

CATALYZED ROUTES TO MOLECULAR HYDROGEN FORMATION AND HYDROGEN ADDITION REACTIONS ON NEUTRAL POLYCYCLIC AROMATIC HYDROCARBONS UNDER INTERSTELLAR CONDITIONS

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ABSTRACT

We present first-principle calculations which reveal the existence of low-barrier routes to molecular hydrogen formation on the polycyclic aromatic hydrocarbon (PAH) molecule coronene via Eley-Rideal abstraction reactions and show that such processes could indeed be active under interstellar conditions. The calculations indicate that in regions of low UV flux, coronene, and larger PAHs might be found in superhydrogenated states. Furthermore, the calculations imply that not only edge carbon atoms but also carbon atoms on the inner rings of the coronene molecule can be hydrogenated. Such superhydrogenated PAHs are expected to exhibit significantly changed absorption and emission spectra.

Subject headings: ISM: lines and bands — ISM: molecules — molecular processes

Online material: color figures

1. INTRODUCTION

The formation of molecular hydrogen in the interstellar medium continues to be a matter of intense debate. Molecular hydrogen is the most abundant molecule in the interstellar medium, it is a key molecule in the chemical reaction networks leading to the formation of more complex chemical species and the energy released in its formation has been shown to significantly influence the thermodynamic evolution in interstellar dust and molecular clouds (Flower & Pineau des Forêts 1990). At the low density and temperature present in most interstellar environments, no efficient gas-phase routes exist for the formation of molecular hydrogen. The present consensus is that molecular hydrogen forms on the surface of interstellar dust grains (Hollenbach & Salpeter 1971). Recent laboratory experiments have shown that H₂ formation from weakly bound physisorbed hydrogen atoms is indeed efficient at temperatures below ~20 K (Katz et al. 1999; Manico et al. 2001; Hornekær et al. 2003). However, at higher temperatures more tightly bound states have to be invoked, such as strong binding sites on highly defected surfaces (Cuppen & Herbst 2005) or chemisorption states on, e.g., graphite (Cazaux & Tielens 2004). Recent experiments have revealed that molecular hydrogen formation on graphitic surfaces could be an efficient formation route under photodissociation region (PDR) and post-shock conditions (Hornekær et al. 2006b, 2006a). However, at intermediate temperatures convincing routes to H₂ formation are still missing. In this paper we propose that under low UV flux conditions molecular hydrogen formation on neutral polycyclic aromatic hydrocarbon (PAH) molecules could be such a route.

PAHs are gaining widespread acceptance as the prime carriers of the infrared emission features at 3.3, 6.2, 7.7, 8.6, 11.3, and 12.7 μm in protoplanetary nebulae, reflection nebulae, H II regions and the general interstellar medium (Allamandola et al. 1999; Le Page et al. 2003). They are also suggested to be the cause of a number of the diffuse interstellar bands (Snow 2001),

the extended red emission (Rhee et al. 2007), and the UV extinction bump (Duley 2006). The charge and chemical state of PAHs depend strongly on the environment in which they exist. In regions of high UV flux smaller PAHs are expected to be photodissociated (Jochims et al. 1994; Allain et al. 1996; Le Page et al. 2003), at intermediate UV flux the PAHs are expected to exist in ionized and dehydrogenated states, and at low UV flux they are expected to be mainly neutral (or even anionic) and possibly superhydrogenated (Le Page et al. 2003; Allamandola et al. 1989). In dense interstellar clouds the PAHs are expected to cluster and/or condense out on the surface of interstellar dust grains (Duley & Williams 1993; Rapacioli et al. 2006). The IR absorption and emission spectra of PAHs change depending on their charge state (Allamandola et al. 1989) and degree of hydrogenation (Schutte et al. 1993; Bernstein et al. 1996; Beegle et al. 2001; Pauzat & Ellinger 2001). Absorption/emission lines which coincide with those of superhydrogenated PAHs have been detected in low UV flux environments (e.g., IRAS 05341), while they are largely absent in sources with higher UV flux (e.g., the Orion bar; Bernstein et al. 1996). Laboratory measurements show distinct changes in the UV spectra of PAHs with excess edge hydrogenation indicating that identification of interstellar superhydrogenated PAHs in the UV could be possible (Halasinski et al. 2005). The results presented in this article indicate that under low UV flux conditions superhydrogenated states of larger PAH molecules could be ubiquitous. These states would not only involve excess edge hydrogenation but also hydrogenation of carbon atoms on the center rings. Such superhydrogenation is expected to influence both the near-IR and UV spectrum of interstellar PAHs (Bernstein et al. 1996; Halasinski et al. 2005).

The superhydrogenated states of PAHs and their role as catalysts for molecular hydrogen formation have been discussed by numerous authors. Stein & Brown (1991) showed that addition of a single hydrogen atom to a PAH outer edge site is energetically

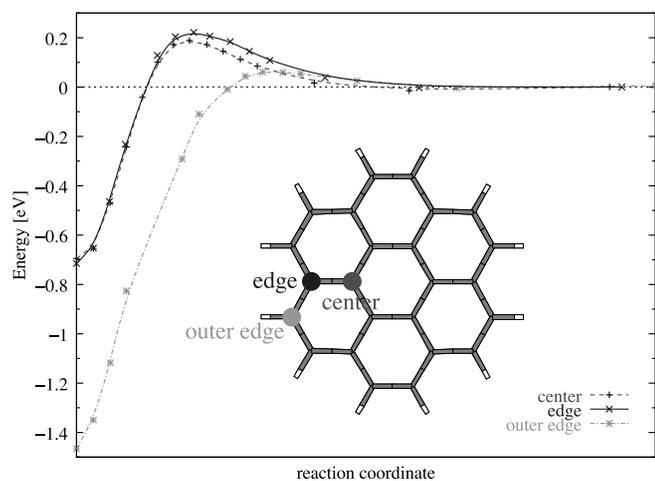


FIG. 1.— Potential energy curve for addition of a single hydrogen atom on the three principally different sites on the coronene molecule. [See the electronic edition of the *Journal* for a color version of this figure.]

favorable and Duley & Williams (1993) suggested that molecular hydrogen might form on PAH covered dust grains in dark clouds. The majority of the attention has, however, been focused on the formation of molecular hydrogen on PAH cations. Cassam-Chenai et al. (1994) suggested that H_2 could form from abstraction reactions between an incoming H atom and one of the edge H atoms on PAH cations. Bauschlicher (1998) suggested that H_2 might form in a two-step process where first an extra H atom is added to an edge site and second this excess H atom is abstracted by an incoming H atom. Hydrogen addition reactions with two H atoms on smaller PAHs was also suggested. Laboratory experiments on benzene and smaller PAHs show that such reactions do indeed occur in the laboratory (Petrie et al. 1992; Scott et al. 1997; Le Page et al. 1997; Snow et al. 1998). The generalization of these results to interstellar conditions was questioned by Herbst & Page (1999), who showed that at low densities, e.g., in the absence of collisions, H-benzene complexes would lose the additional hydrogen atom before being able to stabilize radiatively. However, the calculations showed that even the smallest PAH cation, $C_{10}H_8^+$ (naphthalene), was able to stabilize radiatively in an H addition reaction. Hiramata et al. (2004) showed that not only the edge sites but also carbon atoms in center sites could bind an H atom and thereby act as catalytic sites for H_2 formation via abstraction reactions. In this work we present calculations on competing addition and abstraction reaction mechanisms which lead to the formation of H_2 on and to the superhydrogenation of the neutral PAH molecule coronene.

2. CALCULATIONS

First-principle density functional theory (DFT) calculations on the coronene molecule have been performed using the plane wave based DACAPO code (Hammer et al. 1999; Bahn & Jacobsen 2002) with the PW91 exchange-correlation (xc) functional (Perdew et al. 1992). All calculations include spin polarization. Generally, all atoms in the structure were allowed to relax, while the potential energy curves were obtained by performing single-point calculations with constrained distances between either two H atoms or one H and one C atom, respectively. Barrier heights were determined by iterative calculations of the energies in the critical distance interval. Hence, the calculated barriers are close upper bounds for the activation energies. In the diagrams, the potential energies are plotted against the reaction coordinate defined by the 3N-dimensional movement of all atoms during the process.

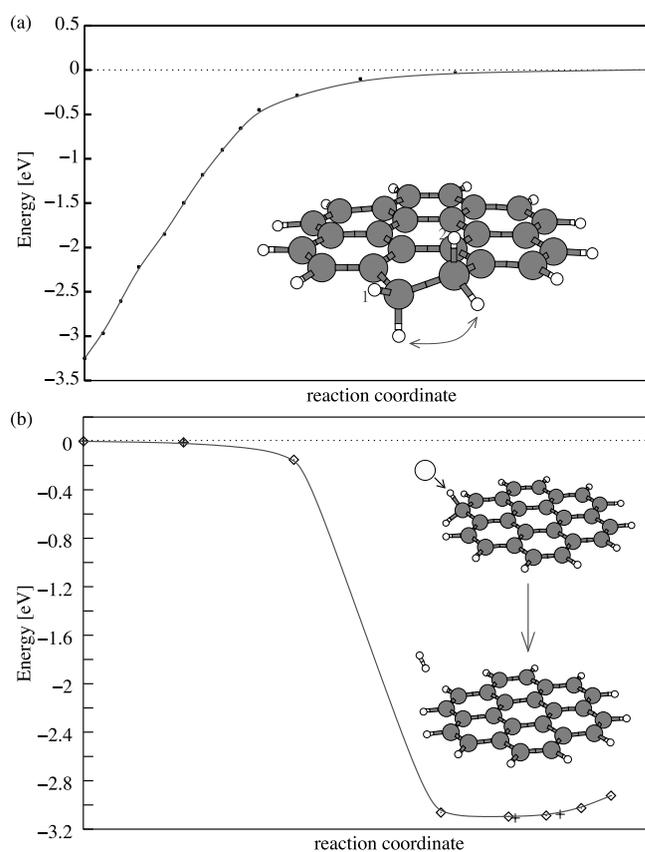


FIG. 2.— (a) Potential energy curve for addition of a second hydrogen atom into the most favorable position, namely, onto the outer edge carbon atom adjacent to the site of adsorption of H atom no. 1. Note the characteristic tilt of the C—C bond. (b) Potential energy curve for molecular hydrogen formation via Eley-Rideal abstraction of hydrogen atom no. 1 by hydrogen atom no. 2 directly impinging on the binding site of hydrogen atom no. 1. [See the electronic edition of the *Journal* for a color version of this figure.]

A similar procedure has successfully been used to describe H atom sticking and hydrogen molecule formation on graphite (Hornekær et al. 2006a, 2006b), in good agreement with experimental results.

3. RESULTS

In Figure 1 the potential energy curves for addition of a single hydrogen atom on top of each of the three principally different carbon sites on the coronene molecule are displayed. No bound states were found for hydrogen atoms on bridge or hollow sites. The three different sites are an outer edge (oe) site which is already occupied by one H atom, an edge (e) and a center (c) site. Bound states exist on all three sites. One site, however, namely, the outer edge site, has a binding energy of 1.45 eV, which is twice the binding energy of the other two sites. Furthermore, all three sites have a barrier to H atom addition, but the barrier to H atom addition into the outer edge site is only 60 meV, i.e., a factor of 3 smaller than the barrier to addition into any of the other two sites. These findings indicate that hydrogen atoms with an energy sufficient to overcome a 60 meV barrier will preferentially bind to outer edge sites of the coronene molecule. The DFT binding energy of the outer edge H atom is in good agreement with the Hueckel-method calculations in Stein & Brown (1991) (1.39 eV). Bauschlicher (1998) have used the B3LYP approach to model H addition reactions with naphthalene. For the neutral molecule they obtained 1.28 eV for the binding energy and 108 meV for the sticking barrier into an outer edge site. This reaction barrier is somewhat higher than our calculated reaction barrier for

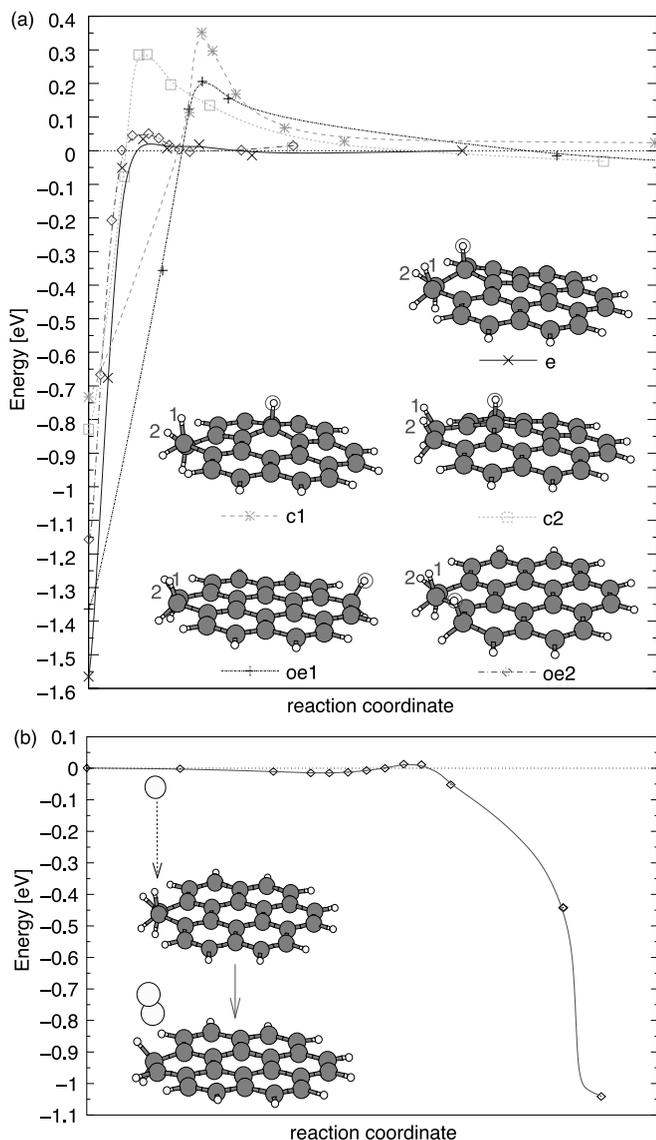


FIG. 3.—(a) Potential energy curves for addition of hydrogen atom no. 3 into five different sites on the coronene molecule. (b) Potential energy curve for molecular hydrogen formation via Eley-Rideal abstraction of hydrogen atom no. 2 by hydrogen atom no. 3 directly impinging on the binding site of hydrogen atom no. 2. [See the electronic edition of the Journal for a color version of this figure.]

H addition to the coronene molecule. This is expected due to the lower flexibility of the smaller naphthalene molecule but could also be caused by the different choice of exchange functionals. PW91 xc functionals have been shown to slightly underestimate barrier heights compared to B3LYP functionals (Nachtigall et al. 1996). Jeloica & Sidis (1999) computed the sticking barrier and binding energy for H atom adsorption into one of the center sites on coronene allowing only the carbon atom above which the H atom adsorbs to relax. They found a sticking barrier in good agreement with the one presented in this work and a somewhat smaller binding energy (0.57 eV as compared to 0.7 eV), as expected for a not fully relaxed system.

Figure 2a displays the potential energy curve for addition of a second hydrogen atom onto the adjacent outer edge carbon atom. Sticking into this site yields the highest energy gain, and the reaction has no energy barrier. The high binding energy of this structure is caused partly by the tilting of the C—C bond where the two excess H are attached. The energy gain due to this tilt amounts to 0.15 eV. We note that the binding energy of

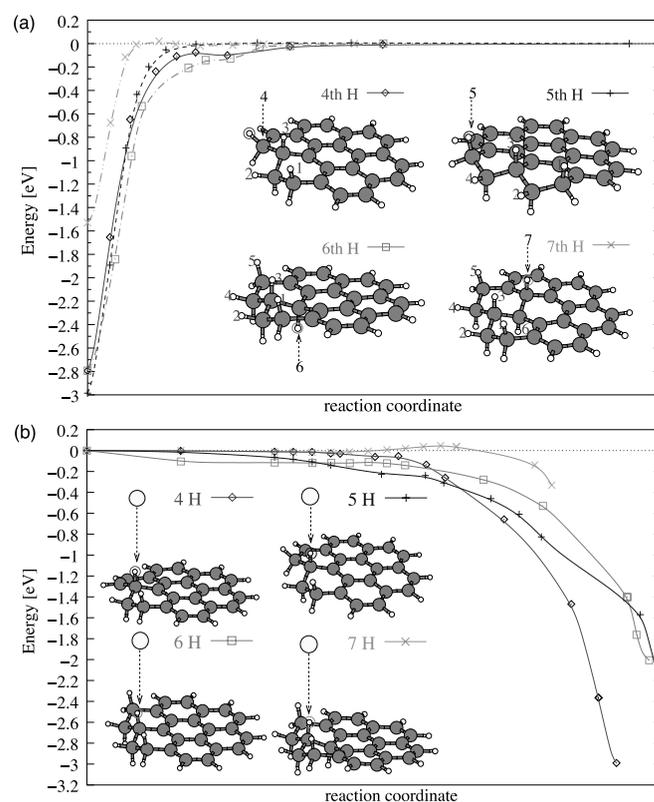


FIG. 4.—(a) Potential energy curves for addition of hydrogen atom nos. 4–7 into the most favorable sites. (b) Potential energy curve for molecular hydrogen formation via Eley-Rideal abstraction of hydrogen atom no. 3 by hydrogen atom nos. 4–7 directly impinging on the binding site of hydrogen atom no. 3. [See the electronic edition of the Journal for a color version of this figure.]

two H atoms bound to adjacent outer edge carbon atoms on coronene is so high (≈ 4.7 eV) that the reaction of the two excess hydrogen atoms to form H₂ (with a binding energy of 4.5 eV) is not energetically favorable. The potential energy curve for an Eley-Rideal abstraction reaction between the incoming second H atom and the already adsorbed first H atom is shown in Figure 2b. This reaction, likewise, has no energy barrier.

In Figure 3a the potential energy curves for addition of hydrogen atom no. 3 into several sites on the coronene molecule are displayed. Sticking into the edge site next to hydrogen atoms 1 and 2 is preferred both based on the binding energy and the reaction barrier. The reaction barrier is 30 meV. The potential energy curve for a competing Eley-Rideal abstraction reaction between the incoming third H atom and the already adsorbed second H atom is shown in Figure 3b. This reaction has a small barrier of 10 meV.

In Figure 4a the potential energy curves for sticking of hydrogen atoms nos. 4–7 into favorable sites are shown.¹ For hydrogen atoms 4–6, there exist sites with high binding energies (2.8–3 eV) and vanishing reaction barrier. In the case of the seventh H atom, an activation barrier of 20 meV has to be overcome, and the binding energy of 1.5 eV is considerably smaller than that of H atoms 4–6. Note that H atom no. 6 is the first to occupy a center site of the coronene molecule. This is, however, only energetically favorable for adsorption on the “bottom side” of the molecule (where the top side is defined as the side where H atom no. 3 is adsorbed). Potential energy curves for several competing sticking reactions for hydrogen atom no. 6 are shown in Figure 5.

¹ Only the processes and structures with the highest probabilities are shown here, determined first by the lowest reaction barrier and second by the highest energy gain on sticking.

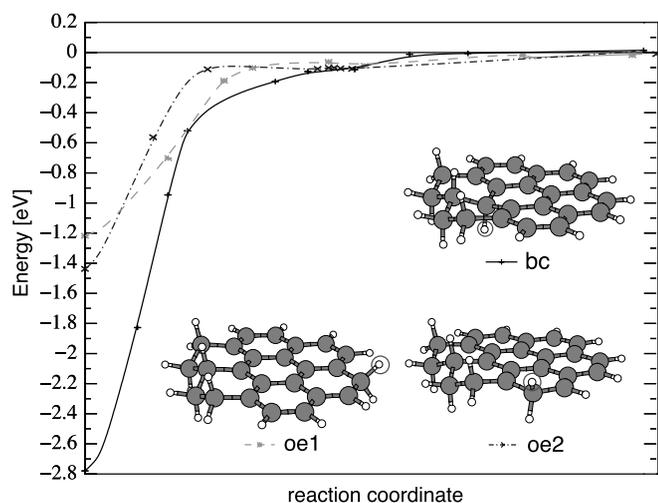


FIG. 5.— Potential energy curves for addition of hydrogen atom no. 6 into three different sites of the coronene molecule. [See the electronic edition of the Journal for a color version of this figure.]

Figure 4b shows the potential energy curves for the Eley-Rideal reaction between H atom no. 3 and an incoming H atom nos. 4–7 directly impinging on the binding site of H atom no. 3. The abstraction of H atom no. 3 is expected to be preferred, since abstraction of an H atom from one of the outer edge sites would mean a stronger geometrical change of the structure, i.e., removal of the stabilizing tilt of the outer edge dimer. For incoming H atoms 4–6 abstraction of H atom no. 3 takes place barrierless. For incoming H atom no. 7 a reaction barrier of 50 meV has to be overcome. Hence, for H atom 4–6 competing sticking and Eley-Rideal abstraction channels exist with zero reaction barrier and high binding energies. For H atom no. 7 the lower barrier to sticking is expected to favor this reaction at low-impact energies.

Figure 6a displays potential energy curves for addition of an eighth hydrogen atom. If the hydrogen atom approaches the coronene molecule from the bottom side (where the sixth H atom is bound) the most energetically favorable outcome is for sticking into the edge site denoted 8b in the figure. Figure 6b displays the situation where the hydrogen atom approaches the coronene from the top side, (the same side where H atom no. 7 is bound). The lowest barrier reaction does not involve sticking to the coronene molecule, but instead abstraction of hydrogen atom no. 7 and H₂ formation. Note that an abstraction reaction occurs both when the incoming H approaches the molecule on top of the center carbon which is nearest neighbor (8t2) and next neighbor (8t1) to the binding site of the seventh H atom. This large capture radius indicates that H atom no. 7 has a very high reactivity. The barrier for this reaction is zero for approach via the nearest neighbor site (which already has attached an H atom on the bottom side) and 20 meV for approach via the next neighbor site. Note that for incidence on site 8t1, a fast reaction, i.e., in which the energy of the incoming H atom is not dissipated, might allow the continuation of the sticking process (Fig. 6b, dashed line). Paths to sticking of the eighth H atom on top of the three other center sites exist but have energy barriers exceeding 0.1 eV.

Molecular hydrogen formation from reactions between two bound hydrogen atoms has also been investigated. However, in all the cases such reactions exhibited energy barriers in excess of 1 eV.

4. DISCUSSION

While the presented calculations do not explore the full set of possible sticking and reaction pathways for multiple hydro-

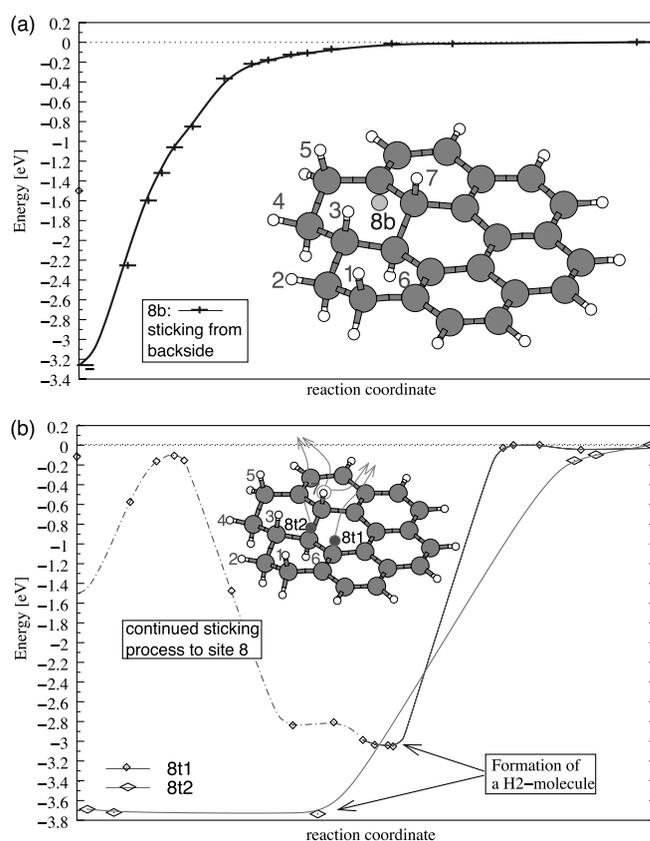


FIG. 6.— (a) Potential energy curves for addition of hydrogen atom no. 8 into a favorable site (denoted 8b in the figure) on the coronene molecule. (b) Potential energy curve for molecular hydrogen formation via Eley-Rideal abstraction of hydrogen atom no. 7 by hydrogen atom no. 8 impinging on either the nearest neighbor (denoted 8t1 in the figure) or next neighbor (denoted 8t2 in the figure) site of hydrogen atom no. 7. [See the electronic edition of the Journal for a color version of this figure.]

gen atoms on the coronene molecule, they do explore the lowest barrier, highest binding energy path for successive hydrogen atom addition and abstraction. An overview of the discussed reactions is shown in Figure 7. Several pathways lead to molecular hydrogen formation via the Eley-Rideal abstraction mechanism. The rate limiting step in these processes is the addition of the first hydrogen atom onto the coronene molecule, exhibiting a reaction barrier of 60 meV. However, it should be noted that a number of pathways exist where this first atom is not removed in the suggested H₂ abstraction processes. In the case of abstraction between hydrogen atoms nos. 2 and 3, the first H atom on the outer edge site remain bound to coronene forming a C₂₄H₁₃ molecule. The C₂₄H₁₃ molecule can then bind another H atom (a new no. 2) in a zero barrier reaction, which can subsequently form molecular hydrogen via an Eley-Rideal abstraction reaction with an incoming H atom (a new no. 3) with a reaction barrier of only 10 meV. Similar H₂ producing reaction loops exist for Eley-Rideal abstraction reactions once four H atoms are adsorbed on the coronene molecule. As can be seen from Figure 6, several of these loops have zero reaction barriers. When an even higher excess of seven hydrogen atoms is obtained on the coronene molecule, the abstraction reaction between hydrogen atoms nos. 7 and 8 becomes active. As stated in the previous section, this reaction has a very large capture radius and forms a reaction loop for H₂ production with a barrier ranging from 0 to 20 meV depending on the impact site for the eighth H atom.

Hence, superhydrogenated coronene molecules with more than three excess H atoms will act as catalysts for H₂ formation with

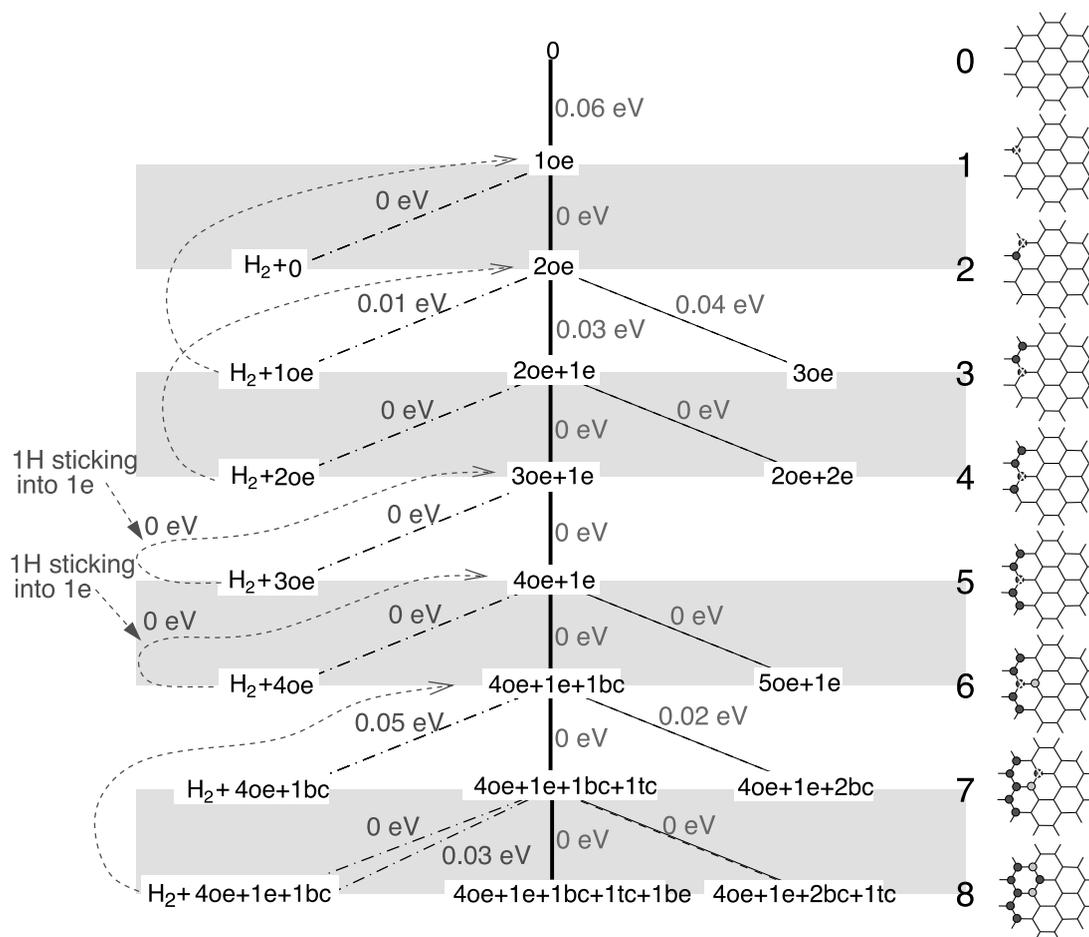


FIG. 7.— Reaction pathways for H₂ formation on coronene from atomic H (normal incidence). The total number of H atoms involved in each step is shown on the right hand side of the figure. Abstraction reaction branch off to the left (*dash-dotted lines*), the most favorable sticking reactions form the center line. The resulting structures are described via abbreviations: "oe" denotes H atoms attached to outer edge sites, "e" to edge sites, "c" to center sites; "t" denotes the top side of the molecule, and "b" the bottom side. To the right the H_n-coronene structures of the central reaction line are shown. Dark dots indicate H atoms adsorbed on the front side of the molecule, while brighter dots indicate H atoms adsorbed on the backside of the molecule. Crosses indicate that this atom is involved in an abstraction reaction with the next incoming H atom. [See the electronic edition of the *Journal* for a color version of this figure.]

vanishing effective reaction barriers, while the C₂₄H₁₃ and C₂₄H₁₄ molecules will act as catalysts for H₂ formation with an effective reaction barrier of 10 and 30 meV, respectively. Other, even more complex superhydrogenated states of coronene which exhibit similar catalytic activity might very well exist. For example, the same reaction pathway can be imagined to happen more or less simultaneously and independently on the opposite side of the molecule, leading to both higher H coverage of the coronene molecule and higher efficiency in H₂ formation.

5. ASTROPHYSICAL IMPLICATIONS

As stated above, the majority of previous work on H₂ formation on PAHs focused on the PAH cations. These generally exhibit vanishing barriers for addition of the first excess H atom into an outer edge site and low or vanishing barriers for abstraction reactions involving excess H atoms (Bauschlicher 1998). The PAH cations might therefore be more efficient catalysts for H₂ formation than their neutral counterparts. It should, however, be noted that the cation and neutral PAHs are not decoupled populations. For example, a superhydrogenated PAH cation could convert to a neutral superhydrogenated PAH molecule via electron attachment reactions (Bauschlicher 1998), thus providing a low-barrier route for the first hydrogenation step of neutral PAHs. As argued above in the case of the coronene molecule, once more than 3 excess H atoms are added to the neutral molecule it will

act as a catalyst for H₂ formation with vanishing effective reaction barriers.

In present models of the hydrogenation state of PAHs, reactions between H atoms and neutral PAHs are generally neglected (Le Page et al. 2003). The calculations presented here indicate that H addition reactions could very well be important also for neutral PAHs in low UV flux environments where large PAHs will be able to retain excess H atoms over a longer time span. Hence in these environments neutral PAHs could well be in superhydrogenated states. Laboratory measurements show that such superhydrogenation will influence both the near-IR (Schutte et al. 1993; Bernstein et al. 1996; Beegle et al. 2001; Pauzat & Ellinger 2001) and UV (Halasinski et al. 2005) spectrum of interstellar PAHs. Absorption/emission lines which coincide with those of superhydrogenated PAHs have already been detected in low UV flux environments (Bernstein et al. 1996).

To summarize, our calculations indicate that in the absence of external sources of H atom desorption (such as UV radiation), PAHs could well exist in superhydrogenated states. Furthermore, they indicate that not only edge sites but also center sites on the PAH molecules are hydrogenated. Such superhydrogenated PAHs could indeed act as catalysts for interstellar H₂ formation.

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