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Ionization of aluminum clusters

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ABSTRACT

Near-threshold photoionization cross sections for several aluminum clusters have been estimated from the ionization efficiency curves. Their magnitude raises the possibility that the edge of a collective electron resonance (surface plasmon) may contribute to the photoemission channel. On the other hand, electron impact ionization efficiently produces multiply charged metal cluster ions and is unaccompanied by noticeable fragmentation. Consequently it does not appear to involve collective excitations.

1. Introduction

Studies of the size-dependent properties of nanoclusters rely on mass spectrometry, and if the clusters are electrically neutral then the mass spectrometer must be preceded by an ionization stage. Therefore insights into the ionization process are important for interpreting cluster formation, abundances, and stabilities.

We present data on the ionization of cold clusters of aluminum. This material lies at the boundary between a free electron-like metal and a more complicated band structure, is technologically important and chemically reactive, and displays behavior ranging from high reflectance to superconductivity. The corresponding properties of free aluminum nanoclusters have been extensively explored, for example see Refs. [1–7].

Their ionization energies also have been determined[8], but the photoionization cross sections have been deduced[9] only for cluster sizes up to $n = 8$. In fact, most measurements of absolute light absorption cross sections of free metal nanoclusters are performed in the vicinity of their giant dipole plasma resonances[10,11]. Aluminum metal has a high bulk plasma frequency ($\hbar\omega_p \approx 15$ eV[12]) and the dipole resonance frequency ω_r is correspondingly high ($\hbar\omega_r = \hbar\omega_p/3^{1/2} \approx 8.7$ eV). This is difficult to access by conventional light sources, and lies significantly above the cluster ionization energy (which is approximately 4.7 eV–5.3 eV for the size range discussed here [8]). Here we provide cross section estimates for several larger clusters at an energy less than an eV above their ionization thresholds by using their photoionization saturation curves (Section 3).

Electron impact ionization is another common technique in cluster beams mass spectrometry. In Section 4 we contrast the evolution of ion abundances under laser ionization with increasing fluence and electron impact ionization with increasing energy.

2. Experiment

We briefly outline the experimental approach [6,13–15]. Neutral Al_n clusters are produced by a magnetron sputtering/gas condensation source[16–18]. A specially designed thermalizing tube at the end of the cluster aggregation chamber allows the particle temperature to be set to a value in the range from 65 K to 215 K. In this experiment temperatures of 90 K and 140 K were used.

In the photoionization mode, clusters exiting the thermalizing tube pass through a skimmer into the extraction region of a collinear Wiley-McLaren time-of-flight mass spectrometer, where they are ionized by 5 ns pulses from a Nd-YAG/OPO laser system, tuned to 220 nm for this experiment. The laser beam is collimated to a 2×2 mm^2 profile 10 cm prior to entering the mass spectrometer's ionization region, and its pulse energy is monitored immediately after crossing this region. The intensity is adjusted by using a continuously variable neutral density filter.

At the end of a 1.5 m-long flight path the extracted cluster ions are detected by a pulse-mode channeltron multiplier equipped with a high voltage conversion dynode, which is important for efficient detection of heavy ions.

In the electron ionization mode, the cluster beam enters the axial ionizer of an Extrel MAX-9000 quadrupole mass spectrometer positioned 1.4 m downstream from the skimmer. At the exit of the quadrupole the cluster ions are again detected by a channeltron with a high-voltage conversion dynode.

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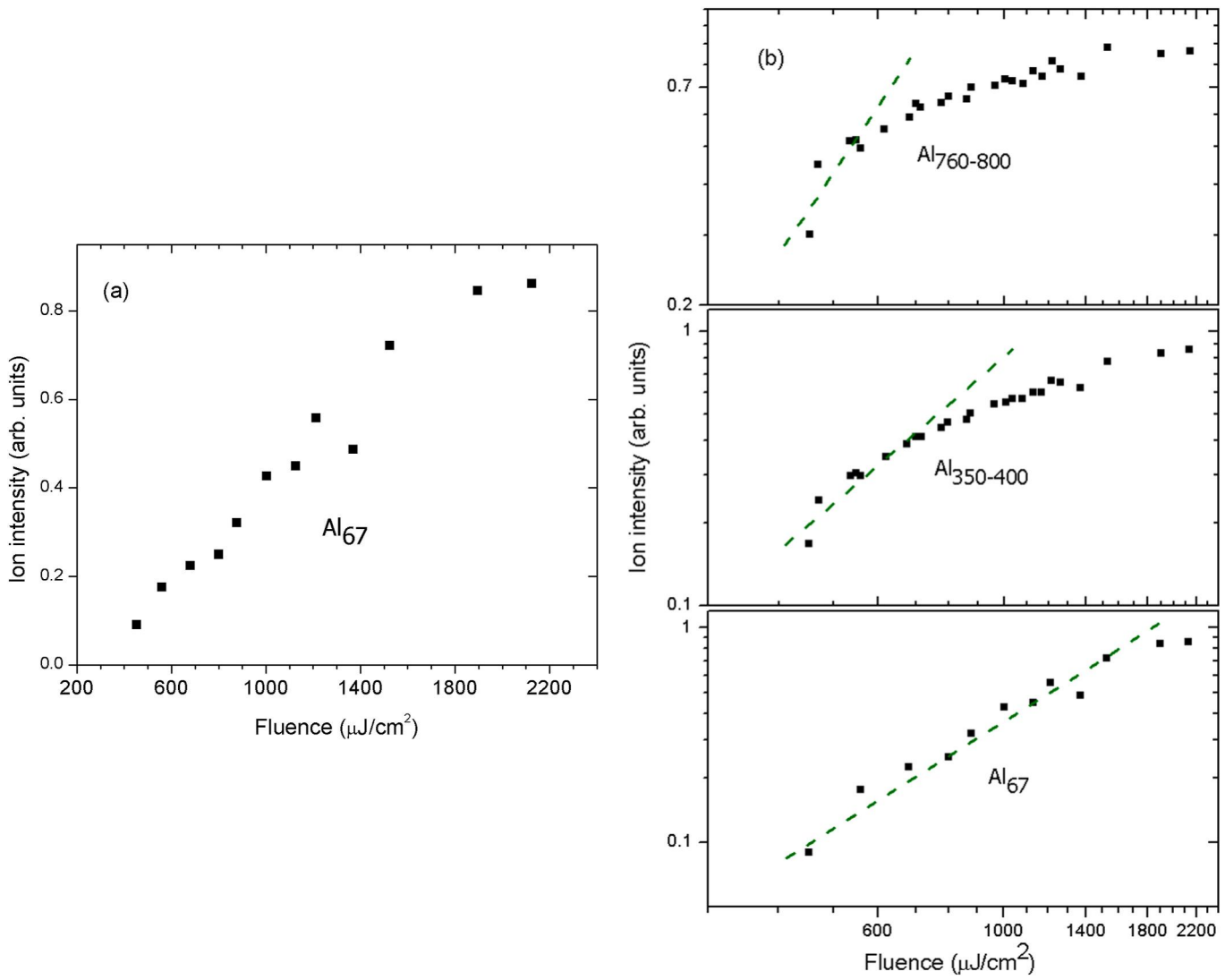

Fig. 1. Intensities of cluster ions in the time-of-flight mass spectra as a function of the ionizing laser fluence, (a) linear scale, (b) log-log scale. For the top two panels, intensities were summed over the indicated mass ranges. Deviations of the data points from dashed straight lines identify the onset of the saturation regime and allow to estimate the photoionization cross section.

3. Photoionization

Fig. 1(a) shows the photoion yield of a cluster as a function of laser fluence F (energy per pulse per unit area). A plateauing of the yield curve is evident. The shape is similar to that observed in UV photoionization measurements on both small [9,19,20] and large [21] clusters, where it was interpreted as saturation of single-photon ionization. The normalized saturation curve has the form

$$S = 1 - \exp(-\sigma F) \tag{1}$$

where σ is the photoionization cross section.

By plotting S on a log-log scale, Fig. 1(b), we can identify the location of the knee in the curve as the point $\sigma F \approx 1$, which allows us to estimate the cross section values for clusters Al_n: 6 Å^2 for $n = 67$, 13 Å^2 for $n =$ 350–400, and 17 Å^2 for $n =$ 760–800. In the latter two cases, cluster intensities were summed over the indicated mass ranges. Based on the reproducibility of the saturation curve and the lack of precise information on the intensity distribution in the laser beam profile, these values are estimated to be valid within a factor of ~2.

It is interesting to note that the magnitude of these cross sections is comparable to the wing of the Mie (plasmonic) photoabsorption resonance of aluminum nanoparticles at this wavelength[22]. [23] This suggests an interaction between collective electron oscillations in the nanoparticle and the photoelectron exit channel. Signatures of such an interaction have been seen in data on alkali clusters[24–26], where the corresponding energy ranges lie closer together, and in synchrotron radiation inner-shell photoelectron spectra of aluminum clusters[27].

4. Fragmentation and electron impact ionization

At higher laser fluences, multiphoton absorption leads to extensive cluster heating, accompanied by the onset of evaporation cascades[28]. As shown in Fig. 2, this is evidenced by the strong migration toward smaller cluster sizes in the abundance mass spectra.

Using Poisson statistics for sequential photon absorption and approximating the total photoabsorption cross section by the values given in Section 2, we can estimate that clusters shown in the inset of the bottom panel of Fig. 2 have absorbed between ~10 and 30 photons.

A similar amount of total energy can be carried by electrons in an electron-impact ionizer. Therefore is it instructive to examine the evolution of the ion abundance spectra, originating from exactly the same cluster beam, as a function of electron energy. This is shown in Fig. 3. Interestingly, increasing the impact energy raises the ion counts and strongly stimulates the production of multiply charged clusters, but is

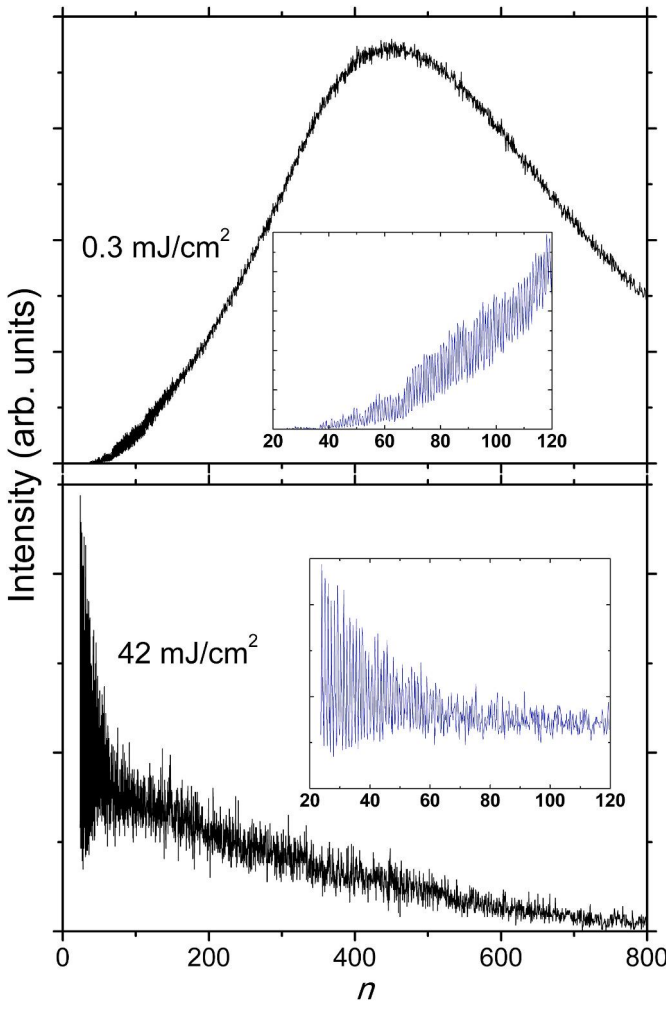

Fig. 2. Time-of-flight mass spectra of singly ionized Al_n clusters for two ionization laser fluences. The insets show an expanded view of the lower mass range. The shift to smaller sizes provides evidence for extensive fragmentation at high laser intensities.

not accompanied by a shift toward lower masses that would signify fragmentation. The absence of significant fragmentation in the course of electron ionization coincides with observations on other metal clusters [13] and contrasts with the behavior of molecular clusters, such as water [29], where the fragmentation is significant.

This implies that the incoming electron does not deposit significant residual energy in the cluster. Therefore, although fast electrons can efficiently excite plasma oscillation in metal clusters and nanoparticles [30–32], here single and multiple electron-impact ionization likely proceeds via a direct "knock-out" channel.

Indeed, the energy required to remove an electron from a metal cluster of charge $+z$ and radius R_n is[33].

$$I_n^z \approx I_n^{z-1} + \frac{e^2}{R_n} \tag{2}$$

For the size range in Fig. 3, $I_n^0 = 5.1$ eV–5.2 eV and $R_n \approx 6.5$ Å (based on the electron density of aluminum). Therefore producing a doubly and a triply ionized aluminum cluster ion from a neutral one requires a sum total energy transfer of ≈12 eV and ≈22 eV, respectively. Ionization proceeding via collective electron excitations would imply the creation and coherent channeling of a minimum of two or three surface plasmon quanta, a low-probability process.

Thus whereas collective electron resonance absorption may contribute to photoelectron emission as discussed in the preceding section, that does not appear to be the case for electron-impact ionization. On the whole, although electron – metal cluster scattering[34] and attachment[35] processes have been explored, there hasn't yet appeared a general rigorous and quantitative treatment of electron-induced ionization and multi-ionization of clusters. In view of both fundamental and applied value of understanding these processes, it is hoped that such work will be forthcoming.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

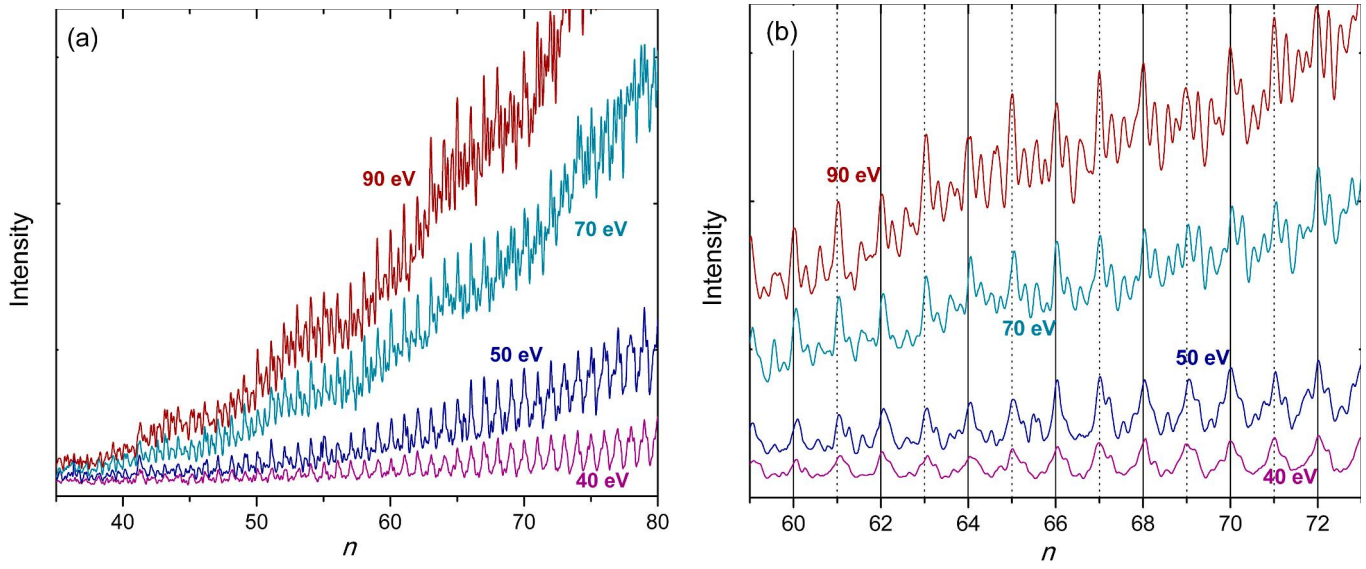

Fig. 3. Mass spectra of Al_n cluster ions from the same beam as previous figures, obtained using a quadrupole mass spectrometer at different electron impact energies. Peaks at seemingly fractional values of n derive from multiply-charged cations. No noticeable shift to lower masses, denoting fragmentation, is observed, but the yield of multiply-charged cations increases with the ionizer energy. This is exhibited in panel (b) which focuses on a smaller size range.

Data availability

Data will be made available on request.

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