

Communication: The formation of helium cluster cations following the ionization of helium nanodroplets: Influence of droplet size and dopant

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The $\text{He}_n^+/\text{He}_2^+$ ($n \geq 3$) signal ratios in the mass spectra derived from electron impact ionization of pure helium nanodroplets are shown to increase with droplet size, reaching an asymptotic limit at an average droplet size of approximately 50 000 helium atoms. This is explained in terms of a charge hopping model, where on average the positive charge is able to penetrate more deeply into the liquid helium as the droplet size increases. The deeper the point where the charge localizes to form He_2^+ , the greater the likelihood of collisions with the surrounding helium as the ion begins to leave the droplet, thus increasing the probability that helium will be ejected in the form of He_n^+ ($n \geq 3$) cluster ions rather than He_2^+ . The addition of a dopant alters the $\text{He}_n^+/\text{He}_2^+$ ratio for small helium droplets, an observation attributed to the potential energy gradient created by the cation-dopant interaction and its effect in drawing the positive charge towards the dopant in the interior of the droplet. © 2011 American Institute of Physics. [doi:10.1063/1.3622764]

Electron impact ionization mass spectrometry is commonly used to provide diagnostic information about doped helium nanodroplets.¹ Ions ejected from helium droplets can be produced either by charge transfer ionization, i.e., a helium atom is first ionized by electron impact and then the He^+ undergoes a resonant hopping mechanism until it localizes,² or by Penning ionization via electronically excited $\text{He}^*(2^3\text{S})$ atoms.³ In the current study, we are interested in the formation of helium cluster cations, He_n^+ , including the effect of adding a dopant molecule. Because Penning ionization generally cannot lead to He_n^+ formation (except its contribution to the increase of He_4^+ in large helium droplets by double Penning ionization^{4,5}), the focus here is on the charge hopping mechanism.

In the charge transfer process, the helium droplet is first ionized by collision of the incoming electron with a helium atom, most likely at or near the surface of the droplet. Once generated, the positive charge is mobile and hops between adjacent helium atoms. The hopping chain is of finite length and terminates in one of two ways: (i) transfer of the positive charge to a dopant (if present) or (ii) charge localization (self-trapping) to form He_2^+ . Both processes are irreversible and both are exothermic, providing the driving force for ions to be expelled into the gas phase. Various models suggest that self-trapping occurs after ~ 10 hops and so if the dopant is a sufficient distance from the initial point of ionization then only process (ii) is possible.^{6–8}

Although He_2^+ is the main product from self-trapping, a variety of other He_n^+ clusters are also observed in mass spectra. Scifoni *et al.* have modelled the collisional relaxation dynamics after the formation of He_2^+ based on the $\text{He}_2^+ + \text{He}$ system.⁹ Their findings suggest that a vibrationally ex-

cited He_2^+ is initially formed, which is then cooled by collisions with surrounding atoms. However, as the He_2^+ ion is cooled it will increasingly act as a nucleation centre for the attachment of further helium atoms, which can remain attached as the ion is ejected into the gas phase.

Callicoatt *et al.* investigated the relative abundances of various He_n^+ ions emitted from pure helium droplets following electron impact ionization.¹⁰ The droplets investigated consisted of a mean number of helium atoms, $\langle N \rangle$, in the range 100 to 15 000 helium atoms. Using the relative ion yields in Table I of Ref. 10, the ratio of abundances of He_3^+ versus He_2^+ can be obtained. The $\text{He}_3^+/\text{He}_2^+$ ratio showed a decline as the average helium droplet size increased for $\langle N \rangle$ larger than 600, but then increased for larger droplet sizes. An approach towards an asymptotic limit was observed for clusters near to the largest studied, $\langle N \rangle \sim 15\,000$, but Callicoatt *et al.* pointed out that the “large cluster limit” is not reached for $\langle N \rangle = 15\,000$ helium atoms. As the authors made clear, it is important not only that larger helium droplets be explored, but also conditions should be employed to avoid contamination from background gases, including water vapor. In the work reported in the current paper, we have (i) re-investigated the He_n^+ abundances for pure helium droplets, extending to larger helium droplet sizes than those used by Callicoatt *et al.* and (ii) we have explored the effect of deliberately adding a dopant. For pure helium droplets, we find, as detailed below, a response to helium droplet size, which is opposite to that reported by Callicoatt *et al.* We also find that the addition of a dopant can significantly alter the relative abundances of He_n^+ ions. For example, the response of the $\text{He}_3^+/\text{He}_2^+$ ratio to the droplet size observed by Callicoatt *et al.* matches our observations when water is added to the helium droplets.

The experimental apparatus and procedure have been described in detail in Refs. 11 and 12. Briefly, a pulsed helium droplet source was employed in combination with a

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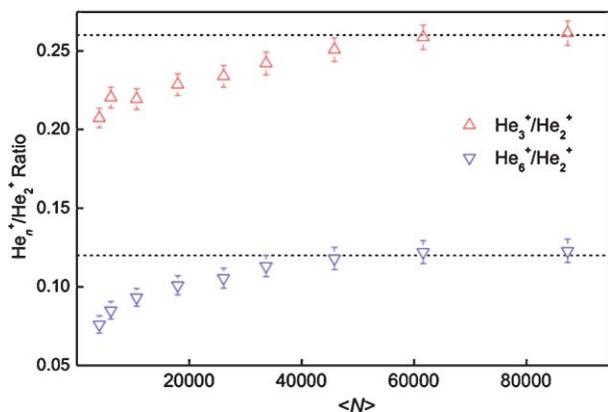


FIG. 1. The dependence of the $\text{He}_3^+/\text{He}_2^+$ and $\text{He}_6^+/\text{He}_2^+$ ratios on the helium droplet size (expressed as the mean number of helium atoms, $\langle N \rangle$). The dashed lines indicate the asymptotic limits for large helium droplets. The error bars shown represent the standard deviation (1σ) of repeat measurements under fixed experimental conditions.

time-of-flight mass spectrometer equipped with a 100 eV electron impact source. The advantage of the pulsed droplet source is that it allows variation of the helium droplet size within a single pulse by simply adjusting the delay between the pulse opening time and the incoming electron pulse, so that no change in source conditions is necessary.¹³ This is possible because large helium droplets have a lower velocity in a pulse train of helium droplets than smaller ones. The pulsed source was operated at a helium stagnation pressure of 16 bars and a temperature of 10.5 K. In the molecule-doping experiments, the partial pressures of foreign gases were high enough to guarantee the pickup of at least one atom or molecule at small helium droplet sizes, $\langle N \rangle \sim 4000$.

The effect of $\langle N \rangle$ on the abundance ratios of He_n^+ ions is illustrated in Fig. 1. This shows the measured intensity ratios for $\text{He}_3^+/\text{He}_2^+$ and $\text{He}_6^+/\text{He}_2^+$ derived from pure (undoped) helium droplets. He_6^+ is included to demonstrate that the variation of the $\text{He}_n^+/\text{He}_2^+$ ratio with droplet size is valid not only for $n = 3$, but also for larger n . He_4^+ and He_5^+ were less suitable for this purpose since the He_4^+ peak overlaps with traces of O^+ in the background mass spectrum. We note in passing that our maximum helium droplet size is below the level ($\langle N \rangle \sim 10^5$) where enhanced formation of He_4^+ is observed.⁵ He_5^+ is affected by the wing of the H_3O^+ signal, which is intense when H_2O is deliberately added to helium droplets (see below).

The $\text{He}_3^+/\text{He}_2^+$ and $\text{He}_6^+/\text{He}_2^+$ intensity ratios show similar trends with the droplet size. Both ratios rise as $\langle N \rangle$ increases, but both reach an asymptotic limit in the region of 5×10^4 helium atoms. For $\text{He}_3^+/\text{He}_2^+$ the ratio changes from 0.20 for small droplets to 0.26 for large droplets, while for $\text{He}_6^+/\text{He}_2^+$ it varies from 0.05 to 0.12. We interpret these data as follows. As the droplet size increases, the possibility of deeper penetration of the electron prior to ionization increases. This leads to an increased probability of self-trapping deeper within a droplet, which in turn will increase the likelihood of multiple collisions with helium atoms as the He_2^+ begins to exit the droplet. This simple explanation accounts for the increase in the $\text{He}_n^+/\text{He}_2^+$ ratio with droplet size. The

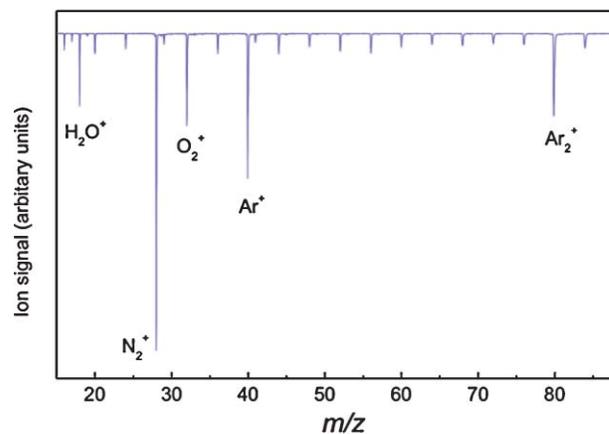


FIG. 2. Part of the mass spectrum obtained when argon was added to the pickup cell. Argon pickup by the helium droplets is demonstrated by the Ar^+ and Ar_2^+ signals. There is also an underlying series of peaks separated by 4 mass units, which correspond to He_n^+ cluster ions. A small air leak is shown by the H_2O^+ , N_2^+ , and O_2^+ peaks (see text for more information).

asymptotic limit is reached for large $\langle N \rangle$ because the incoming electron can penetrate no further beyond a certain droplet size,⁸ and thus further addition of helium atoms just produces an untouched core of liquid helium. Although it is not the purpose of this study, it is interesting to point out that a careful measurement of the $\text{He}_3^+/\text{He}_2^+$ intensity ratio offers the potential for a rapid and simple means for determining the mean droplet size in a helium droplet beam, provided the droplet size is not in the asymptotic region.

The addition of a dopant has a marked effect on the $\text{He}_n^+/\text{He}_2^+$ ratio. We have investigated two dopants, argon and water. Before presenting the findings, we illustrate the cleanliness of our pickup process in order to show that the background water level was insignificant. Figure 2 shows part of the mass spectrum derived from argon pickup and contains clear peaks due to Ar^+ and Ar_2^+ . A small air leak is also present, as evidenced by the H_2O^+ , N_2^+ , and O_2^+ signals. However, this leak is presumably in the mass spectrometer region, since it does not translate into any significant pickup of air by the helium droplets. This is demonstrated by the negligible H_3O^+ signal at $m/z = 19$, which is the major ion derived from water dimer and is always prominent when there is significant background water in the pickup region.

Figure 3 shows the response of the $\text{He}_3^+/\text{He}_2^+$ ratio when argon and water are added. These data were generated using approximately the same partial pressures for both dopants. This partial pressure was not measured directly but equal partial pressures were assured by monitoring the gas carried into the TOF-MS when the nozzle temperature was too high for droplet formation. The signals were corrected for differences in the relative ionization cross sections in order to deliver equal partial pressures. The same asymptotic limit is reached as for the pure helium nanodroplets, as would be expected, but the approach to this asymptote is much faster when argon and water are added and the limit is reached with as few as 10^4 helium atoms in the case of argon. However, there is also a major difference between argon and water in that the $\text{He}_3^+/\text{He}_2^+$ ratios approach the asymptotic limit from

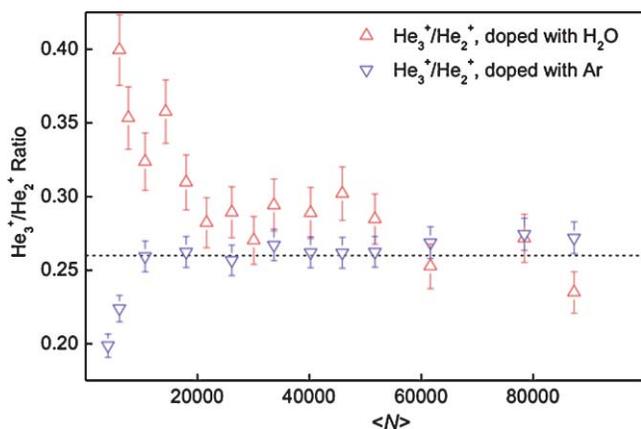


FIG. 3. The dependence of the $\text{He}_3^+/\text{He}_2^+$ ratio on the helium droplet size when doped with H_2O or argon. The dashed line indicates the asymptotic limit for large helium droplets, which reaches the same level as the $\text{He}_3^+/\text{He}_2^+$ asymptotic limit in Fig. 1.

opposite directions. These findings are discussed and interpreted below.

Notice that the asymptotic behaviour for the doped helium droplets is not the result of helium evaporation on pickup, since this should act in the opposite direction and lower the $\text{He}_3^+/\text{He}_2^+$ ratio, given what is seen for pure helium droplets. Instead, the effect of argon and water will be to provide a potential energy gradient between the dopant and the positive hole *prior to* self-trapping. In pure helium droplets, the position of lowest potential energy for the positive charge is the centre of the droplet but the potential gradient is expected to be small and the steering effect will, therefore, be likewise small. Under such conditions, the charge hopping is more likely to be a random walk than a process which is strongly steered by a potential energy gradient.⁸ However, addition of a dopant will markedly increase this gradient. If we assume that the dopant is located near the centre of the helium droplet, then the effect of dopant addition will be to drag the positive hole further into the interior than would otherwise be the case. Based on what we see for pure helium droplets, this steering effect should increase the $\text{He}_3^+/\text{He}_2^+$ ratio compared to pure helium droplets and indeed this is what is observed for both argon and water dopants. Equally, for both argon and water dopants, we can use the enhanced potential energy gradient between He^+ and the dopant prior to self-trapping to account for the more rapid approach to the asymptotic limit than seen for pure helium droplets.

The remaining observation to explain is why, for small droplets, doping with water has the opposite effect on the $\text{He}_3^+/\text{He}_2^+$ ratio as a function of $\langle N \rangle$ when compared to argon doping. Again, the interaction potential can be used to interpret this finding but it is the interaction between the dopant and He_2^+ *after* self-trapping, rather than the interaction between the He^+ and the dopant, that is important here. Helium cluster ions that can be observed in the mass spectrum must have gained enough kinetic energy to overcome the potential energy well generated by the interaction of He_2^+ with the nearby water molecules, otherwise they will eventually be dragged back towards the dopant. If the latter happens then

sooner or later He_2^+ will transfer its charge to the dopant because of its lower ionization energy. For those He_2^+ ions that do escape, they will tend to travel through the helium droplet at a lower velocity compared with pure helium droplets, owing to the energy expended in escaping from the potential energy well in the vicinity of the water molecule.

The impact of the velocity of He_2^+ on its association reactions with helium atoms has not been experimentally investigated in the gas phase. However, there is evidence from numerous studies of other ion + molecule association reactions that the rate of reaction increases as the collision energy decreases. Thus the ability to form He_3^+ and larger He_n^+ clusters should increase if a more slowly moving He_2^+ ion is generated. We therefore propose that in small helium droplets, where the He_2^+ ion is likely to be formed in close proximity to the water dopant, the retarding effect of the ion-dopant interaction accounts for the enhanced production of He_n^+ cluster ions for $n > 2$. This effect will wear off as the droplet size increases, and thus explains why the $\text{He}_3^+/\text{He}_2^+$ ratio *declines* towards the asymptotic limit as a function of $\langle N \rangle$ when water is the dopant.

In summary, we have found that the electron impact mass spectrum of pure helium nanodroplets shows a systematic variation in $\text{He}_n^+/\text{He}_2^+$ ($n \geq 3$) signal ratios with droplet size. This small but easily measurable variation in relative cluster ion abundances is attributed to the site of initial self-trapping of the positive hole (formation of He_2^+). Larger droplets allow deeper penetration of the positive hole, which in turn results in an increased probability for collisions between the outgoing He_2^+ and, therefore, an increased likelihood of forming larger cluster ions. The addition of a dopant introduces a stronger potential energy gradient that steers the charge hopping process towards the droplet centre, which then affects the $\text{He}_n^+/\text{He}_2^+$ ratio when compared to pure helium nanodroplets. The effect is modest when argon is added but far larger when water is the dopant.

However we caution that, while these data can be successfully interpreted in terms of a simple charge hopping model, the actual ionization dynamics is likely to be more complicated than we suggest here. The development of a comprehensive theoretical model that can provide a realistic account of the ionization dynamics in helium nanodroplets, including the findings presented here, would be extremely useful.

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