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DFT investigation of the adsorption of atomic hydrogen on a cluster-model graphite surface

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Abstract

The H-graphite interaction is studied for the first time in the framework of density functional theory. A coronene-like model of the (0001) graphite surface is considered. LSD and LSD + GGA results are presented for both a planar substrate and for considering substrate relaxation. Two adsorption regions separated by a barrier are found: a physisorption region around 3 Å from the surface and a chemisorption region around 1.5 Å. The former is site-independent and compatible with a high mobility of the H atoms parallel to the surface. The latter is located exclusively on top of a carbon atom and requires a significant surface relaxation. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

This work on the H-graphite interaction has been undertaken as a first step in the study of a plausible mechanism of H–H recombination in the interstellar medium. Yet, the H-graphite interaction is also of relevance in other areas, especially technological fields involving graphitic material.

There is a wide consensus in the astrophysical community today to accept the hypothesis that interstellar dust grains play a catalytic role in the formation of H_2 molecules in diffuse interstellar clouds [1–6]. Current knowledge of interstellar dust grains emphasizes a carbonaceous composition [7,8]. This has stimulated the investigation of the role graphitic bonds may have on H_2 formation as a result of elementary interactions between H atoms and graphite-like surfaces or platelets [9,10]. Two mechanisms are thus involved in this respect: (i) the Langmuir–Hinshelwod (LH) mechanism whereby two adsorbed and mobile H atoms interact to recombine and desorb as H_2 molecules, and (ii) the Eley–Rideal (ER) abstraction mechanism whereby H atoms from the gas phase impinge on adsorbed H atoms to finally yield desorbed H_2.

A prerequisite of both mechanisms is that *an H atom is already adsorbed on the surface*. The cogency of one or the other mechanism depends on a few factors among which are the binding energy of the H adatoms to the surface, the potential barriers which govern their mobility, the possibility, or not, of surface reconstruction, the surface coverage, the

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bombardment rate, the bombardment energy and the surface temperature, the actual atomic trapping and molecular desorption processes. Most of these subjects have been discussed to some extent in the literature in relation to the central question of *characterizing the H atom binding to a graphite-like surface* (see for instance Refs. [11–13]).

Scanning this literature reveals that most of the current knowledge of the H-graphite interaction comes from semi-empirical calculations based on approximate Hartree–Fock-type schemes employing minimal basis set expansions of the wavefunctions (CNDO [14,15]; MNDO [16]; INDO [17]; MINDO/3 [12,16,18]). Extended-Hückel-type calculations [19, 20] as well as a perturbation approach [11] have also been reported. There does not seem to be general quantitative (nor sometimes qualitative) agreement between these calculations as concerns the characteristics of the H adsorption to graphite. Given the importance of this topic for the modelling of the physico-chemistry of the interstellar medium, the described situation leaves ample room for a new investigation of this subject.

The present work aims at going beyond the previous approaches by the use of a non-empirical, non-perturbative quantum mechanical treatment that takes provision of electron correlation, spin polarisation and substrate relaxation. Such an ambitious task can be envisaged today within the framework of density functional theory (DFT) [21–23]. Although still in progress, DFT is proving to be quite efficient for the calculation of the ground state electronic energy of complicated polyatomic structures (polyatomic molecules, clusters, zeolites, surfaces, etc.).

2. Method

As suggested by earlier work, we adopt a one-layer cluster model of the graphite (0001) basal surface; large PAH (polycyclic aromatic hydrocarbon) molecules like coronene ($C_{24}H_{12}$), which we consider here (Fig. 1), have often been advocated for this purpose [12,16–18]. The 12 hydrogen atoms serve only to passivate the terminal pending bonds of the C_{24} cluster; they are lying well away from the central ring where the adsorption study is carried out. The recommended C–C and C–H bond lengths of
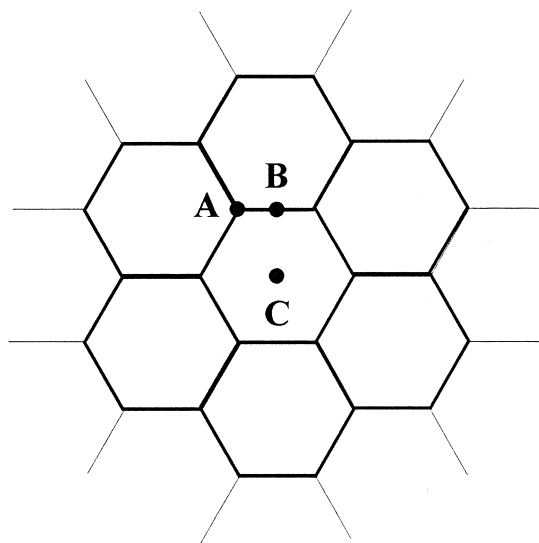

Fig. 1. Wireframe view of the $C_{24}H_{12}$ corenene cluster model of a (0001) graphite surface. The A, B and C sites considered in this work are indicated.

the isolated $C_{24}H_{12}$ cluster in this context are, respectively, 1.415 and 1.084 Å. The inter-layer spacing of graphite (≈ 3.4 Å) is considered to be large enough to exclude any influence from neighbouring layers.

The H–$C_{24}H_{12}$ interaction is determined variationally in the framework of DFT by self-consistently solving the related Kohn–Sham (KS) equations [22]. The calculations are carried out using the ADF [1] computer code [24,25]. The KS molecular orbitals are expanded as linear combinations of atom-centered *Slater-type orbitals*. A double-ζ + polarisation basis of this type has been used for H and the valence shell of the C atoms; the atomic 1s KS orbitals of the C atoms are held frozen during the calculation (ADF[1]). Spin polarisation of the electrons is allowed for by letting the ↑ and ↓ spin densities to be different (unrestricted KS). The exchange-correlation density functional used in this work includes the local (LDA) functional of Vosko et al. [26] and the PW91 [27–29] generalized gradi-

ent (GGA) corrections. Other combinations of exchange (B88 [30], PW86x [31,32], PW91x) and correlation (PW86c [33], PW91c) GGAs have been tried for pinpoint checking purposes in initial stages of the work. There are two main reasons for choosing the PW91-GGA in the present work. Firstly, unlike other functionals, it is non-empirical and, as shown in Ref. [23], it satisfies best the known formal properties of the exact exchange-correlation functional. Secondly, aside from its numerous successes in the description of strong bonding in various ionic and covalent systems, convincing evidence has been given recently by Wesolowski et al. [34] as to its reliability in describing weakly bound van der Waals complexes, namely Benzene $\cdots$ X (X = O_2, N_2, CO).

Proceeding along the track of earlier investigations, we have concentrated our study on vertical approaches of the H atom on top of the specific sites A, B and C indicated in Fig. 1. A few unconstrained searches of most bonding adsorption positions of the H atom to the surface have also been carried out.

3. Results

As a starting point it is worth showing results obtained for an *unrelaxed substrate at the local spin density level* (LSD) that is, without taking GGA corrections into account (Fig. 2). Two features are immediately seen: (i) an *outer* broad well of depth
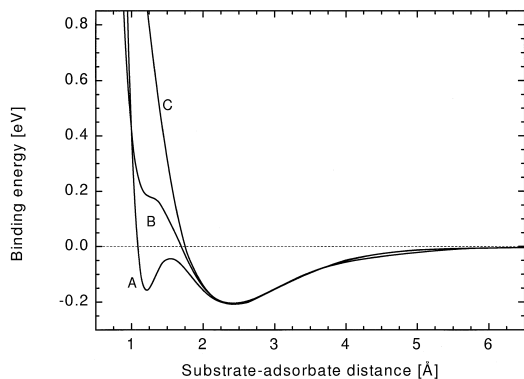
Fig. 2. DFT results, at the local spin density (LSD) level, for the interaction of an H atom with the *unrelaxed* model graphite surface of Fig. 1. The binding energy of the adsorbing H atom as function of its distance to the basal plane above each of the sites A, B and C is shown.
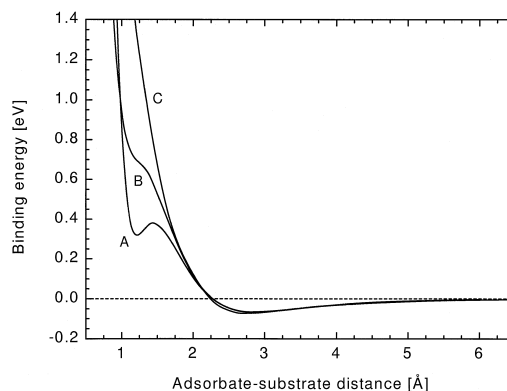
Fig. 3. DFT results, including gradient corrections (LSD + PW91-GGA), for the interaction of an H atom with *unrelaxed* model graphite surface of Fig. 1. The binding energy of the adsorbing H atom as function of its distace to the basal plane above each of the sites A, B and C is shown.

$D_B^{out} = 0.207$ eV $\approx D_C^{out} = 0.211$ eV $\approx D_A^{out} = 0.208$ eV) occurring at rather large H-surface distance ($z_A^{out} = z_C^{out} = z_B^{out} = 2.41$ Å) and, (ii) an *inner* narrow well showing up exclusively at the A site ($D_A^{in} = 0.163$ eV and $z_A^{in} = 1.203$ Å). The appearance of Fig. 2 is quite different from all earlier results. In particular, the existence of a *common outer well* has never been pointed out before. At the inner A-well the interaction energy shows a hierarchy pointed out in previous work, namely the A-site energy is lower than that of the B-site which is lower than that of the C-site; instead of a well, the interaction energy at the B site displays a shoulder on a repulsive wall. Analysis of the electron density at the A inner well shows a clear charge transfer: the binding is of chemical nature.

On the other hand, at the common outer well there is negligible electron transfer indicating that the binding is more of a physisorption type. The lack of electron transfer at the outer well is also an indication that the well itself is not an artefact due to BSSE (basis set superposition error).

However, it is widely known that calculations limited at the local density level overestimate binding energies and underestimate equilibrium distances. Taking the PW91-GGA correction into account, while still maintaining the planarity of the substrate, has the clear effect of introducing more repulsion in the energy curves (Fig. 3). Only the

outer well survives with modified characteristics: $z_A^{out} = 2.81$ Å, $D_A^{out} = 0.074$ eV; $z_B^{out} = 2.66$ Å, $D_B^{out} = 0.074$ eV; $z_C^{out} = 2.81$ Å, $D_C^{out} = 0.067$ eV. The inner A well now hangs on the repulsive wall thereby transforming the inner A site into a 'metastable chemisorption position'. These final results for a *planar substrate* contradict those of earlier calculations. Only the position of the local minimum at the inner A site is close to the one found by Fromherz et al. [12], all other characteristics of the energy curves are different.

In the last batch of PW91-GGA calculations, we considered substrate relaxation. The allowed relaxation for the A and B sites follow the scheme proposed by Fromherz et al. [12]: (i) at a distance z_A of the H atom from the basal plane above the A site, the C atom is displaced vertically by a distance Z_A to minimize the interaction energy; (ii) at a distance z_B of the H atom from the basal plane above the B site, the two nearest C atoms are displaced vertically by a distance Z_B; and (iii) at a distance z_C of the H atom from the basal plane above the C site the six nearest C atoms are displaced vertically by a distance Z_C. As found by Fromherz et al. [12], relaxation at the B site does not change the results in any significant way; the same is found for the C site. The results of the relaxation for the A site are shown in Figs. 4 and 5. Dramatic changes with respect to Fig. 3 are ob-
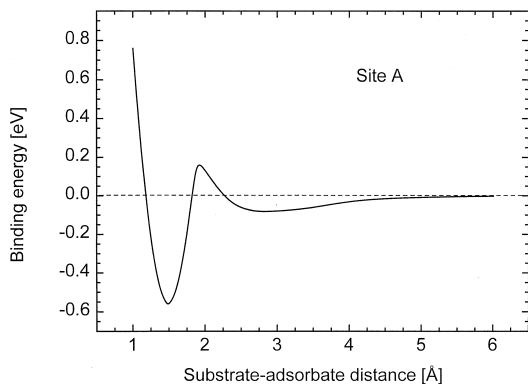

Fig. 5. Distance by which the relaxed carbon atom is displaced at site A (Z_A) as a function of the altitude (z_A) of the adsorbing H atom above the graphite basal plane (d_A in text is the $z_A - Z_A$ distance).

Fig. 4. DFT results, including gradient corrections (LSD + PW91-GGA), for the interaction of an H atom with the model graphite surface of Fig. 1 at the A site when the nearest carbon atom is allowed to relax. The distance Z_A by which the relaxing carbon atom is displaced relative to the basal plane for each adsorbate-substrate distace z_A is shown in Fig. 5.
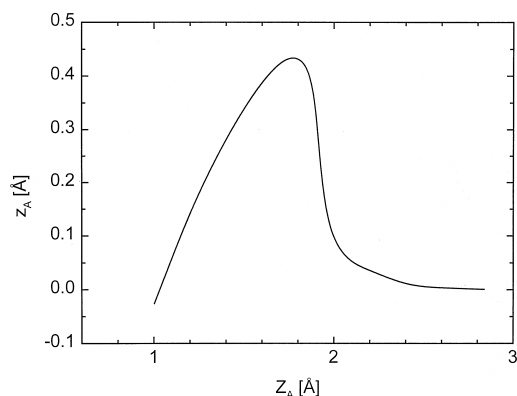
served: the inner chemisorption well reappears quite strongly ($D_A^{in,relax} = 0.57$ eV) and a protruding barrier separates both the inner and outer wells. The chemisorption well builds with a spectacular pull out (tetrahedrization) of the nearest C neighbour ($z_A^{in} = 1.5$ Å, $Z_A^{in} = 0.35$ Å, $d_A^{in} = 1.15$ Å, Fig. 5). Quite the same behaviour has been observed by Fromherz et al. [12] who discussed this feature in relation to earlier findings by Dovesi et al. [15] and Mendoza and Ruette [18]. The potential well found by Fromherz et al. [12] is nearly twice as deep as the present one and their potential barrier is smaller (by a factor 1.6) and smoother than the one seen in Fig. 4. As found for the B and C sites, the outer A-site well is insignificantly affected by substrate relaxation. The outer wells may be compared with the physisorption well deduced by Ghio et al. [35] from an experimental study of the scattering resonances that appear in the specular reflection of H atoms from a (0001) graphite surface. The wells are of comparable breadths but their depths differ: $D_{Ghio\ et\ al.} \approx 0.04$ eV whereas the present calculations yield values 1.5 times larger. To the best of our knowledge, this is the first ab initio DFT estimate of the H-graphite physisorption interaction and we find it rewarding to have such a comparison. Though it is not commonly believed that van der Waals minima can be described correctly by GGA functionals, the detailed comparison of currently used ones for the interaction of benzene with closed shell molecules

[34] lends some confidence in results obtained with the PW91-GGA used in the present work.

4. Conclusions

Two important conclusions emerge from the present calculations. The first one concerns *chemisorption*: it is found that H atoms chemisorb *exclusively* at distances $z_A < 1.8$ Å on top of a carbon atom in the inner A-site well (Fig. 4); although this finding in itself is not new what is specific to our results is that the chemisorption is possible *only* with the help of substantial substrate reconstruction. Chemisorbed H atoms would have no tendency to migrate parallel to the surface. With the present figures, the path along C–C graphite bonds suggested earlier for H migration is unlikely: the classical path from the A site to the B site would lead to the desorption of the H atoms (compare Figs. 3 and 4) and the barrier is too high for quantum tunneling. The second conclusion concerns *physisorption*: to the best of our knowledge, none of the previous calculations have indicated the possibility that H atoms could physisorb with binding characteristics as those appearing in Figs. 3 and 4, for $z > 2$ Å, *independently of the site*. Although there are still doubts as to the ability of LSD-GGA calculations to correctly predict van der Waals wells, the method used to determine the reported physisorption characteristics is supported by the conclusions of the detailed study of Ref. [34]. These characteristics are also supported by the comparison of the present results with data inferred from experiment [35]. The common outer well is compatible with a much higher mobility of H atoms parallel to the surface than ever thought before. According to these findings, H_2 formation near a graphite surface could result from both the LH and ER mechanisms for physisorbed H atoms and from an ER mechanism for chemisorbed H atoms.

Acknowledgements

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