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Abstract. The interaction of vibrationally excited $H_2(D_2)$ with a Cu(111) surface has been studied using molecular beam scattering with state-selected detection of the incident and scattered molecules by resonance-enhanced multiphoton ionization. The ratio of the survival probability for $H_2(v = 1, J = 1)$ in the specular beam to that for $v = 0$, $J = 1$ is 0.67 ± 0.1 for an incident translational energy of 0.34 eV at 45° incidence. This is consistent with efficient dissociative chemisorption of the $H_2(v = 1)$ level, dissociation of the $v = 0$ level being negligible at this energy. Under the same conditions the survival probability for D_2 is 0.8, again consistent with the sticking measurements which show a lower sticking probability for D_2 than for H_2.

1. Introduction

The dissociation of hydrogen on copper surfaces is a highly activated process having a barrier of between 0.5 and 1 eV. The energy and angular dependence of the initial sticking coefficient for $H_2(D_2)$ on Cu(111) and (110) surfaces has been measured by Hayden and Lamont [1] and by Rendulic *et al* [2]. Dissociation is activated by translational energy, having a threshold around 0.2 eV for Cu(110) and 0.16 eV for Cu(111), with a very sharp dependence on incident angle [1,2] consistent with the sharply peaked angular distributions reported by Comsa and David [3] for hydrogen recombinative desorption.

Calculations suggest the potential energy surface shows a barrier pushed significantly back into the exit channel, with the minimum energy path showing a sharp change of co-ordinate from the centre of mass translation to the H-H stretch prior to the barrier [4–7]. Measurements of H_2 and D_2 state distributions from recombinative desorption have shown a significant enhancement in the population of the vibrationally excited states, above that expected for the hot surface [8]. This suggests that the barrier to dissociation may be efficiently overcome by vibrational motion which lies along the correct axis to break the H_2 bond.

Seeded beam experiments [1,2] have shown that the sticking probability, S_0, on Cu(110) and (111) depends both on the translational energy of the beam and on the nozzle temperature and hence the $H_2(D_2)(v, J)$ internal state distribution. Their data indicate that vibrationally (or rotationally) excited levels must have a significantly enhanced sticking coefficient and that sticking is due to a combination of vibrationly activated and translationally activated $H_2(v = 0)$ dissociation. It is not possible to

separate the vibrational state contributions in these experiments [1,2] without assuming both the vibrational populations and some form for the energy dependence [9] but a large fraction of the $H_2(v = 1)$ population must stick to give the observed enhancement.

In order to investigate the internal state dependence of the H_2/Cu interaction, we have performed state selected measurements of H_2 scattering from a Cu(111) surface. Here we report measurements on the relative survival probability of $H_2\{(v = 1), J = 1)/(v = 0, J = 1)\}$ scattered into the specular beam. A direct determination of $S_o(v)$ by resonance enhanced multiphoton ionization (REMPI) would require an accurate measurement and integration over the final state scattering angles (θ,ϕ), velocity distributions (E_t) and rotational states (J), to correlate the incoming and scattered fluxes for the different vibrational levels. This is difficult to perform accurately and our measurement avoids this problem, allowing us to investigate the difference in reflectivity of the two states, without attempting to average over the entire final state $(\theta, \phi, E_T, v, J)$ distribution. By using the $v = 0$ state as a reference, it is possible to investigate the effect of the dissociation channel on the scattering dynamics of higher vibrational states at translational energies where the gound state does not dissociate.

2. Experimental procedure

The experimental arrangement will be described only briefly here [10]. The scattering system (VSW Scientific Instruments) comprises a three-stage beam source and a scattering chamber equipped with a rotatable ion detector, quadrupole mass spectrometer and surface diagnostics (Auger and LEED). The beam source was a molybdenum nozzle and was heated directly using resistive heating, giving a working range up to 1800 K and a few percent of $H_2(v = 1)$ in the beam. Backing pressures for H_2 were between 1 and 3 atm, providing an intense, translationally cold beam. The beam was chopped in the second stage, giving gas pulses of 5 μs or more duration. A low duty-cycle slot allowed the flux of gas onto the crystal to be minimised while maintaining a high instantaneous flux and number density when the laser fired. Translational energies were measured by time of flight using a short gas pulse and laser detection.

The Cu(111) crystal was cleaned by repeated cycles of Ar^+ ion bombardment and annealing. The scattering direction was aligned with a close packed row using LEED. Surface quality was monitored using He atom specular reflectivity measurements, showing a reflectivity of 25–30% for a room temperature beam and sample, comparable with previous measurements [11]. The detection system employed a Nd:YAG pumped dye laser and frequency tripling system to generate radiation tunable between 200 and 220 nm. $H_2(D_2)$ was detected by two-photon resonant, three-photon ionization on the $E,F\ ^1\Sigma_g^+$ transition [12]. The laser was synchronized to the beam chopper to intercept the middle of the gas pulse, which was long compared to the flight times from the surface to the detection volume. The laser was focused to a waist in the chamber, along an axis perpendicular to the scattering plane. Ions generated at the laser focus were extracted into a simple ion time of flight system and detected using a microchannel plate. The reflected beam was typically intercepted 15 mm away from the crystal face.

3. Results and discussion

The $H_2(D_2)$ beam was scattered from the Cu(111) crystal with an incident transla-

tional energy of 0.34 meV ($\theta_i = 45°$) along a close-packed row and showed an intense, specularly scattered peak. No evidence was found for in-plane diffraction of either D_2 or He with a room temperature nozzle ($\theta_i = 45°$) and surface, consistent with the very low degree of corugation in the close-packed (111) surface [13,14].

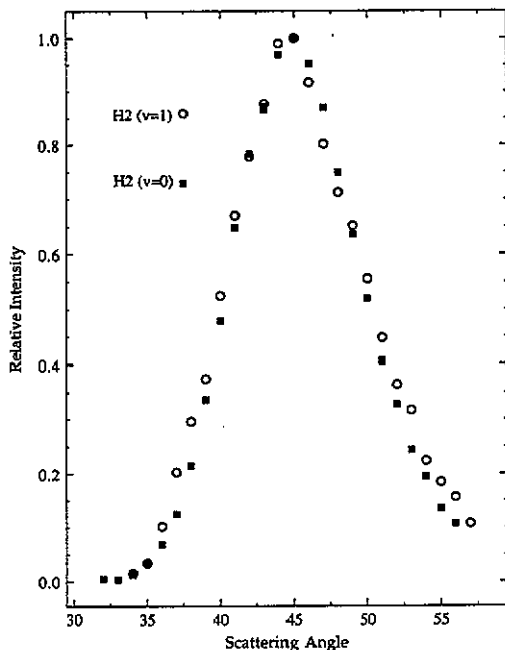**Figure 1.** Angular distribution of H_2 ($J = 1$) scattered close to the specular direction in the $v = 0$ (■) and $v = 1$ (○) vibrational states. The angular resolution ($\approx 6°$) is slightly higher than used in the reflectivity measurements and the distribution for the two vibrational levels is the same within experimental error.

Measurements of the state resolved specular reflectivity were made with the crystal held at 450 K to desorb any hydrogen which sticks during the data acquisition. The flux is in any case so low that less than 2% of a monolayer would be deposited during a typical acquisition period and at 150 °C the equilibrium coverage of hydrogen is negligible [2]. When using the laser to detect scattered H_2 the angular resolution was 8°, defined by the spot size of the beam on the crystal and the distance of the probe point from the scattering centre (15 mm). This resolution was chosen to collect a large fraction of the beam which scatters close to the specular angle but to reject flux scattered at large angles and along the surface normal. Thus scattering events which result in large angle changes will not be detected. The angular distribution of the scattered $H_2(v = 0, J = 1)$ and $H_2(v = 1, J = 1)$ levels is shown in figure 1, for an incident ranslational energy of 0.34 meV at 45° to the surface normal. The peak is broadened by incoherent scattering but no difference is discernable for the two levels and no diffracted beams were seen for D_2 scattering under the same conditions. The specular lobe contains more than 25 % of the incoming flux and the diffusely scattered components were weak. The relative populations of the $H_2(v = 0, J = 1)$ and $H_2(v = 1, J = 1)$ levels was measured in the incident beam (I^i) and then at the

peak of the specularly scattered beam (I^s) giving the ratio α,

$$\alpha = \frac{I^s(v=1, J=1)/I^i(v=1, J=1)}{I^s(v=0, J=1)/I^i(v=0, J=1)} \tag{1}$$

where α is the 'survival probability' of $H_2(v=1, J=1)$ in the specular beam relative to that of $H_2(v=0, J=1)$. This ratio divides out all of the sensitivity factors associated with the REMPI detection of the different vibrational states. For a beam energy of $E_T = 0.34$ eV at $45°$ incidence angle, we obtain a survival probability $\alpha = 0.67 \pm 0.1$ for $H_2(v=1, J=1)$ relative to $H_2(v=0, J=1)$ in the specular beam. For $D_2(J=4)$ under the same conditions the survival probability of the $v=1$ level relative to the $v=0$ is 0.81 and this drops as the normal energy is increased by varying the angle of incidence (figure 2).
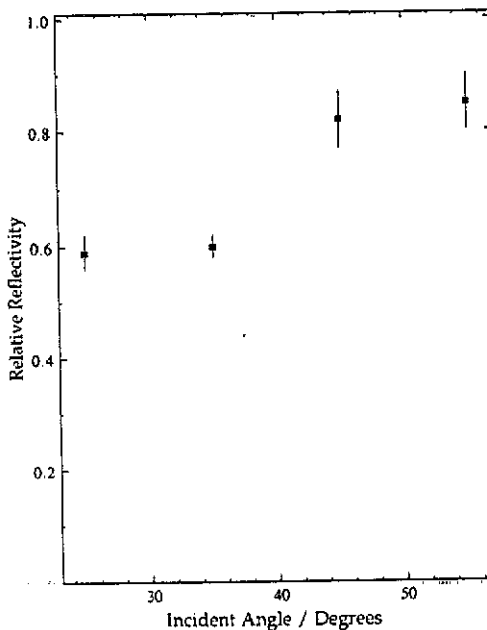

Figure 2. Reflectivity of $D_2(J=4)$ into the specular direction as a function of the incident beam angle θ_i for a translation energy $E_i = 0.34$ eV.

The ratio α reflects *all* of the loss processes which remove or scatter the $v=1$ level *differently* to the $(v=0)$. These might include dissociative chemisorption of $H_2(D_2)(v=1)$ [1,2]; vibrational coupling and de-activation at the surface; vibrational to translational relaxation ($V \rightarrow T$ transfer); translational to rotational ($T \rightarrow R$) transfer and preferential diffraction of $H_2(D_2)(v=1)$ caused by a more corrugated potential for the vibrationaly excited PES.

The probability for dissociative chemisorption of the vibrational ground state is known to be less than 10^{-3} at this energy [2] and, provided the other channels can be neglected, we associate the removal of the $v=1$ state from the specularly scattered beam with preferential dissociative chemisorption of this state, giving an upper limit of $0.33 \pm 0.1(0.19 \pm 0.1)$ for the probability of $H_2(v=1)$ removal from the specular

beam by dissociative chemisorption. This is consistent with the seeded beam measurements [2], for which comparable $v = 1$ removal probabilites may be estimated [10], and with the lower transational threshold expected for ($v = 1$) [15,16].

Direct vibrational relaxation during the collision provides another possible contribution to the reduced reflectivity of $H_2(v = 1)$. The very high frequency of the H_2 vibration (0.515 eV) compared to the copper Debye frequency (30 meV) means that there is a very poor match in the frequency of the motion, making the collisional relaxation of this vibration inefficient at these translational energies [15,17]. Similarly, for a closed shell system like H_2, the coupling of the vibration to electron–hole pair formation may be expected to be less efficient than that to the phonons [17,18]. Vibrational relaxation of NO at an Ag(111) surface has been shown to be inefficient [19] and excited vibrational states of H_2 appear to survive multiple collisions with a metal surface [20]. Vibrational to translational energy redistribution may occur via coupling of the coordinates by the curvature of the potential energy surface near to the barrier region. Calculations exist on the sticking/scattering of $H_2(v = 1)$ from potentials of the predicted form and Hand and Harris [15] suggest that vibrational relaxation will be inefficient, even at translational energies where the $v = 1$ level has a high dissociation probability. These results may be sensitive to the potential energy surface assumed and relaxation of the vibrational energy can not be ruled out as a contribution to α.

For translational to rotational exchange to influence α there has to be a significant difference in probability for T → R transfer between the $v = 0$ and $v = 1$ levels. This might be caused either by a stronger angular dependence to the $v = 1$ potential surface [21], eg. due to a sterically constrained sticking geometry, or possibly by the small change in bond length ($< 3\%$) for $H_2(v = 1)$. Similarly, enhanced diffraction of the $v = 1$ state compared to the $v = 0$ might be caused by the greater probability of sticking for this state *provided* that this is a strong function of surface site. Model calculations have shown that diffraction may occur due to localised sticking but that its onset is rather gradual [22]. Diffraction was not observed here at the low angular resolution employed.

We therefore expect the difference in specular reflectivity of $H_2(D_2)(v = 1)$ compared to $H_2(D_2)(v = 0)$ to be dominated by dissociative chemisorption of the $v = 1$ state, although a contribution from vibrational relaxation can not be ruled out. The observation by Hayden and Lamont [1] and Rendulic *et al* [2] that the sticking probability is dependent on the $H_2(D_2)$ internal state distribution is consistent with our measurements. Energy transfer and vibrational relaxation may be expected to be much more efficient for D_2 than for H_2, due to its larger mass and lower vibrational and rotational quanta. The observation of a lower removal probability for D_2, in agreement with the sticking data [1,2], suggests that relaxation may not be important. The reflectivity of the $D_2(v = 1)$ drops as θ_i, is reduced (figure 2), again in qualitative agreement with the sticking data [2].

4. Conclusion

We have shown that a significant fraction of the $H_2(D_2)(v = 1)$ flux is removed from the specularly scattered beam by collision with a Cu(111) surface at a beam energy $E_\perp = 0.17$ eV. Possible mechanisms for this have been discussed and point to the dominant role of dissociative chemisorption in the removal of the vibrationally excited level. This is in agreement with recent sticking measurements where an increase in the

probability for dissociative chemisorption is seen when high ro-vibrational levels are populated [1,2]. A significant fraction of the $H_2(v=1)$ flux survives the collision, indicating the importance of the impact coordinates (lattice site and H_2 bond orientation) even for the vibrationally excited state. Measurements of the survival probability as a function function of translational energy, incident angle and rotational level J are currently under way.

Acknowledgments

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