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Authors

Lin, T.H.

Somorjai, G.A.

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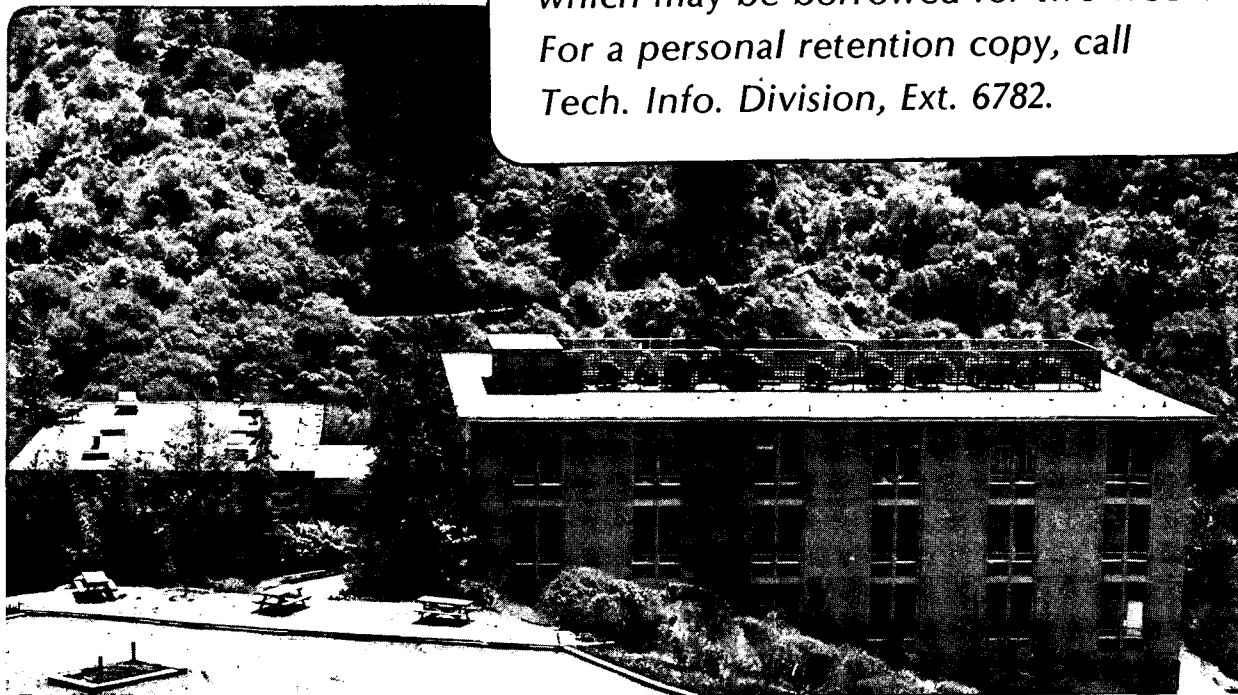
THE DYNAMICS OF ATOMIC HYDROGEN AND DEUTERIUM
RECOMBINATION ON THE STEPPED Pt(557) CRYSTAL SURFACE

T.H. Lin and G.A. Somorjai

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The Dynamics of Atomic Hydrogen and
Deuterium Recombination on the
Stepped Pt(557) Crystal Surface

by

T. H. Lin and G. A. Somorjai
Materials and Molecular Research Division
Lawrence Berkeley Laboratory

and

Department of Chemistry
University of California
Berkeley, California   94720

ABSTRACT

The velocity distribution of HD produced on the Pt(557) crystal surface from atomic hydrogen and deuterium incident beams is measured in the temperature range of 150-700K. The striking results are that (1) the average kinetic energy of the desorbing HD increases as the crystal temperature decreases from 300 to 200K; (2) at 200K, the velocity distribution is considerably wider than the Maxwellian distribution and there is a significant amount of HD leaving the surface with translational energy corresponding to 1900K; (3) for a fraction of the incident atoms, the residence time decreases as the crystal temperature decreases from 300 to 200K. It appears that some of the incident atoms can react with chemisorbed atoms at high coverage before they achieve thermal equilibrium with the surface.

INTRODUCTION

The recombination of hydrogen atoms on surfaces is an exothermic reaction, conceptually one of the simplest surface reactions that can therefore be also subjected to theoretical scrutiny (1-5). The question arises how much of the reaction energy may be carried away by the product molecules in the form of translational energy or in the form of internal excitations and how much is being absorbed by the surface atoms through atomic excitation. While the amount of reaction energy available to the desorbing molecules depends on the strengths of the hydrogen-surface bond, excess energy could still be available to the product hydrogen molecules unless the reaction occurs between two strongly adsorbed hydrogen atoms.

The hydrogen recombination reaction on surfaces is also of great practical importance in many fields of science and technology. The walls of fusion devices are known to degrade in hydrogen plasma (1) and plasma etching and deposition of silicon often involve reactions with fluorine, chlorine, and hydrogen atoms (6). The evolution of inter- stellar gas clouds also requires an understanding of the interactions of hydrogen atoms on surfaces of interstellar grains (7).

In this paper we report an investigation of the interaction of the atomic hydrogen and deuterium with the platinum surface by the use of molecular beam-surface scattering. With separate atomic hydrogen and deuterium incident beams, the velocity distribution of the product HD molecule is measured at substrate temperatures in the range of 150K ~ 700K. Above 500K, the average kinetic energy divided by 2k yields the

average beam temperature which is slightly colder than the correspond-
ing substrate temperature and increases as the crystal temperature
increases. However, below room temperature the HD product temperature
increases as the crystal temperature decreases and becomes higher than
the corresponding substrate temperature. The formation of the hot
product molecules is interpreted by assuming that some of the incident
atoms can react with chemisorbed atoms at high coverage before they are
in thermal equilibrium with the surface. The results of this
nonstatistical distribution of energy among products of chemical
reactions on surfaces are very useful for uncovering information about
the dynamics of the reactive event.

EXPERIMENTAL

The molecular beam-surface scattering apparatus has been described
in detail elsewhere (8,9). For the purpose of these experiments, it
was modified to permit cooling of the crystal to 150K. Briefly, two
incident beams cross at the center of the scattering chamber and one
of the incident beams can be modulated at 150 Hz for residence time
measurement. The scattering chamber is equipped with instrument for
Auger electron spectroscopy (AES), low energy electron diffraction
(LEED), and ion sputtering of the crystal. The two-stage
differentially pumped detector chamber is mounted on a rotatable flange
which rotates about the center of the scattering chamber. The Extra-
nuclear quadrupole mass spectrometer is used for signal detection. The
pseudorandom chopper modulates the scattered product for time-of-flight
measurement and the flight path is about 14.4 cm.

The modification for sample cooling is described in the following. A cryopump with both cold and warm panels removed is mounted to an 8" conflat flange and used to cool the crystal. Because the sample needs to translate ~7.5" from the surface analysis position to the scattering position, a 6" long copper braid is used to connect the cryopump cold stage to a copper rod which is attached to the manipulator with proper insulation. Another 2" copper braid connects the copper rod to a platinum foil on which the crystal is mounted. With this modification, the azimuthal rotation is no longer available and the variation of polar angle is also significantly reduced. Nevertheless, Auger electron spectroscopy and argon ion sputtering can be used. Because of the long distance between the cryopump and the crystal, the sample can only be cooled to 150K while cryopump cold-stage is at 14K. It takes 15 min. to cool the crystal down from 1200K to its ultimate minimum temperature.

The two atomic hydrogen and deuterium beams are produced in the discharges located at the 1mm nozzle tips (10). The plasma is produced in a microwave cavity at a pressure of 2 Torr. By comparing the direct beam intensities with or without the plasma, we estimate that about 35 percent of the hydrogen molecules dissociate. Argon (20 percent) is added to the source whenever the plasma is not stable. The primary beam is incident at an angle of 70 degrees along the step edges of the crystal. The Pt(557) crystal was cleaned by argon ion sputtering and annealing. The background pressure with the cryopump operating is 7×10^{-10} Torr and increases to 8×10^{-9} Torr when both beams are incident on the crystal.

For the measurement of the surface residence time, the incident atomic hydrogen beam was chopped with the tuning fork chopper at 150 Hz and the waveform of the HD product is collected with the 255 multi-channel scalar. The same program which controls the time-of-flight (TOF) distribution collection is used to control the waveform data collection. A trigger from a pick-up coil of the tuning fork chopper is used to trigger the multi-channel scalar.

RESULTS

Figure 1 shows two TOF distributions of the HD product detected at normal to the surface. The open circles represent the distribution at a crystal temperature of 200K and the closed circles 500K. The peak intensities of the distributions were adjusted to be the same. The striking feature is that the velocity of the HD product at a substrate temperature of 200K is higher than that at 500K. Quantitatively, the average kinetic energy divided by 2k for T_S = 200k is 615K which is much higher than the substrate temperature whereas for T_S = 500K it is 300K, lower than the temperature of the platinum single crystal. The distribution for T_S = 200K is also considerably wider than that for T_S = 500K. It should be noted that there is high signal intensity (70 percent of the peak intensity) at the third channel indicated with the arrow in the figure. This channel's signal comes from HD molecules with kinetic energy of .16 ev or 1900 K and exists only if the crystal temperature is below 300K. The average kinetic energy divided by 2k is only 615K because of the wide distribution,

however. This means that there is a significant amount of slow HD molecules produced which brings the average energy down. Nevertheless, a considerable amount of HD product molecules has a temperature of 1900K.

The average kinetic energy divided by 2k of the produced HD as function of the crystal temperature is shown in Fig. 2. If there were complete accommodation between the HD molecules and the surface, the data points would lie on the dashed line. As the substrate temperature increases from 500K to 690K, the average kinetic energy divided by 2k increases and is slightly lower than the corresponding substrate temperature. Similar results were found (9) in this temperature range when the incident beams were H_2 and D_2 rather than H and D. The striking feature is that as the crystal temperature decreases from 500K to 200K, the average energy divided by 2k of the HD product molecules increases from 300K to 615K and for T_s < 300K is higher than the corresponding crystal temperature. As we mentioned before, for T_s < 300K a significant amount of HD leaves the surface with energy as high as 1900K.

The experimental TOF distribution for T_s = 200K is compared with the Maxwellian distribution at 200K (solid curve) in Fig. 3. The theoretical peak intensity is adjusted to be the same as that obtained in the experiment. While the "hot" molecules are definitely not equilibrated with the surface, the tails of the distributions indicate the formation of the "cold" HD product molecules which are colder than the substrate.

To measure the surface residence time, the incident atomic hydrogen was chopped at 150 Hz and the HD product waveform was collected (11). The waveforms as the function of the crystal temperature are shown in Fig. 4. At a substrate temperature of 690K, the waveform does not demodulate because of the short residence time. As the temperature decreases, the residence time increases and the waveform demodulates correspondingly as can be seen for T_s = 500K and 300K. However, the interesting feature is that the waveform appears again, although with low intensity, at 200K indicating that the residence time for some incident atoms becomes shorter.

We have found that the HD signal decreases as the crystal temperature decreases below room temperature and almost completely disappears at 150K. This is concluded from the observation that the time needed to obtain a TOF distribution increases as the crystal temperature decreases.

DISCUSSION

It is useful to review the major features of the measurements before discussing the proposed model. The important results are as follows. The average kinetic energy of the HD product increases as the crystal temperature decreases from 500K to 200K and a significant amount of HD leaves the surface with kinetic energy as high as 1900K at a substrate temperature of 200K. Although the product residence time increases as the substrate temperature decreases from 690K to 300K, it decreases with further lowering of the substrate temperatures.

All the novel features seem to occur below 500K. Above this temperature, the average kinetic energy divided by 2k increases as substrate temperature increases and is slightly lower than the crystal temperature just as in the case of the H_2-D_2 exchange reaction (9). The agreement between these two experimental results confirms that the H_2-D_2 exchange reaction occurs through adsorbed H and D atoms. It also indicates that adsorbed H and D atoms dissipate all of their chemical energy, at least 53 Kcal/mole, and are in thermal equilibrium with the platinum surface before finding another atom with which to recombine and desorbs. The interaction time decreases as the crystal temperature increases in this temperature range, as expected.

Since the formation of HD product molecules with high kinetic energy occurs only below room temperature, this change of reaction mechanism may be related to the surface coverage of adsorbed hydrogen (deuterium) atoms which increases as the temperature of the platinum crystal is lowered. Therefore, we propose the following model which appears to be able to explain all the experimental findings satisfactorily. Consider a hydrogen atom that strikes the platinum surface and is trapped in the potential well which is about 63 Kcal/ mole deep. The trapped atom will not be in thermal equilibrium with the surface instantaneously since the energy transfer is not perfectly efficient. The time between the initial collision and reaching thermal equilibrium will depend on the rate of dissipation of the chemisorption energy. If the trapped hydrogen atom does not have the chance to recombine with other chemisorbed atoms before it is in thermal

equilibrium with the surface, there will not be any recombination energy available for the product HD molecule and the energy of the product will be the same for incident beams that are either atomic or molecular. However, if the trapped hydrogen atom recombines with a chemisorbed deuterium atom before it achieves thermal equilibrium with the surface, there is some chemical energy available that could be carried away by the product. Thus, the amount of chemical energy available for the product is strongly dependent on the elapsed time between the initial collision of the atom with the surface and the recombination reaction. Conceivably, this elapsed time depends on the coverage.

Above room temperature, the coverage is low under our low pressure reaction conditions and the trapped atom dissipates all its chemical energy before recombination takes place, thus, the product kinetic energy is controlled by the interaction potential as discussed in reference 9. As the crystal is cooled below room temperature, the coverage of the hydrogen (deuterium) will be increased. Under these conditions, one can roughly classify the incident atoms into three groups as they impinge on the surface. The first group includes those atoms which collide with the open platinum surface and are within, for example 2Å of any chemisorbed hydrogen (deuterium) atom. These incident atoms can react with the chemisorbed atoms immediately because of the following reasons. There are chemisorbed atoms within 2Å of the incident atoms, and the reaction is probably non-activated. Further-more the reaction is exothermic by 43 Kcal/mole assuming the binding

energy of atomic hydrogen with platinum surface to be 63 Kcal/mole and that there is no energy exchange between the incident atom and the surface before the reaction occurs. If there is some energy exchange but the reaction takes place before the incident atom reaches thermal equilibrium with the surface, which is probably true in this case, the reaction is still exothermic and the liberated energy can be carried away by the product. Thus, the HD kinetic energy divided by 2k can be higher than the substrate temperature.

The second group atoms consists of those which collide with the open platinum surface and are at least 2Å away from any chemisorbed atom. These atoms will have long residence time, keeping the coverage high, and reach thermal equilibrium with the surface before recombination can take place. Thus, the kinetic energy of HD produced from this group's atoms will be determined by the interaction potential and crystal temperature. Extending the results above 500K down to below room temperature, the HD kinetic energy divided by 2k should be slightly lower than the corresponding substrate temperature.

Finally, the third group consists of those which are incident at sites where atoms are already adsorbed. These atoms are probably scattered back into the gas phase instantly. This is concluded from the facts that HD signal decreases as the crystal temperature decreases from room temperature and disappears at 150K when one monolayer coverage is reached.

The experimental results below room temperature can be explained with the above model. As the crystal temperature decreases, the

coverage increases and the percentage of the HD produced from the first group incident atoms increases. Since these HD molecules can be "hotter" than the substrate, the average kinetic energy divided by 2k will increase and can be higher than the crystal temperature as shown in Fig. 2. At a substrate temperature of 200K, HD can be produced from the first group incident atoms as well as the second group incident atoms. As mentioned before, the HD produced from the second group incident atoms is slightly "colder" than the substrate temperature. Thus, the TOF distribution is wide and the hot product is "hotter" and the cold product is "colder" than the substrate temperature as shown in Fig. 3. The appearance of the waveform at 200K in Fig. 4 is due to the HD produced from first group incident atoms. These atoms react immediately with the chemisorbed atoms, thus, the product waveform is not demodulated.

There is a significant amount of HD leaving the surface with translational energy of 1900K which corresponds to 7 percent of the liberated chemical energy. It is very likely that a considerable amount of reaction energy will end up in the product vibrational and rotational modes although no experimental results are available. Theoretically, Tully has studied the reaction of incident oxygen atoms that strike within 2Å of an adsorbed carbon atom on the Pt(111) surface and found that 90 percent of the 6 eV of liberated energy is carried away by the product CO molecule (12). He determined that 30 percent of reaction energy was carried away as the translational energy of the product. A qualitative argument explaining this phenomenon was

suggested by Harris and Kasemo (13). They referred to the trapped atoms which are not in thermal equilibrium with the surface as "hot precursors" and the resulting interaction mechanism as a "precursor mechanism".

There are many experimental results showing product temperatures that are higher than the corresponding substrate temperatures. Examples are N_2 desorbing from sulphur covered Fe (14) and D_2 desorbing from Ni (15), sulphur covered Pd (16), and Cu (17) surfaces. However, the reactants are probably in thermal equilibrium with the surface and the existence of an activation barrier for dissociative adsorption is the origin of the excess energy. The hot HD molecules produced in this study desorb through a non-activated interaction potential and the lack of equilibration in the potential well is the origin of the excess energy. Thus, this is the first experimental result which shows that energy equilibration on solid surfaces is not extremely fast, and thus, that the dynamics of the reactive events can be studied.

CONCLUSION

The velocity distribution of HD produced from atomic hydrogen and deuterium recombination on Pt(557) surface is measured for substrate temperature of 200-700K. The average kinetic energy divided by 2k is slightly lower than the corresponding substrate temperature between 500-700K and increases as the crystal temperature increases. However, it increases as the crystal temperature decreases from 500-200K and

becomes higher than the substrate temperature below 300K. At 200K, the distribution, is considerably wider than the Maxwellian distribution and there is a significant amount of HD leaving the surface with 1900K translational energy. The waveform measurement indicates that the residence time increases as the crystal temperature decreases from 700K to 300K and decreases for some of the incident atoms as the crystal temperature decreases from 300K to 200K.

The striking experimental findings are interpreted by assuming that some of the incident atoms can react with chemisorbed atoms at high coverage before they are in thermal equilibrium with the surface. This mechanism is very different from the previous explanation of hot products (14-19) in which the activation barrier is believed to be the origin of the excess energy.
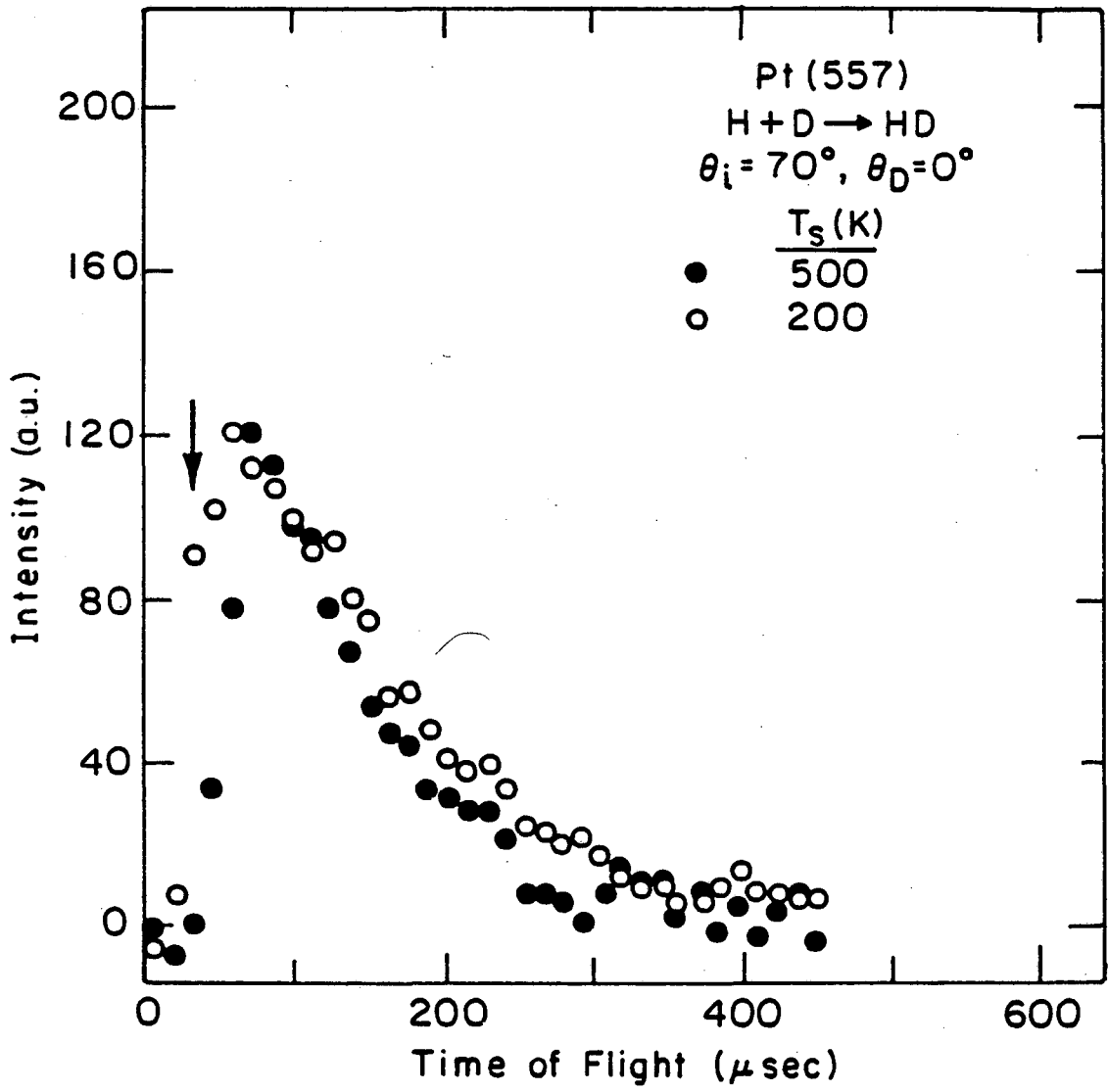
ACKNOWLEDGEMENTS

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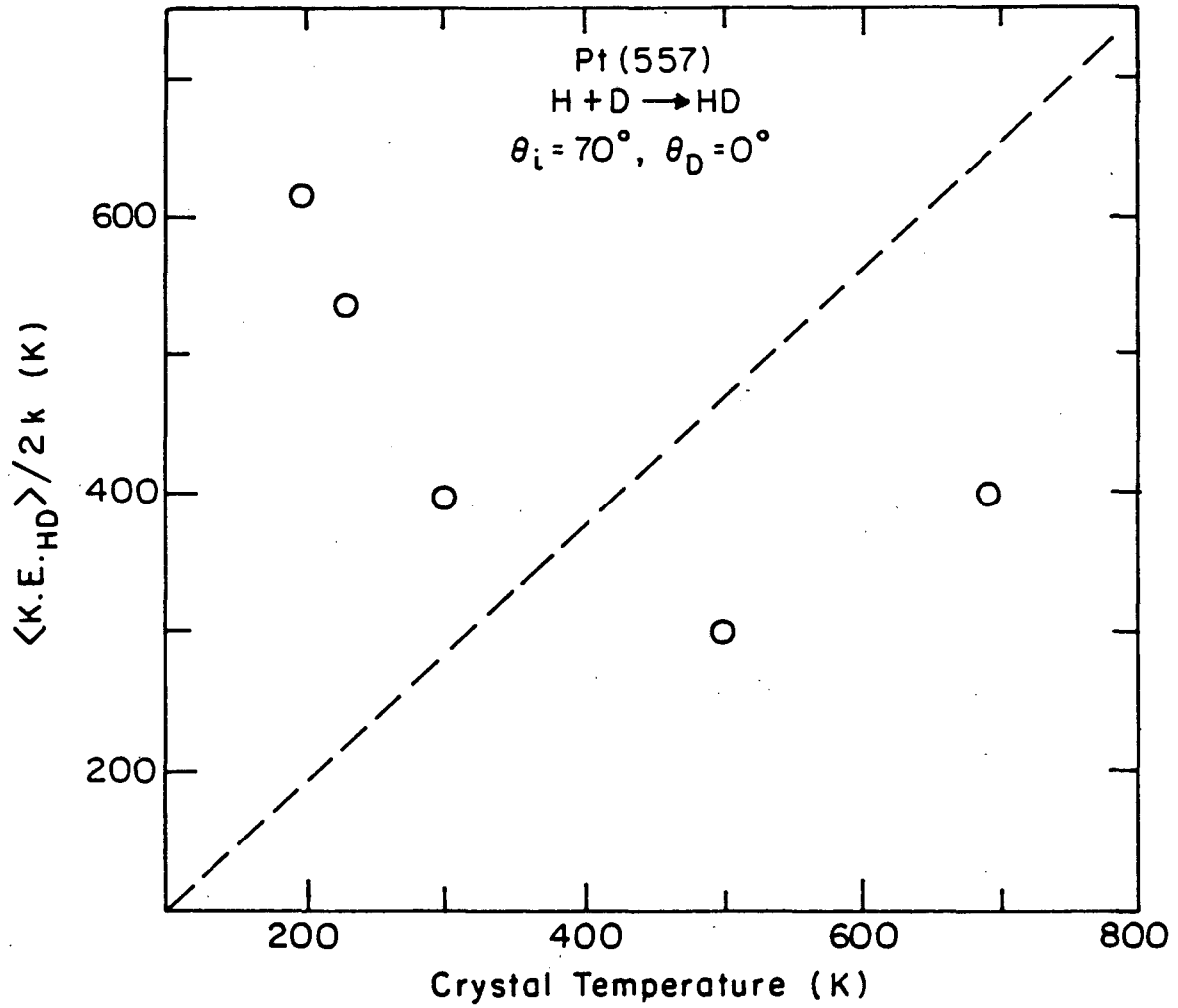
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Figure Captions

Fig. 1 Two time-of-flight distributions for HD produced from atomic

hydrogen and deuterium recombination. The closed circles

represent the TOF distribution for T_s = 500K and the open

circles T_s = 200K. The arrow indicates that there is a

significant amount of HD leaving the surface with translational

energy of 1915K.

Fig. 2 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. 3 Time-of-flight distribution of the produced HD at 200K. The

solid line is the corresponding Maxwellian distribution at

200K.

Fig. 4 Waveforms for HD produced from atomic hydrogen and deuterium

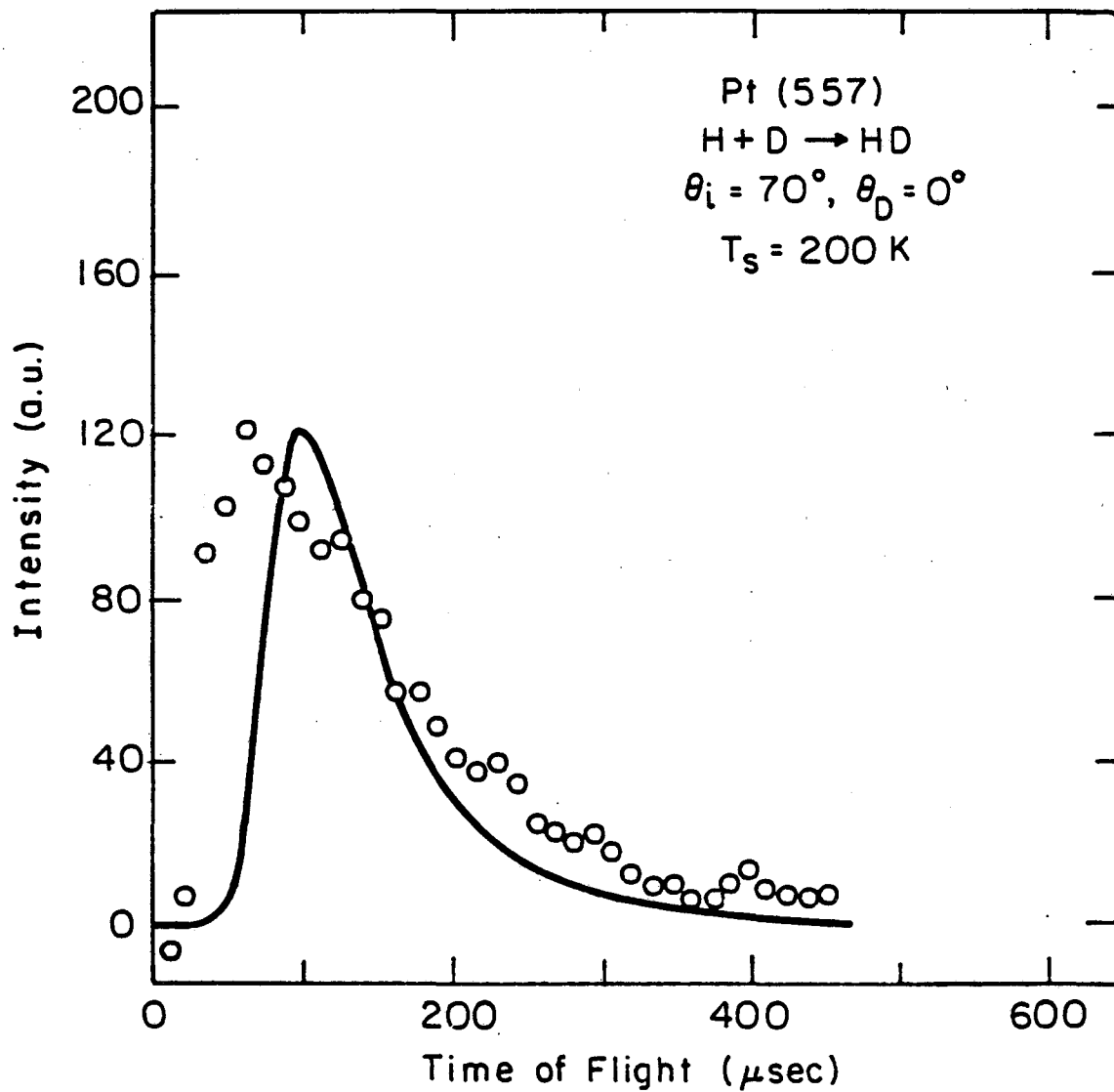recombination on Pt(557) and for temperatures ranging from 200

to 690K.

Fig. 1

Fig. 2

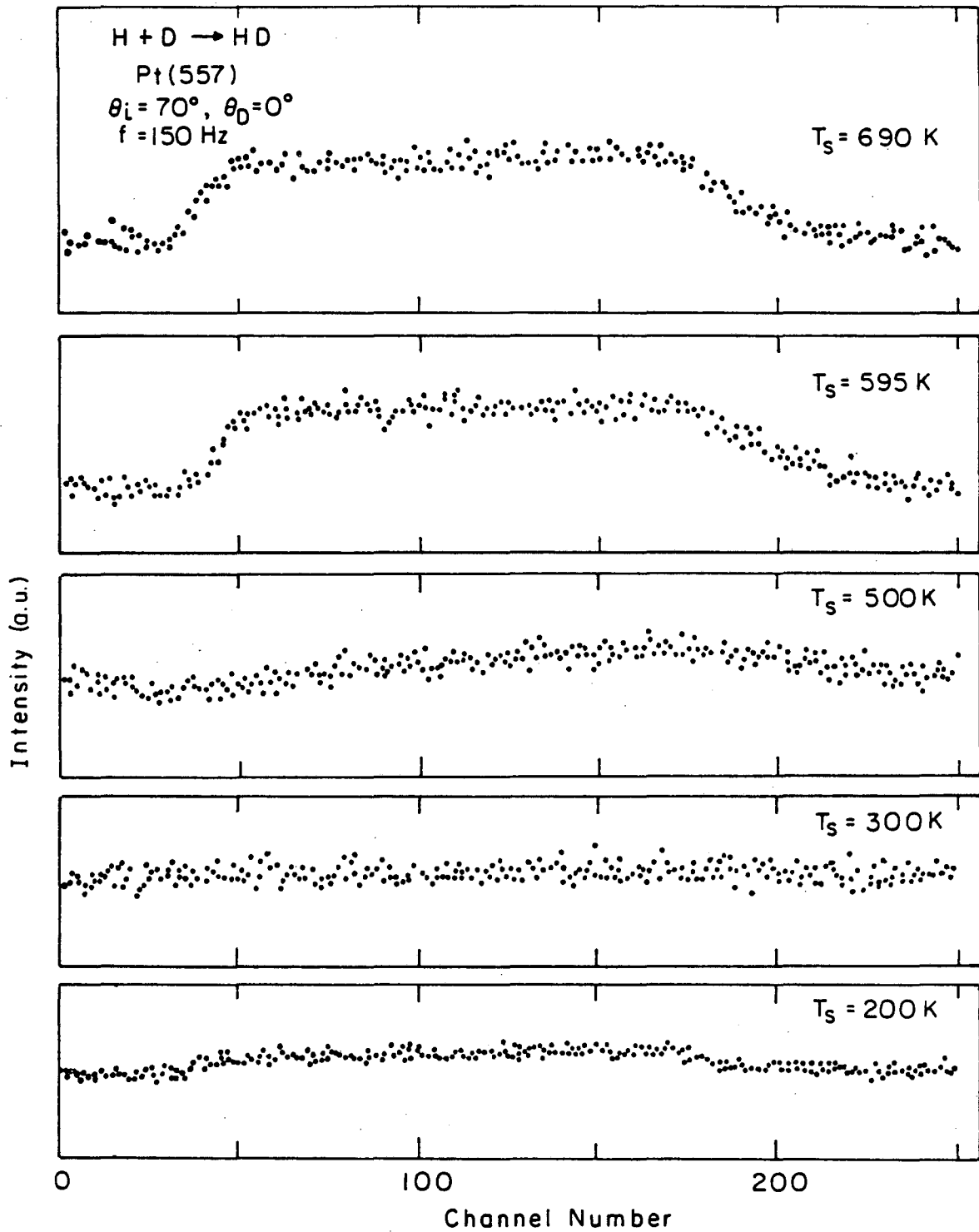XBL 838-6088

Fig. 3

XBL 838-6087

H + D ⟶ HD
Pt (557)
$\theta_i = 70°$, $\theta_D = 0°$
f = 150 Hz

T_s = 690 K

T_s = 595 K

T_s = 500 K

T_s = 300 K

T_s = 200 K

Intensity (a.u.)

Channel Number

XBL 836-5882

Fig. 4