

Eley–Rideal and hot-atom reactions of H(D) atoms with D(H)-covered Cu(111) surfaces; quasiclassical studies

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Quasiclassical molecular dynamics studies are made of H or D atoms incident from the gas phase onto D or H-covered Cu(111) surfaces. Two detailed model potential energy surfaces are used, both based on the results of extensive total energy calculations using the density functional method. The incident H (D) atoms can react directly to form HD via the Eley–Rideal mechanism, or trap onto the surface. These trapped hot atoms can react with the adsorbates to form HD or can eventually dissipate enough energy through collisions with the adsorbates to become immobile. We also observe the formation of D₂ (H₂). Probabilities for these various processes, as well as the rotational, vibrational, and translational energy distributions of the products are computed and compared with experiment. Hot-atom pathways to product formation are shown to make significant contributions. One of the potentials gives excellent agreement with experiment, while the other is less successful.

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I. INTRODUCTION

A sizable number of experimental studies in the past decade have examined Eley–Rideal-type reactions of gas-phase species with particles adsorbed onto metal,^{1–15} semiconductor,^{16–22} and carbon surfaces.^{23–26} Numerous quantum and classical theoretical studies have also appeared.^{27–41} The most detailed experiments have focused on reactions of gas-phase H or D with H, D or halogens adsorbed onto single-crystal surfaces. For these systems the adsorbate–metal bond energies are roughly 2–3 eV while the product bond energies are nearly twice that. This results in a very large exothermicity, with often several eV of energy appearing in the translational and internal motion of the desorbing products. It has become clear in the past few years that many of these reactions proceed via hot-atom pathways,⁴² where the incident atom initially traps onto the surface without reacting. Quantum^{31–34,37} and classical^{33,35,36,39,43,44} studies have shown that H atoms scatter very efficiently from both the surface corrugation and adsorbed H or D atoms, to become trapped. Classical studies have also shown that dissipation of the trapped H atom's energy into the lattice is slow^{43,44} and that these trapped hot atoms lose energy primarily through collisions with other adsorbates.³⁶ The trapped atoms can have energies as high as 2 eV or more above the ground state, and if they react with an adsorbate before dissipating this excess energy the resulting products will be hot and energetically similar to those arising from direct Eley–Rideal (ER) processes. We use the term ER (or direct ER) to refer to reactions which result from the direct encounter of a particle entering from the gas phase with an adsorbate, in contrast to the hot-atom (HA) route.

We focus here on the experimental work of Rettner and Auerbach, who examined reactions of H(g) or D(g) with D or H atoms adsorbed onto Cu(111), and measured detailed final state distributions for the product HD.^{5,7} They observed that the product HD molecules were translationally and internally “hot,” and that about half of the incident atoms reacted to form HD. For the initial coverage of half a monolayer, and assuming a single collision leads to reaction, this corresponds to a reaction cross section of about 5 Å². Quantum mechanical calculations,^{31–33} however, while finding similar product energy distributions, suggested that the cross section for a single direct ER encounter was much smaller, 0.5 Å² or less, and that the cross section for scattering from an adsorbate into a trapped state was very large, roughly 15–20 Å². It was thus postulated that most of the observed reactivity resulted from multiple collisions between trapped hot atoms and adsorbates.⁷ These early quantum calculations were based on a flat-surface approximation (no surface corrugation), however, and not much was known about the potential energy surface (PES). Since then we have put much effort into developing more realistic models and better potentials. The reaction of H(g) or D(g) with a *single* D or H atom adsorbed onto a *corrugated* Cu(111) surface was examined using quasiclassical methods.³⁵ The cross sections for single-collision ER reactions were again found to be small, similar to the flat-surface case. The corrugation was shown to add an additional and efficient pathway to trapping and hot-atom formation. Extensive total energy calculations were performed using the density functional method to examine the interaction of two hydrogens over a Cu(111) surface.^{43,45} In a preliminary study, a model PES based on these calculations was developed, and quasiclassical trajectory methods were used to examine the interaction of H(g) and D(g) atoms with a corrugated Cu(111) surface covered

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by *several* adsorbed D or H atoms. While direct ER processes were observed, most of the HD product resulted from HA reactions, and agreement with experiment was generally good.³⁶ We note that mixtures of direct ER and indirect HA processes have been observed in quasiclassical studies of the $H(g) + D/Si(001)$ reaction³⁹ and in experimental studies of $H + D$ /metal reactions on several metal surfaces by Küppers and co-workers.¹¹

In this paper we present a more detailed study of the reaction of $H(g)$ and $D(g)$ with D and H atoms adsorbed onto Cu(111). A new PES is used which, in certain aspects, provides a better fit to the computed total energies.⁴⁵ Quasiclassical methods are again used, and many adsorbed atoms are included on the corrugated metal surface, simulating the experimental coverage of 0.5 atoms/unit cell. Probabilities for direct and indirect reaction and trapping, as well as the rotational, vibrational, and translational energy distributions of the products are computed and compared with experiment. We describe the theoretical and computational details in Sec. II, present and discuss the results in Sec. III, and conclude with a brief summary in Sec. IV.

II. THEORY

Quasiclassical trajectory methods are used to model $H(g)$ and $D(g)$ atoms incident on D and H-covered Cu(111) surfaces. These methods, our model PES, and the density functional total energy calculations to which this PES is fit are well described in earlier papers.^{36,45} We only provide enough details here to improve the readability of the paper. Because of the large number of particles involved it is necessary to use classical methods. However, for these reactions the energies are high and the barriers are small, tunneling effects should be minor, and classical mechanics should work reasonably well. We have “benchmarked” our methods by comparing quasiclassical and quantum results for the exactly solvable flat-surface single-adsorbate case, and find that the quasiclassical method generally reproduces the essential features of the reaction in a semiquantitative fashion.^{31–33} This comparison suggests that the major source of error comes from our quasiclassical treatment of the large zero point energies of the adsorbed atoms. The Cu surface is kept rigid and an electronically adiabatic PES is used. Thus, we ignore the effects of phonons and electron-hole pair excitations. Energy loss into the substrate should not significantly effect the dynamics of these light high-energy particles, however. We have, in fact, demonstrated that energy loss from the H-atoms to the phonons is slow on reaction timescales,^{43,44} with the dominant energy-transfer mechanism being collisions with adsorbates.³⁶

The experimentally observed⁷ surface coverage of one adsorbate per two surface unit cells is simulated, where each unit cell contains two threefold hollow sites. Our “simulation cell” consists of a 6×6 rhombic array of surface unit cells, containing 18 adsorbed atoms in a graphitic registry. While this honey-comb adsorbate structure has not been proven to exist on Cu(111),⁴⁶ it has been confirmed for half-monolayer coverages of H on Ni(111)⁴⁷ and proposed for $H/Ag(111)$.⁴⁸ A single incident atom is aimed randomly (at normal incidence) at the four unit cells in the center of the

array, and all 19 atoms are evolved in time using Hamilton’s equations of motion. The incident atom has an energy of 0.07 eV, corresponding to the average incident energy in the experiments,⁷ and is initially 7 Å above the surface. The adsorbates are initially bound in the threefold hollow sites with energies corresponding to the quantum zero point energies, using a harmonic approximation for the PES. For our model PES-1, described in the following paragraphs, the initial vibrational energies for adsorbate motion perpendicular and parallel to the surface are 71 and 87 meV, respectively, for H and 50 and 62 meV, respectively, for D. Note that the parallel energies represent the sum of two degenerate modes. For our model PES-2, the zero point energies are not significantly different. The initial oscillator phases are sampled randomly from a uniform distribution. All 19 atoms are evolved until the incident atom or a product molecule is observed more than 7 Å above the surface, or until a total integration time of 2.0 ps is reached. This procedure is repeated 4000 times to average over the impact sites of the incident atom and the initial vibrational phases of the adsorbed atoms. Any product molecules formed are assigned a rotational “quantum number” $j = J/\hbar$, where J is the total classical angular momentum. Unlike in our previous study, where we made a rigid rotor assumption, we here assign vibrational “quantum numbers,” ν , via semiclassical quantization.³¹

Instead of applying periodic boundary conditions, we use reflecting walls perpendicular to the surface. When an atom or molecule reaches the simulation cell boundary its center of mass translation is reflected from the wall (without changing the rovibrational motion for the case of a molecule). We have increased our simulation cell size to an 8×8 array of surface unit cells, with 32 adsorbates, and the results do not change in a significant way.

At a half-monolayer coverage the adsorbates are relatively far apart; the closest spacing is about 2.9 Å, for two adsorbates on opposite sides of a Cu atom. When an incident (or hot) atom collides with an adsorbate, they either react and quickly leave the surface or they scatter without reacting, quickly separating. Thus, three H atoms are never simultaneously sufficiently close together to make three-body (actually, three-H) interactions important, and we expand our PES up to two-body terms:

$$V(\{\mathbf{r}\}) = \sum_i V_a(\mathbf{r}) + \sum_{i < j} V_{aa}(\mathbf{r}_i, \mathbf{r}_j). \quad (1)$$

The particles are located at positions \mathbf{r}_i , and $V_a(\mathbf{r}_i)$ describes the interaction of a single H atom with the corrugated Cu(111) surface. V_{aa} describes the interaction of two H atoms in the presence of the metal.

We present results here for two potentials. Both are very detailed and well described elsewhere, and we will not reproduce their detailed functional forms here. The first model potential,³⁶ which we denote PES-1, uses a chemically reasonable modified LEPS⁴⁹ form to describe the two-H terms, V_{aa} . The LEPS form is based on Morse-like attractive and repulsive terms which decay exponentially with distance. The effects of surface corrugation are included by making the Morse parameters vary across the surface unit cell, ex-

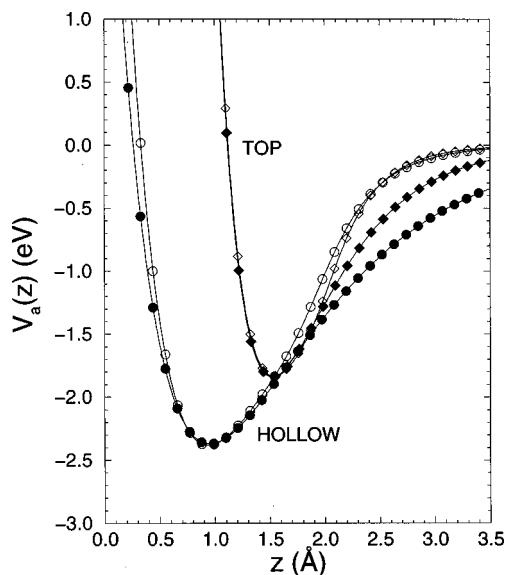


FIG. 1. Plots of the one-body H-Cu(111) interaction potential, V_a , as a function of z , the H-atom distance above the surface plane. The position of the H-atom in the surface plane is held fixed over the top and hollow sites, as indicated. Results are shown for both PES-1 (solid symbols) and PES-2 (open symbols).

panding them in a Fourier series in reciprocal lattice vectors. The single-H term, V_a , was thus a corrugated Morse potential.

Calculations of the total energy were performed for various configurations of one or two hydrogen atoms over a Cu(111) surface,⁴⁵ using the density functional scheme with the generalized gradient approximation for the exchange correlation energy.⁵⁰ Other groups have successfully used these methods to construct potentials for H_2 dissociation on Cu(111).⁵¹⁻⁵⁴ The reader is referred to the literature for further details.^{45,50-54} The PES-1 parameters were chosen by least squares fitting to the computed total energy (density functional) points. Terms in the model PES describing the H-Cu(111) interaction were fit to the computed total energies for H atoms directly over four high-symmetry sites on the Cu(111) surface. The rms (root mean square) error for these fits was 0.09 eV or better,³⁶ and the rms error for the gas-phase H-H interaction was 0.12 eV. The remaining potential parameters were then fit to the computed total energies for several H-H-Cu(111) configurations believed to be important for these reactions. The global rms error for these two-body configurations was 0.17 eV.

While a preliminary quasiclassical study using PES-1 gave good agreement with experiment,³⁶ the exponentially decaying attractive terms did not accurately reproduce the behavior observed in the density functional total energy calculations. A second potential, PES-2, was therefore constructed,⁴⁵ and the form of the attractive parts was modified to improve the fit. While the rms error for the gas-phase H-H and one-body H-Cu(111) interactions improved dramatically to 0.002 eV or better, the overall error in the global two-body fit was only lowered to 0.16 eV.⁴⁵ This small decrease suggests that the modifications did not improve the description of the potential in the interaction region, and a more flexible model is needed to do that. In Fig. 1 we plot V_a

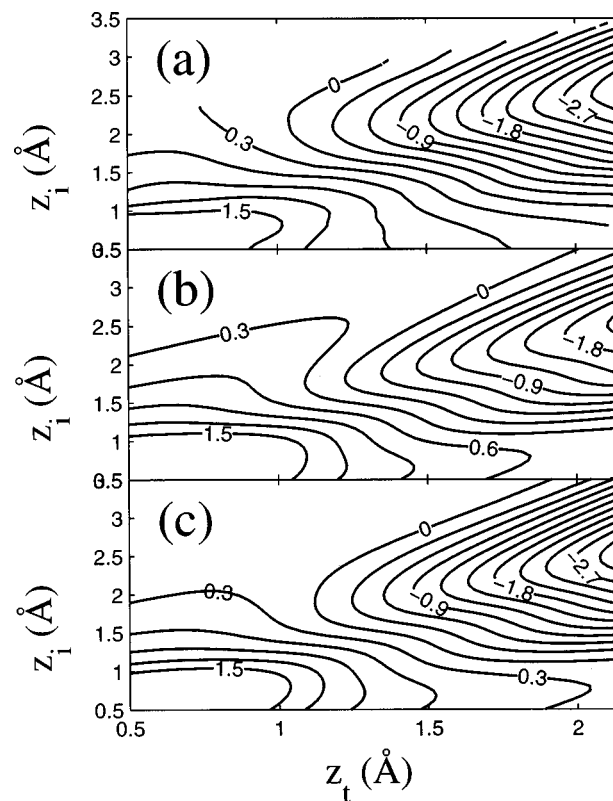


FIG. 2. Contour plots of the two-body interaction, V_{aa} , for both atoms moving only normal to the surface. The distance of the incident and target atoms above the surface plane are z_i and z_t , respectively. The target atom remains directly over a hollow site, and the incident atom remains directly over a neighboring bridge site. Results are shown for the (a) total energy density functional calculations, (b) PES-1, and (c) PES-2. The energy contours are in eV.

as a function of z , the H-atom distance above the surface plane. The position of the H-atom in the surface plane is held fixed over the top and hollow sites, as indicated. It is clear that PES-2 is a much shorter ranged potential than PES-1, in better agreement with the total energy results.

Figures 2 and 3 contain contour plots of the two-body interaction, V_{aa} , for two restricted configurations. In Fig. 2, both H atoms move only normal to the surface, and the distance of the incident and target (adsorbed) atoms above the surface plane are z_i and z_t , respectively. The target atom remains directly over a hollow site, and the incident atom remains directly over the nearest neighboring bridge site, about an H_2 bondlength away. Results are shown for the (a) total energy density functional calculations, (b) PES-1, and (c) PES-2. In Fig. 3 the adsorbate is held fixed in the potential minimum of the hollow site. The incident atom moves in a plane defined by x_i , its distance from the adsorbate along the plane of the surface from the adsorbate hollow site to an adjacent hollow site, through the bridge site, and z_i . In both cases PES-2 more accurately reproduces the results of the total energy calculations. Note that the H-H interaction is repulsive when both atoms are near the Cu surface. The H-H interaction becomes attractive only when the atoms move away from the surface, breaking their bonds to the metal. This is clearly illustrated in Fig. 2, where for z_i and z_t the atoms are about an H_2 bond length apart. Minimum energy

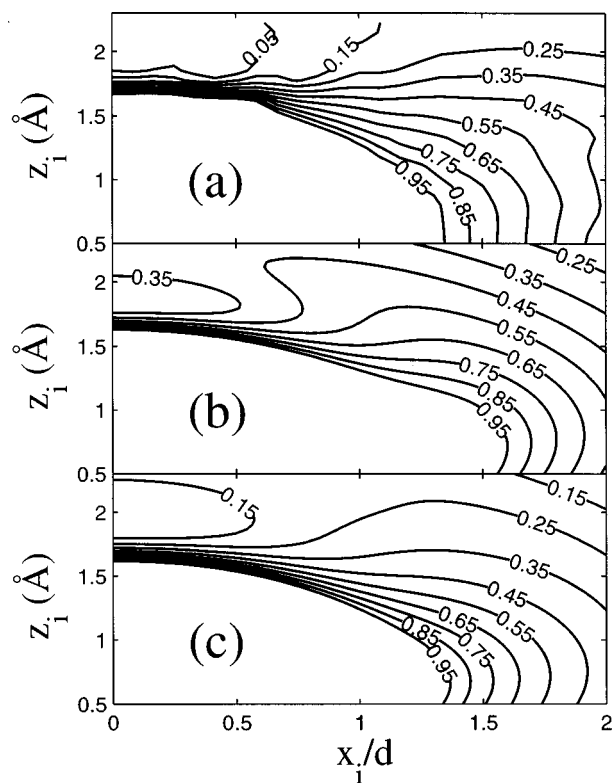


FIG. 3. Same as in Fig. 2, but for the adsorbate held fixed in the potential minimum of the hollow site. The incident atom is at a distance z_i above the surface plane and moves parallel to the surface from the adsorbate hollow site to an adjacent hollow site, through the bridge site. The distance along the surface from the adsorbate is x_i , and $d=0.73$ Å is the hollow-to-bridge site spacing.

paths exist from reactants to products for which there are no barriers; the adsorbate moves away from the metal as it interacts with the approaching incident atom. However, the incident atom is accelerated by its interaction with the metal, and may quickly deflect away from the adsorbate before the adsorbate has time to respond and move away from the surface. That is why trapping can be the dominant outcome for this “barrierless” reaction. An important difference between PES-1 and PES-2 is that PES-2 is more short ranged. In Fig. 2, for PES-2 (and the total energy case), the H–H attraction develops more quickly as the atoms move away from the surface. In Fig. 3, the H–H repulsion for the case of a fixed adsorbate is shorter ranged for PES-2. In the next section we will see how these features effect the dynamics.

III. RESULTS AND DISCUSSION

Results are listed in Table I for the probabilities of various events, for the two potentials. The notation D-on-H refers to D(g) atoms incident on H-covered Cu(111), and so on. Preliminary results based on PES-1 have been published elsewhere,³⁶ although there was an error in that work; the D-on-H results corresponded to an incident energy of 0.28 eV, and not 0.07 eV, as reported. As in our earlier flat-surface studies, we see no exchange processes, where the incident atom knocks an adsorbed atom into the gas phase. This result is in agreement with the experiments where exchange was not observed.⁷

TABLE I. Probabilities for various outcomes, for the two model potentials and isotopic combinations described in the text.

Outcome	H-on-D PES-1	D-on-H PES-1	H-on-D PES-2	D-on-H PES-2
reflection	0.04	0.06	0.19	0.16
primary reaction	0.44	0.32	0.42	0.33
secondary reaction	0.02	0.08	0.03	0.09
sticking	0.50	0.54	0.36	0.42

In the experiments, the probability of the incident atom reflecting from the surface without reacting, P_{ref} , was found to be between 0.02 and 0.1. We see that PES-1 is in good agreement with these observations, while the PES-2 results are a bit too large. Reflection is small because the incident atom interacts strongly with the corrugation and the adsorbates. Note that the asymptotic kinetic energy perpendicular to the surface, 0.07 eV, is small compared with the acceleration in the entrance channel, and it is easy to transfer this amount of energy into other degrees of freedom, leading to trapping. In addition to corrugation-mediated trapping, the similar masses of H and D and the fact that the adsorbates are only weakly bound parallel to the surface makes energy transfer with the adsorbates efficient, and the adsorbate-mediated trapping cross section is also large.^{31–35} The addition of lattice motion would decrease the computed P_{ref} somewhat further.^{43,44} The corrugation and repulsive regions for the *bare* surface (no adsorbates) are essentially the same for the two potentials (see Fig. 1), and scattering from the bare surface should be very similar. In Fig. 4, however, the energy distributions of the reflected atoms are plotted, and the two potentials exhibit very different behavior. Reflection from the bare regions of the (static) surface would produce atoms with energies of 0.07 eV, while scattering from or near adsorbates can lead to asymptotic energies greater or less than this value, due to energy transfer with the adsorbates. It is clear that for the shorter-ranged interaction, PES-2, there is significantly less atom–atom energy transfer. There is thus

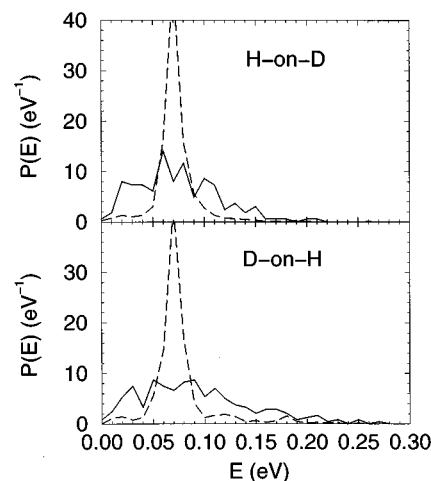


FIG. 4. Probability distribution for the asymptotic kinetic energy of reflected atoms, for both PES-1 (solid lines) and PES-2 (dashed lines).

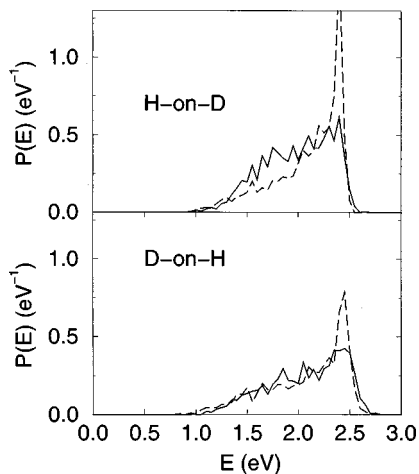


FIG. 5. Probability distribution for the asymptotic total product HD energy, for both PES-1 (solid lines) and PES-2 (dashed lines). The $P(E)$ are normalized such that when integrated over E they equal the primary reaction probabilities of Table I.

less adsorbate-mediated trapping, and more reflection. Also, as illustrated by Fig. 3, for a fixed coverage and shorter range H–H repulsion there is effectively more bare surface to (elastically) scatter from. For PES-1 the incident atom can experience significant energy exchange before reflecting into the gas phase, resulting from one or more collisions with the adsorbates. Note, however, that any energy *gain* from the adsorbates is an artifact of the use of classical mechanics, since the adsorbates have energies which mimic the quantum (zero point) ground state. This suggests that our classical methods may overestimate the reflection probability for a given PES, due to improper behavior of the adsorbate zero point energy.

In Table I, a primary reaction occurs when the incident atom and an adsorbate react to form an HD molecule, via some route. Secondary reactions take place between two adsorbates, to form H_2 or D_2 . This can happen when an incident or hot atom knocks an adsorbate out of its threefold hollow site, such that it becomes mobile on, but still bound to, the surface. We never observe both primary and secondary reactions. If by the end of the simulation (2 ps) the incident atom remains on the surface without having reacted, and there are no secondary reactions, we categorize the event as sticking. We observe that secondary reaction always corresponds to sticking of the incident atom. Thus, the actual probability that the incident atom sticks without reacting is the sticking value in Table I, plus the secondary reaction probability.

In the experiments,⁷ the probability for primary reaction to form HD was reported to be 0.47 ± 0.12 for both isotopic combinations. We see that the PES-1 and PES-2 results are nearly the same, and in good agreement with experiment, although the D-on-H reactivity is a bit low. Also, no isotope effect in the reactivity was resolved in the experiments. As discussed in the Introduction, these primary reactions can result from either direct Eley–Rideal (ER) or indirect hot-atom (HA) pathways, and the relative ER and HA contributions can be deduced from the results in Figs. 5 and 6. In Fig. 5 we plot the total energy distributions of the product HD

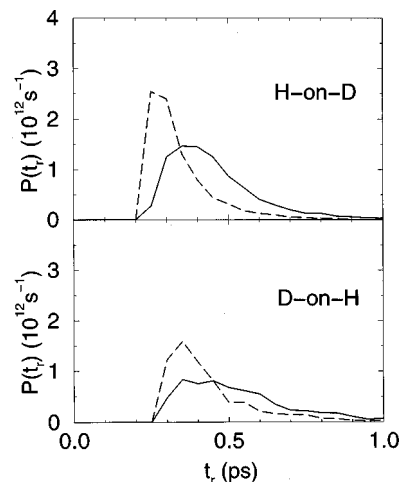


FIG. 6. Probability distribution for the reaction time, for both PES-1 (solid lines) and PES-2 (dashed lines). The $P(t_r)$ are normalized such that when integrated over t_r they equal the primary reaction probabilities of Table I.

molecules for each PES. The curves are normalized such that the integral of $P(E)$ over E is equal to the primary reaction probability. The maximum total energy is about 2.4 eV for H-on-D, with the D-on-H value being slightly larger due to the larger zero point vibrational energy of the adsorbed H. In the absence of energy loss to the substrate, all energies below this maximum value result from nonreactive collisions with the adsorbates. We find that the product molecules leave the surface in a narrow range of angles close to the surface normal (see Fig. 10), and that these nonreactive collisions generally occur prior to the reaction. The peaks near 2.4 eV thus correspond to direct ER processes, while the lower energy components represent HA processes. The probability that the initial encounter between the incident atom and an adsorbate leads to reaction is larger for PES-2 than for PES-1, by roughly a factor of 2. For both potentials we see significant contributions from hot-atom reactions, and the incident atom can lose as much as 1.0 eV or more of energy before reacting. Another probe of the reaction dynamics is the reaction time, defined here as the elapsed time between the start of the trajectory and when the product HD is 7 Å above the surface. In Fig. 6 we plot the reaction time distributions, again normalized so that when integrated over time they equal the primary reaction probabilities. The shortest times correspond to direct ER reaction, and we again see noticeably more ER processes for PES-2. The longer times correspond to multiple collisions and HA processes (slower moving particles), and for PES-1 there are more of these longer-time events. For both potentials, there are many more HA reactions than direct ER reactions. Our studies suggest that the reacting hot atoms typically experience several unreactive collisions with adsorbates prior to reaction. Examination of Fig. 5 would thus suggest that the hot atom loses on the order of a tenth of an eV of energy with each collision. Note finally that all reactions are over by 1 ps, and our total integration time of 2 ps is more than adequate.

Given the initial adsorbate coverage, an apparent reaction cross section of about 5 \AA^2 was deduced from the measured reaction probability, assuming a single reactive en-

TABLE II. Average properties for the product HD molecules formed by primary (secondary) reaction, for the two model potentials and isotopic combinations described in the text. The average vibrational and rotational quantum numbers are $\langle v \rangle$ and $\langle j \rangle$, respectively. The average center-of-mass translational energy, average internal energy, and average total energy are $\langle E_{\text{cm}} \rangle$, $\langle E_{\text{int}} \rangle$, $\langle E_{\text{tot}} \rangle$, respectively.

	H-on-D PES-1	D-on-H PES-1	H-on-D PES-2	D-on-H PES-2
$\langle v \rangle$	0.62 (0.30)	0.75 (0.12)	0.40 (0.14)	0.37 (0.05)
$\langle j \rangle$	7.5 (5.4)	7.9 (4.3)	6.8 (5.4)	6.5 (3.5)
$\langle E_{\text{cm}} \rangle$ (eV)	1.10 (0.99)	1.09 (0.99)	1.37 (1.08)	1.41 (1.06)
$\langle E_{\text{int}} \rangle$ (eV)	0.89 (0.46)	0.99 (0.53)	0.72 (0.37)	0.67 (0.37)
$\langle E_{\text{tot}} \rangle$ (eV)	2.00 (1.46)	2.07 (1.52)	2.09 (1.44)	2.08 (1.43)

counter. However, in our simulations these reactions to form HD occur via both ER and HA routes, often involving several collisions of the incident particle with adsorbates. This demonstrates that the large observed reactivity can be reproduced by *many* atom–atom encounters, *each* with a small *single-collision* reaction cross section. For PES-1, for example, if 10% of the primary reactions are of the ER variety, than the initial-collision ER reaction probabilities are about 0.044 and 0.032 for H-on-D and D-on-H, respectively. These correspond to single-collision ER reactive cross sections of 0.49 \AA^2 and 0.36 \AA^2 respectively, similar to the small single-collision single-adsorbate reaction cross sections computed in earlier studies.^{31–35} The experiments, the quantum calculations, and the finite coverage quasiclassical simulations are thus consistent. Another indication that the probability of reaction for each atom–atom encounter is small can be seen in the large probabilities for sticking without reacting. The experiments⁷ report equal probabilities for reaction and sticking (about 0.5 ± 0.1), and this compares well with our computed values for both potentials. It is perhaps surprising that most atom-adsorbate encounters do not lead to reaction for this barrierless highly exothermic reaction. However, for the reasons discussed earlier the atom–atom energy transfer mechanism is extremely efficient, and it is this competition between reaction and trapping/scattering that makes the single-collision reaction cross sections so small.

In our calculations we find that the probabilities for secondary reaction are 2% and 8% for PES-1, for H-on-D and D-on-H, respectively, with very similar results for PES-2. Rettner and Auerbach did not look for this process in their experiments, but it has been observed by others. Winkler and co-workers¹² report about 4% D_2 formation for H-on-D/Ni(110) and about 6% H_2 formation for D-on-H/Ni(110). On Al(100) they observe secondary reactions for roughly one out of every ten incident atoms.¹³ Küppers and co-workers¹¹ have seen similar behavior on Ni(100) and Pt(111). Our results for both potentials are consistent with these values. Like Winkler and co-workers, we observe that D incident on H is more likely to create mobile H atoms than H incident on D, due to its larger mass. In Table II we list properties of the product molecules, with the values in parenthesis corresponding to secondary reactions. The average total energy, E_{tot} , of the secondary reaction products is about 0.5 eV lower than for the primary reactions, but still considerably ‘‘hot’’; about 1.4–1.5 eV for both potentials. These results

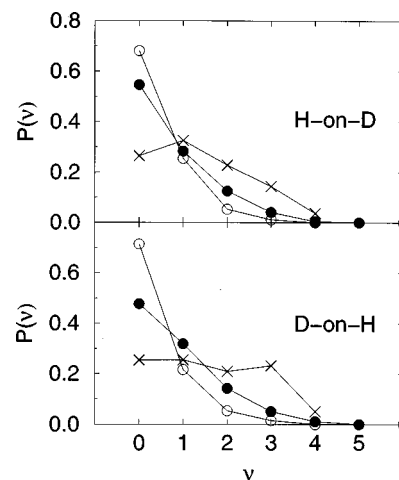


FIG. 7. Product HD vibrational state distributions, from the experiments of Ref. 7 (crosses) and from the calculations for PES-1 (solid circles) and PES-2 (open circles).

suggest that when the incident or hot atom knocks an adsorbate free, it transfers a sizable portion of its energy to that adsorbate.

Rettner and Auerbach measured final state distributions for the product HD and we compare these with our results in Table II and Figs. 7–9. In Fig. 7 are plotted the experimental and computed HD vibrational state distributions, each normalized to unity. The calculations exhibit a fair amount of vibrational excitation, but not as large as is seen in the experiments, with PES-2 having poorer agreement than PES-1. PES-1 does, however, reproduce the slightly larger vibrational excitation seen for D-on-H than for H-on-D. Our quasiclassical treatment of the large adsorbate and product vibrational zero point energies may be a source of some of the error. In comparing quantum and quasiclassical results for the same flat-surface model, we found that the quasiclassical method did not give as much vibrational excitation as in the quantum calculation, particularly for the D-on-H combination.³³ Very recently, quantum calculations have been implemented for a flat-surface version of our PES-1, and the vibrational distributions are in good agreement with experiment, although corrugation effects are ignored.³⁷ The experimental and computed rotational distributions are plotted in Fig. 8. While the broad distributions seen in the experiments are well reproduced by PES-1, the PES-2 distributions are a bit more narrow, but still in reasonable agreement. Because the reactions on PES-2 are more direct, involving a smaller number of pathways, the distributions are perhaps less ‘‘statistical’’ and therefore not as broad. It is interesting that the *lower* energy HA reactions which are somewhat more common on PES-1 lead to *larger* product rotational and vibrational energies than for PES-2. It is tempting to suggest that smaller impact parameters are involved for the shorter-ranged H–H interactions of PES-2, leading to lower rotational angular momentum. However, studies on flat surfaces showed no correlation between impact parameter and final rotational state,³⁴ and the trajectories on the corrugated surface should be even more ‘‘erratic.’’

Rettner and Auerbach reported an anticorrelation be-

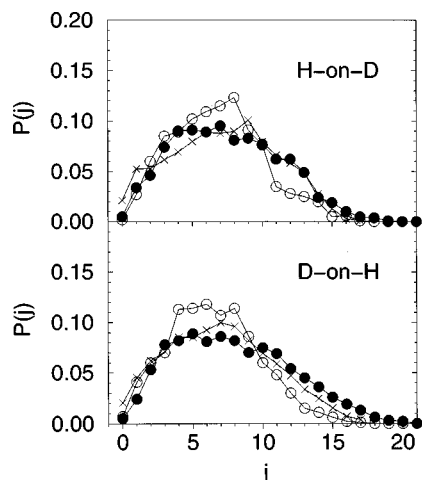


FIG. 8. Product HD rotational state distributions, from the experiments of Ref. 7 (crosses) and from the calculations for PES-1 (solid circles) and PES-2 (open circles).

tween rotational excitation and vibrational excitation,⁷ and similar behavior was seen in our flat-surface model.³¹ As seen in Fig. 9, where we plot the mean rotational energy as a function of vibrational state, the effect is somewhat stronger for H-on-D than for D-on-H. One result of this trend is that the product internal energy distribution (not shown) is a bit more narrow for H-on-D than for D-on-H, which was noted in the experiments⁷ and is seen in these simulations. Once again, PES-1 is in reasonable agreement with the experimental data while PES-2 is less so. The two model potentials exhibit different behavior with regard to the distribution of energy among the product degrees of freedom (see Table II). As noted, there is less product rotational and vibrational excitation for PES-2, even though direct (higher energy) ER processes are more probable and lead to a slightly larger average total product energy, $\langle E_{\text{tot}} \rangle$. A reason for this may be seen in Fig. 2, where for $z_i \approx z_f$ the atoms are about a bond

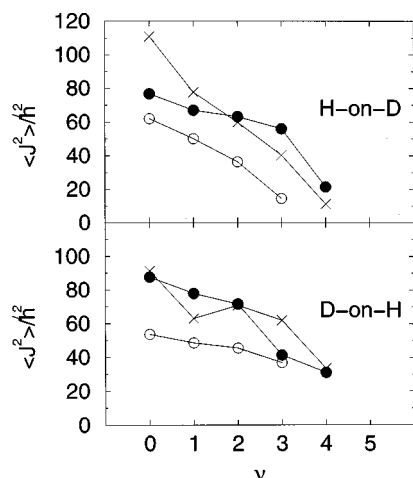


FIG. 9. Correlation between average rotational excitation and vibrational state of the product HD, from the experiments of Ref. 7 (crosses) and from the calculations for PES-1 (solid circles) and PES-2 (open circles). The product vibrational “quantum number” is ν , and $\langle j^2 \rangle / \hbar^2$ corresponds to $\langle j(j+1) \rangle$ in the experiments, where j is the rotational quantum number, and to j^2 in the quasiclassical calculations.

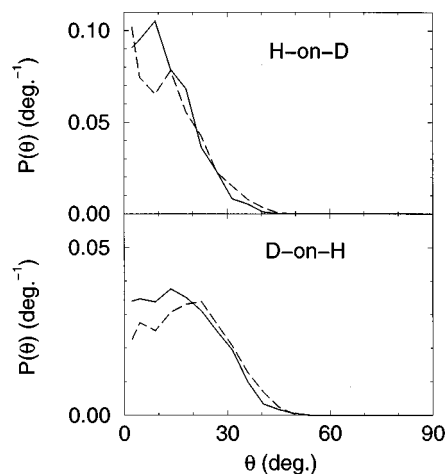


FIG. 10. Angular distributions for the product HD molecules, normalized such that the integral of $P(\theta)$ times $\sin \theta$ is equal to the primary reaction probability. Results for PES-1 (solid lines) and PES-2 (dashed lines) are shown.

length apart. As the HD molecule moves away from the surface (for $z_i \approx z_f$) the kinetic energy release is much more rapid for PES-2 than for PES-1. That is, the force on the molecular center-of-mass is larger, and there is more energy transferred into this coordinate, in competition with internal excitation. As a result, the average center-of-mass translational energies, $\langle E_{\text{cm}} \rangle$, are roughly 0.3 eV larger for PES-2 than PES-1. In their more detailed studies⁷ Rettner and Auerbach do not measure the product translational energies. However, average values of 0.85 ± 0.2 eV and 1.1 ± 0.2 eV were reported for H-on-D and D-on-H in some preliminary studies by Rettner on Cu(111).⁵ Once again, the PES-1 results are in good agreement with experiment and the PES-2 results are not.

In Fig. 10 we plot angular distributions for the product HD molecules, normalized such that the integral of $P(\theta)\sin \theta$ is equal to the primary reaction probability. The distributions are relatively narrow, indicating that the molecules leave the surface in a direction close to the surface normal, and that most of the (large) product translational energy is in that direction. Rettner and Auerbach^{5,7} observed that the product angular distributions for H-on-D were narrower than for D-on-H, and this behavior is reproduced by both model potentials. Compared with PES-1, on PES-2 there are smaller contributions from HA reactions and the product molecules experience a larger repulsive potential gradient for motion normal to the surface. One might thus expect more narrow angular distributions for PES-2, but this effect is not seen in the calculations.

IV. SUMMARY

In conclusion, our results suggest that both ER and HA pathways contribute to the reactivity for reactions of H with D on Cu(111). When an atom incident from the gas-phase collides with an adsorbate, the probability to scatter without reacting is large, leading to some energy transfer and making the single-collision Eley–Rideal reaction cross section small. This also leads to the efficient formation of hot atoms, which

can go on to react, often after several collisions with other adsorbates. This nonreactive scattering is so efficient that hot atoms can eventually stick to the surface without reacting. One reason for this behavior is that the H–H interaction is repulsive when both atoms are near the surface, only becoming attractive (reactive) when the atoms move away from the surface. The probability that a given encounter is reactive is on the order of a few percent, leading to reaction cross sections of roughly a few tenths of an Å², consistent with earlier quantum models.

We observe different behavior between two model interaction potentials, PES-1 and PES-2, which are both based on results from total energy calculations using density functional theory. The major difference between the potentials is that PES-2 is in better agreement with the calculated energy points in the asymptotic interaction region, and is more short-ranged than PES-1. For example, the repulsion between two atoms on the surface is felt over a longer distance for PES-1. We therefore observe more trapping and less reflection and ER reaction on PES-1 during the initial collision. Contributions from the ER channel are a bit more probable for PES-2, but for both potentials the total reactivity is dominated by HA processes. In our earlier quantum and quasiclassical flat-surface studies we also observed a range of behavior upon changing the parameters in the PES.³³ Unlike for many reactions, one cannot relate our PES to observed behavior in terms of barrier heights and locations (early versus late barrier). For this strongly exothermic and barrierless reaction one might guess that the reactivity would be large and insensitive to details in the potential. However, the presence of the surface adds an efficient pathway for nonreactive scattering and trapping, and it is the competition between this mechanism and reaction that makes this a complicated and interesting process.

While PES-1 gives results in excellent (and often detailed) agreement with experiment, PES-2 is less successful, but not inconsistent. Both models reproduce the overall reactivity, direct and indirect reaction pathways, long time relaxation and trapping, and product rotational excitation seen in the experiments. Both fail to reproduce the large product vibrational excitation that is observed. This sensitivity to details in the PES is seen experimentally,^{11–13} where the behavior can vary greatly from metal to metal, and even between different faces of the same metal. Given its better agreement with experiment, it is tempting to believe that PES-1 is closer to the “real” PES in the “important” regions of configuration space than PES-2, even though PES-2 has a slightly better fit to the computed total energies.

The main issue to be resolved now is to more fully understand the connection between the PES and the reaction dynamics. This will help us to understand not only why the theoretical results vary strongly with certain aspects of the interaction, but why the experimentally observed behavior varies from metal to metal.

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- ¹R. I. Hall, I. Cadez, M. Landau, F. Pichou, and C. Schermann, *Phys. Rev. Lett.* **60**, 337 (1988); C. Schermann, F. Pichou, M. Landau, I. Cadez, and R. I. Hall, *J. Chem. Phys.* **101**, 8152 (1994).
- ²P. J. Eenshuistra, J. H. M. Bonnie, J. Los, and H. J. Hopmann, *Phys. Rev. Lett.* **60**, 341 (1988).
- ³E. W. Kuipers, A. Vardi, A. Danon, and A. Amirav, *Phys. Rev. Lett.* **66**, 116 (1991); *Surf. Sci.* **261**, 299 (1992).
- ⁴K. R. Lykke and B. D. Kay, in *Laser Photoionization and Desorption Surface Analysis Techniques*, edited by N. S. Nogar (SPIE, Bellingham, WA, 1990), Vol. 1208, p. 18.
- ⁵C. T. Rettner, *Phys. Rev. Lett.* **69**, 383 (1992).
- ⁶C. T. Rettner, *J. Chem. Phys.* **101**, 1529 (1994); C. T. Rettner and D. J. Auerbach, *Science* **263**, 365 (1994).
- ⁷C. T. Rettner and D. J. Auerbach, *Phys. Rev. Lett.* **74**, 4551 (1995); *J. Chem. Phys.* **104**, 2732 (1996); *Surf. Sci.* **357–358**, 602 (1996).
- ⁸T. A. Jachimowski and W. H. Weinberg, *J. Chem. Phys.* **101**, 10997 (1994).
- ⁹S. A. Buntin, *J. Chem. Phys.* **105**, 2066 (1996).
- ¹⁰C. Lutterloh, J. Biener, A. Schenk, and J. Küppers, *Surf. Sci.* **331–333**, 261 (1995); *J. Chem. Phys.* **104**, 2392 (1996); J. Biener, C. Lutterloh, A. Schenk, K. Pöhlmann, and J. Küppers, *Surf. Sci.* **365**, 255 (1996).
- ¹¹Th. Kammler, J. Lee, and J. Küppers, *J. Chem. Phys.* **106**, 7362 (1997); S. Wehner and J. Küppers, *ibid.* **108**, 3353 (1998); **109**, 294 (1998); Th. Kammler, S. Wehner, and J. Küppers, *ibid.* **109**, 4071 (1998).
- ¹²G. E. Eilmsteiner, W. Walkner, and A. Winkler, *Surf. Sci.* **352–354**, 263 (1996).
- ¹³G. E. Eilmsteiner and A. Winkler, *Surf. Sci.* **366**, L750 (1996); J. Boh, G. Eilmsteiner, K. D. Rendulic, and A. Winkler, *ibid.* **395**, 98 (1998).
- ¹⁴Y.-S. Park, J.-Y. Kim, and J. Lee, *Surf. Sci.* **363**, 62 (1996).
- ¹⁵C. T. Rettner, D. J. Auerbach, and J. Lee, *J. Chem. Phys.* **105**, 10115 (1996).
- ¹⁶C. C. Cheng, S. R. Lucas, H. Gutleben, W. J. Choyke, and J. T. Yates, Jr., *J. Am. Chem. Soc.* **114**, 1249 (1992); J. T. Yates, Jr., C. C. Cheng, Q. Gao, and W. J. Choyke, *Surf. Sci. Rep.* **19**, 79 (1993).
- ¹⁷C. C. Cheng, S. R. Lucas, H. Gutleben, W. J. Choyke, and J. T. Yates, Jr., *Surf. Sci. Lett.* **273**, L441 (1992).
- ¹⁸H. N. Waltenburg and J. T. Yates, Jr., *Chem. Rev.* **95**, 1589 (1995).
- ¹⁹S. M. Gates, *Chem. Rev.* **96**, 1519 (1996).
- ²⁰D. D. Koleske, S. M. Gates, and J. A. Schultz, *J. Chem. Phys.* **99**, 5619 (1993); D. D. Koleske and S. M. Gates, *ibid.* **99**, 8218 (1993).
- ²¹D. D. Koleske, S. M. Gates, and B. Jackson, *J. Chem. Phys.* **101**, 3301 (1994).
- ²²D. D. Koleske, S. M. Gates, B. D. Thomas, J. N. Russel, Jr., and J. E. Butler, *J. Chem. Phys.* **102**, 992 (1995).
- ²³M. Xi and B. E. Bent, *J. Phys. Chem.* **97**, 4167 (1993).
- ²⁴J. Küppers, *Surf. Sci. Rep.* **22**, 249 (1995).
- ²⁵C. Lutterloh, A. Schenk, J. Biener, B. Winter, and J. Küppers, *Surf. Sci.* **316**, L1039 (1994).
- ²⁶C. Su, K.-J. Song, Y. L. Wang, H. L. Lu, T. J. Chuang, and J.-C. Lin, *J. Chem. Phys.* **107**, 7543 (1997).
- ²⁷J. C. Tully, *J. Chem. Phys.* **73**, 6333 (1980).
- ²⁸P. Kratzer and W. Brenig, *Surf. Sci.* **254**, 275 (1991).
- ²⁹B. Jackson and M. Persson, *J. Chem. Phys.* **96**, 2378 (1992); *Surf. Sci.* **269/270**, 195 (1992).
- ³⁰B. Jackson, M. Persson, and B. D. Kay, *J. Chem. Phys.* **100**, 7687 (1994).
- ³¹M. Persson and B. Jackson, *J. Chem. Phys.* **102**, 1078 (1995).
- ³²M. Persson and B. Jackson, *Chem. Phys. Lett.* **237**, 468 (1995).
- ³³B. Jackson and M. Persson, *J. Chem. Phys.* **103**, 6257 (1995).
- ³⁴B. Jackson and M. Persson, in *Elementary Processes in Excitations and Reactions on Solid Surfaces*, Springer Series in Solid State Sciences, Vol. 121, edited by A. Okiji, H. Kasai, and K. Makoshi (Springer, Berlin, 1996).
- ³⁵S. Caratzoulas, B. Jackson, and M. Persson, *J. Chem. Phys.* **107**, 6420 (1997).

- ³⁶D. V. Shalashilin, B. Jackson, and M. Persson, *Faraday Discuss.* **110**, 287 (1998).
- ³⁷C. Kalyanaraman, D. Lemoine, and B. Jackson, *Phys. Chem. Chem. Phys.* **1** (in press).
- ³⁸P. Kratzer and W. Brenig, *Z. Phys. B* **99**, 571 (1996).
- ³⁹P. Kratzer, *J. Chem. Phys.* **106**, 6752 (1997).
- ⁴⁰H. K. Shin, *J. Chem. Phys.* **96**, 3330 (1992); *Chem. Phys. Lett.* **244**, 235 (1995); J. Ree and H. K. Shin, *ibid.* **258**, 239 (1996); J. Ree, Y. H. Kim, and H. K. Shin, *J. Phys. Chem. A* **101**, 4523 (1997); Y. H. Ree, J. Ree, and H. K. Shin, *J. Chem. Phys.* **108**, 9821 (1998).
- ⁴¹X. Y. Chang, M. Perry, J. Peploski, D. L. Thompson, and L. M. Raff, *J. Chem. Phys.* **99**, 4748 (1993).
- ⁴²J. Strömqvist, L. Bengtsson, M. Persson, and B. Hammer, *Surf. Sci.* **397**, 382 (1998).
- ⁴³D. V. Shalashilin and B. Jackson, *J. Chem. Phys.* **109**, 2856 (1998).
- ⁴⁴J. Harris and B. Kasemo, *Surf. Sci.* **105**, L281 (1981).
- ⁴⁵M. Persson, J. Strömqvist, L. Bengtsson, B. Jackson, D. V. Shalashilin, and B. Hammer, *J. Chem. Phys.* **110**, 2240 (1999).
- ⁴⁶E. M. Cash, S. F. Parker, J. Pritchard, and M. A. Chesters, *Surf. Sci.* **215**, 363 (1989); G. Lee, D. B. Poker, D. M. Zehner, and E. W. Plummer, *ibid.* **357–358**, 717 (1996).
- ⁴⁷K. Christmann, R. J. Behm, G. Ertl, M. A. van Hove, and W. H. Weinberg, *J. Chem. Phys.* **70**, 4168 (1979).
- ⁴⁸G. Lee and E. W. Plummer, *Phys. Rev. B* **51**, 7250 (1995).
- ⁴⁹J. H. McCreery and G. Wolken, Jr., *J. Chem. Phys.* **63**, 4072 (1975); **64**, 2845 (1976); **67**, 2551 (1977).
- ⁵⁰J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).
- ⁵¹B. Hammer, M. Scheffler, K. W. Jacobsen, and J. K. Nørskov, *Phys. Rev. Lett.* **73**, 1400 (1994).
- ⁵²J. White, D. Bird, M. Payne, and I. Stich, *Phys. Rev. Lett.* **73**, 1404 (1994).
- ⁵³A. Gross, B. Hammer, M. Scheffler, and W. Brenig, *Phys. Rev. Lett.* **73**, 3121 (1994).
- ⁵⁴G. Weisenekker, G. J. Kroes, and E. J. Baerends, *J. Chem. Phys.* **104**, 7344 (1996).