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PLATINUM SURFACES

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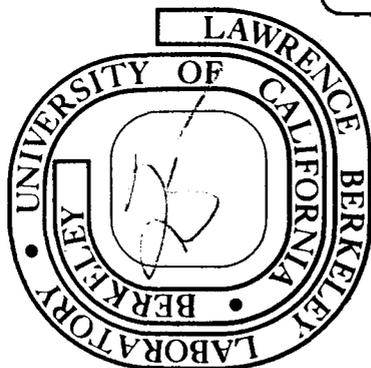
August, 1974

Prepared for the U. S. Atomic Energy Commission  
under Contract W-7405-ENG-48

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SMALL MOLECULE REACTIONS ON STEPPED SINGLE CRYSTAL PLATINUM SURFACES

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ABSTRACT

Ultra high vacuum molecular beam techniques coupled with LEED and Auger Electron Spectroscopy are particularly well suited to the study of surface chemical reactions because of the ability to assess the effect of the surface conditions on the reaction probability. Investigation of the hydrogen-deuterium exchange reaction on a series of low and high Miller Index platinum single crystals has indicated that the steps present on the high index surfaces are necessary for the dissociation and subsequent recombination of hydrogen. We have undertaken a systematic study of a series of small molecule reactions on these stepped surfaces to determine the reaction probability on stepped platinum surfaces. Reactions involving dissociation of  $H_2$ ,  $D_2$ ,  $O_2$ , OH, NH, and CH bonds proceed on the stepped surfaces with much higher reaction probabilities than reactions requiring dissociation of  $N_2$ , or CO bonds. All of the reactions studied resulted in cosine product angular distributions except for the formation of  $CO_2$ , which exhibited a distribution more peaked at the normal to the surface.

## 1. INTRODUCTION

Small molecule decomposition, oxidation, and hydrogenation reactions are important prototype surface reactions. By studying the reaction mechanisms of simple small molecule reactions, and the effect of surface conditions on their catalysis, we can propose models for the initial steps of more complex and technologically more interesting heterogeneous catalytic systems. In order to uncover the mechanisms of these simple surface reactions, a variety of techniques must be used. Of primary importance is the ability to characterize, on an atomic scale, the surface on which the reaction proceeds. This can be done through the use of bulk single crystal surfaces prepared and studied in ultra high vacuum and characterized by Low Energy Electron Diffraction (LEED) and Auger Electron Spectroscopy (AES). The adsorption, reaction, desorption process itself can be studied by the use of molecular beam scattering from these well characterized surfaces. The modulated molecular beam technique<sup>1</sup> is particularly useful in studying reactions at surfaces. Figure 1 shows a schematic diagram of an apparatus<sup>2,3</sup> constructed to use these techniques for the study of surface chemical reactions and energy transfer in gas-solid interactions.

We have investigated several simple reactions of molecules on platinum stepped surfaces, in order to gain information about the reaction probabilities on these surfaces. In each case, 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 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 formed are listed in Table 1.

	<u>Reactants</u>		<u>Product</u>	<u>Reaction Probability</u>
	<u>Beam</u>	<u>Background</u>		
1)	H <sub>2</sub>	D <sub>2</sub>	HD	5.5×10 <sup>-3</sup>
2)	D <sub>2</sub>	H <sub>2</sub>	HD	5.5×10 <sup>-3</sup>
3)	D <sub>2</sub>	O <sub>2</sub>	D <sub>2</sub> O	2.1×10 <sup>-4</sup>
4)	O <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub> O	2.2×10 <sup>-5</sup>
5)	N <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub> O	6 ×10 <sup>-5</sup>
6)	N <sub>2</sub>	O <sub>2</sub>	NO	5 ×10 <sup>-5</sup>
7)	N <sub>2</sub>	O <sub>2</sub>	NO <sub>2</sub>	<1 ×10 <sup>-8</sup>
8)	CO	O <sub>2</sub>	CO <sub>2</sub>	4.7×10 <sup>-5</sup>
9)	O <sub>2</sub>	CO	CO <sub>2</sub>	<1 ×10 <sup>-8</sup>
10)	N <sub>2</sub>	H <sub>2</sub>	NH <sub>3</sub>	1 ×10 <sup>-6</sup>
11)	HCOOH	--	CO <sub>2</sub>	8.2×10 <sup>-5</sup>
12)	CH <sub>3</sub> -NH <sub>2</sub>	--	NH <sub>3</sub>	2.0×10 <sup>-4</sup>

Table 1. Reactants, products and reaction probabilities for several small molecule reactions on the Pt-(S)[5(111)×(111)] surface. Surface temperature<sub>7</sub> = 1000°K; beam temperature = 300°K; P<sub>background</sub> = 4×10<sup>-7</sup> torr; P<sub>beam</sub> = 5×10<sup>-8</sup> torr; modulation frequency = 40 Hz (detection discriminates against residence times > 25 msec.)

If the dissociation of the diatomic molecules on the surface from the background gas gives rise to the build-up of a sufficiently large atom surface concentration then the incident molecules may undergo atom-molecule reactions and the magnitude of the product signal can be used to determine the reaction probability. It should be noted that without the surface atomization of the molecule from the background gas none of the products would be detectable due to the very large activation energies of the largely endothermic molecule-molecule reactions. Thus the appearance of the product yields the reaction probability of the atom-molecule surface reaction which indirectly yields the probability of dissociation of the diatomic molecule on the stepped platinum surface.

## 2. $H_2$ - $D_2$ EXCHANGE

The dissociation of hydrogen can be studied by following the isotope exchange reaction between hydrogen and deuterium on the platinum surface. LEED studies<sup>4</sup> had indicated that hydrogen chemisorption was much more likely on stepped platinum surfaces than on high density low Miller Index (111) surface. In order to test this observation the reaction of deuterium on a platinum surface in a hydrogen ambient to form HD was used to compare the reactivities of low index and stepped surfaces. The stepped surfaces used in this study are the Pt-(S)[9(111)×(111)] and Pt-(S)[5(111)×(111)] and are characterized by terraces of (111) orientation 9 and 5 atoms wide respectively, separated by monatomic height steps also of (111) orientation. A LEED pattern and schematic diagram of the Pt(S)-[9(111)×(111)] surface is shown in Fig. 2.

The results of these comparisons, which are discussed more fully elsewhere,<sup>5,6</sup> indicated a very strong dependence on the presence of steps for the reaction to form HD to proceed. The reaction probability, defined here as the fraction of incident reactant molecules leaving the surface as product at the specular angle, was about three orders of magnitude less for the (111) surface than for the [9(111)×(111)] or [5(111)×(111)] stepped surfaces under identical conditions of surface composition, temperature and pressure. Also noted was the fact that doubling the step density doubled the reaction probability at higher temperatures (> 600°K) in comparisons between the [5(111)×(111)] and [9(111)×(111)] surfaces. This is seen in the surface temperature dependence plot of Fig. 3.

Angular distribution measurements of the product and scattered reactants from these surfaces gives a clue to the working of the steps in promoting the dissociation of hydrogen on a platinum surface. Figure 4 shows the angular distributions of  $H_2$ ,  $D_2$  and HD from the (111) and the two stepped surfaces. The angle of incidence, indicated by the arrow is at the same angle that corresponds to the maximum intensity in the scattered beam (the angles are defined with respect to the surface normal) signifying the specular nature of these patterns. It can be seen that the width of the scattering pattern increases and the specular intensity decreases as the step density is increased from (111) to  $[9(111)\times(111)]$  to  $[5(111)\times(111)]$ . This change is indicative of more complete energy transfer between the incident gas and the surface as the step density is increased. The angular distribution of the desorbed HD reaction product is cosine (peaked at the surface normal) indicating complete thermal accommodation with the surface prior to desorption.

Investigation of the reaction probability and phase shift (related to surface residence time) as a function of surface temperature, incident beam temperature, beam modulation frequency, and incident beam pressure have all indicated a two branch atom-molecule reaction for the formation of HD, with one branch dominant in the temperature range below  $600^\circ K$  and both branches operating in the range of temperature from  $600^\circ$  to  $1300^\circ K$ . These branches can be identified with reactant molecules fed to the dissociating step site via the terrace at low temperatures and directly from the gas phase at higher temperatures. A schematic diagram of this model is shown in Fig. 5.

### 3. OTHER SMALL MOLECULE REACTIONS

The behavior of the steps in promoting the dissociation of  $H_2$  on the platinum surface led to the study of the reaction probability of other small molecule reactions on these stepped surfaces. Could these steps promote the dissociation of any diatomic molecule or small molecule bond, or is there a limit to the dissociating strength of these steps? In order to answer this question a variety of small molecule reactions were studied as indicated in Table 1. By monitoring the reaction probability for the formation of various products in these reactions under identical conditions of incident pressure and surface temperature, the dissociating power of the stepped surfaces for diatomic molecules with varying bond strengths can be determined. The bond strengths tested ranged from the N-H bond for monomethylamine at 4.3 eV to the  $C \equiv O$  bond of carbon monoxide at 11.1 eV.<sup>7</sup> The reaction probabilities for these reactions are listed in Table 1 for the highest step density crystal, the Pt(S)-[5(111)×(111)] at 1000°K. Reaction probabilities for the (997) are roughly half those shown at the same reaction temperature. Reaction probabilities on the (111) surface were about three orders of magnitude lower for the formation of HD by the  $H_2$ - $D_2$  exchange and for water formation by the reactions of  $O_2$  and  $D_2$ , the only direct comparisons made. As noted before, this reaction probability is the product signal at the specular angle (angle of reflection = angle of incidence) divided by the incident reactant beam signal. A total reaction probability defined as total product signal over incident reactant signal can be obtained by integrating over the entire product scattering distribution (assuming a symmetrical in plane

and out of plane distribution) and dividing by the incident beam signal. In the case of products showing a cosine angular distribution (all but  $\text{CO}_2$ ) this amounts to a simple multiplication of the listed reaction probabilities by 4.44. For  $\text{CO}_2$ , which exhibits a  $\cos^2\theta$  distribution, the factor is 2.96.

Several general observations can be made upon inspection of Table 1. The high reaction probabilities of reactions involving  $\text{H}_2$ ,  $\text{D}_2$  and  $\text{O}_2$  in the background indicate that these diatomic molecules readily dissociate on the stepped platinum surface. In the case of reactions with nitrogen molecular beams the formation of  $\text{N}_2\text{O}$  requires the rearrangement but not the rupture of the  $\text{N}\equiv\text{N}$  bond. The equal reaction probability for formation of  $\text{N}_2\text{O}$  and  $\text{NO}$  could indicate that the same intermediate or similar mechanism is operative in their surface reactions. 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 of dissociating the strong  $\text{N}\equiv\text{N}$  bond. The very low  $\text{NO}_2$  and  $\text{NH}_3$  yields seem to indicate that breaking the  $\text{N}\equiv\text{N}$  bond during the surface reaction is an unlikely process.

While the formation of  $\text{CO}_2$  is readily detectable with oxygen in the background (i.e. between atomic oxygen on the surface and  $\text{CO}$  in the molecular beam)  $\text{CO}_2$  will not form when  $\text{CO}$  is in the background and  $\text{O}_2$  is in the molecular beam. This may be explained either by the low sticking probability of  $\text{CO}$  at the reaction temperature of  $1000^\circ\text{K}$  or by the blocking of the reaction sites by carbon, the product of  $\text{CO}$  dissociation. Further studies are necessary to uncover the mechanism of this surface reaction in more detail.

Bonzel and Ku<sup>11</sup> and Palmer and Smith<sup>10</sup> have observed a similar behavior in their studies of CO oxidation on Pt. They ascribe this to a poisoning of the surface by preadsorbed CO. Palmer and Smith observed a sharply peaked distribution of product CO<sub>2</sub>. The peaking was much more pronounced, however, and the angular distribution was well fit by a  $\cos^6 \theta$  dependence.

The decomposition of formic acid and methylamine are readily detectable via the formation of CO<sub>2</sub> and NH<sub>3</sub>, respectively. It is difficult to deduce the bond breaking process that occurs during the surface reaction since the reactant molecules are quite complex. Nevertheless it appears likely that the stepped platinum surface catalyzes the dissociation of the  $\rightarrow\text{C} - \text{H} - \text{O} - \text{H}$  and  $\rightarrow\text{C} - \text{N}$  bonds in these molecules.

Angular distributions of the products of these reactions was cosine in every case except the formation of CO<sub>2</sub>, both by oxidation of CO and by decomposition of formic acid. Figure 6 shows the angular distribution of CO<sub>2</sub> formed by decomposition of formic acid. The curves shown indicate 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<sup>8,9</sup> 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<sub>2</sub> 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.

### CONCLUSION

Studies of several small molecule reactions on stepped platinum surfaces yielded reaction probabilities for several reactions on these surfaces. High reaction probabilities for several of the reactions, involving  $H_2$ ,  $D_2$ ,  $O_2$ , formic acid and methylamine indicate that the stepped surfaces facilitate dissociation of H-H, D-D, O-O, C-H, O-H and C-N bonds. Low reaction probabilities in the cases of the  $N_2$  and CO reactions give evidence that bonds weaker than about 5.5 eV are much more readily broken by the stepped surfaces. The angular distributions of  $CO_2$  formed by CO oxidation or formic acid decomposition indicate the possibility of translationally excited products in these 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, we believe that the work completed thus far offers indication of the reaction probabilities on the stepped platinum surface. Hopefully, information of this type will be useful in unraveling the complexities of heterogeneous catalysis of small molecule reaction.

### ACKNOWLEDGEMENTS

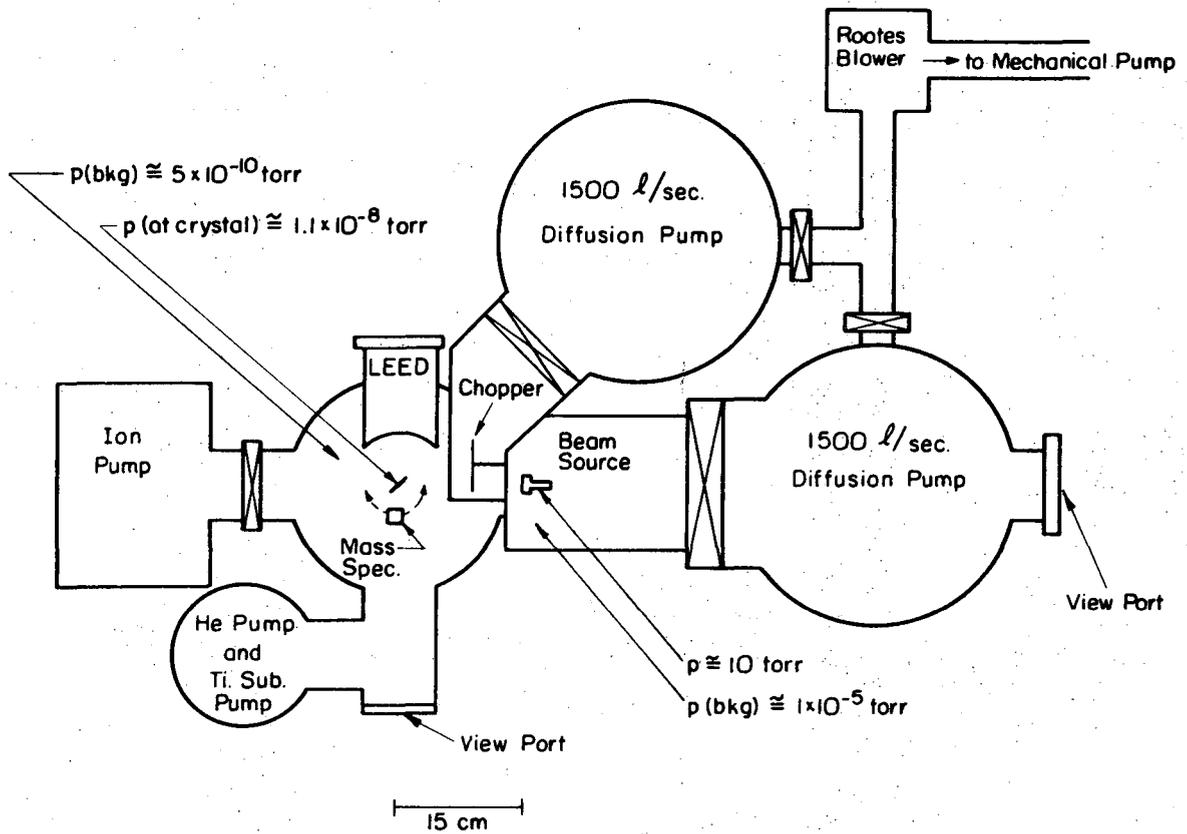
This was done under the auspices of the U. S. Atomic Energy Commission and partially supported by National Science Foundation.

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FIGURE CAPTIONS

- Fig. 1. Schematic diagram of molecular beam apparatus used for surface reaction studies.
- Fig. 2. Low Energy Electron Diffraction Pattern and real space schematic of Pt-(S)[9(111)×(111)] surface.
- Fig. 3. Surface temperature dependence for H<sub>2</sub>-D<sub>2</sub> exchange on Pt-S[5(111)×(111)] and Pt-S[9(111)×(111)] surfaces.
- Fig. 4. Angular distribution of H<sub>2</sub>, D<sub>2</sub> and HD from Pt(111), Pt-S[9(111)×(111)] and Pt-(S)[5(111)×(111)].
- Fig. 5. Model for H<sub>2</sub>-D<sub>2</sub> exchange on stepped platinum surfaces.
- Fig. 6. Angular distribution of CO<sub>2</sub> formed by decomposition of formic acid.



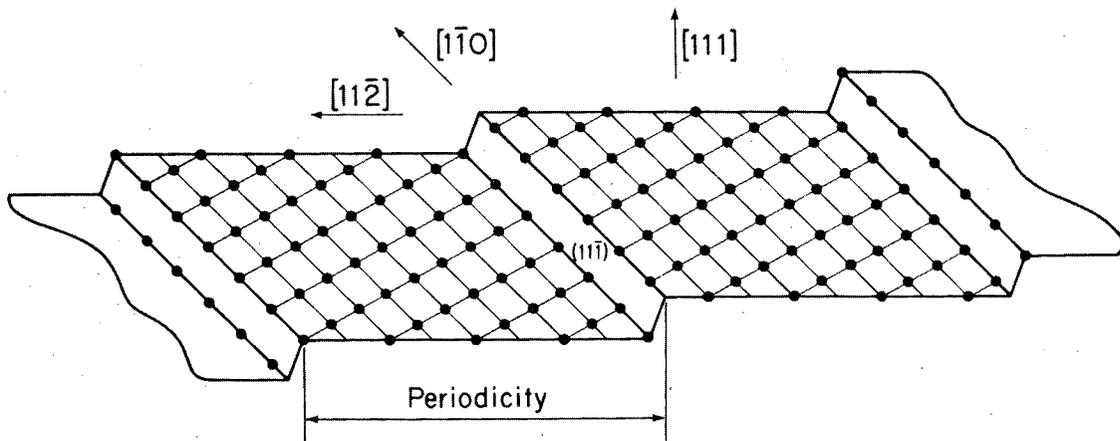
MOLECULAR BEAM SURFACE SCATTERING APPARATUS

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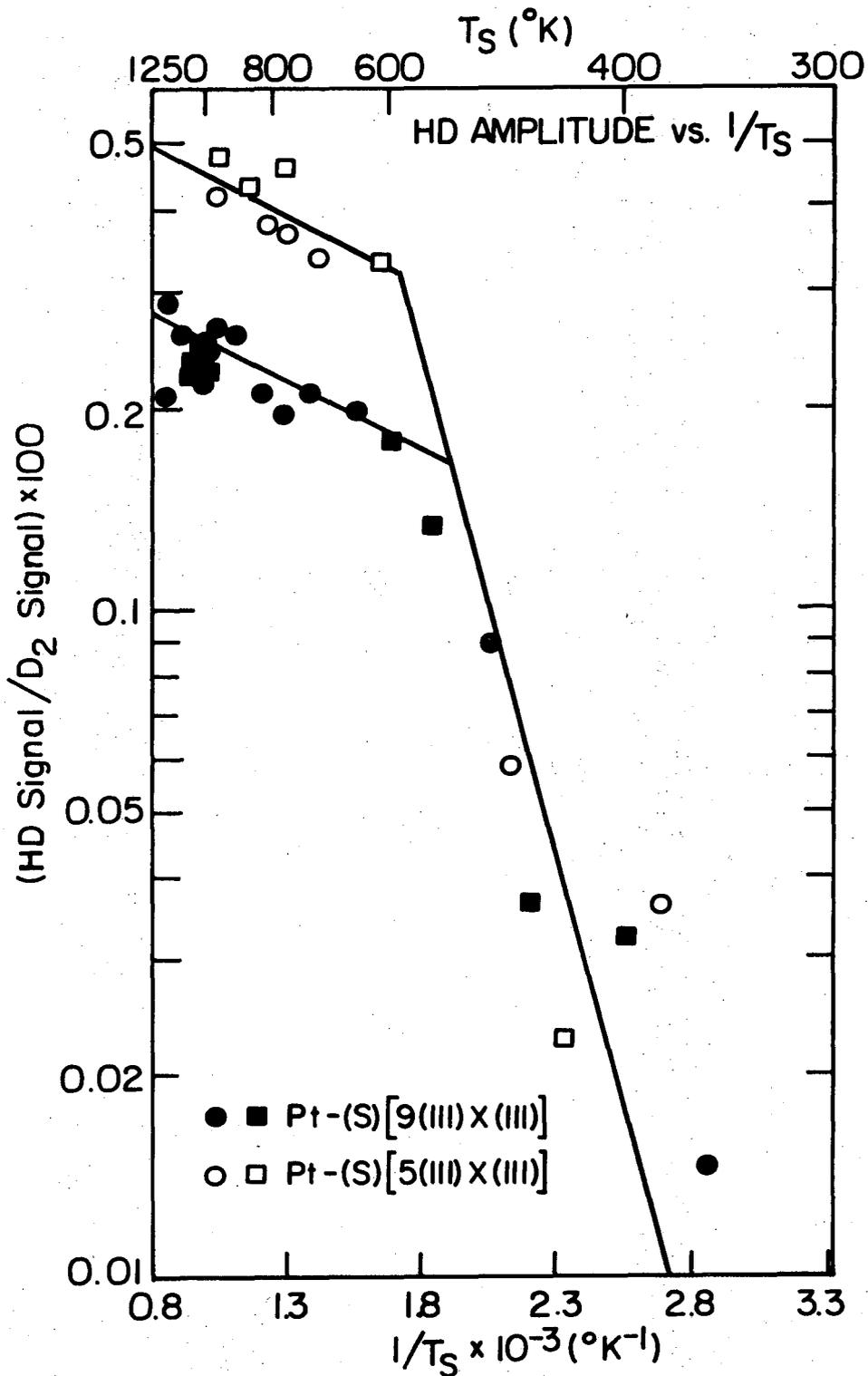
Fig. 1.



Pt-(s)[9(111)X(111)] 86 V

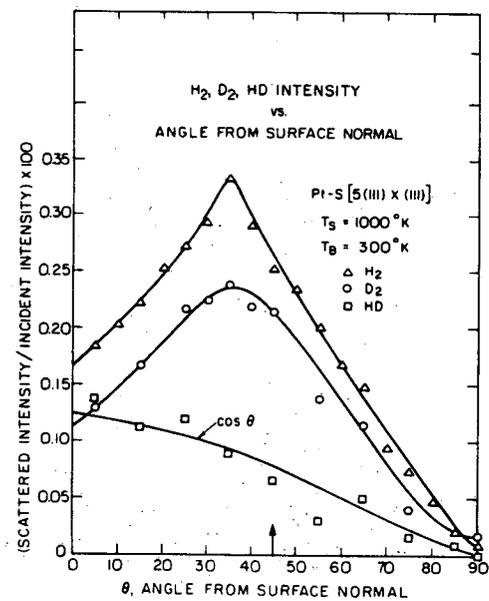
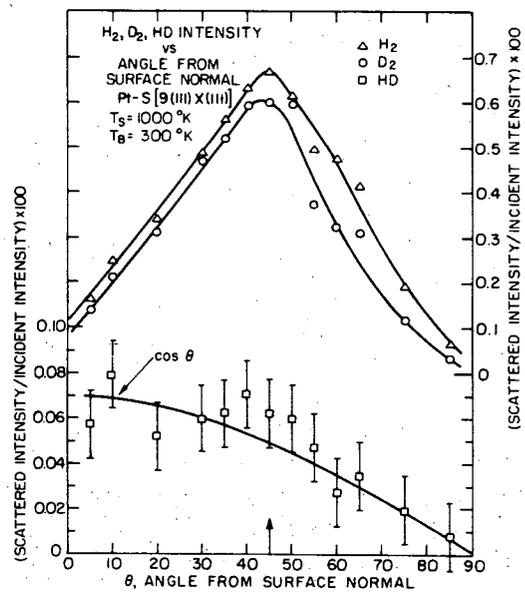
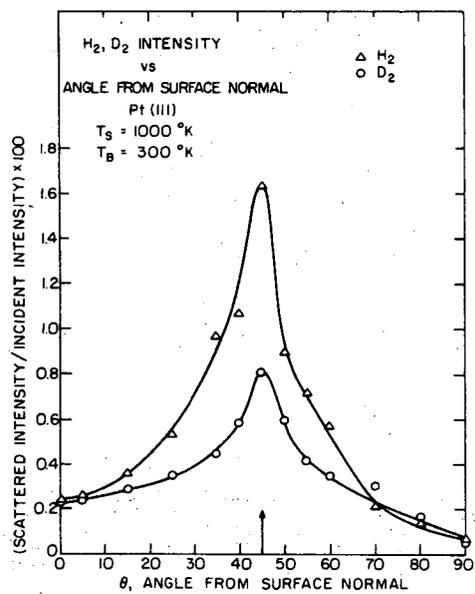


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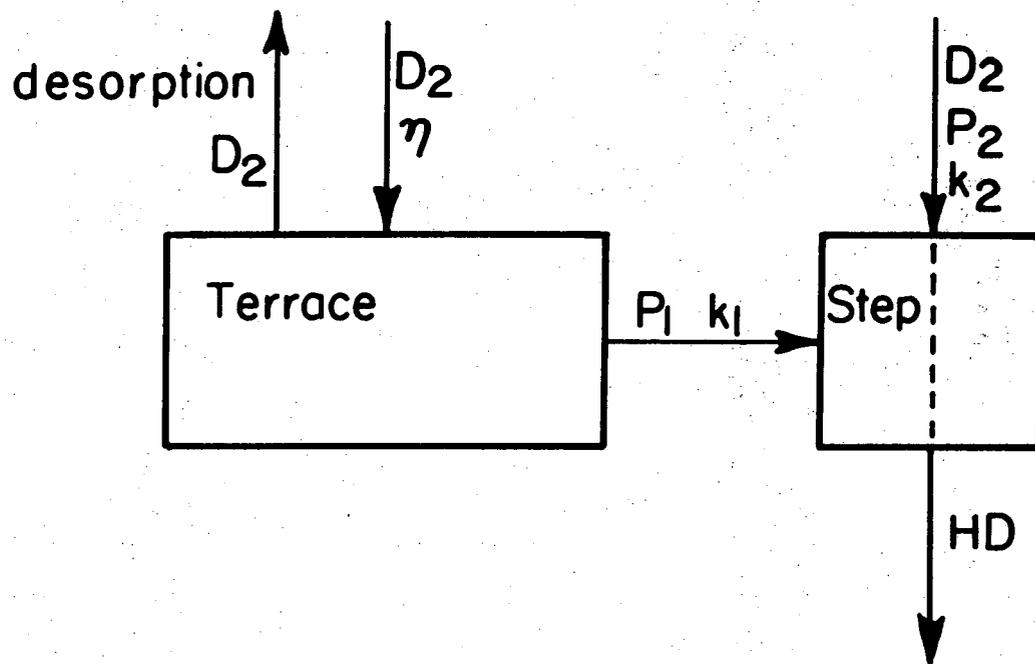
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Fig. 3.



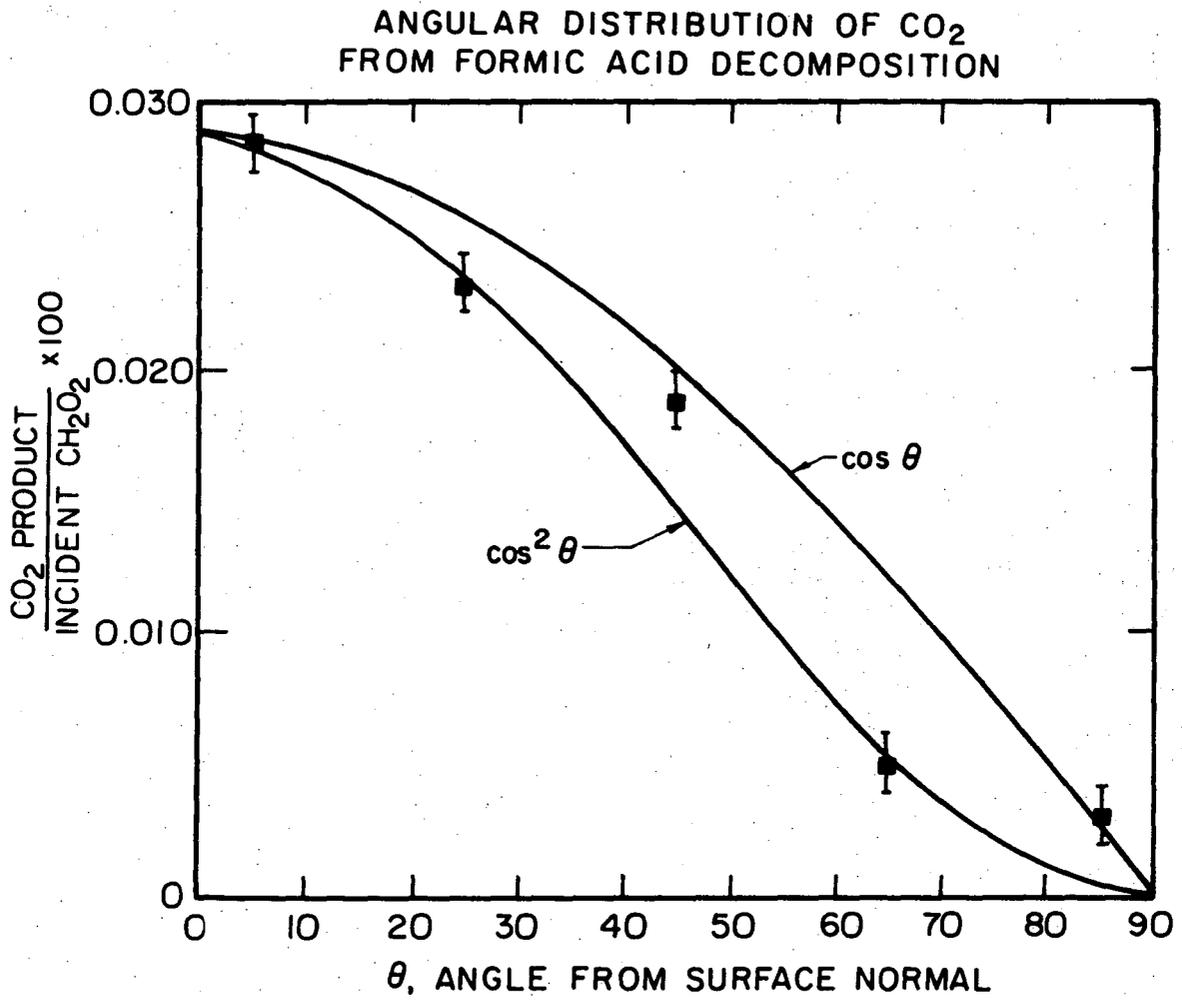
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Fig. 4.



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Fig. 5.



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Fig. 6.

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