Observation of Direct Vibrational Excitation in Collisions of H_2 and D_2 with a Cu(111) Surface

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We have observed the direct vibrational excitation ($v=0 \rightarrow v=1$) of H_2 and D_2 molecules colliding with a Cu(111) surface. The dependence of this process on kinetic energy is found to be similar for both molecules, resembling the function determined for dissociative chemisorption of molecules in the $v=0$ state. This suggests that translational-vibrational coupling is strong only when molecules closely approach the dissociation barrier.

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Studies of the dynamics of energy transfer at the gas-surface interface provide important fundamental input to the understanding of surface chemistry. Inelastic scattering experiments are a natural complement to adsorption studies, providing information both on the form of the relevant interaction potential and on the dynamical couplings effective during the adsorption process. For activated dissociative chemisorption, as the available energy approaches and exceeds the height of the barrier to dissociation, inelastic scattering distributions may become sensitive to the properties of the potential energy surface (PES) in the region of the barrier [1-4]. In particular, the degree of vibrational excitation can provide information on the extension of intermolecular coordinates as the barrier is approached.

We report here the observation of direct vibrational excitation of hydrogen molecules colliding with a Cu(111) surface at energies comparable to the dissociation threshold. While direct vibrational excitation has previously been observed due to electronic [5] or mechanical effects [6], we believe this is the first observation of vibrational excitation resulting from the stretching of a molecule as it approaches the transition state to dissociative adsorption. This observation has a direct bearing on features of the potential energy surface that determine the dissociation dynamics in the hydrogen/Cu system. Specifically, our results appear to require that the barrier to dissociation be "late," involving considerable extension of the internuclear coordinate at the saddle point of the PES.

Experiments were performed in an apparatus that has been described in detail previously [7], but using a rather different approach. Our method permits us to observe directly the dissociation and inelastic scattering of hydrogen molecules in specific quantum states at a Cu(111) surface. Moreover, we can obtain the dependence of these processes on the kinetic energy of the incident molecules over a range of energies comparable to the barrier to dissociation. We direct a molecular beam at a Cu(111) surface using beam conditions chosen to give a wide range of kinetic energies. By chopping such a beam to produce a short pulse far from the surface, we obtain a high degree of temporal dispersion prior to reaching the target. Detecting molecules using state-specific laser ionization a few mm before and after the surface collision thus enables us to follow the loss or gain of molecules in specific quantum states. Making such measurements as a function of the delay after the chopper pulse then provides such information as a function of the molecular velocity (or energy). The advantage of this approach is that species arriving at different delays can be compared directly. If more conventional highly supersonic beams were to be used, separate experiments would have to be carried out at a series of energies, with beams of different fluxes, making comparisons far more difficult. In addition, the use of beams with broad energy spreads has the advantage of providing the highest energies available for a given nozzle temperature, since the high energy tail extends well beyond $4kT_{noz}$, compared to the $\sim 2.7kT_{noz}$ from a supersonic H_2 beam.

We have thus added to the apparatus an assembly for laser-ionization detection of incident and scattered hydrogen using $\sim$205-nm light tuned to discrete two-photon transitions of the E,F-X system [8]. A third photon yields ions, which are extracted onto a multichannel plate detector. In the current study the laser is focused with a 260-mm focal-length lens to a point $\sim$3.5 mm from the crystal. The sample has been prepared with standard techniques and tilted at an angle of 15° to the incident molecular beam. The focus is usually positioned to a point corresponding to the specular scattering angle, with an angular resolution of 15°. With the crystal removed, the focal point could be moved to intercept the molecular beam at the same total distance from its source. The laser pulses had a typical energy of 1.5 mJ, a duration of 8 ns, and a resolution of 0.006 nm at 205 nm.

The molecular beam emerges from a tungsten source operated at about 2000 K with a $\sim$150-μm orifice and is mechanically chopped 230 mm from the surface to give 6-μs pulses that spread to 30 to 60 μs at the point of detection because of the velocity spread in the beam. The fact that the surface-detector distance is short compared to the chopper-surface distance ensures that the total flight times are insensitive to velocity changing collisions at the surface. Measurements were made at a surface temperature of 400 K, except where noted. Doppler shifts are small compared to the laser bandwidth, and

usually cause negligible distortions. The time-of-arrival (TOA) distributions recorded in this manner have a form derived from the kinetic energy distribution of the incident species folded with functions for the loss and gain of the specific quantum state as a function of energy. The form of the distributions is thus sensitive to losses due to dissociation and to vibrational excitation out of a given state and gains due to transitions into that state. The incident beams have vibrational distributions appropriate to the nozzle temperature, giving about 5% and 10% $v=1$ for H_2 and D_2, respectively, at 2000 K.

Such losses and gains are indeed observed as is illustrated in Fig. 1, which displays TOA distributions for D_2 recorded with the laser tuned to detect the $v=1$, $j=4$ state. To observe losses or gains, we compare the TOA distributions of the incident beam [Fig. 1(a)] with those recorded after scattering [Fig. 1(b)]. Figure 1(a) actually shows data recorded after scattering from a surface saturated with deuterium. We find such data to be indistinguishable from measurements made on the beam itself, recorded at the same total chopper to laser distance. This then provides an experimentally convenient method for measuring the beam TOA distribution.

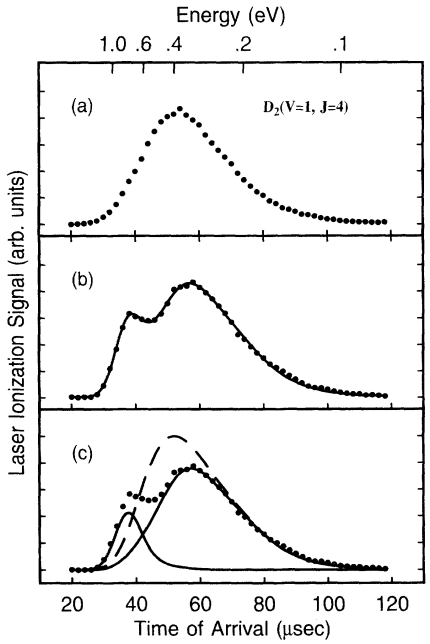

FIG. 1. Time-of-arrival (TOA) distributions of $D_2(v=1, j=4)$ molecules detected after scattering from a Cu(111) surface: (a) scattered from a D-saturated surface, which is indistinguishable from the TOA distribution of the incident beam; (b) scattered from the bare surface; (c) a comparison of (a) and (b) scaled to agree at long times. The solid line in (b) corresponds to a fit based on the change in the incidence distribution, which is indicated as a dashed curve in (c). The two other curves in (c) are the separate components of the fit discussed in the text.

The TOA distribution after scattering from the bare surface [Fig. 1(b)] is clearly bimodal. This distribution shows dramatic examples of both loss and gain of intensity relative to the TOA distribution of the beam. For the lowest energies (longest times) the two distributions are similar. As the energy increases, a loss is seen above about 0.35 eV. Above about 0.6 eV a second peak in the TOA distribution emerges. *We attribute this additional peak to the excitation of high energy (early) $v=0$ species to the $v=1$ state.* Note that the $v=0$ population is much greater than that for $v=1$ so that the excitation of a small fraction of the $v=0$ species can result in a sizable $v=1$ peak. This same behavior has been observed for many different beams with essentially the same result. The additional peak at early times has a constant energetic threshold and is only clearly apparent for beams with a high energy tail extending above ~ 1 eV. No significant dependence on surface temperature is apparent in the range 250–700 K. Note also that the absence of an early peak in Fig. 1(a) indicates that vibrationally inelastic scattering from a saturated surface is improbable.

Figure 1(c) shows a direct comparison of the beam TOA distribution (dashed curve) and the scattered TOA distribution, scaled to agree at low energy. The curve in Fig. 1(b) shows the result of a fit to the data, consisting of two components, which are displayed in Fig. 1(c) as solid curves. The fitting procedure assumes that the $v=1$ signal is composed of two terms: a term $(1-P_{\text{loss}})f_i(t)$ representing loss via adsorption or inelastic scattering out of the $v=1$ state and a term $P_{\text{gain}}F_B(T_v)f_i(t)$ representing gain via inelastic scattering from the $v=0$ to the $v=1$ state; $f_i(t)$ is the TOA distribution of incident species and $F(T_v)$ is a Boltzmann factor giving the ratio of $v=0$ to $v=1$ species. We take the probability of both P's to be of the form [9]

$$P=\frac{A}{2}\left[1+\tanh\left(\frac{E_i\cos^2\theta_i-E_0(v)}{W(v)}\right)\right]. \quad (1)$$

Here E_i and θ_i are the energy and angle of incidence. This form reproduces a curve that rises from zero to a maximum level of "A." E_0 is the point of maximum slope where the function reaches $A/2$, and W is a "width" parameter controlling the range of energies over which the increase occurs. The fitting procedure involves a separate calculation for each measured point in the TOA distribution. It allows for the change in velocity that accompanies vibrational excitation and the fact that signals are proportional to the density, rather than flux, of scattered molecules. It also includes a convolution over the chopper function. The parameters are adjusted by a nonlinear least-squares procedure to achieve the best overall agreement with the data [10].

The components of the fit displayed in Fig. 1(c) as solid curves represent the distribution of reflected $v=1$ and the distribution of $v=0$ molecules excited to the $v=1$

state. The parameters deduced from the fit indicate that the production of $D_2(v=1, j=4)$ follows an excitation function of the form of Eq. (1) with $(E_0/\text{eV}, W/\text{eV}, A) = (0.77, 0.13, 0.32)$ [10]. This is then consistent with an excitation of 32% ($=A$) of the incident molecules for energies that exceed 0.77 eV ($=E_0$) by more than a few times 0.13 eV ($=W$). It is interesting to compare these numbers to those obtained in recent adsorption experiments [11], where it was reported that the energy dependence of the adsorption of $D_2(v=0)$ can be described by Eq. (1) with parameters (0.72,0.07,0.32), indicating a sticking probability of 32% for energies much above 0.72 eV. *These results thus indicate that the degree of vibrational excitation is roughly equal to the degree of dissociation for energies close to the barrier height.* The close agreement between the $E_0=0.72$ eV value for adsorption of $D_2(v=0)$ and the $E_0=0.77$ eV value for excitation of $D_2(v=0)$ indicates that both processes turn on at roughly the same incidence energy. *This strongly suggests that vibrational excitation is governed by the same region of the PES as dissociative adsorption.* The parameters for the loss function for $D_2(v=1, j=4)$ are (0.40,0.13,0.62) as compared to (0.41,0.05,0.32) for the adsorption of $D_2(v=1)$. The larger values for the width W and the maximum loss A (62% loss compared to 32% loss), in the present case are consistent with the fact that loss here involves additional channels.

Figure 2 displays an arrival distribution for $D_2(v=0, j=0)$, for which only a loss is apparent, for energies above about 0.6 eV. Here the D_2 was seeded in H_2 to access higher energies. Again the dashed curve corresponds to the reference distribution and the solid curve to a fit. In this case the parameters deduced from the fit are

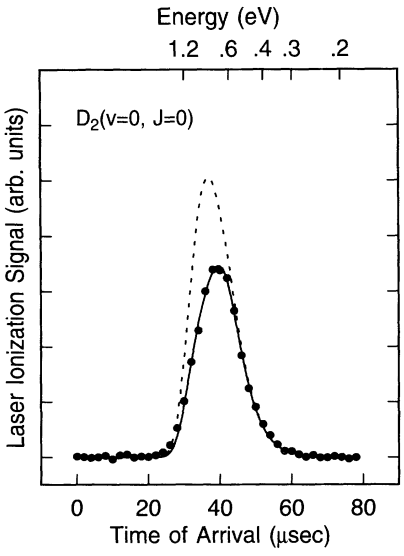

FIG. 2. Time-of-arrival distributions of $D_2(v=0, j=0)$ molecules detected after scattering from a Cu(111) surface. The solid line corresponds to a fit based on the change in the incidence distribution, which is indicated as a dashed curve.

(0.69,0.16,0.47) [10]. Comparing these numbers with those cited previously for adsorption of $D_2(v=0)$ [11] we again note similar values for E_0 and somewhat larger values for W and A, consistent with the availability here of inelastic scattering channels not probed in adsorption measurements.

Similar experiments have been performed with H_2. As for D_2, the TOA curve for $H_2(v=1)$ shows an additional peak, which we attribute to direct vibrational excitation from the high energy tail of the $H_2(v=0)$ population in the beam. The onset energy is similar to that of D_2. There is also a loss seen in the TOA distribution at intermediate energies due to adsorption and inelastic scattering. The TOA curves for $H_2(v=0)$ show only a loss at the highest energies, as in the case of D_2. Separate experiments with near monoenergetic beams with $E_i \sim 0.45$ eV confirm the loss of flux from the $v=1$ state. These latter experiments directly compared the scattering intensity of $v=0$ and $v=1$ molecules with those of the corresponding states in an incident nearly monoenergetic beam in a manner similar to that recently employed by Hodgson, Moryl, and Zhao [12], who report the loss of $v=1$ species from scattered H_2 beams, presumably due to adsorption.

So far we have been concerned only with vibrational states. In fact we find distinct differences in the observed distributions of different rotational states within a given vibrational level. Specifically, the *amount* of adsorption or excitation seems to decrease with increasing j for a given energy. The shapes of the functions nevertheless have the same form. Thus while excitation distributions for $H_2(v=1)$, $j=0$, 3, 5, and 7, are all consistent with the same E_0 and W parameters, the fitted A values decrease by a factor of more than 3 over this range. This suggests that the excitation functions for these j's have the same shape (as determined by the E_0 and W parameters) but different overall scaling factors (as determined by the A parameters). This is illustrated in Fig. 3, which shows arrival distributions for $H_2(v=1)$ with $j=0$, 3, and 5. The constancy of the E_0 and W values is consistent with the finding [11] that (j unresolved) adsorption probabilities of a given vibrational state rise over a narrow energy range (small W), even for experiments involving a broad spread of rotational states. If the energy dependence of each rotational state had a different shape (different E_0 or W), the j-unresolved study would deduce a large W.

These experiments are also sensitive to j-changing collisions, which have not been considered in the analysis. We actually find only slight changes in the rotational distribution of scattered species compared to that for the beam under the conditions of typical measurements. Further, the fact that a gain of signal is seen for all j's for $v=1$ at high energy indicates that the extra flux cannot be derived from within the same vibrational level. Moreover, the good agreement between the loss function obtained here with those based on direct sticking measurements further supports the present interpretation.

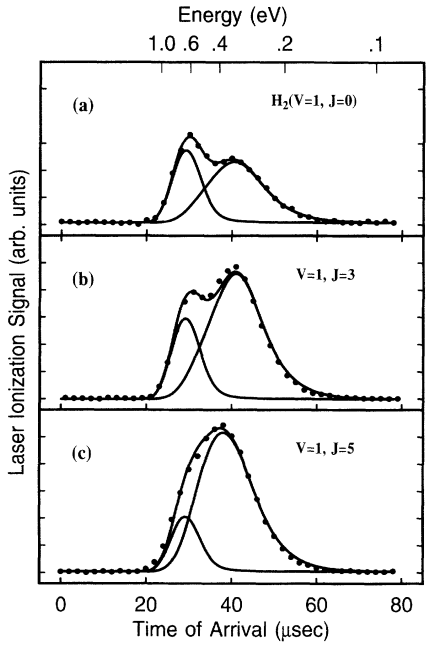

FIG. 3. Time-of-arrival distributions of $H_2(v=1)$ molecules detected after scattering from a Cu(111) surface. Results are displayed for $j=0$, $j=3$, and $j=5$, as labeled. In each case the solid lines correspond to the fit and to the two separate components of the fit.

In summary, we have observed vibrational excitation of H_2 and D_2 in collisions with a Cu(111) surface. Several results support the idea that this vibrational excitation is closely associated with the dissociative adsorption process, which also occurs in such collisions: (1) The excitation function for vibrational excitation resembles the energy dependence of the adsorption probability of $v=0$ species. (2) The similarities in the $v=1$ results for H_2 and D_2 show that the excitation process does not turn on at the energetic threshold for reaching these states. If excitation were to turn on at the energetic thresholds, we would expect the threshold for D_2 excitation to be about 70% of that for H_2, since the vibrational spacing of D_2 is ~ 0.7 of that of H_2. (3) We find no excitation on a covered surface. The current findings suggest that this coupling only reaches sufficient strength relatively close to the top of the barrier to dissociation. Moreover, for translational-vibrational coupling to be reasonably strong, such a barrier needs to be "late," in the sense that reaching the saddle point must entail significant stretching of the internuclear coordinate. These ideas are qualitatively consistent with the many calculations that have explored the dynamics of dissociation in such systems [4,9]. In fact model calculations [4] indicate that vibrational excitation qualitatively similar to that observed here could only be expected on a PES with a late barrier.

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