A Photoelectron Spectroscopic Study of Small Silicon Oxide Clusters: SiO$_2$, Si$_2$O$_3$, and Si$_2$O$_4$

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We present an anion photoelectron spectroscopic study of SiO$_2$, Si$_2$O$_3$, and Si$_2$O$_4$. We obtained the photoelectron spectra of these small silicon oxide anion clusters at 4.66 eV photon energy. All the spectra show broad photodetachment features, suggesting that there is considerable geometry change between the anion and the neutral. The vertical detachment energies are determined to be 2.76 (0.10), 2.75 (0.10), and 3.63 (0.1) eV for SiO$_2^-$, Si$_2$O$_3^-$, and Si$_2$O$_4^-$, respectively. The spectrum of Si$_2$O$_3^-$ shows a weak feature at lower binding energy, suggesting existence of another isomer. The spectra of GeO$_2^-$ and Ge$_2$O$_3^-$ are also obtained and are compared to the silicon analogs. They are similar to the silicon oxide species, but both have higher detachment energies, 2.93 (0.07) eV for GeO$_2^-$ and 3.01 (0.07) eV for Ge$_2$O$_3^-$. The Ge$_2$O$_3^-$ spectrum is consistent with only one isomer. The structure and bonding of these small oxide clusters are discussed.

1. Introduction

Silicon oxide is the most abundant substance on earth and is important in many technological areas. An understanding of the structure, bonding, surfaces, and defects in silicon oxide could aid development in diverse applications such as catalysis, amorphous materials, environmental sciences, and electronic device physics. Small molecules containing Si, O, and H have been used to model properties of bulk silicon oxide.[1,2] It was found that the SiOSi bond angles and bond lengths obtained for the small molecules compare favorably with that in the bulk and yield reasonable bulk properties when used in bulk calculations. However, to model the wide range of structural properties and defects in the bulk and on surfaces, a wider range of structural models may be required. Clusters of the type Si$_x$O$_y$, where x and y can be continuously varied, fulfill these roles, and they now can be synthesized experimentally with cluster beam techniques.[3] We use photoelectron spectroscopy (PES) of size-selected Si$_x$O$_y^-$ anions to obtain electronic and spectroscopic information of these clusters. The PES experiments yield unique structure and bonding information about the neutral clusters and allow systematic studies of a wide range of cluster sizes.

In this paper, we present a study of SiO$_2$, Si$_2$O$_3$, and Si$_2$O$_4$ and the germanium analogs. Although SiO$_2$ is known to be linear in the gas phase,[4,5] there are few studies of their electronic structure.[6] There is no previous study on the Si$_2$O$_3$ species. Si$_2$O$_4$ can be viewed as a dimer of SiO$_2$ and has been studied in a low-temperature matrix experiment[7] and in a theoretical calculation.[8] It has a D_{2h} structure and has been named 2,4-dioxocyclodisiloxane. In a recent calculation, both Si$_2$O$_4^-$ and Si$_2$O$_4^{2-}$ have been studied in an effort to search stable doubly charged anions.[9]

We obtained the photoelectron electron spectra of SiO$_2^-$, Si$_2$O$_3^-$, and Si$_2$O$_4^-$, as well as GeO$_2^-$ and Ge$_2$O$_3^-$, at 4.66 eV photon energy. The spectrum of Si$_2$O$_3^-$ shows one broad feature at higher binding energy and a weak broad feature at lower binding energy and is concluded to be due to two isomers. Only one broad feature is observed in all the other spectra. The germanium analogs both have higher binding energies and show slightly narrow bandwidths. The spectrum of GeO$_2^-$ is similar to that of SiO$_2^-$, while the spectrum of Ge$_2$O$_3^-$ is similar to the higher binding energy feature of the Si$_2$O$_3^-$ spectrum. Significant geometry change from the anion to the neutral in all the clusters is inferred from the broad spectra.

In the following, the experimental apparatus and procedure are presented. In section 3, we report the results and discuss the structure and bonding of these clusters based on the experimental observations. In addition, the structures of all the Si$_2$O$_x$ ($x = 1-4$) clusters are compared, which can be viewed as a sequential oxidation of a Si$_2$ dimer. Finally, a brief summary is presented in section 4.

2. Experimental Section

We generate the Si$_x$O$_y^-$ anions by laser vaporizing a pure silicon target into a helium atmosphere containing 0.05% O$_2$. The cluster beam photoelectron spectroscopic apparatus has been described in detail before.[10,11] Briefly, we employ a magnetic bottle time-of-flight (MTOF) photoelectron analyzer, which has nearly 100% collecting efficiency.[12,13] A Q-switched Nd:YAG laser (20 mJ output of the second harmonic) is used as the vaporization laser. The plasma reactions between the laser-vaporized silicon atoms and the O$_2$ seeded in the carrier gas produce a series of Si$_x$O$_y^-$ clusters. The helium carrier gas and the oxide clusters undergo a supersonic expansion and form a cold molecular beam collimated by a skimmer. The negative clusters are extracted perpendicularly from the beam with a 1 kV high-voltage pulse and subjected to a time-of-flight mass analysis. The desired Si$_x$O$_y^-$ species are mass selected and subsequently decelerated before interacting with the detachment laser. For the germanium oxide clusters, the silicon target is replaced with a germanium one. The fourth harmonic output (266 nm) of another Q-switched Nd:YAG laser is used for photodetachment. The electron energies are calibrated with the
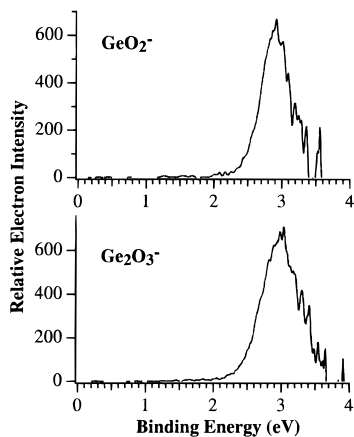
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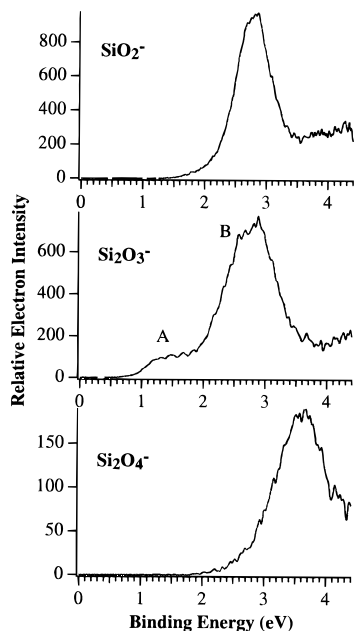
Figure 1. Photoelectron spectra of SiO_2^-, $Si_2O_3^-$, and $Si_2O_4^-$ at 4.66 eV photon energy.

Figure 2. Photoelectron spectra of GeO_2^- and $Ge_2O_3^-$ at 4.66 eV photon energy.

known spectrum of the Cu^- anion and are subtracted from the photon energies to obtain the PES binding energy spectra presented. The spectra are taken at 20 Hz with the vaporization laser off at alternating shots for background subtraction. All the spectra are smoothed with a 10 meV window.

3. Results and Discussion

Figure 1 shows the PES spectra of SiO_2^-, $Si_2O_3^-$, and $Si_2O_4^-$ at 4.66 eV photon energy. The spectra of GeO_2^- and $Ge_2O_3^-$ are displayed in Figure 2. Only one broad band is observed for all the spectra except for that of $Si_2O_3^-$ which appears as two broad features, one at higher binding energy (labeled "B") and one weak feature at lower binding energy (labeled "A"). The spectra of the two germanium oxide species appear narrower. All of these species show quite low detachment cross sections, probably caused by the broad nature of the detachment transitions. Substantial low-energy electron noise (at high binding energies) was present due to the scattered photons. The noise was more severe in the germanium cases due to their lower mass signals, and the background subtraction has affected the tail of the high binding energy side of the two spectra shown in Figure 2. These two spectra were also taken at 3.49 eV (355 nm) photon energy, and similar peak profiles were obtained.

TABLE 1: Adiabatic and Vertical Detachment Energies (eV) of SiO_2^-, $Si_2O_3^-$, $Si_2O_4^-$, GeO_2^-, and $Ge_2O_3^-$

| | SiO_2^- | $Si_2O_3^-$ | | $Si_2O_4^-$ | GeO_2^- | $Ge_2O_3^-$ |
		A	B			
ADE[a]	2.1 (0.1)	0.9 (0.1)	1.9 (0.1)	2.6 (0.1)	2.50 (0.10)	2.43 (0.10)
VDE	2.76 (0.10)	1.4 (0.1)	2.75 (0.10)	3.63 (0.10)	2.93 (0.07)	3.01 (0.07)

[a] Estimate of the upper bound of ADE.

Less noise problem was present for the spectra of the silicon oxide clusters. Nonetheless, the tail at the higher binding energy side for the SiO_2^- and $Si_2O_3^-$ spectra is still partly caused by the imperfect background subtraction.

These spectra represent photodetachment transitions from the ground state of the anion to the neutral states. The vertical detachment energies (VDE) are obtained from the peak maxima. However, the adiabatic detachment energies (ADE) are more difficult to determine due to the lack of vibrational resolution. The broad nature of these spectra, suggesting large geometry changes from the anion to the neutral, also implies that there should be little Franck–Condon factor for the 0–0 transition. An estimate of the upper bound of the ADE is obtained by drawing a straight line at the leading edge of the spectra and taking the intersect with the binding energy axis. The so-obtained ADE and VDE are listed in Table 1. The two germanium oxide species show similar VDEs, which are higher than the silicon analogs. The VDE of SiO_2^- is also quite similar to that of feature "B" of $Si_2O_3^-$. There is a significant increase of VDE from SiO_2^- to $Si_2O_4^-$.

3.1. SiO_2^- and GeO_2^-. The structure of the SiO_2 molecule is well-known, and its electronic structure has also been studied.[4-6] The valence electronic structures of both SiO_2 and GeO_2 should be similar to CO_2, which has a linear symmetric structure. It is also well-known that CO_2 does not have a positive electron affinity and that CO_2^- anion is bent.[14] Indeed, the photoelectron spectrum of CO_2^- shows a rather broad peak with a VDE of 1.4 eV, reflecting the large equilibrium geometry difference between the anion and the neutral.[14] The broad Franck–Condon envelope is along the bending mode. Analogously, the SiO_2^- and GeO_2^- are expected to be bent as well. Indeed, the broad spectra of SiO_2^- and GeO_2^- agree with this analogy. However, both SiO_2 and GeO_2 appear to have positive electron affinities, and their anions show rather high ADEs and VDEs. Another interesting observation is that the width of the observed broad peak decreases from CO_2^- to GeO_2^-, suggesting that the bending angle is probably decreasing from CO_2^- to GeO_2^-; i.e., the anion is closer to the linear structure for the heavier anions. This is consistent with the observation that the heavier molecules should have positive electron affinities.

3.2. $Si_2O_4^-$. Si_2O_4 can be viewed as the dimer of SiO_2, and the dimerization energy has been estimated to be about 4.7 eV.[7,8] However, the main vapor species of silica is the SiO diatomic.[15] The Si_2O_4 molecule was first observed and studied in a matrix infrared experiment where it was formed by reacting Si_2O_2 with O_2.[7] Its ground state structure is concluded to be a symmetric D_{2h} molecule with two terminal O atoms and two bridging O atoms (2,4-dioxocyclodisiloxane).

If we assume that the $Si_2O_4^-$ observed in our experiment corresponds to the D_{2h} neutral molecule, then the broad photoelectron spectrum shown in Figure 1 strongly suggests that there is a considerable geometrical change in the anion. Interestingly, a recent calculation on doubly charged $Si_2O_4^{2-}$ anion found that the two extra electrons enter an antibonding orbital and distorted the anion to a C_s structure, in which one terminal O atom is bent out of the molecular plane.[9] It is expected that the singly charged anion should exhibit a similar
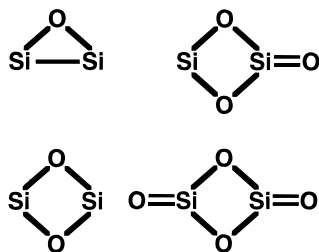
Figure 3. Structures of the Si$_2$O$_x$ ($x = 1-4$) clusters.

distortion, as evidenced by our observed broad photoelectron spectrum. A low-frequency bending mode should be excited in the photoelectron spectrum, making it difficult to resolve vibrational structures. Indeed, more recent calculations obtain similar conclusions.[16]

It is interesting to compare Si$_2$O$_4$ with (CO$_2$)$_2$, whose anion has been studied both theoretically and experimentally.[17,18] While the SiO$_2$ and CO$_2$ molecules are similar, their dimers are very different, reflecting the well-known difference between the carbon and silicon chemistries. The ground state of the CO$_2$ dimer is a weakly bonded van der Waals species with a D_{2h} structure,[17] although it also has a rather high VDE of 2.79 eV. On the other hand, the Si$_2$O$_4$ molecule is a strongly covalent bonded molecule. The solids of the two molecules display exactly the same difference.

3.3. Si$_2$O$_3^-$ and Ge$_2$O$_3^-$. These two species are expected to show similar properties. However, their photoelectron spectra are quite different. The Si$_2$O$_3^-$ spectrum shows two broad features: one strong feature at higher binding energy ("B" in Figure 1) and one weak feature at lower binding energy ("A" in Figure 1). The Ge$_2$O$_3^-$ spectrum displays only one broad feature with a rather high binding energy. It should be noted that the feature "B" of Si$_2$O$_3^-$ is rather similar compared to that of SiO$_2^-$. The same similarity is also observed between the spectra of Ge$_2$O$_3^-$ and GeO$_2^-$. This suggests that the feature "A" in the Si$_2$O$_3^-$ spectrum is most likely due to a different isomer.

The Si$_2$O$_3$ species can be viewed to be formed by removing an O atom from the Si$_2$O$_4$ molecule. There are two ways to do this, either removing a terminal O or a bridging O atom, giving two different Si$_2$O$_3$ structures. In reality, the Si$_2$O$_3$ species are probably the intermediate to form Si$_2$O$_4$ in the laser vaporization source. As a matter of fact, the Si$_2$O$_4$ molecule formed from the reaction between Si$_2$O$_2$ and O$_2$ in the previous matrix experiment is most likely through such Si$_2$O$_3$ intermediates.[7] The isotope substitution experiment using Si$_2$O$_2$ and isotopically labeled ^{18}O$_2$ yields two isomers: ^{18}OSi(OO)Si^{18}O and ^{18}OSi-(^{18}OO)SiO, where the two O atoms in the parentheses indicate the bridging O atoms (Figure 3). The intermediates in the formation of these two Si$_2$O$_4$ isomers are consistent with the two Si$_2$O$_3$ isomers proposed above.

While our experiment cannot distinguish the two isomers, recent calculations predict Si$_2$O$_3$ has a cyclic Si$_2$O$_2$ with a third terminal O atom (Figure 3),[16] i.e., the structure formed by removing a terminal O atom from Si$_2$O$_4$. We attribute the major feature "B" in our spectrum to this isomer. The low intensity of feature "A" indicates the low abundance of this isomer, implying this isomer probably is less stable. The analogous Ge$_2$O$_3$ isomer is negligible, judging from the single feature observed in the Ge$_2$O$_3^-$ spectrum. Therefore, we conclude that the dominating isomer for both Si$_2$O$_3^-$ and Ge$_2$O$_3^-$ is the one with a cyclic M$_2$O$_2$ unit plus a terminal O atom (Figure 3). The broad nature of the M$_2$O$_3^-$ spectra suggests again that there is significant geometry change between the anion and the neutral species.

3.4. From Si$_2$O to Si$_2$O$_4$. Although we are not able to study the smaller clusters, Si$_2$O and Si$_2$O$_2$ due to difficulty to produce the anions in our source, it is still interesting to discuss the structural evolution of this series of clusters as the O content is increased. Si$_2$O has been studied and its structure is known to be C_{2v} with a bridging O atom.[19-21] Si$_2$O$_2$ has also been extensively studied and is known to be a cyclic D_{2h} molecule.[22-27] We previously reported that Ge$_2$O$_2$ has a similar structure.[28] The structures of these molecules are shown schematically in Figure 3, where only the major isomer for Si$_2$O$_3$ is included. This series can be viewed as a sequential oxidation of the Si$_2$ dimer. The oxidation state of the Si atoms are increased from +1 in Si$_2$O to +4 in Si$_2$O$_4$. Similar variation of Si atom oxidation states are known to exist in the important bulk Si/SiO$_2$ interface.[29] Therefore, this series of clusters may be viewed as the smallest models for the oxidation of a Si surface. Large clusters of the kind, Si$_x$O$_y$, will undoubtedly provide better models and are being actively pursued.

4. Conclusions

We report the photoelectron spectra of small silicon oxide clusters involving one and two silicon atoms and the germanium analogs. Broad spectra are observed and suggest that there is considerable geometry change from the anion to the neutral. The SiO$_2^-$ and GeO$_2^-$ spectra indicate that their neutral molecules should possess positive electron affinities, in contrast to CO$_2$. The spectral width suggests that the bending of the anions decreases from CO$_2^-$ to GeO$_2^-$. The Si$_2$O$_4^-$ spectrum shows a considerably high VDE, compared to that of SiO$_2^-$. Two isomers are observed for Si$_2$O$_3^-$, which can be viewed by removing a terminal or bridging O atom from the D_{2h} Si$_2$O$_4$, with the former dominating. These small clusters plus the previously known Si$_2$O and Si$_2$O$_2$ species form a series of oxide clusters which can be viewed as a sequential oxidation of a Si$_2$ dimer and provide the smallest cluster models for the oxidation of a silicon surface.

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