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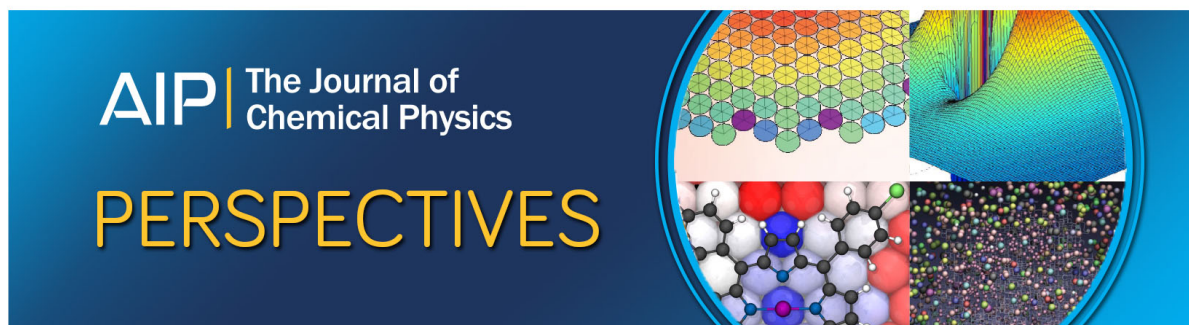
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Kinetic energy and angular dependence of activated dissociative adsorption of N₂ on W(110): Observed insensitivity to incidence angle

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Dissociative chemisorption, the process whereby intramolecular bonds are broken and new bonds formed to surface atoms, is one of the simplest of surface chemical processes. It is a key step in a wide variety of catalytic chemistry and, when accompanied by a sizable activation barrier, is commonly the rate determining steps in such reactions. An understanding of the nature and role of such activation barriers is therefore vital to any detailed picture of surface chemical dynamics. The interaction of H₂ with Cu surfaces has served as a prototype for such studies with interest dating back to Lennard-Jones who introduced the concept of a one-dimensional barrier (1DB) to adsorption.¹ Studies of the dependence of the dissociative adsorption probability at zero coverage S_0 on incident kinetic energy E_i and incidence angle θ_i for H₂/Cu have supported this picture,² as have the observation of noncosine angular distributions and non-Boltzmann kinetic energy distributions of molecules which recombine and desorb.³⁻⁵ A key feature of this 1DB model is that the dissociative adsorption probability scales with the normal component of the incident kinetic energy $E_n = E_i \cos^2(\theta_i)$.

For heavier molecules, far less data is available on the dynamical aspects of activated dissociative chemisorption, despite the great chemical relevance of such processes. Recently, Cosser *et al.*⁶ reported a noncosine angular distribution for N₂ desorbing from W(110). This was also interpreted in terms of a 1DB model, yielding an activation barrier height of $E_a \sim 17$ kJ mol⁻¹. In recent molecular beam experiments^{7,8} performed at $\theta_i = 45^\circ$, we found that S_0 does indeed increase dramatically with E_i . However, the steepest increase occurred at $E_i \sim 80$ kJ mol⁻¹ ($E_n \sim 40$ kJ mol⁻¹). In this Communication we report measurements of the dependence of S_0 on incidence angle.⁹ Contrary to expectations, we find that $S_0(E_i, \theta_i)$ is virtually independent of θ_i for $0 < \theta_i < 45^\circ$, with only a weak dependence at larger angles.

The experiments are performed with a supersonic molecular beam of N₂ incident on a W(110) surface mounted in a UHV chamber (base pressure $< 2 \times 10^{-11}$ Torr). E_i was varied from 9 to 200 kJ mol⁻¹ by seeding in H₂ or He and by changing the nozzle temperature. (Energies are determined by time-of-flight techniques.) The crystal used for the data points reported here was 1.39° off from the W(110) direction. Towards the end of this study, the crystal was repolished to within 0.5° and the data was found to be insensitive to this change. The sample was mounted on a manipulator which permitted accurate control of the incidence angle and provided *e*-beam heating and liquid nitrogen cooling. Temperature, monitored with a thermocouple spot welded to the back of the sample, was controlled by a feedback system

interfaced to a minicomputer. The computer was used to control all the sequencing of the experiment: cleaning, dosing with N₂, temperature ramping, and moving the sample in and out of the beam.

Two methods were used to measure S_0 : determination of the initial slope of a surface coverage vs exposure curve and direct measurement of the fraction of the beam which reflects from the surface (following the approach of King and Wells¹⁰). For the former, coverage measurements were made by recording the area under temperature programmed desorption spectra; exposure was determined by measuring the flux of the molecular beam ($\sim 10^{15}$ – 10^{16} molecules/s/cm²) and controlling the exposure time (down to $\sim 10^{-2}$ s). All the data points presented below were obtained by this method. The latter method, appropriate for $S_0 \geq 0.05$, was used as an independent check. Agreement between these methods was always within a factor of 2, and usually much better. Further details of the apparatus and measurement procedures are given elsewhere.^{8,11-13}

Figure 1 displays S_0 values obtained at various incidence angles plotted against E_i . This data, obtained with a sample temperature of 800 K, clearly indicates the activated nature of the adsorption process. However, the sharp increase in adsorption probability is seen to occur at $E_i \sim 80$

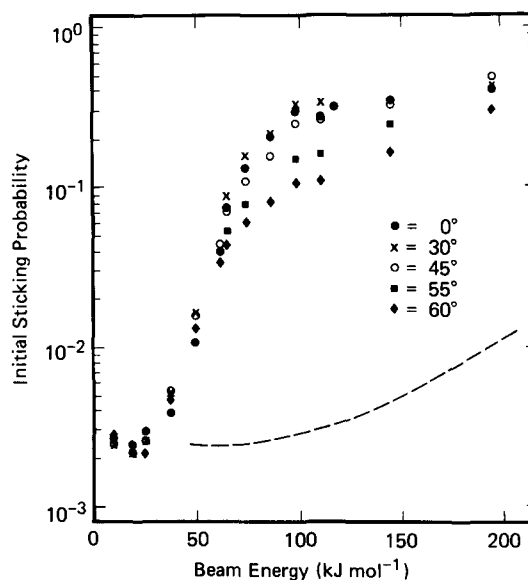


FIG. 1. Initial sticking probability for N₂ on W(110) as a function of beam energy at various angles of incidence for a sample temperature of 800 K. It is seen that the data are insensitive to incidence angle for $0^\circ \lesssim \theta \lesssim 45^\circ$. The dashed line indicates the sticking probabilities predicted for $\theta = 60^\circ$ obtained by assuming normal energy scaling for the $\theta = 0^\circ$ data. Clearly the actual 60° results fall much closer to the uncorrected 0° data. Error bars ($\sim \pm 25\%$) have been omitted for clarity of presentation.

kJ mol^{-1} (point of maximum slope on a *linear* plot), which is much higher than the prediction of Cosser *et al.*⁶ For low beam energies, we find $S_0 \approx 2.5 \times 10^{-3}$, in agreement with the value of $3 \pm 1 \times 10^{-3}$ for N_2 gas at 300 K reported in the literature.¹⁴⁻¹⁶ We also note that the increase of S_0 with E_i is far from a step function, contrary to the behavior expected for a single barrier. In this respect the data are similar to that reported² for H_2 on Cu, although the increase in S_0 observed here is considerably larger than the factor of ~ 5 observed for that system.

It is clear from Fig. 1 that for $\theta_i \leq 45^\circ$, S_0 is virtually independent of θ_i . Thus we find a complete breakdown of the normal energy scaling behavior observed for H_2 on Cu. Normal energy scaling must result from any 1DB model or indeed from any model in which the molecule-surface potential depends on z , the normal coordinate, but not on x or y . A much stronger dependence of potential on z than on x or y (weak corrugation) is quite characteristic of low energy atomic and molecular interactions with low index planes of metal surfaces.¹⁷ Weak corrugation is observed¹⁸ in the Ar-Pt(111) system even at 200 kJ mol^{-1} , the highest energy studied. Rotational excitation of NO in collisions with Ag(111) has been shown to scale with E_n ^{13,19} up to at least 180 kJ mol^{-1} . The breakdown of normal energy scaling reported here is all the more surprising since we have recently observed almost perfect normal energy scaling for CH_4 dissociative chemisorption on this same crystal surface.²⁰

Possible explanations of the observed insensitivity of S_0 to θ , fall into two classes: those which consider the surface to be strongly corrugated or rough on an atomic scale, and those which postulate a long-lived surface intermediate or precursor state which mediates the randomization of the ini-

tial energy modes. He scattering (30% at 500 K) indicates that the surface is smooth as seen by thermal energy atoms.

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COMMENTS

Remarks on the magnitude of van der Waals induced dipole moments in physisorption

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In a recent paper, Wandelt and Hulse¹ presented a detailed analysis of the observed local work function of palladium with less than a monolayer coverage of xenon. It is generally assumed that the change in the work function of the metal is associated with the dipole moment induced in the adsorbed atom. Wandelt and Hulse mentioned three possibilities which could account for the sign and magnitude of the adatom dipole moment and its face specificity. They were: (1) charge transfer, (2) "static" (van der Waals) induced moments, and (3) change in the Xe "dynamic polarization" due to the virtual $5p$ to $6s$ excitation.

The paper by Wandelt and Hulse is an important experimental contribution to the subject of physisorption and has far reaching theoretical implications. In particular, it points out that neither nonbonded charge transfer nor van der Waals induced dipole moment theories can account for face specificity. However, the magnitude of the induced dipole moment, the authors noted, can be reproduced approximately by the model calculations of Antoniewicz^{2,3} and of Sunnen and Schmeits.⁴

The purpose of this note is to point out that, together with Galatry and Girard,⁵ we believe that the use of the