# Survival Probability of $H_2$ ($v = 1, J = 1$) Scattered from Cu(110)

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We have measured the survival probability of $H_2$ in a single rovibrational state ($v = 1, J = 1$) scattering from a Cu(110) surface at 78 meV translational energy, using molecular beam and laser state preparation techniques. The integrated survival probability is found to be only $0.74 \pm 0.13$, compared with 1.00 for the ($v = 0, J = 1$) state. Possible loss channels for the vibrationally excited $H_2$, including dissociation and inelastic scattering, are discussed.

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The hydrogen/copper system has become a prototype for studying activated dissociative adsorption for both experiment and theory [1,2]. On the experimental side, molecular beam studies of adsorption [3–6] and laser-based studies of desorption [7,8] have gone a long way towards characterizing general trends in the translational, rotational, and vibrational state dependence of adsorption and desorption. On the theoretical side, advances have been equally impressive, with multidimensional first-principles potential energy surfaces being published [9–12] and dynamical calculations on these surfaces verifying qualitatively the experimental trends. The dissociative adsorption of $H_2$ on copper is thought to be dominated by vibrationally excited molecules at low (<0.4 eV) incident translational energy [1,2,4]. To explore this possibility, scattering experiments in which the translational and vibrational degrees of freedom of the molecule are controlled independently are needed. These results provide an important test of models for activated sticking and mode-specific surface dynamics.

Several groups have used seeded molecular beams generated with heated nozzles to gain partially independent control over the translational and internal (rovibrational) excitation of the incident molecules [4,6]. Their studies demonstrated that internal excitation can be effective in overcoming the barrier to dissociative adsorption. In these studies, however, the incident molecules have thermal distributions of rovibrational states; this complicates interpretation of the results for individual states. Hodgson, Moryl, and Zhao [5] performed a heated nozzle experiment using laser-ionization detection to measure the survival probability of a selected rovibrational state. Again, however, a thermal distribution is present in their incident beam. In addition, they scale their measured reflectivity to the scattered ground state intensity to avoid integrating over the scattering angle.

Here we present the first results of our scattering experiment using both laser state preparation and detection to gain true quantum state specificity. We report a measurement of the survival probability of $H_2$ ($v = 1, J = 1$) scattered from Cu(110) at low incident translational energy (78 meV). Our measurement is absolute in that we have integrated the incident and scattered signal over flight time and scattering angle and have populated and detected a single excited rovibrational state.

Figure 1 shows a schematic diagram of the apparatus used in our experiment. A pulsed, chopped, doubly deferentially pumped supersonic beam of pure $H_2$ from a room-temperature nozzle is directed at normal incidence against a single-crystal Cu(110) surface held in a UHV scattering chamber. The chamber and method of surface preparation have been described previously [13].

The incident molecular beam is intersected at a right angle 0.28 mm before the surface with a "pump" laser which excites molecules from ($v = 0, J = 1$) to ($v = 1, J = 1$) via stimulated Raman scattering [14,15]. The pump and Stokes light which drive this transition are produced by focusing the second harmonic of a $Q$-switched Nd:YAG laser into a cell of $H_2$ at 5 atm pressure and recollimating the residual Nd:YAG and Raman-shifted orders which emerge. These are focused onto the molecular beam with 20 cm focal length lens and timed to hit the temporal peak of the incident ground state pulse. We estimate that within the volume illuminated

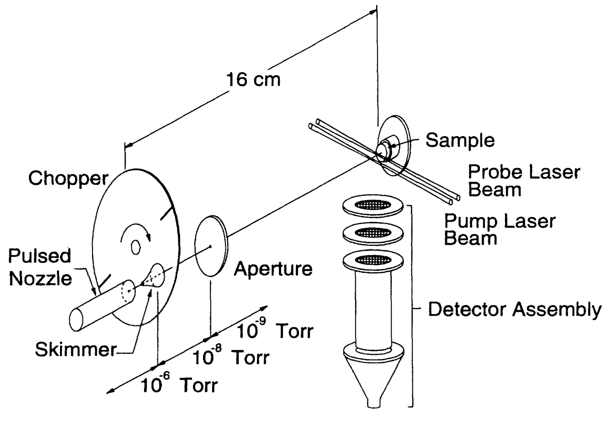

FIG. 1. Schematic diagram of the experiment. A pulsed supersonic beam of $H_2$ is incident normally on a Cu(110) sample in a UHV chamber. The beam is intersected prior to the surface by Raman pump and REMPI probe lasers. Ions created by the probe are collected and detected in a time-of-flight mass spectrometer. Scale is approximate.

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by the focused pump laser, the Raman transition is nearly saturated. Only a single rotational state is promoted to $v = 1$.

State-resolved detection of incident and scattered $H_2$ is done by resonance-enhanced multiphoton ionization (REMPI) [16] using the third harmonic of a Nd: YAG-pumped dye laser (the "probe"). Ionization proceeds via a $Q$-branch transition to the $E, F$ state on the (1,1) band. The probe laser is focused with a 20 cm focal length lens to a point 0.20 mm in front of the surface—slightly closer to the surface than the pump. By scanning the delay between the pump and probe lasers, we record a time-of-flight (TOF) spectrum showing both the incident and scattered molecules. This allows a direct comparison of the incident and scattered intensities and a measure of the survival probability for the vibrationally excited molecules.

Figure 2 shows a TOF curve for $H_2$ at an incident translational energy of 78 meV scattered from clean Cu(110) at 300 K. The signal is from incident and scattered molecules in the $(v = 1, J = 1)$ state. With the pump laser blocked, no signal is seen in either the incident or scattered packet. The flight time is measured from the chopper 15.7 cm upstream of the probe position.

Several aspects of Fig. 2 should be noted. First, the entire spectrum is less than 1 $\mu$s in width, and the time difference between incident and scattered peaks is only 180 ns because of the proximity of the probe to the surface. The incident peak has a FWHM of ≈50 ns. Its probile is determined by the pump laser, which excites only a small part of the incident ground state pulse. Second, the temporal width of the scattered beam, ≈ 150 ns, is considerably larger than that of the incident. This increased width results solely from interaction with the surface: If the sample is moved out of the way and the incident beam is followed downstream, twice the probe to surface distance during scattering, its temporal width increases only a negligible amount. Third, the long time tail of the scattered curve is most likely a result of the angular distribution of the scattered molecules: Those which scatter at large angles reach the probe later than those which scatter along the surface normal. This effect complicates the extraction of the translational energy distribution from the TOF data and is the subject of current investigation.

To measure the survival probability for $H_2$ $(v = 1, J = 1)$ scattered from the surface, we must account for the angular or spatial distribution of the molecules in the plane perpendicular to the laser direction. To do this, we translated the probe position vertically (as shown in Fig. 1) and took a TOF spectrum (like Fig. 2) at each probe position. Figure 3 shows the integrated signal under the incident and scattered peaks in these spectra plotted vs probe height (symbols) along with Gaussian fits to these curves used to reduce the data (solid lines). Note that each point in Fig. 3 effectively includes an integration over the out-of-plane coordinate (parallel to the laser propagation) because of the detection geometry. We estimate the acceptance angle of the integration along this direction to be ±82° from the surface normal, based on the width of the molecular beam (4.8 mm), an estimate of the probe laser interaction length with the beam (8 mm), and the probe to surface distance (0.2 mm). Thus, the ratio of the areas under the fitted scattered and incident curves in Fig. 3 is the survival probability of the $(v = 1, J = 1)$ state, assuming incident and scattered molecules are equally weighted in the TOF scans. This

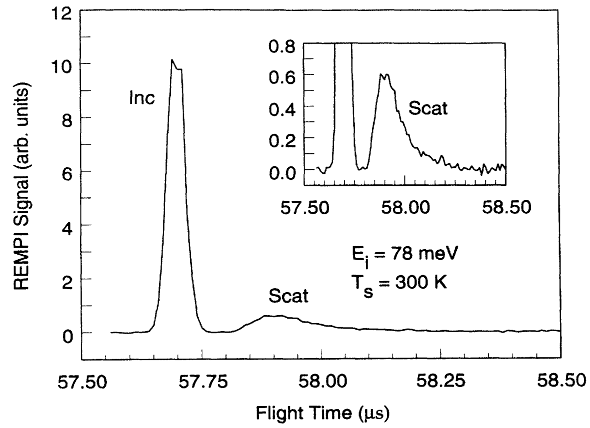

FIG. 2. Measured time-of-flight curve for $H_2$ $(v = 1, J = 1)$ with 78 meV translational energy, scattered at normal incidence from clean Cu(110) at 300 K. Both incident and scattered molecules are shown. Flight time is measured from a chopper 15.8 cm upstream. The vertical scale has been expanded in the inset.

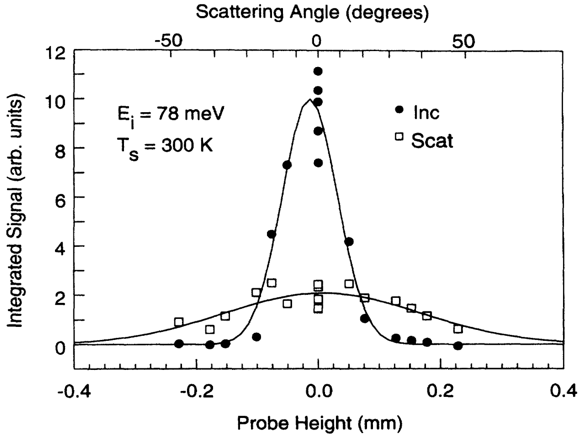

FIG. 3. Measured and fitted spatial profiles for incident (solid symbols) and scattered (open symbols) $H_2$ $(v = 1, J = 1)$. Each point is the integral under the incident or scattered peak in a time-of-flight curve like that of Fig. 2, and scattering conditions were the same as in Fig. 2. The probe was translated parallel to the surface and perpendicular to the laser propagation direction. Fits are with Gaussians.

ratio is 0.74 ± 0.13, where the uncertainty comes from the fitting statistics. However, integration of the TOF scans may overcount the scattered flux relative to the incident, if the scattered molecules have a lower average velocity and/or traverse the probe at larger angles. Thus, the survival probability could be lower than given above; we need a more complete description of the scattered velocity and angular distributions to determine if this is significant. We are currently investigating this as was mentioned above.

The deficit of $H_2$ ($v = 1, J = 1$) in the scattered beam could result from either dissociative adsorption on the surface (sticking) or vibrational relaxation upon collision. Experiments are currently underway to distinguish between these. Either result would be interesting, as we now discuss.

In the first case, previous studies suggest that the translational energy onset for $H_2$ ($v = 1$) sticking on Cu is considerably higher than the 78 meV of our incident beam. For example, Hayden and Lamont [4] concluded from their heated nozzle experiments that the onset of significant sticking for $H_2$ ($v = 1$) on Cu(110) was 130 meV, although they did find a residual sticking at 80 meV. On the theoretical side, reduced-dimensionality dynamical calculations with the most recently computed $H_2$/Cu potential energy surface show a translational energy onset for sticking from $v = 1$ of 140 meV on Cu(110) [12]. The authors estimate the onset would rise some 100–200 meV using higher dimensionality in the calculation.

As for the second possibility, $H_2$ vibrational relaxation could take place by excitation of electron-hole pairs in the solid. Recent experimental and theoretical work in related systems has established that the time scale for this process is comparable with the molecule/surface interaction time in our experiment (<1 ps). For example, vibrational relaxation of CO on copper shows a relaxation time of about 2 ps by this mechanism [17]. For $H_2$ on metal surfaces, theoretical calculations show vibrational lifetime broadening to be almost 20 meV, corresponding to a relaxation time of about 33 fs, if the molecule gets close enough to the surface for the energy of its lowest antibonding orbital to cross the metal's Fermi energy [18]. However, to our knowledge, no theoretical work has been done which would allow us to directly estimate the contribution of vibrational relaxation via electron-hole pair excitation in our experiment. Note that relaxation via phonon excitation is expected to be negligible because of the energy mismatch between the $H_2$ and Cu-Cu oscillations (515 and 10–20 meV, respectively) [19,20].

Rotational excitation from $J = 1$ to $J = 3$ upon collision is a possible, but unlikely, loss channel. Experimental studies have found rotational excitation probabilities for ground state $H_2$ scattered from metals to be only about 1% [21], although they might be higher for the $v = 1$ state. The $J = 1$ to $J = 3$ transition requires 73 meV, which is close to the incident translational energy of 78 meV. (Transitions to $J = 0$ or 2 are not allowed by spin statistics.) If $J = 1 \rightarrow 3$ translational to rotational energy transfer is occurring, however, it would be difficult for us to detect because of the extremely low velocity of the scattered molecules.

An anisotropic spatial distribution of the angular momentum within $J = 1$ could affect our measured survival probability, if the incident and scattered molecules are aligned differently. However, two-photon $\Sigma \leftarrow \Sigma$ $Q$-branch REMPI probing is relatively insensitive to alignment [22], and $Q$-branch Raman excitation is thought to produce no alignment [23]. Furthermore, theoretical calculations indicate that the probability of pure $M$ state changing collisions in $H_2$/surface scattering is small [24]. Therefore, we do not think that angular momentum alignment significantly affects our results.

As a check on the measured survival probability of the excited state, we have measured the survival probability of the ground state $H_2$ ($v = 0, J = 1$), which is known not to dissociatively adsorb at a translational energy of 78 meV [1,2]. Since the temporal width of the ground state pulse is several microseconds, we cannot resolve the incident and scattered molecules in a TOF spectrum recorded at the same probe position used in Fig. 2. Instead, to determine the ground state survival probability, we measured TOF spectra of the ground state (with the pump laser off) both with and without the target present. With the target present, we had 2.02 times as much signal, indicating a measured survival probability for the ground state of unity. Integration over spatial coordinates is unnecessary because the diameter of the ground state beam (4.8 mm) is much larger than the probe to surface distance (≤0.5 mm in this case).

Further confirmation that the excited state survival probability is less than unity on the clean surface is provided by experiments performed at a surface temperature of 100 K. At this low surface temperature, we have observed that the intensity of the scattered $H_2$ ($v = 1, J = 1$) signal increases with time over a period of several hours following sputtering and annealing of the crystal. We attribute this to the accumulation of water or oxygen on the sample since we observe the characteristic oxygen (2 × 1) low energy electron diffraction pattern when the sample is heated to 400 K. (Water decomposes on copper to yield adsorbed oxygen [25].)

The broad spatial distribution of the scattered $H_2$ ($v = 1$) shown in Fig. 3 requires some additional comments. The angular divergence of the incident pumped beam is only 0.04° and is much too small to account for the broad spatial distribution of the scattered molecules. Using the FWHM of the incident and scattered profiles in Fig. 3 (0.10 and 0.38 mm, respectively) and assuming that both curves are represented by Gaussians, we find the FWHM of a Gaussian fit to the deconvolved scattered profile to be 0.36 mm. Using the known probe to surface distance of

0.20 mm, this corresponds to an angular width of ±42° with respect to the surface normal. Hodgson, Moryl, and Zhao [5] found a much narrower scattered angular distribution in their work, but this is partly explained by their use of the less corrugated Cu(111) surface and a much higher incident energy (340 meV) [26]. Our observation of a large angular divergence of the scattered $H_2$ ($v = 1$) is interesting in light of recent theoretical results [10,11,27] suggesting that the potential energy surface at energies where reactive (dissociative) scattering begins to take place is highly corrugated. However, we could not measure the angular distribution of the scattered ground state molecules with equivalent resolution, so we do not know that the broad angular distribution is unique to the excited state.

In conclusion, we find that $H_2$ ($v = 1, J = 1$) with a translational energy 78 meV has a survival probability for scattering from clean Cu(110) of only $0.74 \pm 0.13$. The survival probability increases as the surface becomes covered, most likely with water and/or oxygen, and the angular distribution of the surviving molecules is surprisingly large. These results suggest that either $H_2$ ($v = 1, J = 1$) can dissociatively adsorb at lower incident energies than previously believed, i.e., 80 vs 130 meV, and/or that $H_2$ vibrational relaxation through excitation of electron-hole pairs in copper is rapid compared with the molecule/surface collision time. Experiments are currently underway to distinguish between these possibilities and to characterize the dependence of the $H_2$ ($v = 1, J = 1$) loss channel on incident translational energy and other parameters.

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