

## Dynamics of the Direct Reaction of Hydrogen Atoms Adsorbed on Cu(111) with Hydrogen Atoms Incident from the Gas Phase

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Fast HD molecules are observed in the reaction of a beam of H(D) atoms with D(H) atoms chemisorbed on a Cu(111) surface at 100 K. The mean kinetic energy of these molecules is close to 1 eV, or about half of that available. Angular distributions of the nascent HD product are relatively sharp, are displaced slightly away from the surface normal in the specular direction, and display a small sensitivity to the incidence energy. Both the energy and angular distributions are different for D on H and H on D. Results are discussed in terms of a direct Eley-Rideal mechanism.

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Reactions at the gas-surface interface are often discussed in terms of two idealized mechanisms. Most reactions are believed to occur by way of a Langmuir-Hinselwood (LH) mechanism in which both reagents are considered to be chemisorbed and in thermal equilibrium with the surface [1]. Certain highly reactive reactions are thought to proceed via an Eley-Rideal (ER) mechanism in which a reagent from the gas phase reacts directly on impact with a chemisorbed species [1]. So far the evidence for these processes stems largely from kinetic measurements relating the rate of reaction to the incident flux and to the surface coverage and temperature [1]. Dynamical studies have largely been restricted to cases of recombinative desorption via an LH mechanism, where only very limited control of the interaction conditions is possible. In principle the ER mechanism should be readily amenable to dynamical study and should permit a much greater degree of state preparation, at least for the incident species. In fact, such measurements can potentially provide irrefutable proof for the proposed mechanism, if the energy and momenta of the products are shown to be sensitive to those of the incident reagent. However, only one such study has been reported to date [2] involving the protonation of a relatively large hyperthermal molecule. Here I report a second example of such a study, concerning the formation of a hydrogen molecule from the reaction of an incident atom with a chemisorbed atom. This is therefore the first such study involving a simple prototypical system.

The present study was motivated in part by reports of the observation of highly vibrationally excited hydrogen molecules issuing from cells in which H atoms are produced on a hot tungsten filament [3,4]. The excited molecules have been attributed to ER reactions between the incident atoms and those adsorbed on the metal walls of the cell. In one of these experiments, however, molecules are observed with more vibrational energy than should be available for an incident atom reacting with a chemisorbed atom [3], making the interpretation rather difficult. Considering the importance of these observations (e.g., to the understanding of interstellar chemistry, gaseous discharges, and catalytic processes), I wish to extend

these studies to relatively well-defined conditions. My goal is to clarify the dynamics of such atom-surface reactions. The present study describes the progress in this direction. Specifically, I have examined the reaction of incident H and D atoms with D and H atoms chemisorbed on a Cu(111) surface. I report angular and velocity distributions for the HD product, which cannot be understood in terms of any LH process and which must result from a mechanism close to the ideal ER process. Results are briefly compared with recent calculations [5,6].

The molecular beam apparatus employed in this study has been described in detail previously [7-9]. Beams of H and D atoms are directed at a Cu(111) single crystal contained in an ultrahigh vacuum scattering chamber mounted on a manipulator that provides accurate control of incidence angle  $\theta_i$  and surface temperature  $T_s$ . The crystal surface is within  $\pm 0.2^\circ$  of the (111) plane and contamination levels are determined to be below the  $\approx 1\%$  limit of Auger spectroscopy. The mounting is such that the scattering plane is about  $5^\circ$  from the  $[10\bar{1}]$  azimuth. Time-of-flight (TOF) and angular distributions are obtained using a rotatable differentially pumped mass spectrometer. For TOF measurements, the beam must pass through a high-speed chopper, which also provides a trigger signal for pulse counting by a multichannel scaler.

The measurements reported here are made using two different atomic beam sources installed in a dual beam system. Relatively low-energy ( $\sim 0.06$  eV) H and D atom beams are generated using a microwave discharge source consisting of a quartz tube with a  $\sim 2$ -mm-diam hole [8,9]. This source yields a beam that is about 90% dissociated and has an atomic flux of about 0.2 monolayer/s at the crystal position, which is  $\approx 30$  cm from the orifice [1 ML (monolayer)  $\sim 1.5 \times 10^{15}$  cm $^{-2}$ ]. This beam is directed through a  $\sim 50\%$  chopper for phase-sensitive detection of the nascent HD product. High-energy beams ( $\sim 0.35$  eV) are made by thermal dissociation in a tungsten tube beam source operated at 2300 K. Using a 2-mm-diam hole and a source pressure of a few Torr I obtain an atomic flux of about 0.5 ML/s together with a molecular flux of  $\sim 10$  ML/s (about 5% dissociation). This beam is chopped by the high-speed chopper,

which reduces the flux by a factor of 100 and yields 6- $\mu$ s pulses for TOF measurements.

Measurements are typically made by covering the Cu(111) surface with a saturation dose of H or D from one of the beam sources at a surface temperature of 100 K. This source is then turned off and evacuated to remove all traces of the given isotope from the system. Then a beam of the other isotope, D or H, is directed at the surface, and the HD product is detected. This product is found to be produced promptly but to decay essentially to zero as the incident isotope replaces the initial isotope on the surface. Using temperature-programmed desorption measurements to determine surface coverages, I find that the HD intensity associated with an incident H atom beam is proportional to the D atom coverage. *I find this to be true even when the total H and D coverage on the surface remains much less than saturation throughout the measurements.* These same statements hold for D incident on an H-covered surface, so long as due allowance is made for the HD contamination in the beam (see below). Note that no HD desorption is expected at this surface temperature (100 K) via known LH processes, especially for an unsaturated surface.

Information on the velocity of the HD product molecules is obtained from TOF measurements employing the high-temperature source. The analysis and convolution over the arrival times of the incident atoms and the chopper function are as described previously [7,10], assuming that both the incident atoms and the HD product have velocity distributions of the form  $f(v) \propto v^3 \exp[-(v-v_0)^2/\alpha^2]$ . The distribution function for the incident atoms is determined by using laser multiphoton ionization detection, rather than the quadrupole mass spectrometer. This was necessary because the  $H^+$  and  $D^+$  signals from the mass spectrometer have an unknown contribution due to fragmentation of the excess of molecular hydrogen in the beam. As a check on the methodology, TOF measurements have been made on molecular hydrogen with both laser and mass-spectrometric detection. The two methods yielded energies that agreed to within about 1%. Atoms are detected using  $\sim 205$ -nm radiation, as reported by Bokor *et al.* [11]. Molecules are detected using  $\sim 202$ -nm light as described by Marinero, Rettner, and Zare [12], but using about  $\sim 1$  mJ of light produced by frequency tripling a dye laser.

A representative TOF distribution of HD product is displayed in Fig. 1. This distribution was obtained with an atomic D beam incident on a H-covered Cu(111) surface at a mean energy of 0.33 eV and an incidence angle of  $60^\circ$ , detecting parallel to the surface normal. The solid line added to the data corresponds to a best fit with  $v_0 = 2100$  m/s and  $\alpha = 5200$  m/s, yielding a mean energy of 1.1 eV. From this and other similar measurements, I conclude that the mean energy of the HD produced under these conditions is  $1.1 \pm 0.2$  eV, independent of final angle within a range of  $\pm 20^\circ$  of the surface normal. Similarly, I conclude that the  $\alpha$  value is always large, indicat-

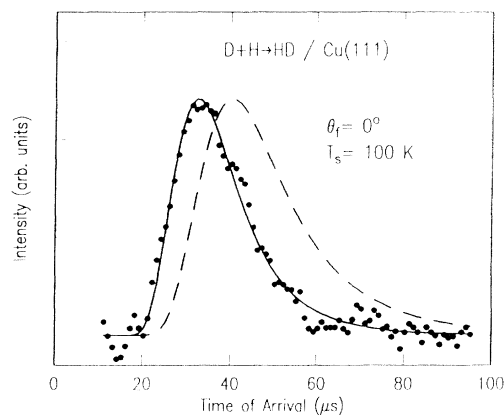


FIG. 1. Time-of-flight (TOF) distribution of the HD product of the interaction of D atoms with an H-covered Cu(111) surface at 100 K. This form reflects both the TOF of the D atoms to the surface and the flight of the HD product to the detector. The solid curve is a fit to the data yielding a mean HD kinetic energy of 1.1 eV, as discussed in the text. The dashed curve indicates the TOF of scattered HD with an energy of 0.45 eV.

ing that the HD is produced with a broad spread of energies. The results are consistent with a spread in energies from essentially zero to about 3 eV. This upper limit is not well determined, but energies in excess of 2 eV are certainly indicated. That the product energy is indeed high can be judged by comparing the data with the dashed line in Fig. 1. This line indicates the form of a TOF distribution of *scattered* HD, present in the beam at trace levels. It is clear that the scattered species are appreciably slower, yet they have an energy of about 0.45 eV. Qualitatively similar results have been obtained for the case of H atoms incident on a D-covered surface. However, in this case the kinetic energy of the HD product is found to be distinctly lower, amounting to about  $0.75 \pm 0.15$  of the D-on-H value, with a mean energy of  $0.85 \pm 0.2$  eV. This value is again independent of angle within  $20^\circ$  of the surface normal.

I have also determined angular distributions of these reactions. Distributions have been measured for high- and low-energy beams for both H and D incident on the other isotope. Since the HD signal decays with time, these distributions are obtained on a point-by-point basis, recording signals on the differentially pumped mass spectrometer at fixed final angles. In all cases, signals are integrated and the relative HD product intensity taken as the modulated component. Thus TOF distributions of the same basic form as displayed in Fig. 1 provide relative signals for each angle. Figures 2 and 3 display angular distributions of the HD product for incident H and D, respectively. Each figure shows results for both incidence energies. It will be apparent that the angular distributions are slightly asymmetrical with respect to the normal, being displaced by a few degrees in the specular direction. The curve added to Fig. 2 corresponds to a

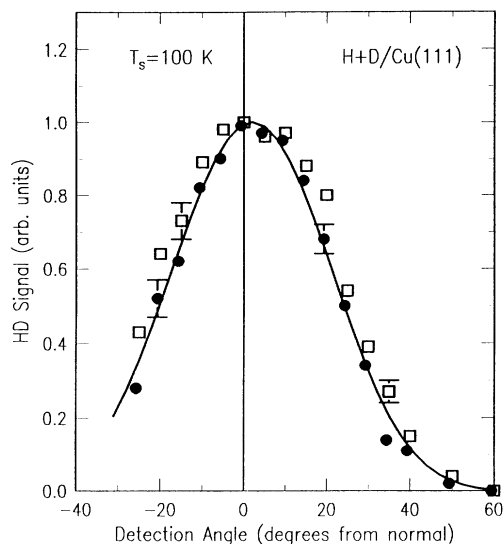


FIG. 2. Angular distribution of the HD product of the interaction of H atoms with a D-covered Cu(111) surface at 100 K. Solid symbols were obtained with H atoms having a kinetic energy of about 0.06 eV incident at  $\theta_i = 70^\circ$  while the open symbols were obtained with H atoms having a kinetic energy of about 0.36 eV incident at  $60^\circ$ . The data points correspond to measurements of the relative ion current signals, and therefore refer to the gas density rather than flux. The curve corresponds to a  $\cos^9\theta_f$  distribution shifted towards the specular by  $2^\circ$ .

$\cos^9\theta_f$  distribution shifted by  $2^\circ$ . Similarly, Fig. 3 displays a  $\cos^3\theta_f$  curve shifted by  $5^\circ$ . While no physical significance is implied by the choice of these functions, they serve to summarize the results and provide an estimate of the size of the shifts with respect to the surface normal. Although the shifts are not large, they are considerably larger than the experimental uncertainties, since He atom scattering is used to define detection angles to about  $0.2^\circ$ . It will be apparent that the distributions are substantially different for incident H and D. Comparing Fig. 2 with Fig. 3 reveals that the D-incident distribution is  $\sim 1.5$  times broader than that for the H-incident case. It is also apparent that the detailed shape of these distributions is slightly sensitive to the incidence energy.

In the case of incident D atoms, due allowance has been made for a contribution to the HD signal from scattered HD present in the beam. This contribution is assessed by covering the surface with D rather than H, thereby eliminating the reactive component, yet providing a virtually identical scattering target. What remains is a scattering lobe that peaks close to the specular direction with a peak height that is comparable to the distributions in Fig. 3. The TOF distributions for this component indicate very little change in energy with respect to the incident HD component of the beam.

Since the relative intensity of the incident D and HD fluxes are known (D:HD  $\sim 15:1$ ), comparison of the rela-

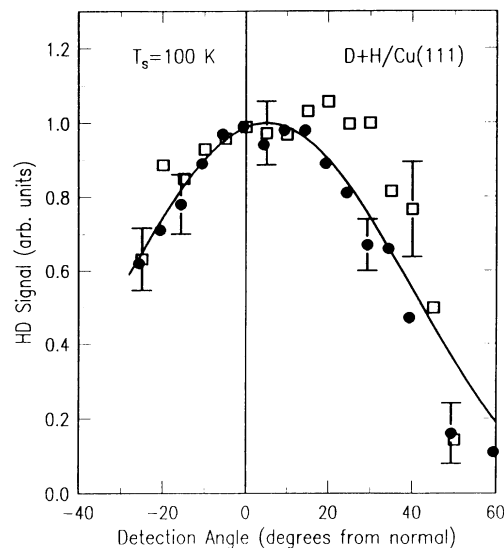


FIG. 3. As for Fig. 2 except for D atoms incident on a H-covered Cu(111) surface. Here the open symbols refer to D atoms incident with a kinetic energy of 0.33 eV. The curve corresponds to a  $\cos^3\theta_f$  distribution shifted towards the specular by  $5^\circ$ .

tive intensity of the scattered HD and the product HD permits the reaction probability to be estimated, since the scattering probability of the incident HD is  $\sim 1$ . This comparison then requires integrating over the respective angular distributions and allowing for the differences in velocity (since signals are proportional to density). Such a comparison gives an estimate of the reaction probability for 0.33-eV D incident on a H-covered Cu(111) surface of  $0.6 \pm 0.4$ , where the uncertainty primarily reflects ignorance of the form of the out-of-plane angular distributions. Here no allowance is made for possible differences in the detection sensitivity due to the differing levels of vibrational excitation of the scattered and product HD. This reaction probability is consistent with estimates made from the total HD yield into the chamber associated with a given incidence dose. For example, I obtain  $0.8 \pm 0.2$  for D incident at 0.06 eV on a H-covered Cu(111) surface. Both estimates are in good quantitative agreement with recent calculations [5,6]. Further studies are required to determine whether or not this probability varies with the incident isotope or the kinetic energy or incidence angle.

While the kinetic energy deduced for the HD products is large compared to  $kT_s$ , the  $\sim 1$  eV of mean kinetic energy accounts for only a fraction of the total energy available. Formation of  $\text{HD}(v=0)$  from two free atoms yields 4.5 eV, while the heat of adsorption of hydrogen atoms is reported to be  $\sim 2.4$  eV on Cu surfaces [6,13]. The reaction  $\text{H}(\text{D})_{\text{gas}} + \text{D}(\text{H})/\text{Cu} \rightarrow \text{HD}_{\text{gas}} + \text{Cu}$  is thus about 2.1 eV exothermic. Allowing for the kinetic energy of the incident atom raises the available energy to over 2.4 eV. The present results indicate that more than half

of this energy is channeled into other modes on average. Moreover, the broad spread in kinetic energies indicated by the measurements requires a complementary spread in the energy appearing in other modes. Thus the low-energy tail of the deduced velocity distribution must be associated with transfer of essentially the full 2.4 eV into other modes. Since energy transfer to the lattice is likely to be inefficient for this system [5,6], the current results suggest that a large fraction of the available energy is channeled into internal motions. While a high degree of rotational excitation is possible, the present results are clearly consistent with previous observations [4,5] and calculations [5,6] which suggest that hydrogen atoms incident on a hydrogen-covered metal surface react to form molecules in very high vibrational states.

That the HD product kinetic energy should be different for incident H and D may at first be surprising. However, consideration of the kinematics of these different systems indicates that different energies are easily rationalized. The basic argument has been elegantly stated recently by Jackson and Persson [6]. Considering a one-dimensional collision in the impulsive limit, it is apparent that the critical difference between H on D and D on H is that an incident H atom can be reflected by a D atom, but an incident D atom will not be stopped by an H atom. Thus for H on D, the H and D atoms may be initially traveling in opposite directions immediately after the encounter, while both atoms will be moving in the same direction for D on H. The former case then leads to more vibrational excitation as a result of the extended bond, at the expense of product kinetic energy. More detailed calculations seem to support this simple picture [5].

The angular distributions are seen to be close to the normal with a small deviation towards the specular. Conservation of the parallel momentum of a D atom incident at  $60^\circ$  with 0.33-eV kinetic energy would require a 1-eV HD product to leave the surface at about  $25^\circ$  to the surface normal. Thus we conclude that the interaction potential must be somewhat corrugated. This behavior is consistent with the idea that incident atoms are accelerated substantially by the attractive potential prior to reaction, penetrating the surface sufficiently deeply to experience the necessary corrugation. One might expect the incident atom to acquire most of the 2.4-eV heat of adsorption before striking the target atom [5,6]. The fact that the angular distributions are relatively narrow and close to the normal suggests that the acceleration occurs primarily in a direction parallel to the surface normal. The increase in deviation towards the specular for D on H compared to H on D may suggest that some tendency towards parallel momentum conservation persists. The increased width of the D-on-H distributions compared to the H-on-D case is consistent with the simple kinematic arguments made above. The incident D atom may simply

penetrate deeper into the surface before turning around with its H partner than for the alternative case. In addition to these effects, the form of the angular and velocity distributions will be sensitive to the extent of the repulsion felt by the nascent molecule as it leaves the surface, just as in recombinative desorption [9]. Detailed calculations are required to further explore these ideas.

In summary, I have shown that when H or D atoms collide with a D- or H-covered Cu(111) surface they may react to form an HD molecule. These molecules are produced with a broad spread of energies with a mean of about 1.1 eV for incident D and 0.8 eV for incident H. Although large, these energies account for less than half of the available energy, suggesting that the HD molecules may be formed with a high degree of internal energy. The angular distributions are quite narrow and peak close to the surface normal, suggesting that incident atoms are accelerated substantially by the gas-surface potential prior to reaction. Differences between incident H and D may be understood in terms of simple kinematic arguments. These observations are inconsistent with a LH mechanism and are attributed to an ER process. The observed differences for H on D and D on H provide particularly strong evidence that the incident atoms react directly on impact.

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