Helium anion formation inside helium droplets

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Abstract. The formation of He$^-$ is examined with improved electron energy resolution of about 100 meV utilizing a hemispherical electron monochromator. The work presented provides a precise determination of the three previously determined resonance peak positions that significantly contribute to the formation of He$^-$ inside helium nanodroplets in the energy range from 20 eV to 29.5 eV. In addition, a new feature is identified located at 27.69 ± 0.18 eV that we assign to the presence of O$_2$ as a dopant inside the droplet. With increasing droplet size a small blue shift of the resonance positions is observed. Also for the relatively low electron currents used in the present study (i.e., 15–70 nA) a quadratic dependence of the He$^-$ ion yield on the electron current is observed.

1 Introduction

Helium droplets offer an interesting and exclusive environment for the study of physical and chemical phenomena [1–7]. This is due to the low temperature of helium droplets (0.37 K), their superfluidity and their capacity of efficient doping with a wide variety of atoms and molecules. Helium droplets provide an ideal cold matrix for spectroscopy that is interacting very little with the dopant [8]. Furthermore, the enormous cooling power of superfluid He has been reported to quench many fragmentation reactions and thus provides a method to investigate short-lived reaction intermediates [9]. For decades, the scientific community has been fascinated by the physics behind electron scattering from helium [10–14]. It has captured the attention of both the experimental and the theoretical communities that have attempted to better understand these fundamental reactions for years. Helium anions are some of the simplest metastable negative ions. The electron affinity of helium was first investigated in 1936 [15]. In the same year, helium anions He$^-$ were first detected by means of mass spectrometry [16]. Later, it was experimentally shown that He$^-$ can be formed by charge-exchange collisions [17]. He$^-$ has a lifetime of a few 100 μs which was determined experimentally utilizing storage rings [18,19]. Therefore the investigation of the physics and chemistry behind it prove to be challenging for this anion in the gas phase. Mauracher et al. [20] recently discovered that He$^-$ is efficiently formed upon electron irradiation of helium nanodroplets (HND) at specific resonance energies. In the meantime several novel processes have been ascribed to the presence of metastable He$^-$ in HND such as the formation and ejection of He$^-$ at electron energies below the ionization threshold of the free atom [21], or the self-assembly of salt nanocrystals from chemical reactions [22]. It has been shown that He$^-$ has a high mobility inside the helium droplet. This mobility enables it to find the dopant and transfer its negative charge and/or electronic excitation energy to it [23,24]. In a separate study, the dopant anions created at electron impact energies of about 22 eV were attributed to the high mobility of He$^-$ inside the helium droplet [20]. It was shown that it is possible for He$^-$ to donate both loosely bound electrons to a fullerene cluster. Multiply charged cations formed inside helium droplets could be mostly attributed to He$^-$ acting as a reagent. Clear experimental evidence of the role of two bound states (1s2s2p 4P) and the (1s2p$^2$ 4P) of He$^-$ was presented [25]. For undoped HND the intensity of the lowest energy resonance (1s2s2p) is exceeding all higher energy resonances by far which therefore only show up as shoulders in the high-energy tail of this dominant resonance. However, He$^-$ in the (1s2s2p) state is most strongly affected by the presence of an impurity, which was ascribed to the highest mobility of this electronic state of He$^-$.

All previous experiments on He$^-$ from HND were performed with poor electron energy resolution which may affect the accurate assignment of both the position and width of the resonance structures.

In the present study we utilized a hemispherical electron monochromator to study the formation of the helium anion He$^-$ in helium droplets. The resonance peak positions as well as the width of the resonances for the formation of He$^-$ were determined with high energy resolution. In addition, we studied the dependence of these positions

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on the initial size of the neutral helium droplet, and the dependence on the ion yield with respect to the initial electron current.

2 Experimental setup

Pure helium nanodroplets were produced via the supersonic expansion of pressurized and pre-cooled He through a small orifice into ultra-high vacuum. A closed cycle cryostat was employed to cool down pure (99.9999%) helium as it passes through a tube. The helium pressure inside the tube is regulated to 20 bar. At the end of the tube, the helium reaches a 5 μm nozzle that is cooled down to low temperatures (6.8–7.6 K) using the same cryostat. When the supercritical fluid of helium expands through the nozzle to high vacuum, the liquid fragments into large droplets as a result of cavitation [26]. Evaporative cooling reduces the temperature of the helium in this experiment had a mean size in the order of 10^{-15} m.

...Israel [27]. We note that due to a small leak a small amount of air (∼1×10^{-5} Pa) was present in the droplet source chamber. The beam is then skimmed passing to a differentially pumped vacuum chamber via a 0.8 mm skimmer. More details on this helium droplet source can be found in [28]. In this differentially pumped chamber, the helium nanodroplet beam intersects with a high resolution electron beam [29]. At first the electrons are produced by a heated tungsten hairpin filament having a diameter of 0.125 mm. After this a hemispherical electron monochromator (HEM) is employed to achieve an electron beam with high energy resolution. The electron beam resolution used for the present work was in the range between 90–110 meV. The resolution of the electron beam is determined by measuring the full width at half maximum (FWHM) of the anion efficiency curve of SF_{6} upon electron attachment to gas phase SF_{6} having a maximum at 0 eV [30]. The latter resonance was also used for the calibration of the energy scale. The electrons are measured at a Faraday cup using a pico-ammeter. In the present work, electron currents were in the range of 15–75 nA at the electron energy of 22 eV. Due to the interaction of the electron beam with the droplet beam, ions are formed. The resulting anions are guided towards a quadrupole mass filter where they are analyzed according to their mass to charge ratio. The detection is achieved by means of a Channeltron type secondary electron multiplier (KBL 510, Dr. Sjuts Optotechnik GmbH). A pulse counting system is used for analyzing and detecting the mass selected ionic products [31]. The channeltron is mounted 90°-off axis to the quadrupole. In the standard configuration the mass selected anions are bent by means of an electrostatic cylindrical sector (the outer electrode consists of a grid, while the inner electrode is a plate). This deflector allows the ions to hit the detector. In the present experiment with helium droplets, the problem occurs that for electron energies higher than 20 eV, neutral metastable species that are created are not affected by the quadrupole mass filter. These metastable species can collide with the grid of the electrostatic bender. As a result of such collisions, electrons and cations are formed and irrespective of the potential set on the detector one of these secondary species is accelerated to the detector. This signal adds to and often exceeds the ion yield of reactions that are investigated. To solve this problem, the cylindrical sector was replaced by a 90° electrostatic quadrupole bender that allows the metastable particles to be dumped without contributing to the signal on the detector.

3 Results and discussions

The attachment of an electron to a helium atom of the nanodroplet proceeds at different resonance energies, each of which corresponds to a specific state. In the present work, clear experimental evidence of four different resonances for the formation of He^{2−} inside helium droplets is observed within a projectile electron energy range between 20 eV and 29.5 eV. The anion yield of He^{2−} is plotted as a function of the projectile electron energy and presented in Figure 1.

Four distinct structures clearly appear in the anion efficiency curve of He^{2−}. The threshold energy for the formation of He^{2−} corresponds to the onset of the first resonance found in the ion efficiency curve of He^{2−}. The threshold was determined to be 21±0.2 eV from the energy where ion yield is 0.1% of the maximum ion yield (vanishing current method). This threshold energy results from two components. The first is the energy required for the electron to penetrate the surface of the helium droplet. Very recently we reinvestigated the surface barrier energy with higher accuracy compared to previous studies [32]. This was possible by investigating low-energy electron attachment to the water dimer inside helium droplets with the HEM described in Section 2. We observed that the...
value for the barrier gets higher when the droplet size increases. In the experiment for the present data the droplet size was relatively big so the value for this barrier is considered to be 0.98 ± 0.05 eV [32]. The second is the energy needed to form the He* (19.82 eV) from ground state helium [20]. Thus the total electron impact energy required to form He"− inside a helium droplet adds up to 20.8 eV. This value is in agreement with the presently determined threshold value for He"− at 21 ± 0.2 eV. Electron attachment to pure helium droplets was previously investigated while utilizing an electron source having an energy resolution of about 250 meV. The onset of the anion formation at the projectile electron energy increases. It was shown in previous experiments employing electron beams with electron currents in the range of μA that the ion yield of He"− formation at a fixed electron impact energy shows a quadratic dependence on the electron current [20, 25]. In the present work, we confirm this quadratic dependence using an electron source producing electron currents in the nA range. A plot of the ion yield of the He"− formation at the projectile electron energy of 22 eV as a function of the electron current is presented in Figure 2. This plot confirms the proposed reaction mechanism that the ejection of He"− upon electron irradiation of large helium droplets is solely possible via a two-electron scattering process.

The first peak appearing around 22 eV is labeled as peak 1 in Figure 1. This peak is assigned to the formation of He"− (1s2s2p 4P) by the attachment of the scattered electron (bubble) to the excited He* (1s2s 3S). We note that in the case of doped helium droplets, ion induced dipole interaction between the He"− and the dopant will attract the two species and lead to several possible reactions, that remove the He"− and ionize the dopant [25]. Some of the possible reactions that can take place between He"− and the dopant are:

\[
\begin{align*}
\text{He}^{*}\text{−} + AB & \rightarrow \text{He}^{*} + AB^{−} \tag{1} \\
\text{He}^{*}\text{−} + AB & \rightarrow \text{He}^{+} + AB^{2−}\text{−} \tag{2} \\
\text{He}^{*}\text{−} + AB & \rightarrow \text{He} + AB^{−\text{−}} \rightarrow AB^{+} + 2e \\
& \quad \rightarrow A^{+} + B + 2e \\
& \quad \rightarrow AB^{2+} + 3e \\
& \quad \rightarrow A^{+} + B^{+} + 3e. \tag{3}
\end{align*}
\]

But only the first two reactions are leading to the formation of an anion, required to push a He"− out of the droplet. The second resonant structure around 23 eV is labelled as peak 2 in Figure 1. This resonance corresponds to the formation of He"− via electron attachment to a higher excited state of the helium atom, i.e., He* (1s2p P). The energy required to form this excited state from the ground state of neutral helium is 20.96 eV [34]. The resulting helium anion upon electron attachment is He"− (1s2p P)}
The excited state He$^*$ may contribute to the appearance of this \(25.78 \text{ eV}\) is labeled as peak 3 in Figure 1. Two different mechanisms may contribute to the appearance of this structure. The first mechanism is electron attachment to the excited state He$^*$ (1s3s $^3\text{S}$) of an isolated helium atom. This state is at an energy of 22.72 eV \[25\] above the ground state of a helium atom. The higher width of this peak also indicates contributions of higher excited states that are located between 22.72 eV and the ionization continuum at 24.59 eV but cannot be resolved due to the width of each individual contribution. Due to the fact that most of this structure is above the ionization threshold of helium, a resonance could come from the mechanism shown in reaction (4). Another possible mechanism is the formation of the He$^*$ accompanied by the formation of another anion. From the energy range of peak 4 we propose that the other anion is O$^-$ formed via dissociative attachment of an electron (DEA) that has been inelastically scattered at one of the He atoms to an O$_2$ dopant. O$^-$ formation from O$_2$ exhibits in gas phase a resonance at 6.5 $\pm$ 0.5 eV \[37\]. Thus the projectile electron requires a energy of 19.82 eV (He$^*$) +1.24 eV (energy barrier for electrons to enter the droplet) + 6.5 eV (DEA to O$_2$) = 27.56 eV.

Anion efficiency curves for He$^*$ were recorded covering the energy range of peak 1, while setting the nozzle temperature to three different values (6.8 K, 7.3 K, 7.6 K). The pressure of the helium gas was kept constant at 20 bar. The HEM was kept at the same conditions with the electron current around 70 nA. Using bi-Gaussian functions, the anion efficiency curves were fitted and the position and width of peak 1, were determined for the three different temperatures (see Fig. 3).

As the temperature of the nozzle drops, the mean droplet size of the formed helium droplets increases to larger values. A reduction of the temperature of the nozzle from 7.6 K to 6.8 K results in an increase of the average droplet size from \(N = 6 \times 10^6\) to \(2 \times 10^7\) helium atoms \[27\]. For higher average droplet size the position of peak 1 is slightly shifted by about 70 meV to higher energy. Such a blue-shift may be ascribed to the change in the anion efficiency curve of He$^*$ at 22 eV at different nozzle temperatures. A blue-shift of 70 meV is observed when changing the temperature of the He before the expansion from 7.6 K to 6.8 K.

### Table 2. The He$^*$ resonance peak position at different nozzle temperatures.

| Nozzle temperature (K) | Peak 1 position (eV) | FWHM     |
|------------------------|---------------------|----------|
| 6.8                    | 21.98 $\pm$ 0.05    | 0.69 $\pm$ 0.05 |
| 7.3                    | 21.95 $\pm$ 0.05    | 0.69 $\pm$ 0.05 |
| 7.6                    | 21.91 $\pm$ 0.05    | 0.69 $\pm$ 0.05 |

\[ e + \text{He} (1\text{S}) \rightarrow 2e + \text{He}^+ (2\text{S}) \rightarrow \text{He}^*_- (4\text{P}) \]. (4)
in the surface barrier of the droplets with different droplet sizes as predicted by Rosenblit and Jortner [38]. Also for large negatively charged He droplets Henne and Toennies reported an energy shift of almost 0.5 eV of the peak positions of the resonances when changing the average droplet size from $9.3 \times 10^{13}$ to $1.54 \times 10^{14}$. The same group also reported a blue-shift of the energy barrier for an electron to penetrate a helium droplet with increasing average droplet size [39]. Therefore, we tentatively assign the blue-shift of the resonance position for the formation of $\text{He}^{+} -$ with increasing average droplet size also to the rise of the energy barrier for the electron entering the He droplet.

4 Conclusion

In the experiments conducted in the present study, the positions of the $\text{He}^{+} -$ resonance peaks were determined with high precision and accuracy. The data were fitted using four bi-Gaussian curves allowing for the reproducibility of the asymmetry of the resonance structures and thus providing a more accurate determination of the maximum peak positions. Evidence of the formation of $\text{He}^{+} -$ via an intermediate $\text{He}^*$ that captures both low-energy secondary electrons was observed. The quadratic dependence of the yield of $\text{He}^{+} -$ on the electron current confirms the proposed model of the ejection of the swift $\text{He}^{+} -$ from a doubly or multiply charged anionic He droplet. The second negatively charged species can either be an electron bubble, another $\text{He}^*$ or a dopant anion. In the present study the latter is formed via dissociative electron attachment to O$_2$ which leads to a unique resonance at 27.7 eV.

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