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An inelastic threshold in electron - alkali cluster collisions

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Abstract. An analysis of integral cross sections for slow electron collisions with neutral sodium clusters and nanoparticles reveals that, in addition to an effective negative ion formation channel, there exists a strong inelastic threshold-type process which appears above a collision energy of 1-1.3 eV. We show that it can be plausibly associated with the onset of direct electron-induced cluster fragmentation. This result highlights the importance of understanding the dynamics of electron-vibrational energy transfer in nanoclusters, including the relative probability of direct *vs.* statistical energy transfer.

PACS. 36.40.-c Atomic and molecular clusters – 36.40.Qv Stability and fragmentation of clusters – 34.80.Ht Dissociation and dissociative attachment by electron impact

1 Introduction

Inelastic electron collisions with atoms, molecules, and solids have provided insight into the fundamental excitations and interactions of quantum systems since the days of the Franck-Hertz experiment [1]. In the last decade or so, such measurements have also begun to contribute information on the properties of atomic and molecular clusters, fullerenes, and helium nanodroplets (see, for example, [2–7] and references therein). For free metal clusters, there have appeared some experimental studies of electron-impact ionization and fragmentation [8–10] and of slow electron attachment [11–15]. A number of theoretical papers have explored various energy loss scenarios in electron-cluster scattering: ionization [16], excitation of particle-hole pairs [17], emission of radiation [18–20], and excitation of collective oscillations (surface and volume plasmons of various multipolarities) [21–24].

In addition to the purely *electronic* energy loss mechanisms treated in these calculations, there exists, of course, the important issue of *vibrational* excitations, including the possibility of direct and evaporative fragmentation. The high density of internal electronic and vibrational states in clusters makes the situation quite distinct from that of electron collisions with small molecules, which has been thoroughly studied. In fact, research on electron-cluster collisions offers a route towards better understanding of (1) electron dynamics in finite systems, and (2) the problem of electron-vibrational coupling in clusters and its evolution from the molecular towards the bulk limit. There is an interesting parallel here with research on carrier scattering dynamics in semiconductor nanostructures [25] and metal quantum dots [26].

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We have performed measurements of absolute cluster beam depletion cross sections resulting from low energy ($\approx$ 0-6 eV) electron scattering. In this paper we describe the appearance of an inelastic channel which rises to dominance above a threshold of ≈ 1 eV in sodium clusters of a wide range of sizes. Its behavior suggests that it may correspond to direct electron-impact fragmentation of the cluster.

2 Measurement and characterization of cross sections

A detailed description of our experimental procedure has been given in Refs. [11–13]. Inelastic electron-cluster interaction cross sections are derived from beam depletion measurements. A tightly collimated beam of neutral sodium clusters or nanoparticles is passed through the scattering region of a low-energy, high-current (50-200 μA) electron gun. Clusters which do not undergo an inelastic collision continue to the beam detector, where they are ionized by UV light from an arc lamp, filtered by a quadrupole mass spectrometer, and detected by an ion counter. On the other hand, both electron attachment and collisional fragmentation lead to cluster removal from the original beam, in the former case by deflection in the gun's magnetic field, and in the latter case by mechanical recoil. The resulting beam depletion, $\Delta n/n$, yields the effective interaction cross sections: $\sigma_{eff}(\langle E \rangle) = A(\Delta n/n)$, where A is determined by the intensities and geometries of the electron and cluster beams. The label "effective" designates that the measured cross section represents a convolution [27,28] of the "true" energy-dependent cross section $\sigma(E_0)$ with the normalized energy distribution function $I(E-E_0)$ of the electron

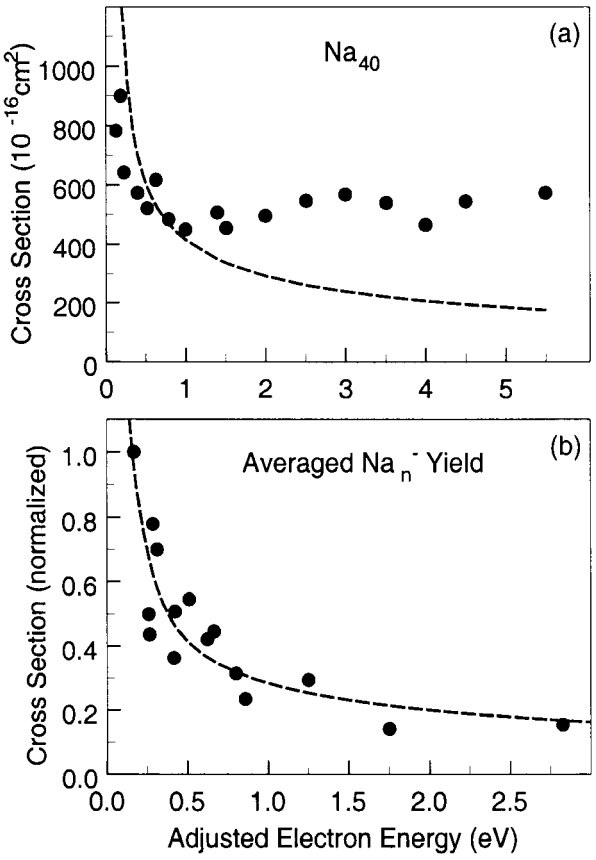

Fig. 1. (a) Total inelastic cross section of $e^- - Na_{40}$ interaction. Solid dots are the experimental data points obtained from the cluster beam depletion measurement. (b) Averaged Na_n anion yield. Solid dots correspond to a direct measurement of the absolute number of negative ions produced by the electron gun. In both panels, the dashed curve is the Langevin cross section for electron capture by a dipole polarization field, convoluted with the experimental energy resolution.

gun (a Gaussian profile with a width of 0.3-0.4 eV). The electron energy is likewise averaged over the distribution: $\langle E\rangle = \int_0^\infty E\, I(E-E_0)dE / \int_0^\infty I(E-E_0)dE$, where the nominal energy E_0 is calibrated to within 0.1 eV.

Interaction cross sections have been measured for small and medium clusters Na_n ($n = 20, 40, 57, 58, 70$), produced by a supersonic cluster source [11] as well as for $\approx$ 4 nm radius particles $Na_{n\approx 8000-9000}$ [12]. All data curves, while different in absolute values and detailed form, exhibited similar behavior in the 0-6 eV collision energy range. They displayed a steep rise for $E \to 0$ and flattened out for energies > 1 eV. An example is shown in Fig. 1(a) for Na_{40}.

The rise region has been identified as originating from efficient negative ion formation *via* attachment of the slow electrons. First of all, for all cluster sizes that we studied, the measured cross sections in the sub-eV region are in quantitative agreement with ones expected for electron capture by the strong polarization field of the cluster. (For the smaller clusters, this is the so-called Langevin capture cross section, $\sigma_L(E) = \sqrt{2\pi^2 e^2 \alpha / E}$, describing electron spiraling into the dipole field $V_{pol} = -\alpha e^2/(2r^4)$ of the polarized particle; α is the cluster polarizability [11,29]. This is illustrated in Fig. 1(a). For the large nanoscale particles, the full image-charge potential must be used, with the result that $\sigma_{capture} = \sigma_L + \pi R^2$, where R is the nanocluster radius [12].) Secondly, we confirmed this identification by direct monitoring of the total yield of negative clusters produced in the scattering region of our electron gun [13] which again yielded a curve precisely matching the aforementioned Langevin form, as shown in Fig. 1(b).

3 Additional inelastic channel

Two facts are apparent from the data. On one hand, Fig. 1(b) demonstrates that the polarization-capture mechanism remains active at least up to an energy of a few eV, smoothly decaying for increasing collision energies. On the other hand, Fig. 1(a) shows that in the region of 1-1.5 eV the experimental points begin to diverge from the capture cross section line. In other words, it is apparent that another inelastic mechanism starts contributing to cluster beam depletion.

This phenomenon is viewed most transparently if we subtract the electron attachment contribution from the full cross section data. The result is shown in Fig. 2(a) for $Na_{20,40,58}$, and in Fig. 2(b) for the $Na_{n\sim 10^4}$ particles. An evident threshold-like process is revealed, with an onset at $\langle E\rangle \approx$ 0.8-1.1 eV for Fig. 2(a) and $\langle E\rangle \approx 1.3$ eV for Fig. 2(b), as determined by a linear regression fit. Note that the large clusters in Fig. 2(b) display much larger cross sections, as expected, but the threshold is close. The precise size dependence of the threshold values is difficult to identify in view of the estimated 10-20% accuracy of the cross section data and the 0.1 eV calibration accuracy of the average electron beam energy.

What mechanism, appearing on top of electron attachment, could contribute to the cluster depletion process depicted in Fig. 2? Note, first of all, that an elastic collision of a few-eV electron with a heavy cluster or nanoparticle would not kinematically be able to deflect the latter away from the detector entrance within the 50 cm flight path. On the other hand, cluster fragmentation can, in principle, provide enough recoil to result in beam depletion.

Fragmentation processes can be roughly divided into direct and evaporative. The latter implies a statistical sharing of the excitation energy between all the vibrational degrees of freedom (cluster heating) followed by the evaporation of a small fragment (see, *e.g.*, [30,31] and references therein). In alkali cluster studies, such events follow, *e.g.*, the decay of optically-induced electronic collective resonance states, or plasmons [32]. It has been predicted that plasmon excitation, followed by evaporative decay, may lead to inelastic electron scattering resonances as well [22]; however, the excitation of a collective resonance requires a minimum energy transfer of $\sim$ 3 eV, which is above the thresholds seen in Fig. 2. Furthermore, it is rather improbable that large clusters (and especially

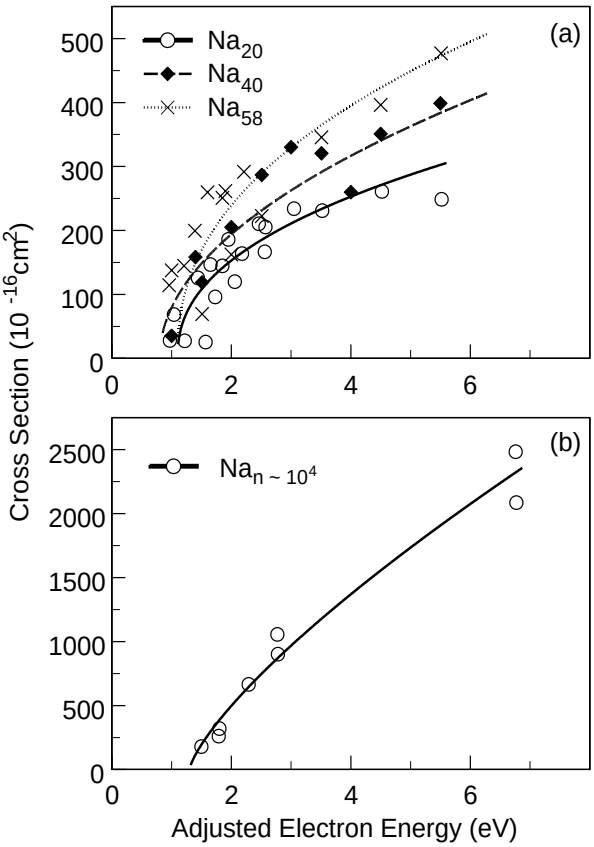

Fig. 2. The result of subtracting the electron attachment contribution from the total inelastic cross section data for (a) sodium clusters and (b) nanoparticles. The thresholds for this inelastic channel are very close to 1 eV for both size ranges. All the lines in the plots above are smoothing fits designed to guide the eye.

nanoparticles) can be heated by the slow electrons from an initial temperature of $\approx$ 400 K [12,33] to a temperature high enough to evaporate fragments which would be sufficiently fast for strong recoil.

Finally, there remains the possibility of a direct fragmentation process (the transfer of all or large part of the electron energy to a single atom or small fragment). For alkali clusters, such a low-energy collisional channel has not been studied in detail either theoretically or experimentally [34]. But it is, in fact, a realistic candidate for the data in Fig. 2. It is especially interesting that the observed thresholds are close to the Na_{20-100} cluster dissociation energies ($\approx$ 0.9-1 eV [35,36]) and to the heat of vaporization of bulk sodium (0.9 eV) [37]. A kinematic estimate shows that an electron within the displayed energy range can indeed knock out a small fragment with an energy sufficient to remove the recoiling (nano)cluster from the collimated beam.

Additional argument in favor of the direct fragmentation proposal comes from our recent data on electron scattering with C_{60} taken with the same electron gun and a similar data acquisition procedure [38]. A strong sub-eV electron attachment channel was again observed, but there was no sign of an over-1 eV threshold process: the inelastic cross sections continued to decay as the collision energy increased to several eV. (Similar results have been shown in [27,28,39].) This is completely consistent with the fact that C_{60} is a much stronger bound molecule that a sodium cluster: its dissociation energy exceeds 8 eV, and may be as high as 11 eV [40]. Hence no low-energy fragmentation channel is expected, and none is observed.

4 Summary

Our study of the depletion of neutral sodium cluster beams by low-energy electron bombardment revealed that in addition to electron capture by the cluster polarization field, a second strong inelastic channel appears above a threshold of approximately 1 eV. We demonstrated that it can be reasonably assigned to direct fragmentation of the particle by an incoming electron. Such processes have not yet been studied in detail, and we hope that this observation, together with earlier work on fragmentation accompanying electron-impact ionization, may draw attention to their prominence. It also highlights the challenging question of formulating criteria for the relative probability of direct *vs.* statistical energy transfer to cluster vibrations.

For the larger clusters, it may be realistic also to consider a process intermediate between purely direct and purely statistical fragmentation. In the field of ion-surface interactions, it is frequently the case that an incoming particle strikes the bulk surface and generates a local impact zone that becomes heated, melts, and evaporates. In the electron-cluster scattering case, it may be possible for the electron's kinetic energy to be transferred to a small group of atoms (instead of the entire cluster), causing one or more of them to evaporate. In the spirit of bridging the zone between clusters and nanoparticles on one hand and surfaces on the other, the dynamics of such a process and the critical size for its appearance represents an interesting problem.

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