DISSERTATION

EXPLORATION OF BASIS SET ISSUES FOR CALCULATION OF INTERMOLECULAR INTERACTIONS

AND

DENSITY FUNCTIONAL THEORY CALCULATIONS OF VANADIUM OXIDE CLUSTERS AND THEIR REACTIONS WITH SULFUR DIOXIDE

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WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY ELENA JAKUBIKOVA ENTITLED EXPLORATION OF BASIS SET ISSUES FOR CALCULATION OF INTERMOLECULAR INTERACTIONS AND DENSITY FUNCTIONAL THEORY CALCULATIONS OF VANADIUM OXIDE CLUSTERS AND THEIR REACTIONS WITH SULFUR DIOXIDE BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

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ABSTRACT OF DISSERTATION

EXPLORATION OF BASIS SET ISSUES FOR CALCULATION OF INTERMOLECULAR INTERACTIONS AND DENSITY FUNCTIONAL THEORY CALCULATIONS OF VANADIUM OXIDE CLUSTERS AND THEIR REACTIONS WITH SULFUR DIOXIDE

The ab initio calculation of intermolecular interactions requires a large basis set in order to describe systems with dominant dispersion interaction accurately. This work focuses on calculation of intermolecular bonding energies of weakly bound systems within the supermolecular method and on issues related to the choice of a basis set for these calculations, in particular size of the basis set, efficiency of 2-electron integral codes, basis set superposition error (BSSE), and the linear dependence of basis functions. In an attempt to find more efficient basis sets for calculations of intermolecular interactions, standard basis sets (10s Huzinaga, 6-311G**, cc-pV6Z), or their parts, are extended (tessellated) by a set of off-centered, s or p functions, symmetrically placed around the nuclei. Standard basis sets (10s Huzinaga, 6-311G**, cc-pVXZ, aug-cc-pVXZ, X = D, T, Q, 5, 6) are also augmented by sets of atom-centered, higher angular momentum functions (p, d, f). Distance from the nucleus of tessellating functions and orbital exponents of tessellating and augmenting functions are optimized with respect to the BSSE-corrected bonding energy at the MP2 or UCCSD level of theory. The two approaches are tested on the model systems with dominant dispersion interactions $^3H_2$, $(CH_4)_2$, and Ne_2 and their efficiency is compared. Both tessellation and augmentation are successful in describing the intermolecular interactions of these model systems, with augmentation being more efficient. Our results draw attention to the linear dependence problems inevitably present in accurate calculations and confirm the need for underlying standard basis sets that provide good descriptions of core and valence electrons in order for the tessellation and augmentation approaches to be reliable.

Vanadium oxide is a catalytic system that plays an important role in the conversion of sulfur dioxide to sulfur trioxide. Density functional theory is employed to study structure and stability of small neutral vanadium oxide clusters in the gas phase. BPW91/LANL2DZ level of theory is used to obtain structures of VO_y (y=1,...,5), V_2O_y (y=2,...,7), V_3O_y (y=4,...,9), and V_4O_y (y=7,...,12) clusters. Energies of growth and fragmentation reactions of the lowest energy isomers of vanadium oxide molecules are also obtained to study the stability of neutral vanadium oxide species under oxygen saturated gas phase conditions. Our results suggest that cyclic and cage like structures are preferred for the lowest energy isomers of neutral vanadium oxide clusters, and oxygen-oxygen bonds are present for oxygen rich clusters. Clusters with an odd number of vanadium atoms tend to have low spin ground states, while clusters with even number of vanadium atoms have a variety of spin multiplicities for their ground electronic state. VO_2, V_2O_5, V_3O_7, and V_4O_{10} are predicted to be the most stable neutral clusters under the oxygen saturated conditions.

Thermodynamics of reactions of vanadium oxide clusters with SO_2 is also studied. BPW91/LANL2DZ is insufficient to properly describe relative V-O and S-O bond strengths of vanadium and sulfur oxides. Calibration of theoretical results with experimental data is necessary to compute reliable enthalpy changes for reactions between V_xO_y and SO_2. Theoretical results indicate SO_2 to SO conversion occurs for oxygen-deficient clusters and SO_2 to SO_3 conversion occurs for oxygen-rich clusters. Some possible mechanisms for SO_3 formation and catalyst regeneration for condensed phase are also suggested. These results are in agreement with, and complement, previous gas phase experimental studies of neutral vanadium oxide clusters.

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CHAPTER 1

INTRODUCTION

OVERVIEW

Computational chemistry methods development and application are equally important areas of quantum chemistry; what is more, they could not exist without each other. As new methods emerge, they allow us to tackle more interesting and complicated problems than ever before. At the same time, the drive to answer important questions of today's chemistry (e.g., How do proteins fold?, How does heterogeneous catalysis work?) serves as a motivation for development of new and better computational methods.

Here I present my contribution to both methods development and applications in two different areas of computational chemistry. The first area encompasses basis set development for ab initio calculations of intermolecular interactions. The second area deals with the application of density functional theory to study heterogeneous catalysis on the model system neutral vanadium oxide clusters in the gas phase.

The organization of this dissertation is as follows: First, a short introduction is devoted to basis sets for electronic structure calculations, heterogeneous catalysis and the place of gas phase metal clusters in catalysis research. Chapters 2, 3 and 4 contain results of my research that have been published (or submitted for publication) as three separate papers. Chapter 5 outlines some future directions for both areas of research presented here. Finally, technical details of calculations and additional material for those interested in pursuing these topics further are included in the Appendices.

BASIS SETS IN ELECTRONIC STRUCTURE CALCULATIONS

Short history of basis set development

A basis set in quantum chemistry is a set of functions (also called basis functions) used to approximate one-electron wavefunctions (orbitals). One-electron wavefunctions are usually expressed as a linear combination of basis functions with expansion coefficients determined iteratively in a self consistent field (SCF) calculation.[1-4] Many-electron wavefunctions are then represented as sums of anti-symmetrized products of one-electron wavefunctions. Note that the final form of a many-electron wavefunction depends on the choice of basis functions as well as the method by which the expansion coefficients are determined.

Efforts to find the best set of basis functions for electronic structure calculations are as old as computational quantum chemistry itself. The very first quantum chemistry computations applied the stationary Schrödinger equation to calculate many-electron atom properties, taking advantage of the central symmetry of these systems as well as their similarity to the exactly solvable case of hydrogen atom. These calculations did not use basis functions in the sense that we use them today, but took different approaches to determine one-electron wavefunctions. For example, Pauling[5] approximated one-electron wavefunctions by analytic, hydrogen-like functions of the form $Np(r)e^{-Zr/n}$, in which N is a normalization constant, $p(r)$ is a polynomial in r, Z is the nuclear charge, and n represents the principal quantum number. Hartree,[1] on the other hand, computed one-electron wavefunctions for a range of atoms by numerically integrating the wave equation for an atom with a non-coulomb spherically symmetric field. Hartree's functions are very accurate, but do not have an analytical representation; they exist only as tables of values.

The concept of a basis set goes back to Slater,[6] who obtained accurate analytical expressions for one-electron wavefunctions by using linear combinations of functions $r^n e^{-ar}$, with exponents a and n varied from one term to another, to approximate Hartree's functions. Slater further used these one-electron wavefunctions to construct orthogonal antisymmetric wave functions in the form of determinants. Both Hartree and Slater functions have been used in various calculations of atomic properties.[7-12] The full potential of Slater functions were realized in 1950s and 1960s, when they were used as basis sets (called "Slater Type Orbitals"[13] or STO) in the Roothaan-Hall implementation of the Hartree-Fock Self Consistent Field method[3,4] for calculations on diatomic[14-18] and polyatomic[19-22] molecules. Unfortunately, integrals arising from Slater functions in the solution of the Schrödinger equation require complicated numerical integration schemes and therefore calculations with large sets of Slater functions can be performed only with great difficulty.

In 1950 Boys suggested the use of Gaussian functions for electronic structure calculations.[23] He defined the class of Gaussian functions to consist of all functions, and of all their linear combinations, of the form $x^l y^m z^n \exp(-ar_A^2)$.[*] He pointed out that Gaussians form a complete system of functions, so they can be used to approximate any function with arbitrary accuracy. Boys also derived simple formulas for integrals over

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[*] In this formula *l, m, n* have any integral value, $a > 0$, and $x_A = x - A_x$, etc., $r_A^2 = x_A^2 + y_A^2 + z_A^2$, A_x, A_y, A_z have any real values.

Gaussians arising in the calculation of atomic and molecular properties. Gaussian functions are less accurate than Slater functions – to approximate one-electron wavefunctions with the same accuracy, more than twice as many Gaussian functions are needed than Slater functions.[24] The main advantage of Gaussians lies in the simplicity and speed of their integral evaluation, making them a very efficient choice for electronic structure calculations.

At first, Gaussian functions were used as an approximation to Slater functions in the calculation of integrals over Slater functions for which it is impossible to obtain explicit formulas.[25] Use of exclusively Gaussian functions in electronic structure calculations have been then explored by Huzinaga, O-ohata, Takata, Reeves and Fletcher,[24,26-28] who proposed to replace Slater type orbitals by a finite expansion of Gaussian functions at every point in the calculations. Gaussian representations of Slater type orbitals have been obtained by least-squares fitting.

The idea of Gaussian functions for electronic structure calculations was further developed by Pople and coworkers,[29] who have obtained STO-*n*G ($n = 2 - 6$) basis sets by using two to six Gaussian functions to represent each Slater type orbital. Subsequently they optimized another series (LEMAO-*n*G) in which coefficients were chosen to minimize the energy of atomic ground state rather than to approximate Slater functions.[30] STO-*n*G and LEMAO-*n*G basis sets are minimal in the sense that they contain only atomic orbitals for shells occupied or partly occupied in the atomic ground state. Later on Pople's group developed split-valence basis sets:[31,32] 4-31G, 5-31G, and 6-31G. In these basis sets, the inner shell is represented by 4, 5, or 6 Gaussian functions and a valence part is represented by an "inner" function composed of 3 Gaussians and an "outer" single Gaussian. Split-valence basis sets are optimized with respect to the total energy of the atomic ground state at the Hartree-Fock level of theory. The 6-311G** basis set[33] was an additional improvement over these basis sets, using 6 Gaussians for the inner shell, triple split (311) representation of the valence, and five uncontracted d-functions on nonhydrogen atoms. Moreover, coefficients of 6-311G** basis set are optimized to give lowest possible energy of the atomic ground state at the MP2 level of theory[34,35] to account for valence electron correlation.

Another step in the basis set evolution was the development of Gaussian basis sets for use in correlated calculations (i.e., configuration interaction). At first, basis sets for correlated calculations were taken from Hartree-Fock calculations. Then Almlöf and coworkers[36,37] showed that better results can be achieved when one optimizes basis functions specifically for correlated calculations. They have developed new basis sets by taking basis functions to be the natural orbitals obtained from correlated atomic calculations. Subsequently, Dunning and coworkers developed correlation consistent basis sets,[38-40] which are noted for their systematic convergence toward the basis set limit (i.e., molecular properties computed with correlation consistent basis sets converge systematically to the basis set limit with increasing basis set size).

Today, the majority of quantum chemical calculations use basis sets composed of Gaussian functions. Among some of the most widely used basis sets are those developed by Pople and Dunning mentioned above. Further development of new basis sets continues even today.[41,42] Gaussian or Slater type orbitals are by no means the only available choices for basis functions. Alternatively, one may use plane wave basis sets,[43] effective core potentials[44] combined with Gaussians, numerical basis functions,[45] or lobe functions.[46] A good starting point to finding more information on this topic is a book of Helgaker, Jorgensen and Olsen[47] and references therein.

Basis sets for intermolecular interactions

Basis sets used for calculations of intermolecular interactions are usually the same as those developed for atomic and molecular calculations (e.g., Pople and Dunning's basis sets). These standard basis sets are in most cases able to provide a proper description of interactions that are about one order of magnitude weaker than covalent bonding (i.e., hydrogen bonding). Unfortunately, they are not as effective in case of interactions dominated by dispersion, such as the interaction between two rare-gas atoms (i.e., Ne_2).[48] The goal of my work was to develop a computationally inexpensive basis set that would be suitable for calculations of these very weak interactions. To achieve this goal, standard basis sets were supplemented with two kinds of basis functions optimized for intermolecular interactions: 1. off-centered tessellating functions; and 2. atom-centered augmenting functions. Results of these efforts are presented in Chapter 2.

HETEROGENEOUS CATALYSIS AND GAS PHASE METAL CLUSTERS

Basic concepts in catalysis

Catalysis plays a very important role in our lives. Photosynthesis, biological reactions occurring in our bodies, as well as many industrial processes (e.g., oil refining, ammonia synthesis, fermentation) are all catalytically assisted reactions.[49] Catalytic materials have special properties that allow them to facilitate chemical reactions (by lowering barriers to these reactions) without being consumed in the process.

Traditionally, two types of catalysis are recognized: 1. homogeneous catalysis, in which catalyst and reactants are in the same phase; and 2. heterogeneous catalysis, in which catalyst and reactants are in different phases. An example of homogeneous catalysis could be the destruction of ozone in the atmosphere catalyzed by chlorine free radicals, where both catalyst and reactants are in the gas phase. Catalysis of $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$ by vanadium pentoxide is an example of heterogeneous catalysis, in which reactants are in the gas phase, while the catalyst is in the molten phase.[50]

There are two limiting approaches to the study and design of heterogeneous catalysts.[51] First, a largely empirical approach finds its roots in the work of Alwin Mittasch,[52] who together with Fritz Haber and Carl Bosch found a new catalyst for the synthesis of ammonia from atmospheric nitrogen by testing about 6500 substances over a period of three years.[53] This empirical approach is still in use today in the form of combinatorial chemistry and high-throughput screening methodologies applied to discovery of new catalytic materials.[54] No a priori knowledge of the processes involved in the catalytic reaction is necessary for these techniques to be successful.

Second, a more conceptual approach stems from the work of Langmuir[55] and focuses on uncovering principles central to heterogeneous catalysis from studies of model systems, such as single crystal surfaces, thin metal films, or supported metal cluster catalysts. The rationale behind this approach is that atomic level understanding of heterogeneous catalysis will facilitate design of new and more efficient catalysts.

The above approaches to catalysis research are highly complementary and much can be learned from both of them. My efforts aimed towards better understanding of vanadium oxide catalysis rely on the second approach, which involves studying the reactivity of small neutral vanadium oxide clusters in the gas phase.

Gas phase metal clusters as models of active sites

At first sight studying heterogeneous catalysis using model systems composed of small clusters in the gas phase might seem like a contradiction. What can these small clusters teach us about complicated processes that occur in the condensed phase? The answer to this question lies in the understanding of mechanistic steps that occur during the heterogeneous catalytic reaction.

In general, heterogeneous catalytic reactions occur in several steps: 1. diffusion of reactants to the surface; 2. adsorption of reactants; 3. chemical reaction (breaking and forming bonds) at the active site; 4. desorption of products; and 5. diffusion of products away from the surface.[56] Recent surface studies[57] also point to three essential features of active heterogeneous catalysts: 1. restructuring of the active metal site during the bond breaking process; 2. mobility of adsorbed molecules along the surface; and 3. catalytic activity of metal oxide – metal interfaces that continues even after the active sites of the supporting metal are deactivated. Although many factors contribute to catalytic activity, at the heart of current theories of heterogeneous catalysis lies the concept of an active site. Metal and metal oxide clusters are often employed as models of the active sites.[58]

The concept of an active site in heterogeneous catalysis is attributed to Taylor,[59] who pointed out that only a small fraction of the heterogeneous catalyst surface is catalytically active and that the "catalyst surface shows a *varying capacity* both to adsorb gas and to promote catalytic change." Active sites are often described as surface defects in the form of steps, kinks, terraces or missing atoms. More than one kind of the active site can be present in the catalyst, especially if the catalyzed reaction involves a complex chemical rearrangement.[60] Mobility of the surface and restructuring of the active site are also considered vital for catalytic activity.[60] Muetterties[61] was the first to suggest the use of discrete metal clusters as model systems for chemisorption and catalytic processes at a metal surface. This approach has since been used in a number of experimental and theoretical studies.[62-69]

Limitations of the cluster approach to the investigation of heterogeneous catalysis should also be understood. Clearly, not all properties of catalysts can be described with model systems consisting of gas phase clusters. Diffusion of reactants and products, mobility of adsorbed molecules along the surface, or any other feature that relies on the presence of an extended lattice would be impossible to study directly based on cluster model systems. On the other hand, metal and metal oxide clusters provide a straightforward representation of active sites central to the heterogeneous catalytic process. Moreover, due to the simplicity of these systems, gas phase theoretical and experimental studies have the ability to examine cluster behavior at the atomic level. As a result, one can gain valuable insights into the mechanisms of reactant adsorption, product desorption, active site rearrangement, and chemical reactions occurring at the active sites.

Vanadium oxide clusters as a model system for vanadium oxide catalyst

Vanadium oxide, V_2O_5, is a catalytic system that plays an important role in the conversion of sulfur dioxide to sulfur trioxide. Although vanadium oxide is a very efficient catalyst with over 95% conversion,[50] the detailed mechanism for its action has not yet been identified. In an effort to understand the behavior of this catalyst better, we have adopted the approach set forth by Muetterties[61] and directed our attention to vanadium oxide clusters. The focus of my work is to use density functional theory calculations to investigate neutral vanadium oxide clusters in the gas phase, with the aim of elucidating the properties that could play a role in the catalytic process. This aim is achieved by: 1. studying the ground state structures and stabilities of neutral vanadium oxide clusters in the gas phase; and 2. exploring the reactivity of gas phase vanadium oxide clusters with SO_2. Results of these investigations are presented in Chapters 3 and 4.

REFERENCES

(1) Hartree, D. R. *Proceedings of the Cambridge Philosophical Society* **1928**, *24*, 89.

(2) Hartree, D. R. *Proceedings of the Royal Society of London Series a-Containing Papers of a Mathematical and Physical Character* **1933**, *141*, 282.

(3) Roothaan, C. C. J. *Reviews of Modern Physics* **1951**, *23*, 69.

(4) Hall, G. G. *Proceedings of the Royal Society of London Series a-Mathematical and Physical Sciences* **1951**, *205*, 541.

(5) Pauling, L. *Proceedings of the Royal Society of London Series a-Containing Papers of a Mathematical and Physical Character* **1927**, *114*, 181.

(6) Slater, J. C. *Physical Review* **1932**, *42*, 33.

(7) Bacher, R. F. *Physical Review* **1933**, *43*, 264.

(8) Brown, F. W.; Bartlett, J. H.; Dunn, C. G. *Physical Review* **1933**, *44*, 0296.

(9) Wetzel, W. W. *Physical Review* **1936**, *49*, 531.

(10) Buckingham, R. A. *Proceedings of the Royal Society of London Series a-Mathematical and Physical Sciences* **1937**, *160*, 0094.

(11) Richtmyer, R. D. *Physical Review* **1939**, *56*, 146.

(12) Lowdin, P. O. *Physical Review* **1953**, *90*, 120.

(13) Mulliken, R. S. *Reviews of Modern Physics* **1960**, *32*, 232.

(14) Ransil, B. J. *Reviews of Modern Physics* **1960**, *32*, 245.

(15) Ransil, B. J. *Reviews of Modern Physics* **1960**, *32*, 239.

(16) Hashino, T.; Huzinaga, S. *Progress of Theoretical Physics* **1958**, *20*, 631.

(17) Huzinaga, S. *Progress of Theoretical Physics* **1958**, *20*, 15.

(18) Phillipson, P. E.; Mulliken, R. S. *Journal of Chemical Physics* **1958**, *28*, 1248.

(19) Palke, W. E.; Lipscomb, W. N. *Journal of the American Chemical Society* **1966**, *88*, 2384.

(20) Pitzer, R. M. *Journal of Chemical Physics* **1967**, *46*, 4871.

(21) Pitzer, R. M. *Journal of Chemical Physics* **1967**, *47*, 965.

(22) Aung, S.; Pitzer, R. M.; Chan, S. I. *Journal of Chemical Physics* **1968**, *49*, 2071.

(23) Boys, S. F. *Proceedings of the Royal Society of London Series a-Mathematical and Physical Sciences* **1950**, *200*, 542.

(24) Huzinaga, S. *Journal of Chemical Physics* **1965**, *42*, 1293.

(25) Foster, J. M.; Boys, S. F. *Reviews of Modern Physics* **1960**, *32*, 303.

(26) Reeves, C. M.; Fletcher, R. *Journal of Chemical Physics* **1965**, *42*, 4073.

(27) Taketa, H.; Huzinaga, S.; Oohata, K. *Journal of the Physical Society of Japan* **1966**, *21*, 2313.

(28) Oohata, K.; Taketa, H.; Huzinaga, S. *Journal of the Physical Society of Japan* **1966**, *21*, 2306.

(29) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *Journal of Chemical Physics* **1969**, *51*, 2657.

(30) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *Journal of Chemical Physics* **1970**, *52*, 5001.

(31) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *Journal of Chemical Physics* **1971**, *54*, 724.

(32) Hehre, W. J.; Ditchfie.R; Pople, J. A. *Journal of Chemical Physics* **1972**, *56*, 2257.

(33) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *Journal of Chemical Physics* **1980**, *72*, 650.

(34) Binkley, J. S.; Pople, J. A. *International Journal of Quantum Chemistry* **1975**, *9*, 229.

(35) Moller, C.; Plesset, M. S. *Physical Review* **1934**, *46*, 0618.

(36) Almlof, J.; Helgaker, T.; Taylor, P. R. *Journal of Physical Chemistry* **1988**, *92*, 3029.

(37) Almlof, J.; Taylor, P. R. *Journal of Chemical Physics* **1987**, *86*, 4070.

(38) Dunning, T. H. *Journal of Chemical Physics* **1989**, *90*, 1007.

(39) Woon, D. E.; Dunning, T. H. *Journal of Chemical Physics* **1993**, *98*, 1358.

(40) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *Journal of Chemical Physics* **1992**, *96*, 6796.

(41) Peterson, K. A.; Puzzarini, C. *Theoretical Chemistry Accounts* **2005**, *114*, 283.

(42) Balabanov, N. B.; Peterson, K. A. *Journal of Chemical Physics* **2005**, *123*.

(43) Andersen, O. K. *Physical Review B* **1975**, *12*, 3060.

(44) Hay, P. J.; Wadt, W. R. *Journal of Chemical Physics* **1985**, *82*, 270.

(45) Benedek, N. A.; Snook, I. K.; Latham, K.; Yarovsky, I. *Journal of Chemical Physics* **2005**, *122*.

(46) Whitten, J. L. *Journal of Chemical Physics* **1966**, *44*, 359.

(47) Helgaker, T.; Jorgensen, P.; J., O. *Molecular Electronic Structure Theory*; John Wiley & Sons Ltd: Chichester, UK, 2000.

(48) Rappe, A. K.; Bernstein, E. R. *Journal of Physical Chemistry A* **2000**, *104*, 6117.

(49) Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; John Wiley & Sons, Inc.: New York, NY, 1994.

(50) West, J. R.; Smith, G. M. Sulfuric Acid and Sulfur. In *Riegel's Handbook of Industrial Chemistry*; Kent, J. A., Ed.; Van Nostrand Reinhold Company Inc.: New York, N. Y., 1983; pp 130

(51) Ertl, G. *The Chemical Record* **2001**, *1*, 33.

(52) Mittasch, A. *Advances in Catalysis* **1950**, *2*, 81.

(53) Mittasch, A. *Geschichte der Ammoniaksynthese*; Verlag Chemie: Weinheim, 1951.

(54) Scheidtmann, J.; Weiss, P. A.; Maier, W. F. *Applied Catalysis a-General* **2001**, *222*, 79.

(55) Langmuir, I. *Transactions of the Faraday Society* **1922**, *17*, 0621.

(56) Ramaswamy, A. V. Catalysis and Theoretical Concepts. In *Catalysis. Principles and Applications.*; Viswanathan, B., Sivasanker, S., Ramaswamy, A. V., Eds.; Narosa Publishing House: New Delhi, India, 2002; pp 206.

(57) Somorjai, G. A.; Contreras, A. M.; Montano, M.; Rioux, R. M. *Proceedings of the National Academy of Sciences of the United States of America* **2006**, *103*, 10577.

(58) van Santen, R. A. The cluster approach to molecular heterogeneous catalysis. In *A Molecular View of Heterogeneous Catalysis*; Derouane, E. G., Ed.; De Boeck Universite: Lucon, France, 1998; pp 73.

(59) Taylor, H. S. *Proceedings of the Royal Society of London Series a-Containing Papers of a Mathematical and Physical Character* **1925**, *108*, 105.

(60) Somorjai, G. A.; McCrea, K. R.; Zhu, J. *Topics in Catalysis* **2002**, *18*, 157.

(61) Muetterties, E. L. *Science* **1977**, *196*, 839.

(62) Dorbon, M. *Revue De L Institut Francais Du Petrole* **1984**, *39*, 497.

(63) Xu, X.; Wang, N.; Zhang, Q. *Surface Science* **1992**, *274*, 378.

(64) Johnson, B. F. G.; Gallup, M.; Roberts, Y. V. *Journal of Molecular Catalysis* **1994**, *86*, 51.

(65) Justes, D. R.; Moore, N. A.; Castleman, A. W. *Journal of Physical Chemistry B* **2004**, *108*, 3855.

(66) Diaz-Ortiz, A.; Aguilera-Granja, F.; Michaelian, K.; Berlanga-Ramirez, E. O.; Montejano-Carrizales, J. M.; Vega, A. *Physica B-Condensed Matter* **2005**, *370*, 200.

(67) Guvelioglu, G. H.; Ma, P. P.; He, X. Y.; Forrey, R. C.; Cheng, H. S. *Physical Review Letters* **2005**, *94*.

(68) Forrey, R. C.; Guvelioglu, G. H.; Ma, P.; He, X.; Cheng, H. *Physical Review B* **2006**, *73*.

(69) Tautermann, C. S.; Clary, D. C. *Physical Chemistry Chemical Physics* **2006**, *8*, 1437.

CHAPTER 2

EXPLORATION OF BASIS SET ISSUES FOR CALCULATION OF INTERMOLECULAR INTERACTIONS

Work presented in this chapter is published in "E. Jakubikova, A. K. Rappé, and E. R. Bernstein, Exploration of basis set issues for calculation of intermolecular interactions. Journal of Physical Chemistry A **110** (31), 9529 (2006)." My contribution to this paper consists of all calculations described below.

INTRODUCTION

Intermolecular interactions play a crucial role in understanding a variety of phenomena involving solids, liquids and gases and their accurate calculation is one of the major challenges for today's computational chemistry.

The calculation of intermolecular interactions usually focuses on computing the properties of weakly bound systems, including geometry, vibrational modes, and bonding energy. The quality of such calculations is often measured by their ability to describe the bonding energy properly. At the ab initio level, bonding energy can be computed in two ways: 1. directly, as a sum of physically distinct contributions from at least first and second order perturbation theory calculations[1]; 2. as a difference between the energy of monomers and the energy of the complex. The second approach is also known as the supermolecular method.

Both approaches have their strengths and weaknesses and are complementary rather than competitive.[2] The advantage of perturbational methods lies in the fact that the interaction energy is calculated directly and not as a difference of two large, almost identical numbers. Also, perturbational methods are free from the basis set superposition error (BSSE) which is a major problem in the application of the supermolecular method. Despite this, the vast majority of calculations use the supermolecular method since it is very simple and straightforward and many standard quantum chemistry programs can be employed in the calculations using this method. The supermolecular method is, unlike perturbation approaches, also valid for any distance between the subsystems and higher order terms with respect to the interaction potential are implicitly taken into account.

The main focus of this paper is computation of total bonding energy for systems with dominant dispersion interaction (i.e., we are not interested in computing different components of bonding energy such as induction or dispersion, but in the bonding energy itself). The bonding energy is, unlike its components, a quantity of direct chemical interest as it is an experimentally accessible number. The supermolecular approach is used in all our calculations due to its simplicity as well as widespread use, and therefore further discussion will refer to the supermolecular approach only.

Once a decision is taken on which method to use to compute the bonding energy (supermolecular or perturbational), one needs to determine the appropriate theory level and basis set. Some ab initio methods are more suitable for calculation of intermolecular interactions than others. For example, Hartree-Fock (HF) calculations completely miss the dispersion interaction, which involves correlation between the electrons on different molecules. Current density functional methods (DFT) also fail to account for dispersion.[3-5] HF and DFT methods can be more successfully used for computations on systems in which charge transfer or electrostatic interactions are dominant (i.e., hydrogen bonded systems). To describe systems for which dispersion plays an important role, methods that treat electron correlation at a higher level (e.g., configuration interaction, coupled-cluster, or perturbational methods) are needed.

Most of the calculations of intermolecular interactions suffer from the basis set superposition error (BSSE). This error was first noted in the calculation of interaction of two ground state helium atoms.[6, 7] The basis functions of each monomer in the supermolecular calculation are usually finite and far from complete; therefore they use basis functions of the other monomer to improve their energies. The lowering of monomer energy lowers the total energy of the dimer; however, it has nothing to do with the interaction energy one is trying to calculate – it is a mere mathematical artifact. This artificial lowering of the energy can be significantly large – of the order of the interaction energy itself.

There has been a considerable amount of discussion about the BSSE and the ways to correct it (see refs. 8-12 and references therein). The most widely accepted is the counterpoise correction scheme,[13, 14] which is also used in our calculations.

Another problem associated with calculations of intermolecular interactions is their remarkable dependence on the quality of the basis set employed. One can argue that to obtain reliable results, large basis sets of cc-pVTZ quality or better should be employed in the calculations.[15, 16] Extensive polarization functions (i.e., d shell for the first row atoms and p shell for hydrogen) and diffuse functions must be included to describe weakly bonded systems with reasonable accuracy.[17-19] Many researchers also use specially tailored basis sets designed to reproduce monomer properties, such as polarizibilities,[2, 20-25] relevant to intermolecular forces. Some also augment standard basis sets with functions optimized with respect to the bonding energies[26] or construct new interaction optimized basis sets.[27] In addition, "bond-centered" basis functions located near the midpoint of the van der Waals bond are also found effective in recovering most of the interaction energy, even in the absence of basis functions with excessively large angular momentum quantum numbers.[28-31]

In 2000, Rappé and Bernstein proposed to supplement standard basis sets with tessellated spherical Gaussians (TSG) optimized for the calculation of intermolecular interactions.[15] TSG functions consist of s basis functions placed at the vertices, faces or edges of an octahedron centered at the atom's nucleus, thus offering a better description of electron density away from the nucleus as well as providing the higher angular momenta components to the basis sets important for the proper description of dispersion electron correlation events. Another reason behind introducing TSG was a general belief that 2-electron integrals over s basis functions are simpler and therefore faster to evaluate than integrals over higher angular momentum functions. Thereby, the extensive use of TSG should lead to substantial computational savings.

Use of basis functions not centered on nuclei but rather allowed to "float" in space for computation of molecular properties is an idea that dates back to the 1950s, when Neumark and Kimball first introduced a "free-cloud" approximation to molecular orbital calculations.[32, 33] Their model has been extended by Frost, who employed floating spherical gaussian orbitals (FSGO) to represent a pair of electrons in a molecule, with radius and position of FSGO optimized to achieve minimum energy.[34] FSGO were later used in a similar manner by Archibald et al.,[35] Spangler et al.,[36] and more recently by Pakiari.[37, 38] A different approach was adopted by Whitten, who instead of explicitly using functions with higher angular momentum (p, d, f, ...), reconstructed them from linear combinations of off-centered gaussian s-functions ("lobe-functions").[39, 40] Bond functions mentioned earlier are another example of the use of the off-centered functions for the ab initio calculations.

The aim of this work is to explore the viability of the tessellation approach for the calculation of intermolecular interactions and compare it with a more standard approach, augmentation. Other issues pertaining to the calculation of intermolecular interactions, such as BSSE and linear dependence of the basis set, are also explored and discussed.

METHOD

Tessellated basis sets are composed of a standard, nucleus centered, valence basis set (or a part of the set) and a set of s or p functions centered away from the nuclei. To place these functions around the nuclei, we use three different tessellation patterns or "shells". The first shell is created by placing s or p functions at the vertices of an octahedron centered at the atom's nucleus; we call this shell the 'v' shell. The second shell of functions, the 'f' shell, is created by placing functions at the centers of the eight triangular faces of the octahedron. The third, 'e' shell, places twelve functions in the middle of the octahedron's edges. Moreover, there can be more than one function centered at the same point of space. See Figure 2.1 for a graphical description of the shells.

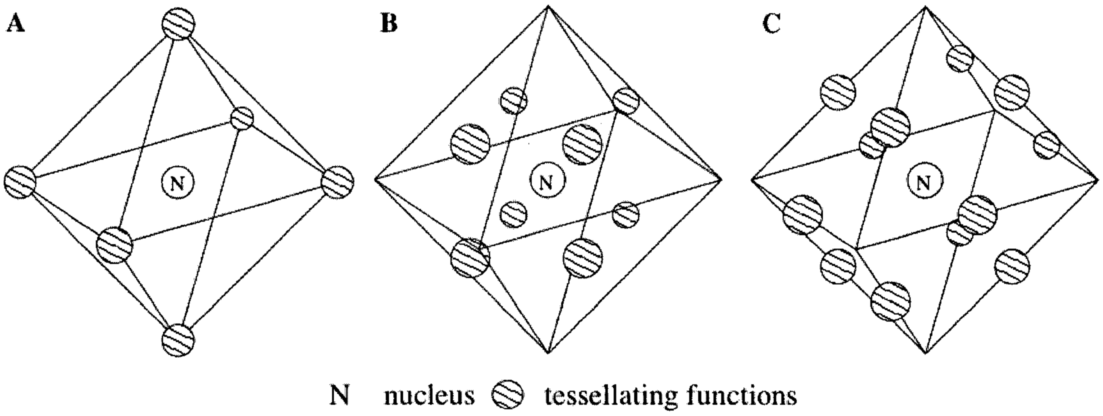


Figure 2.1. Tessellation shells. A - v-shell, functions placed in the vertices of octahedron; B - f-shell, functions placed in the faces of octahedron; C - e-shell, functions placed in the middle of the octahedron's edges.

Each shell of functions is characterized by its radial displacement *R* from the nucleus and an orbital exponent χ. Both of these parameters are variationally hand-optimized in order to maximize the BSSE-corrected intermolecular bonding energy.

Augmented basis sets are created by adding sets of p, d, or f functions centered on nuclei to the standard basis sets. Their orbital exponents χ are hand-optimized with respect to the BSSE-corrected bonding energy.

Geometries of dimers are kept fixed during the basis set optimization and are shown in Figure 2.2. Bond distance for $^3H_2$ is 4.15 Å. Distance between Ne atoms in the dimer is 3.15 Å. Geometry of $(CH_4)_2$ is optimized at the MP2/cc-pVTZ level of theory.

The optimization is done at the MP2 level of theory for Ne_2 and $(CH_4)_2$ and at CISD (UCCSD) level of theory for $^3H_2$. The GAUSSIAN 98 program[41] and MOLPRO 2000.1 and 2002.6[42] are used to perform all computations. Bonding energies are calculated using the supermolecular approach and the counterpoise method is applied to account for BSSE.[13, 14]

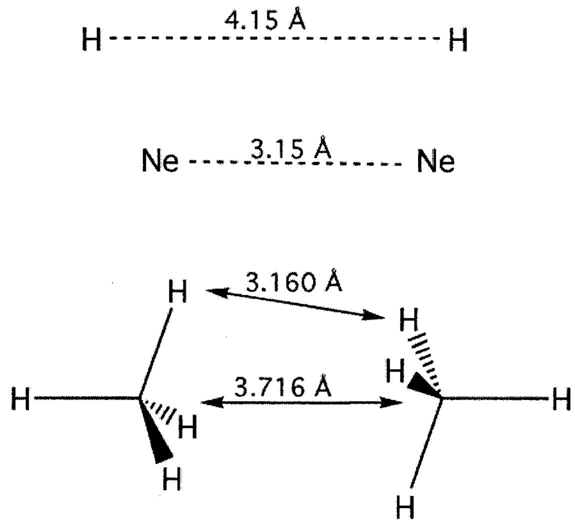


Figure 2.2. Geometries of dimers used in study. A - $^3H_2$; B - Ne_2; C - $(CH_4)_2$

The following naming scheme is introduced for the basis sets we developed. The main part of the name consists of the standard basis set used for description of core and valence (i.e., 6-311G**, Huz for a modified 10s Huzinaga basis set (see Table 2.1), and spd-cc-pV6Z for s, p, and d functions from cc-pV6Z basis set). The prefix stands for the type of functions added to the standard basis set: T for tessellated and A for augmented functions. The suffix describes the angular momentum of functions added: S, P, or D for adding a set of s, p or d functions. In case of tessellated basis sets, the subscript further gives the tessellation pattern (v, f, or e shell) and the number of functions centered at each position. For example, T6-311G**$S_v^2{}_f$ describes a 6-311G** basis set tessellated with two sets of s functions centered at the vertices of an octahedron (both sets centered at the same position) and one set of s functions centered in the faces of octahedron. AHuzP^{2}D is modified 10s Huzinaga basis set augmented with two sets of p functions and one set of d functions. Basis set parameters for optimized tessellated and augmented basis sets are shown in Appendix A.

Exponents	Contraction Coefficients
1776.77556	0.44000×10^{-4}
254.017712	0.37200×10^{-3}
54.6980390	0.20940×10^{-2}
15.0183440	0.88630×10^{-2}
4.91507800	0.30540×10^{-1}
1.79492400	0.90342×10^{-1}
0.71071600	0.213239
0.30480200	0.352350
0.13804600	0.339657
0.06215700	0.107330
1.79492400	1.0
0.71071600	1.0
0.30480200	1.0
0.13804600	1.0
0.06215700	1.0
0.03108000	1.0
0.01554000	1.0
0.00777000	1.0

Table 2.1. Exponents and contraction coefficients for modified 10s Huzinaga basis set used for hydrogen atom.

Finally, it is important to note that all calculations are done with basis sets consisting of spherical gaussians (i.e., we use 5 functions for the d shell, 7 for the f shell, etc.), which is a default choice in the MOLPRO program. A sample MOLPRO file for calculation of bonding energy of neon dimer with tessellated basis set is shown in Appendix B.

RESULTS

$^3H_2$

We have extended (i.e., tessellated and augmented) two standard basis sets for $^3H_2$: modified 10s Huzinaga[43] and 6-311G** basis sets.[44] Radial distance from the nucleus for each tessellation shell and orbital exponents for tessellating, as well as augmenting functions, are optimized at UCCSD level of theory with respect to the BSSE-corrected bonding energy. Note that in the case of the modified 10s Huzinaga basis set, BSSE is of no concern, since the energy of the hydrogen atom computed with this basis set is 0.499 9993 hartree, which suggests a maximal BSSE of 1.4 μh [1 μh = 2.7211 $\times 10^{-5}$ eV = 0.2195 cm^{-1} = 2.6255 $\times$ 10^{-3} kJ/mol = 6.2751 $\times$ 10^{-4} kcal/mol]. BSSE-corrected bonding energies and BSSE for each optimized basis set are shown in Figures 2.3-2.6.

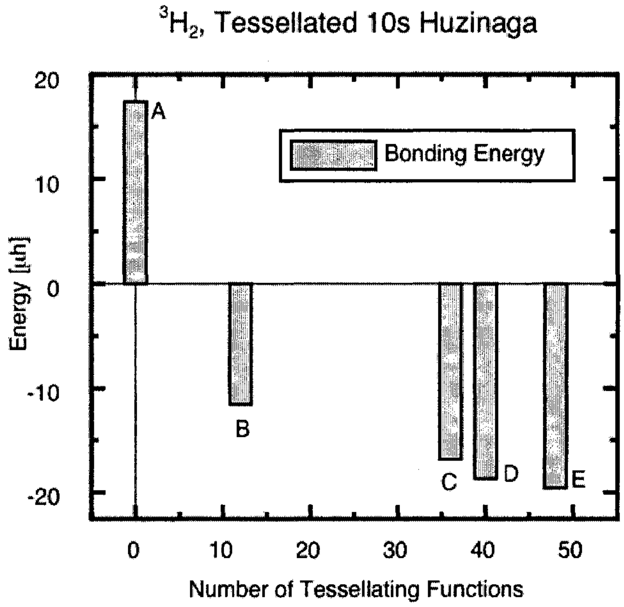


Figure 2.3. Bonding energy for $^3H_2$ computed with tessellated modified 10s Huzinaga basis sets. Radial distance from nucleus and the orbital coefficients for tessellating functions are optimized with respect to the $^3H_2$ bonding energy. The letter labels indicate different basis sets: A - modified 10s Huzinaga basis set, no tessellation; B - THuzS$_v$; C - THuzP$_v$; D - THuzS$_v{}^2{}_f$; and E - THuz(SP)$_v$.

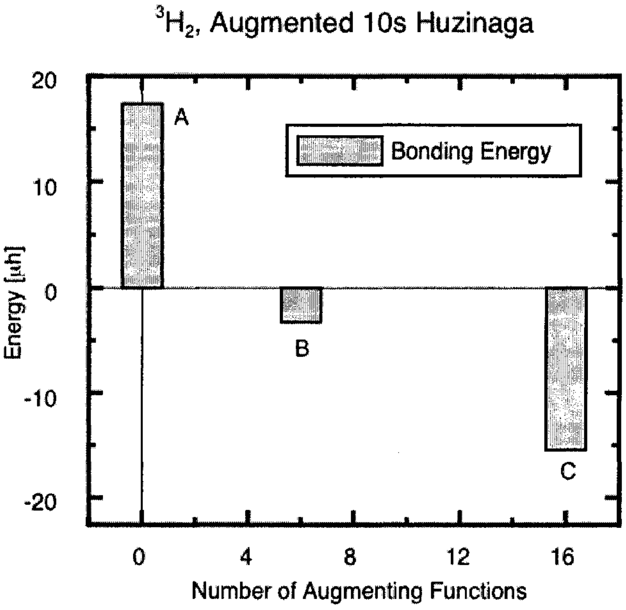


Figure 2.4. Bonding energy for $^3H_2$ computed with augmented modified 10s Huzinaga basis sets. Orbital coefficients for augmenting functions are optimized with respect to the $^3H_2$ bonding energy. The letter labels indicate different basis sets: A - modified 10s Huzinaga basis set, no augmentation; B - AHuzP; and C – AHuzPD.

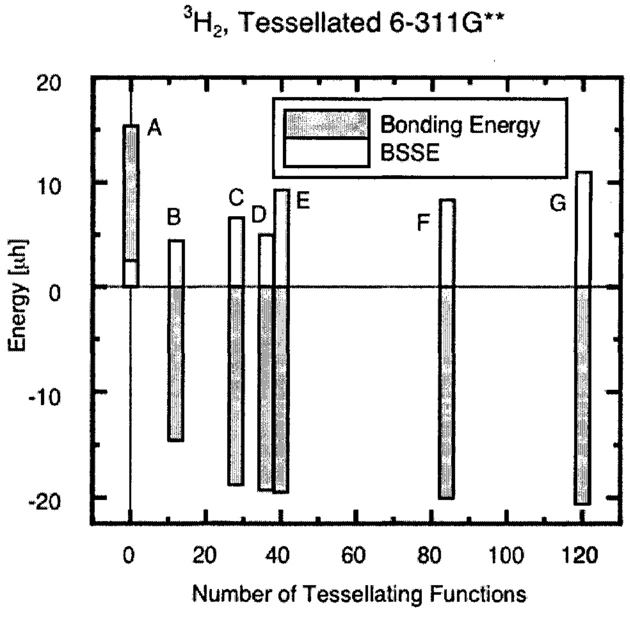


Figure 2.5. BSSE-corrected bonding energy and BSSE for $^3H_2$ computed with tessellated 6-311G** basis sets. Radial distance from nucleus and the orbital coefficients for tessellating functions are optimized with respect to $^3H_2$ BSSE-corrected bonding energy. The letter labels indicate different basis sets: A - 6-311G** basis set, no tessellation; B - T6-311G**S_v; C - T6-311G**S_{vf}; D - T6-311G**P_v; E - THuz$S_v{}^2{}_f$; F - T6-311G**P_{vf}; and G - T6-311G**$P_v{}^2{}_f$.

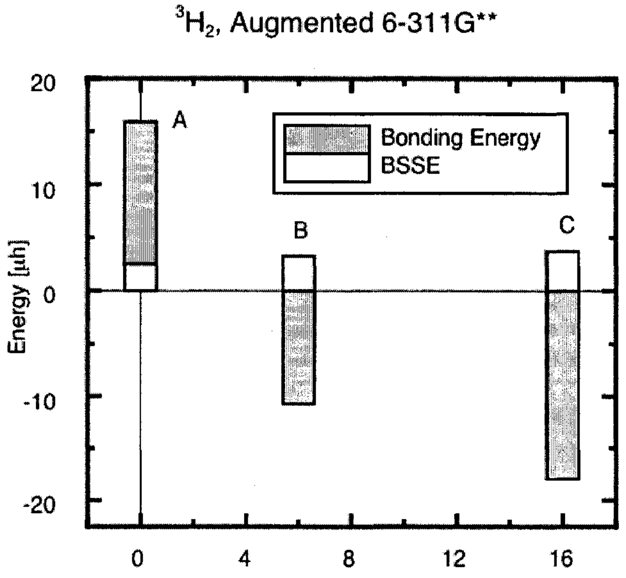


Figure 2.6. BSSE-corrected bonding energy and BSSE for $^3H_2$ computed with augmented 6-311G** basis sets. Orbital coefficients for augmenting functions are optimized with respect to $^3H_2$ BSSE-corrected bonding energy. The letter labels indicate different basis sets: A - 6-311G** basis set, no augmentation; B - A6-311G**P; and C - A6-311G**PD.

Both tessellated and augmented functions are able to recover substantial amounts of the accepted bonding energy for $^3H_2$, -19.52 µh.[45] Tessellated 10s Huzinaga basis sets recover between 59.2 - 100.4% of the accepted bonding energy, while tessellated 6-311G** recover 74.5 - 105.7% of accepted bonding energy. $^3H_2$ bonding energy computed with augmented 10s Huzinaga and augmented 6-311G** basis sets lies between 16.5 - 79.1% and between 55.0 - 92.1% of accepted bonding energy, respectively. In case of 10s Huzinaga and 6-311G** basis sets, higher numbers of functions optimized for bonding recover larger amounts of bonding energy irrespective of whether they are augmenting or tessellating the basis set. Interestingly, bonding energies computed with extended (tessellated or augmented) 6-311G** basis sets recover larger amounts of the bonding energy compared to the 10s Huzinaga basis set tessellated or augmented with the same type and number of functions.

Ne_2

We have extended (tessellated or augmented) s, p and d functions from the cc-pV6Z[46] and 6-311G** basis sets for Ne_2. All parameters are optimized at the MP2 level of theory with respect to the BSSE-corrected bonding energy. The BSSE-corrected bonding energy and BSSE for each optimized basis set are shown in Figures 2.7-2.10.

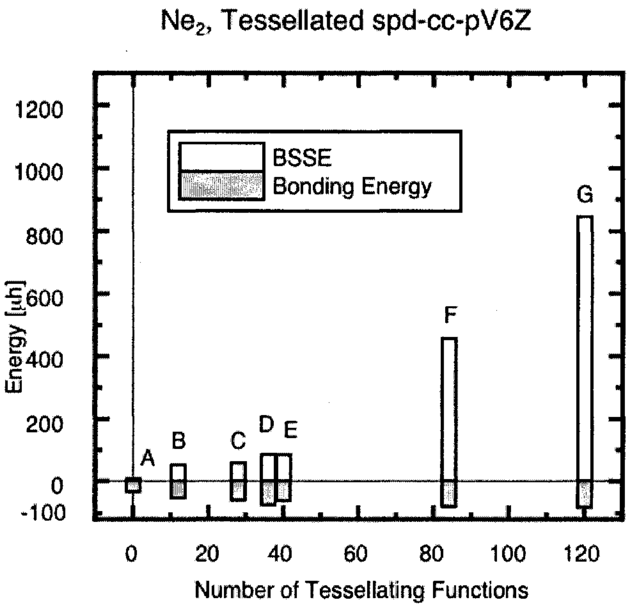

Ne₂, Tessellated spd-cc-pV6Z

Figure 2.7. BSSE-corrected bonding energy and BSSE for Ne_2 computed with tessellated spd-cc-pV6Z basis sets. Radial distance from nucleus and the orbital coefficients for tessellating functions are optimized with respect to the Ne_2 BSSE-corrected bonding energy. The letter labels indicate different basis sets: A - spd-cc-pV6Z basis set, no tessellation; B - Tspd-cc-pV6ZS$_v$; C - Tspd-cc-pV6ZS$_{vf}$; D - Tspd-cc-pV6ZP$_v$; E - Tspd-cc-pV6ZS$_v{}^2{}_f$; F - Tspd-cc-pV6ZGP$_{vf}$; and G - Tspd-cc-pV6ZP$_v{}^2{}_f$.

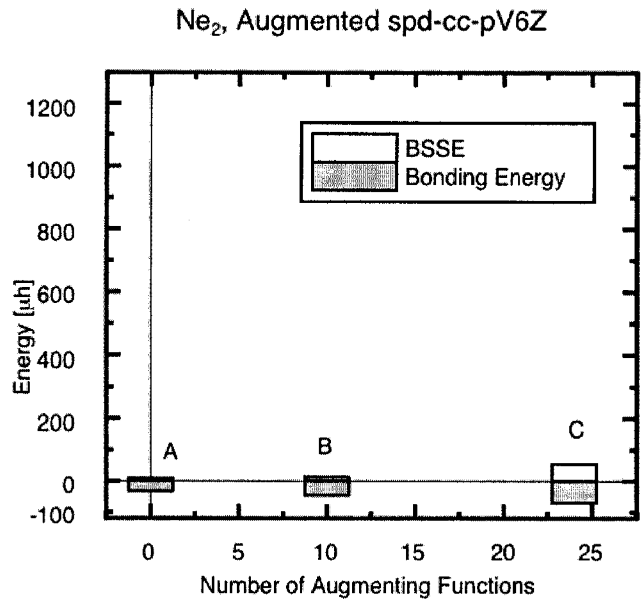


Figure 2.8. BSSE-corrected bonding energy and BSSE for Ne_2 computed with augmented spd-cc-pV6Z basis sets. Orbital coefficients for augmenting functions are optimized with respect to the Ne_2 bonding energy. The letter labels indicate different basis sets: A - spd-cc-pV6Z basis set, no augmentation; B - Aspd-cc-pV6ZD; and C - Aspd-cc-pV6ZDF.

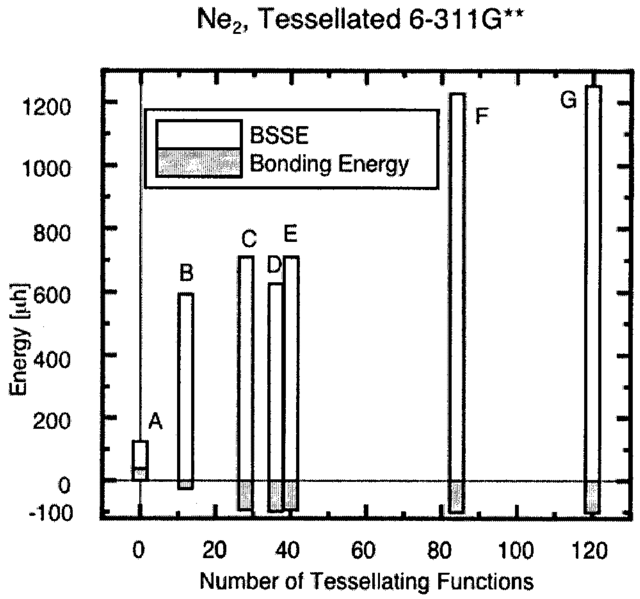


Figure 2.9. BSSE-corrected bonding energy and BSSE for Ne_2 computed with tessellated 6-311G** basis sets. Radial distance from nucleus and the orbital coefficients for tessellating functions are optimized with respect to Ne_2 BSSE-corrected bonding energy. The letter labels indicate different basis sets: A - 6-311G** basis set, no tessellation; B - T6-311G**S_v; C - T6-311G**S_{vf}; D - T6-311G**P_v; E - THuz$S_v^2{}_f$; F - T6-311G**P_{vf}; and G - T6-311G**$P_v^2{}_f$.

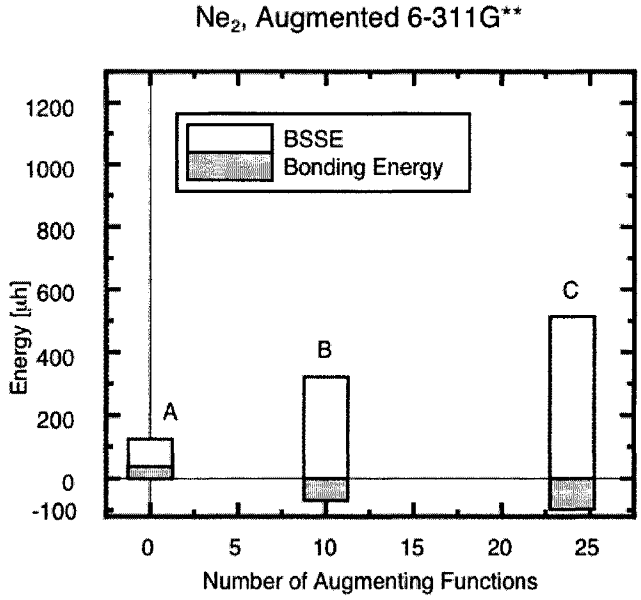


Figure 2.10. BSSE-corrected bonding energy and BSSE for Ne_2 computed with augmented 6-311G** basis sets. Orbital coefficients for augmenting functions are optimized with respect to Ne_2 BSSE-corrected bonding energy. The letter labels indicate different basis sets: A - 6-311G** basis set, no augmentation; B - A6-311G**D; and C - A6-311G**DF.

As in the case of $^3H_2$, both tessellated and augmented basis sets are able to recover substantial amounts of the Ne_2 accepted bonding energy (-134 μh).[47] Tessellated spd-cc-pV6Z basis sets recover 38.9 - 61.1% of the accepted bonding energy, while tessellated 6-311G** basis sets recover 19.3 - 75.6% of the Ne_2 bonding energy. Augmented basis sets recover between 33.6% and 52.6% for spd-cc-pV6Z and between 51.4 and 72.44% for 6-311G** basis sets. Again, with one exception, the higher number of tessellating or augmenting functions recovers more bonding energy, irrespective of the type of the extending function or method employed. Tessellated and augmented 6-311G** basis sets have substantially larger BSSE and recover more bonding energy per shell than tessellated and augmented spd-cc-pV6Z basis sets.

Note that the best available calculation for Ne_2 at the MP2 level of theory employing the t-aug-cc-pVQZ' basis set of Woon[17] recovers only 64% of the accepted bonding energy. To approach Ne_2 bonding energy more closely, one needs to use the MP4 level of theory. Indeed, the MP4 calculation with selected basis sets reveals further lowering of the bonding energy: MP4/Tspd-cc-pV6ZP$_v$ lowers the bonding energy to -108.08 μh from -72.05 μh at MP2 level of theory and MP4/T6-311G**P$_v$ lowers the bonding energy from -98.36 μh to -120.29 μh. Augmented basis sets behave in a similar manner with respect to the MP4 calculations. This shows the importance of using higher levels of theory than MP2 in order to obtain the correct description of the neon dimer interaction.

The BSSE - corrected bonding energy computed with 6-311G** basis sets extended by more than 20 primitives at the MP2 level of theory lies between -93 μh and -101 μh (70-76.5% of the accepted bonding energy). This indicates possible overestimation of the bonding energy with extended 6-311G** basis sets. We attribute this to the approximate nature of the counterpoise model and an undercorrection of the large BSSE that arises with these basis sets.

$(CH_4)_2$

The first family of basis sets constructed for calculation of the bonding energy for $(CH_4)_2$ uses 10s Huzinaga basis set on hydrogen and s, p, and d functions from the cc-pV6Z basis set on carbon. The second family of basis sets consists of the 6-311G** basis sets on both carbon and hydrogen atoms. Basis sets on carbon are extended with augmenting or tessellating functions optimized for BSSE-corrected bonding energy of the methane dimer at MP2 level of theory without the presence of additional functions on hydrogen. We also compute bonding energy for the methane dimer using extended functions on hydrogen which are optimized for bonding energy of $^3H_2$ and their combination with extended functions on carbon. BSSE-corrected bonding energies and BSSE for each of the basis sets are shown in Figures 2.11-2.14.

There are several experimental estimates of the methane dimer bonding energy based on spherically averaged potentials obtained from the fit of experimental data such as viscosity, virial coefficients, and methane-methane scattering.[48-50] The bonding energy given by these empirical potentials lies in the range of 574-797 μh. All bonding energies computed with extended basis sets containing 32 or more augmenting or tessellating functions fall within this range. Extended basis sets with 12 augmenting or tessellating functions recover between 56.0 - 79.9% of the average bonding energy given by empirical potentials.

Interestingly, basis sets for $(CH_4)_2$ do not behave in the same manner as the basis sets for $^3H_2$ and Ne_2. First, a higher number of basis functions does not always generate a larger energy (although this general pattern is roughly followed here too). Second, bonding energies and BSSE computed with extended 10sHuz/spd-cc-pV6Z basis sets and 6-311G** basis sets are of comparable size, with 10sHuz/spd-cc-pV6Z basis sets having noticeably larger BSSE in certain cases. Third, the contribution of MP4 to the bonding energy is not as significant as in the case of Ne_2. For example, the MP4 calculation with 6-311G**on hydrogen and T6-311G**P_v basis set on carbon gives -696.13 μh, while MP2 level of theory with the same basis set recovers -636.80 μh for the methane bonding energy.

In all calculations for $^3H_2$, Ne_2, and $(CH_4)_2$ presented here, tessellated basis sets are more linearly dependent than augmented basis sets. The degree of linear dependence is usually measured by the smallest eigenvalue of the overlap matrix **S** (linear dependence is discussed in greater detail later in this paper). In a few cases the difference is quite significant: difference in the smallest eigenvalue between tessellated and augmented basis set using approximately the same number of extending functions can be two to three orders of magnitude.

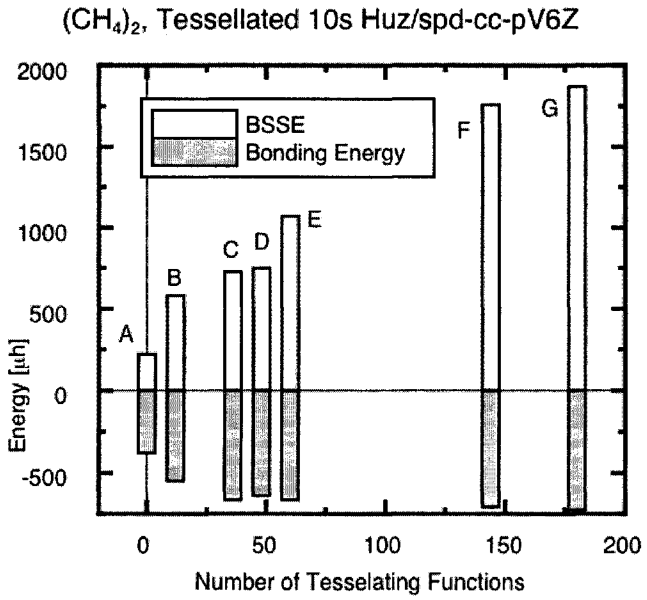


Figure 2.11. BSSE-corrected bonding energy and BSSE for $(CH_4)_2$ computed with tessellated modified 10s Huzinaga basis set on hydrogen and spd-cc-pV6Z basis set on carbon. Radial distance from nucleus and the orbital coefficients for tessellating functions on carbon are optimized with respect to the $(CH_4)_2$ BSSE-corrected bonding energy. Parameters of tessellated 10s Huzinaga basis set are optimized with respect to the $^3H_2$ bonding energy. The letter labels indicate different basis sets: A - 10s Huzinaga/spd-cc-pV6Z basis set, no tessellation; B - Huz/Tspd-cc-pV6ZS$_v$; C - Huz/Tspd-cc-pV6ZP$_v$; D - THuzS$_v$/spd-cc-pV6Z; E - THuzS$_v$/Tspd-cc-pV6ZS$_v$; F - THuzPv/spd-cc-pV6Z; and G - THuzPv/Tspd-cc-pV6ZP$_v$.

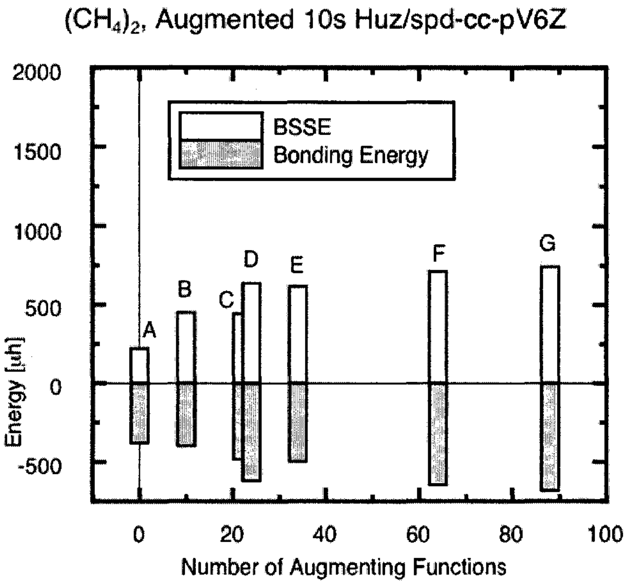


Figure 2.12. BSSE-corrected bonding energy and BSSE for $(CH_4)_2$ computed with augmented modified 10s Huzinaga basis set on hydrogen and spd-cc-pV6Z basis set on carbon. Orbital coefficients of augmenting functions on carbon are optimized with respect to the $(CH_4)_2$ BSSE-corrected bonding energy. Parameters of augmenting functions on hydrogen are optimized with respect to the $^3H_2$ bonding energy. Basis sets C and D have the same number of tessellating functions (24). The letter labels indicate different basis sets: A - 10s Huzinaga/spd-cc-pV6Z basis set, no augmentation; B - Huz/Aspd-cc-pV6ZD; C - AHuzP/spd-cc-pV6Z; D - Huz/Aspd-cc-pV6ZDF; E - AHuzP/Tspd-cc-pV6ZD; F - AHuzPD/spd-cc-pV6Z; and G - AHuzPD/Aspd-cc-pV6ZDF.

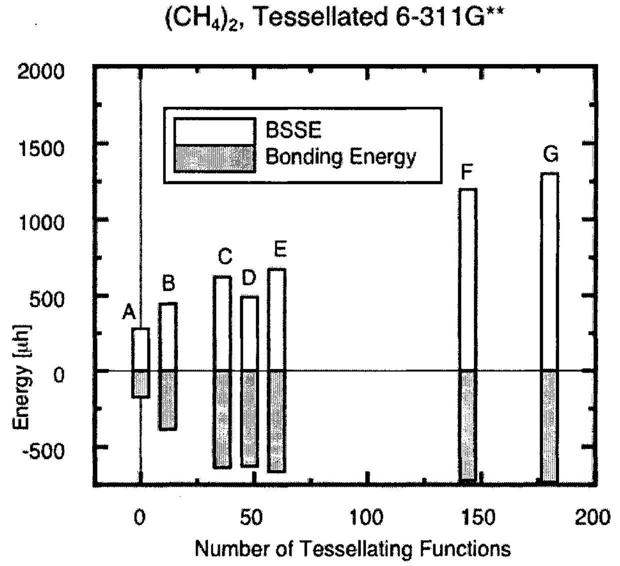


Figure 2.13. BSSE-corrected bonding energy and BSSE for $(CH_4)_2$ computed with tessellated 6-311G** basis set on hydrogen and carbon. Radial distance from nucleus and the orbital coefficients for tessellating functions on carbon are optimized with respect to the $(CH_4)_2$ BSSE-corrected bonding energy. Parameters of tessellated 10s Huzinaga basis set are optimized with respect to the BSSE-corrected $^3H_2$ bonding energy. The letter labels indicate different basis sets: A - 6-311G**/6-311G** basis set, no tessellation; B - 6-311G**/T6-311G**S_v; C - 6-311G**/T6-311G**P_v; D - T6-311G**S_v/6-311G**; E - T6-311G**S_v/T6-311G**S_v; F - T6-311G**P_v/6-311G**; and G - T6-311G**P_v/T6-311G**P_v.

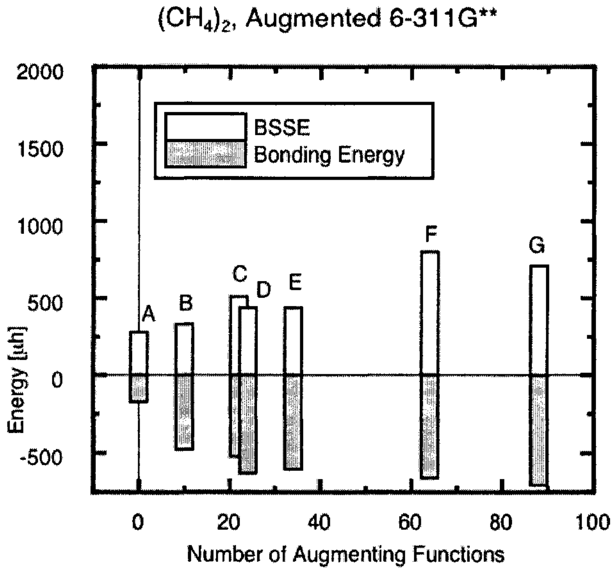


Figure 2.14. BSSE-corrected bonding energy and BSSE for $(CH_4)_2$ computed with augmented 6-311G** basis set on hydrogen and carbon. Orbital coefficients of augmenting functions on carbon are optimized with respect to the $(CH_4)_2$ BSSE-corrected bonding energy. Parameters of augmenting functions on hydrogen are optimized with respect to the BSSE-corrected $^3H_2$ bonding energy. Basis sets C and D have the same number of tessellating functions (24). The letter labels indicate different basis sets: A - 6-311G**/6-311G** basis set, no augmentation; B - 6-311G**/A6-311G**D; C - A6-311G**P/6-311G**; D - 6-311G**/A6-311G**DF; E - A6-311G**P/T6-311G**D; F - A6-311G**PD/6-311G**; and G - A6-311G**PD/A6-311G**DF.

Augmented basis set choices for Ne_2 and $(CH_4)_2$

Comparing the performance of tessellated and augmented basis sets leads us to the conclusion that, at present, augmented basis sets are more suited for calculation of intermolecular interactions. In this section we will focus on augmentation, in particular, how to choose a basis set most suitable for augmentation. The two main criteria this basis set should satisfy are 1. it should provide a good description of the core and valence for the atoms present, so it will not be unbalanced after augmentation, and 2. it should be as small as possible, so the calculation does not take an excessively long time and the basis set can be applied to larger systems (more than 3 or 4 first row atoms). Obviously, choice of such a basis set will require some compromises. For example, aug-cc-pV6Z basis set satisfies the first criterion, but it is too large to be efficient. STO-3G basis set is small and fast, however, it does not provide a satisfactory description of the core and valence, and augmenting it results in an unbalanced basis set leading to erroneous bonding energies even after the application of a BSSE-correction scheme. To illustrate this, we have augmented STO-3G basis set with one p function optimized with respect to the $^3H_2$ bonding energy. The BSSE-corrected bonding energy obtained with this basis set at UCCSD level of theory is -66.82 μh, more than three times the size of the accepted bonding energy for this interaction, -19.52 μh.[45] BSSE is 3631.60 μh.

We have tested a series of Dunning's correlation consistent basis sets[21, 51-53] as well as 6-311G** basis set at MP2 and LMP2 level of theory for Ne_2. Figures 2.15 and 2.16 show bonding energies and BSSE computed with cc-pVXZ, aug-cc-pVXZ (X = D, T, Q, 5) and 6-311G** basis sets. Clearly, the 6-311G** basis set as well as the cc-pVXZ series are not efficient in describing the interaction of Ne_2. The aug-cc-pVXZ family performs better, although even here larger basis sets are required to describe the interaction with satisfactory accuracy. Figures 2.17 and 2.18 show the results of MP2 calculations performed with the same basis sets but with each basis set augmented with a set of d and f functions optimized for the Ne_2 bonding energy. All of the augmented basis sets are able to describe the Ne_2 interaction, with the smallest basis sets (Acc-pVDZDF, A6-311G**DF) overestimating the bonding energy. Bonding energies and BSSE of these augmented basis sets behave smoothly with increasing size of the basis set. In both cases, the BSSE decreases with an increase in number of functions. Bonding energies calculated with Acc-pVXZDF and A6-311G**DF basis sets converge to the Ne_2 bonding energy from below and vary from -111.64 to -73.82 μh. It is far more common for systematic basis set enhancement to converge to an answer from above. Convergence from below is thought to be due to the approximate nature of the counterpoise correction. Bonding energies computed with Aaug-cc-pVXZDF basis sets (with the exception of Aaug-cc-pVQZ basis set) converge to the bonding energy from above and vary between -75.67 and -78.77 μh. Results obtained at the LMP2 level of theory with the same basis sets are shown in Figures 2.19 and 2.20. In all cases, LMP2 bonding energies lie within 13 μh of MP2 bonding energies, most of them being slightly lower than bonding energies computed at the MP2 level of theory. Bonding energies computed with Acc-pVXZDF and A6-311G**DF basis sets still converge to the Ne_2 bonding energy from below, varying between -108.74 and -76.47 μh. Bonding energies computed with Aaug-cc-pVXZ basis sets are almost saturated, varying between -80.77 and 82.38 μh.

We have also computed the methane dimer bonding energy with several augmented and standard basis sets. The results are shown in Figures 2.21 and 2.22. As in the case of Ne_2, augmentation with a set of d and f functions improves bonding energies and the use of LMP2 substantially reduces the BSSE; nonetheless, some differences exist for the two dimers. The A6-311G**DF basis set performs better for the methane dimer than for Ne_2, it does not overestimate the $(CH_4)_2$ bonding energy, and its absolute as well as relative BSSE is smaller. Calculation of the $(CH_4)_2$ bonding energy with the Aaug-cc-pVDZDF basis set, which is quite efficient for Ne_2, shows a very large BSSE for $(CH_4)_2$. LMP2 bonding energies lie within 120 μh of the MP2 bonding energies, all higher than energies computed at the MP2 level of theory, which is opposite to the behavior for Ne_2 LMP2 bonding energies.

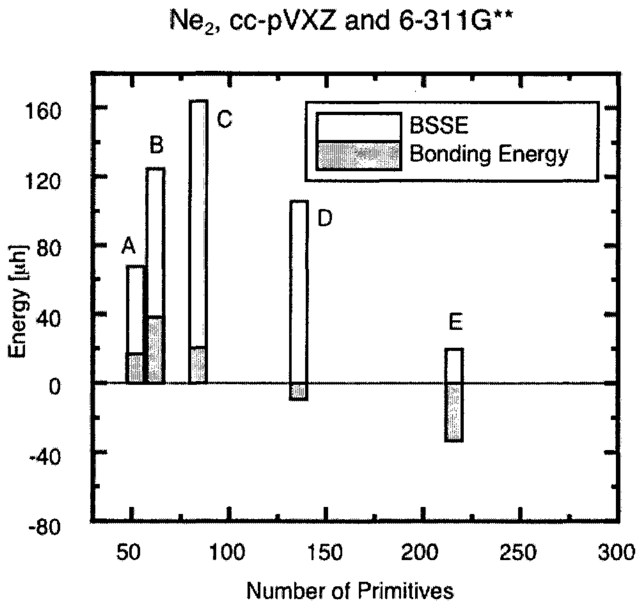


Figure 2.15. BSSE-corrected bonding energy and BSSE for Ne$_2$ computed with cc-pVXZ and 6-311G** basis sets at MP2 level of theory. The letter labels indicate different basis sets: A - cc-pVDZ; B - 6-311G**; C - cc-pVTZ; D - cc-pVQZ; and E - cc-pV5Z.

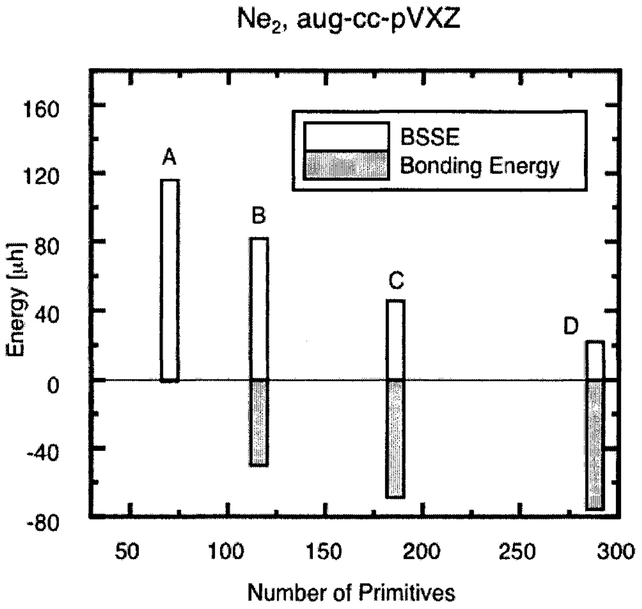


Figure 2.16. BSSE-corrected bonding energy and BSSE for Ne$_2$ computed with aug-cc-pVXZ basis sets at MP2 level of theory. The letter labels indicate different basis sets: A - aug-cc-pVDZ; B - aug-cc-pVTZ; C - aug-cc-pVQZ; and D - aug-cc-pV5Z.

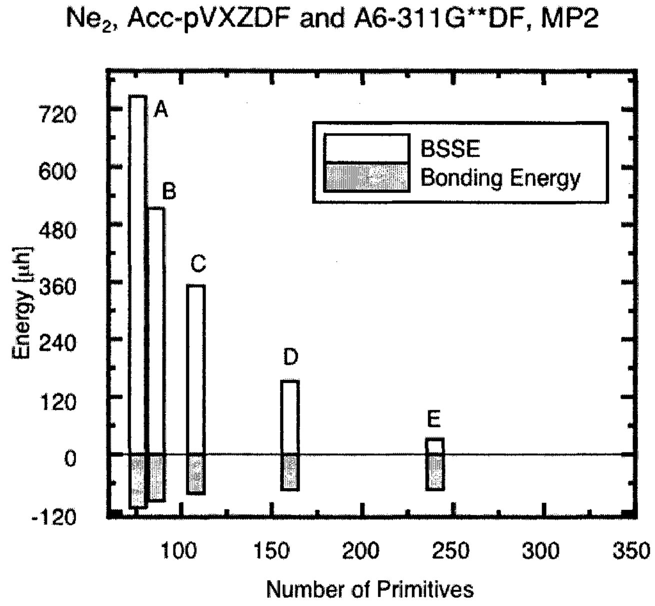


Figure 2.17. BSSE-corrected bonding energy and BSSE for Ne_2 computed with Acc-pVXZDF and A6-311G**DF basis sets at MP2 level of theory. Orbital coefficients of augmenting functions are optimized with respect to the Ne_2 BSSE-corrected bonding energy at MP2 level. The letter labels indicate different basis sets: A - Acc-pVDZDF; B - A6-311G**DF; C - Acc-pVTZDF; D - Acc-pVQZDF; and E - Acc-pV5ZDF.

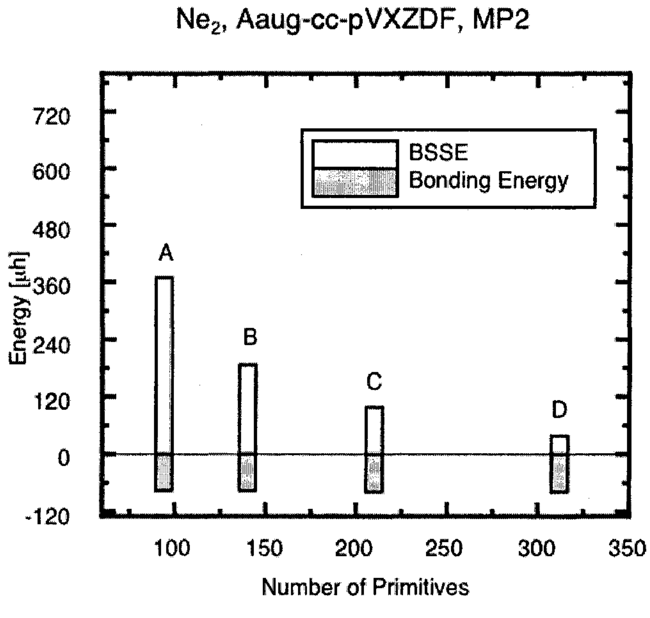


Figure 2.18. BSSE-corrected bonding energy and BSSE for Ne_2 computed with Aaug-cc-pVXZDF basis sets at MP2 level of theory. Orbital coefficients of augmenting functions are optimized with respect to the Ne_2 BSSE-corrected bonding energy at MP2 level. The letter labels indicate different basis sets: A - Aaug-cc-pVDZDF; B - Aaug-cc-pVTZDF; C - Aaug-cc-pVQZDF; and D - Aaug-cc-pV5ZDF.

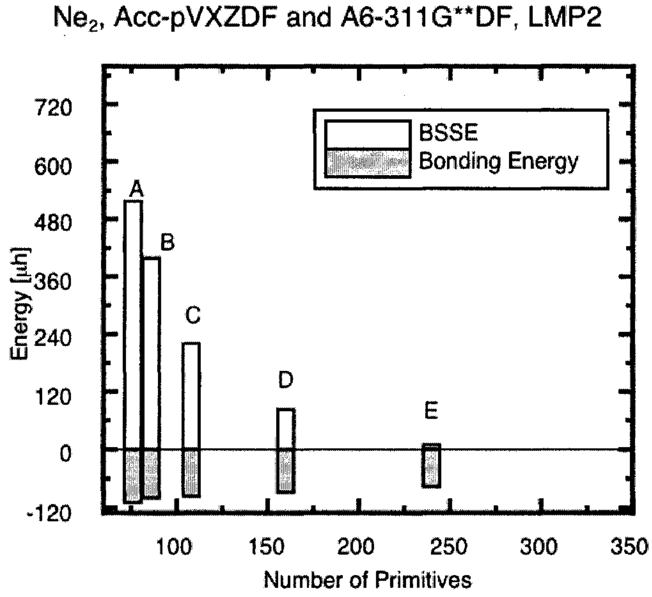


Figure 2.19. BSSE-corrected bonding energy and BSSE for Ne_2 computed with Acc-pVXZDF and A6-311G**DF basis sets at LMP2 level of theory. Orbital coefficients of augmenting functions are optimized with respect to the Ne_2 BSSE-corrected bonding energy at MP2 level. The letter labels indicate different basis sets: A - Acc-pVDZDF; B - A6-311G**DF; C - Acc-pVTZDF; D - Acc-pVQZDF; and E - Acc-pV5ZDF.

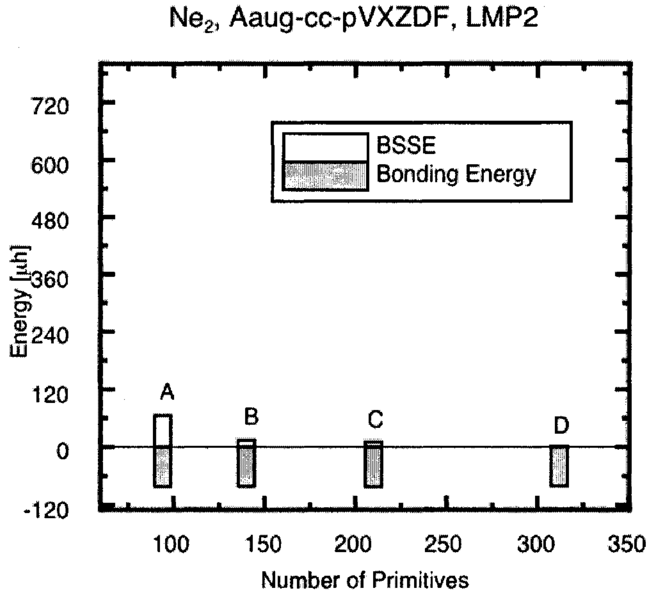


Figure 2.20. BSSE-corrected bonding energy and BSSE for Ne_2 computed with Aaug-cc-pVXZDF basis sets at LMP2 level of theory. Orbital coefficients of augmenting functions are optimized with respect to the Ne_2 BSSE-corrected bonding energy at MP2 level. The letter labels indicate different basis sets: A - Aaug-cc-pVDZDF; B - Aaug-cc-pVTZDF; C - Aaug-cc-pVQZDF; and D - Aaug-cc-pV5ZDF.

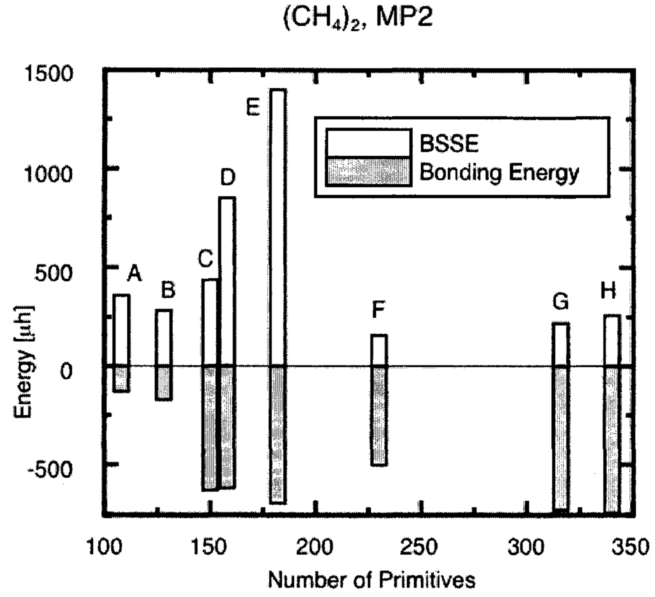


Figure 2.21. BSSE-corrected bonding energy and BSSE for $(CH_4)_2$ computed with a mixture of standard and augmented basis sets at MP2 level of theory. Orbital coefficients of augmenting functions on carbon are optimized with respect to the $(CH_4)_2$ BSSE-corrected bonding energy at MP2 level, hydrogen basis set is not augmented. The letter labels indicate different basis sets: A - cc-pVDZ; B - 6-311G**; C - A6-311G**DF; D - aug-cc-pVDZ; E - Aaug-cc-pVDZDF; F - cc-pVTZ; G - aug-cc-pVTZ; and H - Aaug-cc-pVTZDF.

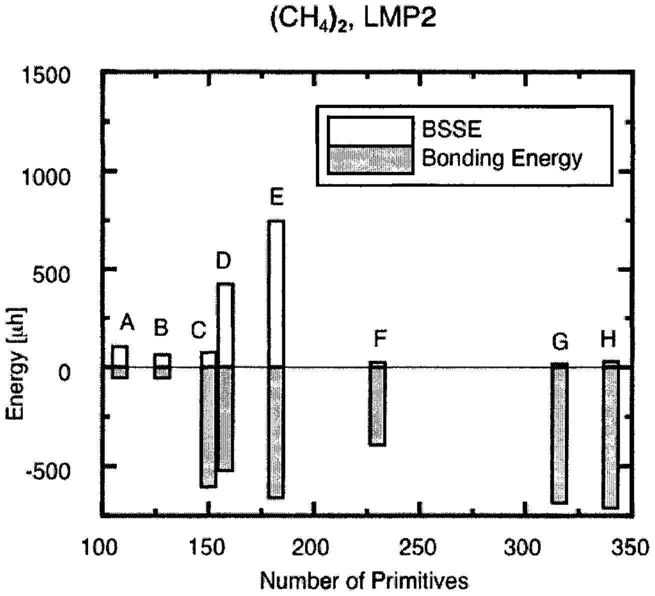


Figure 2.22. BSSE-corrected bonding energy and BSSE for $(CH_4)_2$ computed with a mixture of standard and augmented basis sets at LMP2 level of theory. Orbital coefficients of augmenting functions on carbon are optimized with respect to the $(CH_4)_2$ BSSE-corrected bonding energy at MP2 level, hydrogen basis set is not augmented. The letter labels indicate different basis sets: A - cc-pVDZ; B - 6-311G**; C - A6-311G**DF; D - aug-cc-pVDZ; E - Aaug-cc-pVDZDF; F - cc-pVTZ; G - aug-cc-pVTZ; and H - Aaug-cc-pVTZDF.

DISCUSSION

Overall, our calculations show that both tessellated and augmented basis sets are able to describe bonding in the weakly bound systems we tested - $^3H_2$, Ne_2 and $(CH_4)_2$. The fraction of recovered bonding energy in these dimers roughly scales with the number of augmenting or tessellating functions, irrespective of their type; however, tessellated basis sets have a larger BSSE than augmented basis sets, and they are also more linearly dependent. Additionally, augmented basis sets are much easier to use in conventional electronic structure codes, because one does not need to set up ghost centers for monomer and dimer calculations. Augmented basis sets seem to be more desirable and efficient for use in calculations of intermolecular interactions.

In this section we discuss a number of general issues that arise from the above studies of the calculation of intermolecular interactions for $^3H_2$, Ne_2, and $(CH_4)_2$. In so doing, we will focus on tessellation and augmentation of basis sets, BSSE, and linear dependence problems associated with basis sets.

Further considerations on tessellation

The original proposal of the tessellation approach was motivated by the idea that integrals over s functions are simpler and faster to evaluate than those over the higher angular momentum functions.[15] Therefore, one would expect that tessellating space around the nucleus with a large number of s functions optimized to describe intermolecular interactions rather than augmenting the nucleus centered basis set with higher angular momentum functions should result in substantial computational savings and make the computation of intermolecular interactions more accessible. This hypothesis has, however, two flaws. First, placing a number of s basis functions in close proximity causes a severe linear dependency problem. Second, although it is true that individual two-electron integrals over s basis functions are simpler and therefore faster to evaluate than a single two-electron integral over functions with higher angular momentum, this simplification does not obtain for the modern computation of integrals involving large number of functions.

In modern two-electron integral codes, the calculation of integrals is done in batches. An integral batch consists of all the integrals for a unique combination of four shells. The number of integrals in each batch depends on the number of functions in each shell. For example, an (ss|ss) batch consists of only one integral, a batch (dp|ds) has a total of 75 or 108 integrals since it involves a d shell with 5 (or 6) components, a p shell with 3 components and an s shell with 1 component. Calculation of integrals in the batches allows for intermediate quantities to be computed and reused for many integrals within the batch, thereby avoiding their recalculation. This reduces the number of arithmetic operations needed per uncontracted integral within the batch and causes a relative increase in computational cost for integrals involving low quantum numbers such as (ss|ss) batches, because the cost of setting up each batch (which is quantum number independent) is divided over 81 possible integrals in a (pp|pp) batch, but carried by only one integral in an (ss|ss) batch.[54]

We have performed some timing tests using the computational package Molpro 2000.1,[42] which implements a very efficient scheme for calculation of two electron integrals.[55] As our test system we used the methane molecule with the modified 10s Huzinaga basis set on hydrogen and s, p functions from cc-pV6Z basis set on carbon. We have augmented the carbon and hydrogen basis sets with an increasing number of s, p, and d functions and compared the timings for computation of two electron integrals for these basis sets. For up to about 15 additional primitives the angular momentum dependence of the timing is insignificant. For more than 15 additional functions there is a clear impact of angular momentum. Up to about 30 additional functions, the time needed for calculation of two electron integrals is smallest for basis sets augmented with p functions, and longest for basis sets augmented with d functions. For more than 30 additional functions timings for basis sets augmented with p functions were still the fastest, followed by basis sets augmented with d functions, and finally basis sets augmented with s functions. For example, for basis sets augmented with 45 functions, the time for the computation of two electron integrals for p augmentation functions was half that of s functions.

Tessellation could still be viable if a specific (ss|ss) code were implemented or if p functions were used for tessellation. More efficient implementation of the s integral code or the use of p functions instead of s functions might not, however, bring the desired cost benefit since it seems that a relatively small number of tessellating functions is able to recover a substantial portion of the bonding energy. Moreover, one would still need to deal with the significant linear dependency problem.

Another issue is the relationship between tessellating and bond functions. Bond functions are auxiliary functions centered at the bond midpoints added to standard basis sets to improve the description of intermolecular interactions. The exponents of bond functions are chosen to maximize the correlation contribution to the bonding energy, but at the same time to keep the change in the Hartree-Fock interaction energy minimal. A set of {3s3p2d} bond functions with fixed exponents was found very useful to describe bonding in a variety of van der Waals systems. For a recent review of bond functions see reference 30.

The basic idea behind the use of tessellating functions is therefore very similar to that of bond functions. Both are off-centered and extend standard basis sets; however, some inherent differences between the two approaches exist. For example, due to their construction, bond functions cannot be associated with a particular molecule or atom in the weakly bound complex, so they can not be used to describe bond dissociation potential curves. Tessellating functions, on the other hand, are directly associated with a particular atom. Also since tessellating functions are placed symmetrically around the nucleus they do not bias the basis sets in certain directions. To test whether each of the tessellating functions makes a contribution to the dimer bonding energy and not just those that extend in the bond direction, we have run test calculation on Ne_2 using portions of the Tspd-cc-pV6ZP$_V$ basis set. Figure 2.23 shows the labeling scheme and results are summarized in Table 2.2. Although the functions in the bond region make a larger contribution to the neon dimer bonding energy, other functions contribute as well. The presence of these non-bond functions also somewhat reduces the BSSE.

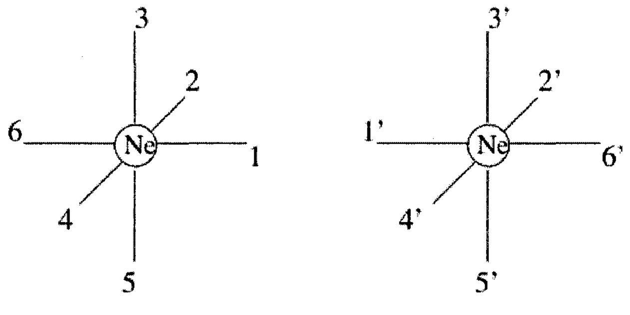


Figure 2.23. Ne_2 with indicated positions of tessellating functions in the vertices of octahedron.

Tessellating Functions Used	Bonding Energy [μh]	BSSE [μh]
1-6, 1'-6'	-72.05	85.84
1, 1'	-67.96	152.39
1-5, 1'-5'	-71.84	96.37
2-5, 2'-5'	-56.25	31.06
2-6, 2'-6'	-59.00	33.95
6, 6'	-37.54	16.77
no tessellation	-32.91	8.62

Table 2.2. Bonding energies and BSSE for Ne_2. Energies and BSSE are computed on MP2 level of theory with spd-cc-pV6Z basis set tessellated with p functions situated in different positions of the vertices of octahedron. Numbers in the first column denote tessellating functions present in the basis set, for more detailed description see Figure 2.23.

Augmentation

Augmenting standard basis sets with d and f functions significantly improves computed bonding energies of van der Waals systems. LMP2 is effective in reducing BSSE, and the reduction is most apparent with larger basis sets for which BSSE arises primarily at the correlated level. It is difficult to assess which of the standard basis sets is the most suited for such augmentation in terms of the computational cost and quality of the calculation. Among the basis sets tested, Aaug-cc-pVDZDF is the most efficient for Ne_2. For methane dimer, the A6-311G**DF basis set is the most efficient. Suitability of a particular basis for one system does not imply the suitability of this basis set for a different van der Waals system. For example, while A6-311G**DF basis set performs well for the methane dimer, it would not be our first choice for Ne_2 due to the overestimation of the Ne_2 bonding energy. Therefore, augmentation of medium-sized basis sets such as 6-311G** or aug-cc-pVDZ should always proceed with caution, especially when confronting a new system, one for which little or no data are available. Use of aug-cc-pVTZ or larger basis sets is desirable for more accurate results. If calculation with a larger basis set is prohibitive, medium size basis sets can be quite useful in obtaining qualitative insights into the behavior of new systems.

Basis Set Superposition Error

Basis set superposition error (BSSE) has been known for a long time to hamper the computation of intermolecular interactions. BSSE arises from incompleteness in the basis set of the monomers; in the dimer calculation, monomers use each other's basis functions to improve their energies and thus artificially lower the energy of the dimer. For a review of BSSE literature see refs. 7, 8 and references therein.

Several schemes can be used to remove the BSSE from calculations. A posteriori schemes (such as counterpoise correction) remove BSSE after the supermolecular calculation has been completed, and a priori schemes (e.g., Chemical Hamiltonian) aim to remove the BSSE from the computational model. For example, in the Chemical Hamiltonian approach (CHA), BSSE effects are removed by modifying the one-electron Hamiltonian in a manner that ensures that free monomer wavefunctions remain unchanged in the extended basis set used for supermolecular calculation.[56, 57] CHA has been successfully used at the SCF, DFT and MP2 level of theory. The drawback of the method is that the CHA Hamiltonian is non-Hermitian and its applicability to different levels of theory is nontrivial. Other examples of a priori schemes for removal of BSSE are the method of Self-Consistent Field for Molecular Interaction for two and multi-component systems,[58-60] Constrained Dimer Function approach,[61] Strictly Monomer Molecular Orbital SCF approach,[62] and the method of Muguet and Robinson that attempts to remove BSSE using a specific localization scheme for Hartree-Fock molecular orbitals.[63]

The most popular scheme for BSSE correction is the a posteriori counterpoise (CP) correction proposed independently by Jansen and Ross[13] and Boys and Benardi.[14] The basic idea is to correct inconsistency in the basis set by using exactly same set of functions for computation of monomer, as well as, dimer properties; that is, calculation on one monomer is done in the presence of basis functions of the other monomer. The complete set of basis functions used for calculation of the dimer is often called dimer centered basis set, and the set of basis functions used for the monomer is called the monomer centered basis set. CP correction scheme is in principle very simple and applicable at any level of theory using conventional quantum chemistry codes.

Much discussion is found in the literature concerning the accuracy of the CP procedure and alternative approaches, such as the virtual-only counterpoise procedure[64] and a variety of a priori approaches mentioned earlier, are suggested. Currently, the CP procedure is widely accepted as a useful tool for eliminating most of the BSSE, some even claim that the CP correction rigorously eliminates BSSE in a supermolecular calculation for closed-shell fragments.[8] Our experience with computing bonding energies of van der Waals dimers at the MP2 level of theory with augmented and tessellated basis sets suggests that although the CP correction is very accurate, it does not necessarily remove BSSE completely. This is especially noticeable in our calculations for Ne_2 with tessellated and augmented 6-311G** basis sets (see Figures 2.9 and 2.10). These basis sets have very large BSSE compared to tessellated or augmented spd-cc-pV6Z (Figures 2.11 and 2.12) with the same number of extending functions. They also overestimate bonding energies. This overestimation is caused by a portion of the BSSE that is not corrected by the CP procedure. Counter to this interpretation is the relatively large Tspd-cc-pV6ZP$_v^{2}_f$ basis set's MP2 BSSE of 846.37 μh and a bonding energy of -81.89 μh, while the smaller A6-311G**DF basis set has a MP2 BSSE of 513.54 μh and a bonding energy of -97.07 μh. In this particular case, the basis set with smaller BSSE overestimates the bonding energy while the basis set with the larger BSSE does not. (Note that the best available calculation at the MP2 level of theory gives -84.5 μh for Ne_2 bonding energy.[17]) Interestingly, a large part of the BSSE for the A6-311G**DF basis set, about 300 μh, arises at the Hartree-Fock (HF) level, while BSSE with Tspd-cc-pV6ZP$_v^{2}_f$ basis set arises almost exclusively at the correlated level (BSSE at HF level is 1 μh). Therefore we speculate that the large BSSE already present at the HF level indicates an imbalanced basis set and a possible (very small) undercorrection of BSSE by the CP procedure.

Another way to remove BSSE partially is to use local correlation methods such as local MP2 (LMP2).[65-68] Removal of BSSE is a byproduct of these methods, their primary purpose being the reduction of computational cost associated with the treatment of electron correlation. Reduction in computational cost is achieved in two ways: 1. pair correlation between the distant orbitals is neglected (or, alternatively, this correlation is treated at a lower level); and 2. virtual space for a given pair is restricted to a subset of atomic orbitals localized in the spatial vicinity of the correlated pair. Restriction of the virtual space also prevents basis functions located on distant centers from contributing with their tails to improve basis set flexibility and as a result, the BSSE is reduced.[69, 70] While local correlation methods will eliminate incremental BSSE arising at the correlated level, they do not impact HF level BSSE.

The positive effect of the LMP2 method on BSSE is also confirmed in this work. Nine different basis sets, aug-cc-pVXZ, aug-cc-pVXZ (X = D, T, Q, 5), and 6-311G**, are augmented with a set of p and d functions optimized with respect to the Ne_2 intermolecular bonding energy at the MP2 level of theory. Figures 2.17-2.20 show Ne_2 bonding energies as well as BSSE for these basis sets computed at the MP2 and LMP2 theory level. The effect of LMP2 on the bonding energy is relatively small - LMP2 bonding energies are between 97-119% of MP2 bonding energies indicating that augmented basis sets are almost saturated with respect to the intermolecular interaction. The impact of LMP2 on BSSE is significant – BSSE computed with the LMP2 method is reduced to 5-78% of the BSSE computed at the MP2 level of theory. LMP2 has an especially favorable effect when used with the augmented aug-cc-pVXZ series, in which BSSE is reduced to 5-18% of the BSSE computed with MP2.

Similar results are obtained for a mixture of standard (cc-pVDZ, 6-311G**, aug-cc-pVDZ, cc-pVTZ, aug-cc-pVTZ) and augmented (A6-311G**DF, Aaug-cc-VDZDF, Aaug-cc-pVTZDF) basis sets for the methane dimer. Figures 2.21 and 2.22 show methane dimer bonding energies and BSSE computed at the MP2 and LMP2 levels of theory with the above basis sets. Two small standard basis sets (cc-pVDZ, 6-311G**) experience a significant reduction in bonding energy as well as BSSE: LMP2 bonding energy is 32-41% of the MP2 bonding energy and LMP2 BSSE is 23-30% of the MP2 BSSE. Bonding energies computed with all other basis sets are not significantly affected (LMP2 recovers between 85-96% of the MP2 bonding energy), while BSSE is substantially reduced (BSSE computed at the LMP2 level of theory is between 9-53% of the MP2 BSSE).

One could also mitigate BSSE by using large, almost complete basis sets. Unfortunately, this approach is costly in terms of the computational time which scales with the number of basis functions N as N^4 or N^6 for correlated methodologies. Moreover, this approach creates linear dependency problems which are discussed next.

Linear Dependence

Calculations performed with large basis sets, especially those containing diffuse functions or those with several closely spaced sets of off-centered functions, often suffer from numerical instabilities due to linear dependency (i.e., two or more functions spanning almost the same physical space). This problem has been known to arise for calculations on periodic systems,[71] calculations using a large set of bond functions,[72] and is also observed for tessellated basis sets.

Two main problems exist for nearly linearly dependent basis sets, one at the HF level and the other for correlated calculations. Solution of the HF equations typically involves construction of an orthogonalizing transformation matrix $\mathbf{S}^{-1/2}$ (**S** is an overlap matrix). For near linear dependence in the basis set, eigenvalues of the **S** matrix will approach zero and construction of $\mathbf{S}^{-1/2}$ involves dividing by quantities that are nearly zero. $\mathbf{S}^{-1/2}$ becomes almost singular, leading to problems in numerical precision. Near linear dependence also leads to very large molecular orbital (MO) coefficients for virtual orbitals. This is problematic for correlated calculations that require transformed integrals. For example, if a MO coefficient is 1000, the product of four such coefficients is 10^{12}. Since two-electron integrals are at best evaluated to an accuracy of 10^{-14}, the transformed integrals will have very large numerical errors and the resulting energies may behave abnormally.

Only a few publications in the literature discuss linear dependence or near linear dependence and the ways to avoid it.[71-73] The severity of this problem is usually measured by the size of the smallest eigenvalue of the overlap matrix **S**. The smaller the eigenvalue, the greater the linear dependence. Serious numerical instabilities arise when the eigenvalues are of the order 10^{-8} or smaller, although sometimes even larger eigenvalues (of the order 10^{-7}, 10^{-6}) generate unreliable results depending on the computational method used.

One way to deal with near linear dependence is to simply omit one or more of the most diffuse basis functions from the basis set, or alternatively omit linear combinations of basis functions that correspond to small eigenvalues of the overlap matrix. Some quantum chemical program packages (e. g., Gaussian) do this automatically for the user. This approach works very well in most cases, but can cause spurious results when applied to the calculation of intermolecular interactions using the supermolecular approach. To compute the bonding energy by the supermolecular method, one usually computes the energy of monomers using a monomer centered basis set and the energy of dimer with dimer centered basis set. This inconsistency in the basis is the cause of BSSE when one uses unsaturated basis sets (see the discussion in the previous section) and is usually not considered to be an issue in calculations using large, almost saturated basis sets. If the basis sets used in a computation are nearly linearly dependent, different linear combinations of basis functions may be deleted from the monomer and dimer centered basis sets making the calculation inconsistent and the computed bonding energies no longer reliable.

This problem can be somewhat alleviated by using the dimer centered basis set for calculations on the monomer in the same way one uses the dimer centered basis set to compute counterpoise corrections. This ensures that the same basis set is used in both monomer and dimer calculations and therefore that the same linear combinations corresponding to small eigenvalues of the **S** matrix are deleted by the program. The bonding energy computed from such a calculation might be smaller than expected, since the basis functions removed by the program are not completely redundant and do provide contribution to the bonding energy of the system. Alternatively, one could turn off the automatic removal of the basis functions by the program and risk the unreliability of a numerically unstable calculation resulting from the nearly linearly dependent basis set. Obviously, it would be best to avoid using linearly dependent basis sets altogether.

One is often tempted to believe that using faster computers, parallel processing, larger disk space, and computer memory will help push computational limits further, by enabling calculations at higher levels of theory with larger basis sets. In reality, this is a rather oversimplified view. Gaussian basis sets that have been used in quantum mechanical computations for the past fifty years with great success suffer from one serious shortcoming: a large number of gaussian functions is required to describe systems with high levels of accuracy, especially for calculations of nonbonded interactions for which dispersion plays an important role. For example, one of the most accurate computations of $(NH_3)_2$ at the MP2 level of theory used 1024 basis functions.[74] Our largest computation on methane dimer with the Tspd-cc-pV6ZP$_v$ basis set on carbon and

$THuzP_v$ basis set on hydrogen uses a total of 466 primitives and the smallest eigenvalue of the **S** matrix is 10^{-7}. The methane dimer basis set could still be extended to give more accurate description of the system, but due to the problems with linear dependence as well as the computational cost we feel that using more than 500 primitives is not advisable. In general, due to the fact that gaussian basis functions are not orthogonal, increasing the number of gaussian functions in a basis set leads to near linear dependency which causes the computation to be numerically unstable. We believe that learning how to deal with the problem of linear dependence in the basis set, whether at the programming level (by finding more efficient ways to treat numerical instabilities) or modeling level (by discovering functions with better spatial properties to replace gaussians) is one of the challenges computational chemistry faces in future years.

CONCLUSION

In this work the role of basis sets in ab initio calculations of intermolecular interactions is explored. The focus of this study is on three systems in which dispersion interactions dominate - $^3H_2$, Ne_2 and $(CH_4)_2$.

Standard basis sets are augmented and tessellated with functions optimized with respect to the BSSE-corrected intermolecular bonding energy of each system. Relatively few tessellating or augmenting functions recover a significant portion of the intermolecular bonding energy. To obtain reliable results, both tessellated and augmented basis sets require underlying standard basis sets that provide a good description of the core and valence electrons. Tessellated basis sets with a large number of s functions do not offer an advantage in terms of the computational speed in comparison with the use of higher angular momentum atom-centered functions. Augmented atom-centered basis sets are less linearly dependent and easier to work with than tessellated basis sets, and therefore more desirable for use in the calculations.

Our results further suggest that the counterpoise correction, applied to the closed shell van der Waals clusters at the MP2 level of theory is very accurate, removing nearly all BSSE, although it is not exact. LMP2 theory is efficient in removing that portion of the BSSE that arises at the correlated level.

Linear dependence of the basis sets is a real problem for the accurate ab initio calculation of intermolecular interactions and we believe more attention needs to be focused on solving this fundamental issue. Current approaches to eliminating linear dependencies from basis sets do so by deleting a linear combination of basis functions corresponding to the smallest eigenvalues of the overlap matrix **S.** This approach inadvertently causes supermolecular calculations to be inconsistent because different combinations of functions may be deleted from monomer and dimer basis sets. Therefore, it is recommended that the same set of functions (i.e., the dimer centered basis set) be used for calculations on both monomer and dimer, even if the monomer basis set is saturated. The use of dimer centered basis sets in all calculations will ensure the removal of the same sets of functions for each calculation.

Overall, at present no shortcut exists to reliable computation of intermolecular interactions.

REFERENCES

1. Szalewicz, K.; Jeziorski, B., Symmetry-Adapted Perturbation Theory of Intermolecular Interactions. In *Molecular Interactions*, Sheiner, S., Ed. Wiley: Chichester, England, 1997; p 1.
2. Chalasinski, G.; Szczesniak, M. M., State of the art and challenges of the ab initio theory of intermolecular interactions. *Chemical Reviews* **2000,** 100, (11), 4227-4252.
3. Kohn, W.; Meir, Y.; Makarov, D. E., vanderWaals energies in density functional theory. *Physical Review Letters* **1998,** 80, (19), 4153-4156.
4. Perez-Jorda, J. M.; Becke, A. D., A Density-Functional Study of Van-Der-Waals Forces - Rare-Gas Diatomics. *Chemical Physics Letters* **1995,** 233, (1-2), 134-137.
5. Cybulski, S. M.; Seversen, C. E., Critical examination of the supermolecule density functional theory calculations of intermolecular interactions. *Journal of Chemical Physics* **2005,** 122, (1).
6. Kestner, N. R., He-He Interaction in Scf-Mo Approximation. *Journal of Chemical Physics* **1968,** 48, (1), 252-&.
7. Liu, B.; McLean, A. D., Accurate Calculation of Attractive Interaction of Two Ground-State Helium-Atoms. *Journal of Chemical Physics* **1973,** 59, (8), 4557-4558.
8. van Duijneveldt, F. B., Basis Set Superposition Error. In *Molecular Interactions*, Sheiner, S., Ed. Wiley: Chichester, England, 1997; p 81.
9. Kestner, N. R.; Combariza, J. E., Basis Set Superposition Error: Theory and Practice. In *Reviews in Computational Chemistry*, Lipkowitz, K. B.; Boyd, D. B., Eds. Wiley-VCH: 1999; Vol. 13, p 99.
10. van Lenthe, J. H.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Duijneveldt, F. B., In Advances in Chemical Physics, 1987; Vol. 69, p 521.
11. Gutowski, M.; Chalasinski, G., Critical evaluation of some computational approaches to the problem of basis set superposition error. *Journal of Chemical Physics* **1992,** 98, (7), 5540-5554.
12. van Duijneveldt, F. B.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Lenthe, J. H., State-of-the-Art in Counterpoise Theory. *Chemical Reviews* **1994,** 94, (7), 1873-1885.
13. Jansen, H. B.; P., R., Non-empirical molecular orbital calculations on the protonation of carbon monoxide. *Chemical Physics Letters* **1969,** 3, (3), 140-143.
14. Boys, F.; Benardi, F., The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. *Molecular Physics* **1970,** 19, (4), 553 - 566.
15. Rappe, A. K.; Bernstein, E. R., Ab initio calculation of nonbonded interactions: Are we there yet? *Journal of Physical Chemistry A* **2000,** 104, (26), 6117-6128.
16. Dunning, T. H., A road map for the calculation of molecular binding energies. *Journal of Physical Chemistry A* **2000,** 104, (40), 9062-9080.
17. Woon, D. E., Benchmark Calculations with Correlated Molecular Wave-Functions .5. the Determination of Accurate Ab-Initio Intermolecular Potentials for He-2, Ne-2, and Ar-2. *Journal of Chemical Physics* **1994,** 100, (4), 2838-2850.
18. Novoa, J. J.; Planas, M.; Rovira, M. C., On the usefulness of the counterpoise method on hydrogen-bonded complexes: A numerical test using near complete basis sets on H2O...HF, (H2O)(2), (HF)(2) and CH4...H2O. *Chemical Physics Letters* **1996,** 251, (1-2), 33-46.

19. Chalasinski, G.; Szczesniak, M. M., Origins of Structure and Energetics of Van-Der-Waals Clusters from Ab-Initio Calculations. *Chemical Reviews* **1994,** 94, (7), 1723-1765.

20. Tsuzuki, S.; Uchimaru, T.; Mikami, M.; Tanabe, K., Basis set effects on the calculated bonding energies of neutral benzene dimers: Importance of diffuse polarization functions. *Chemical Physics Letters* **1996,** 252, (3-4), 206-210.

21. Woon, D. E.; Dunning, T. H., Gaussian-Basis Sets for Use in Correlated Molecular Calculations .4. Calculation of Static Electrical Response Properties. *Journal of Chemical Physics* **1994,** 100, (4), 2975-2988.

22. Sadlej, A. J., Medium-Size Polarized Basis-Sets for High-Level Correlated Calculations of Molecular Electric Properties. *Collection of Czechoslovak Chemical Communications* **1988,** 53, (9), 1995-2016.

23. Sadlej, A. J., Medium-Size Polarized Basis-Sets for High-Level-Correlated Calculations of Molecular Electric Properties .2. 2nd-Row Atoms - Si through Cl. *Theoretica Chimica Acta* **1991,** 79, (2), 123-140.

24. Sadlej, A. J., Medium-Size Polarized Basis-Sets for High-Level-Correlated Calculations of Molecular Electric Properties .5. 4th-Row Atoms - Sn through I. *Theoretica Chimica Acta* **1992,** 81, (4-5), 339-354.

25. Kello, V.; Sadlej, A. J., Medium-Size Polarized Basis-Sets for High-Level-Correlated Calculations of Molecular Electric Properties .6. 5th-Row Atoms - Pb through At. *Theoretica Chimica Acta* **1992,** 83, (5-6), 351-366.

26. Tsuzuki, S.; Uchimaru, T.; Mikami, M.; Tanabe, K., New medium-size basis sets to evaluate the dispersion interaction of hydrocarbon molecules. *Journal of Physical Chemistry A* **1998,** 102, (12), 2091-2094.

27. van Duijneveldt-van de Rijdt, J.; van Duijneveldt, F. B., Interaction optimized basis sets for correlated ab initio calculations on the water dimer. *Journal of Chemical Physics* **1999,** 111, (9), 3812-3819.

28. Tao, F. M., On the Use of Bond Functions in Molecular Calculations. *Journal of Chemical Physics* **1993,** 98, (3), 2481-2483.

29. Tao, F. M., A New Approach to the Efficient Basis-Set for Accurate Molecular Calculations - Applications to Diatomic-Molecules. *Journal of Chemical Physics* **1994,** 100, (5), 3645-3650.

30. Tao, F. M., Bond functions, basis set superposition errors and other practical issues with ab initio calculations of intermolecular potentials. *International Reviews in Physical Chemistry* **2001,** 20, (4), 617-643.

31. Tao, F. M.; Pan, Y. K., An Accurate Abinitio Calculation of the Ne2 Potential. *Chemical Physics Letters* **1992,** 194, (3), 162-166.

32. Neumark, G. F. Columbia University, New York, 1951.

33. Kimball, G. E.; Neumark, G. F., Use of Gaussian Wave Functions in Molecular Calculations. *Journal of Chemical Physics* **1957,** 26, (5), 1285-1287.

34. Frost, A. A., The Floating Spherical Gaussian Orbital Method. In *Methods of Electronic Structure Theory*, Schaefer, H. F., III, Ed. Plenum: New York, NY, 1977; Vol. 3, p 29.

35. Archibald, R. M.; Perkins, P. G.; Armstrong, D. R., Molecular Calculations Using Spherical Gaussian Orbitals. 1. Optimization of Atomic Parameters for First-Row Atoms. *Journal of the Chemical Society-Faraday Transactions II* **1974,** 70, (9), 1557-1569.

36. Spangler, D.; Christoffersen, R. E., Development of Basis Sets for Molecular Calculations - Comparison of Tetrahedral Gaussian Lobe Functions and Cartesian Gaussian Basis Sets. *International Journal of Quantum Chemistry* **1978**, 127-135.

37. Pakiari, A. H., The Reconciliation of Fsgo and Scf Methods, and Evaluation of the Hartree-Fock Energy Limit by Using Entirely the Fsgo Method. *Theochem-Journal of Molecular Structure* **1995,** 331, (1-2), 155-167.

38. Pakiari, A. H.; Keshavarz, M. H., Description of a Pi-System Using the Floating Spherical Gaussian Orbital Method. *Theochem-Journal of Molecular Structure* **1995,** 337, (2), 155-160.

39. Whitten, J. L., Gaussian Expansion of Hydrogen-Atom Wavefunctions. *Journal of Chemical Physics* **1963,** 39, (2), 349-&.

40. Whitten, J. L., Gaussian Lobe Function Expansions of Hartree-Fock Solutions for First-Row Atoms and Ethylene. *Journal of Chemical Physics* **1966,** 44, (1), 359-&.

41. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J. W.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98, Revision A.7*, Gaussian, Inc.: Pittsburgh PA, 1998.

42. Werner, H. J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schutz, M.; Celani, P.; T., K.; Rauhut, G.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Lloyd, A. W.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Schumman, U.; Stoll, H.; Stone, A. J.; Tarroni, A.; Thornsteinsson, T. *MOLPRO, a package of ab initio programs*, 2000.1 and 2002.6.

43. Huzinaga, S., Gaussian-Type Functions for Polyatomic Systems .I. *Journal of Chemical Physics* **1965,** 42, (4), 1293-&.

44. Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A., Self-Consistent Molecular-Orbital Methods .20. Basis Set for Correlated Wave-Functions. *Journal of Chemical Physics* **1980,** 72, (1), 650-654.

45. Kolos, W.; Wolniewicz, L., Potential-Energy Curves for the X 1Sigma_g⁺, b3Sigma_u⁺, and C 1Piu States of the Hydrogen Molecule. *Journal of Chemical Physics* **1965,** 43, (7), 2429-2441.

46. Wilson, A. K.; vanMourik, T.; Dunning, T. H., Gaussian basis sets for use in correlated molecular calculations .6. Sextuple zeta correlation consistent basis sets for boron through neon. *Journal of Molecular Structure-Theochem* **1996,** 388, 339-349.

47. Aziz, R. A.; Slaman, M. J., The Ne-Ne Interatomic Potential Revisited. *Chemical Physics* **1989,** 130, (1-3), 187-194.

48. Matthews, G. P.; Smith, E. B., Intermolecular Pair Potential-Energy Function for Methane. *Molecular Physics* **1976,** 32, (6), 1719-1729.

49. Reid, B. P.; Oloughlin, M. J.; Sparks, R. K., Methane-Methane Isotropic Interaction Potential from Total Differential Cross-Sections. *Journal of Chemical Physics* **1985,** 83, (11), 5656-5662.

50. Bohm, H. J.; Ahlrichs, R.; Scharf, P.; Schiffer, H., Intermolecular Potentials for Ch4, Ch3f, Chf3, Ch3cl, Ch2cl2, Ch3cn and Co2. *Journal of Chemical Physics* **1984,** 81, (3), 1389-1395.

51. Dunning, T. H., Gaussian-Basis Sets for Use in Correlated Molecular Calculations .1. the Atoms Boron through Neon and Hydrogen. *Journal of Chemical Physics* **1989,** 90, (2), 1007-1023.

52. Kendall, R. A.; Dunning, T. H.; Harrison, R. J., Electron-Affinities of the 1st-Row Atoms Revisited - Systematic Basis-Sets and Wave-Functions. *Journal of Chemical Physics* **1992,** 96, (9), 6796-6806.

53. Woon, D. E.; Dunning, T. H., Gaussian-Basis Sets for Use in Correlated Molecular Calculations .3. the Atoms Aluminum through Argon. *Journal of Chemical Physics* **1993,** 98, (2), 1358-1371.

54. Hegarty, D., Evaluation and Processing of Integrals. In *Advanced Theories and Computational Approaches to the Electronic Structure of Molecules.*, Dykstra, C. E., Ed. D. Reidel Publishing: Dordrecht, Holland, 1984; Vol. 133, p 39.

55. Lindh, R.; Ryu, U.; Liu, B., The Reduced Multiplication Scheme of the Rys Quadrature and New Recurrence Relations for Auxiliary Function Based 2-Electron Integral Evaluation. *Journal of Chemical Physics* **1991,** 95, (8), 5889-5897.

56. Mayer, I., The chemical Hamiltonian approach for treating the BSSE problem of intermolecular interactions. *International Journal of Quantum Chemistry* **1998,** 70, (1), 41-63.

57. Mayer, I.; Valiron, P., Second order Moller-Plesset perturbation theory without basis set superposition error. *Journal of Chemical Physics* **1998,** 109, (9), 3360-3373.

58. Gianinetti, E.; Raimondi, M.; Tornaghi, E., Modification of the Roothaan equations to exclude BSSE from molecular interaction calculations. *International Journal of Quantum Chemistry* **1996,** 60, (1), 157-166.

59. Gianinetti, E.; Vandoni, I.; Famulari, A.; Raimondi, M., Extension of the SCF-MI method to the case of K fragments one of which is an open-shell system. In *Advances in Quantum Chemistry, Vol 31: Quantum Systems in Chemistry and Physics, Pt I*, 1999; Vol. 31, pp 251-266.

60. Nagata, T.; Takahashi, O.; Saito, K.; Iwata, S., Basis set superposition error free self-consistent field method for molecular interaction in multi-component systems: Projection operator formalism. *Journal of Chemical Physics* **2001,** 115, (8), 3553-3560.

61. Sadlej, A. J., Exact Perturbation Treatment of the Basis Set Superposition Correction. *Journal of Chemical Physics* **1991,** 95, (9), 6705-6711.

62. Cullen, J. M., *International Journal of Quantum Chemistry* **1991,** S25, 193.

63. Muguet, F. F.; Robinson, G. W., Towards a New Correction Method for the Basis-Set Superposition Error - Application to the Ammonia Dimer. *Journal of Chemical Physics* **1995,** 102, (9), 3648-3654.

64. Daudey, J. P.; Claverie, P.; Malrieu, J. P., Perturbative Ab-Initio Calculations of Intermolecular Energies .1. Method. *International Journal of Quantum Chemistry* **1974,** 8, (1), 1-15.

65. Saebo, S.; Pulay, P., Local Treatment of Electron Correlation. *Annual Review of Physical Chemistry* **1993,** 44, 213-236.

66. Hetzer, G.; Pulay, P.; Werner, H. J., Multipole approximation of distant pair energies in local MP2 calculations. *Chemical Physics Letters* **1998,** 290, (1-3), 143-149.

67. Hetzer, G.; Schutz, M.; Stoll, H.; Werner, H. J., Low-order scaling local correlation methods II: Splitting the Coulomb operator in linear scaling local second-order Moller-Plesset perturbation theory. *Journal of Chemical Physics* **2000,** 113, (21), 9443-9455.

68. Schutz, M.; Hetzer, G.; Werner, H. J., Low-order scaling local electron correlation methods. I. Linear scaling local MP2. *Journal of Chemical Physics* **1999,** 111, (13), 5691-5705.

69. Schutz, M.; Rauhut, G.; Werner, H. J., Local treatment of electron correlation in molecular clusters: Structures and stabilities of (H2O)(n), n = 2-4. *Journal of Physical Chemistry A* **1998,** 102, (29), 5997-6003.

70. Pedulla, J. M.; Vila, F.; Jordan, K. D., Binding energy of the ring form of (H2O)(6): Comparison of the predictions of conventional and localized-orbital MP2 calculations. *Journal of Chemical Physics* **1996,** 105, (24), 11091-11099.

71. Gruneich, A.; Hess, B. A., Choosing GTO basis sets for periodic HF calculations. *Theoretical Chemistry Accounts* **1998,** 100, (1-4), 253-263.

72. van Mourik, T.; Vos, R. J.; van Lenthe, J. H.; van Duijneveldt, F. B., Removal of dependencies from nearly complete basis sets. Calculations on the helium dimer. *International Journal of Quantum Chemistry* **1997,** 63, (4), 805-815.

73. Wallis, A.; McElwain, L. S.; Pritchard, H. O., The Variation Method and the Algebraic Eigenvalue Problem. *International Journal of Quantum Chemistry* **1969,** 3, 711.

74. Stalring, L.; Schutz, M.; Lindh, R.; Karlstrom, G.; Widmark, P. O., The ammonia dimer equilibrium dissociation energy: convergence to the basis set limit at the correlated level. *Molecular Physics* **2002,** 100, (21), 3389-3399.

CHAPTER 3

DENSITY FUNCTIONAL THEORY STUDY OF SMALL VANADIUM OXIDE CLUSTERS

Work presented in this Chapter is to be submitted for publication in "E. Jakubikova, A. K. Rappé, and E. R. Bernstein, Density functional theory study of small vanadium oxide clusters. Journal of Physical Chemistry A, to be submitted (2007)." My contribution consists of DFT calculations of different vanadium oxide isomers as well as calculation of the reaction energies for the fragmentation and growth reactions discussed below.

INTRODUCTION

Vanadium oxide based catalysts play an important role in the manufacture of many chemicals.[1] They are, for example, involved in the oxidation of SO_2 to SO_3 in the synthesis of H_2SO_4[2] or selective reduction of NO_x by NH_3.[3] Studying and understanding catalysis in the condensed phase is a very challenging task and therefore many experimental and theoretical studies focus on neutral or ionic vanadium oxide clusters in the gas phase as acceptable models for presumed "active sites" on catalytic surfaces. This general approach to metal and metal oxide mediated catalysis was first suggested by Muetterties.[4]

In order to gain better understanding of vanadium oxide cluster reactivity and its role in catalysis, one should first understand structure and stability of these molecules. Mass spectroscopy techniques have been applied to study neutral,[5-7] cationic,[8-11] as well as anionic,[12] vanadium oxide clusters in the gas phase. Infrared spectroscopy,[13,14] photoelectron spectroscopy,[15-19] and electron spin resonance spectroscopy[20] have also been used to obtain information about structure, electronic states, and stability of ionic vanadium oxide clusters.

Experimental investigations of gas phase vanadium oxide clusters are complemented by theoretical investigations. Vyboishchikov and Sauer[21] used density functional theory (DFT) with B3LYP and BP86 functionals and a TZVP basis set to obtain structures of neutral VO_y ($y = 1 - 4$), V_2O_y ($y = 4, 6, 7$), V_3O_8, V_4O_{10}, and V_4O_{11} clusters and their anions. They have also determined structures of neutral $(V_2O_5)_n$ ($n = 1 - 5, 8, 10, 12$) clusters at the BP86/DZVP, TZVP levels of DFT.[22] Vyboishchikov also used BP86/DZVP to determine structures and electronic states of $V_2O_y^+$ ($y = 4 - 6$) cations. B3LYP/TZVP and DZP levels of theory were also applied to study structures and reactivity of $V_2O_y^+$ ($y = 2 - 6$) and $V_4O_y^+$ ($y = 8 - 9$) cations.[23] Calatayud et al.[24] employed DFT to study neutral and cationic V_2O_y ($y = 2 - 7$), V_3O_y ($y = 6 - 7$), and V_4O_{10} clusters at the B3LYP/6-31G* level of theory. Pykavy and van Wüllen applied ab initio calculations at the CASSCF level to study electronic ground states of $V_2O_4^{+/0/-}$ and $VO^{+/0/-}$ species.[25,26] CASSCF and MR-SDCI have been also used to characterize ground states of VO_2 and VO_3 molecules.[20]

Despite the abundance of experimental and theoretical work, the question of which neutral clusters are the most stable in the gas phase is still open.[11] Systematic behavior of vanadium oxide clusters is also not completely understood. In this work we employ density functional theory at the BPW91/LANL2DZ level to explore structures and stabilities of small neutral vanadium oxide clusters in the gas phase. Our aim is to gain better understanding of the systematic behavior of vanadium oxide clusters as well as to attempt an explanation of neutral cluster distributions observed in previous experimental studies.[5,6] To accomplish this, a range of oxygen-deficient to oxygen-rich species is considered in our calculations: VO_y ($y = 1 - 5$), V_2O_y ($y = 2 - 7$). V_3O_y ($y = 4 - 9$), and V_4O_y ($y = 7 - 12$). Many of these structures have been calculated previously; however, our calculations consider a larger variety of spin states in determining cluster ground electronic state. Structures of VO_5, V_3O_y ($y = 3, 4, 8, 9$), and V_4O_y ($y = 7, 12$) clusters are investigated for the first time computationally.

COMPUTATIONAL METHODS

All calculations reported in this work are performed employing the BPW91 functional[27,28] and the LANL2DZ basis set.[29] LANL2DZ uses the Los Alamos effective core potential with a double zeta basis set on vanadium atoms, and a D95 basis set[30] on oxygen atoms. The Gaussian 98 program[31] is used for V_xO_y clusters ($x = 1,2,3$), Gaussian 03[32] is used for calculations on V_4O_y clusters. Cluster geometries are optimized without any restrictions on symmetry, and energy minima are confirmed by vibrational frequency calculations. A variety of spin states and isomers are investigated. Broken symmetry calculations are also performed for V_2O_y ($y = 2, 3, 4, 6, 7$) and V_4O_y ($y = 7, 8, 9$) clusters in order to describe their open shell singlet electronic states.

PERFORMANCE OF DFT CALCULATIONS

Table 3.1 shows a comparison between the energetic and structural parameters obtained from experiment and calculated at the BPW91/LANL2DZ level of theory.

Overall, the agreement between experimental and theoretical data is acceptable. The atomization energies of VO and VO_2 are overestimated by about 1 eV. Note that the error in atomization energy of VO_2 is carried over from the error in description of VO. The theoretical value of 5.8 eV for the dissociation energy of VO_2 ($VO_2 \rightarrow VO + O$) compares very well with the experimental value of 5.77 eV.[33] BPW91/LANL2DZ also tends to overestimate slightly the bond lengths and bond angles, with the largest error of 0.08Å for O_2.

An obvious way to improve the level of theory used in this work would be to use an all electron basis set such as TZVP for vanadium and a triple zeta basis set for oxygen. The use of a smaller basis set, however, allows us to perform a large number of calculations to investigate a variety of isomers and spin states of the vanadium oxide clusters.

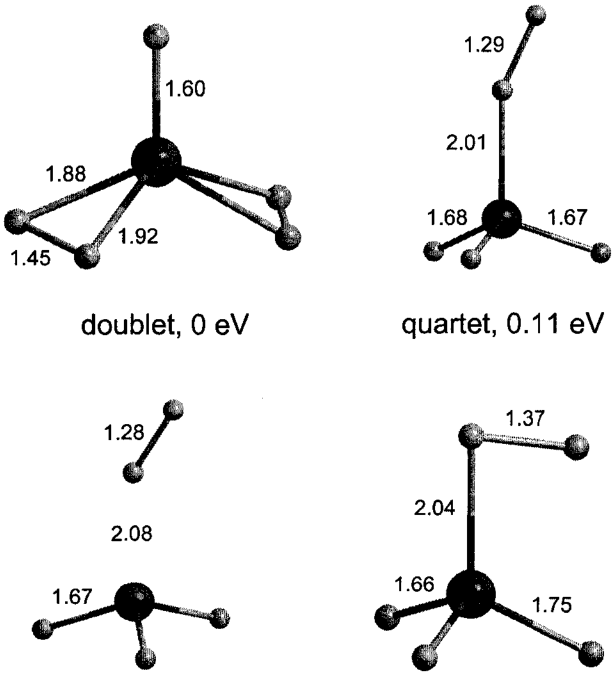
Parameter	**Experiment**	**BPW91/LANL2DZ**
E_a: VO	6.44 eV ± 0.20 eV[34]	7.33 eV
E_a: VO_2	12.20 eV ± 0.19 eV[33]	13.13 eV
E_a: O_2	5.12 eV ± 0.002 eV[35]	4.90 eV
VO: V – O	1.589 Å[35]	1.612 Å
VO_2: V – O	1.589 Å[21,36]	1.633 Å
VO_2: O – V – O	110°[21,36]	110.99°
O_2: O – O	1.208 Å[35]	1.288 Å

Table 3.1. Atomization energies, E_a, and structural parameters of VO, VO_2 and O_2.

RESULTS AND DISCUSSION

VO$_x$ clusters

Optimized lowest energy structures for VO$_y$ (y = 1 – 5) clusters are shown in Figure 3.1. Only low lying spin states (doublet – sextet) are considered in the calculations. While the lowest energy structures of VO$_2$ – VO$_5$ are doublets, the lowest energy structure of VO is a quartet. This is in accord with previous studies of VO$_y$ clusters.[21] The structure of VO$_5$ is reported for the first time. VO$_5$ has several low lying isomers that are shown along with lowest energy structure in Figure 3.1. Based on our calculations, VO$_5$ is a stationary point, though the structures of its low lying isomers suggest that it can easily dissociate into VO$_3$ and O$_2$ and thus might not be observed experimentally. Structural isomers of VO$_3$ and VO$_4$ obtained in our calculations lie at least 0.65 eV above the lowest energy isomers of each cluster.



doublet, 0 eV

quartet, 0.11 eV

doublet, 0.20 eV

doublet, 0.55 eV

Figure 3.1. Lowest energy isomers of VO$_5$ clusters.

V_2O_y structures

Lowest energy structures obtained for V_2O_y clusters (y = 2 – 7) are shown in Figure 3.2. Singlet through nonet spin states for the V_2O_2 cluster, singlet through septet states for V_2O_y (y = 3, 4, 7) clusters, and singlet, triplet and quintet states for V_2O_5 and V_2O_6 clusters are considered in the calculations. Spin states of the lowest energy structures vary between singlet and septet depending on the oxygen saturation of a particular cluster. Oxygen deficient clusters tend to have higher spin states, while oxygen saturated clusters prefer lower spin states. V_2O_4 cluster is an open shell singlet in its ground electronic state, with a triplet state lying 0.11 eV above the open shell singlet. Ground electronic state of V_2O_6 cluster is also an open shell singlet. The energy difference between the open shell singlet and a triplet sate of V_2O_6 is almost negligible (0.004 eV). For V_2O_y (y = 2, 3, 5) clusters, preferred spin states can be determined by simple electron counting with unpaired electrons occupying non-bonding d orbitals.

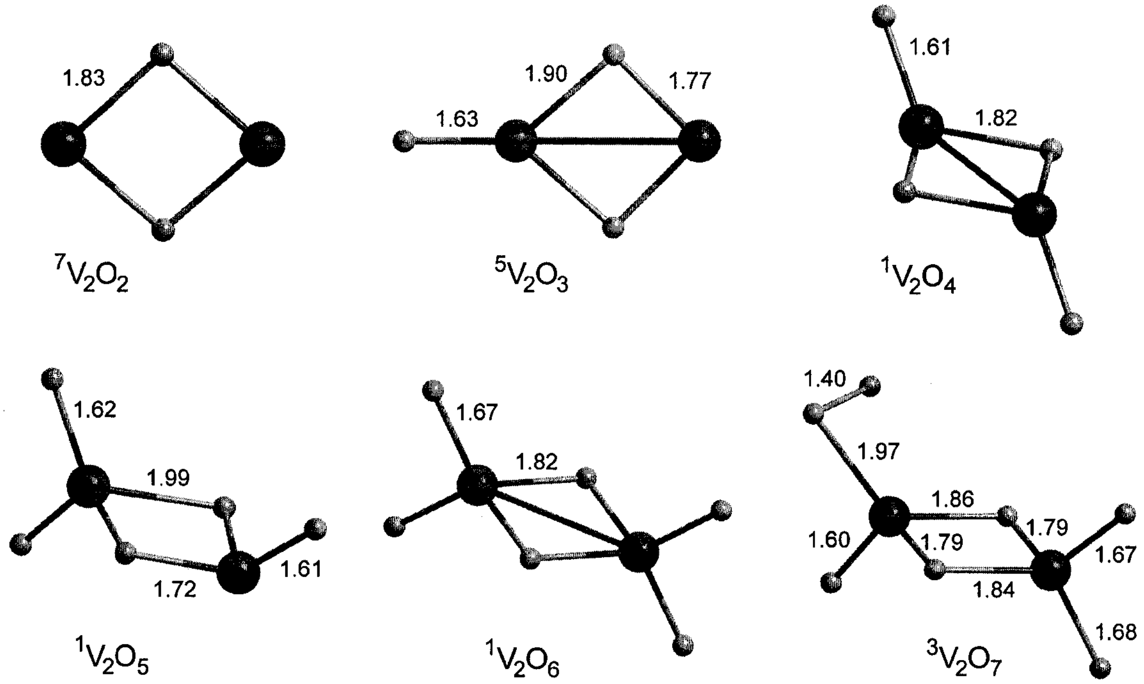


Figure 3.2. Lowest energy structures of V_2O_y (y = 2-7).

Although structures of the lowest energy isomers are similar to those reported elsewhere,[21,24,26] the spin states determined by our calculations differ in several instances. For example, Calatayud et al.[24] report a triplet as the lowest energy state for both V_2O_2 and V_2O_3, while our results indicate septet and quintet states, respectively. This difference is due to the fact that their set of calculations considered only lower multiplicity states. Vyboishchikov and Sauer[21] report singlet states for neutral V_2O_6 and V_2O_7 clusters. Recently Chen and Yang[37] performed spin unrestricted B3LYP calculations on V_2O_6 clusters, concluding that the lowest energy isomer of neutral V_2O_6 cluster is an open shell singlet, which is in agreement with our calculations. It is worth noting than in general, open shell singlets for V_2O_2, V_2O_3 and V_2O_7 lie relatively close to the ground electronic states of these clusters (0.04 – 0.18 eV above the ground state).

$V_2O_y^+$ (y = 2 – 7)

To compare structures of neutral V_2O_y clusters and their cations, we have also optimized geometries of $V_2O_y^+$ (y = 2 – 7). The starting geometry for each optimization is the lowest energy isomer of the neutral structure, except in the case of $V_2O_4^+$, for which both cis and trans isomers are considered. Several spin states (doublet – octet for all clusters, and multiplicity 10 in case of $V_2O_2^+$) are again considered in the calculations. Results are presented in Figure 3.3.

Optimized structures are in general very similar to the structures of neutral clusters. The lowest energy structure of the $V_2O_4^+$ cluster has a trans conformation as is the case for the neutral cluster. Energy differences between cis and trans isomers for both neutral and cation cluster are rather small (see Figure 3.4). The structure of $V_2O_7^+$ can be viewed as $V_2O_5^+$ with weakly bound O_2, indicating that this cluster can easily lose an O_2 subunit upon ionization.

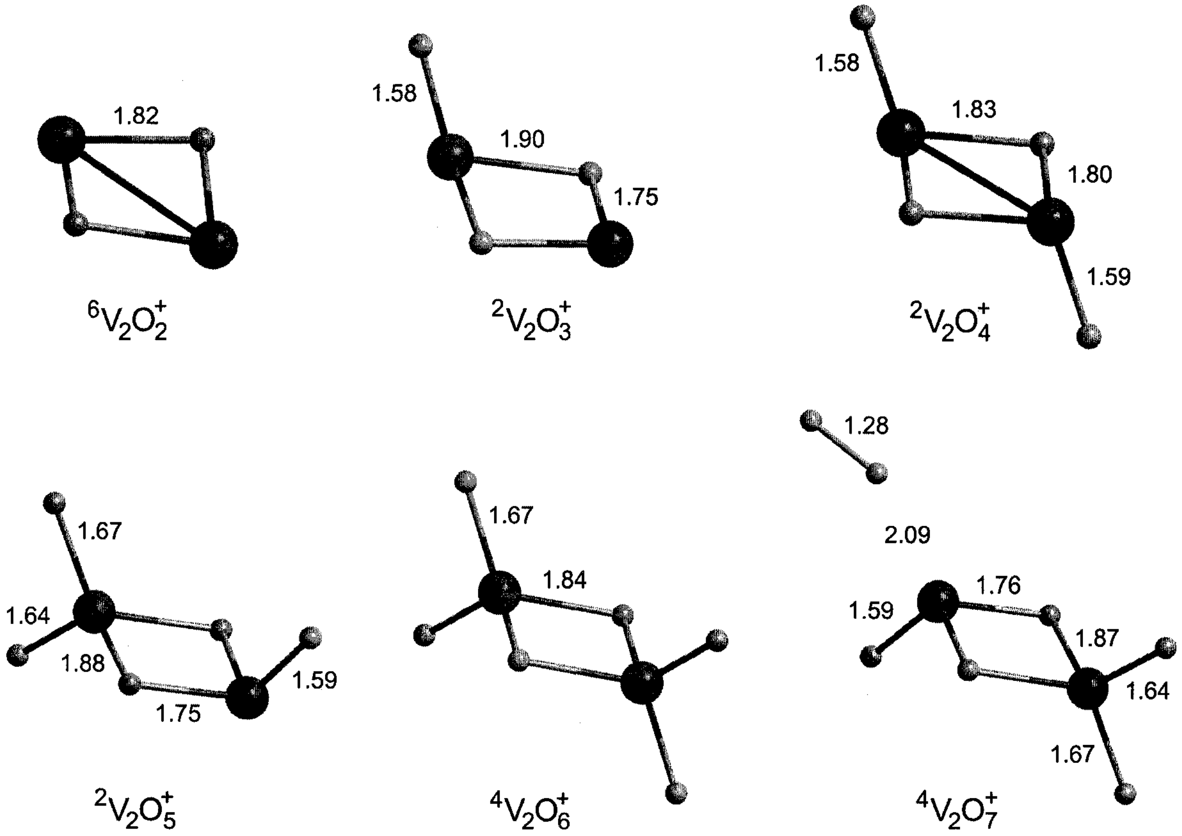
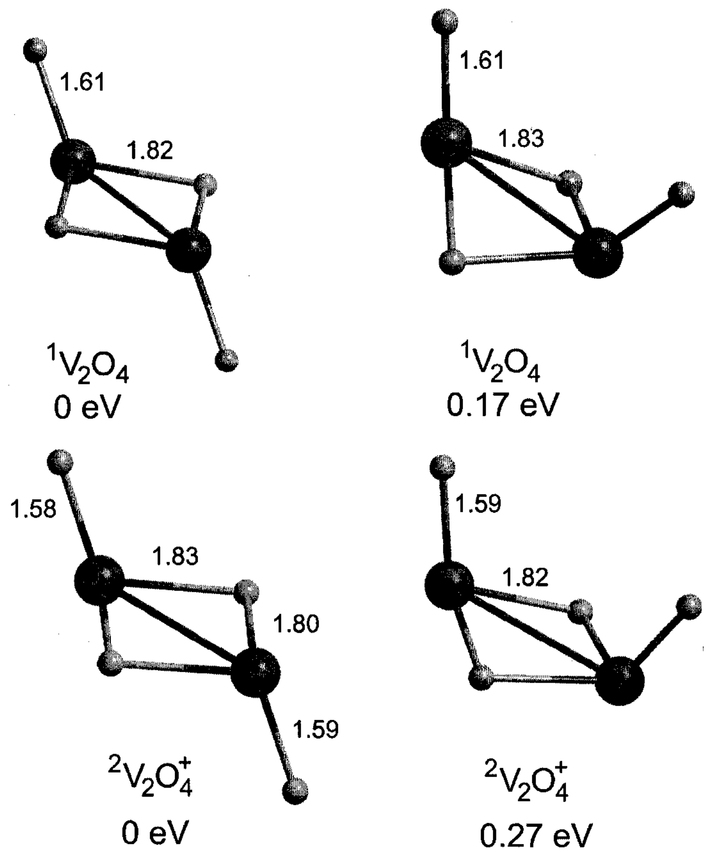


Figure 3.3. Lowest energy structures of $V_2O_y^+$ (y = 2-7) clusters.

Structures presented in Figure 3.3 are not necessarily the lowest energy structures for V_2O_y cations; they are just the lowest energy structures corresponding to the lowest energy neutral isomers of V_2O_y. In other words, these are the isomers we would expect to obtain by ionization of neutral vanadium oxide clusters in a collisionless molecular beam as opposed to the lowest energy isomers of vanadium oxide cations obtained by ablation of vanadium metal into a flow of oxygen. For a more comprehensive study of vanadium oxide cations see references 23, 24, and 38.



$^1V_2O_4$ 0 eV

$^1V_2O_4$ 0.17 eV

$^2V_2O_4^+$ 0 eV

$^2V_2O_4^+$ 0.27 eV

Figure 3.4. Comparison of V_2O_4 and $V_2O_4^+$ lowest energy structures.

V_3O_y (y = 4 – 9)

Lowest energy structures of V_3O_y (y = 4 – 9) clusters are shown in Figure 3.5. We have considered several spin states in the calculations: doublet – multiplicity ten for V_3O_4, doublet – octet for V_3O_5, and doublet – sextet for V_3O_y (y = 6 – 9). All lowest energy isomers are doublets; however, higher spin states for the same general isomeric structures of oxygen deficient clusters (V_3O_4, V_3O_5, and V_3O_6) are energetically very accessible. For example, the energy difference between the sextet and doublet state of the lowest energy isomer of V_3O_4 is only 0.01 eV, and the difference between octet and doublet states for the same isomer is 0.13 eV.

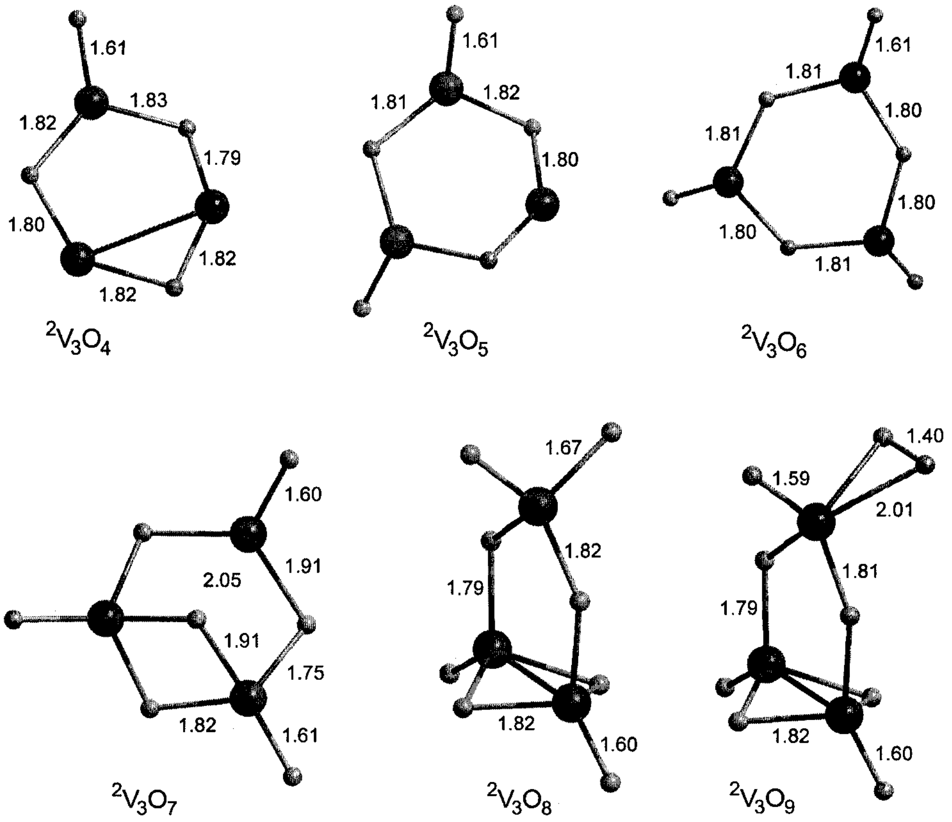
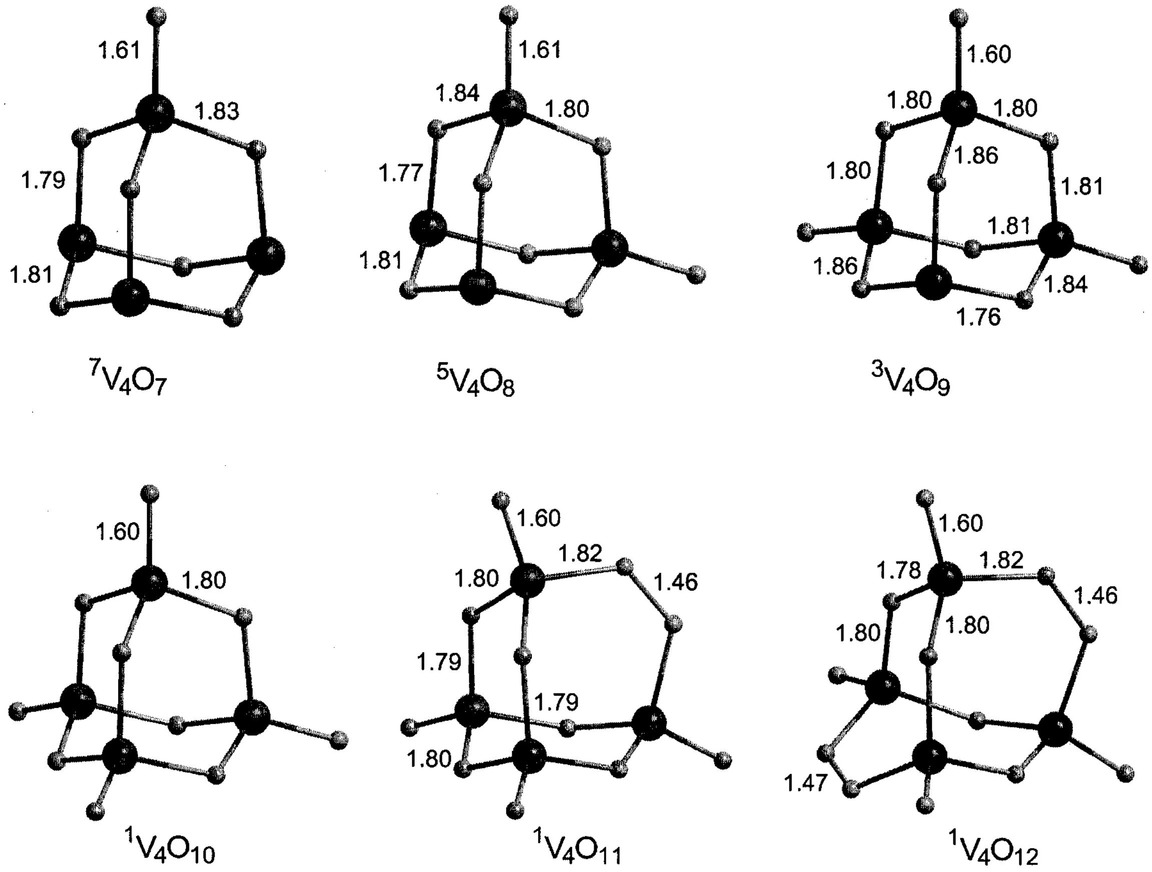


Figure 3.5. Lowest energy structures of V_3O_y (y = 4-9) clusters.

Other reported structures of V_3O_y clusters can be found in the work of Calatayud et al.[24] (V_3O_6 and V_3O_7) and Vyboishchikov and Sauer[21] (V_3O_8).

V_4O_y (y = 7 – 12)

Figure 3.6 shows the lowest energy structures for V_4O_y (y = 7 – 12) clusters. Singlet through nonet spin states are considered for calculations of the V_4O_7 cluster, and singlet through septet spin states are considered for all other V_4O_y (y = 8 – 12) clusters. As in the case of V_2O_y clusters, spin states of the lowest energy structures vary between singlet and septet depending on the oxygen saturation of a particular cluster and can be determined by simple electron counting. Open shell singlets of V_4O_y ($y = 7, 8, 9$) lie 0.14 to 0.61 eV above the ground electronic states.



$^7V_4O_7$ $^5V_4O_8$ $^3V_4O_9$

$^1V_4O_{10}$ $^1V_4O_{11}$ $^1V_4O_{12}$

Figure 3.6. Lowest energy structures of V_4O_y ($y = 7$-12) clusters.

Several different isomers of V_4O_y clusters are explored to find the lowest energy structures, except for V_4O_{10}, for which we considered only the cage-like isomer shown in Figure 3.7. Other isomers of V_4O_{10} are explored in references 21 – 23. A cage-like structure is found for the lowest energy isomer of V_4O_{10}. Lowest energy isomers of oxygen-deficient V_4O_y ($y = 7 – 9$) clusters can be all derived from the cage-like structure of V_4O_{10} by removing an appropriate number of terminal oxygens. Additional isomers considered in our calculation (chain-like, cyclic or bridged isomers) are at least 1 eV above the lowest energy cage isomers of V_4O_y ($y = 7 - 9$), indicating inherent stability of the cage structure.

As for the oxygen-rich V_4O_{11} cluster, the lowest energy isomer determined by our calculations (see Figure 3.6) differs from that reported by Vyboischikov and Sauer,[21] in which an oxygen-oxygen bond is formed with one of the terminal oxygens. The energy difference between these two isomers is, according to our calculations, 0.27 eV. These structural differences are most likely associated with algorithm differences and are probably within the accepted actual calculational uncertainties for the various DFT approaches. V_4O_{12} also has several low lying isomers (0.14 - 0.57 eV above the lowest energy one) with oxygen atoms forming oxo-bonds either at the terminal oxygen sites or bridging oxygen sites. These latter oxo-bonds are thus incorporated into the cage structure.

Stability of neutral vanadium oxide clusters in the gas phase

Previous experimental studies in our laboratory[5,6] address the question of the distribution of neutral vanadium oxide clusters in the gas phase. To understand results obtained in these studies better, we look at the energies of oxidation and reduction reactions of neutral vanadium oxides with oxygen. Under saturated oxygen conditions (i.e., % O_2 in reaction/expansion gas for which the cluster distribution no longer changes, ca. 5 %), newly formed vanadium oxides will react with O_2 and grow further, corresponding to the reaction described by $V_xO_{y-1} + O_2 \rightarrow V_xO_y + O$. During the ionization process, vanadium oxide clusters could also fragment by losing an oxygen atom, corresponding to the reaction $V_xO_y \rightarrow V_xO_{y-1} + O$, or by losing an oxygen molecule $V_xO_y \rightarrow V_xO_{y-2} + O_2$. Interplay between these growth and fragmentation reactions for the neutral clusters determines which species will be the most prevalent in the gas phase. Energies of the three reactions described here are obtained using the energies of ground state vanadium oxide and oxygen structures computed at the BPW91/LANL2DZ level of theory.

The energies of fragmentation and growth reactions for VO_y clusters are shown in Figure 3.7. The plot shows that the oxidation reactions leading to VO and VO_2 formation are exothermic, while the formation of VO_3, VO_4 and VO_5 by oxidation from clusters with lower oxygen content is not energetically favorable. Oxygen-rich clusters, such as VO_4 and VO_5, loose an oxygen molecule more easily than a single oxygen atom, which can be explained by the presence of oxygen-oxygen bonds in their lowest energy isomers (see Figure 3.1). Loss of a single oxygen atom is preferable for clusters with lower oxygen content. Overall, our results suggest VO_2 is the most stable cluster under the oxygen saturated conditions, since the formation of VO_2 is exothermic and at the same time it will not be readily oxidized to form VO_3. Additionally, VO_2 will not be easily fragmented into VO or V. Figure 3.8, Figure 3.9, and Figure 3.10 show energies of fragmentation and growth reactions for V_2O_y, V_3O_y, and V_4O_y clusters. The trends for these clusters follow the general trend described for VO_y clusters. The vanadium-oxygen bond strength decreases with increasing oxygen content of the clusters, meaning that oxygen poor clusters are oxidized more easily than the oxygen rich clusters. Loss of an oxygen molecule is preferred for oxygen rich clusters, while oxygen poor clusters are more likely to loose a single oxygen atom. This is again a consequence of oxygen-oxygen bond formation in oxygen rich clusters. Finally, V_2O_5, V_3O_7, and V_4O_{10} are predicted to be the most stable clusters under the oxygen saturated conditions. Formation of these stable clusters is exothermic, they are not readily oxidized to form clusters with higher oxygen content and at the same time they are not easily fragmented by a loss of an oxygen atom or oxygen molecule.

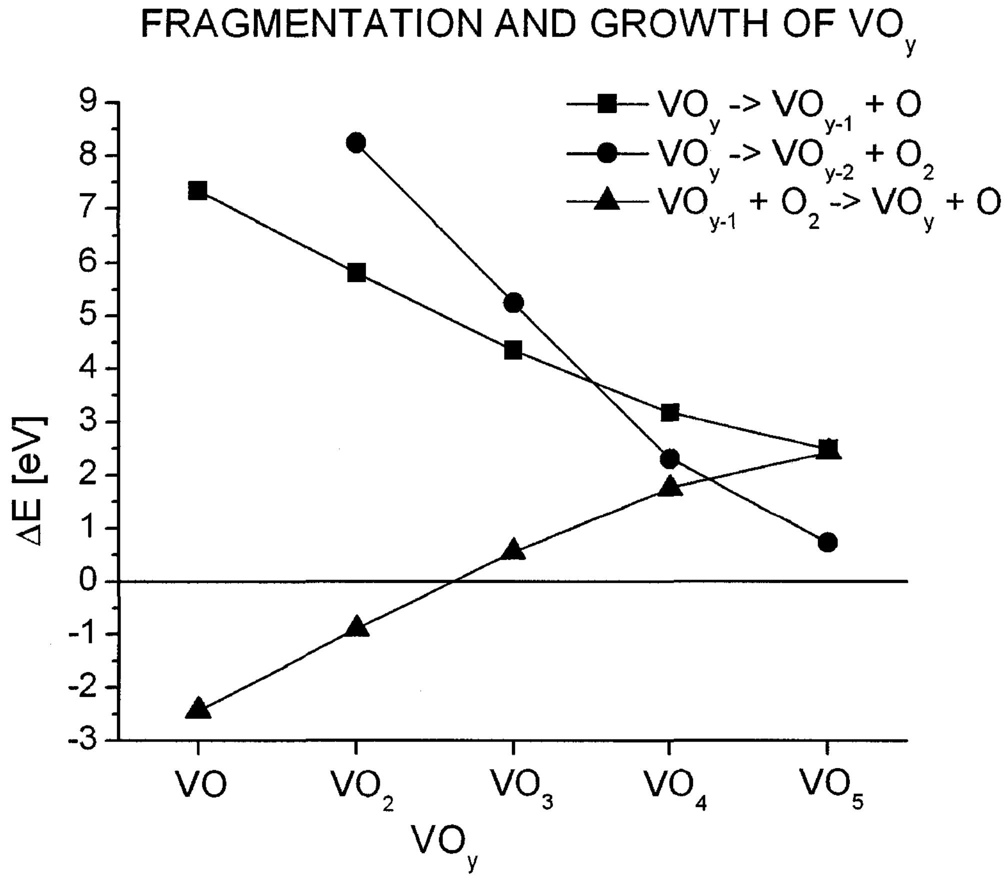


Figure 3.7. Energies of fragmentation and growth reactions for VO_y clusters.

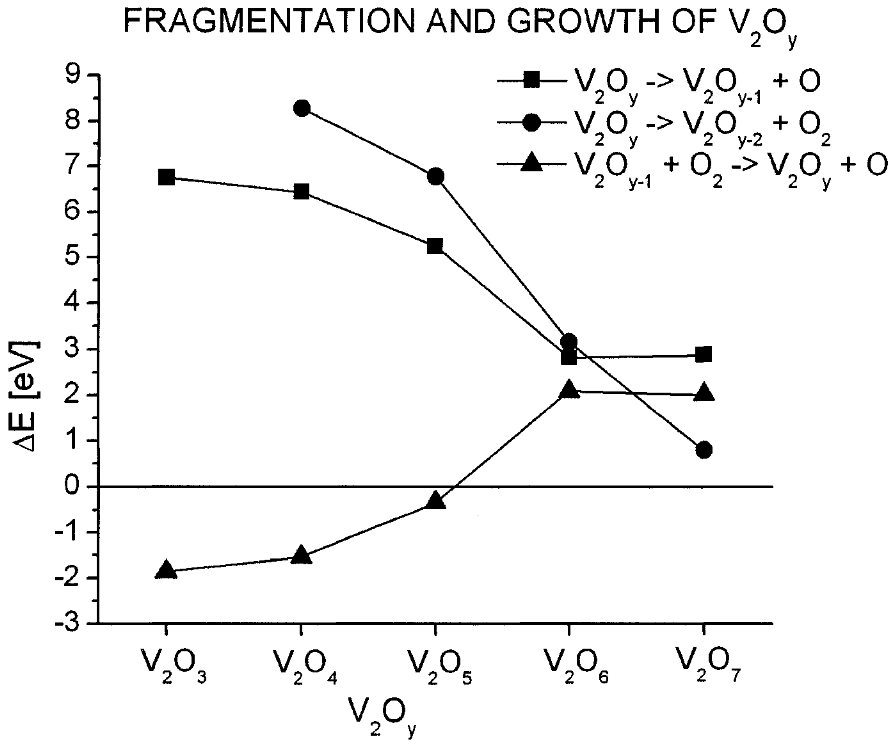


Figure 3.8. Energies of fragmentation and growth reactions for V_2O_y clusters.

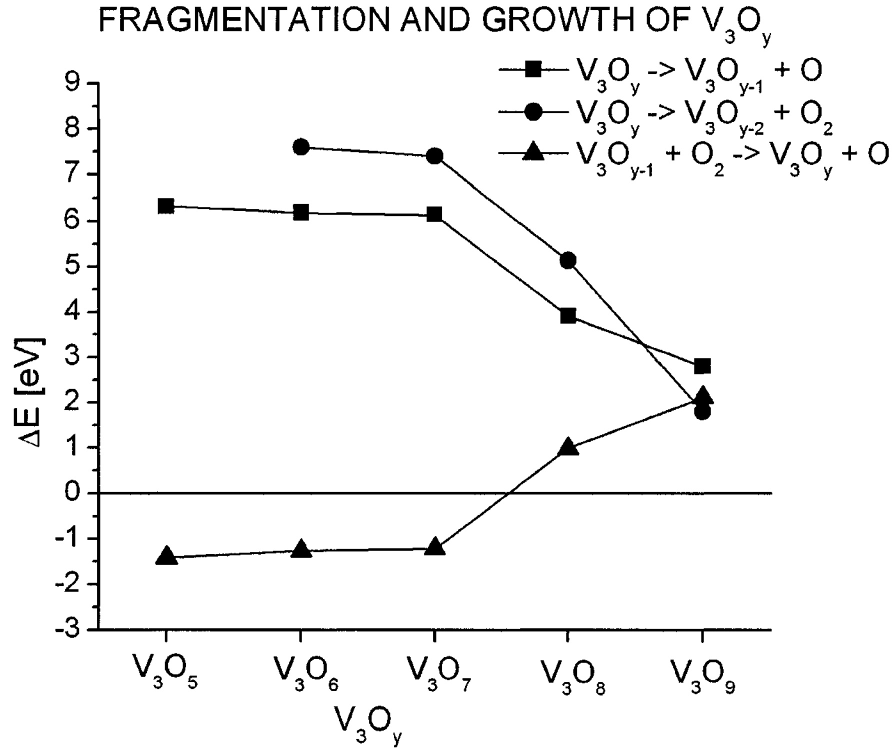


Figure 3.9. Energies of fragmentation and growth reactions of V_3O_y clusters.

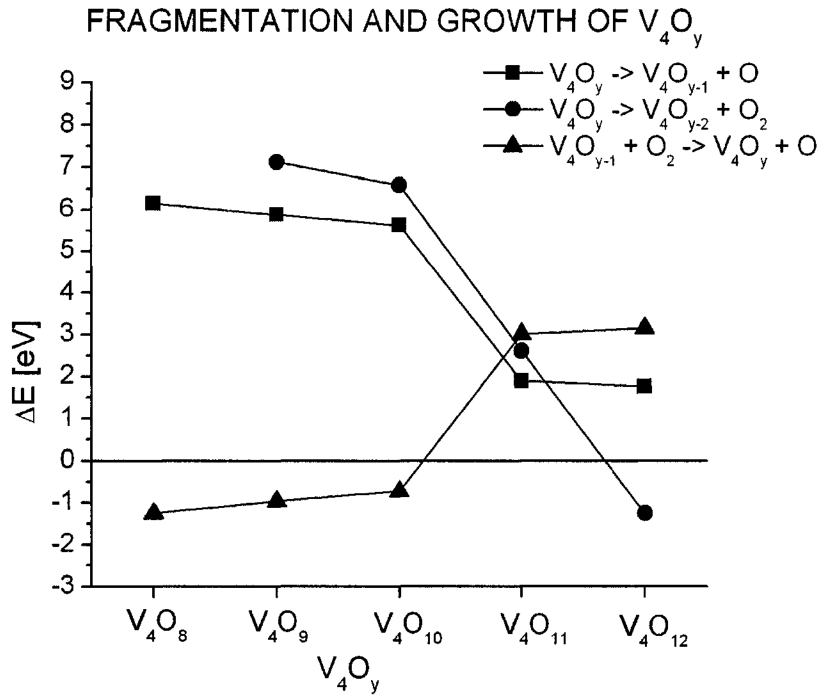


Figure 3.10. Energies of fragmentation and growth reactions for V_4O_y clusters.

Previous molecular beam mass spectroscopy studies using 118 nm (10.5 eV) light for neutral cluster ionization[5] show VO_2, V_2O_5, V_3O_7 and V_4O_9 to be dominant in the beam under the oxygen saturated conditions. V_4O_{10} cluster is not observed in this experiment due to its high ionization energy (> 10.5 eV). Relative increase in the intensity of V_4O_9 peak under the oxygen deficient conditions is also observed, indicating that a vanadium oxide cluster with higher oxygen saturation than V_4O_9 (for example V_4O_{10} as suggested by calculations presented here) is dominant in the molecular beam under the oxygen saturated conditions.

VO_2, V_2O_4, V_3O_7 and V_4O_{10} clusters are found to be the most prominent in the molecular beam under the oxygen saturated conditions detected by single photon ionization studies employing a 26.5 eV x-ray laser.[6] This confirms the stability of V_4O_{10} cluster under the oxygen saturated conditions, but raises an additional question of V_2O_4 versus V_2O_5 cluster stability. There are several possible reasons why 10.5 eV ionization and 26.5 eV ionization experiments could yield different results: 1. ionization cross section for V_2O_5 or V_2O_4 can be wavelength dependent and thus yield different intensities in the mass spectra; 2. special resonance can occur between the 26.5 eV and V_2O_4 cluster leading to the relative increase of the $V_2O_4^+$ intensity; and 3. slight variation in the experimental setup in the ablation region can lead to the differences in the synthesis of V_2O_4 and V_2O_5 clusters and thereby influence their relative abundance in the molecular beam as accessed by mass spectroscopy. Which one of these conditions (if any) is responsible for the differences in the experimental data is not clear. It is also worth noting that except in the case of V_2O_4/V_2O_5 clusters, 10.5 eV and 26.5 eV ionization studies generate consistent results for many systems, not just V_xO_y clusters.[6]

In addition to studies investigating the stability of neutral vanadium oxide clusters, stability of vanadium oxide cluster cations has also been explored.[11] $V_2O_4^+$, $V_3O_7^+$, and $V_4O_9^+$ species have been determined to be the most stable under the oxygen saturated conditions, suggesting differences in the distribution of neutral and cationic vanadium oxide clusters.

To reiterate, DFT calculations predict VO_2, V_2O_5, V_3O_7 and V_4O_{10} to be the most stable clusters in the size range under oxygen saturated conditions. These results are in agreement with the previous experimental studies of gas phase distributions of neutral vanadium oxide clusters.

CONCLUSION

In this work we investigate the structure and stability of small, neutral vanadium oxide clusters in the gas phase. Calculations performed at the BPW91/LANL2DZ level of theory suggest cyclic and cage like structures for lowest energy isomers of neutral vanadium oxide clusters. Oxygen-oxygen bonds are present for oxygen rich clusters. Clusters with an odd number of vanadium atoms (VO_y, V_3O_y) tend to have low spin ground states, while clusters with even number of vanadium atoms (V_2O_y, V_4O_y) have a variety of spin multiplicities for their ground electronic state. Ground spin states of oxygen deficient V_2O_y ($y = 2, 3, 5$) and V_4O_y clusters can be determined by simple electron counting. Whether these trends can be generalized to larger clusters, such as V_xO_y ($x = 5,\ldots,10$; $y = 2x,\ldots,3x$), has not been explored.

Energies of growth and fragmentation reactions of neutral vanadium oxide molecules are obtained to study the stability of neutral vanadium oxide species under oxygen saturated gas phase conditions. Vanadium-oxygen bond strengths in vanadium oxide clusters decrease with increasing cluster oxygen content. Oxygen saturated clusters will lose an O_2 molecule more easily than a single oxygen atom, while the loss of a single oxygen atom is more favorable for oxygen deficient clusters. VO_2, V_2O_5, V_3O_7, and V_4O_{10} are predicted to be the most stable neutral clusters under the oxygen saturated conditions. These results are in agreement with, and complement, previous gas phase experimental studies of neutral vanadium oxide clusters.

ACKNOWLEDGEMENTS

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REFERENCES

(1) Weckhuysen, B. M.; Keller, D. E. *Catalysis Today* **2003**, *78*, 25.

(2) Lapina, O. B.; Bal'zhinimaev, B. S.; Boghosian, S.; Eriksen, K. M.; Fehrmann, R. *Catalysis Today* **1999**, *51*, 469.

(3) Bond, G. C.; Tahir, S. F. *Applied Catalysis* **1991**, *71*, 1.

(4) Muetterties, E. L. *Science* **1977**, *196*, 839.

(5) Matsuda, Y.; Bernstein, E. R. *Journal of Physical Chemistry A* **2005**, *109*, 3803.

(6) Dong, F.; Heinbuch, S.; He, S. G.; Xie, Y.; Rocca, J. J.; Bernstein, E. R. *Journal of Chemical Physics* **2006**, *125*.

(7) Foltin, M.; Stueber, G. J.; Bernstein, E. R. *Journal of Chemical Physics* **1999**, *111*, 9577.

(8) Xu, J.; Rodgers, M. T.; Griffin, J. B.; Armentrout, P. B. *Journal of Chemical Physics* **1998**, *108*, 9339.

(9) Zemski, K. A.; Justes, D. R.; Castleman, A. W. *Journal of Physical Chemistry B* **2002**, *106*, 6136.

(10) Bell, R. C.; Zemski, K. A.; Kerns, K. P.; Deng, H. T.; Castleman, A. W. *Journal of Physical Chemistry A* **1998**, *102*, 1733.

(11) Molek, K. S.; Jaeger, T. D.; Duncan, M. A. *Journal of Chemical Physics* **2005**, *123*.

(12) Bell, R. C.; Zemski, K. A.; Justes, D. R.; Castleman, A. W. *Journal of Chemical Physics* **2001**, *114*, 798.

(13) Asmis, K. R.; Santambrogio, G.; Brummer, M.; Sauer, J. *Angewandte Chemie-International Edition* **2005**, *44*, 3122.

(14) Asmis, K. R.; Meijer, G.; Brummer, M.; Kaposta, C.; Santambrogio, G.; Woste, L.; Sauer, J. *Journal of Chemical Physics* **2004**, *120*, 6461.

(15) Wu, H. B.; Wang, L. S. *Journal of Chemical Physics* **1998**, *108*, 5310.

(16) Zhai, H. J.; Wang, L. S. *Journal of Chemical Physics* **2002**, *117*, 7882.

(17) Pramann, A.; Koyasu, K.; Nakajima, A.; Kaya, K. *Journal of Chemical Physics* **2002**, *116*, 6521.

(18) Green, S. M. E.; Alex, S.; Fleischer, N. L.; Millam, E. L.; Marcy, T. P.; Leopold, D. G. *Journal of Chemical Physics* **2001**, *114*, 2653.

(19) Feigerle, C. S.; Corderman, R. R.; Bobashev, S. V.; Lineberger, W. C. *Journal of Chemical Physics* **1981**, *74*, 1580.

(20) Knight, L. B.; Babb, R.; Ray, M.; Banisaukas, T. J.; Russon, L.; Dailey, R. S.; Davidson, E. R. *Journal of Chemical Physics* **1996**, *105*, 10237.

(21) Vyboishchikov, S. F.; Sauer, J. *Journal of Physical Chemistry A* **2000**, *104*, 10913.

(22) Vyboishchikov, S. F.; Sauer, J. *Journal of Physical Chemistry A* **2001**, *105*, 8588.

(23) Justes, D. R.; Mitric, R.; Moore, N. A.; Bonacic-Koutecky, V.; Castleman, A. W. *Journal of the American Chemical Society* **2003**, *125*, 6289.

(24) Calatayud, M.; Andres, J.; Beltran, A. *Journal of Physical Chemistry A* **2001**, *105*, 9760.

(25) Pykavy, M.; van Wullen, C. *Journal of Physical Chemistry A* **2003**, *107*, 5566.

(26) Pykavy, M.; van Wullen, C.; Sauer, J. *Journal of Chemical Physics* **2004**, *120*, 4207.

(27) Becke, A. D. *Physical Review A* **1988**, *38*, 3098.

(28) Perdew, J. P.; Wang, Y. *Physical Review B* **1992**, *45*, 13244.

(29) Hay, P. J.; Wadt, W. R. *Journal of Chemical Physics* **1985**, *82*, 270.

(30) Dunning Jr., T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum Press: New York, 1976; Vol. 3.

(31) M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople. Gaussian 98 (Revision A.7); Gaussian, Inc.: Pittsburgh PA, 1998.

(32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision D.01; Gaussian, Inc.: Wallingford CT, 2004.

(33) Balducci, G.; Gigli, G.; Guido, M. *Journal of Chemical Physics* **1983**, *79*, 5616.

(34) Pedley, J. B.; Marshall, E. M. *Journal of Physical and Chemical Reference Data* **1983**, *12*, 967.

(35) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(36) Li, J.; Demello, P. C.; Jug, K. *Journal of Computational Chemistry* **1992**, *13*, 85.

(37) Chen, Z. Y.; Yang, J. L. *Chinese Journal of Chemical Physics* **2006**, *19*, 391.

(38) Vyboishchikov, S. F. *Journal of Molecular Structure - Theochem* **2005**, *723*, 53.

CHAPTER 4

REACTIONS OF SULFUR DIOXIDE WITH NEUTRAL VANADIUM OXIDE CLUSTERS IN THE GAS PHASE.

Work presented in this Chapter is to be submitted for publication in “S. G. He, Y. Xie, F. Dong, S. Heinbuch, E. Jakubikova, J. J. Rocca, and E. R. Bernstein, Reactions of sulfur dioxide with neutral vanadium oxide clusters in the gas phase. I. Experimental study employing single photon ionization. Journal of Chemical Physics, to be submitted (2007).” and “E. Jakubikova, and E. R. Bernstein, Journal of Chemical Physics, to be submitted (2007).” My contributions include calculation of enthalpies for reactions of vanadium oxides with sulfur dioxide, optimization of $V_xO_ySO_2$ intermediate structures, and calculation of reaction path for reaction of VO with SO_2. I have also contributed to the design of condensed phase catalytic cycles suggested based on our gas phase theoretical and experimental data. Calculation of reaction path for $VO_2 + SO_2 + O_2$ reaction was performed by Dr. He.

INTRODUCTION

Vanadium oxide is a heterogeneous catalyst that plays an important role in the catalytic conversion of SO_2 to SO_3,[1] selective oxidation of hydrocarbons,[2] and selective reduction of NO_x by NH_3.[3] Due to the importance of vanadium oxide for industrial scale catalysis, a number of experimental and theoretical studies are devoted to vanadium oxide and its reactivity.

Experimental and theoretical studies of vanadium oxide structure and reactivity

Electronic and geometrical structure of small vanadium oxides in the gas phase have been investigated by photoelectron spectroscopy,[4,5] infrared spectroscopy,[6,7] and electron spin resonance spectroscopy.[8,9] Structure and properties of vanadium oxide clusters also have been studied by means of multireference correlation calculations,[8,10,11] and density functional theory (DFT) calculations.[12,13]

Gas phase scattering experiments have been employed to study reactivity of medium-sized vanadium oxide cations with rare gases, hydrocarbons and small inorganic molecules.[14] Reactivity of vanadium oxide and vanadium hydroxide cations with hydrocarbons[15-19] and methanol[20] was explored by the use of mass spectrometric techniques and DFT calculations. DFT was also applied to study gas phase reactions of $V_2O_5^+$ and $V_2O_6^+$ ions with halogenated hydrocarbons,[21] selective catalytic reduction of NO with ammonia on a $V_4O_{16}H_{12}$ cluster,[22] and the interaction of VO^{2+} and VO_2^+ cations with *N*-hydroxyacetamide in the aqueous solution.[23]

Significant efforts have been devoted to studying vanadium oxides as nanosized clusters, the bulk solid, and clusters supported on different metal surfaces. Extended X-ray absorption fine structure spectroscopies, IR and Raman spectroscopy, as well as DFT calculations, were utilized to study the structure of the VO_4 molecule as a function of SiO_2, Nb_2O, and ZrO_2 supports.[24-26] Scanning tunneling microscopy and DFT calculations were used to characterize vanadium oxide nanostructures on the Rh(111) surface.[27] DFT was employed to investigate structure and stability of $(V_2O_5)_n$, $n = 1 - 12$, gas phase clusters and compare them to the bulk solid V_2O_5.[28] Periodic DFT calculations were also applied to study structural and vibrational properties of vanadium oxide aggregates.[29] Furthermore, DFT calculations were utilized to gain insight into the oxidation of methanol to formaldehyde on supported vanadium oxide catalysts[30,31] and oxidative dehydrogenation of propane on vanadium oxide.[32]

Reduction,[33] stability,[34,35] and re-oxidation[36,37] of vanadium oxide surface vacancies were studied by means of DFT calculations. Adsorption of oxygen on reduced $V_2O_3(0001)$ surfaces was also investigated by the use of thermal desorption spectroscopy, infrared reflection absorption spectroscopy, high resolution electron energy loss spectroscopy, X-ray photoelectron spectroscopy, and DFT.[38]

Experimental studies of $SO_2 \rightarrow SO_3$ catalytic conversion

Although there are currently no reports of vanadium oxide cluster reactivity with SO_2 in the gas phase, catalytic conversion of SO_2 to SO_3 was studied experimentally over supported vanadium oxide catalysts and in the molten phase. Kato et al.[39] investigated a mixture of $V_2O_5 - K_2SO_4$ heated to 500, 550, and 600 °C in an atmosphere of $SO_2/SO_3/O_2/N_2$ gases and determined that reduction of V(V) by SO_2 and oxidation of V(IV) with O_2 are in equilibrium and the rate determining step of the reaction is the desorption of SO_3 from the molten catalyst into the gas phase.

Dunn and coworkers[40-43] studied oxidation of SO_2 over supported vanadium oxide catalysts by Raman spectroscopy. They suggested the VO_4 unit attached to the surface has a $O{=}V\text{-}(O\text{-}M)_3$ pyramidal structure, where O – M represents oxygen – support bonds.

They also proposed a catalytic mechanism for SO_3 formation consisting of three steps: 1. adsorption of SO_2 onto V – O – M bridging oxygen; 2. cleavage of the V – O – SO_2 bond and formation of SO_3; and 3. reoxidation of the V atom by dissociatively adsorbed oxygen. The activation energy for this process was determined to be 21 kcal/mol. More recent studies of supported vanadium oxide catalysts suggest that VO_4 is attached to the surface by only one V – O – M bond, and can be described as a chemisorbed O=V – O_2 [oxo] species ("umbrella model").[25,26]

Fouda et al.[44] employed X-ray diffraction techniques, electronic absorption and infrared spectroscopy, and chemical analysis to characterize reaction products of $SO_2 \rightarrow SO_3$. The catalyst in this experiment is composed of ammonium meta-vanadate and potassium sulfate. They have identified a mixture of compounds, including ammonium and potassium polyvanadates, ammonium and potassium bronzes, and ammonium vanadic sulfate ($NH_4V(SO_4)_2$). The presence of $K_2S_2O_7$ in the melt was found to increase catalytic activity of the vanadium based catalyst.

Giakomelou et al. applied in situ Raman spectroscopy to identify vanadium species on the surface of a vanadium oxide based supported molten salt catalyst[45] and supported solid V_2O_5/SiO_2 catalyst.[46] They found that the distorted tetrahedral $O{=}V{-}(O{-}Si)_3$ structure is practically inactive, while impregnation of the surface with Cs_2SO_4 results in a complete structural transformation of the surface and a dramatic improvement in SO_2 oxidation.

A multi-instrumental investigation of molten salt/gas model systems and industrial catalysts for $SO_2 \rightarrow SO_3$ conversion was undertaken by Lapina and coworkers.[1] They have identified $(VO)_2O(SO_4)_4^{4-}$ as the active species and proposed a four step catalytic mechanism consisting of 1. adsorption of O_2 onto the active site, 2. $SO_2 \rightarrow SO_3$ conversion, 3. adsorption of a second SO_2 molecule, and 4. SO_3 desorption.

Despite the significant effort devoted to the experimental studies, complete understanding of the SO_2 oxidation by vanadium oxide based catalysts is still lacking. Available experimental studies provide different views of the catalytic process, suggesting several possible mechanisms for $SO_2 \rightarrow SO_3$ conversion.

Recently, reactions of neutral vanadium oxide clusters V_xO_y with SO_2 have been studied in the gas phase. Much of these studies are reported in the preceding experimental paper, referred to as paper I,[47] in considerable detail.

Goal of this work

The goal of this work is to study the reactivity of small neutral vanadium oxide clusters, VO_y ($y = 1 - 5$), V_2O_y ($y = 2 - 7$), V_3O_y ($y = 4 - 9$), and V_4O_y ($y = 7 - 12$), with SO_2. Our focus lies in investigating the thermodynamics of reactions of vanadium oxides with SO_2. While solid state studies might provide more realistic models for heterogeneous catalysis, gas phase metal oxide clusters also represent a valid model for the active sites of the condensed-phase vanadium oxide catalyst.[48] Gas phase experimental and theoretical work have an advantage of being less complex and thus able to provide insights into catalytic processes at the molecular level. Also, computations of gas phase metal oxide clusters can be performed at a higher level of theory than currently possible for solid state studies.

COMPUTATIONAL METHODS

DFT methods have been successfully employed to study structure and reactivity of various metal oxide systems[15-19,21,22] suggesting DFT is a widely accepted tool to study the properties of metal oxides. Pykavy and Wüllen[11] employed multireference averaged coupled-pair functional (MR-ACPF) and B3LYP density functional theory[49,50] to study properties of $V_2O_4^{+/0/-}$ species and found good agreement between the MR-ACPF and B3LYP results for molecular structures and relative energies of different electronic states, as well as for the ionization energies and electron affinities. Foltin et al.[51] performed benchmark calculation with both BPW91[52,53] and B3LYP functional on zirconium oxides, suggesting BPW91 to be more suitable for computing properties of metal oxides. All calculations described in this work are performed using BPW91 functional.

Structures of VO_y ($y = 1 - 5$), V_2O_y ($y = 2 - 7$), V_3O_y ($y = 4 - 9$), and V_4O_y ($y = 7 - 12$) clusters have been computed at the BPW91/LANL2DZ level of theory and reported previously.[54] The LANL2DZ basis set[55] uses the Los Alamos effective core potential with a double zeta basis set on vanadium atoms, and a D95 basis set[56] on oxygen and sulfur atoms. BPW91/LANL2DZ fails to describe bond strengths and other properties of sulfur oxides properly (for more details see section 3 on Performance of DFT Calculations), therefore experimental enthalpies of formation of sulfur oxides[57] are used to obtain enthalpies for reactions of vanadium oxides with SO_2. Each reaction of a vanadium oxide cluster with SO_2 is divided into two partial reactions. The first reaction involves oxidation (or reduction) of SO_2, with the enthalpy computed from the experimental enthalpies of formation of sulfur oxides and oxygen atom. The second reaction consists of reduction (or oxidation) of a vanadium oxide cluster, and the enthalpy for this reaction is calculated from total energies of vanadium oxide clusters and an oxygen atom obtained from calculations performed at the BPW91/LANL2DZ level of theory. The total enthalpy for the reaction is then computed as the sum of enthalpies for the first and second reactions. To illustrate this, the enthalpy for the reaction of V_2O_5 with SO_2 leading to the formation of SO_3 and V_2O_4 is obtained in the following way:

Partial reaction 1:	$SO_2 + O \rightarrow SO_3 + \Delta H_{exp}$
Partial reaction 2:	$V_2O_5 \rightarrow V_2O_4 + O + \Delta H_{comp}$
Total reaction:	$V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3 + \Delta H_{reaction}$

In the above reactions, ΔH_{exp} is obtained from the experimental enthalpies of formation of SO_2, SO_3 and O; ΔH_{comp} is calculated from the BPW91/LANL2DZ energies of the lowest energy isomers of V_2O_5, V_2O_4 and O. Finally, the total enthalpy of reaction is obtained as a sum of the enthalpies for the two partial reactions: $\Delta H_{reaction} = \Delta H_{exp} + \Delta H_{comp}$.

Structures of VO_y ($y = 1 - 4$) clusters with SO_2 are computed and barriers for reactions of oxygen-deficient VO and oxygen-rich VO_4 clusters with SO_2 are also investigated in an effort to learn more about reaction intermediates and reaction paths. Due to the failure of LANL2DZ basis set to provide proper description of sulfur oxides, these calculations are performed at the BPW91/TZVP level of theory using Gaussian 98 program.[58]

PERFORMANCE OF DFT CALCULATIONS

Vanadium oxides

Table 4.1 shows a comparison between the properties of VO and VO_2 clusters obtained from gas phase experimental data and properties calculated at different levels of theory (density functional as well as ab initio). Density functional methods with the LANL2DZ basis set tend to overestimate bond lengths for VO and VO_2 and the bond angle for VO_2. Use of the TZVP basis set provides better agreement with the experiment, although the calculation still slightly overestimates the O – VO bond length and O – V – O bond angle, and underestimates O – V bond length. Hybrid density functional B3LYP tends to underestimate dissociation energies, while BPW91 and BP86 overestimate them by about 1eV. Note that theoretical values for O-VO bond strength obtained with BP86 and BPW91 functionals employing a LANL2DZ basis set compare rather well to the experimental value of 5.77 eV,[59] suggesting that the error in atomization energy of VO_2 is carried over from the error in the description of VO. Surprisingly, use of TZVP basis set with BPW91 and BP86 functionals to compute atomization energies of vanadium oxides does not provide an improvement over the use of LANL2DZ basis set. BPW91/TZVP overestimates atomization energies of VO and VO_2 by 1.2 eV and 1.65 eV, respectively, while BP86/TZVP overestimates these atomization energies by 1.26 eV and 1.93 eV correspondingly. Ab initio methods with full electron basis sets, on the other hand, tend to slightly underestimate the atomization energies of VO.

From the data presented here, just what method is the best one for calculations of vanadium oxide systems is not entirely clear. While ab initio methods with full electron correlation consistent basis sets provide better accuracy, at this moment they are not practical for use on larger clusters. Density functional methods provide a viable alternative to the ab initio methods; however, one must understand their shortcomings. Additional experimental data are also needed, such as atomization energies and bond strengths of vanadium oxide clusters containing more than one vanadium atom, in order to judge the accuracy of available theoretical methods. We have chosen to use the BPW91 functional, since it provides a correlation component that might be important for proper description of clusters containing more than one vanadium atom, for clusters undergoing reactions, and for calculation of transition states.

	VO		**VO_2**			
Method	**VO [eV]**	**V – O [Å]**	**VO_2 [eV]**	**O – VO [eV]**	**V – O [Å]**	**O – V – O [deg]**
Experimental	6.44 ± 0.20[60]	1.589[61]	12.20 ± 0.19[59]	5.77[59]	1.589[12,62]	110°[12,62]
BPW91/LANL2DZ	7.33	1.612	13.13	5.80	1.633	110.99°
BPW91/TZVP	7.64	1.586	13.85	6.21	1.612	110.59°
BP86/LANL2DZ	7.41	1.611	13.44	6.03	1.632	110.77°
BP86/TZVP	7.70	1.585	14.13	6.43	1.611	110.24°
BP86/basis limit[10]	7.46	1.585				
B3LYP/LANL2DZ	6.92	1.607	11.92	4.98	1.627	114.83°
B3LYP/TZVP	6.33	1.577	11.75	5.42	1.607	114.63°
B3LYP/basis limit[10]	6.22	1.579				
MR-ACPF/basis limit[10]	6.44	1.593				
MCPF[63]	6.06	1.588				
AIMP-MCPF[63]	6.09	1.586				

Table 4.1. Atomization energies, bond lengths and structural parameters for VO and VO_2.

Sulfur oxides and oxygen molecule

Table 4.2 shows structural parameters for the oxygen molecule and sulfur oxides computed at the BPW91/LANL2DZ and BPW91/TZVP level of theory. BPW91/LANL2DZ overestimates O – O bond length, while BPW91/TZVP provides better agreement with the experiment. Performance of BPW91/LANL2DZ for sulfur oxides is much worse, significantly overestimating S – O bond lengths and underestimating O – S – O bond angle in SO_2 molecule. This is due to the lack of polarization functions in description of sulfur and oxygen atoms. Use of the TZVP basis set represents an improvement over LANL2DZ and provides acceptable description of bond lengths and bond angles for sulfur oxides, although it still somewhat overestimates sulfur – oxygen bond lengths.

Parameter	**Experiment**	**BPW91/LANL2DZ**	**BPW91/TZVP**
O_2: O – O	1.208 Å[61]	1.288 Å	1.223 Å
SO: S – O	1.4811 Å[64]	1.653 Å	1.529 Å
SO_2: S – O	1.431 Å[64]	1.636 Å	1.481 Å
SO_2: O – S – O	119.329°[64]	113.448°	118.379°
SO_3: S – O	1.4198 Å[64]	1.632 Å	1.467 Å

Table 4.2. Bond lengths and bond angles for O_2 and SO_y ($y = 1 - 3$).

Table 4.3 compares experimental atomization energy of the oxygen molecule and sulfur – oxygen bond strengths of sulfur oxides to the atomization energy and bond strengths obtained from the DFT calculations. Experimental bond strengths of sulfur oxides are obtained from the enthalpies of formation of sulfur and oxygen atoms and SO_y ($y = 1, 2, 3$) molecules published in NIST Chemistry WebBook[57] based on consideration of the following reactions: $SO \rightarrow S + O$, $SO_2 \rightarrow SO + O$, and $SO_3 \rightarrow SO_2 + O$. S – O and O – SO bond strengths obtained in this way are in excellent agreement with bond strengths published in CRC Handbook.[64]

Parameter	**Experiment [eV]**	**BPW91/LANL2DZ [eV]**	**BPW91/TZVP [eV]**
O_2	5.12 ± 0.002[61]	4.90	5.84
O – S	5.40[57]	4.16	5.46
O – SO	5.71[57]	2.69	5.08
O – SO_2	3.61[57]	1.09	3.24

Table 4.3. Bond strengths for O_2 and SO_y ($y = 1 - 3$).

BPW91/LANL2DZ provides a surprisingly good value for atomization energy of O_2, which is probably just a coincidence considering that the basis set is of only double zeta quality and lacking a polarization function. Use of TZVP basis set to compute atomization energy of O_2 does not provide an improvement over the use of LANL2DZ, overestimating O_2 atomization energy by 0.72 eV.

As can be seen in Table 3, BPW91/LANL2DZ significantly underestimates bonding energies of sulfur oxides, with the largest error being a little over 3 eV for O – SO bond strength. Description of sulfur oxides is dramatically improved by replacing LANL2DZ by TZVP basis set. BPW91/TZVP level of theory, however, still underestimates O – SO and O – SO_2 bond strengths and predicts the largest bond strength for S – O, rather than O – SO. To obtain proper description of sulfur oxide bond strengths one would need to use higher level of theory, such as CCSD(T)/cc-pV(X+d)Z (X = T, Q, 5, 6),[65-68] which is not practical for our calculations.

RESULTS AND DISCUSSION

Thermodynamics of reactions of vanadium oxides with sulfur dioxide

Two main reactions of interest occur between V_xO_y cluster and an SO_2 molecule: 1. oxidation of SO_2 and reduction of V_xO_y, resulting in the formation of SO_3; and 2. reduction of SO_2 and oxidation of V_xO_y, resulting in the formation of SO. These processes can be generally described by the two following reactions: $V_xO_y + SO_2 \rightarrow V_xO_{y-1} + SO_3$; and $V_xO_y + SO_2 \rightarrow V_xO_{y-1} + SO_3$. To determine which product (SO_3 or SO) is more likely to be formed under the reaction of a particular vanadium oxide cluster with SO_2, enthalpy changes for both reactions are computed for the lowest energy isomers of VO_y ($y = 1 - 5$), V_2O_y ($y = 2 - 7$), V_3O_y ($y = 4 - 9$), and V_4O_y ($y = 7 - 12$) clusters.

Figures 4.1 – 4.4 show enthalpy changes for reactions of VO_y ($y = 0 - 5$), V_2O_y ($y = 2 - 7$), V_3O_y ($y = 4 - 9$), and V_4O_y ($y = 7 - 12$) clusters with SO_2. The enthalpies of reactions are computed as described in Section 2 (Computational Methods) above, using experimental enthalpies of formation for sulfur oxides and BPW91/LANL2DZ calculations for vanadium oxides. Enthalpies of reactions for the smallest vanadium oxide clusters are also obtained using available experimental enthalpies of formation for vanadium oxides[64] and are depicted in Figure 4.1. Comparison of the theoretical and experimental enthalpies of reactions indicates that while the agreement of theoretical and experimental data is not perfect, enthalpy changes obtained from the calculations on vanadium oxides should reproduce general trends.

Computed enthalpy changes for reactions suggest that reactions of oxygen-deficient vanadium oxide clusters ($VO_{0,1}$, V_2O_{2-4}, V_3O_{4-6}, V_4O_{7-9}) with SO_2 result in the formation of SO, while reactions of oxygen-rich clusters ($VO_{4,5}$, $V_2O_{6,7}$, $V_3O_{8,9}$, $V_4O_{11,12}$) with SO_2 lead to the formation of SO_3. Each series of vanadium oxides also contains clusters, such as VO_2, V_2O_5, V_3O_7, and V_4O_{10}, which are predicted to be stable with respect to the reaction with SO_2.

These results are in a very good agreement with gas phase molecular beam experiments performed in our laboratory, in which both SO and SO_3 products are observed by 10.5 eV and 26.5 eV ionization, respectively.[22,47]

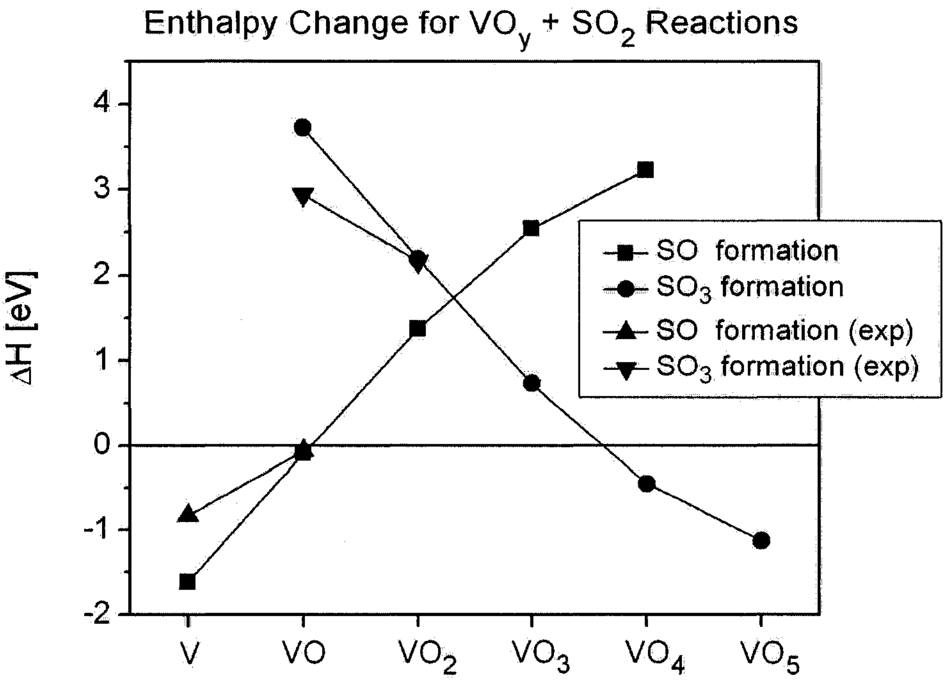

Figure 4.1. Enthalpy changes for $VO_y + SO_2 \rightarrow VO_{y+1} + SO_2$ and $VO_y + SO_2 \rightarrow VO_{y-1} + SO_3$ reactions.

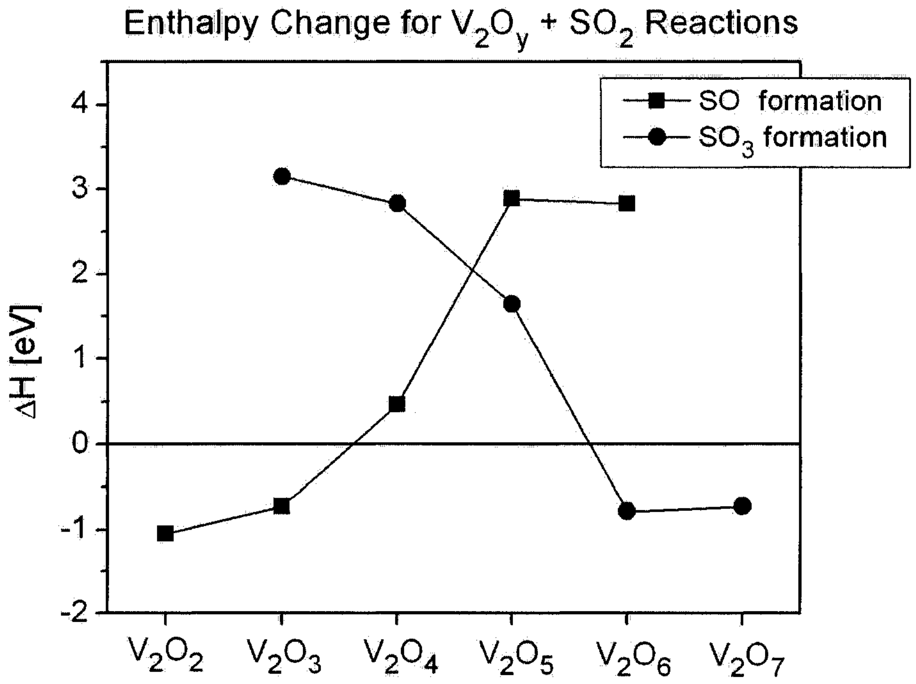

Figure 4.2. Enthalpy changes for $V_2O_y + SO_2 \rightarrow V_2O_{y+1} + SO$ and $V_2O_y + SO_2 \rightarrow V_2O_{y-1} + SO_3$ reactions.

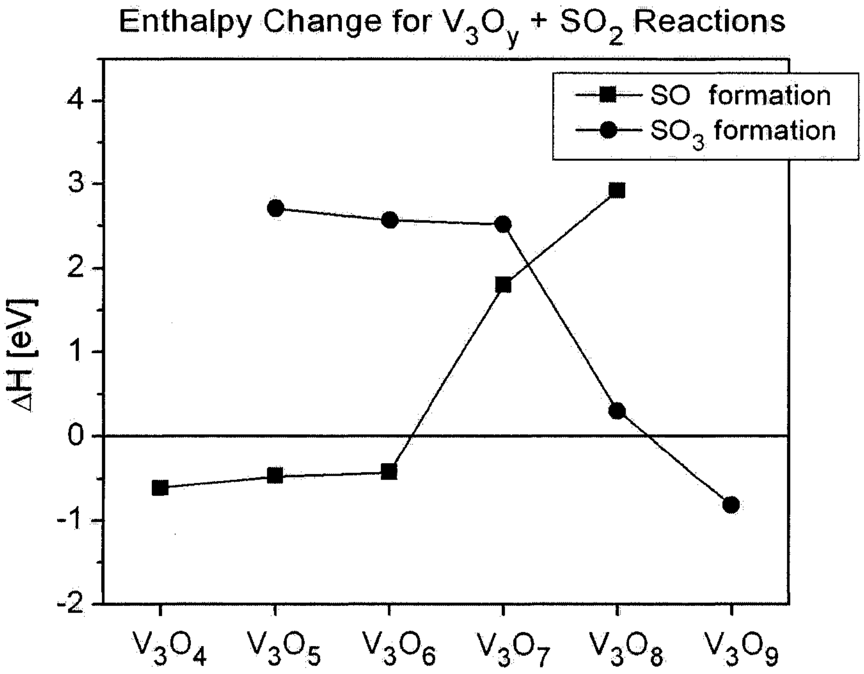

Figure 4.3. Enthalpy change for $V_3O_y + SO_2 \rightarrow V_3O_{y+1} + SO$ and $V_3O_y + SO_2 \rightarrow V_3O_{y-1} + SO_3$ reactions.

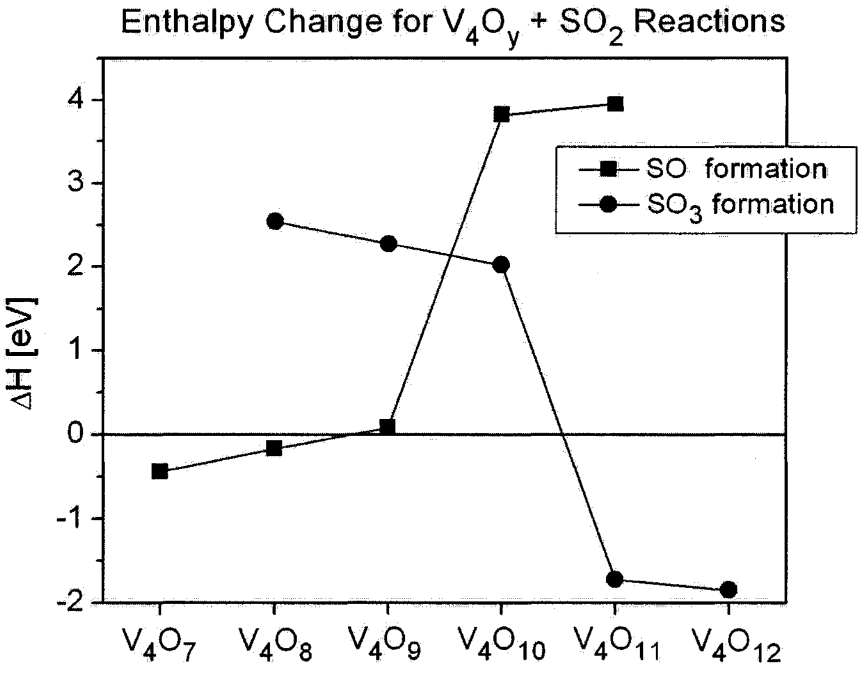

Figure 4.4. Enthalpy changes for $V_4O_y + SO_2 \rightarrow V_4O_{y+1} + SO$ and $V_4O_y + SO_2 \rightarrow V_4O_{y-1} + SO_3$ reactions.

Reaction intermediates, barriers and reaction paths

In an effort to better understand paths for the reactions of vanadium oxides with sulfur dioxide, intermediate structures of the smallest vanadium oxides, VO_{1-4}, with SO_2 are optimized at the BPW91/TZVP level of theory. Structures of various isomers are depicted in Figures 4.5 – 4.8. The ground electronic states of all the isomers are doublets, except the highest energy isomer of VO_2SO_2, which is a quartet.

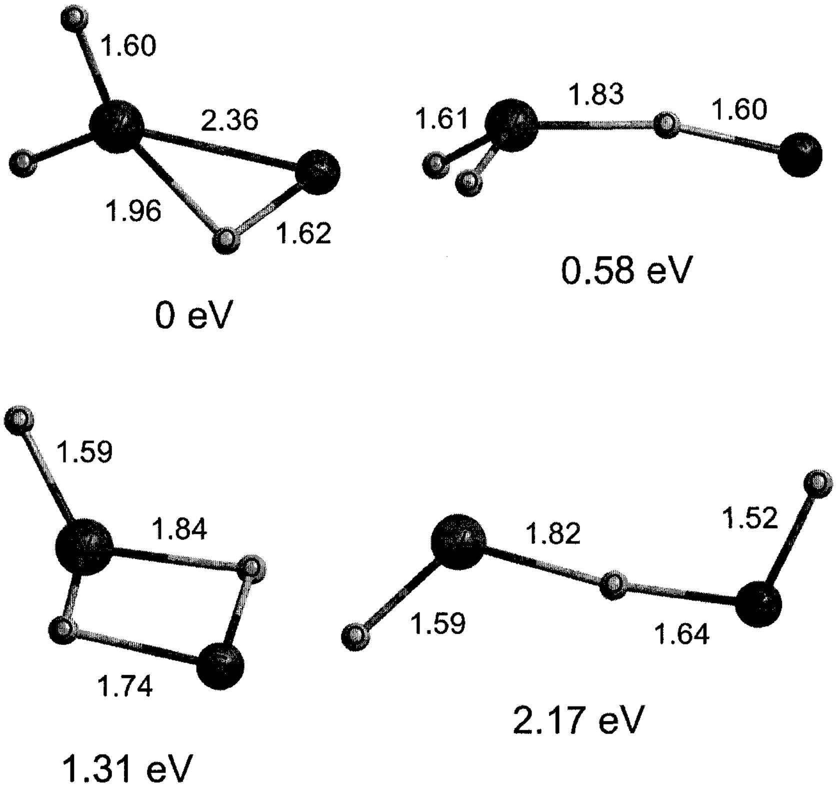

Figure 4.5. $VOSO_y$ structures optimized at the BPW91/TZVP level of theory.

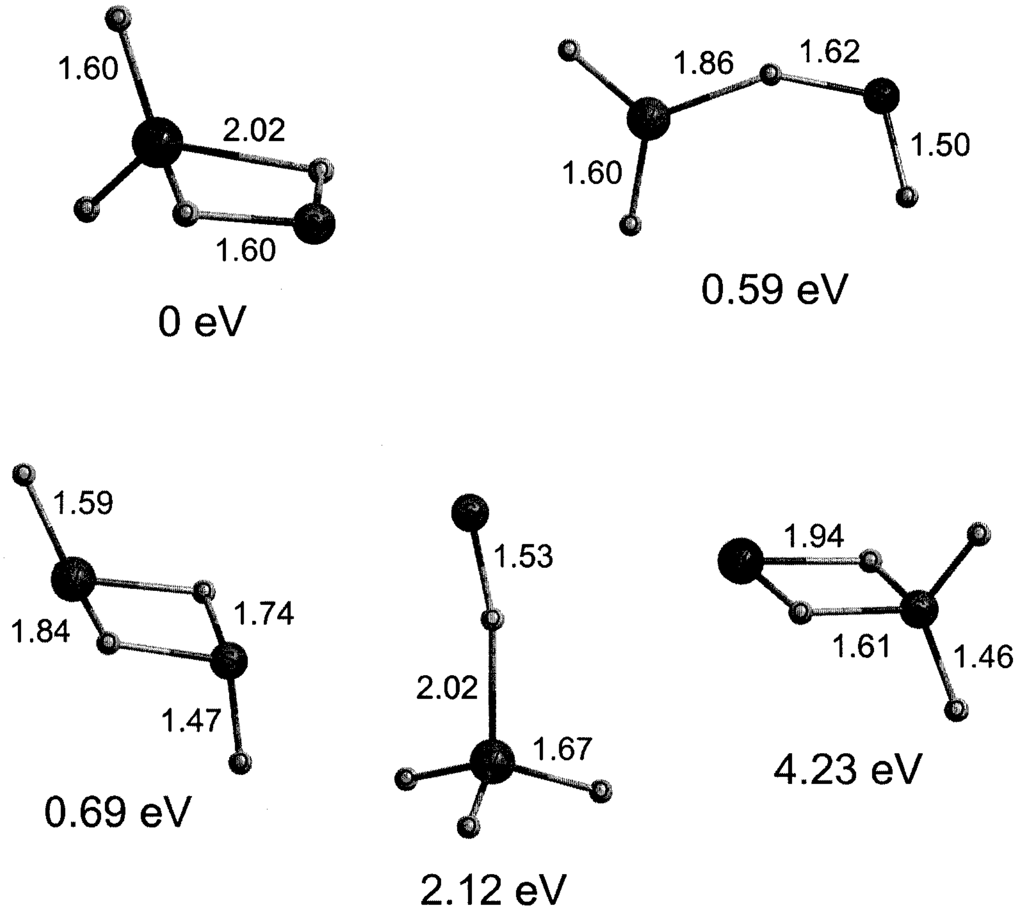

Figure 4.6. VO_2SO_2 structures optimized at the BPW91/TZVP level of theory.

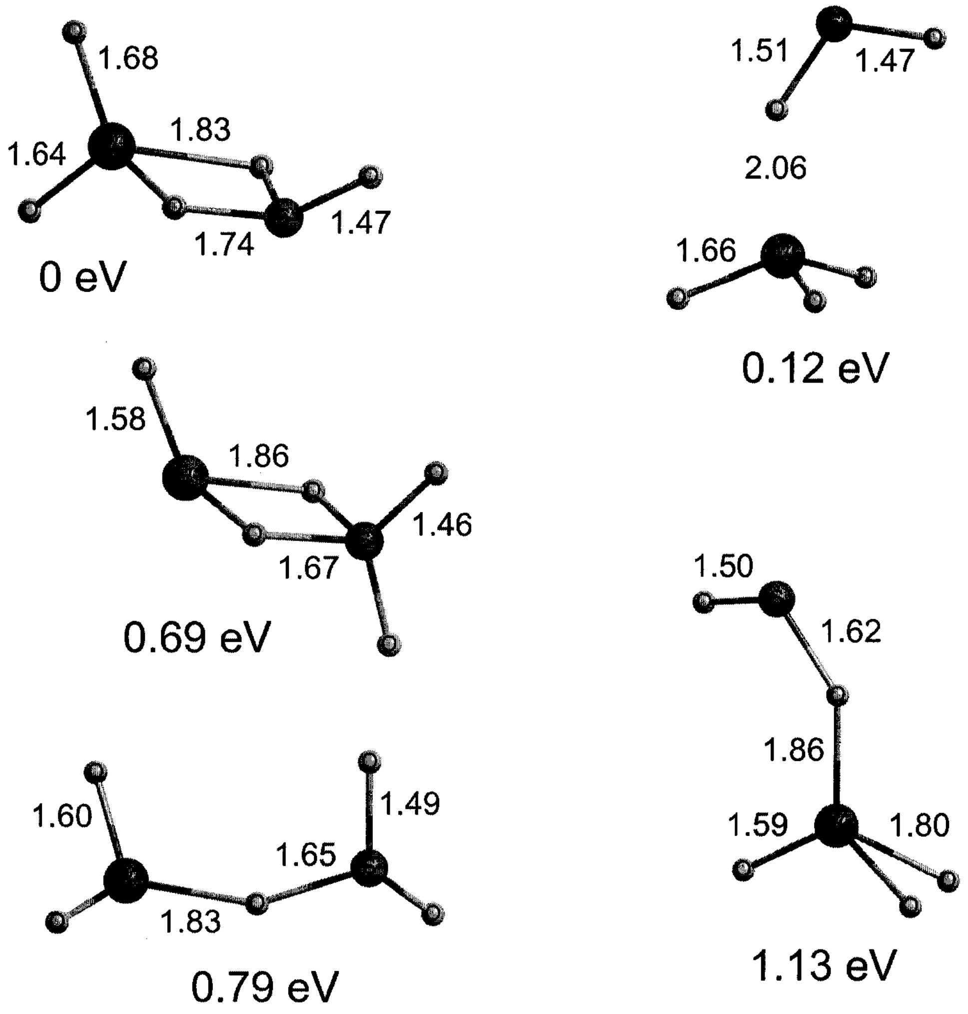

Figure 4.7. VO_3SO_2 structures optimized at the BPW91/TZVP level of theory.

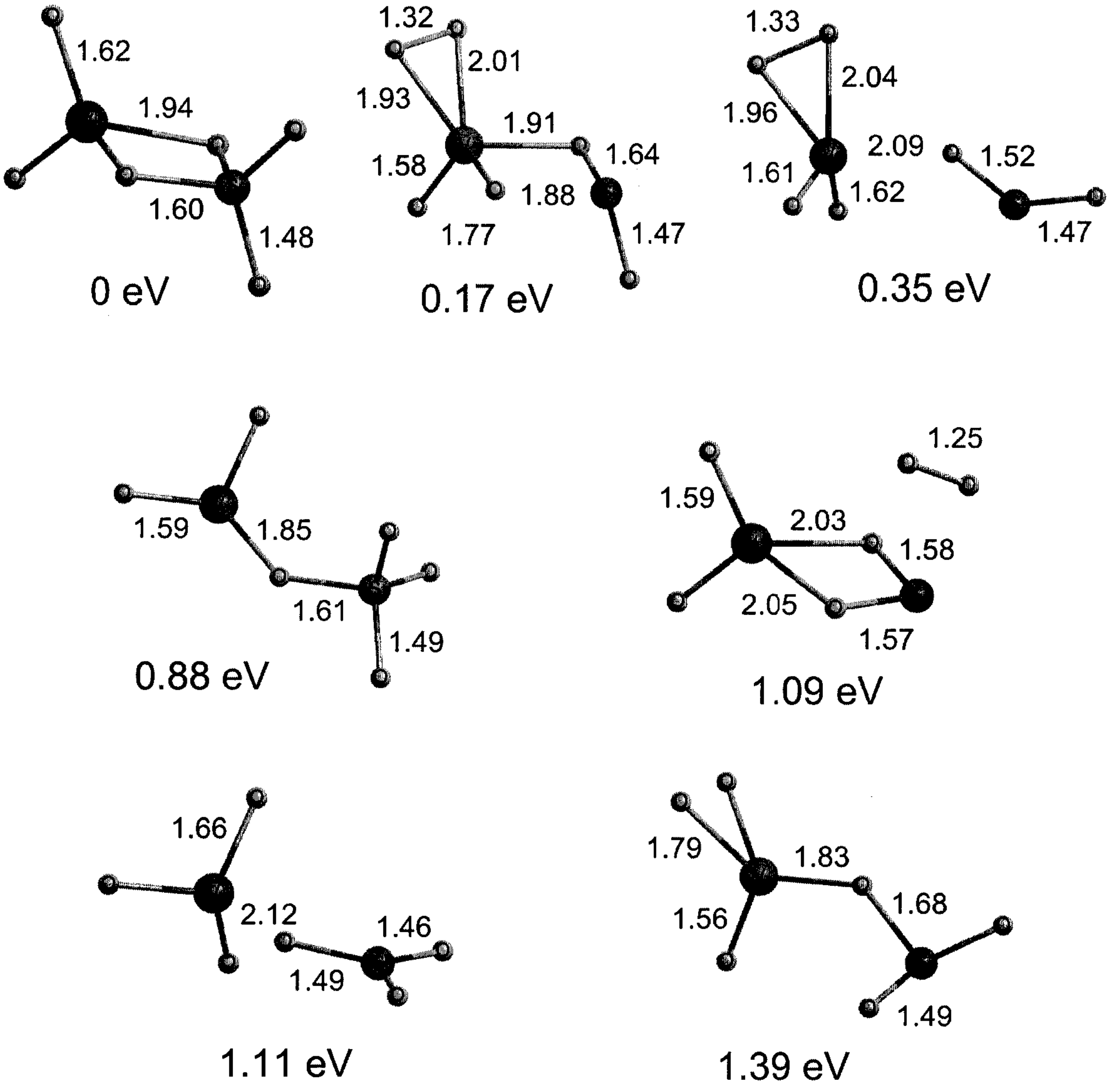

Figure 4.8. VO_4SO_2 structures optmized at the BPW91/TZVP level of theory.

Structures of different VO_ySO_2 isomers give some indication of the possible formation of SO, SO_2, or SO_3 from VO_ySO_2 complexes. The lowest energy structures of $VOSO_2$ (Figure 4.5) hint at SO formation, while structures of VO_2SO_2 (Figure 4.6) and VO_3SO_2 (Figure 4.7) are more indicative of SO_2 formation and suggest that VO_2 and VO_3 should be relatively stable with respect to the reaction with SO_2. Low energy structures of VO_4SO_2 (Figure 4.8) are, contrary to the expectations, also suggestive of SO_2 formation. BPW91/TZVP predicts $\Delta H = +0.63$ eV for the $VO_4 + SO_2 \rightarrow VO_3 + SO_3$ reaction, while BPW91/LANL2DZ calculations calibrated with experimental data for SO_2 predict $\Delta H = -0.45$ eV. The BPW91/TZVP result is a consequence of overestimation of V – O bond strength and at the same time underestimation of O – SO and O – SO_2 bond strengths. If a better theoretical method were used to optimize these structures, most probably the same isomers would be obtained, but with different relative energies. This result is nonetheless within the overall ± 1 eV apparent accuracy of the present level of theory.

Table 4.4 shows the bonding energies of VO_{1-4} with SO_2 for their lowest energy isomers. Even though the bonding energies computed with BPW91/TZVP are probably about 1 eV too strong, we can still conclude that the complexes of V_xO_y clusters with SO_2 should be stable. This is confirmed by the observation of numerous $V_xO_ySO_2$ reaction intermediates in the gas phase experiments.[47]

Structure	**Bonding Energy [eV]**
$VO + SO_2$	4.08
$VO_2 + SO_2$	2.75
$VO_3 + SO_2$	1.51
$VO_4 + SO_2$	1.19

Table 4.4. Bonding energies for lowest energy isomers of VO_ySO_2 (y = 1 – 4) clusters computed at the BPW91/TZVP level of theory.

Calculation of a barrier for the reaction of oxygen-deficient VO with SO_2 is also performed at the BPW91/TZVP level of theory. Despite the shortcomings of this method, calculations can still provide us with valuable insights into the reaction mechanisms. Since the oxidation of SO_2 is suggested to require only one vanadium surface site,[41-43] calculations focused on VO_y clusters should also be representative of a mechanism occurring on larger clusters.

Figure 4.9 shows one possible reaction path for $VO + SO_2 \rightarrow VO_2 + SO$. No overall barrier for the reaction is found, only small barriers for rearrangement of intermediate structures of $VOSO_2$. Note that due to the existence of many different isomers of $VOSO_2$, many possible reaction paths for formation of VO_2 and SO will exist.

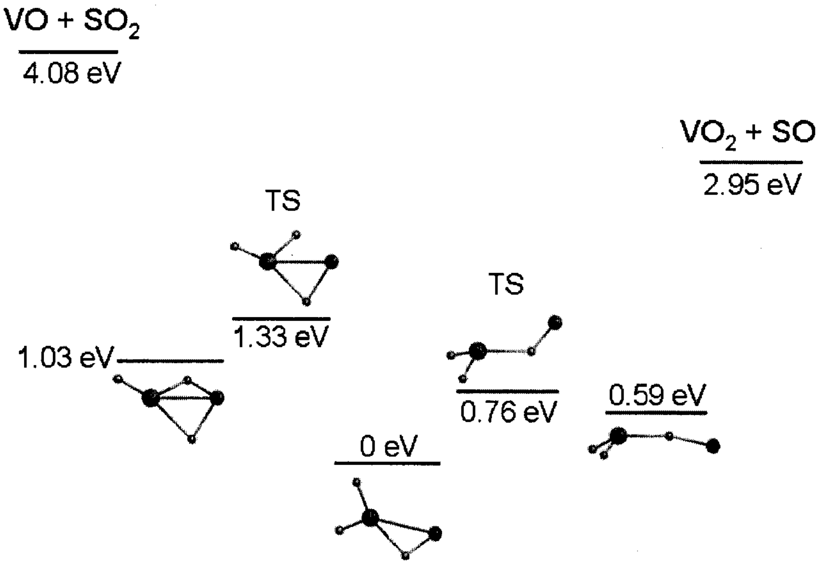

Figure 4.9. Possible reaction path for $VO + SO_2 \rightarrow VO_2 + SO$.

Condensed phase catalytic mechanisms

Based on the calculations presented here, we can propose some possible catalytic mechanisms for $SO_2 \rightarrow SO_3$ catalytic conversion in the condensed phase. First of all, one specific vanadium oxide cluster does not appear to be responsible for the catalytic behavior of vanadium oxides. On the contrary, SO_2 will react with most clusters: reactions with oxygen deficient clusters will lead to the formation of SO, while reactions with oxygen very rich clusters will result in the formation of SO_3. SO can further react with O_2 to produce SO_3 ($\Delta H = -96$kcal/mol, rate gas kinetic), providing another channel for formation of SO_3.[69] Note that other processes, such as SO_2 formation, might compete with the SO_3 formation from SO.[69] Furthermore, "stable clusters" such as VO_2, V_2O_5, V_3O_7, and V_4O_{10} are predicted to be least reactive with SO_2. They will still form intermediate complexes with SO_2 (see also part I[47]), but overall reactions of these clusters with SO_2 leading to the formation of SO or SO_3 are endothermic, requiring extra energy. Note that the general "belief" that catalytic reactions occur at defect condensed phase or surface sites is consistent with these results. In the following paragraphs we will describe two possible catalytic cycles that rely on these oxidation/reduction properties of vanadium oxide clusters. V_mO_n denote the stable sites, while V_mO_{n+i} and V_mO_{n-i} (m, n, i are positive integers, $i < n$) describe oxygen-rich and oxygen-deficient sites, respectively. Enthalpy for the specific reactions involving vanadium oxide clusters is given based on the calculations performed with gas-phase clusters at the BPW91/LANL2DZ level of theory. Enthalpy of SO_3 formation from SO is taken from available experimental data.[64]

Catalytic Cycle 1: $SO_2 \rightarrow SO_3$ occurs on oxygen-rich or oxygen-deficient sites

Step #1: Formation of the oxygen-rich and oxygen-deficient sites from stable sites.

$2V_mO_n \rightarrow 2V_mO_{n-1} + O_2$

$2V_mO_n + O_2 \rightarrow 2V_2O_{n+1}$

$V_mO_n \rightarrow V_mO_{n-2} + O_2$

$V_mO_n + O_2 \rightarrow V_mO_{n+2}$

…

For example,

$2V_2O_5 \rightarrow 2V_2O_4 + O_2$ ($\Delta H = 5.60$ eV)

$2V_2O_5 + O_2 \rightarrow 2V_2O_6$ ($\Delta H = -0.73$ eV)

$V_2O_5 \rightarrow V_2O_3 + O_2$ ($\Delta H = 6.79$ eV)

$V_2O_5 + O_2 \rightarrow V_2O_7$ ($\Delta H = -0.8$ eV)

…

Oxygen-deficient and oxygen-rich sites are formed from the stable sites. This step is endothermic and requires some source of energy, for example in the form of heat. (Note that although reactions like $2V_2O_5 + O_2 \rightarrow 2V_2O_6$ are overall predicted to be exothermic, they will have a significant barrier since O – O bond breaking requires some activation energy.) Additionally, some oxygen-rich or oxygen-deficient sites (or defects) will be naturally present in the condensed phase.

Step #2: Reactions of oxygen-deficient and oxygen-rich sites with SO_2, regeneration of stable sites.

$V_mO_{n+2} + SO_2 \rightarrow V_mO_{n+1} + SO_3$

$V_mO_{n+1} + SO_2 \rightarrow V_mO_n + SO_3$

$V_mO_{n-2} + SO_2 \rightarrow V_mO_{n-1} + SO$, $SO + O_2 \rightarrow SO_3$

$V_2O_{n-1} + SO_2 \rightarrow V_mO_n + SO$, $SO + O_2 \rightarrow SO_3$

…

For example,

$V_2O_7 + SO_2 \rightarrow V_2O_6 + SO_3$ ($\Delta H = -0.73$ eV)

$V_2O_6 + SO_2 \rightarrow V_2O_5 + SO_3$ ($\Delta H = -0.76$ eV)

$V_2O_3 + SO_2 \rightarrow V_2O_4 + SO$ ($\Delta H = -0.73$ eV), $SO + O_2 \rightarrow SO_3$ ($\Delta H = -4.15$ eV)

$V_2O_4 + SO_2 \rightarrow V_2O_5 + SO$ ($\Delta H = 0.46$ eV), $SO + O_2 \rightarrow SO_3$ ($\Delta H = -4.15$ eV)

...

Oxygen-deficient and oxygen-rich sites react with SO_2, leading to the formation of SO and SO_3. SO further reacts with O_2, producing SO_3. These reactions are exothermic and without significant barriers. Stable sites are also regenerated in this step, since oxygen-rich sites are reduced and oxygen-deficient oxidized.

Catalytic Cycle 2: $SO_2 \rightarrow SO_3$ occurs on stable sites

Step #1: Reactions of stable sites with SO_2

$V_mO_n + SO_2 \rightarrow V_mO_{n+1} + SO$, $SO + O_2 \rightarrow SO_3$

$V_mO_n + SO_2 \rightarrow V_mO_{n-1} + SO_3$

...

For example,

$V_2O_5 + SO_2 \rightarrow V_2O_6 + SO$ ($\Delta H = 2.89$ eV), $SO + O_2 \rightarrow SO_3$ ($\Delta H = -4.15$ eV)

$V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3$ ($\Delta H = 1.64$ eV)

...

Stable sites react with SO_2, producing SO_3 and SO as well as oxygen-rich and oxygen-deficient sites. These reactions are endothermic, requiring additional energy.

Step #2: Regeneration of stable sites

$V_mO_{n+1} + SO_2 \rightarrow V_mO_n + SO_3$

$V_mO_{n+1} + V_mO_{n-1} \rightarrow 2V_mO_n$

$V_mO_{n-2} + O_2 \rightarrow V_mO_n$

$2V_mO_{n-1} + O_2 \rightarrow 2V_mO_n$

...

For example,

$V_2O_6 + SO_2 \rightarrow V_2O_5 + SO_3$ ($\Delta H = -0.79$ eV)

$V_2O_6 + V_2O_4 \rightarrow 2V_2O_5$ ($\Delta H = -2.44$ eV)

$V_2O_3 + O_2 \rightarrow V_2O_5$ ($\Delta H = -6.79$ eV)

$2V_2O_4 + O_2 \rightarrow 2V_2O_5$ ($\Delta H = -5.60$ eV)

...

There are several ways by which stable sites can be regenerated in this step: 1. oxygen-deficient and oxygen-rich sites react with leftover SO_2, producing SO_3 and a stable site; 2. oxygen-deficient and oxygen-rich sites react with each other, forming two stable sites; 3. oxygen-poor clusters are oxidized with O_2 present in the system.

In addition to the two mechanisms described above, other mechanisms leading to the SO_3 formation are possible. Experimental evidence exists for reaction of stable sites with SO_2 and O_2 leading to the formation of oxygen-rich sites and SO_3. This mechanism is discussed in more detail in part I.[47] One can imagine other mechanisms as well – for example, two units of SO_2 coming together on a vanadium oxide, producing SO and SO_3 (a $V_2O_4(SO_2)_2$ complex have been also observed experimentally[47]). Additional mechanisms, involving first reduction of a vanadium oxide by SO_2 and then its reoxidation by O_2,[40] or adsorption of O_2 followed by oxidation of two SO_2 molecules,[1] have been suggested based on condensed-phase experimental work. Which one of these mechanisms most closely describes actual processes occurring in the condensed phase should be a subject of further experimental and theoretical studies. Note, however, that the profusion of potential mechanisms is a positive and perhaps important part of the overall efficiency of the catalytic conversion of SO_2 to SO_3 by vanadium oxide. In general, catalytic metal oxide surfaces are very complex and can terminate with multiple surface functionalities.[70] Moreover, vanadium oxide catalytic conversion of SO_2 to SO_3 occurs in molten phase under high temperatures and presence of alkali metal sulfates,[71,72] which leads to formation of a variety of chemical species and adds yet another layer of complexity. Quite possibly, no single mechanism is responsible for catalytic formation of SO_3, but two or more mechanisms occur concurrently, thus making vanadium oxide a very efficient catalyst.

CONCLUSION

Reactions of neutral vanadium oxide clusters with SO_2 are studied with the aim of elucidation of a mechanism for catalytic formation of SO_3.

Theoretical calculations at the BPW91/LANL2DZ level of theory, calibrated with the experimental enthalpies of formation for SO_{1-3} molecules, suggest that both oxidation and reduction of SO_2 occur. $SO_2 \rightarrow SO_3$ formation takes place on the oxygen-rich clusters, while $SO_2 \rightarrow SO$ formation is facilitated by oxygen-poor vanadium oxide clusters. SO formation provides another channel for SO_3 production, since SO readily reacts with O_2: $SO_2 + O_2 \rightarrow SO_3$. SO and SO_3 formation is also confirmed by gas phase experimental studies.[47]

Neutral vanadium oxide clusters form stable reaction intermediates with SO_2, illustrated with the example of the smallest vanadium oxide clusters VO_y, $y = 1 - 4$. Furthermore, BPW91/TZVP calculations find no overall barrier for $VO + SO_2 \rightarrow VO_2 + SO$ reaction, suggesting that reactions of oxygen-poor clusters with SO_2 occur rather easily. In general, many possible reaction paths will be feasible since a variety of $V_xO_ySO_2$ isomers exist that are lower in energy than reactants or products.

Finally, two possible catalytic cycles are suggested based on the facility of vanadium oxide clusters both to oxidize and reduce SO_2. We suggest that more than just one detailed mechanism contributes to the conversion of SO_2 to SO_3 in the condensed phase. Further experimental and theoretical work is necessary to determine the role played by specific mechanisms.

Reported calculations are in a very good agreement with and complement gas phase molecular beam experimental studies of neutral vanadium oxide clusters.

One general extrapolation from these studies of heterogeneous catalysis can be suggested concerning the overall oxidation/reduction catalytic processes we have posited: the profusion of the reactant species, reaction intermediates and transition states, and even mechanisms for the conversion of SO_2 to SO_3 may be a major reason that vanadium oxide is an excellent oxidation/reduction catalyst for the reaction. The fact that many low lying, energy accessible reaction intermediates and transition states are available, that many sites (clusters) can initiate the conversion, that many paths can lead to SO or SO_3, and that the thermodynamics enable and favor both product generation and catalyst regeneration to occur, ensure an overall very efficient and general rate enhancement process for the reaction.

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REFERENCES

(1) Lapina, O. B.; Bal'zhinimaev, B. S.; Boghosian, S.; Eriksen, K. M.; Fehrmann, R. *Catalysis Today* **1999**, *51*, 469.

(2) Oyama, S. T.; Somorjai, G. A. *Journal of Physical Chemistry* **1990**, *94*, 5022.

(3) Bond, G. C.; Tahir, S. F. *Applied Catalysis* **1991**, *71*, 1.

(4) Wu, H. B.; Wang, L. S. *Journal of Chemical Physics* **1998**, *108*, 5310.

(5) Zhai, H. J.; Wang, L. S. *Journal of Chemical Physics* **2002**, *117*, 7882.

(6) Asmis, K. R.; Meijer, G.; Brummer, M.; Kaposta, C.; Santambrogio, G.; Woste, L.; Sauer, J. *Journal of Chemical Physics* **2004**, *120*, 6461.

(7) Asmis, K. R.; Santambrogio, G.; Brummer, M.; Sauer, J. *Angewandte Chemie-International Edition* **2005**, *44*, 3122.

(8) Knight, L. B.; Babb, R.; Ray, M.; Banisaukas, T. J.; Russon, L.; Dailey, R. S.; Davidson, E. R. *Journal of Chemical Physics* **1996**, *105*, 10237.

(9) Zhao, Y. Y.; Gong, Y.; Chen, M. H.; Zhou, M. F. *Journal of Physical Chemistry A* **2006**, *110*, 1845.

(10) Pykavy, M.; van Wullen, C. *Journal of Physical Chemistry A* **2003**, *107*, 5566.

(11) Pykavy, M.; van Wullen, C.; Sauer, J. *Journal of Chemical Physics* **2004**, *120*, 4207.

(12) Vyboishchikov, S. F.; Sauer, J. *Journal of Physical Chemistry A* **2000**, *104*, 10913.

(13) Calatayud, M.; Andres, J.; Beltran, A. *Journal of Physical Chemistry A* **2001**, *105*, 9760.

(14) Fielicke, A.; Rademann, K. *Physical Chemistry Chemical Physics* **2002**, *4*, 2621.

(15) Feyel, S.; Schroder, D.; Schwarz, H. *Journal of Physical Chemistry A* **2006**, *110*, 2647.

(16) Bell, R. C.; Zemski, K. A.; Kerns, K. P.; Deng, H. T.; Castleman, A. W. *Journal of Physical Chemistry A* **1998**, *102*, 1733.

(17) Moore, N. A.; Mitric, R.; Justes, D. R.; Bonacic-Koutecky, V.; Castleman, A. W. *Journal of Physical Chemistry B* **2006**, *110*, 3015.

(18) Justes, D. R.; Castleman, A. W.; Mitric, R.; Bonacic-Koutecky, V. *European Physical Journal D* **2003**, *24*, 331.

(19) Justes, D. R.; Mitric, R.; Moore, N. A.; Bonacic-Koutecky, V.; Castleman, A. W. *Journal of the American Chemical Society* **2003**, *125*, 6289.

(20) Feyel, S.; Scharfenberg, L.; Daniel, C.; Hartl, H.; Schroder, D.; Schwarz, H. Dehydrogenation of Methanol by Vanadium Oxide and Hydroxide Cluster Cations in the Gas Phase, 2007.

(21) Vyboishchikov, S. F. *Journal of Molecular Structure - Theochem* **2005**, *723*, 53.

(22) Anstrom, M.; Topsoe, N. Y.; Dumesic, J. A. *Journal of Catalysis* **2003**, *213*, 115.

(23) de Noronha, A. L. O.; Duarte, H. A. *Journal of Inorganic Biochemistry* **2005**, *99*, 1708.

(24) Gijzeman, O. L. J.; van Lingen, J. N. J.; van Lenthe, J. H.; Tinnemans, S. J.; Keller, D. E.; Weckhuysen, B. M. *Chemical Physics Letters* **2004**, *397*, 277.

(25) Keller, D. E.; Koningsberger, D. C.; Weckhuysen, B. M. *Journal of Physical Chemistry B* **2006**, *110*, 14313.

(26) van Lingen, J. N. J.; Gijzeman, O. L. J.; Weckhuysen, B. M.; van Lenthe, J. H. *Journal of Catalysis* **2006**, *239*, 34.

(27) Schoiswohl, J.; Surnev, S.; Netzer, F. P.; Kresse, G. *Journal of Physics-Condensed Matter* **2006**, *18*, R1.

(28) Vyboishchikov, S. F.; Sauer, J. *Journal of Physical Chemistry A* **2001**, *105*, 8588.

(29) Brazdova, V.; Ganduglia-Pirovano, M. V.; Sauer, J. *Physical Review B* **2004**, *69*.

(30) Khaliullin, R. Z.; Bell, A. T. *Journal of Physical Chemistry B* **2002**, *106*, 7832.

(31) Dobler, J.; Pritzsche, M.; Sauer, J. *Journal of the American Chemical Society* **2005**, *127*, 10861.

(32) Redfern, P. C.; Zapol, P.; Sternberg, M.; Adiga, S. P.; Zygmunt, S. A.; Curtiss, L. A. *Journal of Physical Chemistry B* **2006**, *110*, 8363.

(33) Ganduglia-Pirovano, M. V.; Sauer, J. *Journal of Physical Chemistry B* **2005**, *109*, 374.

(34) Ganduglia-Pirovano, M. V.; Sauer, J. *Physical Review B* **2004**, *70*.

(35) Ganduglia-Pirovano, M. V.; Sauer, J. *Physical Review B* **2004**, *70*.

(36) Tokarz-Sobieraj, R.; Grybos, R.; Witko, M.; Hermann, K. *Collection of Czechoslovak Chemical Communications* **2004**, *69*, 121.

(37) Tokarz-Sobieraj, R.; Witko, M.; Grybos, R. *Catalysis Today* **2005**, *99*, 241.

(38) Abu Haija, M.; Guimond, S.; Romanyshyn, Y.; Uhl, A.; Kuhlenbeck, H.; Todorova, T. K.; Ganduglia-Pirovano, M. V.; Dobler, J.; Sauer, J.; Freund, H. J. *Surface Science* **2006**, *600*, 1497.

(39) Kato, A.; Seiyama, T.; Tomoda, K.; Mochida, I. *Bulletin of the Chemical Society of Japan* **1972**, *45*, 690.

(40) Dunn, J. P.; Koppula, P. R.; Stenger, H. G.; Wachs, I. E. *Applied Catalysis B-Environmental* **1998**, *19*, 103.

(41) Dunn, J. P.; Stenger, H. G.; Wachs, I. E. *Catalysis Today* **1999**, *51*, 301.

(42) Dunn, J. P.; Stenger, H. G.; Wachs, I. E. *Journal of Catalysis* **1999**, *181*, 233.

(43) Dunn, J. P.; Stenger, H. G.; Wachs, I. E. *Catalysis Today* **1999**, *53*, 543.

(44) Fouda, M. F. R.; Saleh, H. I.; Abd-Elzaher, M. M.; Amin, R. S. *Applied Catalysis A - General* **2002**, *223*, 11.

(45) Giakoumelou, I.; Caraba, R. M.; Parvulescu, V. I.; Boghosian, S. *Catalysis Letters* **2002**, *78*, 209.

(46) Giakoumelou, L.; Parvulescu, V.; Boghosian, S. *Journal of Catalysis* **2004**, *225*, 337.

(47) He, S. G.; Xie, Y.; Dong, F.; Heinbuch, S.; Jakubikova, E.; Rocca, J. J.; Bernstein, E. R. *in preparation* **2007**.

(48) Muetterties, E. L. *Science* **1977**, *196*, 839.

(49) Becke, A. D. *Journal of Chemical Physics* **1993**, *98*, 5648.

(50) Lee, C. T.; Yang, W. T.; Parr, R. G. *Physical Review B* **1988**, *37*, 785.

(51) Foltin, M.; Stueber, G. J.; Bernstein, E. R. *Journal of Chemical Physics* **2001**, *114*, 8971.

(52) Becke, A. D. *Physical Review A* **1988**, *38*, 3098.

(53) Perdew, J. P.; Wang, Y. *Physical Review B* **1992**, *45*, 13244.

(54) Jakubikova, E.; Rappe, A. K.; Bernstein, E. R. *in preparation* **2007**.

(55) Hay, P. J.; Wadt, W. R. *Journal of Chemical Physics* **1985**, *82*, 270.

(56) Dunning Jr., T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum Press: New York, 1976; Vol. 3.

(57) *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J.; Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg MD, June 2005.

(58) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J. W.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, Revision A.11; Gaussian, Inc.: Pittsburgh PA, 2001.

(59) Balducci, G.; Gigli, G.; Guido, M. *Journal of Chemical Physics* **1983**, *79*, 5616.

(60) Pedley, J. B.; Marshall, E. M. *Journal of Physical and Chemical Reference Data* **1983**, *12*, 967.

(61) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(62) Li, J.; Demello, P. C.; Jug, K. *Journal of Computational Chemistry* **1992**, *13*, 85.

(63) Rakowitz, F.; Marian, C. M.; Seijo, L. *Journal of Chemical Physics* **1999**, *111*, 10436.

(64) *CRC Handbook of Chemistry and Physics*, 85th ed.; CRC Press: Boca Raton, Fl, 2004.

(65) Dunning, T. H.; Peterson, K. A.; Wilson, A. K. *Journal of Chemical Physics* **2001**, *114*, 9244.

(66) Bell, R. D.; Wilson, A. K. *Chemical Physics Letters* **2004**, *394*, 105.

(67) Wilson, A. K.; Dunning, T. H. *Journal of Chemical Physics* **2003**, *119*, 11712.

(68) Yockel, S.; Wilson, A. K. *Chemical Physics Letters* **2006**, *429*, 645.

(69) Wood, W. P.; Heicklen, J. *Journal of Physical Chemistry* **1971**, *75*, 861.

(70) Wachs, I. E. *Catalysis Today* **2005**, *100*, 79.

(71) Dearnaley, R. I.; Kerridge, D. H. *Thermochimica Acta* **1987**, *121*, 121.

(72) West, J. R.; Smith, G. M. Sulfuric Acid and Sulfur. In *Riegel's Handbook of Industrial Chemistry*; Kent, J. A., Ed.; Van Nostrand Reinhold Company Inc.: New York, N. Y., 1983; pp 130

CHAPTER 5

FUTURE DIRECTIONS

BASIS SETS FOR INTERMOLECULAR INTERACTIONS

Development of efficient basis sets for calculations of intermolecular interactions with large dispersion components is not an easy task. Although relatively few functions (a set of p and d functions for hydrogen, or a set of d and f functions for first row elements) optimized with respect to the interaction dramatically improve computed bonding energies, fairly large basis sets are needed for proper description of core and valence electrons. If the underlying basis sets are too small, deficiencies in the description of core and valence regions combined with the presence of diffuse functions give rise to very large basis set superposition errors (BSSE) in the calculation of bonding energies. On the other hand, large, almost complete basis sets, that provide very good description of core and valence, are computationally expensive and bring about linear dependency problems. There is a need for basis sets that are efficient (i.e., computationally inexpensive), do not cause linear dependency problems, are saturated enough so BSSE is negligible, and provide very accurate bonding energies for systems with dominant dispersion component. At present, no such basis sets are known.

The main issue for basis set development for intermolecular interactions seems to be slow convergence of Gaussian expansions toward the basis set limit. This means that to achieve very accurate descriptions (i.e., within nanohartree accuracy) of higher-order phenomena such as dispersion or, more generally, electron correlation effects, large sets of Gaussian functions are needed.[1] At least two reasons contribute to this slow convergence of Gaussian expansions: 1. use of one-electron wavefunctions as building blocks for many-electron wavefunctions (i.e., many-electron wavefunctions are expressed in terms of antisymmetrized products of one-electron wavefunctions); and 2. the general shape of Gaussian functions. With regard to this latter point, Gaussian functions do not properly reproduce nuclear cusps and fall off too fast in the region away from nuclei.

The first reason for slow convergence (expansion of many-electron wavefunction in terms of one-electron wavefunctions) is not directly related to the choice of Gaussians as basis functions. The same would be true even if different basis functions (for example Slater functions) were used. Slow convergence can be in this case alleviated by considering the explicit dependence of the wavefunction on inter-electronic coordinates r_{12}. The explicitly correlated wavefunction approach is able to describe correlation effects in many-electron systems properly with fewer basis functions than standard methods.[1-3] Since dispersion interactions also originate from electron correlation effects, it might be beneficial to apply r_{12} methods to calculate intermolecular interactions. With this method one might potentially achieve a better description of intermolecular interactions with fewer basis functions, thus eliminating linear dependence problems. One drawback here is that explicit dependence of wavefunction on inter-electronic coordinates vastly complicates the evaluation of 2-electron integrals that are needed in the calculations.

The second issue revolves around the choice of Gaussians as basis functions for calculations of intermolecular interactions. Due to the deficiencies in their shape, large numbers of Gaussians are needed to achieve satisfactory accuracy in the computed energies and other properties of weakly bound systems. Large numbers of Gaussians combined with the presence of diffuse functions required for proper description of intermolecular interactions leads in turn to linear dependence problems. This puts practical limits on the accuracy one can achieve when using Gaussian basis sets, since at some point (once the number of basis functions becomes large enough) calculations becomes numerically unstable.

The finite element method (FEM) offers an alternative approach to the use of Gaussian basis sets. In the FEM, the solution region is divided into a number of smaller regions called elements. Basis functions used in the FEM are traditionally composed of polynomial functions. They are strictly local, defined to be nonzero only on a particular element, and zero everywhere else. This is in contrast to Gaussian basis functions, which have a global character, and are defined over all the solution space. Locality of the finite element (FE) basis functions means that they do not incur global linear dependency problems, and they lead to sparse and band-structured matrices for which efficient algorithms for diagonalization are available. FE basis sets have been implemented for use with various methods, including Hartree-Fock,[4-6] MP2,[7] explicitly correlated methods,[8] and density functional methods.[9,10] Unfortunately, FE basis functions do not reproduce nuclear cusps accurately.[11] Large numbers of polynomials need to be included for elements where nuclei are situated. This then becomes computationally very expensive in the case of polyatomic molecules. Therefore, FEM for polyatomic molecules is not currently competitive with traditional global expansion methods.

One way to solve the basis set problem for calculations of intermolecular interactions would be to combine Gaussian basis sets with FE basis sets. Linear combinations of atom-centered compact Gaussian functions can be used to describe nuclear cusps, thus compensating for the deficiency of FE basis sets in this region. Local FE basis functions would then be used to provide additional flexibility needed to describe electron correlation events properly. This will eliminate the need to add large number of Gaussians to the basis set to improve description of wavefunction in the regions away from nuclei. Since the FE basis functions are local, they will not contribute to BSSE, nor to the linear dependence problems. Calculation of 2-electron integrals should also not pose any difficulties. FE functions are polynomials, so they will not be hard to integrate and standard quantum chemistry program packages already contain efficient codes for calculation of 2-electron integrals over Gaussian functions. Use of compact Gaussian basis functions on nuclei will also minimize the overlap between Gaussians centered on two different atoms thus reducing the number of 2-electron multicenter integrals that need to be evaluated. Moreover, this minimal overlap will also help to prevent conditions that give rise to BSSE.[12] Combined FE-Gaussian basis sets have already been used in density functional theory calculations on several polyatomic molecules[12,13] and based on published results show a great promise for calculations of intermolecular interactions.

DFT CALCULATIONS OF VANADIUM OXIDE CATALYST

Results on structure and reactivity of neutral vanadium oxide clusters in the gas phase presented in Chapters 3 and 4 demonstrate that much can be learned about condensed phase catalytic processes from these simple model systems. This is especially true when computational results are complemented by experimental investigations.

Theoretical as well as experimental[14] studies performed in our laboratory suggest three possible mechanism for SO_3 formation: 1. vanadium oxide catalyzed $SO_2 \rightarrow SO$ conversion (occurs on oxygen deficient sites) with subsequent $SO + O_2 \rightarrow SO_3$ reaction; 2. vanadium oxide catalyzed $SO_2 \rightarrow SO_3$ conversion (occurs on oxygen rich sites); and 3. formation of stable intermediates, $V_xO_y + SO_2 \rightarrow V_xO_ySO_2$, (occurs on stable, oxygen saturated vanadium oxide sites), and subsequent reaction of these intermediates with O_2; $V_xO_ySO_2 + O_2 \rightarrow V_xO_{y+1} + SO_3$. It is important to note that the computational studies of reactions between vanadium oxide clusters and SO_2 presented in this work are concerned with the thermodynamics of these reactions and do not consider reaction kinetics. To learn more about the kinetics and determine preferred mechanism for SO_3 formation, one would need to investigate barriers for the above reactions in more detail. In this respect, optimization of transition states corresponding to steps of the reaction mechanisms proposed above and the application of transition state theory to obtain rate constants should aid us in predicting which of the mechanisms for SO_3 formation is the most likely to occur. SO_2 and O_2 concentrations and temperature effects will also have a considerable influence on SO_3 formation in the condensed phase.

Our results also point out challenges that computational approaches need to overcome to become a better tool for catalysis research. First, while density functional theory (DFT) calculations provide us with qualitatively accurate pictures, they are not yet ready to supply precise quantitative answers. The apparent accuracy of calculations presented here is about ±1 eV, which is acceptable if one wants to gain insight into general trends, but not good enough to provide reliable quantitative results (accuracy within ±2 kcal/mol or ±0.1 eV). Clearly, development of better methodologies is necessary. This problem is compounded by the lack of experimental data, especially for larger metal and metal oxide clusters, that could aid in the design and testing of new computational methods.

Current methods could be improved in two basic areas. First, better functionals are needed. The deficiency of current functionals lies especially in the description of atomization energies and bond strengths. Recently some new functionals have been implemented in the Gaussian 03 computational package, such as PBE[18] and revised PBE,[19] that might provide better atomization energies and bond strengths for metal oxide clusters.

The second area involves development of better basis sets. Most of the basis sets used in DFT calculations have been obtained for use with Hartree-Fock and correlated methods such as MP2 and configuration interaction. One could argue that basis sets developed specifically for DFT calculations would provide more accurate results. Some attempts to develop basis sets for use with DFT methods have already been reported.[20,21] One difficulty with this approach deals with the choice of functional for the basis set optimization. A second difficulty centers about basis set transferability between different functionals.[22] In order to make some progress in this area, careful characterization and benchmark studies of density functionals and basis sets that are already available is necessary. Such benchmark studies are currently underway in several laboratories.[22-26]

REFERENCES

(1) Klopper, W. r12-Dependent Wavefunctions. In *Encyclopedia of Computational Chemistry*; von Rague Schleyer, P., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaefer III, H. A., Schreiner, P. R., Eds.; John Wiley & Sons, Ltd.: Chichester, UK, 1998; pp 2351.

(2) Klopper, W. R12 Methods, Gaussian Geminals. In *Modern Methods and Algorithms of Quantum Chemistry*; Grotendorst, J., Ed.; John von Neumann Institute for Computing: Juelich, Germany, 2000; Vol. 3; pp 181.

(3) Noga, J.; Valiron, P. Explicitly Correlated Coupled Cluster R12 Calculations. In *Computational Chemistry: Reviews of Current Trends*; Leszczynski, J., Ed.; World Scientific: Singapore, London, Hong Kong, New Jersey, 2002; Vol. 7; pp 131.

(4) Flores, J. R.; Clementi, E.; Sonnad, V. *Journal of Chemical Physics* **1989**, *91*, 7030.

(5) Flores, J. R.; Clementi, E.; Sonnad, V. *Chemical Physics Letters* **1989**, *163*, 198.

(6) Murakami, H.; Sonnad, V.; Clementi, E. *International Journal of Quantum Chemistry* **1992**, *42*, 785.

(7) Flores, J. R. *Chemical Physics Letters* **1992**, *195*, 377.

(8) Ackermann, J. *Physical Review A* **1995**, *52*, 1968.

(9) Pask, J. E.; Klein, B. M.; Sterne, P. A.; Fong, C. Y. *Computer Physics Communications* **2001**, *135*, 1.

(10) Tsuchida, E.; Tsukada, M. *Journal of the Physical Society of Japan* **1998**, *67*, 3844.

(11) White, S. R.; Wilkins, J. W.; Teter, M. P. *Physical Review B* **1989**, *39*, 5819.

(12) Yamakawa, S.; Hyodo, S. *Physical Review B* **2005**, *71*.

(13) Yamakawa, S.; Hyodo, S. *Journal of Alloys and Compounds* **2003**, *356*, 231.

(14) He, S. G.; Xie, Y.; Dong, F.; Heinbuch, S.; Jakubikova, E.; Bernstein, E. R. *in preparation* **2007**.

(15) Car, R.; Parrinello, M. *Physical Review Letters* **1985**, *55*, 2471.

(16) Payne, M. C.; Teter, M. P.; Allan, D. C.; Arias, T. A.; Joannopoulos, J. D. *Reviews of Modern Physics* **1992**, *64*, 1045.

(17) Lukkien, J. J.; Segers, J. P. L.; Hilbers, P. A. J.; Gelten, R. J.; Jansen, A. P. J. *Physical Review E* **1998**, *58*, 2598.

(18) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Physical Review Letters* **1996**, *77*, 3865.

(19) Hammer, B.; Hansen, L. B.; Norskov, J. K. *Physical Review B* **1999**, *59*, 7413.

(20) Porezag, D.; Pederson, M. R. *Physical Review A* **1999**, *60*, 2840.

(21) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Canadian Journal of Chemistry-Revue Canadienne De Chimie* **1992**, *70*, 560.

(22) Boese, A. D.; Martin, J. M. L.; Handy, N. C. *Journal of Chemical Physics* **2003**, *119*, 3005.

(23) Wang, N. X.; Venkatesh, K.; Wilson, A. K. *Journal of Physical Chemistry A* **2006**, *110*, 779.

(24) Wilson, A. K.; Prascher, B. P.; Mintz, B.; Wang, X. L. *Abstracts of Papers of the American Chemical Society* **2006**, *231*.

(25) Prascher, B. P.; Wilson, A. K. *Abstracts of Papers of the American Chemical Society* **2006**, *231*.

(26) Delley, B. *Journal of Physical Chemistry A* **2006**, *110*, 13632.

APPENDICES

APPENDIX A

BASIS SET PARAMETERS

Basis sets used in this study are composed of Gaussian basis functions. A primitive Gaussian basis function, g_p, in the spherical-harmonic representation is defined as:

$$g_p = N(\chi, l, m) S_{lm} e^{-\chi(\vec{r}-\vec{R})^2}.$$

In the above equation N denotes a normalization constant, χ represents orbital exponent (χ always has a positive value), $\vec{R}$ orbital center vector, and $\vec{r}$ is the radial distance from the center of the orbital. $|\vec{r}|^2 = x^2 + y^2 + z^2$, in which x, y, and z are cartesian coordinates. S_{lm} represent real solid harmonics, where l can have any integral nonnegative value, and m runs over all integers $|m| \leq l$. S_{lm} for $l \leq 3$ are shown in Table A.1. In the spherical-harmonic representation, one s – function, three p – functions, five d – functions, and seven f – functions correspond to each exponent χ on one center. All calculations presented here used spherical-harmonic representation of Gaussian basis functions, which is a default choice in the MOLPRO program.

Orbital center vector, $\vec{R}$, is in the standard, atom-centered basis sets identical with the atom's coordinates and the only variational parameter is the orbital. In case of the tessellated basis sets, both χ and $\vec{R}$ are determined variationally with respect to the bonding energy of a particular dimer, as described in Chapter 2. For augmented basis sets, only orbital exponent χ is optimized and all basis functions are atom centered.

Appendix A collects basis set parameters for tessellated and augmented basis sets optimized to describe dispersion interactions for $^3H_2$, Ne_2, and $(CH_4)_2$. For tessellated basis sets, they include distance of tessellating functions from the atom's nucleus centered in the vertices of the octahedron ($\boldsymbol{R_v}$) and in the center of octahedron's faces ($\boldsymbol{R_f}$), orbital exponents of functions centered in the vertices of octahedron (χ_{v1} and χ_{v2}, functions with these exponents are centered in vertices of the same octahedron), and orbital exponents of functions centered in the octahedron's faces (χ_f). For augmented basis sets, orbital exponents of augmenting functions are given: χ_p describes the orbital exponent of a set of p – functions, χ_d is the orbital exponent for a set of d – functions, and χ_f corresponds to the orbital exponent for a set of f – functions optimized for the intermolecular interaction.

Other parameters of interest, such as the number of primitive Gaussian functions in each basis set (**No. of Prim.**), smallest eigenvalue of **S** matrix (**S eigen.**), bonding energies ($\boldsymbol{E_{bond}}$), and BSSE ($\boldsymbol{E_{BSSE}}$) are also presented. Number of primitive functions, smallest eigenvalues of **S** matrix, as well as BSSE and bonding energies are also given for some widely used standard basis sets for comparison.

m\l	0	1	2	3
3				$\frac{1}{2}\sqrt{\frac{5}{2}}\left(x^2-3y^2\right)x$
2			$\frac{1}{2}\sqrt{3}\left(x^2-y^2\right)$	$\frac{1}{2}\sqrt{15}\left(x^2-y^2\right)z$
1		x	$\sqrt{3}xz$	$\frac{1}{2}\sqrt{\frac{3}{2}}\left(5z^2-r^2\right)x$
0	1	y	$\frac{1}{2}\left(3z^2-r^2\right)$	$\frac{1}{2}\left(5z^2-r^2\right)y$
-1		z	$\sqrt{3}yz$	$\frac{1}{2}\sqrt{\frac{3}{2}}\left(5z^2-r^2\right)y$
-2			$\sqrt{3}xy$	$\sqrt{15}xyz$
-3				$\frac{1}{2}\sqrt{\frac{5}{2}}\left(3x^2-y^2\right)y$

Table A.1. The real solid harmonics S_{lm} for $l \leq 3$.

Basis Set	**R_v [Å]**	**χ_{v1}**	**χ_{v2}**	**R_f [Å]**	**χ_{v1}**	**No. of Prim.**	**S eigen.**	**E_{bond} [μh]**	**E_{BSSE} [μh]**
Huz						36	2.69×10^{-4}	17.38	0.00
THuzS$_v$	0.14	s 0.18				48	3.69×10^{-5}	-11.55	0.00
THuzP$_v$	0.25-0.35	p 0.17				72	3.96×10^{-5}	-16.85	0.00
THuzS$_v^2{}_f$	0.25	s 0.63	s 0.14	0.70	s 0.16	76	1.56×10^{-8}	-18.70	0.00
THuz(SP)$_v$	0.33-0.38	s 0.45	p 0.13			84	2.17×10^{-5}	-19.59	0.00
6-311G**						16	1.02×10^{-1}	15.39	2.50
T6-311G**S$_v$	0.55	s 0.15				28	4.07×10^{-3}	-14.55	4.44
T6-311G**S$_{vf}$	0.55	s 0.15		0.60	s 0.15	44	3.69×10^{-5}	-18.81	6.57
T6-311G**S$_v^2{}_f$	0.71	s 0.15	s 0.31	0.79	s 0.14	56	9.16×10^{-5}	-19.52	9.26
T6-311G**P$_v$	0.55	p 0.16				52	1.05×10^{-3}	-19.32	4.99
T6-311G**P$_{vf}$	0.57	p 0.16		0.32	p 0.14	100	2.38×10^{-7}	-20.06	8.29
T6-311G**P$_v^2{}_f$	0.58	p 0.16	p 0.39	0.33	p 0.14	136	1.85×10^{-7}	-20.64	10.95

Table A.2. Tessellated basis set parameters for $^3H_2$. Bonding energies and BSSE computed at the MP2 level of theory. R_v – distance from the atomic center to the vertices of octahedron; χ_{v1}, χ_{v2} – orbital exponents of functions centered in the vertices of octahedron; R_f – distance from the atomic center to the middle of octahedron's faces; χ_f – orbital exponent of functions centered in the faces of octahedron; No. of Prim – number of primitive Gaussians in the basis set; **S** eigen. – smallest eigenvalue of the **S** matrix; E_{bond} – bonding energy; E_{BSSE} – BSSE.

Basis Set	**χ_p**	**χ_d**	**No. of Prim.**	**S eigen.**	**E_{bond} [μh]**	**E_{BSSE} [μh]**
Huz			36	2.69×10^{-4}	17.38	0.00
AHuzP	0.1		42	2.69×10^{-4}	-3.22	0.00
AHuzPD	0.16	0.14	52	2.69×10^{-4}	-15.43	0.00
6-311G**			16	1.02×10^{-1}	15.39	2.50
A6-311G**P	0.13		22	1.01×10^{-1}	-10.73	3.24
A6-311G**PD	0.13	0.14	32	9.81×10^{-2}	-17.98	3.72

Table A.3. Augmented basis set parameters for $^3H_2$. Bonding energies and BSSE computed at the MP2 level of theory. χ_p – orbital exponent for a set of p – functions; χ_d – orbital exponent for a set of d – functions; No. of Prim – number of primitive Gaussians in the basis set; **S** eigen. – smallest eigenvalue of the **S** matrix; E_{bond} – bonding energy; E_{BSSE} – BSSE.

Basis Set	**No. of Prim.**	**S eigen.**	E_{bond} **[μh]**	E_{BSSE} **[μh]**
cc-pVDZ	14	9.39×10^{-2}	15.80	7.16
cc-pVTZ	32	1.38×10^{-2}	6.49	2.78
cc-pVQZ	64	2.01×10^{-3}	-1.01	1.48
cc-pV5Z	116	6.44×10^{-4}	-5.83	0.16
cc-pV6Z	190	2.79×10^{-4}	-10.07	0.02
aug-cc-pVDZ	22	6.28×10^{-2}	-10.57	2.02
aug-cc-pVTZ	50	1.31×10^{-2}	-16.24	0.52
aug-cc-pVQZ	114	1.97×10^{-3}	-17.88	0.60
aug-cc-pV5Z	166	6.34×10^{-4}	-18.91	0.06
aug-cc-pV6Z	262	2.77×10^{-4}	-19.49	0.00

Table A.4. Bonding energies, BSSE, and lowest eigenvalues of **S** matrix computed by standard basis sets for $^3H_2$. Bonding energies and BSSE computed at the MP2 level of theory.

No. of Prim. – number of primitive Gaussians in the basis set; **S** eigen. – smallest eigenvalue of the **S** matrix; E_{bond} – bonding energy; E_{BSSE} – BSSE.

Basis Set	R_v **[Å]**	χ_{v1}	χ_{v2}	R_f **[Å]**	χ_{v1}	**No. of Prim.**	**S eigen.**	E_{bond} **[μh]**	E_{BSSE} **[μh]**
spd-cc-pV6Z						164	6.48×10^{-4}	-32.91	8.62
Tspd-cc-pV6ZS$_v$	0.76	s 0.42				176	6.38×10^{-4}	-52.15	52.44
Tspd-cc-pV6ZS$_{vf}$	0.63	s 0.41		0.20	0.53	192	3.98×10^{-6}	-59.58	58.18
Tspd-cc-pV6ZS$_v^2{}_f$	0.45	s 0.37	s 0.50	0.10	0.50	204	4.97×10^{-8}	-61.90	85.50
Tspd-cc-pV6ZP$_v$	0.56	p 0.39				200	5.62×10^{-4}	-72.08	96.19
Tspd-cc-pV6ZP$_{vf}$	0.92	p 0.36		0.44	p 0.45	248	1.66×10^{-5}	-78.94	457.36
Tspd-cc-pV6ZP$_v^2{}_f$	0.99	p 0.38	p 0.27	0.40	p 0.45	284	1.82×10^{-6}	-81.89	846.37
6-311G**						62	8.32×10^{-2}	38.24	124.59
T6-311G**S$_v$	0.58	s 0.46				74	4.14×10^{-3}	-25.86	593.14
T6-311G**S$_{vf}$	0.59	s 0.46		0.59	s 0.56	90	1.47×10^{-4}	-93.48	709.63
T6-311G**S$_v^2{}_f$	0.59	s 0.46	s 1000	0.59	s 0.56	102	1.47×10^{-4}	-93.48	709.63
T6-311G**P$_v$	0.42	p 0.49				98	1.20×10^{-4}	-98.36	626.59
T6-311G**P$_{vf}$	0.49	p 0.44		0.73	p 0.49	146	3.18×10^{-4}	-101.06	1228.26
T6-311G**P$_v^2{}_f$	0.42	p 0.49	p 7.00	0.73	p 0.49	182	4.15×10^{-4}	-101.37	1253.00

Table A.5. Tessellated basis set parameters for Ne_2. Bonding energies and BSSE computed at the MP2 level of theory. R_v – distance from the atomic center to the vertices of octahedron; χ_{v1}, χ_{v2} – orbital exponents of functions centered in the vertices of octahedron; R_f – distance from the atomic center to the middle of octahedron's faces; χ_f – orbital exponent of functions centered in the faces of octahedron; No. of Prim – number of primitive Gaussians in the basis set; S eigen. – smallest eigenvalue of the **S** matrix; E_{bond} – bonding energy; E_{BSSE} – BSSE.

Basis Set	χ_d	χ_f	No. of Prim.	S eigen.	E_{bond} [μh]	E_{BSSE} [μh]
spd-cc-pV6Z			164	6.48×10^{-4}	-32.91	8.62
Aspd-cc-pV6ZD	0.24		174	6.45×10^{-4}	-44.96	13.16
Aspd-cc-pV6ZPDF	0.25	0.36	188	6.43×10^{-4}	-70.42	54.97
6-311G**			62	8.32×10^{-2}	38.24	124.59
A6-311G**D	0.35		72	8.62×10^{-2}	-68.91	320.84
A6-311G**DF	0.34	0.34	86	8.62×10^{-2}	-97.07	513.54

Table A.6. Augmented basis set parameters for Ne_2. Bonding energies and BSSE computed at the MP2 level of theory. χ_d – orbital exponent for a set of d – functions; χ_f – orbital exponent for a set of f – functions; No. of Prim – number of primitive Gaussians in the basis set; **S** eigen. – smallest eigenvalue of the **S** matrix; E_{bond} – bonding energy; E_{BSSE} – BSSE.

Basis Set	χ_d	χ_f	No. of Prim.	S eigen.	MP2		LMP2	
					E_{bond} [μh]	E_{BSSE} [μh]	E_{bond} [μh]	E_{BSSE} [μh]
A6-311G**DF	0.34	0.34	86	8.62×10^{-2}	-111.64	745.71	-108.74	517.25
Acc-pVDZDF	0.32	0.31	76	0.50×10^{-1}	-97.07	513.54	-99.19	398.75
Acc-pVTZDF	0.29	0.35	108	0.17×10^{-1}	-81.29	352.28	-96.22	221.01
Acc-pVQZDF	0.26	0.33	160	0.52×10^{-3}	-74.48	152.13	-87.42	83.34
Acc-pV5ZDF	0.25	0.31	240	0.26×10^{-3}	-73.82	32.20	-76.47	9.82
Aaug-cc-pVDZDF	0.24	0.33	94	0.25×10^{-1}	-75.67	369.16	-81.88	65.04
Aaug-cc-pVTZDF	0.20	0.31	140	0.74×10^{-2}	-76.43	186.56	-81.30	14.13
Aaug-cc-pVQZDF	0.29	0.30	210	0.21×10^{-3}	-78.77	98.17	-82.38	11.17
Aaug-cc-pV5ZDF	0.19	0.32	312	0.25×10^{-3}	-78.59	38.25	-80.77	1.86

Table A.7. Augmented basis set parameters for Ne_2. Bonding energies and BSSE computed at the MP2 and LMP2 levels of theory. χ_d – orbital exponent for a set of d – functions; χ_f – orbital exponent for a set of f – functions; No. of Prim – number of primitive Gaussians in the basis set; **S** eigen. – smallest eigenvalue of the **S** matrix; E_{bond} – bonding energy; E_{BSSE} – BSSE.

Basis Set	**No. of Prim.**	**S eigen.**	E_{bond} [μh]	E_{BSSE} [μh]
cc-pVDZ	52	5.00×10^{-2}	16.98	67.50
cc-pVTZ	84	1.67×10^{-2}	20.48	163.71
cc-pVQZ	136	5.22×10^{-4}	-9.21	105.68
cc-pV5Z	216	2.56×10^{-4}	-33.33	19.70
cc-pV6Z	322	6.70×10^{-5}	-50.00	8.05
aug-cc-pVDZ	70	2.98×10^{-2}	-0.78	116.01
aug-cc-pVTZ	116	1.03×10^{-2}	-50.15	81.59
aug-cc-pVQZ	186	5.10×10^{-4}	-68.70	45.54
aug-cc-pV5Z	288	2.51×10^{-4}	-75.68	22.04
aug-cc-pV6Z	420	6.62×10^{-5}	-79.53	9.50

Table A.8. Bonding energies, BSSE, and lowest eigenvalues of **S** matrix computed by standard basis sets for Ne_2. Bonding energies and BSSE computed at the MP2 level of theory.

No. of Prim. – number of primitive Gaussians in the basis set; **S** eigen. – smallest eigenvalue of the **S** matrix; E_{bond} – bonding energy; E_{BSSE} – BSSE.

Basis Set	R_v **[Å]**	χ_{v1}	**No. of Prim.**	**S eigen.**	E_{bond} **[μh]**	E_{BSSE} **[μh]**
H: Huz			286	6.88×10^{-5}	-378.71	222.45
C: spd-cc-pV6Z						
H: Huz			298	6.86×10^{-5}	-548.18	579.22
C: Tspd-cc-pV6ZS$_v$	1.07	s 0.21				
H: Huz			322	6.59×10^{-5}	-667.85	725.74
C: Tspd-cc-pV6ZP$_v$	0.85	p 0.23				
H: THuzS$_v$	0.14	s 0.18	334	8.18×10^{-7}	-638.64	749.50
C: spd-cc-pV6Z						
H: THuzS$_v$	0.14	s 0.18	346	7.16×10^{-7}	-666.75	1069.08
C: Tspd-cc-pV6ZS$_v$	1.07	s 0.21				
H: THuzP$_v$	0.25	p 0.17	430	2.01×10^{-7}	-706.86	1758.46
C: spd-cc-pV6Z						
H: THuzP$_v$	0.25	p 0.17	466	1.04×10^{-7}	-723.49	1870.05
C: Tspd-cc-pV6ZP$_v$	0.85	p 0.23				

Table A.9. Tessellated basis set parameters for $(CH_4)_2$. Bonding energies and BSSE computed at the MP2 level of theory. R_v – distance from the atomic center to the vertices of octahedron; χ_{v1} – orbital exponents of functions centered in the vertices of octahedron; No. of Prim – number of primitive Gaussians in the basis set; **S** eigen. – smallest eigenvalue of the **S** matrix; E_{bond} – bonding energy; E_{BSSE} – BSSE.

Basis Set	R_v [Å]	χ_{v1}	No. of Prim.	S eigen.	E_{bond} [μh]	E_{BSSE} [μh]
H: 6-311G**			126	1.11×10^{-2}	-171.16	280.92
C: 6-311G**						
H: 6-311G**			138	2.28×10^{-2}	-384.91	445.56
C: T6-311G**S_v	1.14	0.20				
H: 6-311G**			162	7.53×10^{-5}	-636.80	622.06
C: T6-311G**P_v	0.37	0.19				
H: T6-311G**S_v	0.55	0.15	174	1.32×10^{-5}	-626.94	491.61
C: 6-311G**						
H: T6-311G**S_v	0.55	0.15	186	7.86×10^{-6}	-663.39	672.27
C: T6-311G**S_v	1.14	0.20				
H: T6-311G**P_v	0.55	0.16	270	3.28×10^{-6}	-721.50	1196.21
C: 6-311G**						
H: T6-311G**P_v	0.55	0.16	306	3.30×10^{-7}	-734.67	1298.65
C: T6-311G**P_v	0.37	0.19				

Table A.10. Tessellated basis set parameters for $(CH_4)_2$. Bonding energies and BSSE computed at the MP2 level of theory. R_v – distance from the atomic center to the vertices of octahedron; χ_{v1}, χ_{v2} – orbital exponents of functions centered in the vertices of octahedron; No. of Prim – number of primitive Gaussians in the basis set; **S** eigen. – smallest eigenvalue of the **S** matrix; E_{bond} – bonding energy; E_{BSSE} – BSSE.

Basis Set	χ_p	χ_d	χ_f	**No. of Prim.**	**S eigen.**	E_{bond} **[μh]**	E_{BSSE} **[μh]**
H: Huz				286	6.88×10^{-5}	-378.71	222.45
C: spd-cc-pV6Z							
H: Huz				296	6.86×10^{-5}	-397.33	451.18
C: Aspd-cc-pV6ZD		0.13					
H: AHuzP	0.10			310	1.09×10^{-5}	-482.92	444.51
C: spd-cc-pV6Z							
H: Huz				310	6.83×10^{-5}	-618.86	637.79
C: Aspd-cc-pV6ZDF		0.14	0.21				
H: AHuzP	0.10			320	8.09×10^{-6}	-496.87	616.53
C: Aspd-cc-pV6ZD		0.13					
H: AHuzPD	0.16	0.14		350	5.21×10^{-6}	-645.82	713.83
C: spd-cc-pV6Z							
H: AHuzPD	0.16	0.14		374	4.04×10^{-6}	-681.73	743.44
C: Aspd-cc-pV6ZDF		0.14	0.21				

Table A.11. Augmented basis set parameters for $(CH_4)_2$. Bonding energies and BSSE computed at the MP2 level of theory. χ_p – orbital exponent for a set of p – functions; χ_d – orbital exponent for a set of d – functions; χ_f – orbital exponent for a set of f – functions; No. of Prim – number of primitive Gaussians in the basis set; S eigen. – smallest eigenvalue of the **S** matrix; E_{bond} – bonding energy; E_{BSSE} – BSSE.

Basis Set	χ_p	χ_d	χ_f	**No. of Prim.**	**S eigen.**	E_{bond} **[μh]**	E_{BSSE} **[μh]**
H: 6-311G**				126	1.11×10^{-2}	-171.16	280.92
C: 6-311G**							
H: 6-311G**				136	9.10×10^{-3}	-476.18	332.18
C: A6-311G**D		0.17					
H: A6-311G**P	0.13			150	1.25×10^{-3}	-521.71	509.69
C: 6-311G**							
H: 6-311G**				150	1.67×10^{-3}	-628.11	438.52
C: A6-311G**DF		0.16	0.19				
H: A6-311G**P	0.13			160	9.23×10^{-4}	-603.91	438.83
C: A6-311G**D		0.17					
H: A6-311G**PD	0.14	0.14		190	2.10×10^{-4}	-657.28	803.32
C: 6-311G**							
H: A6-311G**PD	0.14	0.14		214	1.47×10^{-4}	-701.82	711.83
C: A6-311G**DF		0.16	0.19				

Table A.12. Augmented basis set parameters for $(CH_4)_2$. Bonding energies and BSSE computed at the MP2 level of theory. χ_p – orbital exponent for a set of p – functions; χ_d – orbital exponent for a set of d – functions; χ_f – orbital exponent for a set of f – functions; No. of Prim – number of primitive Gaussians in the basis set; S eigen. – smallest eigenvalue of the **S** matrix; E_{bond} – bonding energy; E_{BSSE} – BSSE.

Basis Set	χ_d	χ_f	**No. of Prim.**	**S eigen.**	**MP2**		**LMP2**	
					E_{bond} **[μh]**	E_{BSSE} **[μh]**	E_{bond} **[μh]**	E_{BSSE} **[μh]**
A6-311G**DF	0.16	0.19	150	1.67×10^{-3}	-628.11	438.52	-603.93	74.71
Aaug-cc-pVDZDF	0.12	0.17	182	0.17×10^{-3}	-693.31	1397.85	-659.88	746.21
Aaug-cc-pVTZDF	0.19	0.2	340	0.27×10^{-4}	-741.33	258.23	-712.27	29.07
cc-pVDZ			108	1.13×10^{-2}	-127.89	358.52	-52.64	105.80
6-311G**			126	1.11×10^{-2}	-171.16	280.92	-54.00	63.71
aug-cc-pVDZ			158	3.75×10^{-4}	-618.07	850.01	-522.29	422.79
cc-pVTZ			212	1.14×10^{-3}	-502.11	158.28	-392.16	24.71
aug-cc-pVTZ			316	2.90×10^{-5}	-726.42	219.51	-684.29	20.04
cc-pVQZ			392	1.15×10^{-4}	-662.31	57.60	-	-

Table A.13. Bonding energies, BSSE, and lowest eigenvalues of **S** matrix computed by standard basis and augmented sets for $(CH_4)_2$. Bonding energies and BSSE computed at MP2 and LMP2 levels of theory.

χ_p – orbital exponent for a set of d – functions; χ_f – orbital exponent for a set of f – functions; No. of Prim. – number of primitive Gaussians in the basis set; **S** eigen. – smallest eigenvalue of the **S** matrix; E_{bond} – bonding energy; E_{BSSE} – BSSE.

APPENDIX B

SAMPLE MOLPRO INPUT FILE

This appendix contains a sample MOLPRO input file for calculation of Ne_2 bonding energy and basis set superposition error (BSSE) with a tessellated basis set. The input file is presented first and its different components are explained afterward.

```
***,Ne2 dimer

basis
S,Ne,902400.0,135100.0,30750.0,8710.0,2842.0,1026.0;
400.1,165.9,72.21,32.66,15.22
C,1.11,0.551D-05,0.4282D-04,0.22514D-03,0.95016D-03;
0.344719D-02,0.1112545D-01,0.3220568D-01,0.8259891D-01;
0.17990564,0.30605208,0.34012559
S,Ne,902400.0,135100.0,30750.0,8710.0,2842.0,1026.0;
400.1,165.9,72.21,32.66,15.22
C,1.11,-0.129D-05,-0.1005D-04,-0.5293D-04,-0.22312D-03;
-0.81338D-03,-0.26323D-02,-0.77591D-02,-0.2045277D-01;
-0.4797505D-01,-0.9340086D-01,-0.14277215
S,Ne,7.149,2.957,1.335,0.5816,0.2463
P,Ne,815.6,193.3,62.6,23.61,9.762
C,1.5,0.18376D-03,0.158509D-02,0.841464D-02,0.3220033D-01;
0.939639D-01
P,Ne,4.281,1.915,0.8476,0.366,0.151
D,Ne,13.317,5.803,2.529,1.102,0.48
S,Eu,0.41
S,Cf,0.53
end

nogprint,angles,distance

R=0.63,P=3.15+R,Q=3.15-R;
D=0.2,A=D/sqrt(3),B=3.15-A;C=3.15+A

geomtyp=xyz
geometry={
nosym
30
```

```
Ne dimer - 2 levels of tessellation
Ne1  0.0000000000   0.0000000000   0.0000000000
Ne2  0.0000000000   0.0000000000   3.1500000000
Eu   R              0.0000000000   0.0000000000
Eu   0.0000000000   R              0.0000000000
Eu  -R              0.0000000000   0.0000000000
Eu   0.0000000000  -R              0.0000000000
Eu   0.0000000000   0.0000000000  -R
Eu   0.0000000000   0.0000000000   R
Eu   R              0.0000000000   3.1500000000
Eu   0.0000000000   R              3.1500000000
Eu  -R              0.0000000000   3.1500000000
Eu   0.0000000000  -R              3.1500000000
Eu   0.0000000000   0.0000000000   Q
Eu   0.0000000000   0.0000000000   P
Cf   A              A              A
Cf   A              A             -A
Cf   A             -A              A
Cf  -A              A              A
Cf   A             -A             -A
Cf  -A              A             -A
Cf  -A             -A              A
Cf  -A             -A             -A
Cf   A              A              B
Cf   A              A              C
Cf   A             -A              B
Cf  -A              A              B
Cf   A             -A              C
Cf  -A              A              C
Cf  -A             -A              B
Cf  -A             -A              C
}

dummy,Eu,Cf

hf
mp2
Edimer(1) = ENERGY

dummy,Eu,Ne2,Cf
hf
mp2
Eghost(1) = ENERGY
Ebond(1) = Edimer(1) - 2*Eghost(1)

geomtyp=xyz
geometry={
nosym
15
Ne atom - 2 levels of tessellation
Ne1  0.0000000000   0.0000000000   0.0000000000
Eu   R              0.0000000000   0.0000000000
Eu   0.0000000000   R              0.0000000000
Eu  -R              0.0000000000   0.0000000000
Eu   0.0000000000  -R              0.0000000000
Eu   0.0000000000   0.0000000000  -R
Eu   0.0000000000   0.0000000000   R
```

```
90   Cf   A              A              A
91   Cf   A              A             -A
92   Cf   A             -A              A
93   Cf  -A              A              A
94   Cf   A             -A             -A
95   Cf  -A              A             -A
96   Cf  -A             -A              A
97   Cf  -A             -A             -A
98   }
99
100  dummy,Eu,Cf
101
102  hf
103  mp2
104  Eatom(1)=ENERGY
105  Ebsse(1)=2*(Eghost(1)-Eatom(1))
106
107  table,Edimer,Eghost,Eatom,Ebsse,Ebond
```

Line 1: Title section

Lines 3 – 22: Basis set specification

Lines 4 and 5 specify orbital coefficients of s – functions centered on Ne atom. Lines 6 – 8 give values of the contraction coefficients for the 11 s – type basis functions listed in the in lines 4 and 5. Similarly, lines 9 – 19 specify other sets of s, p and d – functions for neon atom. Line 20 gives the orbital exponent for the tessellating functions centered in the vertices of octahedron, represented by dummy atoms Eu. Line 21 denotes orbital exponent for the tessellating functions centered in the octahedron's faces, represented by dummy atom Cf.

Line 24: Output print options

Line 24 contains commands for suppressing the printout of all bond lengths and bond angles of the specified molecular system.

Line 26 – 27: Definition of variables

Variables are defined that will be used to position dummy atoms, Eu and Cf, into the vertices and faces of octahedrons centered on Ne atoms. R represents the distance from the center of octahedron (or from Ne atom) to its vertices, while D denotes the distance from the center of an octahedron to the middle of its faces.

Lines 29 – 64: Geometry specification

This input section specifies the geometry of Ne dimer and position of dummy atoms. Placement of tessellating functions is determined through the positions of dummy atoms. Line 29 indicates that the geometry is given in cartesian coordinates. Line 31 suppresses the use of symmetry in the calculation, which is important for proper treatment of the dummy atoms. Line 32 denotes the number of atoms specified in the geometry input. Line 33 has no effect on calculation – it is merely a title section for the following geometry input. Lines 34 – 64 contain cartesian coordinates of neon and dummy atoms.

Line 66: Removal of charge from dummy atoms

All electrons are removed from Eu and Cf, making them just a place-holders for tessellating basis sets.

Line 68: Hartree – Fock calculation

Hartree – Fock (HF) calculation is requested. This is an important prerequisite to the perturbational theory calculation.

Line 69: Perturbational theory calculation

Moller – Plesset perturbation theory calculation of the 2nd order (MP2) is requested. Line 70 places the calculated energy of neon dimer into the variable Edimer(1).

Lines 72 – 76: Calculation of Ne atomic energy with "ghost" functions

In order to calculate BSSE, energy of single Ne atom is calculated with the presence of basis functions on the second Ne atom. Charge is removed from the second Ne atom the same way it is done for dummy atoms representing positions of tessellating basis functions. Energy of neon atom computed from this "ghost" calculation is placed into the variable Eghost(1), BSSE – corrected bonding energy is computed and saved as Ebond(1) variable.

Lines 78 – 104: Energy calculation for single Ne atom

Lines 78 – 98 specify geometry for a single neon atom with its tessellating functions. Charge is removed from the dummy atoms Eu and Cf in line 100. Lines 102 and 103 request HF calculation followed by an MP2 calculation on neon atom. Calculated energy is saved into the Eatom(1) variable (line 104), and basis set superposition error is computed (line 105).

Line 107: Final printout of computed energies

Final line requests a printout of a table of computed energies, including the neon dimer bonding energy and BSSE .

Input files for calculation of bonding energy and BSSE with augmented basis sets are very similar to the one presented here, albeit much simpler, since the augmenting functions are centered directly at the atoms, so there is no need to use dummy atoms. Other keywords relevant to the calculations performed in this work can be found in the manual for MOLPRO program.

APPENDIX C

SAMPLE GAUSSIAN INPUT FILES

This appendix contains sample Gaussian input files for geometry optimization of a vanadium oxide cluster, internal reaction coordinate (IRC) calculation, and potential energy scan (PES). Each input file is presented first and its different components are explained afterwards.

GROUND STATE GEOMETRY AND TRANSITION STATE OPTIMIZATION

```
%Mem=300MB
%Chk=v3o6s7.chk
#P BPW91/LANL2DZ
# SCF(MaxCycle=800)

single point calculation

0     2
O     -0.118349   -1.709894   -0.756567
O     -1.510705   0.899985    -0.804375
O      1.619344   0.689940    -0.798591
V     -1.412996   -0.664682   -0.027507
V      0.110006   1.643699    -0.120782
V      1.307337   -0.849439   -0.030613
O     -2.783089   -1.355451   0.439047
O      0.213921   3.077226    0.579723
O     -0.001215   -0.016216   1.081338

--Link1--
%Chk=v3o6s7.chk
%Mem=300MB
#P BPW91/LANL2DZ
# Opt(Redundant,MaxCycle=100)
# SCF(MaxCycle=800)
# Guess(Read) Geom=Check freq

geometry optimization
```

```
29
30    0      2
31
```

The input file above is an example of a multi-step input file. The two computational steps are separated by the command in the line 20. The first step (lines 1 – 19) requests a single point energy calculation at the BPW91/LANL2DZ level of theory. Cluster geometry and wavefunction are saved in the checkpoint file v3o6s1.chk. The purpose of the first step is to provide a good initial guess for the wavefunction used for geometry optimization performed in the second step (lines 21 -31).

Lines 1-2: "Link 0" commands

Line 1 sets the amount of dynamic memory to be used in the calculation to 300 MB. Line 2 specifies the name of checkpoint file, in which geometry, wavefunction and other results of calculation will be saved in binary format.

Lines 3-4: Route section

Line 3 specifies the level of calculation (BPW91/LANL2DZ) and the level of desired output (P – generates additional output to the normal print level). Line 4 specifies the maximum number of cycles for iterative self consistent field (SCF) calculation.

Lines 6, 8, 19: Blank lines

Blank lines separate different parts of input. They are important and if omitted the calculation will not run properly.

Line 7: Title section

Lines 9 – 18: Geometry Specification

Line 9 indicates the charge and multiplicity of the molecular system. Lines 10-18 specify Cartesian coordinates of individual atoms in Angstroms.

Lines 21 – 31: Input for Step 2

Commands for the second step of the Gaussian job follow general rules outlined above. Line 24 contains the command for geometry optimization, specifying maximum number of optimization steps to 100. Guess(Read) and Geom=Check commands request that the wavefunction guess and molecular geometry are obtained from the checkpoint file. “freq” keyword calls for the frequency calculation once the geometry optimization is completed.

Additional keywords can be used to achieve geometry convergence in case of difficult optimization cases. For example, Opt(tight) together with Int=Ultrafine keywords might prove helpful in achieving better convergence of the geometry optimization, if negative normal mode frequencies are present after the optimization is completed. Opt(CalcFC) or Opt(CalcAll) keywords, which improve the generation of force constants needed for geometry optimization, are also sometimes useful in achieving the geometry convergence.

Transition state optimization

The input file shown above can be easily modified to request transition state optimization by altering the Opt keyword in the line 24 in the following way: Opt(Redundant,MaxCycle=100,TS,noeigentest).

POTENTIAL ENERGY SCAN CALCULATION

```
1      %Chk=vo3so3pscan.chk
2      %Mem=1000MB
3      #P BPW91/TZVP
4      # SCF(MaxCycle=800)
5
6      single point
7
8      0     2
9      O     1.779400    .359988     1.466285
10     O     -1.924281   1.431723    .240418
11     O     1.678947    1.167181    -.880661
12     S     1.595301    -.017106    .034395
13     O     .121172     -.640014    -.121362
14     V     -1.629231   -.050636    -.261405
15     O     -2.703145   -1.046041   .368316
16     O     2.541346    -1.093047   -.390246
17
18     --Link1--
19     %Chk=vo3so3pscan.chk
20     %Mem=1000MB
21     #P BPW91/TZVP
22     # Opt(ModRedundant,MaxCycle=100)
23     # SCF(MaxCycle=800)
24     # Guess(Read) Geom=Check
25
26     PES
27
28     0     2
29
30     4 5  1.607896  S   50   0.05
31
```

This input file requests a potential energy scan (PES) with respect to the S – O bond of VO_4SO_2 cluster. During the PES calculation, geometry is optimized at each step, while holding the S – O bond fixed at the specified value. The first step of this multi-step input file calls for the single point energy calculation of the VO_4SO_2 cluster. The structure of the input for the second step is very similar to the input file for geometry optimization, with two changes. Opt keyword specified on line 22 uses ModRedundant option, which is a requirement when performing potential energy surface (PES) scan. Line 30 specifies the atoms involved in the PES scan (atoms number 4 and 5 in the input geometry), the initial value of the scanned coordinate, number of steps (50) and the step size (0.05 Å).

INTERNAL REACTION COORDINATE CALCULATION

```
1       %Chk=vo2so2o2irc.chk
2       %Mem=1000MB
3       #P BPW91/TZVP
4       # SCF(MaxCycle=800)
5
6       single point
7
8       0      2
9       O      -.378919    -.431925    1.229169
10      O    -1.473595    1.741734     .000481
11      S    -1.343324    -.541772     .000001
12      O     1.744095    1.493079    -.000654
13      V     1.217092    -.011688    -.000038
14      O    -2.785658    -.248587    -.000298
15      O      -.378849    -.432421   -1.229106
16      O     2.460434   -1.004732     .000515
17
18      --Link1--
19      %Chk=vo2so2o2irc.chk
20      %Mem=1000MB
21      #P BPW91/TZVP
22      # IRC(MaxPoints=40,CalcFC,MaxCycle=100)
23      # SCF(MaxCycle=800)
24      # Guess(Read) Geom=Check
25
26      IRC calc
27
28      0      2
29
```

Internal reaction coordinate (IRC) calculation follows the reaction path from the transition state in both forward and reverse directions. Geometry is optimized at each point along the reaction path. The first step of the above input file calls again for the single point energy calculation. The second step requests the IRC calculation. IRC program is called in line 22, with options specifying the maximum number of points to be computed in each direction from the transition state (MaxPoint=40), and maximum number of the geometry optimization cycles for each point (MaxCycle=100). Force constants required for IRC calculation are computed at the beginning of the calculation (CalcFC).

Other keywords and options relevant to the geometry optimization, IRC calculation or PES scans can be found in the manuals for Gaussian 98 and Gaussian 03 programs.

APPENDIX D

STRUCTURES OF VANADIUM OXIDE CLUSTERS

This appendix collects structures and energies of vanadium oxide clusters computed at the BPW91/LANL2DZ level of theory. Several spin states are considered for each isomer. Bond lengths are reported for every structure in Ångstroms. Cartesian coordinates are shown for each structure. Relative energies of different isomers with respect to the lowest energy cluster with a particular stoichiometry are also given. The name noted for each isomer (i.e., vo2s.log), corresponds to the name of the actual Gaussian output file for a particular calculation. More information about each calculation can be found in my laboratory notebook under these names.

VO_y ($y = 1 - 5$), V_2O_y ($y = 2 - 7$), V_3O_y ($y = 4 - 8$) structures are optimized with Gaussian 98 program using the computer resources of the Department of Chemistry. V_3O_9 and VO_ySO_2 ($y = 1 - 4$) are optimized using Gaussian 98 program, utilizing the resources of the San Diego Supercomputing Center. V_4O_y ($y = 7 - 12$) are optimized with Gaussian 03 program using the resources of the National Center for Supercomputing Applications. Unless noted otherwise, structures presented here are optimized at the BPW91/LANL2DZ level of theory.

In addition to the structures and energies of different molecules, zero point energy correction and thermal corrections to the energy at $T = 298.150$ K and $P = 1$ Atm are given for most of the structures. The sum of the computed energy of a molecule (electronic energy) and a zero-point energy correction gives the total energy of a molecule at 0 K. Sum of the electronic energy and thermal correction to energy gives the energy of a molecule at 298.15 K (E) accounting for the effects of molecular translation, rotation and vibration. Sum of the electronic energy and thermal correction to enthalpy gives the enthalpy of a molecule ($H = E + \mathrm{R}T$) at 298.15 K. Finally, the sum of the electronic energy and thermal correction to Gibbs free energy gives the Gibbs free energy of the molecule ($G = H - TS$) at 298.15 K. All values are given in Hartrees.

O, O_2

BPW91/LANL2DZ
O: E = -75.0686953426 h (triplet)
O_2: E = -150.317550924 h (triplet)

```
                BPW91/TZVP                          O(2)-V(1)    1.2225
                  o2.log
O    .000000      .000000      .611250            E = -150.379106631 h
O    .000000      .000000     -.611250                  triplet
 Zero-point correction=                          .003475 (Hartree/Particle)
 Thermal correction to Energy=                   .005840
 Thermal correction to Enthalpy=                 .006784
 Thermal correction to Gibbs Free Energy=       -.016517
```

SO_y

```
                BPW91/TZVP                          S(1)-O(2)   1.5287
                sotzvp.log
S    .000000      .000000     -.114350            E = -473.405275776 h
O    .000000      .000000     1.414350                  triplet
 Zero-point correction=                          .002429 (Hartree/Particle)
 Thermal correction to Energy=                   .004818
 Thermal correction to Enthalpy=                 .005763
 Thermal correction to Gibbs Free Energy=       -.019489
```

```
                BPW91/TZVP                          O(1)-S(2)   1.4808
                  so2.log                           S(2)-O(3)   1.4807
                                                 O(1)-S(2)-O(3)   118.3786
O   -.098573      .000000      .022540            E = -548.674187793 h
S    .137917      .000000     1.484311                  singlet
O   1.536348      .000000     1.970987
 Zero-point correction=                          .006340 (Hartree/Particle)
 Thermal correction to Energy=                   .009456
 Thermal correction to Enthalpy=                 .010400
 Thermal correction to Gibbs Free Energy=       -.018590
```

```
                BPW91/TZVP                          O(1)-S(2)   1.4808
                  so2.log                           S(2)-O(3)   1.4807
                                                 O(1)-S(2)-O(3)   118.3786
O   -.098573      .000000      .022540            E = -548.674187793 h
S    .137917      .000000     1.484311                  singlet
O   1.536348      .000000     1.970987
 Zero-point correction=                          .006340 (Hartree/Particle)
 Thermal correction to Energy=                   .009456
 Thermal correction to Enthalpy=                 .010400
 Thermal correction to Gibbs Free Energy=       -.018590
```

BPW91/TZVP
so3.log

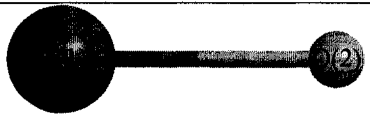
```
S(2)-O(1)    1.4672
S(2)-O(3)    1.4675
S(2)-O(4)    1.4674
```

```
O   1.243039    -.779695     .000066
O    .000036    -.000121    -.000099
O    .053833    1.466360     .000066
O  -1.296943    -.686424     .000066
```

E = -623.875402877 h
singlet

```
 Zero-point correction=                        .011121 (Hartree/Particle)
 Thermal correction to Energy=                 .014800
 Thermal correction to Enthalpy=               .015744
 Thermal correction to Gibbs Free Energy=     -.015429
```

VO clusters



```
O(2)-V(1)    1.6122
```

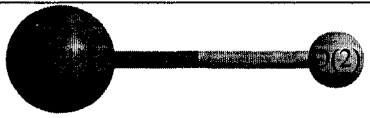
voquartet.com, voquartetfr.log

```
V   .000000     .000000    -.005466
O   .000000     .000000    1.606766
```

E = -146.5862035 h (0 eV)
quartet

```
 Zero-point correction=                        .002281 (Hartree/Particle)
 Thermal correction to Energy=                 .004678
 Thermal correction to Enthalpy=               .005623
 Thermal correction to Gibbs Free Energy=     -.020608
```

Doublet: E = -146.5562050 h (0.82 eV) (V – O bond length: 1.6013)
Sextet: E = -146.4731554 h (3.08 eV) (V – O bond length: 1.8852)



```
O(2)-V(1)    1.5858
```

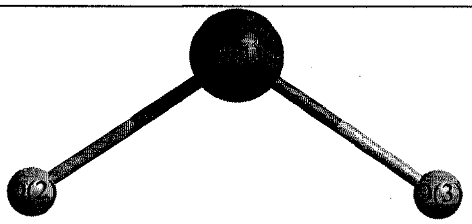
votzvp.log, vo.log

```
V   .000000     .000000     .013235
O   .000000     .000000    1.598965
```

E = -1019.31506181 h
(BPW91/TZVP)
quartet

```
 Zero-point correction=                        .002320 (Hartree/Particle)
 Thermal correction to Energy=                 .004715
 Thermal correction to Enthalpy=               .005659
 Thermal correction to Gibbs Free Energy=     -.020538
```

VO_2 clusters



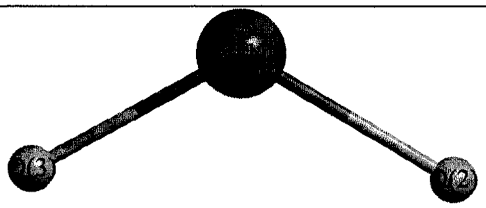
```
 O(3)-V(1)     1.6328
 O(2)-V(1)     1.6328
O(2)-V(1)-O(3) 110.9895
```

vo2opt.log (nosymm), vo2optfr.log

```
V   -.004031      .000000    -.002562
O   -.009860      .000000    1.630219
O   1.522501      .000000    -.581978
```

E = -221.8680388 h (0 eV)
doublet

```
 Zero-point correction=                      .005269 (Hartree/Particle)
 Thermal correction to Energy=               .008573
 Thermal correction to Enthalpy=             .009517
 Thermal correction to Gibbs Free Energy=   -.021253
```



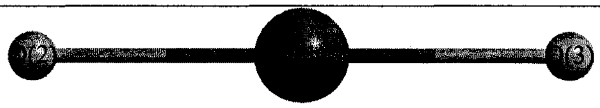
```
 O(3)-V(1)     1.6626
 O(2)-V(1)     1.7312
O(2)-V(1)-O(3) 119.7820
```

vo2qr2.log (nosymm)

```
V   -.023767      .330146      .000000
O   1.479889     -.527740      .000000
O  -1.456122     -.513974      .000000
```

-221.787727016 h (2.19 eV)
quartet

```
 Zero-point correction=                      .002585 (Hartree/Particle)
 Thermal correction to Energy=               .006796
 Thermal correction to Enthalpy=             .007740
 Thermal correction to Gibbs Free Energy=   -.025767
```



```
 O(3)-V(1)     1.7869
 O(2)-V(1)     1.7863
O(2)-V(1)-O(3) 179.9854
```

vo2s.log (nosymm)

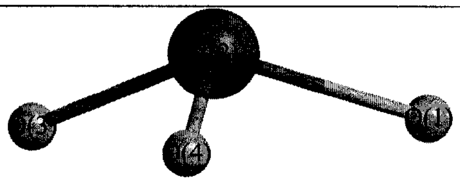
```
V   .000210     -.237343     .000000
O  1.786430     -.249684     .000000
O -1.786640     -.224541     .000000
```

-221.689305813 h (4.86 eV)
sextet

```
 Zero-point correction=                      .002189 (Hartree/Particle)
 Thermal correction to Energy=               .006428
 Thermal correction to Enthalpy=             .007372
 Thermal correction to Gibbs Free Energy=   -.019051
```

VO_3 clusters

Isomer 1



```
O(4)-V(2)    1.6684
O(3)-V(2)    1.6684
V(2)-O(1)    1.6686
```

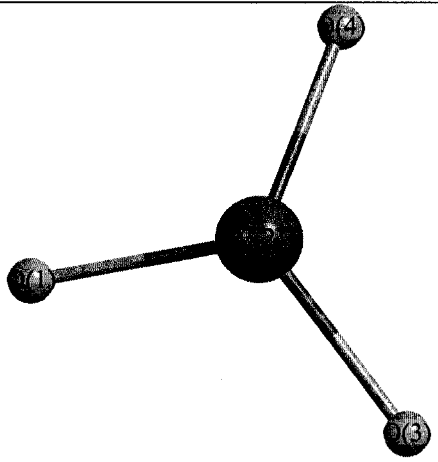
vo3.log

```
O  -1.974207   -0.737213    0.137895
V  -0.693977    0.164885   -0.437798
O  -0.629702    1.627061    0.363038
O   0.732415   -0.669297   -0.207481
```

E = -297.096314838 h (0 eV)

doublet

```
Zero-point correction=                    0.006979 (Hartree/Particle)
Thermal correction to Energy=             0.011537
Thermal correction to Enthalpy=           0.012481
Thermal correction to Gibbs Free Energy= -0.021559
```



```
O(4)-V(2)    1.7587
O(3)-V(2)    1.7584
V(2)-O(1)    1.6501
```

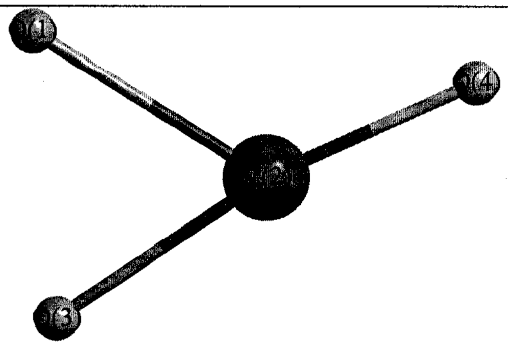
vo3qr1.log

```
O  -2.041097    -.758209     .060136
V   -.671635     .121926    -.209533
O   -.689415    1.797883     .322237
O    .836677    -.776163    -.317187
```

-297.009738701 h (2.36 eV)

quartet

```
 Zero-point correction=                    .005406 (Hartree/Particle)
 Thermal correction to Energy=             .010686
 Thermal correction to Enthalpy=           .011630
 Thermal correction to Gibbs Free Energy= -.025249
```



```
O(4)-V(2)   1.6683
O(3)-V(2)   1.8315
V(2)-O(1)   2.0037
```

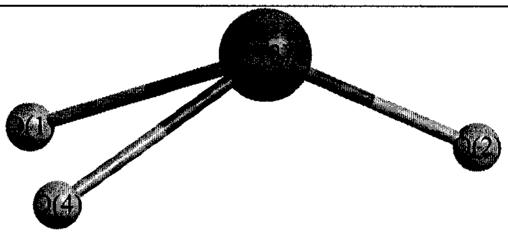
vo3sr1.log

```
O  -2.077104    -.328873     .378438
V   -.207029     .130615    -.175236
O  -1.195941    1.607697     .265869
O    .914603   -1.024003    -.613418
```

-296.899960594 h (5.34 eV)
sextet

```
 Zero-point correction=                          .004838 (Hartree/Particle)
 Thermal correction to Energy=                   .010290
 Thermal correction to Enthalpy=                 .011235
 Thermal correction to Gibbs Free Energy=       -.026263
```

Isomer 2

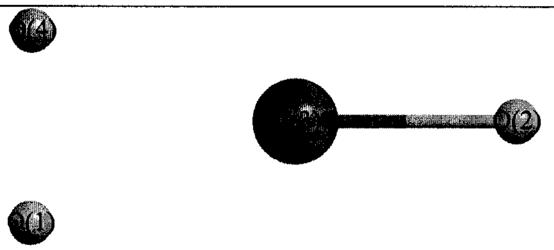


```
O(4)-V(3)   1.8385
V(3)-O(2)   1.6173
V(3)-O(1)   1.8385
```

vo3s2.log

```
O   -1.265068    -.769117     .230554
O    1.660903     .000013     .531983
V     .302349    -.000005    -.345417
O   -1.265088     .769118     .230538
Zero-point correction=                          .007939 (Hartree/Particle)
Thermal correction to Energy=                   .012285
Thermal correction to Enthalpy=                 .013229
Thermal correction to Gibbs Free Energy=       -.020378
```

E = -297.03558247 h (1.65 eV)
doublet



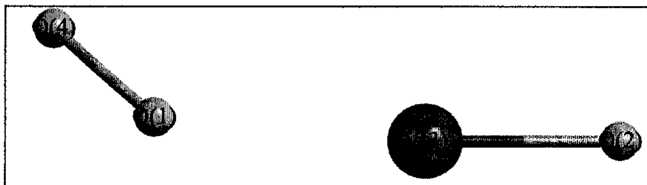
```
V(3)-O(2)    1.6215
V(3)-O(4)    2.0886
O(1)-O(4)    1.4178
O(1)-V(3)    2.0888
```

vo3s2q.log

```
O   1.568676    -.708873     .041596
O  -2.006407    -.000030     .101179
V   -.393306    -.000005    -.064129
O   1.568485     .708918     .041596
```

E = -296.986971000 h (2.98 eV)
quartet

```
 Zero-point correction=                      .006765 (Hartree/Particle)
 Thermal correction to Energy=               .011906
 Thermal correction to Enthalpy=             .012850
 Thermal correction to Gibbs Free Energy=   -.024308
```



```
O(1)-V(3)    2.2467
O(4)-O(1)    1.2975
V(3)-O(2)    1.6434
```

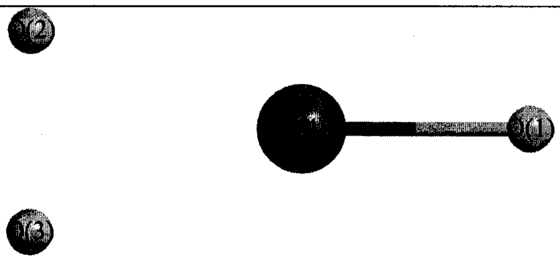
vo3s2sr1.log

```
O   1.573077    -.413700     .000111
O  -2.239865     .313023     .000107
V   -.654260    -.118990    -.000068
O   2.547785     .442773    -.000024
```

E = -296.909263255 h (5.09 eV)
sextet

```
 Zero-point correction=                      .005962 (Hartree/Particle)
 Thermal correction to Energy=               .011744
 Thermal correction to Enthalpy=             .012688
 Thermal correction to Gibbs Free Energy=   -.026312
```

Isomer 3

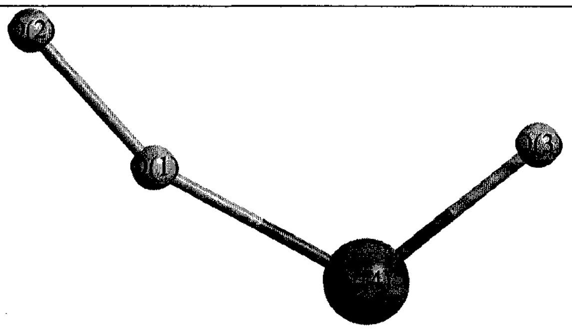


```
V(4)-O(1)    1.6214
O(3)-V(4)    2.0865
O(2)-V(4)    2.0865
O(2)-O(3)    1.4178
```

vo3s3qr2.log

```
O  -2.003175     .000000     .115076
O   1.566067     .708878     .047308
O   1.566067    -.708878     .047308
V   -.392681     .000000    -.072937
Zero-point correction=                      .006767 (Hartree/Particle)
Thermal correction to Energy=               .011910
Thermal correction to Enthalpy=             .012854
Thermal correction to Gibbs Free Energy=   -.024323
```

E = -296.986969324 h (2.98 eV)
quartet



```
V(4)-O(1)   1.7469
V(4)-O(3)   1.6181
O(2)-O(1)   1.3513
```

vo3s3.log

```
O  1.074833    -.213345     .001063
O  2.281087     .395689    -.000578
O -1.455789     .998656     .000182
V  -.660915    -.410783    -.000232
```

E = -296.985906036 h (3.00 eV)
doublet

```
 Zero-point correction=                        .007725 (Hartree/Particle)
 Thermal correction to Energy=                 .012424
 Thermal correction to Enthalpy=               .013368
 Thermal correction to Gibbs Free Energy=     -.021445
```

BPW91/TZVP
vo3tzvp.log

```
V(2)-O(1)  1.6547
V(2)-O(3)  1.6545
V(2)-O(4)  1.6543
```

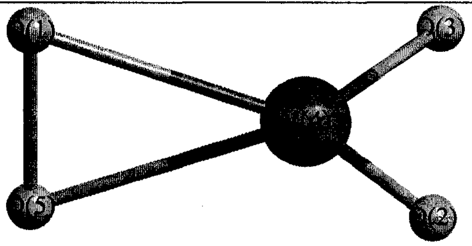
```
O  -1.047861   -2.171064     .293876
V  -1.106515    -.645330    -.343932
O  -1.202964    -.710849   -1.994300
O    .215109     .232580     .124386
```

E = -1169.88116378 h
doublet

```
 Zero-point correction=                        .006854 (Hartree/Particle)
 Thermal correction to Energy=                 .011423
 Thermal correction to Enthalpy=               .012367
 Thermal correction to Gibbs Free Energy=     -.021650
```

VO_4 clusters

Isomer 1



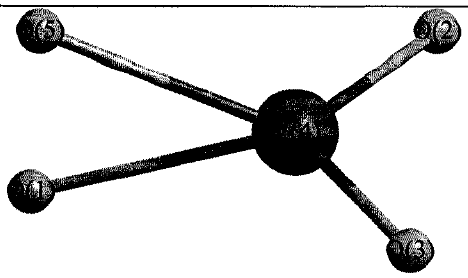
```
O(5)-O(1)   1.4032
O(5)-V(4)   2.0065
V(4)-O(1)   2.0069
V(4)-O(3)   1.6156
V(4)-O(2)   1.6156
```

vo4s2.log

```
O     1.596176    -.000056    -.701341
O    -1.187166   -1.339751     .000228
O    -1.186885    1.339913     .000233
V     -.284331    -.000014    -.000348
O     1.595326    -.000066     .701879
```

E = -372.280963306 (0eV)
doublet

```
Zero-point correction=                         .010903 (Hartree/Particle)
Thermal correction to Energy=                  .016721
Thermal correction to Enthalpy=                .017665
Thermal correction to Gibbs Free Energy=      -.020114
```



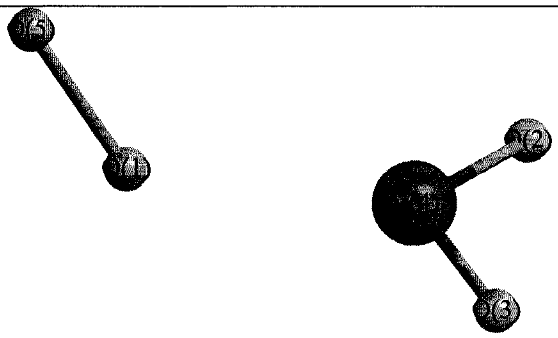
O(5)-O(1)	1.4098
O(5)-V(4)	1.9989
V(4)-O(3)	1.6832
V(4)-O(2)	1.6832
V(4)-O(1)	1.9989

vo4s2q.log

```
O  -1.596000    .002855    .704924
O   1.201557  -1.404911    .001463
O   1.201452   1.404964   -.001428
V    .274464    .000000   -.000030
O  -1.596094   -.002908   -.704871
```

E = -372.211605692 h (1.89 eV)
quartet

```
 Zero-point correction=                      .008354 (Hartree/Particle)
 Thermal correction to Energy=               .014881
 Thermal correction to Enthalpy=             .015825
 Thermal correction to Gibbs Free Energy=   -.023976
```



O(5)-O(1)	1.3060
V(4)-O(2)	1.7051
V(4)-O(3)	1.7027
V(4)-O(5)	3.1060
O(1)-V(4)	2.1237

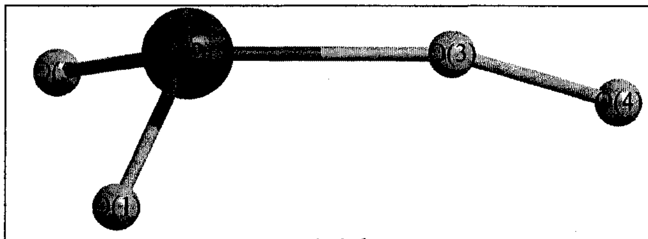
vo4s2s.log

```
O   1.536235    .000352    .472781
O  -1.273603   1.534655   -.069882
O  -1.272486  -1.533702   -.069949
V   -.535635   -.000644    .006240
O   2.549804    .000547   -.350891
```

E = -372.121671031 h (4.33 eV)
sextet

```
 Zero-point correction=                      .007080 (Hartree/Particle)
 Thermal correction to Energy=               .014358
 Thermal correction to Enthalpy=             .015302
 Thermal correction to Gibbs Free Energy=   -.027392
```

Isomer 2

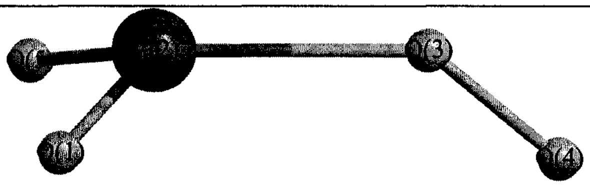


```
O(5)-V(2)    1.6210
O(4)-O(3)    1.3368
O(3)-V(2)    1.8324
V(2)-O(1)    1.6232
```

vo4s3.log

```
O     1.291696   -1.270216     .378007
V      .511025    -.001810    -.267290
O    -1.314482    -.147730    -.205507
O    -2.546892     .032064     .280077
O     1.100483    1.391085     .315882
Zero-point correction=                        .010603 (Hartree/Particle)
Thermal correction to Energy=                 .016772
Thermal correction to Enthalpy=               .017716
Thermal correction to Gibbs Free Energy=     -.021769
```

E = -372.255725646 h (0.69 eV)
doublet

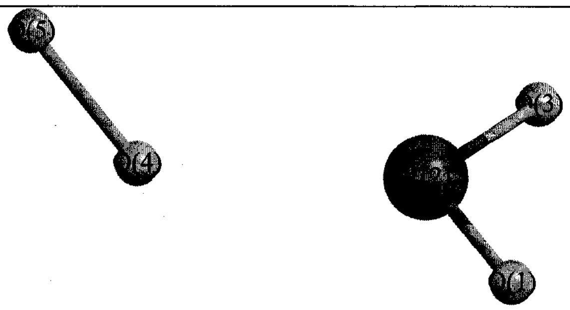


```
O(5)-V(2)    1.6477
O(4)-O(3)    1.3087
O(3)-V(2)    2.0408
V(2)-O(1)    1.6475
```

vo4s3qr1.log

```
O   1.294609   -1.368990     .291446
V    .525056    -.000539    -.207971
O  -1.509423    -.001410    -.369083
O  -2.578878    -.002381     .385186
O   1.284154    1.374330     .290368
 Zero-point correction=                        .009019 (Hartree/Particle)
 Thermal correction to Energy=                 .015793
 Thermal correction to Enthalpy=               .016738
 Thermal correction to Gibbs Free Energy=     -.024867
```

E = 372.208226119 h (1.98 eV)
quartet



```
O(5)-O(4)    1.3059
O(3)-V(2)    1.7036
V(2)-O(1)    1.7046
V(2)-O(5)    3.1052
V(2)-O(4)    2.1237
```

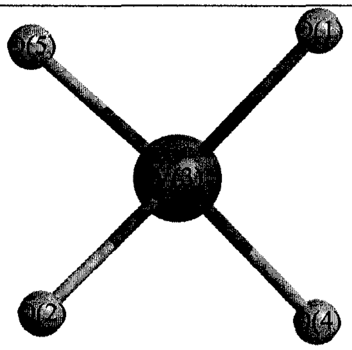
vo4s3s.log

```
O    1.273296    1.534430    -.069901
V     .535266    -.000273     .006213
O   -1.536451     .000173     .473113
O   -2.549282    -.000078    -.351211
O    1.273549   -1.533741    -.069865
```

E = -372.121671264 h (4.33 eV)
sextet

```
 Zero-point correction=                      .007075 (Hartree/Particle)
 Thermal correction to Energy=               .014357
 Thermal correction to Enthalpy=             .015301
 Thermal correction to Gibbs Free Energy=   -.027406
```

Isomer 3



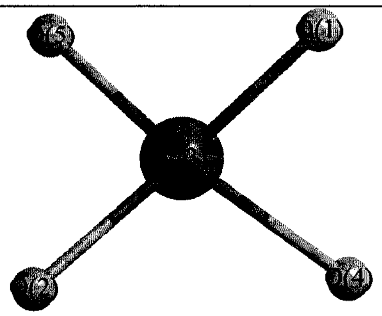
```
O(5)-V(3)    1.7267
O(4)-V(3)    1.7271
V(3)-O(1)    1.7271
V(3)-O(2)    1.7267
```

vo4q.log

```
O    -1.377504    1.042356   -0.022589
O    -0.043893   -0.981326    1.419457
V     0.000046    0.000848   -0.000017
O     1.443039    0.949877    0.000527
O    -0.021775   -1.013347   -1.397344
```

E = -372.246234115 h (0.95 eV)
quartet

```
Zero-point correction=                      0.007558 (Hartree/Particle)
Thermal correction to Energy=               0.014055
Thermal correction to Enthalpy=             0.015000
Thermal correction to Gibbs Free Energy=   -0.024353
```



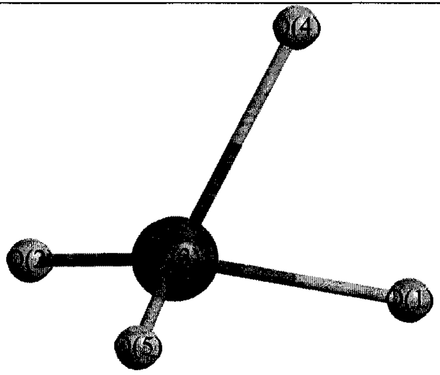
```
O(5)-V(3)    1.7139
O(4)-V(3)    1.7418
V(3)-O(1)    1.7416
V(3)-O(2)    1.7132
```

vo4.log

```
O   1.114258   -0.013995   -1.315144
O  -1.070246    1.359286   -0.011735
V  -0.027578   -0.000059   -0.000201
O   1.112790    0.009574    1.316341
O  -1.077515   -1.354695    0.011115
```

E = -372.230985737 h (1.36 eV)
doublet

```
 Zero-point correction=                           0.007400 (Hartree/Particle)
 Thermal correction to Energy=                    0.013944
 Thermal correction to Enthalpy=                  0.014889
 Thermal correction to Gibbs Free Energy=        -0.023817
```



```
O(5)-V(3)    1.7853
O(4)-V(3)    1.9159
V(3)-O(2)    1.6564
V(3)-O(1)    1.9162
```

vo4sr2.log

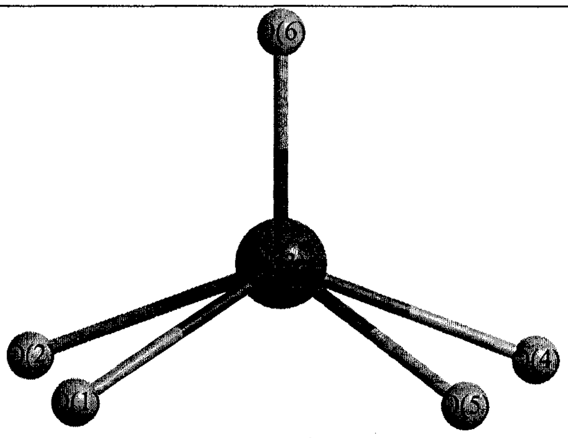
```
O   1.174361   -0.599295   -1.131492
O   0.057777    1.717249    0.000262
V  -0.213981    0.083258   -0.000758
O   1.171346   -0.598551    1.133641
O  -1.788289   -0.758771   -0.000231
```

E = -372.122485966 h (4.32 eV)
sextet

```
 Zero-point correction=                           0.007072 (Hartree/Particle)
 Thermal correction to Energy=                    0.013854
 Thermal correction to Enthalpy=                  0.014798
 Thermal correction to Gibbs Free Energy=        -0.025967
```

VO_5 clusters

Isomer 1

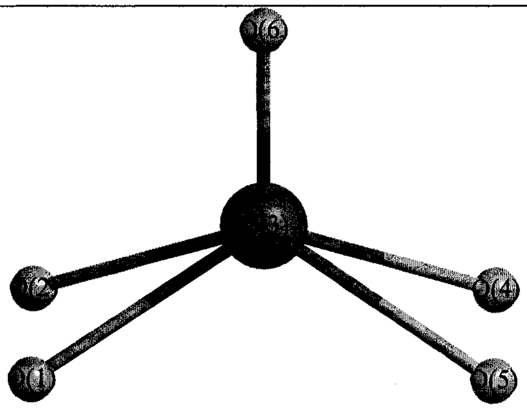


```
O(6)-V(3)    1.5955
O(5)-V(3)    1.9223
O(4)-V(3)    1.8830
V(3)-O(1)    1.9219
V(3)-O(2)    1.8832
```

vo5s3.log

```
O     1.331034    -.941850    -.584864
O     1.730539    -.281327     .644965
V      .000165     .249262     .124772
O    -1.730244    -.280113     .645561
O    -1.333613    -.939236    -.584969
O      .001810    1.725897    -.479412
Zero-point correction=                        .013847 (Hartree/Particle)
Thermal correction to Energy=                 .020400
Thermal correction to Enthalpy=               .021344
Thermal correction to Gibbs Free Energy=     -.017534
```

E = -447.440735276 h (0 eV)
doublet

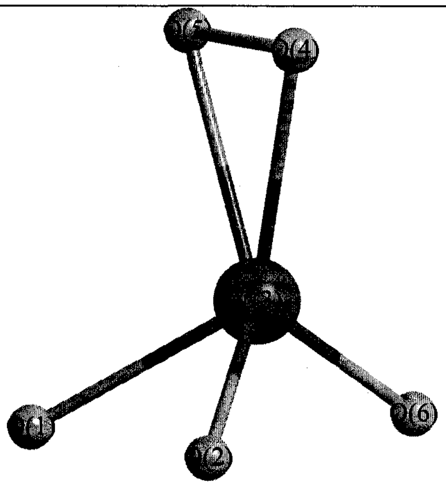


```
O(6)-V(3)    1.5961
O(5)-V(3)    2.0067
O(4)-V(3)    2.0059
V(3)-O(2)    2.0059
V(3)-O(1)    2.0067
```

vo5s3q.log

```
O   1.654540    -.641015    -.704261
O   1.653557    -.640849     .704428
V   -.000001     .249709    -.000141
O  -1.653532    -.640886     .704431
O  -1.654537    -.641016    -.704255
O   -.000024    1.845853     .000061
 Zero-point correction=                       .013027 (Hartree/Particle)
 Thermal correction to Energy=                .020141
 Thermal correction to Enthalpy=              .021085
 Thermal correction to Gibbs Free Energy=    -.020043
```

E = -447.410636568 h (0.82 eV)
quartet



```
O(6)-V(3)    1.6333
O(5)-O(4)    1.4001
O(5)-V(3)    2.0420
O(4)-V(3)    2.0417
V(3)-O(1)    1.9045
V(3)-O(2)    1.9042
```

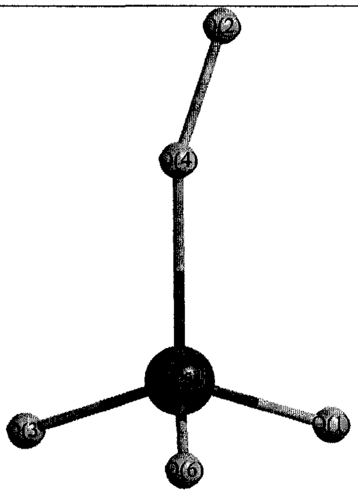
vo5s3s.log

```
O  -1.197221    -.870608    1.157131
O  -1.192214    -.893753   -1.143069
V   -.107322     .176634    -.001474
O   1.775815    -.194636    -.697463
O   1.776430    -.177914     .702512
O   -.854260    1.629088    -.014874
```

E = -447.325065743 h (3.15 eV)
sextet

```
 Zero-point correction=                      .010450 (Hartree/Particle)
 Thermal correction to Energy=               .018407
 Thermal correction to Enthalpy=             .019351
 Thermal correction to Gibbs Free Energy=   -.024491
```

Isomer 2



```
O(6)-V(5)    1.6805
V(5)-O(1)    1.6710
V(5)-O(4)    2.0118
V(5)-O(3)    1.6800
O(4)-O(2)    1.2886
```

vo5qr1.log

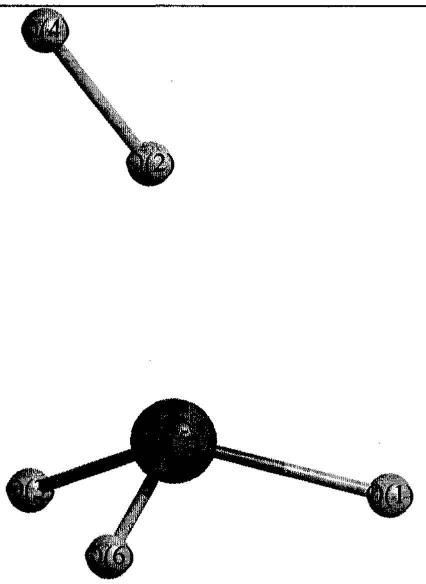
```
O   1.004634     .822267    1.362952
O    .873007   -2.313592    -.912149
O  -1.668471     .406690     .974086
O    .247979   -1.202793    -.722483
V   -.173953     .525938     .216038
O   -.204207    1.786098    -.895320
```

E = -447.436565721 h (0.11 eV)
quartet
[E = -447.436538077 h,
Int=Ultrafine]

```
Zero-point correction=                      .011094 (Hartree/Particle)
Thermal correction to Energy=               .018338
Thermal correction to Enthalpy=             .019282
Thermal correction to Gibbs Free Energy=   -.022933
```

Note that calculation without Int=Ultrafine produces one negative frequency.

```
[Int=Ultrafine
 Zero-point correction=                     .011102 (Hartree/Particle)
 Thermal correction to Energy=              .019279
 Thermal correction to Enthalpy=            .020223
 Thermal correction to Gibbs Free Energy=  -.026036
 All frequencies are positive.]
```



```
O(6)-V(5)    1.6736
V(5)-O(1)    1.6738
V(5)-O(3)    1.6735
O(4)-O(2)    1.2836
O(2)-V(5)    2.0763
```

vo5r1.log

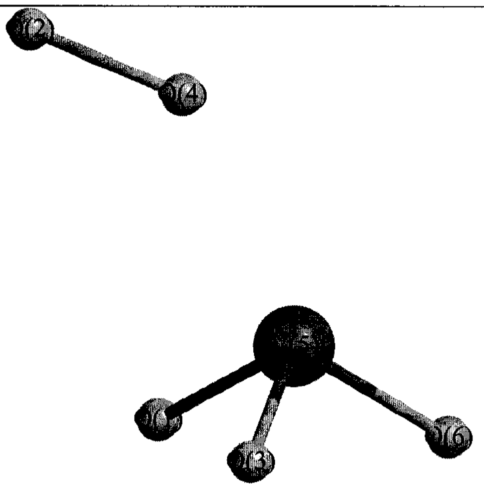
```
O   1.059600     .909867    1.547789
O    .370120   -1.364363    -.442978
O  -1.576254     .584393     .852096
O    .039207   -2.274894   -1.285021
V    .003995     .538403     .303081
O    .182318    1.631203    -.951843
```

E = -447.433234464 h (0.20 eV)
doublet
[E = -447.433226235 h,
Int=Ultrafine]

```
Zero-point correction=                            .011185
(Hartree/Particle)
 Thermal correction to Energy=                     .018461
 Thermal correction to Enthalpy=                   .019406
 Thermal correction to Gibbs Free Energy=         -.022308
```

Note that calculation without Int=Ultrafine produces one negative frequency.

```
[Int=Ultrafine
 Zero-point correction=                      .011237 (Hartree/Particle)
 Thermal correction to Energy=               .019410
 Thermal correction to Enthalpy=             .020354
 Thermal correction to Gibbs Free Energy=   -.024696
 All frequencies are positive.]
```



O(6)-V(5)	1.7773
V(5)-O(1)	1.8519
V(5)-O(3)	1.6403
O(4)-O(2)	1.3018
O(4)-V(5)	2.1181
O(2)-V(5)	3.1735

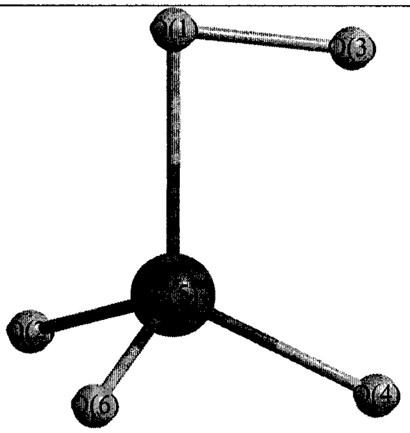
vo5s1s.log

```
O    1.130653     .785252     .880752
O     .962599   -2.326406    -.480096
O   -1.694517     .294597    1.006680
O     .168558   -1.369110    -.864514
V    -.446709     .482945    -.041284
O    -.041596    2.157330    -.478413
```

E = -447.333931543 h (2.91 eV)
sextet

```
 Zero-point correction=                         .010315 (Hartree/Particle)
 Thermal correction to Energy=                  .018616
 Thermal correction to Enthalpy=                .019561
 Thermal correction to Gibbs Free Energy=      -.025588
```

Isomer 3



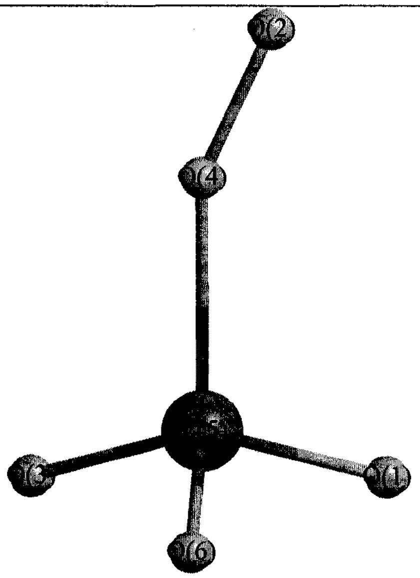
O(6)-V(5)	1.6610
V(5)-O(2)	1.6606
V(5)-O(1)	2.0383
V(5)-O(4)	1.7516
O(3)-O(1)	1.3646

vo5s2d.log

```
O     .176540     .634793    1.596062
O    1.570648    -.899421    -.594361
O   -1.001226    -.054244    1.607520
O   -1.148552    -.972545    -.906511
V     .195941    -.003446    -.339609
O     .285638    1.319472   -1.339979
```

E = -447.420598375 h (0.55 eV)
doublet

```
Zero-point correction=                          .010958 (Hartree/Particle)
Thermal correction to Energy=                   .018828
Thermal correction to Enthalpy=                 .019772
Thermal correction to Gibbs Free Energy=       -.022826
```



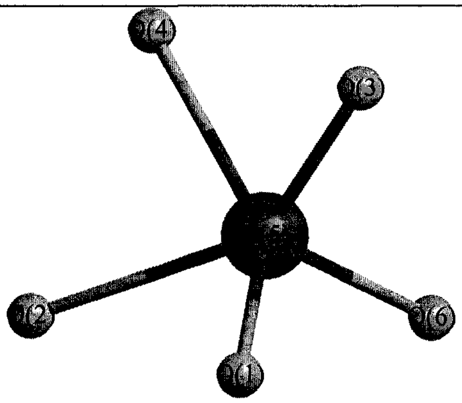
vo5s2qr1.log

```
O(6)-V(5)    1.6798
V(5)-O(1)    1.6714
V(5)-O(4)    2.0115
V(5)-O(3)    1.6803
O(4)-O(2)    1.2888
```

```
O    .996707     .785696    1.396212
O    .888577   -2.266717   -1.007856
O  -1.691731     .495555     .962430
O    .176819   -1.250825    -.658217
V   -.176334     .515671     .236690
O   -.115050    1.745228    -.906136
```

E = -447.436590835 h (0.11 eV)
quartet

```
 Zero-point correction=                        .011190 (Hartree/Particle)
 Thermal correction to Energy=                 .019290
 Thermal correction to Enthalpy=               .020234
 Thermal correction to Gibbs Free Energy=     -.024661
```



vo5s.log

```
O(6)-V(5)    1.6506
V(5)-O(1)    1.8441
V(5)-O(2)    1.8462
V(5)-O(3)    1.8429
V(5)-O(4)    1.8458
```

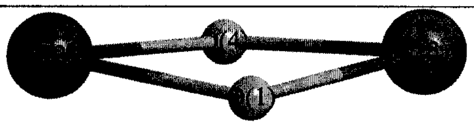
```
O    .807894     .475913    1.532719
O   1.354998   -1.074790    -.469607
O  -1.383506     .280640    1.082470
O   -.830361   -1.268763    -.923754
V    .021471     .148076    -.102729
O    .108491    1.463532   -1.095976
```

E = -447.336646079 h (2.83 eV)
sextet

```
 Zero-point correction=                        .009053 (Hartree/Particle)
 Thermal correction to Energy=                 .017188
 Thermal correction to Enthalpy=               .018133
 Thermal correction to Gibbs Free Energy=     -.025445
```

V_2O_2 clusters

Isomer 1



v2o2s1s.log

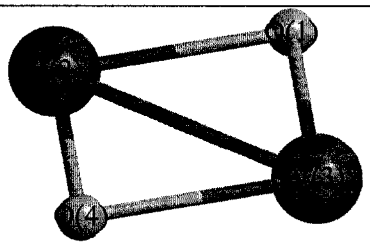
```
O   .000488     1.223330     .089821
V -1.359183      .000000    -.031227
V  1.358843      .000000    -.031257
O   .000488    -1.223330     .089821
```

```
O(4)-V(3)    1.8320
O(4)-V(2)    1.8330
V(3)-O(1)    1.8320
V(2)-O(1)    1.8330
```

E = -293.26100284 h (0 eV)

septet

```
Zero-point correction=                        .006028 (Hartree/Particle)
Thermal correction to Energy=                 .010643
Thermal correction to Enthalpy=               .011587
Thermal correction to Gibbs Free Energy=     -.024677
```



v2o2s1bsopt.log, v2o2s1bsoptfr.log

```
O    .027282    1.557117     .029042
V  -1.014970     .001412     .029566
V   1.015909    -.001371     .029420
O   -.027584   -1.557158     .029130
```

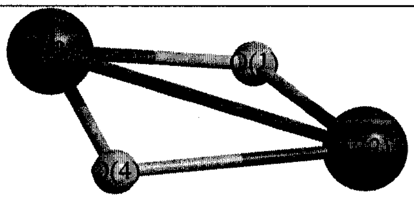
```
O(4)-V(3)    1.8733
O(4)-V(2)    1.8450
V(3)-O(1)    1.8456
V(3)-V(2)    2.0309
V(2)-O(1)    1.8726
```

E = -293.256983332 h (0.11 eV)

broken symmetry

singlet

```
 Zero-point correction=                        .005257 (Hartree/Particle)
 Thermal correction to Energy=                 .010618
 Thermal correction to Enthalpy=               .011562
 Thermal correction to Gibbs Free Energy=     -.025468
```



v2o2s1q.log

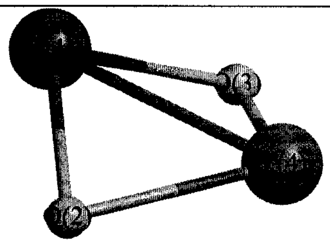
```
O   .125902     .132155    1.343723
V   .125902   -1.288607     .000000
V  -.213486    1.196673     .000000
O   .125902     .132155   -1.343723
```

```
O(4)-V(3)    1.7476
O(4)-V(2)    1.9555
V(3)-O(1)    1.7476
V(3)-V(2)    2.5083
V(2)-O(1)    1.9555
```

E = -293.243520588 h (0.48 eV)

quintet

```
 Zero-point correction=                        .006053 (Hartree/Particle)
 Thermal correction to Energy=                 .010858
 Thermal correction to Enthalpy=               .011802
 Thermal correction to Gibbs Free Energy=     -.024684
```



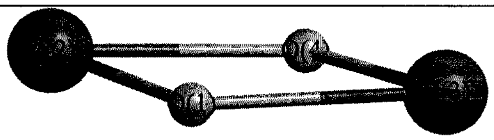
v2o2s1tr.log

```
V   -1.024316    -.015214    -.104601
O    -.030114    1.487841     .300316
O     .030089   -1.487806     .300501
V    1.024325     .015202    -.104379
```

```
V(4)-V(1)    2.0489
V(4)-O(2)    1.8559
V(4)-O(3)    1.8470
O(3)-V(1)    1.8559
O(2)-V(1)    1.8470
```

E = -293.238751142 h (0.54 eV)
triplet

```
 Zero-point correction=                          .006075 (Hartree/Particle)
 Thermal correction to Energy=                   .010851
 Thermal correction to Enthalpy=                 .011795
 Thermal correction to Gibbs Free Energy=       -.023931
```



v2o2s1n.log

```
O   -.035589     .001108    1.116359
V    .060346    1.547682     .000000
V   -.035589   -1.548453     .000000
O   -.035589     .001108   -1.116359
```

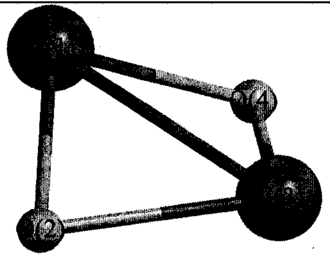
```
O(4)-V(2)    1.9098
O(4)-V(3)    1.9098
V(3)-O(1)    1.9098
V(2)-O(1)    1.9098
```

E = -293.147442583 h (3.09 eV)
nonet

```
 Zero-point correction=                          .004480 (Hartree/Particle)
 Thermal correction to Energy=                   .009990
 Thermal correction to Enthalpy=                 .010934
 Thermal correction to Gibbs Free Energy=       -.028829
```

Optimization of closed shell singlet cyclic isomer is unsuccessful (convergence problems).

Isomer 2



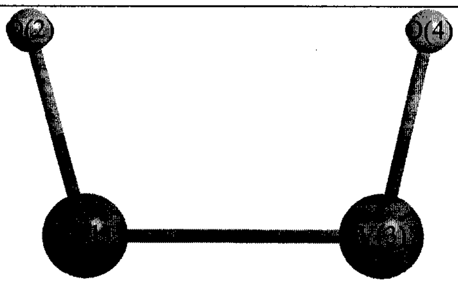
v2o2s2trdi.log

```
V   -1.032884     .000581    -.102895
O    -.001574    1.484154     .294747
V    1.034810    -.000612    -.102155
O    -.003963   -1.484065     .294770
```

```
O(4)-V(3)    1.8540
O(4)-V(1)    1.8496
V(3)-V(1)    2.0677
V(3)-O(2)    1.8537
O(2)-V(1)    1.8501
```

E = -293.238829733 h (0.60 eV)
triplet

```
Zero-point correction=                          .005824 (Hartree/Particle)
Thermal correction to Energy=                   .010728
Thermal correction to Enthalpy=                 .011672
Thermal correction to Gibbs Free Energy=       -.024332
```



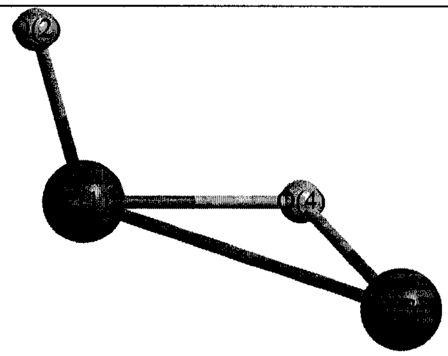
```
O(4)-V(3)    1.5945
V(3)-V(1)    2.1872
O(2)-V(1)    1.5945
```

v2o2line.log

```
V  -1.093485   -0.399613   -0.001426
O  -1.474885    1.148557    0.003041
V   1.093673   -0.399489    0.001426
O   1.474346    1.148860   -0.003040
```

E = -293.195516719 h (1.78 eV)
singlet

```
 Zero-point correction=                      0.006968 (Hartree/Particle)
 Thermal correction to Energy=               0.011931
 Thermal correction to Enthalpy=             0.012875
 Thermal correction to Gibbs Free Energy=   -0.022736
```



```
O(4)-V(3)    1.7958
O(4)-V(1)    1.8281
V(3)-V(1)    2.6166
O(2)-V(1)    1.6156
```

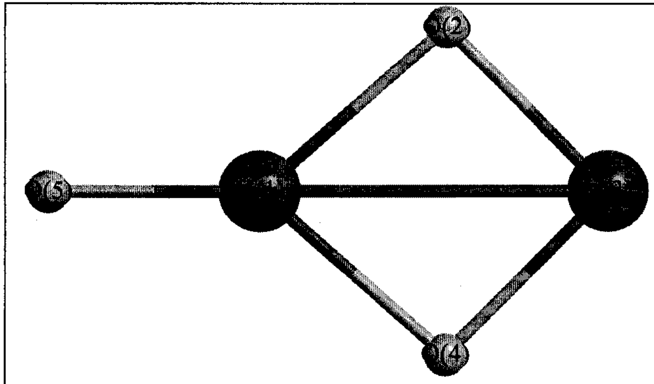
v2o2s2q.log

```
V  -1.015627     .256666    -.310259
O  -1.892575    -.858236     .463204
V   1.532178    -.285719    -.063095
O    .407492     .941764     .610190
```

E = -293.235873665 h (0.68 eV)
quintet

```
 Zero-point correction=                       .006135 (Hartree/Particle)
 Thermal correction to Energy=                .011232
 Thermal correction to Enthalpy=              .012176
 Thermal correction to Gibbs Free Energy=    -.025477
```

V_2O_3 clusters



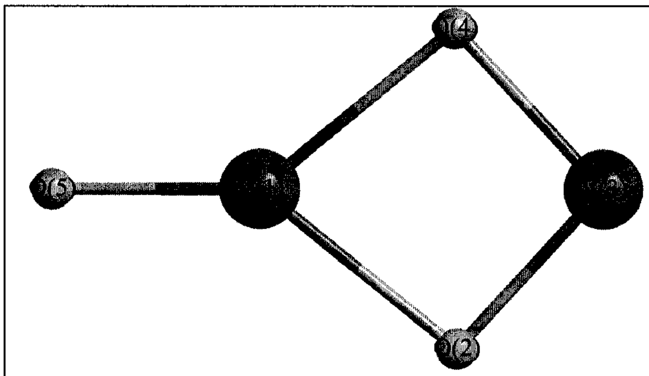
```
O(5)-V(1)    1.6258
O(4)-V(3)    1.7714
O(4)-V(1)    1.9000
V(3)-O(2)    1.7714
V(3)-V(1)    2.6740
O(2)-V(1)    1.9000
```

v2o3opt.log

```
V  -1.018554     .000001    -.000510
O    .406714    1.256460    -.000100
V   1.655414    -.000001     .000242
O    .406712   -1.256459    -.000100
O  -2.644400    -.000002     .000970
```

E = -368.578068044 h (0 eV)
quintet

```
Zero-point correction=                     .009434 (Hartree/Particle)
Thermal correction to Energy=              .015328
Thermal correction to Enthalpy=            .016272
Thermal correction to Gibbs Free Energy=  -.023267
```



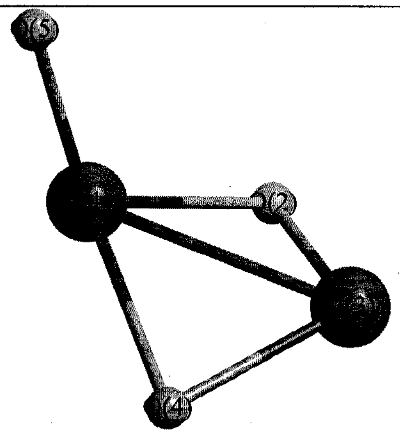
```
O(5)-V(1)    1.6211
O(4)-V(3)    1.7195
O(4)-V(1)    1.9866
V(3)-O(2)    1.7195
O(2)-V(1)    1.9866
```

v2o3bsoptr1.log

```
V  -1.065377     .000002     .001929
O    .464978    1.266710    -.000471
V   1.627821    -.000001    -.003647
O    .464971   -1.266707    -.000467
O  -2.686507    -.000005     .003157
```

E = -368.571476172 h (0.18 eV)
broken symmetry
singlet

```
 Zero-point correction=                     .009528 (Hartree/Particle)
 Thermal correction to Energy=              .015525
 Thermal correction to Enthalpy=            .016469
 Thermal correction to Gibbs Free Energy=  -.021941
```



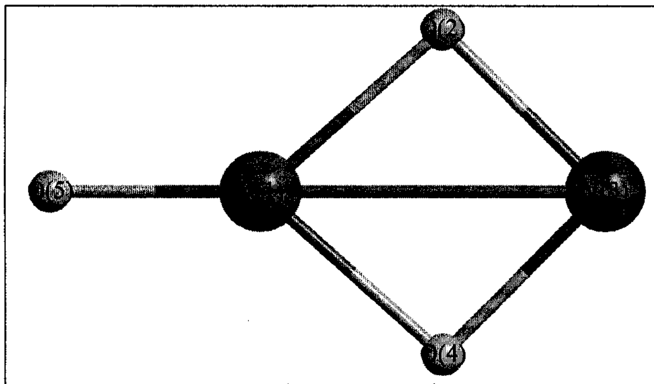
```
O(5)-V(1)    1.6213
O(4)-V(3)    1.7658
O(4)-V(1)    1.9225
V(3)-O(2)    1.7658
V(3)-V(1)    2.2010
O(2)-V(1)    1.9225
```

v2o3.log

```
V   -.855573     .000021    -.320140
O    .459594    1.399827    -.403885
V   1.247378    -.000014     .329449
O    .459561   -1.399821    -.403924
O  -2.045592    -.000026     .781043
```

E = -368.544992977 h (0.90 eV)
singlet

```
 Zero-point correction=                        .009880 (Hartree/Particle)
 Thermal correction to Energy=                 .015568
 Thermal correction to Enthalpy=               .016512
 Thermal correction to Gibbs Free Energy=     -.020475
```



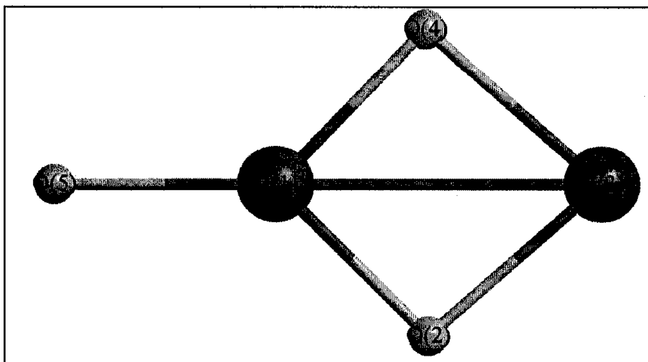
```
O(5)-V(1)    1.6220
O(4)-V(3)    1.7776
O(4)-V(1)    1.8761
V(3)-O(2)    1.7777
V(3)-V(1)    2.6617
O(2)-V(1)    1.8761
```

v2o3trr.log, v2o3trfr.log

```
V  -1.008831     .000116    -.006527
O    .389605    1.250692    -.004432
V   1.652854    -.000070     .004646
O    .389513   -1.250624    -.004437
O  -2.630684    -.000201     .014275
```

E = -368.573575885 h (0.12 eV)
triplet

```
 Zero-point correction=                        .009469 (Hartree/Particle)
 Thermal correction to Energy=                 .015422
 Thermal correction to Enthalpy=               .016366
 Thermal correction to Gibbs Free Energy=     -.023705
```



```
O(5)-V(1)    1.7940
O(4)-V(3)    1.9258
O(4)-V(1)    1.7781
V(3)-O(2)    1.9254
V(3)-V(1)    2.6509
O(2)-V(1)    1.7787
```

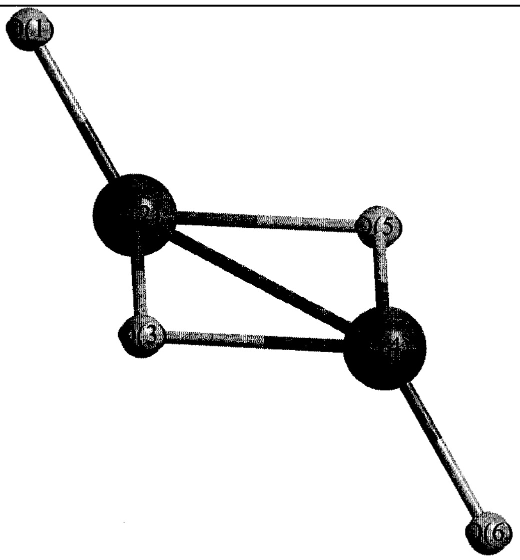
v2o3sp.log, v2o3spfr.log

```
V   -.945432      .000156    -.000326
O    .277691     1.291507    -.000788
V   1.705463     -.000205     .000504
O    .276642    -1.291356    -.000789
O  -2.739423     -.000012     .001065
```

E = -368.481468680 h (2.63 eV)
septet

```
 Zero-point correction=                          .007580 (Hartree/Particle)
 Thermal correction to Energy=                   .014036
 Thermal correction to Enthalpy=                 .014981
 Thermal correction to Gibbs Free Energy=       -.025960
```

V_2O_4 clusters
Isomer 1 – trans



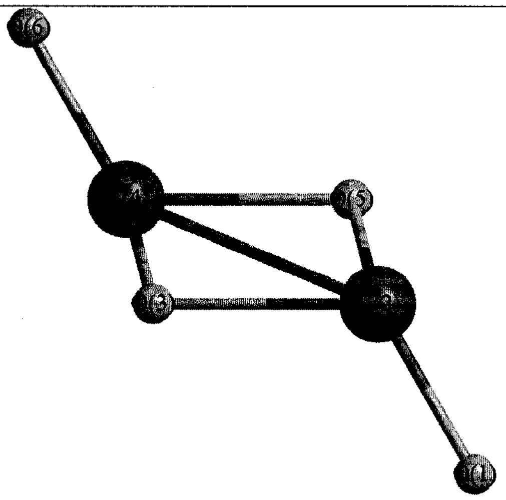
```
O(6)-V(4)    1.6110
O(5)-V(2)    1.8176
O(5)-V(4)    1.8176
V(4)-O(3)    1.8176
V(4)-V(2)    2.5935
O(3)-V(2)    1.8176
V(2)-O(1)    1.6110
```

v2o4bsopt.log

```
O  -2.676125      .000000    -.447752
V  -1.276999      .000000     .352633
O    .000000     1.259520    -.000001
V   1.276999      .000000    -.352633
O    .000000    -1.259520    -.000001
O   2.676123      .000000     .447757
```

E = -443.886798389 h (-0.10 eV)
singlet, broken symmetry

```
 Zero-point correction=                          .013428 (Hartree/Particle)
 Thermal correction to Energy=                   .020203
 Thermal correction to Enthalpy=                 .021148
 Thermal correction to Gibbs Free Energy=       -.018796
```

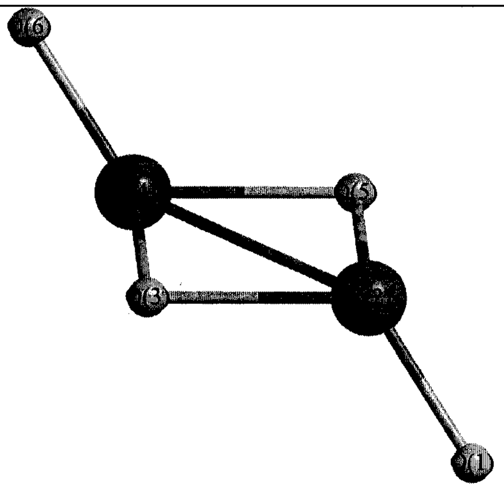


```
O(6)-V(4)    1.6112
O(5)-V(2)    1.8326
O(5)-V(4)    1.8326
V(4)-V(2)    2.6694
V(4)-O(3)    1.8326
O(3)-V(2)    1.8326
V(2)-O(1)    1.6112
```

v2o4s2trtight.log

```
O   2.649387     .000005    -.499832
V   1.285697    -.000003     .358267
O    .000003   -1.255778    -.000021
V  -1.285705     .000004    -.358272
O   -.000004    1.255779    -.000010
O  -2.649363    -.000007     .499877
 Zero-point correction=                         .012868 Hartree/Particle)
 Thermal correction to Energy=                  .019919
 Thermal correction to Enthalpy=                .020863
 Thermal correction to Gibbs Free Energy=      -.020712
```

E = -443.883305207 h (0 eV)
triplet

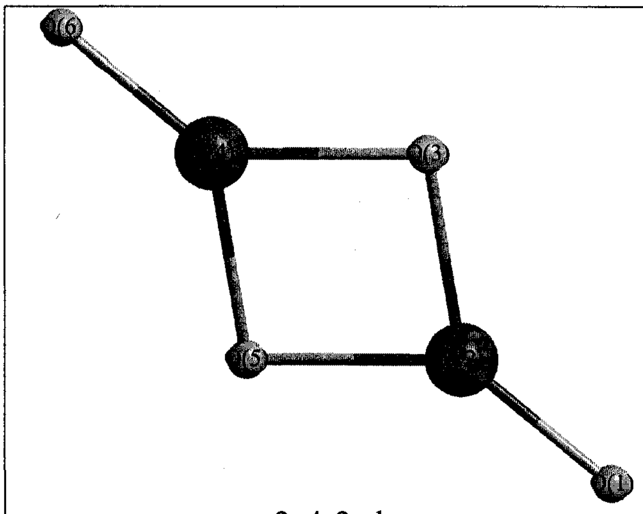


```
O(6)-V(4)    1.6110
O(5)-V(2)    1.8176
O(5)-V(4)    1.8176
V(4)-O(3)    1.8176
V(4)-V(2)    2.5935
O(3)-V(2)    1.8176
V(2)-O(1)    1.6110
```

v2o4s2.log

```
O  -2.676026     .000000    -.436609
V  -1.255700     .000000     .323640
O    .000000    1.273593    -.000003
V   1.255702     .000000    -.323642
O    .000000   -1.273593    -.000003
O   2.676021     .000000     .436620
 Zero-point correction=                       .013585 (Hartree/Particle)
 Thermal correction to Energy=                .020309
 Thermal correction to Enthalpy=              .021254
 Thermal correction to Gibbs Free Energy=    -.018611
```

E = -443.872265868 h (0.30 eV)
singlet



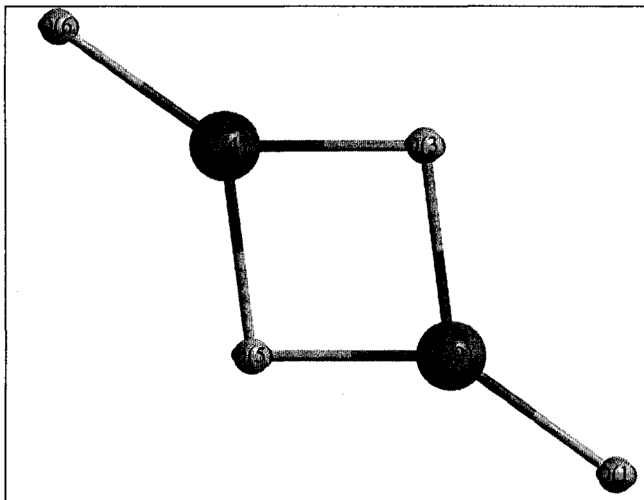
```
O(6)-V(4)    1.6666
O(5)-V(4)    1.8457
O(5)-V(2)    1.8457
V(4)-O(3)    1.8457
O(3)-V(2)    1.8457
V(2)-O(1)    1.6667
```

v2o4s2q.log

```
O  -3.041522     .000000     .000215
V  -1.374872     .000000    -.000137
O   -.000005    1.231373    -.000018
V   1.374876     .000000     .000113
O   -.000005   -1.231373    -.000018
O   3.041519    -.000001    -.000110
```

E = -443.798120181 h (2.32 eV)
quintet

```
 Zero-point correction=                      .009805 (Hartree/Particle)
 Thermal correction to Energy=               .017847
 Thermal correction to Enthalpy=             .018791
 Thermal correction to Gibbs Free Energy=   -.026703
```



```
O(6)-V(4)    1.8272
O(5)-V(4)    1.8892
O(5)-V(2)    1.7797
V(4)-O(3)    1.7798
O(3)-V(2)    1.8903
V(2)-O(1)    1.8273
```

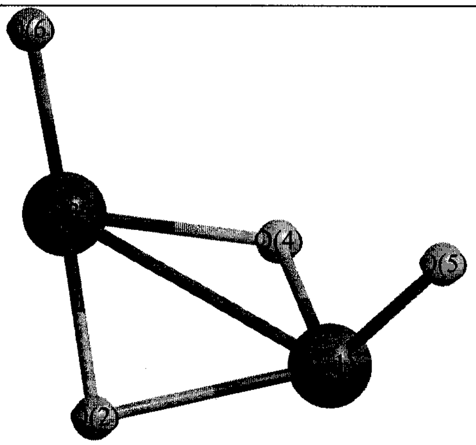
v2o4s2s.log

```
O  -3.193891     .084799     .002267
V  -1.372626    -.063248    -.000952
O    .017834    1.217298    -.000382
V   1.372501     .062915    -.000043
O   -.017304   -1.216667    -.000168
O   3.193722    -.084472     .001145
```

E = -443.684909032 h (5.40 eV)
septet

```
 Zero-point correction=                      .009809 (Hartree/Particle)
 Thermal correction to Energy=               .017667
 Thermal correction to Enthalpy=             .018611
 Thermal correction to Gibbs Free Energy=   -.026033
```

Isomer 2 – cis



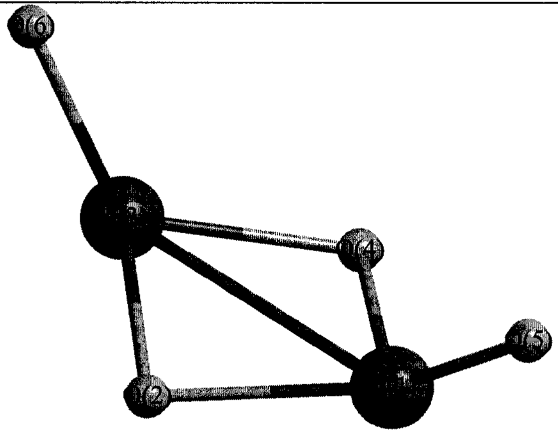
```
O(6)-V(3)    1.6097
O(5)-V(1)    1.6097
O(4)-V(1)    1.8288
O(4)-V(3)    1.8288
V(3)-O(2)    1.8288
V(3)-V(1)    2.3655
O(2)-V(1)    1.8288
```

v2o4r1.log

```
V   1.182736   -0.217511   -0.000004
O   0.000014   -0.624613    1.334166
V  -1.182728   -0.217514    0.000008
O  -0.000007   -0.624646   -1.334152
O   1.844281    1.249987   -0.000010
O  -1.844311    1.249967   -0.000015
```

E = -443.880765993 h (0.07 eV)
singlet

```
 Zero-point correction=                           0.013886 (Hartree/Particle)
 Thermal correction to Energy=                    0.020383
 Thermal correction to Enthalpy=                  0.021327
 Thermal correction to Gibbs Free Energy=        -0.017720
```



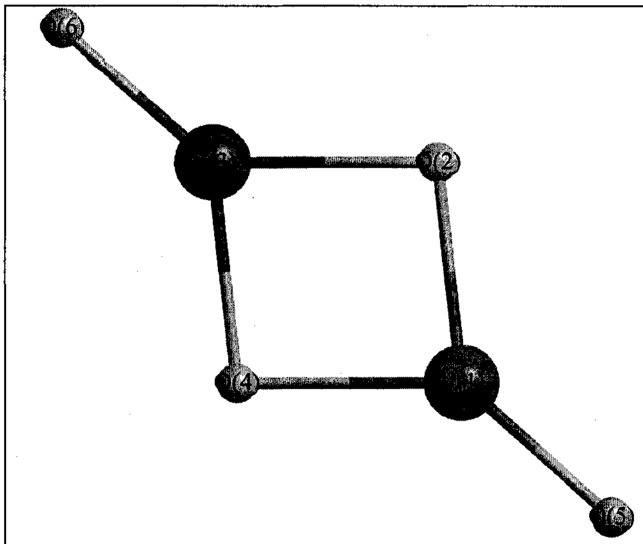
```
O(6)-V(3)    1.6155
O(5)-V(1)    1.6155
O(4)-V(3)    1.8280
O(4)-V(1)    1.8280
V(3)-O(2)    1.8280
V(3)-V(1)    2.5973
O(2)-V(1)    1.8280
```

v2o4trip.log

```
V  -1.298661     .000014    -.199180
O    .000000    1.270325    -.402864
V   1.298661     .000013    -.199179
O   -.000002   -1.270273    -.402995
O  -2.407625    -.000067     .975572
O   2.407627    -.000066     .975570
```

E = -443.876659821 h (0.18 eV)
singlet

```
 Zero-point correction=                            .012793 (Hartree/Particle)
 Thermal correction to Energy=                     .019919
 Thermal correction to Enthalpy=                   .020864
 Thermal correction to Gibbs Free Energy=         -.021828
```



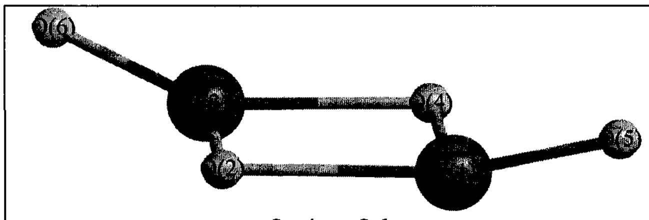
```
O(6)-V(3)    1.6667
O(5)-V(1)    1.6667
O(4)-V(1)    1.8457
O(4)-V(3)    1.8457
V(3)-O(2)    1.8457
O(2)-V(1)    1.8457
```

v2o4qr1.log

```
V   1.375180     .000000    -.000004
O    .000001   -1.231002    -.000006
V  -1.375181     .000000    -.000004
O    .000001    1.231002    -.000006
O   3.041838     .000000     .000017
O  -3.041836     .000000     .000017
```

E = -443.798120128 h (2.32 eV)
quintet

```
 Zero-point correction=                        .009809 (Hartree/Particle)
 Thermal correction to Energy=                 .017848
 Thermal correction to Enthalpy=               .018792
 Thermal correction to Gibbs Free Energy=     -.026662
```



```
O(6)-V(3)    1.7100
O(5)-V(1)    1.9725
O(4)-V(1)    1.8682
O(4)-V(3)    1.8097
V(3)-O(2)    1.8097
O(2)-V(1)    1.8682
```

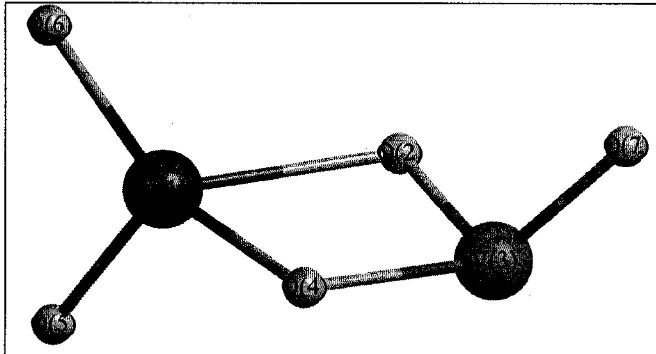
v2o4spr2.log

```
V   1.349326     .000012    -.162428
O   -.051981   -1.233400    -.091110
V  -1.375244    -.000001    -.038143
O   -.051987    1.233409    -.090999
O   3.226684    -.000026     .442893
O  -3.048199    -.000014     .315858
```

E = -443.687488017 h (5.32 eV)
septet

```
 Zero-point correction=                        .008933 (Hartree/Particle)
 Thermal correction to Energy=                 .017219
 Thermal correction to Enthalpy=               .018163
 Thermal correction to Gibbs Free Energy=     -.028488
```

V_2O_5 clusters

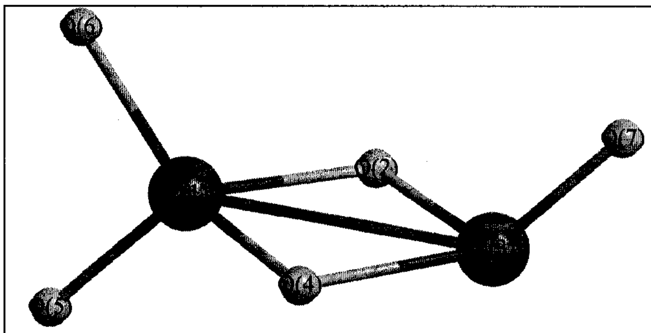


O(7)-V(3)	1.6124
O(6)-V(1)	1.6152
O(5)-V(1)	1.6190
O(4)-V(3)	1.7151
O(4)-V(1)	1.9866
V(3)-O(2)	1.7151
O(2)-V(1)	1.9866

```
V   -1.197038     .062600     .000021
O     .346477    -.085234   -1.241882
V    1.500406    -.345056     .000030
O     .346520    -.085053    1.241946
O   -2.189320   -1.216672    -.000011
O   -2.047414    1.435819    -.000080
O    2.671555     .763199    -.000120
```

E = -519.144980692 h (0 eV)
singlet

```
 Zero-point correction=                        .017267 (Hartree/Particle)
 Thermal correction to Energy=                 .025050
 Thermal correction to Enthalpy=               .025995
 Thermal correction to Gibbs Free Energy=     -.016352
```



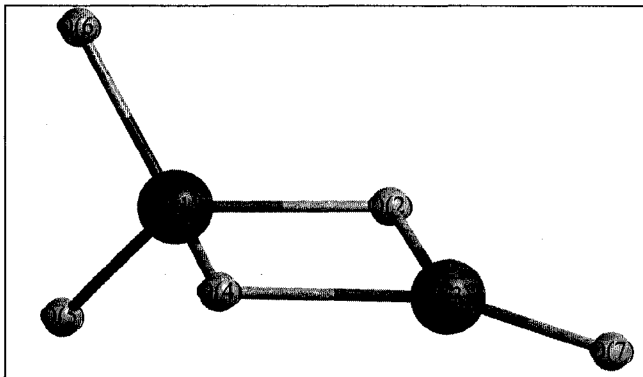
O(7)-V(3)	1.6071
O(6)-V(1)	1.6936
O(5)-V(1)	1.6632
O(4)-V(3)	1.8335
O(4)-V(1)	1.8159
V(3)-O(2)	1.8336
V(3)-V(1)	2.6636
O(2)-V(1)	1.8159

v2o5tr.log

```
V  -1.112063     .039301    -.000019
O    .187920    -.194582   -1.246154
V   1.526707    -.323443     .000066
O    .187903    -.194437    1.246190
O  -2.354349   -1.066635    -.000015
O  -1.934022    1.520085    -.000011
O   2.720449     .752480    -.000145
```

E = -519.103634486 h (1.13 eV)
triplet

```
 Zero-point correction=                        .015505 (Hartree/Particle)
 Thermal correction to Energy=                 .023539
 Thermal correction to Enthalpy=               .024483
 Thermal correction to Gibbs Free Energy=     -.019217
```



```
O(7)-V(3)    1.6805
O(6)-V(1)    1.6970
O(5)-V(1)    1.6970
O(4)-V(3)    1.9034
O(4)-V(1)    1.7899
V(3)-O(2)    1.9034
O(2)-V(1)    1.7898
```

v2o5qr1.log

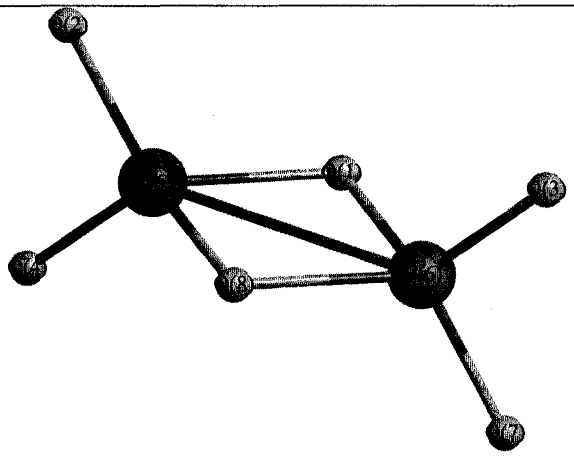
```
V  -1.203070     .000003     .000008
O    .110518   -.000085   -1.215739
V   1.575130   -.000005     .000002
O    .110548    .000063    1.215746
O  -2.273208  -1.317027     .000060
O  -2.273199   1.317038    -.000077
O   3.255668    .000015    -.000017
```

E = -519.012116356 h (3.62 eV)
quintet

```
 Zero-point correction=                        .012802 (Hartree/Particle)
 Thermal correction to Energy=                 .021696
 Thermal correction to Enthalpy=               .022640
 Thermal correction to Gibbs Free Energy=     -.023813
```

V_2O_6 clusters

Isomer 1



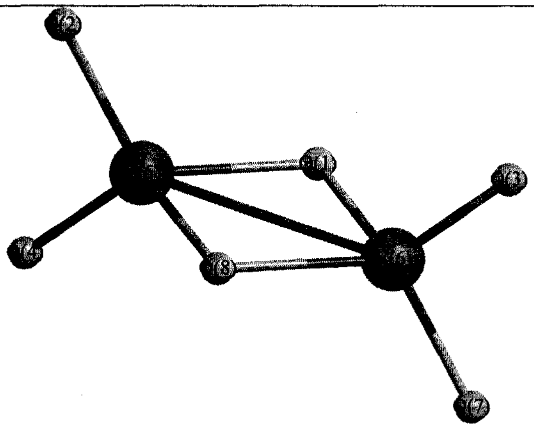
```
O(8)-V(6)    1.8175
O(8)-V(5)    1.8175
O(7)-V(6)    1.6737
V(6)-O(3)    1.6737
V(6)-O(1)    1.8175
V(6)-V(5)    2.6800
V(5)-O(1)    1.8175
V(5)-O(2)    1.6737
V(5)-O(4)    1.6737
```

v2o6s1bsoptr1.log, v2o6s1bsoptfr.log

```
O    .000000    .000002   -1.227915
O  -2.388347   1.304754     .000002
O   2.388348   1.304754     .000002
O  -2.388349  -1.304753    -.000003
V  -1.340024    .000000     .000000
V   1.340024    .000000     .000000
O   2.388348  -1.304754    -.000002
O    .000000   -.000002    1.227915
```

E = -594.317287637 h (-0.004 eV)
broken symmetry
singlet

```
 Zero-point correction=                        .017469 (Hartree/Particle)
 Thermal correction to Energy=                 .026877
 Thermal correction to Enthalpy=               .027821
 Thermal correction to Gibbs Free Energy=     -.017891
```



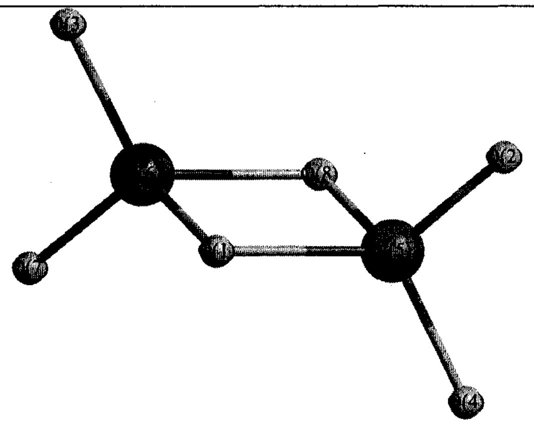
```
O(8)-V(6)    1.8175
O(8)-V(5)    1.8175
O(7)-V(6)    1.6737
V(6)-O(3)    1.6737
V(6)-O(1)    1.8175
V(6)-V(5)    2.6800
V(5)-O(1)    1.8175
V(5)-O(2)    1.6737
V(5)-O(4)    1.6737
```

v2o6s1tr.log

```
O    .000000     .000002   -1.227915
O  -2.388347    1.304754     .000002
O   2.388348    1.304754     .000002
O  -2.388349   -1.304753    -.000003
V  -1.340024     .000000     .000000
V   1.340024     .000000     .000000
O   2.388348   -1.304754    -.000002
O    .000000    -.000002    1.227915
```

E = -594.317126182 h (0 eV)
triplet

```
 Zero-point correction=                      .017433 (Hartree/Particle)
 Thermal correction to Energy=               .026861
 Thermal correction to Enthalpy=             .027805
 Thermal correction to Gibbs Free Energy=   -.019011
```



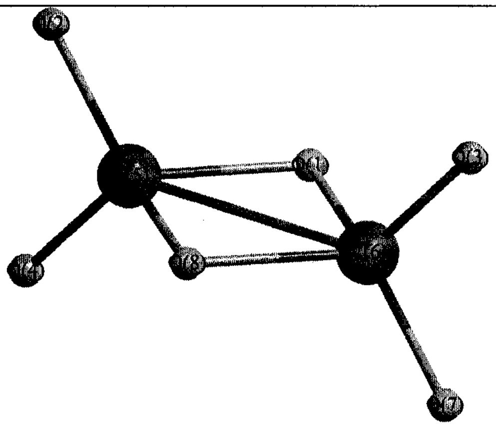
```
O(8)-V(5)    1.8317
O(8)-V(6)    1.8317
O(7)-V(6)    1.6631
V(6)-O(1)    1.8317
V(6)-O(3)    1.6631
V(5)-O(2)    1.6631
V(5)-O(4)    1.6631
V(5)-O(1)    1.8317
```

v2o6s1r1.log

```
O    .000000     .000002    1.239555
O   2.356382    1.322975    -.000001
O  -2.356387    1.322971    -.000003
O   2.356389   -1.322971     .000001
V   1.348540     .000000     .000000
V  -1.348540     .000000     .000000
O  -2.356386   -1.322972     .000002
O    .000001    -.000005   -1.239553
```

E = -594.293150183 h (0.65 eV)
singlet

```
 Zero-point correction=                      .017697 (Hartree/Particle)
 Thermal correction to Energy=               .027097
 Thermal correction to Enthalpy=             .028041
 Thermal correction to Gibbs Free Energy=   -.017689
```



```
O(8)-V(6)    1.8618
O(8)-V(5)    1.8618
O(7)-V(6)    1.6949
V(6)-O(3)    1.6949
V(6)-O(1)    1.8618
V(6)-V(5)    2.6484
V(5)-O(1)    1.8618
V(5)-O(2)    1.6949
V(5)-O(4)    1.6949
```

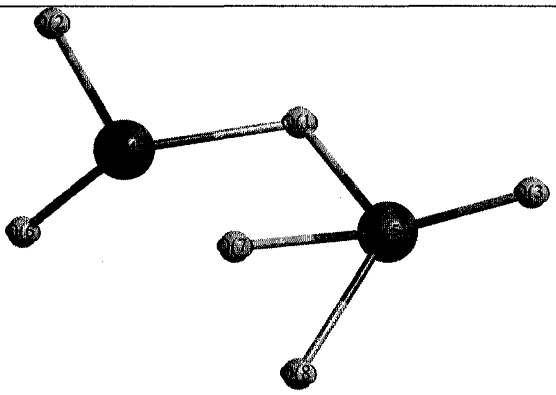
v2o6s1q.log

```
O    .000000     .000002   -1.308770
O  -2.331492    1.363029     .000002
O   2.331493    1.363028     .000003
O  -2.331493   -1.363028    -.000002
V  -1.324181     .000000     .000000
V   1.324181     .000000     .000000
O   2.331492   -1.363029    -.000003
O    .000000    -.000002    1.308770
```

E = -594.219453903 h (2.66 eV)
quintet

```
 Zero-point correction=                        .013680 (Hartree/Particle)
 Thermal correction to Energy=                 .024522
 Thermal correction to Enthalpy=               .025466
 Thermal correction to Gibbs Free Energy=     -.025170
```

Isomer 2

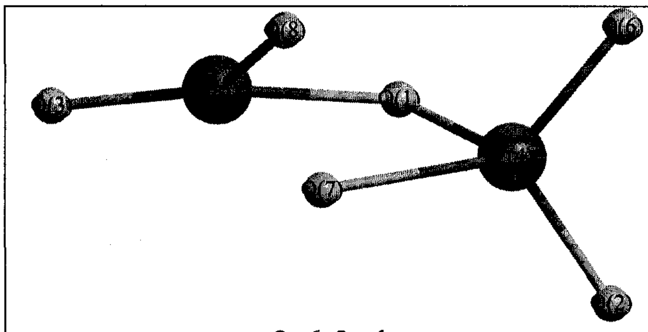


```
O(8)-V(5)    1.8478
O(7)-V(5)    1.9720
O(6)-V(4)    1.6156
V(5)-O(1)    1.7217
V(5)-O(3)    1.6032
V(4)-O(2)    1.6137
V(4)-O(1)    1.9533
V(4)-O(8)    3.0356
V(4)-O(7)    2.0522
```

v2o6s2.log, v2o6s2fr.log

```
O   -.160506   -1.059266    -.761414
O   2.322925    -.934060     .985513
O  -2.826867    -.797148     .233257
V   1.358218    -.095680     .000344
V  -1.463355    -.078816    -.208542
O   2.242090     .795303   -1.017026
O   -.186869     .801895    1.009507
O  -1.088504    1.694953     .148732
Zero-point correction=                         .019444 (Hartree/Particle)
 Thermal correction to Energy=                 .028683
 Thermal correction to Enthalpy=               .029627
 Thermal correction to Gibbs Free Energy=     -.016197
```

E = -594.290344801 h (0.73 eV)
singlet



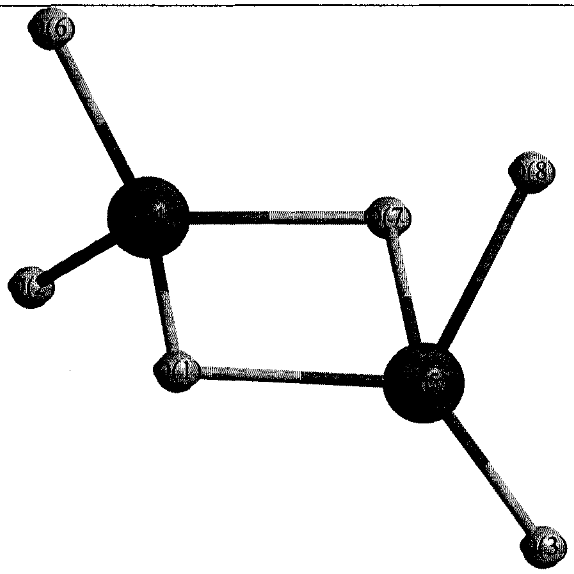
```
O(8)-V(5)    1.9811
O(7)-V(4)    2.0057
O(6)-V(4)    1.6680
V(5)-O(1)    1.8288
V(5)-O(3)    1.6067
V(4)-O(2)    1.6308
V(4)-O(1)    1.8067
O(7)-O(8)    1.5047
V(4)-O(8)    2.6521
V(5)-O(7)    2.0461
```

v2o6s2tr.log

```
O   -.055555   -1.015099    -.810190
O   2.331214   -1.065359     .833731
O  -3.021103    -.559350     .100632
V   1.281533    -.123292     .015031
V  -1.494826    -.114060    -.131084
O   2.161975     .889035    -.976070
O   -.136541     .757582    1.126688
O   -.666771    1.675578     .058865
```

E = -594.245998924 h (1.94 eV)
triplet

```
 Zero-point correction=                         .017359 (Hartree/Particle)
 Thermal correction to Energy=                  .027134
 Thermal correction to Enthalpy=                .028078
 Thermal correction to Gibbs Free Energy=      -.019995
```



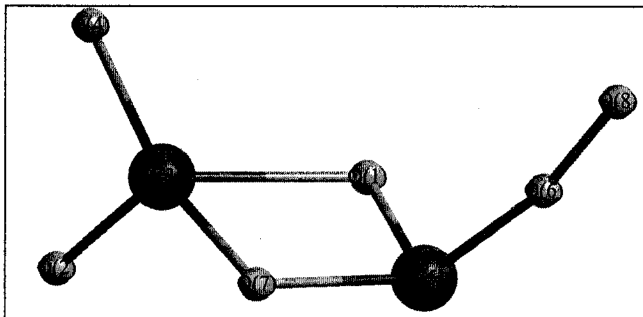
```
O(8)-V(5)    1.9377
O(7)-V(5)    1.9111
O(7)-V(4)    1.8357
O(6)-V(4)    1.6765
V(5)-O(3)    1.6163
V(5)-O(1)    1.8930
V(4)-O(1)    1.7865
V(4)-O(2)    1.6860
```

v2o6s2q.log

```
O   -.097074    -.383310    1.281627
O  -2.282765   -1.325905    -.449871
O   2.574843   -1.145755    -.239392
V  -1.279857    -.042822    -.013292
V   1.419688    -.098084     .185552
O  -2.361321    1.206434     .270162
O    .116572     .265223   -1.164335
O   1.647730    1.788419    -.193438
```

E = -594.214321072 h (2.80 eV)
quintet

Isomer 3



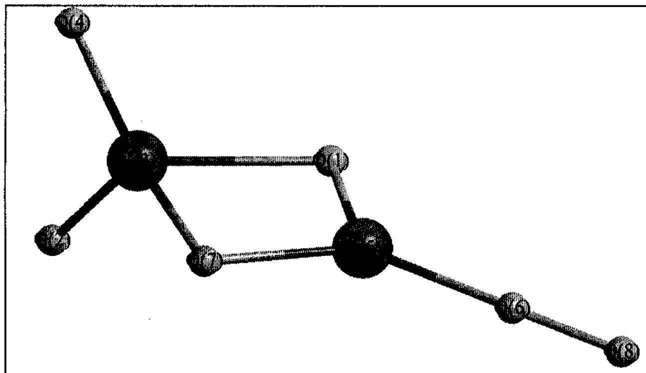
```
O(8)-O(6)    1.3365
O(7)-V(3)    1.9872
O(7)-V(5)    1.7104
O(6)-V(5)    1.7098
V(5)-O(1)    1.7105
O(4)-V(3)    1.6154
V(3)-O(2)    1.6181
V(3)-O(1)    1.9872
```

v2o6s3.log,

```
O     .015076    -.311536    1.232989
O    2.768048    -.799560    -.000401
V    1.489641     .192371    -.000130
O    1.972992    1.733764     .000556
V   -1.081305    -.762615     .000023
O   -2.501332     .189786     .000562
O     .014598    -.310900   -1.232978
O   -3.443346    1.137899    -.000423
```

E = -594.247875282 h (1.88 eV)
singlet

```
 Zero-point correction=                       .019574 (Hartree/Particle)
 Thermal correction to Energy=                .029000
 Thermal correction to Enthalpy=              .029944
 Thermal correction to Gibbs Free Energy=    -.016939
```



```
O(8)-O(6)    1.3370
O(7)-V(3)    2.0016
O(7)-V(5)    1.6968
O(6)-V(5)    1.8177
V(5)-O(1)    1.6968
O(4)-V(3)    1.6162
V(3)-O(2)    1.6162
```

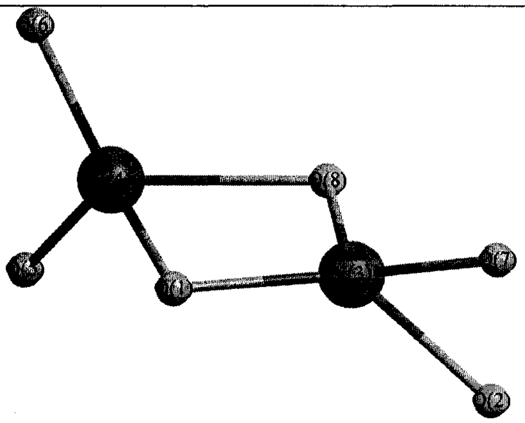
v2o6s3tr.log

```
O    .094525    -.004943   -1.247669
O   2.571569    1.335901    -.000036
V   1.659716     .001542    -.000012
O   2.584788   -1.323698     .000001
V  -1.055356    -.005806     .000032
O  -2.873002     .002811    -.000010
O    .094584    -.004902    1.247690
O  -4.209997     .007090    -.000033
```

E = -594.247709324 h (1.89 eV)
triplet

```
 Zero-point correction=                       .018542 (Hartree/Particle)
 Thermal correction to Energy=                .028561
 Thermal correction to Enthalpy=              .029506
 Thermal correction to Gibbs Free Energy=    -.020872
```

Isomer 4



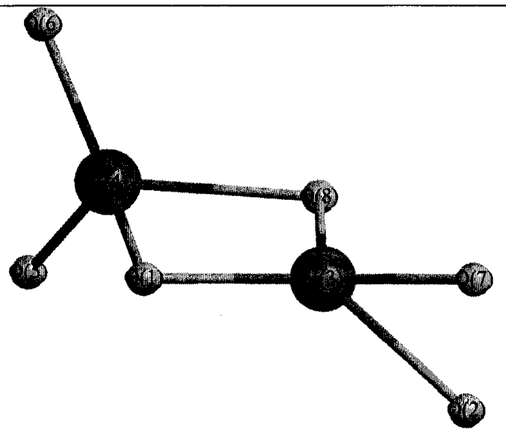
```
O(8)-V(4)    2.0121
O(8)-V(3)    1.6978
O(7)-V(3)    1.8084
O(6)-V(4)    1.6137
O(5)-V(4)    1.6137
V(4)-O(1)    2.0119
V(3)-O(1)    1.6978
V(3)-O(2)    1.8084
```

v2o6s4.log

```
O    -.055454    -.001032   -1.246710
O   -2.843518    -.772122     .000049
V   -1.208309     .000036    -.000271
V    1.523285    -.000084     .000361
O    2.447261   -1.323090     .000609
O    2.446098    1.323724    -.001093
O   -2.843720     .771902     .000083
O    -.056222     .000754    1.246804
```

E = -594.297372710 h (0.54 eV)
singlet

```
 Zero-point correction=                           .019188 (Hartree/Particle)
 Thermal correction to Energy=                    .028648
 Thermal correction to Enthalpy=                  .029593
 Thermal correction to Gibbs Free Energy=        -.017709
```



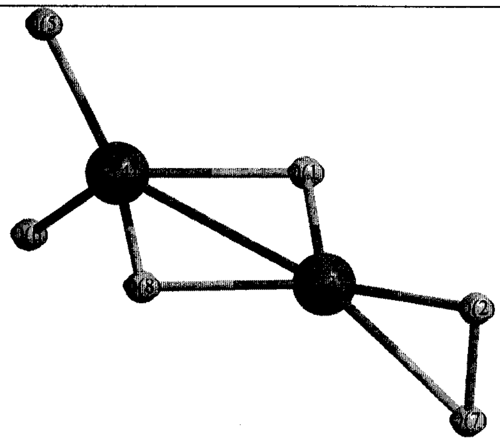
```
O(8)-V(4)    1.9900
O(8)-V(3)    1.6987
O(7)-V(3)    1.9893
O(6)-V(4)    1.6179
O(5)-V(4)    1.6179
V(4)-O(1)    1.9972
V(3)-O(1)    1.6969
V(3)-O(2)    1.9893
```

v2o6s4tr.log

```
O   -.009766    -.000029    1.250384
O  -3.022060     .704802    -.008204
V  -1.161835    -.000027     .004473
V   1.550209     .000009     .003213
O   2.470920    1.330389    -.008546
O   2.470917   -1.330371    -.008564
O  -3.022122    -.704728    -.008202
O   -.004464    -.000012   -1.238966
```

E = -594.272166672 h (1.22 eV)
triplet

```
 Zero-point correction=                           .018478 (Hartree/Particle)
 Thermal correction to Energy=                    .028064
 Thermal correction to Enthalpy=                  .029008
 Thermal correction to Gibbs Free Energy=        -.018821
```



```
O(8)-V(4)    1.8512
O(8)-V(3)    1.8027
O(7)-V(3)    2.0179
O(7)-O(2)    1.3994
O(6)-V(4)    1.6781
O(5)-V(4)    1.6781
V(4)-O(1)    1.8512
V(4)-V(3)    2.6195
V(3)-O(1)    1.8027
V(3)-O(2)    2.0179
```

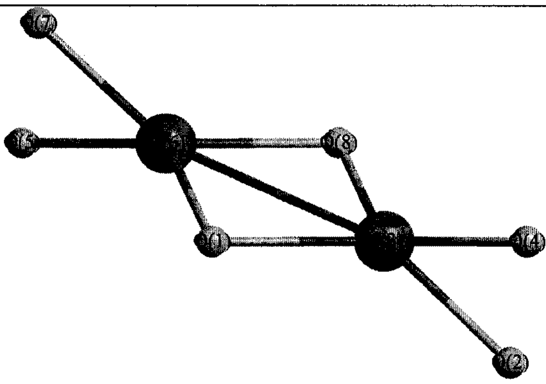
v2o6s4q.log

```
O    .118855    -.000018    1.273508
O  -3.049783     .699723    -.000058
V  -1.157109    -.000013     .000057
V   1.462368    -.000009    -.000002
O   2.492081    1.325051    -.000055
O   2.492245   -1.324955    -.000046
O  -3.049805    -.699710    -.000057
O    .118786    -.000027   -1.273450
```

E = -594.202379931 h (3.12 eV)
quintet

```
 Zero-point correction=                          .016203 (Hartree/Particle)
 Thermal correction to Energy=                   .026327
 Thermal correction to Enthalpy=                 .027271
 Thermal correction to Gibbs Free Energy=       -.022334
```

Isomer 5



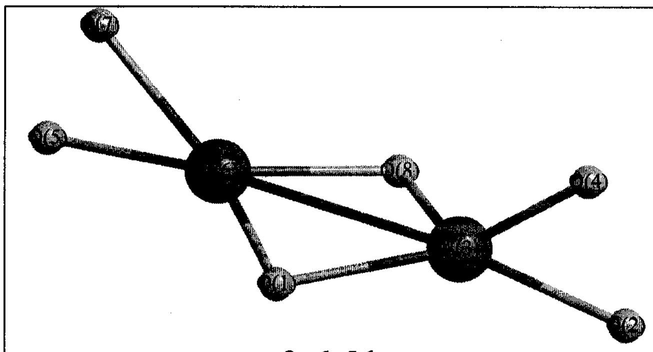
```
O(8)-V(3)    1.8096
O(8)-V(6)    1.8096
O(7)-V(6)    1.8268
V(6)-V(3)    2.6765
V(6)-O(1)    1.8096
V(6)-O(5)    1.8267
O(4)-V(3)    1.8268
V(3)-O(2)    1.8267
V(3)-O(1)    1.8097
```

v2o6s5tr.log

```
O   -.000076    1.218796    -.000326
O   2.999542    -.001278     .759278
V   1.338240     .000644    -.000228
O   3.000338    -.001116    -.758160
O  -2.999467    -.001244     .759336
V  -1.338239     .000541    -.000289
O  -3.000408    -.001075    -.758104
O    .000068   -1.217490    -.000536
```

E = -594.195861086 h (3.30 eV)
triplet

```
 Zero-point correction=                          .018658 (Hartree/Particle)
 Thermal correction to Energy=                   .027667
 Thermal correction to Enthalpy=                 .028611
 Thermal correction to Gibbs Free Energy=       -.017839
```

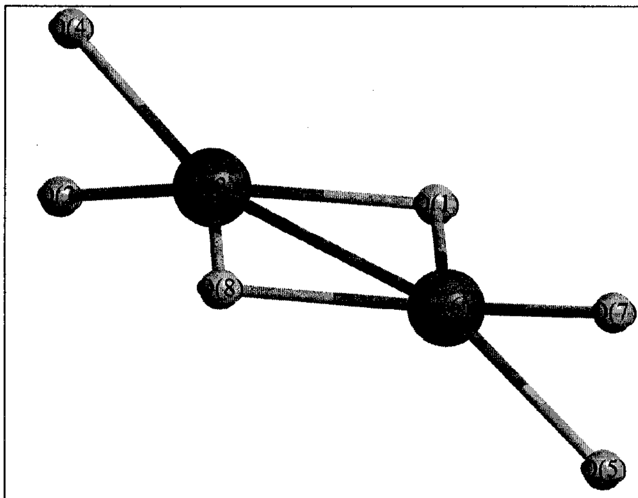


```
O(8)-V(3)    1.7975
O(8)-V(6)    1.7970
O(7)-V(6)    1.8035
V(6)-V(3)    2.6056
V(6)-O(1)    1.7971
V(6)-O(5)    1.8403
O(4)-V(3)    1.8035
V(3)-O(2)    1.8402
V(3)-O(1)    1.7963
```

v2o6s5.log

```
O    .001426   -1.169205    -.475276
O   3.128392     .038529    -.362542
V   1.302771     .020605    -.132216
O   2.641053    -.139684    1.066024
O  -3.128630     .039631    -.362208
V  -1.302806     .018764    -.132620
O  -2.640892    -.139618    1.066129
O   -.001248    1.257161    -.170724
 Zero-point correction=                        .019045 (Hartree/Particle)
 Thermal correction to Energy=                 .027938
 Thermal correction to Enthalpy=               .028883
 Thermal correction to Gibbs Free Energy=     -.017159
```

E = -594.175641266 h (3.85 eV)
singlet



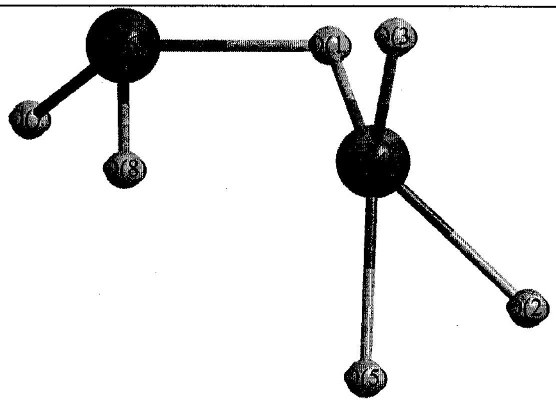
```
O(8)-V(6)    1.8179
O(8)-V(3)    1.7944
O(7)-V(6)    1.9998
V(6)-O(5)    1.9998
V(6)-O(1)    1.8179
V(6)-V(3)    2.6807
O(4)-V(3)    1.8418
V(3)-O(1)    1.7944
V(3)-O(2)    1.8418
```

v2o6s5qr1.log

```
O   -.045798    1.210606    -.000005
O  -3.048019     .000001    -.759779
V  -1.370266     .000001     .000004
O  -3.048020    -.000006     .759791
O   3.179859     .000001    -.710147
V   1.310423     .000001    -.000018
O   3.179824    -.000005     .710191
O   -.045795   -1.210604    -.000012
 Zero-point correction=                        .017081 (Hartree/Particle)
 Thermal correction to Energy=                 .026837
 Thermal correction to Enthalpy=               .027782
 Thermal correction to Gibbs Free Energy=     -.021109
```

E = -594.153819502 h (4.44 eV)
quintet

Isomer 6



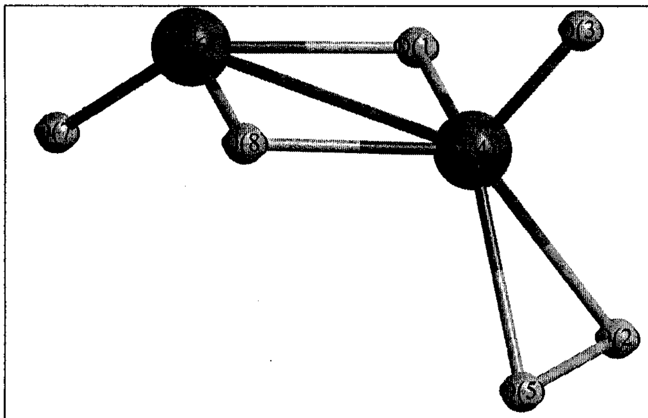
```
O(8)-V(6)    1.6896
O(7)-V(6)    1.6134
V(6)-O(1)    1.7369
O(5)-V(4)    1.8637
V(4)-O(1)    1.9191
V(4)-O(3)    1.6076
V(4)-O(2)    1.8078
V(4)-O(8)    2.0916
```

v2o6s6.log

```
O     .517809     .478593    1.180617
O   -2.483635    -.701813     .687209
O   -1.503857    1.603791    -.520896
V   -1.031816     .191696     .085415
O   -1.806120   -1.412727    -.462010
V    1.701792     .231538    -.066029
O    2.796362    -.909148     .256121
O     .553259    -.275492   -1.196776
```

E = -594.289379148 h (0.76 eV)
singlet

```
 Zero-point correction=                        .019826 (Hartree/Particle)
 Thermal correction to Energy=                 .028710
 Thermal correction to Enthalpy=               .029655
 Thermal correction to Gibbs Free Energy=     -.015057
```



```
O(8)-V(6)    1.8080
O(8)-V(4)    1.8363
O(7)-V(6)    1.6097
V(6)-O(1)    1.8080
V(6)-V(4)    2.6554
O(5)-O(2)    1.4033
O(5)-V(4)    2.0095
V(4)-O(1)    1.8364
V(4)-O(2)    2.0097
V(4)-O(3)    1.5985
```

v2o6s6tr.log

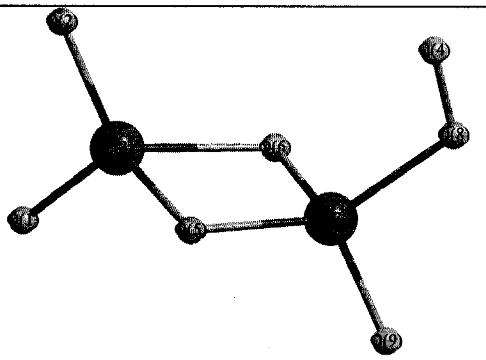
```
O    .413580    -.247378   -1.247825
O  -2.077369    1.235280    -.701572
O  -1.765278   -1.626207    -.000041
V   -.933754    -.261032    -.000020
O  -2.077024    1.235204     .701680
V   1.720937    -.197690     .000014
O   2.829490     .969423    -.000014
O    .413451    -.247497    1.247792
```

E = -594.281037421 h (0.98 eV)
triplet

```
 Zero-point correction=                        .018764 (Hartree/Particle)
 Thermal correction to Energy=                 .028133
 Thermal correction to Enthalpy=               .029077
 Thermal correction to Gibbs Free Energy=     -.018029
```

V_2O_7 clusters

Isomer 1



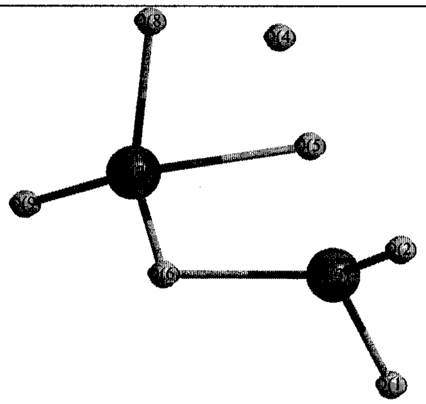
O(9)-V(7)	1.6062
O(8)-V(7)	2.0098
O(8)-O(4)	1.3215
V(7)-O(6)	1.7475
V(7)-O(5)	1.7429
O(6)-V(3)	1.9106
O(5)-V(3)	1.9153
V(3)-O(2)	1.6341
V(3)-O(1)	1.6335

v2o7s4tr.log

```
O   2.880939   -0.799774   -0.094480
O   2.106235    1.738514    0.094659
V   1.586534    0.192176   -0.000214
O  -2.760635    1.881977   -0.153077
O   0.152881   -0.147420   -1.224091
O   0.212012   -0.303477    1.230756
V  -1.019745   -0.520120    0.010289
O  -2.673565    0.608094    0.187336
O  -1.547387   -2.035075   -0.070069
```

E = -669.491822883 h (0.00 eV)
triplet

```
 Zero-point correction=                         0.020883 (Hartree/Particle)
 Thermal correction to Energy=                  0.031541
 Thermal correction to Enthalpy=                0.032485
 Thermal correction to Gibbs Free Energy=      -0.017367
```



O(9)-V(7)	1.5991
O(8)-V(7)	1.8370
V(7)-O(5)	2.0396
V(7)-O(6)	1.7122
O(6)-V(3)	1.9464
V(3)-O(2)	1.6152
V(3)-O(1)	1.6159
O(4)-O(8)	1.5101
O(4)-V(7)	2.4162
O(4)-O(5)	1.5867
V(3)-O(5)	2.0463
V(3)-O(4)	2.8502

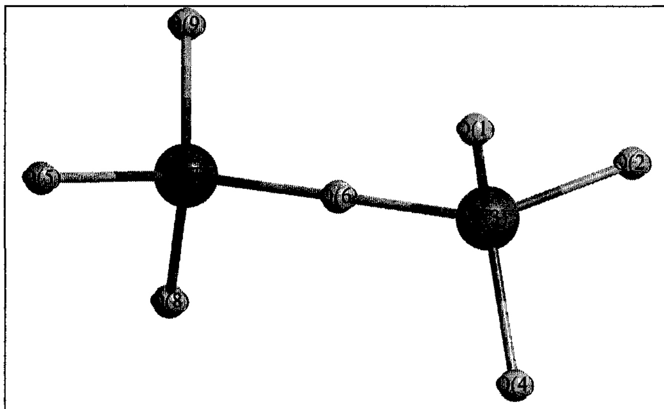
v2o7s1r1.log

```
O  -2.257917   -1.249037    0.825863
O  -2.522605    0.833812   -0.793183
V  -1.471567   -0.140403   -0.048113
O   0.494509    1.895984    0.285648
O   0.020372    0.632339    1.119992
O   0.071522   -0.850716   -0.998315
V   1.393718   -0.321761   -0.047679
O   1.835746    1.450220   -0.246111
O   2.582187   -1.383878    0.081505
```

E = -669.447870051 h (1.20 eV)
singlet

```
 Zero-point correction=                         0.022055 (Hartree/Particle)
 Thermal correction to Energy=                  0.032423
 Thermal correction to Enthalpy=                0.033367
 Thermal correction to Gibbs Free Energy=      -0.014818
```

Isomer 2



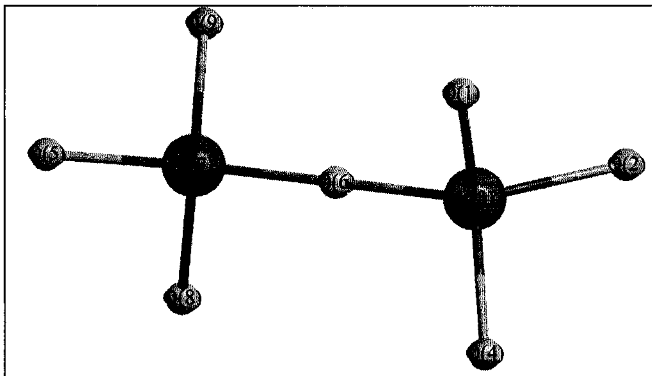
```
O(9)-V(7)    1.7030
O(8)-V(7)    1.7025
V(7)-O(5)    1.7018
V(7)-O(6)    1.8038
O(6)-V(3)    1.8045
O(4)-V(3)    1.7028
V(3)-O(2)    1.7028
V(3)-O(1)    1.7027
```

v2o7s2.log

```
O  -2.432300   -0.886097   -1.307843
O  -2.460624    1.569572   -0.111927
V  -1.803624    0.002757    0.001253
O  -2.450738   -0.696484    1.412557
O   2.423063   -1.525838   -0.424533
O   0.000831    0.019581    0.006637
V   1.804513    0.001377    0.001116
O   2.460991    0.387594    1.523768
O   2.456221    1.119788   -1.105469
```

E = -669.425471572 h (1.81 eV)
quintet

```
 Zero-point correction=                           0.015951 (Hartree/Particle)
 Thermal correction to Energy=                    0.028459
 Thermal correction to Enthalpy=                  0.029404
 Thermal correction to Gibbs Free Energy=        -0.027822
```



```
O(9)-V(7)    1.6758
O(8)-V(7)    1.7395
V(7)-O(6)    1.8149
V(7)-O(5)    1.6879
O(6)-V(3)    1.7809
O(4)-V(3)    1.7124
V(3)-O(1)    1.7140
V(3)-O(2)    1.7002
```

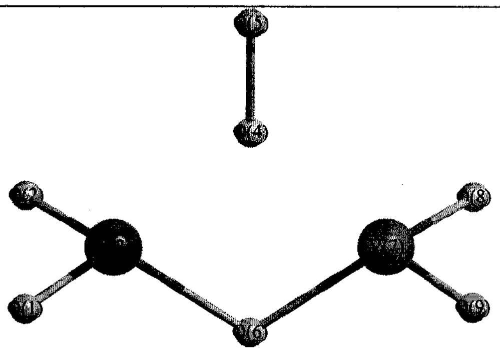
v2o7s2tr.log

```
O   2.452008    1.411422   -0.665702
O   2.454053   -1.314819   -0.888305
V   1.788249   -0.023906   -0.004609
O   2.463885   -0.056082    1.568561
O  -2.398438    1.510624    0.472731
O   0.007411   -0.010759    0.001113
V  -1.807468    0.001734    0.000617
O  -2.487366   -1.206041    1.051793
O  -2.436300   -0.270602   -1.528713
```

E = -669.416230951 h (2.06 eV)
triplet

```
 Zero-point correction=                           0.015772 (Hartree/Particle)
 Thermal correction to Energy=                    0.028495
 Thermal correction to Enthalpy=                  0.029439
 Thermal correction to Gibbs Free Energy=        -0.028312
```

Isomer 3



v2o7s3r2.log

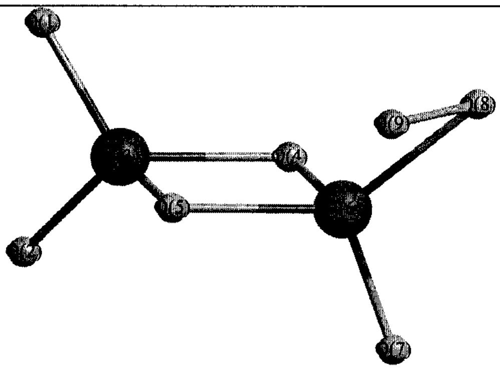
```
O(9)-V(7)    1.6343
O(8)-V(7)    1.6328
V(7)-O(6)    1.8170
O(6)-V(3)    1.8169
O(5)-O(4)    1.3670
V(3)-O(1)    1.6328
V(3)-O(2)    1.6343
O(5)-V(7)    3.1545
O(4)-V(7)    2.0493
V(3)-O(5)    3.1542
V(3)-O(4)    2.0493
```

```
O  -2.439865   -0.291185    1.320232
O  -2.418857   -0.290357   -1.332249
V  -1.477873   -0.227035    0.002461
O   0.000054    1.192620   -0.006484
O  -0.000191    2.559642   -0.008657
O  -0.000012   -1.283968    0.007802
V   1.477908   -0.227079   -0.000661
O   2.437874   -0.306726   -1.319083
O   2.420895   -0.274446    1.333263
```

E = -669.453669362 h (1.04 eV)
triplet

```
 Zero-point correction=                           0.019880 (Hartree/Particle)
 Thermal correction to Energy=                    0.031263
 Thermal correction to Enthalpy=                  0.032207
 Thermal correction to Gibbs Free Energy=        -0.020038
```

Isomer 4



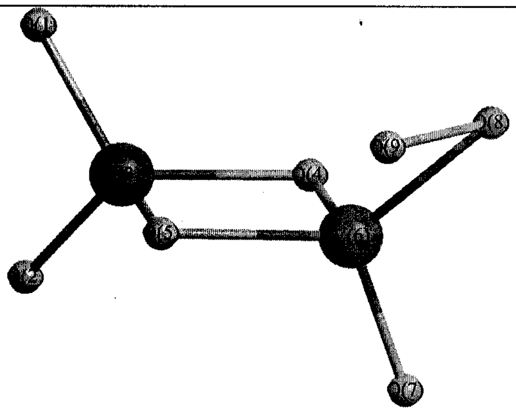
v2o7s4tr.log

```
O(9)-O(8)    1.3982
O(8)-V(6)    1.9701
O(7)-V(6)    1.5958
V(6)-O(4)    1.7904
V(6)-O(5)    1.8576
O(5)-V(3)    1.7940
O(4)-V(3)    1.8354
V(3)-O(2)    1.6775
V(3)-O(1)    1.6679
```

```
O  -2.390091   -1.515249    0.160509
O  -2.750287    1.045685   -0.208780
V  -1.535961   -0.090478    0.011409
O  -0.222321    0.270364    1.241400
O  -0.192786   -0.097760   -1.177844
V   1.130814    0.281810    0.069023
O   1.700441    1.752542   -0.173776
O   2.630386   -0.862365    0.637776
O   2.389456   -1.143297   -0.710527
```

E = -669.491822883 h (0 eV)
triplet

```
 Zero-point correction=                           0.020883 (Hartree/Particle)
 Thermal correction to Energy=                    0.031541
 Thermal correction to Enthalpy=                  0.032485
 Thermal correction to Gibbs Free Energy=        -0.017367
```



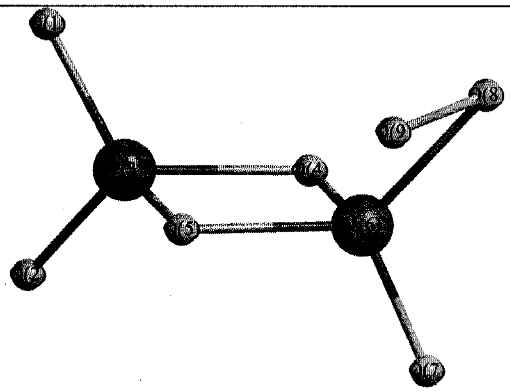
```
O(9)-O(8)    1.3990
O(8)-V(6)    1.9709
O(7)-V(6)    1.5956
V(6)-O(4)    1.7931
V(6)-O(5)    1.8565
O(5)-V(3)    1.7932
O(4)-V(3)    1.8327
V(3)-O(2)    1.6795
V(3)-O(1)    1.6679
```

v2o7s4s1bsopt.log, v2o7s4bsoptfr.log

```
O  -2.399122   -1.509113    .163474
O  -2.750102    1.047653   -.205302
V  -1.534561   -.090919     .010807
O   -.222074    .263735    1.239829
O   -.193470   -.103361   -1.179551
V   1.131289    .278882     .063682
O   1.698150   1.750954    -.176502
O   2.627222   -.865666     .643917
O   2.402319  -1.130913    -.711165
```

E = -669.491690886 h (0.04 eV)
singlet
broken symmetry

```
 Zero-point correction=                        .020982 (Hartree/Particle)
 Thermal correction to Energy=                 .031624
 Thermal correction to Enthalpy=               .032568
 Thermal correction to Gibbs Free Energy=    -.016252
```



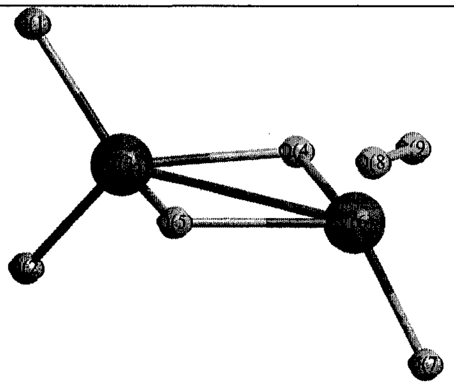
```
O(9)-O(8)    1.3827
O(8)-V(6)    2.0034
O(7)-V(6)    1.5963
V(6)-O(4)    1.7594
V(6)-O(5)    1.8523
O(5)-V(3)    1.8359
O(4)-V(3)    1.8776
V(3)-O(2)    1.6532
V(3)-O(1)    1.6490
```

v2o7s4fr.log

```
O    -2.304141   -1.544657    0.214707
O    -2.720005    1.038332   -0.285592
V    -1.551358   -0.090624    0.019246
O    -0.194613    0.355717    1.238026
O    -0.158980   -0.096454   -1.177391
V     1.132095    0.322813    0.082900
O     1.762872    1.770550   -0.150530
O     2.538890   -1.003953    0.606591
O     2.281359   -1.187079   -0.739482
```

E = -669.464781222 h (0.74 eV)
singlet

```
 Zero-point correction=                       0.021025 (Hartree/Particle)
 Thermal correction to Energy=                0.031731
 Thermal correction to Enthalpy=              0.032675
 Thermal correction to Gibbs Free Energy=   -0.016314
```

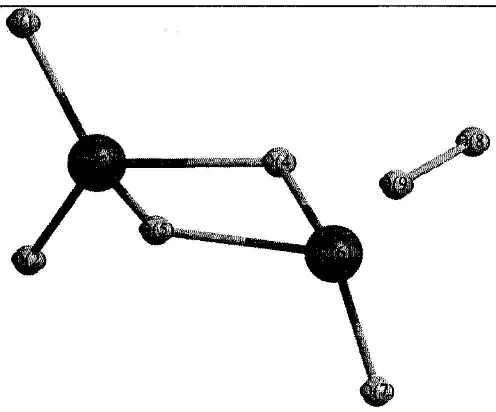


```
O(9)-O(8)    1.2884
O(7)-V(6)    1.6080
V(6)-V(3)    2.6729
V(6)-O(5)    1.8676
V(6)-O(4)    1.8417
O(5)-V(3)    1.8022
O(4)-V(3)    1.8118
V(3)-O(1)    1.6693
V(3)-O(2)    1.6943
V(6)-O(9)    2.1831
```

v2o7s4q.log

```
O    2.372334    1.522085    0.601161
O    2.771691   -0.554778   -0.947875
V    1.566649    0.202781   -0.028752
O    0.634906   -0.824999    1.136696
O    0.001483    0.548744   -0.852509
V   -0.965375   -0.606100    0.251796
O   -1.611954   -1.890507   -0.467868
O   -3.233466    1.596390   -0.455437
O   -2.663658    0.762607    0.344579
 Zero-point correction=                           0.019740 (Hartree/Particle)
 Thermal correction to Energy=                    0.031250
 Thermal correction to Enthalpy=                  0.032194
 Thermal correction to Gibbs Free Energy=        -0.021116
```

E = -669.43389650 h (1.58 eV)
quintet



```
O(9)-O(8)    1.3651
O(7)-V(6)    1.6014
V(6)-O(5)    1.9171
V(6)-O(4)    1.9170
O(5)-V(3)    1.9453
O(4)-V(3)    1.9450
V(3)-O(2)    1.6956
V(3)-O(1)    1.6988
V(6)-O(9)    2.1189
V(6)-O(8)    2.1189
```

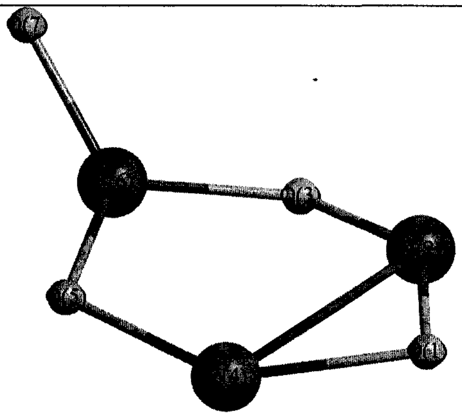
v2o7s4s.log

```
O    2.701121   -1.564179    0.000636
O    2.851025    1.245184   -0.000696
V    1.827931   -0.107007   -0.000226
O    0.210924   -0.041974   -1.079144
O    0.211367   -0.041106    1.079876
V   -1.330642    0.322842    0.000430
O   -1.793728    1.855840   -0.000327
O   -2.804671   -1.037239   -0.683038
O   -2.805744   -1.037052    0.682106
 Zero-point correction=                           0.017101 (Hartree/Particle)
 Thermal correction to Energy=                    0.029484
 Thermal correction to Enthalpy=                  0.030429
 Thermal correction to Gibbs Free Energy=        -0.025029
```

E = -669.321657900 h (4.63 eV)
septet

V_3O_4 clusters

Isomer 1



O(7)-V(6)	1.6131
V(6)-O(3)	1.8296
V(6)-O(5)	1.8189
O(5)-V(4)	1.7990
V(4)-O(1)	1.8183
V(4)-V(2)	2.6458
O(3)-V(2)	1.7904
V(2)-O(1)	1.8184

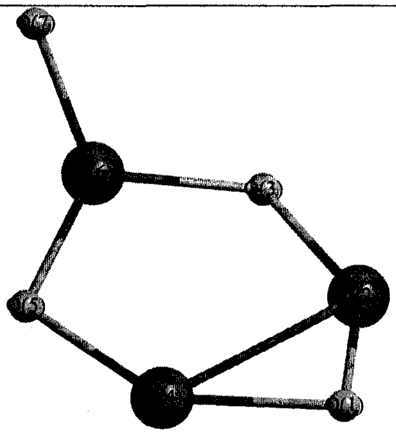
v3o4s1.log, v3o4s1fr.log

```
O   2.296114    0.173723    0.331884
V   0.943367    1.363164    0.083029
O  -0.741643    1.512608   -0.503427
V   1.245068   -1.262418   -0.041048
O  -0.518773   -1.596976   -0.156167
V  -1.548576   -0.097921   -0.183377
O  -2.875295   -0.097475    0.734222
```

E = -515.299842487 h (0 eV)

doublet

```
 Zero-point correction=                          .013977 (Hartree/Particle)
 Thermal correction to Energy=                   .022717
 Thermal correction to Enthalpy=                 .023661
 Thermal correction to Gibbs Free Energy=       -.022712
```



O(7)-V(6)	1.6138
V(6)-O(3)	1.8182
V(6)-O(5)	1.8157
O(5)-V(4)	1.7941
V(4)-O(1)	1.8072
V(4)-V(2)	2.6038
O(3)-V(2)	1.7949
V(2)-O(1)	1.8234

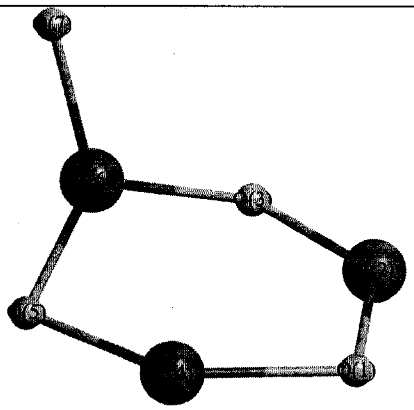
v3o4quart.log

```
O    2.287982      .016941     .418695
V    1.069695     1.311535     .013093
O    -.662945     1.562131    -.382840
V    1.116051    -1.291763    -.005291
O    -.624569    -1.572098    -.337877
V   -1.543602     -.014776    -.173563
O   -2.846630     -.021337     .778582
```

E = -515.277835562 h (0.60 eV)

quartet

```
 Zero-point correction=                          .013976 (Hartree/Particle)
 Thermal correction to Energy=                   .022711
 Thermal correction to Enthalpy=                 .023656
 Thermal correction to Gibbs Free Energy=       -.023657
```



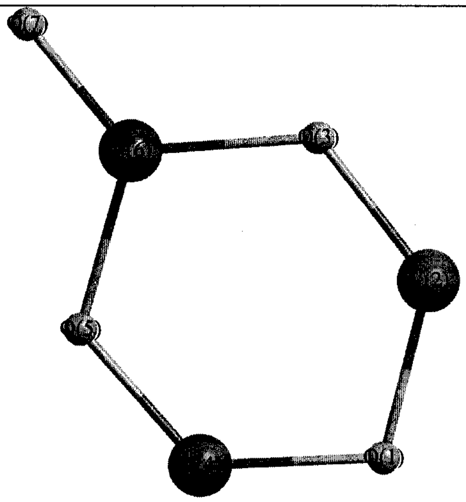
O(7)-V(6)	1.6115
V(6)-O(3)	1.8274
V(6)-O(5)	1.8273
O(5)-V(4)	1.7871
V(4)-O(1)	1.8131
O(3)-V(2)	1.7871
V(2)-O(1)	1.8132

v3o4s1s.log

O	2.046764	.311187	.471095
V	.826692	1.562793	-.011100
O	-.807766	1.450815	-.725029
V	1.198847	-1.275976	.249104
O	-.393870	-1.714978	-.432374
V	-1.425896	-.213502	-.292346
O	-2.569101	-.257804	.842541

E = -515.29958255 h (0.01 eV)
sextet

```
 Zero-point correction=                           .013986 (Hartree/Particle)
 Thermal correction to Energy=                    .022658
 Thermal correction to Enthalpy=                  .023602
 Thermal correction to Gibbs Free Energy=        -.023684
```



O(7)-V(6)	1.6217
V(6)-O(3)	1.8447
V(6)-O(5)	1.8447
O(5)-V(4)	1.7905
V(4)-O(1)	1.8130
O(3)-V(2)	1.7905
V(2)-O(1)	1.8130

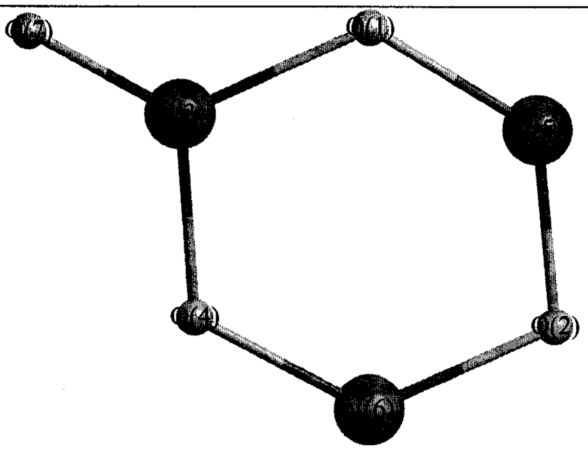
v3o4s1o.log

O	2.282103	.000039	-.035434
V	1.200355	1.453930	.019436
O	-.589013	1.509055	-.012706
V	1.200420	-1.453904	.019479
O	-.588943	-1.509073	-.012823
V	-1.649340	-.000028	-.050539
O	-3.264523	-.000018	.094384

E = -515.295111139 h (0.13 eV)
octet

```
 Zero-point correction=                           .013125 (Hartree/Particle)
 Thermal correction to Energy=                    .022226
 Thermal correction to Enthalpy=                  .023170
 Thermal correction to Gibbs Free Energy=        -.025902
```

Isomer 2



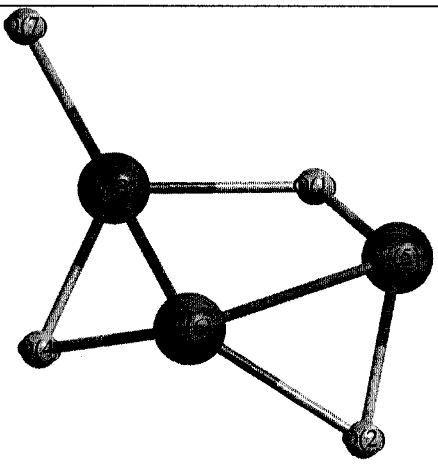
```
O(7)-V(3)    1.6217
V(6)-O(4)    1.7907
V(6)-O(2)    1.8130
V(5)-O(1)    1.7907
V(5)-O(2)    1.8130
O(4)-V(3)    1.8445
V(3)-O(1)    1.8445
```

v3o4s2o.log

```
O   .588869   -1.508606    -.013895
O -2.282153     .000241    -.036666
V  1.649637    -.000196    -.053051
O   .589211    1.508455    -.013818
V -1.200660   -1.453745     .020420
V -1.200299    1.453901     .020383
O  3.264123     .000024     .099591
```

E = -515.295110952 h (0.13 eV)
octet

```
 Zero-point correction=                      .013129 (Hartree/Particle)
 Thermal correction to Energy=               .022226
 Thermal correction to Enthalpy=             .023170
 Thermal correction to Gibbs Free Energy=   -.025857
```



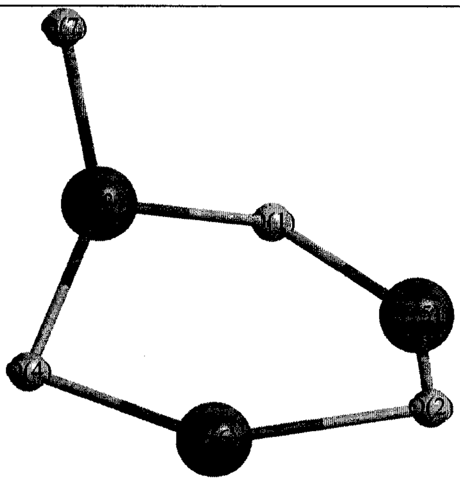
```
O(7)-V(3)    1.6134
V(6)-O(2)    1.7876
V(6)-V(5)    2.2324
V(6)-O(4)    1.8066
V(6)-V(3)    2.6215
V(5)-O(2)    1.8979
V(5)-O(1)    1.8158
O(4)-V(3)    1.8262
V(3)-O(1)    1.7978
```

v3o4.log, v3o4fr.log

```
O   -.566483    1.630913    -.409688
O   2.267965    -.250727    -.374644
V  -1.421429     .056670    -.257805
O   -.561357   -1.480111    -.740946
V   1.069759    1.111752     .182091
V    .857402   -1.106608     .313360
O  -2.594104    -.077794     .842047
```

E = -515.286740086 h (0.36 eV)
doublet

```
 Zero-point correction=                      .014449 (Hartree/Particle)
 Thermal correction to Energy=               .022856
 Thermal correction to Enthalpy=             .023800
 Thermal correction to Gibbs Free Energy=   -.020998
```



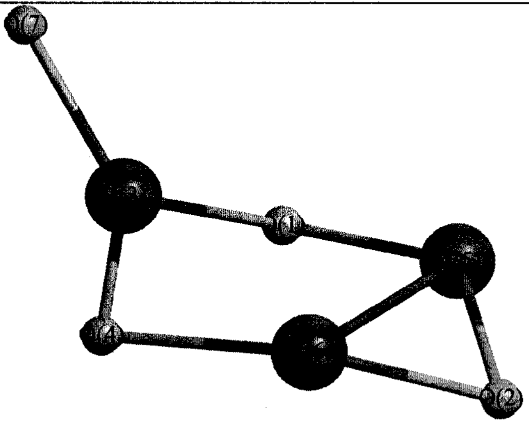
```
O(7)-V(3)    1.6105
V(6)-O(4)    1.7719
V(6)-O(2)    1.8320
V(5)-O(1)    1.7658
V(5)-O(2)    1.7989
O(4)-V(3)    1.8469
V(3)-O(1)    1.8573
```

v3o4s2q.log

```
O    .620804   -1.643707    -.581530
O  -2.036784     .008488     .598118
V   1.425947    -.021134    -.171136
O    .669354    1.607840    -.601109
V  -1.021788   -1.348973    -.004380
V   -.983548    1.381011    -.004399
O   2.412367    -.003970    1.101777
```

E = -515.288421603 h (0.31 eV)
quartet

```
 Zero-point correction=                         .014368 (Hartree/Particle)
 Thermal correction to Energy=                  .022847
 Thermal correction to Enthalpy=                .023791
 Thermal correction to Gibbs Free Energy=      -.022145
```



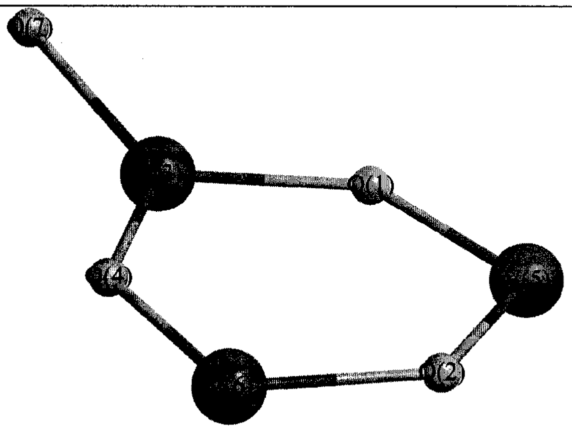
```
O(7)-V(3)    1.6136
V(6)-O(2)    1.8179
V(6)-V(5)    2.6238
V(6)-O(4)    1.7900
V(5)-O(2)    1.8179
V(5)-O(1)    1.7901
O(4)-V(3)    1.8264
V(3)-O(1)    1.8263
```

v3o4s2sr2.log

```
O   -.614812    1.589638    -.538066
O   2.260028     .000170    -.045573
V  -1.432823    -.000151    -.165285
O   -.613896   -1.589366    -.538996
V   1.016099    1.311959     .145702
V   1.016385   -1.311805     .145999
O  -2.755345    -.000451     .759190
```

E = -515.290201016 h (0.26 eV)
sextet

```
 Zero-point correction=                         .013979 (Hartree/Particle)
 Thermal correction to Energy=                  .022596
 Thermal correction to Enthalpy=                .023540
 Thermal correction to Gibbs Free Energy=      -.023133
```



```
O(7)-V(3)    1.8330
V(6)-O(4)    1.8483
V(6)-O(2)    1.8028
V(5)-O(1)    1.8483
V(5)-O(2)    1.8029
O(4)-V(3)    1.7657
V(3)-O(1)    1.7657
```

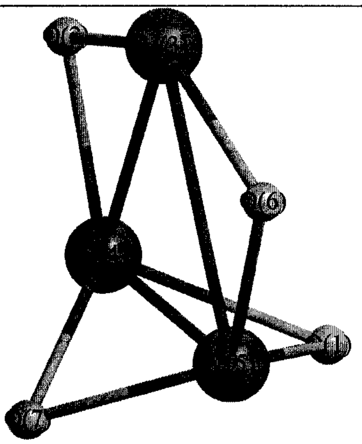
v3o4s2te.log

```
O    .576794   -1.402764    -.059861
O  -2.085376     .000338     .113194
V   1.647414    -.000107    -.122163
O    .577672    1.403254    -.059424
V  -1.259565   -1.599114     .012779
V  -1.258762    1.599278     .012695
O   3.434782    -.000990     .284073
```

E = -515.198064014 h (2.77 eV)
multiplicity = 10

```
 Zero-point correction=                       .011672 (Hartree/Particle)
 Thermal correction to Energy=                .021060
 Thermal correction to Enthalpy=              .022004
 Thermal correction to Gibbs Free Energy=   -.027508
```

Isomer 3



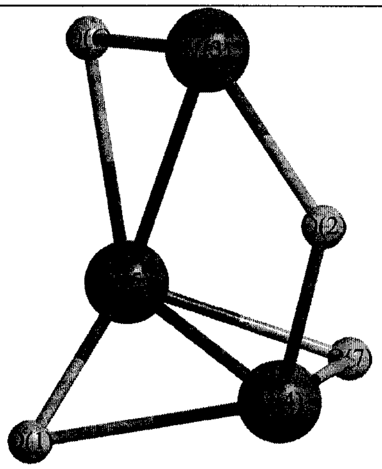
```
O(7)-V(4)    1.9732
O(7)-V(5)    1.7604
O(6)-V(5)    1.8430
O(6)-V(3)    1.8154
V(5)-O(1)    1.7601
V(5)-V(4)    2.1880
V(5)-V(3)    2.6750
V(4)-O(1)    1.9735
V(4)-O(2)    1.8382
V(4)-V(3)    2.6318
V(3)-O(2)    1.8214
```

v3o4s3.log, v3o4s3fr.log

```
O   1.333372     .064484    1.384432
O  -1.283507    1.542389     .000452
V  -1.668734    -.237817    -.000359
V    .525381    1.215601     .000018
V    .913087    -.937772    -.000001
O   -.722561   -1.787136     .000007
O   1.334713     .065228   -1.383910
```

E = -515.294393469 h (0.15 eV)
doublet

```
 Zero-point correction=                       .013961 (Hartree/Particle)
 Thermal correction to Energy=                .022232
 Thermal correction to Enthalpy=              .023177
 Thermal correction to Gibbs Free Energy=   -.020674
```



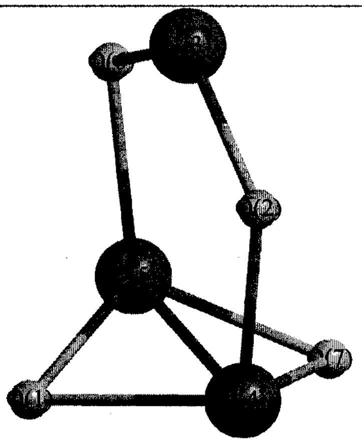
```
O(7)-V(4)    1.9571
O(7)-V(5)    1.7733
O(6)-V(3)    1.7937
O(6)-V(5)    1.8729
V(5)-V(3)    2.6394
V(5)-V(4)    2.1785
V(5)-O(1)    1.7733
V(4)-O(2)    1.8192
V(4)-O(1)    1.9571
V(3)-O(2)    1.8304
```

v3o4s3q.log

```
O  -1.309929    -.127457   -1.396552
O    .973067    1.687854    -.000860
V   1.693152     .005012     .000300
V   -.757623    1.127306     .000087
V   -.725806   -1.050965     .000033
O   1.042940   -1.666735    -.000881
O  -1.309033    -.127552    1.397086
```

E = -515.291838388 h (0.22 eV)
quartet

```
 Zero-point correction=                      .014238 (Hartree/Particle)
 Thermal correction to Energy=               .022326
 Thermal correction to Enthalpy=             .023270
 Thermal correction to Gibbs Free Energy=   -.020732
```



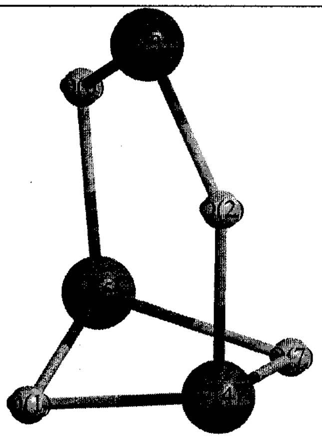
```
O(7)-V(5)    1.7559
O(7)-V(4)    1.9471
O(6)-V(3)    1.8658
O(6)-V(5)    1.7842
V(5)-O(1)    1.7559
V(5)-V(4)    2.4494
V(4)-O(2)    1.8377
V(4)-O(1)    1.9471
V(3)-O(2)    1.8049
```

v3o4s3sr1.log

```
O  -1.165549     .400365    1.311504
O    .524613   -1.756407    -.000011
V   1.729544    -.412572    -.000059
V  -1.167259   -1.038889     .000040
V   -.410223    1.290604     .000012
O   1.369390    1.418145    -.000048
O  -1.165635     .400361   -1.311427
```

E = -515.294351834 h (0.15 eV)
sextet

```
 Zero-point correction=                      .013924 (Hartree/Particle)
 Thermal correction to Energy=               .022110
 Thermal correction to Enthalpy=             .023054
 Thermal correction to Gibbs Free Energy=   -.021649
```



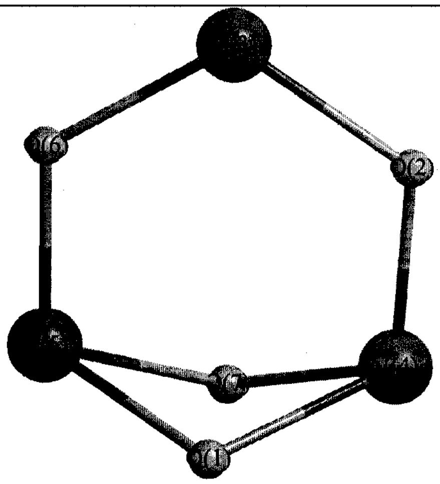
```
O(7)-V(5)    1.8372
O(7)-V(4)    1.8368
O(6)-V(3)    1.8356
O(6)-V(5)    1.7998
V(5)-O(1)    1.8375
V(4)-O(2)    1.7998
V(4)-O(1)    1.8365
V(3)-O(2)    1.8353
```

v3o4s3or1.log

```
O  -1.183017     .003198    1.203461
O    .927660   -1.574418    -.001662
V   1.880060    -.005580     .000331
V   -.857583   -1.345749     .000447
V   -.848051    1.350664    -.000151
O    .938334    1.570045    -.000899
O  -1.184454     .003088   -1.202702
```

E = -515.294455985 h (0.15 eV)
octet

```
 Zero-point correction=                          .013999 (Hartree/Particle)
 Thermal correction to Energy=                   .021953
 Thermal correction to Enthalpy=                 .022897
 Thermal correction to Gibbs Free Energy=       -.021628
```



```
O(7)-V(5)    1.9321
O(7)-V(4)    1.9321
O(6)-V(3)    1.8261
O(6)-V(5)    1.7996
V(5)-O(1)    1.9127
V(4)-O(2)    1.7996
V(4)-O(1)    1.9127
V(3)-O(2)    1.8261
```

v3o4s3ter3.log

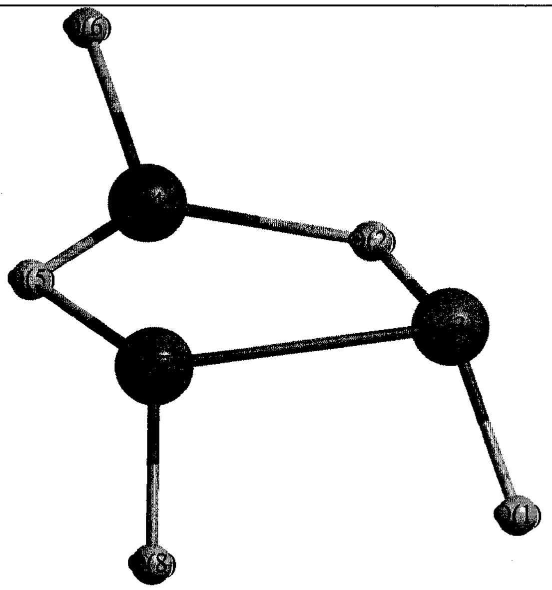
```
O  -1.313466    -.000015    1.132327
O    .967170   -1.527354     .002598
V   1.967813     .000000    -.022123
V   -.831303   -1.463784    -.000573
V   -.831303    1.463784    -.000534
O    .967170    1.527354     .002645
O  -1.498346     .000014   -1.070784
```

E = -515.199267913 h (2.74 eV)
multiplicity = 10

```
 Zero-point correction=                          .012543 (Hartree/Particle)
 Thermal correction to Energy=                   .021264
 Thermal correction to Enthalpy=                 .022208
 Thermal correction to Gibbs Free Energy=       -.025236
```

V_3O_5 structures

Isomer 1



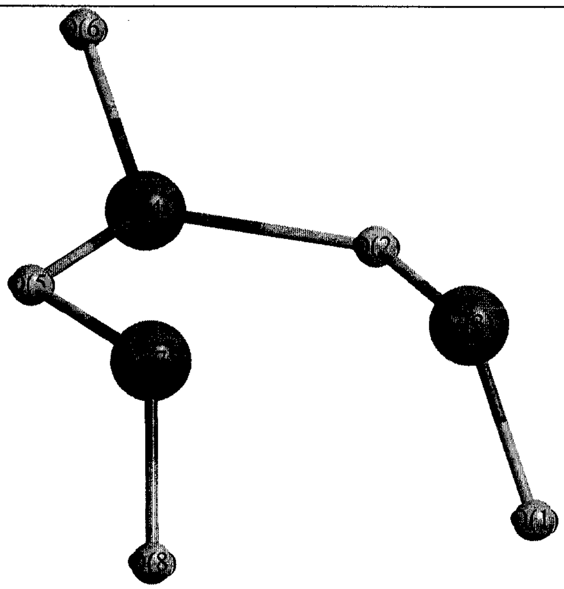
O(8)-V(7)	1.6037
V(7)-V(3)	2.6372
V(7)-O(5)	1.8029
O(6)-V(4)	1.6123
O(5)-V(4)	1.8005
V(4)-O(2)	1.8034
V(3)-O(1)	1.6051
V(3)-O(2)	1.8019

v3o5.log, v3o5fr.log

```
O   2.159951   -1.584477     .654524
O   -.745690   -1.518374     .154003
V    .963055   -1.314990    -.380455
V  -1.720483    -.008759     .305767
O   -.787540    1.516286     .091943
O  -3.220623    -.040902    -.284319
V    .939885    1.322090    -.386288
O   2.069338    1.632237     .709154
```

E = -590.550205173 h (1.38 eV)
doublet
[E = 590.550080666 h,
in frequency calculation]

```
 Zero-point correction=                      .017266 (Hartree/Particle)
 Thermal correction to Energy=               .027632
 Thermal correction to Enthalpy=             .028576
 Thermal correction to Gibbs Free Energy=   -.022056
```



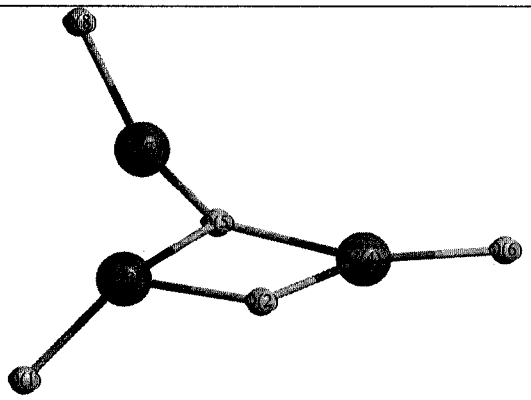
```
O(8)-V(7)    1.6047
V(7)-O(5)    1.7952
O(6)-V(4)    1.6127
O(5)-V(4)    1.8043
V(4)-O(2)    1.8043
V(3)-O(2)    1.7952
V(3)-O(1)    1.6047
```

v3o4s1qr1.log

```
O  -2.102339    1.679849     .690422
O    .758390    1.510664     .138502
V   -.952621    1.395803    -.392403
V   1.727364    -.000027     .324043
O    .758216   -1.510652     .138841
O   3.200016    -.000189    -.333238
V   -.952687   -1.395760    -.392396
O  -2.102692   -1.679720     .690148
```

E = -590.544539131 h (1.53 eV)
quartet
[E = -590.544532729 h,
Int=Ultrafine]

```
 Zero-point correction=                     .016944 (Hartree/Particle)
 Thermal correction to Energy=              .026609
 Thermal correction to Enthalpy=            .027553
 Thermal correction to Gibbs Free Energy=  -.021973
Note that frequency calculation results in one negative frequency
without the use of Int=Ultrafine.
[Int=Ultrafine
 Zero-point correction=                     .016970 (Hartree/Particle)
 Thermal correction to Energy=              .027544
 Thermal correction to Enthalpy=            .028488
 Thermal correction to Gibbs Free Energy=  -.024448]
```



O(8)-V(7)	1.6160
V(7)-O(5)	1.8714
O(6)-V(4)	1.6228
O(5)-V(3)	1.9403
O(5)-V(4)	1.9684
V(4)-O(2)	1.8698
V(3)-O(1)	1.6216
V(3)-O(2)	1.7893

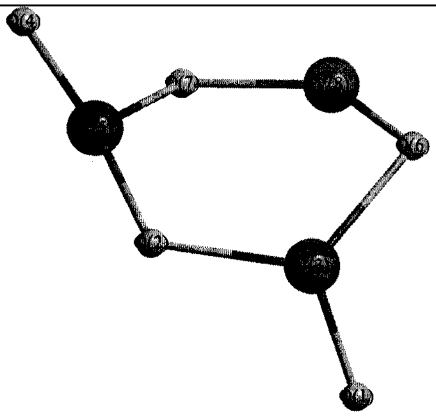
v3o5s1s.log

```
O  1.721955   -2.106764     .801018
O  -.886437   -1.847374    -.679445
V   .767567   -1.319372    -.247115
V -1.777029    -.282991    -.173942
O   .023150     .411912     .214673
O -3.308149     .254548    -.157885
V  1.151550    1.862549     .567530
O  2.040976    2.539646    -.599470
```

E = -590.546408014 h (1.48 eV)
sextet

```
 Zero-point correction=                          .015787 (Hartree/Particle)
 Thermal correction to Energy=                   .026818
 Thermal correction to Enthalpy=                 .027762
 Thermal correction to Gibbs Free Energy=       -.027313
```

Isomer 2



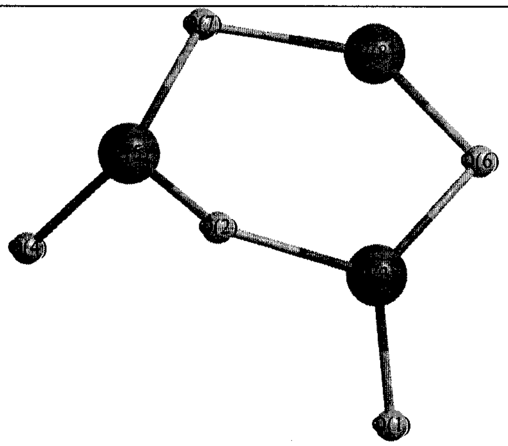
V(8)-O(6)	1.7990
V(8)-O(7)	1.7991
O(7)-V(5)	1.8199
O(6)-V(3)	1.8199
V(5)-O(2)	1.8055
V(5)-O(4)	1.6090
V(3)-O(1)	1.6090
V(3)-O(2)	1.8056

v3o5s2.log, v3o5s2fr.log

```
O     2.666985   -0.876166   -0.862159
O     0.000344   -1.583311   -0.000362
V     1.515323   -0.629410    0.234039
O    -2.666056   -0.876811    0.862823
V    -1.515054   -0.629938   -0.234046
O     1.438648    1.066579    0.889635
O    -1.439299    1.065976   -0.889856
V    -0.000486    1.678038   -0.000021
```

E = -590.600848219 h (0 eV)
doublet

```
 Zero-point correction=                          .017600 (Hartree/Particle)
 Thermal correction to Energy=                   .027463
 Thermal correction to Enthalpy=                 .028408
 Thermal correction to Gibbs Free Energy=       -.020897
```



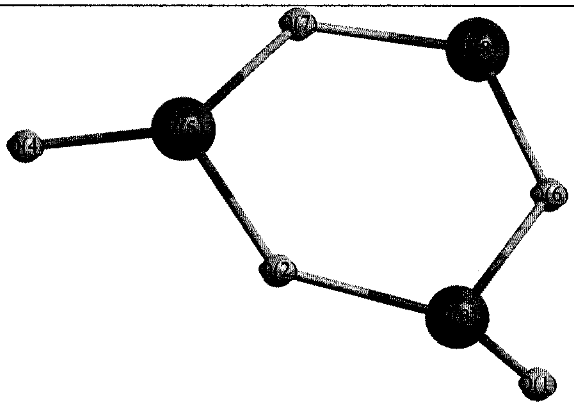
```
V(8)-O(7)    1.7913
V(8)-O(6)    1.7915
O(7)-V(5)    1.8137
O(6)-V(3)    1.8136
V(5)-O(4)    1.6070
V(5)-O(2)    1.8002
V(3)-O(2)    1.8006
V(3)-O(1)    1.6071
```

v3o5quart.log

```
O  -2.128369   -1.485411     .946780
O    .001918   -1.344903   -.988004
V  -1.449103    -.609078   -.216524
O   2.133129   -1.480752     .945491
V   1.450764    -.605485   -.216776
O  -1.638364    1.187490   -.056151
O   1.634659    1.191556   -.054172
V   -.002695    1.886569     .157146
```

E = -590.600333993 h (0.01 eV)
quartet

```
 Zero-point correction=                          .017599 (Hartree/Particle)
 Thermal correction to Energy=                   .027312
 Thermal correction to Enthalpy=                 .028257
 Thermal correction to Gibbs Free Energy=       -.021023
```



```
V(8)-O(7)    1.7870
V(8)-O(6)    1.7870
O(7)-V(5)    1.8237
O(6)-V(3)    1.8237
V(5)-O(4)    1.6143
V(5)-O(2)    1.8115
V(3)-O(2)    1.8115
V(3)-O(1)    1.6143
```

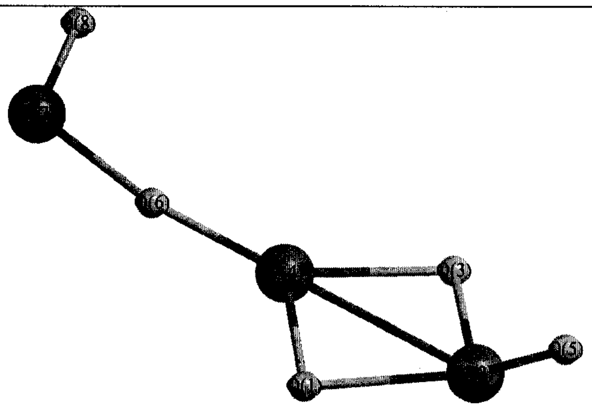
v3o5s2s.log

```
O  -2.953165   -1.375321    -.420686
O   -.000019   -1.455102    -.000107
V  -1.631589    -.696995     .211323
O   2.953043   -1.375364     .420913
V   1.631594    -.697043    -.211367
O  -1.500976    1.121536     .167389
O   1.501006    1.121489    -.167433
V    .000034    2.076738     .000017
```

E = -590.596583885 h (0.12 eV)
sextet

```
 Zero-point correction=                          .016340 (Hartree/Particle)
 Thermal correction to Energy=                   .026708
 Thermal correction to Enthalpy=                 .027652
 Thermal correction to Gibbs Free Energy=       -.024192
```

Isomer 3



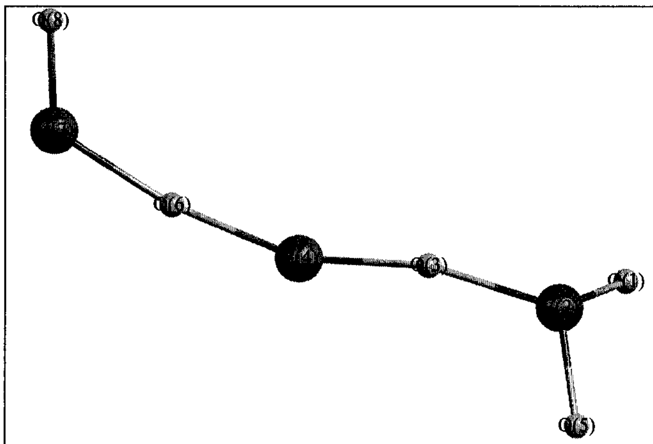
O(8)-V(7)	1.6154
V(7)-O(6)	1.8157
O(6)-V(4)	1.7849
O(5)-V(2)	1.6193
V(4)-V(2)	2.6579
V(4)-O(3)	1.8064
V(4)-O(1)	1.8081
O(3)-V(2)	1.8382
V(2)-O(1)	1.8364

v3o5s3qr1.log

O	1.581240	-1.268525	-.151441
V	2.813953	.092701	-.150918
O	1.357576	1.205260	-.292573
V	.166602	-.142783	-.127109
O	4.093487	.259475	.827365
O	-1.600612	-.365885	-.012397
V	-3.408240	-.281166	.136658
O	-4.202095	1.122015	.035484

E = -590.562295890 h (1.05 eV)
quartet

```
 Zero-point correction=                           .016148 (Hartree/Particle)
 Thermal correction to Energy=                    .026895
 Thermal correction to Enthalpy=                  .027839
 Thermal correction to Gibbs Free Energy=        -.026494
```



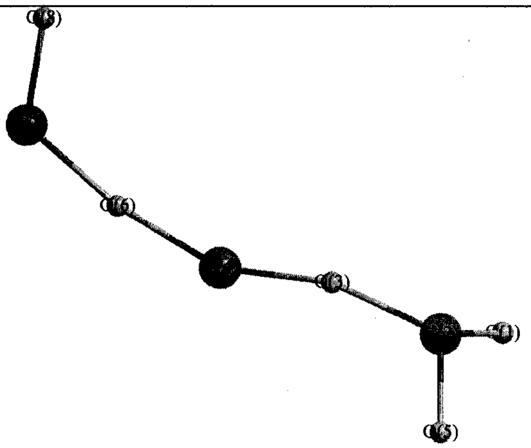
O(8)-V(7)	1.6176
V(7)-O(6)	1.8238
O(6)-V(4)	1.7909
O(5)-V(2)	1.6280
V(4)-O(3)	1.7906
O(3)-V(2)	1.8017
V(2)-O(1)	1.6280

v3o5s3.log, v3o5s3fr.log

O	-3.761989	1.084159	.972887
V	-3.147406	.269736	-.295722
O	-1.353853	.098808	-.298197
V	.244224	-.403489	.334428
O	-3.974531	-1.105935	-.567166
O	2.035092	-.403280	.334046
V	3.821183	-.130245	.086016
O	4.416027	1.085241	-.800145

E = -590.518197812 h (2.25 eV)
doublet

```
 Zero-point correction=                           .015645 (Hartree/Particle)
 Thermal correction to Energy=                    .027082
 Thermal correction to Enthalpy=                  .028026
 Thermal correction to Gibbs Free Energy=        -.028801
```



```
O(8)-V(7)    1.6176
V(7)-O(6)    1.8150
O(6)-V(4)    1.7971
O(5)-V(2)    1.6287
V(4)-O(3)    1.7922
O(3)-V(2)    1.8017
V(2)-O(1)    1.6287
```

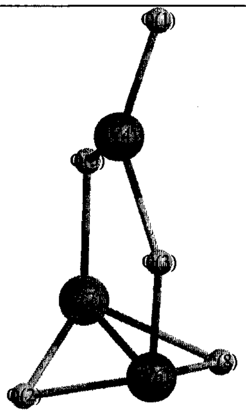
v3o5s3s.log

```
O  -3.722039    1.169711     .936886
V  -3.144155     .267444    -.289691
O  -1.353661     .070200    -.326162
V    .247102    -.434892     .301787
O  -3.997027   -1.109403    -.461522
O   2.044191    -.426161     .304116
V   3.821289    -.136114     .076003
O   4.371358    1.168392    -.706600
```

E = -540.519820777 h (2.20 eV)
sextet

```
 Zero-point correction=                          .015456 (Hartree/Particle)
 Thermal correction to Energy=                   .026948
 Thermal correction to Enthalpy=                 .027893
 Thermal correction to Gibbs Free Energy=      -.030179
```

Isomer 4



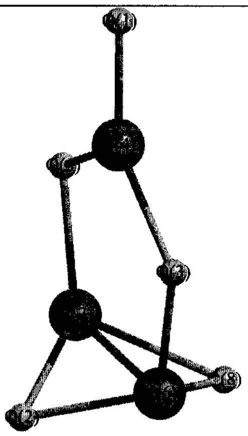
```
O(8)-V(7)    1.9422
O(8)-V(6)    1.7444
V(7)-O(2)    1.9406
V(7)-V(6)    2.4209
V(7)-O(5)    1.8115
V(6)-O(2)    1.7541
V(6)-O(3)    1.7571
O(5)-V(4)    1.8187
V(4)-O(3)    1.8753
V(4)-O(1)    1.6138
```

v3o5s4q.log

```
O  -3.261404    -.056794     .262353
O   1.699062    -.099449   -1.230197
O   -.582836   -1.531543    -.081441
V  -1.702774    -.029188    -.155216
O   -.733583    1.500638     .012261
V   1.128036   -1.153397     .050459
V   1.062527    1.265937    -.006867
O   1.476369    -.052493    1.357944
```

E = -590.599360203 h (0.04 eV)
quartet

```
 Zero-point correction=                          .016922 (Hartree/Particle)
 Thermal correction to Energy=                   .026541
 Thermal correction to Enthalpy=                 .027485
 Thermal correction to Gibbs Free Energy=      -.020607
```



O(8)-V(7)	1.9614
O(8)-V(6)	1.7428
V(7)-O(2)	1.9614
V(7)-V(6)	2.3702
V(7)-O(5)	1.8414
V(6)-O(2)	1.7428
V(6)-O(3)	1.7703
O(5)-V(4)	1.7938
V(4)-O(3)	1.8596
V(4)-O(1)	1.6130

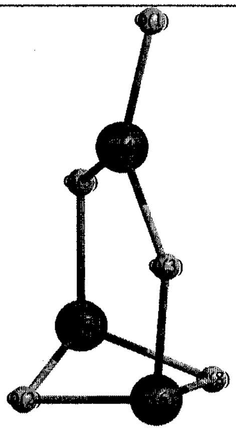
v3o5s4.log, v3o5s4fr.log

```
O  -3.269616    -.127113     .002404
O   1.601673    -.060542   -1.321658
O   -.552562   -1.551288    -.000775
V  -1.658164    -.056095    -.001245
O   -.822046    1.530950    -.000792
V   1.161221   -1.107534     .000205
V    .998838    1.257113     .000317
O   1.599604    -.060772    1.322899
```

E = -590.597683511 h (0.09 eV)

doublet

```
 Zero-point correction=                        .017122 (Hartree/Particle)
 Thermal correction to Energy=                 .026829
 Thermal correction to Enthalpy=               .027773
 Thermal correction to Gibbs Free Energy=     -.020582
```



O(8)-V(7)	1.8299
O(8)-V(6)	1.8299
V(7)-O(2)	1.8330
V(7)-O(5)	1.7989
V(6)-O(2)	1.8330
V(6)-O(3)	1.7987
O(5)-V(4)	1.8319
V(4)-O(3)	1.8320
V(4)-O(1)	1.6173

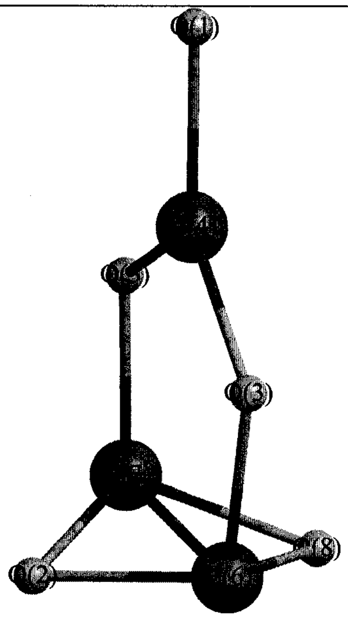
v3o5s4s.log

```
O  -3.263663    -.000302     .179690
O   1.520396     .000050   -1.161009
O   -.665677   -1.530364    -.028712
V  -1.670315     .000015    -.097683
O   -.665958    1.530470    -.028800
V   1.123060   -1.346688     .017277
V   1.122903    1.346721     .017340
O   1.419913     .000007    1.220145
```

E = -590.599253761 h (0.04 eV)

sextet

```
 Zero-point correction=                        .017131 (Hartree/Particle)
 Thermal correction to Energy=                 .026504
 Thermal correction to Enthalpy=               .027449
 Thermal correction to Gibbs Free Energy=     -.021032
```



O(8)-V(7)	1.8404
O(8)-V(6)	1.8430
V(7)-O(2)	1.8407
V(7)-V(6)	2.4792
V(7)-O(5)	1.8080
V(6)-O(2)	1.8428
V(6)-O(3)	1.8581
O(5)-V(4)	1.8397
V(4)-O(3)	1.7980
V(4)-O(1)	1.8152

v3o5s4or1.log

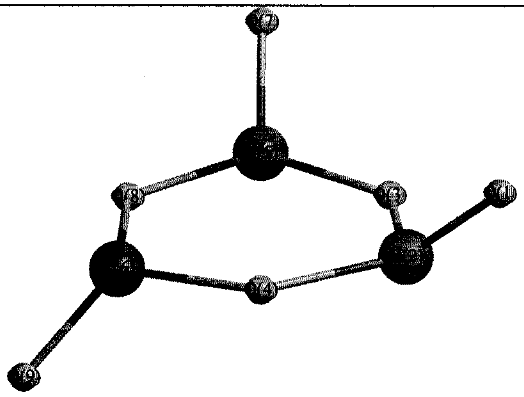
```
O  -3.487366     .080581     .001382
O   1.493924     .028355   -1.319088
O   -.644478   -1.535045     .000393
V  -1.677924    -.063717    -.000833
O   -.671952    1.476638    -.000088
V   1.186864   -1.221110     .000111
V   1.122659    1.257245     .000086
O   1.494023     .028769    1.319228
```

E = -590.485645773 h (3.13 eV)
octet

```
 Zero-point correction=                       .014712 (Hartree/Particle)
 Thermal correction to Energy=                .025000
 Thermal correction to Enthalpy=              .025944
 Thermal correction to Gibbs Free Energy=    -.024741
```

V_3O_6 clusters

Isomer 1



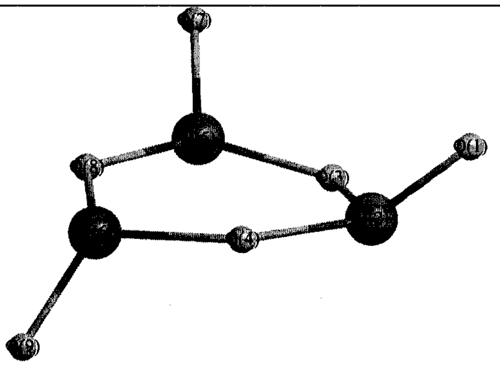
```
O(9)-V(6)    1.6082
O(8)-V(5)    1.8062
O(8)-V(6)    1.8047
O(7)-V(5)    1.6090
V(6)-O(4)    1.8039
V(5)-O(3)    1.8027
O(4)-V(2)    1.8068
O(3)-V(2)    1.8038
V(2)-O(1)    1.6089
```

v3o6s5.log, v3o6s5fr.log

```
O  1.839895   -2.643619     .621958
V   .948252   -1.620598    -.242332
O  1.597046     .047567    -.465686
O  -.815180   -1.526835     .139894
V   .855502    1.676154    -.247612
V -1.844011    -.051536     .278137
O  1.674702    2.731586     .648971
O  -.903343    1.479758     .113298
O -3.277379    -.100015    -.449493
```

E = -665.896512857 h (0 eV)
doublet

```
 Zero-point correction=                        .020501 (Hartree/Particle)
 Thermal correction to Energy=                 .031858
 Thermal correction to Enthalpy=               .032802
 Thermal correction to Gibbs Free Energy=     -.020517
```



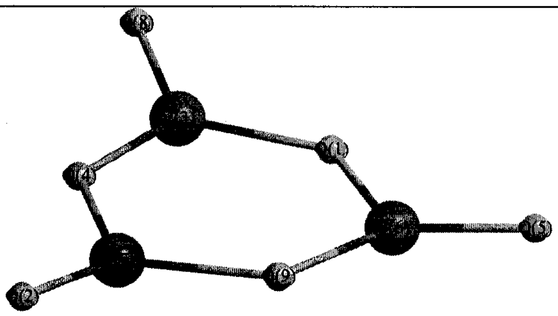
```
O(9)-V(6)    1.6093
O(8)-V(6)    1.8057
O(8)-V(5)    1.8088
O(7)-V(5)    1.6094
V(6)-O(4)    1.8058
V(5)-O(3)    1.8038
O(4)-V(2)    1.8086
O(3)-V(2)    1.8038
V(2)-O(1)    1.6094
```

v3o6quart.log

```
O   -1.792835    2.647357     .631270
V    -.885091    1.656584    -.254561
O   -1.545912     .004398    -.549997
O     .848243    1.475654     .229078
V    -.893700   -1.651050    -.253743
V    1.878218    -.004812     .320872
O   -1.809174   -2.639696     .626478
O     .839330   -1.479222     .234871
O    3.174496    -.010570    -.632833
```

E = -665.895107479 h (0.04 eV)
quartet

```
 Zero-point correction=                        .020303 (Hartree/Particle)
 Thermal correction to Energy=                 .031717
 Thermal correction to Enthalpy=               .032661
 Thermal correction to Gibbs Free Energy=     -.021636
```



v3o6s1sr1.log

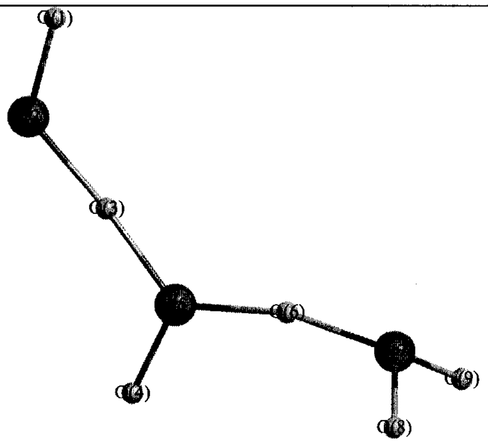
O(9)-V(7)	1.8314
O(9)-V(6)	1.7899
O(8)-V(3)	1.6621
V(7)-O(4)	1.8325
V(7)-O(2)	1.6153
V(6)-O(1)	1.8150
V(6)-O(5)	1.6614
O(4)-V(3)	1.7882
V(3)-O(1)	1.8142

```
O    .191011   -1.697729    -.077269
O   -.386924    3.464167     .149385
V   1.735322    -.745760    -.070032
O   1.407312    1.011532    -.024042
O  -2.827210   -2.099814     .205943
V  -1.523938   -1.103885    -.058400
V   -.212131    1.869090    -.036030
O   3.225742   -1.417526     .230057
O  -1.607782     .683465    -.011247
```

E = -665.808277111 h (2.40 eV)
sextet

```
 Zero-point correction=                          .016875 (Hartree/Particle)
 Thermal correction to Energy=                   .029293
 Thermal correction to Enthalpy=                 .030237
 Thermal correction to Gibbs Free Energy=       -.026984
```

Isomer 2



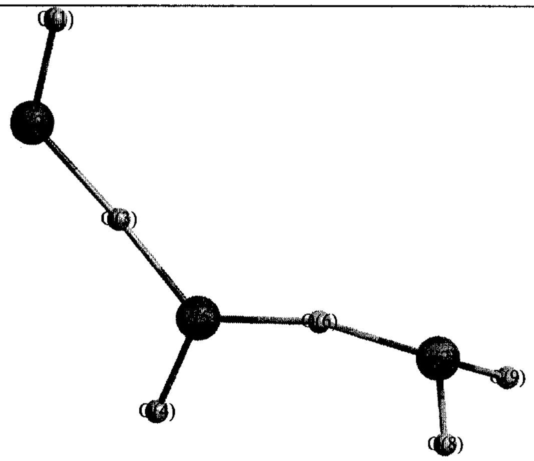
v3o6s2q.log

O(9)-V(7)	1.6231
O(8)-V(7)	1.6232
V(7)-O(6)	1.7899
O(6)-V(5)	1.8026
V(5)-O(4)	1.6143
V(5)-O(3)	1.7802
O(3)-V(2)	1.8091
V(2)-O(1)	1.6157

```
O  -4.115509   -1.772197    -.018865
V  -3.668257    -.219853     .006896
O  -1.916837     .232495    -.018426
O   -.104569    2.453946     .058165
V   -.246157     .847241    -.008574
O   1.256324    -.148432    -.032791
V   2.964485    -.682663    -.012633
O   3.840815    -.243351   -1.306338
O   3.770822    -.363544    1.359400
```

E = -665.819547694 h (2.09 eV)
quartet

```
 Zero-point correction=                          .019125 (Hartree/Particle)
 Thermal correction to Energy=                   .031750
 Thermal correction to Enthalpy=                 .032694
 Thermal correction to Gibbs Free Energy=       -.028801
```

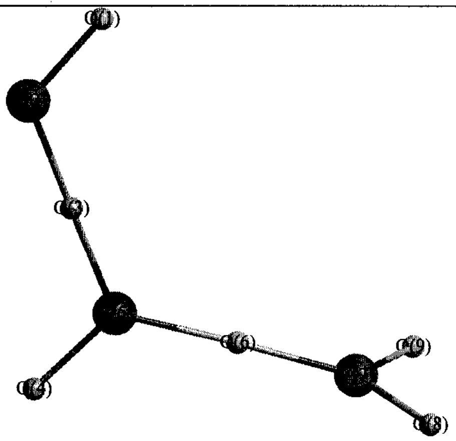


O(9)-V(7)	1.6228
O(8)-V(7)	1.6229
V(7)-O(6)	1.7915
O(6)-V(5)	1.7993
V(5)-O(4)	1.6133
V(5)-O(3)	1.7734
O(3)-V(2)	1.8163
V(2)-O(1)	1.6155

v3o6s2.log, v3o6s2fr.log

O	-4.123003	-1.775335	-.021861
V	-3.663149	-.226979	.011205
O	-1.913131	.257335	-.031824
O	-.084041	2.459019	.080519
V	-.244064	.856545	-.015090
O	1.250707	-.144751	-.041543
V	2.957458	-.688617	-.014913
O	3.844818	-.238838	-1.297082
O	3.755195	-.387656	1.365835

E = -665.818521024 h (2.12 eV)
doublet



O(9)-V(7)	1.6889
O(8)-V(7)	1.6894
V(7)-O(6)	1.7832
O(6)-V(5)	1.8141
V(5)-O(4)	1.6149
V(5)-O(3)	1.7803
O(3)-V(2)	1.8088
V(2)-O(1)	1.6147

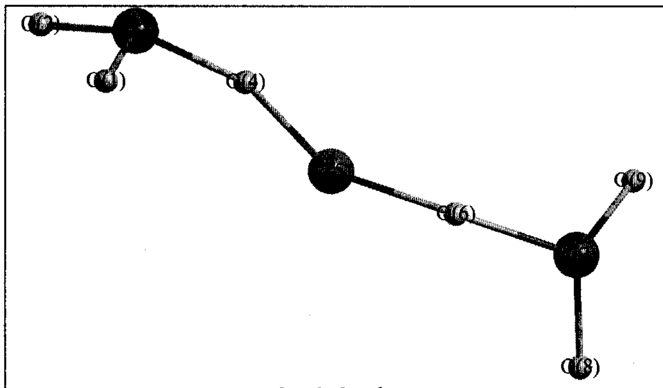
v3o6s2s.log

O	-3.634391	-2.111099	.002740
V	-3.543042	-.499017	.000861
O	-1.933113	.325489	-.001967
O	-.381605	2.735066	.000892
V	-.340261	1.120741	-.002155
O	1.283866	.312621	-.002798
V	2.909459	-.420364	.000120
O	3.732911	-.926738	-1.385400
O	3.732134	-.914248	1.389908

E = -665.753213770 h (3.90 eV)
sextet

```
 Zero-point correction=                           .016569 (Hartree/Particle)
 Thermal correction to Energy=                    .030071
 Thermal correction to Enthalpy=                  .031015
 Thermal correction to Gibbs Free Energy=        -.033999
```

Isomer 3

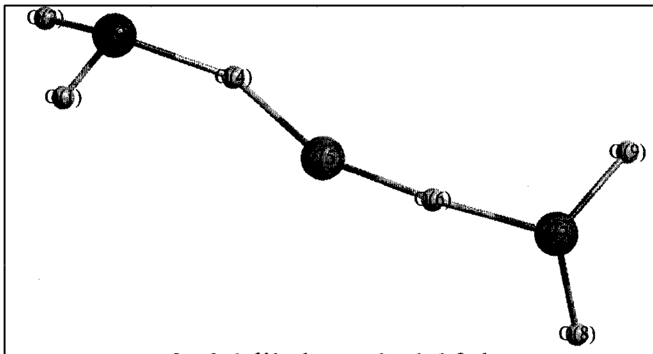


```
O(9)-V(7)    1.6252
O(8)-V(7)    1.6252
V(7)-O(6)    1.8046
O(6)-V(5)    1.7854
V(5)-O(4)    1.7863
O(4)-V(3)    1.8046
V(3)-O(1)    1.6252
V(3)-O(2)    1.6250
```

v3o6s3q.log

```
O  -3.934705    1.398801    -.579935
O  -4.335564    -.785916     .910892
V  -3.462552    -.129496    -.292303
O  -1.679009    -.335341    -.110456
V    .000421    -.048694     .426365
O   1.666992     .286371    -.119463
V   3.460016     .164902    -.283844
O   4.287542     .801929     .961354
O   4.000825   -1.327643    -.631769
 Zero-point correction=                          .019309 (Hartree/Particle)
 Thermal correction to Energy=                   .031602
 Thermal correction to Enthalpy=                 .032546
 Thermal correction to Gibbs Free Energy=       -.026837
```

E = -665.806172088 h (2.46 eV)
quartet



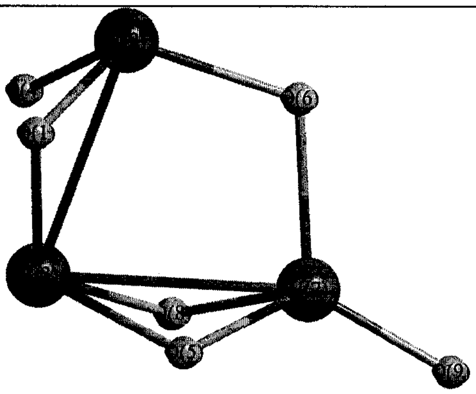
```
O(9)-V(7)    1.6263
O(8)-V(7)    1.6261
V(7)-O(6)    1.8273
O(6)-V(5)    1.7568
V(5)-O(4)    1.7575
O(4)-V(3)    1.8280
V(3)-O(1)    1.6264
V(3)-O(2)    1.6264
```

v3o6s3diis.log, v3o6s3fr.log

```
O  -3.853781    1.435409    -.583973
O  -4.336836    -.780171     .846279
V  -3.421971    -.110164    -.319570
O  -1.625448    -.366653    -.100188
V   -.000690    -.096262     .512900
O   1.606024     .294465    -.080443
V   3.417128     .185507    -.297467
O   4.271342     .760297     .961191
O   3.954608   -1.283205    -.743472
 Zero-point correction=                          .019097 (Hartree/Particle)
 Thermal correction to Energy=                   .031430
 Thermal correction to Enthalpy=                 .032374
 Thermal correction to Gibbs Free Energy=       -.026462
```

E = -665.784747664 h (3.04 eV)
doublet

Isomer 4



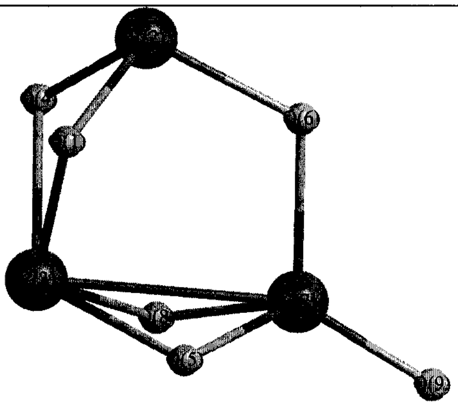
v3o6s4.log, v3o6s4fr.log

```
O   -1.695364     .121044   -1.259108
V   -1.415939   -1.016542    -.005272
V    -.617801    1.290900     .003218
O   -1.695320     .094963    1.266531
O     .795283     .896373   -1.185968
O     .242901   -1.629849    -.007183
V    1.499681    -.235889    -.000636
O     .791438     .884530    1.193508
O    3.096482    -.477659    -.000044
```

```
O(9)-V(7)    1.6150
O(8)-V(7)    1.7841
O(8)-V(3)    1.8889
V(7)-O(5)    1.7842
V(7)-O(6)    1.8769
V(7)-V(3)    2.6105
O(6)-V(2)    1.7686
O(5)-V(3)    1.8886
O(4)-V(2)    1.7120
V(3)-O(1)    2.0306
V(3)-V(2)    2.4416
V(2)-O(1)    1.7159
```

E = -665.859840903 h (1.00 eV)
doublet

```
 Zero-point correction=                          .021523 (Hartree/Particle)
 Thermal correction to Energy=                   .031322
 Thermal correction to Enthalpy=                 .032266
 Thermal correction to Gibbs Free Energy=       -.014506
```



v3o4s4qr1.log

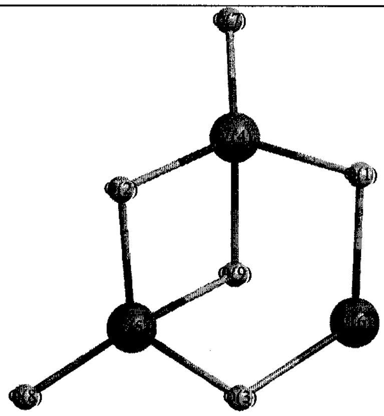
```
O    1.592651     .186477    1.195010
V    1.556160   -1.062356    -.000081
V     .515920    1.417201     .000029
O    1.592465     .186831   -1.194905
O    -.862265     .873453    1.195303
O    -.133219   -1.602706    -.000137
V   -1.475571    -.295091     .000000
O    -.862433     .873659   -1.195179
O   -3.042163    -.689505     .000059
```

```
O(9)-V(7)    1.6155
O(8)-V(3)    1.9036
O(8)-V(7)    1.7806
V(7)-O(5)    1.7806
V(7)-V(3)    2.6264
V(7)-O(6)    1.8740
O(6)-V(2)    1.7737
O(5)-V(3)    1.9036
O(4)-V(2)    1.7290
O(4)-V(3)    2.0250
V(3)-O(1)    2.0253
V(2)-O(1)    1.7289
```

E = -665.850349569 h (1.26 eV)
quartet

```
 Zero-point correction=                          .021515 (Hartree/Particle)
 Thermal correction to Energy=                   .031210
 Thermal correction to Enthalpy=                 .032155
 Thermal correction to Gibbs Free Energy=       -.015048
```

Isomer 5



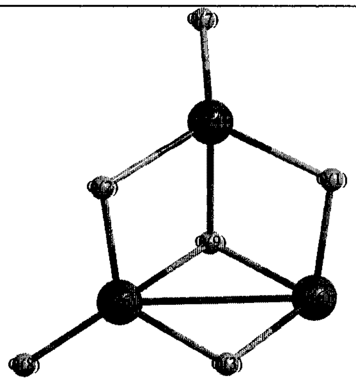
v3o6s7q.log

O(9)-V(4)	1.9221
O(9)-V(5)	1.9222
O(8)-V(5)	1.6106
O(7)-V(4)	1.6106
V(6)-O(1)	1.8743
V(6)-O(3)	1.8743
V(5)-O(2)	1.8183
V(5)-O(3)	1.7805
V(4)-O(1)	1.7805
V(4)-O(2)	1.8183
V(6)-O(9)	2.0619

O	1.596559	1.114349	-0.535722
O	-0.000184	-1.391180	-0.933120
O	-1.596247	1.114587	-0.535464
V	1.362901	-0.580783	-0.043520
V	-1.363012	-0.580562	-0.043204
V	0.000217	1.833770	0.133047
O	2.685412	-1.408364	0.356417
O	-2.686018	-1.407789	0.355836
O	0.000176	0.045176	1.158876

E = -665.898800221 h (0.06 eV)
quartet

```
 Zero-point correction=                           .020349 (Hartree/Particle)
 Thermal correction to Energy=                    .030883
 Thermal correction to Enthalpy=                  .031828
 Thermal correction to Gibbs Free Energy=        -.017867
```



v3o6s7r1.log, v3o6s7r1fr.log

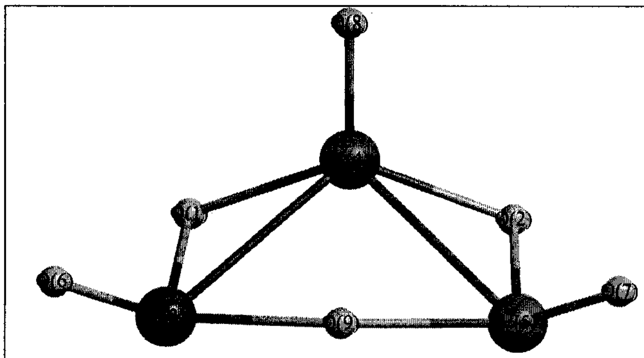
O(9)-V(4)	2.0196
O(9)-V(6)	1.9228
O(9)-V(5)	1.9226
O(8)-V(5)	1.6105
O(7)-V(4)	1.6060
V(6)-O(1)	1.7672
V(6)-O(3)	1.7922
V(6)-V(5)	2.6647
V(5)-O(2)	1.7571
V(5)-O(3)	1.8671
V(4)-O(1)	1.9211
V(4)-O(2)	1.9105

O	1.389033	1.329525	-.577572
O	-.037937	-1.449903	-.910670
O	-1.528906	1.104034	-.701717
V	1.454497	-.539817	-.139712
V	-1.315697	-.625237	-.030616
V	-.132308	1.749395	.217532
O	2.741996	-1.272714	.480279
O	-2.611584	-1.467131	.422721
O	.028731	.076208	1.151247

E = -665.893554917 h (0.08 eV)
doublet

```
 Zero-point correction=                           .020609 (Hartree/Particle)
 Thermal correction to Energy=                    .031033
 Thermal correction to Enthalpy=                  .031977
 Thermal correction to Gibbs Free Energy=        -.016581
```

Isomer 6



v3o6s8r1.log

```
O     -1.673922     0.957304    -0.838504
O      1.674757     0.955878    -0.839965
V     -1.815891    -0.713779    -0.240906
V      0.000867     1.142871    -0.036452
V      1.814938    -0.714889    -0.240968
O     -2.924060    -1.036268     0.877438
O      2.922279    -1.037359     0.878175
O      0.001744     1.941933     1.348240
O     -0.000555    -0.959820     0.064802
```

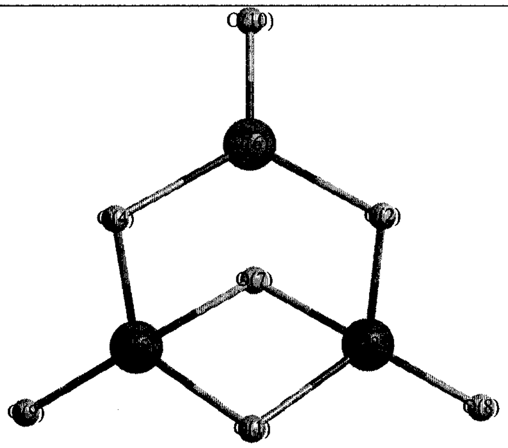
```
O(9)-V(5)    1.8573
O(9)-V(3)    1.8573
O(8)-V(4)    1.5987
O(7)-V(5)    1.6071
O(6)-V(3)    1.6071
V(5)-O(2)    1.7804
V(5)-V(4)    2.6046
V(4)-O(2)    1.8661
V(4)-O(1)    1.8662
V(4)-V(3)    2.6057
V(3)-O(1)    1.7804
```

E = -665.882281541 h (0.39 eV)
doublet

```
 Zero-point correction=                          .021042 (Hartree/Particle)
 Thermal correction to Energy=                   .031902
 Thermal correction to Enthalpy=                 .032846
 Thermal correction to Gibbs Free Energy=       -.018627
```

V_3O_7 clusters

Isomer 7

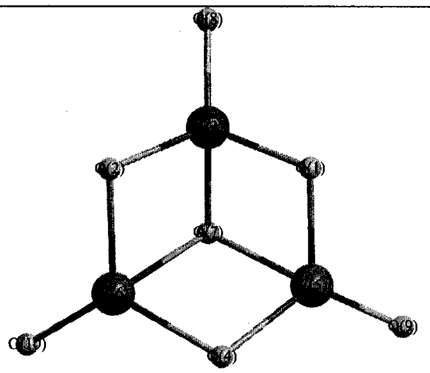


v3o7s7.log

```
O   -.029129   -1.729140    -.737302
O  -1.557103     .808007    -.782016
V  -1.377008    -.751746    -.010969
O   1.585160     .759389    -.778228
V   1.351331    -.796289    -.011093
V    .026960    1.630554    -.101317
O   -.000634    -.033646    1.098222
O  -2.710386   -1.505913     .471817
O   2.657022   -1.597166     .470472
O    .051379    3.061225     .611747
```

```
O(10)-V(6)   1.5987
O(9)-V(5)    1.6057
O(8)-V(3)    1.6062
O(7)-V(5)    1.9079
O(7)-V(3)    1.9080
V(6)-O(4)    1.9092
V(6)-O(2)    1.9103
V(5)-O(4)    1.7502
V(5)-O(1)    1.8175
V(3)-O(1)    1.8165
V(3)-O(2)    1.7492
V(6)-O(7)    2.0516
```

E = -741.191379414 h (0 eV)
doublet



O(10)-V(6)	1.6043
O(9)-V(5)	1.6439
O(8)-V(3)	1.6461
O(7)-V(6)	2.0015
O(7)-V(3)	1.8709
O(7)-V(5)	1.9644
V(6)-O(2)	1.9457
V(6)-O(4)	1.8886
V(5)-O(4)	1.8071
V(5)-O(1)	1.9138
V(3)-O(2)	1.7460
V(3)-O(1)	1.7826

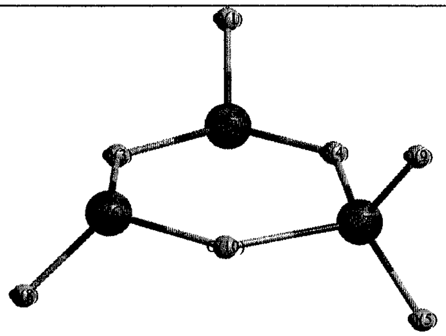
v3o7s7q.log

O	-1.519689	.707829	-.907750
O	1.311641	1.200762	-.781774
V	-.217778	1.523807	-.003995
O	.204183	-1.746806	-.779000
V	-1.280108	-.996984	-.071735
V	1.546060	-.605617	-.097843
O	.008212	-.013470	1.038147
O	-.502718	3.026905	.603544
O	-2.497618	-1.826628	.657386
O	2.857489	-1.122058	.668471

E = -741.110445166 h (2.20 eV)
quartet

```
 Zero-point correction=                           .021973 (Hartree/Particle)
 Thermal correction to Energy=                    .033980
 Thermal correction to Enthalpy=                  .034924
 Thermal correction to Gibbs Free Energy=        -.017838
```

Isomer 1



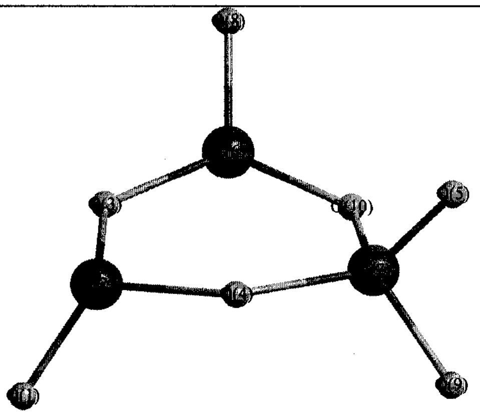
O(10)-V(6)	1.7125
O(10)-V(7)	1.9206
O(9)-V(7)	1.6221
O(8)-V(6)	1.6079
V(7)-O(4)	1.9207
V(7)-O(5)	1.6221
V(6)-O(3)	1.7960
O(4)-V(2)	1.7125
O(3)-V(2)	1.7960
V(2)-O(1)	1.6078

v3o7s1.log

O	1.775977	2.825442	-.502174
V	1.119786	1.588162	.287579
O	1.907614	.000084	-.000543
O	-.582256	1.462635	.146810
O	-2.752922	-.081990	1.323200
V	1.119875	-1.588253	-.287658
V	-1.818362	-.000082	-.000036
O	1.776175	-2.825013	.502837
O	-2.753597	.081990	-1.322799
O	-.582223	-1.462650	-.147003

E = -741.147786373 h (1.19 eV)
doublet

```
 Zero-point correction=                           .023956 (Hartree/Particle)
 Thermal correction to Energy=                    .036266
 Thermal correction to Enthalpy=                  .037210
 Thermal correction to Gibbs Free Energy=        -.017792
```

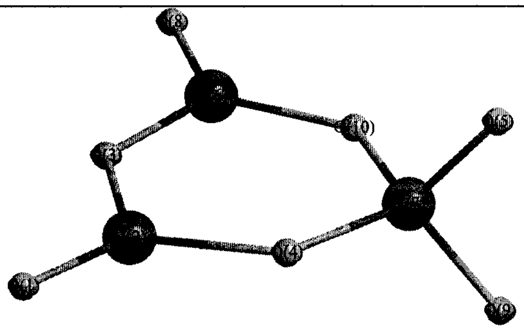


```
O(10)-V(7)   1.7925
O(10)-V(6)   1.8105
O(9)-V(7)    1.6769
O(8)-V(6)    1.6069
V(7)-O(5)    1.6769
V(7)-O(4)    1.7925
V(6)-O(3)    1.8058
O(4)-V(2)    1.8105
O(3)-V(2)    1.8058
V(2)-O(1)    1.6068
```

v3o7s1q.log

```
O  -1.650031   -2.828989    -.573956
V  -1.149568   -1.594152     .324197
O  -1.932828     .000209    -.000369
O    .638057   -1.346369     .468394
O   2.802601     .403127    1.219978
V  -1.149176    1.594507    -.324269
V   1.725080    -.000184     .000007
O  -1.649303    2.829012     .574529
O   2.802380    -.403786   -1.220065
O    .638408    1.346303    -.468326
 Zero-point correction=                        .022668 (Hartree/Particle)
 Thermal correction to Energy=                 .035220
 Thermal correction to Enthalpy=               .036164
 Thermal correction to Gibbs Free Energy=     -.020033
```

E = -741.110900712 h (2.19 eV)
quartet



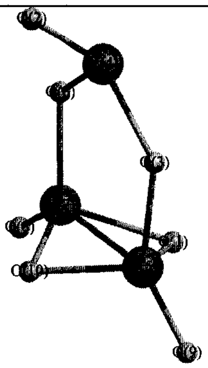
```
O(10)-V(6)   1.8058
O(10)-V(7)   1.8151
O(9)-V(7)    1.6841
O(8)-V(6)    1.7183
V(7)-O(4)    1.7615
V(7)-O(5)    1.6843
V(6)-O(3)    1.7788
O(4)-V(2)    1.8518
O(3)-V(2)    1.8324
V(2)-O(1)    1.6153
```

v3o7s1sr1.log

```
O   1.662066    3.168130    -.000736
V    .938763    1.723862     .000074
O   1.893677     .159897     .000371
O   -.878026    1.365515    -.000887
O  -2.859319    -.283719    1.285860
V   1.272745   -1.507053     .000292
V  -1.780362    -.147268    -.000208
O   2.335080   -2.857667    -.000382
O  -2.860404    -.286576   -1.284800
O   -.532616   -1.465513     .000117
 Zero-point correction=                        .019624 (Hartree/Particle)
 Thermal correction to Energy=                 .032981
 Thermal correction to Enthalpy=               .033925
 Thermal correction to Gibbs Free Energy=     -.024418
```

E = -741.019004528 h (4.69 eV)
sextet

Isomer 2



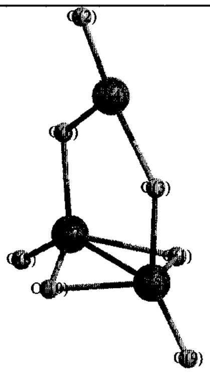
v3o7s2.log

O	1.338872	.000118	-1.145104
O	-3.129527	-.000165	.812123
O	-.913338	1.483457	-.261627
V	-1.980514	-.000127	-.303206
V	.840520	1.296118	.035322
O	-.913208	-1.483581	-.261511
V	.840737	-1.296019	.035273
O	1.733357	-2.628017	.109271
O	1.732903	2.628277	.109303
O	1.011302	-.000006	1.306302

O(10)-V(5)	1.8233
O(10)-V(7)	1.8233
O(9)-V(5)	1.6051
O(8)-V(7)	1.6051
V(7)-O(1)	1.8225
V(7)-V(5)	2.5921
V(7)-O(6)	1.7887
O(6)-V(4)	1.8280
V(5)-O(1)	1.8225
V(5)-O(3)	1.7887
V(4)-O(3)	1.8280
V(4)-O(2)	1.6013

E = -741.190328338 h (0.03 eV)
doublet

```
 Zero-point correction=                           .025324 (Hartree/Particle)
 Thermal correction to Energy=                    .036510
 Thermal correction to Enthalpy=                  .037454
 Thermal correction to Gibbs Free Energy=        -.013238
```



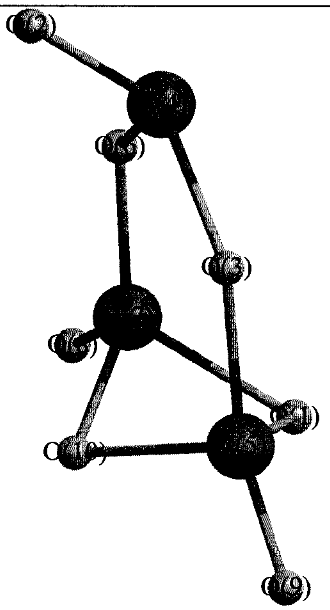
v3o7s2q.log

O	1.151786	-.000447	1.276014
O	-3.508133	.000285	-.359456
O	-.861911	-1.502911	.056996
V	-1.977317	-.000079	.138880
V	.886748	-1.328918	.011039
O	-.861808	1.502519	.057319
V	.886962	1.329061	.011417
O	1.758332	2.717243	-.150535
O	1.758797	-2.716866	-.150250
O	1.148308	-.000007	-1.193926

O(10)-V(7)	1.8132
O(10)-V(5)	1.8128
O(9)-V(5)	1.6471
O(8)-V(7)	1.6470
V(7)-O(1)	1.8539
V(7)-V(5)	2.6580
V(7)-O(6)	1.7580
O(6)-V(4)	1.8732
V(5)-O(1)	1.8534
V(5)-O(3)	1.7579
V(4)-O(3)	1.8733
V(4)-O(2)	1.6099

E = -741.103071624 h (2.40 eV)
quartet

```
 Zero-point correction=                           .020984 (Hartree/Particle)
 Thermal correction to Energy=                    .033562
 Thermal correction to Enthalpy=                  .034506
 Thermal correction to Gibbs Free Energy=        -.020618
```



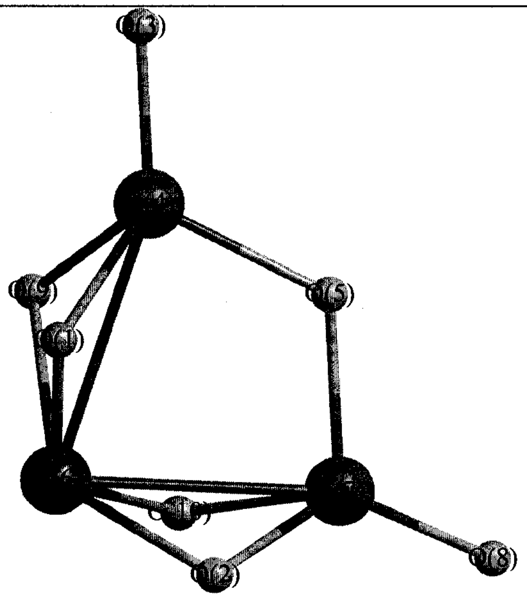
```
O(10)-V(5)   1.9581
O(10)-V(7)   1.9581
O(9)-V(5)    1.6296
O(8)-V(7)    1.6296
V(7)-O(1)    1.9491
V(7)-O(6)    1.8053
O(6)-V(4)    1.8142
V(5)-O(1)    1.9491
V(5)-O(3)    1.8054
V(4)-O(3)    1.8142
V(4)-O(2)    1.6066
```

v3o7s2s.log

```
O   1.530477     .000080    -.970258
O  -3.225543    -.000078     .782875
O   -.951662    1.460307    -.212599
V  -2.025644    -.000033    -.285465
V    .840101    1.549580    -.010332
O   -.951575   -1.460303    -.212569
V    .840200   -1.549551    -.010454
O   1.685433   -2.929119     .184233
O   1.685405    2.929144     .184108
O   1.220328    -.000021    1.124681
 Zero-point correction=                       .021217 (Hartree/Particle)
 Thermal correction to Energy=                .034001
 Thermal correction to Enthalpy=              .034945
 Thermal correction to Gibbs Free Energy=   -.021415
```

E = -741.018106432 h (4.72 eV)
sextet

Structure 3



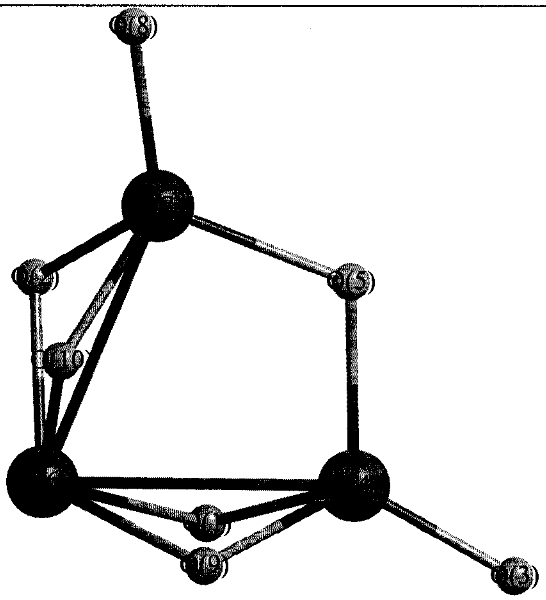
O(10)-V(7)	1.7277
O(10)-V(6)	2.0381
O(9)-V(6)	2.0381
O(9)-V(4)	1.7278
O(8)-V(7)	1.6106
V(7)-O(2)	1.9029
V(7)-V(6)	2.6130
V(7)-O(5)	1.8193
V(6)-O(2)	1.7595
V(6)-O(1)	1.7595
V(6)-V(4)	2.6130
O(5)-V(4)	1.8193
V(4)-O(1)	1.9029
V(4)-O(3)	1.6106

v3o7s3r1.log

```
O  -1.297930   1.073112  -1.022282
O   1.297929   1.073113  -1.022281
O  -2.948872  -1.406572   -.002611
V  -1.585991   -.551270   -.073864
O    .000000  -1.400029   -.346099
V   -.000001   1.519809    .078414
V   1.585991   -.551269   -.073864
O   2.948873  -1.406571   -.002612
O  -1.219669    .433650   1.297582
O   1.219671    .433648   1.297583
```

E = -741.136027398 h (1.51 eV)
doublet

```
 Zero-point correction=                     .025338 (Hartree/Particle)
 Thermal correction to Energy=              .036146
 Thermal correction to Enthalpy=            .037090
 Thermal correction to Gibbs Free Energy=  -.012120
```



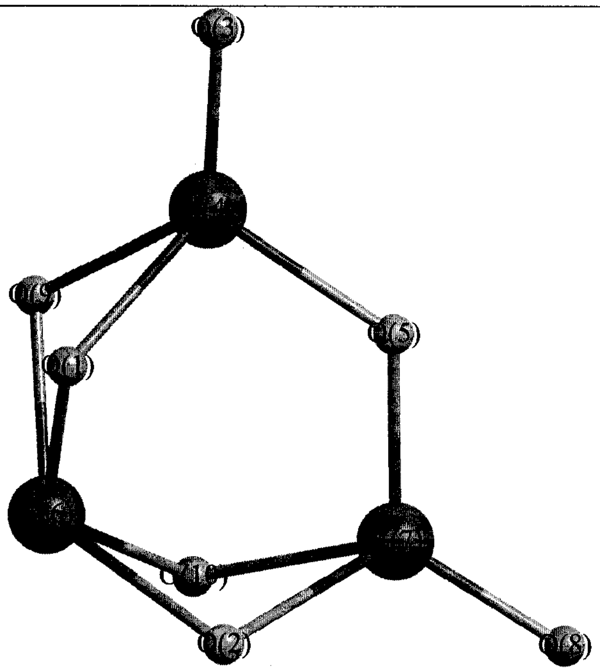
O(10)-V(7)	1.8655
O(10)-V(6)	1.9657
O(9)-V(6)	1.9657
O(9)-V(4)	1.8655
O(8)-V(7)	1.6116
V(7)-O(2)	1.7824
V(7)-V(6)	2.6839
V(7)-O(5)	1.8086
V(6)-O(2)	1.8805
V(6)-O(1)	1.8805
V(6)-V(4)	2.6839
O(5)-V(4)	1.8086
V(4)-O(1)	1.7824
V(4)-O(3)	1.6116

v3o7s3q.log

```
O  -1.329216    .801884  -1.101665
O   1.329216    .801883  -1.101665
O  -2.962138  -1.306454   -.005147
V  -1.515135   -.596963   -.012875
O    .000000  -1.578187   -.124529
V    .000000   1.617991   -.051196
V   1.515134   -.596963   -.012875
O   2.962137  -1.306454   -.005147
O  -1.104691    .684069   1.279688
O   1.104692    .684069   1.279688
```

E = -741.081197863 h (3.00 eV)
quartet

```
 Zero-point correction=                           .023402 (Hartree/Particle)
 Thermal correction to Energy=                    .034693
 Thermal correction to Enthalpy=                  .035637
 Thermal correction to Gibbs Free Energy=        -.014938
```



O(10)-V(6)	1.8721
O(10)-V(7)	1.9128
O(9)-V(4)	1.9128
O(9)-V(6)	1.8721
O(8)-V(7)	1.6082
V(7)-O(2)	1.9382
V(7)-O(5)	1.8081
V(6)-O(1)	1.8923
V(6)-O(2)	1.8923
O(5)-V(4)	1.8081
V(4)-O(1)	1.9382
V(4)-O(3)	1.6082
O(5)-V(6)	3.1494

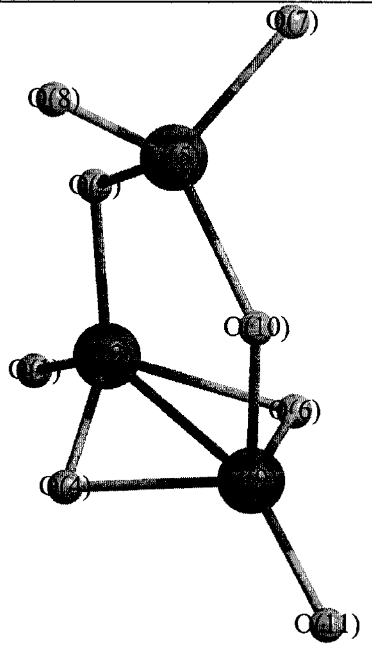
v3o7s3s.log

O	1.336831	.820560	1.104103
O	-1.336825	.820558	1.104104
O	2.978043	-1.479255	.110524
V	1.601400	-.674992	-.100000
O	.000001	-1.496606	.072150
V	.000001	1.652726	.054642
V	-1.601403	-.674992	-.100005
O	-2.978046	-1.479250	.110532
O	1.356136	.971802	-1.041748
O	-1.356135	.971808	-1.041748

E = -741.006158981 h (5.04 eV)
sextet

V_3O_8 structures

Isomer 1

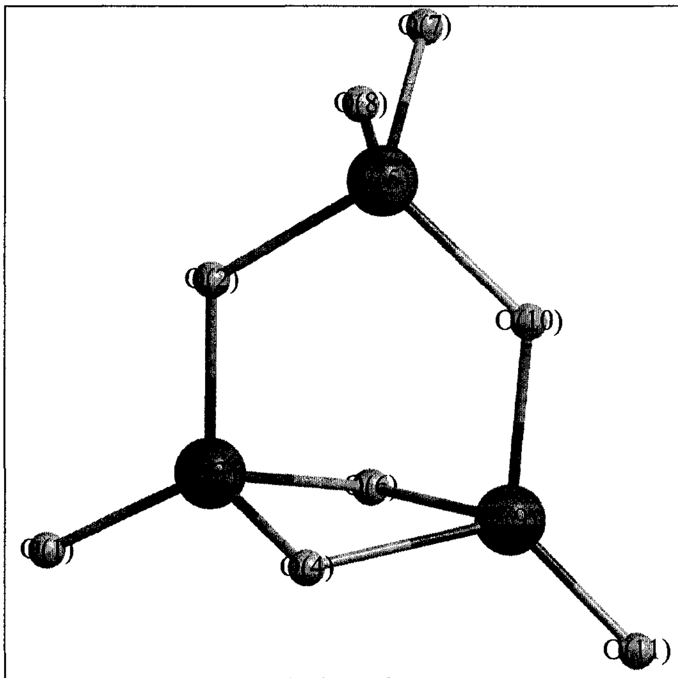


v3o8s1.log

O(11)-V(9)	1.6026
O(10)-V(9)	1.7901
O(10)-V(5)	1.8150
V(9)-O(6)	1.8210
V(9)-O(4)	1.8210
V(9)-V(3)	2.5858
O(8)-V(5)	1.6684
O(7)-V(5)	1.6683
O(6)-V(3)	1.8211
V(5)-O(2)	1.8152
O(4)-V(3)	1.8209
V(3)-O(1)	1.6027
V(3)-O(2)	1.7899

```
O    1.922831    2.629201     .001790
O    -.744843    1.450444    -.005942
V    1.038116    1.292813    -.000206
O    1.386248     .000024   -1.234418
V   -1.836220     .000045    -.000894
O    1.378952    -.000207    1.236000
O   -2.897533    -.000067    1.286337
O   -2.912902     .000195   -1.275333
V    1.037843   -1.292965    -.000341
O    -.745267   -1.450497    -.006147
O    1.923266   -2.628787     .001857
 Zero-point correction=                         .027364 (Hartree/Particle)
 Thermal correction to Energy=                  .039873
 Thermal correction to Enthalpy=                .040817
 Thermal correction to Gibbs Free Energy=      -.012787
```

E = -816.402821525 h (0 eV)
doublet



O(11)-V(9)	1.6123
O(10)-V(9)	1.8358
O(10)-V(5)	1.7861
V(9)-O(6)	1.9918
V(9)-O(4)	1.9936
O(8)-V(5)	1.6721
O(7)-V(5)	1.6724
O(6)-V(3)	1.7473
V(5)-O(2)	1.8304
O(4)-V(3)	1.7465
V(3)-O(1)	1.6786
V(3)-O(2)	1.7818

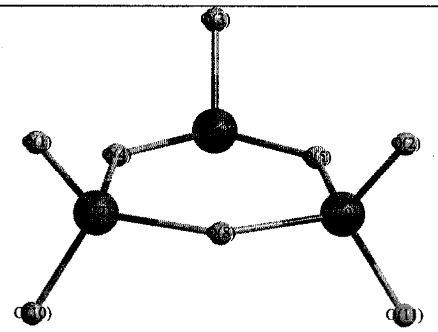
v3o8s1q.log

```
O    1.916900    2.731160     .010181
O    -.764399    1.426464    -.017315
V    1.013881    1.316223    -.001002
O    1.366753     .142208   -1.244909
V   -1.869404    -.032630    -.001347
O    1.343457     .136260    1.244782
O   -2.921101    -.038378    1.298925
O   -2.952329    -.047628   -1.275278
V    1.076460   -1.391574    -.004860
O    -.758909   -1.431513    -.009376
O    2.134431   -2.608127     .013717
```

E = -816.316627895 h (2.35 eV)
quartet

```
 Zero-point correction=                          .023665 (Hartree/Particle)
 Thermal correction to Energy=                   .037418
 Thermal correction to Enthalpy=                 .038362
 Thermal correction to Gibbs Free Energy=       -.019029
```

Isomer 2

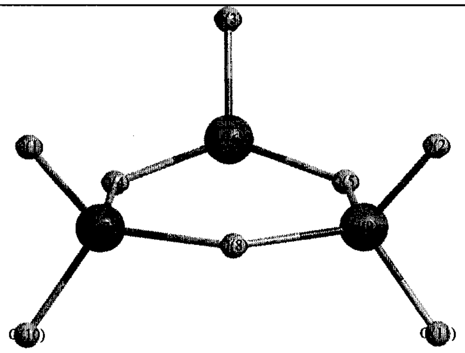


```
O(11)-V(9)   1.6413
O(10)-V(7)   1.6416
V(9)-O(2)    1.6433
V(9)-O(5)    1.9177
V(9)-O(8)    1.8010
O(8)-V(7)    1.8010
V(7)-O(4)    1.9177
V(7)-O(1)    1.6431
V(6)-O(3)    1.6073
V(6)-O(5)    1.7085
V(6)-O(4)    1.7085
```

v3o8s2.log

```
O  -2.543389   -1.202604    1.384460
O   2.534258   -1.198024    1.390518
O    .009335    3.252508     .745071
O  -1.374606    1.065299    -.147211
O   1.376498    1.060079    -.161596
V    .001924    2.060199    -.332763
V  -1.695577    -.816980     .030839
O   -.002066   -1.428651     .069491
V   1.693071    -.821640     .029920
O  -2.554797   -1.371898   -1.253106
O   2.556439   -1.388749   -1.245615
 Zero-point correction=                           .026050 (Hartree/Particle)
 Thermal correction to Energy=                    .039515
 Thermal correction to Enthalpy=                  .040459
 Thermal correction to Gibbs Free Energy=        -.016807
```

E = -816.362960572 h (1.08 eV)
doublet

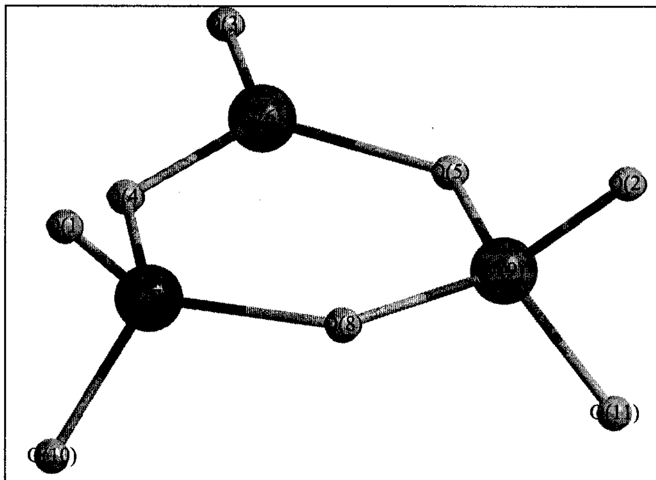


```
O(11)-V(9)   1.6678
O(10)-V(7)   1.6678
V(9)-O(5)    1.7905
V(9)-O(2)    1.6815
V(9)-O(8)    1.7958
O(8)-V(7)    1.7958
V(7)-O(4)    1.7905
V(7)-O(1)    1.6814
V(6)-O(5)    1.8089
V(6)-O(3)    1.6049
V(6)-O(4)    1.8089
```

v3o8s2q.log

```
O  -2.582254   -1.068710    1.405249
O   2.585105   -1.067907    1.404161
O   -.003369    3.263021     .721272
O  -1.459545     .971208    -.324945
O   1.458434     .973616    -.321855
V   -.001420    2.041741    -.319956
V  -1.669742    -.772224     .024427
O    .001041   -1.421627     .132978
V   1.670984    -.770109     .024676
O  -2.607064   -1.545316   -1.118095
O   2.608163   -1.540084   -1.120061
 Zero-point correction=                           .024741 (Hartree/Particle)
 Thermal correction to Energy=                    .038516
 Thermal correction to Enthalpy=                  .039460
 Thermal correction to Gibbs Free Energy=        -.019148
```

E = -816.324441878 h (2.13 eV)
quartet



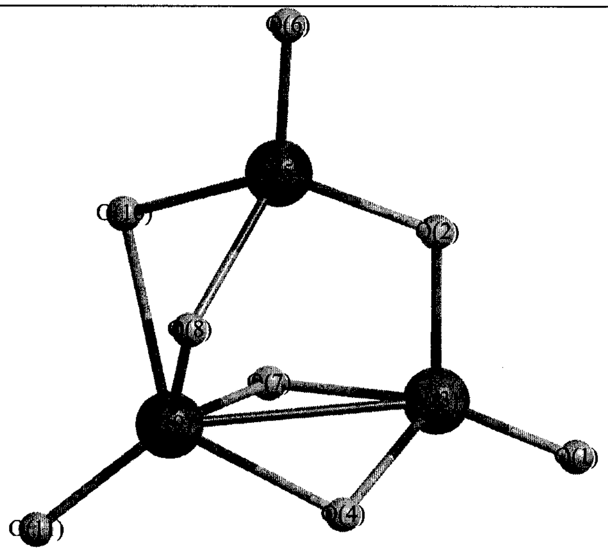
O(11)-V(9)	1.7127
O(10)-V(7)	1.7132
V(9)-O(5)	1.7306
V(9)-O(2)	1.7129
V(9)-O(8)	1.8072
O(8)-V(7)	1.8066
V(7)-O(4)	1.7304
V(7)-O(1)	1.7138
V(6)-O(5)	1.9028
V(6)-O(3)	1.6118
V(6)-O(4)	1.9029

v3o8s2s.log

```
O  -2.649902   -1.384367    1.270608
O   2.649784   -1.384516    1.270378
O   -.001136    3.692254     .001936
O  -1.521342     .937168    -.001074
O   1.521036     .937317     .000310
V   -.000127    2.080423    -.001102
V  -1.667237    -.787080    -.000159
O    .000177   -1.482468    -.000141
V   1.668202    -.786992     .000180
O  -2.650286   -1.386679   -1.268649
O   2.649260   -1.384470   -1.270262
 Zero-point correction=                          .021145 (Hartree/Particle)
 Thermal correction to Energy=                   .036178
 Thermal correction to Enthalpy=                 .037123
 Thermal correction to Gibbs Free Energy=       -.025555
```

E = -816.225385093 h (4.83 eV)
sextet

Isomer 3



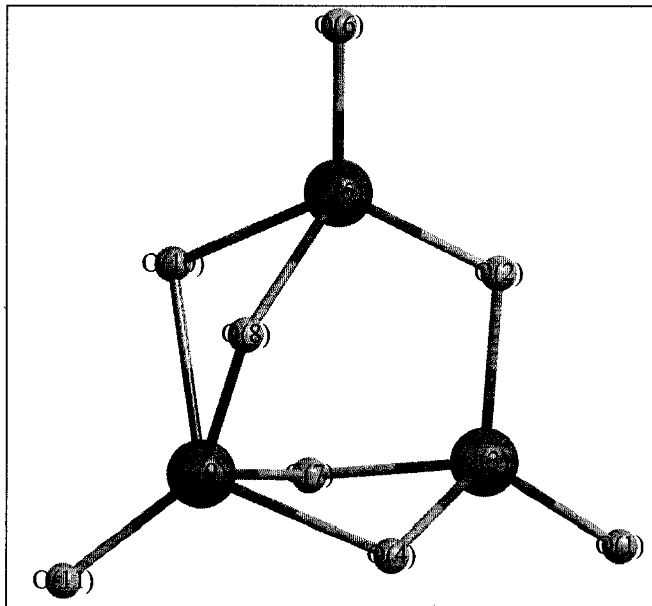
O(11)-V(9)	1.5916
O(10)-V(9)	2.0195
O(10)-V(5)	1.8276
V(9)-O(7)	1.8642
V(9)-O(4)	1.8646
V(9)-V(3)	2.5814
V(9)-O(8)	2.0174
O(8)-V(5)	1.8286
O(7)-V(3)	1.7888
O(6)-V(5)	1.6046
V(5)-O(2)	1.7753
O(4)-V(3)	1.7885
V(3)-O(1)	1.6061
V(3)-O(2)	1.8519

v3o8s3.log

```
O    2.752388   -1.870505    -.000596
O    -.263902   -1.656397    -.000197
V    1.443650    -.939556     .000227
O    1.248834     .345672   -1.228115
V   -1.685688    -.593205    -.000415
O   -3.134973   -1.281803    -.000418
O    1.248772     .345863    1.228885
O   -1.321787     .832990   -1.085509
V     .291178    1.370282     .000604
O   -1.324290     .831292    1.085940
O     .653681    2.920015    -.001187
```

E = -816.361417566 h (1.13 eV)
doublet

```
 Zero-point correction=                          .027159 (Hartree/Particle)
 Thermal correction to Energy=                   .039744
 Thermal correction to Enthalpy=                 .040688
 Thermal correction to Gibbs Free Energy=       -.012411
```

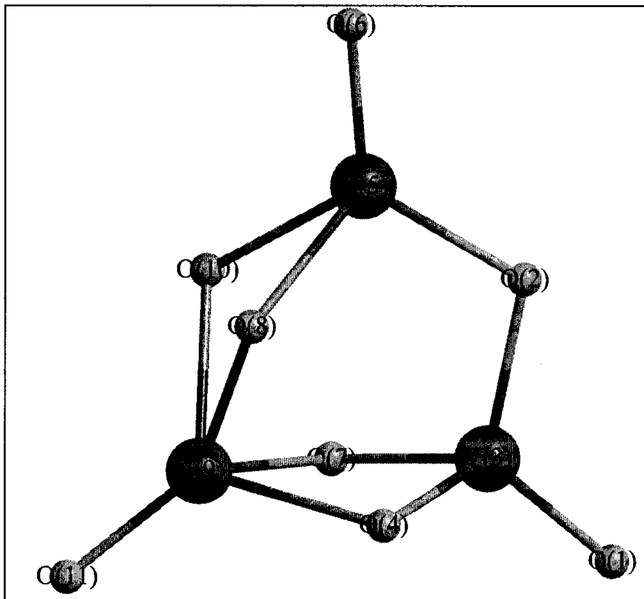


O(11)-V(9)	1.5929
O(10)-V(5)	1.8586
O(10)-V(9)	1.9910
V(9)-O(4)	1.9377
V(9)-O(8)	1.9911
V(9)-O(7)	1.9377
O(8)-V(5)	1.8587
O(7)-V(3)	1.7970
O(6)-V(5)	1.6118
V(5)-O(2)	1.7991
O(4)-V(3)	1.7970
V(3)-O(2)	1.8192
V(3)-O(1)	1.6155

v3o8s3qr1.log

```
O  -2.678257   -1.974119    -.000156
O    .314318   -1.748323     .000076
V  -1.360871   -1.038977    -.000093
O  -1.306649     .299116    1.198215
V   1.697708    -.598118     .000220
O   3.224506   -1.114661     .000331
O  -1.306576     .298996   -1.198404
O   1.240923     .859305    1.059423
V   -.331019    1.468208    -.000147
O   1.241214     .859214   -1.059105
O   -.746205    3.006022    -.000322
 Zero-point correction=                        .024816  (Hartree/Particle)
 Thermal correction to Energy=                 .038252
 Thermal correction to Enthalpy=               .039196
 Thermal correction to Gibbs Free Energy=     -.017746
```

E = -816.301265665 h (2.76 eV)
quartet



O(11)-V(9)	1.6045
O(10)-V(5)	1.9766
O(10)-V(9)	2.0197
V(9)-O(8)	2.0197
V(9)-O(7)	2.0025
V(9)-O(4)	2.0025
O(8)-V(5)	1.9766
O(7)-V(3)	1.8074
O(6)-V(5)	1.6072
V(5)-O(2)	1.8443
O(4)-V(3)	1.8074
V(3)-O(2)	1.7761
V(3)-O(1)	1.6179
V(3)-O(10)	3.2015
V(3)-O(8)	3.2015

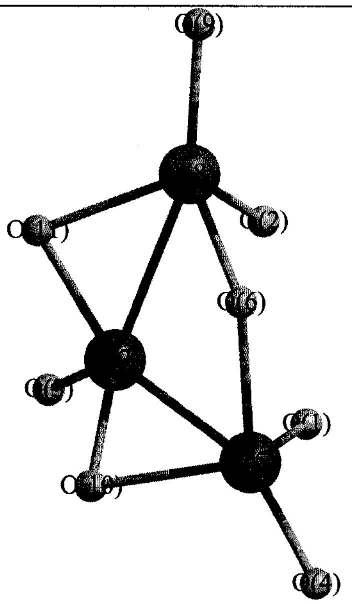
v3o8s3sr2.log

```
O  -1.840390    2.667655     .000118
O    .929336    1.679458    -.000129
V   -.825789    1.407452     .000056
O  -1.152305     .165953   -1.272313
V   1.848406     .080515    -.000199
O   3.442997    -.120203    -.000312
O  -1.152069     .166009    1.272535
O    .752963   -1.158805   -1.082382
V   -.939522   -1.365574     .000125
O    .753180   -1.158734    1.082286
O  -1.972609   -2.593213     .000249
```

E = -816.223255529 h (4.88 eV)
sextet

```
 Zero-point correction=                        .024691 (Hartree/Particle)
 Thermal correction to Energy=                 .038066
 Thermal correction to Enthalpy=               .039010
 Thermal correction to Gibbs Free Energy=     -.019206
```

Isomer 4



```
O(11)-V(7)   1.8346
O(11)-V(8)   1.8023
O(10)-V(5)   1.8033
O(10)-V(7)   1.8332
O(9)-V(8)    1.6085
V(8)-O(2)    1.8147
V(8)-V(7)    2.6641
V(8)-O(6)    1.8079
V(7)-V(5)    2.6654
V(7)-O(3)    1.5928
O(6)-V(5)    1.8090
V(5)-O(4)    1.6087
V(5)-O(1)    1.8116
O(1)-V(8)    3.1306
O(2)-V(5)    3.1265
O(1)-O(2)    2.1352
```

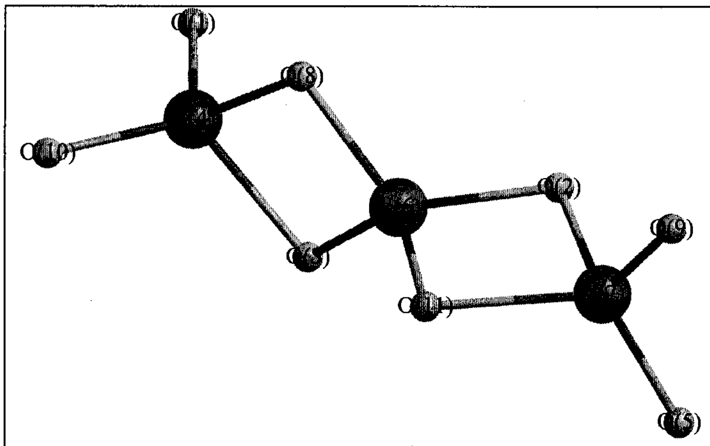
v3o8s4.log

```
O   1.070709     .310890    1.353359
O  -1.064442     .314569    1.350739
O   -.007081    3.009209     .055641
O   2.956751   -1.494882    -.002690
V   1.523459    -.765100    -.031958
O    .001921   -1.703001    -.311035
V   -.003127    1.419736    -.047673
V  -1.520884    -.769698    -.030978
O  -2.951220   -1.504719     .001264
O   1.342914     .702209   -1.064594
O  -1.347964     .696529   -1.064684
```

E = -816.366152337 h (1.00 eV)
doublet

```
 Zero-point correction=                        .027231 (Hartree/Particle)
 Thermal correction to Energy=                 .039676
 Thermal correction to Enthalpy=               .040620
 Thermal correction to Gibbs Free Energy=     -.012153
```

Isomer 5

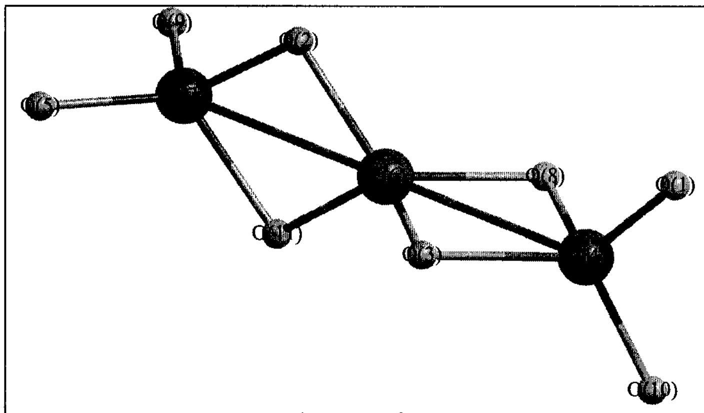


```
O(11)-V(7)   1.9062
O(11)-V(6)   1.7390
O(10)-V(4)   1.6368
O(9)-V(7)    1.6368
O(8)-V(6)    1.7390
O(8)-V(4)    1.9062
V(7)-O(5)    1.6368
V(7)-O(2)    1.9062
V(6)-O(2)    1.7390
V(6)-O(3)    1.7390
V(4)-O(3)    1.9062
V(4)-O(1)    1.6368
```

v3o8s4v2.log

```
O  -3.646724    -.939840    -.935883
O   1.230465    -.870565    -.867332
O  -1.230464    -.870400     .867498
V  -2.687610     .000001     .000001
O   3.646700    -.940313     .935434
V   -.000001    -.000006    -.000003
V   2.687613     .000003     .000001
O  -1.230461     .870391    -.867500
O   3.646733     .940304    -.935414
O  -3.646711     .939853     .935887
O   1.230455     .870578     .867312
 Zero-point correction=                          .026722 (Hartree/Particle)
 Thermal correction to Energy=                   .039612
 Thermal correction to Enthalpy=                 .040556
 Thermal correction to Gibbs Free Energy=       -.014756
```

E = -816.377200185 h (0.70 eV)
doublet



v3o8s5q.log

```
O   3.701742    -.926953    -.931332
O  -1.297964    -.868747    -.872773
O   1.297963     .872835    -.868684
V   2.664994     .000000     .000001
O  -3.701737     .931314    -.926976
V    .000000    -.000001    -.000002
V  -2.664994     .000000     .000001
O   1.297963    -.872837     .868682
O  -3.701741    -.931310     .926978
O   3.701737     .926956     .931336
O  -1.297961     .868746     .872772
```

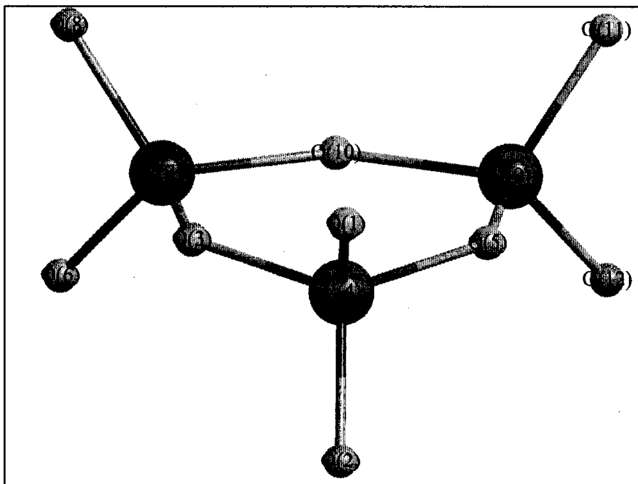
```
O(11)-V(6)   1.7892
O(11)-V(7)   1.8399
O(10)-V(4)   1.6738
O(9)-V(7)    1.6738
O(8)-V(4)    1.8399
O(8)-V(6)    1.7892
V(7)-O(2)    1.8399
V(7)-V(6)    2.6650
V(7)-O(5)    1.6738
V(6)-O(3)    1.7892
V(6)-V(4)    2.6650
V(6)-O(2)    1.7892
V(4)-O(1)    1.6738
V(4)-O(3)    1.8399
```

E = -816.311926669 h (2.47 eV)
quartet

```
 Zero-point correction=                          .024457 (Hartree/Particle)
 Thermal correction to Energy=                   .037847
 Thermal correction to Enthalpy=                 .038791
 Thermal correction to Gibbs Free Energy=       -.018343
```

V$_3$O$_9$ clusters

Isomer 1

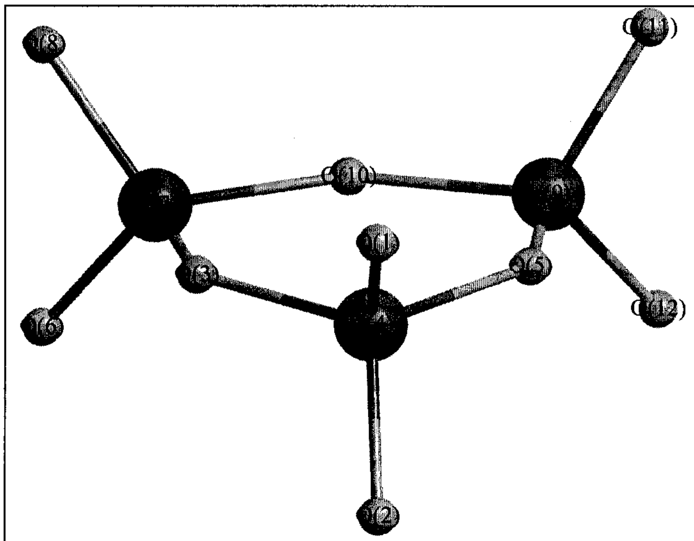


```
O(12)-V(9)   1.6726
O(11)-V(9)   1.6725
O(10)-V(9)   1.7932
O(10)-V(7)   1.7938
V(9)-O(5)    1.7935
O(8)-V(7)    1.6724
V(7)-O(3)    1.7938
V(7)-O(6)    1.6718
O(5)-V(4)    1.7937
V(4)-O(2)    1.6714
V(4)-O(1)    1.6728
V(4)-O(3)    1.7942
```

v3o9s1.log.cluster

```
O   2.155599   -2.106264   -1.269064
O   2.116168   -2.093492    1.293962
O   1.571893     .434489    -.006472
V   1.369211   -1.347937    -.002767
O   -.409058   -1.577503    -.026503
O    .749456    2.890240    1.287781
V    .481584    1.859192    -.000960
O    .757156    2.907123   -1.274481
V  -1.851145    -.511585    -.004055
O  -1.164052    1.145010    -.010517
O  -2.909492    -.800339   -1.266306
O  -2.866666    -.798314    1.293970
 Zero-point correction=                       .026808 (Hartree/Particle)
 Thermal correction to Energy=                .041849
 Thermal correction to Enthalpy=              .042793
 Thermal correction to Gibbs Free Energy=   -.017788
```

E = -891.536414929 h (1.02 eV)
doublet



O(12)-V(9)	1.6712
O(11)-V(9)	1.6715
O(10)-V(9)	1.7952
O(10)-V(7)	1.7947
V(9)-O(5)	1.7952
O(8)-V(7)	1.6716
V(7)-O(3)	1.7946
V(7)-O(6)	1.6713
O(5)-V(4)	1.7945
V(4)-O(2)	1.6711
V(4)-O(1)	1.6721
V(4)-O(3)	1.7944

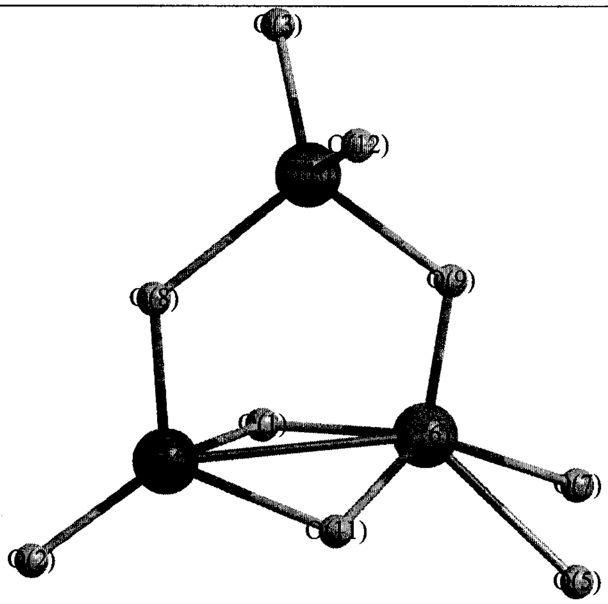
v3o9s1q.log

```
O     .207962    3.060541   -1.234625
O     .190727    2.904578    1.329892
O   -1.352502     .906639    -.072778
V     .129131    1.917322    -.016947
O    1.464404     .719392    -.064952
O   -2.702811   -1.263261    1.290772
V   -1.725216    -.847318     .000637
O   -2.669057   -1.371342   -1.275637
V    1.596282   -1.069663     .001930
O    -.109504   -1.626413     .058239
O    2.459478   -1.711279   -1.277597
O    2.510737   -1.619838    1.288030
```

E = -891.537064900 h (1.00 eV)
quartet

```
 Zero-point correction=                       .026572 (Hartree/Particle)
 Thermal correction to Energy=                .041645
 Thermal correction to Enthalpy=              .042589
 Thermal correction to Gibbs Free Energy=    -.018643
```

Isomer 2



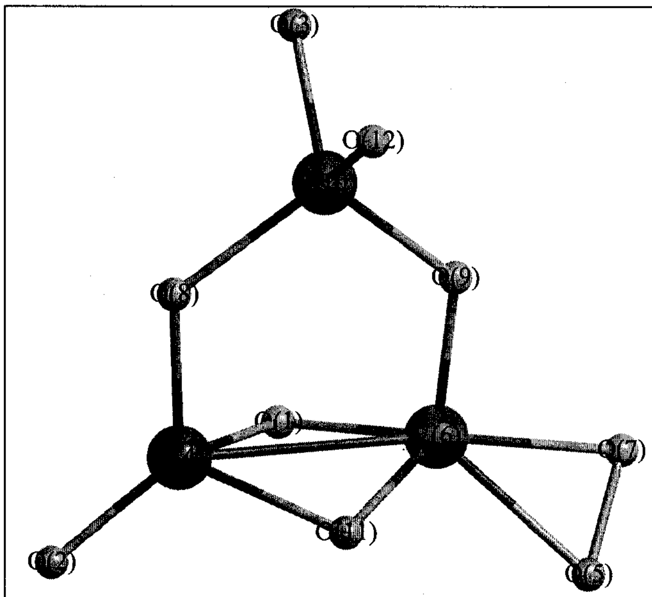
O(12)-V(10)	1.6213
O(11)-V(4)	1.8092
O(11)-V(6)	1.8427
V(10)-O(8)	1.8962
V(10)-O(3)	1.6229
V(10)-O(9)	1.9722
O(9)-V(6)	1.6802
O(8)-V(4)	1.7247
O(7)-V(6)	1.9208
V(6)-O(1)	1.7291
V(6)-V(4)	2.6425
V(6)-O(5)	2.0217
V(4)-O(2)	1.6038
V(4)-O(1)	1.9225

v3o9s2r1.log

```
O  -1.061561    .563601  -1.306035
O   -.429621   3.300013    .078866
O   2.824629  -1.113539  -1.233853
V   -.201449   1.716276   -.030309
O  -2.982936  -1.329991    .812042
V  -1.317054   -.677126   -.129192
O  -2.777944  -1.874225   -.478629
O   1.439404   1.185140   -.045709
O    .147573  -1.489318    .005630
V   1.929569   -.644810    .036137
O  -1.080562    .644811   1.132587
O   2.739204  -1.020221   1.389772
```

E = -891.547215724 h (0.73 eV)
doublet

```
 Zero-point correction=                        .030031 (Hartree/Particle)
 Thermal correction to Energy=                 .044125
 Thermal correction to Enthalpy=               .045069
 Thermal correction to Gibbs Free Energy=     -.012530
```



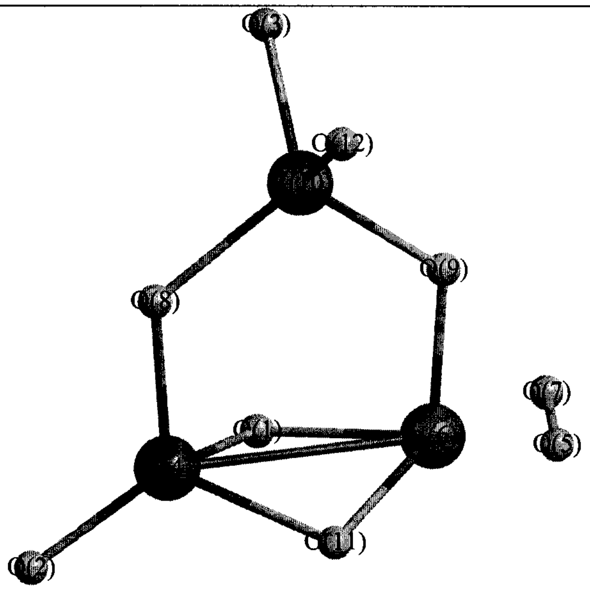
O(12)-V(10)	1.6662
O(11)-V(6)	1.8275
O(11)-V(4)	1.8106
V(10)-O(8)	1.8072
V(10)-O(9)	1.8112
V(10)-O(3)	1.6810
O(9)-V(6)	1.7890
O(8)-V(4)	1.7964
O(7)-V(6)	2.0153
O(7)-O(5)	1.4011
V(6)-O(5)	2.0115
V(6)-O(1)	1.7170
V(6)-V(4)	2.6343
V(4)-O(2)	1.6024
V(4)-O(1)	1.9461

v3o9s2q.log

```
O   1.105109    .589227   1.322224
O    .514850   3.309539   -.110114
O  -2.851764  -1.103684   1.234713
V    .205592   1.744462    .040238
O   3.052488  -1.358208   -.650124
V   1.351160   -.625798    .134221
O   2.537605  -2.245948    .303815
O  -1.488430   1.147591    .010048
O   -.249605  -1.409271   -.021402
V  -1.877800   -.616327   -.045789
O   1.120893    .690299  -1.112627
O  -2.818132  -1.063763  -1.346463
```

E = -891.499509667 h (2.03 eV)
quartet

```
 Zero-point correction=                       .028107 (Hartree/Particle)
 Thermal correction to Energy=                .042624
 Thermal correction to Enthalpy=              .043569
 Thermal correction to Gibbs Free Energy=    -.015381
```



```
O(12)-V(10)  1.6836
O(11)-V(6)   1.8429
O(11)-V(4)   1.8224
V(10)-O(8)   1.7903
V(10)-O(3)   1.6674
V(10)-O(9)   1.8227
O(9)-V(6)    1.7908
O(8)-V(4)    1.8208
O(7)-O(5)    1.2902
V(6)-O(1)    1.8755
V(6)-V(4)    2.6325
V(4)-O(2)    1.6139
V(4)-O(1)    1.7931
O(5)-V(6)    2.2035
```

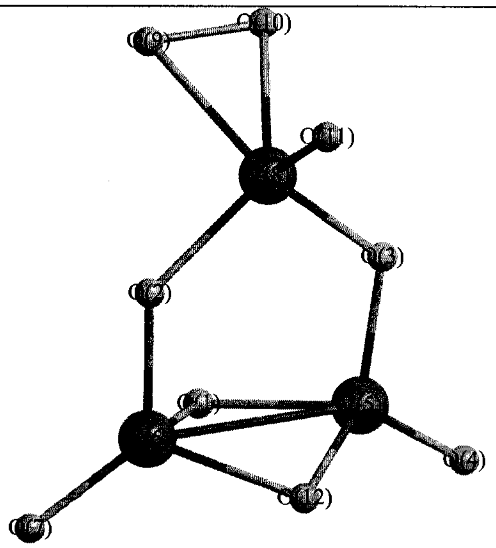
v3o9s2sr2.log

```
O  -1.222744     .706847    -.885656
O   -.086248    3.334911    -.487671
O   2.336469   -1.710874   -1.425007
V    .030010    1.760325    -.153476
O  -3.144510   -1.422261     .096696
V  -1.282866    -.377773     .643218
O  -3.689927   -1.827786   -1.000016
O   1.613107     .892966    -.391947
O    .170849   -1.411464     .484600
V   1.810416    -.860761    -.090515
O   -.605685    1.140774    1.438068
O   3.025701   -1.203262    1.023153
```

E = -891.438736426 h (3.68 eV)
sextet

```
 Zero-point correction=                       .027094 (Hartree/Particle)
 Thermal correction to Energy=                .042340
 Thermal correction to Enthalpy=              .043285
 Thermal correction to Gibbs Free Energy=    -.019654
```

Isomer 7



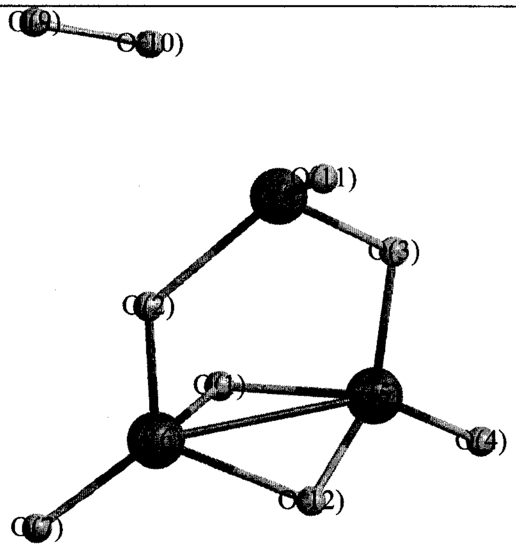
```
O(12)-V(5)   1.8193
O(12)-V(6)   1.8192
O(11)-V(8)   1.5931
O(10)-V(8)   2.0093
O(10)-O(9)   1.3968
O(9)-V(8)    2.0093
V(8)-O(3)    1.8132
V(8)-O(2)    1.8132
O(7)-V(6)    1.6036
V(6)-O(1)    1.8218
V(6)-V(5)    2.5787
V(6)-O(2)    1.7868
V(5)-O(4)    1.6036
V(5)-O(1)    1.8218
V(5)-O(3)    1.7868
```

v3o9s7.log

```
O   1.360140     .000078   -1.313067
O   -.545900   -1.411924     .254401
O   -.546054    1.411951     .254560
O   2.074725    2.634227    -.176540
V   1.212949    1.289367    -.034347
V   1.213177   -1.289287    -.034366
O   2.075081   -2.634074    -.176515
V  -1.682924    -.000079     .293095
O  -2.906627    -.698508   -1.139390
O  -2.906442     .698330   -1.139510
O  -2.497432    -.000102    1.662251
O   1.755804     .000018    1.128714
```

E = -891.573939824 h (0 eV)
doublet

```
 Zero-point correction=                           .030855 (Hartree/Particle)
 Thermal correction to Energy=                    .044641
 Thermal correction to Enthalpy=                  .045586
 Thermal correction to Gibbs Free Energy=        -.011252
```



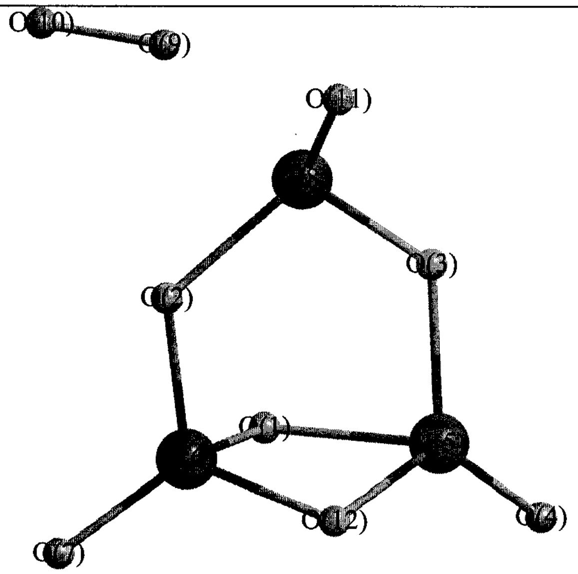
```
O(12)-V(6)   1.8315
O(12)-V(5)   1.8133
O(11)-V(8)   1.6048
O(10)-O(9)   1.2847
V(8)-O(2)    1.8593
V(8)-O(3)    1.8154
O(7)-V(6)    1.6086
V(6)-O(2)    1.7690
V(6)-O(1)    1.8332
V(6)-V(5)    2.5894
V(5)-O(1)    1.8161
V(5)-O(3)    1.7996
V(5)-O(4)    1.6065
V(8)-O(10)   2.2019
```

v3o9s7qr1.log

```
O  -1.323411     .499972   -1.304530
O    .885763    1.015756     .400992
O   -.020430   -1.725657    -.126352
O  -2.902154   -1.876183    -.617031
V  -1.639121    -.950506    -.258241
V   -.809106    1.465127     .166683
O  -1.162264    3.031346     .265961
V   1.444625    -.756176     .331090
O   3.836265     .881030   -1.183240
O   3.146505    -.174995    -.939355
O   2.180169   -1.177566    1.693708
O  -1.755088     .220767    1.121194
```

E = -891.518451772 h (1.51 eV)
quartet

```
 Zero-point correction=                           .029476 (Hartree/Particle)
 Thermal correction to Energy=                    .044240
 Thermal correction to Enthalpy=                  .045185
 Thermal correction to Gibbs Free Energy=        -.015639
```



O(12)-V(6)	1.7613
O(12)-V(5)	1.9444
O(11)-V(8)	1.6110
O(10)-O(9)	1.2842
V(8)-O(2)	1.8710
V(8)-O(3)	1.7907
O(7)-V(6)	1.6399
V(6)-O(2)	1.7716
V(6)-O(1)	1.8126
V(5)-O(1)	1.9823
V(5)-O(3)	1.8770
V(5)-O(4)	1.6106
V(8)-O(9)	2.2181

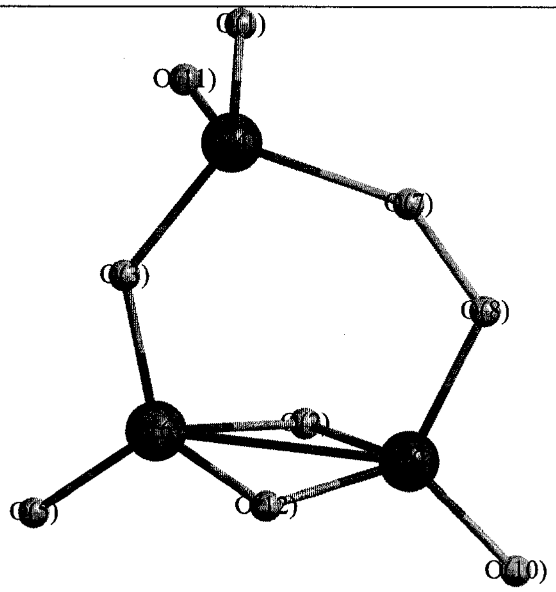
v3o9s7sr1.log

```
O  -1.070422    .492094  -1.276516
O    .953558    .999678    .531960
O   -.039706  -1.685144   -.112069
O  -3.082698  -1.697946   -.833627
V  -1.785405   -.999050   -.183461
V   -.722224   1.473734    .206989
O  -1.070008   3.075573    .156434
V   1.444749   -.796428    .349729
O   3.077139   -.180798  -1.020106
O   3.785745    .866016  -1.246564
O   2.294709  -1.373042   1.590796
O  -1.792534    .428580   1.136579
```

E = -891.430948235 h (3.98 eV)
sextet

```
 Zero-point correction=                          .026312 (Hartree/Particle)
 Thermal correction to Energy=                   .042249
 Thermal correction to Enthalpy=                 .043194
 Thermal correction to Gibbs Free Energy=       -.021478
```

Isomer 5



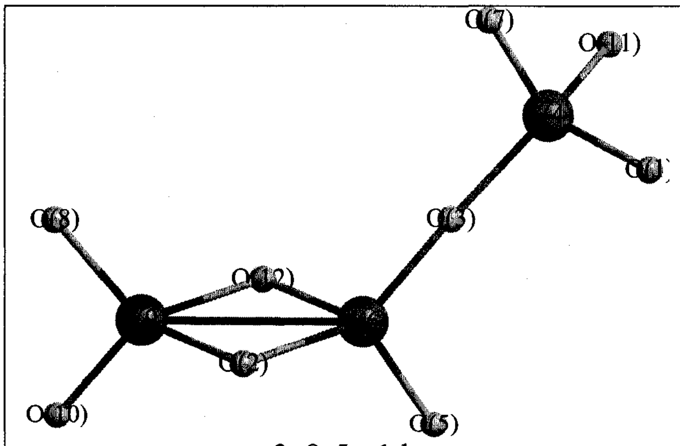
O(12)-V(9)	1.7863
O(12)-V(6)	1.8470
O(11)-V(4)	1.6312
O(10)-V(9)	1.5999
V(9)-O(2)	1.7874
V(9)-V(6)	2.6374
V(9)-O(8)	1.8894
O(8)-O(7)	1.4009
O(7)-V(4)	1.9483
V(6)-O(5)	1.6021
V(6)-O(2)	1.8461
V(6)-O(3)	1.7353
V(4)-O(3)	1.8443
V(4)-O(1)	1.6363
V(4)-V(9)	3.8509

v3o9s5r1.log

```
O  -2.926344    -.203291    1.417711
O   1.351020     .290005    1.234596
O   -.987001    1.338133    -.069883
V  -2.107077    -.125297     .003451
O   1.318568    2.995229     .011853
V    .739808    1.501563    -.017032
O  -1.097352   -1.784327    -.151069
O    .230293   -2.220329    -.051870
V   1.649118    -.973961     .006500
O   3.058556   -1.729112     .061825
O  -3.203949    -.142883   -1.203719
O   1.445891     .299948   -1.229084
```

E = -891.536293344 h (1.02 eV)
doublet

```
 Zero-point correction=                     .029618 (Hartree/Particle)
 Thermal correction to Energy=              .044027
 Thermal correction to Enthalpy=            .044972
 Thermal correction to Gibbs Free Energy=  -.013899
```



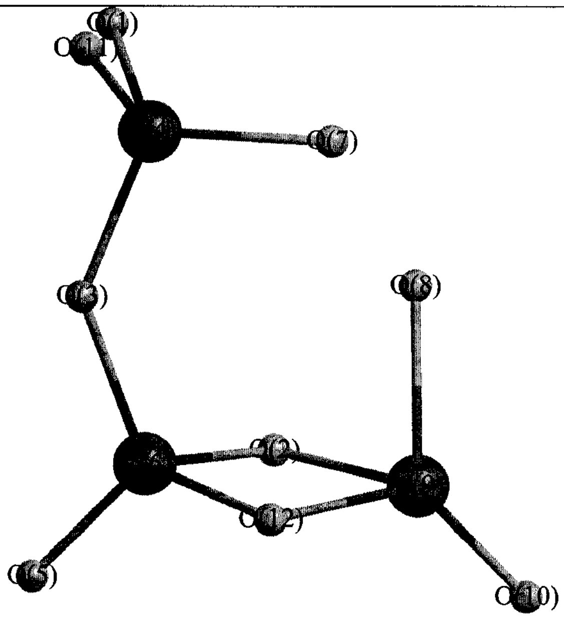
```
O(12)-V(6)   1.8091
O(12)-V(9)   1.8205
O(11)-V(4)   1.6887
O(10)-V(9)   1.6796
V(9)-O(2)    1.8183
V(9)-V(6)    2.6810
V(9)-O(8)    1.6637
O(7)-V(4)    1.7171
V(6)-O(3)    1.7706
V(6)-O(5)    1.6044
V(6)-O(2)    1.8114
V(4)-O(1)    1.7076
V(4)-O(3)    1.8014
```

v3o9s5qr1.log

```
O   3.951857    .568483   -1.029920
O  -1.630128    .226090   -1.229520
O   1.203262    .242985    -.056545
V   2.922137   -.289406     .028210
O   -.435823   2.479575    -.008143
V   -.450175    .875231    -.018107
O   3.128363  -1.896576    -.539960
O  -2.995975  -2.109319    -.004530
V  -2.774661   -.460458     .005286
O  -4.350095    .121237     .031252
O   3.590933   -.201879    1.576411
O  -1.592135    .208976    1.216713
```

E = -891.499025238 h (2.04 eV)
quartet

```
 Zero-point correction=                          .026253 (Hartree/Particle)
 Thermal correction to Energy=                   .041769
 Thermal correction to Enthalpy=                 .042713
 Thermal correction to Gibbs Free Energy=       -.021764
```



O(12)-V(6)	1.7734
O(12)-V(9)	1.8868
O(11)-V(4)	1.6761
O(10)-V(9)	1.6127
V(9)-O(2)	1.9324
V(9)-O(8)	1.9825
O(7)-V(4)	1.8058
V(6)-O(5)	1.6113
V(6)-O(2)	1.8025
V(6)-O(3)	1.8084
V(4)-O(3)	1.7709
V(4)-O(1)	1.6905
O(7)-O(8)	1.8983
V(6)-O(8)	3.1972
V(4)-O(8)	3.1213

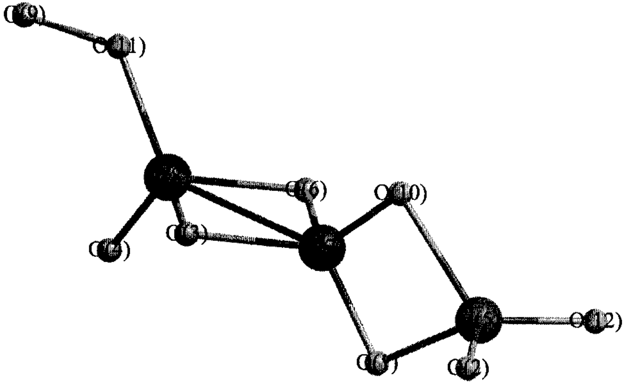
v3o9s5s.log

```
O  -3.180244    -.335190    1.403627
O   1.327790     .229620    1.228023
O  -1.146947    1.126277    -.078626
V  -2.289510    -.225832    -.029057
O   1.155181    2.879309     .197342
V    .643894    1.363433     .005018
O  -1.405047   -1.774588    -.311581
O    .377344   -1.804840     .340962
V   2.084295    -.914916    -.132847
O   3.624201   -1.333467     .100137
O  -3.518826    -.104738   -1.161896
O   1.505347     .477400   -1.266941
```

E = -891.397155657 h (4.81 eV)
sextet

```
 Zero-point correction=                          .025676 (Hartree/Particle)
 Thermal correction to Energy=                   .041131
 Thermal correction to Enthalpy=                 .042075
 Thermal correction to Gibbs Free Energy=       -.020173
```

Isomer 6



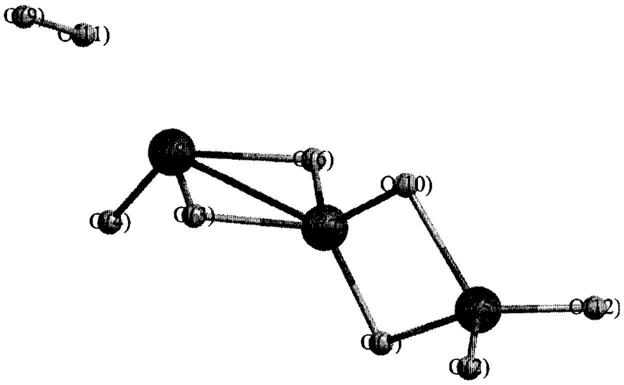
O(12)-V(5)	1.6130
O(11)-O(9)	1.3552
O(11)-V(8)	1.8549
O(10)-V(7)	1.6901
O(10)-V(5)	2.0144
V(8)-O(4)	1.5948
V(8)-O(6)	1.8301
V(8)-O(3)	1.8186
V(8)-V(7)	2.6734
V(7)-O(6)	1.7943
V(7)-O(3)	1.8028
V(7)-O(1)	1.6941
V(5)-O(1)	2.0044
V(5)-O(2)	1.6131

v3o9s6r1.log

O	-1.542520	1.216345	.174131
O	-3.928939	-.371632	1.319012
O	1.030465	-.021540	1.204664
O	3.054479	1.678648	.177205
V	-3.028950	-.117624	.004613
O	.989708	.315835	-1.216377
V	-.306964	.070631	-.000687
V	2.360120	.254550	-.004927
O	4.906119	-1.123756	.140816
O	-1.363786	-1.235755	-.181755
O	3.632134	-1.059004	-.316667
O	-3.972252	.004133	-1.298152

E = -891.530122099 h (1.19 eV)
doublet

```
 Zero-point correction=                          .030316 (Hartree/Particle)
 Thermal correction to Energy=                   .044831
 Thermal correction to Enthalpy=                 .045776
 Thermal correction to Gibbs Free Energy=       -.014628
```



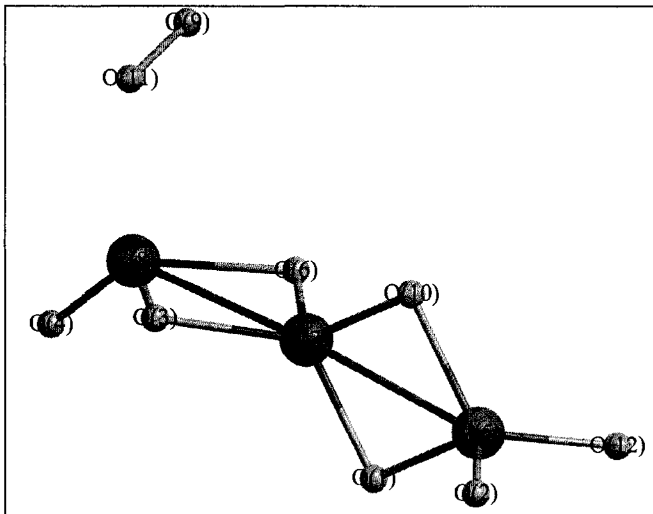
v3o9s6qr1.log

```
O   1.538402    -.938910     .776689
O   3.738591    1.130427    1.059904
O  -1.109640     .534596     .850709
O  -3.034232   -1.631146     .892653
V   2.926979     .169781     .026045
O   -.880351   -1.063439   -1.045959
V    .248771    -.138241    -.049321
V  -2.380799    -.525334    -.059735
O  -4.110689    2.085116    -.013687
O   1.353874     .947743    -.803592
O  -3.761848     .920363    -.503277
O   3.980409    -.565092    -.974785
```

```
O(12)-V(5)   1.6283
O(11)-O(9)   1.3107
O(10)-V(5)   1.9412
O(10)-V(7)   1.7232
V(8)-V(7)    2.6579
V(8)-O(3)    1.8890
V(8)-O(6)    1.8744
V(8)-O(4)    1.5990
V(7)-O(1)    1.7282
V(7)-O(3)    1.7630
V(7)-O(6)    1.7675
V(5)-O(2)    1.6280
V(5)-O(1)    1.9289
V(8)-O(11)   2.0479
V(8)-O(9)    3.1319
```

E = -891.495502904 h (2.13 eV)
quartet
(used SCF=qc, does not converge with DIIS)

```
 Zero-point correction=                           .029098 (Hartree/Particle)
 Thermal correction to Energy=                    .043906
 Thermal correction to Enthalpy=                  .044850
 Thermal correction to Gibbs Free Energy=        -.016553
```



O(12)-V(5)	1.6806
O(11)-O(9)	1.2840
O(10)-V(7)	1.8199
O(10)-V(5)	1.8130
V(8)-O(4)	1.6124
V(8)-O(6)	1.8817
V(8)-O(3)	1.8528
V(8)-V(7)	2.6584
V(7)-O(6)	1.7650
V(7)-O(3)	1.7832
V(7)-O(1)	1.8140
V(7)-V(5)	2.6762
V(5)-O(1)	1.8153
V(5)-O(2)	1.6794
V(8)-O(11)	2.2479

v3o9s2sr2.log

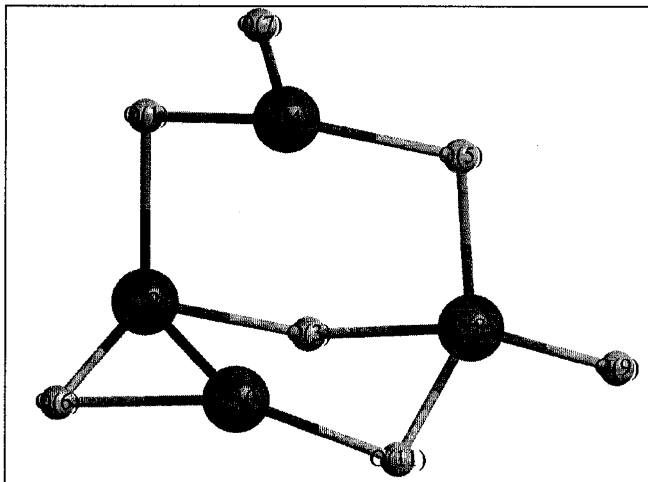
```
O  -1.222744    .706847   -.885656
O   -.086248   3.334911   -.487671
O   2.336469  -1.710874  -1.425007
V    .030010   1.760325   -.153476
O  -3.144510  -1.422261    .096696
V  -1.282866   -.377773    .643218
O  -3.689927  -1.827786  -1.000016
O   1.613107    .892966   -.391947
O    .170849  -1.411464    .484600
V   1.810416   -.860761   -.090515
O   -.605685   1.140774   1.438068
O   3.025701  -1.203262   1.023153
```

E = -891.438736426 h (3.68 eV)
sextet

```
 Zero-point correction=                         .027094 (Hartree/Particle)
 Thermal correction to Energy=                  .042340
 Thermal correction to Enthalpy=                .043285
 Thermal correction to Gibbs Free Energy=      -.019654
```

V_4O_7 clusters

Isomer 2



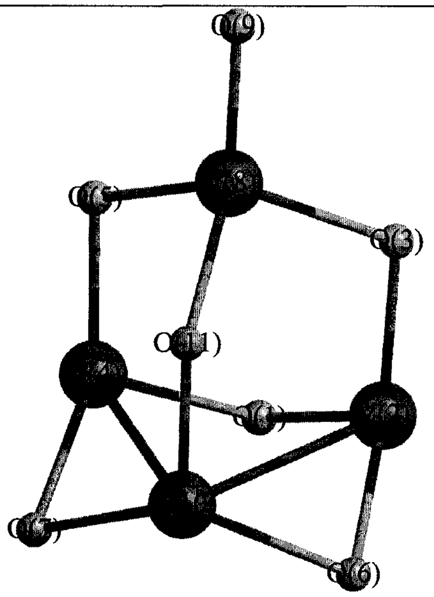
O(11)-V(8)	1.8437
O(11)-V(10)	1.7435
V(10)-V(2)	2.3466
V(10)-O(6)	1.7973
O(9)-V(8)	1.6061
V(8)-O(5)	1.8040
V(8)-O(3)	1.8280
O(7)-V(4)	1.6105
O(6)-V(2)	1.8224
O(5)-V(4)	1.8036
V(4)-O(1)	1.8249
O(3)-V(2)	1.7807
V(2)-O(1)	1.7862
V(4)-V(10)	2.6856

v4o7s2r1.log

```
O  -1.528490    .389951   -1.459273
V   -.705347  -1.136889   -1.032898
O   1.032212   -.832280   -1.275756
V   -.992403   1.365300    -.013021
O    .772626   1.733465    -.058681
O  -1.596168  -1.987411     .310248
O  -2.104570   2.304781     .675587
V   1.813192    .260018    -.035350
O   3.401016    .463748    -.164849
V   -.527989   -.932117    1.298008
O   1.209445   -.796650    1.349600
```

E = -812.612934632 h (1.58 eV)
singlet

```
 Zero-point correction=                           .026809 (Hartree/Particle)
 Thermal correction to Energy=                    .039227
 Thermal correction to Enthalpy=                  .040172
 Thermal correction to Gibbs Free Energy=        -.012197
```



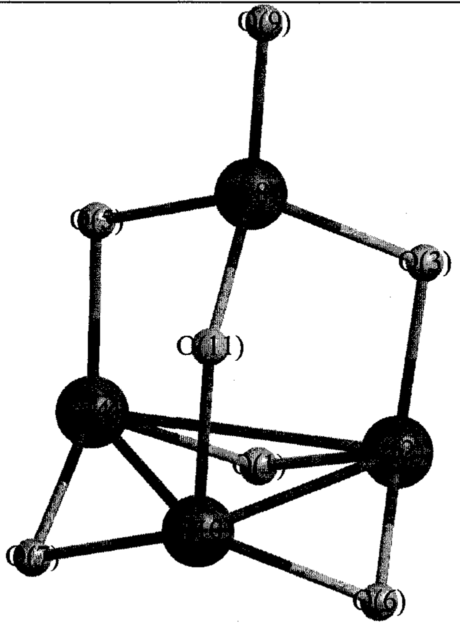
O(11)-V(10)	1.7610
O(11)-V(8)	1.8503
V(10)-O(6)	1.8185
V(10)-V(2)	2.6298
V(10)-O(7)	1.8098
V(10)-V(4)	2.6156
O(9)-V(8)	1.6086
V(8)-O(3)	1.8263
V(8)-O(5)	1.8226
O(7)-V(4)	1.8250
O(6)-V(2)	1.8149
O(5)-V(4)	1.7986
V(4)-O(1)	1.8114
O(3)-V(2)	1.7920
V(2)-O(1)	1.8063

v4o7s2trr3.log

```
O   1.456516    .112638   -1.729791
V    .777174   1.416358    -.680214
O  -1.013944   1.469071    -.703064
V    .759466  -1.311770    -.854347
O  -1.037893  -1.372628    -.878598
O   1.638533   1.433881     .917219
O   1.615589  -1.567555     .736934
V  -1.797563    .000476     .048329
O  -3.406098    .013455     .049794
V    .837773   -.104303    1.464520
O   -.911145   -.091051    1.669927
```

E = -812.661469453 h (0.26 eV)
triplet

```
 Zero-point correction=                           .025002 (Hartree/Particle)
 Thermal correction to Energy=                    .037814
 Thermal correction to Enthalpy=                  .038758
 Thermal correction to Gibbs Free Energy=        -.015256
```

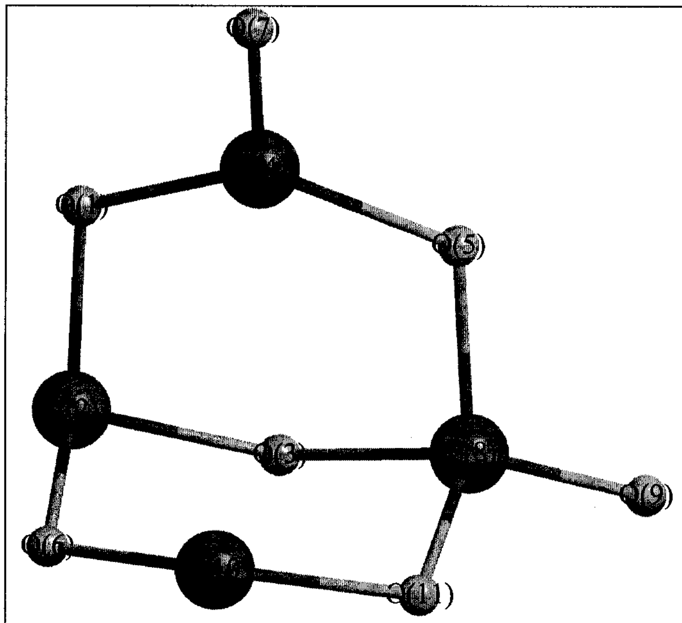


O(11)-V(10)	1.7825
O(11)-V(8)	1.8377
V(10)-V(4)	2.6741
V(10)-O(7)	1.8111
V(10)-O(6)	1.8067
V(10)-V(2)	2.6786
O(9)-V(8)	1.6084
V(8)-O(5)	1.8407
V(8)-O(3)	1.8352
O(7)-V(4)	1.8081
O(6)-V(2)	1.8132
O(5)-V(4)	1.7792
V(4)-O(1)	1.8048
V(4)-V(2)	2.6752
O(3)-V(2)	1.7857
V(2)-O(1)	1.8150

```
O   1.516489   -1.620771    .678730
V    .787887   -1.233071   -.937754
O   -.994461   -1.322487   -.999930
V    .807578    -.194494   1.527566
O   -.967344    -.201068   1.650333
O   1.496962     .223242  -1.752677
O   1.536177    1.390068   1.050623
V  -1.770843     .001186    .006618
O  -3.379230     .002029    .017276
V    .793408    1.424288   -.600810
O   -.985429    1.535000   -.631759
```

E = -812.667360659 h (0.10 eV)
quintet

```
 Zero-point correction=                        .025136 (Hartree/Particle)
 Thermal correction to Energy=                 .037817
 Thermal correction to Enthalpy=               .038761
 Thermal correction to Gibbs Free Energy=     -.015305
```



O(11)-V(10)	1.8164
O(11)-V(8)	1.7992
V(10)-O(6)	1.8367
O(9)-V(8)	1.6107
V(8)-O(3)	1.8422
V(8)-O(5)	1.8034
O(7)-V(4)	1.6144
O(6)-V(2)	1.7723
O(5)-V(4)	1.8129
V(4)-O(1)	1.8566
O(3)-V(2)	1.7798
V(2)-O(1)	1.7654
V(4)-V(10)	3.2621

v4o7s2sp.log

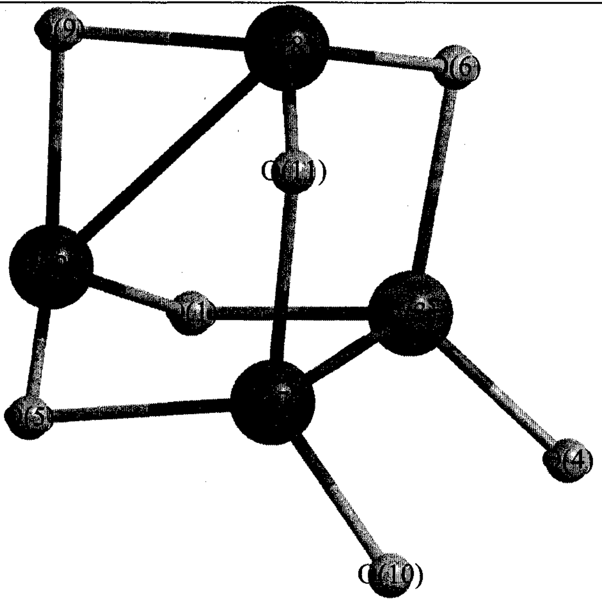
```
O   1.761877     .256638   -1.188419
V    .445638    1.425025   -1.326227
O  -1.060631     .488721   -1.475288
V   1.527784   -1.096675     .060868
O   -.132948   -1.807820    -.089918
O    .371837    2.142156     .292800
O   2.758484   -1.880892     .751342
V  -1.580001    -.737370    -.202183
O  -2.963566   -1.503526    -.507373
V   -.103835    1.154841    1.766650
O  -1.567611     .160486    1.356921
```

E = -812.610681104 h (1.64 eV)

septet

```
 Zero-point correction=                           .024875 (Hartree/Particle)
 Thermal correction to Energy=                    .038133
 Thermal correction to Enthalpy=                  .039077
 Thermal correction to Gibbs Free Energy=        -.017924
```

Isomer 4



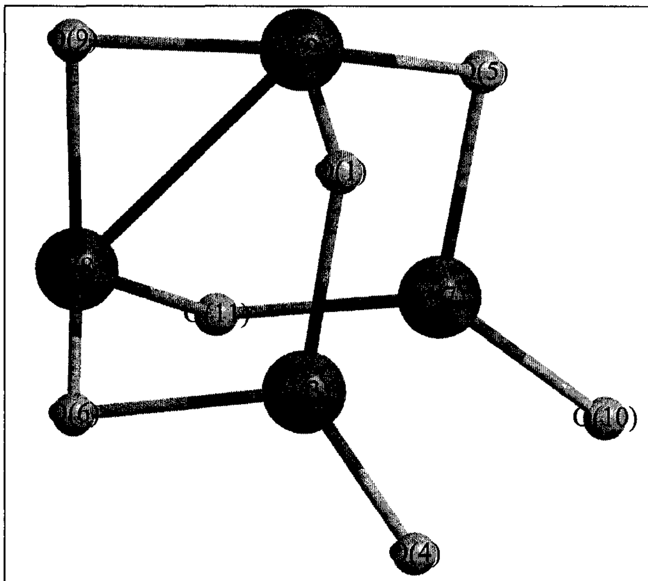
O(11)-V(8)	1.7413
O(11)-V(7)	1.8760
O(10)-V(7)	1.6024
O(9)-V(2)	1.8091
O(9)-V(8)	1.8094
V(8)-V(2)	2.6466
V(8)-O(6)	1.7413
V(7)-V(3)	2.5948
V(7)-O(5)	1.8758
O(6)-V(3)	1.8760
O(5)-V(2)	1.7412
O(4)-V(3)	1.6024
V(3)-O(1)	1.8758
V(2)-O(1)	1.7412

v4o7s4r1.log

```
O     .268546   1.523945   1.487585
V    1.095001    .000128   1.323586
V    -.850801   1.297435   -.000540
O   -2.406972   1.679568   -.000762
O     .268439  -1.523599   1.487899
O     .270501   1.524149  -1.487412
V    -.850863  -1.297401   -.000319
V    1.095968   -.000181  -1.322982
O    2.329323   -.000026    .001004
O   -2.407053  -1.679458   -.000484
O     .270465  -1.524524  -1.487098
```

E = -812.634022559 h (1.01 eV)
singlet

```
 Zero-point correction=                         .026910 (Hartree/Particle)
 Thermal correction to Energy=                  .039393
 Thermal correction to Enthalpy=                .040337
 Thermal correction to Gibbs Free Energy=      -.012082
```



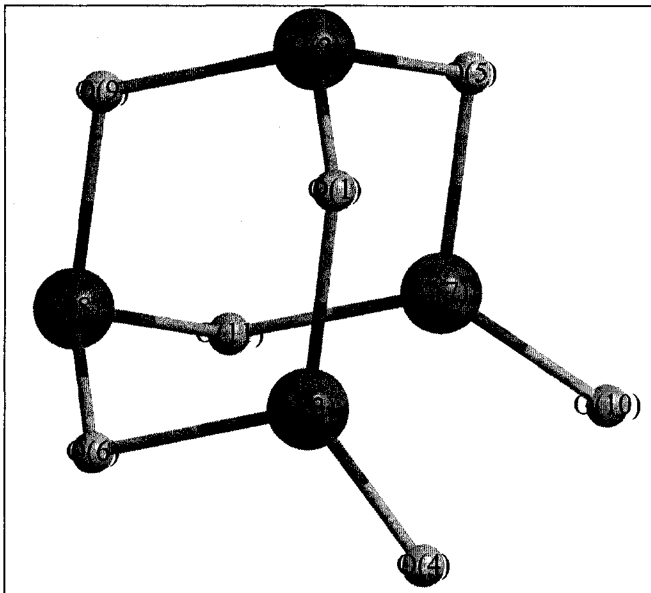
```
O(11)-V(8)   1.7545
O(11)-V(7)   1.8498
O(10)-V(7)   1.6052
O(9)-V(2)    1.8431
O(9)-V(8)    1.7795
V(8)-V(2)    2.6045
V(8)-O(6)    1.7545
V(7)-O(5)    1.8006
O(6)-V(3)    1.8498
O(5)-V(2)    1.8128
O(4)-V(3)    1.6052
V(3)-O(1)    1.8006
V(2)-O(1)    1.8128
V(3)-V(7)    2.8807
```

v4o7s4tr.log

```
O   1.510609     .031796    1.527134
V   -.000099    -.959596    1.382144
V   1.440453     .843492    -.078572
O   2.033109    2.329006    -.214812
O  -1.510611     .032090    1.527140
O   1.515801    -.409896   -1.436938
V  -1.440294     .843764    -.078573
V   -.000121   -1.262193   -1.204733
O   -.000233   -2.366012     .190990
O  -2.032619    2.329409    -.214837
O  -1.515882    -.409609   -1.436939
```

E = -812.627311947 h (1.19 eV)
triplet

```
 Zero-point correction=                           .025214 (Hartree/Particle)
 Thermal correction to Energy=                    .038466
 Thermal correction to Enthalpy=                  .039410
 Thermal correction to Gibbs Free Energy=        -.016269
```



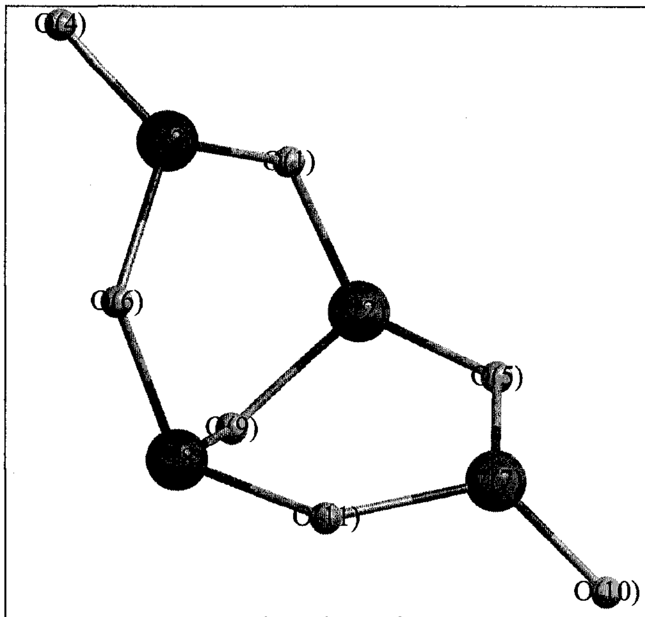
O(11)-V(7)	1.8172
O(11)-V(8)	1.7891
O(10)-V(7)	1.6048
O(9)-V(8)	1.8040
O(9)-V(2)	1.8042
V(8)-O(6)	1.7891
V(7)-O(5)	1.8171
O(6)-V(3)	1.8172
O(5)-V(2)	1.7892
O(4)-V(3)	1.6048
V(3)-O(1)	1.8171
V(2)-O(1)	1.7892
V(3)-V(7)	2.9900

v4o7s4q.log

```
O  -1.529214    -.184127   -1.525766
V   -.000128   -1.113188   -1.517983
V  -1.495007     .802671    -.000328
O  -2.074296    2.299247    -.001311
O   1.528903    -.184049   -1.526028
O  -1.528845    -.182120    1.526498
V   1.495010     .802665    -.000523
V    .000123   -1.111171    1.519036
O   -.000004   -2.086285     .001294
O   2.074312    2.299236    -.001505
O   1.529153    -.182210    1.526236
```

E = -812.626729135 h (1.21 eV)
quintet

```
 Zero-point correction=                       .024734 (Hartree/Particle)
 Thermal correction to Energy=                .038137
 Thermal correction to Enthalpy=              .039082
 Thermal correction to Gibbs Free Energy=    -.017895
```



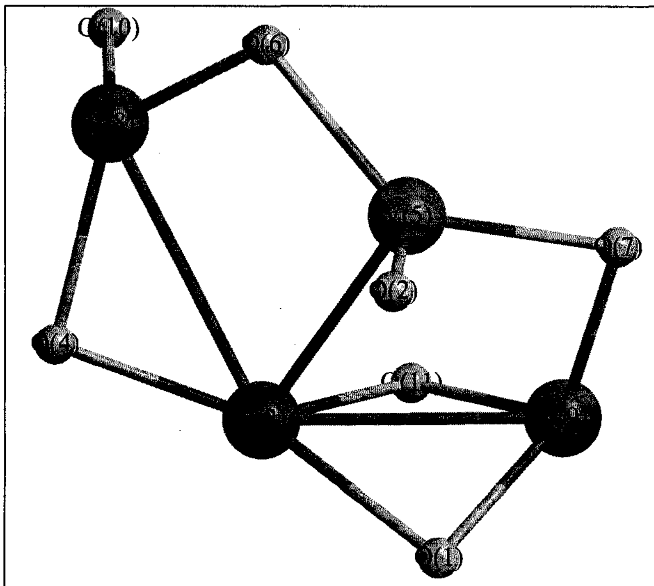
```
O(11)-V(7)   1.8261
O(11)-V(8)   1.7896
O(10)-V(7)   1.6137
O(9)-V(2)    1.7980
O(9)-V(8)    1.7980
V(8)-O(6)    1.7895
V(7)-O(5)    1.8261
O(6)-V(3)    1.8261
O(5)-V(2)    1.7896
O(4)-V(3)    1.6137
V(3)-O(1)    1.8261
V(2)-O(1)    1.7895
```

v4o7s4spr3.log

```
O   1.531069    1.489564    -.134542
V    .000000    1.576722     .787803
V   2.412824     .000000    -.716211
O   4.025869     .000000    -.762701
O  -1.531066    1.489563    -.134548
O   1.531069   -1.489564    -.134542
V  -2.412825     .000000    -.716211
V    .000000   -1.576722     .787803
O   -.000001     .000000    1.651920
O  -4.025870     .000000    -.762697
O  -1.531066   -1.489563    -.134548
```

E = -812.626559600 h (1.21 eV)
septet

Isomer 5



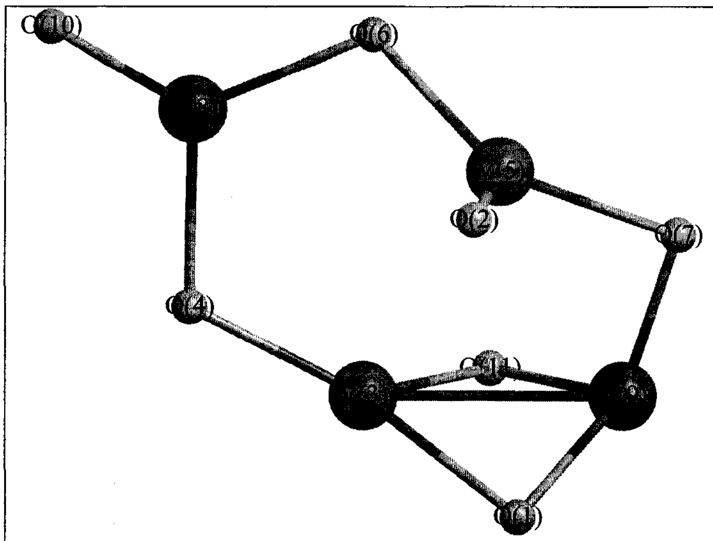
O(11)-V(9)	1.7480
O(11)-V(3)	1.9024
O(10)-V(8)	1.6039
V(9)-O(7)	1.7321
V(9)-O(1)	1.7577
V(9)-V(3)	2.4247
V(8)-V(3)	2.6789
V(8)-O(6)	1.7896
V(8)-O(4)	1.8310
O(7)-V(5)	1.9047
O(6)-V(5)	1.7920
V(5)-O(2)	1.6074
V(5)-V(3)	2.5431
O(4)-V(3)	1.7649
V(3)-O(1)	1.9210

v4o7s5r2.log

O	1.970675	-.603644	1.153998
O	.596125	2.286454	1.267751
V	.135506	-1.020618	.768507
O	-1.560595	-1.132765	1.243231
V	.238713	1.394611	-.020909
O	-1.487443	1.542976	-.478910
O	1.707118	1.058032	-1.186387
V	-2.211270	-.043598	-.076926
V	2.076556	-.528965	-.598941
O	-2.751662	-.844028	-1.357440
O	.837202	-1.736134	-.848469

E = -812.593866056 h (2.10 eV)
singlet

```
 Zero-point correction=                           .026624 (Hartree/Particle)
 Thermal correction to Energy=                    .039374
 Thermal correction to Enthalpy=                  .040318
 Thermal correction to Gibbs Free Energy=        -.013521
```



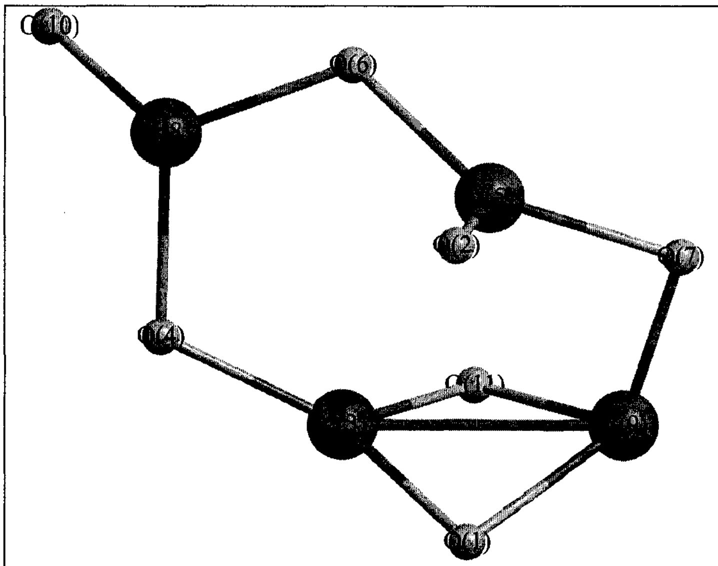
O(11)-V(9)	1.7652
O(11)-V(3)	1.8898
O(10)-V(8)	1.6083
V(9)-O(7)	1.7470
V(9)-O(1)	1.7496
V(9)-V(3)	2.3808
V(8)-O(6)	1.8084
V(8)-O(4)	1.8166
O(7)-V(5)	1.8699
O(6)-V(5)	1.7910
V(5)-O(2)	1.6032
O(4)-V(3)	1.7895
V(3)-O(1)	1.9376
V(3)-V(5)	2.7143

v4o7s5tr.log

```
O   2.118940   -.789690    1.222583
O   -.080009   1.830579    1.576933
V    .447161  -1.278666     .373843
O  -1.321492  -1.511336     .515629
V    .068128   1.388623     .042962
O  -1.513437   1.229607    -.782297
O   1.813482   1.540540    -.610580
V  -2.376973   -.289756    -.317266
V   2.376893   -.094354    -.362032
O  -3.936106   -.204498     .067845
O   1.437398  -1.307012   -1.235450
```

E = -812.600177661 h (1.93 eV)
triplet

```
 Zero-point correction=                        .025398 (Hartree/Particle)
 Thermal correction to Energy=                 .038829
 Thermal correction to Enthalpy=               .039774
 Thermal correction to Gibbs Free Energy=     -.017504
```



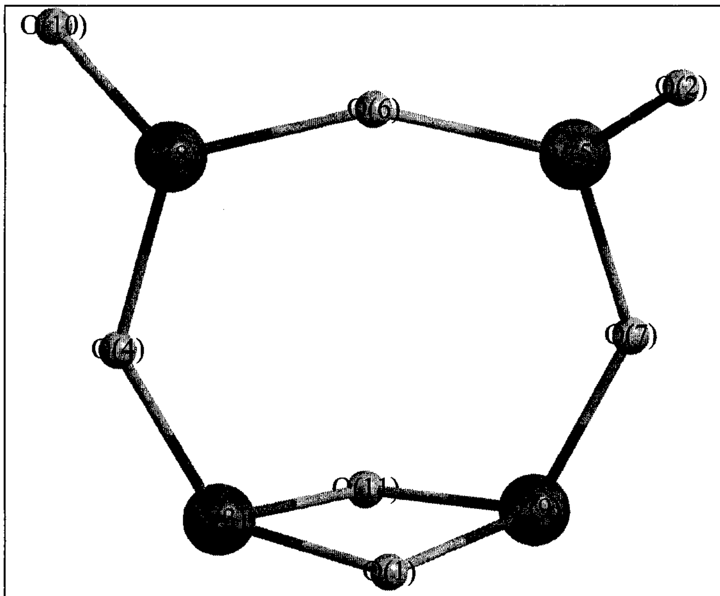
```
O(11)-V(3)   1.7524
O(11)-V(9)   1.9011
O(10)-V(8)   1.6112
V(9)-O(7)    1.7688
V(9)-O(1)    1.9239
V(9)-V(3)    2.4932
V(8)-O(6)    1.7997
V(8)-O(4)    1.8255
O(7)-V(5)    1.8641
O(6)-V(5)    1.8104
V(5)-O(2)    1.6042
O(4)-V(3)    1.7882
V(3)-O(1)    1.7575
V(5)-O(11)   3.1624
V(3)-V(5)    2.7908
O(1)-V(5)    3.1195
```

v4o7s5q.log

```
O   1.815773   -1.059064    1.192821
O    .356229    1.934055    1.581823
V    .283778   -1.344802     .380331
O  -1.474214   -1.388206     .704938
V    .310502    1.427516     .060428
O  -1.380034    1.338533    -.581275
O   1.987204    1.434788    -.754200
V  -2.428382    -.016316    -.029759
V   2.365121    -.270294    -.473712
O  -3.842716    -.293140    -.750151
O   1.011077   -1.380766   -1.213656
```

E = -812.596304296 h (2.03 eV)
quintet

```
 Zero-point correction=                      .024773 (Hartree/Particle)
 Thermal correction to Energy=               .038427
 Thermal correction to Enthalpy=             .039371
 Thermal correction to Gibbs Free Energy=   -.018580
```



O(11)-V(9)	1.8199
O(11)-V(3)	1.8205
O(10)-V(8)	1.6136
V(9)-O(1)	1.8203
V(9)-O(7)	1.7980
V(8)-O(4)	1.8039
V(8)-O(6)	1.8019
O(7)-V(5)	1.8065
O(6)-V(5)	1.8016
V(5)-O(2)	1.6137
O(4)-V(3)	1.8007
V(3)-O(1)	1.8183

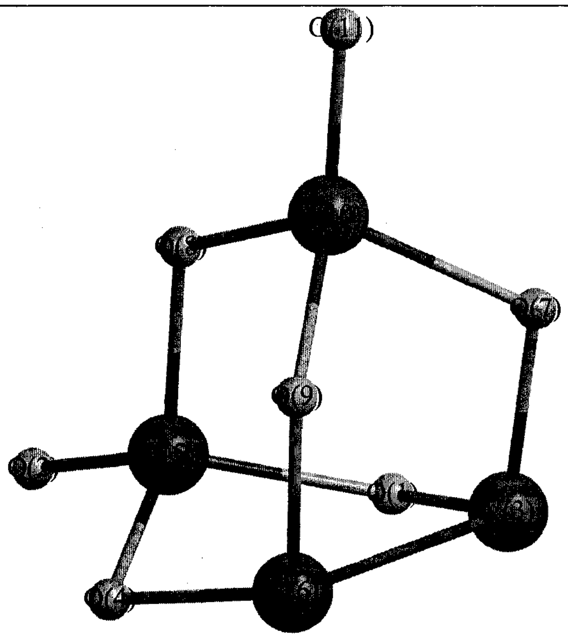
v4o7s5sp.log

```
O   1.957484    -.379422    1.169628
O  -1.509170    3.314553     .743571
V   1.379417   -1.815897     .216467
O   -.378428   -2.190305     .327074
V   -.909680    2.096308    -.128420
O  -1.791135     .525688    -.086106
O    .887337    2.051913    -.308004
V  -1.909993   -1.260866     .116346
V   2.160629     .785957    -.213853
O  -3.104198   -2.026486    -.652662
O   1.867036    -.736761   -1.166301
```

E = -812.600403592 h (1.92 eV)
septet

```
 Zero-point correction=                        .023976 (Hartree/Particle)
 Thermal correction to Energy=                 .038055
 Thermal correction to Enthalpy=               .038999
 Thermal correction to Gibbs Free Energy=     -.021885
```

Isomer 9



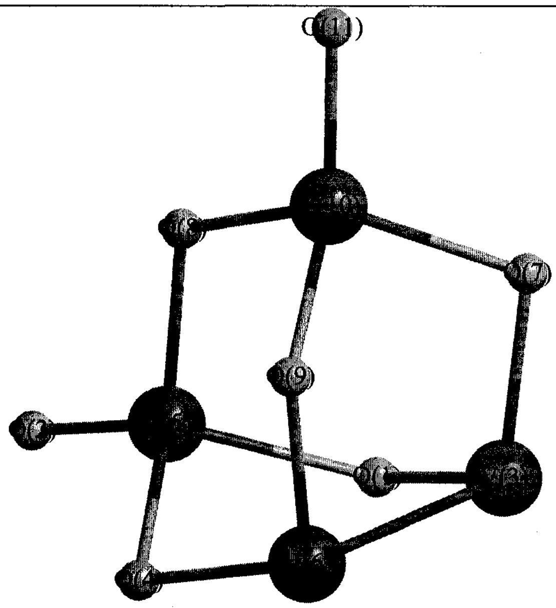
O(11)-V(10)	1.6080
V(10)-O(8)	1.8185
V(10)-O(7)	1.8429
V(10)-O(9)	1.8429
O(9)-V(6)	1.7489
O(8)-V(5)	1.8096
O(7)-V(3)	1.7489
V(6)-O(4)	1.7613
V(6)-V(3)	2.3369
V(5)-O(2)	1.6090
V(5)-O(1)	1.8481
V(5)-O(4)	1.8481
V(3)-O(1)	1.7613

v4o7s9.log

```
O   1.409402    -.255620    1.522212
O   2.841031    1.702084    -.000003
V    .091639   -1.369392    1.168457
O   1.409417    -.255642   -1.522201
V   1.517703     .786857    -.000001
V    .091632   -1.369391   -1.168456
O  -1.437055    -.529420    1.295359
O   -.045297    1.698730    -.000003
O  -1.437049    -.529398   -1.295375
V  -1.608792     .770098     .000003
O  -3.005472    1.567022     .000002
```

E = -812.595268517 h (2.06 eV)
singlet

```
 Zero-point correction=                     .026842 (Hartree/Particle)
 Thermal correction to Energy=              .039155
 Thermal correction to Enthalpy=            .040099
 Thermal correction to Gibbs Free Energy=  -.011897
```

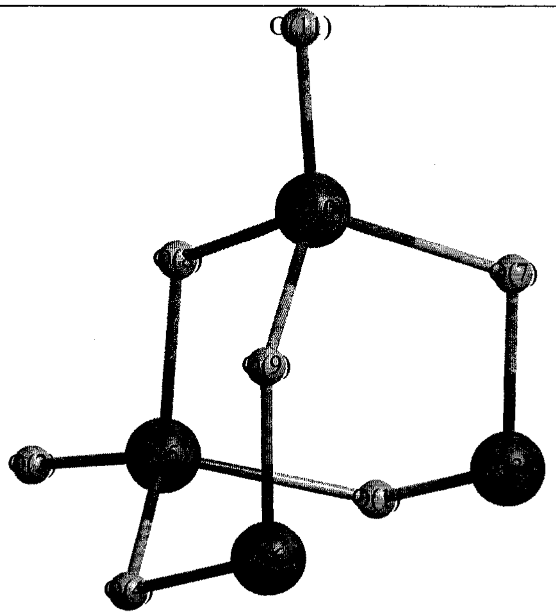


O(11)-V(10)	1.6095
V(10)-O(8)	1.8120
V(10)-O(7)	1.8161
V(10)-O(9)	1.8161
O(9)-V(6)	1.7882
O(8)-V(5)	1.8115
O(7)-V(3)	1.7882
V(6)-O(4)	1.7882
V(6)-V(3)	2.2822
V(5)-O(2)	1.6095
V(5)-O(1)	1.8161
V(5)-O(4)	1.8161
V(3)-O(1)	1.7882

v4o7s9tr.log

```
O   1.466095    -.398003    1.372159
O   2.894867    1.695253     .000003
V    .000115   -1.395573    1.141109
O   1.466098    -.398004   -1.372156
V   1.565667     .787597     .000001
V    .000117   -1.395573   -1.141108
O  -1.465255    -.397227    1.372952
O   -.000029    1.698713     .000000
O  -1.465252    -.397227   -1.372956
V  -1.566027     .787218    -.000001
O  -2.896156    1.693449    -.000003
 Zero-point correction=                        .026925 (Hartree/Particle)
 Thermal correction to Energy=                 .039145
 Thermal correction to Enthalpy=               .040089
 Thermal correction to Gibbs Free Energy=     -.012511
```

E = -812.606750422 h (1.75 eV)
triplet



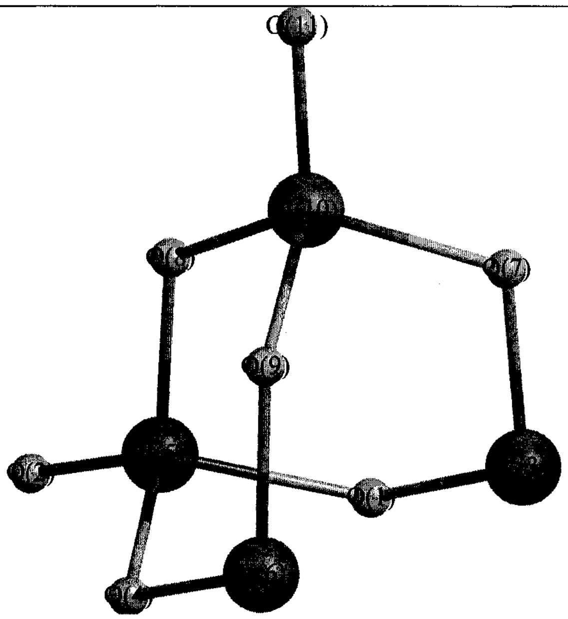
O(11)-V(10)	1.6072
V(10)-O(9)	1.8647
V(10)-O(7)	1.8647
V(10)-O(8)	1.8042
O(9)-V(6)	1.7420
O(8)-V(5)	1.8042
O(7)-V(3)	1.7420
V(6)-O(4)	1.7420
V(5)-O(4)	1.8647
V(5)-O(1)	1.8647
V(5)-O(2)	1.6072
V(3)-O(1)	1.7420
V(3)-V(6)	2.8414

v4o7s9qr1.log

```
O   -1.471175    -.407733   -1.461995
O   -2.857328    1.741957     .000001
V     .000000   -1.339737   -1.420707
O   -1.471178    -.407730    1.461991
V   -1.598408     .742772    -.000002
V     .000000   -1.339732    1.420714
O    1.471175    -.407733   -1.461995
O     .000000    1.579544     .000001
O    1.471178    -.407730    1.461991
V    1.598408     .742772    -.000002
O    2.857328    1.741957     .000000
```

E = -812.613393816 h (1.57 eV)
quintet

```
 Zero-point correction=                       .025415 (Hartree/Particle)
 Thermal correction to Energy=                .038347
 Thermal correction to Enthalpy=              .039291
 Thermal correction to Gibbs Free Energy=    -.015627
```



O(11)-V(10)	1.6107
V(10)-O(9)	1.8177
V(10)-O(7)	1.8177
V(10)-O(8)	1.8067
O(9)-V(6)	1.8023
O(8)-V(5)	1.8064
O(7)-V(3)	1.8023
V(6)-O(4)	1.8020
V(5)-O(4)	1.8179
V(5)-O(1)	1.8179
V(5)-O(2)	1.6107
V(3)-O(1)	1.8020
V(3)-V(6)	3.0642

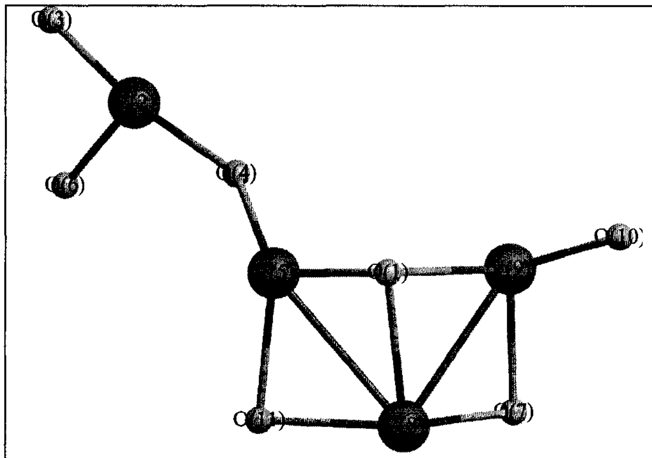
v4o7s9sp.log

```
O  -1.488671    -.374523   -1.409762
O  -2.906253    1.704802    -.000002
V    .000278   -1.382045   -1.532118
O  -1.488673    -.374526    1.409756
V  -1.595847     .768243    -.000002
V    .000278   -1.382045    1.532119
O   1.489332    -.373932   -1.410168
O   -.000304    1.615095     .000000
O   1.489330    -.373929    1.410173
V   1.595580     .768082     .000002
O   2.904405    1.706834     .000002
```

E = -812.601748473 h (1.89 eV)
septet

```
 Zero-point correction=                        .025089 (Hartree/Particle)
 Thermal correction to Energy=                 .038199
 Thermal correction to Enthalpy=               .039143
 Thermal correction to Gibbs Free Energy=     -.016806
```

Isomer 10



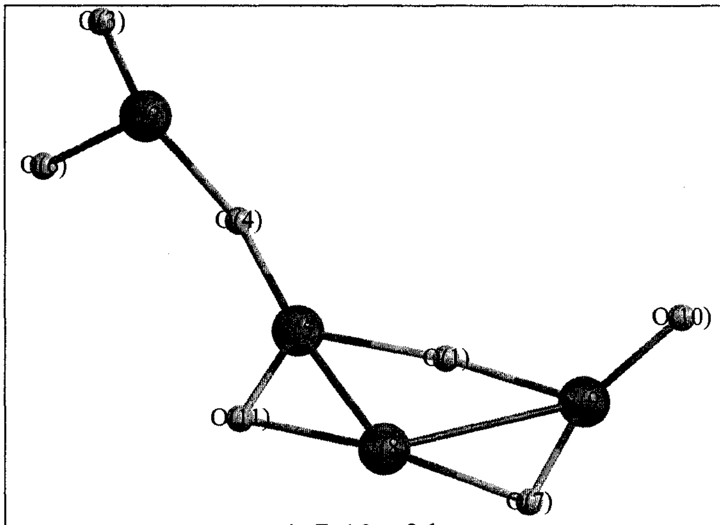
O(11)-V(5)	1.7946
O(11)-V(8)	1.8309
O(10)-V(9)	1.6146
V(9)-O(7)	1.8695
V(9)-O(1)	1.9575
V(9)-V(8)	2.3172
V(8)-O(7)	1.7692
V(8)-O(1)	2.0449
V(8)-V(5)	2.4340
O(6)-V(2)	1.6241
V(5)-O(1)	1.8132
V(5)-O(4)	1.7534
O(4)-V(2)	1.8242
O(3)-V(2)	1.6257

v4o7s10r4.log

O	1.433658	-.241399	-1.321632
V	-3.316880	-.440565	.326381
O	-4.238251	-.723696	-.982693
O	-1.532018	-.346138	-.038393
V	-.114305	.456965	-.686100
O	-3.906071	.802913	1.189147
O	2.562664	.301173	1.443342
V	2.111449	1.184279	-.021766
V	2.011630	-1.102614	.338465
O	3.200564	-2.108088	-.088511
O	.490259	2.033296	-.077576

E = -812.507263843 h (4.46 eV)
singlet

```
 Zero-point correction=                         .025140 (Hartree/Particle)
 Thermal correction to Energy=                  .038997
 Thermal correction to Enthalpy=                .039941
 Thermal correction to Gibbs Free Energy=      -.019780
```



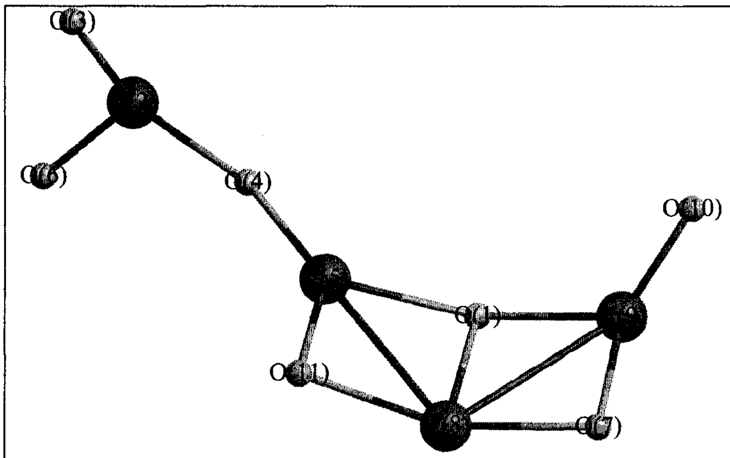
O(11)-V(8)	1.9372
O(11)-V(5)	1.7373
O(10)-V(9)	1.6126
V(9)-O(7)	1.7961
V(9)-V(8)	2.6195
V(9)-O(1)	1.8790
V(8)-O(7)	1.8724
V(8)-V(5)	2.6592
O(6)-V(2)	1.6242
V(5)-O(1)	1.8539
V(5)-O(4)	1.7552
O(4)-V(2)	1.8308
O(3)-V(2)	1.6244

v4o7s10trr3.log

```
O   1.245259    .427560   -.371409
V  -3.806285    .564469   -.010217
O  -4.301045    .571947   1.536934
O  -2.016483    .256591   -.242116
V   -.400657   -.424126   -.321681
O  -4.777076   -.365785   -.921464
O   3.713533   -.639586    .050046
V   2.001690  -1.322782    .379910
V   3.036326    .989414   -.287072
O   3.545012   2.295547    .510316
O    .201461  -1.991328    .124990
```

E = -812.534407642 h (3.72 eV)
triplet

```
 Zero-point correction=                          .023446 (Hartree/Particle)
 Thermal correction to Energy=                   .038218
 Thermal correction to Enthalpy=                 .039162
 Thermal correction to Gibbs Free Energy=       -.025592
```



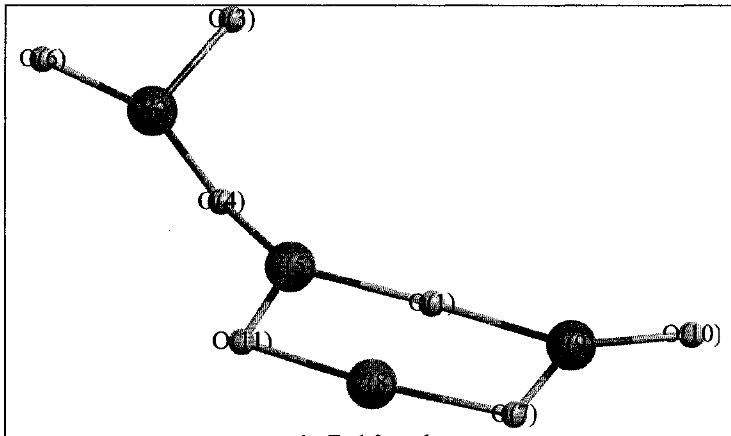
v4o7s10q.log

```
O   1.278940    .327198   -.596205
V  -3.805124    .528384   -.083111
O  -4.449053    .485035   1.407222
O  -2.003991    .318655   -.137135
V   -.381479   -.396283   -.027234
O  -4.625830   -.441540  -1.095265
O   3.732590.  -.521681    .116316
V   2.087352  -1.416581    .074461
V   2.966292   1.061319   -.271846
O   3.239627   2.382344    .613385
O    .334976  -1.908424    .576408
```

```
O(11)-V(8)   1.8880
O(11)-V(5)   1.7788
O(10)-V(9)   1.6135
V(9)-O(7)    1.8010
V(9)-V(8)    2.6519
V(9)-O(1)    1.8685
V(8)-O(7)    1.8733
V(8)-O(1)    2.0357
V(8)-V(5)    2.6733
O(6)-V(2)    1.6244
V(5)-O(1)    1.8985
V(5)-O(4)    1.7764
O(4)-V(2)    1.8141
O(3)-V(2)    1.6241
```

E = -812.544046297 h (3.46 eV)
quintet

```
 Zero-point correction=                           .023484 (Hartree/Particle)
 Thermal correction to Energy=                    .038176
 Thermal correction to Enthalpy=                  .039120
 Thermal correction to Gibbs Free Energy=        -.025278
```



```
O(11)-V(8)   1.8337
O(11)-V(5)   1.8039
O(10)-V(9)   1.6196
V(9)-O(7)    1.8330
V(9)-O(1)    1.8881
V(8)-O(7)    1.8258
O(6)-V(2)    1.6284
V(5)-O(1)    1.8604
V(5)-O(4)    1.7746
O(4)-V(2)    1.8126
O(3)-V(2)    1.6284
O(1)-V(8)    2.1015
```

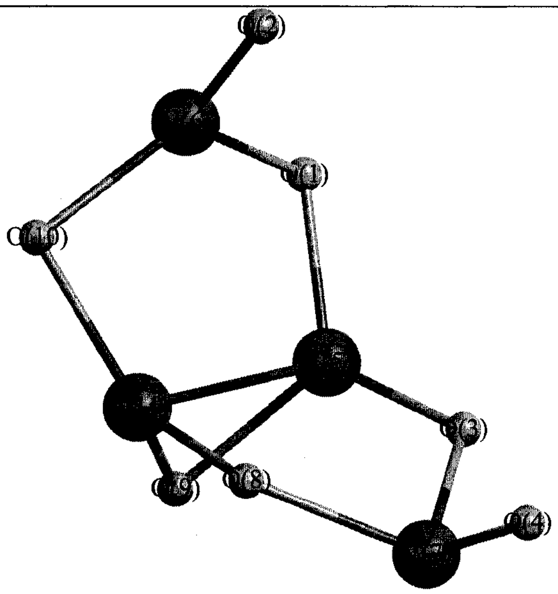
v4o7s10sp.log

```
O   1.218651     .366242    -.038396
V  -3.887059     .369142    -.206921
O  -4.154283    1.844894     .427543
O  -2.132399    -.062390    -.349686
V   -.427620    -.496815    -.117054
O  -4.795450    -.767092     .524806
O   3.683117    -.522117     .138041
V   2.150348   -1.513030     .090818
V   2.935355    1.148513     .038899
O   3.545600    2.645227    -.064076
O    .418070   -2.089718    -.079742
```

E = -812.542580603 h (3.50 eV)
septet

```
 Zero-point correction=                       .022568 (Hartree/Particle)
 Thermal correction to Energy=                .037697
 Thermal correction to Enthalpy=              .038642
 Thermal correction to Gibbs Free Energy=    -.027475
```

Isomer 11

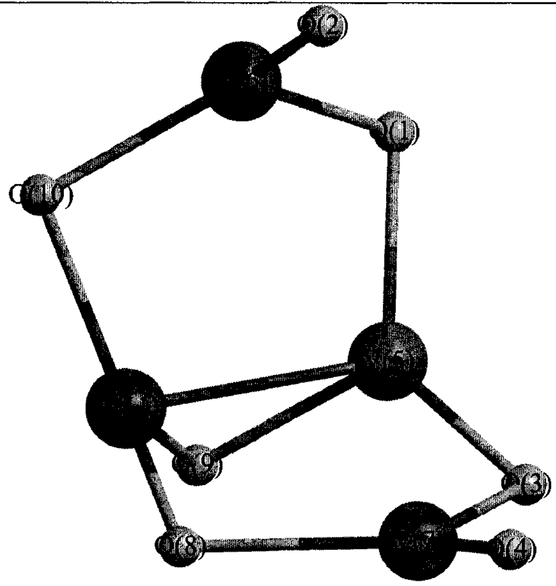


```
V(11)-O(8)   1.8001
V(11)-V(5)   2.2262
V(11)-O(9)   1.8277
V(11)-O(10)  1.8107
O(10)-V(6)   1.8075
O(9)-V(5)    1.8276
O(8)-V(7)    1.7962
V(7)-O(4)    1.6041
V(7)-O(3)    1.7960
V(6)-O(2)    1.6044
V(6)-O(1)    1.8075
V(5)-O(3)    1.8002
V(5)-O(1)    1.8106
```

v4o7s11.log

```
O  -1.847857   -.121265  -1.574501
O  -2.073137   2.290338   -.001029
O   1.337848    .133019  -1.280997
O   3.354353   1.630922   -.000458
V   -.217115   -.758366  -1.112915
V  -2.205674    .691456   -.000152
V   2.593858    .218554   -.000093
O   1.337810    .133576   1.281059
O   -.128869  -2.204850    .000634
O  -1.847646   -.119706   1.574925
V   -.217157   -.757570   1.113288
 Zero-point correction=                       .026422 (Hartree/Particle)
 Thermal correction to Energy=                .039104
 Thermal correction to Enthalpy=              .040048
 Thermal correction to Gibbs Free Energy=    -.013956
```

E = -812.608671217 h (1.70 eV)
singlet



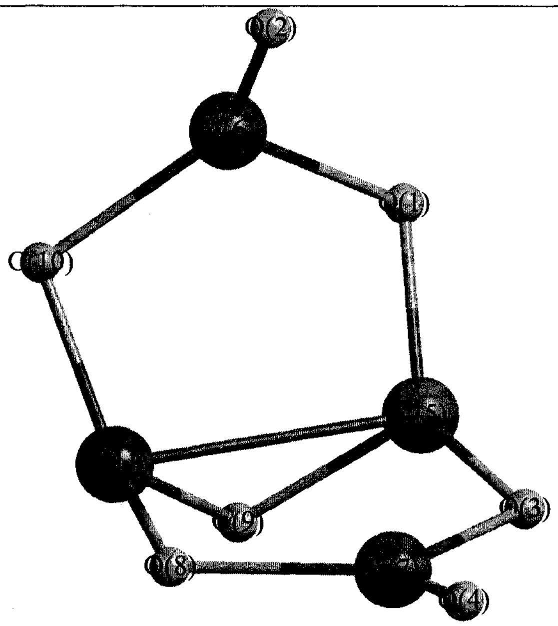
V(11)-O(8)	1.7428
V(11)-V(5)	2.3185
V(11)-O(9)	1.8205
V(11)-O(10)	1.8135
O(10)-V(6)	1.8036
O(9)-V(5)	1.8205
O(8)-V(7)	1.8773
V(7)-O(4)	1.6061
V(7)-O(3)	1.8773
V(6)-O(2)	1.6062
V(6)-O(1)	1.8036
V(5)-O(3)	1.7428
V(5)-O(1)	1.8134
V(6)-V(7)	4.1346

v4o7s11trr1.log

```
O   -1.750073    .050162   -1.564232
O   -1.376103   2.442230    -.000101
O    1.392914   -.368699   -1.535918
O    3.163815   1.640974    -.000075
V    -.235751   -.861618   -1.159240
V   -1.921741    .931557    -.000041
V    2.175258    .375158    -.000006
O    1.392910   -.368560    1.535956
O    -.446627  -2.249284     .000090
O   -1.750112    .050334    1.564216
V    -.235757   -.861500    1.159309
```

E = -812.630670370 h (1.10 eV)
triplet

```
 Zero-point correction=                          .025545 (Hartree/Particle)
 Thermal correction to Energy=                   .038839
 Thermal correction to Enthalpy=                 .039783
 Thermal correction to Gibbs Free Energy=       -.017647
```

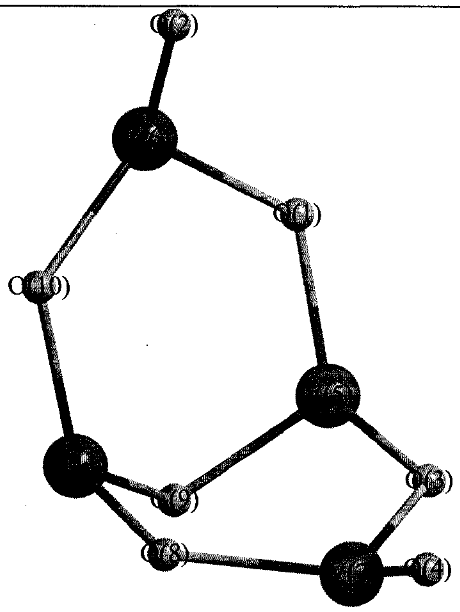


V(11)-V(5)	2.6426
V(11)-O(9)	1.8037
V(11)-O(8)	1.7710
V(11)-O(10)	1.7631
O(10)-V(6)	1.8442
O(9)-V(5)	1.8037
O(8)-V(7)	1.8366
V(7)-O(4)	1.6099
V(7)-O(3)	1.8366
V(6)-O(2)	1.6058
V(6)-O(1)	1.8442
V(5)-O(3)	1.7710
V(5)-O(1)	1.7631

v4o7s11qv2.log

```
O  -1.742135    1.570384    -.087452
O  -1.891738    -.000018    2.409409
O   1.424715    1.536342    -.152323
O   3.425584    -.000012    1.528135
V   -.180938    1.321301    -.867905
V  -2.087891    -.000006     .815592
V   2.234575    -.000004     .445015
O   1.424714   -1.536340    -.152345
O   -.280320     .000016   -2.091684
O  -1.742136   -1.570382    -.087475
V   -.180939   -1.321288    -.867924
 Zero-point correction=                     .024549 (Hartree/Particle)
 Thermal correction to Energy=              .038196
 Thermal correction to Enthalpy=            .039140
 Thermal correction to Gibbs Free Energy=  -.019308
```

E = -812.628642767 h (1.15 eV)
quintet



```
V(11)-O(8)   1.8121
V(11)-O(9)   1.8115
V(11)-O(10)  1.7982
O(10)-V(6)   1.8212
O(9)-V(5)    1.8112
O(8)-V(7)    1.8174
V(7)-O(4)    1.6140
V(7)-O(3)    1.8176
V(6)-O(1)    1.8213
V(6)-O(2)    1.6107
V(5)-O(3)    1.8121
V(5)-O(1)    1.7984
```

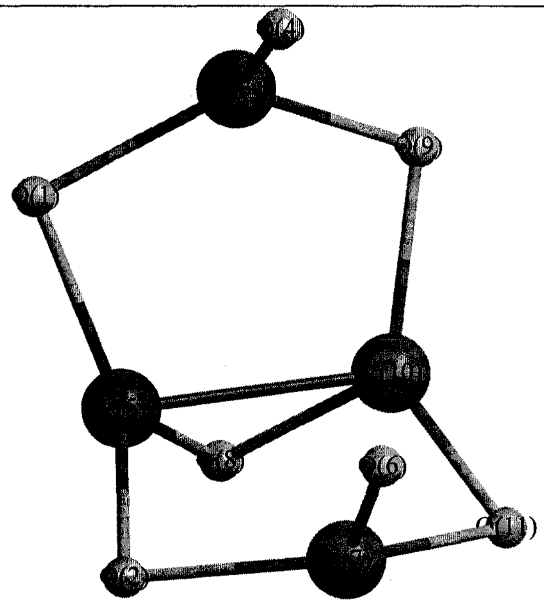
v4o7s11sp.log

```
O  -1.533728    1.441432     .014827
O  -2.973633    -.013838    2.093750
O   1.503831    1.478941     .062514
O   3.136882    -.013126    2.026795
V   -.007236    1.413338    -.935517
V  -2.502459    -.003715     .553549
V   2.417660    -.003836     .581923
O   1.503815   -1.479569     .043236
O    .181098     .013763   -2.069586
O  -1.533107   -1.441356    -.003518
V   -.007150   -1.401003    -.954048
```

E = -812.609167053 h (1.68 eV)
septet

```
 Zero-point correction=                          .024032 (Hartree/Particle)
 Thermal correction to Energy=                   .037809
 Thermal correction to Enthalpy=                 .038753
 Thermal correction to Gibbs Free Energy=       -.020237
```

Isomer 12



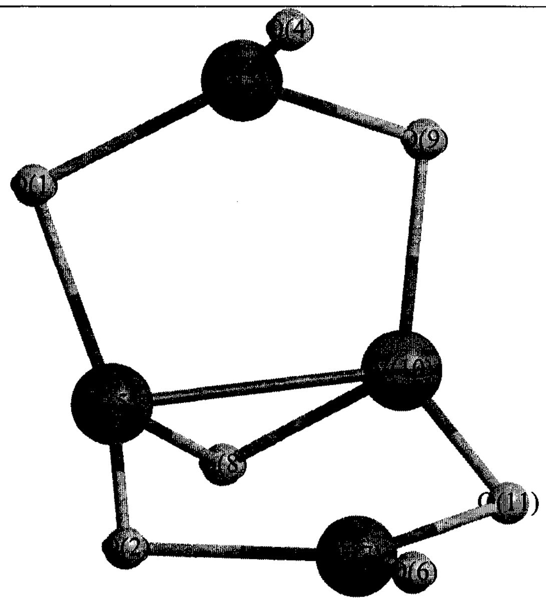
v4o7s12r1.log

O	-1.641364	-.208486	1.570698
O	1.640737	-.208399	1.570943
V	-2.033548	.584688	-.000214
O	-1.890093	2.180117	-.000027
V	-.000254	-.805533	1.105942
O	1.890246	2.180075	-.000114
V	2.033653	.584640	.000152
O	-.000029	-2.255816	.000117
O	-1.640769	-.208384	-1.571009
V	.000132	-.805647	-1.105890
O	1.641322	-.208783	-1.570582

O(11)-V(7)	1.8030
O(11)-V(10)	1.8071
V(10)-V(5)	2.2118
V(10)-O(8)	1.8238
V(10)-O(9)	1.8071
O(9)-V(3)	1.8030
O(8)-V(5)	1.8238
V(7)-O(6)	1.6019
V(7)-O(2)	1.8030
V(5)-O(2)	1.8071
V(5)-O(1)	1.8071
O(4)-V(3)	1.6019
V(3)-O(1)	1.8030
V(3)-V(7)	4.0672

E = -812.647034085 h (0.65 eV)
singlet

```
 Zero-point correction=                           .027257 (Hartree/Particle)
 Thermal correction to Energy=                    .039632
 Thermal correction to Enthalpy=                  .040576
 Thermal correction to Gibbs Free Energy=        -.012251
```

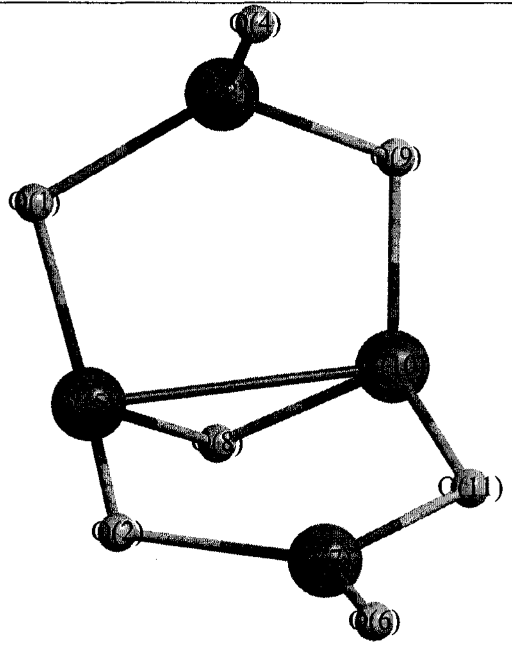


O(11)-V(7)	1.8773
O(11)-V(10)	1.7427
V(10)-V(5)	2.3184
V(10)-O(8)	1.8205
V(10)-O(9)	1.8136
O(9)-V(3)	1.8035
O(8)-V(5)	1.8205
V(7)-O(6)	1.6061
V(7)-O(2)	1.8773
V(5)-O(2)	1.7427
V(5)-O(1)	1.8136
O(4)-V(3)	1.6062
V(3)-O(1)	1.8035
V(3)-V(7)	4.1366

v4o7s12trr1.log

```
O  -1.751710     .050673    1.564053
O   1.391401    -.366825    1.535787
V  -1.922814     .931750    -.000232
O  -1.375375    2.441830    -.000280
V   -.236917    -.860739    1.159255
O   3.175713    1.632281     .000181
V   2.176188     .375040     .000172
O   -.447067   -2.248693     .000106
O  -1.751423     .050470   -1.564370
V   -.236707    -.860904   -1.159192
O   1.391679    -.367035   -1.535486
 Zero-point correction=                          .025547 (Hartree/Particle)
 Thermal correction to Energy=                   .038839
 Thermal correction to Enthalpy=                 .039783
 Thermal correction to Gibbs Free Energy=       -.017634
```

E = -812.630670497 h (1.10 eV)
triplet



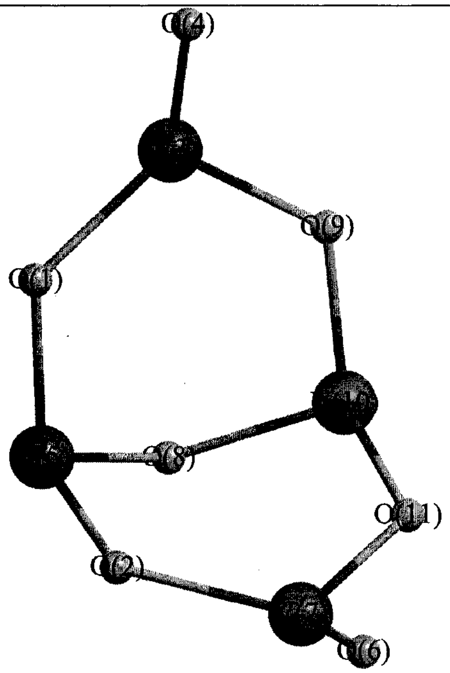
O(11)-V(7)	1.8368
O(11)-V(10)	1.7708
V(10)-O(8)	1.8037
V(10)-V(5)	2.6424
V(10)-O(9)	1.7632
O(9)-V(3)	1.8441
O(8)-V(5)	1.8037
V(7)-O(6)	1.6098
V(7)-O(2)	1.8368
V(5)-O(2)	1.7708
V(5)-O(1)	1.7631
O(4)-V(3)	1.6058
V(3)-O(1)	1.8441

v4o7s12qv2.log, v4o7s12qv2fr.log

O	-1.741107	-1.570147	-.087101
O	1.425336	-1.536420	-.153721
V	-2.087655	-.000019	.815826
O	-1.892811	-.000051	2.409798
V	-.180392	-1.321198	-.868691
O	3.419726	-.000039	1.534339
V	2.234515	-.000006	.444914
O	-.280321	.000046	-2.092445
O	-1.741106	1.570146	-.087018
V	-.180396	1.321234	-.868639
O	1.425326	1.536433	-.153658

E = -812.628642601 h (1.15 eV)
quintet

```
 Zero-point correction=                           0.024551 (Hartree/Particle)
 Thermal correction to Energy=                    0.038196
 Thermal correction to Enthalpy=                  0.039140
 Thermal correction to Gibbs Free Energy=        -0.019284
```



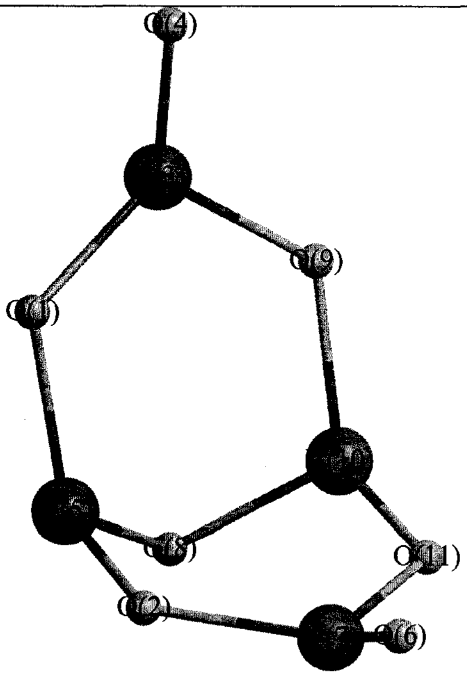
```
O(11)-V(10) 1.7889
O(11)-V(7)  1.8279
V(10)-O(9)  1.7889
V(10)-O(8)  1.7980
O(9)-V(3)   1.8279
O(8)-V(5)   1.7981
V(7)-O(2)   1.8279
V(7)-O(6)   1.6115
V(5)-O(1)   1.7889
V(5)-O(2)   1.7889
O(4)-V(3)   1.6115
V(3)-O(1)   1.8279
```

v4o7s12sp.log

```
O   1.495325    1.517147     .065454
O  -1.495303    1.517151     .065472
V   2.407282    -.000009     .521336
O   3.254476    -.000014    1.892197
V    .000005    1.574150    -.914796
O  -3.254516    -.000003    1.892169
V  -2.407273    -.000002     .521336
O   -.000004     .000012   -1.783750
O   1.495305   -1.517152     .065451
V   -.000004   -1.574133    -.914814
O  -1.495311   -1.517156     .065454
```

E = -812.623517407 h (1.29 eV)
septet

```
 Zero-point correction=                        .024227 (Hartree/Particle)
 Thermal correction to Energy=                 .037898
 Thermal correction to Enthalpy=               .038842
 Thermal correction to Gibbs Free Energy=     -.020089
```



```
O(11)-V(7)   1.7697
O(11)-V(10)  1.8803
V(10)-O(9)   1.8803
V(10)-O(8)   1.8238
O(9)-V(3)    1.7697
O(8)-V(5)    1.8238
V(7)-O(6)    1.6760
V(7)-O(2)    1.7697
V(5)-O(2)    1.8802
V(5)-O(1)    1.8803
O(4)-V(3)    1.6761
V(3)-O(1)    1.7697
```

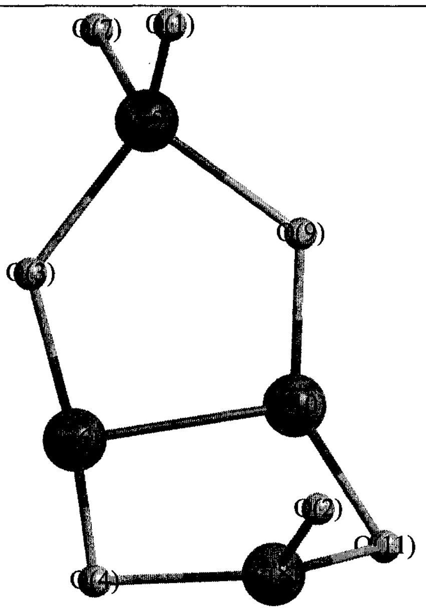
v4o7s12n.log

```
O  -1.601101     .048086    1.436294
O   1.600896     .048174    1.436313
V  -2.495042     .566776    -.000202
O  -3.312382    2.030033    -.000583
V   -.000063    -.936594    1.386290
O   3.312404    2.030001    -.000494
V   2.495043     .566783    -.000102
O   -.000003   -2.122405     .000573
O  -1.600901     .047402   -1.436326
V    .000068    -.937354   -1.385798
O   1.601067     .047326   -1.436316
```

E = -812.511471648 h (4.34 eV)
nonet

```
 Zero-point correction=                           .021407 (Hartree/Particle)
 Thermal correction to Energy=                    .035969
 Thermal correction to Enthalpy=                  .036913
 Thermal correction to Gibbs Free Energy=        -.024338
```

Isomer 13



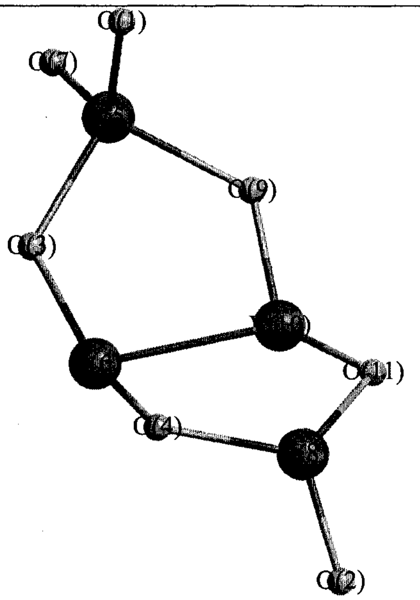
O(11)-V(10)	1.8017
O(11)-V(8)	1.8009
V(10)-V(6)	2.2853
V(10)-O(9)	1.7011
O(9)-V(5)	1.9282
V(8)-O(4)	1.8020
V(8)-O(2)	1.6031
O(7)-V(5)	1.6220
V(6)-O(3)	1.6998
V(6)-O(4)	1.7977
V(5)-O(1)	1.6192
V(5)-O(3)	1.9318

v4o7s13.log

O	2.814011	-.216208	1.893474
O	-2.529740	-.355100	2.012471
O	1.225276	1.391102	-.039416
O	-2.046755	1.571421	-.111645
V	2.444246	-.062700	.324581
V	-.356999	1.277567	-.650138
O	3.804382	.005913	-.556522
V	-2.543906	-.072198	.434600
O	1.180701	-1.380852	-.295070
V	-.363402	-.994502	-.895390
O	-2.090197	-1.442256	-.642545

E = -812.556251029 h (3.12 eV)
singlet

```
 Zero-point correction=                           .025914 (Hartree/Particle)
 Thermal correction to Energy=                    .039615
 Thermal correction to Enthalpy=                  .040559
 Thermal correction to Gibbs Free Energy=        -.017876
```



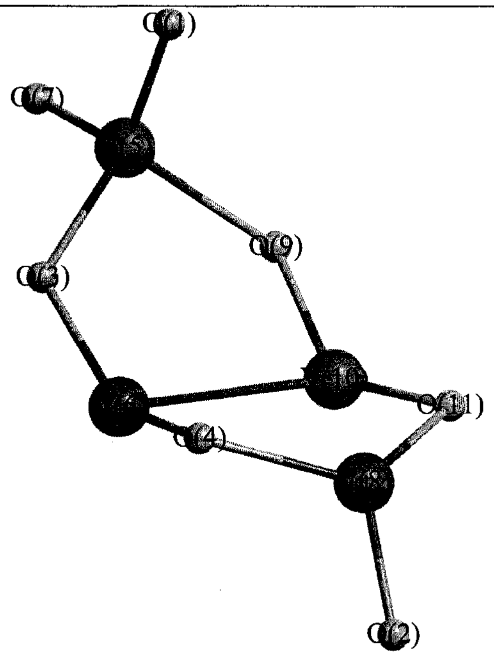
O(11)-V(8)	1.8440
O(11)-V(10)	1.7565
V(10)-V(6)	2.5819
V(10)-O(9)	1.6832
O(9)-V(5)	1.9550
V(8)-O(2)	1.6062
V(8)-O(4)	1.7779
O(7)-V(5)	1.6221
V(6)-O(4)	1.8244
V(6)-O(3)	1.7230
V(5)-O(3)	1.8995
V(5)-O(1)	1.6225

v4o7s13tr.log

```
O   -2.913391   -.226169   1.800222
O    4.196920    .034088   -.124369
O   -1.457434  -1.377472   -.468119
O    1.831873  -1.528080    .331092
V   -2.576622   -.009639    .227876
V     .260939  -1.302053   -.568694
O   -3.953294    .188448   -.606907
V    2.721998    .000405    .510623
O   -1.320181   1.464511   -.037028
V     .255080   1.279692   -.600579
O    1.713997   1.535509    .343582
```

E = -812.562844476 h (2.95 eV)
triplet

```
 Zero-point correction=                          .025302 (Hartree/Particle)
 Thermal correction to Energy=                   .039252
 Thermal correction to Enthalpy=                 .040196
 Thermal correction to Gibbs Free Energy=       -.019347
```



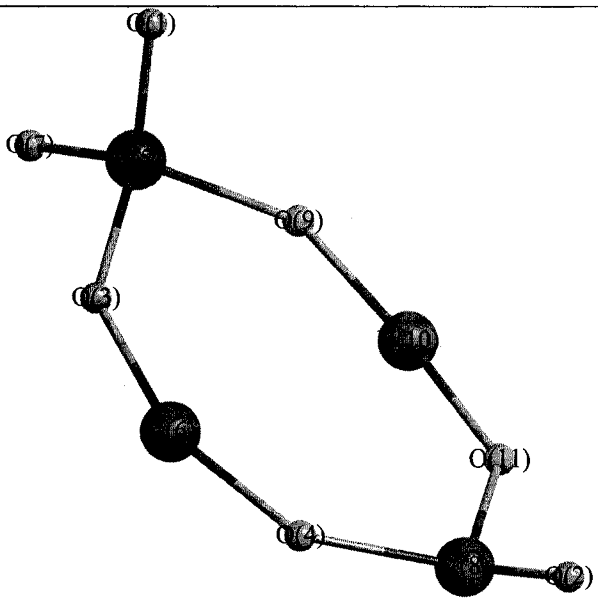
O(11)-V(10)	1.7972
O(11)-V(8)	1.8001
V(10)-O(9)	1.7038
V(10)-V(6)	2.6812
O(9)-V(5)	1.9279
V(8)-O(4)	1.7999
V(8)-O(2)	1.6058
O(7)-V(5)	1.6211
V(6)-O(3)	1.7040
V(6)-O(4)	1.7974
V(5)-O(1)	1.6229
V(5)-O(3)	1.9278

v4o7s13q.log

```
O   2.761128    .000705   1.790403
O  -3.962951   -.000660   -.390344
O   1.380194   1.450181   -.339018
O  -1.747554   1.567521    .503398
V   2.538085   -.000094    .182855
V   -.307380   1.340800   -.547909
O   3.975523   -.000839   -.566703
V  -2.632256    .000046    .508386
O   1.379563  -1.450565   -.337594
V   -.307619  -1.340413   -.548173
O  -1.747036  -1.567318    .503775
```

E = -812.557499041 h (3.09 eV)
quintet

```
 Zero-point correction=                           .025196 (Hartree/Particle)
 Thermal correction to Energy=                    .039180
 Thermal correction to Enthalpy=                  .040124
 Thermal correction to Gibbs Free Energy=        -.020206
```



O(11)-V(10)	1.8268
O(11)-V(8)	1.7969
V(10)-O(9)	1.7250
O(9)-V(5)	1.9048
V(8)-O(4)	1.7969
V(8)-O(2)	1.6111
O(7)-V(5)	1.6249
V(6)-O(3)	1.7250
V(6)-O(4)	1.8268
V(5)-O(1)	1.6256
V(5)-O(3)	1.9048
V(6)-V(10)	3.4022

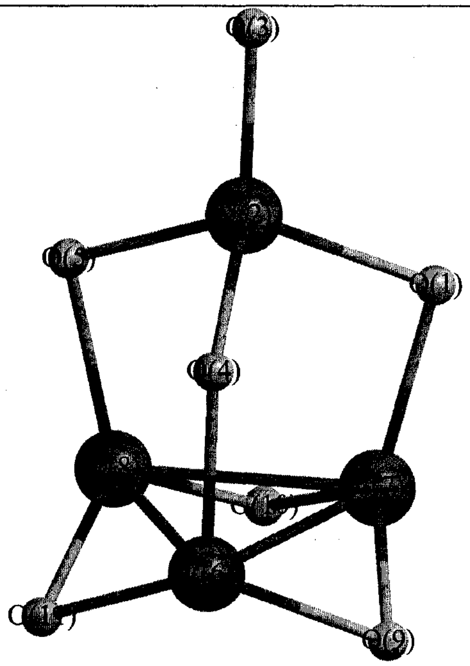
v4o7s13sp.log

```
O   3.326938     .000538    1.682085
O  -4.241707     .000104    1.043760
O   1.509979    1.446692    -.098974
O  -1.983176    1.431112    -.124025
V   2.718314    -.000168     .174724
V   -.184719    1.701352    -.296150
O   3.929374    -.000698    -.908665
V  -3.067793    -.000067    -.059665
O   1.509719   -1.447028    -.097767
V   -.184958   -1.700839    -.296236
O  -1.983553   -1.431522    -.124099
```

E = -812.554586319 h (3.17 eV)
septet

```
 Zero-point correction=                          .024352 (Hartree/Particle)
 Thermal correction to Energy=                   .038894
 Thermal correction to Enthalpy=                 .039838
 Thermal correction to Gibbs Free Energy=       -.023046
```

Isomer 14



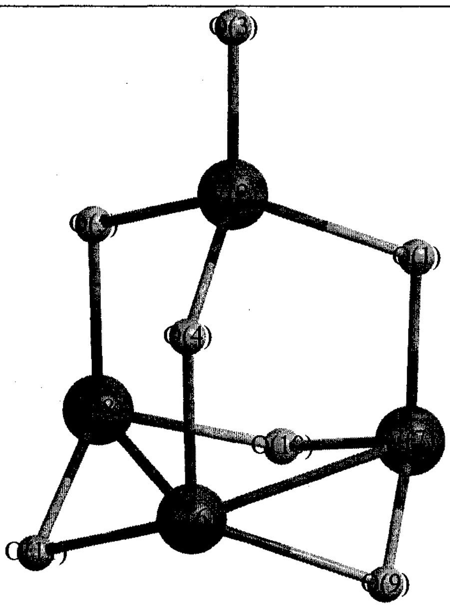
O(11)-V(6)	1.7348
O(11)-V(8)	1.9106
O(10)-V(7)	1.8276
O(10)-V(8)	1.8262
O(9)-V(6)	1.7352
O(9)-V(7)	1.9095
V(8)-O(5)	1.8292
V(8)-V(6)	2.6644
V(8)-V(7)	2.1629
V(7)-O(1)	1.8286
V(7)-V(6)	2.6633
V(6)-O(4)	1.7409
O(5)-V(2)	1.8034
O(4)-V(2)	1.9056
O(3)-V(2)	1.6084
V(2)-O(1)	1.8041

v4o7s14.log

```
O    1.062422    -.685943    1.505229
V    1.716563     .062850    -.000109
O    3.322670     .147991     .001001
O     .806188    1.736913    -.001303
O    1.063539    -.688024   -1.504133
V    -.928963    1.595905    -.001230
V    -.710909    -.827323    1.082040
V    -.710310    -.830135   -1.080873
O   -1.581470     .838786    1.417210
O   -1.270962   -2.190312     .001006
O   -1.580735     .836861   -1.418514
```

E = -812.648768011 h (0.61 eV)
singlet

```
 Zero-point correction=                           .026611 (Hartree/Particle)
 Thermal correction to Energy=                    .038776
 Thermal correction to Enthalpy=                  .039720
 Thermal correction to Gibbs Free Energy=        -.011598
```



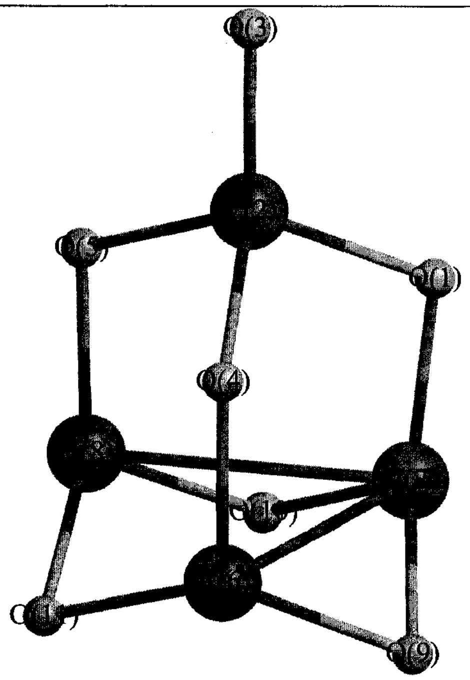
O(11)-V(6)	1.8746
O(11)-V(8)	1.7712
O(10)-V(7)	1.7885
O(10)-V(8)	1.8123
O(9)-V(6)	1.8886
O(9)-V(7)	1.7575
V(8)-V(6)	2.6666
V(8)-O(5)	1.7742
V(7)-V(6)	2.6823
V(7)-O(1)	1.7630
V(6)-O(4)	1.8354
O(5)-V(2)	1.8504
O(4)-V(2)	1.7988
O(3)-V(2)	1.6072
V(2)-O(1)	1.8633

v4o7s14bsoptv2.log

O	1.131050	-0.754586	1.452401
V	1.783675	0.115013	0.033179
O	3.387123	0.247427	0.030989
O	0.850257	1.695348	-0.023975
O	1.041699	-0.727168	-1.423800
V	-0.909119	1.451878	-0.010233
V	-0.715858	-0.833451	1.326143
V	-0.726965	-0.828015	-1.326850
O	-1.596501	0.805645	1.489226
O	-1.384690	-1.883013	-0.067752
O	-1.672638	0.708492	-1.479005

E = -812.657904748 h (0.36 eV)
singlet, broken symmetry

```
 Zero-point correction=                           0.025311 (Hartree/Particle)
 Thermal correction to Energy=                    0.037977
 Thermal correction to Enthalpy=                  0.038922
 Thermal correction to Gibbs Free Energy=        -0.013539
```



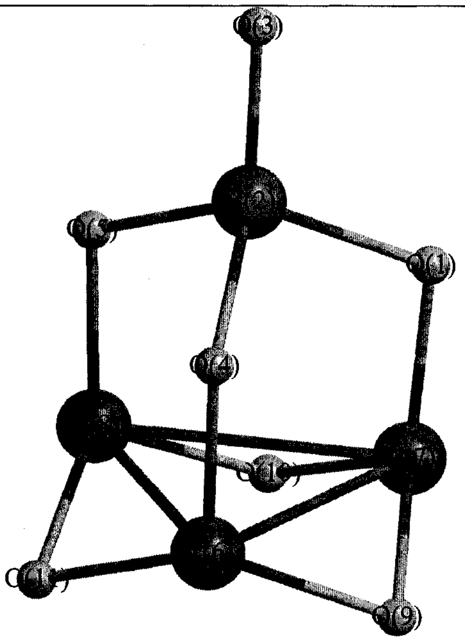
O(11)-V(8)	1.8076
O(11)-V(6)	1.8100
O(10)-V(7)	1.8142
O(10)-V(8)	1.8191
O(9)-V(7)	1.8141
O(9)-V(6)	1.8201
V(8)-V(7)	2.6235
V(8)-O(5)	1.7969
V(7)-V(6)	2.6149
V(7)-O(1)	1.7618
V(6)-O(4)	1.7958
O(5)-V(2)	1.8232
O(4)-V(2)	1.8246
O(3)-V(2)	1.6086
V(2)-O(1)	1.8491

v4o7s14trr1.log

```
O    -.913683    -.080689    1.669825
V   -1.796200    -.005153     .046715
O   -3.404749    -.009771     .049007
O   -1.021571   -1.387127    -.858493
O   -1.032637    1.458090    -.727868
V     .772967   -1.326068    -.827440
V     .836011    -.068609    1.464361
V     .763316    1.403319    -.706130
O    1.631810   -1.540244     .762984
O    1.622414    1.464313     .896127
O    1.462144     .085397   -1.726909
```

E = -812.661452772 h (0.26 eV)
triplet

```
 Zero-point correction=                          .024966 (Hartree/Particle)
 Thermal correction to Energy=                   .037805
 Thermal correction to Enthalpy=                 .038749
 Thermal correction to Gibbs Free Energy=       -.015379
```



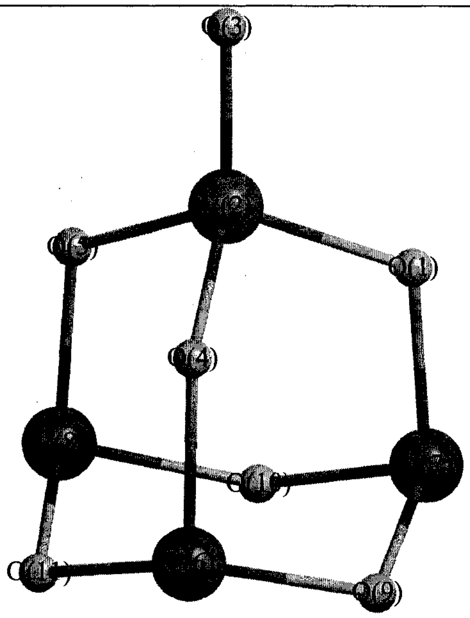
```
O(11)-V(8)   1.8069
O(11)-V(6)   1.8123
O(10)-V(8)   1.8114
O(10)-V(7)   1.8086
O(9)-V(7)    1.8066
O(9)-V(6)    1.8140
V(8)-V(7)    2.6729
V(8)-V(6)    2.6778
V(8)-O(5)    1.7830
V(7)-V(6)    2.6755
V(7)-O(1)    1.7807
V(6)-O(4)    1.7841
O(5)-V(2)    1.8377
O(4)-V(2)    1.8365
O(3)-V(2)    1.6084
V(2)-O(1)    1.8390
```

v4o7s14q.log

```
O   -.980226    -.442217    1.600905
V  -1.771505    -.001725     .000376
O  -3.379931    -.003714     .000113
O   -.980873   -1.165774   -1.179742
O   -.985743    1.607188    -.413205
V    .799679   -1.084793   -1.102473
V    .796472    -.410106    1.486548
V    .793560    1.495803    -.387406
O   1.519921   -1.697391     .445653
O   1.521093    1.230017    1.249991
O   1.508419     .474252   -1.695219
```

E = -812.667331676 h (0.10 eV)
quintet

```
 Zero-point correction=                           .025143 (Hartree/Particle)
 Thermal correction to Energy=                    .037823
 Thermal correction to Enthalpy=                  .038767
 Thermal correction to Gibbs Free Energy=        -.015307
```



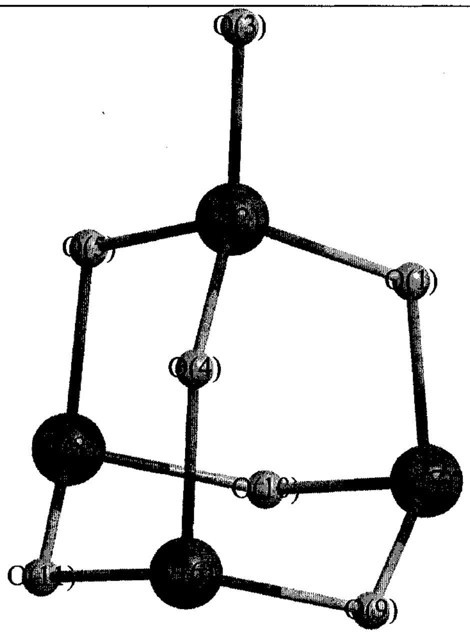
```
O(11)-V(6)   1.8077
O(11)-V(8)   1.8067
O(10)-V(7)   1.8065
O(10)-V(8)   1.8068
O(9)-V(7)    1.8057
O(9)-V(6)    1.8074
V(8)-O(5)    1.7895
V(7)-O(1)    1.7906
V(6)-O(4)    1.7889
O(5)-V(2)    1.8306
O(4)-V(2)    1.8294
O(3)-V(2)    1.6082
V(2)-O(1)    1.8307
```

v4o7s14spr1.log

```
O    -.967366   1.521640   -.686026
V   -1.720082   -.000485   -.001920
O   -3.327811   -.003491    .036509
O    -.950364   -.173398   1.648652
O    -.965791  -1.348538   -.984216
V     .833305   -.184608   1.784861
V     .818612   1.641268   -.733973
V     .819201  -1.455224  -1.054149
O    1.349172   1.341704    .965778
O    1.351056    .170150  -1.637131
O    1.351874  -1.510801    .671331
```

E = -812.671072314 h (0 eV)
septet

```
 Zero-point correction=                           .025781 (Hartree/Particle)
 Thermal correction to Energy=                    .037884
 Thermal correction to Enthalpy=                  .038828
 Thermal correction to Gibbs Free Energy=        -.014139
```



O(11)-V(8)	1.8151
O(11)-V(6)	1.8039
O(10)-V(8)	1.8078
O(10)-V(7)	1.8017
O(9)-V(6)	1.8106
O(9)-V(7)	1.8154
V(8)-O(5)	1.8859
V(7)-O(1)	1.8507
V(6)-O(4)	1.8157
O(5)-V(2)	1.7521
O(4)-V(2)	1.8018
O(3)-V(2)	1.7975
V(2)-O(1)	1.7749

v4o7s14nv2.log

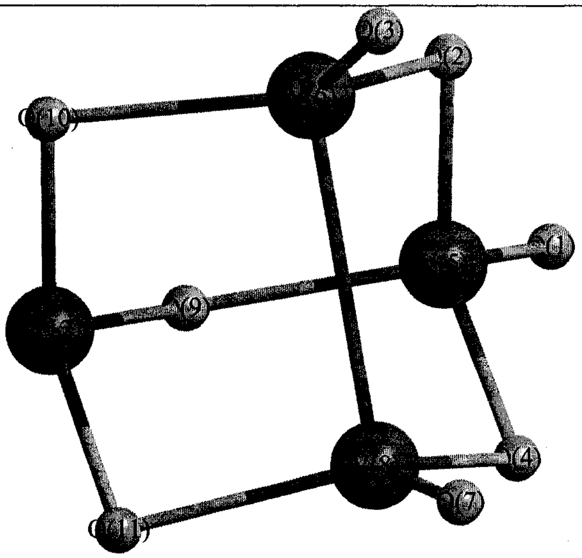
```
O    .997028   -1.191634   -1.095355
V   1.722565     .007025    -.005783
O   3.518245    -.046957     .055273
O    .952321    -.373695    1.577994
O   1.034140    1.549238    -.472065
V   -.856349    -.400935    1.735701
V   -.845195   -1.314973   -1.221872
V   -.842645    1.725717    -.528790
O  -1.423652   -1.574661     .479208
O  -1.342648     .371139   -1.616613
O  -1.373267    1.218173    1.131196
```

E = -812.570279804 h (2.74 eV)
nonet

```
 Zero-point correction=                          .023212 (Hartree/Particle)
 Thermal correction to Energy=                   .036333
 Thermal correction to Enthalpy=                 .037277
 Thermal correction to Gibbs Free Energy=       -.018969
```

V_4O_8 clusters

Isomer 3

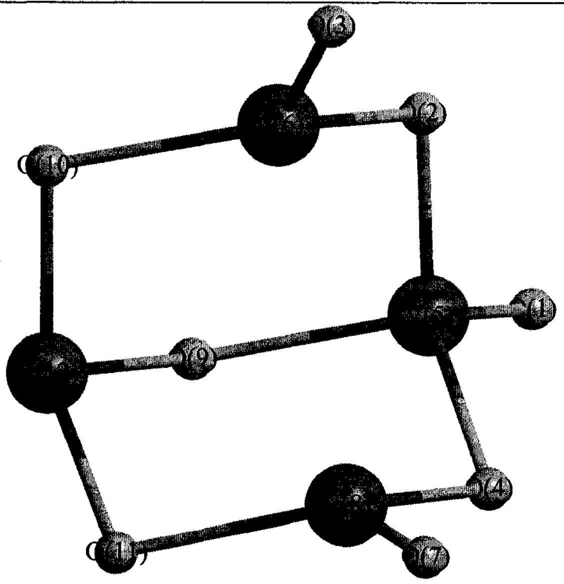


V(12)-O(10)	1.7324
V(12)-O(11)	1.7324
V(12)-O(9)	1.7758
O(11)-V(8)	1.8790
O(10)-V(6)	1.8790
O(9)-V(5)	1.8445
V(8)-V(6)	2.6630
V(8)-O(7)	1.6007
V(8)-O(4)	1.8086
V(6)-O(3)	1.6007
V(6)-O(2)	1.8085
V(5)-O(2)	1.7917
V(5)-O(4)	1.7917
V(5)-O(1)	1.6041
V(8)-O(9)	3.1889
V(6)-O(9)	3.1889

v4o8s3.log

```
O  -3.420346     .000060    -.516203
O   -.976964    1.444941    -.923776
O   1.953168    1.695912   -1.559824
O   -.976943   -1.444686    -.924187
V  -1.831313     .000033    -.297198
V    .784274    1.331595    -.528758
O   1.953195   -1.695438   -1.560300
V    .784296   -1.331449    -.529123
O  -1.311152    -.000223    1.472428
O   1.154825    1.478011    1.307532
O   1.154853   -1.478362    1.307135
V    .425999    -.000254    1.841060
 Zero-point correction=                        .029965 (Hartree/Particle)
 Thermal correction to Energy=                 .043813
 Thermal correction to Enthalpy=               .044757
 Thermal correction to Gibbs Free Energy=     -.010858
```

E = -887.913316322 h (1.43 eV)
singlet



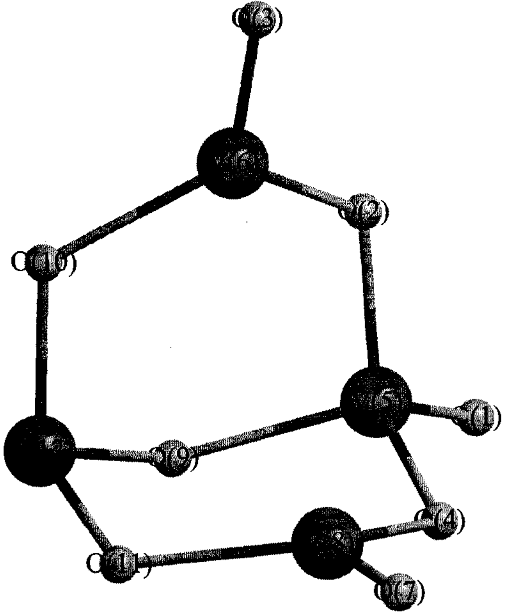
```
V(12)-O(9)   1.7685
V(12)-O(11)  1.7767
V(12)-O(10)  1.7767
O(11)-V(8)   1.8221
O(10)-V(6)   1.8221
O(9)-V(5)    1.8390
V(8)-O(4)    1.7756
V(8)-O(7)    1.6023
V(6)-O(2)    1.7756
V(6)-O(3)    1.6023
V(5)-O(1)    1.6047
V(5)-O(4)    1.8228
V(5)-O(2)    1.8228
V(6)-V(8)    2.9448
```

v4o8s3tr.log

```
O   3.427039    .000000    -.421205
O    .942764  -1.454872    -.938589
O  -1.836377  -2.054830   -1.592939
O    .942764   1.454874    -.938584
V   1.827838    .000000    -.288521
V   -.785729  -1.472376    -.532639
O  -1.836376   2.054834   -1.592936
V   -.785729   1.472378    -.532636
O   1.263723   -.000002    1.461834
O  -1.168287  -1.497290    1.248708
O  -1.168287   1.497287    1.248711
V   -.453584   -.000002    1.884231
```

E = -887.917990794 h (1.30 eV)
triplet

```
 Zero-point correction=                           .028795 (Hartree/Particle)
 Thermal correction to Energy=                    .043124
 Thermal correction to Enthalpy=                  .044068
 Thermal correction to Gibbs Free Energy=        -.014192
```



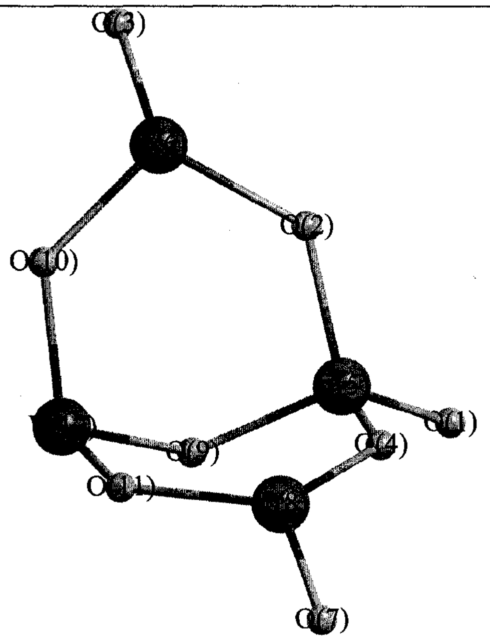
V(12)-O(10)	1.7435
V(12)-O(9)	1.7682
V(12)-O(11)	1.7435
O(11)-V(8)	1.8766
O(10)-V(6)	1.8766
O(9)-V(5)	1.8476
V(8)-O(4)	1.8238
V(8)-O(7)	1.6078
V(6)-O(2)	1.8238
V(6)-O(3)	1.6078
V(5)-O(2)	1.7856
V(5)-O(1)	1.6073
V(5)-O(4)	1.7855
V(6)-V(8)	3.5233

v4o8s3qr1.log

```
O   -.000177    3.384163    -.471993
O   1.433291     .958358    -.929251
O   2.651622   -1.749498   -1.543811
O  -1.433391     .958233    -.929231
V   -.000088    1.790240    -.264728
V   1.761662    -.804262    -.595399
O  -2.651428   -1.749748   -1.543835
V  -1.761597    -.804430    -.595384
O   -.000055    1.261942    1.505690
O   1.397345   -1.155422    1.211684
O  -1.397224   -1.155562    1.211699
V    .000029    -.443275    1.973440
```

E = -887.903551691 h (1.70 eV)
quintet

```
 Zero-point correction=                           .028121 (Hartree/Particle)
 Thermal correction to Energy=                    .042856
 Thermal correction to Enthalpy=                  .043801
 Thermal correction to Gibbs Free Energy=        -.017134
```



```
V(12)-O(9)   1.8165
V(12)-O(10)  1.7916
V(12)-O(11)  1.7916
O(11)-V(8)   1.8165
O(10)-V(6)   1.8165
O(9)-V(5)    1.7818
V(8)-O(4)    1.8529
V(8)-O(7)    1.6194
V(6)-O(3)    1.6194
V(6)-O(2)    1.8529
V(5)-O(1)    1.7128
V(5)-O(2)    1.7763
V(5)-O(4)    1.7763
```

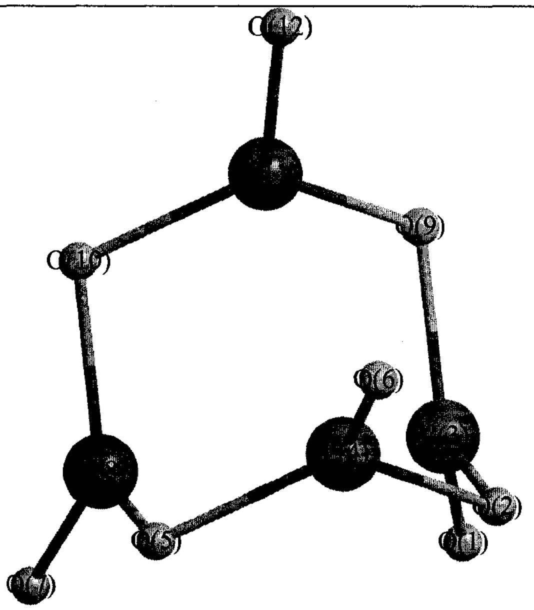
v4o8s3spr2.log

```
O    -.000002    3.200711     .892086
O    1.476403    1.201186    -.606649
O    4.040465    -.402957    -.780157
O   -1.476389    1.201174    -.606656
V     .000004    1.593571     .299733
V    2.421645    -.386779    -.741230
O   -4.040464    -.402925    -.780183
V   -2.421644    -.386783    -.741222
O     .000002     .315325    1.541087
O    1.518813   -1.638282     .216982
O   -1.518833   -1.638290     .217007
V    -.000003   -1.458599    1.150192
```

E = -887.831109976 h (3.67 eV)
septet

```
 Zero-point correction=                          .025298 (Hartree/Particle)
 Thermal correction to Energy=                   .040685
 Thermal correction to Enthalpy=                 .041629
 Thermal correction to Gibbs Free Energy=       -.020885
```

Isomer 4



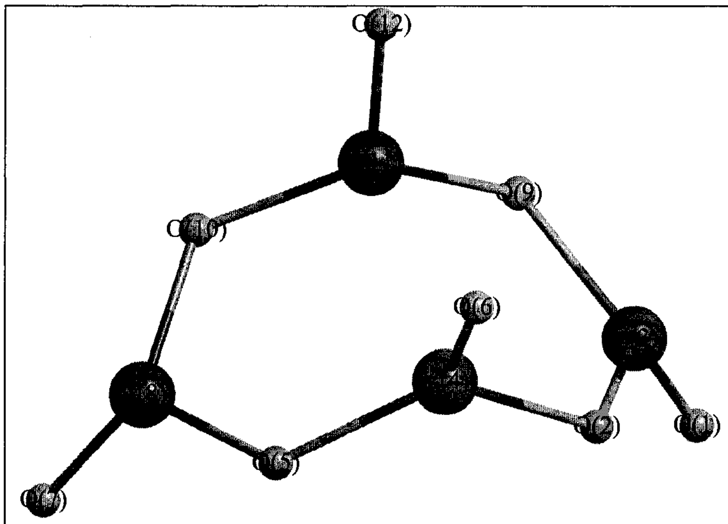
O(12)-V(11)	1.6051
V(11)-O(10)	1.7880
V(11)-O(9)	1.7881
O(10)-V(8)	1.7881
O(9)-V(3)	1.7880
V(8)-O(5)	1.7881
V(8)-O(7)	1.6051
O(6)-V(4)	1.6051
O(5)-V(4)	1.7881
V(4)-O(2)	1.7880
V(3)-O(2)	1.7881
V(3)-O(1)	1.6051
V(4)-V(11)	2.9816
V(3)-V(8)	2.9815

v4o8s4v2r5.log

```
O  -2.548980    -.046086   -1.881202
O    .000254   -1.523082   -1.451049
V   -.992218    -.036262   -1.490255
V    .992326   -1.490254     .036142
O    .000142   -1.451009    1.523140
O   2.548965   -1.881692     .045763
O  -2.548896     .045604    1.881204
V   -.992097     .036117    1.490398
O   -.000324    1.451049   -1.523106
O    .000010    1.523179    1.450998
V    .992046    1.490431    -.036220
O   2.548666    1.881945    -.045935
```

E = -887.878009671 h (2.39 eV)
singlet

```
 Zero-point correction=                          .029268 (Hartree/Particle)
 Thermal correction to Energy=                   .044221
 Thermal correction to Enthalpy=                 .045165
 Thermal correction to Gibbs Free Energy=       -.014357
```



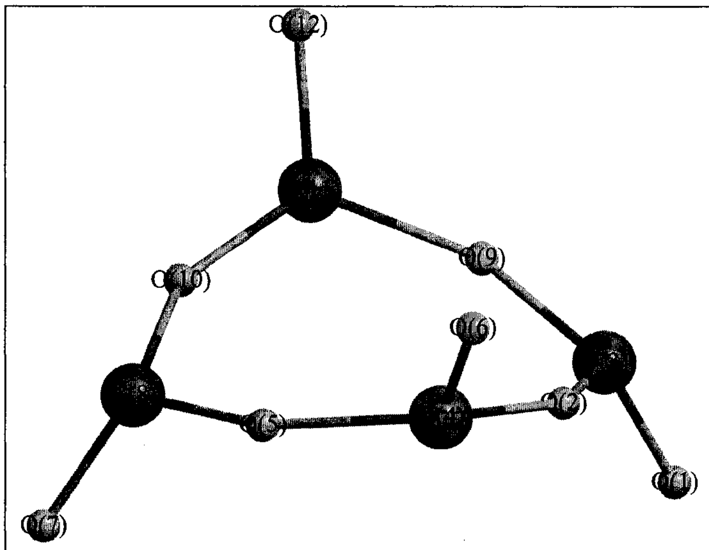
O(12)-V(11)	1.6008
V(11)-O(9)	1.7878
V(11)-O(10)	1.7878
O(10)-V(8)	1.8003
O(9)-V(3)	1.8003
V(8)-O(5)	1.8001
V(8)-O(7)	1.6068
O(6)-V(4)	1.6007
O(5)-V(4)	1.7879
V(4)-O(2)	1.7879
V(3)-O(1)	1.6068
V(3)-O(2)	1.8001
V(4)-V(11)	2.7941

v4o8s4trr1.log

```
O   3.239162    -.027349   -2.067928
O   1.592394   -1.489271    -.095165
V   2.436820    -.009417    -.675857
V   -.000062   -1.386955     .711099
O  -1.593263   -1.489096    -.093736
O    .000841   -1.773880    2.264377
O  -3.238287    -.027959   -2.068530
V  -2.436871    -.009358    -.675935
O   1.593876    1.484625    -.129693
O  -1.593377    1.484770    -.130803
V   -.000046    1.406958     .676355
O   -.000892    1.834629    2.218953
```

E = -887.894149221 h (1.95 eV)
triplet

```
 Zero-point correction=                           .028851 (Hartree/Particle)
 Thermal correction to Energy=                    .044024
 Thermal correction to Enthalpy=                  .044968
 Thermal correction to Gibbs Free Energy=        -.017316
```



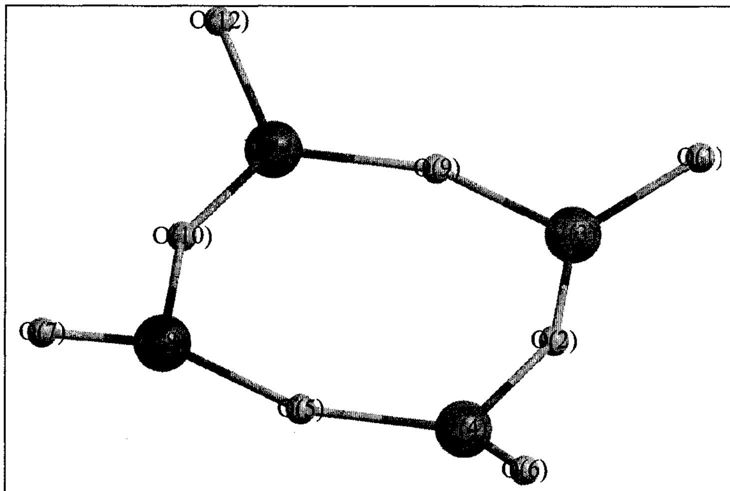
```
O(12)-V(11) 1.6089
V(11)-O(10) 1.7963
V(11)-O(9)  1.7972
O(10)-V(8)  1.7964
O(9)-V(3)   1.7970
V(8)-O(5)   1.7970
V(8)-O(7)   1.6090
O(6)-V(4)   1.6089
O(5)-V(4)   1.7972
V(4)-O(2)   1.7963
V(3)-O(2)   1.7964
V(3)-O(1)   1.6090
```

v4o8s4qr1.log

```
O  -2.667835    1.751353   -1.802827
O   -.434385    2.092802    -.002785
V  -1.994428    1.301920    -.412318
V   1.310495    1.989135     .411329
O   2.126953     .443310    -.005358
O   1.739024    2.650449    1.814002
O   2.667573   -1.751004   -1.803115
V   1.994437   -1.302014    -.412329
O  -2.126928    -.443519    -.005779
O    .434389   -2.092906    -.002817
V  -1.310477   -1.989217     .411353
O  -1.738868   -2.649975    1.814329
```

E = -887.886895985 h (2.15 eV)
quintet

```
 Zero-point correction=                           .027444 (Hartree/Particle)
 Thermal correction to Energy=                    .043519
 Thermal correction to Enthalpy=                  .044463
 Thermal correction to Gibbs Free Energy=        -.022455
```



```
O(12)-V(11) 1.6327
V(11)-O(10) 1.8024
V(11)-O(9)  1.8026
O(10)-V(8)  1.8026
O(9)-V(3)   1.8024
V(8)-O(7)   1.6327
V(8)-O(5)   1.8024
O(6)-V(4)   1.6327
O(5)-V(4)   1.8026
V(4)-O(2)   1.8024
V(3)-O(2)   1.8026
V(3)-O(1)   1.6327
```

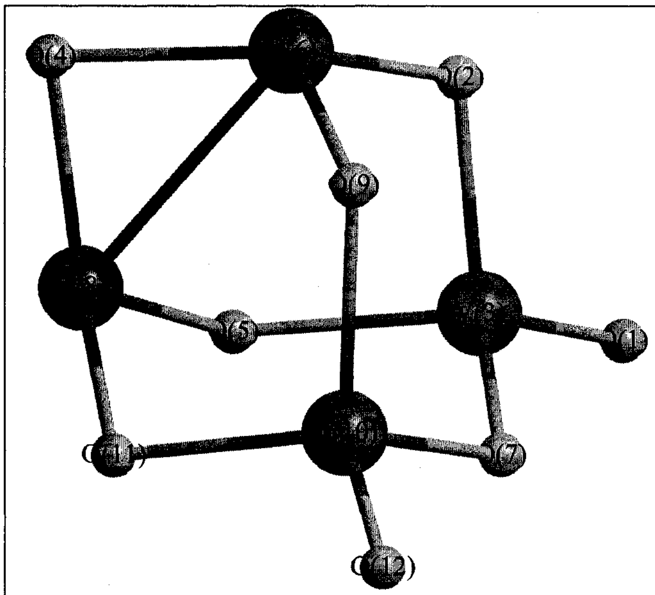
v4o8s4spr4.log

```
O  -3.237827   -2.318085     .508605
O  -2.140944     .354287    -.129577
V  -2.016459   -1.443960    -.131633
V  -1.443968    2.016465    -.131802
O    .354281    2.140917    -.129912
O  -2.317982    3.237816     .508612
O   3.237717    2.317996     .508654
V   2.016472    1.443969    -.131941
O   -.354288   -2.140950    -.129583
O   2.140922    -.354282    -.129946
V   1.443962   -2.016468    -.131764
O   2.318105   -3.237715     .508676
```

E = -887.800572118 h (4.50 eV)
septet

```
 Zero-point correction=                           .023415 (Hartree/Particle)
 Thermal correction to Energy=                    .040301
 Thermal correction to Enthalpy=                  .041245
 Thermal correction to Gibbs Free Energy=        -.026929
```

Isomer 5

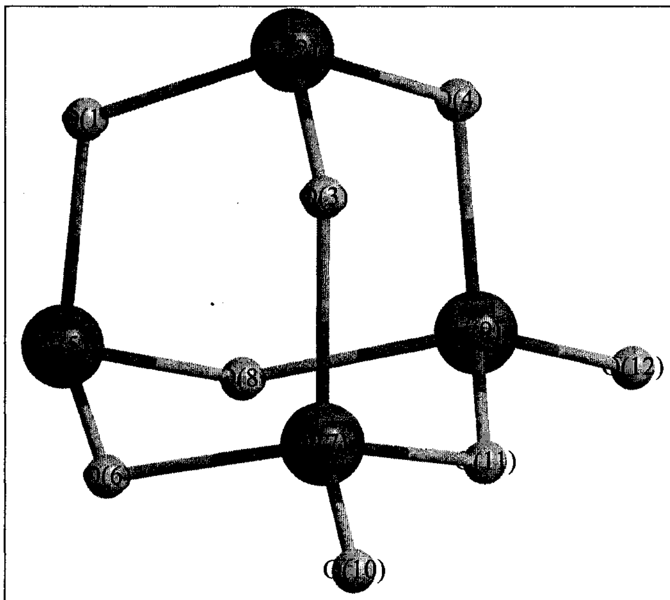


```
O(12)-V(10)  1.6044
O(11)-V(10)  1.8589
O(11)-V(8)   1.7516
V(10)-O(9)   1.8589
V(10)-O(7)   1.8037
O(9)-V(6)    1.7516
V(8)-O(4)    1.8069
V(8)-O(5)    1.7429
V(8)-V(6)    2.5298
O(7)-V(3)    1.8111
V(6)-O(4)    1.8068
V(6)-O(2)    1.7429
O(5)-V(3)    1.8558
V(3)-O(2)    1.8558
V(3)-O(1)    1.6056
```

v4o8s5r.log

```
O  -3.087422   -1.579176    -.000247
O  -1.392301     .405592   -1.361616
V  -1.670246    -.824396    -.000012
O    .364652    2.536706    -.000016
O  -1.392460     .405359    1.361797
V    .117911    1.270246   -1.264885
O   -.158023   -1.821000    -.000396
V    .117609    1.270302    1.264882
O   1.420076     .112748   -1.445983
V   1.474555   -1.054167     .000021
O   1.419619     .112739    1.445977
O   2.711350   -2.076173     .000469
 Zero-point correction=                           .030002 (Hartree/Particle)
 Thermal correction to Energy=                    .043349
 Thermal correction to Enthalpy=                  .044294
 Thermal correction to Gibbs Free Energy=        -.010168
```

E = -887.942880968 h (0.63 eV)
singlet



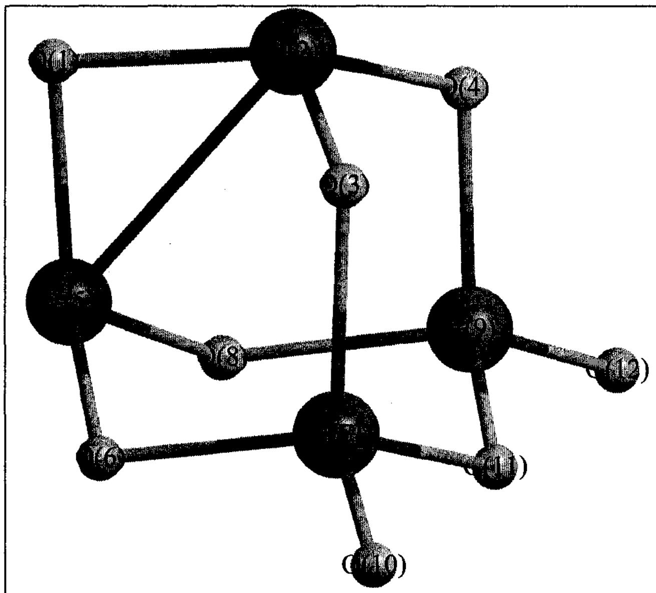
```
O(12)-V(9)   1.6063
O(11)-V(7)   1.8010
O(11)-V(9)   1.8010
O(10)-V(7)   1.6063
V(9)-O(8)    1.8780
V(9)-O(4)    1.8780
O(8)-V(5)    1.7408
V(7)-O(6)    1.8780
V(7)-O(3)    1.8780
O(6)-V(5)    1.7408
V(5)-O(1)    1.8051
O(4)-V(2)    1.7408
O(3)-V(2)    1.7408
V(2)-O(1)    1.8052
```

v4o8bsopt.log

```
O  -0.000514   2.205958   0.000046
V  -0.000196   1.290552  -1.555782
O   1.391322   0.248555  -1.464151
O  -1.391266   0.247940  -1.464358
V  -0.000433   1.290489   1.555836
O   1.391100   0.248496   1.464375
V   1.586824  -0.911036   0.000104
O  -1.391489   0.247881   1.464150
V  -1.586429  -0.911769  -0.000142
O   2.892309  -1.846908   0.000190
O   0.000398  -1.763552  -0.000036
O  -2.891495  -1.848225  -0.000263
```

E = -887.943622266 h (0.61 eV)
singlet, broken symmetry

```
 Zero-point correction=                      0.028767 (Hartree/Particle)
 Thermal correction to Energy=               0.042355
 Thermal correction to Enthalpy=             0.043300
 Thermal correction to Gibbs Free Energy=   -0.011148
```



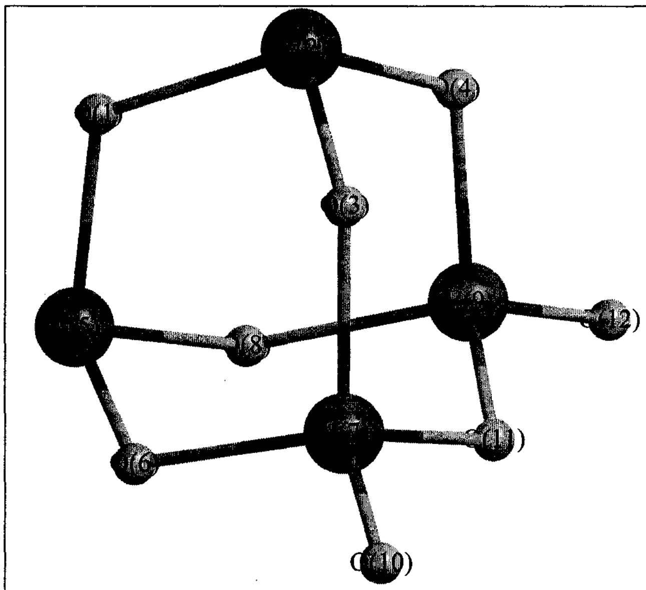
```
O(12)-V(9)   1.6060
O(11)-V(7)   1.8228
O(11)-V(9)   1.7935
O(10)-V(7)   1.6045
V(9)-O(8)    1.8520
V(9)-O(4)    1.8520
O(8)-V(5)    1.7510
V(7)-O(6)    1.8409
V(7)-O(3)    1.8410
O(6)-V(5)    1.7689
V(5)-O(1)    1.8037
V(5)-V(2)    2.6162
O(4)-V(2)    1.7510
O(3)-V(2)    1.7689
V(2)-O(1)    1.8036
```

v4o8s5tr.log, v4o8s5trfr.log

```
O    .259488    2.488197     .000026
V    .108112    1.255686   -1.308083
O   1.474729     .138870   -1.426356
O  -1.395718     .365014   -1.413148
V    .107902    1.255645    1.308122
O   1.474508     .138800    1.426552
V   1.470132   -1.024901     .000087
O  -1.395928     .364925    1.413007
V  -1.656404    -.803507    -.000118
O   2.715957   -2.035971     .000238
O   -.173686   -1.812603    -.000080
O  -3.044858   -1.610637    -.000263
```

E = -887.956332285 h (0.26 eV)
triplet

```
 Zero-point correction=                       0.029276 (Hartree/Particle)
 Thermal correction to Energy=                0.042752
 Thermal correction to Enthalpy=              0.043696
 Thermal correction to Gibbs Free Energy=    -0.011483
```



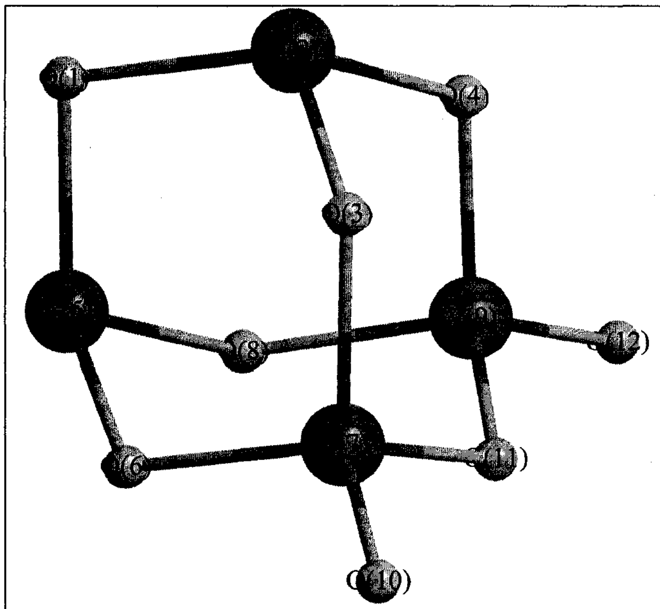
O(12)-V(9)	1.6068
O(11)-V(7)	1.8036
O(11)-V(9)	1.8033
O(10)-V(7)	1.6068
V(9)-O(8)	1.8386
V(9)-O(4)	1.8386
O(8)-V(5)	1.7722
V(7)-O(6)	1.8384
V(7)-O(3)	1.8384
O(6)-V(5)	1.7723
V(5)-O(1)	1.8073
O(4)-V(2)	1.7722
O(3)-V(2)	1.7723
V(2)-O(1)	1.8072

v4o8s5q.log, v4o8s5qfr.log

```
O     .000439   2.208088    .000044
V    -.000281   1.301394  -1.563304
O    1.399678    .220930  -1.446521
O   -1.400646    .221531  -1.446131
V    -.000526   1.301331   1.563360
O    1.399461    .220877   1.446729
V    1.570683   -.900532    .000102
O   -1.400865    .221459   1.445933
V   -1.569945   -.901330   -.000139
O    2.900305  -1.802681    .000205
O     .000426  -1.787805   -.000047
O   -2.898598  -1.804881   -.000262
```

E = -887.965867970 h (0 eV)
quintet

```
 Zero-point correction=                        0.029308 (Hartree/Particle)
 Thermal correction to Energy=                 0.042561
 Thermal correction to Enthalpy=               0.043505
 Thermal correction to Gibbs Free Energy=     -0.011550
```



O(12)-V(9)	1.6627
O(11)-V(7)	1.8141
O(11)-V(9)	1.8234
O(10)-V(7)	1.6740
V(9)-O(8)	1.7791
V(9)-O(4)	1.7791
O(8)-V(5)	1.8448
V(7)-O(6)	1.7759
V(7)-O(3)	1.7760
O(6)-V(5)	1.8476
V(5)-O(1)	1.8165
O(4)-V(2)	1.8448
O(3)-V(2)	1.8476
V(2)-O(1)	1.8166

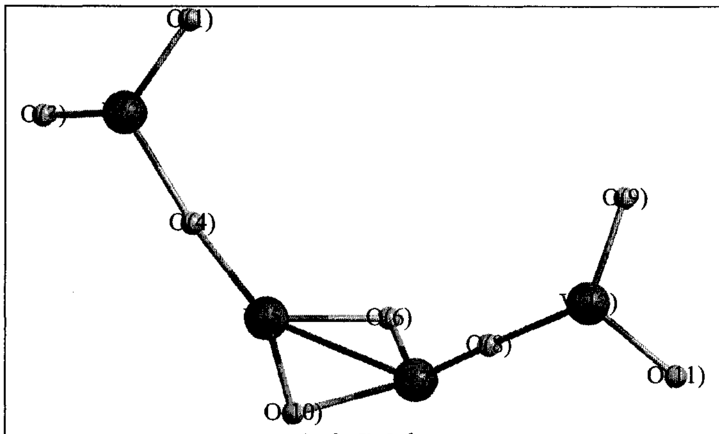
v4o8s5sp.log

```
O   -.013172    2.471195     .000029
V   -.010552    1.323897   -1.408363
O   1.448472     .190795   -1.379063
O  -1.452964     .174121   -1.382397
V   -.010782    1.323873    1.408389
O   1.448247     .190720    1.379287
V   1.597846    -.918073     .000108
O  -1.453174     .174030    1.382227
V  -1.586124    -.938054    -.000119
O   3.009214   -1.818236     .000191
O    .016649   -1.807417    -.000042
O  -2.975638   -1.851180    -.000273
```

E = -887.865711852 h (2.73 eV)
septet

```
 Zero-point correction=                          .025771 (Hartree/Particle)
 Thermal correction to Energy=                   .040263
 Thermal correction to Enthalpy=                 .041207
 Thermal correction to Gibbs Free Energy=       -.017126
```

Isomer 7



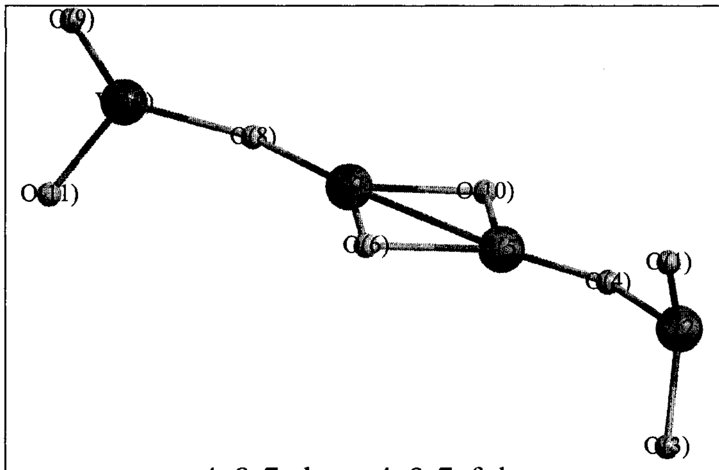
```
V(12)-O(9)   1.6227
V(12)-O(8)   1.8453
V(12)-O(11)  1.6243
O(10)-V(5)   1.7999
O(10)-V(7)   1.7999
O(8)-V(7)    1.7326
V(7)-O(6)    1.7960
V(7)-V(5)    2.5106
O(6)-V(5)    1.7960
V(5)-O(4)    1.7326
O(4)-V(2)    1.8453
O(3)-V(2)    1.6243
V(2)-O(1)    1.6227
```

v4o8s7r3.log

```
O   3.670506    2.346596     .549720
V   3.903428    1.001164    -.327088
O   5.337640     .327207     .029369
O   2.495399    -.191568    -.316989
V   1.255306   -1.309556     .145935
O    .000009   -1.126637    1.417335
V  -1.255291   -1.309534     .145934
O  -2.495378    -.191539    -.316990
O  -3.670563    2.346579     .549758
O   -.000001   -2.064592    -.899915
O  -5.337635     .327158     .029334
V  -3.903435    1.001160    -.327084
```

E = -887.766150359 h (5.43 eV)
singlet

```
 Zero-point correction=                        .027335 (Hartree/Particle)
 Thermal correction to Energy=                 .043301
 Thermal correction to Enthalpy=               .044245
 Thermal correction to Gibbs Free Energy=     -.023454
```



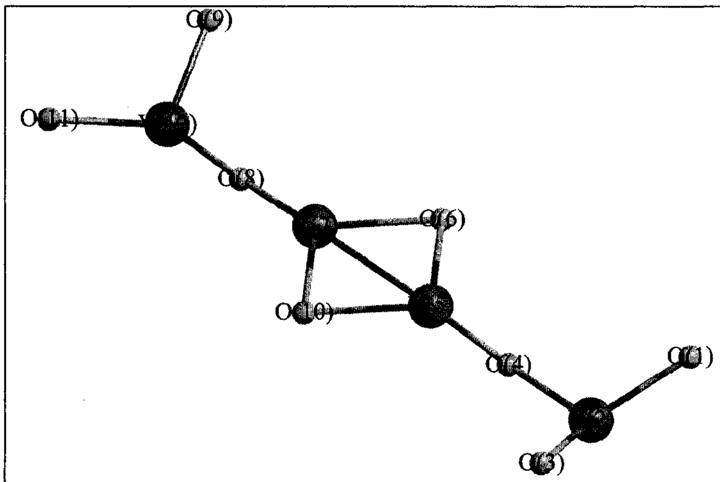
V(12)-O(8)	1.8331
V(12)-O(11)	1.6239
V(12)-O(9)	1.6237
O(10)-V(5)	1.8211
O(10)-V(7)	1.8211
O(8)-V(7)	1.7598
V(7)-O(6)	1.8187
V(7)-V(5)	2.6385
O(6)-V(5)	1.8187
V(5)-O(4)	1.7598
O(4)-V(2)	1.8331
O(3)-V(2)	1.6239
V(2)-O(1)	1.6237

v4o8s7q.log, v4o8s7qfr.log

```
O   5.164683   1.549528   -.723706
V   4.800638    .130420   -.023665
O   5.341331    .078988   1.506706
O   3.073349   -.437178   -.257146
V   1.319226   -.402247   -.120365
O    .000005    .645442    .564947
V  -1.319229   -.402211   -.120409
O  -3.073347   -.437099   -.257276
O  -5.164526   1.549915   -.723228
O   -.000003  -1.465300   -.788252
O  -5.341489    .078423   1.506533
V  -4.800636    .130484   -.023761
```

E = -887.804043404 h (4.40 eV)
quintet

```
 Zero-point correction=                           0.025853 (Hartree/Particle)
 Thermal correction to Energy=                    0.042463
 Thermal correction to Enthalpy=                  0.043407
 Thermal correction to Gibbs Free Energy=        -0.028458
```



V(12)-O(8)	1.8173
V(12)-O(9)	1.6531
V(12)-O(11)	1.6537
O(10)-V(5)	1.8160
O(10)-V(7)	1.8160
O(8)-V(7)	1.7662
V(7)-V(5)	2.6787
V(7)-O(6)	1.8158
O(6)-V(5)	1.8158
V(5)-O(4)	1.7662
O(4)-V(2)	1.8172
O(3)-V(2)	1.6536
V(2)-O(1)	1.6531

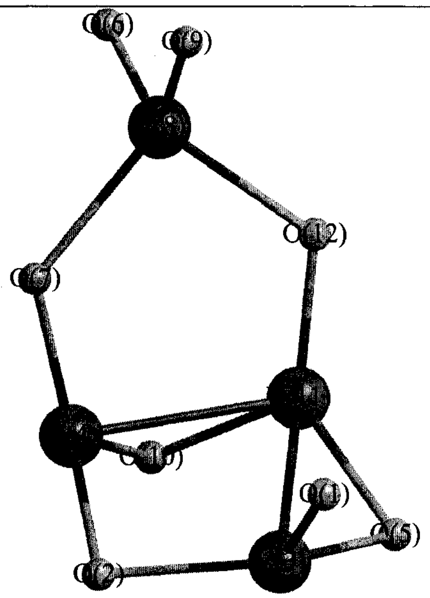
v4o8s7spr1.log

```
O   5.594113    1.433058     .360637
V   4.916670     .029388    -.190348
O   5.712770   -1.294146     .400446
O   3.101820    -.046668    -.136368
V   1.339375    -.045550    -.020546
O   -.000019    1.180438    -.012118
V  -1.339362    -.045567    -.020543
O  -3.101804    -.046710    -.136386
O  -5.594115    1.433093     .360539
O   -.000003   -1.271944    -.024670
O  -5.712825   -1.294109     .400506
V  -4.916661     .029376    -.190332
```

E = -887.743779824 h (6.04 eV)
septet

```
 Zero-point correction=                          .023468 (Hartree/Particle)
 Thermal correction to Energy=                   .040489
 Thermal correction to Enthalpy=                 .041434
 Thermal correction to Gibbs Free Energy=       -.031109
```

Isomer 8



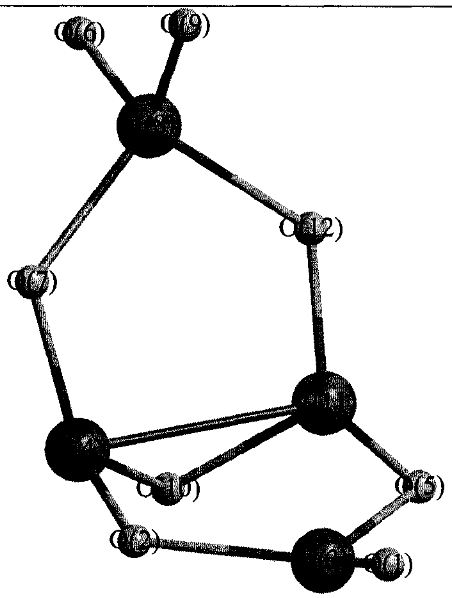
O(12)-V(8)	1.9494
O(12)-V(11)	1.6955
V(11)-O(10)	1.8260
V(11)-V(4)	2.3680
V(11)-V(3)	2.6627
V(11)-O(5)	1.8072
O(10)-V(4)	1.8013
O(9)-V(8)	1.6154
V(8)-O(6)	1.6194
V(8)-O(7)	1.9517
O(7)-V(4)	1.6959
O(5)-V(3)	1.8048
V(4)-O(2)	1.7909
V(3)-O(1)	1.5987
V(3)-O(2)	1.8182

v4o8s8r2.log

```
O  -2.018777   2.271945   -.421361
O  -1.917916   -.407688  -1.534270
V  -2.295876    .719488   -.158548
V   -.345607  -1.089144  -1.013783
O  -2.069945    .179150   1.548570
O   3.613700   -.505905    .228419
O   1.141080   -.370673  -1.400516
V   2.315262    .418914   -.056318
O   2.809441   1.910892   -.429432
O   -.447747  -2.131695    .451628
V   -.418819   -.504534   1.279710
O   1.032153    .362894   1.410163
```

E = -887.897484257 h (1.86 eV)
singlet

```
 Zero-point correction=                     .029787 (Hartree/Particle)
 Thermal correction to Energy=              .044006
 Thermal correction to Enthalpy=            .044950
 Thermal correction to Gibbs Free Energy=  -.014395
```



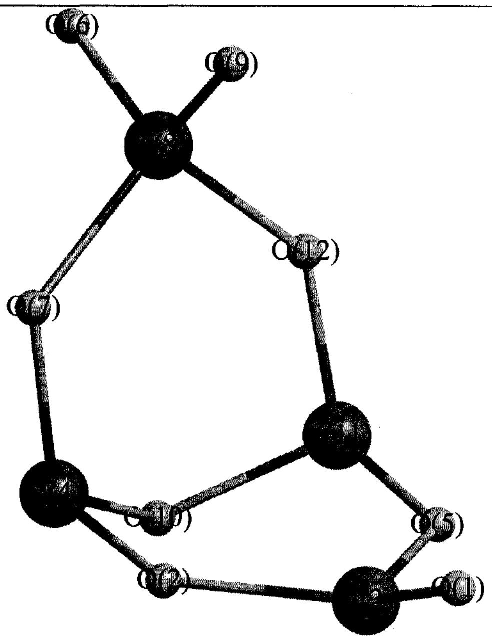
O(12)-V(8)	1.9458
O(12)-V(11)	1.6931
V(11)-O(5)	1.7634
V(11)-O(10)	1.7991
V(11)-V(4)	2.6080
O(10)-V(4)	1.7939
O(9)-V(8)	1.6173
V(8)-O(6)	1.6191
V(8)-O(7)	1.9463
O(7)-V(4)	1.6928
O(5)-V(3)	1.8423
V(4)-O(2)	1.7612
V(3)-O(2)	1.8453
V(3)-O(1)	1.6044

v4o8s8tr.log

```
O  -3.476751   1.891029   -.107064
O  -1.720930   -.113546  -1.506557
V  -2.608165    .544350   -.028311
V   -.191787   -.950528  -1.255509
O  -1.726060    .053893   1.512916
O   3.834720   -.080768    .003902
O   1.265829   -.117027  -1.470359
V   2.364469    .596443   -.030921
O   2.533723   2.202522   -.118380
O   -.166307  -2.111197    .112107
V   -.194464   -.804459   1.348383
O   1.266875    .040902   1.476715
```

E = -887.898503427 h (1.83 eV)
triplet

```
 Zero-point correction=                      .028659 (Hartree/Particle)
 Thermal correction to Energy=               .043377
 Thermal correction to Enthalpy=             .044322
 Thermal correction to Gibbs Free Energy=   -.016553
```



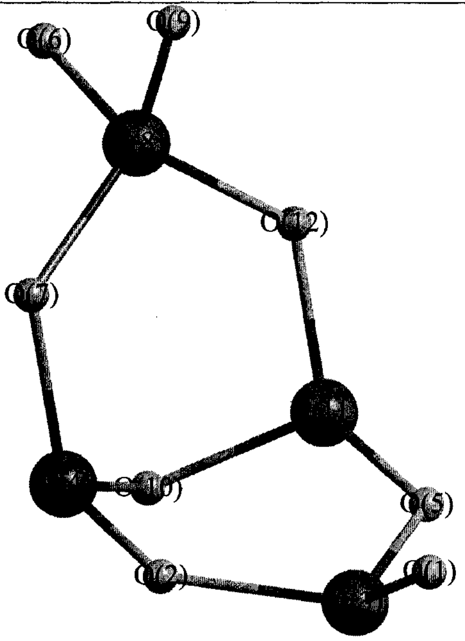
O(12)-V(8)	1.9345
O(12)-V(11)	1.7076
V(11)-O(10)	1.8032
V(11)-O(5)	1.7638
O(10)-V(4)	1.8032
O(9)-V(8)	1.6204
V(8)-O(6)	1.6206
V(8)-O(7)	1.9345
O(7)-V(4)	1.7076
O(5)-V(3)	1.8511
V(4)-O(2)	1.7638
V(3)-O(2)	1.8511
V(3)-O(1)	1.6063

v4o8s8qr2.log

```
O  -3.258908     .000000    2.041174
O  -1.672869    1.492766    -.048292
V  -2.557898     .000000     .595861
V   -.181509    1.539366    -.988824
O  -1.672869   -1.492766    -.048293
O   3.837603     .000001     .157139
O   1.291175    1.477124    -.126750
V   2.286825     .000000     .627632
O   2.229738    -.000001    2.247037
O   -.222037     .000000   -1.927068
V   -.181508   -1.539366    -.988824
O   1.291176   -1.477123    -.126752
```

E = -887.891757752 h (2.02 eV)
quintet

```
 Zero-point correction=                           .027947 (Hartree/Particle)
 Thermal correction to Energy=                    .042805
 Thermal correction to Enthalpy=                  .043750
 Thermal correction to Gibbs Free Energy=        -.018683
```



O(12)-V(8)	1.7978
O(12)-V(11)	1.8179
V(11)-O(5)	1.7948
V(11)-O(10)	1.8074
O(10)-V(4)	1.8074
O(9)-V(8)	1.6760
V(8)-O(6)	1.6912
V(8)-O(7)	1.7979
O(7)-V(4)	1.8178
O(5)-V(3)	1.8213
V(4)-O(2)	1.7947
V(3)-O(2)	1.8213
V(3)-O(1)	1.6097

v4o8s8spr3.log

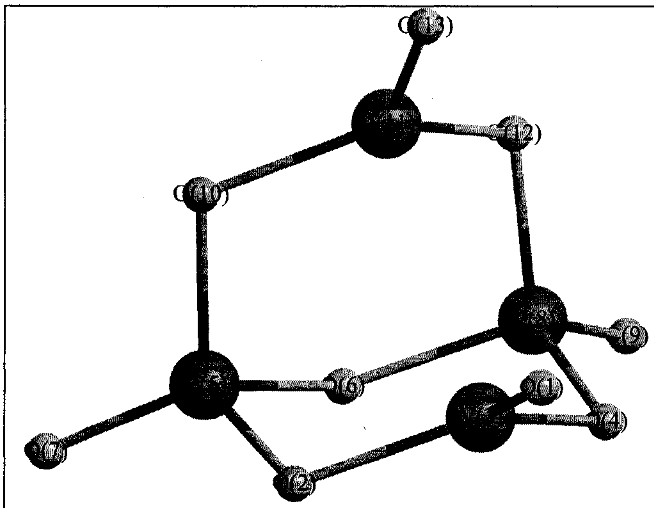
```
O  -3.212904    2.061583    -.011387
O  -1.728390    -.014320   -1.434817
V  -2.712949     .531557    -.003052
V   -.202028    -.957747   -1.399113
O  -1.729749     .001696    1.435599
O   3.805200    -.135979     .000939
O   1.292818     .076442   -1.412854
V   2.280247     .595264    -.002805
O   2.708596    2.215576    -.010981
O   -.018563   -2.073245     .011093
V   -.203392    -.942117    1.408561
O   1.292589     .090743    1.412088
```

E = -887.825683867 h (3.81 eV)
septet

```
 Zero-point correction=                     .026229 (Hartree/Particle)
 Thermal correction to Energy=              .041213
 Thermal correction to Enthalpy=            .042157
 Thermal correction to Gibbs Free Energy=  -.019322
```

V_4O_9 clusters

Isomer 2



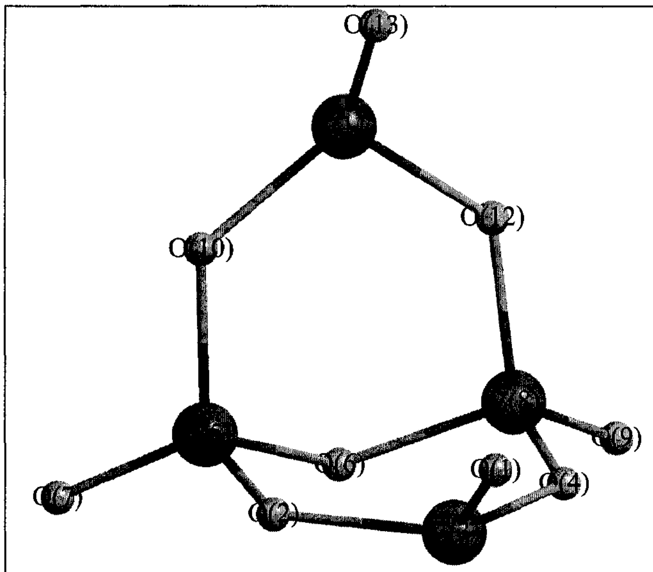
```
O(13)-V(11) 1.5995
O(12)-V(11) 1.7937
O(12)-V(8)  1.7986
V(11)-O(10) 1.7937
O(10)-V(5)  1.7987
O(9)-V(8)   1.6027
V(8)-O(6)   1.8079
V(8)-O(4)   1.7986
O(7)-V(5)   1.6027
O(6)-V(5)   1.8080
V(5)-O(2)   1.7986
O(4)-V(3)   1.7937
V(3)-O(2)   1.7936
V(3)-O(1)   1.5995
V(3)-V(11)  2.8919
```

v4o9s2.log

```
O   -.000296    2.604634   -1.778860
O   1.529464     .103844   -1.419575
V   -.000112    1.040239   -1.445487
O  -1.529439     .103385   -1.420031
V   1.605181    -.998451    -.000305
O   -.000082   -1.830324    -.000157
O   2.845194   -2.013819    -.000663
V  -1.605167    -.998298    -.000280
O  -2.844207   -2.014917    -.000587
O   1.529621     .102999    1.419639
V   -.000072    1.039245    1.446407
O  -1.529524     .102547    1.420116
O   -.000242    2.603788    1.779157
```

E = -963.203067569 h (1.29 eV)
singlet

```
 Zero-point correction=                      .033327 (Hartree/Particle)
 Thermal correction to Energy=               .048526
 Thermal correction to Enthalpy=             .049470
 Thermal correction to Gibbs Free Energy=   -.009473
```



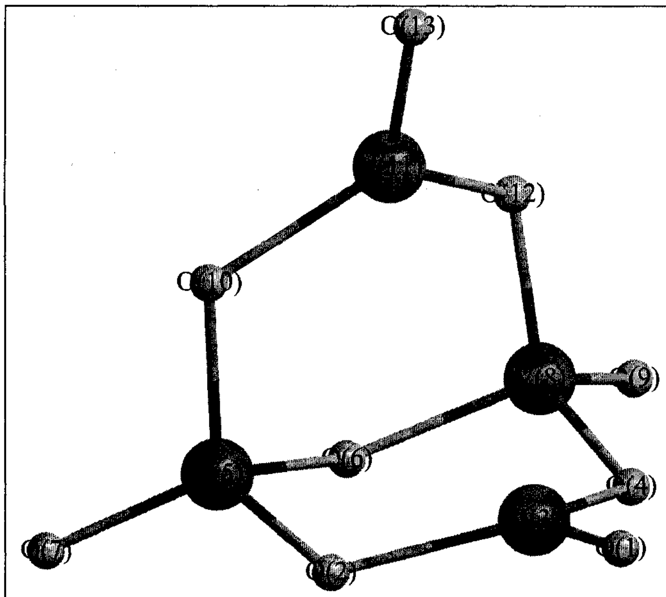
O(13)-V(11)	1.6029
O(12)-V(8)	1.7877
O(12)-V(11)	1.8125
V(11)-O(10)	1.8125
O(10)-V(5)	1.7877
O(9)-V(8)	1.6038
V(8)-O(4)	1.7877
V(8)-O(6)	1.8066
O(7)-V(5)	1.6038
O(6)-V(5)	1.8066
V(5)-O(2)	1.7877
O(4)-V(3)	1.8125
V(3)-O(1)	1.6029
V(3)-O(2)	1.8125

v4o9s2trv2.log

```
O    2.462793    -.000651    2.445404
O    1.473090   -1.474409     .146228
V    2.253572    -.000740     .856245
O    1.474593    1.473560     .145814
V    -.000703   -1.562385    -.861760
O    -.000085     .000022   -1.768701
O    -.000912   -2.834997   -1.837743
V     .000570    1.562409    -.861727
O     .000791    2.835043   -1.837682
O   -1.474654   -1.473652     .145881
V   -2.253437     .000721     .856410
O   -1.473150    1.474493     .146356
O   -2.462472     .000578    2.445586
```

E = -963.210920972 h (1.08 eV)
triplet

```
 Zero-point correction=                          .032811 (Hartree/Particle)
 Thermal correction to Energy=                   .048328
 Thermal correction to Enthalpy=                 .049272
 Thermal correction to Gibbs Free Energy=       -.012844
```



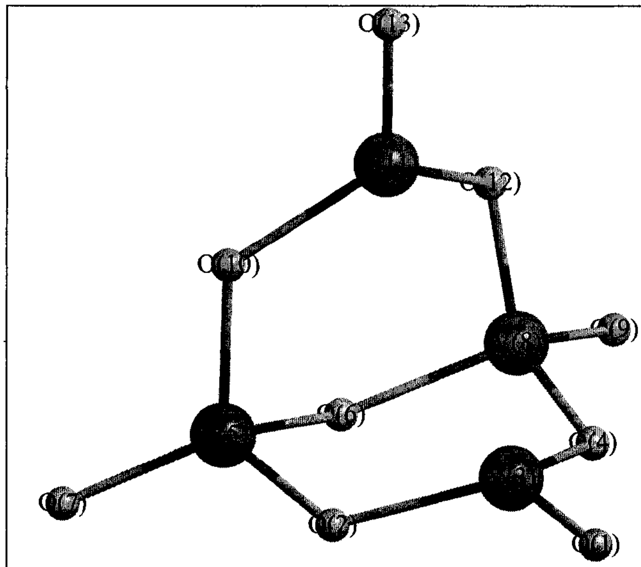
O(13)-V(11)	1.6107
O(12)-V(11)	1.8439
O(12)-V(8)	1.7652
V(11)-O(10)	1.8624
O(10)-V(5)	1.7635
O(9)-V(8)	1.6482
V(8)-O(4)	1.7635
V(8)-O(6)	1.8100
O(7)-V(5)	1.6482
O(6)-V(5)	1.8101
V(5)-O(2)	1.7652
O(4)-V(3)	1.8624
V(3)-O(2)	1.8439
V(3)-O(1)	1.6107
V(3)-V(11)	3.3813

v4o9s2qr1.log

```
O    .094130    2.508225   -2.482754
O   1.542132     .078122   -1.345926
V    .051135    1.107130   -1.689335
O  -1.463901     .052368   -1.442889
V   1.608002   -1.010345     .042130
O    .000067   -1.840399    -.000796
O   2.931363   -1.991988     .084064
V  -1.607921   -1.010421    -.043037
O  -2.931247   -1.992080    -.085928
O   1.463964     .051201    1.442925
V   -.051208    1.105550    1.690366
O  -1.542203     .076848    1.345957
O   -.094328    2.505952    2.484992
```

E = -963.110282505 h (3.82 eV)
quintet

```
 Zero-point correction=                           .028965 (Hartree/Particle)
 Thermal correction to Energy=                    .045325
 Thermal correction to Enthalpy=                  .046269
 Thermal correction to Gibbs Free Energy=        -.017411
```



O(13)-V(11)	1.6372
O(12)-V(8)	1.7908
O(12)-V(11)	1.8178
V(11)-O(10)	1.8180
O(10)-V(5)	1.7905
O(9)-V(8)	1.6806
V(8)-O(4)	1.7905
V(8)-O(6)	1.8219
O(7)-V(5)	1.6806
O(6)-V(5)	1.8219
V(5)-O(2)	1.7908
O(4)-V(3)	1.8180
V(3)-O(2)	1.8178
V(3)-O(1)	1.6372
V(3)-V(11)	3.2775

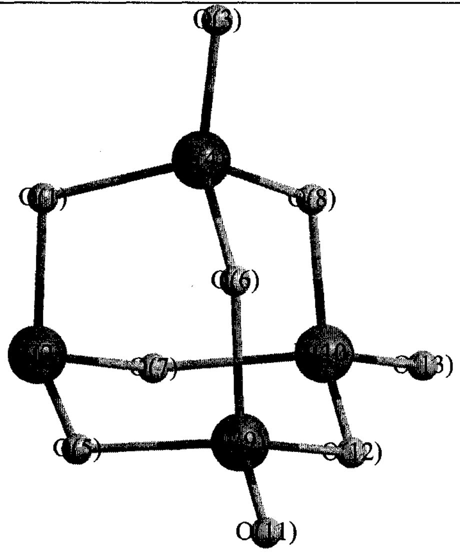
v4o9s2s.log

O	-.005772	2.723877	2.394134
O	1.436753	1.361093	.093738
V	-.003212	1.639238	1.167802
O	-1.441643	1.356696	.092530
V	1.617088	.002310	-1.058757
O	-.000006	-.000847	-1.898037
O	3.042260	.005140	-1.949423
V	-1.617094	-.003272	-1.058746
O	-3.042273	-.006843	-1.949400
O	1.441668	-1.356689	.093666
V	.003218	-1.638247	1.169204
O	-1.436778	-1.361084	.094893
O	.005789	-2.721428	2.396827

E = -963.019335402 h (6.29 eV)
septet

```
 Zero-point correction=                           .025743 (Hartree/Particle)
 Thermal correction to Energy=                    .043029
 Thermal correction to Enthalpy=                  .043973
 Thermal correction to Gibbs Free Energy=        -.022090
```

Isomer 3



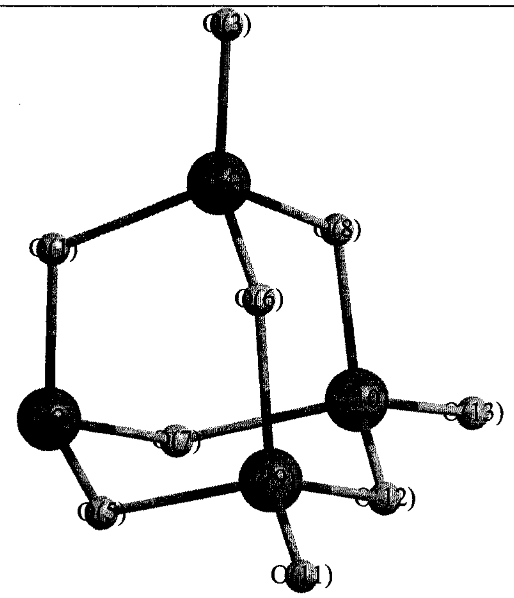
```
O(13)-V(10)  1.6033
O(12)-V(10)  1.8070
O(12)-V(9)   1.8074
O(11)-V(9)   1.6033
V(10)-O(8)   1.7806
V(10)-O(7)   1.8776
V(9)-O(6)    1.7810
V(9)-O(5)    1.8771
O(8)-V(4)    1.8171
O(7)-V(2)    1.7279
O(6)-V(4)    1.8172
O(5)-V(2)    1.7281
V(4)-O(3)    1.6016
V(4)-O(1)    1.8491
V(2)-O(1)    1.7693
```

v4o9s3r1.log

```
O   1.915441    -.013834    1.188808
V    .339679    -.002326    1.993406
O   3.087219    -.017383   -1.480069
V   1.717694    -.011566    -.649673
O   -.510136   -1.402475    1.442411
O    .625534   -1.415028   -1.023418
O   -.489787    1.410278    1.443687
O    .642173    1.404562   -1.023208
V  -1.022235   -1.536453    -.358551
V  -1.002772    1.549770    -.357128
O  -1.786011   -2.886217    -.765024
O  -1.830803     .012241    -.821632
O  -1.746680    2.909506    -.767209
```

E = -963.225450356 h (0.68 eV)
singlet

```
 Zero-point correction=                      .033463 (Hartree/Particle)
 Thermal correction to Energy=               .047829
 Thermal correction to Enthalpy=             .048773
 Thermal correction to Gibbs Free Energy=   -.007212
```

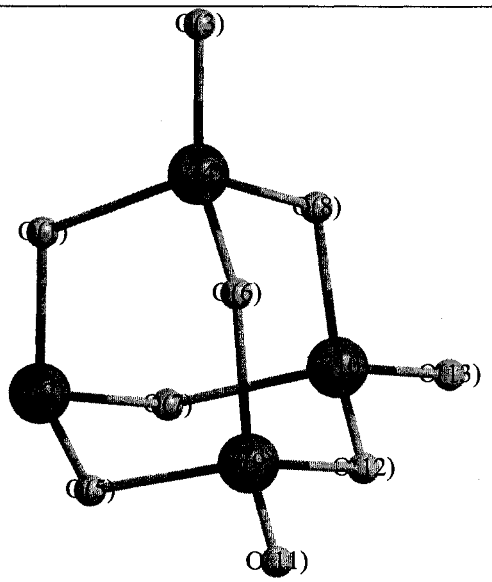


v4o9bsopt.log, v4o9bsoptfr.log

O(13)-V(10)	1.6030
O(12)-V(9)	1.8044
O(12)-V(10)	1.8025
O(11)-V(9)	1.6035
V(10)-O(8)	1.7979
V(10)-O(7)	1.8786
V(9)-O(6)	1.8041
V(9)-O(5)	1.8695
O(8)-V(4)	1.7976
O(7)-V(2)	1.7420
O(6)-V(4)	1.8011
O(5)-V(2)	1.7371
V(4)-O(3)	1.6031
V(4)-O(1)	1.8813
V(2)-O(1)	1.7415

```
O  -0.208366    1.643689    1.382666
V  -0.077397    0.038445    2.045097
O  -0.308174    3.265857   -1.127935
V  -0.128231    1.806307   -0.489850
O   1.386378   -0.638434    1.399454
O   1.385310    0.943164   -0.946041
O  -1.384431   -0.901344    1.379526
O  -1.417456    0.654869   -0.983298
V   1.657262   -0.768705   -0.445686
V  -1.455981   -1.073579   -0.489772
O   3.066536   -1.414283   -0.856172
O   0.180340   -1.677582   -0.944326
O  -2.690617   -1.880458   -1.117674
 Zero-point correction=                          0.032834 (Hartree/Particle)
 Thermal correction to Energy=                   0.047411
 Thermal correction to Enthalpy=                 0.048355
 Thermal correction to Gibbs Free Energy=       -0.008220
```

E = -963.245403548 h (0.14 eV)
singlet, broken symmetry



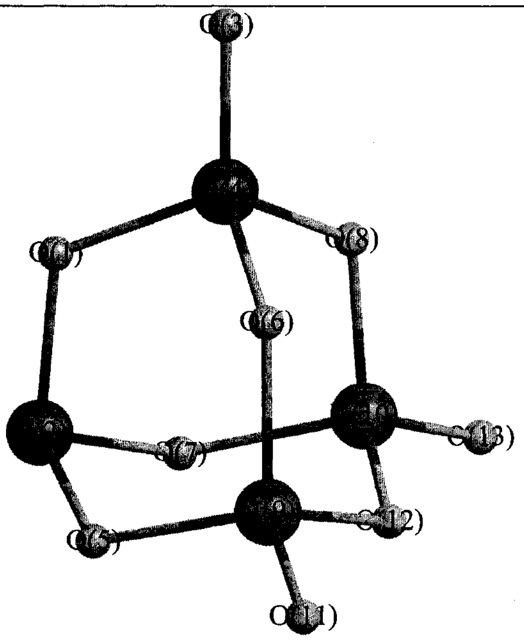
O(13)-V(10)	1.6032
O(12)-V(9)	1.8085
O(12)-V(10)	1.7979
O(11)-V(9)	1.6036
V(10)-O(8)	1.7985
V(10)-O(7)	1.8578
V(9)-O(6)	1.8089
V(9)-O(5)	1.8410
O(8)-V(4)	1.7991
O(7)-V(2)	1.7587
O(6)-V(4)	1.7981
O(5)-V(2)	1.7573
V(4)-O(3)	1.6031
V(4)-O(1)	1.8587
V(2)-O(1)	1.7585

v4o9s3trv2.log

O	-.213755	1.651643	1.359383
V	-.081376	.040586	2.051606
O	-.291948	3.272192	-1.091802
V	-.128539	1.794538	-.491905
O	1.394223	-.642199	1.384858
O	1.383193	.941202	-.960409
O	-1.393898	-.903625	1.359637
O	-1.428303	.658180	-.998052
V	1.657982	-.767055	-.432835
V	-1.450826	-1.066973	-.490059
O	3.065785	-1.417173	-.841458
O	.178650	-1.663590	-.960427
O	-2.686015	-1.899780	-1.082549

E = -963.250508579 h (0 eV)
triplet

```
 Zero-point correction=                           .032872 (Hartree/Particle)
 Thermal correction to Energy=                    .047366
 Thermal correction to Enthalpy=                  .048310
 Thermal correction to Gibbs Free Energy=        -.008991
```



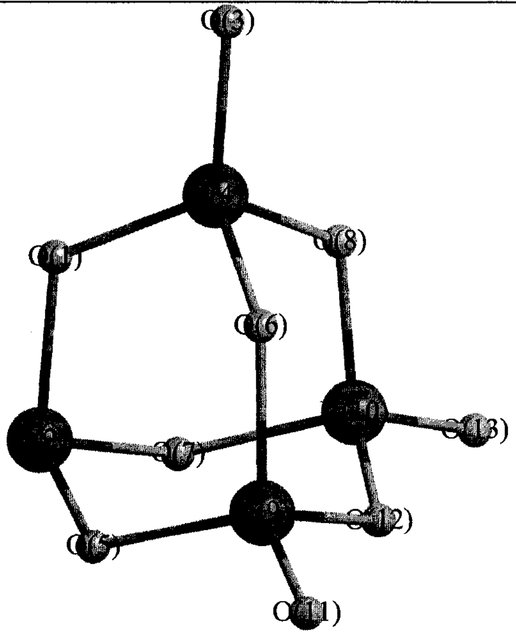
```
O(13)-V(10)  1.6414
O(12)-V(10)  1.7924
O(12)-V(9)   1.8222
O(11)-V(9)   1.6180
V(10)-O(7)   1.8113
V(10)-O(8)   1.8130
V(9)-O(5)    1.8124
V(9)-O(6)    1.8229
O(8)-V(4)    1.8115
O(7)-V(2)    1.7913
O(6)-V(4)    1.7907
O(5)-V(2)    1.7941
V(4)-O(1)    1.8111
V(4)-O(3)    1.6429
V(2)-O(1)    1.7915
```

v4o9s3qr1.log

```
O  -1.452695    -.762102    1.340170
V    .000422     .010325    2.048124
O  -2.997866   -1.597885    -.981537
V  -1.628546    -.854959    -.459949
O    .058005    1.653032    1.329122
O  -1.384642     .841327    -.979216
O   1.394828    -.863363    1.340366
O   -.057694   -1.598519    -.970856
V    .066000    1.823412    -.475194
V   1.563164    -.966945    -.460099
O    .117419    3.354731    -.995079
O   1.445785     .744879    -.978464
O   2.873873   -1.806119    -.981540
```

E = -963.175613701 h (2.04 eV)
quintet

```
 Zero-point correction=                       .030380 (Hartree/Particle)
 Thermal correction to Energy=                .045272
 Thermal correction to Enthalpy=              .046216
 Thermal correction to Gibbs Free Energy=    -.012216
```



```
O(13)-V(10) 1.6710
O(12)-V(10) 1.8025
O(12)-V(9)  1.8368
O(11)-V(9)  1.6361
V(10)-O(7)  1.7848
V(10)-O(8)  1.7815
V(9)-O(5)   1.7825
V(9)-O(6)   1.8171
O(8)-V(4)   1.8327
O(7)-V(2)   1.8263
O(6)-V(4)   1.7927
O(5)-V(2)   1.8333
V(4)-O(1)   1.7567
V(4)-O(3)   1.7865
V(2)-O(1)   1.8533
```

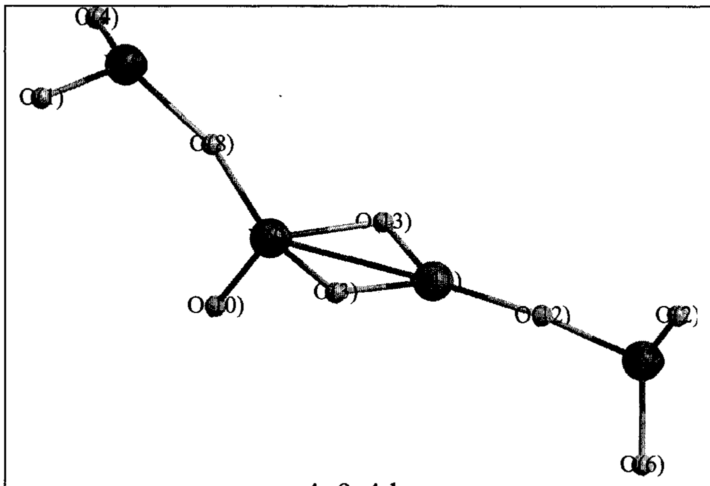
v4o9s3s.log

```
O  -1.445300   -.610761    1.400506
V    .152673    .072373    2.044424
O  -3.285189  -1.353617    -.933395
V  -1.726536   -.722668    -.329897
O    .273665   1.732318    1.275638
O  -1.334108    .926883    -.911944
O   1.423604   -.997503    1.285835
O   -.232807  -1.624235    -.890789
V    .194820   1.819601    -.502965
V   1.432173  -1.130313    -.493955
O    .348110   3.318538   -1.140632
O   1.461652    .593734   -1.019060
O   2.637624  -2.097462   -1.129281
```

E = -963.076066834 h (4.75 eV)
septet

```
 Zero-point correction=                      .028349 (Hartree/Particle)
 Thermal correction to Energy=               .043947
 Thermal correction to Enthalpy=             .044891
 Thermal correction to Gibbs Free Energy=   -.015564
```

Isomer 4



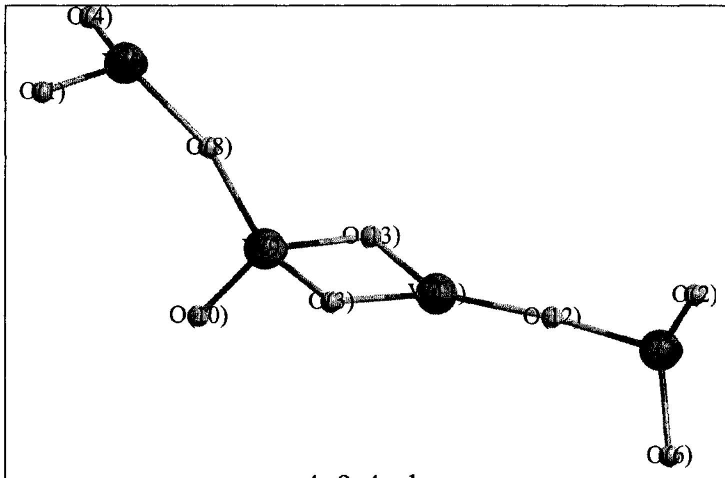
O(13)-V(9)	1.8948
O(13)-V(11)	1.7295
O(12)-V(11)	1.7785
O(12)-V(7)	1.8071
V(11)-V(9)	2.6422
V(11)-O(3)	1.7297
O(10)-V(9)	1.6004
V(9)-O(8)	1.7723
V(9)-O(3)	1.8949
O(8)-V(5)	1.8076
V(7)-O(6)	1.6190
V(7)-O(2)	1.6194
V(5)-O(4)	1.6201
V(5)-O(1)	1.6199

v4o9s4.log

```
O   5.192692    -.684570    1.395082
O  -5.102186   -1.902332     .244307
O   -.158079     .233220    1.133321
O   5.315342    -.351324   -1.237564
V   4.403548    -.878125    -.006333
O  -5.557691     .651083     .789459
V  -4.778786    -.376106    -.189977
O   2.700574    -.271962    -.012602
V   1.296323     .806691     .062618
O   1.634692    2.349486     .320903
V  -1.270645     .234180    -.191085
O  -3.018767    -.021583    -.395229
O   -.001594     .611392   -1.303940
```

E = -963.084775544 h (4.51 eV)
singlet

```
 Zero-point correction=                        .031287 (Hartree/Particle)
 Thermal correction to Energy=                 .048249
 Thermal correction to Enthalpy=               .049193
 Thermal correction to Gibbs Free Energy=     -.020547
```



O(13)-V(9)	1.8114
O(13)-V(11)	1.8169
O(12)-V(11)	1.7900
O(12)-V(7)	1.8010
V(11)-O(3)	1.8132
O(10)-V(9)	1.6076
V(9)-O(8)	1.7835
V(9)-O(3)	1.8139
O(8)-V(5)	1.7957
V(7)-O(6)	1.6191
V(7)-O(2)	1.6194
V(5)-O(4)	1.6200
V(5)-O(1)	1.6197

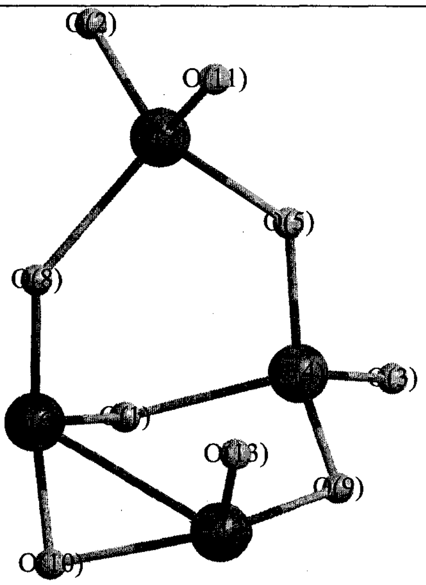
v4o9s4tr.log

```
O    5.157918    -.786482    1.372626
O   -5.015530   -1.994477     .268119
O    -.053995     .452303    1.159247
O    5.260087    -.549507   -1.265550
V    4.331967    -.975026    -.007843
O   -5.631714     .539499     .727599
V   -4.781196    -.466330    -.213927
O    2.684139    -.261422    -.010554
V    1.319443     .884892     .056191
O    1.836468    2.392973     .263296
V   -1.312225     .375558    -.144114
O   -3.044288    -.016121    -.369381
O     .077697     .743338   -1.255034
```

E = -963.095791818 h (4.21 eV)
triplet

```
 Zero-point correction=                           .031239 (Hartree/Particle)
 Thermal correction to Energy=                    .048241
 Thermal correction to Enthalpy=                  .049185
 Thermal correction to Gibbs Free Energy=        -.022452
```

Isomer 5



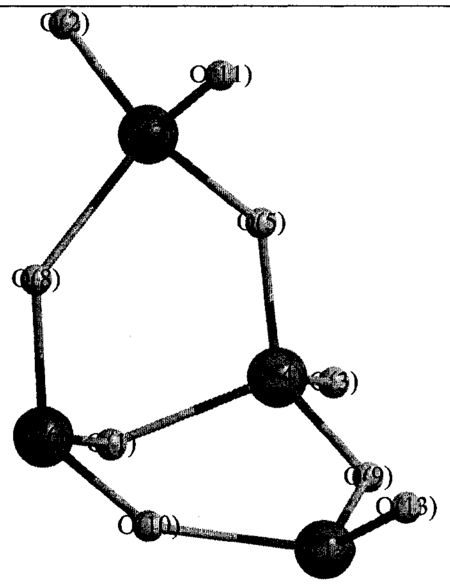
O(13)-V(12)	1.5964
V(12)-V(6)	2.6100
V(12)-O(9)	1.7817
V(12)-O(10)	1.8305
O(11)-V(7)	1.6171
O(10)-V(6)	1.7729
O(9)-V(4)	1.8172
O(8)-V(7)	1.9768
O(8)-V(6)	1.6822
V(7)-O(2)	1.6195
V(7)-O(5)	1.9094
V(6)-O(1)	1.7327
O(5)-V(4)	1.7138
V(4)-O(3)	1.6043
V(4)-O(1)	1.8819

v4o9s5.log

O	-.579001	.920438	1.576348
O	3.481861	-.202592	.728387
O	-.353657	3.376846	-.075537
V	-.286443	1.773938	-.075128
O	1.251748	1.191673	-.556772
V	-.637339	-.805518	1.435604
V	2.194208	-.435647	-.225804
O	.808565	-1.393679	.808578
O	-1.604415	.992802	-1.052359
O	-2.190100	-1.465547	.891111
O	2.672298	-1.198496	-1.569092
V	-2.029193	-.714429	-.770444
O	-1.305844	-1.699184	-1.797818

E = -963.174322156 h (2.07 eV)
singlet

```
 Zero-point correction=                           .033549 (Hartree/Particle)
 Thermal correction to Energy=                    .048685
 Thermal correction to Enthalpy=                  .049630
 Thermal correction to Gibbs Free Energy=        -.009790
```



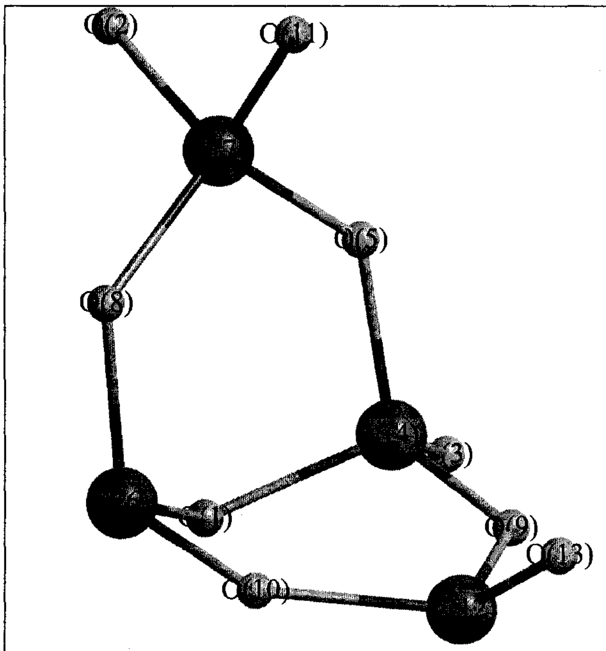
```
O(13)-V(12)  1.6019
V(12)-O(9)   1.7867
V(12)-O(10)  1.8474
O(11)-V(7)   1.6200
O(10)-V(6)   1.7594
O(9)-V(4)    1.8141
O(8)-V(7)    1.9682
O(8)-V(6)    1.6848
V(7)-O(2)    1.6197
V(7)-O(5)    1.8989
V(6)-O(1)    1.7508
O(5)-V(4)    1.7187
V(4)-O(3)    1.6051
V(4)-O(1)    1.8694
```

v4o9s5trrr2.log

```
O   -.242021     .955112    1.646691
O   3.775880    -.101544    -.058566
O   -.301709    3.310122    -.097679
V   -.265818    1.705720    -.065277
O   1.157664    1.056386    -.776533
V   -.158047    -.791451    1.733901
V   2.265895    -.463942    -.518977
O   1.272397   -1.264216     .979769
O  -1.760855     .960343    -.772568
O  -1.597609   -1.366362     .901755
O   2.322811   -1.444661   -1.807172
V  -2.521317    -.636974    -.522253
O  -2.672407   -1.566993   -1.817726
```

E = -963.179760622 h (1.93 eV)
triplet

```
 Zero-point correction=                          .032730 (Hartree/Particle)
 Thermal correction to Energy=                   .048280
 Thermal correction to Enthalpy=                 .049224
 Thermal correction to Gibbs Free Energy=       -.013126
```



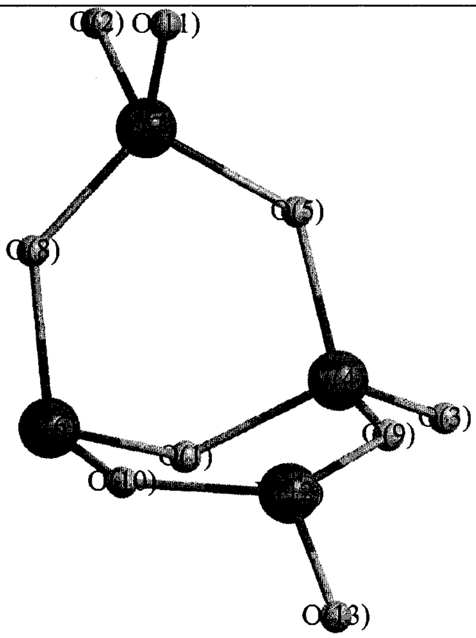
O(13)-V(12)	1.6053
V(12)-O(9)	1.8139
V(12)-O(10)	1.8284
O(11)-V(7)	1.6809
O(10)-V(6)	1.7764
O(9)-V(4)	1.7928
O(8)-V(7)	1.8139
O(8)-V(6)	1.7909
V(7)-O(2)	1.6727
V(7)-O(5)	1.7865
V(6)-O(1)	1.7862
O(5)-V(4)	1.8127
V(4)-O(3)	1.6054
V(4)-O(1)	1.8129

v4o9s5q.log

O	-.211095	.914955	1.600073
O	3.781522	-.082583	-.029827
O	-.244643	3.301263	.066036
V	-.254298	1.699028	-.033970
O	1.224453	1.006632	-.821304
V	-.170199	-.868512	1.690118
V	2.209836	-.442677	-.474971
O	1.326007	-1.343322	.828089
O	-1.726199	1.020080	-.800000
O	-1.629629	-1.414421	.836998
O	2.495762	-1.385041	-1.837217
V	-2.543379	-.572069	-.504100
O	-2.836814	-1.487903	-1.789444

E = -963.128150180 h (3.33 eV)
quintet

```
 Zero-point correction=                           .030262 (Hartree/Particle)
 Thermal correction to Energy=                    .046170
 Thermal correction to Enthalpy=                  .047115
 Thermal correction to Gibbs Free Energy=        -.016052
```



```
O(13)-V(12)  1.6352
V(12)-O(9)   1.8552
V(12)-O(10)  1.7878
O(11)-V(7)   1.6912
O(10)-V(6)   1.8182
O(9)-V(4)    1.7836
O(8)-V(7)    1.7607
O(8)-V(6)    1.8528
V(7)-O(2)    1.6853
V(7)-O(5)    1.8148
V(6)-O(1)    1.8397
O(5)-V(4)    1.8040
V(4)-O(3)    1.6755
V(4)-O(1)    1.7624
```

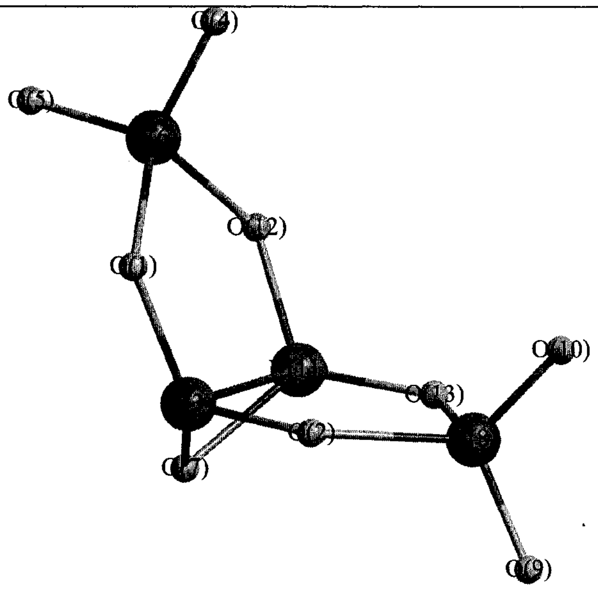
v4o9s5sr1.log

```
O   -.295084     .600283    1.610564
O   3.950595    -.081588    -.060045
O   -.300705    3.278053     .570848
V   -.207486    1.647705     .195930
O   1.349626    1.172329    -.581075
V   -.179411   -1.230080    1.466283
V   2.340137    -.345027    -.480992
O   1.468267   -1.391642     .634564
O  -1.595764    1.096173    -.778679
O  -1.604607   -1.583340     .394008
O   2.548501   -1.066938   -1.996163
V  -2.454079    -.548441    -.790703
O  -4.080917    -.655284    -.916762
```

E = -963.040184720 h (5.72 eV)
septet

```
 Zero-point correction=                           .026824 (Hartree/Particle)
 Thermal correction to Energy=                    .043722
 Thermal correction to Enthalpy=                  .044666
 Thermal correction to Gibbs Free Energy=        -.021398
```

Isomer 6



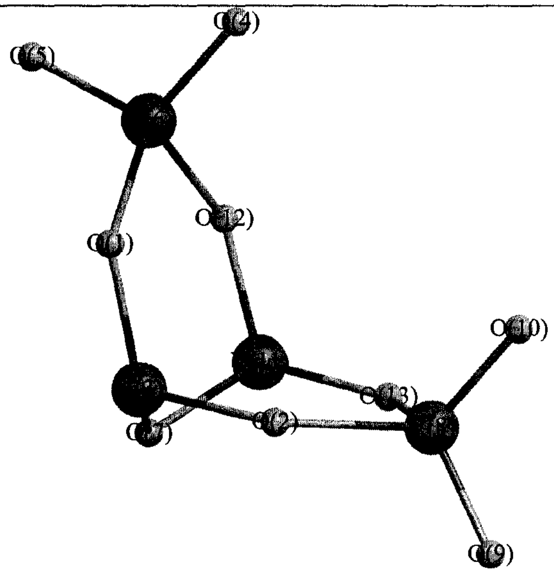
```
O(13)-V(8)  1.9494
O(13)-V(11) 1.6918
O(12)-V(11) 1.6919
O(12)-V(6)  1.9495
V(11)-V(3)  2.5601
V(11)-O(7)  1.7981
O(10)-V(8)  1.6142
O(9)-V(8)   1.6181
V(8)-O(2)   1.9494
O(7)-V(3)   1.7980
V(6)-O(1)   1.9493
V(6)-O(4)   1.6142
V(6)-O(5)   1.6181
V(3)-O(2)   1.6919
V(3)-O(1)   1.6919
```

v4o9s6.log

```
O   -1.441654    -.040173    1.432624
O    1.441288    -.039871    1.432411
V    -.000091    -.912605    1.280287
O   -2.822991    2.197791    -.000356
O   -4.044349    -.127047    -.000064
V   -2.598421     .599331    -.000162
O     .000413   -2.175715     .000627
V    2.598483     .599476    -.000146
O    4.043749    -.128182    -.000007
O    2.824183    2.197772    -.000494
V    -.000047    -.913350   -1.279862
O   -1.441613    -.041047   -1.432686
O    1.441194    -.040478   -1.432391
```

E = -963.163782224 h (2.36 eV)
singlet

```
 Zero-point correction=                      .033445 (Hartree/Particle)
 Thermal correction to Energy=               .048805
 Thermal correction to Enthalpy=             .049749
 Thermal correction to Gibbs Free Energy=   -.011037
```



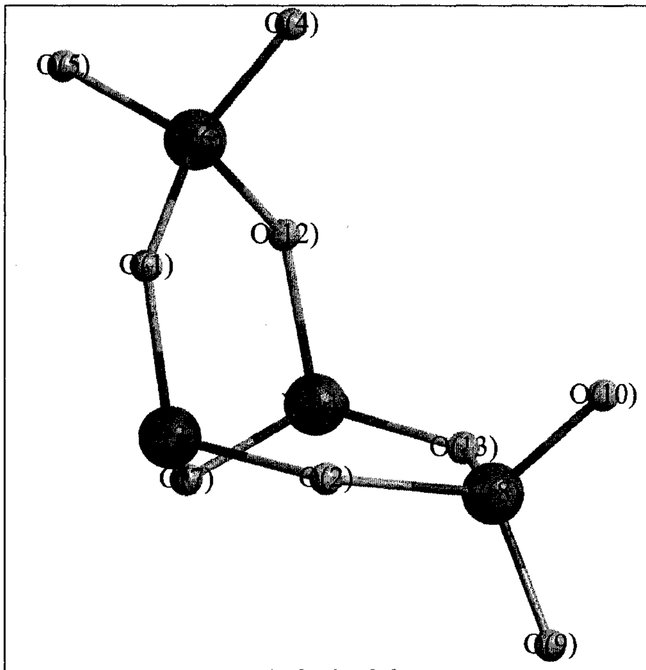
```
O(13)-V(8)   1.9411
O(13)-V(11)  1.6997
O(12)-V(6)   1.9411
O(12)-V(11)  1.6997
V(11)-O(7)   1.8057
O(10)-V(8)   1.6169
O(9)-V(8)    1.6191
V(8)-O(2)    1.9411
O(7)-V(3)    1.8057
V(6)-O(5)    1.6191
V(6)-O(4)    1.6169
V(6)-O(1)    1.9411
V(3)-O(1)    1.6997
V(3)-O(2)    1.6997
```

v4o9s6tr.log

```
O   1.425681    -.119888   -1.458996
O  -1.425569    -.119778   -1.458974
V    .000020   -1.041529   -1.543537
O   2.458881    2.260466    -.000036
O   3.983073     .112671     .000037
V   2.453435     .643538    -.000004
O   -.000013   -1.978479     .000027
V  -2.453441     .643540    -.000012
O  -3.983016     .112491    -.000039
O  -2.459082    2.260468    -.000001
V   -.000003   -1.041497    1.543562
O   1.425631    -.119814    1.458981
O  -1.425616    -.119785    1.458975
```

E = -963.157999299 h (2.52 eV)
triplet

```
 Zero-point correction=                          .032851 (Hartree/Particle)
 Thermal correction to Energy=                   .048371
 Thermal correction to Enthalpy=                 .049315
 Thermal correction to Gibbs Free Energy=       -.013387
```



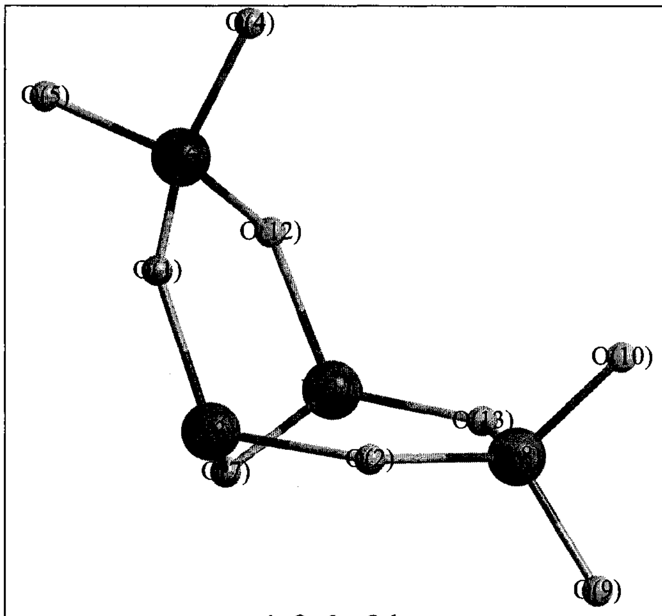
```
O(13)-V(8)   1.8652
O(13)-V(11)  1.7497
O(12)-V(6)   1.8652
O(12)-V(11)  1.7497
V(11)-O(7)   1.7986
O(10)-V(8)   1.6467
O(9)-V(8)    1.6416
V(8)-O(2)    1.8652
O(7)-V(3)    1.7986
V(6)-O(4)    1.6467
V(6)-O(1)    1.8652
V(6)-O(5)    1.6416
V(3)-O(2)    1.7497
V(3)-O(1)    1.7497
```

v4o9s6qr2.log

```
O  -1.443402   -1.476326    -.030252
O   1.443081   -1.476316    -.029786
V    .000008   -1.559455   -1.015651
O  -2.523286    -.000058    2.234361
O  -3.928751    -.000035    -.001439
V  -2.398293    -.000024     .592401
O    .000128     .000063   -1.911671
V   2.398289    -.000016     .592429
O   3.928373     .000033    -.002344
O   2.524297    -.000085    2.234310
V   -.000013    1.559526   -1.015553
O  -1.443446    1.476331    -.030194
O   1.443035    1.476304    -.029657
```

E = -963.106805607 h (3.91 eV)
quintet

```
 Zero-point correction=                          .029833 (Hartree/Particle)
 Thermal correction to Energy=                   .045735
 Thermal correction to Enthalpy=                 .046679
 Thermal correction to Gibbs Free Energy=       -.016930
```



```
O(13)-V(8)   1.8005
O(13)-V(11)  1.8098
O(12)-V(11)  1.8098
O(12)-V(6)   1.8005
V(11)-O(7)   1.7878
O(10)-V(8)   1.6858
O(9)-V(8)    1.6761
V(8)-O(2)    1.8005
O(7)-V(3)    1.7878
V(6)-O(1)    1.8005
V(6)-O(4)    1.6858
V(6)-O(5)    1.6761
V(3)-O(2)    1.8098
V(3)-O(1)    1.8098
```

v4o9s6sv2.log

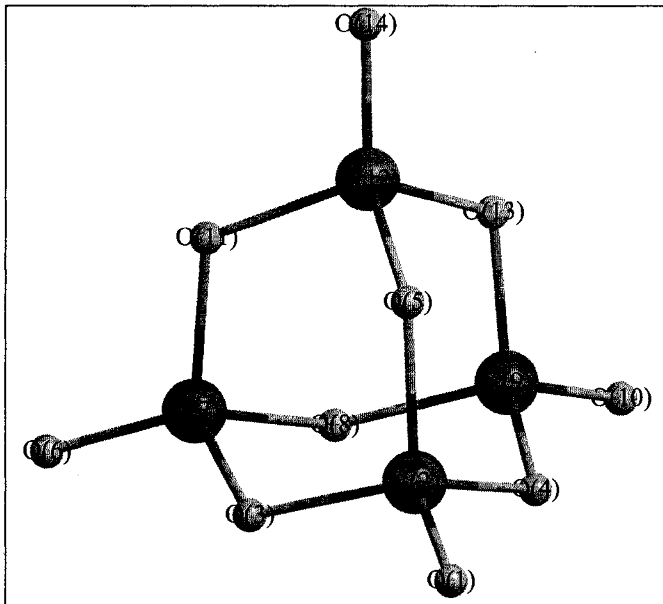
```
O  -1.549371   -1.450935    -.027284
O   1.549323   -1.450934    -.027354
V   -.000045   -1.557277    -.956658
O  -2.730770    -.000072    2.194033
O  -4.048986     .000008     .003584
V  -2.457880    -.000016     .530501
O   -.000063     .000060   -1.834733
V   2.457920    -.000018     .530294
O   4.048945    -.000010     .003128
O   2.731074    -.000067    2.193782
V   -.000039    1.557338    -.956556
O  -1.549360    1.450934    -.027183
O   1.549336    1.450939    -.027271
```

E = -963.048021016 h (5.51 eV)
septet

```
 Zero-point correction=                        .028503 (Hartree/Particle)
 Thermal correction to Energy=                 .044676
 Thermal correction to Enthalpy=               .045620
 Thermal correction to Gibbs Free Energy=     -.018425
```

V_4O_{10} clusters

Isomer 1



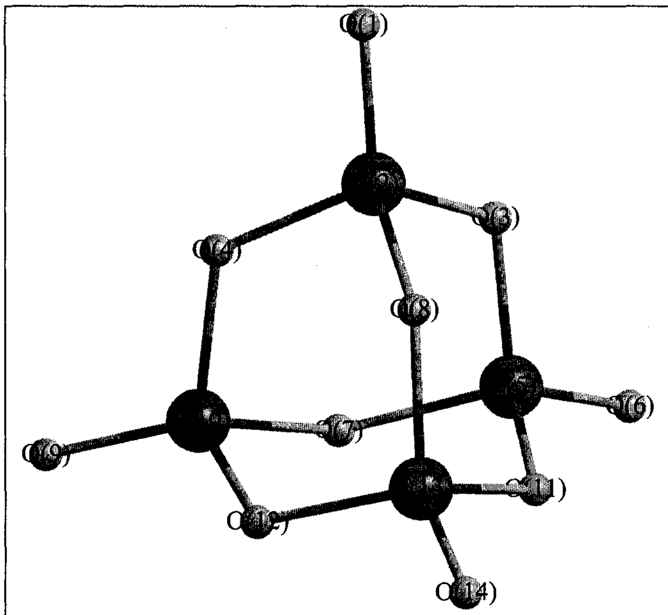
```
O(14)-V(12) 1.6005
O(13)-V(9)  1.8008
O(13)-V(12) 1.8019
V(12)-O(5)  1.8017
V(12)-O(11) 1.8009
O(11)-V(7)  1.8017
O(10)-V(9)  1.6005
V(9)-O(4)   1.8018
V(9)-O(8)   1.8021
O(8)-V(7)   1.8009
V(7)-O(3)   1.8019
V(7)-O(6)   1.6004
O(5)-V(2)   1.8019
O(4)-V(2)   1.8024
O(3)-V(2)   1.8016
V(2)-O(1)   1.6005
```

v4o10s1.log

```
O      .373439    1.271307    3.241347
V      .204238     .690813    1.759481
O    -1.101033    -.539579    1.591674
O     1.673043    -.128286    1.111098
O     -.197845    1.934421     .519087
O    -2.591127   -2.357368    -.036644
V    -1.407325   -1.280429    -.022052
O      .196772   -1.934910    -.513854
V     1.621329    -.831740    -.546879
O     2.986297   -1.529283   -1.007110
O    -1.674237     .131827   -1.108440
V     -.418360    1.419744   -1.193358
O     1.104379     .541901   -1.590380
O     -.769350    2.614603   -2.198703
```

E = -1038.52608132 h (0 eV)
singlet

```
 Zero-point correction=                      .037030 (Hartree/Particle)
 Thermal correction to Energy=               .052666
 Thermal correction to Enthalpy=             .053610
 Thermal correction to Gibbs Free Energy=   -.004903
```



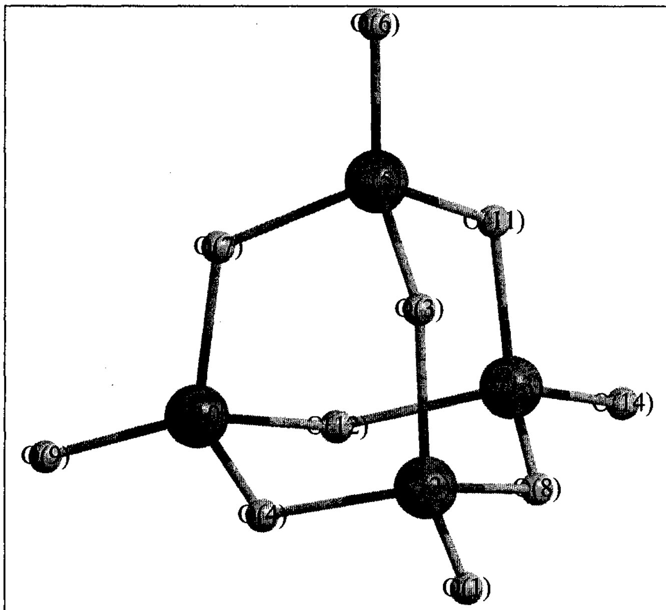
O(14)-V(13)	1.6233
V(13)-O(12)	1.8035
V(13)-O(8)	1.8087
V(13)-O(11)	1.7954
O(12)-V(10)	1.8025
O(11)-V(5)	1.7957
V(10)-O(9)	1.6232
V(10)-O(4)	1.7951
V(10)-O(7)	1.8098
O(8)-V(2)	1.8090
O(7)-V(5)	1.8077
O(6)-V(5)	1.6233
V(5)-O(3)	1.8038
O(4)-V(2)	1.7956
O(3)-V(2)	1.8024
V(2)-O(1)	1.6230

v4o10s1trv2.log, v4o10s1trv2fr.log

```
O  -2.094455   2.041998  -2.010889
V  -1.150689   1.067349  -1.120071
O  -2.012305  -0.052817  -0.001360
O  -0.049754   1.944210  -0.004992
V  -1.093322  -1.124921   1.121070
O  -1.978346  -2.149137   2.017128
O  -0.000906   0.005445   2.013594
O  -0.000681  -0.005684  -2.013735
O   1.983539   2.162048   1.998234
V   1.094203   1.131284   1.114283
O   0.050089  -1.944402   0.005006
O   2.011830   0.053188  -0.001410
V   1.150040  -1.073379  -1.115234
O   2.090322  -2.055810  -2.001714
```

E = -1038.45988264 h (1.80 eV)
triplet

```
 Zero-point correction=                        0.033697 (Hartree/Particle)
 Thermal correction to Energy=                 0.049859
 Thermal correction to Enthalpy=               0.050803
 Thermal correction to Gibbs Free Energy=     -0.010213
```



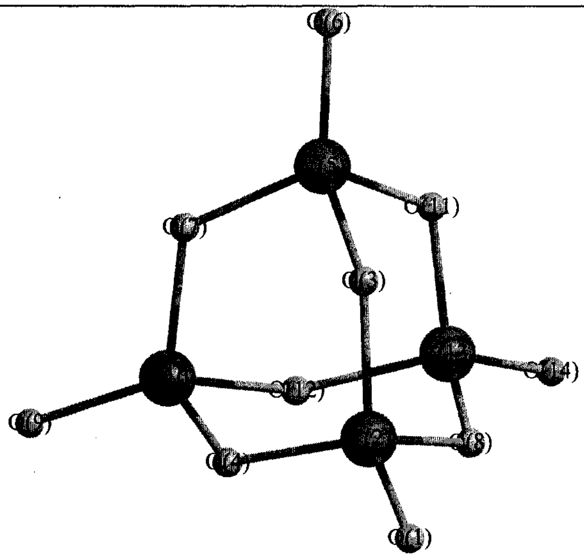
O(14)-V(13)	1.6475
V(13)-O(8)	1.8053
V(13)-O(11)	1.8052
V(13)-O(12)	1.8051
O(12)-V(10)	1.8040
O(11)-V(5)	1.8055
V(10)-O(7)	1.8048
V(10)-O(4)	1.8059
V(10)-O(9)	1.6479
O(8)-V(2)	1.8047
O(7)-V(5)	1.8046
O(6)-V(5)	1.6476
V(5)-O(3)	1.8053
O(4)-V(2)	1.8040
O(3)-V(2)	1.8052
V(2)-O(1)	1.6478

v4o10s1qr1.log

O	-2.069947	0.767369	2.841688
V	-1.122974	0.417410	1.539386
O	-0.376630	1.817360	0.678158
O	-1.912230	-0.470312	0.181694
V	0.692380	1.654527	-0.767476
O	1.273521	3.051007	-1.420687
O	-0.328237	0.625268	-1.842357
O	0.324679	-0.615548	1.846142
O	-1.950846	-1.746574	-2.469848
V	-1.060295	-0.945496	-1.338108
O	1.914153	0.463393	-0.177409
O	0.378109	-1.811678	-0.678531
V	1.491076	-1.126151	0.566315
O	2.746887	-2.081122	1.040813

E = -1038.38287026 h (3.90 eV)
quintet

```
 Zero-point correction=                           0.032141 (Hartree/Particle)
 Thermal correction to Energy=                    0.048534
 Thermal correction to Enthalpy=                  0.049478
 Thermal correction to Gibbs Free Energy=        -0.012104
```



```
O(14)-V(13)  1.6715
V(13)-O(12)  1.7893
V(13)-O(11)  1.7689
V(13)-O(8)   1.7873
O(12)-V(10)  1.8270
O(11)-V(5)   1.8719
V(10)-O(7)   1.7780
V(10)-O(9)   1.7530
V(10)-O(4)   1.7968
O(8)-V(2)    1.8297
O(7)-V(5)    1.8310
O(6)-V(5)    1.6440
V(5)-O(3)    1.8315
O(4)-V(2)    1.7948
O(3)-V(2)    1.7784
V(2)-O(1)    1.7489
```

v4o10s1s.log

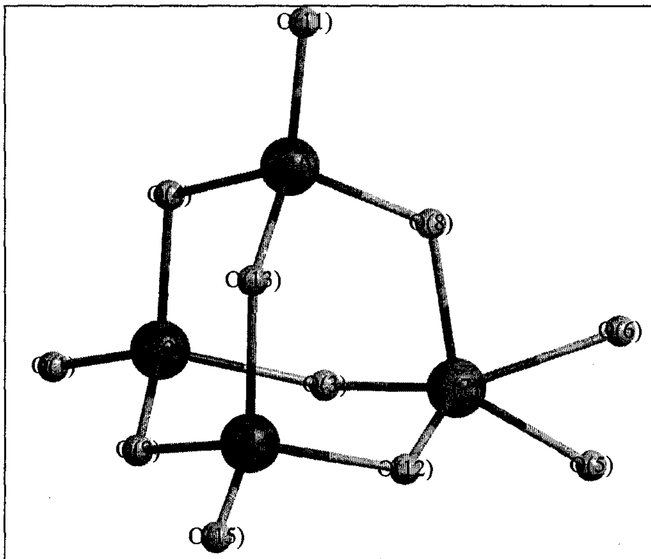
```
O  -2.945887   -1.810833   -1.340438
V  -1.563449   -0.915110   -0.753009
O  -1.532759    0.851875   -0.952024
O   0.070626   -1.376754   -1.334422
V  -0.163038    1.936279   -0.402131
O  -0.289285    3.566791   -0.570590
O   1.321232    1.067780   -1.030695
O  -1.289677   -1.072165    1.049269
O   3.122160   -1.349118   -1.488463
V   1.644721   -0.669412   -0.834047
O  -0.066107    1.390266    1.385742
O   1.496302   -0.862208    0.976692
V   0.074577   -0.295304    1.903432
O   0.134063   -0.567936    3.551476
```

E = -1038.27319153 h (6.88 eV)
septet

```
 Zero-point correction=                           0.029053 (Hartree/Particle)
 Thermal correction to Energy=                    0.046627
 Thermal correction to Enthalpy=                  0.047571
 Thermal correction to Gibbs Free Energy=        -0.017216
```

V_4O_{11} clusters

Isomer 1



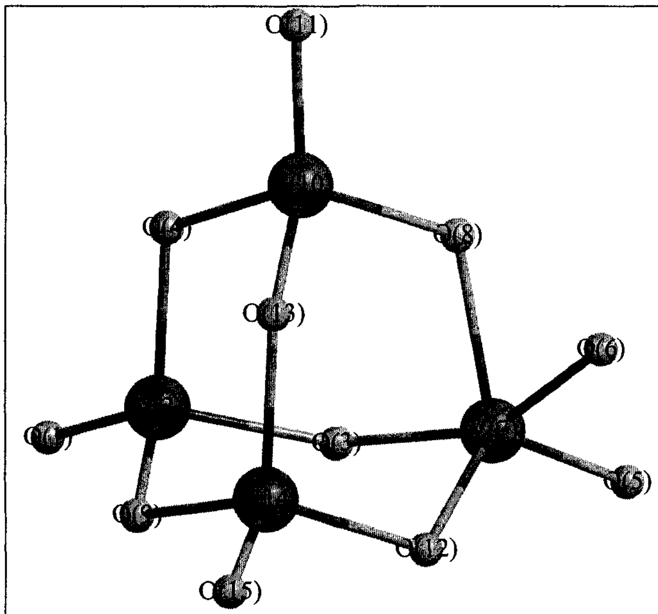
```
O(15)-V(14) 1.6002
V(14)-O(13) 1.7715
V(14)-O(9)  1.8003
V(14)-O(12) 1.8331
O(13)-V(10) 1.8331
O(12)-V(7)  1.7565
O(11)-V(10) 1.6022
V(10)-O(4)  1.8331
V(10)-O(8)  1.7441
O(9)-V(2)   1.8003
O(8)-V(7)   1.8905
V(7)-O(3)   1.7567
V(7)-O(6)   1.8606
V(7)-O(5)   1.8071
O(4)-V(2)   1.7715
O(3)-V(2)   1.8331
V(2)-O(1)   1.6002
```

v4o11s1.log

```
O    1.467220   -1.555993    2.857681
V     .878504    -.826072    1.561032
O    -.947896    -.829881    1.404486
O    1.323317     .884673    1.444483
O   -3.538498    -.778592     .002940
O   -3.421607     .713150    -.002939
V   -1.817026    -.228807     .001223
O   -1.010138    1.480865    -.004511
O    1.434992   -1.541081     .005310
V     .701432    1.816062    -.006730
O    1.008933    3.388470    -.012201
O    -.948156    -.840470   -1.397487
O    1.322807     .874357   -1.451468
V     .878108    -.837284   -1.555313
O    1.466099   -1.576706   -2.846907
```

E = -1113.65425759 h (0.27 eV)
singlet

```
 Zero-point correction=                          .039714 (Hartree/Particle)
 Thermal correction to Energy=                   .056358
 Thermal correction to Enthalpy=                 .057302
 Thermal correction to Gibbs Free Energy=       -.003343
```



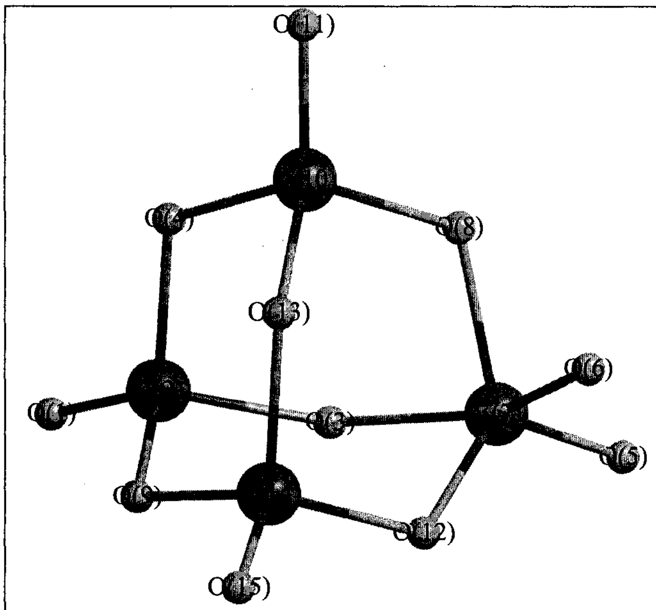
```
O(15)-V(14)  1.6008
V(14)-O(12)  1.8111
V(14)-O(13)  1.8003
V(14)-O(9)   1.7907
O(13)-V(10)  1.8045
O(12)-V(7)   1.8167
O(11)-V(10)  1.6013
V(10)-O(8)   1.8096
V(10)-O(4)   1.7912
O(9)-V(2)    1.8105
O(8)-V(7)    1.9085
V(7)-O(6)    1.9748
V(7)-O(5)    1.6095
V(7)-O(3)    1.8378
O(4)-V(2)    1.8103
O(3)-V(2)    1.7733
V(2)-O(1)    1.6019
```

v4o11s1trr6.log

```
O  -2.919303   -0.439330   -2.052664
V  -1.689179   -0.212850   -1.051871
O  -0.099279   -0.403811   -1.813789
O  -1.578861    1.432344   -0.304543
O   2.676505   -0.621054   -2.111196
O   2.799117    0.372084    0.363218
V   1.548939   -0.306172   -1.006745
O   1.177350    1.500740   -0.517315
O  -1.573578   -1.402674    0.307902
V  -0.135241    1.783469    0.695917
O  -0.150990    3.241987    1.356792
O   1.198005   -1.605930    0.213110
O  -0.096565    0.418215    1.875315
V  -0.148529   -1.314341    1.388704
O  -0.213374   -2.349125    2.608404
```

E = -1113.61444083 h (1.35 eV)
triplet

```
 Zero-point correction=                           0.037936 (Hartree/Particle)
 Thermal correction to Energy=                    0.055316
 Thermal correction to Enthalpy=                  0.056260
 Thermal correction to Gibbs Free Energy=        -0.007185
```



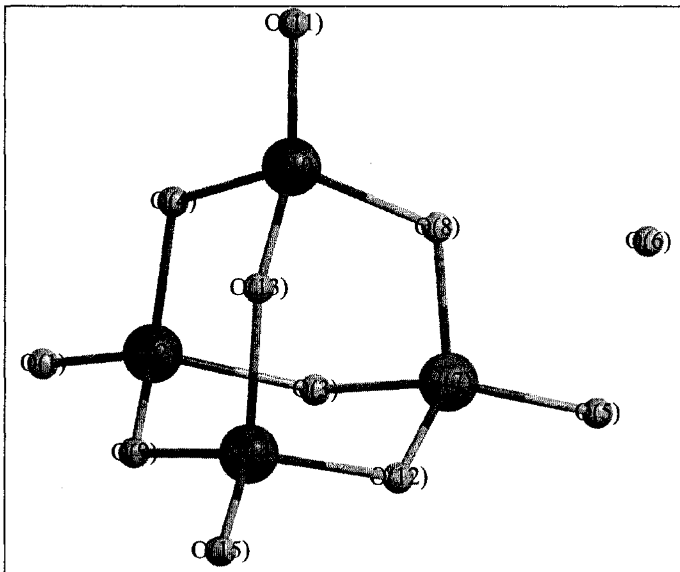
```
O(15)-V(14)  1.6175
V(14)-O(9)   1.8021
V(14)-O(13)  1.8043
V(14)-O(12)  1.7910
O(13)-V(10)  1.7994
O(12)-V(7)   1.8882
O(11)-V(10)  1.6180
V(10)-O(4)   1.7987
V(10)-O(8)   1.7924
O(9)-V(2)    1.8019
O(8)-V(7)    1.9010
V(7)-O(3)    1.8961
V(7)-O(5)    1.6077
V(7)-O(6)    1.9969
O(4)-V(2)    1.8038
O(3)-V(2)    1.7469
V(2)-O(1)    1.6375
```

v4o11s1q.log

```
O   2.939924   -0.157914    2.154229
V   1.717541   -0.082130    1.067243
O   0.144115   -0.122992    1.825097
O   1.615368    1.409219    0.057792
O  -2.689265   -0.169191    2.286335
O  -2.751496    0.084048   -0.528210
V  -1.607534   -0.077095    1.100531
O  -1.198741    1.558700    0.222444
O   1.601864   -1.421210   -0.132944
V   0.150498    1.673669   -0.951848
O   0.171070    3.010015   -1.863861
O  -1.212088   -1.562593    0.004013
O   0.102812    0.133288   -1.880807
V   0.135525   -1.526938   -1.175132
O   0.137853   -2.725451   -2.261369
```

E = -1113.55001485 h (3.11 eV)
quintet

```
 Zero-point correction=                           0.035266 (Hartree/Particle)
 Thermal correction to Energy=                    0.053145
 Thermal correction to Enthalpy=                  0.054089
 Thermal correction to Gibbs Free Energy=        -0.010920
```



O(15)-V(14)	1.6239
V(14)-O(12)	1.8168
V(14)-O(13)	1.8118
V(14)-O(9)	1.8170
O(13)-V(10)	1.7928
O(12)-V(7)	1.7788
O(11)-V(10)	1.6297
V(10)-O(8)	1.8484
V(10)-O(4)	1.8162
O(9)-V(2)	1.7931
O(8)-V(7)	1.7850
V(7)-O(5)	1.7397
V(7)-O(3)	1.7726
O(4)-V(2)	1.8018
O(3)-V(2)	1.8172
V(2)-O(1)	1.6456
O(6)-V(7)	2.5818
O(5)-O(6)	2.0103

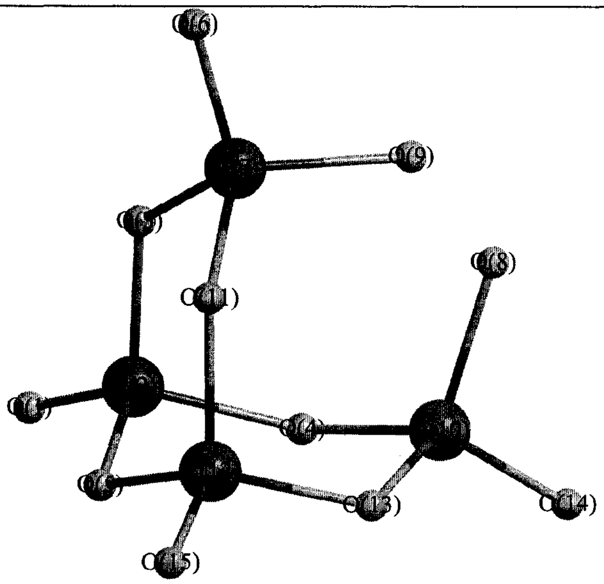
v4o11s1s3.log

```
O  -2.166885   -2.017499   -2.208289
V  -1.271021   -1.093182   -1.183120
O   0.356171   -1.760840   -0.726407
O  -0.845687    0.560432   -1.758428
O   3.044255   -1.647598    0.632287
O   3.845788    0.062133   -0.057427
V   1.491322   -0.918595    0.343284
O   1.624261    0.691290   -0.416180
O  -1.993363   -0.730067    0.417410
V   0.159840    1.745073   -0.818077
O   0.425011    3.191852   -1.519888
O   0.478671   -0.576841    1.765195
O  -0.710056    1.764023    0.749373
V  -1.130142    0.261935    1.671306
O  -1.901912    0.476824    3.083850
 Zero-point correction=                      0.034016 (Hartree/Particle)
 Thermal correction to Energy=               0.052143
 Thermal correction to Enthalpy=             0.053087
 Thermal correction to Gibbs Free Energy=   -0.013243
```

E = -1113.48115269 h (4.98 eV)

septet

Isomer 2



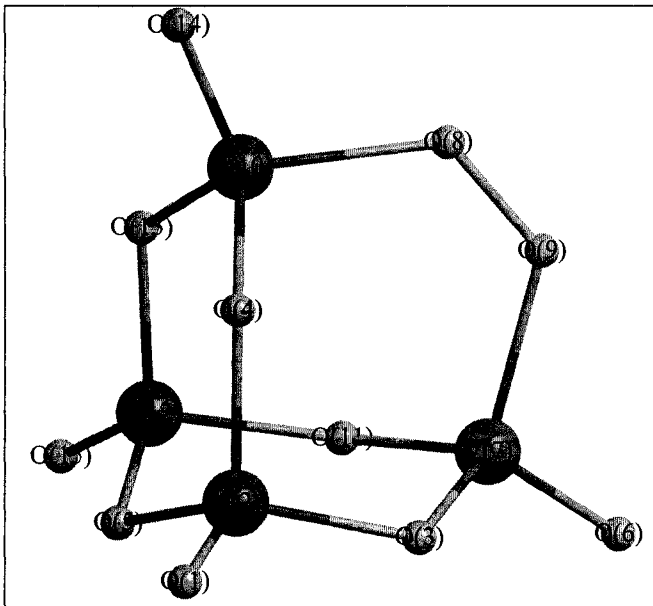
O(15)-V(12)	1.6009
O(14)-V(10)	1.5985
O(13)-V(10)	1.7953
O(13)-V(12)	1.7944
V(12)-O(11)	1.7945
V(12)-O(5)	1.8024
O(11)-V(7)	1.7951
V(10)-O(8)	1.8210
V(10)-O(4)	1.7952
O(9)-V(7)	1.8210
V(7)-O(3)	1.7953
V(7)-O(6)	1.5985
O(5)-V(2)	1.8024
O(4)-V(2)	1.7945
O(3)-V(2)	1.7945
V(2)-O(1)	1.6009
O(9)-V(10)	2.9311
V(7)-V(10)	3.6174
O(8)-O(9)	1.4582
V(7)-O(8)	2.9310

v4o11s2r5.log

```
O   -0.001902   -2.092758   -2.858978
V   -0.001435   -1.168692   -1.551720
O   -1.434083   -0.098339   -1.403658
O    1.430299   -0.096746   -1.405686
O    0.000601   -2.084305    0.000772
O   -3.305974    1.515673    0.003033
V   -1.809036    0.955082    0.000881
O    0.728304    2.422219   -0.001274
O   -0.729936    2.421876   -0.000315
V    1.808318    0.956092   -0.001654
O   -1.429939   -0.096322    1.405643
V    0.002252   -1.167478    1.552535
O    1.434432   -0.096700    1.403634
O    3.304839    1.517764   -0.003822
O    0.003075   -2.090500    2.860531
```

E = -1113.66414866 h (0 eV)
singlet

```
 Zero-point correction=                       0.039595 (Hartree/Particle)
 Thermal correction to Energy=                0.056644
 Thermal correction to Enthalpy=              0.057588
 Thermal correction to Gibbs Free Energy=    -0.004420
```



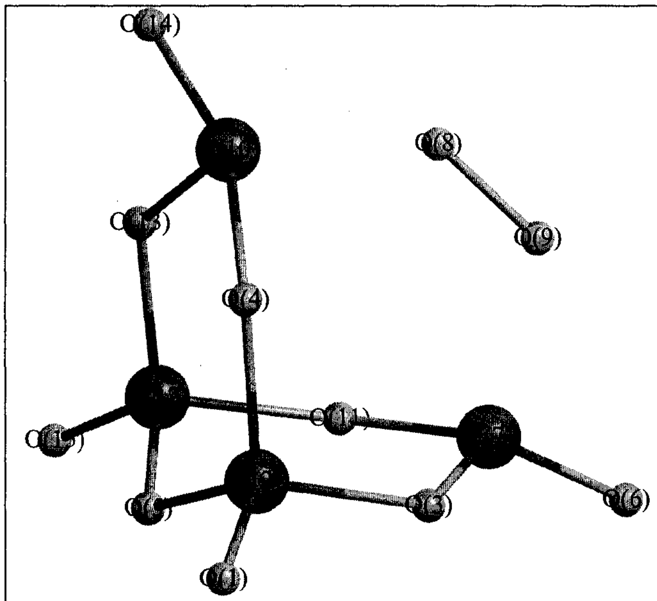
```
O(15)-V(12)  1.6009
O(14)-V(10)  1.6009
O(13)-V(10)  1.7691
O(13)-V(12)  1.8373
V(12)-O(11)  1.8297
V(12)-O(5)   1.8025
O(11)-V(7)   1.7573
V(10)-O(8)   2.0019
V(10)-O(4)   1.7573
O(9)-V(7)    2.0019
O(9)-O(8)    1.3765
V(7)-O(3)    1.7691
V(7)-O(6)    1.6009
O(5)-V(2)    1.8025
O(4)-V(2)    1.8297
O(3)-V(2)    1.8373
V(2)-O(1)    1.6009
V(7)-V(10)   3.7020
```

v4o11s2tr.log

```
O   0.316607   -2.066052    2.855994
V   0.313856   -1.194304    1.513256
O   1.767050   -0.104610    1.236408
O  -1.060665    0.012035    1.457838
O  -0.000005   -2.121909    0.000001
O   3.333352    1.375989   -0.573661
V   1.841459    0.942279   -0.187792
O  -0.688252    2.568175    0.002578
O   0.688255    2.568170   -0.002587
V  -1.841462    0.942285    0.187789
O   1.060682    0.012019   -1.457846
V  -0.313855   -1.194305   -1.513253
O  -1.767044   -0.104610   -1.236410
O  -3.333356    1.375983    0.573668
O  -0.316620   -2.066063   -2.855984
```

E = -1113.60384165 h (1.64 eV)
triplet

```
 Zero-point correction=                           0.037710 (Hartree/Particle)
 Thermal correction to Energy=                    0.055522
 Thermal correction to Enthalpy=                  0.056466
 Thermal correction to Gibbs Free Energy=        -0.008609
```



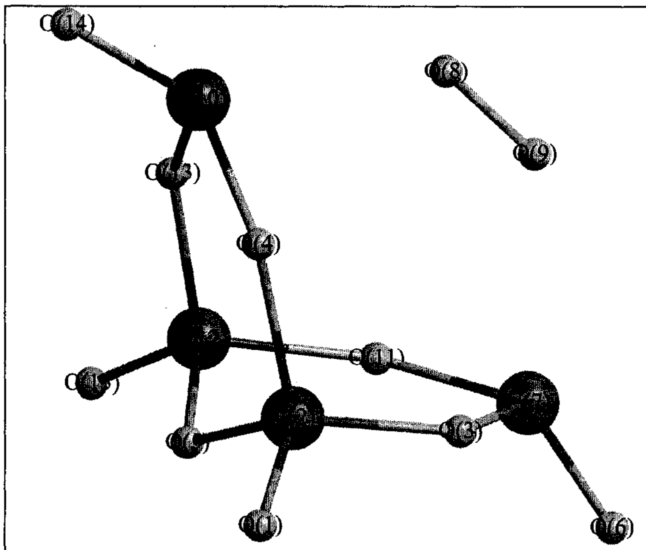
```
O(15)-V(12)  1.6144
O(14)-V(10)  1.6117
O(13)-V(10)  1.7881
O(13)-V(12)  1.8119
V(12)-O(5)   1.8055
V(12)-O(11)  1.8117
O(11)-V(7)   1.7912
V(10)-O(4)   1.8248
O(9)-O(8)    1.3451
V(7)-O(3)    1.7903
V(7)-O(6)    1.6094
O(5)-V(2)    1.8010
O(4)-V(2)    1.7796
O(3)-V(2)    1.8124
V(2)-O(1)    1.6344
O(9)-V(10)   3.1919
O(8)-V(10)   2.0840
V(7)-V(10)   4.0101
V(7)-O(9)    2.0987
V(7)-O(8)    3.0123
```

v4o11s1r2.log

```
O   0.027006    0.418170    3.527891
V  -0.022609    0.236201    1.904377
O  -1.534239   -0.544322    1.279297
O   1.295604   -0.725122    1.193710
O   0.007359    1.760742    0.945951
O  -3.556952   -1.029624   -0.786797
V  -2.030552   -0.658089   -0.437109
O   0.469844   -2.178975   -1.150300
O  -0.848854   -2.321927   -0.926805
V   1.972232   -0.893157   -0.492644
O  -1.309195    0.756183   -1.266499
V   0.149391    1.748448   -0.853884
O   1.591060    0.705791   -1.196431
O   3.530158   -1.302468   -0.439818
O   0.131382    3.215515   -1.527324
```

E = -1113.52524369 h (3.78 eV)
quintet

```
 Zero-point correction=                          0.034760 (Hartree/Particle)
 Thermal correction to Energy=                   0.053490
 Thermal correction to Enthalpy=                 0.054434
 Thermal correction to Gibbs Free Energy=       -0.013651
```



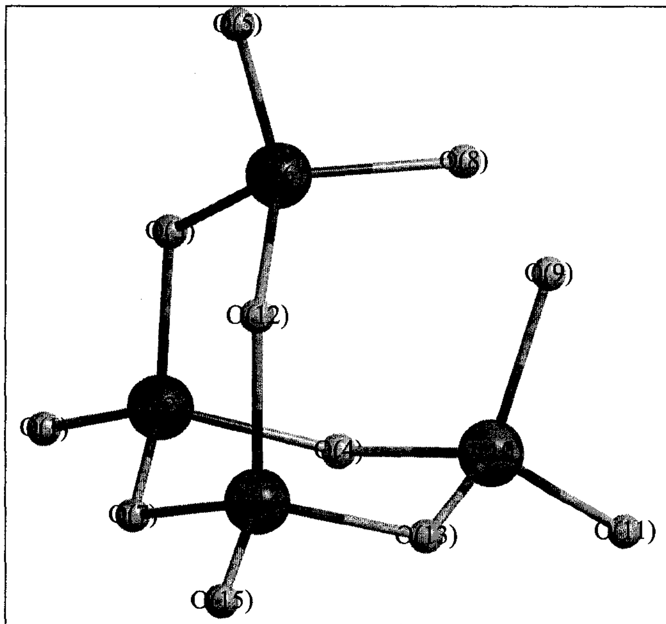
```
O(15)-V(12)  1.6399
O(14)-V(10)  1.6139
O(13)-V(12)  1.8065
O(13)-V(10)  1.8149
V(12)-O(11)  1.8032
V(12)-O(5)   1.7940
O(11)-V(7)   1.8233
V(10)-O(4)   1.8234
O(9)-O(8)    1.2932
V(7)-O(6)    1.6139
V(7)-O(3)    1.8149
O(5)-V(2)    1.7939
O(4)-V(2)    1.8031
O(3)-V(2)    1.8066
V(2)-O(1)    1.6399
O(8)-V(10)   2.5469
V(7)-O(9)    2.5518
```

v4o11s2sr1.log

```
O  -0.004440   -2.860711   -1.953359
V   0.004209   -1.577873   -0.931850
O   1.479892   -1.414996    0.097495
O  -1.461419   -1.412575    0.105393
O   0.001186    0.000268   -1.784914
O   3.970232    0.013200    0.441300
V   2.392520   -0.002983    0.780929
O  -0.650092    0.004177    2.636891
O   0.643093   -0.005088    2.638722
V  -2.392594    0.002796    0.779392
O   1.461618    1.412692    0.107302
V  -0.003051    1.578173   -0.931411
O  -1.479747    1.414855    0.096310
O  -3.970010   -0.013414    0.438384
O   0.006569    2.861264   -1.952572
 Zero-point correction=                     0.032321 (Hartree/Particle)
 Thermal correction to Energy=              0.052505
 Thermal correction to Enthalpy=            0.053449
 Thermal correction to Gibbs Free Energy=  -0.020279
```

E = -1113.44524621 h (5.96 eV)
septet

Isomer 3



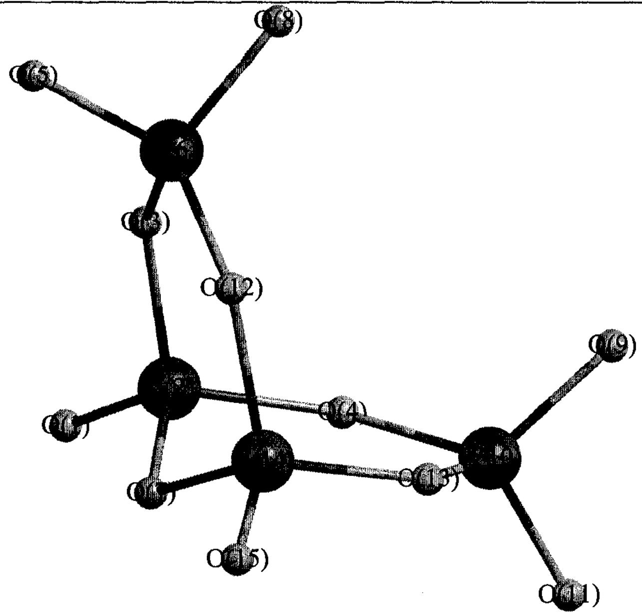
v4o11s3sr5.log

```
O(15)-V(14)  1.6009
V(14)-O(13)  1.7944
V(14)-O(12)  1.7944
V(14)-O(7)   1.8024
O(13)-V(10)  1.7952
O(12)-V(6)   1.7952
O(11)-V(10)  1.5984
V(10)-O(9)   1.8212
V(10)-O(4)   1.7952
O(8)-V(6)    1.8212
O(7)-V(2)    1.8024
V(6)-O(3)    1.7952
V(6)-O(5)    1.5984
O(4)-V(2)    1.7944
O(3)-V(2)    1.7944
V(2)-O(1)    1.6009
O(8)-V(10)   2.9312
V(6)-V(10)   3.6167
O(8)-O(9)    1.4587
V(6)-O(9)    2.9314
```

```
O   -0.000445   -2.092104   -2.859817
V   -0.000162   -1.168561   -1.552167
O   -1.431452   -0.096460   -1.404728
O    1.431416   -0.096698   -1.404912
O   -3.304771    1.517410    0.000009
V   -1.808267    0.955788    0.000117
O   -0.000198   -2.084724    0.000010
O   -0.729011    2.422723   -0.000318
O    0.729649    2.422736    0.000294
V    1.808465    0.955452   -0.000126
O    3.305116    1.516676   -0.000026
O   -1.431505   -0.096455    1.404913
O    1.431362   -0.096672    1.404733
V   -0.000096   -1.168544    1.552178
O    0.000012   -2.092071    2.859838
```

E = -1113.66414825 h (0.00 eV)
singlet

```
 Zero-point correction=                          0.039594 (Hartree/Particle)
 Thermal correction to Energy=                   0.056643
 Thermal correction to Enthalpy=                 0.057587
 Thermal correction to Gibbs Free Energy=       -0.004418
```



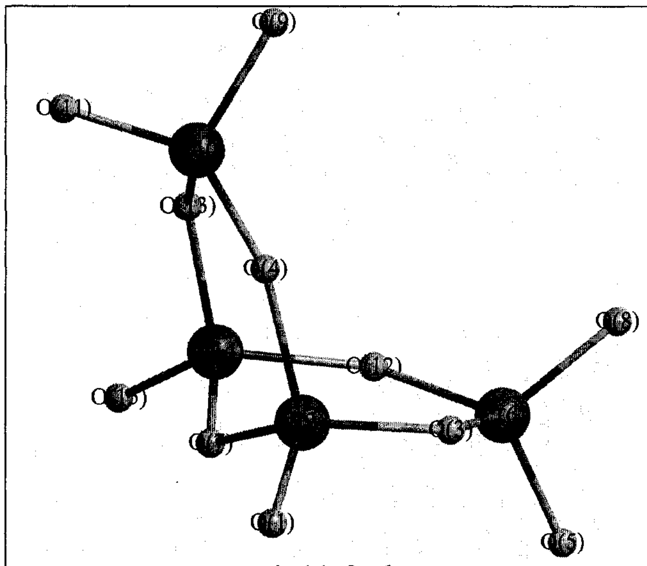
O(15)-V(14)	1.6010
V(14)-O(13)	1.7872
V(14)-O(12)	1.7871
V(14)-O(7)	1.8038
O(13)-V(10)	1.7999
O(12)-V(6)	1.7999
O(11)-V(10)	1.6868
V(10)-O(4)	1.7999
V(10)-O(9)	1.6548
O(8)-V(6)	1.6548
O(7)-V(2)	1.8038
V(6)-O(3)	1.7998
V(6)-O(5)	1.6868
O(4)-V(2)	1.7871
O(3)-V(2)	1.7871
V(2)-O(1)	1.6010

v4o11s3trr2.log

O	0.000029	2.842401	-1.814576
V	-0.000304	1.541615	-0.881194
O	-1.466872	1.415429	0.132180
O	1.465758	1.415313	0.132874
O	-4.006350	-0.000774	0.344932
V	-2.374865	-0.000105	0.773397
O	0.000217	0.000018	-1.817823
O	-2.500928	0.000208	2.423427
O	2.501276	-0.000096	2.423406
V	2.374759	0.000067	0.773448
O	4.006178	0.000769	0.344708
O	-1.465839	-1.415287	0.132758
O	1.466601	-1.415657	0.132699
V	0.000315	-1.541586	-0.881247
O	0.000200	-2.842297	-1.814745

E = -1113.63057846 h (0.91 eV)
triplet

```
 Zero-point correction=                           0.036888 (Hartree/Particle)
 Thermal correction to Energy=                    0.054969
 Thermal correction to Enthalpy=                  0.055913
 Thermal correction to Gibbs Free Energy=        -0.011356
```



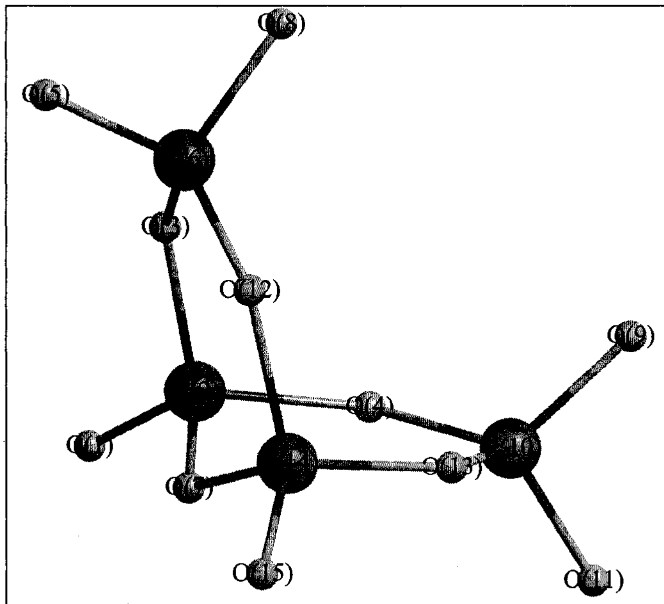
```
O(15)-V(14) 1.6250
V(14)-O(12) 1.8309
V(14)-O(7)  1.7887
V(14)-O(13) 1.8316
O(13)-V(10) 1.7870
O(12)-V(6)  1.7883
O(11)-V(10) 1.6894
V(10)-O(4)  1.7883
V(10)-O(9)  1.6743
O(8)-V(6)   1.6743
O(7)-V(2)   1.7887
V(6)-O(5)   1.6894
V(6)-O(3)   1.7870
O(4)-V(2)   1.8309
O(3)-V(2)   1.8316
V(2)-O(1)   1.6250
```

v4o11s3q.log

```
O  -0.001357   -2.795321   -1.899557
V   0.001204   -1.585210   -0.815041
O   1.505779   -1.404354    0.213658
O  -1.499620   -1.403028    0.217649
O   4.044806    0.004527    0.113725
V   2.476576   -0.000069    0.741889
O  -0.000021    0.000002   -1.643685
O   2.789781   -0.001974    2.386647
O  -2.789824    0.001996    2.386673
V  -2.476560    0.000063    0.741927
O  -4.044767   -0.004569    0.113706
O   1.499678    1.403023    0.217558
O  -1.505772    1.404348    0.213691
V  -0.001215    1.585225   -0.815037
O   0.001300    2.795327   -1.899560
```

E = -1113.54692026 h (3.19 eV)
quintet

```
 Zero-point correction=                         0.032167 (Hartree/Particle)
 Thermal correction to Energy=                  0.051508
 Thermal correction to Enthalpy=                0.052452
 Thermal correction to Gibbs Free Energy=      -0.017967
```



```
O(15)-V(14)  1.8192
V(14)-O(12)  1.8456
V(14)-O(13)  1.8456
V(14)-O(7)   1.7803
O(13)-V(10)  1.7728
O(12)-V(6)   1.7728
O(11)-V(10)  1.6921
V(10)-O(9)   1.6912
V(10)-O(4)   1.7892
O(8)-V(6)    1.6912
O(7)-V(2)    1.8132
V(6)-O(5)    1.6921
V(6)-O(3)    1.7892
O(4)-V(2)    1.8301
O(3)-V(2)    1.8301
V(2)-O(1)    1.6189
```

v4o11s3sep.log

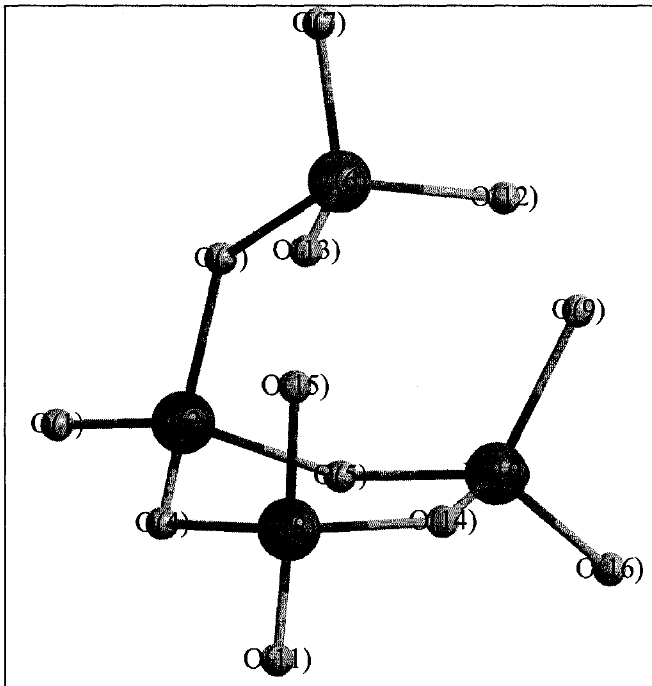
```
O  -0.000008   -2.566634   -2.249433
V  -0.000001   -1.498404   -1.033051
O   1.491612   -1.466659    0.026797
O  -1.491596   -1.466669    0.026824
O   4.018796   -0.015761    0.321288
V   2.388918   -0.107009    0.766686
O  -0.000013    0.191289   -1.690792
O   2.571654   -0.277452    2.439318
O  -2.571735   -0.277475    2.439320
V  -2.388906   -0.107016    0.766701
O  -4.018757   -0.015733    0.321214
O   1.476957    1.347575    0.324921
O  -1.476900    1.347559    0.324993
V   0.000001    1.688687   -0.727864
O  -0.000039    3.268218   -1.630309
```

E = -1113.44706271 h (5.91 eV)
septet

```
 Zero-point correction=                          0.031013 (Hartree/Particle)
 Thermal correction to Energy=                   0.050778
 Thermal correction to Enthalpy=                 0.051722
 Thermal correction to Gibbs Free Energy=       -0.020503
```

V_4O_{12} clusters

Isomer 1

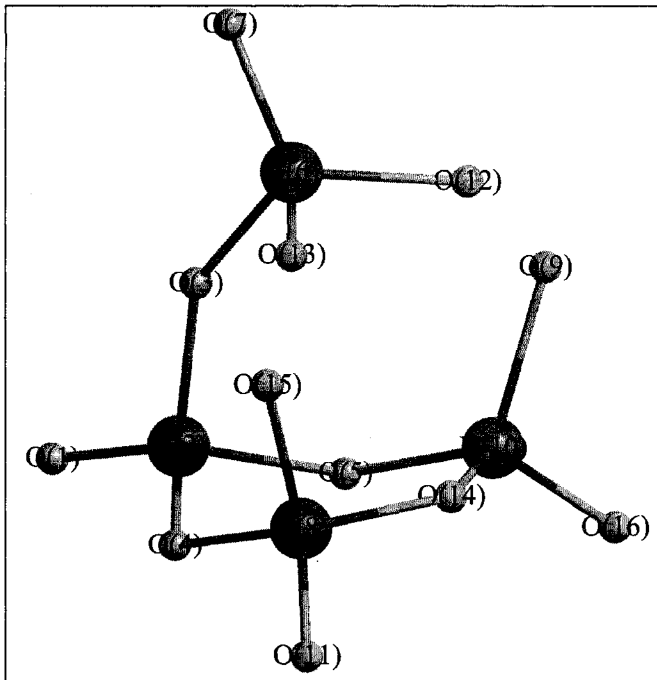


```
O(16)-V(10) 1.5981
O(15)-V(8)  1.8251
O(14)-V(8)  1.7885
O(14)-V(10) 1.7885
O(13)-V(6)  1.8232
O(12)-V(6)  1.8232
O(11)-V(8)  1.5982
V(10)-O(5)  1.8003
V(10)-O(9)  1.8256
V(8)-O(4)   1.8002
O(7)-V(6)   1.5963
V(6)-O(3)   1.7837
O(5)-V(2)   1.7958
O(4)-V(2)   1.7959
O(3)-V(2)   1.7865
V(2)-O(1)   1.6009
O(13)-O(15) 1.4505
V(6)-O(15)  3.0145
V(8)-O(13)  2.8444
V(10)-O(12) 2.8452
O(9)-O(12)  1.4505
V(6)-V(10)  3.6461
V(6)-O(9)   3.0143
V(6)-V(8)   3.6457
```

v4o12s1.log

```
O   0.685029    0.000519    3.500844
V   0.498025   -0.000156    1.910855
O  -1.213880   -0.002471    1.400113
O   1.198145    1.431370    1.082711
O   1.201748   -1.429669    1.082424
V  -2.151418   -0.000569   -0.117324
O  -3.731876   -0.000923    0.106882
V   1.035638    1.673237   -0.693755
O  -0.575274   -2.286649   -1.290239
V   1.037154   -1.672398   -0.693788
O   2.112956    2.686658   -1.299289
O  -1.797623   -1.596608   -0.924521
O  -1.798331    1.595474   -0.924728
O   1.175579    0.000449   -1.311060
O  -0.576562    2.286747   -1.289973
O   2.114315   -2.685226   -1.300377
 Zero-point correction=                       0.042147 (Hartree/Particle)
 Thermal correction to Energy=                0.060638
 Thermal correction to Enthalpy=              0.061583
 Thermal correction to Gibbs Free Energy=    -0.003889
```

E = -1188.79230833 h (0.14 eV)
singlet



```
O(16)-V(10)  1.5994
O(15)-V(8)   1.8773
O(14)-V(8)   1.7938
O(14)-V(10)  1.7936
O(13)-V(6)   1.8864
O(12)-V(6)   1.8872
O(11)-V(8)   1.5994
V(10)-O(5)   1.7626
V(10)-O(9)   1.8779
V(8)-O(4)    1.7628
O(7)-V(6)    1.6025
V(6)-O(3)    1.8076
O(5)-V(2)    1.8418
O(4)-V(2)    1.8415
O(3)-V(2)    1.7494
V(2)-O(1)    1.6019
O(13)-O(15)  1.4352
V(6)-O(15)   3.1134
V(8)-O(13)   2.7988
V(10)-O(12)  2.7997
O(9)-O(12)   1.4347
V(6)-V(10)   3.7336
V(6)-O(9)    3.1131
V(6)-V(8)    3.7333
```

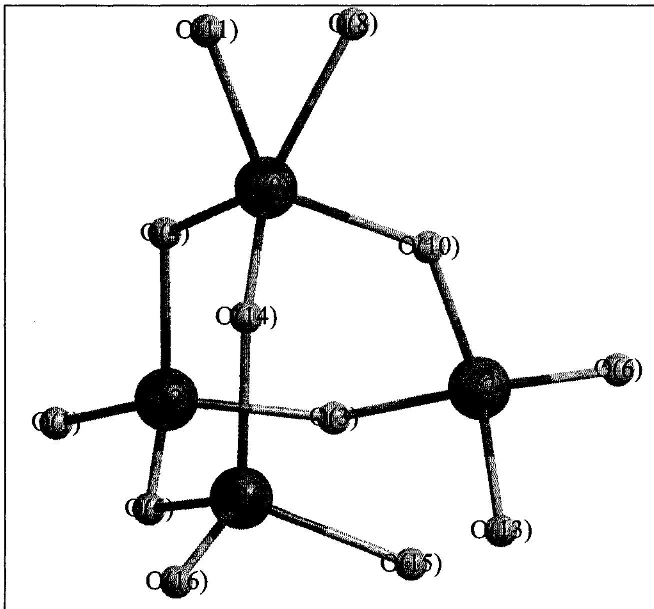
v4o12s1tr.log

```
O   0.421453   -0.000989    3.531263
V   0.426051   -0.000575    1.929390
O  -1.197621   -0.001150    1.278075
O   1.152609    1.473337    1.098228
O   1.153241   -1.474117    1.097532
V  -2.228001    0.000260   -0.207109
O  -3.787556    0.000164    0.161610
V   1.081903    1.668827   -0.652222
O  -0.546139   -2.420228   -1.209181
V   1.082198   -1.668247   -0.652883
O   2.208495    2.684274   -1.159789
O  -1.666249   -1.524724   -1.166545
O  -1.665713    1.524787   -1.165275
O   1.223452    0.000309   -1.295485
O  -0.545641    2.421110   -1.208355
O   2.208485   -2.683537   -1.161460
```

E = -1188.73496350 h (1.70 eV)
triplet

```
 Zero-point correction=                           0.039054 (Hartree/Particle)
 Thermal correction to Energy=                    0.058588
 Thermal correction to Enthalpy=                  0.059532
 Thermal correction to Gibbs Free Energy=        -0.009671
```

Isomer 2

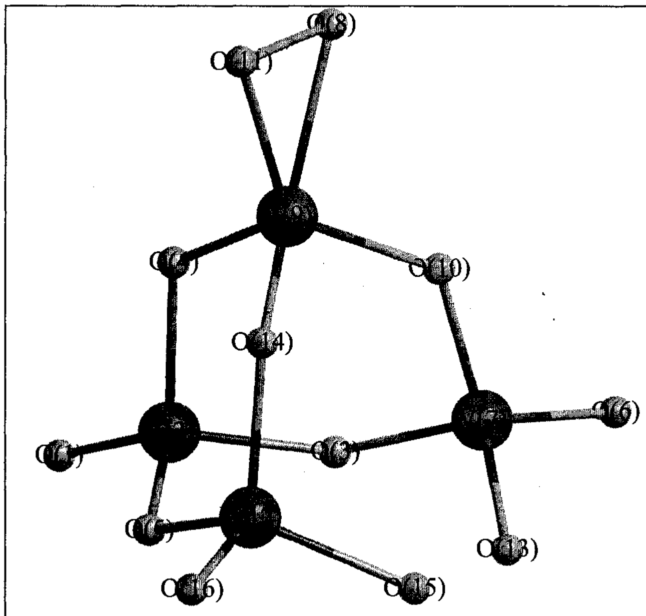


```
O(16)-V(12) 1.5970
O(15)-V(12) 1.8132
O(14)-V(12) 1.8269
O(14)-V(9)  1.7549
O(13)-V(7)  1.8336
V(12)-O(5)  1.7854
O(11)-V(9)  1.8057
O(10)-V(7)  1.7420
O(10)-V(9)  1.8694
V(9)-O(4)   1.7628
V(9)-O(8)   1.8590
V(7)-O(3)   1.8322
V(7)-O(6)   1.6014
O(5)-V(2)   1.8049
O(4)-V(2)   1.8282
O(3)-V(2)   1.7616
V(2)-O(1)   1.6001
O(13)-O(15) 1.4579
V(7)-O(15)  2.9299
V(12)-O(13) 2.9035
V(7)-V(12)  3.5775
```

v4o12s2.log

```
O   0.826372   -0.138130    3.495531
V   0.513094   -0.107191    1.926686
O   1.193326   -1.481419    1.059411
O  -1.262494   -0.141789    1.492486
O   1.092772    1.379302    1.082904
O   1.245945   -3.196757   -1.253130
V   0.908465   -1.719607   -0.734798
O  -3.300647   -0.842994   -0.947410
V  -1.872285    0.041300   -0.151267
O  -0.769518   -1.276895   -0.886741
O  -3.649284    0.360699   -0.121752
V   0.748521    1.851904   -0.604059
O   1.954745   -0.555593   -1.690116
O  -1.018208    1.430299   -0.800049
O   1.771690    0.889462   -1.750590
O   1.059139    3.382896   -0.935661
 Zero-point correction=                           0.042180 (Hartree/Particle)
 Thermal correction to Energy=                    0.060300
 Thermal correction to Enthalpy=                  0.061244
 Thermal correction to Gibbs Free Energy=        -0.002969
```

E = -1188.78939034 h (0.22 eV)
singlet



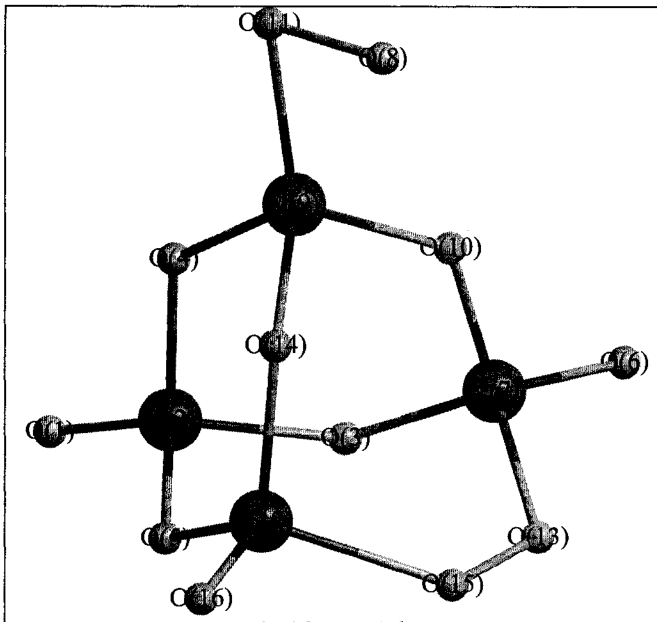
v4o12s2trr1.log

```
O  -0.928845   -0.000064    3.485821
V  -0.587172   -0.000045    1.922083
O  -1.160644    1.443539    1.051334
O   1.234872   -0.000030    1.523543
O  -1.160624   -1.443615    1.051299
O  -1.137124    3.309817   -1.144855
V  -0.826627    1.808082   -0.689956
O   3.665957    0.702380   -0.442610
V   1.815839    0.000001   -0.116019
O   0.911136    1.377521   -0.804167
O   3.665963   -0.702361   -0.442643
V  -0.826626   -1.808049   -0.690020
O  -1.821993    0.725343   -1.776763
O   0.911139   -1.377498   -0.804222
O  -1.822005   -0.725245   -1.776747
O  -1.137149   -3.309756   -1.144995
```

```
O(16)-V(12) 1.5995
O(15)-V(12) 1.8287
O(14)-V(9)  1.7859
O(14)-V(12) 1.7939
O(13)-V(7)  1.8287
V(12)-O(5)  1.8101
O(11)-O(8)  1.4047
O(11)-V(9)  2.0057
O(10)-V(9)  1.7859
O(10)-V(7)  1.7939
V(9)-O(8)   2.0057
V(9)-O(4)   1.7394
V(7)-O(3)   1.8101
V(7)-O(6)   1.5995
O(5)-V(2)   1.7807
O(4)-V(2)   1.8651
O(3)-V(2)   1.7807
V(2)-O(1)   1.6006
O(13)-O(15) 1.4506
V(7)-O(15)  2.9308
V(12)-O(13) 2.9308
V(7)-V(12)  3.6161
```

E = -1188.76134251 h (0.98 eV)
triplet

```
 Zero-point correction=                           0.040302 (Hartree/Particle)
 Thermal correction to Energy=                    0.059246
 Thermal correction to Enthalpy=                  0.060190
 Thermal correction to Gibbs Free Energy=        -0.007576
```



```
O(16)-V(12)  1.6019
O(15)-O(13)  1.3772
O(15)-V(12)  2.0131
O(14)-V(9)   1.8087
O(14)-V(12)  1.7665
O(13)-V(7)   2.0131
V(12)-O(5)   1.7675
O(11)-O(8)   1.4028
O(11)-V(9)   1.9130
O(10)-V(9)   1.8090
O(10)-V(7)   1.7663
V(9)-O(4)    1.8140
V(7)-O(6)    1.6019
V(7)-O(3)    1.7675
O(5)-V(2)    1.8376
O(4)-V(2)    1.7764
O(3)-V(2)    1.8375
V(2)-O(1)    1.6028
V(7)-V(12)   3.7497
```

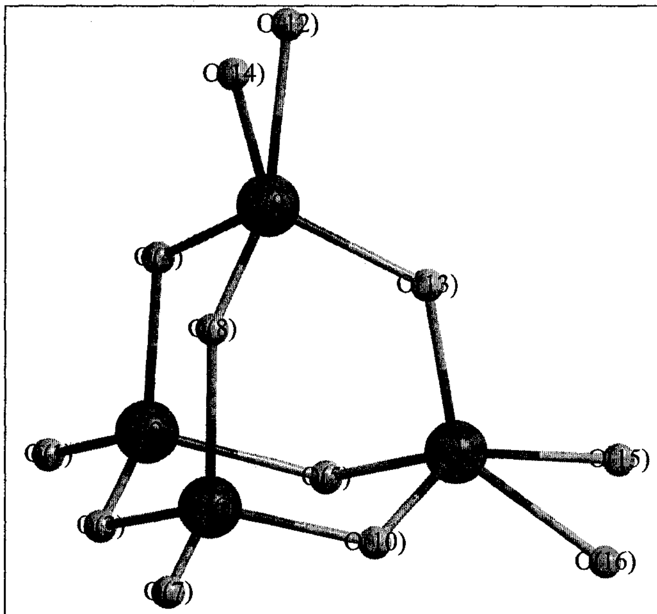
v4o12s1qr1.log

```
O  -1.794560    0.001258    3.187137
V  -1.125179    0.000484    1.730852
O  -1.499297    1.443082    0.656019
O   0.649535    0.000013    1.808627
O  -1.500703   -1.442112    0.656365
O  -0.710973    3.408496   -1.249862
V  -0.596727    1.875046   -0.800997
O   3.773058   -0.002329   -0.556157
V   1.785454   -0.000554    0.394268
O   1.078891    1.404476   -0.499722
O   3.645589   -0.002898    0.840805
V  -0.599137   -1.874703   -0.801092
O  -1.231439    0.689189   -2.298783
O   1.076633   -1.403640   -0.500368
O  -1.233204   -0.687993   -2.298451
O  -0.713715   -3.408329   -1.249324
```

E = -1188.70389658 h (2.54 eV)
quintet

```
 Zero-point correction=                          0.039199 (Hartree/Particle)
 Thermal correction to Energy=                   0.058757
 Thermal correction to Enthalpy=                 0.059702
 Thermal correction to Gibbs Free Energy=       -0.009896
```

Isomer 3

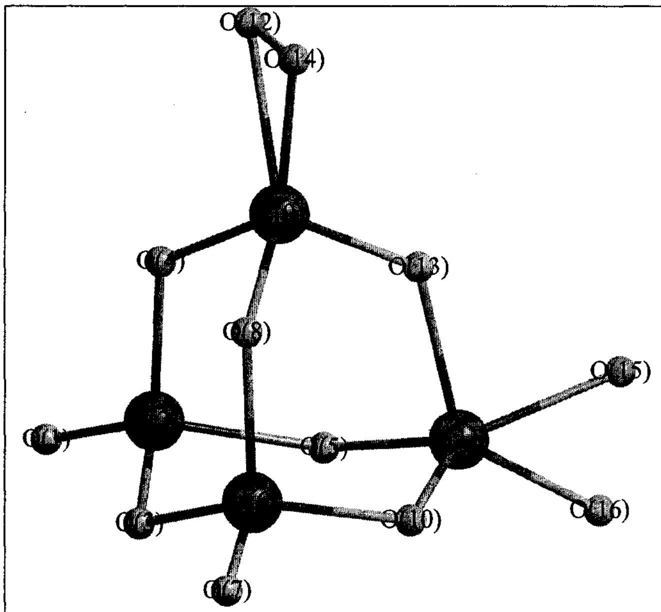


```
O(16)-V(11) 1.8587
O(15)-V(11) 1.8089
O(14)-V(9)  1.8588
O(13)-V(9)  1.7887
O(13)-V(11) 1.7886
O(12)-V(9)  1.8089
V(11)-O(10) 1.8464
V(11)-O(5)  1.7572
O(10)-V(6)  1.7683
V(9)-O(8)   1.8463
V(9)-O(4)   1.7572
O(8)-V(6)   1.7684
O(7)-V(6)   1.6037
V(6)-O(3)   1.8580
O(5)-V(2)   1.8317
O(4)-V(2)   1.8316
O(3)-V(2)   1.7501
V(2)-O(1)   1.59949
```

v4o12s3.log

```
O   0.000195   2.321257  -2.778686
V  -0.000131   1.366091  -1.495808
O   0.000142   2.246642   0.016620
O   1.433978   0.234852  -1.360719
O  -1.434509   0.234969  -1.360975
V  -0.000025   1.222633   1.567009
O  -0.000281   2.018214   2.959398
O   1.392749   0.157429   1.337585
V   1.610659  -0.978224  -0.101786
O  -1.392895   0.157771   1.337207
V  -1.610578  -0.978198  -0.102042
O   2.850829  -2.199717  -0.593637
O  -0.000044  -1.747151   0.015735
O   3.196974  -1.520722   0.700883
O  -2.850599  -2.200164  -0.593400
O  -3.196324  -1.521247   0.701290
 Zero-point correction=                          0.041977 (Hartree/Particle)
 Thermal correction to Energy=                   0.059792
 Thermal correction to Enthalpy=                 0.060736
 Thermal correction to Gibbs Free Energy=       -0.002429
```

E = -1188.77628621 h (0.57 eV)
singlet



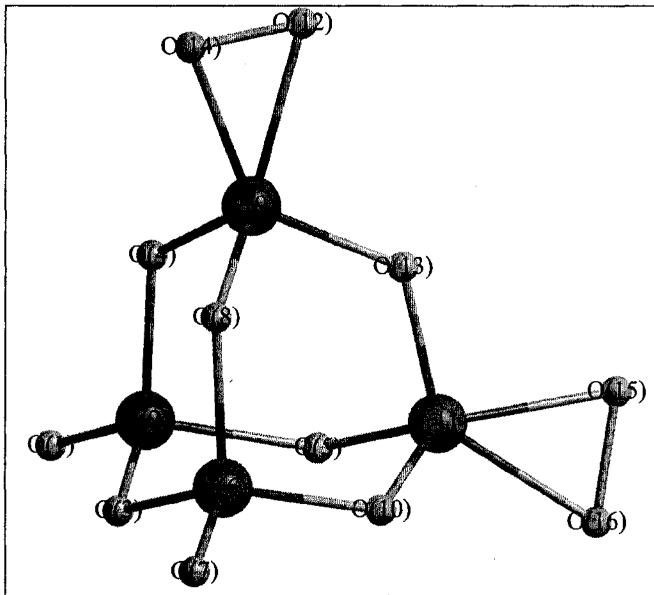
v4o12s3trr1.log

```
O  -0.081482   -2.209889    2.880154
V  -0.075690   -1.319091    1.549746
O  -0.176253   -2.231568    0.000002
O   1.394383   -0.309768    1.361658
O  -1.429161   -0.075578    1.377168
V  -0.075690   -1.319094   -1.549744
O  -0.081483   -2.209894   -2.880151
O   1.394383   -0.309770   -1.361658
V   1.611137    0.838916   -0.000001
O  -1.429160   -0.075581   -1.377167
V  -1.680847    0.967849   -0.000001
O   3.209201    1.821764    0.702931
O   0.151293    1.681459   -0.000003
O   3.209201    1.821764   -0.702931
O  -2.216499    2.757615   -0.000001
O  -3.308791    1.729778   -0.000001
```

```
O(16)-V(11) 1.7974
O(15)-V(11) 1.8682
O(14)-O(12) 1.4059
O(14)-V(9)  2.0035
O(13)-V(9)  1.6855
O(13)-V(11) 1.9662
O(12)-V(9)  2.0035
V(11)-O(5)  1.7460
V(11)-O(10) 1.7460
O(10)-V(6)  1.8461
V(9)-O(4)   1.7946
V(9)-O(8)   1.7946
O(8)-V(6)   1.7931
O(7)-V(6)   1.6011
V(6)-O(3)   1.8012
O(5)-V(2)   1.8461
O(4)-V(2)   1.7931
O(3)-V(2)   1.8012
V(2)-O(1)   1.6011
```

E = -1188.76408275 h (0.91 eV)
triplet

```
 Zero-point correction=                           0.040903 (Hartree/Particle)
 Thermal correction to Energy=                    0.059251
 Thermal correction to Enthalpy=                  0.060195
 Thermal correction to Gibbs Free Energy=        -0.005639
```



v4o12s3q.log

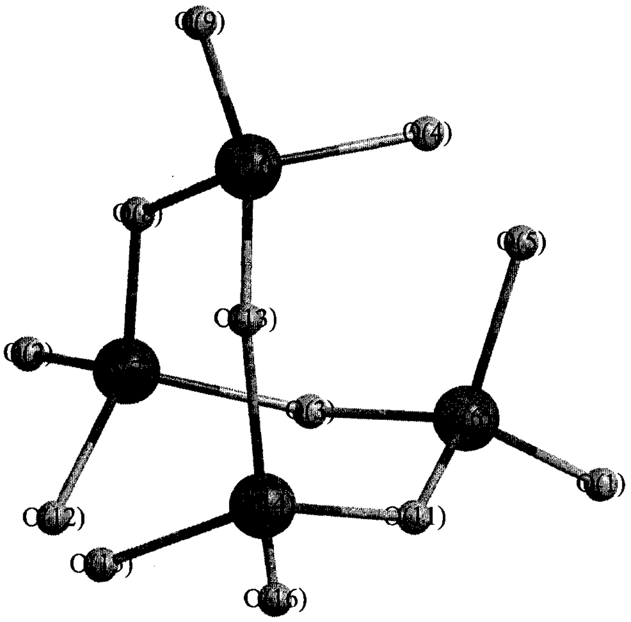
```
O(16)-O(15) 1.4070
O(16)-V(11) 2.0133
O(15)-V(11) 2.0098
O(14)-V(9)  2.0144
O(14)-O(12) 1.4070
O(13)-V(11) 1.7923
O(13)-V(9)  1.7926
O(12)-V(9)  2.0086
V(11)-O(10) 1.7708
V(11)-O(5)  1.7316
O(10)-V(6)  1.8195
V(9)-O(8)   1.7708
V(9)-O(4)   1.7317
O(8)-V(6)   1.8194
O(7)-V(6)   1.6025
V(6)-O(3)   1.8225
O(5)-V(2)   1.8613
O(4)-V(2)   1.8612
O(3)-V(2)   1.7814
V(2)-O(1)   1.6012
```

```
O  -0.000848  -2.233272  -2.889396
V  -0.000414  -1.349625  -1.554103
O  -0.001853  -2.244358  -0.013678
O  -1.427038  -0.168543  -1.370254
O   1.428519  -0.171404  -1.368977
V  -0.001654  -1.314364   1.553709
O  -0.002879  -2.167049   2.910561
O  -1.420711  -0.194416   1.348389
V  -1.607373   0.907344  -0.025313
O   1.419751  -0.197070   1.349024
V   1.609253   0.904635  -0.024359
O  -2.722965   2.569132  -0.193815
O   0.001737   1.695574   0.027747
O  -3.510600   1.498580   0.267984
O   2.726320   2.566713  -0.194506
O   3.511107   1.495640   0.270861
```

E = -1188.73062835 h (2.80 eV)
quintet

```
 Zero-point correction=                           0.039003 (Hartree/Particle)
 Thermal correction to Energy=                    0.058314
 Thermal correction to Enthalpy=                  0.059258
 Thermal correction to Gibbs Free Energy=        -0.010752
```

Isomer 4



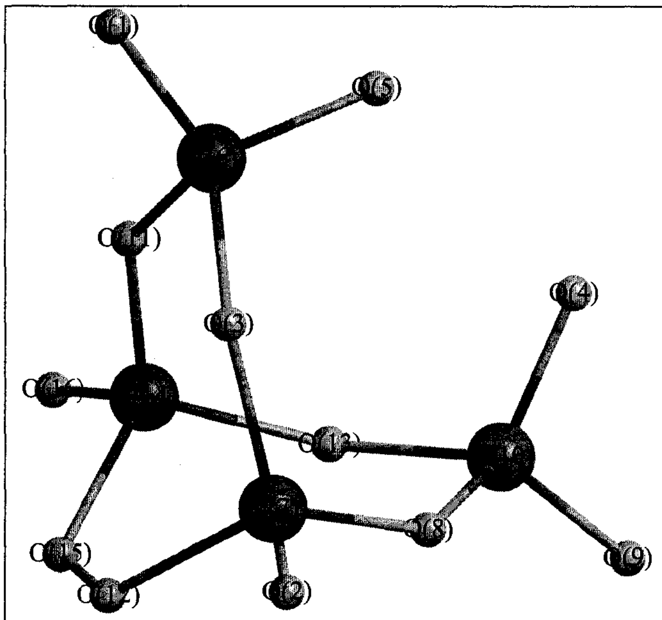
```
O(16)-V(14)  1.5987
O(15)-V(14)  1.8226
V(14)-O(11)  1.7785
V(14)-O(13)  1.8000
O(13)-V(10)  1.7788
O(12)-V(7)   1.8225
O(11)-V(6)   1.7997
V(10)-O(4)   1.8240
V(10)-O(9)   1.5988
V(10)-O(8)   1.7989
O(8)-V(7)    1.7786
V(7)-O(3)    1.7999
V(7)-O(2)    1.5986
V(6)-O(1)    1.5986
V(6)-O(5)    1.8240
V(6)-O(3)    1.7796
O(12)-O(15)  1.4641
V(7)-O(15)   2.9296
O(12)-V(14)  2.9292
V(7)-V(14)   3.6035
V(6)-V(10)   3.6012
O(5)-V(10)   2.9228
O(4)-V(6)    2.9298
O(4)-O(5)    1.4666
```

v4o12s4.log

```
O   1.772631   -2.752108   -1.628004
O  -2.761284   -1.802675    1.584697
O  -0.427436   -1.960937   -0.025767
O  -0.503810    0.595179   -2.486212
O   0.436863   -0.529782   -2.506475
V   0.951711   -1.506055   -1.054348
V  -1.505690   -0.981981    1.031894
O  -1.949137    0.419843    0.030997
O  -1.814669    2.796252   -1.508555
V  -0.978803    1.533416   -0.995868
O   1.953178   -0.429418   -0.016571
O  -0.556518   -0.466421    2.499856
O   0.434906    1.952051   -0.000644
V   1.533183    0.954569    1.018525
O   0.612771    0.414724    2.496114
O   2.801350    1.763440    1.559981
```

E = -1188.79741296 h (0 eV)
singlet

```
 Zero-point correction=                          0.041818 (Hartree/Particle)
 Thermal correction to Energy=                   0.060524
 Thermal correction to Enthalpy=                 0.061468
 Thermal correction to Gibbs Free Energy=       -0.004744
```



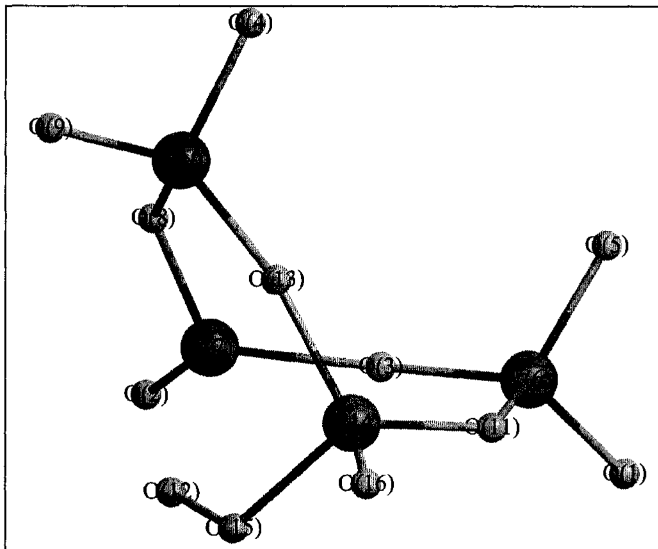
```
O(16)-V(14)  1.6009
O(15)-O(12)  1.3855
O(15)-V(14)  1.9632
V(14)-O(13)  1.7398
V(14)-O(11)  1.7398
O(13)-V(10)  1.8504
O(12)-V(7)   1.9632
O(11)-V(6)   1.8504
V(10)-O(9)   1.6331
V(10)-O(8)   1.8504
V(10)-O(4)   1.6514
O(8)-V(7)    1.7398
V(7)-O(2)    1.6009
V(7)-O(3)    1.7398
V(6)-O(3)    1.8504
V(6)-O(5)    1.6514
V(6)-O(1)    1.6331
V(7)-V(14)   3.6958
V(6)-V(10)   4.1563
```

v4o12s4trr3.log

```
O  -3.700114    0.000470   -1.172591
O   0.000379    3.369264    1.398913
O  -1.432168    1.422403    0.009543
O   1.421781    0.000056   -2.497846
O  -1.421596   -0.000056   -2.497802
V  -2.078157    0.000226   -0.982558
V   0.000238    1.847924    0.900548
O   1.432659    1.422041    0.009713
O   3.700154   -0.000472   -1.172393
V   2.078177   -0.000227   -0.982531
O  -1.432718   -1.422041    0.009743
O   0.000071    0.692738    2.487884
O   1.432108   -1.422406    0.009513
V  -0.000278   -1.847923    0.900549
O  -0.000084   -0.692734    2.487884
O  -0.000412   -3.369262    1.398918
```

E = -1188.76443980 h (0.90 eV)
triplet

```
 Zero-point correction=                        0.039703 (Hartree/Particle)
 Thermal correction to Energy=                 0.059397
 Thermal correction to Enthalpy=               0.060341
 Thermal correction to Gibbs Free Energy=     -0.010253
```



O(16)-V(14)	1.6000
O(15)-V(14)	1.9452
O(15)-O(12)	1.3819
V(14)-O(11)	1.7458
V(14)-O(13)	1.7548
O(13)-V(10)	1.8206
O(11)-V(6)	1.8450
V(10)-O(8)	1.7611
V(10)-O(4)	1.6653
V(10)-O(9)	1.6844
O(8)-V(7)	1.8434
V(7)-O(3)	1.8436
V(7)-O(2)	1.6038
V(6)-O(1)	1.6785
V(6)-O(3)	1.7438
V(6)-O(5)	1.6761
V(7)-O(15)	3.1363
V(7)-V(14)	3.7997
V(7)-O(12)	2.0711

v4o12s4qr1.log

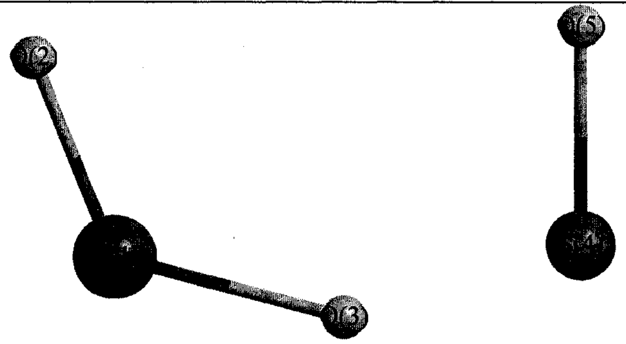
O	4.029204	0.357514	0.523756
O	-0.011434	3.406556	-1.290718
O	1.312480	1.242955	0.156483
O	-2.560136	-0.172612	2.462301
O	2.355685	-0.009866	2.485851
V	2.404126	0.051316	0.811551
V	-0.203230	1.973107	-0.597519
O	-1.750855	1.395366	0.220462
O	-3.993275	-0.407327	0.329981
V	-2.400661	-0.133532	0.805143
O	1.740516	-1.488091	0.040862
O	-0.207224	0.704285	-2.234473
O	-1.219070	-1.360918	0.163191
V	0.214764	-1.800499	-0.747995
O	0.108862	-0.639162	-2.304901
O	0.152125	-3.288579	-1.332442

E = -1188.69455544 h (2.80 eV)
quintet

```
 Zero-point correction=                           0.037067 (Hartree/Particle)
 Thermal correction to Energy=                    0.057879
 Thermal correction to Enthalpy=                  0.058823
 Thermal correction to Gibbs Free Energy=        -0.016714
```

VOSO$_2$ clusters (BPW91/LANL2DZ)

Isomer 1



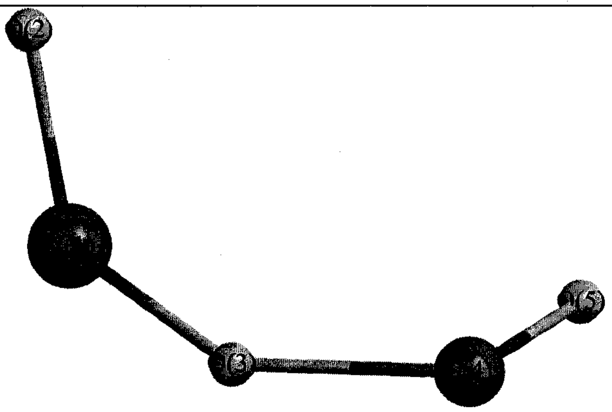
```
O(5)-S(4)    1.6553
O(3)-V(1)    1.7651
O(2)-V(1)    1.6182
O(3)-S(4)    1.8710
V(1)-S(4)    3.4979
 (planar geometry)
```

voso2s1fr.log

```
V   -1.522468    -.031152     .000000
O   -1.695104   -1.640132     .000000
O     .000000     .862059     .000000
S    1.870511     .819194     .000000
O    2.331177    -.770754     .000000
```

E = -307.114666481 h (3.37 eV)
doublet

```
 Zero-point correction=                      .008458 (Hartree/Particle)
 Thermal correction to Energy=               .015085
 Thermal correction to Enthalpy=             .016029
 Thermal correction to Gibbs Free Energy=   -.025195
```



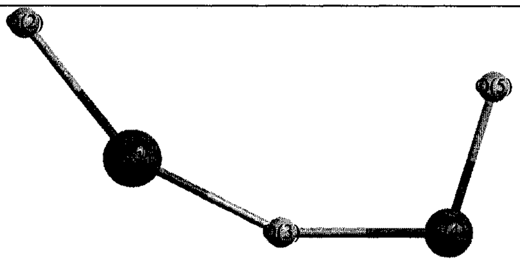
```
O(5)-S(4)    1.6526
S(4)-O(3)    1.7900
O(3)-V(1)    1.8376
O(2)-V(1)    1.6195
```

voso2s1q.log

```
V   -1.344431    -.255807     .488142
O   -1.943587   -1.465593    -.406357
O     .051776     .813148    -.045609
S    1.797650     .718934    -.428983
O    2.422708    -.571466     .392808
```

E = -307.143476211 h (2.59 eV)
quartet

```
 Zero-point correction=                      .008332 (Hartree/Particle)
 Thermal correction to Energy=               .015113
 Thermal correction to Enthalpy=             .016057
 Thermal correction to Gibbs Free Energy=   -.026694
```



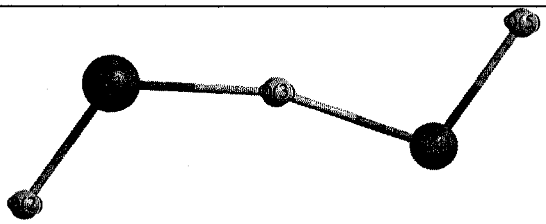
```
O(5)-S(4)    1.6465
S(4)-O(3)    1.8090
O(3)-V(1)    1.7903
O(2)-V(1)    1.8659
 (planar geometry)
```

voso2s1s.log

```
V  -1.370298    -.351351     .000000
O  -2.167302   -2.038487     .000000
O    .000000     .800824     .000000
S   1.758962    1.223248     .000000
O   2.588985    -.198700     .000000
 Zero-point correction=                      .007549 (Hartree/Particle)
 Thermal correction to Energy=               .014335
 Thermal correction to Enthalpy=             .015279
 Thermal correction to Gibbs Free Energy=   -.027563
```

E = -307.049020337 h (5.16 eV)
sextet

Isomer 1b

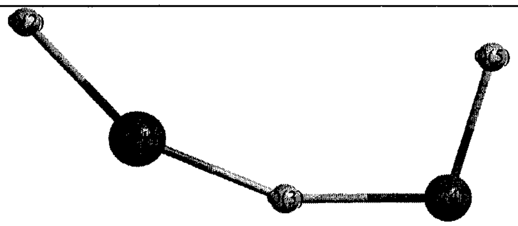


```
O(5)-S(4)    1.6504
S(4)-O(3)    1.8050
O(3)-V(1)    1.7814
O(2)-V(1)    1.6190
```

voso2s1br1.log

```
V   1.523870    -.416497    -.000004
O   2.576731     .813400     .000026
O   -.238182    -.154653    -.000028
S  -1.879924     .595598    -.000009
O  -2.959827    -.652515     .000031
 Zero-point correction=                      .008303 (Hartree/Particle)
 Thermal correction to Energy=               .015159
 Thermal correction to Enthalpy=             .016103
 Thermal correction to Gibbs Free Energy=   -.026560
```

E = -307.145826285 h (2.53 eV)
doublet



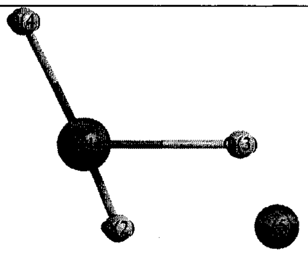
```
O(5)-S(4)    1.6469
S(4)-O(3)    1.8054
O(3)-V(1)    1.7885
O(2)-V(1)    1.8656
```

voso2s1bs.log

```
V  -1.397095    -.271744    -.037687
O  -2.893754     .835272     .085456
O    .347471    -.665838    -.033957
S   2.120627    -.339354     .060372
O   2.321678    1.290538    -.063893
 Zero-point correction=                      .007445 (Hartree/Particle)
 Thermal correction to Energy=               .014321
 Thermal correction to Enthalpy=             .015265
 Thermal correction to Gibbs Free Energy=   -.028355
```

E = -307.048943768 h (5.16 eV)
sextet

Isomer 2



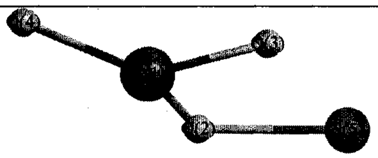
```
O(4)-V(1)    1.6120
O(3)-V(1)    1.8441
O(2)-V(1)    1.8439
O(3)-S(5)    1.8764
O(2)-S(5)    1.8776
V(1)-S(5)    2.7238
```

voso2s2.log

```
V    .857093    -.000358    -.333198
O   -.458723    1.267556    -.086510
O   -.460181   -1.267017    -.086178
O   2.079999     .000044     .717027
S  -1.812618     .000223     .206803
```

E = -307.19784974 h (1.11 eV)
doublet

```
 Zero-point correction=                         .009401 (Hartree/Particle)
 Thermal correction to Energy=                  .015259
 Thermal correction to Enthalpy=                .016204
 Thermal correction to Gibbs Free Energy=     -.021877
```



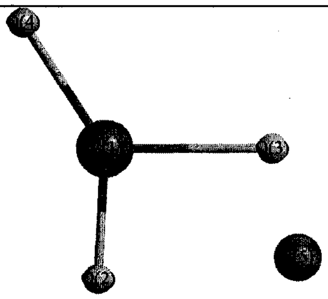
```
S(5)-O(2)    1.7069
O(4)-V(1)    1.6239
O(3)-V(1)    1.6874
O(2)-V(1)    1.9888
```

voso2s2q.log

```
V   -.798867    -.063348    -.093428
O    .893360   -1.106088    -.028150
O   -.455524    1.585071     .016871
O  -2.342152    -.492549     .173240
S   2.100529     .097846     .053322
```

E = -307.186776013 (1.41 eV)
quartet

```
 Zero-point correction=                         .008667 (Hartree/Particle)
 Thermal correction to Energy=                  .015253
 Thermal correction to Enthalpy=                .016198
 Thermal correction to Gibbs Free Energy=     -.025190
```



```
O(4)-V(1)    1.6456
O(3)-V(1)    1.8173
O(2)-V(1)    1.8174
O(3)-S(5)    2.3844
O(2)-S(5)    2.3862
V(1)-S(5)    3.1858
```

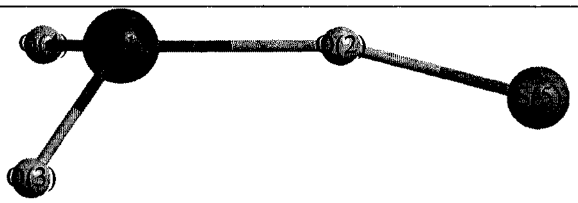
voso2s2s.log

```
V    .966444    -.000331    -.267137
O   -.292804    1.305361    -.377816
O   -.294518   -1.304209    -.378147
O   2.139028    -.000328     .887481
S  -2.165116     .000064     .318250
```

E = -307.08514343 h (4.18 eV)
sextet

```
 Zero-point correction=                         .006740 (Hartree/Particle)
 Thermal correction to Energy=                  .013806
 Thermal correction to Enthalpy=                .014750
 Thermal correction to Gibbs Free Energy=     -.027523
```

Isomer 2b

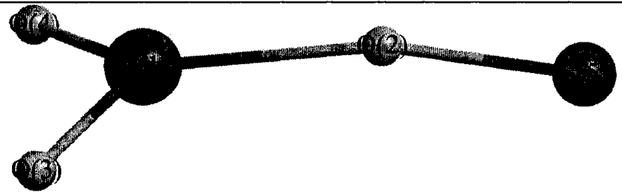


```
S(5)-O(2)   1.6987
O(4)-V(1)   1.6248
O(3)-V(1)   1.6240
O(2)-V(1)   1.8043
```

voso2s2b.log

```
V    -.927548    -.002195    -.248618
O     .873132    -.115728    -.245773
O   -1.543398    1.388850     .319825
O   -1.710962   -1.283641     .371186
S    2.523965     .008415     .134769
 Zero-point correction=                      .009831 (Hartree/Particle)
 Thermal correction to Energy=               .016095
 Thermal correction to Enthalpy=             .017039
 Thermal correction to Gibbs Free Energy=  -.023133
```

E = -307.238701305 h (0 eV)
doublet

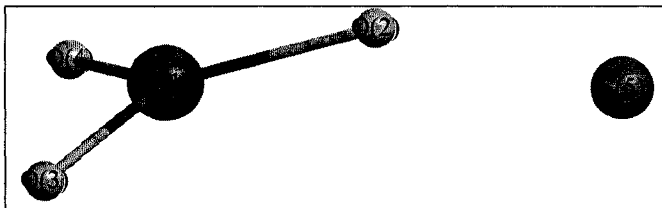


```
S(5)-O(2)   1.6649
O(4)-V(1)   1.6567
O(3)-V(1)   1.6514
O(2)-V(1)   1.9333
```

voso2s2bq.log

```
V     .926718    -.003471     .092296
O   -1.002767    -.092972     .174823
O    1.737395    1.418475    -.127119
O    1.890573   -1.329048    -.149427
S   -2.644757     .006762    -.081815
 Zero-point correction=                      .008088 (Hartree/Particle)
 Thermal correction to Energy=               .014977
 Thermal correction to Enthalpy=             .015922
 Thermal correction to Gibbs Free Energy=  -.027021
```

E = -307.189600656 (1.33 eV)
quartet



```
O(4)-V(1)   1.6934
O(3)-V(1)   1.6936
O(2)-V(1)   1.7952
O(2)-S(5)   2.0912
V(1)-S(5)   3.7507
```

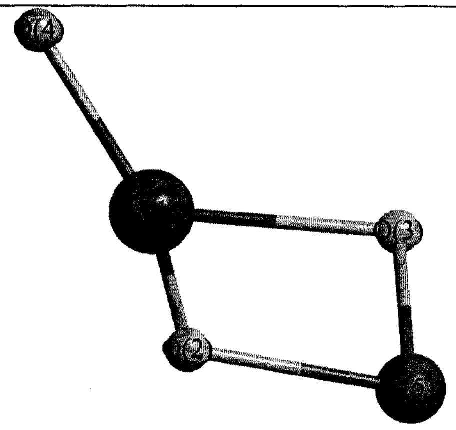
voso2s2bs.log

```
V    -.939343    -.000072     .083116
O     .811976    -.001719     .477753
O   -1.860511   -1.393035    -.198372
O   -1.857733    1.394765    -.197503
S    2.803439     .000097    -.160418
 Zero-point correction=                      .006588 (Hartree/Particle)
 Thermal correction to Energy=               .013832
 Thermal correction to Enthalpy=             .014776
 Thermal correction to Gibbs Free Energy=  -.029301
```

E = -307.112145415 h (3.44 eV)
sextet

VOSO$_2$ clusters (BPW91/TZVP)

Isomer 2



```
S(5)-O(2)    1.7390
S(5)-O(3)    1.7389
O(4)-V(1)    1.5893
O(3)-V(1)    1.8399
O(2)-V(1)    1.8399
```

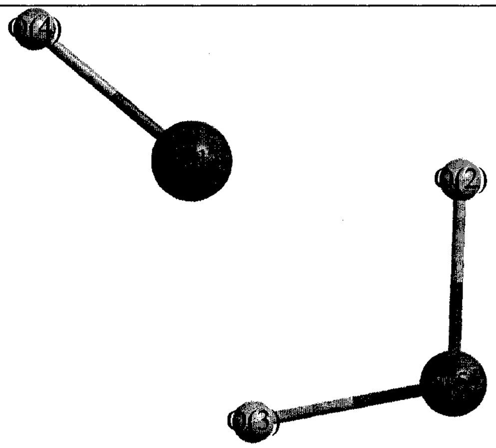
voso2s2tzvp.log

```
V    .785859    -.000005    -.244608
O   -.522570    1.256393     .063075
O   -.522621   -1.256376     .063075
O   2.235195    -.000013     .407561
S  -1.724674     .000005     .084769
```

E = -1568.09102124 h (1.31 eV)

doublet

```
 Zero-point correction=                         .009794 (Hartree/Particle)
 Thermal correction to Energy=                  .015600
 Thermal correction to Enthalpy=                .016544
 Thermal correction to Gibbs Free Energy=     -.021437
```



```
V(1)-S(5)    2.6770
V(1)-O(3)    2.0939
V(1)-O(2)    2.0973
S(5)-O(2)    1.5894
S(5)-O(3)    1.5900
O(4)-V(1)    1.5916
```

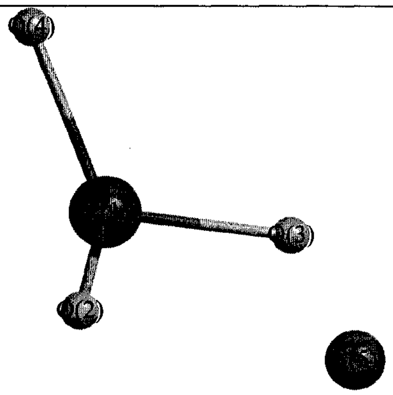
voso2s2tzvpq.log

```
V   -.906119     .002193    -.001322
O    .784198    1.243725    -.000594
O    .776971   -1.243478    -.000610
O  -2.497750    -.001906     .002662
S   1.770836    -.002323     .001171
```

E = -1568.08052912 h (1.59 eV)

quartet

```
 Zero-point correction=                         .010072 (Hartree/Particle)
 Thermal correction to Energy=                  .015992
 Thermal correction to Enthalpy=                .016936
 Thermal correction to Gibbs Free Energy=     -.022028
```



```
O(4)-V(1)    1.7165
O(3)-V(1)    1.7082
O(2)-V(1)    1.7081
O(3)-S(5)    2.4166
O(2)-S(5)    2.4180
V(1)-S(5)    2.9372
```

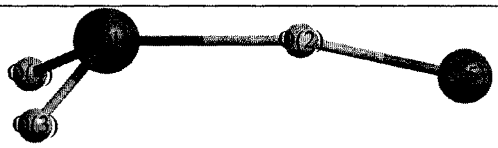
voso2s2tzvps.log

```
V    .804492    -.000081    -.271462
O   -.171655    1.400615    -.219504
O   -.173155   -1.399954    -.219851
O   2.204395    -.000628     .721791
S  -2.086250     .000100     .249009
```

E = -1568.96077758 h (4.58 eV)
sextet

```
 Zero-point correction=                        .006969 (Hartree/Particle)
 Thermal correction to Energy=                 .013848
 Thermal correction to Enthalpy=               .014792
 Thermal correction to Gibbs Free Energy=     -.027156
```

Isomer 3



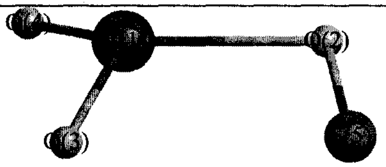
```
S(5)-O(2)    1.6004
O(4)-V(1)    1.6059
O(3)-V(1)    1.6059
O(2)-V(1)    1.8267
```

voso2s3tzvp.log

```
V    -.914387    -.000002    -.240145
O     .912298    -.000184    -.227265
O   -1.614026    1.328530     .329442
O   -1.614272   -1.328376     .329516
S    2.472432     .000017     .129363
```

E = -1568.11753342 h (0.59 eV)
doublet

```
 Zero-point correction=                        .010009 (Hartree/Particle)
 Thermal correction to Energy=                 .016215
 Thermal correction to Enthalpy=               .017159
 Thermal correction to Gibbs Free Energy=     -.022803
```



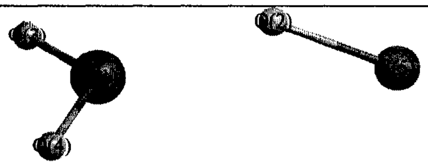
```
S(5)-O(2)    1.5839
O(4)-V(1)    1.6062
O(3)-V(1)    1.6708
O(2)-V(1)    2.0221
O(3)-S(5)    2.8347
```

voso2s3tzvpq.log

```
V   -.792885    -.062284    -.156943
O    .956113   -1.073388    -.070296
O   -.422881    1.557556     .018555
O  -2.267189    -.504271     .302297
S   2.006750     .099585     .100327
```

E = -1568.06781192 h (1.94 eV)
quartet

```
 Zero-point correction=                        .009089 (Hartree/Particle)
 Thermal correction to Energy=                 .015539
 Thermal correction to Enthalpy=               .016483
 Thermal correction to Gibbs Free Energy=     -.024164
```



voso2s3tzvpsb.log

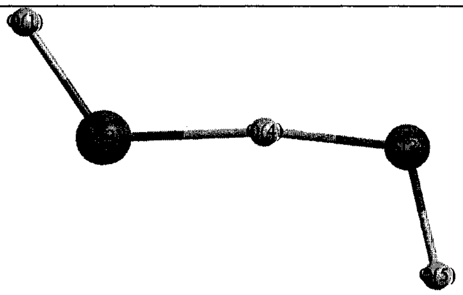
```
S(5)-O(2)   1.5556
O(4)-V(1)   1.6878
O(3)-V(1)   1.6858
V(1)-S(5)   3.4036
V(1)-O(2)   2.0744
```

```
V   -.948586     .000562     .013294
O   1.061502    -.001392     .525647
O  -1.615373    1.544321    -.105481
O  -1.618472   -1.544019    -.105901
S   2.449764    -.000263    -.176243
```

E = -1567.97057805 h (4.58 eV)
sextet

```
 Zero-point correction=                       .006340 (Hartree/Particle)
 Thermal correction to Energy=                .013690
 Thermal correction to Enthalpy=              .014634
 Thermal correction to Gibbs Free Energy=    -.028887
```

Isomer 5

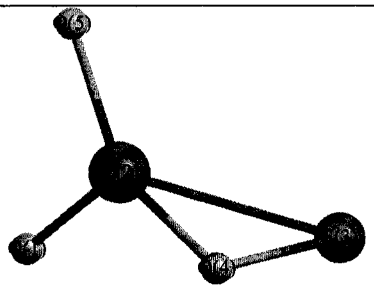


```
O(5)-S(2)   1.5160
O(4)-S(2)   1.6405
O(4)-V(3)   1.8184
V(3)-O(1)   1.5904
```

```
O   -2.670372    -.602736    -.008157
S    1.900221    -.532255    -.000254
V   -1.425266     .386780     .001674
O     .290814    -.214541     .010172
O    2.676755     .769794    -.006320
```

E = -1568.05912695 h (2.17 eV)
doublet

Isomer 7



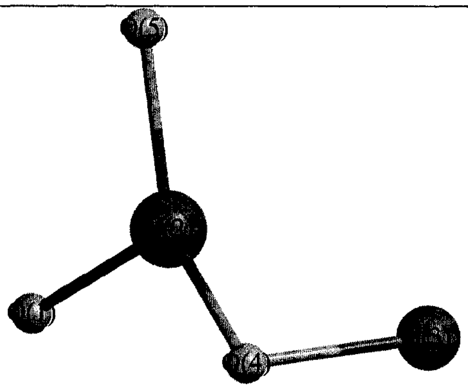
voso2s7tzvp.log

```
O(5)-V(2)   1.6024
O(4)-S(3)   1.6252
O(4)-V(2)   1.9646
S(3)-V(2)   2.3622
V(2)-O(1)   1.6024
```

```
O    -1.454816   -1.334770    -.121570
V     -.578099    -.000060     .010859
S     1.743538     .000272    -.424794
O     1.082926    -.001501    1.060042
O    -1.453152    1.335900    -.120102
```

E = -1568.13905161 h (0 eV)
doublet

```
 Zero-point correction=                       .010265 (Hartree/Particle)
 Thermal correction to Energy=                .016212
 Thermal correction to Enthalpy=              .017157
 Thermal correction to Gibbs Free Energy=    -.021459
```



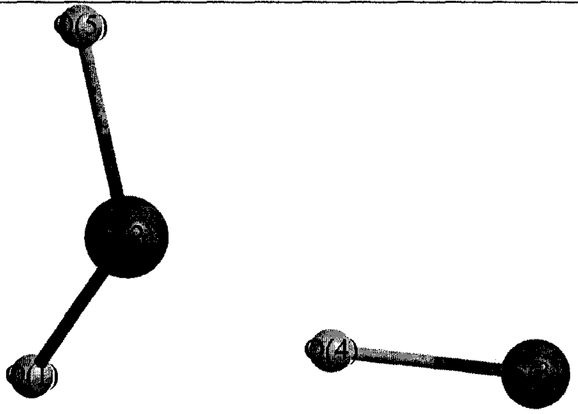
```
O(5)-V(2)   1.6541
O(4)-S(3)   1.6133
O(4)-V(2)   1.9913
V(2)-O(1)   1.6578
```

voso2s7tzvpq.log

```
O  -1.702191   -1.235136    -.213941
V   -.606642    -.002310    -.046042
S   1.846985     .065718    -.364367
O   1.062104    -.377300     .973727
O  -1.309787    1.487641     .101319
```

E = -1568.05894233 h (2.18 eV)
quartet

```
 Zero-point correction=                      .007593 (Hartree/Particle)
 Thermal correction to Energy=               .014366
 Thermal correction to Enthalpy=             .015310
 Thermal correction to Gibbs Free Energy=   -.025977
```



```
O(5)-V(2)   1.6868
O(4)-S(3)   1.5558
V(2)-O(1)   1.6869
V(2)-O(4)   2.0734
V(2)-S(3)   3.4027
```

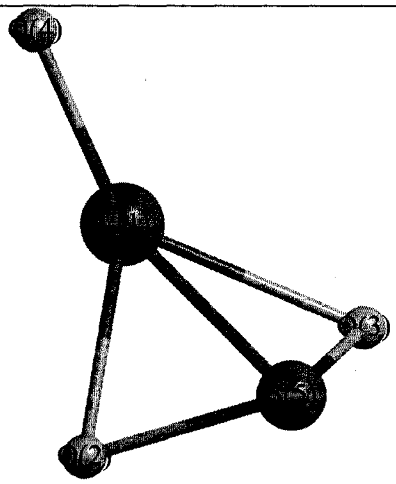
voso2s7tzvps.log

```
O  -1.616977   -1.543952    -.106342
V   -.948123     .000018     .013782
S   2.449259    -.000035    -.176440
O   1.061019    -.000062     .525924
O  -1.616705    1.544034    -.106324
```

E = -1567.97057803 h (4.58 eV)
sextet

```
 Zero-point correction=                      .006336 (Hartree/Particle)
 Thermal correction to Energy=               .013687
 Thermal correction to Enthalpy=             .014631
 Thermal correction to Gibbs Free Energy=   -.028888
```

Isomer 10



```
S(5)-V(1)    2.2175
S(5)-O(2)    1.6620
S(5)-O(3)    1.6620
O(4)-V(1)    1.5917
O(3)-V(1)    1.9574
O(2)-V(1)    1.9574
```

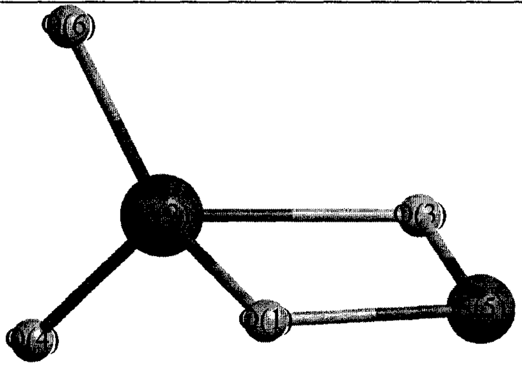
voso2s10.log

```
V     .731986    -.000006    -.194923
O    -.751621    1.256250    -.423044
O    -.751628   -1.256240    -.423041
O    2.171379     .000007     .484608
S   -1.386295     .000001     .460940
 Zero-point correction=                        .010204 (Hartree/Particle)
 Thermal correction to Energy=                 .015774
 Thermal correction to Enthalpy=               .016719
 Thermal correction to Gibbs Free Energy=    -.020469
```

E = -1568.10131965 h (1.03 eV)
doublet

VO_2SO_2 clusters (BPW91/LANL2DZ)

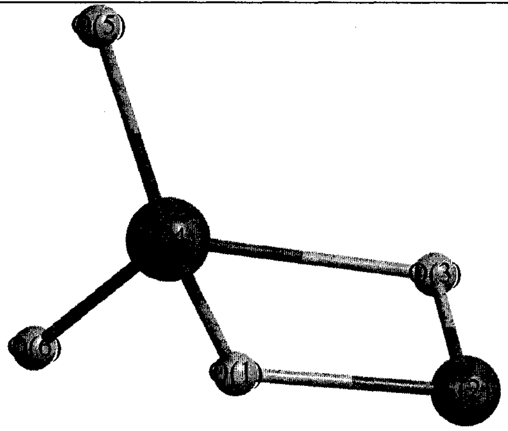
Isomer 1



```
O(6)-V(2)    1.6145
S(5)-O(3)    1.7535
S(5)-O(1)    1.7523
O(4)-V(2)    1.6143
O(3)-V(2)    2.0077
V(2)-O(1)    2.0064
```

```
O   -0.788857   0.000536  -1.292464
V    0.745686  -0.000076   0.000126
O   -0.789733  -0.000877   1.293691
O    1.690449  -1.309015  -0.000876
S   -1.972790   0.000041  -0.000617
O    1.689874   1.309493   0.000520
```

E = -382.4506757 h (0 eV)
doublet



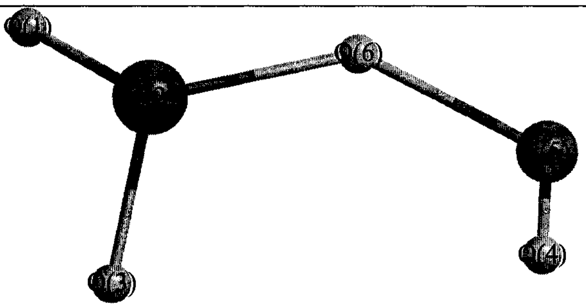
```
O(6)-V(4)    1.6856
O(5)-V(4)    1.6849
V(4)-O(1)    2.0035
V(4)-O(3)    2.0035
O(3)-S(2)    1.7555
S(2)-O(1)    1.7555

Note: structure 4, quartet
```

v2o4s4q.log, vso4s4qfr.log

```
O    .796717   -.000170    1.253625
S   2.025656   -.000282    -.000002
O    .796753   -.000314   -1.253618
V   -.766108    .000068     .000014
O  -1.719977   1.389007    -.000088
O  -1.722243  -1.388153     .000042
 Zero-point correction=                      .010127 (Hartree/Particle)
 Thermal correction to Energy=               .017852
 Thermal correction to Enthalpy=             .018796
 Thermal correction to Gibbs Free Energy=   -.024137
```

E = -382.376999116 h (2.00 eV)
quartet

Isomer 2

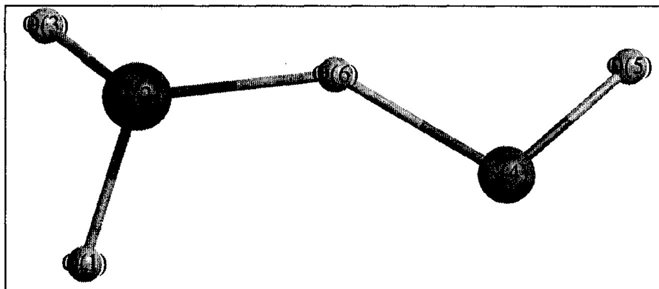


```
O(6)-S(5)    1.8024
O(6)-V(2)    1.8127
S(5)-O(4)    1.6452
O(3)-V(2)    1.6205
V(2)-O(1)    1.6208
```

optlanl1.log, optlanl1freq.log

```
O  -2.461376   -0.800079    0.237636
V  -1.179362    0.057746   -0.259888
O  -1.166054    1.510820    0.457411
O   2.442156    0.997544   -0.319856
S   2.099417   -0.505468    0.254874
O   0.377106   -0.863371   -0.137762
 Zero-point correction=                     0.012350 (Hartree/Particle)
 Thermal correction to Energy=              0.019923
 Thermal correction to Enthalpy=            0.020867
 Thermal correction to Gibbs Free Energy=  -0.022863
```

E = -382.428409402 h (0.61 eV)
doublet



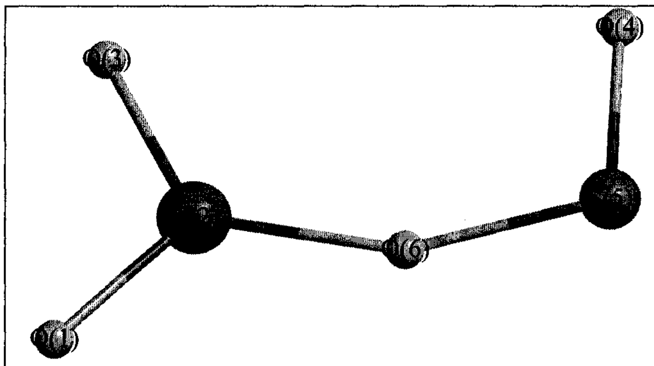
```
O(6)-S(4)    1.8060
O(6)-V(2)    1.7996
O(5)-S(4)    1.6393
O(3)-V(2)    1.6216
V(2)-O(1)    1.6234
```

optlanl2b.log

```
O  -1.763833    1.397730     .318614
V  -1.314627    -.049340    -.264216
O  -2.148466   -1.232460     .466951
S   2.040328     .495433     .084332
O   3.144107    -.716077     .117055
O    .467088    -.298207    -.311664
```

E = -382.425970397 h (0.67 eV)
doublet

```
 Zero-point correction=                      .012264 (Hartree/Particle)
 Thermal correction to Energy=               .019932
 Thermal correction to Enthalpy=             .020876
 Thermal correction to Gibbs Free Energy=   -.023492
```



```
O(6)-S(5)    1.7960
O(6)-V(2)    1.7957
S(5)-O(4)    1.6427
O(3)-V(2)    1.6667
V(2)-O(1)    1.7058
```

Note: structure 1, quartet

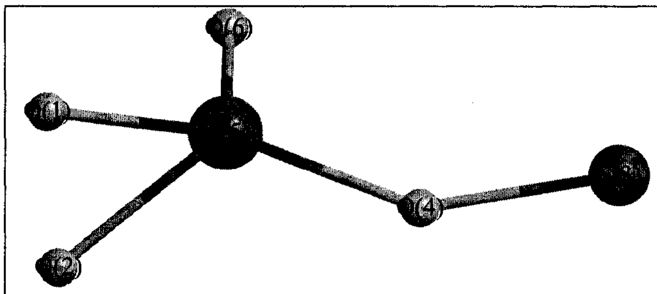
vso4s1q.log, vso4s1qfr.log

```
O  -2.590938    -.977134     .081876
V  -1.199423     .002478    -.035881
O  -1.634764    1.610339     .018858
O   2.659471    1.063500     .028197
S   2.268622    -.531928     .015784
O    .477329    -.639974    -.057340
```

E = -382.362918197 h (2.39 eV)
quartet

```
 Zero-point correction=                      .009693 (Hartree/Particle)
 Thermal correction to Energy=               .018233
 Thermal correction to Enthalpy=             .019177
 Thermal correction to Gibbs Free Energy=   -.031217
```

Isomer 5



```
O(6)-V(5)    1.6071
V(5)-O(4)    1.8047
V(5)-O(1)    1.8270
V(5)-O(2)    1.8331
O(4)-S(3)    1.7117
```

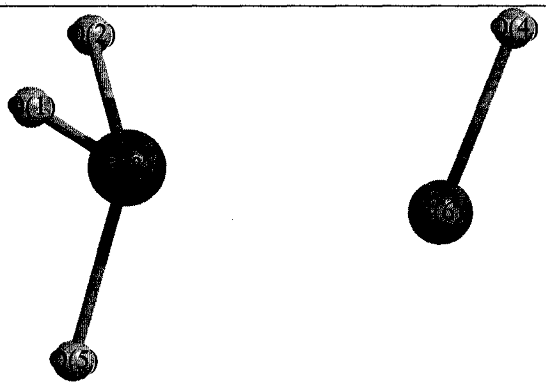
ring2.log

```
O   -2.068862   -0.646583    0.789533
O   -1.944690   -0.854245   -0.720992
S    2.736851   -0.173055    0.078397
O    1.066711   -0.416072   -0.206793
V   -0.623327    0.171606    0.028623
O   -0.734796    1.769642   -0.100831
```

E = -382.395619428 h (1.50 eV)
doublet

```
 Zero-point correction=                           0.012390 (Hartree/Particle)
 Thermal correction to Energy=                    0.019698
 Thermal correction to Enthalpy=                  0.020643
 Thermal correction to Gibbs Free Energy=        -0.021686
```

Isomer 6



```
S(6)-O(4)    1.6607
O(5)-V(3)    1.6722
V(3)-O(2)    1.6749
V(3)-O(1)    1.6792
V(3)-S(6)    2.5331
```

vo3sodoubletb.log

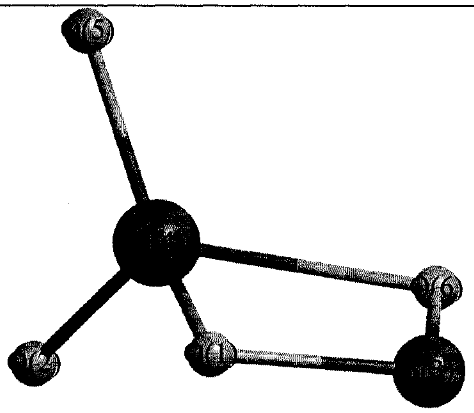
```
O   -1.335185   -0.993283   -1.257767
O   -1.031806   -0.740378    1.487851
V   -0.748181   -0.039445   -0.006631
O    2.483474   -0.864971   -0.030577
O   -1.370064    1.511396   -0.073125
S    1.702300    0.600321   -0.053659
```

E = -382.376311770 h (2.02 eV)
doublet

```
 Zero-point correction=                           0.009905 (Hartree/Particle)
 Thermal correction to Energy=                    0.018313
 Thermal correction to Enthalpy=                  0.019257
 Thermal correction to Gibbs Free Energy=        -0.026545
```

VO_2SO_2 clusters (BPW91/TZVP)

Isomer 1



```
O(6)-V(4)    2.0224
O(6)-S(3)    1.5983
O(5)-V(4)    1.5960
V(4)-O(2)    1.5960
V(4)-O(1)    2.0224
S(3)-O(1)    1.5984
```

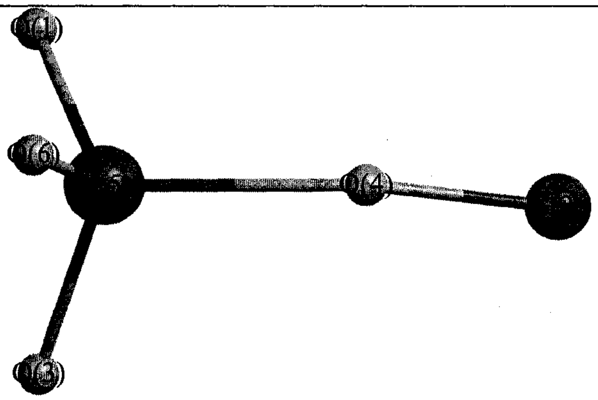
vo2so2s1.log

```
O    -.859521      .000632   -1.231543
O    1.667795    -1.301939    -.000717
S   -1.878366      .000005    -.000002
V     .744600     -.000025    -.000001
O    1.667269     1.302260     .000724
O    -.859535     -.000892    1.231543
```

E = -1643.40059848 h (0 eV)
doublet

```
 Zero-point correction=                       .013956 (Hartree/Particle)
 Thermal correction to Energy=                .020684
 Thermal correction to Enthalpy=              .021629
 Thermal correction to Gibbs Free Energy=    -.018618
```

Isomer 2



```
O(6)-V(5)    1.6651
V(5)-O(4)    2.0244
V(5)-O(3)    1.6641
V(5)-O(1)    1.6652
O(4)-S(2)    1.5284
```

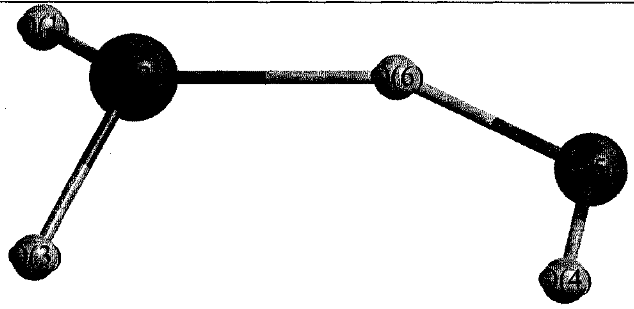
vo2so2s2r2.log

```
O   -1.362527     -.951178   -1.264531
S    2.689913     -.008662     .004694
O   -1.249328     -.705599    1.451056
O    1.172282      .147863    -.086036
V    -.844925      .001057    -.000282
O   -1.511093     1.523200    -.109065
```

E = -1643.32268302 h (2.12 eV)
doublet

```
 Zero-point correction=                       .010608 (Hartree/Particle)
 Thermal correction to Energy=                .018765
 Thermal correction to Enthalpy=              .019709
 Thermal correction to Gibbs Free Energy=    -.026456
```

Isomer 3



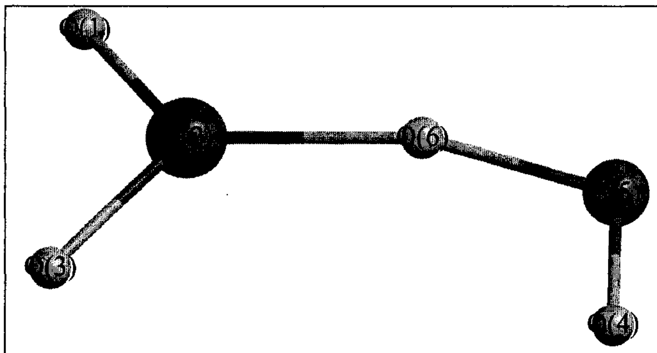
```
O(6)-S(5)    1.6214
O(6)-V(2)    1.8573
S(5)-O(4)    1.5030
O(3)-V(2)    1.6012
V(2)-O(1)    1.6028
```

vo2so2s3.log

```
O   -2.355689    -.915982     .341110
V   -1.203374     .030108    -.247068
O   -1.369391    1.530153     .287999
O    2.509475     .950069    -.067143
S    2.086619    -.477606     .137945
O     .502068    -.695590    -.127534
```

E = -1643.37878723 h (0.59 eV)
doublet

```
 Zero-point correction=                       .013102 (Hartree/Particle)
 Thermal correction to Energy=                .020481
 Thermal correction to Enthalpy=              .021425
 Thermal correction to Gibbs Free Energy=    -.021576
```



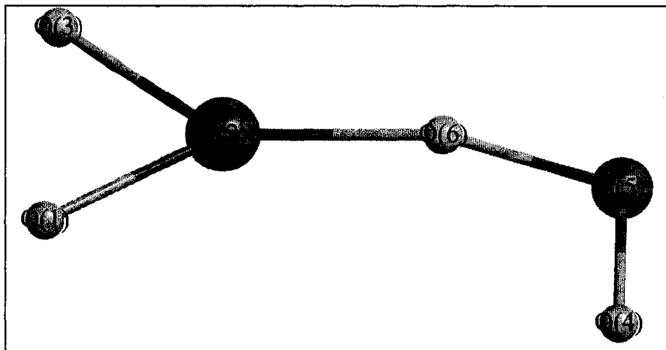
```
O(6)-S(5)    1.6307
O(6)-V(2)    1.8323
S(5)-O(4)    1.5028
O(3)-V(2)    1.6454
V(2)-O(1)    1.6987
```

vo2so2s3q.log

```
O  -2.497191   -1.062778     .116451
V  -1.196805     .014946    -.065470
O  -1.726963    1.567239     .062995
O   2.726184     .918534     .022109
S   2.188194    -.484566     .037379
O    .562396    -.496831    -.088086
```

E = -1643.30376232 h (2.64 eV)
quartet

```
 Zero-point correction=                       .010408 (Hartree/Particle)
 Thermal correction to Energy=                .018733
 Thermal correction to Enthalpy=              .019677
 Thermal correction to Gibbs Free Energy=    -.027027
```



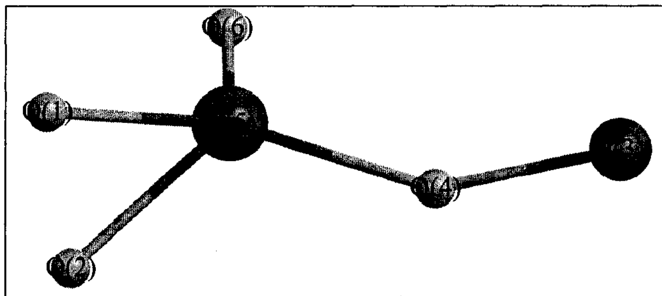
O(6)-S(5)	1.6328
O(6)-V(2)	1.8442
S(5)-O(4)	1.5061
O(3)-V(2)	1.9397
V(2)-O(1)	1.7237

O	-2.208606	1.283621	.009020
V	-1.077586	-.016440	-.033033
O	-2.828966	-.843532	.072622
O	2.788398	.998192	.034817
S	2.325567	-.434902	.012550
O	.696098	-.521212	-.046588

E = -1643.18636680 h (5.83 eV)
sextet

```
 Zero-point correction=                           .010171 (Hartree/Particle)
 Thermal correction to Energy=                    .018538
 Thermal correction to Enthalpy=                  .019483
 Thermal correction to Gibbs Free Energy=        -.027927
```

Isomer 4



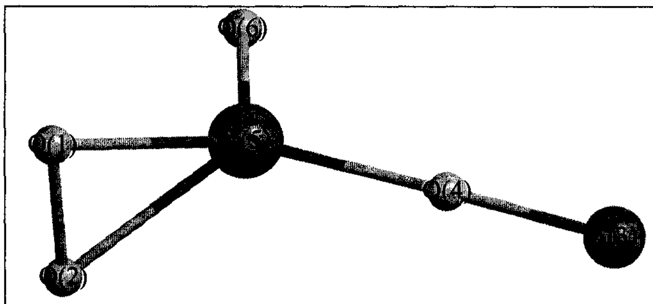
O(6)-V(5)	1.5895
V(5)-O(4)	1.8331
V(5)-O(1)	1.8014
V(5)-O(2)	1.8082
O(4)-S(3)	1.6042

vo2so2s4r1.log

O	-1.991991	-.734201	.748164
O	-1.856198	-.917631	-.686557
S	2.681448	-.188240	.093280
O	1.120309	-.289810	-.261691
V	-.623458	.192953	.032176
O	-.842573	1.763382	-.078982

E = -1643.30824376 h (2.51 eV)
doublet

```
 Zero-point correction=                           .012851 (Hartree/Particle)
 Thermal correction to Energy=                    .020129
 Thermal correction to Enthalpy=                  .021074
 Thermal correction to Gibbs Free Energy=        -.021888
```



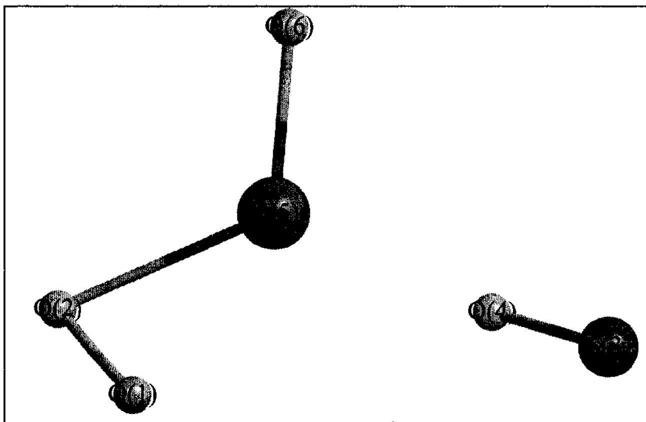
```
O(6)-V(5)    1.5866
V(5)-O(2)    1.9092
V(5)-O(1)    1.9095
V(5)-O(4)    1.8779
O(4)-S(3)    1.5851
O(2)-O(1)    1.3687
```

vo2so2s4q.log

```
O   1.843041   -1.054743    -.681470
O   1.832189   -1.057869     .687171
S  -2.773769    -.227143     .003234
O  -1.207067     .013051    -.010227
V    .652461     .275101    -.003083
O   1.203551    1.762933     .006922
```

E = -1643.28368342 h (3.18 eV)
quartet

```
 Zero-point correction=                       .012246 (Hartree/Particle)
 Thermal correction to Energy=                .019774
 Thermal correction to Enthalpy=              .020719
 Thermal correction to Gibbs Free Energy=    -.023051
```



```
O(6)-V(5)    1.6041
V(5)-O(2)    2.0353
O(4)-S(3)    1.5547
O(2)-O(1)    1.3255
O(4)-V(5)    2.0638
S(3)-V(5)    3.3651
```

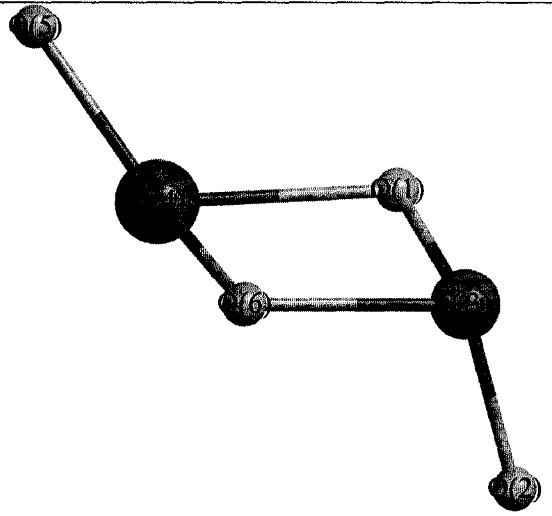
vo2so2s4s.log

```
O   1.343012   -1.590708    -.329530
O   2.317319    -.821941     .135999
S  -2.594466    -.317836    -.186566
O  -1.289574     .012100     .591557
V    .681895     .389381     .111687
O    .857728    1.916751    -.345994
```

E = -1643.20585508 h (5.30 eV)
sextet

```
 Zero-point correction=                       .010770 (Hartree/Particle)
 Thermal correction to Energy=                .019168
 Thermal correction to Enthalpy=              .020112
 Thermal correction to Gibbs Free Energy=    -.026732
```

Isomer 5



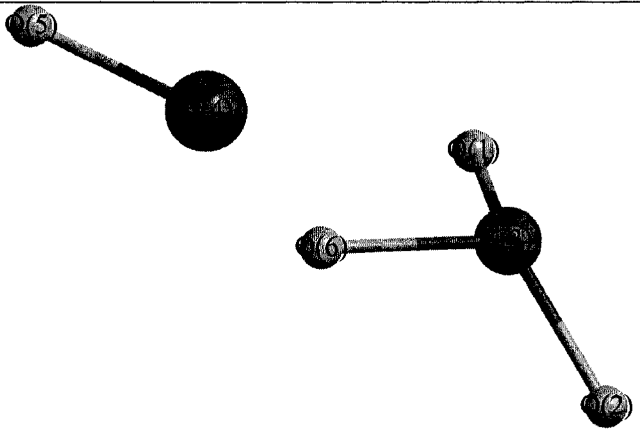
```
O(6)-S(3)    1.7371
O(6)-V(4)    1.8352
O(5)-V(4)    1.5863
V(4)-O(1)    1.8347
S(3)-O(2)    1.4737
S(3)-O(1)    1.7381
```

vo2so2s5.log

```
O     .207385   -1.220858    -.157315
O    2.372447    -.000774     .645101
S    1.404808     .000400    -.466452
V   -1.073423    -.000113     .327991
O   -2.511537     .000246    -.341418
O     .208180    1.220911    -.156438
```

E = -1643.36530872 h (0.96 eV)
doublet

```
 Zero-point correction=                     .014200 (Hartree/Particle)
 Thermal correction to Energy=              .020716
 Thermal correction to Enthalpy=            .021660
 Thermal correction to Gibbs Free Energy=  -.017876
```



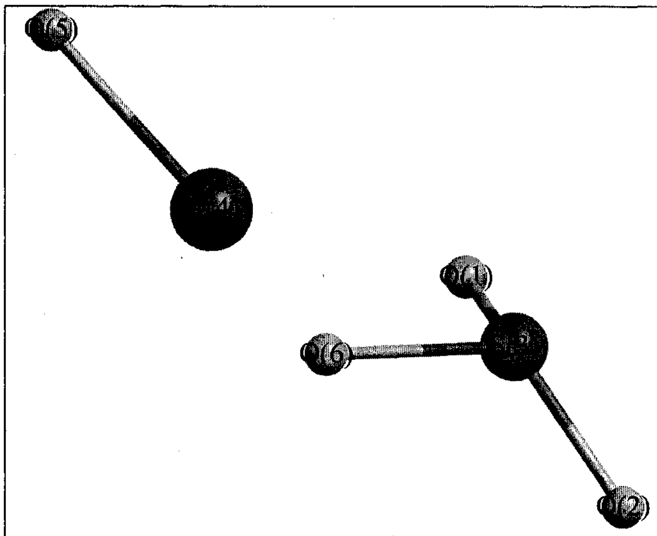
```
O(6)-S(3)    1.5705
O(5)-V(4)    1.5888
S(3)-O(1)    1.5705
S(3)-O(2)    1.4844
V(4)-O(6)    2.1083
S(3)-V(4)    2.6986
O(1)-V(4)    2.1084
```

vo2so2s5q.log

```
O   -.460136    1.224008    -.118274
O  -2.648754    -.000166     .558899
S  -1.429362    -.000018    -.287636
V   1.249693     .000103     .036858
O   2.834673    -.000197     .147046
O   -.459926   -1.223905    -.118366
```

E = -1643.29259938 h (2.94 eV)
quartet

```
 Zero-point correction=                     .014179 (Hartree/Particle)
 Thermal correction to Energy=              .020914
 Thermal correction to Enthalpy=            .021859
 Thermal correction to Gibbs Free Energy=  -.019342
```



O(6)-S(3)	1.5718
O(5)-V(4)	1.8584
S(3)-O(2)	1.4847
S(3)-O(1)	1.5718
V(4)-O(6)	2.0734
S(3)-V(4)	2.6827
O(1)-V(4)	2.0734

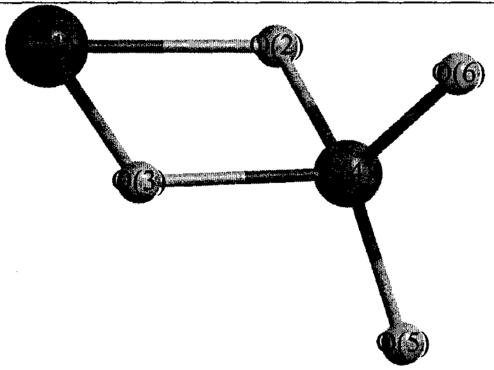
vo2so2s5s.log

```
O    .463693    1.199858    -.040448
O   2.772768    -.000008    -.268559
S   1.411398    -.000002     .323866
V  -1.219725     .000007    -.199750
O  -3.016229    -.000013     .276009
O    .463682   -1.199853    -.040454
```

E = -1643.17623735 h (6.11 eV)
sextet

```
 Zero-point correction=                       .012992 (Hartree/Particle)
 Thermal correction to Energy=                .019984
 Thermal correction to Enthalpy=              .020928
 Thermal correction to Gibbs Free Energy=   -.021430
```

Isomer 9



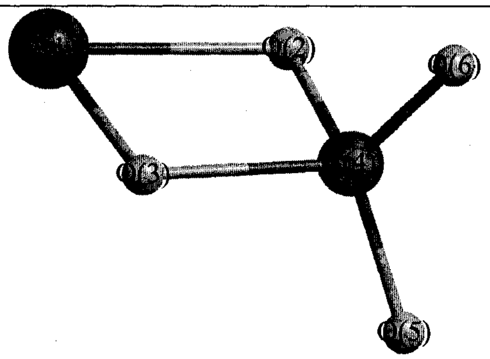
O(6)-S(4)	1.4603
O(5)-S(4)	1.4598
S(4)-O(3)	1.6871
S(4)-O(2)	1.6870
O(3)-V(1)	1.8098
O(2)-V(1)	1.8098

vo2so2s9.log

```
V  -1.635883     .000024    -.000016
O   -.260603    -.001014   -1.176515
O   -.260715    -.000696    1.176537
S    .948429    -.000081    -.000014
O   1.665062   -1.271847     .000173
O   1.662562    1.273651    -.000121
```

E = -1643.21036412 h (5.18 eV)
doublet

```
 Zero-point correction=                       .015999 (Hartree/Particle)
 Thermal correction to Energy=                .021796
 Thermal correction to Enthalpy=              .022740
 Thermal correction to Gibbs Free Energy=   -.015112
```



```
O(6)-S(4)    1.4643
O(5)-S(4)    1.4642
S(4)-O(2)    1.6126
S(4)-O(3)    1.7310
O(3)-V(1)    1.7993
O(2)-V(1)    1.9359
```

vo2so2s9q.log

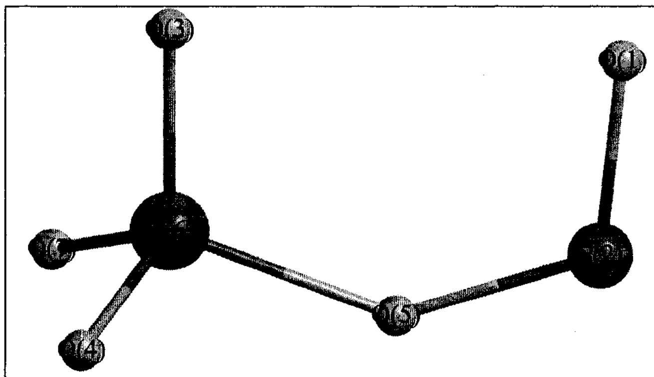
```
V   1.664217   0.000001   0.007163
O   0.147640  -0.000094   1.210330
O   0.303029   0.000077  -1.169528
S  -0.947870  -0.000009   0.026953
O  -1.669784  -1.271100  -0.057733
O  -1.669767   1.271131  -0.057570
```

E = -1643.24513809 h (4.23 eV)
quartet

```
 Zero-point correction=                     .015968 (Hartree/Particle)
 Thermal correction to Energy=              .021803
 Thermal correction to Enthalpy=            .022747
 Thermal correction to Gibbs Free Energy=  -.016014
```

VO_3SO_2 clusters (BPW91/LANL2DZ)

Isomer 1



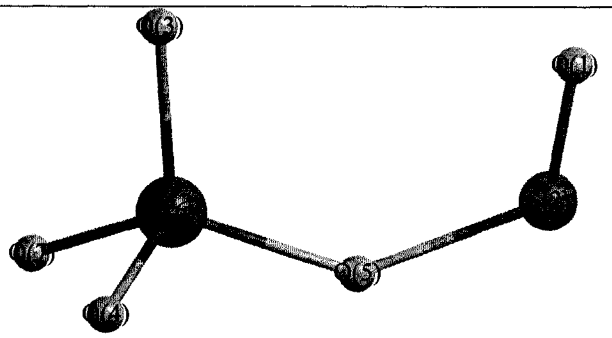
```
O(7)-V(6)    1.6886
V(6)-O(5)    1.9363
V(6)-O(3)    1.6729
V(6)-O(4)    1.6887
O(5)-S(2)    1.6917
S(2)-O(1)    1.6222
```

vso5s1r4.log

```
O    2.602421    1.079667     .000025
S    2.312914    -.516444    -.000048
O    -.951609    1.689619    -.001465
O   -1.926228    -.469212    1.370897
O     .655630    -.855898    -.000094
V   -1.070725     .020939    -.000024
O   -1.927706    -.471488   -1.369198
```

E = -457.596908495 h (0.10 eV)
doublet

```
 Zero-point correction=                     .013182 (Hartree/Particle)
 Thermal correction to Energy=              .022375
 Thermal correction to Enthalpy=            .023319
 Thermal correction to Gibbs Free Energy=  -.025848
```



```
O(7)-V(6)    1.7185
V(6)-O(5)    1.8018
V(6)-O(3)    1.6761
V(6)-O(4)    1.7312
O(5)-S(2)    1.8253
S(2)-O(1)    1.6427
```

vso5s1q.log

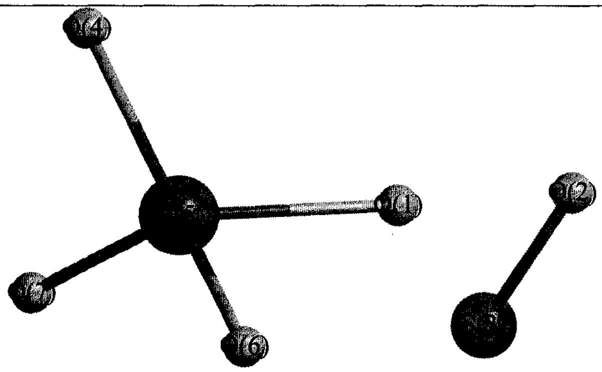
```
O   2.629230    1.068366     .113355
S   2.348124    -.540713    -.060808
O   -.925105    1.532078    -.723783
O  -1.873791     .170305    1.483891
O    .562295    -.820362     .192553
V  -1.019893     .016523    -.014253
O  -2.156686    -.916464    -.903422
```

E = -575582565 h (0.68 eV)

quartet

```
 Zero-point correction=                          .012280 (Hartree/Particle)
 Thermal correction to Energy=                   .021764
 Thermal correction to Enthalpy=                 .022708
 Thermal correction to Gibbs Free Energy=       -.025936
```

Isomer 3



```
O(7)-V(5)    1.6600
O(6)-V(5)    1.8227
V(5)-O(1)    1.8227
V(5)-O(4)    1.6900
S(3)-O(2)    1.5968
S(3)-O(6)    1.9506
S(3)-V(5)    2.7151
O(1)-S(3)    1.9504
```

vso5s3r1.log

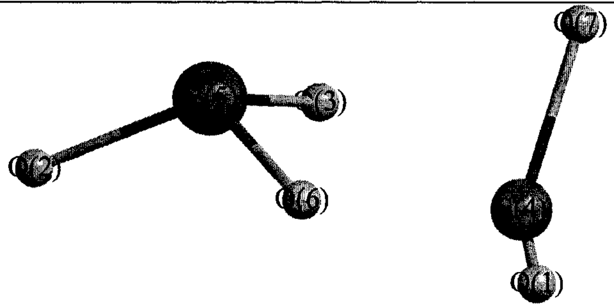
```
O    .295374    -.294767   -1.305819
O   2.602121     .869983    -.000238
S   1.733466    -.469869     .000062
O  -1.657019    1.543892    -.000263
V   -.938096     .014384     .000059
O    .295330    -.294233    1.306075
O  -2.305713    -.926489    -.000049
```

E = -457.600434805 h (0 eV)

doublet

```
 Zero-point correction=                          .014461 (Hartree/Particle)
 Thermal correction to Energy=                   .022848
 Thermal correction to Enthalpy=                 .023792
 Thermal correction to Gibbs Free Energy=       -.019941
```

Isomer 5



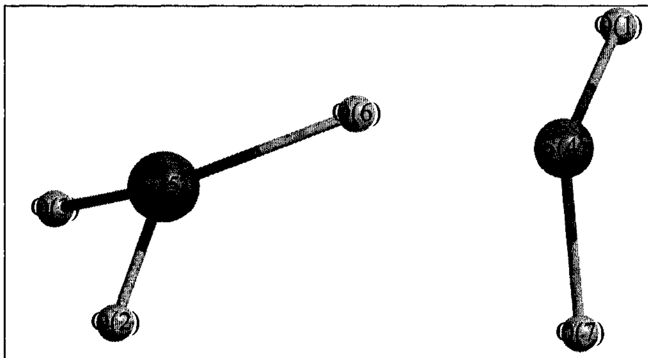
```
O(7)-S(4)    1.6623
O(6)-V(5)    1.8129
V(5)-O(3)    1.6228
V(5)-O(2)    1.6188
S(4)-O(1)    1.6491
S(4)-O(6)    1.8821
S(4)-V(5)    3.2693
```

vo3so2s1r1.log

```
O  -2.943151   -1.063819     .075424
O   2.664139   -1.016539     .007935
O   1.596479    1.304881     .726803
S  -1.777323     .075498     .325164
V   1.441394     .013984    -.244236
O   -.164368    -.809517    -.071512
O  -1.742462    1.393793    -.686801
```

E = -457.550038534 h (1.37 eV)
doublet

```
 Zero-point correction=                       .014336 (Hartree/Particle)
 Thermal correction to Energy=                .023258
 Thermal correction to Enthalpy=              .024203
 Thermal correction to Gibbs Free Energy=    -.024053
```



```
O(7)-S(4)    1.6568
O(6)-V(5)    1.7918
V(5)-O(2)    1.6693
V(5)-O(3)    1.6981
S(4)-O(1)    1.6579
S(4)-O(6)    1.8585
S(4)-V(5)    3.5200
```

vo3so2s1q.log

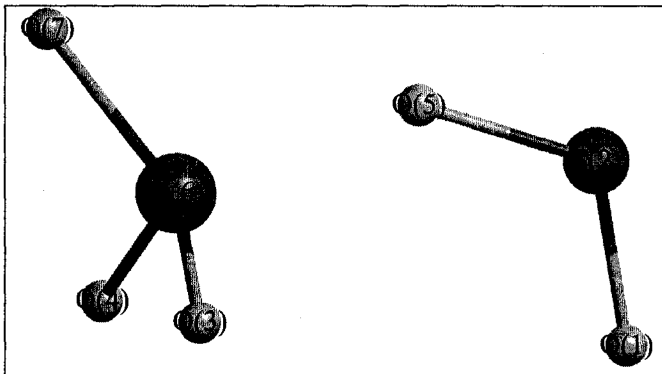
```
O   2.817504   -1.197562    -.025849
O  -2.304043    1.308109    -.301731
O  -2.249988   -1.080845    1.015393
S   1.983764     .217357    -.252556
V  -1.515632    -.160301    -.208043
O    .230661    -.304038    -.582653
O   1.895781    1.300488     .998075
```

E = -457.483888166 h (3.17 eV)
quartet

```
 Zero-point correction=                       .011994 (Hartree/Particle)
 Thermal correction to Energy=                .021616
 Thermal correction to Enthalpy=              .022560
 Thermal correction to Gibbs Free Energy=    -.028167
```

VO_3SO_2 clusters (BPW91/TZVP)

Isomer 1



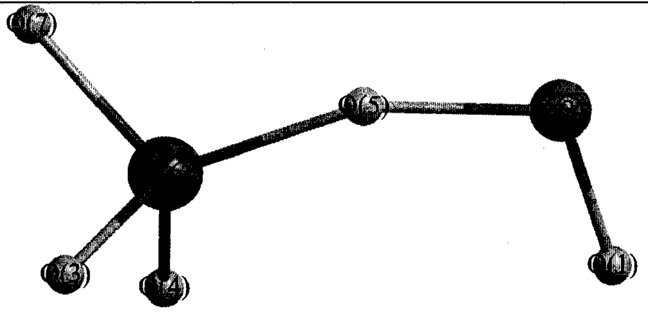
```
O(7)-V(6)    1.6649
V(6)-O(3)    1.6643
V(6)-O(4)    1.6643
O(5)-S(2)    1.5123
S(2)-O(1)    1.4691
O(5)-V(6)    2.0562
S(2)-V(6)    3.3988
```

vo3so2s1tzvpr1.log

```
O   -2.624802     .950439     .000001
S   -2.254765    -.471273    -.000001
O    1.231197     .956028    1.370553
O    1.231185     .956062   -1.370531
O    -.778130    -.797987     .000000
V    1.108392     .019875     .000000
O    2.263453   -1.179137    -.000020
```

E = -1718.59382991 h (0.47 eV)
doublet

```
 Zero-point correction=                          .014724 (Hartree/Particle)
 Thermal correction to Energy=                   .023744
 Thermal correction to Enthalpy=                 .024688
 Thermal correction to Gibbs Free Energy=       -.023013
```



```
O(7)-V(6)    1.6983
V(6)-O(3)    1.7280
V(6)-O(4)    1.6697
V(6)-O(5)    1.8188
O(5)-S(2)    1.6637
S(2)-O(1)    1.5056
```

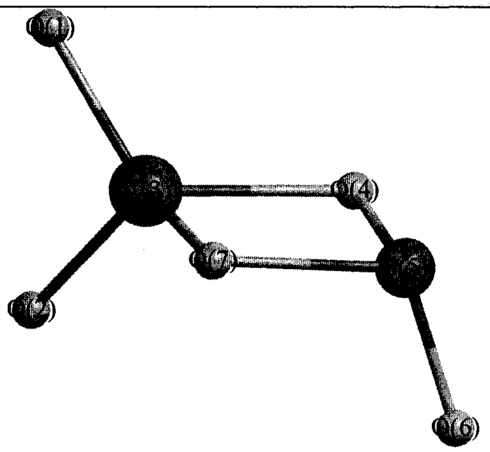
vo3so2s1tzvpq.log

```
O  -2.688023     .946656     .139909
S  -2.297664    -.491993    -.071611
O   1.836322     .012947    1.495695
O   1.079728    1.579890    -.626442
O   -.654692    -.692110     .097448
V   1.012722     .024353    -.023372
O   2.110419    -.933411    -.896192
```

E = -1718.53866270 h (1.97 eV)
quartet

```
 Zero-point correction=                          .012734 (Hartree/Particle)
 Thermal correction to Energy=                   .022212
 Thermal correction to Enthalpy=                 .023156
 Thermal correction to Gibbs Free Energy=       -.025992
```

Isomer 2



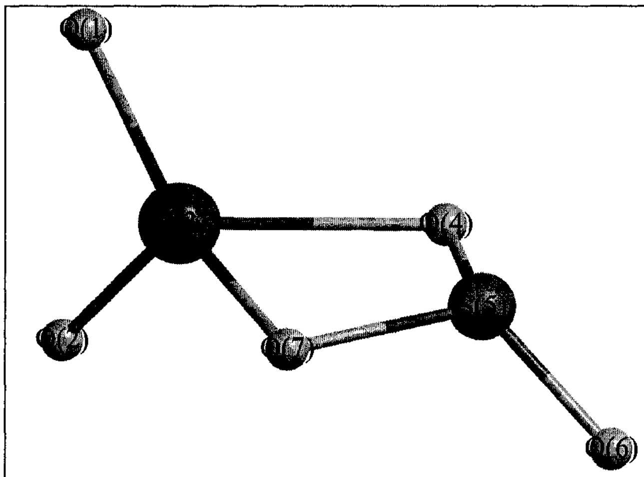
```
O(7)-S(5)    1.7315
O(7)-V(3)    1.8360
O(6)-S(5)    1.4682
S(5)-O(4)    1.7319
O(4)-V(3)    1.8358
V(3)-O(2)    1.6769
V(3)-O(1)    1.6337
```

vo3so2s2tzvp.log

```
O   -2.216547    -.993130     .000170
O   -1.657441    1.526829    -.000294
V    -.931222     .015324    -.000067
O     .406722    -.261203    1.226098
S    1.620723    -.411152     .000102
O    2.495943     .767612    -.000072
O     .407140    -.261862   -1.225915
```

E = -1718.60646820 h (0.12 eV)
doublet

```
 Zero-point correction=                       .015421 (Hartree/Particle)
 Thermal correction to Energy=                .023510
 Thermal correction to Enthalpy=              .024454
 Thermal correction to Gibbs Free Energy=    -.018512
```



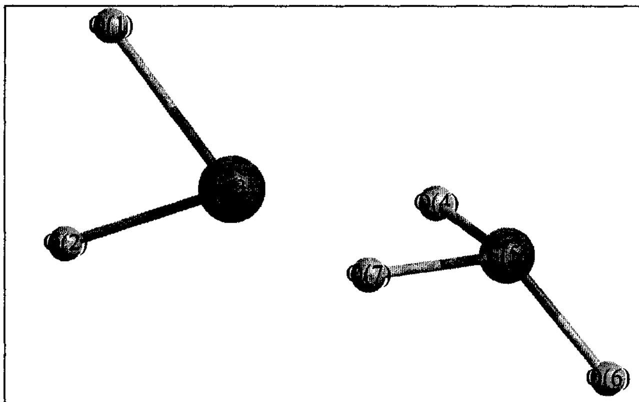
```
O(7)-V(3)    2.0397
O(7)-S(5)    1.5780
O(6)-S(5)    1.4826
S(5)-O(4)    1.5777
O(4)-V(3)    2.0404
V(3)-O(2)    1.6543
V(3)-O(1)    1.6830
```

vo3so2s2tzvpq.log

```
O   2.101893   -1.291110    -.000224
O   1.930488    1.461569    -.000945
V   1.077393     .044174     .000429
O   -.571693    -.067735   -1.195960
S  -1.571951    -.308819     .000104
O  -2.842851     .454583    -.000366
O   -.571439    -.066669    1.196053
```

E = -1718.5280069 h (2.26 eV)
quartet

```
 Zero-point correction=                       .015152 (Hartree/Particle)
 Thermal correction to Energy=                .023635
 Thermal correction to Enthalpy=              .024579
 Thermal correction to Gibbs Free Energy=    -.020836
```



O(7)-S(5)	1.5746
O(6)-S(5)	1.4837
S(5)-O(4)	1.5746
V(3)-O(1)	1.9019
V(3)-O(2)	1.7432
V(3)-O(7)	2.0683
V(3)-S(5)	2.7005
V(3)-O(4)	2.0683

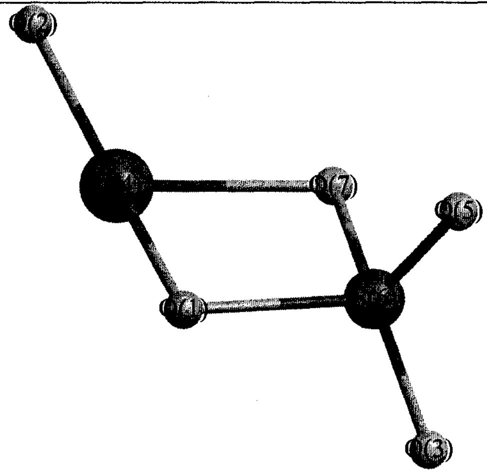
vo3so2s2tzvps.log

```
O   2.538761     .733903     .736896
O   2.335589    -.815330    -.832626
V    .987441    -.044636    -.040622
O   -.694633    -.812242     .886263
S  -1.688249     .211342     .219617
O  -2.952431    -.322841    -.344163
O   -.689682     .922155    -.768814
```

E = -1718.40768073 h (5.53 eV)
sextet

```
 Zero-point correction=                          .014684 (Hartree/Particle)
 Thermal correction to Energy=                   .023360
 Thermal correction to Enthalpy=                 .024305
 Thermal correction to Gibbs Free Energy=       -.022501
```

Isomer 3



O(7)-V(4)	1.8552
O(7)-S(6)	1.6679
S(6)-O(1)	1.6684
S(6)-O(5)	1.4567
S(6)-O(3)	1.4618
V(4)-O(2)	1.5805
V(4)-O(1)	1.8549

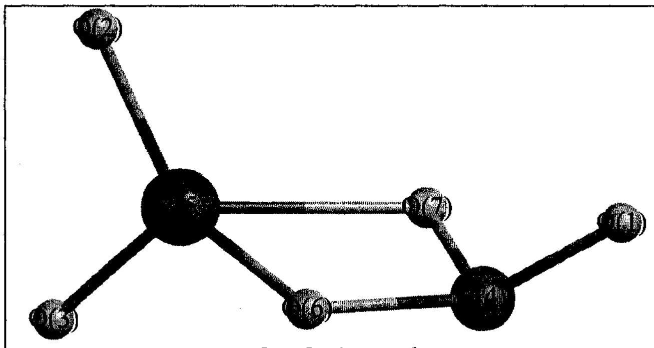
vo3so2s3tzvp.log

```
O    -.059166    -.114984   -1.182034
O    2.521160     .708475    -.000331
O   -2.114193   -1.074705     .000362
V    1.350191    -.353083     .000211
O   -1.729997    1.446220    -.000825
S   -1.220004     .081686     .000055
O    -.059594    -.113266    1.182110
```

E = 1718.58555898 h (0.69 eV)
doublet

```
 Zero-point correction=                          .019657 (Hartree/Particle)
 Thermal correction to Energy=                   .026556
 Thermal correction to Enthalpy=                 .027500
 Thermal correction to Gibbs Free Energy=       -.013104
```

Isomer 4



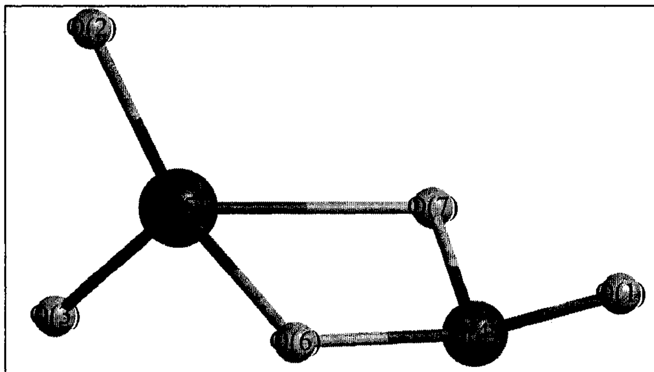
```
O(7)-V(5)   2.0223
O(7)-S(4)   1.5850
O(6)-V(5)   2.0218
O(6)-S(4)   1.5850
V(5)-O(2)   1.5979
V(5)-O(3)   1.5942
S(4)-O(1)   1.4795
```

vo3so2s4tzvp.log

```
O   -2.762896     .531358    -.000016
O    1.790417    1.453601     .000485
O    2.151830   -1.127330    -.000195
S   -1.559845    -.329781    -.000087
V    1.058754     .033097    -.000104
O    -.551649    -.146224   -1.209290
O    -.551930    -.146997    1.209488
```

E = -1718.61099797 h (0 eV)
doublet

```
 Zero-point correction=                       .017641 (Hartree/Particle)
 Thermal correction to Energy=                .025268
 Thermal correction to Enthalpy=              .026212
 Thermal correction to Gibbs Free Energy=    -.016206
```



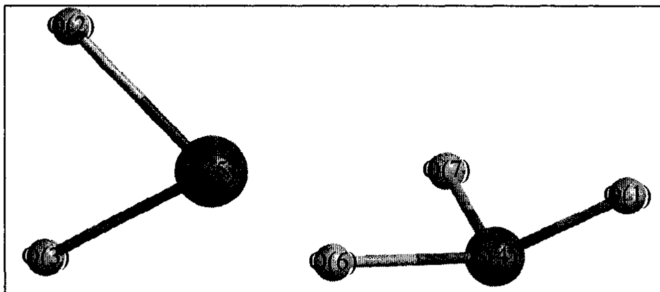
```
O(7)-V(5)   2.0402
O(7)-S(4)   1.5779
O(6)-V(5)   2.0401
O(6)-S(4)   1.5779
V(5)-O(2)   1.6456
V(5)-O(3)   1.6929
S(4)-O(1)   1.4824
```

vo3so2s4tzvpq.log

```
O  -2.842489     .450241     .000004
O   1.907081    1.467796     .000018
O   2.123047   -1.284697    -.000023
S  -1.571433    -.312609    -.000007
V   1.077371     .046619     .000005
O   -.571103    -.071050   -1.196188
O   -.571113    -.071103    1.196190
```

E = -1718.52800995 h (2.26 eV)
quartet

```
 Zero-point correction=                       .015253 (Hartree/Particle)
 Thermal correction to Energy=                .023667
 Thermal correction to Enthalpy=              .024612
 Thermal correction to Gibbs Free Energy=    -.020439
```



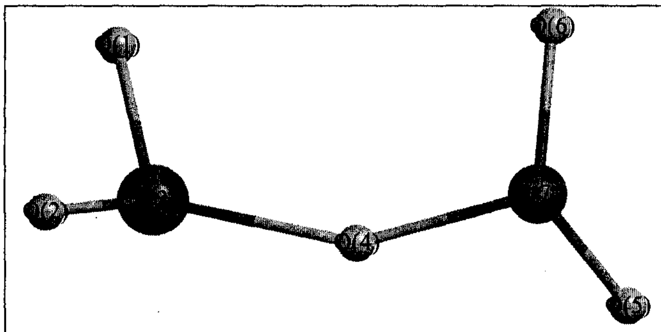
```
O(7)-S(4)    1.5747
O(6)-S(4)    1.5746
V(5)-O(2)    1.7431
V(5)-O(3)    1.9018
S(4)-O(1)    1.4837
V(5)-O(7)    2.0689
V(5)-O(6)    2.0695
S(4)-V(5)    2.7020
```

vo3so2s4tzvps.log

```
O    2.946172     .485210    -.000422
O   -2.321812    1.175933     .000072
O   -2.553058   -1.024539    -.000180
S    1.690676    -.305355     .000066
V    -.987180     .054758     .000009
O     .692951    -.091659    1.199326
O     .692537    -.091665   -1.198954
 Zero-point correction=                        .014688 (Hartree/Particle)
 Thermal correction to Energy=                 .023356
 Thermal correction to Enthalpy=               .024300
 Thermal correction to Gibbs Free Energy=     -.022424
```

E = -1718.40763577 h (5.53 eV)
sextet

Isomer 5

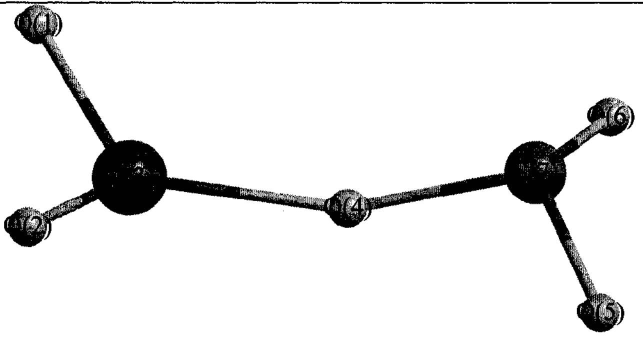


```
S(7)-O(6)    1.4895
S(7)-O(5)    1.4893
S(7)-O(4)    1.6511
O(4)-V(3)    1.8325
V(3)-O(1)    1.5949
V(3)-O(2)    1.5981
```

vo3so2s5tzvp.log

```
O    -1.868616    1.357766    -.537662
O    -2.441354    -.743360     .896517
V    -1.489592    -.164309    -.249230
O      .292023    -.541488    -.045332
O     2.704158    -.735098    -.752100
O     1.898338    1.354096     .565694
S     1.849014    -.109764     .294709
 Zero-point correction=                        .017235 (Hartree/Particle)
 Thermal correction to Energy=                 .025534
 Thermal correction to Enthalpy=               .026479
 Thermal correction to Gibbs Free Energy=     -.020489
```

E = -1718.58212290 h (0.79 eV)
doublet



S(7)-O(4)	1.6396
S(7)-O(5)	1.4911
S(7)-O(6)	1.4911
O(4)-V(3)	1.8436
V(3)-O(2)	1.6593
V(3)-O(1)	1.6597

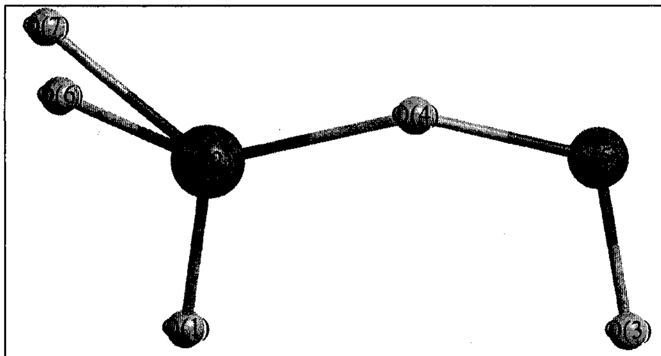
vo3so2s5tzvpq.log

```
O   2.375000   -1.335007     .264540
O   2.372613    1.335872     .264981
V   1.504048    -.000034    -.197929
O   -.336529    -.001664    -.303592
O  -2.497321    1.295874    -.107977
O  -2.499575   -1.295038    -.106835
S  -1.869163     .000030     .278964
```

E = -1718.50912493 h (2.77 eV)
quartet

```
 Zero-point correction=                          .014476 (Hartree/Particle)
 Thermal correction to Energy=                   .023488
 Thermal correction to Enthalpy=                 .024432
 Thermal correction to Gibbs Free Energy=       -.024299
```

Isomer 6



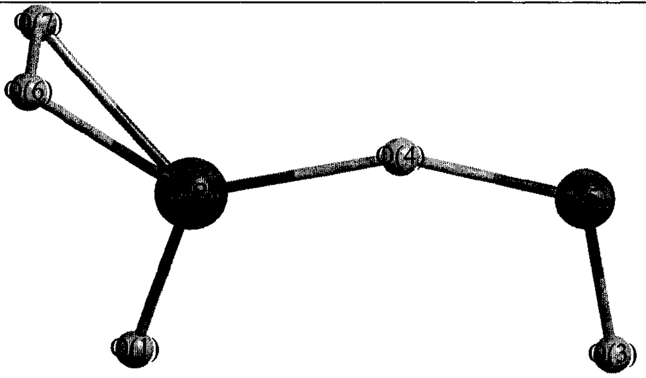
O(7)-V(2)	1.8018
O(6)-V(2)	1.8019
S(5)-O(4)	1.6163
S(5)-O(3)	1.4974
O(4)-V(2)	1.8583
V(2)-O(1)	1.5870

vo3so2s6tzvp.log

```
O     .855521    1.743306    -.110807
V     .926806     .158134    -.085231
O   -2.866327     .749123     .364813
O    -.732373    -.674166     .003059
S   -2.334298    -.544821    -.168813
O    2.239973    -.613034     .877998
O    2.507235    -.570219    -.552400
```

E = -1718.56955553 h (1.13 eV)
doublet

```
 Zero-point correction=                          .015871 (Hartree/Particle)
 Thermal correction to Energy=                   .024388
 Thermal correction to Enthalpy=                 .025333
 Thermal correction to Gibbs Free Energy=       -.020658
```



```
O(7)-V(2)    1.9704
O(7)-O(6)    1.3300
O(6)-V(2)    1.9702
S(5)-O(3)    1.5047
S(5)-O(4)    1.6361
O(4)-V(2)    1.8366
V(2)-O(1)    1.5818
```

vo3so2s6tzvpq.log

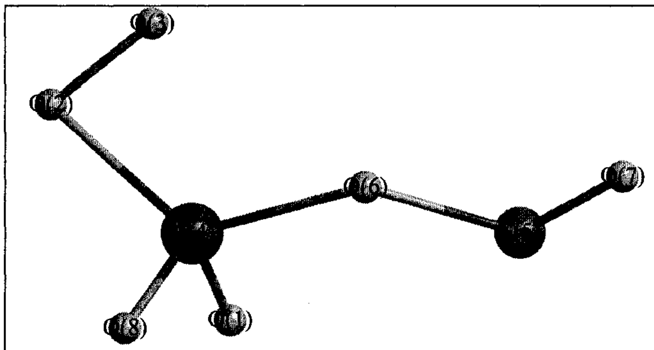
```
O  -1.006512    1.796121    -.000257
V   -.883074     .219172    -.000071
O   2.975521     .776460     .000588
O    .765138    -.591183    -.000284
S   2.401106    -.614235    -.000162
O  -2.498761    -.691535    -.664744
O  -2.498761    -.691515     .665222
```

E = -1718.54121192 h (1.90 eV)
quartet

```
 Zero-point correction=                      .015612 (Hartree/Particle)
 Thermal correction to Energy=               .024390
 Thermal correction to Enthalpy=             .025335
 Thermal correction to Gibbs Free Energy=   -.022064
```

VO_4SO_2 clusters (BPW91/LANL2DZ)

Isomer 1



```
O(8)-V(4)    1.6249
O(7)-S(5)    1.6175
O(6)-S(5)    1.6984
O(6)-V(4)    1.9504
V(4)-O(1)    1.6287
V(4)-O(2)    2.0111
O(3)-O(2)    1.3815
```

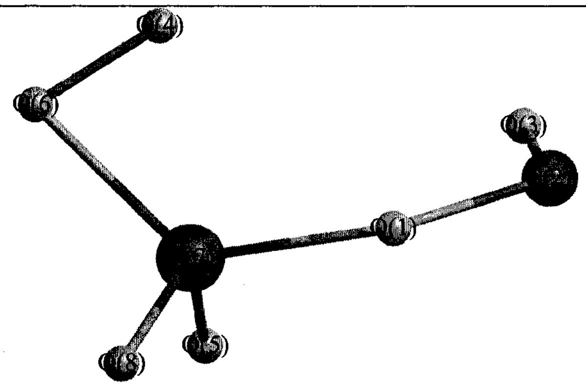
vo4so2s1r1.log

```
O   -.832328   -1.223719   -1.279010
O  -2.546875     .916365    -.230553
O  -1.503790    1.807851    -.069852
V   -.967690    -.296187     .052884
S   2.305278    -.126288    -.380688
O    .859245     .286702     .408536
O   3.524074     .543637     .445098
O  -1.328772   -1.226722    1.335116
```

E = -532.772332038 h (0.05 eV)
doublet

```
 Zero-point correction=                      .016890 (Hartree/Particle)
 Thermal correction to Energy=               .027393
 Thermal correction to Enthalpy=             .028337
 Thermal correction to Gibbs Free Energy=   -.022115
```

Isomer 2



O(8)-V(7)	1.6263
V(7)-O(6)	2.0224
V(7)-O(5)	1.6252
V(7)-O(1)	1.9580
O(6)-O(4)	1.3803
O(3)-S(2)	1.6238
S(2)-O(1)	1.6877

vo4so2s2r2.log

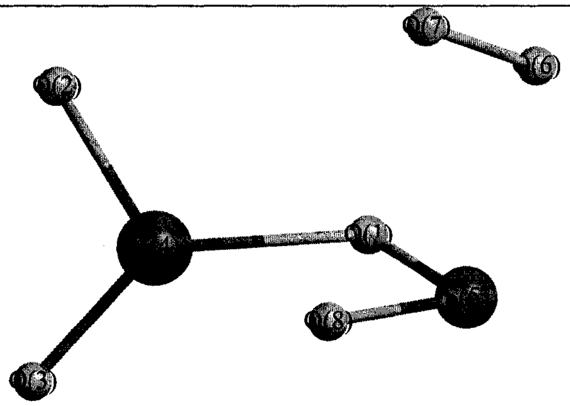
O	-.816434	-.592457	-.768149
S	-2.416003	-.205147	-.394581
O	-2.506376	.781532	.891836
O	.890357	1.741915	-.636580
O	.677605	-.616105	1.648245
O	2.048845	1.385531	.023788
V	.925926	-.295767	.074406
O	1.875970	-1.439791	-.583893

E = -532.774081693 h (0 eV)
doublet

```
 Zero-point correction=                           .017010 (Hartree/Particle)
 Thermal correction to Energy=                    .027406
 Thermal correction to Enthalpy=                  .028350
 Thermal correction to Gibbs Free Energy=       -.021825
```

VO_4SO_2 clusters (BPW91/TZVP)

Isomer 3



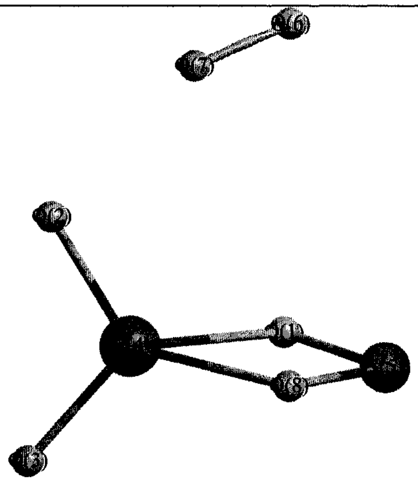
O(8)-S(5)	1.5745
O(7)-O(6)	1.2452
S(5)-O(1)	1.5846
V(4)-O(1)	2.0257
V(4)-O(2)	1.5939
V(4)-O(3)	1.5943

vo2so2o2s3.log

O	.079515	-.950060	-1.153942
O	-1.395044	1.689718	-.402921
O	-2.573265	-.500410	.336679
V	-1.164898	.163057	-.006854
S	1.104691	-1.174481	.033265
O	2.536922	.511324	-.312251
O	2.088571	1.503135	.292500
O	.403002	-.373533	1.193110

E = -1793.78342547 h (1.09 eV)
doublet

```
 Zero-point correction=                           .019525 (Hartree/Particle)
 Thermal correction to Energy=                    .029172
 Thermal correction to Enthalpy=                  .030116
 Thermal correction to Gibbs Free Energy=       -.017632
```



```
O(8)-S(5)    1.5982
O(8)-V(4)    2.0216
O(7)-O(6)    1.2224
S(5)-O(1)    1.5981
V(4)-O(2)    1.5960
V(4)-O(1)    2.0218
V(4)-O(3)    1.5960
```

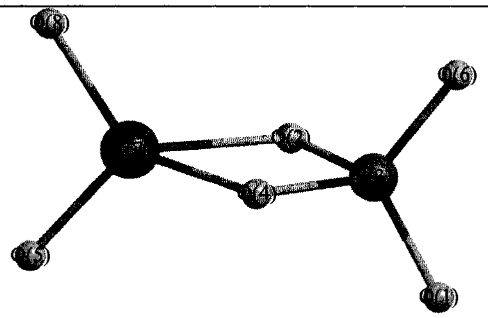
vo2so2o2s3q.log

```
O  -1.951863     .864392     .864115
O   -.117281   -1.629266     .951748
O  -1.992891   -1.714697    -.852682
V  -1.071457    -.749520     .022829
S  -1.113133    1.871576    -.050236
O   4.708213     .515647     .340845
O   4.903399    -.466334    -.360568
O   -.242872     .841977    -.908620
```

E = -1793.77978697 h (1.19 eV)
quartet

```
 Zero-point correction=                          .017687 (Hartree/Particle)
 Thermal correction to Energy=                   .028910
 Thermal correction to Enthalpy=                 .029855
 Thermal correction to Gibbs Free Energy=       -.030019
```

Isomer 4



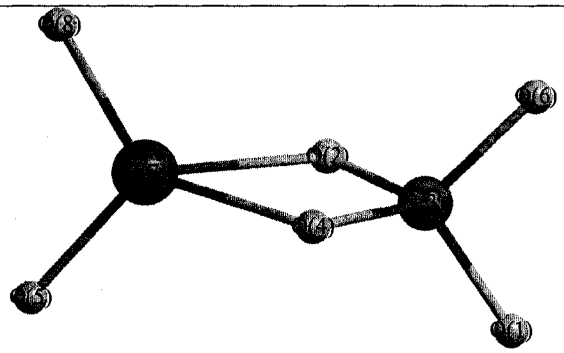
```
O(8)-V(7)    1.6153
V(7)-O(4)    1.9409
V(7)-O(2)    1.9401
V(7)-O(5)    1.6153
O(6)-S(3)    1.4765
O(4)-S(3)    1.6003
S(3)-O(1)    1.4761
S(3)-O(2)    1.6004
```

vo2so2o2s4.log

```
O    2.199273   -1.239715     .000074
O     .322079    -.000147   -1.185056
S    1.397851    -.000124    -.000118
O     .322829    -.000152    1.185304
O   -2.174457   -1.298805    -.000018
O    2.199103    1.240019    -.000200
V   -1.214087    -.000016    -.000039
O   -2.174030    1.299093     .000247
```

E = -1793.82359083 h (0 eV)
doublet

```
 Zero-point correction=                          .020758 (Hartree/Particle)
 Thermal correction to Energy=                   .029221
 Thermal correction to Enthalpy=                 .030165
 Thermal correction to Gibbs Free Energy=       -.013908
```



O(8)-V(7)	1.6662
V(7)-O(5)	1.6662
V(7)-O(2)	2.0373
V(7)-O(4)	2.0373
O(6)-S(3)	1.5052
O(4)-S(3)	1.5501
S(3)-O(2)	1.5501
S(3)-O(1)	1.5052

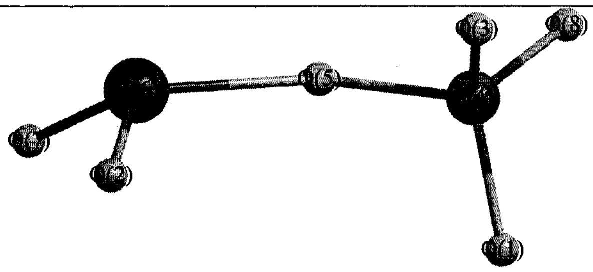
vo2so2o2s4q.log

O	-2.320321	-1.175479	.000167
O	-.376672	-.000040	1.181553
S	-1.380207	-.000016	.000096
O	-.376844	-.000035	-1.181514
O	2.233131	-1.368741	-.000103
O	-2.320235	1.175539	.000162
V	1.282899	-.000003	-.000108
O	2.233021	1.368797	-.000146

E = -1793.73680394 h (2.36 eV)
quartet

```
 Zero-point correction=                          .018520 (Hartree/Particle)
 Thermal correction to Energy=                   .027955
 Thermal correction to Enthalpy=                 .028900
 Thermal correction to Gibbs Free Energy=       -.019044
```

Isomer 7



O(8)-S(4)	1.4941
O(7)-V(6)	1.5939
V(6)-O(5)	1.8527
V(6)-O(2)	1.5926
O(5)-S(4)	1.6078
S(4)-O(1)	1.4922
S(4)-O(3)	1.4992

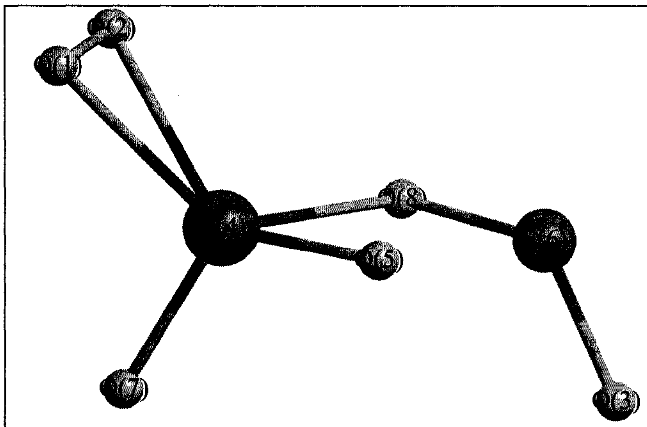
vo2so2o2s7.log

O	1.777501	.364154	1.465375
O	-1.922274	1.432021	.240034
O	1.678491	1.165083	-.883295
S	1.594867	-.017427	.034410
O	.121299	-.641505	-.120826
V	-1.629035	-.050727	-.261684
O	-2.702943	-1.045354	.369185
O	2.541670	-1.093706	-.386951

E = -1793.79111119 h (0.88 eV)
doublet

```
 Zero-point correction=                          .020544 (Hartree/Particle)
 Thermal correction to Energy=                   .029773
 Thermal correction to Enthalpy=                 .030717
 Thermal correction to Gibbs Free Energy=       -.017535
```

Isomer 10



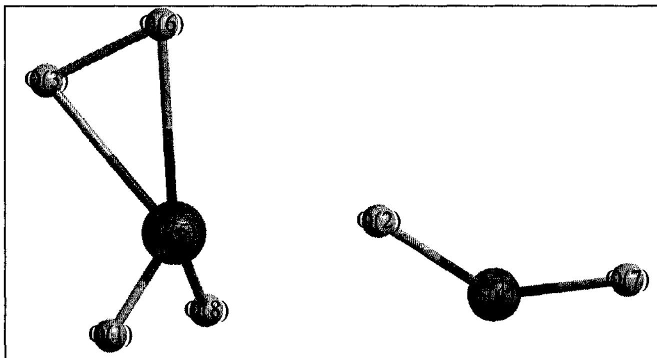
```
O(8)-V(4)    1.9122
O(8)-S(6)    1.6423
O(7)-V(4)    1.5823
S(6)-O(3)    1.4677
O(5)-V(4)    1.7658
V(4)-O(1)    1.9345
V(4)-O(2)    2.0133
O(2)-O(1)    1.3221
O(5)-S(6)    1.8751
```

vo4so2s10.log

```
O    2.433122    -.372785     .623156
O    2.109397   -1.089510    -.439573
O   -2.814495     .417453    -.274575
V     .710210     .278952     .032418
O    -.563594     .374054    1.251618
S   -1.796448    -.539803     .174215
O     .986291    1.671331    -.666759
O    -.599678    -.722925    -.935497
 Zero-point correction=                          .020207 (Hartree/Particle)
 Thermal correction to Energy=                   .029150
 Thermal correction to Enthalpy=                 .030094
 Thermal correction to Gibbs Free Energy=       -.015083
```

E = -1793.81737259 h (0.17 eV)
doublet

Isomer 11



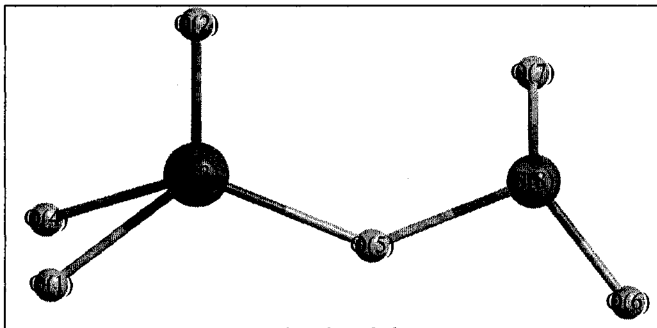
```
O(8)-V(5)    1.6195
O(7)-S(4)    1.4681
O(6)-O(3)    1.3269
O(6)-V(5)    2.0363
V(5)-O(3)    1.9575
V(5)-O(1)    1.6103
S(4)-O(2)    1.5156
S(4)-V(5)    3.1670
O(2)-V(5)    2.0905
```

vo4so2s11r2.log

```
O    1.220166   -1.309763   -1.240094
O    -.952427     .393493    -.501017
O    2.577289     .792546     .258320
S   -2.179212    -.064152     .262351
V     .967039    -.283975    -.024874
O    1.610745    1.647737    -.050233
O   -3.440935     .471383    -.263557
O     .563349   -1.050663    1.343392
 Zero-point correction=                          .019461 (Hartree/Particle)
 Thermal correction to Energy=                   .029381
 Thermal correction to Enthalpy=                 .030325
 Thermal correction to Gibbs Free Energy=       -.019086
```

E = -1793.81077758 h (0.35 eV)
doublet

Isomer 12



```
S(8)-O(5)    1.6816
S(8)-O(7)    1.4904
S(8)-O(6)    1.4851
O(5)-V(3)    1.8250
O(4)-V(3)    1.7932
V(3)-O(2)    1.5854
V(3)-O(1)    1.7926
```

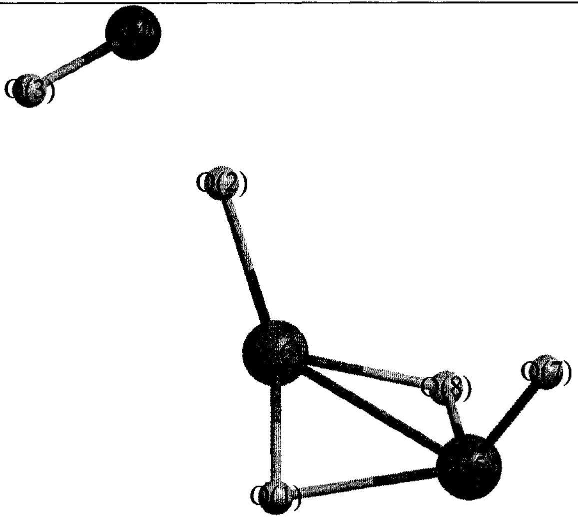
vo4so2s12.log

```
O    2.610035    -.970780    -.279031
O    1.270741    1.546565    -.740745
V    1.184494     .100647    -.096150
O    2.507593    -.342885    1.029976
O    -.508340    -.581305    -.089414
O   -2.982327   -1.119640    -.216607
O   -2.171201    1.082896     .902233
S   -2.065961     .047894    -.164991
 Zero-point correction=                        .020001 (Hartree/Particle)
 Thermal correction to Energy=                 .029397
 Thermal correction to Enthalpy=               .030341
 Thermal correction to Gibbs Free Energy=     -.018317
```

E = -1793.77240408 h (1.39 eV)
doublet

$V_2O_3SO_2$ clusters (BPW91/LANL2DZ)

Isomer 1

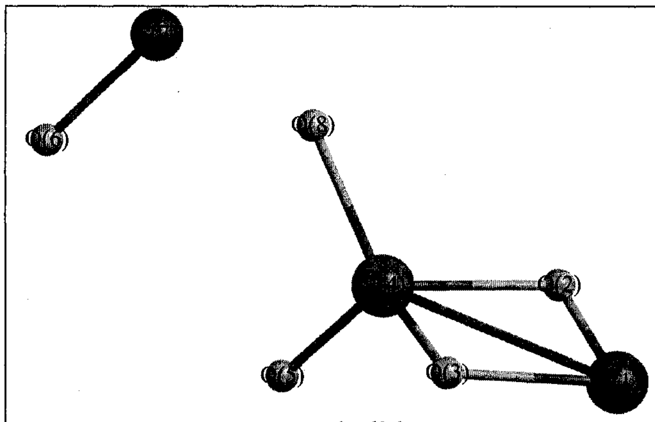


```
O(8)-V(5)    1.8590
O(8)-V(6)    1.7954
O(7)-V(5)    1.6060
V(6)-V(5)    2.3342
V(6)-O(1)    1.7894
V(6)-O(2)    1.7260
V(5)-O(1)    1.8636
S(4)-O(3)    1.6468
S(4)-V(6)    3.5366
O(2)-S(4)    1.8522
```

v2o3so2.log

```
O  1.052125   -0.045525    1.501973
O -1.369060   -0.509426   -0.401532
O -3.480037    0.893125    0.890427
S -3.083629    0.177600   -0.538873
V  2.090796    0.428570    0.029084
V  0.195348   -0.923050    0.198989
O  1.784313    1.839163   -0.674800
O  1.607254   -1.110909   -0.894074
```

E = -529.133221637 h (3.06 eV)
singlet

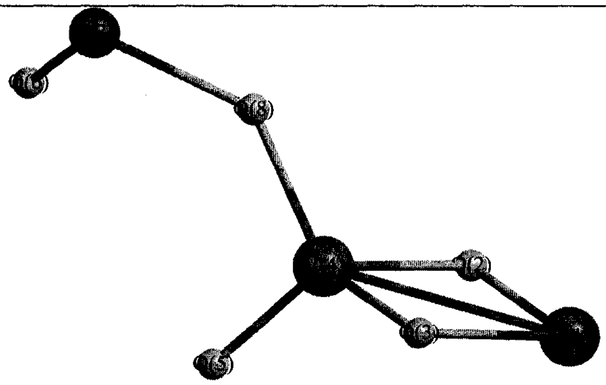


O(8)-V(4)	1.7741
S(7)-O(6)	1.6452
O(5)-V(4)	1.6098
V(4)-O(3)	1.8134
V(4)-V(1)	2.6340
V(4)-O(2)	1.8737
O(3)-V(1)	1.8564
O(2)-V(1)	1.7840
S(7)-O(8)	1.8436
V(4)-S(7)	3.3689

v2so5tripdi.log

V	-2.732378	-0.272708	0.049658
O	-1.506584	-0.209691	-1.245010
O	-1.384078	0.060584	1.281444
V	-0.153874	0.258409	-0.036023
O	0.354806	1.776772	-0.201538
O	3.506609	0.810284	0.118417
S	3.055555	-0.765648	-0.021955
O	1.216113	-0.865445	0.051394

E = -529.157021073 h (2.42 eV)
triplet
Note: The starting structure for optimization does not come from isomer 1 singlet, but from modified structure of isomer 2.



O(8)-V(4)	1.8035
O(8)-S(7)	1.8101
S(7)-O(6)	1.6434
O(5)-V(4)	1.6125
V(4)-V(1)	2.6382
V(4)-O(2)	1.8612
V(4)-O(3)	1.7768
O(3)-V(1)	1.9100
O(2)-V(1)	1.7989

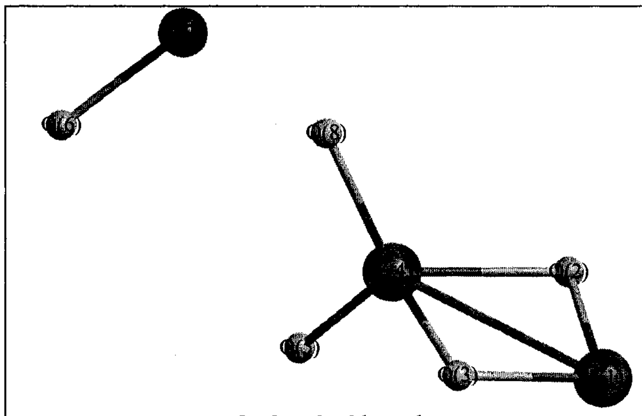
v2o3so2s1quir.log, v2o3so2quifr.log

V	2.717791	-.296929	.214194
O	1.360075	.261856	1.253678
O	1.469621	-.333622	-1.231102
V	.167964	.256844	-.175662
O	-.314420	1.742424	-.576382
O	-3.480515	.714294	.624424
S	-3.044749	-.705969	-.078253
O	-1.241809	-.857769	-.024892

E = -529.129463931 h (3.17 eV)
quintet

```
Zero-point correction=                          .016530 (Hartree/Particle)
 Thermal correction to Energy=                  .026705
 Thermal correction to Enthalpy=                .027650
 Thermal correction to Gibbs Free Energy=      -.023587
```

Isomer 2

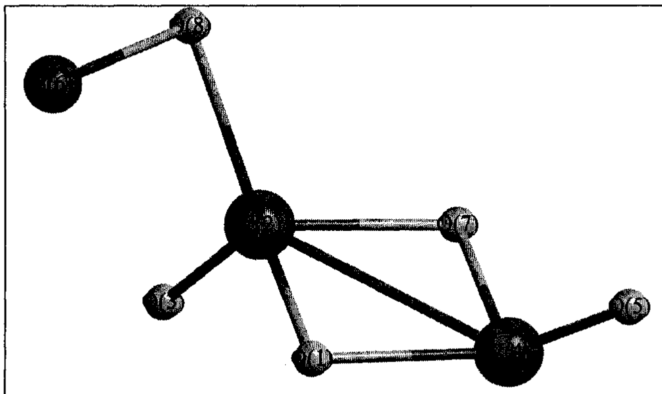


```
O(8)-V(4)    1.7440
S(7)-O(6)    1.6474
O(5)-V(4)    1.6020
V(4)-V(1)    2.6188
V(4)-O(3)    1.9565
V(4)-O(2)    1.9407
O(3)-V(1)    1.7076
O(2)-V(1)    1.7136
S(7)-O(8)    1.8750
V(4)-S(7)    3.3966
```

v2o3so2_2bqc.log

```
V  -2.690969    -.272411     .157626
O  -1.654232    -.361036   -1.203909
O  -1.459195     .087290    1.284166
V   -.150336     .278890    -.157365
O    .271248    1.804992    -.401574
O   3.615541     .717955     .457044
S   3.088258    -.743038    -.091855
O   1.218873    -.781751     .047235
 Zero-point correction=                      .016496 (Hartree/Particle)
 Thermal correction to Energy=               .026849
 Thermal correction to Enthalpy=             .027793
 Thermal correction to Gibbs Free Energy=   -.022923
```

E = -529.096711731 h (4.05 eV)
singlet

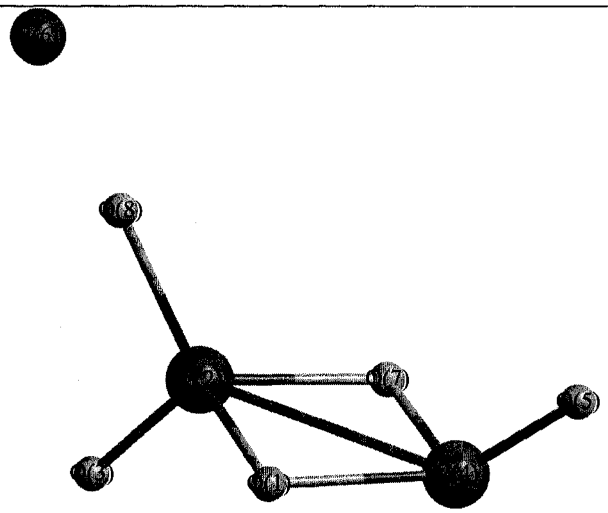


```
O(8)-V(2)    1.8950
O(8)-S(6)    1.7579
O(7)-V(4)    1.8317
O(7)-V(2)    1.8060
O(5)-V(4)    1.6113
V(4)-V(2)    2.6702
V(4)-O(1)    1.7998
O(3)-V(2)    1.6021
V(2)-O(1)    1.8564
```

v2o3so2s2tr.log

```
O  0.529825   -0.327553   -1.151561
V -0.605145    0.529087    0.041777
O -1.191051    1.887594   -0.572883
V  1.997156   -0.037588   -0.150517
O  2.909939   -1.270092    0.343594
S -2.607860   -1.143965   -0.224314
O  0.889300    0.857596    1.001208
O -1.924325   -0.272674    1.140897
```

E = -529.245888901 h (0 eV)
triplet



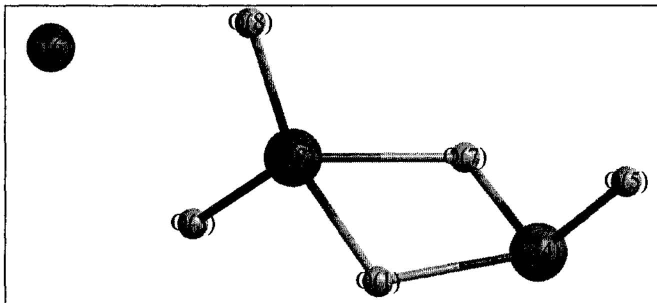
O(8)-V(2)	1.7765
O(7)-V(2)	1.8280
O(7)-V(4)	1.8222
O(5)-V(4)	1.6126
V(4)-O(1)	1.8202
V(4)-V(2)	2.6643
O(3)-V(2)	1.6138
V(2)-O(1)	1.8312
S(6)-O(8)	2.0354
V(2)-S(6)	3.7731

v2o3so2s2qui.log, v2o3so2s2quifr.log

O	-.793427	.132779	1.252644
V	.313279	.835028	-.026130
O	.530314	2.424566	.148565
V	-2.065543	-.362607	.048703
O	-2.518955	-1.904242	-.086342
S	3.477528	-1.219449	.027966
O	-1.010203	.416928	-1.215781
O	1.874974	.010656	-.219915

E = -529.195359100 h (1.37 eV)
quintet

```
 Zero-point correction=                           .016787 (Hartree/Particle)
 Thermal correction to Energy=                    .026865
 Thermal correction to Enthalpy=                  .027809
 Thermal correction to Gibbs Free Energy=        -.023416
```



O(8)-V(2)	1.7396
O(7)-V(2)	1.9403
O(7)-V(4)	1.8088
O(5)-V(4)	1.6263
V(4)-O(1)	1.8089
O(3)-V(2)	1.6978
V(2)-O(1)	1.9404
S(6)-O(8)	2.5362
O(3)-S(6)	2.4943
V(2)-S(6)	2.8826

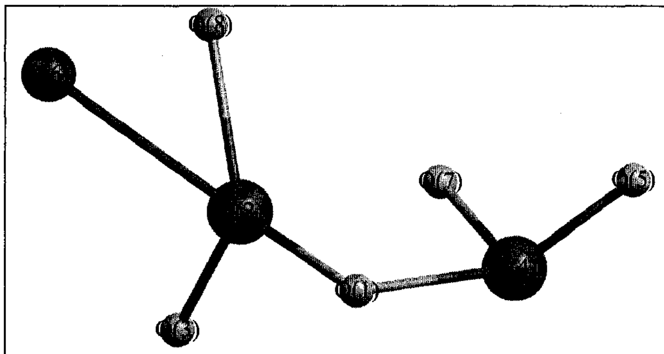
v2o3so2s2sep.log, v2o3sos2sepfr.log

O	-.913155	-.350248	-1.180512
V	.606485	-.102585	.000309
O	1.651597	-1.440596	.000152
V	-2.280144	-.249464	-.000144
O	-3.194570	1.095370	-.000346
S	3.464563	.272470	-.000399
O	-.913564	-.350055	1.180623
O	1.252333	1.512731	.000406

E = -529.092515441 h (4.17 eV)
septet

```
Zero-point correction=                            .014166 (Hartree/Particle)
 Thermal correction to Energy=                    .025168
 Thermal correction to Enthalpy=                  .026112
 Thermal correction to Gibbs Free Energy=        -.027185
```

Isomer 3

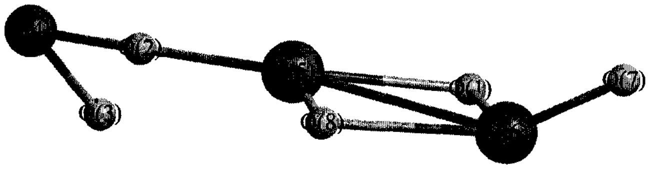


```
O(8)-V(2)    1.8446
O(7)-V(4)    1.6926
S(6)-V(2)    2.3106
O(5)-V(4)    1.6144
V(4)-O(1)    1.7447
O(3)-V(2)    1.6056
V(2)-O(1)    1.9048
V(2)-O(7)    2.0767
```

v2o3so2transb.log

```
O   0.712119    0.180472   -1.263936
V  -0.726727    0.354401   -0.027927
O  -1.118582    1.894242    0.203081
V   1.976938    0.120265   -0.063699
O   2.937238   -1.176601   -0.111234
S  -2.748791   -0.705976   -0.382212
O   0.900784    0.132444    1.242692
O  -1.528331   -0.983270    0.957245
 Zero-point correction=                       .018038 (Hartree/Particle)
 Thermal correction to Energy=                .027587
 Thermal correction to Enthalpy=              .028531
 Thermal correction to Gibbs Free Energy=    -.018247
```

E = -529.239756843 h (0.17 eV)
singlet

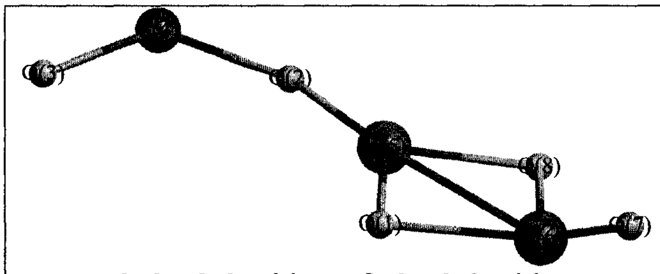


```
O(8)-V(5)    1.7948
O(8)-V(6)    1.8527
O(7)-V(6)    1.6181
V(6)-V(5)    2.6624
V(6)-O(1)    1.8549
V(5)-O(2)    1.7786
V(5)-O(1)    1.7933
S(4)-O(3)    1.6456
S(4)-O(2)    1.8146
```

v2o3so2s3tr.log, v2o3so2s3trfr.log

```
O    -.993034    1.166538    -.251881
O    1.861090    -.599286    -.124612
O    3.895682    1.213586     .445801
S    3.646673    -.283058    -.191514
V     .121145    -.230917    -.104520
V   -2.490516     .176224     .214637
O   -3.965080     .149338    -.451189
O   -1.280060   -1.206816     .448321
Zero-point correction=                        .015601 (Hartree/Particle)
 Thermal correction to Energy=                .026328
 Thermal correction to Enthalpy=              .027273
 Thermal correction to Gibbs Free Energy=    -.026000
```

E = -529.151404256 h (2.57 eV)
triplet



v2o3so2s3qui.log, v2o3so2s3qui.log

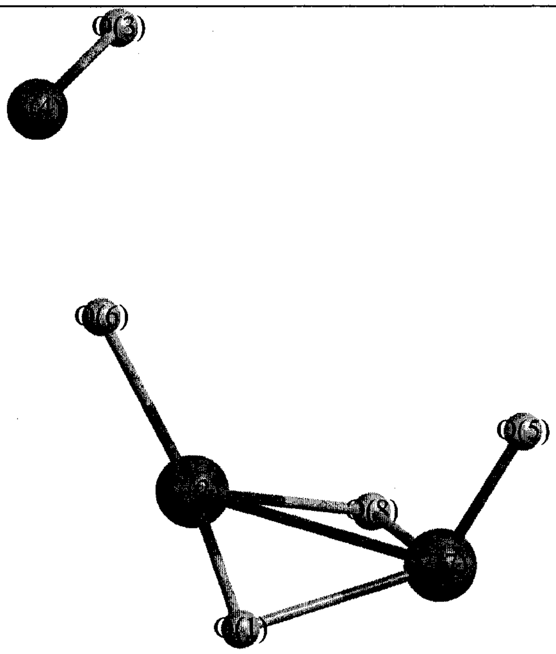
O	-1.010684	1.192665	-.155912
O	1.876212	-.483010	.072207
O	4.035085	1.239851	-.028082
S	3.658693	-.352631	.120525
V	.112635	-.196360	-.047672
V	-2.527966	.114010	-.145429
O	-3.965829	.277158	.581723
O	-1.308090	-1.284647	-.155820

O(8)-V(5)	1.7929
O(8)-V(6)	1.8559
O(7)-V(6)	1.6195
V(6)-V(5)	2.6606
V(6)-O(1)	1.8617
V(5)-O(2)	1.8094
V(5)-O(1)	1.7897
S(4)-O(3)	1.6431
S(4)-O(2)	1.7980

E = -529.152346642 h (2.55 eV)
quintet

```
 Zero-point correction=                           .015687 (Hartree/Particle)
 Thermal correction to Energy=                    .026414
 Thermal correction to Enthalpy=                  .027358
 Thermal correction to Gibbs Free Energy=        -.026813
```

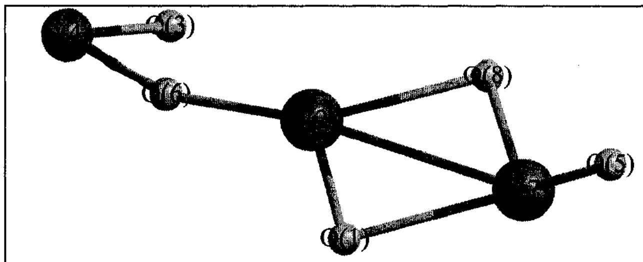
Isomer 4



O(8)-V(2)	1.7894
O(8)-V(7)	1.8635
V(7)-V(2)	2.3344
V(7)-O(5)	1.6060
V(7)-O(1)	1.8591
O(6)-V(2)	1.7260
S(4)-O(3)	1.6469
V(2)-O(1)	1.7953
S(4)-O(6)	1.8522
V(2)-S(4)	3.5367

O	-1.606501	-1.113156	-0.892016
V	-0.194233	-0.920895	0.199640
O	3.482796	0.893942	0.889286
S	3.085817	0.176407	-0.538885
O	-1.790360	1.836897	-0.677241
O	1.369629	-0.506650	-0.401795
V	-2.092812	0.426677	0.029142
O	-1.051943	-0.042971	1.501788

E = -529.133221935 h (3.07 eV)
singlet



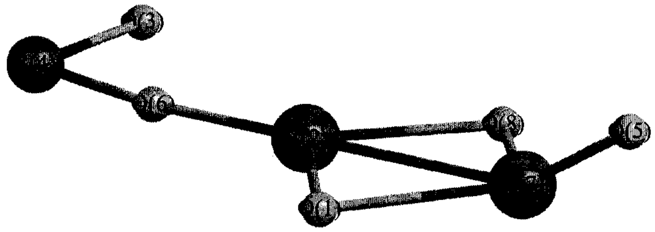
v2o3so2s4trdi.log, v2o3so2s4trfr.log

```
O(8)-V(2)    1.7934
O(8)-V(7)    1.8548
V(7)-V(2)    2.6624
V(7)-O(1)    1.8525
V(7)-O(5)    1.6181
O(6)-S(4)    1.8147
O(6)-V(2)    1.7786
S(4)-O(3)    1.6456
V(2)-O(1)    1.7950
```

```
O  -1.280391   -1.206482     .449324
V    .121154    -.231069    -.104077
O   3.894890    1.213521     .446227
S   3.646516    -.282792    -.192130
O  -3.963952     .148756    -.453091
O   1.860960    -.599946    -.124967
V  -2.490409     .176538     .214925
O   -.992932    1.166512    -.251921
```

E = -529.151404207 h (2.57 eV)
triplet

```
Zero-point correction=                      .015602 (Hartree/Particle)
 Thermal correction to Energy=              .026328
 Thermal correction to Enthalpy=            .027273
 Thermal correction to Gibbs Free Energy=  -.025985
```



v2o3so2s4qui.log, v2o3so2s4quifr.log

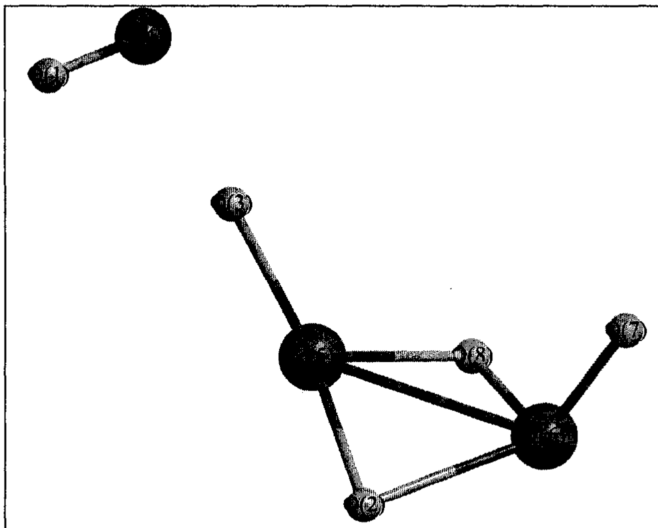
```
O(8)-V(7)    1.8631
O(8)-V(2)    1.7885
V(7)-O(5)    1.6196
V(7)-O(1)    1.8565
V(7)-V(2)    2.6612
O(6)-V(2)    1.7909
O(6)-S(4)    1.7877
S(4)-O(3)    1.6431
V(2)-O(1)    1.7923
```

```
O  1.306794   -1.283916   -0.155125
V -0.113421   -0.196218   -0.044598
O -4.034379    1.240341   -0.029770
S -3.659427   -0.352684    0.116789
O  3.973932    0.275024    0.567656
O -1.877077   -0.484035    0.073993
V  2.527756    0.114524   -0.143600
O  1.008372    1.192823   -0.149263
```

E = -529.152347269 h (2.54 eV)
quintet

```
 Zero-point correction=                     .015683 (Hartree/Particle)
 Thermal correction to Energy=              .026415
 Thermal correction to Enthalpy=            .027359
 Thermal correction to Gibbs Free Energy=  -.026833
```

Isomer 5

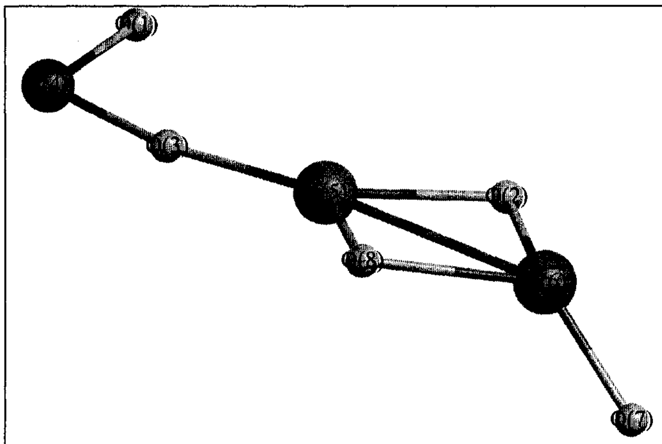


O(8)-V(6)	1.8597
O(8)-V(5)	1.7940
O(7)-V(6)	1.6062
V(6)-O(2)	1.8608
V(6)-V(5)	2.3382
V(5)-O(2)	1.7931
V(5)-O(3)	1.7215
S(4)-O(1)	1.6456
S(4)-V(5)	3.5730
O(3)-S(4)	1.8515

v2o3so2s5diis.log

O	-3.800815	.692029	.880379
O	1.235273	-.331065	1.473381
O	-1.389472	-.351825	-.199781
S	-3.108788	.243059	-.543528
V	.208928	-.905314	.119860
V	2.156473	.384992	.023841
O	1.873127	1.920348	-.353215
O	1.498936	-.919681	-1.126849

E = -529.132820425 h (3.08 eV)
singlet



O(8)-V(5)	1.8044
O(8)-V(6)	1.8342
O(7)-V(6)	1.6156
V(6)-O(2)	1.8455
V(6)-V(5)	2.6617
V(5)-O(3)	1.7955
V(5)-O(2)	1.7949
S(4)-O(1)	1.6440
S(4)-O(3)	1.7838

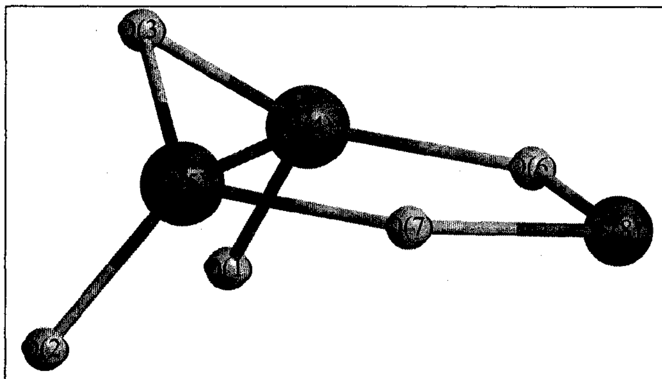
v2o3so2s5tr.log

O	3.946428	1.265728	-0.016260
O	-1.021575	1.181975	-0.252433
O	1.866830	-0.555430	0.055501
S	3.632308	-0.335489	0.184430
V	0.113879	-0.199950	-0.101374
V	-2.527727	0.118276	-0.175782
O	-3.782862	0.287492	0.827327
O	-1.333626	-1.273975	-0.186168

E = -529.149930557 h (2.61 eV)
triplet

```
 Zero-point correction=                           .016107 (Hartree/Particle)
 Thermal correction to Energy=                    .026607
 Thermal correction to Enthalpy=                  .027552
 Thermal correction to Gibbs Free Energy=        -.025050
```

Isomer 6

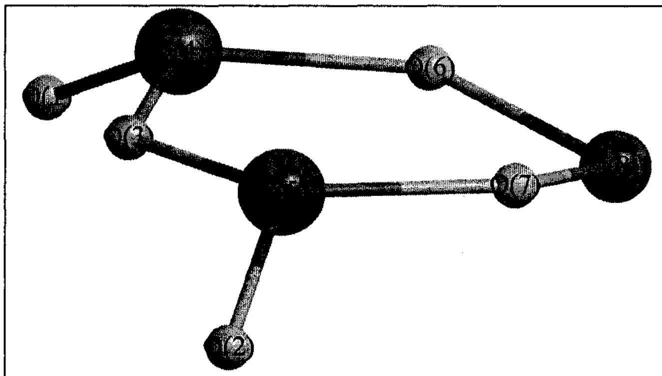


```
S(8)-O(6)    1.7758
S(8)-O(7)    1.7756
O(7)-V(5)    1.8015
O(6)-V(4)    1.8017
V(5)-O(3)    1.7984
V(5)-V(4)    2.6484
V(5)-O(2)    1.6073
V(4)-O(1)    1.6076
V(4)-O(3)    1.7979
```

v2o3so2s6.log

```
O   1.371338    1.940340    1.024702
O   1.423664   -1.921047    1.007720
O   1.379201     .019320   -1.097770
V    .534889    1.332769    -.206367
V    .565347   -1.315461    -.208794
O  -1.257311    1.295551    -.025639
O  -1.225022   -1.326078    -.008754
S  -2.427524    -.028924     .146664
```

E = -529.205574307 h (1.10 eV)
singlet



```
S(8)-O(6)    1.7758
S(8)-O(7)    1.7758
O(7)-V(5)    1.8049
O(6)-V(4)    1.8049
V(5)-O(3)    1.8017
V(5)-O(2)    1.6125
V(4)-O(1)    1.6125
V(4)-O(3)    1.8018
```

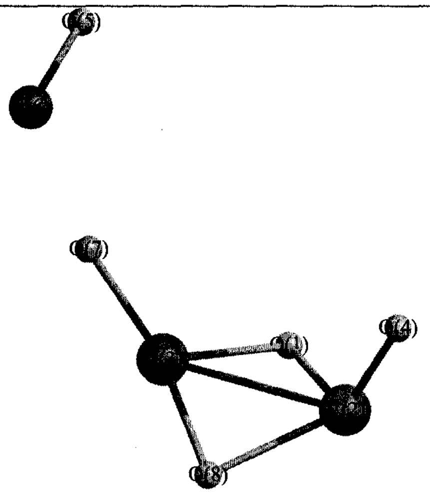
v2o3so2s6tr.log

```
O  2.912616   -1.208968    0.557009
O -2.913439   -1.209308    0.555225
O -0.000017   -1.310636   -0.091149
V  1.639475   -0.571327   -0.199810
V -1.639323   -0.570861   -0.199271
O  1.370970    1.212128   -0.130478
O -1.371170    1.212643   -0.128834
S  0.000302    2.293966    0.192792
```

E = -529.213983149 h (0.87 eV)
triplet

```
 Zero-point correction=                           .017228 (Hartree/Particle)
 Thermal correction to Energy=                    .027175
 Thermal correction to Enthalpy=                  .028120
 Thermal correction to Gibbs Free Energy=        -.021469
```

Isomer 7

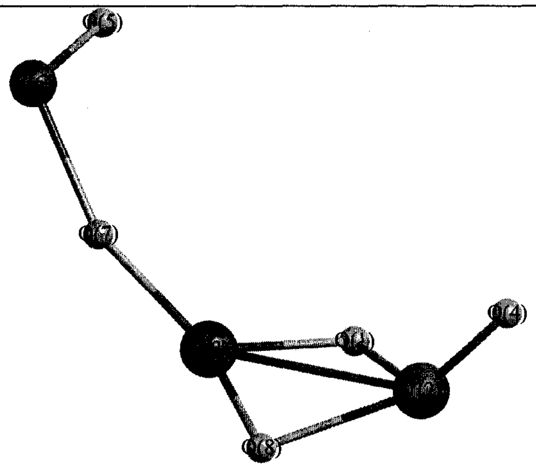


O(8)-V(3)	1.7953
O(8)-V(2)	1.8591
O(7)-V(3)	1.7261
S(6)-O(5)	1.6469
O(4)-V(2)	1.6060
V(3)-V(2)	2.3344
V(3)-O(1)	1.7893
V(2)-O(1)	1.8636
S(6)-O(7)	1.8523
V(3)-S(6)	3.5363

v2o3so2s7qc.log

O	-1.050541	-.041309	1.501730
V	-2.092422	.426795	.029240
V	-.193991	-.920851	.200010
O	-1.790120	1.836131	-.678913
O	3.480598	.894295	.889679
S	3.085475	.176511	-.538934
O	1.369513	-.507507	-.403194
O	-1.606963	-1.114221	-.890526

E = -529.133222189 h (3.07 eV)
singlet
(used SCF(qc))



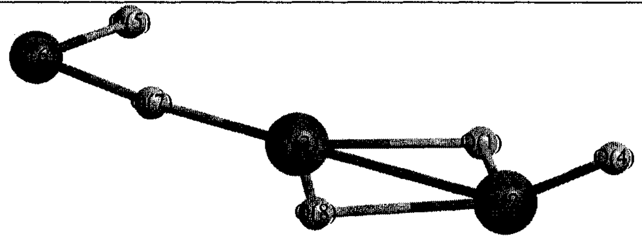
O(8)-V(3)	1.7521
O(8)-V(2)	1.8835
O(7)-S(6)	1.8248
O(7)-V(3)	1.7624
S(6)-O(5)	1.6464
O(4)-V(2)	1.6103
V(3)-O(1)	1.7485
V(3)-V(2)	2.5269
V(2)-O(1)	1.8903

v2o3so2s7tr.log

O	-.912580	.162367	1.369853
V	-2.235202	.299377	.026364
V	.003364	-.846374	.274044
O	-2.674946	1.610585	-.798515
O	3.414464	1.151378	.792653
S	3.210251	.249148	-.569333
O	1.594879	-.589362	-.437940
O	-1.425783	-1.260649	-.651056

E = -529.136341031 h (2.98 eV)
triplet

```
 Zero-point correction=                           .016124 (Hartree/Particle)
 Thermal correction to Energy=                    .026576
 Thermal correction to Enthalpy=                  .027520
 Thermal correction to Gibbs Free Energy=        -.024877
```



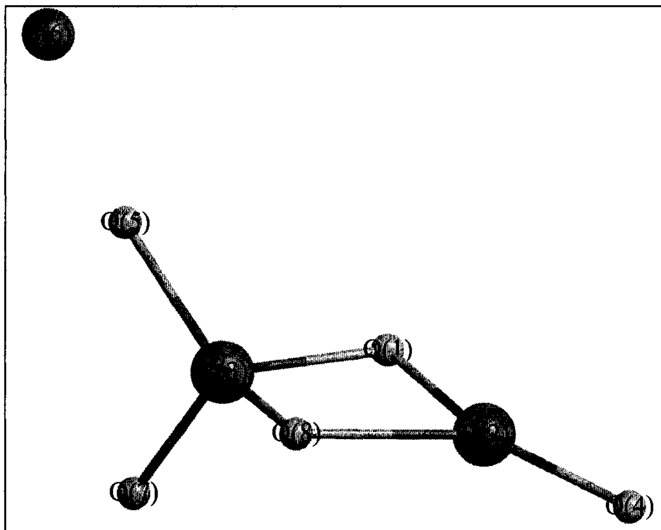
v2o3so2s7qui.log

```
O    1.011451    1.192958   -0.156796
V    2.528094    0.113931   -0.146623
V   -0.112281   -0.195981   -0.047676
O    3.963163    0.276640    0.586038
O   -4.035916    1.239142   -0.028429
S   -3.658399   -0.353015    0.121136
O   -1.875874   -0.482261    0.072711
O    1.308510   -1.284554   -0.157185
```

```
O(8)-V(2)    1.8556
O(8)-V(3)    1.7932
O(7)-V(3)    1.7907
O(7)-S(6)    1.7879
S(6)-O(5)    1.6431
O(4)-V(2)    1.6195
V(3)-O(1)    1.7899
V(3)-V(2)    2.6603
V(2)-O(1)    1.8613
```

E = -529.152346057 h (2.55 eV)
quintet

```
 Zero-point correction=                           .015689 (Hartree/Particle)
 Thermal correction to Energy=                    .026414
 Thermal correction to Enthalpy=                  .027358
 Thermal correction to Gibbs Free Energy=        -.026797
```



v2o3so2s7sep.log

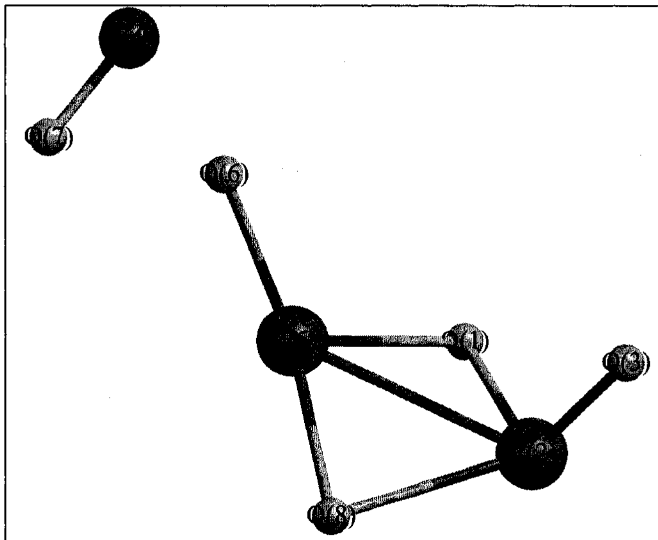
```
O     .686796     .073441    1.240175
V    2.087262    -.528548     .000346
V    -.393208     .715821     .000033
O    3.683261    -.898500    -.000836
O   -2.036261     .037575     .001687
S   -3.731730   -1.110987    -.000247
O    -.426387    2.400669    -.001976
O     .685646     .070378   -1.239644
```

```
O(8)-V(2)    1.9649
O(8)-V(3)    1.7656
O(7)-V(3)    1.6852
O(5)-V(3)    1.7775
O(4)-V(2)    1.6383
V(3)-O(1)    1.7655
V(2)-O(1)    1.9649
O(5)-S(6)    2.0479
V(3)-S(6)    3.8056
```

E = -529.102948809 h (3.89 eV)
septet

```
 Zero-point correction=                           .013694 (Hartree/Particle)
 Thermal correction to Energy=                    .024801
 Thermal correction to Enthalpy=                  .025745
 Thermal correction to Gibbs Free Energy=        -.028350
```

Isomer 8

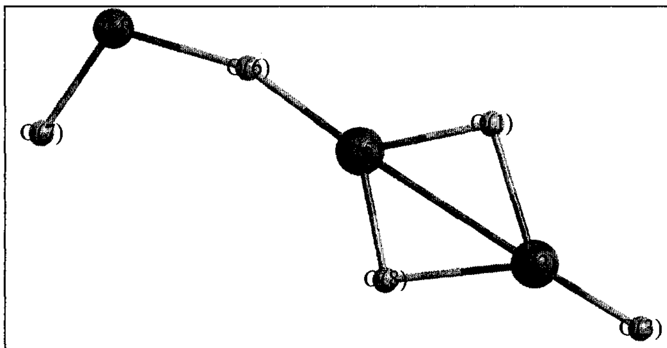


O(8)-V(2)	1.8636
O(8)-V(5)	1.7893
O(7)-S(4)	1.6469
O(6)-V(5)	1.7260
V(5)-V(2)	2.3342
V(5)-O(1)	1.7954
O(3)-V(2)	1.6069
V(2)-O(1)	1.8592
S(4)-O(6)	1.8521
S(4)-V(5)	3.5366

v2o3so2s8qc.log

O	1.607016	-1.111295	-.893883
V	2.091077	.428403	.028944
O	1.784612	1.838769	-.675418
S	-3.084026	.176904	-.538737
V	.195315	-.922671	.199234
O	-1.369207	-.509210	-.401080
O	-3.480106	.894096	.889855
O	1.052357	-.045150	1.501989

E = -529.133221775 h (3.07 eV)
singlet
(used SCF(qc))



O(8)-V(2)	1.9366
O(8)-V(5)	1.7301
O(7)-S(4)	1.6440
O(6)-V(5)	1.7950
O(6)-S(4)	1.7873
V(5)-V(2)	2.6824
V(5)-O(1)	1.7323
O(3)-V(2)	1.6184
V(2)-O(1)	1.9306

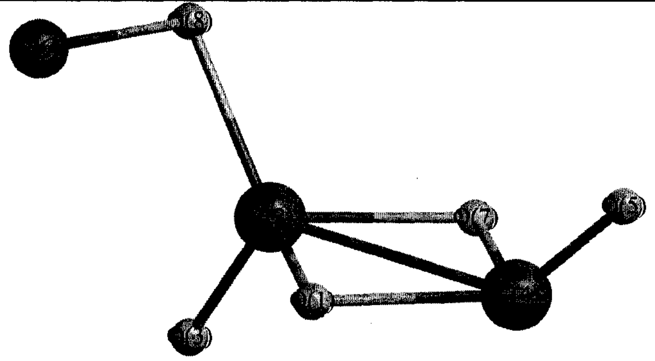
v2o3so2s8tripr.log, v2o3so2s8tripfr.log

O	1.222333	-1.297918	0.083437
V	2.525604	0.125551	0.032899
O	4.131847	0.313281	-0.030048
S	-3.659590	-0.311036	-0.025134
V	-0.132867	-0.225500	-0.036406
O	-1.892565	-0.579422	-0.025438
O	-3.916749	1.307808	0.101390
O	0.895195	1.165676	-0.068993

E = -529.146779669 h (2.70 eV)
triplet
(not completely optimized, one small negative frequency)

```
 Zero-point correction=                           .015735 (Hartree/Particle)
 Thermal correction to Energy=                    .025702
 Thermal correction to Enthalpy=                  .026646
 Thermal correction to Gibbs Free Energy=        -.024878
```

$V_2O_3SO_2$ (BPW91/TZVP)



O(8)-V(2)	1.8950
O(8)-S(6)	1.7579
O(7)-V(4)	1.8317
O(7)-V(2)	1.8060
O(5)-V(4)	1.6113
V(4)-V(2)	2.6702
V(4)-O(1)	1.7998
O(3)-V(2)	1.6021
V(2)-O(1)	1.8564

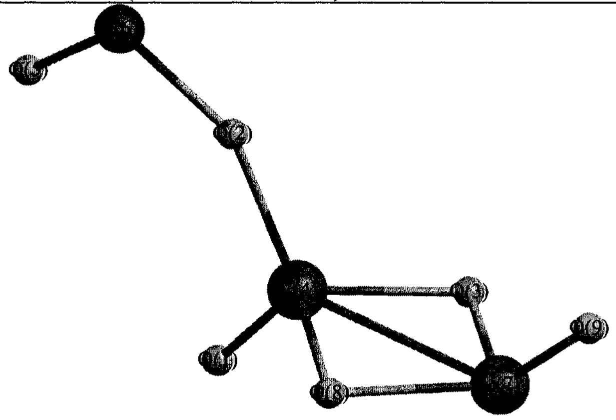
v2o3so2trtzvp.log

```
O    .587239    -.078267   -1.256271
V   -.645046     .512528     .006406
O  -1.250772    1.925115    -.380998
V   1.925870     .025755    -.090732
O   2.798718   -1.275542     .219925
S  -2.344376   -1.152674    -.298663
O    .790754     .658580    1.140912
O  -1.919556    -.472105    1.116196
```

E = -2662.90343133 h
triplet

```
 Zero-point correction=                           .018316 (Hartree/Particle)
 Thermal correction to Energy=                    .027717
 Thermal correction to Enthalpy=                  .028661
 Thermal correction to Gibbs Free Energy=        -.018830
```

$V_2O_4SO_2$ (BPW91/TZVP)



O(9)-V(7)	1.5932
O(8)-V(4)	1.8169
O(8)-V(7)	1.8061
V(7)-O(3)	1.8060
V(7)-V(4)	2.6112
S(6)-O(5)	1.5025
S(6)-O(2)	1.6404
V(4)-O(2)	1.8289
V(4)-O(1)	1.5871
V(4)-O(3)	1.8169

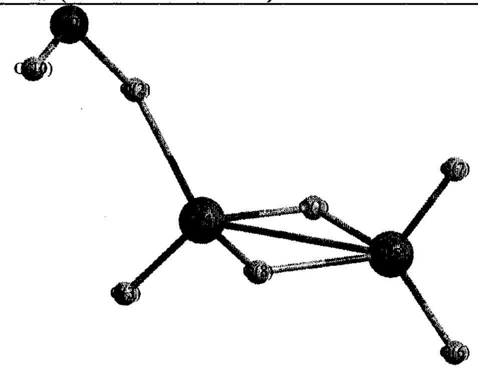
v2o4so2s2.log

```
O    .676087    2.032583     .000001
O   1.442019    -.714225    -.000559
O  -1.172173     .291810   -1.254135
V    .117595     .546968    -.000127
O   3.863668     .264005     .000587
S   3.056757   -1.003469    -.000123
V  -2.417137    -.080370     .000183
O  -1.171702     .291296    1.254227
O  -3.140230   -1.500000    -.000038
```

E = -2738.15837995 h
triplet

```
 Zero-point correction=                           .021311 (Hartree/Particle)
 Thermal correction to Energy=                    .032173
 Thermal correction to Enthalpy=                  .033117
 Thermal correction to Gibbs Free Energy=        -.019346
```

$V_2O_5SO_2$ (BPW91/TZVP)



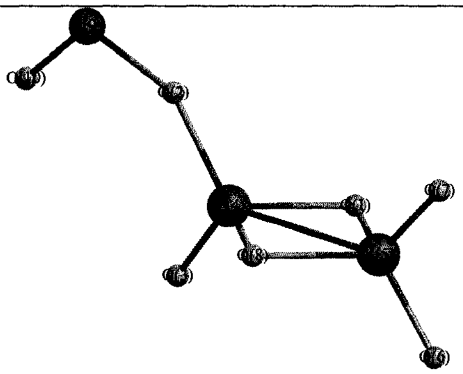
v2o5so2s1r1.log

O(10)-S(9)	1.4724
S(9)-O(2)	1.5278
O(8)-V(4)	1.7207
O(8)-V(5)	1.9438
O(7)-V(5)	1.6145
O(6)-V(5)	1.6115
V(5)-O(1)	1.9411
V(5)-V(4)	2.6759
V(4)-O(3)	1.6009
V(4)-O(2)	2.0081
V(4)-O(1)	1.7224

O	-1.051079	.664125	-1.183751
O	1.953297	.013696	-.657944
O	.527973	2.412555	.306471
V	.241967	.882302	-.067026
V	-2.070233	-.461374	.025499
O	-3.521943	.079101	.469821
O	-2.139015	-2.021151	-.385680
O	-.574588	.012619	1.172984
S	3.266715	-.699846	-.341932
O	3.528188	-.971420	1.081352

E = -2813.42362512 h
singlet

```
 Zero-point correction=                            .024826 (Hartree/Particle)
 Thermal correction to Energy=                     .037026
 Thermal correction to Enthalpy=                   .037970
 Thermal correction to Gibbs Free Energy=         -.017540
```



v2o5so2s1tr.log

O(10)-S(9)	1.4999
S(9)-O(2)	1.6476
O(8)-V(5)	1.8089
O(8)-V(4)	1.8099
O(7)-V(5)	1.6578
O(6)-V(5)	1.6720
V(5)-O(1)	1.8089
V(5)-V(4)	2.6517
V(4)-O(1)	1.8099
V(4)-O(3)	1.5838
V(4)-O(2)	1.8176

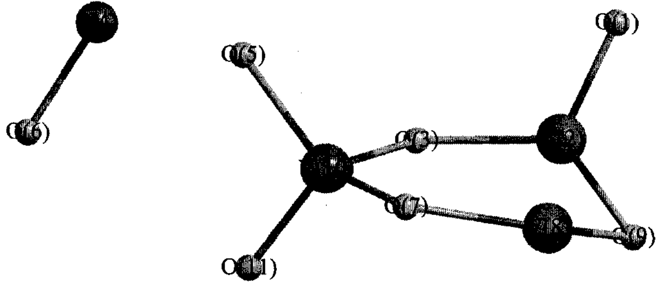
O	.918885	.131117	1.231331
O	-1.763001	-.703854	.000073
O	-.840858	1.970623	.000194
V	-.366469	.459522	.000181
V	2.200437	-.205733	-.000071
O	3.552415	.778040	-.000162
O	2.854668	-1.729011	-.000187
O	.918690	.131169	-1.231231
S	-3.401526	-.876498	.000230
O	-4.110402	.445266	-.000796

E = -2813.39639489 h
triplet

```
 Zero-point correction=                            .023064 (Hartree/Particle)
 Thermal correction to Energy=                     .035404
 Thermal correction to Enthalpy=                   .036349
 Thermal correction to Gibbs Free Energy=         -.019754
```

$V_3O_5SO_2$ clusters (BPW91/LANL2DZ)

Isomer 1

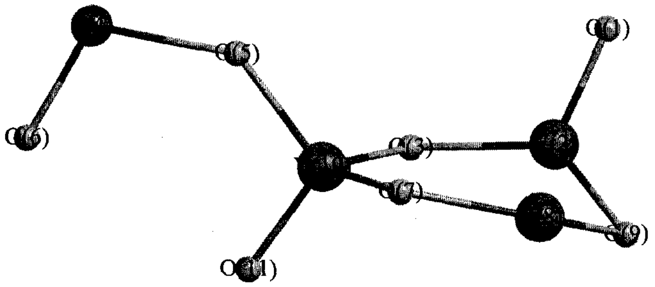


v3o5so2s1.log

O	-2.567231	2.146318	-.829768
V	-2.137104	1.091413	.305154
O	-.390594	1.083881	.731930
S	3.868502	.569208	-.745271
O	2.046802	.393807	-.781071
O	4.453616	-.170863	.595784
O	-.136964	-1.576392	-.510743
V	-1.928273	-1.489640	-.491370
O	-3.121371	-.434850	.344270
V	.769781	-.226478	.292834
O	1.453578	-.784292	1.633614

O(11)-V(10)	1.6051
V(10)-O(5)	1.7801
V(10)-O(3)	1.8045
V(10)-O(7)	1.8139
O(9)-V(2)	1.8165
O(9)-V(8)	1.7984
V(8)-O(7)	1.7935
O(6)-S(4)	1.6397
O(3)-V(2)	1.7979
V(2)-O(1)	1.6081
S(4)-V(10)	3.3635
S(4)-O(5)	1.8305

E = -751.152191495 h (2.81 eV)
doublet



v3o5so2s1quart.log, v3o5so2s1quartfr.log

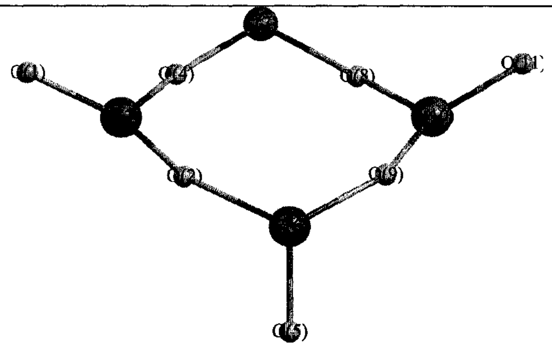
O	-2.595997	2.108740	-.837307
V	-2.161543	1.065636	.306739
O	-.417333	1.091616	.746100
S	3.867143	.655339	-.662763
O	2.055244	.470444	-.742717
O	4.460628	-.377125	.463736
O	-.092820	-1.547954	-.569436
V	-1.884617	-1.497060	-.490926
O	-3.119247	-.474534	.332620
V	.759718	-.195687	.289589
O	1.423763	-.778922	1.629501

O(11)-V(10)	1.6051
V(10)-O(5)	1.7854
V(10)-O(3)	1.8031
V(10)-O(7)	1.8148
O(9)-V(2)	1.8138
O(9)-V(8)	1.8022
V(8)-O(7)	1.7942
O(6)-S(4)	1.6393
O(5)-S(4)	1.8231
O(3)-V(2)	1.7989
V(2)-O(1)	1.6080

E = -751.152029617 h (2.82 eV)
quartet

```
 Zero-point correction=                           .024742 (Hartree/Particle)
 Thermal correction to Energy=                    .038843
 Thermal correction to Enthalpy=                  .039788
 Thermal correction to Gibbs Free Energy=        -.021497
```

Isomer 2



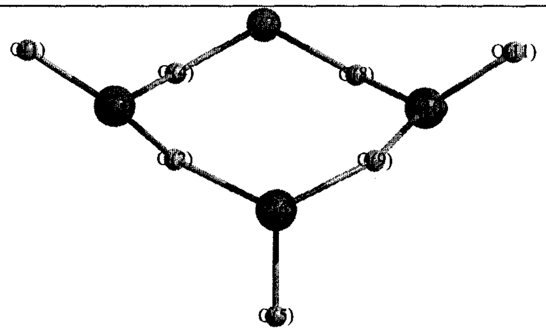
v3o5so2s2rest.log, v3o5so2s2fr.log

O	-3.743179	-.673213	-.749176
O	-1.570590	1.254011	-.300109
V	-2.322891	-.364524	-.059144
O	-1.310234	-1.771023	.380686
O	-.086885	3.252944	1.132051
V	-.060396	2.196640	-.083028
S	.081057	-2.829781	.356726
O	1.417779	-1.702751	.445630
O	1.475312	1.291332	-.276394
V	2.360293	-.258672	-.030407
O	3.721792	-.515388	-.849975

O(11)-V(10)	1.6097
V(10)-O(9)	1.8017
V(10)-O(8)	1.7889
O(9)-V(6)	1.7931
O(8)-S(7)	1.7507
S(7)-O(4)	1.7485
V(6)-O(5)	1.6102
V(6)-O(2)	1.7934
O(4)-V(3)	1.7881
V(3)-O(2)	1.8010
V(3)-O(1)	1.6089

E = -751.202511772 h (1.45 eV)
doublet

```
 Zero-point correction=                           .024321 (Hartree/Particle)
 Thermal correction to Energy=                    .039002
 Thermal correction to Enthalpy=                  .039947
 Thermal correction to Gibbs Free Energy=        -.022455
```



v3o5so2s2quartdi.log

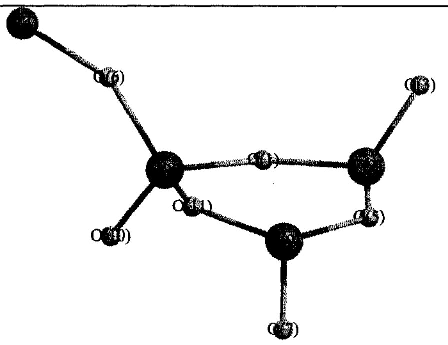
O	-3.690378	-.612848	-.878744
O	-1.510963	1.264620	-.281709
V	-2.348747	-.312178	-.041276
O	-1.368255	-1.726200	.448611
O	.003256	3.240359	1.151897
V	.002153	2.207239	-.083698
S	-.000084	-2.816286	.370786
O	1.362587	-1.719377	.460867
O	1.514669	1.263809	-.282227
V	2.350005	-.313510	-.038169
O	3.679445	-.624751	-.891233

O(11)-V(10)	1.6100
V(10)-O(9)	1.8015
V(10)-O(8)	1.7890
O(9)-V(6)	1.7936
O(8)-S(7)	1.7516
S(7)-O(4)	1.7511
V(6)-O(5)	1.6106
V(6)-O(2)	1.7937
O(4)-V(3)	1.7891
V(3)-O(2)	1.8017
V(3)-O(1)	1.6099

E = -751.201997180 h (1.46 eV)
quartet

```
 Zero-point correction=                           .024241 (Hartree/Particle)
 Thermal correction to Energy=                    .038952
 Thermal correction to Enthalpy=                  .039896
 Thermal correction to Gibbs Free Energy=        -.023403
```

Isomer 3



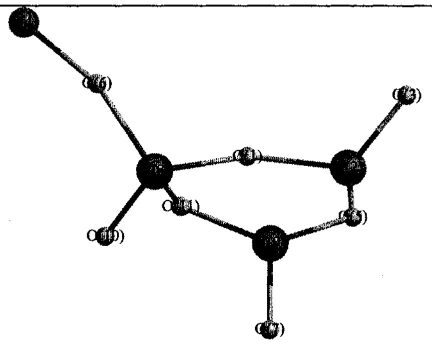
v3o5so2s3rest.log, v3o5so2s3fr.log

```
O      .129619    1.258023     .730664
V    -1.520613    1.720940     .235674
O    -1.659248    2.965306    -.772885
S     4.245511     .073615    -.759668
O    -2.429628     .231647    -.230341
O     2.526247     .011873    -.614447
O    -2.595250   -2.666297     .100306
V     1.155147    -.218865     .485172
V    -1.766694   -1.425808    -.501744
O     1.675283    -.750871    1.907046
O     -.008086   -1.416180    -.230926
```

```
O(11)-V(8)   1.8164
O(11)-V(9)   1.7794
O(10)-V(8)   1.6048
V(9)-O(5)    1.8056
V(9)-O(7)    1.6087
V(8)-O(6)    1.7727
V(8)-O(1)    1.8147
O(6)-S(4)    1.7265
O(5)-V(2)    1.8060
O(3)-V(2)    1.6077
V(2)-O(1)    1.7840
```

E = -751.255637562 h (0 eV)
doublet

```
 Zero-point correction=                           .024571 (Hartree/Particle)
 Thermal correction to Energy=                    .038884
 Thermal correction to Enthalpy=                  .039828
 Thermal correction to Gibbs Free Energy=        -.021458
```



v3o5so2s3quart.log, v3o5so2s3quartfr.log

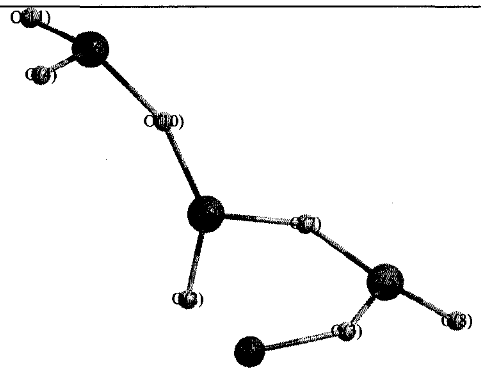
```
O      .219947    1.239944     .665244
V    -1.464029    1.730731     .221734
O    -1.651850    3.080069    -.632870
S     4.267271     .116959    -.768139
O    -2.425661     .290262    -.278832
O     2.586990    -.122596    -.556144
O    -2.685307   -2.613497     .085575
V     1.141801    -.284739     .484542
V    -1.810499   -1.399222    -.505145
O     1.581005    -.812009    1.936839
O     -.028074   -1.430553    -.261783
```

```
O(11)-V(8)   1.7996
O(11)-V(9)   1.7992
O(10)-V(8)   1.6063
V(9)-O(5)    1.8122
V(9)-O(7)    1.6089
V(8)-O(6)    1.7883
V(8)-O(1)    1.7908
O(6)-S(4)    1.7105
O(5)-V(2)    1.8028
O(3)-V(2)    1.6082
V(2)-O(1)    1.8092
```

E = -751.254255294 h (0.04 eV)
quartet

```
 Zero-point correction=                           .025222 (Hartree/Particle)
 Thermal correction to Energy=                    .039429
 Thermal correction to Enthalpy=                  .040373
 Thermal correction to Gibbs Free Energy=        -.020721
```

Isomer 4



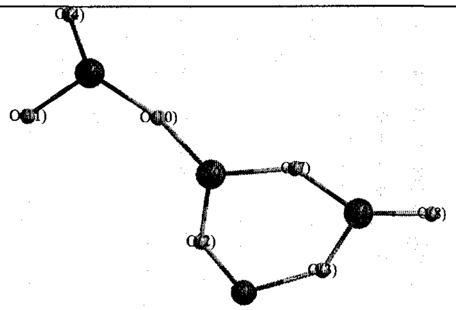
v3o5so2s4qcr.log, v3o5so2s4fr.log

S	1.783853	2.308005	.049698
O	.500906	1.327073	.954735
O	2.810686	1.015598	-.571033
O	-3.902310	1.307272	-.643389
V	2.859039	-.784235	-.393082
V	-3.487154	-.251384	-.454754
O	1.255014	-1.324431	.276123
O	4.244683	-1.560814	-.127365
V	-.147856	-.305477	.679620
O	-1.733501	-.521887	-.061905
O	-4.512268	-1.003168	.557061

O(11)-V(6)	1.6247
O(10)-V(9)	1.7638
O(10)-V(6)	1.8174
V(9)-O(2)	1.7781
V(9)-O(7)	1.7802
O(8)-V(5)	1.6105
O(7)-V(5)	1.8200
V(6)-O(4)	1.6240
V(5)-O(3)	1.8093
O(3)-S(1)	1.7635
S(1)-V(9)	3.3104
S(1)-O(2)	1.8513

E = -751.168269896 h (2.38 eV)
doublet

```
 Zero-point correction=                           .023311 (Hartree/Particle)
  Thermal correction to Energy=                   .038180
  Thermal correction to Enthalpy=                 .039124
  Thermal correction to Gibbs Free Energy=       -.026231
```



v3o5so2s4quart.log, v3o5so2s4quartfr.log

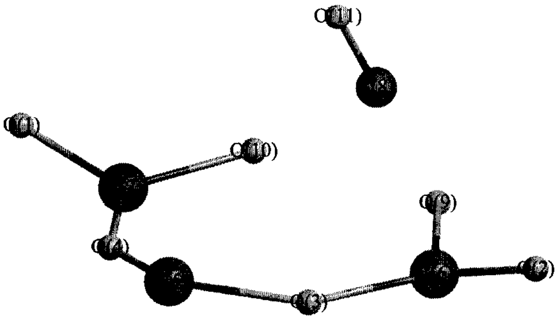
S	-2.309932	2.294696	.179366
O	-.696166	1.604825	-.150380
O	-3.269300	.823365	.239431
O	4.374552	-.398518	1.420181
V	-2.905221	-.963223	.051834
V	3.731597	-.399866	-.069411
O	-1.100785	-1.134892	-.075693
O	-3.986842	-2.128116	-.236005
V	.202773	.063648	-.154764
O	1.928083	-.383196	-.087517
O	4.411520	.763035	-.973268

O(11)-V(6)	1.6222
O(10)-V(6)	1.8037
O(10)-V(9)	1.7835
V(9)-O(2)	1.7842
V(9)-O(7)	1.7726
O(8)-V(5)	1.6155
O(7)-V(5)	1.8171
V(6)-O(4)	1.6224
V(5)-O(3)	1.8329
O(3)-S(1)	1.7575
O(2)-S(1)	1.7857

E = -751.171154934 h (2.30 eV)
quartet

```
 Zero-point correction=                           .023591 (Hartree/Particle)
 Thermal correction to Energy=                    .038332
 Thermal correction to Enthalpy=                  .039276
 Thermal correction to Gibbs Free Energy=        -.025326
```

Isomer 5



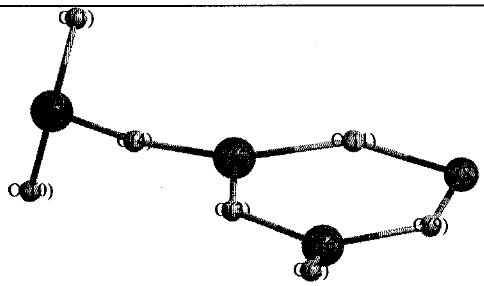
v3o5so2s5qc.log, v3o5so2s5fr.log

```
O    3.901286    -.107871     .058872
O   -3.900834    -.108088     .059635
O   -1.500917    1.546784    -.047481
O    1.501017    1.546379    -.046767
V     .000051    2.379154     .410760
V   -2.357159     .000014    -.397446
V    2.357267    -.000290    -.397122
S    -.000276   -2.416651     .233068
O   -1.397517   -1.513759    -.569439
O    1.398047   -1.514468    -.568082
O    -.000983   -1.854950    1.750576
```

```
O(11)-S(8)   1.6181
O(10)-V(7)   1.8006
O(9)-V(6)    1.8006
V(7)-O(1)    1.6135
V(7)-O(4)    1.8022
V(6)-O(3)    1.8023
V(6)-O(2)    1.6135
V(5)-O(4)    1.7764
V(5)-O(3)    1.7764
S(8)-O(10)   1.8469
S(8)-O(9)    1.8470
V(7)-S(8)    3.4342
V(6)-S(8)    3.4341
```

E = -751.059533384 h (5.34 eV)
doublet

```
Zero-point correction=                          .022806 (Hartree/Particle)
 Thermal correction to Energy=                  .037668
 Thermal correction to Enthalpy=                .038612
 Thermal correction to Gibbs Free Energy=      -.024110
```



v3o5so2s5quartqc.log, v3o5so2s5quartdir.log,
v3o5so2s5quartfr.log

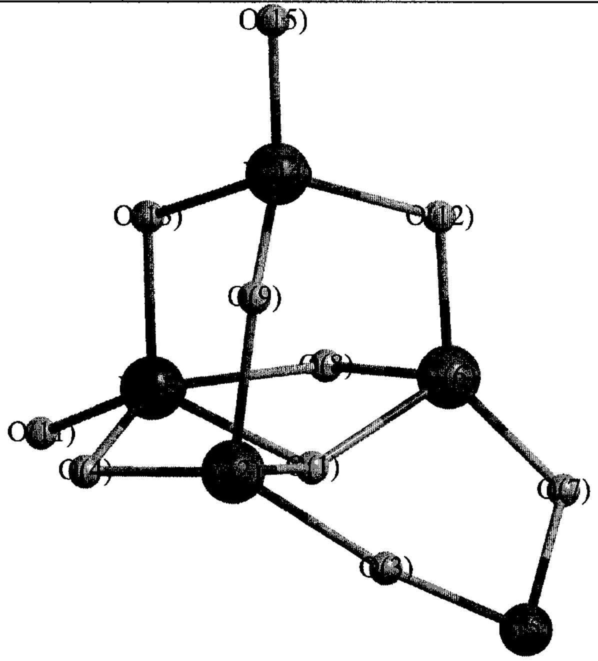
```
O   4.411263      .763724     -.973671
O  -3.986952    -2.126766     -.241473
O  -1.101136    -1.135071     -.072741
O   1.928291     -.384292     -.088532
V    .202796      .062903     -.152915
V  -2.905715     -.963177      .053116
V   3.731767     -.399713     -.070191
S  -2.309649     2.295087      .177559
O  -3.268768      .823669      .240059
O   4.374350     -.398140     1.419583
O   -.695686     1.604165     -.149621
```

```
O(11)-V(5)   1.7838
O(11)-S(8)   1.7858
O(10)-V(7)   1.6224
O(9)-S(8)    1.7577
O(9)-V(6)    1.8328
V(7)-O(1)    1.6222
V(7)-O(4)    1.8035
V(6)-O(3)    1.8172
V(6)-O(2)    1.6155
V(5)-O(4)    1.7837
V(5)-O(3)    1.7725
```

E = -751.171154848 h (2.30 eV)
quartet

```
 Zero-point correction=                         .023595 (Hartree/Particle)
 Thermal correction to Energy=                  .038331
 Thermal correction to Enthalpy=                .039275
 Thermal correction to Gibbs Free Energy=      -.025267
```

$V_4O_8SO_2$ (BPW91/LANL2DZ)



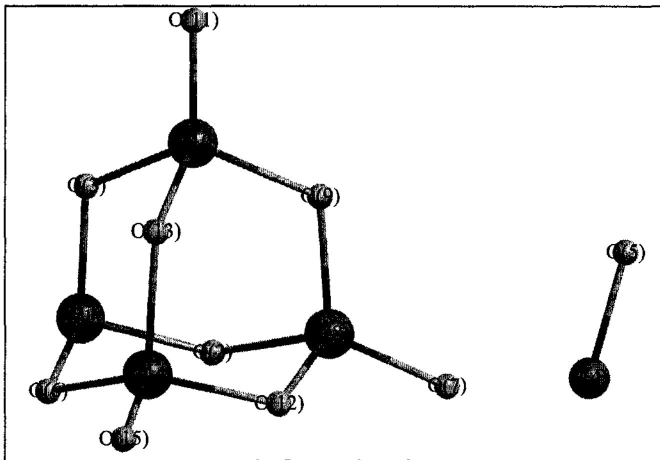
O(15)-V(14)	1.6000
V(14)-O(13)	1.8243
V(14)-O(9)	1.8264
V(14)-O(12)	1.8262
O(13)-V(10)	1.7785
O(12)-V(6)	1.7843
O(11)-V(10)	1.5981
V(10)-O(8)	2.0101
V(10)-O(1)	2.0267
V(10)-O(4)	2.0079
O(9)-V(2)	1.7841
O(8)-V(6)	1.7324
O(7)-V(6)	1.8386
O(7)-S(5)	1.7934
V(6)-O(1)	1.8168
S(5)-O(3)	1.7936
O(4)-V(2)	1.7331
O(3)-V(2)	1.8382
V(2)-O(1)	1.8179

v4o8so2s1.log

```
O  -0.650368    0.659833    0.002082
V  -0.626390    0.010124    1.699780
O  -2.395220   -0.395937    1.407846
O   0.545821    1.272303    1.890943
S  -3.450497   -0.044057    0.000902
V  -0.627781    0.019444   -1.697985
O  -2.398100   -0.385186   -1.410626
O   0.543448    1.281876   -1.887182
O   0.360933   -1.455666    1.455247
V   1.179072    1.532071    0.003295
O   1.831833    2.990796    0.006431
O   0.357639   -1.448968   -1.460444
O   2.277758    0.133537   -0.000861
V   1.458378   -1.496450   -0.004046
O   2.450323   -2.751892   -0.008241
```

E = -1048.49711439 h
singlet

```
 Zero-point correction=                           0.038025 (Hartree/Particle)
 Thermal correction to Energy=                    0.054685
 Thermal correction to Enthalpy=                  0.055629
 Thermal correction to Gibbs Free Energy=        -0.005175
```



v4o8so2s2r1.log

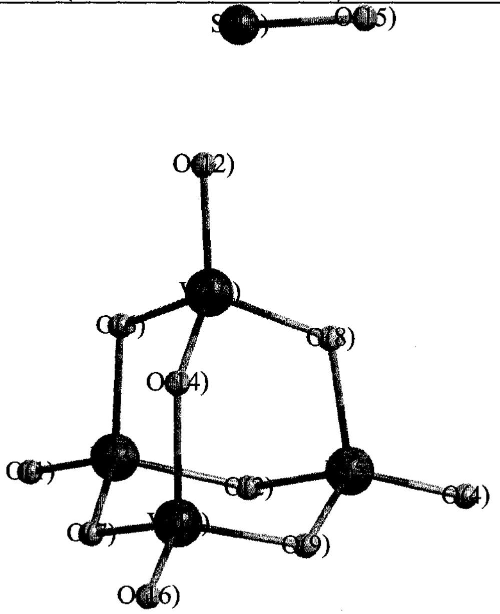
```
V   1.481357   -0.194734    1.916555
O  -0.229025   -0.464011    1.690468
O   1.787126    1.361826    1.215977
S  -4.658063   -0.521725   -0.080627
O  -4.931912    1.069866   -0.366790
O   2.292446   -1.345165    0.860149
O  -2.838320   -0.783396    0.219423
V  -1.175632   -0.318887    0.134634
O  -0.719711    1.299583   -0.433541
V   1.043873    1.784498   -0.450766
O   1.368291    3.240104   -1.036171
O  -0.180941   -1.438761   -0.789403
O   1.831046    0.448027   -1.352735
V   1.646137   -1.280032   -0.885933
O   2.324389   -2.318301   -1.900285
```

```
O(15)-V(14) 1.6022
V(14)-O(13) 1.7995
V(14)-O(6)  1.8630
V(14)-O(12) 1.8365
O(13)-V(10) 1.7943
O(12)-V(8)  1.7599
O(11)-V(10) 1.6021
V(10)-O(3)  1.8733
V(10)-O(9)  1.8291
O(9)-V(8)   1.7749
V(8)-O(2)   1.8269
V(8)-O(7)   1.7284
O(6)-V(1)   1.7599
O(5)-S(4)   1.6401
O(3)-V(1)   1.7341
O(2)-V(1)   1.7461
```

E = -1048.48433852 h
singlet

```
 Zero-point correction=                           0.036334 (Hartree/Particle)
 Thermal correction to Energy=                    0.054218
 Thermal correction to Enthalpy=                  0.055162
 Thermal correction to Gibbs Free Energy=        -0.010936
```

$V_4O_9SO_2$ (BPW91/LANL2DZ)



v4o9so2s1r3.log

```
O(16)-V(11)  1.6012
O(15)-S(13)  1.6328
O(14)-V(11)  1.8395
O(14)-V(10)  1.7716
O(12)-V(10)  1.7225
V(11)-O(9)   1.7980
V(11)-O(7)   1.7975
V(10)-O(8)   1.7547
V(10)-O(6)   1.7607
O(9)-V(5)    1.8005
O(8)-V(5)    1.8320
O(7)-V(3)    1.8007
O(6)-V(3)    1.8316
V(5)-O(2)    1.8040
V(5)-O(4)    1.6014
V(3)-O(2)    1.8017
V(3)-O(1)    1.6017
O(12)-S(13)  1.8612
V(10)-S(13)  3.5072
```

```
O   2.081480   -2.322683   -2.229722
O   1.679558    0.483085   -1.710156
V   1.465401   -1.238599   -1.224404
O   1.182675    3.278060   -1.180005
V   0.986403    1.776102   -0.660308
O  -0.326515   -1.426321   -0.894885
O   2.121748   -1.307935    0.451013
O  -0.753254    1.270777   -0.387388
O   1.685866    1.441434    0.964614
V  -1.208800   -0.331350    0.164664
V   1.495898   -0.184906    1.707288
O  -2.891265   -0.665275    0.321665
S  -4.702169   -0.519514   -0.082523
O  -0.319175   -0.482973    1.689183
O  -5.117760    1.055165    0.034525
O   2.186636   -0.345389    3.142890
```

E = -1123.79017099 h
singlet

```
 Zero-point correction=                           0.039740 (Hartree/Particle)
 Thermal correction to Energy=                    0.058910
 Thermal correction to Enthalpy=                  0.059854
 Thermal correction to Gibbs Free Energy=        -0.009689
```