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VARIATION OF SURFACE REACTION PROBABILITY WITH REACTANT ANGLE OF INCIDENCE. A MOLECULAR BEAM STUDY OF THE ASYMMETRY OF STEPPED PLATINUM CRYSTAL SURFACES FOR H-H BOND BREAKING

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VARIATION OF SURFACE REACTION PROBABILITY WITH REACTANT ANGLE OF INCIDENCE. A MOLECULAR BEAM STUDY OF THE ASYMMETRY OF STEPPED PLATINUM CRYSTAL SURFACES FOR H-H BOND BREAKING

by

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Abstract

A molecular beam of H_2 and D_2 was used to investigate the angular dependence of the reaction probability for H_2-D_2 exchange ($H_2 + D_2 \rightarrow 2HD$) on the Pt(111) and Pt(S)-[6(111)x(111)] surfaces. On the stepped surface, a marked increase in the production of HD is observed when the beam of reactants strikes the open side of the step structure. The Pt(111) surface exhibits a smooth decrease in HD production from normal incidence to grazing angles.

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In this paper, we demonstrate for the first time how the reaction rate ($H_2 + D_2 \rightarrow 2HD$) depends on the angle of approach of the reactants to the atomic step structure on a high Miller index surface, Pt(332). The exchange reaction has been studied as a function of incident azimuthal angle (ϕ) and angle of incidence (θ). These results are compared with those obtained on a Pt(111) surface under identical conditions.

The importance of structural defects such as steps and kinks for catalytic bond breaking on single crystal surfaces has been emphasized in recent years.[1] Since these sites are asymmetrical,[2,3] the reaction probability (efficiency of adsorption, bond breaking, etc.) may be determined by the direction of approach of the reactant molecule.

The dependence of the reactivity at a surface site on the angle of approach of the reactant can only be investigated with a directed flow of molecules to the surface. The ultrahigh vacuum molecular beam-surface scattering apparatus used in this study has been previously described in detail.[4]

A mixed molecular beam of H_2 and D_2 is chopped before impinging on the platinum single crystal surface. Periodic pulses of both the reaction product (HD) and the unreacted species (H_2 and D_2) are emitted from the surface and detected by a rotatable quadrupole mass spectrometer.

The detection was performed using two methods. In one method, the species emitted from the surface within a small solid angle are detected directly (differential mode). Using the second method, the modulated partial pressure due to the reaction product HD is measured with the detector removed from direct line of sight of the surface (integral mode). This signal is proportional to the HD produced by the surface integrated over all

emission angles. Although the absolute intensity of the signal is different in each mode, the reaction probability dependence obtained by these two methods of detection is identical. These techniques will be discussed in more detail in a forthcoming paper.

The surface characterization of the single crystal samples was accomplished using low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and the scattering of light gases (He, H_2 and D_2). The Pt(332) surface was shown by LEED to have an ordered step structure with monatomic height steps separated by terraces on the average six atoms wide. Both the step and terrace planes are of the (111) orientation. In a more descriptive notation, this surface is the Pt(S)-[6(111)x(111)].[5] The orientation of the surface step structure with respect to the incident molecular beam was determined from the LEED pattern and He scattering.[6] The composition of the surface was monitored by AES.

In Figure 1, the total production of HD (integral mode) is shown as a function of angle of incidence (θ). Curves a and b present the results for the Pt(S)-[6(111) x(111)] and curve c, those for the Pt(111). The azimuthal angle, ϕ, is 90° in curve a, i.e., the beam is incident perpendicular to the step edges. The open side of the step structure is facing the incoming beam for positive values of θ. The azimuthal angle ϕ is 0° in curve b, where the projection of the incident beam direction on the surface is parallel to the step edges.

For the stepped surface, the formation of HD depends dramatically on the angle of incidence when the step edges are perpendicular to the incident beam (Figure 1a). The reaction probability[7] changes by roughly

a factor of two between the extreme positions. The probability for exchange is highest when the reactants strike the open side of the step structure. In contrast, there is essentially no variation in HD production with angle of incidence when the azimuthal angle $\phi = 0$ (Figure 1b).

The behavior of the exchange reaction on the Pt(111) surface with angle of incidence is most intriguing. After passing through a maximum, at normal incidence, the production of HD decreases smoothly towards glancing incidence. (The asymmetry observed in the experimental curve is probably due to edge effects.) Between normal incidence and a 60° angle of incidence, the reaction probability decreases by almost a factor of two. A similar trend for the sticking coefficient of H_2 and D_2 on W(110) has been reported.[9,10]

The effect of the steps is also clearly seen in Figure 2, where the HD production (integral mode) for the Pt(S)-[6(111)x(111)] is shown as a function of azimuthal angle ϕ, with a fixed angle of incidence $\theta = 45°$. Again, the reaction probability is highest when the reactants strike the open side of the step structure, $\phi = 90$. The increase in HD production is approximately a factor of two from $\phi = -90$ to $\phi = 90$. In a similar experiment on the Pt(111), no significant variation in the production of HD was found.

The energy of the incident molecules was increased by heating the beam from 25°C to 270°C to investigate the possibility of an activation energy for adsorption, as has been reported for H_2 adsorption on Cu.[8] In our experiment, no variation in the amount of HD produced could be detected. Indeed, the results show that, if any, the activation energy for dissociative adsorption of hydrogen should be below the experimental uncertainty ($\lesssim$0.4 kcal/mole) for both the Pt(111) and the Pt(S)-[6(111)x(111)] surfaces. On the stepped

surface, this result is found regardless of angle of incidence or azimuthal angle.

The experiments were performed using a beam modulation frequency of 10 Hz and a surface temperature of 800°C for both crystals. At these high surface temperatures, the H_2-D_2 exchange reaction is limited by the dissociative adsorption of the reactants.[11] Therefore, this work investigates the probability for dissociative adsorption of hydrogen and deuterium by monitoring the formation of the exchange reaction product HD.

The marked dependence of the exchange reaction probability on the angle of approach of the reactants to the step structure can be associated with the unique activity of the platinum atoms at the step edges for H-H bond breaking. The fact that the reaction probability increases rapidly as θ increases, for $\theta > 0$, $\phi = 90$, indicates that the active sites are at the open side of the step structure.

In a recent paper,[12] using work function change measurements, two types of hydrogen adsorption sites were associated with monatomic height steps. These were tentatively assigned to the top and bottom of the step site. Theoretical calculations[3] indicate that, for certain step structures, the bottom of the step site should be more active for breaking H-H bonds.

With our data we cannot pinpoint the exact location of the active site, i.e., the top or bottom atom. However, we do establish that there is definitely a preferred direction of approach for H-H bond breaking. This is perhaps the direction in which the available bonding orbitals of the surface atoms are pointing.[2]

The production of HD on a stepped surface may be considered as the

sum of the contributions of both step and terrace sites. On the Pt(S)-[6 (111)x(111)] surface, approximately 17% of the surface atoms are in step positions. Assuming that the terrace sites behave like those on the Pt(111), we can estimate, using our results, the relative contribution of the step sites. The result of such a partitioning is that the rate of dissociative adsorption of hydrogen at a step site is on the order of 20 times greater than that of a terrace site, under our experimental conditions.

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7. The true reaction probability is obtained in the limit of zero modulation frequency. However, the discrepancy between the apparent value and the true reaction probability should be very small under our experimental conditions of low frequency (10 Hz) and high surface temperature (800°C).

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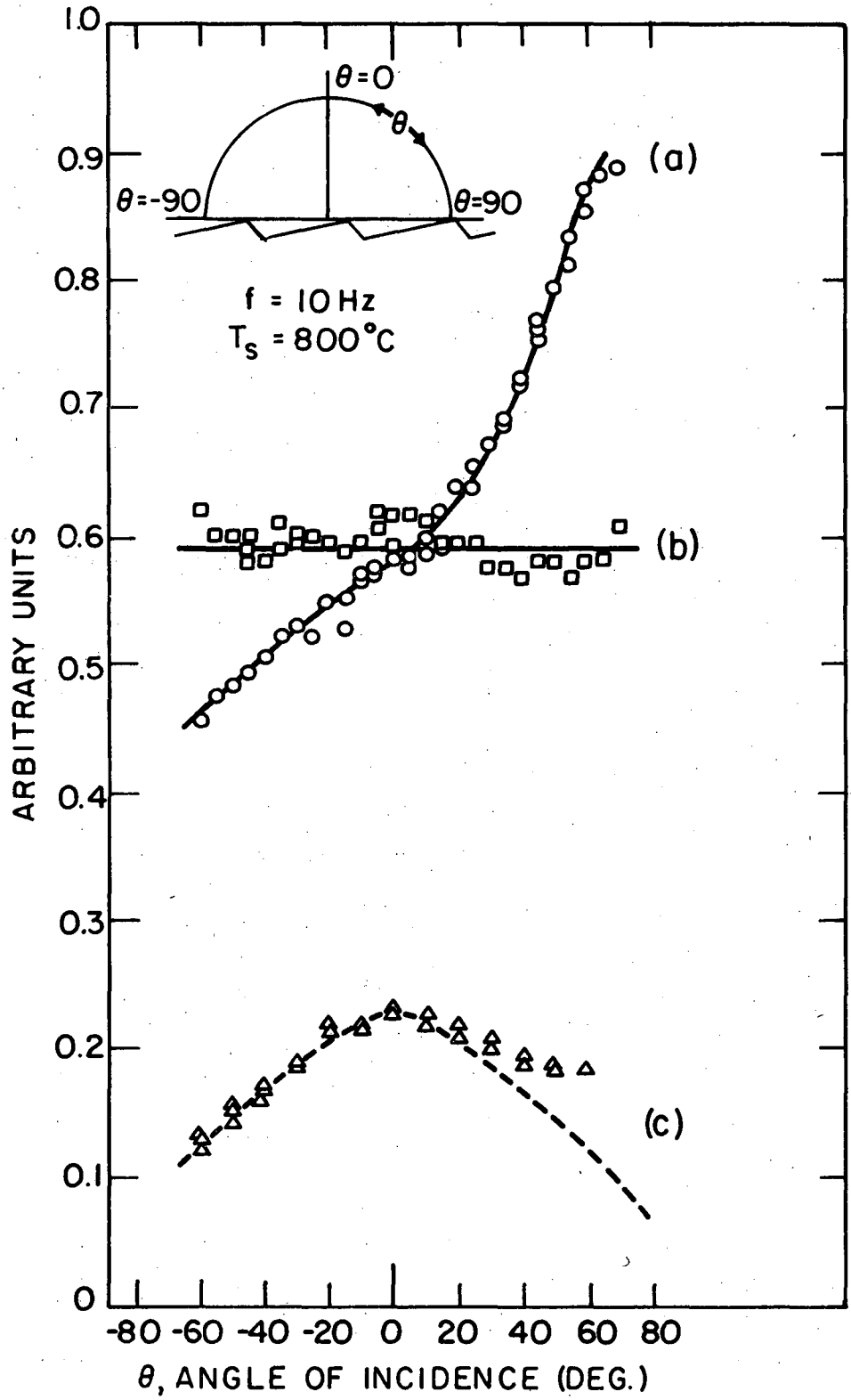
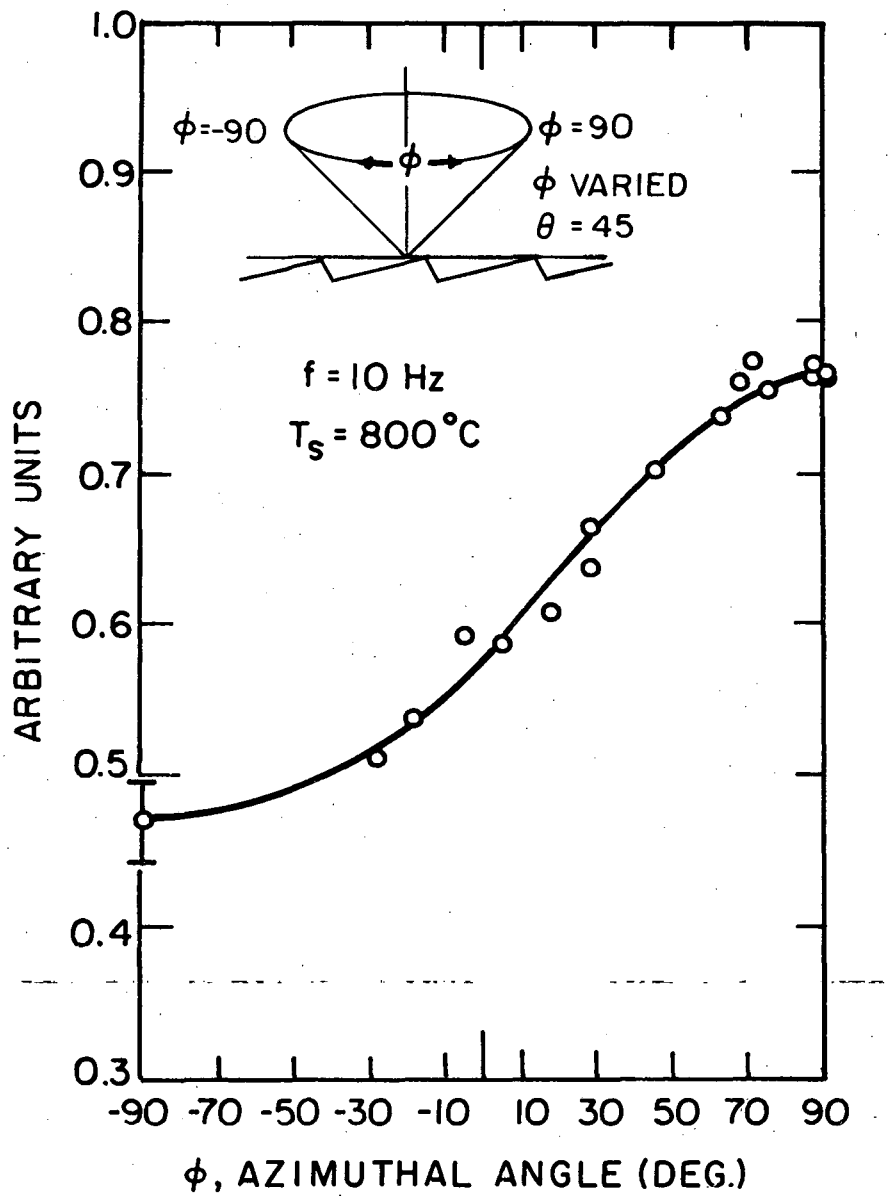
Figure Captions

Fig. 1 Dependence of HD production on angle of incidence (θ), measured from the macroscopic surface normal. a) Pt(S)-[6(111)x(111)] surface, with azimuthal angle $\phi = 90°$, i.e. the beam is incident perpendicular to the step edges as shown schematically in the insert. b) Pt(S)-[6(111)x(111)] surface, with azimuthal angle $\phi = 0°$, i.e. the projection of the incident beam on the surface is parallel to the step edges. c) Pt(111) surface.

Fig. 2 Variation of HD production with azimuthal angle on the Pt(S)-[6(111)x(111)]. The angle of incidence is fixed at 45°, measured from the macroscopic surface normal.


θ=0
θ
θ=-90
θ=90
f = 10 Hz
T_s = 800°C
(a)
(b)
(c)
ARBITRARY UNITS
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-80 -60 -40 -20 0 20 40 60 80
θ, ANGLE OF INCIDENCE (DEG.)

XBL 772-5084


1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
ARBITRARY UNITS
φ=-90
φ=90
φ
φ VARIED
θ = 45
f = 10 Hz
T_s = 800°C
-90 -70 -50 -30 -10 10 30 50 70 90
φ, AZIMUTHAL ANGLE (DEG.)

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