Role of Vibrational and Translational Energy in the Activated Dissociative Adsorption of D_2 on Cu(111)

C. T. Rettner, D. J. Auerbach, and H. A. Michelsen[a]

IBM Research Division, Almaden Research Center, San Jose, California 95120-6099

(Received 23 August 1991)

We report the relative efficacy of vibrational and translational energy in overcoming the barrier to dissociative adsorption of D_2 on a Cu(111) surface. This is determined by measuring variation of adsorption probability with kinetic energies, E_i, and vibrational temperature. At the highest energy ($E_i = 0.83$ eV) adsorption is predominantly due to ground-state D_2; molecules in excited vibrational states play the dominant role for E_i below ~ 0.5 eV. A detailed analysis provides estimated adsorption probability versus energy functions for D_2 in vibrational states $v=0$ to $v=3$.

Recently there has been great interest in the extent to which molecular vibration enhances the dissociative adsorption of hydrogen molecules at Cu surfaces. This interest is stimulated both by general questions concerning the role of internal states in surface chemistry and by specific issues related to the connection between experimental adsorption data and the barrier to dissociative adsorption in the potential hypersurface for the H/Cu system. Both the original [1,2] and more recent [3,4] measurements show that the probability of dissociative adsorption is substantial at energies considerably below theoretical estimates [5] of the barrier height. One possible explanation for this discrepancy is that molecules in vibrational states higher than the ground state are responsible for adsorption probabilities observed at low kinetic energies. Calculations of Harris [6], Hand and Holloway [7], and Brenig and co-workers [8,9] show that the vibrational energy can be effective in overcoming the barrier to dissociation. In experiments performed with heated supersonic beams of pure H_2 there is an exponential increase in $H_2(v=1)$ population as the kinetic energy is increased; thus enhanced sticking for $H_2(v=1)$ could account for the observed adsorption probabilities at low energy. To test this hypothesis, Hayden and Lamont [10,11] and Rendulic and co-workers [12,13] used molecular-beam techniques [14] to vary the kinetic energy and vibrational temperature of the incident molecules. These authors confirm vibrational enhancement of the sticking but disagree about the magnitude of this enhancement and its implications.

There are a number of limitations of the existing data that make it impossible, even with careful modeling [15–17], to establish firmly the translational thresholds for individual vibrational states. Specifically, (1) the incidence energy employed in these studies does not extend to high enough values to sensitively probe adsorption of molecules in the ground vibrational state; (2) the spread in incidence energies is poorly characterized and large enough to influence the results significantly, especially in the case of beams seeded in heavy carrier gases ("antiseeded beams"); and (3) the dynamic range of observed

sticking probabilities is limited. Here we present new data on the adsorption probability of D_2 on Cu(111) that address these limitations. In particular, we have extended the energy range up to 0.83 eV, carefully characterized the beam energy and energy spread for each measured point, and extended the sticking probability range to cover over 5 orders of magnitude. Using a quantitative model analysis [16] we have been able to determine the translational energy dependence of the adsorption of D_2 in the $v=0$, 1, 2, and 3 vibrational states.

Supersonic beams of D_2 are directed at a Cu(111) crystal polished to within $\pm 0.1°$ of the (111) plane. The mounting is such that the $[10\bar{1}]$ vector lies in the scattering plane. Contamination levels are determined to be below the $\simeq 1\%$ limit of Auger spectroscopy. Beams are generated using a tungsten source that can be heated to a nozzle temperature, T_n, of over 2100 K. Energies up to ~ 0.83 eV are obtained by seeding in H_2, while lower kinetic energies with high vibrational temperatures, T_v, are obtained by seeding in Ne or Ar. Under the conditions used here, the rotational temperature is about 80% of T_n [18]. Vibrational relaxation is so slow (requiring $\sim 10^6$ collisions per deactivating collision [19]) that it is safe to assume $T_v = T_n$ [20].

In most cases, sticking probabilities are determined from coverage versus exposure measurements, using temperature programmed desorption (TPD) to determine coverages. Both coverage and exposure are determined by integrating the partial pressure rise in the system over time. The ratio of these two integrals gives the absolute sticking probability. For coverages below 0.1 of saturation (~ 0.05 atomic monolayer), we find that this ratio provides a good measure of the sticking probability at zero coverage, S_0. For beams of D_2 seeded in H_2, this TPD method is not applicable since deuterium will adsorb and desorb as both D_2 and HD. Instead we measure S_0 by comparing the partial pressure rise of D_2 with and without a bare crystal in the beam. Further details of the apparatus and measurement techniques have been given previously [21,22].

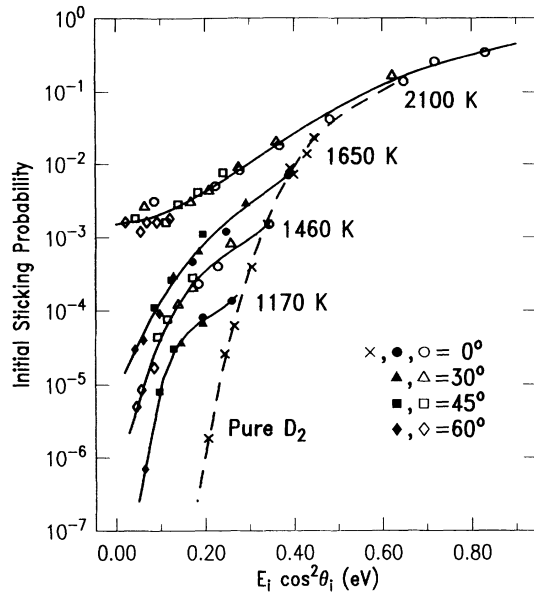Figure 1 displays the adsorption probability S_0 mea-

FIG. 1. Initial adsorption probability for D_2 on $Cu(111)$ plotted as a function of the energy associated with motion normal to the surface for the incidence angles indicated. Data are shown for seeded beams using four nozzle temperatures as indicated, and a solid line is drawn (to guide the eye) through each set of data points recorded at the same nozzle temperature. The $\times$ marks (followed by the dashed curve) represent data for pure D_2 expanded from a nozzle at temperatures ranging from 875 to 2100 K.

sured for various incidence conditions plotted as a function of the mean kinetic energy associated with motion normal to the surface $E_n = E_i \cos^2\theta_i$. S_0 increases by a factor of $> 3 \times 10^5$ over the range of conditions employed here, which we believe is the largest such effect reported to date. The curves labeled with nozzle temperatures correspond to measurements with beams of pure D_2 and several antiseeded mixtures of D_2 at four incidence angles, as indicated. For $T_n = 2100$ K, the results of two experiments with D_2 seeded in H_2 are also shown. These measurements reach a maximum energy of 0.83 eV. The curve labeled "pure D_2" corresponds to measurements performed with nozzle temperatures ranging from 875 to 2100 K for pure D_2 beams at normal incidence. The mean energies are determined from time-of-flight measurements; the energy distributions are also used in the analysis of the data. For beams consisting of a dilute mixture of D_2 in a heavier gas, we find the results are significantly influenced by the high-energy component of the beam. Some of the scatter in the points in Fig. 1 stems from these convolution effects, especially the low-energy measurements with $T_n = 2100$ K.

The dramatic dependence of S_0 on both E_n and T_n is a direct indication that both translational and internal energy play an important role in overcoming the barrier to adsorption. In principle, changes in T_n can affect the re-

sults through changes in both the vibrational and rotational state distributions of the beam. We expect, however, that the sticking probability is relatively insensitive to rotational energy, based on detailed balance arguments [16] and the rotational state distributions that have been reported for recombinative desorption [23]. Thus we believe that the variation of S_0 with T_n at a given energy reflects the changing vibrational populations in the beam. For example, the S_0 values at ~ 0.25 eV increase with T_n roughly in proportion to the $D_2(v=2)$ population. Thus, molecules in the $v=2$ and higher vibrational states dominate the results at low energies, and the rapid increase in S_0 around 0.2 eV originates primarily from an increase in the adsorption probability for $D_2(v=2)$. On the other hand, at the highest energies the populations of all vibrationally excited species are too small to account for the observed S_0 values. The $\sim 14\%$ vibrational excitation at 2100 K is less than half the sticking probability measured at 0.83 eV, indicating that most of the adsorption must be due to $D_2(v=0)$. The picture that emerges from this discussion is that $D_2(v=3)$ determines S_0 at the lowest energies used here, and contributions from $D_2(v=2)$, $D_2(v=1)$, and $D_2(v=0)$ successively become significant as the energy is increased.

We can make a more quantitative determination of the variation of the sticking probability with energy for individual vibrational states by the application of a sticking probability model. We write S_0 as a weighted sum over the contributions from each vibrational state,

$$S_0(E_e, T_n) = \sum_{v=0}^{3} F_B(v, T_n) S_0(v, E_e) + \text{atoms}(T_n, P_n) ,$$

(1)

where $F_B(v, T_n)$ is the Boltzmann factor for state v at a nozzle temperature T_n. The term atoms gives the contribution to S_0 that arises from dissociation of D_2 in the nozzle and is determined by assuming an atomic sticking probability of unity and calculating the dissociation from the stagnation pressure P_n and nozzle temperature using standard methods [24]. For most of our analysis we take

$$S_0(v, E_e) = \frac{A}{2} \left[1 + \tanh\left[\frac{E_e - E_0(v)}{W(v)} \right] \right] ,$$

(2)

where E_e is the effective energy given by

$$E_e = E_i \cos^n\theta_i .$$

(3)

Here E_i and θ_i are the energy and angle of incidence, and n is a scaling factor that describes how strongly the adsorption depends on angle. The application of the model involves a separate calculation for each measured point including a convolution over the energy distribution of the beam used to measure that point. The parameters of the model are then adjusted by a nonlinear least-squares procedure to achieve the best agreement with the data. Details have been given previously [16].

Because of the large number of parameters, performing a fit with all the parameters of the model free to vary does not give reliable results. Thus we must introduce constraints to reduce the number of free parameters. There are a wide variety of ways to do this, and, not surprisingly, each approach leads to a slightly different set of parameters. Nonetheless, the general features are similar, and we can take the differences in the sets of sticking probability curves as a measure of the uncertainty involved in this approach.

We begin the task of reducing the number of free parameters by fixing the value of the energy-angle scaling exponent n. By plotting the data for various values of n we find that $n \simeq 1.8$ does the best job of scaling the data for a given T_n so that they fall on a single curve. This value is slightly less than the value $n = 2$ expected for a completely uncorrugated interaction potential. It indicates that parallel momentum has a small role in promoting adsorption. We take $n = 1.8$ for the remainder of the discussion (although the results remain essentially unchanged if we take $n = 2$). To reduce further the number of free parameters, we introduce constraints on the variation of $E_0(v)$ and $W(v)$ with v so they behave in a "reasonable" manner. One approach to this problem is to require all of the width parameters $W(v)$ to be equal. The results of such a fit are shown in Fig. 2 along with a comparison with the measurements. As shown in Fig. 2, the model provides a reasonable representation of the data. The multiple lines for a given T_n result from different convolution effects for the beams involved. (Points for which the convolution effects are greater than

a factor of 2 have been eliminated from consideration in the fits.) The sticking probability curves that result from this fit are displayed as the dashed lines in Fig. 3.

Another, less arbitrary approach is to require a smooth variation of the values of $W(v)$ and $E_0(v)$ with v. For example, in the calculation of Hand and Holloway [7] the widths and energy spacings decrease smoothly with increasing vibrational state. We can introduce this constraint in our fitting by using a second-order polynomial in v to represent the widths and energies. The sticking probability curves that result are shown by the solid lines in Fig. 3. The largest disagreement with the previous fit is for the $v = 1$ curve.

To investigate the extent to which the results are influenced by the choice of the functional form of Eq. (2), we have performed fits with the following representation of the sticking probabilities:

$$\ln[S_0(v)] = A - B \exp\left[-\frac{E_c - E_0(v)}{C(v)} \right]$$
$$-\exp\left[-\frac{E_c - E_0(v)}{D} \right]. \tag{4}$$

This form is similar to that used by Rettner and Stein to represent the measured sticking probability for N_2 on Fe(111) [25] and allows for a more gradual saturation of the sticking probability at high energy. Here, the term containing C governs the initial rapid rise of the sticking probability, and the term containing D introduces a more gradual rise at high energies. The dotted curve in Fig. 3 displays the results of using Eq. (4) in the fits to the data. This set of curves is considerably broader than the other two sets, but the rise in the sticking probability for a given v occurs at similar energies for all three sets. All three sets give a similarly good description of the measurements.
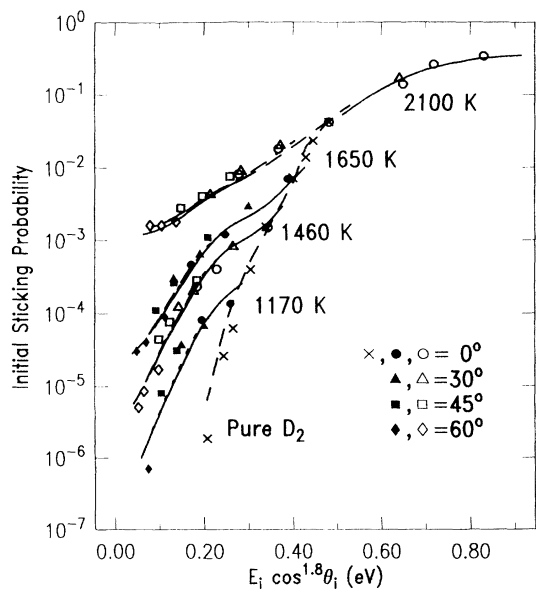

FIG. 2. Comparison of the results of the sticking probability model described in the text with the data of Fig. 1. Points for which the convolution effects exceed a factor of 2 have been eliminated.
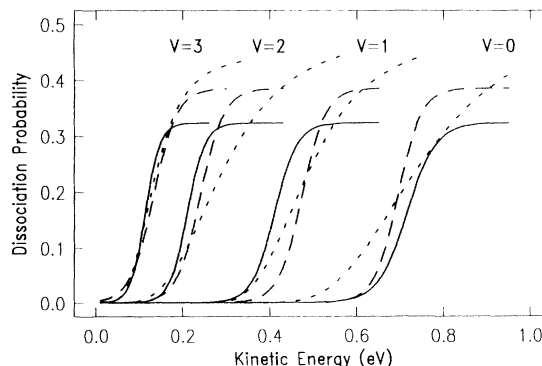

FIG. 3. Sticking probability vs effective energy for the vibrational states of D_2 indicated. The lines show the results of the three fits to the data: dashed lines, Eq. (2) with $W(v)$'s constrained to be equal; solid lines, Eq. (2) with $E_0(v)$'s and $W(v)$'s constrained by a second-order polynomial; dotted lines, Eq. (4).

In conclusion, we have shown that the dissociative adsorption of D_2 on Cu(111) is activated and that both translational and vibrational energy are effective in overcoming the activation barrier. The data extend to high enough energy to probe the adsorption of $D_2(v=0)$. The energy required for the adsorption of $D_2(v=0)$ is consistent with theoretical estimates of the barrier if we suppose that the zero-point energy of D_2 is available for the reaction. Further theoretical work on the form of the sticking probability curves and trends in the energy spacing and widths could greatly improve our ability to interpret these data quantitatively. Further theoretical work is also required to explore the connection of these results to features of the potential energy hypersurface.

(a)Also at Stanford University, Stanford, CA 94305.

[1] M. Balooch, M. J. Cardillo, D. R. Miller, and R. E. Stickney, Surf. Sci. 46, 358 (1974).

[2] M. J. Cardillo, M. Balooch, and R. E. Stickney, Surf. Sci. 50, 263 (1975).

[3] G. Anger, A. Winkler, and K. D. Rendulic, Surf. Sci. 220, 1 (1989).

[4] B. E. Hayden and C. L. A. Lamont, Chem. Phys. Lett. 160, 331 (1989).

[5] J. Harris and S. Andersson, Phys. Rev. Lett. 55, 1583 (1985).

[6] J. Harris, Surf. Sci. 221, 335 (1989).

[7] M. R. Hand and S. Holloway, J. Chem. Phys. 91, 7209 (1989).

[8] W. Brenig and H. Kasai, Surf. Sci. 213, 170 (1989).

[9] W. Brenig, S. Küchenhoff, and H. Kasai, Appl. Phys. A 51, 115 (1990).

[10] B. E. Hayden and C. L. A. Lamont, Phys. Rev. Lett. 63, 1823 (1989).

[11] B. E. Hayden and C. L. A. Lamont, Surf. Sci. 243, 31 (1991).

[12] H. F. Berger, M. Leisch, A. Winkler, and K. D. Rendulic, Chem. Phys. Lett. 175, 425 (1990).

[13] H. F. Berger and K. D. Rendulic, Surf. Sci. 253, 325 (1991).

[14] J. B. Anderson, R. P. Andres, and J. B. Fenn, in Advances in Atomic and Molecular Physics, edited by D. R. Bates and Immanuel Estermann (Academic, New York, 1965), Vol. 1, pp. 345–388.

[15] H. A. Michelsen and D. J. Auerbach, Phys. Rev. Lett. 65, 2833 (1990).

[16] H. A. Michelsen and D. J. Auerbach, J. Chem. Phys. 94, 7502 (1991).

[17] S. Küchenhoff, W. Brenig, and Y. Chiba, Surf. Sci. 245, 389 (1991).

[18] J. E. Pollard, D. J. Revor, Y. T. Lee, and D. A. Shirley, J. Chem. Phys. 77, 4818 (1982).

[19] C. Joffrin and J. Ducuing, Chem. Phys. Lett. 19, 26 (1973).

[20] K-D. Rinnen, M. A. Buntine, D. A. V. Kliner, and R. N. Zare, J. Chem. Phys. 95, 214 (1991).

[21] C. T. Rettner, L. A. DeLouise, and D. J. Auerbach, J. Chem. Phys. 85, 1131 (1986).

[22] C. T. Rettner, H. A. Michelsen, D. J. Auerbach, and C. B. Mullins, J. Chem. Phys. 94, 7499 (1991).

[23] G. D. Kubiak, G. O. Sitz, and R. N. Zare, J. Chem. Phys. 83, 2538 (1985).

[24] Walter J. Moore, Physical Chemistry, Fourth Edition (Prentice-Hall, Englewood Cliffs, 1972), pp. 297–301.

[25] C. T. Rettner and H. Stein, Phys. Rev. Lett. 59, 2768 (1987).