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MOLECULAR BEAM STUDY OF THE H_2 - D_2 EXCHANGE REACTION ON STEPPED
PLATINUM CRYSTAL SURFACES: DEPENDENCE ON REACTANT
ANGLE OF INCIDENCE

by

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Abstract

The exchange reaction $H_2 + D_2 \rightarrow 2HD$ was studied as a function of the angle of incidence (polar and azimuthal) of the beam of reactants on two stepped platinum surfaces, the Pt(S)-[6(111)x(111)] and Pt(S)-[5(111)x(111)]. The reaction probability was found to depend markedly on the direction of approach of the reactants to the step structure. The production of HD is highest when the reactants strike the open side of the step structure, decreasing by approximately a factor of two when the inner corner of the step is shadowed. These variations are intimately related to the geometry of the stepped surfaces and cannot be attributed to an activation energy barrier for adsorption. The observed dependence can be accounted for in a simple model, assigning different activities for H-H bond breaking to the step and terrace sites. For the best fit with the experimental data, we find that the activity of a step site is seven times that of a terrace site at normal incidence.

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1. Introduction

The identification of the active sites on the surface of a catalyst is one of the important goals of research in surface chemistry. These sites may be characterized in terms of the coordination number of the surface atoms. Vacancies, adatoms, steps and kinks are commonly found in even the most carefully prepared low Miller index surface planes. The role that these sites play in the catalytic breaking of C-C, C-H and H-H bonds has been investigated in recent years on platinum surfaces.¹ For the case of H-H bond breaking, for example, the presence of an ordered array of monatomic height steps in a (111) surface has been found to enhance the reaction probability for H_2-D_2 exchange relative to the flat (111) plane.^{2,3,4}

The asymmetry of a stepped surface, as revealed by helium scattering,⁵ raises the question of what effect the direction of approach of the reactants to the step structure may have on the reaction probability. This may be of particular significance if the dissociative adsorption upon impact is the rate limiting step for the reaction.

To investigate this question, a collimated beam of reactants is required, where the angle of incidence with respect to the surface structure is well defined.

In our investigation of the angular dependence of the H_2-D_2 reaction, we find that the reaction probability is highest when the beam of reactants approaches the open side of the step structure. When the reactants are incident such that the inner corner of the step is shadowed, the production of HD is lower by about a factor of two.⁶

This angular dependence can be explained by a geometrical model,

where the terrace sites are assumed to behave like sites on the Pt(111) surface and the step site has a different activity. Such a treatment indicates that a step site is approximately seven times as active for H-H bond breaking as a terrace site at normal incidence.

2. Experimental

2.1 Apparatus

The ultra-high vacuum molecular beam-surface scattering apparatus used for this work, shown schematically in Fig. 1, has been previously described in detail.² Briefly, a molecular beam, formed by effusion from a multichannel glass capillary array, passes through a one millimeter collimating orifice into a differentially pumped chamber containing a slotted disc that serves to modulate the beam in the range of frequencies 10 to 300 Hz. The chopped molecular beam continues through another one millimeter orifice into the UHV chamber containing the single crystal sample(s) under investigation.

The species emitted from the surface after collision of the beam with the sample are detected by a rotatable quadrupole mass spectrometer, in the plane defined by the incident beam and the macroscopic surface normal.

The crystal can be raised and the detector placed in the direct beam line so that the intensity and composition of the incident beam can be measured. The scattered signal can then be normalized to the incident beam intensity.

Under our experimental conditions, the molecular beam so obtained has an intensity of approximately 10^{13} molecules per second and a cross-sectional diameter of approximately 2.5 mm at the surface of the sample.

The range of beam modulation frequencies is extended to below 1 Hz, to approach the conditions of conventional non-modulated experiments, by the use of a flag which swings across the beam path, inside the UHV chamber. The low frequency limit (0.5 Hz) is set by the lowest working frequency of our lock-in amplifier.

The molecular beam source can be resistively heated from 25 to 300°C to vary the energy of the incident reactants.

2.2 Experimental method

To study the reaction between two gases (H_2 and D_2 in our case) on the surface of a catalyst, we have introduced the reactants in two different ways. In one method, one of the reactants is in the form of a modulated molecular beam, while the other is admitted directly into the chamber, up to a pressure of 10^{-7} to 10^{-6} torr, to yield an unmodulated flux of the background gas to the surface, equivalent to that of the chopped molecular beam. Both reactants are in the beam for the second method, producing a mixed molecular beam of H_2 and D_2 in the ratio desired.

The background pressure in the UHV chamber is in the range of 10^{-9} torr with the mixed beam method, resulting in an improved signal to noise ratio relative to the beam-background method.

2.3 Modes of signal detection

Detection of the product signal can be performed in two different modes, differential and integral.

In the differential mode, the mass spectrometer is positioned at a certain scattering angle from the surface normal. The signal detected is composed of two different contributions for a given mass number. One

part is due to the species directly emitted from the surface at that angle. The second contribution is from the modulated partial pressure of the species emitted from the surface due to their finite residence time in the UHV chamber before being pumped away. The modulated background must be subtracted from the total signal measured to obtain the true differential signal. At each scattering angle, the modulated background can be measured by covering the aperture in the ionizer of the mass spectrometer facing the crystal, so that molecules emitted from the surface cannot enter it directly. The true differential signal is then normalized to the incident beam intensity to give the differential reaction probability. To obtain the total reaction probability, these results must be integrated over all angles, which requires knowledge of the angular distribution of the products.

It can be shown, in the first approximation, that the intensity of the modulated background, I_{bkgd} , changes with the frequency of modulation ω as $I_{\text{bkgd}} \propto \frac{1}{\sqrt{1+(\omega/s/v)^2}}$ where s is the pumping speed and v the volume of the chamber. For very low modulation frequencies, $\leq 2\text{Hz}$, for example, the contribution of this modulated background is ~ 10 times larger than the signal due to the species emitted directly from the surface into the solid angle accepted by the ionizer aperture. This is due to two effects. First, the time constant of the pump, v/s , is low enough for the pump to follow the periodic production of HD by the surface at low modulation frequency. The second factor is that the direct signal corresponds to molecules emitted within 3° at a particular scattering angle whereas the modulated background is produced by products emitted in all directions.

For our experimental geometry, that is roughly a factor of 500 for a cosine type emission from the surface. In the high modulation frequency range (≤ 200 Hz), the pump can no longer follow the signal pulses emitted from the surface so that the modulated partial pressure contribution becomes smaller than the true differential signal. At 200 Hz, for example, the true differential signal is a factor of three larger than the modulated background.

At low modulation frequency, it is therefore advantageous to utilize the second method of detection, the integral mode. The mass spectrometer is positioned behind the crystal, out of the direct line of sight of the surface, such that only the modulated partial pressure of the products is measured. This integral signal is proportional to the total amount of HD emitted by the surface and needs not to be integrated as in the differential mode. Furthermore, any possible effects due to the angular distribution of the products is eliminated, i.e., we need not assume that the products are emitted in a cosine distribution.

When the reaction product signal is measured in this manner, an integral mode measurement of the incident beam is also required. This is accomplished by rotating the sample holder such that the beam strikes the back of the crystal support. The scattering geometry is the same so that the incident reactants are distributed in the chamber in the same manner as the products are when the beam strikes the crystal. The relative proportions of H_2 , D_2 and HD measured in this way are not substantially different from those measured in the direct beam, so we know that the beam is scattered, but no reaction occurs. The integral mode measurement of the product signal is then normalized to the integral mode measurement of

the incident beam to give the total reaction probability.

In the integral mode of detection, the angle of incidence and azimuthal angle can be varied by 180° . The angular variation is limited to 90° in the differential mode due to restrictions in the range of rotation of the detector. Since the mass spectrometer needs not to be moved in the integral mode measurements, this restriction is eliminated.

The differential mode of detection is, however, preferable at high frequencies and for studies of angular scattering distributions.

2.4 Reactant gases

The D_2 used for these experiments contained 1% HD, so the scattered HD had to be subtracted from the product signal. The H_2 contained a negligible amount of HD ($\leq .01\%$). Before mixing the H_2 into the beam, the D_2 beam was formed and the scattering distribution of D_2 and HD measured. After the H_2 was admitted into the beam, ^{the} H_2 , HD and D_2 signal were measured so that the scattered HD ^{could} be estimated.

2.5 Single crystal sample preparation

The platinum single crystal surfaces employed in this work were the Pt(553), Pt(332) and Pt(111). After orientation by X-ray diffraction to within $\pm 1^\circ$ of the appropriate plane, the crystals were spark cut from 99.999% pure bulk platinum single crystal rods. The samples were then mechanically polished down to .05 μ alumina and etched in warm aqua regia before being placed in the chamber.

The crystals were mounted on a tantalum support which provided infrared or direct heating. Surface temperatures were measured externally with an optical pyrometer which had been previously calibrated using a thermocouple spot-welded to the crystal.

The crystals were cleaned in vacuum using argon ion sputtering, high temperature annealing and/or heating to 600-800°C in 10^{-7} to 10^{-6} torr of oxygen. All of the results reported here correspond to surfaces which were clean and well ordered as established by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED).

2.6 Definition of angular geometry

The manipulator upon which the crystals were mounted provides several different motions: x, y and z translation as well as two types of rotation. The standard rotary feedthrough motion is used to position the crystal for cleaning and characterization by LEED, AES and argon ion sputtering and to fix the angle of incidence of the molecular beam. Azimuthal rotation, i.e., rotation of the crystal around the macroscopic surface normal, provides positioning of the surface microstructure with respect to the incident beam.

The geometry for the variation of angle of incidence and azimuthal angle is shown schematically for a stepped surface in Fig. 2. The angle of incidence, θ , is measured from the macroscopic surface normal and designated as positive when the open edge of the step structure is directed toward the incident beam. The azimuthal angle, ϕ , is defined as 0° when the projection of the incident beam on the surface is parallel to the step edges; 90° when the beam impinges into the open edge of the step structure (from the right in the figure) and -90° when the open edge of the step structure is directed away from the incoming beam (from the left in the figure).

3. Surface Characterization by LEED, AES and Helium Scattering

3.1 The Pt(332) and Pt(553) crystal faces

The major contaminants detected by AES in the Pt(332) crystal were silicon and phosphorous. The most effective method of removing these impurities was found to be bombardment with 500 eV argon ions for several hours with the crystal at $\sim 600^\circ\text{C}$. After such a treatment, the near surface layers were sufficiently depleted of the contaminants to maintain a clean surface at temperatures up to 900°C .

The Pt(553) crystal employed in this study had been used extensively by earlier workers in this laboratory^{2,5} such that bulk impurities had been depleted. Carbon was the only contaminant detected by AES and was easily removed by flashing to $\sim 1000^\circ\text{C}$ or heating at $600\text{--}800^\circ\text{C}$ in 10^{-7} torr of oxygen.

Presented in Fig. 3 are the LEED patterns for the clean surfaces, which indicate that these surfaces consist of ordered arrays of terraces of the (111) orientation separated by steps. From intensity versus voltage measurements of the (0,0) doublet, the steps are found to be of monatomic height. The ratios of the distances between doublet spots, a , and parallel rows, b , are $\frac{b}{a} = 3.87 \pm 0.04$ for the Pt(553) surface and $\frac{b}{a} = 4.71 \pm 0.04$ for the Pt(332) surface. These results agree quite well with the calculated values 3.84 and 4.69, corresponding to the stepped surfaces denoted⁷ Pt(S)-[5(111)x(111)] and Pt(S)-[6(111)x(111)], respectively. The reciprocal lattice unit cells, shown in Fig. 3, have the geometry characteristic of these two stepped surfaces: oblique for the Pt(S)-[5(111)x(111)] (odd number of atomic rows, n , in the terrace) and rectangular for the Pt(S)-[6(111)x(111)] (even number of atomic rows, n , in the terrace), confirming that the steps are of the (111) orientation. When the steps are of the (100) orientation, the symmetry is reversed, i.e., rectangular for n odd and oblique for n even.

A ball model illustration of the Pt(S)-[6(111)x(111)] surface is given in Fig. 4. The terraces are six atomic rows wide. The Pt(S)-[5(111)x(111)] surface differs only in that the terraces are five atomic rows wide. As can be seen in this model, the atom at the step edge and the inner corner atom of the step structure have unique coordination. The other terrace atoms have the configuration of surface atoms in the (111) plane.

The clean surfaces exhibited thermal stability over the entire temperature range studied (25-1100°C). However, many different, complex surface structures were observed by LEED when the surfaces were contaminated with carbon, silicon, phosphorous or oxygen.

The LEED pattern also allows us to determine the azimuthal angle, ϕ , by measuring the angle between the rows of doublets and the beam line. The sign of the azimuthal angle, i.e., whether the open side of the step structure is facing towards the beam, is determined by helium scattering. The specular reflection peak, which results from the ^{helium} atoms scattering from the terrace planes, appears shifted from the optical specular by twice the angle between the macroscopic surface plane and the (111) plane.⁵ The helium scattering distributions from the Pt(S)-[5(111)x(111)] surface at 1000°C are presented in Fig. 5 for three azimuthal angles. When $\phi = 90^\circ$ (curve a), the open edge of the step structure is perpendicular to the incident beam. In curve b, for $\phi = -90^\circ$, the open edge of the step structure is facing away from the incoming beam. The projection of the beam on the surface is parallel to the step edges when $\phi = 0^\circ$ (curve c). The lower intensity of the specular peak when $\phi = 0^\circ$ is due to the fact that the maximum of the helium scattering distribution is located out of the plane of detection.

-11-

3.2 The Pt(111) crystal faces

In the five Pt(111) samples used for this study, the main impurities detected by AES were silicon, phosphorous, carbon and calcium. The relative proportion of these contaminants varied from sample to sample. Three samples exhibited only carbon as an impurity. One contained calcium and another showed silicon and phosphorous as major contaminants.

The carbon could be removed by heating to 600-800°C in $\sim 10^{-7}$ torr of oxygen. The silicon, phosphorous and calcium were most effectively removed by argon sputtering for several hours with the crystal at $\sim 600^\circ\text{C}$.

The LEED patterns of the clean surfaces exhibited the characteristic hexagonal structure of the (111) plane of an fcc crystal.

Helium scattering was used to probe the degree of perfection of the surfaces. The helium scattering distribution for a surface temperature of 520°C , shown in Fig. 6, consists of a peak at the specular angle with a FWHM of 7° and with an intensity of 16.5% of the incident beam. This result is to be compared with the previously reported values³ of 7° FWHM and 11% scattered intensity for the same plane of platinum and at the same surface temperature, indicating that our sample surface was quite smooth. The other Pt(111) surfaces examined by helium scattering showed broader and less intense scattering distributions, but their reactivity for $\text{H}_2\text{-D}_2$ exchange was not significantly higher.

The results reported here for $\text{H}_2\text{-D}_2$ exchange were obtained on the Pt(111) surface exhibiting the most narrow and highest intensity helium scattering distribution.

4. Results

The exchange reaction $\text{H}_2 + \text{D}_2 \rightarrow 2\text{HD}$ was studied on three platinum

crystal faces, Pt(S)-[6(111)x(111)], Pt(111) and Pt(S)-[5(111)x(111)], at surface temperatures in the range 300-1000°C, as a function of angle of incidence and incident azimuthal angle. The modulation frequency of the beam of reactants employed was between 1.5 and 200 Hz. The majority of the results presented here were obtained at 10 Hz or below.

4.1 Reactive scattering from the Pt(S)-[6(111)x(111)] surface

The angular dependence of the H_2 - D_2 exchange reaction probability on the Pt(S)-[6(111)x(111)] surface was investigated with a mixed beam of H_2 and D_2 , using the integral mode of detection.

In Fig. 7 (a) and (b), the production of HD as a function of angle of incidence is presented. The azimuthal angle, ϕ , is $\pm 90^\circ$ in curve (a), i.e., the step edges are perpendicular to the incident beam as shown in the insert. The projection of the reactant beam on the surface is parallel to the step edges in curve (b), where $\phi = 0^\circ$. These experiments were performed with a beam modulation frequency of 10 Hz and a surface temperature of 800°C. The vertical scale is the reaction probability corrected for the ratio of D_2/H_2 in the beam. The form of this expression will be discussed in section 5.4. The magnitude of this correction is generally ~ 0.1 .

These results, obtained with a mixed beam and the integral mode of detection, reveal the fine details of the variation in reaction probability as a function of angle of incidence. When $\phi = \pm 90^\circ$, the production of HD increases smoothly from $\theta = -60^\circ$ to $\theta = 0^\circ$, where there is an inflection, followed by a rapid increase as the beam of reactants approaches at more glancing angles into the open side of the step structure. The formation of HD is most favorable when the reactant molecules are incident at

glancing angles ($\theta \sim 60^\circ$) into the open side of the step structure. A decrease by approximately a factor of two is observed from $\theta = 60^\circ$ to $\theta = -60^\circ$, where the inner corner of the step site is shadowed. In curve (b), the beam of reactants comes in along the step edges and there is no variation in reaction probability with angle of incidence. The two curves coincide at normal incidence, as expected.

The dependence of the reaction probability for $\text{H}_2\text{-D}_2$ exchange on azimuthal angle is shown in Fig. 8(a), for a fixed angle of incidence, $\theta = 45^\circ$ measured from the macroscopic surface normal. These results were also obtained at 10 Hz and $T_s = 800^\circ\text{C}$. Again, the vertical scale is the reaction probability corrected for the ratio of D_2/H_2 in the beam. As found in the angle of incidence experiments, the production of HD is highest when the reactant beam strikes the open side of the step structure, increasing by approximately a factor of two from $\phi = -90^\circ$ to $\phi = 90^\circ$.

The amount of D_2 withdrawn from the beam and converted to HD, ΔD_2 , was also measured and is plotted in Fig. 8(b). It follows the trend in HD production, as expected.

4.2 Reactive scattering from the Pt(111) surface

The production of HD as a function of angle of incidence and incident azimuthal angle was studied on the Pt(111) surface with a mixed beam of H_2 and D_2 , using the integral mode of detection.

The dependence of HD formation on angle of incidence is shown in Fig. 7 (c), at 10 Hz and $T_s = 800^\circ\text{C}$. These results were obtained on the Pt(111) sample which showed the highest reflectivity for helium. The reaction probability increases from glancing incidence $\theta = \pm 60^\circ$, to a maximum at normal incidence, by approximately a factor of two.

No appreciable dependence of HD production on azimuthal angle was found on the Pt(111) surfaces, although a variation of less than 20% would not have been observed due to scatter in the experimental points.

4.3 Reactive scattering from the Pt(S)-[5(111)x(111)] surface

To demonstrate that the angular dependence of the $\text{H}_2\text{-D}_2$ exchange reaction probability observed on the Pt(S)-[6(111)x(111)] surface is not restricted to this specific stepped surface or to the particular experimental method utilized, we present results obtained on the Pt(S)-[5(111)x(111)] surface using the beam-background method and both modes of detection. These experiments were performed with a beam of H_2 and $\sim 10^{-6}$ torr of D_2 in the background at a variety of surface temperatures and beam modulation frequencies.

The production of HD as a function of angle of incidence is shown in Fig. 9, measured in the integral mode. As depicted in the insert, the azimuthal angle is $\phi = \pm 90^\circ$, such that the step edges are perpendicular to the incident beam. These results correspond to two different experiments, performed at 2.5 Hz and $T_s = 1000^\circ\text{C}$, normalized to 1 at $\theta = 45^\circ$, $\phi = 90^\circ$. The overall trend observed is the same as that on the Pt(S)-[6(111)x(111)] surface, an increase of approximately a factor of two from $\theta = -60^\circ$ to $\theta = +60^\circ$, with the reaction probability highest when the reactants approach the open edge of the step structure at glancing angles.

The azimuthal angle dependence for $\text{H}_2\text{-D}_2$ exchange is shown in Fig. 10, with the angle of incidence fixed at $\theta = 45^\circ$, measured from the macroscopic surface normal. The two curves present results utilizing the two different methods of detection. Curve (a) corresponds to the integral mode and curve (b) to the differential mode.

In curve (a), the results from several experiments measured in the integral mode for surface temperatures from 400-1100°C and beam modulation frequencies of 1.5 to 2.6 Hz were normalized to 1 at $\phi = 90^\circ$. Again, the formation of HD is most probable when the reactants impinge on the open side of the step structure, increasing by approximately a factor of two from $\phi = -90^\circ$ to $\phi = 90^\circ$, as observed on the Pt(S)-[6(111)x(111)] surface.

Presented in curve (b) are the normalized results of two high frequency experiments, at 100 Hz, $T_s = 900^\circ\text{C}$ and 200 Hz, $T_s = 700^\circ\text{C}$, measured in the differential mode with the detector accepting those molecules emitted normal to the surface. Although the azimuthal angle can be varied only from $\phi = 0^\circ$ to $\phi = 90^\circ$ in this mode, the same dependence is observed.

As mentioned in the experimental section, the high background pressure required in the beam-background method gives rise to a poor signal to noise ratio which results in the scatter seen in these experimental measurements. However, these results indicate that the trend observed is the same over a wide range of experimental conditions.

4.4 Beam temperature dependence of the reaction probability

To investigate whether the angular dependence observed can be attributed to an activation energy for adsorption, the molecular beam was heated from 25°C to 300°C and the production of HD monitored. No significant variations were observed within our experimental uncertainty. Our results show that, if any, the activation energy for adsorption is below 0.4 kcal/mole, for both the Pt(111) and Pt(S)-[6(111)x(111)] and is independent of angle of incidence.

5. Discussion

We have found that the $\text{H}_2\text{-D}_2$ exchange reaction probability on stepped platinum surfaces depends markedly on the direction of approach of the reactants to the step structure, reflecting the structural asymmetry of the surface. Since the reaction rate was independent of the thermal energy of the incident reactants, these angular variations cannot be associated with an activation energy for adsorption, either on the steps or on the terrace. The trend may be explained in terms of the geometrical variation of the number of reactant molecules that strike the open side of the step structure, which is more active for H-H bond breaking.

5.1 Structure sensitivity of the reaction probability

For the $\text{Pt(S)}\text{-}[5(111)\times(111)]$ and $\text{Pt(S)}\text{-}[6(111)\times(111)]$ surfaces, the reaction probability for $\text{H}_2\text{-D}_2$ exchange is found to be highest when the reactants approach the open side of the step structure directly. This result clearly reveals the unique properties of the step site(s) for H-H bond breaking.

Work function change measurements⁴ indicate that there are two types of sites for hydrogen adsorption on stepped platinum surfaces with (111) steps not found on the flat $\text{Pt}(111)$ surface. These sites have tentatively been assigned to the top and bottom of the step edges.

The one-hole charge density angular distributions of the orbitals of transition metal ions in various crystalline geometries on stepped surfaces have been calculated by Tsang and Falicov.⁹ The stepped surface examined was of the $n(100)\times(100)$ configuration for fcc metals. These calculations indicate that the available bonding orbitals of the platinum atom at the top of the step edge should be fairly symmetrical, whereas the most

prominent available orbital of the inner corner atom is directed away from the step edge. In this theoretical framework, the activity of the different sites for H-H bond breaking on a stepped platinum surface of the $n(111) \times (100)$ configuration was calculated.¹⁰ The site associated with the inner corner atom was found to be most active. If these results also hold for a stepped surface of the $n(111) \times (111)$ configuration, the angular dependence of the reaction probability that was observed experimentally would then correspond to the change in the number of molecules striking the inner corner of the step structure as a function of the angle of incidence.

We can make a simple calculation of the angular dependence expected on the basis of the arguments above in the following manner. First, we assume that the sites on the (111) terrace behave like those on the Pt(111) surface, for which we have data obtained under identical experimental conditions. We take the step site to be the inner corner atom and its first nearest neighbors. This site then has the geometry of the sites on the unreconstructed Pt(110) surface. (H_2 - D_2 exchange on the Pt(110) surface has also been studied under identical experimental conditions.¹¹) The incident beam is divided between the available area of the step site and that of the terrace. The reaction probability per unit area at the step site is used as an adjustable parameter, while our experimental results for the reaction probability per unit area on the Pt(111) surface is used for the terraces.

The results of such a crude calculation are shown in Figs. 11 and 12 with the experimental data for the variation with angle of incidence and azimuthal angle, respectively. R is the ratio of the reaction probability per unit area of the step site to that of a terrace site at normal

incidence. The agreement is remarkably good when the step site is assumed to be seven times as active as a terrace site. The deviation from the experimental curve at negative glancing angles of incidence may be attributed to the possibility that some defect sites are accessible at all angles of incidence.

As indicated previously, the inner corner atom of the step structure has the nearest neighbor configuration of a site on the unreconstructed Pt(110) surface. The experimental results obtained for this surface under identical conditions give a value of $R = 4$. The calculated curve which gives the best fit to our experimental results on the Pt(S)-[6(111)x(111)] surface corresponds to $R = 7$, indicating that the activity of the step site is higher than the same configuration on the Pt(110) surface.

5.2 Absence of an activation energy barrier for adsorption

The observed dependence of the reaction probability on the angle of incidence of the reactants can be an indication of an activation energy barrier for adsorption. Such a barrier would introduce a term of the form $\exp(-E_a/RT)$ in the sticking coefficient for the optimum incident direction, i.e., perpendicular to the barrier. For other incident directions, the denominator in the exponential would be modified as $RT \cos^2 \theta$.

The existence of an activation energy barrier for adsorption can be probed by varying the energy of the incident reactants. For example, Balooch and coworkers¹² were able to correlate the angle of incidence dependence with the beam energy dependence for hydrogen adsorption on several faces of copper. In our study, the temperature of the beam of reactants was varied from 25-300°C which, in this analytical framework, should be equivalent to varying the angle of incidence by 67°. Over this

range of beam energies, however, no variation in the reaction probability was observed whereas varying the angle of incidence by 60° on the Pt(111) surface resulted in a factor of two change in HD production. On the stepped surfaces, the variation of the reaction probability with angle of incidence may be complicated by the structural asymmetry of the surface. An activation energy barrier associated with the step edge could produce an asymmetric curve. The fact that no dependence on the energy of the reactants was found, regardless of angle of incidence, rules out this as a possible explanation. Thus, the correlation between beam energy and angle of incidence corresponding to an activation energy barrier for adsorption, as found for hydrogen on copper, cannot be made in this case.

Using the model of van Willigen,¹³ which incorporates the activation barrier for adsorption, an activation energy of ~ 2 kcal/mole would be required to approximate the angle of incidence dependence observed on the Pt(111) surface, in clear disagreement with the upper limit of 0.4 kcal/mole established by the beam energy dependence.

From these arguments, we must conclude that the angular dependence found for H_2-D_2 exchange on the three platinum surfaces studied is not due to an activation energy barrier for adsorption. This conclusion is supported by the results reported by other workers. Bernasek² found that the H_2-D_2 exchange reaction probability on the Pt(S)-[5(111)x(111)] and Pt(S)-[9(111)x(111)] surfaces is independent of beam energy. The adsorption of hydrogen on the Pt(111)¹⁴ and Pt(S)-[9(111)x(111)]⁴ surfaces was reported to be non-activated by Ertl and coworkers.

5.3 Angle of incidence dependence of the reaction probability on Pt(111)

The reaction probability for H_2-D_2 exchange on the Pt(111) surface is

also found to depend of the angle of incidence of the reactants. As indicated in the previous section, we cannot attribute this result to an activation energy for adsorption. These variations may possibly be explained in terms of angular dependent energy exchange between the gas and the surface. A comparison of our results with the predictions of the many models which have been proposed for gas-surface energy transfer

is planned for the near future.

5.4 Dissociative adsorption probability of H_2 and D_2

Our experiments were performed in the range of surface temperatures in which the reaction rate was found to be independent of surface temperature. In this regime, the rate determining step in the H_2 - D_2 exchange reaction is the adsorption of the reactants. Flash desorption experiments^{3,4,14} have shown that the long-lived surface species in the adsorption of hydrogen on platinum single crystal surfaces are atomic. The results shown in the preceding sections are best explained by assuming that the dissociation of the hydrogen molecule occurs directly upon impact with the surface. The observed angular dependence on the stepped surfaces suggests that the dissociation is not preceded by diffusion to an active site, such as the step. If diffusion of the molecules before dissociation played an important role, the reaction probability would be independent of the angle of incidence of the reactants. Therefore, we assume that the only surface intermediates are H and D atoms.

With this assumption, under steady state conditions, the mass balance equations would give the rate of HD formation as:

$$R_{HD} = 2\sigma \frac{R_{H_2}^o R_{D_2}^o}{R_{H_2}^o + R_{D_2}^o} \quad (\text{Eq. 1})$$

-21-

where σ is the sticking coefficient for dissociative adsorption (neglecting isotope effects) and $R_{H_2}^0$, $R_{D_2}^0$ are the number of molecules from the beam colliding with a unit area of the surface per unit time.

The sticking coefficient is then expressed in terms of the experimentally measured parameters, from Eq. (1), as:

$$\sigma = \frac{HD_{int}}{2D_{2int}^0} \left(1 + \frac{I_{D_2}^0}{I_{H_2}^0} \right) \quad (\text{Eq. 2})$$

where HD_{int} and D_{2int}^0 are the product and beam signal, respectively, measured in the integral mode and $I_{D_2}^0/I_{H_2}^0$ is the ratio of D_2/H_2 in the incident beam.

The vertical axis in Figs. 7, 8, 11 and 12 is then 2σ and the trend observed is the variation of the sticking coefficient for dissociative adsorption as a function of angle.

The equations shown above should be appropriate for the analysis of our experimental data, since the reaction was studied at low modulation frequency, 10 Hz, and high surface temperature, 800°C. Under these conditions, the reaction time is short compared to the modulation period, such that a steady state treatment is applicable. If the modulation frequency is very high, an apparent decrease in HD production is observed due to demodulation of the first harmonic of the product signal. This demodulation indicates that the reaction time is comparable to or larger than the modulation period. Under such conditions, the modulation frequency must be incorporated into the mass balance equations and the formulas presented

above would not be valid. One can, of course, by choosing the appropriate surface temperature and modulation frequency, avoid this demodulation.

5.5 Comparison with earlier work

It is interesting to compare the sticking coefficient of hydrogen deduced from our data with that reported by other authors. To obtain the isotropic sticking coefficient, our angular data must be integrated over all angles of incidence. To perform the integration, the data for the dependence on azimuthal angle was fit by a sine function, shown as a (curve a). solid line in Fig. 8/ We assume that the functional shape of the curve is the same for all angles of incidence.

The values for the sticking coefficient for H_2 on the $Pt(S)-[5(111) \times (111)]$ surface obtained by such an integration are $\sigma = 0.36$ or 0.35 , depending on how the extrapolation from $\pm 60^\circ$ to $\pm 90^\circ$ angle of incidence is performed. The absolute value should be regarded as correct to within 20%, due to possible differences in the pumping speed for HD and D_2 and the uncertainties in the integration procedure. The data for the $Pt(111)$ surface can also be integrated over all angles of incidence to give a value of $\sigma = 0.07$ with the same 20% uncertainty. The ratio of the sticking coefficient for H_2 on the $Pt(S)-[6(111) \times (111)]$ surface to that on the $Pt(111)$ surface is equal to 5. The uncertainty in the ratio should be lower than ~10%.

These results are in fairly good agreement with those of Ertl and coworkers for the $Pt(111)$ surface,^{4,14} where the reported value is $\sigma = 0.085$. The $Pt(S)-[6(111) \times (111)]$ result is comparable to the value obtained by the same laboratory⁴, for the $Pt(S)-[9(111) \times (111)]$, i.e., $\sigma = 0.35$, although our crystal has 1.5 times the step density. The reported ratio

-23-

of the sticking coefficient for H_2 on the $Pt(S)-[9(111)x(111)]$ surface to that on the $Pt(111)$ is equal to 4.

Since these ratios tend to cancel some of the experimental errors, a comparison of the sticking coefficient ratios with the ratio of step densities may be more instructive. The step density ratio for the two stepped surfaces is $9/6 = 1.5$, while the sticking coefficient ratio is $5/4 = 1.25$, suggesting that the integrated sticking coefficient does not depend linearly on step density.

As mentioned previously, the rate of HD formation was found to be constant over a wide range of surface temperatures, ~ 300 - $1000^\circ C$. This result implies that the sticking coefficient for hydrogen on these platinum surfaces is temperature independent over this range. Ertl and co-workers⁴ found no variation in the sticking coefficient over their range of experimental temperatures, -150 to $300^\circ C$. Since these ranges do overlap, comparison of the sticking coefficients observed in both cases should be valid.

Other measurements of the sticking coefficient for hydrogen on $Pt(111)$ include those of Smith and Merrill,¹⁵ $\sigma = 0.07$, and Lu and Rye,³ $\sigma = 0.016$. Bernasek and Somorjai^{2,16} have reported that the rate of H_2 - D_2 exchange on this surface is three orders of magnitude lower than that on a stepped surface. No clear cut explanation has been found as of yet for the discrepancy between our results and some of these other observations.

6. Conclusions

Our molecular beam study of the H_2 - D_2 exchange reaction on platinum crystal surfaces as a function of the angle of incidence (polar and azimuthal) has shown that:

- (1) The structural asymmetry of the stepped surfaces is reflected in

the reaction probability for H_2 - D_2 exchange. This gives rise to a dependence of the reaction probability on the direction of approach of the reactants to the step structure.

(2) The functional form of the angular dependence can be explained by assigning an activity for H-H bond breaking/at the step site equal to approximately seven times that of a terrace site at normal incidence.

(3) The observed angular dependence on the stepped surfaces cannot be attributed to an activation energy barrier for adsorption.

(4) The increase in HD production found on the stepped surfaces when the reactants approach the open side of the step structure at grazing angles of incidence is best explained by assuming that the most active site is associated with the inner corner platinum atom of the step structure.

(5) The results suggest that dissociation of the hydrogen molecule occurs directly upon impact with the surface, i.e., diffusion of molecular hydrogen is not controlling the rate of reaction.

(6) The angular dependence of the reaction probability on the Pt(111) surface must reflect an energy exchange process between the gas and the surface which depends on the angle of impact and is not due to an activation energy for adsorption.

(7) The isotropic sticking coefficients for hydrogen on Pt(111) and Pt(332) are 0.07 and 0.35 ($\pm 20\%$), respectively.

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Figure Captions

- Fig. 1 Schematic diagram of the experimental apparatus.
- Fig. 2 Diagram defining the geometry of the incident angles (polar, θ , and azimuthal, ϕ) of the molecular beam with respect to a stepped surface. The polar angle of incidence, θ , is measured from the macroscopic surface normal and designated as positive when the molecular beam strikes the open side of the step structure (i.e., incident from the right in the figure). The cones represent variation of the azimuthal angle, ϕ , for different angles of incidence. The azimuthal angle, ϕ , is defined as 0° when the projection of the incident beam on the surface is parallel to the step edges, $+90^\circ$ when the step edges are perpendicular to the beam with the beam impinging on the open side of the step structure, and -90° when the step edges are perpendicular to the incident beam with the open edge of the step pointing away from the incoming beam.
- Fig. 3 LEED patterns (photographs and schematic representations) of the Pt(S)-[5(111)x(111)] surface (A) and the Pt(S)-[6(111)x(111)] surface (B). The schematic representation indicates the symmetry of the step periodicity: oblique for an odd number of atomic rows on the (111) terrace (A) and rectangular for an even number (B).
- Fig. 4 Ball model of the Pt(S)-[6(111)x(111)] surface. A) Top view: the dotted lines show the rectangular symmetry of the periodicity of the step structure. B) Side view.
- Fig. 5 Helium scattering distribution from Pt(553) (or Pt(S)-[5(111)x(111)]) surface at $T_s = 1000^\circ\text{C}$ for three azimuthal angles, with the angle of

incidence fixed at $\theta = 45^\circ$. The arrow on the horizontal axis indicates the macroscopic specular angle. (a) The step edges are perpendicular to the incident beam with the open side directed away from the beam ($\phi = -90^\circ$). (b) The step edges are perpendicular to the incoming beam with the open side facing the beam ($\phi = +90^\circ$). (c) The projection of the beam on the surface is parallel to the step edges ($\phi = 0^\circ$).

Fig. 6 Helium scattering distribution from the Pt(111) surface at $T_s = 520^\circ\text{C}$. The specular angle is indicated by an arrow on the horizontal axis.

Fig. 7 HD production as a function of angle of incidence, θ , of the molecular beam, normalized to the incident D_2 intensity. The expression in the parentheses is a correction factor which accounts for the relative proportions of H_2 and D_2 in the beam, as explained in section 5.4. a) Pt(332) (or Pt(S)-[6(111)x(111)]) surface, with the step edges perpendicular to the incident beam ($\phi = \pm 90^\circ$). b) Pt(332), where the projection of the beam on the surface is parallel to the step edges ($\phi = 0^\circ$). c) Pt(111) surface.

Fig. 8 a) HD production on the Pt(332) (or Pt(S)-[6(111)x(111)]) surface as a function of azimuthal angle, ϕ , normalized to the incident D_2 intensity. The expression in the parentheses is a correction factor which accounts for the relative proportions of H_2 and D_2 in the beam, as explained in section 5.4. The solid line is a sine function fit to the data in order to perform the integration discussed in section 5.5. b) ΔD_2 , the amount of D_2 extracted from the beam and converted to HD, as a function of azimuthal angle,

ϕ , normalized to the incident D_2 intensity. The angle of incidence is fixed at $\theta = 45^\circ$ for both curves.

Fig. 9 HD production on the Pt(553) (or Pt(S)-[5(111)x(111)]) as a function of angle of incidence, θ , of the molecular beam. The azimuthal angle, ϕ , is $\pm 90^\circ$, i.e., the step edges are perpendicular to the incident beam. These are the normalized data from two experiments at $T_s = 900^\circ\text{C}$ and $f = 2.5$ Hz.

Fig. 10 HD production on the Pt(553) (or Pt(S)-[5(111)x(111)]) as a function of azimuthal angle, ϕ , with the angle of incidence fixed at $\theta = 45^\circ$. a) Normalized data from several experiments at $T_s = 400 - 1100^\circ\text{C}$ and $f = 1.5 - 2.6$ Hz, measured in the integral mode. b) Normalized data from two experiments at $T_s = 900^\circ\text{C}$, $f = 100$ Hz and $T_s = 700^\circ\text{C}$, $f = 200$ Hz, measured in the differential mode.

Fig. 11 Comparison of experimental and calculated HD production as a function of angle of incidence, θ , on the Pt(332) (or Pt(S)-[6(111)x(111)]) surface. The azimuthal angle, ϕ , is $\pm 90^\circ$, i.e., the step edges are perpendicular to the incident beam. R is the ratio of the reaction probability per unit area of the step site to that of a terrace site at normal incidence.

Fig. 12 Comparison of experimental and calculated HD production as a function of azimuthal angle, ϕ , on Pt(332) (or Pt(S)-[6(111)x(111)]). The angle of incidence is fixed at $\theta = 45^\circ$. R is the ratio of the reaction probability per unit area of the step site to that of a terrace site at normal incidence.

-29-

MOLECULAR BEAM SURFACE SCATTERING APPARATUS

XBL 732-57448

Fig. 1

XBL 767-7183

Fig. 2

A

Pt(S) - [5(III) x (III)]
 $E_0 = 140 \text{ eV}$

B

Pt(S) - [6(III) x (III)]
 $E_0 = 67 \text{ eV}$

XBB 771-631

Fig. 3

Fig. 4

XBB 774-2692

XBL 771-4927

Fig. 5

XBL772-5102

Fig. 6

-35-

XBL772-5084A

Fig. 7

XBL773-5227

Fig. 8

XBL77I-4926

Fig. 9

XBL77I-4924

Fig. 10

XBL 773-5225

Fig. 11

XBL773-5226

Fig. 12

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