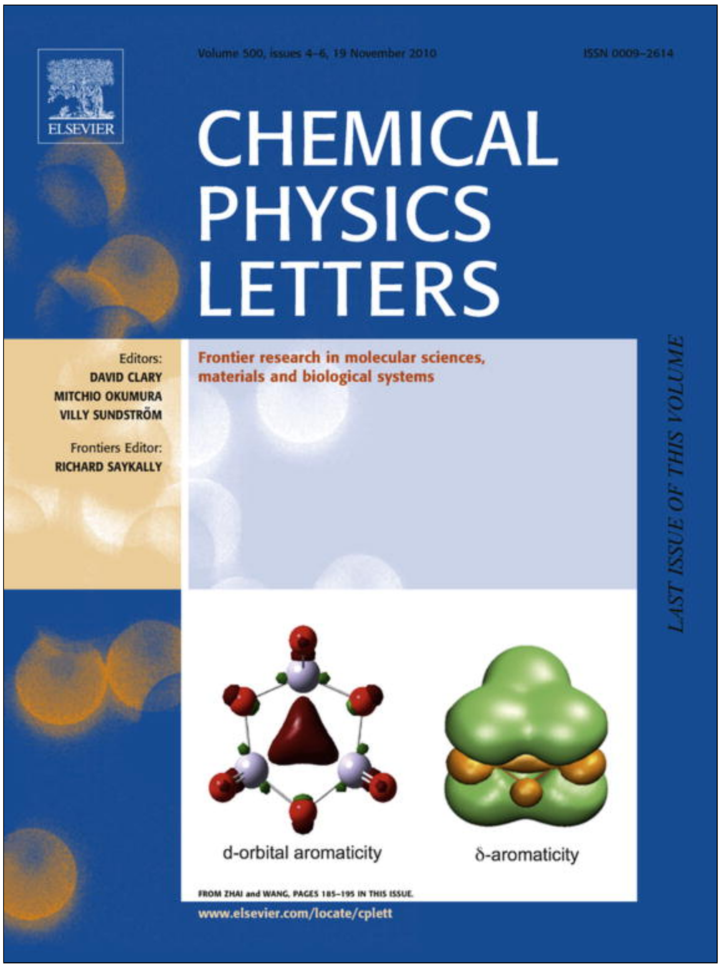
Volume 500, issues 4–6, 19 November 2010
ISSN 0009-2614
ELSEVIER
CHEMICAL PHYSICS LETTERS
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δ-aromaticity
FROM ZHAI and WANG, PAGES 185–195 IN THIS ISSUE.
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Chemical Physics Letters 500 (2010) 283–286

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

On the performance of van der Waals corrected-density functional theory in describing the atomic hydrogen physisorption on graphite

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ARTICLE INFO

Article history:
Received 10 August 2010
In final form 11 October 2010
Available online 14 October 2010

ABSTRACT

The atomic hydrogen physisorption on graphite was studied using the hydrogen–coronene model system and the van der Waals corrected-density functional theory (DFT + vdW). The results show that H preferentially occupies the hollow site. The adsorption energy at this site is calculated as 38.1 meV, in very good agreement with the available experimental measurements on a single graphite layer (39.2 ± 0.5 meV) and with reported MP2/aug-cc-pVDZ calculations (39.7 meV). The results suggest that, in DFT simulations, dispersion corrections should be considered in order to obtain accurate distances, adsorption energies and diffusion barriers in physisorption processes such as those occurring in the cold interstellar medium.

1. Introduction

Atomic hydrogen can interact with graphite surface either physically or chemically with adsorption energies of about 0.04 and 0.8 eV, respectively [1–4]. While the physisorption process is essentially site-independent, the chemisorption takes place exclusively on top with a substantial pull out of the carbon atom involved in the chemical bond. A barrier of nearly 0.2 eV exists in the transition from the physisorbed state to the chemisorbed one.

The physical interaction between atomic hydrogen and graphite surfaces has particular importance in astrochemistry. It is generally accepted that molecular hydrogen, H_2, is catalytically formed from atomic hydrogen on the surface of dust grains present in the interstellar medium (ISM). These grains are believed to be formed by carbonaceous materials [5]. For this reason, the H–graphite system was usually used as a representative system to investigate the H adsorption and the subsequent H_2 formation in the ISM. At the extremely low temperatures present in the ISM atomic hydrogen physisorbs barrierless on a graphite surface but it is unable to surpass the chemisorption barrier. In these conditions, a hydrogen atom is very mobile on graphite and it can eventually react with another surface hydrogen atom via the Langmuir–Hinshelwood mechanism [6].

Current density functional theory (DFT) approaches are unable to describe properly the weak van der Waals (vdW) interactions (also called dispersion interactions) such as those present in H–graphite physisorption. A possible strategy to overcome this deficiency of DFT is the inclusion of a damped correction term to account for the vdW forces. This is a practical way to make use the well-known versatility of DFT instead of using the more computational demanding post-Hartree Fock methods which do correctly describe vdW interactions. In fact, in new versions of several quantum-mechanic programs this type of empirical correction has been included within their DFT calculations. These approximations are usually indicated by DFT + vdW, DFT + E_{dis}, or d-DFT.

Dispersion interactions present in different chemical systems have been recently studied using DFT + vdW. For example, intermolecular interactions of hydrocarbons [7] and the stacking of DNA bases [8] were analyzed using different DFT functionals. Reliable results were found in the study of molecular hydrogen on graphite, single-walled carbon nanotubes (SWCNTs) and SWCNT bundles [9]. The adsorption of simple molecules on transition metal surfaces were also investigated testing different approximations for the empirical dispersion term [10].

Recently, Bonfanti et al. have been performed second-order Møller-Plesset (MP2) calculation on the H–coronene model system to investigate the H physisorption on graphite [4] employing the aug-cc-pVDZ basis set augmented with bond functions. Adsorption on hollow was found to be the preferred site. Furthermore, the energy differences with the other adsorption sites indicate that the adsorbed hydrogen atoms are highly mobile on the surface. On the other hand, using the more simplified H–benzene system they found that MP2 results are very similar than those obtained with the highly correlated and very expensive coupled-cluster singles and doubles with perturbative triples correction method (CCSD(T)); hence, these results give confidence to those obtained at MP2 level for the H–coronene. Indeed, the computed adsorption energy at the hollow site, 39.7 meV, is in very good agreement with the available experimental results for the adsorption on a graphite surface,

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doi:10.1016/j.cplett.2010.10.027

43.3 ± 0.5 meV [11], a value slightly different than that estimated in the same work for a single graphite layer, 39.2 ± 0.5 meV.

In this Letter we present a detailed study of the performance of DFT + vdW approximation in representing the very weak H–graphite interaction. In order to compare our results with those published by Bonfanti et al. at MP2 level [4], we use the coronene molecule to model the graphite surface.

2. Computational method

The graphite (0 0 0 1) surface was represented by a one-layer cluster model (Figure 1). The influence of inner layers can be considered negligible due to the large interlayer distance (3.35 Å), as it will be shown later. The dangling bonds of the C atoms located at borders were saturated by H atoms. In this way, the surface model corresponds to the coronene molecule ($C_{24}H_{12}$), a polycyclic aromatic hydrocarbon. The C–C distance in the coronene molecule was kept fixed at the bulk value of 1.42 Å for graphite. Previously, we checked that the interaction of coronene with physisorbed hydrogen does not produce any relevant surface change. The H adsorption is studied at the three symmetric sites (top, bridge and hollow) along a line perpendicular to the surface plane. For each site, calculations were carried out varying the H-surface distance (z).

We have chosen the PW91-GGA exchange and correlation functional to allow a direct comparison with other similar studies using cluster models [1] and periodic supercells [2] in which this functional was employed. For C atoms and the adsorbed H atom the Pople-type 6-311++G(d,3pd) basis set was used. The H atoms belonging to the coronene molecule were represented by the 6-311++G(d,p) basis set. DFT calculations were performed using the Gaussian03 package [12].

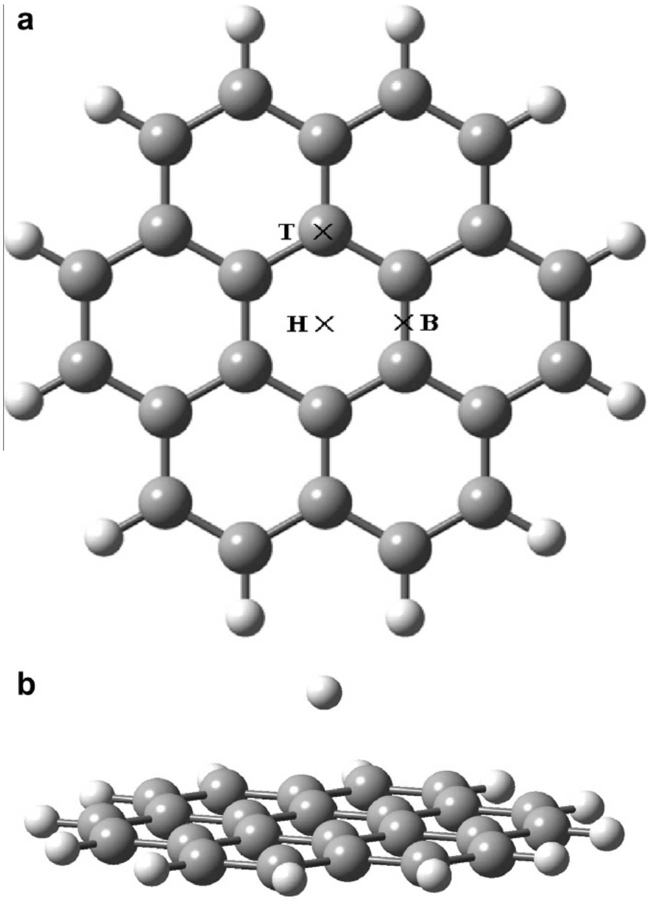

Figure 1. (a) The coronene molecule used to represent the graphite surface. The crosses indicate the adsorption sites (T: top, B: bridge, H: hollow). (b) Hydrogen atom physisorbed at hollow site optimized with the PW91 + vdW approach.

In the DFT + vdW scheme the total energy is obtained by adding a dispersion energy term to the DFT energy

$$E_{tot} = E_{DFT} + E_{dis} \tag{1}$$

The dispersion term is constructed to represent the interaction of two systems with nonoverloapping densities and hence it should be valid only in this regime.

The dispersion energy was calculated as

$$E_{dis} = -\sum_{i,j} f(R_{ij}) C_6^{ij} (R_{ij})^{-6} \tag{2}$$

where R is the interatomic distance for each atom pair contributing to E_{dis}, and $f(R_{ij})$ is the damping function which equals to one at large values of R and zero at small values of R. We have used the damping function proposed by Mooij et al. [13], which has recently provided promising results for H_2 adsorption on graphite [9]:

$$f(R_{ij}) = [1 - \exp(-c_{damp}(R_{ij}/R_0)^3)]^2 \tag{3}$$

R_0 is the sum of the atomic vdW radii [14]. For c_{damp} in Eq. (3) we used the value of 3.54 suggested by Wu and Yang [8]. The atomic C_6 coefficients in Eq. (2) are taken from the work of Halgren [15] (2.8 and 19.1 hartrees $\times$ bohr^6 for H and C, respectively). The H–C diatomic coefficient was calculated according to Slater–Kirkwood combination rule [16],

$$C_6^{ij} = \frac{2C_6^i C_6^j \alpha_i \alpha_j}{\alpha_i^2 C_6^j + \alpha_j^2 C_6^i} \tag{4}$$

where α are the atomic polarizabilities [15].

Each point of the potential energy curve $E(z)$ (Figure 2) was calculated as the following energy difference:

$$E(z) = E_{tot}(\mathrm{H/coronene}) - [E_{tot}(\mathrm{coronene}) + E_{tot}(\mathrm{H})] \tag{5}$$

The adsorption energy, E_a, corresponds to the minimum of the corresponding curve and it is reported here as a positive value. The energy differences calculated with Eq. (5) present an error known as basis set superposition error (BSSE). When two fragments interact each fragment takes the basis functions of the other, and as a consequence, the energy of the system falls down and the magnitude of the energy difference is overestimated. To correct this error the so-called counterpoise (CP) procedure is usually applied [17] in which each fragment is treated with the ghost functions of the other one. Therefore, the CP correction makes intermolecular interactions less stable with longer intermolecular distances than those of the optimized structure obtained with the standard calculation. For typical chemical bonds, the CP correction only affects slightly the final optimized geometry; in these cases, it is a common practice to make an *a posteriori* BSSE correction. However, for weak interactions the CP procedure yields an optimized geometry which could be substantially different than that obtained with the standard uncorrected procedure.

3. Results and discussion

As a first step in our study, we will discuss in detail the magnitude of the BSSE in the hydrogen–graphite interaction and the subsequent effect of the CP correction.

The H physisorption on graphite was previously analyzed using pure DFT in combination with cluster models [1,18] and with periodic supercells [2]. For the H–coronene interaction, Sidis et al. have calculated uncorrected adsorption energies (E_a) of 74 meV (top and bridge sites) and 67 meV (hollow) using a double-ζ + polarization (DZP) Slater-type basis set and the PW91 functional [1,18]. However, the E_a value changes dramatically to about 8 meV with the richer triple-ζ + polarization set (TZP). Thus, the adsorption energy calculation strongly depends on the quality of the basis set when the BSSE is not corrected. Using a slab model, the PW91 functional and plane waves (for which the BSSE is zero) [2], Sha and Jackson have found a broad and site-independent H physisorption region far away from the surface with essentially the same value of adsorption energy, 8 meV.

In Table 1 we present our preliminary calculations performed only on the hollow site of coronene using Pople-type functions of different quality. As the basis set size increases, the CP-corrected adsorption energy tends to a value of about 10.5 meV, which is reached with 6-311++G(d,3pd). At the same time, the distance between H and the surface also reaches a constant value of about 3.42 Å. Besides, we performed a single point calculation at z = 3.42 Å but using the largely extended aug-cc-pVTZ Dunning's functions obtaining a similar CP-corrected E_a value of 10.2 meV.

Therefore, after BSSE correction, or alternatively when it is zero for delocalized functions (plane waves), E_a seems to tend to a value between 8 and 11 meV using PW91. However, these values are significantly underestimated with respect to the experimental value of 39.2 ± 0.5 meV [11] for H physisorption on a single graphite layer.

Using the RPBE functional and the Slater-type DZP basis set, Bergeron et al. [18] obtained a non-CP-corrected E_a value that is in good agreement with the experimental one (about 46 meV). As it was mentioned, a noticeable difference in the E_a values was found comparing DZP and TZP functions at PW91 level (around 60 meV) owing to the large value of BSSE in the former case. Thus, together with the general tendency of RPBE to give lower E_a values than PW91, the good value obtained at RPBE/DZP level seems to be the result of the compensation of two different effects: the very poor description of dispersion contributions of DFT (which destabilizes the interaction) is counterbalanced by the lacking of the BSSE correction (which increases the magnitude of the energy difference).

According to the tendency obtained by varying the basis sets size (Table 1) we have used the 6-311++G(d,3pd) basis set for all the calculations. In Figure 2 the potential energy profiles for CP-corrected PW91, PW91 + vdW and MP2 calculations on the hollow site are presented. For comparison, the MP2/aug-cc-pVDZ results by Bonfanti et al. [4] are also reported. It is clear that the curves are fairly different at MP2 level, depending on the choice of basis sets. However, as it was commented above, the adsorption energy with PW91 reaches the basis set limit using 6-311++G(d,3pd), so that similar energy profiles are expected with other basis sets of similar quality after BSSE correction. It is interesting to note that different trends related to the basis set limit, comparing MP2 with DFT, were also observed in other systems [19,20]. For instance, for the water dimer [20] the interaction energy converges rapidly to a certain value after CP application in DFT, even using a relatively poor basis set. However, at MP2 level, enriching the quality of the basis set continuously stabilizes the interaction and the limit is obtained only with the largely extended aug-cc-pV5Z functions. The same behaviour was observed recently for Xe–benzene and H_2–graphite interactions [21,22].

Table 1
CP-uncorrected and CP-corrected adsorption energies (in meV) for H physisorption on graphite at hollow site using different Pople-type basis functions; z (in Å) is the optimized perpendicular distance to the surface.

Basis set[a]	No correction		CP-corrected	
	z	E_a	z	E_a
6-31G[b]	3.36	12.4	4.00	5.2
6-31G(d,p)[c]	3.32	13.0	4.01	5.1
6-311++G(d,p)[d]	3.32	14.9	3.44	9.0
6-311++G(d,3pd)[d]	3.36	21.7	3.42	10.6
6-311++G(3df,3pd)[d]	3.42	15.2	3.43	10.4

[a] Basis function used for C and adsorbed H.
[b] For H belonging to the coronene molecule the 6-31G basis functions were used.
[c] For H belonging to the coronene molecule the 6-31G(d,p) basis functions were used.
[d] For H belonging to the coronene molecule the 6-311++G(d,p) basis functions were used.

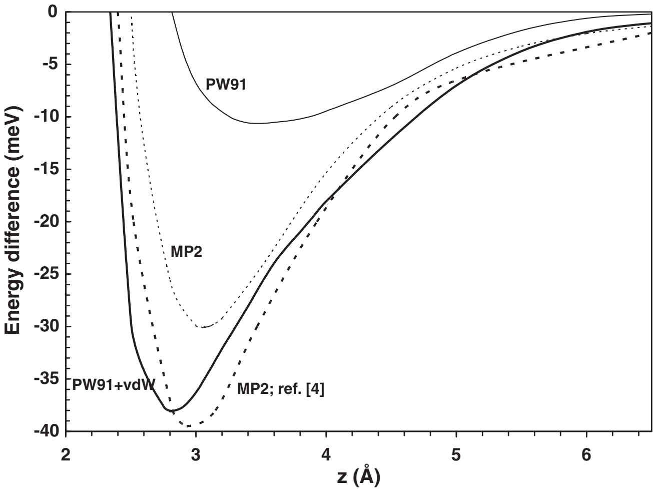

Figure 2. Variation of the interaction energy as a function of the distance of H from the graphite surface at the hollow site. Narrow continuous line: PW91 results. Dotted line: MP2 with Pople-type functions (see text). Broad continuous line: PW91 + vdW results. Dashed line: MP2 results from Bonfanti et al. [4].

On the other hand, the exaggerated long H-surface (z) distance obtained at PW91 level is typical for pure DFT in which the dispersion energy is not properly described. In fact, periodic DFT gives H-surface distances of about 4 Å [2] even higher than our value of 3.4–3.7 Å with pure PW91 (Table 2). While the E_a values are practically the same for all the adsorption sites at PW91 level, the incorporation of the vdW term accentuates the energetic differences among the sites yielding the hollow as the preferred adsorption site, in agreement with the results at MP2/aug-cc-pVDZ level (Table 2). This is the expected result because the hollow site should maximize the dispersion interactions with the C atoms of the ring. Indeed, the values for dispersion contributions ($-E_{dis}$ values of Eq. (2)) are found to be 32.1, 32.7 and 38.1 meV for top, bridge and hollow, respectively. Besides, the inclusion of the vdW term improves the z value for the hollow site (2.81 Å), which is very similar than that for the high level calculation (2.93 Å). The effect of the dispersion component is clearer when the distance d between H and the nearest C is considered, as it shown in Table 2. In the same table, the difference of distances Δd of the hollow site with respect to that of top or bridge is also presented. These Δd are very similar for PW91 + vdW and MP2 from Bonfanti et al. [4]; even the result of MP2 using Pople's functions are in good agreement.

In Table 3 the difference of adsorption energies (ΔE_a) of the hollow site with respect to that of top or bridge sites is also shown. Assuming that local minima exist exactly at these symmetric sites, as one would reasonably expect, the ΔE_a value can be considered as the minimal diffusion barrier. The results are very similar for PW91 + vdW and the high level MP2, indicating the extremely high mobility of physisorbed H atom. For MP2, using the Pople-type basis set, the relative values are somewhat smaller.

To our knowledge, the only reported DFT + vdW study devoted to the H physisorption on graphite was performed by Psofogiannakis and Froudakis [3]. They used the BP86-GGA functional and the dispersion correction proposed by Grimme [23,24]. The pure DFT calculation predicts erroneously the adsorption minimum at top.

Table 2

CP-corrected optimized geometrical parameters (in Å) for H physisorption on graphite; z is the optimized perpendicular distance to the surface and d is the nearest H–C distance. Δd values are calculated as $\Delta d = d(\text{hollow}) - d(\text{site})$.

	MP2[a]			MP2[b]			PW91[b]			PW91 + vdW[b]		
	z	d	Δd	z	d	Δd	z	d	Δd	z	d	Δd
Top	3.07	3.07	0.19	3.16	3.16	0.23	3.73	3.73	−0.03	2.93	2.93	0.22
Bridge	3.03	3.11	0.15	3.14	3.22	0.17	3.65	3.72	−0.02	2.92	3.00	0.15
Hollow	2.93	3.26	0.00	3.08	3.39	0.00	3.42	3.70	0.00	2.81	3.15	0.00

[a] MP2/aug-cc-pVDZ + bond functions calculations, from Ref. [4].
[b] This work, using 6-311++G(d,3pd) for C and adsorbed H, and 6-311++G(d,p) for H of coronene.

Table 3

CP-corrected adsorption energies (in meV) for H physisorption on graphite. ΔE_a values are calculated as $\Delta E_a = E_a(\text{hollow}) - E_a(\text{site})$.

	MP2[a]		MP2[b]		PW91[b]		PW91 + vdW[b]	
	E_a	ΔE_a	E_a	ΔE_a	E_a	ΔE_a	E_a	ΔE_a
Top	34.5	5.0	26.7	3.3	9.9	0.7	32.1	6.0
Bridge	35.5	4.0	27.2	2.8	10.3	0.3	32.7	5.4
Hollow	39.5	0.0	30.0	0.0	10.6	0.0	38.1	0.0

[a] MP2/aug-cc-pVDZ + bond functions calculations, from Ref. [4].
[b] This work, using 6-311++G(d,3pd) for C and adsorbed H, and 6-311++G(d,p) for H of coronene. For the optimized geometries at hollow site, the H/coronene total energies (in hartrees) are −919.872267 (MP2) and −922.248667 (PW91); the E_{DFT} contribution at the distance optimized with the PW91 + vdW approach is −922.248256 hartrees.

The inclusion of the dispersion component leads to the correct preferred site at hollow with an adsorption energy of 30.4 meV.

Taking into account the very weak interaction present in the H/graphite system, an additional study of the adequacy of using the coronene molecule as a model for graphite was performed. For this purpose, the H adsorption at the hollow site on two larger clusters was computed at the PW91 + vdW level. Firstly, we have used the circumcoronene molecule ($C_{54}H_{18}$) which can be obtained by enlarging symmetrically the coronene molecule. In this case the E_a is found to be 39.9 meV, with a z distance of 2.78 Å; in this case the contribution of the vdW term (Eq. (2)) results to be 41.5 meV. In the second additional model, the possible effect of an inner layer of graphite is tested by considering a two-layer model formed by two superimposed coronene molecules separated by an interlayer distance of 3.35 Å (bulk graphite). The results are very similar: $E_a = 39.2$ meV, $z = 2.79$ Å (with a vdW contribution of 40.5 meV). Therefore, the coronene molecule represents very well the graphite surface regarding its weak interaction with H.

4. Conclusions

In the study of H physisorption on graphite, the incorporation of a dispersion term within the DFT approach leads to a significant improvement in the optimized distances, physisorption energies and minimal diffusion barriers.

Other species, such as the O atom, can interact physically with the graphite surface; yet the description of these weak interactions at MP2 level often presents serious convergence problems [18]. Therefore, the DFT + vdW approximation could be an alternative and powerful tool for the study of diffusion or chemical reactions of physisorbed species, such as those present on the surface of dust grains in the cold interstellar medium.

Acknowledgments

The authors acknowledge the financial support of Universidad Nacional del Sur, CONICET and ANPCyT of Argentina.

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