

## Si<sub>3</sub>O<sub>4</sub><sup>-</sup>: Vibrationally Resolved Photoelectron Spectrum and *ab Initio* Calculations

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Study of atomic clusters has received considerable attention over the past decade.<sup>1</sup> Oxide clusters are an interesting class of complex clusters due to the importance of oxide materials in catalysts, surface chemistry, and many other materials applications. In particular, silicon oxide is a key material in many technological and scientific areas,<sup>2</sup> and its surface chemistry plays an important role in understanding the underground transport of waste materials. We have initiated a project to study small silicon oxide clusters and to use these model systems to better understand the structure and dynamics of silicon oxide surfaces and defects. The smaller and controlled sizes of these cluster species provide an excellent testing ground for theoretical models that are intended to simulate large and "real-world" systems.

Information about the structure and spectroscopy of clusters with more than a few atoms is difficult to obtain. Photoelectron spectroscopy (PES) of size-selected anion clusters offers a powerful method to study these clusters and can provide unique information about the cluster structure and bonding. Based on a previous design,<sup>3</sup> we have developed an instrument which combines higher mass resolution with a higher resolution version of a magnetic bottle time-of-flight (MTOF) photoelectron spectrometer.<sup>4</sup> It overcame problems associated with fast ion PES and is designed to study a wide range of clusters.<sup>4–8</sup> In this Communication, we report a vibrationally resolved photoelectron spectrum of a relatively complex cluster, Si<sub>3</sub>O<sub>4</sub><sup>-</sup>, for which we observe a single vibrational progression with a frequency of 800(50) cm<sup>-1</sup>. We use quantum mechanical calculations to determine the structure of the cluster, which is found to be *D*<sub>2d</sub> for the neutral ground state Si<sub>3</sub>O<sub>4</sub> and *C*<sub>2v</sub> for Si<sub>3</sub>O<sub>4</sub><sup>-</sup>. The agreement between the theoretical and experimental vertical and adiabatic detachment energies of the predicted Si<sub>3</sub>O<sub>4</sub><sup>-</sup> geometry, and the frequency and symmetry of the vibrations of Si<sub>3</sub>O<sub>4</sub>, suggest that the predicted structure is correct.

The details of the MTOF photoelectron apparatus have been published elsewhere.<sup>3,4</sup> Briefly, we use a laser vaporization cluster source to generate the Si<sub>3</sub>O<sub>4</sub><sup>-</sup> clusters. A Q-switched Nd:YAG laser is used as the vaporization laser, with 20 mJ of the second harmonic output (532 nm) focused to a 1 mm diameter spot onto a pure silicon target. Helium seeded with

0.05% O<sub>2</sub> (10 atm total stagnation pressure) is used as the carrier gas, which is delivered by two pulsed molecular beam valves. The plasma reactions between the laser-vaporized silicon atoms and the O<sub>2</sub> produce a series of Si<sub>x</sub>O<sub>y</sub><sup>-</sup> clusters which, together with the helium carrier gas, undergo a supersonic expansion and form a cold molecular beam collimated by two skimmers. The negative clusters are extracted perpendicularly from the beam with a 1 kV high-voltage pulse and subjected to a TOF mass analysis. The TOF mass spectrometer has a mass resolution (*M*/*ΔM*) of 500, which is sufficient to resolve all the isotopes for the small Si<sub>x</sub>O<sub>y</sub><sup>-</sup> clusters. The cluster is mass selected by a three-grid mass gate and is subsequently decelerated by a momentum decelerator before it interacts with the detachment laser.<sup>4</sup> The second harmonic output (532 nm) of another Q-switched Nd:YAG laser is used for the photodetachment. More than 98% of all the photoelectrons are collected by the magnetic bottle and parallelized down to a 3.5 m long TOF tube for electron kinetic energy analysis. The electron kinetic energy distributions are calibrated with the known spectrum of the Cu<sup>-</sup> anion. The kinetic energy is subtracted from the photon energy to obtain the binding energy spectra presented. The spectrometer has an energy resolution of better than 30 meV at 1 eV electron kinetic energy, as measured from the spectrum of Cu<sup>-</sup>.

In the theoretical part of this study, we fully optimize Si<sub>3</sub>O<sub>4</sub> and Si<sub>3</sub>O<sub>4</sub><sup>-</sup> using the *ab initio* molecular orbital formalism in the computer program Gaussian92.<sup>9</sup> We first optimize the molecules at the Hartree–Fock level using the 6-31+G\* basis set.<sup>10</sup> We calculate the normal mode frequencies and displacements at the same level of theory. The frequencies are all positive, indicating that the optimized structures represent minima on the potential energy surface. To obtain more accurate geometries and energetics, we then optimize the molecules using second-order Møller–Plesset perturbation theory (MP2)<sup>11</sup> with the 6-31+G\* and 6-311+G\* basis sets.<sup>12</sup> Core electrons are frozen. The accuracy imparted by the electron correlation and the large basis sets is sufficient to determine the preferred geometry and gives excellent agreement with experimentally determined properties. Calculations using similar basis sets and density functional methods give poor agreement with the experiment. The details of these calculations will be reported elsewhere.<sup>13</sup>

The PES spectrum of Si<sub>3</sub>O<sub>4</sub><sup>-</sup> is shown in Figure 1 with the well-resolved vibrational structure. More than 10 peaks are resolved, and the vibrational spacing obtained is 800(50) cm<sup>-1</sup>. Considering the size of this cluster, it is remarkable to observe such a simple and well-resolved vibrational progression. To ascertain the spectral assignment, it merits some comments on the identification of the carrier of the observed PES spectrum for a new species. Either due to fragmentation during the photodetachment laser pulse or because of metastable decay in the flight tube of the mass spectrometer, it is possible for such observed spectrum to be from a fragment of the mass selected cluster. The 800 cm<sup>-1</sup> observed vibrational frequency can be used to exclude O<sub>2</sub>, Si<sub>2</sub>, and SiO, whose ground state frequencies are 1580, 510, and 1242 cm<sup>-1</sup>, respectively.<sup>14</sup> Additionally, theory predicts that SiO will not bind an extra electron,<sup>15</sup> and it is not observed in our Si<sub>x</sub>O<sub>y</sub><sup>-</sup> mass spectra. While the electron

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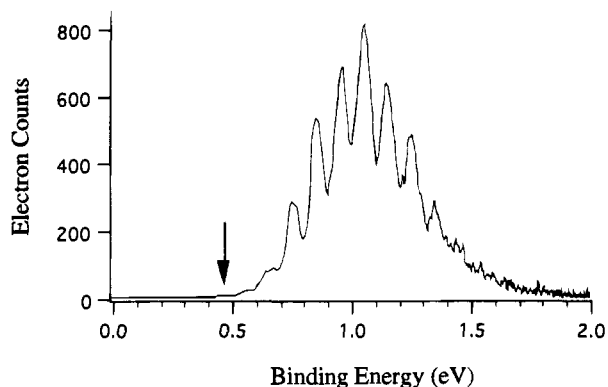
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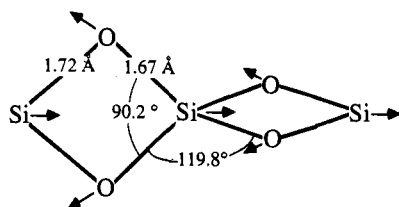
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**Figure 1.** Photoelectron spectrum of  $\text{Si}_3\text{O}_4^-$  at 532 nm, showing a well-resolved vibrational progression. The arrow indicates the detachment threshold.



**Figure 2.**  $D_{2d}$  geometry of  $\text{Si}_3\text{O}_4$ , optimized at MP2/6-311+G\*. The arrows represent the displacements of the atoms in the  $779\text{ cm}^{-1}$  mode.

affinity of  $\text{O}_2$  is rather close to that of the species seen in our PES, the observed PES of  $\text{O}_2^-$  shows excited electronic state structure,<sup>16</sup> which is absent from the current PES spectrum. We have obtained the PES spectra of  $\text{Si}_3\text{O}_y^-$  ( $y = 1-3$ ) and  $\text{Si}_2\text{O}_3^-$ , and each has a different PES spectrum. Hence, it can be concluded that the carrier of the current PES spectrum is neither a diatomic fragment nor a fragment formed by the loss of 1-3 O atoms or  $\text{SiO}$ . Furthermore, the observed spectrum does not depend on the photon fluence used in the photodetachment. We have also taken the spectrum with different detachment photon energies (355 nm and 266 nm) and obtained the same spectrum except that vibrations cannot be well-resolved at the higher photon energies due to the dependence of the spectrometer resolution on the electron kinetic energy. Thus, we see no basis for assigning it to a species other than the parent,  $\text{Si}_3\text{O}_4^-$ .

Determination of the molecular structure requires a theoretical approach. The optimized MP2/6-311+G\* geometry of  $\text{Si}_3\text{O}_4$ , which is shown in Figure 2, has a  $D_{2d}$  symmetry. The anion,  $\text{Si}_3\text{O}_4^-$ , exhibits Jahn-Teller distortion and has a  $C_{2v}$  symmetry, with the  $C_2$  axis running through the three silicon atoms. In both the neutral and the anion, the central Si atom is bonded to four O atoms. The coordination of the Si atom is distorted from an ideal tetrahedral geometry; the O-Si-O angles are close to  $90^\circ$  and  $120^\circ$ . The cluster geometry is reminiscent of bulk  $\text{SiO}_2$ , of which  $\text{SiO}_4$  tetrahedra are the basic building unit.<sup>17</sup> Both the vertical and adiabatic electron affinities are determined. The vertical electron affinity is calculated as the difference in total

**Table 1.** Comparison of Experimental and Theoretical Electron Affinities and Vibrational Frequencies of the  $\text{Si}_3\text{O}_4$  Cluster

	$\text{EA}_a$ (eV) <sup>a</sup>	$\text{EA}_v$ (eV) <sup>b</sup>	$\nu$ ( $\text{cm}^{-1}$ ) <sup>c</sup>
experimental	0.46(0.07)	1.055(0.050)	800(50)
HF/6-31+G*	0.270	0.784	629, 779, 983
MP2/6-31+G*	0.552	1.039	
MP2/6-311+G*	0.491	1.039	

<sup>a</sup> Adiabatic electron affinity. The arrow in Figure 1 at 0.46 eV indicates the detachment threshold. However, its excellent agreement with the theoretically predicted adiabatic EA suggests that that should be assigned to the 0-0 transition, representing the experimental adiabatic EA. <sup>b</sup> Vertical electron affinity. <sup>c</sup> Theoretical HF frequencies of the  $b_2$  modes are multiplied by 0.893.

energy between the optimized geometry of the anion and the energy of the neutral at the optimized anion geometry. The adiabatic electron affinity is the difference in energy between the optimized geometries of the anion and the neutral. The theoretical and experimental values are compared in Table 1. From the selection rules governing photodetachment transitions,<sup>18</sup> only totally symmetric vibrational states are allowed. Based on the geometry change from the anion to the neutral, the observed vibrational structure should be dominated by  $b_2$  vibrational modes of the  $D_{2d}$  neutral, which transform to totally symmetric modes in the  $C_{2v}$  anion. Even though the totally symmetric  $a_1$  modes are also allowed, the dominant Franck-Condon factors should be in the  $b_2$  modes. The calculated frequencies of the three  $b_2$  modes of the neutral are also given in Table 1. The  $b_2$  modes primarily represent the asymmetric stretching of the Si-O bonds, with some contribution due to changes in the O-Si-O angles. Although it is difficult for us to be certain which  $b_2$  mode dominates the experimental spectrum, it seems reasonable to assume that the mode is predominantly that which we calculate as  $779\text{ cm}^{-1}$ . The atomic displacements of this mode are shown in Figure 2. The excellent agreement between the theoretical and experimental electron affinities and the vibrational frequency suggests that the calculated geometries are correct.

Silicon prefers to form four single bonds with oxygen, and the  $\text{SiO}_4$  tetrahedra<sup>17</sup> dominate all materials involving Si and O (e.g., in zeolites).<sup>19</sup> The significance of this work is that detailed studies of the small clusters will provide relevant insight into the structure and reactivity of much more complicated bulk systems. Systematic studies of the  $\text{Si}_x\text{O}_y$  clusters are under way to fully elucidate the growth, structure, and bonding of these systems. A full report of this work is forthcoming.

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