A Study of the Dissociation Dynamics of D₂O on Zirconium Surfaces Using Resonance Enhanced Multiphoton Ionization Spectroscopy

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Abstract

Atomic hydrogen adsorbates on Zr surfaces have much higher probability for dissolution into the bulk than recombinative desorption even when the surface is heated at rates as high as $10^{10}$ K/s. On the other hand, water dissociation on hot Zr surfaces (which takes place at temperatures as low as 80 K) produces molecular hydrogen very efficiently at temperatures above 230 K. To help resolve these apparently contradictory observations and to generally understand the dynamics of heavy water (D$_2$O) dissociation on Zr, we built an UHV chamber equipped with pressure and surface diagnostic tools to probe the rotational, vibrational and translational energy distributions of the evolving deuterium (D$_2$) using resonance enhanced multiphoton ionization (REMPI) spectroscopy and time-of-flight mass spectrometry. The rotational population distributions of the first two vibrational states ($v'' = 0, 1$) of the D$_2$ product were measured and found to fit Boltzmann-like distributions at $T_{rot} \leq 500$ K while the surface was held at 800 K. In addition, the total population of the $v'' = 1$ was found to be four times higher than
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the expected value at the surface temperature, corresponding to temperature of $T_{vib} = 1070 \pm 50$ K. These distributions are consistent with previous observations of hydrogen recombination on metal surfaces. Regarding the translational populations, the population of the $v'' = 0$ was measured and was found to fit a thermal beam model at 1200 K. This indicates the existence a very small energy barrier to desorption. To verify that the observed hydrogen was due to surface recombination, we probed the rotational population distributions of the $v'' = 1$ of hydrogen scattered from or released (through slow thermal desorption of hydrogen dissolved in the bulk) by Zr at $T = 800$ K. These distributions fitted at a Boltzmann-like distribution at $T_{rot} \leq 400$ K. From these observations, we conclude that hydrogen release from the dissociation of water arises from recombinative desorption occurring at the surface. The efficient production of hydrogen when water reacts with hot Zr is explained in terms of competition between hydrogen and oxygen adsorbates for subsurface/bulk sites.
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Chapter 1

Introduction

Water plays a pervasive role in our world. As a result, it is the subject of interest and research in a wide range of scientific fields including meteorology [1], geology [2], electrochemistry [3, 4], corrosion and solar energy conversion [5, 6, 7, 8, 9, 10], and heterogeneous catalysis [11, 12]. Interest in water-surface interaction has been increasing during the past three decades, as attested to by two major reviews [13, 14], as a result of advances in experimental methods.

Water interaction with surfaces can take place in different forms: The molecule may adsorb on the surface physically (physisorption), adsorb dissociatively, or react with other adsorbates. One of the objectives in studying water-surface interactions is determining whether water is molecularly or dissociatively adsorbed on a particular surface. Water is known to dissociate on most metals, oxides and semiconductor surfaces [13, 14]. With regard to reactive metallic surfaces, there exist cases where it is not at all
clear whether water dissociates or not. For metals, whether water dissociates or not depends on structure of the surface (crystalline or not, crystal face etc.) [13]. Recently, there has been a controversy regarding whether water adsorbes molecularly or dissociatively on well characterized Ru(1000) surface [15, 16, 17, 18, 19, 20]. However, water dissociation on Zr surfaces is not controversial[13].

In addition to helping resolve outstanding controversies, better understanding the dynamics of water-surface interaction will enable us controlling and engineering of these reactions. The aim of our experiment is to understand the dynamics of water dissociation on single crystal Zr surfaces at elevated temperatures through the dynamics of evolving hydrogen. While it is not possible to directly measure the dynamics of the dissociation of water, the reaction releases molecular hydrogen which can be detected in a state specific manner. The dynamical information obtained from the evolving hydrogen is expected to shed light on the nature of the water/Zr reaction.

1.1 Dynamics of Surface-Molecule Interactions

In general, studies of reaction dynamics are concerned with the measurement of the energy distribution and the motion of the reaction products. In comparison with gas-phase molecule-molecule reactions, the dynamics
of molecule-surface reactions are much more complex. The increased complexity arises as result of the extremely large number of degrees of freedom required to describe the surface. As a result, our understanding of the dynamics of the molecule-surface interactions is lagging behind that of gas-phase reactions. Despite the added complexity, there has been a considerable success in recent years in the experimental efforts aiming at understanding the dynamics of select molecule-surface systems. Currently there are two major approaches in dynamical studies of molecule-surface interactions. An approach pioneered by Polanyi [21, 22, 23], White [24], Yates [25], Ho [26] and others, is concerned with photochemical processes involving surface adsorbates. The fact that the surface imposes certain geometrical constraints on adsorbed molecules is seen advantageous to study steric effects in molecule-molecule reactions. The reactions are usually initiated by electronic excitation of the surface or the adsorbate(s), by means of coherent light or electrons, to induce a surface reaction, leading to the desorption of some of all of the products. The energy distributions of the products and other dynamical information, which shed light on the nature of the molecule-surface interaction, are obtained from the desorbed products by means of state-specific detection schemes.

The other main approach in the study of the dynamics of surface-molecule
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reactions has been mainly successful for diatomic molecules. In this approach, which is pioneered by among others, Zare [27], Auerbach, Rettner [31] and Wodke [45], precise dynamical information about the reaction is obtainable through the precise control of the initial conditions of the molecule before the reaction (kinetic energy, internal energy, orientation etc) or the measurement of these parameters in a state-specific detection or recombinatively desorbed molecules. Reversibility in most of diatomic-surface interactions provides complementary ways of obtaining dynamical information about these reactions. To obtain dissociation dynamics, for example, the orientation, internal and translational energy of the incoming molecule are controlled in a precise manner while monitoring the available product channels. Oftentimes though, dynamics information is obtained through the state-specific detection of recombinatively desorbing molecules from the surface.

The experiments carried so far largely involve H₂ and D₂ mainly on Cu [27, 31, 32, 33, 34, 35, 36, 37, 38] and Ni [39, 40, 41, 42], but there has been a number of experiments that involve such molecules as NO on Cu [43, 44] and Au [45] and other molecules such as N₂ and CO and surfaces of such metals as well as W, Pt, Pd and Ag and even superlattices [46]. The significance of these experiments is that understanding the dynamics in one
process (dissociation or desorption) allows for prediction of the behaviour of the reverse process.

The photochemical approach is amenable to reactions between species adsorbed on the surface. Therefore it cannot be applied to study the dissociation dynamics of non-diatomic molecules such as water. Since dissociation of water and other non-diatomic molecules is not reversible, recombinative desorption cannot be utilized to obtain dynamical information about the reaction.

1.2 Water Dissociation on Zr Surfaces

Prior to this work, Norton and coworkers had extensively studied D$_2$/Zr and D$_2$O/Zr systems [47, 48, 49, 50, 51, 52]. They observed efficient water dissociation into D(ad) and OD(ad) on Zr at temperatures as low as 80K [50, 51]. Their observations showed that the water dissociation on Zr is a self-catalyzing reaction that requires the co-presence of oxygen and Zr sites and stops when such sites are no longer available as a result of dissociation product coverage of the surface. Furthermore, subsequent heating of the surface does not lead to desorption of intact or recombined products. The hydroxyl adsorbates, in particular, were found to further dissociate into O and H adsorbates, both of which subsequently diffuse into the bulk of the
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At temperatures above 230 K, the dissociation of water on Zr leads to evolution of molecular hydrogen and adsorbed oxygen. The reaction again stops when the surface coverage of the dissociation products is complete. At surface temperatures above 450 K, the oxygen adsorbates diffuse into the bulk of the Zr crystal. The coexistence of transient oxygen on the surface and free Zr sites results sustained dissociation of impinging water molecules. This allows for water to continuously dissociate on the surface, leading to a steady production of molecular hydrogen.

1.3 Behaviour of Hydrogen Adsorbates on Zr Surfaces

At temperatures above 450 K, hydrogen adsorbates are also expected to migrate into the subsurface and bulk sites of the crystal[49, 51]. When Norton et al. heated the surface at a rate as high as $10^{10}$K/s, using pulsed laser radiation, very little ($\leq 2\%$ in comparison with nickel under identical conditions) of the adsorbed D$_2$ was desorbed [48, 49]. They concluded that thermal desorption of hydrogen was highly inefficient process. The production of molecular hydrogen with near-unity efficiency in the case where water
is brought to the surface at elevated temperatures is very surprising. If the water dissociation is caused by the same mechanism in both temperature regimes production of molecular hydrogen should not be expected to occur. To explain the difference, Norton and coworkers proposed a unimolecular concerted mechanism where hydrogen atoms on a single molecule combine before molecules dissociates [51]. For this type of recombination to occur the molecule should land on the surface with the oxygen atom and hydrogen formation taking place rapidly before significant energy is transfer to the surface occurs as a result of weakening of the OH bonds by the interaction with the surface. Hydrogen produced under such mechanism is expected to carry significant amount of the binding energy of the water molecule. Consequently, hydrogen forming under this mechanism is expected to be characterized by high internal energy. Therefore, a first step in understanding water dissociation on Zr should involve testing of this hypothesis by probing of the internal state energy and population distributions of the released hydrogen.
1.4 Recombinative Desorption of Hydrogen on Metal Surfaces

The dynamics of recombinatively desorbing hydrogen from metal surfaces is one of the most studied and easiest to understand of molecule-surface reactions. This is due to the relative ease that desorbing molecules are detected in a state specific manner and also the relative ease with which the resulting data are analyzed and interpreted. The internal and the translational energy of the desorbing molecules reveal wealth of information about the interaction between the molecule and the surface. The rovibrational and translational population distributions of the desorbing molecules, for example, give a measure of the internal energy of the molecules which is compared with the thermal energy of the surface. These distributions can reveal such information as whether the molecules has thermalized at the surface temperature prior to desorption as well as information about the role the different degrees of freedom play in the interaction. The translational energy distribution can reveal information about the potential energy barrier to desorption. Information obtained through the measurement of these distributions can also be inverted to predict the characteristics of the dissociation channels and role the different degrees of freedom in the disso-
ative reaction of the molecule with the surface [37]. Due to the simplicity of the electronic structure of the hydrogen molecule, hydrogen/metal surface system is amenable to theoretical calculations.

The first experiment probing the rovibrational population distributions of recombinatively desorbing hydrogen was done on copper (111) and (110) surfaces by Zare and coworkers more than 20 years ago [27, 28, 29, 30]. They used a permeation Cu source with a thin, high purity single crystal copper termination. The source which was back-filled with about 50 Torr of hydrogen and mounted in an UHV chamber allowed hydrogen to diffuse through the thin single crystal termination. The source was heated to 850 K, with the hydrogen adsorbates from dissociation on the high pressure side of the crystal diffusing through the crystal to recombine and desorb on the UHV side. The recombining hydrogen was then detected using resonance enhanced multiphoton ionization (REMPI) scheme. The average rotational energy of the desorbing molecules were found to be between 80 and 90% of the surface thermal energy and the vibrational population in the first excited vibrational level was found to 100 times higher than the value the thermal energy of the surface would allow for. In a subsequent work, Zacharias and coworkers studied hydrogen (and deuterium) recombinatively desorbing from clean and silicon-covered palladium surfaces [53] using a permeation
source similar to the one used by Zare et al. A two photon resonant ionization scheme (REMPI 1 + 1') through the intermediate \( B^1 \Sigma_u^+ \) state, where the prime signifies the difference in wavelength between the two photons, was used to detect the desorbing hydrogen. Their observations showed that the \( Q_J(0,0) \) population distribution to be Boltzmann-like at a lower temperature \( (T = 281K) \) than the surface which was kept at \( T_s = 570K \).

A number of experiments probing the rovibrational population distribution on recombinatively desorbing hydrogen (or deuterium) from nickel and vanadium and other single crystal surfaces have been carried out since [37, 39]. The overwhelming majority of the experiments on recombinatively desorbing hydrogen from surfaces show cooler rotational population distributions and hotter vibrational population distributions with respect to the surface temperature. Cooler rotational distribution and hotter vibrational distribution emerge as a signature of recombinative desorption. Since surface recombination occurs as result of collision between adsorbates, the lower rotational temperature exhibited by recombinatively desorbing hydrogen molecules can be understood in terms of classical collision theory as follows: Since at high enough temperatures, the adsorbates diffuse on the surface, molecular bond formation will depend on the impact parameter of the collision between the adsorbates. Since the angular momentum of the
resulting molecule ( $\vec{r} \times \vec{p}$ in this simplified picture) is proportional for the impact parameter, the smaller the impact parameter, the higher the probability of the formation a molecule (and vice versa) and the smaller the angular momentum. In the light of such simple classical model, the cold rotational population distribution is understandable. On the other hand, the more direct the collision, the more likely for vibrational excitation to occur. Hence, warmer vibration is also understandable in terms of this simple classical model.

Regarding the translational energy distributions, however, there is the situation is not clear. The standard way of measuring the translational energy is to collect time-of-flight distributions of the desorbing molecules. The average translational energy, which is inferred from these time-of-flight distributions, gives a measure of the potential barrier the recombining molecules overcome to desorb.

\section*{1.5 Langmuir-Hinshelwood vs. Eley-Rideal Mechanism}

Recombination of adsorbates on a surface are believed mainly occur through a mechanism due to Langmuir and Hinshelwood (L-H) \cite{54}. In this mecha-
nism the recombining adsorbates are accommodated to the surface conditions. The overall internal energy of the molecules forming under this mechanism is therefore expected to be comparable to the thermal energy of the surface. Another mechanism proposed by Eley and Rideal (E-R) [55] over sixty years ago but was demonstrated experimentally only recently [56, 57, 58, 59] involves collision between a gas-phase and an adsorbed species. The molecular bond between the reactants forms at a large internuclear distance. As a result, the molecules forming under the ER mechanism are expected to be characterized by significant vibrational excitation, a characteristic markedly different from that of molecules forming under the LH mechanism. Rettner and Auerbach, for example, observed roughly equal population in the five lowest vibrational levels \( v'' = 0 - 4 \) of \( \text{D}_2 \) resulting from the recombination of gas phase atomic D and D atoms adsorbed on Cu surface [31]. In addition to these two mechanisms an intermediate mechanism in which recombinative desorption occurs as a result of recombination between an adsorbate and an energetic surface atom has been also reported [41, 96]. Hodgson and coworkers observed significant translational excitation of up to \( 8k_BT \) in \( \text{D}_2 \) desorbing from Ni(111) as a result of recombination of surface and subsurface (hot) atoms. They attribute the excess energy in the translational degree of freedom to the subsurface atom acquiring energy as a result of overcoming
a barrier of 0.35 – 0.47 eV.

Since the two hydrogen atoms in the water molecule are separated by a larger distance than the equilibrium internuclear distance of the hydrogen molecule, the hydrogen formation under the concerted mechanism proposed by Norton would be expected to lead to population distributions closer to the ER type distributions. Therefore, measuring of the population distributions of the hydrogen released by the dissociation of water on a hot Zr surface would be expected to shed light on the underlying mechanism. While determining the underlying mechanism of the hydrogen does not directly address the dissociation dynamics of the water, it will give a deeper insight into the reaction. Given the fact that, currently there are no experiments addressing the dynamics of dissociation beyond the diatomics, the idea of examining the dynamics of the products to learn more about such reactions seems the best choice. It is noteworthy that not all reaction on surfaces lead to readily detectable and simple products as does water on Zr, however, whenever this is the case this approach will be help our understanding of such reactions.
1.6 Current Study

In the current study the rovibrational and translational energy distributions of deuterium produced by dissociation of D$_2$O on clean single crystal Zr surface in an ultrahigh vacuum environment are measured using resonance enhanced multiphoton ionization (REMPI) spectroscopy and time-of-flight mass spectrometry (TOF-MS) at surface temperatures around 800 K. The measured rovibrational and translation population distributions are then analyzed and compared with rovibrational distribution of deuterium from a thermalized effusive source at the same temperature as the surface. The aim of the measurement of internal and translational energy distribution of the deuterium leaving the "surface" is to directly test the concerted mechanism hypothesis put forward by Norton. The results of this experiment rule out the concerted mechanism hypothesis and instead indicate recombinative desorption as the mechanism underlying the production of the deuterium.

Two more experiments measuring the rovibrational distributions of hydrogen recombinatively desorbed or scattered from a heated Zr surface are carried out. In one of the experiments, the Zr crystal was exposed to deuterium background at $T \sim 500$ K for several hours before it was degassed and detecting the degassed hydrogen. In the other experiment, hydrogen scattering from a hot Zr surface is detected. The aim of these experiments
was to measure the rovibrational populations distributions of hydrogen that recombined on a hot Zr surface and to compare them with those measured in the case of the water dissociation.

1.7 Organization of the Thesis.

Chapter two presents detailed description of the apparatus used to carry out the experiment. Chapter three is concerned with the description of the analytical techniques used to understand and extract the relevant information from the observed rovibrational and time of flight distributions. Chapter four presents results of the D$_2$ released by the dissociation of D$_2$O on zirconium along with rovibrational and time-of-flight distributions from an effusive source at the same temperature as the surface. Chapter five presents rovibrational data from the $Q_J(1,1)$ transition due to deuterium scattered from or desorbed by the zirconium crystal at 800K. Chapter six discusses the role of oxygen in the efficient production of hydrogen and the implications of our observations for the water-zirconium system. Chapter 7 concludes the thesis with a summary of our conclusions as well as suggestions of further experiments.
Chapter 2

Apparatus

2.1 Overview of Experiment

The aim of this experiment is to collect and analyze rovibrational spectra and translational energy distributions of deuterium molecules released in the dissociation of heavy water (D$_2$O) on hot Zr surfaces and as a result of scattering or desorption of D$_2$ from these surfaces. The experiments were carried out in an ultrahigh vacuum (UHV) chamber using high purity D$_2$O or D$_2$ on the (10\overline{1}0) face of single crystal Zr. The deuterium molecules resulting from these reactions were multiphoton ionized using the third harmonic of an Nd:YAG-pumped pulsed dye laser and were subsequently collected using a linear time-of-flight mass spectrometer with a multichannel plate detector. The time of flight allows for the discrimination of other ionized species as well as measurement of velocity distribution of the mass of interest. The amplified output of the microchannel plate detector was digitized by a
digital oscilloscope. The digitized signal was read from the oscilloscope by a computer through a general purpose interface bus (GPIB) port. Under the best experimental conditions, the signal resulting from the ionized deuterium is in the order of one ion per laser shot. The use of a LabVIEW program allows for the construction of either a spectrum or a time of flight distribution by either integrating or histogramming the single ion signal from many laser shots.

This chapter gives a detailed description of the apparatus used to carry out the experiment. The main components of the apparatus are

1. Ultrahigh vacuum (UHV) chamber equipped with vacuum and surface diagnostic tools

2. Nd:YAG-pumped dye laser with doubling and frequency-mixing nonlinear optical crystals to produce tunable UV light

3. Time of flight spectrometer with microchannel plate detectors

4. Effusive D$_2$O and D$_2$ sources

5. Computer programs and electronics for data acquisition and instrument control.

The following sections describe the function of each of these components
Figure 2.1: Overall schematic of the experimental apparatus.
Chapter 2. Apparatus

of the apparatus as well as the conditions under which they are operated to produce desirable experimental conditions.

2.2 UHV Chamber

The main body of the UHV chamber is made of a 12 inch diameter, 28 inch high stainless steel cylinder. The chamber has three sets of ports at different heights. The middle and lower sets each consist of eight ports that are mounted perpendicular to axis (side wall) of the chamber whereas the upper set of ports consists of five ports that are mounted at 45° with respect to the vertical axis of the chamber. The middle set of ports holds the time-of-flight mass spectrometer, the LEED/Auger system, the effusive D₂, two quartz windows for UV light, an 8 inch glass view port and two 4.5 inch glass view ports. Three of the lower set of ports are used to hold the Ar⁺ gun, a glass view port and electrical feedthroughs for the time-of-flight mass spectrometer voltage wiring. A fourth one is connected through a manual gate valve to a second turbo pump dedicated for the gas line manifold. Three of the upper set of ports hold the RGA, a feed-through for the water doser and a view port. The axis through these ports all point to the surface of the crystal when it is placed in front of the time-of-flight mass spectrometer (TOF-MS). The port holding the TOF-MS is extended with a 6" (differential
chamber). The chamber is sealed from the top by a 8 inch port that in its axis holds the a 360° rotatable manipulator which supports the zirconium crystal. The manipulator allows for the crystal to be placed in-front of the different ports. The chamber is sealed from the bottom through an 8 inch port by an ion pump-Ti sublimator system.

2.2.1 Pump Systems

The initial stage of the pumping of the chamber from $10^{-4}$ to $10^{-7}$ Torr is achieved using a 70 L/s turbo-molecular pump through the TOF-MS differential chamber (see Fig. 2.2). This turbo pump is backed by a diffusion pump (Edwards Diffstack 63) which is in turn backed by a mechanical pump. (When in operation the diffusion pump decreases the pressure behind the turbo pump to $10^{-7}$ Torr, but is not always used.) The turbo pump alone brings the chamber down to $\sim 10^{-9}$ Torr. The use of an ion pump is necessary to reach lower pressure below those possible with the turbo pump alone. Hence the second stage of the pumping which drops the pressure to $\leq 2 \times 10^{-10}$ Torr involves the use of a 240 L/s ion pump and getter pump combination (Physical Electronics, Low Profile 300). The getter pump consists of a titanium sublimator surrounded by a liquid nitrogen trap (cryoshroud). The continuous leakage of small amount of gas ($D_2$ or
D_{2}O etc.) into the chamber requires that the TMP to be used during the experiment to help keeping the background pressure low. The turbo pump, which pumps the gas handling system, is backed by a mechanical pump. As shown in Fig. 2.2, this turbo pump can be used to pump the chamber. To avoid contamination of the chamber, this turbo pump is used to help the pumping only during the pump down stage. The titanium sublimator is made of a set of titanium filaments and it fits inside the ion pump. By passing a high current (50 – 55 A), the titanium filaments deposit a layer of evaporated Ti on the surrounding surfaces. To minimize the escape of the titanium vapour into the chamber and deposit Ti on the surfaces surrounding the filaments, liquid nitrogen is used. The titanium getter pump has a higher efficiency for pumping hydrogen (which is the dominant residual gas in the chamber). Filling of the cryoshroud with liquid nitrogen increases the getter pump efficiency up to three times. The lowest pressures observed in this chamber (< 10^{-11} Torr) were observed using liquid nitrogen after the titanium filaments were “flashed” several times.

### 2.2.2 Gas Handling System

As shown in Fig. 2.3, the gas handling system is made of a set of interconnected stainless steel tubes and valves. The system is pumped by a turbo
Figure 2.2: Schematic representation of the pumping system. The abbreviations stand for turbo molecular pump (TMP), diffusion pump (DP), mechanical pump (MP), automatic gate valve (AGV), manual valve (V), ion gauge (IG) and thermocouple gauge (TCG).
pump backed by a mechanical pump. The system has three inputs, two of which hold D$_2$ and D$_2$O reservoirs. The third input line is used to allow for the pumping of the argon line.

Two of the outputs of the system are connected to the chamber through the effusive D$_2$ source and the D$_2$O capillary. The D$_2$O passes through a leak valve (Varian 951 – 5106) and a mechanical valve before it enters the chamber. Both lines are connected to the turbo pump and can be differentially pumped.

### 2.2.3 Pump-down Procedure

After sufficient preparation the base pressure of the UHV system stabilizes around $\leq 2 \times 10^{-10}$ Torr. To reach this level of vacuum or lower, the following pump-down procedure is followed.

#### Roughing Step

After venting the chamber, the initial step of the pump-down stage involves the use of only mechanical pumps. With the turbo pumps and the diffusion pump off, both mechanical pumps are used for faster pumping. The turbo pumps can be turned on after the chamber pressure drops to $\sim 100$ mTorr. With no major leaks and the turbo pumps on, the chamber pressure nor-
Figure 2.3: Schematic representation of the gas handling system. The abbreviations stand for turbo molecular pump (TMP), leak valve (LV), manual valve (V), effusive source (ES), ion gauge (IG), D$_2$O doser (D), deuterium reservoir (D), and D$_2$O reservoir (D$_2$O).
mally drops to the high $10^{-6}$ Torr range within 15 minutes. To minimize accumulation of moisture during venting, it is helpful to keep a positive pressure of nitrogen in the chamber. When this is done, the chamber pressure can reach in low $10^{-6}$ to high $10^{-7}$ Torr range with 2 – 3 hours of pumping. Using the gas handling system turbo pump, which is isolated from the main chamber by manual valves during the venting, shortens the pump-down time to some extent. According to its manufacturer's specifications, it is better to start the ion pump only after the pressure has reached $\leq 10^{-7}$ Torr.

**Leak Testing**

If major leaks are present in the system, the pressure stops decreasing near $10^{-4}$ Torr, which makes the leaks easily detectable. Minor leaks, however, become detectable at pressures around $10^{-6}$ Torr or lower. After reaching this level of vacuum and before starting baking, it is important to check the system for leaks. A quick way of telling whether leaks are present in the system is to measure the proportion of oxygen and nitrogen in the chamber with residual gas analyzer. Note that nitrogen has the same mass as carbon monoxide which is a usual component of the residual gas at this pressure. If the proportions of the nitrogen and oxygen peaks are close to their atmospheric proportions, it is most likely that there is a leak present in the
system. If leaks are found in this way and eliminated, it may still be that smaller leaks exist. Before proceeding to bake the chamber, it is advisable to spray helium all recently opened ports while monitoring the partial pressure of helium inside the chamber. If no helium leaks into the chamber, then there are no leaks and the baking can be started.

2.2.4 Chamber Bake-out

After pumping down the chamber to $10^{-4}$ Torr, over 90% of the residual gas pressure in the chamber is due to water vapour [60]. With the walls at room temperature, water molecules can be stuck on the chamber walls for a long time before evaporating and finding their way into the pumps. With the chamber walls above 100 °C, however, all the water in the chamber turns into gas and can be pumped efficiently as any other gas by the pumps. Hence, for the chamber to reach at operating UHV pressure in a reasonably short time, it must be baked at temperatures above the boiling point of water.

Baking of the chamber is done using a home-made heater which is made of a pair of 300 W heaters (Gamma Vacuum P/N 2190731) mounted on the flat back of, about two inch thick, semicircular aluminum bars which are externally attached to the chamber. In addition to the external heaters, we
use an UV halogen lamp mounted inside the chamber. With heaters on and the chamber wrapped with fibre glass blankets, the chamber temperature stabilizes at 250 °C. The UV lamb was found to be specially efficient in removing the water moisture from the inner walls of the chamber.

**Ion Pump Bake-out**

The ion pump cannot be isolated from the chamber and, as a result, is exposed to atmospheric conditions when the system is vented. This introduces to the ion pump moisture and other gases that degrade its performance. However, the ion pump can be baked to clean it from these contaminants. The ion pump used in this work comes with its own heaters (Gamma Vacuum 2190731). These heaters raise the temperature of the ion pump up to 250 °C. According to the manufacturer's specifications, the ion pump can be heated to 250 °C without affecting the performance of its permanent magnets. These heaters are preset to raise the temperature of the ion pump to the specified value when it is baked in air. Wrapping the chamber with blankets, as is done when baking the chamber, will raise the temperature significantly above the specified value and will cause irreversible damage to the magnets.

Best results were achieved with this system when the baking of the cham-
ber stops when the pressure drops to low $10^{-8}$ or even high $10^{-9}$ Torr.

**Ti Sublimation Pump**

After the chamber cools, pressure can drop to the mid $10^{-10}$ Torr roughly within 24 to 48 hours, depending on the baking and other conditions. To lower the pressure further, the titanium sublimation pump is used. The liquid nitrogen reservoir surrounding the titanium filaments is first filled with liquid nitrogen so that the titanium vapour condenses efficiently on the surrounding walls without escaping into the chamber. To get the best results, the current must be in the 50 – 55 Ampere range for about 45 to 60 seconds at a time. When hot, the titanium filaments release mostly hydrogen gas. The flashing of the titanium can be stopped when the amount of hydrogen released becomes relatively small.

**Cleaning the Crystal Surface**

After venting or prolonged exposure to $\text{D}_2\text{O}$, the Zr crystal surface is highly contaminated with adsorbates. As a result it loses reactivity. It must therefore be cleaned before using it again. The cleaning process involves bombardment of the surface with high energy ions using an $\text{Ar}^+$ gun.

The $\text{Ar}^+$ gun consists of an electron gun and an accelerating magnetic
and electric fields. The electron gun filament must be outgassed sufficiently before using it to minimize contamination of the crystal. The filament is outgassed until the chamber pressure drops to high $10^{-10}$ Torr for best results.

The cleaning cycle of the crystal consists of three steps:

1. Bombardment of the crystal with 2.5 KV Ar$^+$ ions between 5-20 minutes

2. Annealing to 500 – 600 °C for up to 5 minutes

3. Checking surface composition using the Auger spectrometer

Usually, steps 1 and 2 are repeated a few times before the surface composition is checked using the Auger spectrometer. If the Auger spectrometer shows significant amount of adsorbates (usually C and O), steps 1 and 2 need to be repeated.

2.2.5 Pressure Measurement

The UHV chamber is equipped with a high sensitivity nude ion gauge and a residual gas analyzer (Lesker, AccuQuad 300). The nude gauge consists of an ionization filament, an accelerating grid and a positive ion collector. Electrons emitted by the filament ionize gas species in the chamber through
collision. The ionized species are then collected by a collector producing a small ion current which is subsequently converted into a pressure reading by the controller electronics. The ion gauge has no selectivity for different masses. Therefore, it cannot be used to measure the partial pressure of a specific species when the gas in the chamber has more than one component. In addition, at low enough pressures (10^{-10} \text{Torr}) the ion gauge operating range is limited by x-ray emission current. At moderately low pressures the ion gauge gives reasonably accurate reading.

The residual gas analyzer consists of an ionizing filament, a quadrupole mass filter, and ion detector and appropriate electronics and control software. Its software allows for the measurement of either the total pressure or the partial pressure of a specific mass. In the analogue mode, it records a mass spectrum, by scanning the quadruple voltage, and this represents the true partial pressures of the different masses in the chamber. In this mode it can measure up to 200 atomic mass units. Its software allows for corrections for differences in the ionization efficiencies of different molecular and atomic species. In the dynamic mode (pressure vs. time), it can monitor, display and record the changes in the partial pressures of up to ten masses simultaneously. For accurate pressure measurements, we rely on the residual gas analyzer and during the experiment we use it in the dynamic
mode. The RGA is controlled by a dedicated computer using a proprietary software with sophisticated control and display capabilities.

2.2.6 D$_2$O Reservoir

The D$_2$O reservoir is a 100 mL stainless steel vessel. We fill the vessel with high purity (99.9%) D$_2$O. Before filling the stainless steel bottle with D$_2$O, we bake it above 100°C under vacuum. When baking stops, the pressure in the bottle drops to $\leq 10^{-8}$ Torr. The baking minimizes contamination of the D$_2$O with moisture (H$_2$O). To make sure that air and moisture do not get in the bottle when filling it with the D$_2$O, the bottle is mounted on a T with one end blocked by a rubber stopper. The heavy water which is loaded in a syringe is then injected into the bottle through the rubber stopper. When the loading is done, the valve at the neck of the bottle is closed and the bottle is mounted on one of the lines of the gas manifold. To get rid of air and other gases that are dissolved into the D$_2$O, the bottle is frozen in liquid N$_2$ and then pumped out. This step is usually repeated up to three times before the D$_2$O is used.

At room temperature water has a vapour pressure of 25 Torr [61]. Therefore the D$_2$O pressure is about $\sim 25$ Torr at 20°C at the neck of the vessel. The UHV chamber is normally in the low 10$^{-10}$ Torr range. It is therefore
necessary to regulate the D$_2$O pressure very carefully. This is done by a leak
valve placed between the bottle and the chamber. It is found that differen-
tial pumping of the D$_2$O line before it enters the chamber is essential for the
precise control of the D$_2$O beam. The D$_2$O is brought to the the crystal by a
0.12 mm diameter stainless steel capillary that enters the chamber through
a feedthrough.

2.2.7 D$_2$ Reservoir

We use high purity (99.99%) D$_2$ from a commercial vendor for calibration
purposes. Unlike water, D$_2$ is easily controllable, so differential pumping is
not necessary. A leak valve is sufficient to precisely control its pressure. The
D$_2$ gas is brought into the ionization region in the chamber by a heatable
stainless steel capillary with inner diameter 0.2 mm that is mounted on a
translation bellows mounted on a 6 inch flange.

2.2.8 Pacification of the Chamber Walls

Usually, when D$_2$O is introduced into the UHV chamber for the first time, a
significant amount of background D$_2$ is produced, apparently due to water
dissociation on the clean walls of the chamber. Apparently, the baking and
the UV light exposure shift equilibrium of the iron hydroxide/iron oxide
on the surface. This effect is especially strong when the UV lamp is used during the baking. In this case, the level of the $D_2$ partial pressure can reach a level comparable to that of the $D_2$ from the dissociation of water on the hot Zr surface. As a result, the level of background contribution in the $v'' = 0$ spectra can raise to a level comparable to the signal itself. The unwanted $D_2$ background diminishes with exposure of $D_2O$ to the chamber as a result of increased oxide coverage on the chamber walls. To accelerate the "pacification" of the chamber walls, it was found advantageous to raise the $D_2O$ background in the chamber to $\sim 10^{-9}$ Torr for several hours before starting the experiment.

2.2.9 Optimal Pressure Conditions

Typical base pressure of the chamber just before the water is introduced to the chamber is below $2 \times 10^{-10}$ Torr. As mentioned earlier, with only the ion pump on, the base pressure hovers around $2 \times 10^{-10}$ Torr. Further decrease of the pressure is limited by hydrogen permeating from the stainless steel walls. The use of the Ti sublimator temporarily (up to several hours) drops the pressure below this value by producing a fresh trapping surface and cooling walls containing the Ti with liquid nitrogen improves the pumping of hydrogen. It was observed that liquid nitrogen reduces the background
hydrogen pressure by about two thirds. The chamber pressure before the introduction of water ranged from $5 \times 10^{-11}$ to $2 \times 10^{-10}$ Torr.

2.2.10 Auger Electron Spectrometer

Auger electron spectroscopy (AES) is a surface-sensitive spectroscopic technique used for compositional analysis of surfaces. It offers unambiguous identification for all elements except H and He, which do not have Auger spectra due to lack of inner shells ($L, M, ...$), high efficiency, surface specificity and compatibility with cleanliness requirements for ultrahigh vacuum environments [62].

Theory

The physical principle underlying the method is well known. When an atom is ionized through one of its inner shell electrons, the resulting ion is left in a highly excited state. The excited ion can relax either through the emission of an x-ray photon (radiative) or a secondary electron (nonradiative). The latter process, known as the Auger effect (after M. Pierre Auger) is more common in lighter atoms, and involves the filling of the inner shell vacancy by an electron from a higher shell and the simultaneous emission of an (Auger) electron from one of the outer levels. The excess energy is carried by the
Figure 2.4: Schematic representation of the Auger process. a) Atom is bombarded with an energetic electron. b) The atom loses an inner shell electron as a result of electron bombardment. b) An upper shell electron fills the hole and an electron from an upper shell is ejected simultaneously.
Auger electron as kinetic energy. For the case of a K-LII transition, for example, the kinetic energy of the Auger electron is given by \[62\]

\[ E_{\text{Auger}} = E_K - (E_{L_I} + E'_{K_{II}}) \]  

(2.1)

where \( E_{\text{Auger}} \) is the kinetic energy of the Auger electron and \( E_K, E_{L_I} \) and \( E'_{K_{II}} \) are the binding energies of the K \((n = 1)\) and \(L_I (n = 2)\) shells of the atom and the \(L_{II}\) of the ion. Because of the uniqueness of the energy level structure of atoms, the kinetic energy of the Auger electron is characteristic of the energy levels of the emitting atom. Analysis of the kinetic energy of the Auger electron reveals the identity of the emitting species. Schematic representation of the Auger process is shown in Fig. 2.4.

Auger electron spectroscopy (AES) involves an excitation source (usually an electron gun) and an analyzer\(^1\). Cylindrical mirror analyzers (CMA), hemispherical sector analyzers (HSA) and retardation grid analyzers are three possible methods of analyzing Auger spectra. Our setup uses the hemispherical sector analyzer.

The way the hemispherical sector analyzer works is the following: A beam of electrons with a well defined kinetic energy (5 keV) hits perpendic-

\(^1\)Electron excitation method requires simpler equipment than by x-ray excitation
ularly the surface to be analyzed. The electrons which are back-scattered from crystal with a continuum of energies ranging from near zero up to 5 keV, are analyzed by applying a retarding voltage on the hemispherical retardation grid. The Auger electrons resulting from the surface layers make a very small component of the flux of electrons reaching the retardation grid. As the retardation grid voltage is ramped up, more and more of the Auger electrons are stopped from reaching the detector, leading to a stepped electron current as a function of voltage. The current versus retardation voltage curve is differentiated once or twice to recover the Auger electron peaks from the background current. This is usually done in real-time using the techniques of lock-in amplification.

**Practice**

To monitor the cleanliness of the surface, we use a low energy electron diffraction (LEED)/Auger system (Fissons Instruments LEG-24-161) that can be electrically configured either as LEED or Auger electron spectrometer. The LEED mode is more useful if one is specially interested in obtaining detailed geometric information about the adsorbates. When this is not the case but

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2The surface specificity of the Auger method arises from the fact that Auger electrons resulting beyond the surface layer scatter from the surface layers and as a result lose their characteristic energy.
instead one requires to know how the concentration of several species on the surface changes with time or as the surface condition changes, the Auger mode is more useful. We use the Auger spectrometer to monitor the surface contaminant concentration during the different stages of the cleaning process. To record an Auger electron spectra, the retarding potential on the retarding grids is ramped and the collector grid current is fed into a lock-in amplifier (Stanford Research System Model SR510).

In this experiment the major surface contaminants are carbon and oxygen. Therefore, usually the aim of the cleaning process is to reduce the signal due to these species relative to that due to Zr. The lowest Auger transitions of these species lie in the 80-600 eV energy range. Measuring the intensity of these peaks is sufficient to monitor the relative concentrations of these species on the surface. During the scanning, the retarding voltage is ramped up from 100 to 600 V to monitor Auger transition that occur at 147, 266 and 507 V for zirconium, carbon and oxygen, respectfully.

The cleaning process, as described earlier, involves several cycles of Ar bombardment, annealing and diagnosing. The Auger spectrum taken after each cleaning cycle and the cleaning is stopped when the intensities of the zirconium and oxygen are ~ 3.8 : 1. Fig. 2.5 shows a spectra that are collected before and after cleaning the Zr crystal. The shape of the spectra
Figure 2.5: Typical Auger spectra before and after cleaning of the Zr crystal. The cleanliness of the surface is measured in terms of the ratio of the Zr peak amplitude to that of the C peak. The above plots are normalized for the Zr at 147 V peak and significant diminishing of the oxygen and carbon peaks with the Ar⁺ bombardment is clear. The peak shapes result from the second derivative of the Auger electron current.
is resulting from the second derivative of the Auger electron current.

### 2.3 UV Light Production

Isotopes of molecular hydrogen are transparent to light up to an energy of 90,000 cm$^{-1}$. To measure rovibrational spectrum of deuterium and other hydrogen isotopes, resonance enhanced multiphoton ionization (REMPI) is the most convenient method. In our experiment, deuterium molecules are excited from the ground electronic state into the $E, F^1\Sigma_g^+$ state by resonant absorption of two $\sim 201 - 210$ nm (6.17 - 5.91 eV) photons. A third UV photon from the same beam ionizes the molecule. This section is a description of the optical processes and apparatus involved in the production of tunable coherent light in the above wavelength region.

#### 2.3.1 The Laser System

The laser system consists of a dye laser (Sirah Precision Scan) pumped by an Nd:YAG laser (Spectra Physics PR0 290). The fundamental frequency of the dye laser is doubled using a KDP crystal which is subsequently mixed with the residual fundamental frequency beam using a beta barium borate ($\beta$-BBO) crystal. The resulting UV light is steered into the UHV chamber using fused silica prisms (or dichroic mirrors) and subsequently focused by a $f =$
25 cm focal lens into the interaction region of the time-of-flight spectrometer where it ionizes deuterium molecules.

### 2.3.2 Nd:YAG laser

The Nd:YAG laser system used to pump the dye laser is a pulsed (20 Hz), 40 Watt (2J/pulse) Spectra Physics PRO 290 system operating at 1064 nm. The system has KDP crystal in place for second harmonic production. The KDP crystal currently used produces 600 – 650 mJ/pulse at 532 nm. The Nd:YAG laser has a seeder laser system which allows it to be used to pump an optical parametric oscillator (OPO). The function of the seeder is to force the laser into single mode oscillation by seeding one of the cavity modes. The lasing of Nd:YAG laser otherwise builds up from spontaneous emission which results multi-mode oscillation. While the seeder improves the mode quality of the laser, it actually lowers the overall power output as a result of reduction in the mode beam size. Dye lasers are not very sensitive to the pump mode quality, hence use of the seeder in the Nd:YAG laser is not necessary.
2.3.3 Dye Laser

The tunable UV light used to ionize the D$_2$ molecules is generated using Sirah Precision Scan dye laser (Sirah Laser-und Plasmatechnik GmbH PRSC-DA-24) in a double grating (2400 lines/mm) resonator configuration with a linewidth of 0.0012 nm at 450 nm[63].

For the dye laser, the 26% conversion efficiency specified by the manufacturer at the peak of Rhodamine 6G is achievable. In terms of beam quality, however, maximum conversion efficiency is not the best parameter to use when preparing the system. Aiming for maximum conversion efficiency at the fundamental wavelength, the power output of third harmonic (resulting from the mixing of the fundamental and second harmonic) is far from optimum. For applications requiring the third harmonic of the dye laser, it was found better to optimize the UV power instead of the visible when preparing the system. This can be done by monitoring the third harmonic power instead of the fundamental when aligning the system.

\[3\] The 2400 lines/mm double grating setting is optimized for the largest tunable range (330 – 710 nm), according to the Sirah manual. The grating-mirror configuration, on the other hand, has slightly larger tunability range (330 – 740 nm), but with 50% larger linewidth.
2.3.4 Production of UV Light

The production of tunable UV light in the 200 nm range involves two steps of nonlinear optical frequency conversion. First, the fundamental frequency is doubled (second harmonic generation) using a KDP crystal. Secondly, the second harmonic and remaining fundamental frequency beams are mixed (sum frequency generation) using a beta barium borate ($\beta$-BBO) crystal.

Theory

Second harmonic and sum frequency generation result from the nonlinear dependence of the dielectric polarization on the electric field of the light at high power and coherence. The dielectric polarization is given by (in Gaussian units) [64]

\[
P_i(t) = \chi^{(1)}_{ij} E_j(t) + \chi^{(2)}_{ij} E_j^2(t) + \chi^{(3)}_{ij} E_j^3(t) + ... \tag{2.2}
\]

\[
P_i(t) = P^{(1)}_i(t) + P^{(2)}_i(t) + P^{(3)}_i(t) + ... \tag{2.3}
\]

where $P_i(t)$ is a component of the dielectric polarization vector of the medium, $\chi^{(i)}_{ij}$ ($i = 1, 2, 3$) is the optical susceptibility tensor and $E_j(t)$ the electric field of the applied optical field. At low enough intensities, only the first term contributes to the polarization. However, at higher intensities, higher order
(nonlinear) terms can also contribute. The lowest order nonlinear term $P^{(2)}$ is responsible for both second harmonic and sum-frequency generation.

The incidence of high intensity optical radiation is a necessary, but not sufficient, condition for conversion of optical frequencies exploiting nonlinear optical properties of materials. In particular second order nonlinear process are possible to realize only in non-centrosymmetric media [64]. Another requirement for the realization of second order nonlinear processes is to satisfy energy and momentum conservation requirements of the photons at the different frequencies. In the case of sum-frequency generation\textsuperscript{4}, the following two equation must be satisfied simultaneously.

\begin{equation}
\vec{k}_3 = \vec{k}_1 + \vec{k}_2 \tag{2.4}
\end{equation}

and

\begin{equation}
\omega_3 = \omega_1 + \omega_2 \tag{2.5}
\end{equation}

Here $\vec{k}_i$ are the wavevectors of the different waves and $\omega_i$ their frequencies. The first equation can be rewritten with the help of $\vec{k}_i = \frac{\omega_i n}{c} \hat{r}$, where $n$ is the value of the refractive index of the medium along the direction of $\vec{k}_i$, and $\hat{r}$ is a unit vector along the direction of propagation, and assuming parallel

\textsuperscript{4}The second-harmonic generation is a special case of sum-frequency generation.
propagation directions as

\[ n_3 \omega_3 = n_1 \omega_1 + n_2 \omega_2 \]  

(2.6)

Due to dispersion, Equations 2.4 and 2.5 generally cannot be simultaneously satisfied. The most common method used to overcome this limitation takes advantage of birefringence in crystals. In a uniaxial birefringent crystal, for example, there are two different values for the refractive index for different polarization directions. It is also possible to tune the refractive index of the extraordinary direction by tuning the angle between the optic axis of the crystal and propagation direction of the light. The extraordinary refractive index is given by [65]

\[ n(\theta) = \frac{n_e}{(n_0^2 \sin^2 \theta + n_e^2 \cos^2 \theta)^{\frac{1}{2}}} \]  

(2.7)

where \( \theta \) is angle between the beam direction and the optic axis of the crystal.

In practice, the polarization of the low frequency beams are chosen to be along the higher refractive index direction while the high frequency beam is polarized along the low refractive index direction. By tuning angle of incidence with respect to the optic axis, it is possible to find a direction in which both the energy and the momenta of the involved photons are
conserved. In other words, a direction in which the two beams have equal velocities so that energy is coupled out from the lower frequency beams to the higher frequency beam. This technique is called phase (or velocity) matching.

Practice

The production of the UV light involves two stages of nonlinear conversion of visible light form the dye laser. In the first stage, the frequency of the fundamental beam laser is doubled (second harmonic generation). In the second stage, the fundamental and second harmonic beams are mixed to produce light with frequency at the sum of these to frequencies.

There are two types of crystals. Type I crystals require the polarizations of the different beams to be perpendicular to each other whereas type II crystals require parallel polarizations [65]. The second harmonic generation takes place in a type I crystal. The incident dye laser beam has vertical polarization, and the second harmonic beam is horizontally polarized.

The mixing crystal is a type II beta-barium borate ($\beta$-BBO). To make the polarizations of the two input beams parallel, we use a polarization-rotating plate. A polarization rotating plate rotates the polarization of different frequencies of light by different amounts due to dispersion. The
polarization rotating plate we use is optimized for the two wavelengths 600 and 300 nm. As soon as the wavelength departs from these values as a result of frequency tuning, the two polarizations walk out of each other and the mixing efficiency drops. By slightly rotating the polarization rotating plate about an axis perpendicular to the beam axis (increasing the optical paths of the beams), the conversion efficiency can improved. This method is effective up to 10 nm of tuning. However, as the wavelength is tuned further, the angle of incidence of the light becomes large enough such that reflection becomes significant. This challenge can be overcome by having several polarization rotators each optimized for a specific range of interest.

2.4 Linear Time of Flight Mass Spectrometer

The focused power of the laser near $\lambda = 200$ nm can easily multiphoton ionize almost any of the molecules of the background gases. To separate hydrogen ions from unwanted signal due to the background gases, we use a linear time of flight mass spectrometer (TOF-MS). In the simplest configuration, a TOF-MS consists of two regions: The acceleration region and field free region. The principle behind the use of the TOF-MS is that particles with the same initial kinetic energy but different masses travel at different velocities. As a result, if such particles enter the field-free region at the same
time, they will separate themselves in time after the flight in the field-free region, the lighter species arriving earlier. The output of a TOF-MS is a mass spectrum.

As shown in Fig. 2.6, the TOF-MS used in this work has two acceleration stages, a field-free flight tube and microchannel plates detector. Ideally the flight tube entrance and exit would be covered by a high-transparency grid to make the acceleration fields as flat as possible. However, due to low signal, it was realized this was not worthwhile. Simion simulations showed that when the minimum beam waist of the laser is aligned with the axis of the TOF-MS, distortions of the velocity distribution can be minimized by choosing appropriate electrode voltages.

The velocity acquired by an ion accelerated in a two acceleration stage TOF-MS can be calculated by equating the kinetic energy gain of the ion at the end of each stage with the potential difference it crosses [66]. The velocity acquired by an ion with charge $q$ after crossing $P_1$ and $P_2$ is given by

$$ v_{tot} = \sqrt{\frac{2q}{m} \left( \sqrt{V_1} + \sqrt{V_2} \right) } \quad (2.8) $$

where $m$ is the mass and $V$ is the potential difference the ion cross. The time the ion spends in the field-free region depends only on its velocity at the entrance of the field free region. The time an ion takes to cross the
Figure 2.6: Schematic representation of the time of flight spectrometer used in the experiment. \( P_1 \) is a skimmer which is normally grounded. \( P_2 \) is the extraction electrode which is made of fine gold grid (90% transparent). \( P_3 \) is the field free tube. \( P_4 \) is a hollow ring used to shield the flight free tube from the microchannel plate field. MCP is a set of a microchannel plates. \( R \) is a 100 \( \Omega \) resistor and \( C \) is a capacitor. The diagram is not drawn to scale.
field-free region is given by

\[ t = \frac{L}{v} \]  

(2.9)

where \( L \) is the length of the field-free region. When large acceleration voltages are used, the acceleration time due to \( v_{\text{tot}} \) is much smaller than the time the ions spend in the field-free region. In this case, the effect of \( v_{\text{tot}} \) is an unimportant shift in the time axis. An ion with initial kinetic energy \( E_0 \) will take the time

\[ t = \sqrt{\frac{mL^2}{2E_0}} \]  

(2.10)

Since gas molecules or atoms of the same species have a certain velocity distribution, the flight time of an ensemble of ions of the same species (and charge) is represented by a "time-of-flight" distribution.

To calibrate a TOF-MS, it is common to fit measured mass spectra, like those shown in Fig 2.7, to an equation of the form

\[ t = A\sqrt{m} + B \]  

(2.11)

where \( A \) and \( B \) are free parameters. Normally, this type of fit allows for the identification of the masses present in the spectrum. The average flight time of any other mass can then be predicted quite accurately using Eq. 2.11
Figure 2.7: Mass spectra produced by the ionization of gases in the chamber by tightly focused laser pulses at $\lambda = 201$ nm during the pump down. The small ringing in the trace is caused by small impedance mismatch in the detection circuit seen by the relatively large signal (not shown) due to scattered UV light on the microchannel plates.
Figure 2.8: A plot of the $\sqrt{m}$ against the time-of-flights of the mass spectrum shown in Fig. 2.7.
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The TOF-MS used in this experiments consists of a skimmer (P_1), a 90% transparent gold mesh (P_2), a 6 inch long stainless steel flight tube (P_3), a stainless steel hollow plate (P_4), a set of microchannel plates (Chevron), and current-to-voltage RC circuit whose output is fed to a 10\times pre-amplifier before being digitized by a digital the oscilloscope. The hollow electrode has a smaller hole than the tube and therefore shields the flight tube from the high field of the microchannel detector. Figure 2.7 shows a typical mass spectrum resulting from background gases.

The collection of a whole set of a rovibrational spectra at D_2 pressures \( \leq 10^{-8} \) Torr takes several hours while a time-of-flight distribution takes less than an hour. This necessitates the use of two sets of voltages, one set for the collection of the rovibrational spectra and the other for measuring time-of-flight distributions. Typical voltages used in this work are as follows: For rovibrational spectra measurements, electrode P_1 was usually grounded while \(-35\) and \(-220\) V applied to electrodes P_2 and P_3, respectively. These voltage shrink the time-of-flight distribution and this cuts both the data acquisition time and reduces the noise due to "dark" counts. For the time-of-flight distributions, P_1 is usually grounded whereas P_2 and P_3 are kept at \(-4\) and \(-14.5\) V, respectively.
2.5 Data Acquisition Programs

The programs used in this project are written in the LabVIEW Graphical Programming Language. Each of these programs is used to accomplish two tasks: To control the instruments and to extract information from the signals received from these instruments. There are three different programs that are used in this experiment: One program for the collection of spectra; one for collecting time of flight (TOF) distributions; and one for collecting Auger spectra. The rest of this section is a detailed description of these programs.

2.5.1 Tuning Program

The program used for the collection of the spectra is the most complex of the three programs. The major parts of this program are shown in the flowchart shown in Fig. 2.9. The functions of this program can be divided into three parts:

1. Initialization of instruments

2. Tuning the laser and the crystals

3. Acquisition of data
Initialization

Before the program starts to acquire data, it initializes communication devices and instruments to appropriate settings. Before any communication takes place between the data acquisition computer and any of the instruments, the communication ports (GPIB, Serial Port, ADC) must be set up to appropriate settings. This involves specifying the GPIB addresses of the devices, setting up of the serial port parameters to appropriate values and similar details. With the communication ports set to their appropriate settings, initialization commands are sent to the devices. This part is common to all of the three programs used in this experiment. The devices used in this part of the experiment that are controlled by the program are the dye laser, the oscilloscope and the data acquisition card. Initialization of the dye laser involves selecting a scanning mode (trigger scan etc.) and setting of the grating and the second harmonic crystal to their initial positions.

Controlling of the Sirah dye laser is accomplished by sending encoded low level commands to its microprocessor through the serial port (RS232).

Communication with the oscilloscope (Tektronix TDS3050) can be done through either the general purpose interface bus (National Instruments IEEE 488.2) or the serial port (RS232). However, the GPIB is faster, especially when large amounts of data are transferred between the oscilloscope and the
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Figure 2.9: Scanning program flowchart.
data acquisition computer. Our program, therefore, communicates with the oscilloscope through the GPIB. The initialization of the oscilloscope involves specification of the format the data to be transferred (how many bytes per trace point etc.) and setting up of an acquisition window (or a gate).

The data acquisition card (National Instruments PCI6025) does not need to be initialized. However, the program specifies the channel(s) to be read.

The mixing crystal, which is external to the dye laser, is controlled by simple stepper motor. This system does not need to be initialized by the program. Instead, the crystal is phase-matched manually at the beginning of the scan. Subsequent tracing of the phase-matching angle is accomplished by the program.

Tuning the Dye Laser and Optical Crystals

The spectra is produced by tuning the laser wavelength in small increments (usually about 0.002 nm/step) while monitoring the ion signal. The wavelength of the dye laser is related to the position of sine drive stepper motors that control the grating with respect to a specified origin.

We set up the dye laser in a mode that allows for the direct control of the tuning stepper motors. To tune the wavelength or track the phase-matching angle of the crystals, each motor must move a certain number of
steps. The relationship between the wavelength and the motor positions is nonlinear and can be characterized using a polynomial function. The relationship between the grating position and the wavelength, for example, can be expressed as

\[ Y(X) = A_0 + A_1 X + A_2 X^2 + A_3 X^3 \]  

(2.12)

where \( Y(X) \) is the grating or crystal motor position, \( X \) is the current wavelength in nanometer and \( A_i \) are constant coefficients. The relationship between the wavelength and the second harmonic and the mixing crystals also obey the above equation, but each with a different set of coefficients (\( A_i \)'s).

The coefficients for each system are found by fitting the above equation using data for each system. The data for the relationship between the wavelength and the grating positions are provided by the dye laser vendor but can also be generated using a stand-alone tuning program provided by the vendor or by measurement. In both methods, first the laser is set to a specific wavelength then the power is optimized by tuning the crystal. This can repeated at as many step as is necessary to produce a set of values corresponding to the (angular) positions of the crystal corresponding to optimum power at specific wavelengths. A polynomial fit of this data is used to trace
the optimal tuning parameters. The same procedure is used to generate phase matching data for the mixing crystal.

The tuning program uses these coefficients and the above equation to calculate the number of steps each of the stepper motor systems must move in every step of the scanning process. For the dye laser grating and second harmonic crystal this each value of $Y(X)$ corresponds to an absolute position (with respect to a specified origin) of the motors. This data is sent as an encoded single command.

The mixing crystal, however, is external to the dye laser and is driven by a stepper motor with much less resolution (200 steps/revolution or 0.56°/step). The wavelength increments we used require a change of the crystal phase-matching angle that is less than the one produced by a single step of the stepper motor. The program uses an approximate scheme to keep the phase-matching angle as close as possible to its optimum value. To do this, the program calculates the motor position at the new wavelength position using the above polynomial function and compares the new value with the previous one. Based on the difference, the program decides whether to move a step or not. If the change of the function is smaller than one step, as is usually the case, the program saves the change in a shift register adds it to the value of the function at the next wavelength position. It eventually
makes a step when the accumulated differences becomes greater than one. To make a step, the program sends a positive pulse to the stepper motor controller.

Data Acquisition

The sequence of events in this part of the data acquisition is as follows: A photo-diode (Newport 818-BB-22) sends a trigger pulse (due to scattered light from the laser) to the oscilloscope which in turn acquires a voltage signal from the microchannel plates in a specified time window with respect to the trigger. The output of the power meter (Ophir Optronics Ltd. P/N 1701500), which is in front of the UV beam exiting the chamber, is also detected using an A/D channel of the data acquisition card. These steps are repeated for as many laser shots as required (usually $\geq 100$ shots) at each wavelength.

At the pressures the experiment is done, the ion signal is so low that at resonance, the number of detected deuterium ions is less than one per laser shot. After the acquisition of each trace, the data is sent to a routine that detects and counts the single ion pulses in the time window. The number of ions detected in each trace are added to those resulting from the previous shots, which are kept in a shift register, until the maximum number of shots
for that wavelength is reached. The total number of ions are written along with the average power for that wavelength to a data file (as well as the computer screen) before the wavelength is incremented.

### 2.5.2 Time of Flight Program

The time of flight program records the distribution of the ions in the region of interest (gate) of the oscilloscope trace. This program communicates only with the oscilloscope.

Before this program is started, the dye laser must be tuned to the peak of a REMPI resonance. The program acquires a large number of laser shots (2000 – 20000 shots), divides the time window into segments (~ 10 points per segment) and searches for ions in each segment. The number of ions in each segment are written along with the average arrival time of the segment containing them in a two-dimensional array. The number of ions in each segment are accumulated into these bins until the required number of shots is finished. The data is written to a file at the end. A flow chart version of this program is shown on Fig. 2.10
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Figure 2.10: Time of flight program flowchart.
2.5.3 Scanning Program for the Auger Spectrometer

This program accomplishes two tasks: Ramping the electron mesh (retarding) voltage and acquiring Auger (voltage) signal from the lock-in amplifier. The retarding voltage is generated by a power supply whose output can be controlled by external voltage in the range of 0 to 10 volts. The program provides the external driving voltage for the spectrometer's retardation field power supply using the one of the D/A channels of the data acquisition card. The range of retarding voltage is from 0 to 600 V while that of the external driving source must lie between 0 and 10V. The relationship between the two voltages is nonlinear and fits a cubic polynomial equation of the form:

\[ V_{\text{ext}}(V) = B_0 + B_1V + B_2V^2 + B_3V^3 \quad (2.13) \]

where \( V_{\text{ext}} \) is the driving voltage (generated by the program through the DAQ card), \( V \) is the desired retarding voltage and \( B_i \) are fit coefficients. The fit coefficients are obtained by fitting the retardation voltage (displayed by the Auger spectrometer's power supply) versus the driving voltage. The resulting fit coefficients are then used to calculate the driving voltage in a similar way as the scanning program uses the wavelength to calculate the stepper motor positions. The Auger signal is recorded in a file along with
Set initial voltage on power supply

Wait for the electronics to stabilize

Calculate voltage step

Send voltage to power supply

Read Lock-in Amp. output (A/D channel)

Write data to file

End reached?

Stop

Figure 2.11: Auger spectrometer scanning program flowchart.
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the retarding voltage at each voltage step (usually $\Delta V = 1$ V). A flow chart version of the program is shown in Fig. 2.11.
Chapter 3

Data Analysis Methods

3.1 Introduction

This chapter explains in detail the detection scheme and the analytical methods necessary for the understanding and the extraction of the dynamical information from the rovibrational and translational population distributions of the D$_2$ molecules.

The measurement of the rovibrational and translational energy of deuterium molecules at pressures $\sim 10^{-10}$ Torr is a challenging task. The partial pressure of the deuterium from the dissociation of D$_2$O on a hot Zr surface is limited to this extremely small value due to the limitation of the available surface area of the crystal and the efficiency of the D$_2$ production. In the case of the heated effusive source where this limitation does not exist the pressure is still kept near the above value to minimize contamination of the signal from scattered background, especially for the $Q_J(0,0)$ band. In
the $Q_j(1,1)$ and $Q_j(0,1)$ transitions, increasing pressure leads to significant increase in the background noise due to non-resonant ionization processes.

An additional challenge in this experiment is related to the detection of deuterium. Homo-nuclear diatomic molecules, including deuterium, lack a permanent electric dipole moment. Consequently, transitions between rotational or vibrational levels are not possible. Due to this characteristic, deuterium does not emit or absorb electromagnetic radiation in the infrared region of the spectrum [67]. Furthermore, the lowest excited electronic states of deuterium lies above 91000 cm$^{-1}$ ($\sim$ 110 nm) [68]. This means that deuterium is transparent to electromagnetic radiation whose energy lies below this value. Under UHV conditions, it is not easy to generate VUV photons that can be used for the excitation (or ionization) of deuterium. Furthermore, electron impact ionization lacks the necessary resolution for state-specific population measurements. Laser induced fluorescence (LIF) [69], Coherent Anti-Stokes Raman Scattering (CARS) [70, 71] and Resonance Enhanced Multi-Photon Ionization (REMPI) are among alternative methods for detection of hydrogen in a state-specific manner. CARS signal scales with the square of the gas density [70]. Consequently, CARS is not an effective method at very low pressures. In LIF, the fluorescence signal is emitted isotropically and cannot be gathered efficiently. REMPI is most efficient in
situations where the particle density is extremely small since ions created can be collected with near unit efficiency using time-of-flight techniques.

The REMPI scheme used in this experiment to multiphoton ionize deuterium involves two steps: In the first step the molecules are excited into an excited electronic state \((E, F^1\Sigma_g^+)\) by simultaneous absorption of two UV photons \(^7\text{citkligler}\). The second step involves absorption of a third photon from the same beam which ionizes the molecule. When all three photons are of the same wavelength, the REMPI process is termed as \((2 + 1)\) whereas the notation \((2 + 1')\) is used when the ionization step involves a photon with a different wavelength. The REMPI scheme is many orders of magnitude more efficient than the direct multiphoton ionization as a result of significant enhancement due to the resonant intermediate step. Figure 3.1 shows the schematic of the REMPI process for deuterium. The figure shows the potential energy surfaces of only those states involved in the REMPI process.

The REMPI ions are collected by a time-of-flight spectrometer. To record a rovibrational spectra the photon energy is tuned over the region of interest. To obtain a time-of-flight distribution the laser wavelength is fixed on top of a rovibrational transition and the resulting ions are collected into histogram bins according to their time of arrival at the detector.
Figure 3.1: Potential energy curves of D₂ as a function of internuclear distance. The data points are based on *ab initio* calculations due to Sharp [73] and Kolos *et al.* [74]. The vibrational wave functions shown in the potentials are calculated using Le Roy's Level program [75] after using corrections in Ref. [76].


3.2 REMPI Spectra of Deuterium

Transitions involving an even number of photons require that the symmetry of initial and final states involved in the transition to be the same. In the case of deuterium, the lowest excited electronic state that can be reached from the $X^1\Sigma_g^+$ ground state by two photon transition is the $E, F^1\Sigma_g^+$ state. The selection rules for the rotational quantum number for a transition from the ground state into the $E, F^1\Sigma_g^+$ restrict the change of the rotational quantum number to $\Delta J = -2, 0, 2$. The branches corresponding to the different $\Delta J = -2, 0, 2$ are called the O-branch, Q-branch and S-branch, respectively. The Q-branch is orders of magnitude stronger than the two other branches and also preserves the ground state population distributions[77].

The rovibrational transition $E, F^1\Sigma_g^+(v', J') \leftarrow X^1\Sigma_g^+(v'', J'')$ with $\Delta J = 0$ is usually written as $Q_J(v', v'')$, where $v'$ and, $v''$ are the upper and lower state vibrational quantum numbers, respectively\(^1\).

With respect to vibrational quantum number, there are no symmetry selection rules. Transitions can be made from any vibrational state of the ground electronic state to any of the vibrational states of the excited electronic state. Transitions between different vibrational states are restricted,

\(^1\)It is common in spectroscopy to label the quantum numbers of the ground electronic state with double prime and those in the upper state in a transition with single primes.
however, by the overlap between the vibrational wave functions of the states involved. Electronic transitions occur in a much shorter time scale than the period of the vibrational motion of the nuclei. Hence the transition intensity depends on the square of the overlap of the wave functions of the two vibrational levels involved in the transition. This is called the Frank-Condon principle [82]. Fig. 3.2 show a typical REMPI spectrum along with a simulated data.

In the case of the $Q_J(v'', v')$ band, the ion signal generated by the REMPI scheme represents rovibrational spectra and the intensities of the individual peaks are proportional for the populations in the lower levels. The rovibrational populations are measured in the following way: Each time twice the energy of the third harmonic of dye laser matches the energy gap between rotational states in the ground and excited states which satisfy the selection rules ($\Delta J$), molecules in that specific rovibrational state are pumped into the intermediate state and are subsequently ionized through the absorption of another photon from the same beam. The ionization step is usually saturated, therefore, the ion signal depends on the laser intensity only through the intermediate stop. The absorption of the intermediate step by two simultaneous photons through a virtual state (a nonlinear process) is expected to depend on the square of the intensity. With the intensity variations taken
Figure 3.2: REMPI (2 + 1) spectrum of the $Q_J(0,0)$ band of D$_2$. The upper spectrum is a simulation of D$_2$ at 450 K and the lower spectrum is due to deuterium from dissociation of water on a Zr surface at 800 K. The upper spectrum is shifted up for clarity.
into account, the ion signal reflects the population of the rovibrational states of the ground state electronic state. Thus, tuning of the laser wavelength over a rovibrational band maps the ground state population into the ion signal. The result is a set of rotational spectra for each of the ground state vibrational levels which represent the population in these levels.

Under thermal equilibrium, the population distribution in the ground electronic state depends on the temperature through Boltzmann Law. Hydrogen isotopes are particularly special in that at room temperature over ~ 99% of the molecules are in the ground vibrational state. This is a consequence of unusually large energy spacing in the vibrational levels.

The rovibrational spectra of deuterium were generated by tightly focusing the third harmonic (~ 200 nm) of ~ 8 ns dye laser pulses that were generated using either Rhodamine 610 or Rhodamine 640 dyes or their mixture to measure the spectra of the $Q_J(0,0)$, $Q_J(1,1)$ or $Q_J(0,1)$ bands. The REMPI ions were collected using a linear time-of-flight mass spectrometer. Collection of this ion signal as function of the laser wavelength results in the REMPI spectrum. At the pressure levels the experiments were done, the REMPI signal was so weak that there was less than one ion per laser shot at the maximum of strongest rovibrational transitions. As a result, the rovibrational spectra were collected using ion counting techniques.
3.2.1 Dependence of the Ion Signal on the Laser Power

For any particular dye, the power of the dye laser light varies with wavelength. For hydrogen, the variation of the intensity from one rovibrational line to the next can be very large due to the large separation between these lines. In addition, the efficiency of the ionization process is expected to depend on (at least) the square of the intensity [79]. It was thus necessary to measure the power of the laser along with the ion signal at each wavelength increment to subsequently correct the resulting spectrum for the power variations. In order to correct for the ion signal dependence on intensity, the ion signal was measured as a function of UV power by varying the laser power at a fixed wavelength and pressure under typical experimental conditions. In order to deduce the exponent of the relationship a linear function was fit to the logarithm of resulting data. Fig. 3.3 shows the result of one such measurement. The slope of the fit was measured as 2.04 ± 0.05. This result implies quadratic dependence of the ion signal dependence on laser power and independence from the intensity of the third (ionizing) photon.

3.2.2 D₂O/D₂ Pressure Correlation

The evidence for hydrogen evolution as a result of dissociation of water on a hot Zr comes from the changes of the partial pressures of the scattered
Figure 3.3: Log-log plot of the D$_2^+$ intensity at top of the $Q_2(0,0)$ peak vs. average laser pulse energy. The solid line is a fit with slope = 2.04 ± 0.05.
D$_2$ and D$_2$O recorded by the RGA. When the crystal is heated under an impinging beam of D$_2$O, a raise in the D$_2$ partial pressure and accompanying drop of the D$_2$O partial pressure are observed on the RGA. Fig. 3.4 shows correlated changes in the pressure of D$_2$ and D$_2$O due to changes in the temperature of the Zr crystal. At point A the crystal temperature sweep from room temperature to 800 K begins, leading at the same to decrease of the partial pressure of D$_2$O and an increase of the partial pressure of D$_2$. After steady state D$_2$ production for about 30 minutes, the crystal temperature is swept down at point B, leading to an increase in the pressure of D$_2$O and a decrease of the pressure of D$_2$. This is a clear evidence that the dissociation of D$_2$O is the source of the changes in the partial pressure of D$_2$ with temperature. The data shown in Fig. 3.4 were obtained using the hexagonal (0001) face of the Zr crystal. Using the (10\overline{1}0), we find that the correlation between the two partial pressures changes somewhat. Although we have not made a comparison of the production efficiencies in a calibrated manner, it appears that hydrogen production is higher in the case of the (10\overline{1}0) face. Since the structure of the two phases are different it is not surprising to see differences in the behaviour of the water dissociation.
Figure 3.4: Partial pressures of D$_2$ and D$_2$O as function of temperature. The changes in the partial pressures are due to the changes of the temperature of the Zr crystal. The upper curve represents the partial pressure of the D$_2$O and the lower curve represents the partial pressure of the D$_2$. 
3.3 Estimation of D₂ Production Efficiency

In this section we attempt to estimate the ionization efficiency of our experiment. The surface area of the Zr crystal we use is approximately 25 mm². Assuming inter-atomic distance of 3.23 Å [80] for the Zr crystal and one surface site per atom, there are about $1 \times 10^{13}$ sites on the surface of the crystal. The volume of the chamber we use is roughly 0.044 m³. In the absence of pumping, the pressure change in the chamber due to desorption of one monolayer of D₂ from the crystal can be calculated using the ideal gas law as

$$\Delta p = \frac{1}{2} \frac{\Delta N k_B T}{V}$$

where $\frac{1}{2}$ comes from the fact that two deuterium atoms combine to make a deuterium molecule. In the absence of pumping, the increase in the partial pressure of D₂ in the chamber due to the desorption of one monolayer is approximately $7 \times 10^{-6}$ Torr. To get a more accurate estimate the effect of the pumping must be taken into account.

In the more realistic situation where there is a constant gas load as well as pumping, the changes in the amount of gas in the system is described by
the following equation [60]:

\[-V \frac{dp}{dt} + Q_\infty = Sp(t)\]  \hspace{1cm} (3.2)

where \(V\) is the volume, \(p\) is the pressure, \(Q_\infty\) is the constant gas load, and \(S\) is the pumping speed in L/s.

As an illustration, the total gas load can be calculated for our UHV system from the pressure data acquired through the RGA software. For a given time interval \(\Delta t = t_f - t_i\) (ignoring the variation of pumping speed with pressure and assuming a constant gas load) the total gas load can be calculated by integrating Eq. 3.2.

\[Q_\infty \Delta t = V \Delta p + S \int_{t_i}^{t_f} p(t) dt\]  \hspace{1cm} (3.3)

A discrete form of Eq. 3.2 which is more useful in practical situations where discrete pressure data is available takes the form:

\[Q_\infty \Delta t = V \Delta p + S \sum_{i=1}^{N} p(t_i) \Delta t_i\]  \hspace{1cm} (3.4)

For illustration purposes, we apply Equation 3.4 to calculate the total amount of \(\text{D}_2\) gas produced by the crystal using the data Fig. 3.4. Assuming a com-
combined pumping speed of \( \sim 100 \text{ L/s} \) and parameters of the chamber, the amount of \( \text{D}_2 \) produced during the reaction is estimated to be \( \sim 5 \times 10^{14} \) molecules. The number of molecules produced during the steady state is about \( 3.5 \times 10^{14} \) molecules. The water beam impinges on the crystal on an area of with diameter \( \sim 2 \text{ mm} \). Taking this into account, the \( \text{D}_2 \) output of the crystal during the steady state is \( \sim 500 \) monolayers (ML). The production rate of the crystal is then estimated to be about \( 0.5 \text{ ML/sec} \).

### 3.3.1 Estimation of \( \text{D}_2 \) Density at the Focal Region of the Lens

From knowledge of the partial pressure of the deuterium molecules and laser parameters, it is possible to give an estimate of the average density of the deuterium molecules in the focal region of the laser.

**Relevant Focal Volume of the Laser for REMPI**

The efficiency of two photon step in the ionization process, which determines the overall REMPI efficiency, depends strongly on the photon flux density. High photon flux density can be achieved by tightly focusing the laser beam. The photon flux density at the focus of the lens can be calculated using the so-called ABCD transformation matrix for Gaussian beams. (Even though
the laser beam has an oblong shape due to diffraction by the vertical edges of the dye cells, it is not diffracted along the vertical direction. Therefore, the beam is closest to Gaussian along this direction.) In order to understand how we estimate the beam size at the focus of the laser, it necessary to briefly summarize the relevant aspects of Gaussian beam properties.

In general, the properties of a Gaussian beam are contained in the so-called Gaussian beam parameter \( q \) defined as \(^81\)

\[
\frac{1}{q(z)} = \frac{1}{R(z)} + \frac{i\lambda}{\pi w^2(z)}
\]

where \( z \) is the beam position along the propagation axis, \( R(z) \) is curvature of the beam wavefront, \( w(z) \) is the beam waist, and \( \lambda \) is the wavelength. The ABCD transformation of the Gaussian parameters is given by

\[
q' = \frac{Aq + B}{Cq + D}
\]

where \( A, B, C \) and \( D \) form the elements of the following \( 2 \times 2 \) matrix, called the ray transfer matrix or simply the ABCD matrix,

\[
\begin{pmatrix}
A & B \\
C & D
\end{pmatrix}
\]

For propagation in free space, the ABCD matrix becomes
where \( z_2 \) \(-\) \( z_1 \) is the distance of interest. For a lens with focal length \( f \) the ray transfer matrix takes the form

\[
\begin{pmatrix}
1 & z_2 - z_1 \\
0 & 1
\end{pmatrix}
\]

When the beam passes through a series of optical elements, the matrices of the different elements are multiplied from left to right in the order the beam traverses these optical elements. The beam parameters of the resulting beam after the propagation through a set of optical elements are deduced from the elements of the resulting ABCD matrix.

The beam waist at the focus of the lens, which is the relevant parameter here, is deduced from the imaginary part of Eq. 3.6. In order to measure the beam waist of the UV beam used to ionize the hydrogen molecules, an experiment was set up to measure the divergence of the beam. The experiment was set up such that the laser beam first propagates in air for a distance \( \sim 3.3 \text{ m} \) before it is focused by a thin lens. To estimate the beam size at the focus of the lens, the far field divergence angle of the laser beam was measured by measuring the beam size at different distances from the laser resonator. The far field divergence of the laser beam was found to be 0.65 mrad at 202 nm. (The manufacturer stated a far field divergence of 0.5
mrad in the visible.) The volume of the focal region relevant for the REMPI process is estimated as

\[ V_{\text{focal}} = \frac{2\pi}{3} z_R \bar{w}_0^2 \tag{3.7} \]

where \( z_R \) is the Rayleigh range parameter at the focal region of the lens and \( \bar{w} = \frac{1+\sqrt{2}}{2} w_0' \) is the average radius of the beam. The above parameters lead to a focal volume of \( \sim 4 \times 10^{-12} \text{ m}^3 \)

**D\textsubscript{2} Density at Focus of the Lens**

Treating D\textsubscript{2} as an ideal gas, the molecule density in the chamber at pressure \( p \) is given by

\[ n = \frac{p}{k_B T} \tag{3.8} \]

where \( n \) is the molecular density, \( T \) is the temperature and \( k_B \) is the Boltzmann constant. For \( p = 10^{-9} \text{ Torr} \), \( n = 3.2 \times 10^{12} \text{ particle/m}^3 \). Using this estimate of the focal volume, the average number of deuterium molecules in the focal volume at \( 10^{-9} \text{ Torr} \) is \( \sim 140 \) molecules. For background deuterium at room temperature about 38\% (or 53 molecules) will be in the focal volume of the laser on average.
3.3.2 Estimating the Detection Efficiency

Using the estimated number of molecules in focal volume, the efficiency of our detection system can be estimated. The rotational peaks are spread in $\sim 0.01$ nm ranges. The area under the rotational lines gives the total population in that line. Due to the discrete nature of the tuning of laser, we obtain the total population in a line by summing the ions in that line. The total population in all the rotational lines of a vibrational state at a fixed power is the sum of the ions in the populated rotational lines within the vibrational state. The total number of ions in the line are however a result of accumulation of ions resulting from a large number of laser shots ($100 - 1000$ shots). The number of ions detected in a specific rotational line is the fraction of ions in that line with respect to the total number of ions in that vibrational state divided by the number of shots accumulated. Assuming the time of flight efficiency of unity and neglecting other possible factors affecting the detection efficiency (which are known to be negligible), the estimated detection efficiency represents that of the REMPI scheme.

Under equilibrium conditions at $T = 300$ K, the rotational state with $J = 2$ of the ground vibrational state of deuterium contains approximately 39% of the population in that vibrational state. The peak due to this line was collected using the effusive source at room temperature by accumulating 400
laser shots and was found to contain a total of 6012 ions. This corresponds to detecting an average of 15 molecules within the linewidth per laser shot.

For the effusive source, the pressure recorded by the RGA was \( \sim 2 \times 10^{-9} \) Torr. The pressure at the focal volume was measured to be about three times higher than the background seen by the RGA. The total number of molecules in the \( v = 0 \) state in the focal region this pressure was calculated to be about 770 molecules. About 300 (39\%) of which were expected to be in \( J = 2 \). As a result, this puts the detection efficiency of the REMPI process around 5\%.

3.3.3 Rovibrational Spectra of D\(_2\) Under Thermal Equilibrium: An Illustrative Example

Under equilibrium conditions, the rovibrational population distributions obey Boltzmann Law. For deuterium, the ground electronic state rovibrational population is given by [67]

\[
N(J, v) = \frac{1}{Q} g_J (2J + 1) e^{-\frac{E_{rot}(J,v) + E_{vib}(v)}{k_B T}}
\]

(3.9)

where \( N(J, v) \) is the fraction of the population in the rovibrational state specified by \( J \) and \( v \). \( E_{rot}(J,v) \) and \( E_{vib}(v) \) are the rotational and vibrational energies of the the rovibrational state, and \( g_J \) is a nuclear spin degeneracy
factor whereas $Q = \sum_{J,v} N(J,v)$ is the partition function\textsuperscript{2}. The energy of the rotational states is given by

$$E_{\text{rot}} = B_v J(J + 1) - D_v J(J + 1)^2$$

(3.10)

where $B_v$ is equilibrium rotational constant given by

$$B_v = B_e - \alpha_v \left( v + \frac{1}{2} \right)$$

(3.11)

and $D_v$ is the rotational distortion. $\alpha_v$ and $D_v$ have slight vibrational dependence. For the ground electronic state of deuterium $\alpha_v$, according to the NIST database, is given by [68]

$$\alpha_v = 1.0786 + 0.01265(v + \frac{1}{2})^2 - 0.00069 \left( v + \frac{1}{2} \right)^3$$

(3.12)

where the $v$ subscript signifies dependence on the vibrational quantum number. Similarly the rotational distortion constant for the ground electronic state is given by [68]

$$D_v = 0.01141 - 0.00022 \left( v + \frac{1}{2} \right)$$

(3.13)

\textsuperscript{2}g_J = 6 for even values of $J$, $g_J = 3$ for odd values of $J$[82]
These small corrections are necessary for the correct calculation of the rotational line positions for the Boltzmann plots. $E_{\text{vib}}(v)$, on the other hand, is given by

$$E_{\text{vib}}(v) = \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2 + \omega_e y_e \left(v + \frac{1}{2}\right)^3 - \omega_e z_e \left(v + \frac{1}{2}\right)^4$$

(3.14)

The constants for $X^1\Sigma_g^+$ and the inner ($E$) well of the $E^1\Sigma_g^+$ states of $D_2$ are summarized in Table 3.1.

<table>
<thead>
<tr>
<th>State/Constant</th>
<th>$\omega_e$</th>
<th>$\omega_e x_e$</th>
<th>$\omega_e y_e$</th>
<th>$\omega_e z_e$</th>
<th>$B_e$</th>
<th>$\alpha_e$</th>
<th>$D_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^1\Sigma_g^+$</td>
<td>3115.50</td>
<td>61.82</td>
<td>0.562</td>
<td>-0.0228</td>
<td>30.443</td>
<td>1.0786</td>
<td>0.01141</td>
</tr>
<tr>
<td>$E^1\Sigma_g^+$</td>
<td>1784.42</td>
<td>48.10</td>
<td></td>
<td></td>
<td>16.369</td>
<td>0.6764</td>
<td>0.0054</td>
</tr>
</tbody>
</table>

Table 3.1: Rotational and vibrational constants (in cm$^{-1}$) of the $X^1\Sigma_g^+$ and the $E^1\Sigma_g^+$ [68].

### 3.3.4 Boltzmann Plots and Temperature Measurement

The temperature of a gas at equilibrium in a container at a fixed temperature can be inferred from the rovibrational population distribution of the gas. One way to measure the rotational temperature of a gas in equilibrium is to compare the measured spectrum to a simulated spectrum. A more convenient way is to plot the logarithm of the line intensities against the...
rotational energy. In the case of deuterium and hydrogen, the intensity must be divided by the multiplicity $g_J(2J + 1)$ of the rotational line before taking the logarithm. To find the vibrational temperature, the logarithm of the sum of the populations in each vibrational state is plotted against the vibrational energy. Under equilibrium conditions, the resulting data fits a straight line and the temperature is deduced from the slope of the line of best fit. The temperature is related to the temperature by the relation

$$slope = \frac{1}{k_B T}$$

where $k_B = 0.69432 \text{ cm}^{-1}$ when the energy is measured in wavenumbers.

3.3.5 Rotational Spectra of D$_2$ Under Thermal Equilibrium

The rotational spectra of the ground vibrational is measured through REMPI $Q_J(0, 0)$ for calibrational purposes using an effusive D$_2$ source at room temperature. Figure 3.5 is Boltzmann plot of the same spectra. The slope of the line of best fit gives the measured temperature of 308 ± 10 K.
Figure 3.5: $Q_J(0, 0)$ Plot of degeneracy-normalized intensities of the $Q_J(0, 0)$ band of $D_2$ from effusive source at room temperature. The background component present in the low $J$ lines The straight line is a least squares fit.
3.4 Time of Flight Distribution

A convenient way of measuring velocity distributions is to use a time-of-flight spectrometer. Under such an experiment, the gas whose velocity distribution is to be determined is accelerated in a field free time of flight tube to a highly biased microchannel plates. The velocity distribution of the ionized gas has a corresponding time distribution with a different functional form. If the detector response effects and other imperfections are neglected, the two distributions are related mathematically in a simple way. The difference between the two distributions arises from the reciprocal relationship between velocity and the time-of-flight of the particles. In the case of a field free flight tube, the time-of-flight and velocity distributions are related by: a small area under the velocity distribution \( f(v)dv \) (fraction of molecules with their velocities between \( v \) and \( v + dv \)) transforms into

\[
g(t) \propto \frac{1}{t^2} f \left( \frac{L}{t} \right)
\]  

(3.16)

where \( g(t) \) is the the time of flight distribution, \( f(\frac{L}{t}) \) is the velocity distribution with the velocity replaced with the length of the tube \( (L) \) and the time-of-flight of the particles. The \( 1/t^2 \) factor is the Jacobian associated with the transformation of the area under the velocity distribution.
For the case of an isotropic gas, the velocity distribution along the time-of-flight axis has a Gaussian shape of the form

\[ f(v) = C \exp(-\alpha v^2) \] (3.17)

where \( \alpha = \frac{M}{2k_B T} \), \( M \) is the mass of the molecules, \( k_B = 1.381 \times 10^{-23} \text{ J/K} \) is the Boltzmann constant, \( T \) is the temperature and \( C \) is a normalization factor. The corresponding time of flight distribution has the form

\[ g(t) \propto \frac{1}{t^2} \exp \left\{ -\alpha L^2 \left( \frac{1}{t} - \frac{1}{t_0} \right)^2 \right\} \] (3.18)

In the case of an oven source, the probability for the molecules to exit the oven is proportional for their speed. The velocity distribution of the exiting particles is thus proportional for the product of the speed distribution function of the gas inside the oven and the velocity of the particles[83] giving

\[ f(v) \propto v^3 \exp \left\{ -\alpha v^2 \right\} \] (3.19)

The corresponding time of flight distribution is given by

\[ g(t) \propto \left( \frac{1}{t} - \frac{1}{t_0} \right)^5 \exp \left\{ -\alpha L^2 \left( \frac{1}{t} - \frac{1}{t_0} \right)^2 \right\} \] (3.20)
where the flight tube parameters are substituted instead of the velocities.

Figure 3.6 shows a typical raw time-of-flight distribution recorded by the time of flight mass spectrometer. The data were collected using the effusive source at room temperature.

3.4.1 Extracting Temperature from Time of Flight Distributions

Under equilibrium conditions, the shape of the velocity distribution depends on the temperature. Using the above formulas, it is possible to deduce of the temperature information from time-of-flight distributions such as the one shown in Fig.e 3.6. This section is an illustration of how the modeling is done.

Nonlinear Least Square Modeling of TOF Distributions

In order to extract the temperature information from the time-of-flight distributions, we used Mathematica's nonlinear regression routine. For the case of time-of-flight distributions due to isotropic D$_2$, we used a model of the form

\[ f_1(t) = A_0 + \frac{A_1}{t} \exp \left[ - \left( \frac{1/t - A_2}{\sigma_1} \right)^2 \right] \]  

(3.21)
Figure 3.6: \( \text{D}_2^+ \) time-of-flight distribution recorded by the time-of-flight mass spectrometer resulting from the laser ionization of a \( \text{D}_2 \) beam from the effusive source. The data contains a background component resulting from the ionization of the isotropic \( \text{D}_2 \) in the chamber.
where $A_i$ and $\sigma_1$ are model parameters. Similarly, for the case of an effusive source, we use a model of the form

$$f_2(t) = B_0 + B_1 \left( \frac{1}{t} - B_2 \right)^4 \exp \left[ - \left( \frac{1/t - B_2}{\sigma_1} \right)^2 \right] \times \theta(t_0 - t) \quad (3.22)$$

where again the $a_i$'s and $\sigma_2$ are parameters to be varied and $\theta(t_0 - t)$ is a unit step (Heaviside) function which is necessary for the suppression of the second wing of the symmetrical fit function. Note that in the above models, the power of the pre-exponential factors are reduced by one unit. The reason for this is related to the detection mechanism. According to Auerbach [78], a factor of $t$ must be multiplied to the time of flight distribution when a density sensitive, instead of flux sensitive, detector is used. During the ionization by REMPI, the molecules are effectively at rest, rendering REMPI a density sensitive method.

The temperature information is inferred from $\sigma_i$ through the relation

$$T = \frac{ML^2 \sigma_i^2}{k_B} \quad (3.23)$$

Figure 3.7 is an illustration of the fitting procedure described above. The fit to the data is the sum of two functions corresponding to the beam and the background components of the signal. Normally, a discrete form of the
Figure 3.7: Nonlinear least squares fits of the beam and background components of the time-of-flight data in Fig. 3.6. The $v = 0$ label marks the time-of-flight of the zero velocity ions.
model for the background is subtracted from the raw data to isolate the component of the data due to the beam, which is what was done to get the beam-like distribution in Figure 3.6.

When the background is subtracted the resulting data can be converted into a velocity distribution by using the reverse of the transformation described above. Figure 3.8 shows the velocity distribution resulting from the beam component of the data shown in Figure 3.6. We measured the temperature of the velocity distribution by fitting the distribution to a model of the form:

\[ f_2(v) = C_0 + C_1 v^3 \exp \left[ - \left( \frac{v^2}{\sigma} \right)^2 \right] \]  \hspace{1cm} (3.24)

The resulting temperature from the fit was found to be \( T = 307 \pm 4 \text{K} \). Given the level of pressure used, this agrees well with the measured temperature of 307K.

### 3.5 Summary

In the previous sections of this chapter we discussed the REMPI scheme and how it leads to rovibrational spectra and gave a rough estimate of its sensitivity. We also discussed how the rovibrational and translational energy
Figure 3.8: Velocity distribution of $\text{D}_2^+$ ions resulting from the transformed time-of-flight of the beam component of the data on Figs. 3.6 and 3.7. The effusive source was at 300 K and the fit of the velocity distribution gives a temperature of $307 \pm 4$ K.
of a deuterium under equilibrium conditions are measured. The methods used in this chapter will be used in the next two chapters to extract thermal information from deuterium molecules resulting from the dissociation of D$_2$O on Zr as well as D$_2$ scattered from or desorbed by a hot Zr crystal.
Chapter 4

Population Distributions of

$D_2$ Due to Dissociation of

$D_2O$

In this chapter, the results of measurements of rovibrational and translational population distributions $D_2$ produced in the dissociation of $D_2O$ on Zr at $\sim 800$ K are presented and analyzed. The three bands $Q_J(0,0)$, $Q_J(1,1)$ and $Q_J(0,1)$, as well as the time of flight distribution of $Q_4(0,0)$ are measured. The rovibrational distributions for the $Q_J(0,0)$ and $Q_J(1,1)$ band are compared with those of $D_2$ from a heated effusive source and the translational population distributions are compared with that of isotropic background.
Chapter 4. Population Distributions of D\textsubscript{2} Due to Dissociation of D\textsubscript{2}O 100

4.1 Effusive Source Spectra

The effusive source emits a thermalized beam of deuterium. The rovibrational spectra of the beam were measured at the same temperature as surface temperature in the dissociation experiment, namely $T \sim 800$ K. The $Q_J(0,0)$ band up to $J'' = 8$ and the $Q_J(1,1)$ band up to $J'' = 6$ were collected and analyzed.

4.1.1 $Q_J(0,0)$ Band of Effusive Source

The $Q_J(0,0)$ band of the effusive source was measured few times under various levels of optimization of the detection scheme (such as the variation of the source pressure, source exit-ionization region distance, the alignment of the source with the axis of the of TOF-MS and ion extraction voltage and time gate width). Under optimum conditions, the contribution of the isotropic background to the spectrum was minimized such that it was not necessary to subtract it from the data. The optimization procedure took advantage of the high gas density near the exit of the effusive source by bringing the source as close as possible to the ionization region and at the same time aligning it with the time-of-flight axis. As can be seen in Fig. 3.7, the effusive source time-of-flight distributions overlap approximately with the early half of the background time-of-flight distribution. Therefore, to further minimize
the background contributions to the spectra, only the early half of the time-
of-flight gate was collected. The data presented here were collected under optimum conditions at effusive source temperature of 810 ± 10 K, with the uncertainty resulting from a small drift of the source temperature during the time of the experiment.

Fig. 4.1 shows the Boltzmann plot of a $Q_J(0,0)$ data collected under the optimal conditions. The logarithm of the power-corrected, degeneracy-normalized peak intensities fits a straight line whose slope gives $T = 778 ± 56$ K quite well, indicating the thermalization within the associated uncertainty of the gas at the temperature of the source. The slightly larger uncertainty originates in the noise in the the rotational peak shapes and laser power fluctuations.

The dependence of the transition moments of the $Q_J(0,0)$ and $Q_J(0,1)$ REMPI transitions through the $E$ well of the $E, F^1Σ_g^+$ state of deuterium on the rotational quantum number ($J$) were studied both theoretically and experimentally by Zare and coworkers [84, 85]. They found that up to $J = 15$, the variation of the transition moment is less than 7% and smaller for lower $J$'s. This effect is smaller than the uncertainty associated in the measured intensities in Fig. 4.1. Another effect that can influence the REMPI spectra of deuterium is the production of $D^+$ ions through the dissociative ioniza-
Chapter 4. Population Distributions of $D_2$ Due to Dissociation of $D_2O$

Figure 4.1: Boltzmann plot for 800 K $D_2$. The straight line represents the least squares fit of the degeneracy-normalized intensity of the lines in the $Q_J(0,0)$ band versus the rotational energy. The slope of the fit give $T = 778 \pm 56$K while the thermocouple attached to the tip of the source read $T = 813$ K.
Chapter 4. Population Distributions of D$_2$ Due to Dissociation of D$_2$O

Due to dissociation of D$_2$O, Zare and coworkers again found that for deuterium, the ratio of D$^+$/D$_2^+$ production to be approximately constant for states with $J \leq 9$ and $J \leq 7$ for the $Q_J(0,0)$ and $Q_J(1,1)$ bands, respectively [84, 85]. For states with $J \geq 10$, the D$^+$/D$_2^+$ ratio increases rapidly, diminishing the D$_2^+$ ion signal while increasing the D$^+$ signal. All of the reported spectra in this work are within $J < 10$ regime, hence, the D$^+$ production effect is not considered in the analysis of intensity of the REMPI spectra.

4.1.2 $Q_J(1,1)$ Band of the Effusive Source

The $Q_J(1,1)$ REMPI spectra of D$_2$ were measured under conditions similar as the $Q_J(0,0)$ band for $J \leq 6$. The purpose of measuring this band was to use it for comparing it with the $Q_J(1,1)$ spectra of D$_2$ from dissociation of water on hot Zr surface. The REMPI transition of this band has never been measured for population distributions measurement purposes and to the best of our knowledge, never been observed for $J \leq 5$. Perturbations on the REMPI spectra due to the presence of the F well are thought to increase with increasing vibrational quantum number in the E well and with increasing $J$ within the vibrational states. As a result, the alternative $Q_J(0,1)$ REMPI transition which involves the ground vibrational state of the E well is normally used. Because of the proximity in energy of the
Chapter 4. Population Distributions of $D_2$ Due to Dissociation of $D_2O$

Figure 4.2: Semi-logarithmic plot of degeneracy-normalized intensity of the $Q_J(1,1)$ spectrum of the effusive source at 800K versus rotational energy. The straight line represents the least squares fit of the data. The slope of the fit gives $T = 778 \pm 51$K. The thermocouple attached near the tip of the hot source capillary read 780K.
Chapter 4. Population Distributions of D₂ Due to Dissociation of D₂O 105

$Q_J(1,1)$ to the $Q_J(0,0)$ it is possible to scan both bands with a single laser dye.

The spectra shown in Fig. 4.2 were collected with the effusive source temperature at $780 \pm 5$ K. As can be seen in the Figure, the logarithm of the degeneracy-normalized intensity fits a straight line whose slope gives $T = 778 \pm 50$ K very well. Due the the comparatively much smaller population in the $v = 1$ state, the it was necessary to use higher number of laser shots per point to achieve acceptable signal-to-noise ratio within reasonable experimental time. The deviations of the low $J$ population about the line of best fit is most likely due to fluctuations in the power of the laser. The higher $J$ data fit the line of best fit quite well. On the other hand, if significant perturbations were present one would expect the higher $J$ transitions to deviate from the line of best fit more than the lower $J$ transitions. Due to the absence of pronounced perturbations in the in the $J \leq 6$ range, the $Q_J(1,1)$ transition is as useful as the $Q_J(1,0)$ band.

4.1.3 $Q_{10}(0,0)$ versus $Q_3(1,1)$

The $Q_J(1,1)$ REMPI transition has closer proximity to the $Q_J(0,0)$ band in energy than the $Q_J(0,1)$ band. This makes it more convenient in that a single dye mixture (Rhodamine 610 and 640) can be used to scan both bands.
Another advantage of this transition for our study is that the $Q_{10}(0,0)$ and $Q_J(1,1)$ REMPI transition lines are separated by only 3.8 cm$^{-1}$. The proximity of these two lines turns out, as will be discussed later, to be extremely useful in the comparison of the relative intensities of the $Q_J(1,1)$ spectra of D$_2$ from the dissociation of water with the D$_2$ from the effusive source.

Figure 4.9 shows the intensities of the $Q_{10}(0,0)$ and $Q_3(1,1)$ REMPI lines. The measured intensity ratio of the two lines at $T = 800$ K is $\sim 3$. This ratio will be used in Chapter 5 to estimate the relative population of the $v'' = 1$ state of the hydrogen produced by water dissociation on hot Zr.

4.2 Rovibrational Spectra of D$_2$ from the D$_2$O/Zr System

We probed the spectra of the lowest three vibrational levels ($v'' = 0 - 2$) of the ground electronic state ($X^1\Sigma^+_g$) of D$_2$ resulting from the dissociation of D$_2$O on Zr(1010) surface at 800 K. The REMPI spectra of the $v'' = 0$ and $v'' = 1$ were readily measured but no discernible signal was detected in the $v'' = 2$ state.
Figure 4.3: Measured intensities of the $Q_{10}(0, 0)$ and $Q_{3}(1, 1)$ lines of $D_2$ from effusive source at 800 K versus simulated spectra. In the simulation the molecular constants for $D_2$ were used and the $Q_{10}(0, 0)$ peak was divided by the relative transition moment of the $Q_{3}(1, 1)$ transition to fit the data.
4.2.1 \( Q_J(0,0) \) Spectra of the \( \text{D}_2 \) from the \( \text{D}_2\text{O/Zr} \) System

It is difficult to avoid contamination from the isotropic deuterium background when measuring the \( Q_J(0,0) \) REMPI spectra of the crystal. The background contamination is specially significant in the lower \((J \leq 4)\) lines of the spectrum. To get around this difficulty, the background spectrum was measured along with the deuterium from the reaction. Figure 4.4 the deuterium pressure in the chamber recorded by the RGA during a typical experiment. The higher pressure corresponds to the crystal temperature at \( \sim 800 \text{ K} \) and the lower pressure regions correspond to the crystal temperature at \( \sim 350 \text{ K} \). The REMPI peaks are measured twice for each peak; once when the crystal is hot and once after the heat is turned off and the crystal temperature drops to \( \sim 350 \text{ K} \). The pressure measured by the RGA represents the background level in the chamber, which is higher when the crystal is producing \( \text{D}_2 \). The background spectrum is adjusted for the pressure difference before it is subtracted from the signal.

The lower curve in Figure 4.5 shows the resulting \( Q_J(0,0) \) REMPI spectrum of deuterium due to the dissociation of the water on the hot Zr surface for \( J \leq 6 \). The upper curve is a simulation of the rotational population of \( v'' = 0 \) state at 450 K. A Boltzmann plot of the same data is shown in Figure 4.6. The slope of the line of best fit of the logarithm of the degeneracy-
Figure 4.4: Variation of the pressure of $D_2$ with time during the water dissociation experiment. The higher pressure result from the dissociation of water when the crystal is heated to 800 K. The pressure drops as soon as heating is stopped. Data on Figs. 4.5 and 4.6 were collected at top of the pressure peaks.
Figure 4.5: $Q_j(0,0)$ spectrum of D$_2$ released by dissociation of heavy water on Zr(1010) surface at 800 K (lower figure). The upper figure is a simulation at $T = 450$ K. The simulated spectrum is not fitted to the data and the simulation temperature is chosen by visual examination. Boltzmann plots are used for temperature estimation.
Figure 4.6: Semi-logarithmic plot of normalized intensity versus rotational energy of the $Q_J(0,0)$ band of the $D_2$ released reaction of $D_2O$ on Zr surface at $T = 810$ K. The slope of the fit gives an average temperature of $493 \pm 44$ K.
normalized line intensities gives a rotational temperature of $T = 493 \pm 44$ K. The surface temperature was held at $800 \pm 10$ K during the experiment. The disagreement between the crystal temperature and the rotational temperature of the spectrum cannot be accounted for in terms of the experimental uncertainties resulting from the processing of the data. The background intensities subtracted from the spectrum were thermalized at $\sim 300$ K. Hence any random fluctuations resulting from the subtraction process cannot distort the distribution in such a manner as to fit a Boltzmann distribution at a much lower temperature. It is noteworthy to mention that REMPI peaks beyond $J'' = 6$ were very difficult to observe.

4.2.2 $Q_J(1,1)$ Spectra of $D_2$ due to $D_2O/Zr$ System

In addition to the $Q_J(0,0)$ REMPI spectra of the deuterium released by the water dissociation on hot Zr surface, the REMPI spectra of the $Q_J(1,1)$ band was measured under similar conditions. Since the $v'' = 1$ state of $D_2$ lies about 3000 cm$^{-1}$ above $v'' = 0$ state, the $Q_J(1,1)$ REMPI spectrum is effectively background-free. Figure 4.7 shows the logarithmic plot of the degeneracy-normalized intensity of REMPI spectrum versus the rotational energy. The upper curve corresponds to the alternative $Q_J(0,1)$ REMPI transition (which were also able to measure) and lower curve corresponds
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Figure 4.7: Semi-logarithmic plot of degeneracy-normalized $Q_J(0, 1)$ and $Q_J(1, 1)$ population distributions. The slopes of the least square fits give $T = 403 \pm 33$ K and $T = 410 \pm 33$ K, respectively.
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to the \( Q_J(1,1) \) transition. Both transitions fit a straight line reasonably well. The slopes of the lines of best fit of the two transitions give rotational temperature of 403 ± 33 for the \( Q_J(0,1) \) and 410 ± 33 K for the \( Q_J(1,1) \). This temperature is significantly lower than the Zr surface temperature of \( \sim 800 \) K. Since in this transition there was no background contamination, the uncertainties in the data arise from the fluctuation of the laser power and the peak shape distortions arising from the ion counting statistics. While rotational temperatures of the two bands agree remarkably with each other, they are significantly lower than the surface temperature. The rotational temperature of these bands is also slightly lower than that of the \( Q_J(0,0) \).

4.2.3 \( Q_{10}(0,0) \) vs. \( Q_3(1,1) \)

The REMPI spectra due to \( Q_J(0,0) \), \( Q_J(0,1) \) and \( Q_J(1,1) \) transitions of D₂ from water dissociation on hot Zr all fit a lower rotational temperature than the surface temperature. To confirm this effect further, we measured the \( Q_{10}(0,0) \) and the \( Q_3(1,1) \) REMPI lines of D₂ from water dissociation on hot Zr at the same time. Figure 4.8 shows comparison of the intensities of these two lines for the D₂ from the water dissociation on Zr 800 K with those from the effusive source at the same temperature. The dotted curve in Figure 4.8 shows the \( Q_{10}(0,0) \) and \( Q_3(1,1) \) lines of deuterium from the water
Figure 4.8: Measured intensities of $Q_{10}(0,0)$ and $Q_3(1,1)$ lines of $D_2$ from the effusive source (solid curve) and the dissociation experiment (dashed curve).
Figure 4.9: Intensities of the $Q_{10}(0,0)$ and $Q_{3}(1,1)$ lines of $D_2$ from effusive source at different temperatures (solid curves) and simulated data at the same temperatures.
on Zr reaction whereas the solid curve shows the same lines for \( D_2 \) from the effusive source. In the hot source data the \( Q_{10}(0,0) \) line is about 3 times stronger than the \( Q_s(1,1) \) line. However, in the water dissociation data, the \( Q_{10}(0,0) \) is completely absent. Since the two lines are energetically very close to each other, the difference in their populations arise from differences in the degeneracies. To correctly compare the populations of the rotational states giving rise to REMPI intensities of these lines, the Frank-Condon factors must be taken into account.

The fact that the \( Q_j(0,0) \) is absent while \( Q_j(1,1) \) is present can be interpreted as an indication of higher vibrational temperature. To show that this is the case and that no thermal equilibrium conditions explain this observation, we measured the relative intensities of the two lines change with temperature for several temperatures in the range of 470 K to 770 K, using the effusive source. We also simulated the intensities of the two lines at the same temperatures using the molecular constants in Table 3.1 and the Frank-Condon factors. As can be seen in Fig. 4.9 agreement between the experiment and simulation is remarkable. As can be seen in the figure, the \( Q_{10}(1,1) \) line is stronger than the \( Q_s(1,1) \) line at all temperatures. Calculations based on the Boltzmann law also show that the ratio of the intensities \( Q_{10}(0,0):Q_s(1,1) \) diminishes only 30% when the temperature is
to 8000K whereas it increases about 30 times between 800 and 100 K. This implies that there are no thermal conditions that can lead to the ratios of intensities observed in the water dissociation experiment. The only way to explain the observed intensity ratio is to postulate that the vibrational temperature is higher than the rotational. Furthermore, the effusive source data on Fig. 4.8 and the ease with which we detect the $Q_J(1,1)$ spectra (at $5 \times 10^{-10}$ Torr) imply that the vibrational temperature must be hotter than the rotational temperature.

The experimental data in Fig. 4.9 were measured at pressures ranging from $10^{-8}$ to $10^{-7}$ Torr. The data corresponding to 770, 670, 580 and 470 K were measured at pressures of $1 \times 10^{-8}$, $2.5 \times 10^{-8}$, $5.4 \times 10^{-8}$ and $10^{-7}$ Torr, respectively.

### 4.3 $v'' = 1$ Population

The rotational degree of freedom of the hydrogen released in the dissociative reaction of water on a hot Zr surface has been shown in the previous sections of this chapter to be at a lower (average) temperature than the surface. The non-thermal behaviour of the rotational distribution was further confirmed by the absence of the $Q_{10}(0,0)$ line and the presence of the weaker but energetically close $Q_3(1,1)$ line, which has been interpreted as an
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additional evidence of cooler rotational distribution. Although the absence of the $Q_{10}(0,0)$ line and the presence of $Q_3(1,1)$ line suggest vibrational population in the $v'' = 1$ above that of the rotational distribution, measurement of the relative population of the $v'' = 1$ state requires a more elaborate analysis.

To compare the overall population of the $v'' = 1$ and $v'' = 0$ states, we measured the REMPI $Q_J(0,0)$ and $Q_J(1,1)$ spectra under constant chamber and crystal conditions. Figure 4.10 shows Boltzmann plots of the two spectra. The slope of the line of best fit of the $v'' = 0$ distribution gives $T = 470 \pm 30$ K whereas the slope of the $v'' = 1$ fit gives $T = 380 \pm 20$ K. These temperatures are consistent with temperatures obtained from measurements of the populations of these states at different times, such as those presented earlier in this Chapter. It is noteworthy to point out that the $v'' = 0$ rotational population shows a slightly higher temperature than the $v'' = 1$ population.

Under thermal conditions, the relative population of the $v'' = 1$ state can be calculated using Eq. 3.9 and the REMPI spectra of the $v'' = 0$ and $v'' = 1$ states. According to Eq. 3.9, the ratio of the populations any two rotational states specified by $J_0$ and $J_1$ in the $v'' = 0$ and $v'' = 1$ vibrational
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Due to dissociation of \( D_2O \), the population distributions of \( D_2 \) can be observed. The figure below illustrates the degeneracy-normalized intensities of the \( Q_J(0,0) \) and \( Q_J(1,1) \) REMPI spectra of deuterium produced by water dissociation on hot Zr. The lower spectrum is due to \( v'' = 1 \) whereas the upper data is due to \( v'' = 0 \). The slope of the \( v'' = 0 \) fit gives \( T = 380 \pm 20 \) K whereas the slope of the \( v'' = 1 \) fit gives \( T = 470 \pm 30 \) K. The surface temperature was held at 775 K. The \( Q_J(0,0) \) data is shifted down for clarity.

Figure 4.10: Plot of the degeneracy-normalized Intensities of the \( Q_J(0,0) \) (\( J = 4 - 7 \)) and \( Q_J(1,1) \) (\( J = 0 - 4 \)) REMPI spectra of deuterium produced by water dissociation on hot Zr. The lower spectrum is due to \( v'' = 1 \) whereas the upper data is due to \( v'' = 0 \). The slope of the \( v'' = 0 \) fit gives \( T = 380 \pm 20 \) K whereas the slope of the \( v'' = 1 \) fit gives \( T = 470 \pm 30 \) K. The surface temperature was held at 775 K. The \( Q_J(0,0) \) data is shifted down for clarity.
states of the ground electronic state, respectively, is given by

\[
\frac{N(J_1, 1)}{N(J_0, 0)} = \frac{g_{J_1}(2J_1 + 1)}{g_{J_0}(2J_0 + 1)} \exp \left[ -\frac{E_{\text{rot}}(J_0) - E_{\text{rot}}(J_0)}{k_B T} \right] \exp \left[ -\frac{E_{\text{vib}}(1) - E_{\text{vib}}(0)}{k_B T} \right]
\]  

(4.1)

Note that the rovibrational partition function

\[
Q(J, v) = \sum_v \sum_J g_J (2J'' + 1) \exp \left( -\frac{E_{\text{vib}}(v)}{k_B T} \right) \exp \left( -\frac{E_{\text{rot}}(J, v)}{k_B T} \right)
\]

(4.2)

drops from the calculation since it is common to both \(N(J_0, 0)\) and \(N(J_1, 1)\).

The measured populations of any two rotational states can be used, in conjunction with the REMPI transition moments, to calculate the population ratio of the two vibrational states.

Under non-equilibrium conditions, the above scheme cannot be used directly. In the particular case of the water dissociation experiment, the measured rotational populations of the \(v'' = 0\) and \(v'' = 1\) states fit temperatures that are lower than the surface temperatures and the population of the \(v'' = 1\) appears to be higher than what it would be under equilibrium conditions at the surface temperature. In order to estimate the population of \(v'' = 1\), we first note that the population of each of the two detected vibrational states fit a Boltzmann-like distribution and that there was not
detectable population in \( v'' = 2 \). We further assume that the vibrational populations also fit a Boltzmann distribution. This allows us to use the scheme outlined in Appendix E. The last two terms of Eq. E.5 are calculated using the measured temperatures and a Boltzmann model and the difference is \(-0.27\) whereas for \( J_0 = J_1 = 4 \)

\[
\beta_1 E_{\text{rot}}(1) + \beta_0 E_{\text{rot}}(0) = 0.46
\]  

(4.3)

The left hand side of Eq. E.5 was deduced from the data plotted in Fig. 4.10 as 1.2. In the REMPI spectra the transition moment of the \( Q_J(0,0) \) and \( Q_J(1,1) \) bands must be taking into account to estimate the populations of the \( v'' = 0 \) and \( v'' = 1 \) states. The transition moment of the \( v'' = 1 \) inferred from comparison of the \( Q_{10}(0,0)/Q_{3}(1,1) \) intensity ratio is \( 3.0 \pm 0.2 \), which is in agreement with the value measured by Zare and coworkers [85]. After adding the transition moment to the logarithmic difference of the normalized intensities and rearranging the terms, one gets

\[
E_{\text{vib}}(1) - E_{\text{vib}}(0) = 4.01k_BT
\]  

(4.4)

The left hand side is 2991 cm\(^{-1}\) and the resulting temperature is 1070 K. Hence, the population of the \( v'' = 1 \) of the deuterium molecules resulting
from the reaction of D$_2$O on hot Zr surface is the same as that of a system in equilibrium at $T = 1070 \pm 50$ K. This population is four times higher than what one would obtain for a thermal system at the surface temperature of $T = 800$ K. This implies that while the rotational degree of freedom of deuterium released in the dissociative reaction of water on hot Zr surfaces is at a colder temperature than the surface, the vibrational degree of freedom is hotter.

4.4 Time of flight Distributions for the $v'' = 0$ State

The time-of-flights distributions of several lines ($J = 2 - 4$) of the $Q_J(0,0)$ REMPI transition of deuterium from the surface reaction were collected in order to measure the average translational energy of the deuterium molecules leave the surface.

The time-of-flight distributions require collection of much larger number of laser shots than the rovibrational spectrum. To be able to make their analysis easier, the time-of-flight distributions are expanded into a wider time gate by applying smaller extraction and acceleration voltages even though the expansion somewhat degrades the signal to noise ratio of distribution.
Even though the $Q_J(1, 1)$ or $Q_J(0, 1)$ transitions are background free and are ideal for the time-of-flight measurements, their small populations the reduced signal-to-noise ratio by the expansion renders their analysis impractical. This is the reason only $J'' = 2 - 4$ lines of the $Q_J(0, 0)$ band were measured. Of these lines the $J = 4$ resulted the best distribution as a result of its relatively lower background. Figure 4.4 shows the raw $J = 4$ time-of-flight distributions due to deuterium from the surface reaction and isotropic background. The time-of-flight of the deuterium from the surface reaction on average arrives earlier than the background component. In the figure, the background is shown along with nonlinear least squares fit. The time-of-flight distribution due the $D_2$ from the surface reaction was extracted from the composite time-of-flight data by subtracting the fit of the background component from the total signal. The resulting time-of-flight distribution was subsequently converted into a velocity distribution using the transformation outlined in Chapter 3. The resulting velocity distribution was fitted to a function of the form:

$$f(v) = A_0 + A_1v^3 \exp \left[ -\frac{v^2}{\sigma^2} \right]$$

(4.5)

where $\sigma$, $A_0$ and $A_2$ are parameters, with $\sigma$ related to the temperature
Figure 4.11: Time of flight distribution of D₂ molecules due to D₂/Zr interaction (with background contamination). The lower figure shows the pure background time-of-flight distribution (dots) along with least squares fit (solid line).
Figure 4.12: The velocity distribution of the $Q_4(0,0)$ line of $D_2$ resulting from the time-of-flight distribution data in Fig. 4.11 after the background component has been subtracted. The solid line is the least squares fit at $T = 1230 \pm 30$ K. The surface temperature was held at 800 K.
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through

\[ T = \frac{m\sigma^2}{2k_B} \]  

(4.6)

where $m$ is the mass of the gas and $k_B$ is the Boltzmann constant. The resulting velocity distribution is shown in Figure 4.4. The solid line, which represents the least squares fit, gives a translational temperature of $1230\pm30$ K whereas the surface temperature was kept at 800 K. The showing an excess energy of 0.007 eV. This value is one order of magnitude less than that measured for recombinatively desorbing deuterium on Cu(111) by Auerbach and coworkers [34]. In that work, it was observed that the translational energy for $v'' = 0 - 2$ of the desorbing molecules varies both with rotational and vibrational quantum numbers. With regard to rotational state, for example, the variation of the kinetic energy varied about +0.05 eV from $J = 0$ to $J = 5$ and about -0.2 eV from $J = 5$ to $J = 14$. Despite the level of background noise present in the time-of-flight of the detected rotational lines, which made the time-of-flights of the $J < 4$ states difficult, no appreciable change was observable in the shape of these distributions which implies that the translation energy of the observed states does not vary significantly with rotational quantum number.
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4.5 Summary

The spectra of the $Q_J(0,0)$ and $Q_J(1,1)$ bands of deuterium released by dissociation of $D_2O$ on Zr surfaces were measured and analyzed by comparing them with population distributions due to $D_2$ from an effusive source. The population distribution of the $Q_J(0,0)$ band was found to fit a Boltzmann distribution at rotational temperature at $T = 480 \pm 50$ K whereas the population of the $Q_J(1,1)$ also fits a Boltzmann-like distribution at average temperature $T = 400 \pm 50$ K. The cooling of the rotational degree of freedom of the hydrogen produced in the reaction was further confirmed by comparing the relative intensities of the neighbouring $Q_{10}(0,0)$ and $Q_3(1,1)$ REMPI lines with those due to thermalized effusive source at the same temperature as the surface. Furthermore, using the relative transition moments of the $Q_J(0,0)$ and $Q_J(1,1)$ REMPI transitions, measured using spectra from the effusive source and the intensities of the $Q_{10}(0,0)$ and $Q_3(1,1)$ REMPI lines, the vibrational population of the $v'' = 1$ was estimated to be about 4 times higher than the corresponding population at the surface temperature. The agreement between these population distributions with distributions due re-combinatively desorbing hydrogen from other metals in the literature was noted.

Regarding the translational distribution of the hydrogen produced by
dissociation of water on hot Zr, the $Q_{4}(0,0)$ was chosen for analysis due to its minimal background contamination and its strong signal-to-noise ratio. After subtracting the background and converting the time-of-flight distribution into a velocity distribution, the resulting data was fitted to an effusive source model using nonlinear least squares routine. The resulting velocity distribution was found to fit a distribution at a translational temperature of $1230 \pm 30$ K which implies a small excess energy ($\sim 0.007$ eV), with respect to the surface thermal energy, in the translational degree of freedom of the evolving hydrogen. No discernible variation of the translational energy with the rotational quantum number was observed in the detected time-of-flight distributions.
Chapter 5

Scattering and Desorption of Deuterium by Zr(10\bar{1}0)

5.1 Introduction

The results of the measurement of the internal state population distributions of deuterium from the dissociation of heavy water on Zr surfaces in the previous chapter showed cooler rotational population in $v'' = 0, 1$ and above thermal population in $v''$. Cooler rotational temperature and hotter vibrational temperature are among the characteristics of recombinative desorption metallic surfaces. If the detected hydrogen truly results from surface recombination, where does it form? Can hydrogen recombine on a Zr surface at all? If the internal state distribution of hydrogen recombining on Zr is measured and is compared with those of hydrogen evolving from the water/Zr reaction, this will shed light on the mechanism under-
lying this phenomena. The data presented in this chapter is an attempt to detect and measure recombinative desorption of hydrogen on clean Zr. Two experiments were carried out to this effect. In one of the experiments a beam of deuterium is scattered from a hot Zr surface, allowing a fraction of the incident molecules to scatter into the ionization region. In the second experiment, the Zr crystal is loaded with deuterium through exposure to a relatively high pressure ($\sim 10^{-6}$ Torr) of deuterium for several hours at temperature about 625 K. The rest of the chapter is a discussion of the $Q_J(1,1)$ spectra of D$_2$ either desorbed or scattered from Zr surface at 800 K. The time-of-flight distributions were not measured as a result of poor signal-to-noise ratio.

5.2 Scattering Deuterium from Hot Zr Surface

In this experiment, clean Zr(10\text{I}0) crystal at 925 K was bombarded with a beam of molecular deuterium using the capillary used to bring water to the Zr crystal surface, raising the background D$_2$ in the chamber to $2 \times 10^{-8}$ Torr. The higher pressure (more than one order of magnitude higher than the pressure under which the water dissociation experiment was done) was necessary to detect the $v'' = 1$ of the scattered deuterium. The detection efficiency of the scattered deuterium in this experiment was, therefore, more
than ten times lower. Due to the geometry of the set up, very little of the hydrogen impinging on the Zr surface scatters into the ionization region with the possibility of some scattered molecules not exchanging energy with the surface. This results a higher background than usual, which renders the analysis of the $Q_J(0,0)$ spectrum impractical. As a result the $Q_J(0,0)$ spectrum was not collected. Due to the large vibrational specing of deuterium, the $Q_J(0,0)$ was expected to be mainly background free.

5.2.1 $Q_J(1,1)$ Spectrum

The $J = 0 - 4$ lines of the $Q_J(1,1)$ REMPI spectrum of deuterium were analyzed. Figure 5.1 shows the logarithmic plot of degeneracy-normalized intensities of the spectrum versus the rotational energy. The signal-to-noise ratio of the data is lower than that of the effusive source or the surface reaction experiments. Despite the poorer signal-to-noise ratio, as can be seen in Fig. 5.1, the rotational population distribution of the $v'' = 1$ state fits a Boltzmann distribution remarkably well. The slope of the least squares fits a rotational temperature of $240 \pm 20$ K, which is surprisingly below room temperature.
Figure 5.1: Logarithm of the degeneracy-normalized intensity of the $Q_J(1,1)$ band of D$_2$ scattered from Zr(10\overline{1}0) versus rotational energy. The slope of the least squares fit gives $T = 240 \pm 20$ K whereas the surface temperature was held at 925 K.
Figure 5.2: Plot of the $Q_{10}(0,0) - Q_{3}(1,1)$ lines of D$_2$ scattered from Zr surface at 925 K (upper curve) and D$_2$ from the effusive source at 800 K (lower curve).
5.2.2 $Q_{10}(0,0) - Q_{3}(1,1)$ Intensities of Scattered $D_2$

To be sure that the observed rovibrational data does not arise from background, we scanned the $Q_{10}(0,0) - Q_{3}(1,1)$ lines of the REMPI spectrum as in the water dissociation experiment. Figure 5.2 shows the $Q_{10}(0,0)$-$Q_{3}(1,1)$ line intensities of deuterium scattered from the Zr surface at 925 K (dotted curve) versus deuterium due to the heated effusive source at $\sim 800$ K. As can be seen in the figure, the stronger $Q_{10}(0,0)$ REMPI can hardly be observed while the $Q_{3}(1,1)$ is clearly present. This confirms that the observed hydrogen spectrum was not due to background but rather due to surface reaction. Furthermore, the cooler temperature and absence of the $Q_{10}(0,0)$ line are consistent with the observations made with the deuterium from water dissociation reaction.

5.3 Recombinatively Desorbing of $D_2$ from $Zr(10\bar{1}0)$

In this experiment, clean Zr crystal at 625 K was exposed to $D_2$ pressure of about $10^{-6}$ Torr for about 8 hours. At this surface temperature, a significant amount of deuterium is expected to diffuse into the bulk of the crystal. After exposing to hydrogen, the crystal was subsequently cooled and the chamber
was allowed to recover to base pressure below $2 \times 10^{-10}$ Torr. The crystal was then heated to 850 K, where it started desorbing D$_2$ gas, raising the partial pressure of the D$_2$ in the chamber to $\sim 7 \times 10^{-9}$ Torr. The fraction of the desorbing D$_2$ entering the time-of-flight mass spectrometer was ionized and detected. The $Q_J(1,1)$ spectrum of the desorbing deuterium were again collected. As in the previous experiment, it was not possible to measure the $Q_J(0,0)$ spectrum due to the presence of significant background.

5.3.1 $Q_J(1,1)$ Spectrum

As in the scattering experiment discussed above, the $Q_J(1,1)$ band of deuterium desorbing from the surface of hot Zr was collected and analyzed. Figure 5.3 is a plot of the logarithm of the degeneracy-normalized intensities against the rotational energy. As can be seen in the figure, the data fits a straight line reasonably well. The slope of the least squares fit of the gives an average rotational temperature of $T = 346 \pm 40$ K. The surface temperature was maintained at 850 K. The $Q_J(1,1)$ spectrum due to desorbing deuterium from the hot Zr surface repeats the pattern of the experiments described in Chapter 4 and the earlier sections of this chapter. Again to verify that the observed data does not arise from the isotropic background deuterium in the chamber, we measured the intensities of the $Q_{10}(0,0)$ and
Figure 5.3: Logarithm of the degeneracy-normalized intensity of the $Q_J(1,1)$ band of D$_2$ desorbing from Zr(1010) versus rotational energy. The slope of the least squares fit gives $T_{rot} = 346 \pm 40$ K whereas the surface temperature was held at 850 K.
5.3.2 \( Q_{10}(0,0) - Q_3(1,1) \) Intensities of Desorbing \( \text{D}_2 \)

As in the previous experiments of this chapter, the intensities of the \( Q_{10}(0,0) \) and \( Q_3(1,1) \) REMPI bands were measured at surface temperature of 850 K. Figure 5.4 shows plots of the \( Q_{10}(0,0) - Q_3(1,1) \) REMPI lines due to desorbing \( \text{D}_2 \) (upper curve) as well as \( \text{D}_2 \) from the effusive effusive source at 850 K (lower curve). As in the previous experiments, the \( Q_3(1,1) \) REMPI line is clearly observable while the \( Q_{10}(0,0) \) line is totally absent. Taking into account the fact that the rotational population fits a Boltzmann distribution at temperature significantly lower than that of the Zr surface, it is reasonable to conclude that the detected hydrogen in this experiment is due to recombinatively desorbing hydrogen on the hot Zr surface. This experiment also follows the pattern of the two other experiments in that under certain conditions, it is possible for hydrogen atoms to recombine and desorb on hot Zr surfaces.

5.4 Summary

In this chapter, the \( Q_2(1,1) \) REMPI spectra of deuterium scattered or desorbed from a hot Zr surface were analyzed. Due to the significant back-
Figure 5.4: Plot of the $Q_{10}(0,0) - Q_{3}(1,1)$ lines of $D_2$ desorbed from Zr surface at 850 K (solid curve) and $D_2$ from the effusive source at 800 K (dotted curve).
ground presence, the $Q_J(0,0)$ was not considered. The $Q_J(1,1)$ spectra of both experiments fitted Boltzmann distributions at significantly lower temperatures than the surface. The temperature deduced from the Boltzmann plots of the REMPI spectrum of the $D_2$ scattered from the surface were found for the two case to be $240 \pm 20$ K corresponding to surface temperature at 925 K. The REMPI spectrum of the desorbed deuterium yielded a temperature of $350 \pm 40$ K corresponding to a surface temperature at 850 K. The intensity ratios of the $Q_{10}(0,0)$ and $Q_3(1,1)$ lines rule out any significant role for background in these distributions. Despite the slight differences between the rotational temperatures deduced from these distributions, the clear pattern that emerges is that these spectra are all due to recombinatively desorbing hydrogen. The implications this qualitative agreement between rotational population distributions of the scattering and desorption experiments with the water dissociation experiment for the mechanism underlying the production of hydrogen in the latter case will be discussed in the next chapter.
Chapter 6

Implications of the D$_2$ Dynamics for D$_2$O/Zr Reaction

6.1 Introduction

In this chapter, the implications of our observations for the Zr/D$_2$O reaction mechanism are discussed. After summarizing our experimental observations, a short review of relevant work on the characteristics of hydrogen on Zr surfaces is given. So far no mention is made of the role of oxygen in the production of hydrogen in case of the dissociation of water. An obvious difference in the condition of the surface is the transient presence of oxygen in the case of the water dissociation experiments. The chapter concludes with a discussion linking the hydrogen production in the dissociative reaction of
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water with the surface to changes in the hydrogen dissolution kinetics on the surface and subsurface sites by the presence of oxygen.

6.2 Energetics of D₂O

At low temperature (∼ 80 K), water dissociates on Zr into hydrogen and hydroxyl adsorbates, i.e.,

\[ D_2O(g) \rightarrow D(ad) + OD(ad). \]

On the other hand if hydrogen recombination occurs before the molecules dissociates on the surface, as would be the case in the concerted mechanism, i.e.,

\[ D_2O(g) \rightarrow O(ad) + D_2(g) \] (6.1)

this reaction would also be highly exothermic and according to Ref. [13], would dissipate 170 kJ/mol of energy. If a significant portion of this energy is carried away by the D₂ molecule, one would expect to observe vibrational excitation up to \( v'' = 5 - 6 \). Our measurements of the rovibrational and translational populations of the D₂ molecules show much less excitation. The total population in \( v'' = 1 \) is less than 1% of the total population and \( v'' = 2 \) contains no detectable population. The average traslational
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Figure 6.1: Enthalpy changes of adsorption and dissociation of water on Zr crystal. Note that $\Delta H_m$ is the enthalpy change due to desorption of a physically adsorbed water molecule, $\Delta H_f$ is the formation energy of water from gas atoms, $\Delta H_d$ is the enthalpy change due the complete or partial dissociation of a water molecule into adsorbates. The data on this figure are based on Fig. 22 and Table 4 of Ref. [13].

\[ \begin{align*}
H_2(g) + \frac{1}{2}O_2(g) & \rightarrow \Delta H_f(H_2O(g)) = 243 \text{ kJ/mol} \\
H_2O(g) & \rightarrow \Delta H_m = 50 \text{ kJ/mol} \\
H_2O_{ad} & \rightarrow \Delta H_d = 477 \text{ kJ/mol} \\
H_2(g) + O_{ad} & \rightarrow \Delta H_f = 307 \text{ kJ/mol} \\
2H_{ad} + O_{ad} & \rightarrow \Delta H_d(H_2) = 170 \text{ kJ/mol}
\end{align*} \]
energy is only about 10 kJ/mol (7 meV). As will become evident shortly, this point is relevant to the discussion relating to the mechanism underlying the production of the D₂ as a result of water dissociation on a hot Zr surface.

6.3 Summary of Population Distribution Results

The experiments presented in the previous two chapters were concerned with measurement of the internal state population distributions of D₂ due to dissociation of water, and desorption or scattering of hydrogen from a hot Zr surface. In Chapter 4, rovibrational spectra and translational energy distribution of D₂ due to dissociation of water on a hot Zr surface were analyzed. In each case, the measurements of the rotational population distributions of the \( v'' = 1 \) and \( v'' = 0 \) states fitted a Boltzmann distribution at temperatures below 500 K while the surface temperature was held at 800 K. Furthermore, the population of the \( v'' = 1 \) state was found to be approximately four times higher than the expected equilibrium value at the surface temperature. The translational population distribution for \( v'' = 0 \) on the other hand showed a temperature slightly higher than the surface temperature. It was noted that the observed cold rotational and hot vibrational population distributions show characteristics of recombinative desorption observations made with other systems, such as Cu and Ni.
In Chapter 5, rotational population distributions of the $v'' = 1$ state of D$_2$ desorbing or scattering from a hot Zr surface were analyzed. These population distributions were also found to fit a Boltzmann distribution at a significantly lower temperature than the surface. The temperatures inferred from least squares fits of the rotational population distributions for the $v'' = 1$ in the desorption and scattering cases were slightly lower than those measured in the case of D$_2$ due to water dissociation. Presence of significant background made reasonable estimation of the population of the $v'' = 1$ state difficult. Despite the fact that the temperatures deduced from the least square fits for desorption/scattering cases are slightly lower than those deduced from the population distribution due to the D$_2$ from the water dissociation, the general qualitative agreement has significant implications for the mechanism underlying the production of hydrogen in the water dissociation experiment.

In the light of the previous observations on the behaviour of hydrogen adsorbates on Zr, the fact that rotational population distributions of the D$_2$ due to water dissociation Zr fits a Boltzmann distribution at a lower temperature than the surface, as it would if it were due to recombinative desorption, was surprising. The consistency among the rotational population distributions of hydrogen resulting from desorption or scattering and
hydrogen released by dissociation of water on hot Zr surface with prior results of recombinative desorption experiments and the fact that the $v'' = 1$ state contains population four times higher than the expected population at the surface temperature while the $v'' = 2$ contained no detectable population, rules out the concerted mechanism proposed by Norton. The amount of energy carried by the D$_2$ molecules is much smaller than the amount expected if such concerted mechanism was underlying cause. While how hydrogen recombination on the surface occurs in the case of water dissociation, when this process is known to be highly inefficient for clean Zr surfaces, requires an explanation, the population distribution measurements are unequivocal in indicating recombinative desorption on the surface as the underlying mechanism for the production of hydrogen in water/Zr reaction case.

6.4 Characteristics of D$_2$ on Surface Layers of Zr

The work of Norton and coworkers [52] shows, as discussed in the Introduction, that hydrogen recombination on clean Zr surfaces is a highly inefficient process. On the other hand, observations show efficient hydrogen recombination takes place on Zr surfaces when water dissociates on a hot Zr surface. The behaviour of the surface in the two cases is clearly different. In order to
understand the behaviour of hydrogen in the case of the water dissociation experiments, it is important to summarize previous observations regarding hydrogen behaviour on clean Zr surfaces. Of particular importance are work function studies of hydrogen/Zr systems by Norton and his colleagues.

6.4.1 Previous Experiments

One of the ways to monitor adsorbate presence on metallic surfaces is to measure the changes of the work function of the surface as the concentration of the adsorbate on the surface is varied [86]. For example, the variation of the adsorbate concentration on the surface layers can be monitored by measuring the changes of work function with exposure. In this mode, the experiment usually starts with a clean surface.

Another possible use of the work function method is to monitor the kinetics of adsorbates that desorb or dissolve into the bulk at higher temperatures. In this mode, the experiment starts with a surface having a fixed adsorbate coverage, usually deposited on the surface at low temperature, and the crystal is gradually heated while the work function is monitored.

Norton and coworkers used the work function method in both of these modes in an experiment aimed at understanding of the behaviour of hydrogen on Zr surfaces. They monitored hydrogen concentration at the surface
layers on a clean Zr(10\{1\}0) surface as function of coverage and temperature [49]. Starting with a clean Zr surface, they monitored the work function change ($\Delta \Phi$) as a function of exposure at various crystal temperatures. Their observations are summarized in Fig. 6.2. At low temperatures ($T < 150$ K), they found $\Delta \Phi$ to be positive at saturation coverages with magnitude $\geq 50$ mV, even though the $\Delta \Phi$ was initially negative. As can be seen in the low exposure regime of that figure, the magnitude of the initial decrease in $\Delta \Phi$ increases with increasing temperature, the eventual saturation value of $\Delta \Phi$ becoming less positive with increasing temperature. For $T \geq 370$ K, $\Delta \Phi$ is negative at all coverages. Furthermore, $\Delta \Phi \rightarrow 0$ for $T \geq 450$ K. Norton’s interpretation of these results are as follows: for $T \leq 200$ K ($\Delta \Phi \rightarrow +ve$), the hydrogen adsorbates stay on the surface while for $200 \leq T \leq 393$ K ($\Delta \Phi \rightarrow -ve$) the hydrogen adsorbates are still detected but in this case they are occupying a subsurface site located the surface. For ($T \geq 450$ K), however, the work function change becomes negligible which means that hydrogen disappears from the detection range of the work function method. As hydrogen does not desorb under the conditions of this experiment, Norton concluded that hydrogen adsorbates must had diffused into the bulk of the metal. They further supported this hypothesis with evidence from the shift of Zr Auger peaks as a result of hydrogen presence.
Figure 6.2: The change of the work function, $\Delta \Phi$, during hydrogen exposure at 100, 150, 293, 379 and 450 K [49].
Figure 6.3: Model potential energy curve for hydrogen-Zr(10\overline{1}0). $E_{DF}$ is the diffusion barrier energy in the bulk; $E_D$ is the subsurface to bulk diffusion barrier; $\Delta E_S$ is the energy difference between the subsurface and bulk sites; $E_{DS}$ is the desorption energy for adsorbed atomic hydrogen and $E_{H-Zr}$ is the binding energy of hydrogen atoms adsorbed on the surface [49].

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Their observations led them to propose the model potential energy curve, shown in Fig. 6.3, for hydrogen adsorbates on Zr. As shown in the figure, there are three kinds of binding sites for hydrogen on the Zr crystal: One site at the surface; one sub-surface site and a bulk site. Adsorbates at the surface and subsurface sites see a small barrier between the two sites in addition to the larger barriers to desorption and diffusion into the bulk. According to their estimates, hydrogen diffusing into the bulk from the subsurface sites has to overcome a potential barrier of $E_D = 42$ kJ/mol (or 0.44 eV) to diffuse into the bulk and the barrier for desorption for hydrogen in the surface site to be above $\sim 196$ kJ/mol above the surface binding site [49, 52].

6.4.2 Desorption of $D_2$ from Zr Surface

In the light of the high hydrogen dissolution rate observed when a Zr crystal covered with hydrogen adsorbates is heated, the hydrogen desorption from Zr seems unlikely. In Chapter 5 we presented rotational distribution of hydrogen recombinatively desorbing from Zr crystal containing hydrogen adsorbates in its bulk. We concluded from the data that the detected populations were due to recombinative desorption. The discrepancy between these two observations arises as a result of differences in the condition of the crystal. The hydrogen content in the bulk is minimal in the former
case whereas in the latter case there is a significant presence of hydrogen in the bulk. The model potential (see Fig. 6.3) is helpful in illustrating why hydrogen desorbs in the latter case.

Under equilibrium conditions at elevated temperature, the hydrogen desorption depends on the relative concentrations on the surface and bulk sites. The smaller desorption rate is modified in the case where high hydrogen concentration exists in the bulk leading to detectable level of desorbing hydrogen. The small desorption rate is compensated for, in this case, by the higher concentration of the bulk hydrogen.

### 6.4.3 Scattering of $D_2$ from Zr Surface

In Section 6.4.2, we argued that at sufficiently high hydrogen concentration in the bulk at elevated temperatures, hydrogen migrates to the surface and desorbs as a result of recombination on the surface. In the case of scattering hydrogen from a clean Zr surface, the above argument does not apply. Before the scattering experiment, the crystal is annealed at high temperature ($\geq 925$ K) until hydrogen "degassing" drops to a negligible value and then cleaned with Ar$^+$ ions. At the temperatures the scattering experiment was done ($\sim 9250$ K), there is no hydrogen degassing and hydrogen is present in the bulk at a much reduced level. The crystal is then dosed with a beam of
hydrogen from a doser mounted such that the hydrogen beam from it hits a small area (~15 – 20%) of the surface. The condition of the surface is very similar to that under which it is dosed with the D₂O such that there is very little hydrogen presence in the bulk and high hydrogen concentration on the surface. Why is it then possible to observe rovibrational population due to recombinative desorption?

The point of this experiment was to see if hydrogen dissociation on the surface can lead to recombinative desorption. The rovibrational population distributions indicate that the detected hydrogen is due to recombinative desorption. During the experiment, the background D₂ was raised to \(2 \times 10^{-8}\) Torr to improve the signal-to-noise ratio. At this pressure the \(Q_{J}(1,1)\) is still background free as both simulations and data on Fig 5.2 show. Therefore, it is reasonable to think the observed hydrogen as being due to recombination of the dissociated hydrogen molecules. The higher pressure required to observe the data can be attributed to the low recombinative (high dissolution) rate of hydrogen adsorbates on the Zr surface. In this case, the behaviour of the hydrogen adsorbates on Zr is not different from that observed in previous researchers[52, 87].

It is worth noting that the surface conditions under which the hydrogen production occurs in the desorption/scattering experiments are differ-
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ten from those under which the water dissociation experiment is done, the similarities between rotational population distributions is an additional evidence supporting the claim that hydrogen evolution in the case of water dissociation on hot Zr surfaces results from surface recombination of hydrogen adsorbates.

6.4.4 D₂ Released as a Result of Dissociation of Water

In the discussion of the results hydrogen desorption experiment, we explained how desorption of hydrogen is possible when the bulk of the Zr crystal contains high hydrogen concentration. Also, we stated the hydrogen "desorption" in the scattering experiment as resulting from recombinative desorption. We argued that the much poorer signal-to-noise ratio is this case is an indication of the higher dissolution rate for hydrogen adsorbates on the surface that recombination, as expected under clean surface conditions. It is noteworthy to mention once more that the water dissociation experiment is the most efficient of the three experiments in hydrogen production. The background D₂ pressure in the chamber range from $7 \times 10^{-8}$ Torr, in the scattering experiment, and $2 \times 10^{-9}$ Torr in the case of the desorption experiment, to $\leq 5 \times 10^{-10}$ Torr in the case of the dissociation of water experiment. This implies that even though the population distribu-
tion due to the scattering experiment are similar to those of the desorption experiment, the pressure required to detect the signal in the scattering experiment was much higher. Comparison of the partial pressure of the D$_2$ in the chamber in the case of the water dissociation ($\sim 5 \times 10^{-10}$ Torr) with that of the scattering ($7 \times 10^{-8}$ Torr) shows the high efficiency of the hydrogen production by the water dissociation reaction. It is this high efficiency in the production hydrogen in the dissociation case and the high dissolution rate into the bulk under similar thermal conditions, that make this problem much more interesting. The rest of this section is an attempt to identify the mechanism leading to the production of hydrogen in the water dissociation case.

6.4.5 D$_2$ Production Efficiency vs. Temperature

In order to study the efficiency of hydrogen production due to dissociation of water on hot Zr as function of temperature, using the RGA, we measured the hydrogen partial pressure as function of temperature at a constant water flux. Figure 6.4 shows partial pressure of hydrogen as function of temperature. The steps in the graph represent increases in the partial pressure of hydrogen resulting from sudden increases of the surface temperature.

Figure 6.5 is a plot of the logarithm of the partial pressure of D$_2$ as
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Figure 6.4: Dependence of the partial pressure of $D_2$ due to dissociation of heavy water on temperature. The temperature of the Zr crystal was increased in steps at constant water flux impinging on the surface.
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Figure 6.5: Logarithm of the partial pressure of $D_2$ released as a result of water dissociation on hot Zr surface as function of temperature recorded by the RGA. The points represent the data whereas the dotted line represents line of best fit.
Figure 6.6: Logarithm of the partial pressure of D$_2$ released as a result of water dissociation on hot Zr surface as function of $1/T$ recorded by the RGA. The points represent the data whereas the dotted line represents line of best fit.
function of temperature. The points represent the data whereas the dotted line represents least squares fit of the data fitting the linear function 

\[-20.008 + 0.007643T\]. The fit corresponds to an exponential relationship between the surface temperature and partial pressure of the released $\text{D}_2$ of the form:

$$p(T) = p_0 \exp(0.007643T)$$ \hspace{1cm} (6.2) 

where $p(T)$ is the pressure, $p_0 = 2.06 \times 10^{-9}$ Torr and $T$ is the temperature in Kelvin. We observed that increase of the $\text{D}_2$ partial pressure slows down at temperature beyond $T = 925$ K.

In an attempt to infer kinetic information from the data in Fig. 6.4, we plotted the log of the pressure versus $1/T$ (Arrhenius plot). The slope of an Arrhenius plot is related to the activation energy for the reaction. In the simplest situations the slope of the Arrhenius plot is a straight line, indicating simple recombination. As can be seen in Fig. 6.5 data fit a curve better than a straight line. That the data fit a curve, rather than a straight line, could be already deduced from Fig. 6.4. The implication of non-constant slope of the Arrhenius plot is that the recombination process is a complex one. As a result, it is difficult to infer an activation energy from this data. The nonlinear shape of the Arrhenius plot is an indication of a complex process. The slope of the linear fit gives $35.3$ kJ/mol as activation energy.
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6.5 The Role of Oxygen in Hydrogen Production

As noted earlier, at low coverages and relatively low temperatures (230 \(\leq\) \(T\) \(\leq\) 450 K), the presence of oxygen adsorbates on the surface has been found to catalyze the dissociation of water on Zr surfaces, producing molecular hydrogen [51]. In this temperature regime, the hydrogen yield decreases with increasing oxygen coverage and stops when the surface is totally covered with oxygen. At temperatures above 450 K, oxygen adsorbates efficiently diffuse into the bulk leading to sustained production of hydrogen [95]. In the experiments involving water dissociation on Zr, continuous dissolution of oxygen adsorbates into the bulk continually vacates surface sites for the impinging water to dissociate. This is necessary for the sustained production of molecular hydrogen. Other than this fact, however, the actual role the oxygen adsorbates play in the production of the molecular hydrogen is not well understood. To the best of the our knowledge, there are no studies on the role of oxygen in the efficient production of hydrogen from the dissociated water on Zr surfaces. There are number of studies on the oxygen interaction with both crystalline and polycrystalline Zr that are mainly concerned with the adsorption and diffusion characteristics of oxygen on Zr [87, 88, 89, 90, 91, 92]. To the best knowledge of the author, to date there had been only one study in the literature that deals with the effect on
hydrogen behaviour by oxygen presence in the subsurface of Zr [48]. This study compares segregation on the surface by hydrogen originating in the bulk of single crystal Zr containing different amounts of dissolved oxygen. By monitoring the hydrogen concentration in the surface layers as a function of temperature, they observed increase in hydrogen segregation on the surface in the presence of higher concentration of dissolved oxygen. The segregation of hydrogen on the surface, in this case, is a consequence of existence of higher hydrogen concentration in the bulk than on the surface. In a study aimed at understanding the effect of hydrogen on oxidized Zr surfaces, Mitchell et al. found that at 473 K, the presence of hydrogen adsorbates on the surface of Zr facilitates O migration into the bulk [88]. This study, however, does not consider hydrogen kinetics. From these studies, on the one hand, dissolution of oxygen helps diffusion of oxygen from the bulk into the surface and subsurface sites, and on the other hand, hydrogen presence facilitates oxygen to dissolve into the bulk. The behaviour of hydrogen adsorbates is, therefore, difficult to deduce from these studies.

Our data discussed in Section 6.4.5 shows the production of hydrogen increases with increased temperature. This can be understood in the following way: First, since water dissociation on Zr is a very efficient process, especially in the presence of oxygen, dissolution of oxygen is expected to in-
crease [52]. Increasing the temperature of the surface will lead to increasing
dissociation rate until the reaction saturates. In addition, the presence of
hydrogen adsorbates will increase the dissolution rate of oxygen leading to
higher production of molecular hydrogen.

Secondly, efficient recombinative desorption of otherwise highly soluble
hydrogen adsorbates is directly related to the transient oxygen presence on
the surface and in the subsurface layers. In addition, the non-Arrhenius be­
haviour of the hydrogen production (see Fig. 6.6) implies complexity in the
nature of the process underlying this hydrogen production. It is also rea­
sonable to think the role of oxygen adsorbates as competing with hydrogen
adsorbate for a fixed number of dissolution sites, increasing the lifetime of
the hydrogen adsorbates on the surface and subsurface layers, consequently
increasing the surface recombination rate of the hydrogen adsorbates.

6.6 Estimation of Hydrogen Evolution

Parameters

Hydrogen evolution on Zr can be described by a reaction rate equation of
the form:

\[ k = A \exp \left( - \frac{E_a}{k_B T} \right) \] (6.3)
where $E_a$ is the activation energy of the reaction, $T$ is the temperature and $A$ is the reaction rate coefficient. For the evolution of hydrogen adsorbates, $A = \theta^2 v$ where $\theta$ (in ML) is the average (dynamic) coverage and $v$ (in s$^{-1}$) is the reaction frequency (pre-exponential).

Using this Equation 6.3 in conjunction with data in the literature, we can estimate some parameters for the hydrogen evolution on Zr. First, according to Ref. [52], the hydrogen activation energy for desorption is 196 kJ/mol with a pre-exponential of $v \sim 10^{14}$ s$^{-1}$. If a dynamic coverage of hydrogen on Zr of $\theta \sim 0.1$ ML is assumed, which corresponds the maximum rate for the oxygen catalyzed water dissociation reported in Ref. [51] for Zr(0001), according to Eq. 6.3, one finds a desorption of $\sim 0.2$ ML/s at 800 K. For desorption to dominate transfer into the subsurface sites, the transfer rate to the subsurface sites has to be at least 0.2 ML/s. Furthermore, rough transfer rate for hydrogen to the subsurface sites at 200 K can be inferred from the slope $\Delta \Phi$ versus the temperature curve in Fig. 5 of Ref. [49]. Around $T = 200$ K, the slope of the curve, which represents the hydrogen adsorbate transfer rate from the surface to the subsurface sites, is approximately $-3$ mV/s. Assuming a calibration ($\Delta \Phi$ corresponding to the dissolution of a one monolayer) of $\sim -100$ mV/ML, the transfer rate into the subsurface sites can be estimated roughly as $\sim 0.03$ ML/s. To estimate the activation
energy and the pre-exponential for the transfer of hydrogen from the surface to the subsurface sites, the assumption that desorption barely overtaking transfer into the subsurface sites is made. Application of Eq. 6.3 twice leads to an activation energy of 4.2 kJ/mol and a transfer rate of \( \sim 0.4 \text{ ML/s} \). This activation energy for the transfer of the hydrogen adsorbates into the subsurface layer is about 10 times smaller than the activation energy for dissolution into the bulk. This means hydrogen dissolution into the bulk must be much slower than surface-to-subsurface transfer rate, which requires that similarly slow transfer from the bulk back to the surface sites. In this discussion, we ignored the fact that oxygen is present in the case of water dissociation on the Zr. Oxygen, as mentioned before, appears to lower the bulk-subsurface barrier. However, this effect is much too small to affect the slow bulk-subsurface transfer rate predicted above.
Chapter 7

Summary and Future Experiments

7.1 Conclusions

In the previous three chapters, measurements of the rovibrational \( (v'' = 0, 1) \) and translational population distributions due to hydrogen released by dissociative reaction of water on hot Zr and the rovibrational population distributions \( (v'' = 1) \) of hydrogen desorbing or scattering from a hot Zr surfaces were presented and discussed. The rovibrational population distributions of the hydrogen released by the water-Zr reaction was found to fit a Boltzmann distribution at a temperature below 500 K and the relative population of the \( v'' = 1 \) state was found to be about four times higher than the thermal value corresponding to the surface temperature at 800 K. That the rotational degree of freedom is cooler and the vibrational degree of freedom is
hotter was further confirmed by comparing the relative intensities of the $Q_{10}(0,0)$ and $Q_3(0,0)$ REMPI lines of the hydrogen released by the reaction with the corresponding lines due to a thermal source at 800 K. In the discussion of these results, it was noted that the close agreement between rovibrational population distributions of hydrogen from decomposition of water on Zr surface, namely cold rotation and hotter vibration, and those of recombinatively desorbing hydrogen on other metallic surfaces strongly suggests recombinative desorption as the mechanism underlying the hydrogen production in the water/Zr system. On the other hand, it was noted that the hypothesis that hydrogen recombination occurs in a concerted manner could not be supported by our observations. Under a concerted mechanism, the hydrogen molecules are expected to carry a significant fraction of the binding energy of the water molecules, leading to vibrational excitation of up to $v'' = 5 - 6$. The population of the first excited vibrational state was observed to be only slightly hotter (1100 K) than the surface (800 K) and no detectable population was observed in the $v'' = 2$ state. Consequently, the observed vibrational excitation was deemed too small to support this hypothesis. In addition, the translational degree of freedom showed only a temperature only slightly hotter than the surface temperature. The average total energy of the hydrogen molecules was pointed to be much smaller than
what it is expected under the concerted mechanism.

The population distribution of the \( v'' = 1 \) of hydrogen desorbing from hot Zr surface, after the crystal was saturated with hydrogen, fitted a Boltzmann distribution at the same temperature (within associated uncertainties) as the hydrogen from the \( \text{D}_2\text{O}/\text{Zr} \) reaction. The detected hydrogen in this case could only be produced as a result of recombinative desorption. And although the underlying mechanism is not as clear, the population distribution of \( \text{D}_2 \) scattered on a hot Zr also showed qualitative agreement with the other the population distributions of \( \text{D}_2 \) resulting from dissociation of water. The agreement between the population distributions in these experiments strongly suggests the underlying mechanism of hydrogen production in case of the \( \text{D}_2\text{O}/\text{Zr} \) reaction to be similar.

Since hydrogen adsorbates on Zr surfaces are known to have a much higher rate for dissolution into the bulk than desorbing when the surface is heated, the high efficiency of hydrogen production in the case of the \( \text{D}_2\text{O} \) dissociation on Zr surface requires explanation. The high efficiency of the hydrogen desorption in the case of water dissociation on Zr must be related to the transient presence of oxygen in the surface region. On the one hand, both oxygen and hydrogen are known dissolve into the bulk of Zr at temperatures above 450 K. When hydrogen and oxygen coexist
on the surface as a result of dissociation of water, a competition for the available dissolution sites is expected exist between the two species. Since no discernible oxygen desorption is observed in our experiments, it seems reasonable to conclude that oxygen wins the competition for the dissolution sites. The high hydrogen yield in the dissociation of water experiments can be the result of increased lifetime of hydrogen on the surface and subsurface sites as a result of the presence of dissolved oxygen.

The Arrhenius plot of the increase of yield of hydrogen with the of surface temperature between 600 and 920 K does not fit a simple activated model and when forced to fit such a model yields an activation energy that is too small (35 kJ/mol) for a simple activated process. Hydrogen formation can take place either as a result of interaction between adsorbates on the surface site or interaction between surface and subsurface sites. To increase the hydrogen adsorbate lifetime on the surface and subsurface sites such that efficient recombinative desorption can occur requires oxygen to block hydrogen dissolution into the bulk. In any case, while understanding of the proper role of oxygen in the efficient production of the hydrogen when water dissociates on hot Zr surfaces requires further study (both experimentally and theoretically), the conclusion that oxygen is responsible in the modification of the behaviour of hydrogen adsorbates on Zr appears appropriate.
In summary, this thesis presented measurement and analysis of rovibrational and translational population distributions of hydrogen released by the dissociative reaction of water on hot Zr. The strong agreement of these distributions with hydrogen desorbing or scattered from hot Zr on the one hand, and previous observations on hydrogen recombination on hot metallic surfaces on the other, was interpreted as indication of recombinative desorption as the underlying mechanism in the production of hydrogen from water dissociation on hot Zr. The high efficiency of the hydrogen production in this case (as opposed to near zero efficiency in experiments attempting to desorb hydrogen adsorbates deposited on clean Zr surfaces) is attributed to modification of hydrogen dissolution rates due competing oxygen.

7.2 Future Work

The experiment reported in this thesis was the first surface experiment carried out in Prof. Hepburn's laboratory. The rest of this chapter is concerned with supplementary experiments and possible apparatus improvements that can be carried to complement the current work.
7.2.1 Use of D$_2$O Molecular Beam

The water dissociation experiment presented in this thesis could be improved if, instead of using a capillary to bring water molecules to the surface, a molecular beam is utilized. The use of a molecular beam will significantly decrease contaminations from background D$_2$ resulting from the dissociation of scattered water, which also degrades the pumping speed of Ti surfaces. The use of the molecular beam would also allow for more precise control of the flow of the water into the chamber. The addition of a molecular beam requires building of an additional chamber with a differential pumping system. This will also most likely require some re-arrangement of the apparatus.

7.2.2 Orientation of the Released Hydrogen

Recent study on the orientation dependence of the population of hydrogen desorbing from Cu has shown differences between the energetics of the two orientations [102, 103]. While measuring the orientation dependence (steric) effects in the hydrogen recombination on Zr will improve our understanding of the recombinative desorption process, the resulting data can be used to make a comparison between this reaction and that of hydrogen on Cu systems. To measure the orientation of the desorbing hydrogen requires the
use of a $(1 + 1')$ REMPI scheme where the intermediate resonant transition involves a single photon. The lowest state that such a resonant transition can be made is the $B^1\Sigma_u^+$ state which requires light whose wavelength is around 105 nm (which lies in the vacuum ultraviolet (VUV) range of the EM spectrum). As a result of this, the experiment suggested here requires an additional chamber for the production of the VUV light.

7.2.3 Water Dissociation on Ti Surfaces

Titanium is similar to Zr in many respects: The two metals belong to the same group of the periodic table and therefore have similar electronic and crystal structures. In addition, both are very reactive. Both hydrogen and water dissociate on titanium very efficiently. This is the reason that it is used as a getter pump in UHV chambers. Oxygen probably dissolves into the bulk of titanium at a similar rate as it does in Zr. Confirmation of this would require nothing more than changing the Zr crystal with a Ti crystal in crystalline or even polycrystalline form. If water dissociation on hot Ti leads to steady evolution of hydrogen, the same data acquisition and analysis methods used in the Zr case can be directly applied to the water/Ti system. This will be an ideal system to compare with the water/Zr system and will undoubtedly contribute our understanding of the underlying water-metal
interaction dynamics.

7.2.4 Theoretical Work

As noted in Section 7.1, oxygen plays a big role in the production of hydrogen. It is of at most interest to understand the nature of the competition between the hydrogen and oxygen. Is hydrogen produced as a result of hydrogen presence in the subsurface sites only or oxygen presence in all three sites contributes? It is not possible to answer this question experimentally with the equipment used in this experiment. Since the problem is also a dynamical one, usual surface techniques cannot be used. It is however possible to study the problem theoretically using the density functional theory and related methods. Such a theoretical study should at least shed some light on the role of the oxygen in each of the relevant sites.
Appendix A

Uncertainty Estimation

Uncertainties in the data arise as a result of inadequate signal. The data is then analyzed to estimate such parameter such temperature using a certain models. The estimated parameters have uncertainties that are related to the uncertainties in the data. This Appendix is an illustration of the mathematical procedures and justifications used to derive uncertainties for these parameters.

A.1 Logarithm of Data with Uncertainties

Suppose one wants to plot the logarithm of a data in the form of \( x_i \pm \delta x_i \) against a variable. Since the logarithm is a nonlinear function, \( \log(x_i \pm \delta x_i) \neq \log(x_i) \pm \log(\delta x_i) \). We can derive the uncertainty in the following way: We can expand the logarithm in power series as follows [121]:

\[
\ln(x_i \pm \delta x_i) = \ln x_i \pm \frac{\delta x_i}{x_i} \mp \frac{\delta x_i^2}{2x_i^2} + ... \quad (A.1)
\]
Appendix A. Uncertainty Estimation

Since uncertainties are usually smaller than the data, we can ignore the higher order terms and terminate the expansion at the second term. That is

\[ \log(x_i \pm \delta x_i) \sim \log(x_i) \pm \frac{\delta x_i}{x_i} \quad (A.2) \]

In effect, the uncertainties in the logarithm of uncertain data is given by the fractional uncertainty of the data.

A.2 Uncertainties of Areas Under Peaks

The intensities in the rovibrational data presented in the Boltzmann plots are calculated from the areas under the rotational lines in the REMPI spectra. The rotational lines are represented by a discrete data binned in a histogram. The areas under these peaks, when normalized for transition moments, degeneracy factors, power fluctuations of the ionizing radiation and other experimental factors, represent populations of the ground electronic state. The areas under the peaks are calculated by summing all the ions in the relevant bins of the corresponding histograms. The uncertainty of the resulting integrated (summed) ions is derived from the counting uncertainty. The uncertainty associated the counting of \( N_i \) independent ions (events) in a certain wavelength bin is \( \delta N_i = \sqrt{N_i} \). The overall uncertainty
Appendix A. Uncertainty Estimation

corresponding to the sum of $N_0$ bins is given by

$$A = \sum_{i=1}^{N_0} (N_i \pm \sqrt{N_i})$$  \hspace{1cm} (A.3)

The uncertainty associated with the sum of $N_0$ independent data values is given by [$? ]

$$\frac{\delta A}{A} = \sqrt{\sum_{i=1}^{N_0} \left( \frac{\delta N_i}{N_i} \right)^2}$$

$$= \sqrt{\sum_{i=1}^{N_0} \left( \frac{\sqrt{N_i}}{N_i} \right)^2}$$

$$= \sqrt{\sum_{i=1}^{N_0} \left( \frac{1}{\sqrt{N_i}} \right)^2}$$

$$= \sqrt{\sum_{i=1}^{N_0} \frac{1}{N_i}}$$  \hspace{1cm} (A.4)

In order arrive at the last step, which is what is needed to calculate the uncertainties associated with the peak areas, is reached by using the fact that $\delta N_i = \sqrt{N_i}$ for counting of independent ion events.

$$\delta A = \sqrt{\sum \left( \frac{\delta N_i}{N_i} \right)^2}$$  \hspace{1cm} (A.5)
A.2.1 Contributions from the Power Fluctuations

As shown in Chapter 3, the ion signal intensity depends on the square of the power of the ionizing laser light. The effect of fluctuations of the power on the peak intensities are taken into account by dividing the peak ion counts simultaneously recorded power. The uncertainties due to the power fluctuations can be calculated in a similar manner. However, we find that the uncertainty due to the power fluctuations is significantly smaller than the uncertainties associated with the ion counting. As a result, we do not find the inclusion of the power fluctuations in the calculation of the uncertainties associated with data plotted in the logarithmic plots.
Appendix B

Nonlinear Least Square

Fitting Using Mathematica

Nonlinear fitting of the data presented in this thesis was done using Mathematica's nonlinear regression routine. To be able to use this routine it is necessary to specify a model function for the data set with sufficient number of parameters. It is also necessary to supply a good (guess) values so that the regression converges to the best fit parameters. In order to do this, it is necessary to have a rough idea of a model representing the observed data.

In this appendix, we present the detail of the fits of the time-of-flight data presented at the end of Chapter 3. First, the both dark counts, background and the beam of interest are collected under the same conditions. The background is collected by misaligning the source, and the dark counts are collected by detuning the laser from resonance. Both the dark count and the
background contribute the effusive source and water/Zr signal. Therefore, they must both be modeled and subtracted from the signal. Fig. B.1 shows beam and background data that were collected under the same conditions. The shift in the beam signal is due to dark count contribution.

The first step is to subtract the dark count background. To avoid increasing the noise in the data, the curve of best fit of the dark counts is subtracted from the beam-background signal. The next step involves subtraction of the fit of the background from the beam-background signal. The resulting data after the background is subtracted is shown in Fig. B.3. The data is represented by the dotted lines and the solid line is a nonlinear least squares fit.
Figure B.1: The plot of the raw data. The upper text is a list of packages needed for the plotting and analysis of the data. The text in the upper part of the figure is a set of header files that are necessary for plotting, nonlinear regression routine, etc.
Figure B.2: The upper figure represents the background noise accumulated with the same number of laser shots as the beam. The points the data and solid curve represents the line of best fit. The lower figure shows the beam-background signal after the dark counts being subtracted.
Figure B.3: The effusive beam time-of-flight distributions resulting after the subtraction of the background contribution and the dark counts. The data shown at the end of Chapter 3.
Appendix B. Nonlinear Least Square Fitting Using Mathematica

Figure B.4: The explicit format of the Mathematica routine used to fit the time-of-flight data shown in Fig. B.3. The detail the options in the nonlinear regression routine can be found by typing Option[NonlinearFit] at the Mathematica prompt.
Appendix C

Average Energy of an Effusive Beam

In this thesis we are interested in estimating the translational energy of an effusive beam using a model based on an effusive source speed distribution. The velocity distribution of the hydrogen leaving the nozzle of the heated effusive source is expected to be similar to that a gas scaping the small opening of an oven source. The speed distribution of a beam escaping the opening of an oven source is given by

\[ f(v)dv = Av^3 \exp(-\alpha v^2) \]  \hspace{1cm} (C.1)

where \( \alpha = \frac{M}{2k_BT} \), \( M \) is the mass of the gas, \( T \) is the temperature, \( k_B \) is the Boltmann constant and \( A = 2\alpha^2 \) is a normalization factor.

The average kinetic energy of the molecules with mass \( M \) in the beam
Appendix C. Average Energy of an Effusive Beam

is given by:

\[ \bar{E} = \frac{1}{2} M \langle v^2 \rangle \]  \hspace{1cm} (C.2)

where

\[ \langle v^2 \rangle = \int_0^\infty v^2 v^3 e^{-av^2} dv \]  \hspace{1cm} (C.3)

Using the transformation of the coordinate \( u = av^2 \) and the integral identity \( \int_0^\infty u^n \exp(-u) du = n! \) we get

\[ \langle E \rangle = \frac{1}{2} \frac{M}{\alpha} \]

\[ = k_B T \]  \hspace{1cm} (C.4)

The above result shows the average translational energy of the effusive source is equal to \( k_B T \). Note that \( \alpha \) is related to the parameter in the exponential terms in Eq. 3.24 by the relation \( \alpha = 1/\sigma^2 \).
Appendix D

Energy Units Conversion

Table

Different fields of physics and chemistry employ different units for energy measurements. Several of these are used in different parts of this thesis. To have a feel of the magnitudes involved when unfamiliar units are encountered, one makes a conversion to one of his or her more familiar unit. The table below summarizes six different energy units (five of which are used in this thesis) and their conversion factors. Note that the speed of light, \( c \) has to be converted into \( \text{cm/s} \) in the above quantities to get the correct conversion.

<table>
<thead>
<tr>
<th>Unit</th>
<th>J</th>
<th>eV</th>
<th>cm(^{-1})</th>
<th>kJ/mol</th>
<th>kcal/mol</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>J</td>
<td>e</td>
<td>1/(hc)</td>
<td>(\frac{N_A}{1000})</td>
<td>(N_A/4187.5)</td>
<td>1/(k_B)</td>
<td></td>
</tr>
<tr>
<td>eV</td>
<td>e/(hc)</td>
<td>(\frac{N_A \times e}{1000})</td>
<td>(\frac{N_A \times e}{4187.5})</td>
<td>(e/(k_B))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cm(^{-1})</td>
<td>(\frac{N_A}{1000})</td>
<td>(\frac{N_A \times e}{4187.5})</td>
<td>(hc/(k_B))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>kJ/mol</td>
<td></td>
<td>1/4.1875</td>
<td>1000/(k_B)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table D.1: Conversion of energy units.
In laser spectroscopy the spectra are sometimes plotted with (laser) wavelength units (nm) instead of energy units such as cm\(^{-1}\). The conversion between these units are \(\lambda\) (nm) \(\rightarrow\) \(10^7/\lambda\) (cm\(^{-1}\)).
Appendix E

Population Ratios for the

$v'' = 1$ and $v'' = 0$ States

Consider a rovibrational system where the rotational population of each vibrational level is in equilibrium at a different temperature, $T_i$ where $i = 0, 1, ...$ designates the vibrational state. Suppose that the vibrational states are in equilibrium at different temperature $T$. For such a system the ratio of the vibrational population of any two states ($v = 0$ and $v = 1$, for example) is given by

$$
\frac{N(v_1)}{N(v_0)} = \frac{1}{Q_{vib}} e^{-\beta E_{vib}(1)} e^{-\beta E_{vib}(0)}
$$

(E.1)

where $\beta = 1/k_B T$ and $Q_{vib}(v, T) = \sum_{v=0}^{\infty} e^{-\beta E_{vib}(v)}$ is the vibrational energy partition function. Note that, since the partition function is common to both
terms, it is dropped in the last step.

If the ratio of any two rotational states belonging to different vibrational states of such a system is sought, they can be calculated according to Eq. 3.9 as

$$N(J_i, v_i) = \frac{1}{Q_{\text{vib}} Q_{\text{rot}}} e^{-\beta_i E_{\text{rot}}(J_i)} e^{-\beta E_{\text{vib}}(v_i)}$$

(E.2)

where $Q_{\text{vib}}$ is the vibrational partition function defined above and $Q_{\text{rot}}$ is given by

$$Q_{\text{rot}}(T_i) = \sum_{J_i} g_i (2J_i + 1) e^{-\beta_i E(J_i)}$$

(E.3)

where $g_i$ is any additional degeneracy factor and the subscripts in $\beta_i$ signify the fact that rotational temperature may be different for different vibrational states.

The ratio of the degeneracy normalized populations of two rotational states in equilibrium at temperatures $T_0$ and $T_1$ and belonging to, for example, $v = 0$ and $v = 1$ vibrational states is by

$$\frac{N(J_1, 1)/g_{J_1} (2J_1 + 1)}{N(J_0, 0)/g_{J_0} (2J_0 + 1)} = e^{-\beta (E_v(1) - E_v(0))} \times e^{-\beta (E_{\text{rot}}(1) - E_{\text{rot}}(0))} \times Q_{\text{rot}}(J_0, T_0)/Q_{\text{rot}}(J_1, T_1)$$

(E.4)

The last term corresponds to the ratio of the total populations in the two
vibrational states under consideration. In the case where the vibrational population is in thermal equilibrium, these quantities play the role of normalizing factors and can be assumed equal, especially since the population differences in the two vibrational states are included in the vibrational Boltzmann factor.

Taking this fact into account and taking the logarithm of both sides of Eq. E.4, we get

\[
\ln \frac{N(J_1, 1)/g_{J_1}(2J_1 + 1)}{N(J_0, 0)/g_{J_0}(2J_0 + 1)} = -\beta(E_{\text{vib}}(1) - E_{\text{vib}}(0))
- \beta_1 E_{\text{rot}}(1) + \beta_0 E_{\text{rot}}(0)
+ Q_{\text{rot}}(J_0, v_0) - Q_{\text{rot}}(J_1, v_1)
\]  

(E.5)

The left hand side of Eq E.5 represents the logarithmic values degeneracy-normalized that are plotted in Boltzmann plots and the energy terms in the right hand side are given by Eqs. 3.10 and 3.14 in Chapter 3.
Bibliography


[38] H. Hou, Y. Huang, S.J. Guiding, C.T. Rettner, D.J. Auerbach and A.M. Wodke, Science 284, 1647 (1999);


