Enhanced H₂ catalytic formation on specific topological defects in interstellar graphenic dust grain models

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First-principles models of the formation of H₂ on interstellar media carbonaceous grains are usually concerned with processes occurring on ideal graphenic surfaces. Until now these models are unable to explain the formation of molecular hydrogen due to the presence of absorption barriers that cannot be overcome at the low temperatures of the interstellar media. We propose an approach emphasizing the role of specific topological defects for molecular hydrogen catalysis at interstellar dust grain models. Using the nudged elastic band method combined with density-functional techniques, we obtain the full catalytic cycle for the formation of the H₂ molecule on complex carbon topologies involving the presence of pentagonal rings and C adatoms. Depending on structures, reaction paths can be barrierless or have adsorption barriers as low as 10^{-3}–10^{-2} eV, which might be easily overcome at the temperatures of the interstellar medium. Such low adsorption barriers indicate that specific carbon grains topological defects are preferential sites for the molecular hydrogen formation in the interstellar medium.

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I. INTRODUCTION

The study of low-energy interactions and reactions of H atoms at surfaces is of outmost importance for the understanding of H₂ formation mechanisms in diffuse clouds of the interstellar medium (ISM).[1–3] The diffuse interstellar clouds are composed predominantly by atomic and molecular hydrogen and are characterized by a gas-phase density number of approximately 10^6–10^8 m^{-3}.[4,5] Approximately 1% of their mass consists of dust grains whose composition and morphology are extremely complex and still poorly known.[6] It is commonly believed that grains are of carbonaceous or silicaceous nature. Diffuse ISM clouds are at temperatures of a few tens of degree kelvin and are open for penetration by the stellar background flux of UV photons. These photons can easily dissociate molecular hydrogen. Given the significant H₂ abundance in the ISM, there must be an efficient molecule formation mechanism adapted for these environments that can compete with photodissociation.

Due to the inefficiency of direct gas-phase reactions to form H₂ in these very low temperature and atomic density conditions, it has been proposed that ISM dust grains, acting as catalysts, must play a crucial role in the process.[7–10] This hypothesis has stimulated much of the recent experimental investigations on molecular hydrogen formation on grain surfaces of astrophysical interest.[11–15] In this context, different theoretical mechanisms for the H₂ formation have been proposed and studied.[16–24] It is worth mentioning that H₂ formation subsequent to H atom physisorption on grains is quite efficient.[1,2,25] However, the weakness of an H-grain physisorption bond (few tens of millielectron volt)[26] make it quite sensitive to temperature and H atom evaporation readily occurs above 20 K.[27] In diffuse ISM clouds UV absorption by the grains and their subsequent warming up can easily produce such evaporations. Therefore stronger bonds

(0.5–2 eV), of the chemisorption type, are preferable.

Few earlier theoretical studies proposed the existence of a first chemisorbed H atom on the graphenic surface as an essential prerequisite in the Eley-Rideal multistep H₂ formation mechanisms. Once an H atom is adsorbed the chemisorption of additional H atoms at specific sites surrounding the adsorption spot can occur without an energy barrier being encountered.[28,29] Successive hydrogen atoms might subsequently recombine into molecular hydrogen. Yet, numerous theoretical works have shown that the first H atom chemisorption onto a perfect graphitic surface involves an activation barrier of about 0.2 eV.[30–32] This is indeed confirmed by experiments that have to resort to a hot H atom beam source (1600–2200 K) to chemisorb H atoms onto highly ordered pyrolytic graphite.[33] Clearly this barrier is too high to be overcome by H atoms at temperatures $T < 100$ K and probabilities for quantum tunneling across it at these temperatures are far too low to have any relevance for models of H₂ formation in the ISM. Plausible catalysis scenarios should involve barrierless processes or processes having very small activation barriers. The perfect graphitic surfaces might be a too simplistic model and their relevance is thus questionable as concerns H₂ formation in the ISM. To resolve this problem more complex structures for the carbonaceous particles should be taken into account.

During the past decades, in the field of nanoscience, the research of carbon structures developed tremendously since the discovery of fullerene C₆₀ (Ref. 34) and carbon nanotubes.[35] As a result, a vast number of new complex carbon nanoforms have been identified, studied, and reported.[36,37] Carbon nanostructures can range from structurally well-defined molecules to larger complex systems with various defects.

A common topological defect in graphitic systems is the presence of nonhexagonal rings or adatoms. The inclusion of
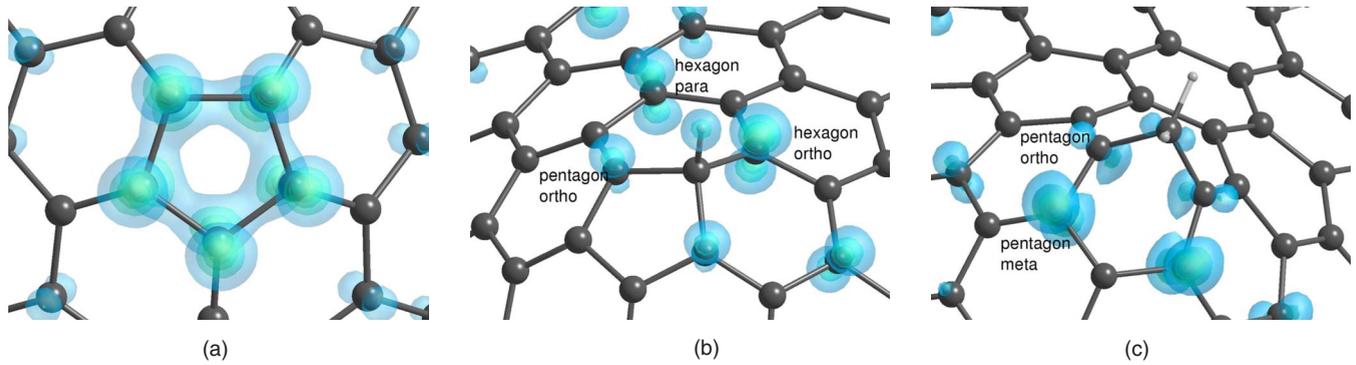
FIG. 1. (Color online) Electron-density distribution isosurfaces for the highest occupied Kohn-Sham orbital for the clusters (a) with a pentagon, (b) with one hydrogen adsorbed on top of a C atom of the pentagon (hexagon para-, pentagon ortho-, and hexagon ortho-sites are indicated), and (c) with a doubly hydrogenated carbon adatom bridging two atoms of the pentagon (pentagon ortho- and meta-sites are indicated). Isosurfaces are plotted at $D_{min} + n \cdot \Delta$, where $\Delta = (D_{max} - D_{min})/6$ and n runs from 1 to 5.

a pentagonal ring induces a local curvature in graphenic flakes. This defect is experimentally and theoretically known to be stable in a number of graphitic structures such as carbon cones and nanotube caps.[38] Adding more pentagons the curvature increases up to the limit case of 12 pentagons in fullerene molecules. In the limit of even smaller structures, the $C_{20}H_{10}$ corannulene molecule has a single pentagon surrounded by hexagonal rings. The valence electron orbitals of a carbon atom in a pentagonal ring are in a mixed sp^2-sp^3 hybridization state making pentagonal sites particularly chemically active. This fact suggests that pentagons in graphitic dust grains might play the sought role for the catalysis of the H_2 molecule. While the occurrence of pentagonal rings (or any kind of nonhexagonal ring) in the structure of carbonaceous ISM grains is difficult to prove experimentally,[39] recent observations show that cold and neutral fullerenes can and do form efficiently in space.[40] As known from nanoscience, pentagons in graphenic structures might appear under similar synthesis conditions.[38] This justifies to look at curved defective graphenic models as possible catalysts in the ISM.

In the present work we propose to consider the role of certain topological defects in carbonaceous interstellar dust grain models in enhancing their reactivity toward hydrogen chemisorption. The pentagonal defect as well as cases of more complex topologies involving the presence of adatoms or additional pentagonal rings are discussed. Using an *ab initio* approach we present several full catalytic cycles for the formation of the H_2 molecule where each step proceeds without (or with very low) energy barrier. In the ISM context, the proposed defective models might be seen not only as individual flakes (defective polyaromatic hydrocarbon molecules) but rather as part of extended grains, i.e., fullerenes, defective carbonaceous platelets, or amorphous carbon.

II. COMPUTATIONAL DETAILS

We have performed electronic-structure calculations and structural optimizations within the DFT framework using the Perdew-Burke-Ernzerhof[41] gradient corrected generalized

gradient approximation (GGA) functional for exchange and correlation as implemented in the AIMPRO code.[42,43] Spin polarization has been taken explicitly into account. Carbon and hydrogen pseudopotentials are generated using the Hartwingsen-Goedecker-Hutter scheme.[44] The code and the basis sets used have been previously successfully applied to the study of H adsorption on perfect graphene, more details are given in Ref. 32.

All structures are clusters formed of a central pentagonal ring surrounded by three concentric circles of hexagonal rings. Edges are saturated by an even number of hydrogen atoms. The cluster with one pentagonal defect is thus formed by 80 C and 20 H atoms and has a fivefold symmetry. Other models considered are the adatom addition on top of the cluster with pentagon and the presence of several pentagons adjacent to the first one.

According to the Eley-Ridel mechanism,[45] the H_2 molecule is formed by direct abstraction of a previously chemisorbed H atom by another H atom from the gas phase; the final molecule is then released in the gas phase. To study the reaction path for H atom chemisorption and abstraction and to correctly estimate the corresponding activation energy barrier, we employed the nudged elastic band method (NEB).[46] This technique only requires structural information concerning the initial and final states, with optionally few other intermediate configurations.[47,48] It is thus a suitable technique for exploring, in an efficient way, a large region of configuration space and deriving complicated minimum-energy paths. No *a priori* assumption for the migration path is required. In order to accurately describe the reaction path, we have used a large number of intermediate images, typically 25, allowing all atoms to move within the NEB optimization process. As initial configuration for the adsorption reaction path we have used the optimized structure for the H atom bound to the cluster and as final configuration the H atom located 5 Å above it. For the abstraction reaction path we have used the optimized structure of the H atom located 5 Å above the hydrogenated cluster as initial point and the bare cluster with an H_2 molecule at 5 Å from it as final point. The distance of 5 Å guarantees a residual zero interactions between the cluster and the atom/molecule in the gas phase.

III. RESULTS

Figure 1(a) presents isosurfaces of the electron-density distribution for the highest occupied Kohn-Sham orbital for the cluster with a pentagonal defect. The curvature leads to the localization of this electronic state predominantly on the tip of the cluster. Thus hydrogen adsorption will occur preferentially onto one of the five equivalent active sites of the pentagon. The actual formation energy for H chemisorption atop one of the C atoms of the pentagon is found to be −1.85 eV, nearly twice as large as that for chemisorption onto a nondefective graphitic surface [−0.94 eV (Ref. 32)]. The characteristic bond lengths between the adsorbent carbon and hydrogen atoms (1.11 Å) and between the adsorbent carbon and its first neighbors (1.51 Å) are similar to those for hydrogen chemisorption on ideal graphene. Due to the adsorption onto an already curved surface, only the adsorbent atom slightly protrudes by 0.29 Å; this puckering is less pronounced than in the case of graphene where the H chemisorption leads to formation of an extended hillock.[32]

Figure 2(a) shows the full catalytic cycle for H$_2$ formation on the cluster with a pentagonal defect. Compared to the adsorption on perfect graphene, the energy barrier for the single H adsorption decreases significantly from 0.2 to 0.02 eV. This makes the H adsorption on atoms at pentagonal sites much more efficient than on atoms in a perfect graphenic environment and it will be feasible already at room temperature. It is worth to note that in agreement with earlier work, we obtain the same energy barrier (0.02 eV) for the hydrogen chemisorption onto a fullerene C$_{60}$ which has the same local pentagon-hexagon arrangement as the cluster considered here.[49] We mention that adsorption on the "inner" concave side of the pentagonal site of the cluster has a very high (∼0.5 eV) energy barrier. This shows the importance of the local topology around the adsorption spot rather than the global morphology of the adsorbent molecule.

We investigate next the succeeding catalysis step [Fig. 2(a), catalytic cycle 1]. The interaction of the formed (H +grain) complex with a second hydrogen atom and the following H-H recombination proceed without barrier leading to the formation of an H$_2$ molecule. The grain restores its initial configuration and is available for successive catalytic reactions.

However, the adsorption of a first H atom perturbs locally the electronic structure of the cluster and new favorable adsorption sites appear. These new active sites have been identified by exploring the isosurfaces of the electron-density distribution for the electronic states associated solely with the addition of the first hydrogen atom, see Fig. 1(b). Thus besides the direct H-H recombination, the second hydrogen atom might be trapped in the vicinity of the first one; this is similar to the formation of hydrogen pairs on graphene.[29,50,51] These additional adsorption sites differ by their formation energies: −2.53 eV on the hexagon ortho-site, −2.69 eV on the pentagon ortho-site and −2.32 eV on the hexagon para-site; these sites are shown in Fig. 1(b). The hydrogenation leads to the puckering of both adsorbent carbon atoms by about 0.30−0.35 Å depending on the adsorption site. In all the cases the characteristic C-H bond length (1.11 Å) is preserved.
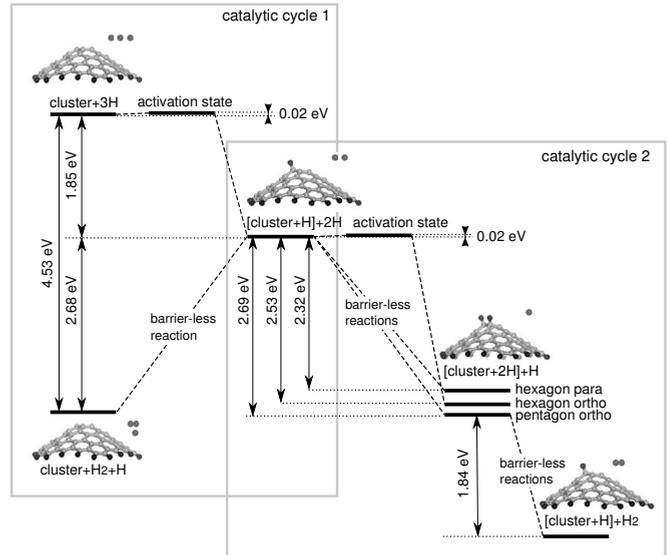
(a) Binding energies and reaction steps for a cluster with a pentagonal ring (catalytic cycle 1) and for a cluster with an H atom adsorbed at the pentagon (catalytic cycle 2).
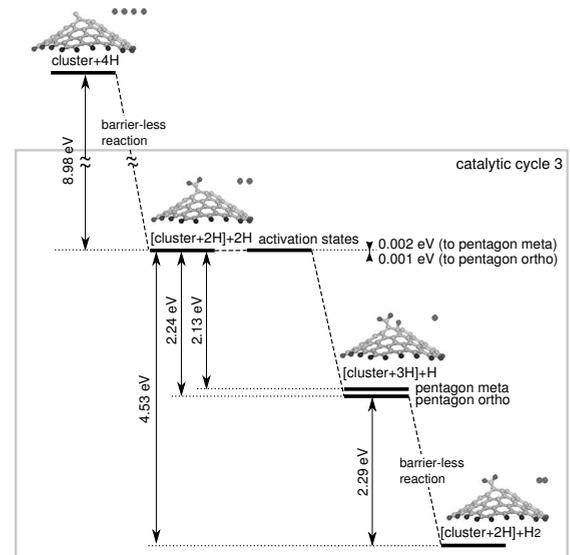
(b) Binding energies and reaction steps for a cluster with an ad-atom bridging two atoms of the pentagon (catalytic cycle 3).

FIG. 2. Schemas for the catalytic molecular hydrogen formation on graphenic ISM dust grain models. The energy gain of each cycle is equal to 4.53 eV, the computed cohesion energy for an H$_2$ molecule.

The adsorption of the second hydrogen takes place without barrier on the pentagon ortho-site and the hexagon para-site. For the H adsorption on the hexagon ortho-site, there is a small barrier of 0.02 eV [Fig. 2(a), catalytic cycle 2]. Finally, for all three sites, the arrival of a third hydrogen atom atop the "second" chemisorbed one leads to the barrierless formation of the H$_2$ molecule and leaves the grain ready for a set of subsequent catalytic cycles. This is similar to the recombination between gas phase H atom and one of para chemisorbed H atoms on a perfect graphitic surface.[52]

As discussed in Sec. I, the chemisorption at the active site should be barrierless or have a very little barrier in the temperature conditions of the ISM. Addition of one pentagon

onto a flat graphenic surface decreases the first hydrogen chemisorption barrier by a factor 10 compared to ordinary graphene. However, the obtained value of 0.02 eV corresponds to the Maxwellian most probable energy at a temperature of ~200 K and thus it might be still a too high energy barrier in the ISM conditions. The reason for the barrier lowering is the particular morphology of the substrate (presence of curvature); localized electronic states create potentially active catalytic spot(s) atop of the considered cluster. Indeed, recently it has been experimentally shown in the case of graphite, fullerenes, and nanotubes that atomic hydrogen adsorption depends on the local curvature of the carbon substrate. This fact was attributed to a higher local sp^3 character of convex sp^2-based carbon structures.[53,54] It is thus reasonable to suppose that by increasing the local curvature, one could be able to further decrease the chemisorption barrier.

In the above we have considered the case when the pentagon is surrounded by hexagonal rings; as in C_{60} the adsorbent carbon atom is characterized by a pyramidal angle[55] of 11.6° (for comparison, the pyramidal angle of atoms in graphene is 0.0°). Structures with higher local curvatures can be obtained by juxtaposing two or three pentagonal rings. In the case of the C_{20} fullerene only pentagonal rings are present and all atoms are at the vertex of three neighboring pentagons with a large pyramidal angle close to that of sp^3-hybridized carbon (19.5°).[56] The same pyramidal angle can be found on the top of cluster with three adjacent pentagons. NEB reaction paths show that the energy barrier for hydrogen adsorption onto these highly curved surfaces vanishes. Moreover, the chemisorption of a second H atom in two possible inequivalent positions in the vicinity of the first chemisorbed H atom happens also without barrier. However, the Eley-Rideal recombinative abstraction of either of these chemisorbed atoms by another atom cannot occur spontaneously due to the strong bonding between the hydrogen and carbon atoms: the abstraction of the single H atom or one of the two H atoms in the pair would require overcoming barriers of 0.16 eV and 0.09 eV, respectively. It is clear that in the ISM conditions the presence of highly curved surfaces as a part of various amorphous structures would contribute rather to the depletion of atomic hydrogen than to H_2 formation. On the contrary, we underline that moderate curvatures would facilitate the H_2 formation if some H atoms would have enough energy to overcome the 0.02 eV chemisorption barrier.

Another way to induce strong local electronic changes and thus to form a potential catalytic spot is to adsorb an additional C atom. The effect may be similar to the barrier lowering promoted by the adsorption of a first H atom shown above. For the sake of consistency with the whole study and for comparison with above results, we place a carbon adatom on the most stable bridge position on the pentagon. We note that the bridge position is known to be the most stable also in the case of graphene.[57] This site is highly reactive: the chemisorption of the first and second H atoms on the C adatom occurs without barrier. However, H atoms are strongly bound at the adatom (the binding energy for the first H is 4.54 eV and for the second is 4.45 eV) and thus can hardly be abstracted by an Eley-Rideal reaction with another gas

phase H atom. This step corresponds to the preactivation of the catalyst and it is outside of the catalytic cycle schema, see Fig. 2(b).

Next, according to the electron-density distribution for the highest occupied Kohn-Sham orbital of the cluster with the hydrogenated adatom, we identify two possible positions where a subsequent adsorption of atomic hydrogen would be most probable [pentagon ortho- and meta-sites, see Fig. 1(c)]. The H atom binding energies for ortho- and meta-sites are, respectively, 2.24 eV and 2.13 eV. The NEB obtained activation barriers are as low as 0.001 eV and 0.002 eV for ortho- and meta-sites, respectively. These energies correspond to a temperature range of ~10–20 K, which is highly relevant to the ISM conditions. Finally, each of these adsorbed H atoms can be abstracted without barrier by a further hydrogen atom with subsequent recombination and formation of an H_2 molecule, see Fig. 2(b).

IV. CONCLUSIONS

In this paper we have investigated the role of topological defects in graphenic interstellar dust grains as models for the H_2 formation catalysis. In particular, we have studied how the curvature induced by the addition of one or several pentagonal rings into the graphenic lattice affects the H adsorption and H-H recombination characteristics. Using the nudged elastic band methodology in the framework of DFT-GGA calculations, we show that the activation barrier against single H atom chemisorption onto the cluster with pentagonal defect is 0.02 eV, ten times less than in the case of a perfect hexagonal lattice. Chemisorption of a second H atom is barrierless for both the pentagon ortho-site and adjacent hexagon para-site whereas a 0.02 eV barrier exists for the adjacent hexagon ortho-site. We have also shown how these barriers might be lowered by combining different defects. In particular, we have investigated the case of a C adatom placed in a bridge position on the pentagon. H chemisorption at the pentagon ortho- and meta-sites relative to the hydrogenated adatom is found to have barriers as small as 0.001 and 0.002 eV. These barriers correspond to the Maxwellian most probable energy at a temperature of ~10–20 K and thus might be easily overcome in the ISM conditions. For several catalytic cycles presented here, the Eley-Rideal recombinative abstraction proceeds without barrier releasing a H_2 molecule and leaving the grain ready for subsequent cycles.

The proposed defective graphenic-like models might be seen not only as individual flakes (defective polyaromatic hydrocarbon molecules) but rather as a part of extended grains, i.e., fullerenes, defective carbonaceous platelets, or amorphous carbon. In previous studies it had been proposed that the hydrogen trapping at defective sites will yield a low recombination efficiency.[10] In agreement with that, our simulations for highly curved surfaces suggest a depletion of atomic hydrogen rather then H_2 molecule formation. However, we underline that once H atoms will be trapped on specific defective sites, other favorable spots for further H adsorption/recombination will be activated. Thus the H_2

catalytic formation might occur more efficiently on certain defective grapheniclike surfaces. The presence of a number of defective carbon structures would be highly feasible since the low temperature in the ISM makes the annealing of the various defects originally produced at the grains formation highly improbable. This leads to the existence of multiple potential catalytic sites, i.e., implying high reaction rates.

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