Role of Surface Temperature in the Precursor-Mediated Dissociative Chemisorption of N_2 on W(100)

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(Received 20 May 1988)

Molecular-beam techniques have been used to probe the dynamical origin of the surface-temperature (T_s) dependence of the precursor-mediated dissociative chemisorption of N_2 on W(100). Measurements of the angular and velocity distributions of scattered molecules have revealed that increasing T_s primarily serves to reduce the fraction of precursor molecules that go on to dissociate, by biasing the kinetics in favor of desorption. In contrast, the trapping probability into the precursor state is found to be relatively insensitive to this parameter, accounting for $\lesssim 20\%$ of the observed effects.

While it is widely accepted that chemisorption often proceeds by way of an intermediate, or precursor, state, the detailed microscope picture of this process is by no means clear.[1,2] A key step in building such a picture is to resolve which of several contrasting proposed explanations gives a correct view of the role of surface temperature in modifying the chemisorption probability.

Precursor-mediated chemisorption is generally viewed as beginning with an initial gas-surface collision where incident species either scatter or are trapped into a relatively weakly bound (precursor) state. Often, this step is not particularly sensitive to occupation of the impact site, which accounts for the observed insensitivity of chemisorption probabilities to surface coverage in these systems.[3-7] Those molecules that trap are expected to rapidly accommodate to the surface temperature, T_s, which will influence the rates of desorption and of diffusion to, and chemisorption at, vacant sites.[7] In principle, this model is supported by the fact that chemisorption, or sticking, probabilities are often found to be sensitive to T_s in these systems. Indeed, such behavior is hard to rationalize in terms of alternative "direct" chemisorption models. However, although precursor-based models are consistent with a sensitivity to surface temperature, the details of this behavior remain controversial. For the case of the clean surface, increasing T_s can inhibit chemisorption in at least two dynamically distinct ways: either by changing the ratio of desorption and chemisorption rates in favor of the desorption channel,[5,7,8] or by reducing the trapping probability into the precursor state.[9,10]

Here we report the results of a molecular-beam study of this question for the case of the dissociative chemisorption of N_2 on W(100). Although this system is arguably one of most carefully examined examples of precursor-mediated dissociation, previous workers have interpreted the surface-temperature dependence for this process in a variety of ways. Thus Clavenna and Schmidt[9] and King and co-workers[5,11] have successfully accounted for rather similar data for this system using

very different models for the origin of the temperature dependence. In these cases the relevant results concerned sticking versus coverage curves obtained over a range of surface temperatures. The former group attributed the observed falloff in sticking with increasing T_s to changes in the trapping probability into the precursor state, while the latter assumed this probability to be constant, attributing the entire effect to changes in the fraction of precursors that reevaporate. It would appear that such measurements alone are insufficient to resolve this issue.

This difficulty was recognized by Janda *et al.*,[10] who examined the angular and velocity distributions of N_2 scattering from polycrystalline tungsten. The basic idea was that changes in the trapping probability should result in an increase in the direct-inelastic-scattering channel, while precursor molecules that reevaporate should contribute to a trapping-desorption component. Unfortunately the results of this study were somewhat inconclusive, in large part because of the polycrystalline nature of the sample which restricted the effective angular resolution as well as presenting an unknown distribution of crystal faces. It was concluded that both variations in the trapping probability and kinetic competition played some role, but in the crucial region around 700 K where the sticking probability drops sharply, it was not possible to assess which of these factors played a dominant role. In the present study we overcome some of these difficulties by employing a single-crystal W(100) target. We find that the greater effective angular resolution which we gain by using a single crystal is particularly useful in resolving the two scattering channels for this system, and conclude that the primary effect of T_s is to change the fraction of precursor molecules that go on to dissociate. In contrast, variations in the trapping probability into the precursor state are found to account for $\lesssim 20\%$ of the observed effects. This picture is thus substantially closer to the model of King and co-workers,[5,11] than to that of Clavenna and Schmidt[9] or that suggested by the study of Janda *et al.*[10]

Experimental techniques and methods follow those described in detail elsewhere.[12-14] Supersonic seeded beams of N_2 are directed at a W(100) crystal mounted in a UHV chamber on a manipulator which permits accurate control of the incidence angle and surface temperature. The crystal was prepared and cleaned with use of standard techniques and gives sharp LEED patterns and contamination levels below 1% as determined by Auger-electron spectroscopy. In addition, He scattering gave a specular peak close to the instrumental resolution. Beams pass through a high-speed chopper which reduces the N_2 flux to 10^{13} molecules cm^{-2} s^{-1} (10^{-2} monolayer per second with unity sticking probability) and produces $\simeq 8$-μs pulses for time-of-flight measurements based on a doubly differentially pumped rotatable mass spectrometer.[12,13] Velocity distributions of scattered species are extracted by time-of-flight analysis as described previously.[10,12,15] In all cases data are obtained under conditions where surface coverages are < 0.03 atomic monolayer, which restricts measurement times to a few seconds between cleaning cycles.[12] Sticking probabilities are determined by a beam-reflection technique first described by King and Wells,[5] and described in detail elsewhere.[12]

Sticking probabilities and angular and velocity distributions have been determined for this system for a wide range of conditions; incidence kinetic energy, E_i, from $\simeq 0.03$ to > 5 eV; incidence angle, θ_i, from $0°$ to $60°$; T_s from $\simeq 100$ to 1600 K; and coverages from bare to saturated surface. Particular emphasis has been placed on the initial sticking probability, S_0, corresponding to the low-coverage limit. This reaches a maximum close to unity for the lowest kinetic energies and surface temperatures. Increasing energy results in a decrease in S_0 to a minimum value of $\simeq 0.15$ at 0.4 eV, above which it rises again, approaching 0.5 at 5 eV, at which point there is little sensitivity to T_s. These results suggest that the dissociation of N_2 on W(100) proceeds via at least two dynamically distinct mechanisms. At energies below about 0.2 eV, a precursor-mediated process dominates, with a more direct interaction applying to collisions above about 0.5 eV. Here we are concerned with the low-energy channel, where the sensitivity to coverage and to T_s are found to be essentially identical to those reported previously,[11] and to be consistent with classical precursor-type behavior. Absolute values obtained for S_0 are also found to be in good agreement with reported measurements for given values of the mean incidence energy.[11]

To clarify the role of surface temperature in the precursor-mediated case, we have recorded S_0 values together with angular and velocity distributions for scattering from the clean surface for a range of temperatures. Here we wish to estimate the fraction of the total scattered flux, $I_{tot} = 1 - S_0$, going into the trapping-desorption and direct-inelastic channels, I_{td} and I_{di}, re-

spectively. If the trapping probability into the precursor state is α, then we expect $I_{td} = \alpha - S_0$ and $I_{di} = 1 - \alpha$. Here it is apparent, for example, that if α remains constant as T_s varies, I_{di} will also be constant and I_{td} will grow to account for the entire increase in $1 - S_0$. In this manner we can, in principle at least, quantify the temperature dependence of α, which can then be distinguished from changes in S_0 resulting from changes in the fraction of precursors which desorb. In practice, this separation is found to be surprisingly difficult to resolve. Thus neither the angular nor velocity distributions show sufficiently clear bimodality to permit unambiguous assignments to the two scattering channels based on any individual distribution.

This behavior is apparent for the case of angular distributions from the data shown in Fig. 1 which show results for $T_s = 800$ and 400 K, with $E_i = 0.088$ eV and $\theta_i = 60°$. These distributions display the total *flux* obtained at each scattering angle, θ_f, which represents the corresponding integrated time-of-flight (TOF) signals multiplied by their respective mean velocities, as obtained from analysis of the form of the TOF waveforms. Thus such measurements may not always be able to distinguish the scattering channels and to permit variations in the trapping probability to be followed. However, in this specific case we find that the effect of T_s can be deduced by the subtraction of distributions recorded at different temperatures. This approach is successful here for a number of reasons. The angular distribution for direct-inelastic scattering for this system is much less
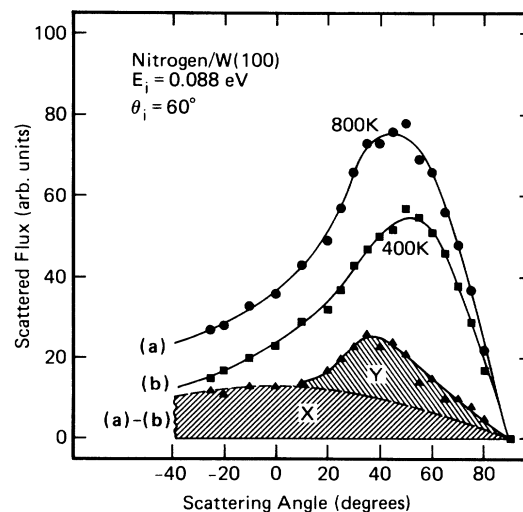

FIG. 1. Angular distributions for N_2 scattered from W(100) for an incidence energy of 0.088 eV and an incidence angle of 60°. Curves a and b were obtained with surface temperatures of 800 and 400 K, respectively. Also displayed is the result of subtracting curve b from curve a. This difference curve has been fitted with a cosine component, region X, and a quasispecular lobe, region Y.

sensitive to surface temperature than is often the case, which will be described more fully elsewhere.[16] Furthermore, α is in fact rather insensitive to T_s. Thus as the temperature is changed, the shape of the direct-inelastic part of the angular distribution does not change drastically, and in this instance subtraction of one angular distribution from another yields a "difference distribution" having a clear cosine contribution, together with a fairly well defined lobular component. The result of the subtraction of the angular distributions mentioned above, recorded at 800 and 400 K, is shown at the bottom of Fig. 1, together with a fitted curve corresponding to a cosine form representing the difference in trapping-desorption components for these two temperatures. Thus the distribution obtained at 800 K resembles that at 400 K with a substantial additional cosine component plus a small additional lobular component. If we take similar pairs of data from 150 to 1600 K, it is possible to resolve all distributions into cosine and lobular components, provided that this separation can be made for any one of them. We assume this to be the case for the 150-K data, i.e., $I_{td}(150\text{ K}) = 0$. The angular distribution for this temperature could, in principle, contain a cosine component equivalent to $\simeq 10\%$ of the incident beam, but such a value would be inconsistent with the observed TOF distributions, as discussed below. Next it is necessary to convert in-plane intensities into absolute fluxes, which could be accomplished by integration over both in-plane and out-of-plane distributions. However, not knowing the precise form of the out-of-plane lobular component, we chose instead to rely on direct calibration of the cosine component. Specifically, the beam was scattered from the machined Cu surface of the manipulator (aligned in the same manner as the sample) giving a cosine angular distribution and a Boltzmann velocity distribution corresponding to the temperature of the manipulator (300 K). The intensities obtained in this manner were then defined as representative of a cosine component with 100% of the incident flux. The lobular fraction could then be estimated by subtraction, knowing that the total scattered flux is $1 - S_0$. It should be noted that the alternative method to estimate I_{di} and I_{td} by integration over all directions gave consistent results, taking the out-of-plane width of I_{di} to be about half of that for the in-plane distribution.

Figure 2 displays the increase in the cosine component of the scattered flux recorded on raising T_s from 150 to 1600 K for $E_i = 0.088$ eV and $\theta_i = 60°$. Also displayed for comparison is the corresponding change in the total scattered flux, as determined from changes in S_0. To complete the picture, we also give an estimation of the variation of the direct-inelastic-scattering flux over this range of temperatures based on the difference between these two curves. Thus on heating the surface from 150 to 1600 K, S_0 falls from 0.60 to 0.05, of which $\lesssim 20\%$ is due to changes in α, the remainder being due to an in-
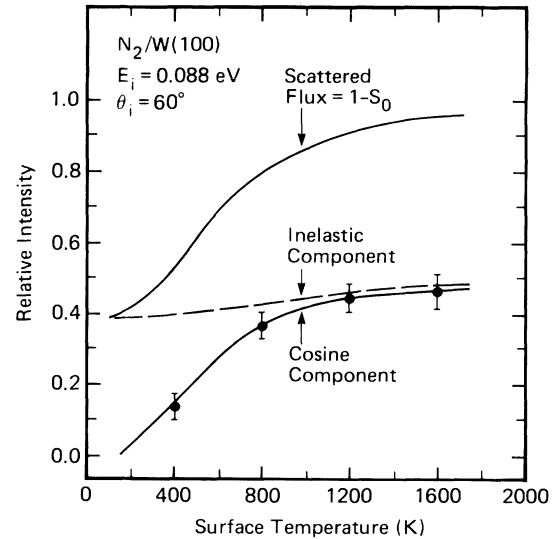

FIG. 2. Comparison of the total scattered flux with the cosine component of this flux and the estimated direct-inelastic-scattering flux as a function of surface temperature.

crease in the fraction of precursor molecules which desorb. Although these results strictly apply only to an incidence angle of 60°, we believe that a similar picture must hold for other angles, since $S_0(T_s)$ values are found to be insensitive to θ_i.[14]

The above conclusions are supported by analysis of the TOF distributions, which are found to be consistent with the deduced fractions of direct-inelastic and trapping-desorption contributions. However, satisfactory agreement could only be obtained if the desorption component was assumed to be somewhat cooler than a Boltzmann velocity distribution corresponding to T_s. For example, good agreement was obtained with the assumption of a Boltzmann distribution having an effective temperature of $T_e \sim 0.8 T_s$. This observation is qualitatively consistent with previous measurements of Ar desorbing from Pt(111),[17] and with trajectory calculations of NO desorption.[18] In both cases this translational cooling has been rationalized on the basis of microscopic reversibility arguments, wherein the excess of cold species in desorption mirrors the higher trapping probability for translationally cold species incident on the surface. In the case of $T_s = 150$ K, no appreciable Boltzmann component could be discerned. However, this could be because desorption occurs after a long residence time at this temperature (> 500 μs).

The overall conclusion of this study is then that the primary effect of T_s on the precursor-mediated chemisorption of N_2 on W(100) is to reduce the fraction of precursor molecules that go on to dissociate, by biasing the kinetics in favor of desorption. The trapping probability into the precursor state is found to be relatively insensitive to this parameter. This insensitivity is support-

ed by calculations based on a simple cube model.[19] However, such calculations also suggest that the situation could be quiet different for systems in which the incident species and surface atoms have similar masses, where the motions of the surface atoms would be relatively more important. Our findings indicate that the approximation made by King and co-workers,[5,7,11] that α is independent of T_s may be reasonable, although as is apparent from Fig. 1, for example, this is not strictly the case. Thus we estimate that neglecting the temperature dependence of α will lead to a $\simeq 10\%$ overestimation of the quantity $E_d - E_a$, the difference in activation energies for desorption and dissociation. Finally, we note that fitting I_{td} with a Boltzmann distribution at T_s may have caused Janda et al.[10] to overestimate the fall in α with increasing temperature. Although an attempt was made by Janda et al. to account for this effect by using a $1/v$ weighted Boltzmann distribution, we find this latter form to be insufficiently flexible and too broad to fit our TOF distributions.

We thank J. A. Barker for helpful discussions and J. E. Schlaegel for assistance in the maintenance and upkeep of the apparatus.

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