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ATOMIC HYDROGEN INTERACTION WITH A CLUSTER-MODEL GRAPHITE SURFACE: CHEMISORPTION, COVERAGE AND H_2 SURFACE RECOMBINATION

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The interaction of atomic hydrogen with a cluster-model graphite surface ($C_{24}H_{12}$) has been examined in detail using the MINDO/3 method. Results on chemisorption, surface diffusion, coverage formation and H_2 surface recombination are discussed, and they found to be in good agreement with experiment.

1. Introduction

In the past fifteen years the hydrogen-graphite interaction has been the subject of a series of both theoretical and experimental studies motivated by the relevance of its related processes in a variety of research fields. For instance, graphite corrosion by hydrogen leading to plasma contamination is a topic of concern in fusion energy technology [1]; molecular hydrogen observed in interstellar clouds could be produced by surface reactions on graphitic grains [2]; there is sustained interest in coal hydrogenation in the comercial production of synthetic liquid fuels [3]; graphite is found to be deposited on the surface of catalysts used in the hydrotreatment of petroleum causing deactivation [4] and since graphite is used in high-vacuum applications most properties and effects belonging to this interaction must be thoroughly established [5].

Pioneering theoretical studies in surface science correspond to Bennett et al. [6,7] and Messmer et al. [8] who used Extended Hückel, CNDO and LCAO band structure methods to study chemisorption on graphite, particularly of hydrogen atoms. Since then *ab initio* Hartree-Fock, semi-empirical methods (CO-NDO, MNDO, MINDO/3, CO-MINDO/3) and band calculations have been extensively used with different graphite models to investigate hydrogen chemisorption [9–11], regular chemisorption [12–15], effects of substrate relaxation in the chemisorption process [16,17], surface migration [18] and dissociative chemisorption of H_2 [19]. In the astrophysical context, the adsorption and recombination of hydrogen atoms on a model graphite grain has been treated in a modified extended Hückel approach [20].

Experimentally, due to the applicability of graphite for first-wall use in fusion plasma reactors, the hydrogen-graphite interaction has received a great deal of attention. Although most experiments agree on reaction products (H_2, methane and other hydrocarbons) measurements can show large discrepancies. For instance, in a critical comparison Stangeby et al. [21] point out that, for low energy ($\leqslant 1$ eV) atomic hydrogen bombardment, reported data for the absolute methane yield span four orders of magnitude, temperature positions of the maximum yield span the range 700–900 K and in some cases a maximum is not observed. Also, values of the activation energy for H_2 surface recombination in two proposed reaction kinetics models [22,23] vary by a large factor.

We have been encouraged to study the hydrogen interaction with graphite due to the astrophysical physical importance of a surface mediated recombination to account for the abundant H_2 molecule in interstellar diffuse clouds. In a previous calculation [20] potential barriers were found in the recombination process on a model graphite surface that, at the low interstellar temperatures, could only be overcome through tunneling, therefore discarding the graphitic grain surface from being an efficient catalyst in such conditions. It is worth mentioning that although graphite is still considered to be an important constituent of the interstellar grain, the degree of crystallinity and grain structure are topics under discussion. For example, hydrogenated amorphous carbon grains have been recently proposed [24] which consist of small (~ 10 Å) graphitic (polycyclic aromatic hydrocarbons, PAH) platelets loosely and randomly arranged to form a larger grain. In this respect cluster models, which are usually used to represent infinite surfaces, could provide realistic theoretical representations for such platelets. In the present letter we report results obtained with the MINDO/3 method on different aspects of the hydrogen-graphite interaction which lead to an H_2 surface recombination mechanism that could be feasible in interstellar conditions. We briefly describe the method and surface model in the next section, and results are discussed in section 3.

2. Method and surface model

The theoretical method employed is the unrestricted Hartree-Fock (UHF) version of MINDO/3 [25]. The computer program is essentially that due to

Rinaldi [26] modified to include symmetry adapted wave functions, selectively occupied molecular orbitals and convergence features using molecular fragments [27].

The graphite substrate is modeled by a coronene cluster shown in fig. 1. The C–C and C–H bond lengths are taken to be 1.415 Å and 1.084 Å respectively. Since the energy difference between the lowest substrate state with spin multiplicity $M = 2S + 1 = 1$ and the excited state with $M = 3$ is ~ 2.28 eV, substrate excitation in the chemisorption process will not be considered. This cluster presents key advantages that can be exploited in computation: it is highly symmetrical; it is large enough to investigate separately plane and edge processes; it allows the study of hydrogen coverage without including sites with edge saturators; the cluster diameter of 9.2 Å is similar to that of the PAH-like platelets proposed in connection with interstellar grains [24].

3. Results and discussion

Regarding substrate properties a cohesive energy per carbon atom of 7.30 eV is obtained in good agreement with an experimental estimate of 7.58 eV/atom [28] and other recent theoretical results [11,14]. Our result for the ionisation potential of 7.87 eV agrees closely with the experimental value given for coronene of 7.36 eV [29], but it is considerably higher than the work function usually quoted for graphite of 4.8 eV.

Atomic hydrogen chemisorption is studied by considering the three characteristic surface lattice sites of high symmetry: A, B and C (see fig. 1). Their corresponding potential energy curves are shown in fig. 2. Site A is the most active with a binding energy of $BE_A = -0.60$ eV at an equilibrium distance from the surface of $z_A = 1.26$ Å. Site B is a saddle point with $BE_B = -0.05$ eV at $z_B = 1.40$ Å. The centre of the carbon ring (site C) is found to be repulsive. Small potential barriers (~ 0.1 eV) for adsorption on sites A and B of can be seen at $z_A = 2.35$ Å and $z_B = 2.00$ Å respectively. Although there is good qualitative agreement with previous theoretical work [7,9,11,18] significant quantitative differences are noticed. In particular the potential barrier for surface migration (taken to occur along the inter-carbon path) of 0.55 eV is considerably larger than that previously reported [18]. Adsorption on a hydrogen-saturated edge site (site K) is also examined; the most stable configuration ($BE_K = -1.95$ eV) is found to be with the two hydrogen atoms equidistant above and below the graphite plane at an H–C–H angle of 96°. This is in qualitative agreement with the findings of Bennett et al. [7] but they quote an angle of 120°. The present theoretical results are consistent with recent experimental observations of sub-eV hydrogen trapping by the graphite surface, the presence of different trapping sites, which would correspond to surface sites and edge sites (lattice defects), and the high substrate temperatures (~ 1000 K) required to mobilise the chemisorbed H atoms [30–32].

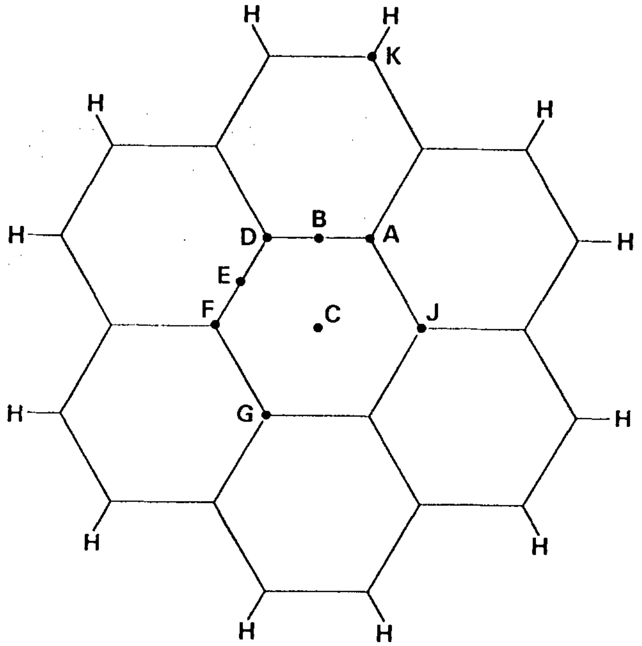

Fig. 1. Coronene cluster ($C_{24}H_{12}$) used to model the graphite surface showing sites of interest (A, B, C, D, E, F, G, J, K).

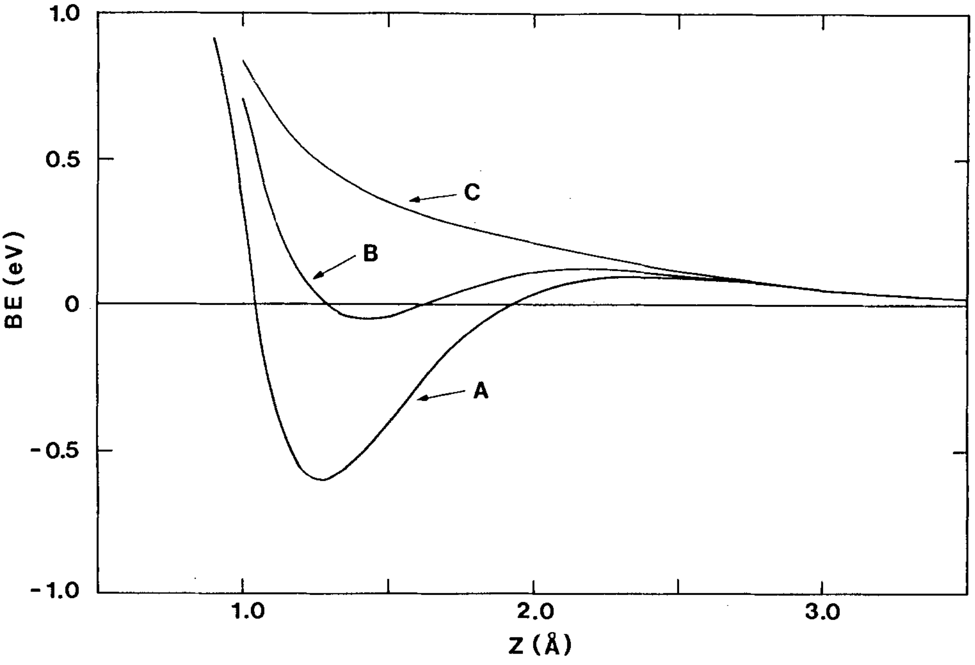

Fig. 2. Potential energy curves for hydrogen adsorption on sites A, B and C of the model graphite surface shown in fig. 1.

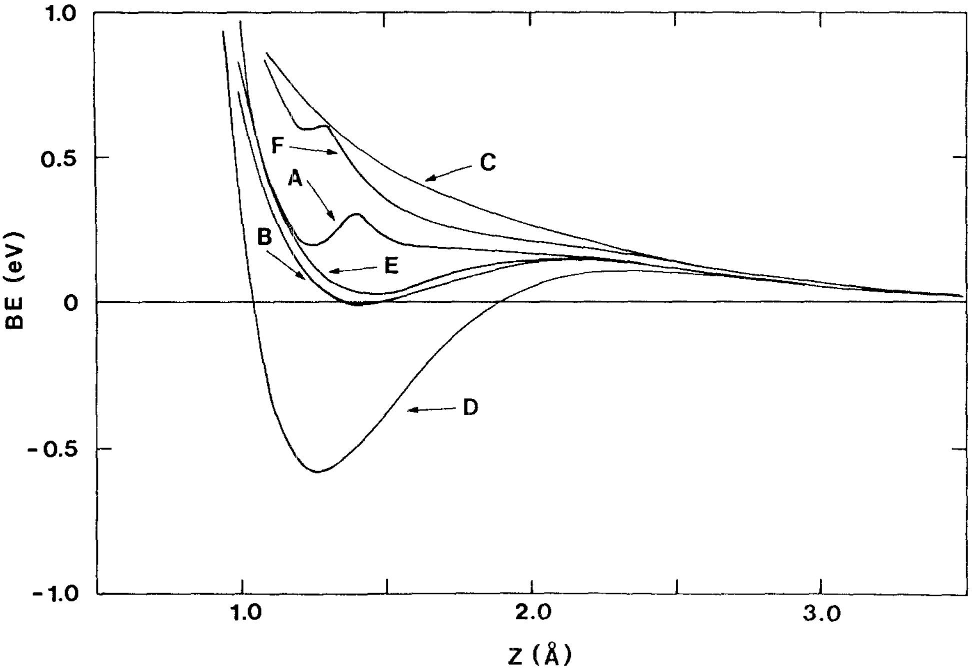

Fig. 3. Potential energy curves for hydrogen adsorption on sites A, B, C, D, E and F of the model graphite surface (fig. 1) in the presence of a chemisorbed hydrogen atom at site G. The multiplicity is $M = 3$.

We then examine the adsorption of an incoming H atom in the presence of a nearby chemisorbed H atom placed at site G of fig. 1 with $z_G = 1.26$ Å, for total system spin multiplicities $M = 1$ and $M = 3$ corresponding respectively to antiparallel and parallel spins of the two adsorbates. Potential energy curves for $M = 3$ (see fig. 3) show that the incoming H atom will only chemisorb at site D (or J by symmetry) with $BE_D = -0.59$ eV. For $M = 1$ no stable configurations are found. Although substrate geometric optimisation is not carried out due to the computation times involved, small tests indicate that these results are consistent with the view held by Dovesi et al. [17], and supported by some experimental evidence [33], that hydrogen chemisorption on graphite destroys substrate planarity caused by partial tetrahedrisation of the carbon atoms. Furthermore, these results appear to have several implications. Firstly, assuming total spin conservation, the catalytic recombination of H_2 on a bare graphite surface in the Langmuir-Hinshelwood sense, even when invoking tunneling, would be spin unfavoured. A recent experimental estimate of a high activation energy (44 kcal/mol) for the thermal release of hydrogen trapped on graphite to form H_2 [34,35] could be interpreted as implying that the H atoms must be detached from the surface before recombination occurs. Secondly, the reverse process of dissociative chemisorption of H_2 on graphite would also be spin unfavoured, in

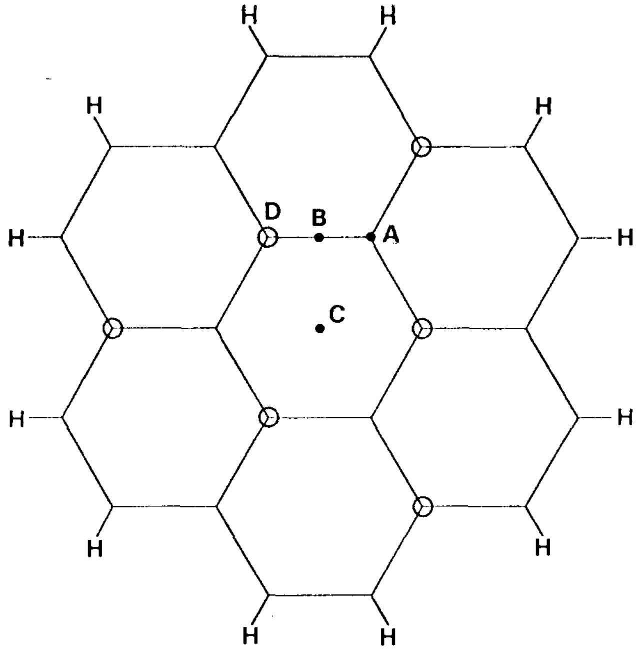

Fig. 4. Model graphite surface showing the resulting 1 : 2 surface phase (the open circles represent hydrogen atoms on the surface). A, B, C and D are sites of interest for interaction with an incoming hydrogen atom.

accord with well established experimental data that H_2 is practically unreactive towards graphite except at very high temperatures [22,23]; that is, the H_2 molecule must be thermally dissociated before chemisorption can proceed [33]. Thirdly, the interaction of atomic hydrogen with a bare graphite surface will lead to a fairly stable surface phase, and saturation effects observed in low-energy H trapping in graphite [30,31] seem to support this view.

Surface coverage formation is investigated by placing hydrogen atoms at sites D and G (fig. 1) and finding stable configurations for different multiplicities as more H atoms are adsorbed. Configurations with up to six H atoms are considered. Results lead to a 1 : 2 surface phase with H adsorbates placed over alternate carbon lattice atoms forming equilateral triangles (see fig. 4) whilst, contrary to previous theoretical work [17], the 1 : 1 surface phase is found to be unstable. Results for the 1 : 2 phase are shown in table 1. As the number of atoms is increased the H-layer distance from the surface is found to remain almost constant at 1.26 Å, but it can be noticed that the absolute value of the binding energy per adsorbate shows a slow decrease (configurations with up to 3 atoms) before edge effects come into play (configuration with 6 atoms). The most stable configurations are those with the H-atom spins parallel, that is, they have spin multiplicities $M = n + 1$ where n is the number of adsorbates. Moreover, an H layer with similar characteristics is found to be stable on the other side of the

Table 1
Binding energy/H atom and spin multiplicity (M) for the most stable configurations as the number of H atoms adsorbed on the model graphite surface is increased leading to a 1 : 2 surface phase. The equilibrium distance of the H atoms from the surface is kept at 1.26 Å. Notice that a second 1 : 2 H layer can form on the other side of the graphite monolayer involving the remaining unbonded carbon atoms (arrangement with 12 H atoms).

No. H atoms	M	BE (eV)	Arrangement
1	2	−0.597	G
2	3	−0.590	G, D
3	4	−0.576	G, D, J
6	7	−0.617	as in fig. 4
12	1	−0.807	as in fig. 4 +6 H underneath

graphite monolayer involving the remaining unbonded carbon atoms. Dovesi et al. [17] also found this arrangement to the most stable. If the same number of H atoms is placed on both top and underneath the graphite monolayer (e.g., a total of 12 atoms), the multiplicity for the most stable system is found to be $M = 1$ (see table 1).

Since the above results indicate that the interaction of H atoms with a bare graphite surface mostly leads to surface coverage rather than recombinations, we then examine the interaction of an incoming H atom with the H covered graphite surface. A six-atom layer is considered at a fixed equilibrium distance (see fig. 4), and potential energy curves are calculated for an incoming H atom at the sites A, B and C. The resulting curves, shown in fig. 5, are very different from those of a single H atom on the bare graphite surface. The covered surface appears repulsive at all tested sides when the spin of the incoming H atom is parallel with respect to that of the H layer ($M = 8$). On the other hand, for antiparallel spins ($M = 6$) the surface is attractive throughout. At sites A and C, corresponding to centres of the H triangles shown in fig. 4, the binding energy is very small, but at site B a strong increase in the absolute value of binding energy (~ 1 eV) is observed showing that H_2 recombination is already taking place (H–H bond order = 0.84 and diatomic energy = −0.29 a.u.). Further calculations show that recombination will also proceed along other paths (e.g., along CD) and that molecular desorption will occur spontaneously once enough energy is liberated from the forming strong H–H bond to break the weaker C–H bond. Considering that a free H atom approaching the surface reacts with a chemisorbed atom to form H_2, this mechanism is of the Eley-Rideal catalytic type as proposed in the experiment of Wood and Wise [22], and the small activation energy that quote of 2 kcal/mol for this process seems to be consistent with present results. Moreover, this recombination mechanism seems to be supported by a recent experiment on surface modification due to the hydrogen-graphite interaction [33], where it has been

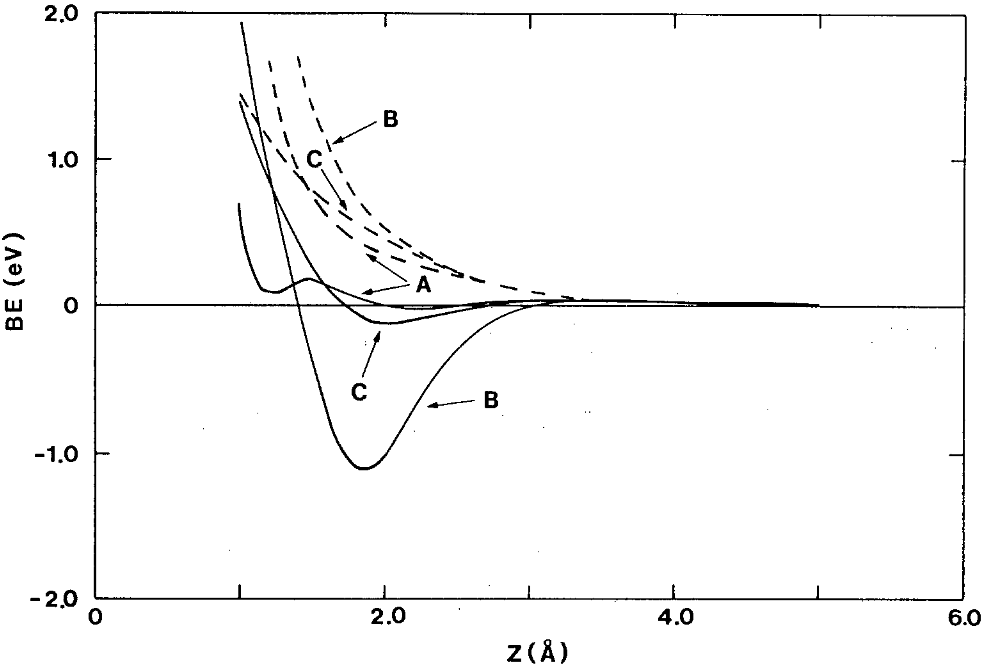

Fig. 5. Potential energy curves for an incoming hydrogen atom interacting with the hydrogen covered graphite surface at sites A, B and C of fig. 4. The solid curves represent results for multiplicity $M = 6$ and the broken curves for $M = 8$.

observed that if deuterium-saturated graphite is exposed to atomic hydrogen the bonded deuterium is predominantly emitted as HD.

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