Dynamics of D$_2$ released from the dissociation of D$_2$O on a zirconium surface

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Hydrogen is efficiently released during water dissociation on zirconium (Zr), while even very rapid temperature programmed heating of a hydrogen covered Zr surface predominantly leads to dissolution (99\% dissolution). To help resolve these apparently contradictory observations, we have studied the dynamics of water (D$_2$O) dissociation on a crystalline Zr surface by probing the rotational and vibrational energy distributions of the D$_2$ produced using resonant enhanced multiphoton ionization spectroscopy. The internal-state energy distribution of the D$_2$ product was found to be rotationally cold and vibrationally hot with respect to the temperature of the surface. The rotational distribution shows slight deviations from Boltzmann’s law, with a mean rotational temperature of 426 K while the surface is at 800 K. The population of the $v'=1$ vibration is at least four times higher than a 800 K temperature would allow, this corresponding to a vibrational temperature of 1100 K. Information on the translational energy of the D$_2$ product have also been obtained by time-of-flight spectroscopy and it is found to be nearly thermally equilibrated with the surface temperature. Similar results were obtained from studies of D$_2$ scattered from a clean Zr surface, and of D$_2$ released by a slow thermal desorption process which involves dissolved hydrogen as the source. The reconciliation of the present results with those for thermal desorption of preadsorbed hydrogen implies a role for both surface and subsurface adsorption sites on the Zr surface and clearly demonstrates that at high temperatures, the release of D$_2$ arises from the recombinative desorption of adsorbed hydrogen formed by the complete dissociation of D$_2$O. © 2006 American Institute of Physics. [DOI: 10.1063/1.2179798]

I. INTRODUCTION

Understanding the structure and reactivity of water has been one of the most interesting and challenging problems of chemistry and physics. As early as 1781 Lavoisier tried to understand the nature of water and for this purpose studied its chemical reactivity with metallic iron.\footnote{Electronic mail: hepburn@chem.ubc.ca} Despite the tremendous amount of research that has been done on the subject since Lavoisier and the level of sophistication of modern experiments, the reactivity of water with metallic surfaces is still not well understood with a number of controversies still attracting attention.\footnote{Electronic mail: hepburn@chem.ubc.ca} Even apparently simple questions relating to whether water dissociates or not remain in dispute on surfaces such as Ru(0001).\footnote{Electronic mail: hepburn@chem.ubc.ca} Water interactions with solid surfaces have been the subject of two very interesting review articles which report studies done mainly under ultrahigh vacuum (UHV) conditions.\footnote{Electronic mail: hepburn@chem.ubc.ca} The reviews provide a good summary of our current understanding of water interactions with surfaces, as well as the difficulties associated with the experimental techniques for probing water on surfaces.

Water dissociation on and release of hydrogen from metal surfaces are always assumed to proceed via step(s) in which water is first adsorbed on the surface and then dissociates into adsorbed oxygen and hydrogen atoms, perhaps sequentially, leading to at least the transient existence of adsorbed hydroxyls. The hydrogen is then assumed to desorb by recombination of two H atoms, largely unaffected by the presence of adsorbed O. Adsorbed oxygen is often found to act as a cocatalyst for reaction, resulting in autocatalytic kinetics.\footnote{Electronic mail: hepburn@chem.ubc.ca}

These ideas are essentially at a kinetic and phenomenological level. The dynamics of the dissociation of water on
metal surfaces is completely unexplored, hence our interest in this project. The specific interest in the Zr/D2O system arose from observations on the presence or nearly the complete absence of hydrogen release during water dissociation and thermal desorption of preadsorbed hydrogen, respectively.

A second advantage of the Zr/water system for our experimental approach is that at sufficiently high temperatures (800 K) the adsorbed oxygen released by the dissociation event can dissolve into the bulk of the Zr sample, thus maintaining a steady-state oxygen coverage and preventing the poisoning of the surface. This situation is essential in the resonant enhanced multiphoton ionization (REMPI) experiments as data accumulation times are long, and the water beam has to be on target for many hours. This advantage of the Zr/water system is not found with most other transition metals such as nickel, iron, or platinum. These transition metals could show high initial reactivity and hydrogen evolution at 800 K but, as none of them dissolve oxygen, rapid poisoning of the surface is expected by the adsorbed oxygen as both bare metal sites and adsorbed O are required for reaction. We now summarize some basic observations of the Zr/water and Zr/hydrogen systems that are relevant in understanding the background to the experiments.

A. Water dissociation on Zr

The dissociation of water on Zr surfaces has been well characterized and is found to be autocatalytic with respect to the adsorbed oxygen product at low temperatures. These earlier studies have shown that at low temperatures the water dissociates into adsorbed H and OH (Had, OHad) followed by the further dissociation of the OHad into adsorbed O (Oad) and Had. Strikingly, upon warming, little release of hydrogen was detected. Mass balance was therefore achieved by assuming that the Had dissolved into the bulk, consistent with the behavior of Had produced by hydrogen exposure.

At elevated temperatures, many metals, including Zr, exhibit high reactivity for water dissociation and autocatalytic behavior with respect to Oad. Reaction is accompanied by the release of hydrogen, assumed to occur by recombinative desorption of two Had. At temperatures at which Oad rapidly dissolves into the Zr bulk, a dynamically stable surface can be produced with the oxygen coverage determined by the pressure in the water beam and the temperature. Under these conditions hydrogen is efficiently released with estimates of 25% of the collisions of water molecules with the surface resulting in hydrogen desorption. This result contrasts with the very limited (∼1) desorption observed from a preadsorbed hydrogen layer, even at extremely high heating rates. This is summarized in the next section.

B. Hydrogen adsorption and desorption from Zr

Studieds of the thermal desorption of hydrogen from Zr surfaces at heating rates of 1–100 K/s showed very little hydrogen desorption, with most of the hydrogen disappearing from the surface via hydrogen dissolution. Even at heating rates of 1010 K/s less than 1% of the adsorbed hydrogen desorbed. The origin of this effect lies in the fact that the activation barrier to dissolution is much smaller than for desorption in this system. The fact that very little hydrogen desorption occurs from a preadsorbed hydrogen layer even at very high heating rates contrasts with the observation of efficient hydrogen release in the case of high temperature water dissociation.

On the basis of this discrepancy, some of the present authors proposed that a different pathway must therefore exist for water dissociation where molecular deuterium release occurs in a concerted manner whereby the hydrogen atoms never equilibrate with the metal surface. Such a mechanism implied an intramolecular hydrogen elimination by the water molecule as it binds to the surface. This mechanism should be characterized by dynamics that are distinct from hydrogen desorbed from a preadsorbed layer, which must originate from recombinative desorption of hydrogen atoms. The idea was that the energy released in the formation of the Zr–O bond (550 kJ/mol) (Ref. 6) would appear in the excitation of the outgoing hydrogen molecule. If true, this mechanism could be valid for many metal/water systems in which a highly exothermic metal-oxygen bond is formed. Since hydrogen release is expected in these other systems, recombinative desorption had always been assumed and there was never any suspicion of a direct unimolecular mechanism.

One way to test these assumptions is to have a careful look at the internal-state energy distribution of the product and this is the focus of the present experiments.

C. Hydrogen desorption and reaction: General comments

Direct gas-surface reaction between an incoming molecule and an adsorbed species is possible, and occurs by way of an Eley-Rideal mechanism, but the so called Langmuir-Hirschelwood mechanism where the reactants combine on the surface before desorbing is believed to be more common. The observation of a high amount of internal energy in the product is generally accepted as evidence for Eley-Rideal and is consistent with the higher exothermicity of the reaction. Rettner and Auerbach have demonstrated that these mechanisms have distinct dynamical signatures. It is therefore reasonable to expect that the exothermicity of the previously proposed concerted water decomposition on the zirconium surface would leave a high amount of internal energy in the product, just as an Eley-Rideal reaction would, assuming that there is no close contact between the surface and the hydrogen atoms prior to desorption. Keeping in mind that the proposed reaction mechanism is not strictly Eley-Rideal, the narrow angular distribution and the correlations between the initial and final state properties observed by Rettner and Auerbach are not expected, but the authors must admit that these have not been verified.

On the other hand, the recombinative desorption of hydrogen from copper surfaces is a Langmuir-Hirschelwood type mechanism, and the dynamics of the H2/D2 products have been extensively studied. Many other hydrogen-surface reactions have been studied but only the H2–D2/Cu and H2–D2/V systems have been investigated.
for all the three degrees of freedom of the desorbing molecule. In the D$_2$O/Zr case, if the hydrogen formation proceeds by recombinative desorption of adsorbed D, then the amount of internal energy of the molecule is expected to be relatively low; this is what we report herein.

To our knowledge this report describes the first experiments on the dynamics of hydrogen which are not produced by desorption from a preadsorbed layer, but rather produced via water decomposition on a metallic surface.

II. EXPERIMENT

The experiments were performed in a stainless steel ultrahigh vacuum chamber (see Fig. 1) equipped with a low-energy electron diffraction (LEED)/Auger spectrometer, a commercial quadrupole mass spectrometer (AccuQuad RGA300D), an Ar$^+$ gun, an oven source for H$_2$/D$_2$ which is a heated stainless steel capillary, a D$_2$O doser, and a zirconium single crystal cut from a 6 mm diam rod along the Zr(0001) or Zr(1010) face. The chamber was pumped with a turbomolecular pump, and a turbomolecular pump (Edward EXT70H). The base operating pressure of the main chamber was in the low 10$^{-10}$ Torr range. Prior to dosing, the crystal surface was bombardded with 2.5 kV Ar$^+$ ions and cleanliness verified with Auger spectroscopy. The crystals had previously been studied and shown to be free of segregatable impurities.$^8$

Heavy water (D$_2$O) was dosed on the crystal surface using a differentially pumped stainless steel capillary (125 μm ID). The use of D$_2$O helped reduce the effect of background hydrogen in the chamber. The crystal was resistively heated to 800 K using four tungsten filaments and the D$_2$ flux produced by D$_2$O decomposition was sent to a differentially pumped (turbomolecular Edward EXT70H) ionization time-of-flight (TOF) chamber. Under these operating conditions the main chamber pressure rose to the low 10$^{-9}$ Torr range.

The D$_2$ flux from the crystal was interrogated by a 6 ns pulsed laser beam focused approximately at 2–3 cm from the crystal surface and was ionized by a 2+1 REMPI process. An electric field was applied to separate the different masses and the ions were collected by a pair of microchannel plates. The signal was collected using a Tektronix TDS3032 oscilloscope and processed using our own software (programed in LABVIEW) to count individual ions, allowing selective D$_2$ detection for partial pressures below 5 × 10$^{-11}$ Torr. To record the spectrum of D$_2$ products, ions arriving at the detector within a defined time window were counted as a function of laser wavelength. The timing of the gate was set early on the oscilloscope to avoid collecting too many background ions as discussed further in Sec. III D.

Comparison of the resolved rovibrational lines with D$_2$ flux produced by an oven source allowed the populations to be determined. Calibration showed that the ion signal varies linearly with pressure (or density of D$_2$) and is quadratic with respect of the laser power. Time-of-flight spectra for the D$_2$ products were recorded at fixed wavelength by accumulating ion counts as a function of arrival time at the detector.

The time-of-flight spectrometer (represented schematically on Fig. 1) utilizes a stainless steel tip, a highly transparent gold mesh, a tube, and a pair of microchannel plates (MCPs). Deuterium was ionized between the tip and the gold mesh. 30 cm separates the ionization region from the pair of MCP. The potentials used for measuring the TOF distributions were different than the potentials used for spectroscopy, typically much lower. Due to the small D$_2$ flux (limited by the available sites on the surface), the TOF distributions were not acquired by field-free TOF but a small potential was used instead to collect ions more efficiently. Ion time-of-flight simulations were performed with Simion and on our homemade software to determine the electrode potentials and to ensure that the velocity distribution was conserved.

In order to excite D$_2$ to the $E,F \, ^1\Sigma^+_g$ state and to observe the $Q_f(0,0)$ and $Q_f(1,1)$ transitions with two photons, the wavelengths needed range from 201 to 205 nm. The light was produced by third harmonic generation (THG) of the output from a dye laser. The laser source includes the frequency-doubled output of a 20 Hz Quanta Ray Pro-290 yttrium aluminum garnet (YAG) laser which is used to pump a tunable Sirah PrecisionScan-DA-24 dye laser (using a 2:1 mixture of rhodamine 610 and rhodamine 640). The output of the dye laser is frequency doubled with a potassium dihydrogen phosphate (KDP) crystal and the two wavelengths are subsequently mixed using a beta-barium borate (BBO) crystal producing the desired wavelength with a typical output power of 1 mJ/pulse and a spectral resolution of approximately 0.002 nm.

III. RESULTS

A 300 K D$_2$ background spectrum was taken with the oven source not aligned with the entrance of the ionization...
chamber. The upper trace on Fig. 2 shows the Boltzmann plot for this background, and it is linear for a rotational temperature of 294±10 K. The spectrum was corrected for the quadratic dependence of the signal on the laser power prior to analysis. No obvious need to include rotational correction factors has been found, for D2 Q(J,0) with J=0–7 as they vary by less than 7%. At very low pressure (<10⁻⁹ Torr) this variation is within the noise level and their influence on the temperature determination is negligible. We concluded that our calculation is a good representation of the background L on the oscilloscope was set early to eliminate as much D2 produced by heavy water decomposition on a 800 K zirconium surface (open squares), and hot D2 at 800 K (full circles). In the ordinate title I(J) stands for the experimental intensity of a given J rotational line and g_a for its nuclear spin statistical weight.

A. Rovibrational populations of 800 K D₂

The lower panel of Fig. 3 shows the D₂ REMPI spectrum obtained from the oven source at 800 K. The spectrum has been corrected for laser power fluctuations and the time gate on the oscilloscope was set early to eliminate as much background D₂ as possible (the gate setting details are given in Sec. III D). The 300 K D₂ background has been consistently found to be 30±5% with an early gate and we consequently corrected the 800 K spectrum for 30% 300 K background. The ratio of the line strength for Q(J,0,0):Q(J,1,1) has been experimentally found to be 1:3:8 when averaged over J=0–4, which is in good agreement with literature values. It is obvious from Fig. 2 that the spectrum shows no important deviation from the 800 K Boltzmann distribution (lower trace, full circles), and the Boltzmann plot is reasonably linear with a rotational temperature of 822±50 K. The data were analyzed exactly the same way as mentioned in the previous section except for the background correction which is partly responsible for the larger error on the temperature (50 K versus 10 K). The gap between 203 and 203.6 nm in Fig. 3 indicates that Q(J,0,0) has not been measured.

Again there is not obvious need to include correction factors for the J dependence of the two-photon line strength. The hot D₂ spectrum shows nothing unusual and its comparison to the D₂ spectrum arising from water decomposition (Fig. 3) is straightforward.

B. Rovibrational populations of D₂ produced via water decomposition

The REMPI spectrum of D₂ produced by water decomposition on a zirconium single crystal at 800 K is presented in the top panel of Fig. 3. The gap between 202.6 and 203.6 nm indicates that the Q(J,0,0) and Q(J,0,0) transitions have not been measured. Calculations have been performed assuming 426 and 1100 K Boltzmann populations for rotations and vibrations, respectively, and are in good agreement with the experimental observations.

A few features arise from this spectrum that should be noted: (1) rotations are clearly colder than in their 800 K hot oven counterpart, (2) the Q(J,1,1) transition is stronger, indicating vibrational heating, and (3) the deviation from Boltzmann’s law, if any, is small.
Points (1) and (2) are better illustrated by Fig. 4, which shows both hot D\textsubscript{2} and D\textsubscript{2} produced via water decomposition on the same plot. The abscissa is expanded to show only the 204.010–204.045 nm region where \( Q_{10}(0,0) \) and \( Q_{3}(1,1) \) are almost coincident. The \( Q_{10}(0,0) \) transition which is the strongest for 800 K D\textsubscript{2} is strikingly absent when D\textsubscript{2} is produced via water decomposition on the zirconium surface. Only rotational cooling and/or vibrational heating of the D\textsubscript{2} product can lead to this situation. Moreover, the proximity of the two transitions ensures that the two lines were rigorously measured under the same experimental conditions.

Point (3) is well illustrated by the middle trace of Fig. 2 which is the Boltzmann plot for the \( Q_{10}(0,0) \) part of the D\textsubscript{2} REMPI spectrum arising from water decomposition. The plot is reasonably linear with an average rotational temperature of 426±50 K, with only \( Q_{2}(0,0) \) showing deviation from linearity. The \( Q_{2}(0,0) \) line is more intense than would be expected from a 426 K rotational temperature in this case. Since both thermal distributions (300 and 800 K) have a \( Q_{2}(0,0) \) line intensity that is consistent with the Boltzmann population, the discrepancy in the case of D\textsubscript{2} from water decomposition does not result from the rotational line strength. Further, the increased intensity for this line was consistently observed under different conditions of dosing and surface temperature. We have no explanation for this deviation from a Boltzmann distribution.

C. Translational energy of D\textsubscript{2} produced via water decomposition

The TOF distributions for single rovibrational states of D\textsubscript{2} produced by water decomposition were collected and compared to hot source distributions, allowing measurements of translational energy of the product. The TOF distributions have been measured for \( Q_{10}(0,0) \), \( Q_{3}(1,1) \), \( Q_{3}(0,0) \), \( Q_{3}(0,0) \), \( Q_{3}(0,0) \), \( Q_{3}(0,0) \), \( Q_{3}(1,1) \), and \( Q_{3}(1,1) \). The best signal to noise for TOF distributions from D\textsubscript{2} produced by water dissociation have been found for \( Q_{10}(0,0) \), which is shown in Fig. 5. The signal to noise in this case is determined not only by the population of the product but also by the population of the 300 K background that has to be subtracted from it. In this case, distributions that are hotter than the background are going to show a bigger signal to background ratio for high \( J \) values, which will translate into more accurate determination of the high velocity part of the total measured distribution. On the other hand, if the chosen \( J \) value is too high, its population will be insufficient, and the signal to noise of the distribution becomes small. As can be seen in the inset in Fig. 5, the background accounts for approximately half the signal (5:9) which gives a product to background ratio of 4:5 for \( Q_{10}(0,0) \). This ratio is even smaller for lower values of \( J \) whereas at higher values of \( J \) the low signal to noise prevents us from accurately measuring it. The background has been found to be very small for \( Q_{3}(0,0) \) and absent for \( Q_{3}(1,1) \), but in each case the signal to noise of the TOF distribution of the D\textsubscript{2} product is too low to accurately measure the translational energies.

This optimum value of \( J \) found again demonstrates that the product D\textsubscript{2} is rotationally hotter than 300 K but colder than what would be expected from an 800 K thermal distribution. In such a case the population should be high up to at least \( J=6 \) (see Fig. 3), which would give a product to background ratio much higher than 4:5.
As mentioned in Sec. II, the gate for spectroscopic measurements was set early to minimize the contribution of background to the spectrum. A typical setting of the gate is showed in the inset of Fig. 5. By counting only early ions the background contribution to the signal is greatly reduced and accounts for 30±5% of the total intensity of a given $Q_j(0,0)$ spectrum and is absent of $Q_j(0,1)$ and $Q_j(1,1)$ spectra. Given that there is no need to determine the individual arriving time of each ion but simply count how many of them are within the gate to record a spectrum, the sensitivity of the spectroscopic measurement is therefore at least one order of magnitude better than the translational energy measurement.

Figure 6 shows the $Q_j(0,0)$ TOF distribution of D$_2$ produced by water decomposition on a crystalline zirconium surface compared with an effusive source at 800 K. The product TOF is very close to its 800 K effusive source counterpart. This figure shows that the velocity of the product is nearly thermally equilibrated with the temperature of the surface. Calibration with the oven source shows that translational temperatures different by 200 K can be distinguished by our techniques.

D. Thermal desorption of D$_2$ from D dissolved in bulk Zr and from scattered D$_2$

It is necessary to compare the D$_2$ released after the dissociation of water, with that whose origin is clearly either adsorbed, absorbed, or scattered deuterium. This will provide further insight as to the origin of D$_2$ released after water dissociation. Accordingly we made additional measurements of the internal energy state distributions of D$_2$ desorbed from the Zr crystal at elevated temperatures (800 K) and scattered from 300 K D$_2$ beam impinging on an 800 K surface.

A word of explanation is in order, as we have previously indicated that deuterium is not thermally desorbed from Zr. For a sample in which the bulk is nearly free of dissolved D, any deuterium deposited on the surface would prefer dissolution over desorption. On the other hand, desorption of D$_2$ can be readily detected and measured if the bulk is “loaded” with deuterium.

The scattering experiment is a little more ambiguous in that the D$_2$ interrogated can arise from both direct molecular scattering and/or dissociation/desorption events. We currently have no means of distinguishing these possibilities.

For simplicity, we present only the data for the $Q_{10}(0,0)$ and $Q_{3}(1,1)$ lines. The $Q_{j}(1,1)$ spectra for the three cases (water dissociation, scattered D$_2$, and D$_2$ originating from dissolved D) show rotational temperatures that are consistent within the error limit and in agreement with the $Q_{j}(0,0)$ temperature of 426±50 K found for water dissociation. The rotational temperatures for the three cases mentioned before are of 358, 362, and 457±100 K, respectively, and all show the absence of the $Q_{10}(0,0)$ line. The top trace (a) in Fig. 4 shows the $Q_{10}(0,0)$ and $Q_{3}(1,1)$ lines for a thermal D$_2$ beam at 800 K. Trace (c) shows the same region for D$_2$ scattered from an 800 K Zr surface and is indistinguishable from trace (b) arising from water dissociation for which the $Q_{10}(0,0)$ line is absent as underlined earlier. Arguably a weak $Q_{10}(0,0)$ transition is apparent for D$_2$ desorption and can be seen around 204.02 nm on trace (d). This $Q_{10}(0,0)$ line is thought to arise from background 300 K D$_2$. As a matter of fact the D$_2$ background pressure measured in the chamber was higher for trace (d) than for any other spectra shown on Fig. 4. The D$_2$ background pressure goes approximately as follows: $10^{-10}$, $10^{-9}$, and $10^{-8}$ Torr for experiments (b), (c), and (d), respectively, and experiment (a) can be performed at even lower background pressures. The dynamics showed by experiments (b), (c), and (d) are indistinguishable; they all show rotational cooling and moderate vibrational heating with less than 2% of the population in $v=1$. There is very little evidence that would support the concerted mechanism here; the total amount of internal energy in the product is too low and the reaction is very exothermic (~307 kJ/mol). Any subtle differences not revealed by this experiment would not have a dramatic impact on our conclusion that the three processes are essentially the same: recombination of atomic deuterium on the Zr surface to form the gas phase molecule D$_2$.

IV. DISCUSSION

A. Implications of the D$_2$ dynamics observed for heavy water dissociation

Our results clearly indicate that the D$_2$ released by water dissociation exhibits a higher vibrational temperature and a lower rotational temperature than the surface, while the translation is found to be nearly thermally equilibrated with the surface. It has already been shown that desorbing H$_2$/D$_2$ exhibits rotational cooling and vibrational heating from many metallic surfaces and so it is logical to attribute the source of D$_2$ arising from water dissociation to adsorbed D atoms, as the dynamics are similar to the dynamics of hydrogen produced by thermal desorption from many metals, including Zr. This supports a mechanism for water...
decomposition that occurs in two steps: first the water undergoes dissociative chemisorption on the surface followed by recombinative desorption of D₂. This is the simplest mechanism and is entirely consistent with kinetic studies of water dissociation. In such a case the rovibrational distribution is explained and the quasithermal translational energy can be interpreted as a low barrier for D₂ adsorption on the zirconium/zirconium-oxygen surface. Overall, when the translational degree of freedom is taken in account, the energy balance cannot accommodate the high exothermicity of a concerted water decomposition/hydrogen desorption (∼307 kJ/mol). This is another argument in favor of the two step mechanism; in this case the heat of the water decomposition (∼477 kJ/mol) (Ref. 6) can dissipate in the metal before recombinative desorption of hydrogen occurs (170 kJ/mol).⁶

A few differences between the Cu/D₂ and Zr/D₂ systems are worth underlining. While the general picture of rotational cooling and vibrational heating still stands, the copper shows a D₂ population in the ν'=1 vibrational state of about 25% at 950 K (Refs. 18 and 23) against only 2% for heavy water decomposition on zirconium at 800 K. The translational temperature of D₂ desorbing from Cu is reported to be at least 3600 K,¹⁸ and we found 800±200 K for D₂ following D₂O decomposition on Zr. We also found that the temperature of the Zr surface does not influence the dynamics dramatically in the temperature range of 750–900 K, and thus the potential energy surface seems to be the determining factor. To understand the fine details of the dynamics, not only the height of the barrier is important but also its position. On a simple two dimensional potential energy surface, an early barrier (the entrance channel) mean translations will be more efficient in activating the reaction, while a late barrier (product channel) will be best activated by vibrations.³²,³³ The data for Cu/D₂ suggest an intermediate barrier with a rather large activation (i.e., the energy needed to activate D₂ chemisorption on Cu is higher than on Zr with translations about twice as effective as vibrations).³³ For a system with a low activation barrier Schröter et al.²⁴ have reported that the difference between the mean energy of D₂ desorbed from Pd and thermal distribution at the surface temperature is small and this is what is observed for D₂ on Zr. It is not possible on the basis of the present data to say anything on the preference over translational or vibrational energy to activate D₂ since everything is nearly thermal with a small excess in vibration. Again, all this is consistent with recombinative desorption of D atoms over a small barrier to form D₂. It is reasonable to expect that a more direct concerted reaction would give high populations up to ν'=6 which is roughly the full exothermicity of the reaction, assuming cold rotations and translations. In an attempt to measure the population of D₂ from Zr in ν'=2 no signal was observed, suggesting that its population is at least smaller than in ν'=1.

However, as we mentioned previously, the major problem of this simple model is to rationalize the release of molecular D₂ under conditions that should favor the dissolution of the D atoms into the bulk.⁸ This bias towards dissolution is especially true for low coverages of oxygen on zirconium since it has been observed that adsorbed O reduces the barrier to dissolution of hydrogen.³⁴ As it has been clearly established that dissolution of deuterium into the bulk is thermodynamically favored over desorption of D₂, the observation of desorbed D₂ resulting from decomposition of D₂O on hot zirconium must result from the kinetics of desorption versus dissolution. This point is discussed in more detail in the next section.

B. Characteristics of hydrogen adsorption and desorption on Zr

To make further progress with the discussion of a possible mechanism for the discrepancy between hydrogen desorption in the two classes of experiment, it is necessary to briefly review the Zr-hydrogen adsorption/desorption system in more detail.

The most important observation relevant to the current questions is the behavior of the work function, ∆Φ, with hydrogen coverage and adsorption temperature.¹¹ At low temperatures (≤150 K), ∆Φ is positive at saturation by ≥50 mV, although the initial change is negative. The magnitude of the initial decrease in ∆Φ decreases with decreasing temperature, and the eventual value of ∆Φ becomes more positive with decreasing temperature. Above ∼200 K, ∆Φ is negative at all coverages. At temperatures at which hydrogen can dissolve into the bulk, ∆Φ is zero. The earlier work¹³ also showed that ∆Φ of a surface prepared by hydrogen exposure at 100 K (∆Φ initially positive) decreased continuously upon heating above T ∼ 150 K. These observations and the semiquantitative determination of the energetics of hydrogen dissolution and diffusion led to a model which postulated the existence of two states of D₉ at the surface of Zr.

In the present case the study was on Zr(1010), but similar observations were made on Zr(0001).¹⁹ These states were described as surface and subsurface adsorbed hydrogen. Our work function data showed clearly that both states must reside very close to the surface, as the screening length of a hydrogen atom (proton) in a d-band metal is very short. By reference to the behavior of adsorbed hydrogen on most transition metals, and consideration of electronegativities and ionization potentials, we attribute the positive ∆Φ to surface adsorption with the hydrogen located just above the surface plane of the Zr atoms, and the negative end of the dipole on the H(D). Conversely, the negative ∆Φ is then attributed to the subsurface species. The data in Ref. 11 indicated that there is a small activation barrier to movement of the surface adsorbed hydrogen to the subsurface sites, but that the subsurface sites are slightly more thermodynamically stable. Once in the subsurface sites, the hydrogen atoms are prevented from diffusing into the bulk by an activation energy barrier of ∼43 kJ/mol. At sufficiently high temperatures they could, in principle, migrate between the surface and subsurface sites or diffuse into the bulk. Once in the bulk, they diffuse with kinetics given by the bulk diffusion parameters [D=0.034 exp(–40 000/RT) mm²/s, in Joule units for the (0001) surface].³⁴ The barrier to desorption as hydrogen molecules is estimated¹² to be much larger, ∼196 kJ/mol; this is why very little desorption is detected, even at heating
rates as high as $10^{11}$ K/s, and why the facile desorption of hydrogen following water dissociation is so puzzling. Our previous suggestion\(^7\) that the hydrogen atoms arising from water dissociation did not equilibrate with the surface and would therefore be distinguishable from thermally desorbed hydrogen must be dismissed on the basis of the present data. To rationalize the observations we are forced to make two new, connected hypotheses. (1) Hydrogen desorption can occur from the surface state at elevated temperatures because transfer to the subsurface state is slow and (2) transfer of adsorbed hydrogen from the surface to the subsurface sites is slow because of a very small preexponential factor.

Basically, these hypotheses require that the lifetime of the hydrogen released by water dissociation into the surface sites at 800 K is small compared to that due to the transfer into the subsurface sites, so that desorption occurs before the subsurface migration, even though the activation energy for desorption is much larger.

We can put very approximate limits on the various parameters. The activation energy for desorption is $\sim 196$ kJ/mol and the expected preexponential\(^{12}\) is $10^{14}$ s\(^{-1}\). If we assume that the dynamic equilibrium coverage of \(D_{\text{eq}}\) in our experiments is $0.1$ ML (this basically assumes we are somewhere near the maximum in the O-catalyzed rate of dissociation), then the desorption rate at 800 K would be $0.2$ ML/s, where ML=monolayer. For desorption to dominate over transfer to the subsurface site, or at least be comparable, we might assume that the transfer rate at 800 K could also be as high as 0.2 ML/s. This would mean that 50% of the hydrogen desorbed and 50% went into the subsurface state. We have at least indirect evidence of the transfer rate at 200 K from the temperature dependent work function data in Ref. 11 (Fig. 5). The slope of the $\Delta \Phi$ versus temperature line at 200 K is $\sim -3$ mV/s, which we attribute to the transfer of the surface state to the subsurface state. Assuming a calibration of $\sim -100$ mV/ML, the transfer rate is $\sim 0.03$ ML/s. These two estimated rates yield a maximum activation energy, $E_{\text{surf to subsur}}$, of 4.2 kJ/mol and a preexponential factor of $\sim 0.4$ ML/s. The value of $E_{\text{surf to subsur}}$ is clearly smaller than that for diffusion by a factor of $\sim 10$, so we cannot explain our results in terms of bulklike diffusion. The transfer of the surface hydrogen to the subsurface sites is slow and very weakly activated. Our model requires a similarly slow transfer back to the surface sites. It is difficult to rationalize the very low barrier and low preexponential factor in terms of low probability collective motions of the surface Zr atoms, but it is possible that the surface adsorbed and subsurface sites are geometrically distinct from the point of view of symmetry (e.g., three-fold hollow and tetrahedral, respectively) that would make the preexponential factor very small. Another possibility that we must consider is that the transfer might be mediated by defects on the surface. If this is correct the transfer back to the surface might also be mediated by defects and be at least as slow.

This model provides an immediate rationalization of the observed lack of desorption in the laser-induced thermal desorption (LITD) experiments in which the surface was exposed to deuterium at 175 K and held at that temperature for some time before the laser-induced heating. Comparison with the $\Delta \Phi$ data in Ref. 11 indicates that the hydrogen would have all gone into subsurface sites before the LITD experiment, from which dissolution rather than desorption is the preferred route. The model also suggests an experiment to test the hypotheses. If hydrogen stays in the surface sites at 100 K, and only migrates to the subsurface sites at a rate of $\sim 1$ ML/s, then rapid heating in a LITD experiment should result in significant desorption. We are planning just such an experiment.

**V. CONCLUSIONS**

The internal energy distribution of the D\(_2\) produced by water decomposition on a zirconium crystal indicates that it is produced by recombinative desorption of adsorbed D. This observation implies that complete dissociation of water occurs on the surface prior to the desorption of D\(_2\). The resolution of the discrepancy between the efficient desorption of hydrogen in high temperature water dissociation, on the one hand, and the near absence of desorption in LITD experiments on preadsorbed hydrogen, on the other hand, lies in the presence of two adsorbed states, surface and subsurface for the hydrogen. Once the hydrogen enters the subsurface state by a slow, weakly activated process, it selectively dissolves upon heating, with virtually no desorption except at very high heating rates. At the high temperatures used in the water dissociation experiments, the short lifetime of D adsorbed in the surface states kinetically limits the population of the subsurface state.

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