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Structural and electronic properties of neutral and charged silicalike clusters

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The electronic and structural properties of neutral and charged $\mathrm{Si}_n\mathrm{O}_n$ clusters, with $n=3$, 4, and 5, and related clusters, are examined using the higher-order finite-difference pseudopotential method. The ground-state structures for these clusters are determined via a simulated annealing procedure. The photoemission spectra for negatively charged clusters $\mathrm{Si}_n\mathrm{O}_n^-$ are simulated at finite temperatures using quantum forces coupled with Langevin dynamics. The simulated spectra are in good agreement with measured spectra. In contrast to previously predicted structures, we find the lowest-energy structures for $\mathrm{Si}_4\mathrm{O}_4$ and $\mathrm{Si}_5\mathrm{O}_5$ correspond to nonplanar rings. [S0163-1829(98)03005-7]

I. INTRODUCTION

Silica is an important technological material. Uses of silica span applications from passivation of electronic materials to vitrification of materials for waste disposal. However, at the microsopic level, our understanding of silica is incomplete. For example, the process by which oxidation occurs, the role of defects in oxides, the nature of amorphous structures, and the evolution of macroscopic properties from atomistic constituents are all important unresolved issues.

Clusters provide an interesting source of information for the bonding properties of matter.[1] The bonds in clusters are often in unusual configurations relative to macroscopic pieces of the solid state. For example, in tetrahedral semiconductor clusters the coordination number may be 2, 3, or 6 in contrast to a diamond crystal value of 4. Also, the surface of a cluster dominates its electronic and structural properties; the atoms in a cluster may be considered all ''surface'' atoms if the cluster is only 10–20 atoms large. In this situation, the cluster can have thermodynamic properties far removed from ''bulk properties.'' These properties may include a reduced melting point and complete solubility between normally insoluble consituents. In short, an understanding of silicalike clusters will allow one to develop insights into bonding in silica and similar materials.[2]

One of the chief problems in understanding clusters is assessing the accuracy of predicted electronic and structural properties. Unlike crystalline matter, where x-ray diffraction can be used to extract an accurate picture of structure, clusters cannot be so easily probed. The procedure for clusters is quite indirect. One can calculate a property such as the Raman spectra[3] or photoelectron spectra,[4,5] and compare the theoretical calculation to experiment. For semiconducting clusters,[3–5] small differences in the structure can result in large differences in the photoelectron spectra. In such cases, which are by no means universal, some candidate structures can be eliminated. In other cases, two structures which might be different in terms of their topology may possess similar photoemission spectra and no distinction between clusters can be determined via the simulation. Here we will consider similar calculations for silica clusters. In particular, we are interested in making comparisons to recent photoelectron spectroscopy measurements of $\mathrm{Si}_n\mathrm{O}_n^-$ clusters[6] and in predicting the structure of both charged and neutral clusters.

II. COMPUTATIONAL METHODS

Our theoretical approach centers on *ab initio* pseudopotentials[7] which have been constructed within the local density approximation using the procedure of Troullier and Martins.[8] The atomic configuration used for the construction of the Si potential was $3s^2 3p^2$ with the core size parameters fixed to $r_s = r_p = 2.50$ a.u. (1 a.u. $=0.529$ Å). For the O potential, the configuration was $2s^2 p^4$ with the core size taken to be $r_s = 1.30$ a.u. and $r_p = 1.65$ a.u. The local part of the pseudopotential was taken to be $l=0$; only $l=1$ nonlocal terms were included in the pseudopotential. The exchange-correlation potential was from the work of Ceperley and Alder[9] as parametrized by Perdew and Zunger.[10]

The resulting one-electron Schrödinger equation was solved in real space on a uniform grid via a higher-order finite-difference method.[11] The grid spacing h was fixed to be 0.325 a.u. We can roughly estimate the plane wave cutoff as $\frac{1}{2}(\pi/h)^2$ or about 90 Ry. This can be compared to a plane wave cutoff of 64 Ry commonly used for crystalline silica.[12] Our use of a uniform grid may be contrasted with other approaches such as adaptive grids.[13] The use of adaptive grids allows one to account for different length scales. For example, the grid may be finer around the oxygen atom and coarser around the silicon atom. Unfortunately, adaptive grids can greatly complicate the calculations. This is especially true for situations in which the atoms are allowed to move. The grids must be updated continuously as the atoms move, and determining accurate forces is complex as the ''basis'' changes with the grid.

An important factor in any real space method is the ''smoothness'' of the pseudopotential. In plane wave calculations, the pseudopotential is expanded in reciprocal lattice vectors. This set of vectors is often terminated by a vector commensurate with the shortest wavelength present in the wave function. The termination procedure in some sense is equivalent to a ''low-pass'' filter. Short-ranged fluctuations in the potential are effectively removed. This issue is non-

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trivial and has resulted in some very poor convergences for some pseudopotentials. In particular, Gygi and Galli found that with a CO_2 molecule, even with a grid spacing of less than 0.25 a.u. the eigenvalues and eigenvectors were not well converged.[13] They attributed this problem to the use of a Hamann-Schlüter-Chiang potential[14] which is not especially well suited for real space grids.[11] These potentials can possess fluctuations in the potential near the core radii. In contrast, work using the Troullier-Martins potentials[8] found the molecular wave functions and eigenvalues to be well converged at these grid spacings.[15]

Our higher-order finite-difference expansion of the kinetic energy operator includes terms up to 12th order. The resulting eigenvalue problem was solved using a generalized Davidson procedure.[16] This method takes advantage of the sparsity and well-defined structure of the Hamiltonian matrix. A block diagonalization procedure was used to find the eigenvalue-eigenvector pair. Preconditioning consisted of averaging over neighboring grid points. This simple preconditioning accelerates the convergence by approximately 30% in terms of the computing time. We also dynamically altered the tolerance criteria for setting the accuracy of the eigenvalue-eigenvector pairs. All eigenvalues were required to be converged within 0.1 eV at the initial self-consistency loop. This criterion was made more stringent by a factor of 2 after each iteration until a value of 0.005 eV was established. This dynamic tolerance can reduce the computational time by a factor of 2. We note that our tolerance criteria is only for the highest eigenvalue computed.[16] The other eigenvalues are converged to much more stringent tolerance, e.g., typically $\sim 10^{-4}$ eV.

The boundary conditions for the eigenvalue problem were to demand the wave function vanish outside a sphere which contains the cluster. The size of the sphere was set so that the surface of the sphere was at least 5 a.u. removed from any atom within the cluster. A multipole expansion was performed to determine the Hartree potential outside of these domains. This expansion was used to fix the boundary condition in solving Poisson's equation with a conjugate gradient method.[16]

The solution of the eigenvalue problem allows one to compute the total electronic energy of the cluster as a function of the atomic coordinates; i.e., it allows the computation of the *quantum* interatomic forces. This is an important issue for clusters of silica as the nature of the Si-O bond is not entirely ionic or covalent. As such, simple interatomic potentials, which do not contain many-body forces, are not likely to be very accurate for Si-O clusters.

A serious consideration in any cluster calculation concerns the determination of the ground-state structure or at least a ''realistic'' description of the structure. This is a highly nontrivial problem owing the numerous degrees of freedom and the existence of numerous energetically degenerate structures. There are several approaches to this problem in the literature. Most approaches are based on either simulated annealing[17,18] or on genetic algorithms.[19] In the genetic algorithm method, a set of ''parent clusters'' are selected and ''offspring clusters'' are created by ''cutting and pasting'' the parents. The cutting procedure is based on bisecting the cluster with a random plane. Often thousands of generations are considered; at each generation, the most energetically endowed offspring are retained and remated. This procedure works very well for escaping from the minimum, or avoiding metastable structures, relative to simulated annealing. Unfortunately, the use of this algorithm is not straightforward. It is still possible in some circumstances to be trapped in a particular structural topology. In these cases, one must introduce ''mutations'' into the process to transit to a new structural type.[19]

In the simulated annealing approach, such as with Langevin dynamics, a random configuration of clusters is considered at a hot temperature.[17,18] The clusters are allowed to interact via interatomic forces as determined by quantum calculations (or by empirical force fields) and with a fictive heat bath. The bath imparts stochastic forces which are dissipated by a viscous damping term. If the system is cooled slowly, one hopes to quench out a reasonable structure. Simulated annealing works quite well for small clusters, e.g., clusters with less than a dozen atoms or so. However, once the number of atoms is increased, the procedure becomes computationally intractable. Larger clusters have been treated directly via Langevin dynamics using physical or chemical insights to expedite the procedure. In this work, we utilize Langevin dynamics to obtain ''realistic structures'' for Si_nO_n and related clusters.

III. STRUCTURAL PROPERTIES OF $H_2Si_2O_3$, $H_2Si_2O_5$ AND Si_3O_4 CLUSTERS

Clusters can be used as models for the bulk to determine bond-stretching forces for the Si-O bond and to determine bond-bending forces for the Si-O-Si and O-Si-O bonds.[20] Several of the most useful interatomic silica potentials have been constructed in this manner. For example, the widely used Tsuneyuki potential[21] was constructed by fitting an *ad hoc* potential to Hartree-Fock calculations. In this case, bond-bending forces were not included.

To test our pseudopotential calculation, we have calculated the structures of H_2SiO_3 and $H_2Si_2O_5$. H_2SiO_3 is the silicon analog of carbonic acid and includes a Si$=$O double bond. $H_2Si_2O_5$ includes two silicons which are in a tetrahedral-like environment. These structures have been treated by a self-consistent field (SCF) molecular orbital method.[22] To initiate our finite-difference pseudopotential calculation, a similar geometry was assumed; this geometry was then allowed to relax fully. For the structural optimization, we have used the initially scaled version of Broyden-Fletcher-Goldfarb-Shanno (BFGS) quasi-Newton method[23] with an inexact line search. The BFGS quasi-Newton method finds the minimum of a function iteratively. In all cases, we iterated the structure until the magnitude of the largest force on any atom was less than 0.005 a.u. Since the role of H in these systems is only to passivate the oxygen dangling bond, we have not tried to obtain a highly accurate potential. For the hydrogen pseudopotential, we used a simple local potential. We do not expect the potential to be highly accurate in terms of the H-O bond. However, we do expect the remaining bonds to be accurately represented.

In Fig. 1, we illustrate the predicted molecular structure. In terms of comparing to the SCF molecular orbital work,[22] the predicted structures are remarkably similar. Ignoring the hydrogen bonds which tend to be about 0.08 Å shorter than the SCF work, the largest difference for H_2SiO_3 occurs in

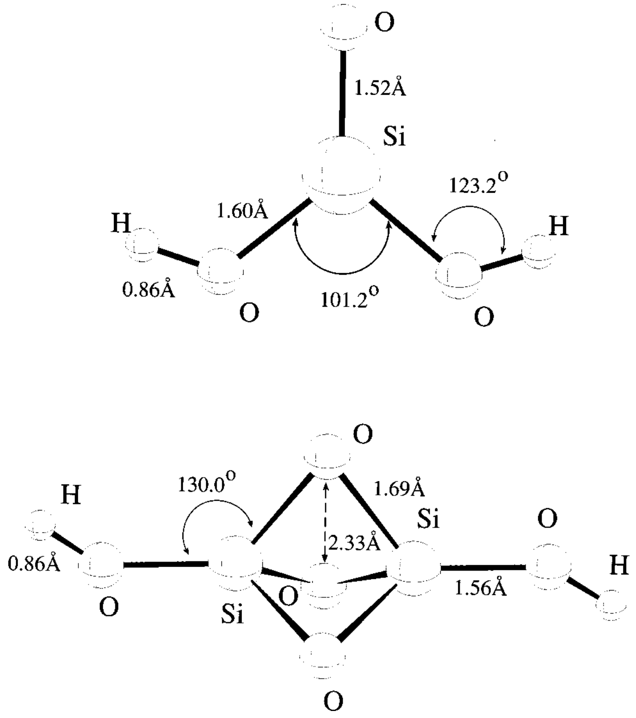

FIG. 1. Predicted ground-state structures for H_2SiO_3 and $H_2Si_2O_5$ clusters.

the Si═O double bond. The molecular orbital work predicts the double bond to be 1.50 Å whereas the pseudopotential local density approximation (LDA) value is 1.52 Å. The O-Si-O bond angle is 106.0° whereas the pseudopotential value is 101.1°. In the case of $H_2Si_2O_5$, the largest difference in bond length is less than 0.01 Å.

We note that the SCF molecular orbital calculations differ in a number of technical details from our work. The SCF molecular orbital calculations include all the electronic states and, more importantly, do not utilize the local density approximation. Also, the molecular orbital method involves an explicit Gaussian basis while the finite-difference method does not use a basis at all. Thus, it is somewhat surprising to find that the calculated structures agree so well.

Another structure we examined is the Si_3O_4 cluster. Previous theoretical[24] and experimental work[6] suggests that this structure has a D_{2h} symmetry with two Si_2O_2 rhombuses sharing one silicon atom. The central silicon atom is in a tetrahedral environment while the two terminal silicon atoms are connected to two oxygens. The predicted structure, optimized as before, is shown in Fig. 2.

We can compare our structure to recent theoretical calculations.[24] The predicted structures are similar. We find a relatively small, but systematic, difference between our calculations and those from quantum chemistry methods. The Si-O bonds are shorter in our work by about 0.03–0.04 Å or about 2% when compared to other calculations. This is the accuracy we expect from the local density approximation. With respect to the bond angles, they are consistent with our ‘‘rescaled’’ bond lengths: the Si-O-Si and O-Si-O angles agree to within a degree.

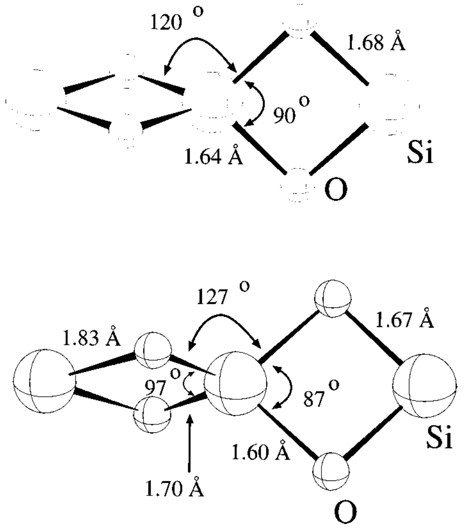

FIG. 2. Predicted ground-state structures for Si_3O_4 and $Si_3O_4^-$ clusters.

This cluster has an intriguing behavior when negatively charged. The lowest unoccupied states are doubly degenerate and are highly localized on opposing terminal silicon atoms. Occupying only one of these states causes some difficulty in obtaining a self-consistent field. In principle, the system should undergo a strong Jahn-Teller distortion and break the symmetry between these states: lowering the energy of the occupied state at the expense of the empty state. However, during the SCF iteration procedure, a small difference in the geometry will result in a large change in the energy of these states. This situation made obtaining a SCF in the traditional manner impossible because of large oscillations in the potential which arose as one state emptied and the other became occupied. The procedure by which we obtained a SCF was to choose one of the wave functions, e.g., the one which results in a dipole pointing to a particular terminal silicon atom. We then constrained this wave function to be occupied regardless of whether it was above or below the competing state.

The structure of the negatively charged Si_3O_4 cluster is also presented in Fig. 2. The Si-O bond lengths involving the charged terminal silicon atom are lengthened from 1.68 Å to 1.83 Å. However, the Si-O bond lengths for the opposite terminal silicon atom remain essentially unchanged. The Si-O bond lengths on the tetrahedrally coordinated silicon atom are equal before charging. After charging, the bond lengths on the side of the charged terminal silicon atom are lengthened from 1.64 Å to 1.70 Å. The other bonds are shortened from 1.64 Å to 1.60 Å.

The electronic configuration resulting from our calculation for the negatively charged cluster is also consistent with previous work.[24] In Fig. 3, we illustrate the charge density

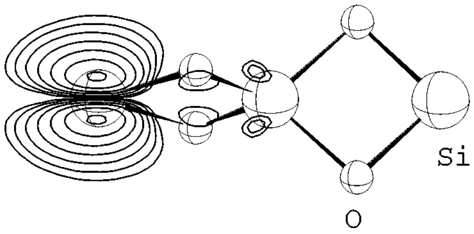

FIG. 3. Charge density for the LUMO in $Si_3O_4^-$. The contours correspond to intervals which double with each contour. The maximum density is 0.8 a.u.

for the highest occupied state. The density is strongly localized on a terminal silicon: in particular the terminal Si atom with the longer Si-O bond length. This is expected as the extra charge weakens the Si-O bond. The charge density for the added electron is p-like with the p state oriented perpendicular to the plane containing the terminal silicon and neighboring oxygens.

IV. STRUCTURAL PROPERTIES OF Si_nO_n CLUSTERS: NEUTRAL AND CHARGED

Ringlike structures such as Si_3O_3 are thought to play an important role in the properties of silica. For example, they have been proposed to account for the anomalies in the Raman spectra of vitreous silica.[25] Here we examine Si_nO_n clusters with $n=3$, 4, and 5 in both the charged and neutral states.

For small rings, a planar geometry is thought to be the ground-state structure.[6,26] We considered a Si-O ring with a planar geometry as the initial candidate structure and used simulated annealing with Langevin dynamics to verify the proposed structure. In terms of some of the computational details, the viscosity of the bath was taken to be 10^{-5} a.u. Initially the cluster was heated to about 2000 K and cooled to a temperature of 300 K. The integration time step was taken to be 100 a.u. (or about 2.4 fs). Typically, several hundred time steps were used with a total annealing time of ~ 1 ps. This simulation time is adequate for the relatively small cluster sizes considered in this work. After the simulated annealing procedure, we then quenched the cluster to the ground-state structure again using the BFGS quasi-Newton minimization procedure. We made no attempt to ''fine-tune'' the clusters by imposing any special symmetry. The resulting structures are shown in Fig. 4 for both the neutral and charged states.

One advantage of using a real space method is that there is no need for a compensating background as would be the case for a supercell calculation. We simply modify the boundary conditions in calculating the charged cluster; i.e., we add a monopole term $(+e^2/r)$ to the Hartree potential outside the spherical domain of the cluster.

For Si_3O_3, we find that the lowest-energy structure is planar. This is consistent with previous theoretical and experimental evidence.[6] The two angles for Si-O-Si and O-Si-O are not equal and are reminiscent of what one might expect from forms of solid silica. In many crystalline silicas,[27] the building block is a tetrahedral unit of SiO_4 in which the O-Si-O angle is close to the tetrahedral value of 109.5°. Also, most crystalline polymorphs of silica differ only in how the tetrahedral units are arranged. Typically, the Si-O-Si bond angle is ''floppy'' with a typical value near ~140°. In Si_3O_3, the O-Si-O bond angle is 102° and the Si-O-Si angle is 134°. If we negatively charge this cluster, the structure deviates somewhat from a planar structure. The additional charge is localized on an oxygen atom which moves out of the plane (Fig. 4). This change in geometry upon charging is also consistent with previous work.[6] As in the case of the Si_3O_4 cluster, the bonds to the charged atom are weakened by the additional charge and they become longer by about 2–3% than in the neutral cluster.

In contrast to the structure of Si_3O_3, the predicted structure of Si_4O_4 is not planar. We find a ''buckled'' ring structure for Si_4O_4. Although we initiated the simulated anneal with a planar structure, the stochastic element of the anneal allows symmetry breaking. We found the original planar cluster quickly deviated to a structure as in Fig. 4. We also examined the Si_4O_4 via a constrained minimization; i.e., we minimized the energy for a planar geometry. The nonplanar structure is favored by an energy difference of more than ~0.3 eV/atom. We found at least one other calculation for the geometry of Si_4O_4.[28] This calculation predicted a planar structure which is at variance with our results. We note that our constrained minimization agrees with the previous planar structure: We find a Si-O bond length of 1.60 Å, a Si-O-Si bond angle of 165°, and an O-Si-O bond angle of 105°. The previous calculation found a bond length of 1.65 Å and bond angles of 166.6° (Si-O-Si) and 103.4° (O-Si-O). It is not clear that the previous work found a global minimum as the phase space explored was considerably smaller than the current work. The bond angles we find are in line with what one would expect for silica. For example, the bond angle of 166.6° for the Si-O-Si angle in the planar structure is much larger than in the Si_3O_3 cluster or what one expects from crystalline silica.

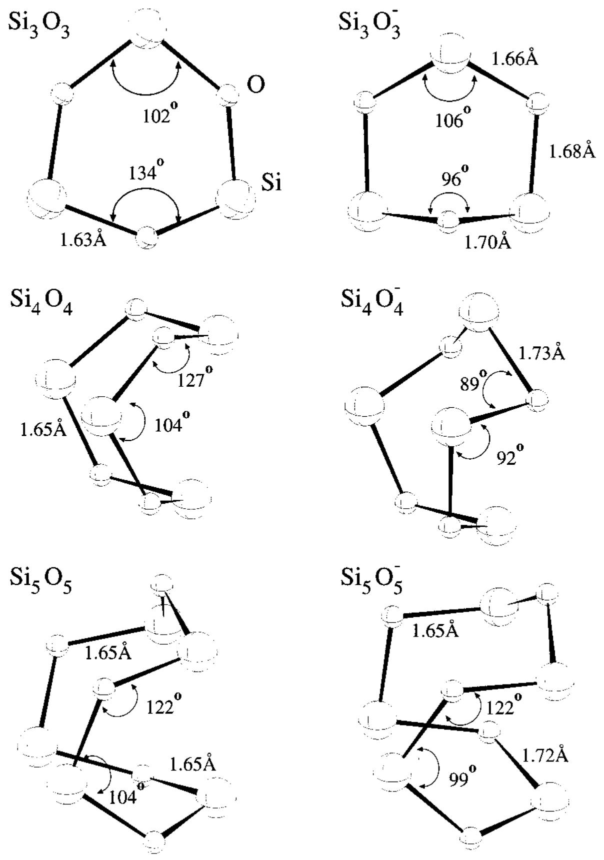

FIG. 4. Predicted ground-state structures for Si_nO_n and $Si_nO_n^-$ clusters.

When negatively charged, the $Si_4O_4^-$ cluster behaves in a similar fashion to the $Si_3O_3^-$ cluster. The extra electron is localized in a state on the anion. Moreover, the bond lengths to this anion are lengthened by about ~3–4 %.

The Si_5O_5 cluster is also buckled with a geometry similar to the Si_4O_4 cluster. One noticeable difference is the lack of change in the cluster geometry when charged. The bond to one of the anions is lengthened, but the angle changes are smaller and the charge localization is not nearly as strong. One would expect that as the cluster increases in size, the role of charging on the structural energy would become less. However, the similarity between the Si_5O_5 cluster and the $Si_5O_5^-$ cluster is somewhat surprising.

The energy differences as a function of cluster size are not large. If we take the total energy for Si_3O_3 as our zero reference, then Si_4O_4 and Si_5O_5 are both within ~ 0.1 eV/atom of the reference energy. The clusters become slightly less stable with increasing size. This is also true for the charged clusters. Perhaps the similarities in total energy are not surprising considering the similarity of the clusters in terms of bond angles and bond lengths.

V. SIMULATED PHOTOEMISSION SPECTRA OF $Si_nO_n^-$ CLUSTERS

A central advantage of our method when compared to other *ab initio* methods is that we can simulate the photoemission spectra via molecular dynamics with quantum forces. Other methods, e.g., quantum chemistry methods which include configuration interactions, are too computationally intensive to permit such simulations. The procedure we use has been used previously for examining the photoemission of negatively charged silicon and germanium clusters.[5,18] Here we focus on the charged clusters $Si_nO_n^-$ with $n=3$, 4, and 5 and compare to recent photoemission work.[6] One significant drawback of the photoemission measurements is the limited energy window. Only a ~ 2–3 eV energy window exists.

Our simulation is initiated by assuming the lowest-energy structure (Fig. 4). Again, the cluster is placed in a fictive heat bath at a temperature commensurate with the experimental conditions. In this case, we are using Langevin techniques as a ‘‘thermostat’’ in contrast to the simulated annealing procedure.[18] Langevin dynamics can be justified as a thermostat for statistical averages in the same fashion as other dynamics, e.g., the use of Nosé dynamics[29] in the Car-Parrinello method.[30] We note that unlike the Car-Parrinello dynamics, we do not use fictitious electron dynamics. Instead, we quench the system to the Born-Oppenheimer surface at each time step in the simulation. We have taken the temperature of the clusters to be 500 K. After a short thermalization time of about 100 time steps, each cluster was examined for an additional 300 time steps or about 0.7 ps. This time scale is sufficient for the cluster to sample a reasonable number of configurations given the relatively low temperature.

In making comparisons to experiment, we average the eigenvalue spectrum of the cluster over the simulation time. We have not included any matrix elements in the averaged eigenvalue spectrum, and so only the peak positions and ‘‘gaps’’ should be compared. This is not a bad approximation as the contributions to the photoemission spectra come primarily from p-like oxygen states and, as such, strong matrix element effects are not likely to be present.

Given that photoemission samples occupied states, we expect that the peak positions should be reasonably accurate. In Fig. 5, we illustrate the averaged eigenvalue spectra for the cluster. In order to simulate the experimental resolution, we have convoluted this spectra with a Gaussian with 0.2 eV for the half-width at half-maximum.

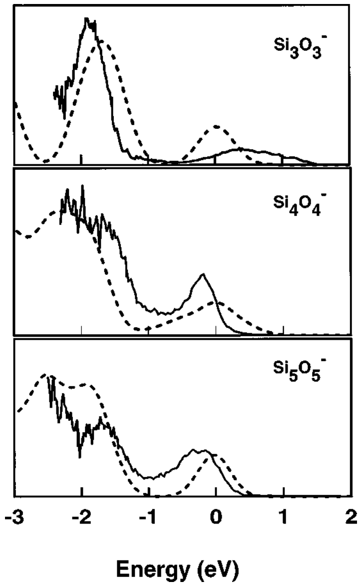

FIG. 5. Simulated photoemission spectra for $Si_nO_n^-$ clusters. The theoretical spectra are shown by dashed lines. The solid lines are from experiment, Ref. 6. The energy zero corresponds to the highest occupied state in the simulation.

The spectra for these clusters all have one feature in common: a small peak separated from the main part of the spectra. For the neutral clusters, a gap of ~1–2 eV exits between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). If an electron is added to the LUMO orbital, and no relaxation occurs, this orbital will appear as a peak in the photoemission spectra. The contribution from this orbital will be separated from the remaining spectra by the HOMO-LUMO gap. Of course, relaxation effects will change this gap. As such, the HOMO-LUMO gap for the neutral cluster need not be accurately reflected in the photoemission spectra for the charged cluster.

In the case of $Si_3O_3^-$, the contribution from the added electron results a broad feature. This feature indicates that there is a large geometry change between the charged cluster versus the neutral cluster.[6] This is consistent with our calculation. In particular, Si_3O_3 becomes nonplanar when charged in contrast to Si_4O_4 and Si_5O_5. The HOMO-LUMO gap for the neutral cluster is 2.9 eV. Upon charging the separation is reduced to 1.7 eV. Experimentally, the separation is difficult to determine because of the broad peak, but a value of 2.2 eV is a reasonable estimate. Given the simplicity of our analysis, the line shapes are in good agreement.

For $Si_4O_4^-$, the HOMO-LUMO gap as indicated by the photoemission spectrum is smaller than in $Si_3O_3^-$. This is consistent with the theoretical predictions. The HOMO-LUMO gap in the neutral cluster is 2.0 eV and when charged it is reduced to about 1.3 eV for the ground-state structure. The gap from the photoemission measurement is about 1.7 eV, or roughly 0.5 eV smaller than in $Si_3O_3^-$. It is interesting to note that the gap from the simulation tends to be larger than for the ground state; i.e., the gap between the peaks in the simulation is about 1.9 eV. This is not surprising. In the simulation, there is no *a priori* reason to believe the levels

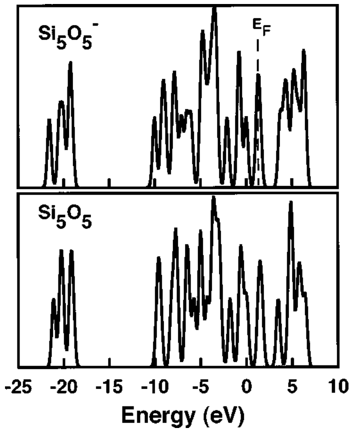

FIG. 6. Comparison of the ‘‘density of states’’ for a neutral and charged Si_5O_5 cluster. The energy zero corresponds to the HOMO state in the neutral case. The position of the Fermi level E_F is indicated for the charged cluster.

will fluctuate in the ‘‘heat bath’’ in a symmetric fashion.

The simulation for $Si_5O_5^-$ is reassuring. For this cluster, there is some additional structure in the photoemission which appears to be accurately replicated by the simulation. In particular, there is a doublet peak in the photoemission spectra at -1.7 eV and -2.5 eV. This is replicated in the theoretical simulation. Consistent with the trend from $Si_3O_3^-$ to $Si_4O_4^-$, the gap is reduced in the photoemission spectrum to about 1.4 eV. In the neutral case, the HOMO-LUMO gap is 1.4 eV and is reduced to about 1.2 eV for the charged case.

In Fig. 6, we illustrate the eigenvalue spectra for Si_5O_5 and $Si_5O_5^-$. The spectra were created by broadening each eigenvalue for the cluster with a Gaussian as done in the simulations of the photoemission spectra. The eigenvalue spectra for the charged and neutral cases appear similar. This confirms a ‘‘band-filling’’ picture; i.e., the addition of an electron fills the lowest empty level without significant rearrangement of the remaining energy levels. In Si_5O_5 there is little structural rearrangement upon charging, and so changes in the eigenvalue spectra represent differences in the electronic potential. The general features of the Si_5O_5 eigenvalue spectrum are shared by the other clusters; e.g., the width of the occupied eigenvalue spectra is about 21 eV and a gap of about 1–2 eV exists between the HOMO and LUMO levels. The cluster spectra cannot be compared directly to a bulk silica density of states. For example, in quartz, the electronic properties are dominated by SiO_4 tetrahedra which are absent in these clusters. Nonetheless, the width of the valence band in quartz is consistent with the spectrum for the cluster. The main spectral difference is the existence of a large gap in quartz which is absent in the clusters.

VI. CONCLUSIONS

We have examined the electronic and structural properties of neutral and charged Si_nO_n clusters, with $n=3$, 4, and 5, and related clusters, using the higher-order finite-difference pseudopotential method. We determined the ground-state structures for these clusters via a simulated annealing procedure. We also simulated the photoemission spectra for the negatively charged clusters $Si_nO_n^-$ at finite temperatures using quantum forces coupled with Langevin dynamics. This simulation allowed us to compare to recent experimental measurements of the photoemission spectra. We found simulated spectra to be in good agreement with measured spectra. This agreement suggested that our predicted structures yield an eigenvalue spectra consistent with experiment and affirm the validity of our predicted structures. In contrast to previous work, we predicted the ground-state structure for Si_4O_4 and Si_5O_5 to correspond to nonplanar rings.

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