Dynamics of the Eley-Rideal Reaction of D Atoms with H Atoms Adsorbed on Cu(111): Vibrational and Rotational State Distributions of the HD Product

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We have determined the internal-state distribution for the HD product of the reaction of gas-phase D atoms with H atoms chemisorbed on Cu(111). The populations of the vibrational states $v = 0$, 1, 2, and 3 are comparable, while that for $v = 4$ is considerably smaller, giving a mean vibrational energy of ~0.7 eV. The mean rotational energy falls with increasing v, from ~0.5 eV for $v = 0$ to <0.2 eV for $v = 4$, with an overall mean rotational energy of ~0.4 eV. The maximum internal energy observed is ~2.3 eV, consistent with the total energy available to the product. Results are compared with recent calculations.

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Most gas-surface reactions are believed to occur after both reagents have come to thermal equilibrium with the surface, by way of a Langmuir-Hinschelwood (LH) mechanism. It has long been suspected that certain highly reactive reactions can occur directly between an adsorbed species and a reagent incident from the gas phase, by way of an Eley-Rideal (ER) mechanism [1]. Until recently, the evidence for this latter process came largely from kinetic measurements relating the rate of reaction to the incident flux and to the surface coverage and temperature [1]. Recent dynamical studies, however, have firmly established that the ER mechanism can indeed occur.

The strongest evidence for the ER mechanism has come from studies that have correlated changes in the properties of the reaction product with changes in the energy of the incident species. In the first such study [2] of which we are aware, Kuipers *et al.* [2] showed that hyperthermal $N(C_2H_4)_3N$ molecules can pick up a proton from a Pt(111) surface, giving an ion whose translational energy depends on that of the incident molecule. More recently, Rettner [3] studied the formation of HD from H atoms incident on D/Cu(111), and from D incident on H/Cu(111). The angular distribution of the HD was found to be asymmetrical about the surface normal and to change with incidence energy. Similar behavior was reported for the ER product of the reaction of H atoms with Cl/Au(111) [4,5], although in this case a clear contribution from a LH mechanism was also apparent, confirming an earlier proposal of Lykke and Kay [6].

Evidence for the ER mechanism has also come from the observation of high internal energy in product molecules, consistent with the much higher exothermicity of ER reactions compared to the corresponding LH processes. Hall *et al.* [7] and Loss and co-workers [8] found highly vibrationally excited hydrogen molecules issuing from cells containing a source of H atoms. These excited molecules have been attributed to ER reactions between the incident atoms and those adsorbed on the metal walls of the cell. These experiments employed a poorly defined collision and collection geometry, however, in which product H_2 molecules could make many gas-surface collisions prior to detection. Moreover, vibrational states were observed with more vibrational energy than should be available for an incident atom reacting with a chemisorbed atom even for a single collision, indicating that the reacting species could be a physisorbed atom, rather than a chemisorbed atom [7]. Lykke and Kay [6] and Rettner [5] have carried out more controlled studies, involving the reaction of H-atom beams with Cl adsorbed on Au(111). In this case, the HCl vibrational state distribution peaks in the first excited state, but much of the available energy appears to be lost to the surface [5].

These experiments have been complemented by a number of detailed computational studies [9–14], which confirm that the reaction can indeed occur on a single gas-surface collision. The most recent work has involved quantum-mechanical models, beginning with the model 2D calculations of Kratzer and Brenig [11] and Jackson and Persson [12], who have examined the ER reaction of H atoms incident on H chemisorbed to metals. Both groups obtain a high degree of vibrational excitation, but the restricted collinear geometry neglected rotational motions. Jackson and Persson [14] have recently rectified this problem by performing 3D quantum calculations, using a flat-surface approximation. In addition to vibrational excitation, their results display a high degree of rotational excitation for each of the four different model potential energy surfaces examined [14]. These surfaces were chosen to model the interaction of a gas-phase H atom with a H atom adsorbed on Cu(111).

As Jackson and Persson point out [14], the H + H/Cu(111) system has several appealing features in the context of model ER studies. The interaction between hydrogen and Cu(111) has been the subject of a large number of experimental and theoretical studies of the dynamics of dissociative adsorption [15,16], and is very much a model system for such studies. Moreover, the

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light hydrogen mass can lead to interesting quantum effects in the dynamics, and the possibility of substituting D for H permits a range of mass combinations to be explored. To date, the experimental information on this reaction has been limited to information on the angular distribution and velocity of the product molecule. In order to test computational studies and to develop a detailed understanding of this important model system for the study of ER reactions, experimental information is needed on the state distributions of the product. The present study provides this information.

Specifically, we report the rotational and vibrational state distributions of the HD product of the reaction of D atoms with H atoms adsorbed on Cu(111) for near-normal incidence and a surface temperature of 100 K. This study extends the earlier measurements [7,8] on the vibrational state distribution of hydrogen formation by H-atom surface reactions to relatively well defined conditions. Results are briefly compared with recent calculations [11–14].

The molecular beam apparatus employed in this study has been described in detail previously [3–5,16,17]. Beams of D atoms (mean energy ~0.07 eV) from a microwave discharge source are directed at a Cu(111) single crystal contained in an ultrahigh vacuum scattering chamber. The crystal surface is within ±0.2° of the (111) plane, and contamination levels are determined to be below the ≃1% limit of Auger spectroscopy. For these experiments, the incidence angle was fixed at 10° and the surface temperature to 100 K. The scattering plane, containing the direction of the incident beam and the surface normal, is close to the $[1\bar{2}1]$ azimuth. Measurements are made by covering the clean Cu(111) surface with a saturation dose of H/H_2 from a 2300 K effusive source. The HD product is found to be produced promptly but to decay essentially to zero as the incident D replaces the H on the surface. Using temperature programmed desorption measurements to determine surface coverages, the HD intensity associated with an incident D-atom beam is found to be proportional to the H-atom coverage, as seen previously for this system [3], and more recently for the H/D/Ru(100) system [18].

The HD product is detected using three-photon ionization via a two-photon resonance to the $E,F^1\Sigma_g^+$ state [19,20]. All measurements are made using $(0,v)$ bands, where v is the vibrational state of the ground electronic state of the species under study, using radiation with a wavelength between 201 [for $Q(0)$ of the (0,0) band] and 232 nm [for $Q(11)$ of the (0,4) band]. This light is obtained from a Nd:YAG-pumped dye laser (Quanta-Ray, DCR2/PDL2), as described previously [5]. The laser beam is focused with a single plane-convex suprasil lens with a focal length of 260 mm to a point about 3 mm from the point where the 3 mm diameter D-atom beam strikes the crystal. The angular resolution is about 50° in the scattering plane, with effective integration over all out-of-plane angles. Relative sensitivity factors for the detection of HD in different v states were determined by calibration experiments similar to those described by Rinnen, Kliner, and Zare [20] employing an effusive beam of HD from the 2300 K source under the same detection conditions. The sensitivities for different J states within a given $(0,v)$ band were found to be indistinguishable within ±10% uncertainties, consistent with previous work [20,21]. Consequently, all J states were assumed to have identical sensitivities. Populations were determined by correcting only for laser power variations (using measured power dependences) and for the sensitivity factors for different $(0,v)$ bands. No allowance was made for small differences in the Doppler linewidths or for differences in the widths of the ion pulses, which were found to vary by less than ~20%.

Figure 1 displays plots of the J distributions obtained for the HD product of the reaction of D atoms with a H-covered Cu(111) surface for molecules in the $v = 0-4$ vibrational states, with $T_s = 100$ K and $\theta_i = 10°$. No attempt was made to look for molecules in the $v = 5$ state. The relative normalized signals have been plotted against total internal energy, the sum of rotational and vibrational energy, but not including zero-point vibrational energy. These results correspond to relative densities of the product species, since the ion signal is proportional to the number of molecules in the ionization volume. These relative number density distributions can be approximately converted to the corresponding relative flux distributions by multiplying the signal for each v-J state by the molecular velocity. This velocity can be estimated by assuming that all of the heat of reaction is carried away by the HD product. The light molecular mass should ensure that

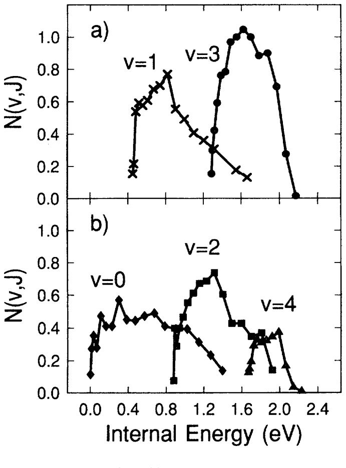

FIG. 1. Quantum-state distributions of the HD product of the interaction of D atoms with a H-covered Cu(111) surface at 100 K. The populations correspond to product densities, as detected by laser ionization. The rotational distributions for $v = 1$ and $v = 3$ states are shown in (a), while those for $v = 0$, 2, and 4 are displayed in (b).

very little energy is transferred to the Cu lattice. For the purpose of this transformation, the available energy is taken as 2.3 eV, consistent with the highest energy states observed (Fig. 1) and with what is known about the energetics of this reaction [14]. The resulting v-J distributions for approximate relative reaction product fluxes are given in Fig. 2. It is seen that the distributions are qualitatively similar to those in Fig. 1, but that the contributions of each of the vibrational states $v = 0$ to 3 are closer to being equal.

Figure 3(a) shows the corresponding vibrational state distributions, summed over J, for HD product density (broken line) and approximate flux (solid line). The points are normalized to a sum of unity in each case. Figure 3(b) shows the mean rotational energy for each state. These rotational energies were also obtained from the approximate fluxes, rather than from densities. The overall mean rotational energy is estimated to be ~0.4 eV, compared to a mean vibrational energy (not including zero-point energy) of ~0.7 eV. Assuming no energy loss to the lattice, the mean translational energy is then ~1.2 eV. This value compares well with the previous experimental measurement [3] of 1.1 ± 0.2 eV, for D atoms with a translational energy of $E_i = 0.33$ eV incident on a H-covered Cu(111) surface at $\theta_i = 60°$. Given that the dynamics may change with θ_i and E_i, as seen in recent calculations for H + H/Cu(111) [14] and that the present experiments average over essentially all final angles, this near-perfect agreement may be somewhat fortuitous.

It is apparent that the HD product is formed with a high degree of both vibrational and rotational excitation. Taken together with previous results on the kinetic energy distribution of the HD product [4], these results provide a rather complete picture of the energy partitioning in this reaction. The energy released couples rather efficiently to all three product energy channels: translation, vibration, and rotation. The ordering of mean energies is $\overline{E}_{\mathrm{trans}} \geq \overline{E}_{\mathrm{vib}} \geq \overline{E}_{\mathrm{rot}}$.

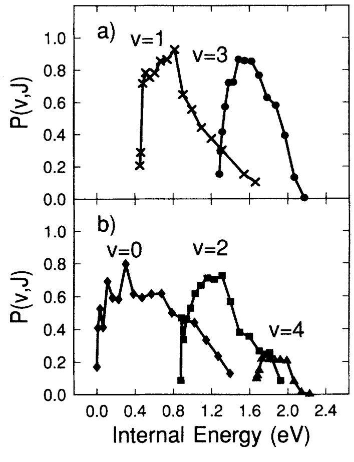

FIG. 2. Quantum-state distributions of the HD product of the interaction of D atoms with a H-covered Cu(111) surface at 100 K. These results are the same as those in Fig. 1, except that they have been approximately corrected to the flux of a given v-J state.

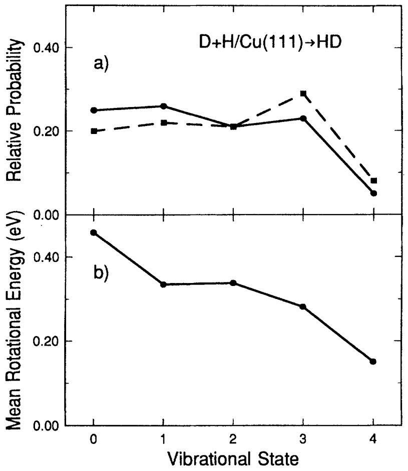

FIG. 3. (a) Vibrational-state distributions of the HD product of the interaction of D atoms with a H-covered Cu(111) surface at 100 K. The broken line corresponds to normalized laser-ionization signals, while the solid line shows the trend for product flux. (b) Mean rotational energy as a function of vibrational state for the HD product of the reaction of D atoms with a H-covered Cu(111) surface at 100 K.

From the high degree of vibrational excitation, we can draw some immediate qualitative conclusions about the form of the potential surface for this reaction. Vibrational excitation is generally associated with an attractive potential energy surface [22], in which energy is released as the reagents approach. Thus the vibrational state distribution is consistent with estimations of the form of the photoemission spectroscopy for this system [14], and with detailed dynamical calculations on those model surfaces [14,23]. Kinematic effects are also expected to be important in determining the detailed form of the vibrational state distribution, however, since recent calculations [23] and preliminary experiments [24] indicate that the reaction of H with D/Cu(111) yields a substantially different state distribution.

From the high degree of rotational excitation of the product, we can immediately conclude that the collinear approximation used in some previous calculations [11–13] is inadequate. It is clear from Fig. 3(b) that the degree of rotational excitation decreases with increasing vibrational energy—there is an anticorrelation between vibrational and rotation excitation. This behavior is expected for a fixed total energy—there is less energy available to rotation for molecules in high v states—and has been seen in recent calculations [14]. It is apparent that this trend is rather weak, however. The high energy tails of the rotational distributions actually move to higher total internal energy as v increases. These tails do not extend to a common internal energy equal to the total energy available. It is possible that angular momentum constraints inhibit the population of very high J states. Such constraints could arise if the reaction probability falls off at large impact parameters or if the maximum effective impact parameter is limited by the spacing of H atoms on the surface. Insight into this latter contention might be obtained by studying the high J cutoff as a function of surface coverage.

In summary, we have shown that when D atoms collide with a H-covered Cu(111) surface, they react to form a HD molecule that leaves the surface with a high degree of vibrational and rotational excitation. In addition to helping to guide theoretical studies of ER reactions, it is expected that these results may aid in the understanding of complex systems in which atom-surface reactions may occur, such as in interstellar chemistry, gaseous discharges, and catalytic processes.

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