

A Photoelectron Spectroscopic Study of Small Silicon Oxide Clusters: SiO₂, Si₂O₃, and Si₂O₄

Lai-Sheng Wang,^{*,†,‡} Hongbin Wu,[†] Sunil R. Desai,[‡] Jiawen Fan,[‡] and Steve D. Colson[‡]

Department of Physics, Washington State University, Richland, Washington 99352, and Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, MS K2-14, Richland, Washington 99352

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We present an anion photoelectron spectroscopic study of SiO₂, Si₂O₃, and Si₂O₄. 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 SiO₂⁻, Si₂O₃⁻, and Si₂O₄⁻, respectively. The spectrum of Si₂O₃⁻ shows a weak feature at lower binding energy, suggesting existence of another isomer. The spectra of GeO₂⁻ and Ge₂O₃⁻ 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 GeO₂⁻ and 3.01 (0.07) eV for Ge₂O₃⁻. The Ge₂O₃⁻ 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_xO_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_xO_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 SiO₂, Si₂O₃, and Si₂O₄ and the germanium analogs. Although SiO₂ 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 Si₂O₃ species. Si₂O₄ can be viewed as a dimer of SiO₂ and has been studied in a low-temperature matrix experiment⁷ and in a theoretical calculation.⁸ It has a D_{2h} structure and has been named 2,4-dioxocyclodisiloxane. In a recent calculation, both Si₂O₄⁻ and Si₂O₄²⁻ have been studied in an effort to search stable doubly charged anions.⁹

We obtained the photoelectron electron spectra of SiO₂⁻, Si₂O₃⁻, and Si₂O₄⁻, as well as GeO₂⁻ and Ge₂O₃⁻, at 4.66 eV photon energy. The spectrum of Si₂O₃⁻ 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 GeO₂⁻ is similar to that of SiO₂⁻, while the spectrum of Ge₂O₃⁻ is similar to the higher binding energy feature of the Si₂O₃⁻ 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 Si₂O_x (*x* = 1–4) clusters are compared, which can be viewed as a sequential oxidation of a Si₂ dimer. Finally, a brief summary is presented in section 4.

2. Experimental Section

We generate the Si_xO_y⁻ anions by laser vaporizing a pure silicon target into a helium atmosphere containing 0.05% O₂. 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 O₂ seeded in the carrier gas produce a series of Si_xO_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_xO_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

[†] Washington State University.

[‡] Pacific Northwest National Laboratory.

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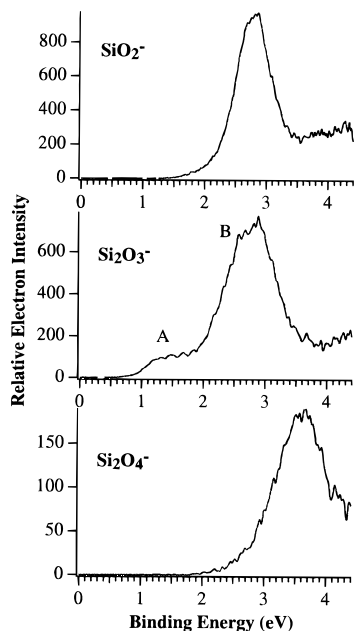


Figure 1. Photoelectron spectra of SiO_2^- , Si_2O_3^- , and Si_2O_4^- at 4.66 eV photon energy.

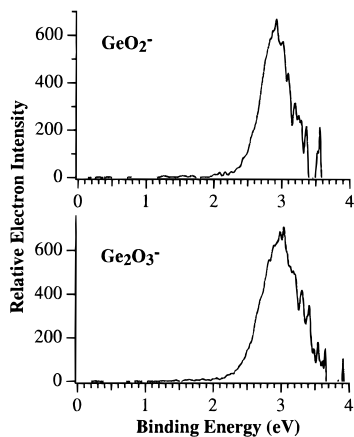


Figure 2. Photoelectron spectra of GeO_2^- and Ge_2O_3^- at 4.66 eV photon energy.

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^-

	Si_2O_3^-		Si_2O_4^-	GeO_2^-	Ge_2O_3^-
	SiO_2^-	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 $\text{Si}_2\text{O}_4^{2-}$ 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

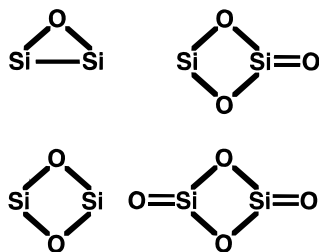


Figure 3. Structures of the Si₂O_x ($x = 1-4$) clusters.

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 Si₂O₄ with (CO₂)₂, whose anion has been studied both theoretically and experimentally.^{17,18} While the SiO₂ and CO₂ molecules are similar, their dimers are very different, reflecting the well-known difference between the carbon and silicon chemistries. The ground state of the CO₂ 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 Si₂O₄ molecule is a strongly covalent bonded molecule. The solids of the two molecules display exactly the same difference.

3.3. Si₂O₃⁻ and Ge₂O₃⁻. These two species are expected to show similar properties. However, their photoelectron spectra are quite different. The Si₂O₃⁻ 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 Ge₂O₃⁻ spectrum displays only one broad feature with a rather high binding energy. It should be noted that the feature "B" of Si₂O₃⁻ is rather similar compared to that of SiO₂⁻. The same similarity is also observed between the spectra of Ge₂O₃⁻ and GeO₂⁻. This suggests that the feature "A" in the Si₂O₃⁻ spectrum is most likely due to a different isomer.

The Si₂O₃ species can be viewed to be formed by removing an O atom from the Si₂O₄ molecule. There are two ways to do this, either removing a terminal O or a bridging O atom, giving two different Si₂O₃ structures. In reality, the Si₂O₃ species are probably the intermediate to form Si₂O₄ in the laser vaporization source. As a matter of fact, the Si₂O₄ molecule formed from the reaction between Si₂O₂ and O₂ in the previous matrix experiment is most likely through such Si₂O₃ intermediates.⁷ The isotope substitution experiment using Si₂O₂ and isotopically labeled ¹⁸O₂ yields two isomers: ¹⁸OSi(OO)Si¹⁸O and ¹⁸OSi(¹⁸OO)SiO, where the two O atoms in the parentheses indicate the bridging O atoms (Figure 3). The intermediates in the formation of these two Si₂O₄ isomers are consistent with the two Si₂O₃ isomers proposed above.

While our experiment cannot distinguish the two isomers, recent calculations predict Si₂O₃ has a cyclic Si₂O₂ with a third terminal O atom (Figure 3),¹⁶ i.e., the structure formed by removing a terminal O atom from Si₂O₄. 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 Ge₂O₃ isomer is negligible, judging from the single feature observed in the Ge₂O₃⁻ spectrum. Therefore, we conclude that the dominating isomer for both Si₂O₃⁻ and Ge₂O₃⁻ is the one with a cyclic M₂O₂ unit plus a terminal O atom (Figure 3). The broad nature of the M₂O₃⁻ spectra suggests again that there is significant geometry change between the anion and the neutral species.

3.4. From Si₂O to Si₂O₄. Although we are not able to study the smaller clusters, Si₂O and Si₂O₂ 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. Si₂O has been studied and its structure is known to be C_{2v} with a bridging O atom.¹⁹⁻²¹ Si₂O₂ has also been extensively studied and is known to be a cyclic D_{2h} molecule.²²⁻²⁷ We previously reported that Ge₂O₂ has a similar structure.²⁸ The structures of these molecules are shown schematically in Figure 3, where only the major isomer for Si₂O₃ is included. This series can be viewed as a sequential oxidation of the Si₂ dimer. The oxidation state of the Si atoms are increased from +1 in Si₂O to +4 in Si₂O₄. Similar variation of Si atom oxidation states are known to exist in the important bulk Si/SiO₂ 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_xO_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 SiO₂⁻ and GeO₂⁻ spectra indicate that their neutral molecules should possess positive electron affinities, in contrast to CO₂. The spectral width suggests that the bending of the anions decreases from CO₂⁻ to GeO₂⁻. The Si₂O₄⁻ spectrum shows a considerably high VDE, compared to that of SiO₂⁻. Two isomers are observed for Si₂O₃⁻, which can be viewed by removing a terminal or bridging O atom from the D_{2h} Si₂O₄, with the former dominating. These small clusters plus the previously known Si₂O and Si₂O₂ species form a series of oxide clusters which can be viewed as a sequential oxidation of a Si₂ dimer and provide the smallest cluster models for the oxidation of a silicon surface.

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