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MOLECULAR BEAM SCATTERING STUDIES OF ENERGY TRANSFER AND CHEMICAL REACTIONS ON WELL CHARACTERIZED PLATINUM SURFACES

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Steven Lynn Bernasek
(Ph. D. thesis)

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MOLECULAR BEAM SCATTERING STUDIES OF ENERGY TRANSFER AND CHEMICAL REACTIONS ON WELL CHARACTERIZED PLATINUM SURFACES

Steven Lynn Bernasek

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ABSTRACT

An existing molecular beam surface scattering apparatus was extensively modified to allow studies of energy transfer and chemical reactions on well characterized platinum surfaces using a modulated beam technique. Low energy electron diffraction and Auger electron spectroscopy were used to characterize the platinum single crystal scattering surfaces, and scattering experiments were carried out under ultra high vacuum conditions. Three platinum surfaces were investigated: the high density (111) face and two stepped single crystal surfaces (Miller Indices (997) and (553)). Energy transfer between a variety of gases and the (111) surface was very poor as indicated by narrow, specular scattering distributions from this surface. The stepped surfaces showed greater energy accommodation which was directly proportional to the density of steps on these surfaces. The stepped surfaces also exhibited an azimuthal orientation dependence on the scattering maximum position which has been termed microscopic specularity. Energy transfer between a variety of gases and a CO covered Pt(111) surface was complete. These results indicated a translational to vibrational channel for the energy transfer.
The exchange reaction of $H_2$ and $D_2$ on the clean surfaces was studied extensively. It was found that the presence of steps on the platinum surface was necessary to produce a significant amount of HD. Studies of the exchange mechanism on the stepped surfaces indicate a two branch mechanism involving the reaction of an adsorbed $D_2$ molecule with atomic hydrogen bound at the step in the surface temperature range of 300-700°K, and the direct reaction of a gaseous $D_2$ molecule with atomic hydrogen bound at the step above 700°K. Further reactive scattering studies on the stepped surfaces indicate that the steps readily dissociate $H_2$, $O_2$, O-H, C-H and N-H bonds, while C=O and N≡N bonds are not readily broken on these surfaces.
The fundamental problem in the study of the gas-solid interaction is the elucidation of the energy exchange between the solid and the gas. An understanding of the chemistry and physics of the gas-solid interaction is fundamental to an understanding of such processes as heterogeneous catalysis, corrosion, vapor deposition, cloud formation, condensation and satellite dynamics. An understanding of the energy exchange between solid and gas is necessary to an understanding of the chemistry and physics of the gas-solid interaction.

More specifically, the problem is one of determining the microscopic initial and final energy states of the gas-solid system. This problem is illustrated schematically in Fig. I-1. An incident particle in the gas phase, in the state $E_i$, collides with the solid in the state $E_i'$. After the collision, the particle is in state $E_f$, while the solid is in the energy state $E_f'$. Depending on the nature of the incident particle, $E_i$ can be a sum of translational, rotational, vibrational and electronic states. $E_i'$ depends on the structure and composition, the temperature, and various other parameters of the solid lattice. After the interaction, the incident particle can leave the solid surface in the same state, in a different (higher or lower energy) state, it can become a part of the solid surface, or it can leave the surface as a chemically different species. The solid surface can, after the interaction, be in the same state as initially, it can be in a different energy state, it can be changed
Before interaction

Gas particle in State $E_i$

$E_i = (\epsilon_t + \epsilon_r + \epsilon_v + \epsilon_e)_i$

Solid in State $E_i$

After interaction

Gas particle in State $E_f$

$E_f = (\epsilon_t + \epsilon_r + \epsilon_v + \epsilon_e)_f$

Solid in State $E_f$

Fig. I-1. Schematic diagram of gas solid interaction.
chemically by the interaction, or surface atoms can leave the solid and enter the gas phase as a result of a gas-surface chemical reaction.

The problem of determining the molecular details of the gas-solid energy exchange is a difficult one for three reasons:

1) The difficulty of characterizing the initial and final states of the system, especially that of the solid surface.

2) The necessity to use approximate, often unrealistic, theories for the interaction, due to the complex many-body nature of the problem.

3) The experimental difficulties arising from dealing with reactive surfaces.

An especially fruitful technique for the study of energy exchange in gas-solid interactions has been the use of molecular beam scattering from surfaces. When molecular beam methods for characterizing the gas phase are coupled with modern surface preparation and characterization techniques, a very powerful tool for the study of this energy exchange results. Several such experimental systems are in use at present.\(^1\)\(^-\)\(^5\) This thesis describes modifications to one of these systems\(^3\) to allow the study of gas-surface chemical reactions as well as non-reactive gas surface interactions, and the results of several investigations of reactive and non-reactive gas-solid interaction systems.

The results of a molecular beam scattering experiment are generally presented in the form of an angular scattering distribution.
Fig. I-2. Diagram showing geometry of surface scattering experiment.
Figure I-2 shows a schematic representation of the surface scattering experiment. The target normal and the incident beam define the plane of incidence. Scattering distributions are normally measured in this plane, with angles of scattering measured from the surface normal.

Typical scattering distributions in rectilinear coordinates are shown in Fig. I-3 for two extremes of energy exchange. The solid curve is a directed distribution, in this case specular. It is characteristic of very poor energy exchange between the solid and the incident gas. The broken curve is termed a cosine distribution, because the intensity decreases as the cosine of the angle from the surface normal. Some reactive scattering studies have resulted in product distributions which are peaked at the normal to the surface. These distributions are often fit by a \( \cos^n \theta \) curve, with \( n \) ranging as high as 8 in some cases. This is entirely a convenience for describing such curves and has no theoretical justification for the particular dependence, unlike the simple cosine distribution which is the result of random desorption from the surface. Several other terms are used to describe the directed distributions, and will be used frequently in this thesis. The maximum intensity is the scattered signal at the maximum angle normalized to the incident intensity.

The full width at half maximum (FWHM) of the distribution is defined similarly to spectroscopic peaks. This figure is usually in degrees.

If the angle of maximum scattering is equal to the angle of incidence, \( \theta_i \), (denoted by the arrow along the abscissa in Fig. I-3) the distribution

---

Recent work by Cardillo, et al. on the microscopic reversibility of the scattering process could well offer a theoretical justification for these distributions.
Fig. I-3. Rectilinear presentation of angular distribution. Solid curve is specular scattering. Dashed curve is random or cosine distribution.
is termed specular. If the angle of maximum scattering is greater than $\theta_i$, it is termed supraspecular scattering, if less than $\theta_i$, subspecular scattering.

The purpose of this brief introduction has been to describe the problem of energy exchange between a gas and solid surface and to define a few of the terms which will be used frequently in the body of this thesis. Chapter II is a short survey of the theoretical and experimental results in this field of study taken from the literature of the last few years. Its purpose is to introduce the reader to some of the results of energy exchange studies and the groups involved in these studies. Chapter III is a detailed description of the apparatus construction and the experimental techniques used in this study. Chapter IV presents the results of these energy exchange studies. Chapter V serves as a short summary of the work presented here along with some comments about future areas of interest in the study of gas surface energy exchange by ultra high vacuum molecular beam methods.
II. LITERATURE REVIEW

Before describing the experimental system and the results which make up the bulk of this thesis, it would be worthwhile to review briefly the theory and experimental results of the last few years which pertain directly to the study of energy exchange in the gas surface interaction. A more extensive review of this subject may be found in reference 6 and the numerous citations contained therein.

A. Theory

1. Classical Scattering Theories

Perhaps the most widely known theory of the scattering of gas atoms from a solid surface is the hard cube model of Logan and Stickney\textsuperscript{7} and its derivatives. This theory has added a great deal to our understanding of the energy exchange between a solid and a gas molecule incident on that solid. The success of these cube theories is based on their simplicity and their ability to qualitatively predict the scattering behavior for a wide variety of gas-solid systems.

The hard cube model is based on four assumptions.\textsuperscript{7-9} These assumptions are:

1) The gas particle and the surface atom are rigid elastic particles.

2) The surface is perfectly smooth. This means that the tangential component of the gas velocity is not changed on collision with the surface.
Fig. II-1. Hard cube scattering model (Reference 7).
3) The surface atoms are independent particles confined by square well potentials.

4) A one-dimensional Maxwellian distribution of velocities is chosen for the motion of the surface atoms normal to the surface. A schematic diagram of this model is shown in Fig. II-1.

The most extensive analysis\textsuperscript{8,10} of these assumptions results in a closed form expression for the complete angular distribution of scattered particles and for their velocity distribution as well. These expressions give the flux of gas particles scattered into a unit angular range as well as the velocity distribution of particles scattered at a given angle. The calculation uses the temperature of the solid and gas and the mass of the solid and gas atoms. The results of the theory can be concisely stated by examining the behavior of \( \eta = \theta_0 - \theta_1 \) (where \( \theta_0 \) = angle of incidence and \( \theta_1 \) = angle of reflection measured from the surface normal) as a function of the four variables mentioned above. This behavior is compared with the experimental behavior in Table II-1. Figure II-2 shows a calculated scattering distribution compared with a measured distribution.

The remarkable qualitative agreement between this model and the observed scattering behavior indicates that the assumptions upon which the model is based are valid assumptions to a first approximation. Stickney\textsuperscript{9} and Logan, \textit{et al.}\textsuperscript{8} discuss the assumptions in detail and suggest modifications which have been incorporated into the theory. Goodman\textsuperscript{11} has indicated a quantum mechanical basis for the assumption of a planar equipotential scattering surface. The assumption of a
Table II-1.

<table>
<thead>
<tr>
<th>Hard cube prediction</th>
<th>Experimental results</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{\partial \eta}{\partial m_g} &gt; 0$</td>
<td>$\frac{\partial \eta}{\partial m_g} &gt; 0$</td>
</tr>
<tr>
<td>$\frac{\partial \eta}{\partial T_s} &gt; 0$</td>
<td>$\frac{\partial \eta}{\partial T_s} &gt; 0$</td>
</tr>
<tr>
<td>$\frac{\partial \eta}{\partial T_g} &lt; 0$</td>
<td>$\frac{\partial \eta}{\partial T_g} &lt; 0$</td>
</tr>
<tr>
<td>$\frac{\partial \eta}{\partial \theta} \leq 0$</td>
<td>$\frac{\partial \eta}{\partial \theta} \leq 0$</td>
</tr>
</tbody>
</table>
Fig. II-2. Comparison of measured (o) and calculated (solid line) scattering distributions, using the hard cube model (Reference 8).
smooth surface and the experimental evidence supporting this assumption say a great deal about the nature of energy transfer in the gas-solid interaction. To a first approximation, change in tangential momentum can be ignored in the scattering of gas particles from a solid surface. Of course, at grazing angles of incidence, or when chemical reaction takes place, the approximation breaks down. In any case, this assumption, and the hard cube theory based upon it, have added significantly to our understanding of gas-surface energy transfer.

Several of the drawbacks of the hard cube model have led to modifications and extensions of the theory to include more physically realistic assumptions. In most cases, these extensions have also led to a more complex theory requiring numerical solution. The first important revision of the model by Logan and Keck\textsuperscript{12} is termed the soft cube model. As its name implies, the gas-solid potential is assumed to be made up of a square well attractive potential resulting in a "soft" gas surface collision with an exponential repulsive potential (Fig. II-3). The attractive potential is assumed fixed in space while the repulsive part of the potential oscillates about the equilibrium position of the surface atom which behaves as if attached to the remainder of the rigid lattice by a single spring. The soft cube model in this form introduces three parameters to describe the gas-surface potential; the well depth, the interaction range, and the surface atom oscillator frequency. This results in the need for numerical solution of the scattering equations. Forman,\textsuperscript{13} and Karamcheti and Scott\textsuperscript{14} have utilized a truncated harmonic potential
Fig. II-3. Soft cube scattering model (Reference 12).
in a similar analysis which simplifies the calculation somewhat. The soft cube model predicts the same trends with experimental variables as does the hard cube model, but greatly improves the quantitative agreement with experiment, especially in the case of the scattering distribution width.

A recent extension of the cube theories is that by Doll.\textsuperscript{15} He has developed the formalism to include scattering of a rigid rotor by the surface. This extension has improved the agreement of theory and experiment for the scattering of diatomic molecules from solid surfaces, particularly the widths of the scattering distributions. The success of the "cube" theories in explaining and predicting gas-surface scattering distributions has added to the understanding of the gas-solid energy exchange. The simplicity of the results and the apparent experimental verification of many of the assumptions upon which the theories are based has led to a physical picture of the processes involved in the gas-surface interaction.

Other classical scattering theories are of the trajectory type. This method consists of numerical solution of the equations of motion for a large number of gas particles incident on an idealized surface. The surface is composed of a lattice of atoms connected by harmonic potentials. The approaches to this theory by different authors differ in numerical techniques and the gas-surface interaction potential used in the calculation. Lorenzen and Raff\textsuperscript{16-20} utilize a Morse potential for the interaction. Calculations for two\textsuperscript{16} and three\textsuperscript{17} dimensional surfaces exhibit semi-quantitative agreement with experimental data.
for He scattering from Ni and Ar from W.\textsuperscript{20} They treat the effect of surface impurities,\textsuperscript{18} finding an increase in energy transfer for surfaces contaminated by submonolayer quantities of contaminants.

McClure\textsuperscript{21-24} uses a 6-12 pairwise interaction potential. His two-dimensional finite range interaction model points out the dependence of the scattering results on the tangential momentum transfer.\textsuperscript{21} This dependence is neglected in the cube models discussed previously. An interesting result of these calculations is the appearance of "surface rainbows" in the calculated scattering distribution.\textsuperscript{22} This structure can be used to extract information about the gas-surface interaction potential. Comparisons have been made with experimental data for Ne/LiF scattering showing very good quantitative agreement.\textsuperscript{23,24}

Several other trajectory type calculations have been done,\textsuperscript{25,36} but all attempts suffer from the same drawback. The convergence characteristics of the numerical techniques used necessitate the calculation of $10^4$ to $10^5$ trajectories for each set of incident conditions. This is an expensive method for extracting information about the gas-surface potential field. Recent work by Steele,\textsuperscript{37,38} Doll\textsuperscript{39,40} and Wolken\textsuperscript{41,42} promise a greater return of information for invested computational time. This work will be discussed briefly in a later section.

2. Quantum Mechanical Theories

Present day quantum mechanical treatments of gas-surface energy exchange have built on the early theory of Lennard-Jones, Devonshire and Strachan.\textsuperscript{43-45} The major problems of this early theory were that it was one-dimensional, it could not account for large non-specular
fluxes (first order perturbation theory), it treated surface atoms as if in the bulk, and the inelastic scattering theory was limited to single phonon processes. Recent developments in the theory have attempted to correct these problems. An extensive review of the state of quantum theories of scattering up to 1966 is given by Beder. More recent reviews by Goodman discuss several of the corrections.

The breakdown of the first order perturbation treatment was discussed initially by Cabrera, Celli, Goodman, and Manson. They developed first an elastic scattering theory and then a one phonon inelastic theory which is based on the conservation of particle flux (a unitary theory).

Beeby's development of a formalism to treat multiphonon encounters indicates that one and even two phonon terms are not sufficient to explain experimental results. The numerical calculation required to deal with multiphonon scattering is so extensive that higher order calculations are not feasible.

The problem of generalization to three dimensions and recognition that the surface atom is not in fact like an atom in the bulk of the solid was treated by Goodman. The surface atom is assumed to behave as if its characteristic temperature were that of the surface Debye temperature rather than the bulk Debye temperature. This theory is extended to be generally applicable in the treatment of elastic and inelastic scattering. The inelastic theory is able to predict phonon creation and annihilation peaks around elastic scattering peaks.
The quantum theory of gas-surface scattering has progressed to the stage where qualitative agreement with experimental results is generally obtained. Recent treatments are yielding quantitative agreement for helium/alkali halide scattering systems.

3. New Developments in Scattering Theory

Several new approaches to the theory of gas surface scattering have appeared in recent years. These approaches range from classical to quantum mechanical including a very interesting semiclassical formalism. The result of each of these approaches has been to greatly reduce the computational time and storage requirements of the calculations, while significantly improving the agreement with experimental scattering data. Three of these approaches will be briefly discussed below, as representative of the classical, semi-classical, and quantum mechanical theories.

The classical theory of Steele\textsuperscript{38} results in an analytically soluble expression for atom scattering distributions. This simple model assumes a rigid solid lattice. A square well attractive potential acts on the incident atom and it is scattered by a hard wall repulsive barrier whose position varies sinusoidally in the plane of the surface. The frequency and amplitude of this sinusoidal variation are dependent on the nature of the solid lattice. This model shows reasonably good agreement with experimental data for Ne/LiF\textsuperscript{60,61} scattering and with the trajectory calculations on this system of McClure.\textsuperscript{23} Better agreement could be obtained by introducing lattice vibrational motion, at the expense of losing the analyticity
of the model. The same author has also shown that the interaction energy of a gas atom with a solid surface can be expressed as a truncated Fourier series.\textsuperscript{37} Potentials calculated using the truncated series compare favorably with those calculated by direct pairwise summation of gas atom solid atom terms, even though the number of terms used in calculating the Fourier series is small (1-3). These potentials can then be used for calculating adsorption energies and energies of isolated adatoms.

Work by Doll and others\textsuperscript{39,40,62} has extended the semiclassical $S$ matrix formalism of gas phase scattering theory\textsuperscript{63,64} to gas-surface scattering. This technique lies between purely classical and purely quantum mechanical calculations. The semiclassical techniques are used for calculation of transition probabilities of the harmonic oscillator for a collinear hard sphere collision.\textsuperscript{40} This method gives closed form results for the transition probabilities which are nearly identical to the tedious numerical calculations of the transition probabilities in the normal quantum mechanical framework. These calculations have been extended to determine transition probabilities for elastic atom scattering from a solid surface.\textsuperscript{62} The effect of lattice motion can also be included in this formalism.

The quantum mechanical treatment of gas surface scattering by Wolken\textsuperscript{41,42,66} has allowed detailed examination of the effect of the assumed scattering potential on the scattering distribution. It is an exact, direct computational method which takes much more calculational time than the previous methods discussed here. By using a close
coupling method up to 41 scattering channels have been investigated for the He/LiF system. This large basis set includes both observable diffracted beams and beams diffracted into the surface. It is found that this large basis set must be used for reasonable experimental comparisons. However, important details in the dependence of scattering on the interaction potential can be investigated using a much smaller basis. In this way, exact details of the gas-surface interaction can be calculated directly, accurately, and quickly. The method has also been extended to include excited states of incident diatomic molecules.

All of the approaches discussed above have led to an increase in both the ability of scattering theories to reproduce experimental results and to predict experimental distributions for particular interaction potentials. At the same time, they have reduced the computational requirements for these theoretical treatments. The next section discusses some of the results of scattering experiments which will perhaps someday be used in these theories to extract the gas-surface interaction potential, and with it direct information about gas-surface energy exchange.

B. Experiment

1. Elastic Scattering

The elastic scattering of gas particles from solid surfaces does not involve energy transfer between the surface and the incident gas. The results of elastic scattering experiments, however, do give a great
deal of information about the interaction potential between the surface and the gas particle. This information is contained in the presence or absence of diffraction and in the temperature dependence of elastic scattering intensity.

Diffraction of gas particles by a solid surface was first observed by Stern and his coworkers in the early 1930's. Their observation of He diffraction by LiF crystals was a proof of the wave-particle duality postulate of the new quantum mechanics. Since that time, the experiment has been repeated with H atoms, $^3$He, $^4$He, $^2$H, $^2$D and Ne scattered from LiF with well defined diffraction peaks being observed in all cases.

Except for the cases to be mentioned shortly, diffraction has not been observed on scattering from surfaces other than alkali halide crystals. Tendulkar and Stickney observed well defined diffraction peaks on scattering helium from a tungsten (112) surface. This surface consists of close packed rows separated by troughs as seen in Fig. II-4. Helium atoms incident perpendicular to the rows showed diffraction, while atoms incident parallel to the rows showed only specular scattering. Weinberg and Merrill have observed diffraction of He and $^2$D from a tungsten carbide surface. This surface was characterized by a stiff WC surface lattice with holes due to stacking faults having the correct periodicity to exhibit a W(110)R-(3×5)LEED pattern. In both cases of diffraction from non-alkali halide surfaces, the diffracting surface had a pronounced periodicity.
Fig. II-4. Schematic diagram of W(112) surface. (a) top view;
(b) side view. (Reference 77).
and a stiff surface lattice. For LiF scattering the same conditions are met. Beeby treats the effect of lattice stiffness as a condition for diffraction. Weinberg points out the necessity for a strongly periodic scattering potential as a diffraction condition. Thus, simply the observation of diffraction from a solid surface tells a good deal about the nature of the gas solid interaction.

Quantitative information about the surface lattice stiffness is contained in the temperature dependence of elastic scattering intensities. In the harmonic oscillator model of the solid, the mean square displacement of the surface atoms is related to the temperature of the surface by

$$\langle u^2 \rangle = \frac{3h^2 T_s}{M_s k \Theta_D}$$  \hspace{1cm} (1)

where $\langle u^2 \rangle$ is the mean square displacement, $T_s$ is surface temperature, $M_s$ is surface atom mass and $\Theta_D$ is the surface Debye temperature which is characteristic of the lattice stiffness. This surface Debye temperature can be determined by measuring the specular scattering intensity as a function of surface temperature since

$$I_{\text{spec}} \propto \exp[-(\Delta k \cdot \vec{u})^2]$$  \hspace{1cm} (2)

where $\Delta k$ is the momentum transfer on impact and $\vec{u}$ is the instantaneous displacement of the surface atom. Hoinkes, Nahr and Wilsch determined the surface Debye temperature of LiF to be 568°K by this method. The bulk Debye temperature is 732°K in the elastic limit.

Doll has treated this problem in more detail. If the gas atom-surface atom potential well depth is large in relation to the incident
gas atom energy, the well depth interaction dominates the scattering. As the ratio of incident energy to well depth increases, the particle is more able to sample the thermal motion of the surface atoms and the standard Debye-Waller attenuation of scattering intensity is observed. This two regime effect (as incident particle energy is increased) is not seen with electron and X-ray scattering because the incident particle energy is much higher than the well depth for atom-surface scattering. This well depth is of the order of kT.

2. Inelastic Scattering

The greatest wealth of information about the gas-solid energy exchange is contained in the results of inelastic molecular beam scattering experiments. A great number of systems have been studied; some well characterized, others not so well defined. Studies of inelastic scattering of molecular beams from two surfaces, silver and LiF, are perhaps typical of the type of experiments performed and the information available from these experiments. This section will discuss scattering from these two materials in order to indicate the type of information which has been obtained from these inelastic scattering experiments. Other materials will be discussed whenever it is thought to be helpful to expand on particular points.

Preparation of well-defined silver scattering surfaces by epitaxial growth on a mica substrate has been used very successfully by Saltsburg, Palmer and Smith.\textsuperscript{82,83} They have determined the scattering distributions for a variety of gases from silver surfaces prepared in this manner. \( \text{NH}_3 \) was found to scatter with a cosine
distribution, indicating complete energy transfer. He, Ne, Ar, Xe and CH₄ gave peaked scattering distributions indicating varying degrees of energy transfer. Scattering of velocity filtered Ar and Xe beams from the silver surface resulted in scattering distributions very similar to those for Maxwellian beams. This indicates that the thermal motion of the scattering lattice is the main reason for the broadness of the scattering patterns and is the most important factor affecting energy exchange in the gas surface interaction.

The same investigators studied the scattering of H₂, D₂ and HD from the silver epitaxial surface. Their remarkable results are shown in Fig. II-5. H₂ alone shows highly specular scattering characteristic of light atoms such as He or Ne. D₂ and HD showed very broadly peaked distributions at much lower intensities. The reason for this difference can be seen by an examination of the nature of internal energy transfer on scattering. The allowed rotational energy transitions of the hydrogenic species are shown in Table II-1. The energy of a Debye phonon in silver is ~ 450 cal/mole, corresponding rather closely to rotational transitions in D₂ and HD. A multiphonon process would be necessary for energy transfer to the internal states of H₂. This rotational coupling has been observed on single crystal Ag(111) and at Pt(111) surfaces as well in experiments to be described in a later section.
Fig. II-5. H\(_2\), D\(_2\), and HD scattered from epitaxial Ag(111) surface. (Reference 84)
Table II-1. Rotational State Transitions

<table>
<thead>
<tr>
<th>Transition (cal/mole)</th>
<th>J(0-2)</th>
<th>J(1-3)</th>
<th>J(0-1)</th>
<th>J(1-2)</th>
<th>J(2-3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>1032</td>
<td>1720</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D₂</td>
<td>516</td>
<td>860</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HD</td>
<td></td>
<td>248</td>
<td>516</td>
<td>775</td>
<td></td>
</tr>
</tbody>
</table>
A study of the speed distributions of Ar scattered from single crystal silver surfaces gives direct experimental verification of the nature of energy exchange indicated by cosine and specular scattering. Bishara and Fisher \(^{86}\) found that thermal energy Ar beams displayed peaked scattering with a large cosine component when scattered from silver single crystal surfaces. Determination of the velocity distribution by time-of-flight techniques indicated nearly Maxwellian distributions with mean speeds near the temperature of the scattering surface for atoms in the cosine component. Measurements of the velocity in the directed lobe indicated tangential momentum conservation and low energy accommodation. A study on Ni surfaces yielded similar results. \(^{87}\)

Scattering from silver single crystal surfaces in the thermal energy range has been exhaustively studied by Sau and Merrill. \(^{85}\) They identify three types of scattering in this incident energy range. He, \(H_2\) and \(D_2\) exhibit quasi-elastic scattering, characterized by peaked scattering distributions and poor energy exchange. Ne, Ar and Kr show inelastic scattering, as evidenced by broad subspecular distributions which are sensitive to surface temperature. Xe exhibits trapping dominated scattering with a large cosine component and high thermal equilibration. Classification of scattering distributions into these three types correlates well with the reduced gas-surface potential well depth, \(D/kT_s\), derived from independent measurements. (\(D\) is a Lennard-Jones type well depth, \(k\) is the Boltzmann constant,
and $T_b$ is the characteristic temperature of the incident gas beam.)

An interesting correlation of the microscopic roughness of the scattering surface with energy transfer is also noted. As the microscopic roughness is increased in going from Ag(111)\(^85\) to Pt(111)\(^88\) to W(110)\(^89\) to Pt(100)\(^90\), the energy accommodation increases as evidenced by the broadening and the decrease in intensity of the directed peak.

Platinum\(^91\text{--}95\) has also been studied extensively, and is the subject of the investigations described in this thesis, due to its utility in heterogeneous catalysis. Studies of diatomic and polyatomic molecular scattering from platinum surfaces have shown broader scattering distributions than for atoms of similar mass.\(^91\) The transfer of energy to internal modes is responsible for the more efficient energy exchange. This hypothesis is supported by recent theoretical studies by Doll.\(^15\)

A very interesting study by Siekhaus, Schwarz and Olander\(^96\) of simple gases scattered from graphite indicate that the speed of the reflected gas reaches a maximum at a particular surface temperature, dependent on the nature of the gas and the surface, and that any increase in surface temperature beyond that point does not change the speed of the reflected gas. Clarification and explanation of the results of this study could add a great deal to our knowledge of energy transfer between gas and solid.
Several of the studies of beam scattering from LiF have been discussed in the section on elastic scattering. However, several points should be discussed regarding inelastic scattering in these systems. In general, gases heavier than neon do not exhibit diffractive scattering from LiF surfaces. For example, Ar scattered from LiF results in a broadened subspecular peak as in Ar scattering from metal surfaces. Even with light gases, if internal mode coupling is possible, diffraction features are broadened and eventually washed out.

Williams observes peaks in He and Ne scattering from LiF that can be attributed to phonon emission and absorption in the neighborhood of the elastic scattering peaks. (Fig. II-6) Coupled with a useable theory of gas-surface scattering, detailed experiments such as these could be used to determine the surface phonon spectrum of solids. With this information, detailed predictions of energy transfer between the gas and solid could be made.

Selective adsorption in molecular beam scattering from solid surfaces was first observed by Stern. This phenomenon gives information about bound surface states and their energies. For example, a difference in bound state energy is found for the two isotopes of He, while H₂ and D₂ have comparable but much larger (than He) bound state energies on LiF.

Detailed measurement of inelastic gas surface scattering can give a great deal of information about the nature of gas-solid energy exchange. Energy accommodation, phonon spectra, and bound state energies
Fig. II-6. He scattering from LiF surface showing phonon emission and absorption peaks around (0,0) and (-1,-1) elastic peaks. (Reference 73).
are some of the experimental parameters that can be measured and used to describe the energy exchange interaction.

3. Reactive Scattering

The study of surface chemical reactions by molecular beam techniques is the logical goal of gas-surface energy transfer studies. The answer to the question of energy partitioning among the surface atoms and the various degrees of freedom of the desorbing gas particle is vital to an understanding of surface chemistry. Surface chemical reactions fall into two categories; those in which the surface acts as a catalyst for the reaction, and those in which the surface is one of the reactants. The simplest of the first type are surface dissociation, decomposition or rearrangement reactions. More complex examples are hydrogenation, exchange and oxidation reactions. The second type of reactions are exemplified by substrate oxidation and corrosion reactions.

Probably the simplest, yet one of the most important, surface chemical reactions is the dissociation of hydrogen on catalytic surfaces. This reaction is an essential initial step to countless technically important catalytic systems. It has been studied by a variety of techniques on a variety of surfaces, but only recently have molecular beam techniques been used to study this problem. Smith and Fite studied the production of H atoms on scattering \( \text{H}_2 \) from tungsten. Using modulated beam techniques, Krakowski and Olander studied H atom formation on tantalum. Both of these studies indicated an increasing reaction probability with increasing
surface temperature and residence times indicating complete thermal accommodation of the atoms before desorption from the surface. Mixed hydrogen-deuterium beams scattered from the tantalum surface did not result in HD formation. Atom evaporation at the high surface temperatures used is thought to account for the lack of HD formation.

Hydrogen-deuterium exchange was observed on scattering deuterium from epitaxial nickel surfaces in an ambient of hydrogen. The angular distribution of the product HD was $\cos^3 \theta$, perhaps indicating incomplete energy accommodation of the product HD. The isotope exchange reaction on platinum single crystal surfaces is the subject of a major part of this thesis, and will be discussed fully in the sections to follow. Molecular beam techniques have also been used to study the exchange reaction on copper single crystal surfaces. This study found evidence for substantial energy barriers to adsorption of hydrogen on copper, with the barrier height depending on the crystallographic orientation of the surface. The HD product was found to have a peaked at the normal, non-cosine, angular distribution.

The dissociation of $\text{N}_2\text{O}$ on catalyst surfaces is a slightly more complicated process. Coltharp et al. have used modulated beam techniques to measure the angular distributions of $\text{N}_2\text{O}$, $\text{N}_2$ and NO formed when $\text{N}_2\text{O}$ is scattered from a polycrystalline tungsten target. Cosine angular distributions for NO and $\text{N}_2$ indicate long residence times for dissociating $\text{N}_2\text{O}$ molecules. West and Somorjai, in a study carried out on the apparatus described in this thesis before its extensive modifications, obtained similar results for the decomposition
of N₂O on clean Pt(100) single crystal surfaces. However, from a carbon covered platinum surface the product angular distribution is peaked near the specular. This indicates direct scattering of the product before thermal equilibration with the surface. The difference in these two cases can probably be attributed to the exothermicity of reactions between C and N₂O giving CN, CO and CO₂ as reaction products. The dissociation of N₂O on the clean surface is an endothermic reaction.

The decomposition of formic acid on polycrystalline platinum foil has been studied by Dahlberg et al.¹⁰⁶ using molecular beam techniques. They find that the main decomposition products are CO₂ and H₂, with H₂O and CO being formed in a lesser amount. They find evidence for oxygen poisoning of the reaction causing limitation of the surface activity for decomposition at moderate surface temperatures.

The oxidation of NH₃ on platinum has been studied by Nutt and Kapur.¹⁰⁷ They find N₂, H₂O and NO products formed at the surface and no evidence of a gas phase radical intermediate. As this was a fixed detector apparatus, no information is available about the product angular distributions. A more extensive study of this important reaction has been undertaken by Ullman and Olander.¹⁰⁸

Smith and Palmer¹⁰⁹ have studied the oxidation of deuterium on an epitaxial platinum surface. They observed formation of D₂O when a modulated D₂ beam was scattered from the platinum substrate in an O₂ ambient. The angular distribution of the product D₂O was cosine, indicating thermal equilibration with the surface. They propose the
mechanism of the oxidation to be the adsorbed state reaction of four D atoms and an O₂ molecule to give 2 D₂O. Pressure dependence and angle of incidence dependence measurements support this mechanism.

Several more complex catalytic reactions have been given preliminary examination. The oxidation of ethylene on silver surfaces was found to produce CO₂ as the major product by Smith et al.\textsuperscript{110} Acharya et al.\textsuperscript{111} have studied the isotope exchange and decomposition of water on pyrolytic graphite surfaces. Their kinetic results are explained by diffusion of water into the bulk of the solid target. Studies of several other more complex catalytic reactions are the subject of parts of this thesis. These studies will be discussed in later sections.

Reactions in which the surface plays the role of a reactant have been more extensively studied, perhaps because of the generally higher reaction probability for surface oxidation and corrosion type reactions. McKinley's investigations of the nickel-chlorine\textsuperscript{112} and nickel-bromine\textsuperscript{113} systems are an example of this type of study. Results of these studies indicate dissociative adsorption of the halogen followed by desorption of NiX or disproportionation and desorption of NiX₂.

The oxidation of silicon and germanium has been extensively studied by molecular beam methods. A reaction probability of ~0.04 was found for the oxidation of germanium and silicon by molecular oxygen.\textsuperscript{114-116}
Atomic oxygen yielded a reaction probability in the range 0.3-0.6.\textsuperscript{117} Oxidation of the semiconductor surface by ozone had a reaction probability of 0.2 to 0.5.\textsuperscript{118} These results indicate that the dissociation of the O\textsubscript{2} molecule by transfer of energy from the surface to the oxygen-oxygen bond is the rate limiting step in surface oxidation of these semiconductors. Similar studies of halogen corrosion of semiconductor surfaces indicated high (0.2-0.5) reaction probabilities for reaction of molecular halogens with the surfaces.\textsuperscript{119,120} There appears to be a large steric hindrance to energy transfer between the "dangling bonds" of the semiconductor surface and the oxygen molecule, while the larger halogen molecules and ozone can more easily interact with the surface to form reactive atomic species.

Other oxidation studies have included the oxidation of pyrolytic graphite,\textsuperscript{121,122} tungsten,\textsuperscript{123} molybdenum,\textsuperscript{124} and tantalum.\textsuperscript{125} The graphite oxidation appears to be the most complex, with diffusion into the bulk at grain boundaries the rate determining step. Surface diffusion of oxygen to an active site appears to be necessary for the oxidation of molybdenum.

The use of molecular beam techniques for studying surface chemical reactions promises to add significantly to our understanding of the details of gas surface interactions. Hopefully, this information will help the chemist to understand the processes occurring in heterogeneous catalysis, corrosion and adsorption.
III. EXPERIMENTAL

A. Introduction

The successful design of an apparatus for molecular beam studies of gas-solid interactions depends largely on the satisfaction of four criteria. These criteria are flexibility, gas phase characterization, solid surface characterization, and signal to noise ratio. As could be expected the methods for satisfying these criteria often work at cross purposes. Therefore, the final design considerations are a compromise among the four goals. For example, the effort to increase signal to noise ratio by increasing beam intensity causes subsequent degradation in surface characterization capability by increasing the background load in the scattering chamber. Flexibility is sacrificed to signal to noise ratio if more sensitive but more specialized surface ionization detectors are substituted for a more universal detector.

This chapter describes in detail design modifications made to an existing molecular beam system to allow its use in studying reactive and non-reactive scattering systems. The experimental techniques which were used in these studies are also described.

B. Design Modifications

The previous experimental apparatus is shown schematically in Fig. III-1. It consisted of three differentially pumped chambers, one containing the source, the next housing a fixed frequency chopper or rotating disk velocity selector, and the third sorption, ion, and sublimation pumped chamber containing the scattering surface and
Fig. III-1. Schematic diagram of original molecular beam scattering apparatus. (Reference 126).
quadrupole mass spectrometer detector. The distance from the source to the scattering surface was 60 cm. The source was aligned externally and fixed in place. The beam was modulated by a fixed frequency tuning fork chopper. The scattering chamber was isolated from the beam production chambers by a large commercial gate valve. The quadrupole mass spectrometer detector was a standard EAI quad 250-A mounted on a 6 in OD conflat flange fitted with a rotary linear motion feedthrough. The scattering chamber was pumped by a 400 l/sec noble Vacion pump (Varian Associates) and a Ti sublimator. A single scattering crystal surface was externally aligned and mounted in the scattering chamber. The diffusion pumped beam production chambers were backed by a mechanical pump (Kinney KC15) and a Rootes blower mounted solidly in the roughing line in series with the mechanical pump. A description of the design and construction of the original apparatus is given in reference 126.

1. Roughing System Modifications:

The roughing lines and back up lines for the diffusion pumps were kept essentially as on the original apparatus, with changes being made in the 2 inch stainless steel tubing to accommodate the new positions of the diffusion pumps necessitated by modifications to the source and selector chambers. The Rootes blower was vibrationally isolated from the back up lines by a flexible 2 inch copper bellows. This eliminated the problem of microphonic noise pickup when operating the Rootes blower under high beam load. The glass system used for controlling the beam pressure was modified somewhat, and a vacsorb pump was added.
Fig. III-2. Schematic diagram of source inlet system.

Legend: x metal angle valves

1| thermal conductivity pressure gauges
2| greaseless teflon-glass valves

MP1 mechanical pump 1 (KC-15)
MP2 mechanical pump 2 (KC-2)
DP diffusion pump

T1,T2 traps
MM main manifold
BTA back to air
WT Wallace and Tiernan gauge
1L,5L one liter and 5 liter bulbs
LS liquid samples
LV1,LV2 leak valves

SC scattering chamber
SO source oven
SP sorption pump
AGM auxiliary gas manifold
BGM beam gas manifold
Fig. III-2.
to the gas inlet system for roughing. A schematic diagram of the source inlet system as modified is shown in Fig. III-2.

2. **Source Chamber Modifications:**

The source chamber was rebuilt as indicated in the cross sectional drawing of Fig. III-3. Three ports are available around the axis of the chamber for mounting molecular beam sources. These ports are aligned so that up to three separate sources could be moved in and out of the beam line independently. At present, only one source is in use. One of the other ports is used as a window, while the third is blanked off. The source in use is a small oven fitted with a multichannel glass capillary array as in the original apparatus. These sources have been adequately discussed in the literature.

An important characteristic of these sources is the very directed angular distribution which they exhibit. This makes the use of a movable source stage a necessity for aligning the maximum flux of the peaked distribution with the beam line. Slight misalignments can result in drastic beam intensity losses due to this very peaked distribution. The three dimensionally adjustable source stage used in this work is shown in Fig. III-4.

Ports have been included for electrical feedthroughs for the variable frequency chopper motor and reference photocell and for cooling water feedthroughs for the chopper motor. These additions will be discussed below. A viewport was added directly behind the source, and a small window installed in the back of the source oven to allow the use of a laser beam for source, crystal and detector alignment.
Fig. III-3. Source chamber cross sections.

Source Chamber
Horizontal Cross-section

Source Chamber
Vertical Cross-section

Chopper mounting plate (1/4" OFHC)

Thermal conductivity gauge TC3

Ion gauge IG3

Auxiliary source (blanked off)

Beam line

Source oven stage

Viewport

XBL 751-5657
Fig. III-4. Source oven mounting stage.
3. **Selector Chamber Modifications:**

The 60 cm. incident beam path of the original apparatus was necessary for the installation of a slotted disk velocity selector\(^1\) used to make the incident molecular beam monoenergetic. This long beam path served to drastically reduce the incident beam flux due to \(1/r^2\) attenuation, and the poor transmission characteristics of the velocity selector reduced this flux even further. There is some evidence as well that the energy distribution of the incident molecules does not markedly affect the details of gas-surface scattering.\(^2\) For these reasons it was decided to forego the use of a velocity selector in the incident beam in favor of increasing the incident beam flux and therefore the signal to noise ratio. This was accomplished by the major modifications made to the selector chamber (and scattering chamber) resulting in shortening the incident beam path to 15 cm. This chamber is shown in horizontal and vertical cross section in Fig. III-5.

This chamber is welded as a continuous piece to the source chamber described above and the scattering chamber to be described below. A large D shaped opening is cut into the bulkhead between it and the source chamber. This opening is closed by a removable copper plate held in place by several machine screws around its perimeter. The copper plate has two copper tubes fixed to it as shown in Fig. III-6. The larger tube holds the variable speed synchronous motor on which the slotted disk chopper is mounted. The second tube, mounted at the outside edge of the slotted disk, houses a light emitting diode-photocell assembly for monitoring the frequency of modulation produced by the
Fig. III-5. Selector chamber cross sections.
Fig. III-6. Chopper motor mounting plate (not to scale).
rotating slotted disk. The entire copper plate assembly is water cooled for longer motor bearing life and smoother operation. A 1 mm hole is cut in the plate for the initial collimation of the beam. This is the only opening between the source and selector chambers. A schematic diagram of the motor circuitry and the LED-photodiode assembly is shown in Fig. III-7.

The bulkhead between the selector and scattering chambers has a 1 cm hole centered on the beam line. A machined valve seat insert was welded into this opening and a 1 mm hole drilled through it for final collimation of the molecular beam. This was accomplished after the final welding together of the three chambers had been completed. This machined insert serves as a seal seat for a specially designed zero length gate valve separating the scattering chamber from the source and selector chambers. This valve allows the operator to break vacuum in either the scattering chamber or the diffusion pumped chambers separately. Pressures below $10^{-9}$ torr can be maintained in the scattering chamber with the rest of the system at atmospheric pressure using this valve. A diagram of the valve is shown in Fig. III-8.

Ports have also been added to this chamber to accommodate future modifications. Ports above and below the beam line are available for addition of a low frequency beam modulator or incident beam state selecting device.
Fig. III-7. Schematic diagram of chopper motor system and reference signal electronics.
Scattering chamber

Valve seats

Through hole

Selector chamber

Source chamber

Welded S.S. bellow

Brass nut

Support

2"

Fig. III-8. Scattering chamber zero length gate valve.
4. Scattering Chamber Modifications:

The scattering chamber was modified to decrease the incident beam path by removal of a wedge shaped section from the upper part of the original scattering chamber cylinder. The selector and source chamber assembles were then welded directly to this modified cylinder, with the selector chamber wall forming the bulkhead between the two chambers. This is shown in cross section in Fig. III-9.

Several ports were added to the scattering chamber to accommodate modifications described here and to increase the system flexibility for possible future modifications. A small window was added in the beam line allowing optical alignment of the crystal and detector. A needle for introducing gases to the background of the scattering chamber replaced the isotropic source of the original design. This directed source is mounted on top of the scattering chamber, at an angle of 46° to the beam line and 1.6 cm from the crystal. Flow rate through this needle is controlled by a Granville-Phillips leak valve. Two ports are available for glancing incidence electron guns for Auger spectroscopy. One port is aligned for use with the scattering surface turned away from the incident beam, while the other is aligned for use when the beam is impinging on the surface. This makes possible the use of the modulated beam technique for Auger study of adsorption intermediates. A 10 inch OD port was added to permit the installation of a liquid helium cryopump (Excalibur model CVR-100) for pumping hydrogen and helium and for reducing the CO background in the scattering chamber. It has not been necessary to use this pump in any of the work.
Fig. III-9. Scattering chamber cross sections.
reported here. An ion gun on a 1 3/4 inch flange replaced the original 4 inch flange mounted ion gun. It is mounted above the beam line and produces an ion beam incident on the sample at 45° to the beam line.

Three copper cryopanels were added to the scattering chamber to increase the system pumping speed for condensible gases. These are flat copper tanks located around the perimeter of the scattering chamber which are periodically filled with liquid nitrogen. These panels, coupled with a titanium sublimator mounted on a separate port reduce the background pressure in the scattering chamber to \( \sim 5 \times 10^{-10} \) torr. Ninety percent of the background is hydrogen with the rest divided among methane, CO, and hydrocarbon fragments. Various other ports are available on the top, sides and bottom of the chamber for future additions. (Fig. III-9)

5. Detector Modifications:

The original detector design employed a standard EAI quad 250-A spectrometer counterbalanced on the 30 cm shaft of a linear-rotary motion feedthrough. This feedthrough was mounted on a 6 inch OD conflat flange. The entire spectrometer assembly was removable by threading the assembly through the 4 inch hole in the chamber bottom.

The inconvenience of the small bottom opening and the desire to convert the detector to an ion counting device resulted in the present modifications. The original 6 inch OD flange and linear-rotary feedthrough were mounted in the center of a 10 inch OD flange. The bottom of the chamber was turned and drilled to produce a mating flange. The 8 inch opening makes removal of the detector for filament replacement and maintenance much simpler.
The conversion of the spectrometer from a current measuring device to one suitable for ion counting involved three major changes from the original design. The original 14 stage Cu-Be multiplier supplied by EAI was replaced with a high gain 18 stage Cu-Be venetian blind type multiplier (EMI model 9642-4B). This multiplier employs a replaceable first dynode assembly. Since the first dynode degrades most rapidly, the multiplier can be returned to original gain conditions without complete (and expensive) replacement of the entire multiplier.

To reduce noise produced by photons and excited neutrals striking the first dynode of the multiplier, it was mounted at right angles to the quadrupole rod assembly. In the original design the multiplier was mounted directly below the quadrupole rods, in direct line of sight to the ionizing filament. This right angle mounting was achieved by attaching the multiplier and quadrupole assemblies to orthogonal faces of a milled out stainless steel cube. Figure III-10 shows a cross sectional diagram of this assembly. The exact shape of the interior of the cube was obtained by calculation of ion trajectories in fields set up by the multiplier and the ground can. The can geometry was varied until the maximum number of ion trajectories were directed to the multiplier opening. Figure III-11 shows a plot of the field and the ion trajectories for the final design. The program used for these calculations is discussed in the appendix.

The signal cable feedthrough was removed from the central flange near the RF feedthroughs of the original design. It was placed on a separate miniconflat flange farther away from the RF leads. This was
Fig. III.10. Cross sectional diagram of right angle electron multiplier assembly.
Fig. III-11. (a) Field lines for geometry of Fig. III-10. (Electron multiplier to right) (b) Ion trajectories for geometry of Fig. III-10.
done to reduce the RF noise pickup which was a problem with the original apparatus and which would prevent the operation of the spectrometer in an ion counting mode. The signal cable was also shielded by a stainless steel tube for about 1/3 of its length nearest the RF leads. The flexible portion was the same double shielded coaxial lead used in the original apparatus. In order to further reduce RF noise, a pass capacitor (bakeable, UHV Corning CY30C 103J) was attached to the last stage of the multiplier, as shown in Fig. III-12.

The spectrometer assembly is mounted on the motion feedthrough so that the ionizer aperture is 3.0 cm from the crystal surface. It is 1.84 cm from the ionizer aperture to the center of the extractor plate. The counterweight was removed to take out the wobble introduced by the delicate balance as the spectrometer is rotated. A schematic diagram in cross section of the modified apparatus is shown in Fig. III-13. Figure III-14 and III-15 show photographs of the present apparatus. Figure III-16 indicates the placement of the various system parts discussed above.

C. Low Energy Electron Diffraction

The characterization of a solid surface for energy transfer and chemical reaction studies must include a determination of the structure of that surface on an atomic scale. This can be accomplished by using single crystal solid surfaces and the technique of low energy electron diffraction or LEED. An electron with energy between 10 and 200 eV
EMI 9642 18 Stage Electron Multiplier

-3 KV ——— CuBe multiplier dynode
(stages connected by 1 meg Ω resistors)

Signal ———— Corning UHV capacitor
(100 μF)
CY 30C 103 J
XBL 7411-7593

Fig. III-12. Electron multiplier wiring diagram.
Fig. III-13. Schematic diagram of modified molecular beam scattering apparatus.
Fig. III-14. Overall view of apparatus. Vacuum control on left, vacuum chamber, data collection electronics in center and on right.
Fig. III-15. Far left electronics racks. From left, LEED, ion bombardment supplies; Auger spectrometer; vacuum interlocks; pump controls and pressure gauges.
Fig. III-16. Photograph of vacuum envelope. A-gate valve, B-scattering chamber, C-ion pump, D-Ti sublimation pump, E-ion gun, F-manipulator, G-LN₂ feed lines, H-diffusion pump gate valves, I-background gas inlet line, J-source chamber, K-source oven stage, L-diffusion pump, M-sorption pump.
has a wavelength of the order of one to several angstroms. This wavelength, given by the deBroglie relationship as

\[ \lambda = \sqrt{\frac{150}{V(\text{eV})}}, \]

is comparable to the spacing between atoms in a crystal lattice. When such electrons elastically scatter from a crystal lattice, a diffraction pattern results, with information about the crystal structure of the scattering lattice.

Slow electrons have a very high cross section for elastic and inelastic scattering by atoms in a solid lattice. This fact gives rise to the major advantage and disadvantage of the LEED technique as a surface structure analysis tool. Significant scattering and attenuation of the incident beam takes place in the first two or three layers of the solid, therefore giving diffraction information about only the surface region. This same scattering and attenuation gives rise to multiple scattering in the first few layers, severely complicating the analysis of the diffraction information to give 3 dimensional structural information about the surface layer. This effect is illustrated in Fig. III-17.

The apparatus used for LEED characterization of the surfaces studied in this work is shown schematically in Fig. III-18. It is a standard Varian Associates three grid optics mounted so that the electron beam intersects the molecular beam line of the apparatus orthogonally at the front surface of the scattering target. The crystal is mounted in the center of curvature of the optics grids. The electron gun utilizes a thoria coated filament in a low energy flood type gun.
Fig. III-17. Diagram showing multiple scattering and attenuation of low energy electrons compared with X-rays.
Fig. III-18. Schematic diagram of 3 grid LEED optics.
The flange on which the optics are mounted is covered with a mu metal can to reduce interference due to earth and ion pump magnetic fields. A small trimming magnet is used outside the vacuum chamber for final alignment of the electron beam.

LEED patterns and real space diagrams of the three surfaces studied in this work are shown in Fig. III-19. Figure III-19a shows the LEED pattern of the Pt(111) surface. This is the close packed hexagonal plane of the face centered cubic platinum crystal structure. The sharp hexagonally symmetric features and low background between diffraction beams indicate a smooth, well ordered surface free of adsorbed contaminants. The real space diagram exhibits the same hexagonal symmetry evident in the diffraction pattern. This surface is the most densely packed of the low index planes of platinum.

Figure III-19b shows the LEED pattern of the Pt(997) surface. This surface, and the one whose LEED pattern is shown in Fig. III-19c, are stepped surfaces. Perhaps a more descriptive nomenclature than the (997) Miller index is the LEED nomenclature developed in this laboratory which describes the step and terrace orientation and relative widths. In this nomenclature the (997) surface is designated the Pt-(s)[9(111)×(111)] surface. This is a stepped surface cut 6.2° away from a (111) plane in the [111] direction, resulting in a surface with monatomic steps of (111) orientation separated by 9 atom wide terraces also of (111) orientation. The LEED pattern shows sharp hexagonally
Fig. III-19. LEED patterns and real space schematics of the three surfaces used in this work. (a) Pt(111) (b) Pt(997) (c) Pt(553).
symmetric spots which are split into multiplets by the extra periodicity of the steps. The distance between the multiplets is one ninth the distance between the major features, indicating an extra periodicity nine times the Pt–Pt distance. This surface is diagrammatically shown below the LEED pattern. The orientation of the splitting in the LEED pattern can be used to determine the orientation of the step edges with respect to the incident beam line. This information will be seen to be important in the discussion of results that follows.

The other stepped surface used in this work is the Pt(553) surface. Its LEED pattern and real space diagram are shown in Fig. III-19c. Its descriptive nomenclature is the Pt-(s)[5(111)×(111)] surface. This surface is characterized by monatomic steps of (111) orientation separated by terraces 5 atoms wide also of (111) orientation. It is prepared by cutting a platinum single crystal 12.5° from the (111) plane in the [111] direction. The LEED pattern again shows the hexagonally symmetric major features split into multiplets. The multiplet spacing is one fifth the major feature spacing indicating an extra periodicity five times the Pt–Pt distance.

The LEED pattern, then, allows characterization of the 2 dimensional structure of the scattering surface. It gives rough information (by the appearance of high background or extra features) about the presence of adsorbed gases on the metal surface. The LEED pattern also gives information about the geometrical orientation of the scattering surface microscopic structure with respect to the incident molecular beam and the
experimental detector.

D. Auger Spectroscopy

In order to more fully characterize the surface on which gas-surface energy transfer takes place, it is important to know the chemical composition of the surface region. This can be conveniently accomplished by the use of Auger electron spectroscopy. Auger spectroscopy is based on the Auger process, an inner shell atomic relaxation phenomena first observed by Pierre Auger in 1925. This process is illustrated by means of a simple energy level diagram in Fig. III-20. It is compared with the perhaps more familiar X-ray fluorescence process. When a vacancy is produced in an inner shell by the ejection of an electron by some form of ionizing radiation (high energy electrons, X-rays, γ rays), this vacancy is filled by relaxation of an upper shell electron. The energy given up in this process can go into two channels. If a photon is emitted, the process is X-ray fluorescence. If the energy is transferred electrostatically to an upper level electron with its subsequent ejection from the atom, the process is the Auger process. The ejected electron is called the Auger electron. Its energy is given by

$$\bar{E}_{w_0 x-y_q} (z) = \bar{E}_{w_0} (z) - \bar{E}_{x_p} (z) - \bar{E}_{y_q} (z') - \phi_c$$

to a first approximation, where the terms are described in Fig. III-20. \(\phi_c\) is the work function of the material. The Auger electron energy is characteristic of the atom from which the electron was ejected. By
Fig. III-20. Energy level diagram of the Auger process compared with X-ray fluorescence.
analyzing the energies of electrons ejected from a solid during bombardment by vacancy creating radiation, information about the chemical composition of the solid can be obtained. This is the basis of Auger electron spectroscopy.

Auger spectroscopy is a surface sensitive technique for much the same reason that LEED gives surface structural information. The ionizing radiation most commonly used is an electron beam of one to 10 kV energy. This electron beam penetrates several layers of the solid, producing vacancies in perhaps the outer 10 atomic layers. More importantly, the Auger electrons themselves, with energies usually less than 1 kV have mean free paths in the solid significantly less than 10 atomic layers. Due to the short mean free paths of these electrons, only those leaving the solid from the outermost two or three layers will reach the electron energy analyzer without prior energy loss by inelastic scattering. Electrons suffering an energy loss do not appear in the characteristic energy peak of a particular atom but contribute to the overall background.

The sensitivity of Auger spectroscopy to certain elements is limited by the ionization cross section of the element and the probability for the Auger process or the competing X-ray fluorescence process to occur. This probability is dependent on the atomic number of the particular element, and favors the Auger process for low z elements. Figure III-21 shows the relative probabilities for the two processes as a function of atomic number. The overall sensitivity of Auger spectroscopy ranges from about 0.1% to 1.0% of a monolayer depending
Fig. III-21. Auger and X-ray fluorescence yield versus atomic number.
on the particular element. [This corresponds to roughly $10^{12}$ to $10^{13}$ atoms detected per cm$^2$.] The understanding of the Auger process has not progressed to the point where extremely accurate quantitative analysis is possible. Rough quantitative comparisons are made by comparing Auger peak heights and utilizing standards of known concentration. Since the work described in this thesis was generally concerned with the presence or absence$^+$ of a certain atomic species on the scattering surface, quantitative considerations were not of great importance.

The apparatus used for Auger spectroscopy in this work is illustrated schematically in Fig. III-22. It uses the three grid LEED optics described above as an electron energy analyzer. Electrons of various energies are allowed to pass through the grid system by sweeping a retarding voltage on the second grid. The outer grids are grounded for shielding. Superimposed on the second grid ramp voltage is a low voltage AC modulation. This modulates the electron current collected on the positively biased LEED screen. The modulated current can then be electronically differentiated by amplifying the second harmonic of the signal with a lock in amplifier tuned to twice the modulation frequency. This modulation and differentiation technique$^{140}$ allows detection of the weak Auger transitions which would otherwise be lost in the steeply sloping background of inelastically scattered electrons.

$^+$Absence must be taken to mean not present in detectable quantities. Therefore, less than 0.1-1.0% of a monolayer of the element in question is present when it is termed absent in an Auger spectrum.
Fig. III-22. Schematic diagram of Auger electronics.

XBL 7412-7778
This technique has been in use only since 1968 and has resulted in a
tremendous growth in the use of the Auger process for surface atomic
identification.

Figure III-23 shows an Auger spectrum of a clean platinum surface.
Above the 240-325 volt region are Auger spectra of surfaces
contaminated with carbon and calcium. These are the major contaminants
which had to be dealt with in this work. Procedures for the removal
of the contaminants are described in detail in a later section.

E. Modulated Beam Technique

In the study of gas-surface energy transfer, the time dependent
behavior of the interaction is very important. Particularly in the
study of energy transfer occurring during a chemical reaction on a
surface, the time evolution of the system describes the mechanism and
kinetics of the reaction. The determination of this information for
reactions on well characterized solid surfaces is basic to an under-
standing of the process of heterogeneous catalysis. The ability to
extract this time dependent behavior in surface reactions has been
realized due to the development of the modulated molecular beam
technique.4,141 This method allows determination of kinetic information
not available by non-molecular beam methods. This section will be
devoted to a brief discussion of the principles behind these techniques
and their use in unraveling surface reaction mechanisms.
Fig. III-23. Auger spectrum of clean platinum with Ca and C contaminated spectra above for comparison.
A beam of molecules impinging on a surface with intensity $I_0$, when mechanically chopped at angular frequency $\omega$, can be thought of as a modulated driving function. When a reaction takes place on the surface, this modulated function is changed by the processes of the surface reaction. The surface acts as a differential operator operating on the modulated incident beam. A beam of products leaves the surface with different modulation. By monitoring the waveform of the product modulated beam as a function of incident beam modulation frequency, incident beam intensity, incident beam energy, surface temperature, surface structure and chemical composition, incident beam angle and scattered beam angle, models for the surface operator (the surface reaction mechanism) can be formulated and compared with the experimental waveform behavior.

The processing of the modulated product beam waveform in a lock-in amplifier (Fig. III-24) results in a signal with amplitude $A$, $\phi$ degrees out of phase with the reference signal produced at the mechanical chopper. $A$ and $\phi$ correspond to the first Fourier components of the scattered waveform. For surface reactions showing first order pressure dependence, the higher order Fourier components do not contain additional reaction information. Therefore, for first order processes, the behavior of $A$ and $\phi$ as a function of the kinetic variables mentioned above gives information about the surface reaction mechanism. An example of the method for a simple adsorption-desorption process should help to illustrate the technique.
Fig. III-24. Block diagram of signal processing electronics for molecular beam experiment.
Consider a beam of diatomic molecules $A_2$ of intensity $I_0$ chopped by a gating function $g(t)$ which is periodic with angular frequency $\omega$. They interact with the surface with sticking probability $\eta$ and desorb with rate constant $k_d$.

\[ A_2(g) + 2S \xrightarrow{g} 2[SA_{ads}] \xrightarrow{k_d} 2S + 2A(g) \] (1)

A surface mass balance on adsorbed A atoms gives

\[
\frac{d[SA_{ads}]}{dt} = 2\eta I_0 g(t) - k_d [SA_{ads}] 
\] (2)

Substituting a sinusoidal function for $g(t)$ and a trial solution for $[SA_{ads}]$ gives

\[
i\omega[SA_{ads}]^* e^{i\omega t} = 2\eta I_0 g_1 e^{i\omega t} - k_d [SA_{ads}]^* e^{i\omega t}
\] (3)

Equation (3) is solved for $[SA_{ads}]^*$ to give

\[
[SA_{ads}]^* = \frac{2\eta I_0 g_1}{k_d + i\omega}
\] (4)

Writing the complex number in polar form and solving for the rate of desorption ($k_d[SA_{ads}]^*$) gives

\[
k_d[SA_{ads}]^* = \frac{2\eta I_0 g_1 e^{-i\tan^{-1}(\omega/k_d)}}{\sqrt{1 + (\omega/k_d)^2}}
\] (5)
A reaction product vector can be defined which is the ratio of scattered product signal to incident reactant flux. In the limit of low reaction probabilities this vector is just the ratio of $k_d[S_{ads}]^*$ to $I_0g_1$ modified by a phase factor related to the surface residence time of the products.

$$\varepsilon = \frac{k_d[S_{ads}]^*}{I_0g_1} e^{-i\phi} = \varepsilon e^{-i\phi}$$  \hspace{1cm} (6)

Equation (5) can then be written

$$\varepsilon e^{-i\phi} = \frac{2\eta e^{-i\tan^{-1}(\omega/k_d)}}{\sqrt{1 + (\omega/k_d)^2}}$$  \hspace{1cm} (7)

$\varepsilon$, the ratio of product to reactant signal, is given by

$$\varepsilon = \frac{2\eta}{\sqrt{1 + (\omega/k_d)^2}}$$  \hspace{1cm} (8)

and $\phi$, the phase difference between product and reactant signals, is given by

$$\phi = \tan^{-1}(\omega/k_d)$$  \hspace{1cm} (9)

By observing the amplitude and phase of the product and reactant signals as a function of chopping frequency $\omega$, $k_d$ can be determined by a plot of $\tan\phi$ vs. $\omega$ and $\eta$ can be determined by a plot of $1/\varepsilon^2$ vs $\omega^2$. Determinations of $k_d$ at several surface temperatures can give the activation energy and pre-exponential factor for an Arrhenius-type
rate equation. Similar analyses of more complex surface reaction models, including series, parallel and combination series-parallel models, enable the experimenter to extract kinetic parameters and to choose appropriate surface reaction mechanisms.

In the above analysis, a sinusoidal gating function was employed. As has been pointed out, for first order surface processes a sinusoidal gating function is allowed in the analysis regardless of the actual waveform of the incident beam due to the lack of information in higher order Fourier components. For processes other than first order the analysis becomes more complex and must take account of the actual gating function waveform. Several examples of non-first order processes have been treated by Olander.\textsuperscript{142} Recent work by Foxon, \textit{et al.},\textsuperscript{143} has shown the advantage of collecting the entire waveform and using fast Fourier transform techniques to extract the kinetic information, even for first order processes. The advantage to this method appears to be mainly in the increased amount of data available from a single experiment, as the higher harmonics of the signal give information at higher frequencies simultaneously. This method is also directly applicable to non-first order processes without the more complex analysis necessary in lock in detection methods. This method will be discussed more fully in the appendix.

In the work described here, lock in detection was used principally. Preliminary experiments were done in the ion counting entire waveform collection mode, and the system could be easily used in this manner for processing weak reaction signals. Most of the work described here
involved signals whose count rate would have saturated the multiplier of the mass spectrometer.

F. Samples

The single crystal scattering surfaces used in this work were cut from bulk single crystal platinum rods and prepared identically. The single crystal rods were purchased from Materials Research Corporation. They were certified 99.999% pure, were 6 mm in diameter and about 2 inches long. Back reflection of X-rays was used to align the crystals for the particular plane of interest. Figure III-25 shows a zone diagram of the three surfaces used in this work. The (111) surface was cut to expose a (111) plane. The (997) surface was cut 6.2° from the (111) plane in the [111] direction, exposing the 9(111)x(111) stepped surface. The (553) crystal was cut 12.5° from the (111) plane in the [111] direction exposing the 5(111)x(111) stepped surface. The crystals were spark machined from the single crystal rod about 1 mm in thickness.

After orientation and slicing, the crystals were polished mechanically on successively finer grades of abrasive, ending with a polish on 1μ diamond paste followed by 0.1μ alumina. The crystals were rinsed in distilled water and methanol and then spot welded to high purity (5N+) polycrystalline platinum support tabs. A Pt-Pt 10%Rh thermocouple was spotwelded to the back face of one of the two crystals to be mounted in the chamber at one time, as described below. The entire crystal, support and thermocouple assembly was etched in hot (100°C) 50% aqua regia, rinsed in distilled water and methanol and mounted on a Varian crystal
Fig. III-25. Crystallographic zone diagram for the two stepped surfaces.
manipulator. Figure III-26 shows the manipulator mounting assembly which allowed two crystals to be mounted in the scattering chamber simultaneously. One crystal was fitted with a thermocouple as described above. The temperature of the other crystal was monitored with an infrared pyrometer (Infrascope 31000-04) calibrated by comparison with the thermocouple fitted crystal.

Once the crystals were mounted in the vacuum chamber they were subjected to a series of oxidation, ion bombardment, and heat treatments to remove residual impurities and give a clean well ordered scattering surface. The major residual impurity in these crystals was carbon, and calcium to a lesser extent. The carbon was purged from the bulk of the crystal by heating to 1000°C in 2×10^{-5} torr oxygen for about 50 hours. This oxidation treatment was sufficient to remove carbon from a freshly prepared crystal. After this initial purging, a similar oxidation for about 1 hour was sufficient to remove carbon from adsorbed background gases (CO, CH₄) prior to an experimental run.

The removal of calcium proved to be slightly more difficult, though the crystals used in this work were not as badly contaminated as other samples used in this laboratory. After prolonged oxidation at 1000°C, the Auger spectrum showed the presence of a fairly large amount of calcium. The calcium appeared to precipitate at the surface from the bulk of the crystal, and in large amounts had the appearance of a whitish scum. This could be removed slowly by ion bombardment annealing cycles. It was found that high temperature annealing was the most efficient method for Ca removal. Heating the crystal in vacuum or in oxygen
Fig. III-26. Diagram of double crystal holder.
to 1300° or 1400°K resulted in the disappearance of the calcium peak from the Auger spectrum. It is not known whether the calcium is volatilized from the surface, or becomes highly soluble in the bulk at these temperatures. In either case, the result of the high temperature treatment is to remove the calcium peak from the Auger spectrum. The surfaces studied in this work exhibit the clean platinum Auger spectrum shown in Fig. III-23. The upper lines in this figure indicate the Auger spectra observed prior to the high temperature oxidation which removes carbon and calcium. Surfaces showing a slight calcium contamination often exhibited very complex LEED patterns. As our interest was in the clean platinum surface, these complex patterns were something of a nuisance and therefore were not extensively studied. A careful study of these patterns, however, could result in some understanding of the calcium-platinum intermetallic bonding. An example of such a LEED pattern is shown in Fig. III-27.

G. Beam Materials

A variety of gases and high vapor pressure liquids were used as beam materials and background reagents in the work described in this thesis. Table III-1 lists these materials, the supplier and impurity levels of these materials.
Table III-1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Purity (%)</th>
<th>Major impurities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>Matheson</td>
<td>99.995</td>
<td>(N_2 &lt; 5 \text{ ppm}) (O_2 &lt; 1 \text{ ppm})</td>
</tr>
<tr>
<td>Deuterium</td>
<td>Matheson</td>
<td>99.5</td>
<td>(H_2 &lt; 0.1%) (HD \sim 0.4%)</td>
</tr>
<tr>
<td>Helium</td>
<td>Matheson</td>
<td>99.995</td>
<td>(Ne &lt; 5 \text{ ppm}) (N_2 &lt; 1 \text{ ppm}) (O_2,Ar,H_2 &lt; 1 \text{ ppm})</td>
</tr>
<tr>
<td>Argon</td>
<td>Matheson</td>
<td>99.995</td>
<td>(N_2 &lt; 5 \text{ ppm}) (O_2,H_2 &lt; 1 \text{ ppm})</td>
</tr>
<tr>
<td>Neon</td>
<td>Matheson</td>
<td>99.995</td>
<td>(He &lt; 50 \text{ ppm}) (H_2 &lt; 5 \text{ ppm}) (N_2,O_2,Ar &lt; 1 \text{ ppm})</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Matheson</td>
<td>99.95</td>
<td>(N_2 &lt; 400 \text{ ppm}) (Ar &lt; 100 \text{ ppm}) (H_2 &lt; 50 \text{ ppm}) (CO_2,CO &lt; 10 \text{ ppm}) (N_2O &lt; 1 \text{ ppm}) (H.C. &lt; 1 \text{ ppm})</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Matheson</td>
<td>99.999</td>
<td>(Ar &lt; 5 \text{ ppm}) (O_2,H_2,He,Ne &lt; 1 \text{ ppm})</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>Matheson</td>
<td>99.5</td>
<td>(CO_2 \sim 0.2%) (N_2 \sim 0.1%) (H_2 \sim 0.1%)</td>
</tr>
</tbody>
</table>
Table III-1. (Cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Purity (%)</th>
<th>Major impurities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide</td>
<td>Matheson</td>
<td>99.995</td>
<td>CO$_2$,N$_2$ &lt; 50 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H$_2$O$_2$ &lt; 10 ppm</td>
</tr>
<tr>
<td>Methane</td>
<td>Matheson</td>
<td>99.97</td>
<td>N$_2$ &lt; 80 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>propane &lt; 50 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ethane &lt; 30 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O$_2$ &lt; 20 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO$_2$ &lt; 10 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H$_2$O &lt; 5 ppm</td>
</tr>
<tr>
<td>Isobutylene</td>
<td>Matheson</td>
<td>99.0</td>
<td>Other H.C. ~ 1%</td>
</tr>
<tr>
<td>Monomethylamine</td>
<td>Matheson</td>
<td>98.0</td>
<td>NH$_3$, ~ 1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>dimethyl,trimethylamine ~ 1%</td>
</tr>
<tr>
<td>Formic acid</td>
<td>Matheson, Coleman &amp; Bell</td>
<td>93(min)</td>
<td>acetic acid .4%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NH$_4$ .005%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>residue .003%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>sulfate .003%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>heavy metal .001%</td>
</tr>
</tbody>
</table>
Fig. III-27. LEED pattern of Ca contaminated Pt surface.
H. System Calibrations and Data Collection

The angular divergence of the incident molecular beam is defined by the diameter of the collimating orifices and the distance between them. This geometry is shown in Fig. III-28. It indicates an angular divergence of \( \sim 2^\circ \). This corresponds to a beam diameter at the crystal of 1.6 mm and 1.8 mm at the downstream detector. The angular profile of the beam as determined by the mass spectrometer detector for a helium beam is shown in Fig. III-29. It can be seen that the calculated geometric divergence and the measured divergence agree quite well.

The acceptance angle of the ionizer detector is determined by the distance from the crystal to detector and the diameter of the ionizer collimating orifices. This geometry is shown in Fig. III-30. The acceptance angle is \( \sim 5^\circ \).

A plot of source oven pressure vs. mass spectrometer signal is shown for a \( \text{D}_2 \) beam in Fig. III-31. It can be seen that the increase in detector signal is nearly linear with the increase in source oven pressure up to a source pressure of \( \sim 6 \) torr. This plot is for a beam temperature of 300\(^\circ\)K.

The measurement of the absolute phase of a modulated signal in the present system involves several corrections to the measured signal phase. These corrections are discussed in detail in a number of places.
\[ \alpha = 2 \arctan \left( \frac{\text{orifice radius}}{b/2} \right) \]

\[ = 2 \arctan \left( \frac{0.5}{30} \right) = 2(57') = 1^\circ 54' \]

Fig. III-28. Beam divergence geometry.
Fig. III-29. Incident He beam angular profile.
\[ \beta = 2 \arctan \left( \frac{1/2 \text{Ionizer Opening}}{d} \right) \]
\[ = 2 \arctan \left( \frac{1.3}{30} \right) = 2(2^\circ 28') = 4^\circ 56' \]

Fig. III-30. Detector acceptance angle geometry.
Fig. III-31. Detector signal vs. beam oven pressure for $D_2$ beam.
in the literature. The measured phase shift, when a modulated beam scatters from a surface, is a combination of factors, given by the following expression.

\[
\phi_{\text{meas}} = \phi_{\text{mech}} + \phi_{\text{tr}_1}(m_r, T_b, \omega) + \phi_{\text{res}} + \phi_{\text{tr}_2}(m_p, T_s, \omega) + \phi_{\text{m.s.}}(m_p, \omega, V_i) + \phi_x(\omega)
\]

\(\phi_{\text{mech}}\) is the mechanical phase shift due to the different positions on the chopper wheel for the initiation of the beam modulation and the light reference signal. It is a constant determined by the chopper geometry. \(\phi_{\text{tr}_1}\) and \(\phi_{\text{tr}_2}\) are phase shifts due to flight time of the molecules from the chopper to the crystal and the crystal to detector respectively. \(\phi_{\text{tr}_1}\) depends on the reactant mass, its temperature and the modulation frequency. \(\phi_{\text{tr}_2}\) depends on the product mass, the surface temperature (complete equilibration assumed) and the modulation frequency. Of course the reactant and product masses and temperatures could be identical for certain cases. \(\phi_{\text{res}}\) is the phase shift due to residence of the molecules on the surface, and is the phase shift containing all the kinetic information about the surface reaction. In a surface reaction study this is the piece of information which must be extracted from the other phase shifts. \(\phi_{\text{m.s.}}\) is the phase shift due to travel time of the detected ions from the ionizing region to the electron multiplier in the mass spectrometer. It is a function of the ion mass, its accelerating voltage and the modulation frequency. \(\phi_x\) is the phase shift due to the complex impedance of the cables from the
electron multiplier to the lock in amplifier. It is a function of frequency and can be readily calculated if the value of the resistance and capacitance of this cable network is known.

For a chemical reaction, the difference in $\phi_{res}$ for the products and reactants is the information necessary for kinetic analysis. This greatly simplifies the phase determination, as all of the phase components cancel in this difference except those due to molecular transit times and surface residence time. If the difference in mass or velocity (temperature) is not great between product and reactant, transit time phase shifts become very small. The measured phase difference is then equal to the residence time phase difference. This is the case for the reactive studies discussed in the main part of this dissertation.

Experiments were conducted, however, to assure that the individual phase components behaved predictably. The phase shift of the signal with the beam directly incident on the detector was measured as a function of modulation frequency for a series of gases. The results of these measurements are shown in Figs. III-32 and III-33. Figure III-32 shows the measured phase plotted vs. modulation frequency for He, $D_2$, CH$_4$, O$_2$ and Ar beams. The lines are least squares fits to the data points. By extrapolation of these plots to zero frequency, the mechanical phase shift can be determined. The average of the intercepts for the five least squares lines gives a value of $235.2 \pm 0.8$ for this $\phi_{mech}$. Figure III-33 shows the measured transit phase shift, after correction for $\phi_{mech}$, $\phi_{m.s.}$, and $\phi_x$ have been applied, for each of the five gases. The solid lines indicate calculated phase shifts for square modulated
Fig. III-32. Determination of $\phi_{\text{mech}}$. 
Fig. III-33. Corrected $\phi$ compared with calculated $\phi$. 
Maxwellian beams as given by Harrison, Hummer and Fite. The agreement is seen to be good. Any remaining disagreement between measured and calculated values must be assigned to a detector bias function as described by Siekhaus, et al. This bias function has not been determined for the present apparatus, as the correction is small and of interest only for the determination of absolute phase and amplitude values.

The effect of the beam oven temperature on the phase shift was also investigated. The oven temperature was varied in the range 300-600°K while modulating the D₂ beam at several frequencies. The results of these experiments along with predicted phase shifts from Harrison, Hummer and Fite are shown in Fig. III-34. As can be seen, only for the fastest chopping frequencies is the effect on phase shift large. It follows the predicted value quite nicely.

A few words should be included concerning the data collection and analysis. The output of the lock-in amplifier at phase settings of 0.0 and 90.0 degrees is recorded for the reactant and product mass spectrometer signals for each frequency, temperature, pressure and angle of interest. A typical recorder trace from the lock-in output is shown in Fig. III-35. The D₂ signal is scattered from the crystal, the much weaker HD signal is the result of surface reaction. The measured phase of each signal is determined from the relation

\[ \phi_m = \tan^{-1} \left( \frac{S_0}{S_{90}} \right) \]
Fig. III-34. $\Delta\psi$ vs. $T_B$ at $f=1000$ Hz.
Fig. III-35. Typical recorder trace for scattered D₂ and HD signal.
and adjusted for the quadrant in which the vector lies. The amplitude of each signal is given by

\[ A_m = \left( S_o^2 + S_90^2 \right)^{1/2} \]

The reaction product vector, \( \xi \), is given by the ratio of product to reactant amplitude and the difference in measured phase between them.

\[ \xi = \frac{A_m^{\text{(prod.)}}}{A_m^{\text{(react.)}}} e^{-i\Delta\phi} \]

where \( \Delta\phi = \phi_m^{\text{(react.)}} - \phi_m^{\text{(prod.)}} \). Corrections for transit time from chopper to crystal, crystal to detector and inside the mass spectrometer are applied if necessary. As noted above these are difference corrections which are mass dependent, the usual case being that reactant and product masses are similar. Therefore, these corrections are very small.

The signals shown in Fig. III-35 used a lock-in time constant of 3 sec and 10 sec for the strong and weak signals respectively. For weaker signals the time constant was sometimes increased to 30 sec. Signals weaker than this would require ion counting techniques. The system has been modified as discussed above to permit this data collection method.
IV. RESULTS AND DISCUSSION

A. Inelastic Scattering

1. Hydrogen, Deuterium and Helium

The angular distributions of hydrogen, deuterium, and helium scattered from three platinum single crystal surfaces are presented in this section. The width, intensity and direction of these distributions give a great deal of information about the range and degree of energy transfer between the solid and the surface. These experiments deal with clean, well ordered surfaces, exhibiting the Auger spectrum of Fig. III-23 and the LEED patterns of Fig. III-19. The following section describes scattering of several other gases from these surfaces as well as from a platinum surface deliberately contaminated with CO. It will be seen that the cleanliness and surface structure of the surfaces studied greatly affects the energy transfer between the solid and the incident gas.

Figure IV-1 shows the angular distributions of hydrogen, deuterium, and helium from the Pt(111) surface. This surface is the most closely packed plane of platinum, and is ideally very smooth and defect free. (A carefully grown platinum single crystal will have about $10^8$ defects per cm$^2$.) The angle of incidence in each case is indicated by the arrow on the horizontal axis of the distribution as 45°. The surface temperature in each case is 1000°K and the beam temperature is 300°K. The chopping frequency used for these measurements is 160 hz. The azimuthal angle of incidence defined as the direction of the incident beam with respect to the atom rows or step edges is as indicated in the
Fig. IV-1. Angular distributions of helium (a), hydrogen, and deuterium (b) scattered from clean Pt(111).
The angular distribution of hydrogen, deuterium and helium is shown for the (997) surface in Fig. IV-3 and for the (553) surface in Fig. IV-4. The angle of incidence is 45°, the surface temperature 1000°K, beam temperature 300°K, and the modulation frequency 160 hz as for the (111) surface. The azimuthal incidence angles are indicated in Fig. IV-2.

It is perhaps simplest to discuss these data for the low index (111) surface first and to relate these results to the data obtained on the stepped surfaces. Helium scattering from the (111) surface is narrow, intense and highly specular. The maximum intensity, which falls at the specular angle (45°) is 10.9% of the incident beam intensity. The FWHM of the scattering distribution is 6°. This distribution agrees quite favorably with that measured by Merrill\textsuperscript{88} for the Pt(111) surface, using an entirely different experimental system. Helium scattering from Pt(111) is indicative of nearly elastic scattering. Energy transfer between the gas and surface is minimal.

The hydrogen angular distribution is again quite specular. The maximum intensity is 1.7% and the FWHM is 18°. This broadening and decrease in intensity is due to increased energy transfer between the solid and gas. Even though hydrogen is lighter than helium, the internal structure of the diatomic molecule as well as the increased polarizability of the molecule leads to increased energy transfer. The effect of internal degrees of freedom in the incident gas is best seen in the angular distribution of deuterium scattered from this surface.
Fig. IV-2. Schematic diagram indicating azimuthal angle of incidence for Pt(111), Pt(997) and Pt(553) surfaces.
Fig. IV-3. Angular distributions of He, H\textsubscript{2} and D\textsubscript{2} from Pt(997).
Fig. IV-4. Angular distributions of He, H$_2$ and D$_2$ from Pt(553).
In this case the distribution is still peaked at the specular angle, but is much less intense, 0.8%, and much broader, FWHM = 24°, than for hydrogen or helium under the same experimental conditions. This can be explained by examination of the energies of rotational levels in hydrogenic molecules. Table II-1 lists these energies for hydrogen and deuterium. As can be seen, the energy for exciting the lowest rotational level of deuterium is much lower than that for hydrogen. In fact, the energy of a single Debye phonon in platinum is ~ 460 cal, corresponding quite nicely with the energy of the (J=1-2) rotational transition in deuterium. The same lowest level transition in hydrogen would require a multi phonon process. This mechanism has also been postulated to explain similar differences in hydrogen and deuterium scattering from silver surfaces. So, we see that the internal structure of the interacting gas greatly affects the degree of energy exchange in an interaction of the gas and solid.

The orientation and microscopic order of the stepped surfaces greatly determines the extent of energy transfer. Helium scattering from the (997) surface, which has roughly 10% of the surface atoms in step sites, is much broader and less intense than scattering from the (111) surface. It is also not precisely specular, in this case the angle of maximum intensity being shifted about 2° toward the surface normal. More will be said of this shift, which occurs for hydrogen and deuterium as well, in the discussion below. The broadening, FWHM = 18°, and decrease in intensity to 2.42%, indicates an increase in energy transfer between the gas and surface.
Similar behavior is observed on comparing the hydrogen and deuterium distributions from the (997) surface with those from the (111) surface. The distributions are broader ($H_2$ FWHM = 48°, $D_2$ FWHM = 43°) and less intense ($H_2=0.65\%$, $D_2=0.58\%$) than for the same conditions from Pt(111), again indicating more efficient energy transfer. However, there is no longer a marked difference between the hydrogen and deuterium scattering distributions. The stepped surfaces display much more efficient rotational energy accommodation than the (111) surface.

The angular distributions of helium, hydrogen and deuterium from the Pt(553) surface are shown in Fig. IV-4. As with the (997) surface, these distributions are much broader and less intense than the corresponding ones from the (111) surface. ($He=0.96\%, \text{FWHM}=37°; H_2=0.48\%, \text{FWHM}=55°; \text{and } D_2=0.32\%, \text{FWHM}=52°$.) They are also broader and less intense than the distributions from the (997) surface. The (553) surface has roughly 20% of the surface atoms in step sites. The degree of energy transfer between the gas and the surface appears to be directly related to the concentration of atomic steps on the surface.

We can propose a crude model to explain the difference in scattering distributions for the three surfaces. If we assume that two types of scattering are occurring on the stepped surfaces, we can use this model to predict the angular distribution of helium for any stepped surface. The two types of scattering are specular scattering from the (111) terraces combined with random reemission (complete energy accommodation) from the step areas. For example, from the (997) surface roughly 10%
of the scattered flux should be randomly reemitted, while 90% of the
flux would be scattered specularly as from the (111) surface.
Similarly, on the (553) surface, 20% of the flux should be random
with 80% scattered specularly. Figure IV-5 demonstrates the calculated
scattering distributions for He compared with the measured distributions
on the two stepped surfaces. This simple model works reasonably well
for helium scattering, but not for H₂ and D₂ scattering. The same
trends are observed, but the quantitative agreement is not as good.
This is possibly due to more complex energy transfer mechanisms
involving the internal modes of the hydrogen and deuterium molecules.

Figure IV-4 shows that all three distributions from the (553)
surface are shifted about 2° away from the surface normal. As mentioned
above, the (997) distributions are shifted about 2° from the specular
in the opposite direction. The scattering distributions from the
(111) surface are precisely specular. After much thought, it became
apparent that these shifts could be explained by the azimuthal orientation
of the molecular beam with respect to the step edges of the stepped
surfaces. In the cases of the distributions of Figs. IV-3 and IV-4,
the molecular beam was incident nearly parallel with the step edges
(8° from parallel on the (997) and 12° from parallel on the (553)).
If the scattering particles were scattering from the terraces rather
than from the macroscopic platinum surface, we would expect a slight
shift away from specular in one direction or the other, depending
on whether the open edge of the step was into the molecular beam or
away from it. Since a He-Ne laser (λ = 6328 Å) was used to line up the
crystal, determining the incident and specular angles by reflection,
Fig. IV-5. Comparison of measured and model angular distributions of He from the two stepped surfaces.
particles scattered from the overall macroscopic surface would be expected to appear at the specular angle determined by light reflection. If the particles scattered from the terraces of the stepped surfaces, they would be expected to appear at a specular angle determined by the normal to the terrace, a microscopic specular angle.

This effect should be most pronounced for azimuthal orientations making the molecular beam perpendicular to the step edges. Figure IV-6 shows a ray diagram for this effect for the (997) stepped surface. If the molecular beam is exactly perpendicular to the step edges, the specular peak in the scattering distribution would be shifted twice the angle of cut from the (111) plane, or 12.4° for the (997) and 25.0° for the (553) surface. The (997) crystal was removed from the scattering chamber and rotated about 90° in order to align the step edges perpendicular to the beam. Figure IV-7 shows the LEED patterns and azimuthal orientation of the crystal with respect to the beam line before and after this rotation. As can be seen the crystal is not aligned exactly perpendicular to the beam line, being about 15° away from perpendicular. The results of scattering helium are shown for this orientation in Fig. IV-8. As can be seen, the angle of maximum intensity has been shifted away from the specular by about 8°. Exact perpendicular alignment would have predicted a shift of 12.4°.

In order to more fully test the evidence for scattering from the terraces, or microscopic specular scattering, it is necessary to be able to rotate the crystal azimuthally while in the chamber. This would preclude the uncertainty of aligning the step edges and would allow data
\[ \beta = \alpha - 2\gamma \]

- \( N_m \) = macroscopic normal
- \( N_t \) = terrace normal
- \( N_s \) = step normal

Fig. IV-6. Diagram indicating microscopic specularity for step edges perpendicular to the incident beam.
Fig. IV-7. LEED patterns and schematic diagrams of azimuthal orientation of Pt(997) before (upper pattern) and after (lower pattern) azimuthal rotation.
Fig. IV-8. Angular distribution of helium from Pt(997) with step edges 75° from beam direction. (Fig. IV-7).
to be taken for a variety of azimuthal angles in a short time. A Varian manipulator, model 981-0523 with "flip" actuating mechanism has been modified to allow these measurements. A diagram of the azimuthally rotating crystal holder is shown in Fig. IV-9. The author is grateful to Peter Stair for help with this design.

Figures IV-10 and IV-11 show the angular distribution of He from the (997) and (553) surfaces for a number of azimuthal angles. As can be seen, the shift in the specular position is maximum when the beam is perpendicular to the step edges and is non existent when the beam is parallel to the step edges. It should also be noticed that the intensity at the scattering maximum increases as the azimuthal orientation approaches perpendicular. Both of these observations can be explained if it is realized that the detector sees only those particles scattered in the plane defined by the incident beam and the macroscopic surface normal. As the azimuthal orientation is changed, the cone shaped scattering distribution, centered about the microscopic specular angle, travels through this plane. The detector sees slices of this conic section. When the step edges are perpendicular to the incident beam, the detector samples directly across the axis of this cone, giving the true maximum intensity and FWHM of the scattering distribution.

2. Other Gases

In general, clean platinum surfaces show poor energy accommodation between the surface and an incident gas. The angular distributions of H₂, He, D₂, O₂, N₂, NO, CO and C₂H₂⁸⁵,⁹¹ peak at or near the specular angle. Direct measurements of the velocity of molecules scattered from graphite surfaces by Siekhaus et al.⁹⁶ also indicate...
Fig. IV-9. Diagram of manipulator assembly for azimuthal rotation.
Fig. IV-10. Angular distribution of helium from Pt(997) for various azimuthal orientations. I-90°, II-45°, III-11° from parallel.
Fig. IV-11. Angular distribution of He from Pt(553) for 2 azimuthal orientations. I-41°, II-68° from parallel.
poor energy accommodation. Even in the absence of direct determination of the scattered beam velocity, from angular distribution studies it can be concluded that energy transfer between translational or vibrational modes of the incident molecules and the phonon modes of the clean surface is not an efficient process.

The nature of energy transfer changes radically however, when molecules are scattered from a layer of adsorbed molecules. Invariably, atoms or diatomic molecules undergo complete thermal accommodation when scattered from an adsorbed layer of carbon monoxide, as indicated by the cosinelike angular distribution of the scattered molecules. Studies of this adsorbed layer scattering indicate that energy exchange is predominantly via the $T_B - V_S$ mechanism (translational modes of incident particles to vibrational modes of the solid), and that the low frequency localized bending modes of the adsorbed molecules are likely to be responsible for the efficient energy transfer.

The scattering distributions reported in this section were recorded using 160 hz modulation, a surface temperature of 1000°K and 550°K for the clean surface distributions, and 300°K for the CO covered surfaces. The CO adsorbed layer was obtained by exposing the clean Pt(111) surface at 300°K to a pressure of $1.5 \times 10^{-8}$ torr CO for about 30 minutes. The resulting LEED pattern is shown in Fig. IV-12. It indicates a very high background and dim c(4x2) features which are very sensitive to electron beam deterioration. 147
Fig. IV-12. LEED pattern of Pt(111) surface exposed to $5 \times 10^{-8}$ torr CO for 30 minutes. Pt(111)-c(4×2)-CO.
Figure IV-13 shows the angular distribution of CO and N$_2$ from the adsorbed CO layer. Both species have the same molecular weights but very different vibrational frequencies and rotational spectra. This figure clearly shows the cosine angular distribution of the scattered molecules, which implies complete energy accommodation of N$_2$ and CO with this surface before reemission. Figure IV-13 also shows the angular distribution of N$_2$ and CO from the clean platinum surface. Both are peaked at the specular angle. Figure IV-14 shows the angular distribution of hydrogen scattered from clean and CO covered Pt(111) surfaces. Again, the distribution is highly specular from the clean surface, while cosinelike from the CO covered surface. Thus, it appears that an adsorbed layer of CO greatly facilitates the energy accommodation of the incident gas molecules.
Fig. IV-13. Angular distributions of N\textsubscript{2} and CO from clean Pt(111) (upper) and CO covered Pt(111) (lower).
Fig. IV-14. Angular distributions of $H_2$ from clean (upper) and CO covered (lower) Pt(111).
The energy transfer mechanism responsible for this efficient accommodation can be either between the translational modes of the diatomic molecule in the beam and the vibrational modes of the CO molecules adsorbed on the surface (TB-VS interaction), or via the vibrational modes of the gas and the CO molecules on the surface (VB-VS interaction). Rotational energy transfer is expected to be rapid and complete for both incident CO and N₂ molecules even with the clean platinum surface. Doll¹⁵ has shown that the width of the angular distribution on scattering a rigid rotor as compared to atom scattering is markedly increased. These calculations are in excellent agreement with a number of experimental results. Thus, it appears that RB-VS energy transfer can readily take place within the gas-surface collision time even on the clean metal surface. Hydrogen appears to be the exception since large differences in the angular distributions of scattered H₂ and D₂ from clean surfaces⁸⁴ have been observed as has been discussed above.

In order to learn which energy transfer process, TB-VS or VB-VS, is responsible for the complete energy accommodation of the incident gas on the adsorbed layer, the angular distribution of argon scattered from the clean and CO covered surfaces was measured. The results of this measurement are shown in Fig. IV-15. Argon scatters subspecularly from the clean Pt(111) surface, while it exhibits a cosine angular distribution when scattered from an adsorbed layer of CO. This observation indicates that the TB-VS energy transfer channel is responsible for the complete thermal accommodation of the argon atom.
Fig. IV-15. Angular distributions of Ar from clean (upper) and CO covered (lower) Pt(111).
Therefore the CO and N\textsubscript{2} molecules scattered from the CO covered surface are likely to be accommodated by the same mechanism.

For the diatomic molecules, however, contribution of $V_B - V_S$ energy transfer to the accommodation process cannot be ruled out, even though complete thermal accommodation of atoms has taken place in the absence of $V_B - V_S$ energy transfer. Similar results, that is complete energy accommodation, have been obtained upon scattering acetylene from an adsorbed layer of acetylene\textsuperscript{91} as well.

It appears that the vibrational modes of the adsorbed molecules that are localized at the surface can readily absorb the kinetic energy of the incident atom or molecule. Upon impact, these adsorbed molecules bend and absorb a portion of the impact energy by excitation of low frequency bending modes. Once the incident particle loses enough kinetic energy that it can no longer desorb within a vibrational time period, it becomes trapped on the surface long enough for complete accommodation to occur.

It must be noted that the scattering experiments from an adsorbed CO layer were carried out at a surface temperature of 300°K, while those from the clean platinum surface were carried out above 500°K. This higher surface temperature was necessary to avoid contamination of the clean crystal surface by CO, which is a major source of ambient contamination in this system. In the absence of surface contamination, the angular distribution of scattered N\textsubscript{2}, H\textsubscript{2} or Ar becomes more peaked with decreasing surface temperature (See Fig. IV-16). Thus, the surface
Fig. IV-16. Angular distribution of Ar from clean Pt(111) for two surface temperatures. Inset shows variation in intensity at θ=45° versus surface temperature.
temperature difference cannot account for the markedly different energy accommodation of the incident gases, but it must be the result of the presence of the adsorbed CO which changes the nature of the molecular collision dynamics.

In many surface chemical reactions, the rate determining step is that of the adsorption of reactants. These experiments indicate that the residence time of the incident molecules can be greatly increased by contaminating the surface with CO. Other diatomic or polyatomic molecules providing this efficient $T_B^{-V_S}$ channel for energy accommodation should be equally effective in increasing the residence time. Thus, the reaction probability should markedly increase in the presence of these impurities for reactions where reactant adsorption is the rate determining step. It would be interesting to investigate the effect of adsorbed gases on the surface reaction rates of a number of reactions. These partial monolayer adsorbates may well catalyze surface reactions by increasing the residence time of the reactants on the surface. For certain other reactions, adsorption of a partial monolayer of a gas giving increased residence time could decrease the reaction rate by poisoning or blocking active sites.

These results also indicate that the sticking probability of incident molecules should drastically depend on the state of cleanliness of the surface. In ultra high vacuum systems, CO is one of the most abundant contaminants. A partial monolayer coverage of adsorbed CO may change the sticking probability of rare gas atoms or of diatomic molecules by orders of magnitude. The controversy in the literature
over the sticking probability of $O_2$ on Pt surfaces could well be explained by this increase in residence time due to efficient energy transfer on surfaces with adsorbed CO layers.

It is important to separate the effect of atomic disorder from the effect of adsorbed CO on the angular distribution of the scattered molecules. Although the adsorbed CO layer is ordered as indicated by the diffraction pattern, it is likely that there are disordered areas in the adsorbate layer. Therefore, the scattering from the adsorbed layer may also show effects due to disorder. Clean stepped surfaces are ideally suited to study the effect of disorder on the scattering without the presence of the adsorbed layer. Comparison of the angular distributions of $H_2$ scattered from two clean stepped surfaces with the angular distributions from clean and CO covered Pt(111) surfaces is shown in Fig. IV-17. Scattering from the clean (111) surface is very strongly peaked. Scattering from the CO covered surface is cosine. Scattering from the stepped surfaces is still quite peaked, even though the surfaces contain roughly 10% (Pt(997)) and 20% (Pt(553)) edge atoms. It appears that the surface would have to be more than 50% disordered for the scattering distribution to become cosine from disorder or atomic roughness alone. In the case of the CO adsorbed layer, the LEED pattern indicates that the surface is more highly ordered than this. The low frequency bending modes of the adsorbed CO molecules appear to be responsible for the efficient energy accommodation of the incident gas particles.
Fig. IV-17. Comparison of angular distributions of $\text{H}_2$ from $\text{Pt}(111)$, $\text{Pt}(997)$, $\text{Pt}(553)$ and CO covered $\text{Pt}(111)$. 
B. Reactive Scattering

1. \( \text{H}_2-\text{D}_2 \) Exchange

The reaction of hydrogen and deuterium to form hydrogen deuteride is a simple reaction which takes place readily on platinum surfaces even at temperatures below 100°K.\(^{151}\) The same reaction is inhibited in the gas phase by the large dissociation energy of the hydrogenic molecules. Once the \( \text{H}_2 \) molecule is dissociated, the successive atom-molecule reaction in the gas phase still has a potential energy barrier of roughly 10 kcal/mole.\(^{152}\)

This section describes studies undertaken to learn how the platinum metal surface facilitates the hydrogen-deuterium exchange and efforts aimed at uncovering the mechanism of the exchange reaction on well characterized platinum surfaces. The results of these studies indicate that atomic steps on the platinum surfaces play an essential role in dissociating hydrogen or deuterium at low pressures. Without the presence of large concentrations of atomic steps the probability for the exchange reaction to occur is very low. Mechanistic studies indicate a two branch mechanism involving an atom-molecule reaction on the surface.

The experiments were generally performed by scattering a deuterium beam from the platinum surface in an ambient hydrogen pressure and monitoring the production of HD. A hydrogen beam with a deuterium ambient and a mixed hydrogen deuterium beam were also used. Separate introduction of the reactants was preferred because of difficulties in
controlling the $\text{H}_2/\text{D}_2$ ratio in the mixed beam. The surface reaction was studied in the temperature range 300°K to ~1300°K.

Figure IV-18 shows the amplitude of $\text{H}_2$, $\text{D}_2$ and HD versus the angle from the surface normal for the three surfaces studied, (Pt(111), Pt(997) and Pt(553)). The amplitude at each angle is normalized to the incident beam amplitude. In each case, the scattering distributions are for a 300°K incident beam and a 1000°K surface. The modulation frequency is 400 hz. As pointed out in the section on inelastic scattering (IV-A), the $\text{H}_2$ and $\text{D}_2$ scattering distributions are directed on all three surfaces. The (111) surface shows narrow, intense specular scattering for $\text{H}_2$ and $\text{D}_2$. The (997) and (553) surfaces show broader, less intense distributions. These results are discussed more fully in section IV-A, but the point to be made here is that the energy transfer between the incident gas and the surface is much more efficient for the stepped surfaces, as indicated by the decrease in specularity in going to surfaces of higher step density.

Figure IV-18 also shows the amplitude of HD versus the angle from the surface normal. No HD was detected desorbing from the Pt(111) surface under experimental conditions which resulted in approximately 5% and 10% of the incident $\text{D}_2$ beam being converted to HD on the (997) and (553) surfaces respectively. On the stepped surfaces, the amplitude of HD decreased as the cosine of the angle from the surface normal. This distribution indicates complete thermal equilibration of the HD on the surface before desorption, and is in conflict with results of Palmer, et al.
Fig. IV-18. Angular distributions of H₂, D₂ and HD from Pt(111), Pt(997) and Pt(553).
Cardillo et al.\textsuperscript{102} on copper single crystals. Both of these investigators observed a distribution more highly peaked at the normal for HD product. There are indications that these peaked distributions could be a consequence of activated adsorption on the smooth epitaxial surfaces of Palmer\textsuperscript{101} or the copper surfaces of Cardillo.\textsuperscript{102}

Measurements of the normalized HD signal amplitude (at $\theta=45^\circ$) under identical experimental conditions for the three surfaces, gave the results shown in Table IV-1. Integrated reaction probability values, obtained by integrating over the HD angular distributions, assuming a symmetric out of plane cosine distribution, and dividing this value by the incident D\textsubscript{2} signal gives the values listed in the third column of Table IV-1. The experimental conditions used for this comparison are $T_s = 1000^\circ$K, $T_b = 300^\circ$K, modulation frequency $= 400$ hz, $P_{H_2} = 8\times10^{-8}$ torr $= P_{D_2}$. These integrated reaction probability values indicate quantitatively the effect of the step density on the production of HD.

The pressure dependence of the formation of HD was investigated by holding the H\textsubscript{2} background pressure constant and varying the incident D\textsubscript{2} beam pressure and conversely holding the D\textsubscript{2} beam pressure constant and varying the H\textsubscript{2} background pressure. The results of these experiments are shown in Figs. IV-19 and IV-20. These figures indicate that the reaction is first order in the incident D\textsubscript{2} flux or equivalent beam pressure up to pressure near that of the fixed background H\textsubscript{2} pressure. The HD signal then levels off and the reaction becomes zero order. The reaction is half-order in background H\textsubscript{2} pressure, indicating first-order dependence on the concentration of H atoms on the surface. Further
Table IV-1. Reaction Probabilities for HD Production

\( T_s = 1000^\circ K, \quad T_B = 300^\circ K, \quad f = 400 \text{ Hz}, \quad P_H^2 = 8 \times 10^{-8}, \quad P_D^2 = 8 \times 10^{-8} \)

<table>
<thead>
<tr>
<th>Surface</th>
<th>Probability Amplitude</th>
<th>Int. Reaction Prob.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(111)</td>
<td>&lt; 1 \times 10^{-6}</td>
<td>&lt; 1 \times 10^{-5}</td>
</tr>
<tr>
<td>Pt-(S)-[9(111)\times(111)]</td>
<td>4.9 \times 10^{-4}</td>
<td>1.6 \times 10^{-2}</td>
</tr>
<tr>
<td>Pt-(S)-[5(111)\times(111)]</td>
<td>9.2 \times 10^{-4}</td>
<td>9.9 \times 10^{-2}</td>
</tr>
</tbody>
</table>
Fig. IV-19. Normalized HD intensity versus H₂ background pressure for D₂ beam pressure fixed at 2×10⁻⁷ torr.
Fig. IV-20. Normalized HD intensity, versus, D₂ beam pressure for H₂ background pressure of $6 \times 10^{-7}$ torr.
experiments were carried out with $P_{\text{H}_2} \approx 10P_{\text{D}_2}$ in order to give constant H atom coverage on the active sites of the stepped surfaces. This forces the reaction to become pseudo first order, allowing the phase and amplitude analysis discussed above.

The production of HD as a function of the incident beam kinetic energy was also investigated. The source oven could be heated to $\approx 600^\circ$K, near the softening point of the glass capillary array. The beam energy dependence was measured on the (997) surface at $1000^\circ$K and on the (553) surface at $1250^\circ$K. The results of these measurements are shown in Fig. IV-21. In both cases, the HD amplitude and phase were not affected. This indicates an absence of activation energy for the adsorption of the deuterium molecules.

The HD amplitude is plotted as a function of reciprocal surface temperature for the two stepped surfaces in Fig. IV-22. There are two temperature regimes that can be distinguished. From 300-600$^\circ$K, the amplitude increases rapidly following the same T-dependence for both surfaces. Above 600$^\circ$K the increase becomes less rapid for both surfaces. The amplitude from the (553) surface levels off at roughly twice the amplitude from the (997) surface. The surface temperature behavior of the phase shift for the two surfaces also shown in Fig. IV-22, exhibits similar behavior. From 300-600$^\circ$K the phase shift decreases rapidly, data from both surfaces falling on the same line. Above 600$^\circ$K, the phase shift for HD formed at the (997) surface goes through a minimum and then increases. The phase shift of the HD formed at the (553) surface goes to a slightly lower minimum and does not increase as much. Since the phase shift is directly related to the residence time of the HD molecules on the surface, a decrease in phase shift with increasing surface temperature is certainly expected. The reversal in this behavior at high temperature indicates the onset of a new mechanism for the formation of HD not present at low temperature.
Fig. IV-21. HD amplitude and phase shift versus reciprocal beam temperature.
Fig. IV-22. Normalized HD amplitude (right) and phase shift (left) versus reciprocal surface temperature. Broken lines from Eq. (13).
Using either the phase or the amplitude data in the low temperature region, an activation energy for the process occurring can be calculated. With either of the data sets used this activation energy is calculated to be 4.5 kcal/mole. The activation energy in the high temperature region (> 600°K) is calculated to be 0.6 kcal/mole. The data of Figs. IV-22 was obtained using a modulation frequency of 40 hz. Increasing the modulation frequency to 160 and 400 hz gives the same two branch behavior, except that the transition temperature is shifted to higher values as the chopping frequency is increased. The activation energies remain the same. This observation indicates that the reaction that dominates at low temperature occurs with shorter characteristic time than the reaction that dominates at high temperatures.

The modulation frequency dependence of the HD phase shift and amplitude are shown in Figs. IV-23 and IV-24 for two surface temperatures, 1000°K and 485°K. The low temperature phase shift increases monotonically with increasing frequency, while the amplitude decreases with unit slope. Calculation of an activation energy from the 485°K frequency data using Eqs. (10-12) below agrees favorably with the activation energy calculated from the surface temperature data in the low temperature range,

\[ A = \text{amplitude} = \frac{n}{\sqrt{1 + (\omega/k_1)^2}} \quad (10) \]

\[ \Delta \phi = \text{phase shift} = \tan^{-1}(\omega/k_1) \quad (11) \]

\[ k_1 = A_1 \exp \left(-E_1/RT\right) \quad (12) \]
Fig. IV-23. HD phase shift (lower) and amplitude (upper) versus modulation frequency for $T_s = 1000^\circ K$. Broken line from Eq. (13).
Fig. IV-24. HD phase shift (lower) and amplitude (upper) versus modulation frequency for $T_s=485^\circ K$. Broken line from Eq. (13).
where $\eta$ is the sticking coefficient, determined by extrapolation of $A$ versus modulation frequency data to zero frequency to be $\sim 3 \times 10^{-1}$ (integrated over all angles), $\omega$ is the angular modulation frequency equal to $2\pi f$ (f in Hz), and the rate constant $k_1$ is written in Arrhenius fashion with pre-exponential $A_1$ and activation energy $E_1$. The high temperature behavior is more complex. The frequency dependence of the phase is S-shaped and the amplitude decreases with a slope of one-fourth.

The very low HD production rate on the (111) surface can be increased by increasing the background reactant pressure and decreasing the modulation frequency. Increasing the background reactant pressure by a factor of ten and decreasing the modulation frequency a factor of ten increases the HD reaction probability about a factor of 30 on the (111) surface. The same changes with either of the stepped surfaces increases their already much higher reaction probability about a factor of six.

Any chemical interpretation of the data presented here for this exchange reaction must be consistent with the conclusions this data suggests. These conclusions are:

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

2) The stepped platinum surfaces produced large amounts of HD under conditions which showed little HD formation on the (111) surface.
3) Angular distributions indicate greater energy accommodation on higher step density surfaces, and that HD product is in thermal equilibrium with the surface before re-emission.

4) Temperature dependence of both amplitude and phase indicate two reaction regimes. The pseudo first order rate constants are given by, at low temperature (300-600°K),

\[ k_1 = (2\pm1) \times 10^5 \exp(-4.5\pm.5 \text{ kcal/RT}) \text{ sec}^{-1} \]

and at high temperature (600-1300°K),

\[ k_2 = (1\pm2) \times 10^2 \exp(-0.6\pm0.3 \text{ kcal/RT}) \text{ sec}^{-1} \]

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

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

7) The reaction is first order in \( D_2 \) beam pressure and one-half order in \( H_2 \) background pressure up to the limiting H atom coverage.

8) Frequency dependence measurements of the amplitude and phase have a simple monotonic dependence in the low temperature region, and more complex behavior in the high temperature region.

9) Increasing background reactant pressure and decreasing chopping frequency increase HD production on the (111) surface much faster than on the stepped platinum surfaces.

The surface temperature data and particularly the phase shift behavior as a function of modulation frequency at high temperature suggest a branched model for the exchange reaction. An expression for the reaction product vector \( \langle A \e^{-i\Delta \phi} \rangle \) can be derived for a two branch model with differing rate constants for each branch. This expression is
assuming an equal probability for each branch to occur. More will be
said about this model and its use to extract kinetic parameters in the
discussion below. Using the low temperature activation energy
(4.5 kcal/mole) and pre-exponential ($1 \times 10^5$) (determined from Eqs. (10)
and (11) and the low temperature region $T_S$ data), along with the high
temperature activation energy (slope of $A$ vs. $1/T_S$ plot in 600-1300°K
range) Eq. (13) can be used to determine a value for the high temperature
preexponential factor. Using these four parameters to determine the
two rate constants in Eq. (13) we can reproduce the behavior of the
reaction product vector over the temperature and frequency ranges
studied. Broken lines on Figs. IV.22-IV.24 indicate the predicted
vector behavior using these parameters and Eq. (13). Each case lends
support to the choice of a branched reaction model to describe the
data.

Other possible models considered varied in degree of complexity.
A simple one step model determines an expression for the reaction
product vector as shown in section III-E. A two step series model
results in the following expression for the reaction product vector.

$$ Ae^{-i\Delta\phi} = \frac{-\tan^{-1}(\omega/k_1)}{\sqrt{1 + (\omega/k_1)^2}} + \frac{-\tan^{-1}(\omega/k_2)}{\sqrt{1 + (\omega/k_2)^2}} $$ (13)
A branched model with three branches results in this expression for the reaction product vector

\[ Ae^{-i\Delta\phi} = \frac{n_1 e^{-i\tan^{-1}(\omega/k_1)}}{\sqrt{1 + (\omega/k_1)^2}} + \frac{n_2 e^{-i\tan^{-1}(\omega/k_2)}}{\sqrt{1 + (\omega/k_2)^2}} + \frac{n_3 e^{-i\tan^{-1}(\omega/k_3)}}{\sqrt{1 + (\omega/k_3)^2}} \]  

(15)

A branched model with two branches, one being a two step series process, the other being a simple one step reaction results in the following expression for the reaction product vector.

\[ Ae^{-i\Delta\phi} = \frac{n_1 e^{-i\tan^{-1}(\omega/k_1)}}{\sqrt{1 + (\omega/k_1)^2}} + \frac{n_2 e^{-i\tan^{-1}(\omega/k_2)} e^{-i\tan^{-1}(\omega/k_3)}}{\sqrt{1 + (\omega/k_2)^2} \sqrt{1 + (\omega/k_3)^2}} \]  

(16)

The frequency and temperature behavior of each of these models was investigated and compared to the experimental behavior. This comparison is shown in Figs. IV.25 - IV.27. This comparison indicated the choice of the two branched model described by Eq. (13). This model is treated in more detail in the discussion of kinetic parameters below.

Let us now discuss the two branches separately by considering first the low temperature (300-600°K) reaction behavior and then the high temperature (600-1300°K) behavior. In the low temperature region we find that the presence of atomic steps on the platinum surface is
Fig. IV-25. Comparison of model behavior of phase (lower) and amplitude (upper) versus modulation frequency at $T_s = 1000^\circ K$. I is 1 step process Eqs. (8) and (9); II is 2 step series process Eq. (14); III is 2 branch model Eq. (13); IV is 3 branch model Eq. (15); and V is 2 branch model with one branch a 2 step series process Eq. (16). Broken line indicates experimental data.
$T_b = 1000 \text{ K}$

Fig. IV-25.
Fig. IV-26. Comparison of model behavior of phase (lower) and amplitude (upper) versus modulation frequency at $T_s = 485^\circ K$. Curves labelled as in Fig. IV-25.
Fig. IV-27. Comparison of model behavior of phase (left) and amplitude (right) versus surface temperature at 40 hz modulation frequency. Curves labelled as in Fig. IV-23.
necessary for the efficient production of HD, as the reaction probability is much lower on the (111) surface. The first order beam pressure dependence indicates that molecular deuterium is involved in the rate limiting step. Possibilities for this rate determining step are diffusion of the molecule to the active step site, or perhaps dissociation of the molecule at this site. The half-order pressure dependence on hydrogen background pressure indicates the involvement of atomic H in the rate determining step. In the low temperature range the concentration of atomic H on the surface should be quite high, most of it bound at the monatomic step sites. Supporting evidence for the assumption of atomic H being bound at the steps is given in an interesting study of hydrogen adsorption on Pd surfaces by Conrad et al. They found that the isosteric heat of hydrogen adsorption on Pd-(s)-(9(111)x(111)) was about 3 kcal/mole higher at low coverages than on Pd(111). Assuming a reasonable Pt-H binding energy of 50 kcal/mole assures a constant coverage of H atoms at the step sites over the temperature range studied.

This information in the low temperature region suggests the following mechanism for the exchange reaction. Molecular D₂, weakly adsorbed on the terrace, diffuses to step sites where strongly bound atomic hydrogen is present. It there undergoes a three-center atom-molecule reaction to form HD which is subsequently desorbed and detected. The possibility of a two-center atom-atom reaction taking place to form HD after dissociation of D₂ at the step cannot be ruled out. The fact that the step density does not affect the reaction probability as drastically in the low temperature region argues for the diffusion, atom-molecule reaction step being rate limiting, since dissociation,
followed by an atom-atom reaction, should be directly proportional to the step concentration. Diffusion rate would only be affected by the shortening of the mean diffusion path length on step density increase. The values of the activation energy and pre-exponential factor also support the choice of molecular diffusion and a three center reaction as the rate limiting step. More will be said about the interpretive value of these parameters below. The reaction in the low temperature region, involving two adsorbed species is commonly termed the Langmuir-Hinshelwood mechanism.\textsuperscript{154}

In the high temperature region, again the steps are necessary for efficient production of HD. The pressure dependence is the same as in the low temperature region, indicating an atom-molecule reaction as the rate limiting step. In this region, however, the step density directly affects the production of HD. Since the surface concentration of H atoms must be much lower at these temperatures, the reaction will be limited to reactions taking place at the steps where the atom binding energy is greater. The appearance of a much lower activation energy in this region indicates the onset of a direct mechanism, where incident D\textsubscript{2} molecules react directly from the gas phase with hydrogen atoms at the steps. This reaction of a gas phase species with an adsorbed species is called the Eley-Rideal mechanism.\textsuperscript{155}

The two-branch mechanism with the associated model descriptions for the high temperature and low temperature branches is shown below.
The broken arrow indicates the possible path resulting from an atom-atom reaction in the low temperature region.

The two branch model can also give information about the expected behavior of the exchange reaction at lower surface temperatures. As the surface temperature is reduced below 300°K, the low activation energy Eley-Rideal process would be expected to again become dominant. Calculations of $k_1$ and $k_2$ and the reaction product vector at lower temperatures using Eq. (13) indicate a transition back to the low activation energy reaction at around 260°K where $k_1$ and $k_2$ are approximately equal. Below this temperature $k_1$ becomes insignificant and the low activation energy $k_2$ branch again dominates. This behavior is shown in Fig. IV.28 where the amplitude vs. $1/T_S$ dependence is shown calculated from Eq. (13). Kuikers et al.\textsuperscript{151} and Breakspeare et al.\textsuperscript{156} have observed the H$_2$-D$_2$ exchange at low temperatures ($< 300°K$) and report a transition from low activation energy to higher activation energy with increasing surface temperature in this region on Pt films and Pt wires, as predicted by extension of Eq. (13) to lower temperatures.
Fig. IV-28. Extrapolation of 2 branch model to low surface temperatures.
The observation of a very slow reaction step (characteristic time $> 10^{-2}$ sec) in this system suggested the possibility of this slow reaction step limiting the formation of HD on the (111) surface. Extending measurements to a chopping frequency of 40 Hz increased the integrated reaction probability on the (111) surface to about $8 \times 10^{-4}$. This is still over two orders of magnitude less than the reaction probability on the stepped surfaces under identical conditions, but it is a significant increase over the reaction probability at high chopping frequencies. If the chopping frequency could be reduced even further, it is conceivable that the reaction probability on the (111) surface could become comparable to that observed on the stepped surfaces. This observation might indicate that as the chopping frequency is decreased, the reaction of molecules diffusing to the active sites present on even the most carefully prepared low index surfaces becomes detectable, perhaps making the stepped surface and low index surface behavior more similar.

Molecular beam techniques have been used to study the $\text{H}_2$-$\text{D}_2$ exchange on platinum surfaces in one other instance. The work of Palmer et al. on epitaxially grown Pt(111) films has found a significant production of HD on these surfaces. The experiment utilized a heated beam. The surfaces were not characterized with LEED or AES, so no conclusions can be drawn as to the surface structure or purity of the scattering surface. They observed a $\cos^3 \theta$ angular dependence for the HD product in disagreement with the work described in this thesis. There has been work on diffusion of $\text{H}_2$ through platinum films showing angular distributions of desorbing $\text{H}_2$ that were described by
cos \theta \) from clean platinum membranes (checked by AES) but \( \cos^n \theta \) \((n>1)\) for platinum contaminated by carbon or sulfur.\(^{157}\) This observation suggests that the platinum surfaces used in the study of Palmer et al.\(^{101}\) were contaminated. Contamination is likely in this case, as the Palmer apparatus is an oil diffusion pumped system with a \(10^{-7}\) torr base pressure in the scattering chamber. Recent work by Cardillo, et al. indicates that the \( \cos^3 \theta \) distribution may be the result of an activated adsorption process. In their work on copper, there was a marked increase in HD production with increasing incident beam energy. This study also showed an HD desorption distribution of \( \cos^3 \theta \). Consideration of microscopic reversibility and equilibrium thermodynamic arguments have shown that \( \cos^n \theta \) distribution \((n>1)\) may be the result of activated adsorption. If this is the case, and noting that the work of Palmer, et al.\(^{101}\) used a heated molecular beam, the observation of a \( \cos^3 \theta \) distribution for HD formed on epitaxial Pt(111) may indicate an activation barrier for adsorption on this smooth surface. The stepped surface, on the other hand, shows no adsorption activation energy over the temperature range of these experiments.

As can be seen from Figs. IV.25 and IV.27, the two branch model fits the observed behavior of the reaction product vector better than any of the other simple models investigated. However, as can be seen from Figs. IV.22-IV.24, the behavior calculated using the activation energies and preexponentials resulting from an "eyeball" fit to the data does not reproduce the experimental data with great accuracy. For this reason a multi-dimensional minimization procedure was employed to fit the model to the experimental data, using the activation
energies and preexponentials as freely adjustable parameters. This
minimization procedure used an available routine called MINUIT which
is described in detail in the appendix. The basic idea was to fit
the observed phase and amplitude behavior as a function of $T_S$ and
modulation frequency to the phase and amplitude calculated using
Eq. (13), by minimizing the sum of the squared vector distances between
the observed reaction product vectors and the calculated reaction
product vectors. Derivation and solution of the model chemical
reactions and material balance leading to the proposed model are shown
in Appendix D. Included is a discussion of the meaning of the rate
constants and the preexponentials and activation energies involved.

2. Other Reactive Scattering Studies

Small molecule decomposition, oxidation and hydrogenation reactions
are important prototype surface reactions. By studying the reaction
mechanisms of these simple reactions on well characterized solid
surfaces, it is possible to propose models for the initial steps in
more complex catalytic systems. In order to utilize the modulated
beam technique to extract this kinetic information, it is necessary
to determine the reaction probabilities for a series of possible
reactions. This will allow comparisons to be made under identical
reaction conditions and should give information about fruitful lines
of future research.

In each case discussed below, the reaction was studied by introducing
one of the reactants to the background of the scattering chamber
in order to produce a significant coverage of dissociated reactant
on the stepped surface. The other reactant in the pair was incident
on the surface from the beam at a pressure about an order of magnitude lower than the pressure due to the background reactant. The reactions studied and the dominant products are listed in Table IV-2, along with the non integrated reaction probability (reaction product vector amplitude at the specular angle). To convert these values to overall reaction probability, this vector must be integrated over the product angular distribution.

The behavior of steps in promoting the dissociation of H₂ on platinum surfaces, as discussed above, led to the study of the reaction probability of the other small molecule reactions listed in Table IV-2. By monitoring the reaction product vector amplitude for the formation of various products under identical conditions of incident pressure and surface temperature, the dissociating power of the stepped surfaces for various bond strengths can be estimated. The bond strengths tested ranged from the N-H bond in methylamine at 4.3 eV to the C=O bond in carbon monoxide at 11.1 eV. The reaction probabilities for these reactions are listed in Table IV-2 for the (553) crystal at 1000°K and beam pressure of ~5×10⁻⁸ torr. As noted before, this reaction probability is the amplitude of the reaction product vector.

Several general observations may be made upon inspection of Table IV-2. The high reaction probabilities of reactions involving H₂, D₂ and O₂ in the background indicate that these diatomic molecules readily dissociate on the stepped platinum surface. In the case of reactions with N₂ in the beam, the formation of N₂O requires the rearrangement but not the rupture of the N≡N bond. The equal reaction probability
<table>
<thead>
<tr>
<th>Reactants</th>
<th>Beam</th>
<th>Background</th>
<th>Product</th>
<th>Reaction Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
<td>H₂</td>
<td>D₂</td>
<td>HD</td>
<td>5.5 x 10^3</td>
</tr>
<tr>
<td>2)</td>
<td>D₂</td>
<td>H₂</td>
<td>HD</td>
<td>5.5 x 10^3</td>
</tr>
<tr>
<td>3)</td>
<td>D₂</td>
<td>O₂</td>
<td>D₂O</td>
<td>2.1 x 10^-4</td>
</tr>
<tr>
<td>4)</td>
<td>O₂</td>
<td>H₂</td>
<td>H₂O</td>
<td>2.2 x 10^-5</td>
</tr>
<tr>
<td>5)</td>
<td>N₂</td>
<td>O₂</td>
<td>N₂O</td>
<td>6 x 10^-5</td>
</tr>
<tr>
<td>6)</td>
<td>N₂</td>
<td>O₂</td>
<td>NO</td>
<td>5 x 10^-5</td>
</tr>
<tr>
<td>7)</td>
<td>N₂</td>
<td>O₂</td>
<td>NO₂</td>
<td>&lt;1 x 10^-8</td>
</tr>
<tr>
<td>8)</td>
<td>CO</td>
<td>O₂</td>
<td>CO₂</td>
<td>4.7 x 10^-5</td>
</tr>
<tr>
<td>9)</td>
<td>O₂</td>
<td>CO</td>
<td>CO₂</td>
<td>&lt;1 x 10^-8</td>
</tr>
<tr>
<td>10)</td>
<td>N₂</td>
<td>H₂</td>
<td>NH₃</td>
<td>1 x 10^-6</td>
</tr>
<tr>
<td>11)</td>
<td>CHOOH</td>
<td>--</td>
<td>CO₂</td>
<td>8.2 x 10^-5</td>
</tr>
<tr>
<td>12)</td>
<td>CH₃-NH₂</td>
<td>--</td>
<td>NH₃</td>
<td>2.0 x 10^-4</td>
</tr>
</tbody>
</table>
for the formation of \( \text{N}_2\text{O} \) and \( \text{NO} \) could indicate that the same intermediate or a similar mechanism is operative in their formation. It is possible that \( \text{NO} \) forms by the fast reaction of \( \text{N}_2\text{O} \) with atomic oxygen on the Pt surface. This route could provide a large concentration of \( \text{NO} \) without the need for dissociating the strong \( \text{N=N} \) bond. The very low \( \text{NO}_2 \) and \( \text{NH}_3 \) yields seem to indicate that breaking the \( \text{N=N} \) bond during the surface reaction is an unlikely process.

While the formation of \( \text{CO}_2 \) is readily detectable with oxygen in the background, \( \text{CO}_2 \) will not form when \( \text{CO} \) is in the background and \( \text{O}_2 \) in the molecular beam. This may be explained either by the low sticking probability of \( \text{CO} \) at the reaction temperature of 1000°K or by the blocking of the reaction sites by carbon from \( \text{CO} \) dissociation. Bonzel and Ku\textsuperscript{159} and Palmer and Smith\textsuperscript{160} have observed a similar behavior in their studies of \( \text{CO} \) oxidation on Pt. They ascribe this to a poisoning of the surface by preadsorbed \( \text{CO} \).

The decomposition of formic acid and methylamine are readily detectable via the formation of \( \text{CO}_2 \) and \( \text{NH}_3 \), respectively. It is difficult to deduce the bond breaking process that occurs during the surface reaction since the reactant molecules are quite complex. It does appear, however, that the stepped platinum surface catalyzes the dissociation of the \( \equiv\text{C - H}, \text{O - H}, \) and \( \equiv\text{C - N} \) bonds in these molecules.

Angular distributions of the products of these reactions was cosine in every case except the formation of \( \text{CO}_2 \), both by oxidation of \( \text{CO} \) and by decomposition of formic acid. Figure IV.29 shows the
ANGULAR DISTRIBUTION OF CO$_2$
FROM FORMIC ACID DECOMPOSITION

Fig. IV-29. Angular distribution of CO$_2$ from formic acid decomposition.
angular distribution of CO$_2$ formed by decomposition of formic acid. The curves show that the data is better fit by a cos$^2\theta$ dependence. This angular distribution is particularly interesting in light of recent work by Madix, Falconer and McCarty\textsuperscript{161,162} on the decomposition of formic acid on Ni surfaces. Flash desorption studies indicate an autocatalytic "surface explosion" mechanism for this reaction. If this were the case, CO$_2$ product leaving the surface could possess excess kinetic energy. An angular distribution sharply peaked at the normal to the surface may therefore be associated with a reaction product having excess translational energy.

The reaction of CH$_4$ with D$_2$ to form deuterated methanes appears to offer a wealth of information about hydrocarbon catalysis. This reaction has been extensively studied by classical methods. The use of molecular beam techniques and well characterized solid surfaces in these studies could answer a number of questions concerning hydrocarbon catalysis. In particular, this system would be well suited to the study of isotope effects in surface chemical reactions.

One must be careful in drawing conclusions about such a wide variety of chemical reactions, due to geometrical and steric considerations which become important as the reaction complexity increases. One must also be cautious in comparing reaction probabilities measured by the modulated beam technique when complete knowledge of the reaction mechanism is not available. Nevertheless, the work completed thus far on small molecule surface reactions offer some indication of the relative reaction probabilities and the dissociating strength of these stepped surfaces. Hopefully, information of this type will be useful in unraveling the complexities of heterogeneous catalysis.
V. CONCLUSION

A. Summary

The combination of modern clean surface preparation and analysis techniques with the use of the modulated molecular beam method has resulted in a number of advances in the understanding of surface chemistry. These advances have been made by several research groups whose work has been mentioned throughout this thesis. The results which make up this thesis have also added to our understanding of processes occurring on solid surfaces. Two areas have been of particular importance in the studies comprising this work: the energy exchange between the gas and solid surface resulting in inelastic scattering and that resulting in chemical reaction on the surface. This concluding chapter will briefly summarize the results obtained in these two areas. Several comments will be made about the flexibility and limitations of the present experimental system, as well as suggestions for future design changes. Finally, comments and suggestions for future areas of research utilizing this combination of techniques will be made.

Inelastic scattering studies of the three platinum surfaces investigated in this thesis have shown the importance of surface steps for efficient energy transfer. The decrease in specular intensity and increase in distribution width as the surface step density increases is evidence of this importance. Azimuthal orientation dependence
studies indicate that the scattering potential for He, H\textsubscript{2} and D\textsubscript{2} is very short range on these platinum surfaces. This is indicated by the microscopic specular scattering, where the incident particle sees only the terrace or step and not the overall macroscopic scattering surface. Scattering distributions of a number of gases from clean and CO covered platinum (111) surfaces indicate that the CO molecules on the surface promote efficient energy transfer. This energy transfer is shown to be due to $T_{\text{B}} - V_{\text{S}}$ energy transfer rather than $R_{\text{B}} - V_{\text{S}}$ or $V_{\text{B}} - V_{\text{S}}$ transfer. The low frequency bending modes of the CO molecules on the surface are thought to be responsible for the increased energy accommodation.

Reactive scattering studies have almost exclusively involved studies of the hydrogen deuterium exchange reaction on these platinum surfaces. It was found that the reaction probability for HD formation was much higher on the stepped surfaces than on the close packed (111) surface. In fact, in the high surface temperature region ($> 600^\circ\text{K}$) the reaction probability was found to be directly proportional to surface step density. Mechanistic studies of this reaction revealed a mechanism with two branches. These branches operate in different temperature regimes. The low temperature branch, whose rate constant was determined to be $k_1 = 10^5 \exp(-4.5/RT)$, appears to be a diffusion controlled branch. Molecules adsorbed on the terraces diffuse to step sites where they undergo atom-molecule reactions to form HD. In the higher temperature region, the reaction is the result of direct interaction of molecules from the gas phase with atoms held at the
steps. The rate constant for this reaction branch is \( k_2 = 10^2 \exp(-0.6/RT) \).

A series of small molecule reaction and thermal decomposition studies indicate a dissociating strength for the steps present on the platinum surfaces studied. This series of reactions included \( \text{N}_2, \text{O}_2, \text{H}_2, \text{CO}, \text{NH}_3, \) and \( \text{CH}_4 \) reactions, as well as decomposition of formic acid and methylamine on the platinum surface. Comparison of reaction probabilities for these reactions indicates that reactions involving \( \text{H}_2, \text{O}_2 \) or \( \text{CH} \) bond fission occur much more readily than those requiring \( \text{N}_2 \) or \( \text{CO} \) bond dissociation. More extensive studies of the \( \text{N}_2-\text{O}_2 \) reaction to form \( \text{NO}, \text{N}_2\text{O}, \) and \( \text{NO}_2 \) are underway, as well as mechanistic studies of the \( \text{CH}_4-\text{D}_2 \) exchange reaction.

B. System Flexibility and Limitations

As the experimental system is presently constructed, it offers a great deal of flexibility in the type of gas surface interaction which can be studied. The rotatable quadrupole detector allows angular distributions of scattered molecules and reaction products to be measured. The crystal mounting allows direct comparison of two scattering surfaces under identical conditions, or alternatively, azimuthal as well as axial orientation of a single surface with respect to the incident molecular beam. It is possible to vary the temperature of the incident surface from liquid nitrogen temperature to the melting point of the sample. The characteristic temperature of the beam can be varied from liquid nitrogen temperatures to about
600°K. LEED and AES can be used to characterize the structure and chemical composition of the scattering surface. The variable frequency mechanical chopper can modulate the beam in the range of 20 to 2000 hz, giving reaction and residence time information in the range of $5 \times 10^{-2}$ to $5 \times 10^{-4}$ seconds.

In the present signal collection mode however, the system is limited to studying reactions exhibiting a reaction amplitude of greater than about $1 \times 10^{-6}$. Residence time information and characteristic reaction times greater than $5 \times 10^{-2}$ seconds or less than $5 \times 10^{-4}$ seconds are lost to the apparatus as well. The characteristic beam energy range is also severely limited by the softening point of the multichannel glass capillary array used for the source. The limitation to in plane detection of the scattered beam does not appear to be a serious one, but could be of some importance in certain cases. These system limitations suggest the design changes discussed below.

C. Future Design Modifications

The most serious limitation in the present system is in the low frequency range of beam modulation. Reaction studies have shown that surface reactions have very long characteristic times. Most of the reaction information appears to be contained in the frequencies below 100 hz. A fairly simple modification to allow lower frequency modulation would be a beam flag operated from an external low speed motor or relay arrangement transmitting the motion through a welded bellows mounted above the beam line in the selector chamber. A
suitable port is already available for this modification.

Connected with the low frequency modulation limitation is the limitation imposed by the lock-in detection signal collection system. The use of the lock-in detector limits the data to the first Fourier component of the reaction signal. This is perfectly acceptable for first order reactions, but becomes a hindrance for reactions other than first order. Use of ion counting digital techniques would allow collection of the entire reaction signal waveform, enabling the studying of any reaction order over a much wider frequency range (by utilizing harmonics of the modulation frequency). This method would increase the detection capabilities of the system by extending the system time constant and increasing the signal to noise ratio.

In conjunction with a small programmable data processor, ion counting techniques would facilitate the study of much more complex chemical reactions. As the number of reaction products increases the time required to record the phase and amplitude of each product for each frequency, temperature and pressure becomes prohibitive. The use of a minicomputer for storing and processing reaction product information, coupled with Fourier transform techniques for extracting the maximum information at each temperature, frequency and pressure would allow the study of complex, low probability surface reactions. With the present system, it appears that this data collection time restriction has already been reached in the studies of CH₄-D₂ exchange which requires the monitoring of five low signal level peaks for each
temperature, frequency or pressure.

The low signal level limitation could also be remedied by increasing the incident beam intensity. This was the main thrust of the modifications described in the third chapter of this thesis. This intensity increase was accomplished by moving the effusion source closer to the scattering surface. Further increase in incident beam intensity could be achieved by converting the source to an aerodynamic nozzle source. These sources have been in use for more than twenty years and are well understood and fairly simple to fabricate. Such a source could increase the incident beam intensity at least one and possibly two orders of magnitude. Another benefit of a nozzle source lies in the fact that the nozzle source is nearly monoenergetic and can be varied in energy over a wide range. This would increase the incident beam energy range of the present apparatus.

Direct measurement of translational accommodation coefficients and information about the kinetic energy of surface reaction products would be available if the system were equipped with a beam chopper between the scattering surface and the detector. Either phase shift or time of flight methods could be used for such a modification. The method of modulation must, however, be compatible with the ultra high vacuum environment of the scattering chamber. Modifications to allow such measurements over a wide range of particle velocities would require much thought and extensive changes to the present system.
The modulated molecular beam technique, by using a mass spectrometer detector, gives information about the reactants and products of a surface reaction after they leave the solid surface. It seems feasible that the same experimental philosophy could be used to study the adsorbed intermediates of a surface reaction. For example, if an Auger spectrometer were used as a detector for the adsorbed species while the surface was in the flux from the modulated molecular beam, detection of the species of interest as a function of the beam modulation frequency would give kinetic information about the adsorption process. Such an experiment could be easily accomplished in the present system by the addition of an electron gun for Auger excitation which would be incident on the scattering surface, along with the molecular beam, while the surface was facing the Auger electron optics. A port for such an electron gun is available on the present system.

Whether or not modifications are made to the present experimental system, there are a number of surface chemical reactions whose mechanisms could be studied using the techniques described in this thesis. The brief paragraphs following suggest areas of future research, which in the author's opinion, are of particular interest to an understanding of surface chemical reactions.

D. Future Studies

Further study of the hydrogen-deuterium exchange is warranted in light of the work mentioned here. It would be particularly interesting to extend the measurements to lower modulation frequencies,
lower surface temperatures, and higher incident beam pressures. Hopefully, such experiments would support the behavior predicted by the branched model proposed in this work. The effect of other surface geometries should be investigated, as well as the poisoning of the reaction by carbon or sulfur impurities. The capability for surface characterization is especially important for such studies.

More information about the dissociating power of the stepped surfaces should be obtained by a systematic study of a wide variety of surface reactions involving chemical bonds of varying strengths. Such information will likely be the result of several years work with different reactions, different surfaces and from different laboratories. These studies will be a prerequisite to an understanding of heterogeneous catalysis.

The reactions of N₂ and O₂ on platinum as well as the CH₄-D₂ exchange reaction are very important reaction systems which have been mentioned previously. Work has begun on kinetic studies of these reactions and should be continued. Other reaction systems which appear to be of interest for a broad understanding of surface chemical reactions are the oxidation of NH₃ on platinum, the formation of NH₃ from N₂ and H₂ on iron surfaces, the decomposition of formic acid on a variety of metal surfaces, and the thermal decomposition of ammonia and the methyl amines on platinum. This last study could perhaps give an insight into the effect of reactant steric factors on simple surface reactions.
Inelastic scattering studies have not been exhausted either. The effect of thermal disorder in a scattering surface could be studied by measuring the angular distribution of helium from a clean crystalline surface, as a function of surface temperature through the melting point of the solid. Scattering from a liquid surface would indicate directly the effect of surface order on gas-surface energy accommodation. Likely candidates for such an experiment would be high surface tension liquid metals such as molten aluminum or lanthanum.

Scattering distributions of a series of gases from several stepped surfaces of varying orientation would give information about the range of interaction between the solid and gas. It would be interesting to see the effect of particle size and surface terrace width and orientation on the energy transfer between gas and solid. Different solids could possibly have different interaction ranges, and a systematic study of these scattering distributions could point out such effects.

The purpose of this concluding chapter has been to briefly summarize the results of this thesis, and also to indicate some areas of future interest for research in molecular beam scattering from surfaces. This particular area of surface chemistry is progressing rapidly, and hopefully the results and comments contained in this dissertation will prove helpful to future workers in this field.
APPENDIX A

Field and Ion Trajectory Calculations

The design of the right angle electron multiplier mounting mentioned in Chapter III was accomplished by Dr. W. Siekhaus. This brief discussion describes the method he used and the computer programs available for design problems of this type. These programs are useful for the solution of a number of design problems which may arise in the construction of surface research equipment involving the motion of charged particles in electric fields.

The design of the multiplier mounting for optimum signal to noise ratio involves moving the multiplier opening out of the line of sight of the quadrupole assembly exit. This can be accomplished by an off axis mounting, or a right angle mounting. Various off axis and right angle geometries were assessed. A particular geometry was evaluated by first determining the electrostatic field in the region between the quadrupole exit and the multiplier entrance, and then using this field to calculate the trajectories of ions exiting the quadrupole assembly and entering this field.

The calculation of the electrostatic field is done by numerical solution of the Poisson equation

$$\nabla^2 (K\psi) + \rho = 0$$

in two dimensions, subject to the boundary conditions imposed by the geometry of the chosen design. This solution is accomplished by the use of a computer program, available in the LBL computer center library,
called JASON.\textsuperscript{169} This program uses a "finite element method"\textsuperscript{169} to
calculate a set of difference equations approximating the Poisson
equation in the correct (cylindrical or 2D cartesian) coordinate system.
These difference equations are then solved by the technique of
"normalized successive block overrelaxation."\textsuperscript{170} The mathematical
development of this solution is discussed in detail in reference 168.

This reference also contains explicit instructions for the
operation of the program. The input data consists of the geometrical
shape of the region, defined by coordinate points, boundary potentials,
and shapes and dielectric constants of subregions in the overall
region. The result of this field calculation has been shown for the
final design geometry in Fig. III-lla.

Once the field has been calculated and a plot of equipotential
lines stored on tape, a number of LBL available programs can be used
to calculate the trajectories of ions in this field. The library
program used in this case is called OPTIK. The trajectories
are determined, of course, by the ion energies and the gradients of the
field in the direction of ion travel. The results of this calculation
for the final design geometry have also been shown previously in
Fig. III-llb.
APPENDIX B

Other Computer Programs

Several other computer programs were used for data analysis and model fitting in the work reported in this thesis. Several of these programs, used infrequently, have been fully described in the dissertations of Al West and Hy Lyon. These programs can be used for data acquisition with the VIDAR system and for geometrical calculations associated with the LEED technique. The reader is referred to discussions in these dissertations concerning their use.

Two programs were written specifically for the work contained in this thesis. Printouts of the Fortran code for these two programs are shown on the following pages. The first is a simple linear least squares fitting routine. It was used for general data fitting and can be easily modified for fitting to other functional dependencies. Its use is self explanatory.

The second code was written to calculate the phase and amplitude behavior of possible surface reaction models as a function of the surface temperature and beam modulation frequency. The program performs calculations in the complex form after the complex vector has been determined. The printout shown is for a temperature sweep from 300 to 1300°K for the five possible models described in section IV. By changing cards containing the vector equation (VECl=...) different model behaviors can be evaluated. Experimentally determined activation energies and Arrhenius factors can be inserted in the calculation by changing the appropriate cards, as well as parameters resulting
HOTEL LEAST SQUARE FIT

INPUTS FIT WITH SLOPE +1.1768
MY LINE WITH SLOPE +1.1768 = INTERCEPT 296.46663 = -62736

A    B    C
44  0.04000  eH=55000  1.0 55000  -44750
40  0.03000  2500000  1.0 55000  -58000
40  0.02000  2500000  1.0 55000  -82489
40  0.01000  2500000  1.0 55000  -106298
40  0.00000  2500000  1.0 55000  -130864
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from the minimization procedure described below. Also included in
the printouts is the correct control card sequence for the use of the
Minnesota Fortran Compiler which uses a wide range of error diagnostics
allowing relatively easy debugging of user programs. This control
card sequence is correct now for use at LBL, but of course may change
at any time. Interested readers should consult the most recent copy
of the computing center manual.

The final program to be briefly described in this appendix is
a routine for multidimensional data fitting. Once the phase and
amplitude data have been collected as a function of surface temperature
and modulation frequency, and a model has been chosen which matches
the data behavior and the chemical intuition of the experimenter,
this routine can be used to extract the "best fit" kinetic parameters
for the given model and collected data.

This fitting is obtained by a variable matrix minimization
procedure known as MINUIT. This program calculates the difference
between an n-dimensional data vector set and an n-dimensional model
vector set and minimizes the difference between the two vectors over
the range of the independent variables ($T_s$ and $\omega$ in this case). It
does this by freely varying the kinetic parameters ($E_i$ and $A_i$) until
the sum squared of the vector differences is a minimum. A detailed
explanation of the use of MINUIT and a discussion of function
minimization in general is available from the CERN Computer Program
Library. 172
The user must supply a subroutine which calculates the vector difference for the particular model in question. The main program then changes parameters in this subroutine until a minimization occurs. The printout on the following pages is typical of the user subroutine FCN which calculates this vector difference. It is quite similar to the previous model calculation program. The minimization procedure uses the gradient of the user difference function, so if the derivative is analytical it is best to calculate it in the user subroutine. If not, MINUIT will numerically determine the needed derivatives. All of this is covered in detail in the CERN write up for MINUIT.
FCN

SUBROUTINE FCN(NPAM*GFLX,IFLAG)
CHARACTER*5 FC,FLX
INTEGER X(100),*507,222,22
DIMENSION X(100),*507,222,22
! IF (IFLAG .GT. 1) .U. 10 100
C
C HEAD IN DATA, CALCULATE EXPIL VECTOR
12 PRINT 600, NOTA
17 PRINT 550
26 WRITE 50, I1,NDITA
33 WRITE 700, PHI(I),AMP(I),TS(I),FH(I)
52 AMP(I)=AMP(I)
57 VECE(I)=CMPLX(AMP(I),COS(PHI(I)/57.3),AMP(I)*SIN(PHI(I)/57.3))
77 OMEGA(I)=2.7*3.141*FH(I)
105 WRITE 500, PHI(I),AMP(I),TS(I),FR(I),OMEGA(I),VECE(I)
C CALCULATE F (UNUSABLE)
140 CONTINUE
140 CF=(0.0,0.0)
143 F=0.0
143 PL=(0.0,0.0)
140 PR=(0.0,0.0)
149 ETA=1.001,0.0
153 WRITE 200, IMN1,N1A
C CALCULATE PHI*AMP** MODEL
154 AK1=X(1)*EXP(-X(3)/(2.3*TS(1))
165 AK2=X(2)*EXP(-X(3)/(2.3*TS(1))
201 ARG1=OMEGA(I)/AK1
202 ARG2=OMEGA(I)/AK2
204 UEN=SQRT(1.0+(AMG/4.)**2)
207 UEN2=SQRT(1.0+(ARG2)**2)
214 A1=ATAN(AH2)
217 A2=ATAN(AH2)
222 Z1=CMPLX(1.3,1.0)
225 Z2=CMPLX(1.3,1.0)
227 VEC=ETA*(Z1*CAP(2)/CEN1)*Z2*EXP(Z2)/DEN2
C CALCULATE ADJUSTION TO MULTIPLE
228 CF=CF**REAL(VEC)+REAL(VCE(1))**2
304 F=REAL(CF)
305 END
600 FORMAT (i3)
650 FORMTAT (1x,P11.3,PHI(1)**AMP,7A*,MTS*8X**FRQ**4X**OMEGA*5X 1UNEPVECTOR)
700 FORMAT *(3F10.4)
800 FORMAT ((1x,7F10.4)
306 END
APPENDIX C

Fourier Transform Method

A recent paper by Foxon, et al.\textsuperscript{143} describes the use of a full waveform collection and signal processing technique which has several advantages over the lock-in detection method used in this thesis. Some of these advantages are: 1) better signal to noise ratio because the lock-in amplifier band pass is no longer limiting, 2) the possible effects due to the velocity distributions of incident and desorbed beams can be removed by deconvolution, 3) information is available at a number of frequencies from a single experiment.

This technique involves digital collection of the product signal waveform using standard ion counting techniques. The behavior of this waveform as a function of the surface reaction parameters is then used to determine a model for the surface process.

For a linear system of elementary processes described by a function $h(\tau)$, an input $x(t)$ results in an output $y(t)$ given by the convolution integral

$$y(t) = \int_{0}^{\infty} h(\tau)x(t-\tau)d\tau$$

(AC-1)

This output $y(t)$ will have the same frequency components as the input $x(t)$, but with different values of phase and amplitude. That is, the values of the Fourier coefficients will be modified, but not the frequency of the waveform.
In the frequency domain, \( h(\tau) \) is described by a frequency response function \( H(f) \) given by

\[
H(f) = \int_{0}^{\infty} h(\tau) \exp(-2\pi i f \tau) d\tau \quad (AC-2)
\]

By writing \( x(t) \) and \( y(t) \) as their Fourier transforms, Eq. (AC-1) becomes

\[
Y(f) = H(f)X(f) \quad (AC-3)
\]

\( H(f) \) can be a sequence of functions, and if there is no interaction between these functions, then

\[
H(f) = \prod_{i=1}^{n} H_i(f) \quad (AC-4)
\]

This transfer function \( H(f) \) is a combination of functions identical to the mechanical, transit time, complex impedance and surface reaction phase shifts discussed in Chapter III. The problem, then, is reduced to a deconvolution of \( Y(f) \) to remove effects due to transit time and so forth, leaving a \( Y(f) \) which is the result of an effective driving function \( X'(f) \).

The remaining function \( Y(f) \) is then compared with expected behavior for the surface model in question. Data at several frequencies, from \( f \) to \( 1/2 Mf \), (where \( M \) the number of channels into which the waveform is divided) are theoretically available from a single measurement. Of course, since successive components are smaller in value, a strong signal is necessary to measure the theoretical
maximum number with reasonable accuracy. These components can then
be used as in the standard lock in detection first Fourier component
method, or proposed models can be fit to the entire waveform. This
last method suffers from the complexity of such models and the
number of parameters involved. A combination of the two methods would
probably be most successful.
APPENDIX D

Model Derivation

In this appendix we list the assumptions and derivations leading to the simple two branch model for H₂-D₂ exchange discussed in the body of this thesis. A detailed treatment leads to a slightly more complicated model which will also be discussed.

The surface region is composed of terraces and steps which can be treated in one dimension since the step edges are essentially infinitely long compared to the terrace width. In this model, the terrace width is \( w \), some fraction of which, \( f \), is in the active vicinity of the step. The distance, \( x \), is taken to be perpendicular to the step edges.

We assume the following:

1) The exchange reaction occurs between an adsorbed or gas phase molecule and an atom bound at the step.
2) Only molecules desorb from the surface. No atoms are directly desorbed.
3) Only atoms are bound at the steps.
4) An incident gas phase molecule can strike the terrace or the step region. The probability of striking the step region is \( f/w \), and that of striking the terrace \( 1-f/w \).
5) A molecule incident on the step region has a probability \( p \) of exchanging an atom with an atom bound at the step. If it strikes an unoccupied portion of the step region it has probability \( \eta_s \) of dissociatively chemisorbing.
6) A molecule incident on the terrace region has probability \( \eta_t \) of associatively adsorbing.

7) A terrace adsorbed molecule incident on the step region has probability \( p' \) of exchanging and \( \eta_s' \) of dissociatively chemisorbing.

8) There are \( N_s \) atom adsorption sites per centimeter of step region.

9) Molecules desorb to the gas phase with rate constant \( k_d \). They can diffuse over the terrace with diffusion coefficient \( D_s \).

For derivation of the differential equations governing the model behavior, the system can be divided into three sets of equilibria. These three sets are gas-terrace, gas-step, and terrace-step equilibria.

Gas-terrace equilibria, with equilibrium constant \( K_{g-t} \),

\[
H_2(g) \rightleftharpoons H_2(t) \quad D_2(g) \rightleftharpoons D_2(t) \quad HD(g) \rightleftharpoons HD(t) \quad (AD-1)
\]

Gas-step equilibria, with equilibrium constant \( K_{g-s} \),

\[
H_2(g) \rightleftharpoons 2H(s) \quad D_2(g) \rightleftharpoons 2D(s) \quad HD(g) \rightleftharpoons H(s) + D(s) \quad (AD-2)
\]

Terrace-step equilibria, with equilibrium constant \( K_{t-s} \),

\[
H_2(t) \rightleftharpoons 2H(s) \quad D_2(t) \rightleftharpoons 2D(s) \quad HD(t) \rightleftharpoons D(s) + H(s) \quad (AD-3)
\]

There are also a series of exchange equilibria which must be satisfied in two cases. Gas-step exchange equilibria
\[
\begin{align*}
\text{H}_2(g) + D(s) & \rightleftharpoons \text{HD}(g) + H(s) \\
\text{D}_2(g) + H(s) & \rightleftharpoons \text{HD}(g) + D(s) \\
\text{HD}(g) + D(s) & \rightleftharpoons \text{D}_2(g) + H(s) \\
\text{HD}(g) + H(s) & \rightleftharpoons \text{H}_2(g) + D(s)
\end{align*}
\]

Terrace-step exchange equilibria

\[
\begin{align*}
\text{H}_2(t) + D(s) & \rightleftharpoons \text{HD}(t) + H(s) \\
\text{D}_2(t) + H(s) & \rightleftharpoons \text{HD}(t) + D(s) \\
\text{HD}(t) + D(s) & \rightleftharpoons \text{D}_2(t) + H(s) \\
\text{HD}(t) + H(s) & \rightleftharpoons \text{H}_2(t) + D(s)
\end{align*}
\]

We assume no direct gas-terrace isotope exchange. At equilibrium these equations must satisfy the following conditions:

\[
K_{eq} = 4 = \frac{[\text{HD}(g)]^2}{[\text{H}_2(g)][\text{D}_2(g)]} = \frac{P_{HD}^2}{P_{H_2}P_{D_2}} \quad (AD-6)
\]

\[
K_{eq} = 4 = \frac{[\text{HD}(t)]^2}{[\text{H}_2(t)][\text{D}_2(t)]} = \frac{N_{HD}^2}{N_{H_2}N_{D_2}} \quad (AD-7)
\]

The fraction of D atoms out of the whole number of atoms must be the same in each phase at equilibrium.

\[
X = \text{fraction D atoms} = \frac{P_{HD} + 2P_{D_2}}{2P_{H_2} + 2P_{HD} + 2P_{D_2}} \quad \text{(gas)} \quad (AD-8)
\]
\[
X = \frac{N_{HD} + 2N_{D_2}}{2N_{H_2} + 2N_{HD} + 2N_{D_2}} \quad \text{(terrace)} \quad \text{(AD-9)}
\]

\[
X = \frac{\theta_D}{\theta_H + \theta_D} \quad \text{(step)} \quad \text{(AD-10)}
\]

\[
P_T = \text{total pressure} = P_{H_2} + P_{D_2} + P_{HD} \quad \text{(AD-11)}
\]

For gas-terrace equilibria,

\[
N_T = K_{g-t} P_T
\]

\[
N_{H_2} + N_{D_2} + N_{HD} = K_{g-t} (P_{H_2} + P_{HD} + P_{D_2}) \quad \text{(AD-12)}
\]

For terrace-step equilibria,

\[
N_T = K_{t-s} \left( \frac{\theta_T}{1-\theta_T} \right)^2
\]

\[
N_{H_2} + N_{D_2} + N_{HD} = K_{t-s} \left( \frac{\theta_H + \theta_D}{1-\theta_H - \theta_D} \right)^2 \quad \text{(AD-13)}
\]

For gas-step equilibria,

\[
P_T = K_{g-s} \left( \frac{\theta_T}{1-\theta_T} \right)^2
\]

\[
P_{H_2} + P_{D_2} + P_{HD} = K_{g-s} \left( \frac{\theta_H + \theta_D}{1-\theta_H - \theta_D} \right)^2 \quad \text{(AD-14)}
\]
These equilibrium conditions involve eight unknowns, $P_{H_2}$, $P_{D_2}$, $P_{HD}$, $N_{H_2}$, $N_{D_2}$, $N_{HD}$, $\theta_H$, $\theta_D$ and eight equations, AD-6 through AD-13 (AD-14 is not independent). Therefore, the unknowns should be determinable.

For the case of the molecular beam experiment there are further constraints on the system which must be taken into account. The incident $D_2$ beam is modulated, so its intensity is given by

$$I_{D_2} = I_{D_2}^0 g(t)$$

where $g(t)$ is the modulation gating function. The background $H_2$ is unmodulated, and its intensity is given by

$$I_{H_2} = I_{H_2}^0 = P_{H_2} \mu_{H_2}$$

where

$$\mu_{H_2} = \frac{1}{\sqrt{2\pi M_{H_2} k_B T}} = 1.06 \times 10^{18} \text{ sec/cm}^2$$

and pressure is measured in dynes/cm$^2$. (One torr equals $1.33 \times 10^3$ dynes/cm$^2$). The conditions of the experiment were such that $I_{H_2} \gg I_{D_2}$.

For strongly bound H atoms at the steps $f_N I_{H_2}^0 / k_R$ is very large. ($k_R$ is the rate constant for production of terrace molecules at the steps by recombination.) This implies that $\theta_H \approx 1$ and

$$\theta_{D} \approx \frac{1}{2} \frac{I_{D_2}^0}{I_{D_2}^0 + I_{H_2}^0} \approx 0$$
Also, since $I_H^0 \gg I_{D_2}^0$, the coverage of $H_2$ on the terrace is uniform,

$$N_{H_2}(x,t) = K_{g-t} P_{H_2} = \left( \frac{\eta_t}{k_{H_2}} \right) P_{H_2} = \text{constant} \quad (AD-15)$$

that is,

$$\frac{\partial N_{H_2}}{\partial t} = \frac{\partial N_{H_2}}{\partial x} = 0$$

The equations governing surface diffusion of HD and $D_2$ on the terrace are,

$$\frac{\partial N_{HD}}{\partial t} = D_s \frac{\partial^2 N_{HD}}{\partial x^2} - k_d N_{HD} \quad (AD-16)$$

$$\frac{\partial N_{D_2}}{\partial t} = D_s \frac{\partial^2 N_{D_2}}{\partial x^2} + \eta_t I_{D_2}^0 g(t) - k_d N_{D_2} \quad (AD-17)$$

subject to the boundary conditions

$$\left( \frac{\partial N_{HD}}{\partial x} \right)_{x=0} = 0 \quad (AD-18)$$

$$\left( \frac{\partial N_{D_2}}{\partial x} \right)_{x=0} = 0 \quad (AD-19)$$

The initial condition for the diffusion is determined by the removal of terrace molecules at the step. The net removal of HD at the step is
We have assumed $\theta_H \sim 1$ and $N_{H_2}$ is given by Eq. (AD-15). Equation (AD-20) then becomes

$$-D_s \left( \frac{\partial N_{HD}}{\partial x} \right)_{N_H} = \frac{1}{2} k' p' N_{HD}^\omega - k' p' N_{H_2}^\omega \theta_D - k' p' N_{D_2}^\omega (\theta_H)$$

(AD-20)

The net removal of $D_2$ at the step is similarly given by

$$-D_s \left( \frac{\partial N_{D_2}}{\partial x} \right)_{N_{HD}} = k' p' N_{D_2}^\omega \theta_H = k' p' N_{D_2}^\omega$$

(AD-22)

where $k'$ is the rate constant for removal of terrace molecules at the step.

Finally we must write a material balance on the number of step adsorbed $D$ atoms.

$$N_s \frac{d\theta_D}{dt} = k' p' N_{D_2}^\omega - f p I_{H_2} \theta_D + \frac{1}{2} k' p' N_{HD}^\omega$$

(AD-23)

This derivation results in three differential equations in three unknowns for the molecular beam case discussed here. They are equations (AD-16, (AD-17) and (AD-23) subject to the boundary conditions
(AD-18), (AD-19), (AD-21) and (AD-22). These equations must be solved for $N_{\text{HD}}$, $N_{D_2}$ and $\theta_D$ in order to fully describe the model behavior.

The simple two branch model discussed previously is equivalent to this more detailed model if the explicit inclusion of molecular desorption is omitted. It can be seen that the simple rate constants derived from the two branch model are effective rate constants which include $K_{g-t}$, $K_{g-s}$ and $K_{t-s}$ as well as the diffusion and desorption constants and the exchange probability factors $p$ and $p'$. A much more extensive treatment of the model described by Eqs. (AD-16) through (AD-22) and comparison of this system with analogous exchange reactions will be necessary before a clear understanding of the quantitative values of these rate parameters is obtained.

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REFERENCES


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