State-Specific Dynamics of D_2 Desorption from Cu(111): The Role of Molecular Rotational Motion in Activated Adsorption-Desorption Dynamics

H. A. Michelsen,[a] C. T. Rettner, and D. J. Auerbach
IBM Research Division, Almaden Research Center, San Jose, California 95120-6099
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We report state-specific kinetic energy distributions for D_2 desorbed from Cu(111), which we have analyzed to obtain state-specific functions for adsorption probability versus kinetic energy. The dependence of these functions on vibrational state is in agreement with previous adsorption measurements. The dependence of the adsorption functions on rotational state J reveals a complex dynamical role for rotation in activated adsorption. As a function of J, the translational energy required for adsorption first increases slightly as J increases from 0 to 5 and then decreases markedly with higher J.

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Recent studies have yielded considerable insight into the roles of kinetic and vibrational energy in activated dissociative adsorption, notably for the important model system of hydrogen and deuterium at Cu surfaces [1]. Electronic structure calculations [2–5] show that the $H_2(D_2)$/Cu potential energy surface possesses a barrier to adsorption of about 1 eV with a substantial increase in the equilibrium H-H internuclear distance near the crest of the barrier or "transition state" region of the potential. Consistent with this stretching of the molecule in the transition state, calculations of dissociation dynamics [6–9] indicate that vibrational energy can help an incident molecule overcome the barrier to dissociation. These calculations are strongly supported by recent experimental results. Measurements of the variation of dissociation probability with vibrational temperature and kinetic energy show a large increase in the adsorption probability with an increase of population in higher vibrational states of incident molecules [10–14]. Additional measurements of the reflection probability of specific vibrational states [15–17] of H_2 and D_2 at a Cu(111) surface confirm this result and reveal another interesting aspect of the vibrational dynamics in these collisions: Vibrational excitation is an important scattering channel at energies comparable to the energy required for dissociation.

In comparison to our breadth of knowledge about the role of vibrational motion in dissociative adsorption and recombinative desorption, our understanding of the role of rotational motion is limited. It has not yet been possible to make adsorption measurements that yield information on the effect of rotation on the probability of activated dissociative chemisorption. The few state-resolved studies of recombinative desorption reported to date have largely concerned systems with small or negligible activation barriers [18–21]. Likewise, the theoretical study of rotational effects in dissociative adsorption has been more limited than that of vibrational effects, at least in part because of the difficulties associated with the larger number of coordinates necessary to treat the rotational problem.

For many reasons, we would like to have more detailed information on the role of rotation in adsorption and desorption. Although the paucity of information about rotational effects severely limits the ability to develop a complete description of the dynamics of these processes, theoretical results hint at interesting effects. Electronic structure calculations [2,3] show a substantial variation of the barrier with molecular orientation. Dynamical calculations [22] indicate that this anisotropy gives rise to a large variation in adsorption probability with M, the projection of the angular momentum vector on the surface normal, and to substantial rotationally inelastic scattering. Other calculations have suggested that putting extra energy into rotation can cause the adsorption probability to increase [23], remain the same [24], or decrease [25,26].

The only experimental results that bear directly on the effect of rotational motion on the kinetic energy barrier to adsorption are rotational state distributions for H_2 and D_2 desorbed from Cu(110) and Cu(111) recorded by Kubiak, Sitz, and Zare [27]. Kubiak, Sitz, and Zare concluded that although these distributions have a mean rotational energy somewhat less than kT_S, they do not deviate dramatically from a Boltzmann distribution. Since the measured distributions appear to have slightly enhanced population at low J, application of the principle of detailed balance indicates that rotational motion may slightly inhibit adsorption. It is not possible from these data to separate the M-state or steric effects (which theory indicates may be substantial) from the J-state effects. It is also not possible from such data to learn about the effect of J on the kinetic energy dependence of adsorption. Although it is possible to obtain this information from desorption data and detailed balance arguments, a different approach is necessary, an approach based on measuring velocity distributions of molecules desorbed into specific (v,J) states.

We report here measurements of the velocity distributions of D_2 molecules desorbed from Cu(111) for vibrational states $v=0$, 1, and 2 and for a wide range of rotational states J up to $J=14$ for $v=0$. These measurements are in accord with predictions based on previous work with respect to vibrational states, but reveal a

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surprising richness to the desorption dynamics with respect to rotational states. As a function of J, the mean energy for desorption is *nonmonotonic*. As J is increased, this energy first increases slightly, reaches a maximum around $J=5$, and then decreases as J is increased further. We have analyzed these velocity distribution measurements via detailed balance to produce sticking probability versus energy curves for each of the states involved. We believe this approach provides the most detailed and precise state-specific information currently available about surface chemical reaction dynamics.

The experiments involved studying D_2 desorbed from Cu(111) after permeation (as atoms) through the bulk. The experiments were conducted in a UHV instrument that will be described more fully in a future publication. The pressure of D_2 behind the crystal was ~ 1 bar. The crystal and heater assembly were the same as those used previously by Kubiak, Sitz, and Zare [27]. We realigned and repolished the crystal to insure that the orientation was within 0.2° [28] of the nominal (111) plane. The crystal was cleaned by Ar^+ ion bombardment, and Auger electron spectroscopy (AES) was used on a regular basis to insure that the crystal was free of contamination. For all of the data reported here, the contamination was less than 0.05 monolayer and often below the limit of detection of AES. Low-energy electron diffraction (LEED) was used at the outset of this study to check the quality of the crystal surface; a sharp 1×1 pattern characteristic of a clean, well-ordered surface was observed.

The desorbed D_2 was detected in a differentially pumped chamber using resonant multiphoton ionization via the E,F-X system [29]. The photoions were formed in a field free region, drifted ~ 24 mm, and were then extracted and focused onto a multichannel plate detector. The angular resolution was $\sim \pm 20°$.

Time-of-flight (TOF) measurements on the ions were used to determine velocity distributions of the desorbed D_2. Distributions were corrected for certain background contributions by subtracting a wave form obtained with the laser tuned away from resonance. In addition, TOF spectra for low J's display a slow component associated with background D_2 gas. A Boltzmann form was fitted by this component and subtracted numerically. Neither correction appreciably changes the parameters derived from fits to the desorption component (see below). An effusive D_2 source, which could be heated to 900 K, was used to check for the influence of electrostatic fields on the TOF spectra. There were small observable effects on very low energy ions (10 meV), but we do not believe these effects substantially influence the results presented here. Zacharias and co-workers have used a similar ion flight time method to study state-specific velocity distributions for hydrogen isotopes desorbed from Pd(100) [19]. The H_2/Pd system does not have a significant activation barrier; correspondingly they found no significant variation of the average kinetic energy of desorbed species with the rovibrational state, which, as we shall show, is in sharp contrast to the present results.

Figure 1 presents TOF distributions for D_2 desorbed from Cu(111) recorded for three vibrational states ($v=0$, 1, and 2) with $J=2$. The distributions shown in this figure shift to longer times (lower energy) with increasing v. This decrease in the translational energy with increasing v is just the trend predicted on the basis of microscopic reversibility from measurements of the kinetic energy requirements for adsorption as a function of v [14,30,31]. Adsorption measurements show that vibrationally excited molecules require less kinetic energy to adsorb. Vibrationally excited molecules are thus expected to desorb with lower kinetic energy, as observed. More quantitatively, we can relate the observed TOF spectra to the initial adsorption probability function, $S_0(E_i,\theta_i,T_S,v,J)$, using detailed balance [30]. We obtained quantitative information on the adsorption function by using a flexible analytical form for the adsorption versus energy function for each (v,J) state. We used [32]

$$S_0(E_i,\theta_i,v,J)=\frac{A}{2}\left[1+\mathrm{erf}\left(\frac{E_n-E_0(v,J)}{W(v,J)}\right)\right], \quad (1)$$

where E_n is the "normal energy" given by $E_n=E_i\cos^2\theta_i$. Here E_0 is the kinetic energy required for the adsorption probability to reach half its maximum value. The application of the model involved a separate calculation for each measured TOF point including a convolution over the angular resolution of the apparatus. The parameters of the model, E_0 and W, were then adjusted by a nonlinear least-squares procedure to achieve the best agreement with the data. The solid lines in Fig. 1 were computed using this procedure. The adsorption functions so determined are in good agreement with those determined previously [14,31], which validates both the previously

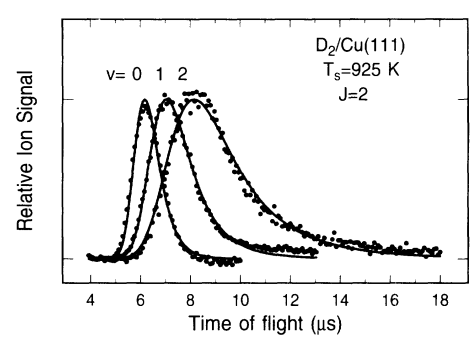

FIG. 1. Time-of-flight distributions obtained for D_2 desorbed from Cu(111) in $v=0$, $v=1$, and $v=2$ states, all for the $J=2$ rotational state. The lines represent the distributions predicted via detailed balance calculations based on the adsorption function given in Eq. (1) with E_0 and W parameters of 0.65 eV and 0.17 eV, respectively, for $v=0$; 0.44 eV and 0.16 eV for $v=1$; and 0.25 eV and 0.15 eV for $v=2$.

determined adsorption functions and the present data and method of analysis.

Although the vibrational effects are easily understood in terms of previous work, the data on the effect of rotation break new ground. To demonstrate the trends observed, TOF distributions for $D_2(v=0)$ are displayed in Fig. 2 for even values of J between 0 and 14. It is apparent that as J is increased from 0 to 4, the distributions shift slightly to shorter times (higher energy); as J is increased further, the trend reverses, and the distributions shift to longer times (lower energy). Qualitatively, the application of detailed balance to these trends indicates that, over the range of conditions relevant to this study, rotational motion *inhibits* adsorption for low J but *enhances* adsorption at high J.

A quantitative description of these trends can be made by fitting adsorption functions to these data as described above. The solid lines in Fig. 2 represent such fits. We found that the $W(v,J)$ values display little or no systematic variations with J for each V. We obtained $W(0,J)=0.17\pm0.02$, $W(I,J)=0.16\pm0.02$, and $W(2,J)=0.15\pm0.02$. The quality of our fits was not degraded by holding the $W(v,J)$ parameters fixed at these values. The values of $E_0(v,J)$ derived from fitting the desorption data in this manner, with $W(v,J)$ so fixed, are plotted as a function of J in Fig. 3. It is apparent that the E_0 values increase for $J=0$ to 5 and then decrease for higher J. The deduced mean energies display an identical trend, but are slightly lower than the E_0 values. The mean energy averaged over quantum state, estimated to be 0.58 ± 0.05 eV for $T_S=925$ K, is in good agreement with the results of Comsa and David [33] who reported a value of about 0.63 eV for a Cu(111) surface at 1000 K.

The observed trends in the variation of E_0 and mean energy with J imply that the barrier to dissociation first increases with increasing rotational state for low-J states, then decreases with increasing J for high-J states. We believe that the predominant effect at low J is a steric one, whereby increasing rotation makes it more difficult for the incident molecule to follow the lowest-energy path. These low-J results are consistent with the observations of Kubiak, Sitz, and Zare [27], who found the mean rotational energy in desorption associated with these low-J states to be slightly less than that appropriate to the surface temperature. The decrease in the effective translational energy barrier with increasing J at high J suggests that some fraction of the large rotational energy associated with these states (up to 0.7 eV) can be coupled to the reaction coordinate, e.g., via rotational-to-vibrational energy transfer prior to the barrier.

It is interesting to compare the relative efficacies of rotational and vibrational energy in promoting dissociation in this system. With respect to a molecule in $v=0$, $J=4$, the translational energy barrier to dissociation can be lowered by about 0.2 eV either by putting about 0.37 eV into vibration (to reach $J=4$, $v=1$) or by putting 0.64 eV into rotation (to reach $J=14$, $v=0$). By this measure, rotational energy can be over half as efficient at promoting dissociation as vibrational energy. As we have seen, however, for low J's, the rotational energy actually has a small negative efficacy, since it causes an increase

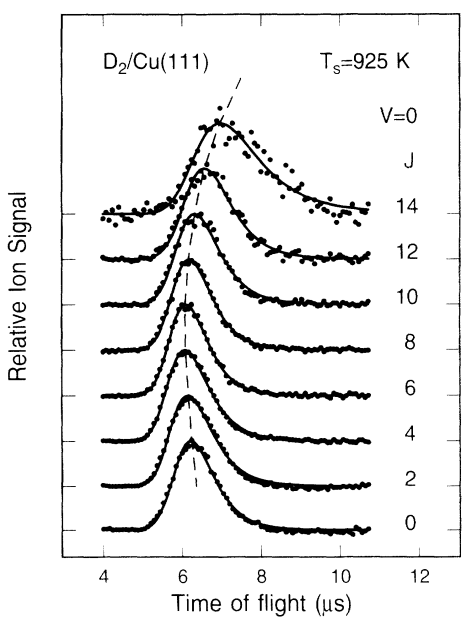

FIG. 2. Time-of-flight distributions obtained for D_2 desorbed from Cu(111) in different rotational states of the ground vibrational state. The lines show fitted distributions based on the adsorption function given in Eq. (1) with parameters as discussed in the text.

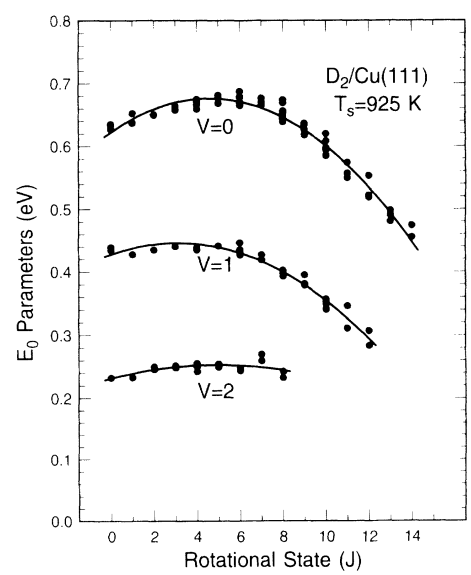

FIG. 3. Values of the parameter E_0 obtained from fits to D_2 time-of-flight distributions for different rovibrational states. These relevant fits were performed holding $W(v,J)$ values fixed for each vibrational state, as discussed in the text.

in the dissociation barrier.

In summary, we have reported the first quantum-state-specific measurements of velocity distributions for recombinative desorption in an activated system. These distributions vary appreciably with rotational and vibrational state. The vibrational energy effects are consistent with the results of previous measurements and calculations. The rotational effects provide new insight into the subtle dynamics of activated dissociative chemisorption.

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[a]Also affiliated with Stanford University, Stanford, CA 94305.

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