

Rotational Excitation and Vibrational Relaxation of H_2 ($v = 1, J = 0$) Scattered from Cu(111)

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(Received 21 October 1996)

We have observed efficient translational to rotational energy transfer for H_2 ($v = 1, J = 2 \leftarrow 0$) scattered from Cu(111), the cross section increasing rapidly from near threshold to reach a maximum at a translational energy of 140 meV. Above this energy a change in the behavior of the H_2 ($v = 1, J = 2 \leftarrow 0$) cross section was seen, coinciding with the abrupt onset of H_2 ($v = 1, J$) removal by coupling of translational and vibrational coordinates. Vibrational relaxation competes with rotational excitation, both processes occurring preferentially at the same impact sites and geometry. [S0031-9007(97)02334-X]

PACS numbers: 79.20.Rf, 68.35.Ja

The potential energy surfaces (PES) and dynamics of activated dissociative chemisorption have become the focus of much attention recently as experiments become available which provide dynamical insight in a relatively direct way [1]. One source of information is energy transfer measurements which can be compared with scattering calculations to investigate the characteristics of the PES. Here we report state selected measurements of rotational energy transfer for H_2 at Cu(111) which is a model system of both experimental and theoretical interest [2]. Dissociation of H_2 at Cu(111) is highly activated and is enhanced by vibrational excitation of H_2 , the translational energy barrier to dissociation decreasing with increasing vibrational state [1,3,4]. This state dependence arises from the location of the barrier to dissociation at extended H-H separations in the exit channel leading to separated atoms. Calculations of the dissociation dynamics on low dimensional model potential energy surfaces [2] show sticking probabilities which depend on vibrational level, the sticking probability following an "S" shaped curve with a rapid increase in sticking as some threshold translational energy is reached. This picture is supported both by deconvolution of the sticking probabilities of individual vibrational levels from seeded beam measurements [4] and by application of microscopic reversibility to recombinative desorption data [1]. Strong coupling between the vibrational and translational coordinates is also evident for $H_2(D_2)$ scattering from Cu(111) [5,6]. For D_2 vibrational relaxation of ($v = 1, J$) occurs at 0.35 eV, while at translational energies above 0.65 eV efficient vibrational excitation of ground state molecules to the excited vibrational level occurs. For D_2 it was shown that the vibrational excitation process scaled with normal energy [5], while the gap between the translational energy thresholds corresponds to the energy separation $D_2(v = 1 \leftarrow v = 0)$. Applying microscopic reversibility implies that the lower threshold is indeed due to $T \leftarrow V$ transfer and cannot be attributed simply to dissociation. For $H_2(v = 1)$ Rettner, Auerbach, and Michelsen observed a loss of flux near

0.3 eV, and vibrational excitation ($v = 1 \leftarrow v = 0$) was again seen at energies above 0.6 eV, just above the threshold for dissociative chemisorption of the ground state [6]. Scattering calculations on model two dimensional potentials, incorporating the H_2 stretching and surface-molecule separation, showed that vibrational excitation was very sensitive to the curvature of the PES in the region prior to the barrier [7]. Darling and Holloway [8] also reported that it was not possible to obtain both the correct $T \rightarrow V$ thresholds as well as the appropriate vibrational efficacy from a single PES, a conclusion supported by recent scattering calculations on an *ab initio* PES [9].

One of the general features to come out of recent total energy calculations of the H_2/Cu PES [10,11] is the sensitivity of the surface to the location of the molecule in the unit cell and the orientation of the bond axis relative to the surface. For dissociation of a H_2 molecule held flat above a Cu(111) surface the barrier was calculated to vary by as much as 0.7 eV for different surface sites [11]. Variation of the barrier height with the orientation of the molecule can be invoked to explain the inhibition of dissociation with rotation at low J [1,3], while for higher rotational energies coupling to the stretching coordinate aids dissociation. Such a corrugation of the PES in the rotational (θ, ϕ) coordinates should produce rotational excitation during scattering. This process will be very sensitive to the vibrational state of the hydrogen since, at energies where a molecule scattering in the ground state ($v = 0$) experiences a simple repulsive potential, a vibrationally excited molecule will be close to the dissociation limit and experience a highly anisotropic potential. This mechanism can lead to enhanced translational to rotational energy transfer for vibrationally excited H_2 [12], a process that will be aided at extended H-H separations by the increased anisotropy of the PES and the reduced energy spacing of the J levels [13].

We have investigated the translational to rotational ($T \rightarrow R$) and vibrational ($T \leftarrow V$) energy transfer cross sections for H_2 scattering from Cu(111) using stimulated

Raman pumping to prepare individual rotational levels of $H_2(v=1, J)$. A similar technique has been used by Sitz and co-workers [14,15] to measure the absolute reflectivity of $H_2(v=1, J=1)$ from Cu(110) to be 0.74 at low energy, similar to that seen on Cu(111) [16], while a reduction in reflectivity was seen between 100 and 200 meV and attributed to dissociation [15]. We have measured rotational energy transfer and the removal of $H_2(v=1, J=0)$ as a function of translational energy. $H_2(v=1, J=2 \leftarrow 0)$ energy transfer was efficient, the cross section increasing rapidly from just above threshold until an abrupt change in cross section is seen near 140 meV as another removal channel for $H_2(v=1, J)$ suddenly becomes available.

H_2 from a supersonic nozzle is collimated, attenuated by a low frequency chopper and then intersected by the Raman pump laser beams. These are provided by a frequency doubled Nd:YAG laser which pumps a tunable dye laser to generate wavelengths around 680 nm, with a second doubling crystal in the YAG providing 532 nm radiation, for Raman excitation on the Q branch. Pumping on this transition provides population of $H_2(v=1, J)$ with negligible alignment of the prepared molecules. Laser pulses are synchronized with the chopper, combined, and focused onto the molecular beam in the second stage of a molecular beam source. Vibrationally excited $H_2(v=1, J)$ molecules are detected in the scattering chamber by two photon resonance enhanced multiphoton ionization (REMPI) on the $E, F^1\Sigma_g^+ - X^1\Sigma_g^+$ transition near 211 nm. The probe laser is delayed with respect to the YAG Q switch by a computer controlled delay, and the resulting ions are extracted, detected on a microchannel plate and counted. The nozzle source can be operated at temperatures up to 2000 K to provide thermal population of the relevant $H_2(v=1, J)$ level and allows simple optimization of the probe laser wavelength and overlap with the molecular beam. The power dependence of the Raman pumped $H_2(v=1, J)$ signal indicates that ($v=1 \leftarrow v=0$) pumping was substantially saturated, with a pumping efficiency greater than 10^{-1} .

Translational energy distributions of H_2 beams are intrinsically much broader than for a rare gas, but by detecting the scattered molecules as a function of the time of flight (TOF) across the 330 mm path between the pump and probe regions we were able to obtain a velocity resolution of better than 1%. The energy resolution was limited by the spatial extent of the pumping volume along the beam which could be controlled by varying the alignment of the pump lasers. Rotational energy transfer was measured at a series of fixed flight times corresponding to translational energies between 30 and 200 meV while the relative fraction of $H_2(v=1, J)$ reflected by the surface was obtained by comparing the TOF for molecules before and immediately after scattering from the surface. In practice reverse seeding in Ne was used with a hot nozzle to increase the populations of higher ro-

tational states and to broaden the H_2 velocity distributions. In this way energy transfer could be measured for $H_2(v=1, 0 \leq J \leq 3)$ at translational energies up to at least 200 meV with an acceptable $H_2(v=1)$ thermal background signal.

Rotational energy transfer was measured as a function of the incident translational energy by detecting $H_2(v=1)$ scattered in $J=0$ and $J=2$ rotational states while pumping on the $Q(0)$ transition to populate $H_2(v=1, J=0)$. Angular distributions of the scattered $H_2(v=1)$ showed only a broadened specular peak, as previously reported for thermal scattering at higher energies [16]. The rotational energy transfer experiment was carried out by scattering $H_2(v=1, J=0)$, incident at an angle of 17° to the surface normal, and placing the probe laser on the peak of the specularly scattered signal as close to the surface as possible. This provides an angular resolution of $\sim 50^\circ$ and ensured that a large fraction of the scattered molecules were detected [5,16], making the experiment insensitive to the scattered $J=0$ and $J=2$ angular distributions. At higher translational energies it was possible to optimize the probe laser on both the scattered $J=0$ and the excited $J=2$ signals, but no difference in ratio was seen with scattering angle, consistent with the intended insensitivity to θ_f . Accurate angular distributions for the scattered $H_2(v=1, J=2)$ were not obtained, but for translational energies near threshold the angular scattering distribution of $H_2(v=1, J=2)$ is expected to deviate from the specular. Assuming that only the normal component of the translational energy contributes to $T \rightarrow R$ transfer, the angular distribution of the scattered $H_2(v=1, J=2)$ will shift away from the surface normal as the incident energy approaches threshold. For this reason we cannot make quantitative energy transfer measurements below $E_i \sim 70$ meV; above this energy our experiment is insensitive to the shift in scattering angle. The relative sensitivity of the probe laser to different $H_2(v=1, J)$ levels was measured by determining the relative signals from the heated molecular beam during the course of each $T \rightarrow R$ measurement.

Figure 1 shows the relative flux weighted population of molecules $H_2(v=1, J=2/J=0)$, corrected for the lower translation energy of $J=2$, scattered from a 300 K Cu(111) surface. Energy transfer $H_2(v=1, J=0 \rightarrow 2)$ requires 42 meV energy and for $T \rightarrow R$ measurements at translational energies below this threshold we were unable to observe any scattered $H_2(v=1, J=2)$ within our experimental precision of $2 \times 10^{-3} [H_2(v=1, J=0)]$. This result is consistent with rotational excitation occurring as a result of direct $T \rightarrow R$ coupling. As the translational energy is increased, the cross section for $J=0 \rightarrow J=2$ transfer increases rapidly, the relative population of these states reaching ~ 0.4 by 140 meV. At energies above 140 meV there is an abrupt change in behavior; the cross section for scattering into $J=2$ no longer increases but falls slightly with increasing translational energy. We also

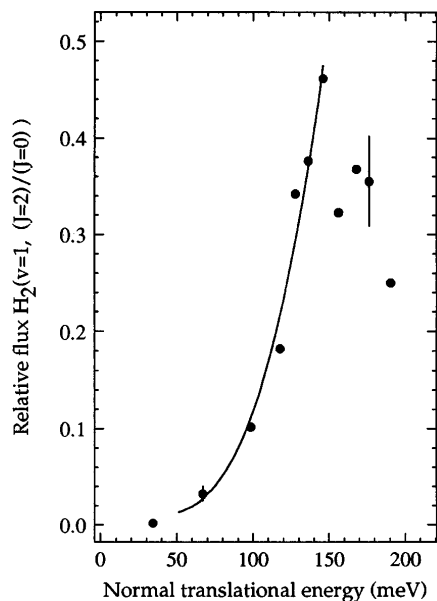


FIG. 1. Scattering of $H_2(v=1, J=0)$ into the $(v=1, J=2)$ state as a function of translational energy. The data are plotted as the ratio of the scattered $J=2$ and $J=0$ intensities and has been corrected from number density to flux by accounting for the lower translation energy of $H_2(v=1, J=2)$. A smooth curve has been fitted to the data below 145 meV to guide the eye.

find that the ratio $H_2(v=1, J=2/J=0)$ in this region becomes more difficult to measure as the scattered flux in both states decreases. Attempts to measure $H_2(v=1, J=3 \leftarrow 1)$ and $H_2(v=1, J=3 \rightarrow 1)$ cross sections at energies up to 200 meV revealed negligible energy transfer, consistent with the apparent absence of any $J=3 \leftarrow 1$ transfer on Cu(110) [15]. For comparison we investigated rotational energy transfer for $H_2(v=0, J=0)$ by measuring the state distributions of a thermal beam scattered from the surface under similar conditions. The experimental precision here is much lower, since both rotational levels are populated in the incident beam, but no transfer $H_2(v=0, J=2 \leftarrow 0)$ could be observed ($\pm 10\%$), consistent with the low cross sections seen for $T \rightarrow R$ transfer in TOF and diffraction experiments.

The reflectivity of $H_2(v=1, J=0)$ from the Cu(111) surface was measured by comparing the scattered signals for different flight times and nozzle energies. This is most conveniently done by comparing the TOF distributions for molecules before and after scattering from the surface, in a manner similar to that used to measure the reflectivity of hot thermal beams [5,6]. Typical TOF data for $H_2(v=1) J=0$ and $J=2$ is shown in Fig. 2 for a beam incident at an angle of 17° to the surface normal. The reflectivity (R) shows an abrupt decrease at flight times corresponding to a normal energy of 142 meV. A loss function given by $R = A/2[1 - \tanh(E_i - E_o)/w]$ was fitted to the data and gave a threshold $E_o = 142$ meV and a width $w = 12$ meV for $J=0$. Different measure-

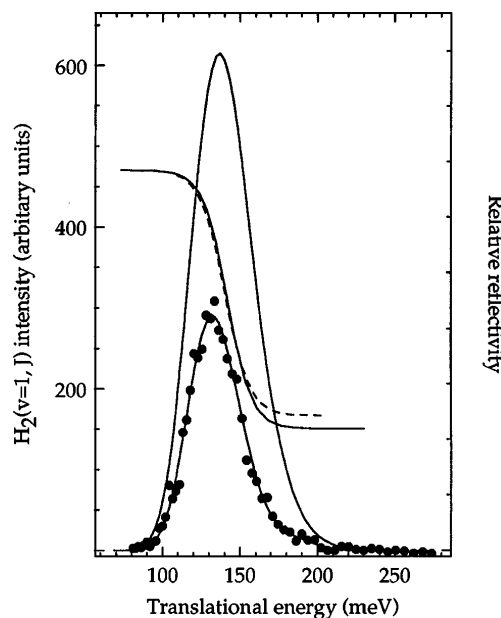


FIG. 2. Relative reflectivity of $H_2(v=1, J=0)$ as a function of translational energy showing the abrupt loss of flux near 140 meV. The relative reflectivity was obtained by comparing the intensity of the scattered signal (solid points) to the incident beam (smooth curve) as a function of flight time or translational energy. The "S" shaped curves show the reflectivity (right-hand scale) obtained, in separate experiments for $J=2$ (dashed line) and $J=0$, by fitting a tanh function to the removal of $H_2(v=1, J)$ as described in the text.

ments gave a removal threshold that was identical within ± 2 meV, consistent with the anticipated error in setting the flight path between the pump and probe regions.

The extremely narrow translational energy range over which $H_2(v=1, J=0)$ removal becomes efficient is remarkable. We have also measured vibrational excitation and relaxation of a thermal beam at incidence angles near 45° and obtain a similar normal energy threshold and width for removal of $v=1$. Similar results were obtained for other rotational states, both using Raman pumping and a thermal beam at large incidence angles, indicating that this threshold is associated with an overall loss of scattered $H_2(v=1)$ flux at the surface and not rotational redistribution, a conclusion confirmed by the decrease in the $T \rightarrow R$ cross section measured here. Scattering experiments with translationally hot H_2 show vibrational excitation of $H_2(v=1 \leftarrow v=0)$ occurring at energies above 0.65 eV, similar to that observed previously [6]. Since $T \rightarrow V$ coupling scales with the normal component of the translational energy [5] the onset of vibrational excitation ($v=1 \leftarrow v=0$) and relaxation ($v=1 \rightarrow v=0$) should be separated by the vibrational quanta, 0.51 eV, just as they are for D_2 [5]. This is entirely consistent with the loss of $H_2(v=1)$ near 140 meV being vibrational relaxation of the scattered molecules by coupling of the vibrational motion into translational energy release. The mean energy

barrier associated with $H_2(v = 1)$ dissociation, obtained from desorption data, is 0.30 eV [1] and indeed thermal scattering experiments also show a second loss near this energy, as reported previously [17]. Similarly, Gostein and Sitz [15] attribute the loss of $H_2(v = 1, J = 1)$ between 100 and 200 meV to dissociative chemisorption, but comparison with the $T \leftarrow V$ threshold seen here for energy transfer at Cu(111) suggests that this loss may be vibrational relaxation, no state specific sticking data being available for Cu(110).

The large cross section for $H_2(v = 1)T \rightarrow R$ transfer is in accord with the predictions of scattering calculations which show an enhanced energy transfer cross section for the vibrationally excited state as the energy becomes sufficient to access regions of the PES close to the barrier to dissociation [12]. Rotational energy transfer is enhanced by the strong anisotropy of the H_2 -surface potential for molecules which experience a chemical interaction with the surface and a weakening of the molecular bond [13]. Recent diffraction measurements of D_2 on Rh(110) [18] showed a strong $J = 0 \rightarrow 1$ peak, with an intensity $\sim 6\%$ of specular at 72 meV, and this was proposed to arise from enhanced $T \rightarrow R$ coupling on the dissociative surface.

The abrupt change in the $T \rightarrow R$ cross section for $H_2(v = 1, J = 0) \rightarrow H_2(v = 1, J = 2)$ energy transfer at 140 meV coincides with the onset of vibrational relaxation, but this does not immediately explain why the cross section turns down. Removal by vibrational relaxation might be expected to decrease the $J = 0$ flux and so decrease the overall $J = 2$ signal, but this would not by itself change the scattered ratio $H_2(v = 1, J = 2/J = 0)$. Moreover the cross sections for vibrational relaxation decrease with J so, if the $T \leftarrow V$ and $T \rightarrow R$ processes were uncorrelated, the scattered ratio $H_2(v = 1, J = 2/J = 0)$ would be expected to go up faster as the threshold for vibrational relaxation is reached. That the cross section actually turns down above this threshold implies that the two processes are correlated, vibrational relaxation preferentially removes those molecules most likely to undergo $T \rightarrow R$ excitation. This must occur because the conditions favored for vibrational to translational coupling also favor rotational excitation. Cruz and Jackson [13] investigated the correlation of rotational excitation and dissociation on a model PES intended to mimic Ni and found that rotational excitation was enhanced at surface sites for which dissociation was easy. Similarly, Darling and Holloway [8] suggested that the inability to reconcile dissociation and $T \rightarrow V$ transfer data in simple 2D scattering calculations was consistent with a site dependence for the two processes. This is supported by recent calculations on an *ab initio* PES [9] which associate vibrational excitation with preferential

impact on the atop site and dissociation with the bridge and hollow sites for Cu(100). The correlation seen here between rotational excitation and vibrational relaxation processes implies that the (atop) site which gives rise to efficient $T \rightarrow V$ coupling also gives a larger cross section for $T \rightarrow R$ transfer than other sites at this energy. $T \rightarrow V$ coupling is enhanced by a strong curvature of the potential well as the bond stretches prior to any dissociation barrier. Such sites are certainly consistent with a very strong angular dependence to the potential as well as a reduced separation of the J levels which further aids coupling. The correlation of rotational and vibrational energy transfer therefore indicates similar steric requirements for both processes and is consistent with the model of a site dependence to energy transfer and dissociative processes on Cu(111).

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