Clustering of Chemisorbed H(D) Atoms on the Graphite (0001) Surface due to Preferential Sticking

L. Hornekær,¹* E. Raulls,¹ W. Xu,¹ Ž. Šljivančanin,² R. Otero,¹ I. Stensgaard,¹ E. Lægsgaard,¹ B. Hammer,¹ and F. Besenbacher¹

¹Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, University of Aarhus, Ny Munkegade bygn. 1520, 8000 Aarhus C, Denmark
²Ecole Polytechnique Fédérale de Lausanne (EPFL), ITP and IRRMA, CH-1015 Lausanne, Switzerland

(Received 2 August 2006; published 31 October 2006)

We present scanning tunneling microscopy experiments and density functional theory calculations which reveal a unique mechanism for the formation of hydrogen adsorbate clusters on graphite surfaces. Our results show that diffusion of hydrogen atoms is largely inactive and that clustering is a consequence of preferential sticking into specific adsorbate structures. These surprising findings are caused by reduced or even vanishing adsorption barriers for hydrogen in the vicinity of already adsorbed H atoms on the surface and point to a possible novel route to interstellar H₂ formation.

DOI: 10.1103/PhysRevLett.97.186102 PACS numbers: 68.43.−h, 68.37.Ef, 82.65.+r, 98.38.Bn

Hydrogen adsorption and the structure of hydrogen adsorbates on surfaces has been studied extensively due to both its fundamental interest and its relevance in connection with numerous technological applications. Preparing and clustering of hydrogen atoms on surfaces have been reported for systems such as H on Si [1] and H on diamond C(111) [2]. For these systems the preparing mechanism is thought to be thermal or “hot precursor” mediated diffusion [2,3]. Here we report on a mechanism for H atom cluster formation on graphite surfaces which does not involve diffusion. The presented results have interesting implications for interstellar H₂ formation in photon dominated regions (PDRs) and in shocked interstellar gases.

Molecular hydrogen is the most abundant molecule in the interstellar medium featuring both in dense and diffuse interstellar molecular clouds, in photon dominated regions (PDRs) [4], and in regions with shocked gasses [5]. In all these regions molecular hydrogen is continuously dissociated by UV radiation and/or cosmic rays. To maintain the abundance of molecular hydrogen, an efficient formation mechanism is required. This mechanism is generally accepted to be H₂ formation on the surface of interstellar dust grains [6]. A substantial fraction of interstellar dust grains are anticipated to be carbonaceous, and onionlike graphite particles have been observed both in presolar dust grains in meteorites [7] and in experiments simulating interstellar grain formation [7,8]. The details of the H₂ formation process have been shown to significantly impact the thermal and chemical evolution in the interstellar medium [4,5,9–11]. In post-shock regions, heating due to H₂ formation has even been suggested to facilitate H₂O maser action [12]. Recent experiments have shown that recombination of chemisorbed H atoms on dust grain analog surfaces is indeed efficient, but at low temperatures only [13–15]. Hence, in regions of higher temperatures, e.g., in PDRs and shocked regions, more tightly bound states have to be invoked, and a chemisorbed state of hydrogen on graphite has been tentatively suggested [16]. However, it was previously perceived that the large barrier for chemisorption (∼0.2 eV) [17,18] would make it unrealistic to obtain a sufficient coverage of H atoms on graphitic surfaces under interstellar conditions. The results presented here challenge this perception by identifying a new mechanism for the formation of H adsorbate clusters. Previous investigations have shown that molecular hydrogen can form on graphite [19] from such H clusters along two paths: either (i) from preparted H dimers on the surface [20,21] or (ii) via Eley-Rideal abstraction reactions [22,23] between adsorbed H atoms and incoming H atoms from the gas phase. In both cases, the identified mechanism for hydrogen cluster formation on graphitic surfaces provides a route for interstellar H₂ formation.

All experiments were performed in a ultrahigh vacuum (UHV) system (base pressure: 3 × 10⁻¹⁰ Torr) equipped with a home built Aarhus STM. Highly ordered pyrolytic graphite (HOPG) samples were cleaved in air immediately prior to being inserted into the UHV chamber. In vacuum the samples were annealed to 1300 K by electron bombardment of the backside of the sample to desorb any hydrogen or oxygen species bound at the surface and at step edges or defects. Atomic hydrogen dosing was performed using a hot (1600–2200 K) hydrogen atom beam source. In the majority of the experiments the D isotope was used.

DFT calculations were performed with the plane wave based DACAPO program package [24], a (4 × 4) Monkhorst-Pack k-point scheme, and the Perdew Wang GGA functional (PW91). The graphite was modeled by a rhombohedral surface slab consisting of either two graphite sheets with 18 carbon atoms each, or of one graphite sheet with 32 carbon atoms separated by five vacuum layers. All atoms were allowed to relax in every step; only one atom per layer was kept fixed to ensure the correct...
spacing of the layers. All calculations were performed spin polarized.

Figure 1(a) shows an STM image of a 210 K graphite (HOPG) surface exposed to a very low dose of hot D atoms. The bright protrusions in the image are ascribed to chemisorbed D atoms since they only appear after D atom dosing and are correlated with molecular deuterium desorption. A close-up of one of these bright protrusions is shown in Fig. 2(a). The threefold symmetry of the structure is as expected for a D monomer adsorbed above a C atom on the graphite surface. By associating each bright protrusion with 1 D atom, a D monomer, we calculate a D atom coverage of 0.03%. After recording STM images like the one in Fig. 1(a), the HOPG sample was removed from the STM and heated to room temperature for 10 min before being put back into the cooled STM. The resulting STM image is shown in Fig. 1(b). As can be seen, the number of bright protrusions is drastically reduced by 80%. By assuming that all the bright protrusions in Fig. 1(a) are D monomers, an upper limit on the lifetime of isolated D atoms on the graphite surface of 6 min can be obtained. This value is in good agreement with the one expected for hydrogen monomer desorption based on the theoretically derived desorption barrier of 0.9 eV [17,18].

Figure 1(c) shows an STM image after a D atom dose roughly a hundred times higher than in Fig. 1(a). Again we ascribe the bright protrusions to chemisorbed D atoms. A close-up on these bright protrusions show that the majority are more complex structures, similar to the ones shown in Fig. 2(b), which we associate with D atom clusters. We calculate a coverage of 0.2% × (number of atoms per protrusion). Figure 1(d) shows an STM image obtained after removing the sample from the STM, heating it to room temperature for 10 min, and then placing it back into the cooled STM. In this case a less drastic reduction of only 20% in the number of bright protrusions is observed. This finding indicates that at the higher integrated flux more stable adsorption complexes are formed on the surface. Based on the upper limit on the D monomer lifetime derived above, a lower limit on the percentage of more stable adsorption complexes can be obtained. We find that

![Image](image1.png)

**FIG. 1 (color online).** STM images of the graphite surface after D atom deposition. During deposition and in the STM the sample temperature is kept below 210 K. (a) STM image after deposition at low integrated flux \( F \sim 10^{12} \text{ atoms/cm}^2 \). (b) STM image after heating the sample in (a) to room temperature (RT) for 10 min followed by recolling in the STM. (c) STM image after D atom deposition at high integrated flux \( F \sim 10^{14} \text{ atoms/cm}^2 \). (d) STM image after heating the sample in (c) to RT for 10 min followed by recolling in the STM. Imaging parameters: (a) \( I_x = -0.58 \text{ nA}, V_y = -312 \text{ mV} \), (b) \( I_x = -0.45 \text{ nA}, V_y = -1250 \text{ mV} \), (c) \( I_x = -0.43 \text{ nA}, V_y = -1250 \text{ mV} \), (d) \( I_x = -0.26 \text{ nA}, V_y = -1486 \text{ mV} \).

![Image](image2.png)

**FIG. 2 (color online).** STM images of the graphite surface after increasing doses of D atoms showing the formation of increasingly more complex adsorption clusters. (a) Zoom in on one of the bright protrusions in Fig. 1(a). (b) STM image showing the formation of hydrogen dimer structures after a 1 min D atom dose at a flux of \( F = 10^{15} \text{ atoms/cm}^2 \). (c) STM image showing the formation of larger and more complex adsorption clusters after a 6 min D atom dose at a flux of \( F = 10^{15} \text{ atoms/cm}^2 \). (d) STM image showing the graphite surface at saturation coverage after a 24 min D atom dose at a flux of \( F = 10^{15} \text{ atoms/cm}^2 \). The underlying carbon lattice is no longer visible and the image is dominated by the electronic reconstruction induced by the hydrogen adsorbates. Imaging parameters: (a) \( I_x = -0.71 \text{ nA}, V_y = -156 \text{ mV} \), (b) \( I_x = -0.16 \text{ nA}, V_y = -884 \text{ mV} \), (c) \( I_x = -0.150 \text{ nA}, V_y = -743 \text{ mV} \), (d) \( I_x = -0.53 \text{ nA}, V_y = -1051 \text{ mV} \).
at least 75% of the D atom adsorbate structures in Fig. 1(c) must be such complexes.

As will become apparent from our calculations it is a fair assumption that stable adsorption complexes consist of D atoms adsorbed within 4th nearest neighbor distance of each other (see discussion below). If the D atoms were distributed uniformly on all carbon surface atoms, then at an adsorbate cluster coverage of 0.2%, as in Fig. 1(c), at most 5% of the D atoms should be part of adsorption clusters containing more than 1 D atom adsorbed within 3rd nearest neighbor distance. This finding contradicts the experimental observation that 75% of the D atoms are associated with more stable structures and indicate that some mechanism favors formation of more stable adsorption clusters.

Figures 2(a)−2(d) show high resolution images of graphite after exposure to increasing doses of D atoms, demonstrating that the tendency to form clusters continues at higher total coverages. Figure 2(a) is a close-up of an adsorption structure on the low coverage surface shown in Fig. 1(a). The threefold symmetry of the bright protrusion is as expected for a D monomer adsorbed above a C atom on the graphite surface. Figure 2(b) shows D adsorbate structures at a slightly higher cluster coverage of ~1%. The elongated bright protrusions, which dominate the image, have been identified as hydrogen (deuterium) dimers [20,25]. At an even higher coverage of ~3% as in Fig. 2(c), the majority of the D atoms are adsorbed in larger D atom clusters. Finally, at saturation coverage, θH ~ 50% [19], the carbon lattice is no longer visible, and the STM image is completely dominated by the electronic effects caused by the deuterium adsorbates.

To determine whether the observed hydrogen (deuterium) atom clusters could be a result of thermal diffusion, the diffusion barrier for an isolated chemisorbed H atom on the graphite surface was calculated, using first principles DFT calculations [24]. The calculations predict a diffusion barrier of 1.14 eV. Since the desorption barrier is only around 0.9 eV this implies that an isolated H atom will desorb rather than diffuse upon heating. This prediction is in good agreement with the experimental findings. STM observations performed both at room temperature and at temperatures of ~200 K show that D atoms are immobile on the graphite surface at all coverages. This finding indicates that the reduction in the number of bright protrusions observed in the STM images in Fig. 1 is due to H atom desorption and that at higher integrated hydrogen atom flux, adsorption complexes which are more stable against desorption are formed.

To investigate under what conditions hydrogen adsorbate clusters can be expected to give rise to increased stability against desorption, the binding energy of various configurations involving 2 H atoms adsorbed within 1st−6th nearest neighbor distances were investigated. Only the ortho- and paradimer configurations shown in Fig. 3(c) show markedly increased binding energies. The next neighbor configuration, NN in Fig. 3(c), has been shown elsewhere to convert to either of the two with a barrier of only ~0.5 eV [20]. This finding justifies the above use of 4th nearest neighbor as the cutoff distance for increased stability of adsorbat clusters.

Since the observed clustering is not a result of diffusion, the influence of the sticking process on clustering was investigated. Figure 3(a) shows the potential energy curves for H atom sticking into the four configurations shown in Fig. 3(b) and 3(c). Two observations stand out: (i) the binding energy of the ortho- and paradimers is much increased compared to the binding energy of 2 H monomers or the next neighbor (NN) dimer state [26], and (ii) the barrier to adsorption into the orthodimer and next neighbor dimer is reduced by roughly 50 meV compared to the sticking of an H atom into a monomer state, while no barrier to adsorption is observed for sticking into the paradimer configuration [29]. The reduced and even vanishing barriers to hydrogen sticking into specific adsorption sites in the vicinity of already adsorbed H atoms will lead to preferential sticking. This observation implies that cluster configurations will become more abundant. According to these calculations, paradimer structures should be the dominant structure at low coverage since no barrier exists for sticking into this state. Experimental observations show that this is indeed the case [20].

![FIG. 3 (color online). (a) Potential energy curves for adsorption of a single H atom monomer (solid line), shown in (b), and for the three dimer configurations shown in (c), the orthodimer (dash-dotted line), the next neighbor site (dashed line), and the paradimer (dash-double dotted line).](image-url)
FIG. 4 (color online). Potential energy curves for adsorption of a third H atom in the vicinity of a paradimer at sites s1–s5 shown in the inset. The reaction coordinate is a sum over all position changes of all atoms in the calculation.

To investigate whether similar mechanisms control the formation of larger clusters at higher coverage, the potential energy curves for adsorption of a third H atom in the vicinity of the hydrogen paradimer were calculated. These are shown in Fig. 4. Reduced barriers to sticking are observed for a third H atom adsorbing into sites 3, 4, and 5 (marked in the figure inset). Further calculations with sticking of a fourth atom also reveal the existence of sites with reduced and even vanishing barriers to adsorption. This finding indicates that also larger clusters form as a result of preferential sticking due to reduced barriers to adsorption in the vicinity of already adsorbed H atoms. The existence of reduced barriers to adsorption into several different cluster structures is in good agreement with the experimental observation of more varied and complex adsorption structures at higher coverages.

The identified mechanism for hydrogen cluster formation differs from the preparing and clustering mechanisms reported on for other systems, e.g., H on Si [1] and H on diamond C(111) [2]. For these systems the preparing mechanism is thought to be thermal or “hot precursor” mediated diffusion [2,3]. In contrast, the mechanism presented here does not involve diffusion. Besides being of fundamental interest, the identified mechanism also has interesting implications for interstellar hydrogen formation. In PDRs and post-shock regions gas temperatures range from several hundred to thousand Kelvin [9,10,30], and hydrogen atoms in the high energy tail of the thermal Maxwell-Boltzmann distribution will have sufficient energy to populate the chemisorbed state on graphitic grain surfaces. Once a first hydrogen atom is adsorbed on the surface, the adsorption barriers for additional H atoms are much reduced or even vanishing, and larger clusters can form. This mechanism enables the buildup of non-negligible H atom coverages from which molecular hydrogen formation may occur either via recombinative desorption or via Eley-Rideal abstraction. Hence, the presented results at the same time reveal a new mechanism for adsorbate cluster formation on surfaces via preferential sticking and contribute to our understanding of interstellar hydrogen formation.

*Electronic address: liv@phys.au.dk

[26] The reported binding energy of the ortho and next neighbor dimer states are in good agreement with earlier findings [20,27,28], while the binding energy of the paradimer state differs from that reported in Miura et al. [28]. This difference can be ascribed to the fact that a smaller carbon unit cell was used in these calculations.
[29] The potential energy curve shown is for adsorption of an incoming H atom with antiparallel spin to the spin of the already adsorbed H atom. In the case of parallel spin, calculations predict a small barrier to adsorption.