Role of Surface Thermal Motion in the Dissociative Chemisorption and Recombinative Desorption of D_2 on Ag(111)

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Although D_2 dissociation exhibits a large barrier on Ag(111), recombinative desorption occurs with minimal translational energy release. A strong surface temperature dependence is seen with a bimodal energy release at high temperatures. We propose that desorption occurs through two channels: by recombination at thermally activated sites, with a high steric constraint but low activation barrier, and directly via a large barrier at high surface temperatures. Surface thermal motion determines the distribution of dissociation barriers, a model which will be important in other activated systems. [S0031-9007(97)03280-8]

Hydrogen dissociative chemisorption on metal surfaces has become a test bed for models of gas-surface reaction dynamics principally because of the simplifications that can be made when comparing experimental results with scattering calculations. These simplifications arise from the low mass of the molecule relative to the substrate and the different time scales associated with the motion of H/D atoms and the metal atoms of the surface [1]. As a result, phonon excitation is far weaker than for other molecules and energy dissipation can generally be ignored without losing the central features of the problem. Similarly, the short time scale for H_2 dissociation ensures that relaxation of the metal lattice occurs only after dissociation is complete, while surface reconstruction of close packed metal faces is minimal compared to that shown by heavier adsorbates such as N, C, and O. Models of the dissociation dynamics generally consider the metal as a rigid lattice and ignore both relaxation and thermal motion, an approach justified by the insensitivity of H_2 dissociative chemisorption on metals to surface temperature.

We have measured the energy release into translational motion for D_2 recombinative desorption from Ag(111) as a function of internal state and surface temperature T_s. We find that the form of the translational energy distributions, $P(E)$, is sensitive to surface temperature, with desorption occurring by different mechanisms to give products with low or high translational energies. At high surface temperatures D atoms can directly overcome a large activation barrier to recombination, resulting in products with considerable translational energy, whereas at lower temperatures desorption gives rise only to products with a low translational energy release. The system therefore has two different paths to desorption, one which relies on thermal activation to overcome a large energy barrier and a second which has a lower energy requirement, but a large entropic constraint, and dominates desorption. The shape of the $P(E)$ distributions

can be related to the sticking probability $S(E)$ by detailed balance and implies a strong surface temperature dependence. This is in contrast to the usual insensitivity of S to T_s for H_2/D_2 dissociation on metals, and we attribute this to a broadening of the barrier distribution caused by thermal activation of the surface.

Although D_2 dissociation on Ag(111) is thought to be endothermic the energetics are not well established [2]. Thermal desorption occurs above 200 K with an activation energy of only 280 meV [3], indicating a weak H-Ag bond. Dissociative chemisorption of D_2 on a 100 K Ag(111) surface is highly activated and has been observed only for gas temperatures above 1000 K and translational energies $E > 200$ meV [4]. Sticking has been modeled using "S" shaped vibrational state dependent sticking functions of the form $S(v) = A(v)/2\{1 - \tanh[E_i - E_0(v)]/w(v)\}$, where the dissociation probability $S(v)$ is determined by three parameters, $A(v)$ the limiting sticking probability at high energy, $E_0(v)$ the median barrier height, and $w(v)$ the effective width of the barrier distribution. For D_2 dissociation, parameters $E_0 = 328$ and 170 meV were obtained for $v = 3$ and 4, with estimates for $v = 1$ and 2 of (700 ± 100) and (510 ± 70) meV, respectively, while dissociation of ground state $D_2(v = 0)$ could not be observed even at 800 meV [5].

An intense beam of D atoms was generated using a microwave powered beam source and collimated before striking a Ag(111) crystal at 45°. The crystal was cleaned and characterized using standard techniques and reproduced the desorption kinetics reported previously [3]. The surface was held above the desorption temperature and an equilibrium established between adsorption and desorption, resulting in an equivalent flux of desorbed D_2. The desorbed molecules were detected by resonance enhanced multiphoton ionization on the E,F-X transition near 200 nm, the ions being extracted by a weak field and detected on a microchannel plate. A fast mechanical shutter interrupts the atomic beam ~ 200 μs before the laser

fires, preventing Eley-Rideal processes contributing to the signal and removing the background due to undissociated D_2 in the incident beam [6]. The REMPI signal showed a time dependence consistent with recombination desorption from Ag(111), allowing the isothermal desorption kinetics to be determined. Translational energy distributions were obtained from the time of flight (TOF) of the D_2^+ ions by signal averaging using a 100 MHz digitizer. For the low rotational states $J \leq 2$, a background due to thermal gas must be removed from the signal. This is simply achieved by recording the thermal 3D signal without the discharge running and fitting this distribution to the tail of the desorption signal at long flight times. TOF distributions were calibrated for each measurement by a global fit to the 300 K thermal signal and to 1D distributions obtained from a Knudsen source ($T \leq 1500$ K), giving an energy calibration with an uncertainty of 4% at 0.8 eV rising to $\leq 11\%$ at $E > 1.3$ eV.

Time of flight distributions have been recorded for surface temperatures between 220 and 570 K as a function of rotational and vibrational state of the desorbed D_2. The TOF data have been converted to flux weighted energy distributions $P(E)$ and are shown for $D_2(v = 0, J = 6)$ in Fig. 1. Similar distributions were obtained following D dosing at 100 K and flash desorption of D_2 near 200 K, although with a reduced signal to noise. It is immediately obvious that the energy release into D_2 product translation is relatively small, much lower than the median barrier to dissociation of the ground state which is expected to lie above 800 meV [4,5]. This contrasts with the result of desorption from a hot Cu(111) permeation source [7] where the mean desorption energy is similar to the barrier inferred from sticking, $E_0(v)$. The energy distribution in desorption $P(E)$ can be related to the sticking function $S(E)$ using detailed balance [7,8] which we will adopt here without discussion [9]. If w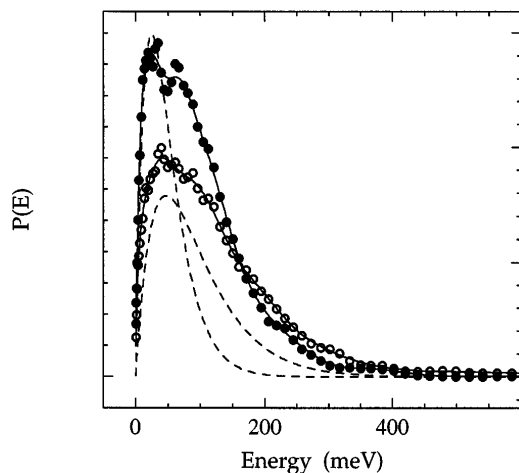e average over the appropriate angular distributions then the energy distribution of a desorbing state $D_2(v, J)$ is related to the sticking probability by $P(E) \propto E \exp(-E/kT)S(E)$ [7], which allows the energy dependence of the sticking probability to be established and relative values $S(E, T_s)$ obtained as a function of quantum state. The dashed lines in Fig. 1 show the distribution $E \exp(-E/kT)$ broadening as the surface temperature is increased. The corresponding $P(E)$ distributions also broaden, but not as rapidly as expected were $S(E)$ independent of T_s. Figure 2 shows the relative energy dependence for sticking at both temperatures for energies $E > 100$ meV. Since absolute coverages and desorption rates are not known for the conditions of the experiment, absolute values of $S(E)$ cannot be obtained for different T_s unless a secondary calibration can be obtained. Nevertheless, the variation in sticking with energy clearly reveals a pronounced difference between the two surface temperatures. In both cases S increases approximately exponentially with energy, indicating an activated dissociation process, but with a slope that depends strongly on T_s, being less severe at high temperatures. At energies below ~ 100 meV the $S(E)$ curves flatten out giving rise to the shoulder to the $P(E)$ distribution which coincides with the peak of the thermal distribution.

As the surface temperature is increased the TOF distributions of D_2 desorbed in ($v = 0, J$) become bimodal (Fig. 3), having in addition to the low energy feature a second, smaller peak at short flight times, corresponding to desorption of $D_2(v = 0, J = 2)$ with an mean energy $\overline{E} = 1090$ meV. This high energy component accounts for some 10% of the desorption flux at 570 K. At the same surface temperature vibrationally excited $D_2(v = 1)$ shows a single desorption peak at longer flight times, corresponding to a mean energy release, $\overline{E} = 775$ meV. This is consistent with dissociative chemisorption being aided by vibrational energy of the molecule, as established by adsorption experiments [5].

FIG. 1. $P(E)$ distributions for $D_2(v = 0, J = 6)$ desorbing from ($\bullet$) 300 and ($\circ$) 570 K surfaces showing the thermal energy distributions $\{E \exp(-E/kT)\}$ as dotted lines. The solid lines through the points are smoothed fits to the data.
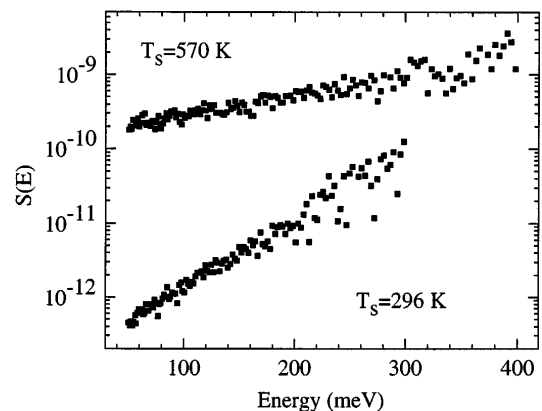

FIG. 2. Relative sticking probabilities $S(E)$ for the data of Fig. 1 showing the effect of changing the surface temperature. The 570 K data have been normalized to $S(E) = 1$ at high energy, but no absolute comparison of S is possible at 300 K.
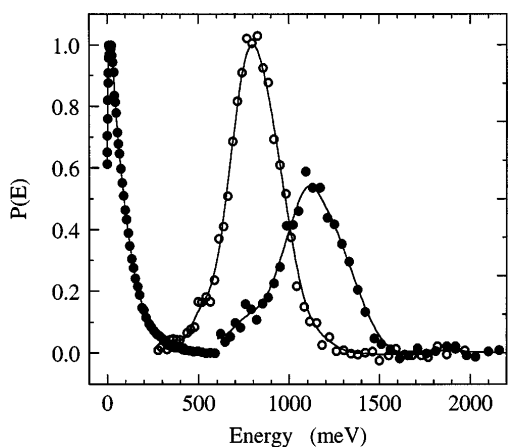
FIG. 3. $P(E)$ distributions for $D_2(v = 0, J = 2)$ ($\bullet$) and ($v = 1, J = 2$) ($\circ$) desorbing from a 570 K surface. The data have been normalized to 1 and the ($v = 0$) data is shown magnified $\times 25$ above 600 meV.

The energy distributions $P(E)$ of Fig. 3 have been converted to sticking functions $S(E) \propto P(E)/[E \exp(-E/kT)]$, and are shown in the form of a log plot in Fig. 4. The enormous range of S accessible is a reflection of "matching" the exponential increase in $S(E)$ to the decay in the available energy by choosing the surface temperature such that the product $S(E) E \exp(-E/kT)$ remains similar over a large energy range. The log $S(E)$ plots show characteristic S shaped curves, the sticking probability tending to a limiting value at high energy and showing a reduced slope at low energy. Absolute sticking coefficients $S(E, v, J)$ can be estimated for desorption data which show the high energy component (Fig. 4) by assuming that S reaches a limiting value ($S \sim 1$) at high energy. At 570 K this gives $S(E) \sim 10^{-9}$ for $D_2(v = 0)$ in the energy range near 100 meV which is responsible for the low energy desorption feature, consistent with the upper limit $S(E) < 10^{-7}$ at low energy obtained from adsorption measurements at 100 K [5]. The high energy component of the ($v = 0$) desorption peak and the ($v = 1$) distribution can both be reproduced using an er-
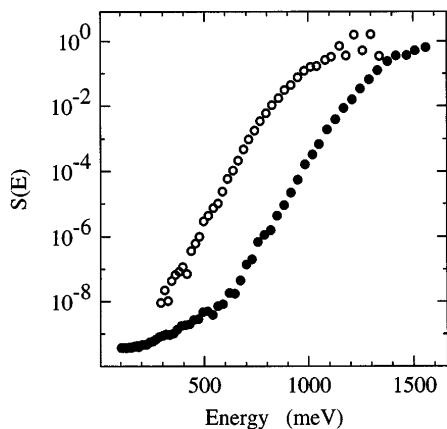
ror function $S(E) = A(v)/2\{1 - \text{erf}[E_i - E_0(v)]/w(v)\}$ to model $P(E)$, but simple functions of this form cannot reproduce the bimodal TOF distributions seen for $D_2(v = 0)$. The low energy tail to $S(E)$, which determines the desorption distribution for low T_s, can be described only by adding a more slowly decaying tail to the simple S shaped sticking functions previously used to model adsorption [5,8]. Both the magnitude and the energy dependence of the low energy adsorption function are sensitive to surface temperature and cannot be described by simply adding a constant term to S to account for some residual nonactivated or defect mediated channel.

The translational energy distribution $P(E)$ for both $D_2(v = 1)$ and for the high energy component of ($v = 0$) desorbed from the hot surface are consistent with recombinative desorption over the large activation barrier found in adsorption experiments. Sticking experiments gave an estimate of (700 ± 100) meV for $E_0(v = 1)$, similar to the mean energy $\overline{E} = 775$ meV seen in desorption, while the energy of the fast component of $v = 0$ is sufficiently high to make this channel inaccessible in sticking. Dissociation of the $v = 3$ and 4 levels showed a shift in the barrier parameter E_0 of ~ 160 meV, corresponding to a vibrational efficacy of ~ 0.5 [5]. In contrast, the mean translational energy of D_2 desorbing in the $v = 0$ and $v = 1$ levels differs by 315 meV, corresponding to a shift of $\sim 0.9\ t\omega$, indicating that vibration plays a more important role in aiding dissociation of the lower vibrational levels. This compares with a vibrational efficacy of ~ 0.5 for dissociation on Cu(111) [7,8] and is consistent with the general trend expected for an increasingly endothermic process from the Polanyi rules [10]. Unlike desorption, sticking measurements are made at 100 K, where the falloff in $S(E)$ is much steeper, and are sensitive to coefficients $S(v, E) \sim 1$, low values of S being masked by dissociation of vibrationally excited states [5].

The dominant desorption feature at all surface temperatures is not, however, the high energy peak, which is associated with a large activation barrier, but the low energy feature associated with flattening of the low energy tail to $S(E)$. Since energy exchange between D_2 and the substrate is expected to be weak, the $P(E)$ distributions must reflect the nascent energy distribution. Molecules desorbing in the low energy channel have avoided the large energy cost of directly overcoming the barrier to desorption. As demonstrated in Figs. 1 and 2, this channel is extremely sensitive to surface temperature. Although no absolute calibration of $S(E)$ was possible at low T_s, the slope of the ln $S(E)$ plot for the 300 K data is only slightly smaller than that of the steep "threshold" region of the high temperature $S(E)$ plots (Fig. 4), the gradients being 0.021 and 0.025 meV^{-1}, respectively, compared to 0.006 meV^{-1} for the 570 K surface for $100 < E < 400$ meV. This is consistent with the sticking function becoming sharper and low energy sticking being strongly inhibited at lower temperatures. In fact the

FIG. 4. $S(E)$ for $D_2(v = 0, J = 2)$ ($\bullet$) and ($v = 1, J = 2$) ($\circ$) for a 570 K surface with S normalized to 1 at high energy.

slope of both $S(E)$ plots is slightly less than that inferred from modeling of the 100 K adsorption data [5], where the widths $w(v)$ of the model sticking function define a slope $d[\ln S(E)]/dE = 2w(v)$ at low energy, about twice that observed here for a 570 K surface. The narrow range of temperature over which the fast desorption feature can be observed prevents the T_s dependence of $S(E)$ being measured in detail for energies near E_0. If we assume that the high energy region, where dissociation is efficient, is relatively insensitive to T_s, then modeling $P(E)$ indicates that the increased slope of $S(E)$ at low T_s is entirely consistent with a reduced sticking coefficient compared to the high temperature data.

Support for the role of substrate activation comes from the observation that, despite the exothermic nature of recombinative desorption, the energy release into product motion [$\overline{E} = 125$ meV for $D_2(v = 0, J = 0)$ at 220 K] is smaller than the activation barrier to desorption (280 meV [3]). The energy associated with activation of the desorption step must therefore remain in the surface and cannot be associated simply with a repulsive barrier to the approach of two D atoms on a rigid Ag surface. This is consistent with a critical role for motion of the surface in determining the desorption dynamics at low T_s. If the activation energy is primarily associated with modifying the Ag lattice, and hence the barrier to desorption, then the energy will remain in the surface, initially as excitation of the Ag surface phonons. An alternative interpretation based on static surface defects can be excluded, since this is not able to explain both the strong T_s dependence and the low energy release. We were also unable to see any significant modification of the $P(E)$ distributions when we deliberately induced defects by sputtering, while the thermal desorption experiments [3] were not especially sensitive to surface preparation.

Desorption experiments for the related Cu(111) system [8] have been made at much higher surface temperatures which, coupled with the lower barrier to dissociation on this surface, makes them relatively insensitive to the form of $S(E)$ at low energy. However, angle resolved desorption measurements did reveal a marked broadening of $P(\theta)$ with T_s that could be associated with thermal broadening of the sticking functions [11]. Another system that shows both a large activation barrier and dramatic T_s dependence is the activated dissociative chemisorption of methane on metal surfaces [12]. As for D_2 on Ag(111), the sticking probability depends strongly on both translational energy and surface temperature and has been attributed to thermally assisted tunneling. Luntz and Harris [12] used a simple cube model to include surface motion and showed that the effective barrier broadened. The change in the barrier height becomes extremely important in the sub-barrier region ($E \ll E_0$) where tunneling dominates dissociation, giving an exponential dependence on barrier height. However, since the effect depends on the relative velocity of the

molecule and the surface mass, it is expected to be less important for D_2 where the sudden approximation is more valid.

A low energy desorption channel has also been observed on Si, where again adsorption is highly activated but desorption gave only a thermal energy release into D_2 translation [13]. Unlike close packed metal surfaces, the covalently bonded Si surface undergoes substantial relaxation on chemisorption with large changes in the Si-Si bond lengths. The directional nature of the bonding and strong T_s dependence in sticking [14] both support a model involving modification of the barrier to adsorption by surface phonons [15]. The thermal activation of desorption sites on the Ag surface is perhaps more surprising than for Si, since not only is the metal surface relaxation relatively weak, but bonding is less directional and the barrier could be expected to be relatively insensitive to Ag positions. It is possible that these activated sites are caused not by a local distortion of the Ag lattice but by thermal creation of an adatom, or some other site with a low desorption barrier. The energy associated with activation of the Ag lattice site remains in the surface, explaining the low energy release to D_2 product motion. In contrast to Cu, desorption is dominated by molecules which sample the tail of the barrier distribution, resulting in the surprisingly low desorption temperature on Ag(111), a trend which continues to Au [16]. We believe that the thermal broadening of the barrier distribution observed here will be important in other highly activated systems where, despite a high entropic requirement, modification of the barrier to adsorption/desorption by thermal motion of the substrate becomes an important channel when the barrier is much greater than the mean energy available to overcome it.

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