Laser induced fluorescence studies of molecular dissociation by electron impact.

Tarek Hussein. Harb

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LASER INDUCED FLUORESCENCE STUDIES OF MOLECULAR DISSOCIATION BY ELECTRON IMPACT

by

Tarek Hussein Harb

A Dissertation submitted to the Faculty of Graduate Studies and Research through the Department of Physics in partial fulfillment of the requirements for the Degree of Doctor of Philosophy at the University of Windsor

Windsor, Ontario, Canada
2002
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ABSTRACT

Laser Induced Fluorescence (LIF) techniques have been used to study the OH (X) and OD (X) radicals produced following electron impact dissociation of water, methanol, and heavy water. Impact energies ranged from the important near threshold region (< 10 eV) up to 300 eV. A magnetically collimated electron beam has been used for this purpose. Absolute dissociation cross section measurements for the production of the OH (X) and OD (X) states have been obtained for the first time and reveal that this dissociation channel is a major contributor to the overall cross section for electron scattering. At 75 eV, the maximum value for the production of OH (X) from dissociation of water is $2.1 \times 10^{-16}$ cm$^2$. The cross section shape reveals that dipole allowed transitions are the dominant channels from which the OH (X) molecules are produced. The OD (X) from heavy water was studied as well to check for any isotopic effects. The OD (X) dissociation cross section was put on absolute scale by comparing to the cross section of that of water. A cross section ratio, $\sigma_{\text{H}_2\text{O}}/\sigma_{\text{D}_2\text{O}} = 0.9$ was obtained.

Finally comparison of the signal from electron impact dissociation of methanol to that of water enabled us to put the production of OH (X) fragments on an absolute scale. The value obtained was $\sigma_{\text{CH}_3\text{OH}}/\sigma_{\text{H}_2\text{O}} = 0.7$. Cross section data and OH (X) rotational distributions from the different target molecules revealed significant details about the dissociation mechanisms and pathways.
“Read! And thy Lord is Most Bountiful. He who taught the use of the pen. Taught man that which he knew not”.

“The Holy Quran” (chapter 96: 3-5)

This work is dedicated to every person who has taught me anything.
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SECTION 1

1.1 Introduction:

The elucidation of the internal structure of atoms and molecules is essential to understand the chemical and physical properties of matter. Scientists have developed many theoretical and experimental techniques that shed light into this sub-microscopic world. Collision of electrons with atoms and molecules is one of these ways that has been of both fundamental and practical importance since the early days of quantum theory [Frank and Hertz (1914)]. Electron-atom collisions are simpler than electron-molecule interactions where more complications arise due to the added degrees of freedom (vibrational and rotational) and also because in electron-molecule collisions the dissociation mechanism can be complicated due to fragmentation into two or more fragments.

The collision of electrons with atoms and molecules is very important in many chemical and physical processes. Electron collision processes are relevant in many environments ranging from atmospheric physics, environmental chemistry, plasma physics, and novel light sources to living tissues where it was found that low energy electrons can cause the break up of the DNA molecules [Boudaiffa et al. (2000)].

Interaction of electrons with molecules can induce different processes (ionization, excitation, dissociation etc...). The quantities most sought in various electron-molecule collisions are the cross sections which are a measure of the
probabilities for specific processes to occur. If upon collision, the resultant species is left in an excited or ionized state, then the cross sections can be measured by monitoring the photon released as the excited molecule cascades down to the ground state or by monitoring the charged particles produced [Mohlmann and de Heer (1977), Beenakker and de Heer (1974), Becker et al. (1980), Nagata et al. (1982), Straub et al. (1998) Kurawaki et al. (1983)]. Experimentally, this is not too hard to do. However, very few studies have been done where neutral, ground state fragments are produced following dissociation, because such cross sections are very much harder to measure [Corrigan (1965), Winters (1975), Motlagh and Moore (1998)]. Corrigan (1965) performed one of the first experiments that attempted to study the neutral fragments produced from electron dissociation of molecules. He used a chemical getter technique to trap the neutral fragments. Other more advanced ways to study neutral fragments produced after dissociation are by using laser related techniques such as Laser Induced Fluorescence (LIF) (e.g. Andresen et al. (1984), Darrach and McConkey (1991), Kawazumi and Ogawa (1986), Abramzon et al. (2000)) or REMPI (Resonance MultiPhoton Ionization, e.g. Kimmel and Orlando (1996)). However, relatively few studies have been done in this area.

In this work we measure the absolute dissociation cross sections of a few molecules (water, heavy water, and methanol) for producing OH (X) fragments using electron impact dissociation followed by LIF. We pay particular attention to the low electron energies (near threshold) where cross section measurements get more
complicated due to the experimental difficulties associated with producing intense and well collimated beams of low energy electrons.

Section 2 describes and discusses the apparatus used in performing this experiment. In section 3 electron impact dissociation of water is investigated. Absolute calibration was achieved using the known electron attachment channel which gives a resonance feature at 6.5 eV (Melton (1972). This procedure has the advantage of an internal calibration technique that eliminates many systematic errors. The absolute dissociation cross section of water is reported here for the first time. Section 4 focuses on the study of any isotopic effects in the excitation of water by comparing D$_2$O with H$_2$O. In section 5 we study the OH (X) radicals produced from electron impact dissociation of methanol. By referencing the fluorescence intensity from methanol to that of water we were able to put the dissociation cross section of methanol on an absolute scale.

Finally in section 6, we give an overview of the results obtained in this experiment and suggest some ideas for future investigations and developments that can be done using our existing setup.

1.2 References:


4
Section 2

Description of the Apparatus

2.1 Introduction:

Figure 2.1 shows a simplified block diagram of the apparatus. This consisted of an electron beam produced by a magnetically collimated electron gun that, at a 90° angle, intersected a supersonic molecular beam produced by a pulsed valve. The resulting collisions led to dissociation of the molecules. The fragments produced after dissociation were then probed via a laser pulse at a 30° angle with respect to the electron beam and orthogonal to the molecular beam. The volume of the overlapping three beams formed the interaction region. A lens collected the resultant fluorescence light from the interaction region and focused it at the entrance of a photomultiplier tube, as shown in Figure 2.2 [Harb (1998), Smalley et al. (1975)]. Great care was taken in order to ensure that the interaction region was imaged properly onto the cathode of the photomultiplier.

The vacuum chamber was made of stainless steel and was evacuated using a 6" Edwards Diffstak oil diffusion pump. The chamber was also Cryogenically pumped using a liquid nitrogen trap seated directly underneath the water beam.

A master oscillator was used to control the timing of the electron (8μs) and laser (~10 ns) pulses with respect to each other and to the gas pulse (~1 ms). A computer controlled the energy of the electron gun, the laser wavelength, and the
Figure 2.1. Simplified block diagram of the apparatus.
Figure 2.2. An over all schematic diagram for the LIF experiment.
photon counter. An overall arrangement of the apparatus is shown in Figure 2.2.

2.2 The Molecular Sources and Pulsed Valve:

Two separate heated stainless steel tanks were used as containers for the molecular source. One tank normally contained pure water and the other, either heavy water or methanol. The heavy water was purchased from “Isotopic Products” and had a minimum isotopic purity of 99.7 % as specified by the company. Two tanks were used in order to stabilize and to ease the control of the conditions of the experiment while comparing the cross sections of different molecules. The tanks were connected to the pulsed molecular valve via 0.25” stainless steel tubing as shown in Figure 2.3. Suitable valves controlled the gas handling system.

The switch from water to heavy water was done in less than 15 minutes. Initially the valve of the water tank was shut and the tube lines were evacuated using a mechanical pump. The vapor from the heavy water tank was then released to the tubing which was evacuated. The tubing system was flushed three times to ensure the purity of the target vapour. When studying hydroxyl radicals produced from the dissociation of alcohol, one of the tanks was emptied, and cleaned thoroughly before filling it with liquid methanol.

The tanks and tubes were heated using heating tapes. Control of pressure was obtained by changing the temperature. A graph of pressure versus temperature for water
Figure 2.3. Schematic diagram showing the connection of the tanks to the molecular valve.
Figure 2.4. Graph of pressure versus temperature for water and methanol.
and methanol is given in Figure 2.4 [Darrach (1990)]. A positive temperature gradient was maintained between the source tanks and the molecular valve. This was done to prevent any condensation outside the tank. If condensation occurred near the valve, droplets of the liquid would clog the valve and produce bursts of gas upon entering the vacuum chamber. Condensation also prevents the molecules from being produced supersonically and might encourage the formation of van der Waals dimers [Liepmann and Roshko (1957)]. The point of connection of the stainless steel tubes to the vacuum wall proved to be difficult to heat sufficiently to avoid condensation. This problem was overcome by placing a flat solid heater (OD=15cm, ID=10cm) against the wall of the vacuum chamber and around the gas feed through, thus heating the entire flange. The temperatures were monitored using copper-constantan thermocouples at five different locations extending from the tanks to the valve (see Figure 2.3).

The molecular valve was a General Valve purchased from Parker Hannifin Corp. (Model # 9-181). A cross sectional diagram of the valve is given in Figure 2.5. It has the ability to operate at temperatures near 150°C. Further, it does not disturb the electron gun since it is electromagnetically quiet. A 12-volt pulse fed to a solenoid produces a magnetic field that activates an armature attached to a teflon poppet. The poppet sits at and normally seals the exit aperture of the valve. This is 0.3 mm in diameter. The nozzle geometry is shown in Figure 2.6. The pulses were produced from a home-made pulser capable of producing pulses of up to 50 V in amplitude and with widths in the range up to 5 ms. A cable heater (24" in length and 0.06" in diameter) was
Figure 2.5. A cross section view of the molecular valve used in producing supersonic expansion of molecules.
Figure 2.6. Graph showing the nozzle geometry of the molecular valve.

Figure 2.7. A figure that demonstrates the behavior of the atoms/molecules prior and after the supersonic expansion through a small nozzle.
wrapped around the valve body. When higher than average temperatures were inadvertently reached due to excessive heating, the solenoid would burn and the valve would have to be rewired. Copper wire #32 was used to rewire the valve. The poppet gradually wears after prolonged use, until it finally fails resulting in a pronounced gas leak. It needed to be replaced every few months.

The physical properties of a supersonic expansion have been well documented by many researchers [Liepmann and Roshko (1957), Anderson and Fenn (1965)]. As a gas expands from a high pressure environment to a vacuum through a small aperture, supersonic expansion occurs (see Figure 2.7). A molecular beam valve produces such a phenomenon and converts the random thermal motion of the particles beyond the nozzle (indicated by arrows in Figure 2.7) into directional flow. Since the probability of any particle experiencing collision with another particle is very low, the rotational temperature will be extremely low, < 20 K. As molecules are cooled, the lowest rotational and vibrational levels will be highly populated while the higher states will be largely vacant. This greatly simplifies the spectroscopy of the molecules. The collision-free nature of the beam expansion also minimizes any perturbing effects that may occur. Another advantage of the expansion is its high density, about $10^{13}$ particles/cm$^3$. Pulsing the valve gave the benefits of less gas use and maintaining a good vacuum ($2 \times 10^{-6}$ Torr) while using moderately sized vacuum pumps.

In 1951 Kantrowitz and Greg [Kantrowitz and Greg (1951)] suggested that supersonic expansion occurs when
\[ \text{d} \gg \lambda_0 \]

where \( \text{d} \) is the orifice diameter, and \( \lambda_0 \) is the mean free path for collisions between the atoms or molecules passing through it. In a thermal source the average flow velocity is zero \( (\nu_x=0) \). In a supersonic expansion this velocity changes to \( \nu_x = v_0 \) and the equation for the molecular flux at a distance \( l \) from the orifice changes from

\[
d\phi = A_0 n_0 \frac{1}{\pi l^2} \frac{1}{\sqrt{\pi}} \left( \frac{m}{2kT_0} \right)^{3/2} v_x \exp \left( -\frac{mv^2_x}{2kT_0} \right) dv_x \tag{2.1}
\]

for an effusive beam to

\[
d\phi = A_0 n_0 v_0 \frac{1}{\pi l^2} \frac{1}{\sqrt{\pi}} \left( \frac{m}{2kT_0} \right)^{3/2} v_x^2 \exp \left( -\frac{m(v_x - v_0)}{2kT_0} \right) dv_x \tag{2.2}
\]

for a supersonic beam. Where \( \nu_x \) is the molecular velocity parallel to the \( x \) axis, \( A_0 \) is the area of the orifice, and \( m \) is the molecular mass. The above equations are usually expressed in terms of the mach number \( M \) defined as the ratio of the stream velocity \( (v_0) \) to the local speed of sound \( (c) \):

\[
M = \frac{v_0}{c}
\]

where,

\[
c = \sqrt{\frac{\gamma kT}{m}}
\]

and \( \gamma = \frac{c_p}{c_v} \) is the ratio of the specific heats at constant pressure and volume. \( \gamma \) is
assumed to be independent of the temperature. Using the mach number, equation 2.2 above becomes:

\[
d\phi = A_0 n_0 v_0 \frac{1}{\pi l^2} \frac{1}{\sqrt{\pi}} \left( \frac{M^2 \gamma}{2} \right)^{3/2} \exp \left( -\frac{M^2 \gamma}{2} \left( \frac{v_x}{v_0} - 1 \right)^2 \right) \left( \frac{v_x}{v_0} \right) d\left( \frac{v_x}{v_0} \right)
\]  

(2.3)

Figure 2.8 shows a theoretical comparison of the velocity distribution for both effusive and supersonic sources. It is clear that a much narrower distribution is accessible via nozzle expansion.

2.3 The Electron Gun:

This experiment focused on measuring the cross sections for electron impact dissociation of molecules particularly in the important near-threshold region (~ 10 eV). Very few researchers have attempted to do this. One of the reasons is the difficulty of operating electron guns, so that a substantial electron current is obtained at these low energies. The present design overcomes these difficulties. It followed that of Ajello et al. [Ajello et al. (1988)] as shown in Figure 2.9. A quadrupole arrangement of permanent magnets inside an aluminum block provided a static magnetic field that collimated the beam. Figure 2.10 is a scale diagram of the aluminum yoke. The electron gun was at one end of the block while the Faraday cup
Figure 2.8. Theoretical velocity distribution for the effusive and supersonic sources. The distribution was given for a mach number of 10 and 25 for the supersonic source, and a value of zero for the effusive source. The curves has been normalized to the same peak.
Figure 2.9. Plan view of the electron gun and the Faraday cup. A section through the gun assembly illustrates the mounting of the permanent magnets.
Figure 2.10. A scale diagram of the aluminum yoke used to host the electron gun and the Faraday cup.
was at the other end (see Figure 2.9). The intensity of the magnetic field along the axis of the electron beam was measured with a magnetometer (RFL Industries inc. model 101). The magnetic field was measured in situ, using a magnetometer probe mounted on a carrier which could slide smoothly along the electron beam axis. As shown in Figure 2.9 the magnetic field was approximately 150 Gauss at the middle of the block. The four magnetic rods were made of Alnico-5 and mounted with like poles reinforcing each other. The rods were 1.25 cm in diameter and 15 cm in length with their axes 3.8 cm apart. The positions of the electron gun and the Faraday cup within the block are shown in Figure 2.9.

The presence of gases inside the chamber and near the gun filament tended to lower the emission current due to cooling of the filament but did not otherwise affect the behavior of the gun. The Faraday cup consisted of inner, middle, and outer cups. Figure 2.11 is a scale diagram of the cups. The Faraday cup was made of non-magnetic, stainless-steel separated by Macor ceramic. The electrical configuration is shown in Figure 2.12. About 95% of the emitted current was collected by the inner faraday cup. The middle and inner cups were attached together and biased at +18 V. This ensured total collection of electron beam current at all energies. The outer cup was grounded and it was observed to collect essentially zero electron current independent of electron-beam energy. This illustrates the effectiveness of the magnetic collimation.

The electron gun was made out of non magnetic stainless-steel but the apertures were made of molybdenum sheet as shown in Figure 2.13. A major development from
Figure 2.11. Scale diagram for the Faraday cup.
A = Ammeter

Figure 2.12. Electrical configuration for the Faraday cups.
Figure 2.13. Scale diagram for the electron gun. A is a 3 mm aperture in molybdenum sheet.
previous work with this apparatus was a system to differentially pump the filament (see Section 2.3), and hence, prolong its lifetime.

The differential pumping system proved to be extremely useful in preventing filament burnout. Before the use of differential pumping, the average lifetime of the filament was approximately 3-4 weeks. After implementing differential pumping, the filament lasted from 5 to 7 months. The electrical configuration of the electron gun is shown in Figure 2.14. Figure 2.15 illustrates clearly the behavior of the electron gun at low energies. The current was monitored using a picoammeter (Keithley 414A).

The filament was made of Thoriated Iridium or Tungsten. For the former case, a filament current of about 5.5 amperes gave a total emission current of about 200μA. As the electron beam current increased it was seen that the threshold of the dissociation process appeared to shift in position, as displayed in Figure 2.16. This was due to space charge effects that increased with electron beam current. The space charge repulsion tends to disperse the electrons in a plane perpendicular to the beam axis. This causes the beam to expand in diameter and introduces screening effects which, in turn, lead to depression of the potential of the electrons in the beam region [9], and hence a shift to higher energies of the molecular excitation process as the current increased. Another problem with space charge is the broadening of the electron energy distribution. Space charge effects were minimized by using as low a current as possible.

Another problem was the formation of low energy secondary electrons produced during ionization of the molecules, or by secondary emission from the surfaces of the
P.W. = Filament Power Supply
A = Ammeter

Figure 2.14. Electrical configuration for the electron gun.
Figure 2.15. Electron current produced from the electron gun versus energy. Different curves correspond to different voltages applied to the grid of the electron gun.
Figure 2.16. Graph showing the shift in the threshold for OH (A-X) fluorescence as the electron current is changed. Different curves corresponds to different currents as shown.
electrodes. At high gas pressures, these secondary electrons can cause additional excitation [Hollas (1996)] with consequent distortion of the excitation function at higher energies. Due to the presence of the confining magnetic field, these low energy electrons can have a long effective path length in the interaction region. This effect is most significant when a process with an excitation function sharply peaked near threshold is being studied. An example is shown in Figure 2.17 where excitation of the $N_2 (C)$ state is being investigated. Lowering the driving pressure of the gas behind the pulsed valve to about 1 atmosphere was sufficient to minimize this effect.

2.3 The Vacuum System:

The chamber was pumped by a 6" Diffstak diffusion pump. An ultimate vacuum of $8 \times 10^{-7}$ Torr was obtained. A liquid nitrogen (LN$_2$) cooled surface was used to provide fast cryogenic pumping when the source gas was introduced, as shown in Figure 2.18. The trap was topped up automatically every 15 minutes from a 200L LN$_2$ reservoir. Using this cryogenic pumping, a typical pressure of about $2 \times 10^{-6}$ Torr could be obtained inside the chamber using a driving gas pressure of about 1 atm. The diffusion pump was backed by an Edwards ED660 rotary pump. The cryogenic pumping was an essential feature of the apparatus. Without it, the experiment would not have been possible.

As previously mentioned in Section 2.2, it was important to have differential
Figure 2.17. Graph showing the variation of the shape of the cross section for $N_2$ (C) state as the gas pressure is varied.
Figure 2.18. Schematic diagram showing the connection of the LN$_2$ trap.
pumping of the filament region in order to extend its useful lifetime. A pumping block made of stainless-steel was designed to house the electron gun. A schematic diagram of the pumping block is shown in Fig. 2.19. This block was designed to fit snugly onto the aluminum yoke which housed the electron gun. A 1.5" diameter copper tube was connected between the block and the mouth of the diffusion pump. This greatly improved the performance of the filament.

2.4 The Electronics and Data Collection:

Accurate control of the relative timing between the three different pulsed beams (gas, electrons, and laser) was crucial for this experiment. A home-made, 30 Hz master oscillator (limited by the allowable laser repetition rate) was used to control the three pulses. The master oscillator has three channels, one for each beam. The first channel activated the molecular valve via a home-made molecular beam driver which outputted positive pulses of 900 µs width and up to 35 V amplitude. The second channel was connected to an electron beam pulser. The electron beam pulser provided a 50 V pulse to the control element of the electron gun (see Figure 2.14) switching the electron beam on for a predetermined time which could be varied in 1 µs steps. The third channel activated the laser pulsing unit via a Gate and Delay Generator (Ortec model 46A) and a fibre optic link to the Q-switch of the laser. The fibre optic connection between the electronics and the laser was important to provide RF isolation between the laser and
Figure 2.19. A schematic diagram showing the pumping block used to differentially pump the filament.
the control electronics. A schematic of the oscillator and associated electronics is shown in Figure 2.20.

The relative timing between the three beams was established as follows. First the direct fluorescence signal was viewed on a fast oscilloscope and the electron beam delay was adjusted until a maximum signal was obtained. This ensured that the electron pulse was properly synchronized relative to the gas pulse. For LIF data collection, the laser pulse was set to occur typically at 2 μs after the termination of the electron pulse as shown in Figure 2.21). This ensured that little direct fluorescence reached the photon counter since the lifetime of the OH (A) state molecule was about 700 ns and thus about three lifetimes had elapsed after the exciting electron beam pulse.

A schematic diagram of the electronics used to collect data is given in Figure 2.22. The computer could change the energy of the electron gun via a digital to analog convertor and an inverting amplifier connected to the electron gun. The computer could also vary the wavelength of the laser through a RS232 connection. A custom designed program allowed data collection from the photon counter (SR400) as a function of changing either the energy (for excitation functions studies) or the laser wavelength (for LIF studies). The SR400 photon counter was interfaced to the computer over the RS232 serial port. The computer could also change the laser delay time through a delay generator and a fibre optics link.

For the excitation cross sections measurements the laser wavelength was tuned to a strong rotational line (usually Q₁(2) at 307.995 nm) and the electron energy was
Figure 2.20. Block schematic of the oscillator and the attached electronics used to vary the time between the three beams.
Figure 2.21. Experimental Timing Sequence. Note that the electron pulser is delayed relative to the centre of the driving pulse and to the supersonic valve to allow the pulse of gas to reach the interaction region.
Figure 2.22. Block schematic of the electronics used to collect data.
ramped. As the energy changed the computer program automatically recorded the photon counter signal. Since the energy ranged from 0 to 300 eV, it was important to normalize the signal to the total current collected at the Faraday cup. Thus before and after the cross section measurements were taken, the current was digitized and stored as a function of electron beam energy. The currents before and after the cross section measurements were compared to check for any change in the behavior of the electron gun with time. The delay time between the laser and the electron pulses was selected prior to collecting the excitation profile, and the photon counter gate was set to be open for 2 μs (see Figure 2.22).

For LIF measurements, the energy was set to a typical value of 75 eV, and the laser pulse was fired 2 μs after the termination of the electron pulse. As the wavelength changed to a new value, the photon counter collected the signal from the photomultiplier tube for typically 10 seconds and sent it to the computer to be recorded before moving to a new wavelength. The wavelength could be tuned to change in 0.001 nm steps. For longer spectra, 0.004 nm steps were used. Since a maximum of 200 points could be collected using the existing computer program, the wavelength range of one run was limited to 0.8 nm.

For direct excitation of OH(A-X), the laser beam was turned off and the electron beam was used in the DC mode to allow for better statistics and faster accumulation of data. Again the data were corrected by dividing by the total current. Near the threshold (<10 eV), the cross section changed sharply, so the energy was varied by 0.5 eV steps.
and was ramped from 0 to 15 eV. For longer energy ranges (0 to 300 eV), 3 eV energy steps were utilized.

2.5 The Laser System:

A Continuum model YG-661-30 Yag Laser was used to probe the OH (A-X) transition state near 308 nm. This laser is capable of producing a 600 mJ/pulse at 1064 nm. The Yag laser pumped a Continuum TDL60 flowing dye laser. The dye laser has three stages; a Moya-Geometry Oscillator, a pre amplifier and a final amplification stage. An optical layout of the dye laser is shown in Figure 2.23. Two 2-liters bottles contained the dyes for the oscillator (14) and for the amplifiers' cells (19 &21). The dyes were circulated continuously.

The Yag pump beam is diverted into the oscillator using an uncoated plate (1) that diverts 5% of the pump beam energy. Another beam splitter (2) diverts 10% of the pump beam into the first amplifier. The rest of the Yag beam, 85%, pumps the final amplifier. A cylindrical lens (7) focuses the pump beam into the oscillator. A grating (12) that has 2400 lines per millimeter is used for wavelength selection. The grating operates in the first order. The diffracted light from the grating is directed towards a flat, rectangular silver mirror (11) that works as the rear mirror of the oscillator cavity. To tune the emission wavelength the silver mirror (11) was rotated around a horizontal axis centered on the grating using a sine drive mechanism (SDM). SDM allows a linear
Figure 2.23. A graph showing the optical lay out of the dye laser. See text for description of numbered items.
mechanical motion to change into linear change in the wavelength. The motion was achieved by using a micro stepper motor.

The pre-amplifier (19) is a flowing rectangular dye cell that is pumped transversely. It is tilted in a vertical plane at the Brewster angle. The pump beam reflected off a second splitter, is focused by a cylindrical lens (6) and expanded by a diverging lens (9). The final amplifier is a 5mm diameter capillary dye cell. The optical path inside the cell is 50mm, and it is pumped transversely. The pump laser is focused using a cylindrical lens (8) that can be longitudinally translated for focusing purposes.

A harmonic generation unit steered the fundamental dye beam into a KDP doubling crystal. Using Rhodamine 640 dye, the dye laser produced a fundamental wavelength that ranged from 605-630 nm. After doubling, the wavelength ranged from 302-315 nm. If a higher wavelength is required, a DCM dye is used that can produce, after-doubling, a wavelength range from 303-338 nm. Figure 2.24 is an optical layout of the harmonic generation unit. DP-1, 2 & 3 are antireflected 90° tuning prisms that are used to steer the dye beam. The DCC, or the doubling crystal, is a quartz compensating crystal that is angle-tuned for the best phase match. This will force the beam traveling through the crystal to change its position, or "walk" when the angle is changed. The QCC-1 is a quartz compensating crystal and is mounted before the DCC crystal in a counter rotating stage. The QCC-1 will compensate for the beam "walking" when the crystals are angle-tuned. A PB-1 Pellin-Broca prism is mounted after the
Figure 2.24. An optical lay out of the Harmonic generation unit.
DCC and QCC to separate the doubled dye beam (ultraviolet) from the fundamental dye beam. After frequency doubling, the output beam yielded a power of 40 mJ/pulse at 308 nm.

The output signal from the harmonic generator was steered to go to the interaction region inside the vacuum chamber using two 45° quartz prisms. The laser system is shown in Figure 2.25. Scattered light was a major experimental problem, particularly as the probing laser has the same wavelength as the fluorescence light. To minimize this problem, all surfaces close to the interaction region were sooted thoroughly using a Benzene flame. This helped slightly, however, the signal to noise ratio was still low. The scattered light problem was solved using carefully designed apertures (Figure 2.26). These ensured that the collection of light by the lens was only from a small volume where the electron, laser, and gas beams all overlapped (see figure 2.26). This helped tremendously in reducing the unwanted scattered light and increased the signal to noise ratio by a factor of about 15.

The fluorescence light was collected using a 30 cm focal length Plano Convex lens that was housed inside a copper tube. The lens focused the light from the interaction region through a window in the vacuum chamber wall and through various interference filters onto the photocathode of an Ampex XP 2233B photomultiplier tube. The P.M. was thermo-electrically cooled to about -30° C and operated at a voltage of 1800 V. Figure 2.27 is a plot of the photomultiplier efficiency versus wavelength. When necessary, data were corrected for the photomultiplier efficiency
Figure 2.25. Schematic diagram of the laser system and the steering prisms.
Figure 2.26. Diagram showing light collection optics which minimized contribution from scattered background light.
using Figure 2.27.

The copper tube surrounding the lens prevented stray light from entering the P.M. The position of this lens was adjusted using the set up shown in figure 2.28. A stainless steel needle was located in the interaction region and a He-Ne laser beam was used to illuminate the tip. The lens position was then moved to maximize the scattered intensity at the photocathode. This was done manually.

The path of the laser beam through the interaction region tended to change with the wavelength. When long wavelength scans were performed this became obvious and had to be compensated for by using the steering prisms (Figure 2.25). It was noticed that a change in room temperature could yield a shift in laser position. However, this problem was not very dramatic and the LIF signal was tested every day to ensure the proper locations of all the beams.
Figure 2.27. A plot of the photomultiplier efficiency versus the wavelength.
Figure 2.28. Diagram showing the method used in aligning procedure.
2.6 References:


Darrach M., Laser Induced Fluorescence Measurements on Electron-Impact Excited

Harb T., laser Induced Fluorescence Studies of Water by Electron Impact, Master’s


Section 3

OH PRODUCTION FOLLOWING ELECTRON-H₂O COLLISIONS

3.1 Introduction and Review of Previous Work:

Water, H₂O, is one of the most abundant molecules in the universe. An understanding of the different processes by which water dissociates is very important for full understanding of many reactions. Thus, water molecules and their constituents play an important role in such areas as the physics and chemistry of the atmosphere, comets, astrophysics, many plasmas, waste management control, and biological processes.

When energetic electrons or photons interact with water molecules, dissociation or ionization might occur and neutral and ionic fragments are formed. These fragments often reveal themselves by emitting characteristic spectra. One of the strongest of these bands occurs in U.V. spectral region around 306 nm. This band is attributable to the formation of electronically excited hydroxyl OH(\(A^2\Sigma^+\)) radicals. The absorption spectrum of water in the vacuum U.V. range has been under investigation by many researchers [Leifson (1926), Henning (1923), Rathenau (1933), Price (1936), Hopfield (1938, 1953), Watanabe (1953)] since the 1920s. In 1926, Leifson (1926) found a continuum in the 1780-1610 Å range. He also reported a maximum intensity at 1392 Å. Henning (1923) observed two continua in the 600-1000 Å region, and Rathenau (1933) found a number of bands and continua in the region from 500-1780 Ä.
Å. Watanabe (1953), in 1953 was the first to identify the broad first and second absorption bands of water in the V.U.V. region 1060-1860 Å. Photo-dissociation via the first electronic excited state of water has been investigated extensively over the past decade both experimentally [Andresen (1984, 1985), Hausler (1987), Vander (1989, 1990, 1991), Schinke (1991), Brouard (1994), Grunewald (1987), Mikulecky (1991), Plusquellic (1994, 1997)] and theoretically [Guo (1988), Henning (1988), Kuhl (1989), Schinke (1985), Anderesen (1987), Imre (1989), Engel (1988)]. The A (1B1) state dissociation is a perfect candidate for comparisons between theory and experiment because it is a relatively easy and straightforward process. It is a purely repulsive state and the bond breaking reaction occurs on a single potential energy surface. Dissociation from the first excited state of water produces fragments that are in their lowest electronic states, i.e. OH (X 2Π) and H (2S). Figure 3.1 [Engel (1992)] shows the electronic absorption spectrum of water in the 5-11 eV photon energy. It can be seen that the transition around 7 eV (A state) exhibits little structure, and that it is well separated from the B and C states at 9 eV and higher. For these reasons, dissociation via the first excited state of water is a prototype process that can be studied from first principles making it one of the most comprehensible processes in molecular spectroscopy.

In using lasers to probe the products of the molecular photo dissociation of water via the first excited state, Andresen et al. (1984) studied the processes involved in great depth. Their experiment demonstrated that the rotational distribution of the
Figure 3.1. The electronic absorption spectrum of water as a function of photon energy
product OH(X) state depended strongly upon the temperature of the parent molecules. The rotational temperature for OH(X) radicals produced from a 10 K water source was 210 K (obtained from Boltzmann plots of P and R lines) and 460 K (via Q lines). This temperature was increased to 460 K (P and R lines) and 610 K (Q lines) when the measurements were made on an effusive source of water at 260 K. For a 300 K water source the rotational temperature increased to 930 °K. The above results of rotational temperatures indicated that the rotation of the parent molecules was not the only source of energy that was transferred to the fragments. If this was the circumstance, then much less cooling would be expected as the temperature of the parent molecules decreased.

It is surprising that the rotational distribution does not have the same value measured via the Q or P and R lines. Andresen et al.'s (1984) findings indicated that the Q line intensities were Boltzmann in nature while the intensities of the P and R lines deviated from being Boltzmann. This means that the concept of having one rotational temperature was meaningless for the R and P lines. They also discovered that the spin distribution, i.e. $^3\Pi_1 /^3\Pi_2$ for the OH(X) state was statistical in nature.

Photodissociation of H$_2$O via the second band state B ($^1A_1$) has been studied extensively [Zanganeh (2000), Hwang (1999), Weide (1987), Simons (1984)], however, this excited state is much more complex than the first excited state A ($^1B_1$). Flouquet and Horsley (1974), as an explanation of the low yield for OH (A $^3\Sigma^+$) fluorescence, suggested that the B state may be coupled with the A and X states that dissociate to give OH (X). The difficulty with the second absorption band arises from
the fact that the excited B state can dissociate via five different dissociation pathways
(See Herzberg (1967) for additional details):

1. \( e + H_2O \rightarrow H_2O^* (B) \rightarrow OH (A \Sigma^+) + H \)  
   \( \rightarrow OH (X \Pi) + H \)  
   Direct dissociation

2. \( e + H_2O \rightarrow H_2O^* (B) \rightarrow H_2O (X) \rightarrow OH (X \Pi) + H \)  
   Renner-Teller coupling

3. \( e + H_2O \rightarrow H_2O^* (B) \rightarrow H_2O (A) \rightarrow OH (X \Pi) + H \)  
   Vibronic coupling

4. \( e + H_2O \rightarrow H_2O^* (B) \rightarrow O (^3D) + H_2 \)  
   Molecular H\(_2\) elimination

5. \( e + H_2O \rightarrow H_2O^* (B) \rightarrow O (^3P) + 2H \)  
   Three body dissociation

The dissociation of the water molecule through the second band becomes even more
complicated due to the strong non-adiabatic coupling with the C (\(^1B\)) and D (\(^1A\))
Rydberg states. Figure 3.1 demonstrates a clear difference in structure between the
first and second absorption bands. At 9 eV and above the structure is seen to be
much more complex than the first absorption band A (\(^1B\)).

In our research, we are interested in the first three processes above because
they produce OH radicals in their ground state. The relative importance of these
channels is still not completely clear and the debate is far from over [Krautwald
(1976) verified that less than 10\% of the molecules that start on the B surface
dissociate directly (process 1) to give excited hydroxyl radicals OH (\(^3\Sigma^+)\). This
et al. (1999) found that the main dissociation process from the B state potential surface leading to OH (X) is through the B-X intersection. However, they observed that as the water temperature is increased, the B-A channel becomes enhanced and the B-X channel is reduced, though the latter dissociation is still the main pathway. Earlier Dunne et al. (1987) had concluded that the B-A transition is more likely to occur than the B-X transition in disagreement with the work of Hwang et al. (1998).

From the OH (\(^2\Sigma\)) \rightarrow OH (\(^2\Pi\)) fluorescence, the rotational distribution of the OH (\(^2\Sigma\)) state was observed by many researchers [Carrington (1964), Jackson and (1986), Hodgson (1984, 1985)] to be highly inverted and peaked close to the highest energetically accessible state. Weide and Schinke (1987) using LIF studies concluded that the OH(X) state rotational distribution peaked at around J = 40 for this particular dissociation channel at 193 nm.

In the present experiment, we compare our results to the photodissociation studies particularly those of Andresen et al. (1984) and Weide and Shinke (1987). Earlier measurements of the dissociation of water by electron impact, are due to Mohlmann (1976), Kawazumi and Ogawa (1987), and Beenakker (1987) Darrach and McConkey (1991). The dissociative attachment at 6.5 eV studied by Melton (1987) also led to the production of OH (X) state. The dissociative attachment process:

\[ e^- + \text{H}_2\text{O} \rightarrow (\text{H}_2\text{O})^- \rightarrow \text{OH} (\text{X}) + \text{H}^- \]

turned out to be very significant for our work since we used their absolute cross section measurement to calibrate our results.
Photodissociation studies using lasers have the important advantage that they allow state specific measurements to be made [Andresen et al. (1984)]. They also allow study of the symmetry of the excited parent state(s) via polarization measurements [Becker and Schulz (1982) (1984)]. When using electrons to dissociate molecules, both dipole and spin forbidden excitations are permitted, in contrast to photo dissociation where only dipole channels are accessible.

In the work of Mohlmann et al. (1976) the OH(A $^2\Sigma^+$) radicals were produced using an electron beam. They indicated that the OH(A) state originated from excitation from both singlet and triplet states of the parent water molecule. They found an excitation cross section that peaked very close to the threshold, an indication that triplet state excitation from the singlet ground state had occurred. This process is due to an electron exchange between the incident electron beam and the molecular beam. The cross section for an electron exchange normally decreases very rapidly with energy after reaching the maximum. However, Mohlmann et al. (1976) found that the cross section for OH(A) decreased quite slowly after its initial sharp rise. Their conclusion was that near threshold, the excitation process was dominated by triplet excitation, whereas at higher energies, optically allowed transitions (i.e. singlet state excitation) played a more important role.

Beenakker et al. (1974) measured an absolute emission cross section of $2.66 \times 10^{-18}$ cm$^2$ at 300 eV for the production of OH(A) state using electron impact dissociation. Tsurubuchi et al. (1974) determined a value of $7.1 \times 10^{-18}$ cm$^2$ for the
same state production, and Sushamin and Kishko [54] reported a maximum value of 4.1 \times 10^{-19} \text{ cm}^2.

Kawazumi and Ogawa (1987) used LIF to study the rotational and translational temperature of OH(X) formed by electron impact on an effusive H₂O beam. They found that the rotational distribution of OH(X) was Boltzmann in type with rotational temperatures of 470 ±50 K and 560 ±50 K for Q lines and for P and R lines respectively. They also evaluated the \Lambda\text{-doublet population and found a ratio } II'/II\text{ of 1.5, which was larger than the expected value of unity. Finally it was discovered that the rotational levels were populated significantly only up to } N=20\text{, unlike the photo dissociation measurements that peaked via the second absorption band at } N=40\text{ [Weide and Schinke (1987)].}

Threshold energy for the production of OH(A) from ground state water using electron impact was evaluated by many researchers [Sushanin and Mishko (1971), Chutjian et al. (1975), Goddard and Hunt (1975), Winter et al. (1975), Johnson et al. (1985)]. For comparison, some of the results are shown in Table 3.1. Since the location of the threshold is very crucial for our own study (see results section), we chose the average value of 9.3 eV.

In our research, water molecules produced supersonically (∼10 K) were studied using electron impact dissociation, followed by LIF excitation of the product OH(X) radicals. The rotational temperature for the P, R, and Q lines were measured.
<table>
<thead>
<tr>
<th></th>
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<th></th>
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<tbody>
<tr>
<td>Threshold</td>
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<td>9.02 eV</td>
<td>9.44 eV</td>
<td>9.5 eV</td>
<td>9.3 eV</td>
<td>9.3 eV</td>
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<tr>
<td>OH(A $^2\Sigma^+$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Table 3.1. Threshold measurements for the production of OH(A) by different researchers.

More importantly, the absolute cross section (0–300 eV) for dissociation into OH(X) was obtained for the first time. The cross section was made absolute using existing measurement of OH(X) production via dissociative attachment [Melton (1972)]. Dissociative attachment is a resonance reaction that occurs when low energy electrons interact with target molecule AB:

$$e^- + AB \rightarrow AB^- \rightarrow A^- + B$$

In the case of water:

$$e^- + H_2O \rightarrow H_2O^- \rightarrow OH(X) + H^-$$

The determination of the absolute cross section for dissociative electron attachment for OH(X)+H⁻ has been the subject of many investigations [Melton (1972), Schulz (1959), Compton (1967), Buchel’nikova (1959)]. Three resonances were observed; the strongest around 6.5 eV; the second which was about 6 times weaker was around 8.6 eV; and the third and weakest one was around 11.3 eV. Table 3.2 is a summary of the different cross sections obtained by different groups.
<table>
<thead>
<tr>
<th>Onset</th>
<th>Peak</th>
<th>Peak Cross Section ($\times 10^{-18}$ cm$^2$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5 ± 0.1 eV</td>
<td>6.5 ± 0.1 eV</td>
<td>7.8</td>
<td>Schulz [59]</td>
</tr>
<tr>
<td>5.45 ± 0.09 eV</td>
<td>6.4 ± 0.1 eV</td>
<td>4.8</td>
<td>Buchel’nikova [61]</td>
</tr>
<tr>
<td>5.7 ± 0.2 eV</td>
<td>6.5 ± 0.1 eV</td>
<td>6.9</td>
<td>Compton [60]</td>
</tr>
<tr>
<td>5.5 ± 0.0 eV</td>
<td>6.4 ± 0.1 eV</td>
<td>6.6</td>
<td>Melton [52]</td>
</tr>
</tbody>
</table>

Table 3.2. Absolute cross section, peak position, and onset data for production of OH(X) and H+ by dissociative attachment of electron to H$_2$O.

Unfortunately, measured cross sections for electron scattering on H$_2$O differ widely in value from one set of data to another. Table 3.3 presents a survey of integral cross section measurements by different groups. Figure 3.2 displays these measurements and those of others on an absolute scale. The data were extracted for the most part from the very recent review on the water molecule by Karwasz et al. (2001).

For total cross sections measurements, experiments that covered the energy range from 0-500 eV were performed by many groups. Szmytkowski’s (1987) measurements ranged from 0.5 to 80 eV; Nishimura and Yano’s (1988) studies ranged from 7 to 500 eV; Saglam’s (1991) work was from 4-200 eV. Finally Saglam and Aktekin (1991) and Zecca et al. (1987) carried out measurements between 25-300 eV and 80-300 eV respectively. From Figure 3.2 we see that above 20 eV, the data for the total cross section agree well. However, at lower energies, large discrepancies occur. A difference as large as 30% exist between the measurements of Saglam and Aktekin.
<table>
<thead>
<tr>
<th>Energy(eV)</th>
<th>Elastic</th>
<th>Vibrational</th>
<th>Ionization</th>
<th>Total SZ</th>
<th>Total SA</th>
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<td>10</td>
<td>16.1 SH</td>
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<td>20.9</td>
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<td></td>
<td></td>
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<td>16.62</td>
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<tr>
<td>13.3 J</td>
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<tr>
<td>20</td>
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<td>0.18 SH</td>
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<tr>
<td>30</td>
<td>11.3 J</td>
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<td>50</td>
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<td>9.7</td>
<td>10.4</td>
<td>10.05</td>
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<tr>
<td>100</td>
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<td>2.25 ST</td>
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<tr>
<td>200</td>
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<td>2.01 ST</td>
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<td>4.8</td>
<td>5.17</td>
<td>4.985</td>
<td>4.12</td>
</tr>
<tr>
<td>300</td>
<td>1.56 K</td>
<td>1.65 ST</td>
<td></td>
<td>3.69</td>
<td>4.01</td>
<td>3.85</td>
<td>3.21</td>
</tr>
<tr>
<td>400</td>
<td>1.32 K</td>
<td>1.42 ST</td>
<td></td>
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<td>2.74</td>
</tr>
<tr>
<td>500</td>
<td>1.04 K</td>
<td>1.21 ST</td>
<td></td>
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<td>2.48</td>
<td>2.25</td>
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<tr>
<td>700</td>
<td>0.82 K</td>
<td>0.93 ST</td>
<td></td>
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<tr>
<td>1000</td>
<td>0.55 K</td>
<td>0.70 ST</td>
<td></td>
<td>1.42</td>
<td>1.42</td>
<td>1.42</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Table 3.3. Integral cross sections for electron scattering on water vapour [10^{-16} cm^2]

DA - Danjo and Nishimura (1985).
K - Katase et al. (1986).
SZ - Szmytkowski (1987).
ST - Straub.
Figure 3.2. Integral cross section for electron scattering on water (taken from Karwasz et al.).
(1991) and those of Nishimura and Yano (1988).

For elastic cross sections, the overall energy ranged from 2.2-1000 eV. Katase et al. (1986) measured the cross section from 100-1000 eV, while Danjo and Nishimura's (1985) data ranged from 2.2-200. At 200 eV the integral cross section of Katase et al. (1986) was 40% higher than that of Danjo and Nishimura (1985).

Figure 3.2, also shows the vibrational and rotational cross sections obtained by Seng and Linder (1976), and by Jung et al. (1982) respectively. The rotational cross section was evaluated at only two energies namely 2.4 and 6 eV. Also, the momentum transfer cross section obtained by Phelps (1999), Tice et al. (1967) and Shinamura (1989) are shown in Figure 3.2.

Around 6.5 eV is the work reported by Melton (1972) for dissociative electron attachment. The curve exhibits three peaks at 6.5, 8.6 and 11.2 eV. The first two peaks are dominated by the production of H⁻ anion radicals. At the third peak, 11.2 eV, the intensity of the H⁻ production is about 600 times smaller than that at 6.5 eV.

Finally, for ionization cross sections, some disagreement exists between different experiments (see Table 3.3 and Figure 3.2). However, the work of Djuric et al. (1988), Straub et al. (1998), and Schutten et al. (1966) agree with each other within the experimental errors. The data of Orient and Srivastava (1987) (not shown on graph) are almost twice as high as those of Djuric et al. (1988). In Table 3.3 only the total ionization cross section of Straub et al. (1998) is shown since their value was very close to the average cross section for all groups.
Summing all of the different cross sections should yield the total cross section value. This is seen in the last two columns in Table 3.3. Clearly large discrepancies exist when comparing the values from different laboratories. An overall check indicates that the summed values are smaller than the total cross section values at most energies. We note that no data for dissociation cross sections are indicated in Figure 3.2. This is because no absolute data were available prior to the present work.

3.2 Overview of the Dissociation Process:

In this section we will develop the necessary notation required for understanding the processes studied in this experiment. Figure 3.3 is a cut through a simplified potential energy surface diagram of water. In its ground state, water which has ten electrons, is described in terms of molecular orbitals [Herzberg (1967)] as:

\[(1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (1b_1)^2\]

Figure 3.4 displays these molecular orbitals taken from Herzberg (1967). The \(1a_1\) orbital is the \(1s\) orbital of O. The \(2a_1\) orbital is mainly the \(O(2s)\) with a small mixture of \(O(2p_y)\) and the symmetric combination \(H(1s)+H'(1s)\). The \(1b_2\) is a mixture of \(O(2p_z)\) and the anti-symmetric combination \(H(1s)-H'(1s)\). The \(3a_1\) bonds strongly and is mainly \(O(2p_y)\) with a mixture of \(O(2s)\) and \(H(1s)+H'(1s)\). The \(1b_1\) orbital is non bonding. The \(4a_1^*\) is anti-bonding and it is a mixture of \(O(2s), O(2p_x)\) and the symmetric combination \(H(1s)+H'(1s)\).
Figure 3.3. Simplified potential energy diagram of water.
Figure 3.4. Molecular orbitals of water of the eight ground state electrons. The \(1a_1\) orbital is not shown. Also shown is the first excited state \(4a_1^*\) orbital.
The incident electron causes an excitation from the ground state X (\(^1\)A\(_1\)) to the first A (\(^1\)B\(_1\)) or the second B (\(^1\)A\(_1\)) excited states. If excitation to the first excited band occurs (process 1), the most loosely bound electron 1b\(_1\) is excited to the lowest anti-bonding orbital 4a\(_1^*\). The A (\(^1\)B\(_1\)) state is represented by a single electron occupying the 1b\(_1\) orbital, and by another electron in the 4a\(_1^*\) orbital. These orbitals are shown schematically in Figure 3.5. The 1b\(_1\) orbital is perpendicular to the H\(_2\)O plane, while the second orbital, 4a\(_1^*\), is in the plane of the water molecule.

In photo dissociation the probability for excitation to excited H\(_2\)O states is proportional to:

\[
|\epsilon, \mu|^2 \propto \cos^2 \theta
\]

where \(\epsilon\) is the electric vector of the photons, \(\mu\) is the transition moment of H\(_2\)O, and \(\theta\) is the angle between the vectors \(\epsilon\) and \(\mu\). In the electron impact dissociation as in our case, \(\epsilon\) is replaced by \(K\), the momentum transfer vector between the incident electron and the scattered electron. The probability for excitation becomes:

\[
|K, \mu|^2 \propto \cos^2 \theta
\]

\(K\) is well defined only very close to threshold where it is parallel to the electron beam or at high energies where it is perpendicular. Therefore, at low energy, excitation occurs predominantly for water molecules whose \(\mu\) is parallel to the \(K\) vector, i.e. to the electron beam. Figure 3.6 shows that this only occurs when the HOH plane is perpendicular to the incident beam direction. It is evident that upon dissociation, if there are no external forces acting on the molecule, the repulsive forces between O-H
Figure 3.5. Schematics of OH excitation. One electron is moved from the $1b_1$ orbital (lower left) to the $4a_1^*$ orbital (upper left). The orientation of the unpaired electron relative to OH angular momentum gives the two $\Lambda$ doublet states (shown right).
Figure 3.6. Diagram showing the orientation of the momentum transfer \( K \) with respect to the transition moment \( \mu_{\text{H}_2\text{O}} \). The linear momentum \( P \) of the H and OH are also shown as they leave the \( \text{H}_2\text{O} \) molecule.
and H-H acts in the plane of the $\text{H}_2\text{O}$ molecule. Figure 3.6 shows the OH and H fragments as they depart away from each other. Upon dissociation the lobe of the OH radicals may have two possible orientations relative to the rotational plane of OH. This is shown in the right side of Figure 3.5. The perpendicular orientation forms the $\Pi^-$, while the inplane orientation forms the $\Pi^+$ state.

In our experiment, the OH(X) state is probed using LIF technique. A partial energy level diagram of OH is shown in Figure 3.7 [Moore (1971)]. Dieke and CrossWhite (1962) studied and developed the spectroscopy of OH. For a $\Sigma$ state molecule, it is best to use Hund’s case (b) [Herzberg (1950)]; however, for states with $\Lambda \neq 0$ ($\Pi, \Delta$, etc...), the rotational states are usually between cases (a) or (b), and the use of any case is appropriate. We will assume the notation of Hund’s case (b) following Dieke and CrossWhite (1962). Hund’s case (b) assumes that the total spin vector $\mathbf{S}$ is coupled to the total angular momentum (apart from spin), $\mathbf{N}$, and is not coupled to the internuclear axis, shown in Figure 3.8. If $\Lambda$ is the total angular momentum along the internuclear axis, then the corresponding quantum number for the total angular momentum $\mathbf{N}$, is:

$$\mathbf{N} = \Lambda, \Lambda + 1, \Lambda + 2, ...$$

In this scheme, the total angular momentum of the molecule including the spin is $\mathbf{N} + 1/2$ which gives rise to $\Pi_{3/2}$ state, and $\mathbf{N} - 1/2$ that gives the $\Pi_{1/2}$ state.

The selection rules for $^2 \Sigma \rightarrow ^2 \Pi$ band are as follows:

$$\Delta J = 0, \pm 1$$

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Figure 3.7. Energy level diagram of OH (not to scale).
Figure 3.8. Hund's case (b), illustrated in vector diagram. $O$ is the angular momentum of the nuclear rotation, $A$ is the total orbital angular momentum component along the internuclear axis, $S$ is the total spin, and $J$ is total angular momentum of the molecule.
\[ \Delta N = 0, \pm 1 \]

Lines satisfying both rules form what are called the "main" branches. The transitions that violate the \( N \) transition rule form the "satellite" branches. The intensities of the main branches are generally much stronger than the satellite ones especially at higher \( N \). \( P, Q, \) and \( R \) transitions are labelled according if \( N \) changes by 1, 0, or -1 respectively. \( P, Q, \) and \( R \) are labelled as a 1 or 2 subscript referring to \( \Pi_{3/2} \) and \( \Pi_{1/2} \) states respectively. Therefore, \( Q_1(5) \), as an example, means \( \Delta N = 0 \), belongs to \( \Pi_{3/2} \) state and has \( N'' = 5 \). The + and - symbols indicate whether the wave function of the molecule is symmetric or antisymmetric with respect to a reflection across any plane containing the nuclear axis. The \( Q \) lines probe \( \Pi^- \) levels while the \( P \) and \( R \) lines probe the \( \Pi^+ \) states.

3.4 Bethe Approximation for High Energy Electron-Molecule Collisions:

Electron molecule collision plays a central role in a vast variety of physical and chemical processes. Understanding the collision process is a very important subject in experimental and theoretical atomic and molecular physics. The quantity that best characterises a particular electron collision with an atom or a molecule is the cross section or probability that a given type of reaction under investigation will take place.

We begin by defining the concept of the cross section. Suppose a parallel beam
of electrons composed of \( N_p \) particles per cm\(^2\)-sec, enters a collision area that contains
\( N_t \) target particles as shown in Figure 3.9. It is assumed that the density of the gas
target is low to prevent any particle from shielding another one and to prevent any
electron from being scattered more than once.

If we draw a solid angle defined by the polar angles \( \theta \) and \( \phi \), then the number of
electrons scattered into the solid angle, \( d\Omega_{lab} \), per sec is:

\[
N_t (\theta, \phi) \ d\Omega_{lab} \propto N_p \ N_t \ d\Omega_{lab}
\]  

(3.1)

inserting a proportionality constant \( \sigma_t (\theta, \phi) \) into equation 3.1 we obtain:

\[
N_t (\theta, \phi) \ d\Omega_{lab} = \sigma_t (\theta, \phi) N_p N_t \ d\Omega_{lab}
\]  

(3.2)

if we now define \( \sigma_t (\theta, \phi) \ d\Omega_{lab} = d \sigma_t (\theta, \phi) \) to be the differential elastic cross section
then:

\[
d \sigma_t (\theta, \phi) = N_t (\theta, \phi) \ d\Omega_{lab} / N_p N_t
\]  

(3.3)

note that \( d \sigma_t (\theta, \phi) \) has the dimension of cm\(^2\) per target particles.

If an electron with mass \( m \) and velocity \( v \) (non-relativistic) collides with a target
molecule, excitation of the molecule from its ground state to the \( n^{th} \) state with energy
\( E_n \) may occur. The electron will lose a portion of its kinetic energy in the process.
According to Inokuti (1971), the differential cross section of this process can be
expressed by:

\[
d\sigma = \frac{4\pi a_0^2 R^2}{E} \frac{f_n(k)}{E_n} d \left[ \ln (ka_0)^2 \right]
\]  

(3.4)
Figure 3.9. Geometry of electron collision with particles. See text for details.
where \( a_0 = \frac{\hbar}{me^2} = 0.52918 \times 10^{-10} \text{ m} \) is the Bohr radius, \( R = \frac{me^2}{\hbar^2} = 13.606 \text{ eV} \) is the Rydberg unit of energy, \( E = \frac{mv^2}{2} \) is the energy of the electron, \( K \) is the momentum transfer between the incident electron and the molecule, and \( f_n(K) \) is the generalized oscillator strength, a quantity introduced by Bethe. \( f_n(K) \) is a generalization of the optical dipole oscillator strength \( f \), given by

\[
f_n = \frac{E_n}{R} M_n^2 \tag{3.5}
\]

where \( M_n^2 \) is the dipole matrix element defined by:

\[
M_n^2 = \frac{1}{a_0^2} \left| \int \psi_o^* \sum_{j=1}^Z x_j \psi_0 \, dr_1 \ldots dr_Z \right| \tag{3.6}
\]

where \( \psi_n \) and \( \psi_o \) are the wave functions of the final and ground states respectively. The generalized oscillator strength \( f_n(K) \) can be written in the form

\[
f_n(K) = \frac{E_n}{K^2 a_0^2 R} |E_n(K)|^2 \tag{3.7}
\]

where \( E_n(K) \) is the matrix element defined by:

\[
E_n(K) = \int \psi_o^* \sum_{j=1}^Z \exp(iK \cdot r_j) \psi_0 \, dr_1 \ldots dr \tag{3.8}
\]
Now if the exponential in equation (3.8) is expanded into a Taylor series and the orthogonality of \( \Psi_n \) and \( \Psi_0 \) is used then it can be shown that:

\[
\lim_{k \to 0} f'_n(K) = f_n
\]  

(3.9)

Therefore, at high energies, \( E \gg E_n \) the generalized oscillator strength can be replaced by the optical oscillator strength that can be measured in absorption spectra experiments. In other words, equation (3.9) is a relationship that connects the collision of high energy charged particles with photon absorption.

By applying the Bethe procedure (Inokuti, 1971) and by neglecting higher order terms, equation (3.4) yields:

\[
\sigma_n = \frac{4 \pi}{E} \left( \frac{a^2 R^2}{E_n} \right) f_n \ln \left( \frac{4C_n E}{R} \right)
\]  

(3.10)

According to Fano (1954), if cascading from higher lying states is negligible then a plot of \( (\sigma E) \) vs. \( \ln (E) \), called a Fano plot, will yield a straight line at sufficiently high energies. The slope of the curve corresponds to \( f_n \), and the intercept with the vertical axis will equal \( E_{int} = R/4C_n \).

Fano (1954) suggested that the asymptotic slope will demonstrate what kind of transition processes dominates the excitation function. If the slope is zero then \( f_n \) is zero, an indication that an optically forbidden transition (two electron excitation or symmetry forbidden excitation) dominates. A positive slope suggests that optically
allowed transitions are dominating (single electron excitation). Finally a negative slope indicates that an electron exchange between the incident electron and the target molecule is dominating. It is possible that a given excitation function may be the result of more than one excitation process. This is the situation for excitation for OH (A) from H₂O (X) as will be discussed later.

One important use of Fano plots is when the cross section is only known relatively. If the absolute value of the oscillator strength is known then the slope may be adjusted until it fits the known \( f_\sigma \). This will put the relative cross section data on an absolute scale.

3.4 Theoretical Calculations of Low Energy Electron-Molecule Collisions:

This section is concerned with the calculations of the cross sections for the scattering of low-energy electrons by an N-electron target. This problem has proven to be a difficult endeavor. The use of low order theories, such as the Born and Ochkur-Rudge approximations [Chung (1975), Cartwright (1967)], the impact-parameter method [Hazi (1981)], and the distorted wave theories [Rescigno (1974), Fliflet (1980), Lee (1983)] cannot be expected to yield reliably consistent cross sections at low and intermediate collision energies [Lima (1988)]. Recently three different variational techniques have been used to approach this problem. These methods are the
multichannel Schwinger variational method [Lippmann et al. (1950), Lima et al. (1985), Lima et al. (1988)], the complex Kohn method [Schneider et al. (1986)], and the R-matrix method [Burke et al. (1983)]. All of these methods rely on bound-state computations for much of their implementation.

Most theoretical studies of electronic excitation of molecules by low energy electrons have been done for diatomic molecules such as H$_2$, N$_2$, CO etc. [Schneider et al. (1985), Baluja et al. (1985), Noble and Burke (1983)]. The simplicity of the electronic structure and the light mass of the hydrogen atoms makes water molecules an obvious extension for further theoretical studies on polyatomic molecules. Pritchard and McCoy (1990) were the first to use the Schwinger-multichannel method to report the differential and integral cross sections for of the $^3A_1$ dissociative state of water. Using the complex Kohn method, Gil et al. (1994) reported both total and differential cross sections for five state coupling calculations. Morgan (1981) on the other hand used the R-matrix method to calculate electron scattering cross sections of the four lowest excited states of water ($^3B_1$, $^1B_1$, $^3A_1$, $^1A_1$). All of the above studies neglect nuclear motion. By means of adaptation of the adiabatic nuclei (AN) approximation to manipulate the R-matrix method, Gorfinkiel et al. (2002) were able to take the nuclear motion into account. In this section, we will briefly discuss each of these methods, present their results for water, and compare them with each other.
3.3.1 The Schwinger Variational Method:

In the process of an electron colliding with a target molecule containing N electrons, the Hamiltonian can be written as:

\[ H = (H_N + T_{N-1}) + V = H_0 + V \]  \hspace{1cm} (3.11)

Where \( H_N \) is the target Hamiltonian, \( T_{N-1} \) is the operator of the kinetic energy of the incident electron, and \( V \) is the potential energy interaction between the incident electron and the nuclei and electrons of the target molecule. For the scattering wave function \( \psi_m \), we can obtain the Lippmann-Schwinger integral equation [Burke and Joachain (1994)] that is used in place of the Schrödinger equation. The Lippmann-Schwinger equation also satisfies the boundary condition that the potential vanishes at large distances. The Lippmann-Schwinger equation is:

\[ \Psi_m = S_m + G_0 V \Psi_m \]  \hspace{1cm} (3.12)

where \( G_0 \) is the Green's function associated with \((E-H_0)\) and \( S_m \) is the free particle solution of the unperturbed Hamiltonian, \( H_0 \), given by

\[ S_m = \phi_m(1,2,...,N)\exp(i\vec{k}_m \cdot \vec{r}_{N+1}) \]  \hspace{1cm} (3.13)

where \( \phi_m \) is an eigenfunction of the target Hamiltonian \( H_N \) with energy \( E_m \).

By defining a projection operator \( P \), that defines the open-channel space in terms of the N-particle eigenfunction of the target Hamiltonian \( H_N \), as:

\[ P = \sum_{m=1}^{N} \langle \phi_m(1,2,...,N) | \phi_m(1,2,...,N) \rangle \]  \hspace{1cm} (3.14)
and applying it to equation (3.12), the following result is obtained:

$$P \Psi_m = S_m + G_F V \Psi_m$$  \hspace{1cm} (3.15)

where

$$G_F = \sum_{m=1}^{N} \frac{e^{ikm}}{2p} \left| \phi_m \right> g_m(r_{N+1}, \bar{r}_{N+1}, \bar{r}_{N+1}) \left< \phi_m \right|$$  \hspace{1cm} (3.16)

And $g_m$ denotes the Green function for $T_{N+1}$ at energy $(E-E_m)$, defined by:

$$g_m(r, \bar{r}) = - \frac{1}{2p} e^{ikm} \frac{\bar{r} - \bar{r}'}{\left| \bar{r}_{N+1} - \bar{r}_{N+1} \right|}$$  \hspace{1cm} (3.17)

To obtain a complete equation for the scattering wavefunction we rewrite the Schrödinger equation as:

$$(E - H) \Psi_m = H \left[ aP \Psi_m + (1 - aP) \Psi_m \right] = 0$$  \hspace{1cm} (3.18)

where $a$ is an arbitrary parameter. With the help of equation (3.15), the Schrödinger equation (equation 3.18) becomes:

$$H \left[ a(S_m + G_F V \Psi_m) + (1 - aP) \Psi_m \right] = 0$$  \hspace{1cm} (3.19)

$a$ is chosen to be equal to $N+1$ in order to ensure that the operator in equation (3.18) is Hermitian. Rearranging equation (3.19) leads to

$$A \Psi' = V S_m \Psi'$$  \hspace{1cm} (3.20)
where
\[ A = \frac{1}{2} (PV + VP) - VG_p + \frac{1}{a} \left[ H - \left( \frac{\alpha}{2} \right) (HP - PH) \right] \] (3.21)

Using the above equations, a variational expression for the scattering amplitude can be derived to be equal to:

\[ f_{m,n} = -\frac{1}{2p} \left( \langle S_m | V | \Psi^+_n \rangle \right) + \left( \langle \Psi^-_m | V | S_n \rangle \right) - \left( \langle \Psi^-_m | A | \Psi^+_n \rangle \right) \] (3.22)

Finally, using the scattering amplitude, the differential cross sections can be obtained using the fact that they are proportional according to the relation

\[ \frac{d\sigma}{d\Omega} \propto |f_{m,n}|^2 \] (3.23)

The total cross section is calculated by performing an average over initial spin states and a sum over final spin states, and integrating over all scattering angles.

3.3.2 The Complex Kohn Variational Method:

This method starts by introducing the radial Schrödinger equation that describes scattering by the central potential which exists between the electron and the nucleus of the molecule:

\[ L_1 \Psi_1 (r) = \left\{ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + K^2 - U(r) \right\} \Psi(r) \] (3.24)
where $\Psi_i(r)$ is the radial wave function, $k$ is the wave vector, $U(r)$ is the reduced potential equal to $2V(r)$, and $l$ is the orbital angular momentum quantum number. The wave function in equation (3.24) satisfies the following boundary conditions $\Psi_i(r=0) = 0$, and

$$\Psi_i(r) \rightarrow \sin(\theta_1 + \gamma) + \tan(\delta_1 - \gamma)\cos(\theta_1 + \gamma) \quad (3.25)$$

where $\gamma$ is a fixed constant and $\theta_i = kr - 1/2l\pi$. The major idea in this theory is the introduction of a trial function $\Psi_i(r)$ that satisfies the same boundary conditions as $\Psi_i(r)$. We now define the functional $I_i$:

$$I_i[\Psi_i] = \int_0^r \Psi_i^* L_i \Psi_i \, dr \quad (3.26)$$

Kato in 1951 introduced the identity:

$$I_i[\Psi_i^i(r)] - I_i[\Psi_i^i(r) - \Psi_1^i(r)] = K[\tan(\delta_1 - \gamma) - \tan(\delta_1^i - \gamma)] \quad (3.27)$$

If the trial function $\Psi_i^i(r)$ is sufficiently close to the exact solution $\Psi_1(r)$, then the second term in equation (3.27) can be neglected.

Using the identities above the variational principle is written as:

$$\delta\left[I_i + K\tan(\delta_1 - \gamma)\right] \quad (3.28)$$

where

$$\delta[\tan(\delta_1 - \gamma)] = \tan(\delta_1^i - \gamma) - \tan(\delta_1 - \gamma) \quad (3.29)$$
and
\[ \delta I_i = I_i[u^i] - I_i[u] = I_i[u^i] \]  
(3.30)

is the change in \( I_i \) under the variation \( \delta \psi_i(r) = \psi_i(r) - \psi_i(r) \).

If the trial function \( \psi'_i(r) \) satisfies the boundary conditions that depends on \( N \) parameters \( c_1, c_2, \ldots, c_N \) and on the phase shift \( \lambda_i \) defined by:
\[ \lambda_i = \tan(\delta_i - \gamma) \]  
(3.31)

then the variation in equation (28) yields:
\[ \frac{\partial I_i}{\partial \lambda} = -K \]  
(3.32)

and
\[ \frac{\partial I_i}{\partial c_i} = 0 \quad , \quad i = 1, \ldots, N \]  
(3.33)

By choosing trial functions that depend linearly on the parameters \( c_1, c_2, \ldots, c_N \) and \( \lambda_i \) equations (3.32) and (3.33) can be solved to generate these parameters from which a solution can be found for equation (3.24).

### 3.3.3 The R-Matrix method:

In the Schwinger and complex Kohn variational methods the trial wave function was defined from \( r = 0 \) to \( r = \infty \). The R-Matrix method on the other hand, takes into account the fact that in most collision problems there exist a region (near the
molecule) where the potential is complicated and another region (far away from the molecule) where the potential is relatively simple to evaluate. R-Matrix method starts by dividing configuration space into two regions. A sphere of radius \( a \), centered at the center of mass of the molecule, separates the two regions. In the inner region, exchange and correlation interactions take place. These effects are negligible in the external region, \( r > a \), allowing for the use of a multipole potential in describing the electron-molecule interaction. This method was first introduced in nuclear reaction theory by Wigner (1946 a,b) and developed by Lane and Thomas (1958).

Initially, we define the "Bloch operator", introduced by Bloch in 1957, as:

\[
L(a, b) = \delta(r-a) \left( \frac{d}{dr} - \frac{b}{r} \right)
\]

(3.34)

where \( b \) is an arbitrary constant. Then if \( L_b \) is introduced into the radial Schrödinger equation defined by:

\[
L \Psi'(r) = \left\{ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + K^2 - U(r) \right\} \Psi(r)
\]

(3.35)

where \( \Psi(r) \) is the radial wave function, and \( l \) is the orbital angular momentum quantum number. It can be proved that \( L - L(a,b) \) is Hermitian with real eigenvalues. After some manipulation, the radial Schrödinger equation can be rewritten as:

\[
[-L + L(a, b)]\Psi'(r) = L(a, b)\Psi'(r)
\]

(3.36)

which has the formal solution

\[
\Psi'(r) = [-L + L(a, b)]^{-1} \Psi(r)
\]

(3.37)
Without loss of generality we can choose a real complete set of basis functions $\chi_i$ that diagonalize the operator $[-L_i + L(a, b)]$ so that

$$\int_0^a \chi_i [-L_i + L(a, b)] \chi_i \, dr = 2(E_i - E)\delta_{ij} \quad (3.38)$$

where $E = k^2/2$. Hence equation (3.37) becomes:

$$\Psi_i (r) = \frac{1}{2a} \sum_{i=1}^\infty \frac{\chi_i (r)\chi_i (a)}{E_i - E} \left( a \frac{d\Psi_i}{dr} - b\Psi_i \right) \quad (3.39)$$

if we introduce the R-matrix defined by:

$$R(E) = \frac{1}{2} \sum_{i=1}^\infty \frac{\chi_i (r)\chi_i (a)}{E_i - E} \quad (3.40)$$

equation (3.40) yields:

$$\Psi_i (r) = R(E) \left( a \frac{d\Psi_i}{dr} - b\Psi_i \right) \quad (3.41)$$

The main idea in this theory involves the calculations of the wave function (equation (3.38)) and the equations of the R-matrix. Kohn (1948) was the first to obtain variational function which enables the R-matrix to be calculated. Using the R-matrix, the cross section can be obtained.
In the external region where \( r \geq a \), the potential is simple and an analytical solution often exists. The potential can be described by the Coulomb potential and other terms vanishing as inverse powers of the distance from the electron to the nucleus of the molecule.

Hence the differential cross section for the outer region is [Burke and Joachain (1994) pp16]:

\[
\frac{d\sigma}{d\Omega} = |f_c(\Theta) + f_s(\Theta)|^2
\]  

(3.42)

where \( f_c \) and \( f_s \) are the scattering amplitudes arising from the Coulomb potential and the potential from the other terms respectively.

3.3.4 Comparison of Different Theories:

Figures 3.10 to 3.13 display the results for the four lowest excited states of water computed using the different methods explained above. The dotted curves in the figures represent the calculations of Morgan et al. (1998) who used the R-matrix method. Gorfinkel et al. (2002) also used the R-matrix theory but took the nuclear motion of the molecule into consideration. Gorfinkel et al. (2002) used two models to manipulate the R-matrix theory: model a: solid curves, and model b: chain curves (see journal article for details). They employed the energy balancing method which is a division of the adiabatic nuclei (AN) approximation. The AN approximation assumes that the excess energy of the incoming electron can be split in any proportion between
Figure 3.10. Cross sections for exciting the $^3B_1$ state of water. Full curves: Gorfinkel et al. (2002) model a; chain curve: Gorfinkel et al. (2002) model b; dotted curve: Morgan (1998); long-dashed curve: Gil et al. (1994).
Figure 3.11. Cross sections for exciting the $^3A_1$ state of water. Full curves: Gorfinkiel et al. (2002) model a; chain curve: Gorfinkiel et al. (2002) model b; dotted curve: Morgan (1998); long-dashed curve: Gil et al. (1994); broken curve: Pritchard et al. (1990).
Figure 3.12. Cross sections for exciting the $^1B_1$ state of water. Full curves: Gorfinkel et al. (2002) model a; chain curve: Gorfinkel et al. (2002) model b; dotted curve: Morgan (1998); long-dashed curve: Gil et al. (1994).
Figure 3.13. Cross sections for exciting the $^1A_1$ state of water. Full curves: Gorfinkiel et al. (2002) model a; chain curve: Gorfinkiel et al. (2002) model b; dotted curve: Morgan (1998); long-dashed curves: Gil et al. (1994).
the outgoing electron and the dissociating fragments. The values obtained using the complex Kohn method [Gil et al. (1994)] are shown as long dashed curves, and finally the results of Pritchard et al. (1990) who used the multichannel Schwinger method are exhibited as broken curves.

It is noticeable that when using the Schwinger and complex Kohn methods, the excitation threshold was between 1 to 2 eV too high compared to the expected experimental value. Morgan (1998) used a complete active space target wave function to manipulate the R-matrix method and obtained an excitation threshold within 0.5 eV of the recommended value.

For the two triplet states, $^3B_1$ and $^3A_1$, shown in Figures 3.10 and 3.11 respectively, a sharp threshold was observed as expected for a spin exchange transition. Gil et al. (1994) and Gorfinkiel et al. (2002) reported cross sections that peaked just above the threshold. This could have a significant error contribution to the magnitude obtained. The cross sections of Gorfinkiel et al. (2002) disagree with those of Morgan (1998) and agree better with those of Gil et al. (1994). This is rather striking since both Gorfinkiel et al. (2002) and Morgan (1998) used a different manipulation of the same theory, the R-matrix method. The results of Pritchard et al. (1990), who only calculated the cross section for the $^3A_1$ state, using the Schwinger method, disagree with the results obtained by others. Gorfinkiel et al. (2002) and Morgan (1998) reported a sharp resonance feature for the dissociative attachment at 9.15 eV and 8.81 eV respectively. Morgan's value is in better agreement with that observed
experimentally at 8.6 eV by Belic et al. (1981). Gil et al. (1994) reported a value of 10.5 eV which is about 2 eV too high and it was not as sharply peaked as that obtained using the R-matrix methods. Another small resonance was observed around 12.5 eV. This was attributed by Gorfinkel et al. (2002) to the $^3A_2$ state which has a threshold energy of 12.3 eV. Although the shapes of different curves disagree with each other, the magnitudes are roughly the same.

For the excitation cross section of the $^1B_1$ state (Figure 3.12), some differences in the curves should be noted. Not only are the threshold positions different, but the overall shapes and magnitudes do not agree well with each other. The magnitudes of the Gorfinkel et al. (2002) data were almost double that of Gil et al. (1994) and 25-50% larger than those of Morgan (1998). Using the R-matrix method, two resonant features were observed around 9 eV and 13 eV corresponding to the $^3B_2$ and $^3A_1$ states. Gil et al. (1994) did not observe these resonances.

Finally, the cross section for excitation to the $^1A_1$ state is shown in Figure 3.13. The results of Morgan (1998) are almost a factor of two larger than both Gorfinkel et al. (2002) and Gil et al. (1994). Using the R-matrix method, the $^3B_2$ state resonance feature is visible around 13 eV, but not observed using the complex Kohn method. Gil et al. (1994) have performed two calculations in two different ways (shown in Figure (3.13)). The threshold of Gil et al. (1994) is about 1 eV higher than those given by the others.

In summary, the results for calculating the cross sections for the four lowest
excited states of water, using different variational methods, do not agree with each other very well. In general they produce different shapes, thresholds, and magnitudes. However, the use of these variational methods to treat polyatomic molecules is still in its infancy stage. It is hoped that better models and better manipulation of these theories will provide values that agree better with experiments and with each other. We note that although there are major discrepancies between the different predictions, all of them indicate large cross sections ($\sim 10^{-17} \text{ cm}^2$) within a few eV of threshold. Our own experimental studies to find the total cross section for the dissociation process are presented in Section 3.6, where our results are compared to the values obtained using the theories above.

3.5 Results and Discussion:

3.5.1 Rotational Spectrum and Dissociation Dynamics:

A typical Laser Induced Fluorescence (LIF) spectrum obtained by exciting the OH($^2\Pi$) radical to the OH($^2\Sigma$) state is shown in Figure 3.14. The OH fragments were produced by dissociation of water molecules by electron impact at 75 eV. Figure 3.14 covers the wavelength range from 306 to 316 nm where the first two vibrational bands ($v'' = 0 \rightarrow v' = 1$) and ($v'' = 1 \rightarrow v' = 0$) are located. Figure 3.15 shows a more highly resolved region of the LIF spectrum where different rotational transitions ($Q_1, P_1, R_1, R_2$) are indicated. (see the previous section). The water vapour head pressure was about one
Figure 3.4. OH (X) rotational LIF spectra obtained after dissociation of water using 75 eV. The LIF signal was obtained after 2 μs delay between the end of the electron beam pulser and the probing laser. The first and second vibrational states are indicated.
Figure 3.5. A highly resolved OH (X) LIF spectrum ranging from 306 to 309 nm. Different rotational lines have been identified.
atmosphere and the data accumulation was started 2 µs after the termination of the electron gun pulse. This delay of about 3 radiative lifetimes of the OH (2Σ) state allowed any direct fluorescence from this state to decay, thus greatly reducing background effects. The electron gun was pulsed on for 8 µs, at 30 Hz such that a typical operating current monitored at the Faraday cup was 10 nA (equivalent to 40 µA DC operation).

In obtaining the rotational spectrum, it was difficult to maintain laser power stability because of the large wavelength range (> 9 nm). Continuous laser scans were not performed. The spectrum was obtained in short wavelength segments keeping all the variables constant (laser power, pressure, current, etc...).

The LIF spectrum seen in Figure 3.14 can be analyzed as follows. Information about the Λ-doublet population can be obtained by comparing the intensity ratio of Q₁ and P₁ or Q₁ and R₁ lines. Andresen et al. (1984) for photodissociation of water in the first absorption band found a substantial preference for Π⁻ that increased markedly with the rotational quantum number. They observed that it rose from Π⁺/Π⁻=1 for N = 1 to about 20 for N = 9. This means that for high rotational states OH (2Π) was almost exclusively generated in the Π⁻ state. They also studied the Λ-doublet inversion for molecular beams at room temperature and found that they were populated as expected based on statistical considerations (Π⁺/Π⁻=1). The results of Andresen et al. (1984) indicate that initial rotation of the ground state water molecule can destroy the preferential population of Π⁻ eventually leading to the statistical limit. Kawazumi and
Ogawa (1987) found a ratio of 1.5 for $\Pi/\Pi^-$ for electron impact dissociation of an effusive beam of water.

We compared the $Q_1$ and $P_1$ lines and found the ratio to be $1.9 \pm 0.3$. This ratio did not change with higher rotational states, a result that disagreed with Andresen et al.'s (1984) photodissociation findings for a similar supersonic beam. Our results are very similar to the results of Kawazumi and Ogawa (1987) also for electron impact.

A possible explanation for the deviation of our finding from that of the photodissociation experiment is the fact that the electrons used for dissociation do not have a well defined momentum transfer vector $\mathbf{K}$ at medium energies (75 eV). Since the excitation probability by electron impact is given by

$$|\mathbf{K} \cdot \hat{\mu}| \propto \cos^2 \theta$$

(3.43)

and $\hat{\mu}$ is perpendicular to the plane of the $\text{H}_2\text{O}$ molecule then the molecules selected for dissociation are distributed along many different planes depending on the particular direction of the $\mathbf{K}$ vector in a particular scattering event. This means that the transition moment of the OH radical is also not well defined. Therefore, upon dissociation of water by electron impact, the argument presented in Section 3.1 for photodissociation is no longer valid. Thus a strong preferential population of $\Pi^-$ or $\Pi^+$ is not expected to occur. In practice we still see some preferential population of $\Pi^-$ as discussed.

The LIF spectrum can also be used to get information about the two different spin orbit states in OH ($^2\Pi_{1/2}$) and OH ($^2\Pi_{3/2}$). Unlike the $\Lambda$-doublets, the spin orbit
states were found to be populated according to their statistical weight \((2J+1)\). The two spin states \(^2\Pi_{1/2}, ^2\Pi_{3/2}\) were measured by comparing the \(Q_1\) and \(Q_2\) rotational lines respectively. The average value from a number of measurements was \(1.82 \pm 0.3\). Our results agree with Andresen et al. (1984) who found the two states to behave according to their statistical weights. Kawazumi and Ogawa (1987) found a preference for \(\Pi_{3/2}\) but did not report on the value obtained.

The signal under the line envelope for each rotational line was integrated to get the intensity of the specific line. In Figure 3.16, the LIF intensity \(I_N\) is plotted versus laser power for the transition \(Q_1(2)\) transition. The arrow in Figure 3.16 indicates the position where the transition is unsaturated and where the LIF signal is directly proportional to the rotational population \(n_N\) according to:

\[
\begin{align*}
n_N &= \frac{I_N}{BP} \\
\end{align*}
\]  

(3.44)

here \(B\) is the Einstein transition probability for absorption (tabulated by Chidsey and Crosely (1980)) and \(P\) is the laser power. The Einstein transition coefficients are proportional to the product of HönL-London and Frank-Condon factors. If, on the other hand, the power of the laser was strong enough to saturate all the transitions then the population would have been independent of laser power and the transition probabilities, i.e. \(n_N \propto I_N\).

If an equilibrium situation exists at a temperature \(T\), the population distribution
Figure 3.16. $Q_1(1)$ LIF signal versus laser power. The arrow indicates the unsaturated transition mode.
of the initial rotational states is determined by the Boltzmann distribution function, i.e.

$$n_N \propto (2N+1)\exp\left(-\frac{B_{\text{rot}}N(N+1)}{kT}\right)$$  
(3.45)

where $B_{\text{rot}}$ and $k$ are the rotational constant of the molecule and Boltzmann's constant respectively. By equating $n_N$ in equations 3.44 and 3.45 we get:

$$\frac{I_N}{B(2N+1)} = \exp\left(-\frac{B_{\text{rot}}N(N+1)}{kT}\right)$$  
(3.46)

From equation 3.46 it is observed that a plot (called Boltzmann plot) of Log [$I_N/(2N+1)BP$] versus N(N+1) should yield a straight line from which the "temperature" can be obtained. Figures 3.17 and 3.18 represent the Boltzmann plots of the Q$_1$ and P$_1$ lines respectively. It is clear that no "one" straight line can be drawn to fit the data. If the first few rotational lines are considered then rotational temperature of 400 ±120 K and 350±60 K are obtained for the Q$_1$ and P$_1$ lines respectively. Photodissociation measurements via the first excited state of water obtained by Andresen et al. (1984) and calculated by Shinke et al. (1985) yield rotationally "cold" OH radicals with measured temperatures of 475 K in reasonable agreement with the above values. Thus, it seems reasonable to conclude that low rotational states of OH(X) are produced predominantly via dipole allowed channels similar to those probed by photodissociation.
Figure 3.17. Boltzmann plot for $Q_1$ branch at 75 eV. If the first few points are taken (low rotational lines) then a rotational temperature of $400 \pm 120$ K is obtained.
Figure 3.18. Boltzmann plot from which the rotational temperature of the $P_1$ line is extracted. By taking the first few lines a rotational temperature of $350 \pm 60 \text{ K}$ is estimated.
Two major sources that contribute to the rotational state distributions are the initial rotation of the parent molecule and the torque generated by the dynamics of the dissociation process. By using a supersonic molecular beam, the parent water molecules are rotationally cold (~ 10 K) and thus have minimal rotational energy. Therefore, following Weide and Schinke (1987) we suspect that the rotational excitation of OH is mainly due to the details of the potential energy surfaces involved. This can be seen from Figure 3.19 where a three dimensional schematic representation of the potential energy surfaces involved in the dissociation of water [taken from Weide and Schinke (1987)] is shown. For excitation via the first absorption band (A(1B) state) we note (see left hand diagram, Figure 3.19) that near the equilibrium position of 104.5° the A (1B) state has a potential energy surface that is almost isotropic with included molecular angle \( \gamma \) \( (dV/d\gamma \sim 0) \). The resultant torque that the A (1B) state produces as dissociation occurs is very small and the rotational distribution should remain peaked at low N values in accord with our data.

The observation of significant population of higher rotational states is an indication that the A (1B) state is not the only pathway possible. Krautwald et al. (1986) and Mordaunt et al. (1994) showed that dissociation via the second absorption band preferentially populates high rotational states. According to the Frank-Condon model when the incident electron excites the water molecules from the ground state \( X (1A) \) to the B (1A) state, it prepares a wave packet that is localized around the ground state equilibrium position (\( \gamma = 104.5^\circ \)) as seen in Figure 3.19. The minimum of the B
Figure 3.19. Three dimensional schematic representation of the first and second absorption band of water (obtained from Weide and Shinke (1987)). Also shown are the trajectories of the B state molecules as they go to the OH (X) state through the A and X states.
(1A) state on the other hand occurs at linearity (γ=180°), hence providing the torque required for excitation to higher rotational states as the molecule swings across the steep potential surface. A number of routes to dissociation are possible.

One possibility is that the B(1A) state of water dissociates to give OH (2Σ) which then fluoresces yielding the ground OH (2Π) state. Another possibility is that as the B (1A) state swings across the potential surface it can make radiationless transitions to the ground state thus producing the observed highly rotationally excited OH (2Π) radicals. This view is consistent with the theoretical work of Weide and Schinke (1987) and by Mordaunt et al. (1994) who demonstrated that the large degree of rotational excitation of OH gained in the first part of the fragmentation (H₂O (B 1A) state) as the molecule goes to a linear configuration is increased in the second part of the break up (as it goes through the B-X or B-A potential surface crossings).

3.5.2 Vibrational Distribution:

To date there have been no vibrational state distributions reported following electron impact dissociation of water. For a comparison with photodissociation, Table 3.4 lists the vibrational state distributions of OH (X) produced from photodissociation of water by different groups along with our own results.
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<td>Engel (1986)</td>
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<td>1.34</td>
<td>0.18</td>
<td>0.1</td>
<td>3D ab initio calc.</td>
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<td>0.25</td>
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<td>0</td>
<td>H tagging, 300 K</td>
</tr>
<tr>
<td>Welge (1967)</td>
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<td>&lt;0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Photodiss.</td>
</tr>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>e⁻ impact (20 K)</td>
</tr>
</tbody>
</table>

Table 3.4. Comparison of the vibrational state distribution of the OH radical produced from photo dissociation and by electron impact (our work).

To obtain vibrational distributions we assumed that rotational populations were similar and that we could get relative vibrational populations by comparing intensities of similar rotational lines in the different bands. This was checked by obtaining the rotational temperature in both the v"= 0 and v"= 1 vibrational states. We found the rotational temperatures of the Q₁ lines to be 400 K and 380 K for v"= 0 and v"= 1 respectively. Thus by using equation 3.44 we were able to obtain the relative population of the v"= 0 and v"= 1 vibrational states. It was found that 20 (± 5)% of the dissociation contributed to the population of the v"= 1 band. Comparisons were made on the Q₁, Q₂, Q₃, and Q₄ lines in the two vibrational states. Care was taken to keep the laser power constant while probing the two states. The third vibrational state, v"= 2, was not observed in our experiment even though rotational spectra involving this state were expected in the wavelength range 318-325 nm, well within the range of our laser.

It is well known that the v"= 2 in the OH (A) state predissociates [Becker (1984, Zanganeh et al. (2000)]. The lifetime of the OH (A, v"= 2) before predissociation is
about 200 ns [Herzberg]. This fact might explain why we were not able to observe any vibrational states higher than the first while Hwang et al. (1999) using the H Rydberg tagging technique were able to observe up to the 6th vibrational state (see table 3.4). Upon dissociation of the water molecule, the Rydberg tagging technique excites the H atom to a high Rydberg state. The H Rydberg atom is then allowed to reach a detector from which the kinetic energy of the H fragment can be obtained. Then by using conservation of energy and momentum the electronic, vibrational, and rotational excitation of the OH radical may be calculated. The advantage of this technique is that it is capable of obtaining vibrational state distributions without being concerned about the lifetime of the state being probed. Another advantage is that the H Rydberg tagging technique does not have the problems associated with obtaining longer laser wavelengths for high vibrational states. Predissociation can cause problems for the LIF technique, but this is not a problem with the H Rydberg tagging technique. Upon dissociation of water by electron impact or by photodissociation, the excess energy transferred to the molecules is shared between the translational, vibrational, and rotational energies of the fragments. According to Andresen et al. (1984), the fragments produced from photodissociation of water shared the following energy partitioning:

\[ f_t : f_v : f_r = 0.885 : 0.095 : 0.02 \]

where \( f_t, f_v, f_r \) are the fraction of the energy transferred to translational, vibrational, and rotational excitation respectively. According to Kawazumi and Ogawa (1987) who
studied the dissociation of water by electron impact on an effusive beam, the translational energies of OH(X) and H were in the 0.073-0.171 eV and 1.25-2.91 eV range respectively. Darrach and McConkey (1991), by analyzing a LIF-TOF profile of OH(X) produced from electron impact of water vapour from supersonic jet, directly measured a translational energy of about 0.026 eV for OH and 0.434 eV for H which was considerably less than that of Kawazumi and Ogawa (1987).

From the potential energy surface of water (see Section 3.1), about 2 eV is transferred to the OH and H fragments. Due to conservation of momentum, the H atom momentum should be seventeen times larger than that of the OH radical. Therefore, the energy transferred to the OH is about 0.11 eV. This energy corresponds to a speed of about 1 mm/μs. Since the diameter of the electron beam is about 3 mm, the loss of the OH fragments from the interaction volume prior to the introduction of the probing laser beam could be significant for the OH(X, v'' = 0) state. When exciting the higher vibrational state OH(X, v'' = 1), one vibrational quantum of energy (0.43 eV) has been removed from the translational energy and hence, OH(X, v'' = 1) will be slower. Hence our signal from v'' = 1 will be somewhat enhanced over v'' = 0. In order to check this, we plot in Figure 3.20 the LIF (and direct) signal as a function of delay time between the formation of the OH (A) and the laser pulse. It is noted that the OH (A) (circles) molecules decay down quickly since the life time of that state is about 700 ns. However, the OH (X) (squares) state is slow and the molecules in that state are still observable even after 10 μs. Based on these results we neglect the translational energy
Figure 3.20. Diagram showing the direct and LIF signal as a function of delay time between the probing laser and the termination of the electron pulse.
effect of the different vibrational fragments.

The observation of low vibrational excitation in our experiment is expected since the equilibrium bond lengths of $\text{H}_2\text{O} (r_e = 0.956 \, \text{Å})$ and of $\text{OH} (r_e = 0.9706 \, \text{Å})$ are very close to each other. According to the Frank-Condon model, if the bond lengths in the lower and in the upper electronic states are very similar then the fragment will not experience any restoring force as it dissociates along the energy surface. It will be born predominantly in its first vibrational state.

The impulsive model [Holdy et al. (1970)] also predicts very low vibrational excitation for the OH radical as it leaves the water molecule. Since the angle between HOH is close to $90^\circ$ ($104.5^\circ$), the force exerted on the oxygen atom (in the OH bond) by the departing H atom will be almost perpendicular to the OH bond. This force cannot produce large stretching or compressing modes upon the OH fragment, therefore, not much vibration will take place.

### 3.5.3 Low Energy Cross Sections:

The excitation of water by electron impact displays its strongest feature at 306 nm as the hydroxyl radical OH ($^2\Sigma$) radiates to the OH ($^2\Pi$) ground state. The relative emission cross section of OH (A-X) measurements as a function of energy is shown in Figure 3.21. The energy ranges from 0 to 100 eV. For comparison we plot the results of Beenakker (1974). Their results were very similar to ours. Threshold
Figure 3.21. Relative OH (A-X) emission cross section as a function of electron impact energy following the dissociation of water. Also shown are the data of Beenakker et al. (1974).
energies were calibrated by comparison with the well known threshold of Nitrogen (C-B) (337 nm) at 11 eV.

Our experiment was performed at relatively low driving pressure ( < 1 atm. ) to minimize the effect of secondary electron production, and at a low current to eliminate space charge effects that might broaden the electron energy distribution. The threshold result obtained was 9.5 ± 0.5 eV which is consistent with that obtained by Beenakker (1974) of 9.5 eV and close to the result found by Sushanin and Kishko (1971) of 9.3 eV. As discussed in Section 3.1, the sharp increase of the cross section followed by a slow decay indicates that, near threshold electron exchange is the dominant process while at higher energies dipole-allowed transitions are the major contributors.

Excitation function of the ground state OH (X) was made possible by using LIF technique. The LIF signal was monitored as a function of electron impact energy. The strong Q1(2) rotational line was chosen as the probing line for the OH(X) excitation function. Data were obtained 2 μs after the termination of the electron beam to avoid the direct fluorescence OH (A-X). It was very hard to get a LIF signal at a delay time of less than 1 μs (see Figure 3.20) due to the relatively weak LIF signal compared to the direct one where the entire rotational manifold is detected. A further geometrical effect is shown in Figure 2.22 where the path of the electron beam through the water vapour beam (direct fluorescence volume) is much bigger than that of the laser beam intersecting the OH(X) fragments produced by the electron beam (LIF fluorescence volume).
Figure 3.22. Diagram showing that the electron beam, water beam overlap is much bigger than that of the laser and the electron beams.
A relative excitation cross section of OH (X) as a function of energy (0-16 eV) is shown in Figure 3.23. The direct fluorescence is also shown for comparison. The cross section near threshold was extracted carefully (0.5 eV steps) to observe any abrupt behaviour as the OH (A) function rises around 9 eV. The shapes of the two curves in Figure 2.23 clearly demonstrate the completely different behaviour of the OH (A) (electron exchange) and the OH(X) transitions near threshold.

The curves in Figure 3.23 indicate that the OH (A) state did not contribute significantly to the population of OH (X). If the contribution of the OH (A) state had been large then the slope would have shown some changes as the direct fluorescence rose sharply near the threshold. The results are in agreement with those of Kawazumi and Ogawa (1986) who did not observe any cascading process from the OH (A) to the OH (X) states. They used LIF techniques following the dissociation of water at room temperature. Beenaker et al. (1974) measured the absolute cross section for the formation of OH (A). The value they reported was about $6.6 \times 10^{-18}$ cm$^2$ at 40 eV. The cross section for an individual rotational line close to threshold is at least one or two orders of magnitude lower. Therefore, most of the OH (X) are produced directly and not via cascade.

To put the dissociation cross section (shown in Figure 3.23) on an absolute scale, the following technique was implemented. It is based on the fact that the dissociative attachment process

\[ e^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^- \rightarrow \text{OH(X)} + \text{H}^- \]
Figure 3.23. Relative cross section measurement of OH (X) near the threshold region. Note the difference shapes of the two curves. OH (X) represents a dipole allowed transition while OH (A-X) is a typical electron exchange process occurring near the threshold.
is very similar to the direct dissociation process except the two surfaces are displaced from one another by the electron affinity of H⁺ (see Figure 3.3). It is reasonable to assume that similar rotational and vibrational distributions of OH (X) will result in each case. Since the cross section of H⁺ production via this channel has been measured [Melton (1972), Schulz (1959), Compton and Christophorou (1967), Buchel’nikova (1959)] it provides a convenient internal calibration for our measurements. The attachment process is a resonant process peaked at 6.5 eV and so the calibration takes place at this energy. We can obtain the absolute cross section at any desired energy by simply comparing the signal at that energy to the absolute cross section at 6.5 eV obtained as discussed above.

The calibration technique explained above has many advantages and some disadvantages. A major advantage is the fact that the detection system, laser wavelength, optics, pressure, and electron current are exactly the same for the two processes and thus cancel out. Hence a large number of possible systematic errors that are usually inherent in measuring absolute cross sections are removed.

A disadvantage of the technique is the fact that the comparison has to be made at 6.5 eV where signals are small and where it is not possible to obtain a full LIF rotational spectrum to confirm the assumptions listed above. Measurements were however made using a number of the strongest rotational transitions and similar results were obtained within experimental error.

In Figure 3.24, the near threshold region (2-12 eV) of the cross section is
Figure 3.24. Excitation function for OH (X), stars, and OH (A), solid squares near the threshold region. The OH (X) curve has been deconvoluted into dissociation attachment product, solid triangles, and direct dissociation, open squares. Dissociative attachment results of that of Melton (1972) are shown as a dashed curve. Note however that Melton's results have been convoluted with a 2 eV energy resolution.
presented. The dashed curve is the OH (X) obtained for dissociative attachment by Melton (1972). Their data were very similar to those of Christophorou (1967). This curve has been convoluted with the energy distribution of our electron beam. Our measured OH (X) cross section (stars) was deconvoluted into two parts, one representing the dissociative attachment process (solid triangles) and the other representing the direct dissociation (open squares). Comparison between the dissociative attachment curve of Melton (1972) and our own (see dashed and solid triangles curves) illustrates the level of uncertainty in the procedure. Also shown is the direct fluorescence curve (solid squares) that was used to calibrate the energy scale. Its threshold was chosen by extrapolating the linearly rising excitation function to intersect the energy axis at 9.3 eV. Finally, the direct excitation threshold was forced to match the known 7.3 eV threshold for the first absorption state of water. Note that the absolute scale in Figure 3.24 refers only to the OH (X) state.

The OH (X) curve in Figure 3.24 was obtained by summing a large number of runs collected over a long period of time. Although this gave us relatively good statistical data (< ± 5 %), it presented the unavoidable problem of having slight variations in the pressure, current, and laser power. These problems together with errors involved in the deconvolution process lead to an estimated error of about 30 %. The absolute cross section for the electron attachment has an associated error of about 20%. Therefore adding in quadrature we give a final error estimate of 36 % to our data.

Our results in the lower energy region were compared to the theoretical
calculations of Gorfinkel et al. (2002), Morgan (1998), and Gil et al. (1994) as shown in Figure 3.25 and tabulated in Table 3.5. We added the contributions of the four lowest states of water ($^3B_1$, $^1B_1$, $^3A_1$, $^1A_1$) obtained by different groups. Since these all eventually lead to OH (X) production either directly or via cascade, our curve is in reasonable agreement with theory at around 19 eV where the maximum difference is about 10%. The values of all of the cross sections are within the same order of magnitude with respect to each other. More discrepancy occurs at lower energies. Our results agree best with the curve of Gil et al. (1994) who used the complex-Kohn theory. The Morgan (1998) and Gorfinkel et al. (2002) data were much larger than ours in the whole energy range covered, but are particularly different around 10 eV where their results are nearly 3.5 and 2.5 times respectively bigger than ours. Resonance features clearly appear in the work of Morgan (1998) but not in that of Gorfinkel et al. (2002). This is somewhat surprising since the two techniques are similar for both works. In general, our results are lower in value than the theoretical calculations. Clearly much additional work needs to be done on this difficult problem.

3.5.4 High Energy Cross Section:

The absolute OH (X) cross section measurements following the dissociation of water by electron impact as a function of energy is shown in Figure 3.26. The electron energy was varied from 0 to 300 eV in 3 eV steps. The data has been put on an absolute
Figure 3.25. Comparison of our OH (X) absolute dissociation cross section (squares) to those obtained theoretically at low energies by Morgan (1998) (long-dashed curve), Gorfinkiel et al. (2001) (chain curve), and by Gil et al. (1994) (short-dashed curve). Representative error bars are shown for the 14.5 eV data.
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Table 3.5. Absolute cross section values obtained from dissociation of water by low energy electron impact \([10^{-17} \text{ cm}^2]\).
scale using the procedure described in Section 3.5.3. The cross section obtained has a broad peak around 75 eV and has a maximum value of $2.1 \times 10^{-16}$ cm$^2$ at that energy. The broad shape of the curve with a maximum at approximately 10 times the threshold energy indicates that dipole-allowed transitions in the parent water molecule are the dominant processes that lead to the formation of the OH (X) radicals.

No other experimental work is available with which to compare our results. However, by using the Bethe approximation, we can try to extract a value for the cross section from a Fano plot, as discussed in Section 3.4. Using data such as in Figure 3.26, a Fano plot ($\sigma E$ vs ln $E$) may be constructed. This is shown in Figure 3.27. The positive slope in the Fano plot at the highest energies provides further evidence that optically allowed excitation processes leading to OH (X) production are the dominant ones.

It is difficult to make qualitative use of the Bethe-Fano equation 3.42 in the present instance for the following reasons. First, we should take data at much higher energies to make sure that we really have reached the Bethe limit. Second, because a number of optically allowed process are contributing each with their own excitation energy and optical oscillator strength, the experimental data curve would somehow need to be deconvoluted. Third, other processes will almost certainly be contributing to OH (X) production at higher incident electron energies and we have no idea of the oscillator strengths which should be attributed to these. If we lump together the oscillator strengths for the first and second absorption bands (0.091, Watanabe (1953))
Figure 3.26. Absolute cross section for the production of OH (X) following the dissociation of water by electron impact. The Q₁ (2) line has been probed by LIF technique.
Figure 3.27. Fano plot of the cross section for the production of OH (X).
and normalize the slope of the Fano plot to this we obtain cross sections which are much too low. Thus we conclude that this technique is not useful in the present instance.

Another way to discuss our total dissociation cross section values at high energies is to examine the results reported in the review by Karwasz et al. (2001) discussed in Section 3.1. We noted in Section 3.1 that the sum of all the individual integral cross sections should agree with the total cross section measurements. In Table 3.6 we show the values of our absolute cross section for dissociation, other integral cross sections (elastic, vibrational, and ionization) values and the measured total cross section. Figure 3.28 is a plot of the summed absolute cross sections and the total ones. The two results are seen to agree well over the complete energy range. A maximum difference of about 20 % is observed around 300 eV. The results in Figure 3.28 give us confidence that our experiment provides good values for the total dissociation cross section. Prior to our work, a significant gap, between the total absolute cross section existed at energies near 100 eV. We finally plot in Figure 3.29 the results for the total dissociation cross section on a similar diagram to that shown by Karwasz et al. (2001). For clarity we have omitted some of the ionization cross sections and only show those of Straub et al. (1997). We note the similar shape of the total dissociation cross section to that of the total ionization cross section and also the fact that their maximum values are very comparable.
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Table 3.6. Integral cross section for electron scattering on water vapour including our values for total OH (X) dissociation [10^{-16} cm^2].
(See also table 3.3).
Figure 3.28. Total cross section measurements obtained by absolute experiments (squares) and the sum of all integral cross sections including our dissociation cross section (triangles). Representative error bars are shown for the 50 eV (sum of integral cross sections) and for the 400 eV (total) data.
Figure 3.29. Integral cross sections for electron scattering on water [Karwasz et al. (2001)]. The absolute dissociation cross section obtained by our experiment has been added. For other measurements see Figure 3.2.
Conclusion:

Laser Induced Fluorescence measurements have been carried out on OH (X) produced from electron impact dissociation of water molecules. We found that the rotational states were populated by more than one channel of dissociation. The rotational "temperatures" for the 6 lowest rotational states were 400 ± 120 K and 350 ± 60 K for the Q1 and P1 lines respectively. About 20% of the fragments are produced in the OH (X, v" = 1) state.

The two spin states \( ^2\Pi_{3/2} \) and \( ^2\Pi_{1/2} \) were found to be populated as expected according to their statistical weighting. We found that the \( \Lambda \)-doublet states ratio \( ^2\Pi^+ / ^2\Pi^- \) to be equal to 1.9 ± 0.3. Unlike the photodissociation experiments this ratio did not change as the rotational states increased. Finally the absolute dissociation cross section of water was obtained for the first time by comparing to the known dissociative attachment cross section. We found that the OH (X) excitation function increases slowly (a dipole allowed process behaviour) and peaks around 75 eV where the maximum value reached is about \( 2.1 \times 10^{-16} \) cm\(^2\). Our results represents the first attempt to measure the absolute dissociation cross section of water for OH (X) production.
3.6 References:


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SECTION 4

LIF MEASUREMENTS ON OD(X) PRODUCED BY ELECTRON IMPACT DISSOCIATION ON HEAVY WATER

4.1 Introduction and Overview of Previous Work:

Water is a prominent constituent of many planetary atmospheres and it plays an important role in biological systems and in radiation chemistry. The interaction of water with electrons resulting in dissociation, ionization and electron attachment are important processes leading to the formation of various neutral and ionic fragments. The cross sections for electron scattering on D₂O will be discussed in this chapter. Comparison to water cross sections will be made to check for any isotopic effects.

According to the Born-Oppenheimer approximation, when an atom is replaced by its heavier isotope, there are no changes in the potential energy curves [Zanganeh et al. (2000)] and in the electronic transition moment but there are changes in the vibrational frequencies, and hence, a change in the zero point energy. In most cases the zero point energy difference is the dominant factor in any isotope effects. Electron impact excitation of H₂O and D₂O were reported by Chutjian et al. (1975). A difference of thresholds was observed, confirming the different zero point energy between the two parent molecules.

Another factor that may give rise to isotope effects is the different rotational
constants that might produce different rotational distributions. The photodissociation of water and heavy water via the first absorption band was carried out by Andresen et al. (1984). They obtained the rotational distribution in order to measure the influence of mass upon energy partitioning. The rotational temperature for the production of OD ($^2\Pi_c$) from heavy water (at 300 °K) was 840 K, while that of OH ($^2\Pi_c$) from water (at 300 °K) was 930 K. Plusquellic et al. (1998) studied the photo-dissociation of H$_2$O and D$_2$O in the non-Frank-Condon region using 193 nm laser radiation. They found that the A-doublet population ratio $\Pi^- / \Pi^-$ of OH was twice that of OD. This was attributed to the rotational constant difference between the two molecules.

Photo-dissociation of water and heavy water in the second absorption band was investigated by Weide and Schinke (1987) and by Zanganeh et al. (2000). They reported that the rotational distributions of OH (A) and OD (A) were highly inverted. The general trends of both distributions were very similar, however, the OD (A) peaked at higher states. This was attributed to the smaller rotational constant of OD with respect to that of OH ($B_o^{\text{OH}} = 18.535$ cm$^{-1}$, $B_o^{\text{OD}} = 9.878$ cm$^{-1}$).

Total cross sections measurements for D$_2$O were measured by Nishimura and Yano (1998) in the 7 to 500 eV region. Szmytkowski et al. (1991) also measured the total cross section ranging from 0.4 to 2700 eV. Comparisons with the water data revealed very close resemblance in overall shape and value. However, the total cross section below 1 eV, where direct rotational excitation occurred, was 10 % higher for water than for heavy water. The difference was attributed to the larger moment of
inertia of D₂O.

Cross sections for electron impact ionization of H₂O and D₂O were studied by Straub et al. (1998) from threshold to 1000 eV. The data presented were for the production of H₂O⁺, OH⁺, O⁺, O²⁻, H₂⁺, and H⁻ from water, and for the production of D₂O⁺, OD⁺, O⁺, O²⁻, D₂⁺, and D⁻ from heavy water. The cross sections were the same for water and heavy water for all ions except for H₂⁺ and D₂⁺. The cross section was approximately a factor of 2 greater for H₂⁺ produced from water than that of D₂⁺ from heavy water.

Compton and Christophorou (1966) determined the dissociative electron attachment cross section for H₂O and D₂O. They found that the formation of H⁻ from H₂O and D⁻ from D₂O both peaked at 6.5 eV. However, big isotope effects were discovered. The cross sections were 5.2 × 10⁻¹⁸ cm² and 6.9 × 10⁻¹⁸ cm² for H⁻ and D⁻ respectively. They also determined the cross section for the formation of O⁻ from both water and heavy water. A significant difference was reported. Using swarm experiments, energy integrated cross sections for the formation of H⁻ from water and D⁻ from heavy water were reported by Hurst et al. (1961) and Stockdale et al. (1964). The values reported were 7.7 × 10⁻¹⁸ cm² eV and 4.6 × 10⁻¹⁸ cm² eV for H⁻ and D⁻ respectively.

By using electron impact dissociation of D₂O Becker and Schulz (1982) found that the dissociation mechanism leading to OD (A) resembled that of OH (A) produced from dissociation of H₂O. They also measured the threshold energy for production of
the OD (A) state and found it to be 9.4 ± 0.3 eV.

Isotope effects in total dissociation cross section measurements were observed for ethane (C₂H₆) by Winters (1979). He reported a ratio of $\sigma_{C_2H_6}/\sigma_{C_2D_6} = 1.09$. Vroom and de Heer (1969) also observed isotope effects for dissociative excitation of hydrogen molecules (H₂ and D₂) and methane (CH₄, CD₄). A difference of up to 20% was observed in the H₂ (D₂) case. This difference was explained for all of the above cases by Platzman (1962), who assumed that preionization and dissociation were two competing paths for highly excited states. A simplified version of the Platzman (1962) model assumed that the dissociation rate was inversely proportional to the square root of the reduced mass of the dissociating particle.

Kedzierski et al. (1998) measured the cross section for the formation of the O (¹S) state from H₂O and D₂O and found no difference within the experimental errors. Freund (1971) demonstrated that electron impact dissociation of H₂O with D₂O into metastable fragments showed no signs of any isotope effects in the kinetic energy measurements from the two parent molecules. Kurawaki et al. (1983) measured the Balmer Lines of H* (n=3,4) and D* (n=3,4) from water and heavy water respectively. They found that the translational energy distribution of H* and D* are similar. This is an indication that the dissociative excitation for both atoms proceeds in a similar manner.

In the next section, the total dissociation cross section for D₂O by electron impact will be compared to that of H₂O. Also, the rotational distributions for the
production of OH ($^3\Pi$) and OD ($^3\Pi$) are reported. An excitation cross section for the production of OD ($^3\Pi$) from D$_2$O ranging from threshold up to 300 eV will be presented for the first time. The shape and magnitude of the excitation cross section will be compared to that for OH production from H$_2$O to check for any isotope effects that may by occurring.

4.2 Comparison of Absolute Cross Sections From Two Different Molecules:

As mentioned in Section 3.1, the quantities of most interest for atomic and molecular studies are the cross sections for the processes being investigated. Comparisons of two cross sections from two different species can be done only if their target densities and other excitation parameters are identical. However, due to different molecular weights and velocities of different molecules and other factors, the target densities are not always the same in a crossed beam experiment. Some form of relative flow procedure must be employed when comparing one cross section to another [Leclair (1993)].

The count rate $R_m$ registered at a detector can be described as [LeClair (1993)]:

$$R_m = q \eta \sigma \frac{\Omega}{4\pi} \int N_s(x, y, z) \nu(x, y, z) N(x, y, z) dV$$  \hspace{1cm} (4.1)

where $q$ is the quantum efficiency of the detection system, $\eta$ is an attenuation factor to account for loses between the interaction region and the detector, $\sigma$ is the cross section
for the process under investigation, $\Omega$ is the solid angle subtended by the detector, $N_e(x, y, z)$ is the density of the electrons, $v (x, y, z)$ is the velocity of the electrons, and $N(x, y, z)$ is the density of the gas in the interaction volume.

The electron density $J$ for a well collimated beam is $N_e v$, and the average electron density $J$ is:

$$J = \frac{I}{eA} \quad (4.2)$$

where $I$ is the electron beam measured by the Faraday cup, $A$ is the cross sectional area of the electron beam, and $e$ is the electron charge. If $N(x, y, z)$ is replaced by its average value $\bar{N}$ over the collision volume, and $\eta$ is taken to be constant which is the case for 308 nm photon detection as in the present instance and may be put equal to unity, then integration of equation 4.1 yields:

$$R_m = q\sigma \frac{\Omega}{4\pi} \frac{I}{eA} \bar{N} \quad (4.3)$$

It is now possible to compare cross sections for production of the same species from two different targets. Thus if one target gas has a known absolute cross section (water in this case, Section 3.5.2, 3.5.3) then the cross section for a different gas ($D_2O$, Methanol) can be put onto an absolute scale by taking the ratio of the two detector count rates

$$\frac{R_m}{R_m'} = \frac{\sigma}{\sigma'} \frac{I}{I'} \frac{\bar{N}}{\bar{N}'} \quad (4.4)$$
Therefore,
\[ \sigma' = \sigma \frac{R_m}{R_m} \frac{I}{I'} \frac{N}{N'} \] (4.5)

Note that most of the parameters in equation 4.3 cancel out. If the currents are also the same for exciting the two molecular species then:
\[ \sigma' = \sigma \frac{R_m'}{R_m} \frac{N}{N'} \] (4.6)

Equation 4.6 gives the cross section \( \sigma' \) of the unknown fragment, in terms of the known cross section \( \sigma \). \( R_m' (R_m) \) is the photon count rate measured experimentally, and \( N' (N) \) is the molecular density in the interaction region.

If the molecules are undergoing "molecular flow" where the mean free path of the fragment is greater than the dimension of the nozzle, then \( N' (N) \) can be replaced by the source pressure \( P' (P) \) [Latimer and McConkey (1965)]. However, if the molecular beam is being operated outside the molecular flow region, a normalization procedure must be implemented. To estimate the relative number density \( N (N') \), the photons produced in the direct dissociation process as the OH(A) state decays down to OH (X) state at 306 nm are plotted as a function of source pressure (see Figure 4.1). In the absence of collisional or other disturbing effects the intensity \( I (I') \) of the signal will be directly proportional to the target density \( N (N') \). Therefore, if the two gases are at different source pressures, the molecular density \( N (N') \) can be replaced by the
Figure 4.1. The production of OH (A) (squares) and OD (A) (stars) from dissociation of water and heavy water as a function of pressure. It is clear that the signal from both radicals is identical.
measured intensity \(I (I')\) (see Figure 4.1), and equation 6 becomes:

\[
\sigma' = \sigma \frac{R'_m \cdot I}{R_m \cdot I'}
\]  (4.7)

4.3 Results and Discussions:

4.3.1 Rotational State Distribution:

A LIF rotational spectrum of OD (X) ranging from 306 to 312 nm taken after dissociation of D₂O by electron impact at 75 eV is shown in Figure 4.2. The position of the ground and the first vibrational states are indicated with long arrows. In Figure 4.3, a highly resolved spectrum ranging from 307 to 309 nm is shown. Some of the Q₁ and P₁ rotational lines are identified. By using the integrated intensity of different rotational lines from the LIF Figures, Boltzmann plots can be produced as shown in Figures 4.4 and 4.5 for Q₁ and P₁ lines respectively. The slopes in the Boltzmann plots are used to calculate the rotational temperatures of the Q₁ and P₁ lines as described in Section 3.5.1. The rotational distribution of OH (X) produced from electron dissociation of water has also been plotted on the same graphs for comparison. The similarity between the rotational distributions of OH (X) and OD (X) are obvious. As in the case of OH (X) the first few lines were considered to obtain the “cold” rotational temperatures. The values obtained were 260 ± 50 K and 230 ± 50 K for the Q₁ and P₁ lines respectively. The magnitude of the errors is an indication of the uncertainty in this procedure. Clearly the whole rotational distribution cannot be defined by a single
Figure 4.2. LIF rotational spectrum of OD (X) taken after dissociation of D₂O by electron impact at 75 eV incident energy.
Figure 4.3. Highly resolved LIF spectrum of OD (X). Excitation conditions are the same as in Figure 4.2.
Figure 4.4 Boltzmann plot for the $Q_1$ lines representing the OD (X) rotational population distribution. The temperature obtained from the first six lines of the progression was $260 \pm 50$ K. Also shown are the $Q_1$ lines rotational lines for OH (X) (squares).
Figure 4.5. Boltzmann plot for the $P_1$ rotational lines. The temperature obtained using the first four lines of the progression was $230 \pm 50$ K. $P_1$ lines from OH (X) are also shown for comparison (squares).
temperature.

The rotational excitation is caused by the dependence of potential energy upon the angle between the H-O-H atoms on the dissociative potential energy surfaces. According to the Born-Oppenheimer approximation the electronic properties of molecules are independent of the nuclear mass [Zanganeh et al. (2000)]. Therefore, the potential energy surfaces are considered to be the same for both H$_2$O and D$_2$O. So we expect the rotational distribution for OH (X) and OD (X) to be similarly cold, as indeed was found in our experiment. The same arguments, that explained the behaviour of the rotational distribution in the water case hold for heavy water as well. For the first few rotational lines we expect the D$_2$O A ($^1$B) state to be the main contributor for populating these states. The higher states are a product of radiationless transitions from the D$_2$O (B $^1$A)) state to the D$_2$O (X $^1$A) state via B-A or B-X curve crossing.

Our results for rotational distribution of OD (X) are consistent with those of Andresen et al. (1984) and Becker et al. (1980). For photodissociation of heavy water leading to OD ($^2\Pi$) Andresen et al. (1984) found no isotopic effects. Becker who used an electron impact dissociation of D$_2$O leading to OD ($^2\Sigma$) also concluded that the dissociation paths are the same for both H$_2$O and D$_2$O. Zanganeh et al. (2000) studied photodissociation into OH (A) and OD (A) and found significant variation in the vibrational branching ratio with wavelength.

The two spin states distribution of OD ($^2\Pi_{3/2}$ and $^2\Pi_{1/2}$) can be extracted by probing the Q$_1$(i) to Q$_2$(i) lines. A few lines were investigated and the average value
obtained for the $^2\Pi_{3/2}$/$^2\Pi_{1/2}$ ratio was $1.9 \pm 0.2$ in agreement with the expected statistical weighting $(2J + 1)$. Within experimental errors this result agrees with that obtained for OH from water dissociation. The fact that the spin states are populated in accordance with their statistical weights is an indication that there are no forces in the exit channels of the excited heavy water (water) molecules that act on the spin of the unpaired electron of the OD (X) or OH(X) molecule.

Using the rotational spectra shown in Figures 4.2 and 4.3 the $\Lambda$ doublet population can also be obtained. This was determined by comparing the $Q_1(i)$ and $P_1(i)$ lines. Six separate lines were compared to each other; the average value obtained for the ratio $^2\Pi^\prime / ^2\Pi^\prime$ was $2.15 \pm 0.25$. This value agrees with our result for OH (X) within statistical errors. Plusquellec et al. (1997) using photo dissociation of jet cooled water and heavy water at 193 nm found that at low rotational states, the ratio $\Pi^\prime / \Pi^\prime$ was the same from both OH (X) and OD (X). However, for higher rotational states they found that the ratio of $\Pi^\prime / \Pi^\prime$ from OH (X) is almost twice that from OD (X). They attributed this variation to the different rotational constants of the products OD ($B_0^{OD} = 18.535 \text{ cm}^{-1}$) and OH ($B_0^{OH} = 9.8788 \text{ cm}^{-1}$). When using electron impact dissociation instead of photons we were not able to observe any changes in the ratio for both OH (X) and OD (X) as the rotational number increased (see section 3.5.1).

In order to obtain the vibrational distribution for OD (X) the first three rotational states of $v^\prime = 0$ and $v^\prime = 1$ were compared to each other. The translational energy of the first vibrational state is lower than that of the ground vibrational state.
However, as in the water case, this did not seem to affect our ability to detect the two states with essentially equal sensitivity.

By using the H atom Rydberg tagging technique following 157.6 nm absorption by water and heavy water in the second absorption band Yang et al. (2000) found that the vibrational distribution in OD (X) is higher than that in OH (X). Yang et al.'s (2000) findings for the ground and first vibrational states of the OH (X) and OD (X) states are listed in Table 4.1 along with our results.

We found that about 29% of the OD radicals populated the first vibrational state \( v'' = 1 \). This result is bigger than that observed for OH (X) which gave a value of only 20% in the first vibrational state. Becker et al. (1982) using electron impact dissociation of water and heavy water suggested that the \( v'' = 1 \) in OD(A) should be stronger than that in OH(A).

We were not able to explain the origin of the difference in the vibrational distribution between OD (X) and OH (X). Based on the Frank-Condon model the vibrational distribution of both OH (X) and OD (X) should be very similar since the equilibrium bond length of D₂O \( (r_e = 0.951) \) and of OD \( (r_e = 0.969) \) are very close to each other and to that of H₂O \( (r_e = 0.956 \text{ Å}) \) and of OH \( (r_e = 0.9706 \text{ Å}) \).

We were not able to detect the OD (X) second vibrational state, that starts to contribute around 314 nm, even though the laser beam was still intense at that wavelength. The lack of evidence of any \( v'' = 2 \) signal is a clear indication that vibrational population higher than \( v'' = 1 \) is scarce. It should be noted that because of
<table>
<thead>
<tr>
<th>Species</th>
<th>( v'' = 0 )</th>
<th>( v'' = 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>OD (X)</td>
<td>1.0 (This work)</td>
<td>0.40 (This work)</td>
</tr>
<tr>
<td>OH (X)</td>
<td>1.0 (This work)</td>
<td>0.25 (This work)</td>
</tr>
<tr>
<td>OD (X)</td>
<td>1.0 (Yang et al. (2000))</td>
<td>1.49 (Yang et al. (2000))</td>
</tr>
<tr>
<td>OH (X)</td>
<td>1.0 (Yang et al. (2000))</td>
<td>1.11 (Yang et al. (2000))</td>
</tr>
</tbody>
</table>

Table 4.1. Vibrational state distribution of OH (X) and OD (X) for the ground and first vibrational states.

different vibrational constants the vibrational spacing for OH (X) is much wider than that for OD (X). The second vibrational state of OH (X) starts to contribute at wavelengths around 318 nm. Predissociation of OH (X, \( v'' \geq 2 \)) is well known [Zanganeh et al. (2000), Becker and Schultz (1982)] and this may account for our observations

### 4.3.2 Absolute Dissociation Cross Sections:

The relative excitation function of OD (A-X) at 306 nm is shown in Figure 4.6. The energy ranges from 0 to 75 eV. The steep increase followed by a gradual decrease is an indication of an electron exchange process dominating the excitation near threshold. At higher energies both electron exchange and dipole-allowed excitation contribute to the formation of the OD (A) state. This behavior is similar to the formation of OH (A) radicals following dissociation of water by electron impact. The
Figure 4.6. Relative excitation function of OD (A) produced from electron impact dissociation of D₂O.
energy positions of the thresholds for the formation of OH (A) and OD (A) measured by various groups are listed in Table 4.2. The value of the threshold we chose for the OD (A) formation was taken as the average (9.45 eV) of all the values in table 4.2. However, because of the poor energy resolution of the electron gun in use we were not able to observe any difference in the threshold between the OD (A) and OH (A) radicals.

To get the excitation function of OD (X $^2\Pi$), the YAG laser probed the strong Q1(2) transition. A relative excitation function of OD (X) ranging from 0 to 15 eV is shown in Figure 4.7. The slope did not change its slow rise around the OD (A) threshold, an indication that the OD (A) cascade contribution to the OD (X) is not very prominent. Also shown for comparison is the OH (X) excitation function. It is clear that the two curves are very similar, an indication that same excitation processes

<table>
<thead>
<tr>
<th>Reference</th>
<th>e+H2O→OH(A) Threshold</th>
<th>e+D2O→OD(A) Threshold</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chutjian (1975)</td>
<td>9.3 eV</td>
<td>9.42 eV</td>
<td>energy loss exp.</td>
</tr>
<tr>
<td>Bose (1978)</td>
<td>9.4</td>
<td>9.6 eV</td>
<td>Static Gas Target</td>
</tr>
<tr>
<td>Becker (1980)</td>
<td>9.3 ± 0.25 eV</td>
<td></td>
<td>Crossed beam exp.</td>
</tr>
<tr>
<td>Becker (1982)</td>
<td></td>
<td>9.4 ± 0.3 eV</td>
<td>Crossed beam exp.</td>
</tr>
</tbody>
</table>

Table 4.2. Threshold measurements for the production of OH (A) and OD (A) by different groups (see also table 3.1).
Figure 4.7. Relative excitation function of OD (X) (circles) ground state at low energies, also shown is the excitation function of OH (X) (squares). Note that we were not able to observe any threshold difference between the two radicals due to the limited resolution of the electron gun in use and also the gradual onset of the excitation function.
produce OD (X) and OH (X). An extended excitation function of OD (X) is shown in Figure 4.8 where the energy range is from 0 to 250 eV. Again the OH (X) excitation function is shown for comparison. We note that the shapes of the two cross sections are similar over the entire energy range.

The absolute dissociation cross section of \( \text{D}_2\text{O} \) exhibited in Figure 4.8 has been obtained by directly comparing the LIF intensity signals of different rotational lines obtained from OD (X) to those of OH (X) from water. Care was taken to carry out the comparison under conditions of identical electron current, and head pressure. Any small differences in target density, due to differences in gas beam velocity were taken into account by making measurements of the direct OH (A→X) and OD (A→X) fluorescence as a function of pressure as discussed in Section 4.2. Figure 4.1 shows the OH (A) and OD (A) signal versus pressure. Data in Figure 4.8 were obtained under the same experimental conditions. It is clear that the signals from both OH (A) and OD (A) are essentially identical as a function of pressure suggesting that LIF signals from the two targets could be directly compared. Furuya et al. (1996) used electron impact (at 17 eV) dissociation of water and heavy water to measure the emission cross section ratio \( \sigma_{\text{OH}(A)}/\sigma_{\text{OD}(A)} \). They found that the production of OD (A) from \( \text{D}_2\text{O} \) dissociation is almost twice that of OH (A) from water dissociation. Because the cross sections are changing rapidly at this low energy, and because of the dominance of triplet excitation, direct comparison with our work is invalid.

As explained in Section 4.2, to compare an unknown cross section \( \sigma \) (heavy
Figure 4.8. Relative excitation function of OD (X) (stars) extended to medium energy range (0-250 eV). The cross section was put on an absolute scale as explained in the text. The squares are the data for OH (X).
water) to a known cross section \(\sigma'\) (water) the following Equation is used:

\[
\frac{\sigma'}{\sigma} = \frac{R_m'}{R_m} \frac{I}{I'}
\]

\(R_m'\) and \(R_m\) are the count rates obtained experimentally from the LIF of OH (X) and OD (X), and \(I\) (\(I'\)) are the direct fluorescence intensities. From Figure 4.8 we see that \(I\) and \(I'\) are identical at all pressures.

The first step was to obtain the intensity of the lowest three \(Q_1\) rotational lines from OH (X) under carefully controlled experimental conditions. Then the molecular source was changed to heavy water. This was accomplished in less than 15 minutes as explained in Section 2.2. Care was taken to ensure that the experimental conditions (head pressure, current, laser power, etc...) were still the same after changing to heavy water. This was readily achieved since after 15 minutes the experimental parameters can be controlled without much effort.

The comparison between the two molecules was done several times on different days under different pressures and currents, and using several different rotational lines. We assume that by comparing the first few rotational lines of the ground vibrational state all the rotational lines will be accounted for. This is valid because as shown in Figures 4.3 and 4.4, for the ground vibrational state, the rotational distribution is the same for both molecules. The measured ratio for \(\sigma_{H_2O}/\sigma_{D_2O}\) was 1.05 \pm 0.05. However, we note that this ratio refers to OH (X, \(v'' = 0\)) and OD (X, \(v'' = 0\)) and hence, because
of the different vibrational distributions described earlier (Section 4.3.1), the ratio must be corrected before a cross section for total OD (X) can be obtained. On taking the vibrational distribution of the two states into account the final ratio of \(\sigma_{\text{H}_2\text{O}}/\sigma_{\text{D}_2\text{O}}\) is 0.93 ± 0.2.

Using the maximum cross section obtained for water \((2.1 \times 10^{-16} \text{ cm}^2)\) the maximum value of the absolute dissociation cross section for heavy water into ground state OD is calculated to be \(2.26 \times 10^{-16}\text{cm}^2\). The OD data in Figure 4.7 were put on an absolute scale based on this ratio. This result might indicate that the O-H bond is harder to break than the O-D bond. To date no one else has reported the absolute dissociation cross section for heavy water following electron impact dissociation.

Using photodissociation in the non-Frank-Condon region at 193 nm Plusquellic et al. (1997) found a relative cross section of \(\sigma_{\text{OH}(X)/\sigma_{\text{OD}(X)}} = 64 \pm 10\). Plusquellic et al.'s (1997) value is four times smaller than the theoretical predcitions of Schroeder and Schinke (1998). It is clear that there is a big difference between the results obtained using electron impact dissociation (as in our case) and photodissociation (Plusquellic et al. 1997). However the two cannot be compared directly because the photon data select non-Frank-Condon dissociation.
4.4 Conclusion:

By monitoring the OD (X) ground state produced from electron impact dissociation of D₂O with LIF techniques, the rotational and vibrational distributions have been obtained. We have found a rotational temperature of 260 ± 50 K and 230 ± 50 K for the Q₁ and P₁ lines respectively. We were not able to assign a single rotational temperature for the rotational distribution. This is the same as was observed for water in Section 3. The two spin states distribution of OD (X) was also studied. A value of 1.9 ± 0.2 was obtained for the ratio $^{3}\Pi_{1/2}/^{3}\Pi_{3/2}$. This is in accordance with the expected statistical weighting ($2J + 1$). Also the A-doublet population was investigated. The average value obtained for the $^{3}\Pi'/_{}^{3}\Pi$ ratio was 2.15 ± 0.25. We have also obtained the vibrational distribution. We found that about 28% of the OH radicals populated the first vibrational state v''=1. We did not observe any higher vibrational states.

By collecting the direct fluorescence from the OD (A) and comparing it to OH (A) we found that the intensities of the two signals are the same, i.e. the cross sections for the production of OH (A) from water and OD (A) from heavy water are the same. Finally we were able to find the absolute dissociation cross section of D₂O by comparing it to that of H₂O. We found that the absolute dissociation cross section of D₂O peaks around 75 eV and has a value of $2.26 \times 10^{-16}$ cm². This value is a factor of 1.08 higher than that of water. This absolute dissociation cross section for D₂O using electron impact had not been obtained before.
4.5 References:


SECTION 5

DISSIPATION OF METHANOL BY ELECTRON IMPACT

5.1 Introduction and overview of previous work:

The interaction of electrons with molecules has played a major role in providing information about the internal structure of molecules and their excited states. In low energy electron-molecule collisions, all electronic transitions including spin exchange are allowed. However at higher electron energies the selection rules are similar to those of optical excitation.

Methanol is a natural extension to our studies on water since methanol is the simplest organic molecule which contains two kinds of hydrogen bonds. The study of methanol, CH₃OH, is of crucial importance because it stands between very big molecules and relatively simple ones (water). Methanol has relatively few electrons so this makes it accessible to high level theoretical calculations. This allows details of the excited states and fragmentation channels to be calculated with some degree of accuracy. Many theoretical studies [Buenker et al. (1984), Curtiss and Pople (1991), Bauschlicher et al. (1992), Wadt and Goddard III (1976), Kassab et al. (1983), and Martson et al. (1993)] have been performed to complement the experimental work that has been going on [Harich et al. (1999 a), Harich et al. (1999 b), Wen et al. (1994), Satyapal et al. (1989), Kindvall et al. (1986), Bialkowski et al. (1977), Donohue et al.]

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(1977), and Knoop et al. (1971)].

Knoop et al. (1971) have studied the electronic excitation of water and methanol using low energy electron energy loss spectroscopy. They found that the methanol spectrum closely resembled that of water. For both water and methanol they observed two dominant transitions. In the case of water they found two transitions one at 7.2 eV and the other at 9.7 eV. They assigned triplet excitation for both of those transitions, namely A (3B) and B (3A). In the case of methanol, it is known that the first optical singlet state peaks at 6.75 eV [Harrison (1959)]. Knoop et al. (1971) observed a transition at 6.5 eV which is lower than that of the singlet state. Therefore, in analogy with water, a triplet excitation was assigned. The other transition of methanol was seen at 8.3 eV and a triplet excitation was assigned as well.

The electron configuration of the lowest state of methanol is:

\[(1a')^2 (2a')^2 (3a')^2 (4a')^2 (5a')^2 (1a'')^2 (6a')^2 (7a')^2 (2a'')^2\]

and for the first excited state is:

\[(1a')^2 (2a')^2 (3a')^2 (4a')^2 (5a')^2 (1a''')^2 (6a')^2 (7a') (2a'') (3s a')\]

Robin and Kuebler (1972) obtained the electron impact energy loss spectrum of methanol using electron energies of 100.7 eV. Their results are shown in Figure 5.1. The broad weak band seen at 6.7 eV was ascribed to the to the \((2a'' \rightarrow 3sa')\) band in agreement with other researchers [Robin (1974) and Tam et al. (1974)]. This corresponds to the observation of the featureless band at 7.44 eV (see Figure 3.1) in water which is assigned \(1b_1 \rightarrow 3s\). Other transitions in Figure 5.1 are labeled
Figure 5.1. Electron impact energy loss spectrum of methanol obtained from Robin and Kuebler (1972). The equivalent wavelength for photo-absorption are indicated.
appropriately. Also indicated on top of Figure 5.1 are the vertical ionization potentials listed in Table 5.1.

<table>
<thead>
<tr>
<th>Orbital State</th>
<th>Vertical Ionization Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>2σ''</td>
<td>10.96 [eV]</td>
</tr>
<tr>
<td>7σ'</td>
<td>12.62 [eV]</td>
</tr>
<tr>
<td>6σ'</td>
<td>15.21 [eV]</td>
</tr>
<tr>
<td>1σ''</td>
<td>15.64 [eV]</td>
</tr>
<tr>
<td>5σ'</td>
<td>17.62 [eV]</td>
</tr>
<tr>
<td>4σ'</td>
<td>22.65 [eV]</td>
</tr>
<tr>
<td>3σ'</td>
<td>32.2 [eV]</td>
</tr>
<tr>
<td>2σ'</td>
<td>292.3 [eV]</td>
</tr>
<tr>
<td>1σ'</td>
<td>538.9 [eV]</td>
</tr>
</tbody>
</table>

Table 5.1. Vertical ionization potential energies for ground state orbitals of methanol obtained from Robin and Kuebler.

The optical absorption spectrum of methanol has been studied by many groups [Harrison et al. (1959), Tsubomura et al. (1964), Salahub et al. (1971), Nee et al. (1985)]. The photo absorption spectrum of methanol from 105 nm to 200 nm reported by Nee et al. (1985) resembles the electron impact spectrum of methanol to a large extent. Photodissociation of methanol in the first absorption band at 193 nm has been studied by many researchers [Wen et al. (1984), and Satayapal et al. (1989)]. Unlike water which has only one dissociation channel at the first absorption band, methanol has a variety of dissociation channels. Some of these processes are as follows:

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$\text{CH}_3\text{OH} + \text{hv} \rightarrow \text{CH}_3\text{OH}^* \rightarrow \text{CH}_3\text{O} + \text{H} \quad 1$

$\text{CH}_3\text{OH} + \text{H} \quad 2$

$\text{CH}_3 + \text{OH} \quad 3$

$\text{CH}_2 + \text{H}_2\text{O} \quad 4$

$\text{CH}_2\text{O} + \text{H}_2 \quad 5$

$\text{CH}_2\text{O} + 2\text{H} \quad 6$

$\text{C} + \text{H}_2\text{O} + \text{H}_2 \quad 7$

$\text{CH} + \text{OH} + \text{H}_2 \quad 8$

Satyapal et al. (1989) concluded that by using photodissociation at 193 nm, only those channels involving the breaking of the two oxygen bonds are of significance. They found that process 1 is the main channel of dissociation of electronically excited methanol with a quantum yield of $0.86 \pm 0.10$. They also concluded that the dissociation process through the first absorption band is direct and fast like the water molecule in its first excited state ($A^1\text{B}$).

Harich et al. (1999) studied the dissociation through the second absorption band at 157 nm. They noted the appearance of several $\text{H}_2$ elimination channels:

$\text{CH}_3\text{OH} + \text{hv (157nm)} \rightarrow \text{CH}_3\text{OH}^* \rightarrow \text{HCOH} + \text{H}_2 \quad 9$

$\text{CH}_3\text{O} + \text{H}_2 \quad 10$

$\text{HCO} + \text{H}_2 + \text{H} \quad 11$

Although attainable, not all of these channels were observed using 193 nm excitation. The appearance of additional dissociation processes is due to the opening of several
dissociation pathways as the molecule is excited to higher and more complex electronic excited states. Harich et al. (1999) determined that the relative branching ratio of H and H₂ eliminations is: 1: 0.15. They also concluded that dissociation via the second absorption band of methanol is fast and direct similar to dissociation via the first band.

Using electron dissociative attachment on methanol Kuhn et al. (1989) observed a resonance at 10.5 eV. They obtained a cross section in the order of 10⁻¹⁹ cm² for the production of the O⁻ ion using electron attachment. The cross section for the OH⁻ ion formation was about 14 times less than that of O⁻.

Dissociation of jet cooled methanol using electron impact at very high energies (20 keV) was done by Kindvall et al. (1986). The rotational temperature of CH (A² Δ ←X ²Π) radicals was evaluated to be 4380 ± 540 K, and the overall rotational distribution was assigned a single temperature.

Bialkowski et al. (1978) used LIF to measure the rotational temperature of OH (X) produced by infra-red multiphoton dissociation of methanol. They found that the OH (X) radicals are formed with a rotational temperature of 1250 ± 400 K. However due to rotational relaxation to lower rotational states this temperature was seen to decrease rapidly. 210 ns after the formation of the OH (X) products, the rotational temperature had decreased to 800 ± 90 K. After about 1.5 µs a value of 400 ± 25 K was reached. They concluded that “the rotational relaxation of the product species occurs via collisions with the cold surrounding CH₃OH gas”.

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In Figure 5.2 the emission spectrum of methanol obtained by Ogawa et al. (1984) using 100 eV electron impact is shown. Figure 5.2 reveals the complexity and the variety of the species formed by the dissociation of methanol. In addition to the molecules and atoms observed by Ogawa et al. (1984), Donohue et al. (1977) using electron impact dissociation of methanol at 100 eV were able to observe additional species (C, CO⁺B(Σ), CO⁻A(Π)) by gathering light at shorter wavelengths. Donohue et al. (1977) reported the emission excitation functions of various excited states ranging from 0 to 50 eV as shown in Figure 5.3. According to Donohue et al. (1977) the OH (A) excitation function appears to have two distinct onsets. The first onset at 10.1 eV and the second one at around 30 eV. Donohue et al. (1977) attributed the first appearance potential to the following process:

\[ e^- + \text{CH}_3\text{OH} \rightarrow (\text{CH}_3\text{OH})^+ \rightarrow \text{OH} (A) + \text{CH}_3 (X) \]

The second onset at around 30 eV is probably the result of total break up of the molecule as shown in the following processes:

\[ e^- + \text{CH}_3\text{OH} \rightarrow (\text{CH}_3\text{OH})^+ \rightarrow \text{OH} (A) + \text{C}^- + 3\text{H} \]

or

\[ e^- + \text{CH}_3\text{OH} \rightarrow (\text{CH}_3\text{OH})^+ \rightarrow \text{OH} (A) + \text{C} + \text{H}_2 + \text{H}^- \]

For the CH (A) excitation function, at 430 nm, two potential onsets were observed as well, one at 13.1 eV and the second one at 42 eV. The first onset was correlated to the process:

\[ e^- + \text{CH}_3\text{OH} \rightarrow (\text{CH}_3\text{OH})^+ \rightarrow \text{CH} (A) + \text{OH} + \text{H}_2 \]
Figure 5.2. Emission spectrum of methanol by electron impact at 100 eV obtained from the work of Ogawa et. al. (1984).
Figure 5.3. Emission excitation functions for various fragments produced from dissociation of methanol by Donhoue et. al. (1977). The superimposed arrows and numbers indicate the location and the value of different appearance potentials.
The second onset at 42 eV was not assigned to any process. They suggested that this higher potential is the result of excitation to multiply excited states of methanol.

Finally using Fano plots from 0 to 2000 eV, Donohue et al. (1977) were able to deduce that the formation of CO\(^{-}\) (B) and OH (A) fragments is dominated by optically allowed transitions. This implies that single electron transitions dominate the production of the species and that photoabsorption experiments will produce the same fragments.

Darrach and McConkey (1991) using the LIF technique after dissociation of methanol by electron impact obtained a rotational temperature of about 350 ± 30 K for the OH (X) radicals. They measured the relative cross sections for the formation of OH (A) from both water and methanol, and found that the production of OH (A) from methanol was down by a factor of 9 to OH (A) produced from water dissociation. They also found the relative cross section for the formation of ground OH (X) from water and methanol and they normalized them relative to each other. At 150 eV the absolute dissociation cross section for methanol was 0.6 that of water at the same energy.

In the next Section, the rotational distribution of OH (X) is discussed. Electron impact dissociation studies of methanol ranging from threshold to 250 eV were carried out. We were able to acquire the relative excitation function of OH (A) and CH (A) and we compare them to the ones obtained by Donohue et al. (1977). The OH (X) radicals produced were excited and studied using LIF. The dissociation cross section for OH (X) production from methanol was put on absolute scale by direct comparison to that
of OH (X) produced from water.

5.2 OH Rotational Distributions:

The break up of the C-O bond creates the excited OH A (2Σ) state as discussed above. It also produces the ground OH (X) state. In order to characterize some of the OH (2Π) state dynamics the Q₁ rotational transition lines were probed using LIF. The Q₁ lines are chosen because of their easy accessibility. We were able to probe the lowest ten rotational lines of the Q₁ transition.

The Q₁ rotational line was probed 2 µs after the termination of the electron gun pulse. The rotational temperature was determined by plotting \( \ln(1/(2N+1)BP) \) vs. \( N(N+1) \) as explained in Section 3.5.1. From the Boltzmann plot, shown in Figure 5.4, the rotational temperature was determined to be 300 ± 70 K. This temperature is close to the rotational temperature (400 ± 120 K) obtained from OH (X) produced from water dissociation when only the first few rotational lines are considered. Darrach and McConkey (1991) found a rotational temperature of 360 ± 30 K for the production of OH (X) produced from dissociation of cold methanol by electron impact at 100 eV. Darrach and McConkey’s (1991) results agree with ours within the statistical errors of the experiments. Bialkowski et al. (1978), who studied multiphoton dissociation of methanol, measured a nascent rotational temperature of 1250 K in a room temperature static gas target.
Figure 5.4. Boltzmann plot for the $Q_1$ rotational line of OH (X) produced from dissociation of methanol by electron impact at 75 eV.
The rotational distribution for the production of OH (X) from methanol was assigned a single rotational temperature. This finding indicates that mainly one channel or process is producing the OH in its ground state. This differs from the case of water where the rotational distribution was not assigned a single temperature. We found that for higher rotational states, the OH(X) rotational temperature produced from water dissociation was much hotter (about 1600 K) than for the lowest states (360 K).

We recall that Kindvall et al. (1986) assigned a single rotational temperature of 4380 ± 540 K to the formation of CH (A) produced in the dissociation of process.

From the work of Donohue et al. (1977), Satyapal et al. (1989), and Harich et al. (1999), the production of OH (X) radicals is mainly a byproduct of the dissociation of methanol via the first and the second absorption bands. Satyapal et al. (1989) and Harich et al. (1999) concluded that these states are fast and direct. When dissociation occurs via fast and direct repulsive energy surfaces, not much torque is transferred to the product species. This was demonstrated in the case of water in Section 3.5.1. Therefore, the low rotational distribution found in our experiment for methanol is expected based on this simple argument.
5.3 Potential Energy Data:

One of the most important results in molecular physics is the positioning of the potential energy curves of the different species and the identifications of the different dissociation pathways. The dissociation limits can be determined from the minimum heat of reaction required to produce different species from the parent molecule. This can be calculated from the thermodynamical data available [NIST 2002]. At the electron energy used in this experiment, 75 eV, there are many channels that are thermodynamically accessible. In Table 5.2 the minimum energy required to produce certain species via specific processes are listed. By using the data calculated in Table 5.2 we plot a simplified potential energy level diagram as shown in Figure 5.5.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Fragments</th>
<th>Value [eV]</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{OH} + e^- \rightarrow \text{CH}_3 + \text{OH} \ (X)$</td>
<td>3.99</td>
<td>calculated [NIST]</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + e^- \rightarrow \text{CH}_3 + \text{OH} \ (A)$</td>
<td>8.04</td>
<td>calculated [NIST]</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + e^- \rightarrow \text{CH}_3\text{O} + \text{H}$</td>
<td>4.55</td>
<td>calculated [NIST]</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + e^- \rightarrow \text{CH}_3\text{O} + 2\text{H}$</td>
<td>5.36</td>
<td>calculated [NIST]</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + e^- \rightarrow \text{CH}_3\text{O} + \text{H}_2$</td>
<td>0.91</td>
<td>calculated [NIST]</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + e^- \rightarrow \text{CH}_3\text{OH} + \text{H}$</td>
<td>4.25</td>
<td>calculated [NIST]</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + e^- \rightarrow \text{CH}_3 + \text{H}_2\text{O}$</td>
<td>3.58</td>
<td>calculated [NIST]</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + e^- \rightarrow \text{H}_2\text{O} + \text{H}_2 + \text{C}$</td>
<td>15</td>
<td>calculated [NIST]</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + e^- \rightarrow \text{CH} (A) + \text{OH} + \text{H}_2$</td>
<td>11.49</td>
<td>Donohue et al. (1977)</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + e^- \rightarrow \text{CH} (A) + \text{H}_2\text{O} + \text{H}$</td>
<td>11.54</td>
<td>Donohue et al. (1977)</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + e^- \rightarrow \text{OH} (A) + \text{C} + \text{H}_2 + \text{H}^-$</td>
<td>29</td>
<td>Donohue et al. (1977)</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + e^- \rightarrow \text{OH} (A) + \text{C}^- + 3\text{H}$</td>
<td>31</td>
<td>Donohue et al. (1977)</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + e^- \rightarrow \text{CO}^- + 2\text{H}_2$</td>
<td>21</td>
<td>Donohue et al. (1977)</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2. Calculated and measured values for the formation of some of the different species obtained after dissociation of methanol.
Figure 5.5 Simplified energy level diagram for methanol. The dissociation limits are taken from Table 5.2.
5.4 Cross Sections:

The excitation functions over the energy range 0 to 75 eV for emission from OH (A) and CH (A) fragments produced from dissociation of methanol by electron impact are shown in Figure 5.6 and Figure 5.7 respectively. Observation of CH(A) was achieved by using a 420 nm filter before the photomultiplier. The gradual rise of the functions indicates that dipole allowed transitions dominate the production of these excited states. We note that this behavior is not similar to that obtained for the production of OH (A) state from dissociation of water, where, near the threshold region, electron exchange processes were shown to be the main contributors to the formation of that state (see Figure 3.23).

The results of Donohue et al. (1977) from 0 to 50 eV for the production of excited OH and CH states after dissociation of methanol are also shown on Figures 5.6 and 5.7. The thresholds in Figures 5.6 and 5.7 were forced to match those of Donohue et al. (1977) since their energy resolution (300 meV) is much better than ours. Overall, the shapes of the excitation functions are very similar. However, we were not able to observe the second onset around 31 eV. The location of the first onset around 10.1 eV is obvious. From Table 5.2 and Figure 5.5 we see that the process

\[ e^- + CH_3OH \rightarrow (CH_3OH)^+ \rightarrow OH (A) + CH_3 (X) \quad (8.04 \text{ eV}) \]

is the most likely process that produces the OH (A) state starting around 10.1 eV. The excess 2.05 eV is partitioned among various degrees of freedom (rotational,
Figure 5.6. Excitation function for OH (A) produced from dissociation of methanol (open circles). The results of Donohue et al. (1977) are also shown (dots). The superimposed arrows and numbers refers only to the work of Donohue et al. (1977). Our data have been shifted so that the first onsets of the excitation functions coincide.
Figure 5.7. Excitation function for CH (A) produced from dissociation of methanol (open circles). The results of Donohue et al. (1977) are also shown (dots). The superimposed arrows and numbers refers only to the work of Donohue et al. (1977).
vibrational, and translational) of the fragment molecules.

The production of CH (A) obtained from dissociation of methanol in this experiment agrees quite well with the results obtained by Donohue et al. (1977) from 0 to 50 eV. As in the case of OH (A) we were not able to see the second appearance potential this time around 42 eV. The first threshold for CH (A) excitation, shown in Figure 5.7, lies about 13.2 eV. From Figure 5.5 we can attribute the formation of the CH (A) state at 13.2 eV to the following processes:

\[ \text{e}^- + \text{CH}_3\text{OH} \rightarrow (\text{CH}_3\text{OH})^+ \rightarrow \text{CH (A)} + \text{OH} + \text{H}_2 \quad (11.49 \text{ eV}) \]

or

\[ \text{e}^- + \text{CH}_3\text{OH} \rightarrow (\text{CH}_3\text{OH})^+ \rightarrow \text{CH (A)} + \text{H} + \text{H}_2\text{O} \quad (11.54 \text{ eV}) \]

As in the case of OH (A) the excess energy (\(-1.7 \text{ eV}\)) is partitioned among the various degrees of freedom of the fragments. From Figure 5.5 we see that 42 eV is much higher energy than any dissociation thresholds that might result in simple production of the CH (A) state. Donohue et al. (1977) suggest that this higher appearance potential is the result of excitation to multiply excited states of methanol.

The excitation function for the production of OH (X) following electron dissociation of methanol has been obtained by varying the electron energy while probing the Q_1(2) line via LIF. In Figure 5.8 we show the relative excitation function of OH (X) in the low energy region, up to 20 eV. The OH (A) excitation function is also shown for comparison. The shape of the two slopes are very similar indicating that similar processes are taking place. The slow rise of the curve indicates that OH (X) production is accessed via dipole allowed transitions.
Figure 5.8. Relative excitation function for OH (X) (squares) and OH (A) (circles) production after dissociation of methanol.
There is a difference of about 1.5 eV between the threshold onsets of the OH (X) and OH (A) curves. We note that this is the approximate separation of the first and second absorption bands, Figure 5.1.

In the case of water we were able to conclude that the H₂O (B) state did not contribute significantly to the formation of OH (X) via a cascade process from OH (A). This conclusion was based on the fact that the OH (X) excitation function did not exhibit any structure at the onset of OH (A) production (see Figure 3.23). However, for methanol we cannot come up with a similar conclusion because of the gradual onsets of the excitation functions for both OH(X) and OH (A) and thus a noticeable cascade onset structure would not be expected.

In Figure 5.9 the excitation function of OH (X) ranging from 0 to 250 eV is displayed. The OH (X) cross section has a broad peak around 100 eV which is an indication that dipole allowed transitions dominate the production.

To put the dissociation cross sections of methanol on an absolute scale we need a procedure for comparing the target densities of H₂O and CH₃OH. To obtain this we use the same procedure as was used for D₂O normalization (see Section 4.2). A plot of direct fluorescence signal intensity of OH (A) vs. pressure for water and methanol molecules is shown in Figure 5.10. For head pressures below about 1 atmosphere the fluorescence intensities are seen to increase approximately linearly with pressure. The LIF signals from both methanol and water were acquired under the same experimental conditions (e-beam current, head pressure, laser power, etc.). See section 4.2 for more
Figure 5.9. Production of OH (X) produced from dissociation of methanol by electron impact.
Figure 5.10. The signal of OH (A) produced from dissociation of water (squares) and methanol (circles) as a function of pressure.
details on this procedure. This enabled the cross section in methanol to be estimated relative to that of water.

The ratio of the dissociation cross sections for production of OH (X) from water and methanol at 75 eV, $\sigma_{\text{CH}_3\text{OH}}/\sigma_{\text{H}_2\text{O}}$ was determined to be 0.7. Because of the uncertainty in relative beam densities, experimental fluctuations (laser power, electron beam current) and statistical errors in the measured LIF intensities, a maximum error of 60% is estimated for the measured relative cross sections. In Figure 5.11 the dissociation cross sections of water and methanol are put on an absolute scale. It is seen that the shape of the cross sections for the two molecules are very similar. Our result agrees with the results obtained by Darrach et al. (1991) who found the absolute dissociation cross section of methanol to be less than that of water by a factor of 0.6 at 150 eV.

It was also found that production of OH(A) from methanol was down by a factor of about 4 over the production of OH (A) from water dissociation. In Figure 5.12 we show the production of OH (A) from 0 to 250 eV. Darrach et al. (1991) found that methanol signal was down by a factor of 9.
Figure 5.11. Absolute dissociation cross section of methanol (circles) and water (squares) ranging from 0 to 250 eV.
Figure 5.12. Production of OH (A) produced from dissociation of methanol by electron impact.
5.5 Conclusions:

The rotational distribution for the formation of OH (X) following the dissociation of methanol by electron impact has been measured and found to be represented by a single rotational temperature. We have obtained a value of $350 \pm 70$ K for this. This value is in good agreement with the work of Darrach and McConkey (1991). We have calculated a simple potential energy diagram for methanol based on its thermodynamical properties. The relative excitation functions ranging from 0 to 75 eV for the production of OH (A) and CH (A) were measured and compared to those obtained by Donohue et al. (1977).

We have also measured the excitation function for the ground state of OH following electron impact dissociation of methanol. The OH (X) excitation function ranging from threshold to 270 eV was obtained. We found that dipole allowed transitions dominate the OH (X) production. We referenced our methanol measurements to those previously obtained for water (see Section 3). We found that at 75 eV the OH (X) dissociation cross section from methanol was a factor of 0.7 lower than that from water obtained under the same conditions. We emphasize that the technique for obtaining absolute dissociation cross sections of unknown species by comparison to a known cross section for production of the same fragment is very useful and relatively easy to do as long as the conditions for the experiment can be controlled accurately so that they are the same for both species.
5.6 References:


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Tam W. C., and Brion C. E., J. Electron Spectrosc. 3 (1974) 263.


SECTION 6

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

The dissociation of a number of different molecules using electron impact has been studied in our experiment. Special attention has been given to the low (near threshold) and medium energy range. Our system proved to be very successful in obtaining some very interesting information about the internal structure and dynamics of the molecules investigated. Specific rotational information has been obtained.

In water we found that the rotational states of OH (X) were populated by more than one process and thus, the rotational temperature could not be assigned to a single value. The vibrational distribution was also measured. We found that most of the OH (X) fragments populated the two lowest vibrational states. The ground to the first vibrational states branching ratio was \( \frac{v''=0}{v''=1} = 1:0.25 \). The excitation functions of both OH (A) and OH (X) were studied. We found that near the threshold region electron spin exchange processes dominate the production of the OH (A) state while dipole allowed transitions dominate the production of the OH (X) state.

We have reported for the first time the dissociation cross section of water. We found that at 75 eV the total cross section for fragmentation into OH (X) is \( 2.1 \times 10^{-16} \text{cm}^2 \). The dissociation cross section for water peaked around 75 eV. At low energies, \(<15 \text{ eV}\), our results are in reasonable agreement with the theoretical work using the Complex Kohn, R-matrix, and the Schwinger variational methods.

In section 4 isotope effects were studied by comparing similar processes in
H$_2$O and D$_2$O. The rotational distribution was found to be the same for both water and its isotope. However, we found a difference in the vibrational distribution in the ground state of OD (X). The branching ratio of the lowest two vibrational states were (v"=0) : (v"=1) = 1:0.4.

The relative cross sections for the formation of OH (A) from dissociation of water and OD (A) from dissociation of heavy water were found to be similar. The total OH (X) dissociation cross section of heavy water was evaluated by comparing the signal to that of water. We found that the ratio of the cross sections of the two molecules $\sigma_{\text{H}_2\text{O}} / \sigma_{\text{D}_2\text{O}}$ to be 0.93 ± 0.2. This allows us to put the absolute dissociation cross section of heavy water on an absolute scale. This result had not been reported before.

Finally the rotational distribution of OH (X) produced from dissociation of methanol by electron impact at 75 eV was reported. A rotational temperature of 300 ± 70K was found. This value is close to that obtained for OH (X) produced from dissociation of water by electron impact under the same conditions. The OH (A) excitation function was studied from 0 to 250 eV. We found that dipole allowed transitions dominate the production of OH (A) state at all energies. This is in contrast to the production of OH (A) from water where electron exchange processes dominate at low energies. Also the excitation function of CH(A) from 0 to 75 eV was reported. This channel is also populated by dipole allowed transitions.

The methanol OH (X) signal was referenced to that of OH (X) from water. This allowed us to find the ratio of the dissociation cross sections of water and methanol.
The ratio $\sigma_{\text{CH}_3\text{OH}} / \sigma_{\text{H}_2\text{O}}$ was found to be $0.7 \pm 0.4$.

One avenue that might be taken in order to improve the signal to noise ratio would be to copropagate the electron and laser beams. This would greatly increase the effective interaction region. Inserting a spherical analyzer to do this (would have the additional advantage of increasing our electron energy resolution. However the practical design of such a system might be difficult due to the presence of the magnetic field in the present setup.

Very little work has been done on probing the neutral products of electron molecule collisions at low energies ($< 15$ eV). So an obvious extension to our work is to study different molecules in the low and medium energy regions. The existing apparatus can study a whole range of molecules by using available dyes to access different wavelengths where LIF transitions might lie. Electron impact ionization of various molecules can also be studied in our experiment with rotational resolution.
VITA AUCTORIS

I was born in Borj El-Barajneh, Beirut, Lebanon in 1970. I graduated from high school in 1987. For the next four years I was unable to continue my education. However in 1991 I attended University of Windsor and received my B.Sc. in physics in the spring of 1995. Then under the supervision of Dr. J. W. McConkey I finished my M.Sc. in 1998.