

# The Effects of Lattice Motion on Eley-Rideal and Hot Atom Reactions: Quasiclassical Studies of Hydrogen Recombination on Ni(100)<sup>†</sup>

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Quasiclassical methods are used to simulate the interactions of H or D atom beams with D- or H-covered Ni(100) surfaces. The Ni substrate is treated as a multilayer slab, and the Ni atoms are allowed to move. The model potential energy surface is fit to the results of detailed total-energy calculations based on density functional theory. Most of the incident atoms trap to form hot atoms, which can eventually react with an adsorbate, or dissipate their energy and stick. The incident atom is found to lose several tenths of an eV of energy into the metal, upon initially colliding with the surface. This limits reflection to a few percent, at all coverages, and secondary reactions between adsorbates are significantly lowered. Long time hot atom reactions are also found to be damped out by the inclusion of lattice motion, leading to increased sticking, even at high coverages where dissipation into the adsorbates should be the primary energy loss mechanism. Overall, the inclusion of lattice motion is found to improve agreement with experiment.

## I. Introduction

Over the past decade, numerous experimental studies have appeared of Eley-Rideal and hot atom reactions of hydrogen atoms with hydrogen-covered single-crystal Ni, Cu, W, Pt, Ru, Al, Re, and Nb surfaces.<sup>1–16</sup> Most of these experiments have been kinetics studies, in which the surface is initially prepared with a known coverage of H and/or D atoms, and then exposed to a beam of D or H atoms. The formation (and desorption) of HD, D<sub>2</sub>, and H<sub>2</sub> products is then monitored as the coverages change over time. In some cases the internal product state and kinetic energy distributions have been measured.<sup>1–4,12</sup> For the direct Eley-Rideal (ER) reaction of an incoming gas-phase H atom with an H adsorbed on a metal surface, the recombination can be exothermic by over 2 eV, leading to very “hot” products. However, theory has suggested that the cross section for this direct ER reaction on metals is small,<sup>17–20</sup> typically below 1.0 Å<sup>2</sup>, and that most of the incident H or D atoms scatter from the adsorbates and/or the surface corrugation, forming trapped hot atoms.<sup>18–22</sup> These hot atoms are initially weakly bound to the metal, perhaps 2 eV or so above the ground state, and are highly mobile. If they react with another surface-bound species before fully equilibrating with the substrate, the product molecular hydrogen formed will also be highly excited. Both quasiclassical simulations<sup>21,22</sup> and kinetic modeling<sup>16,23–25</sup> of the experiments have demonstrated that this hot atom (HA) pathway dominates the formation of molecular hydrogen on several metals.

We recently studied these reactions on Ni(100), using quasiclassical trajectory methods and a potential energy surface fit to density functional theory-based total energy calculations.<sup>22</sup> Reactivity and sticking were examined as a function of the

surface coverage, to make a connection with the kinetics experiments<sup>6</sup> and several kinetic models developed for these reactions.<sup>16,23–25</sup> Earlier classical studies of H atom trapping on bare metal surfaces had shown that energy dissipation from the hot atom into the vibrations of the metal lattice was relatively inefficient.<sup>26,27</sup> Because of the small H-to-metal atom mass ratio, numerous H-substrate collisions were required before the atoms became fully accommodated, and relaxation times were on the order of a picosecond. Consequently, at high coverages, the primary mechanism for hot H atom relaxation should be scattering from the adsorbed H and D, due to the excellent mass match. Thus, as in our earlier quasiclassical studies on Cu-(111),<sup>21</sup> the metal lattice in the Ni(100) study was held fixed. While agreement with experiment<sup>6</sup> was good in many respects, our computed ER and HA reactivity was consistently too large, as was the probability for secondary reactions between the adsorbates, induced by the incident atom. We also found unusually large probabilities for reflection of the incident H or D atom. This is not surprising in the low-coverage limit, since scattering from the adsorbates is the only mechanism for relaxation of trapped hot atoms on a rigid lattice. However, we observed high reflectivity and high reactivity at relatively large coverages, where energy loss to adsorbates should be more important than lattice phonon excitation.

In this paper we present the results of quasiclassical studies of the reaction of gas-phase H and D atoms with D- and H-covered Ni(100), where the lattice atoms are allowed to move. We compare the rigid and moving lattice cases, and show that moving lattice effects can be important even at high adsorbate coverage. In particular, we will show that energy transfer into the lattice can be significant during the initial gas–surface collision, and that this leads to increased hot atom sticking and less molecular hydrogen formation. Allowing the lattice atoms

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to move also reduces the low-coverage reflectivity to nearly zero, in agreement with experiment. We note that in a recent study, Billing and co-workers have shown that lattice motion plays a role in ER reactions of H with H adsorbed onto graphite,<sup>28</sup> although the incident-to-substrate atom mass ratio is much larger in this case than for H atom reactions on metals. We also note that electron–hole pair excitations can contribute to adsorbate relaxation on metal surfaces.<sup>29–31</sup> While we do not include such excitations here, their contribution to hot H atom relaxation may be comparable to that of the lattice phonons. In section II we briefly describe our quasiclassical methods, the potential energy surface, and the total energy calculations used to fit this surface. In section III we compare the rigid and moving lattice results with each other, and with the experimental studies of Küppers and co-workers.<sup>6</sup> We close with a brief summary in section IV.

## II. Theory

In our previous paper<sup>22</sup> we provide detailed descriptions of our potential energy surface (PES) and the electronic structure calculations used to construct it, and we make only a few comments here. Ab initio total-energy calculations were performed using VASP (the Vienna ab initio simulation package), developed at the Institut für Materialphysik of the Universität Wien.<sup>32–34</sup> In this approach, based on density functional theory (DFT), the system is modeled using a slab supercell with periodic boundary conditions. The Kohn–Sham equations are solved using a plane wave basis set. The Ni slab is eight layers thick, with a vacuum space corresponding to 8 nickel layers separating the substrate and its repeatable images. Nonlocal exchange–correlation effects are considered in the form of a generalized gradient approximation, using the Perdew–Wang functional PW91.<sup>35</sup> The interactions between the ionic cores and the electrons are described by fully nonlocal optimized ultrasoft pseudopotential.<sup>36,37</sup> First, the interaction of a single H atom with the metal was computed as a function of the distance above the metal, over several high-symmetry sites. Our results were in excellent agreement with similar calculations using both ultrasoft pseudopotentials<sup>38</sup> and the projector augmented wave method,<sup>39</sup> as well as with experimental results.<sup>40,41</sup> We then computed the total energy for roughly 100 configurations of two H atoms over the Ni(100) surface. The adsorbed (target) H was placed in the hollow site and moved about the minimum, while the incident H atom was moved from the asymptotic region toward the target in a collinear and various noncollinear configurations important for ER and HA reactions.

We wish to accurately simulate the evolution of a large slab of Ni atoms, a sizable number of surface adsorbates, H migration into the bulk, and the reaction of two H atoms on the surface. Thus, the relatively straightforward approaches commonly used for rigid, periodic and impenetrable surfaces are not useful. We require a form where the H–metal and the H–H interactions in the presence of the metal are a function of the instantaneous positions of the Ni atoms. However, standard forms based on summed pair potentials have well-known difficulties. In this study we utilize a many-body PES of the form:

$$V(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}) = V_{\text{Ni}}(\{\mathbf{R}_\alpha\}) + \sum_i V^{\text{a}}(\mathbf{r}_i; \{\mathbf{R}_\alpha\}) + \sum_{i < j} V_{\text{aa}}(\mathbf{r}_i, \mathbf{r}_j; \{\mathbf{R}_\alpha\}) \quad (1)$$

where the  $i$ th H atom is located at position  $\mathbf{r}_i$ , and the  $\alpha$ th Ni atom is at  $\mathbf{R}_\alpha$ . The first term,  $V_{\text{Ni}}$ , describes the potential energy of the Ni slab. We use a form based on the embedded atom

model,<sup>42–44</sup> which accounts for the many-body character of the interatomic interactions in metals, and has been successfully used to study the dynamics and structure of Ni clusters.<sup>45,46</sup> The energy of each Ni atom is described to a large extent by an embedding term, which depends on the total electron density (of the other Ni atoms) at the location of the atom. There are also pairwise-additive Ni–Ni terms modifying the energy. The parameters in the potential were chosen to accurately reproduce numerous properties of bulk Ni and Ni<sub>2</sub>.<sup>43</sup>

In eq 1,  $V_{\text{a}}(\mathbf{r}_i)$  describes the interaction of a single H atom at  $\mathbf{r}_i$  with the Ni slab, and  $V_{\text{aa}}$  describes the additional interactions when two H atoms are near each other and the metal. In our simulations, most of the adsorbates remain in the hollow sites, with only the hot atom, and perhaps a few other mobile atoms, diffusing. Thus, we only very rarely have three H atoms in close proximity, and we monitor this in the simulations. We therefore truncate the expansion in eq 1 at the two-H terms  $V_{\text{aa}}$ . A PES of LEPS<sup>47,48</sup> (London–Eyring–Polanyi–Sato) form,  $V_{\text{L}}$ , is used to model the 2-H terms, where we define

$$V_{\text{aa}}(\mathbf{r}_i, \mathbf{r}_j) = V_{\text{L}}(\mathbf{r}_i, \mathbf{r}_j) - V_{\text{a}}(\mathbf{r}_i) - V_{\text{a}}(\mathbf{r}_j) \quad (2)$$

to avoid overcounting the H–metal interactions. The form used for  $V_{\text{L}}$  is that developed by DePristo and co-workers in their studies of H<sub>2</sub> and D<sub>2</sub> dissociation on Ni and Cu.<sup>49,50</sup> The H–metal components are described using ideas from effective medium theory,<sup>51</sup> and like the Ni–Ni interactions, consist of two terms. The first is an embedding energy determined by the total electron density at the position of the H, which describes the interaction with the conduction electrons. The second term describes the remaining localized interactions, and is defined by a sum over all two-body components. The electron densities, embedding terms, and adjustable parameters describing  $V_{\text{L}}$  were originally taken from or fit to lower-level theory or experiment by DePristo and co-workers. In this study, we instead fit all parameters to our computed DFT energies describing the single- and two-H configurations over Ni(100). Further details of this very complex PES will not be presented here, and the reader is referred to refs 22, 43–46, 49, and 50.

In our quasiclassical (QC) simulations the metal is represented by a slab of 1197 Ni atoms, seven layers thick, with a surface area of roughly 30 Å × 32 Å. At the start of each trajectory, the surface contains some coverage of D (or H) atoms, which are initialized with the ground state zero-point energy. The Ni atoms are initialized classically (no zero-point energy), corresponding to a temperature of 20 K. While the experiments of interest are at 120 K, our studies have shown that the thermal (at these relatively low temperatures) and zero-point energies of the lattice are not that important for these systems. The reason, as we shall see in the next section, is that the hot atom energies are on the order of eV, and the product distributions have temperatures of thousands of degrees. The incident H (or D) atoms, with an asymptotic energy of 0.07 eV, are aimed at a representative section of the surface, and the full system is evolved for up to 2.0 ps, using periodic boundary conditions. Finally, we note that because our PES is defined at each time step by the instantaneous positions of all the H, D, and Ni atoms, the potential gradient calculations and overall propagation are relatively computer time intensive. As a result, we run only about 2000 trajectories at each coverage for the moving lattice case, and 5000 trajectories for the rigid case.

## III. Results and Discussion

We begin by summarizing the essential features of our PES. First, the adsorbed H atoms are located in the hollow sites,

**TABLE 1: Quasiclassical Probabilities for Various Outcomes as a Percentage of the Total Trajectories Run<sup>a</sup>**

collision system	lattice type	coverage (ML)	HD formation	H <sub>2</sub> or D <sub>2</sub> formation	sticking	bulk H or D	reflection
D-on-H	rigid	0.93	0.64	0.18	0.04	0.10	0.03
D-on-H	moving	0.93	0.51	0.14	0.24	0.08	0.03
H-on-D	rigid	0.93	0.51	0.13	0.20	0.15	0.02
H-on-D	moving	0.93	0.34	0.07	0.43	0.14	0.01
H-on-D	rigid	0.50	0.22	0.04	0.25	0.26	0.23
H-on-D	moving	0.50	0.11	0.003	0.64	0.22	0.03
H-on-D	rigid	0.10	0.04	0.004	0.13	0.41	0.42

<sup>a</sup> The initial coverage is given in monolayers (ML). H-on-D refers to gas-phase H atoms incident on D-covered Ni(100). The Ni lattice is either rigid or moving, as indicated. If an atom penetrates into the bulk without returning to the surface by the end of the trajectory, we label it “bulk H or D.” Sticking and reflection refer to sticking and reflection of the incident atom, with no molecular hydrogen formation.

bound by 2.62 eV in the model PES, which is a bit less than in the DFT calculations. The H–metal binding over the other surface sites is less, but still on the order of 2 eV or more, and H atoms incident from the gas phase are strongly accelerated toward the metal. Second, with an adsorbed H fixed in the equilibrium binding site, an incident H is attracted to the adsorbate with a maximum attraction of about 1.0 eV (relative to the gas phase) in the collinear configuration, and about 1.7 eV when the H–H bond lies parallel to the surface.<sup>22</sup> Third, as the adsorbate and the incident particle both move away from the surface, this H–H attraction continues to increase (slowly, at first), such that there is no barrier. Thus there is no barrier to the formation of H<sub>2</sub>(g) via the direct ER pathway, which is exothermic by 2.1 eV. However, it is important to note that the nonreactive pathway, which leads to sticking of the incident H atom, also involves no barrier and is exothermic by 2.6 eV. In fact, the tendency of the PES is to steer the incident H atom away from the adsorbates and toward “unblocked” sites. The resulting reactivity per H–H collision is small. For our model PES, we computed the single collision ER cross section by placing a single D adsorbate on a rigid surface, and aiming the incident H atoms (at normal incidence) at impact points in the vicinity of the adsorbate. Integrating the resulting opacity function over the impact area gives a cross section for direct ER reaction of about 0.1–0.2 Å<sup>2</sup>, depending upon how one defines “direct”.<sup>25</sup> Thus, the tendency is for the incident or trapped/hot H atoms to inelastically collide with several adsorbates, losing energy along the way, before eventually reacting or sticking.

In Table 1 we summarize the results of seven QC studies. “H-on-D” refers to the case of gas-phase H incident on D-covered Ni(100), and “D-on-H” corresponds to the other isotopic combination. The lattice atoms move or are held rigid, as indicated, and the initial coverage is in monolayers (ML). The probabilities for primary reaction to form HD includes both direct ER and longer time HA contributions. The HA pathways dominate the formation of HD for all seven cases, for the reasons outlined in the preceding paragraph. Secondary reactions to form D<sub>2</sub> (H<sub>2</sub>) occur when incident or hot H (D) atoms knock adsorbed D (H) atoms free from the hollow sites, and after diffusing these D (H) atoms react with another adsorbed D (H). “Bulk H or D” refers to atoms which penetrate into the bulk and do not return to the surface by 2.0 ps. The remaining trajectories eventually stick into unoccupied hollow sites.

We see in Table 1 that allowing for lattice motion can significantly change reactivity and sticking, even at high coverages where energy transfer into the adsorbates should be the primary mechanism for hot atom relaxation. Consider first the rigid surface results, where for an initial coverage of 0.93 ML, molecular (HD plus D<sub>2</sub>) formation is the dominant outcome. This appears to be inconsistent with experiment.<sup>6</sup> In the experiments, to prepare some initial desired coverage, a bare

surface is exposed to beams of H or D. The saturation coverage is reached when the rate of adsorbate removal via (primary and secondary) molecular formation is equal to that of sticking. Experimentally, for D incident on Ni(100), this occurs at a coverage of  $\Theta = 0.97$  ML.<sup>6</sup> Ignoring isotope effects in the sticking and reactivity, the saturation coverage for our rigid surface model PES appears to be closer to 0.5 ML for H-on-D, and thus, our model PES appears to be too reactive. However, allowing the lattice to move significantly lowers the reactivity. For H-on-D, molecular (HD plus D<sub>2</sub>) formation roughly balances the rate of sticking at  $\Theta = 0.93$  ML, and this theoretical saturation coverage (again, ignoring isotope effects) is in excellent agreement with experiment. At coverages below saturation, experiment<sup>6</sup> has demonstrated that the initial rate of HD formation drops faster than linear in  $\Theta$ . The kinetic models have shown that this happens because trapped hot atoms are much more likely to stick than react when the coverage is below saturation.<sup>23,25</sup> For example, Küppers and co-workers<sup>6</sup> show that the initial rate of HD formation drops to roughly one-third for H-on-D when the D coverage drops from about 0.9 ML to 0.5 ML. Again, this is in excellent agreement with the moving lattice QC results. Note also that the attenuation in primary reactivity due to lattice motion is larger at lower coverages, where the hot atom-adsorbate collision (and reaction) rate is slower. We will show below how the inclusion of lattice motion can significantly damp out these longer time HA reactions.

The experiments do report small isotope effects in the primary reactivity, with the D-on-H combination being roughly 20% more reactive than H-on-D.<sup>6</sup> Both the rigid and moving surface results reproduce this trend, and more approximately, the magnitude. This small effect suggests that molecular formation and sticking should balance for D-on-H at a lower coverage than for H-on-D, but not significantly below 0.9 ML or so. For the rigid surface this is clearly not the case, with only 4% sticking. Allowing the lattice to move greatly improves things, although the D-on-H combination appears to be more reactive for our model PES than in the experiment.

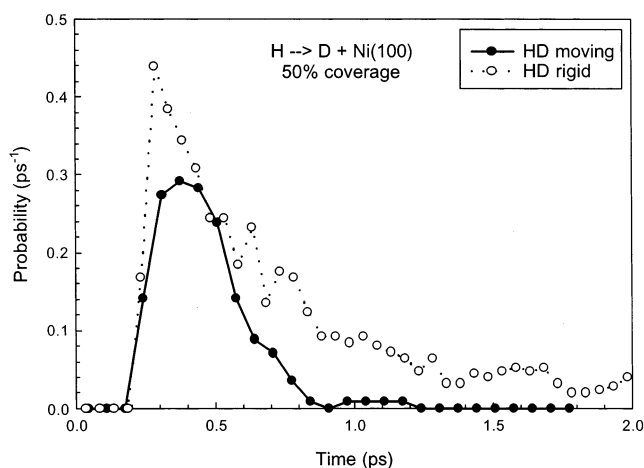
The rate of secondary reaction to form H<sub>2</sub> or D<sub>2</sub> is even more strongly effected by lattice motion, especially at lower coverages. Our kinetic model study contained a parameter  $\epsilon$ , the cross section for the creation of a mobile adsorbate, due to the collision of the incident atom with an atom initially at equilibrium in the hollow site.<sup>25</sup> Fitting this parameter to the experimental D<sub>2</sub> yield for the H-on-D case<sup>6</sup> lead to a value of  $\epsilon = 0.44$  Å<sup>2</sup>. At saturation coverage, where roughly half of these mobile hot atoms react, and half-trap, the rate of D<sub>2</sub> formation would be  $0.5 \epsilon \Theta$ . Using the experimental saturation coverage of 0.97 ML, and the fact that 1 ML = 0.16 atoms/Å<sup>2</sup> on Ni(100), we find that about 3.4% of the incident H atoms leads to D<sub>2</sub> formation in the experiments. Other kinetic models have derived similar relationships.<sup>23,24</sup> We observe that the rigid lattice model is again too reactive for the H-on-D case at saturation



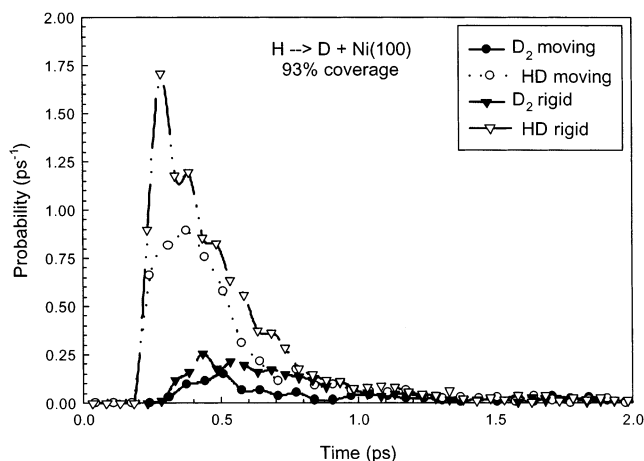
(13% D<sub>2</sub> formation), and that allowing the lattice to move greatly improves the agreement with experiment, although D<sub>2</sub> formation is still too large (7% vs 3.4%). The experiments also report that the rate of secondary reaction drops off rapidly with coverage. The kinetic models show that as the coverage drops below saturation, the probability that a hot atom sticks without reacting increases rapidly. For H-on-D, the rate of D<sub>2</sub> formation at  $\Theta = 0.5$  ML is over an order of magnitude smaller than for the  $\Theta = 0.97$  saturated surface.<sup>6</sup> Again, for the 0.5 ML H-on-D case, the moving lattice results are in better agreement with experiment, and the effects of lattice motion on secondary reactivity are large. Finally, experiment reports a greater rate of H<sub>2</sub> formation for the D-on-H case than D<sub>2</sub> formation for the H-on-D case. This is consistent with our model, and reflects the greater propensity for a heavy particle to perturb a light particle, than vice versa.

At lower coverages, for the rigid lattice case, we see an unusually large reflection, increasing to 42% at  $\Theta = 0.1$  ML. In contrast, the inclusion of lattice motion limits reflection to a few percent at all coverages examined. While the reflection of H atoms from Ni(100) has not been measured, our moving lattice results are consistent with what has been observed on other metals. For example, the sticking coefficient of H on bare Ni(111) and Ni(110) has been found to be 1.0<sup>14,52</sup> and 0.9,<sup>11</sup> respectively, and Rettner and Auerbach report only a few percent reflectivity of H and D atoms from D- and H-covered Cu(111) surfaces.<sup>4</sup> It is not surprising that reflection (plus bulk penetration) should approach unity at zero coverage, since there is no mechanism for relaxation of surface-trapped atoms at  $\Theta = 0$  in our rigid surface model. However, it is surprising that the effect is so large at 0.5 ML, where the highly mobile hot atoms undergo numerous collisions with the adsorbates, and one would not expect collisions with the considerably more massive Ni atoms to be important. We will show below that there is a significant amount of energy transfer into the lattice on the initial collision with the surface. As a result, most trajectories trap, and there is near zero reflectivity and near unity sticking, even at zero coverage. Finally, we observe a significant amount of penetration into the bulk, which is not significantly modified by lattice motion. This behavior has been observed for a number of metals, and Küppers and co-workers report that large amounts of H and D enter the subsurface region upon exposure of Ni(100) to atomic beams.<sup>5</sup>

We now look more closely at the reactions. In Figures 1 and 2 we plot probability distributions for HD reaction times, defined as the total time from the start of the trajectory to the time at which a product HD is 7 Å above the surface. The curves are normalized such that the area under each curve is equal to the probability for HD formation, as listed in Table 1. In Figure 2 we also plot the reaction time distributions for D<sub>2</sub>, similarly defined, and normalized to the probability for D<sub>2</sub> formation. Thus, the probabilities  $P(t)$  in Figures 1 and 2 are proportional to reaction rates for hot atoms surviving at time  $t$ . The maximum at 0.3 ps corresponds to direct ER processes, where HD is formed during the initial collision of the H atom with the surface. It is clear in both figures that a significant portion of the HD product is formed at longer times via HA pathways. For a coverage of 0.5 ML, lattice motion causes the long-time HA reactivity to damp out more quickly, lowering the overall reactivity. Because we add an additional mechanism for hot atom relaxation, this is expected. However, the short time direct ER component is also smaller. This is even more dramatic for the 0.93 ML case in Figure 2, where allowing the lattice to move lowers the ER component by roughly 50%, a significant



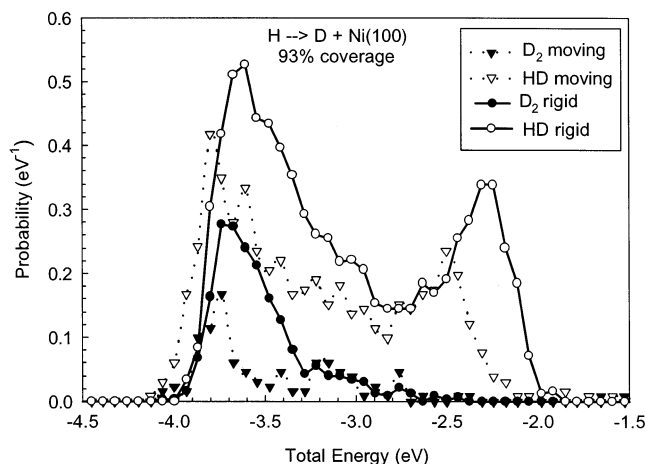
**Figure 1.** Probability distribution of reaction times, for H incident on a D-covered Ni(100) surface, with an initial D coverage of 0.5 ML. Results are shown for both a rigid and moving Ni lattice. The reaction time is defined as the total time between the start of the trajectory and the point at which the product molecule is 7 Å above the surface.



**Figure 2.** Same as Figure 1, but for 0.93 ML coverage. Results are shown for both primary HD and secondary D<sub>2</sub> products.

and unexpected result. There is also a sizable decrease in the hot atom component at this high coverage. This is also a bit surprising, since at this coverage one would expect that energy loss due to H–D collisions would be far more important than for H–Ni collisions. Comparing Figures 1 and 2, we see that the drop in HD formation with lattice motion is larger at lower coverages, when long time HA processes are more dominant. While secondary reactions to form D<sub>2</sub> also become less probable when the lattice is allowed to move, the distributions  $P(t)$  are of similar form, except for a scaling factor of roughly 2.

In Figure 3 we plot the probability distributions for the total product energy,  $P(E)$ , for both HD and D<sub>2</sub>, for the 0.93 ML H-on-D case. Again, the curves are normalized such that the area under each is equal to the reaction probability of Table 1. The minimum product energy is given by the model PES gas-phase HD binding energy of  $-4.7$  eV. The maximum product energy, equal to the adsorbate binding and zero-point energy, plus the incident H atom energy, is about  $-2.4$  eV.  $P(E)$  consists of two components. The first, peaked around the maximum energy, corresponds to direct ER and short time HA processes, where little energy is lost to the lattice and the nonreacting adsorbates. We find nonzero probability above  $-2.4$  eV because the incident/hot atom can (unphysically) gain energy from the zero-point energy of the adsorbates prior to reacting. The second component corresponds to longer time HA processes. There is

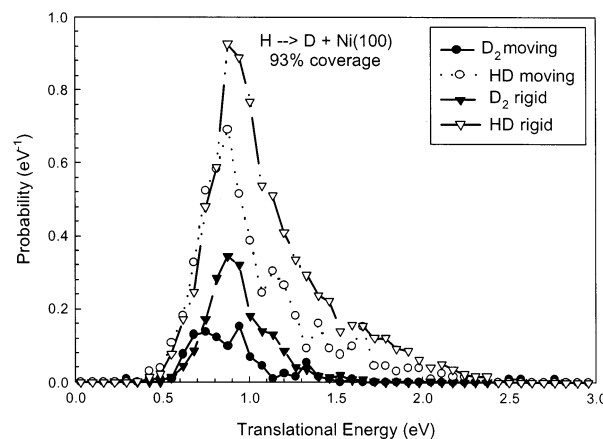


**Figure 3.** Probability distributions for the total (rotational plus vibrational plus translational) asymptotic energy of the product D<sub>2</sub> and HD molecules. Results are shown for the case of H incident on an D-covered Ni(100) surface, with an initial D coverage of 0.93 ML, for both a rigid and moving surface, as indicated. The potential energy minimum for HD is  $-4.7$  eV.

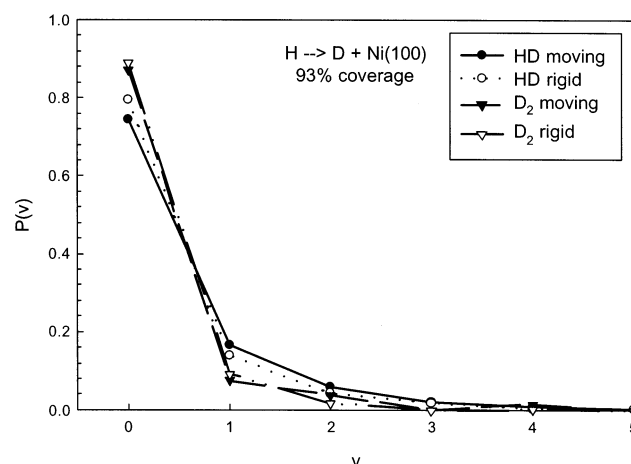
significant energy loss to the adsorbates and lattice, and the “thermal” form of this component suggests a certain amount of equilibration, which is not surprising since the hot atom residence times are on the order of a picosecond (see Figure 1). Lattice motion changes  $P(E)$  noticeably, attenuating both the short time ER and long-time HA components, as noted for Figure 1. In addition,  $P(E)$  shifts by roughly 0.15 eV, with the rigid and moving lattice average HD product energies being  $-3.08$  and  $-3.23$  eV, respectively.

While still relatively “hot,” the secondary product (D<sub>2</sub>) energies are much lower than for HD, since both D atoms are initially equilibrated with the surface. Given an initial energy for two adsorbed D atoms of  $-5.0$  eV, the incident H atom appears to transfer roughly an eV or more into a D atom, making it mobile. This energy transfer is significantly lowered by allowing the lattice to move, with average secondary product energies dropping by several tenths of an eV. Figure 2 suggests that the diffusion and reaction times of these mobile D atoms are similar to the long-time HA processes for the trapped incident H. The inclusion of lattice motion appears to lower secondary reactivity mostly by reducing the number of mobile D formed, in this case by roughly one-half.

In Figure 4 we plot the product center-of-mass translational energy distributions,  $P(K)$ , for the same cases as in Figure 3, with the same normalizations as in Figure 3. First, we see that a significant fraction of the HD product energy, and nearly all of the D<sub>2</sub> energy, is in translational motion. Second, this energy is noticeably lowered by the inclusion of lattice motion. The average kinetic energy for HD drops from 1.11 to 1.02 eV, when the lattice is allowed to move, accounting for much of the 0.15 eV shift in the total energy distributions of Figure 3.  $P(K)$  does not shift to lower energies, however, and we instead observe an attenuation of the high energy components due to lattice motion. All four curves have the same relatively sharp cutoff around 0.5 eV, a result of barriers to hydrogen recombination in the exit channel, along the center-of-mass translational coordinate.<sup>22</sup> For our PES, the barriers to recombination over the (most favorable) bridge and hollow sites are roughly 0.5 eV above the energy of the gas-phase product. We note, however, that we did not compute DFT energies or fit our PES in this region of configuration space, and that in a study of dissociation and recombination on Ni(100), Kress found barriers of 0.15 and 0.35 eV over the bridge and hollow sites,



**Figure 4.** Center-of-mass translational kinetic energy distributions for both the product HD and D<sub>2</sub> molecules formed for H incident on D-covered Ni(100). The initial coverage is 0.93 ML, and results are shown for both a rigid and moving surface, as indicated.

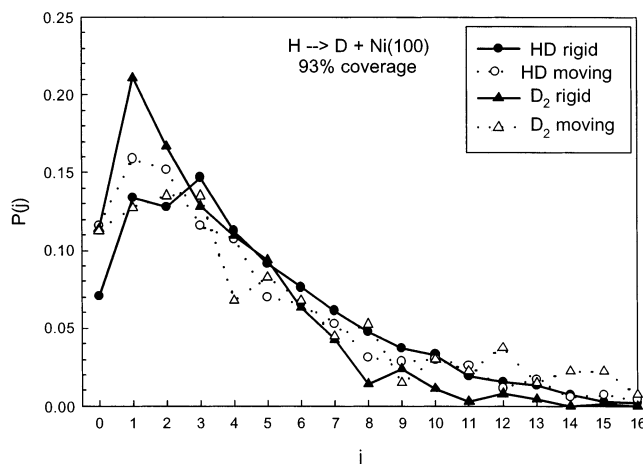


**Figure 5.** Rotationally summed vibrational distributions for both the HD and D<sub>2</sub> molecules formed for H incident on D-covered Ni(100). The initial coverage is 0.93 ML, and results are shown for both a rigid and moving surface, as indicated.

respectively.<sup>53</sup> The sharp cutoff in  $P(E)$  in Figure 3, well above the minimum allowed energy of  $-4.7$  eV, is also a consequence of these barriers.

In Figures 5 and 6 we plot the product vibrational and rotational distributions, respectively, for the same cases as in Figures 3 and 4. Each distribution is normalized to 1. There is relatively little internal excitation of the product, with the rotational and vibrational degrees of freedom containing only a few tenths of an eV (above the vibrational zero-point energy). Some of this is due to the small per-collision reaction probability on Ni(100); the hot atoms diffuse for a longer time, and lose more energy to the nonreacting adsorbates and the lattice. However, for Ni(100), even molecules formed via direct ER or short time HA pathways are not significantly excited internally. The effect of lattice motion is only very minor for product internal energies. Average rotational and vibrational energies drop by only tens of meVs each when the lattice is allowed to move. For the secondary products we see similar results, with even less internal excitation than in the primary products, as expected. Finally, we note that the product energy distributions at lower initial coverages are not significantly different from those in Figures 3–6.

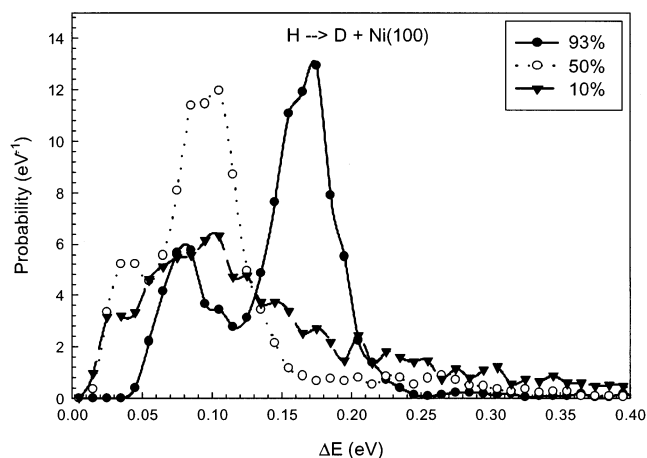
While hot atom processes dominate on both surfaces, the product state distributions of HD formed on Ni(100) are very different from HD formed on Cu(111). For example, on Cu-



**Figure 6.** Vibrationally summed rotational distributions for both the HD and D<sub>2</sub> molecules formed for H incident on D-covered Ni(100). The initial coverage is 0.93 ML, and results are shown for both a rigid and moving surface, as indicated.

(111), both experiments<sup>3,4</sup> and rigid-lattice QC simulations<sup>21</sup> find products with much more internal excitation, similar to that found in the translational degrees of freedom.<sup>3,4,21</sup> There is more energy in the products overall, and there is no low-energy component to  $P(E)$  for Cu(111). We have observed that the reactivity per H–D collision is larger on Cu(111) than on Ni(100), and thus the HA reaction time scales are shorter and there is less energy loss to the adsorbates and the lattice.<sup>21,22</sup> This is in agreement with Küppers and co-workers, who were able to reproduce the different kinetics observed for molecular Hydrogen formation on Ni(100) and Cu(111), by assuming in their kinetic models<sup>23,24</sup> that hydrogen atom collisions on Cu(111) were 10 times more reactive than on Ni(100). The relatively long HA reaction times on Ni(100) lead to energy distributions which look more Boltzmann-like, particularly the low-energy component of  $P(E)$  in Figure 3, and the internal state distributions  $P(v)$  and  $P(j)$ . However, close inspection reveals that these are only very approximately Boltzmann, and correspond to very high “temperatures.” For example, the low-energy component of  $P(E)$  and the translational distribution  $P(K)$  have “temperatures” of roughly 5000 K, the vibrational temperature is on the order of 4000 K, and the rotational distribution is much cooler, around 1000–2000 K. The products are thus still quite hot.

We now examine more closely why lattice motion has a larger effect than expected. The observed behavior is not consistent with the simple addition of an extra energy sink for the long time HA processes. In Figure 7 we plot probability distributions for  $\Delta E$ , which is approximately equal to the energy transferred from the incident H atom into the lattice during its initial collision with the surface. Unfortunately, it is not possible to rigorously separate the energy of an H atom from that of the lattice when the H atom is on the surface, and this  $\Delta E$  is approximate. The incident H is aimed at a target area containing four surface Ni atoms. We monitor the total kinetic energy of these four Ni atoms for a period of 0.028 ps immediately following the initial collision of the incident H with the surface. The largest value for this total kinetic energy during this period is set equal to  $\Delta E$ . Given that the initial kinetic energy of the atoms is negligible compared to the energies of Figure 7, and that the time interval is short compared to Ni–Ni and adsorbate–Ni energy transfer time scales, this is a very reasonable measure of energy transfer into the Ni lattice. We see that the energy transfer is large, complicated, and coverage dependent. The magnitude makes sense when we consider that the incident H



**Figure 7.** Probability distributions for  $\Delta E$ , the amount of energy transfer into the metal lattice during the initial collision of an H atom with a D-covered Ni(100) surface. The initial D coverages are 0.1, 0.5, and 0.93 ML, as indicated.

atom is strongly accelerated toward the surface. For a gas-phase collinear hard-sphere collision between a Ni atom and an H atom with energy equal to the asymptotic energy (70 meV) plus an average attraction to the metal of 2.2 eV, the energy transfer  $\Delta E$  is about 0.15 eV, in good agreement with the distributions in Figure 7. Understanding the details of  $P(\Delta E)$ , including the coverage dependence, is nontrivial. First, adding D to the surface changes the properties of the surface phonons. A good discussion and list of references for this can be found in ref 54. Typically, the surface layer of a bare metal relaxes inward. An excess surface (pseudo)charge leads to a radial Ni–Ni force constant that is weaker than in the bulk. The addition of surface Hydrogen, acting as an electron acceptor, lowers the excess charge on the surface Ni atoms, increasing the radial force constant, and often reversing the surface relaxation.<sup>54</sup> Thus, the lattice “stiffness” is increased. Changes in the detailed nature of the surface phonons can also change the H-metal phonon couplings.<sup>54</sup> The D overlayer also changes the H-metal interaction, weakening the attraction, and possibly lowering  $\Delta E$  in the presence of adsorbates. When the incident H hits a D adsorbate more-or-less directly, much of the energy should go into the D, again lowering  $\Delta E$ . While the average  $\Delta E$  decreases from 0.16 eV to 0.11 eV as  $\Theta$  increases from 0.1 to 0.5 ML, it goes back up to 0.15 eV for  $\Theta = 0.93$  ML. However, the transfer of large amounts of energy, i.e.,  $\Delta E$  above about 0.2 eV, does decrease consistently as the coverage increases. Finally, we note that the distributions in Figure 7 exhibit a peaked structure, which shifts with coverage, whose origins are not clear to us.

During this initial collision with the surface, the energy of the incident H atom is directed normal to the surface, optimizing energy transfer into the metal due to lattice recoil. After this initial collision, much of the atom’s energy is parallel to the surface, and the energy dissipation into the lattice is considerably slower. The primary consequence of including lattice motion appears to take place during this initial collision. The (average) loss of total product HD energy due to lattice motion of 0.15 eV corresponds well to  $P(\Delta E)$  in Figure 7. Because of the energy loss during the initial impact, it is much less likely that an adsorbed D atom will be knocked out of its (laterally) bound state, leading to a sizable suppression of secondary product formation. Also, because this  $\Delta E$  is typically comparable to or larger than the incident asymptotic H atom energy, reflection drops to only a few percent.



#### IV. Summary

In conclusion, we have implemented quasiclassical studies of the interaction of H and D atom beams with D- and H-covered Ni(100) surfaces, using a PES fit to DFT calculations. The PES allows for motion of the Ni atoms, as well as penetration of H and D atoms into the bulk. This study focuses primarily on the effects of lattice motion. We find that upon the initial collision with the moving surface, the incident atom, because of its significant acceleration directed normal to the surface, transfers a relatively large amount of energy into the lattice, on the order of 0.15 eV. This limits reflection of the incident atom to only a few percent at all coverages, consistent with experiment, and in contrast to rigid-lattice models at low coverages. This energy loss also decreases the probability that an adsorbate is knocked out of its (lateral) bound state during the initial collision. The resulting decrease in secondary product formation further improves our agreement with experiment. This lattice recoil effect also lowers the direct ER reaction probability. The moving lattice also acts as an energy sink for the hot atoms, even at relatively high coverages, where collisions with adsorbates should be the dominant mechanism for relaxation. Overall, this energy loss into the lattice significantly increases the probability for sticking of the incident atom, at the expense of reaction, especially at low coverages. While dissipation of the hot atom's energy into the lattice lowers the energy of the HA products, this effect seems to be secondary to the energy loss during the initial collision, which scales closely with the shift in the HD product total energy distribution when the lattice is allowed to move. Most of this energy loss (due to lattice motion) comes out of product center-of-mass translational motion. The product rotational and vibrational distributions are not significantly affected by lattice motion.

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