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November 1983

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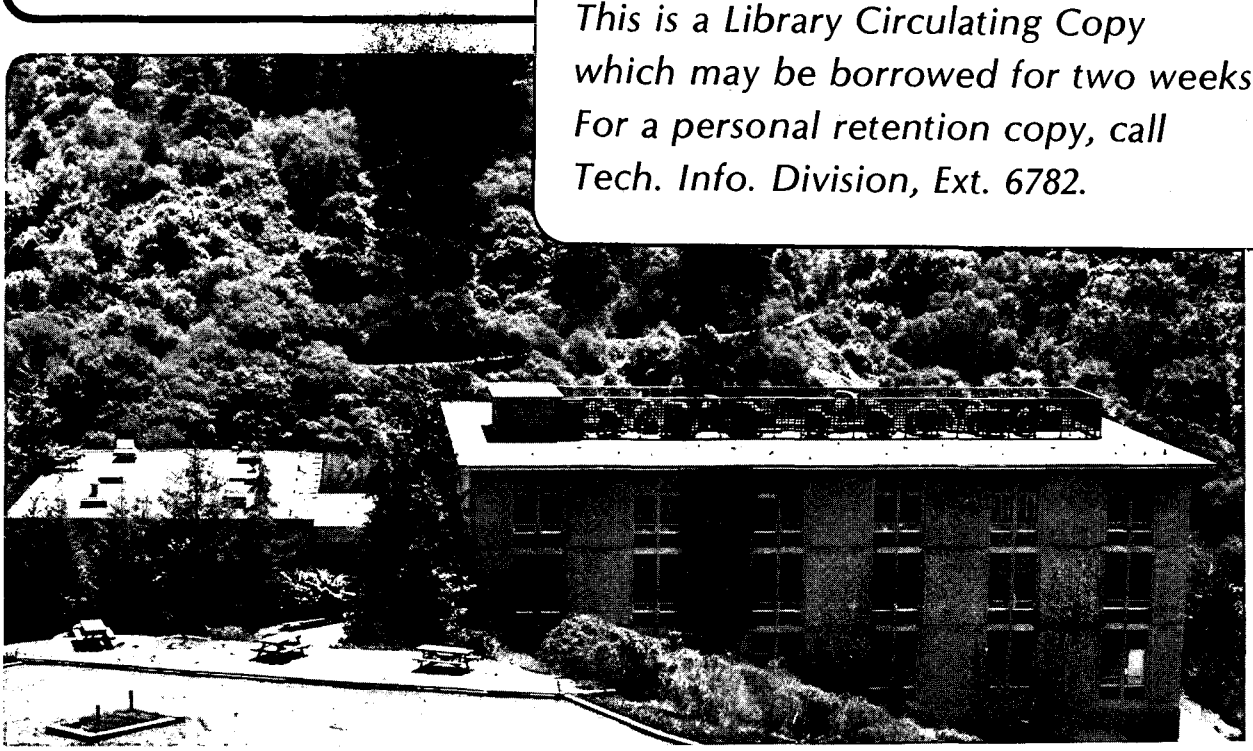

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Angular and Velocity Distributions of HD molecules produced by the H_2-D_2 Exchange Reaction on the Stepped Pt(557) Crystal Surface

by

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ABSTRACT

The H_2-D_2 exchange reaction on Pt(557) crystal surface was investigated using a molecular beam-surface scattering technique. The angular and velocity distributions of the HD product were measured at various crystal temperatures (500-1170K). It was found that the exchange reaction occurred via interactions of adsorbed H and D atoms (Langmuir-Hinshelwood mechanism). Although the HD that is produced desorbs with a $\cos^2\theta$ angular distribution, its translational energy corresponds to a temperature slightly colder than that of the substrate with the mean energy of the desorbing molecules depending on the desorption angle. As the desorbing angle increases away from the surface normal the mean translational energy decreases. The exchange reactivity was found to be incident azimuthal angle dependent while the translational energy of the product HD is independent of the azimuthal angle of detection. Models explaining the results are discussed.

INTRODUCTION

The study of the interaction of a molecular beam with a surface is a useful tool for exploring the dynamics of the gas-surface interactions. One way of investigating the interaction is by measuring the angular distribution and velocity distribution of a reaction product as a function of the desorption angle and substrate temperature. There are many experiments that show that the angular distribution of the desorbing species need not necessarily follow a cosine distribution. Also, the velocity distribution need not be Maxwellian at the substrate temperature and is often strongly desorption angle dependent (1-14). Because of these deviations from the simple laws, the results of angular and velocity distribution measurements are very useful for extracting detailed adsorption and desorption mechanisms.

Over the last few years, Comsa and his group have been studying the interaction of hydrogen (deuterium) on Ni(111), Pd(100), Cu(100), and Cu(111) surfaces by measuring the angular and velocity distributions and the angular dependence of the velocity distribution of the desorbing molecules (9-13). The general features of their results are that (1) the angular distribution is peaked at the normal (2) the velocity distribution at the normal is "hotter" than the corresponding Maxwellian distribution at the substrate temperature (3) except for the case of Cu, the mean kinetic energy decreases as one moves the detector away from the surface normal and becomes "colder" than the substrate temperature at the grazing angle of detection. Although

their explanation of these results is not completely satisfactory as will be discussed in more detail in the discussion section, these results do provide a great deal of information about the associative desorption mechanisms that could operate when HD forms on metal surfaces. Since the deuterium atoms are supplied to the surface by permeation through the bulk from the backside of the crystal, there is some uncertainty of the initial state, chemisorption or subsurface state, of the atoms that participate in the associative desorption.

In this paper, the results of experiments in which HD is desorbed from the stepped platinum single crystal surface are presented. The HD molecules are produced via the H_2-D_2 exchange reaction and the reactants are supplied to the surface by two separate incident molecular beams. The angular distribution of the desorbing HD and its velocity distribution as a function of desorption angle and substrate temperature are measured. We have found that although the angular distribution is slightly peaked at the normal, the velocity distribution of the desorbing HD is slightly colder than the substrate temperature and the deviation increases as the detection angle increases away from the surface normal. Various models explaining the results will be discussed.

Salmeron et al. have found that the H_2-D_2 exchange probability on a stepped platinum surface, Pt(s)[6(111)x(111)], is a strong function of the incident azimuthal angle (15). The reaction probability is highest when the reactants strike the open side of the step structure, decreasing by approximately a factor of two when the inner corner of the step is shadowed. The result was explained by the

geometrical variation of the number of reactant molecules that strike the open side of the step structure and cannot be attributed to an activation energy barrier for adsorption. The incident azimuthal angle dependence of the reaction probability is also observed on Pt(s)[6(111)x(100)] in our studies presented here which has (100) step structure rather than (111). Results of our time-of-flight support the explanation suggested by Salmeron et al. (15).

EXPERIMENTAL

A schematic diagram of the molecular beam-surface scattering apparatus is shown in Fig. 1. It has been modified from an existing apparatus (16) and a detailed description of the modification is described elsewhere (17). Only a brief review of its essential features is included here. The two incident beams, in this case H_2 and D_2, intersect at an angle of 30° on the crystal surface. Unless otherwise stated, the beam sources are two 0.003" diameter nozzles at a stagnation pressure of 100 Torr. A fixed frequency (150 Hz) tuning fork chopper is used to modulate the primary beam for the angular distribution and surface residence time measurements. The scattering chamber, which is pumped by a liquid nitrogen trapped diffusion pump and a titanium sublimator, is equipped with instruments for Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and ion sputtering of the crystal surface. The sample is heated by electron bombardment and a chromel-alumel thermocouple is used to monitor its temperature, T_s. Both the polar and azimuthal angle of the incident beam can be varied by rotating the crystal.

The two-stage differentially pumped detector is mounted on a 24" diameter rotatable flange. The rotatable flange is a modified configuration of a design using a spring-loaded teflon seal described by Auerbach et al. (18). The buffer of the detector is pumped by a 60 l/s ion pump and the mass spectrometer chamber is pumped with a 60 l/s ion pump and a LN_2 cooled titanium sublimator. The background pressure is about 5×10^{-10} Torr. The mass spectrometer (Extra-nuclear) contains a modified ionizer. A pseudorandom chopper is used for the time-of-flight measurement. The chopper motor is mounted on the detector, so that, the angular distribution of the product as well as the velocity distribution at each angle can be measured. Since the scattered beam is chopped instead of the incident beam, the TOF distributions are not affected by the unknown surface residence time. The flight path from the chopper to the mass spectrometer ionizer has been made as long as possible and is about 14.4 cm.

The stainless steel chopper blade with two identical sequences, each consisting 255 elements is made by photoetching rather than machining. The time resolution is 13 μsec per channel for this experiment. The initial channel of the time-of-flight distribution is determined by measuring a TOF distribution using a helium-neon laser as the incident beam and a photo-multiplier as the detector.

The single crystal Pt(557) surface (Pt(s)[6(111)x(100)]) is cleaned by argon ion sputtering and annealing. The cleanliness is determined by AES. The orientation of the crystal is confirmed by helium diffraction (19). For most of the experiments, the primary beam is

incident at an angle of 70° from normal, oriented along the stepped edge and the secondary beam is incident at an azimuthal angle of 30 degrees from the open side of the step. The angular distributions and TOF distributions of the product HD were measured at several substrate temperatures and detector angles. The data accumulation time for the TOF distribution varied from 1 hour to 6 hours depending on angle of detection and the substrate temperature.

RESULTS

In Fig. 2 we present the angular distribution of HD produced by the H_2-D_2 exchange reaction on Pt(557) at a substrate temperature of 690K. The angle of incidence of the primary beam is 60 degrees from the surface normal. The dashed line is the cosine function and the solid line is the square of the cosine function. One can see that the number density distribution of the HD is proportional to the square of the cosine of the desorption angle. As will be shown below, the average energy of the desorbing HD decreases as the desorption angle increases. Therefore, if the relative molecular flux is plotted as a function of the desorption angle, the angular distribution will be even sharper than a $\cos^2\theta$ distribution.

A typical time-of-flight distribution is shown in Fig. 3. The open circles represent the experimental data and the solid line a corresponding Maxwellian distribution at the substrate temperature (690K). It is evident from the figure that the desorbing HD is slightly colder than the substrate. The average kinetic energy of the

HD flux divided by 2k (Boltzmann constant) has been calculated in the same way as in reference (20) and is about 480K for this distribution. The results for other substrate temperatures are shown in Fig. 4. The open circles represent the average kinetic energy divided by 2k at various crystal temperature. The angle of incidence of the primary beam is 70 degrees with respect to the surface normal. If the desorbing HD is equilibrated with the surface, the circles representing the experimental results should lie along the dashed line. However, the average kinetic energies divided by 2k are always lower than the substrate temperature when the temperature is varied between 500 and 1170K, and the average kinetic energy is proportional to T_s over the temperature range. All the TOF distributions are slightly wider than the corresponding Maxwellian distributions at their average temperatures.

The dependence of the mean HD kinetic energy on polar angle is presented in Figs. 5 and 6. Figure 5 shows examples of two TOF distributions. In both cases, the substrate temperature is 690K and the angle of incidence is 60 degrees. The closed circles represents the TOF distribution for normal detection, and the open circles the TOF distribution for detector at 60 degrees from the surface normal. The peak of the $\theta_D = 0^\circ$ (closed circles) distribution occurs at a shorter flight time than that of the $\theta_D = 60^\circ$ (open circles) distribution. This implies that HD molecules desorbing normal to the surface have a higher average kinetic energy than those desorbing at 60° to the normal. The average kinetic energy divided by 2k as a function of the

HD desorbing angle is shown in Fig. 6, and, as can be seen, as the desorption angle increases, the average kinetic energy decreases.

As mentioned above, the reactivity of the H_2-D_2 exchange reaction has been found to be a strong function of the incident beam azimuthal angle for the stepped surface, Pt(s) [6(111)x(111)] (15). The maximum reactivity is observed when the incoming molecules are incident onto the open side of the step. A similar result is found with Pt(s)[6(111)x(100)] as can be seen in Fig. 7, where HD intensity is plotted as a function of azimuthal angle (the zero of azimuthal angle is also shown in Fig. 7).

In order to see if the average kinetic energy of the desorbing HD depends on the azimuthal desorption angle, the following experiment was carried out. With 45° polar angle and zero degree azimuthal angle of detection, a TOF distribution was taken for 70° incident angle at a surface temperature of 690K. Without changing any experimental conditions except rotating the azimuthal angle of the crystal such that the detector is at 45 degrees polar angle and 90 degrees azimuthal angle, another TOF distribution is obtained. Within the experimental error, no difference is observed between these two distributions.

The rate of the HD production is found to be independent of substrate temperature above 650K and to decrease rapidly below 650K. We also observed that the average kinetic energy of the desorbing HD does not depend on incident beam energy. This was determined by varying the incident beam energy by replacing the supersonic sources with effusive sources operating at a stagnation pressure of 2 Torr behind 1 mm diameter nozzles.

DISCUSSION

The following experimental findings indicate that the H_2-D_2 exchange reaction occurs via a Langmuir-Hinshelwood (LH) rather than an Eley-Rideal (ER) mechanism. In other words, the HD molecules are formed via reaction between adsorbed species. If the ER mechanism was to operate, one would expect that the angular distribution of the product should peak towards the specular angle, and that the kinetic energy of the products should depend on the incident beam energy but only very weakly on the substrate temperature. Since the angular distribution is $\cos^2\theta$, the kinetic energy of the products does not depend on the incident beam energy but is proportional to the substrate temperature, it is concluded that the reaction proceeds via a LH mechanism. This mechanism is also believed to hold for the H_2-D_2 exchange reaction on other platinum and transition metal surfaces (21-23).

So far, we have concluded that the reaction occurs between adsorbed species. Now we shall argue that the reaction between adsorbed hydrogen atoms is much more likely than the reaction between molecules. It has been found by bound level resonances of HD scattered from the Pt(111) surface that the heat of adsorption of a HD molecule is about 1 kcal/mole (24). Assuming that heats of adsorption of H_2, HD, and D_2 on the platinum surface are reasonably similar, it can be concluded that the heats of adsorption of H_2, HD and D_2 will be no more than 5 kcal/mole greater even at the step site. The heat of adsorption of hydrogen atoms is much greater than that of the hydrogen

molecules. Although the reported heat of dissociative adsorption varies somewhat depending on measurement techniques, it is about 20 kcal/mole. Poelsema et al. have found that heat of dissociative adsorption is 22 kcal/mole at the step site and 19 kcal/mole on the terrace (25). Since the surface temperature at which the H_2-D_2 exchange reaction was carried out is relatively high, only the dissociative adsorption states of H_2 and D_2 are significantly populated. Thus, it is believed that the HD molecules are formed by the recombination of the adsorbed H and D atoms. This was also concluded by other authors (23,25-30). The recombination is most likely to take place at the step edges since the residence time of H and D atoms is likely to be greater at these sites.

The next step is to explain the $\cos^2\theta$ angular distribution and the angular and substrate temperature dependence of the mean kinetic energy of the desorbing HD molecules within this reaction model framework. We propose the following model which involves no activation energy barrier for dissociative adsorption of $H_2(D_2)$ on the Pt(557) surface. We shall argue that as the surface hydrogen (deuterium) atoms recombine, they are repelled from the surface without completely equilibrating with the surface. This repulsive force is the strongest at the direction normal to the platinum surface. The desorbing HD molecules could be colder or hotter than the crystal temperature depending on their potential energy at the time of recombination.

Consider the one dimensional potential energy diagrams for the interaction between the hydrogen (deuterium) and transition metals

shown in Figs. 8(a) and 8(b). Depending on the position where the atomic and molecular potential energy curves cross, there is an activation barrier (Fig. 8a) or there is no activation barrier to dissociative adsorption (Fig. 8b). For the case involving an activation barrier, the incident $H_2(D_2)$ molecule needs to have high enough kinetic energy in order to reach the region where both atomic and molecular states coexist and be dissociatively adsorbed. Thus, increasing the incident beam energy will increase the sticking coefficient as has been experimentally shown in the case of H_2 on Cu (8).

For the case of H_2 on the stepped platinum surface, the potential energy diagram that is applicable is the one shown in Fig. 8(b). There are systems for which there is no activation energy barrier for adsorption even though the angular distributions of the associative desorption are peaked at the surface normal (23,31). The fact that the desorbing HD is slightly colder than the substrate leads us to believe that this is plausible. The reasons for this conclusion will be clear after the discussion of the model. The shaded area in Fig. 8(b) is where both atomic and molecular states can coexist, so that this is where recombination is expected to occur. We like to point out that although all the incident molecules can reach the shaded area, the sticking coefficient is not necessarily equal to unity because there is only a certain probability for those molecules in the shaded area to dissociate and be trapped in the atomic potential well. Experimental evidence can be seen from studies of the O_2/Pt(111) (31) and H_2/Pt(332) (23), where these two systems have no activation

barrier for dissociative adsorption while the sticking coefficients are less than one.

Now, let us consider the associative desorption process. Since the recombination can occur only in the shaded area, and if H and D recombine in the region of low potential energy, the HD produced will immediately feel a repulsive force from the molecular potential. This repulsive force is most likely to be normal to the surface and if it is strongly repulsive, the HD will have insufficient time to equilibrate and will desorb with an angular distribution peaked at the normal, and its mean kinetic energy will be higher at the normal than at the grazing angle. At the normal direction, the average kinetic energy divided by 2k could be higher or lower than the substrate temperature depending on the potential energy at which recombination occurs. Of course, if there is an activation barrier for the dissociative adsorption (Fig. 8a), the recombination can occur only in the high potential energy region, so that the product will desorb at "higher" temperature than that of the substrate. The substrate temperature dependence of the mean kinetic energy is not difficult to explain with this model. As the substrate temperature increases, the atomic H and D are excited up in the atomic potential well and recombine at higher potential energy level, so that it is reasonable that the mean kinetic energy of the desorbing HD be proportional to the substrate temperature.

This model seems to explain satisfactorily the peaked angular distribution and the angular dependence of the mean kinetic energy of

the desorbing product. The model utilizes the fact that H(D)-Pt bond length is shorter than the distance between the trapped molecular hydrogen and the surface, thus, H and D will recombine near the repulsive molecular potential and feel the normal repulsive force immediately after forming HD. Calculation by Tully (32) have shown that CO produced from atomic oxygen reacting with adsorbed carbon has an angular distribution that is peaked at the surface normal and its normal component of translational energy is considerably higher than the tangential component. The result was interpreted by assuming that CO feels the repulsive interaction with the surface at short C-Pt distances corresponding to the adsorption site of the carbon atom. The experimental facts of hydrogen recombination on nickel (9) and CO oxidation on platinum (33) are consistent with this model.

The rotational and vibrational energy distributions of the HD desorbing from the surface might be important in the interpretation of our experimental results. Unfortunately, no such information is available, so that, it is not appropriate to discuss in detail how rotational and vibrational energy distributions affect the product translational energy distribution. However, one can expect that if the axis of the HD molecules is at 45° to the surface normal immediately after formation, it is possible that the repulsive force will excite rotation and produce a cold translational distribution.

There are other models proposed to explain this type of experimental results, however, they all have drawbacks. Van Willigen's model predicts that the average kinetic energy of the desorbing

molecules increases as the desorption angle changes from normal to parallel to the surface (1). This is the opposite to all the experimental findings that indicate that the average kinetic energy decreases as the detector moved from normal to grazing angle of desorption. Comsa's "activation barrier with hole" model is quite complex and its difficulties were discussed by Horton and Masel (34,35). Horton and Masel did provide a model which concludes that the molecules could desorb preferentially in the surface normal direction if the surface is sufficiently corrugated in the region of the desorption site. However, as the authors have pointed out, the model should predict that the angular distribution of the desorption flux will vary with crystallographic and azimuthal orientation, however, no variations have been observed. Indeed, Salmeron et al. (23) have found that the angular distributions of HD produced from the stepped Pt(332) crystal surface have $\cos^2\theta$ form for two azimuthal angle orientations, $\Phi = 0^\circ$ and 90°. Balooch and Stickney have also found that the angular distributions of H_2 desorbed from the copper surfaces are not azimuthal angle dependent (7).

The fact that in our studies the reactivity of the H_2-D_2 exchange reaction increases as the azimuthal angle of the incident beam increases is similar to the result on the Pt(s) [6(111)x(111)] surface (15) reported previously. Since our crystal surface is Pt(s)[6(111)x(100)], this property appears to be the same for both (100) and (111) orientation steps. Although the step structures might influence the exchange probability somewhat, the steps, no matter what

structures they are, are probably the main cause of the high exchange probability. Tsang and Falicov have calculated H-H bond breaking activity for the different sites on a stepped Pt(557) surface and found the most active site is that associated with the inner corner atom of the step (36). Based on this calculation, Salmeron et al. explained the azimuthal angular dependence by the geometrical variation of the number of reactant molecules that strike the open side of the step structure, which is more active for H-H bond breaking (15). We believe this is also applicable to our angular dependence observation with further support from the fact that the mean kinetic energy of the desorbing HD is not azimuthal angle dependent. If the variation of the exchange probability with respect to the incident azimuthal angle is due to the variation of the activation energy barrier for bond breaking, the desorbed HD velocity should not be independent of the azimuthal angle of desorption.

CONCLUSION

The angular and velocity distributions of HD produced from the H_2-D_2 exchange reaction on Pt(557) surface have been measured. The fact that the angular distribution is peaked at the normal and that the average kinetic energy of the product does not depend on the incident beam energy but is proportional to the substrate temperature indicates that the reaction proceeds via recombination between two adsorbed hydrogen atoms (Langmuir-Hinshelwood mechanism). Although HD desorbs with $\cos^2\theta$ angular distribution, its average kinetic energy

corresponds to a temperature slightly colder than that of the substrate. As the desorption angle increases, the mean kinetic energy of the desorbing molecules decreases. We proposed a model that assumes no activation energy barrier for dissociative adsorption and that as soon as H and D recombine, they will immediately feel a repulsive force which is the strongest perpendicular to the surface.

The H_2-D_2 exchange probability is found to be incident azimuthal angle dependent on Pt(s)[6(111)x(100)] surface. This is similar to that found on the Pt(s)[6(111)x(111)] surface, thus, the steps, not the detailed steps structure, are the main cause of the high exchange probability. The dependence can be understood in terms of the scattering geometry and the enhanced bond breaking properties of the sites at the bottom of the step.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Fig. 1. Schematic diagram of the molecular beam-surface scattering apparatus.

Fig. 2 Angular distribution of HD produced from H_2-D_2 exchange reaction.

Fig. 3 Time-of-flight distribution of the produced HD at 690K and normal angle detection. The solid line is the corresponding Maxwellian distribution at 690K.

Fig. 4 The HD mean kinetic energy divided by 2k as a function of the crystal temperature. Dashed line indicates the temperature that would result for equilibrium between the surface and the produced HD.

Fig. 5 Two time-of-flight distributions for HD produced from H_2-D_2 exchange reaction. The closed circles represent the TOF distribution for the normal angle detection and the open circles 60 degrees from the normal angle detection.

Fig. 6 The HD average kinetic energy divided by 2k is plotted as a function of the desorption angle.

Fig. 7 Production of HD on the Pt(557) surface as a function of the azimuthal angle of incidence, Φ. Φ equals to 90 degrees when the primary incident beam impinges perpendicularly onto the open side of the step.

Fig. 8 Potential energy diagrams showing the interaction of the hydrogen with a metal surface. The atomic potential curve and the molecular curve cross at 7(a) a level higher than that of H_2 or 7(b) a level lower than that of H_2.

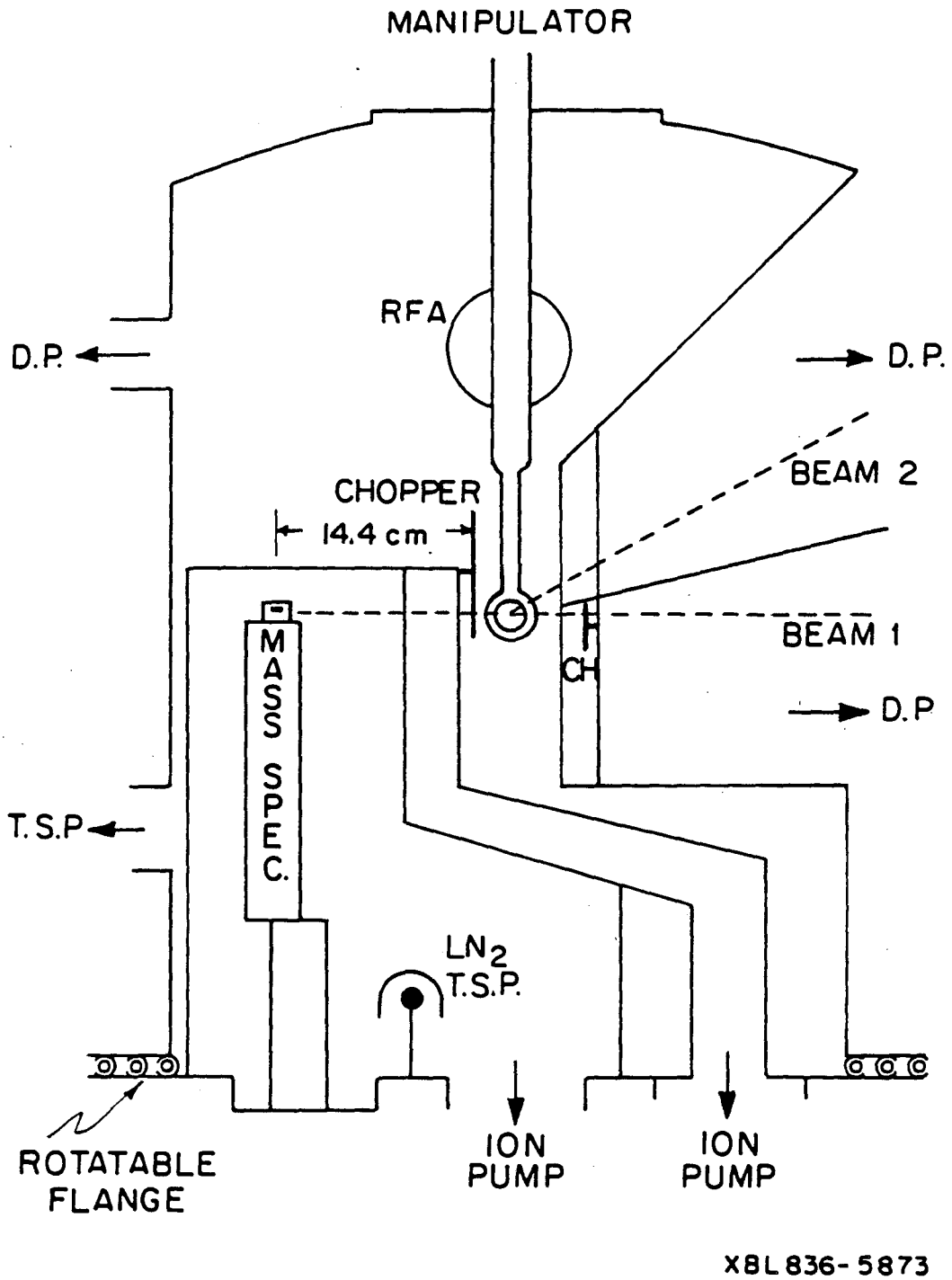
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Fig. 1

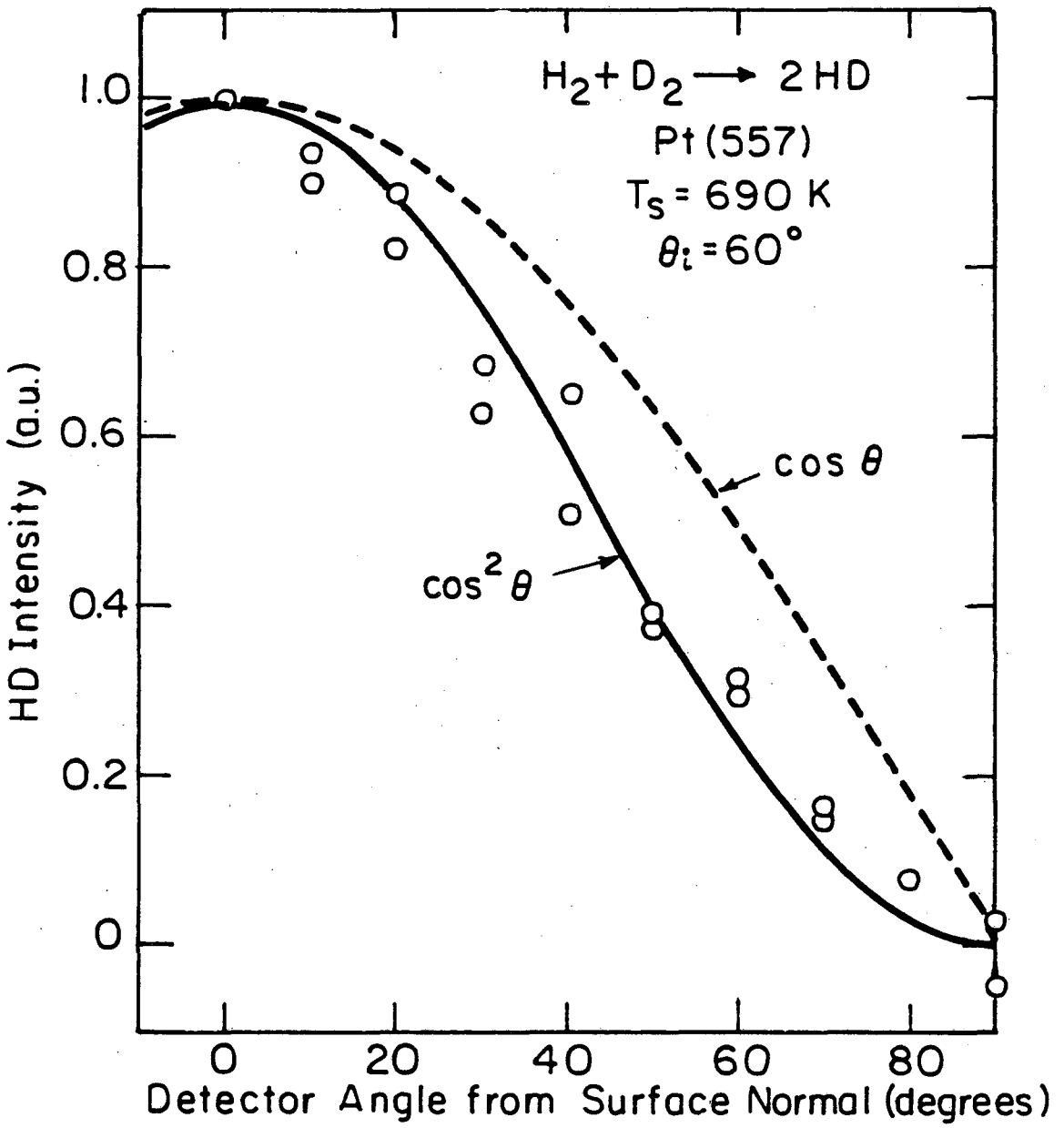

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Fig. 2

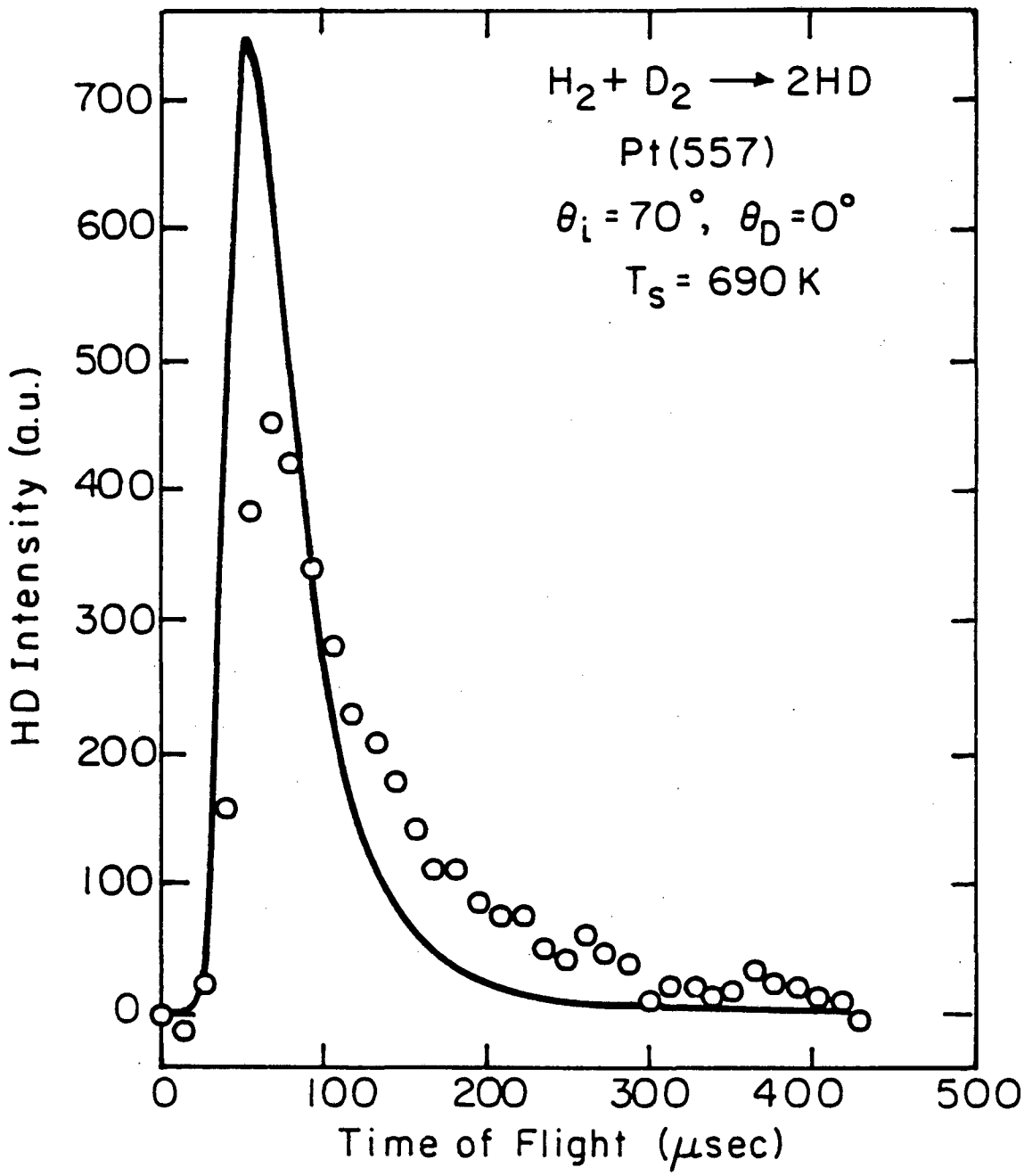

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Fig. 3

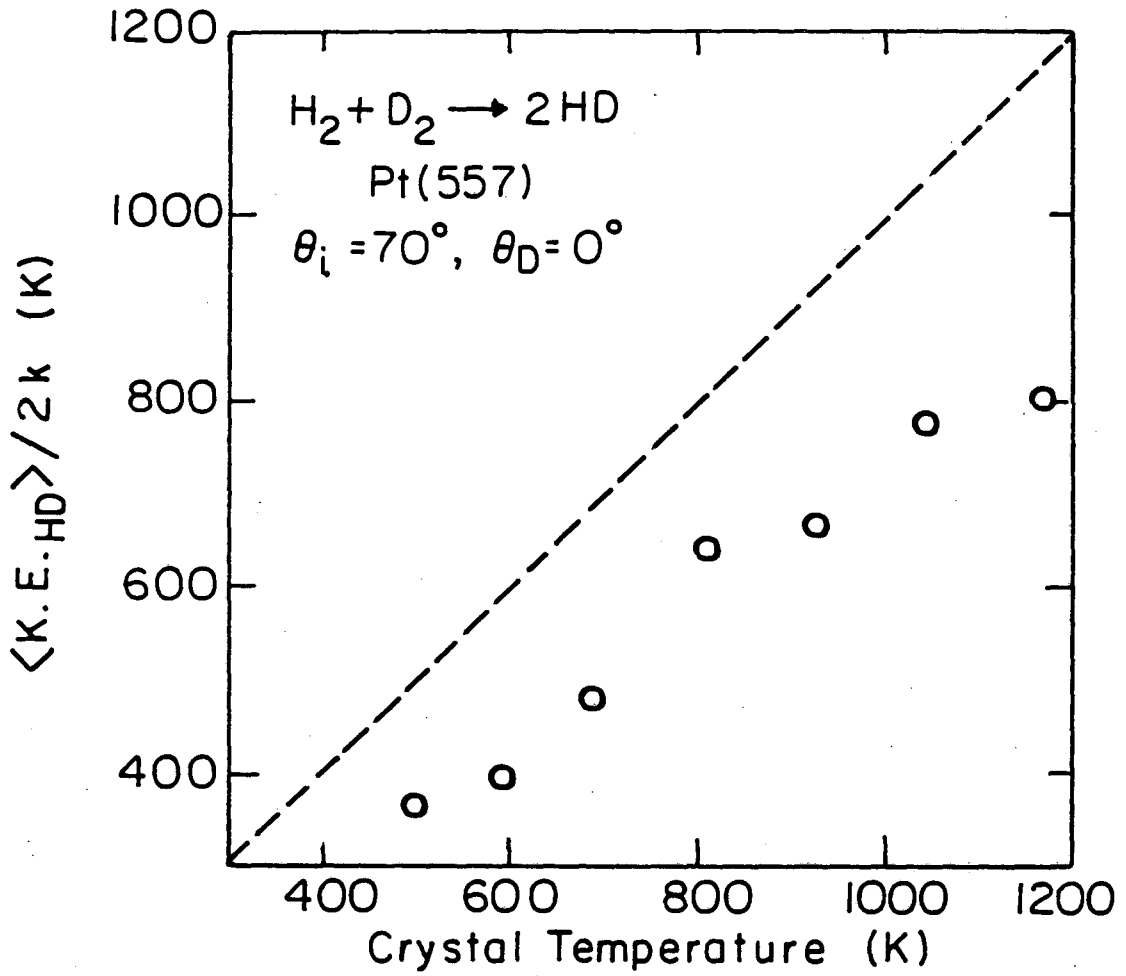

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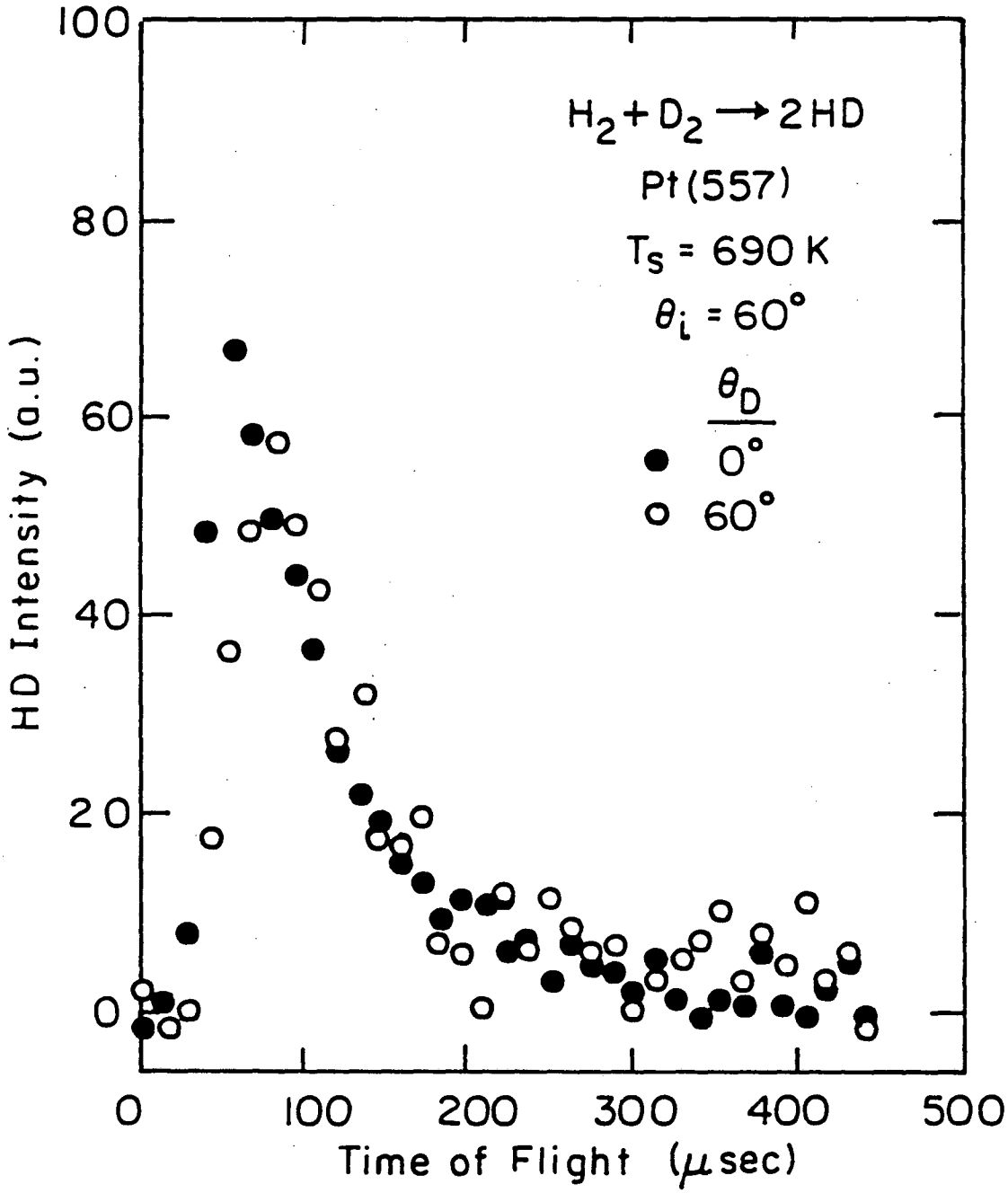
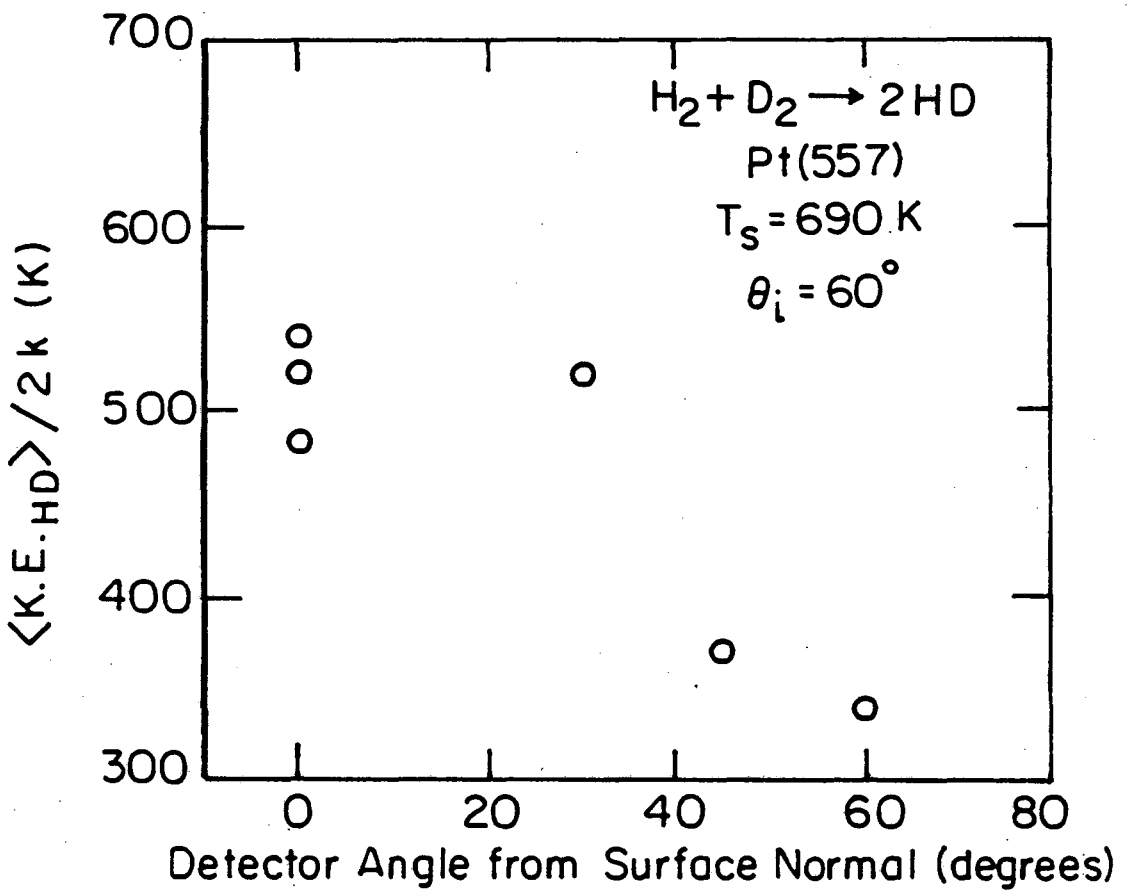
Fig. 4



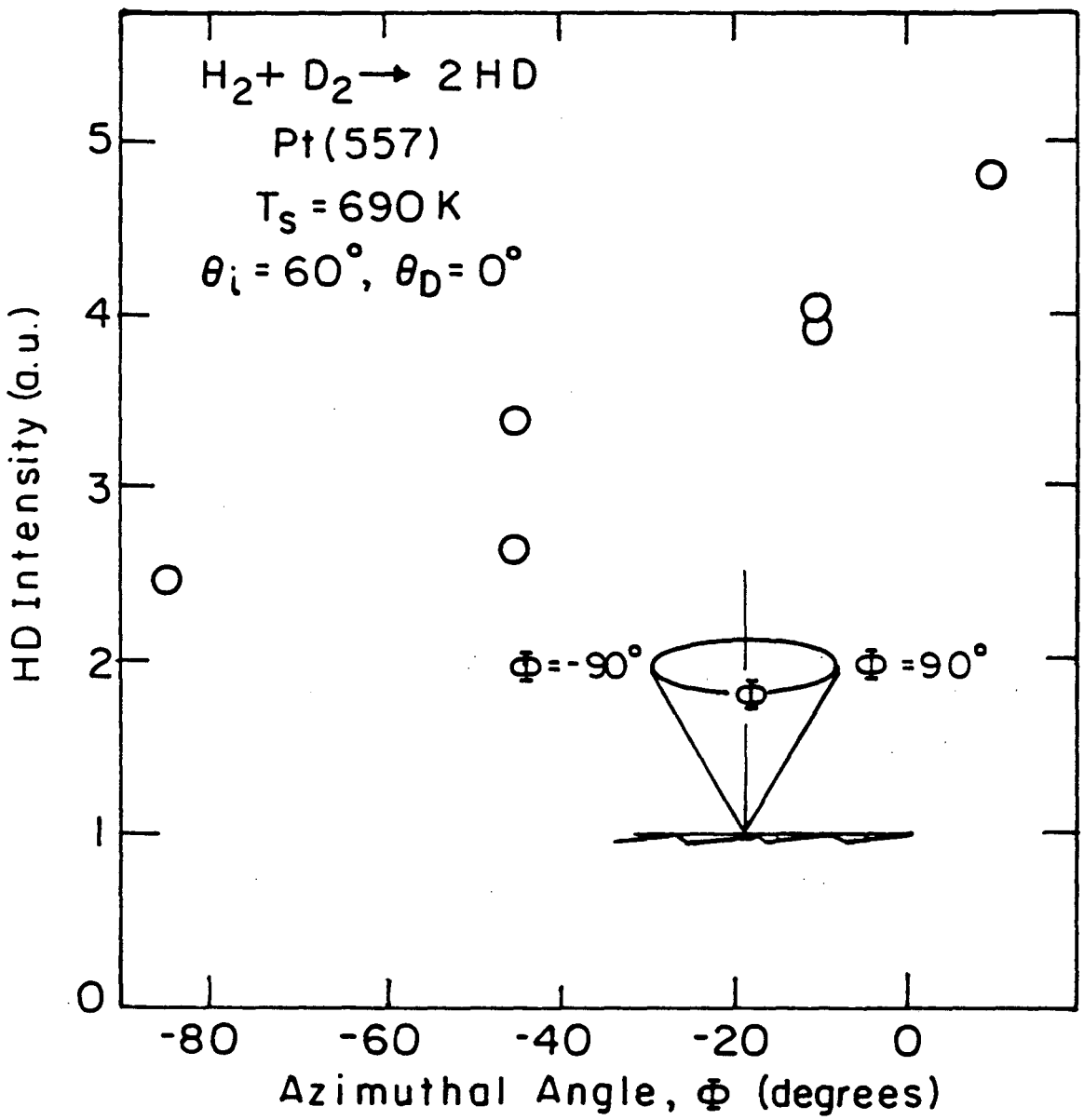
XBL 836-5877

Fig. 5



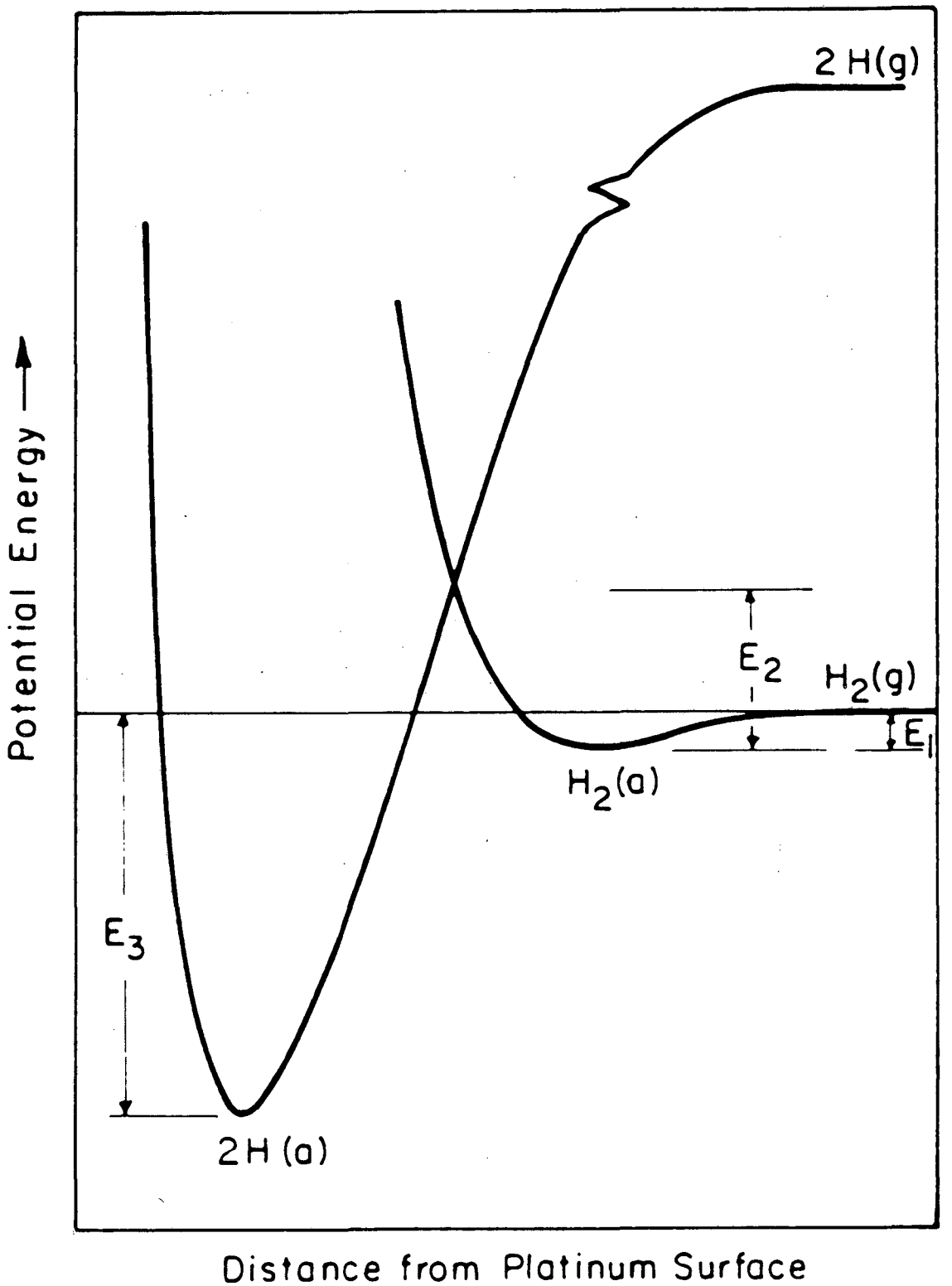
XBL836-5878

Fig. 6



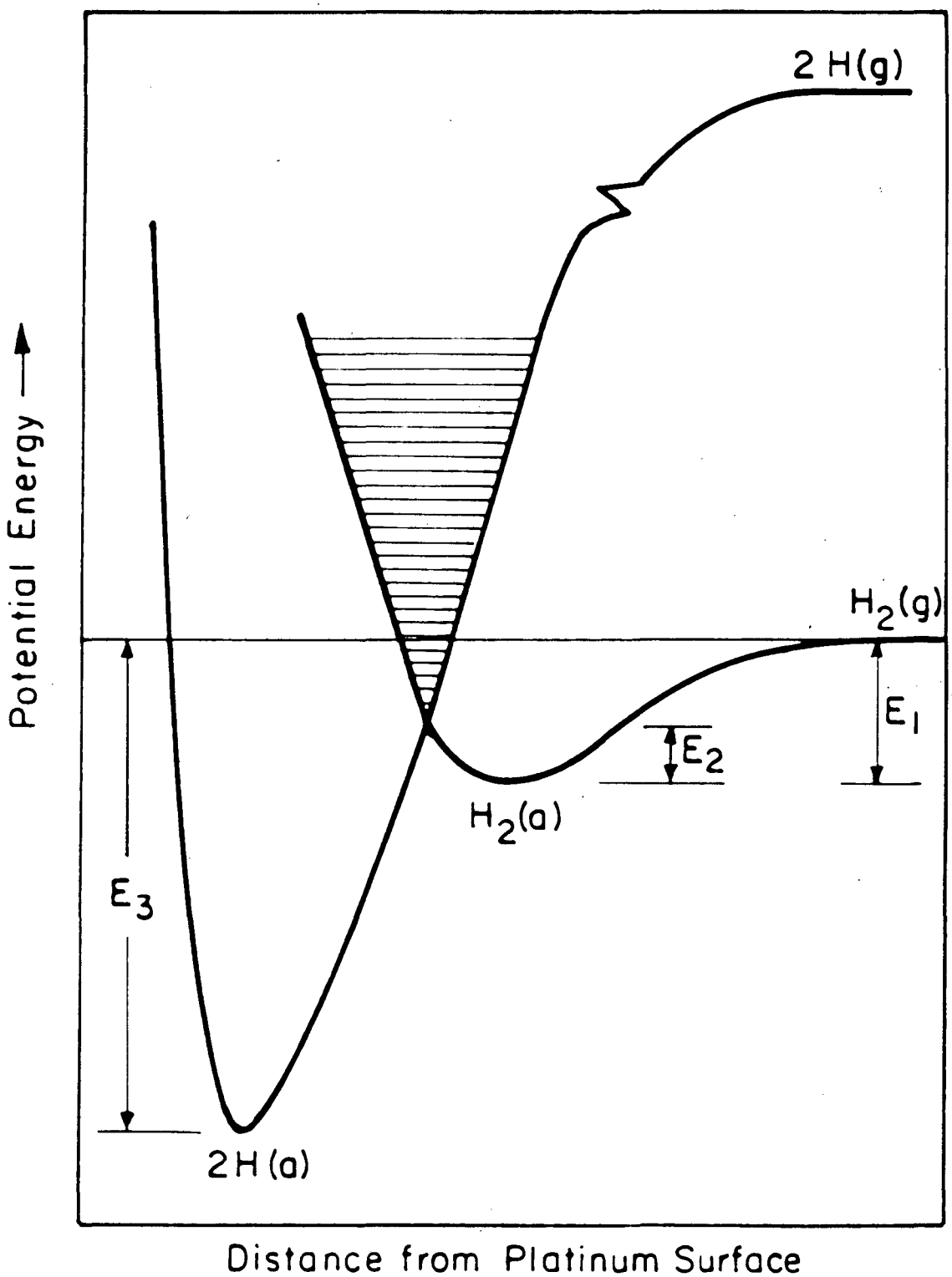
XBL836-5879

Fig. 7



XBL 836-5880A

Fig. 8a



XBL 836-5881A

Fig. 8b

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