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Solvation of carbonaceous molecules by *para*-H₂ and *ortho*-D₂ clusters. I. Polycyclic aromatic hydrocarbons

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This work theoretically examines the progressive coating of planar polycyclic aromatic hydrocarbon (PAH) molecules ranging from benzene to circumcoronene (C₅₄H₁₈) by *para*-hydrogen and *ortho*-deuterium. The coarse-grained Silvera-Goldman potential has been extended to model the interactions between hydrogen molecules and individual atoms of the PAH and parametrized against quantum chemical calculations for benzene-H₂. Path-integral molecular dynamics simulations at 2 K were performed for increasingly large amounts of hydrogen coating the PAH up to the first solvation shell and beyond. From the simulations, various properties were determined such as the size of the first shell and its thickness as well as the solvation energy. The degree of delocalization was notably quantified from an energy landscape perspective, by monitoring the fluctuations among inherent structures sampled by the trajectories. Our results generally demonstrate a high degree of localization owing to relatively strong interactions between hydrogen and the PAH, and qualitatively minor isotopic effects. In the limit of large hydrogen amounts, the shell size and solvation energy both follow approximate linear relations with the numbers of carbon and hydrogen in the PAH. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4952957>]

I. INTRODUCTION

Hydrogen is the most abundant element in the universe and is present under broad ranges of astrophysical conditions of density and temperature.¹ The phase diagram of hydrogen is also more complex than its chemical simplicity would suggest at first sight, especially under high pressure where the possible transition to a superconducting metallic state^{2,3} remains under debate.⁴ At normal pressures, the bosonic character of its two isomeric forms of *para*-hydrogen (*p*-H₂) and *ortho*-deuterium (*o*-D₂) leads to the prediction⁵ that like helium both hydrogen systems should exhibit superfluidity at sufficiently low temperatures. However, hydrogen molecules are more strongly bound to each other than helium and crystallize into hexagonal close-packed structures, preventing so far any manifestation of the Bose condensation to be observed in the bulk, even under conditions of metastable supercooled liquids.⁶

In the gas phase, *para*-hydrogen and *ortho*-deuterium aggregate at very low temperatures of a few Kelvin, the clusters thus produced exhibiting a peculiar quantum melting transition upon cooling^{7–13} in which nuclear delocalization effects overcome thermal excitations and lead to a superfluid. These theoretical predictions, which have since received experimental support,^{14–16} have also raised the interesting question of a possible “supersolid” state that some specific clusters could exhibit, possessing simultaneously the characteristics of a solid and a superfluid.¹⁷ Besides the possibly preferential occurrence of superfluidity at the surface^{11,18} as well as its non trivial size dependence,¹⁷ intriguing segregation phenomena have

also been reported in simulations of mixed *para*-H₂/*ortho*-D₂ clusters, with deuterium molecules acting as a frozen localized core surrounded by parahydrogen shells showing different amounts of fluidlike quantum behavior.^{17,19,20}

In contact with graphitic substrates, submonolayers of *para*-H₂ readily freeze at temperatures where they would otherwise be fluid,²¹ even forming the perfect $\sqrt{3} \times \sqrt{3}$ commensurate structure at 1/3 coverage.²² A similar behavior is known in helium, where the contact layer is pinned in a commensurate lattice.^{23,24} In the case of graphene, the interaction with helium is weaker and the situation appears less clear,²⁵ the corrugation of the substrate being essential in stabilizing ordered structures.²⁶ In the submonolayer regime, *para*-H₂ on graphitic substrates can form solidlike clusters surrounded by vapor,²¹ and remain largely localized. The presence of 2D gas in the commensurate solid phase has also been evidenced by positronium annihilation measurements.²⁷ In graphene, and similarly to ⁴He, the stable phase changes between the $\sqrt{3} \times \sqrt{3}$ commensurate solid and the liquid depending on the pressure or surface density.^{28,29} For both quantum gases, the reconciling view of supersolidity has also been suggested to occur in adsorbed clusters.³⁰

Polycyclic aromatic hydrocarbons (PAH) are planar, graphene-like molecules that contribute to combustion products³¹ and whose presence in the interstellar medium has been increasingly supported by spectroscopic measurements.³² Experimental³³ and theoretical^{34–39} investigations of PAHs coated by ⁴He clusters have shown that nuclear localization is enhanced for solvent atoms in contact with the aromatic faces, but not so much in the vicinity of peripheral hydrogen atoms, the helium belt being largely disordered and fluid. Such effects were recently predicted to possibly lead to the

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formation of metastable PAH clusters frozen in high-energy conformations.⁴⁰

Carbonaceous molecules coated by hydrogen clusters have been experimentally studied by mass spectrometry in the Scheier group,⁴¹ who determined the size of the first solvation shell for the C_{60}^+ and C_{70}^+ fullerenes and reported essentially no effect of deuteration. Calculations at zero temperature using quantum Monte Carlo methods have also been performed for various fullerenes containing up to 80 carbon atoms,⁴² the results showing a suppression of superfluidity at the contact with carbon, and a strong dependence of the shell structure on the fullerene corrugation.

In the present investigation, we consider by means of computational modeling how solvation of *para*-H₂ and *ortho*-D₂ proceeds around various hydrocarbon molecules, starting here with PAHs. Fullerenes will be treated separately in a subsequent publication. The questions we wish to address are directly connected to existing or future experimental detection (size of the solvation shells, solvation energy) but also more fundamental and related to the amount of delocalization in the solvent and its possible isotropy. To tackle those issues, we have carried path-integral molecular dynamics (PIMD) simulations of hydrogen clusters around different PAH molecules, also varying occasionally the number of *para*-H₂ or *ortho*-D₂ in order to evaluate the rate at which size-dependent properties converge to the bulk limit. To achieve these simulations, a simple effective potential of the Silvera-Goldman (SG) type⁴³ was implemented and parametrized to reproduce the rotationally averaged interactions between H₂ and benzene.

Our results suggest that the first solvation shell is generally well defined for both isotopic species and all PAHs ranging from benzene to circumcoronene, its size being appreciably larger for deuterated clusters. The extent of delocalization, as measured either from the spatial spreading of the ring polymers around the solute in the PIMD description or from the fluctuations among inherent structures visited in the PIMD trajectory, is found to be relatively moderate, no clearly fluid state being identified even away from the solute. Interestingly, both the size of the first solvation shell and the solvation energy follow approximate linear relationships with the numbers of carbon and hydrogen atoms in the PAH. This finding should facilitate experimental comparison on a broader diversity of PAH compounds not covered in the present study.

The article is organized as follows. In Sec. II, we describe the potential we have chosen for modeling the interactions between hydrogen molecules and the PAHs and its parametrization based on quantum chemical data. We also briefly describe the PIMD methodology employed to simulate hydrogen-coated PAHs at 2 K, and the tools used to analyse the structural and energetic results, and those more specific to quantify the magnitude of nuclear delocalization. The results are presented and discussed in Sec. III, before some concluding remarks are finally given in Sec. IV.

II. METHODS

The approach followed in this work relies on path-integral molecular dynamics using a simplified potential energy surface

in which the atomic structure of hydrogen molecules is neglected. This approximation commonly employed in quantum simulations of *para*-hydrogen is relevant at moderate temperatures and sufficiently low densities for the H₂ molecules to freely rotate and behave as effective pointlike particles.

A. Potential energy surface

The systems of interest are finite clusters of molecular hydrogen around various PAHs, the solute being assumed as fixed in the laboratory reference frame. We also consider a sufficiently high temperature of 2 K that is above the quantum melting transition temperature of ~ 1 K,¹⁷ ensuring that the bosonic nature of *para*-H₂ and *ortho*-D₂ can be safely neglected. At such a low temperature, the solute is frozen in its ground vibrational state and owing to its much larger mass, it can be treated as rigid. We further assume its center of mass to lie at the origin of the reference frame.

Our next approximation is to simplify the atomic structure of the hydrogen molecules, as performed in the Silvera-Goldman (SG) potential describing their effective mutual interaction. The neglect of atomic structure is justified by the free rotations experienced by H₂ molecules in their $J = 0$ state at the low pressures of finite clusters. The SG pair potential has been successfully used in the past to describe clusters and bulk assemblies of *para*-H₂ and *ortho*-D₂^{13,17,18,21,24,29,42} and their mixtures.^{17,19,20} Here for low-density systems, we use the “isolated” form and parameters of this potential,⁴³

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

$$V_{SG}^{\text{rep}}(r) = \exp(\alpha - \beta r - \gamma r^2), \quad (1)$$

$$V_{SG}^{\text{att}}(r) = -\frac{C_6}{r^6} - \frac{C_8}{r^8} - \frac{C_{10}}{r^{10}} \quad (2)$$

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

$$= 1, \quad r > 1.28r_m. \quad (3)$$

The values of the various parameters of the SG potential can be found in the original publication.⁴³

In neglecting the rotational degrees of freedom of H₂, we impose a similar constraint on the interaction between these molecules and the PAH. For computational efficiency and consistency with the SG potential, we describe the interaction between the PAH and each H₂ molecule i , effectively assimilated as a structureless particle, as consisting of three contributions,

$$V_i = \sum_{j \in \text{PAH}} \left[V_{\text{rep}}^{(j)}(r_{ij}) + V_{\text{disp}}^{(j)}(r_{ij}) \right] + V_{\text{pol}}^{(i)}, \quad (4)$$

where the first two terms in the sum denote the short-range repulsion and long-range dispersion forces, respectively, between the hydrogen molecule and atom j of the PAH. The last term designates a simple polarization correction originating from the partial charges carried by the atoms of the PAH molecule, added here to model the multipolar electrostatic distribution. Although this contribution is expected to be minor for neutral PAHs, it could become essential for cationic or protonated solutes and thus was included from the start.

The pair potentials V_{rep} and V_{disp} between H_2 molecules and the PAH atoms use a form similar to the Silvera-Goldman potential,

$$V_{\text{rep}}^{(j)}(r_{ij}) = A_j \exp(-b_j r_{ij}), \quad (5)$$

$$V_{\text{att}}^{(j)}(r) = -f_{\text{cut}}(r_{ij}) \left[\frac{C_{6,j}}{r_{ij}^6} + \frac{C_{8,j}}{r_{ij}^8} \right], \quad (6)$$

$$f_{\text{cut}}(r_{ij}) = \exp \left[- \left(\frac{r_c}{r_{ij}} - 1 \right)^2 \right], \quad r_{ij} \leq r_c, \\ = 1, \quad r_{ij} > r_c, \quad (7)$$

with 2×4 parameters A_j , b_j , $C_{6,j}$, and $C_{8,j}$ for $j = \text{C}$ and H . The polarization contribution reads

$$V_{\text{pol}}^{(i)} = -\frac{1}{2} \alpha_{\text{H}_2} \vec{E}_i^2 \quad (8)$$

$$\vec{E}_i = \sum_{j \in \text{PAH}} q_j \frac{\vec{r}_{ij}}{r_{ij}^3} \quad (9)$$

where $\vec{E}_i$ is the electric field vector created at site i by the partial charges q_j located at the PAH atomic sites j . Here the polarizability tensor is assumed to be isotropic for consistency with the neglect of rotational degrees of freedom, and the effective atomic polarizability is taken as the experimental value of $\alpha_{\text{H}_2} = 0.787 \text{ \AA}^3$.⁴⁴ The partial charges themselves q_j were determined by fitting the external electrostatic potential (so-called restrained electrostatic potential or RESP procedure), as predicted by density-functional theory calculations on the optimized geometries of the PAH, obtained here using the standard B3LYP functional and the 6-311G(d,p) basis set through the Gaussian09 software package.⁴⁵ It should be emphasized here that polarization forces were included here for generality, anticipating our future use of the model for other possibly charged dopants. For the present neutral PAHs, the polarization energy appears relatively minor: In the coronene(H_2)₁₀₀ system at equilibrium configuration, the total binding energy decreases from 26.9785 K/molecule to 27.2825 K/molecule upon including polarization forces, or a change of about 1.1%.

The eight parameters of the potential were adjusted by least square minimization of an error function measuring the deviation between the present potential and reference potential energy curves obtained for H_2 approaching the benzene molecule along the three most symmetric directions at the MP2/aug-cc-pVDZ level of theory using the MOLPRO package.⁴⁶ Since MP2 is known to overestimate the interactions between closed-shell species, the so-called spin-component-scaled MP2 (SCS-MP2) method⁴⁷ was employed to calculate the numerical potential functions. In SCS-MP2, both the singlet and the triplet ground state energies are scaled by 1.2 and 1/3, respectively. In dimers of PAHs, we have shown that SCS-MP2 provides almost CCSD(T) quality interaction energies at a much lower computational cost.⁴⁸ Here a further averaging of the MP2 and SCS-MP2 energies was used, which corresponds to the scaling factors of 1.1 and 1/6. With these factors, the potential energy values are very close to those from CCSD(T).

The parameters of the effective potentials to be used in the simulations were fitted to reproduce these *ab initio* data using a zero temperature Monte Carlo procedure. The resulting

FIG. 1. Potential energy curves of benzene- H_2 along different directions from the molecular center of mass, averaged over H_2 orientations. Symbols: quantum chemical calculations; solid lines: analytical model.

potential performs well against these calculations, as depicted in Fig. 1, provided that the following parameters are chosen (all in atomic units), $A_{\text{C}} = 73.828$, $A_{\text{H}} = 36.051$, $b_{\text{C}} = 1.999$, $b_{\text{H}} = 2.287$, $C_{6,\text{C}} = 19.406$, $C_{6,\text{H}} = 1.188$, $C_{8,\text{C}} = 139.526$, $C_{8,\text{H}} = 46.828$. As judged from this figure, the binding energy of a H_2 molecule to benzene is approximately one order of magnitude larger than to another H_2 and binding in the peripheral regions of the aromatic plane is much disfavored. This indicates that the solvation process will be similar as with the helium solvent^{38,39} and be ruled by the progressive coating next to the aromatic facets, before the shell completes near the peripheral region.

B. Path-integral molecular dynamics simulations

Owing to their weak binding and cyrogenic nature, aggregates of *para*- H_2 and *ortho*- D_2 molecules require a proper treatment of nuclear quantum effects. Here we have chosen the approach of path-integral molecular dynamics, which is rigorous and describes vibrational delocalization and tunneling despite lacking, at least in its standard version, exchange statistics. The PIMD approach is well documented^{49,50} and we only briefly describe here its most salient features of relevance to the present problem.

Denoting as $\mathbf{R}$ the collective $3N$ degrees of freedom of the N -particle system of hydrogen molecules around a PAH solute, $V(\mathbf{R})$ the classical potential energy of this configuration, the PIMD method consists in replacing the classical positions by a cloud of P replicas or “beads,” $\{\mathbf{R}_\alpha, \alpha = 1, \dots, P\}$ interacting with each other through the physical potential $V(\mathbf{R}_\alpha)$ within a replica, and through cyclic harmonic bonds between the successive beads of a given hydrogen particle. In canonical equilibrium at temperature T , the quantum statistics of the N -particle system is obtained from the large P limit partition function of the $N \times P$ -particle extended system driven by the effective potential $V_{\text{eff}}(\{\mathbf{R}_\alpha\})$,

$$V_{\text{eff}}(\{\mathbf{R}_\alpha\}) = \frac{1}{P} \sum_{\alpha} V(\mathbf{R}_\alpha) \\ + \sum_{\alpha} \sum_{i \in \text{particles}} \frac{mP}{2\beta^2 \hbar^2} \|\vec{r}_{\alpha,i} - \vec{r}_{\alpha+1,i}\|^2, \quad (10)$$

where $\vec{r}_{\alpha,i}$ denotes the position of bead α of particle i , the cyclic condition $\vec{r}_{P+1,i} = \vec{r}_{1,i}$ being applied. In this equation, m and $\beta = 1/k_B T$ denote the mass of the particle and the inverse temperature with k_B the Boltzmann constant, respectively. Having transformed the quantum system into a higher-dimensional classical system allows standard computational techniques such as Monte Carlo or molecular dynamics to be used to sample the canonical ensemble. In the PIMD case, it is customary to couple the dynamical variables to individual thermostats, which is achieved using the massive Nosé-Hoover technique.⁴⁹ Another useful trick in the path-integral framework is to change variables into a normal mode representation where the harmonic contribution to Eq. (10) is diagonal. This linear transformation is convenient for integrating the equations of motion, but also for interpreting the results using the centroid positions, or the normal mode associated with the zero eigenvalue which is just the position $\mathbf{R}_c$ averaged over all beads,

$$\mathbf{R}_c = \frac{1}{P} \sum_{\alpha} \mathbf{R}_{\alpha}. \quad (11)$$

The PIMD trajectories were integrated using a time step of 0.2 fs and for increasing values of the Trotter number (P) from $P = 1$ (classical regime) to $P = 512$. As discussed below, Trotter convergence appears to affect structural and energetic properties to a similar extent, however a satisfactory value of 256 was used throughout. Trajectories of 100 ps were performed after an equilibration of 20 ps not contributing to the averages.

The starting configuration taken for the clusters were obtained using basin-hopping global optimization,⁵¹ initially placing the atoms randomly around the PAH, performing large-step collective moves followed by local optimization and accepting the step in a Monte Carlo procedure based on a Metropolis criterion at 10 K. For each system studied, only 10^4 basin hopping steps were performed, this procedure only serving to generate starting points for the PIMD trajectories. Although we most likely missed the true global minimum for most systems, this specific configuration may not be so relevant for quantum system exhibiting zero-point induced structural transitions⁵² or even highly fluxional states owing to delocalization.

C. Observables

From the PIMD trajectories, several indicators were determined to characterize the structure of the solvent and its layering. The first solvation shell corresponds to H_2 particles that lie closest to the PAH. In spherical solutes such as C_{20} or C_{60} , structural information about the shells would be provided by the radial distances from the center of the solute and their distribution. In highly anisotropic solutes such as the presently studied planar hydrocarbons, the radial distribution is misleading and instead we considered the geometric distance to the solute, that is, the minimum distance between the hydrogen molecule and all atoms of the PAH. In the PIMD framework, the equilibrium distribution is accumulated from the individual contributions of all replicas.

From the PIMD trajectory, the energy $E_{PAH}(N)$ of the N -particle quantum systems in contact with the PAH at finite temperature was evaluated using the virial expression. Additional simulations were performed without the solute for both *para*- H_2 and *ortho*- D_2 clusters, from which the pure solvent energies $E_0(N)$ were likewise evaluated. The solute being kept frozen, the solvation energy associated with coating the solute with the finite-size solvent is simply defined as $E_{solv}(N) = E_{PAH}(N) - E_0(N)$.

Although the effects of exchange statistics cannot be accessed from the PIMD approach employed here, the extent of vibrational delocalization can be quantified from the spatial fluctuations experienced by each hydrogen molecule along the trajectories.³⁸ More precisely, for each particle i we define the fluctuation index,

$$\sigma_i = \frac{1}{P} \sum_{\alpha} [\langle \vec{r}_{\alpha,i}^2 \rangle - \langle \vec{r}_{\alpha,i} \rangle^2]^{1/2}, \quad (12)$$

and as a global indicator of delocalization we thus take the average $\bar{\sigma}$ over all particles. Large values of $\bar{\sigma}$ comparable to the PAH size would be expected for a fluid, whereas $\bar{\sigma}$ not exceeding a few Å would be associated with classical-like, localized behavior.

We have also pursued a more qualitative approach to delocalization by considering the inherent structures explored along the PIMD trajectories, followed pioneering ideas from the physics of liquids.⁵³ For classically localized dynamics, only one structure would show up corresponding to the stable structure. In contrast, a broader range of configurations would arise for a disordered, liquidlike phase. By systematically quenching the centroid configuration every picosecond, we can thus access the distribution of inherent structures and correlate the diversity of underlying minima in the energy landscape to the amount of fluctuations in the system. Such an approach was used earlier for other quantum systems such as cationic neon clusters⁵⁴ and more recently for the similar problem of PAH cations coated by helium.³⁸

Finally, we also evaluated the fluctuations of distances between hydrogen molecules, from which the normalized Lindemann index measures the overall extent of rigidity in the system.³⁸ In all situations considered, this index was found to be below 6%, indicating a high degree of crystallinity and no major fluidlike behavior.

III. RESULTS AND DISCUSSION

A. Trotter convergence

The evolution of the structural and energetic properties with Trotter number is considered first, taking as an example the coronene PAH coated by 100 *para*- H_2 or *ortho*- D_2 molecules. The distributions of minimum distance between hydrogen and the PAH obtained from the PIMD trajectories at $T = 2$ K and increasing values of P are shown in Fig. 2 in a mirror representation. At all values of P , the distributions exhibit three main peaks that are indicative of distinct solvation shells. For $P = 4$, the systems still behave mostly classically, with the first shells displaying some finer structure. However, as P is increased beyond $P = 16$, this atomic

FIG. 2. Distributions of minimum distance between hydrogen molecules and coronene at $T = 2$ K, as obtained from PIMD simulations of coronene(H_2)₁₀₀ at different Trotter numbers $P = 4, 16, 64$, and 256 .

structure becomes smooth and the distributions for each peak even overlap with the neighboring peaks. As expected, the distributions obtained for *para*- H_2 appear generally broader than for the heavier *ortho*- D_2 , even though the overlap between neighboring peaks remains. These features reflect the significant role of vibrational delocalization and confirm the need for an explicit account of quantum effects.

To get more insight into the convergence of physical a quantitative definition for the size and width of the first solvation shell is needed distribution of minimum distances, we have tried to isolate the contribution of atoms from the leftmost peak by assigning a decreasing weight to particles lying beyond $r_{\max} \approx 4$ Å in the averaging process. However we found this threshold somewhat arbitrary and possibly size- and PAH-dependent. Instead we followed a more practical procedure by fitting the first peak of the minimum distance distribution using a simple Gaussian shape, the area, and width at mid-height providing the size and thickness of the first solvation shell. In addition to monitoring these structural quantities, we also consider the average delocalization index $\bar{\sigma}$ and the solvation energy E_{solv} and their variations as the Trotter number is increased.

The variations of these properties with P are represented in Fig. 3 for the coronene(H_2)₁₀₀ system. Generally we find the properties to vary accordingly to power laws with inverse P , but with different exponents depending on the specific property. Convergence is fastest for the delocalization measure $\bar{\sigma}$, then for the shell thickness. However it is very satisfactory already for $P = 256$, especially for the solvation energy where a marginal change by less than 1% is noted upon increasing P to 512. Based on this preliminary investigation, we also conclude that while the shell sizes reported below should be considered as upper bounds, the values for the shell thickness, delocalization index and solvation energies are rather lower bounds.

B. Varying the amount of solvent

The progressive solvation of selected PAHs was investigated in the cases of benzene and coronene, the number n of hydrogen molecules being varied from 10 to 100.

FIG. 3. Convergence of various physical properties of coronene(H_2)₁₀₀ clusters at $T = 2$ K, as obtained from PIMD simulations at different Trotter numbers $P = 2^k$, $k = 1-9$. (a) Size of first solvation shell; (b) thickness of first solvation shell; (c) average delocalization index $\bar{\sigma}$; (d) solvation energy.

Although interesting, we did not specifically study the smallest size regimes $n < 10$ that lie far away from the completion of the solvation shell. We show in Fig. 4 the distributions of minimum distance to coronene for such different numbers by steps of 10, distinguishing in the figure the slightly different behaviors of *para*- H_2 and *ortho*- D_2 . For both choices of mass, the numbers of solvation shells manifested by as many peaks in the distribution of minimum distances varies from 1 for approximately $n < 50$ to 3 for $n > 70$. The peaks are always narrower and higher for *ortho*- D_2 , as expected for this more classical and localized isotope. In larger clusters, the position

FIG. 4. Distributions of minimum distances between the H_2 and coronene molecules in coronene(H_2) _{n} clusters, as obtained from PIMD simulations at 2 K for increasing sizes of $n = 10-100$.

FIG. 5. Variations of the first shell size and shell thickness in benzene(H₂)_n and coronene(H₂)_n clusters as a function of n , as obtained from the distributions of minimum distances. (a) Shell size; (b) shell thickness.

of the second peak is also shifted to lower distances in *ortho*-D₂ relative to *para*-H₂, which is consistent with a higher volumic density in the heavier system.

From these distributions, the numbers of hydrogen molecules composing the first shell and its thickness were evaluated by fitting the first peak onto a Gaussian shape. The variations of the two structural characteristics with increasing amount of hydrogen are represented in Fig. 5 for benzene and coronene. The size of the first solvation shell exhibits a monotonic behavior, growing linearly exactly as the number of hydrogen molecules and stabilizing near $n = 42$ ($n = 43$) for *para*-H₂ (*ortho*-D₂) around coronene, and $n = 24$ ($n = 25$) around benzene. These numbers approximately match the occurrence of the change in slope in the curves with increasing n . In contrast, the thickness of the shell displays some non-monotonic variations at small sizes, before the shell is complete, superimposed to globally increasing trends. These variations are mostly preserved upon changing the molecular isotope, but are also larger in the smaller benzene, both effects that point their origin to structural defects in the shell, in the disturbing presence of peripheral hydrogen atoms of the PAH and their completion in the range $20 < n < 40$.

The shell is also thicker around benzene than around coronene, and in *para*-H₂ relative to *ortho*-D₂, an effect that has already been identified and discussed above. Comparing to existing results for helium,³⁸ the thinner shell in coronene is likely related to the greater localization experienced by the hydrogen molecules in contact with the aromatic plane, the

FIG. 6. Solvation energy of benzene(H₂)_n and coronene(H₂)_n clusters as a function of the number n . (a) Benzene; (b) coronene.

solvent in the peripheral region being less tightly bound and more delocalized. As the PAH grows, the peripheral region becomes relatively less important and the shell thickness is dominated by those molecules that are on both sides of the aromatic plane.

The solvation energy per H₂ molecule, $E_{\text{solv}}(n)/n$, is given in Figs. 6(a) and 6(b) as a function of increasing number of coating hydrogen molecules, for both benzene and coronene solutes and, as always, for the two hydrogen isotopes. For this energetic property, *para*-H₂ always lie above *ortho*-D₂, which is the anticipated behavior owing to higher zero-point vibrational contribution to the energy. This quantum correction to the solvation energy remains approximately constant when comparing *para*-H₂ and *ortho*-D₂ after dividing E_{solv} by n , as done in this figure. Hence it scales nearly linearly with the number of hydrogen molecules, which indicates that it is due to interactions between hydrogen molecules rather than solute-solvent interactions. This observation is consistent with the much weaker nature of H₂–H₂ interaction.

Minor finite size effects are again noticeable for benzene in the size range where the solvation shell completes. However the general behavior consists of two smoothly varying regimes, with a stronger slope at small sizes corresponding to the preferential filling of the shell next to aromatic planes, followed by the more isotropic growth of the solvent energetically associated with H₂–H₂ interactions. In the large size limit, and assuming the solvent to be a continuum medium, the solvation energy would correspond to the creation of a fixed cavity into an approximately spherical droplet of growing radius $R_{\text{ext}}(n)$. The cavity being of fixed size for a given solute, the variations of the solvation energy with increasing n then lead to a fixed contribution E_{solv}^0 related to the surface tension of the solute/solvent interface and driven by the H₂–PAH interactions, plus a varying contribution $\delta E_{\text{solv}}(n)$ corresponding to the enlarging droplet of solvent by the radius $R_{\text{ext}}(n)$. This interaction is dominated at long range by the $1/r^6$ dispersion forces, and integrating over the solvent shell yields

a $1/R_{\text{ext}}^3 \sim 1/n$ leading term for this contribution $E_{\text{solv}}(n)$. Overall the solvation energy in this simplistic continuum model should thus vary as $E_{\text{solv}}(n)/n \simeq E_{\text{solv}}^0/n + \alpha/n^2$ with α a fixed coefficient. The size range covered in the present study is not broad enough to test the validity of this simple scaling argument, but it would be interesting to challenge it in the future. This would notably require a specific determination of the surface tension of the pure and doped hydrogen clusters, following earlier efforts for the PIMD methodology.⁵⁵

At 2 K pure *para*-hydrogen and *ortho*-deuterium clusters are essentially solidlike and localized,¹⁷ and in presence of the even stronger binding provided by the dopant nuclear delocalization should thus be further reduced. The average delocalization index $\bar{\sigma}$ has been computed as a function of n for the two solutes, and the results are shown in Fig. 7. A first comment that can be made is that these indices are always relatively moderate and lie below 3 Å. Even though an average over all atoms is taken to compute $\bar{\sigma}$, a fully delocalized, liquidlike solute can thus be ruled out as it would show values closer to the PAH size. Therefore hydrogen molecules tend to be localized once in contact with the PAH solutes, at least partially.

Here the extent of average delocalization also exhibits significant finite size effects until approximately 40 hydrogen molecules are present, especially in the case of benzene. The high similarity between the variations exhibited by the two delocalization indices for *para*-H₂ and *ortho*-D₂ indicates that these nontrivial variations are robust, and we anticipate that they reflect the interplay between specific positions around the solute and the diverse dynamical behaviors they lead to. This claim can be substantiated by looking specifically at the largest size n onto the archetypal coronene case, but at the resolution of individual molecules. The correlations between the individual average minimum distance and delocalization

FIG. 7. Average delocalization index $\bar{\sigma}$ in benzene(H₂)_n and coronene(H₂)_n clusters as a function of n . (a) Benzene; (b) coronene.

FIG. 8. Molecule-resolved minimum distance versus delocalization index σ_i in coronene(H₂)₁₀₀ clusters.

index in coronene(H₂)₁₀₀ clusters are shown in Fig. 8 for both *para*-H₂ and *ortho*-D₂ isotopes. The average distances arrange into three groups corresponding to the three solvation shells, but what this plot clearly shows is that molecules closer to the PAH are also much more localized. The scatter plots are also remarkably similar for the two molecules, the delocalization index in *ortho*-D₂ clusters being essentially shifted by 1.5–2 Å relative to its value in *para*-H₂. This similarity indicates that the properties under consideration are robust and that there is indeed a close connection between the position of each solvent molecule around the solute and its degree of nuclear delocalization.

A few molecules close to the solute can be delocalized ($\sigma_i > 2$ Å), but show a slightly larger minimum distance and thus lie near the molecular plane rather than being in contact with the aromatic units. Several molecules in the *para*-H₂ system also exhibit a highly delocalized regime with $\sigma_i > 3$ Å and upon visual inspection of the PIMD trajectory appear to experience large excursions in the second shell from one side of the PAH to the other.

Simulations of pure hydrogen clusters of the same size indicate that the individual delocalization indices σ_i vary roughly between 2 and 9 Å accordingly with the distance from the center, the clusters showing overall crystalline behavior except at the surface. However, the molecule-resolved Lindemann index remains below 6% even for the outermost molecules. The dopant thus contributes to further localizing the hydrogen molecules, even though some limited degree of disorder remains, especially at the surface.

C. Varying the solute

We now discuss finite size effects related to the solute itself, varying the PAH by increasing the number of aromatic rings along one direction from benzene to pentacene through naphthalene, anthracene and tetracene, or alternatively by keeping the sixfold symmetry in an oblate fashion from benzene to circumcoronene through coronene, ovalene, hexabenzocoronene, octobenzocoronene. The additional molecules of pyrene and perylene were also included in our set. In this section, the number of solvent hydrogen

FIG. 9. Distribution of minimum distance between various PAH molecules and H_2 molecules coating the PAH, in numbers of $n = 100$. Solid and dashed lines refer to *para*- H_2 and *ortho*- D_2 molecules, respectively. The PAHs are roughly sorted by increasing size from the smallest (benzene, bottom) to the largest (circumcoronene, top).

molecules is fixed to a value that is large enough to cover the first solvation shell in the largest PAH, namely $n = 100$.

Fig. 9 shows the distributions of minimum distance between hydrogen molecules and these various solutes, for both *para*- H_2 and *ortho*- D_2 isotopes. These distributions exhibit always two peaks, but most often three peaks or a

high-distance shoulder on the second peak in smaller PAHs. Such a shoulder does not mean that the shells are less sharply defined, but only reflect the anisotropy of the first solvation shell.

Comparing *para*- H_2 and *ortho*- D_2 with each other is easier on these plots, which confirms our earlier numerical observations for coronene, namely, that the shells are slightly thinner and contain more molecules for the heavier isotope, possibly resulting in the absence of a third shell in the case of ovalene, hexabenzocoronene, and octobenzocoronene. The distributions also become remarkably sharper for larger PAHs, the first and second shells no longer overlapping beyond ovalene.

We have tried to rationalize the dependence of the various properties of shell size, shell thickness, average delocalization index $\bar{\sigma}$ and solvation energy E_{solv} with the numbers of carbon and hydrogen atoms, as well as the number of aromatic units. However, it turns out that no single one of these three size defining parameters is sufficient to yield highly correlated variables. Fig. 10 shows for instance the variations of the properties against the number n_C of carbon atoms in the PAH.

If we put aside the case of the delocalization index and the shell thickness, for which the complex variations with n_C are to be related with the also complex variations with the number of coating H_2 [see Figs. 5(b) and 7], the shell size and solvation energy both appear correlated, nonlinearly in the case of the shell size. One missing variable is the number n_H of terminating hydrogen atoms, which will directly impact the size of the solvation shell (as well as the solvation energy) whereas the number of carbon atoms only measures the dominant contribution of the H_2 molecules in contact with the aromatic units. While the number of carbon atoms drives the global size of the system, correcting for the number of

FIG. 10. Variations of various properties in $PAH(H_2)_{100}$ clusters, as a function of the number of carbon atoms in the PAH. (a) Size of the first solvation shell; (b) shell thickness; (c) delocalization index $\bar{\sigma}$; (d) solvation energy.

TABLE I. Optimal coefficients A_0 , a_C and a_H of the linear relation connecting the size of the first solvation shell and the solvation energy (in K/H₂ molecule) to the number of carbon and hydrogen atoms in the PAH.

	<i>para</i> -H ₂			<i>ortho</i> -D ₂		
	A_0	a_C	a_H	A_0	a_C	a_H
Shell size	12.74	0.534	1.440	16.57	0.718	0.983
Solvation energy	-3.685	-1.488	-0.238	-3.071	-1.591	-0.415

FIG. 11. Size of the first solvation shell in coronene(H₂)₁₀₀ clusters as a double function of the numbers n_C and n_H of carbon and hydrogen atoms in the PAH. The red dots are the raw results from the PIMD simulations, the small blue dots are the corresponding projections on the optimal plane.

peripheral H₂ is equivalent to taking the next order of a liquid drop expansion for a 2D system.

A linear relation coupling n_C and n_H to the property of interest was indeed found to hold very well for both the shell size and the solvation energy, with the form

$$A(n_C, n_H) \simeq A_0 + a_C n_C + a_H n_H, \quad (13)$$

where A_0 , a_C , and a_H are three coefficients that were adjusted by minimizing a least-square error function on each property of interest over the different PAHs.

The resulting parameters are reported in Table I for the shell sizes and solvation energies corresponding to *para*-H₂ and *ortho*-D₂ clusters. The quality of the linear expression can be gauged by looking at the 3D plot of Fig. 11 where the shell size is now represented as a dual function of n_C and n_H together with the plane corresponding to Eq. (13) and the projections of the numerical data onto the plane.

The linear expression works nicely throughout the entire range of PAHs, the residual error in shell size amounting at worst to 2% and similar errors being found for *ortho*-D₂ and also for solvation energies. It thus provides a simple way of estimating the experimentally most accessible properties of regular polyaromatics.

Finally it is important to evaluate and discuss again the role of the solute on the degree of nuclear delocalization in such quantum clusters. Earlier works have shown that carbonaceous impurities bind strongly enough to suppress superfluidity^{21,42} and, even in the case of helium, localize the atoms in contact with the aromatic units.^{57,58} In this respect, it is instructive to consider first the three-dimensional atomic densities obtained from the PIMD trajectories for both isotopes, and to compare them with the results of a purely classical simulation ($P = 1$) for which no such isotopic effect takes place. Density plots are shown in Fig. 12 for coronene coated with 100 H₂ molecules.

The extent of delocalization is obviously larger in *para*-H₂ clusters, but the vast majority of molecules remain distinctly localized in a quasiclassical position, only particles from the third shell appearing as a blurred region of the density plot in Fig. 12(b). These particles are clearly seen in Fig. 8 as those with a high delocalization index and a large minimum distance to the PAH. Among these distant particles, some of them are also rather delocalized in *ortho*-D₂ with $\sigma > 2$ Å; they can be visualized in the third shell in Fig. 12(c). In contrast, all molecules appear well localized around their starting positions in the classical system [Fig. 12(d)]. In the pure *para*-H₂ cluster depicted in Fig. 12(a), outer molecules appear definitely more delocalized and even blur the true crystalline nature of the inner region.

Besides the index σ , delocalization can also be quantified by looking at the classical minima explored along the PIMD trajectory, and especially the fluctuations among these inherent structures. The centroid positions were periodically taken as the starting configuration of a local minimization and the resulting minima were sorted according to their energy relative to the global minimum. The distributions of minima obtained for benzene(H₂)₁₀₀ and coronene(H₂)₁₀₀ are represented in Figs. 13(a) and 13(b), respectively. For all four systems considered, the distributions are significantly broad and extend over hundreds of K in energy. This spreading is directly connected to the fluxional motion of the PIMD trajectories and provides a clear evidence for qualitative delocalization effects.

FIG. 12. Visual depiction of the atomic densities of (H₂)₁₀₀ clusters either (a) free and for *para*-H₂; or around the coronene molecule at 2 K for different treatments of hydrogen: (b) *para*-H₂; (c) *ortho*-D₂; (d) classical H₂. Plots realized with the Mayavi2 suite of Python scripts.⁵⁶

FIG. 13. Distributions of inherent structures visited in the PIMD simulations of (a) benzene(H_2)₁₀₀ and (b) coronene(H_2)₁₀₀ clusters at 2 K.

The distributions associated with *para*- H_2 are both especially broad, shifted to higher energies and consistent with a more disordered state and a higher zero-point energy for this isotope. The much narrower distributions in *ortho*- D_2 clusters are undoubtedly connected to the lower delocalization index and less fluxional dynamics. Even in *ortho*- D_2 clusters, vibrational delocalization is marked but does not predominantly involve the same isomers as *para*- H_2 clusters. More interestingly, the distributions show two rather different behaviors between the two PAHs, with fewer minima that contribute more to the distribution in the coronene case and a greater spreading for benzene, fewer minima dominating the distribution of inherent structures in the case of coronene solvated with *ortho*-deuterium. Care should be taken though not to interpret the energies of the inherent structures straightforwardly as zero-point energies, because the kinetic contribution, including that of the nuclei through the harmonic potential, is missing in these purely configurational values. The different shapes of the distributions between benzene- and coronene-coated clusters thus highlight the different topologies of the landscapes and a much broader basin associated with the most probable structure near 360 K above the global minimum.

IV. CONCLUDING REMARKS

As is well known in the physics and chemistry of helium droplets, the low-temperature equilibrium state of hydrogen clusters is strongly altered by the presence of a molecular impurity. The present investigation was focused

on a specific type of dopant consisting of a planar but possibly large polycyclic aromatic hydrocarbon and was aimed to determine their stepwise solvation mechanisms by *para*- H_2 and *ortho*- D_2 . Following the isotropically averaged description neglecting the atomistic details for hydrogen and using the Silvera-Goldman potential for the interaction between H_2 molecules, a dedicated but functionally similar potential to model H_2 -PAH interactions was developed and parametrized based on quantum chemical calculations. The equilibrium state at 2 K was then simulated using path-integral molecular dynamics simulations, for various PAH molecules ranging from benzene to circumcoronene. The formation and completion of the first solvation shell and its thickness were monitored from the distribution of minimum distance between H_2 and the PAH solute, whereas the solvation energy was evaluated from the difference of quantum energies between doped and pure hydrogen clusters.

The results generally indicate a well defined first solvation shell, delocalization arising mostly from the more distant shells. With respect to pure hydrogen clusters, which are also essentially crystalline, the dopant contributes to further pinning the molecules near the aromatic facets. Some results were rationalized in terms of molecular properties resolved as a function of their distance to the dopant, a procedure that was meaningful owing to the mostly localized nature of the hydrogen molecules. Despite such a classical like behavior at the PAH contact, inherent structure analyses clearly show a broad diversity of minima and excitation energies of several hundreds of Kelvin in the 100-molecule clusters. The variations with the number of *para*- H_2 or *ortho*- D_2 molecules can be non-monotonic until the first shell is well completed, and then become smooth and steady. In the limit of large clusters, the variations of shell size and solvation energy with the PAH itself were rationalized by simple linear relationships with the number of carbon and hydrogen atoms in the PAH.

The neutral compounds investigated in this work will be difficult to observe experimentally, but extending the present models to ionic solutes, making them detectable by mass spectrometry, would require some care. For instance, cationic PAHs are radical species and could spontaneously react with H_2 . Protonated PAHs would be more prone to classical modeling, but further refinement would be needed in order to treat properly the carbon atoms with different hybridization levels. In this respect, fullerenes appear as more convenient to test the possible effects of charge, owing to their greater capacity to hold additional electrons or lack thereof and the availability of measurements for them.⁴¹ In our subsequent effort, we will thus apply the same methodology to the solvation of various fullerenes by *para*- H_2 and *ortho*- D_2 and quantify the effects of size, but also charge and even shape.

Other extensions include more complete characterizations of how the individual properties of the hydrogen molecules vary with the distance to the dopant, ideally taking into account its highly anisotropic nature. The role of temperature on the rigidity and the extent of delocalization would be interesting as well, notably to address the question of the possible dependence of the melting point on the presence of the dopant and its size. Methodological improvements could

also by considered, starting with a proper inclusion of bosonic statistics, either through quantum Monte Carlo techniques⁵⁹ or by combining similar ideas to the PIMD framework.⁶⁰ A more ambitious development could consist in employing a fully atomistic description of the hydrogen solvent, at least with simple potentials such as the Darkrim-Levesque model⁶¹ previously used in the similar context of absorption in carbon nanotubes. Such an approach would enable a more precise characterization of the interaction with the dopant and its influence on the dynamics of the hydrogen molecules and their degree of translational and rotational rigidity as a function of the distance to the dopant. Although such a more realistic model would not necessarily be justified for the global properties addressed here at a temperature above the quantum melting transition,¹⁷ it would allow finer details to be tackled with possible experimental connections, notably the vibrational response in Raman spectroscopy.

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