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NEW VIEWS OF COLLISIONAL VIBRATIONAL RELAXATION: ENERGY REMOVAL RATES AND ENERGY DISTRIBUTIONS OF TRIPLET STATE PYRAZINE

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE DOCTOR OF PHILOSOPHY

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ABSTRACT

New Views of Collisional Vibrational Relaxation:
Energy Removal Rates and Energy Distributions of Triplet State Pyrazine

by

Derek R. McDowell

Collisional energy removal rates from vibrationally excited T₁ pyrazine are measured using the refined and validated Competitive Radiationless Decay (CRD) method. Optical excitation followed by intersystem crossing prepares a vibrationally excited vapor sample of T₁ pyrazine. T₀ ← T₁ transient absorption kinetics, measured with a S/N ratio of ca. 1000, provides the collisional dependence of the average triplet radiationless decay rate constant. Using a calibration between this decay constant and the triplet vibrational energy, the collisional history of the sample’s vibrational energy content is deduced. This leads to the rate of collisional energy removal as a function of the triplet pyrazine’s vibrational energy content. Results with a variety of small relaxers comprise the most useful database to date on collisional vibrational relaxation of a triplet state polyatomic. We find the following order of relaxer effectiveness per collision:

He < H₂ < Ne < D₂ < Ar < N₂ < Kr < Xe < CO < CH₄ < CO₂ < H₂O

These triplet state energy removal rates exceed those recently reported for vibrationally excited ground state pyrazine by a factor of ca. 7.

In addition, a new method for determining the distribution of vibrational energy contents in an excited polyatomic sample is applied to vibrationally excited T₁ pyrazine. The T₁ population decays with a distribution of rate constants corresponding to the underlying distribution of vibrational energies. This rate constant distribution is extracted from decay kinetics through the use of a multi-Gaussian distribution model. The calibration between decay constant and triplet vibrational energy is used to deduce the molecular vibrational energy distribution, providing the first experimental view of an excited sample’s vibrational energy distribution. Relatively narrow nascent vibrational energy distributions are progressively broadened during the early collisional encounters with a relaxer. These new vibrational energy distributions and the collisional energy removal results suggests a threshold for enhanced relaxation near 2000 cm⁻¹ of donor vibrational energy. These intriguing results should stimulate further theoretical and experimental research into the collisional relaxation of electronically excited molecules.
ACKNOWLEDGMENTS

Please forgive me but I'm going to break that emerging trend of writing an 8 page acknowledgments. I feel as if I have already written enough words in this manuscript. Besides, as William Strunk Jr. said "Rule Seventeen. Omit needless words! Omit needless words! Omit needless words!" But bear with me as there is a great need of the following words of acknowledgment.

But of course, Dr. Bruce Weisman is first on the list. I cannot thank him enough for his persistent support in all of my endeavors. He could step back from the situation and point out the positives when I thought progress looked grim. His optimism and encouragement, in addition to his skills as a scientist, played important roles in my scientific and personal development, not to mention the completion of this thesis.

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I can honestly say that my most unconditional support has come from my patient and loving wife, Grace. She has been at my side though out this long journey. She sometimes kept me busy outside of the lab, but I’m sure that salvaged my sanity. My progress sometimes tested her patience, and I am grateful for her understanding, even though she often said that she’s not exactly sure of what I’m doing.

Finally, I want to thank my family. I am proud to know that my mother and father are very proud of my accomplishments. Those Sunday morning conversations with Mom allowed her to express her love and support, which made coming back for more on Monday a little easier.

I would like to dedicate this dissertation to the memory of Glenda Catt. My heart aches for Grace and her family’s loss of this loving mother and wife.
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CHAPTER 1
INTRODUCTION

1.1 Motivation

Illuminating a typical organic molecule with ultraviolet light normally results in absorption to produce an electronically excited singlet state. This optically prepared singlet state commonly proceeds to nonradiatively decay into a lower-lying triplet electronic state. Such intersystem crossing conserves the molecule's total energy producing a triplet state containing excess vibrational energy equal to the difference in electronic energies between the triplet and excited singlet potential energy surfaces. This vibrationally energized metastable triplet species may dissociate, isomerize, phosphoresce, or radiationlessly decay back to the ground state. In order to fully understand the competition between these and other photochemical and photophysical pathways, we need to know how resistant these vibrationally excited triplet molecules are to collisional deactivation.

Whether or not the excited triplet sample can access any of the above mentioned relaxation channels may depend on the amount of vibrational excitation. For example, in order for any unimolecular reaction to occur, the reactants must have sufficient energy to overcome the activation barrier that leads to product formation. As the longest-lived electronic excited state, the triplet is more susceptible to collisional deactivation that might remove enough energy to prevent certain reaction pathways. Thus, the chemical and physical behavior of molecules excited to a triplet state depends on their retention of excess vibrational energy.
Because vibrationally excited polyatomic molecules play central roles in several areas of chemical kinetics and dynamics, more understanding is needed of the mechanisms involved in intermolecular energy transfer. This work provides experimental information concerning triplet state collisional vibrational relaxation under various collisional conditions. Such knowledge improves our understanding of intermolecular energy transfer in the gas phase. By comparing our triplet state results with findings from ground and excited singlet studies, we hope to discern the mechanisms that govern the collisional deactivation of vibrationally excited polyatomic molecules.

1.1.1 Previous Energy Transfer Studies

A broad range of experimental investigations concerning collisional vibrational energy transfer have been performed using a variety of approaches and samples. These investigations fall into one of two categories. The first involves excited molecules with low vibrational energy contents and correspondingly sparse densities of vibrational states. These studies typically prepare donors with only one or two quanta of vibrational excitation and measure the depopulation of this well-specified quantum state. Studies of this type, recently reviewed by Krajnovich et. al.¹, include measurements on electronic ground states and first excited singlet states. Vibrational energy transfer is quite efficient in these studies, with noticeable selectivity in the energy levels that participate in the process. It is often the case that energy transfer in this category is more efficient with the transfer of small amounts of energy per collision rather than larger amounts. Also, it is found that the nature of the relaxer molecule strongly affects the overall efficiency of the energy transfer process.
The second category, recently reviewed by Gordon\textsuperscript{2} and by Oref and Tardy\textsuperscript{3}, involves large, ground electronic state, polyatomic molecules prepared with vibrational energy contents for which the vibrational density of states is very high. In this regime, on the order of 15,000 cm\textsuperscript{-1} of vibrational excitation, the vibrational states can only be characterized by their total energy because of the enormous density of vibrational states. Here, there is no possibility of preparing well-defined vibrational states or measuring any state-specific information. In these studies, the vibrational relaxation is monitored by measuring the time-dependence of some observable physical property that can be directly related to the excited molecule's vibrational energy content. Then the use of a previously determined "calibration curve", which relates the value of this physical property to the vibrational energy content, allows the deduction of the average energy lost per collision as a function of the donor's vibrational energy content. The results of these studies all indicate a fairly linear dependence of the collisional energy removal rate on vibrational energy content over the range of vibrational energy contents above approximately 5000 cm\textsuperscript{-1}. There have been a few observations of a leveling-off of this linear dependence above 20,000 cm\textsuperscript{-1} of internal energy\textsuperscript{3}, but the growing consensus suggests a linear dependence of the average energy lost per collision on the internal energy of an excited polyatomic molecule.

Currently there is little information about vibrational energy persistence in between the two regimes described above. The first half of this dissertation describes continued exploration of the collisional vibrational relaxation of triplet state pyrazine molecules having vibrational energy contents in this intermediate range\textsuperscript{4-6}. The results further
attempt to fill in this vibrational energy gap and help discern any connection between high-
and low-energy collisional vibrational relaxation. They also enhance the only available
information concerning vibrational energy removal from a triplet state molecule. Direct
comparison with ground state vibrational relaxation studies suggests the possibility of
different collisional vibrational energy transfer mechanisms for triplet and singlet state
molecules.

1.1.2 Previous Energy Distribution Studies

Much of the research concerning the fundamental energy transfer properties of
vibrationally excited polyatomic molecules has involved the laser preparation of highly
vibrationally excited molecules in a narrow distribution of energies. This initial narrow
distribution is presumed to broaden as these molecules are collisionally deactivated.
Although a number of measurements have been reported on average vibrational energy
changes during deactivation, far less information exists regarding the shape or evolution of
the excited molecule’s vibrational energy population distribution.

Theoretical studies have included Master equation simulations and classical
trajectory calculations of collisional energy transfer. Most of this work emphasized
average energy transfer behavior, with little investigation into determining the vibrational
energy distribution. Schatz\(^7\) has performed classical trajectory calculations concerning
very large energy transfer that occurs in single collisions. His “successive collisions”
method models experimental situations where collisional energy transfer is studied by
observing the relaxation of initially excited molecules of known vibrational energy content.
This method can be used to simulate the time evolution of the vibrational energy
population distribution over several hundred collisions. The calculated distributions are initially very narrow and begin to broaden due to collisions before approaching a relatively narrow thermalized distribution.

Other work has attempted to provide a general theoretical analysis of the collisional deactivation sequence. The above mentioned experiments create initial vibrational energy distributions with substantial thermal widths and measure the average vibrational energy of the molecules during a collisional deactivation sequence. However, they do not provide any information about the vibrational energy distribution of the excited molecules during the collisional deactivation. Troe has simulated the collisional deactivation sequence of such highly vibrationally excited molecules using Master Equation calculations. This Master Equation is obtained from considering the total population and depopulation rates of vibrationally exited molecules at a particular vibrational energy content. These calculations predict the time evolution of the population using various energy transfer models. In Troe’s work, this evolution is found to begin in a narrow vibrational energy distribution which broadens as collisions occur until reaching another narrow distribution as the population approaches a thermal distribution. It should be noted that these numerical solutions of the Master Equation predict Gaussian energy profiles between the initial and thermal distributions.

To date, there are very few experimental techniques that have acquired information about vibrationally excited population distributions. Work by Luther et. al. used multiphoton ionization to monitor the deactivation of excited molecules through a narrow energy “window” at lower energy. This technique provides a detailed representation of
the distribution of arrival times into this energy range. However, it is not fully extensible to higher vibrational energy contents and is limited to determining population distributions only in the lower vibrational energy windows.

In an extension of the infrared fluorescence technique, Barker and coworkers\textsuperscript{10} have deduced information about the population distribution of highly vibrationally excited polyatomic molecules over a wide range of energies. Emission intensities of two widely separated spectral bands monitor well-defined subsets of the vibrational energy population distribution. These relative intensities constitute a measure of the relative populations of the two emitting subsets, thus providing a direct measure of the width of the overall vibrational energy population distribution. Master Equation simulations are then used to deduce appropriate population distribution widths based on the sensitivity of the relative emission intensities to this width. In searching for a distribution function, these workers assumed a Gaussian form because it provides a simple, well-defined width parameter and because Gaussian distributions have previously emerged from many Master Equation models. This assumption was verified by the results of partial moments analyses that mimicked Gaussian behavior. In benzene-$h_6$ and benzene-$d_6$, initially prepared with $\approx 40,000 \text{ cm}^{-1}$ of vibrational energy, the population distribution was found to differ significantly from the initially prepared delta-function after collisional relaxation to lower vibrational energy contents. The distribution widths were on the order of 5000 \text{ cm}^{-1} when centered around 20,000 \text{ cm}^{-1}, but then began to narrow again as the population approached a room temperature thermal distribution. It should be noted that the distribution width for benzene-$h_6$ was larger than for benzene-$d_6$ because benzene-$h_6$ has a
50% enhancement in average vibrational energy removal, which illustrates that larger relaxation effectiveness leads to greater broadening of the population distribution.

Most recently, Dai and coworkers\textsuperscript{11} reported a technique for studying the collisional deactivation of highly vibrationally excited molecules using time-resolved Fourier transform infrared emission spectroscopy. This technique monitors the complete time evolution of all of the sample's IR-active vibrational modes in a single experiment. This information can give the vibrational energy distribution of the collisionally relaxing vibrationally excited population. By modeling IR emission spectra with different collisional histories using Gaussian profiles, a time evolution for a population distribution undergoing collisional deactivation can be generated. Using NO\textsubscript{2} prepared with \(\approx20,000\) cm\(^{-1}\) of vibrational energy content, measurements were not possible until after relaxation to below 13,000 cm\(^{-1}\) where a very large distribution width of \(\approx4500\) cm\(^{-1}\) was found. This method therefore provides no record of the broadening of the distribution from the initial narrow one prepared by laser excitation, but it does observe the narrowing of the broadened distribution via collisional deactivation to an asymptotic width consistent with a room-temperature population distribution.

As with the average vibrational energy transfer studies, all of the prior vibrational energy distribution studies concern collisional energy transfer in systems containing very large amounts of vibrational energy. The second half of this thesis provides the first views of evolving vibrational energy population distributions for a polyatomic sample with only moderate amounts of vibrational excitation. It demonstrates the first kinetics-based, experimental determination of vibrational energy population distributions. It is applicable
to any excited system whose population decay rate constant varies with vibrational energy content. The observed distribution of rate constants corresponding to the underlying distribution of vibrational energies is mapped into a vibrational energy distribution. The results provide a record of the early broadening of the initial laser-prepared population distribution, as well as contain features that verify observations in the average energy removal results.

1.2 The Pyrazine System

The molecule of interest for our studies is 1,4-diazabenzene, or pyrazine. There has been extensive experimental and theoretical study of pyrazine’s electronic spectroscopy and photophysics because its $S_1 \rightarrow T_1$ relaxation is a prototype of “intermediate case” radiationless decay$^{12-15}$. As the name implies, this behavior lies between the “small molecule” and “statistical limit” cases of radiationless decay. The former describes a system in which both the prepared (singlet) and coupled (triplet) levels have a sparse density of states so that the singlet character is diluted into a fairly small pool of coupled eigenstates. The latter specifies that the coupled manifold contains a quasi-continuum of levels that results in irreversible, complete dephasing of the singlet character. In the theory of “intermediate case” radiationless decay, the radiatively prepared molecule with initially pure $S_1$ character rapidly dephases into mixed states that have some singlet but mostly triplet character. These mixed states then evolve into states of pure triplet character through collisional interactions. Studies of the time resolved
fluorescence emission from $S_1$ pyrazine have clarified the intramolecular couplings and level structure of this molecule.

### 1.2.1 Previous Studies

The absorption spectrum of pyrazine vapor in the near ultraviolet region comprises a series of relatively sharp bands that have been assigned to $(n,\pi^*)$ $S_1 \leftarrow S_0$ transitions$^{16-18}$. Utilizing pyrazine's ability to both fluoresce and phosphoresce in the gas phase, early work by Frad et al.$^{12}$ measured luminescent properties following excitation to several of these $S_1$ levels. They found the fluorescence and phosphorescence yields to be pressure and wavelength dependent, as is characteristic of "intermediate case" radiationless decay. Another distinguishing attribute of "intermediate case" behavior was recognized in the non-exponential fluorescence decay kinetics. They observed a lifetime component shorter than their few nanosecond experimental resolution and a second longer-lived, pressure-dependent component with a zero-pressure lifetime of $\approx 200$ ns. They also report a thermally equilibrated phosphorescence decay lifetime of 63 $\mu$sec.

Among several studies of the pyrazine vapor absorption spectrum, that by McDonald and Rice$^{18}$ contains the most detailed measurements of the vibrational structure of the $S_1 \leftarrow S_0$ electronic transitions. The zero-point level of the $S_1$ state was precisely located at 30,876 cm$^{-1}$ above the $S_0$ ground state and assigned to the $^1B_{3u}$ representation. Of the more than 40 assigned bands, the strongest transitions included those denoted by $0^0$, $6a^1$ (31,461 cm$^{-1}$), $6a^2$ (32,048 cm$^{-1}$), and $8a^1$ (32,253 cm$^{-1}$). In a comparison study, McDonald et al.$^{19}$ also measured fluorescence decay kinetics for several vibrational levels of the $S_1$ state. As did Frad et al., they found the lifetime of the rapidly decaying
fluorescent component to be independent of pressure. Its lifetime was found to be 120 ps for all of the levels investigated. Also, these workers observed that the long-lived component decayed more rapidly at higher pressures. However, this decay was not strictly exponential, and apparent lifetimes increased at longer delay times. Nonetheless, the early region of this slowly decaying fluorescence was used to determine a lifetime of 130 ns after excitation at the $S_1$ origin, a value smaller than reported by Frad et al.

The McDonald et al. results characterize the dephasing processes mentioned above for pyrazine’s “intermediate case” radiationless decay from the optically excited $S_1$ state. The rapidly decaying fluorescence corresponds to the dephasing of the pure $S_1$ states into mixed states. The long-lived fluorescence reflects the radiative plus nonradiative decay of these mixed states and their collisional conversion into pure triplet states. A comparison of the two fluorescence components indicates that these mixed states have mostly triplet character. This implies that pyrazine, prepared in the $S_1$ electronic state, becomes nearly pure triplet in nature within approximately 100 ps and entirely triplet in character within a collisional interval. An alternative view of this behavior has been presented by Amirav$^{20}$. He suggests that the two fluorescence components represent an inhomogeneous population of excited states that differ in their sub-rotational precessional quantum number, $K''$. Amirav's model implies that the $K'' = 0$ states behave in the small molecule limit, giving the slower component, while the more numerous $K'' \neq 0$ states decay in the statistical limit, resulting in the fast decay component. As will be discussed in later chapters, this view appears relevant to an unexpectedly fast component that is found throughout all of our decay kinetics.
The intersystem crossing process from the optically prepared $S_1$ state discussed above leads to the lowest lying triplet state of pyrazine, $T_1$. This $T_1$ state has also been the subject of previous studies\textsuperscript{18-33}. Direct optical excitation of the spin-forbidden $T_1 \leftrightarrow S_0$ transition in the gas phase has located the origin\textsuperscript{21} of the electronic system at 26,820 cm$^{-1}$. The decay kinetics of $T_1$ prepared by intersystem crossing has been measured by molecular beam photoionization, as well in Frad \textit{et al.}'s\textsuperscript{12} gas phase bulb studies, by Dietz \textit{et al.}\textsuperscript{28} and Knee and Johnson\textsuperscript{29}. These groups used laser photoionization to measure the decay of $T_1$ pyrazine following optical excitation of several of the $S_1$ state's well-defined vibrational levels. They found decay rates much higher than the bulb studies, with lifetimes under 1 $\mu$sec that varied with the $T_1$ vibrational energy content. It should be noted that the dominant decay mechanism for $T_1$ pyrazine is radiationless intersystem crossing from $T_1$ to $S_0$, which is indicated by the small phosphorescence yields in Frad \textit{et al.}'s work and the absence of any photochemistry\textsuperscript{21}. Thus, the variation in these $T_1 \rightarrow S_0$ lifetimes was attributed to the increase of the $S_0$ density of vibrational states with energy, which influences the $T_1 \rightarrow S_0$ intersystem crossing rate. In the collision-free environment of the molecular beam studies, the prepared $T_1$ state retains its initial vibrational energy until it either decays back to the $S_0$ state or is ionized by the probe laser. However, in the bulb work of Frad \textit{et al.} the vibrationally excited $T_1$ molecules undergo collisional deactivation during the observation period. The longer lifetimes in the bulb studies can be explained by smaller $T_1 \rightarrow S_0$ decay rates at these lower, thermalized vibrational energy levels. In extremely relaxing conditions, a low temperature solid solution of pyrazine, the phosphorescence decay lifetime is reported to be 19 msec\textsuperscript{30}. 
Spectroscopic absorptions originating in the T₁ state of pyrazine have been observed in both liquid and solid solution and in a molecular beam. Essentially the same transitions were detected between 200 and 900 nm in two principal regions of absorption. The first was in a range from 200 to 400 nm with a sharp peak at 260 nm, and the second ranged from 450 to 900 nm with some structure between 650 and 850 nm. The first gas phase observation of pyrazine transient absorption was performed previously in our laboratory in the region from 625 nm to 750 nm. The spectrum contained only broad, fairly weak features with a maximum near 690 nm. By analogy with the previous observations, this spectrum was assigned to the T₂(7), ← T₁ electronic transition of the vibrationally excited T₁ pyrazine. Note that the question mark implies disagreement between theoretical and experimental results concerning the exact locations of the higher triplet states.

1.2.2 Experimental Overview

Figure 1.1 is a schematic energy level diagram for pyrazine that helps to illustrate our experiments. The excitation process uses a tunable ultraviolet laser pulse to promote pyrazine into a well-defined vibrational level of the S₁ state. These levels consist of the 0⁰ origin at 30,876 cm⁻¹, the 6a¹ level at 585 cm⁻¹ above the origin, and the 8a¹ level at 1377 cm⁻¹ above the S₁ origin. As discussed earlier, this optically prepared state rapidly intersystem crosses into the T₁ vibrational manifold within approximately 100 ps. This monoenergetic intersystem crossing prepares the T₁ state with a vibrational energy content equal to the difference between the S₁ level and T₁ origin. This generates T₁ states containing 4056, 4641, or 5433 cm⁻¹ of vibrational energy content, depending on the
selected $S_1$ level. Creation of this $T_1$ state is monitored by a continuous diode laser that probes the $T_{2(7)} \leftarrow T_1$ transition at 676 nm. By measuring the absorption of the diode laser beam as a function of delay time after optical excitation, the decay kinetics of the $T_1$ state can be probed in our static gas phase samples under various collisional conditions.
Figure 1.1 Pyrazine energy level diagram describing the states and transitions involved in our experiments. Upward arrows denote optical absorptions, downward arrows denote collisional vibrational relaxation, and horizontal dotted arrows represent intersystem crossing processes. The varying lengths of the $T_1 \rightarrow S_0$ dotted arrows symbolize the vibrational energy dependence of this intersystem crossing rate constant.
Depending on the sample pressure conditions, we apply one of two data analysis methods. For moderate pressure conditions, above 1 torr of total pressure, our analysis determines the average vibrational energy loss per collision with a relaxer molecule as a function of the T₁ pyrazine's average vibrational energy content. With low pressure samples of less than 0.5 torr total, we analyze for the vibrational energy population distribution within T₁.

The first analysis begins with the determination of the collisional history of the T₁ → S₀ decay rate constant, based on the transient absorption decay kinetics and the known pressure conditions. An empirical calibration relationship between the T₁ decay rate constant and T₁ vibrational energy content then allows conversion into T₁ vibrational energy content as a function of collisional history. Numerical differentiation then leads directly to the average vibrational energy removed per collision as a function of number of collisions, which can be converted to an average vibrational energy dependence.

The second method involves determining the frequency distribution of T₁ → S₀ decay rate constants from the decay data using a kinetic model that contains several Gaussian components with adjustable amplitudes, widths, and center frequencies. Again, the empirical relationship between the T₁ decay rate constants and T₁ vibrational energies is used to map the decay rate constant distribution into a molecular vibrational energy distribution.
CHAPTER 2
DATA COLLECTION METHOD

2.1 Transient Absorption Apparatus

The method of transient absorption spectroscopy, sometimes called flash photolysis, is a pump-probe technique. A pulsed light source is first directed onto a sample of interest, thus creating a transient species through absorption. A second light source is then used to monitor the changes within the sample produced by the first light pulse. This work involves a pulsed excitation laser that generates tunable ultraviolet light pulses, while the probing laser is of the continuous-wave (CW) type, emitting in the red at 676 nm. Figure 2.1 displays a schematic diagram of the apparatus used in this work. The probe laser is used to measure the transient electronic absorption of the excited state molecule prepared by the excitation laser. The CW probe allows us to continuously monitor the presence of the excited state molecule by observing the attenuation of the probe laser intensity with a photodiode. This time-multiplexed method relies on the use of a digitizing oscilloscope to process the detected probe laser intensity. The detector output is fed to the oscilloscope and the resulting waveform is digitized and averaged over many excitation laser pulses. This averaged waveform provides us with the kinetic behavior of the excited sample, which is then passed to a computer for further data analysis.
2.1.1 Excitation Laser System

The excitation source originates in a commercial Q-switched Nd:YAG laser system. This Lumonics model YM-600 laser generates up to 700 mJ/pulse in the 1064 nm first harmonic emission at a repetition rate of 10 Hz. The YM-600 is electro-optically Q-switched to generate fundamental, 1064 nm light pulses with a duration of 8 ns. The first harmonic transverse beam profile is nearly Gaussian with a nominal beam diameter of 6 mm. The YM-600 incorporates a highly deuterated KD*P harmonic generation crystal which is capable of generating up to 340 mJ/pulse of 532 nm second harmonic light. The vertically polarized second harmonic green light exiting the YM-600 is used to pump a commercial dye laser system.
The Lumonics model HD-500 dye laser employs a Littman-type oscillator and a single amplifier stage, both of which are side-pumped. The dye solution used for these studies was a $5 \times 10^{-4}$ M solution of DCM (Exciton Corp.) in HPLC-grade methanol (Aldrich). The dye reservoir is equipped with a cooling coil to allow cooling of the dye solution for optimum power output and dye lifetime. Tuning of the dye laser emission is microprocessor controlled by a stepping motor and control keypad. As used in this work, the HD-500 dye laser system is tunable between 610 and 660 nm and generates pulse energies in the range of 30 to 50 mJ in a near-Gaussian beam approximately 1 to 2 mm in diameter with a pulse duration of 6 ns.

The red output beam of the dye laser travels approximately 5 m before being passed through a Galilean telescope consisting of two AR-coated lenses (Newport Research Corp.) of focal length +200 and -100 mm. This telescope corrects for the far-field divergence of the dye laser beam and reduces its size, enhancing the efficiency of frequency doubling in a KD*P crystal (Lasermetrics) immediately downstream from the telescope. The output of this second harmonic generator is a collimated ultraviolet beam, tunable between 310 and 324 nm, with an energy on the order of 1-2 mJ/pulse, a beam diameter of 3-4 mm, and a pulse duration below 6 ns. This UV light pulse is directed through our sample cell to generate the excited state molecules.

2.1.2 Probe Laser System

The probe source for these studies is a much simpler diode laser. The Power Technology Inc. model ACM15/1928 is a packaged diode laser system containing a Phillips 20 mW diode, model #2B2. Commercially packaged in a canister 5 cm in length
and 2.5 cm in diameter, the ACM diode laser system makes anamorphic and astigmatic optical corrections to emit a circularized, collimated CW beam at 676 nm with a diameter of approximately 4 mm and an output power of 15 mW. This probe beam is then overlapped in a co-propagating geometry with UV excitation beam in order to probe the volume of excited sample molecules.

2.1.3 Transient Absorption Optics

Figure 2.2 shows the optical layout used to overlap the probe and excitation laser beams within the sample cell. This layout has evolved into a rather complicated arrangement in an effort to remove any artifactual induced transient signals produced in optical elements. The current setup achieves overlap of the excitation and probe beams only within the sample cell but not in any optical material or coating along the beam paths. Immediately after the UV light is generated, a steering prism directs the excitation beam through a fused silica equilateral dispersing prism, which separates it from residual dye fundamental light. Just as a dispersing prism is used to spatially separate laser beams of different wavelengths, it can be used to combine two beams if they are directed into the prism at the appropriate angles so that refractive dispersion results in their exit from the prism in a collinear, co-propagating spatially overlapped geometry. Thus a second dispersing prism is mounted near the entrance of the sample cell to direct the excitation beam into the sample cell. Simultaneously, a steering prism directs the CW probe beam (after passing through a Galilean telescope consisting of two AR coated lenses (Newport Research Corp.) of focal length +400 and -500 mm to reduce the beam diameter to approximately 2 mm) into this dispersing prism at the appropriate angle so that the two
laser beams overlap inside the sample cell. However, they cross at a small angle to keep them separated by *ca.* 2 mm at the exit and entrance windows. This near-collinear geometry avoids any excitation-induced transient signal from the optical material of the sample cell windows. After exiting the sample cell, a third dispersing prism is used to further separate the excitation and probe beams. A narrow beam stop blocks the excitation beam, while the probe beam is directed by turning mirrors onto the detection photodiode.

**Figure 2.2** Schematic diagram of the optical components used to combine then separate the excitation and probe beams, which creates spatial overlap within the sample cell.
As for the polarization orientations of the excitation and probe beams, they are perpendicular to one another. The excitation UV laser beam is vertically polarized throughout its beam path. The probe laser is mounted so that is it also polarized in the vertical direction. A 670 nm one-half wave zero-order retarder (Meadowlark Optics) is used early in the probe path to rotate the polarization 90 degrees, resulting in horizontal polarization of the CW 676 nm diode laser beam. It was found that the kinetic decay traces were independent of the polarization orientation, so the horizontal polarization arrangement of the probe beam was advantageous in that it reduced Fresnel reflection losses at the many dispersing prism faces along the beam path.

Other precautionary measures include the placement of an OG570 Schott filter immediately downstream of the diode laser. This prevents any back-reflected UV excitation light from entering the diode laser and disturbing its performance. Also, the probe beam must travel approximately 3 m after exiting the sample cell before reaching the detection system. Therefore, two converging lenses of focal length +800 mm and +100 mm are placed in the probe path downstream from the sample cell. The large focal length lens is near the sample cell exit to control divergence in the far-field path of the diode laser beam. The smaller lens is placed near the detection photodiode to focus the probe beam well within the photodiode active area. This lens’s main role is to compensate for any thermal lensing effects due to excitation heating of the sample, which might otherwise cause the probe beam to be partly deviated off of the photodiode active area. Finally, a 75% transmitting interference bandpass filter (CVI Laser Corp.), centered at
670 nm with a FWHM of 16 nm, is placed immediately prior to the detector to prevent stray light within the room from producing artifacts in the detected signal.

2.1.4 Probe Detection System

The CW diode laser probe beam is detected by an FND-100Q photodiode (EG&G) used in the photoconductive configuration, which has an active area of 5.1 mm². The photodiode is reverse-biased using a 90 V bias generated from ten 9 V batteries in series. The unamplified photocurrent is measured as a function time by a Tektronix Model TDS 744A 500 MHz digitizing oscilloscope. Because the photocurrent corresponding to the detected light level is low, a resistive external termination of 240 Ω is used instead of the 50 Ω internal termination of the oscilloscope. This arrangement allows us to increase the R value in V = iR. The value of i is fixed by the photocurrent generated by the diode laser beam’s intensity on the photodiode active area. By increasing R with the external terminator, we can increase the voltage magnitude of the detected signal, thereby improving amplitude resolution. The use of a larger termination does require a penalty in time response, but studies have shown consistent kinetic shapes at both termination settings. Also, the oscilloscope is set at a bandwidth-limit of 20 MHz to help filter out high frequency noise in the diode laser intensity and further improve the amplitude resolution.

2.2 Data Acquisition and Automation

The signal from the photodiode detector is a current source and is measured as a proportional voltage that is converted into digital form for computer processing. The
time-multiplexed mode of data acquisition used in these studies relies entirely on the
digitizing oscilloscope to process the detector signal. The photodiode detector output is
fed into the oscilloscope and the resulting waveform is digitized, averaged over repeated
excitation shots, and made available to a computer for induced absorbance calculations.

The oscilloscope has 8-bit digitizer voltage resolution for a single sweep over the
observation time range, but the resolution improves to 12 bits for an averaged signal. The
oscilloscope is used at a 1 GSample per second digitizing rate, allowing for signal
sampling at one digitizer point every nanosecond over a time range of 5000 ns. The
vertical voltage scale covers 10 divisions at a sensitivity of 2 mV/division. A vertical
voltage offset on the order of 700 mV is required to properly display the measured voltage
pedestal corresponding to the CW diode laser beam’s intensity. The averaged signal
12-bit resolution then provides for a minimal vertical granularity of approximately 5 μV.
The most valuable ability of the digitizing oscilloscope is acquiring a complete probe
waveform for each excitation laser shot, plus internally averaging up to 10,000
waveforms. This averaging is performed in firmware and requires no data transfer from
the oscilloscope to the computer. These capabilities enable fast data acquisition with
superior signal-to-noise ratios. Deep averaging reduces the random fluctuations inherent
in the probe diode laser intensity, particularly at high frequencies. Our waveform quality
makes it possible for us to resolve minute transient signals that would otherwise be
undetectable above the diode laser noise.

The digitization process is initiated by computer command through the
oscilloscope’s GPIB interface. Upon completion, the digitally averaged waveform is
transferred to the computer over the GPIB bus. This transferred waveform is in the form of an ASCII string of integers, which are converted to voltages using factors transferred separately from the waveform. In addition, the temporal information for the waveform is calculated using timebase conversion factors that are also transferred separately.

The experimental timing control for these measurements is very simple. Because the CW diode laser is a non-pulsed probe source, there is no need for synchronizing the timing between the firing of the excitation laser and the firing of a probe laser at an appropriate delay, as had been done in earlier work on this project. The trigger event for acquisition is the rising edge of a signal coming from the excitation monitor photodiode (EG&G, FND-100Q, 9V battery bias), as seen in Figure 2.1. This trigger event defines the zero time delay for the experiment, but data at negative time delays can be recorded because the oscilloscope continuously monitors and digitizes the probe diode laser intensity. This capability allows for accurate determination of the absorbance zero while allowing the time zero to be accurately synchronized with the excitation laser pulse.
Table 2.1 Experimental oscilloscope internal settings during data acquisition.

<table>
<thead>
<tr>
<th>Vertical</th>
<th>Horizontal</th>
<th>Trigger</th>
<th>Acquisition Mode</th>
</tr>
</thead>
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<td>Coupling</td>
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<td>Average</td>
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<td>500 ns/div</td>
<td>Pulse</td>
<td>1000</td>
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<td>Record length</td>
<td>Class</td>
<td>Repetitive signal</td>
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<tr>
<td>20 MHz</td>
<td>5000</td>
<td>Runt</td>
<td>ON</td>
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<tr>
<td>Vertical scale</td>
<td>Trigger position</td>
<td>Polarity</td>
<td>Stop after Single Acquisition</td>
</tr>
<tr>
<td>2 mV/div</td>
<td>10%</td>
<td>Positive</td>
<td>Sequence</td>
</tr>
<tr>
<td>Vertical offset</td>
<td></td>
<td>Thresholds</td>
<td>2.5 V to 3.0 V</td>
</tr>
<tr>
<td>≈700 mV</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vertical position</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The apparatus measures the probe laser absorption induced by the excitation laser through the creation of transient excited molecules. The time dependent induced absorbance is found by acquiring only two different waveforms, taken under conditions described in Table 2.1. These waveforms provide the intensities, I and I₀, used to calculate the induced absorbance of the excited sample from the following equation:

$$\Delta A'(t) = -\log \left( \frac{I(t)}{I_0(t)} \right)$$

Here, I₀(t) represents the time dependent intensity of the probe laser beam after passing through the ground state sample, the background, and I(t) is the time dependent intensity of the probe laser after passing through the excited sample, the signal. These intensity waveforms are known to contain contributions from electronic noise components, but the characteristics are identical in both waveforms so they are removed by the ratio in the induced absorbance calculation. Because of slight long term variations in the diode laser
intensity, we need to reference the induced absorbance to a zero level defined by averaging the pre-excitation induced absorbance values. The adjusted result is:

$$\Delta A(t) = \Delta A'(t) - \Delta A_{\text{ref}},$$

where $\Delta A_{\text{ref}}$ is the averaged negative time reference induced absorbance and $\Delta A(t)$ is the adjusted time-dependent induced absorbance.

All data acquisition and calculations are computer controlled and automated. An IBM-compatible 486 personal computer controls the experimental operation. The computer's internal GPIB card (CEC 488) links it with the digitizing oscilloscope and controls data transfers and instrumentation. The data acquisition code is entirely written in FORTRAN and proceeds through initializing instrumental settings, acquiring the waveforms, and then processing the data to calculate the time dependent induced absorbance. The data acquisition code first sets user-selectable parameters that define the data collection conditions, such as the timebase, the number of averages to perform, and the number of repetitions. After hardware settings are initialized, the background and signal waveforms are collected and stored to computer hard disk. For this, the computer initiates the multi-shot digitization average and then repetitively queries the oscilloscope until the average is complete. Then the computer transfers the averaged waveform from the oscilloscope queue into temporary files for later use in calculating the induced absorbance. The remainder of the code reads the averaged background and signal waveforms from the temporary files, calculates the time dependent induced absorbance, and writes that result into an output file in an appropriate file format.
2.3 Sample Handling

The sample cell is constructed of 25 mm dia. Pyrex tubing with window flanges made from 25 mm. dia. O-ring seal joints (Ace Glass Inc.). The cell is 50 cm long with an 18 cm extension attached via an O-ring joint giving a sample cell length of 68 cm. All valves are Ace Model 8194 “high vacuum” Teflon stopcock with O-rings of Ace Glass’s FEP fluoro-elastomer, which is highly resistant toward pyrazine. The cell is sealed at each end with slightly wedged (approx. 5 arc-minutes) 1.5 in. dia. fused silica windows (CVI Laser Corp.). The pressure within the cell is monitored by two capacitance manometers having operating ranges 0 to 10 Torr (MKS Instruments Inc. Model 221-AHS), and 0 to 1000 Torr (Datametrics Dresser Industries Inc. Model 600A-1000T-R12-H21X-4). The cell is connected through a 5 mm O-ring joint to the sample holder and through brass metering valves (Whitey Model B-21RS4) to buffer gas tanks or lecture bottles. The sample holder is constructed of a Ace Glass high vacuum valve which seals the sample container and allows addition of sample into the cell. The buffer gas connections are made with copper tubing and brass Swagelok fittings. The cell and sample and buffer gas manifolds are evacuated by a mechanical roughing pump (Precision Instruments Model DD-20) in conjunction with a 2 in. oil diffusion pump (Varian Associates). Typical vacuum levels in the cell are less than 0.1 mTorr with total pressure increase rates, including leaks and outgassing, of less than 0.1 mTorr per minute.

The pyrazine sample (Aldrich Chemical Co.) has a stated purity of 99+%. Upon loading the sample container with pyrazine, it was subjected to several freeze-pump-thaw cycles using liquid nitrogen. In addition, at least one freeze-pump-thaw cycle was
performed each day prior to use to remove any leaked atmospheric gases. Table 2.2 describes the purity and vendor for each of the buffer gases used in these studies.

**Table 2.2** Stated purities of the buffer gases used in these studies.

<table>
<thead>
<tr>
<th>Buffer Gas</th>
<th>Purity(%)</th>
<th>Vendor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>99.999</td>
<td>Matheson Gas Products</td>
</tr>
<tr>
<td>Neon</td>
<td>99.999</td>
<td>Cryogenic Rare Gas</td>
</tr>
<tr>
<td>Argon</td>
<td>99.998</td>
<td>Big Three Industries</td>
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<tr>
<td>Krypton</td>
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<td>Cryogenic Rare Gas</td>
</tr>
<tr>
<td>Xenon</td>
<td>99.995</td>
<td>Cryogenic Rare Gas</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>99.99</td>
<td>Matheson Gas Products</td>
</tr>
<tr>
<td>Deuterium</td>
<td>99.8</td>
<td>ISOTEC Inc.</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>99.995</td>
<td>Tri-Gas Industrial Gases</td>
</tr>
<tr>
<td>CO</td>
<td>99.5</td>
<td>Matheson Gas Products</td>
</tr>
<tr>
<td>CO₂</td>
<td>99.8</td>
<td>Matheson Gas Products</td>
</tr>
<tr>
<td>CH₄</td>
<td>99.0</td>
<td>Big Three Industries</td>
</tr>
<tr>
<td>H₂O</td>
<td>OmniSolv</td>
<td>EM Science</td>
</tr>
</tbody>
</table>
CHAPTER 3
DATA ANALYSIS FOR AVERAGE ENERGY LOSS

3.1 Overview

Our experiments involve the preparation of vibrationally excited triplet state pyrazine via intersystem crossing for a laser-excited $S_1$ state. Triplet-triplet optical absorption is then used to determine the population decay kinetics of this triplet state under intermediate buffer pressures. The population decay kinetics must first be corrected for changes in the pyrazine $T_1$ molar absorptivity, which is deduced from high buffer pressure kinetics. These corrected decay kinetics are analyzed to obtain the collisional dependence of the unimolecular triplet decay rate constant. Prior knowledge of the vibrational energy dependence of the decay rate constant is used to deduce the triplet sample’s vibrational energy content as a function of collision. This allows for the deduction of the rate of energy removal per collision as a function of collision or of vibrational energy content. This chapter provides representative results and describes in detail the Competitive Radiationless Decay (CRD) method for obtaining collisional vibrational energy removal rates from raw kinetic data.

3.2 High Buffer Pressure Kinetic Scans

The emission of the 676 nm probe diode laser falls within the broad red band of pyrazine’s $T_n \leftarrow T_1$ triplet-triplet absorption, providing us with a means to determine the time-dependent total triplet concentration. Under our experimental collisional conditions, vibrational relaxation occurs and redistributes the sample population to vibrational levels
with different molar absorptivities at our probe wavelength. This results in a variation of the triplet population's average molar absorptivity during collisional deactivation.

Absorbance, in a Beer's law representation, can be defined as the product of the path length, the triplet concentration, and the effective molar absorptivity. To deduce the triplet concentration from the measured induced absorbance, we must first find the collisional change in pyrazine's effective $T_n \leftarrow T_1$ molar absorptivity. For this purpose we measure the time-dependent transient absorbance of pyrazine with high buffer pressures, at which the population decay is very small. Figure 3.1 provides an example of a typical kinetic trace. At higher pressures, the induced absorbance increases with time following the excitation period. This effect implies that either more absorbing molecules are being created or that the molecules present are beginning to absorb more strongly. The loss of the triplet population through intersystem crossing back to the ground state is in the statistical limit, thus ruling out the possibility of a slow return of the triplet population. This increase in the transient absorbance is therefore due to the triplet population's increasing effective molar absorptivity with time. Another way of expressing this effect is that as the average vibrational energy content is collisionally reduced, the triplet population finds itself in lower vibrational energy levels with different, and apparently larger, Frank-Condon factors for the electronic transition we are probing.
3.2.1 Collisional Dependence of the Triplet-triplet Molar Absorptivity

Our measured triplet-triplet transient absorbance kinetics can initially be considered as a competition between the radiationless decay back to the ground state and collisional deactivation which slows the radiationless decay. This simplicity is disrupted by the increase in the molar absorptivity for the $T_n \leftarrow T_1$ transition with the collisional deactivation. The kinetic trace in Figure 3.2 demonstrates the factors within this competition. After its creation near the zero of probe delay, the triplet population initially decays rapidly, but then slows as collisions relax the population to lower vibrationally energy levels whose radiationless decay rate to the ground state is slower. However, as this vibrational relaxation progresses, the population begins to absorb more strongly at
676 nm, and we see a gradual increase in induced absorbance around 1500 ns. In order to remove the variation of the molar absorptivity with time, we use higher pressure transient absorbance results such as shown in Figure 3.1. Here, the kinetic shape is the result of collisions occurring rapidly enough to quickly relax the triplet population to the lowest vibrational energy levels where the radiationless decay rates are very small and the transient absorbance kinetics are dominated by the change in the effective triplet-triplet molar absorptivity. By kinetically modeling this high buffer pressure data, we can obtain a smooth representation for the time dependence of the molar absorptivity.

![Graph of induced absorbance vs probe delay](image)

**Figure 3.2** Pyrazine transient absorption kinetics under intermediate buffer pressure. (0.02 torr pyrazine plus 5.0 torr xenon with 8a\(^1\) excitation)

For the kinetic modeling, we have a general purpose computer program, written in Microsoft FORTRAN for a PC environment, for fitting kinetic data using the Marquardt
algorithm to fit parameters of a selected kinetic model to kinetic data so as to minimize the weighted least-squares error. We have provided this RBWFTT program with the following kinetic model:

\[ A_1 \xrightarrow{k_1} S_0 \]
\[ A_1 \xrightarrow{k_2} A_2 \xrightarrow{k_3} A_3 \xrightarrow{k_4} A_4 \xrightarrow{k_5} A_5 \]

where species \( A_n \) represents a triplet molecule in a particular range of vibrational energy levels with an associated molar absorptivity and \( S_0 \) is the non-absorbing singlet ground state. Here, \( k_1 \) represents the initial radiationless decay constant of the triplet population back to the ground state. Constants \( k_2 \) through \( k_5 \) represent collisional processes that remove vibrational energy to produce a triplet species with a different molar absorptivity. Because radiationless decay is significantly rapid only at the higher vibrational energy contents, only species \( A_1 \) is given a channel back to the ground state. The starting parameters for the relative absorptivities begins with species \( A_1 \) at 1.0 and the remaining \( A_n \) at higher values to reflect the stronger absorption of the collisionally relaxed molecules. The initial estimates for the first-order rate constants, \( k_i \), give fairly large values to \( k_2 \) through \( k_4 \) with a relatively smaller value for \( k_5 \). Table 3.1 gives an example of the starting parameters used to model the kinetic trace in Figure 3.1.

<table>
<thead>
<tr>
<th>Table 3.1</th>
<th>Initial parameters for fitting the high buffer pressure kinetics in Figure 3.1. (0.02 torr pyrazine plus 100 torr xenon with 8a¹ excitation)</th>
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</thead>
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<tr>
<td>Molar Absorptivity, ( C_i )</td>
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<tr>
<td>Rate Constant, ( k_i )</td>
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</tr>
<tr>
<td>Initial Concentration, ( I_i )</td>
<td>1</td>
</tr>
</tbody>
</table>
The parameters varied in the fit, denoted by the \( v \) subscript, are optimized by the Marquardt routine to minimize of the value of \( \chi^2 \). The shape defined by the parameters is first convoluted with an experimentally determined instrument response function to generate a fit that is compared to the kinetic data to determine the \( \chi^2 \) value, which reflects the mean squared difference between the fit and the kinetic trace. Upon convergence of the iterative parameter adjustments, the quality of the fit can also be inspected by viewing residuals generated by the RBWFIT routine. Much attention is paid to the region of the decay near zero time to insure we have properly set the data file's time origin.

![Graph](image)

**Figure 3.3** The line represents the optimized kinetic model fit of the data in Figure 3.1. (0.02 torr pyrazine plus 100 torr xenon with 8a\(^1\) excitation)

Figure 3.3 shows the data in Figure 3.1 along with a high quality kinetic fit typical of our analysis. The resulting fit provides a smooth representation of the kinetic shape from the
high buffer pressure conditions. Although, the shape of the data is mostly due to the increase in the sample's average triplet-triplet molar absorptivity, there are also minor contributions from population loss and from the instrument response function. To correct for the latter effect, a new fit is manually generated with the optimized parameters, but without convoluting with our experimentally determined instrument response function. This new shape, shown in Figure 3.4, is a first approximation to the underlying time-dependence of the molar absorptivity, but it does not account for the small amount of unimolecular loss through $T_1 \rightarrow S_0$ radiationless decay. In order to generate a shape that properly defines the variation in the molar absorptivity, we must remove any component in the curve of Figure 3.4 due to this population loss. The iterative method used for this removal will be described in the next section. Its starting point is the result of Figure 3.4, in which the molar absorptivity normalized to 1.0 at zero time. Through use of a bimolecular collision frequency, expressed as the product of the Lennard-Jones rate constants, $k_{L-J}$, and the pressure of the added buffer gas, we convert this time-dependence of the molar absorptivity to the collisional dependence shown in Figure 3.5. (Lennard-Jones rate constants were calculated as shown in Hippler et al.\textsuperscript{34}. Lennard-Jones parameters reported therein were used for the relaxer gases, while parameters for pyrazine were available from previous work on this project.\textsuperscript{5}) With this information we can correct the absorbance kinetics in Figure 3.2 for the changing molar absorptivity, leaving the true triplet population kinetics.
Figure 3.4  Time-dependence of relative pyrazine molar absorptivity with 100 torr of xenon as a collision partner. The curve is generated using parameters from the fit in Figure 3.3.

Figure 3.5  Collisional dependence of the relative molar absorptivity with xenon. The curve is created by scaling the x-axis of Figure 3.4 by the known collision frequency.
3.3 Intermediate Buffer Pressure Kinetic Scans

The kinetic trace in Figure 3.2 is an example of raw transient absorbance data suitable for our analysis. The criteria followed for acceptable kinetic shapes requires the asymptotic slow decay to be at an amplitude approximately half that of the peak induced absorbance signal. This is found to require on the order of 2-5 torr of buffer pressure for the relaxer gases used in these studies. It is data from these collisional conditions that are used to determine the collisional dependence of the radiationless $T_1 \rightarrow S_0$ decay rate. This information is used to iteratively correct the first approximation for the collisional dependence of the molar absorptivity, until convergence is reached. This converged variation of the molar absorptivity is then used in the refined analysis of data such as in Figure 3.2 to give the true triplet population as a function of time. For such triplet population kinetics we find the collisional dependence of the radiationless decay rate constant, which is then converted into a collisional dependence of the triplet vibrational energy content using a calibration connecting radiationless decay rate and energy content. By calculating the derivative of the vibrational energy content vs. collision number, we obtain energy loss per collision vs. collision number. Finally, the energy loss per collision is plotted as a function of the pyrazine triplet vibrational energy content.

3.3.1 Iterative Correction for the Variation in the Molar Absorptivity

As discussed above, the high buffer pressure kinetic data provides a first approximation to the collisional dependence of the molar absorptivity. With this information we can extract the approximate triplet population kinetics from our observed
transient absorbance data. This is done by simply dividing the raw kinetic trace, Figure 3.2, by this first approximation to the variation in the molar absorptivity shown in Figure 3.5. In this procedure we first account for any time offset in the intermediate pressure data to correct the definition of the experimental time zero. We then scale the collision axis of the absorptivity curve by an appropriate collision interval, given by the reciprocal of the product of $k_{L,J}$ and the intermediate partial pressure of the buffer species. This scaling puts the two curves on the same time basis. We can then divide the intermediate pressure data by the absorptivity function. This result, shown in Figure 3.6, is our first approximation for the time dependence of the relative triplet population. Recall, however that our high pressure data actually includes some loss of triplet population, so our correction has not provided us with the exact triplet population kinetics. However, we can use this approximate result to estimate the collisional dependence of the triplet radiationless decay rate constant using a procedure that will be described in detail in Section 3.3.2, and then go back to correct the molar absorptivity variation in order to obtain a refined view of the triplet population kinetics.
To correct the molar absorptivity function, we need to consider loss of triplet population at the high buffer pressure conditions. The total loss of population at any time is equal to the integral of the collisionally-varying radiationless decay rate. This integral, representing the converging total population loss as a function of number of collisions, can be added to our first approximation to the molar absorptivity function to account for the loss mechanism. In this procedure we first scale the x-axis of the decay rate vs. collision number curve by an appropriate Lennard-Jones collision interval, $k_{LJ}$ divided by the high buffer pressure, to match the time axis of the original molar absorptivity curve, before it was converted to a collisional dependence. We then numerically integrate the horizontally scaled decay rate vs. time curve. After vertical scaling to correct units, this integral is
added to the time dependent molar absorptivity function. This correction removes the
effect of population loss. Figure 3.7 displays the effect this correction has on the first
approximation to the absorptivity function. Note that the correction increases the
steepness of the initial rise. This can be easily understood, because the uncorrected
shape's initial slope is artificially lowered from triplet population loss at early times, before
the triplets are collisionally stabilized. Thus, the correction removes this error resulting in
a shape that better describes the true variation in average molar absorptivity. We repeat
this cycle of corrections until convergence is reached in the absorptivity function. In this
iterative procedure, the initial corrected absorptivity function is used to re-correct the
original intermediate pressure data. Analysis provides a second, slightly refined shape for
the collisional dependence of the triplet radiationless decay rate. This radiationless decay
rate vs. collision number shape then provides a second-generation correction for the
absorptivity function, giving a new correction to the original intermediate pressure data,
which in turn produces a third decay rate vs. collision curve to perform a third correction
to the absorptivity function, and so on. It should be noted that convergence is normally
reached with the second iteration, that is only one correction to the absorptivity function is
needed. There is typically a negligible difference between the second and third corrections
to the absorptivity function. Once we have determined the converged shape of the
absorptivity function, it is used to analyze the intermediate pressure kinetic data. This
yields kinetics reflecting only the relative triplet population convoluted with our
instrument response function, which can be analyzed as described below to produce the
collisional dependence of the radiationless decay rate constant.
3.3.2 Collisonal Dependence of the Triplet Decay Rate Constant

Our objective in the analysis of the intermediate buffer pressure data is to determine the time variation of the radiationless decay rate constant. Because the $T_1 \rightarrow S_0$ intersystem crossing is a first-order process, the change in the pyrazine triplet population can be expressed by the following rate law expression:

$$ R = \left( \frac{d[T_i(t)]}{dt} \right)_{t'} = -k_1(t')[T_i(t)] $$

This expression solved for $k_1$ at time, $t'$ yields:

$$ k_1(t') = \left( \frac{1}{[T_i(t)]} \right) \left( \frac{d[T_i(t)]}{dt} \right)_{t'} $$

Figure 3.7 First approximation for the variation of the molar absorptivity compared to the corrected kinetics as discussed in the text.
Thus, the time dependence of the radiationless decay rate constant can be determined by calculating the time derivative of the triplet population kinetics at any delay time after preparation and then dividing by the population amplitude at that delay time. Because derivatives are very sensitive to noise in the data, we need to generate a smooth fit of the data to differentiate. We have found that the sum of six independent exponentials provides a flexible, accurate fit without introducing the bias of a specific kinetic model. Each exponential term is characterized by a relative amplitude coefficient and a decay constant, as shown below:

\[ [T_i(t)] = \sum_{i=1}^{6} C_i e^{-k_i t} \]

Again, we use the RBWFTT fitting program discussed in Section 3.2.1, with a decay function given by the exponential sum instead of integrated rate laws. Typical starting values for a fit are shown in Table 3.2.

<table>
<thead>
<tr>
<th>Table 3.2</th>
<th>Initial parameters for fitting the intermediate buffer pressure kinetics in Figure 3.8. (0.02 torr pyrazine plus 5.0 torr xenon with 8a1 excitation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exponential Term</td>
<td>1</td>
</tr>
<tr>
<td>Coefficient, ( C_i )</td>
<td>0.3</td>
</tr>
<tr>
<td>Decay Rate Constant, ( k_i (10^6 \text{ s}^{-1}) )</td>
<td>20</td>
</tr>
</tbody>
</table>

The decay corresponding to the sum of the exponential terms is first convoluted with our experimentally determined instrument response function and then compared to the measured triplet population kinetics. The Marquardt method optimizes the exponential parameters to produce a fit with a minimized \( \chi^2 \). Again, we carefully check for a proper
time offset in the data being fit. Figure 3.8 shows the fully corrected triplet population kinetics with the excellent 6-term exponential fit generated by the RBWFIT program.

![Graph](image)

**Figure 3.8** The line represents the optimized sum of exponentials fit of the true pyrazine triplet population kinetics extracted from Figure 3.2. (0.02 torr pyrazine plus 5.0 torr xenon with 8a1 excitation)

It should be noted that the large rate constant for the first exponential term is needed to adequately fit a rapid decay component apparent in the first ca. 20 ns. This initial fast decay is unexpected, but appears in all of our triplet population kinetics. We think that this feature is probably due to a small portion of the excited population that retains some of its singlet character rather than forming pure triplet states. The implications of this systematic effect on our analysis are discussed below. With a smooth representation of the triplet population, we can easily evaluate analytical derivatives from the sum of exponentials. This derivative at time t' divided by the population amplitude at that time yields the rate constant, k1, at time t'. This is equivalent to taking the logarithmic
derivative as a function of time. This resulting time variation of the radiationless decay rate constant, \( k_1(t^\prime) \), is shown in Figure 3.9. Using Lennard-Jones rate constants, \( k_{\text{LJ}} \), and the pressure of the added buffer gas, we can convert this time-dependence of the triplet decay rate constant to a collisional dependence as shown in Figure 3.10. This curve demonstrates the dramatic effect that collisions have on the nascent triplet states. Upon preparation, the triplet sample decays at a fast rate corresponding to its considerable vibrational energy content. As collisions occur, energy is removed, on average, from the triplet population. The average population decay rate constant then decreases to a rate that corresponds to the lower vibrational energy content. As collisions continue, the average decay rate constant continues to decrease until it eventually reflects the decay of a thermalized distribution.

![Graph](image)

**Figure 3.9** Time variation of the pyrazine triplet decay rate constant after preparation at the \( 8a^1 \) excitation level with xenon buffer gas.
Figure 3.10 Collisional variation of the pyrazine triplet decay rate constant after preparation at the 8a¹ excitation level with xenon buffer gas. Created by scaling the x-axis of Figure 3.9 by the known collision frequency.

The calculated $k_1$ vs. collision number curve should show a y-intercept equal to the collisionally unrelaxed rate constant, which of course depends on the amount of initially deposited vibrational energy. These nascent values are shown in Table 3.3, along with previous measurements. Such information is obtained from measuring the $T_1 \rightarrow S_0$ decay under collision free conditions, such as in Knee and Johnson's molecular beam measurements²⁹. In such cases, the pyrazine $T_1$ population retains the initially deposited vibrational energy content, resulting in an unchanging decay rate. Using an earlier apparatus in our laboratory, Bevilacqua⁵ found that low pressure pyrazine kinetics were adequately represented by a single exponential decay. However, with the improved accuracy and precision of our current data, we have determined that the $T_1 \rightarrow S_0$ decay is
not strictly single exponential. Nonetheless, the agreement with the molecular beam results suggests that our low pressure conditions provide a sufficient collision-free environment to obtain accurate results. Our reported values in Table 3.3 represent our measured collisionally unrelaxed decay rate constants, but the alternative method used in their determination will be discussed further in Chapter 4.

<table>
<thead>
<tr>
<th>$S_1$ level excited</th>
<th>$T_1$ Energy (cm$^{-1}$)</th>
<th>Knee and Johnson$^{29}$</th>
<th>Bevilacqua$^5$</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0^0$</td>
<td>4056</td>
<td>1.99</td>
<td>2.0 ± 0.2</td>
<td>1.99 ± 0.02</td>
</tr>
<tr>
<td>$6a^1$</td>
<td>4641</td>
<td>2.86</td>
<td>3.5 ± 0.3</td>
<td>3.01 ± 0.02</td>
</tr>
<tr>
<td>$8a^1$</td>
<td>5433</td>
<td>4.08</td>
<td>4.5 ± 0.5</td>
<td>5.01 ± 0.05</td>
</tr>
</tbody>
</table>

The example shown in Figure 3.10 is the result of data collected following excitation to the $8a^1$ level of the $S_1$ state, implying that the initial decay rate constant should be approximately $5.0 \times 10^6$ s$^{-1}$. However, inspection of Figure 3.10 shows that the initial $k_1$ is well above the value expected. This error is believed due to the presence of a small amount of residual singlet character, as mentioned above, which causes the initial population decay to be too steep. The derivative of this artifactual steep decay produces $k_1$ values that are too large at early delay times. After several collisions, sample molecules with this singlet character should be completely converted to the triplet state. Therefore, we remove the early points on the $k_1$ vs. collision number curve to avoid the distortion produced by the singlet component. In order to reconstruct the $k_1$ as a function of collision number curve at early collisions, we back-extrapolate a biexponential fit of the
truncated curve to zero collisions. This extrapolation is anchored at the zero collision value corresponding to the collisionally unrelaxed rate constant found independently for that excitation level. Figure 3.11 illustrates the corrected collisional history of the triplet radiationless decay constant compared to the original determination.

![Graph showing corrected collisional history of triplet decay rate constant](image)

**Figure 3.11** Corrected collisional history of the pyrazine triplet decay rate constant after excitation to the $8a^1$ level with xenon buffer gas, compared to original result of Figure 3.10.

3.3.3 The “Calibration Curve”

Now that we have a best estimate for the collisional dependence of the triplet decay constant, we want to convert that information into a collision dependence of the triplet vibrational energy content. To do this, we use an empirical relationship between the radiationless decay rate constant and the vibrational energy content. This “calibration curve”, shown in Figure 3.12, displays $k_1$, the $T_1 \rightarrow S_0$ decay rate constant, as a function
of the triplet population's vibrational energy content, $E_{\text{vib}}$. The data points, shown in Table 3.4, are a collection of $T_1 \rightarrow S_0$ radiationless decay constants measured at specific vibrational energy contents.

![Graph](image)

**Figure 3.12** The "calibration curve": pyrazine's $T_1 \rightarrow S_0$ intersystem crossing rate constant data as a function of its triplet vibrational energy content. The line represents the 5th order polynomial fit. (The error bars for the circles and triangles are comparable to the symbol size)
Table 3.4  Experimental values of pyrazine’s $T_1 \rightarrow S_0$ intersystem crossing rate constant as a function of $T_1$ vibrational energy content.

<table>
<thead>
<tr>
<th>$E_{\text{vib}}$ (cm$^{-1}$)</th>
<th>Rate Constant $(10^6 \text{ s}^{-1})$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$5.1 \pm 2.2 \times 10^{-4}$</td>
<td>a</td>
</tr>
<tr>
<td>473</td>
<td>$8.3 \pm 3.1 \times 10^{-4}$</td>
<td>a</td>
</tr>
<tr>
<td>620</td>
<td>$1.0 \pm 0.27 \times 10^{-3}$</td>
<td>a</td>
</tr>
<tr>
<td>980</td>
<td>$1.61 \pm 0.82 \times 10^{-3}$</td>
<td>b</td>
</tr>
<tr>
<td>1045</td>
<td>$2.33 \pm 1.14 \times 10^{-3}$</td>
<td>b</td>
</tr>
<tr>
<td>1145</td>
<td>$5.0 \pm 1.0 \times 10^{-3}$</td>
<td>c</td>
</tr>
<tr>
<td>1220</td>
<td>$6.06 \pm 1.1 \times 10^{-3}$</td>
<td>a</td>
</tr>
<tr>
<td>1458</td>
<td>$4.0 \pm 2.0 \times 10^{-2}$</td>
<td>d</td>
</tr>
<tr>
<td>1560</td>
<td>$4.17 \pm 1.0 \times 10^{-2}$</td>
<td>b</td>
</tr>
<tr>
<td>1626</td>
<td>$6.25 \pm 0.79 \times 10^{-2}$</td>
<td>a</td>
</tr>
<tr>
<td>1745</td>
<td>$0.111 \pm 0.026$</td>
<td>a</td>
</tr>
<tr>
<td>1760</td>
<td>$0.10 \pm 0.021$</td>
<td>a</td>
</tr>
<tr>
<td>3356</td>
<td>$0.87 \pm 0.30$</td>
<td>e</td>
</tr>
<tr>
<td>3656</td>
<td>$1.19 \pm 0.40$</td>
<td>e</td>
</tr>
<tr>
<td>4056</td>
<td>$1.99 \pm 0.02$</td>
<td>f</td>
</tr>
<tr>
<td>4641</td>
<td>$3.01 \pm 0.02$</td>
<td>f</td>
</tr>
<tr>
<td>5433</td>
<td>$5.01 \pm 0.05$</td>
<td>f</td>
</tr>
</tbody>
</table>

a) Ref. 35.  b) Ref. 35; uncertainty twice that reported.  c) Ref. 35; uncertainty three times that reported.  d) Ref. 35; used average of two near-degenerate energies.  
e) Ref. 29; assumed 20% uncertainty.  f) New values reported in this work.

Our experiments can determine these collision rate constants only at vibrational energy contents above 4056 cm$^{-1}$. The data from lower vibrational energy regimes are available from other research groups. Knee and Johnson$^{29}$ used photodissociated van der Waals complexes to measure the radiationless decay rate constant for $T_1$ pyrazine at two energies just below the $S_1$ origin. The remainder of the data below 1800 cm$^{-1}$ of vibrational energy was acquired by Sneh and Chesnovsky$^{35}$ through direct triplet excitation. We generated the smooth line through these three sets of data shown in Figure 3.12 through an uncertainty-weighted five-term polynomial fit. Not shown on the
The calibration curve in Figure 3.12 is a data point at 6000 cm$^{-1}$ of vibrational energy content and a decay rate constant of 6.5 x 10$^6$ s$^{-1}$. This manually placed data point helped to guide the polynomial fit more accurately through our data points, as well as to extrapolate the calibration curve beyond the vibrational energies experimentally investigated. This extension of the calibration was to accommodate measured $k_1$ data with initial decay rate constants exceeding those found for the collision-free data.

3.3.4 Collisional Energy Relaxation Rates

Since we want to convert decay constants into vibrational energy contents, we transpose the axes of the $k_1$ versus vibrational energy data in Figure 3.12 to generate a vibrational energy content versus $k_1$ curve shown in Figure 3.13.

![Figure 3.13](image)

**Figure 3.13** The transpose of the "calibration curve" shown in Figure 3.12; pyrazine's triplet vibrational energy content as a function of the $T_1 \rightarrow S_0$ intersystem crossing rate constant.
This provides a means to determine the energy corresponding to any decay rate constant by evaluating the curve in Figure 3.13 at the decay rate constant values in the corrected result in Figure 3.11. This re-mapping of the y-axis in Figure 3.11 is shown in Figure 3.14; it is the collisional history of the triplet pyrazine sample’s average vibrational energy content, \( \langle E_{\text{vib}} \rangle \). Most collisions will remove energy, but some will add energy to triplet pyrazine molecules, so the brackets denote an average over all sample molecules.

To deduce the amount of energy removed per collision, we simply differentiate the curve in Figure 3.14. A standard five-point numerical derivative algorithm\(^{41}\) is used to calculate the derivative. Figure 3.15 shows the result. Note that the energy removal y-axis is labeled as \(-\left(\frac{d\langle E_{\text{vib}} \rangle}{dZ}\right)\). We show the negative of the derivative because we are interested in the removal of vibrational energy from the triplet population, and the brackets again denote our determination of the average energy removal rate from the triplet population.
Figure 3.14  Deduced average vibrational energy content of $T_1$ pyrazine as a function of xenon collision number after the initial deposition of 5433 cm$^{-1}$ ($8a^1$ excitation) of vibrational energy.

Figure 3.15  Average vibrational energy loss from $T_1$ pyrazine per xenon collision as a function of xenon collision number after the initial deposition of 5433 cm$^{-1}$ ($8a^1$ excitation) of vibrational energy.
3.3.5 Vibrational Energy Dependence of the Average Vibrational Energy Loss per Gas Kinetic Collision

In Figure 3.15 we have arrived at the collisional dependence of the average energy loss per collision. What we seek is the vibrational energy dependence of this average energy removal. Note that Figure 3.14 contains an empirical relationship between average vibrational energy content and gas kinetic collision number. We can use this information in the same manner as the “calibration curve” to map the collisional x-axis of Figure 3.15 into the corresponding average vibrational energy content. This result, shown in Figure 3.16, is the information we are seeking: the vibrational energy dependence of the average vibrational energy removed from $T_1$ pyrazine per collision by an added buffer molecule. Although the experimental sample from which this figure is derived contained a mixture of xenon and pyrazine, the large donor-to-relaxer partial pressure ratio insures that the rate at which the triplet pyrazine collides with a xenon atom greatly exceeds the rate at which it encounters an unexcited pyrazine molecule. Therefore, any contributions to the collisional energy removal rate by rare collisions with pyrazine are assumed negligible. The omission of this correction differs from previous generations of the CRD method which made corrections to the deduced average energy loss curves for a small pyrazine contribution.

Because there are no other methods for measuring triplet energy loss, we must rely on internal checks to validate our CRD method. We find that energy loss curves deduced from replicate experimental runs agree within a few percent. In addition, energy loss curves measured for samples with different buffer or pyrazine pressure are consistent, and variations in the pyrazine-to-relaxer partial pressure ratio or total pressure have no
systematic effect on our results. The deduced energy loss curves are also found to be independent of excitation beam energy and size. It should also be noted that the near-collinear overlap of the excitation and probe beams discussed in Chapter 2 seems to produce no diffusional artifact in our kinetic data as judged by the agreement of the deduced energy loss curves with those obtained from collinearly overlapped kinetic data. This series of checks provides strong validation of the refined CRD method.

![Graph](image)

**Figure 3.16** Average vibrational energy loss from T1 pyrazine per xenon collision as a function of the average T1 vibrational energy content after the initial deposition of 5433 cm\(^{-1}\) (8a\(^1\) excitation) of vibrational energy.
CHAPTER 4

DATA ANALYSIS FOR VIBRATIONAL ENERGY DISTRIBUTIONS

4.1 Overview

It should be pointed out that in the previous chapter concerning energy removal rates, the radiationless decay constants and vibrational energy contents represented average values over the entire triplet population. Our experiment initially prepares the triplet population with a very narrow distribution of vibrational energy. This distribution quickly broadens at normal buffer pressures due to randomness in the amount of vibrational energy exchanged in each collision with a buffer molecule. Some collisions remove energy while others add energy to the $T_1$ pyrazine molecules. The previous method can only measure the change in this average vibrational energy content of an already broadened vibrational energy distribution. In order to better interpret and understand the relaxation process, we would like information about the time-dependent evolution of the vibrational energy population distribution for the relaxing pyrazine triplets. This chapter describes the first version of a new kinetics-based method for determining this distribution of vibrational energy contents.

Under very low buffer pressure conditions where very few collisions occur during the time scale of the observation, the initially narrow laser-prepared vibrational energy distribution is only slightly perturbed, so the decay deviates only slightly from the collisionally unrelaxed kinetic behavior, as shown in Figure 4.1. Due to the dependence of the radiationless decay rate constant on vibrational energy content, the population develops a distribution of decay constants corresponding to the underlying distribution of vibrational energies. Our analysis procedure attempts to recover this distribution of decay
components from the measured low pressure transient absorption kinetics. The decay rate constant distribution can then be converted into a vibrational energy distribution using the calibration relationship between decay constant and energy content. Thus, by extracting decay rate constant distributions from decay kinetics under different collisional conditions, we can observe changes in the narrowly prepared vibrational energy population distribution due to early collisional encounters.

![Graph showing induced absorbance vs probe delay for two conditions: 0.01 torr pyrazine alone and 0.01 torr pyrazine plus 0.3 torr helium.](image)

Figure 4.1 Pyrazine transient absorption decay kinetics in the absence of a buffer gas compared to decay kinetics in the presence of low pressures of helium. ($0^\circ$ excitation)

4.2 Implementation

4.2.1 Initial Analysis using CONTIN

There are numerical techniques available that use the inversion of the Laplace transform of a given kinetic decay, which is convoluted with an instrument response.
function, to determine the frequency distribution of exponential decay components present in the sample. Most recently, the maximum entropy method\textsuperscript{37} has been applied to the analysis of time-resolved pulse-fluorescence decay data in biochemical systems. Our first attempts at extracting a decay constant distribution from our data involved a program package called CONTIN\textsuperscript{38,39}, which has been widely used in the analysis of positron annihilation lifetime data\textsuperscript{40}. After the user provides data plus experimentally determined instrument response information through a reference file, CONTIN employs a constrained, regularized least-squares analysis to calculate a continuous frequency distribution of decay constants that is the most parsimonious solution consistent with the experimental data. (There are generally many distributions consistent with the data.) Our application of CONTIN was successful in fitting the $T_1$ decay data and generating the corresponding decay rate constant frequency distribution. The resulting distribution contained symmetric, Gaussian-like peaks located in appropriate regions of the decay constant spectrum. Unfortunately, CONTIN has no provision for entering an approximate solution at which to start the analysis, so it can converge on unrealistic solutions. Although we sometimes obtained plausible distributions, the consistency of outcomes from file to file was unacceptably poor. Therefore, this analysis procedure was abandoned and replaced by the method described below.

4.2.2 Analysis using a Gaussian Model

By application of a kinetic model containing Gaussian peaks along the decay constant axis with adjustable amplitudes, widths, and center positions, we were able to extract the radiationless decay rate constant distribution from the triplet population
kinetics under these low buffer pressure conditions. This decay rate constant distribution may then be easily converted into a molecular vibrational energy distribution using the "calibration curve" discussed in Section 3.3.3.

4.2.3 Example Gaussian Analysis

Rather than assuming that the collisionally unrelaxed triplet population kinetics follow a single exponential decay, as discussed in Section 3.3.2, it is more realistic to assume that some early collisional effects have slightly broadened the vibrational energy distribution of the triplet population, resulting in decay through an inhomogeneous distribution of single exponential components. The experimental signal, $S$, can be expressed by the following form:

$$\frac{S_t}{S_0} = \int e^{-kt} f(k) dk$$

where $f(k)$ is a distribution function of decay constants modeled as a sum of independent Gaussian peaks with width parameters $\sigma_i$ and center frequencies $k_i$, as shown below:

$$f(k) = \sum_i \frac{A_i}{\sigma_i \sqrt{\pi}} e^{-\frac{(k-k_i)^2}{\sigma_i^2}}$$

The kinetic model used for fitting decay constant distributions to experimental data is also incorporated into the RBWFIT fitting program. The Marquardt algorithm performs a weighted, nonlinear least-squares fit to the kinetic decay using the following model:

$$\frac{S_t}{S_0} = \sum_{peaks,i} \int \frac{A_i}{\sigma_i \sqrt{\pi}} e^{-\frac{(k-k_i)^2}{\sigma_{asy}^2}} e^{-kt} dk$$
where each \( k_i \) represents the center position of a decay rate peak, \( \sigma_i \) determines the width of that peak, and \( A_i \) is its amplitude. The presence of multiple Gaussian peaks in this model provides flexibility similar to that of CONTIN. The values of \( k_i \), \( \sigma_i \), and \( A_i \) are adjusted during fitting in order to minimize the \( \chi^2 \) value, which provides a quantitative measure of agreement between the data and the simulation. The \( \sigma_{asym} \) factor, defined by
\[
\sigma_{asym} = \sigma_i + H(k_i - k) \sigma_a,
\]
allows for some asymmetry to be applied to the dominant Gaussian feature. The \( H(k_i - k) \) expression is a Heaviside function that adds an incremental width, \( \sigma_a \), to only one side of the Gaussian peak, thus introducing the asymmetry. The integration over the Gaussian distributions were numerically calculated using Gauss’s integration formula for an arbitrary interval\(^{41}\). The abscissa and weight factors for 10th order Gaussian quadrature\(^{41}\) were written into the RBW FIT program to permit the numerical integration.

Fitting of the low buffer pressure data proceeds in much the same manner as has been described for the energy removal measurements. The fitting program is provided with the experimentally determined instrument response function for convolution with the generated fit before comparison with the kinetic data. A proper time offset is applied to the data to define the accurate time origin of the experiment. Initial estimates are entered for the Gaussian peaks’ centers, widths, and amplitudes. Typical values for these parameters are shown in Table 4.1 for the data in Figure 4.1. As suggested by the CONTIN results, at least three rate constant peaks are required to properly represent the triplet population kinetics under these low collisional conditions. The first peak is assumed to be the dominant feature and corresponds to the collisionally unrelaxed
"single exponential" decay rate constant previously listed in Table 3.3. The peak at the small rate constant accounts for the slow decay component apparent at the later delay times. The presence of this component was unexpected for low pressure data, but it was found to be necessary to adequately fit the decay kinetics. Finally, a peak at a high decay constant is required to account for the fast decay features evident at very early delay times, as discussed in Section 3.3.2.

Table 4.1 Initial Gaussian method parameters for fitting the low buffer pressure kinetics in Figure 4.1. (0.01 torr pyrazine plus 0.3 torr helium with O³ excitation)

<table>
<thead>
<tr>
<th>Gaussian Peak</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amplitude, A_i</td>
<td>1.0</td>
<td>0.01</td>
<td>0.1</td>
</tr>
<tr>
<td>Center Rate Constant, k_i ( (10^6 \text{ s}^{-1}) )</td>
<td>2.0</td>
<td>0.2</td>
<td>20</td>
</tr>
<tr>
<td>Width, ( \sigma_i ) ( (10^6 \text{ s}^{-1}) )</td>
<td>0.5</td>
<td>0.01</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Figure 4.2 shows the excellent fit to the population data that typically results after optimization of the parameters, which then define the radiationless decay constant distribution through which the triplet population is decaying. The deduced rate constant distribution is shown in Figure 4.3., except for the highest frequency peak, which we assign to singlet rather than triplet decay. Figure 4.3 illustrates that most of the triplet population is decaying with rates near \( 2.0 \times 10^6 \text{ s}^{-1} \). From the optimized parameter defining the center of this dominant Gaussian feature, we obtain the \( T_1 \rightarrow S_0 \) decay rate constant value shown in Table 3.3. The deduced decay constant distribution also indicates that some small fraction of the triplet population is decaying at a much slower rate near \( 0.2 \times 10^6 \text{ s}^{-1} \).
Figure 4.2 The line represents a Gaussian method fit to the helium buffered data in Figure 4.1. (0.01 torr pyrazine plus 0.3 torr helium with $0^\circ$ excitation)

Figure 4.3 Resulting decay rate constant distribution generated from the optimized Gaussian parameters from the fit in Figure 4.2. (0.01 torr pyrazine plus 0.3 torr helium with $0^\circ$ excitation)
4.2.4 The "Calibration Curve", Revisited

Now that we have obtained the distribution of triplet decay rate constants, we want to convert that information into a distribution of the triplet vibrational energy contents. Recall that the "calibration curve" in Figure 3.12 provides an empirical relationship between the triplet radiationless decay rate constant and the triplet vibrational energy content. The polynomial parameters from the fit in Figure 3.12 provide an analytical expression for the radiationless decay constant as a function of vibrational energy content, \( k_1 = f(E_{vb}) \). In order to calculate the vibrational energy content from a corresponding rate constant, we again transpose the "calibration curve" as shown in Figure 3.13. Rather than using an interpolation procedure as described in Section 3.3.3, a smooth fit of the transposed "calibration curve" data was generated using a modified polynomial function, as shown in Figure 4.4. The modified polynomial parameters then provided an analytical expression for the vibrational energy content as a function of the decay rate constant, \( E_{vb} = g(k_1) \). This result allows us to convert the x-axis in Figure 4.3 from rate constant to vibrational energy content.
4.2.5 Distribution of the Triplet Vibrational Energy Content

The result of mapping the decay rate constant distribution into a triplet vibrational energy distribution is shown in Figure 4.5. Note that the distribution seems narrower over the vibrational energies compared to the rate constants. This is due to the steepness of the "calibration curve" in the region of vibrational energy contents for our experiments. That is, the rate constants undergo a considerable change over a small change in vibrational energy content. It should also be noted that a scaling was applied to the vertical axis of the rate constant distribution during the conversion to the vibrational energy distribution in order to maintain normalized amplitudes. Our decay constant distribution, denoted by $f_{r}(k)$, can be viewed as the probability of finding the decay rate constant within the
range \( k \pm dk \). By definition, then \( \int f_k(k)dk = 1 \). Similarly, normalization of our vibrational energy distribution, \( f_e(E) \), leads to \( \int f_e(E)dE = 1 \). By equating these two expressions, we find that the derivative of the “calibration curve”, \( \left( \frac{dk}{dE} \right) \), provides a varying scaling factor between the rate constant and vibrational energy amplitude distribution functions. Because we can more easily determine the derivative of the transposed, \( E_{\text{ vib}} = g(k) \), “calibration curve”, the y-axis of the \( f_k(k) \) is divided by \( \left( \frac{dE}{dk} \right) \) after the x-axis has been mapped into vibrational energy. Our result, displayed in Figure 4.5, is view of the pyrazine’s vibrational energy distribution averaged over the characteristic time interval of the kinetic measurements. Because our method does not take a “snapshot” of the vibrational energy distribution, the result is essentially an integration over the evolution of the vibrational energy distribution from initial preparation through the end of our observation time window. Nonetheless, we can experimentally monitor the shape of the triplet vibrational energy content distribution and deduce some collision-induced changes. The implications of the \( T_1 \) pyrazine vibrational energy distribution results and their relation to the vibrational energy loss measurements will be discussed later.
Figure 4.5 Vibrational energy population distribution deduced from the rate constant distribution in Figure 4.3.
CHAPTER 5
RESULTS AND DISCUSSION

5.1 Average Vibrational Energy Loss per Collision vs. Vibrational Energy Content

The data analysis method described in Chapter 3 was applied to time-resolved absorption data collected from vibrationally excited T\textsubscript{1} pyrazine in the presence of 12 buffer gases: helium, neon, argon, krypton, xenon, hydrogen, deuterium, nitrogen, carbon monoxide, carbon dioxide, methane, and water. It should be noted that the results from this series of relaxer molecules generate a valuable database of the first quantitative measurements of collisional vibrational relaxation of a triplet state polyatomic molecule. Using helium as our standard relaxer molecule in the refining of the CRD method, we initially prepared T\textsubscript{1} pyrazine with three different amounts of vibrational energy, 4056 cm\textsuperscript{-1} (0\textsuperscript{0}), 4641 cm\textsuperscript{-1} (6a\textsuperscript{1}), and 5433 cm\textsuperscript{-1} (8a\textsuperscript{1}). Figure 5.1 shows the results obtained for these three initial T\textsubscript{1} vibrational energy contents. If our method is reliable, then the vibrational energy losses measured with these three different initial excitation levels should agree over their range of overlap. The excellent consistency seen in Figure 5.1 provides validation of our method and shows that there should be no need to routinely study a variety of excitation levels. Therefore, for the remaining relaxers, we worked at the 8a\textsuperscript{1} level of optical excitation (5433 cm\textsuperscript{-1} of initial vibrational energy) in order to extend our observation window to the highest vibrational energy contents.
Figure 5.1 Average vibrational energy content removed per helium collision from vibrationally excited $T_1$ pyrazine as a function of the average $T_1$ vibrational energy content after the initial deposition of three different vibrational energy contents: 4056 cm$^{-1}$ ($0^6$), 4641 cm$^{-1}$ ($6a^1$), and 5433 cm$^{-1}$ ($8a^1$ excitation).

Figures 5.2 through 5.5 display the rates of collisional energy removal from vibrationally excited $T_1$ pyrazine for the various relaxer species studied. Note that the general shapes of these curves have strong similarities. There is a very steep dependence of the average energy loss on the average energy content within the range of energies between approximately 1800 cm$^{-1}$ and the maximum initial energy content of our experiments, $\approx$5500 cm$^{-1}$. This approximately linear dependence follows the trends found in other studies$^{2,3,42,43}$, but is much steeper in slope than reported for those systems. This steep slope describing the energy removal rate abruptly approaches zero near 1800 cm$^{-1}$ for each of the curves. It appears that as the triplet population is relaxed to a vibrational
energy content in this threshold region, it becomes resistant to further collisional energy removal. The noticeable trend among collision partners is an increase in the collisional relaxation efficiency with increasing mass and complexity of the relaxer.

![Graph showing rate of collisional energy removal from vibrationally excited T₁ pyrazine relaxed by the inert gases.](image)

**Figure 5.2** Rate of collisional energy removal from vibrationally excited T₁ pyrazine relaxed by the inert gases. (8a¹ excitation).
Figure 5.3 Rate of collisional energy removal from vibrationally excited \( T_1 \) pyrazine relaxed by the diatomics, hydrogen and deuterium. (8a' excitation).

Figure 5.4 Rate of collisional energy removal from vibrationally excited \( T_1 \) pyrazine relaxed by the diatomics, nitrogen and carbon monoxide. (8a' excitation).
Figure 5.5  Rate of collisional energy removal from vibrationally excited T₁ pyrazine relaxed by the small polyatomics. (8a¹ excitation).

In an effort to parametrize the removal rate effectiveness, Table 5.1 contains the slopes corresponding to a linear fit of the nearly linear regions of the curves in Figures 5.2 through 5.5. This slope represents the fraction of the donor's energy above the threshold energy removed per collision.
Table 5.1  Quantitative expression of relaxer effectiveness determined by a linear fit of the energy removal rate curves in Figures 5.2 through 5.5.

<table>
<thead>
<tr>
<th>Relaxer Molecule</th>
<th>Fraction of energy removed per collision (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.12</td>
</tr>
<tr>
<td>H₂</td>
<td>1.49</td>
</tr>
<tr>
<td>Ne</td>
<td>1.90</td>
</tr>
<tr>
<td>D₂</td>
<td>2.03</td>
</tr>
<tr>
<td>N₂</td>
<td>2.97</td>
</tr>
<tr>
<td>Kr</td>
<td>3.17</td>
</tr>
<tr>
<td>Ar</td>
<td>3.31</td>
</tr>
<tr>
<td>Xe</td>
<td>3.82</td>
</tr>
<tr>
<td>CH₄</td>
<td>3.98</td>
</tr>
<tr>
<td>CO</td>
<td>4.15</td>
</tr>
<tr>
<td>CO₂</td>
<td>6.47</td>
</tr>
<tr>
<td>H₂O</td>
<td>19.97</td>
</tr>
</tbody>
</table>

Before comparing pyrazine's triplet state collisional relaxation with previous studies of pyrazine's ground electronic state vibrational relaxation, I would like to consider in detail the implications of the individual triplet state results for the collisional vibrational relaxation mechanism.

5.1.1 The Rare Gas Series

Figure 5.2 shows the vibrational energy removal rates from T₁ pyrazine by the inert gases. Because collision partners in this series are atoms, the only vibrational energy transfer processes are vibrational to translational or rotational, V → T,R. This is not to say that the noble gas leaves the collision with rotational energy, but the recoil from the collision may change the pyrazine molecule's rotational state, thus converting vibrational energy into rotational energy within the pyrazine molecule. A comparison of the inert gas
series results provides information on the role that the mass of the collision partner plays in vibrational relaxation. As the mass of the inert gas atom increases, its effectiveness in relaxing the T₁ pyrazine increases. Using the slopes as a measure of effectiveness, neon is approximately 1.7 times more effective than helium. This increase of 1.7 is also seen in comparing argon to neon. However, this trend does not persist when continuing to krypton and xenon, as these two appear to have nearly the same effectiveness as argon.

There exists the possibility of forming "collision complexes" which are favored by the greater polarizability of the donor's open shell excited triplet state. Also, it is known that the polarizability of the noble gases increases steadily with increasing atomic number⁴⁴. Consider the following relationships concerning a triplet state pyrazine-inert gas collision. The more massive the collision partner, the more slowly it approaches the pyrazine molecule and the stronger its long-range attractive interactions. The slower this approach, the longer the inert gas atom remains in the proximity of the pyrazine. If a short-lived "collision complex" is formed in this way, energy can be readily coupled from pyrazine vibrational, translational, and rotational modes. This view would imply that the mass of the collision partner reflects its effectiveness at energy removal. However, a limit appears to have been approached in the case of argon. Thus, the argon collisional relaxation results may indicate the maximum average amount of energy that can be transferred via the V → T,R energy transfer channel.

Our experimental results are in disagreement with the predictions of a widely accepted model of impulsive vibrational relaxation by Schwartz, Slawsky, and Herzfeld (SSH)⁴⁵. The SSH theory suggests that the less massive relaxer molecules will
be more effective because they travel at higher speeds. This higher speed allows the collision partner to approach the donor, encounter the repulsive wall, and then recoil on a time scale more similar to that of a molecular vibrational period. Because the time scale of a vibration is much faster than most translational encounters, the lighter collision partners provide enough time scale overlap for enhanced vibrational energy removal.

5.1.2 Hydrogen and Deuterium

Figure 5.3 shows the results for H₂ and D₂ as relaxer molecules. These diatomic molecules introduce the possibility of V → V energy transfer into vibrational energy of the collision partner, in addition to the V → T,R processes. However, the lowest vibrational frequencies for H₂ and D₂ are 4159 and 2990 cm⁻¹, respectively⁴⁶. It is therefore very unlikely for these high vibrational modes to become activated by the pyrazine donor, as this would require the removal of essentially all of the donor’s vibrational energy. This is supported by the presence of the faster decay rates in our transient absorption kinetics. If the triplet population were completely thermalized in a few collisions, we would observe only very slow decay rates. This indicates that this V → V energy transfer process may not be playing a role in the vibrational energy removal. Even though hydrogen has less mass than helium, we find that it is a more effective relaxer by ≈33%. This seems to imply that the V → R process is being enhanced by transfer to the rotational mode of H₂, thus facilitating energy transfer. In our “collision complex” view, a collision with hydrogen should occur rapidly, allowing little chance for complex formation and efficient V → T transfer. However, its ability to remove considerable vibrational energy from the triplet molecules suggests that the V → R transfer plays an important role in the mechanism for
triplet vibrational energy relaxation. Although deuterium has the same mass as helium, we find it to be approximately twice as effective for vibrational relaxation. This again suggests the role of the \( V \rightarrow R \) mechanism in the collisional energy removal.

The hydrogen and deuterium results allow us to compare relaxer molecules with similar electronic characteristics but different vibrational and rotational level structures. We find that deuterium is approximately 1.4 times as effective a relaxer as hydrogen. This factor is unlikely due to the mass difference, based on the results of the inert gas series. With the vibrational modes of both relaxers unlikely to participate, this would imply that the lower rotational constant of deuterium, approximately half that of hydrogen\(^{46}\) allows more efficient \( V \rightarrow R \) transfer.

5.1.3 Nitrogen and Carbon Monoxide

Figure 5.4 displays the vibrational energy removal results from nitrogen and carbon monoxide. Again, these diatomics should remove the triplet’s excess vibrational energy through only \( V \rightarrow T,R \) energy transfer processes because the lowest vibrational frequencies, 2331 and 2143 cm\(^{-1}\) respectively\(^{46}\), are not comparable to the donor’s energy. In comparison with hydrogen and deuterium, they have higher mass and are found to be more effective relaxers. Note because \( \text{N}_2 \) and CO have nearly the same mass, vibrational frequency, and rotational constant, their relative vibrational energy removal effectiveness provide interesting information. We find carbon monoxide to be more effective as a relaxer than nitrogen by a factor of 1.4. CO, the only heteronuclear diatomic studied, has a small permanent dipole moment of 0.112 D\(^{44}\) and a slightly larger polarizability than \( \text{N}_2 \)\(^{44}\). These factors may increase its ability to form short-lived complexes with the
pyrazine donor and transfer energy into translational and rotational motions. The presence of CO’s transition dipole may allow for some long range interactions with the vibrationally excited pyrazine. This IR-active dipole may accept vibrational energy from the donor through a “radiative” transfer via a near-resonant vibrational energy transfer mechanism\textsuperscript{50}. These aspects may account for the increase in relaxer effectiveness with CO.

5.1.4 Small Polyatoms

Figure 5.5 shows the results for the vibrational energy removal rates for these small polyatomic relaxers: carbon dioxide, methane, and water. As discussed above, these molecules’ lowest vibrational frequencies, 667, 1306, and 1596 cm\textsuperscript{-1} respectively\textsuperscript{45}, are not likely to gain one quantum of vibrational energy through collision with a pyrazine molecule, limiting the role of any V $\rightarrow$ V process. The striking results from this set of relaxers is the ineffectiveness of CH\textsubscript{4} as a relaxer and the extremely large effectiveness of H\textsubscript{2}O. The CO\textsubscript{2} results follow expected trends concerning increasing mass and complexity, resulting in a more effective relaxer species. A triatomic, it is found to be approximately 1.5 times more effective than CO, the most effective diatomic relaxer molecule that we studied.

It is surprising that CH\textsubscript{4}, despite its nine vibrational modes, is essentially equal in effectiveness to carbon monoxide. Methane’s smaller mass and large rotational constant\textsuperscript{45} may be hindering the V $\rightarrow$ T,R processes and limiting the vibrational relaxation process.

The most unexpected results within our set of relaxers comes from H\textsubscript{2}O. Because it is a low mass triatomic, we expected an effectiveness similar to that of CO\textsubscript{2}. As discussed with CO, the presence of water’s large dipole moment, 1.85 D\textsuperscript{44}, might cause a
strong attractive interaction with the open shell triplet pyrazine, favoring formation of a "collision complex". This transient "complex" would allow for large amounts of vibrational energy to be transferred before or during dissociation. It is also true that water has hydrogen-bonding capabilities. This characteristic could cause a specific attraction with the triplet pyrazine through interaction with the $\pi$-electrons on the nitrogens of the pyrazine.

5.1.5 Comparison to Ground Singlet State Pyrazine Relaxation

As mentioned above, Miller and Barker\textsuperscript{42} have recently reported the average energy removal rates for the vibrationally excited ground electronic state of pyrazine with all of the relaxers used in our studies. This allows a direct comparison of the persistence of excess vibrational energy in ground state singlet and triplet state pyrazine. Table 5.2 summarizes the deactivation of both the ground and triplet states of pyrazine containing 5000 cm$^{-1}$ of vibrational energy by the set of collision partners. It should be noted the singlet pyrazine results are from the low end of the range of energy contents studied. The singlet values reported in Table 5.2 were calculated in the overlap region between the two energy ranges using least-squares fit expressions from a conventional exponential model reported by Miller and Barker\textsuperscript{42}.
Table 5.2  Comparison of average vibrational energy loss per collision between triplet and singlet ground state pyrazine with 5000 cm\(^{-1}\) of vibrational energy.

\[
\frac{d\langle E_{\text{vib}} \rangle}{dZ} \text{ at } \langle E_{\text{vib}} \rangle = 5000 \text{ cm}^{-1}
\]

<table>
<thead>
<tr>
<th>Relaxer</th>
<th>Pyrazine (T(_1))</th>
<th>Pyrazine (S(_0))</th>
<th>Enhancement Factor (T(_1)/S(_0))</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>37</td>
<td>4</td>
<td>9.25</td>
</tr>
<tr>
<td>Ne</td>
<td>62</td>
<td>11</td>
<td>5.64</td>
</tr>
<tr>
<td>Ar</td>
<td>98</td>
<td>9</td>
<td>10.89</td>
</tr>
<tr>
<td>Kr</td>
<td>106</td>
<td>15</td>
<td>7.07</td>
</tr>
<tr>
<td>Xe</td>
<td>118</td>
<td>16</td>
<td>7.38</td>
</tr>
<tr>
<td>H(_2)</td>
<td>50</td>
<td>11</td>
<td>4.55</td>
</tr>
<tr>
<td>D(_2)</td>
<td>65</td>
<td>9</td>
<td>7.22</td>
</tr>
<tr>
<td>N(_2)</td>
<td>103</td>
<td>15</td>
<td>6.87</td>
</tr>
<tr>
<td>CO</td>
<td>144</td>
<td>19</td>
<td>7.58</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>217</td>
<td>32</td>
<td>6.78</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>147</td>
<td>41</td>
<td>3.58</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>655</td>
<td>93(^a)</td>
<td>7.01</td>
</tr>
</tbody>
</table>

\(^a\) Determined from S\(_0\) relaxation of benzene as the donor\(^{13}\)

The general trend that arises in this comparison is that regardless of the collision partner, the triplet state is much more easily relaxed than the singlet ground state. The triplet energy removal rates are approximately 7 times higher. These differences suggest that collisional vibrational relaxation of the ground and triplet states of pyrazine involves different mechanisms. The somewhat larger differences between triplet and singlet relaxation for the noble gases than for the polyatomics might imply that the V \(\rightarrow\) T,R processes are more enhanced for the triplet state than are the V \(\rightarrow\) V processes. Since the vibrational densities of states are similar for both the singlet and triplet states of pyrazine,
it appears that the electronically excited triplet state has some relaxation mechanism open to it that is not available to the ground state species. In considering our "collision complex" picture as discussed above, an open shell triplet state will have an enhanced polarizability compared to the ground singlet state, because molecules in their excited triplet state are believed to be more "loose" compared to the ground singlet state. This "floppiness" would allow the electron cloud to be more responsive to any collision encounter-induced electric field and increase the rate of complex formation. By comparison, a collision with a ground state pyrazine molecule would occur more elastically due to weaker long-range interactions.

Another possible explanation for the excited triplet state having different mechanisms for vibrational relaxation than the ground singlet state is the involvement of some nearby excited electronic state. A mechanism might involve the coupling between the vibrational levels of the triplet state pyrazine and the levels of another electronic state. This other electronic state could possibly be a T_2 state lying between the T_1 and S_1 origins^{47,48}. There has been some speculation about whether pyrazine actually has such a state within the energy range included in this study^{25,26}.

5.1.6 The "Threshold"

As mentioned above, a dominant characteristic of the vibrational energy removal curves is the abrupt change in slope near 1800 cm^{-1} of vibrational energy content. This "threshold" phenomenon is present in all of the results, indicating that is a characteristic of the triplet state pyrazine, not the relaxer molecule. This type of behavior has not been observed in the ground singlet state studies, but it should be noted that their included
energy range does not extend down to such low vibrational energy contents. What is so special about 1800 cm\(^{-1}\) of vibrational energy content in triplet state pyrazine? It might indicate the onset of some efficient \(V \rightarrow T,R\) energy transfer process, discussed in Section 5.1.5, that is absent for the ground singlet state. Once "activated", it may lead to the steep increase in energy removal rate found in the triplet state relaxation results. More evidence for the existence of the "threshold" will be presented in the discussion of the vibrational energy distributions to follow.

5.2 Triplet Vibrational Energy Distributions

As described in Chapter 4, we have obtained experimental vibrational energy distributions for vibrationally excited \(T_1\) pyrazine. This new method was pioneered using kinetic information from samples containing very low pressures of pyrazine alone or with low pressures of helium or hydrogen as a relaxer molecule. We have measured vibrational energy distributions for two different initial vibrational energy contents, 4056 (\(0^0\)) and 5433 cm\(^{-1}\) (\(8a^1\)) for all of the above sample conditions. Figures 5.6 through 5.9 show the vibrational energy distributions deduced from analysis of these data. As mentioned in Section 4.1.1, the distribution feature at very high decay rate constants attributed to the singlet component of the population is omitted from the figures. Upon general inspection, similarities among the resulting vibrational energy distributions emerge. All of the distributions at these low pressure conditions show that the bulk of the triplet population has a vibrational energy near the initially deposited value. In addition, all of the results show the presence of some small population of triplet molecules containing a much lower
vibrational energy content between 2000 and 3000 cm\(^{-1}\). Also noted in the results from buffered samples is the general broadening of the dominant feature with addition of buffer gas. These characteristics will be discussed in detail in the following sections.

![Graph showing vibrational energy content](image)

**Figure 5.6** Deduced vibrational energy distributions from vibrationally excited T\(_1\) pyrazine from samples of 0.01 torr of pyrazine alone. Initial vibrational energy contents: 4056 cm\(^{-1}\) (\(0^0\)) and 5433 cm\(^{-1}\) (8a\(^1\)).
Figure 5.7  Deduced vibrational energy distributions from vibrationally excited $T_1$ pyrazine from samples of 0.01 torr of pyrazine with various pressures of helium. Initial vibrational energy content of 4056 cm$^{-1}$ (0$^0$ excitation) The appropriate pyrazine alone result from Figure 5.6 is included for comparison.

Figure 5.8  Deduced vibrational energy distributions from vibrationally excited $T_1$ pyrazine from samples of 0.01 torr of pyrazine with and without helium buffer gas after the initial deposition of 5433 cm$^{-1}$ (8a$^1$ excitation) of vibrational energy. The result without helium is from Figure 5.6.
Figure 5.9 Deduced vibrational energy distributions from vibrationally excited T1 pyrazine from a sample of 0.01 torr of pyrazine with various pressures of hydrogen after the initial deposition of 5433 cm\(^{-1}\) (8a\(^{1}\) excitation) of vibrational energy content. Again, the no helium result from Figure 5.6 is included for comparison.

It should be noted that the implementation of the asymmetry factor in the analysis, as discussed in Section 4.1.1, resulted in vibrational energy distributions very similar to those without it. This observation supports our assumption that the distribution features can be described as nearly Gaussian in nature.

As mentioned in Section 4.1.3, our deduced vibrational energy distributions are not “snapshots” of the population distributions. In our experiment, the triplet population is continuously changing due to collisional perturbation, and what we obtain is a picture representing a time integration over the changing vibrational energy distribution. Our measurement therefore does not directly show the time-dependence of the vibrational energy distribution for the relaxing pyrazine triplets. A true time-dependent measurement
would take a "snapshot" of the distribution at many points in time, much like the individual frames of a motion picture. When viewed consecutively, we would then see the time evolution of the distribution due to collisional effects. Initially, the vibrational energy distribution would be very narrow due to monoenergetic intersystem crossing after optical preparation, but the first collisional encounters would randomly add or remove energy from the pyrazine molecules, broadening the vibrational energy distribution. However, our analysis covers the entire time-scale of the decay kinetics, and includes distributions from narrow to collisionally broadened within the experimental window. Our deduced distributions are thus like long exposure photos that average over the time-scale of the experiment. Therefore, our vibrational energy distribution shapes may lie somewhere between the initial narrow distribution and a final broadened distribution present at the end of our experimental observation. Nonetheless, these results supply the first experimentally determined vibrational energy distributions for an electronically excited polyatomic molecule and provide information to help understand vibrational energy transfer from T₁ pyrazine.

5.2.1 Pyrazine alone

The vibrational energy distributions measured for very low pressures of pyrazine alone can be found in Figure 5.6. Although we do find our narrowest distributions in these unbuffered pyrazine results, the width characteristic of these distributions is larger than expected. At these collisional conditions, there is on average less than one hard-sphere collision in the time scale of our experiment. Therefore, we anticipated extremely narrow, collisionally undisturbed distributions prepared by intersystem crossing from a
well-defined optically excited $S_1$ level. The considerable width of these distributions could be the result of minor collisional effects that are present even at these low pressures. We did not measure energy removal rates for pyrazine self-relaxation in this project, but previous results from this lab$^{4,5}$ showed that pyrazine self-relaxation follows a similar form to that with other buffers and is very efficient (on the order of 300 cm$^{-1}$ of vibrational energy removed per collision at a vibrational energy of 5000 cm$^{-1}$). Efficient self-relaxation might therefore broaden the nascent population distribution. The analysis of decay kinetics for pyrazine at the limit of our pressure sensitivity, 0.001 torr, found a lack of further narrowing in deduced vibrational energy distributions, implying the reported pyrazine alone results to contain the narrowest distributions currently obtainable from the method.

We also find similar distribution widths for the two different initial vibrational energy contents. Our average energy loss results apparently suggest that any early collisional effects would result in a larger width for the higher initial vibrational energy content, for which the average loss per collision is greater. The fact that we find the higher vibrational energy distribution slightly narrower may be due to the dependence of the $T_1 \rightarrow S_0$ decay constants on vibrational energy, because at the higher energy the population returns to the ground state much faster and has less opportunity to be collisionally relaxed. This may lead to the smaller width following 8a$^1$ excitation. Given the uncertainty in the measurements, however, the difference between the widths of these two distributions may not be sufficient to support such an explanation.
5.2.2 Helium-Buffered Pyrazine

Figure 5.7 contains the vibrational energy distribution results for triplet pyrazine prepared with 4056 cm$^{-1}$ ($0^0$) of vibrational energy in the presence of several low pressures of helium. Also included is the result for pyrazine alone from Figure 5.6. With the addition of a small amount of helium as a buffer gas we see broadening in the vibrational energy distribution compared to the relatively narrow vibrational energy distribution for pyrazine with no added helium. As the pressure of helium is increased, we see a monotonic broadening of the vibrational energy distribution’s main peak. Also present in all of the helium buffered results is a small secondary peak at a vibrational energy content near 2000 cm$^{-1}$. This seems to indicate that most of the triplet population has remained near the initially deposited amount of vibrational energy while a small subset has been substantially collisionally relaxed to a vibrational energy content lower by $\approx2000$ cm$^{-1}$.

In an effort to quantify the changes in the distribution widths, Figure 5.10 contains a plot of the vibrational energy distribution width as a function of added helium pressure. Note that the widths plotted in this figure represent the helium component of the width after that from the pyrazine alone result has been subtracted. The plot at first appears linear but can also be viewed as slightly curved toward an asymptotic maximum. This maximum might be defined by the width of a thermalized vibrational energy distribution at the same average energy. Density of states information for the triplet pyrazine with 4056 cm$^{-1}$ of vibrational energy at 730 K indicates this maximum thermalized width to be approximately 4500 cm$^{-1}$. Figure 5.10 appears to be approaching a much lower value, $\approx1500$ cm$^{-1}$, but this may be a result of the time averaging from narrow to broadened
distribution, which gives an apparent width intermediate between these two. The decreasing slope of the plot in Figure 5.10 implies that the initially narrow distribution is broadened more quickly by the first few collisional encounters than by subsequent ones.

Figure 5.10 Pyrazine’s $T_1$ vibrational energy distribution widths from Figure 5.7 as a function of added helium pressure after the initial deposition of 4056 cm$^{-1}$ ($0^9$ excitation) of vibrational energy content.

Figure 5.8 shows the vibrational energy distribution deduced for triplet state pyrazine in the presence of helium, after preparation with 5433 cm$^{-1}$ ($8a^1$) of initial vibrational energy. Again, the pyrazine alone result for this optical excitation level is included for comparison. As before, we observe some small fraction of the population with a much lower vibrational energy content. Note that it appears near 2500 cm$^{-1}$ as opposed to 2000 cm$^{-1}$ for the $0^9$ results. Following the description above, this also suggests that collisional energy removal has relaxed some of the pyrazine triplets to this
value. The fact that it lies higher in energy than those found in Figure 5.7 may be due to the faster $T_1 \rightarrow S_0$ decay rate for the more energetic molecules. The population with more vibrational energy is being removed faster, so this subset of the population has less time in which to be relaxed. Therefore, at the end of integration averaging over the evolving distribution, the low energy feature may not be equally relaxed. In addition, of course, the $8a^1$-excited pyrazine molecules begin with an extra 1377 cm$^{-1}$ of triplet excitation.

In comparing the width of the helium buffered distribution in Figure 5.8 to those of comparable helium pressures at the $0^0$ excitation level, we find that the peak centered about 5400 cm$^{-1}$ is approximately twice as broad. This seems to indicate that the higher the initial vibrational energy content, the more rapidly the initial collisional broadening occurs. This follows from the earlier discussion concerning the pyrazine alone widths at the two different vibrational energy levels. At higher vibrational energy contents collisional relaxation is more efficient, so the first collisional encounters are more disturbing to the initial distribution, resulting in a broader vibrational energy distribution for the $8a^1$ level of excitation. However, further data will be required for other helium pressures at this level of vibrational energy to confirm this preliminary assessment.

Another trend to be noted from the results in Figure 5.7 is the increase in the distribution feature at low vibrational energy contents. Figure 5.11 shows a plot of the normalized amplitude of this secondary peak, a parameter optimized in the Gaussian kinetic analysis, as a function of added helium pressure. The linear nature of this plot implies that this lower energy population is collisionally induced. However, under these low helium pressures, few hard-sphere collisions occur on the timescale of our kinetic
measurement. The large change in vibrational energy content resulting in these few collisions suggests some "super-channel" for relaxation. But, it should be noted that this linearity is not strictly observed in other buffer pressure dependent plots, leaving some speculation in the current assessment.

![Graph showing population in low-energy peak vs. added helium pressure](image)

**Figure 5.11** Low-energy peak normalized amplitude from Figure 5.7 as a function of added helium pressure after the initial deposition of 4056 cm\(^{-1}\) (0\(^0\) excitation) of vibrational energy content.

5.2.3 Hydrogen-Buffered Pyrazine

Figure 5.9 contains the results for hydrogen buffered pyrazine with an initial vibrational energy content of 5433 cm\(^{-1}\). Similar to the previous results, we see a progressive broadening of the main peak in the vibrational energy distribution with added hydrogen pressure and a lower energy peak containing a portion of the population around 2500 cm\(^{-1}\). A plot of the hydrogen induced width, as was done with helium above, is
shown in Figure 5.12. Here we see much steeper initial slopes and the curvature is much more evident. The predicted thermal width at this higher energy is 4500 cm$^{-1}$. Although the asymptote in Figure 5.12 appears higher than that in Figure 5.10, it also falls below the predicted thermal width.

![Graph showing distribution width vs. added hydrogen pressure](image)

**Figure 5.12** Pyrazine's $T_1$ vibrational energy distribution widths from Figure 5.9 as a function of added hydrogen pressure after the initial deposition of 5433 cm$^{-1}$ ($8a_1^1$ excitation) of vibrational energy content.

Hydrogen's mean collision time with pyrazine is half that of helium's at the same pressure, but the nascent decay constant after $8a_1^1$ preparation is twice that for $0^0$ preparation. Therefore, the collisional conditions for Figures 5.10 and 5.12 are approximately the same, allowing a direct comparison of the vibrational energy distributions. For 0.1 torr of either buffer gas, we find the hydrogen broadening width to be approximately a factor of 2.5 greater than that from helium after $0^0$ excitation. This
factor is very close to the ratio of average energy losses per collision found earlier for hydrogen at 5433 cm⁻¹ relative to helium at 4056 cm⁻¹. \(60/23 \approx 2.6\) This seems to confirm that at the higher donor energy contents, initial collisional perturbation is more extreme causing more measurable broadening in the vibrational energy distribution. We can also compare the distribution widths for helium- and hydrogen-buffered pyrazine, both at the 8a¹ level of excitation. In doing so, we find that at similar pressures the distribution widths for hydrogen and helium are very much in agreement. This also indicates that the excess broadening is similar for these two relaxers and depends significantly on the donor's initial vibrational energy content. Again, further work should be done with hydrogen-buffered pyrazine at the 0⁰ excitation level in order to confirm this view.

5.2.4 Connection to Average Vibrational Energy Loss Results

In interpreting the general features of our vibrational energy distribution results, perhaps the most unexpected and interesting aspect is the small distribution peak near 2000 cm⁻¹ of vibrational energy content. How did this subset of the population arrive at this specific amount of vibrational energy? One possibility is through "super-collisions" that would remove very large amounts of vibrational energy in one collisional encounter. But the average vibrational energy removal rate results do not suggest such an effect. A more believable explanation would entail normal collisional relaxation of some of the pyrazine triplets until they reach approximately 2000 cm⁻¹ of vibrational energy content. At this level of vibrational energy, they become much less susceptible to the efficient energy removal mechanism that had relaxed them. Therefore, the rate of adding population to this vibrational energy range will exceed the rate of its removal. Thus, the
population of pyrazine triplets begins to pile up, or "bottleneck" near this particular vibrational energy. This explanation leads to a direct connection with the persistent "threshold" seen in all of the average energy loss results. Recall that the "threshold" behavior, regardless of relaxer, was found at a vibrational energy content near $1800 \text{ cm}^{-1}$. The "threshold" in the energy loss curves can similarly be viewed as the result of the relaxing pyrazine triplets reaching energies at which they become resistant to further vibrational relaxation. The similarity between the location of this small collisionally relaxed population in the vibrational energy distributions and the "threshold" behavior in the energy loss results reinforces the uniqueness of the energy region near $2000 \text{ cm}^{-1}$. Thus, the rapid onset of some efficient vibrational energy removal mechanism in the energy removal results seems consistent with the vibrational energy distribution results.
CHAPTER 6

CONCLUSIONS

6.1 Conclusions

This project has refined and validated the Competitive Radiationless Decay (CRD) method for determining the rates of collisional vibrational relaxation from vibrationally excited triplet state molecules. In this method, high definition triplet-triplet optical absorption is used to measure the population decay kinetics of the vibrationally excited triplet sample in the presence of collision partners. From this information, the $T_1 \rightarrow S_0$ decay rate constants are determined as a function of collision number. Knowledge of the vibrational energy dependence of the decay rate constants provides a calibration by which the average vibrational energy of the triplet molecules is deduced from the measured decay constants. This method should be applicable to any molecule that has large $S_1 \rightarrow T_1$ and $T_1 \rightarrow S_0$ intersystem crossing quantum yields, significant $T_n \leftrightarrow T_1$ molar absorptivities, and available calibration data.

In applying this refined method, we have measured collisional vibrational energy removal rates for $T_1$ pyrazine with 12 relaxer gases. These results form the most secure database concerning the collisional vibrational relaxation of a triplet state polyatomic. We find a strong variation of the energy removal rates with vibrational energy content between roughly 1800 and 5500 cm$^{-1}$. For a pyrazine donor containing 5000 cm$^{-1}$ of vibrational energy content, we find the following order of relaxer effectiveness:

$$\text{He} < \text{H}_2 < \text{Ne} < \text{D}_2 < \text{Ar} < \text{N}_2 < \text{Kr} < \text{Xe} < \text{CO} < \text{CH}_4 < \text{CO}_2 < \text{H}_2\text{O}$$
The excellent consistency of our measurements made following different initial levels of excitation, in concert with the agreement of replicate measurements, indicates that our curves of energy loss per collision vs. donor energy content should be reliable to within 5 to 10%.

Comparison of our $T_1$ pyrazine energy loss results with those reported recently for $S_0$ pyrazine indicates that the triplet state energy removal rates are approximately 7 times greater for all relaxers studied. This implies that our large triplet state energy removal rates are linked to the electronic state of the donor.

This project has also developed a new method for determining the distribution of vibrational energy contents in an excited polyatomic sample. The distribution of decay rate constants is extracted from the $T_1 \rightarrow S_0$ kinetic decay of vibrationally excited $T_1$ pyrazine using a Gaussian kinetic model. This decay constant distribution is then mapped into a molecular vibrational energy distribution using a calibration between triplet decay constant and vibrational energy. Increasing buffer pressure in the sample results in progressive broadening of an initially narrow nascent vibrational energy distribution. These deduced distributions, which are time-averaged over the sample’s decay lifetime, provide the first experimental view of an excited sample’s vibrational energy distribution.

Both the energy distribution and the energy loss results indicate a unique “threshold” behavior in the energy region near 2000 cm$^{-1}$. In this region of vibrational energy, the vibrationally excited pyrazine triplets appear to become much less susceptible to efficient energy removal. This is indicated in the vibrational energy distributions results by the pile-up of population near this particular vibrational energy, and in the energy loss
curves as the abrupt change in slope near 1800 cm\(^{-1}\). This "threshold" phenomenon suggests the rapid onset of some efficient vibrational relaxation process.

6.2 Future Directions

The results of these studies suggest several avenues for future work, both experimental and theoretical. Although the implementation of the CRD method has been successful in analyzing the triplet decay kinetics of pyrazine with a few relaxers, this triplet state relaxation information is very limited in comparison to the large databases of relaxer information for molecules in the electronic ground singlet state. Much more information can be gained by greatly extending the list of relaxers to include larger molecules with more varied vibrational structure. This will provide more insight into the energy loss mechanisms.

Comparison of our triplet state pyrazine results to ground state pyrazine energy removal rates suggested that the donor's electronic excitation greatly enhances the relaxation. Further studies of other triplet state donor molecules are clearly needed. Now that the CRD method is fully refined and validated, it can be easily applied to other donors, provided that their radiationless decay properties are suitable and that their "calibration curve" information is available, or can be measured. The foremost candidate is pyrazine-\(d_x\), which is nearly identical to pyrazine in all respects save its rotational and vibrational frequencies. Its "calibration curve" can be constructed with the aid of Cheshnovsky's recent reports of \(T_1 \rightarrow S_0\) decay rate constants for pyrazine-\(d_x\)\(^{49}\), and methylpyrazine\(^{35}\). The results with new donors should provide more insight into which
characteristics of the donor are pertinent to the efficiency of relaxation and the location of the "threshold" in donor energy.

Our results from the Gaussian method of determining triplet vibrational energy distributions represent the earliest stages of a exploratory work on the subject. As presented above, it has so far been applied only to vibrationally excited pyrazine with two relaxer gases, helium and hydrogen. Studies need to continue with pyrazine and other relaxers to measure relative broadening rates and to clarify the source of the low-energy component. It would be very interesting to observe the distribution results from pyrazine relaxed by water, our most effective relaxer. This species may produce greatly broadened vibrational energy distributions approaching thermalized distributions.

The limitations of the current form of the Gaussian analysis method suggest a need for theoretical work. For example, the deduced vibrational energy distributions represent time averages whose exact nature needs to be clarified. In future work, it might be possible to perform a piece-wise analysis of segments of the decay in an attempt to extract truly time-dependent distributions. Another very important step is to perform Master Equation calculations to simulate the measured data from both Gaussian and energy loss experiments. The Master Equation results should stimulate theoretical research on triplet vibrational energy loss. We predict that further experimental work combined with more elaborate analyses will provide unique insight into the early stages of collisional vibrational relaxation.
REFERENCES


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