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MOLECULAR BEAM STUDY OF THE MECHANISM OF CATALYZED HYDROGEN-DEUTERIUM EXCHANGE ON PLATINUM SINGLE CRYSTAL SURFACES

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ABSTRACT

The hydrogen-deuterium exchange reaction was studied by molecular beam scattering on low and high Miller index crystal faces of platinum in the surface temperature range of 300–1300°K. Under the condition of the experiments which put strict limitation on the residence time of the detected molecules, the reaction product, HD, was readily detectable from the high Miller index, stepped surfaces (integrated reaction probability, defined as total desorbed HD flux divided by D2 flux, is $\sim 10^{-1}$) while HD formation was below the limit of detectability on the Pt(111) low Miller index surface (reaction probability $< 10^{-5}$). Atomic steps at the platinum surface must play a controlling role in dissociating the diatomic molecules. The exchange reaction is first-order in D2 beam pressure and half-order in H2 background pressure. This observation indicates that an atom–molecule reaction or possibly an atom–atom reaction is the rate-limiting step in the exchange. The absence of beam kinetic energy dependence of the rate indicates that the molecular adsorption does not require activation energy. The surface is able to store a
sufficiently large concentration of atoms which react with the molecules by a two branch mechanism. The rate constants for this two branch mechanism were determined under conditions of constant H atom coverage, reducing the bimolecular reaction to a pseudo first order reaction. At lower temperatures (<600 K) the rate constant for the exchange is 
\[ k_1 = (2 \pm 1) \times 10^5 \exp(-4.5 \pm 0.5 \text{ kcal/RT}) \text{ sec}^{-1}. \]

The rate determining step appears to be the diffusion of the D$_2$ molecule on the surface to a step site where HD is formed via a three-center (atom-molecule) reaction, or via a two-center (atom-atom) reaction subsequent to D$_2$ dissociation at the step. At higher temperatures (>600 K) the reaction between an adsorbed H atom and an incident D$_2$ gas molecule competes with the low temperature branch. The rate constant for this branch is 
\[ k_2 = (1 \pm 2) \times 10^2 \exp(-0.6 \pm 0.3 \text{ kcal/RT}) \text{ sec}^{-1}. \]

The catalyst action of the platinum surface for the exchange reaction is due to its ability to adsorb and dissociate hydrogen molecules with low activation energy and to store atomic hydrogen on the surface thereby converting the gas phase molecule-molecule reaction to an atom-molecule or atom-atom reaction of low activation energy.

**INTRODUCTION**

One of the fundamental questions of heterogeneous catalysis is how surfaces lower the activation energy for simple reactions on an atomic scale so that they proceed readily on the surface while the same reaction in the gas phase is improbable. The reaction of hydrogen and deuterium molecules to form hydrogen deuteride is one of these simple reactions which takes place readily on metal surfaces even at temperatures below 100°K. The same reaction is completely inhibited in the gas phase by the large dissociation energy of hydrogen or deuterium (~103 kcal/mole).
Once the $H_2$ molecule is dissociated the successive atom-molecule reaction

\[ (H + D_2 \rightarrow HD + D) \]

in the gas phase still has a potential energy barrier of roughly 10 kcal/mole.\(^2\)

We have studied the mechanism of the hydrogen-deuterium surface exchange reaction on platinum by a combination of techniques that are available in modern surface science. We have employed molecular beam scattering techniques to determine the angular distributions and obtain kinetic information about products and reactants. We have used platinum single crystal surfaces whose surface structures were characterized by low-energy electron diffraction (LEED) and whose surface chemical compositions were monitored by Auger electron spectroscopy (AES).

We have found that atomic steps on the platinum surfaces play an essential role in dissociating hydrogen or deuterium at the low pressures used in these experiments. Without the presence of large concentrations of atomic steps the probability for the exchange reaction to occur is very low. In the presence of these atomic steps the hydrogen molecules dissociate and then the surface is able to store a large concentration of atoms. These atoms then react with incident molecules by a two-branch mechanism. At low temperatures, the reaction has an activation energy of 4.5 kcal/mole and the rate limiting step appears to be the diffusion of the adsorbed molecule on the surface to a site where the hydrogen deuteride can be formed. At high temperatures, the reaction between an adsorbed atom and a gas molecule incident at an atomic step competes with the diffusion controlled low temperature branch.
EXPERIMENTAL

The experiments described in this study were carried out with an ultra-high vacuum molecular beam surface scattering apparatus which has been described previously. Several modifications to the original apparatus were necessary for the work reported here. These modifications to the original apparatus are discussed in detail in reference 4. Their purpose was to increase the signal to noise ratio of the original system and to allow kinetic studies of surface reactions by the modulated beam technique. Improvement in the signal to noise ratio was achieved by reducing the incident beam path, increasing the pumping speed in the scattering chamber, and shielding and modifying the quadrupole mass spectrometer detector. Either current measurement or ion counting techniques can be used for detection of signals due to reaction products. Current measurement using lock-in amplification was used in the experiments reported here. The apparatus was modified for use of the modulated beam technique by installation of a variable frequency chopper replacing the fixed frequency chopper of the original apparatus.

A schematic diagram of the modified apparatus is shown in Fig. 1. The system consists of (1) an ultra-high vacuum scattering chamber with LEED and AES capabilities, ion sputtering and gas introduction facilities, a rotatable quadrupole mass spectrometer used as a density sensitive detector, and a base pressure of $\sim 7 \times 10^{-10}$ torr achieved by ion pumping, cryopumping, and titanium gettering. (2) A molecular beam source chamber containing an oven fitted with a multichannel glass capillary source array. The properties of these sources have been discussed previously.
The source used in these experiments produces an equivalent pressure at the crystal surface in the range of $1 \times 10^{-7}$ torr, corresponding to an incident flux of roughly $10^{14}$ particles/cm$^2$sec. (3) A chopper chamber, containing a slotted disk rotated by a variable speed synchronous motor for modulating the incident beam. The range of modulation frequencies is from 20 to 2000 hz.

The installation of a variable frequency chopper is essential for the use of the modulated beam technique of studying surface reactions. This technique has been described extensively in the literature. It is essentially a modeling technique wherein the waveform of modulated reaction products leaving the surface is measured as a function of reaction variables such as surface temperature, modulation frequency, reactant concentrations, surface topography, and so forth. For first order reactions, i.e. when the rate of product formation depends only on the first power of the reactant beam pressure, the waveform information is contained in the first Fourier component of the scattered signal, or the phase and amplitude of the scattered signal. Examples of these model calculations utilizing the phase and amplitude of the scattered beam obtained as a function of modulation frequency and other reaction variables are given in the literature. Thus, if the surface reaction is first order, analysis of the kinetics of
the gas solid interaction can be determined directly from the measurement of the phase and amplitude of the scattered product signal as a function of the reaction variables. This is easily accomplished using a phase sensitive (lock-in) amplifier tuned to the modulation frequency. The measured phase shift is the difference between the phases of the scattered reactant and the surface reaction product as measured by the PAR model HR-8 lock in amplifier. This phase difference has an uncertainty ranging from ±2° at low modulation frequencies to ±4° at higher frequencies. The uncertainty is determined by the size of instrumental time corrections compared to the chopping time. Details of the method of phase shift measurements are given in the literature.\textsuperscript{5,8,9} The uncertainty in the signal amplitude is of the order of 2% for the strongest signals, ranging to roughly 10% for the weak signals at low temperatures, low pressures and high modulation frequencies. Figure 2 shows a schematic diagram of the signal processing electronics.

Three platinum single crystal surfaces were used in this study. They are designated by Miller indices as Pt(111), Pt(997), and Pt(553) surfaces. The (111) surface is the hexagonal close packed plane in which each atom has six nearest neighbors. The (997) and (553) surfaces are cut 6.5° and 12.2° respectively from the (111) plane in the (111) direction resulting in a surface characterized
by ordered monatomic height steps of (111) orientation. These steps are separated by terraces of (111) orientation on the average nine atoms wide in the (997) and five atoms wide in the (553). A more descriptive nomenclature designates the (997) surface as Pt(S)-[9(111)×(111)] and the (553) surface as Pt(S)-[5(111)×(111)]. Figure 3 shows the LEED patterns and real space schematic diagrams of these three surfaces.

Of course even the (111) surface is far from being perfectly smooth. It contains a large number of steps of atomic height as well as those of many atomic layers in height. This is unavoidable due to the finite dislocation density originally present in the platinum crystal (~$10^8$ dislocations/cm$^2$). However, the step density in the stepped surfaces is orders of magnitude higher than in the (111) crystal face, roughly 10% in the [9(111)×(111)] and 20% in the [5(111)×(111)] of all surface atoms being in the steps of monatomic height. In addition, the atomic environment around atoms in steps is uniform due to the well defined orientation, while in the (111) surface many different step orientations are present simultaneously.

All of the crystals were identically prepared by spark cutting from high purity bulk single crystal rods 6 mm in diameter (MRC) after being
oriented to \( \pm 0.5^\circ \) of the desired plane by X-ray diffraction. The surfaces were polished mechanically ending with 1\( \mu \) diamond paste, etched in hot 50\% \textit{aqua regia} and spot welded to high purity polycrystalline platinum supports. A Pt-Pt 10\% Rh thermocouple was spot welded to the back of the surface and the whole assembly etched once more and rinsed in distilled water and methanol. Two crystals could be mounted in the scattering chamber at one time, one above the other on a Varian crystal manipulator. This allowed comparative studies to be carried out under identical experimental conditions.

Once the crystals were in the scattering chamber, they were subjected to extensive heat treatments in oxygen and ion bombardment annealing cycles to prepare clean, well ordered surfaces. Oxygen and argon used for cleaning the surfaces and the hydrogen and deuterium used in the experimental studies were Matheson research grade purity. After cleaning, the surfaces were characterized by LEED and AES. Figure 4 shows the Auger spectrum of the clean surface. All of the experiments were performed on surfaces exhibiting the clean surface Auger spectrum of Fig. 4 and the LEED patterns of Fig. 3 which indicate the presence of well ordered atomic domains on the crystal surfaces.

The surfaces were also characterized by He scattering. This technique has been shown to be very sensitive to surface disorder and to the presence of adsorbed layers of impurities.\textsuperscript{14} The scattering distributions can be described by a specular intensity and FWHM of the specular peak. A comparison of these values for the three surfaces is given in Table I. The presence of steps increases the surface roughness as evidenced by
the decrease in specular intensity and increase in FWHM as the step density is increased.

The experiments were generally performed by scattering a deuterium beam from the platinum surface in an ambient hydrogen pressure of \( \sim 6 \times 10^{-7} \) torr. Background pressures are measured with a Varian nude ionization gauge. The uncertainty in the measured pressure arises from the normal uncertainties in ion gauge measurements, and is taken to be about 10\% of the measured value. The equivalent beam pressure is determined by flow calculations for the particular multichannel source used, in conjunction with source oven pressure measurements with a Wallace & Tiernan absolute pressure gauge. These pressure determinations should be good within a factor of two as far as absolute pressure is concerned. Relative pressure measurements are much more accurate, however, being limited only by the pressure measurement in the source oven and the linearity of the source. This uncertainty is estimated to be less than 5\%. A hydrogen beam with a deuterium ambient and a mixed hydrogen deuterium beam were also used. The results appeared to be independent of the method of reactant introduction. Separate introduction of the reactants was preferred because of difficulties in controlling the \( \text{H}_2/\text{D}_2 \) ratio in the mixed beam.

The surface reaction was studied in the surface temperature range 300\(^\circ\)K to \( \sim 1300\(^\circ\)K. Great care had to be taken at surface temperatures below 450\(^\circ\)K due to the possibility of adsorption of CO on the Pt surface from the scattering chamber background.

The mean velocity, or characteristic temperature of the incident beam was varied from 300\(^\circ\)K to \( \sim 600\(^\circ\)K by resistance heating of the source oven. Higher temperatures could not be attained because of the low melting point of the soft glass multichannel source.
All reaction products and scattered reactants were detected in the plane of the incident beam and the surface normal. No information is therefore available about product which may appear out of plane.
RESULTS

Figure 5 shows the amplitude of \( \text{H}_2 \), \( \text{D}_2 \) and \( \text{HD} \) versus the angle from the surface normal for the three surfaces. The amplitude at each angle is normalized to the incident beam flux determined by placing the detector in the molecular beam with the crystal surface raised above the beam line. In each case the scattering distributions are for a 300°K incident beam and a 1000°K surface. The modulation frequency is 400 hz. The \( \text{H}_2 \) and \( \text{D}_2 \) distributions are directed on all three surfaces. The (111) surface shows narrow, intense specular scattering for both \( \text{H}_2 \) and \( \text{D}_2 \). The \( \text{H}_2 \) distribution is definitely narrower and more intense than the \( \text{D}_2 \) distribution. This behavior has been attributed to rotational coupling between the surface and the incident \( \text{D}_2 \).\(^{15}\) The \([9(111)\times(111)]\) surface shows a broader, less intense directed distribution, and \( \text{H}_2 \) and \( \text{D}_2 \) angular distributions from this surface are very similar. The \([5(111)\times(111)]\) exhibits the broadest, least specularly intense scattering distribution. Again the \( \text{H}_2 \) and \( \text{D}_2 \) angular distributions are very similar. If we assume that the molecules appearing at the specular position are the only ones scattered elastically, these results indicate more efficient energy transfer between the incident gas and the stepped surfaces than with the (111) crystal face. The specular intensity and FWHM for these distributions are summarized in Table 2.

Figure 5 also shows the amplitude of \( \text{HD} \) versus the angle from the surface normal. No \( \text{HD} \) was detected desorbing from the Pt(111) surface under experimental conditions which resulted in approximately 5% and 10% of the incident \( \text{D}_2 \) beam being converted to \( \text{HD} \) on the \([9(111)\times(111)]\) and
[5(111)×(111)] surfaces respectively. The experiments reported here were performed using a modulated D\textsubscript{2} beam with H\textsubscript{2} approximately equal to the D\textsubscript{2} equivalent pressure in the ambient of the scattering chamber. For the stepped surfaces, which produced detectable amounts of HD, the amplitude of HD decreased as the cosine of the angle from the surface normal. This cosine distribution indicates complete thermal equilibration of the reaction product molecules with the surface before desorption.

Measurements of the normalized HD signal amplitude (HD signal at the specular angle (θ=45°) normalized to the incident D\textsubscript{2} signal) at identical experimental conditions for the three surfaces, gave the results shown in Table 3. Integrated reaction probability values, obtained by integrating over the HD angular distribution, assuming a symmetric out of plane cosine distribution, and dividing this value by the incident D\textsubscript{2} signal gives the values listed in the third column of Table 3. The experimental conditions used for this comparison are $T\textsubscript{s} = 1000\,^\circ\text{K}$, $T\textsubscript{b} = 300\,^\circ\text{K}$, modulation frequency = 400 hz, $P\textsubscript{D\textsubscript{2}} = 8\times10^{-8}\ \text{torr} = P\textsubscript{D\textsubscript{2}}$. These reaction probability values indicate quantitatively the effect of the step density on the production of HD.

The pressure dependence of the H\textsubscript{2}-D\textsubscript{2} reaction was investigated by holding the H\textsubscript{2} background pressure constant and varying the incident D\textsubscript{2} beam pressure and conversely holding the D\textsubscript{2} beam pressure constant and varying the H\textsubscript{2} background pressure. The results of these experiments are shown in Figs. 6 and 7. These figures indicate that the reaction is 1st order in the incident D\textsubscript{2} flux or equivalent beam pressure up to pressures near that of the fixed background H\textsubscript{2} pressure. The HD signal
then levels off and the reaction becomes zero order. The observation of a first-order dependence on the beam pressure allows the use of phase and amplitude data for the mechanistic description of the reaction as mentioned above. The reaction is half-order in background H\textsubscript{2} pressure, indicating first-order dependence on the concentration of H atoms on the surface. This implies an atom-molecule reaction or possibly an atom-atom reaction in the rate limiting step. Kinetic rate determination experiments were performed with \( P_{H_2} \sim 10 P_{D_2} \), on the zero order part of the \( P_{H_2} \) dependence curve. This gives a constant coverage of H atoms as evidenced by the coincidence of low and high T\textsubscript{s} points on Fig. 6. This is essential to the further analysis which assumes a constant H atom coverage.

The production of HD as a function of the incident beam kinetic energy was also investigated. By heating the source oven in the temperature range 300°-600°K, a near Maxwellian beam of particles at characteristic temperature greater than room temperature could be produced. The velocity distribution of the multichannel source used in this work has been previously studied.16 This beam energy dependence was measured on the low step density stepped surface, [9(111)×(111)], at 1000°K surface temperature and on the high step density surface, [5(111)×(111)] at 1250°K. In both cases, the HD amplitude and phase were unaffected over this temperature range indicating the absence of an activation energy for the adsorption of the molecules. Figure 8 shows the results of these experiments.

The HD amplitude at \( \theta=45 \) normalized to the incident D\textsubscript{2} signal is plotted as a function of the reciprocal surface temperature for the two stepped surfaces in Fig. 9. There are two temperature regimes that can be distinguished. From 300-600°K, the amplitude increases rapidly following the same T-dependence for both surfaces. Above 600°K, the increase becomes less rapid for both surfaces and starts to level off.
The amplitude of the higher step density surface, however, levels off at a higher value, roughly twice that of the [9(111)x(111)] surface.

The surface temperature dependence of the phase shift for the two surfaces, shown in Fig. 10, exhibits similar behavior. From 300-600°K, the phase shift decreases rapidly, data from both surfaces falling on the same line. Above 600°K, the phase shift of HD formed at the [9(111)x(111)] surface goes through a minimum and then increases. The phase shift of the HD formed at the [5(111)x(111)] surface goes to a slightly lower minimum and does not increase as much. Since the phase shift is proportional to the residence time of the HD molecules on the surface, a decrease in phase shift with increasing surface temperature is certainly expected. The reversal in this behavior at high temperature indicates the onset of a new mechanism for the formation of HD not present at low temperature.

Using either the phase or the amplitude data in the low temperature region, an activation energy for the process occurring can be calculated. With either of the data sets used, (phase or amplitude vs. \(1/T_s\)) this activation energy is calculated to be 4.5 kcal/mole.

The activation energy in the high temperature region (>600°K) is calculated to be 0.6 kcal/mole. Figures 9 and 10 are obtained with a modulation frequency of 40 hz. Increasing the modulation frequency to 160 and 400 hz gives the same two branch behavior, except that the transition temperature is shifted to higher values as the chopping frequency is increased. The activation energies remain the same. This observation indicates that the reaction that dominates at low temperatures.
occurs with a faster rate than the reaction that dominates at high temperatures.

The modulation frequency dependence of the phase and amplitude are shown in Fig. 12 and Fig. 13 for two surface temperatures, 1000°K and 485°K. The low temperature phase shift increases monotonically with increasing frequency, while the amplitude decreases with unit slope. Calculation of an activation energy from the 485°K frequency data using Eqs. 1-3 below agrees favorably with the activation energy calculated from the surface temperature data in the low temperature range.

\[ (1) \quad \varepsilon = \text{amplitude} = \frac{\eta}{\sqrt{1 + (\omega/k_1)^2}} \]

\[ (2) \quad \Delta \phi = \text{phasshift} = \tan^{-1}(\omega/k_1)^2 \]

\[ (3) \quad k_1 = A_1 \exp(-E_1/RT) \]

where \( \eta \) is the sticking coefficient, determined by extrapolation of \( \varepsilon \) versus modulation frequency data to zero frequency to be \( \sim 3 \times 10^{-1} \). \( \omega \) is the angular modulation frequency equal to \( 2\pi f (f \text{ in hz}) \), and the rate constant \( k_1 \) is written in Arrhenius fashion with pre-exponential \( A_1 \) and activation energy \( E_1 \). Both \( k_1 \) and \( k_2 \) (discussed below) are pseudo first order rate constants.

For first order reaction the signal amplitude, \([HD]/[D_2]\), is related to the rate constant by Eqs. (1) and (2). By holding the background \( \text{H}_2 \) pressure constant in the range of zero order \( P_{\text{H}_2} \) dependence the exchange reaction becomes pseudo-first order. Thus the units of \( k \) are \( \text{sec}^{-1} \) as indicated by Eq. (1) and Eq. (2).

*Integrated over all angles.
The high temperature behavior is more complex. The frequency dependence of the phase appears to be S-shaped and the amplitude decreases with a slope of $1/4$ as the frequency increases.

The very low HD production rate on the (111) surface (at about the limit of detection at $f=400$ hz), can be increased by increasing the reactant pressures and decreasing the modulation frequency. Increasing the reactant pressures by a factor of 10 and decreasing the modulation frequency a factor of 10 increases the HD reaction probability about a factor of thirty on the (111) surface. The same changes with either of the stepped surfaces increases the already much higher reaction probability about a factor of six.
DISCUSSION

Any chemical interpretation of the data presented in the previous section must be consistent with the conclusions this data suggests. These conclusions are:

1) The low index Pt(111) surface did not produce a significant amount of HD in our molecular beam scattering experiment in the frequency, pressure, and temperature range studied.

2) The stepped platinum surfaces produced large amounts of HD under conditions which showed little HD formation on the (111) surface.

3) Angular distributions indicate greater energy accommodation on higher step density surfaces, and that HD product is in thermal equilibrium with the surface before re-emission, with residence times in the range of milliseconds.

4) Temperature dependence of both amplitude and phase indicate two reaction regimes. At constant \( H_2 \) pressure of \( 6 \times 10^{-7} \) torr in the background, the pseudo first order rate constants for the exchange reaction have been determined. They are at low temperature (<600°K), \( k_1 = (2 \pm 1) \times 10^5 \exp(-4.5 \pm 0.5 \text{ kcal/RT}) \text{ sec}^{-1} \) and at high temperature (>600°K), \( k_2 = (1 \pm 2) \times 10^2 \exp(-0.6 \pm 0.3 \text{ kcal/RT}) \text{ sec}^{-1} \).

5) In the high temperature region, the surface step density increases the rate of production of HD proportionately while in the low temperature region, the step density does not have as great an effect.

6) Beam temperature dependence measurements indicate that the molecular adsorption is not an activated process.

7) The reaction is first order in \( D_2 \) beam pressure and one-half order in \( H_2 \) background pressure.

8) Frequency dependence measurements of the amplitude and phase have a simple monotonic dependence in the low temperature region, and more complex behavior in the high temperature region.
9) Increasing reactant pressure and decreasing chopping frequency increase HD production on the (111) surface much faster than on the stepped platinum surfaces.

The $H_2 - D_2$ exchange studies are carried out in the presence of excess hydrogen in the scattering chamber. Since the $H_2$ pressure is about an order of magnitude greater than the pressure calculable from the $D_2$ flux to the surface, the hydrogen atom concentration on the platinum surface remains constant during the exchange reaction. By varying the hydrogen pressure in the chamber in the range $5 \times 10^{-8} - 7 \times 10^{-7}$ torr we have found the rates of HD formation and the observed rate constants are independent of $H_2$ pressure. Also, the activation energies in both the high and low temperature region were independent of $H_2$ pressure in the studied pressure range. It appears that the hydrogen atom coverage of the active sites (most likely of the step sites) is unity or near unity in the studied temperature range. Thus, by carrying out the reaction this way, we have converted the bimolecular reaction to a pseudo first order reaction with the incident $D_2$ flux as the only concentration variable.

The surface temperature data and particularly the phase shift behavior as a function of modulation frequency at high surface temperature suggest a branched model. An expression for the product amplitude and phase shift as a function of surface temperature and modulation frequency can be derived as with Eqs. (1) and (2). \[ \epsilon e^{-i\Delta\phi} = \frac{ne^{-i\tan^{-1}(\omega/k_1)}}{\sqrt{1 + (\omega/k_1)^2}} + \frac{ne^{-i\tan^{-1}(\omega/k_2)}}{\sqrt{1 + (\omega/k_2)^2}} \]
with the terms defined as before for Eqs. (1-3). Using the low temperature activation energy and pre-exponential factor (determined from Eqs. (1 & 2) and the low temperature range \( T_s \) data) along with the measured activation energy for the high temperature branch, Eq. (4) can be solved to determine a rough value for the preexponential of the rate constant \( k_2 \). Using these four parameters to evaluate the two rate constants in Eq. (4) we can reproduce the behavior of the reaction product phase and amplitude over the temperature and frequency ranges studied. Broken lines on Figs. 9-12 indicate the predicted phase and amplitude behavior using these experimental values and Eq. (4). The good agreement lends support to the choice of a branched reaction model to describe the data.

Let us now discuss the two branches separately by considering first the low temperature (300-600K) reaction behavior and then the high temperature (600-1300K) behavior. In the low temperature region we find that the presence of atomic steps on the platinum surface is necessary for efficient production of HD, as the reaction probability is much lower on the low index (111) surface. The first-order beam pressure dependence indicates that molecular deuterium is involved in the rate limiting step if we assume equilibrium between the adsorbed and gas phase \( \text{D}_2 \) molecules. Possibilities for this rate determining step are diffusion of the molecule to the active step site, or perhaps dissociation of the molecule at this site. The half-order pressure dependence on the hydrogen background pressure indicates the involvement of \( \text{H} \) atom in the rate determining step. In the low temperature range the concentration
of atomic H on the surface should be quite high, most of it bound at the monatomic step sites. Supporting evidence for the assumption of atomic H being bound at the steps is given in an interesting study of hydrogen adsorption on Pd surfaces by Conrad, Ertl and Latta. They found that the isosteric heat of hydrogen adsorption on Pd-(S)-[9(111)×(111)] was about 3 kcal/mole higher at low coverages than on Pd(111).

This information in the low temperature region suggests the following mechanism for the exchange reaction. Molecular $D_2$, weakly adsorbed on the terrace, diffuses to step sites where strongly bound atomic hydrogen is present. It there undergoes a three-center atom-molecule reaction to form HD which is subsequently desorbed and detected. We cannot rule out the possibility of a two-center, or atom-atom reaction, taking place to form HD after dissociation of the $D_2$ at the step. The fact that the step density does not affect the reaction probability as drastically in the low temperature region argues for the diffusion, atom-molecule reaction step being rate limiting, since dissociation, followed by atom-atom reaction should be directly proportional to the step concentration, while diffusion rate would only be affected by the shortening of the mean diffusion path length on step density increase. The values of the activation energy and pre-exponential factor also support the choice of molecular diffusion and a three-center reaction as the rate limiting step. A study of $H_2$ electron impact desorption from tungsten by Menzel resulted in the observation of a very low pre-exponential. This was postulated to be due to a curve crossing in the transition state.
Suhl\textsuperscript{20} has connected the low pre-exponential to the existence of a transition state involving coupling between a tightly bound (H atom in this case) and weakly bound (D$_2$ molecule) species. The reaction in the low temperature region, involving two adsorbed species is commonly termed the Langmuir-Hinshelwood\textsuperscript{21} mechanism.

The reported rates of HD formation are referenced to the incident D$_2$ flux at a given hydrogen pressure (or constant H atom coverage). Thus, the rate constants that were determined are affected by the various reaction steps the D$_2$ gas molecule participates in prior to the proposed rate determining atom-molecule reaction. In the low temperature region, adsorption of D$_2$(gas) and subsequent diffusion to a reaction site is likely to precede the surface reaction. The activation energy may be modified by these reaction steps. The observed 4.5 kcal activation energy may well be smaller than the true activation energy for the surface reaction, being reduced due to the contribution from the exothermic heat of adsorption of molecular D$_2$ (about 2 kcal/mole)\textsuperscript{34}. The preexponential factor may include terms such as the density of active sites and the coverage of hydrogen atoms in addition to the probability factor and the partition function ratio. The estimation of the magnitudes of these various parameters is uncertain and is dependent on our chosen reaction model. Thus we refrain at present from direct comparison of either the activation energies or the pre-exponential terms we have determined for the surface reaction with the rate parameters of the bimolecular gas phase reaction.
In the high temperature region, again the steps are necessary for efficient production of HD. The pressure dependence is the same as in the low temperature region, indicating an atom-molecule reaction as the rate limiting step. In this region, however, the step density directly affects the production of HD. Since the surface concentration of adsorbed \( D_2 \) molecules must be much lower at these temperatures, the reaction probability of the fast Langmuir-Hinshelwood reaction between the adsorbed species must be markedly reduced. The much lower activation energy that characterizes the reaction in this region indicates the onset of a reaction mechanism where incident \( D_2 \) molecules react directly from the gas phase with hydrogen atoms at the steps. Similarly in this region, the preexponential includes terms involving the density of active sites and reactant coverage as well as the bimolecular collision frequency. This precludes a direct comparison of these values with similar gas phase values at this time.
This mechanism is not dominant at lower temperatures (300-600°K) because of the abundance of molecular deuterium available on the surface. Due to the experimental condition of large H₂ background pressure, the H atoms, strongly bound at the steps, remain available at sufficiently large concentration over the entire temperature range, while the weakly bound molecules have markedly reduced residence times as the temperature is increased. Because of this circumstance the rate of the slow direct reaction with the low preexponential becomes dominant at high temperatures (>600°K). This reaction of a gas phase species with an adsorbed species is commonly termed the Eley-Rideal mechanism.

The two-branch mechanism with the proposed models for the high temperature and low temperature branches is shown below.

The broken arrow indicates the possible path resulting in an atom-atom reaction in the low temperature region.
The two branch model can also give information about the expected behavior of the exchange reaction at even lower surface temperatures. As we extend the surface temperature below 300K, the low activation energy Eley-Rideal process would be expected to again become dominant. Calculations of $k_1$ and $k_2$ and the phase and amplitude at lower temperatures using Eq. (4) indicate a transition back to low activation energy reaction at around 260K where $k_1$ and $k_2$ are approximately equal. Below this temperature $k_1$ becomes insignificant and the low activation energy $k_2$ branch again dominates. This behavior is shown in Fig. 13 where the amplitude vs. $1/T_S$ dependence is shown calculated from Eq. (4).

Kuikers et al. and Breakspeare et al. have observed the $H_2$-$N_2$ exchange at low temperatures (<300K) and report a transition from low activation energy to higher activation energy with increasing surface temperature on Pt films and Pt wires, as predicted by our extension of Eq. (4) to lower temperatures.

The low activation energy Eley-Rideal mechanism becomes predominant for the $H_2$-$D_2$ exchange at high (>600°K) and at very low (<250°K) temperatures, for different reasons. At high temperature, the rate of the competing Langmuir-Hinshelwood reaction ($H_{ads} + D_{2ads} \rightarrow H_D_{ads}$) is attenuated by the very short residence time of adsorbed $D_2$ molecules which reduces their surface concentration. At very low temperatures, although both adsorbed molecules and adsorbed atoms should be available in large concentration, the reaction that would have a higher probability is the one with the lower activation energy.

The observation of a very slow reaction step (characteristic time $> 10^{-2}$ sec) in this system lead us to investigate the possibility of
a very slow reaction step limiting the formation of HD on the (111) surface. Extending measurements to the lowest practical chopping frequency of 40 hz increased the integrated reaction probability on the (111) surface to about $8 \times 10^{-4}$. This is still over two orders of magnitude less than the reaction probability on the stepped surfaces under identical conditions, but is a significant increase. If the chopping frequency could be reduced even further, it is conceivable that the HD reaction probability on the (111) surface could be comparable to that observed on the stepped surface. As the chopping frequency is reduced, the reaction of molecules that need more time to diffuse to the active step sites which are present on even the most carefully prepared low index surface are also detectable, possibly making the stepped surface and low index surface behavior more similar. Also, at higher pressures the increase in surface concentration of H atoms increases the probability of an atom-molecule reaction to occur away from the step sites.

It is worthwhile to compare the results and model discussed here with work on this system done by other methods and workers. The angular distributions of H$_2$ and D$_2$ from Pt(111) are identical to those reported by Merrill$^{24}$ on similarly prepared surfaces. On the other hand, the HD angular distributions are much different than those obtained by Palmer, et al.$^{25}$ in their molecular beam study of the reaction on epitaxial Pt surfaces. There is some indication$^{26}$ that angular distributions sharply peaked at the normal, such as those observed by Palmer et al., could be related to carbon or sulfur contamination on platinum surfaces.
Weisendanger\textsuperscript{27} measures a sticking probability of $H_2$ on polycrystalline platinum of $1 \times 10^{-3}$. Lewis and Gomer\textsuperscript{18} assign adsorption energies to two states of adsorbed hydrogen of $<15$ kcal/mole for a molecular state and 16 kcal/mole for an atomic state. They also measure an activation energy for diffusion of hydrogen atoms on a platinum field emitter tip of 4.5 kcal/mole. The agreement between the measured activation energy in this work and that measured by Lewis and Gomer\textsuperscript{18} could indicate that the diffusing species is the same in each case. It was indicated above that we cannot rule out the possibility of an atomic diffusion step as the precursor for the atom-atom reaction ($H_{\text{ads}} + D_{\text{ads}} \rightarrow \text{HD}_{\text{ads}}$) that can occur in addition to the atom molecule reaction. The relative importance of the atom-atom or atom-molecule reactions, depends on the rate of dissociation of $D_2$ upon single scattering. At present we cannot distinguish between HD molecules produced by these two possible reactions. Merrill\textsuperscript{28} has postulated the existence of two molecular ad states with binding energies of 2 kcal/mole and 17 kcal/mole. Norton and Richards\textsuperscript{29} have performed a careful flash desorption study of the $H_2$-$D_2$ exchange on polycrystalline platinum. They see evidence for a precursor ad state, measure a first-order reactant pressure dependence at $870^\circ$K, a sticking coefficient of $<.01$, and an absolute reaction rate of $4 \times 10^{-1}$/sec at a coverage of 0.5 and surface temperature of 244$^\circ$K.

A very recent flash desorption study of the $H_2$-$D_2$ exchange has been performed by Rye and Lu.\textsuperscript{30} Their work compared a series of four platinum single crystals for reactivity to $H_2$-$D_2$ exchange. They found only a factor of five difference in reactivity between the (111) surface (low reactivity) and the (211) surface (high reactivity). The (211) surface is the [3(111)$\times$(100)] stepped surface. Their reaction probability is of the same order of magnitude ($\sim 10^{-1}$) as ours for the stepped surfaces, but much
higher for the Pt(111) crystal face. We believe that the differing results of these two studies (Rye's and the present work) are the results of differing experimental techniques. The flash desorption technique gives no time dependent information about the initial adsorption and diffusion of molecules on the surface. Indeed, given the infinite residence time of adsorbates in such a flash desorption experiment, diffusion to active sites for dissociation could not possibly be rate-limiting. In the molecular beam system, however, the modulation of the incident beam enables one to probe processes, such as diffusion, taking place on a much shorter time scale.

Using the values of activation energy (4.5 kcal/mole) and preexponential (1x10⁵) sec⁻¹ determined for the rate limiting step in the low temperature region, one can calculate the diffusion times involved. These calculations give times of 2x10⁻¹ sec at 300°K and 5x10⁻³ sec at 600°K. Assuming a root mean square diffusion distance on the [9(111)×(111)] surface for instance to be one-half the terrace width, or 6.5x10⁻⁸ cm, yields a diffusion velocity of ~1x10⁻⁵ cm/sec on the stepped surfaces. The stepped surfaces have a monatomic height step density of roughly 10¹⁴/cm² on the surface. If we assume that the density of monatomic steps on the (111) surface is comparable to the dislocation density (~10⁸/cm²), then the rms diffusion distance to an active site on this surface would be roughly 10⁻⁴ cm. Even at the very low diffusion velocity measured in this work, this distance corresponds to a diffusion time of 1-10 sec, which could not be resolved in the flash desorption experiment. Therefore, under these conditions, the stepped and low-index surfaces would be expected to behave similarly.
Table IV lists pre-exponentials and activation energies for several surface reactions. Low pre-exponential values have been observed by Olander et al.\textsuperscript{31} in their studies of graphite oxidation and by Madix and Schwarz\textsuperscript{32} in a study of molecular chlorine interactions with germanium and silicon. In both cases, the low pre-exponential value was ascribed to a surface migration step. Tables of pre-exponentials for gas phase unimolecular reactions\textsuperscript{33} often indicate pre-exponentials in the $10^2$ to $10^8$ range. In each case, the low pre-exponentials are ascribed to reactions occurring on vessel walls or in the presence of a heterogeneous catalyst. As mentioned previously, the work of Menzel\textsuperscript{19} and Suhl\textsuperscript{20} has also dealt with the significance of the low pre-exponential in surface chemical reactions.

Table IV.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A$ (sec\textsuperscript{-1})</th>
<th>$E_a$ (kcal/mole)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cl}_2 + \text{Ge}$</td>
<td>$9 \times 10^6$</td>
<td>22.6</td>
<td>32</td>
</tr>
<tr>
<td>$\text{Cl}_2 + \text{Si}$</td>
<td>$3 \times 10^7$</td>
<td>33</td>
<td>32</td>
</tr>
<tr>
<td>$\text{O}_2 + \text{Graphite}$</td>
<td>$2.5 \times 10^7$</td>
<td>30</td>
<td>31</td>
</tr>
<tr>
<td>$\text{D}_2 + \text{H}(\text{low T}_s)$</td>
<td>$2 \times 10^5$</td>
<td>4.5</td>
<td>this work</td>
</tr>
<tr>
<td>$\text{D}_2 + \text{H}(\text{high T}_s)$</td>
<td>$1 \times 10^2$</td>
<td>0.6</td>
<td>this work</td>
</tr>
<tr>
<td>$\text{HCOF}$ decomposition</td>
<td>$2 \times 10^2$</td>
<td>10.0</td>
<td>33</td>
</tr>
<tr>
<td>$\text{HCOOH}$ decomposition</td>
<td>$6.2 \times 10^4$</td>
<td>30.6</td>
<td>33</td>
</tr>
<tr>
<td>$\text{Ni(CO)}_4$ decomposition</td>
<td>$3 \times 10^9$</td>
<td>19.1</td>
<td>33</td>
</tr>
<tr>
<td>$1,2$ dichloroethene isomerization</td>
<td>$2 \times 10^2$</td>
<td>16.0</td>
<td>33</td>
</tr>
</tbody>
</table>
CONCLUSION

The purpose of the present study has been to investigate the primary reaction steps involved in hydrogen dissociation on platinum by a molecular beam study of hydrogen-deuterium exchange. The reaction appears to follow a two-branch mechanism on surfaces containing step sites active for $\text{H}_2$ dissociation. One branch, dominant at low temperatures, results from the reaction of H atoms that are stored on the surface in sufficiently large concentration with molecular $\text{D}_2$ arriving at the step sites by diffusion from weakly bound precursor states on the (111) terraces. The second branch appears to be fed by direct reaction of adsorbed H atoms with arriving $\text{D}_2$ molecules in the vicinity of the steps from the incident gas beam. Extension of the model to temperatures below 300°K predicts a return to the low activation energy Eley-Rideal branch as the dominant mechanism for the $\text{H}_2$-$\text{D}_2$ exchange.

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REFERENCES


30. K. E. Lu and R. R. Rye, to be published.
TABLE I
SPECULAR INTENSITIES AND FWHM FOR He SCATTERING

<table>
<thead>
<tr>
<th>Surface</th>
<th>Specular Intensity (%)</th>
<th>FWHM (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(111)</td>
<td>10.9</td>
<td>6</td>
</tr>
<tr>
<td>Pt-(S)-[9(111)×(111)]</td>
<td>1.85</td>
<td>15</td>
</tr>
<tr>
<td>Pt-(S)-[5(111)×(111)]</td>
<td>0.96</td>
<td>25</td>
</tr>
</tbody>
</table>

$T_s = 800^\circ K$, $T_B = 300^\circ K$
### TABLE II

**SPECULAR INTENSITIES AND FWHM FOR H₂, D₂ SCATTERING**

<table>
<thead>
<tr>
<th>Surface</th>
<th>H₂</th>
<th>D₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Int.(%)</td>
<td>FWHM(deg.)</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>1.68</td>
<td>18</td>
</tr>
<tr>
<td>Pt-(S)-[9(111)×(111)]</td>
<td>0.65</td>
<td>48</td>
</tr>
<tr>
<td>Pt-(S)-[5(111)×(111)]</td>
<td>0.33</td>
<td>61</td>
</tr>
</tbody>
</table>

\(T_s = 1000\degree K, \quad T_B = 300\degree K\)
TABLE III
REACTION PROBABILITIES FOR HD PRODUCTION

\[ T_s = 1000^\circ K, \quad T_B = 300^\circ K, \quad f = 400 \text{ hz}, \quad P_{H_2} = 8 \times 10^{-8}, \quad P_{D_2} = 8 \times 10^{-8} \]

<table>
<thead>
<tr>
<th>Surface</th>
<th>Probability Amplitude</th>
<th>+ Int. Reaction Prob.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(111)</td>
<td>(&lt;1 \times 10^{-6})</td>
<td>&lt;1 \times 10^{-5}</td>
</tr>
<tr>
<td>Pt-(S)-[9(111)\times(111)]</td>
<td>4.9 \times 10^{-4}</td>
<td>1.6 \times 10^{-2}</td>
</tr>
<tr>
<td>Pt-(S)-[5(111)\times(111)]</td>
<td>9.2 \times 10^{-4}</td>
<td>9.9 \times 10^{-2}</td>
</tr>
</tbody>
</table>

+ HD signal integrated over total cosine distribution divided by incident \(D_2\) signal.
FIGURE CAPTIONS

Fig. 1. Schematic diagram of ultra-high vacuum molecular beam scattering apparatus.

Fig. 2. Schematic diagram of signal processing electronics. The first Fourier component of the scattered signal is given by the signal amplitude $S$ and the phase shift $\phi$.

Fig. 3. LEED patterns and schematic diagrams of the platinum surfaces studied in this work. (a) Pt(111), (b) Pt(997) or Pt(S)-[9(111)$\times$(111)], (c) Pt(553) or Pt(S)-[5(111)$\times$(111)].

Fig. 4. Auger spectrum of the clean platinum surfaces.

Fig. 5. Angular distribution of hydrogen, deuterium, and hydrogen deuteride for the three surfaces. (a) Pt(111), (b) Pt(S)-[9(111)$\times$(111)], (c) Pt(S)-[5(111)$\times$(111)].

Fig. 6. Production of HD versus H$_2$ pressure at surface for fixed D$_2$ pressure of $2\times10^{-7}$ torr.

Fig. 7. Production of HD versus D$_2$ pressure at surface for fixed H$_2$ pressure of $6\times10^{-7}$ torr.

Fig. 8. Phase and amplitude of HD signal versus incident beam temperature ($\bullet$=$T_s=1000^\circ$K on Pt(S)-[9(111)$\times$(111)]; $\circ$=$T_s=1250^\circ$K on Pt(S)-[5(111)$\times$(111)].

Fig. 9. HD amplitude vs. $1/T_s$ for both stepped surfaces. $f=40$ hz. Broken line from eqn. (4).

Fig. 10. HD phase shift vs. $1/T_s$ for both stepped surfaces. $f=40$ hz. Broken line from eqn. (4).
Figure Captions, contd.

Fig. 11. Phase of HD signal versus modulation frequency for
   (a) $T_s = 1000^\circ K$ and (b) $T_s = 485^\circ K$. Broken line from eqn. (4).

Fig. 12. Amplitude of HD signal versus modulation frequency for
   (a) $T_s = 1000^\circ K$ and (b) $T_s = 485^\circ K$. Broken line from eqn. (4).

Fig. 13. Amplitude vs. $1/T_s$ calculated from eqn. (4) over temperature range 50-1300$^\circ K$. 
p(bkg) \cong 5 \times 10^{-10} \text{torr}

p(\text{at crystal}) \cong 1.1 \times 10^{-8} \text{torr}

MOLECULAR BEAM SURFACE SCATTERING APPARATUS

Fig. 1
Narrow Band Amplifier at $f_0$ → Synchronous Mixer → RC Integrator → Signal Output, $S$

Reference Signal, $f_0$ → Phase Shifter, $\phi$ → Signal, $f_0$
Fig. 4

(d^2I/dV^2)

Electron Energy (eV)

XBL 719-7306A
Fig. 5
Fig. 6

\[ \frac{\text{HD}}{\text{D}_2} \text{ (arb. units)} \]

\[ T_s = 1000^\circ \text{K} \]

\[ T_s = 485^\circ \text{K} \]

Slope = 0.5

\[ \text{D}_2 \text{ Pressure} \]

\[ \text{H}_2 \text{ Pressure at Surface (torr)} \]
Fig. 7

HD/D₂ (arb. units)

D₂ Pressure at Surface (torr)

H₂ Pressure

Slope = 1.0

\( T_s = 1000 \, ^\circ \text{K} \)

\( T_s = 485 \, ^\circ \text{K} \)
Fig. 8
Fig. 9
Fig. 10
HD/D₂ vs f

H₂-P₂/Pt (997)

Tₛ = 1000°K

f (Hz)
AMPLITUDE vs. f

$T_0 = 485 \, ^\circ K$

$\left( \frac{HD}{D_2} \right) \times 100$

$H(D_2)$

$10^1$  $10^2$  $10^3$  $10^4$

$(H(D_2)) \times 100$

$10^1$  $10^2$  $10^3$  $10^4$

Fig. 12b
Fig. 13
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