Size-Dependent Electron-Impact Detachment of Internally Cold C_n^- and Al_n^- Clusters

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The cross sections for electron detachment of internally cold C_n^- and Al_n^- clusters were measured using an electrostatic ion beam trap fitted with an internal electron target. The measured electron-impact detachment cross sections for the C_n^- ($n = 1$–9) clusters exhibit even-odd oscillations reflecting the binding energy trend, namely, higher cross sections for weaker binding. Surprisingly, however, these cross sections increase on the average with cluster size, n, in spite of the increase in electron binding. In contrast, the Al_n^- ($n = 2$–5) clusters follow the known scaling laws for electron detachment. We suggest that the size-dependent polarizability of these clusters is responsible for the observed behavior.

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Atomic clusters are aggregates of a few and up to many thousands of atoms that show properties intermediate between those of molecules and bulk matter. From a fundamental point of view, they provide us with relatively simple model systems for studying dynamic behavior when many but still finite degrees of freedom are involved. Many properties, such as optical, electronic, and magnetic, change dramatically with cluster size, i.e., the number of atoms in the cluster [1]. A systematic investigation of the cluster properties or of their response to external perturbations enables us to discover size-dependent scaling laws. Several systematic cluster properties have been established, the most famous one being the connection between the electronic structure (shell model) and the intensities in mass spectra [2]. Other properties such as the size dependence of the melting point or the optical response have also been studied for specific cases [3,4]. Systematic studies of the external perturbation of clusters were conducted also, such as collision induced fragmentation [5] or ionization [6] of large clusters.

In the present work, we investigated the size dependence of the electron detachment process of negatively charged clusters. Electron-impact detachment is a process that has been extensively studied for atoms and small molecules [7–15]. Because of the high degree of electron correlation in the negative systems, these experiments are sensitive to the electronic structure. It has been shown that, for these simple species, the electron binding energy E_b is the most important parameter in the determination of both the threshold behavior and the magnitude of the cross section above threshold, and a simple scaling law has been obtained [8,12,13]. Among the different theoretical methods leading to this simple scaling law, two can be singled out: The first is a classical phenomenological derivation, where the detachment cross section is estimated to be the cross section for a classical electron moving in a "reaction zone" [13]. The second method is based on the distorted-wave Born approximation [12]. Interestingly, these classical and quantum mechanical methods lead to the same scaling law for electron energies larger than the binding energy, except for some rescaling of the cross sections (with differences smaller than 15% for electron binding energies larger than 1.5 eV). Explicitly, the cross section is inversely proportional to the square of the binding energy of the least bound electron. This scaling law has been quite successful in reproducing existing experimental data for negative ions of small molecules [8,13,15]. Most of the modern experiments related to electron-impact detachment have been carried out using heavy ion storage rings, in which ions can be stored for a time that is long enough for relaxation of internal excitations (electronic and nuclear), so that measurements can be made on species in a well-defined internal state [13]. However, due to the limited magnetic rigidity of these rings, it is difficult to extend systematic size-dependent studies of electron-anion collisions to very large clusters.

In the following, we describe an experiment performed with the combination of a recently developed electrostatic linear ion beam trap [16,17] and an electrostatic electron target [18,19] that allows studies of electron-impact processes for fully relaxed ions of any mass. The results demonstrate that, although the binding energy is indeed an important parameter, a size-dependent effect appears, yielding an overall trend in the impact detachment cross section *opposite* to the common scaling law with binding energy, and we suggest that the change in cluster polarizability is responsible for this surprising behavior. The experiments were performed with carbon (C_n^-, $1 \leq n \leq 9$) and aluminum (Al_n^-, $1 < n \leq 5$) clusters. These clusters were chosen because they differ dramatically in their structure: linear chain for the former [20,21] and compact planar geometry for the latter [22].

The ion beam trap [16,17] allows trapping of keV ion beams between two electrostatic mirrors. The concept and stability criteria of the trap have already been dis-

cussed [23], and only the details relevant to the present experiment are presented here. Since the region between the two innermost mirror electrodes is field-free, it is possible to introduce an electron beam, perpendicular to the ion beam (see Fig. 1). A completely electrostatic design for the electron target was chosen, avoiding the presence of magnetic fields that would perturb the ion trajectories. The cross section of the electron beam in the interaction region is rectangular, about 7.5 by 50 mm, and the interaction occurs in a nearly field-free region between grounded electrodes of the electron target. The ion beam intersecting the center of the electron beam is much smaller, with a diameter of about 3 mm. This electrostatic arrangement guarantees a constant form factor at a fixed electron and ion energies for all cluster masses. The electron beam ($5 \leq E_e \leq 30$ eV), typically, 42 μA at 20 eV, has an energy spread of about 0.1 eV. More details about the experimental setup can be found in Refs. [18,19].

Since the trap is electrostatic, there is no limit to the mass which can be stored. Moreover, since trapping is sensitive only to the beam energy (for a given ionic charge), no tuning is necessary when changing ion species, and the ion trajectories are identical, thus allowing for high precision relative measurements. The clusters were produced in a standard sputter ion source; for aluminum clusters larger than Al_5^- the current was too weak (< 1 nA) for the experiment. The ions are accelerated to an energy of 4.2 keV, chopped by an electrostatic chopper, mass selected by a 90° magnet, and injected into the trap by switching the voltages of the entrance electrodes (left-hand side in Fig. 1) [17]. The ions then oscillate between the two mirrors, with a lifetime of the order of 500 ms at a residual pressure of $\sim 2 \times 10^{-11}$ Torr. A cooling time of 100 ms following the injection was used in order to allow for electronic and vibrational relaxation of the clusters. This relaxation could be monitored through the nonexponential decay of the number of ions (for C_n^-) [24] and by the fact that the measured cross sections at short times were time dependent (for Al_n^-). All measurements performed after this initial delay were found to be time independent. The data were acquired during 650 ms, after which the cycle repeated.

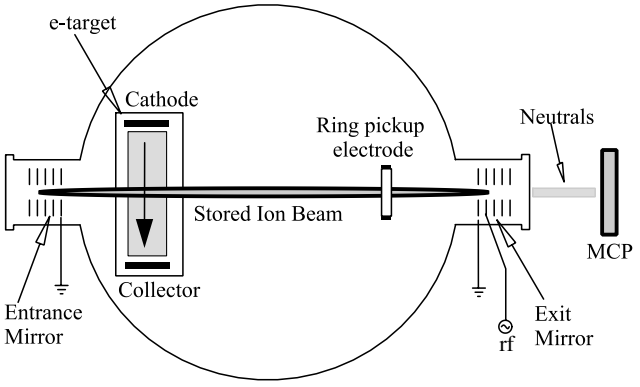

FIG. 1. Schematic view of the experimental setup. The diameter of the chamber is 451 mm.

The relative detachment cross section was determined as a function of the electron energy by measuring the rate of neutral particles exiting the trap using a microchannel plate (MCP) detector located downstream (see Fig. 1). These neutral particles are produced by both an electron-impact detachment (signal) and by stripping collisions with the residual gas (background). In order to subtract the background from the signal, the electron beam was modulated at a rate of 20 Hz (10 ms "on" and 40 ms "off"). The respective rates R_{on} and R_{off} were recorded by two multiscalers synchronized with the electron beam modulation. The clock gating the electron beam was not synchronized with the trapping cycle so that all trapping times were probed equally. The ratio of the rate of neutrals produced by electron impact to those produced by collisions with residual gas atoms is given by

$$F \equiv \frac{R_{\mathrm{on}} - R_{\mathrm{off}}}{R_{\mathrm{off}}} = \frac{\sigma_e I_e}{\sigma_b n_b f_e v_i}, \tag{1}$$

where σ_e and σ_b are the cross sections for neutralization by collisions with the electron beam and the residual gas, respectively, n_b is the target density of the residual gas, f_e is the electron-ion form factor, v_i is the velocity of the ions, and I_e is the current of the electron beam. Equation (1) allows the determination of σ_e relative to σ_b, but note that the latter is also size dependent [25]. Thus, Eq. (1) is insufficient for a systematic relative electron-impact cross section measurement, and an additional normalization procedure that relates directly R_{off} to the number of trapped particles N_t is needed. For a bunched beam, a signal proportional to N_t can be obtained by measuring the charge induced on a pickup electrode (Fig. 1). Bunching was achieved by applying an rf voltage, whose frequency is equal to the natural oscillation frequency of the clusters in the trap, to one of the trap electrodes (see Fig. 1) [26]. The amplitude of the fast Fourier transform (FFT) at the rf frequency, S_{FFT}, is proportional to N_t [19,26]. Both R_{off} and S_{FFT} were measured simultaneously for a given period of the trapping time, and their ratio was calculated:

$$\beta \equiv \frac{|S_{\mathrm{FFT}}|}{R_{\mathrm{off}}} = \frac{C}{\sigma_b n_b v_i}, \tag{2}$$

where C is a constant that depends on the trap parameters (physical and electrical) and the pickup geometry [19]. Finally, dividing Eq. (2) by Eq. (1), we obtain the relative electron-impact detachment cross section:

$$\sigma_e = \frac{C f_e}{I_e} \frac{F}{\beta}, \tag{3}$$

which is independent of both the residual gas charge

stripping cross section σ_b and the density of the residual gas n_b, hence eliminating the effect of pressure fluctuations. The bunching normalization measurement was repeated every ten injections during the duration of the experiment. More details about this procedure can be found in Ref. [19].

The electron-impact detachment cross section was measured for each cluster in the range $5 \leq E_e \leq 30$ eV, but only results at $E_e = 20$ eV are presented here. The conclusions are not sensitive to the value of E_e, and similar trends are observed as long as $E_e \gg E_b$. This choice avoids the effect of the resonances caused by doubly negative states near threshold [27,28]. The lack of structure in the energy scans around 20 eV verified that such resonances play no role in the results presented here. The results are shown in Figs. 2(a) and 2(b) as a function of the number of atoms in the clusters for carbon and aluminum. All data sets are normalized to the measured absolute cross section of C_2^- (merged beam technique, heavy ion storage ring) [28]. Also shown are the absolute cross sections previously measured for C (crossed beam technique, no trapping) [29] and C_4^- (merged beam technique, heavy ion storage ring) [30]. The insets in Figs. 2(a) and 2(b) show the corresponding electron binding energies for the negative carbon [20] and aluminum clusters [22].

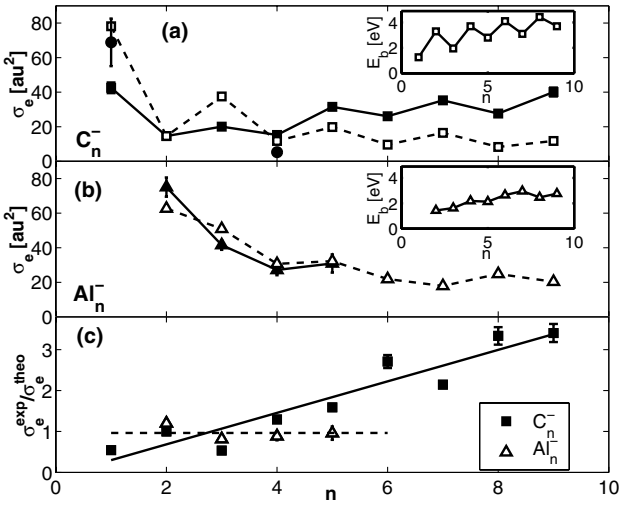

FIG. 2. Measured cross sections σ_e at $E_e = 20$ eV as a function of the number of atoms n for (a) C_n^- (solid squares connected by a line) and (b) Al_n^- (solid triangles connected by a line). Also shown are the calculated cross sections for C_n^- (open squares connected by a dashed line) and Al_n^- (open triangles connected by a dashed line) using the theory of Andersen *et al.* [13,15]. Data and theory are normalized to the absolute cross section of C_n^- [28]. The filled circles (a) are the measured absolute cross sections for C [29] (interpolated to 20 eV) and C_4^- [30]. Insets: electron binding energy for (a) carbon and (b) aluminum clusters as a function of n [20,22]. (c) Ratio between the experimental and theoretical cross sections for C_n^- (squares) and Al_n^- (open triangles) at $E_e = 20$ eV as a function of n. The theoretical cross sections σ_e^{theo} were computed using the functional dependence on the electron binding energy, as suggested by Andersen *et al.* [13,15]. The lines are drawn to guide the eye.

We first concentrate on the carbon cluster results. The most important feature is related to the conflicting dependence of the electron detachment cross section for the C_n^- clusters on their binding energies. On one hand, the odd-even oscillations in the cross section follow nicely the expectation that a stronger binding energy of the electron should result in a smaller cross section (a $1/E_b^2$ scaling is predicted theoretically based on either classical [8,13] or quantum mechanical [12] arguments). On the other hand, the overall average increase in the cross section as a function of n is in contradiction with the argument above, as the binding energy increases as well. Thus, the carbon cluster data show one trend and its opposite at the same time. Direct comparison of the results with the theoretical model developed by Andersen *et al.* [13,15] (also normalized to C_2^-) shows clearly the discrepancy [see Fig. 2(a)]. Explicitly, the general trend for the experimental cross sections is an increase with n, while the trend for the theoretical cross sections is a decrease with n. The same result is obtained if Robicheaux's scaling law [12] is used instead, and for $n > 4$ the two theoretical models coincide.

The results for the aluminum clusters, in contrast to the carbon clusters, are in good agreement with the model predictions in the range where measurements were possible, and the overall trend seems to follow the expected scaling laws, i.e., a decreasing cross section for higher electron binding energies [see the inset of Fig. 2(b)]. To further probe the difference between the carbon and aluminum, we have divided our measured cross sections by the theoretical values predicted using the model of Andersen *et al.* [13,15], thus removing the predicted dependence on the binding energy. The results are shown in Fig. 2(c) where it can be seen that the theory-normalized data of the aluminum clusters seem to be size independent (in the measured range), i.e., roughly agreeing with the $1/E_b^2$ scaling law. The theory-normalized carbon data, in contrast, still show a strongly increasing dependence on n (a factor of about 7 when changing n from 1 to 9), though the odd-even oscillations are effectively removed by the division. Hence, the odd-even dependence of the detachment cross section apparently reflects the change in binding energy, in accordance with the $1/E_b^2$ scaling law. In contrast, the surprising increase of the detachment cross section for C_n^- clusters with n, clearly revealed in Fig. 2(c) and occurring even though the binding energy of the electron increases, seems to indicate an additional size-dependent effect not included in the scaling law. Normalizing the theoretical predictions of Esaulov or Robicheaux [8,12] leads to the same result.

Why does the electron detachment cross section increase with cluster size for carbon and not for aluminum? It is important to note that the electron detachment process depends predominantly on the characteristics of the weakly bound electron. Furthermore, removing that electron does not change the structure of the C_n^- and Al_n^- clusters (except minor bond length adjustments) [20–22]. Therefore, one would expect the detachment cross section to be indeed a function of the binding energy, a dependence which was already demonstrated and "removed" in Fig. 2(c). The next electronic property to consider is the cluster polarizability, as already discussed by Andersen [15], Pindzola [11], and Ostrovsky and Taulbjerg [9]. Several theoretical works have included a polarization potential in their calculations [9,11], but the contribution of the polarizability to the electron detachment process has never been studied systematically, mostly due to the lack of relevant data. To our knowledge, no calculations exist for the polarizability of the negative clusters studied in this work. However, it is well known that in the classical approximation the polarizability is proportional to the volume occupied by the electrons [31,32]. The carbon clusters have a linear structure (in their ground state) for $n < 10$ [20,21], so that the volume occupied by the electrons, hence the polarizability, increases strongly with n. A simple calculation based on the classical jellium model [31,32] shows that the polarizability increases by a factor of 8 when the number of atoms increases from 1 to 9. On the other hand, because of the compact planar structure of the aluminum clusters ($n \leq 5$) [22], the volume occupied by the weakly bound electron increases much slower than for the linear carbon clusters. Therefore, their polarizability does not change much with the increasing number of atoms in the range studied in this work. The present data suggest that an increase in polarizability leads to an increase in the electron detachment cross section. This can be understood directly from Robicheaux's argument [12] that electron detachment mainly occurs at the point of closest approach when the incoming electron has minimum kinetic energy. The attractive nature of the polarization potential will reduce the distance of closest approach, thus resulting in larger distortion of the initial wave function and enhanced electron detachment. Further theoretical work is needed to establish the complete scaling law that depends on both the binding energy and the polarizability.

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