Photoemission Spectra and Structures of Si Clusters at Finite Temperature

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We examine the electronic spectra of small Si_n^- ($n \leq 7$) clusters from first-principles simulations at finite temperature. The calculated spectra yield an accurate description for existing ultraviolet photoelectron data on the negatively charged clusters. The detailed agreement between theoretical and experimental features and the high sensitivity of the electronic spectra to the cluster geometry are exploited to identify the relevant isomers. Our results show the importance of atomic relaxation within the charged cluster, as opposed to photoemission-induced relaxation effects, in determining the observed spectra.

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Semiconductor clusters generally undergo important reconstruction relative to bulk crystalline fragments, as evidenced by the existence of "magic number" effects in their physical and chemical properties [1]. The cluster structural parameters affect the chemical reactivity, photofragmentation, and Raman and photoelectron spectra [2–5], but a systematic approach to extract the geometrical structures from such data is still lacking. For these nanosystems in their unsupported form, no direct experimental probe of the atomic structure exists which is comparable to x-ray diffraction for bulk periodic materials, or scanning tunneling microscopy for surfaces.

Theoretical approaches such as *ab initio* methods for structure prediction are confronted with major difficulties when applied to clusters. Most problems arise from the existence of multiple local minima in the potential-energy surface of these systems. For cluster sizes exceeding a few atoms, one generally relies on simulated annealing procedures for global geometry optimization [6,7]. Simulated annealing times, however, are still orders of magnitude shorter than experimental annealing times, and trapping by local minima in the simulation is a problem. In addition, the accuracy of *ab initio* methods and dynamical effects become critical as the cluster size and the number of competing structures increases. Even for some small clusters, such as Si_6, these effects are already of the same order of magnitude as the energy difference between the lowest energy isomers [8].

Comparison between theory and experiment is essential to identify the relevant isomers, in particular, at finite temperature. Here we will show that systematic comparison of calculated and experimental photoemission spectra can be exploited as a sensitive tool to assign structures. Based on the photoelectron analysis, we confirm that the structures formed by Si_4^-, Si_5^-, and Si_7^- are a planar rhombus, a trigonal bipyramid, and a pentagonal bipyramid, respectively. For Si_6^-, the photoelectron spectra reflect the structure of a bicapped tetrahedron. At zero temperature, the bicapped tetrahedron is quasidegenerate in energy with a distorted octahedron. Using the electronic spectra, however, one can unambiguously identify the former structure as the stable isomer in the experimental conditions.

Comparative studies of photofragmentation and electron affinity have been performed earlier to explain general trends in the stability of some small clusters as a function of their size [9,10], e.g., for Si_n, $n \leq 10$. Very recently, a comparison of theoretical and experimental Raman spectra for size-selected Si_4, Si_6, and Si_7 clusters embedded in a solid nitrogen matrix was successfully used to determine the relevant isomers [4]. Here we elected to focus on photoemission, which has been the spectroscopic method of choice in the past twenty years to monitor the electronic structure of solids.

For clusters, there are a number of unresolved issues in the interpretation of the photoemission spectra. Cheshnovsky *et al.* [5] performed ultraviolet photoelectron spectroscopy (UPS) measurements on the negatively charged silicon clusters (Si_n^-, $n \leq 12$) using the 6.4 eV ArF excimer laser. UPS spectra, interpreted in terms of the neutral cluster properties, were used to gauge the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Large gaps were assigned [5] to the magic number clusters, while other clusters appeared to have vanishing gaps. The existing theoretical estimates [11] for these gaps showed, however, substantial disagreement with the measured values. It was proposed [5] that elaborate calculations including transition cross sections and final state effects were necessary to identify the cluster geometry from the photoemission data. In contrast with this, we find that excellent agreement between the calculated electronic structure and the

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UPS data is obtained when *atomic relaxation* within the charged cluster is properly taken into account. Our results also indicate that electronic relaxation following the photoemission process has a negligible influence on the observed valence spectra from the clusters.

Recently, photoelectron spectra for three- and four-atom silicon clusters were interpreted [12] with some success, assuming complete atomic relaxation to the neutral cluster configuration. We find, however, that, in general, this is not true, and it is only for these very small clusters that atomic relaxation has a negligible impact on the photoelectronic spectrum.

The electronic spectra of the Si_n^-, $4 \leq n \leq 7$, clusters were investigated at finite temperatures via *ab initio* Langevin molecular dynamics simulations. The computational method and the cluster geometries employed in this study have been described in detail elsewhere [13]. The calculations have been performed within the local-density-functional (LDF) framework using the pseudopotential supercell approach. The Si pseudopotential was generated following the prescriptions by Troullier and Martins for soft pseudopotentials [14]. We have used a plane-wave basis with an energy cutoff of 10 Ry, and carried out the simulations in a face-centered cubic supercell with an edge $a = 36$ a.u. With these parameters, a convergence of ~ 0.03 eV was obtained on the relative position of the valence electronic levels of the clusters [15].

Only the Γ point is used for reciprocal space sampling, as is appropriate for a cluster calculation. To simulate charged clusters, we exploited the Gaussian broadening technique [13,16] with an electronic level broadening width of $\sim kT$, T being the nominal temperature of the simulation. We note that our calculated spectra are relatively insensitive to the value of the broadening parameter. Increasing the latter by a factor of 3 had no bearing on our results. The simulations were performed using a Langevin friction parameter $\gamma = 5 \times 10^{-4}$ a.u., as in previous studies [13,17]. The equations of motion were integrated with the algorithm described in Ref. [18], and using a time step of $\sim 7 \times 10^{-15}$ s (~ 300 a.u.).

In Fig. 1 we present the calculated electronic density of states for the highest occupied orbitals of Si_4^-, Si_5^-, Si_6^-, and Si_7^- clusters at $T = 500$ K (left) and at $T = 1500$ K (center) together with the UPS data by Cheshnovsky *et al.* [5] (right). The clusters in the experiment were in a supersonic beam, and their temperature was not known. For each cluster, we chose the zero of the energy scale in the density of states plots so as to align the dominant theoretical and experimental features. The calculated spectra were generated in the constant matrix approximation, and using an average of the density of states [19] over a 3 ps isothermal simulation. We do not expect transition cross sections to modify qualitatively the spectra, since the electronic levels involved here mostly derive from the same type of silicon atomic $3p$ states. The runs for sampling the electronic structures were performed after having slowly heated the lowest-energy isomers obtained from the *ab initio* calculations [10,13].

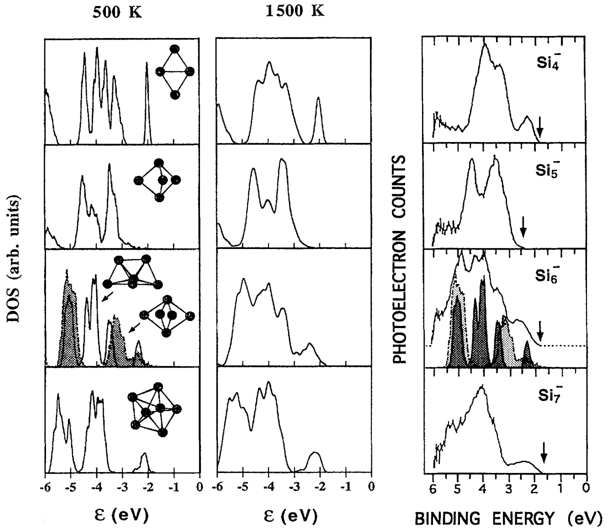

FIG. 1. Calculated density of states for the Si_n^-, $n = 4$ to 7 clusters as obtained from Langevin simulations at $T = 500$ K (left-hand side panel) and $T = 1500$ K (central panel). The spectrum indicated by the dashed curve and shaded area corresponds to the distorted octahedron isomer of Si_6^-. The experimental photoelectron data by Cheshnovsky *et al.* [5] are shown on the right-hand side panel. The calculated spectra for the bicapped tetrahedron (dark shaded area and solid line) and distorted octahedron (light shaded area and dashed line) isomers of Si_6^- have been reported in the right-hand side panel for comparison with experiment.

The theoretical atomic structures corresponding to the calculated spectra have also been sketched in Fig. 1 and are the planar rhombus, trigonal bipyramid, and pentagonal bipyramid for Si_4^-, Si_5^-, and Si_7^-, respectively. Si_6^- has two competing low-energy isomers: a distorted octahedron and a bicapped tetrahedron. In our LDF calculations we find the bicapped tetrahedron slightly lower in energy (by 0.02–0.03 eV/atom) than the distorted octahedron, while Hartree-Fock calculations [10] including correlations at the MP4 order seem to favor the distorted octahedron. In Fig. 1, we reported the spectra for both isomers at 500 K. At 1500 K, only the bicapped tetrahedron remained stable in the simulations, and a single spectrum was obtained.

If one excludes the spectrum for the Si_6^- distorted octahedron (dot-dashed line in Fig. 1), detailed agreement in the relative position and intensity of calculated and measured spectral features is found for all of the remaining clusters. We note, in particular, the striking similarity between the theoretical and experimental structures near the onset of the density of states and the photoemission threshold (indicated by the vertical arrow). The results at $T = 500$ and 1500 K show that temperature does not induce important modifications in the position of the spectral features. The thermal broadening, however, is significant. We find linewidths which are ~ (3−6)kT, which reflects a relatively important coupling to vibrations. The outer valence molecular-orbital levels probed in Fig. 1 critically depend on the cluster structure, and provide us with a sensitive tool for atomic structure identification.

As can be seen from Fig. 1, the spectra for the two isomers of Si_6^- differ substantially from each other. The density of states for the distorted octahedron (dot-dashed line) is characterized by three main features, with a large separation between the two dominant peaks ($\Delta\epsilon >$ 1.5 eV), and a relatively small separation (~0.5 eV) of the third feature at higher energy. The spectrum for the bicapped tetrahedron (solid line) exhibits, instead, four main features, with a larger separation (~1 eV) between the two topmost features, and a separation of only 0.5–1 eV for the others. Comparison with the experimental photoemission results reveals that the theoretical spectrum for the bicapped tetrahedron is consistent with the experiment, while the calculation for the distorted octahedron does not reproduce the experimental data. We conclude that the bicapped tetrahedron is the stable isomer of Si_6^- in the experiment. This is in contrast with the case of neutral clusters, for which Raman investigations showed [4] the distorted octahedron to be the stable isomer.

For the magic number clusters (Si_n with $n = 4$, 6, and 7), the experimental spectra of the charged species exhibit a small peak near the photoemission threshold. This peak, corresponding to the first photodetached level, was assigned [5] to the LUMO of Si_n, singly occupied in Si_n^-, and the following larger signal at higher energy to the many electrons of the HOMO. The energy difference between these peaks yielded HOMO-LUMO gaps of 1–1.5 eV for Si_4, Si_6, and Si_7, and a small or vanishing gap for Si_5. Except for Si_4, the existing calculated LDF gaps [11] were in substantial disagreement with the measured gaps, the theoretical gaps being larger. In the case of Si_5, in particular, a gap of ~2 eV had been predicted [11], in strong contrast to the UPS data in Fig. 1. Here we find, instead, that the measured gap [5] compares quite well with the separation between the highest occupied levels of the *charged* clusters (~1 eV for Si_4^- and Si_6^-, and ~1.5 eV for Si_7^-).

To understand the origin of the earlier discrepancies on the HOMO-LUMO gap, we have investigated to what extent the relaxation associated with the extra electron in Si_n^- modifies the electronic structure. Except for Si_6, which has a quasidegenerate ground state, the type of structure formed by the small silicon clusters is known to remain unchanged with the additional charge, based on first-principles calculations [10]. The bond lengths and bond angles, however, were found to be somewhat modified [10,13] in the negatively charged state of the cluster. In Fig. 2, we show the highest occupied electronic levels of Si_5^-, Si_6^-, and Si_7^- ($T = 0$) calculated using the atomic geometry corresponding to the neutral cluster [Fig. 2(a)], and for the fully relaxed atomic structure of the charged clusters [Fig. 2(b)]. The spectra for Si_4^- were not displayed, since the atomic relaxation is negligible in this case (1%–2%).

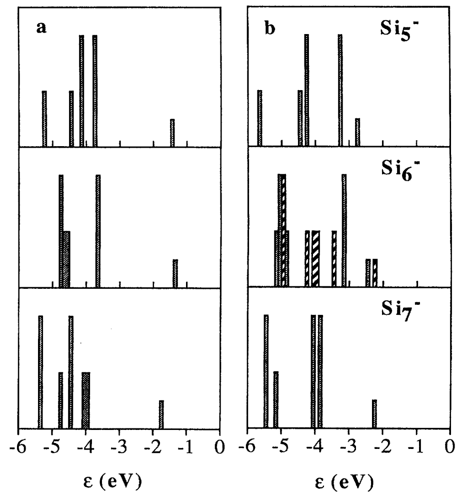

FIG. 2. Relative energy levels ($T = 0$) of the highest occupied orbitals of the Si_5^-, Si_6^-, and Si_7^- clusters calculated with the atomic geometry of the neutral cluster (a), and for the fully relaxed atomic structure of the charged cluster (b). For Si_6^-, the solid bars correspond to the distorted octahedron isomer, and the dashed bars to the bicapped tetrahedron isomer.

For Si_5^- the largest relaxation in bond angle or bond length is ~12%. As can be seen from Fig. 2, this relaxation drastically modifies the electronic spectrum. The gap between the highest occupied levels decreases from ~2 to ~0.5 eV. Such a small value of the gap for the charged cluster explains the structure observed in the experimental spectrum near the photoemission threshold (Fig. 1). For Si_6^-, if one considers only the distorted octahedron structure, i.e., the stable isomer of Si_6, the largest relaxation occurring with the additional electron is a bond angle change of about 6%. This relaxation already significantly alters the electronic structure [solid vertical bars in Figs. 2(a) and 2(b)]. When the geometry is modified from the distorted octahedron to the bicapped tetrahedron, the electronic spectrum totally changes (dashed vertical bars). For Si_7^- the relaxation is relatively small; the largest changes in bond angle are 4%. This still induces noticeable displacements ($\Delta\epsilon \approx 0.5$ eV) in the electronic level structure.

The substantial change that atomic relaxation induces on the electronic spectra of the charged clusters explains the discrepancies observed in earlier studies [5,9]. We emphasize that it is the *atomic* relaxation, as opposed to the *electronic* relaxation, which leads to the drastic modification in the electronic spectra. The relative positions of the electronic levels in Fig. 2 show only weak deviations when the electronic occupation is changed *without* *relaxing* the geometry. In fact, it is because the electronic relaxation is small that good agreement can be obtained between the photoelectron spectra and the computed LDF density of states. The photoelectron experiment of Fig. 1 probes the outer valence orbitals of the clusters. Similar to the atomic case, such valence excitations do not cause major changes in the separation between the electronic levels.

In conclusion, we find that photoelectron spectra can be exploited as a sensitive tool to probe the cluster atomic structures. By comparing theoretical and experimental spectra, we could identify the relevant isomers of small Si clusters at finite temperature in the cluster beam experiments. In the case of Si_6^- the spectra allowed us to distinguish between the two low-energy isomers, and identify the stable experimental structure. This approach appears as a promising tool which could help elucidate the structure of other puzzles in present cluster physics, such as Si_{13}^+, which has an anomalously low chemical reactivity, and a very controversial structure [20].

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