Electronic to Vibrational Energy Transfer from Cl* \((3^2P_{1/2})\) to N₂O(ν₁): Failure of a Simple Kinetic Mechanism

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ELECTRONIC TO VIBRATIONAL ENERGY TRANSFER FROM Cl* ($^3P_{1/2}$) TO
$N_2O(v_1)$: FAILURE OF A SIMPLE KINETIC MECHANISM

A thesis submitted in partial fulfillment
of the requirements of the degree of
Master of Science

By

Brian Elliott Brumfield
B.S. Wright State University 2003

2005
Wright State University
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Brian Elliott Brumfield ENTITLED Electronic to Vibrational Energy Transfer from Cl* (3^2P_{1/2}) to N_2O(v_1): Failure of A Simple Kinetic Mechanism to be accepted in partial fulfillment of the requirements of the degree of Master of Science.

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ABSTRACT

Brumfield, Brian Elliott. M.S., Department of Chemistry, Wright State University, 2005. Electronic to Vibrational Energy Transfer from Cl* (3^2P_{1/2}) to N_2O(ν₁): Failure of A Simple Kinetic Mechanism.

Experimental kinetic studies were carried out examining the electronic to vibrational (E-V) energy transfer from spin-orbit excited Cl* (3^2P_{1/2}, 882 cm⁻¹) to N_2O(ν₁) (symmetric stretch 1285 cm⁻¹). All studies were carried out in the gas phase at room temperature (298 ± 2 K). Cl* was generated by pulsed laser photolysis of ICl at 532 nm in the presence of various mixtures of N_2O, ICl, Ar, and SO_2. Time-resolved IR signals of N_2O(ν₁) fluorescence at 7.8 μm were analyzed to obtain rate coefficients for Cl* quenching and N_2O(ν₁) relaxation. E-V branching ratios, measured in ICl/N_2O mixtures show that all Cl*/N_2O quenching collisions result in the excitation of the N_2O(ν₁). Additional studies were carried out, observing the competitive Cl* quenching between N_2O and SO_2. An indirect measurement of the rate coefficient for N_2O quenching of Cl* was obtained from time-resolved IR signals of SO_2(ν₃) fluorescence at 7.3 μm with varying N_2O concentrations. Kinetic studies carried out in ICl/N_2O gas mixtures found the total Cl* quenching rate coefficient for N_2O to be k*_{N_2O} = (9.8 ± 1.6) x 10⁻¹² cm³·molecule⁻¹·s⁻¹. An E-V branching ratio, k*_{E-V}/k*_{N_2O} = 1.09 ± 0.28, was determined in these experiments. This value indicates that all of the quenching collisions excite N_2O(ν₁) via the E-V pathway, and the absolute rate coefficient for E-V quenching may be determined as k*_{E-V} = (9.8 ± 3.0) x 10⁻¹² cm³·molecule⁻¹·s⁻¹. The rate coefficient for N_2O(ν₁) relaxation by N_2O was determined to be (1.0 ± 0.2) x 10⁻¹² cm³·molecule⁻¹·s⁻¹.
in ICl/N$_2$O mixtures. The N$_2$O competitive quenching studies in ICl/N$_2$O/SO$_2$ gas mixtures yielded a Cl* quenching rate coefficient for N$_2$O of $k_{N2O}^* = (1.59 \pm 0.13) \times 10^{-11}$ cm$^3$·molecule$^{-1}·$s$^{-1}$

It was discovered in this project that the kinetic results in the presence of argon are quite different than in argon’s absence. N$_2$O kinetic studies carried out in a ~5 Torr argon bath yield a quenching rate coefficient for N$_2$O of $k_{N2O}^* = (7.3 \pm 1.7) \times 10^{-12}$ cm$^3$·molecule$^{-1}·$s$^{-1}$, and an N$_2$O($v_1$) relaxation rate coefficient of $k_{N2O}^V = (2.3 \pm 0.4) \times 10^{-12}$ cm$^3$·molecule$^{-1}·$s$^{-1}$. This relaxation rate coefficient agrees with previous studies carried out by J.C. Batson (M.S. Thesis, Wright State University, 2003), but is in poor agreement with literature values. Batson’s rate coefficient assignments are reversed because she was unaware of the unusual and unexplained argon effects discovered here.

Argon kinetic studies yielded an upper limit of the Cl* quenching rate coefficient of $k_{Ar}^* \leq 5 \times 10^{-14}$ cm$^3$·molecule$^{-1}·$s$^{-1}$. The rate coefficient for the relaxation of N$_2$O($v_1$) by argon was found to be $k_{Ar}^V = (2.9 \pm 0.8) \times 10^{-13}$ cm$^3$·molecule$^{-1}·$s$^{-1}$. Argon kinetic studies indicate that the rise portion of the N$_2$O($v_1$) fluorescence signal is due to vibrational relaxation. This assignment is in direct conflict with competitive quenching studies carried out in this project with CD$_4$ and CCl$_4$. The unexplained behavior of N$_2$O($v_1$) fluorescence with addition of argon suggests that a simple Cl*→N$_2$O($v_1$)→N$_2$O mechanism may not apply.
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1. Introduction

This following thesis work involves an experimental investigation of the quenching of spin-orbit excited chlorine atoms, Cl* (2P\(_{1/2}\)). Using pulsed laser photolysis ICl was photodissociated to yield Cl*. Time resolved infrared (IR) fluorescence signals were observed for the N\(_2\)O(\(v_1\)) population excited via an electronic to vibrational (E-V) energy transfer mechanism.

Spin-orbit excited halogen atoms (X* 2P\(_{1/2}\)) can be created by photodissociation of halogen and interhalogen diatomic molecules. In the presence of a small molecular collision partner this excess electronic energy may be deposited into discrete vibrational energy levels of the small molecule. This process of excitation of the vibrational modes of a small molecule through the transfer of excess electronic energy from another comprises an electronic-to-vibrational (E-V) energy transfer. Such E-V processes may play active roles in the chemistry of the atmosphere, plasmas, and chemical lasers.

The impetus for studying Cl* E-V energy transfer to N\(_2\)O(\(v_1\)) vibrational state is two-fold. The overall goal is to test E-V energy transfer theory and to provide E-V branching ratios and quenching rate coefficients for a variety of small polyatomic molecules. The second goal was to resolve conflicting results found in the Masters work done by J.S. Batson [1], a previous group member, regarding the Cl*/N\(_2\)O E-V mechanism where experiments were always done in the presence of argon. In the previous work a disparity existed between the accepted literature values for the rate
constant for Cl* quenching by N₂O, and the value assigned from the experimental studies. This occurred because of the misleading behavior argon dependence illustrated on the time constants for the rise and decay of the N₂O (ν₁) time resolved IR signals.

In this study examining the Cl*/N₂O E-V mechanism an attempt is being made to clear up the confusing conclusions from the previous study. Experiments examining the dependence of time resolved IR N₂O (ν₁) signals with varying concentration of N₂O were carried out in the absence of argon, under pseudo first-order conditions, in order to obtain the second order bimolecular rate coefficients for Cl* quenching and N₂O (ν₁) relaxation. E-V branching ratio measurements were established in the experiments with an absence of argon. Similar experiments were carried out testing argon dependence, and N₂O dependence in the presence of a fixed amount of argon on the rise and decay of the N₂O (ν₁) IR signals. To add resolution to the assignment of the rise and decay of the IR signals the concentration dependence of the N₂O (ν₁) signal with varying CD₄ and CCl₄ concentrations was examined. Both molecules are efficient Cl* quenchers and could aid in verifying the assignment of the rise to a Cl* quenching process. Finally, in another attempt to measure the Cl* quenching rate constant the dependence of the rise of the SO₂ (ν₃) time resolved IR signal with varying N₂O concentrations was carried out.

Chapter one provides a basic background encompassing the electronic configuration, spin-orbit excited properties, detection methods, and experimental history relevant to the discussion of spin-orbit electronically excited halogen atoms. At the end of chapter one a brief review of the theoretical treatments of E-V transfer is provided. Chapter two provides the experimental details regarding the design of the experiments and the apparatus. Included in chapter two are a kinetic scheme and the description of
the pseudo first order reaction conditions. Chapter three comprises the results and discussion surrounding the experimental results.

I. Electronic Configuration and Spin-Orbit Properties of Halogens

Central to the study of an E-V transfer process is an understanding of the electronic configuration and properties of the spin-orbit electronic states of the halogens utilized in the experimental studies. The halogens, which belong in group VII of the periodic table, all bear a ground state electron configuration of ns\(^2\)np\(^5\). Each atomic orbital is filled with electrons, starting first from the orbital with lowest energy and then progressing to each subsequent orbital of higher energy. This order of adding the electrons to the orbitals is termed the Aufbau ("building up") principle. In addition to filling orbitals from lowest to highest energy the "building up" principle also states that the electrons will half-fill different orbitals in a given subshell before attempting to pair. The Pauli exclusion principle forces electrons paired in a given orbital to be of opposed electron spin in order to provide a unique quantum state. Following the accepted rules the ground valence electron configuration of a given halogen atom will be:

\[
\begin{array}{c}
\uparrow \downarrow \\
\text{ns}
\end{array}
\begin{array}{c}
\uparrow \downarrow \\
\text{np}
\end{array}
\begin{array}{c}
\uparrow
\end{array}
\]

A term symbol provides a brief way to describe the electronic state of a given atom. The basic structure of a term symbol follows the given format:

\[
(2S+1)L_J
\]

The total electron angular momentum is described by the capital letter L. Angular momentum is a vector quantity, and the summation of individual electron orbital angular
momenta $\ell$ leads to the total electron angular momentum value of $L$ for an atom. $L$
values of 0, 1, 2, and 3 are represented by the capital letters S, P, D, and F. The
multiplicity of the term symbol is described by the expression $2S+1$, where capital $S$
represents the overall electron spin momentum. The capital letter $J$ represents the vector
sum of the overall electron angular momentum and the overall electron spin momentum.
The coupling of the spin and orbital angular momentum of each electron can be
simplified by the assumption that spin-orbit coupling is weak, and this allows term
symbols to be crafted by determining permitted values of $J$ in the fashion of a Clebsch-
Gordon series using $L$ and $S$:

$$\left| L+S \right\rangle \ldots \left| L-S \right\rangle$$

Analysis of the valence electron configuration of a halogen reveals one unpaired
electron in a p orbital which contributes a value of 1 to the overall angular momentum
($L$). The same electron is also unpaired, yielding an overall electron spin momentum
value of 1/2. The two possible values for $J$ are 3/2 and 1/2. The two possible term
symbols generated are $^2P_{3/2}$ and $^2P_{1/2}$. By referencing Hund’s rules it is possible to
determine which of these term symbols represents the ground state. The higher $J$ state
lies lower in energy when the valence subshell is more than half filled, and the lower $J$
state lies lower in energy when the valence subshell is less than half filled. In the halogen
electron configuration the valence subshell is more than half filled so the ground state
term symbol is $^2P_{3/2}$.

An optical transition for a given halogen between $^2P_{1/2} \leftrightarrow ^2P_{3/2}$ is forbidden
because the selection rule regarding $\Delta L = \pm 1$ is broken. The forbidden nature of such a
process deals with the spin angular momentum of a photon having a value of $\hbar$. The
angular momentum lost or gained by the electron during the optical transition from a higher to lower state must accordingly increase or decrease by an angular momentum value of $h$. Despite being a forbidden transition absorption or emission can occur between these states with increasing probability as the atomic number of the halogens increase. Absorption or emission between these two states has been observed for all of the halogens.

Table 1-1 provides an overview of the spin-orbit properties of the halogen atoms. The energy gap between the two states increases with increasing atomic number of the halogen. This is because the spin-orbit coupling grows stronger as the nuclear charge grows longer. The term $A$ is referred to as the Einstein coefficient of spontaneous emission. The inversion of $A$ yields the radiative lifetime of the transition. Long radiative lifetimes of 830 s and 83 s should be noted for fluorine and chlorine. This illustrates the forbidden nature of the optical transition, however as atomic number increases the assumption of weak spin-orbit coupling is further violated such that the term symbols shown from Russell-Sunders coupling do not actually describe the change in the angular momentum of an electron during the transition. Spontaneous emissions from F ($^2P_{1/2}$) and Cl ($^2P_{1/2}$) have not been observed because they are very weak. Contrasting with this are the much shorter radiative lifetimes of Br ($^2P_{1/2}$) and I ($^2P_{1/2}$). Many E-V studies involving excitation of vibrational quanta of small polyatomic molecules with I* and Br* have been performed [2]. The degree of spontaneous emission from I* and Br* permit direct observation of the population of electronically excited halogen atoms via fluorescence detection.
II. Spin-Orbit Excited Halogen Detection Methods

A variety of experimental methods have been employed in the study of E-V energy transfer between spin-orbit excited halogens and small molecules or atoms. The detection methods fall into two broads categories: direct detection of the forbidden \(^{2}P_{1/2} \leftrightarrow ^{2}P_{3/2}\) transition, or methods where an allowed electronic transition is utilized.

### A. Allowed Electronic Transition Detection Methods

Methods taking advantage of an allowed electronic transition involve atomic resonance absorption in the vacuum ultraviolet (ARA-VUV) [3] and resonant-enhanced multiphoton ionization (REMPI) [4].

Donovan and Husain [3] utilized a technique called atomic resonance absorption in the vacuum ultraviolet (ARA-VUV) in order to directly measure the E-V quenching rate of Cl \(^{2}P_{1/2}\) by H\(_{2}\), HCl, CCl\(_{4}\), and CF\(_{3}\)Cl. A flash photolysis lamp was used to generate electronically excited halogen atoms from CCl\(_{4}\). A delayed electronic pulse from the flash lamp then triggers the firing of a spectral flash lamp and the atomic absorption spectrum was recorded on photographic plates. Using plate photometry the time resolved change in absorption of light at 135.17 nm, corresponding to the transition

<table>
<thead>
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<th>Atom</th>
<th>(\Delta E) (cm(^{-1}))</th>
<th>(\lambda) ((\mu)m)</th>
<th>(\tau_{\text{rad}}) (s)</th>
<th>(A) (s(^{-1}))</th>
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<td>F</td>
<td>404</td>
<td>24.8</td>
<td>830</td>
<td>0.00120</td>
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<td>882</td>
<td>11.4</td>
<td>83</td>
<td>0.0120</td>
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<td>3685</td>
<td>2.713</td>
<td>1.1</td>
<td>0.909</td>
</tr>
<tr>
<td>I</td>
<td>7603</td>
<td>1.315</td>
<td>0.13</td>
<td>7.69</td>
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Table 1-1: Spin-Orbit Properties of the halogen atoms \(^{2}P_{1/2} \rightarrow ^{2}P_{3/2}\) [2]
4p^45s(^2P_{3/2}) \leftarrow 4p^5(^2P_{3/2})$, allowed a relative comparison of that population to the ground state by examining absorption at 134.73nm corresponding to the transition 4p^45s(^2P_{3/2}) \leftarrow 4p^5(^2P_{3/2}). Since absorption is related to population the bimolecular rate constant for quenching with another molecular species could be determined by varying its pressure and observing the reduction in absorption from Cl*.

Resonance-enhanced multi-photon ionization (REMPI) has been used to detect Cl* from ICl photodissociation in combination with time-of-flight (TOF) techniques by Flynn and Ni [4]. The REMPI technique relies upon tuning the photon energy to match an allowed VUV electronic transition, and then a second photon of the same wavelength ionizes the specific excited state. In the study a frequency-doubled dye laser tuned to 237.808 nm promoted the photodissocation of ICl, and then acted additionally as a photofragmentation probe by specifically ionizing Cl* (^2P_{1/2}). The Cl^+ ions then enter a double field TOF mass spectrometer and were detected by a micro-channel plate charged particle detector.

**B. Forbidden Transition Detection Methods of X**

A multitude of methods have been employed to detect the optically forbidden electronic transition in the halogens. Direct detection of IR fluorescence Br* and I* from photolytic precursors has been performed [5]. General “pulse and probe” techniques have been carried out using color center lasers [6,7], diode laser absorption spectroscopy (DLA) [8,9,10,11], laser magnetic resonance (LMR) [12,13,14], and photodissociation lasers (PL) [15].
The first direct detection methods of E-V energy transfer were carried by Leone and Wodarczyk [5] involving time resolved fluorescence studies observing Br* E-V transfer to HCl(ν=1) and HBr(ν=1). A frequency doubled Nd$^{3+}$:YAG laser provided the energy necessary to photolyze Br$_2$ and produce a nearly 1:1 population of Br* and Br. Bandpass filters were used to specifically monitor fluorescence from Br* and HX(ν=1). Leone and Wodarczyk concluded that more than 50% of the total quenching of Br* excites HCl(ν=1) or HBr(ν=1).

The use of diode laser absorption (DLA) and color center laser absorption follows the general scheme of “pulse and probe” techniques. A pulsed photolysis source is used to generate a given population of spin-orbit excited and ground state halogen. A probe beam tuned to the wavelength of the optically forbidden $^2P_{1/2} \leftrightarrow ^2P_{3/2}$ transition is passed through the region of interest. Either absorption or gain will occur at the probe wavelength, and that is dependent upon the population ratio of the spin-orbit excited state to ground state population. Taking into account the degeneracy of both of the halogen electronic states, $g^* = 4$ and $g = 2$, absorption will occur when the population ratio $[X^*]/[X] < 1/2$, and stimulated emission will occur when the population ratio is $[X^*]/[X] > 1/2$. When the population ratio is $[X^*]/[X] = 1/2$ no gain or absorption is detected with the probe source.

Haugen et al [5,6] used a color center laser source as a probe beam to observe the gain and absorption in studies of the Br* quantum yield in IBr or Br$_2$ photodissociation. In both studies a dye laser pumped by a XeCl excimer source was used to photodissociate a small portion of the IBr or Br$_2$ present. The precursors were both present in a dilute gas bath of CO$_2$ and Kr. Krypton was present to thermalize Br and Br* to avoid Doppler
broadening of the hyperfine atomic transitions. Hyperfine transitions arise from coupling the nuclear spin momentum along with the electron spin momentum and electron angular momentum. The color center laser was tuned to the Br ($^2P_{1/2} \leftrightarrow ^2P_{3/2}$) transition, and after the initial pulse from the photolysis source a gain in intensity from the forbidden transition can be observed, and then the time resolved IR signal decays into absorption as the CO$_2$ quenches Br*. Finally, the absorption decays to “zero” as Br ground state atoms are lost. Both the back extrapolated intensity from the induced CO$_2$ decay, and the longer time absorption signal allow for the determination of the nascent Br*/Br ratio in the photodissociation process.

In a DLA study carried out by Leone et al. [8] I* quantum yields for the photolytic dissociation ICN, i-C$_3$F$_4$I, n- C$_3$F$_4$I, and CH$_3$I were carried out in the presence of O$_2$. An InGaAsP semiconductor diode laser was used to probe the I* ($^2P_{1/2} \leftrightarrow ^2P_{3/2}$) transition state after photolysis of an I* source. O$_2$ gas was present in the experiment to quench I*. The diode laser gain/absorption signals are analyzed to obtain the nascent I*/I ratio in photolysis. Temporal analyses of these signals yield rates of X* quenching and X reaction. Hirota and Tiemann [9] performed similar DLA studies to examine quantum yields of Cl* from PCl$_3$, CH$_2$Cl$_2$, phenyl chloride, HCl, and CH$_3$Cl, along with the rate constants for quenching Cl* by each of these precursors. A KrF or ArF excimer laser was used to photolyze a Cl* precursor, and then an IR diode was used to probe the Cl* transition ($^2P_{1/2} \leftrightarrow ^2P_{3/2}$). Akin to studies done by Haugen [6,7,8] the early portion of the signal was examined and fitted based upon the concept of the statistical population [Cl*]/[Cl] = 1/2. Similar DLA studies on the quantum yield and quenching rate constants of various Cl* sources was carried out by Park et al. [10]. The weak F* $\leftrightarrow$ F
\(^{2}\text{P}_{1/2} \leftarrow^{2}\text{P}_{3/2}\) absorption at 25\(\mu\)m has been observed in DLA experiments by Loge et al [11]. A temperature controlled lead salt laser diode was used, and \(\text{F}_2\) was photolyzed by a \(\text{XeCl}\) excimer laser to generate \(\text{F}\) atoms.

The LMR technique used by Chichinin and Krasnoperov [12,13,14] has been used to measure quantum yields for \(\text{Cl}^*\) sources, as well as quenching rate coefficients with various small molecular or atomic collision partners. In the LMR technique an excimer laser is first used to photolyze a \(\text{Cl}^*\) source. The cell where the photolysis occurs is wrapped by a series of field jump coils in a solenoid arrangement. The arrangement is such that when a current is passed through the coils a strong magnetic field is generated through the cell where \(\text{Cl}^*\) is generated. The \(\text{Cl}^*\) \(^{2}\text{P}_{1/2} \leftarrow^{2}\text{P}_{3/2}\) transition is tuned to the energy of the 11P(36) line of a \(^{13}\text{CO}_2\) laser until they are in resonance using the magnetic field. Time-resolved gain or absorption of the \(^{13}\text{CO}_2\) laser probe signal is observed, and the time resolved signals can allow the elucidation of \(\text{Cl}^*\) quenching rate constants for various small molecules or atoms present in the cell. The back extrapolated intensity allows for an effective calculation of the \(\text{Cl}^*\) yield from various photolytic sources of interest.

ARA-IR is another “probe and pulse” technique used by Sotnichenko et al [15] to explore the rate at which various molecular or atomic species will quench \(\text{Cl}^*\) and \(\text{I}^*\). The probe source in Sotnichenko’s \(\text{Cl}^*\) study was a photodissociative laser (PL) generated by pulse photolysis of \(\text{ICl}\) or \(\text{Cl}_2\) using a flashlamp. The precursor \(\text{Cl}^*\) source is first photolyzed in the presence of the precursor and another gas of interest. The absorption or gain signals of the probe PL beam passing through the sample are analyzed to determine quenching rate coefficients.
III. Correlation of $\Delta E$ and $\Delta v$ to E-V Transfer

A review of the experimental results from I* and Br* quenching studies done from 1971 to 1979 by Paul Houston [2] reveals a strong correlation between the X* quenching rate coefficient with the energy gap ($\Delta E$) and number of vibrational quanta excited ($\Delta v$) of a supposed E-V channel. Figure (1-1) is a recreation of the figure found in Houston’s review [2], and provides a plot of the quenching rate coefficients for I* and Br* plotted against the absolute value of the energy gap $\Delta E$ (cm$^{-1}$). Open symbols represent Br* quenching data, and filled symbols represent I* quenching data. The amount of vibrational quanta excited in the quenching event is coded by the shape of the data point on figure 1-1: Circles represent $\Delta v=1$, squares represent $\Delta v=2$, triangles represent $\Delta v=3$, and diamonds represent $\Delta v=4$. The three lines represent correlations drawn from the data. The first highest line is fitted with data from Br* quenching where $\Delta v=1$. The second line represents the quenching rates from Br* or I* that involved excitation of $\Delta v=2$. The third lowest line represents data from quenching of Br* and I* that includes excitation of $\Delta v=3$ or 4.

Figure (1-2) is similar to figure (1-1) recreated from Houston’s review [2], but is constructed from Cl* rate quenching rate coefficients provided in a review of Cl* quenching compounds by Chichinin [14]. All the processes involve vibrational excitation of $\Delta v=1$. Every $\sim 450$ cm$^{-1}$ corresponds to a one order of magnitude decrease in the Cl* rate quenching coefficient.
Figure 1-1: A plot of quenching rate constants for Br* and I* plotted against $|\Delta E|$ as found in reference [2].
Examination of the top fit line in figure (1-1) reveals the dependence of $|\Delta E|$ on the quenching rate. Every $\sim 650$ cm$^{-1}$ increase in the energy gap correlates to a decrease in quenching by one order of magnitude. The other two linear fits for the data have much more scatter, and the steeper slopes indicate a stronger dependence on $|\Delta E|$ as more vibrational quanta are excited via quenching.

Figure 1-2: A plot of quenching rate constants for Cl* taken from reference [14] plotted against $|\Delta E|$.

The Br* quenching rate for BrNO represents a notable outlier in the data presented in figure 1-1. In the experimental study by Sedlacek and Wright [16] it was found that quenching of Br* (3685 cm$^{-1}$) primarily excited the (100) (1800 cm$^{-1}$).
fundamental despite the near resonance of the (200) (3570cm\(^{-1}\)) overtone level. Cold gas filter studies have shown that quenching by the (100) state in BrNO is six times more probable than the (200) overtone even though quenching 1770cm\(^{-1}\) excess energy must be partitioned into the recoiling species.

Dolson et al. [17] have reported similar conclusions based upon studies of Br\(^*\) quenching by SO\(_2\). SO\(_2\) (001) (1361cm\(^{-1}\)) was preferentially excited over the (300) or (102) overtone combination levels which are only ~20cm\(^{-1}\) out of resonance of the Br\(^*\) (3570cm\(^{-1}\)) energy. The authors concluded that a favorable matrix dipole moment of the \(\nu_3\) mode mattered more than closing the energy gap with a greater change in the number of vibrational quanta.

**IV. Theoretical Treatments of E-V Transfer**

The basic theoretical problem of E-V energy transfer involves a non-adiabatic collision between two different electronic potential energy surfaces. Three theories have taken the forefront in attempting to explain E-V energy transfer. A curve crossing mechanism has been postulated in order to predict E-V transfer. Quantum mechanical methods have been employed with limited success. Also, long range attractive forces interactions typically used to describe V-V energy transfer have been adapted to predict E-V energy transfer. In general all three theories agree that the energy gap (\(\Delta E\)), and the number of vibrational quanta (\(\Delta \nu\)) excited are the key determining factors for the probability of E-V transfer.
A. Curve Crossing Treatment of E-V Transfer

The theoretical treatment of E-V transfer as a curve crossing event between two adiabatic zero order electronic potential energy curves was first evoked by Bjerre and Nikitin [18]. Figure (1-3) presents the repulsive portion of four zero order potential energy curves for four different interactions between a halogen and a molecular collision partner M. On the horizontal axis of the figure the distance between the halogen atom and the molecule is depicted, and on the vertical axis the potential energy is depicted. The topmost curve represents the interaction between a spin-orbit excited halogen (X*) and the molecule M(v=0). The curve below the top curve represents the potential interaction between a ground state halogen atom (X) and a molecule M(v=2). The second curve up from the bottom curve represents the interaction between a ground state halogen atom and a molecule M(v=1). The bottom potential energy curve represents the interaction between a ground state halogen atom and the molecule of interest that is not vibrationally excited. As shown in figure (1-3), if the repulsive portion of the energy curve is stronger than the curve for the interaction of X* with M(v=0) then a nonadiabatic crossing event occurs. Following the X*+M(v=0) curve from left to right as a collision begins X* and M(v=0) approach one another, and where this curve crosses another X* and M(v=0) it is possible that the system jumps to a lower curve, X+M(v=2) or X+M(v=0), as the collision is completed. This corresponds to a quenching of the spin-orbit excited halogen and an excitation of the molecule into the v=1 or v=2 state.
Figure 1-3: Depiction of the repulsive portion of four zero order potential energy curves between a halogen atom and a molecule M(v=x) in various vibrational excited states.

The probability \( P_{EV} \) that nonadiabatic cross over will occur can be predicted by the Landau-Zener formula [19]:

\[
P_{EV} \approx 1 - \exp\left( -\frac{2\pi |V_{if}|^2}{\alpha \hbar \Delta E} \right)
\]

\( \Delta E \) represents the energy difference between the two curves. The symbol \( \alpha \) represents the length of the interaction between the two potential curves. \( V_{if} \) is the matrix element of the interaction. From the form of this equation it is apparent that this curve crossing probability is enhanced by small \( \Delta v \) and \( \Delta E \). As more vibrational quanta are excited the
matrix element of interaction $V_{if}$ becomes a small. This causes the exponential to trend closer to 1. As the energy gap between the two curves becomes larger the exponential approaches a value of 1. In both situations this corresponds to a crossing probability approaching 0.

**B. Long Range Attractive Forces**

Long range attractive forces have been called into play to explain the coupling of vibrational degrees of freedom between two interacting molecules in order to explain the rate of V-V energy transfer. Ewing [20] co-opted the Sharma-Brau [19] theory and attempted to modify it to couple together electronic and vibrational degrees of freedom in order to predict the cross sections for reactions between electronic excited states in atoms. Using first order perturbation theory yields the following formula for predicting the probability of E-V energy transfer:

\[ P_{if} = \frac{\hbar}{2} \int_{-\infty}^{\infty} \langle i | V(t) | f \rangle \exp\left(-\frac{i\Delta E t}{\hbar}\right) \]  

Restricting this consideration only to electric dipole-allowed vibrations, $V(t)$ represents the time dependent interaction potential between the quadrupole of the electronically excited state and the dipole of the molecule. It is necessary to use the quadrupole moment for the halogen because it does not have a dipole moment. $\Delta E$ represents the energy gap between the final and initial states of the system. The terms $i$ and $f$ represent the initial and final states of the system. The interaction potential $V(t)$ is represented by the following formula:
Because this interaction potential is present in formula (1-2) ultimately the quadrupole moments of both the halogen and the molecule will be squared. Because of the squared dependence of the quadrupole moments the E-V transfer probability will drop off sharply with increases in $\Delta v$. An increase of $\Delta E$ will shrink the probability of E-V transfer because it is part of the negative exponential term shown in (1-2). It is important to realize that this formula was developed by Ewing for studies of E-V transfer between the electronic excited states of Pb and Te with D$_2$ and H$_2$. D$_2$ and H$_2$ each lack a dipole moment, and this is why the quadrupole moment is used in place of a dipole moment for the molecule in the formula.

When the energy transfer is near resonance ($\Delta E$~0), and the molecule attempting to quench the electronic excited state has a dipole moment, the following equation can be used calculate the cross section for a given E-V energy transfer between the quadrupole moment of the spin-orbit excited halogen and the dipole moment of the quenching molecule [2]:

$$
\sigma(T) = \frac{3\pi^2 \mu |\mu_{if}^M|^2 |Q_{if}^4|^2}{64\hbar^2 d^2 kT}
$$

This formula reveals the temperature dependence of the cross section for the quenching reaction of a spin-orbit excited halogen with a molecule. The term $d$ is the hard sphere collision cross section. $\mu_{if}^M$ is the dipole matrix element of the molecule and $Q_{if}^4$ is the quadrupole matrix element for the halogen $X^* \rightarrow X$ transition. The square of
the dipole matrix element is found in the formula for the strength of a vibrational transition induced by absorption of light, and the value of this term shrinks with increasing $\Delta v$.

Quantum Mechanical Treatments

Zimmerman and George have performed quantum mechanical treatments [21, 22] regarding X*-H$_2$ collinear collisions. For these calculations two adiabatic electronic energy surfaces are utilized for both spin-orbit halogen states, $^2P_{1/2}$ and $^2P_{3/2}$, and included in both surfaces are Morse potentials representing the vibrational energy wells for H$_2$ and H$_2$(v). Both surfaces were constructed from a “diatomics in molecule” approach (DIM). The probabilities for quenching Br* and I* were determined for H$_2$, HD, and D$_2$.

It was found that values of $\Delta v$ larger than 1 had a much smaller probability of successful E-V energy transfer. The cross sections obtained from the quantum mechanical treatments of Br* quenching by H$_2$, HD, and D$_2$ provide the given order of magnitude: $\sigma_{\text{HD}} > \sigma_{\text{H}_2} > \sigma_{\text{D}_2}$. The ordering of cross sections can be related to the increasing size of the energy gap between the first vibrational level of the diatomic and the Br* energy [21,22]. This result is supported by actual experimental work done by Grimley and Houston [23, 24]. In the experimental findings by Grimley and Houston the number of vibrational quanta excited per Br* quenched was calculated. For every Br* quenched the following number of vibrational quanta were excited: 0.78±0.22 for HD, 0.60±0.11 for H$_2$, and 0.094 ± 0.033 for D$_2$ [23]. These trends for the number of quanta
excited follow what is predicted by quantum mechanical measurements for the cross sections.

The ordering of cross sections from quantum mechanical calculations of I* quenching of HD, H₂, and D₂ follow the same order as Br*. The cross sections are smaller than those calculated for Br* quenching. The rate constants calculated for I* quenching by HD, H₂, and D₂ are also smaller than those for Br* quenching. These results are supported by actual experimental work done by Grimley and Houston [23, 24]. Due to the large amount of electronic energy of an I* atom the probability for quenching leading to a $\Delta v = 2$ transition in H₂ is greater than the probability of a $\Delta v = 1$ or 0 transition.

The trends anticipated by the quantum mechanical calculations agree with experimental results collected in E-V transfer studies. The calculations indicate that the probability for an energy transfer to a given E-V channel is dictated by $\Delta E$ and $\Delta \nu$ of the transition. There are two primary concerns with the quantum mechanical studies carried out. The calculations require an accurate potential energy surface, and the quantum mechanical calculations disregard rotational effects and long range attractive forces.
2. Experimental

I. General Overview of the Experimental Design

This first section in the experimental portion of the thesis will describe the general setup of the experimental apparatus and design. Beyond this introductory section the following topics will be presented in the following order: ICl vacuum line synthesis, ICl/IBr photochemistry, N2O vibrational energies, experimental apparatus, kinetic scheme, rise and decay signal analysis, and pseudo first order reaction conditions.

Figure 2-1 presents a simple schematic of the experimental apparatus. Sample gases are maintained in a vacuum line where degassing and distillation of gas samples can be carried out. In addition to processing sample gases, ICl synthesis is carried out in the vacuum line. ICl and IBr gas mixtures are stored in one of the four 12L bulbs attached to the vacuum line.

During experiments ICl and IBr gas mixes flow from the vacuum line and are allowed to enter the photolysis cell at a controlled flow rate dictated by electronic mass flow controllers. Cl* and Br* are generated by pulsed laser photolysis at 532nm by a frequency doubled Q-switched Nd: YAG laser.

Perpendicular to the cell is a HgCdTe photoconductive detector cooled by liquid nitrogen (77K). Infrared fluorescence from the photolysis cell induced by quenching and concomitant excitation of the molecule of interest is observed through a salt window and
a bandpass interference filter designed to only allow a specific window of IR radiation through to the detector. The signal from the detector is amplified and then sent to a digital oscilloscope. The time resolved IR signals traced on the oscilloscope are stored, and later transferred to a computer. The signals are then fit to a non-linear regression analysis in SigmaPlot®.

Figure 2-1: Simple schematic layout of the experimental apparatus. The triangle before the scope represents the preamplifier circuit.
II. ICl Vacuum Line Synthesis

Due to impurity concerns from commercially available sources of ICl a viable means of synthesizing a quality sample of ICl within the vacuum line was devised. The synthesis of ICl follows the straightforward stoichiometry:

$$I_2 + Cl_2 = 2 ICl$$

The stoichiometry indicates that with a given molar quantity of $I_2$ an equal molar amount of $Cl_2$ should be added.

The reaction is carried out in a glass sample vessel made of pyrex® and equipped with a vacuum stopcock or valve. The sample vessel has an approximately cylindrical volume of $\sim 200 \text{ cm}^3$ (20 cm high x 3.5 cm diameter). The top and bottom parts of the sample vessel are connected with a 35/45 standard taper joint and sealed with a halocarbon wax. The sample vessel is first attached to the line and pumped on under vacuum for over 24 hours to draw off any absorbed gases on the glass surface on the inside of the vessel. During this time interval the bottom portion of the sample vessel is warmed using a heat gun in order to further the desorption of water from the glass surface. The evacuated sample vessel is then sealed, removed from the line and weighed on a digital top loading balance. The evacuated and weighed sample vessel is reconnected to the vacuum line in order to receive the iodine reactant.

A 25-35 gram sample of iodine from Sigma Aldrich (99.99%) is mixed with anhydrous calcium sulfate (Drierite®), placed into a different glass vessel and attached to the line. After drying for one to two hours, the iodine sample is pumped under vacuum
for a brief period of time (~10 minutes). This action removes unwanted air and some of the iodine sample. The lower portion of the ICl sample vessel is immersed in liquid nitrogen. The iodine sample vessel is wrapped in resistive heat tape along with the section of the line leading to the ICl sample vessel. Both sample vessels are opened, and the heating of the iodine in conjunction with the liquid nitrogen cooling of the ICl sample vessel forces a re-sublimation of the iodine into the ICl sample tube over the course of several hours (often overnight). After an adequate amount of iodine is transferred into the ICl sample vessel both vessels are sealed. The ICl sample vessel is once again removed from the line and weighed on the top loading digital balance to determine the iodine reactant mass. Iodine samples of lesser purity are subjected to one or two resublimation steps before a final sublimation into the sample vessel. The iodine-loaded ICl sample vessel is then reattached to the vacuum line and ready to receive the chlorine reactant.

Semi-conductor grade (99.999%) or high purity grade (99.9%) chlorine gas from Mattheson is introduced into a 12L bulb connected to the vacuum line. The chlorine gas sample is degassed by exposing a portion of the 12L sample bulb surface to liquid nitrogen. This cold surface freezes out the chlorine gas, and all that remains are gases that are non-condensible at 77K (primarily air, CO and H₂). Any non-condensible impurities are pumped away from the 77K sample.

The stoichiometric number of moles of chlorine required for complete reaction is calculated from the iodine reactant mass. The chlorine reactant is added stepwise to a calibrated volume of the vacuum line manifold from the degassed 12L chlorine sample. After each filling of the manifold the initial chlorine pressure is noted, the ICl sample
vessel is opened and chlorine is allowed to react with the iodine until the manifold chlorine pressure decreases substantially. The lower pressure value is recorded in order to calculate the quantity of chlorine added in each step. The pressure cannot decrease below the ICl vapor pressure so that typical lower pressure stopping points are 35-40 Torr. Chlorine addition to the iodine results in a noticeable reaction that forms dark liquid ICl and some orange ICl$_3$ solid with evolution of heat. This stepwise method of addition and reaction is continued until ideal gas calculations indicate that approximately 98% of the required chlorine is added. At this point the ICl sample vessel is removed and weighed to verify the extent of reaction. The ICl vessel is returned to the line and chlorine addition continues until the reaction is stoichiometrically complete.

When the stochiometric addition of chlorine is completed, the lower half of the ICl sample vessel is immersed in water at 35-40°C and allowed to set overnight. The sample melts, and the remaining iodine and chlorine react. On setting overnight, the water bath cools to room temperature and the ICl sample solidifies.

III. ICl/IBr Photochemistry

The study of photochemistry entails the study of how electrons in molecules and atoms are excited by the absorption of light, and what unique chemistry evolves as a result of this absorption of light. An atom or molecule can absorb a photon and be excited into a new electronic state with a new electron arrangement. In addition to being in a new electronic state, molecules will also find themselves in vibrational and rotational states bound within the excited electronic state. When ICl or IBr absorb a quantum of light from a photon with a wavelength of 532nm they are excited above the dissociation
limit of the B electronic state so that most of the excited molecules dissociate creating Br* or Cl* and a ground state iodine atom.

A greater understanding of the photochemistry of IBr an ICl can be gleaned from molecular orbital theory. In molecular orbital theory atomic orbitals from the two parent atoms coming together to form a molecule merge into molecular orbitals (MO’s) that span both atoms. The combination of such orbitals is termed the linear combination of atomic orbitals (LCAO). The halogens have a valence shell configuration of ns²np⁵. Accordingly only the electrons in the p orbitals will be involved in forming LCAO molecular orbitals. Each halogen contributes 5 electrons to fill the MO’s formed between the two halogens. Along the z internuclear axis both pz orbitals of the halogen atoms can overlap forming a sigma bonding (σg) orbital. The px and py orbital can overlap to form two bonding πu orbitals, and two antibonding πg* orbitals. Placing the 10 electrons into the MO’s requires filling the lowest bonding MO first, and then “building up” similar to the Aufbau principle utilized for treating the filling of atomic orbitals. This yields a (σg)²(πu)⁴(πg*)⁴(σu*)⁰ ground state electronic configuration (X 1Σ⁺) for both interhalogens.

Absorption of a photon with a wavelength of 532nm excites an electron from the uppermost πg* anti-bonding orbital into the σu* anti-bonding orbital yielding an excited state configuration of a (σg)²(πu)⁴(πg*)³(σu*)¹. Two electronic excited states correlate to this gross electronic configuration. The B³Π(0⁺) electronic state, which is the dominant state excited by light at 532nm, has the orientation of the spin of the excited electron parallel with the spin of the electron it was originally paired with in the πg* MO.
Clyne and McDermid [26] have measured the spectroscopic constants for IBr and ICl in the \( B^3\Pi(0^+) \) electronic state. Figure (2-2) presents the Morse potentials (red and blue curves) and RKR energy curves (black curves) for the \( X(1\Sigma^+) \) and \( B(3\Pi(0^+)) \) electronic states for ICl. The spectroscopic constants used to generate the figure are found in table (2-1). The vertical arrow in the figure illustrates that the energy in one photon of light at 532nm is sufficient to excite the ICl molecule to its dissociation limit.

**ICl Potential Energy Curves**

![Potential Energy Curves](image)

Figure 2-2. Potential Energy Curves for the ground state \( X(1\Sigma^+) \) and the excited state \( B(3\Pi(0^+)) \) of ICl [26].
The process of photodissociation will occur when the energy imparted by absorption of a quantum of light is sufficient to break the weakest molecular bond [27]. The photodissociation quantum yields of Br* and Cl* are important because the concentrations of the electronic excited states produced by pulsed laser photolysis is crucial in the experimental studies carried out in this thesis. Seery and Britton [28] carried out room temperature absorption measurements of the halogens and interhalogens, including ICl and IBr, over a broad range of wavelengths. The extinction coefficient for ICl at 532nm is interpolated from their results to be $\varepsilon = 28.2 \text{ M}^{-1}\cdot\text{cm}^{-1}$, which corresponds to a cross section of $1.08 \times 10^{-19} \text{ cm}^2$. The quantum yield value for Cl* from ICl at 532nm used in these experimental studies is $0.58 \pm 0.03$ taken from studies by Mashnin [29]. The quantum yield for Br* produced by the photolysis of IBr at 532nm was found experimentally to be $0.68 \pm 0.05$ by Haugen et al [7].

Because the energy gained by the ICl or IBr molecule after absorbing a photon at 532nm is greater than the energy necessary for photodissociation the remaining energy is imparted as electronic excitation of Cl* or Br* and as translational energy in the recoiling

---

Table 2-1. Spectroscopic Constants of Molecular Iodine Monochloride, $^{127}$I$^{35}$Cl. [26]

<table>
<thead>
<tr>
<th>State</th>
<th>$T_e$(cm$^{-1}$)</th>
<th>$\omega_e$(cm$^{-1}$)</th>
<th>$\omega_e\chi_e$(cm$^{-1}$)</th>
<th>$B_e$(cm$^{-1}$)</th>
<th>$\alpha_e$(cm$^{-1}$)</th>
<th>$r_e$(Å)</th>
<th>$D_e$(cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi^1\Sigma^+$</td>
<td>0</td>
<td>384.3</td>
<td>1.501</td>
<td>0.11415</td>
<td>0.000534</td>
<td>2.31868</td>
<td>17577.5</td>
</tr>
<tr>
<td>$B^3\Pi(0^+)$</td>
<td>17375.4</td>
<td>204.5</td>
<td>2.595</td>
<td>0.08705</td>
<td>0.00200</td>
<td>2.66</td>
<td>1063.8</td>
</tr>
</tbody>
</table>

---

...
atoms. The amount of translational energy carried by each atom is of interest because it could potentially influence the excitation of low lying vibrational states in polyatomic molecules present in the photolysis cell that are being studied for Br* and Cl* quenching.

The assumption made in the kinetic studies in the following thesis work is that all reactants are thermalized. Thermalization means that the translational energy possessed by a recoiling atom after dissociation is close to the translational energy it should possess at room temperature.

The dissociation energy \( D_e \) plus the energy of the spin-orbit electronic state for Cl* and Br* provide the necessary information to calculate the energy that is left over to be partitioned into translational energy. The energy \( E_{\text{excess}} \) remaining after photodissociation occurs can be given by:

\[
E_{\text{excess}} = \frac{hc}{\lambda} - \left( D_o + E_{\text{Cl}^*} \right),
\]

Where \( D_o \) is the dissociation energy from the zero point vibrational energy level in the ground electronic state:

\[
D_o = D_e - \frac{1}{2} \left( \omega_e \right)
\]

\( D_o \) for ICl is 17349 cm\(^{-1} \), and \( D_o \) for IBr is 14655 cm\(^{-1} \) [27]. \( E_{\text{Cl}^*} \) is 881 cm\(^{-1} \), and \( E_{\text{Br}^*} \) is 3685 cm\(^{-1} \). The energy of a photon with a wavelength of 532 nm is 18782 cm\(^{-1} \). From these values \( E_{\text{excess}} \) for the photolysis of ICl is 552 cm\(^{-1} \), and \( E_{\text{excess}} \) for the photolysis of IBr is 442 cm\(^{-1} \).

In order to determine the translational energy imparted to Br* and Cl* specifically the conservation of momentum and energy must be called into play:

\[
E_{\text{excess}} = \frac{1}{2} m_{\text{Cl}} v_{\text{Cl}}^2 + \frac{1}{2} m_{I} v_{I}^2
\]

\[
m_{\text{Cl}} v_{\text{Cl}} = m_{I} v_{I}
\]
The results from equations (2-5) through (2-8) indicate that after ICl or IBr photodissociation at 532 nm a Cl* atom has 419 cm\(^{-1}\) of translational energy, and a Br* atom has 245 cm\(^{-1}\). The Cl* atoms have roughly 2kT (kT/hc = 208 cm\(^{-1}\)) translational energy, while the Br* atoms are given ~1kT translational energy.

IV. \(\text{N}_2\text{O} \) Vibrational Energies

Nitrous oxide (\(\text{N}_2\text{O}\)) is a linear triatomic belonging to the symmetry point group \(\text{C}_{\infty v}\). The simple structure of \(\text{N}_2\text{O}\) is:

\[
\text{N}_1=\text{N}_2=\text{O}
\]

The \(\text{N}_2\text{O}\) molecule has nine degrees of freedom. Three degrees of freedom belong to translational motion in three dimensions. Two translational degrees of freedom belong to rotational motion. The remaining four degrees of freedom are reserved for vibrational modes. There is a symmetric stretch (\(\nu_1\)), an asymmetric stretch (\(\nu_3\)), and a doubly degenerate bending mode (\(\nu_2\)). The symmetric stretch occurs at 1285 cm\(^{-1}\). The asymmetric stretch occurs at 2224 cm\(^{-1}\), and the degenerate bending mode occurs at 589 cm\(^{-1}\). The intensity strength of absorption and emission of these bands in the IR spectrum can be correlated to their Einstein coefficients. Table (2-2) presents the wavenumber region of absorption in the IR spectrum along with the Einstein coefficient for each of the vibrational modes. The most intensely absorbing vibrational mode is the asymmetric stretch with an Einstein coefficient of 236 s\(^{-1}\). This is also the most brightly emitting vibrational state. The second brightest emitting band is the symmetric stretch with an
A coefficient of 12 s\(^{-1}\). The weakest emitting and absorbing band in the N\(_2\)O band is the bending mode with a coefficient of 0.38 s\(^{-1}\).

Table 2-2: Presentation of IR absorption region for each vibrational band along with the appropriate Einstein coefficient [30]

<table>
<thead>
<tr>
<th>Vibrational Mode</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Einstein Coefficient (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_2)</td>
<td>589</td>
<td>0.38</td>
</tr>
<tr>
<td>(\nu_1)</td>
<td>1285</td>
<td>12</td>
</tr>
<tr>
<td>(\nu_3)</td>
<td>2224</td>
<td>236</td>
</tr>
</tbody>
</table>

V. Experimental Apparatus

The following topics in this section will attempt to describe in some detail the components of the experimental apparatus shown in Figure (2-1).

A. Nd:YAG Laser System

A laser operates on the principle of stimulated emission of radiation. Light passing through a sample is absorbed according to Beer’s Law. However if the molecule exposed to the light already exists in an excited state this exposure will cause the molecule to emit a photon from that state with some probability. This emission is said to
have been stimulated by exposure to light radiation, and as a result rather than the beam of light passing through the sample losing intensity it actually experiences an intensity gain. This concept is called light amplification by stimulated emission of radiation, giving rise to the “laser” acronym.

The pulsed photolysis laser used in these experimental studies is a Spectra Physics DCR-11 pulsed Nd:YAG laser [31]. The Nd:YAG laser is a solid-state laser in which the active medium for generation of photons is a yttrium aluminum garnet (YAG) rod doped with a low concentration of Nd$^{3+}$ ions. A flashlamp placed in close proximity to the rod emits light that is absorbed by several Nd$^{3+}$ absorption bands in the red and near infrared regions. The Nd:YAG laser operates by a four step mechanism as shown in figure (2-3). In figure (2-3) optical pumping excites ground state Nd$^{3+}$ ions (E1) primarily into two excited states labeled E2 and E3. These excited states relax through a nonradiative process into the metastable state E4. A state is said to be metastable if it requires a relatively long time to relax. For Nd$^{3+}$ state E4 has a lifetime of 230μsec. Relaxation to the E5 state occurs through stimulated emission of a photon of light at 1064 nm. The E5 state has a very short lifetime. In combination with the short lifetime of the E5 state, and the relatively long lifetime of the E4 state, a population inversion is maintained. A population inversion is necessary for lasing to occur because a greater than equilibrium population must be present in the E4 state, otherwise stimulated emission could not occur.
The Nd:YAG laser is capable of operating in a long pulse or Q-switched mode. In the long pulse mode the laser output pulse approximately matches the $\approx 200 \mu s$ duration of the exciting flashlamp. In the Q-switched mode the resonant character of the laser cavity is blocked for most of the flashlamp pulse duration and restored quickly only after population has built up in the lasing level. Blocking the resonant character of the laser cavity involves the use of Pockel’s cell. A Pockel’s cell is an electro-optical device composed of crystals of potassium dihydrogenphosphophate (KH$_2$PO$_4$). When an electrical potential is applied to the crystal material of a Pockel’s cell any light passing through will be circularly polarized before it reaches the high reflector at the back of the laser cavity. Returning from the high reflector the light is polarized further to the point that it is now perpendicularly polarized from when it first passed through the Pockel’s cell. This light is not capable of stimulating emission of radiation. The flashlamp excites Nd$^{3+}$ ions for $\approx$
200μs, amassing population in the E4 state. When the potential is no longer applied to
the Pockel’s cell the resonant characteristics of the laser cavity are restored and short
powerful pulse (< 10nsec) of laser light is dumped from the cavity.

The Spectra Physics DCR-11 pulsed Nd:YAG laser uses an “unstable resonator”
design. At both ends of the laser cavity are mirrors. The high reflector has a concave
shape, and the output mirror is convex in shape with a highly reflective spot in the center
of the convex mirror. Laser light reflecting from this spot diverges as it heads towards
the high reflector, and sweeps through a large portion of the Nd:YAG medium picking up
gain. This divergent light strikes the concave high reflector and is reflected back towards
the convex mirror where beam intensity spills over the edges of the highly reflective spot.
This produces a “donut” shaped beam profile.

The fundamental wavelength of the Nd:YAG laser is 1064 nm, but making use of
a nonlinear optical phenomena known as sum frequency generation it is possible also to
generate light at the harmonic wavelengths of 532, 355, and 266 nm. In the classical
sense, a new output frequency is generated that is the sum of two input frequencies. A
single beam input is equivalent to two identical input frequencies, and the output is
“frequency-doubled”. In the quantum sense, two input photons are exchanged for a
single output photon of twice the energy. This harmonic generation process is
accomplished with a potassium dideuterium phosphate (KD*P) crystal. Only a fraction
of the input beam energy is converted to the sum frequency; a significant fraction of the
original beam emerges from the crystal along with the harmonic beam. Each desired
harmonic wavelength requires a specific incident angle with respect to one of the crystal
axes. To generate the 532 nm second harmonic beam, the fundamental 1064 nm beam is
passed through the crystal face and the second harmonic beam is generated in the crystal and emerges collinearly with the fundamental beam. The beam of light, now composed of multiple wavelengths, passes through a Pellin-Broca prism where separation of the harmonics occurs. The angle at which the beam strikes the Pellin-Broca prism is Brewster’s angle, the angle that minimizes loss due to reflectance for one of the linear polarizations. A 90° prism is positioned to direct the 532 nm beam through the photolysis cell.

**B. Vacuum System**

The vacuum system provided for gas sample purification and introduction of various gases into the photolysis cell. The vacuum line also provided an air-free environment for the synthesis of ICl.

The vacuum system used for these experiments had four 12L pyrex sample bulbs connected to a glass manifold by Cajon® fittings. At various intervals, sections of the manifold could be closed off through the use of stopcocks that would seal by an o-ring contact with the inner glass surface. Gas pressure could be measured using one of the two MKS Baratron capacitance manometers. The manometer on the front portion of the manifold was calibrated for 1-10 Torr pressure readings, and the monometer attached to the back portion of the manifold was calibrated for 1-1000 Torr readings. The back portion of the manifold held the large 12L sample bulbs, and could be separated from the front portion of the manifold where a cold-finger trap was placed ahead of an oil diffusion pump and a rotary mechanical pump. Valved connections were made from the
back manifold of the vacuum line to the MKS electronic mass flow controllers for flowing sample gases such as ICl and N₂O.

N₂O gas samples from Aldrich (≥99%) and Liquid Carbonic (≥99.5%) were used to create the ICl/N₂O gas mixes. Some N₂O samples were distilled from an ethanol slush while others were multiply degassed at 77K. No differences in results were observed with different N₂O samples or treatments. IR scans of the absorption spectrum for both samples presented no IR bands from noted impurities. Non-condensable impurities (air, H₂) at liquid nitrogen temperature (77K) amounted to <15 ppm.

Argon gas samples from Matheson (99.999%) and Air Products (99.998% UHP zero grade) were used in the current study. To remove any trace water impurity the argon samples were flowed through a molecular sieve cooled by an ethanol slush bath (~156K).

C. Photolysis Cell

The photolysis cell is a crucial part of the experimental studies carried out in the thesis project. Sample gases flow into the cell from electronic mass flow controllers. During experiments the gases are pumped through the photolysis cell by a mechanical rotary pump (Sargent-Welch Duo-Seal® model 1375, 500L/min). A stopcock and a needle valve were used in parallel paths to control the rate at which gases were pumped from the cell, thereby controlling the total pressure of gases in the photolysis cell. Total gas pressure in the cell could be monitored through the use of two MKS Baratron capacitance manometers with one manometer calibrated from 1-10 Torr, and the other calibrated for 1-100 Torr pressure measurements. Ahead of the mechanical rotary pump is a cold gas finger trap that is immersed in liquid nitrogen (77K) during experiments.
When experiments are ended, this trap can be isolated from the pump and photolysis cell and allowed to warm to room temperature while purging with nitrogen gas to force the halogens into a neutralizing solution of sodium hydroxide. The pulsed laser beam is passed through the cell in order to generate Cl* or Br* from the interhalogen precursor in the cell. The infrared detector is positioned perpendicular to the incident photolysis beam in order to observe the transient fluorescence from the molecular vibrational states excited by Cl* or Br* quenching.

The photolysis cell used in the experiments was crafted by John Dryden from a piece of Pyrex tubing 38 cm in length, and 41 mm O.D. Two fused silica windows were position diametrically opposed to one another on each side of the photolysis cell so that the pulsed photolysis laser beam could pass through the cell. Perpendicular to the beam path, a 38mm diameter KCl window is attached to the cell with Apiezon black wax. The IR detector window, with an interceding spectral bandpass interference filter attached, could be brought up flush with this salt window so that IR fluorescence observations could be made. The photolysis cell has six gas inlets, with five positioned along one side of the glass tube, and one directly on the top of the cell.

**D. Spectral Filters**

Spectral filters were used in the experimental studies in order to minimize the influence from scattered laser light, and to optimally allow for the observation of IR emission from selected vibrational states of interest. The general design of a spectral filter involves layering high and low refractive index dielectric compounds on a transparent substrate, and then sealing the stack of layers with another transparent
material. At each interface between a layer of two different materials light will be reflected or transmitted to varying degrees according to wavelength, and the stack of multiple interfaces leads to destructive and constructive interference that allows a filter to transmit only a portion of the light spectrum. The filters used in the following experimental studies are bandpass filters. Bandpass filters are created such that a transmission “window” exists between two wavelength limits. Light of wavelengths falling outside this window will not be transmitted through the filter.

Various spectral bandpass filters were used in the experimental studies depending on the emission region of interest. Figure (2-4) presents the N$_2$O spectrum with appropriate ($v_1$, $v_2$, $v_3$) labels for each identifiable vibrational band. N$_2$O($v_1$) emission at 1285 cm$^{-1}$ (100 → 000) was observed using the 24R spectral bandpass filter in the Cl* studies. Figure (2-5) presents the filter transmittance scan of the 24R filter using a Genesis FT-IR laid over the N$_2$O spectrum. Fluorescence from overtone or combination levels of $v_1$ are only slightly shifted from the fundamental $v_1$ band and also are passed by the 24R filter. This includes the transitions 101 → 001 and 200 → 100, which are unlikely to make a noticeable contribution to emission intensity in the kinetic studies carried out for Cl* quenching by N$_2$O. In this figure it is apparent that 020 → 000 emission at 1173 cm$^{-1}$ also will be passed through the 24R filter. The degree to which this impacted the $v_1$ IR fluorescence signals is minor due to the weak emission probability of the 020 state compared to the much stronger emission probability of the 100 quantum state. This qualitative comparison can be made by looking at the absorption strengths of both of the vibrational bands lying side by side in the spectrum. Experimental determination of the $v_1$ E-V branching ratio, which will be presented in
Chapter 3, requires knowledge of the percent transmittance of 100 $\rightarrow$ 000 emission through the 24R filter. It is determined to be 94% over the 1285 cm$^{-1}$ band.

Figure 2-4: N$_2$O spectrum with labels for each N$_2$O vibrational band and the position of the Br* transition ($^2P_{1/2}$ $\leftarrow$ $^2P_{3/2}$) at 3685 cm$^{-1}$ and Cl* transition ($^2P_{1/2}$ $\leftarrow$ ($^2P_{3/2}$) at 882 cm$^{-1}$.

![N2O spectrum with labels for each N2O vibrational band and the position of the Br* transition (2P_{1/2} \leftarrow 2P_{3/2}) at 3685 cm^{-1} and Cl* transition (2P_{1/2} \leftarrow 2P_{3/2}) at 882 cm^{-1}.]
The final experimental studies to determine the rate at which N\textsubscript{2}O quenches Cl\textsuperscript{*} were done by observing its effect as a competitive Cl\textsuperscript{*} quencher on SO\textsubscript{2}(\nu\textsubscript{3}) fluorescence intensity. Figure (2-6) illustrates the absorption band intensity of SO\textsubscript{2}(\nu\textsubscript{3}), which is curve B in the figure. A transmission curve for the N07355-9A bandpass filter is presented as curve A. Curve C represents the product of the filter transmission and absorption band curves for the filter and SO\textsubscript{2}(\nu\textsubscript{3}). Curve D is the absorption band intensity for N\textsubscript{2}O(\nu\textsubscript{1}). Curve E represents the product of the curve for the absorption band intensity for N\textsubscript{2}O(\nu\textsubscript{1}) and the transmission curve for the N07355-9A bandpass filter.
The % transmission of a vibrational band through the filter can be expressed in equation (2-9):

\[
\left( \frac{\int (A(\nu) \times T(\nu))d\nu}{\int A(\nu)d\nu} \right) \times 100
\]

(2-9)

A(\nu) represents the absorption band curve, and T(\nu) represents the transmission curve over the wavelength region \( \nu \) cm\(^{-1}\). The integral of the area underneath the curve resulting from the product of the filter transmission curve and the vibrational band...
divided by the area under the vibrational band absorption curve gives you the fractional value of the absorption band that passes through the filter. Multiplying this value by 100 gives you the % transmission of the emission that can pass through the interference filter. These calculations indicate that 66% of the SO$_2$(ν$_3$) emission passes through the interference filter. By contrast only 0.2% of the N$_2$O(ν$_1$) emission passes through the transmission filter. The fluorescence contribution from N$_2$O(ν$_1$) in experiments observing SO$_2$(ν$_3$) fluorescence is negligible.

E. HgCdTe Detectors

A photoconductive HgCdTe detectors (MCT2) was used in this study in order to measure the fluorescence intensity from emitting excited states. The detector has a 4 mm x 4 mm active surface area that was cooled to 77K with liquid nitrogen inside a metal dewar. MCT2 incorporates a ZnSe lens between a ZnSe window and the detector element in an attempt to direct more light onto the detector element. The MCT2 detector is sensitive in the range of ~2-21 μm. The spectral response curve for the MCT2 detector is presented in figure (2-7). Detector response values used in branching ratio determinations are taken from the response curves supplied by the manufacturer.

The resistance of a photoconductive MCT detector decreases as the light intensity falling on it increases. The detector resistance is placed in series with a bias resistor of larger value, and a constant current is flowed through the two resistors from a constant voltage source (battery). A simple circuit diagram is shown in figure (2-8) to illustrate the electrical set-up. The bias resistance was effectively ten times that of the MCT photoconductive detector. Light intensity is measured by the voltage drop across the
detector resistor. An AC coupled pre-amplifier magnifies changes in this voltage drop when the detector resistance decreases due to the absorption of photons in the spectral response region. The preamp is powered by a ±15V NiCd or ±12V lead-acid gel cell battery pack. The change in voltage is negative when the resistance of the detector element is reduced due to light exposure. After passing through the preamp the signal then goes to a digital oscilloscope. In order to make physical sense this change in potential is inverted and then interrupted as a measure of the fluorescence emission intensity.

Figure 2-7: Diagram of the amplifier circuit for the MCT2 detector.
VI. Kinetic Mechanism for Cl*/N$_2$O

Based upon previous Cl* quenching studies in this group the following kinetic mechanism is expected in the Cl* quenching by N$_2$O. The simplified Cl*/N$_2$O mechanism, when taking into consideration pseudo-first order reaction conditions, lacks reversible steps and provides a firm foundation to draw a correlation between experimental time-resolved fluorescence signals and the postulated kinetic mechanism presented. The following processes present the steps in the kinetic mechanism where Cl* is quenched:
(2-10) \[ \text{Cl}^* + \text{N}_2\text{O} \rightarrow \text{Cl} + \text{N}_2\text{O}(v_1) \]

(2-11) \[ \text{Cl}^* + \text{N}_2\text{O} \rightarrow \text{Cl} + \text{N}_2\text{O}(01^1\text{O}) / \text{N}_2\text{O}(00^0\text{O}) \]

(2-12) \[ \text{Cl}^* + \text{ICl} \rightarrow \text{Cl} + \text{ICl} / \text{I} + \text{Cl}_2 \]

(2-13) \[ \text{Cl}^* + \text{M} \rightarrow \text{Cl} + \text{M} (\text{Ar, CCl}_4, \text{CD}_4) \]

Equation (2-10) represents the E-V quenching process that excites \text{N}_2\text{O}(v_1). Equation (2-11) is a process by which \text{N}_2\text{O} quenching \text{Cl}^* and does not excite \text{N}_2\text{O}(v_1). Equation (2-12) is the process by which \text{ICl} quenches \text{Cl}^*, either by physical or reactive channels. Equation (2-13) encompasses the addition of any other gas or gases capable of quenching \text{Cl}^* to the system, which for studies carried out in this thesis the added gases were \text{Ar}, \text{CCl}_4, \text{and CD}_4.

Pseudo first-order conditions were maintained in the experiments by keeping the concentrations of \text{N}_2\text{O}, \text{Ar}, \text{ICl}, \text{CCl}_4, \text{and CD}_4 many fold greater than the concentration of \text{Cl}^*. Under pseudo first-order conditions the rate at which \text{Cl}^* concentration changes with time can be given by:

\[
(2-14) \quad \frac{d[\text{Cl}^*]}{dt} = -\left\{ k^*_{\text{N}_2\text{O}}[\text{N}_2\text{O}] + k^*_{\text{ICl}}[\text{ICl}] + k^*_{\text{Q}}[\text{M}] \right\}[\text{Cl}^*] = k^*[\text{Cl}^*] 
\]

Where \( k^* \) represents the pseudo first-order rate coefficient for \text{Cl}^* quenching by all processes. This first order differential equation can be solved to yield a simple exponential decay function as presented in equation (2-15). \([\text{Cl}^*]_0\) represents the initial concentration of \text{Cl}^* at \( t = 0 \) prepared by the nearly instantaneous 8ns laser pulse.
\[ [Cl^*] = [Cl^*]_0 e^{-k't} \]

Obtaining the pseudo first-order rate constant for Cl* quenching by direct observation is not possible with the IR fluorescence technology used in the Laser Laboratory at Wright State University. The long radiative lifetime of 83 seconds for Cl* decay provides a very low intensity signal that is not detectable with currently available technology. The pseudo first-order rate constant for Cl* quenching can be determined via the E-V process that excites N\textsubscript{2}O(\nu_1). Time-resolved IR fluorescence observations of N\textsubscript{2}O(\nu_1) contain the necessary information to determine the rate of Cl* quenching by N\textsubscript{2}O and other gases present, as well as the rate of collisional relaxation of the emitting vibrational excited state.

The relaxation of N\textsubscript{2}O(\nu_1) can occur in a collision with a molecule or atom M. The process of vibrational relaxation may be expressed as:

\[ (2-16) \quad N_2O(10^00) + M \xrightarrow{k^V_M} N_2O(0n^0) / N_2O(000) + M \]

From the expression in equation (2-16) the following rate equation (2-17) can be expressed for the time dependent population of N\textsubscript{2}O(\nu_1):

\[
\frac{d[N_2O(\nu_1)]}{dt} = k^*_{EV}[N_2O][Cl^*] - \sum_M k^V_M[M][N_2O(\nu_1)]
\]

\[ (2-17) \quad \Rightarrow \frac{d[N_2O(\nu_1)]}{dt} = k^EV[Cl^*] - k^V[N_2O(\nu_1)] \]

The second rate equation presents the form after pseudo first-order conditions are invoked. \(k^EV\) and \(k^V\) represent pseudo first-order rate constants, respectively, for the Cl* quenching.
quenching process generating $N_2O(v_1)$ and for the relaxation of $N_2O(v_1)$. The solution to the differential equation presented in (2-17) can be achieved by substituting equation (2-15) for the $[Cl^*]$ concentration. The integrated rate law for equation (2-17) becomes:

$$\begin{align*}
(2-18) \quad [N_2O(v_1)] = & \left( \frac{k^{EV}}{k^*-k^V} \right) [Cl^*]_0 \left( e^{-k^V t} - e^{-k^* t} \right)
\end{align*}$$

The difference of exponential functions in equation (2-18) describes a rise and decay of population. Physically, the rise is associated with the faster process and the decay is associated with the slower process. Mathematically, the rise is described by the negative term, and the positive term describes the decay. Accordingly it is possible that the population rise is due to either the production process or the relaxation processes. The intensity of IR fluorescence of the time-resolved IR signal for $N_2O(v_1)$ is proportional to its population. Taking into account this correlation the experimental signals observed can be fitted to an equation of the form:

$$\begin{align*}
(2-19) \quad I_f = I_o \left( e^{-k^V t} - e^{-k^* t} \right)
\end{align*}$$

The term $I_o$ is linearly related to the pre-exponential coefficient $\left( \frac{k^{EV}}{k^*-k^V} \right) [Cl^*]_0$ found in equation (2-18). Through non-linear regression analysis of the time resolved IR signals the values for $I_o$, $k^*$, and $k^V$ can be determined from experimental observations.

**VII. Association of Signal Rise and Decay with Kinetic Processes**

Section IV presented a pseudo first-order kinetic mechanism for $Cl^*$ quenching by $N_2O$. The mechanism follows the simple kinetic path:
\[(2-20) \quad X^* \xrightarrow{k_{EV}} N_2O(\nu_x = 1) \xrightarrow{k_V} N_2O(0n^10)\]

$X^*$ represents Cl*, and $\nu_x = 1$ indicates one quantum of $\nu_1$ that has been excited by Cl* quenching. Deactivation of $N_2O(\nu_1)$ can populate $0n^10$ states. The deactivation of $\nu_1$ can proceed through the 020 level to 010 and ultimately to 000. This simple mechanism is a three step chemical mechanism that is similar to the first-order textbook mechanism in equation (2-21):

\[(2-21) \quad A \xrightarrow{k_1} B \xrightarrow{k_2} C\]

$k_1$ is equivalent to $k_{EV}$ in the Cl* quenching mechanisms, and $k_2$ is equivalent to $k_V$. The solution to the time dependence of state B is:

\[(2-22) \quad [B] = \frac{k_i}{k_i - k_2} [A]_0 \left( e^{-k_2t} - e^{-k_1t} \right)\]

In equation (2-22) when $k_1$ is taken to be the larger rate coefficient, the pre-exponential coefficient is positive and the $k_1$ exponential function dominates the rising portion of the concentration dependence of B with time. If the magnitude of the rate coefficients were switched then the pre-exponential coefficient in equation (2-22) would be negative and the $k_2$ exponential function would describe the rising portion of the $[B]$ vs. time function. This latter case is counter-intuitive to the common expectation that the rise of the signal should correlate to the production of B. Nonetheless, the rise of the population function is associated with the faster pseudo first-order process, whether it is the production or the loss of the intermediate species. The only way to determine the association of the population rise and decay functions with production and loss is through experimental means.
The two-step mechanism in (2-21) is analogous to the kinetic mechanism proposed in Cl* E-V excitation of N2O \( \nu_1 \) fluorescence. In the quenching mechanism the emitting state is represented by the intermediate B. A single rise and decay is observed for the fluorescence signals, and assignment of the rise and decay to the processes for quenching and relaxation is accomplished via the following experimental methods. Ideally, one would like to alter conditions such that either the quenching or the relaxation rate is increased while the other process is left relatively unaffected. Observing either an increased rate of population rise or its decay resulting from the altered conditions would associate one of the kinetic features with the correct process and the other would be known by default. The research work in this thesis used the addition of gases that are either efficient Cl* quenching agents, or poor quenching agents but effective relaxing agents. Argon was used to identify relaxation processes, and CCl\(_4\) and CD\(_4\) were used to identify the quenching processes. In this thesis a conflict arises because the results from the CCl\(_4\) and CD\(_4\) studies are at odds with the argon studies. All three added gases impact the rise portion of the fluorescence signal, and leave the decay portion relatively unaffected by comparison.

**VIII. Pseudo First-Order Reaction Conditions**

A cursory review of the Cl*/N\(_2\)O mechanism presented in section IV reveals that all the elementary steps are bimolecular, and hence their rate laws are second order. To simplify analyses of experimental observations pseudo first-order reaction conditions were invoked with the following conditions: \([\text{Cl}^*]_0 \ll [\text{N}_2\text{O}], [\text{ICl}], [\text{Ar}], [\text{CD}_4], [\text{CCl}_4]\)
The initial concentration of Cl* or Br* generated by pulsed laser photolysis can be estimated provided the laser beam pulse energy, beam diameter, and ICl pressure. With these values the application of Planck’s and Beer’s Law then allows for an estimate of the concentration of Cl* at $t = 0$. Beer’s Law, which is shown in equation (2-23), can be used to calculate the absorbance of light at 532nm by IBr or ICl. $I_0$ and $I$ represent the incident and transmitted light intensities after passage through a given length $l$ of a number density $N$ of absorbing molecules with an absorption cross section $\sigma$.

\[
(2-23) \quad I = I_0 e^{-\sigma N l}
\]

Equation (2-23) can be written in terms of the fraction of light at a specific wavelength absorbed by the species present in the beam path as:

\[
(2-24) \quad f_{abs} = \left(1 - \frac{I}{I_0}\right) = 1 - e^{-\sigma N l} \approx \sigma N l
\]

The approximation used in equation (2-24) is valid if the product $\sigma N l \ll 1$, and the quadratic and higher terms of the Taylor series polynomial expansion are ignored due to their small value.

Planck’s law, illustrated in equation (2-25), allows for the calculation of the number of photons generated in a monochromatic pulse of laser light.

\[
(2-25) \quad N = \frac{E \lambda}{h c}
\]

$E$ is the energy of the laser pulse. $\lambda$ represents the wavelength of the photons in that laser pulse. $h$ is Planck’s constant, and $c$ is the speed of light. The number of Cl* or Br* atoms produced from a pulse of laser light, $N_{X^*} = N_{abs} \cdot \phi_{X^*}$, is equal to the product of the number of photons in the laser pulse, the fraction of light absorbed at 532nm, and the $X^*$
photolysis quantum yield at 532nm for IBr and ICl. This product divided by the volume traced out by the laser beam in the photolysis cell leads to equation (2-26) for the initial concentration of Br* or Cl* produced.

$$\left[ X^* \right]_o = \frac{(5.03 \times 10^{-12}) E \lambda \sigma N \phi_{X^*}}{A}$$

In equation (2-26) the volume swept out by the laser beam is equal to the product of the cross-sectional area $A$ of the beam and the path length $l$. Pathlength entries (from $\sigma N l$ in the numerator and from $A l$ in the denominator) in equation (2-26) cancel so that $l$ does not appear in the equation. The constant value $5.03 \times 10^{-12}$ is $1/\hbar c$ with a factor of ten alteration to account for the use of units as described. The quantum yield, $\phi_{X^*}$, is a unitless value less than one. The cross section, $\sigma$, for IBr or ICl is given in cm$^2$. $E$ represents the energy in the laser pulse in mJ, and $\lambda$ is taken to be the photolysis wavelength in nm.

The cross sections for both IBr and ICl were interpolated from molar extinction coefficient $\varepsilon$ (M$^{-1}$cm$^{-1}$) data from Seery and Britton [28]. It was necessary to interpolate the values because Seery and Britton only measured $\varepsilon$ values in 10 nm intervals. For ICl $\varepsilon$ at 530 nm was 30.0 M$^{-1}$cm$^{-1}$, and at 540 nm 20.9 M$^{-1}$cm$^{-1}$. Interpolation yields a value of 28.2 M$^{-1}$cm$^{-1}$ at 532 nm. For IBr $\varepsilon$ at 530 nm is 224.5 M$^{-1}$cm$^{-1}$, and 176.6 M$^{-1}$cm$^{-1}$ at 540 nm. This interpolates to an $\varepsilon$ of 214.9 at 532 nm. The molar extinction coefficients can be converted into cross sections simply by converting molar units (mole/L) to the number density (molecules per cm$^3$) and multiplying the resulting value by natural logarithm of 10. This yields an absorption cross section of $\sigma = 1.09 \times 10^{-19}$ cm$^2$ for ICl at 532 nm, and $\sigma = 8.22 \times 10^{-19}$ cm$^2$ for IBr at 532 nm. The photolysis quantum yield of
Cl* from ICl at 532 nm is 0.58±0.03 as determined by Mashnin et al. [29]. The photolysis quantum yield of Br* from IBr at 532 nm is 0.68±0.05 as determined by Haugen et al. [6].

Cl*/N_2O kinetic runs were done with an average pressure of 120 mTorr of ICl. In the Cl*/N_2O study the laser pulse energy was 60 mJ. This corresponds to a Cl* atom concentration of 4.2 x 10^{13} atoms·cm^{-3} respectively. This corresponds to an initial Cl* pressure of 1.3 mTorr, respectively. The [ICl]/[Cl*]₀ pseudo first-order ratio in most experiments is ~100. This is an ample excess of ICl such that pseudo first-order conditions will be observed. The critical concern is that pseudo first-order reaction conditions are maintained with respect to N_2O. At low pressures the amount of N_2O present is near 50 mTorr in Cl*/N_2O studies, and the [N_2O]/[Cl*]₀ pseudo first-order ratio is ~38. By comparison with typical rate coefficient uncertainties of 20% or more, in the Cl*/N_2O study ample pseudo first-order excess is present with respect to the N_2O concentration. This also ensures that the concentration of the excited vibrational states prepared in the kinetic study is quite small compared to the excess concentrations of collision partners that can vibrationally relax the states.
3. Results and Discussion

I. Cl*/N₂O Kinetic Study

This portion of the thesis project centers around resolving the conflicts in the thesis work of J.S. Batson [1] regarding the rate coefficients for the Cl* quenching and relaxation of N₂O(v₁) by N₂O. N₂O kinetic studies done by J.S Baton [1] were carried out in the presence of a constant argon bath around 5 Torr. The assignment of the rise and decay processes in the study to vibrational relaxation and Cl* quenching was based upon the behavior of argon. The rise of the signal was associated with vibrational relaxation of N₂O(v₁), and the decay was associated with Cl* quenching. Based upon these assignments k⁺N₂O was found to be (3.5 ± 0.3) x 10⁻¹² cm³ molecule⁻¹ s⁻¹, and k⁻N₂O was found to be (5.9 ± 1.2) x 10⁻¹² cm³ molecule⁻¹ s⁻¹. Chichinin’s value [14] for Cl* quenching by N₂O strongly suggested that the value for k⁻N₂O was actually k⁺N₂O. Even if the assignment of the rate constants to specific processes was switched the new value for k⁻N₂O is nearly three times greater than the average accepted literature value [32,33,34,35].

The first studies carried out in the present work were in ICl/N₂O mixtures where argon was excluded. A second set of kinetic studies was then performed by bringing argon back into the gas mixtures. In an attempt to verify the association of the N₂O(v₁) fluorescence rise with Cl* quenching a third set of experiments were carried out with the
Cl* quenchers, CCl₄ and CD₄. Finally, an attempt was made to measure the rate coefficient for Cl* quenching by N₂O, k*ₙ₂₀, in competition with SO₂. Pseudo first-order quenching rates were obtained from the rise of SO₂(ν₃) time-resolved IR signals while adding increasing partial pressures of N₂O to fixed concentrations of SO₂ and ICl. It is disconcerting that there remain significant differences in the k*ₙ₂₀ values determined in ICl/N₂O mixtures with and without argon and in the competitive studies with SO₂.

A. Studies of N₂O(ν₁) Dependence On N₂O In The Absence of Argon

Previous Cl*/N₂O studies done by J.S. Batson [1] included the presence of ~5 Torr of argon. In Batson’s experiments ~20 Torr of the ICl sample typically were mixed with ~400 Torr of argon to provide sufficient backing pressure to flow ICl through the flow controllers. Additionally, an inert gas such as argon ensures thermalization of the photolytically prepared Cl* atoms. Batson also used added pressures of argon to identify the N₂O(ν₁) IR fluorescence rise as the vibrational relaxation feature. By default the IR decay was then assigned as the Cl* quenching feature, and rate coefficients were determined with these assignments. The assignment of these processes however was in serious doubt as neither the rate coefficient for Cl* quenching by N₂O nor the rate coefficient for vibrational relaxation of N₂O(ν₁) by N₂O compared favorably with available literature values [13,32,33,34,35]. In an attempt to clarify Batson’s curious results, the first sets of experiments in this thesis were performed in binary gas mixtures of ICl and N₂O without argon.

A typical Cl*/N₂O kinetic experiment involved collecting time-resolved IR signals of N₂O(ν₁) fluorescence at 5 to 10 different pressures of N₂O. The pressure of ICl
was held constant for all of the kinetic trials. Two time-resolved IR fluorescence signals from N$_2$O($\nu_1$) emission at two different pressures of N$_2$O are provided in Figure (3-1). Both signals consist of 2500 points at 200 ns per point. The signal was averaged over 5000 laser shots in order to reduce the random room temperature background noise level. The Q-switching of the laser provides an additional interference near t=0, and 60 Hz pick-up can lead to sloping baselines on the time scale of our observations. To remove the Q-switch and 60 Hz baseline interferences from IR observations, background signals were obtained by allowing the laser to fire for 5000 shots, but keeping the beam blocked. Subtracting the IR “signal” observations from the “background” removes the interferences and inverts the IR signals to be proportional to excited state concentrations.

![Figure 3-1: Two time-resolved IR signals from N2O($\nu_1$) emission due to E-V excitation via Cl* quenching at different N2O partial pressures.](image_url)
Typically the first 20% of each recorded signal is devoted to the pre-trigger t<0 detector response before the laser fires. The pre-trigger detector response is due to thermal background, and it provides a “zero” intensity reference for the IR fluorescence observations.

Both signals presented in Figure (3-1) are characterized by a single exponential rise and a single decay. This is the expected physical behavior from the Cl*/N₂O kinetic mechanism outlined in Chapter 2. The curves drawn through the data points in Figure (3-1) were obtained by fitting the IR signals in SigmaPlot® using the following non-linear regression analysis function:

\[
I_t = (I_0 - I_{SS}) \exp(-k'_d t) - I_0 \exp(-k'_r t) + I_{SS}
\]

\[
= I_0 [\exp(-k'_d t) - \exp(-k'_r t)] + I_{SS} [1 - \exp(-k'_d t)]
\]

\(I_t\) represents the fluorescence intensity as a function of time. \(I_0\) corresponds to a back extrapolated intensity value at \(t = 0\) from the signal decay, and it is linearly related to the pre-exponential coefficient \(k^{EV}[Cl^*]_0/(k^Q - k^V)\) in equation (2-18) for the Cl*/N₂O kinetic mechanism presented in Chapter 2. \(I_{SS}\) refers to the apparent steady-state intensity to which the decay appears to fall in the viewing time of 400 μs. The parameters \(k'_d\) and \(k'_r\) are the pseudo first-order rate coefficients for the decay and rise portions of the signal, respectively. At this point assignment of the rates to specific processes in the kinetic mechanism (Cl* quenching or \(N_2O(v_1)\) relaxation) cannot be made without further study.

Examination of the signals reveals that the rates of the signal rise and the decay increase with higher N₂O pressures. Additionally it is noted that the \(I_0\) values trend to smaller values at higher N₂O pressures. As expected both rate constants in the rise and decay should occur on a quicker time scale with an increase in N₂O pressure.
The pseudo first-order rates for the fluorescence rise and decay from each set of observations are plotted against \([N_2O]\) as in Figure (3-2) to obtain the second order bimolecular rate coefficient for the processes mediated by \([N_2O]\). The contribution to the pseudo first-order processes is dominated by ICl and \(N_2O\). The contributions from Cl, I, Cl*, or \(N_2O(v)\) are considered to be negligible due to their small concentrations. This assumption allows the rate of the pseudo first-order rise to be written as \(k'_r = k_r^{N_2O} [N_2O] + k_r^{ICl} [ICl]\) and the decay as \(k'_d = k_d^{N_2O} [N_2O] + k_d^{ICl} [ICl]\). \(k_r^X\) represents the bimolecular rate coefficient for the kinetic process found in the rise for species \(X\) (\(N_2O\) or ICl), and the bimolecular rate coefficient \(k_d^X\) represents the bimolecular rate coefficient for the kinetic process found in the decay for species \(X\) (\(N_2O\) or ICl). In the kinetic experiments carried out \([ICl]\) was held constant so that a plot of \(k'_r\) and \(k'_d\) vs. \([N_2O]\) is expected to be linear with a slope of \(k_r^{N_2O}\) and \(k_d^{N_2O}\) respectively for both pseudo first-order rates. The y-intercept for the linear plot of the pseudo first-order rise or decay will be \(k_r^{ICl} [ICl]\) or \(k_d^{ICl} [ICl]\) respectively. In figure (3-2) the pseudo first-order rate coefficients for the rise and the decay are plotted against \([N_2O]\), and a linear fit provides a value for \(k_r^{N_2O}\) and \(k_d^{N_2O}\) from the slope of a linear fit of the data for the rise and decay. Error bars are provided for each data point in the experiment, and represent three times the standard error values from the non-linear regression analysis of the IR signals.

Another notable aspect of figure (3-2) is that the y-intercepts appear to overlap at the same point. This is misleading because the uncertainty in the y-intercept for the rise is as large as the intercept value itself. Unfortunately reducing the \(N_2O\) concentration in order to get an accurate determination of the intercept is not possible owing to signal-to-noise constraints and the requirements for pseudo first-order conditions. Intercept values
from the fluorescence decay typically have lower relative uncertainty in the N$_2$O kinetic plots. When the preliminary assignments are discussed later in this section the analysis of the decay intercept will be performed.

Overall six kinetic experiments were carried out using just ICl/N$_2$O gas mixes. Table (3-1) summarizes the results from each experiment. The table provides the N$_2$O pressure range for each kinetic experiment and the constant ICl pressure. In addition the average of the rate coefficients obtained in these six experiments are provided at the bottom of table (3-1).

Figure 3-2: Kinetic plot showing N$_2$O dependence of the pseudo first-order rise and decay rates in ICl/N$_2$O mixtures.
Table 3-1. A summary of results from kinetic studies carried out with ICl/N₂O gas mixtures.

<table>
<thead>
<tr>
<th>P_{N₂O}a</th>
<th>P_{ICl}b</th>
<th>k_{r}^{N₂O}c</th>
<th>k_{d}^{N₂O}c</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1403-0.5301</td>
<td>0.1397</td>
<td>9.9±1.1</td>
<td>0.7±0.2</td>
</tr>
<tr>
<td>0.2002-0.5532</td>
<td>0.1298</td>
<td>11.0±1.3</td>
<td>0.8±0.2</td>
</tr>
<tr>
<td>0.1744-0.4997</td>
<td>0.1256</td>
<td>12.2±0.6</td>
<td>1.0±0.1</td>
</tr>
<tr>
<td>0.1649-0.6669</td>
<td>0.1351</td>
<td>7.5±0.7</td>
<td>1.1±0.2</td>
</tr>
<tr>
<td>0.1349-0.4517</td>
<td>0.1351</td>
<td>8.9±1.9</td>
<td>1.1±0.1</td>
</tr>
<tr>
<td>0.1447-0.4389</td>
<td>0.1425</td>
<td>9.2±0.6</td>
<td>1.2±0.1</td>
</tr>
<tr>
<td>Average Value ± 1σ</td>
<td></td>
<td>9.8±1.6</td>
<td>1.0±0.2</td>
</tr>
</tbody>
</table>

a. range of partial pressures in Torr  
b. constant partial pressure in Torr  
c. 10⁻¹² cm³·molecule⁻¹·s⁻¹ ± 1 standard error of the slope

If the simple kinetic mechanism suggested in Chapter 2 is correct, one of k_{r}^{N₂O} or k_{d}^{N₂O} should be k^{*}_{N₂O} from the mechanism and the other should be k^{V}_{N₂O}. Preliminary assignments of k_{r}^{N₂O} and k_{d}^{N₂O} can be made based upon comparison with currently available literature values for k^{*}_{N₂O} and k^{V}_{N₂O}. Two literature values exist for k^{*}_{N₂O} and three for k^{V}_{N₂O}.

Clark and Husain [36] reported a value of (3.7±0.6) x 10⁻¹³ cm³·molecule⁻¹·s⁻¹ for k^{*}_{N₂O}. This is an extremely slow rate coefficient for this process and falls well below both k_{r}^{N₂O} and k_{d}^{N₂O} obtained in this study. Cl* quenching experiments in the Husain group were accomplished using VUV absorption spectroscopy to probe Cl* concentrations following flash photolysis initiation of the experiments. Husain’s experimental method has been critiqued by Tyndall et al [37] because their experiments had a built-in 60 µs delay after the flash-lamp pulse before Cl* observations began. This
delay limits the amount of the early decay signals of Cl* that can be observed, and data fit to the decay will not represent the earlier time behavior missed with rapid Cl* quenching species. This could explain the very small rate coefficient reported for the Cl* quenching process by N$_2$O.

Chichinin [14], using an LMR technique, has determined that the Cl* quenching by N$_2$O proceeds by $k_{N2O}^* = (6.3 \pm 2.0) \times 10^{-12}$ cm$^3$·molecule$^{-1}$·s$^{-1}$. Within the stated uncertainties Chichinin’s value overlaps with the value of $k_r^{N2O}$ obtained from the N$_2$O ($\nu_1$) fluorescence rise in this study. Using equation (3-2) Chichinin was able to predict within a factor of 2 the rate coefficients for Cl* quenching for 18 different compounds with the adjustment of two parameters: A and B. $I_i$ is the integrated absorption intensity of the vibrational band at frequency $\nu_i$. $\Delta E_i$ is the difference in energy between Cl* and the fundamental vibrational frequency $\nu_i$. This equation has the essential features for the E-V quenching probability from the theoretical treatment of long range attractions.

Optimization of A and B values to have maximal accuracy in predicting the expected Cl* quenching coefficients for the 18 different compounds led to values of A = 145 cm$^{-1}$ and B = 77 cm$^{-1}$.

$$k^*_M = A \left\{ \Sigma (I_i/\nu_i) \exp(-|\Delta E_i|/B) \right\}$$

Evaluating this expression for N$_2$O yields a rate coefficient for Cl* quenching of $k_{N2O}^* = 4.0 \times 10^{-12}$ cm$^3$·molecule$^{-1}$·s$^{-1}$. From a very simple relationship this comes reasonably close to Chichinin’s value determined experimentally, and is nearly half that of $k_r^{N2O}$ determined in these studies.

Previous work done on this system by J.S. Batson [1] yielded a $k_r^{N2O}$ value of $(5.9 \pm 1.2) \times 10^{-12}$ cm$^3$·molecule$^{-1}$·s$^{-1}$. This value agrees with Chichinin’s value for $k_{N2O}^*$.
however, Batson assigned the rise to vibrational relaxation rather than to Cl* quenching. Thus Batson reported $k^V_{\text{N}_2\text{O}} = (5.9 \pm 1.2) \times 10^{-12}$ cm$^3$·molecule$^{-1}$·s$^{-1}$, describing the vibrational relaxation of N$_2$O($v_1$) by N$_2$O. Batson’s assignment of the fluorescence rise to the relaxation process was made from her observation that additions of argon, a poor Cl* quencher but good vibrational relaxer, increased the rate of the rise of N$_2$O($v_1$) fluorescence. By default, this observation pointed to the rate of fluorescence decay as the Cl* quenching rate, and Batson reported $k^*_{\text{N}_2\text{O}} = (3.5 \pm 0.3) \times 10^{-12}$ cm$^3$·molecule$^{-1}$·s$^{-1}$ from the [N$_2$O] dependence of the fluorescence decay. While this value compares favorably to the prediction of equation (3-2), Batson’s reported $k^V_{\text{N}_2\text{O}}$ value from the fluorescence rise is in better agreement with Chichinin’s Cl* quenching rate coefficient. Experiments described in the next section reveal a curious behavior of argon that suggests Batson may have been mistaken in the assignments of fluorescence rise and decay. For a preliminary assignment, the propinquity of Batson’s $k^V_{\text{N}_2\text{O}}$ value [1] to that of Chichinin’s $k^*_{\text{N}_2\text{O}}$ [14], and (within the stated uncertainties) to $k_r^\text{N}_2\text{O}$ found in this work leads to the assignment of $k_r^\text{N}_2\text{O}$ to $k^*_{\text{N}_2\text{O}} = (9.8 \pm 1.6) \times 10^{-12}$ cm$^3$·molecule$^{-1}$·s$^{-1}$. Table (3-2) provides a summary of the literate values for $k^*_{\text{N}_2\text{O}}$ compared to the recently measured value in this experimental study.

Table 3-2: Summary of rate constants for $k^*_{\text{N}_2\text{O}}$ obtained in this work and from literature values from previous experimental studies.

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</tr>
</thead>
<tbody>
<tr>
<td>$k^*_{\text{N}_2\text{O}}$</td>
<td>6.3±2.0</td>
<td>5.9±1.2</td>
<td>0.37±0.06</td>
<td>9.8±1.6</td>
</tr>
</tbody>
</table>

a. rate constants in units of $10^{-12}$ cm$^3$·molecule$^{-1}$·s$^{-1}$. 

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By default this leaves the assignment of $k_d^{N_2O} = k_V^{N_2O} = (1.0 \pm 0.2) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. This assignment compares favorably to three other literature values for $k_V^{N_2O}$.

Kung [32] determined $k_V^{N_2O}$ to be $(6.6\pm1.3) \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ by time-resolved fluorescence observations of the $(200) \to (100)$ transition. In work done by Kung a DF laser was used to excite N$_2$O to the $(200)$ overtone level. The pressure of N$_2$O in the gas cell was so high that the $(100) \to (000)$ fundamental emission was absorbed before reaching the detector. This radiative trapping meant that only emission from the $(200) \to (100)$ state was observed in the 7.8 \mu m region. Using a series of assumptions, Kung concluded that relaxation from the $(200)$ state should be twice as fast as from the $(100)$ state. The rate coefficient for the $(100)$ level relaxation was taken to be one half of the rate coefficient measured for $(200)$ relaxation.

Huddleton and Weitz [33] reported $k_V^{N_2O} = 28 \pm 1.6$ msec$^{-1}$ Torr$^{-1}$, which is equivalent to a value of $(8.6 \pm 0.5) \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. This rate coefficient was obtained by pumping population out of N$_2$O$(v_1)$ using an N$_2$O laser to promote the 100$\to$001 transition. The time-resolved IR signal then represents the refilling of the $(100)$ level from lower lying states – the reverse of the $(100)$ relaxation process. Relaxation of the $(001)$ state is too slow relative to the time-scale of $(100)$ equilibration to make a contribution to the refilling of this state.

In photoacoustic studies carried out by Slobodskaya and Rityn [34, 35] a value of $k_V^{N_2O} = 2.3 \times 10^4$ s$^{-1}$ Torr$^{-1}$ that is equivalent to a rate coefficient of $k_V^{N_2O} = 7.1 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was reported. In these studies the phase delay of pressure waves

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resulting from chopped IR excitation of an N₂O sample in a gas cell was correlated to a complex model depending upon the values of five rate coefficients.

Table (3-3) provides a summary of the literature values for $k^V_{N₂O}$ compared to the value obtained in these experimental studies. All three literature values of $k^V_{N₂O}$ lie close to the value obtained in this study for $k_d^{N₂O}$. This respectable agreement is in stark contrast to the value of $k_d^{N₂O} = (3.5 \pm 0.3) \times 10^{-12}$ cm³·molecule⁻¹·s⁻¹ obtained in Batson’s [1] previous study of the Cl*/N₂O system but assigned to Cl* quenching. The current studies were carried out in the absence of argon, while Batson’s studies were done in an argon bath of ~ 5-6 Torr. If the proposed mechanism for the Cl*/N₂O system is flawed with respect to steps mediated by argon then the $k_d^{N₂O}$ rate coefficient obtained by J.S. Batson might not represent the relaxation of N₂O($v_1$).

Table 3-3: Summary of rate constants for $k^V_{N₂O}$ obtained in this work and from literature values from previous experimental studies.

<table>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$k^V_{N₂O}$</td>
<td>7.1</td>
<td>6.6±1.3</td>
<td>8.6±0.5</td>
<td>35.0±3.0</td>
<td>10.0±2.0</td>
</tr>
</tbody>
</table>

a. rate constants in units of $10^{-13}$ cm³ molecule⁻¹·s⁻¹

The disparity between Batson’s value [1] for $k^V_{N₂O}$ compared to the value obtained in this current study in the absence of argon suggested repeating Batson’s experiments. Two additional kinetic studies were carried out testing the N₂O($v_1$) dependence on [N₂O] in the presence of a ~ 5 Torr argon bath. The average value obtained for $k^*_{N₂O}$ in the studies was $(7.3 \pm 1.7) \times 10^{-12}$ cm³ molecule⁻¹·s⁻¹, and $k^V_{N₂O} = (2.3 \pm 0.4) \times 10^{-12}$ cm³ molecule⁻¹·s⁻¹. The quenching rate coefficient inhabits a region
overlapped by both Batson’s value and the current value obtained in the absence of argon for \( k_{N2O}^* \). The value found for \( k_{N2O}^V \) in these two current studies approaches that found by Batson [1], and is twice as fast as \( k_{N2O}^V \) determined in experiments in the absence of argon. This illustrated that the behavior observed by Batson [1] in the presence of argon was reproducible, and indicates a failure of the simple Cl*/N2O kinetic mechanism to simultaneously explain the N2O(\( v_1 \)) observations with and without added argon.

Based upon the preliminary assignments, \( k_r^{N2O} = k_{N2O}^* \) and \( k_d^{N2O} = k_{N2O}^V \), the y-intercept of the rise plot in figure 3-2 represents the pseudo first-order rate of Cl* quenching by ICl, and the intercept of the decay plot represents the pseudo first-order rate of N2O(\( v_1 \)) relaxation by ICl. \( k_{ICl}^V \) was estimated in each experiment by dividing the decay intercept by the constant ICl concentration for that experiment. The six values were averaged to yield \( k_{ICl}^V = (2.2 \times 0.6) \times 10^{-12} \text{ cm}^3\text{-molecule}^{-1}\text{·s}^{-1} \), where the reported uncertainty is one standard deviation about the mean. \( k_{ICl}^* \) was not determined by this method because the inherent uncertainty in the y-intercept in all six studies was on the same order of magnitude as the value. As such a value determined by examining the y-intercepts would be meaningless. Two literature values exist for \( k_{ICl}^* \). Chichinin [14] found \( k_{ICl}^* \) to be \( (3.3 \times 10) \times 10^{-13} \text{ cm}^3\text{-molecule}^{-1}\text{·s}^{-1} \) through LMR studies. Park et al [9] determined \( k_{ICl}^* \) through DLA studies looking at the direct decay of the Cl* state after the photolysis of ICl at 532 nm. Using this method they determined \( k_{ICl}^* \) to be \( (4.0 \pm 1.0) \times 10^{-12} \text{ cm}^3\text{-molecule}^{-1}\text{·s}^{-1} \). These literature values differ by one order of magnitude. It is entirely possible that the rate coefficient for Cl* quenching and relaxation is roughly equivalent, and this could explain the nearly overlapping y-intercepts observed in many of the N2O kinetic plots.
B. Studies of N$_2$O($\nu_1$) Dependence on Argon

Huddleston and Weitz [33] report a value for $k^V_{Ar}$ that is equivalent to $(1.5 \pm 0.5) \times 10^{-12}$ cm$^3$·molecule$^{-1}$·s$^{-1}$, and the general consensus from Chichinin’s review [14] is that $k^*_{Ar} \leq 1.0 \times 10^{-14}$ cm$^3$·molecule$^{-1}$·s$^{-1}$. Thus, argon collisions are much more likely to relax N$_2$O($\nu_1$) than to quench Cl*. Accordingly, here and in previous Cl* E-V quenching studies at WSU, argon addition has been used to associate either the fluorescence rise or its decay with the vibrational relaxation process.

Figure (3-3) is a composite of three IR fluorescence signals at varying argon concentrations and constant ICl and N$_2$O concentrations. These signals were background-corrected, just as the N$_2$O/Cl* signals were treated. Each trace consists of 2500 points at 200 ns per point. The signals with 0.096 Torr and 2.217 Torr of argon did not return to the pre-trigger level during the observation time so that a steady-state term was added to the non-linear regression analysis. As the argon pressure is increased the peak intensity drops because the N$_2$O($\nu_1$) population is being relaxed more quickly. At 18.958 Torr of argon three time constants are evident. In addition to the faster fluorescence rise and decay, the apparent steady-state intensity observed at lower argon pressures decays with a third, slower, pseudo first-order rate.
This slower decay or apparent steady-state level has been noted in previous time-resolved fluorescence studies of SO₂ [13, 38, 39] and SF₆ [40], and is attributed to heating by V-T,R relaxation. Using SigmaPlot® the IR signals at 0.096 Torr and 2.217 Torr of argon were fit to the non-linear regression algorithm in equation (3-1). The IR signal for the 18.958 Torr time-resolved signal was fitted to a non-linear regression function that accounts for the measurable second decay:

\[
I_t = I_0 \{\exp(-k'_d t) - \exp(-k'_r t)\} + I_{SS} \{\exp(-k'_d t) - \exp(-k'_d t)\},
\]

where \(k'_d\) is the slower, second pseudo first-order decay coefficient.

Figure 3-3: Three time-resolved IR signals of \(\text{N}_2\text{O}(\nu_1)\) fluorescence with fixed amounts of \(\text{N}_2\text{O}\) and ICl, but differing pressures of Ar.
Figure (3-4) presents a kinetic plot for the dependence of N$_2$O($v_1$) emission with varying concentrations of argon. The data relating to the second, slower decay V-T,R process has been excluded from this plot because the slope will be relatively flat and smaller than its uncertainty. The slope for the rise data in this experiment is $(3.2\pm0.5) \times 10^{-13}$ cm$^3$·molecule$^{-1}$·s$^{-1}$, which is nearly within a factor of two of Huddleston and Weitz’s $k^V_{N2O}$ value [33]. The slope of the decay data is $(5.0\pm1.8) \times 10^{-14}$ cm$^3$·molecule$^{-1}$·s$^{-1}$, which is somewhat larger than Chichinin’s limiting value for $k^*_{N2O}$ [14].

Figure 3-4: Kinetic plot illustrating the dependence of the time-resolved N$_2$O($v_1$) fluorescence intensity with respect to [Ar]. $k^r_{Ar}$ and $k^d_{Ar}$ are assigned to the slopes of the linear fits of the pseudo first order rates of the rise and decay, respectively, based upon arguments presented in the text. Error bars are three standard errors of the pseudo first-order rates.
Table (3-4) summarizes the results of nine kinetic studies in which the argon concentration was varied over a broad range. The table includes the range of argon pressures used, and the constant partial pressures of ICl and N₂O in each experiment.

The rate coefficients and one standard error uncertainties are stated, and at the bottom of the table the average value ±1σ is stated.

Table 3-4: Summary of results from kinetic studies with ICl/N₂O/Ar gas mixtures examining the N₂O(ν₁) dependence on Ar of the pseudo first-order rise and decay of time resolved fluorescence signals.

<table>
<thead>
<tr>
<th>P_{Argon} a</th>
<th>P_{N₂O} a</th>
<th>P_{ICl} a</th>
<th>k^{V}_{Ar} b</th>
<th>k^{*}_{Ar} c</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-6.218</td>
<td>0.174</td>
<td>.125</td>
<td>3.1±0.5</td>
<td>5.0±1.8</td>
</tr>
<tr>
<td>0-10.229</td>
<td>0.339</td>
<td>.160</td>
<td>3.3±0.5</td>
<td>2.9±2.4</td>
</tr>
<tr>
<td>0-10.193</td>
<td>0.349</td>
<td>.160</td>
<td>2.8±0.3</td>
<td>5.5±1.7</td>
</tr>
<tr>
<td>0-12.668</td>
<td>0.217</td>
<td>.153</td>
<td>3.3±0.2</td>
<td>1.9±1.2</td>
</tr>
<tr>
<td>0.087-9.519</td>
<td>0.145</td>
<td>.132</td>
<td>4.1±0.8</td>
<td>1.5±1.0</td>
</tr>
<tr>
<td>0.096-18.958</td>
<td>0.204</td>
<td>.102</td>
<td>2.1±0.7</td>
<td>7.1±1.0</td>
</tr>
<tr>
<td>0.096-18.958</td>
<td>0.229</td>
<td>.128</td>
<td>3.7±0.3</td>
<td>0.8±1.3</td>
</tr>
<tr>
<td>1.238-16.247</td>
<td>0.144</td>
<td>.135</td>
<td>2.3±0.4</td>
<td>0.5±0.4</td>
</tr>
<tr>
<td>1.225-21.896</td>
<td>0.170</td>
<td>0.131</td>
<td>1.5±0.2</td>
<td>-0.3±0.5</td>
</tr>
</tbody>
</table>

Average Value ± 1σ | 2.9±0.8 | 2.7±2.5 |

a. partial pressure in Torr
b. 10⁻¹³ cm³·molecule⁻¹·s⁻¹ ± 1 standard error of the slope
c 10⁻¹⁴ cm³·molecule⁻¹·s⁻¹ ± 1 standard error of the slope

The average value of (2.9 ± 0.8) x 10⁻¹³ cm³·molecule⁻¹·s⁻¹ for k^{V}_{Ar} from these kinetic studies is in excellent agreement with Batson’s [1] value of (2.5 ± 0.7) x 10⁻¹³ cm³·molecule⁻¹·s⁻¹. All nine kinetic plots indicate that argon has the greatest impact upon
the rise portion of the IR signal. This says that the rise represents the vibrational 
relaxation of N$_2$O($\nu_1$). This is in direct conflict with the assignment of the rise to Cl$^*$ 
quenching based upon a review of literature values discussed in the previous section.

Three other reported literature values exist for the rate coefficient for argon 
relaxation of N$_2$O($\nu_1$). Kung’s study [32] yielded a value of $p\tau = 0.38$ \(\mu\text{sec}\cdot\text{atm} \pm 20\%\), 
which is the inverse of $k_{V,\text{Ar}}$, so that $k_{V,\text{Ar}} = (1.1 \pm 0.2) \times 10^{-13}$ \(\text{cm}^3\cdot\text{molecule}^{-1}\cdot\text{s}^{-1}\). This 
value is roughly a third of the value obtained in this study, and in the study by Batson [1]. 
The values clearly do not overlap within the given uncertainties. Slobodskaya and Rityn 
[34] found the rate constant for $k_{V,\text{Ar}}$ to be $4 \times 10^3$ s$^{-1}\cdot\text{Torr}^{-1} \pm 30\%$, and this converts to a 
value of $(1.2 \pm 0.4) \times 10^{-13}$ cm$^3$·molecule$^{-1}$·s$^{-1}$. This experimental value is in agreement 
with Kung’s value but distinctly different from the value found in the present study. 
Huddleston and Weitz [33] determined $k_{V,\text{Ar}}$ to be $5 \pm 1.5$ msec$^{-1}\cdot\text{Torr}^{-1}$, which is 
equivalent to a value of $(1.5 \pm 0.5) \times 10^{-13}$ cm$^3$·molecule$^{-1}$·s$^{-1}$. This result is in agreement 
with Kung and with Slobodskaya and Rityn, and it agrees with the rate coefficient 
determined in this work within a little more than the combined stated uncertainties of the 
measurements.

The three literature values are in fairly good agreement. The values of $k_{V,\text{Ar}}$ 
quoted by Slobodskaya and Rityn [34] and Kung [33] are obtained through indirect 
methods, and an argument can be made for favoring the results from the more direct IR 
observations of N$_2$O($\nu_1$) in the studies by Batson [1] and Huddleston and Weitz [33] and 
in the present work. While there is not complete agreement between all five of the $k_{V,\text{Ar}}$ 
measurements, there is agreement that its value is in the low $10^{-13}$ cm$^3$·molecule$^{-1}$·s$^{-1}$ 
region.
The average value of \((2.7 \pm 2.5) \times 10^{-14} \text{ cm}^3\text{-molecule}^{-1}\text{-s}^{-1}\) for \(k^*_{\text{Ar}}\) with a large uncertainty indicates a rate coefficient that is too small to be measured within the experimental sensitivity. This low value must be assigned to \(\text{Cl}^*\) quenching on the basis of previous studies that show argon to be a very weak quencher of \(\text{Cl}^*\).

One additional experiment was done to observe the appearance and loss rates of \(\text{N}_2\text{O}(\nu_1)\) with respect to \(\text{N}_2\) addition. \(\text{N}_2\) is a homonuclear diatomic molecule, and as such lacks a transition dipole moment so that its vibration is IR inactive. According to Ewing’s modification of Sharma-Brau theory for long range attractive forces, one major requirement to efficiently couple and transfer electronic to vibrational energy is that the polyatomic molecule must possess a dipole moment. This lack of a dipole moment should give \(\text{N}_2\) a comparable \(\text{Cl}^*\) quenching probability to that of a monoatomic gas because energy transfer to the \(\text{N}_2\) vibration is not favorable. The anticipated rate constant for quenching should be close to that of neon, which is of comparable mass. Chichinin [14] reports \(k^*_{\text{N}_2} = (3.9 \pm 1.5) \times 10^{-14} \text{ cm}^3\text{-molecule}^{-1}\text{-s}^{-1}\) and \(k^*_{\text{Ne}} \leq 4.2 \times 10^{-14} \text{ cm}^3\text{-molecule}^{-1}\text{-s}^{-1}\) from LMR experiments.

Figure (3-5) provides the kinetic plot and the results of the \(\text{N}_2\) study performed here with \(\text{N}_2\text{O}(\nu_1)\) fluorescence observations. \(\text{N}_2\) partial pressures were varied from 0.09 to 19.958 Torr. The constant partial pressures of \(\text{ICl}\) and \(\text{N}_2\text{O}\) were 0.136 Torr and 0.140 Torr, respectively. The rate coefficient \(k^V_{\text{N}_2}\) has been assigned the value \((2.2 \pm 0.4) \times 10^{-13} \text{ cm}^3\text{-molecule}^{-1}\text{-s}^{-1}\) from the rise data, and \(k^*_{\text{N}_2}\) has been assigned the value \((1.4 \pm 0.8) \times 10^{-14} \text{ cm}^3\text{-molecule}^{-1}\text{-s}^{-1}\) from the decay data.
The value for $k^*_{N_2}$ determined here agrees with Chichinin’s value within a little more than their combined stated uncertainties. The $k^*_{N_2}$ quenching rate coefficient obtained here also is reasonably close to that determined for argon. Accordingly, assignments of the fluorescence rise and decay rates to vibrational relaxation and quenching, respectively, are supported by the nine kinetic experiments performed with argon and the one carried out with $N_2$. These apparently solid assignments conflict with the closer association of $k^*_{N_2O}$ with the fluorescence rise and $k^V_{N_2O}$ with the decay in experiments with ICl/$N_2O$ mixtures - without argon. In an attempt to further resolve the
conflict between assignments based upon agreement with $k^*_{N_2O}$ and $k^{V}_{N_2O}$ literature values and assignment based upon observations with added argon and N$_2$, further studies were carried out using competitive Cl* quenching compounds. These are described in the next section.

C. Studies of N$_2$O($\nu_1$) Dependence on CCl$_4$ and CD$_4$

Experiments in ICl/N$_2$O mixtures associate $k^{V}_{N_2O}$ with the fluorescence decay and $k^*_{N_2O}$ with the fluorescence rise. Experiments with additions of argon or nitrogen to these mixtures supports the opposite assignments. In order to provide resolution of these assignments a set of experiments were performed with the addition of gases that strongly quench Cl* relative to their ability to vibrationally relax N$_2$O($\nu_1$).

A review of Chichinin’s [14] table of quenching rate constants for Cl* indicated that CCl$_4$ and CD$_4$ were two prime candidates that were currently available in the lab. The quenching rate coefficient for Cl* by CD$_4$ ($k^*_{CD4}$) and by CCl$_4$ ($k^*_{CCl4}$) were found to be $(1.3 \pm 0.4) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $(1.8 \pm 0.6) \times 10^{-10}$ cm$^3$·molecule$^{-1}$·s$^{-1}$, respectively, in Chichinin’s LMR experiments [14]. These rate coefficients are quite large, and approach a theoretical hard sphere value of $\sim 3 \times 10^{-10}$ cm$^3$·molecule$^{-1}$·s$^{-1}$. These large quenching rate coefficients can be attributed to the small energy gaps between the Cl* energy and that of IR active vibrational modes in CCl$_4$ and CD$_4$. CCl$_4$ has a degenerate stretching mode at $\nu_3 = 776$ cm$^{-1}$, for which $|\Delta E| = 104$ cm$^{-1}$ with respect to the 882 cm$^{-1}$ energy of the Cl* spin-orbit electronic state. CD$_4$ has a degenerate bond deformation mode at $\nu_4 = 996$ cm$^{-1}$, and this corresponds to $|\Delta E| = 114$ cm$^{-1}$ from Cl*. 
Literature values were not available for the rate coefficients for relaxation of \( \text{N}_2\text{O}(v_1) \) mediated by either \( \text{CCl}_4 \) or \( \text{CD}_4 \). The assumption can be made that for both compounds their \( k^*_M \) value is much greater than their potential \( k^V_M \) value, and that the \( k^V_M \) values should be in the region of \( k^V_{\text{N}_2\text{O}} \). This assumption is based upon the larger energy gap between \( \text{N}_2\text{O}(v_1) \) and the nearest IR active modes mentioned in the previous paragraph for both compounds in comparison to the energy gap with \( \text{Cl}^* \).

Figure (3-6) presents three time-resolved IR signals of \( \text{N}_2\text{O}(v_1) \) fluorescence with increasing amounts of \( \text{CCl}_4 \) added. The non-linear regression fits were done using all 2500 data points, but for ease of presentation only every tenth point has been plotted. The signals were fitted using equation 3-2. An appreciable increase in \( k'^r \) with addition of \( \text{CCl}_4 \) causes the fluorescence to “peak” at earlier times. A decrease in the peak intensity to a steady-state level also occurs quickly with added \( \text{CCl}_4 \) because it competes with \( \text{N}_2\text{O} \) to quench \( \text{Cl}^* \), and this leads to a reduction in the number density of excited \( \text{N}_2\text{O}(v_1) \) molecules.
Figure 3-6: Three N$_2$O($\nu_1$) time-resolved IR signals with differing partial pressures of CCl$_4$ fitted via non-linear regression analysis.

In figure (3-7) the kinetic plot for CCl$_4$ provides strong evidence for the quenching process to be assigned to $k'_r$. In this study the concentration of CCl$_4$ ranged from 0-42 mTorr. The constant partial pressures of ICl and N$_2$O were 0.1425 Torr and 0.5575 Torr respectively. The value for $k^*_{CCl4}$ is $(3.3 \pm 0.4) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, and is 75 times faster than the $k^V_{CCl4}$ of $(4.4 \pm 2.7) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. With inclusion of the large uncertainty for the $k^V_{CCl4}$ it is fair to say that it is in reasonable proximity to $k^V_{N2O}$. The $k^*_{CCl4}$ value is larger than Chichinin’s, $(1.8 \pm 0.6) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, and does not overlap within the stated uncertainties of either value. The primary result of this study is that CCl$_4$ points to the $k'_r$ as the Cl* quenching process, and this is in conflict with the assignment to vibrational relaxation as dictated by argon.
and \( \text{N}_2 \) studies. The large uncertainties for both values also indicate the difficulties in carrying out these kinetic studies with competitive \( \text{Cl}^* \) quenching compounds. \( \text{N}_2\text{O}(v_1) \) has an Einstein coefficient of 12 \( \text{s}^{-1} \), indicating a fairly weak fluorescence intensity.

Under normal experimental conditions the peak signal intensity can be expected not to get much larger than 1 mV. The amount of noise visible in figure (3-6) couples with the weak intensity profiles of the signals to make accurate fitting to equation (3-2) difficult.

![Figure 3-7: Kinetic plot illustrating the dependence of the time-resolved \( \text{N}_2\text{O}(v_1) \) fluorescence intensity with respect to \([\text{CCl}_4]\). \( k'_{\text{CCl}_4} \) and \( k^V_{\text{CCl}_4} \) are assigned to the slopes of the linear fits of the pseudo first order rates of rise and decay, respectively based upon the literature values for the rate of quenching \( \text{Cl}^* \). Error bars represents three standard errors of the first-order rates.](image)
Figure (3-8) provides the results from the single CD₄ kinetic experiments. The pressure of CD₄ ranged from 0 to 82 mTorr. The constant partial pressures of ICl and N₂O were 0.1397 and 0.3604 Torr respectively. The value of $k^{*}_{\text{CD}_4}$ was determined to be $(3.9 \pm 2.1) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. With the large value of uncertainty the quenching value does overlap with Chichinin’s rate coefficient for CD₄.

The value of $k^{V}_{\text{CD}_4}$ was found to be $(2.8 \pm 1.2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. Despite the large uncertainties the qualitative results are the same as in the CCl₄ studies. Competitive
Cl* quenching agents associate the fluorescence rise with the Cl* quenching step and, by default, implicate the fluorescence decay association with the vibrational relaxation step for \( \text{N}_2\text{O}(\nu_1) \).

**D. Studies of \( \text{SO}_2(\nu_3) \) Dependence on \( \text{N}_2\text{O} \)**

Results detailed in sections A, B, and C all reveal conflicting assignments of specific kinetic processes (Cl* quenching vs. \( \text{N}_2\text{O}(\nu_1) \) relaxation) to the rise and decay of the time-resolved \( \text{N}_2\text{O}(\nu_1) \) fluorescence. One interpretation of this unusual and unanticipated behavior is that the simple Cl*/\( \text{N}_2\text{O} \) mechanism presented in Chapter 2 may be flawed. To remove the measurements from dependence upon an uncertain mechanism, the idea arose that \( k^*_{\text{N}_2\text{O}} \) could be measured in competitive quenching experiments with \( \text{SO}_2 \) using observations of the E-V excited \( \text{SO}_2(\nu_3) \). \( \text{SO}_2 \) has a firm assignment of specific pseudo first-order time constants to Cl* quenching and \( \text{SO}_2 \) V-V relaxation processes, and \( \text{SO}_2(\nu_3) \) is a fairly bright emitter.

Previous work by Dolson and West [41] in the Laser Chemistry Lab at Wright State University examined E-V energy transfer from Cl* to \( \text{SO}_2(\nu_3) \). In these studies a kinetic mechanism was firmly established, and three pseudo first-order rate coefficients were assigned to specific kinetic processes in the mechanism. Figure (3-9) provides an example of a time-resolved IR fluorescence curve obtained from \( \text{SO}_2(\nu_3) \) emission obtained during the studies carried out in this project. The rise portion of the \( \text{SO}_2(\nu_3) \) time-resolved fluorescence signal represents Cl* quenching by \( \text{SO}_2 \). The faster of two decays represents a \( \nu_3 \leftrightarrow \nu_1 \) V-V equilibration process, and finally the slower decay represents the stretch to bend relaxation in the vibrational manifold. Fortunately the
interference bandpass filter for viewing SO$_2$(v$_3$) still is available, and it passes a negligible amount of (~0.2%) fluorescence from the N$_2$O(v$_1$) band.

Three kinetic experiments were carried out with ICl/N$_2$O/SO$_2$ mixtures. The N$_2$O concentration was varied and kinetic plots were constructed in order to obtain values for $k^*_{N_2O}$. Figure (3-9) provides an example kinetic plot from one of the three experiments. The dependence of the second slower stretch to bend decay constant with respect to N$_2$O concentration is not plotted. The slope of the pseudo first-order rise rates in the kinetic plot yield $k^*_{N_2O} = (1.46 \pm 0.03) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

Figure 3-9: Time-resolved SO$_2$(v$_3$) IR fluorescence emission observed through a spectral bandpass filter. Cl$^*$ quenching, V-V relaxation, and Stretch-to-Bend relaxation labeled in the figure represent three distinct kinetic processes that are associated with the three pseudo first-order kinetic rates observable in the signal.
This rate constant is roughly ~50% greater than was determined through direct observations of N_2O(ν_1) fluorescence in the absence of argon. It is also approximately double the rate coefficient values determined by Chichinin [14] and Batson [1]. The rate coefficient for the relaxation of SO_2(ν_3) is k_{N_2O}^{V-V} = (1.0 ±0.2) x 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. This value for a vibrational relaxation process is reasonable.

The smaller error bars for the data points in figure 3-10 are due to two factors. In large part it is due to the increased signal to noise from the brighter SO_2(ν_3) emission. At the lowest pressures of N_2O a peak intensity of greater than 3 mV is possible. As more N_2O is added the SO_2(ν_3) intensity decreases, and the pseudo first-order rates increase as do their uncertainties. Secondly, a new digital oscilloscope was used to collect the SO_2(ν_3) time-resolved fluorescence decays. The LeCroy 6030A digital oscilloscope enabled data collection with a greater density of data point sampling at earlier times than was possible with the older digital oscilloscope.
Table (3-5) summarizes the results of the three kinetic studies examining the SO($\nu_3$) time dependence with variations in N$_2$O concentration. The average value for $k^*_N$O is $(1.59\pm0.13) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. It was frustrating to find yet a different value for the quenching depending upon the type of observations made. There are no literature values with which to compare the average $k^{V-V}_{N_2O}$ value of $(8.2\pm2.0) \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$; however, it is only a factor of $\sim$2 smaller than the rate coefficient for $\nu_3$-$\nu_1$ equilibration mediated by SO$_2$ collisions, $k^{V-V}_{SO_2} = (1.9\pm0.5) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$[40].

Figure 3-10: Kinetic plot illustrating the dependence of the time-resolved SO$_2$(v$_3$) fluorescence intensity with respect to [N$_2$O]. $k^*_N$O and $k^{V-V}_{N_2O}$ are assigned to the slopes of the linear fits of the pseudo first order rates of rise and decay based upon the previous assignment of these processes in SO$_2$(v$_3$) studies [41]. Error bars are three standard errors of the pseudo first-order rates.
Table 3-5: Summary of results from kinetic studies with ICl/N₂O/SO₂ gas mixtures.

<table>
<thead>
<tr>
<th>Pₜ₈O [a]</th>
<th>Pₜ₈₂ [a]</th>
<th>PₐCl [a]</th>
<th>k₋₈N₂O [b]</th>
<th>k₋₈⁻Vₐ₈O [c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-0.5010</td>
<td>0.1481</td>
<td>0.1319</td>
<td>1.46±0.03</td>
<td>10.0±0.2</td>
</tr>
<tr>
<td>0-0.5630</td>
<td>0.1462</td>
<td>0.1338</td>
<td>1.59±0.06</td>
<td>6.0±2.7</td>
</tr>
<tr>
<td>0-0.3950</td>
<td>0.1398</td>
<td>0.1402</td>
<td>1.72±0.11</td>
<td>8.5±3.7</td>
</tr>
<tr>
<td>Average Value ± 1σ</td>
<td></td>
<td></td>
<td>1.59±0.13</td>
<td>8.2±2.0</td>
</tr>
</tbody>
</table>

a. partial pressure in Torr  
b. 10⁻¹¹ cm³·molecule⁻¹·s⁻¹ ± 1 standard error of the slope  
c. 10⁻¹³ cm³·molecule⁻¹·s⁻¹ ± 1 standard error of the slope

To lend support to the fact that the rise of the SO₂(ν₃) fluorescence is the process involving Cl* quenching one additional kinetic experiment was done examining the dependence of SO₂(ν₃) with respect to CD₄. The kinetic plot presented in Figure (3-11) provides the result of this experiment. The concentration of CD₄ was varied from 0 to 70 mTorr. The constant partial pressures of ICl and SO₂ were 0.1286 and 0.1280 Torr, respectively. The rate constant for the quenching of Cl* by CD₄ was found to be (1.8 ± 0.3) x 10⁻¹⁰ cm³·molecule⁻¹·s⁻¹. This is in good agreement with Chichinin’s value of (1.3 ± 0.4) x 10⁻¹⁰ cm³·molecule⁻¹·s⁻¹ [14]. The better agreement of kₚₜ₄ from SO₂(ν₃) observations in comparison to kₚₜ₄ determined from competitive quenching of Cl* against N₂O is probably due in large part to the improved signal to noise ratio and the higher density of data sampling. These CD₄/SO₂/ICl experiments further support the association of the SO₂(ν₃) fluorescence rise with Cl* quenching.
E. Exploration for a Potential “Cross-Over” Event

The phenomenon of a “cross-over” potentially could lead to the conflicting behavior in the assignments of the fluorescence rise and decay to specific kinetic processes such as that observed in the present work. A “cross-over” occurs when the slower pseudo first-order rate (decay) at lower collider concentrations becomes the faster pseudo first-order rate (rise) at higher collider concentrations. This would be more likely to occur in Cl* quenching experiments when the rate coefficient for vibrational relaxation
is larger than that for Cl* quenching. Such is the case for the rare gases and other inefficient Cl* quenchers such as N₂.

Figure (3-12) is a hypothetical kinetic plot that provides a qualitative example of a cross-over event; all the values used are arbitrary and were not results of experimental studies. The simple Cl*/N₂O E-V mechanism of Chapter 2 is assumed with additions of a non-reactive collider gas, M. The pseudo first-order quenching rates are plotted as the open circles, and the vibrational relaxation rates are the closed circles. The non-zero y-intercepts are the sums of the pseudo first-order rates due to the constant pressures of ICl and N₂O. The key difference separating the y-intercepts is the larger rate for quenching Cl* by ICl and N₂O compared to their lower probability for vibrational relaxation of N₂O(ν₁).

Because the collider, M, has a greater probability of relaxing N₂O(ν₁) than for quenching Cl* eventually the pseudo first-order relaxation rate will exceed the pseudo first-order quenching rate as M is added. Recall that N₂O(ν₁) in the simple Cl*/N₂O E-V mechanism has a similar time dependence as the intermediate B in the first-order A→B→C mechanism discussed in Chapter 2. [B] and [N₂O(ν₁)] are described by a difference of exponential terms, f(t) ∝ [exp(-k_decay t) − exp(-k_rise t)], and the faster of the two rates will appear in the rise, regardless of its association with creation or destruction of the intermediate. In the hypothetical Cl*/N₂O/M mechanism quenching of Cl* is the faster rate at low [M] so that the rise reflects k* and the decay k⁺. When [M] is sufficiently large that k⁺ > k* the rise will be governed by k⁺ and the decay by k*. The influence of the quenching “crosses over” from the rise to the decay as [M] increases.
In figure (3-12) the equivalence point, where \( k_{\text{rise}} = k_{\text{decay}} \), appears to occur at \([M] \approx 4 \times 10^{17} \text{ molecule cm}^{-3}\), which is a pressure of about 10 Torr of added collider. At this point the pseudo first-order rise adopts the slope that the pseudo first-order decay has before the equivalence point. This is because the relaxation now dominates the rise of the time-resolved IR signals. If a cross-over event is occurring in the argon kinetic studies, figure (3-4) provides no firm indication of such an event. The paradox is that the \( y \)-intercept for the data for \( k' \) in Figure (3-12) represents \( \text{Cl}^* \) quenching contributions from ICl and \( \text{N}_2\text{O} \), but the slope of the fitted line is quite steep and is assigned to the vibrational relaxation process. The inverse is true for the \( y \)-intercept of the decay. Here the intercept is due to vibrational relaxation of \( \text{N}_2\text{O}(v_1) \) by ICl and \( \text{N}_2\text{O} \), and the slope of the fitted line is assigned to the very slow \( \text{Cl}^* \) quenching by argon. This disconnect between the processes associated with intercepts and slopes has no explanation at present. It seems as if an “instantaneous” cross-over event has occurred, but this is not physically possible.
No obvious cross-over behavior was observed in any of the nine Cl*/N₂O/Ar kinetic experiments. Yet at the same time a linear fit of the rise data yields a slope that is consistent with N₂O(ν₁) relaxation by argon but an intercept that is consistent with Cl* quenching by ICl and N₂O. And a linear fit of the decay data yields a slope that is consistent with Cl* quenching by argon but an intercept that is consistent with N₂O(ν₁) relaxation by ICl and N₂O.

Even though a cross-over was not observed in these experiments, it would be reasonable to estimate where a cross-over would be anticipated. The argon
concentrations necessary for potential equivalence points can be estimated with available literature values for the rate constants of the relaxation and quenching processes, along with values for the ICl and N$_2$O partial pressures. The point where the “cross-over” begins occurs when the sum of the pseudo first-order rates for the rise process is equivalent to decay process as shown in equation (3-4):

\[
(3-4) \quad k^*_{ICl}[ICl] + k^*_{N2O}[N2O] + k^*_{Ar}[Ar] = k^V_{ICl}[ICl] + k^V_{N2O}[N2O] + k^V_{Ar}[Ar]
\]

Simple algebraic manipulation of equation (3-4) leads to equation (3-5) which presents the algebraic relationship between the equivalence point argon concentration and the concentrations of ICl and N$_2$O:

\[
(3-5) \quad [Ar]_{Equivalence} = \frac{[N_2O](k^*_{N2O} - k^V_{N2O}) + [ICl](k^*_{ICl} - k^V_{ICl})}{k^V_{Ar} - k^*_{Ar}}
\]

Table (3-6) provides a summary of calculated argon pressures at the equivalence points and includes references for the rate coefficients used in the evaluation of cross-over points calculated using the expression in equation (3-4). The rate coefficients selected were chosen on the basis of maximizing the amount of argon pressure necessary to see a cross-over point. This was done in order to give a potential maximum limit up to what pressure argon kinetic observations would have to be carried out in order to reach the cross-over event. In the 9 kinetic studies carried out the constant N$_2$O pressure ranged from 0.144-0.339 Torr. Given the ranges of argon pressures used in each study a cross-over event should have occurred in at least one kinetic study. The bulk of the studies were carried out under argon pressures, which according to the calculated equivalence points, would not have seen the cross-over point. The behavior of the slopes
and y-intercepts however indicates that there will never be a cross-over point at higher pressures.

Table 3-6: Parameters used to evaluate the argon equivalence pressure with specified partial pressures of N₂O and ICl.

<table>
<thead>
<tr>
<th>Rate Constants(^a)</th>
<th>Partial Pressures(^b)</th>
<th>Equivalence Pressure(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k^V\text{Ar}[35])</td>
<td>1 x 10(^{-13})</td>
<td>(P_{\text{ICl}})</td>
</tr>
<tr>
<td>(k^*_\text{Ar}[14])</td>
<td>1 x 10(^{-14})</td>
<td>0.1200</td>
</tr>
<tr>
<td>(k^V\text{N}_2\text{O}[35])</td>
<td>8.7 x 10(^{-13})</td>
<td>0.1200</td>
</tr>
<tr>
<td>(k^*_\text{N}_2\text{O}[35])</td>
<td>10 x 10(^{-12})</td>
<td>0.1200</td>
</tr>
<tr>
<td>(k^V\text{ICl}[9])</td>
<td>2.2 x 10(^{-12})</td>
<td>0.1200</td>
</tr>
<tr>
<td>(k^*_\text{ICl}[9])</td>
<td>4 x 10(^{-12})</td>
<td>0.1200</td>
</tr>
</tbody>
</table>

\(^a\) rate constants in units of cm\(^3\)-molecule\(^{-1}\)-s\(^{-1}\)
\(^b\) pressures are expressed in Torr
\(^c\) rate coefficients from the present work

F. The Branching Ratio for \(k^*_\text{EV} / k^*_\text{N}_2\text{O}\)

\(k^*_\text{N}_2\text{O}\) represents the overall quenching of Cl\(^*\) by the multiple possible E-V and very improbable E-T,R energy transfers. The bimolecular rate coefficient for quenching that excites a specific E-V channel is just a fraction of this overall quenching rate. The branching ratio for Cl\(^*\) collisions that excite N₂O(\(v_1\)) can be represented as \(k^*_\text{EV} / k^*_\text{N}_2\text{O}\).

The branching ratio value is determined through the linear relationship between \(I_0\) and the pre-exponential factor in equation (2-17):

\[
(2-17) \quad [N_2O(v_1)] = \left( \frac{k^EV}{k^V - k^*} \right) [Cl^*]_0 \left( e^{-k^*_t} - e^{-k^V t} \right)
\]
The relationship that can be drawn between the time dependence of the fluorescence intensity $I_f$ and the pre-exponential coefficient from equation (2-17) is provided in equation (3-6):

$$\text{(3-6)} \quad I_f = C \left[ N_2O(\nu_1) \right] T_\lambda \; D_\lambda \; A_\nu = I_0 \left( \exp(-k^* t) - \exp(-k^V t) \right)$$

$T_\lambda$ represents the transmittance of the bandpass interference filter at the wavelength of emission, and $D_\lambda$ represents the detector sensitivity at the emission wavelength. $A_\nu$ is the Einstein coefficient for spontaneous emission from the $N_2O(\nu_1)$ state. The $C$ value is a constant that encompasses the fraction of emitted light that actually falls upon the detector surface and a conversion factor that relates the light intensity to a change in voltage from the detector/pre-amplifier. The $C$ value also depends on the distance of the detector from the source of fluorescence emission.

The pre-exponential factor in equation (2-17) can be defined as $[N_2O(\nu_1)]_0 = 0 \cdot \exp\left( \frac{k^*}{k^V - k^*} \right) [Cl^*]_0$. $I_0$ and $[N_2O(\nu_1)]_0$ can be related to one another in equation (3-7):

$$\text{(3-7)} \quad [N_2O(\nu_1)]_0 = \frac{I_0}{C \; T_\lambda \; D_\lambda \; A_\nu}$$

Both sides of equation (3-7) can be divided by $[Cl^*]_0$ leading to:

$$\text{(3-8)} \quad \frac{[N_2O(\nu_1)]_0}{[Cl^*]_0} = \frac{I_0}{C\; [Cl^*]_0 \; T_\lambda \; D_\lambda \; A_\nu} \frac{k^*_{EV}}{k^V - k^*}$$

$k^*_{EV}$ could be determined from a single observation if the value of $C$ were known. Because the value of $C$ is unknown and difficult to determine from first principles, a photolytic reference is used to determine the E-V branching ratios in our laboratory.

Photolysis of IBr at 532 nm produces spin-orbit excited Br$^*$ atoms, which emit IR
fluorescence at 2.713 μm. The photolytically prepared Br* atoms follow a nearly instantaneous rise within the 8 ns laser pulse, and then decay with a single time constant. Equation (2-23) represents the time dependence of Br* fluorescence:

\[
[B r^*] = [B r^*]_0 e^{-k^*t}
\]

[Br*]_0 can be related to the time=0 Br* fluorescence intensity, I_0, in a manner similar to equation (3-6). This relationship may be rearranged to find an expression for C in equation (3-9):

\[
C = I_0 / ([B r^*]_0 T_\lambda D_\lambda A_\nu)
\]

Equation (3-9) can be substituted into equation (3-6), providing equation (3-10):

\[
[N_2O(v_1)] / [C l^*]_0 = I_0^N [B r^*]_0 T_\lambda^* D_\lambda^* A_\nu^* / I_0^* [C l^*]_0 T_\lambda^N D_\lambda^N A_\nu^N = k^*_{EV} / k^V - k^*
\]

The terms with superscript N and * refer to values for N_2O(v_1) and Br*, respectively. Using the Beer-Lambert law and Planck’s law, equation (2-33) allows for the calculation of [Br*]_0 and [Cl*]_0. IR spectral scans of the filters provided values for the transmission, and the detector sensitivity is provided by the detector manufacturer. The Einstein coefficients for spontaneous emission for Br* can be found in Houston’s review [1], and the Einstein coefficient for N_2O are provide by Gribov and Smirnov [29]. k^V and k^* are both pseudo first-order coefficients that are determined experimentally along with I_0^N, for each N_2O(v_1) fluorescence observation through non-linear regression analysis. I_0^* is determined from an exponential fit of the Br* fluorescence decay. Table (3-6) provides a summary of the values used to determine the Cl* E-V branching ratio for exciting N_2O(v_1).
### Table 3-7: Parameters for determination of the branching ratio.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Br*</th>
<th>N₂O(ν₁)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tₜ a</td>
<td>0.56</td>
<td>0.94</td>
</tr>
<tr>
<td>Dₜ (MCT1) b</td>
<td>0.145</td>
<td>0.70</td>
</tr>
<tr>
<td>Dₜ (MCT2) b</td>
<td>0.232</td>
<td>0.612</td>
</tr>
<tr>
<td>Aᵥ c</td>
<td>0.909 (Ref. [1])</td>
<td>12 (Ref. [29])</td>
</tr>
<tr>
<td>σ d</td>
<td>8.21 (Ref. [27])</td>
<td>- - - - -</td>
</tr>
<tr>
<td>φ* e</td>
<td>0.68 (Ref. [6])</td>
<td>- - - - -</td>
</tr>
</tbody>
</table>

a. filter transmittance measured on Mattson Genesis II FTIR  
b. detectivity values from calibration by detector manufacturer  
c. spontaneous emission coefficient in units of s⁻¹  
d. absorption cross-section for IBr at 532 nm in units of 10⁻¹⁹ cm²  
e. Br* photolysis quantum yield from IBr at 532 nm

In two kinetic experiments 15 individual branching ratio measurements were made. The average value of these 15 measurements was 1.09 ± 0.28. A value greater than one is not physically sensible because the E-V rate coefficient cannot exceed the overall quenching rate coefficient. Figure (3-13) shows a plot of the branching ratio value vs. the pressure of N₂O. The scatter of data points is fairly broad as indicated by the large uncertainty value attached to the branching ratio value. Despite this scatter it appears as if there may be a relationship between the pressure of N₂O and the branching ratio. As the pressure of N₂O increases the calculated branching ratio decreases. At higher values the branching ratio appears to approach unity. All 15 of these measurements were carried out in the absence of any argon. In the previous Cl*/N₂O/Ar study Batson’s [1] average N₂O(ν₁) E-V branching ratio value was 0.48 ± 0.09, and all 35 of the measurements were made in the presence of a ~5 Torr argon bath. It has already
been illustrated in preceding sections that something bizarre is occurring with regards to the addition of argon. The potential for a cross-over event has already been discussed and discounted. Because these measurements are so reliant on the kinetic mechanism used to interpret the results, it is not possible to be certain of the E-V branching ratio determined in this work.

![Graph](image)

**Figure 3-13:** A plot of the branching ratio $k_{EV}^* / k_{N2O}^*$ against the pressure of N$_2$O (Torr).

Work carried out by J.S. Batson [1] discounted the effects of second-order behavior by examining the variation of the pseudo first-order rate constants at the same partial pressures of ICl, N$_2$O, and argon when the photolysis source laser power was cut in half from 80 mJ to 40 mJ. There was a negligible change in the pseudo first-order rates in the time-resolved IR signals. Additionally, Batson [1] determined that $\geq 85\%$ of
the $\text{N}_2\text{O}(\nu_1)$ emission arises from the fundamental transition. Because ICl pressures and laser energies are similar in the studies carried out by Batson [1] and the current study the results of these tests should still apply to the current experimental work.

II. Conclusions

Kinetic studies have been carried out studying the E-V excitation of $\text{N}_2\text{O}(\nu_1)$ via Cl* quenching. These E-V kinetic studies were carried out with the motivation of collecting data to test current E-V theories, and to obtain quenching rate coefficients and branching ratio values for the Cl*/$\text{N}_2\text{O}$ system. E-V processes may contribute to chemical processes in the atmosphere, in plasmas, and in E-V chemically pumped laser systems. In addition to these goals there was also a desire to resolve conflicts in the conclusions reached by J.S. Batson [1] in an earlier kinetic study of the Cl*/$\text{N}_2\text{O}$ system. The gas phase experiments were carried out at room temperature (298 ± 2 K). Kinetic rate coefficients for Cl* quenching by $\text{N}_2\text{O}$ and $\text{N}_2\text{O}(\nu_1)$ relaxation by $\text{N}_2\text{O}$ and argon were obtained from time-resolved IR fluorescence observations of $\text{N}_2\text{O}(\nu_1)$. These fluorescence observations were characterized by a single exponential rise and a single decay, which is the expected behavior of $\text{N}_2\text{O}(\nu_1)$ if excited via E-V quenching of Cl* and collisionally relaxed to lower vibrational levels. It was not possible to discern any multi-exponential character in the fluorescence rise in any experiment. In ICl/$\text{N}_2\text{O}$ mixtures (without argon) the second-order rate coefficient for Cl* quenching by $\text{N}_2\text{O}$ was found to be $k_{\text{N}_2\text{O}}^* = (9.8 \pm 1.6) \times 10^{-12}$ cm$^3$·molecule$^{-1}$·s$^{-1}$ from the fluorescence rise, and the second-order rate coefficient for $\text{N}_2\text{O}(\nu_1)$ relaxation by $\text{N}_2\text{O}$ was determined to be $k_{\text{N}_2\text{O}}^\nu = (1.0 \pm 0.2) \times 10^{-12}$ cm$^3$·molecule$^{-1}$·s$^{-1}$ from the decay. An E-V branching ratio for
the fraction of quenching collisions that lead to excitation of N$_2$O($\nu_1$) was found to be $k^{*}_{\text{EV}}/k^{*}_{\text{N}_2\text{O}} = 1.09\pm0.28$ in ICl/N$_2$O mixtures.

In similar ICl/N$_2$O mixtures with the addition of a fixed amount (~5 Torr) of argon, the quenching rate coefficient decreased slightly to a value of $k^{*}_{\text{N}_2\text{O}} = (7.3 \pm 1.7) \times 10^{-12}$ cm$^3$·molecule$^{-1}$·s$^{-1}$, and the vibrational relaxation rate coefficient increased significantly to $k^{V}_{\text{N}_2\text{O}} = (2.3 \pm 0.4) \times 10^{-12}$ cm$^3$·molecule$^{-1}$·s$^{-1}$. The Cl* quenching rate coefficients agree within one stated error; however, the difference between the rate coefficients for N$_2$O($\nu_1$) vibrational relaxation is real and these two rate coefficients may pertain to different V-V processes in N$_2$O.

In ICl/N$_2$O/Ar mixtures with varying argon, some unexplained behavior was observed in the kinetic plots. The N$_2$O($\nu_1$) fluorescence observations still were characterized by a single exponential rise and a single decay (apart from heating effects at longer times). Plotting the pseudo first-order rise rates vs. [Ar] yielded linear fits for which the intercept was consistent with N$_2$O($\nu_1$) vibrational relaxation by ICl and N$_2$O but the slope was consistent with Cl* quenching. Conversely, plots of the pseudo first-order decay rates vs. [Ar] yielded linear fits for which the intercept was consistent with Cl* quenching by ICl and N$_2$O but the slope was consistent with N$_2$O($\nu_1$) vibrational relaxation by argon. This switch from one kinetic process in the intercept to the other process in the slope appears to be unprecedented, and no explanation can be offered at this time. From the pseudo first-order decay data, the Cl* quenching rate coefficient for Ar was found to be $k^{*}_{\text{Ar}} = (2.7 \pm 2.4) \times 10^{-14}$ cm$^3$·molecule$^{-1}$·s$^{-1}$, which may be better stated as $k^{*}_{\text{Ar}} \leq 5 \times 10^{-14}$ cm$^3$·molecule$^{-1}$·s$^{-1}$. From the pseudo first-order rise data, the rate coefficient for relaxation of N$_2$O($\nu_1$) by argon was taken to be $k^{V}_{\text{Ar}} = (2.9 \pm 0.8) \times 10^{-13}$ cm$^3$·molecule$^{-1}$·s$^{-1}$.
cm$^3$·molecule$^{-1}$·s$^{-1}$. Additional kinetic studies were carried out in order to obtain an indirect measurement of $k_{\text{N}_2\text{O}}^*$ in competition with SO$_2$. In this work the Cl$^*$ quenching rates were obtained from the rates of the pseudo first-order rise of SO$_2$(v$_3$) time-resolved IR fluorescence signals as N$_2$O was added. These competitive experiments yielded a $k_{\text{N}_2\text{O}}^*$ of $(1.59 \pm 0.13) \times 10^{-11}$ cm$^3$·molecule$^{-1}$·s$^{-1}$ in ICl/SO$_2$/N$_2$O mixtures.

The conflicts that existed in Batson’s [1] previous work on Cl$^*/$N$_2$O are highlighted in this study. Table (3-8) provides a summary of the $k_{\text{N}_2\text{O}}^*$ results determined in this work through various methods and literature values from previous experimental studies. In the presence of argon the quenching rate coefficient determined here approaches Batson’s [1] and Chichinin’s [14] values. Without argon present the N$_2$O rate coefficient for Cl$^*$ quenching found in this work is roughly 50% faster than Chichinin’s and Batson’s values, and is in agreement with Chichinin’s value within their combined stated uncertainties.

Table 3-8: Summary of $k_{\text{N}_2\text{O}}^*$ values.

<table>
<thead>
<tr>
<th>$k_{\text{N}_2\text{O}}^*$</th>
<th>reference/comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.8 ± 1.6</td>
<td>this work, ICl/N$_2$O mixtures</td>
</tr>
<tr>
<td>7.3 ± 1.7</td>
<td>this work, ICl/N$_2$O mixtures with ∼5 Torr of argon</td>
</tr>
<tr>
<td>15.9 ± 1.3</td>
<td>this work, ICl/N$_2$O/SO$_2$ mixtures; SO$_2$(v$_3$) fluorescence</td>
</tr>
<tr>
<td>11 ± 5</td>
<td>this work, a single value to encompass all results</td>
</tr>
<tr>
<td>6.3 ± 2.0</td>
<td>Chichinin [14], in 10 Torr of argon</td>
</tr>
<tr>
<td>5.9 ± 1.2</td>
<td>Batson [1], in ∼5 Torr of argon (attributed to $k_{\text{V,N}_2\text{O}}^*$)</td>
</tr>
</tbody>
</table>

a. $10^{-12}$ cm$^3$·molecule$^{-1}$·s$^{-1}$

The three different values determined for $k_{\text{N}_2\text{O}}^*$ in this study can be averaged together to yield a final value of $k_{\text{N}_2\text{O}}^* = (1.1 \pm 0.5) \times 10^{-12}$ cm$^3$·molecule$^{-1}$·s$^{-1}$. The one standard deviation about this mean value encompasses all three values determined individually in the three different kinetic studies carried out.
Table (3-9) provides a review of the rate coefficients determined for $k^V_{N_2O}$, and table (3-10) provides a review of the rate coefficients determined for $k^V_{Ar}$ in this work and from literature values. The $k^V_{N_2O}$ value determined in ICl/N$_2$O mixtures in this work, $(1.0\pm0.2) \times 10^{-12}$ cm$^3$·molecule$^{-1}$·s$^{-1}$ overlaps within the combined stated uncertainties with the values determined by Kung [32] and Huddleston and Weitz [33]. The apparent vibrational relaxation rate coefficient, obtained from N$_2$O($v_1$) fluorescence decays, increased to $k^V_{N_2O} = (2.3\pm0.4) \times 10^{-12}$ cm$^3$·molecule$^{-1}$·s$^{-1}$ when a fixed amount (~5 Torr) of argon was added to the ICl/N$_2$O mixtures. This value for $k^V_{N_2O}$ approaches the value obtained by Batson [1] in the previous study. There is agreement between Batson and this work with regards to the value of $k^V_{Ar}$, but both values are roughly 2 to 3 times greater than the currently accepted literature values.

Table 3-9: Summary of $k^V_{N_2O}$ values

<table>
<thead>
<tr>
<th>$k^V_{N_2O}$ a</th>
<th>reference/comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0 ± 2.0</td>
<td>this work, ICl/N$_2$O mixtures</td>
</tr>
<tr>
<td>23.0 ± 4.0</td>
<td>this work, ICl/N$_2$O mixtures with ~5 Torr of argon</td>
</tr>
<tr>
<td>6.6 ± 1.3</td>
<td>Kung [34]</td>
</tr>
<tr>
<td>8.6 ± 0.5</td>
<td>Huddleston and Weitz [33]</td>
</tr>
<tr>
<td>11 ± 5</td>
<td>this work, a single value to encompass all results</td>
</tr>
<tr>
<td>7.1 ± NA</td>
<td>Slobodskaya and Rityn [36], no uncertainty provided</td>
</tr>
<tr>
<td>35.0 ± 3.0</td>
<td>Batson [1], in ~5 Torr of argon (attributed to $k^V_{N_2O}$)</td>
</tr>
</tbody>
</table>

a. $10^{-13}$ cm$^3$·molecule$^{-1}$·s$^{-1}$

Table 3-10: Summary of $k^V_{Ar}$ values

<table>
<thead>
<tr>
<th>$k^V_{Ar}$ a</th>
<th>reference/comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.9 ± 0.8</td>
<td>this work, ICl/N$_2$O/Ar mixtures</td>
</tr>
<tr>
<td>2.5 ± 0.7</td>
<td>Batson [1]</td>
</tr>
<tr>
<td>1.1 ± 0.2</td>
<td>Kung [32]</td>
</tr>
<tr>
<td>1.5 ± 0.5</td>
<td>Huddleston and Weitz [33]</td>
</tr>
<tr>
<td>1.2 ± 0.4</td>
<td>Slobodskaya and Rityn [36]</td>
</tr>
</tbody>
</table>

a. $10^{-14}$ cm$^3$·molecule$^{-1}$·s$^{-1}$
The bizarre behavior that added Cl* quenchers and vibrational relaxing agents, alike, increase the rate of N$_2$O($\nu_1$) fluorescence rise in conjunction with the differences in $k^V_{N2O}$ and $k^*_{N2O}$ in the presence or absence of argon suggests that a more elaborate kinetic mechanism is at work than one similar to the simple A-B-C kinetic mechanism. The proposal that a cross-over or switching of the fluorescence rise/decay associations with quenching/V-V relaxation might lead to incorrect assignments of the kinetic processes in the mechanism has been discounted as an explanation of the results. Preliminary kinetic modeling efforts with the simple mechanism support the expectation that argon addition should increase only the rate of N$_2$O($\nu_1$) fluorescence decay and leave the rise unaffected. Another unexpected and unexplained behavior is that the y-intercepts of the argon kinetic plots are in direct conflict with the assignments of the slopes. The current discrepancy defies any plausible explanation despite lengthy consideration and experimental attempts to formulate a coherent understanding of the results of this study.

Kinetic modeling of alternative mechanisms may lead to an improved understanding of the present experimental results. Replacing the IR fluorescence observation method with a diode laser absorption method would enable time-resolved observations of the 010, 020, 100 and 110 levels with improved selectivity and sensitivity whereas, at present, only the 100 level can be observed. This expanded capability to observe the populations of all of the energetically accessible states would be a valuable improvement in these E-V pathway investigations.
References


25. ICl thermodynamic values. NIST at www.nist.gov


