Ab Initio Study of the \( \text{Si}_2\text{O} \) and \( \text{Si}_3\text{O} \) Molecules

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The structures and vibrational frequencies of various structures and electronic states of \( \text{Si}_2\text{O} \) and \( \text{Si}_3\text{O} \) have been studied at the MP2(full)/6-311+G* level, with geometries also calculated at the MP4SDTQ/6-311+G(2df) and QCISD(T)/6-311+G(2df) levels. Triangular \( \text{Si}_2\text{O} \) \((\text{C}_3\text{v}, \text{A}_1)\) and planar-rhombus \( \text{Si}_3\text{O} \) \((\text{C}_2\text{v}, \text{A}_1)\) structures are found to be the most stable, but several other low-lying local minima are also found. The calculated dissociation energies for the lowest energy decompositions of \( \text{Si}_2\text{O} \) into \( \text{Si} + \text{O} \) and of \( \text{Si}_3\text{O} \) into \( \text{Si}_2 + \text{Si} + \text{O} \) are 50.1 and 59.8 kcal/mol, respectively. The energies for \( \text{Si}_2\text{O} \rightarrow \text{Si}_n + \text{O} \) are much larger. Even the lowest decomposition energies are larger than those found for \( \text{Li}_2\text{O} \), \( \text{Li}_3\text{O} \), \( \text{Mg}_2\text{O} \), \( \text{Mg}_3\text{O} \), and \( \text{Al}_2\text{O} \), \( \text{Al}_3\text{O} \). In both \( \text{Si}_2\text{O} \) and \( \text{Si}_3\text{O} \), the \( \text{O} \) atom does not insert into coordination sites of highest symmetry; rather, the most stable structures involve coordination of the \( \text{O} \) atom to two \( \text{Si} \) atoms without destroying the \( \text{Si}_2\text{O} \) bonding. Again, this is different than in \( \text{Li}_2\text{O} \), \( \text{Li}_3\text{O} \), \( \text{Mg}_2\text{O} \), \( \text{Mg}_3\text{O} \), \( \text{Al}_2\text{O} \), and \( \text{Al}_3\text{O} \), where the \( \text{O} \) atom inserts into the site of highest coordination and highest symmetry.

Introduction

Hypermetallic molecules such as \( \text{Li}_2\text{X} \), \( \text{Na}_2\text{X} \), \( \text{K}_2\text{X} \), \( \text{Mg}_2\text{X} \), and \( \text{Al}_2\text{X} \) with electronegative atoms \( \text{X} \) and with stoichiometries exceeding normal valence expectations have been practiced theoretically and studied experimentally. Metal–metal bonding is found to contribute significantly to the stability of these species. However, similar hyperstoichiometric molecules with nonmetallic ligands are still unknown. One of the important results found in refs 1–3 is that for \( \text{X}=\text{O} \), the oxygen atom occupies a high-coordination site in which it is bonded to as many other atoms as possible.

In the present work, we investigate the hypersilicon molecules, \( \text{Si}_2\text{O} \) and \( \text{Si}_3\text{O} \). Experimental and theoretical studies of the \( \text{Si}_2\text{O} \) monomer and of clusters of \( \text{Si} \) atoms are extensive,6–10 and preliminary experimental11 and theoretical12 results are available on \( \text{Si}_2\text{O} \). According to experimental ESR spectra, the \( \text{Si}_2\text{O} \) molecule has a linear \( \text{SiSiO} \) structure with a triplet \( \Sigma \) state. However, in CISD and CASSCF calculations by DeKock and others,13 the linear symmetric \( \text{SiOSi} \) triplet (\( \Sigma \)) structure is more stable by 10 kcal/mol than the linear asymmetric \( \text{SiSiO} \) triplet (\( \Sigma \)) structure. These authors considered only triplets and found that bent triplet states of \( \text{SiSiO} \) are higher in energy. We have not been able to find any information on isolated \( \text{Si}_2\text{O} \). Our interest in these two molecules was stimulated by the fact that they are prototypes of small silicon clusters interacting with an impurity—oxygen atom. Results of our study of such interactions may be of importance to scientists interested in how \( \text{O} \) atoms and molecules react with various crystal surfaces (or terraces, kinks, or steps) of solid \( \text{Si} \).

Computational Details

The geometries of \( \text{Si}_2\text{O} \), \( \text{Si}_2\text{O} \), \( \text{Si}_3\text{O} \), and \( \text{Si}_3\text{O} \) in the singlet and triplet states were first optimized by employing analytical self-consistent-field (SCF) gradients13 with a polarized split-valence basis set (results at this level are denoted SCF/6-31G*14,15) and subsequently at the correlated second-order Møller–Plesset (MP2-full) level. Further optimized geometries were obtained using MP2(full) calculations with triple-\( \gamma \) plus polarization and diffuse bases (denoted 6-311+G*8,16,17). The fundamental vibrational frequencies, normal coordinates, and zero-point energies (ZPE) were calculated by standard FG matrix methods. Finally, higher quality correlated total energies were evaluated in the frozen-core approximation both by fourth-order Møller–Plesset perturbation theory18 (MP4) and by the quadratic configuration interaction including singles and doubles with approximate triples QCISD(T)19 method using 6-311+G-(2df,2p) basis sets. The Gaussian 90 program suite20 was used to perform all of the calculations, whose results are discussed here.

Results and Discussion

Our calculated molecular properties of the various electronic states of \( \text{Si}_2\text{O} \), \( \text{Si}_2\text{O} \), and \( \text{Si}_3\text{O} \) are presented in Tables I–V, and dissociation energies for various decompositions of \( \text{Si}_2\text{O} \), \( \text{Si}_3\text{O} \), and \( \text{Si}_3\text{O} \) are shown in Table VI. The corresponding molecular structures are depicted in Figure 1, and the simulated IR spectra of the lowest energy minima of \( \text{Si}_2\text{O} \) and \( \text{Si}_3\text{O} \) are shown in Figure 2.

\( \text{Si}_2\text{O} \) and \( \text{Si}_3\text{O} \). It is well-known that the \( \text{Si}_2\text{O} \) molecule has a singlet \((1\Sigma^+, 1\sigma^2\pi^21\pi^2\pi^2\pi^2)\) ground state and that the \( \text{Si}_2 \) dimer is a triplet \((\Sigma^+, 1\sigma^21\pi^2\pi^22\pi^2\pi^2)\) in its ground electronic state.6

\( \text{Si}_3\text{O} \) is known to have a linear CCO singlet structure.21 However, for \( \text{Si}_3\text{O} \) we

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### Table I: Calculated Molecular Properties of the Singlet and Triplet States of SiO and Si₂

<table>
<thead>
<tr>
<th></th>
<th>SiO (Σ⁺)</th>
<th>SiO (Π)</th>
<th>SiO (Σ⁻)</th>
<th>Si₂ (Σ⁻)</th>
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<td>R(Si–O)</td>
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</tr>
<tr>
<td>E_MFP</td>
<td>-364.2533</td>
<td>-364.09022</td>
<td>-578.11043</td>
<td>-578.12997</td>
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<td>ωₐ</td>
<td>1183 cm⁻¹</td>
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<tr>
<td>ZPE</td>
<td>1.69 kcal/mol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MP2(full)/6-311+G*</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

### QCISD(T)/6-311+G(2df) State

<table>
<thead>
<tr>
<th></th>
<th>SiO (C₃v, 1A₁)</th>
<th>SiO (C₃v, 1B₁)</th>
<th>SiO (C₃v, 1Σ⁻)</th>
<th>SiO (C₃v, 1Σ⁺)</th>
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<tr>
<td>E_MFP</td>
<td>-653.3328Å</td>
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<td>-653.7018Å</td>
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<td>ωₐ</td>
<td>810 cm⁻¹</td>
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<td>1207 cm⁻¹</td>
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<tr>
<td>r(b2)</td>
<td>613 cm⁻¹</td>
<td>1389 cm⁻¹</td>
<td>1220 cm⁻¹</td>
<td>514 cm⁻¹</td>
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<tr>
<td>ZPE</td>
<td>2.66 kcal/mol</td>
<td>3.63 kcal/mol</td>
<td>2.81 kcal/mol</td>
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<td>MP2(full)/6-311+G*</td>
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</table>

### Table II: Calculated Molecular Properties of the Lowest Energy SiO Structures

<table>
<thead>
<tr>
<th>Structure</th>
<th>SiO (C₃v, 1A₁)</th>
<th>SiO (C₃v, 1B₁)</th>
<th>SiO (C₃v, 1Σ⁻)</th>
<th>SiO (C₃v, 1Σ⁺)</th>
</tr>
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<tbody>
<tr>
<td>1a₁2a₂1b₁2b₂1b₂⁻</td>
<td>1a₁2a₂1b₁2b₂1b₂⁻</td>
<td>1a₁2a₂1b₁2b₂1b₂⁻</td>
<td>1a₁2a₂1b₁2b₂1b₂⁻</td>
<td>1a₁2a₂1b₁2b₂1b₂⁻</td>
</tr>
<tr>
<td>3a₁2b₂2a₄1b₂⁺</td>
<td>3a₁2b₂2a₄1b₂⁺</td>
<td>3a₁2b₂2a₄1b₂⁺</td>
<td>3a₁2b₂2a₄1b₂⁺</td>
<td>3a₁2b₂2a₄1b₂⁺</td>
</tr>
<tr>
<td>2a₇2e₃3ε⁴</td>
<td>2a₇2e₃3ε⁴</td>
<td>2a₇2e₃3ε⁴</td>
<td>2a₇2e₃3ε⁴</td>
<td>2a₇2e₃3ε⁴</td>
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</tbody>
</table>

### Table III: Calculated Molecular Properties of the Lowest Energy Si₂ Structures

<table>
<thead>
<tr>
<th>Structure</th>
<th>SiO (D₁h, 1A')</th>
<th>SiO (C₃v, 1A')</th>
<th>SiO (C₃v, 1A')</th>
<th>SiO (C₃v, 1A')</th>
<th>SiO (C₃v, 1A')</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a₁2e₄1a₂⁻</td>
<td>1a₁2e₄1a₂⁻</td>
<td>1a₁2e₄1a₂⁻</td>
<td>1a₁2e₄1a₂⁻</td>
<td>1a₁2e₄1a₂⁻</td>
<td>1a₁2e₄1a₂⁻</td>
</tr>
<tr>
<td>2a₂2e₂3ε⁴</td>
<td>2a₂2e₂3ε⁴</td>
<td>2a₂2e₂3ε⁴</td>
<td>2a₂2e₂3ε⁴</td>
<td>2a₂2e₂3ε⁴</td>
<td>2a₂2e₂3ε⁴</td>
</tr>
</tbody>
</table>

### MP2/SDTQ/6-311+G* Level

- Frequencies were not calculated at the MP2/6-311+G* level due to difficulties with convergence.
- Frequencies calculated at the MP2(full)/6-31G* level.

The bent singlet C₂⁺ (1A₁, 1a₁2a₂1b₁2b₂1b₂⁻) SiO₂ structure has been found to be the global minima (see Table II), which is unlike the case for CO₂. Five other local minimum structures were also identified, and some of them are characterized in Table II.

The triplet C₃ (1B₁, 1a₁2a₂1b₁2b₂1b₂⁻) SiO₂ triplet linear D₈h (3Σ⁺, 1ε₂2ε₃2ε₄2ε₅2ε₆2ε₇2ε₈) SiO₂, and linear C₃ (3Σ⁺, 1ε²2ε₃2ε₄2ε₅2ε₆2ε₇2ε₈) SiO₂ structures lie higher in energy than the global minimum C₂⁺ (1A₁) structure by 17.3, 20.7, and 27.0 kcal/mol, respectively (at the QCISD(T)/6-311+G* level). The geometrical structure of the C₂⁺ (1B₁) triplet state does not differ much from that of the singlet C₂⁺ state.

Our results do not agree with the previous conclusion by DeKock and others that the bent triplet SiO₂ is higher in energy than the linear molecules. At our largest 6-311+G(2df) basis set, the
The lowest energy Si2O structure is different from those of Li2O, Mg2O, and Al2O3, in which the oxygen atom breaks the metal-metal bond to form stable linear SiOSi (2.337 Å) structures. The equilibrium SiSi bond length (2.340 Å), as in the previous structure. There is a low-lying triangular triplet state of SiSiO (2.317 Å), and the SiO distances (1.723 Å) are also close to the normal single Si-O bonds in H3Si-OH (1.66 Å) at all MP2(full)/6-31+G* levels. The bonding in this molecule may be represented as a single Si-O bond and two single Si-O bonds with one lone electron pair on each silicon atom, which will coordinate outside of rather than insert into such clusters. The bent C5v (1B1) structure of Si2O is more stable than the linear $D_{4h}$ ($\Sigma^+$) at all levels of theory, from PUSCF to QCISD(T). In our calculation, we also found that the linear SiO3 (D5h, $\Sigma^+$) structure is more stable than SiO2 (C5v, $\Sigma^+$), as in the previous calculations by DeKock and others. However, we assume that the C5v (1B1) structure of Si2O is more stable than the linear D4h (1Σ+) state of SiO2. The equilibrium Si-Si bond length (2.173 Å) will coordinate outside of rather than insert into such clusters.

The lowest energy SiO3 structure is different from those of Li2O, Mg2O, and Al2O3, in which the oxygen atom breaks the metal–metal bond to form stable linear X–O–X structures. In Si2O, the oxygen is coordinated to both Si atoms, but a single SiSi bond remains intact. This result provides us the first hint that when oxygen atoms interact with larger silicon clusters, they will coordinate outside of rather than insert into such clusters.

The bent singlet-state global minimum of the SiO3 molecule is thermodynamically stable with respect to dissociation into SiO–(\(\pi^*\)) + Si(2P) by 50.1 kcal/mol (this value is somewhat less than $D_a$(SiO) = 74.7 kcal/mol, as well as into Si3(2Σ+) + O(2P) by 162.4 kcal/mol. The equilibrium Si–Si bond length (2.340 Å) in Si2O (C2v, 1A1) is close to the “normal” Si–Si single bond in HSiSi–H3 (2.337 Å), and the Si-O distances (1.723 Å) are also close to the normal single Si–O bonds in H3Si–OH (1.661 Å) at all MP2(full)/6-31+G** levels. Therefore, the bonding in this molecule may be represented as a single Si–Si bond and two single Si-O bonds with one lone electron pair on each silicon atom. The calculated infrared (IR) spectrum is presented in Figure 2 to help identify this molecule in the gas phase or in matrix isolation.

The lowest energy SiO2 structure is different from those of Li2O, Mg2O, and Al2O3, in which the oxygen atom breaks the metal–metal bond to form stable linear X–O–X structures. In Si2O, the oxygen is coordinated to both Si atoms, but a single SiSi bond remains intact. This result provides us the first hint that when oxygen atoms interact with larger silicon clusters, they will coordinate outside of rather than insert into such clusters.

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### TABLE VI: Calculated (with 6-311+G(2df) Basis Set) and Experimental Dissociation Energies of the Si₃O Species (kcal/mol)

<table>
<thead>
<tr>
<th>reaction</th>
<th>PUHF</th>
<th>PMP2</th>
<th>PMP3</th>
<th>PMP4</th>
<th>QCISD(T)</th>
<th>QCISD(T)+ZPE</th>
<th>expt(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si₂ → Si + Si</td>
<td>39.8</td>
<td>68.9</td>
<td>68.9</td>
<td>70.4</td>
<td>70.5</td>
<td>69.7</td>
<td>74.0</td>
</tr>
<tr>
<td>SiO → Si + O</td>
<td>104.7</td>
<td>194.3</td>
<td>171.1</td>
<td>189.0</td>
<td>183.7</td>
<td>182.0</td>
<td>190.0</td>
</tr>
<tr>
<td>Si₂O → SiO + Si</td>
<td>28.3</td>
<td>48.3</td>
<td>51.7</td>
<td>48.8</td>
<td>51.1</td>
<td>50.1</td>
<td></td>
</tr>
<tr>
<td>Si₂O → Si₂ + O</td>
<td>93.1</td>
<td>173.8</td>
<td>153.8</td>
<td>167.3</td>
<td>164.3</td>
<td>162.4</td>
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<tr>
<td>SiO → Si + Si₂</td>
<td>133.0</td>
<td>242.6</td>
<td>222.7</td>
<td>237.8</td>
<td>234.8</td>
<td>232.2</td>
<td></td>
</tr>
<tr>
<td>Si₂O → Si₂ + Si</td>
<td>36.9</td>
<td>86.0</td>
<td>76.0</td>
<td>83.0</td>
<td>81.7(^b)</td>
<td>81.7(^b)</td>
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</tr>
<tr>
<td>Si₂O → SiO + Si₂</td>
<td>25.4</td>
<td>65.5</td>
<td>58.7</td>
<td>61.4</td>
<td>59.8(^b)</td>
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<tr>
<td>Si₂O → Si₂ + O</td>
<td>94.0</td>
<td>161.6</td>
<td>143.1</td>
<td>155.3</td>
<td>153.2(^b)</td>
<td>153.2(^b)</td>
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</tr>
<tr>
<td>Si₂O → Si₃ + O</td>
<td>169.9</td>
<td>328.7</td>
<td>298.8</td>
<td>320.8</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

\(^a\) Experimental data from ref 6. \(^b\) At the MP4SDTQ/6-311+(2df)//MP2(full)/6-31+G*+ZPE level. \(^c\) Geometries and frequencies of Si₃ calculated at the MP2(full)//6-311+G* level.

**Figure 1.** Molecular structures and geometrical parameters examined at MP2(full)//6-311+G* for Si₂O and Si₃O.

**Threelfold Coordinated Oxygen.** The first structures examined for Si₃O (see Figure 1) involve the insertion of an oxygen atom into the triangle of Si₃ in a threefold site. The resultant high-symmetry $D_{3h}$ structure ($'A_1$, $1a_1'^2e'^4'1a_2'^2'2a_1'^2'2e'^4'3e'^4'2a_2'^6'$)
was found to have one imaginary vibrational frequency $v_2(a_1')$, allowing this mode to distort leads to a pyramidal $C_{2v}(A_1', a_1'' 2a_2'' 3a_1'' 2b_2'' 4a_1'' 2b_1')$ local minimum which is 31.3 kcal/mol lower in energy. However, the Si-Si distances (2.617 Å) in the $C_{2h}(A_1')$ structure are larger than single Si-Si bonds in molecules such as $H_2Si-SiH_2$ ($R(Si-Si) = 2.337$ Å). Therefore, silicon-silicon interactions do not contribute significantly to the stability of this structure. Probably as a result, this $C_{2v}(A_1')$ structure is not thermodynamically stable with respect to dissociation into $SiO + Si$ (i.e., its lowest energy decomposition path).

Deforming the $D_3h$ singlet structure while retaining planar symmetry leads to two lower energy structures: $C_{2h}(A_1', a_1'' 2a_2'' 3a_1'' 2b_2'' 4a_1' 2b_1'')$ and $C_{2h}(A_1', a_1'' 2a_2'' 3a_1'' 2b_2'' 4a_1'' 2b_1'')$. In the $C_{2h}(A_1')$ structure, two Si-Si bonds elongate (by 0.429 Å) and one Si-Si bond shortens (by 0.773 Å) relative to the $D_3h$ starting point. As a result, two silicon atoms approach close enough ($R(Si-Si) = 2.253$ Å) to form a bond. In the $C_{2h}(A_1')$ structure, one silicon-silicon distance increases, relative to the $D_3h$ starting point, but the two other decrease to form two Si-Si single bonds ($R(Si-Si) = 2.446$ Å). The $C_{2v}(A_1')$ structure is a saddle point, and the $C_{2h}(A_1')$ structure is a local minimum (see Tables III-V).

In contrast, the triplet states $C_{2v}(A_1', a_1'' 2a_2'' 3a_1'' 2b_2'' 4a_1' 2b_1'')$ and $C_{2h}(A_1', a_1'' 2a_2'' 3a_1'' 2b_2'' 4a_1'' 2b_1'')$ (with $R(Si-Si) = 2.253$ Å) correspond to these two $C_{2v}$ structures are both local minima. However, the most stable of these structures, $C_{2v}(A_1')$ (8B$_1$), lies only 27.3 kcal/mol below the energy of the dissociation products $SiO + Si$. From these data, we speculated that lower energies might arise from structures that do not place the oxygen atom inside the silicon cluster; again, this is unlike $Na_2O$, $Mg_2O$, and $Al_2O_3$, where the most stable structures have the oxygen atom inside the cluster.

Another $C_{2v}$ pyramidal structure involves binding of the oxygen atom in a threefold site of $Si_2$ without breaking the silicon–silicon bonds (see Tables III-V). The corresponding $C_{2h}(A_1', a_1'' 2a_2'' 3a_1'' 2b_2'' 4a_1' 2b_1'')$ structure is a local minimum but lies ~34.4 kcal/mol (at the (MP4SDTQ/6-311+G(2df) level) higher in energy than the global minimum $C_{2v}(A_1')$, structure, to be discussed shortly.

**Twofold Coordinated Oxygen.** Structures in the next group examined begin by coordinating the oxygen atom to the exterior (edges and vertices) of the most stable $C_{2v}(A_1')$ structure of $Si_2$. Both singlet and triplet structures have been optimized, and our findings are summarized in Tables III-V.

A singlet rhombus $C_{2v}(A_1', a_1'' 2a_2'' 3a_1'' 2b_2'' 4a_1' 2b_1'')$ structure (Figure 1) with the oxygen atom coordinated to an edge of the $Si_3$ triangle was found to be the most stable structure. The optimized $Si_3-O$ (1.731 Å) and $Si-Si_2$ bonds (2.311 Å) as well as the angle $\angle SiOSi$ (82.9°) are very close to the corresponding $Si$ bond (1.723 Å) and $Si$ bond (2.340 Å) bond lengths and angles $\angle SiOSi$ (85.5°) in the most stable structure of $Si_2O$ (see Tables II and III-V). All silicon–silicon bond lengths are comparable to "normal" single Si–Si bond lengths.

**Singly Coordinated Oxygen.** In the vertex-bonded structure $C_{2h}(A_1', a_1'' 2a_2'' 3a_1'' 2b_2'' 4a_1' 2b_1'')$ shown in Figure 1, the oxygen atom is coordinated to only one of the $Si$ atoms. Thus, the oxygen–silicon bond (1.536 Å) is 0.20 Å shorter than that in the $C_{2v}(A_1')$ rhombus structure and is the same as that in diatomic $SiO$ (1.536 Å at the MP2(full)/6-311+G* level). The Si–$Si_2$ bond length (2.284 Å) is close to the length of normal single Si–Si bonds, and the Si–Si bond length is 0.07 Å shorter. However, this $C_{2h}(A_1')$ structure is a saddle point whose Hessian eigenvector of imaginary frequency leads to the twofold coordinated $C_{2v}(A_1')$ structure discussed earlier. The barrier for the intramolecular movement of the oxygen atom between the $C_{2v}$ and $Y$ structures is high (18.8 kcal/mol at QCISD(T)/6-311+G(2df) level) and probably too high to display rovibrational spectral manifestations.
vibrational spectrum agree well with the experimental data. A rhombus $C_{2h}$ ($A_{1}$) minimum-energy structure has been found for $Si_{2}C$; this structure can be viewed as the rhombus $D_{2h}$ ($A_{2}$) structure of $Si_{4}$ in which one carbon atom is replaced by a silicon atom. The $Si_{4}$ molecule examined here has a similar rhombus structure; however, the chemical bonding is different in $Si_{2}O$ and $Si_{2}C$. In $Si_{2}C$, the carbon atom is coordinated to all three silicon atoms and silicon–silicon bonding between the two bridge atoms is absent; in $Si_{2}O$, the oxygen atom is coordinated to only two silicon atoms and silicon–silicon bonding between the two bridge atoms is retained (as evidenced by the Si–Si bond lengths).

### Overview

$SiO$ and $Si_{2}O$ may provide prototypes for the interaction between an O atom and the simplest silicon clusters or sites that are accessible on various solid silicon surfaces, kinks, steps, and terraces. Therefore, it is important to now compare results of our calculations with available experimental data on oxygen chemisorption to silicon surfaces. We begin by summarizing our results.

**Our Findings.** First, we found that the most energetically stable structures involve an oxygen atom coordinated to two silicon atoms on the periphery of the cluster. This twofold coordination is favored over monodentate coordination, which, in turn, is favored over threefold coordination.

We found that the energy required to desorb atomic oxygen or atomic silicon is much higher than the energy required for desorption of an intact SiO molecule. Thus, SiO should be the most abundant species observed in desorption from oxidized silicon surface.

We calculated vibrational frequencies of the Si–O–Si symmetric stretch (810 cm$^{-1}$) and antisymmetric stretch (613 cm$^{-1}$) vibrations for the lowest energy bent structure of $Si_{2}O$; our calculations produced 705 and 471 cm$^{-1}$, respectively, for these vibrations in the lowest energy rhombus structure of $Si_{2}O$. In contrast, the calculated Si–O frequency of the monodentate–bonded structure of $Si_{2}O$ is 1207 cm$^{-1}$; for monodentate–bonded $Si_{3}O$, it is 1189 cm$^{-1}$.

**Experimental Information.** In a real-time study of oxygen reacting with Si(100) by Yu and Eldridge, only SiO was detected as a desorbed reaction product. This result has been supported by other experimental observations. The energy required to activate the SiO desorption process from Si(100) was found to be 69 kcal/mol, which is similar to our $Si_{2}O \rightarrow Si_{2} + SiO$ dissociation energy (60 kcal/mol).

On silicon surfaces, two types of oxides have been observed by high-resolution electron energy loss spectroscopy, ultraviolet photoelectron spectroscopy, and low-energy electron diffraction. A feature corresponding to an energy loss of 1226 cm$^{-1}$ was attributed to one oxide, and features at 444, 686, and 1032 cm$^{-1}$ were attributed to a second oxide.

The former oxide is consistent with diatomic SiO adsorbed on the surface. Its 1226 cm$^{-1}$ band is close to the vibrational frequencies we obtain for monodentate–bonded species (e.g., 1183 cm$^{-1}$ in SiO, 1207 cm$^{-1}$ in $Si_{2}O$, 1190 cm$^{-1}$ in SiO ($C_{2v}$, Y), 1187 cm$^{-1}$ in SiO ($C_{2v}$, $Y$, $A_{1}$), and 1187 cm$^{-1}$ in SiO ($C_{2v}$, $Y$, $B_{1}$)).

The second oxide was proposed to closely resemble SiO in a local environment similar to that in bulk silicon monoxide. While the nature of the bulk SiO is still controversial, Yasaitis and Kaplow and Bianconi and Bauer concluded that their X-ray diffraction data are consistent with ring structures involving SiO$_{n}$ in which each oxygen atom is coordinated to two silicon atoms and in which there is substantially reduced Si–Si bonding. Our calculated frequencies for the twofold coordinated lowest energy structures of $Si_{2}O$ ($\nu_{1}(a_{1})$ = 810 cm$^{-1}$) (symmetric stretch O–Si$_{2}$ vibration), $\nu_{2}(b_{2})$ = 613 cm$^{-1}$ (asymmetric stretch O–Si$_{2}$ vibration), and $\nu_{3}(a_{1})$ = 437 cm$^{-1}$ (symmetric stretch Si–Si vibration) and SiO ($C_{2v}$, $A_{2}$) ($\nu_{1}(a_{1})$ = 795 cm$^{-1}$) (symmetric stretch O–Si$_{2}$ vibration), $\nu_{2}(b_{2})$ = 471 cm$^{-1}$ (asymmetric stretch O–Si$_{2}$ vibration), and $\nu_{3}(a_{1})$ = 461 cm$^{-1}$ (symmetric stretch Si–Si vibration) are similar to the observed vibrational bands ascribed to the second oxide (1065, 686, and 428 cm$^{-1}$ in ref 29a and 992, 871, 774, and 403 cm$^{-1}$ in ref 29b). In particular, the Si–Si vibrational frequencies clearly match well. Therefore, it seems most likely that, in this oxide, each O atom resides in a twofold coordination site in which significant Si–Si bonding is intact.

### Conclusions

The results of our calculations on $Si_{2}O$ and $Si_{3}O$ have shown that an oxygen atom favors coordination to the periphery of silicon clusters rather than insertion into Si–Si bonds. Structures with the oxygen atom inside the cluster that result in monodentate Si–Si bonding are much higher in energy. This result is in sharp contrast with the structures of other oxygen–metal clusters, such as Li$_{2}$O, Li$_{2}$O, Mg$_{2}$O, Mg$_{2}$O, Al$_{2}$O, Al$_{2}$O, and AlO$_{2}$, where the most stable structures have the oxygen atom in the interior of the cluster in a high-coordination location.

Particularly important findings include the following:

1. $Si_{2}O$ and $Si_{3}O$ are thermodynamically stable species with singlet triangular $C_{2h}$ ($A_{1}$) and planar–rhombus $C_{2h}$ ($A_{1}$) structures, respectively. Therefore, they are viable molecules that might be found in gas-phase and matrix isolation experiments.

2. The lowest energy decomposition path for both species involves loss of an SiO molecule. For $Si_{2}O \rightarrow SiO + Si$, the energy difference is 60 kcal/mol, and for $Si_{3}O \rightarrow SiO + Si$ it is 50 kcal/mol. For SiO, loss of atomic Si or of O requires 82 or 153 kcal/mol, respectively.

3. All structures of SiO with the oxygen atom inside the $Si_{3}$ cluster are less stable than the planar–rhombus $C_{2h}$ ($A_{1}$) structure in which the oxygen atom is coordinated to an edge of $Si_{3}$ cluster.

4. Structures with the O atom coordinated to a single Si site are less stable than the twofold coordinated species but more stable than the threefold coordinated species.

5. Our computed vibrational frequencies seem to shed light on the geometrical and bonding nature of two oxide structures that have been studied experimentally.

It is our hope that the results presented here stimulate further experimental study of small SiO$_{n}$ clusters, where results of such calculations may be useful guides to interpreting the experimental data.

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### References and Notes

Ab Initio Study of Si₃O and Si₃O


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