Vibrational Relaxation of NH$_3$ ($\nu_2$)

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Abstract
The V - T, R rate of NH$_3$ ($\nu_2$) is measured using the method of laser excited vibrational fluorescence. Self deactivation at room temperature occurs in about 7 collisions and requires 1100, 1100, 670, and 530 collisions for deactivation by He, Ar, N$_2$, and O$_2$, respectively.
Vibrational relaxation of \( \text{NH}_3(v_2) \)

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The method of laser-excited vibrational fluorescence is used to measure the vibrational relaxation rates of \( \text{NH}_3(v_2) \) in collisions with \( \text{NH}_3, \text{He}, \text{Ar}, \text{N}_2, \) and \( \text{O}_2 \). The rates are found to be 3.8 \( \times 10^{-11} \), 2.8 \( \times 10^{-13} \), 1.8 \( \times 10^{-13} \), 3.6 \( \times 10^{-13} \), and 4.2 \( \times 10^{-13} \) cm\(^3\) molecule\(^{-1}\) sec\(^{-1}\), respectively. Exciting to different rotational levels gives the same result within 10%.
I. INTRODUCTION

The rate of vibration-to-translation and rotation (V + T, R) energy transfer of the v_2(±) fundamental vibration of NH_3 is known to be fast. Recently reported rates cover the range from 1/35 to 1/4 of the gas kinetic collision rate. Such rapid V + T, R relaxation rates are also observed in other hydrogen bonding systems such as H_2O and HF, and are of theoretical interest. The rates are of importance in the design of two-photon pumped NH_3 lasers having 2v_2(-) as the upper level and 2v_2(+) or v_2(±) as the lower level.

In this paper measurements of the V + T, R rates for NH_3(v_2 = 1±) relaxed by NH_3, He, Ar, N_2, and O_2 are given. The rate constants were measured by the method of laser-excited vibrational fluorescence. A CO_2 TEA laser was used to pump Q- or R-branch transitions of the v_2(±) state. The time-resolved infrared emission from the P- and Q-branches of the same level was analyzed to extract the deactivation rate constants.

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A CO_2 TEA laser was directed single pass through a fluorescence cell and into a photon drag detector, which monitored the pulse shape and triggered the signal averaging equipment (a Biomation 8100 transient recorder, a Tracor-
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In this paper measurements of the V→T, R rates for \( \text{NH}_3(v_2 = 1\pm) \) relaxed by \( \text{NH}_3 \), He, Ar, \( \text{N}_2 \), and \( \text{O}_2 \) are given. The rate constants were measured by the method of laser-excited vibrational fluorescence. A \( \text{CO}_2 \) TEA laser was used to pump Q- or R-branch transitions of the \( v_2(\pm) \) state. The time-resolved infrared emission from the P- and Q-branches of the same level was analyzed to extract the deactivation rate constants.

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Northern NSS75A digital signal analyzer, and a Hewlett-Packard 7004B X-Y recorder. A liquid He cooled Cu:Ge detector is mounted to look at fluorescence perpendicular to the excitation beam. The signal from the detector is amplified and averaged for enough laser pulses to give a signal-to-noise greater than 10 for the fluorescence intensity versus time traces, typically 100 to 200 shots.

The CO$_2$ TEA laser was constructed from a Tachisto model 215 discharge head and made to oscillate on single rotation-vibration transitions. The output beam is 6 mm in diameter and has a pulse width of 50 nsec FWHM with no observable tail. The pulse energies were 30 - 50 mJ for all experiments using the (00$^0_1$) - (02$^0_0$) R(16) laser line and 35 - 75 mJ for experiments using the (00$^0_1$) - (10$^0_0$) R(6) or R(14) lines.

Chang and McGee$^{11}$ have shown that the (00$^0_1$) - (02$^0_0$) R(16) line pumps the aR(6,0) transition of NH$_3$(v$_2$). The spectroscopic data of Shimizu$^{12}$ and Garing et al.$^{13}$ show that the (00$^0_1$) - (10$^0_0$) R(6) and R(14) laser lines pump the sQ(5, 4) and aR(1, 1) transitions, respectively.

The fluorescence cell, which is 25 cm long and 2.5 cm in diameter, has Brewster angle ZnSe input and output windows to minimize scattered light. There are 2.5 cm fluorescence viewing holes which are covered with NaCl windows in the top and bottom of the cell. A 2.5 cm focal length parabolic mirror directs the fluorescence coming out the bottom window back toward the detection system. A 6.1 cm diameter f/1 NaCl lens
collects and focuses the fluorescence onto the detector.

For experiments using only pumping by the (00°1) - (02°0) R(16) line the interference filter inside the detector Dewar was an OCLI wide band pass filter with half power points at about 770 cm\(^{-1}\) and 960 cm\(^{-1}\). The external filter was a wide band filter with half power points at about 780 cm\(^{-1}\) and 970 cm\(^{-1}\). This combination of filters transmitted most of the P- and Q-branch transitions of the NH\(_3\)(v\(_2\)) band.\(^{13}\) For the experiments which used (00°1) - (10°0) R(6) and R(14) pumping two long pass filters were used externally. They had cut on frequencies (~ 5% transmitting) of about 920 cm\(^{-1}\) and 880 cm\(^{-1}\). This combination of filters transmitted most of the P-branch of the NH\(_3\)(v\(_2\)) band. For all experiments a liquid He cooled 2 mm thick BaF\(_2\) window directly in front of the detector element eliminated radiation frequencies less than 650 cm\(^{-1}\).

All of the measurements described were done on mixtures of NH\(_3\) with either Ar, He, N\(_2\), or O\(_2\) at 20 ± 2°C. The buffer gas prevented unwanted heating effects and enhanced the absorption of the excitation beam. Even though the added buffer gas increased the energy absorbed, it increased the total sample heat capacity at a faster rate.

The cell plus the glass and grease manifold to which it is connected have a leak rate of less than 10\(^{-3}\) Torr/hr. A Celesco pressure transducer in the manifold allowed continuous monitoring of the pressure. To minimize uncertainties in the NH\(_3\) pressure, the system was first saturated with NH\(_3\) and then
allowed to equilibrate until the NH₃ pressure changed less than 1% in 15 minutes. At this time the desired buffer gas was added.

The NH₃ used was Matheson anhydrous grade with a minimum purity of 99.99%. The buffer gases were Matheson research grade of the following purities: Ar, 99.9995%; He, 99.9999%; N₂ 99.999%; O₂, 99.99%. In addition, each of the buffer gas samples was held over liquid N₂ before an experiment.

III. RESULTS AND ANALYSIS

Since the two inversion levels of NH₃ (v₂) are separated by only 35 cm⁻¹ their fluorescence was not resolved in these experiments and the kinetics are treated as a single level at 950 cm⁻¹.

The relaxation time τ of this level is given by

\[ \frac{1}{p \tau} = (k_{\text{NH}_3} - k_M) X_{\text{NH}_3} + k_M, \]

where \( p \) is the total pressure, \( X_{\text{NH}_3} \) the mole fraction of NH₃, \( k_{\text{NH}_3} \) the rate constant for NH₃ (v₂) deactivation by collisions with other NH₃ molecules, and \( k_M \) the rate constant for deactivation by collisions with M.

To be sure that the observed fluorescence was due to v₂ fundamental fluorescence and not hot band fluorescence, an experiment was done with a 4 cm gas filter cell containing ~170 Torr of NH₃ between the fluorescence cell and detector. The peak fluorescence intensity seen with the NH₃ in the filter
cell was about 3% of that seen with the cell empty for a sample containing 0.67 Torr of NH₃ and 66 Torr of Ar. Thus population of higher levels is not sufficient to interfere with the ν₂ fundamental fluorescence analysis. Values of \( \tau \) are deduced from semilog plots such as Fig. 1.

A series of Ar and He mixture measurements, using (00'-1) - (02'-0) R(16) excitation, was done to establish \( k_{NH₃} \), \( k_{Ar} \), and \( k_{He} \). The Ar data include measurements on samples with eight different NH₃ pressures, ranging from 0.106 to 0.671 Torr. The total sample pressures used ranged from 8 to 153 Torr. For the He data four different NH₃ pressures ranging from 0.109 to 0.636 Torr were used. The total sample pressures ranged from 21 to 144 Torr. The results of the measurements are shown in Figs. 2 and 3. Different points of about the same \( X_{NH₃} \) represent samples with different total pressures. The Ar data gives \( k_{NH₃} = 1.3 \mu sec^{-1} \) Torr\(^{-1} \) and \( k_{Ar} = 5.9 \times 10^{-3} \mu sec^{-1} \) Torr\(^{-1} \). The He data gives \( k_{NH₃} = 1.2 \mu sec^{-1} \) Torr\(^{-1} \) and \( k_{He} = 9.3 \times 10^{-3} \mu sec^{-1} \) Torr\(^{-1} \). These values were obtained from a weighted least squares analysis of the data. The weighting was done so that each point had the same % uncertainty. The least squares analysis gave estimates for uncertainties in the k's of only a few percent. Since the pressures and lifetimes have experimental uncertainties of ~ 5% a generous estimate of the total random and systematic uncertainties in \( k_{NH₃} \), \( k_{Ar} \), and \( k_{He} \) is ± 10%.
A value of $k_{\text{NH}_3} = 1.25 \text{ usec}^{-1} \text{ Torr}^{-1}$ from the He and Ar measurements was used to analyze the $N_2$ and $O_2$ results. A rearrangement of Eq. (1) shows that $k_M = \frac{1}{p\tau} - k_{\text{NH}_3}X_{\text{NH}_3}$ for $p \sim p_M$. Values of $k_M$ were calculated from each experiment and averaged to obtain the reported value. Figure 4 graphically displays the $N_2$ and $O_2$ results from experiments pumping with the $(00^01) - (02^00) R(16)$ line. The $N_2$ measurements were made on two samples with $\text{NH}_3$ pressures of 0.084 and 0.128 Torr and total pressures between 51 and 120 Torr. The $O_2$ measurements were done on a single $\text{NH}_3$ sample of 0.079 Torr and total pressures between 33 and 117 Torr. The standard deviations of $k_{N_2}$ and $k_{O_2}$ were small and the uncertainties again estimated to be $\pm 10\%$.

An additional $\text{NH}_3$-Ar measurement not shown in Fig. 2 was done to see if any effect on $k_{\text{NH}_3}$ due to the initial rotational state could be observed. The sample had $X_{\text{NH}_3} = 0.050$ with $p_{\text{NH}_3} = 0.377$ Torr and $p_{\text{Ar}} = 7.17$ Torr. The fluorescence decay time $\tau$ was measured after excitation by the $(00^01) - (10^00) R(6)$, $(00^01) - (10^00) R(14)$, and $(00^01) - (02^00) R(16)$ laser transitions. Using the previously measured $k_{\text{Ar}}$ all of the $\tau$'s yielded the same value of $k_{\text{NH}_3}$ within about 10% of the previously measured value. Since the $S/N$ for these experiments was not as good as for much of the data, this difference is not significant.

At high laser powers or high $\text{NH}_3$ pressures significant sample heating is observed as a long time fluorescence tail.
For a sample of 0.5 Torr of pure NH₃ and laser pulse energies of 50 mJ the data of Chang & McGee on absorption of the (00°₁) - (02°₀) R(16) laser line show that the excitation volume in the cell should absorb about 0.1 mJ. Comparison of fluorescence intensities with and without Ar shows that addition of ~10 Torr of Ar causes a roughly fivefold increase in absorption. Thus for the most concentrated sample used for rate measurements, X_{NH₃} = 0.05, about 0.5 mJ laser energy was absorbed. The excitation volume is heated by 13°C. Nearly all of the other samples measured were heated much less. The heating effect analyzed for CD₄ results in rate constant changes of less than 1%. Rate constant measurements are reported only for samples which displayed no heating effects.

IV. DISCUSSION

The results presented here are summarized in Table I. As has been found in other strongly hydrogen bonding systems such as H₂O⁷ or HF⁸ the V → T, R rate of the lowest excited level is quite fast, even though a significant amount of energy must go into rotation and translation. In addition, the ratios of k_{NH₃}/k_M are similar to the analogous ones reported for H₂¹⁸O(v₃).⁷ The k_{NH₃}/k_M values for argon, nitrogen, and oxygen are 200, 100, and 90, respectively. For k_{H₂O}/k_M they are 170, 50, and 70.

Most of the more recent measurements of k_{NH₃} by acoustic
techniques are in reasonable agreement with that reported here, considering the difficulties of large corrections for classical absorption and rotational relaxation. Lambert and Salter\textsuperscript{1} saw no sound velocity dispersion over the f/p range they studied and thus concluded $k_{\text{NH}_3} > 1.1 \mu\text{sec}^{-1} \text{Torr}^{-1}$. Cottrell and Matheson\textsuperscript{2} did similar measurements and report similar results. Jones et al.\textsuperscript{4} measure both velocity dispersion and absorption at larger f/p values. By fitting their results with the same relaxation time for both rotational and vibrational relaxation they obtain a value for $k_{\text{NH}_3}$ of $1.8 \mu\text{sec}^{-1} \text{Torr}^{-1}$, but report no uncertainties. By measuring ultrasonic absorption and fitting the data by varying both the rotational and vibrational relaxation times Bass and Winter\textsuperscript{5} obtain $k_{\text{NH}_3} = 0.73 \mu\text{sec}^{-1} \text{Torr}^{-1}$. However, their estimated uncertainties in $k_{\text{NH}_3}$ due to a 10% uncertainty in the absorption measurements include values ranging from about $0.45 \mu\text{sec}^{-1} \text{Torr}^{-1}$ to $1.8 \mu\text{sec}^{-1} \text{Torr}^{-1}$. They note that the difference between their value and that of Jones et al. can be largely attributed to the different methods used to extract relaxation times from absorption data. Of the recent measurements by acoustic techniques, the value of $\sim 0.22 \mu\text{sec}^{-1} \text{Torr}^{-1}$ for $k_{\text{NH}_3}$ estimated by Strauch and Decius\textsuperscript{3} from velocity data is the furthest from the $k_{\text{NH}_3}$ reported here.

An infrared-ultraviolet double resonance technique used by Ambartzumian et al.\textsuperscript{6} to study the $V \rightarrow T, R$ rate of $\text{NH}_3(\nu_2)$
gave values of $k_{\text{Ar}}$ and $k_{\text{O}_2}$ of $7.0 \times 10^{-3}$ $\mu$sec$^{-1}$ Torr$^{-1}$ and $1.1 \times 10^{-2}$ $\mu$sec$^{-1}$ Torr$^{-1}$, in good agreement with those reported here. However, their value of $k_{\text{NH}_3}$ was $0.69 \pm 0.15$ $\mu$sec$^{-1}$ Torr$^{-1}$, almost a factor of 2 slower than found here. An error in their NH$_3$ pressures could lead to a significant change in the $k_{\text{NH}_3}$ value without greatly affecting the $k_M$'s.

Shin has investigated the $V \rightarrow T$, $R$ rates for NH$_3$ theoretically using two models. One assumes $V \rightarrow T$ transfers take place at preferred orientations and the other is a quasi-classical $V \rightarrow R$ calculation. Both models give essentially the same room temperature result for $k_{\text{NH}_3}$ with a value about half of that reported here. The $V \rightarrow T$ model predicts that $k_{\text{NH}_3}$ should go through a minimum at 600 K which is about 1/3 of the 300 K value. The $V \rightarrow R$ model predicts a much weaker temperature dependence. By comparison to the temperature dependence seen by Bass and Winter Shin concludes $V \rightarrow R$ is the dominant mechanism. The results of Cottrell and Matheson showing that ND$_3$ deactivates more slowly than NH$_3$ more strongly supports a $V \rightarrow R$ mechanism.

Orbiting collisions have been shown to be important in vibrational relaxation of HF. Billing and Poulsen semiclassically calculate $V \rightarrow T$, $R$ and $V \rightarrow V$ rates for several vibrational levels of HF using an ab initio SCF HF-HF potential surface. They show that roughly half of the vibrational deactivation of HF($v = 1$) by HF is a result of orbiting collisions at 300 K. Orbiting collisions are
several times more effective per collision than non-orbiting collisions. For a given translational-rotational energy and impact parameter, orbiting collisions will occur less frequently for NH$_3$-NH$_3$, with an attractive potential well depth of between 2.8 and 4.5 kcal/mole$^{17-20}$, than for HF-HF with 6 kcal/mole.$^{21}$ However, for NH$_3$-NH$_3$, with a vibrational quantum about four times smaller and relaxation rate twenty times larger than HF, collision energies smaller by at least a factor of two should be important. Thus the contribution of orbiting trajectories to relaxation of NH$_3$ may be comparably as important as for HF.

ACKNOWLEDGMENTS

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REFERENCES


TABLE I. Measured rates of vibrational deactivation of $\text{NH}_3(v_2)$ by M (293 K).\(^a\)

<table>
<thead>
<tr>
<th>M</th>
<th>$k(\mu\text{sec}^{-1} \text{ Torr}^{-1})$</th>
<th>$k(\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1})$</th>
<th>$p^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NH}_3$(^b)</td>
<td>1.3</td>
<td>$3.9 \times 10^{-11}$</td>
<td>0.15</td>
</tr>
<tr>
<td>$\text{NH}_3$(^c)</td>
<td>1.2</td>
<td>$3.6 \times 10^{-11}$</td>
<td>0.14</td>
</tr>
<tr>
<td>He</td>
<td>$9.3 \times 10^{-3}$</td>
<td>$2.8 \times 10^{-13}$</td>
<td>$8.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Ar</td>
<td>$5.9 \times 10^{-3}$</td>
<td>$1.8 \times 10^{-13}$</td>
<td>$8.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\text{N}_2$</td>
<td>$1.2 \times 10^{-2}$</td>
<td>$3.6 \times 10^{-13}$</td>
<td>$1.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>$1.4 \times 10^{-2}$</td>
<td>$4.2 \times 10^{-13}$</td>
<td>$1.9 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

\(^a\) Uncertainties are estimated to be ± 10%. See Results and Analysis.

\(^b\) Measured with Ar as buffer gas.

\(^c\) Measured with He as buffer gas.

\(^d\) $P = k/k_{gk}$ where $k_{gk}$ is calculated using the molecular diameters $d_{\text{NH}_3} = 3.17$ Å, $d_{\text{He}} = 2.24$ Å, $d_{\text{Ar}} = 2.86$ Å, $d_{\text{N}_2} = 3.15$ Å, and $d_{\text{O}_2} = 2.93$ Å.
Figure 1. Fluorescence intensity versus time for an NH$_3$-Ar mixture.

Figure 2. Results of NH$_3$-Ar measurements. Slope = 1.3 µsec$^{-1}$ Torr$^{-1}$, intercept = 5.9 x 10$^{-3}$ µsec$^{-1}$ Torr$^{-1}$.

Figure 3. Results of NH$_3$-He measurements. Slope = 1.2 µsec$^{-1}$ Torr$^{-1}$, intercept = 9.3 x 10$^{-3}$ µsec$^{-1}$ Torr$^{-1}$.

Figure 4. Results of NH$_3$-N$_2$ and NH$_3$-O$_2$ measurements.
\[ P_{NH_3} = 0.46 \text{ torr} \]
\[ p_{tot} = 76.4 \text{ torr} \]
\[ \tau = 0.69 \mu\text{sec} \]
$k_{O_2} = 0.0142 \, \mu\text{sec}^{-1} \, \text{torr}^{-1}$

$k_{N_2} = 0.0116 \, \mu\text{sec}^{-1} \, \text{torr}^{-1}$