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SCATTERING OF DIATOMIC AND POLYATOMIC MOLECULES FROM THE (100) CRYSTAL FACE OF PLATINUM

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ABSTRACT

The angular distribution of diatomic (CO, N₂, O₂, NO, H₂, D₂) and polyatomic (CO₂, N₂O, C₂H₂, NH₃ and methylene cyclobutene) molecules were monitored upon scattering from the clean and carbon covered (100) crystal face of platinum. All of the scattered molecules (except ammonia) exhibit directed scattering with intensity maxima at or near the specular angle, indicating poor energy accommodation during collision. On scatterings CO and C₂H₂ from an adsorbed layer of carbon monoxide or acetylene the angular distributions were cosine-like that indicate significant energy accommodation between the incident gas molecules and the surface. It appears that if the vibrational energy of surface atoms and the translational energy of the incident molecules are of the same magnitude, the incident particles will be reflected. The near complete energy accommodation of the scattered molecules in the presence of adsorbed gases could take place if high frequency surface modes are created on adsorption of these low molecular weight gases. This way, there is matching of vibrational frequencies of the collision pairs (gas molecules—adsorbed molecules) which allow strong vibrational (V-V) energy transfer.

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I. INTRODUCTION

Studies of the scattering of atomic and molecular beams from solid surfaces reveal the nature of energy transfer between an incident atom or molecule and surface atoms. For monatomic gas atoms energy can only be exchanged between the translational modes of the incident atom and the vibrational states of atoms in the surface. The interaction of monatomic gases with solid surfaces has been studied sufficiently to allow the development of the "hard-cube" and "soft-cube" scattering models. These models, and more sophisticated models, explain qualitatively many of the scattered beam properties: its surface and beam temperature dependence and its dependence on the mass ratio \( \frac{m_{\text{gas}}}{m_{\text{surface}}} \). The major assumption of the cube models, that momentum changes only along its perpendicular component while the magnitude of the parallel component is conserved, stands up well under experimental scrutiny.

For diatomic molecules, however, the interaction between the gas and the solid is more complex due to the possibility of additional energy exchange between the internal states of the molecule (rotation and vibration) and the vibrational modes of the surface atoms. That such energy exchange takes place efficiently has been demonstrated by the striking observations of Saltsburg et al. in their studies of the scattering of \( \text{H}_2, \text{D}_2 \) and \( \text{HD} \) molecules from the Ni(100) surface. \( \text{H}_2 \), whose rotational energy states were separated by \( \Delta E_{\text{rotation}} > kT \) at the experimental temperatures, showed a sharp intensity maximum at the specular angle when directed at the solid in the form of a molecular beam, while beams of HD and D\(_2\) for which \( \Delta E_{\text{rotation}} \) is of
the order of $kT$, produced broad angular distributions, indicating efficient energy exchange. Further evidence that surface scattering involves the excitation of rotational energy states was obtained by increasing the beam temperature and observing changes in the angular distribution of scattered $H_2$. An energy accommodation model, developed by Feuer for the case of diatomic molecules scattered from surface atoms, does indeed predict efficient energy exchange between surface vibrations and the rotational modes of diatomic molecules. Experimental studies have indicated that energy transfer takes place efficiently when the magnitude of the surface vibrational energy quantum is comparable to the energy to be transferred to or from the internal states of the gas molecule. At temperatures above the Debye temperature, the thermal energy, $3RT$, may be used to estimate the maximum quanta of vibrational energy that is transferred by a surface atom.

In order to investigate further the nature of energy transfer between the internal modes of molecules and the vibrational modes of surface atoms, we have studied the angular distribution of several diatomic and polyatomic species ($CO, NO, O_2, NO_2, H_2, D_2, CO_2, N_2O, C_2H_2$, methylene cyclobutene and $NH_3$), scattered from the clean (100) face of a platinum single crystal and from the same surface covered by a layer of graphite. We have also monitored the angular distribution of molecules scattered from a layer of like molecules ($CO, C_2H_4$) adsorbed on the surface.

The energy transfer appears to be poor (except for ammonia) when scattering takes place from clean or carbon covered platinum surfaces. On the other hand, efficient energy transfer takes place on scattering
CO or C$_2$H$_2$ in the presence of adsorbed (CO or C$_2$H$_2$) molecules. These results can be explained assuming the presence of high frequency vibrational modes associated with the adsorbed molecules. This way, there is a matching of vibrational frequencies of the collision pairs (surface atoms--gas molecules) which produces the efficient vibrational-vibrational (V-V) energy transfer. These vibrational frequencies may be estimated from the simple models that were proposed.
II. EXPERIMENTAL

The apparatus used for these experiments has been described in detail elsewhere. In brief, the molecular beam emanates from a source consisting of a multi-channel array and a reservoir maintained at a pressure of several torr. Differential pumping is used between the source and the scattering chamber to reduce the ambient gas pressure to UHV levels. At the single crystal surface, the incident flux is approximately $10^{13}$ molecules/cm$^2$/sec, modulated at 150 Hz to allow phase sensitive detection of the scattered signal. During the experiments a high speed ion pump maintains the background pressure in the scattering chamber in the low $10^{-9}$ torr range. The scattered beam is detected by a quadrupole mass spectrometer with an ionizer acceptance angle of 7°. Due to the open construction of the ionizer, the ion intensity is proportional to the number density of molecules in the range of the acceptance angle. Scattered signals are reported in the plane of incidence; no attempt was made to analyze the out-of-plane scattering intensity.

Surface structures of the clean surface or of those resulting from adsorbed gases were monitored by low energy electron diffraction (LEED) optics built into the scattering chamber. The Pt(100) single crystal surface was characterized by a LEED diffraction pattern indicating a (5x1) surface structure when clean, and a (1x1) structure following the adsorption of carbon monoxide, carbon or hydrocarbons. Its cleaning required heating in an oxygen pressure of $10^{-5}$ torr at 800°C for an extended period (10 minutes-100 minutes depending on the amount of carbon on the surface). A layer of surface carbon was the
the major impurity encountered in these experiments. Surface cleanliness was determined by Auger electron spectroscopy (AES), carried out using the LEED electron optics. Typical Auger spectra of a clean and of a CO covered platinum surface are shown in Fig. 1. An auxiliary titanium sublimation pump was used to reduce the partial pressure of CO in the ambient when desired. In each experiment it was possible to monitor not only the scattered beam intensity as a function of scattering angle, but also to detect the incident beam intensity. This way the data could be presented in terms of the normalized beam intensity $I(\theta)/I(\text{beam})$ that allows a direct comparison of all of the scattering curves for different gases.
III. RESULTS

A. Scattering from the Clean Pt(100)-(5x1) Surface

Figures 2-4 show the angular distributions of CO, N₂ and O₂ scattered from the clean platinum surface. The cleanliness of this surface during an experiment could easily be checked since the diffraction beam intensities due to the (5x1) surface structure are known to deteriorate rapidly upon the adsorption of ambient gases (mostly CO). Scattered beam intensities have been normalized to the incident beam intensity so that all of the beam intensities in these figures can be compared directly. The angular distribution of the scattered beam is peaked at or near the specular angle for all of these diatomic gases. It should be noted that for these experiments the source temperature (which defines the beam temperature $T_{beam}$ for a Maxwellian velocity distribution) was 300°C while the surface temperature was somewhat hotter (475°C). It was necessary to maintain this slightly elevated temperature during the scattering experiments with the clean platinum surface because the surface temperature must be above the point at which CO in the $\alpha$ binding state desorbs. Otherwise, the surface would soon be covered with a layer of $\alpha$-CO.  

Figure 5 shows the angular distribution of nitric oxide, NO, scattered from the (100) face of platinum. The surface temperature for this experiment was 1200°C because the thermal dissociation of N₂O was also being investigated. Due to the higher surface temperatures, the angular distribution is broader than those previously shown and the peak intensity appears at the position nearer to the surface normal, than the specular angle, as it should according to various models for
momentum transfer from the hot surface to the colder gas. The angular distribution is still peaked however, and not cosine in nature, thus indicating the lack of complete energy accommodation as in the case of all the other incident diatomic molecules.

The scattering of molecular beams of hydrogen and deuterium was also studied. The results are shown in Figs. 6 and 7 for a clean platinum surface maintained at 1175°K. Compared to other diatomic gases scattered from hot surfaces, these curves are intense and the maxima fall at the specular position as noted in previous studies. While the angular distributions are surprisingly broad for both molecules, it appears that the angular distribution of scattered deuterium beam may be somewhat narrower than that of hydrogen and that the overall intensity may be slightly higher, although the experimental uncertainty does not permit a definitive answer at this time. Neither the presence of oxygen nor hydrogen in the ambient of the scattering chamber seemed to effect the D\textsubscript{2} scattering, but there was a large amount of scatter in the data and a high background noise level.

Several polyatomic gases were also scattered from the clean (100) face of platinum. Figures 8 and 9 show the angular distribution of the scattered beams of two tri-atomic molecules, CO\textsubscript{2} and N\textsubscript{2}O. Again, the angular distributions are peaked at or near the specular angle. The higher surface temperature in the N\textsubscript{2}O study\textsuperscript{9} has shifted the peak intensity somewhat toward the surface normal. Figures 10 and 11 show the angular distributions of scattered beams of two hydrocarbons, acetylene and methylenecyclobutane. As in the previous cases the intensity maximum occurs near the specular position.
for low surface temperature (acetylene) and is backscattered at high surface temperatures (methylenecyclobutane). In summary: the scattered diatomic and polyatomic molecules we have investigated have angular distributions with intensity maxima at or near the specular angle.

The only exception to this type of directed scattering from the Pt(100) is that of ammonia. Ammonia molecular beams had a cosine-like scattered angular distribution as can be seen in Fig. 12. The ammonia-platinum interaction appears to be strong that leads to near thermal equilibrium between the gas molecules and the surface during the collision time.

B. Scattering from Molecules Adsorbed on the (100) Face of Platinum

Carbon monoxide and acetylene both chemisorb readily on platinum at 300°K. Carbon monoxide forms several ordered surface structures depending on the surface concentration and surface temperature.\(^8\) Acetylene forms a \((\sqrt{2} \times \sqrt{2})\)-R\(^{45}\)\(^{\circ}\) surface structure.\(^{12}\) Although the surface order is easily discernible by low energy electron diffraction the high background intensities in the diffraction pattern indicate a fair amount of disorder in the adsorbed layer and this has been substantiated by molecular beam studies.

The angular distribution of carbon monoxide scattered from an adsorbed layer of carbon monoxide on platinum is shown in Fig. 13. The scattered beam has a very broad angular distribution that does not change with differing angle of incidence, thus indicating a change in the nature of gas-solid interaction. This result should be contrasted
with the scattering of CO from the clean platinum surface (Fig. 2) that had an intensity maximum at the specular angle. The angular distribution of acetylene scattered from a layer of adsorbed acetylene is shown in Fig. 14. The scattered beam again has a broad, cosine-like distribution. These observations seem to indicate that complete energy accommodation occurs between the surface and the incident molecules within the collision time.

Carbon forms a graphitic overlayer on the (100) face of platinum. The resultant ring-like diffraction pattern indicates the presence of domains of graphite that lie with their basal plane parallel to the surface and yet show rotational disorder. We have scattered the molecular beams of several diatomic molecules from this carbon layer. Figures 15a and b show examples that in every case the angular distribution of the scattered beam was peaked near or at the specular angle, indicating incomplete energy accommodation between the incident molecules and the carbon covered surface.
IV. DISCUSSION

One of the general conclusions one may draw from the results obtained by monitoring the angular distribution of the scattered beams of diatomic and polyatomic molecules from the clean platinum (100) surface is that in every case (with the exception of ammonia) the angular distribution is non-cosine, it has an intensity maximum at or near the specular angle. The peak intensities and the widths of the angular distributions may vary depending on the surface temperature. The kinetic energy of the scattered molecules at the various angles has not been determined in these experiments. Thus, any conclusion as to the nature of energy transfer between the surface atoms and the incident molecules has to be arrived at from the inspection of the angular distribution. The absence of a cosine-like scattering distribution and the large intensity maximum near the specular angle does indicate, however, that there is incomplete energy accommodation between the platinum surface atoms in the single crystal surface and the incident gas molecules. It is likely that some fraction of the molecules that appear at the specular angle have velocities identical to the incident velocity, while others also appear at this angle after undergoing inelastic scattering.

Results also indicate that energy transfer is inefficient when the incident molecules are scattered from carbon-covered platinum surfaces. It appears that the vibrational modes of platinum atoms at the surface, or of carbon atoms in the graphite layer on the platinum surface, impart enough momentum to reflect the diatomic or polyatomic species with high efficiency before adsorption can take place and permit
complete energy accommodation. It should be noted that directed scattering occurs from both of these surfaces regardless of the large difference in atomic weights between platinum and carbon.

Once a layer of adsorbed CO is present on the surface, however, energy accommodation of the incident CO molecules is entirely different from that on clean platinum or on carbon covered surfaces. The incident molecule collides with the carbon monoxide layer and is then reflected with a near-cosine angular distribution indicating significant energy accommodation. Thus, the carbon-oxygen bond of the adsorbed CO molecule has suitable vibrational modes that permit efficient energy transfer between the CO(gas) and CO(adsorbed) while no such modes exist between CO(gas) and C(adsorbed) or CO(gas) and Pt(surface). In the same way, C₂H₂(gas) shows complete energy accommodation with an adsorbed C₂H₂ layer within the collision time as indicated by the distribution of scattered beam that again exhibits cosine character. It appears that these low molecular weight adsorbed gases have vibrational modes that allow rapid energy transfer on collision, while adsorbed carbon, with an even smaller atomic weight, and platinum itself, do not.

Recently Beebe and Dobryzhnsky have suggested that if vibrational modes that are closely similar in energy to the thermal translational energy of the incident particle exist for surface atoms, the incident particles will be reflected. In the absence of such modes, the particle may be adsorbed and must wait for desorption until the surface modes come into phase. Thus translational(T)-vibrational(V) energy transfer between incident molecules and the surface is not very likely if the two are matched in energy, but such an energy transfer
results in a reflection of the molecule from the surface. For these relatively high temperature experiments \((T > \text{Debye temperature})\), the thermal energy of surface atoms that is due to the various modes of lattice vibrations is of the same magnitude as the kinetic energy of the incident molecule. The energy of excitation of diatomic molecules to their first excited vibrational state, however, is so high \((\approx 0.1 \text{ eV})\) that the surface phonon energies \((\approx 0.02 \text{ eV})\) are insufficient to cause vibrational excitation in the diatomic molecule at the experimental temperatures.

Armand et al.\(^6\) have suggested that adsorption of a low molecular weight gas on a surface creates high frequency surface modes, the frequencies being similar to the vibrational frequency of diatomic gas molecules. On the other hand, the adsorption of high molecular weight gas molecules with respect to the atomic weight of the adsorbing surface atoms creates low frequency surface modes whose frequencies are lower than the vibrational modes of the adsorbing solid. This theory is yet to be tested rigorously, but it would predict the thermal accommodation of \(\text{CO} \) molecules by a layer of adsorbed \(\text{CO} \) or the accommodation of \(\text{C}_2\text{H}_2 \) molecules by adsorbed \(\text{C}_2\text{H}_2 \), as due to very efficient V-V energy transfer processes between the high frequency vibrational modes of the adsorbed molecule and the incident molecule. Also, the vibrational modes of adsorbed molecules of higher energy than the kinetic energy of the incident molecule would not allow, according to the Beebe model, reflection of the incident particles.

So far we have not considered the possibility of the exchange of energy between the rotational modes of the incident diatomic molecule
and vibrational states of the surface atoms. While the ground and first excited vibrational energy states of the gas molecules are 0.1-0.2 eV apart for most of the diatomic and polyatomic molecules considered here, the first two rotational energy states are \( \sim 10^{-3} \) eV apart for nitrogen and for all other molecules with the exception of \( H_2 \) and \( D_2 \). It has been shown by Saltsburg et al. that coupling between the vibrations of surface atoms and the rotations of diatomic molecules can yield strong V-R interactions that may rotationally excite diatomic molecules (at least in the case of \( H_2, D_2 \) or HD). However, due to the small energy separation of rotational states for all other molecules, many of the higher rotational states are already excited. Feuer's model predicts that whenever the temperature of the solid exceeds that of the gas (or beam), not only can vibrational energy be transferred from the lattice into rotational modes of the gas, but also some of the rotational energy of the gas may be converted into translational energy. The net effect of these V-R and R-T energy transfer processes should be to broaden the angular distribution of the scattered beam and to impart a diffuse component to the scattered gas. This energy transfer mechanism might be especially effective in the case of ammonia due to its large number of rotational and vibrational modes, and may give rise to the observed cosine-like distribution.

In summary, the absence of high frequency vibrational modes for surface atoms that would match the vibrational excitation energies of incident diatomic molecules is the likely cause of the poor energy accommodation on platinum or carbon covered platinum single crystal surfaces. Adsorbed carbon monoxide or acetylene facilitate efficient
energy transfer between the surface and the incident molecules. This can be explained by assuming the creation of high frequency surface modes on adsorption of these gases that allow strong V-V energy transfer between the collision pairs.
V. COMPARISON WITH OTHER SCATTERING RESULTS

It is possible to compare the scattering results above, with data previously obtained for scattering various diatomic and polyatomic molecules from the (111) surface of several other fcc metals, at the (110) face of tungsten and different polycrystalline solids. In general, there is good agreement with our observations of poor accommodation of the incident beam on clean surfaces and efficient accommodation on gas covered surfaces. Coltharp, Scott and Muschlitz$^{14,15}$ have studied the scattering of nitrous oxide from a tungsten ribbon composed primarily of crystallites having the (112) orientation. At room temperature they detected a cosine angular distribution for the reflected gas. The ambient pressure in their scattering chamber was $10^{-6}$ torr, high enough to insure that the surface was covered by adsorbed gases. They also observed, however, that high surface temperatures yielded pronounced lobular distribution with broad intensity maxima in the vicinity of the specular position. These same authors report that both nitrogen and nitric oxide are backscattered from a tungsten surface heated to $2500^0$K. Although our platinum surface temperature was considerably lower, we have also observed that nitric oxide scattered back toward the surface normal from the hot surface in agreement with their observation. The scattering of nitrogen molecules has been studied by several authors.$^{15,16,17}$ Hurlbut$^{16}$ found that nitrogen was scattered diffusely (i.e. with a cosine angular distribution) from polished steel, polished aluminum, and unpolished glass except at near-grazing incident angles ($\theta_{\text{incident}} > 80^0$) where some peaking was observed. In view of the poor residual vacua achieved, $(10^{-6}$ torr) and the presence in the
work chamber of hydrocarbon vapors from the diffusion pump oil, the specimen surfaces were undoubtedly contaminated and we would thus expect them to yield distribution of scattered gas molecules close to the cosine pattern. Stickney and Hurlbut\textsuperscript{18} and Stickney\textsuperscript{19} have measured the momentum transfer between several gases (He, Ne, Ar, N\textsubscript{2}, H\textsubscript{2}, CO\textsubscript{2}) and the surfaces of tungsten, aluminum and platinum, through the use of a sensitive torsion balance. Angular distributions are not determined and thus, direct comparison of their data with those reported in this paper cannot be carried out. In the only other systematic investigation of the scattering of polyatomic gases besides the studies reported here, Saltsburg et al.\textsuperscript{17} have reported the scattering of several molecules, H\textsubscript{2}, HD, D\textsubscript{2}, O\textsubscript{2}, CO and CO\textsubscript{2} from an epitaxially grown (111) silver single crystal. Their results for nitrogen show a slight backscatter but the surface was held at 560\textdegree K in their experiment, as compared to T = 475\textdegree K in our work where not backscatter was observed. A better comparison between their work and our work may be achieved by looking at the scattering of nitrogen and oxygen. Their data indicated that both curves have maxima at the same location and are similar in intensity and peak shape. From our figures (Figs. 3 and 4) we can see that the scattering of nitrogen and oxygen from the Pt(100) surface yields the same results. Additionally, CO\textsubscript{2} scattering in their system produces a lower intensity maximum than the scattering of either N\textsubscript{2} or O\textsubscript{2}, although all three gases have peak intensities at the same angle. Comparing our data with theirs shows that similar trends exist for the platinum surface.
There are no data in the literature for hydrocarbon scattering except for methane, which shows backscatter from a (111) silver surface at $T_S = 560^\circ K$. Smith and Merrill have studied the irreversible chemisorption of ethylene on a Pt(111) single crystal by combined LEED and helium beam techniques, but evidently did not attempt to scatter the gas. Thus, our results for acetylene and methylene-cyclobutane must stand alone. The likelihood of electronic or vibrational excitation of C$_2$H$_2$ by the clean platinum surface is small, although we already know from our work that this gas readily adsorbs and decomposes on platinum. Methylene-cyclobutane seems to be the largest projectile (13 atoms) used to date in gas-solid scattering experiments.

In their investigation of the scattering behavior of polyatomic gases on (111) silver, Saltsburg et al. found that the CO and CO$_2$ scattering distributions are quite similar. This is in agreement with our observations of CO and CO$_2$ scattering from the (100) platinum surface if we take into account the adsorption of CO on Pt surfaces and that CO does not adsorb on silver at 300$^\circ$K. The surface of silver was also employed in a study of the angular distribution of scattered ammonia. The pattern was found to be very broad and almost completely diffuse in nature, which is similar to the data shown in Fig. 12 for ammonia scattered from Pt(100).

Much attention has been directed toward the scattering of hydrogen and deuterium from metal surfaces, and data now exist for experiments conducted on Ni, Au, Ag, Pt, and W. For all of these solids, provided the surface is clean, the maximum intensity occurs at the specular positions, although the dispersion or half-width...
of the scattered beam varied somewhat. In order to explain the broad peak that was observed in many experiments between the surface normal and the specular angle in the angular distribution of \( \text{H}_2, \text{HD}, \) and \( \text{D}_2 \), Palmer et al.\(^3,10,24\) invoked energy transfer between the rotational energy states of the incident hydrogenic species and the vibrational modes of the surface atoms in the silver and nickel lattices. Their model for R-V energy transfer is further supported by the beam temperature dependence of the deuterium scattering distribution. There can be no doubt about the markedly different scattering distributions observed by Palmer et al. when hydrogen isotopes were impinged on the epitaxially grown thin film. Our studies of \( \text{H}_2 \) and \( \text{D}_2 \) scattering from the Pt(100) surface and those of Smith\(^28\) for \( \text{D}_2 \) from the Pt(111) surface show no peaks other than the specularly directed one, and we find no evidence for marked differences between the angular distributions of scattered \( \text{H}_2 \) and \( \text{D}_2 \) molecular beams. Smith and Merrill,\(^11\) however, have found a spatial distribution reminiscent of those observed by Palmer et al. when \( \text{D}_2 \) is scattered from an unetched Pt(111) crystal surface. This result indicates that perhaps surface roughness is important in effecting R-V energy transfer between incident diatomic molecules and the solid. It appears that the epitaxial silver and nickel surfaces used in the experiments by Palmer et al. could have been considerably rougher on an atomic scale than the well-characterized platinum single crystals used in our work and the work cited above. In addition, the surface temperature in our studies was higher (1175°K) than the surface temperature used in the scattering studies with silver (570°K). If microscopic
disorder enhances rotational coupling to the solid, even a surface
"disordered" through heating (due to the large mean square displacement
of surface atoms) could possibly cause significant internal excitation
of hydrogenic molecules. Unfortunately, systematic variation of the
surface temperature during the scattering of H\textsubscript{2} and D\textsubscript{2} beams have not
been carried out mostly because of the likely contamination of the
platinum surface at lower temperatures by the adsorption of carbon
monoxide from the ambient. Such study will be carried out in the near
future to uncover the causes of the discrepancy between the deuterium
beam scattering characteristics reported by the various investigators.

We have already pointed out that the hydrogen and deuterium data
presented here (Figs. 6 and 7) show rather broad peaks. At T\textsubscript{S} = 775\textdegree K
Smith\textsuperscript{28} reported a half-width of 29.5\textdegree for D\textsubscript{2} scattering from Pt(111)
and a maximum intensity of 1.5\%, down from 3.6\% at T\textsubscript{S} = 375\textdegree K. These
values may be compared to those we find at 1175\textdegree K for D\textsubscript{2} scattering
from the Pt(100): the maximum intensity 0.9\% and the half-width 50\textdegree.
One would expect a lower intensity and perhaps broader dispersion due
to the higher surface temperature. Feuer's analysis of the energy
exchange between rigid rotors of diatomic molecules and a solid surface
also helps to explain the observations as discussed earlier.

Although there is the possibility of V-T energy transfer for diatomic
molecules from the clean surface and our date indicates that there is
evidence for efficient V-V energy transfer between the incident diatomic
molecules and diatomic molecules adsorbed on the platinum surface, it
is difficult to obtain accurate information on the details of the energy
transfer without an energy analysis of the scattered beam. It appears that to obtain reliable V-V, V-T and T-R energy transfer information one must measure the kinetic energy of the scattered beam by time-of-flight techniques that would modulate the scattered beam and measure the time-of-flight after scattering. Experiments are in progress in our laboratory on a modified apparatus that allows us to measure the translational energy (velocity) of the scattered beam to obtain more detailed information about energy transfer between surface atom vibration and internal energy states of diatomic and polyatomic molecules.
VI. CONCLUSION

Unlike monatomic gases, diatomic molecules may exchange energy with the vibrational modes of surface atoms (i.e. surface phonons) through their vibrational and rotational energy states. From clean surfaces, we infer from the angular distributions that many diatomic and polyatomic molecules scatter without complete energy accommodation. This can be explained by the strong recoil effect due to matching of the translational energy of the incident molecule with the vibrational energy of the surface atoms. The energy accommodation of the incident diatomic molecule appears to be complete when scattered by an adsorbed layer of the same diatomic molecule. Armand's model that postulates, upon the adsorption of low molecular weight gases, the creation of high frequency vibrational modes that have the same magnitude as the vibrational frequencies of the incident diatomic molecules and much higher frequencies than the lattice phonons, can explain these findings. The complete energy accommodation in this case is due to V-V energy transfer that, apparently, is very efficient. V-R and R-T transitions are also possible and when they take place angular distribution of the scattered beam is broadened.

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8. On most crystal faces, diffraction features are, in general, not very sensitive to the presence of an adsorbed gas unless it forms an ordered surface structure. For these surfaces, Auger electron spectroscopy is a much more sensitive probe of surface cleanliness than LEED. In the case of platinum, however, the (5×1) surface structure is sensitive to the presence of ambient gases and gives one a probe of surface cleanliness.
20. R. E. Stickney, Phys. Fluids 5, 1617\(1962\).


FIGURE CAPTIONS

Fig. 1 Auger spectra of clean and carbon and carbon monoxide covered platinum surfaces.

Fig. 2 Carbon monoxide scattering distribution taken by flashing the Pt(100) sample between data points ($I_{\text{Beam}}$ = incident beam intensity).

Fig. 3 Angular distribution of a nitrogen beam scattered from a clean Pt(100) surface ($I_{\text{Beam}}$ = incident beam intensity).

Fig. 4 Angular distribution of an oxygen beam scattered from the clean Pt(100) surface.

Fig. 5 Nitric Oxide scattering distribution from a clean (100) platinum surface.

Fig. 6 Angular distribution of hydrogen beam scattered from a clean Pt(100) surface.

Fig. 7 Angular distribution of a deuterium beam scattering from a clean Pt(100) surface.

Fig. 8 Angular distribution of a CO$_2$ beam scattered from a clean Pt(100) surface.

Fig. 9 Angular distribution of a nitrous oxide beam scattered from a clean Pt(100) surface.

Fig. 10 Angular distribution of an acetylene beam scattered from a Pt(100) surface.

Fig. 11 Angular distribution of a beam of methylene cyclobutane scattered from a Pt(100) surface.

Fig. 12 Angular distribution of an ammonia beam scattered from a clean (100) crystal face of platinum.
Fig. 13 Angular distribution of a carbon monoxide beam scattered from a carbon monoxide covered Pt(100) surface.

Fig. 14 Angular distribution of an acetylene beam scattered from an acetylene covered (100) crystal face of platinum.

Fig. 15a Angular distribution of a beam of nitric oxide scattered from a carbon covered (100) face of platinum.

Fig. 15b Angular distribution of a beam of nitrous oxide scattered from a carbon covered (100) platinum surface.

Fig. 15c Angular distribution of a beam of nitrogen dioxide scattered from a carbon covered (100) platinum surface.

Fig. 15d Angular distribution of a beam of carbon monoxide scattered from a carbon covered (100) platinum surface.
Fig. 1

Platinum + Carbon and Carbon Monoxide

Clean Platinum
CO/Pt (100)
Surface: (5x1)
$T_S = 450^\circ K$
$T_B = 300^\circ K$
$\theta_i = 45^\circ$

Fig. 2

$\frac{I_{\theta_r}}{I_{\text{BEAM}}} \times 100$, scattered intensity

$\theta_r$, angle from surface normal

XBL 708-1971
Fig. 3

$\frac{I_{\theta_r}}{I_{\text{BEAM}}} \times 100$, scattered intensity vs. $\theta_r$, angle from surface normal

- $N_2/\text{Pt (100)}$
- Surface: $(5x1) + C(4x1)$
- $T_S = 475^\circ K$
- $T_B = 300^\circ K$
- $\theta_i = 45^\circ$
$O_2/Pt\ (100)$

$T_s = 475^\circ K$

$T_B = 300^\circ K$

$\theta_l = 45^\circ$

- Fig. 4 -
Fig. 5
$H_2/\text{Pt (100)-(5\times1)}$

$\theta_i = 45^\circ$

$T_B = 300^\circ \text{K}$

$T_S = 1175^\circ \text{K}$

Fig. 6

Scattered % of Incident Beam

$\theta_r$, Angle from Surface Normal (Degrees)
$D_2/Pt(100)-(5 \times 1)$

$\theta_i = 45^\circ$

$T_B = 300^\circ K$

$T_S = 1175^\circ K$

**Fig. 7**
CO$_2$/Pt (100)
Surface: (5x1)
$T_S = 475^\circ K$
$T_B = 300^\circ K$
$\theta_i = 45^\circ$

Fig. 8
N$_2$O/Pt (100)
Surface: (5x1)
$T_s = 1125^\circ$K
$T_B = 300^\circ$K
$\theta_i = 45^\circ$

Fig. 9
$C_2H_2$ / Pt (100)
Surface: (5x1) carbon ring

$T_S = 475^\circ K$
$T_B = 300^\circ K$
$\theta_i = 45^\circ$

Fig. 10
Fig. 11

\[ \text{\(\triangle / \text{Pt}(100)\)} \]

\[ \theta_i = 45^\circ \]

\[ T_B = 300^\circ K \]

\[ T_S = 1175^\circ K \]
NH₃/Pt(100) - (5×1)

θᵢ = 45°

T_B = 300°K

T_S = 900°K

□ P₀₂ = 5×10⁻⁸ torr

○ P_BG = 1×10⁻⁹ torr

Fig. 12
Fig. 13

CO/Pt (100) - CO

\( T_S = 300 \, ^\circ \text{K} \)

\( T_B = 300 \, ^\circ \text{K} \)

\( \theta_i \)

\( \frac{\theta_i}{45^\circ} \)

\( \frac{\theta_i}{50^\circ} \)

\( \frac{\theta_i}{55^\circ} \)

PERCENT OF INCIDENT BEAM

\( \theta_r, \text{ANGLE FROM SURFACE NORMAL} \)

STANDARD DEVIATION

XBL715-6731

Fig. 13
Fig. 14
NO/Pt(100) C-ring

θ_i = 45°

T_B = 300°K

T_S = 1200°K

Fig. 15a
N$_2$O/Pt (100)
Surface: Carbon Ring
$T_S = 1125 \degree K$
$T_B = 300 \degree K$
$\theta_l = 45\degree$

Fig. 15b
NO$_2$/Pt (100) - C-ring

$\theta_i = 45^\circ$

$T_B = 300^\circ K$

$T_S = 1200^\circ K$

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Fig. 15c
CO/Pt (100)
Surface: (5x1) + C(4x1)
$T_s = 925 \degree K$
$T_B = 300 \degree K$
$\theta_i = 45 \degree$

$\frac{I_{\theta_r}}{I_{\text{beam}}}$ x 100, scattered intensity

$\theta_r$, angle from surface normal

Fig. 15d
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