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Shell completion of helium atoms around the coronene cation

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ABSTRACT

Recent mass spectrometry measurements carried out for the coronene ($C_{24}H_{12}$) cation coated with helium atoms have revealed special stabilities associated with 'magic numbers' at sizes 38, 41, and 44, the latter being interpreted as the signature of a complete first solvation shell. In the present contribution we examine by means of path-integral molecular dynamics simulations employing a polarizable potential the equilibrium structures of such clusters and how they differ from the classical global minima. Our results confirm the special energetic stability of the suggested sizes and the highly symmetric geometric arrangement of the helium atoms around the aromatic cation. However, they also indicate that the helium atoms in the vicinity of the aromatic plane are highly fluxional and not associated with a unique local minimum in the energy landscape. Above the size of 44, the shell expands but remains stable with no immediate evidence for a second shell.

1. Introduction

Helium binds very weakly to graphitic surfaces and at sufficiently low temperature forms a $\sqrt{3} \times \sqrt{3}$ commensurate monolayer in which superfluidity is suppressed [1]. Graphene also binds helium, but the interaction and corrugation are both lower, resulting in the melting of the adsorbed helium film [2]. Polycyclic aromatic hydrocarbons (PAHs) can be seen as a finite piece of graphene in which the outer carbon atoms are saturated by hydrogens. PAHs have been the subject of an increasing attention in the recent years owing to their relevance in soot formation mechanisms [3], their possible role in health sciences as pollutants [5] or carcinogenic products [6] but also their likely presence in interstellar media [4] and capability to host a significant fraction of carbonaceous matter in such cold environments. PAHs have been synthesized in helium droplets by irradiation of smaller hydrocarbon partners [7], and very recently the controlled adsorption of ^{4}He on the coronene cation has been experimentally addressed by mass spectrometry in the Scheier group [8]. The measurements have revealed a series of particularly stable sizes or 'magic numbers', the coronene$^+$He$_n$ complex exhibitting higher abundances at the sizes 38, 41, and 44 and a strong drop above this size. These numbers were interpreted based on geometric considerations on commensurate filling at $n = 38$, then with the additional adsorption of 3 and 6 atoms at threefold symmetric sites in the aromatic plane [8].

Magic numbers in cluster physics usually convey the filling of geometric or electronic shells [9] but for chemically heterogeneous systems such as helium-coated carbonaceous cations the situation appears not trivial in general. For example, $C_{60}^+He_n$ display two magic numbers at sizes 32 and 60, only the first being clearly associated with the complete coverage of the fullerene with helium atoms above the centers of 12 pentagonal and 20 hexagonal rings [10]. In contrast, the enhanced stability at 60 atoms was shown [11,12] to result from the particular conditions met by the helium monolayer, which at this size occupies an optimal shell with a particular radius around the fullerene, allowing it to be locked and move as a whole, clusters with neighboring sizes displaying disorder and a fluxional dynamics.

The coating of PAHs by helium atoms has been theoretically addressed in the past [13–19], and it was generally shown that the adsorption process is strongly anisotropic, atoms next to aromatic facets being much more tightly bound than atoms close to the aromatic plane. In a recent computational exploration of such compounds [20] these weakly bound peripheral atoms were described as forming a 'slush' phase intermediate between the solidlike state experienced by the atoms adsorbed on either side of the graphitic plane and the liquidlike phase characteristic of the more distant helium shells.

In the present contribution we revisit coronene$^+$He$_n$ van der Waals complexes in the light of the more recent experimental data of Kurzthaler and coworkers [8], focusing on the magic numbers

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identified in this study, using the methodology already developed in Ref. [20] but also some ideas borrowed from a related work [21] in order to assist data interpretation. Of particular interest here is the relation between classical and quantum results, geometric magic numbers being necessarily connected to a well-defined structure whereas quantum effects may either reorder minima among each other through different zero-point energy corrections or even compromise the structural stability of specific structures.

We have thus investigated the stability of helium clusters coating the coronene cation in the size range relevant to the mass spectrometry measurements, and identified whether the structural motifs proposed by these authors can indeed be responsible for the observed behavior. Our computational work confirms the interpretation of the magic number at 38 atoms as resulting from commensurate adsorption on the aromatic facets, but sheds a different light on the two other remarkable sizes of 41 and 44 atoms: Although they can indeed be depicted as the additional adsorption of 3 or 6 atoms in threefold symmetric sites, they do not correspond to well-defined structures in the classical sense but to partially delocalized clouds covering multiple minima in the energy landscape. In addition we find that above the size of 44 additional atoms are much less bound, but also contribute to expanding the single shell around the cationic dopant. No sign of a second shell is still found at 55 atoms, indicating that as in the case of $C_{60}^{+}He_n$ at size 60 [11] the drop seen experimentally [10] in the mass abundances above size 44 may not necessarily be associated with geometric shell closing, but merely to a drop in binding energy.

2. Model and methods

The general computational strategy relies on a fully atomistic modeling of the (fixed) coronene cation in contact with n (mobile) ^{4}He atoms. These atoms interact with each other through the accurate Aziz-Jenzen pair potential [22], and with the PAH via a sum of pairwise terms with all carbon and hydrogen atoms, as well as a polarization contribution. The carbon-helium and hydrogen-helium interactions account for the short-range Pauli repulsion and the long-range dispersion attraction, with a functional form similar to the Aziz-Jenzen potential given in Ref. [22]. The polarization contribution arises from the global charge carried by the coronene cation, represented by a set of partial charges on each carbon or hydrogen atom and derived from the standard RESP procedure and that can be found in the supplementary material of Ref. [20]. The polarization interaction is also explicitly detailed in Ref. [20] and was used here without any modification.

We first search for low-energy structures by performing basin-hopping [23] global optimization for systems containing between 35 and 55 helium atoms. For each size, 5 series of 10,000 Monte Carlo steps followed by local minimization were attempted and accepted based on a Metropolis criterion at 10 K, the maximum amplitude of the collective random displacements being fixed to 5 Å. Once good low-energy candidate structures were located, path-integral molecular dynamics (PIMD) trajectories were conducted at $T = 1$ K and using a Trotter discretization number of $P = 128$. More details about the PIMD methodology can be found in our earlier paper [20], and will not be repeated here for the sake of brevity. The PIMD trajectories were propagated over 1 ns using a time step of 1 fs, and several properties or indicators were calculated along them. The quantum energies were evaluated using the standard virial estimator [24], and we also quantified the amount of delocalization in the system from the overall spreading $\langle\sigma\rangle$ of the nuclear wavefunction [20],

$$\langle\sigma\rangle = \frac{1}{n}\sum_{i=1}^{n}\sigma_i \tag{1}$$

$$\sigma_i = \frac{1}{P}\sum_{\alpha=1}^{P}\left[\left\langle \mathbf{r}_{\alpha,i}^2\right\rangle - \left\langle \mathbf{r}_{\alpha,i}\right\rangle^2\right]^{1/2} \tag{2}$$

where we have denoted by $\mathbf{r}_{i,\alpha}$ the position of monomer α ($1 \leqslant \alpha \leqslant P$) of helium atom i in the path-integral representation, the cyclic condition $\mathbf{r}_{i,\alpha+1} = \mathbf{r}_{i,1}$ being used for all atoms.

The atom-resolved Lindemann index δ_i is defined from the fluctuations of the interatomic distances with other helium atoms, here taken from the centroids of the ring polymers [11,20]:

$$\delta_i = \frac{1}{n-1}\sum_{j\neq i}\frac{\sqrt{\left\langle r_{ij}^2\right\rangle - \langle r_{ij}\rangle^2}}{\langle r_{ij}\rangle} \tag{3}$$

The Lindemann index yields direct insight into the degree of mobility of individual atoms, low values of $\delta_i < 5\%$ being associated with a rigidlike vibrating motion whereas values above 10–15% are indicative of well-developed fluidlike, delocalized motion. As shown earlier [20] the fluxional dynamics in the present systems may not be so clear cut between solid and liquid, helium atoms closer to peripheral hydrogens undergoing some 'slushy' dynamics manifested by intermediate values of the Lindemann index.

The amount of delocalization in the energy landscape was also monitored, following our own earlier work [20,25], by systematically optimizing configurations sampled from the PIMD trajectories to their closest local minimum or inherent structure (IS). Here again a classical behavior would correspond to a single IS, whereas a broad distribution of IS's would be associated to disordered, fluidlike motion.

The most direct way of visualizing delocalization is finally provided by the probability density itself accumulated over the different monomers in the path-integral description and the simulation time. In addition to the 3D density, two-dimensional plots projected perpendicular or parallel to the PAH plane were also determined.

3. Results and discussion

Specially stable clusters in mass spectra originate from their greater resistance to evaporation than neighboring sizes. The second energy difference $\Delta_2E(n) = E(n+1) + E(n-1) - 2E(n)$, where $E(n)$ is the energy of the n-particle cluster, is a natural indicator of such special stabilities from the pure energetic point of view. The variations of Δ_2E with n in the range 36–54 and obtained from the classical global minima or from the quantum PIMD trajectories are represented in Fig. 1. In the classical regime, only one prominent peak is found at size 38, and a secondary peak at size 51. The structure obtained for $n = 38$ corresponds to the adsorption of an helium atom on the two opposite sides of each aromatic ring, including the incomplete rings saturated with peripheral hydrogens, hence two layers of 19 atoms on either side of the PAH plane [see Fig. 1(a)].

However, correcting for quantum effects in the PIMD framework alters the second energy difference quite dramatically, by now showing three peaks at $n = 38$, 41 and especially 44. The classical global minimum for $n = 44$, shown along two views in Fig. 1 (b) and (c), consists of six atoms added to the side of the 38-atom cluster along the main symmetry axis of the coronene cation but lying rather away from its plane. The most stable structure obtained for $n = 41$ is similar to the one for $n = 44$, with the three peripheral atoms arranged in an approximate equilateral triangle but again lying off the coronene plane by about half an angström.