III. PHYSICAL ELECTRONICS AND SURFACE PHYSICS

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A. MOLECULAR BEAM STUDY OF THE APPARENT ACTIVATION BARRIER ASSOCIATED WITH ADSORPTION OF HYDROGEN ON COPPER

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Molecular beam techniques have been employed to study the adsorption and desorption of H_2 on the (100), (110), and stepped (310) crystal faces of copper. Each crystal was exposed simultaneously to a supersonic molecular beam of H_2 (energy variable from 1.6-10.7 kcal/mole) and a highly dissociated beam of deuterium. The majority of H_2 molecules are scattered while a portion adsorb dissociatively and react catalytically with adsorbed deuterium atoms to form HD molecules. These HD molecules desorb, and their angular distributions are measured by a rotatable mass spectrometer. For all three crystal faces the angular distributions of desorbed HD deviate significantly from diffuse emission and are in excellent agreement with the results of our previous permeation study (Fig. III-1).

From the dependence of the HD signal on the energy and incident angle of the H_2 beam, it appears that there are substantial energy barriers to adsorption. These barriers depend on crystallographic orientation and can be correlated by the parameter $E_\perp = \bar{E}_i \cos^2 \theta_i$, where θ_i is the angle of the incident beam with respect to the surface normal, and $\bar{E}_i$ is the average incident energy;
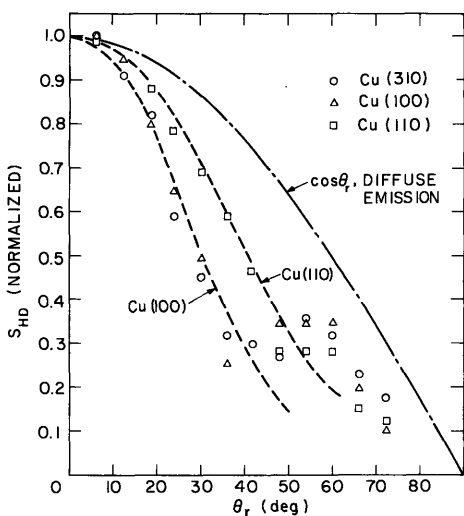

Fig. III-1.

Angular distributions of desorbed HD from Cu(100), Cu(110), and Cu(310). The dashed lines represent the angular distributions obtained from a previous permeation study.[1]
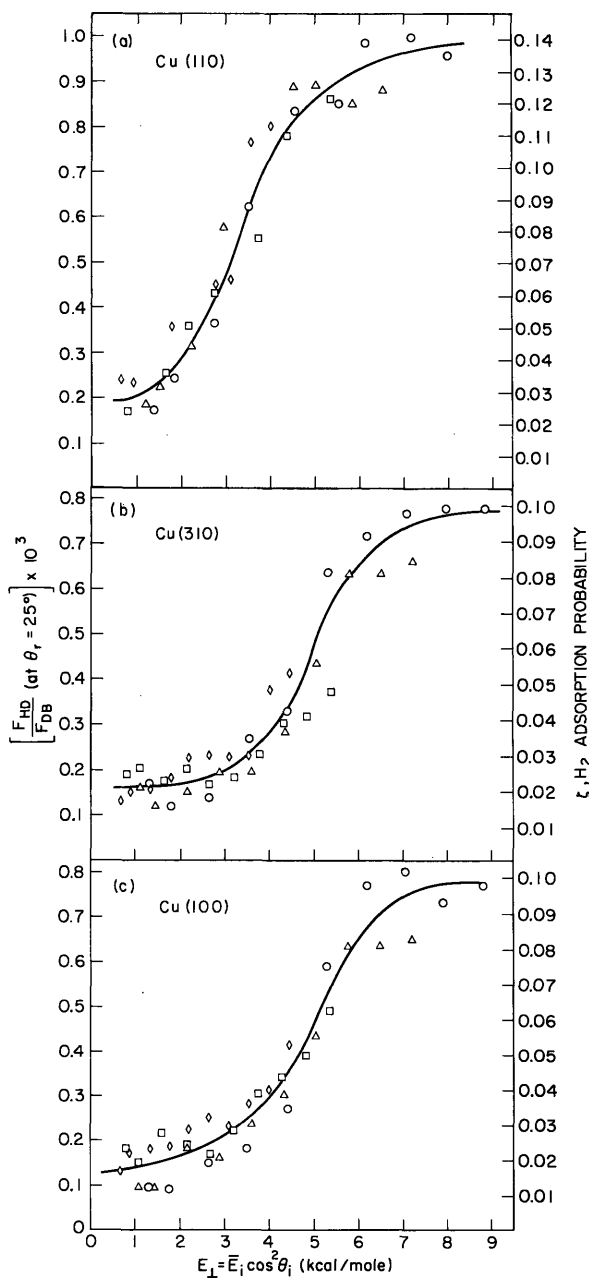
Fig. III-2. Relative HD fluxes (left ordinate) and the dissociative adsorption probabilities for hydrogen, ζ_{H_2} (right ordinate), for Cu(110), (310) and (100). They are plotted against the correlating parameter $E_\perp = \bar{E}_i \cos^2 \theta_i$ for a range of incident angles (θ_i) from 25-50° with respect to the surface normal.

this suggests that a one-dimensional potential to the point of dissociation is sufficient to explain our results. The estimated adsorption probabilities vs $E_\perp$ are S-shaped curves that appear to level off at values considerably less than unity. They are summarized in Fig. III-2. Both the energy dependence and the shape of the HD angular distributions are nearly identical for the stepped (310) and (100) surfaces (the stepped (310) may be described as a sequence of (100) terraces, 3 atoms wide, separated by steps 1 atom high), thereby suggesting that ledge sites are not the principal regions responsible for adsorption of hydrogen on copper. Switching the roles of deuterium and hydrogen in the two incident beams yields a dissociative adsorption probability for D_2 which is higher than that for H_2 by approximately the square root of the mass ratio.

We have compared our results with a simple model[2] with a single energy barrier to adsorption and obtain qualitative but not quantitative agreement for the angular distributions of desorbed HD (Fig. III-3). Consideration of the adsorption probabilities when
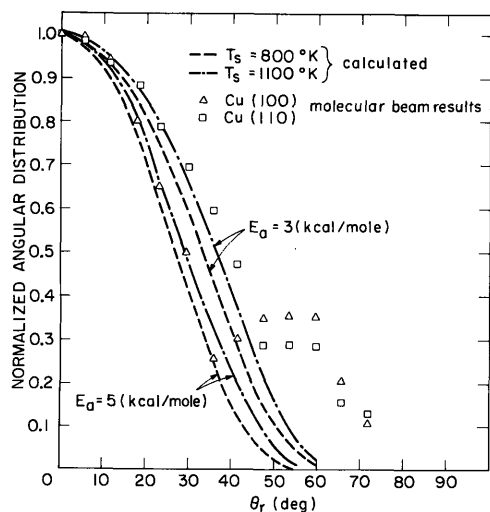
Fig. III-3.

Angular distributions calculated from van Willigan[2] for the (110) and (100) surfaces at two temperatures using the point of inflections from Fig. III-2 to obtain the activation energies E_a. The experimental molecular beam results, which are surface temperature-independent from 800-1100°K, are also shown.

the effect of the nonzero energy spread of the incident beam is removed, together with the results for isotopic switching, suggests that the simplest model must include (i) a distribution of barrier heights associated with the oscillatory nature of the potentials near the surface and (ii) a dynamic factor such as a characteristic collision time to account for the change in dissociation probability with incident particle mass.

References

1. M. Balooch and R. E. Stickney (submitted to Surface Sci.).
2. J. E. Lennard-Jones, Trans. Faraday Soc. 28, 333 (1932); W. van Willigan, Phys. Letters 28A, 80 (1968).