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Electronic Structure of the $^3\Sigma^-$ States of SiOSi and SiSiO

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We have completed theoretical studies on SiOSi and SiSiO in their linear $^3\Sigma^-$ ground electronic states. The theoretical methods that we employed were ab initio self-consistent field (SCF), configuration interaction including single and double excitations from the dominant configuration (CISD), and complete active space (CASSCF). The SiOSi isomer is shown to be symmetrical and about 10 kcal/mol more stable than SiSiO.

Introduction

There are very few references to the molecule Si_2O in the literature. In 1977 Weltner and co-workers[2] reported the optical spectrum of Si and Si_2 in argon matrices. One of the optical absorptions exhibited a progression of about 870 cm^{-1} and could not be ascribed to either Si or Si_2. The experimental technique utilized evaporation of silicon from a tantalum resistance tube; these workers concluded that the absorptions could be due to Si_2O, since oxygen is a known impurity in tantalum metal and optical transitions assignable to SiO were often observed in the matrix spectra. In 1986 Margrave and co-workers[3] reported a study of the photochemistry of group 14 metal atoms with water in matrix isolation experiments. In their Si-H_2O experiments they observed a similar progression (spacing of $\approx$770 cm^{-1}), but since no SiO contaminated their experiments, they ruled out Si_2O as the cause of the absorption.

More recently,[4] Weltner and co-workers have reported the ESR spectra of C_2O and SiCO with ^{17}O isotopic labeling. In the course of this work they obtained signals that could not be due to either of the above molecules and which they tentatively assigned to Si_2O. The spectra attributed to Si_2O were due to the ^{29}Si ($I = {}^1/_2$) nucleus and were observed in a number of different experiments. The signals were most intense upon vaporization of very finely powdered silicon from a tantalum cell that was heated resistively. The appearance of these lines were assumed to be due to oxidation that had occurred on the large surface area samples. Vaporization of a mixture of solid Si and SiO_2 produced only small signals. However, vaporization of Si from one cell and SiO_2 from another produced good signals. A more intense signal also could be produced by laser vaporization of Si and doping the argon matrix gas with 0.5% oxygen. But surprisingly, a similar experiment with Ne as the matrix gas did not yield any of the requisite ESR signals. The spectra are indicative of a triplet molecule and show a hyperfine interaction with only one Si atom, so that the molecule could not be symmetric SiOSi but might be due to SiSiO if most of the spin density were on one of the Si atoms.

In summary, very little is known about the molecule for which some optical and ESR spectra have been assigned to "Si_2O". This experimental background and our recent theoretical work[5] on the homologous compounds C_2O, CN_2, SiCO, and SiN_2 form the background to the theoretical studies reported in this paper. Since Weltner and co-workers observed an ESR signal due to a triplet molecule and since our earlier work on the homologous compounds dealt with the linear triplet electronic states, we restricted the present study to the $^3\Sigma^-$ states of linear SiSiO and SiOSi. (Some perfunctory studies on bent triplet states of SiOSi were carried out, and in all cases they resulted in a higher energy than that of the linear molecule.)

The Si-O bond is of immense importance in the field of mineralogy and materials science. As a consequence, much theoretical work has been devoted to a study of the Si-O-Si framework. It is interesting to note that theoretical work[6] on $(HO)_3Si-O-Si(OH)_3$ predicts the two Si-O bond lengths to be unequal. Part of our interest in this project was to determine whether or not the isomer SiOSi would have equal Si-O bond lengths.

Silicon-oxygen chemistry is also of interest to the astrochemical community. For example, the diatomics SiO and SiS have been detected in interstellar space.[7] In order to assist in such work, it would be useful to know the relative stability of both isomers of Si_2O; if only linear symmetric SiOSi were stable, the likelihood of its detection in interstellar space is much less due to the lack of a permanent dipole moment.

We first examine qualitative arguments regarding which topology is expected to be more stable based upon recent theoretical and experimental work in the area of silicon chemistry. Later we present the theoretical methods that were employed and the results that were obtained.

Qualitative Discussion Regarding the Expected Topology of Si_2O

The most stable isomers of both B_2O and Al_2O are linear with the oxygen in the middle,[8,9] whereas other molecules have the oxygen atom in the terminal position: C_2O,[10] N_2O,[11] S_2O.[11] That is, all of the molecules for which the octet rule is satisfied have the oxygen atom in the terminal position, except for the halogen-containing systems (F_2O,[12] Cl_2O[12]) where it is expected to be in the central position on the basis of formal charge and electronegativity considerations.[13] For the electron-*deficient* systems we find both sorts of topologies (e.g. BOB vs. CCO). What will be the outcome for Si_2O?

We note first that if carbon chemistry is taken as the norm, then silicon chemistry is perverse when it comes to predictions of structure and topology. A few examples will suffice: (1) The analogue of benzene, Si_6H_6, has a structure in which the Si atoms form a trigonal prism rather than the planar hexagon of benzene.[14] (2) The analogue of C_4H_4 exhibits a structure not at all like either a cyclobutadiene or tetrahedrane structure.[15] (3) The triatomic

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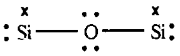
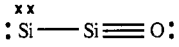
C_3 is (weakly) linear[11] whereas SiC_2,[16] Si_2C,[17] and Si_3[18] are all cyclic. (4) The molecule H_2CO has the topology of formaldehyde, but H_2SiO has that of HSiOH.[19] Likewise, the most stable form of [H, C, O] is HCO whereas the corresponding silicon compound is HOSi.[20] (5) SiO readily polymerizes in matrix isolation experiments[21] to form $(SiO)_n$ whereas such polymerization of CO is unknown. (6) The most stable form of C_4H_6 is that of bicyclobutane, but Si_4H_6 adopts a structure in which there is no bridgehead Si–Si bond and the angles around the bridgehead Si atoms are near 90°.[22]

Discussions on the perverse character of Si compared to C often focus on the inability of Si to form strong multiple bonds. For example, it has been estimated that a CC double bond is 105.1 kcal/mol more stable than such as SiSi bond and that the difference for the corresponding triple bonds is 130 kcal/mol.[23] Much of this structural chemistry also can be understood by noting the so-called "inert-pair" effect that inorganic chemists employ to explain the tendency of the heavier elements in group 14 to remain divalent rather than to be tetravalent.[24] From a theoretical viewpoint, the inert-pair effect is called the "s-orbital contraction".[25] No matter whether one wishes to think in terms of lack of π bonding or the inert-pair effect, the result is the same: Structures in which the Si atom is divalent are often favored whereas the corresponding structures for C chemistry are not.

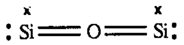
If we apply the inert-pair concept to the Si_2O molecule, we conclude that SiOSi should be the more stable topology. In that form both of the Si atoms can maintain an inert pair. (The symbol "x" refers to the unpaired electrons.)



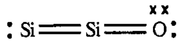
$:\overset{\times}{\mathrm{Si}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}-\overset{\times}{\mathrm{Si}}:$



$:\overset{\times\times}{\mathrm{Si}}-\mathrm{Si}\equiv\mathrm{O}:$

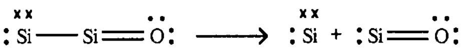


$:\overset{\times}{\mathrm{Si}}=\mathrm{O}=\overset{\times}{\mathrm{Si}}:$



$:\mathrm{Si}=\mathrm{Si}=\overset{\times\times}{\mathrm{O}}:$

For molecules that satisfy the octet rule, one can formulate a simple rule which states that the more electronegative atoms are terminal. Gimarc[26] and Burdett and co-workers[27] have explained this as due to the fact that the upper occupied MOs of the octet rule systems have nodes that pass through the center of the molecule. Hence, the more electronegative atoms prefer terminal positions in order to have maximum access to the valence-electron density. For a triatomic molecule the two lowest valence π MOs have the following character:



$:\overset{\times\times}{\mathrm{Si}}-\mathrm{Si}=\overset{\cdot\cdot}{\mathrm{O}}: \longrightarrow :\overset{\times\times}{\mathrm{Si}} + :\mathrm{Si}=\overset{\cdot\cdot}{\mathrm{O}}:$

Now, ignoring the σ electrons, molecules that have only four valence π electrons (two in $1\pi_x$ and two in $1\pi_y$) should have the more electronegative atom in the central position (e.g. BOB), whereas molecules with eight π electrons should be the opposite (e.g. CO_2). Since Si_2O has six π electrons, we are unable to use this nodal argument to favor one topology over the other. Burdett and co-workers also have employed the method of moments to rationalize topology in both molecular systems and in the solid state.[28]

In summary, we have no a priori method of predicting which isomeric form of Si_2O will be more stable. In the absence of experimental information on the structures or relative energetics, we are led to carry out a theoretical study.

Theoretical Methods

We have considered each of the two topologies of Si_2O in the $^3\Sigma^-$ ground state with the following valence electronic configuration:

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi_x)^2(1\pi_y)^2(2\pi_x)^1(2\pi_y)^1$$

Although the above numbering scheme does not include the "core" electrons (O 1s; Si 1s, 2s, 2p), they were explicitly included in these all-electron ab initio studies.

In our theoretical studies we have employed the standard Huzinaga–Dunning[29–32] double-ζ basis set of contracted Gaussians augmented with a set of (six) d-like functions on each of the atoms. The complete double-ζ plus polarization (DZ+P) basis set is designated (9s5p1d/4s2p1d) for oxygen and (11s7p1d/6s4p1d) for silicon. The polarization function exponents are α_d = 0.85 and 0.5 for O and Si, respectively. Previous theoretical work on Si_3[18a] and SiH_n[33] has shown that in some cases even this flexible basis set needs to be improved. Thus, we carried out some of the calculations with a triple-ζ basis set including two sets of polarization functions (TZ+2P). For oxygen this TZ basis was derived from the same 9s5p primitive set that was mentioned above; the TZ basis on Si was obtained from McLean and Chandler.[34] The α_d values were chosen to be 1.5, 0.35 for O and 1.0, 0.25 for Si. The full specification of this more complete basis set is (9s5p2d/5s3p2d) for O and (12s9p2d/6s5p2d) for Si.

Analytic SCF gradient techniques[35,36] were used to determine geometrical structures. The harmonic SCF vibrational frequencies were obtained by using analytic second derivatives,[37] and analytic determination of dipole derivatives were employed to obtain intensities of infrared spectra.[38]

The effect of electron correlation on the geometries, vibrational frequencies, and energetics of these molecules has been investigated via use of configuration interaction methods (CISD and CASSCF). In the CISD method,[39] only the valence electrons have been included in the CI. That is, the "core" electrons (as defined above) and their virtual orbital counterparts have been omitted. Otherwise, all singly and doubly excited configurations relative to the SCF reference configuration have been included (CISD), which resulted in 10 554 configurations. Geometrical structures were determined by using CI gradient techniques.[40]

The CASSCF studies employed the method of Werner and Knowles,[41] which is incorporated in the CADPAC program.[42] The active space was composed only of electrons in the valence π space in order to use a sufficiently large space to overcome the restricted Hartree–Fock broken-symmetry problem.[43] The active space consisted of the 1π, 2π, 3π, 4π, and 5π orbitals and resulted in a 6-electron/10-orbital designation. Precise stationary points were located by using analytic MCSCF gradient methods.[44] Harmonic frequencies were obtained from the CASSCF

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Table I. Theoretical and Experimental Results for SiO

	SCF		CISD		
	DZ+P	TZ+2P	DZ+P	TZ+2P	expt[a]
energy, hartrees	−363.805 43	−363.832 13	−364.052 89[b]	−364.116 37[c]	
r_{SiO}, Å	1.483	1.479	1.510	1.505	1.5097
ω, cm^{-1}	1412	1406	1307		1241.6
F_{SiO}, mdyn/Å	11.96	11.85	10.24		9.24
I, km/mol	106	99	46		
dipole moment, D	3.52	3.43	3.18	3.14	3.088
bond order					
Mull.[d]	1.87	1.77	1.88	1.81	
Low.[e]	2.24	2.47	2.19	2.39	
Pol.[f]	1.58	1.57	1.45		

[a] Reference 49. [b] With Davidson correction, −364.076 47 hartrees. [c] With Davidson correction, −364.144 24 hartrees. [d] Reference 45. [e] Reference 46. [f] Reference 47. The value calculated from the experimental bond length and force constant for SiO is 1.38.

Table II. Theoretical Results for SiSiO

	SCF		CISD		CASSCF	
	DZ+P	TZ+2P	DZ+P	TZ+2P	DZ+P	TZ+2P
energy, hartrees	−652.638 44	−652.695 43	−653.939 54[a]	−653.040 73[b]	−652.717 77	−652.774 80
r_{SiSi}, Å	2.371	2.286	2.316	2.296	2.369	2.297
r_{SiO}, Å	1.481	1.479	1.508	1.503	1.502	1.498
$\omega_1(\Sigma)$, cm^{-1}	1408	1393	1309		1327	
$\omega_2(\Sigma)$, cm^{-1}	239	345	328		238	
$\omega_3(\Pi)$, cm^{-1}	118	168	172			
I_1, km/mol	215	235	125		88	
I_2, km/mol	0.2	1.2	0.2		2.0	
I_3, km/mol	77	64	52			
F_{SiSi}, mdyn/Å	0.58	1.21	1.09		0.58	
F_{SiO}, mdyn/Å	11.88	11.59	10.20		10.48	
$F_{SiSi,SiO}$, mdyn/Å	0.10	0.16	0.12		0.0	
F_{bend}, mdyn Å/rad^2	0.10	0.21	0.23			
dipole moment, D	2.30	2.71	2.35	2.65	1.76	2.27
Si–SiO bond energy, kcal/mol	2.1	9.6	9.2[c]	15.7[d]		
bond order						
Mull.[e] SiSi	0.77	1.06	0.81	1.00		
Mull.[e] SiO	1.84	1.70	1.81	1.73		
Low.[f] SiSi	1.13	1.29	1.14	1.22		
Low.[f] SiO	2.10	2.34	2.01	2.26		
Pol.[g] SiSi	0.28	0.42				
Pol.[g] SiO	1.58	1.55				

[a] With Davidson correction, −652.975 81 hartrees. [b] With Davidson correction, −653.084 35 hartrees. [c] With Davidson correction, 10.8 kcal/mol. [d] With Davidson correction, 16.4 kcal/mol. [e] Reference 45. [f] Reference 46. [g] Reference 47.

wave function by use of finite difference methods.

Within the framework of the SCF and CISD methods, we have also calculated bond orders by three methods, which we refer to as the Mulliken method,[45] the Löwdin method,[46] and the Politzer method.[47] The former two methods utilize the ab initio density matrix to partition the electron density in a manner different from that originally proposed by Mulliken in his population analysis method.[48] The Politzer method employs a simple equation that needs only the force constant and bond length for a given bond to obtain the bond order:

$$\text{bond order} = 0.55747(k/R_e)^{1/2}$$

The force constant k should be expressed in mdyn/Å and the equilibrium bond length R_e in Å.

Results and Discussion

In Table I we present the results obtained for the diatomic SiO. Since this molecule was not the main point of our study, we discuss only the results obtained with the DZ+P basis. The bond length in the diatomic is calculated to be 1.483 Å (SCF) and 1.510 Å (CISD), in good agreement with the experimental value of 1.5097 Å.[49] The experimental harmonic vibrational frequency is 1241.6 cm^{-1}; after scaling[50] the SCF theoretical value by 0.89, we obtain 1257 cm^{-1}. The theoretical bond orders indicate roughly double-bond character. The bond order computation for the homologous CO molecule gave a bond order of 2.4–2.9, depending upon which method was employed.[5] The bond orders and the dipole moment both indicate that there is much more charge polarization in the SiO molecule than in the CO molecule, a result not unexpected on the basis of the relative electronegativities of C compared to Si. There is very little change in any of the computed properties upon going to the TZ+2P basis set.

We now turn to the results for SiSiO (Table II). The Si–O bond length differs from the value for diatomic SiO by only 0.002 Å at all levels of theory. The Si–Si bond length is 2.371 Å (DZ+P) and 2.286 Å (TZ+2P). This indicates that an accurate description of the Si–Si bond is sensitive to the level of basis set.[18a] The geometrical structure also was optimized at the CISD and CASSCF (DZ+P) levels, and the results show an expected lengthening of the SiO bond and a shortening of the SiSi bond.[51]

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(51) For a molecule that is electronically saturated (i.e., for which electron octets are satisfied), the CISD procedure brings in configurations that are antibonding between atoms and hence bond lengths typically increase compared to the case for the SCF method. However, SiSiO is electronically unsaturated. One of the configurations that can participate in the CISD has the configuration with a half-occupied 1π valence orbital and a doubly occupied 2π valence orbital. The former is mainly SiO bonding whereas the latter is SiSi bonding and SiO antibonding. With these orbitals in mind, it is easy to rationalize the lengthening of the SiO bond and the shortening of the SiSi bond upon going from the SCF to the CISD method. This phenomenon was also observed in our studies on other 14-valence-electron systems with $^3\Sigma^-$ electronic states.[5]

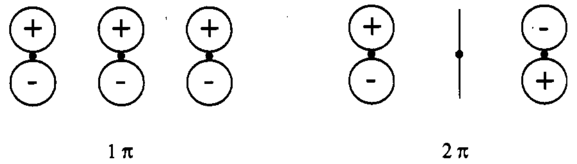
Table III. Theoretical Results for SiOSi

	SCF		CISD		CASSCF	
	DZ+P	TZ+2P	DZ+P	TZ+2P	DZ+P	TZ+2P
symm of wave function	$C_{\infty v}$	$C_{\infty v}$	$C_{\infty v}$	$C_{\infty v}$	$D_{\infty h}$	$D_{\infty h}$
energy, hartrees	−652.683 50	−652.723 46	−652.970 99[a]	−653.059 01[b]	−652.751 14	−652.793 66
r_{SiO}, Å	1.636	1.630	1.650	1.645	1.639	1.635
$\omega_1(\Sigma_u)$, cm^{-1}	1113	1078	1062		1042	
$\omega_2(\Sigma_g)$, cm^{-1}	588	583	571		586	
$\omega_3(\Pi)$, cm^{-1}	168	106	180			
I_1, km/mol	697	745	367		63	
I_3, km/mol	6	2	8			
F_{SiO},[c] mdyn/Å	5.12	4.93	4.76		4.82	
F_{bend}, mdyn Å/rad^2	0.14	0.06	0.16			
bond order						
Mull.[d] SiO	0.73	0.59	0.76	0.65		
Low.[e] SiO	1.13	0.41	1.11	1.37		
Pol.[f] SiO	0.99	0.97	0.95		0.96	

[a] With Davidson correction, −653.002 62 hartrees. [b] With Davidson correction, −653.099 37 hartrees. [c] Using the simple internal coordinate SiO stretch. [d] Reference 45. [e] Reference 46. [f] Reference 47.

The bond lengths, bond orders, vibrational frequencies, force constants, and potential energy distribution of the vibrational frequencies all show that the SiO part of the SiSiO molecule has barely been perturbed by the terminal silicon atom. This is a picture quite different from that which we obtained for the homologous molecule C_2O,[5] where the CO bond length, vibrational stretching frequency, and force constant all changed significantly as a result of reaction of the terminal C atom with the CO "ligand". The force constant associated with the Si–Si stretch is about 1 mdyn/Å at all levels of theory. For such a small force constant, it is not surprising that the computed bond length is sensitive to basis set. The bond dissociation energies (to Si ^3P and SiO) also are presented in Table II. They range from a low of about 2 kcal/mol at the smaller basis SCF level to a high of 16 kcal/mol at the larger basis CISD level.

Why then is the dissociation energy so small for this bond? One qualitative explanation is that the central Si atom is able to go from what could formally be written as a trivalent state to a divalent state upon bond rupture:



The net result is that very little energy is needed to break the SiSi bond. This argument is analogous to that employed in rationalizing the large difference between the first and second bond dissociation energies for a group 2 or group 12 metal atom. For example, the values[52] for MgH_2 are as follows:

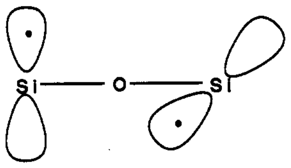
$$MgH_2 \rightarrow {}^{\bullet}Mg\text{—}H + H \qquad 74.1\ \text{kcal/mol}$$

$$MgH \rightarrow :Mg + H \qquad 29.9\ \text{kcal/mol}$$

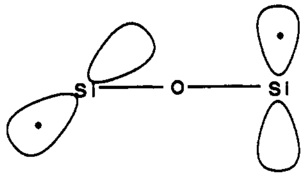
Looked at from the point of view of bond formation between Si and SiO, a qualitative explanation for the weak Si–Si bond is that the SiO bond is very polar (by the Mulliken population analysis the charge is about +3/4 on the Si atom) and hence there is very little frontier valence electron density available for the Si atom to attack. Furthermore, the π-electron density will be so localized on the O end of SiO that it will not be available for "back-donation" to the attacking Si atom.

We now turn to a discussion of SiOSi (Table III). The initial results that we obtained were in the D_{2h} subgroup of $D_{\infty h}$. The propensity for restricted Hartree–Fock symmetry breaking was confirmed by evaluation of the harmonic frequencies that showed a negative eigenvalue in the Σ_u vibrational stretching motion. We next determined an SCF wave function in C_{2v} symmetry (subgroup of $C_{\infty v}$); in the initial run we maintained the SiO bond lengths at the values obtained in the D_{2h} study. Examination of the eigenvectors revealed that symmetry breaking of the wave function had indeed taken place in the π type orbitals of the linear molecule. Although we expected the molecule to undergo an energy lowering along the σ_u coordinate so that the two Si–O bond lengths would be unequal, this is not what happened when we carried out a structure optimization in C_{2v} symmetry. Even when the optimization was started with unequal bond lengths, the result was again one in which the two SiO bond lengths were equal but 0.02 Å longer than they had been in D_{2h} symmetry. The energy was 21.4 kcal/mol lower than the result obtained with the wave function constrained to D_{2h} symmetry. We also carried out a CISD study in C_{2v} symmetry and found the SiO bond lengths to be only 0.014 Å longer than at the SCF level.

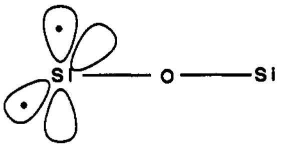
The driving force for symmetry breaking in SiOSi at the single-reference SCF level of theory is the "desire" of the unpaired electrons to localize on one end of the molecule or the other. Under C_{2v} symmetry this leads to either



or



as the one-reference SCF solution. Either of these resonance structures would result in a symmetrical geometry. On the other hand, a third resonance structure



would lead to a geometry with unequal Si–O bond lengths, but only at the cost of raising the energy.[53]

The CASSCF results are very similar to those obtained at the CISD level of treatment. Important to note is that the CASSCF method included the various resonance structures described above and provided identical results whether the molecule was run under D_{2h} or C_{2v} symmetry. In other words, this MCSCF wave function is sufficiently flexible to overcome the familiar artifactual broken-symmetry problem that can arise in restricted Hartree–Fock theory.[54] In addition, we performed a potential energy surface

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(52) Pople, J. A.; Luke, B. T.; Frisch, M. J.; Binkley, J. S. *J. Phys. Chem.* **1985**, *89*, 2198.

(53) We eventually found a $C_{\infty v}$ geometry for SiOSi at the SCF DZ+P level of theory with r_{SiO} = 1.500 and 1.987 Å. This structure is 17.9 kcal/mol higher in energy than the structure with equal Si–O bond lengths (C_{2v} wave function). No unsymmetrical structures were found with the CISD method.

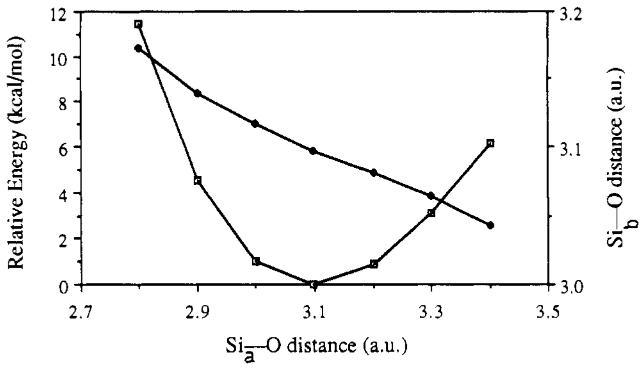

Figure 1. CASSCF results for SiOSi determined by using the DZ+P basis set. The "straight" line shows the variation of the optimized Si–O bond length for each fixed Si–O bond length shown on the horizontal axis. The variation in total energy at each point is shown by the "curved" line.

Table IV. Relative Energies of the SiSiO and SiOSi[a] Linear Isomers (kcal/mol)

method	geometry	rel energy[b,c] DZ+P	rel energy[b,c] TZ+2P
SCF	optimized	28.3	17.6
CISD	SCF geometry	20.3	11.7
CISD	optimized	19.7	11.5
CISD[d]	SCF geometry	17.7	9.9
CISD[d]	CISD geometry	16.8	9.4
CASSCF[e]	optimized	20.9	11.8

[a] SiOSi wave function has $C_{\infty v}$ symmetry unless otherwise noted. [b] Without zero-point vibrational energy correction. [c] Positive number indicates that SiOSi is more stable. [d] With Davidson correction. [e] SiOSi wave function has $D_{\infty h}$ symmetry.

scan using the CASSCF wave function. These results are summarized in Figure 1 and show conclusively that at this level of treatment the SiOSi molecule is symmetrical.

The SiO bond length (≈1.65 Å) is about 0.15 Å longer than it was for either SiSiO or SiO. The SiO bond order has decreased from about 2 for these latter molecules to 1 in SiOSi. The SiO bond length in α-quartz is about 1.6 Å for an Si–O–Si work.[55]

Comparison of the Energies of SiSiO and SiOSi. At all levels of theory we find that the SiOSi topology is the favored isomer. Since we did numerous calculations at single points (e.g. CISD at the SCF geometry), the energy differences between the two isomers are reported in Table IV. Of all the values obtained, the smallest energy difference is 9.4 kcal/mol, and it ranges to a high of 28.3 kcal/mol. The smaller of these values comes from the theoretical results obtained by using the CISD method with the larger basis set. Hence, we tend to favor an energy difference of about 10 kcal/mol between the two isomers. Such a large energy difference is not likely to be reversed with the use of larger basis sets or higher levels of theory,[56] so that we can say with some confidence that SiOSi is more stable than SiSiO.

Relationship of This Work to the Matrix Isolation Experiments. How then do we correlate the present results with those of Weltner and co-workers, who have tentatively assigned optical spectra and ESR signals to "SiSiO"?[2,4] The present results indicate that SiSiO is less stable than SiOSi. Given the wide variety of ways in which these ESR signals could be produced (see Introduction), it would be surprising if all of them involved a mechanism that exclusively generated the SiSiO isomer. One would expect that some of these methods would involve Si and SiO diffusing together at the surface of the matrix during the initial cooling process. If such is the case and if the ESR signals are indeed due to SiSiO, it is surprising that signals were not also observed for SiOSi. Experiments employing ^{17}O could profitably be done to be sure that the carrier of these signals in the ESR experiments is due to a molecule that contains only one O atom.

Although SiOSi is more stable than SiSiO by a considerable extent, we considered the possibility that there might be an energy barrier for the reaction of Si with SiO to form SiOSi. Since only the CASSCF wave function was sufficiently flexible to overcome the artifactual broken-symmetry problem, we used this method to examine the $^3\Sigma^-$ potential energy surface for the linear molecule. The results presented in Figure 1 were carried out at a few additional longer Si–O bond distances, but there was no evidence that any reaction barrier exists.

Conclusions

The most stable topology of Si_2O is the isomer SiOSi, at least for linear configurations. The calculated bending frequency is on the order of 100–200 cm^{-1}. There is little reason to expect these molecules to be bent, although since we have not thoroughly examined bent structures, they cannot be ruled out on the basis of the present work. As Weltner and co-workers have stated,[4] further experimental work is necessary before a thorough identification of the ESR signals can be assigned to "SiSiO". This theoretical study cannot eliminate this molecule as the one that has been observed in the matrix, but it is surprising that signals are not also observed for SiOSi.

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Registry No. Si_2O, 12192-10-8.

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(54) Davidson, E. R.; Borden, W. T. *J. Phys. Chem.* **1983**, *87*, 4783. Allen, W. D.; Horner, D. A.; DeKock, R. L.; Remington, R. B.; Schaefer, H. F. *Chem. Phys.*, in press

(55) Levien, L.; Prewitt, C. T.; Weidner, D. J. *Am. Mineral.* **1980**, *65*, 920.

(56) Note added in proof: We have now completed more sophisticated calculations which confirm these conclusions. Improving the electron correlation treatment with a multireference CI wave function changes the relative energy by only 0.1 kcal/mol. Improving the basis set by adding f-like polarization functions (α_f values of 1.4 and 0.32 for O and Si, respectively) increases the energy separation by 1.0 kcal/mol at the CISD level and by 0.5 kcal/mol with the Davidson correction.