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REACTIVE AND NONREACTIVE SCATTERING OF MODULATED MOLECULAR BEAMS FROM WELL CHARACTERIZED PLATINUM SINGLE CRYSTAL SURFACES

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Reactive and Nonreactive Scattering of Modulated Molecular Beams from well Characterized Platinum Single Crystal Surfaces

By

Rebecca Johnson Gale

ABSTRACT

Reactive and nonreactive gas-surface interactions have been studied by modulated molecular beam mass spectrometry on Pt(111) and stepped Pt(111) surfaces under ultrahigh vacuum conditions. The three platinum single crystal surfaces used in this investigation, Pt(111), Pt(553) or \text{Pt(S)}-[5\text{(111)}\times\text{(111)}], and Pt(332) or \text{Pt(S)}-[6\text{(111)}\times\text{(111)}], were characterized as to structure by low energy electron diffraction (LEED) and as to composition by Auger electron spectroscopy (AES).

The angular distribution of helium atoms scattered from the stepped Pt(553) surface was measured as a function of the angle of incidence (polar, $\theta$, and azimuthal, $\phi$). Rainbow scattering was observed when the helium atoms were incident perpendicular to the step edges, with the open side of the step structure directed away from the incoming beam, indicating that the ordered array of steps and terraces exhibits a strongly periodic surface potential.
In contrast, from the Pt(lll) surface, the angular distribution of scattered helium atoms exhibits a sharp peak at the specular angle, characteristic of a smooth and well ordered surface.

The interaction of hydrogen with platinum was investigated by studying the H$_2$-D$_2$ exchange reaction on the Pt(lll) and the two stepped surfaces, Pt(553) and Pt(332). The production of HD was monitored as a function of the angle of incidence (polar, $\theta$, and azimuthal, $\phi$) of the beam of reactants. A marked dependence on the direction of approach of the reactants was observed. On the stepped surfaces, the apparent reaction probability 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. HD production on the Pt(lll) surface increases from glancing incidence, $\theta = \pm 60^\circ$, to a maximum a normal incidence, by approximately a factor of two. The angular dependence of the apparent reaction probability on the stepped surfaces is intimately related to surface geometry and cannot be attributed to an activation energy barrier for adsorption, whereas that observed on the Pt(lll) surface can be explained by the presence of an activation energy of $\approx 0.5$ kcal/mole.

The mechanism of the H$_2$-D$_2$ exchange reaction was investigated on the Pt(lll) and stepped Pt(332) surfaces. The dependence of the apparent reaction probability on surface temperature also indicates that the adsorption of
hydrogen is an activated process on the Pt(111) surface, but not on the stepped Pt(332) surface. The energy barrier for hydrogen adsorption on Pt(111) deduced from this type of experiment is \( \sim 1.5 \) kcal/mole. On both surfaces, the mechanism of the recombination of adsorbed H and D atoms to form HD consists of a branched process at high crystal temperatures, with one of the branches connected in series with another reaction step at low temperatures. The process that is operative over the entire temperature range studied, 25 - 800°C, has an activation energy and an apparent pre-exponential factor of \( E_1 = 13.0 \pm 0.4 \) kcal/mole and \( A_1 = (8 \pm 3) \times 10^4 \) sec\(^{-1}\) for the Pt(332) surface and \( E_1 = 15.6 \pm 0.5 \) kcal/mole and \( A_1 = (2.7 \pm 1) \times 10^5 \) sec\(^{-1}\) for the Pt(111) surface. The values of the pre-exponential factors and activation energies for the reaction step which occurs in parallel with branch 1 for crystal temperatures above \( \sim 300^\circ \)C could not be uniquely determined on either of the two crystals. The scatter in the data due to the small signal amplitude at low crystal temperatures prevents accurate determination of the rate constants for the process which occurs in series with branch 1 below \( \sim 300^\circ \)C.
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1. INTRODUCTION

In order to understand the fundamental processes of catalysis by metals, it is necessary to study gas-surface interactions under well defined conditions. A technique that is particularly suitable for such investigations is molecular beam scattering from solid surfaces. The single crystal surface, which is maintained under ultrahigh vacuum conditions, can be characterized as to structure and composition by low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The gases may be introduced in the form of a collimated beam, with an equivalent pressure at the surface on the order of $10^{-7}$ torr. With a directed flow of molecules, the gases interact only with the surface under study and the angle of incidence with respect to surface microstructure can be specified.

Studies of molecular beam scattering from solid surfaces may focus on different aspects of the gas-surface interaction. Elastic scattering and diffraction provide information about the gas-surface interaction potential and surface properties such as the structure or surface Debye temperature. Energy transfer between the gas and the solid can be investigated by inelastic or reactive scattering. Modulated molecular beam techniques can be used to study the kinetics and mechanism of reactions catalyzed by the surface or reactions of gases with the surface. Advances in technology continue to expand and
diversify the information that can be obtained experimentally, further improving our understanding of these interactions.

Since this is a field which is rapidly changing and growing, it is frequently reviewed in detail. In the past year, comprehensive reviews of the current experimental\textsuperscript{1} and theoretical\textsuperscript{2} developments have appeared. The earlier reviews are referenced in these articles. Therefore, no attempt will be made to review the field again here. The experimental and theoretical results which are pertinent to the work presented here will be included in the discussion of this work.
2. EXPERIMENTAL

2.1 Description of the Apparatus

The construction of the apparatus has been described in detail in Reference 3. Modifications that were made in the course of this investigation will be discussed in Section 2.2.

The system, depicted schematically in Figure 1, consists of three separately pumped chambers. The first diffusion pumped chamber contains the molecular beam source, a multichannel array of glass capillaries (diameter 5μ, length to diameter ratio 100). Connected to this chamber by a 1 mm collimating orifice is the second diffusion pumped chamber, which serves as a buffer chamber. Located in the second chamber is the slotted disk chopper used to modulate the beam in the range 10-300 Hz. Another 1 mm hole connects this chamber to the ultrahigh vacuum scattering chamber. This orifice can be closed by means of a zero length gate valve to isolate the UHV chamber from the diffusion pumped chambers.

The UHV scattering chamber which is the heart of the apparatus is pumped by a Varian 400 l/sec ion pump and a water cooled titanium sublimation pump. The single crystal samples are mounted on a Varian manipulator equipped with a flip mechanism. The three grid Varian LEED optics are located opposite a window through which the diffraction
Figure 1. Schematic diagram of the molecular beam-surface scattering apparatus.
patterns can be viewed and photographed. A glancing incidence electron gun is used with the LEED optics for AES. A Varian ion bombardment gun is available for cleaning the samples by argon ion sputtering. The EAI QUAD 250A mass spectrometer is mounted on a rotary feedthrough such that it can be rotated around the sample. A beam flag which serves as a low frequency chopper (5 Hz and below) is located directly in front of the beam hole.

2.2 Modifications

2.2.1 Signal detection

As discussed in Reference 3, the detector is a modified EAI QUAD 250A mass spectrometer. Two further modifications have been made.

To improve the signal collection of the EMI electron multiplier, a 28V battery in series with a 1 MΩ resistor was connected to the collecting plate as shown in Figure 2. For DC signal measurements, output A is connected to a Keithley picoammeter and output B is left open. For detection of AC signals, output A is grounded and output B is connected to the lock-in amplifier. Three lock-in amplifiers have been used, a PAR HR-8, a PAR 124A and an Ortholoc 9502.

The ionizer of the mass spectrometer, which was described in detail in Reference 4, was replaced by an EAI model 1908, shown schematically in Figure 3. The new ionizer is designed such that the highest electron density
Figure 2. Electron multiplier wiring diagram.
Figure 3. Schematic diagram of the new ionizer.
is directly above the ion exit aperture, increasing the ion collection efficiency. There are two separate filament block assemblies each holding a coil of 8 mil tungsten wire which can produce emission currents of up to 5 mA. To provide angular resolution, a stainless steel plate with a 4 mm hole was spot welded to the ionizer. The distance from the crystal to the ionizer collimating orifice is 31 mm, such that the acceptance angle is 7.4°.

2.2.2 Scattering chamber pumping

To provide exhaust pumping for the scattering chamber during bakeout, the ion pump was modified to accommodate a 4" ID elbow. A 4" NRC oil diffusion pump equipped with a 4" Granville-Phillips Series 250 Cryosorb cold trap was connected to this port with a 4" Thermionics gate valve. The diffusion pump is backed with a Welch Duoseal mechanical pump with a molecular sieve trap. A miniflange was welded into the neck of the cold trap so that an ion gauge could be installed. The pressure can then be measured before opening the gate valve to the ion pump.

This auxiliary pumping was also used during argon ion bombardment in the flow mode.

2.2.3 Choppers

In order to compare the modulated molecular beam results with conventional nonmodulated experiments, it was necessary to provide a means of low frequency chopping.
To this end, the four bladed slotted disk chopper was replaced by a three bladed wheel, such that stable modulation frequencies as low as 10 Hz could be obtained.

To further extend the low frequency range available for these experiments, a beam flag was mounted in the scattering chamber on a bellows. The back-and-forth chopping motion was achieved using a motor with an eccentric bearing. The range of modulation frequencies is 5 Hz and below. The lower limit is set by the lowest working frequency of the lock-in amplifier, 0.5 Hz.

2.2.4 Gas handling system

The gas handling system, depicted in Figure 4, was modified as follows.

A second Varian leak valve (LV 2) was added to the source inlet system to permit controlled mixing of two gases in the beam.

Copper coils (T3-T5) were added in the gas lines, which can be cooled with liquid nitrogen to trap impurities.

A line connecting gas manifold 2 with mechanical pump 2 was added as an alternative to the sorption pump.

The Wallace-Tiernan pressure gauge was changed from one which operates from 0-20 torr to one which operates from 0-50 torr.

A metal valve which separates T4 from the beam source was added so that the trap could be pumped on through the gas handling system as it warmed up, rather than through the beam source.
Figure 4.

Legend:

- **X**: metal valves
- **G**: greaseless teflon-glass valves
- **O**: ground glass valves
- **MP**: mechanical pump
- **GM**: gas manifold
- **T**: trap
- **DP**: diffusion pump
- **1L**: one liter bulb
- **5L**: five liter bulb
- **WT**: Wallace-Tiernan gauge
- **LS**: liquid samples
- **BTA**: back to air
- **SP**: sorption pump
- **LV**: leak valves
- **G**: thermal conductivity pressure gauges
Figure 4. Schematic diagram of the gas handling system.
2.3 Samples

The platinum single crystal samples were prepared in the following manner. After orientation to ± 1° of the appropriate plane by Laue X-ray diffraction, slices 1-2 mm thick were spark cut from 99.99% pure bulk platinum single crystal rods. The Pt(111) surface was cut along the (111) plane. The Pt(332) and Pt(553) surfaces were cut 10° and 12.3°, respectively, from the (111) plane in the [110] zone. The crystals were mechanically polished with successively finer abrasives down to 0.05μm alumina. Before mounting in the UHV chamber, the crystals were etched in warm aqua regia (≈ 50°C). Depending on the experiment, the crystals were mounted in several different ways, which will be described with the appropriate experimental results.

2.4 Surface Characterization

The surface sensitive techniques used for characterization of the single crystal samples were low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). Since the electron optics required for the post acceleration technique of LEED can be used as a retarding field analyzer for the Auger electrons, these two techniques are compatible and complementary, providing information as to the structure and composition of the surface, respectively. Both of these techniques are in wide use in surface studies and have been extensively discussed in the literature. An in-depth review of LEED has been made by
Somorjai and Farrell\(^5\). The recent developments in surface crystallography by LEED have been reviewed by Somorjai and Kesmodel\(^6\) and Jona\(^7\). Reviews of the theory and use of AES have been written by Chang\(^8\) and Sickafus.\(^9\)

2.5 Experimental Method

After the surface had been determined to be clean by AES and well ordered by LEED, the experiments were performed in the following manner.

With the crystal moved out of the way, the mass spectrometer was rotated into the direct beam line and tuned to the peaks of interest, using up to five channels of the programmable peak selector. This was performed with the chopper off, using the picoammeter. The chopper was then turned on and the reference signal connected to the lock-in amplifier. When using the PAR lock-in amplifiers, the gain was adjusted and the amplifier tuned to the proper frequency. With the Ortholoc 9502, the gain does not need to be adjusted (but can be checked on TEST) and the frequency is automatically tuned to the reference signal.

The experimental data was collected by recording the output of the lock-in amplifier at \(0^\circ\) and \(90^\circ\) on a chart recorder for each of the peaks selected. When using the PAR lock-in amplifiers, the signals were measured consecutively at \(0^\circ\) and \(90^\circ\). The Ortholoc 9502 has dual outputs so that both phases can be recorded simultaneously.
The reactant and product (or incident and scattered) signals can be monitored in two different modes, differential and integral.

For measurements in the differential mode, the mass spectrometer is positioned at a particular scattering angle from the surface normal. For a given mass number, there are two different contributions to the signal detected. 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, which is due to its finite residence time in the UHV chamber before being pumped away.

The intensity of the modulated background, $I_{\text{BKG}}$, changes with the frequency of modulation, $\omega$, as $I_{\text{BKG}} \propto [1 + (\omega V/S)^2]^{-1/2}$, where $S$ is the pumping speed and $V$ the volume of the chamber. Therefore, at low modulation frequency and when dealing with species that are pumped very rapidly, the modulated background will be higher than the signal due to species emitted directly from the surface into the scattering angle accepted by the ionizer aperture. Two factors are responsible for this effect. The time constant of the pump, $V/S$, may be low enough to follow the periodic production of the species by the surface at low modulation frequency. The second factor is that the direct signal corresponds to molecules emitted within the scattering angle accepted by the ionizer aperture ($\sim 5^\circ$ for the
old ionizer and ~7° for the new one) whereas the modulated background is due to products emitted in all directions.

The modulated background must be measured independently and subtracted vectorially from the total signal to obtain the true differential signal. The phase and amplitude of the differential product signal is referenced to that of the direct beam measurement of the reactants, 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 distributions at all angles of emission.

In the second method of detection, the integral mode, only the modulated partial pressure of the reactants and products is measured. For the products, this is accomplished by positioning the mass spectrometer behind the crystal, out of the direct line of sight of the surface, such that the species emitted from the surface cannot enter the ionizer directly. The integral signal is proportional to the total amount of products emitted from the surface and does not need to be integrated as in the differential mode. Furthermore, any possible effects due to the angular distribution of the products are eliminated. The integral mode measurement of the reactants can be performed in two ways, which give the same result. The sample holder can be rotated such that the beam strikes the back of the crystal support or, alternatively, the
flag can be placed in the beam line. In either case, the beam is scattered from a nonreactive surface, as established by monitoring the HD partial pressure. The phase and amplitude of the product signal are referenced to that of the reactant signal, to give the total reaction probability.

The differential mode must be used for measuring angular scattering distributions, but the integral mode is better suited for reactive scattering studies such as $H_2$-$D_2$ exchange.

2.6 Definition of Angular Geometry

Several different motions are provided by the crystal manipulator: $x$, $y$, 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 argon ion sputtering, LEED and AES and to fix the angle of incidence of the molecular beam. The surface microstructure is positioned with respect to the incident beam by azimuthal rotation, i.e. rotation of the crystal around the macroscopic surface normal.

Depicted in Figure 5 is the geometry for the variation of the angle of incidence and azimuthal angle for a stepped surface. The polar angle of incidence, $\theta$, is measured from the macroscopic surface normal and defined as positive when the open edge of the step structure is directed toward the incident beam. The azimuthal angle, $\phi$, is designated as $0^\circ$ when the projection of the incident beam
Figure 5. Diagram defining the angular geometry for a stepped surface.
on the surface is parallel to the step edges; $90^\circ$ when the beam impinges perpendicular to the step edges, into the open side (from the right in the figure) and $-90^\circ$ when the open edge of the step structure is directed away from the incoming beam (from the left in the figure).

Alignment of the crystal, detector, and beam source was achieved by shining a laser beam through the beam source.
3. THEORETICAL MODELS OF SURFACE REACTION MECHANISMS
STUDIED BY MODULATED MOLECULAR BEAM MASS SPECTROMETRY

3.1 Introduction

The response of a modulated molecular beam system to a variety of surface reaction mechanisms has been derived and reported in the literature.\textsuperscript{10-14} Presented below is a summary of these results.

In general, the treatment is for a system which uses phase sensitive lock-in detection, where the signal output is the first Fourier component of the signal from the mass spectrometer detector. The \textit{amplitude} and the \textit{phase} of the product signal are referenced to that of the incident reactants to give the apparent reaction probability, \( e \), and the phase lag of the product signal relative to the reactant signal, \( \phi \). The reference state may be the direct beam, or the reflected beam under conditions where the surface processes are simple enough to be well understood. Various corrections are made to account for instrumental factors, which depend on the particular experimental method and conditions. References \textsuperscript{10} and \textsuperscript{11} discuss these corrections in detail. The phase lag of the product signal, \( \phi \), is related to the characteristic time of the surface process. In the limit of zero modulation frequency, where the phase lag is also zero, the value of \( e \) is the true reaction probability.
The basic method of analyzing a reaction mechanism is to write the kinetic equations as a sequence of elementary steps. The differential equations representing the mass balances for all of the adsorbed species are then solved, assuming a wave form for the incident reactant beam, during the beam-on and beam-off periods, with cyclic steady state boundary conditions. The complete solution is then expanded in a Fourier series about the modulation frequency in which the amplitude and phase of the fundamental component represent the signal amplitude and phase measured by the lock-in detector.

For linear surface processes, the analysis can be simplified, due to the fact that each Fourier component behaves independently. The system response to the fundamental component of the modulated molecular beam can be evaluated using any wave form which has the appropriate periodicity rather than the actual wave form of the incident beam. A sinusoidal gating function is generally used for simplicity.

Obtaining the exact solution and then extracting the fundamental Fourier component is the only method of predicting the exact response of the system to nonlinear surface processes. However, in most cases, this is an extremely complicated and time consuming process, so two alternative approaches have been suggested. In one case, the theoretical treatment has been simplified,
using truncated Fourier expansions to obtain approximate solutions.\textsuperscript{14} The second method is to experimentally linearize the system.\textsuperscript{12,13}

The summary which follows includes the results which have been reported for both linear and nonlinear processes.

3.2 Linear Surface Processes

3.2.1 Simple adsorption-desorption

An example of a simple first order reaction is the dissociation of a diatomic molecule at a surface, under conditions where surface recombination is neglected.

A beam of A\textsubscript{2} molecules with modulation frequency \( \omega = 2\pi f \) strikes the surface and adsorbs with sticking coefficient \( \sigma \). The atomic product A desorbs subsequently with a rate constant \( k_d \). Schematically, this process is

\[
\begin{align*}
\text{A}_2(\text{gas}) & \rightarrow 2\text{A(ads)} \rightarrow 2\text{A(gas)} \\
\sigma & \quad k_d
\end{align*}
\]

The apparent reaction probability and the phase lag are given by\textsuperscript{11}:

\[
\varepsilon = \frac{2\sigma}{\left[1 + \left(\frac{\omega}{k_d}\right)^2\right]^{1/2}} \quad (1)
\]

\[
\phi = \tan^{-1}\frac{\omega}{k_d} \quad (2)
\]

where \( k_d = A_d \exp(-E_d/RT) \).
Presented in Figures 6 and 7 are Arrhenius plots of \( \varepsilon \) and tan \( \phi \), calculated using Equations 1 and 2, for \( A_d = 10^{13} \) sec\(^{-1} \), \( \sigma = 0.1 \), and \( E_d = 20 \) kcal/mole, at various modulation frequencies. In the limit \( \omega \ll k_d \), the apparent reaction probability \( \varepsilon \) approaches the true reaction probability \( 2\sigma \) and the phase lag approaches zero. When \( \omega \sim k_d \), \( \varepsilon \sim \sqrt{2\sigma} \) and \( \phi \sim 45^\circ \). For \( \omega > k_d \), \( \varepsilon \rightarrow 0 \) and \( \phi \rightarrow 90^\circ \). The slope of a plot such as given in Figure 6, ln \( \varepsilon \) vs. \( 1/T \), is

\[
m = -\frac{E_d}{R} \frac{\omega^2}{k_d^2 + \omega^2}
\]

so that for \( \omega \sim k_d \), \( m \rightarrow -E_d/2R \); \( \omega \gg k_d \), \( m \rightarrow -E_d/R \); and \( \omega \ll k_d \), \( m \rightarrow 0 \). For a plot such as given in Figure 7, ln tan \( \phi \) vs. \( 1/T \), the slope is \( E_d/R \) and the intercept is ln \( \omega/A_d \), from which the activation energy, \( E_d \), and the pre-exponential factor, \( A_d \), can be determined in order to obtain \( k_d \).

### 3.2.2 Series processes

If the surface reaction mechanism includes two or more sequential steps with similar characteristic times, it is called a series process. The case for which both reaction steps are first order can be readily formulated, for example, adsorption into a precursor state prior to desorption. Again, a molecular beam of \( A_2 \) with modulation frequency \( \omega = 2\pi f \) impinges on the surface and dissociatively adsorbs with sticking coefficient \( \sigma \). The rate constant
Figure 6. Calculated Arrhenius plots of the apparent reaction probability, $\epsilon$, for a reaction mechanism with first order desorption as the rate limiting step.

$E_d = 20 \text{ kcal/mole}$

$A_d = 10^{13} \text{ sec}^{-1}$

$\sigma = 0.1$
Figure 7. Calculated Arrhenius plots of the tangent of the phase lag, $\phi$, for a reaction mechanism with first order desorption as the rate limiting step.
for the transfer of atoms into the precursor state is $k_1$ and the rate constant for desorption is $k_d$. This process can be depicted as

$$A_2(\text{gas}) \rightarrow 2A(\text{ads}) \rightarrow 2A(\text{ads}^\ast) \rightarrow 2A(\text{gas})$$

The apparent reaction probability and the phase lag for such a two-step process are given by\textsuperscript{11}:

$$\varepsilon = \frac{2\sigma}{1 + \left( \frac{w}{k_d} \right)^{1/2}}$$

$$\phi = \tan^{-1}\frac{w}{k_d} + \tan^{-1}\frac{w}{k_1}$$

where $k_d = A_d \exp(-E_d/RT)$ and $k_1 = A_1 \exp(-E_1/RT)$.

In the limit that one of the reaction steps is very fast relative to the other, the slow step is rate limiting and the process reduces to simple adsorption-desorption, which was discussed in the previous section. For the intermediate case, $k_1 = k_d$, the apparent reaction probability and phase lag are given by:

$$\varepsilon = \frac{2\sigma}{1 + \left( \frac{w}{k_d} \right)^{1/2}}$$

$$\phi = 2 \tan^{-1}\frac{w}{k_d}$$

Equations 6 and 7 were solved for $E_1 = E_d = 20$ kcal/mole, $A_1 = A_d = 10^{13}$ sec\(^{-1}\), and $\sigma = 0.1$ at various modulation frequencies. Arrhenius plots of the solutions
to Equation 6 are given in Figure 8. As for the case of simple adsorption-desorption, in the limit \( w \ll k_d \), the apparent reaction probability approaches the true reaction probability \( 2\sigma \) and for \( w \gg k_d \), \( \varepsilon \to 0 \). However, for the two step process, when \( w \sim k_d \), \( \varepsilon \to \sigma \). The slope of the curves in Figure 8 is:

\[
m = \frac{-2E_d}{R} \frac{w^2}{k_d^2 + w^2}
\]

such that, for \( w \sim k_d \), \( m \approx -\frac{E_d}{R} \); \( w \gg k_d \), \( m \to -2\frac{E_d}{R} \); and \( w \ll k_d \), \( m \to 0 \).

The most striking feature of the series process is that the phase lag varies from 0° to 180°. Presented in Figure 9 are Arrhenius plots of the absolute value of tan \( \phi \), for comparison with Figure 7. In this case, \( \phi = \tan^{-1} \phi_d + \tan^{-1} \phi_1 = 2 \tan^{-1} \phi_d \), so that tan \( \phi \) is not meaningful. The qualitative behavior of tan \( \phi \) is quite different for the two types of processes. For the series process, as the phase lag approaches 90°, tan \( \phi \to \infty \). When the phase lag exceeds 90°, tan \( \phi \) becomes negative. As \( \phi \to 180° \), tan \( \phi \to 0 \). If \( k_1 \) and \( k_d \) are different, it may be possible to separate them by adjusting the experimental conditions so that one process dominates. The Arrhenius plot of tan \( \phi \) may then have a linear region similar to that found for simple adsorption-desorption, with slope \( E/R \) and intercept \( \ln \frac{w}{A} \).
Figure 8. Calculated Arrhenius plots of the apparent reaction probability, $\varepsilon$, for two first order processes acting in series.
Figure 9. Calculated Arrhenius plots of the absolute value of the tangent of the phase lag, $\phi$, for two first order processes acting in series.
3.2.3 Parallel processes

When the surface reaction mechanism consists of two different processes which simultaneously give the same reaction product, it is called a parallel or branched mechanism. Again, the case for which both branches are first order processes will be considered for simplicity. For example, there may be two (or more) types of sites on the surface where dissociative adsorption of the incident \( \text{A}_2 \) molecules and subsequent desorption of the atomic products may occur. In this case, the adsorption probability is \( p \) for branch 1 and \( (1-p) \) for branch 2. The desorption rate constants are \( k_1 \) and \( k_2 \), respectively. This type of mechanism can be written as:

\[
\begin{align*}
2 \text{A}_2(\text{gas}) & \rightarrow p \sigma \text{A(ads)}_1 + (1-p)\sigma \text{A(ads)}_2 + (1-p)\sigma \text{A(gas)}_1 + k_2 \text{A(gas)}_2
\end{align*}
\]

The apparent reaction probability and phase lag are given by:

\[
\begin{align*}
\varepsilon &= 2\sigma (a^2 + b^2)^{1/2} \\
\phi &= \tan^{-1} \frac{b}{a}
\end{align*}
\]

where

\[
\begin{align*}
a &= \frac{p}{1 + (\frac{\sigma}{k_1})^2} + \frac{(1-p)}{1 + (\frac{\sigma}{k_2})^2} \\
b &= \frac{p (\frac{\sigma}{k_1})}{1 + (\frac{\sigma}{k_1})^2} + \frac{(1-p)(\frac{\sigma}{k_2})}{1 + (\frac{\sigma}{k_2})^2}
\end{align*}
\]
Arrhenius plots of the amplitude and phase lag obtained using Equations 9-12 are given in Figures 10 and 11, for $A_1 = A_2 = 10^{13}$ sec$^{-1}$, $\sigma = 0.1$, $E_1 = 20$ kcal/mole, $E_2 = 23$ kcal/mole, and $p = 0.25$. As can be seen in Figure 10, at high crystal temperature, where $\omega \ll k_1$ and $k_2$, the apparent reaction probability approaches the true reaction probability, $2\sigma$, and at low crystal temperature, where $\omega \gg k_1$ and $k_2$, $\varepsilon = 0$. The decrease in the apparent reaction probability with decreasing crystal temperature exhibits a knee which is more distinct at low modulation frequency. The phase lag approaches, but never exceeds, 90°. The Arrhenius plots of tan $\phi$, given in Figure 11, display a feature which is characteristic of branched processes, an inflection in the transition region between the high temperature regime where both processes are acting and the low temperature regime where the branch with the lowest activation energy is dominant. This behavior is more pronounced at low modulation frequency. Figures 12 and 13 demonstrate the effect of the branching ratio on the predicted behavior of the apparent reaction probability and tan $\phi$, respectively, at a fixed frequency of 10 Hz. Presented in Figures 14 and 15 are the Arrhenius plots of the apparent reaction probability and tan $\phi$, respectively, calculated for different values of the activation energy in branch 2, at $f = 10$ Hz and $p = 0.5$. The calculated Arrhenius plots given in Figures 10-15 exhibit distinct
Figure 10. Calculated Arrhenius plots of the apparent reaction probability, \( \varepsilon \), for two first order processes acting in parallel. 

PARALLEL PROCESS

\[
E_1 = 20 \text{ kcal/mole} \\
E_2 = 23 \text{ kcal/mole} \\
A_1 = A_2 = 10^3 \text{ sec}^{-1} \\
\sigma = 0.1 \\
p = 0.25
\]
Figure 11. Calculated Arrhenius plots of the tangent of the phase lag, $\phi$, for two first order processes acting in parallel.
Figure 12. Calculated Arrhenius plots of the apparent reaction probability, $\epsilon$, for two first order processes acting in parallel, at various values of $p$, the branching parameter.
Figure 13. Calculated Arrhenius plots of the tangent of the phase lag, $\phi$, for two first order processes acting in parallel, at various values of $p$, the branching parameter.
Figure 14. Calculated Arrhenius plots of the apparent reaction probability, $\varepsilon$, for two first order processes acting in parallel, at various values of $E_2$, the activation energy of branch 2.
Figure 15. Calculated Arrhenius plots of the tangent of the phase lag, $\phi$, for two first order processes acting in parallel, at various values of $E_2$, the activation energy of branch 2.
features which are characteristic of a branched process and strongly dependent on the values of the kinetic parameters.

3.3 Diffusion Limited Processes

A surface chemical reaction can be limited by two different diffusional processes, surface diffusion or bulk solution and diffusion. These types of reaction mechanisms have been treated in detail by Olander\textsuperscript{10} and discussed in the reviews of Jones et al.\textsuperscript{11} and Schwarz and Madix.\textsuperscript{12}

For example, the case of a molecular beam of $A_2$ with modulation frequency $\omega = 2\pi f$ which dissociatively adsorbs with sticking coefficient $\sigma$ will be considered. The atomic products can either desorb or diffuse in and out of the bulk before desorption, with solubility coefficient $H$, diffusion coefficient $D$, and desorption rate constant $k_d$. This process can be represented by

$$A_2(\text{gas}) + A(\text{ads}) \rightarrow A(\text{gas})$$

The apparent reaction probability and phase lag are given by\textsuperscript{11}:

$$\varepsilon = \frac{2\sigma}{[1 + Q(\frac{w}{k_d})^{1/2}]} \frac{1}{2} \frac{2\sigma}{[1 + Q(\frac{w}{k_d})^{1/2}]} \frac{1}{2} \frac{1}{2}$$

$$\phi = \tan^{-1} \frac{\frac{w}{k_d} + Q(\frac{w}{k_d})^{1/2}}{1 + Q(\frac{w}{k_d})^{1/2}}$$
where

\[ Q = \left( \frac{H^2D}{2k_d} \right)^{1/2} \] (15)

When the reaction is strongly controlled by solution-diffusion, \( Q \to \infty \), the phase lag is constant at 45\(^\circ\), independent of modulation frequency, and the apparent reaction probability varies as \( \omega^{-1/2} \).

If \( k_d \gg H^2D (Q \to 0) \), Equations 13 and 14 simplify to those obtained for simple adsorption-desorption.

3.4 Nonlinear Processes

Finding the exact solution for the apparent reaction probability and the phase lag for a surface reaction with a nonlinear mechanism is a difficult and time consuming task.\(^{12-14}\) Recently, two different methods have been proposed to simplify the treatment.\(^{12-14}\)

In the analysis of nonlinear reaction mechanisms, the dc impingement rate of reactants from the background must be considered as well as the ac impingement rate of the modulated molecular beam.\(^{10}\) Schwarz\(^{12,13}\) has shown that this property can be used to experimentally linearize certain processes such that the ac flux is a perturbation and the kinetic equations can be solved using a perturbation treatment. This method was used to solve the equations for a simple second order reaction and a first order reaction with a coverage dependent adsorption probability. In both cases, the solutions were derived for conditions where
the modulated flux was small compared to the total flux.

A more general method has been described in detail by Olander and Ullman. Their approach is to truncate the Fourier expansions of the gating function and the concentrations of the surface intermediates, retaining the zero order and first order terms, neglecting higher order terms. Using this approximation, the case of adsorption with parallel first and second order desorption has been treated and compared with the exact solution, with very good agreement. The case of adsorption with m-th order desorption was also solved using this technique and compared with the exact solution for m = 2 and m = 3. Again, the agreement was found to be quite good, with a maximum deviation of the approximate solution from the exact solution of 5% in amplitude and 3° in phase for the second order process and 6% in amplitude and 4° in phase for the third order process. First order reactions with a linear coverage dependent adsorption probability and a generalized coverage dependent adsorption probability were also treated using the approximate theory and compared with the exact solutions. In general, the agreement is reasonable. As the coverage becomes large, the discrepancies between the exact and approximate theories also become large. Under these conditions, the amplitude of the product signal is small, such that the experimental data may be poor due to the difficulty of detecting the
small signal above noise and background. Thus, even in this case, the approximate method should be sufficient in the region where the experimental data is good.

Schwarz\textsuperscript{12,13} has used a similar approximation to treat the cases of coverage dependent adsorption-desorption, first order desorption and second order desorption, including the effect of the beam to background ratio.

The conclusion that can be drawn from these detailed treatments\textsuperscript{12-14} is that the approximate theory, used with care, is generally applicable and greatly simplifies the complexities of dealing with nonlinear mechanisms.

3.5 An Alternative Analytical Method

It should be noted that a different approach to the analysis of the mechanisms of surface chemical reactions studied by modulated molecular beam mass spectrometry has been proposed recently.\textsuperscript{15} This method consists of uncoupling the differential equations representing the surface mass balances by matrix manipulations and then obtaining the fundamental component, resulting in a general expression for the "reaction product vector", $\mathbf{s} \exp(-i\phi)$, in terms of a rate coefficient matrix. This technique, which can only be applied to linear processes, has also been used to treat the cases of bulk diffusion and surface reaction, bulk diffusion and bulk reaction, and surface diffusion with reaction in a surface boundary zone.\textsuperscript{16} The expressions for the apparent reaction probability and phase
lag obtained using this method are the same as those found using the method of Jones et al.\textsuperscript{11}, discussed above. The authors indicate plans to apply this technique to mathematically linearized nonlinear reaction mechanisms.\textsuperscript{16} It remains to be seen whether this method can provide better approximate solutions to complex reaction mechanisms than those described above.\textsuperscript{*}

\textsuperscript{*}In a recent publication (H. -C. Chang and W. H. Weinberg, Surface Sci. 72, 617 (1978)), this method has been extended to treat nonlinear processes, using the approximation of Olander and Ullman.\textsuperscript{14} Since the same approximation was used, these results are subject to the same uncertainties discussed in 3.4. Chang and Weinberg state that for complex reaction mechanisms, their formalism is simpler than that due to Olander and Ullman\textsuperscript{14}, although the expressions obtained for the apparent reaction probability and phase lag are identical.
4. SURFACE CHARACTERIZATION BY LEED AND AES

4.1 The Pt(553) and Pt(332) Crystal Faces

The Pt(553) crystal employed in this work had been used by an earlier worker such that bulk impurities had been depleted. The only contaminant detected by AES was carbon, which was removed by flashing the crystal to ~1000°C or heating it at 800-1000°C in 10⁻⁷ to 10⁻⁶ torr of oxygen.

Silicon and phosphorus were the major contaminants observed by AES on the Pt(332) surface. Bombardment with 500 eV argon ions for several hours with the crystal at ~600°C proved to be the most effective method of removing these impurities. The near surface layers were sufficiently depleted of the contaminants after such a treatment to maintain a clean surface at temperatures up to 900°C.

Displayed in Figure 16 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. The steps are found to be of monatomic height from the intensity versus voltage measurements of the (0,0) doublet. The ratios of the distance between doublet spots a and parallel rows b are b/a = 3.87 ± 0.04 for the Pt(553) surface and b/a = 4.71 ± 0.04 for the Pt(332) surface. These results are in good agreement with the calculated values 3.84 and 4.69, corresponding to the stepped surfaces denoted \( \text{Pt}(5)-(5(111)\times(111)) \) and
Figure 16. LEED patterns (photographs and schematic representations) of the two stepped surfaces.
Pt(S)-[6(111)x(111)], respectively. The reciprocal lattice unit cells, shown schematically in Figure 16, 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.

Figure 17 is a ball model illustration of the Pt(S)-[6(111)x(111)] surface. The Pt(S)-[5(111)x(111)] surface differs only in that the terraces are five rather than six atomic rows wide. The atom at the step edge and the inner corner atom of the step structure have unique coordination, while the other terrace atoms have the configuration of surface atoms in the (111) plane.

The clean surfaces were found to be stable over the entire temperature range studied, 25-1100°C. When the surfaces were contaminated by carbon, silicon, phosphorus or oxygen, many different, complex LEED patterns were observed.

The azimuthal angle $\phi$ was determined from the LEED pattern by measuring the angle between the rows of doublet spots and the beam line. The sign of the azimuthal angle,
Top view. The dotted lines show the rectangular symmetry of the step periodicity.

Side view.

\[ \text{fcc (332)} \leftrightarrow 6 \text{ (III) x (III)} \]

Figure 17. Ball model of the Pt(S)-[6(111)x(111)] or Pt(332) surface.
i.e. in which direction the open side of the step structure faces, was established by helium scattering, as will be discussed in Chapter 5.

4.2 The Pt(111) Crystal Faces

The main impurities detected by AES in the five Pt(111) samples examined in this work were silicon, phosphorus, carbon and calcium. The relative proportions of these contaminants varied from sample to sample. Only carbon was observed as an impurity in three of the samples. Silicon and phosphorus were major contaminants in one crystal and calcium in another.

Heating the crystals at 600-800°C in ~10^-7 torr of oxygen removed the carbon contamination. The silicon, phosphorus, and calcium were most effectively eliminated by bombarding the crystals at ~600°C with 500eV argon ions for several hours.

The clean surfaces exhibited LEED patterns with the characteristic hexagonal structure of the (111) plane of a face centered cubic crystal.
5. NONREACTIVE SCATTERING: HELIUM

5.1 He/Pt(553)

The first phase of this work was a study of the scattering of helium atoms from the stepped Pt(553) surface, as a function of angle of incidence, \( \theta \), and azimuthal angle, \( \phi \).

The crystal was mounted as shown in Figure 18, spot welded to polycrystalline Pt tabs which were then bolted to the alumina bar. This mounting allowed variation of the azimuthal angle from \( \phi \approx -90^\circ \), where the beam impinges perpendicular to the step edges, with the open side of the step structure directed away from the incident beam, to \( \phi \approx 0^\circ \), where the projection of the beam on the surface is parallel to the step edges. The crystal was heated resistively and its temperature was measured using an optical or infrared pyrometer which had been previously calibrated with a thermocouple spot welded in the crystal.

This series of experiments was performed with a beam modulation frequency of 160 Hz and a crystal temperature of 800°C. The equivalent pressure of helium on the surface was \( \approx 10^{-7} \) torr.

Presented in Figures 19-24 are the helium scattering distributions from the Pt(553) surface for various azimuthal angles, measured in the plane defined by the incident beam and the macroscopic surface normal. The angle of incidence \( \theta \) is 45°, measured from the macroscopic
Figure 18. Schematic diagram of the crystal holder which provides azimuthal rotation.
Figure 19. Angular distribution of helium atoms scattered from the Pt(553) surface, for $\theta_i = 45^\circ$ and $\phi = -86^\circ \pm 5^\circ$. 
Figure 20. Angular distribution of helium atoms scattered from the Pt(553) surface, for $\theta_i = 45^\circ$ and $\Phi = -80^\circ \pm 5^\circ$. 
Figure 21. Angular distribution of helium atoms scattered from the Pt(553) surface, for $\theta_i = 45^\circ$ and $\Phi = -66^\circ \pm 5^\circ$. 

He/Pt (553) 

$\theta_i = 45^\circ$ 

$f = 160$ Hz 

$T_s = 800^\circ$C
Figure 22. Angular distribution of helium atoms scattered from the Pt(553) surface, for $\theta_i = 45^\circ$ and $\phi = -53^\circ \pm 5^\circ$. 
Figure 23. Angular distribution of helium atoms scattered from the Pt(553) surface, for $\theta_i = 45^\circ$ and $\Phi = -39^\circ \pm 5^\circ$. 
Figure 24. Angular distribution of helium atoms scattered from the Pt(553) surface, for $\theta_i = 45^\circ$ and $\Phi = -12^\circ \pm 5^\circ$. 
surface normal. Each curve, except for $\phi = -66^\circ$, is the average of two or more experiments. The error bars indicate the standard deviation of the data. The macroscopic specular angle is shown by the arrow.

The general features are a large peak which is shifted towards the surface normal and a smaller shoulder near the macroscopic specular angle. The maximum shift and maximum intensity of the large peak are observed when the helium atoms are incident perpendicular to the step edges, $\phi \sim -90^\circ$. As $\phi$ is varied from $\sim -90^\circ$ to $\sim 0^\circ$, the overall intensity of the scattering distribution and the separation of the peaks decreases.

Figures 25-28 show the helium scattering distributions from the Pt(553) surface, measured in the plane defined by the incident beam and the macroscopic surface normal, for various angles of incidence. The azimuthal angle $\phi$ is $\sim -90^\circ$, such that helium atoms impinge perpendicular to the step edges, with the open side of the step structure directed away from the incident beam. Except for $\theta_i = 25^\circ$, these results are the average of two or more experiments. The standard deviation of the data is shown by the error bars. The arrow indicates the macroscopic specular angle.

The same general features are observed in these curves. As the angle of incidence becomes more grazing, the scattered intensity increases and the two peaks coalesce.
Figure 25. Angular distribution of helium atoms scattered from the Pt(553) surface, for $\Theta_1 = 25^\circ$ and $\Phi = -85^\circ \pm 5^\circ$. 
Figure 26. Angular distribution of helium atoms scattered from the Pt(553) surface, for $\theta_i = 35^\circ$ and $\Phi = -83^\circ \pm 5^\circ$. 

He/Pt (553) 

$\theta_i = 35^\circ$

$f = 160$ Hz

$T_s = 800^\circ$C

OPEN SIDE OF STEP EDGES
Figure 27. Angular distribution of helium atoms scattered from the Pt(553) surface, for $\theta_i = 45^\circ$ and $\phi = -86^\circ \pm 5^\circ$. 

He/Pt (553)

$\theta_i = 45^\circ$

$f = 160$ Hz

$T_s = 800^\circ$C

OPEN SIDE OF STEP EDGES
Figure 28. Angular distribution of helium atoms scattered from the Pt(553) surface, for \( \theta_i = 65^\circ \) and \( \phi = -86^\circ \pm 5^\circ \).
The behavior of the large peak in the scattering distribution as a function of azimuthal angle can be understood in terms of the geometry of the surface and the detector. The scattering geometry of the surface is depicted schematically in Figure 29. If the helium atoms scatter from the (111) terraces rather than the macroscopic surface plane, the specular peak is shifted twice the angle between the macroscopic surface plane and the (111) terraces. This angle, $\gamma$, corresponds to the angle at which the crystal was cut from the (111) plane in the [110] zone, $12.3^\circ$ for the Pt(553) surface. Therefore, the maximum peak shift which occurs when the helium beam is incident perpendicular to the step edges ($\phi = \pm 90^\circ$), will be $2\gamma = 24.6^\circ$. As can be seen in Figure 19, the shift observed is $\approx 25^\circ$, in good agreement with this prediction. As the azimuthal angle is varied from $\phi = -90^\circ$ to $0^\circ$, the maximum in the scattering distribution is rotated out of the plane of detection. Figure 30 is a diagram of the scattering and detector geometry for the two limiting cases, (a) $\phi = -90^\circ$ and (b) $\phi = 0^\circ$. In Figure 30(a), the incident beam, the scattered beam, the macroscopic surface normal, the terrace normal and the detector are all in the same plane, such that the detection plane includes the maximum in the scattering distribution. As depicted in Figure 30(b), when the projection of the beam on the surface is parallel to the step edges ($\phi = 0^\circ$), the incident beam, the macroscopic surface normal and the detector lie in the same plane, but the
\( \gamma = 12.3 \) Angle of cut from (III) surface

\[ \alpha + 2\gamma = \beta \]

\( N_m = \text{Macroscopic normal} \)

\( N_t = \text{Terrace normal} \)

Figure 29. Schematic diagram of macroscopic and microscopic specular scattering from a stepped surface.
$\phi = -90^\circ$. The beam impinges perpendicular to the step edges, away from the open side of the step structure.

$\phi = 0^\circ$. The beam strikes into the paper, in the plane defined by the macroscopic surface normal and the detector.

--- In the plane of the paper

----- Below the plane of the paper

Figure 30. Schematic diagram of the scattering geometry from a stepped surface for the two extremes in azimuthal angle accessible to this study.
terrace normal and the maximum in the scattering distribution do not. In this case, the detector measures only slices of the scattering distribution. This is why, as the azimuthal angle approaches $0^\circ$, the intensity of the scattering distribution decreases.

The presence of the second peak near the macroscopic surface normal and the behavior of the two peaks as a function of polar angle of incidence, $\theta$, are indicative of rainbow scattering. This phenomenon is most apparent when the beam of helium atoms strikes perpendicular to the step edges. Since no out-of-plane measurements were made, only the results for $\phi \sim -90^\circ$ will be commented on in this context.

Rainbow scattering was first predicted by the classical calculations of McClure$^{18,19}$. The behavior of the two peaks as a function of angle of incidence, for $\phi \sim -90^\circ$ shown in Figures 25-28, follow the qualitative predictions of these calculations$^{20}$, i.e. as the angle of incidence becomes more grazing, the intensity of the two peaks increases and they move towards each other. When the helium atoms are incident near the macroscopic surface normal, the full strength of the corrugated surface potential is sampled, such that the rainbow peaks are widely separated. The lower intensity of the peaks near normal incidence can be attributed to a preferential transfer of normal momentum and the increased apparent roughness of the surface. At more grazing angles of incidence, the periodic surface
potential is less well resolved and the surface appears smoother to the incident helium atoms, such that the rainbow peaks merge and increase in intensity.

The relative intensities of the two peaks may be explained in terms of the geometry of the surface. Since the terrace is five atomic rows wide and the step is monatomic, the flat region around the inflection point in the terrace potential will be larger than that of the step. Therefore, there will be a higher probability of directed scattering from the terrace. The step inflection point may also be shadowed\(^{21}\) by the step edge because the open side of the step structure is directed away from the incident helium atoms.

A recent review article\(^2\) has discussed in detail the classical, semiclassical and quantum mechanical theories which have been developed since the work of McClure, and compared these theories with the available experimental data. One of the quantum mechanical theories, called the RR\(^1\) method, has been applied to the scattering of monoenergetic helium atoms from a Pt(S)-[5(111)x(111)] surface, for \(\phi = -90^\circ\).\(^{22}\) This is a numerical method which can treat rigorously any bounded surface corrugation. The hard corrugated surface model used in the calculation corresponds to the depicted in Figure 29. This is, of course, a rather crude model, such that only the large peak associated with scattering from the terraces is reproduced. A softer potential would be more realistic, and perhaps would produce
the second peak observed experimentally. The calculation gave diffraction features which generally lie within the rainbow envelope of the experimental results shown in Figures 25-28, and reproduced the position of the larger peak.

In a recent study of helium scattering from the stepped Cu(117) surface\textsuperscript{23} at 100\(^\circ\)C, diffraction was observed. The intensities of the diffracted beams were modulated by the rainbow envelope. This work was performed using a nozzle beam with a narrow velocity distribution and an angular aperture of 0.25\(^\circ\). The detector aperture was also 0.25\(^\circ\). The helium atoms were incident perpendicular to the step edges, into the open side of the step structure, with an angle of incidence of 60\(^\circ\). The qualitative shape of the rainbow envelope is quite similar to the results presented here, with the maximum intensity at the specular angle to the terraces, a bump around the macroscopic specular and a small subspecular peak which they attribute to the interaction potential in the vicinity of the step edges. The authors indicate qualitative agreement with the RR' predictions and the possibility of fitting this model to the experimental data to obtain the helium-metal interaction potential near the step edges.

The absence of well resolved diffraction features in the experimental results presented here may be attributed to several factors in the experimental conditions. The surface temperature was high, 800\(^\circ\)C, the incident helium
beam was at room temperature with an approximately Maxwellian velocity distribution and an angular divergence of \( \sim 2^\circ \), and the acceptance angle of the detector was \( \sim 5^\circ \). Under these conditions, it is reasonable that the rainbow envelope was observed, with no distinct diffraction features.

The conclusion that can be drawn from these results and comments is that the helium atoms are sensitive to the periodic potential introduced by an ordered array of steps and terraces on a metal surface. In order to determine the interaction potential, the experiments must be performed at low surface temperature with a monoenergetic beam such that the quantum theory is applicable.

5.2 He/Pt(111)

Several Pt(111) surfaces were studied by helium scattering, in order to probe the degree of perfection of the surfaces for use in reactive scattering studies. Presented in Figure 31 is the helium scattering distribution for the crystal used in the reactive studies which will be described in Chapter 6. For a crystal temperature of 520°C, the scattering distribution consists of a peak at the specular angle with a FWHM of 7° and with an intensity of 16.5% of the incident beam. The previously reported values for the same plane of platinum at the same surface temperature are 7° FWHM and 11% of the incident beam, indicating that the
Figure 31. Angular distribution of helium atoms scattered from the Pt(111) surface, for $\theta_i = 50^\circ$. 
Pt(111) surface used for the work presented here was quite smooth. The helium scattering distributions for the other Pt(111) samples examined were broader and less intense.
6. REACTIVE SCATTERING: $\text{H}_2$-$\text{D}_2$ EXCHANGE

Although the interaction of hydrogen with platinum has been extensively studied over the past twenty years, it is not well understood on the atomic scale. However, it has been established that the presence of monatomic steps in a (111) surface enhances the adsorption and dissociation of hydrogen relative to the flat surface.\textsuperscript{25-27}

The helium scattering results presented in 5.1 raise the question as to whether the direction of approach of the hydrogen molecules to the step structure will affect the probability of adsorption. To investigate this question, the $\text{H}_2$-$\text{D}_2$ exchange reaction has been studied as a function of the polar and azimuthal angle of incidence on two stepped surfaces, the Pt(S)-[5(111)X(111)] or Pt(553) and the Pt(S)-[6(111)X(111)] or Pt(332) and the Pt(111) surface utilizing the integral mode of detection. The results of this study will be presented in 6.1.

In an effort to extend and clarify earlier work in this laboratory on the mechanism of $\text{H}_2$-$\text{D}_2$ exchange on the Pt(111) and two stepped surfaces, the Pt(997) and Pt(553)\textsuperscript{25}, more detailed studies of the reaction have been made on the Pt(111) and stepped Pt(332) surfaces. By using the integral mode of detection and a mixed beam of reactants, at lower modulation frequencies than the previous study, the overall quality of the data has been improved. This work will be discussed in 6.2.
6.1 Dependence on Reactant Angle of Incidence (Polar and Azimuthal)

6.1.1 The Pt(553) or Pt(S)-[5(111)X(111)] surface

The Pt(553) crystal used in the helium scattering studies presented in 5.1 was also employed in this work. The crystal was remounted in the same manner, but rotated ~180° such that the open side of the step structure was accessible to the incident beam.

These experiments were performed with a modulated beam of H₂, with an average equivalent pressure of ~10⁻⁷ torr at the surface, and ~10⁻⁶ torr of D₂ in the scattering chamber. The integral mode of detection was utilized. The H₂ beam was modulated at 2.5 Hz by the flag chopper. Since this chopper is mounted inside the scattering chamber, no integral mode measurement of the beam could be made. The HD product signal was normalized to the direct beam measurement of H₂, and therefore is given in arbitrary units. The crystal temperature was 1100°C, measured with an optical pyrometer.

Presented in Figure 32 is the production of HD as a function of the polar angle of incidence, θ, of the H₂ beam. As depicted in the insert, the azimuthal angle is φ = 90°, such that the beam impinges perpendicular to the step edges. The apparent reaction probability is highest when the beam is incident at grazing angles into the open
Figure 32. HD production on the Pt(553) surface as a function of the polar angle of incidence, $\theta$, of the $H_2$ beam, with $10^{-6}$ torr of $D_2$ in the scattering chamber, for $\phi = 90^\circ$.
side of the step structure, decreasing by approximately a factor of two from $\theta = 60^\circ$ to $\theta = -60^\circ$.

Figure 33 gives the results for the variation in HD production as a function of azimuthal angle. The polar angle of incidence is $\theta = 45^\circ$, measured from the macroscopic surface normal, as indicated in the insert. Again, the apparent reaction probability is highest when the beam strikes into the open side of the step structure. As $\phi$ varies from $-90^\circ$ to $+90^\circ$, the production of HD increases by almost a factor of two.

6.1.2 The Pt(332) or Pt(553)[6(111)X(111)] surface

In order to compare the results on different crystal surfaces under identical conditions, three crystals were mounted on the alumina bar. A strip of polycrystalline tantalum foil was bolted to the alumina bar and the three crystals were mounted by spot welding the tantalum to the edges of the crystals. The Pt(332) crystal was placed in the center of the bar with a Pt(111) crystal on one side and a new Pt(553) crystal on the other. Indirect heating of the crystals was achieved by passing a current through the tantalum foil. The crystal temperatures were measured using an optical or infrared pyrometer.

The new Pt(553) crystal was so contaminated with silicon and phosphorus that it could not be cleaned. Therefore, no results were obtained from this second sample.
Figure 33. Production of HD on the Pt(553) surface as a function of the azimuthal angle of incidence, Φ, of the H₂ beam, with 10⁻⁵ torr of D₂ in the scattering chamber, for θ = 45°.
The experiments on the Pt(332) surface were performed with a mixed beam of H$_2$ and D$_2$ with an H$_2$/D$_2$ ratio of $\sim$5/1 to 12/1 and an average intensity on the order of $10^{13}$-$10^{14}$ molecules/cm$^2$ sec at the surface with the chopper on. The method of detection was the integral mode. The HD product signal was normalized to the integral mode measurement of D$_2$ in the beam and multiplied by $[1 + (I_{D2}/I_{H2})]$, where $I_{D2}/I_{H2}$ is the ratio of D$_2$ to H$_2$ in the beam.

To assure that the beam of reactants strikes the center of the crystal at each angle of incidence, scans were made of the HD production as a function of the crystal position, both across and up and down. These scans also revealed the importance of spot weld damage on the edges of the crystal. Shown in Figure 34 are scans across the Pt(332) surface at normal incidence after three different mechanical polishing and chemical etching treatments prior to mounting the crystal. In particular, curve A, obtained when the crystal had considerable spot weld damage at the edges, demonstrates the enhancement in the production of HD due to crystal imperfections. For all of the results reported here, the crystal was positioned such that the beam was incident in the central flat position of the scan.

In Figure 35(a), the production of HD as a function of azimuthal angle is presented. As depicted in the insert, the angle of incidence is $\theta = 45^\circ$, measured from the macroscopic surface normal. These results were obtained with a
Figure 34. HD production as a function of the position of the mixed H$_2$-D$_2$ beam on the Pt(332) surface, for three different mechanical polishing and chemical etching treatments.
Figure 35. Dependence on the azimuthal angle of incidence, Φ, for θ = 45°, of the mixed beam of H₂ and D₂ on the Pt(332) surface of: (a) HD production and (b) the amount of D₂ withdrawn from the beam by conversion to HD.
beam modulation frequency of 10 Hz and a crystal temperature of 800°C. The vertical scale is the apparent reaction probability corrected for the ratio of D₂/H₂ in the beam. For the typical beam composition used in this work, the correction was ~ 0.1-0.2. The form of this expression will be discussed below. As found for the Pt(553) surface, the apparent reaction probability is highest when the beam of reactants strikes the open side of the step structure, increasing by approximately a factor of two from φ = -90° to 90°.

Plotted in Figure 35(b) is ΔD₂, the difference between the integral mode measurements of D₂ in the beam and emitted from the Pt(332) surface, which should correspond to the amount of D₂ converted to HD. As expected, this data follows the trend observed for the production of HD.

Presented in Figure 36(a) and (b) are the results for the production of HD as a function of polar angle of incidence, also at 10 Hz and 800°C. For curve (a), the azimuthal angle is φ = 90°, 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), for φ = 0°. When φ = 90°, the production of HD increases smoothly from θ = -60° to 0°, 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. When the reactant
Figure 36. HD production as a function of the polar angle of incidence, $\theta$, of the mixed beam of H$_2$ and D$_2$. (a) On the Pt(332) surface, for $\Phi = 90^\circ$. (b) On the Pt(332) surface, for $\Phi = 0^\circ$. (c) On the Pt(111) surface.
beam is incident at glancing angles into the open side of the step structure, the formation of HD is most favorable, as found on the Pt(553) surface. Again, a decrease of approximately a factor of two is observed as θ varies from 60° to -60°, where the inner corner of the step structure is shadowed. There is no variation in the apparent reaction probability with angle of incidence for φ = 0°, shown in curve (b). As expected, the two curves coincide at normal incidence.

To investigate whether this angular effect is present at lower crystal temperatures, a series of experiments were performed for crystal temperatures down to 200°C, with a beam modulation frequency of 1.8 Hz. Shown in Figure 37 is the variation in HD production as a function of polar angle of incidence, for φ = 90°, at various crystal temperatures. Since the flag chopper was used to modulate the reactant beam, no integral mode measurement of the beam was possible. Therefore, the HD was normalized to the direct beam measurement of D₂ and is reported in arbitrary units. As can be seen in Figure 37, the angular dependence of the apparent reaction probability is even more drastic at the lower temperatures. At 200°C, the production of HD increases by almost a factor of five as θ varies from -60° to +60°. However, as shown in Figure 38, when the crystal temperature is 100°C, a continuous decrease in the formation of HD is observed with time. The arrows in the figure indicate the order, in time, of the measurements. Despite the
Figure 37.
HD production on the Pt(332) surface as a function of the polar angle of incidence, $\theta$, for $\theta = 90^\circ$, at several crystal temperatures.
Figure 38. Production of HD as a function of the polar angle of incidence, $\theta$, of the mixed beam of $H_2$ and $D_2$ on the Pt(332) surface, for $\phi = 90^\circ$ and $T = 100^\circ$C. The arrows indicate the order in time of the measurements.
decrease with time, which is probably due to adsorption of background gases, the strong angular dependence does not seem to be present, but no definite statements can be made to this effect.

6.1.3 The Pt(111) surface

The mounting and experimental procedure described in the previous section for the Pt(332) surface were also used for the reactive scattering studies for the Pt(111). As mentioned in 5.2, the crystal used in this work was the Pt(111) sample which exhibited the highest reflectivity for helium, indicating that this surface was quite smooth.

In Figure 36(c) is shown the dependence of HD production on the polar angle of incidence, \( \theta \), for a crystal temperature of 800°C and a beam modulation frequency of 10 Hz. The apparent 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 on azimuthal angle was observed for the \( \text{H}_2-\text{D}_2 \) exchange reaction on Pt(111), although a variation of less than \( \pm 10\% \) is possible due to scatter in the experimental data.

6.1.4 Beam temperature dependence

The production of HD was monitored as the molecular beam was heated from 25°C to 300°C to investigate whether the angular dependence observed can be attributed to an activation energy barrier for adsorption. Within the experimental
uncertainty, no significant variations were observed. The results indicate that, if any, the activation energy for adsorption is below 0.5 kcal/mole for the Pt(111), Pt(332), and Pt(553) surfaces.

6.1.5 Discussion

The H$_2$-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. Although the cross-sectional area of the beam on the surface changes with polar angle of incidence, no change in the phase lag of the HD product signal is observed, indicating that the concentration of surface intermediates is not affected significantly. The same trend in the production of HD is observed with variation in azimuthal angle, where the cross-sectional area of the beam on the surface is constant. The angular dependence may be explained by 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.

For the two stepped surfaces, Pt(S)-[5(111)X(111)] and Pt(S)-[6(111)X(111)], the apparent reaction probability is highest when the reactants strike the open side of the step structure directly, revealing the unique properties of the step site(s) for H-H bond breaking.
Measurements of the variation of the work function with coverage indicate that there are two types of sites for hydrogen adsorption on the stepped Pt(S)-[9(lll)X(lll)] surface not found on the flat Pt(lll) surface, which were tentatively associated with the top and inner corner of the step edges.

Tsang and Falicov have calculated the one-hole charge density angular distributions of the orbitals of transition metals ions in various crystalline geometries on stepped surfaces. For fcc metals, the stepped surface treated was of the n(100)X(100) configuration. 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 at an angle. The activity for H-H bond breaking of the different sites on a stepped platinum surface of the n(lll)X(100) configuration was calculated in this theoretical framework. The most active site was found to be that associated with the inner corner atom. If these results also hold for a stepped surface of the n(lll)X(lll) configuration, the experimentally observed angular dependence of the apparent reaction probability would correspond to the change in the number of reactant molecules striking the inner corner of the step structure as a function of angle of incidence.
A simple calculation of the angular dependence predicted by the above arguments can be made in the following manner. The step site is taken to be the inner corner atom and its next nearest neighbors. The incident beam is divided between the available area of the step site and that of the terrace. Since no angle of incidence dependence was observed experimentally on the Pt(332) surface when the projection of the incident beam on the surface is parallel to the step edges ($\phi = 0^\circ$), the reaction probability per unit area on the terraces is taken to be that for the Pt(111) surface at normal incidence. The reaction probability per unit area of the step site is used as an adjustable parameter.

Figures 39 and 40 present the results of such a crude calculation, with the experimental data for the variation with angle of incidence, azimuthal, $\phi$, and polar, $\theta$, respectively. The parameter $R$ is the ratio of the reaction probability per unit area of a step site to that of a terrace site. The agreement between the calculated curves and the experimental data is remarkably good when the step site is assumed to be seven times more active than a terrace site.

Dependence of the apparent reaction probability on the angle of incidence of the reactants can be an indication of an activation energy barrier for adsorption. The fraction of reactant molecules that have a component of velocity
Figure 39. Comparison of the calculated dependence of HD production on the azimuthal angle of incidence, Φ, with the experimental data from Figure 35(a), for θ = 45°, on the Pt(332) surface. R is the ratio of the reaction probability per unit area of a step site to that of a terrace site.
Figure 40. Comparison of the calculated dependence of HD production on the polar angle of incidence, $\theta$, with the experimental data from Figure 36(a), for $\Psi = 90^\circ$, on the Pt(332) surface. $R$ is the ratio of the reaction probability per unit area of a step site to that of a terrace site.
perpendicular to the surface large enough to overcome the
barrier $D$ is given by $\exp(-D/RT\cos^2\theta)$ such that
\[ \sigma = \sigma_0 \exp(-D/RT\cos^2\theta) \] (16)
where $\theta$ is the angle of incidence of the molecular beam.
In Figure 41, the angle of incidence dependence predicted
by Equation 16 for various values of $D$ are shown as continuous lines. The data points are the results of two experiments on the Pt(111) surface at a crystal temperature of 800°C and a beam modulation frequency of 10 Hz. The vertical axis is the apparent reaction probability corrected for the ratio of $D_2$ to $H_2$ in the beam. The values of $D$ that best fit the experimental data are below 0.5 kcal/mole.

Another probe of the existence of an activation energy barrier for adsorption is to vary the energy of the incident reactants. Balooch and coworkers\textsuperscript{30}, for example, were able to correlate the beam energy dependence with the angle of incidence dependence for hydrogen adsorption on several faces of copper. As mentioned previously, the temperature of the beam of reactants was varied from 25-300°C in this work, which should be equivalent to varying the angle of incidence by 45°. The results of the beam temperature variation experiments indicate that the activation energy must be less than 0.5 kcal/mole, in agreement with the calculated values for $D$ on the Pt(111) surface.

The apparent reaction probability was independent of angle of incidence on the Pt(332) surface when the projection of the beam of reactants on the surface was parallel
Figure 41. Comparison of the experimental dependence of HD production on the polar angle of incidence, $\theta$, on the Pt(111) surface with that predicted by Equation 16, for various values of the activation energy for adsorption, $D$. 
to the step edges (Figure 36(b), for $\phi = \eta^0$). The relative proportion of reactants striking the step and terrace sites is constant in this experiment. It therefore seems reasonable to conclude that although a small activation energy barrier, less than 0.5 kcal/mole, may be present on the Pt(111) surface, adsorption of hydrogen on the Pt(332) surface is not an activated process. This point will be commented on further in the discussion of the reaction mechanism in 6.2.

These experiments were performed in the range of crystal temperatures and beam modulation frequencies where the phase lag of the product HD signal was zero for both the Pt(111) and Pt(332) surfaces and the apparent reaction probability on the Pt(332) surface was independent of crystal temperature. The rate determining step in this regime is the adsorption of the reactants. The long lived surface species in the adsorption of hydrogen on platinum single crystals have been shown to be atomic by flash desorption experiments. 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 angular dependence observed suggests that the dissociation is not preceded by diffusion to an active site, such as the step. If molecular diffusion played an important role, the reaction probability would be independent of the direction of approach of the reactants.
Therefore, the only surface intermediates will be H and D atoms.

Let us assume that the exchange reaction is a simple second order process, represented as:

\[ 2H_2(gas) + 2D_2(gas) \xrightarrow{\sigma} 4H(ads) + 4D(ads) \xrightarrow{k_r} \]
\[ H_2(gas) + D_2(gas) + 2HD(gas) \]

where \( \sigma \), the sticking coefficient is assumed to be the same for \( H_2 \) and \( D_2 \) and \( k_r \) is the rate constant for recombination.

The surface mass balances for the atomic intermediates are:

\[
\frac{dn_H}{dt} = 2\sigma I_{H2} g(t) - 2k_r n_H^2 - 2k_r n_H n_D
\]  

(17)

\[
\frac{dn_D}{dt} = 2\sigma I_{D2} g(t) - 2k_r n_D^2 - 2k_r n_H n_D
\]  

(18)

where \( n_H \) and \( n_D \) are the number of H and D atoms, respectively, per cm\(^2\) on the surface, \( I_{H2} \) and \( I_{D2} \) are the number of \( H_2 \) and \( D_2 \) molecules, respectively, striking the surface per cm\(^2\) sec and \( g(t) \) is the gating function of the mixed molecular beam.

Solving Equations 17 and 18, using the approximate method of Olander and Ullman\(^{14}\), the following expressions for the apparent reaction probability, \( \varepsilon \), and the phase lag, \( \phi \), are obtained.
where \( \omega \) is the beam modulation frequency.

As indicated by the absence of any measurable phase lag for the HD product signal, the reaction time is short compared to the modulation period, under the experimental conditions of low modulation frequency, 10 Hz, and high crystal temperature, 800°C. For \( \phi = 0 \), \( \tan \phi = 0 \) and Equation 19 simplifies to:

\[
\varepsilon = \frac{2\sigma}{1 + \frac{I_{D_2}}{I_{H_2}}} \tag{21}
\]

By definition, \( \varepsilon = \frac{HD}{D_2} \) where HD represents the product signal and \( D_2 \) the incident \( D_2 \) signal. Rearranging Equation 21, we have

\[
\frac{HD}{D_2} (1 + \frac{I_{D_2}}{I_{H_2}}) = 2\sigma = \tau \tag{22}
\]

where \( \tau \) represents the apparent reaction probability corrected for the ratio of \( D_2 \) to \( H_2 \) in the beam.

The vertical axis in Figures 35, 36, and 39-41 is then \( 2\sigma \) and the trend observed is the variation of the sticking coefficient for dissociative adsorption as a function of angle of incidence, polar and azimuthal.
At very high modulation frequencies, an apparent decrease in the production of HD is observed, as well as a phase lag between the reactant and the product signals, due to demodulation of the first harmonic of the product signal. This demodulation indicates that the reaction time is comparable to or greater than the modulation period. Under such conditions, Equations 19 and 20 are appropriate and Equation 21 is no longer valid. By choosing the appropriate surface temperature and modulation frequency, the demodulation can be avoided.

The mechanism of the \( \text{H}_2-\text{D}_2 \) exchange reaction on the Pt(111) and Pt(332) surfaces, the topic of 6.2, is more complex than a simple second order process. However, the conditions under which these angular dependence experiments were performed are such that only the interpretation of \( \sigma \) changes. This will be discussed more fully in 6.2 in the context of the proposed reaction models.

In order to compare the sticking coefficient deduced from these data with that reported by other authors, the isotropic sticking coefficient must be calculated by integrating the angular data over all angles of incidence. The data for the dependence on azimuthal angle were fit by a sine function, shown as the solid line in Figure 35(a). The functional shape of this dependence is assumed to be the same for all angles of incidence. For the polar angle of incidence dependence, the solid lines drawn through the
data points in Figure 36(a) and (b) and the dotted line in (c) were used to perform the integration.

Such an integration procedure gives values for the sticking coefficient for hydrogen on the Pt(332) surface of $\sigma = 0.36$ or 0.35, depending on how the extrapolation from $\pm 60^\circ$ to $\pm 90^\circ$ angle of incidence is performed. Due to possible differences in the pumping speed and mass spectrometer sensitivity for HD and D$_2$ ($\sim$20%) and uncertainties in the integration procedure ($\sim$5%), the absolute value of $\sigma$ should be regarded as correct to within $\sim$25%.

The data for the Pt(111) surface was integrated over all angles of incidence to give a value of $\sigma = 0.07$, with the same 25% uncertainty.

The ratio of the sticking coefficient on the Pt(332) surface to that on the Pt(111) surface is equal to five. The uncertainty in the ratio should be less than $\sim$10%.

The result for the Pt(111) surface is in fairly good agreement with that reported by Ertl and coworkers,$^27,31$ $\sigma \sim 0.1$. The same laboratory$^27$ has obtained a value of $\sigma = 0.35$ for the Pt(S)-[9(111)X(111)] surface, which is comparable to the result for the Pt(S)-[6(111)X(111)] in this work, although the step density differs by a factor of 1.5. The ratio of the sticking coefficient for hydrogen on the Pt(S)-[9(111)X(111)] to that on the Pt(111) was reported to be equal to four.$^27$
Since the ratio between the sticking coefficients measured in the same laboratory tends to cancel some of the experimental uncertainties, a comparison of the ratios of the results on the stepped surfaces to those on the Pt(111) with the ratio of the step densities may be instructive. The ratio of the sticking coefficient ratios is \( \frac{5}{4} = 1.25 \), and the step density ratio is \( \frac{9}{6} = 1.5 \), suggesting that the isotropic sticking coefficient does not depend linearly on the step density.

Other measurements of the sticking coefficient for hydrogen on Pt(111) include those of Smith and Merrill\(^{34} \), \( \sigma = 0.07 \), Lu and Rye\(^{26} \), \( \sigma = 0.016 \), and McCabe and Schmidt\(^{33} \), \( \sigma = 0.1 \). The rate of \( \text{H}_2\)-\( \text{D}_2 \) exchange on this surface has been reported by Bernasek and Somorjai\(^{25} \) to be three orders of magnitude lower than that on a stepped surface. No clear cut explanation has been found for the discrepancy between the results reported here and some of the other observations.
6.2 The Mechanism of the $H_2$-$D_2$ Exchange Reaction on Pt(111) and Pt(332) Crystal Surfaces

As discussed in Chapter 3, the modulated molecular beam technique can be used to examine the kinetics and mechanism of surface catalyzed chemical reactions. The experimentally observed behavior of the product signal amplitude and phase lag relative to the incident reactants as a function of the temperature of the surface and the modulation frequency, pressure, and temperature of the beam of reactants must be fit to a theoretical reaction model in order to obtain the kinetic parameters.

Since the surface temperature is an important variable for these studies, the Pt(111) and Pt(332) crystals were remounted as shown in Figure 42, such that a chromel-alumel thermocouple could be spot welded to the edge of each crystal. Thermocouples could be used with the mounting for angular variation, but they tended to short and fall off after changing the angle a few times. As depicted in Figure 42, three crystals could be mounted simultaneously. The Pt(111) crystal was mounted on top, the Pt(332) in the middle, oriented such that the step edges were perpendicular to the incident beam direction, and a Pt(110) crystal at the bottom, oriented such that the rows and troughs were perpendicular to the incident beam direction.
Figure 42. Schematic diagram of the crystal holder.
The surface structure of the Pt(110) crystal was found to be extremely sensitive to small amounts of contamination, particularly oxygen. The LEED pattern for this surface was different almost every day, and often varied for different areas on the surface. Since the surface could not be well characterized, no systematic studies were made on this crystal.

For both the Pt(111) and Pt(332) surfaces, the experiments were performed in the following manner. A mixed beam of \( \text{H}_2 \) and \( \text{D}_2 \) was used, with a ratio of \( \text{H}_2/\text{D}_2 \) of \( \sim 5/1 \) to \( 1:1 \) and an average intensity on the order of \( 10^{13} - 10^{14} \) molecules/cm\(^2\) sec at the surface with the chopper on. The crystal to be studied was heated to \( \sim 1000^\circ \text{C} \) and the HD signal was monitored in the integral mode as the crystal temperature decreased to room temperature. The output of the appropriate thermocouple was simultaneously recorded. Integral mode measurements of the reactants were made at the beginning and end of each run. The HD product signal was corrected phase by phase for the contribution of HD from the beam, normalized to the integral mode measurement of \( \text{D}_2 \), and multiplied by \( [1 + (I_{\text{D}_2}/I_{\text{H}_2})] \) to obtain the apparent reaction probability corrected for the ratio of \( \text{D}_2 \) to \( \text{H}_2 \) in the beam, \( r \), as discussed in 6.1.5.

6.2.1 The Pt(332) surface

The amplitude, \( r \), and the absolute value of the tangent of the phase lag, \( \phi \), of the HD product signal are
plotted in Figures 43 and 44 as a function of reciprocal crystal temperature, for various modulation frequencies. As shown in the insert, the angle of incidence is $\theta = 45^\circ$, measured from the macroscopic surface normal and the azimuthal angle is $\phi = 90^\circ$, such that the reactant beam impinges into the open side of the step structure. Each set of data points corresponds to experiments that were performed on different days and thus with slightly different beam intensities and composition. Measurements were also made for $\theta = 45^\circ$ and $\phi = -90^\circ$, where the open side of the step structure is directed away from the incident beam. The shape of the experimental curves is identical to that shown in Figures 43 and 44, but the amplitude is almost a factor of two smaller, as found in the experiments discussed in 6.1.

The predictions of the theoretical models given in Chapter 3 indicate that the behavior of the phase lag is more sensitive to the mechanism of the reaction than is the amplitude. As can be seen in Figure 44, the variation in the absolute value of $\tan \phi$ as a function of reciprocal crystal temperature is quite complex. The scatter in the experimental data at high temperature is due to the fact that the phase lag approaches zero, and must be obtained by subtracting two measured phases, corresponding to the incident $D_2$ (or $H_2$) and the reaction product HD. The phase lag and therefore $\tan \phi$ increases
Figure 43. Arrhenius plots of the amplitude of the HD product on the Pt(332) surface, for various beam modulation frequencies. The calculated curves for reaction model II are shown as continuous lines.
Figure 44. Arrhenius plots of the absolute value of tan φ for the HD product on the Pt(332) surface, at various modulation frequencies. The filled circles and squares correspond to negative values of tan φ. The continuous lines are the predictions of model II. The dashed curve was calculated using model I at f = 50 Hz. The dotted and dashed curves were computed for a series process.
as the crystal temperature decreases. An inflection in
the curves is observed between ~300 and 200°C, followed
by an approximately linear increase. At the lowest tem­
peratures, the phase lag increases sharply to greater than
90°, such that \( \tan \phi \) becomes very large and changes sign.
The filled circles and squares in Figure 44 represent nega­
tive values of \( \tan \phi \). The temperature at which \( \phi = 90° \)
depends on the modulation frequency and is lower at low
frequency. The scatter in the data is again large at low
crystal temperatures because the amplitude of the product
signal is small, as can be seen in Figure 43.

For crystal temperatures below ~100°C, the cool­
ing rate was controlled by the thermal conductivity of the
support, and was therefore quite slow. Each set of data
points was obtained in 30-60 minutes. The results were
reproducible from day to day, except for a variation of
approximately 10° in the phase lag, most probably due
to changes in the beam intensity and composition. For a
second order reaction, the phase lag depends on the re­
actant pressure.12

As shown in Figure 43, the amplitude of the HD
product is constant over a wide range of crystal temper­
atures, but decreases at the lower temperatures. The
temperature at which the production of HD decreases is
higher at high modulation frequency. A decrease in the
HD product amplitude is also observed at the highest
crystal temperatures studied, above ~800°C.
6.2.2 The Pt(111) surface

Presented in Figures 45 and 46 are the variations in the amplitude, \( r \), and the absolute value of the tangent of the phase lag, \( \phi \), for the HD product as a function of reciprocal crystal temperature, for various modulation frequencies. The mixed beam of reactants was incident normal to the surface, \( \theta = 0^\circ \).

The qualitative behavior of the absolute value of \( \tan \phi \) as a function of crystal temperature is quite similar to that observed for the stepped Pt(332) surface, although the slope of the linear region below \( \sim 300^\circ \)C is somewhat steeper. (Compare Figures 44 and 46.)

The dependence of the amplitude of the HD product on the crystal temperature on the Pt(111) surface differs from the results on the stepped surface in that the apparent reaction probability is not constant at high temperatures. On the Pt(111) surface, the HD amplitude is observed to decrease continuously with decreasing temperature. The shallow slope of the high temperature region is followed by a steeper decrease at lower temperatures. The temperature at which the change in slope is observed depends on the modulation frequency, and is higher at high frequency.

A hysteresis was observed in the behavior of the amplitude and the phase lag between results obtained as the crystal was cooled and those obtained as the crystal...
Figure 45. Arrhenius plots of the amplitude of the HD product on the Pt(111) surface, for various beam modulation frequencies. The continuous lines were computed using reaction model II.
Figure 46. Arrhenius plots of the absolute value of tan $\phi$ for the HD product on the Pt(111) surface, at various modulation frequencies. The filled circles and triangles correspond to negative values of tan $\phi$. The predictions of model II are shown as continuous lines.
was heated over the same temperature range. This effect was present for both the Pt(111) and Pt(332) crystals. An example of this behavior is given in Figure 47, for the phase lag of the HD product on the Pt(111) surface. As can be seen in the figure, the phase lag is greater in the high temperature region for the heating cycle. The hysteresis may be due to adsorption of background gases while the crystal is at low temperature, which are desorbed as the crystal is heated. For a heating cycle, the amplitude of the product signal is found to be lower than that observed for a cooling cycle up to ~600°C, in many cases. Above this temperature, the same result is found for both heating and cooling cycles. The reproducibility of the results is excellent for the cooling cycles, but only fair for the heating cycles. This could be caused by different exposure times at low temperature. The data obtained by cooling the crystal appears to be more reliable and therefore only these results that are plotted in Figures 43 - 46 were used in the determination of the mechanism of the reaction.

Segregation of silicon to the surface was observed in some of the experiments on the Pt(111) crystal, as the temperature decreased from ~1000°C to room temperature. As shown in Figure 48, the amplitude of the HD product signal is lower than that found on the clean
Figure 47. Hysteresis observed between heating and cooling cycles for the phase lag of the HD product on the Pt(111) surface.
Figure 48. The effect of silicon segregation to the Pt(111) surface on the production of HD. The dashed line represents the HD amplitude for the clean surface.
surface, indicated by the dotted line in the figure. The behavior of the phase lag was not markedly different for the clean or silicon contaminated surface. This suggests that the silicon may block sites on the surface, but does not change the mechanism of the reaction.

6.2.3 Discussion

The experimental results clearly indicate that the mechanism of the H₂-D₂ exchange is similar for both the Pt(111) and Pt(332) surfaces, despite the obvious differences in surface structure. In particular, the Arrhenius plots of the absolute value of the tangent of the phase lag of the HD product exhibit the same general features on both crystal surfaces. Below ~800°C, the absolute value of tan ϕ increases linearly with decreasing crystal temperature to around 350°C. Between ~300 and 200°C, an inflection is observed, followed by a second linear region. As the crystal temperature decreases further, the phase lag exceeds 90°, such that tan ϕ becomes very large, then changes sign. At high modulation frequencies, the phase lag reaches 90° at higher temperatures, distorting the linear region following the inflection. This behavior is indicative of a branched mechanism at high temperatures (two reaction steps acting in parallel) and a series mechanism at low temperatures (two or more sequential reaction steps). Other mechanisms could also possibly explain these results, as will be discussed below.
Studies of the adsorption of hydrogen and H₂-D₂ exchange on flat and stepped Pt(111) surfaces by thermal desorption indicate that the adsorbed species are atomic and that the recombination is a second order reaction. The observation in this work that the phase lag of the product signal depends on the reactant pressure is also characteristic of a second order process. No systematic study was made of this dependence due to the difficulties in maintaining the same ratio of H₂/D₂ while varying the total reactant pressure. However, in comparing the phase lag data from experiments performed on different days and thus with slightly different beam pressure and composition, a vertical displacement on the order of ± 5° was required to make the curves coincide.

In order to extract the kinetic parameters from the experimental results, the simplest theoretical model that is physically reasonable and best fits the data must be found. Several simplifying assumptions were made in order to derive a model for the kinetics of this reaction. In view of the angular dependence of the exchange reaction on the Pt(332) surface discussed in 6.1, the diffusion of molecular H₂ and D₂ is neglected. Since the apparent reaction probability is highest when the beam of reactants strikes most directly into the open side of the step structure, at least for temperatures above 200°C, the molecular diffusion distance must be less than the
terrace width, \( \sim 13 \, \text{\AA} \), i.e., the \( \text{H}_2 \) and \( \text{D}_2 \) molecules dissociate upon impact. Isotope effects in the adsorption and dissociation of \( \text{H}_2 \) and \( \text{D}_2 \) and in the diffusion and recombination of \( \text{H} \) and \( \text{D} \) atoms are not included. Although this assumption may not be strictly valid, the error introduced into the pre-exponential factors should be less than that due to the uncertainty in the absolute beam intensity, and will not change the order of magnitude. The flux of \( \text{H}_2 \), \( \text{D}_2 \) and \( \text{HD} \) from the background of the scattering chamber was \( \sim 10^{-2} - 10^{-3} \) times less than that from the beam and therefore was neglected in the model derivations. The pumping speed was assumed to be the same for \( \text{H}_2 \), \( \text{D}_2 \) and \( \text{HD} \).

Calculations of the predictions of various reaction models were made and compared to the experimental data of Figures 43-46 by Dr. Miquel Salmeron. The \( \text{H}_2-\text{D}_2 \) exchange reaction was treated as the recombination of two H atoms in the reaction models, on the basis of the assumptions above and that the expression for the HD amplitude, \( r \), explicitly takes into account the ratio of \( \text{H}_2/\text{D}_2 \) and is equal to twice the sticking coefficient for dissociative adsorption. A single step second order reaction, even with a coverage dependent adsorption probability, activation energy, or pre-exponential factor, was found to be insufficient to explain the experimental data. The model which yields the best fit to the results is a branched mechanism, including a series process at low temperatures.
In a review paper which discussed approximate methods for dealing with nonlinear surface processes, it was noted that maxima in the Arrhenius plot of the phase lag could be observed due to coverage dependence of the sticking coefficient or rate constant. This was examined as a possible explanation of the experimentally observed phase reversal as follows.

Consider a single step second order recombination of the form

\[ \sigma \frac{k}{H_2(\text{gas}) \rightarrow 2H(\text{ads}) \rightarrow H_2(\text{gas})} \]

The mass balance equation for the concentration of H atoms, \( n \), adsorbed on the surface is:

\[ \frac{dn}{dt} = 2\sigma s(\theta) I(t) - 2kn^2 \]           \hfill (23)

where the coverage dependent occupation factor \( s(\theta) \) is explicitly separated from the bare surface sticking coefficient \( \sigma \). \( I(t) \) is the number of molecules striking the surface per unit area and unit time at time \( t \), equivalent to \( Ig(t) \), where \( g(t) \) is the gating function. The rate constant \( k \) is expressed in the usual Arrhenius form as \( A_0 \exp (-E/RT) \) where \( A_0 \) is the pre-exponential factor and \( E \) is the activation energy.

The approximate method of Olander and Ullman was used to solve Equation 23 for \( s(\theta) = (1 - \theta)^2 \). The periodic function \( I(t) \) is approximated by:

\[ I(t) = I_0 + I_1 \exp (i\omega t) \]           \hfill (24)
where $I_0$ is the dc term of the Fourier expansion of $I(t)$, equal to $I/2$, $\omega = 2\pi f$, and $f$ is the beam modulation frequency. The variation of $\tan \phi$ with crystal temperature predicted by these equations does not show an inflection or any other of the experimentally observed features.

Calculations were then performed including a coverage dependent activation energy with a coverage dependent sticking coefficient of the form $s(\theta) = (1 - \theta)^2$. Two different expressions for the dependence of $E$ on $\theta$ were examined, $E(\theta) = E_0 - B\theta^2$ and $E(\theta) = E_0 \exp(-\theta/\theta_0)$. By choosing appropriate values of $B$ and $\theta_0$, the qualitative behavior of the Arrhenius plots of the values for $\tan \phi$ calculated using either of these expressions for $E(\theta)$ was similar to the experimental results. However, at low temperature, the calculated values for $\tan \phi$ were at least two orders of magnitude greater than the experimental data. This difference was not very sensitive to the analytical form of $E(\theta)$. The reason for the discrepancy is that at the transition temperature (between 200 and 300°C in this case) these models imply that the coverage becomes very large (near unity) such that the phase lag approaches 90°. Therefore, the predictions of this type of model are not consistent with the experimental results.

The effect of a coverage dependent pre-exponential in the Arrhenius expression for the rate constant, $k = A(\theta)\exp(-E/RT)$, was also investigated and found to be
inappropriate as an explanation of the experimental observations.

Apparently, a model which includes only a single step second order reaction, even with a coverage dependent sticking coefficient and rate constant, is insufficient to explain the experimental data. The rate constant and the sticking coefficient may be coverage dependent, but this dependence is not what determines the variation of \( \tan \phi \) with crystal temperature observed experimentally.

Calculations were performed for two models with two reaction steps acting in parallel, depicted schematically below. The parameter \( p \) is the branching probability.

\[
\begin{align*}
I. & \quad 2H_2(gas) \quad (l-p)\sigma \quad k_1 \quad 2H(ads)_1 \rightarrow H_2(gas) \\
& \quad p\sigma \quad k_2 \quad 2H(ads)_2 \rightarrow H_2(gas)
\end{align*}
\]

\[
\begin{align*}
II. & \quad 2H_2(gas) \quad (l-p)\sigma \quad k_1 \quad 2H(ads)_1 \rightarrow H_2(gas) \\
& \quad p\sigma \quad k_2 \quad 2H(ads)_2
\end{align*}
\]

Model I consists of two second order recombination processes which may occur simultaneously with different rate constants \( k_1 \) and \( k_2 \). The recombination in each branch is the rate limiting step. The surface mass balance equations for this mechanism are:
In model II, the rate limiting step in branch 1 is a second order recombination process with rate constant \( k_1 \). The transfer of atoms from sites 2 to sites 1 is the rate limiting step in branch 2, a first order process. The reverse transfer of atoms from sites 1 to sites 2 is neglected because at low crystal temperatures (\( T \leq 300^\circ C \)), sites 2 are completely covered (a result confirmed a posteriori) and at high crystal temperatures, the coverage of sites 1 is too small for any significant transfer of atoms to sites 2, as compared with the contribution from the incident beam to the occupancy of sites 2. For this reaction model, the surface mass balance equations are:

**Type 1 sites**

\[
\frac{dn_1}{dt} = 2(1-p)\sigma I(t) - 2k_1n_1^2
\]  
(25)

**Type 2 sites**

\[
\frac{dn_2}{dt} = 2p\sigma(1-\theta)^2 I(t) - 2k_2n_2^2
\]  
(26)

Expressions for the amplitude, \( r \), and the phase lag, \( \phi \), predicted by models I and II were obtained by
solving Equations 25 and 26, respectively, using the approximate method of Olander and Ullman. In both models, adsorption in branch 2 was assumed to be coverage dependent, with \( s(\theta) = (1 - \theta)^2 \). The periodic function \( \theta(t) \) is approximated by:

\[
\theta(t) = \theta_0 + \theta_1 \exp(\omega t)
\]  

(27)

Using the approximations of Equations (24) and (27) to solve the mass balance equations for each of the branches, the following expressions were found for the amplitude, \( r \), and the phase lag, \( \phi \).

**Model I**

\[
r \exp(-i\phi) = r_1 \exp(-i\phi_1) + r_2 \exp(-i\phi_2)
\]  

(28)

\[
\tan \phi_1 = \frac{\omega}{4[(1-p)\sigma I_o k_1]^{1/2}}
\]  

(29)

\[
r_1 = \frac{2(1-p)\sigma}{[1 + \tan^2 \phi_1]^{1/2}}
\]  

(30)

\[
\tan \phi_2 = \frac{\omega}{4[p\sigma I_o k_2]^{1/2}}
\]  

(31)

\[
r_2 = \frac{2p\sigma (1-\theta_0)^3}{[1 + \tan^2 \phi_2]^{1/2}}
\]  

(32)

\[
\theta_0 = [1 + \left( \frac{k_2 N_2}{p\sigma I_o} \right)^{1/2} - 1]
\]  

(33)
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$I_0$ is the average number of molecules from the beam impinging on the surface per unit area per unit time, $\theta_0$ is the mean coverage of type 2 sites, and $N_2$ is the number of sites 2 per unit area.

**Model II**

$$r \exp(-i\phi) = r_1 \exp(-i\phi_1)[(1 + \frac{P}{1-P} r_2 \exp(-i\phi_2)]$$ (34)

$$\tan \phi_1 = \frac{w}{2[4(1-p) \sigma I_0 k_1 + 2k_1 k_2 N_2 \theta_0]^{1/2}}$$ (35)

$$r_1 = \frac{2(1-p)\sigma}{[1 + \tan^2 \phi_1]^{1/2}}$$ (36)

$$\tan \phi_2 = \frac{w(1-\theta_0)}{k_2(1+\theta_0)}$$ (37)

$$r_2 = \frac{(1-\theta_0)^3}{(1+\theta_0)[1 + \tan^2 \phi_2]^{1/2}}$$ (38)

$$\theta_0 = \frac{1 - [1 - y]^2}{y}$$ (39)

where

$$y = [1 + \frac{k_2 N_2}{4 \rho \sigma I_0}]^{-1}$$

As the crystal temperature is varied, if the values of the pre-exponentials and activation energies are sufficiently different, there will be regions where one of the branches is dominant and other regions where both branches are active. In the fitting of these models to
the experimental data, it appears that the inflection observed around \(10^3/T \approx 1.9\) is the transition region between the two regimes, i.e. one branch dominates at low crystal temperatures and both are acting at high temperatures.

The low temperature branch is common to both models. When the crystal temperature is low, such that branch 2 is not active, \(k_2 = 0\), both models give:

\[
\tan \phi = \frac{w}{4\sigma I_o A_1^o \frac{1}{2} \exp(E_1/2RT)} = \frac{\pi f}{2A_1} \exp(E_1/2RT)
\]

where the rate constant \(k_1\) has been written in Arrhenius form as \(A_1^0 \exp(-E_1/RT)\). At low crystal temperatures, the Arrhenius plot of \(\tan \phi\) will be a straight line with slope \(E_1/2R\). The intercept at the origin provides the value for \(A_1 = [\sigma(1-p)I_o A_1^o]^{1/2}\), from which the pre-exponential factor \(A_1^0\) can be obtained if the other parameters are known.

The high temperature limit of the amplitude for both models is \(r = 2\sigma\), since in both cases \(\phi_1\) and \(\phi_2\) approach zero.

As discussed in Chapter 3, phase lags greater than \(90^\circ\) are characteristic of reactions with two or more sequential steps. The experimental observation that, at low crystal temperatures and high modulation frequencies, the phase lag exceeds \(90^\circ\) such that \(\tan \phi\) becomes negative indicates that another reaction path is acting in series with branch 1 of the preceding models. This is depicted schematically as:
or other similar processes. The phase lag for this model is given by:

\[ \phi = \phi_1 + \phi_3 \]  

\[ \tan \phi_1 = \frac{w}{k_1} \]  

\[ \tan \phi_3 = \frac{w}{k_3} \]

where \( k_1' = 4(\sigma(1-p)I_o k_1)^{1/2} \) for a second order process.

For the Pt(332) surface, the activation energy \( E_1 \) and the apparent pre-exponential factor \( A_1 \) corresponding to the low temperature branch were obtained directly from the experimental curves in Figure 44 for \( 10^3/T > 1.9 \). The average of the values measured for each set of experimental data are \( E_1 = 13.0 \pm 0.4 \text{ kcal/mole} \) and \( A_1 = (6 \pm 3) \times 10^4 \text{ sec}^{-1} \).

An estimate of \( A_1^0 \) can be made by substituting the values for the various parameters into the expression for \( A_1 \) given by both models, \( A_1 = [\sigma(1-p)I_o A_1^0]^{1/2} \). The value for \( \sigma \) is obtained directly from the high temperature limit of \( r, 2\sigma = 0.6 \text{ to } 0.7 \), such that \( \sigma \approx 0.33 \pm 0.03 \) for \( \theta = 45^\circ \) and \( \phi = 90^\circ \). The \( H_2 \) beam intensity is approximately \( 10^{13} - 10^{14} \text{ molecules/cm}^2 \text{ second} \). From the fitting of models I and II to the experimental data, the value of the
branching probability $p$ is $\approx 0.25$ for both models. The pre-exponential factor $A_1^0$ is therefore on the order of $10^{-3}$ cm$^2$/sec.

For a second order reaction which takes place on a surface, the pre-exponential factor predicted by transition state theory is given as $A = (kT/h)(Q^*/Q_H^2)$, where $Q^*$ is the partition function for the transition state, an H-H molecule, and $Q_H$ is the partition function for an adsorbed H atom. With $q_T$ and $q_R$ as the translational and rotational partition functions, respectively, $Q^* = q_T^2 q_R$ and $Q_H = q_T^2$, from which an order of magnitude estimate for $A$ of $10^{-3}$ cm$^2$/sec is obtained. The estimate for $A_1^0$ determined above is in good agreement with this prediction, confirming the assumption of second order kinetics.

Least squares fitting of Equations 28-33, for model I, and Equations 34-39, for model II, to the experimental data at 50 Hz was performed in order to obtain $p$, $A_2^0$, and $E_2$, where $k_2 = A_2^0 \exp(-E_2/RT)$. The values of $A_2^0$ and $E_2$ could not be uniquely determined due to the scatter in the results for tan $\phi$ at high crystal temperatures. Pairs of values of $A_2^0$ and $E_2$ related through the expressions $4 \log[\sigma \rho A_2^0 I_c]^{1/2} \approx E_2$ for model I and $2 \log(A_2^0) \approx E_2$ for model II were found to fit the experimental data approximately as well. Good agreement between the experimental results and the curves calculated for both models was obtained for values of $E_2$ ranging from...
20-50 kcal/mole. For the second order reaction step included in model I, the pre-exponential factor $A_2^0$ should be on the order of $10^{-3} - 10^{-1}$ cm$^2$/sec, such that $E_2 \sim 20-30$ kcal/mole. The rate limiting step for this branch in model II is first order, for which the pre-exponential factor $A_2^0$ should be on the order of $10^{11} - 10^{13}$ sec$^{-1}$, giving again $E_2 \sim 20-30$ kcal/mole. The branching probability which gives the best fit is $p \sim 0.25$, for both models. Using Equations 34-39, for model II, with the measured values of $A_1$ and $E_1$, $A_2^0 = 10^{-12}$ sec$^{-1}$, and $E_2 = 25$ kcal/mole, the curves shown as solid lines in Figures 43 and 44 were calculated. Similar results were obtained for model I. For example, the dashed curve in Figure 44 was computed using Equations 28-33, for model I, with $A_2^0 = 10^{-1}$ cm$^2$/sec, $E_2 = 25$ kcal/mole, and $f = 50$ Hz.

The predictions of the two branched models fit the data reasonably well over most of the temperature range studied. Another reaction step which acts in series with the low temperature branch of the parallel models must be included to account for the observation that the phase lag exceeds 90° at low crystal temperatures. This was accomplished by fitting Equations 41-43 to the low temperature experimental data.
An estimate of the pre-exponential and activation energy for this process can be made by comparison of the temperatures at which the phase lag is observed experimentally to reach 90° (tan φ + ω) to those predicted theoretically. The values obtained in this manner were $A_3^0 = 10^4 \pm 10^1$ sec$^{-1}$ and $E_3 = 2 \pm 1$ kcal/mole, where $k_3 = A_3^0 \exp(-E_3/RT)$. Using Equations 41-43 with these values for $A_3^0$ and $E_3$, the curves plotted as dotted and dashed lines (\ldots) in Figure 44 were computed. The order of magnitude of the pre-exponential $A_3^0$ is similar to that obtained for the apparent pre-exponential factor for branch 1, $A_1$, indicating that the series step may also be a second order process. How the two second order processes could be connected in series is difficult to rationalize.

Since the behavior of the amplitude as a function of crystal temperature predicted by the two parallel models I and II is very similar, only the values of r calculated for model II are plotted as solid lines in Figure 43. The agreement between the theoretical curves and the experimental results is quite good over the whole temperature range for high beam modulation frequencies. The experimental amplitudes for low modulation frequencies show a steeper decrease at low temperatures than that predicted by the models. This discrepancy is not appreciably reduced by the inclusion of a series step. The cooling rate in this range of crystal temperatures was very slow, such
that adsorption of background gases is possible, which could cause the observed decrease in the production of HD. The major component of the background, besides H₂, is CO, and therefore this is the most likely contaminant. An Auger spectrum of the surface was measured at the end of each experiment and only very small carbon peaks were observed, with a ratio C_{272}/Pt_{237} ≲ 1/6. However, it is possible that the adsorbed CO could have been desorbed by the electron beam by the time that the carbon peak was recorded.

For Pt(111) surface, as for the stepped surface, the activation energy \( E_1 \) and apparent pre-exponential factor \( A_1 \) for the low temperature branch were measured directly from the experimental curves. From the results in Figure 46, for \( 10^3/T > 1.9 \), the average values are \( E_1 = 15.6 \pm 0.5 \) kcal/mole and \( A_1 = (2.7 \pm 1) \times 10^5 \) sec⁻¹.

The estimate for \( A_1^0 \) is deduced in the same manner as for the Pt(332) surface, by substituting the values of the various parameters into the expression for \( A_1 \) given by both of the parallel reaction models for the low temperature branch, \( A_1 = [σ(1-ρ)I_o A_1^0]^{1/2} \). As indicated in 6.2.2, the behavior of the amplitude of the HD product as a function of crystal temperature on the Pt(111) surface differs from that observed on the stepped surface. At high crystal temperatures, where the phase lag approaches 0°, the amplitude is not demodulated, such that \( r \approx 2σ \). For the Pt(332) surface, the amplitude is independent of
temperature in this regime, whereas the amplitude on the Pt(111) surface continues to increase with increasing temperature. This behavior indicates that the sticking coefficient on the Pt(111) surface is not temperature independent, i.e. there is an activation barrier for dissociative adsorption. The sticking coefficient is therefore given as:

$$\sigma = \sigma_0 \exp(-D/RT)$$  \hspace{1cm} (44)

From the slope and the intercept at the origin of the Arrhenius plots of the amplitude, $r$, at high crystal temperatures, the values of $D$ and $\sigma_0$ can be measured directly to be $D = 1.5$ kcal/mole and $\sigma_0 = 0.28$, for $\theta = 0^\circ$. The branching probability, from the fitting of models I and II to the experimental data is again found to be $p \approx 0.25$. With the $H_2$ beam intensity of $10^{13} - 10^{14}$ molecules/cm$^2$ sec, the estimated value of $A_1^0$ is on the order of $10^{-2}$ cm$^2$/sec.

The value of $A_1^0$ for the Pt(111) surface, although somewhat higher than that observed on the stepped surface, is still consistent with a second order process, by the same arguments used in the discussion of the Pt(332) surface.

The activation energy $E_1$ measured from the slope of the Arrhenius plots of $\tan \phi$ includes the activation barrier for dissociative adsorption, $D$, as can be seen by substituting Equation 44 into Equation 40. The activation energy for the recombination process can be obtained from
the difference of these two values to be $E_1^* \approx 14$ kcal/mole, similar to that found on the stepped surface, $\sim 13$ kcal/mole.

The solid curves shown in Figures 45 and 46 were computed by the same procedure described for the Pt(332) crystal, for model II, with $A_2^o = 10^{12}$ sec$^{-1}$ and $E_2 = 27$ kcal/mole. As indicated above, the branching probability was found to be $p \approx 0.25$. The values of $A_2$ and $E_2$ for the high temperature branch exhibited the same uncertainty as observed on the stepped surface.

No calculations were made for the series process on the Pt(111) surface due to the absence of well defined structure in the phase data at low crystal temperatures. The phase lag does exceed $90^0$, indicating that there is a reaction step in series with the low temperature branch of the parallel models, but the scatter in the data is too large to attempt a meaningful theoretical fit.

The apparent reaction probability, $e$, is defined as the ratio of the product signal to the reactant signal, $H_D/D_2$ in this case. In order to examine the validity of the assumption in Salmeron's calculations that the isotope exchange reaction can be treated simply as a hydrogen recombination reaction by multiplying the apparent reaction probability by $(1 + \frac{I_{D_2}}{I_{H_2}})$, the expressions for the apparent reaction probability and the phase lag were obtained for models I and II, distinguishing between the isotopes.
The surface balance equations for model I, analogous to Equations 25, are:

Type 1 sites

\[
\frac{dn_{H1}}{dt} = 2(1-p)\sigma I_{H2}(t) - 2k_1n_{H1}^2 - 2k_1 n_{H1} n_{D1}
\]

\[
\frac{dn_{D1}}{dt} = 2(1-p)\sigma I_{D2}(t) - 2k_1n_{D1}^2 - 2k_1 n_{H1} n_{D1}
\]

Type 2 sites

\[
\frac{dn_{H2}}{dt} = 2\sigma(1-\theta)^2 I_{H2}(t) - 2k_2n_{H2}^2 - 2k_2 n_{H2} n_{D2}
\]

\[
\frac{dn_{D2}}{dt} = 2\sigma(1-\theta)^2 I_{D2}(t) - 2k_2n_{D2}^2 - 2k_2 n_{H2} n_{D2}
\]

For model II, the surface balance equations, analogous to Equations 26, are:

Type 1 sites

\[
\frac{dn_{H1}}{dt} = 2(1-p)\sigma I_{H2}(t) + k_2n_{H2} - 2k_1n_{H1}^2 - 2k_1 n_{H1} n_{D1}
\]

\[
\frac{dn_{D1}}{dt} = 2(1-p)\sigma I_{D2}(t) + k_2n_{D2} - 2k_1n_{D1}^2 - 2k_1 n_{H1} n_{D1}
\]

Type 2 sites

\[
\frac{dn_{H2}}{dt} = 2\sigma(1-\theta)^2 I_{H2}(t) - k_2n_{H2}
\]

\[
\frac{dn_{D2}}{dt} = 2\sigma(1-\theta)^2 I_{D2}(t) - k_2n_{D2}
\]
Equations 45 and 46 were solved by the approximate method of Olander and Ullman. The following expressions were obtained for the apparent reaction probability, $\epsilon$, and the phase lag, $\phi$.

**Model I**

$$\epsilon \exp(-i\phi) = \epsilon_1 \exp(-i\phi_1) + \epsilon_2 \exp(-i\phi_2)$$  \hspace{1cm} (47)

$$\tan \phi_1 = \frac{w}{4[(1 + \frac{I_D}{I_{H2}})(1-p)\sigma I_{H2}^0 k_1]}^{1/2}$$  \hspace{1cm} (48)

$$\epsilon_1 = \frac{2(1-p)\sigma}{(1 + \frac{I_D}{I_{H2}})[1 + \tan^2 \phi_1]}^{1/2}$$  \hspace{1cm} (49)

$$\tan \phi_2 = \frac{w}{4[(1 + \frac{I_D}{I_{H2}}) p\sigma I_{H2}^0 k_2]}^{1/2}$$  \hspace{1cm} (50)

$$\epsilon_2 = \frac{2p\sigma (1-\theta_0)^3}{(1 + \frac{I_D}{I_{H2}})[1 + \tan^2 \phi_2]}^{1/2}$$  \hspace{1cm} (51)

$$\theta_0 = [1 + \left(\frac{k_2 N_2^2}{(1 + \frac{I_D}{I_{H2}}) p\sigma I_{H2}^0}\right)^{1/2}]^{-1}$$  \hspace{1cm} (52)

**Model II**

$$\epsilon \exp(-i\phi) = \epsilon_1 \exp(-i\phi_1)[1 + \frac{p}{(1-p)} \epsilon_2 \exp(-i\phi_2)]$$  \hspace{1cm} (53)
\[ \tan \phi_1 = \frac{w}{2[4(1 + \frac{I_{D2}}{I_{H2}})(1-p)\sigma I_{H2}^0 k_1 + 2k_1 k_2 N_2 \theta_o]^1/2} \]  

(54)

\[ \varepsilon_1 = \frac{2(1-p)\sigma}{(1 + \frac{I_{D2}}{I_{H2}})[1 + \tan^2 \phi_1]} \]  

(55)

\[ \tan \phi_2 = \frac{w (1-\theta_o)}{k_2 (1+\theta_o)} \]  

(56)

\[ \varepsilon_2 = \frac{(1-\theta_o)^3}{(1 + \theta_o)[1 + \tan^2 \phi_2]} \]  

(57)

\[ \theta_o = 1 - \frac{[1 - y^2]^{1/2}}{y} \]  

(58)

where \[ y = \left[1 + \frac{k_2 N_2}{4p\sigma I_{H2}^0 (1 + \frac{I_{D2}}{I_{H2}})}\right]^{-1} \]

Comparing Equations 28-33 to 47-52 and 34-39 to 53-58, with \( \varepsilon = \frac{r}{(1 + \frac{I_{D2}}{I_{H2}})} \), it is obvious that Salmeron's assumption was oversimplistic. The factor of \( (1 + \frac{I_{D2}}{I_{H2}}) \) not only appears in the expression for the apparent reaction probability but also in the phase lag. However, since \( I_{D2}/I_{H2} \) is at most 0.2, the error involved cannot be very large. The best way to evaluate the error is to compare...
the predictions of the two sets of equations. In Figures 49 and 50 are the Arrhenius plots of the absolute value of the tangent of the phase lag, calculated for models I and II, respectively, with \( I_o = I_{H2}^o = 3 \times 10^{13} \) molecules/cm\(^2\) sec, \( N_2 = 2 \times 10^{14} \) sites/cm\(^2\), \( p = 0.25 \), \( \sigma = 0.33 \), \( I_{D2}/I_{H2} = 0.2 \), \( E_1 = 13 \) kcal/mole, \( E_2 = 25 \) kcal/mole and \( A_1^o = 10^{-3} \) cm\(^2\)/sec, at 1, 10, 100 and 1000 Hz. For model I, with \( A_2^o = 10^{-1} \) cm\(^2\)/sec, the predictions of Equations 28-33 are shown in Figure 49 as solid lines and those of Equations 47-52 are plotted as points. In Figure 50, for model II, with \( A_2^o = 10^{12} \) sec\(^{-1}\), the solid lines were calculated from Equations 34-39 and the plotted points from Equations 53-58.

The differences are quite small, negligible compared to the fit of the theoretical models to the experimental data. (See Figures 44 and 46.) Since the apparent pre-exponential factors and activation energies for branch 1 were obtained directly from the experimental curves, only the interpretation of the apparent pre-exponential changes. In any case, the values of the pre-exponential factors are only order of magnitude estimates.

The angle of incidence dependence of the apparent reaction probability discussed in 6.1 can now be evaluated in terms of the predictions of models I and II. Under the experimental conditions of high crystal temperature, 800°C, and low modulation frequency, 10 Hz, there was no measurable phase lag for the HD product. Substituting \( \phi = 0 \)
Figure 49. Comparison of the predictions of Equations 28-33 (plotted as lines) with those of Equations 47-52 (plotted as points), at various modulation frequencies.

MODEL I
Figure 50. Comparison of the predictions of Equations 34-39 (plotted as lines) with those of Equations 53-58 (plotted as points), at various modulation frequencies.
into Equations 47-52 for model I and into Equations 53-58 for model II, the apparent reaction probability $\varepsilon$ is found to be:

**Model I**

$$\varepsilon = \frac{2(1-p)\sigma}{(1 + \frac{I_D^2}{I_{H2}})} + \frac{2p\sigma(1-\theta_o)^3}{(1 + \frac{I_D^2}{I_{H2}})}$$  \hspace{1cm} (59)

At 800°C, $k_2 \sim 10^{-6}$ sec$^{-1}$ and $\theta_o \sim 10^{-5}$, so that Equation 59 simplifies to:

$$\varepsilon = \frac{2\sigma}{(1 + \frac{I_D^2}{I_{H2}})}$$  \hspace{1cm} (60)

**Model II**

$$\varepsilon = \frac{2(1-p)\sigma}{(1 + \frac{I_D^2}{I_{H2}})} + \frac{p}{1-p} \frac{2(1-p)\sigma}{(1 + \frac{I_D^2}{I_{H2}})} \frac{(1-\theta_o)^3}{(1 + \theta_o)}$$  \hspace{1cm} (61)

At 800°C, $k_2 \sim 10^7$ sec$^{-1}$ and $\theta_o \sim 0$, so that Equation 61 simplifies to:

$$\varepsilon = \frac{2\sigma}{(1 + \frac{I_D^2}{I_{H2}})}$$  \hspace{1cm} (62)

Equations 60 and 62 are identical to Equation 21. The only difference is that the total sticking coefficient actually includes contributions from two different processes acting in parallel.
The activation barrier for dissociative adsorption of hydrogen on the Pt(111) surface deduced from the dependence of the sticking coefficient on crystal temperature, $D \approx 1.5$ kcal/mole, is clearly in disagreement with the result obtained from the beam temperature and angle of incidence dependence, $D \leq 0.5$ kcal/mole, presented in 6.1. This may be due to the difference in the experimental conditions, since in one case the properties of the surface are varied, whereas the properties of the incident molecules are changed in the other. The molecules that have enough initial energy to overcome the barrier will dissociate upon impact. Those that do not still may be trapped or adsorb into a precursor state and dissociate due to energy transfer from the surface. If this second process has a characteristic time shorter than the modulation period, these molecules will contribute to the measured signal. The condensation coefficient and its dependence on angle of incidence, as well as the steric factors for the energetic molecules must be known in order to separate the different contributions to the total sticking coefficient.

The observation that the amplitude, $r$, of the HD product is independent of the crystal temperature in the high temperature range, where the signal is not demodulated, indicates that the adsorption of hydrogen on the stepped Pt(332) surface is not an activated process. This is in
agreement with the results reported in 6.1. The beam
temperature dependence of the $^3H$-$^2D$ exchange reaction on
this surface put an upper limit of 0.5 kcal/mole on the
activation barrier. The lack of any angle of incidence
dependence for $\phi = 0^\circ$ is also consistent with this result.

The important conclusion that can be drawn from
these observations is that the terraces on the stepped
surface, which are six atomic rows wide and of the (111)
orientation, do not have the same properties as the in­
finite (111) plane. The presence of steps in a (111) sur­
face not only introduces new sites on the surface associ­
ated with the step edges, but also modifies the H-H bond
breaking properties of the (111) sites of the terraces.

The previous investigation in this laboratory of
the mechanism of the $^3H$-$^2D$ exchange reaction on the Pt(111)
and the stepped Pt(997) and Pt(553) surfaces was performed
in the differential mode of detection with one of the
reactant gases in the beam and the other in the background
of the scattering chamber. Most of the measurements
were made at high crystal temperatures and high beam modu­
lation frequencies. The main feature observed in the
Arrhenius plots of the phase lag for the stepped surfaces
was a minimum near $10^3/T \sim 1.3$. At higher crystal tem­
peratures, the phase lag increased again up to the highest
temperatures investigated, $\sim 1000^\circ C$. This phase reversal
was attributed to a branched mechanism. In the
present study, more detailed structure has been revealed in the Arrhenius plots of tan $\phi$ for crystal temperatures below $\sim 800^\circ C$ due to the increased number of data points obtained and the use of the integral mode of detection, a mixed beam of reactants and low beam modulation frequencies. A phase reversal at high crystal temperatures has also been observed in this work, although at somewhat higher temperatures than the earlier study. However, since the phase lags approach zero at the minimum in the present study, the results show considerable scatter above $10^3/T \sim 1.3$. An alternative explanation for the high temperature phase reversal may be that dissolution of hydrogen into the bulk may increase the residence time at the crystal, resulting in a greater phase lag for the product HD. A decrease in the apparent reaction probability above $\sim 800^\circ C$ is observed, accompanying the increased phase lag, which could be attributed to a decrease in the surface concentration of H and D atoms due to bulk diffusion.

The low reaction probability for $H_2$-$D_2$ exchange on the Pt(111) observed in the previous study$^{3,25}$ cannot be readily explained in view of the results of the present investigation. Several Pt(111) samples were used in an attempt to reproduce the unreactive surface. No experimental conditions could be found where the apparent reaction probability differed by more than an order of magnitude on the flat Pt(111) surface relative to the stepped Pt(332).
The $\text{H}_2$-$\text{D}_2$ exchange reaction has been found to have an activation energy of $2.5 \pm 0.5$ kcal/mole on both the Pt(111) and stepped Pt(997) surfaces at crystal temperatures below $300^\circ$C by Christmann et al. The results were obtained by thermal desorption, a nonmodulated technique, and therefore can only be compared with the results of the present study at zero modulation frequency, or where the phase lag is zero such that the signal is not demodulated. Since the apparent reaction probability is
\[
\varepsilon = \frac{2\sigma}{1 + \frac{I_{\text{D}_2}}{I_{\text{H}_2}}},
\]
under these conditions for the modulated molecular beam experiment, the activation energy measured from an Arrhenius plot of the sticking coefficient is appropriate for comparison. On the Pt(111) surface, the activation energy for dissociative adsorption was found to be 1.5 kcal/mole, which is smaller than that measured by Christmann et al., 2.1 kcal/mole, but larger than that reported by Lu and Rye, 1.2 kcal/mole. No activation energy for dissociative adsorption was observed on the stepped Pt(332) surface. Since the step density on the Pt(332) surface is ~1.5 times that on the Pt(997) surface, it is not clear that the same activation energy should be found on the two surfaces. A question which deserves investigation is how wide the terrace region must be to exhibit the properties of the infinite (111) plane, which in this case would be an activation energy for dissociative adsorption of hydrogen.
Smith et al.\textsuperscript{37} have reported an activation energy barrier for adsorption of D\textsubscript{2} on Pt(111) of \textasciitilde 1.8 kcal/mole, in good agreement with the work presented here.

Thermal desorption studies of hydrogen adsorption on Pt(111) surfaces have indicated that one\textsuperscript{26}, two\textsuperscript{27,32} or three\textsuperscript{33} types of sites are present on the surface. Two investigations have compared the adsorption of hydrogen on the flat (111) and stepped (111) surfaces (Pt(S)-[9(111)X(111)]\textsuperscript{27} and Pt(S)-[6(111)X(111)]\textsuperscript{32}). In both of these studies, the two types of adsorption sites that were found on the flat (111) surfaces were also observed on the stepped (111) surface, as well as a third higher energy site. The results of the present work indicate that on both the flat (111) and stepped (111) surfaces at least two types of sites are present which control the recombination reaction simultaneously at high crystal temperatures.
7. SUMMARY AND CONCLUSIONS

The work presented in this thesis demonstrates that the presence of an ordered array of monatomic steps in a Pt(111) surface significantly affects reactive and nonreactive gas-surface interactions relative to the flat surface.

Helium scattering is predominantly specular from the flat Pt(111) surface. On the stepped Pt(553) or Pt(S)-[5(111)X(111)] surface, rainbow scattering is observed when the helium atoms are incident perpendicular to the step edges. These results indicate that the periodic step structure introduces a corrugation into the smooth surface potential of the (111) plane of platinum.

The studies of the hydrogen isotope exchange reaction reveal both similarities and differences in reactive encounters with stepped and flat Pt(111) surfaces. The dependence of the apparent reaction probability on the angle of incidence, polar and azimuthal, of the reactants is markedly different. For the stepped surfaces, Pt(553) or Pt(S)-[5(111)X(111)] and Pt(332) or Pt(S)-[6(111)X(111)], the apparent reaction probability is highest when the reactants strike the open side of the step structure. This dependence can be understood in terms of the scattering geometry and the enhanced H-H bond breaking properties of the step sites. The production
of HD on the Pt(111) surface is highest at normal incidence. This behavior can be explained by an activation energy for adsorption.

The mechanism of $\text{H}_2$-$\text{D}_2$ exchange on both the flat Pt(111) and stepped Pt(332) surfaces consists of two processes operating in parallel at high crystal temperatures and another process acting at low crystal temperatures in series with the branch that is operative over the entire temperature range studied. The dependence of the apparent reaction probability on crystal temperature also indicates that the adsorption of hydrogen is an activated process on the Pt(111) surface, but not on the stepped Pt(332) surface.
REFERENCES

REFERENCES (cont.)

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