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Electron - Cluster Interactions

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Abstract

Beam depletion spectroscopy has been used to measure absolute total inelastic electron-sodium cluster collision cross sections in the energy range from $E \sim 0.1$ to $E \sim 6$ eV. The investigation focused on the closed shell clusters Na_8 , Na_{20} , and Na_{40} . The measured cross sections show an increase for the lowest collision energies where electron attachment is the primary scattering channel. The electron attachment cross section can be understood in terms of Langevin scattering, connecting this measurement with the polarizability of the cluster. For energies above the dissociation energy the measured electron-cluster cross section is energy independent, thus defining an electron-cluster interaction range. This interaction range increases with the cluster size.

Introduction

Electron-atom as well as electron-surface and electron-bulk interactions have been studied for decades to provide a basic understanding of atoms, molecules and condensed matter (1,2,3). Although many aspects of these interactions are well understood, our knowledge of the electron interaction with finite systems, that is systems, containing from several to several thousand atoms, is still very limited. Such finite systems are commonly called clusters.

Many aspects of cluster properties, such as electronic states, magnetic properties, intra- and intermolecular potentials are the subject of intense research (4). Generally, cluster physics studies the transition from the atomic to the bulk state, two extremes which exhibit very different properties. It is natural to extend these questions to the important subject of electron-cluster interactions in order to gain a full understanding of finite systems.

Studies of neutral clusters are usually carried out in molecular beams, which makes it possible to measure the properties of free particles (5). In contrast to atomic beams, these cluster beams present a number of special problems. They contain a broad distribution of cluster sizes and, furthermore, the neutral fluxes of individual cluster sizes are not known. Some of these problems can be overcome by studying charged clusters, where both the mass and the flux can be well defined in the experiment. Unfortunately, this option is not usable for the study of electron-cluster interactions because the latter would be overwhelmed by the Coulomb force between the electron and the ion.

The electron-cluster interaction manifests itself via a number of channels:

(1) *Electron attachment*: For low electron energies, electron attachment, frequently followed by fragmentation of the cluster, is the dominant scattering channel (6). The cross section of this process typically shows a strong increase for decreasing energies. Relative electron attachment efficiencies have been measured for many molecular clusters such as $(\text{O}_2)_N$, $(\text{SF}_6)_N$ and $(\text{CO}_2)_N$, showing distinct fragmentation patterns of the ion cluster (7,8,9). Absolute attachment cross sections have been measured for some metal clusters (see below) (10). Cluster

fragmentation channels resulting from electron attachment have, to the authors' knowledge, not yet been determined.

(2) *Electron impact-induced ionization, typically accompanied by cluster fragmentation:* This is one of the most important of all electron-cluster interactions, since it underlies a basic experimental method of cluster detection. Unfortunately, strong fragmentation of the cluster after electron impact ionization is common, as the impact energy (60 -100 eV) significantly exceeds the bond- and ionization energies of all clusters (11,12). These bond energies are in the meV range for loosely bound van der Waals systems (e.g. $\text{He}_N < .8 \text{ meV}$) (13) and in the eV range for stronger bound metallic systems (e.g. $\text{Na}_N \sim 1 \text{ eV}$) (14,15).

Fragmentation channels resulting from electron impact ionization have been measured in collision experiments for some small rare gas clusters such as Ar_N ($N=2-6$) and small metal clusters such as Na_N (11,16). Fragmentation is dominated by the formation of a dimer-ion within the ionized cluster leading to cluster evaporation (12). The fragmentation channels and their electron energy dependence have been measured (11), and theoretically analyzed (12). It is possible to manipulate and custom-tailor the fragmentation in mixed clusters such as $\text{Ar}_N\text{C}_2\text{H}_4$ and He_NSF_6 , where $N > 100$ (17,18).

In contrast to the relative ionization efficiencies, absolute ionization cross sections are much less known. This arises mostly because the neutral flux of the cluster beam must be determined in order to relate efficiencies to absolute ionization cross sections. Most cluster beam experiments are not able to do so directly. Therefore some experiments approach this problems by scaling the electron impact ionization efficiencies of small clusters to the known atomic cross sections (19), or by comparing the measured average ion yield with the estimated cluster size and flux in the beam (20). It was found that for inert gas clusters such as $(\text{H}_2)_N$ or $(\text{N}_2)_N$, the ionization cross section scales directly with the number of atoms N for small clusters, and becomes proportional to $N^{2/3}$ for larger systems. The maximum of the ionization cross section increases with the cluster size. These findings were interpreted in terms of geometrical effects and the energy loss of ionizing electrons penetrating a large cluster (21).

(3) *Direct collision -induced cluster fragmentation:* While fragmentation channels caused by electron impact ionization have been studied for several systems, the total collision cross sections for electron-cluster collisions have only been measured for the sodium clusters Na_8 , Na_9 , Na_{20} , and Na_{40} (see below) (10). This experiment did not monitor the fragmentation products.

(4) *Rotational excitation by electron-impact; elastic electron scattering:* Pure rotational excitation and elastic scattering do not result in cluster fragmentation. These processes have been studied on alkali dimers by observing recoil deflection of the molecules. In this way, integral elastic (22,23) and differential rotational-excitation (24,25) cross sections have been measured. If feasible, similar experiments on larger metallic clusters would be of considerable interest.

To summarize, an ideal collision experiment between an electron and a cluster should be able to determine the different interaction channels and to measure the individual cross sections as a function of the energy and cluster size. However, such an experiment would require both size selection of the cluster beam before the collision in order to determine the fragmentation pattern, and knowledge of the neutral cluster flux prior to the electron scattering in order to determine absolute cross sections. Unfortunately, no cluster experiment is currently able to do so. The existing techniques are capable of measuring one of the following (1) ionization and attachment efficiencies, (2) fragmentation channels of small clusters, or (3) total inelastic and elastic scattering cross sections.

In the following section we will describe an experiment to measure the total inelastic electron-cluster scattering cross sections for sodium clusters containing 8, 9, 20, and 40 atoms in the energy range from $E \sim 0.1$ eV to $E \sim 30.0$ eV. The experiment has been described earlier (10,26). The measured electron attachment cross sections will be discussed in the framework of the Langevin scattering theory (1,27,28,29).

Experimental Set Up

The experiment is carried out using the technique of beam depletion spectroscopy: A beam of sodium clusters is intersected with an electron beam. The loss of signal on a specific cluster mass due to inelastic electron-cluster collisions determines the inelastic collision cross section. This technique has been successfully applied by our group to photoabsorption spectroscopy and to atomic scattering of metal clusters (30,31,32).

The general set up of the experiment is shown in Fig. 1. The cluster apparatus has been described in detail before (30,10,33). A supersonic beam of sodium clusters is produced by expanding sodium vapor (950K, 80 mbar) together with the argon carrier gas ($P_0 = 5$ bar for the $\text{Na}_{8/9}$ measurements, $P_0 = 8$ bar for others) through a hot, small orifice into vacuum. The central part of the beam is skimmed ($d = 0.4$ mm) and, after passing through three differential pumping stages, enters the electron gun chamber. After leaving the electron gun, the beam enters the detector chamber where the clusters are ionized with UV light from a filtered arc lamp ($\lambda = 240\text{-}420$ nm). The cluster ions are mass selected in a quadrupole field prior to detection in a dynode-photomultiplier unit. The total length of the flight pass is 2 m, the beam area is 3×2 mm at the detector entrance, typical count rates are $2\text{-}5 \cdot 10^4$ counts/sec for the closed shell clusters $\text{Na}_{8/20/40}$. The cluster velocity, 1000 to 1100 m/sec. is measured by laser induced depletion of the beam (34).

The near-threshold ionization of the metal clusters with UV light does not lead to significant fragmentation of the clusters (16,30). Therefore this arrangement allows us to measure the beam depletion of neutral metal clusters size-selectively. It should be mentioned that we do not detect the scattered electrons, because such a measurement would not be size-selective as the scattering volume contains many cluster sizes.

The electron gun design follows one described by R. E. Collins et. al. (35). The electron beam intersects the cluster beam at a right angle and is pulsed at a rate of 3 Hz with a 50/50 duty cycle. The electrons are emitted from an oxide-coated cathode, extracted by a series of grids and guided by a 1400 gauss magnetic field. Typical electron current densities have been 1.2 mA/cm^2 with a full width half

maximum (FWHM) of 0.25 eV for $E > 1$ eV and $200 \mu\text{A}/\text{cm}^2$ with a FWHM of 0.4 eV below 1 eV.

An inelastic electron collision can remove a cluster out of the molecular beam by three mechanisms:

(1) *Electron attachment*: The negatively charged clusters are removed out of the molecular beam by the Lorentz force of the magnetic field guiding the electrons in the gun.

(2) *Vibrationally inelastic collision*: The cluster evaporates an atom after an inelastic electron collision, the recoil of the ejected atoms removes the cluster out of the beam. The electron energy must be greater than the bond energy of the cluster ($E \sim 1$ eV (14,15)) for this channel to occur.

(3) *Electron impact ionization*: Similar to (1), the positively charged cluster will be removed from the beam by the magnetic field of the electron gun. The electron energy must be above the ionization potential of the cluster ($\text{IP}(\text{Na}_8) \sim 3$ eV (36,37)).

Elastic electron collisions will not remove the cluster from the molecular beam due to the large cluster size and the low energy of the electrons in the collisions. Therefore, elastic scattering will not contribute significantly to the measured cross section. We determine the total inelastic collision cross section through the depletion of the cluster signal on a specific cluster mass:

$$\sigma = \frac{\Delta N}{N} \frac{v_{\text{cluster}}}{J_{\text{electron}} L} \quad (1)$$

Here $\Delta N/N$ is the measured depletion rate, v_{cluster} the cluster velocity, J_{electron} the electron flow density, and L the length of the interaction volume. The measured depletion rate was between 0.3% and 1%.

Results

Total absolute inelastic scattering cross sections for the closed-shell clusters Na₈, Na₂₀, and Na₄₀ as function of the electron energy are presented in Fig. 2. The measurements cover the energy range from $E \sim 0.1$ eV to $E \sim 6$ eV. Dots represent individual measurements, and solid lines are least-square fits to the data. The scatter reflects the aforementioned fact that the attainable depletion ratios are very small. The accuracy in the experiment is $\pm 50\%$ for the Na₈ and $\pm 30\%$ for the Na_{20,40}. Measurements on the Na₉ cluster, not given in the figure, shows within the experimental uncertainty the same cross sections as the Na₈.

The major features in the results are: (1) a strong increase of the signal at the lowest energies for the Na₈ and Na₂₀, (2) a flat plateau regime for energies above $E \sim 1$ eV, and (3) very large, size-dependent cross sections. As we will show below, this behavior reflects the long-range electron-cluster interaction. Similar effects of very large interaction cross section due to the large polarizability of the cluster has been observed in Na_N scattering with molecules and in Na_N - Na scattering (38,31,32). We will now discuss these aspects of the data.

(1) Electron attachment is the primary scattering mechanism which can remove the cluster out of the beam at collision energies below the bond energy of the cluster. The attachment cross section can be described in terms of Langevin scattering, assuming a polarization interaction between the electron and the cluster polarized by the approaching charge (1,27):

$$V(r) = \frac{-1}{2} \frac{\alpha e^2}{r^4} \quad (2)$$

Here α is the polarizability of the cluster and e the electron charge. Using the measured polarizabilities of Na clusters (39), we can calculate the Langevin cross section for electron capture in the polarized field of the cluster:

$$\sigma = \pi \sqrt{\frac{2\alpha e^2}{E_{\text{collision}}}} \quad (3)$$

Fig. 3 compares the calculated and measured attachment cross section for Na₈, Na₂₀, and Na₄₀ for $E = 0.5$ eV and $E = 1$ eV. We find good agreement of the data with the proposed model.

(2) The plateau regime: For collision energies above the dissociation energy ($E > 1$ eV) the cross section is, within our resolution, independent of the collision energy, but rather dependent on the cluster size. In this regime, cluster fragmentation can be expected to be the primary interaction channel. If A is the characteristic inelastic interaction range, then partial waves with angular momenta up to $l_{\text{max}} = kA$, with k the wave number of the electron, will contribute to the scattering process. In this case the upper bound of the collision cross section can be written as (40)

$$\sigma_{\text{max}} = \pi A^2 \quad (4)$$

Our experimental data shows that the inelastic interaction range A is a function of the cluster size:

$$A = (1.4 - 1.7) R \quad (5)$$

R is the radius of the cluster and depends on the cluster size $R = a_0 r_s N_e^{1/3}$, where a_0 the Bohr Radius, r_s the Wigner-Seitz radius of sodium, and N_e is the number of valence electrons in the cluster. The large interaction cross section reflects the long-range character of the electron-cluster collision. It exceeds the core size of the cluster significantly. At a distance of $r = A$, the density of the cluster valence electrons is extremely small, less than 1% of its value at the center of the cluster (41).

For Na_{40} the total inelastic cross section has been measured up to $E = 30$ eV in 10 eV steps (see Fig. 4). We did not observe any significant changes of the cross section in this regime, which confirms the validity of Eq. 4 and Eq. 5 to describe the total inelastic cross section. Electron impact-induced ionization is expected to occur at collision energies above the ionization threshold, with increasing cross section in the measured energy regime (42,1). Such a behavior is not seen in our measurements (see Fig .4) indicating that electron impact ionization is overshadowed by non-ionizing fragmentation of the cluster. This suggestion is further supported by the size of the measured cross section per atom $\sigma_{\text{Na40/atom}} \sim 9 \text{ \AA}^2$, which exceeds typical ionization cross sections of metal atoms which are in the order of one $\text{\AA}^2$ depending on the energy (19,43,1,42). Further, in a cluster the ionization cross section per atom will be even smaller (44,21). However, this important question has to be addressed in a direct measurement for a definite answer.

Summary

Beam depletion spectroscopy has been applied to measure absolute inelastic collision cross sections for electron- Na_N ($N=8,9,20,40$) cluster collisions in the energy range from $E = 0.1$ eV to $E= 6.0$ eV. For collision energies below the dissociation energy of the cluster ($E \sim 1$ eV) cross sections increase with decreasing energy. In this energy regime electron attachment is the primary process for inelastic electron scattering. The attachment cross section is explained in terms of Langevin scattering linking the measured cross section to the polarizability of the cluster. For collision energies above the energy of the bond, collision-induced fragmentation is the primary inelastic scattering channel. The scattering cross section is essentially constant thus defining a range for the inelastic electron-cluster interaction. This interaction range increases with the cluster size. The strong polarizability of the cluster leads to large cross sections. This property is also responsible for very strong van der Waals forces observed in recent experiments on sodium cluster collisions with atoms and molecules.

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Figure List

Fig 1: Experimental set up for the measurement of inelastic collision cross sections. A supersonic beam of sodium clusters is intersected at right angle by an electron beam. Inelastic collisions remove clusters out of the molecular beam. The depletion rate on a specific cluster mass determines the absolute inelastic collision cross section for the electron-cluster interaction.

Fig 2: Absolute electron impact depletion cross section for the clusters Na₈, Na₂₀, and Na₄₀. The dots represent the individual measurements, solid lines are least square fits to the data.

Fig 3: Comparison of the measured cross sections with calculated Langevin electron attachment cross sections for an electron in the polarization field of a cluster. Diamonds represent the calculated cross sections (Eq. 2, Eq. 3), the circles show the measured values.

Fig 4: Electron impact depletion cross section of Na₂₀ for energies up to E = 30 eV.

PLASMA SOURCE AND SKIMMER

**DETECTOR
APERTURE**

UV-LIGHT

QMA

DALY-DYNODE

CROSS SECTION ($\text{\AA}^2$)

ELECTRON ENERGY (eV)

CROSS SECTION ($\text{\AA}^2$)

DATE

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