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The dynamics of H absorption in and adsorption on Cu(111)

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Abstract

We have studied theoretically the dynamics of H adsorption on and absorption in Cu(111) using a classical molecular dynamics approach. A key ingredient of this study is plane wave and pseudopotential calculations of potential energy curves for the major high symmetry sites. These calculations are based on density functional theory and the generalized gradient approximation. The extracted chemisorption bond parameters from the energy curves are in good agreement with available experimental data. We find that the calculated energy barriers for absorption of an adsorbed atom are lowered dramatically by relaxations of the Cu atoms and these barriers are so low even in the rigid surface lattice situation that the absorption of an incident H atom is non-activated for impacts close to the so-called fcc and hcp hollow sites. The model interaction potential that we have used in the dynamics calculations is determined from the calculated potential energy curves and its form is taken from a semi-empirical effective medium theory for binary compounds. The main results of the dynamics calculations are: the relaxations and thermal fluctuations of the Cu atom do not affect the absorption of H in the surface; the energy transfer to the phonons is rather inefficient so the H atom has to make a large number of collisions with the surface atoms before it sticks either in the surface adsorption well or in the subsurface absorption well; a simple estimation shows that the energy transfer to electron-hole pairs can be as efficient as the energy transfer to phonons; our results are consistent with experiments, which indicate that subsurface sites can be populated by an incident atomic H beam and show that the scattering probability is small.

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I. INTRODUCTION

The understanding of how atomic H interacts with surfaces are of direct interest in many technologically important processes such as hydrogen storage, nuclear fusion in Tokamaks, and growth of diamond thin films and also from a basic scientific point of view, for instance, H is the simplest atom. In particular, the interaction of atomic and molecular hydrogen with Cu(111) have attracted a lot of attention as a model system for experimental and theoretical studies of surface reactions such as activated molecular dissociation [1] and the Eley-Rideal mechanism for atom recombination [2,3]. There have been a number of theoretical studies of the dynamics for this latter surface reaction based on simplified model potential energy surfaces [4–7]. These studies have been valuable but in order, for example, to understand the role of "hot" H atoms on the reaction, we need a PES that describes the effects of the surface corrugation on the H atom adsorption dynamics. Another interesting aspect in the context of surface reactions involving H atoms is the role of absorption of incident H atoms in subsurface sites. The importance of subsurface hydrogen has been stressed by Maynard and coworkers [8] for the Ni-surface-catalyzed reaction of the CH_3 radical with H to form CH_4 and may also play a role in the same reaction on Cu(111), which have recently been studied experimentally by Rettner, Auerbach, and Lee [9] using atomic H beams.

As a first step towards the goal to develop a first principle total energy surface that can be used for dynamical studies of the reaction between H atoms on a Cu(111) surface, we have performed plane wave and pseudopotential calculations of the total energy [10] for the interaction of a single H atom with a Cu(111) surface. We have calculated potential energy curves for the major high symmetry sites for a range of positions of the H atoms so that we can determine, for example, subsurface sites and absorption energy barriers. Based on these curves, we have constructed a model potential energy surface that we have used in classical molecular dynamics calculations of H adsorption on and absorption in Cu(111). The aims of these dynamical studies have been to investigate the effects of relaxations and thermal fluctuations of the Cu atoms on the absorption of incident H atoms and the role and efficiency of energy transfer to the surface lattice in relation to electronic friction.

The paper is organized as follows. In Section II, we present some of the details behind our first principle total energy calculations, the model interaction potential, and the classical molecular dynamics calculations. The calculated energy curves for the different high symmetry sites are presented and discussed in relation both to experimental data and previous calculations in Section III A. The results of the classical molecular dynamics calculations are presented and discussed in relation to experimental data in Section III C. Finally, we sum up and stress the main points of our work in Section IV.

II. THEORY

A. Some details of the total-energy calculations

Our total-energy calculations of the interaction of an H atom with a Cu(111) surface were based on the density functional scheme using the generalized gradient approximation for the exchange correlation energy. The total energy was computed in a super-cell geometry using a plane-wave and pseudopotential code. In this code, the Kohn-Sham equations were solved by alternating conjugate gradient minimizations and subspace rotations. The occupation numbers were updated using a recently developed technique that is based on a minimization of a free energy functional. [11]

The Cu(111) surface was represented in the super cell by a slab of four atomic layers in an ABCA stacking and the vacuum region was 6 layers thick. Each substrate layer contained 3 Cu atoms and the lattice parameter of the slab was 3.56 Å. The cell contained a single H atom, which corresponds to a coverage of 1/3 and results in a large H-H distance of about 4.4 Å. The ion cores of the Cu atoms were represented by the fully separable pseudopotential of Troullier and Martins [12], which includes the $3d$ states as valence states. The hydrogen atom was represented by its bare Coulomb potential. The plane wave set was cut off at a kinetic energy of 50 Rydberg. The surface Brillouin zone was sampled by 54 special k points with 6, 15 and 15 points in the irreducible wedge for hollow, bridge and top configurations, respectively, (Convergence with respect to the k point set and kinetic energy cut off were investigated in Ref. [13]) . The calculations were performed selfconsistently in the LDA with gradient corrections calculated from the LDA densities using GGA [14]. The electronic temperature was 0.1 eV and the energy was extrapolated to zero temperature in a standard manner [15]. The calculations were performed in parallel over k-points on the SP2 machine at PDC, Stockholm. Typically, the total energies were converged after about 20 iterations.

The reference energy, that is the energy of the system for the separated Cu surface and the H atom, was obtained from two separate calculations in the super cell; one for the isolated slab and one for the isolated H atom. In the latter case, it is necessary to do a spin-polarized calculation in order to get an accurate description of the H atom, which gave a value for the H atom energy of -13.54 eV. In two cases, we also calculated the energy gained by in-plane relaxation of the Cu atoms in the surface plane using a damped molecular dynamics method [10]. All our calculated total energies for the H/Cu(111) system are presented in Fig. 1.

The representation of the Cu(111) surface and the choice of the plane wave set were based on the experience gained by Hammer and coworkers [13,16] in their calculations of the potential energy surface (PES) for hydrogen dissocation on Cu(111).

B. Model potential

Here we present in detail our construction of a model PES from the calculated energy points. This PES is based on semi-empirical effective medium theory, which is efficient to use in classical molecular dynamics calculations of the H absorption and adsorption dynamics.

For a metallic system like the H/Cu(111) system, a pair-functional interaction potential such as the effective medium theory or the embedded atom method, has been shown in many cases to be a good description of the interatomic interactions, whereas, for instance, a simple pair-potential model is inadequate. We have adopted a semi-empirical effective medium theory expression for the interaction potential that have been developed by Jacobsen and coworkers [17] to describe binary metallic compounds in which the total energy is given by the following expression:

$$E_{\rm tot} = \sum_i \bar{E}_c^{(s)}(\bar{n}_s(i)) + \bar{E}_c^{(a)}(\bar{n}_a) + \sum_{j>i} V_s(r_{ij}) + \frac{1}{2}\sum_i (V_{sa}(r_i) + V_{as}(r_i)). \qquad (2.1)$$

Here the subscript a and s refer to the adsorbate and substrate atoms, respectively, the index i labels the Cu atoms, r_{ij} is the distance between the two Cu atoms i and j, and r_i is the distance between the H atom and the Cu atom i. Here $\bar{E}_c^{(s)}(\bar{n}_s(i))$ and $\bar{E}_c^{(a)}(\bar{n}_a)$ are many-body embedding energies of the Cu atom i and the H atom, respectively, which depend on the corresponding quasi-embedding electron densities $\bar{n}_s(i)$ and $\bar{n}_a$, whereas the remaining energy terms in Eq. (2.1) are repulsive pair potentials. The functional form of the many-body embedding energies, the quasi-embedding electron densities, and the repulsive pair potentials are detailed in Ref. [17].

An attractive feature of the effective medium theory expression for $E_{\rm tot}$ in Eq.(2.1) is that it contains a relatively small number of parameters compared to other pair-functional methods but we have still to determine 14 independent potential parameters. For the subset of parameters that determines the interaction potential of the isolated Cu system, we have used the set that was suggested by Jacobsen and coworkers [17] for Cu bulk. This parameter set was choosen such that the measured cohesive energy, bulk moduli and the shear modulus were reproduced for Cu. We have determined the remaining 7 parameters by adjusting the model PES to a subset of the calculated total energy points (solid symbols in Fig. 1) so that the root mean square error was minimized. This non-trivial multidimensional minimization problem was solved numerically by a downhill simplex method. All our potential parameters are presented in Table I and the resulting model PES is discussed in Section III B.

C. Classical molecular dynamics

Our classical molecular dynamics calculations have been performed using the so-called ART program [18], which was developed by Stoltze and collaborators and provides an efficient implementation of the semi-empirical effective medium theory. Here we shall just discuss those aspects that are relevant for the absorption and adsorption dynamics.

The Cu(111) surface was represented by a slab with periodic lateral boundary conditions. The slab consists of 6 layers with 36 atoms in each layer where the bottom layer was kept fixed and the lattice constant was set to 3.61 Å. The light mass of the H atom required a rather small value of 0.1 fs for the integration of the trajectories by the velocity Verlet algorithm. The initial position of the H atom were sampled randomly over the surface unit cell at a distance of $\sim$ 4.9 Å from the surface. Typically, we ran about 500 trajectories for each incidence energy. The error bars for the calculated probabilities were estimated by assuming that the results sampled a Gaussian distribution and corresponds to a 90% confidence interval.

The problem of determining when the particle sticks in a subsurface well or in the chemsisorption well is complicated by the many-body interaction potential. To avoid a complete thermalization of the H atom, we have formulated a sticking criteria based on the behaviour of its kinetic energy, E_{k}, with time. Along each trajectory, we have calculated running averages of E_{k} and E_{k}^2 over time intervals of a length, 0.35 ps, that corresponds to many oscillations of the H atom in the potential wells and from these averages, $\langle E_{\mathrm{k}}\rangle(t)$ and $\langle E_{\mathrm{k}}^2\rangle(t)$, we have calculated the variance $\sigma_{\mathrm{k}}^2(t) = \langle (E_{\mathrm{k}} - \langle E_{\mathrm{k}}\rangle)^2\rangle(t)$. In the harmonic approximation of the potential energy around a potential minimum, such a running time average of the potential energy is equal to $\langle E_{\mathrm{k}}\rangle(t)$ and $\sigma_{\mathrm{k}}(t) = \langle E_{\mathrm{k}}\rangle(t)/\sqrt{2}$. Inspired by this fact, we have formulated the following sticking criteria for a trajectory. The trajectory is regarded to be stuck in a potential well when

$$\langle E_{\mathrm{k}}\rangle(t) + 2\sigma_{\mathrm{k}}(t) < D - 3k_{\mathrm{B}}T_s, \tag{2.2}$$

where T_s=500 K is the surface temperature and D is the height of the rigid potential energy barrier to cross the surface plane from the outside to the inside and from the inside to the outside for sticking in the chemisorption well and the subsurface well, respectively. We have tested this criteria by decreasing $D - 3k_{\mathrm{B}}T_s$ by a factor of two and we find that this stricter criteria does not change our results for the number of trajectories sticking in the subsurface well and the chemisorption well, respectively. Finally, the H atoms that passes the initial perpendicular distance from the surface are counted as scattered.

III. RESULTS AND DISCUSSION

A. Calculated potential energy curves

Here we present and discuss our calculated first-principle total-energy points for the interaction of an H atom with the (111) face of Cu. We show that the calculated binding parameters are in good agreement with available experimental data. We end by discussing previous calculations for the same system.

In Fig. 1, we present our calculated total energies for various high symmetry configurations of the H atom with respect to the rigid Cu(111) surface. The set of configurations comprises the two inequivalent hollow sites, fcc (No underlying substrate atom in the second layer) and hcp (One underlying substrate atom in the second layer), the bridge and the atop sites as a function of the perpendicular coordinate, z, of the atom with respect to the first Cu surface plane. The total energy is referenced with respect to the sum of the energies of the isolated Cu(111) surface and the isolated H atom. The potential energy curves exhibit a wealth of stationary points of which some, as we shall show, correspond to interesting adsorption sites, absorption sites or potential barriers. The energies and positions of these sites and barriers are tabulated in Table II.

Outside the surface, the potential energy curves reveal that the H atom prefers to adsorb in an hollow site at z =0.95 Å with a slight preference of about 5 meV for the fcc site, which probably is within the error bars of the calculation. Note that the presence of Cu atom in the second layer for the hcp configurations starts first to influence significantly the energies well inside the surface plane; the values for the potential energies for the fcc and hcp hollow configurations are almost equal (differ with at most 20 meV) outside the first surface plane. The potential energy curves show also that there is a small potential energy barrier for diffusion of about 0.15 eV at the bridge site, whereas the potential barrier at the top site is much larger and is located much farther away from the surface. A somewhat surprising result is the relatively low potential barrier of about 1.3 eV, relative to the chemisorption mimimum for the H atom, to cross the surface plane at the two hollow sites, whereas at the bridge site the potential barrier is much larger and is about 2.7 eV. In fact, the energy of the absorption barrier at the hollow site is well below the vacuum energy with $\sim$ 1.1 eV, which suggests that it is possible for an incident gas-phase H atom to penetrate the surface plane and possibly populate available subsurface sites. The dynamics associated with this absorption process is one of the key issues adressed in this work and is investigated in Section III C.

Inside the surface plane, the potential energy curves reveal the existence of several metastable subsurface sites. At z =-1.0 Å between the first and second substrate layer in the fcc hollow configuration, there is a local potential energy minimum with the same coordination as for the bulk octahedral interstitial site and is $\sim$ 0.9 eV above the chemisorption minimum. The potential barrier to escape out of this subsurface site is only about 0.4 eV. We find that the potential energy of the subsurface site is very close to the potential energy for the bulk-like octahedral site located about -3.2 Å below the surface plane of the top site. Between the second and third substrate layer in the fcc hollow configuration at z =-2.7 Å, there is a local minimum, which has the same coordination as the bulk tetrahedral interstitial site, of $\sim$ 0.5 eV above the energy of the octahedral subsurface site.

Previous work based on simple model PES such as the effective medium theory [19,20] have shown that the relaxations of the substrate atoms influence significantly the absorption potential energy barriers. We have calculated the effects of in-surface-plane relaxations of the Cu atoms on the absorption barrier at bridge and hollow sites. As indicated in Fig. 1, these potential energy barriers decrease dramatically for both the hollow and bridge sites. This behaviour raises the interesting question, which we address in Section III C, whether the penetration probability for an incoming beam of H atoms is influenced by the relaxations of the surface atoms.

There are numerous calculations [13,16] that show that density functional theory based on the GGA is able to give an accurate description of binding parameters and potential barriers. The experimental data [21–23] of H adsorption and absorption parameters on Cu(111) are relatively scarce and do not allow a very critical assessment of the calculated potential energy curves. However, we find that the calculated potential energy curves are in good agreement with the available experimental data such as the chemisorption energy and perpendicular adsorbate vibrational frequencies.

There exists no direct measurement of the chemisorption energy of H on Cu(111) but the experimental data give a rather narrow range of about 0.1 eV for the possible values of the chemisorption energy, which is in good agreement with our total energy calculations. The binding energy of about 2.24 eV per atom in the hydrogen molecule gives a lower bound for the chemisorption energy because H adsorption is observed to be thermodynamic stable on Cu(111) at coverages below 2/3. An upper bound of the chemisorption energy is provided by the measured maximum internal energy of about 2.3 eV for HD molecules that are formed in recombinative desorption of an incident D beam with adsorbed H atoms. [2] From the kinetic energy of about 0.07 eV for the incident atomic beam and the measured binding energy of 4.475 eV for an HD molecule, we deduce an upper bound of about 2.3 eV for the chemisorption energy. These two bonds gives a range of 2.24-2.3 eV for the chemisorption energy of an H atom. Thus the dissociation of hydrogen on Cu(111) is weakly exothermic, which is consistent with the estimates of 0.1 -0.15 and 0.2 eV for the heats of adsorption by Lee and coworkers [21] from thermal and recombinative desorption data and by Alexander and Pritchard [22] from measurement of adsorption isotherms, respectively. To make a direct comparison of the measured range of the chemisorption energies for an H atom with the calculated welldepth of the H adsorption potential, we have to substract the zero-point energy. The infrared measurement by Lamont and coworkers [23] of the two vibrational energies for the adsorbate modes of H (and D) on Cu(111) gives in the harmonic approximation a value of 0.16 eV for the zero-point energy of the adsorbed H atom. Thus we extract from the experimental data a welldepth in the range of about 2.4-2.5 eV, which is in good agreement with our calculated value of about 2.4 eV for a H atom in the fcc and hcp hollow sites on a rigid Cu surface.

In Table II, we have also listed vibrational energies of the adsorbed and absorbed H atom in the perpendicular direction, as calculated in the harmonic approximation. The calculated vibrational energy in the hollow site is $\sim 10\%$ larger than the measured vibrational energy of ~ 129 meV by Lamont and coworkers [23]. As demonstrated by Mattson and coworkers [24] from the solution of the Schrödinger equation for the eigenstates of H and D atoms in the full three-dimensional PES, calculations of vibrational energies that are based on the harmonic approximation tend to overestimate the excitation energies of the lowest vibrational states with about 15 %. Thus, a large part of the small difference between our vibrational energies and the measured ones may be attributed to such multidimensional anharmonic effects. Note that the potential energy curve at top site is similiar to the binding energy curve for the CuH dimer [25,26], whose equilibrium distance is 1.46 Å and vibrational energy is 239 meV but its binding energy of 2.86 eV is much larger. Finally, we find that the vibrational energies in the harmonic approximation are significantly smaller for the bulk and subsurface sites than for the hollow adsorption sites. This finding is consistent with the assingmnent of vibrational spectra for H on Ni(111) made by Johnson and coworkers [27] that the vibrational energy is substantially lower for embedded H than for chemisorbed H.

There exist a few other density functional calculations of the total potential energy for an H atom interacting with a Cu(111) surface but they have only been limited to the calculation of binding parameters. The first calculation, which was based on the LAPW method and LDA, was performed by Feibelmann and Hamann [28] for a monolayer of H, who found that H prefer to bind in the fcc sites by 0.1-0.2 eV over the hcp hollow site, a higher vibrational energy for the perpendicular mode with about 20 meV than our value, and a bond length of about 1.70 Å that is close to our calculated value about 1.74 Å. A more recent calculation by Gundersen and coworkers [29], which was based on a pseudopotential and plan wave method for a (1x1) monolayer, gives a also preference for binding in a hollow site and with similar curvatures around the potential minima normal to the surface for hollow and bridge sites (i.e. perpendicular vibrational energies) but the potential energy barrier for diffusion, that is, the energy difference between adsorption at the bridge site and at the hollow site, is about twice as large. The corresponding results for the binding curves in the high symmetry sites by Forni and coworkers [30] from band structure calculations using a density functional formalism are more or less consistent with our results. The largest discrepancies are in the binding energies, whereas the curvatures and the position of the local minima are similiar.

B. Model potential energy surface

Here we present and discuss the results of our model PES for the interaction of an H atom with the (111) face of Cu. These results make us believe that our model potential describes most of the key ingredients of the interactions that are important in the adsorption and absorption dynamics. The procedure for determining its parameters from the first-principle energy points have already been discussed in Section II B.

As shown in Fig. 1, we find that the overall agreement between the model potential energy curves for various configurations of the H atom outside and inside the Cu surface and the first principle energies to be rather good; the root mean square error is about 0.2 eV. In particular, the description of the potential barriers for the H atom to enter the subsurface region is accurate. The model potential reproduces also with reasonable accuracy the energies in the regions where the first-principle energy points have not been used in the construction of this potential. The most notable disagreement appears around the subsurface site at z=-1.0 Å in the fcc hollow configuration where the deviations between the model potential energies and the first-principle energies are as large as 0.5 eV. Also the details of the potential energy curves around the local minima outside the surface such as the potential energy barrier at the bridge site between two hollow sites, are not reproduced.

We have also investigated how well the model interaction potential describes the effects of the relaxations of the Cu atoms on the interaction energy of the H atom with the Cu surface. To this end, we have calculated first-principle energies for the fcc hollow and bridge configuration of the H atom in the surface plane for the in-surface-plane relaxations of the Cu surface atoms. The calculated values of these first principle relaxation energies 0.44 and 1.4 eV for the hollow and bridge sites, respectively, are in rather good agreement with the corresponding values, 0.62 and 1.6 eV, calculated from the model interaction potential when the relaxations of the Cu atoms are restricted to the nearest neighboring surface atoms.

In Fig. 1, we have also presented the results for potential energy curves for the H atom from the model interaction potential for the fully relaxed Cu slab. The relaxation energies for the octahedral subsurface site and the chemisorption site are less than 0.1 eV, whereas the relaxation energy for the bulk tetrahedral site is much larger and is 0.5 eV. The relaxation energies of the absorption barriers at hollow and bridge sites are 0.7 and 1.8 eV, respectively. These values for the relaxation energies are close to the corresponding values for the relaxations of the Cu atoms that are restricted to the nearest neighboring surface atoms, which show that a large part of the relaxation energies in these two situations comes from these restricted relaxations.

A more informative picture of the topography of the parts of the model PES that are relevant for the absorption and adsorption dynamics than the potential energy curves in Fig. 1 is provided by the contour plots of the model PES for H on the rigid surface in Fig. 2. The contour plot in Fig. 2(a) of the PES in the surface plane shows how the area of impact parameters, where the atom is classically allowed to cross the absorption barrier, varies with incidence energy. For instance, at an incidence energy approaching zero (dashed contours in Fig. 2(a)), this area is a relative small fraction of only about 14 % of the surface unit cell. Note that the PES contours are essentially identical around the two inequivalent fcc and hcp hollow sites. The differences in the PES between these two sites are revealed in the contour plot in Fig. 2(b) of the PES.

C. Absorption and adsorption dynamics

After all key ingredients of our classical molecular dynamics calculations of the absorption and adsorption probabilities have been covered, we now present and discuss the results. Besides ignoring quantum mechanical effects, we have also ignored electronically non-adiabatic effects such as electronic friction. We have restricted our calculations to normal incidence because the large gain in energy of the H atom in the adsorption well should make the dependence on incidence angle weak. The results obtained at zero surface temperature, T_s=0 K, should only be viewed as a gauge of the importance of thermal effects, whereas the results obtained at T_s=500 K are in a regime where a classical treatment of the surface lattice is valid. We end by a discussion of our results in relation to experiments.

An important result of our calculated potential energy curves is that the absorption of H in Cu(111) should be non-activated. This behaviour is demonstrated by the zero energy contour in Fig. 2(a), which shows that there is a region in the surface plane – the absorption hole in the model PES – where an incident atom is energetically allowed to cross this plane. As shown in Fig. 3(a), we find that the fraction, $P_{\rm hole}$, of the surface cell that is occupied by this absorption hole is in good agreement with the probability, $P_{\rm p}$ for an H atom to *cross* the surface plane during the first round trip in the adsorption well in the rigid surface situation.

An important question raised in Section III A from the calculated PES is whether the large effect of the relaxations of the Cu atoms on the absorption energy barrier heights influences significantly the absorption dynamics. There are two conceivable ways these relaxations can influence the absorption. The barriers are lowered, with a concommitant increase of the absorption hole area, from the rigid surface situation either by a fast response of the surface atoms to the motion by the incident atom or by a thermal fluctuation of the surface atoms. We have studied these two effects by comparing the results for $P_{\rm p}$ in the rigid surface situation with the calculated results for $P_{\rm p}$ at two different surface temperatures $T_{\rm s}$: $T_{\rm s}$ = 0 and 500 K. As shown in Fig. 3(a), we find that the results for $P_{\rm p}$ in the rigid surface situation and at $T_{\rm s}$ = 0 K are essentially equal. Thus, this result shows, as expected in view of the light H atom mass compared to the Cu atom mass, that the time scale for the interaction of the H atom with the Cu surface is so short that the substrate atoms do not have time to respond to the motion of the H atom and decrease the energy barriers.

We also find that the lowering of energy barriers by thermal fluctuations plays a minor role in the absorption. As can be seen in Fig. 3(a), the results for P_{p} at $T_{\mathrm{s}} = 500$ K are essentially equal to those at 0 K. This result is consistent with the value of ~ 0.1 Å for the average root-mean square displacements of the Cu atoms at $T_{\mathrm{s}} = 500$ K being smaller than, for instance, the value of ~ 0.25 Å for surface relaxations induced by an H atom in the surface plane at the bridge site. In addition, thermal fluctuations have opposing effects on crossing a barrier for a non-activated process. They can both increase and decrease the absorption hole area and a net effect is only obtained in a situation where this area varies in an highly non-linear manner with the displacements of the substrate atoms.

The absorption probability, P_{ab}, is not simply given by P_{p} because of two important effects: (1) the H atom has to stick in the subsurface well by losing at least 1.0 eV of its energy gained in the adsorption well; (2) the H atom can make several attempts to cross the surface plane by making multiple roundtrips in the adsorption well. The energy transfer from the light H atom to the surface lattice, or more precisely the phonons, is rather inefficient. For example, the Baule formula gives that the H atom loses $\sim 6\%$ of its energy in the adsorption well in a binary collision with a Cu atom. In order to lose a large fraction of the energy gained by the interaction of the H atom with the Cu surface, the atom has to make several collisions with the Cu atoms. This point is illustrated in Fig. 4, which shows a single trajectory and its energy as a function of time for an H atom on a 0 K surface with incidence energy E_i= 1.1 eV. The H atom makes a large number of collision with the surface until it has lost about 2.0 eV of its energy in the adsorption well to the phonons, which takes about 1.2 ps. This energy loss corresponds roughly to an energy relaxation rate of about 0.7×10^{12}/s. When taking an average over 500 trajectories, we find that the average lateral root-mean-square distance traveled by the H atom on a 0 K surface with E_i= 0.1 eV is about 19 Å before it either absorps or adsorps.

In fact, these results show that the energy loss rate to the phonons is so slow that electronic friction cannot be neglected. For example, a simple estimate based on the electron-hole pair contribution to the vibrational linewidth, as measured by infrared vibrational spectroscopy by Lamont and coworkers [23], suggests an energy relaxation rate of 1.6×10^{12}/s. This rate is of the same magnitude as the estimate done in the previous paragraph for the energy loss rate to phonons. We find that the surface corrugation of the H-Cu(111) potential is so strong that the kinetic energies of the lateral and perpendicular motion of the H atom are statistically mixed after a time period of only about 0.2 ps, which is short compared to the calculated and estimated time scales for energy transfer to phonons and electron-hole pairs, respectively. A similar result was obtained from classical trajectory studies of the transient mobility of adsorbed O on Al(111) by Wahnström and coworkers [31,32] and they stressed that this mixing limits the transient mobility on the surface. The total energy transfer rate to phonons and electron-hole pairs seems to be rather small so we expect that the adsorption of H atoms can create "hot" atoms [33], which can catalyze surface reactions.

Before we discuss our classical molecular dynamics results for absorption, adsorption, and scattering probabilities, we would like to stress that energy transfer to electron-hole pairs is not included in these calculations so these results cannot be viewed as predictive and cannot be directly compared with experiments. However, we do believe that these results are meaningful in the sense that they illustrate the relative importance of surface corrugation and energy transfer on the dynamics behind these processes.

Our results for the absorption probabilities in Fig. 3(b), shows that both the effects (1) and (2) are important for $P_{\rm ab}$. Our finding that the results for $P_{\rm ab}$ at 0 K are a bit smaller than the corresponding results for $P_{\rm p}$ shows that only a fraction of the atoms that crosses the surface plane sticks in the subsurface well. A somewhat surprising effect is the large temperature dependence of $P_{\rm ab}$ at low $E_{\rm i}$.

Two other outcomes of the interaction of an incoming H atom with the Cu surface are possible; adsorption or scattering. In Fig. 3(c), we have presented our calculated results for the adsorption and scattering probabilities. As expected from the behaviour of $P_{\rm p}$ in Fig. 2,

$P_{\rm ad}$ is much larger than $P_{\rm ab}$ for low E_i, whereas at higher E_i, $P_{\rm ad}$ decreases rapidly but is always larger than $P_{\rm ab}$. The temperature dependence of $P_{\rm ad}$ mirrors the corresponding dependence for $P_{\rm ab}$.

At T_s=0 K, the scattering probability, P_s, increases more or less monotonically with E_i to a value of about 0.5. This behaviour is not expected from a simple consideration that is based only on the energy transfer from the incident H atom to the surface lattice and ignores the surface corrugation of the potential. In this situation, $P_{\rm s}$ should be equal to zero for E_i below the characteristic value of about 0.15 eV for the energy transfer during the first round trip in the adsorption well and above this energy $P_{\rm s}$ should switch rapidly to unity. Thus, the suppression of $P_{\rm s}$ at higher E_i is an effect of the strong geometric surface corrugation of the PES, as can be seen from the contour plot in Fig. 2(b), which promotes multiple round trips in the adsorption well and subsequent sticking by transfering energy of the normal motion of the incident H atom to the lateral motion. Finally, we note that the sticking probability, S is simply related to $P_{\rm s}$ as $S = 1 - P_{\rm s}$.

We have also investigated the isotope dependence of $P_{\rm ab}, P_{\rm ad}$ and $P_{\rm s}$ by making also trajectory calculations for D. As shown in Fig. 5, we find no dramatic isotope effects on these probabilities. Note that any isotope effects are caused only by the difference in time scales for the motion of the H and D atoms, which results in different values for the energy transfer from the atom to the surface lattice. For instance, in the rigid lattice situation and for the same incidence energy, the classical trajectories H and D are identical after an appropriate mass scaling of the time variable. The larger values of $P_{\rm s}$ for H than for D is consistent with the energy transfer in each surface collision being larger for D than for H. The effects of the isotope differences in the energy loss on $P_{\rm ab}$ and $P_{\rm ad}$ is more subtle because of two compensating effects. First, the number of roundtrips in the adsorption well made by the D atom until its energy is below the potential energy barrier for absorption should roughly be half of the corresponding number for the H atom because a simple Baule argument gives that the energy transfer in each collision with the surface is about twice as large for D than for H. Thus this effect makes the probability larger for the H atom to cross the surface plane than for D. Second, the larger energy transfer in each collision for D than for H should make the sticking probability in the subsurface well of an atom that crosses the surface plane larger for D than for H. As shown in Fig. 6(a), we find no statistically significant isotope effect on $P_{\rm ab}$, which indicates that these two effects are more or less compensating each other.

So far there have been no detailed experimental studies of absorption and adsorption of H atoms on Cu(111) and there exists only indirect evidences for these processes. Two different experimental groups – Rettner and Auerbach [2] and Lee and coworkers [21] – have recently suggested that subsurface sites on Cu(111) can be populated after exposure to atomic H or D at high coverages, whereas population of these sites are not possible by exposure to hydrogen molecules. These suggestions are based on the identification of a low temperature feature around 230 K in the thermal desorption spectrum and by making an analogy with the corresponding results for H on Ni(111), where subsurface H was identified from electron energy loss spectroscopy by Johnson and coworkers [27]. Rettner and Auerbach even produces a value of ~ 0.05 for $P_{\rm ab}$ for a saturated surface. In this high coverage situation, other competing processes such as the formation of hydrogen molecules by an Eley-Rideal mechanism dominates and we cannot make a direct comparison with our calculated data that pertains to a low coverage situation.

Our calculated values of the scattering probabilities of H are very small but consistent with results from atomic beam measurements by Rettner and Auerbach [2]. They find independently of coverage an upper limit for the scattering probability of ~ 0.1 for E_i = 0.07 and 0.3 eV at near normal incidence. This result is not consistent with the measured sticking data of H on Cu(110) by Bischler and coworkers [34]. They find a value of ~ 0.18 for the sticking of an quasithermal beam of H atoms with an average kinetic energy in the range 0.16 – 0.3 eV. This value is surprisingly small in view of our results that the surface corrugation is effective in trapping the H atoms on the surface in the initial collision.

IV. CONCLUDING REMARKS AND SUMMARY

We have studied theoretically the dynamics of H adsorption on and absorption in Cu(111) using a classical molecular dynamics approach. This approach is based on a model interaction potential that has been constructed from plane wave and pseudopotential calculations of the total energy within density functional theory using the generalized gradient approximation. The functional form of this model interaction potential is taken from a semi-empirical effective medium theory for binary compounds and its potential parameters associated with the H/Cu interaction were adjusted so that the potential reproduces the calculated total energies. The extracted chemisorption bond parameters from the calculated total energies are in good agreement with available experimental data. We find that the calculated energy barriers for an adsorbed atom are lowered dramatically by relaxations of the Cu atoms and these barriers are so low even in the rigid surface lattice situation that the absorption of an incident H atom is non-activated for impacts close to the so-called fcc and hcp hollow sites.

The main points from the results of the classical molecular dynamics calculations that we would like to stress are the following. An incident H atom moves so fast that the Cu atoms do not have time to relax and decrease the absorption barriers. The thermal fluctuations of the Cu atoms have a negligible effect on the probability to cross the surface plane. The energy transfer from the H atom to the surface lattice, or more precisely, to phonons, is rather inefficient. A simple estimation based on the measured electron-hole pair contribution to the vibrational relaxation rate for an adsorbed H atom on Cu(111) from infrared vibrational spectroscopy shows that the energy transfer to electron-hole pairs can be as efficient as to phonons and requires further attention. The total energy transfer rate as calculated to phonons and as estimated to electron-hole pairs is so small that the H atom makes a large number of round trips in the surface adsorption and absorption wells before it sticks either in the adsorption well or in the absorption well. The surface corrugation of the hydrogen-surface interaction potential plays an important role in the scattering and sticking processes by transferring efficiently the energy of the normal motion of the incident atom to lateral motion.

Finally, we find that our results are consistent with experimental data for H on Cu(111). The experiments indicate that subsurface sites can be populated by an incident atomic H beam and show that the scattering probability is small.

ACKNOWLEDGMENTS

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FIGURES

FIG. 1. A comparison between model potential energy curves (lines) and calculated first-principle total energies (symbols) as a function of the perpendicular coordinate, z, with respect to the outermost surface plane for various configurations. (a) fcc and hcp hollow sites. (b) bridge and top sites. Only the total energy points represented by solid symbols have been used in the construction of the model interaction potential. The zero of the energy scale corresponds to the total energy of the isolated H atom and Cu(111) slab.

FIG. 2. Two sections of the rigid model PES. (a) Surface plane. x is the coordinate along the [100] surface direction.(b) The plane spanned by the surface normal and direction in the surface plane along the line (dotted line in (a)) through top, hollow(fcc), bridge, hollow(hcp), and top sites. The dashed contours contours correspond to zero incidence energy.

FIG. 3. Calculated probabilities for various outcomes of the scattering of an H atom from the Cu (111) surface as a function of energy, E_i, at normal incidence. (a) P_{h} is the fraction of the surface unit cell where the atom is energetically allowed to cross the surface plane. P_{p} is the calculated probabilities to cross this plane under various conditions as indicated; in the rigid surface lattice situation and for two surface temperatures, $T_s = 0$ K and a 500 K. (b) Absorption probability, P_{ab}, for two different surface temperatures; $T_s = 0$ K and a 500 K. (c) Adsorption, P_{ab}, and scattering , P_{s}, probabilities for for two different surface temperatures; $T_s = 0$ K and a 500 K.

FIG. 4. A trajectory for a H atom incident normal to the surface as a function of time. z is the distance from the surface plane and E is defined as the sum of the kinetic energy of the atom and its potential energy in the rigid lattice situation. The incidence energy of the H atom is 1.1 eV and $T_s = 0$ K.

FIG. 5. Isotope dependence of probabilities P_{ab}, P_{ad}, and P_{s} for absorption in, adsorption on, and scattering from the Cu(111) surface, respectively, as a function of the energy at normal incidence. The surface temperature is 500 K.

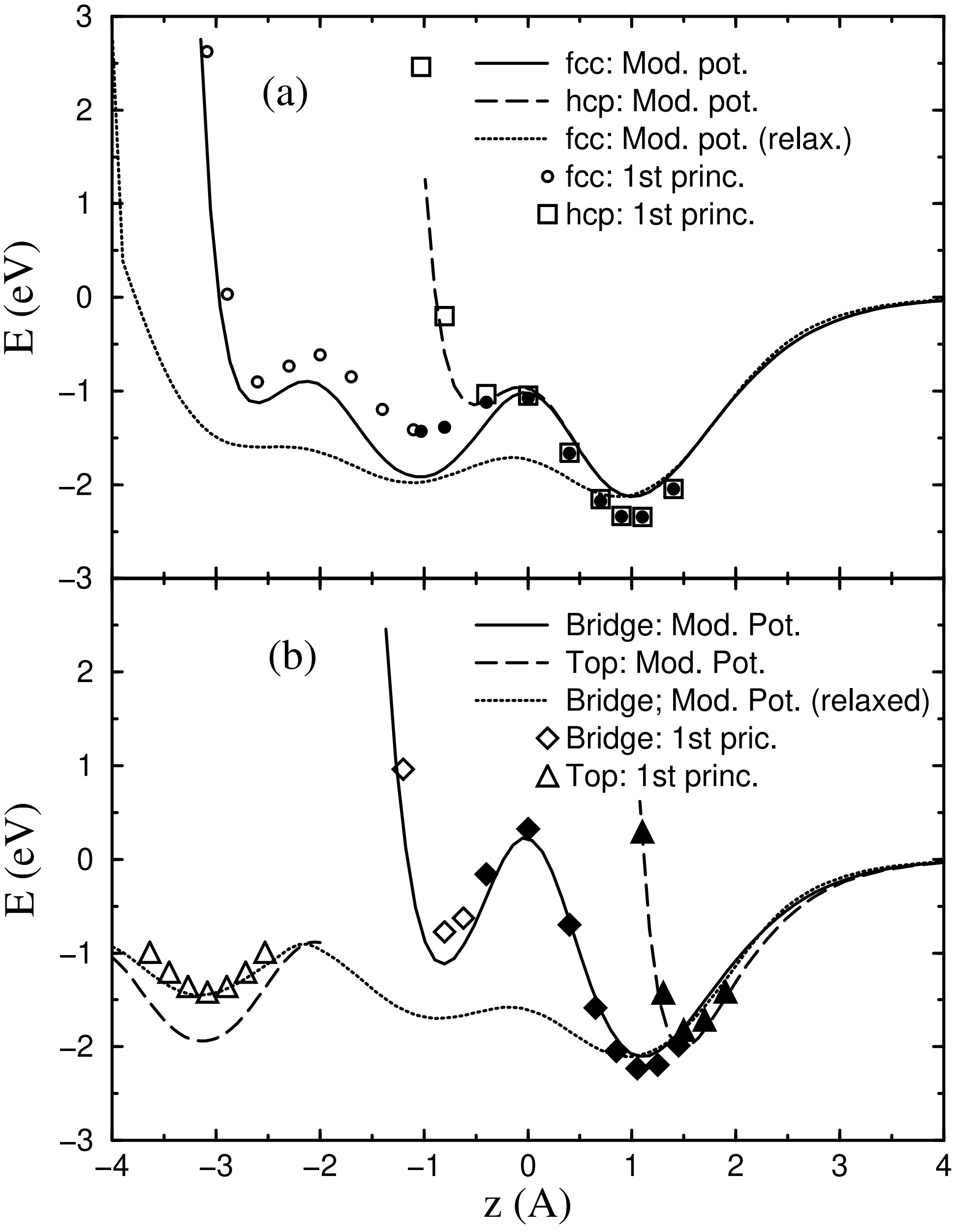

(a)
fcc: Mod. pot.
hcp: Mod. pot.
fcc: Mod. pot. (relax.)
fcc: 1st princ.
hcp: 1st princ.
(b)
Bridge: Mod. Pot.
Top: Mod. Pot.
Bridge; Mod. Pot. (relaxed)
Bridge: 1st pric.
Top: 1st princ.
E (eV)
z (A)

Fig. 1

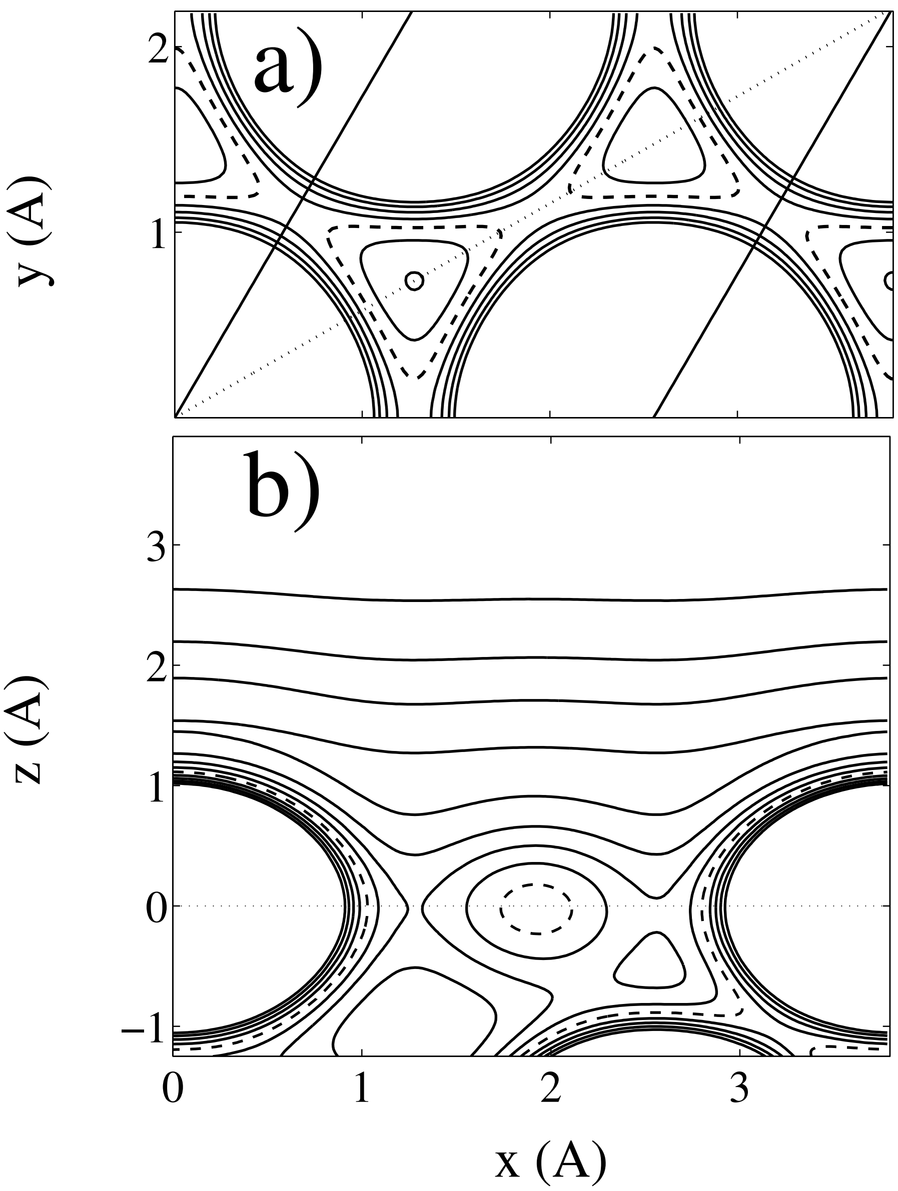
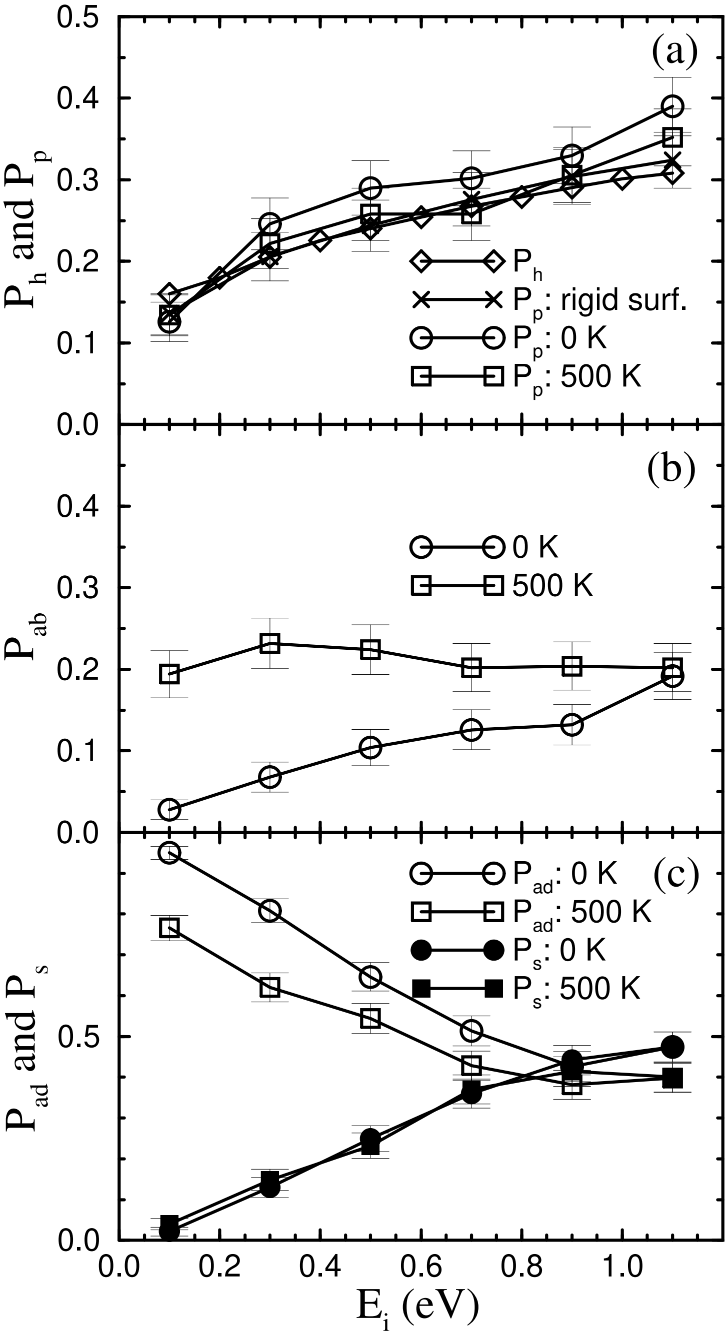


Fig. 2



(a)
(b)
(c)
P_h and P_p
P_ab
P_ad and P_s
E_i (eV)
P_h
P_p: rigid surf.
P_p: 0 K
P_p: 500 K
0 K
500 K
P_ad: 0 K
P_ad: 500 K
P_s: 0 K
P_s: 500 K
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.8
1.0

Fig. 3

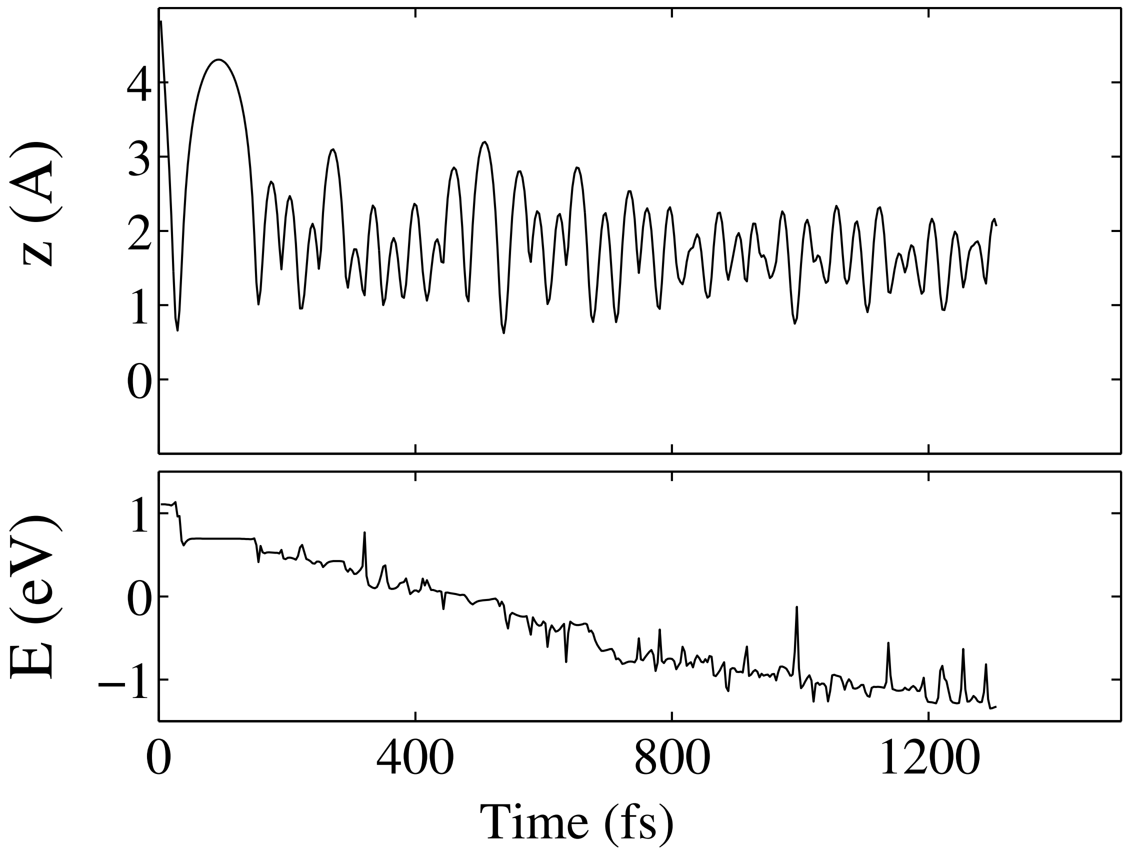


Fig. 4

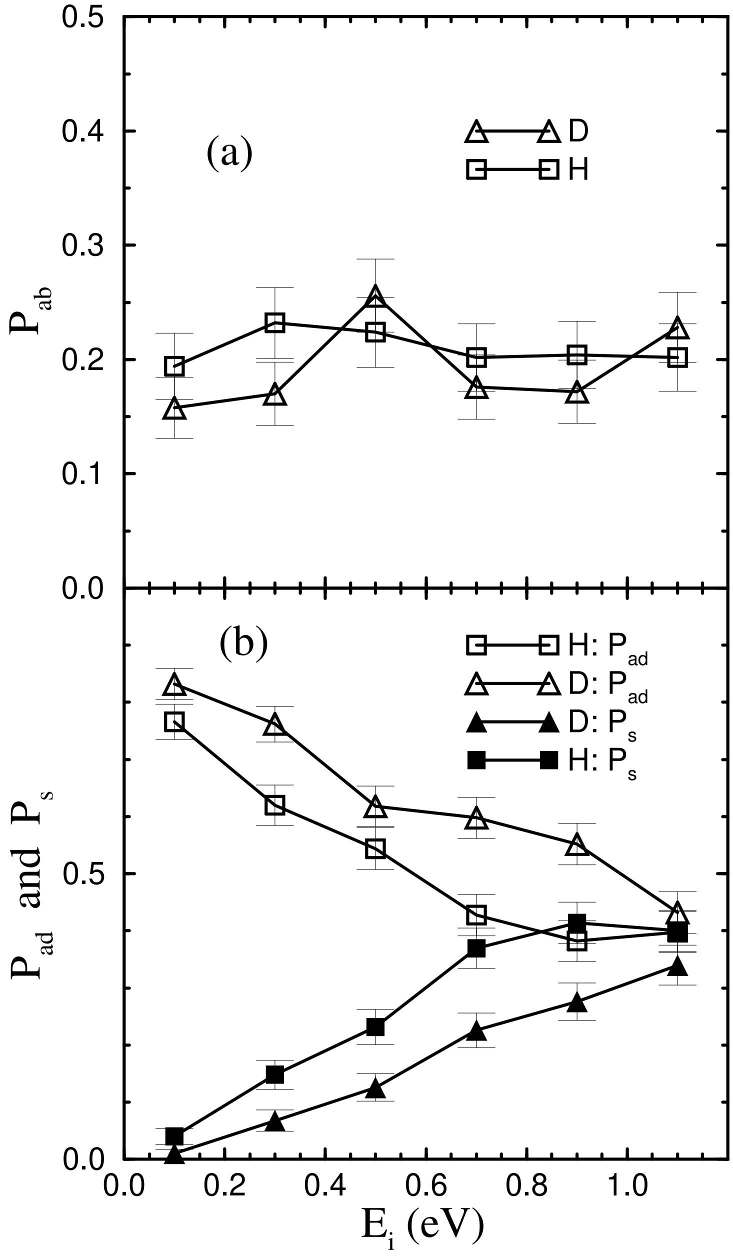

0.5
0.4
0.3
0.2
0.1
0.0
(a)
D
H
P_{ab}
(b)
H: P_{ad}
D: P_{ad}
D: P_s
H: P_s
0.5
0.0
P_{ad} and P_s
0.0
0.2
0.4
0.6
0.8
1.0
E_i (eV)

Fig. 5

TABLES

TABLE I. Potential parameters in the model potential.

$\sigma =$	s	a
$n_{\sigma 0}$ (a_0^{-3})	0.091	0.027
$\eta_{\sigma 2}$ (a_0^{-1})	1.652	2.871
$r_\sigma 0$ (a_0)	4.83	2.326
$E_{0\sigma}$ (eV)	-3.51	-2.371
λ_σ (a_0^{-1})	1.906	4.089
κ_σ (a_0^{-1})	2.74	4.69
$V_{0\sigma}$ (eV)	2.476	0.427

TABLE II. Calculated binding parameters. E_{ad} is the potential energy of the minima located at z_{ad} with respect to the position of the surface plane. $\hbar\omega_{\rm h}$ is the calculated vibrational energies for the H atom normal to the surface in the harmonic approximation. D_{ab} is the potential energy barrier for absorption with respect to the adsorption minima. The values in the parentheses corresponds to the value when the atoms in the surface plane are relaxed.

site	E_{ad}	z_{ad}	$\hbar\omega_{\rm h}$	D_{ab}
	[eV]	[Å]	[meV]	[eV]
top	-1.83	1.52	215	—
bridge	-2.22	1.08	139	2.7(1.3)
hollow(fcc)	-2.37	0.953	145	1.3(0.9)
hollow(hcp)	-2.36	0.957	144	1.3(0.9)
sub-surface	-1.43	-1.0	$\sim$ 110	—
bulk	-1.41	-3.1	120	—