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Solvation of carbonaceous molecules by *para*-H₂ and *ortho*-D₂ clusters. II. Fullerenes

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The coating of various fullerenes by *para*-hydrogen and *ortho*-deuterium molecules has been computationally studied as a function of the solvent amount. Rotationally averaged interaction potentials for structureless hydrogen molecules are employed to model their interaction with neutral or charged carbonaceous dopants containing between 20 and 240 atoms, occasionally comparing different fullerenes having the same size but different shapes. The solvation energy and the size of the first solvation shell obtained from path-integral molecular dynamics simulations at 2 K show only minor influence on the dopant charge and on the possible deuteration of the solvent, although the shell size is largest for *ortho*-D₂ coating cationic fullerenes. Nontrivial finite size effects have been found with the shell size varying non-monotonically close to its completion limit. For fullerenes embedded in large hydrogen clusters, the shell size and solvation energy both follow linear scaling with the fullerene size. The shell sizes obtained for C₆₀⁺ and C₇₀⁺ are close to 49 and 51, respectively, and agree with mass spectrometry experiments. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4961159>]

I. INTRODUCTION

Among cryogenic media, *para*-hydrogen and *ortho*-deuterium exhibit a fairly rich physics owing to the interplay between their very low mass but relatively high binding energy, especially under high pressures owing to the possible metallic transition.^{1–3} Unlike ⁴He, it is unclear whether bosonic hydrogen could undergo a superfluid transition at sufficiently low temperatures because under normal pressure conditions it would first crystallize.⁴ Away from the bulk limit, hydrogen clusters can display much lower densities and actually were suggested as possible candidates exhibiting superfluidity together with some residual localization of the nuclei.^{5–12} Superfluidity in hydrogen clusters has mostly been predicted from numerical investigations but has also found experimental support from spectroscopy measurements of solvated chromophores.^{13–15} In addition to this so-called supersolid state, some hydrogen clusters were theoretically predicted to melt upon cooling, vibrational nucleation prevailing over thermal localization under specific circumstances.^{5–12,16}

Besides decreasing temperature, one way of crystallizing assemblies of hydrogen molecules consists of adsorbing them on carbonaceous substrates such as graphite.^{17–21} For instance, the submonolayer at 1/3 coverage forms the $\sqrt{3} \times \sqrt{3}$ commensurate structure^{20–22} and finite *para*-H₂ clusters can be solidlike and also display supersolidity.²³ Freezing on graphitic substrates is largely driven by the stronger binding of the adsorbed molecules, which tends to pin them on particular sites and usually suppress bosonic exchange,^{20–22,24,25} as also known in the case of helium.^{26,27} To a large extent, similar phenomenology has been found to occur

for helium around polycyclic aromatic hydrocarbons (PAHs), which can be considered as flat finite-size graphene units. Various investigations of helium-coated PAH molecules^{28–34} have revealed the strong anisotropic character of nuclear delocalization in these helium clusters, solvent atoms in direct contact with the aromatic units being much more localized than peripheral atoms. Such conclusions seem to hold for fullerene dopants coated with helium.^{35–37}

In a previous paper (herein referred to as Paper I),³⁸ the coating of PAHs by *para*-H₂ and *ortho*-D₂ clusters was addressed by means of computational modeling and shown to proceed qualitatively similarly to the coating by helium with some enhanced localization for molecules in contact with the hydrocarbon dopant.³⁸ However, in contrast with helium clusters, hydrogen clusters from either isotope are almost rigidlike even away from the dopant, although zero-point motion remains strong with the dynamics having a clear fluxional character and the nuclear wavefunction being spread over many minima of the potential energy landscape. In the present contribution we consider a different type of carbonaceous dopant, namely fullerenes, which present an apparently simpler situation than the very anisotropic PAHs and only consist of one atom type. Yet they display different facets (pentagons and hexagons), different curvatures depending on their size, and also possibly non-spherical shapes. Recently, mass spectrometry experiments in the Scheier group have shed light onto the coating of hydrogen clusters on the cationic fullerenes C₆₀⁺ and C₇₀⁺, for which strong drops in abundances at sizes 49 and 51, respectively, were interpreted as the manifestation of shell completion.³⁹ These experimental results are at variance with the only existing theoretical investigation that we are aware of,⁴⁰ which predicted that shell closure takes place much earlier, near 40 *para*-H₂ molecules for the neutral dopant C₆₀.

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The current investigation aims to revisit the coating of such fullerenes by hydrogen clusters using the same computational framework as previously employed for hydrogen-coated PAHs, but also focusing on related aspects that were overlooked in Paper I.³⁸ We first wish to clarify the role of the charge, polarization forces being potentially stronger than those binding the neutral dopant to the hydrogen molecules, possibly resulting in a different threshold for shell completion. Another objective is to critically evaluate the accuracy of our modeling and notably the hydrogen-fullerene interaction by comparing the predictions based on our potential to experimental data, as well as related results originating from alternative potentials from the literature. This specific investigation is important also in the perspective of calibrating the H₂-carbon interaction which is essential for related problems involving hydrogen storage in carbon structures.^{41,42} Third, and following our earlier efforts for hydrogen-coated PAHs,³⁸ we aim to generalize the results obtained on a selected set of dopants to a broader range of systems by extracting approximate scaling laws of the most important energetic and geometrical properties of interest. Finally, and as also carried out in Paper I,³⁸ the role of deuteration, which conveys most of the quantum effects and appears minor on the experimental results, should also be characterized for the fullerene dopants.

We use path-integral molecular dynamics (PIMD) simulations with an explicit polarizable force field to explore the quantum mechanical equilibrium properties of C_m⁽⁺⁾(H₂)_n for *m* ranging from 20 to 240 and *n* from 10 to 500. We find shell completion to occur near 49 and 51 molecules for C₆₀⁺ and C₇₀⁺, respectively, in agreement with experimental measurements.³⁹ However, our results also indicate that the appearance of the second shell is not strictly sharp, fluctuations in the shell occupancy being significant near these sizes. Deuteration effects turn out to be indeed quite minor, although they generally tend to increase the shell size by reducing the density as a result of reduced delocalization and a lower de Broglie wavelength.

In Sec. II, we briefly describe the main features of our computational modeling, not entering into the details already covered in Paper I³⁸ but emphasizing the few new ingredients of relevance here. Sec. III presents our results with the discussion being extended in Sec. IV, and the article finally ends on some possible perspectives laid out in Sec. V.

II. METHODS

The computational methodology followed in the present contribution builds on the same path-integral molecular dynamics framework described in Ref. 38. The PIMD approach is rigorous but also convenient for simulating rather large systems containing hundreds of particles.

A. Potential energy surface

The explicit polarizable potential developed for modeling an assembly of *para*-H₂ or *ortho*-D₂ molecules around a rigid PAH molecule has first been used without modification to describe similar assemblies exohedrally adsorbed around

a fullerene dopant C_m⁽⁺⁾. This potential assumes the hydrogen molecules to be effectively simplified as structureless pointlike particles, which is justified by the free rotations they experience in their *J* = 0 state at the low pressures of finite clusters in vacuum. Neglecting the internal structure of H₂ molecules, a similar approximation is made to model their interactions with the dopant, although its geometric extension can of course not be neglected.

The well-established Silvera-Goldman (SG) potential⁴³ was chosen for its accurate representation of the interaction between hydrogen molecules. A similar energy function was employed to describe the interaction between H₂ and the carbon atoms. A polarization contribution added to better account for the effects of the dopant charge was included as well, so the total potential energy of the *N*-molecule system in contact with the dopant (D) is written as

$$V(\{\mathbf{r}_i\}) = \sum_{i < j; i, j \in \text{H}_2} V_{\text{SG}}(r_{ij}) + \sum_{i \in \text{H}_2; j \in \text{D}} V_c(r_{ij}) + \sum_{i \in \text{H}_2} V_{\text{pol}}^{(i)}, \quad (1)$$

$$V_{\text{SG}}(r) = V_{\text{SG}}^{\text{rep}}(r) + f_{\text{SG}}^{\text{cut}}(r)V_{\text{SG}}^{\text{att}}(r), \quad (2)$$

$$V_{\text{SG}}^{\text{rep}}(r) = \exp(\alpha - \beta r - \gamma r^2), \quad (3)$$

$$V_{\text{SG}}^{\text{att}}(r) = -\frac{C_6}{r^6} - \frac{C_8}{r^8} - \frac{C_{10}}{r^{10}}, \quad (4)$$

$$f_{\text{SG}}^{\text{cut}}(r) = \begin{cases} \exp\left[-\left(\frac{1.28r_m}{r} - 1\right)^2\right], & r \leq 1.28r_m, \\ 1, & r > 1.28r_m \end{cases}, \quad (5)$$

$$V_{\text{pol}}^{(i)} = -\frac{1}{2}\alpha_{\text{H}_2}\vec{E}_i^2, \quad (6)$$

$$\vec{E}_i = \sum_{j \in \text{D}} q_j \frac{\mathbf{r}_{ij}}{r_{ij}^3}, \quad (7)$$

where *r_{ij}* denotes the distance between particles *i* and *j*, *α*, *β*, *γ*, *C*₆, *C*₈, *C*₁₀ and *r_m* parameters of the “isolated form” of the SG potential,⁴³ and *α_{H₂}* = 0.787 Å³ the effective atomic polarizability of H₂ taken as the experimental value,⁴⁴ *q_j* being the partial charge carried by atom *j* of the dopant. The interaction potential *V_c*(*r_{ij}*) between each hydrogen molecule and each carbon atom uses the same form as the Silvera-Goldman potential without *C*₁₀ van der Waals contribution. The parameters chosen for the H₂-carbon potential were initially adjusted to reproduce quantum chemical reference data for the (rotationally averaged) interaction between H₂ and benzene.³⁸

In order to assess the performance of this explicit potential for the case of fullerenes, we show in Fig. 1 the interaction energies between H₂ and C₆₀ or C₆₀⁺ as a function of the distance between centers of mass. For the sake of simplicity, the extra charge of +1 is spread evenly among atoms of the cationic dopant, each atom of C_m⁺ carrying a charge of +1/*m*. More accurate models to account for the multipolar distribution of fullerenes are available (also for neutral compounds)⁴⁵ but were not deemed as necessary in the present work. For comparison, we have also represented the effective potential energy curves obtained by assuming simple Lennard-Jones (LJ) forms for the H₂-carbon interaction, with parameters

FIG. 1. Rotationally averaged potential energy of a H_2 molecule approaching C_{60} or its cation along a sixfold symmetry axis, as obtained from the present potential and from alternative Lennard-Jones potentials from Refs. 41 and 46. The results of electronic structure calculations at the levels of SAPT/DFT⁴⁷ and DFT (with the PBE0 and wB97xD functionals³⁹) are also highlighted. A modified (“scaled”) version of the potential adjusted to reproduce the DFT/wB97xD results is also shown.

taken from Stan and Cole (SC)⁴¹ or from Levesque, Darkrim and co-workers (LD),⁴⁶ both employed for related problems of hydrogen adsorption into carbon nanostructures. When using these potentials for cationic dopants, the same polarization energy was included in order to model the effects of the dopant charge.

Quantum chemical data are also available for the $H_2-C_{60}^{(+)}$ systems, obtained either from density-functional theory (DFT) with the PBE0 and wB97xD functionals³⁹ or from symmetry-adapted perturbation theory (SAPT)/density-functional theory.⁴⁷ These quantum chemical data are limited to the equilibrium positions and binding energy but are still very insightful owing to the notorious difficulty of evaluating accurate non-covalent forces in many-electron systems.

All potentials and electronic structure calculations find H_2 to bind preferentially at the center of an hexagon of the fullerene, at a distance ranging from 6.3 to 6.5 Å from the center. The present analytical potential and the two LJ potentials predict rather similar energy curves with the binding energy amounting to about 300 K (LJ LD), 380 K (LJ SC), or 390 K (present potential). These values increase by about 40–50 K in the case of the cationic dopant as the result of the additional and attractive polarization forces. While the three potentials predict rather similar adsorption sites and strengths, electronic structure calculations are clearly more diverse with the binding energy lying in the approximate range of 300 K (DFT/PBE0) to 570 K (DFT/wB97xD) and the SAPT/DFT

value of 380 K in between those limits. Charging the dopant also has a stronger effect on the DFT results and amounts to about 100–120 K extra binding depending on the functional used.

Overall, the present potential and the two LJ potentials all perform rather well against quantum chemical data except those obtained at the DFT/wB97xD level. In order to assess the possible effects of such a discrepancy, we have adjusted our potential to reproduce the equilibrium positions and well depths for both neutral and cationic dopants obtained with the dispersion-corrected functional. The carbon parameters of the original potential, which can be found in Paper I,³⁸ were thus modified into the following values in order to mimic the DFT/wB97xD results: $A_C = 88.594$, $b_C = 2.039$, $C_6 = 23.287$, $C_8 = 167.431$ (all in atomic units). The effective polarizability of the hydrogen molecules was also increased by a significant amount in order to reproduce the binding energy for the cationic system, $\alpha_{H_2} = 1.338 \text{ Å}^3$. This “scaled” potential was only employed to assess the robustness of some results.

B. Path-integral molecular dynamics simulations

Except at high temperature, hydrogen clusters behave quantum mechanically and it is important to account for zero-point motion and possibly tunneling. However, we choose a temperature of 2 K that is high enough for bosonic exchange effects to be neglected, especially for molecules in stronger contact with a dopant.¹² At high temperature, simple corrections such as the Feynman-Hibbs potential are sufficient to capture the most important effects of vibrational delocalization,⁴⁸ but they are clearly insufficient under the cryogenic conditions of isolated clusters.

Path-integral molecular dynamics simulations were performed to describe the thermal equilibrium state of the $C_m^{(+)}(H_2)_n$ systems for both *para*-hydrogen and *ortho*-deuterium isotopes, under the same conditions as in Paper I³⁸ and notably a Trotter number taken as $P = 256$.

The initial conditions of the PIMD trajectories were carefully examined by first carrying out a broad survey of the energy landscapes of the different clusters and locating the putative global minimum using the basin-hopping method.⁴⁹ While this specific structure may not be ultimately relevant for a quantum system with a wavefunction spread over different fluxional states, it provides the most reasonable starting point in absence of further information.

All PIMD trajectories were propagated over 100 ps after an equilibration stage of 50 ps, using a time step of 1 fs. Additional details about the PIMD methodology can be found in Paper I³⁸ as well as recent review articles.^{50,51}

C. Observables

Various structural properties were recorded from the simulation data. Following our previous work dealing with the very anisotropic PAHs, the instantaneous distance between each hydrogen molecule and the fullerene is evaluated as the minimum distance between this molecule and all carbon atoms for each configuration, from which the corresponding

distributions and averages are accumulated along the PIMD trajectories. For spherically symmetric solutes such as C_{20} or C_{60} , the radial distance from hydrogen molecules to the fullerene center was also evaluated. In both cases, vibrational delocalization is accounted for from the contributions of all beads in the path-integral description.

Several indicators were evaluated to quantify the importance of quantum effects and the overall spreading of the nuclear wavefunction. The fluctuations σ_i of the individual position of each particle i ,

$$\sigma_i = \frac{1}{P} \sum_{\alpha=1}^P \left[\langle \vec{r}_{\alpha,i}^2 \rangle - \langle \vec{r}_{\alpha,i} \rangle^2 \right]^{1/2}, \quad (8)$$

are a direct measure of the spatial extension with $\vec{r}_{\alpha,i}$ the instantaneous position of replica α of particle i and $\langle \cdot \rangle$ a time average along the PIMD trajectory. The degree of fluxionality associated with the motion of individual particles was quantified from the distance fluctuations with the remaining hydrogen particles, which we denote as δ_i ,

$$\delta_i = \frac{1}{n(n-1)} \sum_{j \in H_2, j \neq i} \frac{[\langle \vec{r}_{ij}^2 \rangle - \langle \vec{r}_{ij} \rangle^2]^{1/2}}{\langle \vec{r}_{ij} \rangle}, \quad (9)$$

where we have denoted by $\vec{r}_{ij}$ the distance between the centroids of particles i and j . The Lindemann index δ_i should remain below a few % for particles that only vibrate around their equilibrium position, whereas disordered particles causing isomerization could have δ_i in excess of 10%–15%. The global isomerization index δ obtained by averaging over δ_i , which was particularly insightful in the case of helium-coated C_{60}^+ , appears not as useful here because it remains below 10% and in the solidlike regime for all systems considered.

The extent of fluxionality can also be investigated from the broader perspective of the underlying energy landscape, as was initially pioneered in the physics of liquids.⁵² Instantaneous configurations of centroids from the PIMD trajectories were locally minimized into their closest inherent structure (IS). The spreading of the IS distribution over different minima is another qualitative feature of the disordered or liquidlike nature of the nuclear dynamics, a perfectly localized system being entirely associated with a single, well-defined structure.⁵³

The energetic properties of the hydrogen-doped clusters were addressed using the virial expression of the energy estimator in the PIMD trajectory. The solvation energy $E_{\text{solv}}(N)$ associated with coating the fullerene with a finite amount N of hydrogen molecules was determined simply by subtracting the quantum energy $E_0(N)$ of the pure hydrogen cluster from the energy $E(N)$ of the doped cluster. The solvation energies were obtained from three independent simulations PIMD trajectories for a better confidence in the averages.

III. RESULTS AND DISCUSSION

Before discussing finite-size effects associated with changing the amount of hydrogen molecules around the

fullerene dopants, we begin by illustrating the generic behavior of this solvent in the large size limit of 500-molecule clusters, $C_{60}^{(+)}(p\text{-H}_2)_{500}$ and $C_{60}^{(+)}(o\text{-D}_2)_{500}$. Fig. 2 shows the equilibrium distributions of the minimum distance between hydrogen molecules and the C_{60} fullerene at 2 K, for both neutral and cationic dopants and for the two hydrogen isotopes. These distributions show multiple peaks that are naturally interpreted as successive solvation shells. For the 60-atom fullerenes, four peaks are found (also in the radial distribution, not shown) and remain clearly resolved even at large distances exceeding 10 Å, thus confirming the strong role of the fullerene-hydrogen interaction. This multiple-peak structure suggests a soft solid behavior rather than a fully developed liquid. The softness of the solid itself originates from the combined thermal and nuclear delocalizations, as will be examined in further details below. Comparing now the neutral and cationic dopants, the effects of charge are rather moderate but for both isotopes clearly increase the distributions near the maxima of the first peaks. The distributions for *ortho*-D₂ are also slightly more peaked than those obtained for *para*-H₂, consistently with the stronger localization expected for the heavier isotope.

To characterize these distributions more quantitatively, we turn to the shell size N_s , or average number of molecules contained under the first peak. However, it is important to compensate for the overlapping between the first and second peaks which will lead to an overestimation of the shell size. Following Ref. 38, we found more convenient to replace the first peak by its best fitting Gaussian. The size of the first solvation shell was thus obtained, not only for the large 500-molecule clusters but also for smaller systems across the filling of the shell. In Fig. 3, we have represented the shell sizes for $C_{60}^{(+)}(p\text{-H}_2)_n$ and $C_{60}^{(+)}(o\text{-D}_2)_n$ clusters with $n = 40$ –60 together with the values obtained for $n = 500$ using the data of Fig. 2. The shell size below $n = 40$ follows the same exact trend, and the corresponding results have been omitted. The shell size is equal to the number of coating hydrogen molecules up to 49 in all four cases but begins to deviate shortly above this limit and depending on the dopant charge and hydrogen isotope stabilizes between 49 and 52, most often with non-integer values. As is the case for the large 500-molecule clusters, the shell is slightly smaller for neutral

FIG. 2. Distributions of minimum distance between hydrogen molecules and C_{60} or C_{60}^+ in the large clusters of $(p\text{-H}_2)_{500}$ and $(o\text{-D}_2)_{500}$.

FIG. 3. Size of the first solvation shell in $C_{60}(H_2)_n$ clusters and their cations, for *para*- H_2 and *ortho*- D_2 in the range $n = 40$ – 60 and for $n = 500$, as obtained from integrating the distribution of minimum distance assumed to have a Gaussian shape.

dopants and for *para*- H_2 . In addition to the non-integer values, which reflect partial completion of the shell, the shell size varies non-monotonically with increasing number of hydrogen molecules, with differences among the various systems although the depletion near $n = 57$ – 59 seems more robust. Such non-monotonic variations, studied in more details below, are indeed observed in the mass abundances reported by Kaiser *et al.*³⁹ and may thus be genuine phenomena rather than computational artifacts.

The shell size in the large cluster limit is about one molecule smaller than in these smaller clusters, the general ordering between the four different systems remaining the same. This result is somewhat counter-intuitive, because in larger droplets the pressure at the center is expected to be larger than in outer regions, hence the solvation shell should be able to accommodate more molecules.⁵⁴ To interpret this discrepancy, we first note that experiments do not directly measure the solvation shell size in large cryogenic droplets but at the onset of shell completion. Moreover, it is well possible that finite size effects also operate in this size range and even beyond, until the droplet undergoes the crystalline transition to hexagonal close-packed. However, it is unclear whether the shell size obtained for precisely 500 coating hydrogen molecules would remain so in a true hydrogen matrix imposing crystalline constraints.

More insight into finite-size effects can be gained from considering now the global Lindemann index and the average minimum distance between hydrogen molecules and the fullerene, both properties being depicted in Fig. 4 for the specific case of $C_{60}^+(p-H_2)_n$ with n in the range 10–60. The very similar results obtained for deuterated clusters or neutral dopants are omitted for brevity. The variations of both properties mimic one another, being smooth until $n = 32$, changing more dramatically at $n = 33$, and also showing a clear optimum at the shell completion near $n = 49$.

A first observation is that the dynamics is always poorly fluxional, the global Lindemann index remaining below 10% in the entire size range. This is in strong contrast with helium coated C_{60}^+ , where clearly melted states were identified between 32 and 60 coating atoms.^{36,37} However, clusters

FIG. 4. Average minimum distance between *para*-hydrogen molecules and C_{60}^+ (solid red circles) and global Lindemann index (open black squares) in $C_{60}^+(p-H_2)_n$ clusters as a function of n .

having fewer than about 15 molecules or between 32 and 49 show some degree of disorder, which is confirmed by the distributions of inherent structures for these clusters (data not shown).

The minor increase in the average minimum distance at $n = 33$ suggests some structural rearrangements above the size of 32 at which commensurate adsorption is expected. The *decrease* in the average minimum distance as the coverage increases from 33 to the completion of the shell indicates that the structural disorder introduced orientationally by making room for the additional molecules is associated with some radial disorder as well. The growth of a second shell above size 49 is clearly manifested in the steady increase in the minimum distance between hydrogen molecules and the fullerene. More interestingly, that the dynamics exhibits a minimum in fluxionality as the shell is just complete is very similar to what was theoretically predicted for $^4He_{60}C_{60}^+$ clusters with a nearly rigid layer of solvent atoms stabilized by an ideal surface density and distance to the dopant.³⁶

The energetic properties of hydrogen-coated C_{60} and its cation are illustrated in Fig. 5 on the solvation energy per *para*- H_2 or *ortho*- D_2 molecule, for the same size range as in Fig. 3. The variations obtained for the two isotopes are parallel to each other, the zero-point shift between them being constant and equal to approximately 15 K. The strongest changes occur as the hydrogen-hydrogen interactions become increasingly important, first at $n = 33$ with the initial completion of the shell, then above about $n = 46$, where it eventually becomes energetically preferable to eject one molecule from the shell. The average *radial* distance, shown in Fig. 5(b), complements the average minimum distance considered previously in Fig. 4 in that the decrease found in the range 33–50 is now mostly washed away as the shell expands in radius, giving also more room for molecules to approach the carbon atoms. As expected, the phenomenology remains identical for deuterated clusters, with the only difference that vibrational delocalization brings the molecules closer to the fullerene surface.

Finite size effects were shown in Figs. 3 and 4 to be non-trivial around the completion of the first solvation shell, and we now address them in more details. In this purpose, we focus

FIG. 5. (a) Solvation energy in $C_{60}(p\text{-H}_2)_n$ and $C_{60}(o\text{-D}_2)_n$ per hydrogen molecule versus n ; (b) average radial distance from the fullerene center in the same systems.

on the two fullerene sizes of 20 and 60 carbon atoms. Fig. 6(e) shows the distributions of minimum distances obtained for 32 and 35 hydrogen molecules around the dodecahedral cages C_{20} and C_{20}^+ in logarithmic scale. For this small fullerene, the first shell is complete exactly at 32 *para*-H₂ or *ortho*-D₂ for both neutral and cationic dopants, an additional molecule forming the precursor of an additional shell seen as an extra peak. For the heavier isotope, there is no overlap between the two peaks at the resolution of the present simulations,

vibrational delocalization being manifested more distinctly for *para*-H₂.

The completion of the shell size at 32 hydrogen molecules would suggest some simple geometrical filling of the solvation shell into highly symmetric sites respecting the I_h point group of C_{20} , e.g., with molecules first adsorbed above the 12 pentagonal faces and 20 additional molecules above the dual hexagonal faces formed by these 12 first molecules. However, inspection of the equilibrium distribution accumulated along the PIMD trajectory indicates otherwise, the dynamics appearing somewhat fluxional. The distribution of inherent structures for the $C_{20}(p\text{-H}_2)_{32}$ cluster, shown in the inset of Fig. 6(e), is not exhaustively contained in a single very stable minimum but spreads over nearly isoenergetic structures within a few K from the global minimum. A visual depiction of the equilibrium density for this cluster [Fig. 6(a)] confirms the significant spreading of the nuclear wavefunction even though individual particle sites can be identified but without providing any evidence of a specific symmetry.

The fluxional character of the wavefunction is much stronger for the $C_{20}(p\text{-H}_2)_{33}$ cluster, the extra atom lying above the first shell exhibiting a clear floating behavior better seen for $C_{20}(p\text{-H}_2)_{35}$ [see Fig. 6(b)], with inherent structures now spreading over more diverse minima and at least 20 K above the global minimum which is no longer markedly populated. The Lindemann indices δ_i , which remain below 3% for all particles from the first shell, reach about 6% for the floating *para*-H₂ molecule. In *ortho*-D₂ clusters, these numbers change to 2% and 3%, respectively, the outer molecule no longer showing transversal motion on the time scale of the PIMD trajectory. Interestingly, for *para*-H₂ clusters around C_{20}^+ also

FIG. 6. Logarithmic distributions of minimum distances between hydrogen molecules and $C_m^{(\pm)}$ fullerenes in $C_m^{(\pm)}(H_2)_n$ clusters for (e) neutral and cationic $m = 20$, $n = 32, 35$; (f) cationic $m = 60$, $n = 50-52$. In (e) the distributions are shown for the *para*-H₂ and *ortho*-D₂ isotopes and for the neutral and cationic fullerene dopants. In (f) only *para*-H₂ clusters around C_{60}^+ are considered. Representative molecular densities of *para*-H₂ clusters around the neutral C_{20} and C_{60} dopants at 2 K thermal equilibrium are depicted in panels (a)-(d). Plots realized with the Mayavi2 suite of Python scripts.⁵⁵

display less fluxional motion, with Lindemann indices of all particles being similar to their values in $C_{20}(o\text{-D}_2)_{33}$. This result is consistent with the stronger binding experienced with cationic dopants, leading to a more classical behavior similar here to changing the isotope from *para*-H₂ to *ortho*-D₂.

In Fig. 6(f), the distributions of minimum distances in *para*-H₂ clusters around C_{60}^+ are shown, again for sizes 50–52 close to the completion of the first shell. These three clusters exhibit non-monotonic size effects with the intermediate size $n = 51$ being the only one-shell system, both neighboring sizes being associated with a clear additional peak ($n = 52$) or at least a shoulder on the large distances side ($n = 50$). As was the case for the smaller clusters adsorbed on C_{20} , the distributions of inherent structures for these systems are not limited to single minima, even though the global minimum contributes to more than 95% of the nuclear wavefunction for $n = 50$ and 51 with the 5% remaining lying in peaks less than 50 K in energy above [and barely visible in the inset of Fig. 6(f)]. For $n = 52$, the diversity in inherent structures is larger and exceeds 150 K above the global minimum. The particle-resolved Lindemann indices do not show any deviation from any molecule in the $C_{60}^+(p\text{-H}_2)_{51}$ cluster, despite the clear presence of a shoulder on the distribution of minimum distance. Inspection of the PIMD trajectories reveals that the equilibrium state predicted by the model is that of occasional but reversible excursions of one molecule from the first shell into a floating particle, possibly reinserting itself after some time followed by the subsequent excursion of a possibly different molecule.

In contrast, in the $C_{60}^+(p\text{-H}_2)_{52}$ system, one hydrogen molecule distinctly floats over the first shell and another one from the first shell occasionally jumps out and back in, giving a size of the first shell between 50 and 51. These highly size-sensitive behaviors are difficult to visualize directly, but the density plots below ($n = 40$) and above ($n = 60$) the completion of the first shell near the size 50, as depicted in Figs. 6(c) and 6(d), confirm that the second shell emerges in this broad size range. Interestingly, qualitatively similar distributions are found for the deuterated clusters and for the neutral dopant, with only the 51-molecule system in the range 50–52 exhibiting a single shell without any floating particle. However these excursions are less likely and the resulting sizes of the first shell are higher by a significant fraction (see Fig. 3).

Besides the effects of dopant charge, cluster size, and deuteration, we have investigated the possible role of the fullerene shape, choosing the C_{80} dopant that exists in three conformers with either spherical symmetry (D_{5h} point group) or with prolate (D_{5d}) or oblate (D_3) deformations, and represented in Figs. 7(a)–7(c). The distributions of minimum distance between *para*-H₂ molecules and the fullerenes in the large cluster $C_{80}(p\text{-H}_2)_{500}$ at 2 K thermal equilibrium are shown in Fig. 7(d), with the distributions of *radial* distances around the fullerene center as an inset in Fig. 7(e). From the radial distributions, the peak at the shortest distance indicative of the first solvation shell naively looks like it depends on the shape of the fullerene, being broader and shifted in the case of the deformed conformers of C_{80} . The distributions of minimum distance remove this shape dependence and provide a more local account of the actual contact between the

FIG. 7. (a)–(c) Oblate, prolate, and spherical isomers of C_{80} with point groups D_3 , D_{5d} , and D_{5h} , respectively. (d) Distributions of minimum distance between *para*-H₂ molecules and the three isomers of C_{80} . The inset in panel (e) shows the radial distributions of *para*-H₂ molecules around the geometrical centers of these fullerenes.

hydrogen layer and the curved graphitic surface, resulting in first solvation peaks that are now essentially similar in shape and height. Integration of the peaks through the intermediate Gaussian fitting procedure yields shell sizes in the range of 55–56 depending on the conformer, the spherically symmetric dopant accommodating the fewest particles. More precisely, the shell sizes for the D_{5h} , D_3 , and D_{5d} fullerenes are evaluated to be 55.0, 55.2, 55.3, and thus grow with the effective carbon areas estimated from their convex hulls to be 190.17, 190.20, and 190.23 Å², respectively, whereas the volumes of the same dopants decrease accordingly from 237.73 to 236.90 and 233.79 Å³, respectively. That the shell size correlates with the exposed area of the fullerene but not with its volume indicates that the adsorption phenomenon is locally driven, but it would be interesting to determine whether this result holds for more dense dopants such as multishell fullerenes.

While it depends only weakly on the dopant shape, the size of the solvation shell unsurprisingly exhibits much stronger variations with the dopant mass. We have represented in Fig. 8(a) these variations obtained for $(p\text{-H}_2)_{500}$ clusters around C_m and C_m^+ fullerenes as well as $C_m(o\text{-D}_2)_{500}$, the results for $C_m^+(o\text{-D}_2)_{500}$ being very similar. All results for the shell size N_s can be fairly well represented with a linear function $N_s(n) \approx an + b$ with $a = 0.39$ and $b = 24.9$, the last digit varying a little depending on the specific system. The coefficient a is of comparable magnitude as its counterpart in hydrogen-coated PAHs.³⁸

The approximate linear scaling obtained for the solvation shell, together with the expected constant surface area of graphitic sheets due to covalent constraints, suggests that the adsorbed hydrogen layer also has a nearly constant

FIG. 8. (a) Size N_S of the first solvation shell and (b) solvation energy per hydrogen molecule in $C_m(H_2)_{500}$ clusters and their cations, for *para*- H_2 and *ortho*- D_2 isotopes, as a function of the fullerene size m between 20 and 240. The solid lines are linear fits to the data.

surface density. From the radial distributions obtained for large hydrogen clusters coating the spherically symmetric fullerenes, these surface densities are found to be approximately 0.095 molecule/ $\text{\AA}^2$ around C_{20} , decreasing to 0.088 – 0.090 molecule/ $\text{\AA}^2$ for larger fullerenes, with a minor dependence on dopant charge or deuteration.

Similarly, the solvation energy per H_2 [Fig. 8(b)] in the 500-molecule clusters exhibits linear variations with increasing fullerene size. This behavior is consistent with the constant surface density of the first solvation shell and its linear growth with dopant size but shows more interesting differences with dopant charge or deuteration. Upon ionization, the solvation energy increases with respect to the neutral dopant, which results from the significant polarization energy carried by the molecules especially in the first solvation shell. The shift is found to decrease with increasing fullerene size, a feature that can be interpreted by noticing that the fullerene radius approximately scales as the square root of its size m , hence the electric field experienced by the adsorbed molecules scales as $1/m$, and their polarization energy as $1/m^2$. This effect is mitigated by the fact that all molecules are polarized even away from the fullerene surface (and polarization forces are longer ranged than the dispersion attraction), leading to an apparently softer decrease in the solvation energy. Deuteration has a steady influence on the solvation energy, as was already found in the case of PAH dopants.³⁸ Here the increase in magnitude of the solvation energy simply results from the much lower zero-point energy for this heavier isotope.

Our simulations on size-specific clusters have previously highlighted some degree of fluxionality near the completion of the first solvation shell. To address this issue further, we discuss the case of large hydrogen clusters around the C_{60} dopant, focusing now on indicators of delocalization and mobility. More precisely, the fluctuations in the minimum distance to the fullerene and the individual Lindemann index are shown against each other for both $C_{60}(p-H_2)_{500}$ and $C_{60}(o-D_2)_{500}$ clusters in Fig. 9. These indicators appear

FIG. 9. Correlation between fluctuations in the minimum distance to the fullerene and the particle-resolved Lindemann index for hydrogen molecules in $C_{60}(p-H_2)_{500}$ and $C_{60}(o-D_2)_{500}$.

strongly correlated and behave very similarly for the two systems, the *ortho*- D_2 cluster showing lesser fluctuations. Except a few tens of particles, the vast majority of the clusters exhibit only vibrating motion and remain locked in their shell. Fluxionality with Lindemann indices exceeding 10% is associated with strong fluctuations in the distance to the fullerene exceeding 2 $\text{\AA}$. Correlation with the minimum distance itself indicates that these particles are usually, but not exclusively, the most distant from the center, at less dense locations where they have more radial freedom. However, occasional jumps between shells take place, including between the first and second shell, even though only about 15 molecules among the 500 present undergo such larger amplitude motion within the limited 100 ps long trajectory. In a fully equilibrated system and in the ergodic limit, all molecules should thus be expected to have a small but nonzero propensity for diffusion especially at the cluster surface.

Finally, we have investigated the sensitivity of the results to the interaction potential between hydrogen molecules and the fullerenes, noting from Fig. 1 that the potential employed so far significantly deviates from the density functional theory calculation with the $wB97xD$ functional, with a binding nearly 50% stronger in the latter case and with a slightly shorter equilibrium distance. We have thus repeated some of the path-integral MD simulations using the “scaled” potential adjusted to reproduce these specific DFT data, and we show in Fig. 10 the distributions of minimum distance between hydrogen particles and neutral or cationic C_{60} dopants in clusters containing either 500 or 50–52 *para*- H_2 molecules, respectively. The distribution for the $C_{60}(p-H_2)_{500}$ system, represented against the same data using the potential originating from Ref. 38 in Fig. 10(a), unsurprisingly displays peaks that are sharper but also shifted to shorter distances. The overlap between the first and second peaks is lower, consistently with the greater localization induced by stronger forces. Integrating the distribution yields a shell size of 50 for the scaled potential that is about one unit larger than the value obtained with the other potential.

Clusters of 50–52 molecules around the cationic dopant, whose distributions of minimum distance are depicted in Fig. 10(b), show a single solvation shell for $n = 50$ and 51,

FIG. 10. Distributions of minimum distance between *para*-H₂ molecules and (a) C₆₀ in (H₂)₅₀₀; and (b) size-selected clusters around C₆₀⁺, in logarithmic scale, as obtained from PIMD simulations with the scaled or reference potential. (a) C₆₀(*p*-H₂)₅₀₀. (b) C₆₀⁺(*p*-H₂)_n.

but one floating molecule over a 51-molecule shell for $n = 52$. Compared to the distributions obtained in Fig. 6(f), the size effects thus appear qualitatively different and especially for size 50, but the same trends as in Fig. 10(b) are generally noted, with sharper peaks indicative of greater localized molecules also associated with a larger first shell with higher surface density.

IV. DISCUSSION

Our modeling predicts the first solvation shell of *para*-H₂ around C₆₀⁺ and C₇₀⁺ to contain about 49 and 51 molecules, respectively, and slightly larger values for *ortho*-D₂ clusters. These values are remarkably close to mass spectrometry measurements,³⁹ in which the completion of the shell was inferred from a drop in the abundances associated with the appearance of an extra outer molecule less bound to the fullerene. The agreement indicates that our overall approach is rather realistic, and that the interaction potential between the hydrogen molecules and the fullerenes is reasonably well described. The larger deviation between our results and experimental data when the calculations are performed with a potential mimicking DFT/wB97xD results³⁹ further suggests that this method overestimates the binding energy quite significantly and that the SAPT/DFT and DFT/PBE0 calculations are probably more accurate.

The first solvation shell was found to be incommensurate with the fullerene structure, very clearly in the cases of C₂₀ (shell size of 32) and C₆₀ (shell size close to 50), and even once it is complete it remains mostly solidlike and only locally fluxional. However, some quantitative changes in the collective behavior above the commensurate covering size of 32 were noted, though not as dramatic as the defect-induced melting seen in helium-coated C₆₀⁺ at the same coverage.³⁶ The present results are also at variance with previous quantum Monte Carlo results by Turnbull and Boninsegni⁴⁰ who reported the first solvation shell to be complete with 40 *para*-H₂ molecules (in an incommensurate arrangement). The

LJ potential used by these authors (LD parameters) to model the H₂-carbon interaction⁴⁶ is similar to our own potential, hence the reason for this discrepancy could lie in the higher temperature of 2 K considered in the present investigation. Although the detailed effects of temperature on the structural and energetic properties lie beyond the scope of the present paper, it is unlikely that a difference of 10 molecules could be explained this way. It may thus well be that exchange effects, which were neglected here, contribute to reducing the shell occupancy as predicted by Turnbull and Boninsegni.⁴⁰

The incommensurate nature of the solvation shell, also found in the case of the helium solvent, originates mainly from the interplay between the competition between the H₂-H₂ and H₂-carbon interactions, but also from the corrugation of the fullerene surface which above 32 molecules hinders regular arrangements. The initially dominant H₂-carbon interaction makes hydrogen molecules bind preferentially in contact with the fullerene and remain rather distant from each other. Upon growth the surface density increases and at some point the hydrogen molecules interact sufficiently for the shell to expand away from the fullerene, as shown in Fig. 5. But the single shell arrangement is of course not optimal and it soon becomes preferable to eject some molecules into a second layer to maximise the binding of the first layer to the dopant. Turnbull and Boninsegni concluded that corrugation of the fullerene is essential on the adsorption properties,⁴⁰ consistently with earlier results on ⁴He_nC₆₀⁺ clusters,³⁶ but also on helium clusters on graphene.⁵⁶ Yet it would be interesting to repeat the present calculations with a coarse-grained description of the fullerenes assimilated as point particles but having the same effective interaction energy with hydrogen than the fully atomistic model.

The present calculations have also shed light onto nontrivial finite size effects, with the first shell varying non-monotonically near the shell completion. Such effects well known in clusters physics⁵⁷ are sensitive to many factors including the details of the interactions as well as external parameters and could appear differently in experiments, if they could be evidenced at all in the first place. Vibrational delocalization was found to be essentially moderate and to mostly act on energetic properties, rather than on the size of first solvation shell which remains barely affected by deuteration. However, it is unclear whether the occurrence of “quantum melting” reported in pure *para*-H₂ clusters^{5–12,16} could affect the overall rigidity and degree of disorder at lower temperature. While the stronger interaction to carbon should attenuate delocalization effects along the radial direction, the lateral motion could be enhanced and influence the size at which the shell is complete. These issues would be better clarified using more advanced (but also more demanding) simulation techniques that account for exchange statistics.^{58,59}

V. CONCLUDING REMARKS

The interaction between hydrogen and carbon nanostructures has received a lot attention owing to potential applications for reversible energy storage.^{41,42,60,61} It also has implications in astrochemistry especially since the observation of fullerenes in the interstellar medium,^{62,63} and the ubiquity

of hydrogen in the Universe. The present investigation has focused on some much more fundamental aspects, namely how the coating of various fullerenes by *para*-H₂ or *ortho*-D₂ molecules proceeds below, at, and far away from the completion of the first solvation shell. We used computational modeling based on an explicit polarizable potential for the hydrogen-carbon interaction, a structureless representation of the hydrogen molecule consistent with the accurate Silvera-Goldman potential⁴³ all within the framework of path-integral molecular dynamics simulations. From this approach previously employed to describe hydrogen-coated polycyclic aromatic hydrocarbons,³⁸ the arrangement of hydrogen molecules into solvation shells, the extent of vibrational delocalization, and their propensity for fluxional behavior were characterized for neutral and cationic fullerenes containing between 20 and 240 atoms and possibly displaying anisotropic shapes.

Our results generally show that the first solvation shell completes at 32 molecules for the 20-atom dodecahedral fullerene, near 50 molecules for buckminsterfullerene, and scales linearly with the fullerene size. Fluctuations are significant near the first shell completion, as also suggested in the experimental measurements by Kaiser and co-workers.³⁹ Deuteration effects, although small, were found to increase slightly the shell size similarly as the results obtained for PAH dopants.³⁸ Charge effects were also found to be quite minor and marginally increase the shell size owing to stronger binding to the fullerene. Comparison with existing measurements yields a very satisfactory agreement for the shell size, and indicates that the binding potential between hydrogen and C₆₀ does not exceed 500 K in energy, as predicted (and overestimated) by DFT calculations using the wB97xD functional.³⁹

Several issues deserve further attention in future investigations, and two natural extensions of the present work would be to look at temperature effects and at the possible influence of the internal structure of *para*-H₂ and *ortho*-D₂ molecules. The neglect of internal degrees of freedom in hydrogen molecules could become questionable at low temperature, and fully atomistic models such as the Darkrim-Levesque potential⁶⁴ could be employed though at a significantly higher computational cost. Another assumption possibly questionable made in the present work is related to the additive nature of the van der Waals interaction employed to model the forces between hydrogen and fullerene molecules. The electron cloud is rather delocalized in such carbon nanostructures, and the van der Waals interaction involving extended bodies is partially shielded.⁶⁵ Unfortunately, such an effect is also difficult to account when the electronic structure is described explicitly, but it would contribute to decrease the binding energy and reduce the size of the solvation shell.

As usual when dealing with finite-size systems, the issue of how the results converge to the large size limit is of fundamental interest, and in the present case, the asymptotic behavior should be compared to adsorption on the graphene substrate. However, large icosahedral fullerenes are decreasingly stable (and rather academic objects), increasingly flat in the hexagonal aromatic regions and sharp at the pentagonal defects.⁶⁶ Adsorption over large fullerenes could thus become anisotropic because of such curvature effects, a

feature that could also be addressed for exohedral adsorption over nanotubes. More realistic fullerenes in the large size limit would be of the onion-ring type and bind hydrogen more strongly. Although linear scaling in the size of the first solvation shell is still anticipated with the number of fullerenes layers, we thus expect that the first hydrogen layer could accommodate more molecules.

Of course, another extension worth pursuing would consist in considering exohedral adsorption around carbon nanotubes, thus bridging the 1D gap intermediate between the present 0D nanostructures and the 2D case of graphene, or in the case of multiwall nanotubes, between onion-ring fullerenes and 3D graphite. Modeling adsorption on large-scale materials would still be feasible by path-integral MD but become computationally expensive, and such simulations would highly benefit from methodological improvements such as auxiliary colored-noise thermostats,^{67,68} in order to treat hundreds or thousands of hydrogen molecules.

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