

Photoelectron spectra of aluminum cluster anions: Temperature effects and *ab initio* simulations

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Photoelectron (PES) spectra from aluminum cluster anions, Al_n^- ($12 \leq n \leq 15$), at various temperature regimes, were studied using *ab initio* molecular dynamics simulations and experimentally. The calculated PES spectra, obtained via shifting of the simulated electronic densities of states by the self-consistently determined values of the asymptotic exchange-correlation potential, agree well with the measured ones, allowing reliable structural assignments and theoretical estimation of the clusters' temperatures. [S0163-1829(99)51640-8]

Photoelectron spectroscopy (PES) is a rich source of information pertaining to the electronic structure and excitation spectra of atoms, molecules, and condensed phases. Materials clusters exhibit a high sensitivity of the electronic spectrum to the geometrical structure, which often differs from that of the bulk, and show a high propensity to form structural isomers that may dynamically interconvert at finite temperatures. Consequently, high-resolution PES emerges as an important tool in cluster science, particularly in the face of severe difficulties in applying common direct structure-determination techniques to such systems.

However, a reliable interpretation of PES spectra is often theoretically challenging due to several factors, including finite-state effects, electronic and ionic relaxations, thermal ionic motions, and structural isomerizations. With the advent of accurate *ab initio* methods for electronic structure calculations, theoretical investigations of some of these issues have been pursued.¹⁻³ Particularly pertinent to our study is the development of methods which allow practical and reliable simulations of PES spectra including dynamical (finite-temperature) effects.^{2-4(a)}

In this paper, we address, via the use of *ab initio* Born-Oppenheimer local-spin-density molecular dynamics (BO-LSD-MD) simulations,^{4(a)} methodological issues pertaining to simulations and analysis of finite-temperature PES spectra. We performed accurate (and practical) calculations of PES spectra from recorded density of states of the clusters using a "generalized Koopmans' theorem" (GKT),⁵ concurrent with simulations of the ionic dynamics. Furthermore, in conjunction with measured⁶ high-resolution PES spectra for Al_n^- ($12 \leq n \leq 15$) cluster anions, we illustrate that the simulated spectra provide a (quantitatively) faithful description of the measured ones, including thermal effects, thus allowing reliable assignments of ground as well as isomeric structures. Additionally, we demonstrate that through comparisons between simulated PES spectra and those measured in three

(experimentally undetermined) temperature regimes, estimates of the clusters' temperatures can be obtained.

In the BO-LSD-MD method, the motions of the ions evolve in time according to classical equations of motion, with the electronic Hellmann-Feynman forces evaluated at each MD time step via a self-consistent solution of the Kohn-Sham (KS) equations, using the LSD exchange-correlations after Ref. 7, and in conjunction with nonlocal norm-conserving pseudopotentials.⁸ An important element of the method, distinguishing it from those used previously in PES studies,^{2,3} is the fact that it does not employ supercells (periodic replicas of the system), and consequently charged systems as well as those having permanent and/or dynamically developed multipole moments, are simulated accurately in a straightforward manner on equal footing with neutral ones (i.e., alleviating the need for an artificial neutralizing background, large calculational cells, and/or approximate treatment of long-range multipole image interactions).

The ground state structures of Al_{12}^- - Al_{15}^- , determined by us through structural optimization starting from those of the corresponding neutral clusters,^{4(b)} are displayed in Fig. 1. Aluminum clusters in this size range favor energetically icosahedral-based structures,⁹ Al_{12}^- having an oblate deformed shape, that of Al_{13}^- being close to an ideal icosahedron, and those of Al_{14}^- and Al_{15}^- being capped icosahedra. For Al_{15}^- , we find that in the energy-optimal structure, the two capping atoms are located on the opposite sides of a "core" icosahedron, resulting in a strongly deformed prolate shape (see Fig. 1).¹⁰

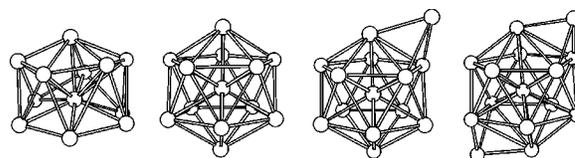


FIG. 1. The ground state geometries of Al_{12}^- - Al_{15}^- (left to right).

TABLE I. Number of valence electrons (N) in the cluster anions, HOMO-LUMO gap (E_g), vertical detachment energy (vDE) of 0-K ground state anion, and numerically determined asymptotic exchange-correlation shift (v_{xc}^∞). Energies in eV.

	N	E_g	vDE	v_{xc}^∞
Al_{12}^-	37	0.25	2.82	1.63
Al_{13}^-	40	1.89	3.59	1.64
Al_{14}^-	43	0.32	2.67	1.57
Al_{15}^-	46	0.79	3.07	1.57

The electronic structure of the ground state cluster anions exhibits sizable gaps (E_g) between the highest-occupied KS molecular orbitals (HOMO) and the lowest unoccupied ones (LUMO), as well as odd-even alternation (as a function of the number of electrons) in the vertical detachment energy (vDE) shown in Table I. Al_{13}^- is electronically “magic” (i.e., 40 valence electrons), having an exceptionally high vDE,⁶ and the largest E_g . Its electronic structure reflects the corresponding neutral cluster, which was found^{4(b)} to exhibit a clear jellium-type filling sequence $1s^2 1p^6 1d^{10} 2s^2$ for the lowest 20 single-particle states. The remaining 20 states, which would correspond to jellium $1f^{14} 2p^6$ states, are grouped into two broadly overlapping subbands (finite temperature broadening of these bands is displayed in Fig. 2) and show significant pf mixing; this level scheme is known to be a consequence of the I_h icosahedral symmetry.

Although the KS states are not necessarily the “true” molecular orbitals of the system, it has been observed that the KS HOMO eigenvalue of the N -electron system, $\epsilon_{\text{HOMO}}(N)$, bears a well-defined relation to the ionization potential $I(N)$ and electron affinity $A(N)$ ^{11,5} through Janak’s theorem.¹² Following these ideas, we make use here of a “generalized Koopmans’ theorem” (GKT).^{5,13}

$$\epsilon_{\text{HOMO}}(N) - v_{xc}^\infty = -I_{\text{GKT}}(N), \quad (1)$$

where v_{xc}^∞ is the asymptotic limit of the exchange-correlation potential. This nonvanishing energy shift is required for an accurate description of the asymptotic KS equations.⁵ While rigorously, the vertical detachment energy would be given by $E(N-1) - E(N)$, where $E(N)$ and $E(N-1)$ are, respectively, the total energies of the anion and neutral (unrelaxed) clusters, Eq. (1) suggests a practical approach for evaluation of the threshold region of finite-temperature PES spectra through MD simulations. Accordingly, neglecting hole-relaxation effects, the vDE for removing the electron from the HOMO state may be well estimated by $(-\epsilon_{\text{HOMO}} + v_{xc}^\infty)$, provided that v_{xc}^∞ remains constant to a good approximation, regardless of spatial details of the N -electron system (such as isomeric atomic configurations of the cluster). To explore the validity of this condition, we have calculated for each of the cluster anions the energy shift $v_{xc}^\infty = E(N-1) - E(N) + \epsilon_{\text{HOMO}}(N)$, for a selected set of structures (including the ground state structure and ten other configurations chosen randomly from finite-temperature MD trajectories). The calculated values of v_{xc}^∞ were found to have a spread of no more than 0.04 eV for each of the clusters, and furthermore, we found that the dependence of v_{xc}^∞ on N ($37 \leq N \leq 46$) is very weak (see Table I).

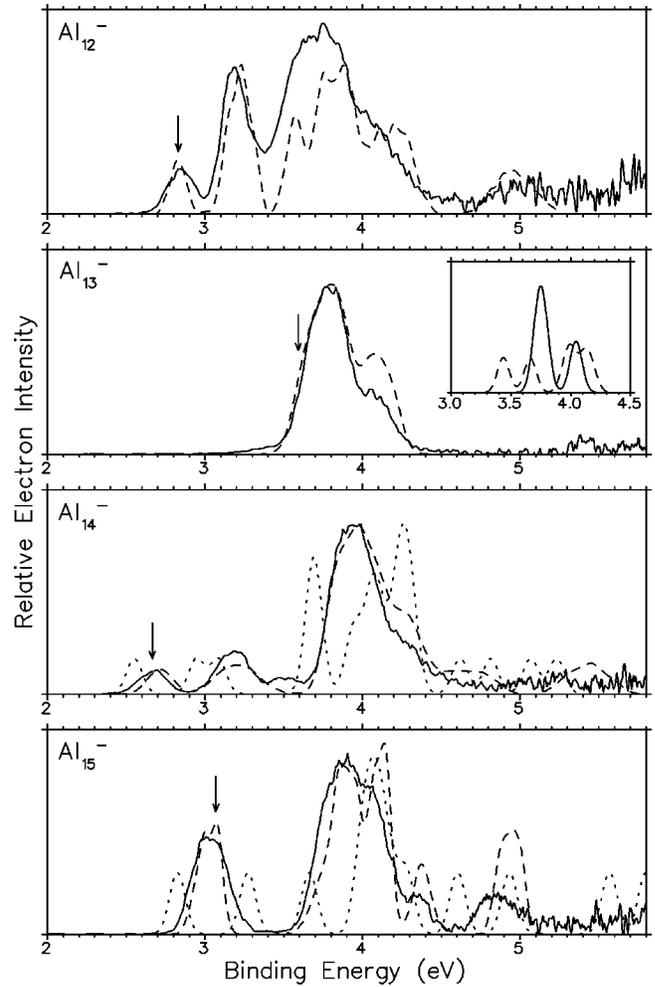


FIG. 2. Measured photoelectron spectra of cold (long residence time) Al_{12}^- - Al_{15}^- at 193 nm (solid lines) compared to the simulated spectra (dashed lines). The simulation temperatures are 160, 260, 200, and 130 K for Al_{12}^- - Al_{15}^- , respectively. The arrows correspond to the vDE of the ground state structure at 0 K, given in Table I. The inset shows the 0-K PES spectra for the ground state (solid line) and the decahedral isomer (dashed line) of Al_{13}^- . The dotted line for Al_{14}^- is the 0-K spectrum of the decahedral isomer, and that for Al_{15}^- is the 0-K spectrum of an icosahedral-based isomer (see text).

While this procedure could be repeated to determine v_{xc}^∞ values for vDE’s from deeper (lower-energy) KS states, we have chosen to use a simpler (and more practical) procedure, whereby we also use the shift calculated for the HOMO level for the deeper states.¹⁴ In this way, we generate the full PES spectra from the density of states (DOS) recorded in the course of the BO-LSD-MD simulations.¹⁵ As shown below, this theoretically founded procedure yields a faithful description of the experimental data, and it is a viable and reliable alternative to previously used methods for finite-temperature *ab initio* MD simulations of PES spectra which were based on either ad hoc shifts (aligning the theoretical DOS with the dominant features in the measured spectra)² or on a first-order perturbative treatment.^{3(b)} Furthermore, the comparative analysis of the simulated PES spectra and the measured ones (see below) validates a posteriori certain general assumptions underlying MD simulations of PES spectra, i.e., neglect of finite-lifetime effects of the hole (see also Ref. 2 where it is

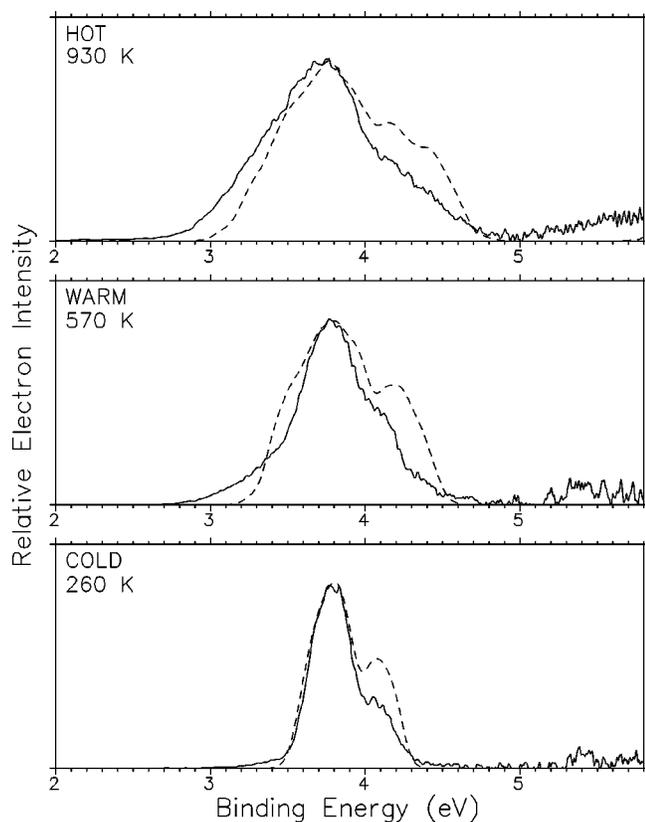


FIG. 3. Measured temperature-dependent PES spectra of Al_{13}^- (solid lines) compared to the simulated ones at 930, 570, and 260 K (dashed lines). Hot: short residence time; warm: medium residence time; cold: long residence time.

noted that such effects may contribute only for very small clusters); the use of vDEs (i.e., neglect of ionic relaxations following the detachment process); and, assumed equal weights for all states contributing to the PES spectrum (i.e., neglect of photoelectron transition-matrix effects, which may affect line-shape features and certainly the absolute PE cross sections, but not the locations of spectral features, i.e., binding energies).

The measured PES spectra for Al_{12}^- - Al_{15}^- are shown in Figs. 2 and 3 (solid line). It is found that clusters leaving the nozzle early (short residence time) are quite “hot” whereas clusters leaving the nozzle late (long residence time) are “colder.” Indeed, the PES spectra for the cold clusters shown in Fig. 2 and the bottom panel of Fig. 3 exhibit well-defined features. On the other hand, hot clusters exhibit much broader and diffused spectral features, as shown in Fig. 3 for Al_{13}^- , where we display spectra measured for three different residence times, labeled as “cold,” “warm,” and “hot.” Comparisons between the locations (binding energies) of the peaks and shoulders in the measured and simulated spectra for the cold clusters (simulation temperatures of 130 K to 260 K, see caption to Fig. 2) validate the V_{xc}^∞ -shifting procedure of the calculated DOS described above. The widths of the peaks in the theoretical PES spectra originate solely from atomic thermal vibrations, since at these low temperatures isomerization effects and/or strong shape fluctuations do not occur. The good agreement achieved here, without any adjustable parameters other than the ionic temperature in the MD simulations, strongly indi-

cates that the “cold” clusters in the experiments are indeed well below room temperature.

Theoretical PES spectra corresponding to isomeric structures of Al_{13}^- - Al_{15}^- , calculated at 0 K, are also shown in Fig. 2 (see inset for the threshold regions of Al_{13}^- , and the dotted line in the panels for Al_{14}^- and Al_{15}^-). The isomers for Al_{13}^- and Al_{14}^- are the aforementioned decahedral ones,⁹ and in the Al_{15}^- isomer, two neighboring triangular facets are capped. Comparison between these spectra and those calculated for the ground state clusters as well as with the measured ones, suggests overall that at low temperatures either these isomers do not occur, or that their abundance in the cluster beam is rather low. In this context, we note that starting from the decahedral isomer of Al_{13}^- , it transformed readily during short MD simulations into the icosahedral one at about room temperature. This supports our conclusion pertaining to the low abundance in the cold beam of clusters “trapped” in isomeric structures; however, an even small relative (quenched) concentration of such isomer in the cold Al_{13}^- beam may be sufficient to account for the low-binding energy tail observed in the measured PES spectra for Al_{13}^- (see inset in Fig. 2).

Both the experimental and theoretical PES spectra, shown in Fig. 3 for Al_{13}^- , which were measured at the three temperature regimes mentioned above and simulated at the indicated temperatures, exhibit gradual broadening and “smearing” of the PES spectral features as the temperature increases. We also observe that the binding energy of the main peak is rather insensitive to the thermal conditions, while the line shape near the threshold region (lower binding energies) exhibits a rather pronounced temperature dependence.

The broadening of the spectral features and the (so-called) “thermal tail effect” near threshold originate from the variations of the electronic structure caused by enhanced vibrational motions at the higher temperatures, as well as from increased isomerization rates (e.g., in the “warm” regime) governed by the free energy of the cluster (that is enhanced contributions of lower frequency modes to the vibrational entropy),¹⁶ and from disordering (“melting”) of the cluster in the “hot” regime (where inspection of the atomic trajectories reveals frequent transitions between a broad assortment of configurations). Indeed, examination of the vibrational DOS of the simulated clusters (obtained via Fourier transformation of the atomic velocity autocorrelation functions) revealed a marked gradual softening of the clusters at the “warm” and “hot” regimes (that is shifting of the vibrational spectrum to lower frequencies) coupled with increasing overlap between the frequency regions of the various modes due to large anharmonicities.

In light of the above, we judge the overall agreement between the simulated and measured spectra and their thermal evolution as rather satisfactory, and the remaining discrepancies (mainly in line shapes) may be attributed to insufficient sampling during the 5-ps MD simulations of the thermally expanded phase space of the clusters.

The methodology developed in this study for practical calculations of finite-temperature PES spectra, through *ab initio* MD simulations of aluminum cluster anions with no adjustable parameters other than the clusters’ temperatures,

was demonstrated to yield results in agreement with high-resolution PES spectra measured at various thermal conditions of the cluster beam. Such comparative analysis allows reliable structural assignments and theoretical estimation of the clusters' temperatures, as well as gaining insights into the electronic and structural properties of clusters and their thermal evolution.

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part on an IBM RISC 6000/SP2 at the GIT Center for Computational Materials Science. Work in the University of Jyväskylä was supported by the Academy of Finland, and at Georgia Tech by the US DOE. The experimental work was supported by the NSF and performed at EMSL, a DOE user facility located at PNNL, which is operated for DOE by Battelle Memorial Institute. L.S.W. acknowledges support from the Alfred P. Sloan Foundation. J.A. wishes to thank the Väisälä Foundation for support.

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- ¹⁰The pattern of shape deformations for all the cluster anions shown in Fig. 1 correlates well with that obtained via jellium calculations for clusters with the number of electrons corresponding to that in this size range (37 to 46 electrons). For a review, see C. Yannouleas and U. Landman, in *Large Clusters of Atoms and Molecules*, edited by T. P. Martin (Kluwer, Dordrecht, 1996), p. 131.
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- ¹⁴Restricted (spherical) jellium calculations [$r_s(\text{Al}) = 2.07 a_0$] for a 40-electron system (Al_{13}^-), where electrons are removed from deeper levels (with a "frozen-orbital" approximation), show that the v_{xc}^∞ shifts for these deeper levels are approximately constant to within 0.2 eV [M. Manninen (unpublished)].
- ¹⁵Microcanonical MD simulations were performed at various temperatures around and below room temperature, and Al_{13}^- was also simulated at 570 and 930 K. A 5-fs time step was used in integration of the classical equations of motion, and the DOS data was recorded in 5-ps simulations (after equilibrating the system at the desired temperature for about 2 ps). The DOS spectra were smoothed by replacing every data point by a 0.05-eV FWHM Gaussian. These spectra were then shifted by the v_{xc}^∞ values given in Table I for each cluster anion. This gives the absolute binding energy scale on which the calculated spectra are plotted in Figs. 2 and 3. The height of the calculated spectra are scaled to the main peak of the experimental spectra in Al_{13}^- to Al_{15}^- and to the second peak in the case of Al_{12}^- .
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