Spectroscopic wavelength shifts characterizing the phase transition of helium adsorbed on fullerene cations

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Synopsis Using high-precision spectroscopy and elaborate MD simulations, we have studied the absorption lines of the $He_nC_{60}^+$ ($n \leqslant 100$) complex formed via electron ionization of helium nanodroplets doped with C_{60}. The observed variation of wavelengths with the number of He atoms provides clear evidence of the phase transition of helium adsorbed on C_{60}^+ cations.

The mysterious character of the diffuse interstellar bands (DIBs) had puzzled scientists until very recently, when four DIBs were unequivocally assigned to C_{60}^+ by laboratory spectroscopy [1]. Inspired by this seminal work, we have conducted a combined spectroscopic and molecular dynamics (MD) simulation study on the $He_nC_{60}^+$ complex with n exceeding 100 via electron ionization of helium nanodroplets doped with C_{60} [2]. In the experiments, C_{60}^+ is solvated in helium nanodroplets, with a few to several thousand He atoms attached to the molecular ion. By studying the influence of the weakly interacting matrix helium on the absorption spectra, the absorption lines of the bare ion can be deduced with outstandingly high precision.

Fig. 1 shows the center positions for the photodepletion of $He_nC_{60}^+$ ($n = 2$–100) as a function of n. For the two electronic transitions around 958 nm and 963.5 nm, we observe a remarkably linear redshift of 0.07 nm per He atom until $n = 32$, where He atoms fully occupy the hexagonal and pentagonal faces of C_{60}^+. The addition of more He atoms gives rise to a pronounced blueshift, due to the displacement of He atoms from pentagonal faces into a farther adlayer, as revealed by MD simulations [3]. In this second adlayer, He atoms are mobile behaving like liquid. The blueshift continues to be observed up to $n = 60$, where the adlayer consists of 20 immobile He atoms above hexagons and 40 mobile delocalized ones. Beyond $n = 80$, the absorption lines do not change, implying the onset of superfluidity.

The observed phase transitions are supported by elaborate MD simulations including quantum effects [3]. By combining MD results with a model that describes the van der Waals interaction of the ground and first excited states of C_{60}^+ with the surrounding He atoms, the wavelength shifts have been evaluated, showing an impressive similarity to the experiments.

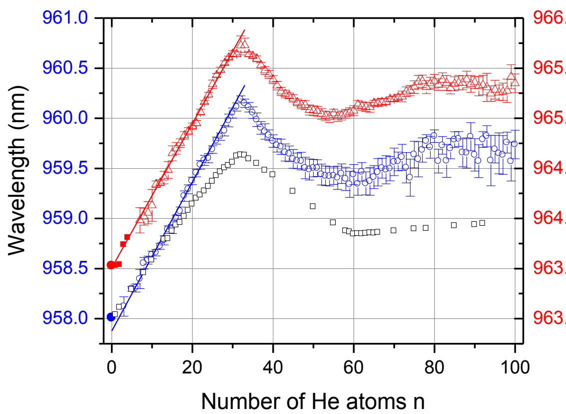

Figure 1. Center positions for the absorption spectra of $He_nC_{60}^+$ around 958 nm (blue circles, left y-axis) and 963.5 nm (red triangles, right y-axis), as a function of n. Simulated wavelengths are plotted as black squares.

References

[1] E. K. Campbell *et al.* 2015 *Nature* **523** 322

[2] M. Kuhn *et al.* 2016 *Nat. Commun.* **7** 13550

[3] C. Leidlmair *et al.* 2012 *Phys. Rev. A.* **108** 076101

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