RICE UNIVERSITY

PHOTODISSOCIATION DYNAMICS OF OZONE USING RAMAN EXCITATION PROFILES (REP's)

by

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Abstract

The Photodissociation Dynamics of Ozone Using Raman Excitation Profiles (REP’s)

By

Erik Siavash Lotfi

Because of the environmental importance, ozone has long been one of the prominent research topics in the scientific community. Surprisingly, in spite of all the research, the UV photodissociation dynamics of ozone has not been completely understood yet. More specifically, the origin of the small structural features overlapping the broad-band feature in the UV absorption spectrum of ozone still remains a mystery. However, theoretical calculations done in our lab predict, subject to UV radiation, a great majority of ozone molecules fall apart in roughly 6 femtoseconds while a very minute portion, about 1% corresponding to small structural features take much longer to dissociate (up to 150 femtoseconds). Even with the fastest lasers currently available, it would not be possible to learn about the photodissociation dynamics of ozone using Femtosecond chemistry. However, a unique technique called continuous-scan Raman Excitation Profiles developed and tested on iodobenzene in our lab has proven to be a powerful method in learning about extremely fast dissociating processes such as ozone. One of the features that make REP’s a powerful tool is that, it provides valuable knowledge of time domain behavior based on only the intensity and frequency of the emitted photons. However, primarily because of its extremely low photon yield, one must overcome several significant and challenging experimental problems associated with the apparatus before achieving any reliable ozone REPs. The main objective of this thesis is to demonstrate how these problems were solved and to discuss and analyze some recently obtained preliminary data to be the guide for those pursuing full-scale ozone REP’s in the future.
Acknowledgements

The Journey of my Ph. D has been the most challenging yet the most wonderful experience in my life. The biggest lesson I learned from my graduate work is that with enough dedication one can achieve almost everything in life. As far as I can remember, I had always dreamed of becoming a scientist, and finally today that dream has come true. When I was visiting Rice University as a prospective graduate student, after taking a tour around Professor Kinsey’s lab, I knew that I wanted to work for him. Kinsey’s group is definitely one of the best groups in the world of science. Over the last several years on this road, I have my family, mentors, colleagues, and friends to thank in all different categories in life. Above all, I would like to thank my parents Mr. Rassuel Zehtab Lotfi and Mrs. Khanoom Nassirin Lotfi for all the sacrifices they have made and the sufferings they bore to send me to graduate school. Mom and Dad, none of this would be possible without your help and I appreciate all you have done for me in my life. I would also like to thank all the other members of my family for their help and support through my graduate work. Second, I would like to thank my advisor, professor James Kinsey for his guidance when things were not clear, for his support when I needed help, for his leadership whenever our team needed a leader and above all for his patience during the entire time that I was a graduate student in his lab. Jim, I thank you for all your help. I also would like to thank Bruce Johnson, our theoretician, who has been an instrumental in helping me with the theory behind our experiment. Thank you Bruce for all the theoretical discussions. And Finally, I want to thank Carter Kittrell who has been a great mentor and wonderful teacher during all my graduate years at Rice. I must admit without Carter’s help this journey would be a lot more difficult, and I would like to thank him for his tremendous help with the apparatus, all the science and the experimental skills that he taught me. Carter, I appreciate all the things you have taught me and I hope one day I will teach others some of the things I have learned from you. Finally, I would like to mention that I am honored to have had the opportunity to be working in such a great scientific team as Kinsey’s group and Rice University. Finally, I would like to express the most critical fact that science is the wave of the future, it not only helps humanity eliminate terrible diseases that have been inflicting human kind for eons, but also every discovery brings us one step closer to answering the biggest question of all, where we have come from and where we are going. And finally the most wonderful result of all the discoveries and the analyses is that we are getting closer and closer to our creator.
I Would Like To Entirely Dedicate This Ph. D
To My Dearest Parents:

Mr. Rassuel Zehtab Lotfi & Mrs. Khanoom Nassirin Lotfi

With All My Love,
Your Youngest Son,
Erik Siavash Lotfi
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Chapter 1
Introduction

1.1 The Background Theory on Raman Scattering

To understand extremely fast phenomena in nature one needs to apply a tool that is even faster than the process. Femtosecond chemistry essentially uses direct temporal resolution to extract dynamical information of fast dissociating molecules by fluorescence from at least one of their excited electronic states. This technique cannot be used to study extremely fast photodissociation processes of molecules such as ozone that do not fluoresce from their higher excited electronic surfaces. Dissociative Resonance Raman Spectroscopy (DRRS) is an alternative approach that has proven to be the right tool for such applications\(^1\text{-}^4\). Unlike femtosecond chemistry\(^6\), DRRS relies on the intensities of the photons emitted \textit{during} the dissociation process to interpret the dynamics of the photodissociation. By using one excitation frequency of a very narrow bandwidth, depending on the position and width of the initial wave function, DRRS enables one to probe a region on the dissociative excited surface. As figure 1.1 shows, in DRRS of ozone, the stationary ground vibrational wave function is pumped
from its ground electronic state to a dissociative excited electronic state.

Now being in a repulsive state, the ground electronic wave function
becomes a wave packet propagating towards the dissociation channel.
During the propagation of the wave packet, the majority of ozone
molecules exit the dissociation channel and turn into an O₂ and an O
photoproducts. However, after absorbing a photon, an extremely small
percentage of ozone molecules [less than one in a million] return to one of
the vibrational levels within the ground electronic state by emitting a
photon. The following formula [equation 1.1] known as Kramer,
Heisenberg and Dirac²-⁸ equation or KHD expression shows how Raman
cross section for those minute percentage of Ozone molecules are
mathematically calculated. In this equation, i, m and f are the initial,
intermediate and final wave functions, ω and ω,

\[
\sigma_{0\rightarrow n}(\omega) = A \left[ \sum_i \frac{\langle f | \mu_s | m \rangle \langle m | \mu_i | i \rangle}{(E_i + h\omega - E_f - i\Gamma + NRT)} \right]^2
\]  

1.1
Figure 1.1 Dissociative Resonance Raman Spectroscopy (DRRS)

Experiment of Ozone
correspond to the frequency of the incident and scattered photons, $E_i$ and $E_f$ are the energy of the initial, and final vibrational levels, $\mu_l$ and $\mu_s$ are the transition dipole moments corresponding to absorption and scattering, respectively, $\Gamma$ is a phenomenological level width to account for processes like spontaneous emission, $A$ is a constant, and finally NRT stands for the non-resonant term. Because of the absence of any explicit time dependence and enormous number of intermediate states involved in equation 1.1, it might not be the best choice to learn about dynamical information. Although equivalent to the KHD expression, the following formula that was derived by Heller and coworkers\textsuperscript{8-10} provides a more natural framework for thinking about the dynamical processes in fast photodissociations such as ozone, where the Raman scattering is strongly determined by a single excited state. However, if there is more than one excited electronic state involved in the process, one must account for their contribution. In the formula below, $\sigma_{0\rightarrow n}(\omega)$ is the Raman cross section, $B$ is a constant, $\omega$ and $\omega_s$ are the frequencies of the incident and scattered photons, $E_0$ corresponds to the energy of the vibrational level within the
ground electronic state, $\Gamma$ is the same phenomenological factor as above, 
$\mu_i$ and $\mu_s$ are the molecular transition dipole moments from the initial to 
the intermediate and from the intermediate to the final electronic states 
respectively. $\chi_i$ and $\chi_f$ are the initial and final vibrational wave functions 
within the ground electronic state. $H_x$ is the Hamiltonian in the 
dissociative excited electronic surface and accordingly $|\Psi_i(t)\rangle$ is the wave 
packet on that surface.

\[
\sigma_{0\rightarrow n}(\omega) = B\omega \omega_s^3 \left| \int_0^\infty e^{i(\omega + E_0)t - \Gamma t} \langle \phi_f | \Psi_i(t) \rangle dt \right|^2
\]

1.2

Where

$|\phi_f\rangle = \mu_s |\chi_f\rangle$

$|\Psi_i(t)\rangle = \exp(-iH_x t).\mu_i |\chi_i\rangle$
1.2 Ozone Absorption Spectrum

The first strong UV absorption continuum of ozone$^{11-22}$ is shown in figure 1.2. This band, which is known as the Hartley ($X^1A_1 \rightarrow ^1B_2$) continuum, is primarily responsible for preventing the harmful UV from reaching the earth according to the following two-photodissociation exit channels:

$$O_3 + UV \rightarrow O_3(a, ^1\Delta_g) + O(^1D) \quad (\sim 85\%)$$

$$O_3 + UV \rightarrow O_3(X, ^3\sum_e^-) + O(^3P) \quad (\sim 15\%)$$

As shown above, the photodissociation is predominantly through the singlet exit channel with a yield of 85%. The additional triplet exit channel is the result of a nonadiabatic interaction between $\tilde{D}^1B_2$ and R state whose existence has been predicted by Heller et al$^{17}$. By taking a closer look at the ozone UV spectrum, one can see that there are essentially two distinguishing features that can be analyzed within the Hartley band. One is the broad band feature and the other is the intriguing small oscillatory structures on the top of the broad band feature. The time dependent ozone
Figure 1.2 Ozone UV Absorption Spectrum
absorption formulation, which is similar to that of DRRS, is shown in the following equations.

\[ \varepsilon(\omega) = \kappa \omega \int_{-\infty}^{\infty} \exp[i(\omega + E_0 / h)t] \langle \phi | \Psi_i(t) \rangle dt \]  \hspace{1cm} (1.3)

Where

\[ \langle \phi | = \langle \chi_i | \mu_i \]

In this equation, \( E_0 \) corresponds to the energy of the vibrational ground level of ground electronic state, \( \omega \) is the frequency of the incident photon, \( \phi_i \) and \( \Psi_i(t) \) corresponds to the eigenfunction of the ground vibrational state in the ground electronic state and wave packet in the dissociative excited surface respectively. In eq 1.3, the quantity \( \langle \phi | \Psi_i(t) \rangle \), which is called the auto-correlation function, is the projection of the wave packet in the dissociative excited electronic surface onto the eigenfunction of the ground vibrational state in the ground electronic state. This time dependent auto-correlation function plays a critical role in the excited state dynamics. If the dependence of \( \mu \) on vibrational coordinates is neglected, \( |\langle \phi | \Psi_i(t) \rangle|^2 \) is proportional to the survival probability of the wave packet in the Frank-
Condon region. In fact the function $\Psi_i(t)$ contains all the dynamical information in the process of photodissociation. Therefore, to understand the photodissociation process and the small oscillatory features on the top of the broad Hartley band, one has to learn about the behavior of the wave packet, $\Psi_i(t)$ in the dissociative excited surface. Therefore, to that end, by taking the inverse Fourier transform of ozone UV absorption spectrum, Johnson and Kinsey’s elegant calculations$^{12-14}$ showed that during the photodissociation, the majority of ozone molecules fall apart in the first few femtoseconds, however a very small percentage ($< 1\%$) do not dissociate right away but revisit the region after some time. Figure 1.3 shows the result of their analysis. The UV absorption spectrum is included in this figure for a quick reference. The bottom graph shows the Fourier transform of the UV absorption spectrum. In this spectrum, the x-axis is the time and the y-axis is the magnitude of the normalized auto-correlation function, $\langle \phi | \Psi_i(t) \rangle$. The first peak in this spectrum, near $t = 0$, corresponds to the broad band feature of the ozone Hartley UV absorption. As expected, this is the highest peak and it decays very rapidly in about 6 Femtosecond. However, at much smaller amplitude other peaks
Figure 1.3 Ozone Absorption and Correlation Functions
show up in this spectrum at later times. Johnson and Kinsey attributed these additional peaks to the wave packet, $\Psi_i(t)$ revisiting the Franck-Condon region after absorbing the incident photon. In simple terms, the return of the wave-packet to the Frank-Condon region helps build up overlap with the ground vibrational level in the ground electronic state that result in small oscillatory features on the top of the broad Hartley band. However, $\leq 1\%$ of the O$_3$ molecules travel on these semi-classical trajectories that go in and out of the Frank-Condon region before finally dissociating into photoproducts. It is this small portion of O$_3$ molecules that cause the oscillatory structures on the top of the broad Hartley ozone UV absorption spectrum.

1.3 DRRS Experiments of Ozone and the Summary

To summarize, using Fourier transform, the ozone UV absorption spectrum has been analyzed to understand the ozone photodissociation in terms of wave packet overlap. As mentioned above, $\Psi_i(t)$ holds the key to the photodissociation process. Taking the inverse Fourier transform of the UV ozone absorption spectrum ($\varepsilon(\omega)$ in eq 1.3), mainly help us to
understand how quickly the wave packet, $\Psi_i(t)$ exits the dissociation channel or how fast the molecule photodissociates.

In other words, the ozone absorption spectrum mainly tells us about the Frank-Condon region at the instant when the absorption occurs, but it does not provide any information about the direction of the wave packet throughout the dissociation process. This is where DRRS proves to be a very valuable tool. DRRS can help us learn about later times or all the dynamical information of the wave packet throughout the entire photodissociation process. However, one has to point out that there are two fundamental differences between the ozone UV absorption and Raman scattering formulations (eq’s 1.3 and 1.2). First, in Raman scattering formulation, unlike the UV absorption equation the limits of integral are from zero to infinity. Second, unlike the UV absorption spectrum, the Raman cross section is proportional to the square of the wave packet, $\Psi_i(t)$. Because of these two significant differences, one can not obtain the correlation function, $\langle \phi_j | \Psi_i(t) \rangle$ by simply applying the inverse Fourier
transform method. However, one can theoretically model $\langle \phi_i | \Psi_i(t) \rangle$ and test the model against the experimentally obtained Raman scattering cross section, $\sigma_{0 \rightarrow n}(\omega)$. In order to understand the photodissociation dynamics, one has to understand the behavior of this wave packet from the moment of absorbing a photon until its exit through the dissociation channel. In other words, how $\Psi_i(t)$ behaves during the entire photodissociation process.

Since every DRRS experiment is done with only one particular excitation wavelength, this only tells us part of the story about the wave packet behavior. In order to extract the complete dynamical information, one has to conduct a series of DRRS experiments to acquire the Raman cross section with respect to all wavelengths (refer to eq 1.2). This means in order to fully understand the UV photodissociation of ozone, one has to obtain ozone Raman Excitation Profiles (REP's) in the entire range of the Hartley band (roughly 230-280 nm). However, this would be an immense undertaking to finish within only one project. Therefore, at the outset of this investigation, it was decided to divide the entire range into two regions of longer (250-280 nm) and shorter wavelengths (230-250 nm). Prior to the work of this thesis, although not carefully analyzed, a fair amount of
ozone REP data in the longer wavelengths (250-270 nm) was collected. Therefore, original focus of this thesis was to investigate the shorter wavelengths (230-250 nm), which would be complimentary to the previous work. However, as we began our investigation in the shorter wavelengths range, we encountered a number of serious issues that were extremely critical in obtaining reliable ozone REP data. Most of these serious problems had not been addressed in the previous work. As a result, the main objective of this work evolved into a careful examination of how these serious problems can be addressed and a discussion of some preliminary ozone REP data that was recently collected in our lab to guide the way for those pursuing reliable and reproducible ozone REP data in the future.
Chapter 2
The Experimental Setup for Ozone REP

Overview

The experimental setup is basically the same as described in the thesis of Chih Wei Hsiao\(^1\). However, some modifications have been made on the system to help facilitate achieving ozone REP. This chapter will describe the entire experimental setup with emphasis on the recent modifications and improvements made on the system. Figure 2.1 shows the schematic diagram of the experimental apparatus for ozone REP. A Questek 2860 series XeCl Excimer laser (308 nm) is used to pump a tunable FL 3002 Lambda Physik dye laser which generates visible photons (480-560 nm). The visible output of the dye laser is then passed through a \(\beta\)-BB0 (Beta Barium Borate) crystal to produce the UV photons for the experiment. A homemade auto-tracking device is used to maintain the phase matching angle of the \(\beta\)-BBO crystal as the dye laser scans through different excitation wavelengths.
Since the conversion efficiency of the $\beta$–BBO crystal is only about 5%, the beam emerging on the other side of the crystal is mostly visible light. To separate the UV from the visible photons, the output beam of the $\beta$–BBO crystal is then put through 4 prisms. This separated UV beam will then intersect the ozone flow in the cell at a 90° angle. Ozone is made using a commercial ozone generator (OREC 03V5-5) and supplied to the cell through an in-house made ozone trapping system. Using helium as a carrier gas, a steady flow of ozone is established to intersect the UV beam in the cell. Scattered light is collected at a 90° angle to the incident beam and focused onto the entrance slit of a dual-channel Czerny-Turner spectrometer. This spectrometer was configured to allow simultaneous monitoring of the Rayleigh scattering signal in one channel while measuring a specific Raman feature in an ozone REP experiment in the other channel. In this experiment, the ozone Rayleigh signal is collected to normalize the ozone REP with respect to variations in the laser intensity and the ozone flow. At the exit slits of the spectrometer, the Rayleigh and Raman signals are detected by their respective photomultiplier tubes (PMTs). The output of Rayleigh and Raman PMTs are then sent to the
data acquisition board by their corresponding boxcars which are externally triggered by the XeCl laser to be stored for later analysis. The data acquisition process is controlled by a Labview program running on a Mac IICI using two interface boards.

2.1 Light Source
2.1.1 The XeCl Excimer Laser

Although Nd-YAG lasers provide a stable source of energy, they can only pump red dyes efficiently. The ozone Hartley band extends approximately over the range of 230-280 nm, which requires frequency doubling of the blue end of the visible spectrum. Excimer lasers have proven to be an excellent choice to pump tunable dye lasers in the far end of the visible spectrum (460-560 nm). A Questek 2860 series excimer laser is used to pump a FL 3002 Lambda Physik dye laser in our lab. Figure 2.2 shows the overall layout of the excimer laser. In this figure, thick lines correspond to components that have either been modified or replaced. Although they pump tunable dye lasers efficiently, excimer lasers require a
Figure 2.2 Schematic Diagram of the XeCl Excimer Laser
Figure 2.3 Schematic of Modified and Problematic Areas of XeCl Excimer Lasers
great deal of maintenance. There are essentially three common problems with these excimer lasers: leakage, noise interference and contamination. Figure 2.3 mainly shows the problematic areas of Excimer lasers. Charge at a potential of about 30 KV must be discharged across the electrodes in a very short time (<100 ns) just before every laser pulse. This discharge can create high frequency electromagnetic noise, which can interfere either with the data collection process or with the laser operations. We succeeded in suppressing the noise interference with respect to the data collection process by the following two measures: First, our PMTs have been shielded extremely well using Faraday cages to minimize induced noise generated by the excimer laser. Second, the Rayleigh and Raman signals are delayed by running them through a 100 m cable. Our boxcar gates are delayed by a corresponding time. This 100 m cable is long enough to separate our signals in arrival time from the prompt high frequency noise created by the excimer laser. Another noise problem was penetration of these high frequency oscillations through the main power cable and to interfere with the discharging process. This was eliminated by installing a high frequency filter right after the main switch (as shown in Fig 2.3). We
also installed a water relay to protect our laser from a failure in the cooling water. In order to optimize the lasing process, the gas inside the chamber is circulated. Therefore, we need a device that can transfer rotary motion for gas pumping while keeping the chamber completely sealed. Ferro Fluid Seals meet this need. Using ferromagnetic fluids, these devices can provide seals with the leakage rate of $10^{-11}$ [He] mbar s$^{-1}$ with roughly 10 years of lifetime for normal usage. However, the highly corrosive gases in an excimer laser reduce the failure lifetime of Ferro Fluid Seals to not more than a couple of years. This is most likely due to reaction of the HCl gas with the magnetic fluid. During the course of this work we have had to replace these seals several times. Contamination is another major problem with these excimer lasers. A very minute amount of contaminants such as oxygen, water, and different types of hydrocarbons or any other compounds that interfere with the lasing process can dramatically diminish the output power. These contaminants diminish the laser power by interfering with the discharge process across the electrodes, which powers the lasing process inside the laser chamber. By using only high purity gases and an efficient circulation system, we were able to eliminate the
contamination problem. At its optimal condition, running at 10 Hz, the excimer laser’s average energy is about 200 mj/pulse. Under normal operating conditions the average chamber pressure is about 2700-3000 mb. The gas inside the chamber consists of a mixture of approximately 0.015% HCl, 3% Xe and about 97% He (99.9995% purity). The aluminum chamber walls are covered with a layer of nickel to prevent exposing the aluminum layer to reactive HCl gas or other corrosive contaminants. However, as the laser is used, this nickel layer gradually starts to flake off the chamber walls, producing dusts of aluminum chlorides or other aluminum-containing compounds. Therefore, having an efficient gas filtration system is essential for sustained use of excimer lasers. As shown on Figure 2.2 there are three valves directly connected to the chamber (A, B, L). In order to avoid dust clogging and corrosion, A and L are of the type Whitey 33VVCO4 ball valve. The simple straight-through bore design in this valve eliminates any dust clogging cavities. In order to remove aluminum chloride and other aluminum compound dusts from the chamber, there are 3 filters in this circulation system. Downstream from the outlet valve A, there are two Balston 1-in. x 7-in. hollow glass-fiber
cylindrical volume filters. The first one is a grade-D coarse filter, which is followed by a grade-A fine filter in series. After removing the large or intermediate sizes of the dust particles through these two volume filters, the finer sized dust particles are removed through a membrane filter which is located before the gas circulator. After going through an Oxford circulator, the gas flow is measured using a rotameter gauge with a tantalum (Ta) float. Since the gas returning to the chamber is cleared of any dust, the valve B is a simple Linde SG5461 brass diaphragm valve. The solenoid valves (1-6) that are used to introduce different gases into the chamber tend to leak. To minimize leakage and to facilitate detection of leaks that do occur, a manifold extension was added. The valves D, F and G (inert gas supply) along with pump out valves (I and J) are of the type Nupro B-2T4P4 brass plug valves. These valves are sealed with Viton-O-rings lubricated with a thin layer of silicone grease. Since HCl is not compatible with this silicone grease, a Nupro SS-DSVCR4 (greaseless) Stainless diaphragm valve (E) with a Kel-F stem seat is used for the HCl supply line. In order to monitor and eliminate the leaks throughout the circulation lines (3/8-in copper lines), two Bourdon pressure gauge
(P1 and P2) are used before and after the circulator. Finally, to avoid overpressurizing the chamber, a safety check pressure valve (SS-4CPA2-3) K with a cracking pressure of 3400 mb was put in the exhaust line.

2.1.2 The Gas Circulator

The gas circulator in this system is the commercially used GP 2000 gas purifier made by Oxford Lasers. The cryogenic trap in these GP gas purifiers significantly increases the single gas-fill lifetime of these excimer lasers by selectively removing gaseous contaminants. As shown in figure 2.4 the essential elements of these Oxford gas processors are the liquid nitrogen dewar, the temperature control, the heat exchanger and the diaphragm pump. At the time of purifying, the built in dewar (~ 7 liters) is filled with liquid nitrogen and, based on the nature of the contaminants, the temperature of the trap can be set using the temperature control unit (100 K–300 K), depending on the vapor pressure of the impurities. For instance, temperatures of less than 250 K will remove water vapor from the chamber. After setting the appropriate temperature, the middle outlet valve is closed. This forces the gas to go through the heat exchanger section.
The heat exchanger consists of several feet of two different metals with different heat conductivity soldered together in a number of loops. Therefore, as the incoming gas (carrying the contaminants) approaches the central shaft (directly connected to the temperature control), it is cooled down and contaminants are settled out of the flow. After going through the central shaft of the heat exchanger, this purified flow is slowly warmed up to room temperature before it leaves the gas circulator to enter the chamber. Since there are two Questek series excimer lasers interchangeably used in our lab, there are also two GP 2000 series interchangeably used in this experiment. To achieve sufficient purification, circulation times of up to 10-20 hours are sometimes needed. We are able to minimize the downtime by determining the vapor pressure of primary components of the laser (Xe and HCl) gas versus the temperature (Appendix A1). This allows one to operate the excimer laser while purifying the gas inside the chamber.
Figure 2.4 Schematic Diagram of the Gas Processor 2000
2.1.3 Dye Laser

The Questek 2800 series excimer laser described above is used to pump a tunable Lambda Physik dye laser. The dye laser is a tunable pulsed (10 ns) device with an output wavelength range of 400-800 nm (visible) depending on the dye. With Coumarin 480 nm dye, the average energy of the laser is about 10 mj/pulse. One of our modifications on the REP system was to update the dye laser from 2002 FL model to 3002 FL. In the 2002 FL model, at the outset of every scan, the starting excitation wavelength had to be manually set. Since the built in counter was rather slow, this would contribute to increase the amount of time needed for a scan. However, the newer model 3002 FL takes advantage of the GPIB (Appendix A2) interface, which enables the user to operate and control all the dye laser functions remotely via GPIB software within the Labview application.
2.1.4 Second Harmonic Generation, Compensator Prisms

and the UV Path to the Cell

The well-collimated visible beam coming out of the dye laser is passed through the $\beta$–BBO crystal to produce UV photons for the REP experiment by the second harmonic generation. When two visible photons of a particular wavelength are incident onto the $\beta$–BBO crystal which must be precisely at the right angle with respect to the incident beam (phase matching angle), they can be converted to a UV photon of exactly half the original wavelength. As the dye laser scans in the REP setup, this phase matching angle must be adjusted by an auto-tracking system to be described below. Since the $\beta$–BBO crystal conversion efficiency is about 5%, 95% of the $\beta$–BBO output remains in the visible. This must be separated from the desired UV. As shown in figure 2.5 this is done by a set of four prisms. The visible and UV beams are separated by prism 1. The function of prisms 2, 3 and 4 is to bring the UV beam back to the same exact line (dashed line in Figure 2.5) as the main beam was going before hitting prism 1. This four-prism configuration not only separates the UV
beam from the visible beam, it also compensates for optical path
differences generated as the dye laser scans through different excitation
wavelengths. The output of the dye laser has a vertical polarizability,
which is suitable with our reaction cell geometry. However, the UV output
of the β-BBO crystal has a horizontal polarizability. Therefore, on exiting
from prism 4, the UV beam passes through a pair of dihedral $90^\circ$ right
angle prisms to change the polarizability of the UV beam back to vertical.
Figure 2.5 Schematic Diagram of the UV Path
2.1.5 The Optical Layout & Auto-Tracking System

As shown in figure 2.6, after going through the 45° UV mirror, this visible beam is reflected back onto the β–BBO crystal as a non-collimated beam using two cylindrical (f = + 150, f = + 300) lens and three right prisms. Having the returning visible beam be diverging rather than collimated is a crucial element in the mechanism of the auto-tracking system. Figure 2.7 demonstrates the operating concept of this system. First, the phase matching angle of the β–BBO crystal must be manually adjusted to give optimal doubling for a particular wavelength. Second, in order to maximize the UV conversion of the returning beam, that beam must be focused inside the crystal. After satisfying the above two conditions, as shown in figure 2.7, the return visible beam (cone labeled 1) will be partially converted to UV (is indicated by circle A in the figure). In this configuration, photodiodes P1 and P2 are receiving the exact same signals. As the dye laser scans to a different excitation wavelength (cone labeled 2), the UV image on the dual photodiode is gradually shifted (labeled B) due to the fact that the new excitation wavelength corresponds
Figure 2.6 Schematic of the Auto-Tracking System and the Optical Path of the Return UV
Figure 2.7 Schematic Diagram of the Optical Layout of the Auto-Tracking System
to a different phase matching angle. This gradual shift in the UV image, which results in generating an error signal, only comes about if the returning beam is not collimated. Now, in this new configuration, one of the photodiodes (P1) is receiving more UV signal than the other and there is a non-zero difference signal. This difference in signals becomes an error signal in a feedback circuit. Depending on the sign and the magnitude of the error signal, this feedback circuit sends signals to the stepper motor to move the crystal in order to the point the new UV image (B) exactly where the old (A) UV image was. At that point, the error signal is exactly zero again. This auto-tracking device thus serves two different purposes. First, it keeps the β–BBO crystal tuned for optimal doubling efficiency as wavelength is scanned. Second, it maintains tight control of constancy of the UV beam’s direction. Since these UV Hamamatsu dual photodiodes are also sensitive to visible light, we needed to block the remaining visible light on the returning beam to the dual photodiodes. Almost all the standard visible filters would also absorb much of the UV. We needed a filter that would block out the range of 480-560 nm and would pass the range 240-280 nm as much as possible. We found a solution filter of
cadmium chloride serves our application (Appendix A3). After testing this solution for our range, a filter holder was specifically made to keep the solution vial in front of the dual photodiodes at all time.

2.1.6 Auto-Tracking Circuit

Figure 2.8 shows the original schematic diagram of the auto-tracking system circuit. The output signals from the photodiodes are amplified by operational amplifiers (C & D). When the main dye laser output is at the correct angle with respect to the β–BBO crystal for a particular excitation wavelength, the UV that goes into the reaction cell (thin line in Figure 2.6) is at its maximum intensity. Some of the visible photons also go through the crystal, and these are used by the auto-tacking system to generate a returning UV beam. As the dye laser scans to a slightly new excitation wavelength, the crystal converts far less to UV. As a result of that, there are a lot more visible photons that go through the crystal to be reflected and to create the return UV. This return UV image is now shifted on
Figure 2.8 the Auto-Tracking System Circuit
photodiodes (circle B in figure 2.7), but it is more intense than in the previous configuration (circle A in figure 2.7). To prevent saturation of the circuit with this intense UV beam, we use Zener diodes. As figure 2.8 shows, one can use a combination of Zener diode and a variable resistor to clip the incoming signals (I and II) to prevent circuit saturation. This clipper circuit combination resembles and functions as an integrator circuit. Since ours is a pulsed system, a pair of peak detectors (A1 and A2) are used to detect the peak of each amplified signal. The difference of the two peaks is measured by a differential amplifier (E), whose output is further amplified (amplifier F). An LM675 power operational amplifier (B) which provides good shielding against the noise induced by the excimer laser discharge is used to drive the DC motor that adjusts the angle of the β–BBO crystal in response to an error signal. In order to provide further shielding against the noise induced by the excimer laser, the whole circuit is placed in an aluminum box. Further depression of high frequency pick-up was provided by strategic insertion of ferrite inductors and by adding high frequency filters to the input and output of power amplifier B.
Figure 2.9 the Modified Auto-Tracking System Circuit
2.2 Ozone Trapping and Storage System

Overview

This section will describe a special trapping and storage system that is capable of safely delivering ozone at a pressure of several torr in a monitored and controlled fashion\(^{(2)}\). In addition to being toxic, ozone is also highly likely to detonate in liquid form. This makes the storage of ozone in liquid form very unsafe in a laboratory. Our system uses silica gel to trap and store ozone safely. Ozone adsorbed onto silica gel no longer presents a hazard of explosion. This section will begin with synthesis and storage ozone in our lab. The process for monitoring and controlling stable flow conditions for the REP experiment will then be described. Finally, the section will end with description of the electronic circuits for controlling the trapping system.

2.2.1 The Ozone Trap and the New Cooling System

Figure 2.10 shows the schematic diagram of the ozone silica gel trap. The vital parts of the trap consist of a Pyrex trap (1) filled with silica gel
(6-12 mesh), an aluminum jacket with embedded heating wire (2), a finned aluminum cooling cylinder (3, 4, and 5), a precooled tube (6), four stainless steel inserts (7), and a stainless steel dewar. All the joints and tubes in this trap are made of either glass or Teflon, two of the very few materials that do not react with ozone. In the old system, dry ice was used to keep the trap cool. But dry ice was very problematic in several ways. Therefore, one of the main modifications made on the system was to install a cryogenic refrigerator as a heat sink instead of dry ice. Figure 2.11 shows the schematic diagram of this refrigerator. The essential parts of this refrigeration system include a Cryocool CC-100 Refrigerator and an over extended tube. The cooling end of this tube is sealed. This tube contains freon, which can simply remove heat from the surrounding by going from the liquid phase to the gas phase. A metal plate to house the sealed end of the tube is attached onto the well between two fins inside the original ozone trapping system (dashed line area in figure 2.11) was specifically designed in our laboratory. After its installation, the new cooling system was calibrated with respect to ozone flow conditions.
Figure 2.10 Schematic Diagram of Ozone Trap
Figure 2.11 Schematic Diagram of the Modified Ozone Trap
2.2.2 Ozone Flow Conditions

In the new cooling design, at the time of the experiment, depending on the amount of ozone flow needed (capable of delivering 10-25 torr of ozone), a certain current (0.2-0.8 amps) would be sent to the thermocouple heating wires that had already been wrapped around the aluminum sleeve containing the Pyrex glass (figure 2.11). Starting with a full load of ozone in the trap and using helium (15 ml/min) through the trap as a carrier gas it would approximately take 2 hours to deliver a stable flow of 16 torr of ozone into the reaction cell. This 2-hour delay was the time needed to raise the trap temperature from 195 K to about 220 K. As ozone supply depleted, higher temperatures (220-250 K) were needed to achieve the same flow of 16 torr of ozone. This was because ozone is trapped onto the silica gel in various layers, and as higher layers of ozone leave the silica gel, more heat is required to remove the more tightly bound deeper layers. At the time of flowing ozone, a constant pressure of 2/3 atmosphere (O₃ and He) was needed to maintain a stable flow. Therefore, a pressure gauge was added directly to the outlet valve of the trap to monitor the pressure. The main problem encountered with the refrigerator system was that even
with currents as high as 1.0 amps (maximum range of the heater), the trap
temperature could not be raised beyond 210 K, which would result in
insufficient flow of ozone. After trying a few options such as loosening the
screws that connected the well to the fins (figure 2.11) and a piece of
nylon, this problem was solved by putting a piece of cardboard on one side
of the contact next to two screws and adjusting the pressure on the screws.
With this piece of cardboard, the thermal contact was reduced enough that
one could raise the temperature of the trap as high as 260 K with currents
of less than 1.0 amp.

2.2.3 Ozone Monitor and Controller

An ozone monitor is located between (figure 2.1) the ozone trap and the
reaction cell to measure the partial pressure of ozone going into the cell
monitors the flow of ozone according to the following (Figure 2.12). This
monitor is primarily composed of two identical cells (4) with a pen-Ray Hg
lamp (1) in the middle. One of these cells will contain the ozone to be
measured, and the other will be a blank containing air. The UV generated
by this lamp (powered by 120 V/60 Hz AC) is passed through identical
pairs of UV fused silica lenses on either side of the lamp (2, $f = 45$ mm) to be collimated. These collimated beams on either side of the lamp are passed through interference filters to select 253.7 nm wavelength Hg resonance line which has a high ozone absorption cross section. The UV beam then passed through the absorption cells on either side of the lamp. The UV that goes unattenuated through the air cell is focused by a UV lens (2) onto a photodiode (5, UV 100B, EG&G). On the other side, the UV that goes through ozone absorption cell is partially absorbed by the helium/ozone mixture flowing out of the ozone trap. The outputs of the two photodiodes are then fed into the ozone monitor circuit to monitor and control the ozone flow.
Figure 2.12 Schematic Diagram of Ozone Monitor System

2 = Lens, 3 = UV Filter
4 = Channel, 5 = Photodiode
2.2.4 Ozone Monitor and Controller Circuits

Figure 2.13 shows the schematic diagram of the ozone flow monitor circuit. The output current of each of the photodiodes of the ozone monitor is first converted to voltage using two current-to-voltage converters (A, B). Voltage amplifiers C and D (gain factor = 60), further amplify the outputs of A and B. The outputs of C and D are then passed through two unity gain butterworth low-pass filters (E and F). These two filters, along with two RC filters ($R_1 = 10 \, k\Omega$ and $C_1 = 82 \, nF$), are used in this circuit to smooth out some of the sinusoidal nature of the photodiode signals coming from the AC Hg lamp. They also attenuate high-frequency noise induced by the excimer laser in our lab. The outputs of E and F feed into an integrated divider chip (G, AD535, Analog Devices). Two RC filters ($R_2 = 100 \, \Omega$ and $C_2 = 10 \, \mu F$) were added to the power supply to suppress noise. Finally, the output of divider chip G (the ratio of the two photodiode signals) is fed into the controller circuit. Figure 2.14 shows the schematic diagram of ozone controller circuit. The ratio signal and a reference voltage is fed into a noninverting differential amplifier (H). The value of the reference
A, B, C, D, E and F are all LF 411CN
JFET Op-amps and G is a multiplier divider
Analog Devices (AD 535JD)

Figure 2.13 Schematic Diagram of Ozone Flow Monitor Circuit
voltage determines the desired ozone partial pressure. The output of the differential amplifier H is amplified by amplifiers J and K in parallel. Amplifier J provides a signal that is proportional to the instantaneous value of the differential amplifier H. On the other hand, the amplifier K (with a time constant of \( \sim 20 \) minutes) produces a time average of this signal. These two signals are then added, with relative contributions determined by the ratio of \( R_3 = 51 \, \text{k}\Omega \) and \( R_4 = 20 \, \text{k}\Omega \). This summed signal from amplifiers is fed into a voltage-controlled current source (VCCS), which consists of an amplifier L, and a Darlington power transistor \( (M, \text{TIP-141}) \). The power transistor \( M \) controls the current flowing into the heater according to the incoming error signal. A 15 \( \Omega \) power resistor \( (20 \, \text{W}) \) limits the maximum current to 0.8 Amps to prevent overheating the circuit. In order to achieve a preset ozone partial pressure in a steady and stable fashion without long delays, the values of the most critical parameters of the controller circuit that consist of the time constant of \( K \) amplifiers and \( R_3 \) and \( R_4 \) have to be selected precisely.
H, J, K and L are all LF 411 CN and M is a Darlington Power Transistor (TIP-141)

Figure 2.14 Schematic Diagram of Ozone Controller Circuit
2.3 Light Detection System

Overview

This section will describe the entire process of signal detection beginning with the Czerny-Turner dual channel spectrometer and its calibration. This will be followed by a description of our Hamamatsu PMTs’ and their calibration. Finally, this chapter will end by introduction and discussion of how Labview programs are employed for the data collection process.

2.3.1 The Spectrometer

In order to make precise measurements, ozone REP signals need to be normalized with respect to laser power and ozone flow fluctuations. One idea for doing this is to refer the REP signal to the Rayleigh Excitation Profile signal. The physical process that produces ozone Rayleigh scattering signals depends on UV power and ozone concentration in exactly the same way as Raman scattering signal. Although the ozone Rayleigh cross section has been accurately calculated\(^{(24)}\), after normalizing the ozone REP signal with respect to ozone Rayleigh signal, the ozone Rayleigh
signal in turn must be normalized with a known standard such as N₂ Rayleigh. Figure 2.15 shows the schematic diagram of our dual channel Czerny-Turner spectrometer (SPEX 1401, focal length = 75 cm). In this dual channel spectrometer a Labview program is used to precisely locate and track the Rayleigh signal in one channel while tracking one particular Raman band in the other channel simultaneously throughout the ozone REP experiment. Using a (f/1) collection optics, light from the cell is focused onto the entrance slit of the spectrometer. A custom-made beam splitter (B1, zero degree, wavelength range = 225-308 nm, peak = 248 nm, Reflectance ≈ 20%) is used to pick off some of the incoming light for the Rayleigh channel while letting most of the light continue in the Raman channel. In order to avoid a secondary reflection, an anti-reflection coating is used on the back surface of this beam splitter. Mirrors M7 (flat) and M3 (focal length = 75 cm) guide the reflected beam onto the Rayleigh grating G2 (blaze angle = 17.5°, 1200 grooves/mm, used in the 2nd order). Light leaving the Rayleigh grating (set by Labview to the appropriate angle) is focused by UV mirrors M6 (flat) and M4 (focal length = 75 cm) onto the exit slit. The other ~ 80% of the collected light that passes through the B1
beam splitter is reflected from an UV mirror \((M2 = 75 \text{ cm})\) onto the Raman
G1 grating (blaze angle = 36.8°, 1200 grooves/mm, used in the 4\(^{\text{th}}\) order).
Again, Labview sets the angle of the grating to correspond to the chosen
Raman feature. The beam leaving the Raman grating is then focused onto
the Raman exit channel using another UV mirror \((M1, \text{ focal length} = 75
\text{ cm})\). Although both channels of the spectrometer come equipped with
fairly accurate wavelength counters, the accuracy for REP experiment
required even more precise wavelength calibration. Because of this
multiple and sharp emissions, Hg lines were the choice for this calibration.
Before the Rayleigh channel could be calibrated, the damaged Mirrors of 3
and 4 needed to be replaced. After doing some ray tracing calculations, the
best location of mirrors was determined with many iterative fine
adjustments. After replacing the mirrors in the Rayleigh channel, both
counter settings for these two channels were recorded for multiples of Hg
lines which in turn were least square fitted \((\text{error} = +/- 0.5 \text{ cm}^{-1})\) to a
polynomial \((n = 6)\) and finally incorporated into the main Labview
scanning program.
Figure 2.1 Schematic Diagram of Dual Channel Spectrometer
2.3.2 Rayleigh and Raman PMTs and Their Calibrations

Two PMTs are used in our system, one for the Raman signal (31000, Burle [RCA]) and one for the Rayleigh signal (R331, Hamamatsu). Both tubes are end-on type, and they have similar operating characteristics. Both tubes have two features that make them suitable for our application. One is their fast response feature (< 3ns) compared to our laser pulse (~ 10ns). Since our signal level is extremely low (only a few photons per each laser pulse) the second feature that makes these tubes very attractive is the special design for low-light detection. Figure 2.16 shows the schematic diagram of the voltage divider layout of our PMTs. All the values of circuit components of the socket have been selected to optimize performance for our application. For example, the photocathode resistor (K2 = 602 kΩ) has higher resistance than the typical factory value of (~ 400 kΩ) in order to provide a relatively high voltage between the first and the second dynode. This increases the number of electrons, which in turn contributes to bigger output signals at the anode.
Figure 2.16 Schematic Diagram of PMT and Amplifiers
The outputs of the two anodes are connected to two identical amplifiers (VV100BTB) with a gain of 10. The capacitor shown in figure 2.16 represents the equivalent capacitance of all the wires and dynodes within the PMTs. This has a value of approximately 20-30 pF. The first resistor plays two critical functions in the circuit. First, it provides a required input voltage for the first amplification by dynodes in the PMT. Second, it allows for the current coming from the photocathode to discharge in the appropriate time interval. Choosing the right value for this resistor is very critical since values that are too high would stretch the time constant beyond the time of the laser pulse (> 10 ns). This would result in some emissions from the photo fragments being picked up and be mistaken as the real signal. On the other hand, values that are too low would result in very weak signals (since the gain of the circuit is proportional to this resistor). The value of 300 Ω appears to be suitable for this circuit, since this would give an RC constant of ~ 10 ns. The next three resistors are essentially there to provide the proper output voltages for these two amplifiers to function optimally. The amplifiers used in this circuit are VV00BTB fast response (~ 2 ns) with a gain of 10. In order to eliminate high frequency
noise induced by the excimer laser, low-pass filters were installed for the voltage power supply of amplifiers (+6, -12 V) and that for the PMTs power supply (1500 V>). The lines that supply high voltage for the PMTs are the special type of RG-59 (Belden) with SHV connectors on each end for better shielding. Depending on operating conditions such as the particular choice of ozone Raman band, the available laser power and the ozone concentration, different PMT voltages may be used for different scans. Therefore, it is also important to calibrate the sensitivity of the two PMTs to voltage. In the ozone experiment, depending on the vibrational level and the ozone concentration and UV power for the scan, Rayleigh and Raman REP's are collected at various PMT voltage settings. After taking REP scans within different regions of ozone Hartley band (237-275 nm) these different scans with different voltage settings need to be patched together to extract the dynamical information of ozone photodissociation. Therefore, one of the most important modifications made over the previous system was to calibrate all our PMTs.
2.3.3 PMT Calibration Setup

Our PMT calibration was greatly facilitated by the existence of a setup for this purpose in the T.W. Bonner Nuclear Laboratory. We are very grateful to Dr. W. Lloge and his group for making this facility available to us and for their help in carrying out the calibration process. The light source used in this setup is a 337 nm ND Nitrogen Laser (figure 2.17). Optical fiber cables guide the laser beam into the "Dark Box". The Dark box is covered with black paper on the inside walls to prevent any extraneous light from penetrating into the box. Inside the Dark Box, a splitter splits the laser beam. One part of this split beam is sent to a reference PMT, which serves as a monitor of the laser power from one run to another. The other part of the beam goes to the tube being calibrated (the "main" tube). The outputs of the anodes are then sent to a channel selector. A discriminator, which is triggered by the laser, provides the gates for the detections. Finally, a pulse height analyzer sorts individual pulses into bins corresponding to the pulse amplitude which are then sent to the computer
Figure 2.16 Schematic Diagram of the PMT Calibration Setup
for final analysis. The software used to analyze and plot the data was called POW.

Calibration Process

Obtaining the gain curve of a PMT involves determination of how the anode current (output) of the tube changes as the voltage is varied, for a constant incident light intensity. There are two types of calibration. One is the absolute gain calibration, which determines the absolute number of electrons coming out of the anode dynode at a particular voltage for every photon falling on the photocathode window. The second type is the relative gain of one voltage setting to another for a fixed number of incident photons. Since in our experiment we vary the voltage, our goal was to obtain a relative gain calibration. The Photomultiplier Handbook\(^{(23)}\) provided us with the formula that shows the relationship of the anode current with voltage as the following: \( G = K \cdot V^{(n,b)} \). In this formula, \( n \) is the number of stages in the PMT socket (12 in our setup) and \( K \) is a constant (which is not critical in calculating a relative gain). Therefore, the parameter \( b \) is the most important factor in obtaining a relative gain curve.
of a tube. A log-log plot of gain (G) vs voltage (V) should be a straight line with the slope of (n/b) and the intercept of Log (K). In our experiment, the voltage range for our tubes is roughly 1400-2000 V. Therefore, we had to calibrate our tubes in that voltage range. Since the reference PMT in the Bonner Lab setup used no amplification, we had to remove the amplifiers and place them in special housing that we constructed for them. With the above modifications we were able to calibrate all our PMTs (Appendix A4). The data were analyzed with and without the reference tube. The final calculations showed that the exponent factors (b) for the relative gain calibration were accurate with a small error margin of +/- 5%. In order to confirm that our data were within an acceptable range, the curve gain of a typical Hamamatsu tube was calculated. Comparing the slope of this tube to ours, showed that our data were well within the acceptable range. Therefore, this setup proved to be a very efficient way of calibrating our PMTs.
2.4.4 Labview Data Collection Programs

The computer control and the data acquisition process in this system is essentially the same as described in Chih-Wei Hsiao thesis\(^1\). The purpose of this section is to explain the modifications made on the system since that work. This section also briefly explains the structure and the subroutines involved in the main data acquisition program. The main components of the data collection process (figure 2.18) are a Mac IICI computer, an eight-channel analogue to digital converter (A/D), three data acquisition boards and two boxcars. Three interface boards include NB-TIO-10\(^{25}\), NB-GPIB/TNT\(^{26}\) and Lab-NB\(^{27}\). The TIO-10 board is used to control the photon counting program used at the time of calibrating the Raman and Rayleigh gratings within our spectrometer. The NB-GPIB/TNT, which has been incorporated as part of the current system, controls the 3002 Lambda Physik dye laser. The rest of the data collection process is controlled and monitored by the main Lab-NB interface board. The boxcars integrate the Raman and Rayleigh signals, respectively, and send their output to the NB board to be processed. Two of the A/D channels are assigned to two photodiodes used in the system. Two of the remaining channels are used to
monitor the ozone flow and the amount of current in the ozone trap heater. The 7\textsuperscript{th} channel is used as a ground reference. The 8\textsuperscript{th} channel is not used in our system. Before collecting ozone data, a program called NB-2 Config Auto program is run first. This program configures all the I/O digital ports (with 8 channels in each port) and resets the two counters used in the Lab-NB board. Then, it finds a starting reference point (called index) pulse for the Raman grating counter. Since there is no counter for the Rayleigh grating, the starting wavelength for the Rayleigh channel must to be set manually. Finally, this program saves all the reference and starting points along with the Rayleigh and Raman grating orders as global variables to be used later throughout the main program. Raman-REP-GPIB.vi is the name for the main scanning program used in this system to collect ozone REP data. Before running the program, the user needs to input the following 4 parameters: the starting excitation wavelength (nm), the stepsize (nm), the number of shots/point and the Raman shift (determined by which vibrational level is being studied). This program can be divided into 4 stages. In the first (initialization) part, all the analogue input channels are configured and the Raman grating is moved to the starting point. The
starting point for the Rayleigh grating is calculated and manually set, the
dyelaser grating is moved to the starting excitation wavelength and all the
parameters including the reference points for both Raman and Rayleigh
grating, Raman shift, stepsize and shots/point are saved to be used
throughout the data collection scan. The second stage is the data
collection. Once the program checks to see if all the gratings are at their
 corresponding positions and the motors have stopped, then the program is
ready to collect data. The entire data collection process is externally
triggered by the excimer laser. As mentioned above, the computer receives
7 analogue signals. A shutter in front of the reaction cell provides a way to
obtain a baseline for Raman and Rayleigh signals. At the very initial data
collection point, this shutter is closed and 10 data points are collected to be
used as a baseline for the Raman and Rayleigh signals. Once the baseline
is obtained, depending on the number of shots per point, the output of those
7 analogue channels are converted to digital numbers and temporarily
stored. The third stage is to move all the gratings to their new
corresponding positions. After checking if all the gratings are
Figure 2.18 Schematic Diagram of Collection Process of Ozone REP Experiment
moved to their corresponding positions and the motors are stopped, new data are collected and temporary stored. The scanning and collecting stages will be inserted until the program is stopped by the user. After the program is stopped, all the collected data are permanently stored using an Excel write file.
Chapter 3
Ozone Photodissociation: A 2nd Order Kinetics Reaction

Overview:

This section will start by briefly reviewing Beer’s law, and first and second order kinetics reactions. This will be followed by explaining ozone photodissociation as a second order kinetics reaction. Some theoretical calculations along with empirical data will then be presented. Finally, an in depth analysis will demonstrate how ozone photoabsorption can be used as a predictor for ozone Raman and Rayleigh signals in an REP experiment.
3.1 Beer’s Law

When a beam of light is incident on a sample of solution, some of the light will be absorbed by the molecules in the solution. To calculate the amount of light being absorbed through the sample, one usually applies the following equation known as Beer’s law:\(^\text{(29)}\):

\[ I = I_0 e^{-C\sigma L} \]

Where:

- \( I \) = final intensity [photons/(s\(^{-1}\) cm\(^2\))]
- \( I_0 \) = initial intensity [photons/(s\(^{-1}\) cm\(^2\))]
- \( C \) = concentration (molecules/cm\(^3\))
- \( \sigma \) = absorption cross section (cm\(^2\)/molecule)
- \( L \) = the length of penetration of light (cm)

In order to keep things simple in the above equation, the light source is considered monochromatic, and the sample consists of only one species.
The above familiar form for Beer's law treats the concentration \( C \) constant even though every photon absorbed removes one molecule from the electronic ground state and promotes it to an excited level. Hence, the validity of this simple expression requires the assumption that the rate of restoring the ground state population is much faster than the rate of removal. The restoration process can be either relaxation of the excited molecules, or diffusion or flow of fresh absorbers into the viewing zone (or all of these). The weaker the exciting source the better this assumption be. Therefore, normally the only significant variable in a typical Beer's law is the length (\( x \)) of the absorption cell. However, in photodissociation processes where both the concentration and the flux vary, in addition to the variable (\( x \)), we must consider other variables.

### 3.2 Ozone Photodissociation, A 2\textsuperscript{nd} Order Kinetics Reaction

During a photodissociation process, a molecule such as ozone, after absorbing a photon falls apart into some photoproducts. In this, assuming other processes such as stimulated or spontaneous emissions are negligible, the molecule or the absorber and the photon are both permanently removed
from the reaction cell. Since there are two reagents involved, one has to
treat the above process like a second order kinetics reaction. Problems
with some similarity to ours have previously been considered in exposure-
bleaching of positive photoresists in chip manufacture\(^{(28)}\).

We begin our theoretical analysis with the following assumptions:

1) The absorber is contained in a “Cell” of length \(L\).

2) The light arrives in a pulse of length \(T\).

3) The incident light is uniform across an area \(A\), which is
   perpendicular to the direction of travel.

4) The concentration of absorber is uniform throughout a volume \(A \times L\)
   before the light pulse arrives.

5) The pulse incident intensity is constant during the time \(0 \leq t \leq T\).

In addition to the above assumptions, we define some of the experimental
parameters used for the absorption process in the ozone REP experiment.
In the subsequent equations, \(L\) and \(A\) correspond to the length and the area
of the cross section of the absorption reaction cell accordingly. \(C(x,t)\) and
\( \phi(x,t) \) denote the concentration and the flux of photons in the reaction cell respectively. Unlike a typical second order kinetics reaction, in which both reagents depend on a single variable (usually the concentration of individual reagents), each one of the reagents involved in our photoabsorption process depends on two variables of length and time. This adds to the complexity of the process under the investigation.

The following two equations give the rate of change for the concentration and photon flux:

\[
\frac{\partial C(x,t)}{\partial t} = -\sigma C(x,t) \phi(x,t)
\]  
(1)

\[
\frac{\partial \phi(x,t)}{\partial x} = -\sigma C(x,t) \phi(x,t)
\]  
(2)

With the following boundary conditions:

\[
C(x, t = 0) = C_0
\]  
(3)

\[
\phi(x = 0, t) = \phi_0.
\]  
(4)
The boundary condition equation (3) implies that the concentration is uniform throughout the absorption cell before any light arrives.

The boundary condition equation (4) implies that the photon flux is constant or uniform for the region \( x < 0 \).

Integrating eq's (1) & (2) at \( x = 0 \) and \( t = 0 \), respectively, results in the following equations:

\[
C(x = 0, t) = C_0 e^{-\sigma \phi_s t} \tag{5}
\]

\[
\phi(x, t = 0) = \phi_0 e^{-\sigma C_0 x} \tag{6}
\]

Differentiating eq 1 with respect to \( x \) gives:

\[
\frac{\partial}{\partial t} \left( \frac{\partial \ln C}{\partial x} + \sigma C \right) = 0 \tag{7}
\]

Equation (7) shows that the function inside the parenthesis is independent of time. One can solve the above differential equation to arrive at the following equation:

\[
\sigma dx = \frac{dC}{C(C - C_0)} \rightarrow \sigma C_0 x = Ln \left[ \frac{C(x, t)}{C_0 - C(x, t)} \cdot \frac{C_0 - C(0, t)}{C(0, t)} \right]. \tag{9}
\]
Substituting eq (4) into eq (9) and some rearranging results in the following:

\[
C(x, t) = \frac{C_0 e^{\sigma C_0 x}}{e^{\sigma C_0 x} + e^{\sigma \phi_0 t} - 1}
\]

(10)

Similarly one can obtain an equivalent function for the flux:

\[
\phi(x, t) = \frac{\phi_0 e^{\sigma \phi_0 t}}{e^{\sigma C_0 x} + e^{\sigma \phi_0 t} - 1}
\]

(11)

Whenever it is the case that \(\sigma \phi_0 t \ll 1\), one can make the approximation:

\[e^{\sigma \phi_0 t} \approx 1 + \sigma \phi_0 t\]

Using this approximation in equations (10) and (11) result in the following equation:

\[
\phi(x, t) / \phi_0 = e^{-\sigma C_0 x} + (\sigma \phi_0 t)(e^{-\sigma C_0 x} - e^{-2\sigma C_0 x}) + \cdots
\]

(12)

The leading term in the eq 12 is just Beer’s law again. The fact that the first correction term is positive reflects that some of the absorber is destroyed during the process.

On the other hand if \(\sigma C_0 x \ll 1\), we can use the approximation:

\[e^{\sigma C_0 x} \approx 1 + \sigma C_0 x\]
which gives the Beer-law like result.

\[ C(x, t) / C_0 = e^{-\sigma \phi_0 t} + (\sigma c_0 x) \left( e^{-\sigma \phi_0 t} - e^{-2\sigma \phi_0 t} \right) + \cdots \] (13)

To simplify thinking about the results in eqs 10 and 11, it is convenient to define the following two dimensionless parameters:

\[ \Theta = \sigma C_0 L \] Where L = the length of the cell

\[ \Lambda = \sigma \phi_0 T \] Where T = the duration of the laser pulse.

For our experimental conditions, values of both dimensionless parameters lie in the range of 1-5. In many of the figures, we have taken typical experimental values of \( \Theta = 3, \Lambda = 1.2 \). Figure 3.1 shows the plot of \( \phi / \phi_0 \) vs \( x \) for those values of \( \Theta \) and \( \Lambda \). For \( t = 0 \), this plot essentially obeys the Beer's law. However, as time passes by, more and more absorber molecules are removed, which results in flux penetrating deeper and deeper into the absorption cell. By the time the end of the pulse is passing through the absorption cell, most of the ozone molecules have been removed and the photons at the trailing end of the pulse “see” very few molecules on their way through the cell. This is clearly reflected on in figure 3.1 on the
plot when \( t = 10 \text{ ns} \) by the fact that \( \phi/\phi_o \) is about 90% of the pulse. Figure 3.2 shows the behavior of \( C/C_0 \) vs \( x \). For \( t = 0 \) the \( C/C_0 \) is constant and uniform throughout the absorption cell (this was one of our boundary conditions). However, as times goes on, more ozone molecules are removed and by the time the end of the pulse is passing through the absorption cell very few ozone molecules left to interact with the oncoming photons. This is clearly evident in the plots of \( t = 6, 8, 10 \). By \( t = 10 \text{ ns} \), only about 5% of the molecules near the front of the cell have survived, and the survival rate is \( \sim 20\% \) near the end of the cell. Viewing the concentration dependence vs time might be a better alternative to discover the behavior of concentration throughout the absorption process. Figure 3.3 shows \( C/C_0 \) vs \( t \). At the entrance to the cell \( (x = 0) \), the concentration decays exponentially with time. This is similar to Beer’s law. Since there are fewer photons left towards the end of the cell, the concentration drop is less than at the entrance of the cell.
Figure 3.1 $\phi/\phi_0$ as a Function of $X$ for Various Times

During the Pulse, for $\Theta = 3$, $\Lambda = 1.2$. 
Figure 3.2 $C/C_0$ as a Function of $X$ for Various Times

During the Pulse, for $\Theta = 3$, $\Lambda = 1.2$. 

$C/C_0$ vs $x$, for $\Theta=3, \Lambda=1.2$
Figure 3.3  $C/C_0$ as a Function of $T$ for Various Depths into the Cell, for $\Lambda = 1.2, \Theta = 3.0$. 
3.3 Raman and Rayleigh Scattering Intensity

Until now the discussion was about the absorption process in the cell. Now one needs to investigate how the knowledge of absorption process can be used towards measuring the intensity of Raman and Rayleigh scattering. Since it is already known that the intensity of a secondary process is extremely small, the few photons emitted during Raman or Rayleigh scattering will have a negligible effect on the equations derived on the absorption process in the previous section. As discussed in chapter 2, a dual channel spectrometer is used in the ozone REP setup to separate the Raman from Rayleigh photons. The rate at which these Raman or Rayleigh photons are produced between \( x \) and \( x + dx \) and \( t \) to \( t + dt \) can be described by the following equation:

\[
d^2S(x, t) = Q C(x, t) \phi(x, t) dx dt
\]  

(14)

Where \( Q \) is the cross section for the specific Raman or Rayleigh process being selected by the spectrometer. The rest of the variables are the same as in the previous sections. In order to see how the scattering rate behaves with respect to length and time, one needs to look at the product of \( C \) and
\( \phi \) vs \( x \) and \( t \). This is demonstrated in figure 3.4. For \( x = 0 \), the product function \((\phi/\phi_0)(C/C_0)\) behaves exponentially versus time. For \( x = 1.0 \), this product function does not show significant change until \( t = 5 \text{ ns} \). However, the behavior of this product function becomes complicated at greater depths into the cell. This is a reflection of the fact that more ozone molecules and photons have been used simultaneously at greater depths into the cell. In order to show the relative contribution of different parts of the cell during the entire pulse, one has to integrate eq 14 over the duration of the pulse.

\[
S_x = \int_0^T d^2S(x, t) dt = \frac{QAC_0}{\sigma} \left| \frac{e^\Theta - 1}{e^{\Lambda x/L} + e^\Theta - 1} \right|
\]  

(15)

One must note that the maximum of this function \( (S_x) \) is always at \( x = 0 \) and for \( x > 0 \) it drops monotonically. Figure 3.5 shows this for various values of \( \Lambda \) and \( \Theta \). In order to get total scattering intensity (Raman or Rayleigh) one has to integrate eq 15 over the entire absorption cell (0-L).

\[
S_{\text{tot}} = \frac{QA}{\sigma^2} \ln \left( \frac{e^\Theta e^\Lambda}{e^\Theta + e^\Lambda - 1} \right)
\]  

(16)
Figure 3.4 $\phi C / \phi_0 C_0$ as a Function of Time for Various Depths in the Cell, for $\Lambda = 1.2$, $\Theta = 3.0$. 
Figure 3.5 Relative Contributions to Scattering Signal from Different Parts of the Cell, for Various $\Lambda$ and $\Theta$. 

$S_x/S_{x=0}$ for different $\Lambda, \Theta$ values
3.4 Loss of Photons and Absorber:

If one assumes the following:

\[ N_b = \text{the number of photons in a pulse at } x = 0 \]

(before entering the absorption cell)

\[ N_a = \text{the total number of photons in the same pulse at } x = L \]

(after exiting the absorption cell),

\[ N_b = A \phi_0 T \quad (17) \]

\[ N_a = A \int_0^T \phi(L, t) \, dt \quad (18) \]

By substituting the expression for \( \phi \) in eq 11 and some rearrangements, one can show the number of photons leaving the cell is given by the following equation:

\[ N_a = \frac{A}{\sigma} \ln \left( \frac{e^{\Lambda} + e^{\Theta} - 1}{e^\Lambda} \right) \quad (19) \]

A little bit more manipulation will show the following:

\[ N_a = AT \phi_0 - \frac{A}{\sigma} \ln \left( \frac{e^{\Theta} e^\Lambda}{e^\Theta + e^\Lambda - 1} \right) \quad (20) \]
Therefore, the number of photons absorbed in the cell is given by the following expression:

$$\Delta N = N_b - N_a = \frac{A}{\sigma} \ln \left( \frac{e^\Theta e^\Lambda}{e^\Theta + e^\Lambda - 1} \right).$$

(21)

The number of absorbers (ozone molecules) is computed in a similar fashion:

The number of ozone molecules before the light pulse enters the absorption cell is:

$$M_b = ALC_0.$$  

(22)

and the number of ozone molecules after the light pulse leaves the absorption cell is:

$$M_a = A \int_0^L C(x, T) dx = \frac{A}{\sigma} \ln \left( \frac{e^\Lambda + e^\Theta - 1}{e^\Theta} \right) = M_b - \frac{A}{\sigma} \ln \left( \frac{e^\Theta e^\Lambda}{e^\Theta + e^\Lambda - 1} \right)$$

(23)

and hence

$$\Delta M = M_b - M_a = \frac{A}{\sigma} \ln \left( \frac{e^\Theta e^\Lambda}{e^\Theta + e^\Lambda - 1} \right)$$  

(24)
The expressions of (21) and (24) are equivalent, since for every absorber being destroyed one photon is absorbed simultaneously. Furthermore, comparing these two equations to eq 16 shows the following equation for the total scattering intensity:

$$S_{\text{tot}} = \frac{Q \Delta N}{\sigma}$$ (25)

One has to bear in mind that the above equation (25) is a very general case. Since the absorption process depends on the concentration and the flux in exactly the same way as the scattering (Raman and Rayleigh) intensity process does. The expression (25) holds for all Rayleigh and Raman scattering due to the fact that the amount of scattered light in a photodissociation process is so small that has very little effect on all the equations derived up to now. A keynote with regard to equation 25 is that $S_{\text{tot}}$ corresponds to the total scattering in the cell. However, a small fraction of the total scattered light is actually collected through the collection optics in our system. Therefore, normalizing with respect to the geometry of the cell, the number of photons absorbed is a very good predictor of the total amount of scattered light.
3.5 Rayleigh Scattering

Since every ozone Raman band shows up at a particular wavelength different from the wavelength of the incident light (Raman shift), it is highly unlikely for the light collected at a specific Raman shift characteristic of ozone to originate from any source other than ozone molecules. However, the situation is entirely different with Rayleigh signals. One can group the "Rayleigh" signal into three different sources: 1) ozone and its photoproducts 2) cell and its components 3) He atoms.

We have managed to suppress the cell scattering down to ~ 1% of the total scattered light by very precise alignment, which needs to be checked regularly. Since He has always been used as a carrier gas for ozone, one would inevitably get a certain amount of Rayleigh scattering coming from He. The helium Rayleigh cross section has been calculated to be $Q_{\text{He}} \approx 1.96 \times 10^{-28} \text{ (cm}^2\text{)}^{(24)}$. One can compare this value to that of ozone at the same wavelength $Q_{\text{O}_3} \approx 1.26 \times 10^{-25} \text{ (cm}^2\text{)}^{(24)}$ and to the ozone absorption cross section $\sigma \approx 1.1 \times 10^{-17} \text{ (cm}^2\text{)}^{(11-22)}$ at 250 nm. Just by comparing the above values, one can conclude that about 1 in $10^8$ absorptions produces a Rayleigh photon and there is even a smaller yield
for any individual Raman process. In fact by adding all the Raman and Rayleigh transitions one can roughly estimate that about one excited ozone molecule in \(10^7\) scatters light rather dissociating. Although the Rayleigh cross section is about 3 orders of magnitude smaller than that of ozone, there are a lot more He atoms (600 torr) than ozone (10 torr) in the absorption cell. Since both the intensity and the ozone concentration vary with time and location in the cell, one needs to refer to eq 14 for both He and ozone. One can consider three different regimes that eq (1) needs to be applied: 1) for scattering by He when no ozone is present, both \(C\) and \(\phi\) are constant; 2) for scattering by He when there is ozone present, \(C_{He}\) is constant, but \(\phi\) is a function of both \(x\) and \(t\) because of interception with ozone (eq 11); 3) for scattering by ozone, in this case it is necessary to take into account variation of both \(C_{O3}\) and \(\phi\) (eqs 10 and 11). When there is no ozone present, the intensity of Rayleigh scattering from He is given by the following equation:

\[
S^o_{He} = C_{He}Q_{He}\phi_0ATL
\]  

(26)

Integrating eq 14 when ozone is present would lead us to calculate the Rayleigh intensity for He with the following equation.
\[
S_{\text{He}} = \frac{S_{\text{He}}^0}{LT} \int_0^L \int_0^T dx \int_0^t dt \frac{e^{\sigma \phi_0 t}}{e^{\sigma \phi_0 t} + e^{\sigma C_0 x} - 1}
\]  
(27)

Where \( C_0 \) is the ozone concentration at the beginning of the laser pulse as in eq (11).

One can analytically integrate the time integral:

\[
\int_0^T dt \frac{e^{\sigma \phi_0 t}}{e^{\sigma \phi_0 t} + e^{\sigma C_0 x} - 1} = \frac{1}{\sigma \phi_0} \int_0^q \frac{dq}{q + e^{\sigma C_0 x} - 1} = \frac{1}{\sigma \phi_0} \ln \left[ \frac{e^\Theta + e^{\sigma C_0 x} - 1}{e^{\sigma C_0 x}} \right]
\]  
(28)

Thus

\[
S_{\text{He}} / S_{\text{He}}^0 = \frac{1}{\sigma \phi_0 LT} \int_0^L dx \ln \left[ \frac{e^\Theta + e^{\sigma C_0 x} - 1}{e^{\sigma C_0 x}} \right]
\]  
(29)

\[
= \frac{1}{\Theta \Lambda} \int_0^\Lambda dy \ln \left[ \frac{e^\Theta + e^y - 1}{e^y} \right]
\]

The remaining integral can only by evaluated numerically. For the “typical” values \( \Lambda = 1.2, \Theta = 3.0 \) this numerical integral gives:

\[
S_{\text{He}} / S_{\text{He}}^0 = 0.815.
\]  
(30)
If both \( C_{\text{ozone}} \) and \( \phi \) were unchanged by absorption and photodissociation, the ozone Rayleigh intensity would be given by an expression similar to eq (26):

\[
S_{O_3}^0 = Q_{O_3} C_0 \phi_0 \Lambda \Theta T
\]

(31)

One has to note that the above expression eq (31) is an entirely fictitious but useful one. The actual Rayleigh scattering intensity for ozone can be calculated by substituting the results of eqs (10) and (11) into eq (14):

\[
S_{O_3} = Q_{O_3} A \int_0^L \int_0^T \frac{C_0 e^{\sigma C_0 x} e^{\sigma \phi_0 t}}{(e^{\sigma C_0 x} + e^{\sigma \phi_0 t} - 1)^2} \, dx \, dt.
\]

(32)

If we define \( u = \sigma C_0 x \) and \( v = \sigma \phi_0 t \), the double integral can be evaluated analytically:

\[
S_{O_3} / S_{O_3}^0 = \frac{1}{\Lambda \Theta} e^\Lambda \int_0^\Lambda e^\Theta \int_0^\Theta 1 \, du \, dv \frac{1}{(u + v - 1)^2}
\]

(33)

\[
= \frac{1}{\Lambda \Theta} ln \left[ \frac{e^\Lambda e^\Theta}{e^\Lambda + e^\Theta - 1} \right]
\]

Now in order to calculate the entire Rayleigh scattering intensity one needs to combine eqs (29) and (33):
\[
\frac{S_{Ray}}{S_{He}^0} = \frac{1}{\Theta \Lambda} \int dy \ln \left[ \frac{e^\Theta + e^y - 1}{e^y} \right] + \frac{P_{01}Q_{01}}{P_{He}Q_{He}} \frac{1}{\Theta \Lambda} \ln \left[ \frac{e^\Theta e^\Lambda}{e^\Theta + e^\Lambda - 1} \right]
\] (34)

Where \( P_x \) is the partial pressure of component \( X \) (He or \( O_3 \)).

Using the following values:

\[ P_{O_3} \approx 10 \text{ Torr} \]
\[ P_{He} \approx 600 \text{ Torr} \]

One would get:

\[ \frac{P_{01}Q_{01}}{P_{He}Q_{He}} = 10.71. \] (35)

And substituting the eqs (30) and (35) into eq (34) gives:

\[ \frac{S_{Ray}}{S_{He}^0} \approx 0.815 + (10.71) \cdot (0.303) = 4.06 \] (36)

Therefore, according to eq (36) when ozone is introduced into the cell the observed “Rayleigh” signal should increase by about a factor of 4.

Alternatively one could write:

\[ \frac{S_{O_3}}{S_{Ray}} \approx 0.80. \] (37)
To conclude, under normal operating conditions, about 80% of the observed Rayleigh scattering would be due to ozone. If the percentage of Rayleigh scattering was much higher (99%) or alternatively the above 80% was known with a lot more precision (3-4 significant digits) the Rayleigh intensity would have been a very useful normalizing factor since ozone Rayleigh and Raman both depend on the concentration and the flux fluctuation in exactly the same way.
Chapter 4
Ozone REP Data

Overview:

This chapter will begin by explaining the original plan of this project. This will be followed by describing the ozone REP apparatus and its operation as used in the previous work, with a critical analysis of problems that were discovered during the course of this work. During the discussions of solving these problems with the apparatus, two methods of obtaining ozone REP will be explained. Finally, this chapter will conclude with a brief summary of the problems that were solved and some suggestions to guide the way to obtain full-scale ozone REP data in the future.

4.1 The Original Plan

As mentioned at the end of chapter one, since some ozone REP data (250-270 nm) had already been collected in the previous work, the original plan for this thesis was to refine and extend that work. More specifically,
the main objective of this thesis was to collect ozone REP in the shorter wavelength range (230-250 nm) to compliment the previous work (250-270 nm). However, during the course of taking measurements, we discovered a series of problems with the apparatus. In fact the discovery of these problems cast serious doubts as to the validity of the ozone REP data. At that point, our main objective shifted from refining and extending the data collected in the previous project to understanding and solving these important issues before obtaining any reliable ozone REP data.

4.2 Weak Signal

To put things in perspective, one needs to learn about the magnitude of signal in our experiment. In a typical ozone REP experiment, every time the laser fires \( (T = 10 \text{ ns}) \), the number of photons that are absorbed by ozone in the absorption cell is \( \sim 6 \times 10^{14} \). Since an absorbed photon usually results in photodissociating one ozone molecule, this number is also the number of ozone molecules that dissociate. However, as mentioned in previous chapters, our Raman or Rayleigh signal comes from an extremely minute fraction of ozone molecules that undergo Raman or
Rayleigh scattering in the course of dissociating, thereby returning to one of the vibrational levels in the ground electronic state. In fact, out of the total number of scattered photons, approximately 5% is imaged by the collection optics into the entrance slit of the spectrometer. Depending on the slit width (usually 1.0 mm), only 30% of the light actually enters the spectrometer. After entering the spectrometer, the light is split by the beam splitter and sent to the Raman and Rayleigh channels with the ratios of 20% and 80% respectively (refer to chapter 2). After entering each channel, only 50% of the light actually reaches the first mirror (vignetting effect). Only roughly 75% of this light is reflected onto the grating (since our UV mirrors absorb roughly 25% of the light incident). Since the grating absorbs 75% of the light, only 25% of the light being incident onto the grating is actually reflected onto the second mirror, and similar to the first mirror, only 75% of this light actually reaches the detector, and based on the quantum efficiency of our PMTs, only roughly 20% of this light is converted into an electrical signal inside our PMTs. Bearing in mind the several stages of loss of photons mentioned above, in order to estimate the number of photons actually collected in our REP experiment, we applied
two separate ways. First the voltage output of our PMTs was measured, using all the parameters such as the properties of amplifier, the values of the resistor and the capacitor, this number was converted to the number of photons. The second approach was to actually measure the shot noise in the signal. If \( X \) = the standard deviation of the collected data and \( Y \) = the signal magnitude, then \( N = (Y/X)^{1/2} \) is a reasonable estimate of number of photons collected. These two approaches gave estimates that were consistent with one another, and which showed that the number of photons collected per laser shot was in the range (1-10). Because of this extremely low photon yield, we had to average very many laser pulses per data point. Therefore, one important point to consider is that out of \( \sim 6 \times 10^{14} \) in a laser shot, on average, only \( \sim 5 \) are actually collected as a signal. Having a very small signal such as this, only increases the level of complexity of ozone REP experiment with respect to many issues. Some of these issues include precise measurement of the number of UV photons absorbed, shot to shot noise, reproducibility, normalization and calibration of the signal, these will be discussed in the next sections.
4.3 Measuring UV Photons Absorbed

One of the significant improvements made on the ozone REP apparatus was the direct measurement of the UV photons absorbed in every ozone REP scan precisely. In the previous work, the number of photons absorbed in ozone REP experiments was not measured. Instead, the Rayleigh signal was used to normalize the Raman signal with respect to ozone concentration and UV power fluctuations. Theoretically, this is an efficient way of normalizing since the desired Raman and ozone Rayleigh signals both depend on the ozone concentration and the laser intensities in the same way. However, as discussed earlier, the signal observed in the "Rayleigh channel" of the spectrometer is not all from ozone. There are contributions from stray light in the cell (a minor effect) and from Rayleigh scattering by the carrier gas He. As indicated in chapter 3, the latter is not negligible under our operating conditions. Hence, the observed Rayleigh signal cannot be used as a reliable normalizing factor. If the ozone Rayleigh signal cannot be measured precisely, an alternative reliable method to take into account the effects of fluctuations in the UV power and ozone concentration would be to normalize the ozone Raman signal with
respect to the number of photons absorbed in the reaction absorption cell. The following method was implemented to obtain the number of absorbed photons in a typical ozone REP experiment. The number of UV photons absorbed in the cell is simply the difference between the number of UV photons before entering the absorption cell and the number exiting the cell. Measuring the UV photons after going through the cell (called "UVA") is easily done by directly placing a photodiode in front of the exit window of the reaction cell. However, to measure the UV photons before (called "UVB") the cell is trickier, since putting a photodiode in front of the cell would block the laser beam. Therefore, to measure the UVB, a small pick off signal from reflection of the UV beam from a lens in front of the cell was used. These two photodiodes were calibrated by running a normal scan except with the cell under vacuum. Since the pick off signal from the lens is directly proportional to the UVB beam, almost independent of the wavelength, plotting the UVB vs UVA should produce a line with a reproducible slope and a negligible intercept. Figures 4.1 and 4.2 show two typical plots of UVB vs UVA. Although these two scans have been taken at different time intervals, and also the fact that they are about 12 nm
wavelength range, one can see how reproducible the slopes are (the difference between these two slopes is only 0.2%). Although the optical realignment of the system can affect the slope, this effect is small and quite reproducible slopes are achieved over an extended period of time (up to a few weeks) in our system. Once a reproducible slope is obtained, it is multiplied by the UVB and subtracted from the UVA to calculate the number of UV photons absorbed in a typical REP experiment.

4.4 Early Ozone REP’s Using Rayleigh as Reference

At the start of this work, since we were not aware of the major problems with the ozone REP setup and especially the fact that Rayleigh signal cannot be used as a normalizing factor, we were using the methods previously used in this project, in particular relying on the Rayleigh signal as a reference. At the beginning of the data collection we would choose a particular Raman band and a starting excitation wavelength, then the dye laser, and the Raman and Rayleigh gratings would simultaneously scan at a 0.1 nm stepsize. Depending on which ozone vibrational Raman band being
Figure 4.1 UVB vs UVA

Figure 4.2 UVB vs UVA
under study, the Raman grating was programmed to track the dye laser with a constant shift (Raman shift) in frequency, while the Rayleigh grating was programmed to follow the wavelength of the dye laser exactly without any shift in wavelength. As mentioned above, all the ozone REP data collected in the previous project were normalized with respect to Rayleigh signal. Early into our investigation we realized the need to determine the reliability of Rayleigh scans, otherwise the data collected in the previous project could not be trusted. At this point in our data acquisition we did not have the analysis presented in chapter 3 regarding the lack of reliability of Rayleigh signal. The Ozone Rayleigh Excitation Profile spectrum has already been theoretically calculated by Fourier manipulation of the absorption cross section. Figure 4.3 shows this spectrum in the range of our ozone REP experiments (235-275 nm). One can notice that the magnitude of the broad band feature increases as wavelength increases (235 nm → 253 nm). Moreover, the relative magnitude of the small structural oscillations to the overall broad band feature is fairly small. Figure 4.4 shows a Rayleigh Excitation Profile collected in this work. This plot is an average of a number of ozone
Rayleigh Excitation Profiles scans in our Rayleigh channel of our spectrometer in the range 235-250 nm. All these scans were normalized with respect to the number of photons absorbed in the reaction cell. First, the broad shoulder in the range 235-239 nm is actually an artifact of the instrument. The dielectric mirror coating inside the Rayleigh channel (the Raman channel does not exhibit similar abnormal behavior) in our spectrometer transmits part of the light at wavelengths less than about 239 nm (this feature was incorrectly interpreted as part of the O₃ REP in the previous project). Second, the overall trend of this scan for \( \lambda \gtrsim 239 \) nm is decreasing with increasing wavelength, except the opposite of the theoretical expectations. Third, the structural oscillations that appear in this spectrum for \( \lambda \gtrsim 245 \) nm seem to be much larger than what the theory predicts. Soon after obtaining similar results with numerous scans with both channels of our spectrometer for \( \lambda \gtrsim 239 \) nm to the one just explained (for \( \lambda \lessim 239 \) nm our Raman channel behaves normally), our focus shifted towards determining how much of the "Rayleigh" signals that we observed was actually due to ozone. Since helium is used as a carrier gas to carry
Figure 4.3 Ozone Rayleigh Excitation Profile x 10^25 Spectrum (Calculated) vs nm
Figure 4.4 All Rayleigh’s Averaged (raych) Signals vs nm
ozone molecules into the reaction cell, even though the He Rayleigh cross section is much smaller than that of ozone (see chapter 3), it is inevitable that some of the total Rayleigh scattering will come from helium. In order to determine the exact contribution of helium; we introduced a bypass valve to go around the ozone trap while allowing the normal flow of helium into the reaction cell. This allowed us to measure the helium Rayleigh scattering and compare it to the total "Rayleigh" signal when both ozone and helium flowed together into the reaction cell. By doing this, we were able to measure helium Rayleigh scattering and compare it to the time we had measured the total Rayleigh signal when flowing the ozone and helium together in a typical ozone REP experiment. These two separate measurements (pure He) and (O₃ and helium) were done with the exact same sample flow rates and PMT voltages. Several repeats of these measurements allowed us to conclude that the helium contribution to Rayleigh scattering was not reproducible and it varied in the range (20-40%) of the total Rayleigh signal. We believe the cause of having a variable helium Rayleigh scattering instead of being a constant contribution to the total Rayleigh scattering can be explained by the following two
factors, one minor and the major factor. The minor factor is the inherent problem with the tube that carries the He/O$_3$ mixture to the reaction cell. Some of the inner tubes can slightly move during the course of the experiment, which can affect the flow inside the reaction cell. In other words, the direct result of the movements of the flow tubes is that the beam hits areas with slightly (depending on how much the tube moves, which we believe is a small amount) concentrations (of both helium and ozone), which in turn affect the Rayleigh signal. The second and more important factor is the beam shape of the laser beam. We determined that the UV beam entering the reaction cell contains two "hot spot". In other words, there were two small areas (0.1 mm diam) within the actual main area of the beam (1.0 mm). Discovering these small hot spots was a central observation in understanding the unexpected ozone Rayleigh Excitation Profiles discussed above. The intensity of UV photons in these hot spots is much greater than that of the other areas of the beam. Since the entrance slit within our spectrometer images a very small volume (< 1.0 mm$^3$, where beam meets the ozone flow) in the absorption cell, a slight movement of the beam could have a disproportionate impact on the total Rayleigh signal
collected. In order to test our hypothesis that a slight amount of beam moving would have a big impact on our collected signal and would interfere with obtaining reproducible results, we conducted the following tests. We took two sets of emission scans. In the first set, we deliberately turned on our auto-tracking system while taking several emission scans. Since in an emission scan the excitation wavelength is fixed, there is no need to run the auto-tracking system (refer to chapter 2). The data within these several scans in the first set were quite consistent and reproducible. In the second set of data the same emission scans as in the first set were repeated except half of the scans were taken after deliberately moving the UV beam slightly and not running the auto-tracking system. And the other half of the emission scans in the second set were done identical to the first data set (with the auto-tracking system running and not moving the beam). Comparing the first data set to the second data set helped confirm our hypothesis and helped us reach the following conclusion. First, even a small movement of the beam can have an impact on the amount of scattered light collected. Second, The auto-tracking system appears to compensate for the small movements of the beam during an emission scan.
However, in an REP experiment, where the dye laser scans through different wavelengths, we believe that the problem of beam movement is even more pronounced and more difficult to eliminate compared to an emission scan. This is due to the fact that the response function of our auto-tracking system depends partially on the wavelength of our laser beam. In other words, the sensitivity of our auto-tracking system varies as one scans through different wavelengths. This results in the fact that our auto-tracking being unable to track optimally sometimes during the entire scanning range. In essence, this is equivalent to the UV beam not being exactly at the “right” spot sometimes. Therefore, any slight movement of our beam that contains two hot spot could easily shift the beam and its hot spots to a region with different concentrations of He and O₃, which would have a dramatic effect on our signal. Therefore, the crucial lessons we learned from the above were that among other significant conditions required for REP experiment are a uniform and spacially stable UV beam.
4.5 Ozone Emission Scans

In an ozone Emission scan, a particular excitation wavelength is chosen to excite the ozone molecules, the spectrometer gratings are then scanned at 0.1 nm steps with the dye laser fixed at this chosen wavelength. In principal, either of the two spectrometer channels would suffice for an emission experiment. However, we decided to scan both channels in tandem to test for consistency. In these Emission scans, both gratings start at the red side of the excitation wavelength and scan towards longer wavelengths. Since ozone Raman bands appear at unique wavelengths, one can be assured that the signal obtained comes entirely from ozone. In contrast, in a typical REP experiment, both the dye laser and the grating scan (in synchrony) over different wavelengths maintaining a fixed frequency difference that corresponds to one particular vibrational level in the ground electronic state (as described above). In a typical Emission experiment, the excitation wavelength is fixed while the spectrometer scans over different vibrational levels in the ground electronic state. After collecting all vibrational and wavelengths, these two types of experiments
should provide the same information with regard to the photodissociation
dynamics of ozone. There are however essentially two main differences
between these two experiments. In a continuous ozone REP scan, a range
of wavelengths, for example 240-250 nm is covered within a single scan,
but one only obtains information about one Raman band. On the other
hand, in an Emission experiment, to cover the same range of excitation
wavelengths, one has to conduct many (in this case 100) different scans.
However, since experimental conditions such as UV power, ozone
concentration, noise level, and baseline might vary from one scan to
another, it might be difficult to batch and normalize these different
emission scans into one spectrum. The second significant difference
between these two experimental methods is that the ozone Emission
experiment due to the enormous number of scans simply takes a lot longer
experimental time compared to the continuous ozone REP experiment.
Before launching into a new phase of ozone emission scans we had to do a fair amount of programming that would eventually facilitate analysis of the data would be acquired. Therefore, a Labview code was written in our lab to help us with the processing (Appendix A5). This Labview code was designed to integrate the area of each vibrational band of ozone that appeared in all ozone Emission scans. In order to obtain an REP spectrum (of [100] for example) using emission scans, all the integrated [100] of different emissions (different excitation wavelengths) would be assembled. However, regardless of which experimental method is applied either Emission scans or REP experiment, ultimately all vibrational bands must be collected with respect to all excitation wavelengths. In other words, Emission scans or REP scans seek the same matrix of data with only taking different paths to get there. In the initial stage of our ozone Emission scans, we were still concentrating on the shorter wavelengths (235-250 nm). The scans taken in this region did not reflect any discernable structural features corresponding to the features in the ozone absorption spectrum. In retrospect, this is not surprising. Figure 4.5 shows an ozone absorption spectrum in the same region as our
Emission scans. It is easily seen that features around 230-245 nm are several times smaller in magnitude than those in 250-260 nm. Since the error bars reflecting the reproducibility of our emission scans were too large, it was not feasible to see any structures in the shorter wavelength range (235-245 nm). The features in this region were simply too weak to bring out with this apparatus. Therefore, we turned our attention towards the longer wavelengths (250-260 nm) where the structural features should be intense. We began collecting ozone Emission data in this range of longer wavelengths (≥ 250 nm), as described above, with the dye laser fixed at a particular wavelength and both Raman and Rayleigh gratings scanning through different vibrational levels. The normalization factor used in this data was the number of UV photons absorbed in the reaction cell. Analysis of these early data revealed much poorer reproducibility than we had expected (10-20%). As a reminder, in order to trust any features or patterns in our ultimately seeking ozone REP data, the error bars of reproducibility can not be more than 4-5%. With the beam jitter essentially eliminated with the aid of auto-tracking system, we believe the
Figure 4.5 UV Ozone Absorption Spectrum
power issue was a critical factor that prevented us from achieving reproducible results. In a typical ozone Emission scan, at a stepsize of 0.1 nm, any of our spectrometers scans over 30 nm range to cover the emission lines that correspond to the vibrational band of [100] to about [500]. This roughly corresponds to over 2 hours in time. Initially, our strategy with respect to ozone Emission scans was to scan over a very long range to collect as many vibrational bands as possible. In order to facilitate normalizing our data, in a typical ozone Emission experiment, the incoming UV power inside the absorption cell had to be maintained at a constant level. However, soon into our data collection, we discovered the following problem. During this long scan our UV power would drop by as much as a factor of two in an unpredictable fashion. The problem was our Excimer laser. In order to maintain the same power level, our Excimer laser requires an HCl boost every 0.5 an hour. Since obviously it was not possible to optimize our Excimer laser power during an Emission scan, we had to come up with a different scheme to solve this problem. As a result of these considerations we decided to abandon taking very long scans over many vibrational bands. Instead, we decided to park both
gratings at the center of a particular vibrational band (for example [100]) and collect data for about 30 minutes, so the UV power would be approximately constant. This mode of collecting data actually served at least two purposes. First it eliminated the issue of power drop, and the second, which was equally important, it increased the total number of data points that were averaged. Figure 4.6 exemplifies all the ozone Emission scans. On this figure, x-axis corresponds to the number of averaged shots and y-axis corresponds to the intensity of the scattered light. Each point on this plot is the result of averaging 200 laser shots, since there are approximately 50 points on a single scan like above, this roughly amounts to averaging 10,000 shots. A quick calculation shows that the shot noise within this scan (and similarly with the rest of the scans), is well within the statistical fluctuations (1.0-1.5%). With the noise level suppressed and beam jitter eliminated, and the power stable, we ventured into taking many similar measurements as above to obtain the long sought ozone REP data.
Figure 4.6 Ozone Raman/(UV Absorbed) Parked at [100] Band
4.6 Preliminary Ozone REP Data

As discussed in the introduction chapter, the absorption and the scattering (Raman and Rayleigh) processes are both governed by the same wave packet in the dissociative excited electronic state. Hence, one would expect to observe similar structural oscillations appear in ozone Raman or Rayleigh excitation profiles. However, it is not yet known exactly how similar these structural features must be in magnitude and placement to their counterparts in the ozone absorption spectrum. However, one would not be surprised if the ozone REP spectrum contained different pattern of oscillations from one vibrational level to another. Each of the vibrational wave functions in the ground electronic state is orthogonal to all the others. This essentially means that no two vibrational levels behave similarly either in the ground or in the excited state. Since any feature in an ozone REP (of a particular band) spectrum originates from the overlap of the excited wave packet and a particular vibrational level in the ground electronic state, any two-ozone REP spectra are likely to have different structure. Since the average spacing between the small structural features in the ozone absorption spectrum is approximately 1.0 nm, an ozone REP
spectrum collected at stepsize of 0.25 nm should reveal any similar structural features. As a result, all the ozone REP data presented in the next few pages were taken at a stepsize of 0.25 nm in the wavelength of the laser. In the final stage of this work, we would like to present ozone REP of 5 different vibrational bands. In order to facilitate the analysis of these following ozone REP scans of different vibrational bands, UV power (0.8 +/- 0.05 mj), ozone concentration (11 +/- 0.5 torr) have both been maintained at an almost constant level throughout. The data in figure 4.6 and all the subsequent figures for ozone REP data of different bands shown in the following pages have been taken in the excitation wavelength range of 250 nm to 252 nm. Figure 4.7 shows ozone REP of the band [100]. The x-axis in this figure is the excitation wavelength and the y-axis is the intensity of ozone Raman [100] band at a particular excitation wavelength. Every point shown on figure 4.7 (and similar with the other ozone REP bands shown in the next few pages) is the averaged result of an ozone emission experiment similar to the one shown earlier in figure 4.6. In other words, every point on figure 4.7 is the result of averaging 10,000 laser shots. In order to assess the reproducibility of these points, some of these
data points have been repeated. In other words, more than one emission scans have been conducted for some of these data points to obtain their reliability. In order to provide a visual aid with the trend of all the data points shown in the following ozone REP bands, a 6th degree polynomial has been used as a curve fitting function. These curves have no physical significance. As shown on figure 4.7, the error bars are approximately 5-6% on REP of [100]. There seems to be a definite pattern of oscillations in this figure. There appear to be two oscillations having their maxima at approximately 250.5 nm and 251.5 nm. Due to the error bars, the oscillation appearing at 250.5 nm might be just an experimental artifact. However, on the other hand, the oscillation occurring at 251.5 nm clearly stands out as a peak. Even though, there is an error bar of 5-6% on this figure, the high point at 251.5 nm is definitely a maximum compared to the point 251 nm well outside the error bars. Our next spectrum is shown in figure 4.8. In this figure, ozone REP of [200] band shows two oscillations around 250.25 nm and 251.75 nm. However, again based on the error bars, we have more confidence in the first peak appearing at around 250.25 nm than the second peak around 251.75 nm. Figure 4.9 shows the REP of
[300] band. In this figure, unlike the first two ozone REP’s shown already ([100] and [200]), the error bars are only 2%. This indicates that the UV power and ozone concentration fluctuations were even smaller than those in the previous bands shown. As a result, we are able to state with a high level of confidence that there are two oscillations appearing around 250.25 nm and 251.5 nm in this figure. The REP band of [202] is shown in figure 4.10. Similarly on this spectrum, one can see that the error bars are only about 3%. This is reassuring in the fact that there are actually two distinct oscillations occurring at around 250.5 nm and 251.5 nm in this spectrum. Finally, the last ozone REP band presented in this work is shown in figure 4.11. In this spectrum, even though one might observe three oscillations, based on the error bars (3%) we would like to only report two peaks, one around 250 nm and the other around 251 nm.
Figure 4.7 Ozone REP [100] Spectrum
Figure 4.8 Ozone REP [200] Spectrum
Figure 4.9 Ozone REP [300] Spectrum
Figure 4.10 Ozone REP [202] Spectrum
Figure 4.11 Ozone REP Spectrum [400]
4.7 Conclusion

These recently collected ozone REP data presented in the above figures are unique for the following three fundamental reasons. First, unlike any previous ozone REP data collected, the intensity shown here is normalized only with respect to the number of photons absorbed in the absorption cell. And the magnitude of the signal reported here is purely due to ozone and no other potential source (such as cell scattering, He scattering, O₂, O and other contaminants such as OH, etc). Second, each point shown in these scans is the result of averaging 10,000 shots (50 times more averaging than previously done). And finally, one can see there is definitely a discernable and unique pattern within every particular band. Although we have a considerable confidence that the structural features (oscillations) in the several bands of ozone REP spectra presented here do correspond to the structural features (oscillations) overlaying the ozone UV absorption spectrum, this investigation is still an early stage. Finally, although the ozone REP data presented here is preliminary, it definitely shows promise as a guide for pursuing further investigation of ozone REP data in the future.
Endnotes

1 Towards the end of our REP experiments, the photodiodes were replaced with a pair of J3-09 Molelectron Joulemeters to measure the UV absorbed in the reaction cell.
Bibliography


24 B. R. Johnson, private communication.


Appendix A1

Vapour Pressure (mb) vs Temperature (K)

$D_d = XeCl$

$S_q = HCl$

Temperature (K)

Vapour Pressure (mb)
Appendix A3

Transmission Spectrum of Ni(SO₄)₂ & Co(Cl)₂

Ni(SO₄)₂ = 0.46 M
CoCl₂ = 0.094 M
Appendix A4

Typical Hamamatsu Tube Current Gain

\[ y = 6.6657x - 15.664 \]

\[ R^2 = 1 \]
Raych PMT Curve Gain

\[ y = 6.804x - 19.168 \]

\[ R^2 = 0.9981 \]
Spare Gain Curve

\[ y = 6.8607x - 19.263 \]
\[ R^2 = 0.9973 \]
Appendix A5