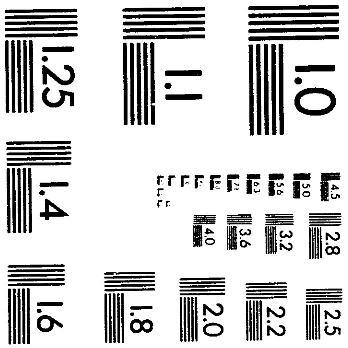
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LOW-ENERGY ELECTRON COLLISIONS WITH METAL CLUSTERS: ELECTRON CAPTURE AND CLUSTER FRAGMENTATION

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INTRODUCTION

Clusters are aggregates of a finite number of identical atoms or molecules, containing from a few to thousands of particles. They represent a form of matter intermediate between atoms and small molecules on one end and bulk solids and liquids on the other. Cluster research is motivated by the interest in mapping out the transition between the aforementioned limits, as well as by the fact that clusters possess a number of unique properties of their own [1]. In order to be able to monitor the atom-by-atom evolution of cluster properties, and to avoid their distortion by substrate effects, a large number of studies are performed on free clusters, making use of molecular beam techniques and mass spectrometry.

It is found that many properties of metal clusters are governed by the valence electron cloud [2-4]. This cloud is formed when the constituent atoms lose their weakly bound outer electrons which then become delocalized throughout the volume of the cluster. These delocalized electrons organize into quantized energy levels, giving rise to the shell structure of metal cluster spectra. The valence electron cloud determines such major cluster properties as shapes,

stabilities (including the appearance of "magic numbers" which mark enhanced abundances of certain cluster sizes and are associated with the closing of electronic shells), ionization potentials, electric and magnetic susceptibilities, and optical spectra. Correlated motion of the highly mobile valence electrons gives rise to a large electric polarizability of metal clusters, as well as to the appearance of intense dipole resonances [5]. As we shall see, these characteristics also manifest themselves in scattering processes involving clusters.

Electron scattering spectroscopy has a lot of potential as a tool for probing the evolution of cluster properties [6]. In particular, the cluster valence electrons can be expected to strongly react to an external electron beam. There is also practical need for understanding electron-cluster interactions which control such processes as cluster ion formation and electron-impact ionization. Unfortunately, the density of particles in a cluster beam is extremely low ($\sim 10^6$ cm^{-3}, or $\sim 10^{-10}$ torr), which makes electron scattering studies difficult. Earlier studies of collisions between electrons and metal clusters have been limited to ionization efficiency measurements [7,8]; absolute cross sections have been reported only for dimers [9,10].

We have carried out the first measurement of absolute electron-impact cross sections for free neutral metal clusters Na_n (n=8,9,20,40). Integral inelastic scattering cross sections were measured as a function of both cluster size and electron energy (E=0.1-30 eV). The cross sections are very large, reflecting the strong polarization force induced between an electron and a cluster. The data indicates that for collision energies below 1 eV electron capture is the principal process, while impact-induced fragmentation dominates at higher energies. This picture is in quantitative agreement with known cluster properties and provides a bridge between studies of electron scattering and cluster response.

In the following, we describe the experimental procedure and the data, and discuss the analysis of electron attachment and cluster fragmentation processes. The experiment and preliminary interpretation were originally described in Refs. [11,12].

EXPERIMENTAL METHOD

The experimental arrangement is shown in Fig. 1. A supersonic beam of neutral sodium clusters is generated in a seeded expansion using an oven source. At the end of the flight path, clusters are photoionized by a UV lamp, mass separated with the help of a quadrupole mass analyzer (QMA), and counted by a

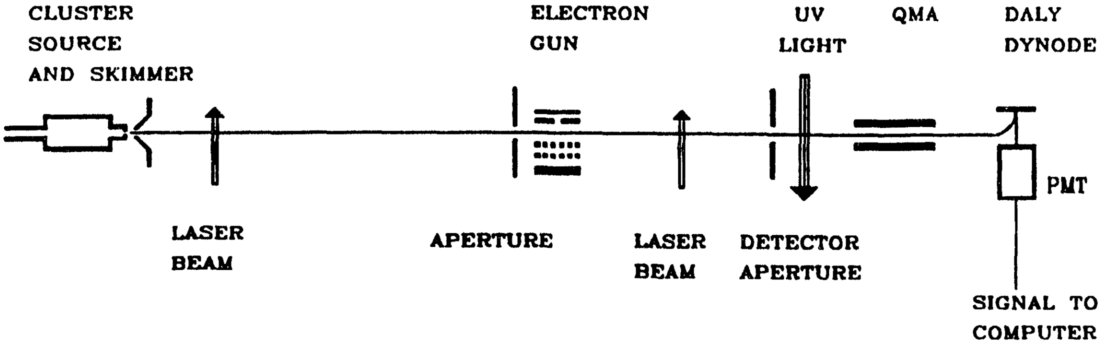

Figure 1. Outline of the depletion experiment. The beam of neutral clusters is intersected at a right angle by a pulsed electron beam. Inelastic collisions result in removal of clusters from the tightly collimated cluster beam.

Daly ion detector. Cluster velocities are measured by the laser-induced beam depletion technique [13].

The essential feature of the experiment is that we determine the scattering cross sections by measuring the electron-induced depletion of the cluster beam, rather than by detecting the scattered electrons. The latter would be impractical due to the tenuous nature of the cluster beam. The present approach is analogous to that used in photoabsorption spectroscopy of giant dipole resonances in clusters [14] and in measurements of elastic electron scattering by beams of atoms and alkali dimers [9].

The electron gun is mounted approximately halfway between the cluster source and the detector; the electron beam is perpendicular to the cluster beam. The electron gun is based on the design described in Ref. [15]. Electrons are emitted by an oxide-coated cathode, extracted by a series of grids and masks, and collide with the cluster beam inside a bounded equipotential region. To prevent dispersal of the electron beam, the gun assembly is placed in a uniform magnetic field (B=1400 gauss). Typical electron current densities in the interaction region were ≈1.2 mA/cm^2 at energies above 1 eV and <200 μA/cm^2 at energies below 0.5 eV. Energy resolution ranged from ≈0.25 eV at energies below 1 eV to ≈0.4 eV at higher energies. More details about the cluster beam apparatus and the electron gun are given in Refs. [11,16].

Following an inelastic collision, a cluster is removed from the tightly collimated beam, resulting in a decrease in the counting rate at the detector. In the experiment, the QMA is set to a chosen mass, and the counts with electron beam on/off are collected. This measurement yields the absolute electron-induced depletion cross section. It is important to note that in our experiment the kinematic conditions are such that cluster beam depletion can be caused only by inelastic scattering.

Typical counting rates for a particular cluster size were ≈30,000 per second, and the amount of depletion varied from ≈0.3% for Na_8 to ≈0.8% for Na_{40}, requiring data acquisition times of one to two hours for every data point.

RESULTS

Fig. 2 shows the integral inelastic scattering cross sections for spherical closed-shell clusters [2] with n=8, 20, and 40 valence electrons. To within the experimental accuracy, cross sections for the open-shell spheroidal cluster Na_9 were similar to those of Na_8. Dots represent individual measurements, and solid lines are fits to the data. The scatter reflects the aforementioned fact that the attainable depletion ratios are very small. Note that the cross sections are very large and increase with cluster size. As will be shown below, this behavior reflects the action of long-range forces.

The cross section curves display a rise at the low-energy end of the spectrum ($E \leq 1$ eV) and are essentially flat at higher energies. The latter point is confirmed by an expanded spectrum (Fig. 3) which shows that the cross sections of Na_{40} at electron energies of 10, 20 and 30 eV do not differ from those at lower energies. In the analysis which follows, we discuss the processes which determine these two regimes.

ANALYSIS

In general, several mechanisms can remove a neutral Na_n cluster from the beam in our experiment as a result of an inelastic collision: electron attachment (forming Na_n^-), electron-induced ionization (forming Na_n^+), or fragmentation. In the first two cases, the charged clusters will be swept out of the beam by the strong force of the electron gun's magnetic field. In the last case, recoil momentum of the fragments will result in depletion. Fragmentation may proceed either directly or via an intermediate stage, with sufficient excess energy deposited into the cluster. However, in order for direct fragmentation to take place, the amount of energy carried by the incident electron must exceed the cluster binding energies of the neutral clusters, which are ≈1 eV [17]. This criterion matches the location of the transition from the level part of the cross section curves to the rising part.

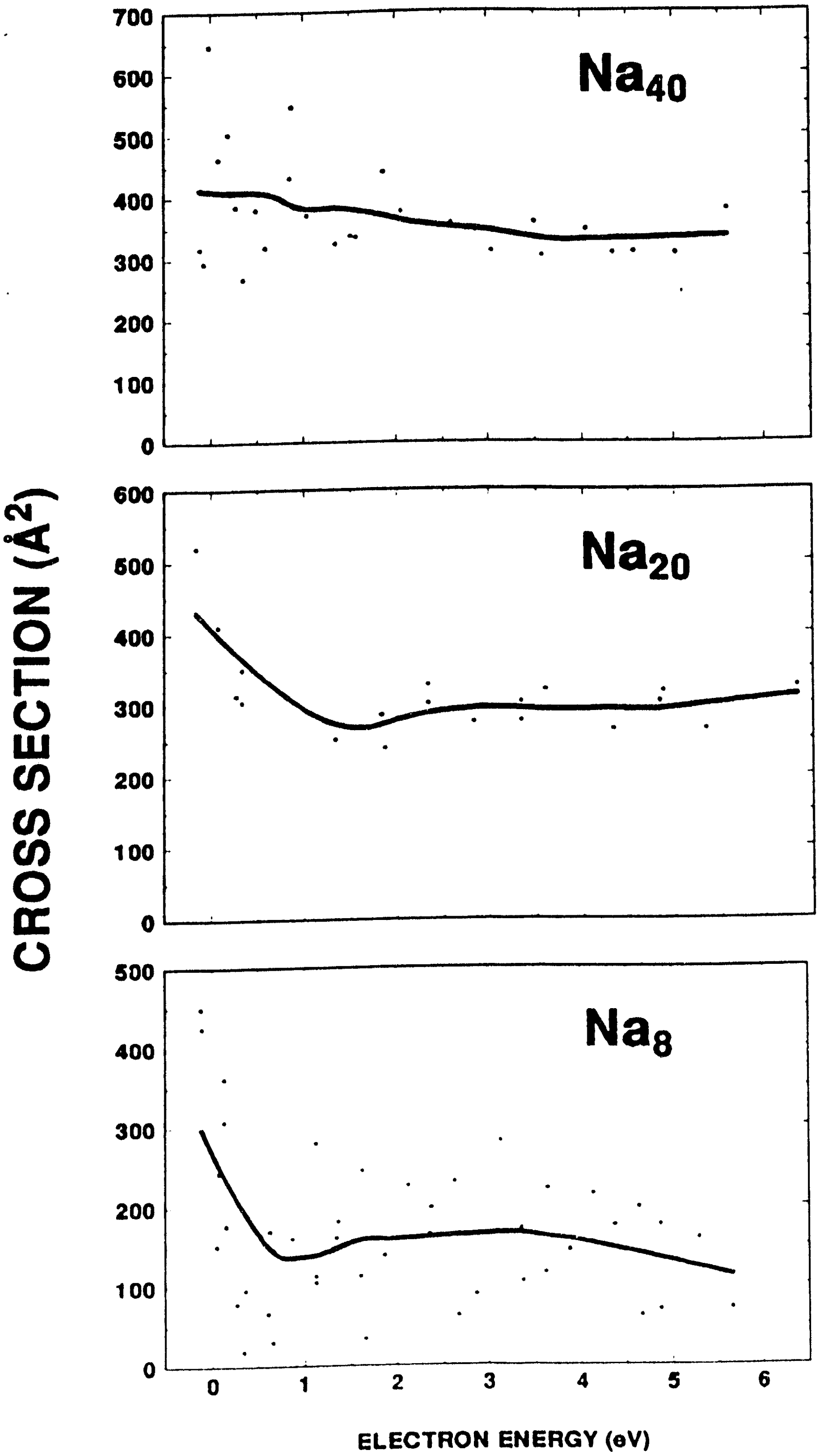

Figure 2. Absolute integral electron-impact depletion cross sections for three clusters with closed valence electron shells. Dots represent individual measurements, solid lines are least-square fits to the data. Note the large magnitude of the cross sections.

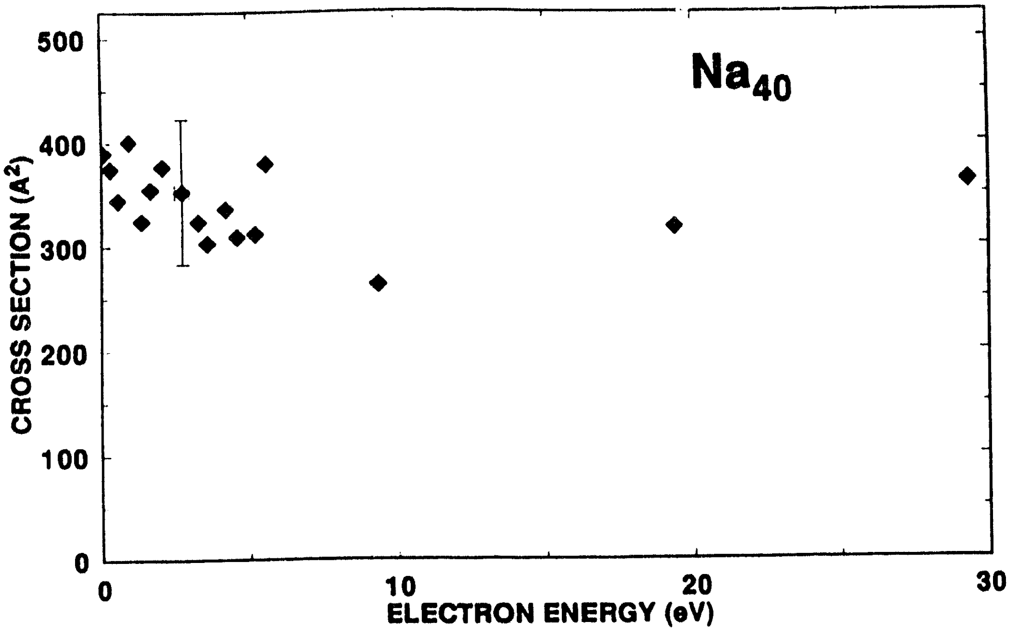

Figure 3. Extended electron-impact depletion spectrum for Na$_{40}$.

Rise Region: Electron Capture by Polarization Field

In this region, the kinetic energy of the incident electrons ($E \leq 1$ eV) is insufficient to cause direct fragmentation of the cluster or to ionize it. It follows that electron attachment must be the primary channel of cluster depletion at low impact energies.

A slow electron approaching a neutral cluster polarizes the latter and is subsequently attracted by the induced dipole field. In the limit of scattering by a perfect conductor, this interaction corresponds to the image charge potential. In the case of a spherical cluster the polarization potential seen by the incident electron is given by [18,19]

$$V_p = -\frac{\alpha e^2}{2r^4}, \tag{1}$$

where α is the electric polarizability of the cluster. Electrons approaching the cluster with impact parameters smaller than a certain critical value spiral into the center of force and are captured. Metal clusters are highly polarizable [5], and the strong long-range potential (1) will provide for efficient electron attachment.

The cross section for electron capture by the dipole polarization field (1) ("Langevin process") is given by [20]

$$\sigma_c = \pi\sqrt{\frac{2\alpha e^2}{E}}, \tag{2}$$

where E is the energy of the incoming electron. Static electric polarizabilities α of alkali clusters have been measured experimentally [21,22], and it is therefore possible to use Eq. (2) to calculate the expected electron attachment cross sections and compare them with the experimental results.

Fig. 4 presents a comparison between measured and calculated values at two collision energies. The quantitative agreement confirms that collisions in the low-energy regime indeed result in electron capture by the clusters [23]. Note also that the low-energy inelastic cross sections significantly exceed the geometrical hard-sphere dimensions of the sodium clusters (the radius of the cluster ion core is $R_n \cong r_s a_0 n^{1/3}$, where a_0 is the Bohr radius and r_s is the

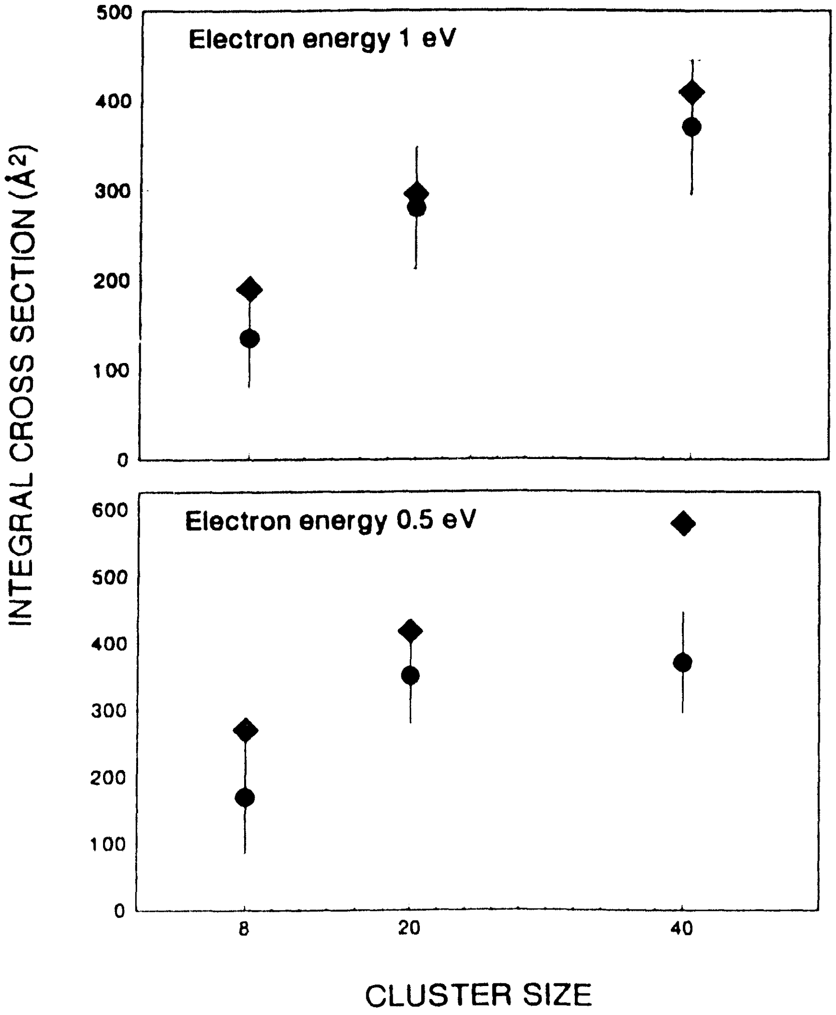

Figure 4. Circles: integral inelastic cross sections measured for three closed-shell clusters. Diamonds: electron capture cross sections calculated from Eq. (2) based on experimental cluster dipole polarizabilities.

Wigner-Seitz density parameter of the metal [2]; for Na $r_s \cong 4$ so that, for example, $R_8 \cong 4$Å). This illustrates the long-range character of the observed polarization interaction.

An important question requiring further study has to do with the fate of the captured electron. A possible relaxation channel would involve a transfer of energy to ionic vibrations of the cluster. Due to the high density of vibrational states, such transfer may represent a very fast process, in analogy with the rapid decay of collective electronic states in clusters excited by resonant photoabsorption [17,24-26]. In order to address this problem, it is necessary to detect and analyze the products of the electron attachment reaction.

Plateau Region: Cluster Fragmentation

At impact energies above $\cong$1 eV, electrons carry sufficient energy to cause cluster fragmentation, and this can be expected to become the primary inelastic interaction channel. It is, in fact, known that electron bombardment leads to substantial fragmentation of small clusters [27]. A level scattering profile can be interpreted in the following manner.

If $\mathcal{A}$ is the characteristic inelastic interaction range, then partial waves with angular momenta up to $\ell \cong k\mathcal{A}$ will contribute to the scattering process (k is the wave number of the incident electron). It can be shown [28] that there exists an upper bound to the inelastic scattering cross section given by

$$\sigma_{in}^{max} = \pi\mathcal{A}^2. \qquad (3)$$

The fact that clusters break up readily makes it plausible that above the fragmentation threshold the cross section would be close to its limiting value (3). The fact that for impact energies from $\gtrsim$1 eV up to 30 eV the integral cross sections are essentially constant confirms this picture.

We can use the experimental data to determine the interaction range $\mathcal{A}$. From the plateau segments of the cross section curves we find

$$\mathcal{A} \cong (1.4\text{-}1.7)R_n, \qquad (4)$$

where R_n is the radius of the cluster ion core introduced in the preceding subsection. This result shows that at higher electron energies the inelastic interaction is still governed by long-range forces. Indeed, at distances $r \simeq \mathcal{A}$ from the center, the density of the cluster valence electrons is extremely small (less than 1% of its value at the center [5,29]), thus, roughly speaking, fragmentation can occur without the incident electron coming in contact with the cluster. Further experimental and theoretical analysis is needed to understand the detailed dynamics of electron-impact fragmentation; it is clear, however, that, as in the case of low-energy electron capture, long-range polarization forces play an essential role.

At sufficiently high energies, additional channels can come into play above their respective thresholds (e.g., excitation of collective excitations, or surface plasmons, above ≈2.3eV [5] and ionization above ≈3eV [2,30]); however, these do not appear as prominent features on top of the overall cross section data. This confirms that fragmentation must be the primary mechanism of cluster depletion in the plateau region.

Related Polarization Effects in Cluster Spectroscopy

The importance of polarization effects has been noted in other work on cluster electron spectroscopy. Low-energy electron collisions with C_{60} and C_{70} fullerene clusters result in very efficient electron capture [31]; a large cross section for this process has been estimated. Similarly to the measurements described here, this must reflect the high polarizability of the fullerenes. Effects of the polarization interaction have been observed in photoelectron spectra of metal and carbon cluster anions [32,33]. Calculations of elastic electron scattering by small Be [34] and Na [35] clusters also demonstrate the necessity to account for the polarization term.

In electron-cluster scattering described in the present work, incident electrons induce a real dipole moment in the neutral cluster. Interaction between virtual induced dipoles, on the other hand, is responsible for the long-range van der Waals attraction between neutral particles. Experiments on collisions between neutral alkali clusters and neutral atoms and molecules [36,37] have shown that the high polarizability of metal clusters again results in extremely high scattering cross sections. For example, the integral elastic cross section for a thermal collision between a Na_{20} cluster and a Na atom is found to be $\cong 2500\text{Å}^2$ [37], exceeding by over an order of magnitude the geometrical cross section of the cluster. This once again illustrates that in scattering processes involving highly polarizable clusters the effects of polarization-related interactions can be quite dramatic.

SUMMARY

We have carried out the first measurement of absolute cross sections for the interaction between electrons and size-resolved free metal clusters. Integral inelastic scattering cross sections have been determined for electron-Na_n cluster collisions in the energy range from 0.1 eV to 30 eV.

At energies ≤ 1 eV, cross sections increase with decreasing impact energies, while at higher energies they remain essentially constant. The dominant processes are electron attachment in the low-energy range, and collision-induced fragmentation at higher energies.

The magnitude of electron capture cross sections can be quantitatively explained by the effect of the strong polarization field induced in the cluster by the incident electron. The cross sections are very large, reaching values of hundreds of $Å^2$; this is due to the highly polarizable nature of metal clusters.

The inelastic interaction range for fragmentation collisions is also found to considerably exceed the cluster radius, again reflecting the long-range character of electron-cluster interactions.

The important role played by the polarization interaction represents a bridge between the study of collision processes and the extensive research on cluster response properties. Furthermore, insight into the mechanisms of electron scattering is important for understanding production and detection of cluster ions in mass spectrometry and related processes.

Acknowledgements

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