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Energy Surfaces and Structure of S_7O

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Abstract: The geometries corresponding to local minima in the energy surfaces of cycloheptasulfur monoxide, S_7O, have been determined by the combined molecular dynamics/density functional (MD/DF) method. Beginning from the ground-state structure of S_8, we show that the ring structure (i.e. with a -S-O-S- bridge bond) is a stable local minimum in the energy surface. Applying kinetic energy corresponding to a temperature of 2000 K to the atoms triggers a chemical rearrangement: The O atom moves out of the ring and forms a double bond outside an S_7 ring. The parameter-free MD/DF scheme allows us to follow the evolution of the structure and, on cooling, to find other stable minima. The lowest energy we find ($\sim$0.1 eV below the ring structure) is in remarkably good agreement with experimental data. The results provide a striking demonstration of the value of the MD/DF technique in a system where the energy surfaces have many local minima and the ground state has a geometry qualitatively different from the initial one.

I. Introduction

Small molecules of group VIA elements are unusual in that a substantial number can be prepared as single crystals, so that accurate X-ray structure analyses can be performed. The different allotropes of sulfur, in particular, mostly comprise regular arrays of ring molecules, S_n, and X-ray structure analyses have been performed for n = 6-8, 10-13, 18, 20.[1,2] Two cyclic allotropes of selenium, Se_6 and Se_8, have also been measured,[1,3] as well as mixed clusters of sulfur with both selenium[4] and oxygen.[2,5] While the substitution of Se into S-rings leads to little change in ground-state topologies, molecules containing oxygen are found to have the O atoms bonded to a closed S_n ring; i.e., -S-O-S- bridge bonds are not favored. To the best of our knowledge, compounds of the type R-S-O-S-R′ have only been postulated[6] as unstable reaction intermediates. (This applies also to the aromatic sulfenic anhydrides Ar-S-O-S-Ar reported repeatedly as stable products.[7] Rather, the corresponding hydrolysis of aromatic sulfenic chlorides ArSCl was shown to lead to mixtures of thiosulfonates Ar-SO_2-S-Ar and disulfides ArSSAr, presumably via the thiosulfinate Ar-SO-S-Ar.[8])

In the present work we apply the combined molecular dynamics (MD)/density functional (DF) scheme[9] to calculate the geometries of several local minima in the energy surfaces of cycloheptasulfur monoxide (S_7O). The DF method,[10,11] with the local spin density (LSD) approximation for the exchange-correlation energy, is parameter-free and has been applied with success to triatomic group VIA molecules (O_3, S_3, SO_2, SOS)[11,12] and to polymeric sulfur.[13] Calculated geometries agree well with experimental values where available, and bond strengths are overestimated systematically by $\sim$1 eV/bond, so that bonding trends are given reliably. Finite-temperature MD techniques are particularly valuable in larger molecules, since the ground-state structures are often unknown and the energy surfaces contain many local minima. The use of the DF method in conjunction with molecular dynamics is free of the assumptions about the nature of interatomic forces common in other MD approaches.[14]

We have used this scheme previously to study the energy surfaces and ground-state structures of selenium clusters Se_n (n = 3-8).[15] Our results for Se_6 and Se_8 give ground-state geometries in excellent agreement with experiment, so that the predictions for n = 3, 4, 5, 7 should be reliable. This is also true for an extensive study we have performed for sulfur clusters S_n (n = 2-13).[16] The method makes no assumptions about the ground-state structures (in molecules up to n = 5 we have started from a linear structure, in larger systems from a planar ring), and it is striking that these are identified correctly in all cases where experimental results are available. In the case of S_9, for which single crystals have not been prepared, the calculated ground state is consistent with the available spectroscopic data. Atomization energies are overestimated consistently, as found previously for smaller molecules containing group VIA elements.[11]

Details of the method of calculation have been given elsewhere.[16] In section II we outline those aspects of the method that are relevant to the present work and in section III give details of how the calculations for S_7O were performed. A discussion of our results and our concluding remarks comprise sections IV and V, respectively. A detailed, comparative study of different energy minima in S_7O, S_7S, and S_7Se is currently in progress.

II. Method of Calculation

The DF formalism shows that the ground-state properties of a system of electrons in an external field, V_{ext}, can be determined from a knowledge of the electron density, $n(\mathbf{r})$, alone. One such ground-state property, the total energy, E_{gs}, can be found by minimizing the relationship between energy and density, $E[n]$, and this minimum is found for the ground-state density, n_{gs}. It is convenient to write[17]

$$E[n] = T_0[n] + \int d\mathbf{r}\, n(\mathbf{r})\, (V_{ext}(\mathbf{r}) + (1/2)\Phi(\mathbf{r})) + E_{xc}[n] \qquad (1)$$

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(1) Donohue, J. *The Structures of the Elements*; Wiley: New York, 1974; Chapter 9.

(2) Steudel, R. In *Studies in Inorganic Chemistry*; Müller, A., Krebs, B., Eds.; Elsevier: Amsterdam, The Netherlands, 1984; Vol. 5, p 3.

(3) Steudel, R.; Strauss, E. M. *Adv. Inorg. Chem. Radiochem.* **1984**, *28*, 135.

(4) Steudel, R.; Strauss, E. M. In *The Chemistry of Inorganic Homo- and Heterocycles*; Academic: London, 1987; Vol. 2, p 769.

(5) Bitterer, H., Ed. *Schwefel: Gmelin Handbuch der Anorganischen Chemie*, 8. Aufl.; Springer: Berlin, 1980; Ergänzungsband 3, p 8.

(6) See, for example: Haas, A. ; Peach, E. *Z. Anorg. Allg. Chem.* **1965**, *338*, 299.

(7) Zincke, T.; Lenhardt, S. *Justus Liebigs Ann. Chem.* **1913**, *400*, 1. Zincke, T.; Farr, F. *Justus Liebigs Ann. Chem.* **1912**, *391*, 55. Kharash, N.; Potempa, S. J.; Wehrmeister, H. L. *Chem. Rev.* **1947**, 327. Kharash, N.; King, W.; Bruice, T. C. *J. Am. Chem. Soc.* **1955**, *77*, 931.

(8) Oae, S.; Kawamura, S. *Annu. Rep. Radiat. Cent. Osaka Prefect.* **1961**, *2*, 120.

(9) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471.

(10) Applications are described by: von Barth, U.; Williams, A. R. In *Theory of the Inhomogeneous Electron Gas*; Lundqvist, S., March, N. H., Eds.; Plenum: New York, 1983.

(11) DF calculations for molecules are discussed in: Jones, R. O. *Adv. Chem. Phys.* **1987**, *67*, 413.

(12) Jones, R. O. *J. Chem. Phys.* **1986**, *84*, 318.

(13) Springborg, M.; Jones, R. O. *Phys. Rev. Lett.* **1986**, *57*, 1145; *J. Chem. Phys.* **1988**, *88*, 2652.

(14) A molecular dynamics study of liquid sulfur is given in: Stillinger, F. H.; Weber, T. A. *J. Phys. Chem.* **1987**, *91*, 4899. This calculation assumes that the interatomic interactions in S can be described by a potential with two- and three-body interactions.

(15) Hohl, D.; Jones, R. O.; Car, R.; Parrinello, M. *Chem. Phys. Lett.* **1987**, *139*, 540.

(16) Hohl, D.; Jones, R. O.; Car, R.; Parrinello, M. *J. Chem. Phys.* **1988**, *89*, 6823.

0002-7863/89/1511-0825$01.50/0

where T_0 is the kinetic energy that a system with density n would have in the absence of electron–electron interactions, $\Phi(\mathbf{r})$ is the Coulomb potential, and E_{xc} defines the exchange–correlation energy. The last is the only term for which an approximation is necessary, and we adopt the widely used LSD approximation

$$E_{xc}^{LSD} = \int dr\ n(\mathbf{r})\ \epsilon_{xc}[n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})] \qquad (2)$$

Here $\epsilon_{xc}[n_\uparrow, n_\downarrow]$ is the exchange and correlation energy per particle of a homogeneous, spin-polarized electron gas with spin-up and spin-down densities $n_\uparrow$ and $n_\downarrow$, respectively. We use the parametrization of Vosko et al.[18]

The energy minimization required for structure determination can be performed by standard MD techniques,[9] since the evolution of the system of electrons and ions can be reproduced exactly by the evolution of a classical dynamical system defined by the Lagrangian

$$L = \sum_i \mu_i \int_\Omega dr\ |\dot{\psi}_i{}^* \dot{\psi}_i| + \sum_{1} \frac{1}{2} M_1 \dot{\mathbf{R}}_1{}^2 - E[\{\psi_i\}, \{\mathbf{R}_1\}] + \sum_{ij} \Lambda_{ij} \left(\int_\Omega d\mathbf{r}\ \psi_i{}^* \psi_j - \delta_{ij} \right) \qquad (3)$$

Here M_1 and R_1 denote the ionic masses and coordinates, μ_i are fictitious "masses" associated with the electronic degrees of freedom, dots denote time derivatives, and the orthonormality of the single particle orbitals, $\psi_i(\mathrm{r}, t)$, is guaranteed by the Lagrangian multipliers Λ_{ij}. From these orbitals and the resultant density $n(\mathbf{r}, t) = \sum_i |\psi_i(\mathrm{r}, t)|,^2$ we use eq 1 to evaluate the total energy E, which is the classical potential energy in eq 3. The dynamics given by the Lagrangian L can be used to generate Born–Oppenheimer (BO) trajectories of the nuclei by an appropriate choice of the μ_i and initial conditions.

The MD procedure is initiated by displacing the atoms randomly from an arbitrary geometry, with velocities $\dot{\psi}_i$ and $\dot{R}$ set equal to zero. For this geometry we diagonalize the Hamiltonian matrix using a small plane wave basis set and determine those ψ_i that minimize E for this geometry. This is the only point where an explicit matrix diagonalization is necessary. With appropriate values of μ (300 au) and integration time step (7.3×10^{-17} s), we find that the subsequent motion of the nuclei departs little from the BO surface. Furthermore, after every 1000–2000 time steps, we fix the ionic positions and bring the electrons back into their ground state. The energy change observed was small (no more than ~0.1 eV) in all cases. This strategy ensures that the molecular configurations observed during the "simulated annealing" process actually represent physical molecules at elevated temperatures. The energy surfaces are probed by varying the average kinetic energy of the nuclei ("temperature" T), and the optimum geometries found by slowly reducing $T \rightarrow 0$. In the present work each time step required approximately 5 s of CPU time on a Cray X-MP computer.

In the present work, we have treated the S and O atoms by nonlocal pseudopotentials,[19] simplifying the calculation by setting the d and higher l components of the pseudopotential equal to the p component ($v_{l\geq2}(r) = v_1(r)$[16]). Calculations on S_n clusters[16] have shown that this approximation causes a negligible change in the relative stabilities of different structures and leads to bond length overestimates of 1–2%. The cluster is placed in a unit cell of constant volume 1000 Å^3 [fcc lattice constant 15.9 Å] with periodic boundary conditions. This choice of cell means that the distance between the S_7O clusters is large, much greater than in the single crystals where the shortest intermolecular S–S and S–O distances are 3.23 and 2.87 Å, respectively.[5] A plane wave expansion is used for the electronic eigenfunctions, and the rapid spatial variation of the pseudopotential[19] for O means that this expansion must be very large. We have used an energy cutoff of 45 Ry, corresponding to ~36 000 plane waves for a single point ($\mathbf{k} = 0$) in the Brillouin zone.[20]

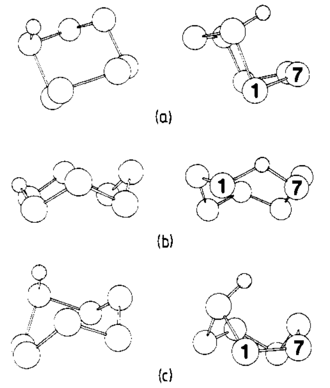

Figure 1. Structures of the (a) ground-state, (b) "ring", and (c) "intermediate" forms of S_7O. The sulfur atoms are numbered cyclically; the oxygen atom is shaded.

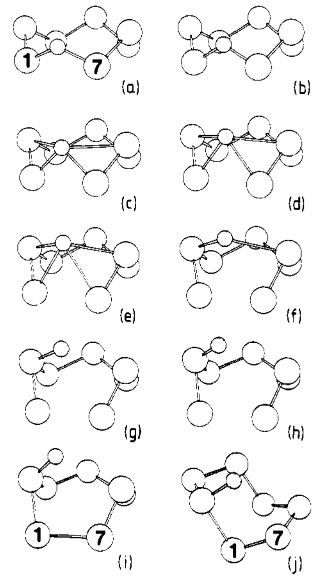

Figure 2. (a–i) Evolution of the ring structure into the intermediate structure. The interval between each frame is 150 time steps. (j) The ground-state structure from the same perspective.

Table I. Molecular Parameters d, α, and γ for the Fully Relaxed C_s ("ring") Isomer of S_7O (See Figure 1b)[a]

$d_{O1,O7}$	1.78	$\gamma_{O1,O7}$	102
$d_{12,67}$	2.06	$\gamma_{12,67}$	94
$d_{23,56}$	2.15	$\gamma_{23,56}$	95
$d_{34,45}$	2.11	$\gamma_{34,45}$	98
α_O	119		
α_1, α_7	110		
α_2, α_6	109		
α_3, α_5	106		
α_4	108		

[a] Bond lengths d_{ij} (between atoms i and j) in Å, bond angles α_i (at atom i) and torsion angles γ_{ij} (at bond ij) in degrees. Sulfur atoms are numbered 1–7; the oxygen atom is denoted by O.

III. Molecular Dynamics for S_7O

An important advantage of the present technique is its ability to locate energy minima corresponding to geometries far removed from the starting structure. In the present work, we have started with the calculated geometry for the ground state of S_8 (D_{4d}), perturbed each of the coordinates by a random amount (between –0.1 and +0.1 au), and located the nearest minimum. In practice, this procedure can be accelerated by increasing electron mass and time step to $\mu = 50000$ au and $\Delta t = 8.5 \times 10^{-16}$ s and following a steepest descents path to the local minimum $\min\{E[\{\mathbf{R}_1\}, \{\psi_i\}]\}$ at $T = 0$. The resulting ring structure (C_s) is shown in Figure 1b and corresponds to a stable local minimum. The structural parameters are given in Table I.

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(17) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133.

(18) Vosko, S.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(19) Bachelet, G. B.; Hamann, D. R.; Schlüter, M. *Phys. Rev. B* **1982**, *26*, 4199.

(20) Gillert, R.; Scheffler, M., private communication. These authors derived a pseudopotential of identical type for O that decays faster in momentum space. They obtain convergence of geometries and relative energies in Si–O condensed matter systems for plane wave energies of ~30 Ry. Using their potential parameters for O [$\alpha_1^{core} = 4.07$, $\alpha_2^{core} = 1.61$, $c_1^{core} = 1.1360$, $c_2^{core} = -0.1360$; $\alpha_1 = 4.99$, $\alpha_2 = 6.15$, $\alpha_3 = 7.21$, $C_1 = -1.1374$, $C_2 = 0.2008$, $C_3 = 0.0584$, $C_4 = 0.1253$, $C_5 = 0.0699$, $C_6 = 0.0153$ ($l = 0$); $\alpha_1 = 1.05$, $\alpha_2 = 3.19$, $\alpha_3 = 4.22$, $C_1 = 0.5255$, $C_2 = -0.2293$, $C_3 = 0.0149$, $C_4 = 0.0897$, $C_5 = 0.1298$, $C_6 = 0.3884$ ($l = 1$)] yields geometries and energy differences for the minima of S_7O in Figure 1 that are virtually identical with those obtained with the sharper potential in the original work.[19] The S–O distances agree within ~0.01 Å and the energy differences within ~0.001 eV. Thus, the plane wave basis set with a cut-off energy of 45 Ry is sufficient to represent the rapidly varying pseudopotential[19] for O, but the softer potential of Gillert and Scheffler and a reduced basis set should be applied wherever appropriate.

Table II. Molecular Parameters d, α, and γ for C_1 Conformations of S_7O[a]

	$C_1^{\text{int}\,b}$	$C_1^{\text{int},T\to 0\,c}$	$C_1^{\text{gs}\,d}$	expt
d_{12}	2.20	2.25	2.46	2.28
d_{23}	2.60	2.39	2.28	2.16
d_{34}	1.95	2.04	2.04	2.01
d_{45}	2.05	2.15	2.21	2.12
d_{56}	2.32	2.12	2.02	1.99
d_{67}	2.02	2.10	2.29	2.20
d_{71}	2.45	2.12	1.99	1.96
d_{7O}			2.88	2.96
d_{O2}	1.69	1.54	1.56	1.47
α_1	100	105	95	99.9
α_2	84	91	95	97.0
α_3	112	104	100	100.4
α_4	118	106	106	102.9
α_5	112	98	102	105.7
α_6	94	112	103	105.7
α_7	112	112	106	106.5
α_{32O}	113	109	108	107.0
α_{O21}	117	111	98	101.5
γ_{12}	113	111	113	111.9
γ_{23}	104	105	75	78.4
γ_{32}	63	84	92	81.0
γ_{45}	65	79	114	112.3
γ_{56}	98	103	82	80.5
γ_{67}	78	67	7	6.3
γ_{71}	13	29	94	89.5
γ_{712O}	17	17	4	2.9
γ_{O234}	13	7	26	25.9

[a] Bond lengths d_{ij} (between atoms i and j) in Å, bond angles α_i (at atom i) and torsion angles γ_{ij} (at bond ij) in degrees. [b] Intermediate C_1 structure; see Figure 2i. [c] Quenched intermediate C_1 structure; see Figure 1c. [d] Ground-state C_1 structure; see Figure 1a and Figure 2j.

From this structure we allowed the system to evolve at 2000 K (mean kinetic energy of the ions, second term in eq 3) for 1000 time steps. In spite of the large ionic motion, this produced no significant changes in either the total energy or the basic structural "motif",[21] i.e. the pattern of torsion angles. A further 1200 time steps, however, brought the dramatic structural changes shown in Figure 2a–i at intervals of 150 time steps. The S_1–O and S_7–O bonds become longer, the S_1–O–S_7 angle is reduced sharply, and the O atom is pushed out of the ring, forming a bond with the sulfur atom (number 2), which was originally its next nearest neighbor. The structure at this point (Figure 2i) is an oxygen atom outside the familiar S_7 ring structure. However, the topology is different from the measured ground state, where the oxygen is attached to an S_3 group, with long bonds to an S_4 group, which is approximately planar. If the system is now cooled, the structural motif remains the same and the lowest energy of this conformation is 0.47 eV above that of the ring structure. The fully relaxed structure is shown in Figure 1c, and the parameters are given in Table II.

We have also continued the high-temperature simulation from the geometry shown in Figure 2i, reducing the temperature in stages to a low value (<100 K) and finally reaching the bottom of the minimum via steepest descents techniques. We have found that the structure changes continuously into the ground-state form shown in Figure 1a and Figure 2j. The total number of time steps used in this stage of the calculation, including the cooling procedure, was approximately 6000. The lowest energy we find is a stable minimum 0.13 eV below that of the ring structure (Figure 1b). The calculated geometry is compared with that determined from X-ray diffraction[5] in Table II. The overall agreement is very good. Experimental bond and torsion angles are generally reproduced to within 2–3° and lengths of shorter bonds are overestimated by 1–4%, while the particularly long bonds d_{12} and d_{23} are overestimated by slightly more. The calculated distance between the oxygen atom and the remote neighbor S_7 (2.88 Å) is shorter than the measured value (2.96 Å). The d_{7O} separation is associated with a small torsion angle and is correspondingly long.[5] The discrepancies in the bond lengths are due to the pseudopotential description we have adopted and to the extreme flatness of the energy surface near the minimum. While the agreement between theory and experiment is very good, it is perhaps even more remarkable that this structure has been found in only 8000 time steps (~ 10^{-12} s) from a starting configuration with a very different topology.

Table III. Calculated and Measured S–O and S–S Bond Lengths (Å)[a]

	S–O(expt)	S–O(calc)	S–S(expt)	S–S(calc)
SO	1.481[b]	1.54[c]		
OSO	1.432[d]	1.46[c]		
SSO	1.465[d]		1.884[d]	
S_7O(gs)	1.474[e]	1.56[f]	2.163, 2.283[e]	2.28, 2.46[f]
SOS(open)		1.70[g]		
SOS(ring)		1.76[g]		
S_7O(ring)		1.78[f]		2.06, 2.15[f]
S_2			1.889[b]	1.98[g]
S_3				2.00[g]
S_8			2.05[h]	2.11[h]

[a] For both the ground-state (gs) and ring structures of S_7O, the S–S lengths refer to the bonds closest to the O atom. [b] Reference 27. [c] Reference 28. [d] Reference 23. [e] Reference 5. [f] This work. [g] Reference 12. [h] Reference 16.

IV. Discussion

Although the ground-state structure of S_7O is well established,[5] the unusual behavior of oxygen in only forming rings *outside* homocyclic sulfur rings is not well understood.[22] In fact, it has not been clear whether the ring structure corresponds to a stable local minimum in the energy surface or deforms spontaneously into another structure with lower energy.[22] The existence of the molecule ClOCl with an "open" ground-state structure[23] suggests that there is no fundamental reason why S–O–S bond angles near 90° should not occur. As noted above, Se substitution into a S_n ring proceeds with comparatively small structural changes—modest increases in bond lengths and no change in the structural motif and the topology.

Our calculations shed some light on these issues. We find that the C_s ring structure is a stable local minimum lying approximately 0.13 eV above the lowest energy for the C_1^{gs} structure. The energy barrier for the change from "ring" to ground state is substantial, and the structural change involved is very interesting. As the simulation proceeds, the S–O–S bond angle becomes substantially less and, together with the lengthening of the S_7–O and S_1–O bonds, results in the O atom being pushed out of the ring. In the structure in Figure 2e, for example, $\alpha_{S_1OS_7} = 65°$, $r_{S_1O} = 2.41$ Å, and $r_{S_7O} = 2.51$ Å. The energy of this structure is close to the top of the barrier between the ring (Figure 2a) and "intermediate" (Figure 2i) structures. The height of the barrier is ~5 eV, which is substantially larger than the thermal energy available initially. The energy fed into the system to maintain the average kinetic energy of the nuclei means that the system is far from equilibrium during most of the simulation.

The tendency of α_{SOS} to be of smaller values than α_{SSS} is apparent in calculations for triatomic molecules.[11,12] Calculations for O_3, SO_2, SOS, and S_3 all lead to two low-lying singlet states ($^1A_1$) with minima for bond angles near 60° (closed) and 115° (open). The relative stabilities of these states, however, shows a pronounced variation from molecule to molecule. In SOS, for example, the ground state is a closed structure with α ~75°, whereas the corresponding minimum in SO_2 is over 4 eV above the open ground state. This remarkable difference can be traced directly to the fact that the valence p eigenvalue lies much higher in S than in O,[12] which is consistent with the small core in O and the more compact p orbitals in first-row atoms. By contrast, the

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(21) Tuinstra, F. *Structural Aspects of the Allotropy of Sulphur and Other Divalent Elements*; Waltman: Delft, The Netherlands, 1967.

(22) Steudel, R., private communication.

(23) Herzberg, G. *Electronic Structure and Electronic Spectra of Polyatomic Molecules*; Van Nostrand: Princeton, NJ, 1969.

valence eigenvalues and the extent of the valence eigenfunctions in Se are very similar to those in S, consistent with the minor structural changes observed in Se substitution.[24]

Some interesting trends in bond lengths in sulfur rings have been noted by Steudel and co-workers.[2,25,26] They observed that the shortest bonds were always adjacent to the longest and that there was an inverse relationship between the bond length, d_2, and the mean length of the neighboring bonds, $^1/_2(d_1 + d_3)$. Our results for S_4–S_{13} were more extensive than available experimental data and provide further support for this correlation.[16] The present results show that the bond lengths we find in the present work are consistent with similar arguments applied to S–O bonds. In Table III we compare experimental bond lengths for diatomic[27] and triatomic[23] molecules with the results of density functional calculations.[12,28] Also shown are the corresponding results for S_8 and S_7O. The S–O bond lengths are remarkably similar if the oxygen atom is at the extremity of a small molecule or outside a ring, as in the ground state of S_7O (i.e. double bonds). In SOS and in the ring conformation of S_7O (i.e. single bonds), however, d_{SO} is substantially greater, with the bond in the latter being 5% longer than in SOS. A similar effect can be seen in S_3 and in S_8, where the bond in the ring structure is also 5% longer. As we may expect from the alternation in bond strengths in sulfur ring molecules noted above, the extremely long S–O bond in cyclic S_7O is associated with neighboring S–S bonds, which are respectively 2% shorter and 2% longer than in S_8.

The results we have obtained show that trends in the di- and triatomic molecules are indeed apparent in larger systems. DF calculations indicate that the closed conformation of SOS is more stable than the open structure and make plausible the tendency of the –S–O–S– bridge structure to break up on increasing the kinetic energy. However, the energy difference between the ring and ground-state structures is so small (~0.1 eV) that qualitative arguments cannot be expected to predict the ground state. The situation is similar to that in S_7 or S_9, where several structures have similar total energies and detailed calculations are essential to determine the most stable conformation.

V. Concluding Remarks

We have described here calculations of the energy surfaces of the S_7O molecule using a parameter-free MD/DF method, which requires no assumptions about the equilibrium structure. This is a decisive advantage in such a molecule, where the energy surface is very complex and has many local minima. It is unrealistic to expect that conventional methods, either using correlated wave function or density functional techniques, will be able to find a path in configuration space between low-lying minima. This situation will be true even if gradient techniques are used, as the analytical properties of the energy as a function of the coordinates are by no means simple. The introduction of kinetic energy (temperature) terms in eq 3 enables the system to locate the most favorable geometry in a large region of configuration space. In principle, the same method could be applied to Hartree–Fock or configuration interaction techniques, but the CPU time required with current implementations of these methods would be much greater than the 5 s a combined diagonalization/self-consistency/MD step requires with the present approach.

The S_7O molecule is a difficult test for any computational method, and the agreement with experiment for the ground state is very satisfactory. We note, however, that there is no guarantee that this method can sample all regions of configuration space and that the absolute minimum of the energy can be found. The success of the calculation depends to some extent on an appropriate choice of the initial geometry. Entropy arguments suggest, for example, that it would be more difficult to locate a highly symmetric minimum if we start in a conformation with low symmetry, such as the ground state of S_7O. Nevertheless, we are confident that the approach will be of value in other systems where the pseudopotential approximation is appropriate and that the MD/DF method should be a valuable complement to other techniques in studying energy surfaces in general.

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(24) For a discussion of the relationship between core size, valence eigenfunctions and bond strengths, see: Harris, J.; Jones, R. O. *Phys. Rev. A* **1979**, *19*, 1813.

(25) Steudel, R. *Angew. Chem.* **1975**, *87*, 683 (*Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 655); *Z. Naturforsch.* **1975**, *38B*, 543.

(26) Steudel, R.; Sandow, T.; Reinhardt, R. *Angew. Chem.* **1983**, *89*, 757 (*Angew. Chem., Int. Ed. Engl.* **1983**, *16*, 716).

(27) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1974.

(28) Jones, R. O. *J. Chem. Phys.* **1985**, *82*, 325.