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Adsorption of molecular hydrogen on coronene with a new potential energy surface

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Benchmark interaction energies between coronene, C₂₄H₁₂, and molecular hydrogen, H₂, have been computed by means of high level electronic structure calculations. Binding energies, equilibrium distances and strengths of the long range attraction, evaluated for the basic configurations of the H₂-C₂₄H₁₂ complex, indicate that the system is not too affected by the relative orientations of the diatom, suggesting that its behavior can be approximated to that of a pseudoatom. The obtained energy profiles have confirmed the noncovalent nature of the bonding and served to tune-up the parameters of a new force field based on the atom-bond approach which correctly describes the main features of the H₂-coronene interaction. The structure and binding energies of (para-H₂)_N- coronene clusters have been investigated within an additive model for the above mentioned interactions and exploiting basin-hopping and path integral Monte Carlo calculations for $N = 1-16$ at $T = 2$ K. Differences with respect to the prototypical (Rare Gas)_N-coronene aggregates have been discussed.

1 Introduction

The interest on polycyclic aromatic hydrocarbons (PAHs) within an astrophysical context has made this sort of systems subject of a large number of studies in recent years¹⁻⁵. The role played by PAHs in the formation of interstellar molecular hydrogen consists in providing an optimal platform for encounters of H atoms rather than supplying hydrogen to the environment after photodissociative fragmentation⁶. Thus, the mobility of H on defective graphene was treated in an attempt to understand the molecular hydrogen formation catalysis⁷. Graphite represents one of the best examples of inert surface to host both the formation of H₂⁸⁻¹³ and its ortho-para conversion¹⁴. As opposed to chemical dissociative processes, physical adsorption energy is typically in the meV regime and therefore the overall mechanism becomes relevant at low temperatures¹³⁻¹⁵. Physisorption on PAHs can be directly considered, on the other hand, as a model to study hydrogen storage^{16,17}. The characterization of phase diagrams and the heat capacity of systems formed by layers of H₂ on either graphite or graphene has been the goal of numerous investigations in the

past¹⁸⁻²⁵. Attachment of H₂ and D₂ to fullerenes has been also experimentally investigated in comparison with some other physisorbed species such as rare gases (RG) or N₂: The electronic absorption spectra recorded by Holt *et al.*²⁶ revealed a marked influence of the corresponding ligand. The theory versus experiment comparison performed by Kaiser *et al.*²⁷ on helium droplets doped with fullerenes and hydrogen (H₂ or D₂) revealed the effect of the surface curvature to accommodate hosting species inside the PAH.

It is therefore important to have an accurate description of the interaction between molecular hydrogen and PAH surfaces. Different works have treated the corresponding potential between H₂ and PAHs such as coronene, graphene or graphite^{15,28-32}. Density functional theory (DFT) calculations of the potential energy curves of up to seven H₂ molecules approaching coronene in a direction parallel to the C₆ symmetry axis were performed by Yeamin *et al.*³⁰. Energies obtained by averaging on a number of randomly generated conformations of H₂ at each distance to the center of mass (CM) of the coronene were fitted to an improved Lennard-Jones (ILJ) analytical function. Špirko *et al.* also performed DFT calculations to calculate the interaction potential separating the stretching and translational motions of molecular hydrogen on the graphene surface²⁹. A similar investigation by de Lara-Castell and Mitrushchenkov²⁸ concluded that the global minimum corresponds to the orthogonal orientation of the hydrogen molecule with respect to the surface plane of the graphene.

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The comparison of the theoretical results with experimental binding energies of the H₂ bound states on a graphite surface revealed a fairly good agreement. Most of the structural properties obtained on those calculations indicate that the relative orientation of the H₂ unit has little influence. The path integral molecular dynamics (PIMD) calculation by Calvo and Yurtsever³³ on H₂-solvated PAH clusters employed a simplified potential energy surface (PES) in which H₂ internal degrees of freedom are neglected.

In a series of previous papers, we treated coronene clusters doped with RG atoms^{34–36}, such as He, Ne, Ar and Kr. Energies and structures of (RG)_N-coronene systems (including also combinations of different RG atoms) were calculated by means of basin-hopping (BH) and path integral Monte Carlo (PIMC) calculations employing a PES developed by some of us³⁷. An experimental investigation on He atoms adsorbed on coronene cations³⁸ revealed an interesting agreement with some of the findings reported for the neutral species³⁶. In particular the theoretically predicted stability for the He₃₈-coronene cluster was found to match the anomalously high intense peak in the spectra of Ref.²⁷ interpreted as the formation of a rigid layer composed with 38 He atoms completely covering both faces of (C₂₄H₁₂)⁺. Analogously, a similar magic signal at $N = 44$ seen in the measured spectrum for the cationic coronene²⁷ agrees with the prediction of the PIMC calculation of the first complete solvation shell for He₄₄-coronene³⁶. In the same spirit, we present here a new H₂-coronene analytical PES obtained by exploiting the atom-bond procedure whose parameters are fine-tuned on benchmark *ab initio* calculations of the interaction energies for several orientations of H₂ on the main sites of the C₂₄H₁₂ plane. The resulting potential, which considers H₂ as a pseudoatom with no internal degrees of freedom, is then employed to calculate the structure and binding energies of the (H₂)_N-coronene clusters, where $N < 17$, employing both BH and PIMC methods at $T = 2$ K.

The structure of the paper is as follows: Section 2 presents theoretical details of the PES calculation; Section 3 summarizes BH and PIMC methods; in Section 4 results for both the interaction energies and the clusters structure and binding energies are presented; results are discussed in Section 5 and, finally, conclusions are reported in Section 6.

2 Potential Energy Surface Calculations

2.1 Computational Methods

Intermolecular interaction energies between H₂ and coronene have been computed at levels of the “coupled” supermolecular second-order Møller-Plesset perturbation theory (MP2C)³⁹ and density functional theory-symmetry adapted perturbation theory (DFT-SAPT)⁴⁰. The choice of the MP2C approach relies on its capability to provide accurate estimations for the interaction energies in weakly bound noncovalent systems, ranging from RG-coronene³⁷ or benzene-benzene⁴¹ up to molecule-annulenes^{42–44}, at an affordable computational cost. DFT-SAPT estimations of the interaction energies are in general more expensive in terms of computing time, but they have been also performed in order to provide alternative results of well known reliability^{45,46} and unaffected by the basis set superposition error

(BSSE). Moreover, one of the advantages of SAPT approaches is to obtain a decomposition of the interaction energy into its different physical contributions, a very helpful feature to get more insights into the properties of the cluster.

For a proper estimation of the involved noncovalent interactions, the use of large basis sets (including diffuse functions) is required. Our previous experience on the RG-coronene systems³⁷ has suggested that a modified version (with the exponents of the most diffuse functions of each angular momentum type multiplied by 2.3) of the aug-cc-pVTZ⁴⁷ basis set should be employed for coronene, while for H₂ we have tested that the aug-cc-pVQZ⁴⁷ set is sufficiently large to lead to well converged energies. MP2C interaction energies have been corrected for the BSSE by the counterpoise method of Boys and Bernardi⁴⁸.

In the DFT-SAPT approach, the exchange-correlation functional has been approximated by the the Perdew-Burke-Ernzerhof (PBE) generalized gradient functional⁴⁹, whose asymptotic behavior is corrected as described by Grüning *et al*⁵⁰ through a shift parameter obtained as the difference between the ionization and HOMO energies of each monomer. These latter energies have been calculated at the DFT level of theory with the corresponding basis set as used for DFT-SAPT computations, while the experimental ionization potentials are taken from Ref.⁵¹.

Finally, the δE_{HF} contribution⁵² has been added to the DFT-SAPT energies; this is a term obtained at the Hartree Fock level of theory that accounts for induction and exchange-induction effects higher than second-order and which is generally small for neutral or highly symmetric systems even if not negligible. In order to make both MP2C and DFT-SAPT calculations computationally affordable, the density-fitting method⁵³ has been applied to approximate the two-electron repulsion integrals. Both MP2C and DFT-SAPT computations have been performed by using the Molpro2012.1 package⁵⁴. All reported interaction profiles refer to a rigid monomers approximation, that is, the molecular configurations are not allowed to relax during the calculations. In particular the following geometrical parameters have been employed: for coronene the C-C bond lengths and C-C-C angles are those⁵⁵ typical for graphite, namely 1.420 Å and 120°, respectively, whereas the C-H bond lengths and C-C-H angles are 1.090 Å and 120°, respectively; for H₂ the bond length is 0.746 Å.

Table 1 Optimized parameters for the H₂-(C-C) and H₂-(C-H) atom-bond pair potentials. Perpendicular and parallel components of R_m and ϵ are in Å and in meV, respectively. λ is dimensionless.

Pair	$R_m^\perp$	$R_m^\parallel$	$\epsilon^\perp$	$\epsilon^\parallel$	λ
H ₂ -CC	3.596	3.958	2.089	2.685	6.5
H ₂ -CH	3.446	3.668	2.714	2.163	9.0

2.2 Analytical Representation

The atom-bond approach^{56,57} has been used to represent the H₂-coronene interaction with the diatom considered as a pseudoatom. In this approach the chemical bonds of coronene are the interaction centers on the PAH frame and the total intermolecular energy V_{tot} is given as a sum of atom-bond pair contributions (i), each one represented by a potential term V^i :

$$V_{\text{tot}} = \sum_i V^i. \quad (1)$$

The atom-bond pair potential, V^i , depends both on the distance R_i between the H_2 pseudoatom (fixed as a point mass at the H_2 CM) and the bond reference point, as well as on θ_i , the Jacobi angle describing the orientation of the pseudo-atom relative to the bond axis. The above reported sum runs over all bonds on coronene and the reference point for each bond coincides with the geometric bond center.

The parameterization adopted for the pair potential V^i is of the ILJ type⁵⁸:

$$\frac{V^i(R_i, \theta_i)}{\varepsilon_i(\theta_i)} = \frac{6}{n(x_i) - 6} \left(\frac{1}{x_i} \right)^{n(x_i)} - \frac{n(x_i)}{n(x_i) - 6} \left(\frac{1}{x_i} \right)^6 \quad (2)$$

where x_i is a reduced distance

$$x_i = \frac{R_i}{R_{mi}(\theta_i)}, \quad (3)$$

the n exponent is given by

$$n(x_i) = \lambda + 4.0 x_i^2, \quad (4)$$

λ is a parameter defining the shape of the potential and depending on the nature and hardness of interacting particles, and $\varepsilon_i(\theta_i)$ and $R_{mi}(\theta_i)$ are the angle dependent well depth and minimum location of the atom-bond interaction, respectively. Their dependence with the Jacobian angle can be easily expressed⁵⁷ as a function of $\varepsilon_i^\perp$, $\varepsilon_i^\parallel$, $R_{mi}^\perp$ and $R_{mi}^\parallel$, respectively, which are the well depths and equilibrium distances for the perpendicular and parallel approaches of the pseudo-atom to the bond. Together with λ , these parameters are optimized by exploiting the comparison of the analytical potential with the benchmark *ab initio* results. During the optimization procedure they have been varied within limited ranges with respect to the zero order values predicted by the polarizability components of the involved partners, in order to maintain a proper physical meaning and not to treat them as simple fitting parameters. This assures that the adopted formulation of the PES, providing an internally consistent analytical representation of the interaction both in the less and the most stable configurations of the investigated system, is suitable to perform molecular dynamics calculations.

The final fine-tuned values for $R_m^\perp$, $R_m^\parallel$, $\varepsilon^\perp$, $\varepsilon^\parallel$ and λ are presented in Table 1 for both H_2 -(C-C) and H_2 -(C-H) pairs.

For the interaction between H_2 pairs we have employed the Diep and Johnson PES^{59,60}, which is suitable to describe the dimer gas phase behaviour. However, in order to be consistent with the pseudoatom approximation for H_2 considered for the H_2 -coronene interaction, we have retained just the first term of the H_2 - H_2 potential expansion which accounts for the spherically averaged component. Note that the interaction anisotropy in H_2 - H_2 , basically determined by the electrostatic permanent quadrupole-permanent quadrupole contribution, makes the potential deviates from the spherically averaged component about 2 meV at maximum in the minimum region. This difference roughly corresponds to less than 5 % of the average total binding energy of

the H_2 -coronene system (see Fig. 1, Table 2 and Section 4.1) and it is comparable (or lower) in absolute scale to its interaction anisotropy. Moreover, such anisotropic component tends to vanish for free rotating molecules as it is for H_2 monomers at low temperature and density, since the attractive and repulsive contributions seem to balance. The spherical average approximation for para- H_2 , on the other hand, has been analyzed in detail by Li and coworkers⁶¹, proving its good performance for the ground state of (para- H_2)₂ by comparison with accurate calculations.

3 Structure and Energy Calculations

3.1 Basin-Hopping Method

Global minima were obtained using the BH⁶² or Monte Carlo (MC) minimization⁶³ method, successfully employed before for both neutral^{62,64,65} and charged atomic and molecular clusters^{66–71}, along with many other applications.⁷² This technique is a stochastic method that involves perturbation followed by minimization at each step. This method transforms the PES into a collection of basins and explores them by hopping between local minima. This transformation of the PES preserves the global minimum and all local minima. The steps are accepted or rejected following a Metropolis criterion using the energies of the initial and final minima and a fictitious temperature. The procedure is particularly efficient because the downhill barriers between different basins are removed. Hence, this approach avoids trapping, and the step sizes can be much larger than those typically used for thermal sampling in MC simulations.

The results were obtained at a constant fictitious temperature such that $k_B T = 5$ meV. A total of 4 runs of $2 \cdot 10^4$ BH steps each were performed for all clusters sizes. The same global minima were obtained in all trajectories. This should ensure a reasonably high degree of confidence.

In order to include quantum effects in this classical method, we have calculated the zero-point-energy (ZPE) in the harmonic approximation as in Ref.³⁶. In doing so we have built a database of local minima closed to the global minimum to each cluster size. The ZPE correction has been added to the local and global minima. In some cases, the geometry of the BH-ZPE global minimum differs from the BH one as shown in Table 3.

3.2 Path Integral Monte Carlo Method

The PIMC approach was already explained in previous publications^{34,36} and therefore we will simply present the numerical details of the calculation. The total Hamiltonian $\hat{H}$ can be written as:

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + V(\mathcal{R}) \quad (5)$$

where m is the mass of H_2 , $\mathcal{R}$ is the vector with the $3N$ positions of the H_2 pseudoatoms, $\hbar$ is the Planck constant, and

$$V(\mathcal{R}) = \sum_{i=1}^N V_{\text{H}_2-\text{cor}}(\mathbf{r}_i) + \sum_{i<j}^N V_{ij}(r_{ij}) \quad (6)$$

is the total potential: the first term corresponds to the pairwise H_2 -coronene interaction and the last term refers to the interaction

potential between the two i and j H₂ molecules separated by a distance $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$.

The internal energy have been calculated by means of the estimator given in Refs.^{73,74}:

$$\begin{aligned} \langle E(T) \rangle = & \frac{3N}{2\beta} - \left\langle \frac{1}{2M} \sum_{\alpha=0}^{M-1} \sum_{i=1}^N (\mathbf{r}_i^{\alpha} - \mathbf{r}_i^C) \cdot \mathbf{F}_i^{\alpha} \right. \\ & \left. + \frac{1}{M} \sum_{\alpha=0}^{M-1} V(\mathcal{R}_{\alpha}) \right\rangle, \end{aligned} \quad (7)$$

where M is the number of beads considered in the calculation once the total density matrix at temperature T is assumed fractioned in M density matrices at higher temperatures MT ^{34,36}; $\beta = 1/k_B T$, k_B is the Boltzmann constant; $\mathbf{r}_i^C = M^{-1} \sum_{\alpha=1}^M \mathbf{r}_i^{\alpha}$ defines the centroid of the M beads describing the i -th H₂ molecule. The first term in Eq. (7) is the classical kinetic energy with subtraction of the CM degrees of freedom; the second one is a quantum correction with $\mathbf{F}_i^{\alpha}$ as the force experienced by the i -particle on the α slice and the third term describes the interaction between each pair of particles on that α slice. Calculations performed with the thermodynamic estimator⁷⁵ yield to almost identical results for the energy.

The calculations involve a total of 10^5 MC sweeps for each simulation with about 100 staging moves. The position of 10 % of the beads are updated after each staging move. Error bars for the energy values are obtained using the block average method⁷⁶. The PIMC calculation has been performed at $T = 2$ K with $M = 1$ for the classical Monte Carlo (CMC) version and up to a total of $M = 1000$, a value which guarantees converged results.

The PIMC simulations are started from the optimized minimum energy configurations obtained by means of the BH + ZPE algorithm explained in the previous section.

4 Results

4.1 Interaction Energies

Interaction energies have been computed for three different perpendicular approaches of H₂ towards the central ring of the coronene plane: in analogy with our previous studies on the RG-coronene system³⁷ they are the hollow (H), top (T) and bridge (B) approaches and for each of them three different orientations of the H₂ molecule have been taken into account corresponding to two parallel (labelled with the "1" and "2" indexes) and one perpendicular (labelled with the "3" index) geometries as shown in Fig. 1.

Nine different interaction profiles have been then globally computed and reported in Fig. 1 as a function of z , the distance to the coronene plane. In particular, the MP2C results have been obtained in a range of distances comprised from 2.25 to 10.5 Å, while those corresponding to the DFT-SAPT level have been calculated over a shorter interval (from 2.5 to 4.5 Å) due to its higher computational cost. In Fig. 1 a good agreement between the results carried out at both levels of theory can be noticed, even if globally the DFT-SAPT profiles are somewhat less attractive in the well region.

Fig. 1 (Upper part) Sketch of the coronene molecule and bridge (B), top (T) and hollow (H) approaches of the H₂ molecule towards its inner ring. For each approach three different orientations of H₂ have been considered: "1" and "2" are parallel, and "3" is the perpendicular configurations. (Lower part) *Ab initio* intermolecular interactions for the H₂-coronene system as a function of z , perpendicular coordinate with respect to the coronene plane). The different energy profiles correspond to the H₂ approaches depicted above: black and red colours are used to distinguish between H₂ parallel and perpendicular orientations, respectively. Notice that both parallel orientations ("1" and "2" labels in each panel) provide practically indistinguishable results. MP2C and DFT-SAPT interaction energies are reported as full circles joined with lines and open squares, respectively. Previous results⁷⁷ obtained at the DFT/CC level of theory have been also depicted as crosses for comparison.

Previous results⁷⁷ obtained around the minima with the DFT/CC correction scheme, which combine DFT and CCSD(T) levels of theory to obtain reliable values of the interaction energies, are also reported in Fig. 1 and they provide a good comparison with present findings.

For each (B, T, H) approach it can be also seen that the interaction profiles corresponding to the two parallel orientations of H₂ are practically indistinguishable. Moreover, even if they are globally less attractive in the long range, they correspond to the most stable intermolecular structure for the hollow approach (bottom panel): in this case a slightly larger binding energy is found with respect to the interaction related to the H₂ perpendicular orientation while for the top and bridge approaches (middle and top panel) an opposite trend can be observed with more marked differences between the energy profiles in the minimum. This behavior of the interaction with the H₂ orientation can be under-

Table 2 DFT-SAPT contributions to the total binding energies for the hollow and top approaches. The reported values refer to intermolecular distances equal to 2.91 and 3.18 Å, roughly the corresponding equilibrium distances for the H and T configurations, respectively. Induction and dispersion components also include the respective exchange contributions. The $\delta(\text{HF})$ term is also added to the induction contribution. All values are in meV.

	H1	H3	T1	T3
Electrostatic	-32.4	-35.7	-15.1	-20.8
Exchange repulsion	101.1	129.3	52.4	70.8
Induction	-8.8	-14.7	-4.6	-10.6
Dispersion	-106.5	-119.1	-72.8	-83.1
Total	-46.6	-40.2	-40.1	-43.7

Table 3 Total energy of the $(\text{H}_2)_N$ -Coronene clusters (in meV) for $N = 1 - 16, 38$ and the number of H_2 units at each side of the molecular plane, (n_a, n_b) , (second column) according to the BH (third column), the CMC (fourth column), the BH+ZPE (fifth column) and PIMC (sixth column) approaches. * means that the minimum for the BH+ZPE case comes from a different structure than the BH global minimum. Temperature for the CMC and PIMC calculations is 2 K.

N	(n_a, n_b)	BH	CMC	BH+ZPE	PIMC
1	(1,0)	-44.3	-43.8	-31.3	-32.8
2	(1,1)	-88.8	-87.8	-62.8	-65.7
3	(3,0)	-128.5	-127.0	-89.1*	-92.8
4	(3,1)	-173.2	-171.1	-115.5*	-120.1
5	(3,2)	-212.9	-210.3	-140.3	-147.3
6	(3,3)	-257.8	-254.7	-165.2	-174.6
7	(4,3)	-294.8	-291.2	-182.8	-196.0
8	(4,4)	-331.9	-327.7	-200.4*	-217.5
9	(5,4)	-364.3	-359.6	-214.5	-234.3
10	(7,3)	-399.0	-393.8	-230.0*	-252.0
11	(7,4)	-436.2	-430.4	-246.0*	-270.0
12	(7,5)	-468.7	-462.5	-260.1*	-286.9
13	(7,6)	-502.8	-495.9	-275.7*	-304.9
14	(7,7)	-540.8	-533.6	-291.8*	-322.7
15	(8,7)	-567.6	-559.8	-301.0*	-334.0
16	(9,7)	-594.9	-586.6	-308.3*	-346.6
38	(19,19)	-1180.3	-1160.5	-530.3*	-619.0

stood by looking into the different contributions provided by the DFT-SAPT calculations and reported in Table 2 for the distances around the minima of the hollow and top approaches: it can be seen that globally for the H_2 perpendicular orientation the attractive components (electrostatic, induction and dispersion) are generally higher than those pertaining to the parallel orientation. This steric effect has been also shown in previous theoretical estimations²⁸ obtained at the DFT-SAPT level of theory and for the same interaction partners. The exchange repulsion contribution is also larger for the perpendicular than for the parallel approach and it is worth noting that the difference between both orientations becomes significantly larger (about 30 meV) for the hollow approach, while for the top case such a difference is more moderate (about 18 meV). Therefore, it can be inferred that the parallel oriented H_2 molecule penetrates more easily towards the center of the inner ring due to a reduced exchange repulsion (compare H1 with H3 values and T1 with T3 in Table 2).

Despite the aforementioned discussion, the anisotropy of the interactions with respect to the H_2 orientation is rather small: in the long range and around the minimum, parallel and perpendicular profiles of Fig. 1 are shifted from one to another by just few meV, a difference that is smaller than the rotational constant

of the molecular hydrogen (≈ 7.35 meV). This suggests that H_2 nearly behaves as a free rotor when adsorbed on coronene thus making the treatment of the diatom as an effective pseudoatom a reasonable approximation. Effective potentials have been then obtained by simply summing the results for the three orientations of H_2 , each one weighted by a 1/3 factor. We have found that building effective potentials adiabatically (i.e. solving a hindered rotor problem⁷⁸ at every value of the position of the H_2 CM) leads to almost identical profiles to those of the orientation averaged potentials, a further support for the approximation adopted in the present study neglecting the internal degrees of freedom of H_2 .

Fig. 2 Effective intermolecular interactions for the H_2 -coronene system obtained by considering H_2 as a pseudoatom as a function of z the perpendicular coordinate with respect the coronene plane. MP2C and DFT-SAPT interaction energies are reported as full circles and open squares, respectively, and they correspond to average values obtained by combining (see text) the related results reported in Fig. 1. The solid black lines correspond to the analytical atom-bond potentials whose parameters are reported in Table 1.

The resulting orientationally-averaged interactions are shown in Fig. 2 together with the related atom-bond analytical profiles. A good agreement can be observed between the *ab initio* predictions and the analytical representation, especially in the case of the top and bridge approaches. For the hollow approach the atom-bond profile slightly underestimates the *ab initio* interactions in the well region but it is globally close to the DFT-SAPT curve, even if with a slightly larger minimum position. From the comparison with analogous results previously obtained for different RG (See Figures 2–5 of Reference³⁷), it can be also noticed that present interaction curves lie between those of Ne and Ar.

This behavior could be somehow expected since it follows the trend of an increasing value of the Ne, H₂ and Ar polarizabilities (0.4, 0.79 and 1.64 Å³, respectively)⁷⁹ and it confirms the noncovalent nature of the H₂-coronene bonding.

Additional interaction profiles (not shown here) calculated for parallel approaches of H₂ towards the coronene plane at outside locations (following either one of the C–H bonds or one of the C–C bonds leading to any of the vertexes of the central hexagon) reveal a similar good agreement between MP2C and atom-bond options. This result confirms the reliability of the presently obtained atom-bond force field for configurations with the H₂ located far from the center of the coronene and the convenience of the MP2C result for a valid global description of the interaction.

4.2 (H₂)_N-Coronene Clusters

The BH approach was employed to obtain the classical optimized configurations for (H₂)_N-coronene with $N = 1 - 16$ and 38. The resulting structures are shown in Figure 3 and their corresponding energies are listed in Table 3. H₂ molecules are located mainly over the hollow positions of the coronene with the only exception of those situations with two, four or five molecules at one of the sides of the PAH plane (see the $N = 5, 7-9$ cases). (H₂)₁₄-coronene corresponds to the first cluster with hollows at both sides of the molecule occupied by H₂. When more units of molecular hydrogen are added to the cluster, the additional H₂ occupy peripheral positions at the border of the coronene plane (see Fig. 3).

$N = 14$ certainly seems to be a special case as manifested also by the evaporation energy, $E_{\text{evap}} = E_N - E_{N-1}$, as a function of N , given in Figure 4. The BH values show in fact a local minimum at $N = 14$, in comparison with the immediately closest cases $N = 13$ and $N = 15$. A similar situation is found for (H₂)₄-coronene and (H₂)₆-coronene, thus suggesting the special stability brought to the cluster by an arrangement of three H₂ molecules surrounding the central hollow.

A tentative comparison with the PIMC results can be made by adding the ZPE estimations to the pure BH energies as explained in Section 3.1. In particular, the trend followed by the evaporation energy as a function of N obtained with this BH+ZPE approach reproduces qualitatively well the PIMC energies shown in Figure 4 almost for the entire range of sizes under investigation.

Table 3 and Figure 4 also include values of the total energies. The comparison between the BH and CMC results reveals a fairly good agreement for the smallest sizes, with slight deviations as N increases, which can be due to the temperature, a factor not included in the BH algorithm. Differences are more noticeable when PIMC and BH+ZPE results are compared, with E_{tot} values obtained by the latter approach remaining clearly above the PIMC energies for the largest N . As in the case of (He)_N-coronene clusters investigated in Ref.³⁶, anharmonic effects and the additive character of the interaction as the size of the cluster increases can be the reason for this feature.

Probability density functions for the (H₂)_N-coronene clusters are also obtained with the PIMC approach. The cases $N = 5, 9, 13$ and 16 are illustrated in Figure 5 showing both sides of the coronene plane. For those situations with a number between two

and six H₂ molecules on one side of the coronene (see cases (a), (b) and (c) in Figure 5), the coexistence of different isomers or locations on the PAH surface indicates certain degree of unlocalized behavior. For $N = 13$, the seven units of H₂ on one side of the coronene are close to occupy localized top positions above the C atoms of the outer ring. As seen in our previous paper on RG atoms on coronene³⁴ the precise location is driven by the equilibrium distance between consecutive H₂ molecules, a feature which seems to explain why the hollow sites are not occupied in this case.

Interestingly, for (H₂)₁₆-coronene (case (d) in Figure 5) the PIMC distribution agrees with the BH minimum arrangement with the two units of molecular hydrogen located outside the PAH plane. There is however a discrepancy regarding the precise position since the H₂ unit prefers a different kind of dimple according to each method prediction.

Our study includes the case of a larger cluster, (H₂)₃₈-coronene as a further test of the capabilities of the present PES for different approaches of H₂ to the coronene plane. For He_N-coronene, $N = 38$ was found to be the first case where the solvating He atoms occupy both all hollow sites and all outer cavities formed between C-H bonds (see Figure 5 of Ref.³⁶). Therefore extra He atoms added subsequently to the coronene cluster are free to explore $z \approx 0$ regions. The corresponding energy according to the PIMC calculation, shown in Table 3, -619 meV, is about 1.7 times more negative than the binding energy of $N = 16$. Its probability density as a function of the distance to the coronene plane (not shown here) exhibits some non-negligible values around $z \approx 0$ which are indication of certain probability of passage between both sides of the plane rather than evidences of the onset of a proper solvation layer. This tendency is also found for the structure of the BH+ZPE minimum where 17 H₂ units are seen at each side of the coronene and the remaining 4 are located at the plane. The BH geometry, on the contrary, predicts a (19,19) structure for (H₂)₃₈-coronene.

5 Discussion

An interesting issue to discuss regards the convenience of including a correct description of the internal degrees of freedom of the H₂ molecule to obtain the analytical expression of its interaction with coronene. The present PES has been obtained under the assumption of a pseudoatom behavior for the molecular hydrogen. This is, on the other hand, the usual procedure followed in previous investigations on similar systems formed by H₂ on either molecules or surfaces^{22,23,29,33,80,81}. Thus, for example, Špirko *et al.*²⁹ neglected internal rotations of absorbed molecular hydrogen keeping an equilibrium orientation with a frozen H-H distance, and Nho *et al.* assumed H₂ as spherical particles interacting via a semiempirical Silvera and Goldman potential⁸¹. Analogously, in their recent PIMD study, Calvo and Yurtsever³³ assumed structureless H₂ molecules. Their choice was justified by the free rotations experienced by hydrogen molecules in their $J = 0$ state at the low pressures of finite clusters. The dispersionless density functional (dLDF) investigation of H₂-graphene performed by de Lara-Castells and Mitrushchenkov²⁸ reveals weak dependence of the PES on the molecular hydrogen orientation with respect to the graphene surface. Moreover, it has been ex-

Fig. 3 Global minimum energy configurations of the Coronene-(H₂)_N for $N = 2 - 16$ obtained by means of the BH approach. Present calculations do not provide orientation of H₂ with respect to the coronene surface so an arbitrary one has been chosen for each cluster.

Table 4 Binding energies (in meV) of the bound states (first column) of H₂ on graphite from experiment by Mattera *et al.*⁸⁴ (second column); present results (third column); DFT/CC energies of Ref.²⁹ (fourth column); and dIDF energies of Ref.²⁸ (fifth column).

	Exp ⁸⁴	Present	DFT/CC ²⁹	dIDF ²⁸
0	41.61	46.83	50.21	40.24
1	26.43	30.96	32.45	25.52
2	15.33	18.90	18.87	14.72
3	7.96	10.45	9.30	7.49
4	3.61	5.13	3.37	3.22
5	1.46	2.19	0.51	1.10

perimentally observed that physisorbed H₂ molecules on graphite nearly behave as free rotors^{82,83} These findings thus support the assumptions considered here to obtain the effective PES and validate the corresponding BH and PIMC calculations carried out for the coronene molecule.

Test calculations of H₂-coronene bound states employing a model average potential constructed with B, T and H contributions at different values of the z distance and the angle of the H-H bond with respect to the coronene plane reveal that differences with a pseudoatom approximation are not larger than 1 meV, a clear indication of the validity of such an approach for the present investigation.

A comparison of the present PES with some of those previously reported potentials can be attempted. Despite the lower theory level of calculations employed by Yeamin *et al.*³⁰ (DFT plus empirical dispersion corrections), values of the minimum energy and equilibrium distance for a single H₂ in perpendicular approach to the coronene surface and equilibrium distance (45.7 meV and

3.09 Å, respectively) are in good accord with the values here obtained: 45.5 meV and 3.15 Å. The only significant discrepancy arises with the equilibrium distance (3.57 Å) for the averaged potential in Ref.³⁰, surprisingly larger, not only than the present result (~ 3.1 Å) but also than the value reported by authors of Ref.³⁰ for the H₂ molecular axis in a perpendicular direction with respect to the coronene surface. An analogous comparison with the potential interaction employed by Calvo and Yurtsever³³ revealed noticeable similarities with the only exception of H₂ 'in-plane' approaching H₂ configurations for which the present potential remains slightly deeper.

The present potential has been extrapolated to describe the interaction between H₂ and graphene/graphite by summing pair potentials over all the C-C bonds needed for a prescribed convergence and by a further representation in a Fourier series, as reported in detail in Ref.³⁷ for the case of RG-graphene/graphite. For H₂-graphite, bound states of the first term of the Fourier series (the laterally averaged potential) have been obtained and in Table 4 the results are reported and compared with binding energies estimated either from experiment⁸⁴ or from other theoretical approaches^{28,29}. As can be seen, present calculations (third column) overestimate the binding energies experimentally determined (second column) although to a lesser extent than those obtained from a DFT/CC study²⁹ (fourth column), while the dIDF calculation by de Lara-Castells *et al.*²⁸ achieves a remarkable agreement with experiment (fifth column). It is worth noting that qualitatively similar results were reached for He-graphite within the same methodology³⁷, i.e., the computed binding energies were found to be somewhat larger than the measurements.

Fig. 4 Total energies in meV for the $(\text{H}_2)_N$ -Coronene clusters with $N = 1 - 16$ obtained by means of the PIMC (full squares), CMC (empty squares), BH (empty circles) and BH+ZPE (empty triangles) methods. Temperature for the PIMC and CMC calculations is 2 K; (Inset) Evaporation energies calculated as $E_N - E_{N-1}$ with $N > 1$.

In that work, overestimation of the He-graphene/graphite interaction energies was attributed to a poorer description of the extended π -electron conjugation (that could slightly modify the C-C bond polarizability) and/or to screening effects (that would reduce the long range attraction in the case of graphite). We believe that the discrepancies found for the present system are also due to these factors and that the neglect of the H_2 rotation plays a smaller role. Indeed, as in the present *ab initio* calculations, de Lara-Castells *et al.*²⁸ also found within their extended calculation on graphene that the PES exhibits a very weak dependence on the orientation of the hydrogen molecule.

Regarding the energetics and structures of the $(\text{H}_2)_N$ -coronene clusters, present results can be compared with previous studies on different RG-doped coronene clusters^{34,36}. For instance, the BH minimum structures shown in Fig. 3 are in good agreement with respect to those preferred in the case of He and Ne atoms found in Ref.^{34,36}, the only difference being the cases of He_5 -coronene, Ne_5 -coronene and $(\text{H}_2)_5$ -coronene. For the latter the (3,2) arrangement, in which three units of H_2 are located at one side of the coronene surface and the remaining two are positioned at the other side, differs from the (4,1) structure obtained for He and Ne clusters on coronene. However, this discrepancy does not occur when comparing with the behavior of other heavier RG atoms (see Table III and Figure 4 of Ref.³⁴). Actually, even if H_2 is isoelectronic with He, its larger polarizability ($0.79 \text{ \AA}^3$ versus $0.2 \text{ \AA}^3$, respectively) leads to a larger equilibrium distance for the H_2 - H_2 interaction which lies between those of Ne-Ne and Ar-Ar (see Reference⁶⁰ and Figure 1 of Ref.³⁴). This enhanced repulsion tends to penalize those compact configurations with several particles on one coronene side and could explain the agreement found with the results for RG heavier than Ne.

The minimum energy structures predicted by PIMC simulations may differ from the global minimum classical structure, as in pre-

vious studies on He and Ne-coronene clusters^{34,36}. Thus, for $N = 3$ and $N = 4$ the classical results indicate that the minima are found for (3,0) and (3,1), respectively whereas the PIMC found the (2,1) and (2,2) structures as the most stable. None of these discrepancies have been observed in the present calculations performed on the $(\text{H}_2)_N$ -coronene clusters, at least up to $N = 16$ (see Table 3). Interestingly when the temperature is increased up to $T = 10 \text{ K}$, PIMC results (not shown here) point to those configurations with an almost equal number of H_2 units at both sides of the substrate surface, (that is, (2,1) and (2,2)), as the corresponding minimum energy structures for $(\text{H}_2)_3$ -coronene and $(\text{H}_2)_4$ -coronene, respectively.

Some sort of inversion feature occurs when the ZPE is added to some BH minimum structures. Those values marked with * in Table 3 correspond to cases in which the BH+ZPE absolute minimum is not obtained from the total minimum energy of the BH case. For $N = 3$ and 4, for instance, the structures differ on the number of H_2 at both sides, whereas, for the rest ($N = 8, 10-16$) the differences simply correspond to the positions of the H_2 on the surface. In this sense, it is worth noticing that the PIMC cluster structures and energies are in good agreement with the BH+ZPE predictions.

Calculations performed for the $(\text{H}_2)_N$ -coronene clusters at different values of the temperature (up to 10 K) show that $T = 2 \text{ K}$ represents some kind of limit between localized and delocalized behavior for the classical predictions. The obtained PIMC probability density distributions exhibit for $T \geq 2 \text{ K}$ the same degree of delocalization shown in Figure 5 at 2 K, but CMC distributions, on the contrary, manifest features of a change of behaviour with non-localized probability distributions for $T > 2 \text{ K}$.

The probability density functions shown in Figure 5, on the other hand, reveal a strong similitude with results obtained for coronene doped with different RG atoms. Thus, locations of H_2 on the coronene plane are comparable to those found in previous studies on these systems^{34-36,85}.

The present PIMC investigation has been also extended to $(\text{D}_2)_N$ -coronene clusters, for some selected values of N . Previous investigations³³ did not reveal significant qualitative differences between the isotopic variants D_2 and H_2 of these systems. Thus, distributions of minimum distances and solvation energies exhibited a similar trend for both types of clusters. In particular, solvation energies for (ortho- D_2) $_N$ -coronene clusters were found more negative than those for (para- H_2) $_N$ -coronene for the entire range of different sizes considered in the PIMD study of Ref.³³. The total energies calculated in our work with the PIMC method for $(\text{D}_2)_N$ -coronene for $N = 6, 7, 14, 16$ and 38 are -197, -222.4, -379.5, -410 and -754 meV, respectively. Results obtained by means of the BH+ZPE approach yield, on the other hand, energies -192.6, -215.9, -364.6, -391.1 and -715.4 meV for the same clusters. The comparison with the corresponding $(\text{H}_2)_N$ -coronene cases shown in Table 3 suggests then larger stability when the coronene is surrounded by D_2 molecules. A similar investigation of the probability density as a function of z for $N = 38$ as discussed at the end of Section 4.2, reveals that the probability of finding D_2 units close to coronene plane, $z \approx 0$, is null.

Estimations, on the other hand, of the isotopic difference be-

Fig. 5 Probability density distributions for $(\text{H}_2)_N$ -Coronene clusters with (a) $N = 5$, (b) $N = 9$; (c) $N = 13$ and (d) $N = 16$ calculated with the PIMC approach at $T = 2$ K. H_2 units located at both sides of the coronene molecular plane, $(n_a n_b)$ are shown in each case. Units for x and y are Å.

tween binding energies for bound states of the complex formed between either H_2 or D_2 and coronene, graphene and graphite (3.8, 2.9 and 2.6 meV, respectively) reveals an expected decrease as the size of the PAH increases.

6 Conclusions

Interaction energies between H_2 and coronene have been computed by means of MP2C and DFT-SAPT calculations providing benchmark results which have been exploited to build up a new analytical formulation of the multidimensional PES, based on the atom- bond approach, where H_2 , because of its limited interaction anisotropy, is treated as a pseudoatom having a polarizability equal to the average molecular value. The features of this potential confirm the noncovalent nature of the H_2 -coronene interaction, whose strength lies between those of Ne and Ar-coronene systems, as expected by the relative values of the Ne, H_2 and Ar polarizabilities. BH and PIMC simulations at $T = 2$ K have been performed for $(\text{para-H}_2)_N$ -coronene clusters with $N \leq 16$ and the corresponding equilibrium structures and energies are shown. The addition of the ZPE terms to the BH predictions yield results in a fairly good agreement with the PIMC results. A comparison with the corresponding $(\text{RG})_N$ -coronene aggregates have been provided and similarities with those heavier RG cases (Ar and Kr) have been evidenced. The proposed force field, even if specifically determined for the H_2 -coronene system, is in principle suitable to describe the interaction between H_2 and larger molecules, such as ovalene and circumcoronene, since the additivity of atom-bond pair components can be exploited to formulate the force fields in systems involving H_2 and PAH at increasing

complexity.

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