Vibrational Relaxation of H_2 ($v = 1, J = 1$) on Pd(111)

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We have observed the relaxation of H_2 from the rovibrational state ($v = 1, J = 1$) into ($v = 0$, $J = 5$, and $J = 7$) upon scattering from Pd(111). The relaxation probability is 0.04 ± 0.01 into $J = 5$ and 0.03 ± 0.01 into $J = 7$. Relaxation does not occur when the surface is saturated with H atoms at low temperature. Furthermore, relaxation occurs with significant loss of vibrational energy, 50–120 meV, to the substrate. The relaxation mechanism is most likely electronically nonadiabatic. The survival probability of the incident H_2 ($v = 1, J = 1$) is 0.05 ± 0.01 for a clean surface, but nearly unity for an H-saturated surface. [S0031-9007(97)04200-2]

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The dissociative adsorption of a molecule upon a solid surface is a fundamental step in many surface chemical processes and has therefore been the subject of intense study [1,2]. Considerable attention has been focused on the role of molecular vibration in activated dissociation. In the model system of H_2 adsorption on copper, for example, molecular vibration promotes dissociation [2,3]. This occurs because the activation barrier is located "late" along the reaction pathway, i.e., at a significant extension of the molecular bond. The late barrier also results in the coupling of translational and vibrational degrees of freedom during a scattering event, permitting vibrational excitation and deexcitation [4]. State-resolved measurements which explore these effects provide a stringent test of the calculated potential energy surface (PES) and dynamics. While vibrational excitation in gas-surface scattering has been directly observed for H_2 on Cu [5] and for NO on Ag [6] and Cu [7], so far vibrational deexcitation channels have not been directly observed. However, the loss of H_2 ($v = 1$) upon scattering from Cu at low translational energies has been interpreted in terms of vibrational deexcitation [8–10].

For H_2 on Pd, dissociation occurs readily, implying the absence of an activation barrier. Nonetheless, vibrational heating of H_2 desorbing from Pd(100) has been observed [11]. From the principle of detailed balance, this suggests that the sticking coefficient of vibrationally excited H_2 on Pd should be larger than that of the ground state molecule. Several authors have tried to reconcile this observation with the apparent lack of an activation barrier. Darling and Holloway pointed out that one must consider a distribution of barrier heights to dissociation for different approach geometries of the incident molecule [12]. In this case some paths will be activated and others will be nonactivated. Gross and Scheffler examined this point in more detail in their study of vibrational effects in H_2 dissociation on Pd(100) [13]. They performed dynamical simulations on an *ab initio* potential energy surface, which included all six coordinates of the two H atoms. They found that while some reaction pathways are nonactivated, the majority of pathways are activated, such that an average over impact parameter and orientation gives a nonzero energy barrier to dissociation. Furthermore, their calculations show that molecular vibration does enhance dissociation. However, they argued that the vibrationally enhanced dissociation of H_2 on Pd is not due to a late activation barrier or strongly curved reaction path, as assumed previously. Instead, they argued that the softening of the molecular vibration near the surface results in vibrational energy becoming available to carry the molecule along the reaction path. Because of the absence of a late barrier, they predicted that vibrationally inelastic transitions in the scattering event should be weak.

To explore these effects further, we have investigated the scattering of vibrationally excited H_2 from Pd(111), using stimulated Raman pumping to prepare H_2 in the single rovibrational state ($v = 1, J = 1$).

The experimental apparatus used has been described previously [8,9,14] and will be only briefly reviewed here. A pulsed, chopped, supersonic H_2 beam is directed at near normal incidence against a single-crystal Pd(111) sample in ultrahigh vacuum (UHV). A pulsed "pump" laser crosses the molecular beam at a right angle ≈2.5 mm before the Pd target. It excites a portion of the incident molecules from ($v = 0, J = 1$) to ($v = 1, J = 1$) by stimulated Raman scattering. A counterpropagating pulsed "probe" laser crosses the beam 0.24–2.5 mm before the target. It is used to state-selectively ionize the incident and scattered molecules, which are then detected with a microchannel plate electron multiplier. By scanning the delay between the pulsed pump and probe lasers, time-of-flight (TOF) spectra are recorded which show the molecules incident upon and scattered back from the target as they cross the probe axis. A clean Pd(111) surface is prepared according to the methods described in Ref. [14]. The surface is held at $T_s = 450$ K during the scattering experiments, and flashed above 850 K every 15 min, to keep it clean. For comparison, scattering experiments are also performed with the surface saturated with H atoms, achieved by cooling the sample to 100 K and exposing it to a dose of ≈15 L H_2.

Figure 1 shows a pair of H_2 TOF spectra taken with the probe laser tuned to detect the prepared $(v = 1, J = 1)$ state, for different conditions of the surface. The early peak is from incident molecules prepared by the pump laser, and the later smaller peaks are from scattered molecules still in the excited state. The plot shows that the reflectivity is very low on the clean surface and quite high on the H-saturated surface (noting the scale change). For this figure the average incident translational energy was 74 ± 1 meV and the probe laser was 0.46 mm from the target. The time axis zero was set to the peak arrival time of the incident excited packet at the target. The curves are fits to a model [15,16]. Similarly low reflectivities to the $(v = 1, J = 1)$ state on the clean surface were also found for incident translational energies of 22 and 151 meV, achieved by varying the nozzle temperature and seed gas ratio.

To determine the absolute survival probability of the excited state, we integrated over the spatial distribution of incident and scattered flux. The probe laser was translated over a range of positions in a plane perpendicular to the molecular beam. At each position, a TOF spectrum like those shown in Fig. 1 was taken. The measured, density-weighted spectrum was then transformed to a flux-weighted one using a model described previously [15,16], and the flux under the incident and scattered peaks in each spectrum was integrated. The integrated flux versus probe laser position is plotted in Fig. 2 for both the clean surface and the H-saturated surface. By comparing the areas under the scattered flux profiles to that of the incident profile, the survival probabilities were determined. We thus found that, for an incident translational energy of 74 meV, the H_2 $(v = 1, J = 1)$ survival probability is only 0.05 ± 0.01 on clean Pd(111), versus 0.97–1.00 (i.e., almost unity) on H-saturated Pd(111).

The difference in the results for the clean and H-saturated surface is striking. Essentially the H-saturated surface is inert to the H_2 molecules incident in the $(v = 1, J = 1)$ state, which are simply reflected. However, upon scattering from the clean surface, almost none of the incident H_2 $(v = 1, J = 1)$ survives.

There are three possible loss channels for the incident H_2 $(v = 1, J = 1)$ upon collision with the Pd surface: dissociative adsorption (i.e., sticking), rotational excitation to odd J's within $v = 1$, and relaxation to odd J's in the ground vibrational state. (Conversion to even J is forbidden by nuclear spin symmetries.) Of the three loss channels, sticking is almost certainly the dominant one, since H_2 adsorption on Pd occurs readily. The sticking coefficient is already ≈ 0.6 for the ground vibrational state $(v = 0, J = 1)$ on Pd(111) [14], and is expected to be higher for $v = 1$ as discussed above. We looked for rotational excitation to $(v = 1, J = 3)$, but did not observe any. We therefore assume that excitation to higher J states within $v = 1$ is also negligible, since the energy gap for these transitions is even larger.

Vibrational relaxation, however, was directly observed, with vibrational energy converted to both rotation $(V \longrightarrow R)$ and translation $(V \longrightarrow T)$. This is shown in Fig. 3, where TOF spectra for various states have been plotted together. For $(v = 1, J = 1)$, the signal results from excitation by the pump laser. For the other states, however, there is a significant population over the whole molecular beam pulse, whose width of ≈ 10 μs is too large to be seen in the figure. The figure then shows an almost constant background for these states, given by the initial population in the beam and rotationally inelastic scattering [14]. The dip in the $(v = 0, J = 1)$ spectrum shows depletion of the ground state by the pump laser. The peaks which appear in the $(v = 0,\ J = 5$, and $J = 7)$ spectra at positive times, i.e., after the excited

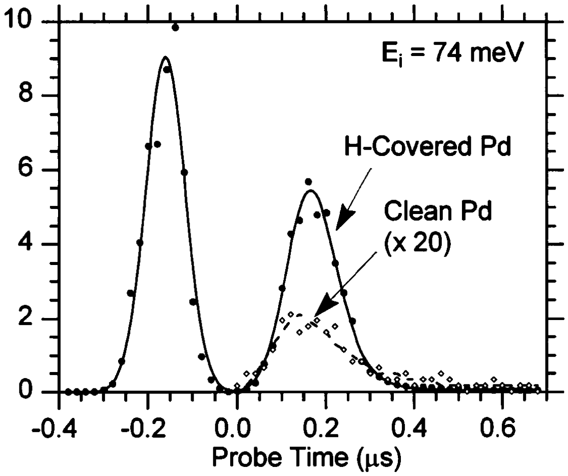

FIG. 1. TOF spectra of H_2 $(v = 1, J = 1)$ incident on and scattered from clean $(T_s = 450$ K) and H-covered $(T_s = 100$ K) Pd(111).

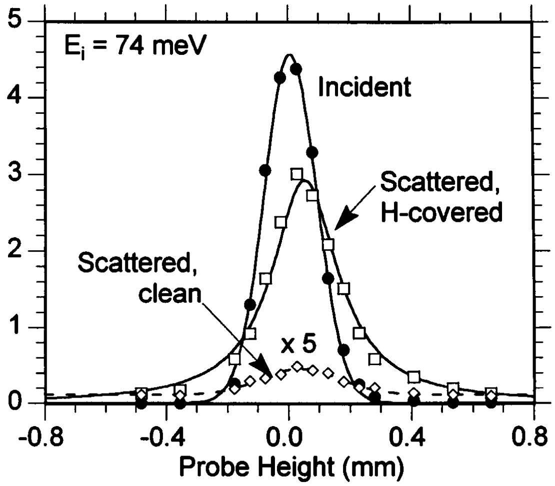

FIG. 2. Vertical profiles of incident and scattered flux of H_2 $(v = 1, J = 1)$ for clean $(T_s = 450$ K) and H-covered $(T_s = 100$ K) Pd(111).

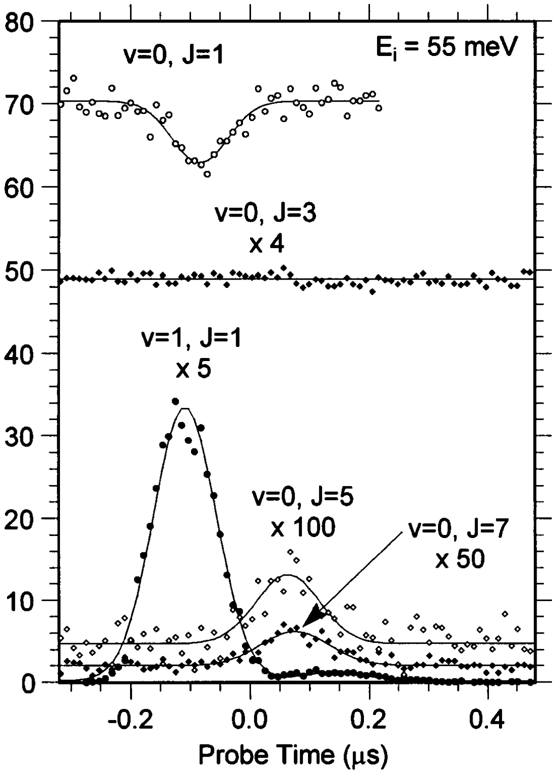

FIG. 3. Time-of-flight spectra of H_2 in various rovibrational states scattered from clean Pd(111). The incident prepared $(v = 1, J = 1)$ packet collides with the surface at time 0. Relaxation into $(v = 0, J = 5, 7)$ then gives peaks in these states at positive times.

state $(v = 1, J = 1)$ packet has hit the surface, arise from relaxation of the excited state on the clean surface. They disappear if the pump laser is blocked, or if the surface is cooled and saturated with H atoms. Note that they also appear at an earlier time than the small, rovibrationally elastically scattered $(v = 1, J = 1)$ peak, indicating $V \rightarrow T$ conversion. We determined the average translational energy of the molecules scattered into $(v = 0,\ J = 5$, and $J = 7)$ by measuring the TOF peak times for these states versus probe laser distance from the surface. This gave final translational energies of 250 ± 33 meV and 137 ± 14 meV, respectively, while the average incident translational energy was 55 ± 1 meV.

We would also expect relaxation to occur to $(v = 0,\ J = 1$, and $J = 3)$. However, given the high background in these states, as shown in Fig. 3, relaxation to them on the order of that found for $(v = 0,\ J = 5$, and $J = 7)$ could not be detected with the available signal to noise. We did not look for scattering into $(v = 0, J = 9)$, since this state is considerably higher in energy than $(v = 1, J = 1)$. We did check for relaxation into the even J states $(v = 0,\ J = 4$, and $J = 6)$, but found none.

We determined the absolute magnitude of the vibrational relaxation probabilities for the observed channels in a manner similar to that used to determine survival probabilities for the excited state. The density-weighted TOF spectra were roughly rescaled to flux-weighted ones using the measured velocities of incident and scattered molecules. The incident and scattered flux in the relevant states was then integrated over a plane perpendicular to the molecular beam. The relaxation probabilities determined are listed in Table I. The resonance-enhanced multiphoton ionization (REMPI) rates are nearly independent of rotational state but do depend on the vibrational band probed [17]. Allowance for this was made in comparing the signals for different states [15]. Table I shows that the relaxation probabilities are at least several percent into each of the observed channels.

Although there is significant $V \rightarrow T$ and $V \rightarrow R$ energy transfer, the total vibrational, rotational, and translational energy of the scattered vibrationally relaxed molecules in $(v = 0,\ J = 5$, and $J = 7)$ is significantly less than that of the incident molecules in $(v = 1, J = 1)$. The difference is listed in Table I. The missing vibrational energy must be dissipated in the surface. If the initial energy were conserved within the molecule, then vibrational relaxation during the scattering event could be considered as arising solely from the dynamics of the molecule on a six-dimensional PES, e.g., as calculated for H_2 on Cu(100) [4]. However, the fact that energy is dissipated to the surface indicates that this is not the case. Surface degrees of freedom, which are usually neglected in dynamics calculations for simplicity, must be included to explain the present results.

Incident vibrational energy may be dissipated in the surface either to electronic excitations or to excitation of phonons. However, phonon excitation seems to be an unlikely explanation for the observed energy transfer. Given the Pd Debye temperature of 275 K [18], corresponding to 24 meV, dissipation of ~100 meV would require simultaneous excitation of at least four phonons. However, an estimate of the time scale for adsorbate vibrational relaxation by excitation of multiple phonons [19] is orders of magnitude longer than the interaction time in a single molecule-surface collision. Furthermore, the large mass mismatch between H and Pd suggests that mechanical energy transfer in a single collision should be inefficient. In addition, the disappearance of the vibrational relaxation peaks in the TOF spectra when the Pd surface saturated with H atoms shows that the relaxation depends sensitively on the details of the molecule-surface interaction

TABLE I. Vibrational relaxation probabilities for H_2 $(v = 1, J = 1)$ on Pd(111), and energy dissipation to surface for each channel, for incident translational energy of 55 ± 1 meV.

Transition	Probability	Energy loss to substrate (meV)
$(v=1, J=1) \rightarrow (v=0, J=1)$	···	···
$(v=1, J=1) \rightarrow (v=0, J=3)$	<0.05	···
$(v=1, J=1) \rightarrow (v=0, J=5)$	0.04 ± 0.01	120 ± 34
$(v=1, J=1) \rightarrow (v=0, J=7)$	0.03 ± 0.01	54 ± 15

potential, which is obviously different on the clean and H-covered surfaces. Thus the absence of relaxation on the H-covered surface, for which the mass match is greatly improved, suggests that the relaxation does not occur by mechanical energy transfer, but rather by an electronic interaction.

Theoretical understanding of the role of substrate electronic excitations in dissociative scattering is not well developed [1]. However, the time scale for vibrational relaxation via surface electronic excitation may be comparable to the molecule-surface collision time. Calculations for H_2 on metals, for example, show a vibrational lifetime broadening due to electronic interactions [20] corresponding to decay times on the order of 100 fs. Since the damping rate is enhanced when the adsorbate antibonding level passes through the Fermi level, strong vibrational damping should be expected in a system which is dissociative, such as H_2 on Pd. Further theoretical work should be done to assess the importance of electronic interactions in direct scattering.

In conclusion, we have investigated the dynamics of vibrationally excited H_2 scattering from Pd(111), and have found a significant probability for vibrational deexcitation during the scattering. This vibrational deexcitation occurs only on the clean surface, and disappears when the surface is cooled and covered with H atoms. Furthermore, a significant amount of vibrational energy is dissipated to the surface during deexcitation. These facts strongly suggest that the relaxation is due to an electronic or chemical interaction with the surface. This is supported by the fact that vibrational damping lifetimes by phonon-mediated processes are too long to explain the energy loss observed in a direct scattering event. We find an overall survival probability of the incident H_2 $(v = 1, J = 1)$ molecules of only about 0.05 on the clean Pd(111), versus nearly unity on the H-atom saturated surface. The majority of the loss in the vibrationally excited state is probably due to dissociative adsorption, but a significant fraction is due to vibrational relaxation.

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