DETERMINATION OF VIBRATION-TO-VIBRATION ENERGY TRANSFER RATES OF NITROGEN, OXYGEN, AND HYDROGEN USING STIMULATED RAMAN SCATTERING

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

BY

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The Ohio State University
2005

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ABSTRACT

Stimulated Raman scattering is used to vibrationally excite N\textsubscript{2}, O\textsubscript{2} and H\textsubscript{2} molecules in the pressure range 300-760 Torr at room temperature. The subsequent vibration-to-vibration (VV) collisional energy transfer processes causes the excited vibrational levels of these molecules to be populated well above their equilibrium distribution at room temperature. The temporal evolution of the populations of vibrational levels as high as v=6 of these molecules is probed by spontaneous Raman scattering. The experimental results are compared to predictions from a Master Equation kinetics modeling code, incorporating VV energy transfer rate coefficients derived from several published theoretical models. Predictions using the rate coefficients given by three dimensional semi-classical trajectory calculations give good overall agreement with the experimental data for N\textsubscript{2}, with those of the Forced Harmonic Oscillator Free Rotator (FHO-FR) model giving the best overall agreement followed by the rates from models of Billing and Fisher and the models of Bogdanov et al. Rate coefficients calculated using one dimensional theory failed to give good agreement with experiment. For the O\textsubscript{2}-O\textsubscript{2} and H\textsubscript{2}-H\textsubscript{2} VV rates, even the rate coefficients from three dimensional semi-classical theory fails to give accurate predictions and new sets of rate coefficients are needed. Intensities of
spontaneous Raman scattering transitions originating from H$_2$(v=1), populated by stimulated Raman scattering were measured and compared to those from ground level. The experimentally determined Raman cross section ratio between v=1 and v=0 is consistent with theoretical predictions of Schwartz and LeRoy.
ACKNOWLEDGMENTS

I thank God for leading me to meet the people to whom I am grateful for helping me with my graduate studies.

I wish to thank my adviser Dr. Walter R. Lempert for his intellectual support, encouragement, and for his patience without which writing this thesis would not have been achieved.

I thank Dr. J. William Rich, and Dr. Igor V. Adamovich for many insightful discussions. I also wish to thank members of my group, Wonchul Lee, Naibo Jiang, Robert Leiweke, and Kraig Frederickson for their various contributions in performing the experiments.

This research was supported by the Air Force Office of Scientific Research (AFOSR) and the National Science Foundation (NSF).
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CHAPTER 1

INTRODUCTION

Nitrogen (N\textsubscript{2}) and oxygen (O\textsubscript{2}) are the most abundant molecules in the earth’s atmosphere while hydrogen (H\textsubscript{2}) is the most abundant molecule in the universe. Despite their abundances in nature, spectroscopic studies of these molecules have been limited since they are homonuclear diatomics that have no dipole moment. The molecules in the upper atmosphere and outer space are in non-equilibrium conditions\textsuperscript{1} - i.e., the population distribution of the vibrational and/or rotational levels cannot be explained by a thermal Boltzmann distribution. The relaxation of vibrationally excited molecules in the upper atmosphere is of great importance in atmospheric chemistry\textsuperscript{2}. For example, reaction between vibrationally excited O\textsubscript{2} (\(v \gg 0\)) and O\textsubscript{2} (\(v = 0\)) has been proposed as a source of ozone formation in the earth’s stratosphere\textsuperscript{3,4}.

\begin{equation}
O_2 (v \gg 0) + h\omega \rightarrow 2O \tag{1.1}
\end{equation}

\begin{equation}
O_2 + O + M \rightarrow O_3 + M \tag{1.2}
\end{equation}
These processes compete with collisional relaxation that quenches vibrational excitation\textsuperscript{4}.

\[ \text{O}_2 (v \gg 0) + \text{O}_2 (0) \rightarrow \text{O}_3 + \text{O} \]  \hspace{1cm} (1.3)

\[ \text{O}_2 (v) + \text{O}_2 \rightarrow \text{O}_2 (v - 1) + \text{O}_2 \]  \hspace{1cm} (1.4)

Although the latter process has been suggested to be much faster than the former\textsuperscript{5 6 7 8}, quenching of vibrational energy at these high vibrational levels cannot be accounted for by the above reaction (equation 1.4) alone. More studies are needed to fully understand the processes that control the fate of these vibrationally excited molecules.

Non-equilibrium conditions can also occur in combustion processes, advanced plasma propulsion and control systems\textsuperscript{9}, gas dynamic lasers\textsuperscript{10}, and novel material synthesis methods\textsuperscript{11} to name a few. Detailed knowledge of vibration-to-vibration (V-V) collisional energy transfer rates is essential for quantitative modeling of these non-thermal systems. Non-intrusive spectroscopic determination of collisional V-V energy transfer rates in homonuclear diatomic molecules has been difficult due to the absence of a dipole moment for rotational or vibrational transitions. Moreover, all electronic transitions from the ground level in nitrogen and hydrogen require X-ray or vacuum ultraviolet radiation and cannot be achieved with ordinary laser frequencies. Diagnostic methods based on laser absorption are inappropriate for these molecules.

Absorption of infrared radiation, which accompanies direct vibrational excitation is also the most efficient method of producing a vibrationally excited non-equilibrium medium,
but since it is forbidden for these molecules due to basic optical selection rules, other methods have to be used.

\[ A_2(v = 0) + h\nu \not\rightarrow A_2(v = 1) \quad (1.5) \]

Electric discharge is another method of creating non-equilibrium conditions. However, the discharge also causes ionization and dissociation processes to occur, consequently forming plasmas containing free electrons, atoms and atomic/molecular ions.

\[ A_2 + e^- \rightarrow 2A + e^- \quad (1.6) \]
\[ A_2 + e^- \rightarrow A_2^+ + 2e^- \quad (1.7) \]
\[ A_2 + e^- \rightarrow A + A^+ + 2e^- \quad (1.8) \]

The charged species and atoms can recombine to form molecules or undergo collisions with other molecules leading to an increase in the internal energy of the molecules and promote secondary ionization or dissociation processes.

\[ A_2^+ + e^- + A_2 \rightarrow 2A_2 \quad (1.9) \]
\[ 2A + A_2 \rightarrow 2A_2 \quad (1.10) \]
\[ A_2(v = 0) + e^- \rightarrow A_2(v > 0) + e^- \quad (1.11) \]


In fact, the recombination of free electrons with oxygen molecules has been proposed to be a reaction critical to reducing the density of free electrons in high pressure plasmas\textsuperscript{12}.

\[ \text{O}_2 + e^- + M \rightarrow \text{O}_2^- + M \]  \hspace{1cm} (1.12)

The reactions mentioned above also affect the molecular vibrational energy distribution since vibrational excitation or relaxation often accompanies collisions with atoms or free electrons. In order to assess the dynamics purely due to V-V transfer, formation of ionic and/or atomic species must be avoided. A method other than gas discharge should be employed to achieve a non-equilibrium vibrational excitation.

Photochemical and chemical reactions have also been used to create vibrationally excited molecules since they are easy to apply\textsuperscript{13,14,15}.

\[ \text{NO}_2 + O \rightarrow \text{O}_2(v > 0) + \text{NO} \]  \hspace{1cm} (1.13)

Nature produces vibrationally excited oxygen molecules by photodissociation of ozone molecules in the stratosphere. This is the very mechanism by which ozone molecules in the ozone layer block the sun’s UV radiation from reaching the earth’s troposphere.

\[ \text{O}_3 + h\nu \rightarrow \text{O}_2(v > 0) + \text{O} \]  \hspace{1cm} (1.14)

A disadvantage of using chemical reactions to produce vibrationally excited molecules is that they also produce unwanted byproducts that can interfere with the analysis of pure
V-V dynamics. Another disadvantage is that molecules are produced over a wide range of vibrational levels, which complicates the analysis of the kinetic behavior of the populations in the individual states. Efforts have been made to solve this problem by combining optical pumping with chemical reactions and this method remains popular for producing vibrationally excited O$_2$ molecules$^{14}$.

Stimulated emission pumping (SEP) or “pump-dump” methods can be used for vibrational excitation when there exists an upper electronic energy level accessible by a laser photon$^{16}$. The pump frequency photon excites the molecule to the upper electronic state while the dump frequency causes stimulated emission back down to the ground electronic energy level. The difference in energy between the two laser frequencies is the energy of the vibrational excitation.

\[
A_2(S_0, v = 0) + \hbar \nu_{\text{pump}} \rightarrow A_2(S_1) \tag{1.15}
\]

\[
A_2(S_1) + \hbar \nu_{\text{dump}} \rightarrow A_2(S_0, v) + 2 \hbar \nu_{\text{dump}} \tag{1.16}
\]

\[
E(v) - E(0) = \hbar \nu_{\text{pump}} - \hbar \nu_{\text{dump}} \tag{1.17}
\]

In the case of O$_2$, the existence of the well-known Schumann-Runge transition (\( X^3\Sigma_g^- - B^3\Sigma_u^- \)) band allows vibrational pumping through SEP$^4$$^{17}$. A minor disadvantage of utilizing SEP comes from the spontaneous emission (fluorescence) from excited electronic states back down to the ground state levels that are not resonant with the dump laser, a process known as “Franck-Condon pumping”. The amount of
population transferred to these levels is typically on the order of 1% of transition to vibrational levels in resonance with the dump laser wavelength\textsuperscript{18}.

\[ A_{2}(S_{t}) \rightarrow A_{2}(S_{o},v)+h\nu, \quad v \neq v_{\text{dump}} \]  

Laser absorption to an electronically excited level can also cause molecules to predissociate\textsuperscript{19}, and this phenomenon is also observed in O\textsubscript{2}, B \textsuperscript{3}\Sigma_{u}^{-}.

Stimulated Raman pumping\textsuperscript{20} is a nonlinear optical method that is analogous to SEP, except that the transition to the intermediate upper level is to a non-resonant virtual state.

\[ A_{2}(v = 0) + h\nu_{\text{pump}} + h\nu_{\text{dump}} \rightarrow A_{2}(v = 1)+2h\nu_{\text{dump}} \]  

Figure 1 shows a comparison of the two methods.

Although it is a much more efficient process than spontaneous Raman scattering which does not use a “dump” frequency light to stimulate the scattering process, a high laser intensity is usually needed for the excitation, leaving the sample susceptible to laser breakdown due to high electric fields. Nevertheless, stimulated Raman scattering (SRS) has previously been used to vibrationally pump N\textsubscript{2}\textsuperscript{21}, O\textsubscript{2}\textsuperscript{22} and H\textsubscript{2}\textsuperscript{23,24}.

Valyanskii et al. pumped v=1 level of N\textsubscript{2} by SRS and probed its population decay by coherent anti-Stokes Raman spectroscopy (CARS) to infer the V-V rates\textsuperscript{21}. Diskin pumped the v=1 level of O\textsubscript{2} by SRS and probed the population change in v=2 and 3 with
Figure 1. Stimulated emission pumping “pumps” the molecule to an existing excited state then “dumps” it to a lower energy state while stimulated Raman pumping uses a virtual state as the intermediate state.
LIF signals from excitation of the O$_2$ Schumann-Runge band$^{22}$. The $v=2$ and 3 levels (and higher vibrational levels) were populated by V-V transfer through molecular collisions.

\[ \text{O}_2(v) + \text{O}_2(v=1) \rightarrow \text{O}_2(v=1) + \text{O}_2(v=0), v = 1, 2, \ldots \]  

(1.20)

Ducuing and co-workers measured the vibration-to-translation (V-T) rates out of $v=1$ in H$_2$, D$_2$ and HD by utilizing SRS and Schlieren detection of the change of index of refraction of the gas$^{25, 26, 27}$.

\[ \text{H}_2(v=0) + \text{H}_2(v=1) \rightarrow 2\text{H}_2(v=0) \]  

(1.21)

Miles and co-workers measured V-T and V-V relaxation rates out of excited vibrational levels in H$_2$ and HD using time-resolved photoacoustic detection following direct overtone pumping into $v=2$–6 vibrational levels$^{24, 28, 29}$.

\[ \text{H}_2(v=0) + \text{H}_2(v=2) \rightarrow 2\text{H}_2(v=1) \]  

(1.22)

Several experiments have measured rotation-to-rotation (R-R) rates as well as V-V rates of H$_2$ using SRS to populate the $v=1$, $J=1$ level and monitored its population transfer using either CARS, laser induced fluorescence (LIF) or resonance enhanced multiphoton ionization spectroscopy (REMPI)$^{23, 30, 31}$.

\[ \text{H}_2(v=1, J=1) + \text{H}_2(v=0) \rightarrow \text{H}_2(v=1, J=3) + \text{H}_2(v=0) \]  

(1.23)
Similarly Sitz and coworkers measured rotational energy transfer rates of $N_2(v=1)$ through stimulated Raman pumping$^{32}$.

All of the experiments mentioned above observed population dynamics for a limited range of vibrational levels and did not measure the absolute time dependent concentration of excited states, partly limited by the nature of the detection scheme. Determining the absolute concentration from data obtained by spectroscopic methods such as LIF is not always straightforward and calibration of the signal is necessary.

In this study, vibrational pumping of the homonuclear diatomic molecules to $v=1$ is achieved by SRS. The higher levels are subsequently populated by collisional V-V processes and the kinetics of the V-V transfer is monitored by spontaneous Raman scattering. The choice of Raman spectroscopy as the probe method will be discussed later. Under our experimental conditions, the timescale for the Raman pumping (~20 ns) is short compared to that of the V-V processes (~μs) so the temporal laser width can be regarded as infinitely short.

A feature of this study that is different from most previous measurements of vibrational energy transfer rates is that we observe the rise in the population of higher vibrational levels from VV collisional excitation of lower levels instead of the VV decay rate of higher vibrational levels relaxing to lower levels. The two processes are related to each other since one is the reverse reaction of the other.

$$A_2(v-1) + A_2(l) \xrightarrow{k_{-1}} A_2(v) + A_2(0)$$  \hspace{1cm} (1.24)
The ratio of the two rates can be expressed as

$$\frac{k}{k_{-1}} = \exp \left[ -\frac{(E(v) + E(v = 0)) - (E(v - 1) + E(v = 1))}{kT} \right]$$

(1.25)

from the detailed energy balance relation, where $E(v)$ is the vibrational energy of $A_2(v)$. Due to the anharmonic nature of the vibrational levels the forward rate will be larger than the reverse rate, that is $k \geq k_{-1}$.

The advantage of using spontaneous Raman spectroscopy as the probe method comes from its non-resonant nature. Unlike other forms of spectroscopy, the frequency of the incident photon (or in the case of multiphoton processes, their sum or difference) does not need to match the energy difference between the state under probe and a high (or low) lying state. In spectroscopic methods where the resonance conditions must be met, only the states that satisfy these criteria can be detected at a certain wavelength. The probe laser frequency must be scanned and the change in laser power and other experimental conditions during the scan must be accounted for.

For Raman scattering, the incident light wavelength can be of any value and the population of the ground vibrational level can be measured simultaneously along with that of the Raman pumped v=1 level as well as the population of higher vibrational levels rising from subsequent V-V collisions. Therefore, quantitative analysis can be performed in a straightforward way and scanning the probe laser wavelength is unnecessary. This enables extraction of absolute concentrations of the vibrational levels and its evolution in time with relative ease compared to LIF or other spectroscopic techniques. The
disadvantage of spontaneous Raman spectroscopy, as will be mentioned in Chapter 2, is its low sensitivity which requires longer integration times and/or higher sample density for collection of spectra with reasonable signal-to-noise ratios. Chapter 2 will also mention other specific details of experimental conditions that were used to study the V-V dynamics of N_2, O_2 and H_2.

Chapter 3, 4 and 5 contain experimental data for V-V kinetics of N_2, O_2 and H_2 respectively. In all three cases, molecules in the ground vibrational level, v=0 are excited to v=1 by stimulated Raman pumping. Higher vibrational levels are populated by collisional V-V processes. The highest level of vibrational energy observed is v~6 for all three cases. Processes such as diffusion of energetic molecules out of the probe volume, and vibration-to-translation (V-T) relaxation of vibrational energy result in decreasing the already small population of higher v levels created by VV excitation, and make their detection by Raman spectroscopy even more difficult.

Notwithstanding, due to the advantages mentioned above, the time evolution of the population in each vibrational level and hence the V-V kinetics is monitored with Raman spectroscopy. The experimental results are compared with simulations using the theoretically calculated V-V rate coefficients for each gas molecule. The agreement/disagreement between experiments and simulations are discussed.

The vibrational level dependence of the Raman transition intensities for each molecule is also discussed as well as the effect of anharmonicity on the Raman scattering cross sections.

Chapter 3 also mentions the effect of the relative size of the focused pump and probe laser beams on the observed signal under our experimental conditions. We find that for
our experimental conditions, the size of the probe beam relative to the pump beam has little effect on the time evolution of the population in vibrational levels.

The final chapter concludes with possible future directions in this study.
CHAPTER 2

DETERMINATION OF VIBRATIONAL POPULATION

2.1 Introduction

Spontaneous Raman scattering has several advantages as a non-intrusive laser diagnostic technique compared to absorption spectroscopy or laser induced fluorescence (LIF). Absorption is a “line of sight” probe method where the entire laser beam path becomes the sampling region and contributes to the observed signal. LIF, along with Raman spectroscopy collects the fluorescence or light scattering at an angle with respect to the laser beam and hence only the region in the laser beam path that intersects the detection path contributes to the signal making them “point of sight” probe methods. However, processes such as non-radiative relaxation (quenching), saturation and amplified
spontaneous emission of the fluorescence cause deviation from a linear response of the LIF signal as a function of the concentration of the species under detection\textsuperscript{22,33}.

The advantages of Raman spectroscopy as a “point of sight” detection method and the linear relationship between species concentration and its observed signal intensity, are compensated by its low sensitivity compared to the other two methods mentioned above. Consequently, data must be collected for a longer period of time, which makes Raman spectroscopy unsuitable for probing systems where the sampling conditions aren’t highly reproducible from laser shot to laser shot, such as shock flow measurements.

Under our experimental conditions, vibrationally excited molecules are only produced in a small region around the focal point of the pump laser, making absorption methods inappropriate for obtaining information about the number densities of the excited species in the region where they are formed. The pressure inside the sample cell is \(~760\) Torr giving a concentration of \(2\times10^{19}\text{cm}^{-3}\) at 300 K which is sufficient for molecules of our interest with relatively large Raman cross sections to be studied by Raman spectroscopy. All Raman spectra, each obtained by integration of 100 laser shots, yielded a fraction of molecules pumped to the first vibrational level within 10\% of the mean value. This confirms the reproducibility of the system and also the validity of Raman spectroscopy as the diagnostic tool of choice.
2.2 Experimental Setup

The experimental layout and the excitation scheme for nitrogen is shown in figure 2. The setup for oxygen and hydrogen are similar. Approximately 200 mJ per pulse of the second harmonic output (532 nm) of a Q-switched Nd:YAG laser (Quanta Ray GCR 230) was focused with a 1.5 m focal length plano-convex lens into a high pressure (70 bar) stimulated Raman shifting cell containing a 1:1 mixture of N\textsubscript{2}:He. Approximately 25% of the incident pump photons (532 nm) are converted to either the first or second Stokes frequencies (607 and 707 nm, respectively) by the SRS process\textsuperscript{34}. The helium inside the cell served primarily to increase the thermal conductivity of the gas mixture, which is important for dissipation of the excess energy associated with the conversion of a pump photon (532 nm) to a Stokes photon (607 / 707 nm). The cell was 2.4 m in length and a heating tape whose temperature was maintained approximately at 40° C, was attached to the bottom of the cell to help with the convection of the gases inside. This, along with the addition of the helium buffer gas is known to help improve the spatial beam profile of the Raman cell output\textsuperscript{35}. A small fraction (~20 mJ) of the second harmonic output of the Nd:YAG pump laser was used to excite a simple dye laser oscillator consisting of a cuvette containing a flowing mixture of Rhodamine 610 and 640 laser dye solution (total concentration ~70 mg/L in methanol), a high reflector (radius of curvature $r_c = 5.0$ m), and a 30% reflectivity (at 600 nm) – flat output coupler. The oscillator output from the output coupler had a broad bandwidth of ~10 nm with peak emission frequency at 607 nm. It was transmitted through a dichroic mirror and used as a seed source in order to enhance the SRS conversion efficiency inside the Raman cell. Introduction of the seed
Figure 2. Schematic diagram of the experimental setup.
beam into the Raman cell increased the Stokes conversion efficiency by a factor of ~2 at pump beam power of 200 mJ. Since the bandwidth of the oscillator output was several nanometers, the mismatch between the peak emission frequency and the first Stokes frequency by 50 cm$^{-1}$ has no observable effect on the conversion efficiency. The dye cell cuvette was tilted at Brewster’s angle in order to match the polarization of the dye oscillator output to that of the pump YAG beam entering the Raman cell. The optical path of the pump beam was time delayed to permit the pump beam and the seed beam to overlap temporally as well as spatially inside the Raman cell. The SRS pump, consisting of the residual second harmonic and the first and second Stokes frequency beams after exiting the Raman shifting cell, was recollimated by another 1.5 m focal length lens and focused with a 300 mm focal length lens into a second cell containing pure N$_2$ at room temperature and variable pressure between 300 and 760 Torr. The total power of the final pump pulse incident to the measurement cell was ~100 mJ (~50 mJ of 532 nm, ~40 mJ of 607 nm, and ~10 mJ of 707 nm). Through a second stimulated Raman process, a fraction (~$\frac{1}{3}$) of the N$_2$ molecules in the second cell were initially prepared in the first (v=1) excited vibrational level. The second harmonic of a second Q-switched Nd:YAG laser (Continuum Surelite), counter propagating to the SRS pump beam, formed a probe beam which was focused with a 250 mm focal length lens to overlap the volume excited by the pump. A shorter focal length lens was used with the intent of creating a probe volume with a smaller radius than that of the pump. This was necessary in order to avoid spatial averaging over a volume element in which the molecules are not excited by the pump laser, and to properly account for diffusion of excited molecules out of the probe volume.
The time delay between the pump and probe beams was varied between 150 ns and 20 µs by an electronic pulse delay generator (Stanford Research Systems). All spectra were signal averaged for between 1 and 5 minutes, with a pump and probe repetition rate of 5 Hz, which was limited by energy dissipation effects in the SRS conversion cell.

Spontaneous $Q$-branch Raman scattering signal from the probe beam was used to determine the vibrational distribution as a function of time with respect to the pump pulse, using the detection scheme also illustrated in figure 2. A pair of $f/4$ lenses was used to 1:1 image the spontaneous scattering from an approximately 1 cm segment of the probe region onto the slit of a 0.3 cm, $f/4$ spectrometer (Acton Spectrapro 300i), equipped with a gated ICCD detector (Princeton Instruments) which collected the vibrationally resolved Stokes ($v \rightarrow v+1$) $Q$ branch Raman data. The slit of the spectrometer was opened to a width of 100 µm, its optimal value due to compromise between signal intensity and spectral resolution.

As will be described in more detail in the following chapters, accounting for mass diffusion requires that the dimensions of the pumped and probed volumes be determined. We have determined the convolution of the two by translation of the pump beam relative to the probe, and recording the initial $v=0$ and 1 population fractions. This is performed by moving the 300 mm focal length lens which is used to focus the pump beam into the measurement cell. The lens is mounted on a X-Z translation stage and translated in both the X and Z directions with respect to the fixed path of the probe beam (the path of the laser is chosen as the $Y$ axis). The fixed path of the probe beam allows the positions of the collection optics and that of the spectrometer to remain fixed. Figure 3 shows the
schematics of the translation of the pump beam along with the directions of laser polarizations.

Since the pump beam and the probe beam both contain 532 nm photons, and the two beams travel collinearly in counter propagating directions, the output of the pump laser could potentially enter the exit aperture of the probe laser and vice versa. To avoid this, a polarizer was placed between the probe laser and the measurement cell. We manipulated the linear polarizations of the pump (X) and the probe (Z) to be orthogonal to each other. The pump beam exiting the measurement cell was reflected out of the probe laser beam path by the polarizer. The probe beam was transmitted through the polarizer and focused into the region excited by the pump laser. The low power probe laser beam was inevitably allowed to travel directly into the pump laser, but no effect on the pump laser output was observed.

Another consequence of the two beams containing photons of the same frequency was limitation on the shortest time delay between the two pulses that could be achieved. This was also due to the fact that the pump and probe methods both employed the same vibrational Raman transition. The Stokes frequency of the pump beam matched the frequency of the Raman Stokes spectrum (for v=0) being collected. Any 607 nm pump beam photons reaching the detector interfered with the signal. The pump region could only be probed after the pump beam had completely passed through the probe region. Although the pump beam had a temporal width of ~20 ns FWHM, photons scattering off objects inside the room, despite attempts at baffling, reached the detector as much as 100 ns after the pump laser had passed through the probe region. Therefore the fastest time that the nitrogen vibrational distribution could be observed after pumping was ~150 ns.
Figure 3. Schematic of translating the pump beam in X-Z plane with respect to the probe laser by moving the focusing lens. Also shown are the directions of polarizations and propagation of the two lasers as well as the direction of observation (collection lens) of Raman scattering.
By this time, the pumped molecules go through numerous collisions and any orientation of the molecules that resulted from the polarization of the pump laser is relaxed to a spatially isotropic distribution. The polarization of the probe beam being orthogonal to that of the pump therefore does not introduce any bias to the observed signal.

The spontaneous Raman cross section for the $\nu \rightarrow \nu + 1$ $Q$ branch signal from vibrational level $\nu$ scales as being proportional to $\nu + 1$ in harmonic oscillators. For real diatomic molecules, the cross sections deviate from the $\nu + 1$ proportionality dependence at higher vibrational levels. At low vibrational energy levels, the molecule behaves close to a harmonic oscillator and the intensities of each vibrational peak are be divided by $\nu + 1$ to extract the vibrational level population. The highest level observed in nitrogen was $\nu = 6$, which is well below the dissociation energy ($< 25\% D_0$), and the $\nu + 1$ dependence of the spontaneous Raman cross sections was assumed. Recent theoretical calculations are in agreement with the assumptions within 10% at $\nu = 6$ for nitrogen$^{36}$. A more detailed discussion on the vibrational level dependence of the Raman cross sections will be given later.

The excitation scheme for oxygen was similar to the experimental setup for nitrogen. The output of the pump laser was increased to 250 mJ per pulse. The Raman shifting cell consisted of the oxygen and helium gas with $O_2$:He ratio of 1:1 and total pressure of 70 bar. The solution for the dye laser oscillator was a mixture of Rhodamine 590 and 610 in methanol with a total concentration of 70 mg/L. The ratio of the dyes was adjusted to match the emission peak frequency to the first Stokes frequency of 581 nm.

The Raman cell output entering the measurement cell after focusing was approximately 100 mJ per pulse in total energy. The content of the measurement cell was 21% oxygen.
and 79% nitrogen with a total pressure of 760 torr, similar to room air. The purity of the sample was \(~99.99\%\) and no quenching effects from possible contaminants such as H\(_2\)O could be observed. The oxygen concentration was adjusted to make the timescale of the oxygen VV transfer kinetics appropriate for probing with our nanosecond laser system. Nitrogen was added as a buffer gas to slow down diffusion of pumped oxygen molecules out of the probe region. N\(_2\)-O\(_2\) VV transfer rates are three orders of magnitude slower than that of O\(_2\)-O\(_2\) and the role of nitrogen as a VT relaxer of vibrationally pumped oxygen is also negligible on our probe timescale of within 10 \(\mu\)s\(^{37}\). Therefore the only effect of nitrogen on the energy transfer kinetics of vibrationally excited oxygen molecules is decreasing its diffusion rate out of probe volume.

For hydrogen, the gain for stimulated Raman scattering is substantially higher compared to nitrogen or oxygen. As a result, the Raman cell was filled with only 3 bar of pure hydrogen. The seed beam, used to improve the Raman conversion efficiency in nitrogen and oxygen was not employed for hydrogen. The power of the pump laser was 70 mJ per pulse. The output of the Raman cell incident to the measurement cell was 20 mJ (12 mJ of 532 nm, 6 mJ of 1\(^{st}\) Stokes and 2 mJ of 2\(^{nd}\) Stokes) per pulse and sufficient in energy to pump \(\frac{1}{3}\) of hydrogen molecules from the ground level to the first vibrationally excited level.

For probing, in addition to the vibrational \(Q\)-branch Raman spectrum collected in the cases of nitrogen and oxygen, the pure rotational \(S\) branch spectrum could also be obtained for hydrogen owing to its large rotational energy spacing. \(v, J \rightarrow v, J+2\) transitions corresponding to each \(v\) and \(J\) value could be resolved by the spectrometer.
This allowed the probing of the change in population of individual rotational quantum states with time. Also, since the $S$ branch spectrum was far removed in frequency from the $Q$ branch, interference by the pump Stokes beam on the signal is minimal and probing of the population distribution at $t=0$ was possible. However, as noted earlier, due to the polarizations of the pump and the probe beams being linear and orthogonal to each other, initially all molecules Raman pumped to $v=1$ are aligned along the pump laser polarization axis ($X$) while the probe laser detects molecules aligned along its polarization axis ($Z$). For accurate determination of population in $v=1$, the shortest time delay monitored should be at least long enough to allow any spatial alignment of vibrationally excited hydrogen molecules produced from the polarization of the pump beam to be removed by intermolecular collisions. At 760 Torr, this relaxation process occurs on the order of $100 \text{ ps}^{32}$, and the effects of laser polarizations on measuring the vibrational level population can be ruled out. The pump laser pulse is 20 ns long and fittingly, the population in $v=1$ reaches its maximum at 20 ns. The pump laser beam has the same frequency as the probe and a small amount of $S$ branch rotational signal due to scattering of the pump beam was observed at 20 ns. Although scattering signal from the pump beam is qualitatively the same as that from the probe, the shortest delay was chosen to be 30 ns. At 30 ns, no Raman scattering from the residual pump laser was observed, and $S$ branch signal at this time delay is compared with the signal without Raman pumping for measurement of pure rotational Raman cross section ratios between $v=1$ and $v=0$.

Hydrogen has a higher anharmonicity compared to nitrogen or oxygen, and its $v, J \rightarrow v+1, J$ transition Raman cross section cannot be assumed to be proportional to $v+1$ like a harmonic oscillator even at low vibrational levels. We used the polarizability
matrix elements calculated by LeRoy and coworkers\textsuperscript{38} to obtain the ratio of both the \( Q \) branch and \( S \) branch Raman cross sections between different vibrational and rotational levels. But as will be seen later, the \( v \) dependence of the Raman cross section for hydrogen is similar to that of oxygen and nitrogen.

Figure 4(a) shows an image of a ruler placed in the probe region. The spectrometer grating was set to 0 nm to act as a reflecting mirror instead of as a diffraction grating. The distance between each reading of the ruler is \( \frac{1}{16} \) of an inch. Figure 4(b) shows an image of the oxygen Raman spectrum of the same region as (a). The image was taken \( \sim 1 \) \( \mu \)s after the region was Raman pumped. The grating wavelength was centered to the oxygen vibrational Raman Stokes frequency of 581 nm. As a result, the image was frequency resolved to several lines with each line corresponding to a Stokes line from a different vibrational level. When compared with (a), the image of the Stokes line for \( v=0 \) is \( \sim \frac{5}{16} \) inches (~8 mm) in length. The width of the image is substantially shorter due to the 100 \( \mu \)m width of the spectrometer slit opening and the narrow spatial profile of the probe laser at its focus.
Figure 4. (a) Image of a ruler placed at the probe region. Spacing between each reading corresponds to 1/16 of one inch. (b) Image of the probe region resolved in frequency by the spectrometer. Each line corresponds to one vibrational level of O$_2$. 
2.3 Extracting Population Data from Raman Scattering Spectrum of Diatomic Molecules

Intensity of a rotational Raman transition is described\(^{39}\) by the equation of the form

\[
I = \frac{16\pi}{c^4} I_0 \frac{N_{v,J}}{2J+1} \sum_{m,m'} \left| \langle vJm | \alpha_{ij} | v'J'm' \rangle \right|^2
\]  

(2.1)

where \(I\) is the energy flux scattered from unit volume per unit solid angle. \(\nu\) represents the frequency of the scattered radiation, \(I_0\) is the energy flux density of the incident radiation, \(N_{v,J}\) is the number density of molecular scatterers in the initial energy level specified by \(v\) and \(J\). Therefore \(\frac{N_{v,J}}{2J+1}\) becomes number density of molecules in the initial rotational state \(vJm\). \(\langle vJm | \alpha_{ij} | v'J'm' \rangle\) is the matrix element of the \(ij\) component of the polarizability tensor for the transition \(vJm \rightarrow v'J'm'\), where \(vJm\) and \(v'J'm'\) are the vibrational, rotational and magnetic quantum numbers of the initial and final states respectively.

Since the polarizability tensor of a diatomic molecule is not spherically symmetric, one has to consider the matrix elements of the various components. Each of these in turn gives information about the intensity and state of polarization of the radiation scattered in various directions for all different polarizations of the incident radiation. In view of the separability of the Schrödinger equation for diatomic molecules, the matrix elements of the polarizability \(\alpha=\alpha(r,\theta,\phi)\) can be written\(^{40}\)
\[ \sum_{m,m'} \left| \langle \nu Jm | \alpha(r, \theta, \phi) | \nu' J'm' \rangle \right|^2 = \left| \langle \nu J \alpha(r) | \nu' J' \rangle \right|^2 \sum_{m,m'} \left| \langle Jm | f(\theta, \phi) | J'm' \rangle \right|^2 \] (2.2)

where we have written \( \alpha(r, \theta, \phi) = \alpha(r) f(\theta, \phi) \). Therefore the calculation consists of two parts, the evaluation of \( \langle \nu J \alpha(r) | \nu' J' \rangle \) and \( \sum_{m,m'} \left| \langle Jm | f(\theta, \phi) | J'm' \rangle \right|^2 \).

In the molecule fixed coordinate system \( x,y,z \) with \( z \) direction corresponding to the molecular axis, the polarizability tensor has the particular simple form, \( \alpha_{xx} = \alpha_{yy} \neq \alpha_{zz} \) and \( \alpha_{ij} = 0; \quad i \neq j \) where \( i,j = x,y \) or \( z \). Since it is the space fixed \( X,Y,Z \) coordinate system in which observations are made, it is necessary to transform the molecular polarizability to this system. If the orientation of the molecular axis is described by the conventional polar angles \( \theta \) and \( \phi \), components of the polarizability in the space-fixed \( XYZ \) system are

\[
\begin{align*}
\alpha_{zz} &= (\sin^2 \theta) \alpha_\perp + (\cos^2 \theta) \alpha_\parallel \quad \text{(2.3a)} \\
\alpha_{xy} &= \alpha_{yx} = \sin^2 \theta \cos \phi \sin \phi (\alpha_\parallel - \alpha_\perp) \quad \text{(2.3b)} \\
\alpha_{xz} &= \alpha_{zx} = \sin \theta \cos \theta \cos \phi (\alpha_\parallel - \alpha_\perp) \quad \text{(2.3c)} \\
\alpha_{yz} &= \alpha_{zy} = \sin \theta \cos \theta \sin \phi (\alpha_\parallel - \alpha_\perp) \quad \text{(2.3d)}
\end{align*}
\]

where \( \alpha_\parallel = \alpha_{zz} \) and \( \alpha_\perp = \alpha_{xx} = \alpha_{yy} \) for polarizability parallel and perpendicular to the molecular axis. \( \alpha_{XX} \) and \( \alpha_{YY} \) are omitted since they can be eliminated by choice of orientation of coordinate axes. If we assume that the incident light propagating in the \( Y \)
direction and polarized in the X direction is scattered along the X direction, that is parallel to the direction of the polarization of the incident light, the intensity is given by

\[ I_\parallel = \frac{16\pi \nu^4}{c^4} I_0 \frac{N_v J}{2J + 1} \left\{ \sum_{m,m'} \left| \langle v J m | \alpha_{yx} | v' J' m' \rangle \right|^2 + \sum_{m,m'} \left| \langle v J m | \alpha_{zx} | v' J' m' \rangle \right|^2 \right\} \]  \hspace{1cm} (2.4)

Similarly, if the incident light is polarized in the Z direction and we make the observation from the X direction, which is now perpendicular to the direction of polarization of the incident light, the intensity is given by

\[ I_\perp = \frac{16\pi \nu^4}{c^4} I_0 \frac{N_v J}{2J + 1} \left\{ \sum_{m,m'} \left| \langle v J m | \alpha_{yz} | v' J' m' \rangle \right|^2 + \sum_{m,m'} \left| \langle v J m | \alpha_{zz} | v' J' m' \rangle \right|^2 \right\} \]  \hspace{1cm} (2.5)

The contribution from component \( \alpha_{ij} \) to the intensity gives rise to scattered light polarized in the i direction from incident light polarized in the j direction. When the incident light isn’t plane polarized, it can be resolved into two components so that the intensity measurements on natural light can be considered as the sum of the intensities from observations parallel and perpendicular to the direction of polarization of a plane polarized incident beam. As shown in figure 3, in our experimental conditions, the incident light is linearly polarized (Z), while the scattered light is observed in a direction (X) that is perpendicular (at 90 degrees) to both the direction of polarization of the incident beam as well as the direction of beam propagation (Y), and therefore we shall only consider this particular case here. The evaluation of the angular part of these matrix...
elements involves only the rotational wavefunctions, which are the same as for the rigid rotor and are given by

\[ |Jm\rangle = Y_{jm} = \Theta_{jm} \Phi_m \] (2.6)

where \( \Theta_{jm} = \left[ \frac{2J + 1}{2} \frac{(J + |m|)!}{(J - |m|)!} \right]^{1/2} P_{jm}^{|m|}(\cos\theta) \) and \( \Phi_m = \frac{1}{\sqrt{2\pi}} \exp(im\varphi) \). \( P_{jm}^{|m|}(\cos\theta) \) is an associated Legendre polynomial in \( \cos\theta \). These functions are orthonormal to each other so that

\[ \langle Jm | J'm \rangle = \int_0^\pi \int_0^{2\pi} \Theta_{jm} \Phi_m \Theta_{j'm} \Phi_{m'} \sin\theta d\theta d\varphi = \delta_{jj'} \delta_{mm'} \]. We therefore obtain the following integrals for the matrix elements of our interest:

\[ \langle Jm | \alpha_{iz} | J'm \rangle = (\alpha_{||} - \alpha_{\perp}) \int_0^\pi \int_0^{2\pi} \Theta_{jm} \Phi_m \sin\theta \cos\theta \sin\varphi \Theta_{j'm} \Phi_{m'} \sin\theta d\theta d\varphi \] (2.7a)

\[ \langle Jm | \alpha_{zz} | J'm \rangle = \int_0^\pi \int_0^{2\pi} \Theta_{jm} \Phi_m (\alpha_{||} \cos^2\theta + \alpha_{\perp} \sin^2\theta) \Theta_{j'm} \Phi_{m'} \sin\theta d\theta d\varphi \] (2.7b)

These integrals are seen to be a product of \( \theta \) integrals and \( \varphi \) integrals. The evaluation of the \( \varphi \) integrals is straightforward. The \( \theta \) integrals can be evaluated by making use of the recursion relations

\[ \cos\theta \Theta_{jm} = K(J + 1, m)\Theta_{j+1,m} + K(J, m)\Theta_{j-1,m} \] (2.8a)

\[ \sin\theta \Theta_{jm} = G(J + 1, |m| + 1)\Theta_{j+1,|m|+1} - G(J, |m|)\Theta_{j-1,|m|+1} \] (2.8b)
where \( K(J, m) = \left[ \frac{J^2 - m^2}{(2J + 1)(2J - 1)} \right]^{\frac{1}{2}} \) and \( G(J, \pm |m|) = \left[ \frac{(J - 1 \pm |m|)(J \pm |m|)}{(2J + 1)(2J - 1)} \right]^{\frac{1}{2}} \). After a somewhat lengthy and detailed evaluation,

\[
\sum_{m,m} \left| \langle \nu J^m | \alpha_{zz} | \nu' J - 2, m \rangle \right|^2 = \frac{2}{15} \frac{(J - 1)J}{(2J - 1)} \left| \langle \nu J | \gamma | \nu' J - 2 \rangle \right|^2 \tag{2.9a}
\]

\[
\sum_{m,m} \left| \langle \nu J^m | \alpha_{zz} | \nu' J + 2, m \rangle \right|^2 = \frac{2}{15} \frac{(J + 1)(J + 2)}{(2J + 3)} \left| \langle \nu J | \gamma | \nu' J + 2 \rangle \right|^2 \tag{2.9b}
\]

\[
\sum_{m,m} \left| \langle \nu J^m | \alpha_{zz} | \nu' J, m \rangle \right|^2 = (2J + 1) \left| \langle \nu J | \alpha | \nu' J \rangle \right|^2 + \frac{4J(J + 1)(2J + 1)}{45(2J + 3)(2J - 1)} \left| \langle \nu J | \gamma | \nu' J \rangle \right|^2 \tag{2.9c}
\]

for scattered light polarized parallel to the polarization of the incident laser and,

\[
\sum_{m,m} \left| \langle \nu J^m | \alpha_{yz} | \nu' J - 2, m \rangle \right|^2 = \frac{1}{10} \frac{(J - 1)J}{(2J - 1)} \left| \langle \nu J | \gamma | \nu' J - 2 \rangle \right|^2 \tag{2.9d}
\]

\[
\sum_{m,m} \left| \langle \nu J^m | \alpha_{yz} | \nu' J + 2, m \rangle \right|^2 = \frac{1}{10} \frac{(J + 1)(J + 2)}{(2J + 3)} \left| \langle \nu J | \gamma | \nu' J + 2 \rangle \right|^2 \tag{2.9e}
\]

\[
\sum_{m,m} \left| \langle \nu J^m | \alpha_{yz} | \nu' J, m \rangle \right|^2 = \frac{J(J + 1)(2J + 1)}{15(2J + 3)(2J - 1)} \left| \langle \nu J | \gamma | \nu' J \rangle \right|^2 \tag{2.9f}
\]

for scattered light perpendicularly polarized to the polarization of the incident probe laser. \( \alpha \) is the mean polarizability while \( \gamma \) is called the polarizability anisotropy. Their expressions are as follows.
\[ \alpha = \frac{1}{3} (\alpha_\parallel + 2\alpha_\perp) \]  
\[ \gamma = (\alpha_\parallel - 2\alpha_\perp) \]

(2.10a)  
(2.10b)

The \( J' = J - 2 \) terms correspond to the anti-Stokes (O branch), \( J' = J + 2 \) terms correspond to the Stokes (S branch) and \( J' = J \) terms correspond to the rotational Q branch transitions.

The factors involving the rotational quantum number \( J \), such as the term \( \frac{J(J + 1)(2J + 1)}{(2J + 3)(2J - 1)} \) for the Q branch signals is written in abbreviated form as \( S(J) \), termed line intensity factors and \( \frac{S(J)}{2J + 1} \), termed Placzek-Teller factors\(^{41} \). Under our experimental conditions, the photon flux of \( Z \) polarized incident light Raman scattered in the \( X \) direction is given by

\[ J_\perp = \frac{16\pi^4 v^3}{hc^4} I_0 \frac{N_{v,J}}{2J + 1} \left\{ \sum_{m,m'} \left| \langle vJm | \alpha_{yz} | v'J'm' \rangle \right|^2 + \sum_{m,m'} \left| \langle vJm | \alpha_{zz} | v'J'm' \rangle \right|^2 \right\} \]

(2.11)

For \( \Delta J = 0 \) Q branch signals, the flux is

\[ J_\parallel = \frac{16\pi^4 v^3}{hc^4} I_0 \frac{N_{v,J}}{2J + 1} \left\{ (2J + 1) \left| \langle vJ | \alpha | v'J \rangle \right|^2 + \frac{7}{45} \frac{J(J + 1)(2J + 1)}{(2J + 3)(2J - 1)} \left| \langle vJ | \gamma | v'J \rangle \right|^2 \right\} \]

(2.12a)

while for \( \Delta J = 2 \) S branch signals, it becomes
\[ J_s = \frac{16\pi^4 \nu^3}{hc^4} I_0 N_v J \left\{ \frac{7}{30} \frac{(J + 1)(J + 2)}{(2J + 3)} \left| \langle v J \| \gamma \| v' J + 2 \rangle \right|^2 \right\} \] (2.12b)

Since Q branch peaks have small J splitting, we can consider them to fall on the same frequency and write

\[ J_q(v) = \sum_j \frac{16\pi^4 \nu^3}{hc^4} I_0 \cdot N_v \cdot f(v, J) \left\{ \left| \langle v J \| \alpha \| v' J \rangle \right|^2 + \frac{7}{45} \frac{J(J + 1)}{(2J + 3)(2J - 1)} \left| \langle v J \| \gamma \| v' J \rangle \right|^2 \right\} \] (2.13)

where \( N_v \) is the total population in vibrational level \( v \) and \( f(v, J) \) is the fraction of number of molecules in rotational state \( J \). It is this quantity \( J_q(v) \), that is measured by the CCD camera in the laboratory for various \( v \)'s, from which we infer the vibrational population distribution. Since the rotational distribution within a vibrational level is at thermal equilibrium, if we know the vibrational polarizability matrix elements and the energy levels of the rotational levels, we can calculate the \( v \) dependence of the Raman cross sections for \( J_q(v) \) for all temperatures. Figure 5 shows such \( v \) dependence in \( N_2 \), \( O_2 \) and \( H_2 \) at 300 K.

For evaluation of the vibrational matrix elements, we expand the polarizability about the equilibrium internuclear distance, \( r_e \) of the diatomic molecule.
**Figure 5.** Raman cross section ratios of the $Q$ branch $v, J \rightarrow v+1, J$ transition (due to vibrational matrix elements) at 300 K divided by the scaling factor $v+1$. Solid line represents oxygen, the filled circles hydrogen and the open circles nitrogen.
\[
\alpha(r) = \sum_i \alpha_i (r - r_c) \tag{2.14a}
\]
\[
\gamma(r) = \sum_i \gamma_i (r - r_c) \tag{2.14b}
\]

where \( \alpha_i \) and \( \gamma_i \) are constants. More specifically, \( \alpha_i = \left( \frac{\partial \alpha(r)}{\partial r} \right)_{r=r_c} \) and likewise for \( \gamma_i \).

If we only consider the first two terms in these expansions, they become

\[
\alpha(r) = \alpha_0 + \alpha_1 (r - r_c) \tag{2.15a}
\]
\[
\gamma(r) = \gamma_0 + \gamma_1 (r - r_c) \tag{2.15b}
\]

In the rigid rotor approximation where the “centrifugal potential” term in the radial Schrödinger equation

\[
\frac{\hbar^2}{2\mu r^2} \left[ \frac{d}{dr} \left( r^2 \left( \frac{d}{dr} \right) \right) \right] + J(J+1) \mid v, J \rangle = \mid E - V(r) \rangle \mid v, J \rangle \tag{2.16}
\]

is considered to be constant ( \( \frac{J(J+1)\hbar^2}{2\mu r_{\text{c}}^2} = \frac{J(J+1)\hbar^2}{2\mu r_{\text{c}}^2} \) ), the calculated vibrational wavefunctions have no \( J \) dependence. The vibrational matrix elements thus can be expressed in terms of the vibrational quantum number only.

\[
\mid \langle v | \alpha | v' \rangle \mid = \mid \langle v | \alpha_0 + \alpha_1 (r - r_c) | v' \rangle \mid \tag{2.17a}
\]
The first term on the right hand side of the equation \( \| \langle v | \alpha | v' \rangle \| = \delta_{v,v'} \) and therefore only contributes to a \( \Delta v=0 \) pure rotational transition. For harmonic oscillator wavefunctions the second term has a selection rule of \( \Delta v = \pm 1 \) and they can be written as

\[
\| \langle v | \alpha | v' \rangle \|^2 = \alpha_i^2 (v + 1) \left( \frac{h}{8\pi^2 c \mu \tilde{v}} \right) \Delta v = 1
\]

\[
\| \langle v | \alpha | v' \rangle \|^2 = \alpha_i^2 v \left( \frac{h}{8\pi^2 c \mu \tilde{v}} \right) \Delta v = -1
\]

where \( \mu \) is the reduced mass and \( \tilde{v} \) is the frequency of the vibrational transition which is constant for harmonic oscillators.

Thus, for Raman scattering accompanying vibrational transitions, the scattered light intensity is proportional to \( v+1 \) for the Stokes band ( \( v \rightarrow v+1 \) ) and \( v \) for the anti-Stokes band ( \( v \rightarrow v-1 \) ). For our measurements, we probe the vibrational \( Q \) branch ( \( v, J \rightarrow v+1, J \) ) transition to obtain the population in vibrational level \( v \).

Since the internuclear potential and the resulting vibrational wavefunctions of the diatomic molecule are actually not harmonic\(^{42} \), the simple \( v+1 \) dependence of the line intensity on vibrational quantum number \( v \) is not an accurate description and anharmonicities must be taken into account\(^{43} \). Moreover, since the diatomic molecule is actually not a rigid rotor, the rotational angular momentum of the molecule contributes a
centrifugal term, \( \frac{J(J+1)\hbar^2}{2\mu r^2} \) to the internuclear potential, so the interaction between rotation and vibration (Coriolis coupling) also affects the values of the polarizability matrix elements. If we separate the effect of rotation-vibration coupling from the effects of anharmonicity, we can write

\[
\left| \langle vJ | \alpha, \gamma | v'J' \rangle \right|^2 = F_{vv'}^{\alpha,\gamma}(J) \left| \langle v | \alpha, \gamma | v' \rangle \right|^2
\]  

(2.19)

where \( F_{vv'}^{\alpha,\gamma}(J) \) is called the Herman-Wallis factor \( n \) which represents the effect of interaction between rotation and vibration while \( \left| \langle v | \alpha, \gamma | v' \rangle \right| \) is the anharmonic oscillator term. Buldakov et al. have calculated the polarizability matrix elements of \( \text{N}_2 \) and \( \text{O}_2 \) for various vibrational transitions \( 36 \). For the low vibrational levels of concern in this study, the results using their Raman cross section values did not differ appreciably from analysis using the \( v+1 \) dependence of the line intensities on \( v \) as in the case of the harmonic oscillator. For hydrogen, which becomes highly anharmonic even at low vibrational levels, the \( v+1 \) dependence was not expected and accurate Raman cross sections in literature were searched for. The best values to date on polarizability matrix elements of hydrogen are from calculations performed by LeRoy and coworkers \( 38 \). Their values were used for obtaining vibrational level population from \( \Delta v=1 \) \( Q \) branch spectra as well as extracting the population in the \( v,J \) quantum state from the pure rotational \( S \) branch spectra where each \( v,J \rightarrow v,J+2 \) line can be resolved by the spectrometer grating. It is interesting to note that much to our surprise, figure 5 shows that the thermally averaged
(at 300 K) $v$ dependence of the $Q$ branch cross sections for hydrogen doesn’t differ much from that of nitrogen and oxygen. The cross sections for $\text{N}_2$ and $\text{O}_2$ in figure 5 were calculated using Buldakov’s formulae while $\text{H}_2$ used LeRoy’s polarizability values. Nonetheless, the cross sections from LeRoy were still used for data analysis in $\text{H}_2$. 
3.1 Introduction

Previous studies, both theoretical and experimental, of the N$_2$-N$_2$ V-V transfer process gave results that varied widely. Since the first study of N$_2$-N$_2$ V-V rates by Billing and Fisher using semi-classical trajectory calculations, the reported values of the rate coefficient for the simple reaction

\[ \text{N}_2(1) + \text{N}_2(0) \rightarrow \text{N}_2(0) + \text{N}_2(1) \]  

at 300K have varied by more than one order of magnitude in the range $9 \times 10^{-15} \text{cm}^3 \text{s}^{-1} \leq k_{1,0}^{0,1} \leq 1.5 \times 10^{-13} \text{cm}^3 \text{s}^{-1}$. The discrepancy between the experimental measurements is most likely attributed to the difficulty in obtaining comprehensive...
accurate data sets due, in turn, to the difficulty in preparing substantial vibrational excitation at room temperature.

Akishev et al. experimentally studied the dynamics of the V-V process in N$_2$ by exciting nitrogen with a pulsed discharge of $\sim$5 ms$^{46}$. The vibrational distribution was measured by spontaneous Raman scattering. However, as a result of the strong luminosity of the gas, the vibrational distribution could not be measured during the discharge lifetime. Valyanskii et al. used coherent anti-Stokes scattering (CARS) as the probe method to overcome this problem and study vibrationally excited nitrogen molecules under the conditions of glow discharge and also shortened the duration of the discharge pulse to $\sim$40 ns$^{47}$. Although the CARS spectrum showed that the rotational/translational temperature remained relatively constant at $\sim$320 K during and after the discharge, creating vibrational excitation by discharge methods carries the disadvantage that free electrons and atomic nitrogen may remain in the gas after the discharge pulse. These species can interact with the molecules by collision or through ion-electron/atom-atom recombination processes, affecting the vibrational distribution. It follows that in order to determine the rate constant of the elementary process of collisional vibration-to-vibration (V-V) exchange of energy, it is preferable to perform experiments under conditions in which this V-V exchange process dominates and only a small number of vibrational levels are involved in the exchange of vibrational energy.

Valyanskii et al. acknowledged the difficulties involved in describing V-V kinetics under the conditions of a recombining atomic molecular plasma and performed another experiment where the vibrational excitation was produced by what they term “biharmonic” excitation, more commonly referred to as stimulated Raman excitation$^{21}$. 
The determination of the V-V rate constants by this experiment was made difficult by the absence of kinetic data for the population of vibrational levels other than v=1. A more comprehensive set of data involving more vibrational levels is desired for better understanding of the VV kinetics. Another factor subject to uncertainty in the extraction of VV rates in this experiment was the effect of mass diffusion due to the uncertainty in the laser “pumped” excitation volume. The diameters of the pump beam (second harmonic of the Nd:YAG laser) and Stokes beam (from dye laser) were measured and assumed to be identical to that of the pumped region, while no measurement of the excitation volume itself and/or the diffusion kinetics was made.

In the present experiments, as mentioned in Chapter 2, Raman pumping of N\textsubscript{2} v=1 was achieved similar to the Valyanskii’s “biharmonic” excitation but using stimulated Raman scattering of the Nd:YAG second harmonic by high pressure N\textsubscript{2} molecules (instead of a dye laser) to produce the Stokes frequency at 607 nm. Population in v=1 is transferred to higher vibrational levels by collisional vibration-to-vibration (V-V) energy transfer processes.

\[
N_2(v = 1) + N_2(v = 1) \rightarrow N_2(v = 2) + N_2(v = 0) \tag{3.2a}
\]

\[
N_2(v = 2) + N_2(v = 1) \rightarrow N_2(v = 3) + N_2(v = 0) \tag{3.2b}
\]

\[
N_2(v) + N_2(v = 1) \rightarrow N_2(v + 1) + N_2(v = 0) \tag{3.2c}
\]

The rate of rise in the population of higher vibrational levels (and the fall of v=1) depends on the rate of these V-V reactions, and their rates were studied by monitoring the time dependent population of the vibrational levels of interest (0 ≤ v ≤ 6). “Spontaneous”
Raman scattering from a second Nd:YAG “probe” laser at 532 nm, delayed in time with respect to the pump laser was collected as mentioned in Chapter 2. The time delay between the pump and probe laser was varied from 150 ns to 15-20 µs depending on the V-V rates. As noted earlier, spectra at a delay time shorter than 150 ns could not be obtained due to interference of the Raman signal from stray room scattering of the pump beam entering the spectrometer.

3.2 Extracting Vibrational Population and Experimental Conditions from Raman Spectra

Figure 6 shows the Raman spectrum of pure N\textsubscript{2} at a pressure of 760 Torr and temperature of 300 K, at several time delays after the Raman excitation pulse, specifically at 150 ns, 1 µs, 5 µs, and 10 µs. Each peak corresponds to a $Q$ branch Stokes ($\Delta v=1$) vibrational band with the rightmost peak representing the $N_2(v = 0, J) \rightarrow N_2(v =1,J)$ transition which is proportional to the fractional population of N\textsubscript{2} in v=0. The rotational structure of the $Q$ branch could not be resolved by the spectrometer. At a short time delay of 150 ns, we can see that about one third of the nitrogen molecules in the ground vibrational level have been pumped to v=1 by the Raman excitation pulse (if we assume the simple scaling factor $v+1$ for the Raman cross section of the $Q$ branch $N_2(v,J) \rightarrow N_2(v+1,J)$ $\Delta v=1$ spectrum, the cross section for $v=1$ is twice that of $v=0$). A small signal corresponding to $v=2$ produced by the collisional reaction,
\[ N_2(v = 1) + N_2(v = 1) \rightarrow N_2(v = 2) + N_2(v = 0) \] (3.3)

is also observed. At \( t=1 \) \( \mu \)s, population in \( v=2 \) has further increased while a small population in \( v=3 \) can be detected, produced by subsequent V-V processes. These processes should lead to a decrease in \( v=1 \) population while increasing the population in \( v=0 \) and other vibrational levels, and this is exactly what is observed at \( t=1 \) \( \mu \)s. At \( t=5 \) \( \mu \)s, population in \( v=4 \) and \( v=5 \) start to show up while that of \( v=1 \) has further decreased. At \( t=10 \) \( \mu \)s, an appreciable amount of vibrationally excited molecules have diffused out of the volume being probed by the probe laser. Pumping of higher vibrational levels by collisional excitation is more evident in figure 7, where the intensity axis is magnified to reveal small but measurable population in those higher levels. Here, we can see that there is also quite a small population in \( v=3 \) at \( t=150 \) ns (upper panel). At \( t=8 \) \( \mu \)s (lower panel), vibrational levels up to at least \( v=6 \) can now be seen to have been populated by V-V transfer.

Raman signal from the vibrational levels must now be converted to their corresponding population which is proportional to signal intensity. Except in a few cases, fluctuations in the probe laser beam intensity were not monitored. As a result, the intensity scale in each spectrum could not be normalized to an absolute scale. The relative intensity of two peaks corresponding to the same vibrational level in different spectra (corresponding to different time delays) cannot be compared directly. However, the relative intensities of peaks, and therefore the fractional population corresponding to different vibrational transitions in the same spectra can be directly compared to each other since they are collected from the same laser pulse probing the same space at the same time.
Figure 6. Spontaneous Raman signal of Raman pumped $\text{N}_2$ at 150 ns, 1 µs, 5 µs, and 10 µs after Raman pumping.
Figure 7. A blow up of the $\text{N}_2$ Raman spectrum at $t=150$ ns (top) and $t=8$ $\mu$s (bottom).
The population of a vibrational level at time $t$ is extracted by comparing its signal intensity to those from other levels in the same spectrum.

Unless the translational/rotational temperature of the sample probe region changes (from its original value of 300 K) during our experiment (150 ns – 10 $\mu$s), the sample’s total number density should remain constant. The total number density, $N$ is the sum of the vibrational level populations,

$$N = \sum n(v,t) \quad (3.4)$$

where and $N = 2.4 \times 10^{16}$ cm$^{-3}$ in a gas sample at 760 Torr and 300 K.

The intensity of each peak in a spectrum divided by its Raman cross section should be proportional to the number density in vibrational level $v$. We saw from Chapter 2 that for the low $N_2$ vibrational levels ($v \leq 6$) being probed in this study, assumption of Raman cross sections as simply being proportional to $v+1$ (as for a harmonic oscillator) should be sufficient. Since the Raman cross section of a $\Delta v = 1$ Raman transition is proportional to $v+1$, we can write,

$$n(v,t) = c \frac{I(v,t)}{v+1} \quad (3.5a)$$

$$\sum_v c \frac{I(v,t)}{v+1} = N \quad (3.5b)$$
$c$ in the above equations is the proportionality constant. Thus, the absolute number density of each vibrational level at time $t$ can be obtained. The possibility of obtaining absolute densities is the reason we chose spontaneous Raman spectroscopy as our probe method over LIF despite its low sensitivity.

While not directly relevant to this work, it is interesting to note that the observed $\sim 30\%$ (37% after spectral analysis) fractional population in $v=1$ directly after SRS pump pulse exceeds the population in any one rotational sublevel (which peaks at $\sim 10\%$ for $J=10$ in $\text{N}_2$ at ground level, $v=0$). This implies that the population is moved from multiple rotational levels simultaneously. This, as described in more detail by Diskin\textsuperscript{22}, occurs in part because of the relatively broad spectral linewidths ($\sim 0.5 \text{ cm}^{-1}$) of the Stokes output from the Raman cell. The Stokes bandwidth covers 2-3 rotational levels. However, even if the Raman transition reached complete saturation and half the population in the three rotational levels ($J=9,10,11$) were excited to $v=1$, that would account for a fractional population of only $\sim 15\%$ in $v=1$. The rest of the population in $v=1$ comes from the rapid rotational “refilling” of the rotational distribution which occurs during the duration of the pump beam pulse. The molecules in other rotational levels quickly “refill” the population depleted by Raman pumping in $v=0,J=10$ by collisions while those excited to $v=1,J=10$ are quickly transferred “out” by collisions to a different rotational level in $v=1$. These processes maintain the population difference between the two states and enable further pumping of population into $v=1$ by the laser.

$$N_2(v=0,J=10) + h\omega_{\text{pump}} + h\omega_{\text{Stokes}} \rightarrow N_2(v=1,J=10) + 2h\omega_{\text{Stokes}}$$ \hspace{1cm} (3.6a)  

$$N_2(v=0,J \neq 10) + N_2 \rightarrow N_2(v=0,J=10) + N_2$$ \hspace{1cm} (3.6b)
\[ \text{N}_2(v = 1, J = 10) + \text{N}_2 \rightarrow \text{N}_2(v = 1, J \neq 10) + \text{N}_2 \]  

(3.6c)

The rate constant for the last reaction at 300 K and 760 Torr has been experimentally measured to be \(\sim 10^{10} \text{ s}^{-1}\), meaning collisional relaxation out of the \(\text{N}_2\) \(v=1, J=10\) state occurs in about \(\tau=100 \text{ ps}\), far less than the laser pulse duration of \(\sim 20 \text{ ns}^{32}\). Rotational relaxation rate in the ground vibrational level is expected to be on a similar timescale, and therefore the large fractional population observed in \(v=1\) after the Raman pulse can be accounted for by “rotational refilling”. Also, the short rotational relaxation time enables us to assume that the rotational distribution is at thermal equilibrium throughout the experiment, both during and after the laser pulse. The high collision rate also ensures that the rotational energy is in equilibrium with kinetic energy.

The measured value of fractional population in \(v=1\), \(f_{\text{meas}}(v = 1) = 0.37\) also confirms that the Raman pump beam has a bandwidth wide enough to pump at least two rotational levels. Since rotational levels with odd/even \(J\) values have different nuclear spin, rotational transfer between odd \(J \leftrightarrow\) even \(J\) does not occur on the timescale as fast as the laser pulse. Resonant VV processes which can populate odd \(J\) molecules in \(v=1\) are also not as fast as the laser pulse duration\(^{45}\). In nitrogen 2/3 of the molecules have even \(J\) values at 300 K. Even if these molecules were pumped to saturation, that would lead to \(v=1\) fractional population of only 33%. Pumping of odd \(J\) molecules is necessary to achieve \(f(v=1)\) higher than 33%. It is not certain if the odd/even \(J\) ratio in \(v=1\) is in its equilibrium value immediately after the pump laser pulse.

Figure 8 shows the horizontal (\(X\)) and vertical (\(Z\)) spatial profile of the fractional population of \(\text{N}_2\) \(v=1\) at \(t=150 \text{ ns}\). The results suggest that the pump beam has an
elliptical shape that has $1/e^2$ radius (where the intensity falls to $1/e^2$ its value at center) of 70 $\mu$m in one direction ($Z$) and 90 $\mu$m in another ($X$).

Figure 9 shows the decay of total vibrational quanta, $\sum_{v=1}^{v} N(v,t)$, during the experiment along with the expected loss of vibrational quanta from the probe region through mass diffusion. In calculating the expected loss of vibrational quanta, the initially Raman pumped region was assumed to have a spherically symmetric spatial distribution with $1/e^2$ radius of 70 $\mu$m. From the figure, we can see that this assumption predicts the diffusion behavior rather well, both at 760 Torr and 300 Torr, and actually better than the elliptical pumped region model. Therefore, in the next section, we take the pumped region to initially have a spherical distribution of $1/e^2$ radius equal to 70 $\mu$m in our numerical modeling. We will further discuss the validity of our assumptions on the volume of the Raman pumped region later.

In all of our analysis that proceeds, we assume the experimental conditions to be quite ideal. The size of the focused probe beam is infinitesimally small compared to the pump beam size. The waists of the two beams are uniform along the segment of laser travel being imaged onto the detector. The Raman pumped region has a spherically Gaussian radial profile in the plane perpendicular to the beam propagation axis. These assumptions are likely to be unrealistic. We must examine if taking into account these non-ideal conditions changes the outcome of our VV rates which are determined from spectral measurements assuming the ideal conditions mentioned above.
Figure 8. Spatial distribution of the fractional population of $N_2 \; v=1$ in the $z$ direction (top) and the $x$ direction (bottom). The filled circles indicate experimental data while the solid line represents a Gaussian fit. The empty circles are predictions of profiles that would be measured for a wider spatial width for the probe compared to the pump. The bold line is what the actual profile of $v=1$ would be under such conditions. The details are mentioned in the text.
Figure 9. Decay of total vibrational quanta initially produced by Raman pumping at 760 Torr (top) and 300 Torr (bottom). The closed circles are experimental data while the solid line is the predicted decay from diffusion of excited molecules out of the probe region. Dashed line in the lower panel is predicted diffusion of an elliptically shaped pumped region.
First, let’s see if movement of the pump lens results in translation of the entire probe segment.

Figure 8 shows the horizontal (X) and vertical (Z) spatial profile of the fractional population of \(N_2\) \(v=1\) at \(t=150\) ns, measured by moving the lens which focuses the pump beam onto the probe region in increments of \(10\ \mu m\). The focusing lens for the pump laser beam was mounted on a translational stage and moved horizontally and vertically to achieve the translation of the pump beam relative to the probe beam and determine the convolution of the two beams. From simple geometrical optics, moving the pump beam focusing lens position by a certain distance in the \(X-Z\) plane causes the lens focal point position to shift by the same amount of distance. Since the pump beam is parallel to the lens axis when it falls on the lens, the position of its focus will reflect the translation of the lens. The probe beam traveling path remains fixed, and this brings about a lateral movement of the Raman pumped area relative to the area being probed by the probe laser. The focal length of the pump laser focusing lens is \(300\) mm while the length of the area being imaged onto the CCD camera is \(\sim 1\) cm. This means that the farthest point from the focus that contributes to the signal is \(5\) mm from the focal point. Once again from geometrical optics, while moving the lens by \(10\ \mu m\) would move the focal point also by \(10\ \mu m\), the points \(5\) mm away from focus would be moved by \(\frac{(300\ \text{mm} \pm 5\ \text{mm})}{300\ \text{mm}} \times 10\ \mu m = 10 \pm 0.2\ \mu m\) which is within \(2\%\) of the distance moved by the focal point. Therefore, we can basically treat the whole pumped area to have moved by \(10\ \mu m\) or the same distance as that of focal lens translation.
Another assumption we make is the uniform profile along the laser propagation direction despite the fact that the pump and probe beams are focused beams with waist sizes that vary with their distance from the focal lens. However, collecting spectra by integrating only the center segment of ±1 mm from the focal point instead of the whole pumped image segment of ~1 cm did not produce a noticeable change in the fraction of molecules pumped to v=1. Diskin observed similar results from earlier work\(^\text{22}\). Therefore, we concluded that the fractional population in v=1 is uniform after Raman pumping along the laser propagation axis (Y in conjunction with the notation given in Chapter 2. We note that our coordinate system differs from the conventional one where the Z axis is chosen as the laser propagation axis).

The confocal parameter, \(b\), which is a measure of the length of the focused region\(^\text{48}\), is ~8 mm beam if we assume a \(1/e^2\) radius of \(\omega_0 = 70 \mu m\) at the focus and \(\omega = 5 \text{ mm}\) before focusing.

\[
\omega^2(z) = \omega_0^2 \left[ 1 + \left( \frac{z = 300 \text{ mm}}{z_0} \right) \right] \approx 5 \text{ mm}
\]

\[z_0 \approx 4 \text{ mm}, \quad b = 2z_0 \approx 8 \text{ mm}\]  

(3.7)

From Chapter 2, this corresponds to about the length of image, and our assumptions seem reasonable. But the same analysis for our probe beam assumed to have \(\omega_0 \sim 8 \mu m\) gave \(b\) of only ~1.5 mm and \(\omega \sim 50 \mu m\) at the edges of the image. However, as stated above, taking only the portion of the image corresponding to ~ ± \(z_0\) did not change the outcome. This might suggest that the probe beam confocal parameter is actually longer than 1.5
mm due to a larger focused beam size that is perhaps comparable to that of the pump beam. In our work, we continue with the assumption of uniform profile along the Y axis (at least in the segment from which signals are collected) for both the pump and probe beams.

Now let’s check the size of the focused pump and probe beams and its effect on the measured spectrum. The effect of the dimension of the spectrometer slit width should also be considered. Stimulated Raman scattering involves two laser beams both of high intensity at the pump and Stokes frequencies. If a laser beam profile is Gaussian, then we can write as,

\[
I(x,z) = \frac{2P}{\pi \sigma_x \sigma_z} \exp \left[ -2 \left( \frac{x^2}{\sigma_x^2} + \frac{z^2}{\sigma_z^2} \right) \right]
\]

where \( \sigma_{x,z}(y) = \sigma_{x,z} \) for a uniform profile along the Y direction. \( P \) is the laser power, \( P = \iint I(x,z) dx dz \) and \( \sigma_x(\sigma_z) \) is the position along the X(Z) axis where the laser intensity decreases to \( 1/e^2 \) of the intensity at \( x=z=0 \).

Assuming \( \sigma_x = \sigma_z = \sigma \) for simplicity,

\[
I = \frac{2P}{\pi \sigma^2} \exp \left[ -2 \frac{x^2 + z^2}{\sigma^2} \right]
\]

(3.9)
The Raman pumping rate is proportional to the product of the pump and Stokes laser beam intensities, $I_L I_S$.

$$I_L \cdot I_S = \frac{2P_L}{\pi \sigma_L^2} \exp \left[ -\frac{x^2 + z^2}{\sigma_L^2} \right] \left( \frac{2P_S}{\pi \sigma_S^2} \right) \exp \left[ -\frac{x^2 + z^2}{\sigma_S^2} \right]$$

$$= \frac{2 \cdot (2P_L P_S)}{\pi^2 \sigma_L^2 \sigma_S^2} \exp \left[ -2 \left( \frac{\sigma_L^2 + \sigma_S^2}{\sigma_L \cdot \sigma_S} \cdot (x^2 + z^2) \right) \right]$$

which we can write as

$$I_L I_S = I_1 = \frac{2P_1}{\pi \sigma_1^2} \exp \left[ -2 \frac{x^2 + z^2}{\sigma_1^2} \right]$$

where, $P_1 = \frac{(2P_L P_S)}{\pi (\sigma_L^2 + \sigma_S^2)}$ and $\sigma_1 = \frac{\sigma_L \cdot \sigma_S}{\sqrt{\sigma_L^2 + \sigma_S^2}}$.

As will be shown later, if the fraction of Raman pumped $v=1$ molecules is small, i.e. $f(v=1) \ll f(v=0)$, then the spatial distribution of $v=1$ population will follow that of the pump beam intensity, $I_1 = I_L I_S$ since $\frac{df(v=1)}{dt} \propto I_L I_S$.

$$f_{v=1}(x,z) = f_{v=1}(x=z=0) \cdot \exp \left[ -2 \frac{x^2 + z^2}{\sigma_1^2} \right]$$

(3.11)
If the pump beam is moved by a distance of \( x_0 \) along the x axis, the profile would be

\[
I(x,z) = \frac{2P}{\pi\sigma^2_1} \exp\left[ -2\frac{(x-x_0)^2 + z^2}{\sigma^2_1} \right] \tag{3.12}
\]

\[
f_{v=-1}(x,z) = f_{v=-1}(x = 0) \cdot \exp\left[ -2\frac{(x-x_0)^2 + z^2}{\sigma^2_1} \right] \tag{3.13}
\]

The \( v=1 \) profile Raman pumped by an elliptically shaped beam would be,

\[
f_{v=+1}(x,z) = f_{v=+1}(x = 0) \cdot \exp\left[ -2\frac{(x-x_0)^2 + z^2}{\sigma^2_1} \right] \tag{3.14}
\]

Moving the pump beam along the Z axis would be analogous and straightforward.

The probe laser is also assumed to have a Gaussian profile where

\[
I_{\text{probe}} = \frac{2P_{\text{probe}}}{\pi\sigma^2_2} \exp\left[ -2\frac{x^2 + z^2}{\sigma^2_2} \right] \tag{3.15}
\]

The measured fractional population for \( v=1 \) would be spatial average of the signal that enters the spectrometer slit opening, weighted by the probe laser intensity.

\[
f_{\text{meas}}(v=1) = \left\langle f_{v=1}(x,z) \right\rangle = \frac{\iint f_{v=1}(x,z) \cdot I_{\text{probe}} \, dx \, dz}{\iint I_{\text{probe}} \, dx \, dz} \tag{3.16a}
\]
\[
\begin{align*}
    f_{\text{meas}}(v = 1) = & \int \int f_{x=1}(x = z = 0) \cdot \frac{2P_{\text{probe}}}{\pi \sigma_z^2} \cdot \exp \left[ -2 \frac{(x-x_0)^2 + z^2}{\sigma_1^2} \right] \\
    & \cdot \exp \left[ -2 \frac{x^2 + z^2}{\sigma_z^2} \right] \, dx \, dz
\
    (3.16b)
\end{align*}
\]

We must now consider the integration domain in the X and Z directions. The X direction is parallel to the Raman signal collection axis. All Raman scattering signal coming from in front of or behind the lens focal point in the X direction will “bloom” at image focal plane unless the scattering is from within the vicinity of the focus called the “depth of field” of the imaging system\(^49\). The depth of field is defined from Levi\(^50\) to be

\[
\delta a = \frac{2 \lambda F^2 a^2}{f^2}
\]

(3.17)

where \(a\) is the nominal distance of the object from the lens, \(f\) is the focal length, \(F\) is the focal length:lens diameter ratio, and \(\lambda\) is the laser wavelength. Since \(a=f\), \(\lambda \approx 600\) nm and \(F=4\), the depth of field is less than 20 \(\mu\)m in our system, which seems quite shallow. Although this seems bad, the slit width is 100 \(\mu\)m, so it is able to collect spots equal to or less than 50 \(\mu\)m in diameter at the position of the slit. From simple geometric optics, a point \(\pm 40\) \(\mu\)m off the lens focal plane \((a=\pm 40\) \(\mu\)m) becomes a spot \(\approx 20\) \(\mu\)m in diameter at the imaged plane, the plane of the spectrometer slit. So a Raman scattering signal from a focused laser with \(1/e^2\) radius of \(\omega_0 \leq 40\) \(\mu\)m will be completely collected by our
detection system although some resolution may be lost. Most of the signal along the X axis should be collected as long as the probe laser has a $1/e^2$ radius of $\omega_0 \leq 100 \mu m$. Since the $1/e^2$ radius of the probe laser should be less than 100 µm, we set the integration domain limits in the X direction as $\pm \infty$.

Meanwhile signal collection of scattered light from points along the Z axis is more directly limited by the width of the spectrometer slit opening. Signal from points imaged outside the slit opening will not be collected at all, and only scattering from within $\pm 50 \mu m$ from the focus will be collected. Consequently, $\pm 50 \mu m$ becomes the integration domain in the Z direction. As will be seen later, this finite slit width can cause the spatial profile measured by translation of the pump beam to “seem” elliptic despite actually being spherically symmetric.

In our assumption $\sigma_2 << \sigma_1$, and the measured population in v=1 simply becomes,

$$f_{\text{meas}}(v = 1) = f_{v=1}(x = z = 0) \exp \left[ -2 \frac{x_0^2}{\sigma_1^2} \right]$$ \hspace{1cm} (3.18a)

$$f_{\text{meas}}(v = 1) = f_{v=1}(x = -x_0, z = 0)$$ \hspace{1cm} (3.18b)

regardless of the slit width.

Another feature of the v=1 spatial distribution to consider is saturation of Raman pumping. A large fraction ($\sim 37\%$) of the molecules are pumped from v=0 to v=1. When such a high percentage of the molecules are pumped, saturation of the Raman transition, similar to saturation effects in absorption should be considered since stimulated Raman
scattering is also a resonant process. This means that the forward and backward reactions in

\[ N_2(v=0) + 2\hbar \nu_L + \hbar \nu_S \rightleftharpoons N_2(v=1) + \hbar \nu_L + 2\hbar \nu_S \]  

(3.19)

are equally likely to occur since the \( \nu_L \) and \( \nu_S \) photons are present in abundance. Although the Raman transitions occur for only a few number rotational states, since the rotational relaxation is fast and occurs in less than 1 ns, we can assume the rotational distribution in \( v=0 \) and \( v=1 \) to be in equilibrium during the 20 ns pulse. Since the V-V transition rates occur on a timescale of \( \mu \)s, population in higher vibrational levels such as \( v=2 \) are still low and \( f(v=0) + f(v=1) \) can be assumed to be constant and equal to 1 for the duration of the laser pulse. Since the rotational spacing, \( [B_v - \alpha_v(v + \frac{1}{2})] \) in \( v=0 \) and \( v=1 \) are within 1% of each other\(^5\), their rotational distribution can be considered as identical. For \( Q \) branch transitions, which involve rotational levels with the same \( J \), the population difference between the upper state and the lower state will reflect the population difference of the two vibrational levels. Therefore, we can treat the two vibrational levels as a simple two level system. The steady state pumping rate in a two level system is given by Zhang\(^5\).

\[
\frac{\partial n}{\partial t} + \frac{n - n_{eq}}{T_1} = \frac{1}{T_2} \left[ \left( \omega_v^2 - \omega_r^2 \right) / 2\omega_r \right]^2 \frac{1 - 2n}{32m\hbar\omega_0} \left( \frac{\partial \alpha}{\partial q} \right)^2 A_v^2 A_s^2
\]  

(3.20)
where \( n = f(v=1) \), and \( n_{eq} = 0 \) at room temperature. \( T_1 \) is population decay lifetime of \( v = 1 \) (V-T relaxation time), while \( T_2 \) is the dephasing time of molecular vibrations in phase with electromagnetic oscillations of the two laser beams. For nitrogen and oxygen \( T_2 \) is taken as the collision lifetime of the molecules. \( \omega_0 \) is the natural frequency of the molecular vibration and \( \omega_v = \omega_L - \omega_S \) is the difference in frequency between the pump beam and the Stokes beam. \( m_r \) is the reduced mass of the molecule and \( \frac{\partial \alpha}{\partial q} \) is the polarizability derivative with respect to the vibrational coordinate. \( A_L \) and \( A_S \) are the electric field amplitude of the pump and Stokes beam respectively. They are connected to the intensity by

\[
I_i = \left( \frac{c}{8\pi} \right) A_i^2, \quad i = L, S
\]  

(3.21)

Since \( T_1 \) is long and vibrational relaxation is negligible during the laser pulse, we can write,

\[
\frac{\partial n}{\partial t} = k (1 - 2n) I_L I_S  
\]

(3.22a)

\[
k = \frac{1/T_2}{(1/T_1)^2 - \left[ (\omega_v^2 - \omega_0^2)/2\omega_0 \right]^2} \frac{(8\pi/c)^2}{32m_r\hbar\omega_0} \left( \frac{\partial \alpha}{\partial q} \right)^2.
\]

(3.22b)

Solving for \( n \) gives
\[ n = \frac{1}{2}(1 - \exp[-2ki_LI_s]) \]  

(3.23)

We modeled the pump beam as, 

\[ I_LI_s = \frac{2P_1}{\pi\sigma_1^2}\exp\left[-2\frac{x^2 + z^2}{\sigma_1^2}\right]. \]

At low intensities \((2ki_LI_s \ll 1)\), we can expand the exponential so that

\[ n = f_{v=1}(x,z) = \frac{1}{2}(1 - \exp[-2ki_LI_s]) = ki_LI_s = k\frac{2P_1}{\pi\sigma_1^2}\exp\left[-2\frac{x^2 + z^2}{\sigma_1^2}\right] \]

(3.24)

and the spatial distribution of \(v=1\) population will follow the Gaussian pattern of the pump beam.

However, since,

\[ f_{\text{meas.}}(v = 1) = \langle f_{v=1}(x,z) \rangle = 0.37 \rightarrow \langle \exp[-2ki_LI_s] \rangle = 0.26 \ll 1 \]

(3.25)

the distribution will deviate from a Gaussian profile, due to partial saturation of the Raman transition. We tried to replicate the measured spatial profile in figure 8 under conditions where the probe beam radius is finite and larger than that of the pump beam. We also took into account saturation effects and the finite slit width. We could replicate the observed profile using parameters \(\sigma_1 = 27 \ \mu m, \ \sigma_2 = 67 \ \mu m\) and \(\frac{4kP_1}{\pi\sigma_1^2} = 270\). The open circles in figure 8 represent the \(v=1\) signal spatial distribution profile predicted to be
observed by translation of the Raman pump beam. Note that they are wider in the $X$ direction than in the $Z$ direction despite assuming spherical distribution for both the pump and probe beams. This comes from saturation effects and the $1/e^2$ probe diameter being slightly larger than the finite slit width of the spectrometer. The bold line represents the actual radial $v=1$ spatial profile that would be needed to produce the signal profile represented by open circles. It resembles a uniform laser beam profile that has uniform intensity inside $40 \, \mu m$ and zero intensity outside. For $r \leq 40 \, \mu m$, the Raman pumping would have reached saturation and $f(v = 1) = 0.5$. Note that the initial population of $v=1$ on the laser “centerline”, $r \approx 0$ (bold line), needs to be higher than that displayed as the measured value (open circles) in order for the spatial average to replicate the experimental data.

Having said all this, we find in the next section that the predicted time evolution of the vibrational level populations is actually relatively indifferent to whether we assume the size of the probe beam to be infinitesimally small or finite and larger than that of the pump.

3.3 Comparison of experimental data to kinetic models

Time dependence of each vibrational level can be expressed by the master equation kinetic model$^{53}$. 
\[
\frac{dN_{i,v}}{dt} = \text{VV}_{i,v} + \text{VT}_{i,v} + \text{VE}_{i,v} + \text{SRD}_{i,v} + \text{PL}_{i,v} + D_i \nabla^2 N_{i,v}
\] (3.26a)

\[
\rho c_p \frac{dT}{dt} = \eta \nabla^2 T + \text{HVR}
\] (3.26b)

\[N_{i,v} = N_i f_{i,v}(x,y,z,t)\] is the number density of species \(i\) in vibrational level \(v\) and \(N_i\) is the total number density of species \(i\), and \(f_{i,v}(x,y,z,t)\) its time and space varying fractional population. \(D_i\) and \(\eta\) are the mass diffusion and heat conduction coefficients respectively. The diffusion coefficient is assumed to be independent of vibrational level. \(\rho\) and \(c_p\) are density and specific heat of the gas at constant pressure. \(\text{VV}_{i,v}\) represents the species and \(v\) dependent \(V-V\) energy transfer term, \(\text{VT}_{i,v}\) is the \(V-T\) relaxation term, \(\text{SRD}_{i,v}\) is the spontaneous radiative decay term, \(\text{VE}_{i,v}\) is the vibration-electronic coupling term, \(\text{PL}_{i,v}\) is the laser absorption term and \(\text{HVR}\) is the term describing gas heating by vibrational relaxation (both \(V-T\) and non resonant \(V-V\) processes). Flament gives explicit expressions for each term in the master equations. The two equations are primarily coupled through the strong temperature dependence of the \(V-T\) relaxation and \(V-V\) transfer rates as well as the temperature dependence of the laser absorption and spontaneous radiative decay cross sections.

In our experiment, nitrogen is the only species present, and at 300 K, its \(V-T\) rate coefficients are slower than the \(V-V\) rate coefficients by several orders of magnitude especially for \(v<7\) where they are predicted to be less than \(10^{-20}\text{ cm}^3\text{s}^{-1}\) by Billing\(^{45}\) as to the \(V-V\) rate coefficients on the order of \(10^{-14}\text{ cm}^3\text{s}^{-1}\). For our experimental conditions of \(P=760\text{ Torr}\) and number density, \(N\), equal to \(2.4 \times 10^{19}\text{ cm}^{-3}\), the \(V-T\) decay rate is
\( \sim 10^{-1} \text{s}^{-1} \). Therefore, the V-T rates \((VT_v)\) can be neglected on the probe timescale of our experiment (< 20 µs).

The lowest excited electronic state for nitrogen, \( A^3\Sigma_u^+ \), is energetically 50,000 cm\(^{-1}\) above the ground vibrational level in \( X^1\Sigma_g^+ \). This would require a vibrational excitation at \( v \sim 25 \) for V-E transfer processes to occur. At low vibrational energies of \( N_2 \) in the ground electronic state, coupling pathways to other electronic levels are not available and the V-E rates \((VE_v)\) can be ignored. Processes such as dissociation, ionization, dimerization, and recombination that follows dissociation and ionization are also similarly negligible under our experimental conditions.

Since the vibrational motion of homonuclear diatomic molecules does not absorb radiation, its emission is also forbidden and the spontaneous radiative decay term \((SRD_v)\) is also neglected (quadrupole and higher order transition moments will also be neglected here).

Stimulated Raman pumping process contributes to the laser absorption term \((PL_v)\) and is only present during the initial 20 ns pump laser pulse duration. It also involves only the transition between \( v=0 \) and \( v=1 \) and has no terms involving higher vibrational levels.

As in the previous section, we will assume a spatial profile of \( N_v \) to be cylindrical and Gaussian in the \( X-Z \) plane and uniform along the \( Y \) axis, that is

\[
N_v = N_v(x = z = 0) \exp \left[ -\frac{x^2 + z^2}{\sigma^2} \right] \quad (3.27)
\]
the value of $\nabla^2 N_v$ and the effects of diffusion will be maximum at the center ($x=z=0$).

We take $\sigma=70 \mu m$ and $D = 2 \times 10^{-5} m^2 s^{-1}$ for nitrogen at 760 Torr\textsuperscript{54}. The diffusion term at the center will be

\begin{equation}
DV^2 N_v = D \left( \frac{1}{r} \frac{\partial}{\partial r} \left[ r \frac{\partial}{\partial r} \right] \right) N_v \\
= 2 \times 10^{-5} m^2 s^{-1} \left[ -\frac{8}{(7 \times 10^{-5} m)^2} \right] N_v = 3.2 \times 10^4 s^{-1} N_v \tag{3.28}
\end{equation}

which is about an order of magnitude of smaller than the V-V rates but much larger than the V-T rates. Therefore the diffusion terms will not be neglected in the equation.

Since the $VT_v$ terms do not contribute significantly to changes in vibrational level population, their effect on temperature change can also be neglected. As for the effect of non resonant V-V processes on temperature, let’s consider the change in the population distribution of the vibrational levels brought about by V-V transfer. From our analysis above, the only processes that change vibrational level populations after Raman excitation are V-V transfer and mass diffusion. Mass diffusion does not change the temperature since the temperature profile remains homogenous at $T=300$ K throughout the sample even after Raman pumping. Therefore, only non resonant $VV_v$ terms with vibrational energy mismatch will contribute to temperature change of the gas sample.

The amount of vibrational energy converted to thermal energy can be described by

\begin{equation}
\Delta E_T = \sum_{v=2}^{\infty} (vE(v=1) - E(v)) \times N_v \tag{3.29}
\end{equation}
and $vE(v = 1) - E(v) > 0$ due to the anharmonicity of the vibrational levels. The maximum value of $\Delta E_T \approx 4\text{cm}^{-1}$ and occurs ~7 $\mu$s after Raman pumping. Since this energy is distributed among the three translation degrees of motion and two rotational degrees, the resultant temperature increase will be ~1 K. After 7 $\mu$s, the value of $\Delta E_T$ decreases due to mass diffusion of vibrationally excited molecules out of the probe region.

A temperature change of 1 K at room temperature has negligible effect on the value of the rate coefficients or the density of the gas. We conclude that gas heating and the increase in temperature that follows vibrational relaxation is minimal, and consider the gas to be at constant temperature during the entire experiment.

From figure 9, we see that the fraction of vibrational quanta that have diffused out of the probe volume

$$\Delta(N(v, t = 0) - \sum_{v \in 1} N(v, t)) = \frac{N_{\text{total}}}{N_{\text{total}}}$$

after 14 $\mu$s is about 30% of the initial vibrational quanta at 760 Torr. We can conclude from the figure that the decay of total vibrational quanta inside the probe volume during the first 15-20 $\mu$s is well accounted for by diffusion alone.

After omitting all equations and processes that make negligible contribution to our system under study, the rate of change of vibrational level populations after Raman excitation in equation 3.26 can be rewritten as
\[ \frac{dN_v}{dt} = VV_v + D \nabla^2 N_v \]  

(3.31)

The notation \( i \), is omitted since nitrogen is the only species present. The temperature stays constant at \( T=300 \) K.

We now turn our attention to the \( VV_v \) terms in the master equation (equation 3.31). They can be expressed in the following form.

\[ VV_v = \sum_{v'} \left[ k_{v+1,v}^{v',v'+1} N_{v+1} + k_{v-1,v}^{v',v'-1} N_{v-1} - \left( k_{v,v}^{v',v'+1} + k_{v,v+1}^{v',v'-1} \right) N_v \right] N_{v'} \]  

(3.32)

The term \( k_{v,v+1}^{v',v'+1} \) is the rate coefficient for the following reaction.

\[ \text{N}_2 (v) + \text{N}_2 (v') \xrightarrow{k_{v,v+1}^{v',v'+1}} \text{N}_2 (v+1) + \text{N}_2 (v'-1) \]  

(3.33)

\( k_{v,v+1}^{v',v'-1} \) and \( k_{v,v+1}^{v'-1,v} \) are related to each other by detailed balance,

\[ k_{v,v+1}^{v',v'-1} = k_{v+1,v}^{v'-1,v} \exp \left[ \frac{(E(v+1) - E(v)) - (E(v') - E(v'-1))}{kT} \right] \]  

(3.34)

The rate coefficients for transfer of two vibrational quanta

\[ \text{N}_2 (v) + \text{N}_2 (v') \xrightarrow{k_{v,v+2}^{v',v'-2}} \text{N}_2 (v+2) + \text{N}_2 (v'-2) \]  

(3.35)
are predicted to be on the order of \( \sim 10^{-24} \text{cm}^3 \text{s}^{-1} \) and have been neglected\(^{45}\). Since the system is thought to be at constant temperature (300 K) and pressure (760 Torr) throughout the experiment, the total number density is constant and \( N = 2.4 \times 10^{19} \text{cm}^{-3} \). So \( N_v = N \cdot f_v(x, y, z, t) \) and we can mention the vibrational population in terms of its mole fraction \( f_v(x, y, z, t) \) which we term as “fractional population”.

For the values of the rate coefficients, \( k_{v_v,v_v+1}^{v_v,v_v+1} \), five sets of theoretical \( \text{N}_2 \) V-V rate coefficients were used in the kinetic modeling calculations. Rate coefficients of Billing\(^{45}\) are obtained from three-dimensional semiclassical trajectory calculations where the change in the density of vibrational wavefunctions upon molecular collisions was calculated by solving the time dependent Schrödinger equation while treating the translational and rotational motions classically. For the intermolecular potential Billing used a potential energy surface which incorporates both short term repulsive interaction and long term attractive forces (both quadrupole quadrupole forces and dispersive forces). Bogdanov’s rates\(^{55}\) are obtained from three-dimensional quasiclassical trajectory calculations for two different potential energy surfaces and are presented as an analytic fit to the numerical data.

The FHO-FR (Forced Harmonic Oscillator – Free Rotor) V-V rate model of Admovich\(^{56}\) is a three-dimensional non-perturbative semiclassical model which considers realistic collision dynamics (non-collinear collisions of rotating molecules) and analytically solves both the classical equations of motion and the time dependent Schrödinger equation to predict analytic V-V and V-T transition probabilities. Essentially, it provides an analytic
solution of the inelastic scattering problem using the same semiclassical approach as developed by Billing for the repulsive part of the potential energy surface and will give the same results as Billing’s for systems where the V-V dynamics is mainly affected by the repulsive part of the potential. However, it is unsuitable for systems where the attractive well of the potential becomes important in V-V processes. The FHO-FR model has the advantages of both being analytic and not containing any adjustable parameters.

The analytic rate coefficients of Kirilov\textsuperscript{57,58} and those of Chauveau\textsuperscript{59}, which are based on the earlier work of Jeffers and Kelley\textsuperscript{60}, are obtained using the one-dimensional first order perturbation theory. The V-V and V-T rates predicted by such one-dimensional models always contain adjustable parameters such as “steric factors” and “potential parameter factors” needed to reconcile the predictions based on the simplified collision model used (i.e. collinear collisions of non-rotating molecules) with realistic collision dynamics. Therefore, predictive capability of such models is rather limited and the adjustable parameters are typically determined from the available experimental data. The three-dimensional models, which are primarily limited by the accuracy of the potential energy surface used, are considered to be superior to these one-dimensional theories. A further disadvantage of perturbation theory based models is that they can only be used for prediction of single quantum V-T and V-V processes at fairly low temperatures. However, these models have the advantage of relative simplicity and have therefore been widely used. There is no calculation of V-V rate coefficients based on fully quantum three-dimensional theory for N\textsubscript{2}-N\textsubscript{2} collisions, leaving the three-dimensional semiclassical approaches as most accurate.
Since Billing does not provide a full set of V-V rate coefficients in earlier published work, the rates have been recalculated for the same potential energy surface using a trajectory calculation code DIDIAV developed by Billing\textsuperscript{61}. In these calculations, V-V cross sections have been evaluated for 15 different values of the collision energy using a total of 15,000 trajectories, compared to 2000 trajectories used in the original calculations. The recalculated rate coefficients are typically somewhat higher than the originally published values by up to 30-50%.

Figure 10 shows the recalculated values of Billing’s V-V rate coefficients along with those originally published as well as the rate coefficients from the FHO-FR model. Notice the similarities between the FHO-FR rates and those of Billing’s original calculation. Although the values of Billing’s original calculation seem closer to those from the FHO-FR model than the recalculated values using more trajectories, we cannot use them in our master equation since the complete set of rates from the original calculation are not available. Figure 10 shows the values of several rate coefficients from each theoretical model. We can see that Kirilov’s rates, which have the highest rate coefficient values are approximately one order of magnitude faster than those of FHO-FR, the set with lowest values.

For all simulations, comparisons between experimental results and theory are done for all observed vibrational levels simultaneously, with a single set of theoretical rates employed.

Figure 11 shows the experimental and calculated values for the population of the vibrational levels $v=0$ and 1 as a function of time with respect to the pump pulse at 300 K and 760 Torr. Although predictions were obtained for all five sets of rate coefficients, we
Figure 10. V-V rate coefficients for the reaction, $N_2(v-1) + N_2(1) \rightarrow N_2(v) + N_2(0)$.

The filled circles are the FHO-FR rates, while the solid line indicates the originally published Billing’s rates. The open circles are for the recalculated Billing’s rates. As mentioned in text, they are 30-50% higher than the published values.
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<td>2.9</td>
<td>3.5×10^{-14}</td>
</tr>
</tbody>
</table>

**Table 1.** Calculated rate coefficients for the reaction $N_2(v-1) + N_2(l) \rightarrow N_2(v) + N_2(0)$ in units of cm$^3$/s at 300 K.
have, for clarity displayed only three. While the predictions of the FHO-FR model are seen to give the best overall agreement, it is also clear that the predictions derived using the rates of Billing, also agrees quite well with experiment, meaning that the repulsive part of the potential is the determining factor for V-V rates. While not plotted, it was also found that the predictions using the rates of Bogdanov also gave good agreement with experiment, which is not unexpected since it is also based on three-dimensional semiclassical trajectory theory. The rate coefficients from both one-dimensional models predict similar, significantly more rapid, temporal evolution than is observed experimentally, although only the results using Kirilov’s rates are presented. The same qualitative conclusions can be made from figure 12, which is identical to figure 11, except that the results for v=2 and 3 are now displayed. Note however, that in this case, the rise in excited level population is observed, as opposed to the decay. Similar to the data of figure 11, the predicted rate of V-V transfer is significantly higher for the simulations using the rate coefficients derived from the one dimensional model than any of the three dimensional models.

The rise in population of levels v=4-6 is presented in figure 13. While the signal to noise in the experimental data is somewhat low, it can be seen that simulations using both the FHO-FR and Billing’s rate coefficients are in reasonable, if not perfect agreement with the data. Again, the one-dimensional models predict vibrational level populations that rise too rapidly by approximately one order of magnitude. We conclude that rate coefficients derived from accurate, three-dimensional potential surfaces and which incorporate rotation and non-linear trajectories provide, not surprisingly, the best agreement with experimental data. We also note that for nitrogen, the dynamics of the
Figure 11. Time dependent population of v=0 (top) and v=1 (bottom) at 300 K and 760 Torr. Filled circles indicate experimental data with error bars corresponding to $2\sigma$. The bold line corresponds to computational simulation using rates by Kirilov, while the dotted lines use those by Billing. The solid line uses rates of FHO-FR.
Figure 12. Time dependent population of $v=2$ (top) and $v=3$ (bottom). Details are analogous to figure 11.
Figure 13. Time dependent population of \( v=4 \) (top) and \( v=5 \) and 6 (bottom). Details are analogous to figure 11. The filled squares in the bottom panel represent experimental data for \( v=6 \). For clarity, only theoretical predictions of the FHO-FR model are shown for \( v=5 \) and 6.
collision appear to be successfully captured by inclusion of the repulsive part of the potential only, and that the effects from the attractive part are minimal, demonstrated by the agreement of predictions using rates of the FHO-FR model with experimental data. Although one-dimensional model rates can be reconciled with experimental data by varying adjustable parameters such as steric factors and potential parameters, the predictive use of these models wherever the experimental data are not available becomes problematic.

As a further test of the consistency of both the experimental data and the theoretical rate coefficients, theory/data comparisons for pressures of 300 and 520 Torr were performed. Since the vibrational level population relaxation time by V-V processes is approximately inversely proportional to the pressure of the system (1/$\tau$ $\sim$ $k_{v,v+1}$ $N$ and $N$ $\propto$ $P$), the V-V relaxation time (timescale of the V-V dynamics) should slow down by a factor of 2 by changing the pressure from 760 Torr to 300 Torr. In all cases, the calculations utilize the same rate coefficients as employed for the 760 Torr case.

Figure 14 and figure 15 summarize the 520 Torr data, while figure 16 and figure 17 summarize the 300 Torr data. Due to relatively poor signal to noise ratio in the raw data, comparisons were only possible for vibrational levels v=0-3. Nonetheless, it can again be seen that the rate coefficients from the FHO-FR model agree best with the data, while the rates of Billing and Bogdanov also were found to agree quite well. As is the case for 760 Torr, the predictions derived using the rates of Kirilov and Chauveau appear to be too fast by approximately one order of magnitude.
Figure 18 shows the calculated time dependence of the vibrational level populations at 300 Torr assuming a spatial average over a Gaussian probe volume as mentioned in the previous section, where the $1/e^2$ radius of the pump and probe laser are $\sigma_1 = 27 \, \mu m$ and $\sigma_2 = 67 \, \mu m$ respectively. The actual $v=1$ profile follows the bold line in figure 8. The V-V rates used are from the FHO-FR model. The results are compared with the calculations using the same FHO-FR rates but with an infinitesimally thin probe laser volume and a Gaussian $v=1$ profile with $1/e^2$ radius of $\sigma_1 = 70 \, \mu m$. We can see from the figure that the different methods resulted in essentially no change in predicted level populations.

In conclusion, it is found that the three-dimensional FHO-FR model provides the best overall agreement with the entire data set, although other published three-dimensional models are also in reasonable agreement. The rate coefficients predicted by the one-dimensional models of Chauveau and Kirilov appear too fast by approximately one order of magnitude. Under our experimental conditions, kinetic modeling using a set of V-V rate coefficient values seems to give the same predictions for the time evolution of vibrational level populations regardless of our assumptions on the relative size of the pump and probe beams.
Figure 14. Time dependent population of v=0 (top) and v=1 (bottom) at 300 K and 520 Torr. The filled circles are data points while the solid line is predictions using FHO-FR model.
Figure 15. Time dependent population of $v=2$ (top) and $v=3$ (bottom) at 520 Torr and 300 K. Details are analogous to figure 14. Here the predictions of Billing (dotted line) are also shown.
Figure 16. Time dependent population of $v=0$ (top) and $v=1$ (bottom) at 300 K and 300 Torr. The rest of the details are analogous to figure 11.
Figure 17. Time dependent population of v=2 (top) and v=3 (bottom) at 300 Torr and 300 K. The details are analogous to figure 16.
Figure 18. Time dependent population of v=0 and 1 (top) and v=2 and 3 (bottom) at 300 K and 300 Torr. The solid line assumes infinitely narrow spatial profile for the probe laser while the dotted line assumes the spatial profile of the probe to be finite but larger than that of the pump laser. Both lines use the same FHO-FR rate coefficients. Details are mentioned in the text.
4.1 Introduction

As mentioned in Chapter 1, relaxation rates of $O_2$ vibrational energy have long been of interest in atmospheric chemistry due to their importance in the chemical reaction cycle of ozone in the upper atmosphere\(^{62}\). Previous experimental studies of $O_2$ vibrational relaxation focused on higher vibrational levels ($v \geq 8$)\(^{4,13}\) since these molecules can be photodissociated by radiation with wavelengths longer than 300 nm, which is abundantly present in the sunlight that reaches the earth’s stratosphere. Photodissociation of vibrationally excited $O_2$ molecules was proposed as a possible source of significant amounts of ozone in the atmosphere\(^{63}\).

\[
\begin{align*}
O_3(X^3\Sigma_g^-, v \gg 1) + h\nu & \rightarrow 2O & \quad (4.1a) \\
2O + 2O_3(X^3\Sigma_g^-, v=0) + 2M & \rightarrow 2O_3 + 2M & \quad (4.1b)
\end{align*}
\]
This process was viewed as a possible explanation for the “ozone deficit problem” in atmospheric chemistry, where current theoretical models underestimate the ozone concentration level in the atmosphere.

Wodtke and coworkers\textsuperscript{4} vibrationally excited O\textsubscript{2} molecules (19 \leq v \leq 28) by Stimulated Emission Pumping (SEP) and measured their relaxation rates at 300K and 450 K. Slanger and coworkers\textsuperscript{63} created vibrational excited oxygen (8 \leq v \leq 22) through photodissociation of O\textsubscript{3}. Smith and coworkers\textsuperscript{13} employed chemical reactions to produce vibrational levels 8 \leq v \leq 11. These experiments, along with other studies, established that the rate of collisional removal of vibrational energy should dominate over that of photodissociation by sunlight in the stratosphere. Thus production of significant amounts of ozone by photodissociation of vibrationally excited O\textsubscript{2} as a possible source of explanation for the “ozone deficit problem” became unlikely.

Recently, the relaxation of vibrational energy of O\textsubscript{2} at low vibrational levels has also gained interest because relaxation of O\textsubscript{2} (X^3\Sigma_g^-, v=1) by H\textsubscript{2}O molecules lead to H\textsubscript{2}O emission, which can be used to measure water vapor in the atmosphere\textsuperscript{64}. This process competes with relaxation by other O\textsubscript{2} molecules, where at low vibrational levels, V-V relaxation rates are much faster than the V-T rates\textsuperscript{65}. Accurate collisional relaxation rates of O\textsubscript{2} (X^3\Sigma_g^-, v=1) are needed for interpretation of atmospheric H\textsubscript{2}O emission spectrum.

Slanger and coworkers have experimentally measured the collisional removal rates of O\textsubscript{2} (X^3\Sigma_g^-, 1 \leq v \leq 3) by O\textsubscript{2} at room temperature\textsuperscript{66}. The population in the low vibrational levels is prepared by collisional relaxation of an a^1\Delta_g(v) excited electronic level distribution formed by photodissociation of ozone.
Most theoretical calculations of O₂-O₂ V-V rates to date have used semi-classical methods. Billing and coworkers published a set of O₂-O₂ vibrational energy transfer rates\(^65\) that is consistent with both the experimental rates for high vibrational levels and the newly measured rates at low vibrational levels. The rate coefficients are approximately four times larger than their values from earlier calculations\(^67\). The two calculations used the same theoretical approach but different intermolecular potential energy surfaces. Clary and coworkers performed \textit{ab initio} calculations of O₂-O₂ V-V rates\(^68\) and their values agreed well with experimental results, but rate coefficients for lower vibrational levels (v<8) are not available.

This study bridges the gap created by earlier studies of O₂ vibrational relaxation rates between those for high vibrational levels (v≥8) and those for lower levels (v=2,3). By studying vibrational levels 0 ≤ v ≤ 6, a nearly comprehensive set of experimental data in O₂-O₂ relaxation rates of vibrational energy and their vibrational level dependence is achieved. This provides a test ground for a theoretical model’s ability to completely predict V-V rates at all vibrational levels in the ground electronic level, X\(^3\Sigma^−\).

The same method used to measure V-V rate coefficients for N₂ molecules at 300 K was employed to study V-V transfer in O₂. As in the case of N₂, about one-third of O₂
molecules in the ground state ($X^3\Sigma_g^-, v=0$) at room temperature are pumped to the first vibrationally excited level ($X^3\Sigma_g^-, v=1$), by stimulated Raman scattering (SRS).

$$\hbar\omega_p + \hbar\omega_s + O_2(v=0) \rightarrow 2\hbar\omega_s + O_2(v=1) \quad (4.3)$$

Here $\omega_p$ is the laser “pump” beam frequency at 532 nm and $\omega_s$ is the Stokes beam frequency at 581 nm.

A difference from nitrogen is that the sample is synthetic “air” containing 79% $N_2$ and 21% $O_2$, equal to their respective mole fractions in air. Nitrogen is added to the sample as a buffer gas due to rapid $O_2$-$O_2$ V-V rates. At atmospheric pressure of 760 Torr, the V-V rates are too fast$^{65}$ to be studied by our nanosecond resolution of the probe laser. The V-V rates are proportional to the pressure, so a low $O_2$ partial pressure is required and it was reduced by a factor of 5. However, the mass diffusion rate is inversely proportional to pressure. Since we only excite a small volume of the sample with a focused pump laser, $N_2$ is added as a buffer gas to reduce the diffusion rate and prevent vibrationally excited molecules from diffusing out of the Raman pumped volume quickly. Nitrogen is chosen as the buffer gas because it quenches vibrational excitation in oxygen slowly$^{37}$. Although Ar is also a good candidate as a buffer gas$^{69}$, we observed laser breakdown more easily with samples containing argon as the buffer gas in other experiments and chose $N_2$.

The large fraction of molecules vibrationally excited (>30%) by Raman pumping enables the initially prepared molecules in $v=1$ to subsequently be excited to higher vibrational levels by collisions with other vibrationally excited molecules.
\[ O_2(v) + O_2(v = 1) \rightarrow O_2(v + 1) + O_2(v = 0), \ v = 0, 1, 2, 3... \] (4.4)

Although SRS is not efficient in producing molecules with large vibrational quanta, it creates vibrational excitation in a clean environment devoid of free radicals and molecules in upper electronic states. In fact, only one vibrational level, \( v=1 \) is pumped by the Raman pump beam. This gives SRS an advantage over ozone photolysis in producing vibrationally excited oxygen to study pure \( O_2-O_2 \) V-V kinetics, especially at low vibrational energy.

The time evolution of the population in each vibrational level due to the above reactions are detected and compared to predictions from a Master Equation kinetics modeling code, which incorporates V-V energy transfer rate coefficients derived from several published theoretical models. As will be shown later, comparison of the kinetic modeling predictions with experiment shows that the rate coefficients predicted by theory are smaller than their actual values at low vibrational levels \( (0 \leq v \leq 6) \). This leads to the conclusion that while the currently available semi-classical models accurately predict \( O_2-O_2 \) vibrational energy transfer rates for oxygen molecules with high vibrational energy \( (v \geq 8) \), they underestimate the rates at low vibrational levels.
4.2 Temperature Analysis

As mentioned previously, at our temperature of 300 K and pressure of 760 Torr, the translation and rotational energy distribution should be at thermal equilibrium. The upper panel in figure 19 shows the $O$ and $S$ branch lines of the $v = 0 \rightarrow v = 1$ Stokes spectrum of cold $O_2$ before Raman pumping. The $v = 0, J = 3 \rightarrow v = 1, J = 1$ and $v = 0, J = 1 \rightarrow v = 1, J = 3$ transition peaks of the $O$ and $S$ branches respectively are buried inside the intense broad $v = 0 \rightarrow v = 1$ $Q$ branch transition band and are indiscernible. The most intense line in the $O$ branch corresponds to the $v = 0, J = 9 \rightarrow v = 1, J = 7$ transition, while the most intense line in the $S$ branch corresponds to the $v = 0, J = 7 \rightarrow v = 1, J = 9$ transition. The most intense line for the two branches corresponds to different rotational levels in $v=0$ due to the different line strengths, $S(J)$ of the $O$ and $S$ branches. The line intensity factors for vibrational-rotational Raman transitions in linear molecules with $\Lambda = 0$ (S electronic state) are

$$
\Delta J = -2 \ (O \ branch) : \quad S(J) = \frac{3J(J-1)}{2(2J-1)} \\
\Delta J = 2 \ (S \ branch) : \quad S(J) = \frac{3(J+1)(J+2)}{2(2J+3)}
$$

where $J$ corresponds to the rotational state in the ground vibrational level, $v=0$. The values of $J$ corresponding to the most intense lines ($J_{\text{max}} = 9$ for the $O$ branch and $J_{\text{max}} = 7$ for the $S$ branch) gives a temperature range of $260 \, \text{K} < T < 330 \, \text{K}$ which contains
the temperature of our experiment (300 K). Assuming the wavelength dependence of the
CCD camera and the spectrometer’s sensitivity to be constant over the range of the
collected spectrum, a rotational temperature analysis was performed using the S branch
peaks (figure 20). The rotational temperature was found to be \( 309 \pm 6 \) K. A temperature
analysis taking wavelength dependence (using manufacturer’s specs) of the CCD camera
into account gave \( T_{\text{rot}} = 310 \) K. This is essentially the same result without factoring in the
wavelength sensitivity of the instruments but \( \sim 10 \) K higher than the actual room
temperature. We thought this difference could be attributed to the assumption that the
polarizability anisotropies of the transition peaks with different \( J \) values are constant.
However, according to Buldakov\(^{36}\), the Herman-Wallis factors, \( F_{\nu,\nu'}^{\alpha,\gamma}(J) \) (which is
proportional to the signal intensity, i.e. \( I \propto F_{\nu,\nu'}^{\alpha,\gamma}(J) \)) for S branches with \( \Delta \nu=1 \) decrease
with increasing \( J \) values and this would lead to an increase in the rotational temperature
from the analysis. A spectral response calibration of the detection apparatus using a
blackbody light source would be needed to obtain a more accurate measurement of line
intensities.

The lower panel in figure 19 shows an analogous spectrum 4 \( \mu \)s after the Raman pumping
laser pulse. The \( O \) branch peaks are overlapped by the \( v,J \rightarrow v+1,J \quad (v > 0) \) \( Q \) branch
transitions and are hard to identify. The \( S \) branch peaks are unaffected by such lines and
have been used in previous studies to measure rotational temperature by Lee et al\(^{70}\). A
possible source of systematic error in obtaining rotational temperature by such methods
comes from the overlap of \( v,J \rightarrow v+1,J + 2 \) \( S \) branch peaks originating from higher
vibrational levels. If we ignore such effects and assume that the peaks are those of the
v = 0, J \rightarrow v = 1, J + 2 \text{ transitions only, we get a rotational temperature of } 308 \pm 11 \text{ K from analysis. Figure 20 shows such temperature analysis of both cold, and vibrationally excited oxygen gas corresponding to the spectra in figure 19.}

The logarithmic of the signal intensity is proportional to the energy of the rotational level.

\[
I = cS(J) e^{\frac{E_J}{kT}}
\]

\[
\ln\left(\frac{I}{S(J)}\right) = -\frac{E_J}{kT} + \ln(c)
\]

(4.6)

We expressed the proportionality constant as \(c\) in the above equation. Plotting \(\ln\left(\frac{I}{S(J)}\right)\) versus \(E_J\) gives a straight line with the slope as \(-1/kT\), enabling us to find the temperature from the slope.

The \(v = 0, J = 7 \rightarrow v = 1, J = 9\) transition remains the highest peak in the \(S\) branch (bottom panel of figure 19) which gives \(T_{rot} < 330\) K. This leads to the conclusion that the rotational/translational temperature remains relatively unchanged at least in the time period being probed (<10 \(\mu\)s) and confirms that the rates of O\(_2\)-O\(_2\) V-V processes (observed to be vibrant during this time period) are much faster than the V-T/R rates at low vibrational levels. A pure rotational Raman spectrum where the lines for the \(v, J \rightarrow v, J \pm 2\) transition with the same values of \(J\) but different \(v\) closely overlap each other in wavelength, would probably be more effective in measuring the rotational temperature. Although Lee has performed such measurements in CO plasmas\(^{71}\), due to a
large amount of stray light of the laser beam entering the spectrometer, pure rotational O$_2$

Raman signals near the laser frequency could not be detected with our apparatus.
Figure 19. $O$ and $S$ branch lines of the $v \rightarrow v+1$ Stokes Raman spectrum of $O_2$ before (top) and 4 µs after (bottom) Raman pumping. The noted $J$ values correspond to rotational levels in $v=0$. 

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Figure 20. Plot of logarithmic of peak intensity/line strength vs. rotational energy, before (top) and 4 µs after (bottom) Raman pumping. Rotational temperature is proportional to inverse of slope.
4.3 Comparison to kinetic models

The same master equation used in predicting the time dependent vibrational level population of N\textsubscript{2} was used for O\textsubscript{2}.

\[
\frac{dN_{i,v}}{dt} = V_{i,v} + VT_{i,v} + VE_{i,v} + SRD_{i,v} + PL_{i,v} + D_{i} \nabla^{2}N_{i,v}
\]  
(4.7a)

\[
\rho c_{p} \frac{dT}{dt} = \eta \nabla^{2}T + HVR
\]  
(4.7b)

From the same arguments used in Chapter 3 and the actual rotational temperature measurement in the previous section, temperature can be regarded to be constant during the experiment, and the equation for temperature change need not be considered. The only excited electronic level that is accessible from low vibrational levels is \(a^{1}\Delta_{g}\), which is \(\approx 7900 \text{ cm}^{-1}\) above the \(X^{3}\Sigma^{-}_{g}\) ground state. However, the direct collisional transition to this electronic state from the ground state is spin forbidden, so V-E transfer is unlikely to occur. Like nitrogen, O\textsubscript{2} does not emit in the infrared and the spontaneous radiative decay term \(SRD_{i,v}\) can be omitted. The laser absorption term \(PL_{i,v}\) needs only to be considered during the pump laser pulse and only the vibrational levels \(v=0\) and \(1\) of O\textsubscript{2} are involved in Raman pumping. A qualitative feature that is different from the case of N\textsubscript{2} in Chapter 3 is that O\textsubscript{2} molecules are not the only species present in the sample. The quenching rates of vibrational excitation in O\textsubscript{2} by N\textsubscript{2} must be considered for both V-T and V-V processes.
where the O$_2$ vibrational quantum number can be relaxed by one or two quantum numbers in the O$_2$-N$_2$ V-V process.

At vibrational levels, $8 \leq v \leq 10$ and 300 K, the total quenching rate coefficients for O$_2$ vibrational excitation by O$_2$-N$_2$ interaction$^{37}$, which is the sum of the three rates above, is expected to be $\leq 3 \times 10^{-16}$ cm$^3$s$^{-1}$. Although we expect the value to be even smaller at lower vibrational levels, no experimental data is yet available to confirm this.

The O$_2$-O$_2$ V-T relaxation rate coefficients for low vibrational levels are considered to be $<10^{-17}$ cm$^3$s$^{-1}$ while O$_2$-O$_2$ V-V rates are predicted to be $>10^{-14}$ cm$^3$s$^{-1}$. The O$_2$-O$_2$ V-V rates should be about two orders of magnitude higher than the O$_2$-N$_2$ quenching rates$^{72}$ and at least three orders higher than O$_2$-O$_2$ V-T rates. So we will assume for now that O$_2$-N$_2$ and O$_2$-O$_2$ V-T relaxation rates are unimportant. This means that immediately after Raman excitation, O$_2$-O$_2$ V-V transfer and diffusion are the only relevant processes that take place.

The O$_2$-O$_2$ V-V rates of vibrational level $v$ can be written as follows.

$$ VV_v = \sum_{v'} \left[ k_{v',v+1,v} N_{v+1} + k_{v',v-1,v} N_{v-1} - \left( k_{v',v+1} + k_{v',v-1} \right) N_v \right] N_{v'} \quad (4.9) $$
The term $k_{v',v''}^{v''v'+1}$ is the rate coefficient for the following reaction.

$$
O_2(v) + O_2(v') \xrightarrow{k_{v',v''}^{v''v'+1}} O_2(v+1) + O_2(v'-1)
$$

(4.10)

Three sets of $O_2-O_2$ V-V rate coefficients were used in the modeling calculations. Rate coefficients of Billing$^{65,67}$ are obtained from the same semiclassical trajectory method he used for calculating $N_2-N_2$ V-V rates. Although he calculated two sets of such rates using different potential energy surfaces, we used the more recent one$^{65}$, which agreed better with recent experimentally measured $O_2-O_2$ V-V rates at low vibrational levels. FHO-FR V-V rate model of Adamovich$^{56}$, which gave very accurate predictions for the $N_2-N_2$ V-V rates in Chapter 3, was used again here for $O_2$. However as will be seen later, in the case of oxygen, it failed to provide a good agreement with experimental data. This suggests that unlike nitrogen, the attractive well of the intermolecular potential plays an important part in the $O_2-O_2$ V-V dynamics. Since no other set of theoretical $O_2-O_2$ V-V rate coefficients exist for low vibrational levels, the values from the FHO-FR model were multiplied by a constant factor to reach satisfactory agreement with experimental data. Multiplication of the FHO-FR values by a constant factor of 8 seemed to give the best agreement with the data.

The rate coefficients of Billing were recalculated using its theoretical model to produce a sufficient set of rate coefficients necessary for kinetic modeling, as was done in Chapter 3. The average cross sections were calculated for 17 values of classical energy (translational + rotational) ranging from $10^2$-$10^4$ cm$^{-1}$ and 500 trajectories were used for
each energy value. Energies outside this range made little contribution to the overall rate. The resulting rate constants matched the published values within 25%.

Figure 21 shows the experimental and calculated values for the population of the vibrational levels v=0 and 1 as a function of time with respect to the pump pulse. The rate coefficients of Billing and the FHO-FR model are seen to predict a significantly slower temporal evolution than is observed experimentally. The predictions derived from employing the values of the FHO-FR rate coefficients multiplied by a factor of 8 seem to give good agreement with experimental data. This implies that the actual V-V kinetics is about 8 times faster than predicted by the FHO-FR model. The same qualitative conclusions can be made from figure 22 which displays the results for v=2 and 3. Diskin\textsuperscript{22} similarly predicts rates that are faster than Billing’s calculations.

The values of the rate coefficients, \( k_{v,v'}^{v-1,v} \), for the reaction

\[
O_2(v-1) + O_2(v=1) \rightarrow O_2(v)+ O_2(v=0)
\]

from the “FHO-FR times 8” model for v=2 and 3 are \( k_{1,0}^{1,2} = 2.9 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \) and \( k_{1,0}^{2,3} = 4.3 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \) respectively. From the detailed balance relation,

\[
k_{v,v+1}^{v',v-1} = k_{v+1,v}^{v-1,v'} \exp\left[-\frac{(E(v+1)-E(v'))-(E(v')-E(v'-1))}{kT}\right]
\]  

(4.11)

the rate coefficients for the reverse decay process

\[
O_2(v) + O_2(v=0) \rightarrow O_2(v-1) + O_2(v=1)
\]

becomes \( k_{0,1}^{2,1} = 2.6 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \) and \( k_{0,1}^{3,2} = 3.4 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \) respectively. These values are higher than the experimental values.
of Slanger\(^6\) ( \( k_{\text{ul}}^{2.1} = 1.3 \pm 0.4 \times 10^{-13} \text{cm}^3 \text{s}^{-1} \) and \( k_{\text{ul}}^{3.2} = 1.9 \pm 0.3 \times 10^{-13} \text{cm}^3 \text{s}^{-1} \) ) by approximately a factor of 2.

The observations from figure 23 seem to suggest that the V-V kinetics for the reaction

\[
\text{O}_2(v = 3) + \text{O}_2(v = 1) \rightarrow \text{O}_2(v = 4) + \text{O}_2(v = 0)
\]

might be faster than the prediction from the “FHO-FR times 8” model, while the

\[
\text{O}_2(v = 4) + \text{O}_2(v = 1) \rightarrow \text{O}_2(v = 5) + \text{O}_2(v = 0)
\]

process may be slower than the predictions. Both predictions are within the statistical error margin of experimental data, so we take the rate coefficient of the “FHO-FR times 8” model as our value. The predictions using the rate coefficients of Billing and FHO-FR model once again seem too slow for \( v = 4 \) and 5. While the signal to noise in the experimental data of the \( v = 6 \) population (figure 24) is rather low, it can be seen that the “FHO-FR times 8” prediction is in reasonable, if not perfect agreement with the data.

To obtain a set of theoretical rate coefficients that give agreement with our experimental data, Billing’s rates were recalculated using a modified potential energy surface. Billing’s potential\(^6\) consists of several parts; a short range part, \( V_{\text{SR}} \), a long range part from quadrupole interactions, \( V_{\text{LR}} \), and the dispersion potential due to van der Waals forces, \( V_{\text{disp}} \).

\[
V = V_{\text{SR}} + V_{\text{LR}} + V_{\text{disp}}
\]  \hspace{1cm} (4.12)
Figure 21. Time dependent population of $v=0$ (top) and $v=1$ (bottom). Filled circles indicate experimental data with error bars corresponding to $2\sigma$. The bold line corresponds to computational simulation using rates by FHO-FR model, while the dotted lines use those by Billing$^{65}$. The solid line uses FHO-FR rates multiplied by a factor of 8.
Figure 22. Time dependent population of $v=2$ (top) and $v=3$ (bottom). The details are analogous to figure 21.
Figure 23. Time dependent population of $v=4$ (top) and $v=5$ (bottom). The details are analogous to figure 21.
Figure 24. Time dependent population of $v=6$. The details are analogous to figure 21.
Details of each part of the potential are given in reference 65. From our calculations, modifications to the long range potential and the dispersion part of the potential had little effect on the resulting values of the rate coefficients.

The short range part, $V_{SR}$, is expressed as the following.

$$V_{SR} = Ce^{-\alpha R} \left[ e^{\alpha (1-\varepsilon) \gamma_i} + e^{-\alpha \gamma_i} \right] \left[ e^{\alpha \gamma_1} + e^{-\alpha (1-\varepsilon) \gamma_1} \right]$$

$$-Fe^{-\eta R} \left[ e^{\eta (1-\varepsilon) \gamma_i} + e^{-\eta \gamma_i} \right] \left[ e^{\eta \gamma_1} + e^{-\eta (1-\varepsilon) \gamma_1} \right]$$

(4.13)

$R$ is the distance between the two molecules, while $r_1$ and $r_2$ are the internuclear distances of the two molecules. $c_i = \cos \gamma_i$ and $\varepsilon = m_O/(m_O + m_O) = 0.5$, where $\gamma_i$ (and $\delta_i$ mentioned in reference 65) define the orientation of the vector $r_i$ with respect to $R$, and $m_O$ is the atomic mass of oxygen. The parameters $a$ and $\eta$ were taken from another reference 73 while $C$ and $F$ were chosen to fit the potential in reference 73. Since $a$ and $\eta$ were determined by experiment, only the parameters $C$ and $F$ were varied. The resultant calculated values of the rate coefficients were mainly affected by the change in the ratio $F/C$ of the two parameters, which is proportional to the well depth of the potential.

Figure 25 shows the predicted time dependence of vibrational levels $v=1$ and $2$ using rate coefficients that were calculated using a potential well depth ($F/C$ ratio) of 150%, 175%, and 200% of the original ratio used by Billing. It seems that using a well depth 175% of the original value gives the set of rate coefficients that best reproduce the experimental results, at least for $v=1$ and 2. The initial decay of $v=1$ and rise of $v=2$ is mainly affected by the V-V process $O_2(v=1) + O_2(v=1) \rightarrow O_2(v=2) + O_2(v=0)$. The rate coefficient
for this process calculated from the 175% well depth potential is \( k_{1,0}^{1.2} = 2.8 \times 10^{-13} \text{ cm}^3 \text{s}^{-1} \), similar to the value from the FHO-FR model times 8. Using potential well depth of 150% gave \( k_{1,0}^{1.2} = 2.1 \times 10^{-13} \text{ cm}^3 \text{s}^{-1} \) which seems too slow. Using potential well depth of 200% gave \( k_{1,0}^{1.2} = 3.6 \times 10^{-13} \text{ cm}^3 \text{s}^{-1} \) and seems too fast compared to experimental data in figure 25. Considering the 2s error bars of the experimental data shown in the figure, these values could be regarded as the lower and upper limits of \( k_{1,0}^{1.2} \) respectively.

Another method for obtaining the lower limit of the rate coefficient \( k_{1,0}^{1.2} \) is through analysis of the rate equation for \( v=1 \) population. The master equation for the population of \( v=1 \) immediately after the Raman pump pulse can be written as follows.

\[
\frac{dN(v=1)}{dt} = \sum_{v'=1}^{2} k^{0,1}_{v,v'-1} N(v=0) N(v') + \sum_{v'=0}^{2} k^{2,1}_{v',v'+1} N(v=2) N(v') - \left( \sum_{v'=1}^{2} k^{1,2}_{v,v'-1} N(v') + \sum_{v'=0}^{1} k^{1,0}_{v',v'+1} N(v') \right) N(v=1)
\]  

(4.14b)

Initially at \( t=0 \), it can be assumed that only vibrational levels \( v=0 \) and 1 are populated immediately after the Raman pulse. Then the only V-V process that accompanies a change in vibrational level population would be formation of \( v=2 \).

\[
O_2(v=1) + O_2(v=1) \rightarrow O_2(v=2) + O_2(v=0)
\]  

(4.15)
Figure 25. Time dependent population of $v=1$ (top) and $v=2$ (bottom). Filled circles indicate experimental data. The bold line corresponds to computational simulation using rates calculated with the same method as Billing’s but using a potential well depth of 150% of the nominal (published) value. The dotted line uses well depth of 200%. Billing. The solid line uses well depth of 175%.
The V-V rate can be written as follows.

\[
VV_{v=1} \approx -2k_{1,0}^{1,2} N(v = 1)^2
\]  
(4.16)

Since V-V processes are much faster than diffusion, we can write the following.

\[
\frac{dN(v = 1)}{dt} \approx -2k_{1,0}^{1,2} N(v = 1)^2 \\
\frac{1}{N(v = 1, t)} \approx \frac{1}{N(v = 1, t = 0)} + 2k_{1,0}^{1,2} t
\]  
(4.17)

Figure 26 shows a plot of \( \frac{1}{N(v = 1)} \) vs. \( t \) along with several predictions using predetermined values of \( k_{1,0}^{1,2} \) and assuming that no other process occurs. Soon, population in \( v=2 \) starts to build up. If we consider V-V processes that involve only vibrational levels \( v=0, 1 \) and \( 2 \), the V-V rates can be written as follows.

\[
VV_{v=1} \approx -2k_{1,0}^{1,2} N(v = 1)^2 + 2k_{2,1}^{0,1} N(v = 0)N(v = 2) \\
- k_{2,3}^{1,0} N(v = 1)N(v = 2) + k_{2,3}^{2,1} N(v = 2)^2
\]  
(4.18)

Resonant processes that do not change overall vibrational level population have been excluded in the equation. After sufficient time has elapsed, V-V processes involving higher vibrational levels start to contribute along with diffusion.
**Figure 26.** Inverse of the time dependent population of v=1. Filled circles indicate experimental data. Solid line is a least squares fit line taking into account only the initial linear portion of the data. The bold line uses the $k_{1,0}^{1,2}$ value from Slanger\textsuperscript{66} while the dotted line uses the value of Billing\textsuperscript{65}.
Before all these processes become important, the most important process other than
\[ \text{O}_2(v = 1) + \text{O}_2(v = 1) \rightarrow \text{O}_2(v = 2) + \text{O}_2(v = 0) \] would be its reverse reaction,
\[ \text{O}_2(v = 0) + \text{O}_2(v = 2) \rightarrow 2\text{O}_2(v = 1) \], which leads to an increase in v=1 population. If this
is faster than all processes in equation (other than equation) that decrease v=1 population,
we could write,

\[ 2k_{2,1}^{0,1}N(v = 0)N(v = 2) - k_{2,3}^{1,0}N(v = 1)N(v = 2) + k_{2,3}^{2,1}N(v = 2)^2 \geq 0 \]  (4.19)

This causes us to write as follows.

\[ \frac{dN(v = 1)}{dt} \geq -2k_{1,0}^{1,2}N(v = 1)^2 \]
\[ \frac{1}{N(v = 1, t)} \leq \frac{1}{N(v = 1, t = 0)} + 2k_{1,0}^{1,2}t \]  (4.20)

The slope of the solid line \((k_{1,0}^{1,2} = 2.5 \times 10^{13} \text{ cm}^3 \text{ s}^{-1})\) in figure 26, obtained by least squares
fitting of the first few data points can be interpreted as the lower limit for the rate
coefficient \(k_{1,0}^{1,2}\).

Figure 27 shows a summary of several V-V rate coefficient values obtained from various
experiments and theoretical calculations. The filled circles are the values of rate
coefficients from the FHO-FR model multiplied by 8, which seemed to give the best
agreement with our experimental data. Although Slanger’s rate coefficients are smaller
Figure 27. Theoretical and experimental values for the rate coefficient, $k_{0.1}^{v,v-1}$ of reaction $O_2(v)+O_2(v=0) \rightarrow O_2(v-1)+O_2(v=1)$. The filled circles represent this work, open circles are from Slanger$^{66}$, open triangles are from Smith$^{13}$, - ▲ - from FHO-FR, and - × - from Billing$^{65}$, while the dotted line, solid line and dash-dotted line use the potential used by Billing but with a well depth of 200%, 175%, and 150% respectively.
than our values by approximately a factor of 2, they are within our error range and can be considered as being consistent with our experimental results.

Figure 28 shows the effect of using Buldakov’s $Q$ branch Raman cross sections\textsuperscript{36} compared to the simple $v+1$ dependence for harmonic oscillators. The absolute population in vibrational levels $v=4$ and $5$ decreased by small amounts from corrections, but their rise time behavior did not change. The rate of change in vibrational level population is still best predicted by the rate coefficients of the FHO-FR model multiplied by 8. Although not plotted in the figure, population in the lower levels changed even less after corrections, and we conclude that the simple $v+1$ dependence of the Raman cross sections is sufficient for our purposes.

Figure 29 shows the spatial profile of population in $v=1$ at 150 ns and 10 µs after the Raman pump pulse. The solid line in the figure is the predicted spatial profile assuming V-V processes and diffusion only. Taking vibrational quenching into account had little effect on the predicted time dependent spatial profile. We assumed an infinitely narrow probe laser beam and a Gaussian profile pump beam with $1/e^2$ radius of 80 µm. Since the profile after 10 µs is predicted with reasonable accuracy, it seems that using these assumptions to model the time dependent behavior of the O$_2$ vibrational level populations are satisfactory.

Figure 30 shows the predicted time evolution of population of vibrational levels $v=1-4$, assuming a finite probe beam radius that is wider than that of the pump beam. The results show that using this assumption had no effect on $v=1$ and 2 while the $v=3$ and 4 are predicted to decay more slowly which actually agreed less with experimental data.
Figure 28. Fractional population of $v=4$ (top) and $v=5$ (bottom). Filled circles assumed scattering cross sections to be proportional to $v+1$, while open circles used the polarizability matrix elements of Buldakov.
Figure 29. Spatial profile of \(v=1\) population 150 ns (top) and 10 \(\mu s\) (bottom) after Raman excitation. Solid lines are predictions from the master equation.
Figure 30. Time dependence of fractional population of \( v=1,2 \) (top) and \( v=3,4 \) (bottom). Solid line corresponds to simulation using pump laser radius \( \sigma_{\text{pump}} = 80 \) µm and probe laser radius \( \sigma_{\text{probe}} = 8 \) µm, while the dotted line uses \( \sigma_{\text{pump}} = 47 \) µm and \( \sigma_{\text{probe}} = 67 \) µm.
However, the rise time behavior in $v=3$, 4 and all other levels were not affected by this assumption, and it is the rise time of the vibrational population that is more sensitive to the rate coefficient values than that of the decay. The time dependence of predicted vibrational level population being relatively invariant to the relative size of the pump and probe beams provides another justification for our choice of pump and probe beam dimensions.

We now revisit our assumption of neglecting the $\text{O}_2$-N$_2$ rates. Although a difference by two orders of magnitude is large, before neglecting the quenching rates by N$_2$, we must consider that there are about 4 times more N$_2$ molecules than O$_2$ molecules in the sample. In addition, the dominant collision partner in the O$_2$-O$_2$ V-V process is O$_2$(v=1), which is only ~30% of the total O$_2$ concentration. This additional factor decreases the difference between the two processes to approximately one order of magnitude. Under such circumstances, relaxation rates by nitrogen molecules become comparable to that of diffusion and cannot be neglected. On the other hand, the relaxation time of the O$_2$-O$_2$ V-T decay processes is ~20 ms$^{65}$ which can indeed be ignored during our experimental timescale of 10 µs.

\[
\frac{1}{\tau_{v-T}} = kN(O_2) \approx 10^{-17} \text{cm}^3\text{s}^{-4} \cdot (0.21) \cdot 2.4 \times 10^{19} \text{cm}^3 = 50 \text{s}^{-1}
\]

\[
\tau_{v-T} \approx 20 \text{ ms}
\]  

(4.21a)

The relaxation of vibrational energy by O$_2$-N$_2$ collisions is expected to occur on the timescale of 200 µs or slower$^{37}$. 

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Although t~200 µs is also much longer than 10 µs, the experimental data for quenching of vibrational quanta suggests that the decay rate might be even faster than 200 µs.

Figure 31 shows the decay of average vibrational quanta possessed by an O₂ molecule inside of the probe volume. If we assume that all loss of vibrational quanta during 10 µs in figure 31 is due to diffusion, we must set the diffusion coefficient to $D \sim 3 \times 10^{-5} \text{ m}^2\text{s}^{-1}$ in order to match the data. This value of the diffusion coefficients is about 50% higher than that of other measurements at atmospheric pressure\textsuperscript{54}. The diffusion coefficient for O₂ molecules in N₂ at 760 Torr is widely considered to be $D \sim 2.1 \times 10^{-5} \text{ m}^2\text{s}^{-1}$. The dashed line in figure 31 shows the expected decay of vibrational quanta by the diffusion process alone with $D = 2 \times 10^{-5} \text{ m}^2\text{s}^{-1}$. To replicate the actual decay observed from our data, we must assume another loss channel with a decay rate of $1/\tau = 1.1 \times 10^4 \text{s}^{-1}$, $\tau \sim 100 \mu\text{s}$, which is twice as fast as the maximum O₂ vibrational energy loss rate expected from O₂-N₂ collisions. No vibrational excitation in nitrogen was observed, although the fraction of vibrationally excited N₂ molecules would be less than 1% even if they were present. The loss mechanism could also be due to quenching by species other than oxygen or nitrogen present inside the sample in small amounts, such as water, carbon dioxide etc. In the end, despite the presence of this relatively fast loss channel that is comparable in speed to diffusion, numerical solution of the vibrational level populations taking this loss rate into account did not have a noticeable effect on the
O$_2$-O$_2$ V-V dynamics which happened to be even faster than predicted with a timescale on the order of ~1 µs.

In conclusion, we have presented a new set of O$_2$-O$_2$ V-V energy transfer data at a temperature of 300 K. Approximately one third of the O$_2$ molecules are initially prepared in the first vibrationally excited level v=1, by means of stimulated Raman pumping. Higher vibrational levels become populated by V-V processes. Spontaneous Raman scattering is used to probe the temporal evolution of the populations of vibrational levels as high as v=6, providing a comprehensive data set for comparison to predictions from existing theoretical models. It is found that currently available models underestimate the V-V rate coefficients by at least a factor of 2. A full dimensional quantum calculation or semiclassical calculations employing highly accurate intermolecular potential energy surfaces seem to be needed for more accurate treatment of the V-V dynamics.
**Figure 31.** Decay of average vibrational quanta in O₂. The bold line represents decay due to diffusion alone while the solid line incorporates quenching processes to fit the data.
5.1 Introduction

Collisional energy exchange between two hydrogen molecules is the simplest process that exists for a molecule-molecule interaction and therefore the system that can be most accurately explained by theory. However, the study of energy transfer between hydrogenic molecules has been hampered by the experimental difficulty in optically exciting molecules that have no dipole moment. Stimulated Raman scattering has enabled excitation of rotational and vibrational energy of hydrogen to upper energy levels. Several experiments were previously performed which populated \( \text{H}_2 \) in a single rotational level \((j=1)\) in \(v=1\) using stimulated Raman pumping. Ducuing and coworkers measured the vibration-to-translation (V-T) relaxation rate of \( \text{H}_2 \ (v=1) \) formed by Raman pumping\(^{25}\).

\[
\text{H}_2(v = 1) + \text{H}_2(v = 0) \rightarrow 2 \text{H}_2(v = 0)
\]

\[(5.1)\]
As mentioned in Chapter 1, rotation-to-rotation (R-R) energy transfer rates in H\textsubscript{2} (v=1) were measured using Raman pumping and compared to R-R rates in v=0 obtained from crossed molecular beam scattering experiments. Vibration-to-vibration (V-V) energy transfer rates between H\textsubscript{2}, D\textsubscript{2} and HD were also measured using stimulated Raman pumping\textsuperscript{74}.

\[
\text{H}_2(v=1) + \text{D}_2(v=0) \rightarrow \text{H}_2(v=0) + \text{D}_2(v=1)
\]  \hspace{1cm} (5.2)

In addition to measuring the rotation-rotation energy transfer rates in v=1 and the V-V rates between H\textsubscript{2}, D\textsubscript{2} and HD, Chandler and coworkers\textsuperscript{23} also measured the V-V rates between two H\textsubscript{2} molecules at 295 K.

\[
p-\text{H}_2(v=1) + o-\text{H}_2(v=0) \rightarrow p-\text{H}_2(v=0) + o-\text{H}_2(v=1)
\]  \hspace{1cm} (5.3)

They obtained a rate coefficient value of \(7.1 \pm 3.0 \times 10^{-14} \text{s}^{-1} \text{cm}^3\) for the above reaction, which is 2-3 times faster than the rate for a similar reaction

\[
\text{H}_2(v=2) + \text{H}_2(v=0) \xrightarrow{k_{21}} \text{H}_2(v=1) + \text{H}_2(v=1)
\]  \hspace{1cm} (5.4)
measured by Miles and coworkers\textsuperscript{24} where $k_{0,1}^{2,1} = (1-4) \times 10^{-14}$ s$^{-1}$ cm$^3$ at 298 K. Chandler and coworkers attributed the difference to the near resonance of reaction in equation 5.3, while the above reaction in equation 5.4 has an energy mismatch of 235 cm$^{-1}$.

The only theoretical calculation of V-V rates in H$_2$ at 300 K were performed by Billing and coworkers\textsuperscript{75, 76} using semiclassical collision models. They published two sets\textsuperscript{75, 77} of theoretical calculations using different potential energy surfaces and found that the values of the rate constants differ by almost two orders of magnitude. For instance, the value for $k_{0,1}^{2,1}$ in reaction at 300 K differs between $3 \times 10^{-15}$ s$^{-1}$ cm$^3$ and $2 \times 10^{-13}$ s$^{-1}$ cm$^3$. The above mentioned experimental value from Miles and coworkers, lies between the two calculated values.

Augustine and coworkers\textsuperscript{78} used stimulated Raman scattering to measure the rotational Raman transition intensity (and hence the polarizability anisotropy) for H$_2$(v = 1, J = 1) relative to that of H$_2$(v = 0, J = 1). Due to the use of high intensity laser beams for Raman pumping, the transition from v=0, J=1 to v=1, J=1 was assumed to have reached complete saturation, resulting in 1:1 ratio between the population of the two states.

In this study, the investigation of V-V relaxation rates between two hydrogen molecules at room temperature is extended to vibrational levels higher than v=2 (and up to v=6) using the same methods described in Chapter 3 and Chapter 4. The experimentally measured V-V rate coefficients are found to lie within the error range of previous experimental results. The rotational Raman transition intensity in v=1 relative to v=0 is also measured in the same way as Augustine’s but using a different analysis which yields different results.
In addition to using spontaneous Raman scattering of the $Q$ branch, $v, J \rightarrow v+1, J$ transitions to probe the time dependent population of vibrational levels, pure rotational $S$ branch, $v, J \rightarrow v, J + 2$ transitions are also used to measure vibrational level population. It is difficult to use $S$ branch spectrum in $N_2$ and $O_2$ to infer vibrational level population since the $v, J \rightarrow v, J + 2$ transitions with same $J$, but from different vibrational levels essentially overlap each other in frequency with very small energy splitting that cannot be resolved by our spectrometer. $H_2$ $S$ branch peaks have much larger energy splitting values and each $v, J \rightarrow v, J + 2$ transition line could be resolved by our spectrometer for the most part.

Figure 32 shows the $Q$ branch Raman spectra obtained at several time delays between the pump and probe pulses. Figure 33 shows a magnified intensity axis revealing the small but measurable population in higher vibrational levels. Figure 34 and figure 35 show pure rotational $S$ branch Raman spectra at several time delays analogous to figure 32 and figure 33, respectively. The intensity scale in all spectra are arbitrary and do not relate from one spectrum to another. Although the $S$ branch signals have smaller signal to noise ratios compared to $Q$ branch, they have the advantage of having lines rotationally resolved by our spectrometer. As will be seen later, this enables us to measure the rate of the reaction $H_2(v = 1, J) + H_2(v = 0, J') \rightarrow H_2(v = 0, J) + H_2(v = 1, J')$, which is difficult to measure without rotational resolution.

As mentioned in Chapter 2, polarizability matrix elements of Schwartz and LeRoy$^{38}$ were used to obtain Raman cross sections for both the $Q$ branch and $S$ branch signals. It will
beseeved later that their calculated values of the polarizability matrix elements are in agreement with our experimental results.
Figure 32. Spontaneous $Q$ branch Raman signal of Raman pumped H$_2$ at 100 ns, 500 ns, 1.6 µs, and 3 µs after Raman pumping.
Figure 33. A blow up of the $\text{H}_2$ $Q$ branch Raman spectrum at $t=100$ ns (top) and $t=1.6 \, \mu$s (bottom).
Figure 34. Spontaneous rotational $S$ branch Raman signal of Raman pumped $H_2$ at 30 ns, 500 ns, 1 $\mu$s, and 1.5 $\mu$s after Raman pumping.
Figure 35. A blow up of the H$_2$ S branch Raman spectrum at t=30 ns (top) and t=1.5 µs (bottom).
5.2 Comparison to kinetic models

Once again, the master equation for kinetic modeling can be written in the following form.

\[
\frac{dN_v}{dt} = \text{VV}_v + \text{VT}_v + \text{VE}_v + \text{SRD}_v + \text{PL}_v + D\nabla^2 N_v
\] (5.5)

\[
\rho c_p \frac{dT}{dt} = \nu\nabla^2 T + \text{HVR}
\] (5.6)

As in the case for nitrogen, hydrogen is the only gas inside the sample cell. We will ignore the vibration-electronic coupling term \(\text{VE}\) (energy of the lowest excited electronic state, \(B^1\Sigma_u^+\), is above the ground state dissociation energy, \(D_0 = 4.48\ eV\)) and the spontaneous radiative decay term, \(\text{SRD}\), as was done in previous chapters. The laser absorption term \(\text{PL}\) is only relevant for the first 20 ns duration of the pump pulse. The diffusion coefficient \(D\) is \(1.5\times10^{-4}\ m^2s^{-1}\) for \(H_2\). We also assume vibration-to-translation energy transfer processes (the \(\text{VT}\) term) to be negligible and that the temperature remains constant during the experiment partly due to the fact that no set of theoretical VT rates was available. Although predictions from Billing and Miles suggests that the \(H_2-H_2\) VT rates are significant even for low vibrational levels, analysis from the previous chapter showed that the rise time behavior of population in \(v \geq 2\) depended mostly on the VV rates even in the presence of other relevant decay mechanisms. It will be seen that this holds true for hydrogen as well; kinetic modeling considering only VV processes and
diffusion can be fitted to match the kinetics of the rise in vibrational level population, while VT rates need to be incorporated to match its decay. Therefore, other than diffusion, only vibration-to-vibration (VV) processes are considered as relevant to change in vibrational level population at short times.

\[
VV_v = \sum_{v'} \left[ k_{v\rightarrow v+1} N_{v+1} + k_{v\rightarrow v-1} N_{v-1} - (k_{v,v+1} + k_{v,v-1}) N_v \right] N_{v'}
\] (5.7)

The term \( k_{v,v+1} \) is the rate coefficient for the following reaction.

\[
H_2(v) + H_2(v') \xrightarrow{k_{v\rightarrow v+1}} H_2(v+1) + H_2(v'-1)
\] (5.8)

The modeling also assumed the initially Raman pumped v=1 spatial distribution to be Gaussian and symmetric around the pump laser propagation axis,

\[
N(v=1, r) = N(v=1, r=0) \times \exp \left[ -\frac{2r^2}{\sigma^2} \right] \text{ with } \sigma = 76 \, \mu m. \text{ The probe laser was assumed to have a small beam radius of less than 10 } \mu m. \text{ For such cases, the results of the kinetic modeling are essentially the same as the results for modeling assuming an infinitely small probe beam radius.}
\]

Figure 36 shows the spatial profile of v=1 from experimental measurements. The solid lines represent the predicted spatial profile from our assumptions of an initially Gaussian profile, with 1/e² radius \( s = 76 \, \mu m. \) It shows that the predicted profile after 3 μs is consistent with if not in perfect agreement with experimental results.
Billing’s VV rate coefficients were recalculated using the same semiclassical trajectory calculation method and the intermolecular potential energy surface mentioned in reference 75, similar to the recalculation of \( N_2 \) and \( O_2 \). Unlike the case of \( N_2 \) and \( O_2 \) where the recalculated rate coefficients were higher than the originally published values by only 30-50\%, the recalculated \( H_2-H_2 \) VV rate coefficients are higher than the original values by about one order of magnitude. Since there is no other way to obtain a complete set of \( H_2-H_2 \) VV rate coefficients, we used the values obtained from this recalculation and compared the results of kinetic modeling with experiment. As will be seen later, the results did not match the experiment. Specifically, the rate coefficients predicted the VV kinetics to be faster than they actually are. However, using rate coefficient values that are an order of magnitude smaller and which more closely resembles the original published values predicts kinetic behavior that is slower than that observed experimentally. Billing acknowledges that the potential energy surface was not fitted to match any previously reported VV kinetic data\(^{75} \). To achieve agreement between kinetic modeling and experimental data, all of Billing’s rate coefficients were multiplied by a constant factor as was done in Chapter 4 for oxygen. It was found that multiplying the rate coefficients by 0.4 gave the best agreement with data.
Figure 36. Spatial profile of $v=1$ population 30 ns (top) and (3 µs) after the Raman pump pulse. The solid lines correspond to predictions from kinetic modeling.
Figure 37 shows the experimental and calculated values for the population of vibrational levels v=0 and 1. The experimental measurement of vibrational level populations in the figure was achieved by using spontaneous $Q$ branch ($v, J \rightarrow v+1, J$ transitions) Raman scattering, as was used for nitrogen and oxygen. It is clear that the predictions derived using the recalculated Billing rate coefficients predict a more rapid temporal evolution than is observed experimentally. The predictions using rate coefficients multiplied by a constant factor of 0.4 are seen to give good agreement with experimental data. The same qualitative conclusions can be made from figure 38, except that v=2 and 3 are now displayed. The same can be said for figure 39, which displays v=4 and 5 and figure 40, which displays v=6. A feature that is different in these figures from the figures representing lower vibrational levels, is that the populations decay more rapidly than predicted by kinetic modeling. This could be due to V-T processes that become significant at higher vibrational levels. The VT rate coefficients are predicted by Billing to become comparable in magnitude to those for VV processes near v=5 at 300 K. A complete set of VT rates as well as VV rates is necessary to replicate the decay of population in higher vibrational levels.

The population loss in higher vibrational levels could also be due to collision induced dissociation of $\text{H}_2$ molecules.

$$\text{H}_2(v \geq 5) + \text{H}_2(v \geq 5) \rightarrow \text{H}_2 + 2\text{H} \quad (5.9)$$

Vibrational energy of $\text{H}_2$ molecule at v=5 is over 50% of the dissociation energy and collisions between two $\text{H}_2$ molecules in vibrational levels 5 and higher could result in
Figure 37. Time dependent population of $v=0$ (top) and $v=1$ (bottom) at 300 K and 760 Torr. Filled circles indicate experimental data with error bars corresponding to $2\sigma$. The bold line corresponds to computational simulation using rates by Billing, while the thin lines use Billing’s rate times 0.4. Dotted lines and $\times$ represent 0.4 times Billing’s rates increased/decreased by 30% respectively.
**Figure 38.** Time dependent population of $v=2$ (top) and $v=3$ (bottom). Details are analogous to figure 37.
Figure 39. Time dependent population of $v=4$ (top) and $v=5$ (bottom). Details are analogous to figure 37.
Figure 40. Time dependent population of $v=6$. Details are analogous to figure 37.
dissociation\textsuperscript{79}, although the rate would likely be small at room temperature. The presence (or absence) of H atoms after Raman pumping could be verified experimentally using methods such as two photon absorption laser induced fluorescence (TALIF)\textsuperscript{80}.

It can be seen from figure 41 that using pure rotational \(S\) branch ( \(v, J \rightarrow v, J + 2\) transitions) Raman scattering to measure the time dependent vibrational level population gives a result that is consistent with results using the \(Q\) branch peaks. It also seems possible that for higher vibrational levels, the inferred population from \(S\) branch signals might be lower than that obtained from \(Q\) branch signals. However, due to the large uncertainty in population derived from \(S\) branch signals, this cannot be claimed with certainty. The range of error for populations obtained from the two spectra overlap each other and the inferred populations can be considered to be consistent with each other.

The value of rate coefficient for the process,

\[
H_2(v = 1) + H_2(v = 1) \xrightarrow{k_{1,0}^{1,2}} H_2(v = 2) + H_2(v = 0)
\]

(5.10)

that gives agreement with experiment is \(k_{1,0}^{1,2} = 4.5 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}\). From detailed energy balance relation, the rate coefficient for its reverse reaction becomes \(k_{0,1}^{2,1} = 1.5 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}\). The experimental result obtained by Miles and coworkers\textsuperscript{24} is \(k_{0,1}^{2,1} = (1 - 4) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}\) which is consistent with our result. However, the bold line in figure 37 and figure 38 are obtained using \(k_{0,1}^{2,1} = 3.7 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}\) and certainly
Figure 41. Time dependent population of v=0-3 from rotational S branch measurements (open circles and squares). The populations from Q branch measurements (filled circles and squares) are also shown for comparison. Circles and squares indicate v=0 and v=1 respectively on top while circles and squares indicate v=2 and 3 respectively on the bottom. Error bars are 2 S.D.
overestimates the VV rates. Therefore the upper limit of \( k_{01}^{2,1} \leq 4 \times 10^{-14} \text{ cm}^3 \text{s}^{-1} \) given by Miles seems too high and a more reasonable range would be \( k_{01}^{2,1} = (1-2) \times 10^{-14} \text{ cm}^3 \text{s}^{-1} \).

We tried to find the lower limit for \( k_{1,0}^{1,2} \) from the relation

\[
\begin{align*}
\frac{dN(v = 1)}{dt} & \geq -2k_{1,0}^{1,2}N(v = 1)^2 \\
\frac{1}{N(v = 1, t)} & \leq \frac{1}{N(v = 1, t = 0)} + 2k_{1,0}^{1,2}t
\end{align*}
\]

(5.11)

analogous to the analysis performed in Chapter 4 for oxygen.

Figure 42 shows the plot of \( 1/N(v=1) \) versus \( t \). The solid line is a least squares fit of the linear portion of the data with the resulting rate coefficient value of \( k_{1,0}^{1,2} = 4.7 \times 10^{-14} \text{ cm}^3 \text{s}^{-1} \) obtained from the slope of the fitted line. This is actually higher than the value obtained by fitting the kinetic modeling to experimental data. It seems that the large energy defect of the reaction (-235 cm\(^{-1}\)) makes the reverse process, which increases the population in \( v=1 \), less competitive relative to diffusion, VT relaxation and other VV processes such as \( H_2(v=2) + H_2(v=1) \rightarrow H_2(v=3) + H_2(v=0) \) which all result in depletion of population in \( v=1 \). The result would be that the above relations no longer hold true. From the figure, it is also obvious that the predictions from using Billing’s recalculated rate coefficients are probably too fast.

Figure 43 shows the ortho/para ratio in vibrational levels \( v=0 \) and 1. The Raman pump pulse involves transition between \( H_2(v=0, J=1) \) and \( H_2(v=1, J=1) \). Therefore initially after the pulse, all molecules in \( v=1 \) will have ortho parity \( (J=1) \). Rotational
Figure 42. Inverse of the time dependent population of v=1. Filled circles indicate experimental data. Solid line is a least squares fit line taking into account only the initial linear portion of the data. The dotted line is the prediction using the $k_{1,0}^{1,2}$ value from Billing.
Figure 43. Fraction of odd $J$, *ortho* (top) and even $J$, *para* (bottom) molecules in vibrational levels $v=0$ (open circles) and $1$ (filled circles). Dotted lines are predictions using Billing’s rates while the solid line uses Billings rate times $2$. 
energy transfer rates are quite high and the \(v=1,J=3\) state becomes quickly populated by collisions in less than 1 ns.

\[
o - H_2(v = 1, J = 1) + H_2 \rightarrow o - H_2(v = 1, J = 3) + H_2
\]

(5.12)

However, the molecule cannot change its nuclear spin very easily and the true ortho-para conversion can be ignored here.

\[
o - H_2(v = 1, J = 1) + H_2 \not\xrightarrow{p} p - H_2(v = 1, J = 0,2) + H_2
\]

(5.13)

Therefore, states in \(v=1\) with even \(J\) values can only be populated by VV processes.

\[
H_2(v = 1, J = 1) + H_2(v = 0, J = 0,2) \rightarrow H_2(v = 0, J = 1) + H_2(v = 1, J = 0,2)
\]

(5.14)

So the rise in population of molecules with para parity (even \(J\)) in vibrational level \(v=1\) will depend on the rate of the reaction

\[
H_2(v = 1) + H_2(v = 0) \xrightarrow{k_{10}^{10}} H_2(v = 0) + H_2(v = 1)
\]

(5.15)

\(k_{10}^{10}\) is the rate coefficient for this reaction.

From figure 43, it is obvious that the recalculated Billing’s value for this rate coefficient predicts VV processes that are actually slower than that observed in the experiment. This
is in contrast to the kinetics of other VV processes that accompany a change in population of the vibrational levels in which the recalculated Billing’s rate coefficients overestimated the VV rates. The solid line, which gives the best agreement with experimental data, uses a rate coefficient value that is twice the value of Billing’s recalculated values for the above near resonant reaction, specifically $k_{10}^{10} = 9.9 \times 10^{-14} \text{cm}^3\text{s}^{-1}$. This is consistent with previous experimental results of Chandler and coworkers whose result gave $k_{10}^{10} = 7 \pm 3 \times 10^{-14} \text{cm}^3\text{s}^{-1}$. Chandler attributed the fact that the rate coefficient for this reaction is several times higher than the rate coefficient for $\text{H}_2(\nu = 2) + \text{H}_2(\nu = 0) \rightarrow \text{H}_2(\nu = 1) + \text{H}_2(\nu = 1)$ to the near resonance of the former process while there is an energy defect of 235 cm$^{-1}$ for the latter. However, it should be noted that despite the energy mismatch, semiclassical calculations predict the value of $k_{10}^{1.2}$ to be higher than $k_{10}^{1.0}$, while our experimental results and those of others suggest otherwise ($k_{10}^{1.0} = 9.9 \times 10^{-14} \text{cm}^3\text{s}^{-1} > k_{10}^{1.2} = 4.5 \times 10^{-14} \text{cm}^3\text{s}^{-1}$). This suggests that semiclassical methods, which treat the rotational motion classically, may not be adequate in calculating VV rate coefficients for H$_2$ since the rotational energy spacing for H$_2$ is unusually large with a rotational constant $B_c=60$ cm$^{-1}$ while O$_2$ and N$_2$ have $B_c \approx 2$ cm$^{-1}$.
<table>
<thead>
<tr>
<th>$\nu$</th>
<th>This work</th>
<th>Chandler</th>
<th>Miles</th>
</tr>
</thead>
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<tr>
<td>0</td>
<td>$(10 \pm 3) \times 10^{-14}$</td>
<td>$(4 - 10) \times 10^{-14}$</td>
<td></td>
</tr>
<tr>
<td>1</td>
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<td></td>
<td>$(3 - 12) \times 10^{-14}$</td>
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<tr>
<td>2</td>
<td>$(7.9 \pm 2.4) \times 10^{-14}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$(1.2 \pm 0.4) \times 10^{-13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$(1.5 \pm 0.5) \times 10^{-13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>$(1.6 \pm 0.5) \times 10^{-13}$</td>
<td></td>
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</tr>
</tbody>
</table>

**Table 2.** Experimental V-V Rate coefficients in cm$^3$/s at 300 K for the reaction $\text{H}_2(\nu) + \text{H}_2(\nu = 1) \rightarrow \text{H}_2(\nu + 1) + \text{H}_2(\nu = 0)$.
Augustine and coworkers measured the Raman polarizability anisotropy for v=1 pure rotational Raman transition in H2 by rotational Raman spectroscopy. They pumped the v = 0, J = 1 → v = 1, J = 1 Q branch transition to saturation, achieving a 1:1 population ratio between the ground rotational level and the upper level. They then measured the intensity ratio of the pure rotational S branch transitions from the two levels, v = 0, J = 1 → v = 0, J = 3 and v = 1, J = 1 → v = 1, J = 3. The number density of the ground levels in the two transitions are the same and intensity factor, S(J) is identical for the two transitions since they involve the same rotational quantum number J for the upper and lower states of the S branch transition. Therefore the ratio of the two peaks is proportional to the square of polarizability anisotropy, \( \langle \gamma \rangle^2 \). Augustine found the intensity ratio to be 1.115 and hence
\[
\frac{\langle \gamma_{11,13} \rangle^2}{\langle \gamma_{01,03} \rangle^2} = 1.115.
\]

It is clear from our experimental data that we do not completely saturate the Raman pumping transition. Therefore, we measured the S branch spectrum with and without the Raman pump pulse. If all other experimental conditions are the same, the intensity ratio of the v = 0, J = 1 → v = 0, J = 3 transition in the cold spectrum to that in the Raman pumped spectrum will be equal to the ratio of the v = 0, J = 1 population before and after Raman pumping. All population lost from v = 0, J = 1 should be in v = 1, J = 1, populated by Raman pumping. From the intensity of the v = 1, J = 1 → v = 1, J = 3 transition peaks, we can obtain the polarizability anisotropy ratio of the two transitions.
\[
\frac{I_{\text{pump}}(v = 0, J = 1)}{I_{\text{cold}}(v = 0, J = 1)} = \frac{N_{\text{pump}}(v = 0, J = 1)}{N_{\text{cold}}(v = 0, J = 1)}
\] (5.16)

\[
\frac{I_{\text{pump}}(v = 1, J = 1)}{I_{\text{pump}}(v = 0, J = 1)} = \left( \frac{\gamma_{11,13}}{\gamma_{01,03}} \right)^2 \frac{N_{\text{pump}}(v = 1, J = 1)}{N_{\text{pump}}(v = 0, J = 1)}
\] (5.17)

\[
N_{\text{pump}}(v = 1, J = 1) = N_{\text{cold}}(v = 0, J = 1) - N_{\text{pump}}(v = 0, J = 1)
\] (5.18)

\[
\frac{I_{\text{pump}}(v = 1, J = 1)}{I_{\text{pump}}(v = 0, J = 1)} = \left( \frac{\gamma_{11,13}}{\gamma_{01,03}} \right)^2 \left( \frac{I_{\text{cold}}(v = 0, J = 1)}{I_{\text{pump}}(v = 0, J = 1)} - 1 \right)
\] (5.19)

Unlike in the experiment by Augustine, rotational collisions occur rapidly under our experimental conditions of 760 Torr and 300 K. This leads to the \( v, J = 3 \) state being in thermal equilibrium with the \( v, J = 1 \) state. This causes an additional complication in that at 300 K, the number density ratio between \( v = 0, J = 1 \) and \( v = 0, J = 3 \) is approximately 7:1 while the ratio becomes 6:1 in \( v = 1 \) due to the energy difference between \( J = 1 \) and \( J = 3 \) being different in \( v = 0 \) and \( v = 1 \). We must take into account the different population ratios between \( J = 1 \) and \( J = 3 \) in the two vibrational levels.

We tried to make the probe laser power and other experimental conditions identical for the two cases of pump laser on and pump laser off by taking signals under each condition alternately. Since collisions accompanying VV transfer processes also occur quickly (~1 µs) in our experiment, the Raman pumped sample must be probed quickly before any VV processes cause vibrational levels other than \( v = 0 \) or 1 to be populated. However, due to the fact that the pump laser contains a 532 nm component, which is the wavelength of the
probe laser, the sample could not be probed immediately after pumping. Spontaneous
Raman scattering of the pump laser’s 532 nm component contributes to the observed
signal for $t < 30$ ns, making the overall intensity of the signal higher for the Raman
pumped spectrum. Therefore the probe pulse was delayed by 30 ns in collecting the
Raman pumped pure rotational $S$ branch spectrum to avoid these types of interferences.
From figure 41, population in vibrational levels other than $v = 0$ or 1 should be less than
1% of the total number density at 30 ns. We also note that the temperature should remain
unchanged after 30 ns, maintaining a constant total number density of hydrogen
molecules.

Figure 44 shows the rotational $S$ branch, $v, J = 1 \rightarrow v, J = 3$ spectrum before and 30 ns
after Raman pumping. The analysis of the peak intensities gave
\[
\frac{\langle Y_{11,13} \rangle^2}{\langle Y_{01,03} \rangle^2} = 1.6 \pm 0.3
\]
which is a little higher than the value obtained by Augustine. We also have from the
analysis,
\[
\frac{\langle Y_{13,15} \rangle^2}{\langle Y_{03,05} \rangle^2} = 1.5 \pm 0.3.
\]
The $\frac{\langle Y_{11,13} \rangle^2}{\langle Y_{01,03} \rangle^2}$ and $\frac{\langle Y_{13,15} \rangle^2}{\langle Y_{03,05} \rangle^2}$ values calculated by LeRoy\textsuperscript{38}
are both 1.5. This agrees with our results and also justifies using LeRoy’s polarizability
anisotropy values to derive vibrational/rotational level population from the
$S$ branch Raman spectra.

Extracting the
\[
\frac{\langle \alpha_{1J,2J} \rangle^2}{\langle \alpha_{0J,1J} \rangle^2}
\]
ratio from the $Q$ branch signal becomes even more problematic
because the $v, J \rightarrow v+1, J$ transitions with different $J$ values all lie in a narrow frequency
range and cannot be resolved by our spectrometer. Even if we assume no $J$ dependence of
the polarizability ratios, $Q$ branch peaks also have contributions from polarizability anisotropy, $\gamma$ terms, as seen from Chapter 2. Therefore, we can only measure the temperature dependent Raman cross section, $s$ of the $Q$ branch, which is the sum of the $v, J \rightarrow v+1, J$ transitions over all $Js$, for $v=0$ and 1 experimentally and compare their ratio with that predicted from theory. Figure 45 shows the $Q$ branch spectrum before and immediately after the Raman pumping.

Another complication in obtaining $Q$ branch cross section ratios comes from the fact that the stray room scattering of the 683 nm component of the pump laser enters the spectrometer as much as 100 ns after the pump pulse passed through the sample. This interferes with the $Q$ branch peaks corresponding to $v=0, J \rightarrow v=1, J$ transitions. Consequently, the probe laser delay was set to 100 ns to avoid this. At this time, the population in $v=2$ has risen to above 1% of the total number density, as seen from figure 38. Our assumption that all population lost in $v=0$ by Raman pumping is in $v=1$ will cause to overestimate the population in $v=1$, leading to an underestimation of the Raman cross section for the $v=1, J \rightarrow v=2, J$ transitions. Nonetheless, we can regard our result as the lower limit and find $\frac{\sigma(v=1 \rightarrow v=2)}{\sigma(v=0 \rightarrow v=1)} \geq 2.4 \pm 0.4$. The cross section ratio predicted by LeRoy is 2.16, which is actually lower than our lower limit. The value of 2.16 was obtained by taking into account that only molecules with $ortho$ parity ($J=1,3$) are initially populated in $v=1$ while there is a depletion in the fraction of such molecules in $v=0$. However, the predicted cross section ratio for a thermal equilibrium rotational distribution at 300 K was 2.14 so the rotational non-equilibrium can be neglected. The predicted ratio is within the error margin of our experimental result and can be considered
as consistent with our experiment, although at this point, more studies clearly need to be conducted before any conclusions can be made.

Figure 46 shows the vibrational $S$ branch ($v, J \rightarrow v + 1, J + 2$) Raman scattering transitions before and after Raman pumping. The peaks are situated on the right tail wing of the $v = 0 \rightarrow v = 1$ $Q$ branch transition peak, making quantitative measurements of vibrational $S$ branch peak intensities non-trivial. Nonetheless, this can be done for vibrational levels $v=0$ and $1$. The vibrational $S$ branch peaks from higher vibrational levels are swamped by the more intense $Q$ branch peaks and their intensity cannot be measured. The vibrational $O$ branch peaks are also overlapped by $Q$ branch peaks as seen from oxygen, and this makes it difficult to measure their intensity. Due to low signal to noise ratio of the spectrum, the gamma ratio, $\frac{\langle y_{13,25} \rangle^2}{\langle y_{03,15} \rangle^2}$ extracted from the intensities of $v, J = 3 \rightarrow v + 1, J = 5$ transition peaks could not be considered to be reliable and we did not try to estimate its value. The extracted value for $\frac{\langle y_{11,23} \rangle^2}{\langle y_{01,13} \rangle^2}$ is equal to $2.6 \pm 0.4$ while the value predicted by LeRoy is 2.4. Once again, our experimental value is a lower estimate since at 100 ns, vibrational levels other than $v=0$ and $1$ start to become populated. Nonetheless, our measured ratio is closer to the predicted value than it was for the averaged $Q$ branch Raman cross section at 300 K. Since the population in $v=0$ and $1$ should still account for over 98% of the total number of $H_2$ molecules at 100 ns, the measured lower estimates of vibrational $Q$ branch and $S$ branch Raman cross section ratios should be close to the actual values and we’ll just treat them as experimentally
measured ratios. Table 3 gives a summary of the Raman cross section ratios of the transitions measured in this experiment.
Figure 44. Pure rotational \((v, J \rightarrow v, J + 2)\) \(S\) branch spectrum before Raman pumping (top) and 30 ns after Raman pumping (bottom).
Figure 45. $v, J \rightarrow v+1, J$ $Q$ branch spectrum before Raman pumping (top) and 30 ns after Raman pumping (bottom).
Figure 46. $v, J \rightarrow v + 1, J + 2$ $S$ branch spectrum before Raman pumping (top) and 30 ns after Raman pumping (bottom). The noted levels in the figure correspond to the initial level of the Raman transition, $v, J$.
Table 3. Raman cross section ratios $\frac{\sigma_{v=1,J \rightarrow \Delta v + 1, J + \Delta J}}{\sigma_{v=0, J \rightarrow \Delta v, J + \Delta J}}$ at 300 K for the rotational $S$ branch $v, J \rightarrow v, J + 2$ vibrational $Q$ branch, $v, J \rightarrow v + 1, J$ and vibrational $S$ branch, $v, J \rightarrow v + 1, J + 2$ transitions.
5.4 Conclusion

We have presented a new set of VV energy transfer data for pure H\textsubscript{2} at a temperature of 300 K and pressure of 760 Torr. Approximately one third of the H\textsubscript{2} molecules are initially prepared in the first vibrationally excited level, v=1, J=1 by means of stimulated Raman scattering. Similar to N\textsubscript{2} and O\textsubscript{2}, spontaneous Raman scattering of the \textit{Q} branch \( v, J \rightarrow v+1, J \) transitions is used to probe the temporal evolution of the populations of vibrational levels as high as \( v=6 \), providing a comprehensive data set for comparison to predictions from existing theoretical rate models. Raman scattering signal of the pure rotational \textit{S} branch \( v, J \rightarrow v, J+2 \) transitions is also used as a probe and gives results that are consistent with those derived from \textit{Q} branch signals. The value of the VV rate coefficients are obtained by varying their values until the kinetic modeling predictions match experimental data. Despite their low precision, the VV rate coefficient values obtained from other previous experiments are found to be consistent with our value. The observed rate for \( \text{H}_2(v=1)+\text{H}_2(v=0) \rightarrow \text{H}_2(v=0)+\text{H}_2(v=1) \) is faster than for \( \text{H}_2(v=1)+\text{H}_2(v=1) \rightarrow \text{H}_2(v=0)+\text{H}_2(v=2) \), which disagrees with predictions from semiclassical calculations. This suggests that semiclassical calculation methods that treat the rotational motion classically may be unsuitable for H\textsubscript{2}, which has large rotational energy level spacing.

The ratio of Raman cross sections and polarizability matrix elements of \textit{Q} branch and \textit{S} branch (\( \Delta v = v' - v'' = 0,1 \)) transitions for \( v''=1 \) relative to those for \( v''=0 \) were measured and found to be consistent with theoretical values predicted by LeRoy. However, the
measured ratio for $\frac{\langle \gamma_{11,13} \rangle^2}{\langle \gamma_{01,03} \rangle^2}$ was found to be larger than the experimentally determined value by Augustine.
Vibration-to-vibration (V-V) energy transfer rates of three homonuclear diatomics have been measured experimentally at room temperature and near atmospheric pressure (300 - 760 Torr).

\[ A(v_0) + A(v = 1) \rightarrow A(v + 1) + A(v = 0) \]  \hspace{1cm} (6.1)

\( A=N, O \) and \( H \) in the above equation and \( 0 \leq v \leq 6 \).

The molecules are excited from the ground vibrational level, \( v=0 \), to \( v=1 \) by stimulated Raman scattering.

\[ A(v = 0) + h\omega_{pump} + h\omega_{Stokes} \rightarrow A(v = 1) + 2h\omega_{Stokes} \]  \hspace{1cm} (6.2a)

\[ h\omega_{pump} - h\omega_{Stokes} = E(v = 1) - E(v = 0) \]  \hspace{1cm} (6.2b)
After Raman excitation, molecules in v=1 are further excited to higher vibrational levels by collisional V-V transfer processes of equation 6.1. The time evolution of the vibrational level populations is measured by Raman spectroscopy. The experimentally measured time dependence of the populations is compared to predictions of kinetic modeling that use rate coefficient values from theoretical calculations. For nitrogen, the currently available rates from semi-classical theory accurately predict experimental results, while new calculations for the VV rate coefficients are needed for oxygen and hydrogen.

The Raman scattering cross sections in H₂(v=1) relative to those in v=0 have also been measured for the rotational S branch (Δν = 0, ΔJ = 2), vibrational Q branch (Δν = 1, ΔJ = 0), and vibrational S branch (Δν = 1, ΔJ = 2) transitions. Our results are closer to the calculations from LeRoy than the experimental measurements of Augustine. For future work, measuring the VV rates involving higher vibrational levels (v=6) of N₂ and O₂ and comparing to other previous measurements is a possibility in addition to measuring the VV transfer rates between these two molecules.

\[ \text{N}_2(\nu = 0) + \text{O}_2(\nu) \rightarrow \text{N}_2(\nu = 1) + \text{O}_2(\nu - \Delta \nu), \quad \Delta \nu = 1, 2 \]  \quad (6.3)

Multi-quantum transitions are possible because at v=18, this two quantum jump in the above equation becomes a near resonant process. Two quantum collisional transition of a vibrationally excited CO molecule is also possible and measuring such rates are potential experiments in the near future.
For hydrogen, looking for H atoms possibly formed by collision between two vibrationally excited H\(_2\) molecules is also a good candidate.

\[
\text{H}_2 (v \geq 5) + \text{H}_2 (v \geq 5) \rightarrow 2\text{H} + \text{H}_2
\]  

(6.4)

v=5 is chosen since at this level, the vibrational energy is over half the dissociation energy. We have already set up apparatus to explore the last two reactions mentioned above in our laboratory.


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