Determination of nitrogen V–V transfer rates by stimulated Raman pumping

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Abstract

Stimulated Raman scattering is used to vibrationally excite pure \( \text{N}_2 \) in the pressure range 300–760 Torr at room temperature. The subsequent temporal evolution of the populations of vibrational levels as high as \( v = 6 \) is probed by spontaneous Raman scattering. The experimental results are compared to predictions from a Master Equation kinetics modeling code, incorporating V–V energy transfer rate coefficients derived from several published theoretical models. Predictions using the rate coefficients given by the three-dimensional Forced Harmonic Oscillator Free Rotator (FHO-FR) model are found to give the best overall agreement with the experimental data, although agreement with the three-dimensional models of Billing and Fisher, and Bogdanov et al. is also found to be quite good.

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1. Introduction

Vibration-to-Vibration (V–V) collisional energy transfer rates for simple diatomic molecules are an essential element for quantitative modeling of non-equilibrium systems and processes, examples of which include gas dynamic lasers [1], advanced plasma propulsion and control systems [2], and novel material synthesis methods [3], to name only a few. As a particular example, despite the fact that over the last two decades \( \text{N}_2–\text{N}_2 \) V–V transfer has been extensively studied, both theoretically [4–8] and experimentally [9–11], the reported values of the rate coefficient for the simple reaction

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

vary by more than one order of magnitude in the range \( 9 \times 10^{-15} \text{ cm}^3 \text{s}^{-1} \leq k_{10}^{01} \leq 1.5 \times 10^{-13} \text{ cm}^3 \text{s}^{-1} \). This discrepancy is most likely attributed to the difficulty in obtaining comprehensive accurate data sets due, in turn, to the difficulty in preparing substantial vibrational excitation. Since \( \text{N}_2 \) does not have a dipole moment, the absorption of infrared radiation and accompanying direct vibrational excitation is prohibited due to basic optical selection rules. Valyanskii et al. have produced vibrational excitation both by pulsed discharge [9], and by what they term “biharmonic” excitation [10], more commonly referred to as Raman excitation. In both cases, however, the data presented was limited to measurement, by coherent anti-Stokes Raman spectroscopy, of the decay of population with time. While this approach is conceptually sound, extraction of V–V rate coefficients in such an experiment is subject to uncertainty in the effects of mass diffusion, either due to uncertainty in temperature, in the case of the discharge studies, or of the excitation volume, in the case of the laser pumped studies.

In this paper, we present new experimental results in which \( \text{N}_2 \) molecules are laser excited to the \( v = 1 \) vibrational level by a process known as stimulated Raman scattering (SRS),

\[
\hbar \omega_p + \hbar \omega_s + \text{N}_2(0) \rightarrow 2\hbar \omega_s + \text{N}_2(1),
\]

where \( \omega_p \) is the laser “pump” beam frequency and \( \omega_s \) is the Stokes beam frequency.

The initially prepared molecules in \( v = 1 \) are subsequently excited to higher vibrational levels by molecular collisions,
N\(_2\)(1) + N\(_2\)(1) \rightarrow N\(_2\)(2) + N\(_2\)(0),  
(3)

N\(_2\)(v) + N\(_2\)(w) \rightarrow N\(_2\)(v + 1) + N\(_2\)(w - 1),  
\( v > w. \)  
(4)

The time evolution of the population of vibrational levels as high as \( v = 6 \) is experimentally measured and compared with predictions from a Master Equation modeling code, incorporating theoretical rate constants from a variety of published energy transfer models. It is found that predictions from a recently presented three-dimensional analytical Forced Harmonic Oscillator Free Rotator (FHO-FR) model [8] are in best overall agreement with all of the experimental data. The agreement is also found to be quite good for rates based on the semiclassical trajectory models of Billing and Fisher [5] and Bogdanov et al. [6].

2. Experimental

The generation of the stimulated Raman pump beams, illustrated in Fig. 1, is essentially identical to that described by Zhang et al. [12]. Approximately 200 mJ per pulse of the second harmonic output (532 nm) of a Q-switched Nd:YAG laser is 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\(_2\):He. As described in [12], the helium buffer serves primarily to increase the thermal conductivity of the mixture, which is important for dissipation of the excess translational energy associated with the conversion of a pump photon (532 nm) to a Stokes photon (607 nm). Approximately 25\% of the incident pump photons are converted to either the first or second Stokes frequencies of the pump photon (532 nm) to a Stokes photon (607 nm).

The SRS process, consisting of the collinear residual second harmonic and first and second Stokes frequency beams, is collimated and refocused 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 is \(~100\) mJ (~50 mJ of 532 nm, ~40 mJ of 607 nm, and ~10 mJ of 707 nm). Through a second stimulated Raman scattering process, a fraction (~\(\frac{1}{3}\)) of the N\(_2\) molecules in the second cell are initially prepared in the first \((v = 1)\) excited vibrational level. The second harmonic of a second Q-switched Nd:YAG laser, counter propagating to the SRS pump beam, forms a probe beam which is focused with a 250 mm focal length lens to overlap the volume excited by the pump. A shorter focal length lens is used with the intent of creating a probe volume with smaller radius than that of the pump. This is necessary in order to avoid spatial averaging over a volume element in which molecules are not excited, and to properly account for mass diffusion.

The time delay between the pump and probe beams is varied between 150 ns and 10 \(\mu\)s. For all the data to be presented in this paper, spectra are signal averaged for between 1 and 5 min, with a pump and probe repetition rate of 5 Hz, which is limited by energy dissipation effects in the SRS conversion cell [12].

Spontaneous Q-branch Raman scattering is used to determine the vibrational distribution function as a function of time with respect to the pump pulse, using an apparatus which is very similar to that described by Lee et al. [13]. A pair of \(f/4\) lenses is used to 1:1 image the spontaneous scattering from an approximately 1 cm segment of the probe beam on to the input slit of a 0.3 m, \(f/4\) spectrometer, equipped with a gated ICCD detector. The intensity of the vibrationally resolved Stokes Raman signal from each vibrational level, \(v\), is scaled by the \(v + 1\) dependence of the spontaneous Raman cross-section (assuming harmonic oscillators [13]) to extract the vibrational distribution function, \(f(v)\), which is defined as the fraction of total N\(_2\) molecules which reside in vibrational level \(v\).

As will be described in more detail below, 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 in both the horizontal and vertical directions,
with results that indicate an elliptical pump volume, as indicated by the discrete circles (horizontal axis) and squares (vertical axis) in Fig. 2. (The solid curves in Fig. 2, labeled “modeling distribution,” will be described in the next section.) The displacement from centerline at which the \( v = 0 \) population falls to \( 1/e^2 \) of its original value is \( \sim 65 \) \( \mu \)m in the horizontal direction and \( \sim 130 \) \( \mu \)m in the vertical direction. Also note that the diffraction limited radius \((1/e^2)\) of the probe beam is \( \sim 6 \) \( \mu \)m, assuming a 7 mm diameter beam focused with a 250 mm focal length lens.

3. Results and discussion

3.1. Experimental spectra

Fig. 3 shows a set of typical Raman spectra obtained at a pressure of 760 Torr and a temperature of 300 K. The time delay between the pump and probe pulse is 150 ns, 1, 5 and 10 \( \mu \)s, respectively, from top left to bottom right. Each peak corresponds to a single Stokes vibrational band (the rotational structure is unresolved) with the rightmost peak in each spectrum corresponding to the fractional population of the \( v = 0 \) level. Note that the relative intensity scales, while comparable, are not directly relatable from one spectrum to the other. (In other words, one cannot quantitatively infer the changes in population with time of a given level, for example \( v = 0 \), by comparing the relative intensities of the right most peak in different spectra.) Also note that 150 ns is selected for the minimum delay time in order to avoid interferences due to stray room scattering from the first and second Stokes pump beams, some of which, despite baffling, was found to enter the spectrometer. Finally, and very importantly, unlike spontaneous infrared emission spectroscopy, spontaneous Raman scattering provides a direct measurement of the fractional population of the \( v = 0 \) level. This is very important for the extraction of rate coefficients.

![Fig. 2. Experimental horizontal (circles) and vertical (squares) spatial distribution of initial \((\Delta t = 150 \text{ ns})\) \( v = 0 \) and 1 populations, along with distribution employed for modeling purposes.](image1)

![Fig. 3. Raman spectra of the pumped region at 760 Torr and 300 K. The time delay between the pump and probe pulse is (a) 150 ns, (b) 1 \( \mu \)s, (c) 5 \( \mu \)s and (d) 10 \( \mu \)s.](image2)
From the 150 ns delay spectrum it can be seen that approximately one third of the total N₂ molecules are initially excited to the \( v = 1 \) level. (Since the vibrational Raman cross-section scales as \( v + 1 \), the \( v = 1 \) cross-section is twice that of \( v = 0 \).) While not directly relevant to this work, it is interesting to note that this exceeds the fractional population (which peaks at \( \sim 10\% \) for \( J = 10 \)) in any one rotational sublevel, implying that population is moved from multiple rotational levels simultaneously. This, as described in more detail in Diskin et al. [14] occurs because of the relatively broad spectral linewidths (\( \sim 0.5 \) cm\(^{-1} \)) of the Stokes output from the Raman cell, as well as because of rapid collisional “refilling” of the rotational distribution which occurs during the duration of the pump beam pulse. From Fig. 4 it can be seen that after a delay of 1 µs, substantial population has been transferred to the \( v = 2 \) level and a detectable population has been transferred to \( v = 3 \). Substantial population continues to be transferred for longer delay times, reaching a maximum, for levels as high as \( v = 5 \), at a delay time of order 5 µs. The bottom right spectrum, corresponding to a 10 µs delay, indicates that the excited population has begun to decay, primarily due to mass diffusion. Fig. 4 shows similar 760 Torr spectra obtained with pump probe time delay of 1 (left) and 8 (right) µs, respectively, in which the intensity axis is magnified to reveal measurable population in levels as high as \( v = 6 \).

The 760 Torr data is summarized in Fig. 5, which gives the experimental vibrational distribution functions (open circles, filled squares, and filled triangles) as a function of time delay between pump and probe for levels \( v = 0–6 \), along with predictions based on a variety of published rate coefficients (described in more detail in the next section). Similar data sets were also obtained at pressures of 300 and 520 Torr. For all conditions, a minimum of three data sets was obtained. The indicated experimental uncertainties in the level populations were derived from the standard deviation in the mean of the observed experimental data for each vibrational level.

### 3.2. Comparison to kinetic models

Using the V–V rate coefficients predicted by several theoretical models, time dependent vibrational level populations were calculated by numerical solution of the master equation which takes into account spatial diffusion of the vibrationally excited molecules out of the laser-pumped volume,

\[
\frac{\partial n_v(r,t)}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[ r D \frac{\partial n_v(r,t)}{\partial r} \right] + VV_v + VT_v + PL_v, \quad (5)
\]

\[
VV_v = \sum_v \left[ k_{v+1,v}^{r,r} n_{v+1}(r,t) + k_{v,v-1}^{r,r} n_{v-1}(r,t) \right]
- \left( k_{v+1,v}^{r,r} + k_{v,v-1}^{r,r} \right) n_v(r,t) \quad (6)
\]

In Eqs. (5) and (6), \( n_v(r,t) = N f_v(r,t,v) \) is the total number density of N₂ molecules and \( f_v(r,t,v) \) is the time-space dependent \( v \) level population (i.e., the time and space varying vibrational distribution function); \( D \) is the coefficient of mass diffusion for N₂, assumed independent of \( v \); \( k_{v,v-1}^{r,r} \) are the V–V energy transfer rate coefficients, a variety of which have been incorporated into Eqs. (5) and (6); \( VT_v \) is the vibration–translation energy transfer term; and \( PL_v \) is the Raman laser excitation term. Explicit expressions for each of the terms in Eqs. (5) and (6) can be found in Flamet et al. [15]. It is noted, however, that for the relatively low vibrational levels \( v < 7 \) and low rotational/translational temperature probed in this work, V–T processes in N₂ are slow compared to V–V processes, such that they are completely negligible at the time scales studied in the experiment. This also implies that the rotational/translational temperature is constant (at 300 K), a result which was approximately confirmed by integration, suitably weighted by the \( v + 1 \) level dependence of the Raman cross-section, of the total Raman signal as a function of time. This integrated Raman signal is proportional to the N₂ number density and, therefore, inversely proportional to temperature at constant pressure. Such measurements show that the temperature remains constant to within \( \pm 3 \) K. It should also be noted that,

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Fig. 4. Raman spectra of the pumped region at 760 Torr and 300 K in which the intensity axis is blown up to reveal detected population in levels as high as \( v = 6 \). The probe delays are (a) 1 µs and (b) 8 µs.
while formally included in the Master Equations, the rate for multiple vibrational quantum jump transitions, at the low temperature and for the range of vibrational levels probed in this work, is slower than that for single quantum transitions by many orders of magnitude. For example, the FHO model [8] predicts a value of approximately $10^{-18}$ cm$^3$ s$^{-1}$ for the rate coefficient $k^0_{2,0}$ at 300 K, which is $\sim 10^{-4}$ of that for the coefficient $k^1_{1,0}$. Essentially, the probability for the two quantum transition is given by the product of the probabilities for the individual single quantum transitions, which are of order $10^{-4}$ for processes such as $k^0_{1,0}$ and $k^1_{2,1}$.

For purposes of modeling it was assumed that the convolution of the pump and probe volumes results in a measurement volume defined by an axisymmetric Gaussian profile, $\exp[-2r^2/\sigma^2]$, with $\sigma = 65 \mu$m. This value of $\sigma$ was found to result in an excellent fit to the horizontal profile data, as illustrated by the solid curves in Fig. 2. The horizontal profile was selected because the role of diffusion is greatest for the shorter dimension. Two sets of calculations were performed. For the first set, the Raman pump laser is assumed to initially excite a Gaussian spatial profile, with $\sigma = 46 \mu$m. The calculated temporal evolution of the $v$ level populations was then modeled assuming a spatial average over a Gaussian probe volume, with $\sigma$ also equal to 46 $\mu$m. (Note that the convolution of two Gaussian profiles with $\sigma$ equal to 46 $\mu$m results in a Gaussian with $\sigma$ equal to 65 $\mu$m.) The initial excitation was defined to match the experimentally determined populations at $t = 150$ ns. (In other words, the initial population of $v = 1$ on true “centerline” was somewhat higher than that displayed in Fig. 5, in order that the spatial average would replicate the experimental data.) For the second set of calculations an infinitesimally thin probe volume was assumed, and the entire 65 $\mu$m measurement volume was assigned to the pump. This difference resulted in essentially no change in the predicted level populations.

Five sets of theoretical N$_2$ V–V rate coefficients were used in the modeling calculations. Rate coefficients of [5] are obtained from three-dimensional semiclassical trajectory calculations for an accurate potential energy surface which incorporates both short-term repulsive interaction and long-term attractive forces (both quadrupole–quadrupole and dispersive). V–V rates in [6] are obtained from three-dimensional quasiclassical trajectory calculations for two different potential energy surfaces and presented as an analytic fit to the numerical data using the SSH parameterization. In the absence of a fully quantum three-dimensional theory, these models are considered to be superior to one-dimensional theories, and their predictive capability is primarily controlled by the accuracy of the potential energy surface used.

Analytic rate coefficients of Kirilov et al. [7] and those recently presented by Chauveau et al. [4], which are based on the earlier work of Jeffers and Kelley [16], are obtained using the one-dimensional first-order perturbation theory. Note that V–V and V–T rate sets predicted by such one-dimensional models always contain adjustable parameters such as “steric factors” and “potential pa-
rameter factors” needed to reconcile the predictions based on the simplified collision model considered (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. In addition, the perturbation theory based models can be used only for prediction of single-quanta 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.

The FHO-FR V–V rate model of Adamovich [8] 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 accurate analytic solution of the inelastic V–V and V–T transition probabilities [8] over the impact parameters, orien-
tation angles, angular momentum angles, and rotational coefficients, we have recalculated them for the same po-
tential energy surface using a trajectory calculation computer code DIDIAV [17] developed by Billing. 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 of [5]. The recalculated rate coefficients are typically somewhat higher than the originally published values, by up to 30–50%.

Table 1 gives the value of \( k_{1,0} \) resulting from each model.

For all cases to be presented below the comparison between experimental results and theory is done for all observed levels simultaneously, with a single set of theoretical rates employed. Fig. 5(a) shows the experimental and calculated values for the population of vibrational levels \( v = 0 \) and 1 at 760 Torr pressure as function of time with respect to the pump pulse. Although predictions were obtained for all five sets of rate coefficients, we have, for clarity, displayed only those from [5,7,8], in the figure. While the predictions of the FHO-FR model are seen to give the best overall agreement, it is also clear that the

\[
k_{v+1,w}(v+1,w+1) = \frac{1}{16} \frac{x^2 kT}{2\omega^2 m} (v+1)(w+1) \times (3 - e^{-2\lambda}) e^{-\lambda v} \exp \left( \frac{\Delta E}{2kT} \right),
\]

with

\[
\lambda = \frac{1}{3\sqrt{2}} \left( \frac{\theta'}{T} \right) \frac{|\Delta E|}{\omega h},
\]

where \( v \) and \( w \) are the vibrational quantum numbers, \( \omega = 4.0 \) A\(^{-1} \) is the exponential repulsive potential parameter [5], \( k \) is the Boltzmann constant, \( \omega \) is the oscillator frequency, \( m \) is the collision reduced mass, \( \theta' = \frac{4\omega^2 x_w}{\omega^2} \), and \( \Delta E = E_{v+1} + E_w - E_v - E_{w+1} \) is the vibrational energy defect. Eq. (7) was obtained by approximate analytic averaging of the FHO-FR transition probabilities [8] over the impact parameters, orientation angles, angular momentum angles, and rotational energies of the collision partners, as well as the total collision energy. However, the FHO-FR rates used for comparison with the present experiments were obtained by a more accurate Monte Carlo numerical averaging of the analytic FHO-FR probabilities over these collision parameters using \( 10^8 \) randomly selected points in the phase space. Both analytically averaged FHO-FR rates of Eq. (7) and numerically averaged FHO-FR rates for \( N_2-N_2 \) at room temperature are plotted in Fig. 6.

Table 1

| Rate coefficients for reaction (1) according to each theoretical model |
|--------------------------|----------------|
|                         | \( k(1, 0 \to 0, 1) \) (cm\(^3\)/s) |
| Chauveau                | \( 6.0 \times 10^{-14} \) |
| Kirillov                | \( 1.1 \times 10^{-13} \) |
| Bogdanov                | \( 2.0 \times 10^{-14} \) |
| Billing                 | \( 1.8 \times 10^{-14} \) |
| FHO-FR                  | \( 0.9 \times 10^{-14} \) |
predictions derived from [5], which is also a three-dimensional model and employs a similar repulsive contribution to the potential, also agree quite well. While not plotted, it was also found that predictions derived from [6] are quite similar to those from [5], which is not unexpected since both are based on three-dimensional semiclassical trajectory theory. The rate coefficients from both one-dimensional models [4,7] predict similar, significantly more rapid, temporal evolution than is observed experimentally, although only [7] results are presented. The same qualitative conclusions can be made from Fig. 5(b), which is identical to Fig. 5(a) except that the results for levels $v = 2$ 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 Fig. 5(a), the predicted rate of V–V transfer is significantly higher for the rate coefficients derived from the one-dimensional model [7] than either of the three-dimensional models. While not shown, predictions derived from [6,7] are, once again, found to be similar to those from [4,5], respectively. The rise in population of levels 4–6 is presented in Fig. 5(c). While the signal to noise in the experimental data is somewhat low, it can be seen that both the FHO-FR [8] and Billing and Fisher [5] predictions are in reasonable, if not perfect, agreement with the data. Again, the one-dimensional models from [4] (plotted) and [7] (not plotted) predict level populations which 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 unsurprisingly, the best agreement with experimental data. We also note that for nitrogen, the dynamics of the collision appear to be successfully captured by inclusion of the repulsive part of the potential only, and that effects from the attractive part are minimal. Note that although the one-dimensional model rates can be reconciled with the experimental data by varying adjustable parameters such as steric factors and potential parameters, the predictive use of these models wherever the experimental data are unavailable is 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. In all cases the calculations utilize the same rate coefficients as employed for the 760 Torr case, illustrated in Fig. 5. Fig. 7 summarizes the 300 Torr data. In this case, due to relatively poor signal to noise in the raw data, comparisons were only possible for vibrational levels 0–3. Nonetheless, it can again be seen that the rate coefficients from [8] agree best with the data, while the rates of [5] (plotted) and [6] (not plotted but similar) also were found to agree quite well. As for the 760 Torr case, the predictions derived from the rates of [4] (plotted) and [7] (not plotted) appear to be too fast, by approximately one order of magnitude. Essentially identical conclusions were drawn from the 520 Torr data, for which we were able to obtain population data for vibrational levels 0–6.

It should also be noted that the fact that a single set of rate coefficients provides good agreement with the 300, 520, and 760 Torr data sets, including both the decay in level 1 and the rise in the other levels, implies that the effects of diffusion are being accounted for with sufficient accuracy. More specifically, it provides a justification for the somewhat approximate method which was used to define the pump and probe volumes. Finally, kinetic modeling calculations show that the time-dependent vibrational level populations measured in the present experiments are most sensitive to the non-resonance V–V rates $k(1, v - 1 \rightarrow 0, v)$.

### 4. Conclusions

We have presented a new set of V–V energy transfer data for pure N$_2$ at a temperature of 300 K and pressure in the range 300–760 Torr. Approximately one third of the N$_2$ molecules are initially prepared in the first vib-
rationally excited level, \( v = 1 \), by means of stimulated Raman pumping. 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 rate models. It is found that the three-dimensional FHO-FR model \([8]\) provides the best overall agreement with the entire data set, although previously published three-dimensional models \([5,6]\) are also in reasonable agreement. The rate coefficients predicted by the one-dimensional models of \([4]\) and \([7]\) appear to be too fast by approximately one order of magnitude.

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**References**


