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Atomically resolved phase transition of fullerene cations solvated in helium droplets

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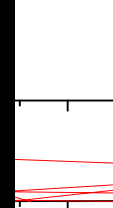
Helium has a unique phase diagram and below 25 bar it does not form a solid even at the lowest temperatures. Electrostriction leads to the formation of a solid layer of helium around charged impurities at much lower pressures in liquid and superfluid helium. These so-called 'Atkins snowballs' have been investigated for several simple ions. Here we form $\text{He}_n\text{C}_{60}^+$ complexes with n exceeding 100 via electron ionization of helium nanodroplets doped with C_{60} . Photofragmentation of these complexes is measured by merging a tunable narrow-bandwidth laser beam with the ions. A switch from red- to blueshift of the absorption frequency of $\text{He}_n\text{C}_{60}^+$ on addition of He atoms at $n = 32$ is associated with a phase transition in the attached helium layer from solid to partly liquid (melting of the Atkins snowball). Elaborate molecular dynamics simulations using a realistic force field and including quantum effects support this interpretation.

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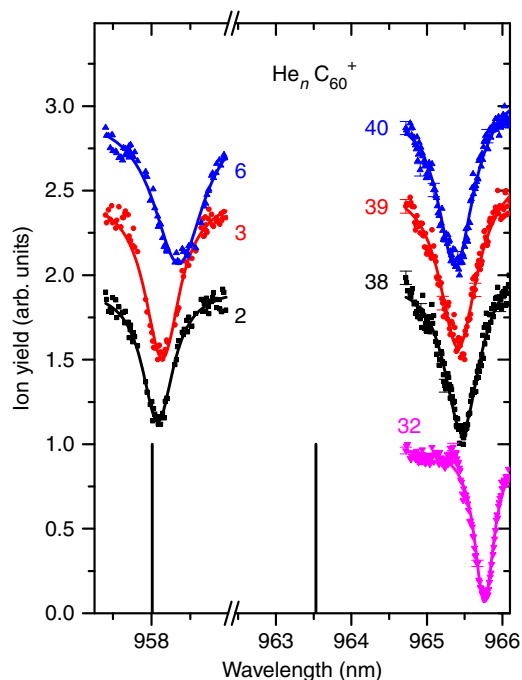


Figure 2 | Ion signal depletion. Wavelength scans near 958 and 964 nm for seven different cluster sizes (solid symbols) together with the position of the resonance of the electronic transition for the bare C_{60}^+ , taken from ref. 9 and corrected from air to vacuum (vertical lines). Error bars indicate the s.d. of the ion yield. Photoabsorption depletes the ion signal to minima at different wavelength positions with a line width of about 0.2 to 0.6 nm (full width at half maximum). The solid lines represent Lorentzian profiles fitted to the data.

number of helium atoms results in a sharp kink to smaller absorption wavelengths due to the displacement of helium atoms from the pentagonal central sites. Theoretical studies predict, at this point, the formation of a mobile (liquid) layer intermixed with a solid part (the 20 He atoms that occupy the positions above the centre of the hexagons)^{24,25}. A pronounced intensity drop in the mass spectra (see Fig. 1) at around $n = 60$ indicates a shell closure at this cluster size. We note that the red shift for $He_{60}C_{60}^+$ is the same as for $He_{20}C_{60}^+$, thus—in agreement with the theoretical studies^{24,25}—indicating that only He atoms positioned above the centre of the 20 hexagonal faces of the fullerene cage are significantly involved in the interaction with C_{60}^+ . The increased red shift from 60 to 80 attached helium atoms can be attributed to the influence of the outer helium ad-layer. Beyond $n = 80$, we observe an almost constant resonance wavelength. It is possible that this constant absorption wavelength coincides with the onset of superfluidity.

To support the above picture, we have performed elaborate MD simulations by using the realistic force field introduced in ref. 25 and including quantum effects. By combining the results of these simulations with a simple model that describes the van der Waals (vdW) interaction between C_{60}^+ and the surrounding helium atoms, we have evaluated the energy shifts in the ground and first excited states of C_{60}^+ as a function of the number of helium atoms. The calculated line shifts are also included in Fig. 3 (open squares). The theoretical results show an impressive qualitative similarity to the experiments, with an initial linear increase in the peak wavelength, culminating in a peak in this red shift at $n = 32$, followed by a gradual decrease and bottoming out around $n = 60$, before slightly increasing again. The Supplementary Fig. 4 shows calculated line shifts including and neglecting quantum effects in comparison with the experimental data. Without quantum effects,

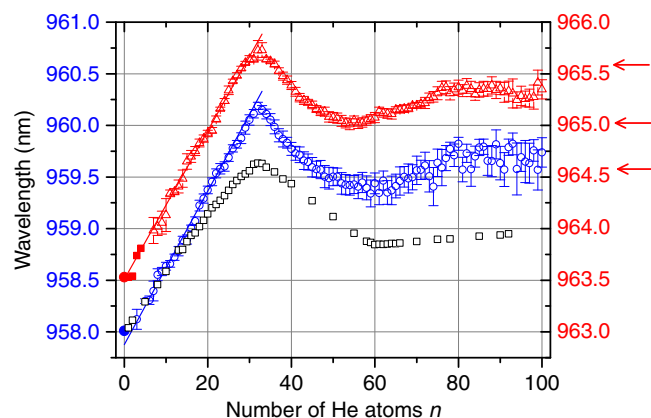


Figure 3 | Absorption wavelength as a function of He atoms attached.

Centre positions for the absorption spectra of $He_n C_{60}^+$ around 958 nm (blue open circle, left y axis) and 964 nm (red open triangle, right axis) plotted as a function of n , the number of helium ad-atoms on the fullerene ion surface. The error bars indicate s.e.m. of the centre position of the Lorentzian profiles fitted to the ion signal depletion (see Fig. 2). The absorption wavelengths (corrected to vacuum) that were obtained for zero to a few helium atoms by Maier and colleagues⁹ are indicated by the bold symbols. The red arrows indicate the wavelengths at which the mass spectra shown in Fig. 1 were measured. The open grey squares represent calculated absorption wavelengths for $He_n C_{60}^+$ including quantum effects, renormalized by a factor of 1.0008.

the local minimum in the line shift is located around $n = 70$, whereas calculations including quantum effects and the experiment reveal such a minimum at $n = 60$. Furthermore, also the slope of the blue shift from $n = 32$ to this minimum agrees better with the experiment when including quantum effects.

The trends in the shifts of absorption wavelength with increasing number of helium atoms is reminiscent of the vibrational bandshifts measured by McKellar and colleagues^{27,28} in neutral molecule— He_n clusters, which were also interpreted in terms of solvation shell closures. As in the present case, the shifts clearly depend on the helium–dopant interactions.

The weaker lines close to the 937 and 943 nm C_{60}^+ electronic absorption bands show similar wavelength shifts for helium physisorption (see Supplementary Fig. 3). Extrapolation of all spectra to bare C_{60}^+ yields the line positions of 936.74 ± 0.01 , 943.02 ± 0.02 , 957.91 ± 0.016 and 963.52 ± 0.03 nm, in agreement with the data from Campbell *et al.*^{9,16} once corrected to vacuum, since all present data are obtained in vacuum.

The spectroscopic investigation of an Atkins snowball provides unprecedented details about the solvation of ions by helium. By choosing ions with different corrugation and curvature, the balance between surface and mutual interaction can be systematically varied and its effect on the helium phase transitions studied in detail. The theoretical procedure applied in this study is a suitable routine for prescreening the effect of messenger helium atoms to various molecules prior their experimental investigations. In addition, our study demonstrates that doped helium nanodroplets provide a powerful tool to study the spectroscopic characteristics of cations or transient species under isolated and cold conditions relevant to outer space. The weak matrix effect of helium has been used by Maier and colleagues⁹ to convincingly attribute two DIBs to the cation C_{60}^+ and predict—and recently tentatively confirmed—three additional DIB transitions^{15,16}. The linear wavelength shift in our study demonstrates that the absorption wavelength of species isolated in He droplets can be accurately predicted to better than 0.05 nm through extrapolation, and in the wavelength domain of the C_{60}^+ bands investigated here, this is comparable to the accuracy

of astronomical observations. Therefore, this technique provides a convenient way to systematically investigate the absorption spectra of astrophysically relevant species, including smaller fullerenes, polycyclic aromatic hydrocarbons and their derivatives that were shown to be linked to fullerene formation in space²⁹, and may be possible carriers of the other unidentified DIBs.

Methods

Experimental. We have prepared fullerene–helium ion complexes by loading C₆₀ molecules into helium nanodroplets and subsequent ionization via electron impact. The resulting ions are analysed by a high-resolution reflectron, time-of-flight mass spectrometer (Tofwerk AG, model HTOF). The details of this experiment have been described previously³⁰. The high resolution of the mass spectrometer is used to assign the fullerene–helium ion clusters to their specific atomic composition, because isobaric mass differences of clusters with nominally the same mass are easily resolved. For example, pure He_(180+n) clusters are distinguished from He_nC₆₀⁺ due to their mass difference of 0.469 u. After ionization and before detection in the mass spectrometer, the cluster ions are subjected to the radiation of a continuous-wave titanium sapphire (Ti:Sa) laser (Sirah Matisse TR, 10 MHz bandwidth and 0.6 W power). If the Ti:Sa laser hits an electronic transition in the C₆₀⁺ core, the photo-absorption followed by radiative or non-radiative decay heats up the ion. This triggers evaporation of the weakly bound helium atoms, which is detected as a depletion of the respective cluster signal. In the experiment, mass spectra of all helium cluster ions are taken at the same time, whereas the laser frequency is scanned. An animated sequence of a section of the mass spectra from $m/z = 730$ until $m/z = 990$ as a function of the laser wavelength is shown in the Supplementary Movie 1. This new technique allows for an efficient parallel recording of the absorption spectra of all cluster ions simultaneously and enables systematic studies on the effects of size on the interaction of helium adsorbents.

General theoretical model. The vdW interaction between helium atoms and the C₆₀⁺ cation comes from two parts: (i) the charge/induced dipole interaction between the C₆₀⁺ cation and the helium atoms, and (ii) the London dispersion interaction between helium atoms and the cage. As a simple approximation, we consider the highly symmetrical C₆₀⁺ cage as an isotropic sphere. Then, the vdW interaction energy between a single He atom and the C₆₀⁺ cage can be estimated as^{31–33}

$$E_{\text{int}} = E_{\text{ind}} + E_{\text{disp}} = -\frac{e^2 \alpha_{\text{He}}}{2(4\pi\epsilon_0)^2 R^4} - \frac{3}{2} \frac{\text{IP}_{\text{He}} \text{IP}_{\text{C}_{60}^+}}{\text{IP}_{\text{He}} + \text{IP}_{\text{C}_{60}^+}} \frac{\alpha_{\text{He}} \alpha}{(4\pi\epsilon_0)^2 R^6} \quad (1)$$

where R is the distance of the He atom to the centre of the C₆₀⁺ cage, α_{He} and α are the polarizabilities of He and C₆₀⁺, respectively, and IP_{He} and $\text{IP}_{\text{C}_{60}^+}$ are the first ionization potentials of He and C₆₀⁺, respectively. As can be seen, E_{ind} only depends on the polarizability of the helium atom and the distance between the latter and the cage centre. Therefore, E_{ind} is expected to be the same for the ground and the first excited state of C₆₀⁺. The dispersion interaction E_{disp} depends on the polarizability of C₆₀⁺ (as we will see below), which can change noticeably on electronic transition, thus leading to different shifts on the energy levels of the ground and excited states of C₆₀⁺. Therefore, here we only need to consider the dispersion interaction to account for the line shifts observed in the experiments.

Hence, the variation of the energy difference between the first excited state $|1\rangle$ and the ground state $|0\rangle$ of He_nC₆₀⁺ (that is, the line shift) will be given by

$$h\Delta\nu = E_{\text{int}}^1 - E_{\text{int}}^0 = -\frac{3}{2} \frac{\text{IP}_{\text{He}} \text{IP}_{\text{C}_{60}^+}}{\text{IP}_{\text{He}} + \text{IP}_{\text{C}_{60}^+}} \frac{\alpha_{\text{He}}}{(4\pi\epsilon_0)^2} \left(\sum_{i=1}^n \frac{1}{R_i^6} \right) \Delta\alpha \quad (2)$$

where R_i is the distance between the i -th helium atom and the cage centre, and $\Delta\alpha = \alpha_1 - \alpha_0$ is the difference of polarizability between the ground and the first excited state of C₆₀⁺. In equation (2), we can use the experimental values: $\alpha_{\text{He}} = 1.383746$ a.u.^{34,35}, $\text{IP}_{\text{He}} = 24.59$ eV³⁶ and $\text{IP}_{\text{C}_{60}^+} = 11.59$ eV³⁷. The distances R_i have been obtained from the MD simulations described below (see section MD simulations). To calculate $\Delta\alpha$, which, as we will show below, is of the order of a few tens of atomic units, ideally one should perform high-level *ab initio* calculations. However, these are not feasible for such large systems. Instead, we have used a straightforward model that allows us to estimate the magnitude of $\Delta\alpha$.

Particle-on-a-sphere model to estimate $\Delta\alpha$. For the polarizability of aromatic molecules such as C₆₀, it has been pointed out that σ -orbitals give the same contribution to the excited state as to the ground state³⁸. Therefore, we will only consider π -orbitals to calculate $\Delta\alpha$. The simplest way to describe the π electrons of C₆₀⁺ is by using the particle-on-a-sphere model, that is, a particle confined to the 2D surface of a sphere, which is known to have exact solutions of the Schrödinger equation³⁹. The eigenfunctions are spherical harmonics $Y_l^m(\theta, \varphi)$ ($l = 0, 1, 2, \dots; m = 0, \pm 1, \dots, \pm l$) and the eigenenergies are given by

$$E_{l,m} = \frac{\hbar^2}{2m_e R_s^2} l(l+1) = \frac{e^2 a_0}{(4\pi\epsilon_0) 2R_s^2} l(l+1) \quad (3)$$

where R_s is the radius of the sphere and a_0 the Bohr radius.

The wave function of the ground state of C₆₀⁺ can be written as a 59×59 Slater determinant:

$$\Psi = \left| Y_0^0 \bar{Y}_0^0 \dots Y_5^2 \bar{Y}_5^2 Y_5^{-2} \bar{Y}_5^{-2} Y_5^1 \bar{Y}_5^1 Y_5^{-1} \bar{Y}_5^{-1} Y_5^0 \right| \quad (4)$$

$$\equiv \left| \dots 5_2 \bar{5}_2 5_{-2} \bar{5}_{-2} 5_1 \bar{5}_1 5_{-1} \bar{5}_{-1} 5_0 \right| \quad (5)$$

In the last abbreviated notation, only unpaired electrons and the highest occupied molecular orbitals are indicated.

According to perturbation theory, polarizability only comes from the second-order interaction energy, since the first-order perturbation is vanishing due to the odd parity of the dipole operator. The polarizability tensor of the ground state C₆₀⁺ is then calculated as

$$\alpha_{0}^{uv} = 2 \sum_i \frac{\langle \Psi_0 | \mu_u | \Psi_i \rangle \langle \Psi_i | \mu_v | \Psi_0 \rangle}{E_i - E_0} \quad (6)$$

As a result of spherical symmetry, the polarizability tensor is isotropic:

$$\alpha_0 \equiv \alpha_{0}^{uv} = \alpha_{0}^{zz} = 2e^2 \sum_{i>0} \frac{|\langle \Psi_0 | \mu_z | \Psi_i \rangle|^2}{E_i - E_0} \quad (7)$$

By using the above expression, it is easy to evaluate the polarizabilities for the ground and first excited states of C₆₀⁺ (see Supplementary Methods, in particular Supplementary Equations 14 and 28). Hence, the polarizability difference between the first excited and the ground state of C₆₀⁺ is

$$\Delta\alpha = 2e^2 \left[\frac{(3_0 | 4_0)^2}{E_4 - E_3} + \frac{(5_0 | 6_0)^2}{E_6 - E_5} - 2 \frac{(4_0 | 5_0)^2}{E_5 - E_4} \right] \quad (8)$$

which from equation (3) and (Supplementary Methods 2) can be written as

$$\Delta\alpha = \frac{80}{9,009} \cdot \frac{4\pi\epsilon_0 R_s^4}{a_0} \quad (9)$$

By using the actual value of the C₆₀ radius, which is $6.7 a_0$ (refs 40,41) equivalent to the distances between the geometrical centre of the cage and the carbon atoms, the estimated value of $\Delta\alpha$ is 18 a.u.

Molecular dynamics simulations. To determine the values of the R_i distances required in equation (2), we have performed MD simulations for the He_nC₆₀⁺ systems by

using the DL-POLY2 code⁴² and the force field introduced in ref. 25. This force field, obtained by fitting a large set of density functional theory (DFT) and coupled-cluster calculations (on the CCSD(T) level), was successfully used in ref. 25 to explain the multi-shell structure of He_nC₆₀⁺ observed in the experiments.

Quantum effects and dispersion corrections have also been included. The dispersion correction to the DFT energy is included for helium–carbon interactions, following Grimme's DFT-D2 scheme⁴³:

$$E_{\text{disp}} = -\frac{s_6}{2} \sum_{i,j} \frac{C_6^{ij}}{r_{ij}} f_{\text{damp}}(r_{ij}) \quad (10)$$

where the summation is over all pairs of atoms i and j ; C_6^{ij} is the dispersion coefficient for atom pairs i and j ; s_6 is a scaling factor depending on the functional, r_{ij} is the distance between atoms i and j , and $f_{\text{damp}}(r_{ij})$ is a damping function so that the dispersion correction takes effects only for long-range interactions. In our simulations, instead of using the recommended values⁴³, we have calibrated parameters s_6 and C_6^{ij} , on the basis of high-level *ab initio* calculations (MP2 with complete basis set) for He-pyrrylene⁺ systems.

The quantum effects have been taken into account using Feynman–Hibbs model, where the distribution of quantum particles is approximated by using a Gaussian packet. Accordingly, we have generated an effective Feynman–Hibbs potential from our *ab initio* potential $U(r)$ to second order in $\hbar^{44,45}$:

$$U_{\text{FH}}(r) = U(r) + \frac{\hbar^2}{24\mu k_B T} \left[U''(r) + 2 \frac{U'(r)}{r} \right] \quad (11)$$

where μ is the reduced mass of the two particles, k_B the Boltzmann constant and T the simulation temperature.

We have tried different initial configurations, including low- and high-energy ones, to guarantee a meaningful statistical sampling of the system. In all calculations, the system was initially heated to 10 K and then slowly cooled at a rate of 0.1 K per 50 ps. Once the system reached 4 K, which is close to the estimated temperature of He_nC₆₀⁺ under our experimental conditions, the simulation was run for another 5 ns, to ensure full equilibration and to collect statistical information. In all cases, periodic boundary conditions were applied to prevent escape of He atoms.

With all the ingredients at hand, we are now able to predict the line shifts observed in the absorption spectra of He_nC₆₀⁺, by substituting in equation (2) the calculated values of $\Delta\alpha$ (section 2) and $\sum_{i=1}^n \frac{1}{R_i^6}$ (section 3). In the latter case, the summation is averaged over the last 2 ns of the simulation. We have also used a cutoff radius of 6.7 Å to exclude He atoms from the second and further shells²⁵, because, as indicated by the experimentally measured line shifts and widths, the He–C₆₀⁺ interaction is much more effective for He atoms belonging to the first shell.

Data availability. The data that support the findings of this study are available from the corresponding author upon request.

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Author contributions

A.L., R.W. and P.S. conceived the project. M.K., S.S., M.S., M.R., J.P. and S.R. carried out the bulk of the experimental work. Y.W., M.A. and F.M. carried out theoretical calculations. H.L., A.G.G.M.T., J.C., M.K.B., A.M., A.L. and P.S. wrote the manuscript. P.S. oversaw all the works. All the authors discussed the results and commented on the manuscript.

Additional information

Supplementary Information accompanies this paper at <http://www.nature.com/naturecommunications>

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