Electronic Structure and Potential Energy Surfaces of Positive Ions of Group IV Tetrarners (Ge\(_4^+\)-Pb\(_4^+\))

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We compute the geometries and energy separations of 17 electronic states of Ge\(_4^+\), Sn\(_4^+\), and Pb\(_4^+\). The complete active space multiconfiguration self-consistent field (CAS-MCSCF) followed by multireference singles + doubles configuration interaction (MRSDCI) calculations are employed in this investigation. Spin-orbit effects are also included using the relativistic configuration interaction (RCI) method for Pb\(_4^+\). The ground state of Ge\(_4^+\) is found to be a \(^{1}A_2\) state with an equilibrium geometry of a rhombus. For Sn\(_4^+\) we find two nearly-degenerate electronic states of \(^{2}B_1\) and \(^{2}A_1\) symmetries as candidates for the ground state both with rhombus equilibrium geometries. We find three nearly-degenerate electronic states (\(^{2}B_1\), \(^{2}B_3\), and \(^{2}A_1\)) for Pb\(_4^+\) as candidates for the ground state in the absence of spin-orbit interaction. Upon introduction of spin-orbit interaction, the ground state of Pb\(_4^+\) becomes a \(^{2}B_1\) state with an equilibrium geometry of a rhombus. The leading configuration is composed of 1a\(_1\)2a\(_2\)3a\(_8\)1b\(_1\)2b\(_1\)1b\(_2\)1b\(_3\). Removal of an electron from the 3a\(_1\) orbital would lead to a \(^{2}A_2\) state with the 2B\(_1\) state for the positive ion while the 2B\(_1\) state can be formed by removing an electron from the 2b\(_1\) orbital. Since the 1b\(_2\) orbital is primarily composed of the valence s orbitals of two of the group IV atoms, this is not an attractive candidate for ionization. On the other hand, removal of an electron from 1b\(_1\) or 1b\(_2\) could lead to \(^{2}B_1\) and \(^{2}B_3\) states, respectively. Consequently, in the present study on Ge\(_4^+\)-Pb\(_4^+\), we consider \(^{2}B_1\), \(^{2}A_1\), \(^{2}B_3\), and \(^{2}B_2\) states with rhombus geometries.

The tetrahedral geometry is somewhat more complex due to the degeneracy of the \(t_2\) and \(e\) orbitals. The A\(_1\) state of the neutral structure \(4\Sigma^+\) arises from the 1a\(_1\)2a\(_2\)3a\(_8\) configuration. Hence removal of an electron from the 3a\(_1\) orbital leads to the \(2T_2\) state. On the other hand, the spin-exchange stabilization energy could favor the \(A_2\) state arising from the 1a\(_1\)2a\(_2\)3a\(_8\) configuration due to the near proximity of the 2t\(_2\) and 1e orbitals as well as spin-stabilization energy. Consequently, in addition to these states we also considered electronic states of \(T_2\), \(E\), and \(T_2\) symmetries for the tetrahedral structure.

For the linear structure of neutral Si\(_4\), the \(^3\Sigma^+_g\) state was found to be the lowest state. This state arises from the \(1s^22s^22p^0\) configuration. A few lowest-lying electronic states for the positive ion with linear geometry are \(^2\Sigma^+_g\), \(^2\Pi_u\), \(^2\Pi_g\), \(^2\Delta_g\), \(^2\Sigma^+_u\), \(^2\Sigma^+_u\), \(^2\Pi_u\), \(^2\Pi_g\), \(^4\Pi_g\), \(^2\Delta_g\), and \(^2\Sigma^+_g\). We considered these states with linear geometry. All computations of Ge\(_4^+\)-Pb\(_4^+\) were made using the relativistic effective core potentials (RECPs) which retained the outer ns\(_2\)np\(_2\) (\(n\) = principal quantum number) shells in the valence space for Ge-Pb, replacing the rest of the electrons by RECPs. Computation of the rhombus and square structures were made in the \(D_4h\) group. However, the computations of the tetrahedral structure were made in the \(C_2h\) group. The RECPs for Ge-Pb were taken from ref 41. We start with the (3p3p) valence Gaussian basis set in ref 41 which was further augmented by one set of six-component

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1 Camille and Henry Dreyfus Teacher-Scholar.
configurations. The CASSCF calculations used the method to address the effect of spin-orbit coupling. The RCI calculations included up to two double excitations from each reference configuration, three of which arise from the \( 3 \Sigma^+ \) state, and three from the \( 2 \Sigma^- \) state.

The rhombus and square geometries were considered in the \( D_4h \) group. The active space in the \( D_4h \) group consisted of four \( a_1 \), three \( b_2 \), two \( b_1 \), two \( b_3 \), one \( b_1 \) and one \( b_3 \) orbitals. All four valence \( s \) orbitals for both the rhombus and square geometries were kept inactive in the CASSCF calculations. Two \( a_1 \), two \( b_2 \), two \( b_1 \), two \( b_3 \), two \( b_3 \), one \( b_1 \) and one \( b_3 \) orbitals were included in the CASSCF active space. The active space of the linear structure \( (D_{2h}) \) consisted of four \( a_1 \), four \( b_2 \), two \( b_1 \), two \( b_3 \), one \( b_1 \) and one \( b_3 \) orbitals. Two \( a_1 \) and two \( b_2 \) orbitals which correlated into four valence \( s \) orbitals were kept inactive. Consequently, in this method all geometries were treated in a consistent manner. Separate CASSCF calculations were carried out for each state of different spatial symmetry, spin multiplicity, and geometry. The geometries of all states were optimized using a multidimensional harmonic approximation near the potential well.

Multireference singles + doubles configuration interaction (MRSDCI) calculations were carried out for some low-lying states of different geometries with the intent of incorporating the effects of higher-order electron correlations. The MRSDCI calculations also included excitations from all four valence \( s \) orbitals. All configurations in the CASSCF with coefficients \( \geq 0.1 \) were included as reference configurations in the MRSDCI. Subsequently, single and double excitations were allowed from these reference configurations. The CASSCF calculations on \( \text{Ge}_4^+ \) included up to 141577 configuration spin functions (CSFs) depending on the spatial symmetry, spin multiplicity, and geometry, while the MRSDCI calculations included up to 650000 CSFs.

The spin-orbit effects could be important for \( \text{Pb}_4^+ \). Consequently, we used the relativistic configuration interaction (RCI) method to address the effect of spin-orbit coupling. The RCI calculations were made in the \( C_2^h \) double group. All electronic states which have the same symmetry in the double group were mixed. Note that the RCI of \( \text{Pb}_4^+ \) has to be done in the \( E \) double group representation since \( \text{Pb}_4^+ \) is a system of an odd number of electrons. The RCI computation of \( \text{Pb}_4^+ \) included 13 reference configurations, three of which arise from the \( 3 \Sigma^+ \) state, two from the \( 1 \Sigma^+ \) state, five from the \( 2 \Sigma^- \) state, and three from the \( 3 \Sigma^- \) state. Single + double excitations from these reference configurations resulted in a total of 5919 configurations. The spin-orbit integrals were evaluated using Pitzer's ARGOS codes which were subsequently transformed into the MRSDCI natural orbital basis. The integrals thus computed were added to the CI matrix in the RCI.

All CASSCF/MRSDCI calculations were made using one of the author's modified versions of ALCHEMY II codes to include relativistic effective core potentials (RECPs) as described in ref 43. The spin–orbit integrals for the RCI were obtained using R. Pitzer's modified version of ARGOS codes. The RCI was made using the method described in ref 42.

Results and Discussion


Table I shows the optimized geometries and energy separations of 18 electronic states of \( \text{Ge}_4^+ \) among which the geometry of the linear \( \text{B}_4^+ \) state was not optimized. We also show in that table the dissociation limit \( (\text{Ge}_2^+ + \text{Ge}_2^+) \) obtained by using the CASSCF and MRSDCI calculations. Figure 1 shows the potential energy surfaces of four low-lying electronic states with the rhombus geometry and corresponding electronic states with the square geometry. In Figure 1 for each \( \theta \) the \( \text{Ge}-\text{Ge} \) bond lengths were optimized and the optimized energies are plotted. Computations were carried out varying \( \theta \) in steps of \( 5^\circ \). As seen from Table I and Figure 1, the ground state of \( \text{Ge}_4^+ \) is a \( \text{B}_2^+ \) state with the equilibrium structure of a rhombus. The \( \text{Ge}-\text{Ge} \) bond lengths along the four sides of the rhombus structure are 2.447 Å, which are 0.03 Å shorter than the \( \text{A}_2^+ \) ground state of the neutral \( \text{Ge}_2^+ \). The acute apex angle of 72.5° at the MRSDCI level is 8.6° larger than the \( \text{A}_2^+ \) ground state, suggesting more repulsive force between the \( \text{Ge} \) atoms located on the \( y \) axis (the distance between these two atoms is 2.894 Å). The first excited state is found to be the \( \text{A}_2^+ \) state with the rhombus geometry which is \( 1.73 \) eV above the \( \text{B}_2^+ \) ground state. As seen from Table 1, the bond lengths decrease by 0.02–0.08 Å at the MRSDCI level compared to the CASSCF method while the bond angle changes 0.2–1.4° for the rhombus geometry.

The \( \text{B}_2^+ \) state of square geometry is higher in energy compared to the \( \text{B}_1^+ \) and \( \text{B}_3^+ \) states with the rhombus geometry at the
TABLE II: Geometries and Energy Separations of Electronic States of Sn₄⁺

<table>
<thead>
<tr>
<th>geometry</th>
<th>state</th>
<th>( R_{12}, \text{Å} )</th>
<th>( R_{34}, \text{Å} )</th>
<th>( \theta, \text{deg} )</th>
<th>( E, \text{eV} )</th>
<th>( R_{12}', \text{Å} )</th>
<th>( R_{34}', \text{Å} )</th>
<th>( \theta', \text{deg} )</th>
<th>( E', \text{eV} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>rhombus</td>
<td>( ^2\text{B}_1 )</td>
<td>2.869</td>
<td>72.5</td>
<td>0.00</td>
<td>2.805</td>
<td>71.8</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( ^4\text{A}_1 )</td>
<td>2.942</td>
<td>59.8</td>
<td>0.14</td>
<td>2.893</td>
<td>59.3</td>
<td>0.04</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>( ^2\text{B}_2 )</td>
<td>2.979</td>
<td>65.2</td>
<td>0.20</td>
<td>2.925</td>
<td>65.7</td>
<td>0.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( ^4\text{B}_2 )</td>
<td>2.976</td>
<td>61.2</td>
<td>0.48</td>
<td>2.943</td>
<td>58.3</td>
<td>0.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>square</td>
<td>( ^2\text{B}_1 )</td>
<td>2.877</td>
<td>90.0</td>
<td>0.58</td>
<td>2.810</td>
<td>90.0</td>
<td>0.48</td>
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<td>( ^4\text{A}_1 )</td>
<td>3.178</td>
<td>109.47</td>
<td>1.13</td>
<td>3.067</td>
<td>109.47</td>
<td>0.96</td>
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<tr>
<td></td>
<td>( ^2\text{B}_2 )</td>
<td>3.184</td>
<td>109.47</td>
<td>1.37</td>
<td>3.083</td>
<td>109.47</td>
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<td></td>
<td>( ^3\text{T}_2 )</td>
<td>3.194</td>
<td>109.47</td>
<td>1.53</td>
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</tr>
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<td>( ^2\text{B}_1 )</td>
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<td>2.970</td>
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<td>1.77</td>
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<td>3.196</td>
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<td>( ^2\text{B}_2 )</td>
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<td>1.91</td>
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<td>109.47</td>
<td>2.06</td>
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<td>2.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>linear</td>
<td>( ^4\text{E} )</td>
<td>3.314</td>
<td>2.858</td>
<td>180.0</td>
<td>3.355</td>
<td>2.759</td>
<td>180.0</td>
<td>2.32</td>
<td></td>
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<tr>
<td>Sn₂⁺+Sn₂⁺⁺</td>
<td>( ^2\Sigma )</td>
<td>3.988</td>
<td>2.872</td>
<td>180.0</td>
<td>3.18</td>
<td>2.735</td>
<td>180.0</td>
<td>3.12</td>
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</tr>
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</table>

* \( R_{12}, R_{34}, \text{and} \theta \text{ as in Table I.} \)

Table II shows the optimized geometries and energy separations of 17 electronic states of Sn₄⁺ and the dissociation limit (Sn₂⁺+Sn₂⁺⁺) obtained using the CASSCF and MRSDCI levels. Figure 2 shows the potential energy surfaces of four low-lying electronic states with the rhombus geometry and the corresponding electronic states with the square geometry. As seen from Table II and Figure 2, the ground state of Sn₄⁺ is a \(^2\text{B}_1\) state with the equilibrium structure of a rhombus at both the CASSCF and MRSDCI levels. The Sn–Sn bond lengths corresponding to the four equal sides of the rhombus are 2.805 Å, and the acute apex bond angles are 71.8° at the MRSDCI level. The energy of the first excited state \(^2\text{A}_1\) with the rhombus geometry is 0.14 eV above the ground state at the CASSCF level and at the MRSDCI level it is only 0.04 eV above the ground state. Hence the \(^2\text{A}_1\) state with the rhombus geometry is considered also as a potential candidate for the ground state of Sn₄⁺.

A comparison of the results obtained at the CASSCF and MRSDCI levels of theory reveals that the bond lengths change

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**Figure 1.** Potential energy surfaces of low-lying electronic states of Ge₄⁺.

CASSCF level while at the MRSDCI level the two states were found to be reversed in order. As seen from Figure 1, the energies of all states with the square geometry are very high with the exception of the \(^2\text{B}_1\) state of square geometry. In any case for all states considered here the square geometries are saddle points in the potential energy surfaces. All these states exhibit rhombic distortions from their ideal square structures to rhombic structures.

The lowest \(^4\text{A}_1\) state of the tetrahedral geometry is found to be 1.41 eV higher than the rhombus ground state at the MRSDCI level. The Ge–Ge bond lengths of the tetrahedron are longer than the Ge–Ge side bond lengths of the rhombus, as expected. As seen from Table I, the bond lengths of all states with the tetrahedral geometry are 2.80–2.83 Å at the CASSCF level and about 2.72 Å at the MRSDCI level while the corresponding bond lengths are 2.50–2.60 Å for the rhombus structure at the CASSCF level and 2.45–2.57 Å at the MRSDCI level.

The lowest state with the linear geometry is the \(^6\Sigma^+\) state, but it is much higher (2.7 eV) in energy compared to the \(^2\text{B}_1\) ground state with the rhombus geometry. The central bond length is 0.6–0.7 Å longer than the terminal bond length at both CASSCF and MRSDCI levels. Other electronic states such as \(^2\Pi\) and \(^2\Sigma^+\) are higher in energy.

We also calculated the CASSCF vertical energy separations of electronic states with the rhombus geometries for Ge₄⁺. These vertical energy separations provide approximate regions for these excited electronic states of Ge₄⁺. For example, all sextet states with the rhombus geometry are much higher in energy (3.8–5.0 eV above the ground state).

2. **Dissociation Energy.** The dissociation energy for the process

\[
\text{Ge}_4^+(2\text{Bl}, \text{rhombus}) \rightarrow \text{Ge}_2^+(\Sigma_g^+) + \text{Ge}_2^+(\Sigma_g^+) + e^-
\]

is computed at both CASSCF and MRSDCI levels of theory. The \( D_\text{e} \) was computed by treating Ge₄⁺ and Ge₂⁺⁺ as a linear Ge₄⁺ supermolecule in which the central bond length was set to 10.0 Å while the terminal bond lengths were optimized. The \( D_\text{e} \) values obtained this way are 88 and 85 kcal/mol, respectively, at the CASSCF and MRSDCI levels. We also note that all 18 electronic states of Ge₄⁺ listed in Table I are more stable than the \( \text{Ge}_2^+(\Sigma_g^+) + \text{Ge}_2^+(\Sigma_g^+) \) dissociation limit.

3. **Ionization Potential of Ge₄⁺.** Using the CASSCF and MRSDCI energies of the ground state of Ge₄⁺ in ref 39 and the ground-state energies of Ge₂⁺⁺ we obtained in this investigation, the adiabatic ionization potential of Ge₄⁺ for the process

\[
\text{Ge}_4^+(1\text{A}_1, \text{rhombus}) \rightarrow \text{Ge}_2^+(2\text{Bl}, \text{rhombus}) + e^-
\]

is computed at both CASSCF and MRSDCI levels of theory. The adiabatic IP values computed are 7.33 and 7.44 eV at the CASSCF and MRSDCI levels, respectively. Since the acute bond angle of the ground state of Ge₄⁺ is near 63°, the ground-state geometry of Ge₂⁺⁺ in its \(^2\text{B}_1\) state is quite different from the ground state of Ge₂⁺⁺. Hence we expect considerable vibrational progression in the \(^1\text{A}_1\rightarrow^3\text{B}_1\) transition. However, the envelope corresponding to the \(^1\text{A}_1\rightarrow^3\text{B}_1\) transition is likely to be narrow and sharp in the photoelectron spectrum of Ge₄⁺.
TABLE III: Geometries and Energy Separations of Electronic States of Pb4+

<table>
<thead>
<tr>
<th>geometry</th>
<th>state</th>
<th>( R_{12} ) Å</th>
<th>( R_{23} ) Å</th>
<th>( \theta ) deg</th>
<th>( E ) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>rhombus</td>
<td>( ^2B_{3u} )</td>
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<td>0.00</td>
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<td></td>
<td>( ^2A_g )</td>
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<td>65.0</td>
<td>0.05</td>
<td>3.168</td>
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<tr>
<td></td>
<td>( ^2B_{2g} )</td>
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<td>61.0</td>
<td>0.22</td>
<td>3.115</td>
</tr>
<tr>
<td></td>
<td>( ^2B_{1g} )</td>
<td>3.180</td>
<td>61.0</td>
<td>0.34</td>
<td>3.161</td>
</tr>
<tr>
<td>square</td>
<td>( ^2B_{1u} )</td>
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<td>90.0</td>
<td>0.50</td>
<td>3.013</td>
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<td>tetrahedron</td>
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<td>3.360</td>
</tr>
<tr>
<td></td>
<td>( ^2T_{2g} )</td>
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<td>109.47</td>
<td>0.72</td>
<td>3.326</td>
</tr>
<tr>
<td></td>
<td>( ^2T_{1g} )</td>
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<td>109.47</td>
<td>0.89</td>
<td>3.326</td>
</tr>
<tr>
<td></td>
<td>( ^2E )</td>
<td>3.387</td>
<td>109.47</td>
<td>1.23</td>
<td>3.360</td>
</tr>
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<td>( ^2B_{2u} )</td>
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<td>90.0</td>
<td>1.44</td>
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<tr>
<td></td>
<td>( ^2T_2 )</td>
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<td>109.47</td>
<td>1.66</td>
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<td>2.998</td>
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<td>( ^2T_2 )</td>
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<td>3.012</td>
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<td></td>
<td>( ^2E )</td>
<td>3.436</td>
<td>3.025</td>
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<td>2.36</td>
</tr>
<tr>
<td>Pb2 + Pb2*</td>
<td>( ^2E + ^2T_2 )</td>
<td>10.0</td>
<td>2.995</td>
<td>180.0</td>
<td>2.83</td>
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</tbody>
</table>

\( ^a R_{12}, R_{23}, \text{and} \theta \text{ as in Table I.} ^b \text{The zero energy for CASSCF is -13.41068 hartrees; for MRSDCI it is -13.51883 hartrees.} \)

Figure 2. Potential energy surfaces of low-lying electronic states of Sn4+.

Figure 3. Potential energy surfaces of low-lying electronic states of Pb4+.

The dissociation energy for the process

Sn4+(2B1u;rhombus) \rightarrow Sn(2Σg) + Sn(2Σg)'(Σg')

is computed at both CASSCF and MRSDCI levels of theory. The \( D_e \) values are 73 and 72 kcal/mol, respectively, at the CASSCF and MRSDCI levels. The dissociation energy was computed the same way as Ge4+, using supermolecular computation.

We calculated the adiabatic IP from Sn4+(2A1u;rhombus) to Sn(2Σg) + Sn(2Σg)'(Σg') as 6.76 and 6.86 eV at the CASSCF and MRSDCI levels of theory, respectively. Again we find a large change in the geometry of the \( 2B_{1u} \) state compared to the \( 2A_1 \) ground state of the neutral structure. However, the \( 2A_1 \) state has a geometry not too far from the neutral ground state. Hence we expect the peak corresponding to this transition to be sharp in the photoelectron spectrum.

C. Pb4+. 1. Electronic States and Potential Energy Surfaces. Table III shows the optimized geometries and energy separations of 17 electronic states of Pb4+ and the dissociation limit (Pb2 + Pb2+) obtained by using the CASSCF and MRSDCI calculations. Figure 3 shows the potential energy surfaces of Pb4+ electronic states with the rhombus geometry and the corresponding electronic states with the square geometry. As seen from Table III and Figure 3, the Pb4+ ion has three nearly-degenerate electronic states as candidates for the ground state, all with rhombus geometries. Although the \( 2B_{2g} \) state prevails at both the CASSCF and MRSDCI levels of theories, the small energy separation between \( 2B_{1u} \) and \( 2B_{2g} \) states as well as \( 2A_2 \) and \( 2B_{1u} \) states makes it difficult to draw an unequivocal conclusion on the ground state of Pb4+. As we see subsequently, there is further complicated by the spin-orbit coupling of electronic states in the near proximity of each other. The \( 2B_{1u} \) electronic state has an equilibrium structure of a rhombus at both the CASSCF and MRSDCI levels of theory. The Pb-Pb bond lengths are 3.020 Å and the acute apex bond angles are 71.1° at the MRSDCI level. The Pb4+ ion differ from Ge4+ and Sn4+, in that the first excited state is not \( 2A_1 \) state but the \( 2B_{1u} \) state with the rhombus geometry. The \( 2B_{1u} \) and \( 2A_2 \) states are only 0.03 and 0.08 eV above the ground state, respectively.
The energy separations of the excited electronic states of Pb$^+$ are smaller compared to Ge$^+$ and Sn$^+$. A significant lowering almost the same as the 2B2 state with the rhombus geometry. This makes the 6A1 state with the tetrahedral geometry state which is 0.74 eV above the ground state at the CASSCF level while at the MRSDCI levels it is only 0.39 eV above the ground state. It is not the case of Ge$^+$ and Sn$^+$.

We computed the effect of spin–orbit coupling for the ground state with the rhombus geometry of Pb$^+$ since lead is a very heavy atom. The relativistic configuration interaction (RCI) method was employed. Table IV shows the result of the RCI calculations of Pb$^+$. As seen from Table IV, the spin–orbit coupling elongates the Pb–Pb bond length by 0.033 Å and decreases the acute apex angle by 1.4°, which suggests enhancement of bonding along the y axis due to the spin–orbit effect. The energy of the E(1) relativistic electronic state is lowered by 0.09 eV (~2 kcal/mol) relative to the D2, symmetry state with the rhombus structure. The contribution of the 3B2 and 1A1 states to the E(1) state are predominantly of the 2Blu and 2A1 states, respectively.

1. Rhombus and Square Geometries.

The leading configurations of the 2B3u, 2B3, and 2B3, electronic states, respectively. This stronger mixing results in the energy of the E(II) state to be 0.19 eV above the E(I) state. Hence the RCI description of Pb$^+$ is somewhat less ambiguous in that the E(I) state is predominantly 2Bl1u.

2. Tetrahedral Geometry.

The adiabatic IP of Pb$^+$ for the process Pb$^+(2Blu;rhombus) \rightarrow$ Pb$^+(2B1u;rhombus)$ was computed. The adiabatic IP value is 6.23 eV at the CASSCF level while at the MRSDCI level it increased to 6.39 eV. After consideration of the spin–orbit effect, the IP of Pb$^+$ increased further to 6.48 eV.

The Nature of Electronic States

A. Cl Compositions. 1. Rhombus and Square Geometries.

The analysis of the leading configuration of the MRSDCI wave function reveals that the 2B1u ground states with the rhombus geometry and the corresponding saddle point with the square geometry of Ge$^+$, Sn$^+$, and Pb$^+$ are predominantly represented by their leading configurations (the coefficients are between 0.86 and 0.89), namely, 1a1g2a2d3a1b1g2b1u2b1g1b1u. Compared to the 1A1 ground states with the rhombus geometry of the neutral Ge, Sn, and Pb, we found that an electron from the 2b1u orbital is removed for the positive ions. Thus, we can assign the 2b1u orbital as the highest occupied molecular orbital (HOMO) for both neutral molecules and their positive ions.

Figure 4 shows the orbital interaction diagrams for the occupied orbitals of the 3B2 state with the rhombus geometry of Ge$^+$, Sn$^+$, and Pb$^+$ as derived from the natural orbital compositions. As seen from Figure 4, the 1a1 orbital is composed predominantly of the ns orbitals (n is the principle quantum number of the valence s and p orbitals of Ge, Sn, and Pb) of all four atoms. If we labeled the atoms located on the z axis as M1

![Figure 4. Orbital interaction diagrams for the occupied orbitals of the 3B2 state with the rhombus geometry of Ge$^+$, Sn$^+$, and Pb$^+$](image-url)

and M4, while the atoms located on the y axis as M2 and M3 (M = Ge, Sn, and Pb), we find that

$$\psi(1a_1) = M_1(s) + M_2(s) + M_3(s) + M_4(s)$$

Following this model we obtain

$$\psi(2a_2) =$$

$$-M_1(s) + M_2(s) + M_3(s) - M_4(p_z) + M_4(p_y)$$

$$\psi(3a_2) =$$

$$-M_1(s) + M_2(s) + M_3(s) - M_4(s) + M_1(p_z) - M_2(p_z) + M_3(p_z) - M_4(p_z)$$

$$\psi(2b_{1u}) =$$

$$-M_1(p_z) + M_2(p_z) + M_3(p_z) - M_4(p_z) - M_4(s) - M_3(s)$$

$$\psi(1b_{1u}) =$$

$$M_1(p_z) + M_2(p_z) - M_3(p_z) - M_4(p_z)$$

The 1b1u orbital is the only occupied orbital which is perpendicular to the molecular plane. This is analogous to the pz bonding among all four atoms. In this orbital, four px orbitals make significant contributions to bring about bonding among all four atoms.

Figure 5 shows the orbital energy diagrams of the 4A1 and 3T1 states with the tetrahedral geometry.
TABLE V: Mulliken Population Analysis for the Low-Lying Electronic States of Ge4+ a

<table>
<thead>
<tr>
<th>geometry</th>
<th>state</th>
<th>M1</th>
<th>M2</th>
<th>M1(s)</th>
<th>M1(p)</th>
<th>M1(d)</th>
<th>M2(s)</th>
<th>M2(p)</th>
<th>M2(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rhombus</td>
<td>2B1</td>
<td>3.64</td>
<td>3.86</td>
<td>1.63</td>
<td>1.74</td>
<td>0.27</td>
<td>1.56</td>
<td>2.00</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>2A1</td>
<td>3.61</td>
<td>3.89</td>
<td>1.70</td>
<td>1.65</td>
<td>0.26</td>
<td>1.53</td>
<td>2.08</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>2Bn</td>
<td>3.62</td>
<td>3.88</td>
<td>1.69</td>
<td>1.66</td>
<td>0.27</td>
<td>1.59</td>
<td>2.00</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>2B1</td>
<td>3.56</td>
<td>3.94</td>
<td>1.70</td>
<td>1.59</td>
<td>0.27</td>
<td>1.58</td>
<td>2.05</td>
<td>0.31</td>
</tr>
<tr>
<td>square</td>
<td>2B1</td>
<td>3.77</td>
<td>3.73</td>
<td>1.61</td>
<td>1.88</td>
<td>0.28</td>
<td>1.58</td>
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<td>tetrahedron</td>
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<td>3.75</td>
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<td>1.67</td>
<td>1.78</td>
<td>0.30</td>
</tr>
<tr>
<td>linear</td>
<td>4 2T2</td>
<td>3.86</td>
<td>3.64</td>
<td>1.71</td>
<td>1.96</td>
<td>0.19</td>
<td>1.78</td>
<td>1.67</td>
<td>0.19</td>
</tr>
</tbody>
</table>

* M1 stands for one of the two atoms along the z axis for the rhombus and square geometries; M2 stands for one of two atoms along the y axis. For the linear geometries, M1 is the central atom and M2 is one of the terminal atoms.

TABLE VI: Mulliken Population Analysis for the Low-Lying Electronic States of Sn4+ a

<table>
<thead>
<tr>
<th>geometry</th>
<th>state</th>
<th>M1</th>
<th>M2</th>
<th>M1(s)</th>
<th>M1(p)</th>
<th>M1(d)</th>
<th>M2(s)</th>
<th>M2(p)</th>
<th>M2(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rhombus</td>
<td>2B1</td>
<td>3.58</td>
<td>3.92</td>
<td>1.75</td>
<td>1.67</td>
<td>0.16</td>
<td>1.72</td>
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<tr>
<td></td>
<td>2A1</td>
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<td>3.95</td>
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<td>0.15</td>
<td>1.70</td>
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<tr>
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<td>2Bn</td>
<td>3.56</td>
<td>3.94</td>
<td>1.82</td>
<td>1.59</td>
<td>0.15</td>
<td>1.78</td>
<td>2.03</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>2B1</td>
<td>3.53</td>
<td>3.97</td>
<td>1.82</td>
<td>1.56</td>
<td>0.15</td>
<td>1.77</td>
<td>2.06</td>
<td>0.14</td>
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<td>square</td>
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<td>3.74</td>
<td>3.76</td>
<td>1.74</td>
<td>1.853</td>
<td>0.17</td>
<td>1.70</td>
<td>1.90</td>
<td>0.16</td>
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<td>3.75</td>
<td>3.75</td>
<td>1.85</td>
<td>1.76</td>
<td>0.14</td>
<td>1.85</td>
<td>1.76</td>
<td>0.14</td>
</tr>
<tr>
<td>linear</td>
<td>4 2T2</td>
<td>3.89</td>
<td>3.61</td>
<td>1.77</td>
<td>2.02</td>
<td>0.10</td>
<td>1.83</td>
<td>1.65</td>
<td>0.13</td>
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</table>

* M1 and M2 as in Table VII.

TABLE VII: Mulliken Population Analysis for the Low-Lying Electronic States of Pb4+ a

<table>
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<tr>
<th>geometry</th>
<th>state</th>
<th>M1</th>
<th>M2</th>
<th>M1(s)</th>
<th>M1(p)</th>
<th>M1(d)</th>
<th>M2(s)</th>
<th>M2(p)</th>
<th>M2(d)</th>
</tr>
</thead>
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<tr>
<td>rhombus</td>
<td>2B1</td>
<td>3.66</td>
<td>3.84</td>
<td>1.96</td>
<td>1.64</td>
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<td>1.94</td>
<td>1.84</td>
<td>0.06</td>
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<tr>
<td></td>
<td>2B1</td>
<td>3.64</td>
<td>3.86</td>
<td>1.98</td>
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<td>0.07</td>
<td>1.95</td>
<td>1.86</td>
<td>0.05</td>
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<tr>
<td></td>
<td>2A1</td>
<td>3.61</td>
<td>3.89</td>
<td>1.98</td>
<td>1.57</td>
<td>0.06</td>
<td>1.95</td>
<td>1.88</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>2B1</td>
<td>3.63</td>
<td>3.87</td>
<td>1.98</td>
<td>1.58</td>
<td>0.07</td>
<td>1.98</td>
<td>1.81</td>
<td>0.08</td>
</tr>
<tr>
<td>square</td>
<td>2B1</td>
<td>3.71</td>
<td>3.79</td>
<td>1.92</td>
<td>1.71</td>
<td>0.08</td>
<td>1.91</td>
<td>1.81</td>
<td>0.07</td>
</tr>
<tr>
<td>tetrahedron</td>
<td>4A1</td>
<td>3.75</td>
<td>3.75</td>
<td>2.00</td>
<td>1.68</td>
<td>0.07</td>
<td>2.00</td>
<td>1.68</td>
<td>0.07</td>
</tr>
</tbody>
</table>

* M1 and M2 as in Table VII.

Figure 5. Orbital energy diagrams of the 6A1 and 2T2 states with the tetrahedral geometry of Ge4+, Sn4+, and Pb4+.

For the 6A1 state the leading configuration is la1lt22a12t12e (the coefficients are 0.912, 0.914, and 0.922 for Ge4+, Sn4+, and Pb4+, respectively) while for the 2T2 state the leading configuration is 1a1lt22a12t12e (the coefficients are 0.840, 0.825, and 0.823 for Ge4+, Sn4+, and Pb4+, respectively). As seen from figure 5, the 2t1 and the 1e orbitals of the 6A1 state are all half-filled; hence, these five electrons with the same spin result in the 6A1 state. Such occupation and spin will result in spin-exchange energy stabilization. This explains partially why the energy of the 6A1 state is lower than the 2T2 state. For the 2T2 state the next configuration is formed by transferring two electrons from 2t1 to 1e (forming three 2t1 and two 1e singly-occupied orbitals) and the coefficients are 0.206, 0.199, and 0.214 for Ge4+, Sn4+, and Pb4+, respectively. The Jahn–Teller distortion from the ideal tetrahedral structure of the 2T2 state could lower the energy of the 2T2 state further.

Figure 6 shows the orbital interaction diagram for the occupied orbitals of the 6A1 state with the tetrahedral geometry for Ge4+, Sn4+, and Pb4+. From the natural orbital configurations we obtain

\[
\psi'(1a1) = M_1(s) + M_2(s) + M_1(p) + M_2(p) \\
\psi'(1t2(I)) = M_1(s) - M_2(s) - M_1(p) + M_2(p) \\
\psi'(1t2(II)) = M_1(s) - M_2(s) \\
\psi'(1t2(III)) = M_2(s) - M_1(s)
\]

In the 2a1 and 2t2 orbitals we find strong sp hybridization:

\[
\psi'(2a1) = -M_1(s) - M_2(s) - M_4(s) + M_3(p) + M_3(p) - M_1(p) - M_2(p) + M_3(p) + M_2(p) - M_4(p)
\]

\[
\psi'(2t2(I)) = -M_1(p) - M_2(p) - M_3(p) + M_4(p) - M_1(s) - M_2(s) - M_4(s) \\
\psi'(2t2(II)) = -M_1(p) - M_2(p) + M_1(p) + M_4(p) - M_1(s) + M_4(s) \\
\psi'(2t2(III)) = -M_1(p) - M_2(p) + M_3(p) - M_4(p) - M_4(s) + M_3(s)
\]

The 1e orbitals consist primarily of atomic p orbitals:

\[
\psi'(1e(I)) = -M_1(p) + M_2(p) + M_3(p) - M_1(p) - M_2(p) + M_3(p) - M_4(p)
\]

\[
\psi'(1e(II)) = M_1(p) - M_2(p) + M_3(p) - M_4(p)
\]

We do not show the relatively small contribution of d orbitals for clarity.
respectively.

6A, state with the tetrahedral geometry of Ge4+, Sn4+, and Pb4+, respectively. For the rhombus geometry, as we found in a previous study of Ge4+, Sn4+, and Pb4+, the s populations of the M2 atoms located on the y axis have an average population of s1.63p1.74d0.27 while the p populations of M2 are larger than those of M1. This suggests that although an electron is removed from the neutral Ge4, Sn4, and Pb4, there is a strong interaction between the np orbitals located on the y axis. Hence the rhombus structure is a consequence of enhanced np-mp interaction of the atoms located on the y axis.

As seen from Table V, for the 2Blu ground state, the M1 atoms on the z axis have an average population of s1.64p1.67d0.16 and s1.72p2.04d0.16, respectively (see Table VI). For the 2Blu state of Ge4+, Sn4+, and Pb4+, we found that the Ge4+ ion is formed by removal of 54% of the electronic charge from M1 atoms and 46% from M2 atoms. The removed electron comes predominantly from the p orbitals of the group IV atoms.

For the ground state of Sn4+, the populations of M1 and M2 are s1.78p1.67d0.16 and s1.73p1.30d0.18, respectively (see Table VI). For the ground state of Pb4+, the M1 and M2 atoms have populations of s1.86p1.69d0.16 and s1.87p1.30d0.18, respectively (see Table VII). From Ge4+ to Pb4+, the s populations increase while the d populations decrease. This trend is also observed for the tetrahedral and linear structures. This is an evident manifestation of the relativistic stabilization of the 6s orbital of Pb. As seen from Tables VI and VII, we find an increase of 0.21 s population in going from Sn to Pb. Hence, we conclude that relativistic effects are quite important for Pb+n.

Comparison of Ge4+, Sn4+, Pb4+, and Neutral Ge4, Sn4, and Pb4

All three positive ions have rhombus structures with nearly the same acute bond angles (72.5°, 71.8°, and 71.1° for Ge4+, Sn4+, and Pb4+, respectively), although these bond angles are 8.6°, 7.4°, and 6.9° larger than the acute bond angles of their corresponding neutral clusters, respectively, implying more repulsive force between the atoms located on the y axis for the positive ions. This is comprehensible since some of the positive charge is on the atoms located on the y axis which are much closer than the atoms located on the z axis. The side bond lengths for the ground state with the rhombus geometry are 2.447, 2.805, and 3.020 Å for Ge4+, Sn4+, and Pb4+, respectively.

The 2Bu state with rhombus geometry is the second excited state for both Ge4+ and Sn4+, while for Pb4+ it is the first excited state. The T2 values for the 2Bu state, relative to the ground state, are 13, 7, and 0.7 kcal/mol for Ge4+, Sn4+, and Pb4+, respectively. We find a triangle formed by the energy curves of the 2Bu, 2Blu, and 2Bu states between θ = 61° and 65° for Ge4+ in Figure 1, while this triangle becomes smaller near one point at θ = 64° for Sn4+ (Figure 2) since the 2Bu curve of Sn4+ is lowered. The further lowering of the 2Bu state makes it even lower than the 2Bu state for Pb4+ as seen from Figure 3.

The energy separations of the excited electronic states of Ge4+, Pb4+ are found to decrease, especially the splitting between the rhombus and tetrahedral structures, as one goes down the group. The T2 values for the tetrahedral structure relative to the rhombus structure are 32, 22, and 9 kcal/mol for Ge4+, Sn4+, and Pb4+, respectively, while for the neutral Ge4, Sn4, and Pb4 these values are 42, 32, and 19 kcal/mol, respectively. There is a significant drop in the energy separation between the rhombus and tetrahedral geometries in going from Sn4+ to Pb4+ (also from Sn4 to Pb4). This is a consequence of relativistic mass-velocity stabilization of the 6s orbital of Pb.

The ionization potentials of Ge4, Sn4, and Pb4 are 7.48, 6.86, and 6.39 eV at the MRSDCI level without the spin-orbit effect, respectively, while with consideration of the spin-orbit effect the IP of Pb increases by 0.09 eV.

Conclusion

In this investigation, we studied 17 low-lying electronic states of Ge4+, Sn4+, and Pb4+, respectively, using CASSCF/MRSDCI methods. We also computed the CASSCF vertical energy separations of several electronic states with the rhombus and linear geometries of both Ge4+ and Sn4+. The ground states of Ge4+, Sn4+, and Pb4+ were found to be of 2Bu symmetry with equilibrium geometries of a rhombus. The spin-orbit effects were found to be significant for Pb4+. The bond lengths of four equal sides of the rhombus structure of Ge4+, Sn4+, and Pb4+ are 2.45, 2.81, and 3.02 Å, respectively. The acute apex angle of the ground states of Ge4+, Sn4+, and Pb4+ are between 71.1° and 72.5°. The ionization potentials of M4 (M = Ge, Sn, Pb) are between 71.4, 71.8, and 72.5 eV. The ionization potentials of M4, M = Ge, Sn, Pb, are between 71.4, 71.8, and 72.5 eV. The ionization potentials of M4, M = Ge, Sn, Pb, are 7.48, 6.86, and 6.39 eV at the MRSDCI level without the spin-orbit effect, respectively.

The population analysis indicated that the sp hybridization and d polarization effect are quite significant for the ground state and the excited states of Ge4+ and Sn4+. We found that the 6s population is enhanced for Pb4+ due to the relativistic mass-velocity contraction of the 6s orbital of Pb. The orbital interaction diagrams of the rhombic and tetrahedral structures give us more information to understand further the nature of the electronic states of Ge4+, Sn4+, and Pb4+.

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References and Notes

(1) Balasubramanian, K. Chem. Rev. 1990, 90, 93.
(44) The major authors of ALCHEMY II are B. Liu, B. Lengsfield, and M. Yoshinine.

Structure and Electron Density of Solid Dimethoxysulfane, (CH$_3$O)$_2$S$^1$

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High-resolution X-ray data were collected at a low temperature (110 (1) K) to determine the crystal and molecular structure and the deformation electron density (DED) of CH$_3$OSOCH$_3$. Crystal data: $a = 9.156$ (5), $b = 7.451$ (6), $c = 6.593$ (3) Å, Pbcn (centric), $Z = 4$. The molecules are in special positions of $C_2$ symmetry with bond lengths SO = 1.6212 (7), CO = 1.4444 (6), and CH = 1.067 (7) Å (av), bond angles OSO = 104.78 (5)°, COS = 115.76 (2)°, OCH = 108.3 (av), and torsional angle COSO = 81.75 (2)°. The OCH$_3$ units deviate considerably from C$_2$ symmetry. The deformation electron density is analyzed in terms of static (SDD) and dynamic deformation density (DDD) calculated from the fitted multipole populations and X−X Fourier synthesis. The lone pairs at S and O are clearly discernible in these maps but there is no indication of any anomeric effect. The torsional angle of 82° at the S−O bonds must therefore be the result of the lone pair interaction only. The molecules form layers with the OSO units in parallel planes and the methyl groups separating these planes from each other. There are no intermolecular contacts shorter than the van der Waals distances, but the sulfur atoms are coordinated by two nonbonded oxygen atoms of neighboring molecules from the same plane resulting in a 2 + 2 coordination of local symmetry C$_2$.

Introduction

The SO single bond originating from two-coordinated sulfur has so far been only insufficiently characterized. Species of type RSOR are the intermediates between the well-studied peroxides, ROOR, and the disulfides, RSSR. While numerous structural investigations are known for both peroxides and disulfides, few species of type RSOR are stable enough to allow a detailed structural analysis; the latter compounds are isomeric to the well-known sulfides, RS(O)R. Two sulfenic acids were shown by X-ray crystallography and microwave spectroscopy to possess the structure RSOH, and the methyl ester of an aromatic sulfenic acid, RSOCH$_3$, has been characterized by X-ray diffraction on single crystals. These species are formally derivatives of the oxadisulfane HSOH and the unstable sulfoxylic acid, HOSOH, the most stable isomer of which is of C$_2$ symmetry according to an ab-initio MO calculation; the rotamer of C$_2$ symmetry is less stable by 8.4 kJ/mol, while the sulfoxide form, HS(O)OH, is less stable by 56 kJ/mol. SO$_2$ is structurally related to the species SF$_2$ and S(NR$_3$)$_2$, the structures of which are well-known. Since S(OH)$_2$ is too unstable to allow an