Quantum studies of H atom trapping on a graphite surface

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The trapping and sticking of H and D atoms on the graphite (0001) surface is examined, over the energy range of 0.1–0.9 eV. For hydrogen to chemisorb onto graphite, the bonding carbon must pucker out of the surface plane by several tenths of an angstrom. A quantum approach in which both the hydrogen and the bonding carbon atoms can move is used to model the trapping, and a potential energy surface based on density functional theory calculations is employed. It is found, for energies not too far above the 0.2 eV barrier to chemisorption that a significant fraction of the incident H or D atoms can trap. The forces on the bonding carbon are large, and it can reconstruct within 50 fs or so. After about 100 fs, most of the trapped H atoms scatter back into the gas phase, but the 5%–10% that remain can have lifetimes on the order of a picosecond or more. Calculations of the resonance eigenstates and lifetimes confirm this. An additional lattice degree of freedom is included quantum mechanically and is shown to significantly increase the amount of H that remains trapped after 1 ps. Further increasing the incident energy destabilizes the trapped state, leading to less H remaining trapped at long times. We estimate that for a full dissipative bath, the sticking probabilities should be on the order of 0.1. © 2005 American Institute of Physics. [DOI: 10.1063/1.1827601]

I. INTRODUCTION

There has been much scientific activity in recent years directed towards understanding the interactions of hydrogen atoms with graphite surfaces. Much of this work is aimed at elucidating the mechanisms for H\(_2\) formation from H atoms in interstellar space, where the large abundance of H\(_2\) cannot be explained by gas phase collision mechanisms. It is generally believed that H atom recombination takes place on interstellar dust particles,\(^1\) perhaps via an Eley–Rideal mechanism, and while the composition of these dust particles is not well known, there is strong spectroscopic evidence that they contain graphitic components.\(^2\) Research has also been motivated by the erosion of graphite-lined walls in fusion reactors by H atoms, and studies of hydrogen adsorption and storage in graphite nanostructures.\(^3\) These problems have stimulated several electronic structure studies of the interaction of H atoms with graphite surfaces.\(^3–14\) While lower-level calculations found varying results,\(^4,8,9\) recent density functional theory (DFT) based studies by Sidis and co-workers,\(^5,6\) and Sha and Jackson\(^7,11\) are in general agreement with respect to chemisorption on the basal plane. These authors find that a H atom can form a chemical bond to a carbon atom on a graphite surface, with a binding energy of about 0.67 eV. They also found that a significant amount of surface reconstruction was necessary, with the carbon atom puckering out of the surface plane by 0.36 Å, and that there was a barrier to sticking of about 0.25 eV. Other recent electronic structure studies have more-or-less reproduced these findings.\(^12–14\) The Eley–Rideal reactions of gas phase H atoms with these chemisorbed H atoms to form H\(_2\) have been studied by several groups.\(^7,10,11,15–21\) In one study,\(^11\) extensive DFT calculations were used to construct fully three-dimensional potential energy surfaces (PESs), and the Eley–Rideal reaction cross sections were computed quantum mechanically to be on the order of 10 Å\(^2\),\(^2\) in agreement with some earlier predictions.\(^17\) Exposing graphite to H atom beams in UHV, Zecho et al. were the first to demonstrate H-graphite chemisorption in the laboratory.\(^22\) They also studied the Eley–Rideal recombination of gas phase and chemisorbed H atoms.\(^23\) Their results were in excellent agreement with theory with regard to both the vibrational properties of the chemisorbed H atoms and the Eley–Rideal reaction cross sections.\(^7,11,22,23\) In addition, they deduced a barrier to sticking of 0.2±0.1 eV,\(^24\) in agreement with Jeloaica and Sidis’\(^5\) and our predictions.\(^7\) Other UHV laboratory studies are currently in progress examining H-graphite sticking and Eley–Rideal processes,\(^25,26\) as well as sticking and recombinative desorption at terrace and edge sites.\(^27\) Studies of these various processes on amorphous carbon also exist.\(^28–31\)

One of the unresolved and perhaps most fundamentally interesting aspects of these H-graphite reactions is how H atoms trap and stick on graphite surfaces in the first place. Sticking is one of the most fundamental processes in surface science, and while seemingly straightforward it is complicated by the need to dissipate energy into the many-body excitations of the lattice. The case of H sticking on a graphite (0001) surface is further complicated by the significant

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amount of lattice reconstruction required, and it is not obvious that the bonding carbon atom should have the time to distort by several tenths of an angstrom during the brief H-surface collision. Having said that, the experiments by Zecho et al. are quite convincing that chemisorbed H is indeed formed,22 and they extract probabilities for the initial sticking of H and D atoms on graphite that are surprisingly large: 0.4±0.2 at a surface temperature of 150 K. We note that lattice reconstructions are probably also important for H sticking on organic or semiconductor surfaces, and to a much lesser extent, on metals. For the case of sticking on graphite, however, a significant reconstruction is necessary to form a stable bond.

In this paper we examine this problem in detail. In Sec. II we present the results of total energy calculations based on DFT, where the H-graphite interaction examined as a function of both the H atom position and the displacement of the bonding carbon. In Sec. III time-dependent quantum scattering methods are used to examine the trapping process. We conclude with a summary in Sec. IV.

II. THE PES

We first consider the interaction of a H atom with a graphite (0001) surface. We calculate total energies from first principles using the well-known VASP (Vienna ab initio simulation package) developed at the Institut für Materialphysik of the Universität Wien,32–34 which uses a plane wave basis set. Nonlocal exchange-correlation effects are introduced via a generalized gradient approximation (GGA), using the Perdew–Wang functional PW91.35 The interactions between the ionic cores and the electrons are described by fully nonlocal optimized ultrasoft pseudopotentials,36,37 and spin-polarized calculations have been performed. A four-layer slab supercell with periodic boundaries has been used to model the graphite, with eight carbon atoms per layer, and a H atom coverage of 1/8 monolayer. We direct the reader to Ref. 7 for more details.

We consider a collinear configuration, where the H atom is directly over a carbon atom in the lattice (the “bonding carbon”). We have computed the energy at 35 points along $z_H$, the distance of the H atom above the plane of the surface, for each of 21 different values of $z_C$, the displacement of the bonding carbon from the surface plane. The results are presented as a contour plot in Fig. 1. Our earlier studies7 showed that there was negligible lattice relaxation of the remaining carbon atoms, and in this study they are kept fixed. Note first that for the flat surface ($z_C=0$), there is a quasi-bound state near $z_H=1.2$ Å, but no stable chemisorption. There is a shallow physisorption well, about 0.01 eV deep, roughly 4 Å above the surface. While this version of DFT does not accurately describe physisorption, the well depth is known to be small, and has been estimated to be 0.043 eV in selective adsorption experiments.38 As the bonding carbon moves out of the surface plane ($z_C>0$) and towards the incoming H atom, a stable chemical bond begins to form. The maximum binding energy of 0.67 eV occurs for $z_C=0.36$ Å. If the lattice relaxes adiabatically as we move the H atom towards the surface, there is a barrier to chemisorption of about 0.25 eV. These results are consistent with the work of Sidis and co-workers,6 who performed a similar DFT-GGA-PW91 study, but used a cluster model with an atomic orbital basis set. Our calculated equilibrium properties for bulk graphite and the graphite (0001) surface are in good agreement with experimental data.7 Also, our computed vibrational frequencies for H and D chemisorbed onto graphite (0001) are in good agreement with those measured by the Küppers group,22 and the computed barrier to chemisorption agrees well with the value measured by that group, 0.2±0.1 eV.24

In this paper we use standard definitions of trapping and sticking. Our zero of energy corresponds to a flat surface ($z_C=0$) with the H atom far above the surface. If the H is bound to the carbon, but the energy of the C–H complex is positive, the H is trapped. The H can stick only if, through dissipation of energy to the substrate excitations, this energy becomes negative. For trapping or sticking to occur, the bonding carbon must pucker rapidly when the incident H atom is close by, before the fast-moving H atom scatters away. Note how the forces on the carbon atom change dramatically as the H atom crosses the barrier region: for $z_H$ less than about 2 Å, there are strong forces pushing the carbon away from the surface plane. Note also that half of the time, on average, the carbon atom is already moving away from the surface when the H atom crosses the barrier. In addition, if the H atom has an energy just above the barrier, say 0.3 eV, it can become trapped in the chemisorption region if the carbon puckers out by only 0.2 Å. That is, the carbon does not need to pucker the full amount to trap the H atom. Sticking may occur via a trapping resonance; i.e., H may initially become trapped in the binding well of Fig. 1, and then relax as energy is dissipated away from the newly formed and highly excited C–H bond and into the substrate excitations. This relaxation is, of course, in competition with the dissociation of this metastable complex. Excitation of any lattice phonons or electron hole pairs during the initial collision will
generally increase trapping, and if there is sufficient lattice excitation during this initial collision, sticking may occur more directly.

III. TRAPPING DYNAMICS

A. The model

In this paper we consider the collision of a H atom, at normal incidence, with a graphite surface. While we will only consider the collinear case here—the H atom is directly over the bonding carbon—we allow this carbon to move freely according to the PES depicted in Fig. 1, and we also allow for some motion of the surrounding lattice, all quantum mechanically. Inclusion of this second lattice degree of freedom allows energy to move away from the newly formed and highly excited C–H bond. We denote the potential depicted in Fig. 1 as \( V_0(z_H, z_C) \). Note that \( z_C \) describes the position of the bonding carbon relative to the surrounding (planar) lattice. We wish to allow the lattice atoms surrounding the bonding carbon to also vibrate, due to the collision of the incident H and their coupling to the bonding carbon. For example, we could allow the three carbon atoms surrounding the bonding carbon to move normal to the plane of the surface, but require them to all have the same displacement \( q \). We thus define a lattice coordinate \( q \) that describes the displacement of the surrounding lattice from its equilibrium position. We define the direction \( q>0 \) to be away from the graphite substrate (normal to the surface). Since the bonding carbon vibrates relative to this surrounding lattice, the full Hamiltonian can be written as

\[
H = -\frac{\hbar^2}{2m_H} \frac{\partial^2}{\partial z_H^2} - \frac{\hbar^2}{2m_C} \frac{\partial^2}{\partial z_C^2} - \frac{1}{2} M_q \omega_q^2 q^2 + V_0(z_H - q, z_C - q) + \frac{1}{2} M_q \omega_q^2 q^2,
\]

where \( m_H, m_C \), and \( M_q \) are the masses of the H and C atoms, and the effective mass of the additional lattice vibration, respectively. For our model, there is no transfer of parallel momentum into the lattice, and for graphite, there are two nonzero frequency phonons with zero parallel momentum: the vertical and longitudinal optical modes at about 0.11 and 0.20 eV, respectively. The optical mode with the vertical displacement should couple most strongly, and we thus take \( \hbar \omega_q = 0.11 \) eV. However, for the more general scattering case, other phonons can also couple and we will consider the effects of changing this frequency over a relatively wide range. Similarly, the choice for the “effective mass” is not unique, and \( M_q \) is varied between 12 and 36 amu, corresponding to the motion of between one and three neighboring carbon atoms. We note that Hamiltonians of this form have been used to describe lattice vibration and recoil effects in dissociative adsorption.\(^{40,41}\)

We examine the time evolution of this three-dimensional system using standard quantum methods. To write the initial wave function we must consider the case where the H atom is far above the surface. In this limit, \( V_0(z_H, z_C) \) reduces to the PES for the vibration of the bonding carbon normal to the surface, and for small values of \( z_C \) this is well described by a harmonic potential with a frequency \( \hbar \omega_C = 0.07 \) eV. The Hamiltonian in this limit is thus

\[
H = -\frac{\hbar^2}{2m_H} \frac{\partial^2}{\partial z_H^2} - \frac{\hbar^2}{2m_C} \frac{\partial^2}{\partial z_C^2} + \frac{1}{2} m_C \omega_C^2 (z_C - q)^2 + \frac{1}{2} M_q \omega_q^2 q^2.
\]

The \( q \) and \( z_C \) oscillations are, of course, coupled, and the initial wave function is written

\[
\Psi(z_H, z_C, q; 0) = G(z_H)\Phi_{e_+}^{(+)}(Q_+)\Phi_{e_-}^{(-)}(Q_-)
\]

where the normal coordinates \( Q_+ \) and \( Q_- \) are linear combinations of \( q \) and \( z_C \), and the corresponding vibrational eigenfunctions of the normal modes are \( \Phi_{e_+}^{(+)} \) and \( \Phi_{e_-}^{(-)} \), with initial quantum numbers \( v_+ \) and \( v_- \) respectively. For \( M_q = 12 \) amu and the frequencies given above, the \( Q_+ \) mode corresponds most closely to \( q \), with a frequency of 0.137 eV, and the \( Q_- \) mode corresponds most closely to \( z_C \), with a frequency of 0.057 eV. The motion of the incident H atom is initially described by the gaussian wave packet \( G(z_H) \), centered far above the surface. The width of this wave packet is different for H and D, and defined such that for an incident energy of 0.3 eV the kinetic energy uncertainty is 35 meV for both H and D. Thus, while our results are not energy resolved, the energy uncertainty is relatively small.

We consider incident H and D atom energies in the range 0.1–0.9 eV. As we are primarily interested in the terrestrial experiments of Küppers and co-workers,\(^{22-24}\) we will not explore the very low energies relevant to H chemisorption on interstellar dust grains. For incident energies of a few meV, tunneling into the chemisorption well is certainly very weak. Standard fast Fourier transform (FFT) methods are used to represent and evolve the wave function,\(^{32}\) with the split operator method being used to propagate \( \Psi \) in time.\(^{33}\) The wave function is represented by its values on a rectangular grid of 256×64×32 points along \( z_H, z_C, \) and \( q \), respectively, corresponding to maximum kinetic energies of 3.0, 2.5, and 2.5 eV, respectively. These energies need to be large, since at the highest incident energy considered, and for \( v_+ = v_- = 1 \), there is 1.84 eV of energy in the trapped state relative to the potential minimum. To use the FFT we need to know the potential energy \( V \) at these grid points. Rather than fit a model PES to our DFT energies, we compute \( V_0(z_H - q, z_C - q) \) at these grid points using a bicubic spline fit to our grid of 735 DFT total energy points. The trapped state can be relatively long lived, and to propagate our system over long times we need to absorb \( \Psi \) at large values of \( z_H \) (corresponding to reflected and dissociated H). This is done with an optical potential\(^{44}\) which is zero for \( z_H < z_0 \), and equal to \(-ia(z - z_0)^3/L^3\) otherwise. The length \( L \) over which the optical potential is nonzero is 8 Å for D and 11.8 Å for H, and \( a=0.6 \) eV.
over the region of configuration space given by trapped fraction as the square of the wave function integrated various initial states of the graphite lattice. We define the all z as defined in the text. The q = 0 case corresponds to having a fixed lattice about the moving carbon.

B. Results

In Fig. 2 we plot the trapped fraction of the wave function vs time, for H with an incident energy E, of 0.3 eV, and various initial states of the graphite lattice. We define the trapped fraction as the square of the wave function integrated over the region of configuration space given by z_C=2 Å, for all z_C, which corresponds approximately to H in the chemisorption region. For the case labeled “q = 0,” the lattice surrounding the moving bonding carbon is held fixed at q = 0, and the bonding carbon is initially in its ground vibrational state with an energy of 0.035 eV. For this case about 70% of the incident H atoms cross the barrier, but many of them reflect back within 30 fs or so, before the carbon has time to pucker. However, for roughly 50% of the incident H atoms the carbon does pucker sufficiently to trap the H, at least for a few vibrations of the C–H complex. The expectation value of z_C for this trapped fraction increases from 0 to 0.4 Å in only about 50 fs. The forces on the carbon are indeed quite large. The wave function describing the C–H complex consists of a linear combination of trapping resonances, the quasibound eigenstates of H, which all have different lifetimes. In Fig. 2 we see that most of this trapped state decays (i.e., the H leaves the surface) rapidly, within a hundred fs or so, but that there is some probability remaining in the trapping region at long times. The lifetimes of the trapped states that remain at long times (after about 0.6 ps propagation time), appear to be on the order of a picosecond or longer.

The amount of H that eventually sticks is in part determined by the lifetimes of these trapping resonances, and we have thus computed them for the two-dimensional q = 0 case, using a complex-symmetric form of the Lanczos algorithm. A negative imaginary potential is added to the real Hamiltonian, which is diagonalized in a two-dimensional basis of sine functions to yield the energies and widths of the resonance states. The Lanczos calculations rely on standard strategies that need not be detailed here. They will, however, be discussed in a forthcoming three-dimensional application. It is harder to converge the imaginary parts of the eigenvalues than the real parts, so we expect only two significant digits of accuracy for most lifetimes less than 100 ps. The results are listed in Table I for the first 34 states with lifetimes greater than 100 fs. The system is very well described in terms of a nearly-harmonic carbon vibration with an excitation energy of hω_C=0.07 eV and quantum number n_C, and a relatively weakly anharmonic C–H stretch with energy hω_H=0.28 eV and quantum number n_H. Because the C–H stretch frequency is approximately four times hω_C, there are several near degeneracies. There are 12 bound states, the first four being isolated and corresponding to (n_C = 0–3, n_H = 0), and the rest consisting of four pairs of nearly degenerate states arising from the mixing of doublets.

![FIG. 2. The fraction of the wave packet remaining trapped on the surface as a function of propagation time for H incident at 0.3 eV. The initial vibrational quantum numbers for the lattice modes are v_+ and v_- as defined in the text. The q = 0 case corresponds to having a fixed lattice about the moving carbon.](image-url)
\( n_C = 3 + i, \quad n_H = 0 \) and \( n_C = i - 1, \quad n_H = 1 \) where \( i = 1 - 4 \). In addition to nearly degenerate pairs from the mixing of the \( n_H = 0 \) and 1 states, the resonance states also include the more highly excited states \( n_H = 2 \) and 3. However, Table I does not list states that are too short lived, and notice that the anharmonicity of the C–H stretch results in nondegenerate states already with \( n_H = 2 \) (states 13, 16, 19, and 22 for \( n_C = 0 - 3 \)). Only \( n_C = 0, \quad n_H = 3 \), state 23, has been retained in Table I according to a threshold lifetime of 100 fs, among the highly excited C–H stretch modes. Indeed, it is obvious that exciting the C–H stretch favors dissociation and efficiently kills resonances, as illustrated by the small lifetimes of states 22 and 23. States 24–27 correspond to four pairs of \( n_H = 0 \) and 1 doublets \( (n_C = 10 + i, \quad n_H = 0) \) and \( (n_C = 6 + i, \quad n_H = 1) \), where \( i = 1 - 3 \). Finally, only the \( n_C = 0 \) states remain not too short lived at higher energies. Thus excitation of the C-lattice stretch stabilizes the trapped state. These assignments and lifetimes will help to understand the trapping results in the rest of this paper.

The average incident energy of 0.3 eV in Fig. 2 corresponds to an average total energy of 0.335 eV, for the \( q = 0 \) case, when we include the C-lattice stretch zero point energy. Since the kinetic energy uncertainty is 35 meV, this particular case samples at least the five quasidegenerate states numbered 23–27 in Table I. Three of them are quite long lived, with lifetimes of 4–10 ps, confirming our observation in Fig. 2 for the \( q = 0 \) case that the trapped fraction remains trapped for several picoseconds. While there are many short-lived resonances, and while the lifetimes generally decrease with increasing energy, given a particular value of \( n_C \), we find that relatively long-lived resonances (with lifetimes on the order of a picosecond) exist for energies up to at least an eV.

The other curves in Fig. 2 correspond to cases where the surrounding lattice can vibrate, and are labeled by the initial quantum numbers of the two normal vibrational modes corresponding to \( Q_+ \) and \( Q_- \). For the ground state case, \( v_+ = v_- = 0 \), the initial lattice energy is 0.097 eV. The small increase in total initial energy leads to a slight increase in the initial barrier crossing. More importantly, the amount of probability remaining in the trapping region at longer times increases significantly. This is not surprising, since there is an additional degree of freedom orthogonal to the coordinates \( z_C \) and \( z_H \) into which some energy can be deposited. Of course, two lattice modes do not make a bath, and even with the addition of \( q \) our model still only describes trapping and not sticking, and eventually the trapped fraction will go to zero. By 0.3 ps the shorter-lived resonances have decayed, and what remains appears to have lifetimes, again, on the order of several picoseconds. We will henceforth refer to this trapped state as the “trapping complex,” which includes the surrounding lattice vibration \( q \) in addition to the motion of the H and C atoms. If our system were coupled to an infinite dissipative bath, this trapping complex would probably relax to a truly bound state (\( E < 0 \)) within a picosecond or so. Thus, the trapped fraction at about 1 ps is a rough estimate of the (collinear) sticking probability.

Initially exciting the lattice modes has several effects. Increased lattice excitation can increase the probability for crossing the barrier, but this is not a dramatic effect for the small amounts of vibrational excitation considered here. The major effect is that initial lattice excitation increases the amount of energy in the trapping complex, populating higher energy trapping resonances with shorter lifetimes. The result is less overall trapping at long times. In general, exciting the \( Q_+ \) mode (similar to \( q \)) has a much greater effect than exciting the \( Q_- \) mode (similar to the bonding carbon vibration). This is simply a reflection of the total energy added to the trapping complex: for the \( v_+ = 0 \) and \( v_- = 1 \) case, the initial lattice energy is 0.153 eV, while for the \( v_+ = 1 \) and \( v_- = 0 \) case, the initial lattice energy is 0.234 eV.

In Fig. 3 we plot the trapped fraction vs time for three values of the incident energy. As expected, we observe increased barrier crossing and more trapping at short times as we increase \( E_i \). However, as we observed in the preceding paragraph, for higher total energies of the trapping complex, we populate more of the higher energy shorter lifetime trapping resonances, and less of the longer-lived lower energy resonances (see Table I). Note how the lifetimes of the trapped fractions after about 0.6 ps decrease with increasing \( E_i \). The overall effect is that long time trapping, and thus sticking, decreases as the incident energy is raised above about 0.35 eV.

The incident energy influences the effects of vibrational excitation on trapping. In Fig. 4 we consider a low \( E_i \) case and a high \( E_i \) case. At incident energies well above the barrier (0.4 eV), adding energy to the lattice destabilizes the trapping complex, leading to shorter lifetimes and less trapping at long times, as discussed earlier. However, at energies near or below the barrier (0.2 eV), exciting the lattice, particularly the puckering carbon (the \( Q_- \approx z_C \) vibration), can significantly increase the amount of barrier crossing, short time trapping, and even long time trapping. The net result can be increased sticking with increased lattice excitation. However, when we thermally average by summing our results for various initial values of \( v_+ \) and \( v_- \) (weighted with the proper Boltzmann factors), these effects are not significant for temperatures of a few hundred kelvins or less.

In Fig. 5 we plot the fraction of H atoms that remain trapped at 1.0 ps vs the incident energy \( E_i \), for three cases. For the \( q = 0 \) case, where the surrounding lattice is not al-
followed to vibrate, we observe only a few percent trapping after 1 ps of propagation time, and only in a narrow range of energy. For the remaining two plots, the surrounding lattice is free to vibrate, with the results thermally averaged over the $Q_+$ and $Q_-$ modes. The $T=0$ K case is simply the result for $v_+ = v_- = 0$, and as noted earlier, the addition of even one degree of freedom to the trapping complex significantly increases long time trapping. At 300 K we observe the behavior noted earlier: increased trapping at lower $E_i$ and less trapping at higher $E_i$. However, because the normal mode frequencies are large relative to $kT$, the effects are small, and the 300 K results do not vary significantly from the $v_+ = v_- = 0$ results. Again, long time trapping is limited to a narrow region of energy, where $E_i$ must be near of above the barrier, but not so large as to destabilize the trapping complex. For the noncollinear case, long time trapping should extend to higher energies, due to a higher density of states and a probable increase in the lifetimes of the trapping resonances. Note the structure in the plot for the case of $q = 0$. If we were to energy resolve our results by projecting the trapped wave function onto the trapping eigenstates, the plots in Fig. 5 would be a series of narrow peaks centered at the positions of the trapping resonances (eigenvalues). When we add an additional degree of freedom $q$ to our trapping complex, the density of states of the trapping resonances increases greatly, the trapping probability increases, and the curves in Fig. 5 become much smoother. Again, while we do not energy resolve our results, our intent here is to understand how and why the experimentally measured H-graphite sticking probabilities are relatively large, and to explore the dynamics of the lattice rearrangement. Our approach is quite adequate for this, and the energy uncertainty of our incident "beam" is similar to that in the experiments.

Note that the C–H well depth is $-0.67 \text{ eV}$ relative to our zero of energy. Thus, for $E_i = 0.3 \text{ eV}$ and $v_+ = v_- = 0$, there is $1.03 \text{ eV}$ of vibrational energy in the trapping complex. While the three degrees of freedom in the trapping complex are highly coupled, we can get a rough idea of how much energy is in the C, the H and the vibration $q$ by monitoring the average kinetic energies along $z_C$, $z_H$, and $q$, respectively. We find that while much of this vibrational energy is initially in the H atom (roughly the C–H stretch), both the C and the $q$ vibration rapidly gain energy, and this energy rapidly distributes itself roughly equally between all three degrees of freedom. This is consistent with our observation in the context of the $(q = 0)$ resonance assignments that too much energy in the C–H stretch leads to dissociation whereas putting energy in the C-lattice stretch stabilizes the trapping complex. The additional lattice vibration $q$ has a role analogous to that of the C-lattice stretch, stabilizing the trapped state by taking energy away from the C–H stretch. For the $E_i = 0.3 \text{ eV}$ and $v_+ = v_- = 0$ case, after a total propagation time of only about 0.5 ps, all three degrees of freedom contain roughly one-third of an eV of energy.

Our choices for $M_q$ and $\omega_q$ do not significantly affect the trapping dynamics. In Fig. 6 we plot the trapped probability vs time for the case of H incident at $E_i = 0.3 \text{ eV}$ and $v_+ = v_- = 0$, with several different values of $M_q$ and $\omega_q$, as indicated. In general, we find that varying $M_q$ between 12 amu and 36 amu can increase or decrease the trapping at longer times, but not dramatically. Varying $\omega_q$ over a reasonable range has a similar effect, and the curves plotted in Fig. 6 are representative of numerous calculations where we vary

![Image](78x89 to 271x234)

![Image](78x591 to 271x740)
behavior. In the limits that lap with the incident wave packet could lead to this observed resonance states, particularly long-lived states, which over-trapping resonances, and a small variation in the number of trapping with and decreases the trapping at long times by a few percent. The variation of trapping with and increases the trapping at long times. We also include results for the 0 K case reveals that the energy initially localized in the lattice modes being in the vibration 0 corresponds to having a fixed lattice about the moving carbon.

The lattice can reconstruct within 50 fs or so. After about 100 fs, most of the trapped H atoms scatter back into the gas phase, but the 5%–10% that remain can have lifetimes on the order of a picosecond or more. Including the extra lattice vibration q significantly increases the fraction of H atoms that remain trapped. Increasing the incident H atom energy, and/or the initial vibrational energy of the carbon lattice generally destabilizes the trapping complex, causing less H to remain trapped at long times. The overall result is that for energies above about 0.2 eV, the fraction remaining trapped after 1 ps is on the order of 5%–10%, for both H and D. Above about 0.6 eV this drops off rapidly.

So what does this tell us about the sticking probability of H on graphite? We merely have to extrapolate our results to include an impact parameter and an infinite dissipative bath. First, there should be no sticking at low incident energies (below about 0.15 eV), and this is consistent with experimental observation. Quantum scattering calculations were implemented using this PES data, and it was found that for energies above the barrier to chemisorption, a significant fraction of the incident H atoms can trap. The lattice can reconstruct within 50 fs or so. After about 100 fs, most of the trapped H atoms scatter back into the gas phase, but the 5%–10% that remain can have lifetimes on the order of a picosecond or more. Including the extra lattice vibration q significantly increases the fraction of H atoms that remain trapped. Increasing the incident H atom energy, and/or the initial vibrational energy of the carbon lattice generally destabilizes the trapping complex, causing less H to remain trapped at long times. The overall result is that for energies above about 0.2 eV, the fraction remaining trapped after 1 ps is on the order of 5%–10%, for both H and D. Above about 0.6 eV this drops off rapidly.

IV. SUMMARY

In conclusion, total energy calculations based on DFT have been used to explore how the H-graphite interaction varies as the bonding carbon atom moves. For hydrogen to chemisorb, the bonding carbon must pucker out of the surface plane by 0.36 Å, and when H is very close to the surface, the forces on the carbon are large. Quantum scattering calculations were implemented using this PES data, and it was found that for energies above the barrier to chemisorption, a significant fraction of the incident H atoms can trap. The lattice can reconstruct within 50 fs or so. After about 100 fs, most of the trapped H atoms scatter back into the gas phase, but the 5%–10% that remain can have lifetimes on the order of a picosecond or more. Including the extra lattice vibration q significantly increases the fraction of H atoms that remain trapped. Increasing the incident H atom energy, and/or the initial vibrational energy of the carbon lattice generally destabilizes the trapping complex, causing less H to remain trapped at long times. The overall result is that for energies above about 0.2 eV, the fraction remaining trapped after 1 ps is on the order of 5%–10%, for both H and D. Above about 0.6 eV this drops off rapidly.
atively weak—the PES increases by only 0.1 eV as the H moves laterally from 0 to 0.5 Å away from the atop site. If we assume that the sticking probability is roughly 0.2±0.1 for impact parameters between 0 and 0.5 Å, and zero beyond this, the sticking cross section would be 0.16±0.08 Å². Given that there is one carbon atom per 2.6 Å² on the graphite surface, our estimate for the sticking probability would then be 0.06±0.03, or, roughly, on the order of 0.1. The experiments, for a surface temperature of 150 K, report zero-coverage D atom sticking probabilities between 0.25 and 0.5, where the variation is from graphite sample-to-sample. For H, the sticking probabilities are about 0.4, with similar sample-to-sample variation. Overall, these numbers are not grossly inconsistent with our calculations. The observed weak isotopic variation in sticking is also consistent with our studies.

Admittedly, it is quite an extrapolation to go from collinear trapping probabilities to sticking probabilities, but the approximations in the preceding paragraph seem reasonable. However, this is an important and interesting problem, and we are currently attempting to compute the trapping cross sections. That is, we are computing total energies for numerous non-collinear configurations, and are developing a higher dimensional model PES. If we assume cylindrical symmetry of this PES with respect to the bonding carbon, we can compute cross sections for H-graphite trapping on a static lattice using methods we have developed for the study of Eley–Rideal reactions. We also intend to compute the trapping resonances so as to fully energy resolve the trapping probabilities and better understand the trapped state. These can be computationally demanding calculations, and it is not yet clear to what extent it will be possible to extend this to include one or more lattice modes. This would certainly be feasible in a classical study, which should be reasonable for energies above the barrier.

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