



High-resolution ion mobility measurements of indium clusters: electron spill-out in metal cluster anions and cations

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Received 12 January 1999; in final form 16 February 1999

Abstract

High-resolution ion mobility measurements have been used to examine In_n^- and In_n^+ clusters with $n = 2\text{--}30$. The cluster–He scattering cross-sections of the anions are systematically larger than those of the cations. The difference ($\sim 25\%$ for In_2 to $\sim 2\%$ for In_{30}) is attributed to the electron density extending further from the surface of the cluster in the anions than in the cations. Geometric cross-sections estimated from electron densities determined from a charged jellium model are in good agreement with the experimental data: the change in cross-section with charge state is reproduced over the entire range. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Ion mobility measurements have been used in the past few years to probe the geometric structure of atomic clusters (for recent reviews, see Refs. [1,2]). This approach has been particularly useful in resolving structural isomers with different shapes for both covalent [3,4] and ionic clusters [5,6]. There have been only a few studies of the mobilities of metal clusters [7,8]. For metal clusters, previous work has shown that the mobilities can be influenced by the electronic shell structure [8]. Clusters with closed electronic shells are expected to be near spherical, and the distortion from a near-spherical geometry between the shell closings is reflected in the mobili-

ties. While mobilities of clusters are usually considered to only reflect their geometric structure, for atoms different electronic states have been resolved [9,10], indicating that electronic effects can also influence the mobilities.

The properties of clusters of free electron metals can be largely accounted for using a jellium model where the ionic cores are replaced by a uniformly charged background [11–15]. Calculations indicate that the electron density spills out over the edge of the jellium background [12]. How far the electron density extends depends on the charge state, and so the mobilities of metal cluster anions and cations are expected to be different. The only previous comparisons of the mobilities of cluster cations and anions were for small [3] and large [16] carbon clusters, where it was found that mobilities for anions and cations do not differ significantly. Here we describe high-resolution ion mobility studies of In_n^+ and In_n^-

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clusters. Indium is ideal for these studies because the clusters are believed to be metallic and liquid at room temperature [17]. Being liquid, both the anionic and cationic clusters should be close to spherical. We find that there are large, size-dependent differences in the collision cross-sections of the In_n^+ and In_n^- clusters, with the cross-sections for the anions being systematically larger. The differences in the measured cross-sections are reproduced by a model where the geometric cross-sections are estimated from the electron densities determined from a charged jellium model. These studies show that the mobility of a cluster is not only sensitive to the atomic coordinates but also depends on the electronic structure through the physical extent of the electron density.

2. Experimental

The high-resolution ion mobility apparatus used for these studies has been described in detail previously [18]. The apparatus consists of a source region coupled directly to a 63 cm long drift tube. Indium clusters were produced by pulsed laser vaporization (308 nm) of an indium rod. Cluster ions pass from the source region into the drift tube through an ion gate. The ion gate consists of a cylindrical channel 0.5 cm in diameter and 2.5 cm long. A helium buffer gas flow of around 900 sccm prevents neutral clusters from entering the drift tube from the source region. An electric field of 200 V/cm carries the ions through the ion gate against the buffer gas flow, and into the drift tube. The drift tube, ion gate, and source region contain helium buffer gas at a pressure of around 500 Torr. A voltage divider coupled to 46 guard rings provides a uniform electric field along the drift tube. A drift voltage of 10000 V was employed. This provides a drift field of 158.7 V/cm. The high drift voltage is primarily responsible for the much higher resolution as compared to conventional injected ion drift tube experiments [1,2,18]. After traveling through the drift tube, ions exit through a 0.125 mm aperture. The ions are then focused into a quadrupole mass spectrometer, and after mass analysis, they are detected with an off-axis collision dynode and dual microchannel plates. Drift time distributions are recorded with a multichannel analyzer

synchronized with the laser pulse that generates the clusters. Cationic or anionic clusters can be studied by using drift, guiding, and focusing voltages of the appropriate polarity. All measurements were performed at room temperature. Cross-sections were derived from the drift times, t_D , using [19]:

$$\Omega_{\text{avg}}^{(1,1)} = \frac{(18\pi)^{1/2}}{16} \left[\frac{1}{m} + \frac{1}{m_B} \right]^{1/2} \frac{e}{(k_B T)^{1/2}} \frac{t_D E}{L \rho}$$

where m is the mass of the ion, m_B is the mass of a buffer gas atom, e is the charge on the ion, ρ is the buffer gas number density, L is the length of the drift tube, and E is the drift field.

3. Results and discussion

Cross-sections determined for In_n^- and In_n^+ clusters with $n = 2-30$ are shown in Fig. 1. The measurements are typically reproducible to within 0.5%. The cross-sections for the In_n^- clusters are systematically larger than the In_n^+ cross-sections. For around half of the cluster sizes, an In_{n+1}^+ cluster has a smaller cross-section than the corresponding In_n^- cluster, even though it contains an additional atom. Fig. 2 shows a plot of the relative difference between the cross-sections of the anionic and cationic cluster ions ($\{\Omega(\text{anion}) - \Omega(\text{cation})\} / \Omega(\text{cation})$). This difference steadily decreases with size, while for the

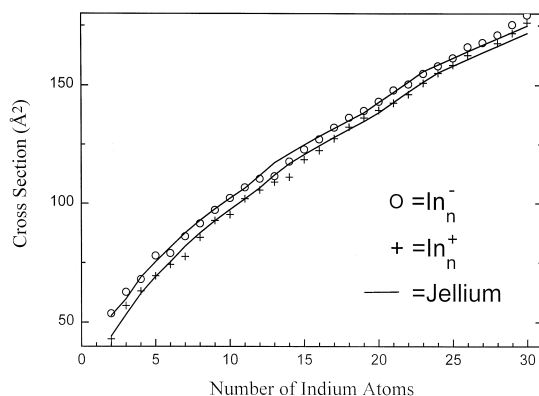


Fig. 1. Plot of cross-sections of indium cluster cations (crosses) and anions (circles) versus cluster size. The lines are fits from spherical jellium model calculations described in the text. The measurements are typically reproducible to within 0.5%.

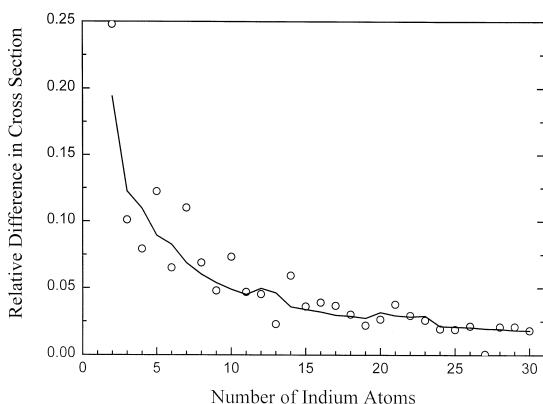


Fig. 2. Plot of the relative difference between the cross-section of the indium cluster anions and cations ($\{\Omega(\text{anion}) - \Omega(\text{cation})\} / \Omega(\text{cation})$) versus cluster size. The measurements are typically reproducible to within 0.5%. The line is a fit from spherical jellium model calculations described in the text.

small sizes, there are relatively large fluctuations from one size to another.

Since the indium clusters are liquid at room temperature [17] they can be treated as small, nearly spherical droplets. The geometric cross-section of this spherical droplet is given approximately by $\pi(r + r_{\text{He}})^2$ where r_{He} is the radius of the helium atom and r is the radius of the droplet. A value of 1.0 Å was used for the radius of the helium atom. To account for the differences between indium cluster anions and cations we have computed effective radii for indium clusters with a model which takes into account the spill-out of the electron density from the cluster's surface. Electron densities for positively and negatively charged clusters were obtained from standard spherical jellium calculations [13]. We used a local density exchange correlation functional (the standard parameterization of Gunnarsson and Lundqvist [20]) and the bulk value of 1.84 Å for the Wigner–Seitz radius of the indium atom.¹ In order to calculate the geometric cross-section, it is necessary to define the effective radius of the cluster. Moving away from the cluster surface, the electron

density falls off nearly exponentially. We found that an effective radius defined by the distance where the electron density falls to 10% of the bulk value provided a good fit to the experimental data for both anions and cations. This cutoff value is the only adjustable parameter in the model. For a given cluster size the radius obtained for the anion is larger than the radius obtained for the cation, due to the two extra electrons. The geometric cross-sections obtained with this model are plotted as solid lines in Figs. 1 and 2. The calculated geometric cross-sections reproduce the measured cross-sections for both anions and cations over the entire size range. In particular, the difference between the cross-sections of the anions and cations (which decreases from $\sim 10\%$ for small clusters to $\sim 3\%$ for large ones) is reproduced by this simple model (see Fig. 2). The good agreement between the measured and calculated cross-sections confirms that the mobilities of the indium clusters are influenced by the electron density spilling out from the cluster surface.

Close inspection of the results shown in Fig. 1 shows that there are small discontinuities or steps in the mobilities for clusters with around 7 and 14 atoms. For cations steps occur between sizes 7–8 and 14–15, and for anions between sizes 6–7 and 13–14. These sizes correspond to the closure of the 2s and 2p electron shells (20 and 40 valence electrons, respectively). These two shell closings have been identified previously in photoionization experiments on neutral indium clusters [17], in abundance distributions, and in dissociation experiments [21]. The shell closings with 20 and 40 electrons have also been observed in mobility measurements performed for Al_n^+ clusters [8]. The reduced cross-sections observed for clusters with closed electronic shells was attributed to the fact that these clusters are predicted to be spherical, while clusters with open electronic shells are predicted to be ellipsoidal, which measurably increases the cross-section. The simple model employed above to determine the effective size of the indium clusters is restricted to spherical symmetry and so it cannot account for ellipsoidal deformations [22]. So while our model reproduces the overall behavior of the measured cross-sections for the anion and cation clusters, it does not reproduce the local fluctuations which result from the effects of shell closings.

¹ We used the Wigner–Seitz radius for the solid at room temperature. Extrapolation of the liquid density to room temperature leads to a Wigner–Seitz radius of 1.85 Å.

4. Conclusion

We have performed high-resolution mobility measurements for cationic and anionic indium clusters. The cross-sections of the negatively charged clusters are systematically larger than those of the positively charged ones. The differences in the measured cross-sections are reproduced by geometric cross-sections derived from a spherical jellium model. The differences between anions and cations is due to the electron density spilling out from the ionic core. These results show for the first time that mobility measurements are sensitive to the surface electron density of a cluster and not only to its atomic geometry.

Acknowledgements

This work was supported by the National Science Foundation (CHE-9618643) and NATO (CRG-971066).

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