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

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Photoelectron (PES) spectra from aluminum cluster anions, $\text{Al}_{12}^-$ ($12 \leq n \leq 15$), 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.

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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 \cite{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 \cite{2-4a}.

In this paper we address, via the use of ab-initio BO-LSD-MD (Born-Oppenheimer local-spin-density molecular dynamics) simulations \cite{4a}, 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) \cite{5}, concurrent with simulations of the ionic dynamics. Furthermore, in conjunction with measured \cite{6} high-resolution PES spectra for $\text{Al}_{12}^-$ ($12 \leq n \leq 15$) 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. \cite{7}, and in conjunction with non-local norm-conserving pseudopotentials \cite{8}. An important element of the method, distinguishing it from those used previously in PES studies \cite{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 $\text{Al}_{12}^- - \text{Al}_{15}^-$, determined by us through structural optimization starting from those of the corresponding neutral clusters \cite{4b}, are displayed in Figure 1. Aluminum clusters in this size range favor energetically icosahedral-based structures \cite{9}; $\text{Al}_{12}^-$ having an oblate deformed shape, that of $\text{Al}_{13}^-$ being close to an ideal icosahedron, and those of $\text{Al}_{14}^-$ and $\text{Al}_{15}^-$ being capped icosahedra. For $\text{Al}_{15}^-$ 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) \cite{10}.

The electronic structure of the ground state cluster anions exhibits sizable gaps (E\textsubscript{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. $\text{Al}_{13}^- is
electronically “magic” (i.e. 40 valence electrons), having
an exceptionally high vDE [6] and the largest $E_g$. Its ele-
tronic structure reflects the corresponding neutral clus-
ter, which was found [4b] to exhibit a clear jellium-type
filling sequence $1s^21p^61d^{10}2s^2$ 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 Figure 2) and
show significant $p$-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”
orbital molecular orbitals of the system, it has been observed
that the KS HOMO eigenvalue of the $N$-electron sys-
tem, $\epsilon_{HOMO}(N)$, bears a well-defined relation to the ion-
ization 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]

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

where $v_{xc}^\infty$ is the asymptotic limit of the exchange-
recommand potential. This vanishing energy shift is required for an accurate description of the asymptotic
KS equations [5]. While rigorously the vertical detach-
ment 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) sug-
ests a practical approach for evaluation of the threshold
region of finite-temperature PES spectra through MD
simulations. Accordingly, neglecting hole-relaxation ef-
fects, the vDE for removing the electron from the HOMO
state may be well estimated by ($\epsilon_{HOMO}$)

$$v_{xc} = \epsilon_{HOMO}(N) - E(N),$$

where $v_{xc}$ remains constant to a good approxima-
tion, regardless of spatial details of the $N$-electron sys-
tem (such as isomeric atomic configurations of the clus-
ter). To explore the validity of this condition we have
calculated for each of the clusters arising the energy shift
$v_{xc} = E(N - 1) - E(N) + \epsilon_{HOMO}(N)$ for a selected set of
structures (including the ground state one and 10 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 de-
pendence of $v_{xc}$ on $N$ (37 $\leq N$ $\leq$ 46) is very weak (see
Table I).

While this procedure could be repeated to deter-
mine $v_{xc}$ values for vDEs from deeper (lower-energy) KS
states, we have chosen to use a simpler (and more prac-
tical) procedure whereby we use the shift calculated for
the HOMO level also 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 experi-
mental 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 [3b]. 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 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.
bounding energies).

The measured PES spectra for $\text{Al}_{13}$−$\text{Al}_{15}$ are shown
in Figures 2 and 3 (solid line). It is found that clus-
ters 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 Figure 3 for $\text{Al}_{15}$, where we display
spectra measured for three different residence times, la-
beled as “cold”, “warm”, and “hot”. Comparisons be-
tween 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 tem-
peratures isomerization effects and/or strong shape fluc-
tuations 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 $\text{Al}_{15}$−$\text{Al}_{15}$, calculated at 0 K, are also shown
in Fig. 2 (see inset for the threshold regions of $\text{Al}_{15}$, and
the dotted line in the panels for $\text{Al}_{14}$ and $\text{Al}_{15}$). The
isomers for $\text{Al}_{13}$ and $\text{Al}_{14}$ are the aforementioned deca-
chedral ones [9], and in the $\text{Al}_{15}$ 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 $\text{Al}_{15}$, it transformed readily during short MD
simulations into the icosahedral one at about room tem-
perature. 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\textsubscript{13}\textsuperscript{−} beam may be sufficient to account for the low-binding energy tail observed in the measured PES spectra for Al\textsubscript{13}\textsuperscript{−} (see inset in Fig. 2).

Both the experimental and theoretical PES spectra, shown in Figure 3 for Al\textsubscript{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.

Computation were performed mainly on Cray T3E at the Center for Scientific Computing, Espoo, Finland, and in part on an IBM RISC 6000/SP2 at the GIT Center for Computational Materials Science. Work in the University of Jyväskylä is supported by the Academy of Finland, and at Georgia Tech by the US DOE. The experimental work is 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.

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

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>E\textsubscript{g}</th>
<th>vDE</th>
<th>v\textsubscript{∞\textsuperscript{xc}}</th>
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<td>1.89</td>
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<td>1.57</td>
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<tr>
<td>Al\textsubscript{15}</td>
<td>46</td>
<td>0.79</td>
<td>3.07</td>
<td>1.57</td>
</tr>
</tbody>
</table>
FIG. 1. The ground state geometries of $\text{Al}_{15}^- - \text{Al}_{15}^-$ (left to right).

FIG. 2. Measured photoelectron spectra of cold (long residence time) $\text{Al}_{15}^- - \text{Al}_{15}^+$ at 193 nm (solid lines) compared to the simulated spectra (dashed lines). The simulation temperatures are 160, 260, 200, and 130 K for $\text{Al}_{15}^- - \text{Al}_{15}^+$, 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 $\text{Al}_{15}^-$. The dotted line for $\text{Al}_{14}^-$ is the 0 K spectrum of the decahedral isomer, and that for $\text{Al}_{15}^-$ is the 0 K spectrum of an icosahedral-based isomer (see text).

FIG. 3. Measured temperature-dependent PES spectra of $\text{Al}_{15}^-$ (solid lines) compared to the simulated ones at 930 K, 570 K and 260 K (dashed lines). HOT - short residence time, WARM - medium residence time, COLD - long residence time.

[6] X. Li et al., Phys. Rev Lett. 81, 1909 (1998). The experimental setup described in this paper is the same as that used in the current study, where in addition, here PES spectra were measured also at various temperature regimes (see discussion in connection with Figs. 2 and 3).
[8] N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993 (1991). For the aluminum 3$s^23p^1$ valence electrons, we use s-nonlocal and $p$-local components with cut-off radii of 2.1 and 2.5 $a_0$, respectively. The KS orbitals are expanded in a plane wave basis with a cutoff of 15.4 Ry.
[9] In Ref. [4b] it has been noted that a truncated decahedral motif, obtained from the icosahedron by a $\pi/5$ rotation of the two opposing capped pentagons with respect to each other, is energetically close to the icosahedral geometry of $\text{Al}_{13}^- - \text{Al}_{15}^-$. On the other hand, fcc-based cuboctahedral structure are much higher in energy in this size range. For other recent ab-initio studies of aluminum clusters in this size range, see references in [4b].
[10] The 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", T. P. Martin, Ed. (Kluwer, Dordrecht, 1996), p. 131.
[13] Koopmans’ theorem, $\epsilon_{\text{HOMO}}(N) = -I(N)$, originally proposed in the context of the Hartree-Fock method, provides often a reasonable estimate for $I$ (within the method), and is in a wide use in quantum chemistry.
[14] Restricted (spherical) jellium calculations ($\epsilon_{c}(\text{Al})=2.07 a_0$ for a 40 electron system (Al$_{15}$), where electrons are removed from deeper levels (with a “frozen-orbital” approximation), show that the $\epsilon_{c}$ shifts for these deeper levels are approximately constant to within 0.2 eV [M. Manninen, unpublished].
[15] Microcanonical MD simulations were performed at various temperatures around and below room temperature, and Al$_{15}$ was also simulated at 570 K 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 $\epsilon_{c}$ values given in Table I for each cluster anion. This gives the absolute binding energy scale on which the calculated spectra are plotted in Figures 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$_{14}$. 