

Surface Temperature Dependence of Rotational Excitation of H₂ Scattered from Pd(111)

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Classical dynamics simulations are performed to study rotational excitation of H₂ scattered from Pd(111), taking into account energy exchange with surface phonons through a 3D surface oscillator model. We show that dynamic trapping, identified recently in the study of dissociation dynamics, plays a prominent role. The corresponding long interaction time due to several recollisions allows an efficient energy exchange between H₂ molecules and surface phonons. This microscopic mechanism explains the puzzling experimental finding on the role of surface temperature in H₂($\nu = 0, J = 1 \rightarrow 3$) excitation.

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Studies on H₂-surface interactions have an intrinsic interest and are also used as a prototype for understanding some chemical reactions on surfaces. Many theoretical and experimental works have been devoted to dissociative adsorption, desorption, and inelastic scattering of H₂ from different metal surfaces (see [1–4] and references therein). In most theoretical studies, the H₂-surface energy exchange (through electronically nonadiabatic effects and coupling with phonons) is neglected. Such an approximation appears to be justified for the study of some observables such as the initial sticking coefficient S_0 , because experimental results do not show an appreciable variation of S_0 with surface temperature, T_s . Nevertheless, experimental evidence of important H₂-surface energy exchange effects has been recently reported [5–8]. For H₂/Pd(111), state-to-state rotational excitation probabilities are strongly dependent on T_s , and rotational excitation occurs even when the incident H₂ translational energy, E_i , is lower than the energy level spacing between the initial and the final rotational states [8]. In this case, part of the excitation energy comes obviously from the surface and not only from energy transfer from translational to rotational molecular degrees of freedom.

Usually, H₂-surface phonon energy exchange is believed to be unimportant due to the large mass mismatch since the energy exchange in a H-metal atom elastic collision is $4m_M m_H E_i / (m_M + m_H)^2$ (m_M and m_H : metal and H atomic masses). Accordingly, the important energy exchange observed in [8] appears very puzzling if one pictures the reflection process as consisting of a single collision with the surface and no compelling explanation has been proposed. The main purpose of this work is to try to unveil the dynamic mechanism behind the important energy exchange effects leading to the unexpected experimental results found for H₂/Pd(111).

The large energy gap between H₂ rotational states might be considered as an argument against the use of classical methods in the description of excitation processes such as H₂($\nu = 0, J = 1 \rightarrow 3$). On the other hand, for sys-

tems such as H₂/Pd(111) (for which dissociative adsorption is nonactivated), it is important to consider all six molecular degrees of freedom in the dynamics. Therefore, the inclusion of molecule-phonon coupling requires a model of dimensionality higher than six. Though full six-dimensional quantum calculations for H₂ interacting with a *frozen* surface are now possible [2,4], the addition of molecule-phonon coupling is still beyond the scope of current state-of-the-art quantum methods. Therefore, until now, all quantum calculations including molecule-surface energy exchange have discarded some of the molecular degrees of freedom. Semiclassical methods, in which the thermal bath of phonons is treated classically, meet with difficulties [1] and are still under development even for the simpler case of atom/surface interactions (see [9] and references therein). Accordingly, we have adopted here a classical approach. This choice is supported by several studies showing that, as far as rotation is concerned, classical trajectory calculations give usually the same qualitative results as the quantum ones and, often, the agreement is quantitative [1,2,4,10].

To describe the H₂-surface phonon coupling, we use the *surface oscillator model* [11,12]. The motion of surface atoms is described through a 3D harmonic oscillator with coordinates $(X_S, Y_S, Z_S) = \mathbf{R}_S$. The H₂-surface phonon coupling is described by a space rigid shift \mathbf{R}_S of the 6D potential energy surface (PES) V_{6D} , corresponding to H₂ interacting with a frozen Pd(111) surface [13]. The 9D PES in this approximation is given by

$$V_{9D}(\mathbf{R}_A; \mathbf{R}_B; \mathbf{R}_S) = V_{6D}(\mathbf{R}_A - \mathbf{R}_S; \mathbf{R}_B - \mathbf{R}_S) + \frac{m_{\text{Pd}}}{2} (\omega_x^2 X_s^2 + \omega_y^2 Y_s^2 + \omega_z^2 Z_s^2), \quad (1)$$

where $\mathbf{R}_{A,B}$ define the positions of H atoms (denoted by A and B) and $\omega_{x,y,z}$ the surface oscillation frequencies. A classical description of the lattice dynamics is suitable because, in the present case, it is expected that multiphonon

processes dominate the molecule-surface energy exchange. Even for low initial energies, H_2 molecules acquire an important amount of translational energy before *knocking* a repulsive part of the PES because the $H_2/Pd(111)$ PES is attractive and presents a deep molecular chemisorption well in the entrance channel [13].

Using the surface oscillator model, we obtain results in excellent agreement with the experimental data. From a detailed inspection of the results of our dynamical simulations, we present a simple physical interpretation of the experiments [8].

This work is focused on the $H_2(\nu = 0, J = 1 \rightarrow 3)$ rotational excitation process. We perform simulations within the so-called *classical* approach, without the initial molecular vibrational zero point energy. The criteria for dissociation and reflection are the same as in [14]. The 6D PES V_{6D} , has been obtained from *ab initio* calculations [13] and is very similar to that described in [15]. Some improvements have been made especially in the entrance reaction channel which is very important for the dynamics of $H_2/Pd(111)$ [16,17]. The initial position and velocity of the surface atoms are generated from a Boltzmann distribution. It is expected that the most important contribution to the molecule-surface coupling comes from the localized surface phonon modes. Then, we have chosen the oscillation frequencies: $\omega_x = \omega_y = 6 \times 10^{-4}$ a.u. and $\omega_z = 4 \times 10^{-4}$ a.u. which correspond to the well localized surface modes [18] at the symmetry point \bar{K} found for Pd(111). The above value of ω_z is in very good agreement with the available experimental data [19]. Although the surface modes at point \bar{K} are associated with some distortion of the surface plane, the wavelength of this distortion is larger than the equilibrium Pd-Pd distance. Obviously, this distortion is not described by the surface oscillator model used in this work. However, due to the quite large distortion wavelength, the impinging H_2 molecule can still encounter a local plane patch of the surface. To evaluate the sensitivity of the results given below to the frequencies used in the simple oscillator model, we have done additional calculations with $\omega_x = \omega_y = \omega_z = 4 \times 10^{-4}$ a.u. corresponding to another localized surface mode and found a very small variation of the results. This implies that the presence of a thermal bath is important, but the more detailed dynamics of the surface atoms is less crucial. All statistical quantities are obtained with 10000 trajectories for each value of E_i and T_s .

Figure 1 shows the distribution of the total energy change, ΔE , of molecules scattered from the surface at $T_s = 450$ and 850 K with $E_i = 48$ meV. Each distribution is normalized to the corresponding total reflection probability: $P_{\text{ref}}(T_s = 450 \text{ K}) = 0.39$ and $P_{\text{ref}}(T_s = 850 \text{ K}) = 0.42$. P_{ref} does not vary much with T_s in agreement with the experimental observation that the initial sticking probability is nearly independent of the surface temperature [8]. The dispersion of ΔE ($-50 \text{ meV} < \Delta E < 150 \text{ meV}$) shown in Fig. 1 results directly from

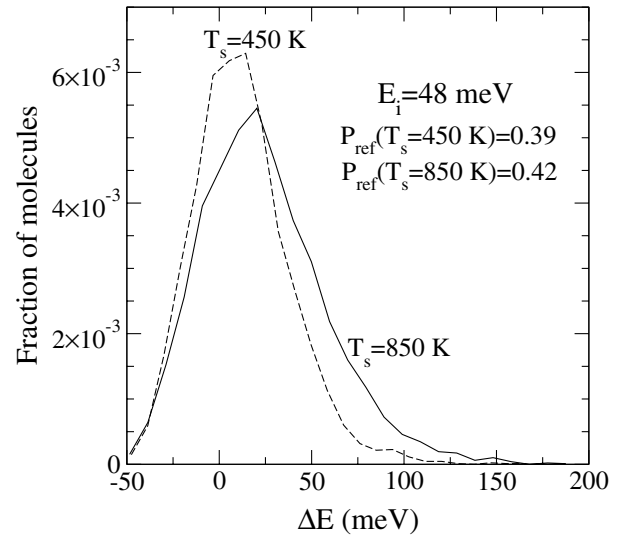


FIG. 1. Distribution in total energy change of molecules scattered from the surface with $E_i = 48$ meV. Dashed line: $T_s = 450$ K; full line: $T_s = 850$ K.

the H_2 -surface energy exchange since a δ -function distribution centered at $\Delta E = 0$ would be obtained in the case of a frozen surface. Dynamical coupling between H_2 and surface atom motions has been also found by Olsen *et al.* in a low dimensional (3D) quantum study of direct subsurface absorption of H_2 on Pd(111) [20].

In Fig. 1 we see that the distribution is broadened and shifted to larger positive values of ΔE when T_s increases. This shows clearly that the reflected molecules gain more energy from the surface at higher temperatures. Nevertheless, this does not mean that the surface supplies energy to all impinging molecules. What is shown in Fig. 1 is that the majority of reflected molecules have gained energy. Molecules losing energy are more likely to be adsorbed.

To characterize the rotational state $J = 3$ in our classical simulations, an energy window, $[E_{\text{rot}}^<, E_{\text{rot}}^>]$, is defined ($E_{\text{rot}}^< = 0.5 [E_{\text{rot}}(2) + E_{\text{rot}}(3)] = 66$ meV and $E_{\text{rot}}^> = 0.5 [E_{\text{rot}}(3) + E_{\text{rot}}(4)] = 119$ meV with $E_{\text{rot}}(J)$ denoting the energy of a quantum rigid rotor representing the H_2 molecule in state J). A reflected molecule with E_{rot} within this window is considered as in the $J = 3$ state.

In Table I, we present the mean translational energy of scattered molecules undergoing the $J = 1 \rightarrow 3$ transition

TABLE I. Mean translational energy of scattered molecules undergoing the $J = 1 \rightarrow 3$ transition at $T_s = 850$ K.

Initial energy (meV)	Final energy (meV)	
	Experiments [8]	Theory
35	35 ± 9	32.0
48	34 ± 7	32.1
75	30 ± 5	34.8

at $T_s = 850$ K. There is an excellent agreement with the experimental results [8]. Moreover, we have checked that this agreement does not deteriorate if we slightly modify the energy window in the definition of the $J = 3$ state. The 3D surface oscillator model proposed here accounts accurately for the magnitude of the H_2 -surface energy exchange.

One very interesting experimental observation of Watts and Sitz [8] is that the surface temperature dependence of the rotational excitation probability is well described by an Arrhenius-type expression. Moreover, the corresponding apparent activation energy, E_a , is lower than the rotational energy level spacing and decreases as E_i increases. In Fig. 2, we plot the logarithm of the $J = 1 \rightarrow 3$ rotational excitation probability as a function of T_s^{-1} for $E_i = 35$, 48, and 75 meV together with the experimental data [8]. The absolute values of the probabilities have not been determined in Ref. [8]. What is really important in this comparison between theory and experiment is the linear dependence on T_s^{-1} and the variation of slope (associated to E_a) with E_i . Both behaviors are very well reproduced by our simulations. The apparent activation energies obtained from our calculations are very close to those found by Watts and Sitz [8]. We have also compared the absolute values of $P_{\text{ref}}(J = 1 \rightarrow 3)$ with the available experimental data [6] obtained at $T_s = 423$ K (very close to the value of 450 K considered in our calculations). For $E_i = 35$, 48, and 75 meV, we obtain absolute $J = 1 \rightarrow 3$ rotational excitation probabilities equal to 0.0086, 0.0166, and 0.0394 in good agreement with the experimental data shown in Fig. 6 of [6].

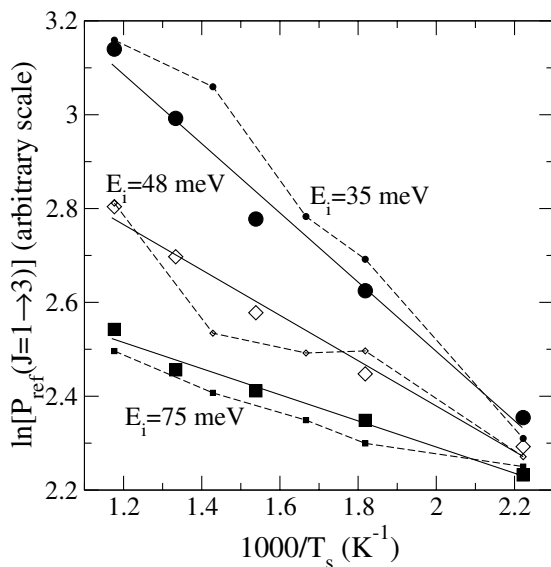


FIG. 2. Probability of the $J = 1 \rightarrow 3$ rotational excitation as a function of T_s^{-1} for $E_i = 35$, 48, and 75 meV. Large symbols: experimental data [8]; full lines: linear fit to experimental data; small symbols connected by dashed lines: present theoretical results.

We have now to understand the microscopic mechanism behind the efficient H_2 -surface energy exchange which is puzzling having in mind the traditional viewpoint based on the mass difference. In our previous studies on H_2 interacting with a frozen Pd(111) surface [16,17], we have found that *dynamic trapping* plays an important role at low energies. In the case of a frozen surface, *dynamic trapping* results from an energy transfer between the various degrees of freedom as the molecule approaches the surface. Because of this transfer, the energy of motion perpendicular to the surface may be reduced to such an extent that the escape from the attractive potential well is no longer possible during some time. A study of interaction times shows that, in the present case, *dynamic trapping* is the microscopic mechanism allowing an important molecule-surface energy exchange through recollisions. Let $t_{\text{min}}^{\text{diss}}$ ($t_{\text{min}}^{\text{ref}}$) be the minimum time required for dissociation (reflection). We have found that, for many molecules, dissociation (reflection) takes place after a period equal to several times $t_{\text{min}}^{\text{diss}}$ ($t_{\text{min}}^{\text{ref}}$): There is a large dispersion in interaction times. The molecules reflected after a time close to $t_{\text{min}}^{\text{ref}}$ have made only one collision with the surface. The others undergo recollisions with the surface before being reflected. For instance, for $E_i = 48$ meV and $T_s = 450$ K, we find that the reflection of molecules excited into the $J = 3$ state starts at $t = 1.4t_{\text{min}}^{\text{ref}}$ and most of these molecules are reflected after more than twice $t_{\text{min}}^{\text{ref}}$. One important thing we learn from these results is that the efficiency of molecule-surface energy exchange is determined not only by the mass difference between the molecule and surface atoms: The interaction time plays an important role.

The above microscopic mechanism provides an explanation for the dependence of the rotational excitation probability on T_s and the variation of E_a with E_i observed experimentally as well as in our simulations. The interaction of the molecule with the surface proceeds through three steps. In the first step, it approaches the surface. In the second, the molecule is dynamically trapped near the surface. In the last step, it recedes from the surface. In all of these steps, energy exchange takes place between the various degrees of freedom, in particular, with rotation (as in the case of a frozen surface). We denote by $E_{\text{rot}}(T \rightarrow R)$ the corresponding transfer of energy from translation to rotation over the whole collisional process. In addition, in the second step, the molecule gains energy through its interaction with surface phonons which play the role of a thermal bath at temperature T_s . The probability for a molecule to gain the rotational energy ΔE_{ph} is proportional to $\exp(-\Delta E_{\text{ph}}/k_B T_s)$ where k_B is Boltzmann constant. (This expression is justified for molecular energies close to the mean energy of the surface phonons. For the impact energy and surface temperature ranges considered here, this condition is satisfied.)

For molecules undergoing the $J = 1 \rightarrow 3$ transition, ΔE_{ph} must be equal to $E_{\text{rot}}(3) - E_{\text{rot}}(1) - E_{\text{rot}}(T \rightarrow R)$.

Accordingly, the probability for a $J = 1 \rightarrow 3$ excitation is proportional to $\exp(-E_a/k_B T_s)$ with

$$E_a = E_{\text{rot}}(3) - E_{\text{rot}}(1) - E_{\text{rot}}(T \rightarrow R). \quad (2)$$

Beside $E_{\text{rot}}(3) - E_{\text{rot}}(1)$, the apparent activation energy involves a term resulting from the energy transfer from translation to rotation, $E_{\text{rot}}(T \rightarrow R)$. Considering the attraction felt by H_2 molecules in the entrance channel, the clearly different values of E_a for initial energies which are small and close to each other (see Fig. 2) might seem surprising. However, it must be noted that, for reflected molecules, the kinetic energy gained in the approach to the surface is *lost* on the way back to the vacuum. So, the rotational energy that must be gained from the thermal bath (i.e., E_a) varies only with $E_{\text{rot}}(T \rightarrow R)$ which is mainly determined by E_i [e.g., $E_{\text{rot}}(T \rightarrow R) \leq E_i$]. For the lowest values of E_i , $E_{\text{rot}}(T \rightarrow R)$ is necessarily small and E_a must be close to the rotational energy gap, i.e., $E_{\text{rot}}(3) - E_{\text{rot}}(1)$. As E_i increases, $E_{\text{rot}}(T \rightarrow R)$ increases also, which leads to a decrease in E_a . This is precisely what has been found in both experiments and our calculations (see Fig. 2 where the slope is smaller when E_i increases).

In summary, we have studied rotational excitation of $\text{H}_2(\nu = 0, J = 1)$ scattered from Pd(111) taking into account molecule-surface phonon energy exchange. For a given initial translational energy, the surface temperature dependence of the rotational excitation probability follows an Arrhenius law as found experimentally. The variation of the apparent activation energy with the initial translational energy and the mean translational energy of molecules scattered in the $J = 3$ rotational state are in remarkably good agreement with experimental data. It has been shown that the rotationally excited reflected molecules have undergone recollisions with the surface before being scattered back into the gas phase.

The fact that molecules can be *dynamically trapped* near the surface as a result of energy exchange from translation to the other molecular degrees of freedom is a simple idea that has been considered by several authors. In this Letter, we show that this microscopic scattering mechanism provides the explanation for the puzzling experimental finding that H_2 can efficiently exchange energy with the Pd(111) surface so as to produce its rotational excitation. Accordingly, the experimental findings of Watts and Sitz [8] support the idea that dynamic trapping is an important dynamic process for some molecule-surface collision processes [e.g., $\text{H}_2/\text{Pd}(111)$] at low energies. An important H_2 -surface energy exchange has been also found in the $\text{H}_2(\nu = 1, J = 1 \rightarrow \nu = 0, J = 3)/\text{Pd}(111)$ process but Gostein and co-workers concluded that it is due to electron-

hole excitations [5]. We plan to extend our work to study this vibrational relaxation process.

Similar experimental results on surface temperature dependence of $\text{H}_2(\nu = 0, 1; J = 1 \rightarrow \nu = 0, 1; J = 3)/\text{Cu}(100)$ excitation probabilities have been published after submission of this article [21,22]. Some of the arguments used here might be also valid for $\text{H}_2/\text{Cu}(100)$. However, given the important differences between the corresponding PESs, a separate study is necessary.

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