accurate accounting of electron correlation and an extension of the basis sets beyond those that we have used in explicit geometry optimizations would result in an additional lowering of the barrier. Specifically, we would expect that the effects of triple substitutions and f functions would lead to a lowering of the barrier. On the basis of a comparison of the classical barriers determined at the optimized levels with those found with the single point calculations, we would expect a lowering of the classical barrier with respect to our "best" optimized level, CCSD/TZ+2P, due to these effects of ~3.0–3.2 kcal/mol. This leads to a best estimate of ~3.0 kcal/mol for the classical barrier to rearrangement of vinylidene to acetylene. Although the augmentation of the basis with additional sets of f functions beyond the one set used in this study may lead to an additional lowering of the barrier, the combined effect of additional f functions and triple substitutions will likely be partially cancelled, as CCSDT-1 tends to overestimate the true effect of triple substitutions. Thus, we do not expect that the classical barrier will vanish.

Finally we return to the question raised in the title of this paper.

Specifically, is this the "Final Chapter" for vinylidene? With respect to the existence/nonexistence of $H_2C=C$: as a genuine minimum on the ground-state acetylene potential energy hypersurface, our answer to this question is "Yes". Vinylidene is a genuine minimum. With respect to other important chemical questions, we have just begun to scratch the surface for vinylidene. The precise value of the classical barrier remains uncertain, although we doubt that it will fall much below 2 kcal/mol. Theoretical questions pertaining to the dynamical aspects of this elementary reaction should continue to be of great interest. And, of course, a variety of new gas-phase experiments will be critical to unfolding the properties of vinylidene, the simplest unsaturated carbene.

Resolution of a Long-Standing Problem in Elemental Sulfur Chemistry: A Theoretical Study of Tetrasulfur

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Abstract: Theoretical studies of the potential energy surface of a poorly understood allotrope of elemental sulfur, S_4, have been performed with use of ab initio electronic structure theory. Eleven different isomers have been considered. Singlet states have been studied with SCF, two-configuration SCF (TCSCF), CISD (single and double excitation configuration interaction), and TC-CISD levels of theory, and selected triplet states have also been investigated with SCF and CISD theory. A few studies have also been performed on the most stable isomers with MR (multi-reference)-CISD, CCSD (coupled cluster theory with single and double substitutions), and CCSDT-1 (CCSD with linearized triple substitutions) methods. Two basis sets, of double-ζ plus polarization (DZP) and triple-ζ plus double polarization (TZ2P) quality, respectively, have been used. The effects of f-functions on the S–S bond have been investigated with a TZ2P+f basis set. Harmonic vibrational frequencies, infrared, and some Raman intensities have been evaluated, as have the ionization energies and the lowest energy electronic transitions for the most stable isomers. Experimental data for these properties are compared with our theoretical results. The global minimum of S_4 is predicted to have a singlet cis planar structure (C_{2v} symmetry); there are several low-lying states, of which the closest to the global minimum are a singlet trans isomer (≈ 10 kcal mol^{-1} above the cis), followed by triplet trans and helical isomers that are almost degenerate, and a singlet four-membered puckered ring and branched three-membered ring isomers that are also almost degenerate. We have been able to assign most of the vibrational spectra previously attributed to S_4 to fundamentals of the cis and trans singlet isomers, and the electronic absorptions assigned to two isomers of S_4 match satisfactorily with the theoretically predicted transition energies for these isomers.

Introduction

Of all the elements, it is sulfur that has by far the most extensive, complex, and interesting allotropy,[1] an allotropy that is dominated by rings. The astonishing temperature variation in the color and viscosity of liquid sulfur has attracted much attention, and while the molecular changes that give rise to these variations are not established in detail, it seems clear that some very large S_n molecules must be involved. Sulfur vapor is a complicated mixture; all S_n in the range $2 \leq n \leq 10$ have been detected, but surprisingly little is known about several of the smaller S_n molecules, no doubt because they cannot be prepared in a "pure" state. Despite much effort over recent years, which has included the use of most components in the spectroscopic arsenal and several theoretical studies, there is no consensus as to the electronic or

geometrical structure of S_4 in its most stable form. No fewer than *six* different isomers have been reported to be the global minimum by various authors! This startling lack of unanimity for such a small molecule, one of the basic allotropic forms of one of the best-studied elements, reflects rather poorly on our structural knowledge and understanding of fundamental bonding principles. In an attempt to overcome at least some of these difficulties, we have undertaken an extensive theoretical study of S_4. In addition

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(1) (a) Schmidt, M. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 445; *Angew. Chem.* **1973**, *85*, 474. (b) Meyer, B. *Chem. Rev.* **1976**, *76*, 367. (c) Meyer, B. *Sulfur, Energy, and Environment*; Elsevier: Amsterdam, 1977. (d) Meyer, B. *Adv. Chem. Ser.* **1977**, *110*, 53. (e) Steudel, R. *Sulfur: Its Significance for Chemistry, for the Geo-, bio- and cosmosphere and Technology*; Müller, A., Krebs, B., Eds.; Elsevier: Amsterdam, 1984. (f) Tamura, K.; Seyer, H. P.; Hensel, F. *Ber. Bunsenges. Phys. Chem.* **1986**, *90*, 581. (g) *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic Press: London, 1987; Vol. 1.

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† University of Georgia.
‡ University of Melbourne.
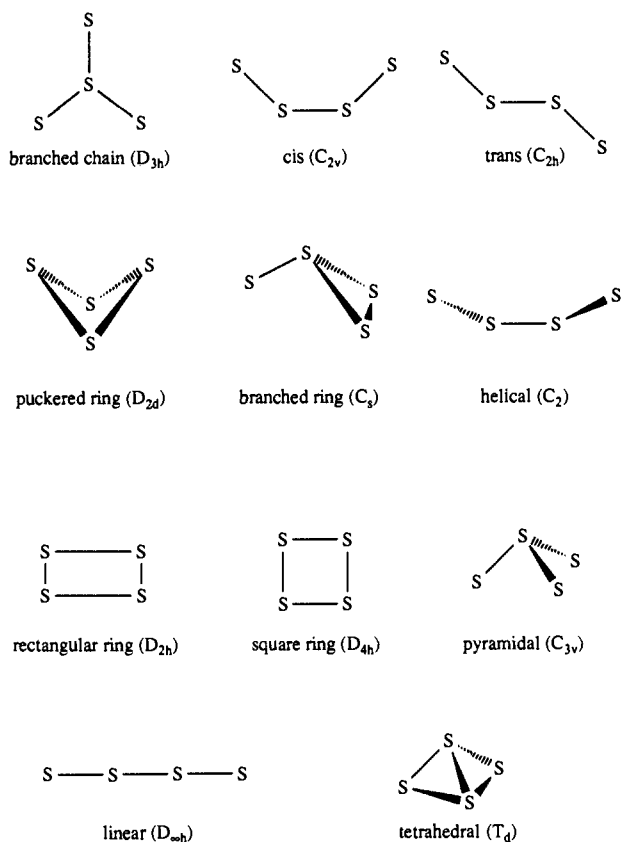
Figure 1. Structures of S_4 isomers.

Figure 2. Orbital interaction diagram for the cis open chain isomer of S_4.

to optimizing the geometries of a wide range of isomers, we have evaluated vibrational frequencies, probed the electronic spectrum, and estimated the ionization potential. With the aid of these results we attempted to provide a consistent interpretation for the various experimental data that have been reported for S_4.

We consider first some qualitative features of the bonding in sulfur clusters, for which a surprisingly large number of isomers can potentially exist. S_4 can exist in one of two main forms, i.e. rings and chains. Branching within these two forms is also possible. The eleven different isomers we have studied in this work, and their point-group symmetries, are displayed in Figure 1. Several of these isomers were studied more for the sake of completeness than in any serious expectation that they would turn out to be the lowest energy structure for S_4. However, in view of the surprising structural features revealed recently for several second-row small molecules such as Si_3^2 and P_3^+ or $P_3^{-3,4}$ and the rich isomerism of S_2O_2,[5] we felt it prudent to cast our net widely. Since a triangular state of S_3 lies only some 9 kcal mol^{-1} above the "open" ozone-like C_{2v} ground state,[6] the C_s isomer of S_4 based on a branched three-membered ring warrants attention, especially since the comparable isomer of S_2O_2 is only about 12 kcal mol^{-1} above the global minimum.[5]

For an S_4 ring the octet rule of Lewis[7] can be obeyed, using $S = N - A$ (a modified expression from ref 8), where $N = 8 \times 4$ is the number of electrons needed to complete the octet for 4 atoms, and $A = 6 \times 4$ is the number of valence electrons available in S_4. Therefore the number of bond pairs (S) is 4. For a chain molecule the realization of 4 bond pairs is not possible if only single
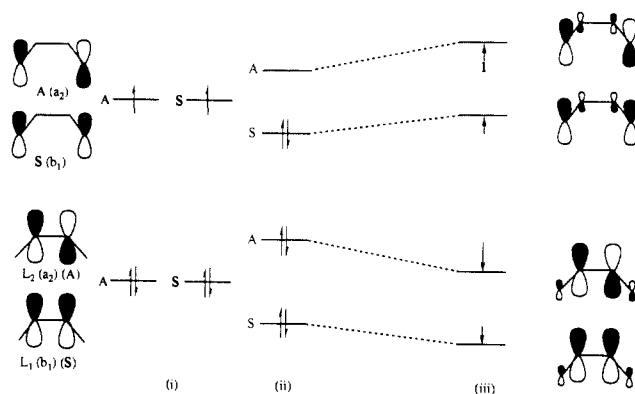
bonds are considered. Three traditional Lewis structures may be envisaged, each of which could exist in planar cis or trans forms
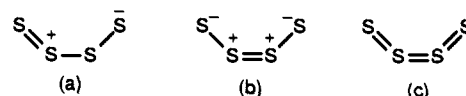
of these, (a) is probably the most reasonable, since (b) violates Pauling's adjacent charge rule,[9] and (c) implies hypervalent central S atoms, which are unlikely for a homoatomic molecule such as S_4.[10] It is interesting to note that (a) implies shorter terminal bonds than central bonds, (b) implies the opposite, while (c) suggests similar central and terminal bond lengths.

An alternative way of looking at the open-chain form of S_4 is to think of it as a broken *ring*, as in the work of Hoffmann.[11] If one starts with a square-planar ring and simply breaks one of the bonds we obtain, after a rotation of the resulting fragment orbitals to prevent recombination, two orbitals A and S on the terminal atoms [the upper pair in Figure 2i], assuming for the moment no interaction between the orbitals. L_1 and L_2 are symmetric and antisymmetric combinations of the out-of-plane lone pairs on the central sulfur atoms, and these are the only other orbitals that can interact with the two fragment orbitals (A, S, L_1, and L_2 are all of π symmetry). The first perturbation on the system splits A and S (also L_1 and L_2 denoted by A and S symmetry labels) orbitals about their center of gravity. This is termed the through-space interaction, and the size of the splitting is dependent on the spatial separation of the interacting components, i.e. the lone-pair splitting is greater than that of the fragments, and gives the situation in Figure 2ii. The second perturbation occurs as a result of interaction between pairs of orbitals of the same symmetry, where the lower energy orbital of the pair is preferentially lowered and the upper level raised. Here both A and S fragment orbitals are raised in energy but A is raised more than the S since the lone-pair A combination is closer in energy to the A fragment orbital. This effect is termed the through-bond interaction. The final orbitals are sketched at the right-hand side of Figure 2; notice that they resemble the π orbitals of cis butadiene. An exactly

(2) (a) Diercksen, G. H. F.; Gruner, N. F.; Oddershede, J.; Sabin, J. R. *Chem. Phys. Lett.* **1985**, *117*, 29. (b) Grev, R. S.; Schaefer, H. F. *Chem. Phys. Lett.* **1985**, *119*, 111. (c) Raghavachari, K. *Chem. Phys.* **1985**, *84*, 3520. (d) Balasubramanian, K. *Chem. Phys. Lett.* **1986**, *125*, 400.

(3) Burdett, J. K.; Marsden, C. J. *New J. Chem.* **1988**, *12*, 797.

(4) Hamilton, T. P.; Schaefer, H. F. *Chem. Phys. Lett.* **1990**, *166*, 303.

(5) Marsden, C. J.; Smith, B. J. *Chem. Phys.* **1990**, *141*, 335.

(6) Rice, J. E.; Amos, R. D.; Handy, N. C.; Lee, T. J.; Schaefer, H. F. *J. Chem. Phys.* **1986**, *85*, 963.

(7) Lewis, G. N. *J. Am. Chem. Soc.* **1916**, *38*, 762.

(8) Langmuir, I. *J. Am. Chem. Soc.* **1919**, *41*, 868.

(9) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, 1960; p 270.

(10) There is an enormous literature that discusses the possible participation of d orbitals in the chemistry of second-row elements, and it is not possible to quote all the important articles. In much (but not all) of the recent work, the tendency has been to downplay the importance of these d orbitals. The following articles are representative: Coulson, C.; Gianturo, F. A. *J. Chem. Soc. (London) A* **1968**, 1618. Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54. Kwart, H.; King, K. G. *d-Orbitals in the Chemistry of Silicon, Phosphurus and Sulfur*; Springer: Berlin, 1977. Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272. Cruickshank, D. W. J.; Eisenstein, M. *J. Mol. Struct.* **1985**, *130*, 143. Magnusson, E.; Schaefer, H. F. *J. Chem. Phys.* **1985**, *83*, 5721. Reed, A. E.; Weinhold, F. *J. Am. Chem. Soc.* **1986**, *108*, 3586. Mayer, I. *J. Mol. Struct.* **1987**, *149*, 81. Patterson, C. H.; Messmer, R. P. *J. Am. Chem. Soc.* **1989**, *111*, 8059. Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434. Magnusson, E. *J. Am. Chem. Soc.* In press.

(11) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

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analogous argument can be followed for the trans isomer, the main difference being that the through-space interaction is smaller due to the greater spatial separation of the two fragment orbitals.

There are two important consequences of this discussion; if the S–A molecular orbital separation is large enough then the singlet state will be preferred to the triplet, with the trans form yielding a smaller singlet–triplet gap than the cis isomer due to the smaller through-space interaction. Second, the description of the singlet state will require at least two configurations in any theoretical treatment that aims at quantitative accuracy, since the two states that are derived from double occupancy of either of the A or S fragment orbitals will be close in energy.

Finally in this qualitative introductory section we draw attention to the series of articles by Harcourt[12,13] in which he has discussed species such as cis planar S_2O_2 which are closely related to cis S_4 and shown that the central bond in these molecules can be expected to be relatively long and weak. Harcourt's work[12,13] provides further reasons for believing that the Lewis structures b and c will not be of prime importance for cis S_4, and he has discussed alternative "long-bond" structures for these systems.

We now summarize the extensive literature concerning S_4. Perhaps the first and most definitive evidence for the presence of S_4 in sulfur vapor came from mass spectrometry experiments conducted by Berkowitz and co-workers.[14,15] The appearance potential for S_4^+ measured in the most recent electron impact experiment is 10.1 eV.[16] This value is substantially higher than that found for other sulfur allotropes that are known to exist as rings, such as S_6 (9.2 eV), S_7 (9.0 eV), or S_8 (9.3 eV), and it has been used to argue[16] that the most stable isomer of S_4 is, therefore, not a four-membered ring. Unfortunately, while the ionization energy by itself can probably rule out a possible contender, it provides little direct evidence as to what the global minimum for S_4 actually *is*.

There have been several studies of the visible and UV spectra of S_n for both liquid and gaseous phases.[17-19] It is generally agreed that S_3 is responsible for an absorption at 400 nm, which shows extensive vibrational structure in the gas phase, and that a rather broad featureless band at about 530 nm is caused by S_4. Like the ionization energy, this visible absorption by itself provides little positive evidence for the structure of S_4, though since S_n rings such as S_8 have no absorption maximum to longer wavelength than 300 nm,[17] the very different wavelength assigned to S_4 also suggests that its lowest energy isomer is not a four-membered ring. A longer wavelength band in the sulfur vapor spectrum at 620 nm was originally attributed to S_5, but it has very recently been assigned to a second isomer of S_4.[19]

No fewer than thirteen (!) apparently different vibrational frequencies have been assigned, with varying degrees of confidence, to S_4. The maximum number of fundamental vibrational frequencies for a tetraatomic molecule is, of course, six. One possible interpretation of this embarrassment of riches is that at least one additional isomer of S_4 is very close in energy to the most stable form and that different species are preferentially produced and/or detected under different experimental conditions. In general, however, it is clear that there is acute difficulty in knowing which molecular species in a complex mixture gives rise to a particular spectral feature. Unless that feature can in some way positively identify the species from which it arises, for example by spin coupling or isotopic abundance ratios, the interpretation of any

spectroscopic data for a mixture as complicated at S_n must be regarded as somewhat equivocal.

Irradiation with visible light of matrices containing S_2 produces infrared absorptions at 681, 660, 636, 483, 320, and 270 cm^{-1}, which have all been attributed to S_4.[20] The products of a radiofrequency discharge in SO_2 vapor give Raman bands at 668, 601, and 440 cm^{-1}, which have also all been assigned to S_4.[21] Since none of these bands could be detected in the infrared spectrum of the discharge products, it was argued that S_4 probably has a center of symmetry, though the alternative possibility of its simply being a weak infrared absorber could not be excluded.[21] In comparing the vibrational frequencies reported in ref 20 and 21, it should be realized that the particular matrix used may perturb the vibrational frequencies slightly. Since energy was fed into the system in both cases, either by irradiation or discharge, it is also possible that neither spectrum arose from the lowest energy form of the molecule(s) studied.

In a careful study of sulfur vapor,[22] Raman bands at 682 and 605 cm^{-1} were assigned to S_4. By use of the resonance Raman technique, which detects symmetric stretching modes with particularly high sensitivity, the authors showed[22] that both these bands are due to molecules that have an electronic absorption near 520 nm, thereby strengthening their assignment to S_4. From studies of the variation in Raman intensity with temperature and pressure, it appeared[22] that the two bands are due to different isomers. Other Raman bands at 440, 384, 305, 250, and 190 cm^{-1} were thought to arise from S_4 or possibly a sulfur chain containing more than four atoms.[22] Since the highest stretching frequency in S_n ring molecules (n = 6-13) is usually about 500 cm^{-1},[23] the assignment of vibrational bands in the 650–680-cm^{-1} region is inconsistent with a four-membered single-bonded ring structure for S_4. Higher vibrational frequencies would be expected for the branched chain isomer, for the cis and trans isomers, and possibly also for the branched ring form, though it is not entirely clear how much multiple bond character is to be anticipated for the branched-chain or -ring isomers, since the use of d orbitals on sulfur as "hybridization functions" is somewhat controversial.[10] The harmonic vibrational frequency in the doubly bonded $^3\Sigma_g^-$ ground state of S_2 at 726 cm^{-1}[24] provides a convenient point of comparison.

Many different theoretical techniques have been applied to the study of S_4.[25-34] In view of the relatively large size of the molecule by theoretical standards (64 electrons), and the substantial number of isomers to be studied, a high-quality ab initio approach has not been feasible until very recently. The different methods used have given startlingly variable predictions concerning the electronic and geometrical structure of the lowest energy isomer of S_4; readers could be excused for doubting whether theoretical methods have, so far, contributed anything of unequivocal reliability to our

(12) Harcourt, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5195; **1981**, *103*, 5623; *Lecture Notes in Chemistry*; Springer: Berlin, 1082; Vol. 30, Chapters 7, 10, 11, 13, 17.
(13) Harcourt, R. D. *J. Mol. Struct.* **1988**, *169*, 193; **1989**, *186*, 131.
(14) Berkowitz, J.; Marquart, J. R. *J. Chem. Phys.* **1963**, *39*, 275.
(15) Berkowitz, J.; Lifshitz, C. *J. Chem. Phys.* **1968**, *48*, 4346.
(16) Rosinger, W.; Grade, M.; Hirschwald, W. *Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 536.
(17) (a) Meyer, B.; Oommen, T. V.; Jensen, D. *J. Phys. Chem.* **1971**, *75*, 912. (b) Meyer, B.; Stroyer-Hansen, T.; Oommen, T. V. *J. Mol. Spectrosc.* **1972**, *42*, 335.
(18) Casal, H. L.; Scaiano, J. C. *J. Photochem.* **1985**, *30*, 253.
(19) Steudel, R.; Albertsen, J.; Zink, K. *Ber. Bunsenges. Phys. Chem.* **1989**, *93*, 502.

(20) Meyer, B.; Stroyer-Hansen, T. *J. Phys. Chem.* **1972**, *76*, 3968.
(21) Hopkins, A. G.; Tang, S.; Brown, C. W. *J. Am. Chem. Soc.* **1973**, *95*, 3486.
(22) Lenain, P.; Picquenard, E.; Corset, J.; Jensen, D.; Steudel, R. *Ber. Bunsenges. Phys. Chem.* **1988**, *92*, 859.
(23) Steudel, R. *Spectrochim. Acta A* **1975**, *31*, 1065.
(24) Freedman, P. A.; Jones, W. J.; Rogstad, A. *J. Chem. Soc. Faraday Trans. 2* **1975**, *71*, 286.
(25) Meyer, B.; Spitzer, K. *J. Phys. Chem.* **1972**, *76*, 2274.
(26) Kao, J.; Allinger, N. L. *Inorg. Chem.* **1977**, *16*, 35.
(27) (a) Foti, A. E.; Smith, V. H., Jr.; Salahub, D. R. *Chem. Phys. Lett.* **1978**, *57*, 33. (b) Salahub, D. R.; Foti, A. E.; Smith, V. H., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 7847.
(28) Dewar, M. J. S.; McKee, M. L. *J. Comp. Chem.* **1983**, *4*, 84.
(29) Baird, N. C. *J. Comp. Chem.* **1984**, *5*, 35.
(30) Bolotin, A. B.; Pipiraite, P. P.; Ruzhene, A. Y.; Gorbunov, B. N.; Tarkhov, G. V.; Simanenkova, L. B. *J. Struct. Chem.* **1988**, *29*, 182.
(31) (a) Jug, K.; Iffert, R. *J. Comp. Chem.* **1987**, *8*, 1004 and references cited therein. (b) Jug, K.; Iffert, R. *J. Mol. Struct. (Theochem)* **1989**, *186*, 347.
(32) (a) Stillinger, F. H.; Weber, T. A.; LaViolette, R. A. *J. Chem. Phys.* **1986**, *85*, 6460. (b) Stillinger, F. H.; Weber, T. A. *J. Phys. Chem.* **1987**, *91*, 4899.
(33) Hohl, D.; Jones, R. O.; Car, R.; Parrinello, M. *J. Chem. Phys.* **1988**, *89*, 6823.
(34) Kao, J. *Inorg. Chem.* **1977**, *16*, 2085.

knowledge of the relative energies of S_4 isomers.

In the first theoretical treatment of S_4, the extended Hückel method was used.[1d,25] Suitable parameters were obtained from studies of S_8 for which experimental data were available. The branched chain isomer of D_{3h} symmetry was predicted to be the most stable form of S_4, with the C_{2h} trans chain 9 kcal mol^{-1} higher, followed in order of increasing energy by cis, helical, square-ring, and puckered-ring isomers. However, the energy levels of the trans form were more compatible with an electronic absorption at 520 nm than were those of the branched ring.

S_4 was included in a molecular mechanics study of several S-containing species, but the parametrization available allowed only four-membered rings to be considered.[26] It was concluded that the ring form of S_4 would be planar rather than puckered, due to ring strain.[26] Five different isomeric forms of S_4 were treated in a study that used the SCF-Xα-SW method to probe electronic energy levels.[27] The authors did not claim to have established which isomer of S_4 is the most stable, since values for the total electronic energy were not obtained, but they favored the planar cis form. The agreement between their values (0.88 and 1.12 eV) and the observed (2.3 eV or 530 nm) electronic transition energies was thought to be "adequate".[27]

The MNDO method has been applied to many S-containing molecules, including S_4.[28,29] In the more complete study of S_4, Baird predicted that the puckered ring isomer is the global minimum, with the square ring only 0.3 kcal mol^{-1} higher.[29] The trans isomer was predicted to be 41 kcal mol^{-1} above the puckered ring isomer, but inclusion of a 2 × 2 (π–π^*) CI reduced this gap to 16 kcal mol^{-1}. Baird claimed[29] that his MNDO results were more reliable than those obtainable from the ab initio SCF studies which were feasible at that time, in which small basis sets were necessarily used (see below). An MNDO/3 study of S_4 has been reported recently,[30] in which the authors agreed with Baird[29] that the puckered ring is the most stable form of S_4, followed by trans and then cis. Triplet chain structures were shown[30] to be less stable than the singlet puckered ring by 7 kcal mol^{-1}. Another semi-empirical MO-based technique known as SINDO1 has been used to study S_4.[31] Direct application of this method leads to the prediction that the branched ring isomer is the lowest energy form of S_4, but since SINDO1 is known to overemphasize the stability of three-membered rings, the authors concluded that the puckered four-membered-ring isomer is the true global minimum.[31]

Molecular dynamics techniques have been applied to study several allotropes of sulfur, using a potential function that contains two-body and three-body terms.[32] Only two local minima were found for S_4. The lowest energy isomer with this potential function is the helical structure, while the square ring is 30 kcal mol^{-1} higher. Since electron spin is not explicitly included in this type of method, spin states are not defined in the work reported in ref 32, and direct comparison with other studies is rather difficult.

One of the most recent theoretical studies of S_4 employed the density functional method, in combination with molecular dynamics and simulated annealing techniques.[33] The authors claim two main advantages for this approach: first it is "parameter-free", and second it enables them to overcome the problem of finding sensible starting points for geometry optimizations. This second point is of considerable importance, since there are many possible isomers even for a tetraatomic molecule, and if some are overlooked, as can easily happen with traditional geometry searches, there is no guarantee that the true global minimum will be located. The rectangular ring isomer was predicted to be the most stable form of S_4, but the cis species is only some 2 kcal mol^{-1} higher, and this region of the potential surface was found to be extremely flat. The trans isomer lies about 10 kcal mol^{-1} above the rectangular ring, and the barrier to internal rotation that separates cis and trans structures was found to be about 24 kcal mol^{-1}. The puckered ring isomer was found to be 18 kcal mol^{-1} above the ground state, while all triplet states were reported to lie "well above" the ground state. This combination of techniques is unconventional and has several potentially attractive features. In assessing its probable accuracy, it should be noted that comparable studies on S_3 produce structural parameters and relative energies

for the "open" C_{2v} and "closed" D_{3h} states that agree rather well with those obtained in a recent high-quality ab initio study[6] (insufficient experimental data are available for S_3 to enable the accuracy of theoretical results to be deduced directly), but the results obtained for S_2 agree no better than moderately with experiment; it is particularly disturbing to anyone used to ab initio results that the bond energy of S_2 is *over*estimated by 25% in the density functional work.[33]

There have been only two ab initio studies of S_4 published to date. In the earlier, more comprehensive of these, Kao reported that the ^3B helical chain isomer was the most stable form.[34] However, his work did not include any electron-correlation effects, and at the SCF level it is clear that the stability of triplets relative to singlets is systematically overestimated. Kao used two basis sets, one minimal (STO-3G) and the other split-valence (44-31G), which gave rise to substantially different geometrical parameters. Both of these basis sets are small by current standards. Since neither basis included polarization functions, which are now known to be essential for studies on sulfur compounds if accurate results are desired,[35,36] his findings cannot be regarded as definitive. The most stable singlet state in Kao's work was the puckered ring isomer, followed by the square ring. Only singlet states were considered in the second ab initio study of S_4, in which a split-valence basis was again used at the SCF level.[37] The authors agreed with Kao[34] that the puckered ring isomer is the most stable singlet state of S_4. Dixon has very recently studied cyclic S_4 as part of an ab initio investigation of S_n rings (n = 4–8).[38a] By comparing MP2 energies (at SCF geometries) with experimental data, he has shown that the lowest energy structure of S_4 is not a four-membered ring, but he did not perform studies of other possible isomers of S_4.

In the work reported here, we have attempted to overcome the deficiencies in the earlier ab initio studies by (1) studying a large range of possible isomers, (2) using much larger basis sets, and (3) using several theoretical methods to assess the importance of electron correlation. We believe that we are able to provide a balanced theoretical account of the isomers of S_4, whose characters are very different, and establish beyond reasonable doubt which is the true global minimum on the S_4 potential surface.

Computational Methods

Ab initio theoretical studies at various levels of theory have been performed on all the isomers of S_4 shown in Figure 1. Two Gaussian-type orbital basis sets have been used. The smaller basis, denoted double-ζ plus polarization (DZP), was based upon the 10s6p primitive set of Huzinaga,[39] with the addition of a d-function exponent (α_d) of 0.55, and contracted to 6s3p1d.[40] This basis is therefore not a "true" DZP set which would require a contraction of 6s4p1d; however, it has been shown to be a cost-effective basis in previous studies of sulfur compounds.[35] Comparisons using both this basis set and the standard "full DZP" basis, which is the Dunning-Hay 11s7p1d/6s4p1d set,[41] for the puckered ring isomer show that the differences in geometry are small. The "full DZP" total energies are however significantly lower than those from the other, smaller, basis set, due to the larger number of primitives in the "full DZP" basis and the more energy efficient contraction scheme in which one primitive appears in two different contracted functions.

The larger basis set used for S_4 was a triple-ζ plus double polarization (TZ2P) set based on the 11s7p primitive set of Huzinaga[39] augmented by the addition of two d functions with α_d = 1.6 and 0.4. This basis was contracted to 7s5p2d.[42] The effects of f functions on the S-S bond in S_2 were investigated by adding a set of f functions, with α_f = 0.55, to the TZ2P basis described above. Spherical harmonic d-type functions were

(35) Marsden, C. J.; Smith, B. J. *J. Mol. Struct.* **1983**, *105*, 385.

(36) Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1976**, *64*, 5142. Mezey, P. G.; Haas, A. *J. Chem. Phys.* **1982**, *77*, 870.

(37) Feng, W. L.; Novaro, O. *Int. J. Quantum Chem.* **1984**, *26*, 521.

(38) (a) Dixon, D. A.; Wasserman, E. *J. Phys. Chem.* **1990**, *94*, 5772. (b) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(39) Huzinaga, S. *Approximate Atomic Functions*; Chemistry Department, The University of Alberta, Edmonton, Canada, 1971.

(40) Contractions were 5 1 1 1 1 1 in the s and 4 1 1 in the p spaces, respectively.

(41) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol. 3, pp 1–27.

(42) Contractions were 5 2 1 1 1 1 1 in the s space and 3 1 1 1 1 in the p.
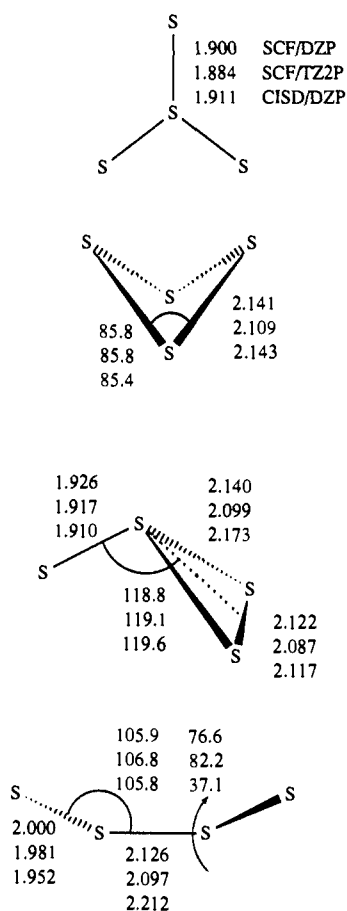
Figure 3. Geometrical structures (bond lengths in Å and angles in deg) predicted for the branched-chain ($^1A_1'$), puckered-ring ($^1A_1$), branched-ring ($^1A'$), and helical (^3B) isomers of S_4. Values are (from top to bottom) for DZP SCF, TZ2P SCF and DZP CISD.
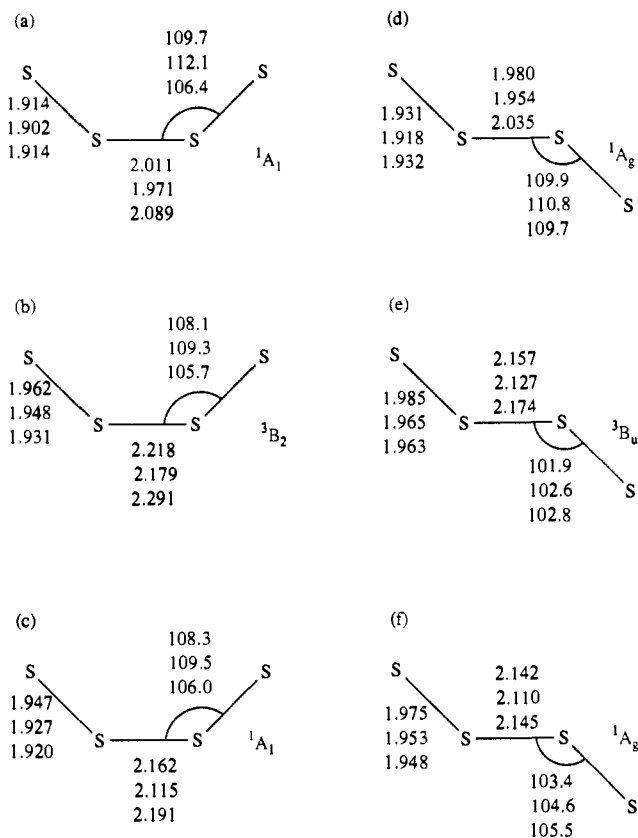

Figure 4. Geometrical structures (bond lengths in Å and angles in deg) predicted for the cis and trans isomers of S_4. Values in the same order as for Figure 3: (a) $^1A_1$ SCF, (b) $^3B_2$ SCF, (c) $^1A_1$ TCSCF, (d) ^1A_g SCF, (e) ^3B_u SCF, and (f) ^1A_g TCSCF.

used for all SCF studies with the DZP basis set, but Cartesian functions (6 d-type or 10 f-type functions) were used for all other calculations. The effects of this difference were investigated on the branched chain and puckered ring isomers and were shown to result in insignificant geometry changes (one or two thousandths of an Å for bond lengths) and an energy lowering at the optimized geometries of 11.1 and 11.3 mH, respectively. With the larger TZ2P basis no doubt the differences in energy between 5d and 6d representations would be much smaller.

Single-reference closed-shell SCF studies were performed with use of standard techniques, with restricted open-shell Hartree–Fock theory[43] used for all open-shell studies. Optimized geometries were obtained by using analytic SCF first derivatives.[44] Harmonic vibrational frequencies were evaluated at SCF equilibrium geometries with the use of analytic second derivatives.[45] Infrared[46] and selected Raman[47] intensities were also evaluated analytically within the double harmonic approximation. All DZP SCF level studies were performed with the Gaussian 86[48] program.

The effects of electron correlation at the single-reference level were included by the use of configuration interaction single- and double-excitation (CISD) theory. Geometry optimizations at the CISD level were performed by utilizing CISD analytic gradients.[49] Harmonic frequencies

at the CISD level were evaluated for selected isomers from central finite differences of gradients in internal coordinates. Corrections for the unlinked quadruple excitations in the CISD formulation (denoted by +Q in the text and tables) have been applied.[50] The active space for all CISD studies included all orbitals except the 1s, 2s, and 2p; no virtual orbitals were excluded.

Open-chain isomers of S_n species are expected to have substantial diradical character, as outlined in the Introduction and in ref 1b, and hence a zeroth-order description of the singlet chain species must incorporate two configurations, i.e. TCSCF.[51] The energy difference between singlet and triplet states has been found to be reliably predicted with use of a TCSCF approach for the singlet and SCF theory for the triplet in the carbenes,[52] for example. Geometry optimizations at the TCSCF level have been performed with TCSCF analytic gradients,[43b,53] with harmonic vibrational frequencies and infrared intensities evaluated from analytic second derivatives.[54] In addition, the barrier to internal rotation between the cis and trans isomers, which is necessarily a two-configuration problem as described in recent studies on S_2O_2,[5] was also evaluated by TCSCF gradient methods. In subsequent discussions SCF will denote single reference only, with TCSCF or TC-CISD indicating two-reference results.

The effects of adding dynamic electron correlation to the TCSCF wave function were estimated by the use of TC-CISD theory with geometries optimized by the use of analytic gradients of the energy.[55]

(43) Roothaan, C. C. J. *Rev. Mod. Phys.* **1960**, *32*, 179.

(44) (a) Pulay, P. *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1977. (b) Goddard, J. D.; Handy, N. C.; Schaefer, H. F. *J. Chem. Phys.* **1979**, *71*, 1525.

(45) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1979**, *S13*, 225.

(46) Yamaguchi, Y.; Frisch, M. J.; Gaw, J. F.; Schaefer, H. F.; Binkley, J. S. *J. Chem. Phys.* **1986**, *84*, 2262.

(47) Frisch, M. J.; Yamaguchi, Y.; Gaw, J. F.; Schaefer, H. F.; Binkley, J. S. *J. Chem. Phys.* **1986**, *84*, 531.

(48) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohfling, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Pople, J. A.; Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh PA, 1987.

(49) Brooks, B. R.; Laidig, W. D.; Saxe, P.; Goddard, J. D.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1980**, *72*, 4652. Rice, J. E.; Amos, R. D.; Handy, N. C.; Lee, T. J.; Schaefer, H. F. *J. Chem. Phys.* **1986**, *85*, 963. Osamura, Y.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1981**, *75*, 2919. Osamura, Y.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1982**, *77*, 383.

(50) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61.

(51) Das, G.; Wahl, A. C. *J. Chem. Phys.* **1966**, *44*, 87. Wahl, A. C.; Das, G. *Adv. Quantum Chem.* **1970**, *5*, 261.

(52) Bauschlicher, C. W.; Schaefer, H. F.; Bagus, P. S. *J. Am. Chem. Soc.* **1977**, *99*, 7106.

(53) Kato, S.; Morokuma, K. *Chem. Phys. Lett.* **1979**, *65*, 19.

(54) Yamaguchi, Y.; Osamura, Y.; Fitzgerald, G.; Schaefer, H. F. *J. Chem. Phys.* **1983**, *78*, 1607. Yamaguchi, Y.; Osamura, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1983**, *105*, 7506. Yamaguchi, Y.; Frisch, M. J.; Lee, T. J.; Schaefer, H. F.; Binkley, J. S. *Theor. Chim. Acta* **1986**, *69*, 337.
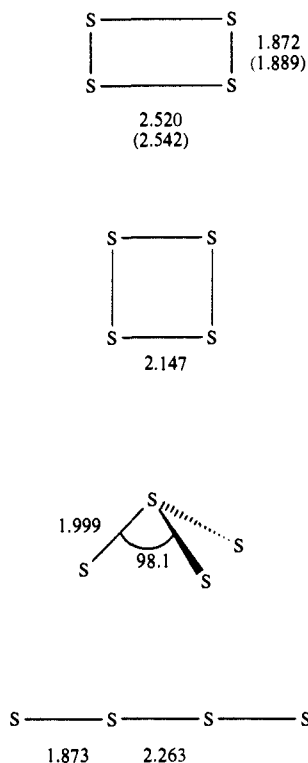
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Figure 5. Geometrical structures predicted (bond lengths in Å and angles in deg) for the rectangular-planar (^1A_g), square-planar ($^1A_{1g}$), pyramidal ($^1A_1$), and linear ($^1\Sigma_g^+$) isomers of S_4. All values are at the SCF level (values in parentheses for the rectangular isomer are at the CISD level) with the DZP basis set.

Analogous corrections for unlinked quadruple excitations in the TC-CISD energy studies were estimated by a two-configuration generalization of the Davidson method[50] due to Shavitt et al.[56] Estimates of the vertical electronic transitions for the cis and trans isomers of S_4, for comparison with experimental data, were obtained by performing an open-shell singlet SCF calculation followed by evaluation of the CISD energy at the TCSCF ground-state geometry with the TZ2P basis set. An alternative method was also used for the cis isomer where the CASSCF method of Werner and Knowles[57] was used to calculate the $^1A_1$, $^1B_2$, and lowest energy triplet states of each symmetry. The active space for the CASSCF studies spanned the entire 3p space for sulfur, i.e. 16 electrons in 12 orbitals. This resulted in close to 62 000 configurations for the singlet states of the neutral S_4 molecule and approximately 44 000 for the triplet states. For the S_4 cationic states, the number of configurations was approximately 100 000. The vertical ionization potentials for the cis and trans isomers were also predicted by an explicit CISD energy evaluation of the lowest lying doublet state as determined by CASSCF studies.

Results

(a) Molecular Geometries. The geometrical parameters predicted at the DZP SCF, TZ2P SCF, and DZP CISD levels of theory are given in Figure 3 for the branched-chain, puckered-ring, branched-ring, and helical isomers of S_4. Results for the cis and trans isomers in various electronic states are given in Figure 4, with those for the square, rectangular, pyramidal, and linear isomers, which turn out not to be true minima but transition states, as described in part d of the Results section, in Figure 5. Detailed description of all results does not seem necessary; here we concentrate on a few main themes.

The structural results displayed in Figures 3 and 4 show some familiar general trends[58] in that increasing the basis set size at the SCF level of theory generally decreases bond lengths, whereas

Table 1. Theoretical Results for S_2 ($^3\Sigma_g^-$)[a]

	SCF			CISD		
	DZP	TZ2P	TZ2P+f	TZ2P	TZ2P+f	expt[b]
r_e	1.878	1.870	1.864	1.897	1.885	1.889
ω_e	810	820	826	758	778	726

[a] Bond lengths in Å, vibrational frequencies in cm^{-1}. [b] Data from ref 24.

improvement in the theoretical method from SCF to CISD, at a given basis set level, increases bond lengths. Bond angles change rather little (range $\approx 6°$) with these changes in theoretical approach with the exception of the torsional angle in the helical isomer. However, the singlet cis and trans isomers, which have been studied more thoroughly than other isomers, do not behave in this "standard" way; single-reference results are particularly erratic for these two species. At the TCSCF and triplet SCF levels the central bond of the cis and trans isomers shows the trends described above, but the terminal bonds decrease in length not only with improvement of the basis set but also with the addition of electron-correlation effects, and this is also true for the helical isomer. In addition the magnitudes of the geometry changes for the basis set and correlation improvements have been reduced markedly from the SCF results. These observations can be rationalized from the qualitative discussion of the bonding in open chain S_4 isomers in the Introduction; to be even qualitatively correct, the singlet wave function must be of two-configuration form.

Geometrical parameters predicted for S_2 with the TZ2P and TZ2P+f basis sets are given in Table I. The bond length in S_2 is reliably predicted with the TZ2P+f basis set at the CISD level of theory although the harmonic vibrational frequency is still somewhat high considering that the experimental value is a harmonic frequency also. The conclusion is that f functions will make only small structural differences to a complex such as S_4. If the typical S–S double bond length is taken to be 1.889 Å, as in S_2,[16] all bond lengths for all isomers of S_4 are greater than this value. The typical S–S single bond distance is taken to be 2.061 Å,[1c] derived from structural characterization of long sulfur chains; the gas-phase S–S distance in H_2S_2 of 2.060 Å is also very close to this value.[59] For a cyclic sulfur molecule such as S_4, single bonds might be expected to deviate from this value somewhat since steric factors will presumably be more important, although since P_4 with 60° bond angles is more stable than cubic P_8 with 90° angles, one should not assume that the structural concepts that apply for first-row atoms will necessarily be so reliable for other parts of the periodic table. Despite this qualification, the bonds in the puckered four-membered-ring isomer and the ring bonds of the branched three-membered-ring form are indeed several hundredths of an angstrom longer than the standard single bond value mentioned above. The typical S–S–S angle is $\approx 106°$,[1c] and all isomers in this study of S_4 (unless constrained in a ring, for example) show bond angles of this order.

For the S_4 isomers studied here which are true minima, the shortest bonds are those in the branched chain isomer (≈ 1.91 Å) and the exocyclic bond in the branched ring (also ≈ 1.91 Å). In the former molecule the central sulfur atom is formally in a VI oxidation state (double bonds to the terminal atoms by analogy with SO_3) and in the latter a IV oxidation state with an exocyclic double bond (as in isomer 8 in ref 5 where the exocyclic S–S bond distance is 1.862 Å, i.e. shorter than in S_2). Such high oxidation states in a homoatomic molecule such as S_4 are unlikely to be favorable.[10] The terminal bonds in the cis and trans isomers are only slightly longer (≈ 1.92–1.96 Å for cis and ≈ 1.95–1.98 Å for trans) and can therefore be said to have some double bond character. This simple observation demonstrates that Lewis structure b for cis S_4 in the Introduction is unrealistic, since it predicts a double bond only in the central position. The central bonds in the cis and trans structures are clearly effectively single, since they are consistently (excepting the single-reference SCF values) greater than the "typical" single bond length of 2.061 Å.

(55) Lee, T. J.; Allen, W. A.; Schaefer, H. F. *J. Chem. Phys.* 1987, 87, 7062.

(56) Shavitt, I.; Brown, F. B.; Burton, P. G. *Int. J. Quantum Chem.* 1987, 31, 507.

(57) Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* 1985, 115, 259. Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* 1985, 82, 5053.

(58) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; J. Wiley and Sons: New York, 1986.

(59) Marsden, C. J.; Smith, B. J. *J. Phys. Chem.* 1988, 92, 347.

These facts provide further evidence that Lewis structures b and c are not useful representations of cis S_4.

The geometrical structures given in Figure 5 are unusual in that they have a wide range of bond lengths, but since they are all first-order transition states at the SCF level (one imaginary frequency as discussed below), normal bond lengths are not necessarily expected. We initially felt that further study of these four transition-state isomers was not warranted, but since Raghavachari, Rohlfing, and Binkley have shown that the rectangular isomer is greatly stabilized by correlation effects,[60] we decided to obtain vibrational frequencies for this species at the CISD level also. It turned out still to be a transition state whose imaginary frequency leads to the cis isomer, though Raghavachari et al.[60] found all real frequencies with MP2 methods. We believe that MP2 techniques are substantially less reliable than CISD methods, especially for cases that have strong multireference character as for cis, trans, and rectangular S_4, described below. The rectangular and linear isomers are simply two S_2 molecules singlet coupled in either a side-on (resulting in a rectangular ring) or end-on (giving a linear molecule) fashion. In each isomer, the shorter S—S bond is in fact shorter than the S=S bond in S_2, due to delocalization of the antibonding π electrons. The long S—S bond for the rectangular isomer is longer than that for the linear since the π^* orbitals have greater spatial extent perpendicular to the axis than along it. The square-planar isomer is simply a transition state between two forms of the puckered-ring isomer and has bond lengths that deviate little from those in the puckered ring. The pyramidal isomer is in a sense derived from the hypothetical tetrahedral isomer by a C_{3v} distortion. A tetrahedral form of S_4 will Jahn–Teller distort on both the singlet and triplet surfaces, since the LUMO for tetrahedral P_4 is triply degenerate t_2, which cannot accommodate the four extra electrons in S_4 without structural distortion. Or it may alternatively be viewed as a transition state between the branched ring and branched chain isomers.

We searched at the SCF level for a planar T-shaped (C_{2v} symmetry) isomer of S_4, which we anticipated might be a transition state linking the D_{3h} branched chain isomer with two S_2 molecules. It became clear that a single-reference approach would not be an appropriate way to locate any such stationary point, since there is a change in configuration. We did not feel it worthwhile to perform multireference calculations to locate this possible stationary point, which appeared to be at high energy at the SCF level.

(b) Relative Energies of S_4 Isomers. The main thrust of this work on S_4 has been to investigate low-lying isomers and determine the lowest isomer on the potential energy hypersurface. The experimental results obtained so far, as summarized in the Introduction, have produced quite a range of data for S_4, without being able to determine definitively which is the most stable form. Most notable in this regard are the 13 apparently different vibrational frequencies that have plausibly been assigned[12-14] to S_4. This suggests that there are at least two, and possibly more, experimentally accessible low-lying states on the S_4 potential energy hypersurface.

The energies of all the singlet stationary points located here for S_4 (relative to the single-reference cis results) are given in Table II at six different levels of theory ranging from DZP SCF to TZ2P CISD+Q. Absolute energies (au) for the planar cis isomer, from which energies of the other isomers can be obtained if desired, are as follows: DZP SCF, -1589.43150; TZ2P SCF, -1589.97871; DZP CISD, -1589.92825; DZP CISD+Q, -1590.01153; TZ2P CISD, -1590.49044; TZ2P CISD+Q, -1590.58146. The substantial magnitudes of the estimated corrections for quadruple excitations should be noted; they are just one indication that a single-reference account of the cis isomer of S_4 is unreliable. Table III contains a more selective set of results, including those for the singlet trans and puckered ring isomers relative to the two-configuration cis values for the singlet cis isomer, and data for some

(60) Raghavachari, K.; McMichael Rohling, C.; Binkley, J. S., private communication.

Table II. Energies (kcal mol⁻¹) of S_4 Isomers Relative to the Single-Reference Cis Isomer[a]

	DZP	TZ2P
Branched Chain ($^1A_1'$)		
ΔE_{SCF}	14.4	10.5
ΔE_{CISD}	21.8	15.7
ΔE_{CISD+Q}	25.9	18.5
Trans (^1A_g)		
ΔE_{SCF}	7.3	6.3
ΔE_{CISD}	9.2	7.8
ΔE_{CISD+Q}	9.8	8.0
Puckered Ring ($^1A_1$)		
ΔE_{SCF}	-19.0	-11.8
ΔE_{CISD}	-3.3	-0.7
ΔE_{CISD+Q}	+2.9	+3.6
Branched Ring ($^1A'$)		
ΔE_{SCF}	-1.0	-0.5
ΔE_{CISD}	+8.0	+6.0
ΔE_{CISD+Q}	+11.9	+8.8
Rectangular Ring (^1A_g)		
ΔE_{SCF}	13.5	
ΔE_{CISD}	4.0	
ΔE_{CISD+Q}	0.9	
Square Ring ($^1A_{1g}$)		
ΔE_{SCF}	-14.9	
Pyramidal ($^1A_1$)		
ΔE_{SCF}	69.7	
Linear ($^1\Sigma_g^+$)		
ΔE_{SCF}	74.4	

[a] Values headed DZP are derived from fully optimized geometries (either SCF or CISD), while TZ2P values were obtained at the TZ2P SCF geometry.

Table III. Energies (kcal mol⁻¹) of S_4 Isomers Relative to Two-Reference Theoretical Treatments of the $^1A_1$ Ground State of the Cis Isomer[a]

	DZP	TZ2P
Cis ($^3B_2$)		
ΔE_{SCF}	10.6	5.4
ΔE_{CISD}	6.5	
ΔE_{CISD+Q}	7.1	
Trans (^3B_u)		
ΔE_{SCF}	8.7	2.5
ΔE_{CISD}	7.2	7.7
ΔE_{CISD+Q}	9.1	9.3
Trans (^1A_g)		
ΔE_{TCSCF}	1.3	1.3
$\Delta E_{TC-CISD}$	4.9	4.7
$\Delta E_{TC-CISD+Q}$	6.1	5.6
Puckered Ring ($^1A_1$)		
ΔE_{SCF}	22.8	16.5
ΔE_{CISD}	15.0	15.6
ΔE_{CISD+Q}	15.0	15.8
Helical (^3B)		
ΔE_{SCF}	7.8	1.6
ΔE_{CISD}	6.4	7.9
ΔE_{CISD+Q}	7.8	9.8
Rectangular (^1A_g)[b]		
ΔE_{SCF}	10.9	
ΔE_{CISD}	3.7	
ΔE_{CISD+Q}	0.3	

[a] Column headings as for Table II. [b] All results at the DZP CISD geometry.

triplet states which are described below. Absolute energies (au) for cis S_4 relevant to the results in Table III are as follows: DZP TCSCF, -1589.49801; TZ2P TCSCF, -1590.02385; DZP TC-CISD, -1589.95743; DZP TC-CISD+Q, -1590.03086; TZ2P TC-CISD, -1590.51630; TZ2P TC-CISD+Q, -1590.60015. The DZP values in Tables II and III are comparisons between energies evaluated for all species at optimized geometries, i.e. either SCF

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or CISD. However, all values in the TZ2P columns were determined at the SCF geometry, since geometry optimization at the TZ2P CISD level was not felt to be worth the enormous computing effort that would have been necessary. Geometry changes due to correlation are not large enough to alter the relative energies significantly, compared to the differences discussed below which emerge when multireference methods are used in place of standard single-reference CISD techniques; for example, the difference in CISD energies for the cis isomer, which is the species whose geometry is most affected by correlation, when evaluated with the DZP basis at the SCF and CISD geometries, is some 2.8 kcal mol⁻¹. While this is not a negligible energy change, it is of relatively minor significance compared with the remaining theoretical uncertainties. For the same reason, zero-point vibrational corrections have also been omitted from the relative energies in Tables II and III.

Perhaps the single most important point to be made concerning our studies on the various S_4 isomers is that their relative energies are *extremely* sensitive to the sophistication of the theoretical method employed. At the single-reference level (Table II) some interesting trends are evident. As electron correlation is described with increasing accuracy (SCF to CISD to CISD+Q), the cis isomer is preferentially stabilized with respect to all other isomers except the trans; this suggests that there must be some significant multireference character in the singlet states of the cis and trans isomers, as was predicted by the qualitative considerations in the Introduction. For example, the puckered ring isomer is lower than the cis isomer by nearly 19 kcal mol⁻¹ at the DZP SCF level but is only 3.3 kcal mol⁻¹ lower at the CISD level and is 2.9 kcal mol⁻¹ *above* the cis isomer with the inclusion of the Davidson correction. This energy difference becomes much larger with the CCSD, CCSDT-1, and multireference (MR)-CISD methods, which are discussed below. Comparable changes are found with the TZ2P basis; a difference of 11.8 kcal mol⁻¹ at the SCF level is reduced to 0.7 kcal mol⁻¹ at the CISD level, with the Davidson correction resulting in the cis isomer being *lower* than the puckered ring by 3.5 kcal mol⁻¹. It is also notable that the cis isomer is stabilized relative to the puckered ring by use of the TZ2P basis even at the SCF level, by more than 7 kcal mol⁻¹, while the branched chain isomer is most affected by expansion of the basis from DZP to TZ2P at the SCF level, gaining almost 4 kcal mol⁻¹ relative to the cis structure. Presumably the improved description of the branched chain and cis isomers with the TZ2P basis has arisen from its more complete set of d functions, as both these isomers contain S in positive environments (the central S in the branched chain isomer is formally in oxidation state VI, while structure c in the Introduction for the cis isomer also contains hypervalent central S atoms). At the single-reference CISD+Q level, all other isomers are over 6 kcal mol⁻¹ higher in energy than the cis structure, except the square-planar transition state which is similar in nature to and only slightly less stable than the puckered ring.

At the SCF level, the energy of the LUMO, which is of a_2 symmetry in Figure 2iii, is *negative* for both the planar cis and trans isomers. (Although one might not expect an antibonding orbital with three nodes to be so close in energy to its bonding counterpart, it must be remembered that p_π-p_π overlap is weak for second-row atoms such as sulfur.[61]) This implies that there may be low-lying triplet states for these two isomers. Indeed, the ^3B_u state of the trans isomer is the global minimum for S_4 at the SCF level, being 40.3 and 31.5 kcal mol⁻¹ below the trans singlet with the DZP and TZ2P bases, respectively, while the planar $^3B_2$ cis structure is also more stable than its closed-shell singlet counterpart (though evaluation of the vibrational frequencies reveals that the cis triplet is in fact not a true minimum, but a transition state between two equivalent helical forms). Since the HOMO is S–S bonding for the central atoms whereas the LUMO is antibonding, as shown in Figure 2iii, the central S–S bond is much longer for the triplets than the singlets, by some 0.21 (cis) or 0.17 Å (trans). Triplet states of the branched chain isomer

were studied at the DZP SCF level, but they were found to be very high in energy.

(c) **Multiconfigurational Results.** The use of the TCSCF wave function enables a better zeroth-order description of the cis and trans isomers to be made and also provides a balanced comparison between the singlet and triplet states of the isomers. Results are shown in Table III for the closed-shell singlet states of the cis, trans, and puckered ring isomers and for the lowest triplet states of the cis, trans, and helical isomers, relative again to the TCSCF and TC-CISD data for the cis singlet. (We have not provided data for the energies of triplet states relative to singlets evaluated at single-reference levels, since we do not feel such comparisons would be very meaningful.) Here the most striking observation is that energy differences are now more stable with respect to increasing the level of electron correlation. With the sole exception of the DZP SCF results, the puckered ring is seen to be consistently some 15 kcal mol⁻¹ above the cis isomer. The cis triplet state is now higher than the singlet, by 6.5 kcal mol⁻¹ (DZP CISD result), but this triplet is a transition state between the helical isomers. Thus the "true" cis triplet is the helical form which is 6.4 kcal mol⁻¹ higher than the cis singlet at the same level of theory. The singlet and triplet states of the trans isomer are both higher than the cis singlet, with the singlet–triplet splitting in the trans (≈3 kcal mol⁻¹) being appreciably smaller than in the cis isomer due to the smaller through-space interaction, as described in the Introduction.

To summarize these SCF, TCSCF, CISD, and TC-CISD results, the puckered four-membered-ring isomer is clearly the most stable singlet at the SCF level, followed by the branched three-membered ring and the planar cis species; the two latter isomers are almost degenerate. Inclusion of electron correlation effects stabilizes the planar cis and trans isomers compared to all others, by substantial amounts. (The rectangular isomer is lowered even more with the inclusion of electron correlation than are the cis and trans forms, but it is still a transition state, rather than a true minimum, even at the CISD level.) Triplet isomers of S_4 are more stable than any singlets at the SCF level, but the lowest triplet lies about 8 kcal mol⁻¹ above the cis singlet once a realistic theoretical description of the cis form is employed.

In view of the indications provided by the TCSCF studies that a single-reference treatment is not very suitable for the cis and trans isomers of S_4, we felt it important to attempt to obtain the relative energies of the most important isomers from a multireference approach in which more than two configurations are explicitly considered. To this end, a few studies were undertaken on the cis, trans, rectangular, puckered four-membered-ring and branched three-membered-ring isomers with a DZP pseudopotential basis (441/221, d exponent 0.55)[62] at the all-electron DZP CISD geometries. The PSHONDO[63] and CIPSI[64] programs were used: the philosophy of these crude methods is to try to recover the qualitative effects of a full MR-CISD procedure, without incurring the crippling computational expense, as follows. Determinants are divided into four classes, imaginatively labeled A, B, C, and D in order of decreasing importance. Starting from an SCF calculation, the importance of individual determinants is estimated by second-order perturbation theory; the most important, whose coefficient in the final wave function exceeds a threshold that turned out to be about 0.01 for S_4, define a reference space B. The dimension of class B cannot exceed 200. The few most important determinants in B, whose coefficients exceeded 0.03 in the calculations on S_4, make up class A, and the final orbitals are obtained from an MCSCF calculation that includes all configurations arising from class A determinants. Membership of classes A and B is determined iteratively and self-consistently. The number of configurations in the MCSF treatment was 9 for

(61) See, for example: Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1987,** *109,* 5217.

(62) Durand, P.; Barthelat, J. C. *Theor. Chim. Acta* **1975,** *38,* 283.

(63) The PSHONDO program is a modification by J. P. Daudey of the HONDO package described in Dupuis, M.; Rys, J.; King, H. F. *J. Chem. Phys.* **1976,** *65,* 111.

(64) Huron, B.; Malrieu, J.-P.; Rancurrel, P. J. *J. Chem. Phys.* **1973,** *58,* 5745. Evangelisti, S.; Daudey, J.-P.; Malrieu, J.-P. *Chem. Phys.* **1975,** *75,* 91. Pelissier, M. Ph.D. Thesis, Universite Paul Sabatier, Toulouse, 1980.

the cis isomer, 10 for the trans, 17 for the puckered four-membered ring, and 14 for the branched three-membered ring.

All single and double excitations from the reference space B are considered. Class C comprises those determinants arising from those excitations whose coefficients are of intermediate value, being too small for class B membership, but which exceed a second threshold that was varied down to about 0.003, with the dimension of C never exceeding 5000. The correlation contribution from classes B and C is determined variationally, but only those determinants in B act as generators. Second-order perturbation theory is used to estimate the contribution from the remaining determinants in class D, which numbered $3.0–3.6 \times 10^6$ for S_4. Finally, one extrapolates class C to encompass all of D, to obtain the final energy.[64] The performance of this method has been reviewed very recently,[65] and it has been shown in some cases to give qualitative agreement with full CI, providing that the number of determinants in class C is sufficiently large.

The following results were obtained (energies relative to the cis isomer are given in kcal mol⁻¹, since absolute energies are of no importance with a pseudopotential basis): SCF, rectangular +17.8, trans +7.1, puckered ring −15.1, branched ring +0.5; single-reference CISD, rectangular +9.0, trans +10.0, puckered ring −0.3, branched ring +11.5; MR-CISD, rectangular +2.3, trans +13.4, puckered ring +22.1, branched ring +23.6; MR-CISD with the generalized quadruples correction,[56] rectangular +1.8, trans +14.7, puckered ring +29.0, branched ring +28.5. It is clear that the multireference treatment substantially stabilizes the cis and trans isomers over the puckered- and branched-ring forms, even beyond what has already been shown in the TC-CISD results. To a lesser extent, cis is favored over trans by the multireference treatment. The branched ring gains about 12 kcal mol⁻¹ compared to the puckered ring from the multireference approach, so that these two ring forms become almost degenerate. Thus the high relative stability of three-membered rings in sulfur chemistry, already suggested by studies of S_3,[6] is emphasized by our results. It is important to note that the pseudopotential relative energies of the different isomers at SCF and CISD levels are similar to those obtained with the all-electron DZP basis; this observation suggests that the selection and extrapolation procedures employed may be reliable.

Our MR-CISD results concerning the relative stability of the rectangular isomer are in conflict with those recently reported by Raghavachari et al.,[60] who found this isomer to be the global minimum at their highest level of theory for S_4. These workers used the 6-31G* basis set at the 3-21G* SCF geometry; at the HF, MP2, MP3, MP4, and QCISD(T) levels, the rectangular isomer was found to be +19.3, −15.2, +1.6, −6.9, and −1.7 kcal mol⁻¹, relative to the cis isomer. In our work, the rectangular isomer is always less stable than the cis, though only by small amounts at correlated levels. The most telling evidence against the rectangular isomer is its imaginary frequency at the CISD level. In addition, our interpretation of the vibrational spectra reported for S_4 is inconsistent with the presence of the rectangular isomer as discussed below.

In the present MCSCF study of cis S_4, the Hartree–Fock reference configuration had a coefficient of 0.89, while that for the HOMO-LUMO double excitation was 0.41. These two configurations made up the bulk of the wave functions, as the next most important coefficient was 0.10, which was for the double excitation from the highest occupied to lowest unoccupied orbital of σ symmetry. In the MR-CISD studies, these coefficients changed modestly, to 0.90, 0.33, and 0.085, respectively, indicating that the importance of the additional configurations is somewhat overestimated by the MCSCF procedure in which only a rather small number of configurations are explicitly considered. The multireference character of the rectangular isomer is very similar to that of the cis species. These data suggest that while the all-electron TCSCF method should recovery at least the bulk of the multireference character in cis S_4, the SCF-TCSCF structural

changes are probably unrealistically large.

Since the approximate MR-CISD studies described above produced rather dramatic stabilization of the cis isomer, over and above that produced by TC-CISD compared to standard single-reference CISD, we felt it desirable to obtain some confirmation of the importance of multireference effects in S_4, preferably by using some method that is "automatic" and "objective", and which does not rely on possibly subjective selection by the operator of particular configurations or thresholds, or on extrapolations. It is widely agreed[66] that the CCSD approach, which approximates a multireference treatment, is the best available single-reference technique, particularly when the effects of triple excitations are incorporated. CCSDT-1[67] energies were evaluated with the DZP basis at the DZP CISD geometries for the cis, trans, and puckered ring isomers of S_4. The cis isomer was found to be the most stable, with absolute CCSD and CCSDT-1 energies of −1590.02869 and −1590.07165 au, respectively; relative to the cis form, CCSD and CCSDT-1 energies are +4.6 and +17.6 kcal mol⁻¹ for the puckered ring isomer and +9.7 and +8.7 kcal mol⁻¹ for the planar trans species. The degree of multireference character in a coupled cluster study may be estimated from the parameter known as T_1, which is normalized for the number of valence electrons; its value is 0.014 for the puckered ring isomer, 0.023 for the cis species, and 0.029 for the trans species. A value greater than 0.02 has been taken to indicate strong multireference character.[68] These results and the approximate MR-CISD findings therefore agree that the lowest energy isomer of S_4 is the planar cis structure, for which a single-reference description is not adequate. The much greater importance of triple substitutions for the cis and trans isomers than for the puckered ring is particularly noteworthy, and again it points to the multireference nature of the cis and trans isomers. Quantitatively, the approximate MR-CISD and CCSDT-1 results are not in perfect agreement, but since they did not use the same basis set, and since neither could be described as full CI, some relatively small discrepancies are to be expected. We strongly suspect that the CCSDT-1 results provide a more accurate account of the relative energies of the various S_4 isomers.

One further point to note regarding the ΔE(cis-puckered ring) is that the results reported here agree with the conclusion of Dixon and Wasserman[38a] that the lowest energy structure for S_4 is 25 kcal mol⁻¹ lower than that of the puckered ring. This value (25 kcal mol⁻¹) is derived from experimental and theoretical results assuming a ring structure. The theoretical studies performed by Dixon and Wasserman[38a] utilized a DZ contraction of the McLean and Chandler[38b] primitive set with the addition of a single set of d functions. The results from this DZP-type basis set are remarkably close to those presented here for geometry and vibrational frequencies, using a TZ contraction with the addition of two sets of d-type polarization functions. The best energy differences presented in this work for the ΔE(cis-puckered ring) are the CCSDT-1 value of 17.6 kcal mol⁻¹ and the approximate MR-CISD+Q value of 29.0 kcal mol⁻¹, supporting the conclusion that the puckered ring isomer is higher than the lowest isomer for S_4(cis) by a value of approximately 20 kcal mol⁻¹.

We have also investigated the torsional potential that links the cis and trans planar singlet isomers. TCSCF theory was used, since, as explained in recent work[5] on the related molecule S_2O_2, this is quintessentially a two-configuration problem. The transition state separating the cis and trans isomers is characterized by a dihedral angle of 134.4° (where the cis and trans isomers have dihedral angles of 0° and 180°, respectively). Other structural parameters for the transition state differ only marginally from the values for the cis and trans isomers; the central and terminal bond lengths are 2.134 and 1.986 Å, respectively, while the bond

(65) (a) Illas, F.; Rubio, J.; Ricart, J. M. *J. Chem. Phys.* **1988**, *89*, 6376. (b) Novoa, J. J.; Mota, F.; Arnau, F. *Chem. Phys. Lett.* **1990**, *165*, 503.

(66) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. Scuseria, G. E.; Scheiner, A. C.; Lee, T. J.; Rice, J. E.; Schaefer, H. F. *J. Chem. Phys.* **1987**, *86*, 2881.
(67) Lee, Y. S.; Bartlett, R. J. *J. Chem. Phys.* **1984**, *80*, 4371. Scuseria, G. E.; Schaefer, H. F. *Chem. Phys. Lett.* **1988**, *146*, 23. Scuseria, G. E.; Schaefer, H. F. *Chem. Phys. Lett.* **1988**, *148*, 205.
(68) Lee, T. J.; Rice, J. E.; Scuseria, G. E.; Schaefer, H. F. *Theor. Chim. Acta* **1989**, *75*, 81. Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem.* **1989**, *S23*, 199.

Table IV. Harmonic Vibrational Frequencies (cm^{-1}) and Infrared ($km\ mol^{-1}$) and Raman ($A^4\ amu^{-1}$) Intensities for the D_{3h} Symmetry Branched Chain Isomer ($^1A_1'$)[a]

mode (assgn)	SCF (DZP)	SCF (TZ2P)	CISD (DZP)
ω_1 (sym str)	506	525	497 (a_1')
ω_2 (asym str)	740	768	746 (e')
ω_3 (sym def)	258	269	247 (e')
ω_4 (o.o.p.)	288	306	277 (a_2'')
I_1^{IR}	0	0	0
I_2^{IR}	410	490	122
I_3^{IR}	2	2	3
I_4^{IR}	3	1	4
I_1^{Raman}	83		
I_2^{Raman}	2		
I_3^{Raman}	16		
I_4^{Raman}	0		

[a] In this and subsequent tables the following abbreviations will be used: sym, symmetric; asym, antisymmetric; cent, central; str, stretch; def, deformation; o.o.p., out-of-plane; exo, exocyclic; and assgn, assignment; IR, infrared.

Table V. Harmonic Vibrational Frequencies, Intensities, and Dipole Moments for the Global Minimum Cis Isomers and the Triplet Cis Isomer[a]

(a) Global Minimum Cis Isomer ($^1A_1$)

mode (assgn)	SCF (DZP)	SCF (TZ2P)	CISD (DZP)
ω_1 (sym str)	696	734	701 (a_1)
ω_2 (cent str)	517	561	421 (a_1)
ω_3 (sym def)	146	139	141 (a_1)
ω_4 (torsion)	219	224	222 (a_2)
ω_5 (asym str)	626	643	693 (b_2)
ω_6 (asym def)	366	372	353 (b_2)
I_1^{IR}	7	17	3
I_2^{IR}	7	2	8
I_3^{IR}	0	0	1
I_4^{IR}	0	0	0
I_5^{IR}	392	431	81
I_6^{IR}	2	2	1
μ	2.21	2.15	1.73
I_1^{Raman}	26		
I_2^{Raman}	291		
I_3^{Raman}	25		
I_4^{Raman}	1		
I_5^{Raman}	1		
I_6^{Raman}	11		

(b) Triplet Cis Isomer ($^3B_2$)[b]

mode (assgn)	SCF (DZP)	SCF (TZ2P)	SCF (DZP)	SCF (TZ2P)
			I_1^{IR} 11	10
ω_1 (sym str)	576	605 (a_1)	I_2^{IR} 0	0
ω_2 (cent str)	387	416 (a_1)	I_3^{IR} 0	0
ω_3 (sym def)	159	157 (a_1)	I_4^{IR} 0	0
ω_4 (torsion)	85i	97i (a_2)	I_5^{IR} 2	1
ω_5 (asym str)	574	595 (b_2)	I_6^{IR} 1	1
ω_6 (asym def)	296	303 (b_2)		
			μ 0.11	0.02

(c) Cis Isomer ($^1A_1$)[c]

mode (assgn)	TCSCF (DZP)		TCSCF (DZP)
		I_1^{IR}	18
ω_1 (sym str)	605 (a_1)	I_2^{IR}	5
ω_2 (cent str)	394 (a_1)	I_3^{IR}	0
ω_3 (sym def)	156 (a_1)	I_4^{IR}	0
ω_4 (torsion)	97 (a_2)	I_5^{IR}	2
ω_5 (asym str)	621 (b_2)	I_6^{IR}	1
ω_6 (asym def)	320 (b_2)		
		μ	0.27

[a] Units as for Table IV with dipole moments in D. [b] The CISD/DZP dipole moment in 0.34 D. [c] The CISD/DZP dipole moment is 0.87 D.

angle is 104.5°. Astonishingly, this transition state is only 1.5 kcal mol^{-1} above the planar cis isomer, or 0.22 kcal mol^{-1} above the trans, showing that the cis and trans isomers can interconvert very readily. Such a low barrier to internal rotation is especially

Table VI. Harmonic Vibrational Frequencies and Intensities for the Trans Isomers and the Triplet Trans Isomer[a]

(a) Trans isomer (^1A_g)

mode (assgn)	SCF (DZP)	SCF (TZ2P)	CISD (DZP)
ω_1 (sym str)	674	711	678 (a_g)
ω_2 (cent str)	593	627	528 (a_g)
ω_3 (sym def)	271	279	252 (a_g)
ω_4 (torsion)	110	113	101 (a_u)
ω_5 (asym str)	594	616	681 (b_u)
ω_6 (asym def)	153	159	140 (b_u)
I_1^{IR}	0	0	0
I_2^{IR}	0	0	0
I_3^{IR}	0	0	0
I_4^{IR}	3	3	2
I_5^{IR}	705	785	128
I_6^{IR}	15	16	5
I_1^{Raman}	16		
I_2^{Raman}	1305		
I_3^{Raman}	26		
I_4^{Raman}	0		
I_5^{Raman}	0		
I_6^{Raman}	0		

(b) The Triplet Trans Isomer (^3B_u)

mode (assgn)	SCF (DZP)	SCF (TZ2P)	SCF (DZP)	SCF (TZ2P)
			I_1^{IR} 0	0
ω_1 (sym str)	564	599 (a_g)	I_2^{IR} 0	0
ω_2 (cent str)	496	525 (a_g)	I_3^{IR} 0	0
ω_3 (sym def)	225	234 (a_g)	I_4^{IR} 0	0
ω_4 (torsion)	23	24 (a_u)	I_5^{IR} 14	15
ω_5 (asym str)	559	587 (b_u)	I_6^{IR} 0	1
ω_6 (asym def)	130	138 (b_u)		

(c) Trans Isomer (^1A_g)

mode (assgn)	TCSCF (DZP)		TCSCF (DZP)
ω_1 (sym str)	570 (a_g)	I_1^{IR}	0
ω_2 (cent str)	479 (a_g)	I_2^{IR}	0
ω_3 (sym def)	230 (a_g)	I_3^{IR}	0
ω_4 (torsion)	26 (a_u)	I_4^{IR}	0
ω_5 (asym str)	583 (b_u)	I_5^{IR}	16
ω_6 (asym def)	137 (b_u)	I_6^{IR}	1

[a] Units as for Table IV.

surprising when compared to the cis and trans barriers in H_2S_2[69] (skew C_2 conformation) of 8.1 and 5.8 kcal mol^{-1}, or the much larger barriers of the order of 24 kcal mol^{-1} in $FSSF$[70] (which also has a skew C_2 conformation). However, it should be recalled that the more complete studies described above, i.e. CCSD, CCSDT-1, and MR-CISD levels of theory, indicated that the energy difference between the cis and trans isomers is substantially larger than the 1.3 kcal mol^{-1} result from TCSCF theory, so we anticipate that the cis/trans barrier is really rather greater than suggested by TCSCF theory.

(d) Vibrational Frequencies and S–S Force Constants. The evaluation of vibrational frequencies for all isomers of S_4 serves two important purposes. First, the vibrational frequencies are essential for the complete characterization of the stationary points which have been located by optimization procedures. Second, the evaluated vibrational frequencies and their intensities provide additional ways in which the identity of the most stable isomer may be determined, by comparison with experimental results. Force constants are of interest because of the detailed information they convey about the character of bonds. It is more meaningful for polyatomic molecules to compare force constants than vibrational frequencies, where this is possible, since the frequencies in general are determined by several different force constants.

Vibrational frequencies evaluated for the different isomers of S_4 are given in Tables IV–XI. First, as already mentioned, we

(69) Urban, S.; Herbst, E.; Mittler, P.; Winnewisser, G.; Yamada, K. M. T.; Winnewisser, M. *J. Mol. Spectrosc.* **1989**, *137*, 327.

(70) Marsden, C. J.; Oberhammer, H.; Losking, O.; Willner, H. *J. Mol. Struct.* **1989**, *193*, 233.

Table VII. Harmonic Vibrational Frequencies and Intensities for the Puckered Ring Isomer ($^1A_1$)[a]

	SCF (DZP)	SCF (TZ2P)	CISD (DZP)
mode (assgn)			
ω_1 (ring str)	533	561	520 (a_1)
ω_2 (pucker)	178	195	187 (a_1)
ω_3 (ring def)	498	530	474 (b_1)
ω_4 (ring def)	352	357	335 (b_2)
ω_5 (ring def)	471	502	446 (e)
I_1^{IR}	0	0	0
I_2^{IR}	0	0	0
I_3^{IR}	0	0	0
I_4^{IR}	0.4	0.2	0.3
I_5^{IR}	0.2	0.2	0.2
I_1^{Raman}	63	56	
I_2^{Raman}	3	2	
I_3^{Raman}	34	12	
I_4^{Raman}	10	9	
I_5^{Raman}	8	12	

[a] Units as for Table IV.

Table VIII. Harmonic Vibrational Frequencies and Intensities for the Branched Ring Isomer ($^1A'$)[a]

	SCF (DZP)	SCF (TZ2P)	CISD (DZP)
mode (assgn)			
ω_1 (exo str)	617	650	680 ($a\mu$)
ω_2 (basal str)	576	613	551 (a')
ω_3 (sym str)	435	463	400 (a')
ω_4 (wag)	231	245	223 (a')
ω_5 (asym str)	380	410	(a'')
ω_6 (twist)	185	199	(a'')
I_1^{IR}	195	222	
I_2^{IR}	11	2	
I_3^{IR}	11	8	
I_4^{IR}	4	2	
I_5^{IR}	12	12	
I_6^{IR}	0	0	
μ	2.15	2.22	1.60
I_1^{Raman}	13		
I_2^{Raman}	70		
I_3^{Raman}	41		
I_4^{Raman}	21		
I_5^{Raman}	31		
I_6^{Raman}	21		

[a] Units as for Table Va.

Table IX. Harmonic Vibrational Frequencies and Intensities for the Lowest Triplet State of the Helical Isomer (^3B)[a,b]

	SCF (DZP)	SCF (TZ2P)		SCF (DZP)	SCF (TZ2P)
mode (assgn)			I_1^{IR}	3	3
ω_1 (sym str)	533	562 (a)	I_2^{IR}	0	0
ω_2 (cent str)	456	488 (a)	I_3^{IR}	1	1
ω_3 (sym bend)	184	195 (a)	I_4^{IR}	0	0
ω_4 (torsion)	38	45 (a)	I_5^{IR}	2	2
ω_5 (asym str)	540	596 (b)	I_6^{IR}	1	1
ω_6 (asym bend)	258	259 (b)	μ	0.04	0.09

[a] Units as for Table Va. [b] The CISD/DZP dipole moment is 0.04 D.

note that the triplet state of the cis isomer ($^3B_2$, Table Vb) is a transition state since it has exactly one imaginary frequency, which is the torsional motion. The isomers in Figure 5 are also transition states (results in Tables X and XI), with the square-planar ring being a transition state between two equivalent puckered ring structures. The rectangular isomer and the linear isomer can be thought of as transition states between equivalent forms of the cis isomer, while the pyramidal structure links the branched ring and branched chain species. The pyramidal isomer is however very high in energy (at the DZP SCF level) and would be essentially inaccessible.

To place the evaluated vibrational frequencies for the various isomers in context, we recall that typical stretching frequencies for S–S single bonds are around 500 cm^{-1},[23] while the harmonic

Table X. Harmonic Vibrational Frequencies for the Rectangular Isomer (^1A_g)[a]

	SCF (DZP)	CISD (DZP)		SCF (DZP)	CISD (DZP)
mode (assgn)			I_1^{IR}	0	
ω_1 (sym str)	817	877 (a_g)	I_2^{IR}	0	
ω_2 (sym str)	344	334 (a_g)	I_3^{IR}	0	
ω_3 (trans def)	375	355 (b_{3g})	I_4^{IR}	0	
ω_4 (pucker)	277	262 (a_u)	I_5^{IR}	885	
ω_5 (asym str)	667	782 (b_{1u})	I_6^{IR}	38	
ω_6 (cis def)	257i	120i (b_{2u})			

[a] Units as for Table Va.

Table XI. Harmonic Vibrational Frequencies and Intensities for the Square Ring ($^1A_{1g}$), Pyramidal ($^1A_1$), and Linear ($^1\Sigma_g^+$) Isomers of S_4 Calculated at the SCF/DZP Level[a]

mode	square ring	pyramidal	linear
ω_1	512 (sym str)	563 (sym str)	833 (sym str)
ω_2	327 (trans def)	266 (sym def)	265 (cent str)
ω_3	543 (asym str)	605 (asym str)	313 (trans def)
ω_4	132i (pucker)	379i (asym def)	759 (asym str)
ω_5	505 (asym str)		173i (cis def)
I_1^{IR}	0	3	0
I_2^{IR}	0	3	0
I_3^{IR}	0	42	0
I_4^{IR}	0	1178	749
I_5^{IR}	10		0
μ	0	0.90	0

[a] Units as for Table Va.

frequency in doubly bonded S_2 is 726 cm^{-1}.[24] Stretching frequencies for the branched chain isomer (Table IV) are rather high, especially for the antisymmetric motion, which is at 740 cm^{-1} at the DZP SCF level, and only small changes in value are seen at TZ2P SCF and DZP CISD levels. The frequency changes mirror the changes in geometry, as expected from Badger's rules.[71] These values reinforce the deductions from the geometry discussed above in that there is considerable double bond character in the S–S bonds in the branched chain isomer. Vibrational frequencies for the cis isomer from single-reference studies (Table Va) also show some double bond character for the terminal bonds, in keeping with the geometrical predictions. However, results for the triplet state (Table Vb) and from TCSCF theory (Table Vc) show considerably smaller values. One point of interest is that most of the vibrational bands for this isomer have very small infrared intensities but reasonably large Raman intensities. This suggests that Raman spectroscopy will probably give more reliable and complete information about S_4 isomers than can infrared spectroscopy.

Results for the trans isomer (Table VI) show similar trends in frequency and intensity values to those of the cis isomer, but there is one intriguing difference concerning the relative ordering of the symmetric and antisymmetric deformation modes which, though it has been observed before in the closely related molecule S_2O_2,[5] has yet to be explained satisfactorily. In the cis isomer the antisymmetric bend is higher than the symmetric but for trans they are reversed. The effect is very large, as there is nearly a factor of 2 separating the frequencies in both isomers. It arises because the off-diagonal force constant which couples the two in-plane bending motions is negative for the cis isomer, but positive for the trans isomer. For the triplet and TCSCF studies the torsional frequency is predicted to be very low, and this, coupled

(71) Badger, R. M. *J. Chem. Phys.* **1934**, *2*, 128; **1934**, *3*, 710. Herschbach, D. R.; Laurie, V. W. *J. Chem. Phys.* **1961**, *35*, 458.

(72) See, for example: Johnson, D. A. *Some Thermodynamic Aspects of Inorganic Chemistry*, 2nd ed.; Cambridge University Press: Cambridge, U.K.; 1982, pp 197–203.

(73) Pulay, P.; Lee, J.-G.; Boggs, J. E. *J. Chem. Phys.* **1983**, *79*, 3882. Fogarasi, G. Pulay, P. *Annu. Rev. Phys. Chem.* **1984**, *35*, 191.

(74) Marsden, C. J.; Smith, B. J. *J. Mol. Struct. (Theochem)* **1989**, *187*, 337.

Table XII. Harmonic S–S Stretching Force Constants Predicted for Singlet S_4 Isomers[a]

| isomer | | SCF | | CISD |
		DZP	TZ2P	DZP
branched		4.336	4.689	4.352
cis	r_{cent}	3.232	3.761	2.375
	r_{term}	4.252	4.557	4.739
trans	r_{cent}	3.316	3.837	2.472
	r_{term}	3.806	4.096	4.412
puckered ring		2.493	2.591	2.086
branched ring	r_{exo}	3.721	4.014	4.469

[a] Units are aJ $Å^{-2}$.

to the barrier to internal rotation discussed earlier, indicates that there is likely to be ready interconversion of the cis and trans isomers in S_4 vapor. Vibrational frequencies of the puckered four-membered-ring isomer (Table VII) are relatively conventional single bond values with no fundamentals above 520 cm^{-1}, but the infrared intensities predicted for this isomer are strikingly low. Clearly this molecule will be very hard to detect in the infrared unless appreciable amounts can be produced. Here again the Raman technique could provide more information.

Vibrational frequencies for the branched three-membered-ring isomer are given in Table VIII. While the exocyclic stretching frequency at 617 cm^{-1} (DZP SCF), 650 cm^{-1} (TZ2P SCF), and 680 cm^{-1} (DZP CISD) is indicative of some double bond character, it is lower than the stretching frequencies in the branched chain isomer. The atypical increase in the highest frequency as correlation effects are included is particularly notable. Infrared intensities for the branched ring isomer are substantial. Frequencies for the helical isomer (Table IX) are typical of single S–S stretching motions, with the symmetric deformation occurring at lower frequency than the antisymmetric mode as for the cis isomer. Infrared intensities for this helical triplet species are again vanishingly small.

Theoretically predicted vibrational frequencies for the remaining isomers, which are all transition states, are given in Tables X and XI. Frequencies for the square ring and pyramidal isomers are typical values for single bonds, while somewhat higher values are found for the pyramidal isomer since it is related to some degree to the branched-ring and branched-chain isomers. The rectangular and linear isomer frequencies show some very large values for the shorter S–S bond stretch and very low frequencies for the long S–S bonds. These results are in line with the structural results above; the shorter S–S bond in both these isomers is shorter than that in S_2, and the stretching frequency is somewhat higher.

Stretching force constants for the most important singlet isomers of S_4 at the DZP SCF, TZ2P SCF, and DZP CISD levels of theory are presented in Table XII. To put these results in their proper context, we note that the standard experimental values for S–S single and double bonds are 2.77 and 4.96 aJ $Å^{-2}$ in H_2S_2[59] and S_2,[24] respectively. It is worth noting that the ratio of these force constants (1.79) is rather similar to the ratio of the bond energies (1.63), for which standard values[72] are 102.6 and 63 kcal mol^{-1} in S_2 and H_2S_2 or S_8, respectively. Consistently accurate prediction of force constants by ab initio methods is very difficult, though fortuitously good results are sometimes obtained; for example, the DZP basis used here gives a remarkably accurate prediction of 2.80 aJ $Å^{-2}$ for H_2S_2 at the SCF level,[59] but as shown in Table I it overestimates the force constant in S_2 by nearly 25%. The success and utility of Badger's rules[71] imply that force constants depend sensitively on bond lengths, and the results in Table XII certainly show how this is true for S–S bonds. The changes in a given force constant from one column to another are strongly correlated with the corresponding changes in bond length, so the variations in force constant with level of theory are to a significant extent revealing the success of that level in geometry prediction. It is for this reason that Pulay and co-workers have insisted[73] that it is advisable where possible to use the experimental rather than theoretical optimum geometry as reference if accurate force constants are to be obtained, and recent work on nitrogen oxides[74] tends to support this contention. Of course, the fact that ex-

Table XIII. Evaluation of Adiabatic Electronic Excitation Energies for the Cis and Trans Isomers with the TZ2P Basis Set at the TCSCF/TZ2P Geometries[a,b]

	cis ($^1B_2$)	trans (^1B_u)
E_{SCF}	−1589.88844	−1589.89625
E_{CISD}	−1590.39811	−1590.40453
E_{CISD+Q}	−1590.49041	−1590.49652
ΔE_{SCF}[b]	48.7, 85.0	45.5, 78.8
ΔE_{CISD}[b]	57.9, 74.2	46.1, 65.5
ΔE_{CISD+Q}[b]	57.1, 69.4	45.3, 59.9
λ_{SCF}[b]	588, 337	629, 363
λ_{CISD}[b]	494, 386	621, 437
λ_{CISD+Q}[b]	501, 412	632, 477

[a] Energies in hartrees, ΔE in kcal mol^{-1}, and λ in nm. [b] Where two energies or wavelengths are given, the first is relative to a single-reference theoretical treatment and the second relative to a two-reference theoretical treatment.

perimental geometries are not usually available is a pragmatic criticism of Pulay's thesis.

If the relationship between force constants and bond energies that was suggested above is really valid, then the data in Table XII highlight the weakness of the bonds in the four-membered puckered ring isomer and also show the substantial difference between central and terminal bond strengths in the planar cis and trans isomers. Presumably the CISD force constants in Table XII are more reliable than those obtained at the SCF level; it is striking that while the SCF results vary over a wide range, the CISD values fall neatly into only two classes, namely "more-or-less double" (the branched isomer, the terminal bonds in the cis and trans isomers, and the exo bond in the branched ring) and "rather weak single" (the central bonds in the cis and trans isomers and the puckered ring).

While detailed comparisons between the theoretical and experimental frequencies will be given in the discussion below, two general points noted in previous work[22] can be emphasized. First the puckered ring form is expected not to have a vibration above about 520 cm^{-1}, which is supported by the theoretical results here (after reducing the SCF results by a typical factor[58] of 10%). Also the branched ring form is expected to have only one frequency above 520 cm^{-1} (at perhaps 680 ± 25 cm^{-1}, which is the exocyclic stretch); this is a consequence of the previous point, and our theoretical results again support this expectation.

(e) Other Properties for S_4 Isomers. Of the experimental results for S_4 the most unequivocal are the ionization potential of 10.1 eV, measured by Rosinger et al.,[16] and the electronic absorption at 530 nm, first assigned by Meyer[17] and confirmed by Casal et al.[18] Recent work has also assigned a second electronic absorption at 620 nm to S_4.[19] The lowest energy electronic transition in the cis isomer will be to the $^1B_2$ state, which arises from an excitation from the HOMO to the LUMO (see Figure 2). The energy evaluated for this transition is given in Table XIII along with that for the analogous transition to the ^1B_u state for the trans form. We have presented the energy changes and wavelengths calculated for this transition in two ways, relative either to the energy of the appropriate ground-state singlet derived from single reference or to that from TC calculations. We have done this not only because the choice of reference leads to a considerable difference in the results but also more particularly because one can argue with reasonable conviction that either choice of reference is the more suitable. Since we have shown above that the single-reference results for cis S_4 are inadequate, it might seem obvious that the proper choice of reference for the ground state is the more satisfactory TC theory. Alternatively, one could say that if a single-reference method is inadequate for the ground state, it is just as likely to be inadequate for an excited state also, and so a comparison should most properly be made of single-reference energies in both cases, if multireference energies cannot be compared.

The results in Table XIII show that our correlated studies predict absorption wavelengths of about 500 nm for cis S_4 and 630 nm for the trans isomer, if the single-reference method is used

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Table XIV. Evaluation of Electronic Excitation Energies for the Cis Isomer from the CASSCF Method with the DZP Basis Set at the One-Reference CISD Stationary Point Geometries[a]

state	energy	μ	ΔE	λ
$^1A_1$	−1589.57192	1.03	0.0	
$^3B_2$	−1589.54835	0.40	14.8	1934
$^3B_1$	−1589.50512	0.50	41.9	682
$^3A_2$	−1589.50309	0.50	43.2	662
$^1B_2$	−1589.46172	0.97	69.2	414
$^3A_1$	−1589.43403	0.50	86.5	331

[a] Energies in hartree, μ in D, ΔE in kcal mol^{-1}, and λ in nm.

Table XV. Evaluation of Ionization Potentials for the Cis and Trans Isomers by the ΔSCF+CISD Method with the TZ2P Basis Set at the TCSCF Ground-State Equilibrium Geometry

	cis ($^2B_1$)	trans (^2A_u)
E_{SCF}	−1589.68663	−1589.67850
E_{CISD}	−1590.18969	−1590.18152
E_{CISD+Q}	−1590.28074	−1590.27323
ΔE_{SCF}	9.2	9.3
ΔE_{CISD}	8.9	8.9
ΔE_{CISD+Q}	8.7	8.7
expt	10.1	

[a] Energies in hartrees, ΔE and experimental ionization potential in eV.

Table XVI. Evaluation of Ionization Potentials for the Cis Isomer from the CASSCF Method with the DZP Basis Set at the One-Reference CISD Ground-State Equilibrium Geometry[a]

state	energy	ΔE
$^2B_1$	−1589.28263	7.87
$^2A_1$	−1589.25650	8.59
$^2B_2$	−1589.25446	8.64
$^2A_2$	−1589.23085	9.28

[a] Energies in hartrees and ΔE in eV.

for the ground-state energies. These values are in very satisfactory agreement with the experimental values of 530[17,18] and 620[19] nm. However, if the reference energies of the ground state are taken from TC evaluations, the predicted wavelengths are substantially reduced to about 400 and 450 nm, though since the values are very sensitive to the level of theory employed it is not clear exactly which result to take as "best"; it does seem evident that reasonable agreement with the experimental values cannot be found on this basis. While one might be tempted to use the very satisfactory agreement with the experimental results as a clear indication that the appropriate choice of reference energy for the ground state is derived from a single-reference type of study, some doubt arises when one considers an evaluation of the lowest excited states of the cis isomer by a CASSCF method with the DZP basis, presented in Table XIV. Here we see that there is excellent agreement between the electronic excitation predicted by the TZ2P CISD+Q and the DZP CASSCF methods, provided that in the former the TC-CISD+Q energy is used as reference for the ground state. Since the CASSCF technique should treat both ground and excited states equally well, one's first thought might be to assume that it would give more reliable results than the "Δ-CI" approach; a second thought might then be that since the CASSCF method necessarily recovers only a small fraction of the total correlation energy, and since the excitation energy is clearly rather strongly influenced by the effects of correlation (see Table XIII), perhaps the CASSCF result is not superior to that obtained by CISD methods from a single-reference wave function. It should also be noted that the CASSCF method could only be used with the DZP basis, which is perhaps insufficiently flexible to give a good description of excited states, even though it seems adequate for the ground state. These two qualifications together are sufficient, in our judgment, to suggest that the DZP CASSCF value should not be preferred over the TZ2P CISD+Q result.

The results of the evaluation of ionization potentials by a TZ2P ΔSCF+CISD+Q method are given in Table XV for the lowest energy excitations of the cis ($^2B_1$) and trans (^2A_u) isomers. The DZP CASSCF results for the cis isomer are given in Table XVI. We believe that the ΔSCF+CISD+Q method should give a good estimate of the competing effects of relaxation and changes in correlation energy implicit in the ionization process. Unfortunately the result (8.7 eV) is significantly below the measured ionization potential for S_4 of 10.1 eV.[16] It is particularly disappointing that the disagreement between the experimental value of the ionization potential and our results *increases* as the level of theoretical sophistication increases. from SCF to CISD to CISD+Q. One

possible reason for the discrepancy is that the measured ionization potential was not obtained from either the cis or trans isomer of S_4, but in the light of the CCSD, CCSDT-1, and MR-CISD studies described above, we are confident that the cis isomer is the lowest energy form of S_4. As the theoretically predicted value of the ionization potential is too low, our theoretical description is relatively more accurate for the ion than for the ground state; presumably this is an indication that multireference effects are less important for the ion than for the ground state, which is at least plausible in view of the qualitative discussion in the Introductory section.

Several of the isomers of S_4 studied in this work are necessarily nonpolar, but the cis planar isomer will have a non-zero dipole moment, whose magnitude will be of crucial importance in determining whether the microwave spectrum of this isomer can be readily detected. The branched three-membered-ring isomer is also polar. Theoretical values of the dipole moment for the singlet cis isomer, which we predict to be the global minimum for S_4, are rather sensitive to the level of theory used. Our most reliable result, which comes from DZP TC-CISD and is reported in Table Vc, is 0.87 D: since the dipole moment increases at the TCSCF level from 0.27 D with the DZP basis to 0.52 D with the TZ2P basis, presumably the TZ2P TC-CISD value would be of the order of 1.0 D. This is quite sufficient for the pure rotation spectrum to be detectable. The most stable triplet form of S_4 is the helical isomer, for which a rather small dipole moment of only 0.40 D has been evaluated at the CISD level. Although the branched three-membered-ring isomer is predicted to be appreciably higher in energy than the planar cis form, its dipole moment of 1.60 D (CISD) is almost twice as large, so its detection by microwave spectroscopy will be much easier than its relative energy might suggest.

Discussion

In this section we compare our theoretical results for the various S_4 isomers with the diverse experimental data that have been reported and attempt to reconcile the apparent conflicts where they arise. We concentrate on the vibrational spectra of S_4, since they appear to give more direct structural information on S_4 than do the other experimental data; we have already commented on the electronic spectra and the ionization potential in part d of the Results section. Our most sophisticated theoretical studies, of the CCSDT-1 and MR-CISD type, predict that the planar cis isomer of S_4 is more stable than any other minimum by a margin of about 10 kcal mol^{-1}. We therefore attempt first to correlate our predicted frequencies for this isomer with the experimental results, to see how compelling is the evidence for the detection of more than one isomer of S_4. Our task is made particularly difficult by the discrepancies between different experiments, which means that we are forced to evaluate the reliability not only of our work but also of various experiments.

The most comprehensive vibrational study of sulfur vapor is due to Corset, Steudel, and co-workers.[22] They assigned Raman peaks at 682 and 605 cm^{-1} to S_4, but they felt that these bands arise from different isomers which both, however, have electronic absorptions near 515 nm. At least some of the bands at 440, 384, 305, 250, and 190 cm^{-1} were also thought to be caused by S_4. Unfortunately, several of the theoretically evaluated vibrational frequencies for cis S_4 are unusually sensitive to the level of theory used, reflecting the rather sophisticated methods necessary to give a good description of these species. At the SCF level ω_1 increases from 696 to 734 cm^{-1} as the basis is enlarged from DZP to TZ2P,

and with the DZP basis the change from SCF to CISD results in a very modest increase (which of course is rather unusual[58]) to 701 cm^{-1}, but the SCF-to-TCSCF change with the DZP basis is substantial, decreasing from 696 to 605 cm^{-1}. It was unfortunately not feasible to obtain any multireference CISD vibrational frequencies in this work. We suspect that the change in frequencies from CISD to TC-CISD would be substantially smaller than the SCF-TCSCF change, since the CISD method already incorporates much of the influence of the important second configuration, and we have described earlier how the MR-CISD results suggested that the majority of the multireference character in cis S_4 should be obtained from two-configuration work. In the absence of any specific information, one's expectation is that CISD stretching frequencies will be slightly too high, since the influence of triple substitutions is usually to lengthen bonds and reduce stretching frequencies. Our results for S_2 in Table I show that the CISD frequencies are indeed too high by a few percent: they further suggest that extension of the basis beyond TZ2P to incorporate f functions would have a relatively minor effect on the vibrational frequencies at the SCF level but might well result in an increase of a few percent once correlation effects are included. All these considerations lead us to estimate a "best value" of 670 ± 50 cm^{-1} for ω_1, and with this level of uncertainty, we may neglect the differences between harmonic (ω) and observed (ν) vibrational frequencies. In view of the rather small basis size and the evident deficiencies of SCF theory for cis S_4, it seems unwise[75] to place too much weight on the theoretical Raman intensities in Table V but the indications are that ω_1 should have at least a reasonable Raman intensity. Our best value for ω_1 therefore correlates very satisfactorily with the Raman peak[22] at 682 cm^{-1}, and the experimental association[22] of this Raman peak with a species having an electronic absorption near 515 nm also matches our results for the cis isomer very satisfactorily (see part e of the Results section).

The estimation of a best value for ω_2 is perhaps more difficult than for ω_1, since ω_2 changes dramatically from SCF to CISD (517 to 421 cm^{-1} with the DZP basis) and from SCF to TCSCF levels of theory (517 to 394 cm^{-1} with the DZP basis), in the same direction. It is also slightly more sensitive to the size of the basis at the SCF level than is ω_1. We believe that 450 ± 50 cm^{-1} is a reasonable prediction for ω_2. Corset, Steudel, and co-workers observe[22] a rather weak Raman peak at 440 cm^{-1}, which appears to match our predictions for ω_2 satisfactorily, though the low intensity perhaps indicates caution. Encouragingly, a weak Raman peak at 440 cm^{-1} was also seen by Brown and co-workers[21] in their experiments on the products of a discharge in SO_2 vapor which were trapped at 80 K; the highest frequency peak Raman band that they assigned to S_4 was at 668 rather than 680 cm^{-1}, but a peak at 680 cm^{-1} was observed and attributed to S_2O, for which the gas-phase frequency is now known[76] to be 679 cm^{-1}. As S_2O was positively identified in Brown's experiments[21] by the detection of ν_1 at 1125 cm^{-1}, it is possible that ν_1 of S_2O and ν_3 of cis S_4 (or perhaps ν_5, as discussed below) are accidentally almost coincident, which would of course add to the difficulty in interpretation of any experiments in which both S_2O and S_4 might be present.

It seems difficult to match the Raman feature seen at 605 cm^{-1} in sulfur vapor[22] (or at 601 cm^{-1} in Brown's work[21]) with any fundamental vibration of cis S_4. The remaining stretching frequency, ω_5, is less sensitive to the level of theory used for its evaluation than are ω_1 and ω_2, though unusually[58] it *increases* from SCF to CISD, so it is possible to give its "best value" with rather smaller uncertainty bars as 700 ± 25 cm^{-1}. If the 682-cm^{-1} gas-phase Raman peak is due to ω_1, as suggested above, then there does not appear to be a candidate for ω_5 in the right frequency region. This would therefore imply either that ω_1 and ω_5 are accidentally almost degenerate, which is unlikely but conceivable given the frequency uncertainties we feel are appropriate, or that

ω_5 has not been observed in the Raman spectrum; note that the DZP SCF Raman intensity of ω_5 is very low. Three of the four methods used for vibrational frequency prediction indicate that ω_5 is the most intense infrared band for cis S_4. It is therefore tempting to assign the most intense of the multiplets observed by Meyer[20] in his infrared matrix isolation experiment as due to ω_5 of cis S_4, and since this feature is at 681 cm^{-1} in a Kr matrix, the tentative possibility of ω_1 and ω_5 being accidentally degenerate is slightly reinforced. However, since a change of the "inert" matrix gas from Kr to Ne altered the infrared frequencies observed by Meyer[20] by several wavenumbers, one should probably not attach too much weight to this coincidence. Meyer observed[20] another intense infrared peak at 660 cm^{-1} in Kr matrices, which could be either ω_1 or ω_5 of cis S_4 on frequency grounds, though our infrared intensities for ω_1 are much less than those for ω_5 at all levels of theory except TCSCF. It is puzzling that the infrared spectrum recorded by Brown[21] is so different from Meyer's.[20] Since Meyer's was obtained from sulfur vapor (S_2 at a very high temperature of 1000 K was deposited at a low pressure), while Brown's experiments were carried out on a more complex mixture, with the added complication of a discharge, in the event of discrepancies between them we are inclined to regard Meyer's spectra as more likely to be due to S_4 molecules.

So far we have not considered whether Meyer's medium-strong infrared band[20] at 483 cm^{-1} might be a fundamental vibration of cis S_4. The remaining frequencies for cis S_4 are expected at 340 ± 30 cm^{-1} for ω_6, 145 ± 15 cm^{-1} for ω_3 and 150 ± 50 cm^{-1} for ω_4; the large uncertainty for ω_4, particularly on a relative basis, is due to the very large difference between SCF (219 cm^{-1}) and TCSCF (97 cm^{-1}) values. Meyer's strong infrared peak at 320 cm^{-1} can therefore plausibly be assigned to ω_6 of cis S_4, and the medium Raman band[22] at 190 cm^{-1} may possibly be due to ω_4, but the 483-cm^{-1} band in the infrared remains unassigned. Unfortunately, no infrared data are available in the region below 200 cm^{-1}.

If the 605-cm^{-1} Raman feature is not due to cis S_4, then the next most likely candidate on energetic grounds is its singlet trans counterpart. The theoretically evaluated frequencies for ω_1 and ω_5 for the trans isomer are consistently some 10–30 cm^{-1} lower than those for their cis counterparts, at all levels of theory used in this work. Our best estimates are therefore 650 ± 50 cm^{-1} for ω_1 and 690 ± 25 cm^{-1} for ω_5. Since the trans isomer is centrosymmetric, the mutual exclusion principle operates and ω_1 will be Raman-active only, while ω_5 will appear only in the infrared spectrum. The indications from the DZP SCF results are that ω_2 will have a much higher Raman intensity than ω_1; the best value we can predict for ω_2 is 550 ± 50 cm^{-1}. With these estimates, neither ω_1 nor ω_2 matches the as-yet unassigned 605-cm^{-1} Raman frequency very closely. We note that Meyer observed a weak infrared band at 647 cm^{-1}, which was correlated with the visible band at 625 cm. If we accept that the 625-nm band is due to trans S_4, as suggested by the theoretically evaluated electronic excitation spectrum as reported in Table XIII, then the only infrared-active fundamental vibration for planar trans S_4 which could be near 647 cm^{-1} is ω_5, for which the frequency was estimated above as 690 ± 25 cm^{-1}. The weakness of the 647-cm^{-1} infrared band is quite consistent with its being due to trans S_4, which would be present in substantially lower concentration than the cis isomer if our CCSDT-1 or MR-CISD predictions of its relative energy (about 10 kcal mol^{-1} above the cis structure) are reasonably accurate. If the frequency for ω_5 has somehow been overestimated by about 40 cm^{-1}, then perhaps that for ω_1 has been also; in that case, the revised frequency for ω_1 would be near 610 cm^{-1}, and so it would match the remaining Raman band at 605 cm^{-1} very satisfactory.

One possible difficulty with this assignment is the claim by Corset and Steudel et al.,[22] based on the variation of Raman intensity with the frequency of the exciting radiation (the resonance Raman effect), that the species giving rise to the 605-cm^{-1} Raman band has an electronic absorption near 515 nm, whereas we have argued above that the absorption wavelength for the trans isomer is actually 630 nm. It is not clear to us how precisely electronic

(75) Amos, R. D. *Advances in Chemical Physics*; Lawley, K. P., Ed.; J. Wiley: Chichester, U.K., 1987; Vol. 67, pp 99–153.

(76) Lindenmayer, J.; Rudolph, H. D.; Jones, H. *J. Mol. Spectrosc.* **1986**, *119*, 56.

absorption wavelengths may be estimated by the resonance Raman technique, but we feel inclined to overlook this possible difficulty. It is also slightly surprising that ω_1 for trans S_4 should be observed more readily than ω_2, in view of the Raman intensities presented in Table VIa, but we have already emphasized that these Raman intensities are fortunately not very reliable. With this combination of ifs and slight inconsistencies, two vibrational frequencies have been more or less plausibly assigned for trans S_4. Together with the reasonable match between the wavelength of the lowest energy electronic transition evaluated for trans S_4 and the observed wavelength of a peak recently assigned to a second isomer of S_4,[19] the indication is that trans S_4 has been identified with reasonable certainty.

Raghavachari et al.[60] have predicted that the rectangular isomer of S_4 is the global minimum. This species would have only one fundamental vibration active in each of the infrared and Raman spectra in the S–S stretching region, and it seems inconceivable that it and the cis planar isomer could both be true minima. Therefore we believe that the observation of a very rich spectrum in the 600–700-cm^{-1} region precludes the rectangular isomer from being the global minimum for S_4.

We now must consider whether there is any indication from the observed vibrational spectra that any other isomers of S_4 have been observed, besides the planar cis and trans singlet forms discussed above. On energy grounds, the next most likely isomer is either the trans triplet or the helical triplet; these are most degenerate, as shown in Table III. Since the trans triplet is centrosymmetric, the mutual exclusion principle will simplify its vibrational spectra. Unfortunately we have evaluated vibrational frequencies for the triplet states of S_4 only at the SCF level, but we may expect these to be more reliable than the analogous results for the cis and trans singlets. In the stretching region we anticipate two Raman bands at about 550 and 480 cm^{-1} and one infrared peak near 540 cm^{-1}. There does not seem to be any feature in the observed spectra that could be assigned to any of these three modes, though it must be acknowledged that a Raman band has been observed[22] at 555 cm^{-1} and assigned to resonance fluorescence from S_2, and that the infrared bands for the trans triplet are expected to be rather weak. Therefore it seems best to consider that while there is no evidence for the detection of the trans triplet isomer of S_4, the available evidence cannot rule out its existence either. Frequencies evaluated for the helical triplet (Table IX) are not very different from those of the trans triplet, though all the stretching modes are slightly lower; once again, there is no hard evidence either in favor of or against its detection.

The most characteristic features of the vibrational spectrum for the branched three-membered-ring isomer are expected to be a rather high-frequency exocyclic stretching mode with substantial infrared intensity, near 680 cm^{-1}, and a basal stretching band with considerable Raman intensity near 550 cm^{-1}. There are infrared peaks at 681 and 660 cm^{-1},[20] but these have already been assigned to vibrations of planar cis S_4, so their presence cannot be used as evidence for the branched ring. The Raman peak at 555 cm^{-1} which was assigned to fluorescence from S_2 has already been mentioned. As for the triplets discussed above, it seems that no evidence can be found in the vibrational spectrum of sulfur vapor either in favor of or against the presence of the branched ring isomer. The data in Table VII show that the puckered ring isomer will be effectively undetectable by infrared spectroscopy and that its most intense Raman peak will probably be the symmetric stretch near 520 cm^{-1}; as the experimental spectrum[20,21] is apparently blank between 475 and 555 cm^{-1}, we may perhaps conclude that the vibrational evidence argues against the presence of the puckered ring form of S_4. We may summarize our discussion of the experimental vibrational spectra of S_4 as follows: most of the fundamental vibrations of cis S_4 have been plausibly

assigned (ν_1 682 cm^{-1}, ν_2 440 cm^{-1}, ν_4 190 cm^{-1}, ν_5 681 or 660 cm^{-1}, and ν_6 320 cm^{-1}), as have two stretching modes for the singlet trans isomer (ν_1 605 cm^{-1} and ν_5 647 cm^{-1}). There is no evidence in the reported vibrational spectra for the presence of other isomers, but we are still left with an infrared band of medium intensity at 483 cm^{-1},[20] which we cannot satisfactorily assign at present to any isomer of S_4.

Conclusions

We have studied many isomers of S_4 by ab initio methods at sophisticated levels of theory using large basis sets. The most stable isomer has been definitively shown to be a planar cis singlet form; there are several other isomers within about 25 kcal mol^{-1} of this species, of which the lowest is the planar trans counterpart, followed by trans and helical triplets. A puckered four-membered ring and branched (or substituted) three-membered ring are almost degenerate. By comparing the vibrational spectra reported for sulfur vapor with our theoretical frequencies, we have been able to provide reasonably convincing assignments for most of the fundamental vibrational modes of the cis singlet and of two of the modes for the trans singlet. There is no direct vibrational evidence consistent with the detection of any other isomer of S_4. The theoretical electronic excitation wavelengths for the cis and trans singlet structures match satisfactorily the two bands assigned to different isomers of S_4, but agreement with the measured ionization potential is poor.

Note Added in Proof. An important new experimental study of the infrared spectra of sulfur vapor has recently been submitted by Andrews and co-workers to the *Journal of Physical Chemistry*. From the Ar matrix spectra produced by a 1:1 ^{32}S:^{34}S isotopic mixture, they were able to assign definitively bands due to S_3 and S_4 and thereby greatly reduce the experimental uncertainty concerning the vibrational spectra of these species. They have shown that strong infrared bands at 661.6 and 642.4 cm^{-1} arise from two different S_4 isomers. Both isomers contain two pairs of equivalent S atoms, with the isomer responsible for the 661.6-cm^{-1} peak being the more stable. These peaks were assigned as ν_5 of planar cis and trans isomers of S_4, respectively. The vibrational assignment in our Discussion section is consistent with, and therefore strengthened by, these new secure results, when allowance is made for possible small shifts in frequency due to "matrix effects". The definitive detection of two different but related S_4 isomers is particularly significant, as it appears to eliminate the possibility, suggested by Raghavachari and co-workers,[60] that the global minimum for S_4 is the rectangular D_{2h} isomer. In addition, the fact that both structures have two pairs of equivalent sulfur atoms also rules out a D_{2h} isomer, which has four equivalent atoms. Andrews and co-workers also describe an infrared peak at 683.2 cm^{-1} which they believe to be due to a cyclic species substituted by a terminal =S group, such as S_5=S. However, we suggest that this band may reasonably be assigned to the branched ring isomer of S_4, as our best estimate of the exocyclic stretching frequency for this isomer is 680 cm^{-1}, and we have shown that this band will have a high infrared intensity. We thank Professor Andrews for communication of his results prior to their publication.