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Electron ionization of superfluid helium nanodroplets doped with C\textsubscript{60} and small molecules

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Abstract. Helium droplets were co-doped with C\textsubscript{60} and ammonia, water or carbon dioxide and the resulting cluster size distributions of the produced cationic complexes are presented. Mass spectra obtained by electron ionization were recorded with high mass resolution of \(m/\Delta m\approx 6000\) (FWHM). Series of C\textsubscript{60}(H\textsubscript{2}O)\textsubscript{n}\(^{+}\), C\textsubscript{60}(NH\textsubscript{3})\textsubscript{n}\(^{+}\) and C\textsubscript{60}(CO\textsubscript{2})\textsubscript{n}\(^{+}\) complexes for \(n\) up to 20 molecules attached to the C\textsubscript{60} were observed among other cations. For C\textsubscript{60}-water cluster ions, the resulting size distribution revealed magic numbers for \(n=4\) and \(n=7\) water molecules attached to the fullerene. Ionic C\textsubscript{60}-ammonia complexes showed an enhanced stability in the cluster size distribution for \(n=4\) ammonia molecules attached as well. However, no intensity anomalies were observed for larger \(n\). For the nonpolar carbon dioxide, no magic numbers were found in the cluster size distribution of C\textsubscript{60}(CO\textsubscript{2})\textsubscript{n}\(^{+}\). These findings suggest that single carbon dioxide molecules are homogeneously distributed on the C\textsubscript{60}; in contrast to ammonia and water, where clusters are attached to the fullerene. In addition, dehydrogenation and protonation reactions of water and ammonia clusters on C\textsubscript{60} were observed in the present study.

1. Introduction

Helium nano-droplets offer a new avenue for the synthesis of novel and exotic molecular complexes and clusters [1,2]. Due to their high cooling efficiency, any molecule embedded will be quickly cooled down by evaporative cooling to the temperature of the droplet (0.37 K). Recently we started investigations of electron ionized C\textsubscript{60}-water complexes which revealed a local intensity maximum for 4 water molecules attached to the fullerene and in addition, ion-molecule reactions triggered by the double ionization of C\textsubscript{60} were observed [3,4]. Numerous experimental and theoretical studies address the interaction of water with C\textsubscript{60} cations or other carbonaceous seeds and provide new insights in many scientific fields, like astrophysics, medicine or atmospheric science [5]. A comparison of the findings for C\textsubscript{60}-water complexes with other C\textsubscript{60}-molecular complexes may contribute further to a better understanding of the reactions induced. For instance, ammonia is a good candidate due to its

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permanent dipole moment and its large proton affinity and indeed similar ion-molecule reactions can be observed for ammonia clusters on fullerenes [6].

In the present work, we compare the size distributions of $\text{C}_{60}(\text{H}_2\text{O})_n^+$, $\text{C}_{60}(\text{NH}_3)_n^+$ and $\text{C}_{60}(\text{CO}_2)_n^+$ clusters obtained after electron ionization of helium nanodroplets doped with the corresponding neutral clusters. By using a mass spectrometer with high resolution, each single peak of the isotope pattern of $\text{C}_{60}$ can be resolved and yields for the different ions can be compared. We focus here on local intensity maxima (magic numbers) in the cluster size distributions. Since water and ammonia are both polar molecules a similar behavior in the size distribution of the $\text{C}_{60}$-water/ammonia complexes may be expected. Enhanced stabilities for 4 and 7 water molecules attached to the $\text{C}_{60}$ can be found and furthermore a drop in intensity between 4 and 5 ammonia molecules attached to the fullerene is observed. In addition, a suppression of the proton-transfer reaction for small $n$ can be found for both systems on $\text{C}_{60}$. In contrast to $\text{C}_{60}(\text{H}_2\text{O})_n^+$ and $\text{C}_{60}(\text{NH}_3)_n^+$, the $\text{C}_{60}(\text{CO}_2)_n^+$ distribution shows no intensity anomalies up to $n=20$.

2. Experimental Setup

The present measurements were performed with a recently developed experimental setup in Innsbruck. The apparatus combines a powerful helium droplet source with a high-resolution time-of-flight mass spectrometer. A scheme of the setup is shown in Figure 1 and a detailed description can be found in [7]. The setup can be divided into 4 different stages: Helium droplet formation, pick up process, ionization and mass analysis.

A brief discussion of the experimental setup will be given: Helium droplets were formed by supersonic expansion of $^4\text{He}$ gas (purity 99.9999 \%) with high pressure and low temperature through a 5 $\mu$m nozzle. The new droplet source is able to cover a wide variety in temperature and He pressure (5 to 15 K and 15 to 30 bar). Within this operation range we were able to reach subcritical and supercritical expansion conditions. In a transition from a subcritical to a supercritical expansion the average helium droplet size changes from a few times $10^2$ to several $10^5$ - $10^6$ helium atoms (for the
exact cluster size dependencies on the expansion conditions see the diagrams presented in [2]). The pressure in the droplet formation region was kept below $5 \times 10^{-5}$ mbar with two turbomolecular pumps with a total pumping speed of 3300 l/s.

After formation, the He droplet beam passed a 0.8 mm skimmer to avoid shock waves and entered a differentially pumped chamber where the pick-up processes took place. The pick-up length was around 10 cm. It can be extended to 20 cm by an additional pick-up chamber. For this study, water, ammonia and carbon dioxide were introduced into the chamber by a pressure-controlled valve and a pick-up length of 10 cm was chosen. The base pressure in the pick-up chamber was kept below $10^{-6}$ mbar by two 70 l/s turbomolecular pumps. The $\text{C}_{60}$ was vaporized in an oven at a temperature of around 700 K. Leaving the pick-up region, the He droplet beam entered another differentially pumped chamber through a 2 mm skimmer. In this chamber the droplets crossed an electron beam of variable energy (from ~ 0 to 150 eV) and current (from 10 to 200 $\mu$A) and cations were formed. For the present measurements, the energy of the electrons was 70 eV. Ions, which were formed by interaction of the electron beam and the doped He droplets, were guided by a weak electrostatic field and accelerated to ~ 40 eV towards the entrance of the time of flight mass spectrometer. For the mass separation, a commercial reflectron time-of-flight mass spectrometer (Tofwerk AG, model HTOF) with a mass resolution $m/\Delta m \sim 6000$ (FWHM) was used. The ions were orthogonally extracted by a pulsed acceleration voltage (4.8 kV, 4 µs pulse length) and detected by a multi-channel plate after a flight length of about one meter. The base pressure in the ionization region and in the mass spectrometer was $10^{-7}$ mbar. The acquisition time of the time-of-flight spectra for these studies ranged from 30 min to 2 hours. The spectra were recalibrated (4th order polynomial function) after the measurement and the accuracy of the mass calibration exceeded 0.01 u.

3. Results and Discussion

3.1. Water Clusters on $\text{C}_{60}$

The helium droplets were doped with the fullerene $\text{C}_{60}$ and with water molecules. Expansion temperature and pressure of the helium were 8 K and 23 bar, respectively. For these measurements, the $\text{C}_{60}$ was evaporated in the oven at around 750 K and water vapour was introduced into the pick up region at a pressure of around $1.2 \times 10^{-5}$ mbar. In Figure 2 a section of the resulting mass spectrum is shown. Next to the dominant signal of pure $\text{C}_{60}^{+}$ at mass 720 u, a series of $\text{C}_{60}$-water complexes $\text{C}_{60}(\text{H}_{2}\text{O})_{n}^{+}$ appears. It is worth to mention, that the pure $\text{C}_{60}$ and the $\text{C}_{60}$-water cations appear in the mass spectrum not just as one single peak but as a series of several peaks, which are due to the isotopes of carbon. The natural abundance of $^{13}\text{C}$ is 1.07 % which is reflected in the isotopologues of $\text{C}_{60}^{+}$ (720 u – 100%, 721 u – 64.9%, 722 u – 20.7% and so on) [8]. For the evaluation of relative intensities of $\text{C}_{60}(\text{H}_{2}\text{O})_{n}^{+}$ complexes, this isotopic pattern has to be considered. A detailed description of our isotope correction treatment is given in [6]. Due to the high mass resolution of $m/\Delta m \sim 6000$ (FWHM) it is possible to fully resolve each peak, and the isotopic pattern can be taken into account in the determination of ion intensities. The inset in Figure 2 displays the size distribution of $\text{C}_{60}(\text{H}_{2}\text{O})_{n}^{+}$ for up to 20 water molecules attached to the fullerene. A correction of the isotopic distribution was included in this diagram.

The mass spectrum reveals two local intensity maxima in the ion yield; they are found at four and seven water molecules attached to the $\text{C}_{60}$ and are labelled in the inset of Figure 2. Magic numbers in a cluster size distribution often indicate enhanced thermodynamic stability with respect to monomer evaporation or reduced stability of the next larger cluster [9]. Computation of the evaporation energies of neutral water clusters shows a maximum for $n=4$ [10]. However, this calculated intensity anomaly cannot explain the observed magic numbers, as the energetics play no role in the assembling process of neutral clusters inside the helium droplet [11]. Hence, considering the energetics of charged clusters may explain the existing cluster size distribution. For example, for pristine water clusters the
stability of \((\text{H}_2\text{O})_4\text{H}^+\), which contains of an \(\text{H}_3\text{O}^+\) core and three water molecules bound to it by strong ion-induced dipole interaction, is well known [12]. Recent calculations of the binding energies of water clusters to \(\text{C}_{60}\) cations show clearly a maximum at \(n=4\) in the energy difference between clusters having \(n\) and \(n-1\) water molecules attached \((\Delta E(n)=E(n)-E(n-1))\) [13]. These calculations agree well with our observed cluster size distribution. The second observed magic number at \(n=7\) is less easy to explain. Although the calculations show a slightly enhanced difference in the binding energy for \(n=7\) with respect to \(n=6\), which would agree with our measurements, the computed \(\Delta E(n)\) for 8 water molecules attached is even higher. In contrast, the experimentally obtained size distribution does not show an enhanced yield for \(n=8\) and thus further investigations will be necessary in order to explain this local intensity maximum. We note that preliminary measurements of water attachment to \(\text{C}_{60}\) dimers show magic numbers for \((\text{C}_{60})_2(\text{H}_2\text{O})_4^+\) and \((\text{C}_{60})_2(\text{H}_2\text{O})_7^+\) as well (not shown).

3.2. Ammonia Clusters on \(\text{C}_{60}\)

A section of a mass spectrum of ammonia clusters and \(\text{C}_{60}\) embedded in helium droplets is shown in Figure 3. Experimental conditions were: source temperature 9.5 K, helium pressure 24 bar, \(\text{C}_{60}\) oven temperature 710 K and pressure in the ammonia pick up region \(1.7 \times 10^{-5}\) mbar. Series of dehydrogenated \(\text{C}_{60}\text{NH}_2(\text{NH}_3)_n^+\), unprotonated \(\text{C}_{60}(\text{NH}_3)_n^+\) and protonated ammonia \(\text{C}_{60}\text{NH}_4(\text{NH}_3)_n^+\) attached to the fullerene are observed. The inset of Figure 3 displays the size distribution of unprotonated water clusters attached to \(\text{C}_{60}\). Two pronounced intensity maxima are found at \(n=4\) and \(n=7\).

![Figure 2](image_url)
consistent with calculations of the bond energies by Petrie [14]. The computed energies were < 1.01 eV for \((C_{60}NH_3)^+\)-\(NH_3\) and < 0.25 eV for \(C_{60}^-\)-\(NH_3\) [14].

In contrast to \(C_{60}\)-water complexes, the ion series of \(C_{60}(NH_3)_n^+\) does not show pronounced local maxima at \(n=4\) and \(n=7\). However, there is a slight drop in the \(C_{60}(NH_3)_n^+\) yield between \(n=4\) and \(n=5\) that can be interpreted as a reduced stability of the \(C_{60}(NH_3)_5^+\) cluster compared to the \(C_{60}(NH_3)_4^+\) cluster.

**Figure 3.** Ammonia-\(C_{60}\) cluster ion yield arising from ionization of helium droplets doped with ammonia and \(C_{60}\) is shown. A series of \(C_{60}NH(NH_3)^+\)\(C_{60}(NH_3)_n^+\) and \(C_{60}NH_2(NH_3)^+\) complexes appear. In addition to the local intensity minimum at \(n=1\), a drop in the intensity between \(n=4\) and \(n=5\) can be found in the cluster size distribution of \(C_{60}(NH_3)^+\) (see inset).

3.3. Ion-molecule reactions of cold \(C_{60}\) covered with water and ammonia

The present results show that \(C_{60}\) suppresses the proton-transfer reaction that usually favors the appearance of protonated ammonia or water clusters. This leads to a pronounced change of the fragmentation patterns compared to studies of pure \(NH_3\) and \(H_2O\) clusters embedded in helium droplets [6]. A detailed discussion of the ion-molecule reactions of water or ammonia clusters with \(C_{60}\) can be found in [6]. To point out similarities between both systems, the key observations of our measurements are displayed in Figure 4 and summarized in the following itemized list.

- **\(C_{60}\) & ammonia**
  - The ion series \(C_{60}(NH_3)_n^+\) (unprotonated) and \(C_{60}NH_4(NH_3)_{n-1}^+\) (protonated) have a pronounced abundance minimum at \(n=1\).
  - The dehydrogenated component is strongest, in relative terms, for \(C_{60}NH_2^+\).
  - The unprotonated signal exceeds the protonated signal for small values of \(n\); the signals are about equal at \(n=5\); the protonated signal is largest for \(C_{60}NH_4(NH_3)_{4}^+\).

- **\(C_{60}\) & water**
The dehydrogenated component is strongest, in relative terms, for C$_{60}$OH$^+$. The unprotonated signal C$_{60}$(H$_2$O)$_n^+$ is stronger than the protonated signal C$_{60}$H$_3$O(H$_2$O)$_{n-1}^+$ for small $n$; the protonated ions have a maximum value at $n=4,7$. The akin behavior of dehydrogenated, unprotonated and protonated C$_{60}$-water and C$_{60}$-ammonia complexes may be a result of the large and very similar proton affinities, namely 8.84 eV for H$_2$O and 7.16 eV for NH$_3$ [15]. Another parallel is the large difference between the first ionization energy of C$_{60}$ (7.60 eV) and H$_2$O (12.62 eV) or NH$_3$ (10.07 eV) [15]. This suggests that the ion complex consists of a neutral water or ammonia cluster weakly attached to C$_{60}$. With increasing cluster size $n$, an increase in the net charge that is localized on the ammonia or water cluster can be expected and thus would tend toward the formation of protonated cluster ions for larger $n$. A similar behavior was also observed for water and ammonia clusters with (C$_{60}$)$_n$-aggregates ($n=2,3$) [6].

Figure 4. Comparison of the cluster size distribution of charged C$_{60}$-water and C$_{60}$-ammonia complexes. Distributions are given for the dehydrogenated, unprotonated and protonated clusters.

3.4. Carbon dioxide on C$_{60}$
In addition to the measurements described in section 3.1 to 3.3 we also doped helium droplets with the nonpolar CO$_2$ molecule and the fullerene C$_{60}$. The helium was expanded at 8.5 K and 23 bar, the CO$_2$ pick up pressure was $1.9 \times 10^{-5}$ mbar and the evaporation temperature of C$_{60}$ was $\sim 700$ K. Under these conditions we were able to detect a series of C$_{60}$(CO$_2$)$_n^+$ peaks; a section of the mass spectrum of this measurement is shown in Figure 5. At mass 720 u the pure C$_{60}^+$ appears as the dominant signal followed by C$_{60}$(CO$_2$)$_n^+$ with $n$ up to 20 carbon dioxide molecules. Furthermore, a peak at mass 738 u is apparent that corresponds to C$_{60}$H$_2$O$^+$, which is due to residual water. There are also several peaks between the main series of C$_{60}$(CO$_2$)$_n^+$. These additional peaks are combinations of water, carbon dioxide, carbon monoxide and oxygen attached to the C$_{60}$, like C$_{60}$(CO$_2$)$_n$(H$_2$O)$_m^+$, C$_{60}$(CO$_2$)$_n$CO$^+$.
$C_{60}O(CO_2)_n^+$ and so on; the latter two products likely arise from ion molecule reactions in the ionized $C_{60}$-carbon dioxide complex.

Even though $C_{60}$ was substantially covered with carbon dioxide and complexes of the form $C_{60}(CO_2)_n^+$ were observed, no pronounced intensity anomalies appeared for $n<20$. This observation may lead to the suggestion that $C_{60}$ is homogeneously covered with carbon dioxide molecules and no structures with enhanced stability are present. In very recent measurements investigating the decoration of fullerenes with other nonpolar molecules like H$_2$ or CH$_4$, we have obtained the same behavior [16,17]. At this point it is worth to mention that for example the complexes of $C_{60}(H_2)_n^+$ show no intensity anomalies for $n<32$. However, from $n=32$ to $n=33$ a pronounced drop in the yield occurs which coincides with the number of faces of the fullerene. It would be interesting to see, if $C_{60}(CO_2)_n^+$ also shows a drop in intensity between $n=32$ and $n=33$. This question will be addressed in future experiments.

![Graph](image)

**Figure 5.** Section of a mass spectrum of $C_{60}$ and CO$_2$ embedded in helium droplets. Next to the $C_{60}^+$, a series of $C_{60}(CO_2)_n^+$ appears. The cluster size distribution for $C_{60}$-carbon dioxide complexes is displayed in the inset for up to 20 CO$_2$ molecules attached.

4. **Summary**

In the present study we showed that a variety of reactions occurs in helium nano-droplets doped with clusters of fullerenes and small molecules upon electron ionization. The results for three molecular dopants studied, water, ammonia and carbon dioxide, indicate that the dipole moment of the co-embedded small molecule controls the arrangement of these dopants on the surface of $C_{60}$. While for polar molecules (water and ammonia) magic numbers can be observed in the mass spectra, the non-polar carbon dioxide shows smoothly changing cluster abundance in the corresponding mass spectrum. Water and ammonia molecules may therefore form compact clusters which are attached to a
fullerene unit. In contrast, carbon dioxide molecules may homogenously cover the fullerene surface as recently observed for molecular hydrogen.

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