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D_2O product angular and translational energy distributions from the oxidation of deuterium on Pt(111)

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The angular and translational energy distributions of D_2O produced from the oxidation of deuterium on the (111) crystal face of platinum have been measured over the surface temperature range of 440–913 K. Although the angular distributions are described by a cosine function, the translational energy distributions deviate from the corresponding Maxwell–Boltzmann distributions. At the normal angle, the D_2O mean translational energy $\langle E \rangle / 2k$ varies from 220 to 400 K over the temperature range investigated. Two mechanisms for the production of translationally cold product molecules are discussed.

INTRODUCTION

The dynamics of the last bond formation step or the desorption step determine the spatial and translational energy distributions of the products from a surface chemical reaction. Measurements of these distributions in a molecular beam reactive scattering experiment provide information on the mechanism and dynamics of the exit process. For example, they can provide a means of determining the concertedness of the final step of the reaction and the desorption process, the amount of the exoergicity channeled into translation, the relative rates of thermal excitation of an adsorbate to desorption, or the shape of the potential energy surface in the exit channel region. The translational energy distribution measurements of H_2 produced from the recombination of $H_{(a)} + H_{(a)}$ on polycrystalline nickel,[1,2] Ni(111),[3] Pd(100),[4] and of CO_2 produced from the reaction $CO + O_2$ on polycrystalline platinum[5] are examples of the determination of the shape of the potential energy surface. The large translational energies observed result from the presence of a barrier in the exit channel which, in the case of CO_2, may be related to the formation of a bent O=C=O bond[6–8] in the transition state. The peaking of the H_2 and CO_2 angular distributions at the surface normal is due to the parallel orientation of the barrier equipotentials which causes focusing of the product molecules towards the normal.

To date, this is the only type of dynamics that has been observed and the only reactive systems that have been studied. The fact that the exit barrier is very effectively channeled into translation indicates that the rate of energy dissipation into the surface is slow relative to the velocity of the newly formed molecule. Thus, it is reasonable that systems can be found where the exoergicity of the last bond formation step is effectively channeled into translation. However, if the exoergicity of the reaction is small or nonexistent, then the newly formed product molecule has a greater probability of becoming trapped on the surface thereby uncoupling the final reaction step and the desorption step. A product angular distribution described by a cosine function and a product translational energy distribution characterized by a Maxwell–Boltzmann function at the temperature of the surface is a signature for this type of dynamics.

At first glance the reaction $D_2 + O_2 \rightarrow D_2O$ on Pt(111) might be cited as an example of this latter mechanism. The D_2O product angular distribution has been observed to fit a cosine function.[9] By conventional interpretations this implies that the translational energy should be in equilibrium with the solid. We have expanded on this previous study to include energy distribution measurements as a function of surface temperature and scattering angle. We report here both the angular and energy distributions of D_2O produced in this reaction. Our angular distribution measurements agree with the earlier measurements. However, the translational energy distributions indicate that the conventional interpretation is incorrect. It is shown that this combination of measurements provides a solid basis for a discussion of the mechanism and dynamics of the desorption process.

EXPERIMENTAL

The apparatus was constructed to study energy partitioning in surface chemical reactions.[8,10] A schematic of it is shown in Fig. 1. The reactants, D_2 and O_2, were each expanded from a 0.08 mm diameter orifice at a stagnation pressure of 200 Torr. The D atom beam was produced from an effusive microwave discharge source, previously described in detail.[10] The twice differentially pumped beams intersect at an angle of 30° at the crystal surface. The angle of incidence is 49°. The incident flux at the surface is approximately 1×10^{15} cm^{-2} s^{-1}. The product flux is detected by a twice differentially pumped quadrupole mass spectrometer. The detector is rotatable about the single crystal sample allowing measurement of product angular distributions and velocity distributions at each angle. A tuning fork chopper at 150 Hz modulated one of the reactant beams during the angular distribution measurements. A cross correlation time-of-flight technique[11] was used for the velocity distribution measurements. The product flux was modulated in these measurements.

The Pt (111) sample was cleaned by argon ion sputtering, and when needed by chemical cleaning in oxygen

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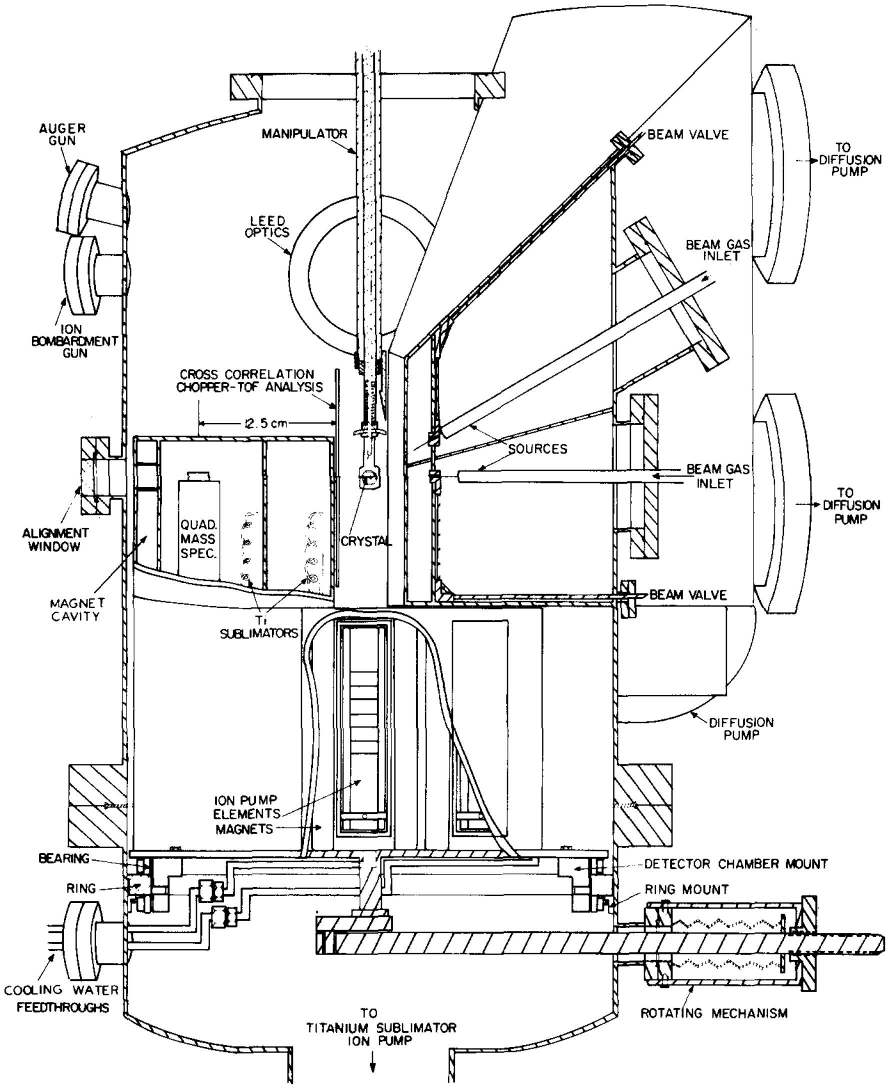

FIG. 1. Schematic diagram of the scattering apparatus.

at a surface temperature of 700 K. Surface cleanliness was determined by Auger electron spectroscopy (AES). The crystal was annealed at 1100 K and then lowered to the reaction temperature. The crystal temperature was determined by a Pt–Pt 10% Rh thermocouple. After each hour of data collection, the crystal surface cleanliness was checked by AES. There was always oxygen contamination on the order of 10%–20% of a monolayer regardless of the temperature at which the reaction occurred. Coverage was based on a calibration by Gland.[12] The crystal was cleaned if the oxygen coverage exceeded 20% or if other contaminants were present.

The D_2O signal count rates were typically 30–80 ions/s against a background count rate at $m/e = 20$ of 7000 ions/s. With the low count rates, approximately 20 h of real data collection time were required for each distribution and approximately two to three times that in actual experimental time.

The low product count rates and the pronouncedly slow TOF distributions caused some concern that spurious sources of signal might be affecting the distributions. Since the resolution of the mass spectrometer was decreased in order to increase transmission, we measured a TOF distribution with no D_2 incident on the surface to determine if incomplete filtering of the $O^+ (m/e = 16)$ ionization fragment produced from the scattered O_2 was occurring. After 3 h, no distribution was observed with the mass filter tuned to $m/e = 20$. The O^+ fragment contributed at most 0.5 ions/s to the signal. Inelastic scattering of background D_2O from the crystal into the detector is another possible spurious source of signal. The background D_2O is produced from the reaction of D_2 and O_2 on filaments, chamber surfaces, and in the ion pump. Blank experiments with both beams entering the scattering chamber, but only one incident on the crystal, showed that the effect of background D_2O is negligible.

The time-of-flight spectrum was calibrated against the flight times for a series of four inert gases from an effusive source at 300 K and against the flight times of D_2O from an effusive source at two temperatures. The effusive source was a 0.08 mm diamter hole in an oven operated at a stagnation pressure of 8×10^{-2} Torr. Figure 2 shows the TOF distributions observed for a source

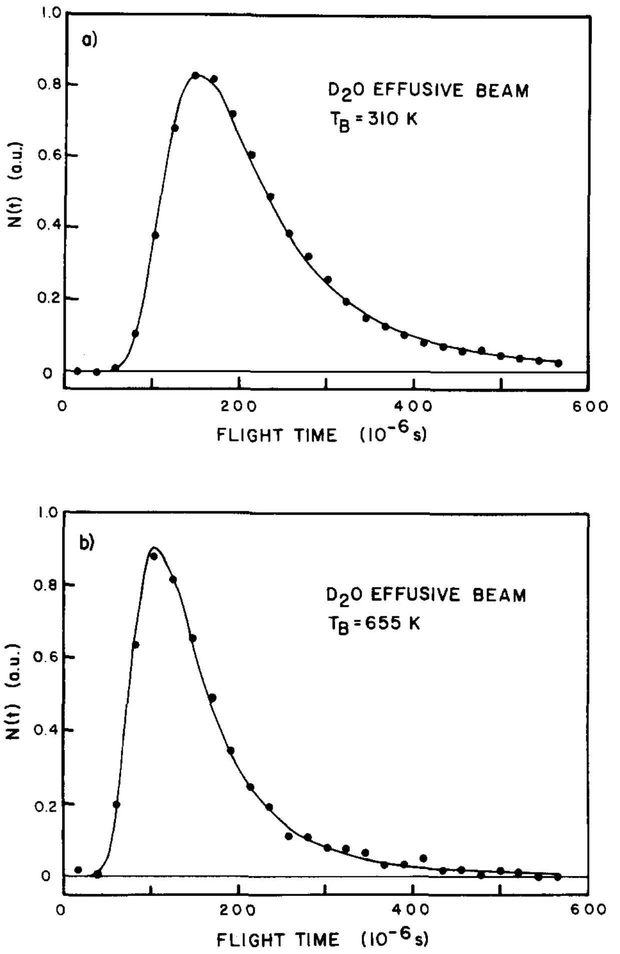

FIG. 2. TOF distributions of D_2O from an effusive source. The solid line is a Maxwell–Boltzmann distribution at the temperature indicated by a thermocouple on the source. (a) 310 K. (b) 655 K.

temperature of 310 and 655 K. The solid curves represent Maxwell–Boltzmann distributions at the source temperature, convoluted with the known chopper gate and electronic gate functions. As can be seen, the experimental distributions agree with the expected Maxwell–Boltzmann distributions.

RESULTS

Figure 3 (a) shows the angular distribution observed for product D_2O taken from the reaction $D_2 + O_2$ at a surface temperature $T_s = 700$ K. Figure 3 (b) shows the product D_2O angular distribution from the reaction $D + O_2$ at the same temperature. Within the uncertainty, the angular distributions resulting from the atomic or molecular deuterium reactants are identical. As discussed below, depending on the desorption mechanism, this similarity may indicate that D atoms rather than D_2 are the essential intermediates in this reaction. Plotted with the data is a cosine function (solid line), showing that the number density is proportional to the cosine of the desorption angle, as reported previously by Smith and Palmer.[9] By microreversibility arguments, cosine angular distributions are commonly taken to imply equilibration of the desorbing gas with the surface.[13] However, the TOF distributions are far from equilibrium distributions.

The time-of-flight distributions, transformed to energy distributions, are shown in Figs. 4 and 5. The collected TOF distributions are number density distributions $P_d(t)$ and are multiplied by the velocity to transform to flux distributions $P_f(t)$. The transformation to an energy distribution is made by multiplication by the Jacobian so that $P(E) \propto t^3 P_f(t) \propto t^2 P_d(t)$. The data for the surface temperatures 913, 870, and 765 K are shown in Figs. 4(a)–4(c). Two distributions for $T_s = 664$ K at detector angles $\theta = 7°$ and 40° from the surface normal are shown in Fig. 5. Plotted as the open circles is a Maxwell–Boltzmann distribution at the corresponding surface temperature, convoluted with the chopper and electronic gating function and normalized to the total counts of the experimental distribution. The striking feature of these distributions is that they lack the high energy tail of the corresponding Maxwell–Boltzmann distributions and hence, the product molecules are said to be transla-

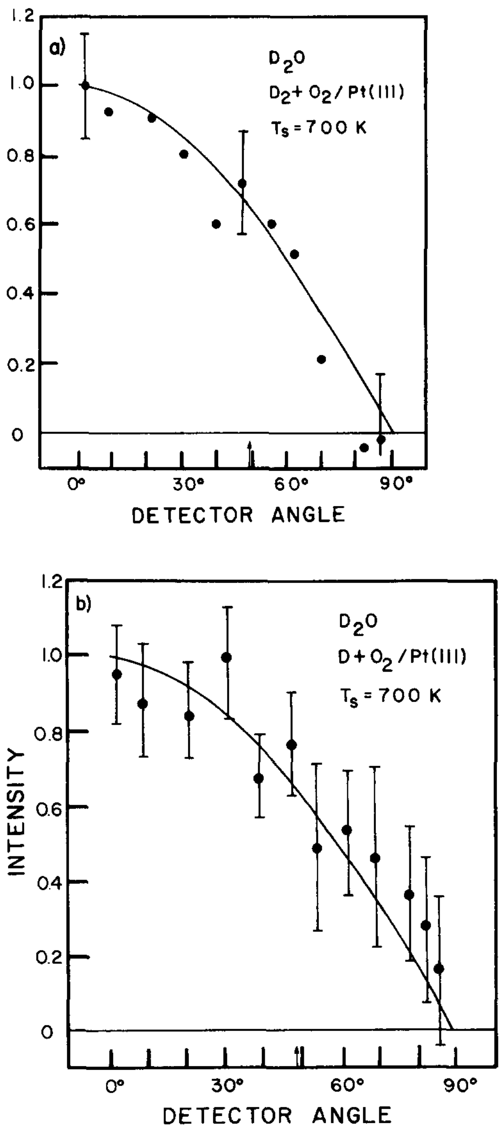

FIG. 3. Product D_2O angular distribution $T_s = 700$ K. (a) $D_2 + O_2$; (b) $D + O_2$.

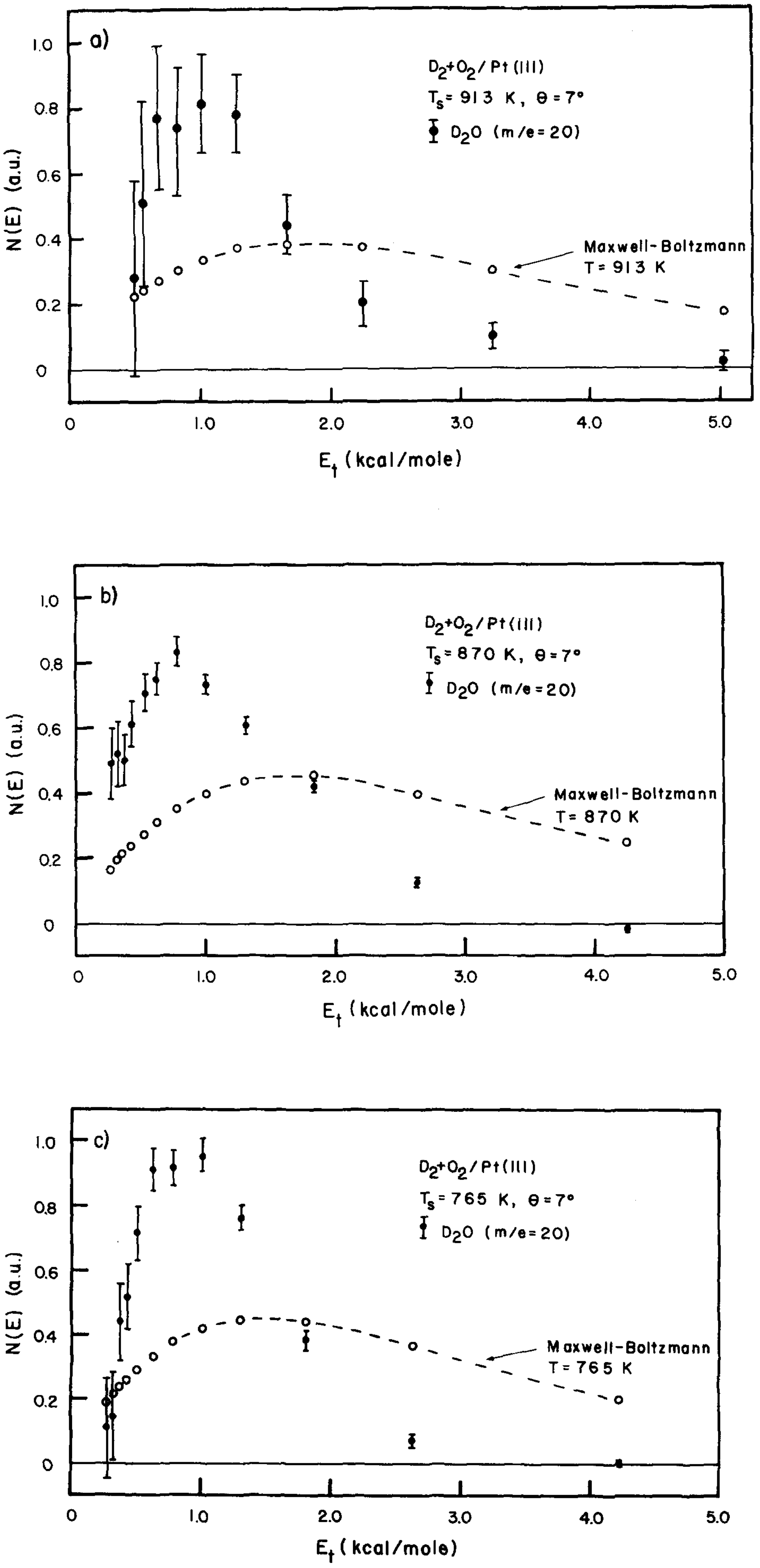

FIG. 4. D_2O translational energy distributions for (a) T_s = 913 K, θ = 7°; (b) T_s = 870 K, θ = 7°; (c) T_s = 765 K, θ = 7°. Open circles represent the corresponding Maxwell–Boltzmann distributions normalized to the total signal of the experimental distributions.

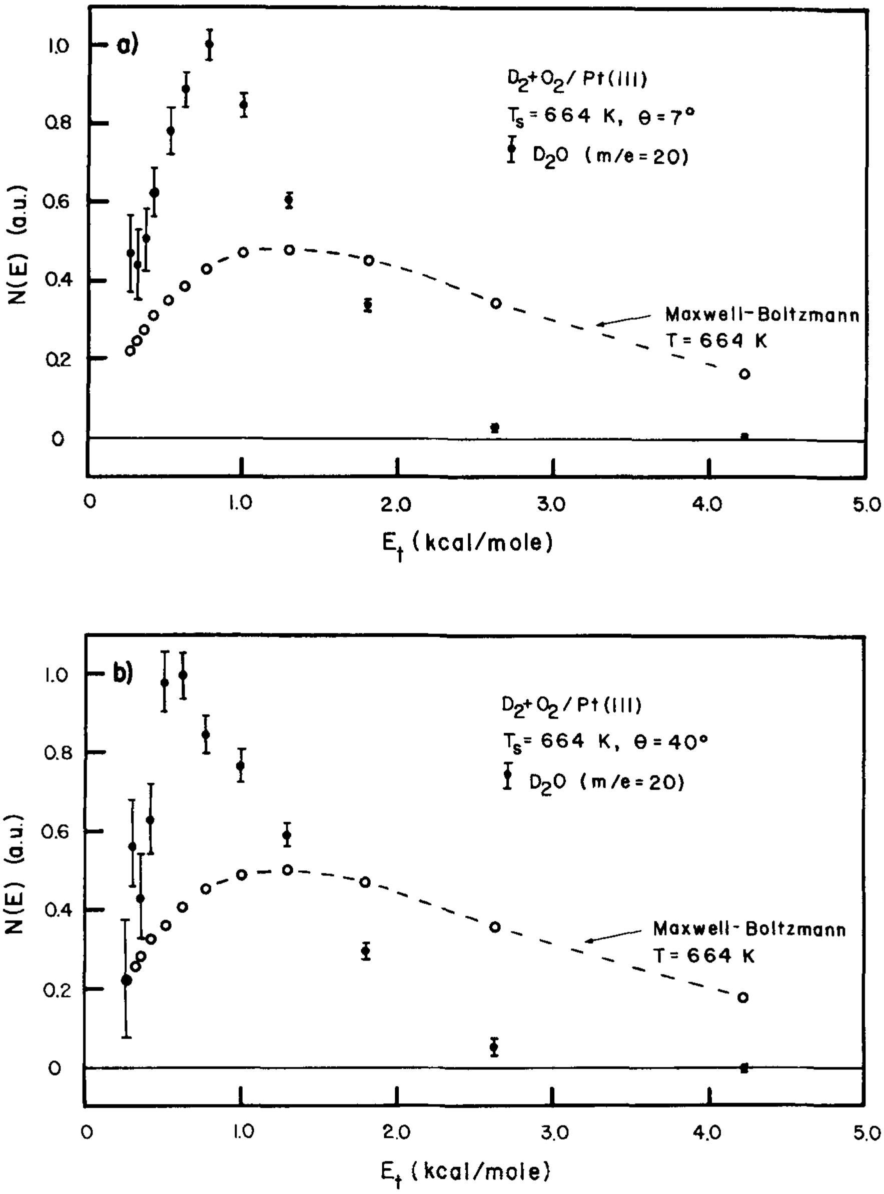

FIG. 5. D_2O translational energy distributions for T_s = 664 K (a) $\theta = 7°$; (b) $\theta = 40°$. Open circles represent the corresponding Maxwell–Botlzmann distributions.

tionally cold. The mean energies in terms of equivalent temperature $\langle E\rangle/2k$, the statistical errors of the mean energies, and the widths $\sigma^2 = (\langle v^2\rangle - \langle v\rangle^2)/\langle v\rangle^2$ are tabulated in Table I.

The relative D_2O production rates at the five temperatures examined in this study are shown in Fig. 6(a). The D_2O production rate as a function of the O_2 source stagnation pressure is shown in Fig. 6(b). The production rate is approximately linear with O_2 intensity. The production rate is nearly independent of D_2 intensity and was essentially unchanged when the D_2 source stagnation pressure was reduced from 200 to 100 Torr. The H_2 sticking coefficient for dissociative adsorption has been measured to be approximately 0.10 on Pt(111).[14-16] A wide range of values has been reported for the O_2 dissociative adsorption probability[12,17-21] which appears to fall exponentially with decreasing defect density and with increasing oxygen coverage.[12,17-19] In this study, it appears that the O_2 dissociative adsorption probability is limiting the rate.

DISCUSSION

These observations of translationally cold molecules produced in a surface chemical reaction are unusual. Previously measured translational energy distributions of product molecules are substantially more energetic than the equilibrium, Maxwell–Boltzmann distributions

TABLE I. Mean D_2O translational energies and distribution widths $\sigma^2 = (\langle v^2\rangle - \langle v\rangle^2)/\langle v\rangle^2$ as a function of surface temperature and scattering angle.

Temperature, angle	Translational energy	Distribution width
664 K, 7°	283 ± 11 K	0.065 ± 0.013
664 K, 40°	277 ± 11 K	0.067 ± 0.013
765 K, 7°	305 ± 12 K	0.065 ± 0.013
870 K, 7°	321 ± 11 K	0.071 ± 0.013
913 K, 7°	400 ± 53 K	0.101 ± 0.028
913 K, 47°	470 ± 53 K	0.101 ± 0.029

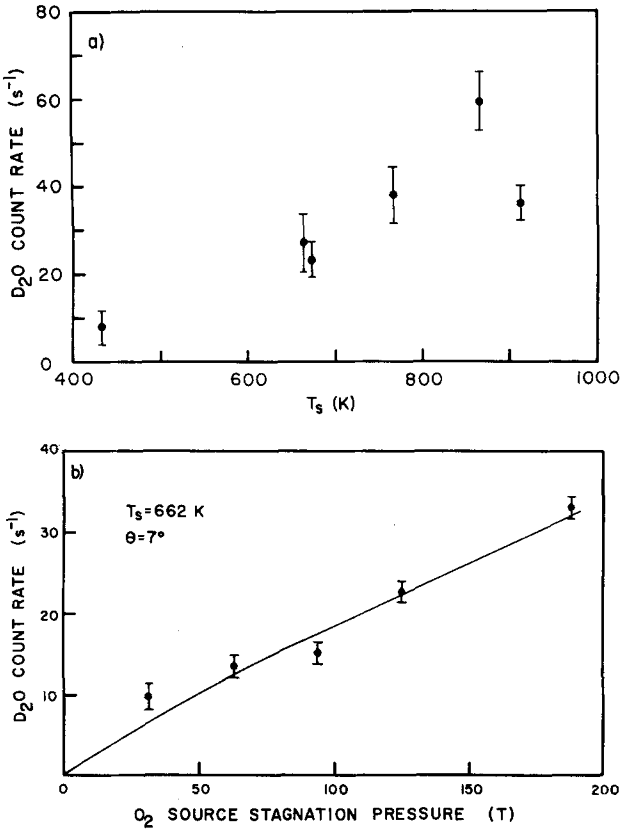

FIG. 6. D_2O production rate (a) as a function of surface temperature; (b) as a function of O_2 stagnation pressure.

at the temperature of the solid. This is the case for H atom recombination on Ni and Pd[1-4] and for the oxidation of CO on Pt.[5]

In order to discuss the possible mechanisms for the production of translationally cold product molecules, it is necessary to understand the energetics of the adsorption of D_2, O_2, OD, and D_2O on Pt(111). An energy level diagram is shown in Fig. 7. The overall reaction

$$D_{2(g)}+O_{2(g)}\rightarrow D_2O_{(g)}+O_{(a)}$$

is exoergic by 83 kcal/mol. The majority of this energy is not available to translation of the molecule away from the surface but is released and dissipated into the solid during the dissociative adsorption of the reactants. The dissociative adsorptions of D_2 and O_2 on Pt(111) liberate 15 kcal/mol[15,16,22] and 50 kcal/mol,[12,23] respectively. A weaker dissociative state of hydrogen on Pt(111) is populated at high coverages[16] with a heat of adsorption of 5 kcal/mol. In addition to these states, evidence for a H_2 molecular precursor state with a heat of adsorption of much less than 5 kcal/mol[15] and a O_2 molecular precursor state with a heat of adsorption of 8 kcal/mol[12,23] has been cited. However, since the surface temperatures at which this reaction was carried out are high, only the deeper dissociative states of D_2 and O_2 are significantly populated. Additional support for the dissociative state of D_2 comes from the fact that the D_2O angular distributions are identical whether the starting reactant is D_2 or D. Now, if the three adsorbed atomic species, 2D and O, shown if Fig. 7 simultaneously collided and then desorbed immediately following their reaction forming D_2O, 18 kcal of energy would be available to translational energy. However, a two-body collision forming an OD species followed by a second collision with $D_{(a)}$ or $OD_{(a)}$ is more likely than a three-body collision. This two-step mechanism requires the presence of stable OD radicals on the surface. Recently, OH radicals adsorbed on the Pt(111) surface have indeed been observed[24] and Lin and co-workers have observed desorption of OH radicals during the water production reaction on an un-

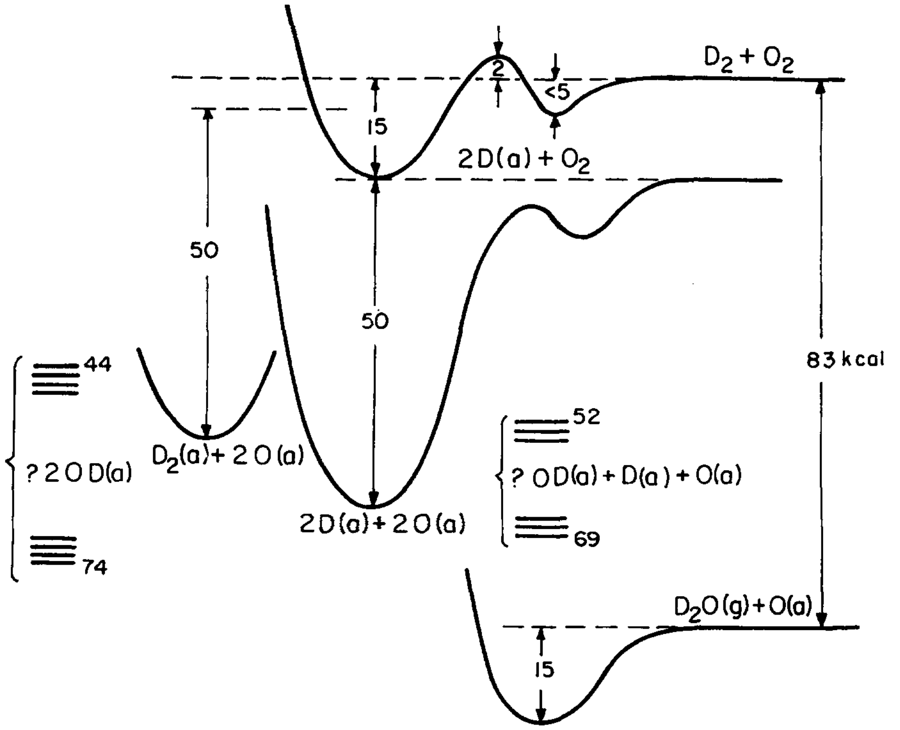

FIG. 7. Energy levels of reactants, intermediates and products. D binding energy from Ref. 22, O binding energy from Refs. 12 and 23, OD binding energy from Ref. 25, D_2O binding energy from Ref. 26, gas phase bond energies from Ref. 38.

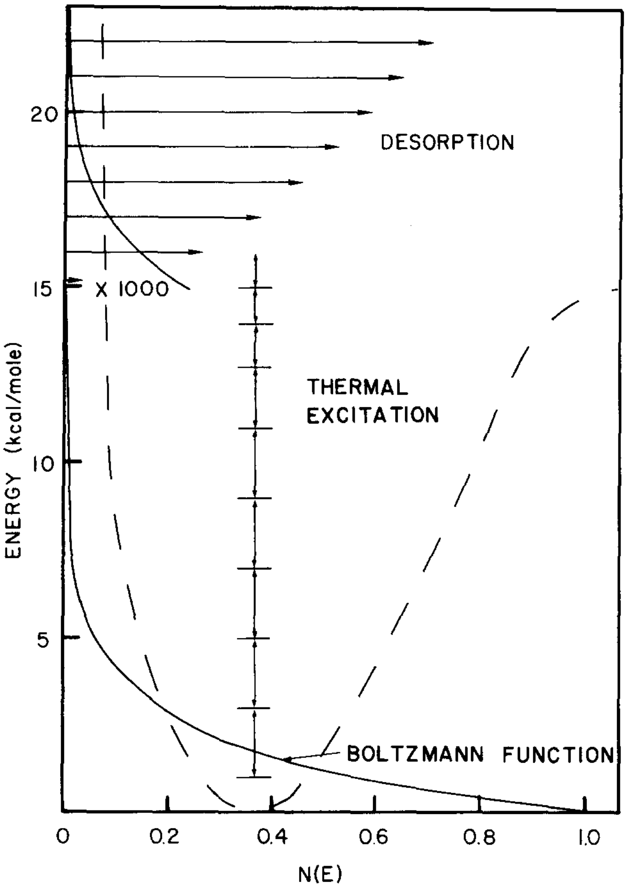

FIG. 8. Diagrammatic representation of D_2O desorption. The solid curve is the equilibrium population of energy levels given by the Boltzmann function $\exp(-E/R\ 870\ \mathrm{K})$ for energy E, and is drawn relative to the 15 kcal/mol Pt–D_2O well depth (Ref. 26) (dashed line). The appearance into the gas phase is proportional to v_z (Ref. 27), and increases with energy above the edge of the potential energy well, as indicated by the arrows. Molecules are thermally excited to the higher energy states.

characterized polycrystalline Pt surface. They reported an apparent activation energy of 31 kcal/mol[25] for OH appearance in the gas phase. In the two-step mechanism the amount of energy available to translation is dictated by the exoergicity of the second step $\mathrm{OD}_{(a)}+\mathrm{D}_{(a)}\rightarrow \mathrm{D_2O}_{(g)}$. Since the bond energies of D–Pt and of $\mathrm{D_2O}_{(g)}$ are known, the amount of energy believed to be available for translation depends acutely on knowledge of the binding energy of the OD radical to the Pt surface. If the apparent activation energy quoted above represents the OH binding energy on a clean platinum single crystal surface, then the exoergicity of the reaction, or the total energy available to translation is about 30 kcal/mol for the $\mathrm{OD}_{(a)}+\mathrm{D}_{(a)}\rightarrow \mathrm{D_2O}_{(g)}$ reaction and 39 kcal/mol for the $\mathrm{OD}_{(a)}+\mathrm{OD}_{(a)}\rightarrow \mathrm{D_2O}_{(g)}$ reaction. It is likely, however, that this measurement of the OH binding energy is not applicable to a clean Pt(111) surface since the binding energy of water in this same experiment was measured to 14 kcal/mol less than that known for water on Pt(111).[26] Consequently, if we assume that the OH binding energy is similarly in error by 14 kcal/mol error, then the total energy available to translation is 17 kcal/mol for the $\mathrm{OD}_{(a)}+\mathrm{D}_{(a)}$ reaction and 9 kcal/mol for the $\mathrm{OD}_{(a)}+\mathrm{OD}_{(a)}$ reaction. The uncertainty in the energetics involving the OD intermediate is shown in Fig. 7.

It is clear that the chemical energy released is not predominantly transferred into translation of the molecule away from the surface. The average energies of the measured distributions are hardly a tenth of these exoergicities. It might be suggested that the OH binding energy is actually larger than the values discussed above, such that the final bond formation step has really very little or no excess energy. However, a final reaction step with a small exoergicity cannot explain these velocity distributions. Kinetic measurements have shown that reaction times are long; 63 μs at 850 K to 1 ms at 600 K.[9] Since these times are long, the intermediates attain equilibrium with the surface and thus, the energy of the D_2O molecule should be at least that which would correspond to the equilibrium state of the reactants $\mathrm{OD}_{(a)}$ and $\mathrm{D}_{(a)}$. Consider, however, a mechanism in which the bond formation step and the desorption process are not concerted. That is, once the D_2O molecule is formed, it remains on the surface for many vibrational periods, dissipating the energy released in the bond formation step to the surface and thereby attaining equilibrium with the surface. Figure 8 represents such an ensemble of equilibrated D_2O molecules. The solid curve is the Boltzmann function for a temperature of 870 K and it is shown relative to a representation of the 15 kcal/mol D_2O–Pt potential energy well[26] (dashed curve). Approximating the density of vibrational levels by the density of levels for an harmonic oscillator and integrating over the well depth, one finds that more than 99% of the initial ensemble is trapped in the well.

As indicated in Fig. 8, the rate of desorption increases with increasing energy and is proportional to the normal component of the velocity v_z, i.e., $v\cos\theta$.. The probability of observing a given translational energy in the gas phase is proportional to the desorption rate, the probability of populating an energy level above the well and the density of states. For adsorbed molecules whose energies are characterized by a Boltzmann distribution, the translational energy distribution of the desorbing flux is given by the Maxwell–Boltzmann distribution $v^3\exp(-mv^2/2kT)$, and the angular distribution of the flux is given by $\cos\theta$ where θ is measured from the surface normal.[27] These distributions hold, however, only if the rate of thermal excitation of the adsorbed molecules by the solid is fast relative to the desorption rate.[27–29] If the desorption rate is fast relative to the excitation rate, then the desorption process depletes molecules from the upper energy levels thereby perturbing the energy distribution away from equilibrium.[30] The result is that the observed velocity distribution is slower than that expected from adsorbed molecules in equilibrium with the surface.[28,29,31] Our observations are not out of line with this mechanism. Early studies of gas phase reactions indicated that nonequilibrium effects are important when the ratio of the activation energy to temperature E_a/kT is less than 5–10.[32–34] In our case, E_a/kT ranges from 17 to 9, the upper limit set by those studies. Tully and co-workers have predicted strong nonequilibrium effects for Xe and Ar desorption from Pt(111) for $E_a/kT=10$, and that these effects persist for somewhat larger ratios.[29,31] Attempts to confirm this mechanism by scattering a beam of low energy (0.2 kcal/mol) water molecules from the surface, subsequently trapping them and then measuring their velocity distribution were unsuccessful because of the low sticking probability of H_2O at the surface temperatures at which the reaction was carried out. It was not possible in either the angular or velocity measurements to separate clearly the inelastically scattered molecules from the small number of desorbing molecules.

The amount of energy that can be transferred from the solid to perpendicular motion of the adsorbed molecule is limited because energy in that coordinate leads to desorption. Since motion parallel to the surface does not lead to desorption, the average parallel velocity component is larger than the perpendicular component. This has two consequences: the angular distribution will be slightly broader than cosine and the mean velocities will be larger as the desorption angle increases.[31] These trends are observed in calculations of Ar and Xe desorption from Pt(111).[29] If coupling between the parallel and perpendicular motion is strong, then the angular distribution should become more similar to a cosine function and the mean velocities more angle independent. The motions of the structurally complex and strongly bound D_2O molecule should exhibit more efficient coupling than those of Ar or Xe, so that the cosine angular distribution and apparent angular independence of the velocity (Fig. 5) are not inconsistent with nonequilibrium desorption.

This mechanism for desorption predicts that the mean translational energy dependence on surface temperature should be linear at low surface temperatures. As the surface temperature is increased, the mean translational energy will gradually decrease from the equilibrium value and finally arrive at some asymptotic value. This behavior was observed in an early study of the mean energies of a variety of molecules scattered from a graphite surface.[35] The mean energies were independent of incident beam energy which indicates that the molecules were indeed trapped and that what was being observed was nonequilibrium desorption. Since the rate of the production of D_2O on Pt decreases drastically at low T_s, it is impossible to carry out the TOF measurements at low T_s. Thus, it is reasonable that this linear region is not observed in Table I. In the intermediate range of T_s, the mean values of the D_2O translational energies have a weak positive dependence on surface temperature as shown in Fig. 9. However, instead of reaching an asymptotic value they increase more rapidly at higher temperatures. This is an interesting observation. If nonequilibrium desorption is occurring, then the interaction between D_2O and the surface must have become substantially more attractive at the higher surface temperature 913 K. This could be a result of a change in coverage of the reactants whose presence modifies the interaction between D_2O and the Pt surface. Oxygen is the more likely of the reactants to be the cause of this shift since the recombination–desorption temperature of O_2 on Pt(111) occurs between 850–900 K, depending on coverage. However, there is no correlation between the amount of oxygen remaining on the surface after the reaction and the surface temperature. There was always an oxygen coverage of 10%–20% of a monolayer after the reaction, regardless of the temperature (440–920 K) of the reaction. The temperature stability of this adsorbed oxygen indicates that it is probably in an oxide form.[23] There remains the question as to whether the steady state concentration of chemisorbed oxygen has changed at the highest temperature studied. This is likely because, as discussed below, the rate of the reaction also levels off here, presumably because of recombination and desorption of O_2 or of the desorption of the OH radical. However, thermal desorption experiments of the coadsorption of water and oxygen on Pt(111)[26] and on Ag[36,37] have shown that the effect of chemisorbed oxygen is to increase the binding energy of water. The loss of the source of increased attraction at $T_s = 913$ K would have the effect of decreasing the mean energy of the D_2O molecules desorbing from the 913 K surface relative to desorption from the 870 K surface. The opposite effect is observed.

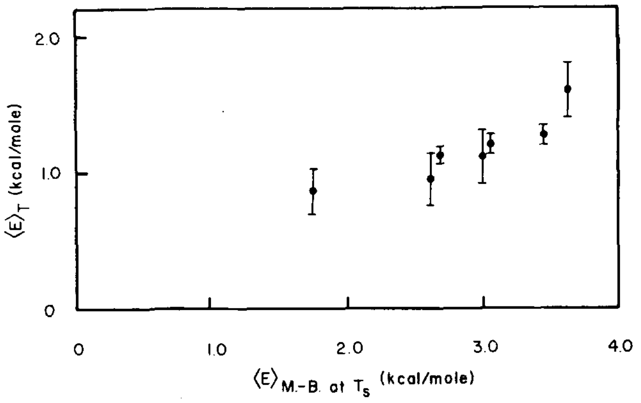

FIG. 9. Mean D_2O translational energy vs $2kT_s$.

Because of this observation at $T_s = 913$ K, another mechanism for the production of unequilibrated cold product molecules is considered. As discussed above, it is likely that the reaction proceeds through the formation of an OD intermediate. The DO–D distance is then the primary reaction coordinate for the final step of the reaction. Since the potential energy surface is multidimensional, the potential energy as a function of that coordinate is also likely to be a strong function of the Pt–OD distance. If the DO–D bond formation step and the desorption step are concerted, no energetic or dynamical restrictions on the reaction exist and no exoergicity is channeled into translation, the D_2O translational energy distribution will reflect the distribution of energies of the Pt–OD bond since OD(*a*) is the heavier reactant. For long surface residence times, this distribution of energies will be Boltzmann at the temperature of the surface. However, if the reaction occurs for a limited range of positions and momenta of the Pt–OD oscillator then a Boltzmann distribution at T_s is not expected. The observation of a cold product translational energy distribution implies that two restrictions on the position and energy of the Pt–OD bond at the time of the reaction are in effect. First, a minimum in the potential energy of interaction must exist when the Pt–OD bond is extended from its equilibrium position. This minimum in the interaction energy may be a result of a lack of the steric hindrance present between a bent Pt–OD oscillator nearer to its equilibrium position and the $D_{(a)}$ which approaches slowly compared to the Pt–OD rotational period. Second, because the Pt–OD species are an ensemble with a Maxwell–Boltzmann distribution of energies, the range of vibrational energy levels of the Pt–OD species that are reacting must be restricted. That is, only a very small range of vibrational levels of the Pt–OD species will effectively form the product molecule. The minimum excitation energy may be set by the amount of excitation in the Pt–OD oscillator necessary to attain an extended position. Thus, when only a small number of vibrational levels are reactive and when the reaction occurs as the Pt–OD bond is extended and hence moving slowly near its classical turning point, the translational energy of the D_2O molecule will reflect the low kinetic energy of the Pt–OD oscillator at the time of the reaction. The observed translational energy distribution will then be colder than an equilibrium distribution. Of course, half of the reactive events are occurring when the Pt–OD oscillator is extended but is moving towards the surface. Any energy transfer as these newly formed molecules are reflected from the surface will modify the nascent energy distribution. Thus, it is likely that the nascent distribution is even colder than that observed.

This simple picture for the origin of translationally cold D_2O suggests three trends. First, a sharp delineation between reactive and nonreactive vibrational levels of the Pt–OD oscillator should not result in translational energy distributions that are dependent on surface temperature. As can be seen in Fig. 9, the mean translational energy is not strictly independent of surface temperature. However, the picture presented here depicts the Pt–OD species as a diatomic molecule but, realistically, the adsorbed OD radical has other vibrational and librational modes which may be coupled weakly to the reaction coordinate. The weak temperature dependence could result from the population of these modes on which there are no restrictions. The more rapid increase in the mean translational energy and in the width of the energy distribution at higher temperatures indicates, however, that these restrictions on the position and energy of the reacting Pt–OD oscillator have been relaxed above 870 K. Secondly, this model predicts an increase in reaction rate as a function of surface temperature. Our measurements show a sixfold increase in rate over a temperature range of 450 to 870 K. Previous measurements[9] indicate a larger increase in rate by a factor of 10–15. In both sets of measurements, however, the rate of the reaction begins to level off at about 920 K, presumably because of a significant desorption rate of O_2[23] and OD.[25] Lastly, if the probability of the reaction is determined strictly by the extension and energy of the Pt–OD bond, the velocity of the newly formed molecule is isotropic. Since the arrival rate of the product molecules at the detector is proportional to the perpendicular component of the velocity, the angular distribution of both the flux and density of molecules will fit a cosine function. This is indeed the case for all temperatures to 870 K. At 913 K, however, some anisotropy of the velocity is apparent as indicated in Table I.

In general, the angular distribution of any reaction product formed through a concerted final bond formation step and desorption step can be described by a cosine function if the velocity of the newly formed molecule is isotropic. The dynamics of the reaction determine how the isotropy is achieved. It is unnecessary for the velocity to have the equilibrium value. Thus, the common association of a cosine angular distribution with equilibrium between the gas and the surface is not always correct. Angular distribution measurements as the sole means of determining energy exchange are inadequate.

CONCLUSION

The product angular and translation energy distributions of D_2O have been measured for the temperature range $T_s = 440–913$ K. Although the angular distributions can be described by a cosine function, the translational energies are low, $\langle E \rangle / 2k = 280$ K at $T_s = 664$ K. The low translational energies may be due to nonequilibrium desorption of the reaction product. Assuming this mechanism, the cosine angular distribution and the isotropy of the translational energy imply efficient coupling of tangential and perpendicular motion of the adsorbate. If, however, the final bond formation step and the desorption step are concerted, then the dynamics of the reaction are limiting the velocity. Features of a dynamical mechanism that would lead to the production of translationally cold molecules are discussed.

Finally, it is becoming increasingly apparent that product molecules do not necessarily thermalize on the surface leading to the loss of the desired dynamical information. These types of measurements are beginning to provide and hold further promise of providing distinctive clues about the dynamics of the molecule–surface interaction.

ACKNOWLEDGMENTS

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[1] A. E. Dabiri, T. J. Lee, and R. E. Stickney, Surf. Sci. **26**, 522 (1971).

[2] G. Cosma, R. David, and K. D. Rendulic, Phys. Rev. Lett. **38**, 775 (1977).

[3] G. Cosma, R. David, and B.-J. Schumacher, Surf. Sci. **85**, 45 (1979).

[4] G. Cosma, R. David, and B.-J. Schumacher, Surf. Sci. **95**, L210 (1980).

[5] C. A. Becker, J. P. Cowin, L. Wharton, and D. J. Auerbach, J. Chem. Phys. **67**, 3394 (1977).

[6] D. A. Mantell, S. B. Ryali, B. L. Halpern, G. L. Haller, and J. B. Fenn, Chem. Phys. Lett. **81**, 185 (1981).

[7] S. L. Bernasek and S. R. Leone, Chem. Phys. Lett. **84**, 401 (1981).

[8] S. T. Ceyer, Ph.D. thesis, University of California, Berkeley, 1979.

[9] J. N. Smith, Jr. and R. L. Palmer, J. Chem. Phys. **56**, 13 (1972).

[10] S. T. Ceyer, W. J. Siekhaus, and G. A. Somorjai, J. Vac. Sci. Technol. **19**, 726 (1981).

[11] G. Cosma, R. David, and B.-J. Schumacher, Rev. Sci. Instrum. **52**, 789 (1982).

[12] J. L. Gland, Surf. Sci. **93**, 487 (1980).

[13] G. Cosma, *Proceedings of the Seventh International Vacuum Conference and Third International Conference on Solid Surfaces* (IVC-ICSS, Vienna, 1977), p. 1317.

[14] D. L. Smith and R. P. Merrill, J. Chem. Phys. **53**, 3588 (1970).

[15] M. Salmeron, R. J. Gale, and G. A. Somorjai, J. Chem. Phys. **67**, 5324 (1977); **70**, 2807 (1979).

[16] K. Christman, G. Ertl, and T. Pignet, Surface Sci. **54**, 365 (1976).

[17] H. Hopster, H. Ibach, and G. Cosma, J. Catal. **46**, 37 (1977).

[18] D. R. Monroe and R. P. Merrill, J. Catal. **65**, 461 (1980).

[19] H. P. Bonzel and R. Ku, Surf. Sci. **40**, 85 (1973).

[20] B. Lang, R. W. Joyner, and G. A. Somorjai, Surf. Sci. **30**, 454 (1972).

[21] W. H. Weinberg, R. M. Lambert, C. M. Comrie, and J. W. Linnett, Surf. Sci. **30**, 299 (1972).

[22] K. E. Lu and R. R. Rye, Surf. Sci. **45**, 677 (1974); J. Vac. Sci. Technol. **12**, 334 (1975).

[23] J. L. Gland, B. A. Sexton, and G. B. Fisher, Surf. Sci. **95**, 587 (1980).

[24] G. B. Fisher and B. A. Sexton, Phys. Rev. Lett. **44**, 683 (1980).

[25] L. D. Talley, D. E. Tevault, and M. C. Lin, Chem. Phys. Lett. **66**, 584 (1979); D. E. Tevault, L. D. Talley, and M. C. Lin, J. Chem. Phys. **72**, 3314 (1980); L. D. Talley, W. A. Sanders, D. J. Bogan, and M. C. Lin, *ibid.* **75**, 3107 (1981).

[26] G. B. Fisher and J. L. Gland, Surf. Sci. **94**, 446 (1980); The peak water desorption temperature was increased by 5 K after 0.3 ℓ exposure of water at 100 K to Pt (111) surface pre-exposed to 0.35 ℓ of oxygen.

[27] G. Armand, Surf. Sci. **66**, 321 (1977).

[28] A. T. Modak and P. J. Pagni, J. Chem. Phys. **65**, 1327 (1976).

[29] J. C. Tully, Surf. Sci. **111**, 461 (1981).

[30] P. J. Pagni and J. C. Keck, J. Chem. Phys. **58**, 1162 (1973).

[31] E. K. Grimmelmann, J. C. Tully, and E. Helfand, J. Chem. Phys. **74**, 5300 (1981).

[32] H. A. Kramers, Physica (Utrecht) **7**, 284 (1940).

[33] I. Prigogine and E. Xhrouet, Physica (Utrecht) **15**, 913 (1949).

[34] E. W. Montroll and K. E. Schuler, Adv. Chem. Phys. **1**, 361 (1958).

[35] W. J. Siekhaus, J. A. Schwarz, and D. R. Olander, Surf. Sci. **33**, 445 (1972).

[36] E. M. Stuve, R. J. Madix, and B. A. Sexton, Surf. Sci. **111**, 11 (1981).

[37] S. T. Ceyer and J. T. Yates, Jr. (in preparation).

[38] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, New Jersey, 1950), *Electronic Spectra of Polyatomic Molecules* (Van Nostrand, Princeton, New Jersey, 1966).