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Author
Hess, Peter

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Peter Hess, A. H. Kung, and C. Bradley Moore

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Vibration → vibration energy transfer in methane

Peter Hess,a) A.H. Kung, and C. Bradley Moore
Department of Chemistry, University of California,
and Materials and Molecular Research Division of
the Lawrence Berkeley Laboratory, Berkeley CA 94720

(Received )

Vibrational energy levels of methane in the range 2800 to 6000 cm\(^{-1}\) were excited by a pulsed tunable laser. Infrared fluorescence decays were observed at 294 K and analyzed to yield \(V \rightarrow V\) energy transfer pathways and rates. Symmetric stretching excitation is converted to asymmetric stretching in the same molecule with a rate constant \(k_1 = (3.6 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} (P = 0.09)\). The \(\nu_2\) and \(\nu_4\) bending vibrations are interconverted somewhat less rapidly. Stretching excitation is converted to bending with a rate constant of \((0.8 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} (P = 0.022)\) for the stretching fundamentals and about twice that for overtone or combination levels. The rate of almost exactly resonant transfer of a vibrational quantum from one molecule to another was about \((1.8 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} (P = 0.05)\) for transfer of a bending quantum from \(\text{CH}_4(2\nu_4)\) and about three times less for transfer of a stretching quantum.
I. INTRODUCTION

Methane is a relatively simple polyatomic molecule whose structure and spectroscopy are well studied. The presence of four fundamental vibrations makes the energy level diagram, Fig. 1, sufficiently complex that methane should be a useful prototype for understanding energy transfer processes in larger molecules. In many molecules CH stretching vibrations are clustered near 3000 cm\(^{-1}\) and bending vibrations in the 1200 - 1500 cm\(^{-1}\) range. The proximity of bending overtones and stretches provides a relaxation path which is undoubtedly important in most hydrocarbons.

In methane energy transfer among the vibrational modes, \(V \rightarrow V\) transfer, is complete in a few microseconds at 1 Torr pressure. Vibrational deactivation to translation and rotation, \(V \rightarrow T, R\) energy transfer, occurs only on the millisecond timescale at 1 Torr. \(V \rightarrow T, R\) relaxation rates have been measured by many methods in pure methane and in mixtures with many other gases. These results have helped to establish a good qualitative understanding of the role of rotation in vibrational relaxation. Laser-excited vibrational fluorescence experiments have given rates for \(V \rightarrow V\) transfer between stretching and bending vibrations. Recent spectrophone data give some qualitative information on the overall mechanism of \(V \rightarrow V\) transfer.

In this work a new powerful tunable ir laser system is used to excite a variety of combination and overtone levels as
well as the fundamental asymmetric stretching level in the 2800 to 6000 cm\(^{-1}\) range. Emission is monitored from both infrared active modes. Hot fluorescence (originating on combination and overtone levels) is distinguished from fundamental fluorescence. There are too many levels even in methane for a complete determination of rate constants coupling each possible initial and final vibrational level. However, rates are determined for the various types of V \(\rightarrow\) V transfer processes and overall relaxation pathways are mapped in a general way.
II. EXPERIMENTAL

The basic experimental method has been described previously.\textsuperscript{4, 9, 10} However, a new much more powerful tunable infrared laser was developed for this work. A Raytheon model SS-404 Nd-YAG laser was used to pump an angle-tuned LiNbO\textsubscript{3} parametric oscillator (OPO). The master oscillator of the Nd:YAG laser is followed by three amplifiers. The bandwidth of the 1.06 µm pump beam was reduced by an etalon in the master oscillator. The Nd:YAG laser output consisted of pulses about 15 nsec in duration with energy limited to 190 - 200 mJ/pulse to avoid damage in the OPO. A repetition rate of 10 sec\textsuperscript{-1} was used in all experiments. The design of the OPO was similar to that described by Byer et al.\textsuperscript{11} and utilised a grating and an etalon as line narrowing elements in the OPO cavity. This reduced the bandwidth of the OPO output to 0.15 cm\textsuperscript{-1}. The signal and idler waves of the OPO output were not separated because in all cases studied here only one of the two wavelengths was coincident with a CH\textsubscript{4} line. Typically, pulses with 3 mJ - 10 mJ were obtained depending on the pump power, the wavelength and whether the idler or the signal was used for excitation. To tune the OPO to desired wavelength the OPO output was reflected into a spectrometer. For fine tuning about 10% of the radiation was reflected into a spectrophone by a quartz beam splitter. The signal and idler were focused into the fluorescence cell, beam diameter one mm, and reflected back through this cell
into a pyroelectric detector which provided the trigger for the signal averaging system. In experiments with a low signal-to-noise the spectrophone was inserted between the fluorescence cell and the trigger detector. The infrared fluorescence was focused by a 5 cm diameter f/1 CaF$_2$ lens onto a Hg:Ge infrared detector cooled with liquid helium. To study hot fluorescence a 3.8 cm long gas filter cell containing 50, 150, 250 or 500 Torr CH$_4$ was placed between the fluorescence cell and the CaF$_2$ lens which focused fluorescence onto the detector. To block the scattered laser radiation three interference filters have been used in all experiments: one cooled inside the detector dewar and the other two external in front of the detector assembly. The preamplified detector signal was further amplified by a Keithley model 104 wideband amplifier and then averaged and recorded with an X-Y plotter. Depending on the line being excited several hundreds to 10,000 pulses were averaged. The signal-to-noise changed from better than 100-to-1 to only about 3 to 1 in two cases. The system response time was shorter than 300 nsec.

A Celesco pressure transducer was used to monitor the pressure in the fluorescence cell continuously. The errors introduced into the pT values are less than 5% in the pressure range studied. The leak rate of the whole glass manifold including pressure gauge and fluorescence cell was below $10^{-3}$ Torr/h.
Matheson research-grade CH$_4$ was used without further purification (impurities in ppm: O$_2$ - 5, N$_2$ - 20, CO$_2$ - 50, C$_2$H$_6$ - 75, and C$_3$H$_8$ - 5). The $^{13}$CH$_4$ sample was provided by Stohler Isotope Chemicals and contained about 90% $^{13}$CH$_4$. $^{12}$CH$_4$ plus $^{13}$CH$_4$ were 98% - 99%. According to the manufacturer there are traces of air and CO. These impurities are far too dilute to affect measurements of the fast V $\rightarrow$ V rates described here. For accurate measurements of the much slower V $\rightarrow$ T, R rates these impurity levels are too high.$^{12}$
III. RESULTS

A. $\nu_3$ fluorescence

The $\nu_3$ band at 3.3 $\mu$ is the strongest infrared-active fundamental of CH$_4$. In this work different bands were excited and the fluorescence from the $\nu_3$ band observed. In the cases of $2\nu_3$, $\nu_3 + \nu_4$, and $\nu_1 + \nu_4$ excitation the interference filters were selected to transmit most of the $\nu_3$ band fluorescence. Inside the detector dewar a broadband filter with 94% maximum transmission and half-transmission points at 2100 and 3150 cm$^{-1}$ was used. At 2000 cm$^{-1}$ and 3250 cm$^{-1}$ the transmission of this filter was less than 1%. Two identical narrowband interference filters were placed outside the detector. These filters had 85% maximum transmission and half-transmission at 2915 - 3060 cm$^{-1}$ and less than 1% outside 2780 - 3175 cm$^{-1}$. For excitation in the P-branch of the fundamental $\nu_3$, fluorescence was observed only in the short wavelength part of the R-branch by using two narrowband interference filters. These had a maximum transmission of 57% and 83%, respectively, about half the maximum value at 3070 and 3205 cm$^{-1}$ and less than 1% transmission outside the R-branch region. In the following subsections the results obtained by exciting different levels and observing the $\nu_3$ fluorescence are described in detail.

Excitation of $2\nu_3$

The excitation of the overtone $2\nu_3$ was performed by
tuning the OPO signal wavelength to 6002.5 cm$^{-1}$, Q(6), and to 6077 cm$^{-1}$, R(6). The relaxation time was independent of the rotational level excited. Hot $v_3$ fluorescence was studied using the gas filter cell with 50 to 500 Torr CH$_4$. The data for 250 and 500 Torr CH$_4$ in the filter cell give the same rates as for pressures down to 50 Torr. The relaxation time derived from these data, Fig. 2, is $1.2 \pm 0.3$ µs Torr. Some experiments were performed without the filter cell. The $\tau_T$ value found for the decay of the total $v_3$ fluorescence was $2.3 \pm 0.5$ µs Torr. By subtracting the hot $v_3$ fluorescence from the total $v_3$ fluorescence a time of $3.3 \pm 0.7$ µs Torr, Fig. 2, was found for $1 + 0$ relaxation of $v_3$. Clearly the total fluorescence decays as the sum of at least two exponentials; thus the fit to a single decay time of 2.3 µsec Torr is meaningless.

**Excitation of $v_3 + v_4$**

Essentially the same experiments as for $2v_3$ were carried out for the combination band $v_3 + v_4$. The Q-branch of this band at 4313 cm$^{-1}$ was excited. The $\tau_T$ values for the fall of the hot and fundamental $v_3$ fluorescence are the same within experimental error as those obtained for $2v_3$ excitation, Fig. 2.

**Excitation of $v_1 + v_4$**

For excitation of the Q-branch at 4216 cm$^{-1}$ the $v_3$ fluorescence decay times are the same as for $2v_3$ and $v_3 + v_4$. 


Fig. 2. The amplitudes of hot and total $v_3$ fluorescence extrapolated to $t = 0$ are the same within a 30% experimental uncertainty. A fluorescence rise time was observed in this case and could be analyzed in the pressure region below 1.5 Torr, Fig. 3. The $\tau$ value for the rise of the hot $v_3$ fluorescence is about 20% smaller than for the rise of the fundamental $v_3$ fluorescence. The rise of the total $v_3$ fluorescence is halfway between, $\tau = 0.55 \pm 0.2$ µsec Torr.

**Excitation of $v_3$**

Experiments carried out for $P(9)$ and $P(6)$ excitation at 2927 cm$^{-1}$ and 2959 cm$^{-1}$ respectively gave the same relaxation time for the fall of $v_3$ fluorescence, Fig. 4. This value of $\tau = 3.2 \pm 0.6$ µsec Torr agrees with the values obtained before within the error limit. Similar experiments performed with a sample containing approximately 90% $^{13}$CH$_4$ and 10% $^{12}$CH$_4$ lead to a slightly longer relaxation time, $\tau = 3.5 \pm 0.6$ µsec Torr than for the normal CH$_4$ sample (see Fig. 4).

B. $n_4$ fluorescence

The fundamental $v_3$, the overtone $2v_3$ and the combination bands $v_1 + v_4$ and $v_2 + v_4$ were excited while $v_4$ fluorescence was observed utilizing 3 interference filters. A long pass filter was used inside the detector with more than 85% transmission around 1300 cm$^{-1}$, half-transmission at 1950 cm$^{-1}$ and less than 1% transmission beyond 2000 cm$^{-1}$. Outside the
detector a second long pass filter was inserted with more
than 90% transmission around 1300 cm$^{-1}$, half-transmission
point at 1510 cm$^{-1}$, and less than 1% transmission beyond
1590 cm$^{-1}$. In addition a wideband pass interference filter
was employed outside the detector. This filter had between
80% and 90% transmission in the $v_4$ band region, half-trans-
mission at 1357 cm$^{-1}$ and 853 cm$^{-1}$, and less than 1% trans-
mission outside 820 cm$^{-1}$ and 1410 cm$^{-1}$. In the following
subsections the $v_4$ fluorescence experiments performed with
this filter combination are described in detail.

**Excitation of $v_3$**

The Q-branch lines Q(3) and Q(4) of the $v_3$ band were
excited at 3018 cm$^{-1}$ with the OPO. Figure 5 shows the
results obtained for the rise of the total $v_4$ fluorescence.
The $p_T$ values derived from this figure are 3.2 ± 0.6 μsec
Torr for the rise of the total $v_4$ fluorescence. The signal-
to-noise was about 50 in these experiments. The rise and
fall of the hot $v_4$ fluorescence were observed by using the
CH$_4$ gas filter cell. Signal intensities are much weaker than
for the total $v_4$ fluorescence. In addition the fall of the
hot $v_4$ fluorescence did not return to the base line on the
μsec timescale but rather on the msec timescale. Therefore,
the uncertainty in the data analysis was much larger in this
case than usual. In Fig. 5 the rise data are displayed.
The approximate value determined from this figure is $p_T$
= 1.8 ± 0.6 μsec Torr for the rise of the hot $v_4$ fluorescence.
The fall data showed even larger scattering due to the baseline problem mentioned above and the low signal-to-noise ratio. Thus the fall time was set equal to the \( v_3 \) fluorescence fall time in order to analyze for the rise times above.

**Excitation of \( v_2 + v_4 \)**

This weak combination band was excited with the idler at 2825 cm\(^{-1}\). The best signal-to-noise achieved by averaging 5,000 to 10,000 shots was about 4, Fig. 6. The comparison of these data for the fall of the hot \( v_4 \) fluorescence with the results for the rise of the hot \( v_4 \) fluorescence exciting \( v_3 \) in Fig. 5 shows that the relaxation time for these two processes is approximately the same (\( \tau_{\text{rel}} = 1.8 \pm 0.6 \) \( \mu \)sec Torr).

**Excitation of \( v_1 + v_4 \)**

The Q-branch of the combination band \( v_1 + v_4 \) was excited at 4217 cm\(^{-1}\). Part of the rise of the total \( v_4 \) fluorescence was instantaneous in this case. By subtracting the hot \( v_4 \) fluorescence from those traces the rise time of the fundamental \( v_4 \) fluorescence was measured. This value agrees with the result obtained for the fall of the hot \( v_4 \) fluorescence using the \( \text{CH}_4 \) gas cell between the fluorescence cell and detector. The \( \tau_{\text{rel}} \) value for these two measurements is 3.0 \( \pm 0.8 \) \( \mu \)sec Torr.

**Excitation of \( 2v_3 \)**

The lines Q(6) and R(6) were excited as in the \( v_3 \)
fluorescence experiments. The rise of the total $v_4$ fluorescence was relatively slow and could therefore be investigated. The rise time was $\tau = 1.5 \pm 0.3$ µsec Torr. Subtraction of the hot $v_4$ fluorescence from the total $v_4$ fluorescence leads to a $\tau$ value of $3.0 \pm 0.8$ µsec Torr for the rise of the fundamental $v_4$ fluorescence.
IV. DISCUSSION

The relaxation time data show that V → V energy transfer processes equilibrate all of the vibrational levels within a few microseconds at 1 Torr pressure. V → T, R relaxation of the equilibrated distribution, 82% CH₄(v₄) and 18% CH₄(v₂), occurs on a millisecond timescale at 1 Torr.³, ⁸

The multitude of overtone and combination levels and of energy transfer processes connecting them permits the determination of only a few rate constants for individual processes. The experimental data consist of intensity versus time for fluorescence from the v₃ mode and from the v₄ mode. The hot fluorescence from each of these modes gives the fraction of excitation in a mode which is associated with overtone and combination levels. In principle each fluorescence vs time curve may be decomposed into a sum of n exponentials where n is the total number of excited levels (Fig. 1) which are populated at some stage of the relaxation process. In practice because the V → V decay times are all of the same order of magnitude only one or two times may be determined from a given decay curve and many of these are identical within experimental error. Conclusions can be drawn regarding classes of processes and approximate rates for overall transfers from overtone and combination levels to fundamental levels and from one fundamental to another.
A. \( v_1 \leftrightarrow v_3 \) stretching equilibration

The most rapid energy transfer observed is the appearance of \( v_3 \) fluorescence following excitation of \( v_1 + v_4 \). The only process which can lead to hot \( v_3 \) is

\[
\text{CH}_4(v_1+v_4) + M \xrightarrow{k_1} \text{CH}_4(v_3+v_4) + M \quad -98 \text{ cm}^{-1}.
\]

(1)

CH\(_4(v_3)\) may be produced subsequently by

\[
\text{CH}_4(v_3+v_4) + \text{CH}_4 \xrightarrow{k_2} \text{CH}_4(v_4) + \text{CH}_4(v_3) - 4 \text{ cm}^{-1},
\]

(2)

or directly by

\[
\text{CH}_4(v_3+v_4) + \text{CH}_4 \xrightarrow{k_3} \text{CH}_4(v_4) + \text{CH}_4(v_3) - 102 \text{ cm}^{-1},
\]

(3)

or by the sequence

\[
\text{CH}_4(v_1+v_4) + \text{CH}_4 \xrightarrow{k_4} \text{CH}_4(v_1) + \text{CH}_4(v_4) + 1 \text{ cm}^{-1}
\]

(4)

\[
\text{CH}_4(v_1) + \text{CH}_4 \xrightarrow{k_5} \text{CH}_4(v_3) + \text{CH}_4 - 103 \text{ cm}^{-1}
\]

(5)

Stretching energy may also be converted to two quanta of bending, \( v_b = v_2 \) or \( v_4 \),

\[
\text{CH}_4(v_1+v_4) + \text{CH}_4 \xrightarrow{k_6} \text{CH}_4((3-n)v_b) + \text{CH}_4(nv_b)
\]

(6)

\[
\text{CH}_4(v_1) + \text{CH}_4 \xrightarrow{k_7} \text{CH}_4((2-n)v_b) + \text{CH}_4(nv_b)
\]

(7)

\[
\text{CH}_4(v_3+v_4) + \text{CH}_4 \xrightarrow{k_8} \text{CH}_4((3-n)v_b) + \text{CH}_4(nv_b)
\]

(8)

\[
\text{CH}_4(v_3) + \text{CH}_4 \xrightarrow{k_9} \text{CH}_4((2-n)v_b) + \text{CH}_4(nv_b)
\]

(9)
For completeness

\[ CH_4(v_3+v_4) \xrightarrow{k_{10}} CH_4(v_1) + CH_4(v_4) + 99 \text{ cm}^{-1} \]  \(\text{(10)}\)

should be considered.

Inspection of the rate equation for this system shows that the concentration of \(CH_4(v_1+v_4)\) decays with the same rate constant, \(k_a\), as for the rise of hot \(v_3\) fluorescence which all comes from \(CH_4(v_3+v_4)\) by process (1). The loss of \(v_1\) quanta, \(CH_4(v_1+v_4)\) and \(CH_4(v_1)\) combined, and production of \(v_3\) quanta, \(CH_4(v_3+v_4)\) and \(CH_4(v_3)\) combined, lead to a smaller rate constant for exponential rise in total \(v_3\) emission, \(k_b = k_a - k_4\). Here it is assumed that \(k_5 = k_1 + k_3\) and \(k_6 - k_7 \ll k_a\). Figure 3 shows that \(k_a\) is greater than \(k_b\) by roughly 5 - 15%. A generous allowance for systematic error due to self-absorption increases the range to 5 - 30%.

Therefore

\[ 0.3 k_a = 0.6 \mu\text{sec}^{-1} \text{Torr}^{-1} \geq k_4 \geq 0.1 \mu\text{sec}^{-1} \text{Torr}^{-1}. \]

The equal (± 25%) amplitudes of hot and total \(v_3\) fluorescence when extrapolated to \(t = 0\) permit the conclusion, after allowing for possible self-absorption, that

\[ k_1 > 3k_3. \]

The relative amplitude of \(v_3\) fluorescence excited through \(v_1 + v_4\) and \(v_3 + v_4\) normalized to the respective spectrophone signals were 1.0 ± 0.3 for hot fluorescence extrapolated to \(t = 0\) and for both hot and total fluorescence for pressure • time = 4 \mu\text{sec} \text{Torr}. Thus \(v_1 + v_4\) equilibrates rapidly with
\( v_3 + v_4 \), process (1), before processes (3), (4) and (6) have proceeded significantly. Thus the \( v_1 \) and \( v_3 \) modes are equilibrated by collision-induced intermode transfer within the excited molecule at a rate fast compared to loss of stretching quanta or transfer from molecule to molecule. When the two stretching modes are equilibrated, 64\% is \( v_3 \) and 36\% is \( v_1 \). The rate constant \((k_1 + k_{-1}) = 1.56 \) \( k_1 \) is the rate constant for approach to this equilibrium. Thus \( k_1 = k_b / 1.56 = 1.2 \pm 0.3 \) \( \mu \)sec\(^{-1}\) torr\(^{-1}\). Rate constants involving \( v_3 \) on the reactants side which are for an equilibrated \( v_3 \) and \( v_1 \) mixture are denoted by a prime, e.g., \( k'_2 = 0.64(k_2 + k_{10}) + 0.36(k_3 + k_4) \). Since \( v_3 \) and \( v_1 \) products are not distinguished, both are included.

**B. Stretch-to-bend deactivation**

Deactivation of \( CH_4(v_3) \) by energy transfer to the bending vibrations has been studied previously by exciting the fundamental band with a chopped He-Ne laser\(^3\) and with a low power pulsed OPO.\(^4\) Here a much higher power OPO is used. The original value for the relaxation time of \( 5.3 \pm 0.8 \) \( \mu \)sec Torr is in reasonable agreement with the low power OPO value of \( 3.9 \pm 0.6 \) \( \mu \)sec Torr. The still shorter value found here, \( 3.2 \pm 0.6 \) \( \mu \)sec Torr, for excitation of the fundamental band may result from some heating by the laser or from the population of hot bands during the relaxation. The decay of "fundamental" fluorescence from overtone and combination excitations, \( 3.3 \) \( \mu \)sec Torr, can be distorted by subtracting
too much (\(\tau\) too long) or too little (\(\tau\) too short) hot fluorescence from the total. Notwithstanding these uncertainties, it can safely be concluded that the total rate of deactivation of \(\text{CH}_4(v_3)\) to bending levels is

\[ k_3' = 0.28 \pm 0.06 \text{ \mu sec}^{-1} \text{ Torr}^{-1}. \]

The \(v_4\) fluorescence observed following the excitation of the \(v_3\) fundamental band was qualitatively the same as observed previously except that S/N was about five times larger. The rise time for hot \(v_4\) fluorescence is the same as the decay time discussed below for \(2v_4\) in \(V + V\) equilibrium with \(v_2 + v_4\). The decay of hot \(v_4\) fluorescence is fit well by the decay constant observed for the \(v_3\) fundamental fluorescence. However, the signal-to-noise is not high enough to make an accurate independent measurement of this decay time. The rise time for the total \(v_4\) fluorescence in previous studies\(^3,\ 4\) was shorter than for the decay of \(v_3\) fluorescence. Here, however, the \(v_3\) fall and \(v_4\) rise are the same within the error margins. We have previously concluded that \(v_3\) was primarily relaxed by transfer to \(2v_4\). All of our data remain consistent with this conclusion. However, the equilibration between \(v_2\) and \(v_4\) proceeds three to four times faster than the stretch bend relaxation and limits the possible difference between \(v_3\) fall and \(v_4\) rise. Furthermore, the possibility of systematic errors caused by self-absorption, by the difficulties of multiple exponential decay analyses, and perhaps, by other unidentified sources suggests
caution with respect to this conclusion.

Observations of \( \nu_4 \) fluorescence following excitation of \( 2\nu_3 \) and \( \nu_3 + \nu_4 \) give similar decay times to those discussed above. However, analysis of these results in terms of single and double exponentials does not give additional information on rate constants. There are just too many processes occurring simultaneously.

C. Relaxation of combination and overtone levels of \( \nu_3 \)

The excitation of \( \text{CH}_4(2\nu_3) \) is followed by rapid equilibration of the \( \nu_3 \) and \( \nu_1 \) vibrations. At the lowest pressures the decay time was observed to be approximately the same as for the rise of \( \nu_3 \) fluorescence following \( \nu_1 + \nu_4 \) excitation. The amplitude of this initial rapid decay was about \( \frac{1}{3} \) as expected from the 36\% population of \( \nu_1 \) when equilibrated with \( \nu_3 \). Further relaxation may occur via the following processes,

\[
\text{CH}_4(2\nu_3) + \text{CH}_4 \rightarrow \text{CH}_4(\nu_3) + \text{CH}_4(\nu_3) - 33 \text{ cm}^{-1}
\]  
(11)

\[
\rightarrow \text{CH}_4(\nu_3 + 2\nu_b) + \text{CH}_4
\]  
(12)

\[
\rightarrow \text{CH}_4(\nu_3 + \nu_b) + \text{CH}_4(\nu_b)
\]  
(13)

\[
\rightarrow \text{CH}_4(\nu_3) + \text{CH}_4(2\nu_b)
\]  
(14)

\[
\text{CH}_4(\nu_3 + 2\nu_b) + \text{CH}_4 \rightarrow \text{CH}_4((4-n)\nu_b) + \text{CH}_4(n\nu_b)
\]  
(15)

\[
\rightarrow \text{CH}_4(\nu_3) + \text{CH}_4(2\nu_b)
\]  
(16)

and by process (9).
The small amplitude of the $\nu_3 = 1 \rightarrow 0$ "cold" fluorescence, 0.3 ± 0.15 of the total after $\nu_3 \leftrightarrow \nu_1$ equilibration, shows that processes (11) and (14) are less important than (12) and (13). The total rate of decay for hot $\nu_3$ fluorescence following $\text{CH}_4(2\nu_3)$ excitation is 0.85 $\mu$s/cm Torr$^{-1}$. The rate for transfer of a $\nu_3$ quantum to bending for $\text{CH}_4(\nu_3)$ is 0.3 $\mu$s/cm Torr$^{-1}$. The rate per quantum of $\nu_3$ should be about the same for $\text{CH}_4(2\nu_3)$ and thus $k'_{12} + k'_{13} + k'_{14}$ might be about 0.6 $\mu$s/cm Torr$^{-1}$. Since (14) requires not only conversion of stretching to bending but also transfer to another molecule, $k'_{14}$ is probably much less than $k'_{12}$.

The major process producing $\text{CH}_4(\nu_3)$ is probably (11). The product of total observed rate and fractional amplitude of "cold" $\nu_3$ fluorescence gives,

$$k'_{11} + 2k'_{14} = (0.85 \, \mu\text{s/cm Torr}^{-1}) \times 0.3 = 0.25 \pm 0.15 \, \mu\text{s/cm Torr}^{-1}.$$ 

Most of the stretching quanta are lost without production of $\text{CH}_4(\nu_3)$ via process (12) and perhaps (13) followed by (15). Thus

$$k'_{12} + k'_{13} = (0.85 \, \mu\text{s/cm Torr}^{-1}) \times 0.7 = 0.6 \pm 0.2 \, \mu\text{s/cm Torr}^{-1}.$$ 

The decays of $\nu_3$ fluorescence following either $\nu_1 + \nu_4$ or $\nu_3 + \nu_4$ excitation give the same relaxation times. The decay of hot $\nu_3$ fluorescence gives the total decay rate from $\nu_3 + \nu_4'$.
The fast initial decay due to equilibration between the $v_3$ and $v_1$ modes is not included in the analysis of the $v_3 + v_4$ results; rates are measured for the last half of the decay. The difference of less than 10% between the rates for $v_3 + v_4$ and $v_1 + v_4$, Fig. 4, is a measure of the systematic error involved.

Following $v_3 + v_4$ excitation and $v_1 \leftrightarrow v_3$ equilibration, excited state concentrations are

$$N_{v_3 + v_4} = N_0 \exp[-k_c t]$$

$$N_{v_3} = N_0 \frac{k_2}{k_2 + k_8 - k_9} \left[ e^{-k_9 t} - e^{-k_c t} \right].$$

If Einstein A coefficients are equal for $v_3$ emission and if the filter transmissions are equal and there is no self absorption, then the fluorescence intensity ratios give the rate constant ratio $[k_2/(k_2 + k_8 - k_9)]$. The total $v_3$ fluorescence was analyzed as the sum of two exponentials with decay rate constants $k_c$ and $k_9$. Since both decay constants are determined independently, the amplitude ratio was determined relatively well. In the pressure range 0.4 to 1 Torr it is constant at $0.25 \pm 0.05$. The constant ratio indicates that self-absorption is negligible below 1 Torr. However, some saturated absorption in the Q-branch may be possible. The true population amplitude ratio could be as high as 0.40.

$$k_c = k_2 + k_8 = 0.85 \pm 0.2 \text{ sec}^{-1} \text{ Torr}^{-1}.$$
The range 0.20 to 0.40 must be considered possible. The ratio \( k'_2/k_c \) is thus in the range 0.12 - 0.34 and \( 2.0 \leq k'_8/k'_9 \leq 3.5 \). Values for \( k'_2 \) and \( k'_8 \) are

\[
0.1 < k'_2 < 0.3 \text{ \mu sec}^{-1} \text{ Torr}^{-1}
\]

\[
k'_8 = 0.7 \pm 0.2 \text{ \mu sec}^{-1} \text{ Torr}^{-1}.
\]

Thus the \( \nu_3 + \nu_4 \) level is primarily relaxed by stretch-to-bend transfer rather than resonant intermolecular transfer. The rate of stretch-to-bend transfer is increased by about a factor of two for \( \nu_3 + \nu_4 \) compared to \( \nu_3 \).

D. Nearly resonant transfers of bending quanta

The bending combination level \( \nu_2 + \nu_4 \) may be relaxed by the process

\[
\text{CH}_4(\nu_2 + \nu_4) + \text{CH}_4 \leftrightarrow \text{CH}_4(2\nu_4) + \text{CH}_4 + 218 \text{ cm}^{-1} \quad (17)
\]

\[
\rightarrow \text{CH}_4(\nu_4) + \text{CH}_4(\nu_2) - 11 \text{ cm}^{-1} \quad (18)
\]

\[
\rightarrow \text{CH}_4(\nu_4) + \text{CH}_4(\nu_4) + 216 \text{ cm}^{-1} \quad (19)
\]

\( V \rightarrow V \) equilibration is then completed by

\[
\text{CH}_4(2\nu_4) + \text{CH}_4 \rightarrow \text{CH}_4(\nu_4) + \text{CH}_4(\nu_4) - 2 \text{ cm}^{-1} \quad (20)
\]

\[
\text{CH}_4(\nu_2) + \text{CH}_4 \leftrightarrow \text{CH}_4(\nu_4) + \text{CH}_4 + 227 \text{ cm}^{-1} \quad (21)
\]

and finally \( V \rightarrow T, R \) relaxation occurs on a much longer timescale. Endoergic transfers to \( \text{CH}_4(2\nu_2) \) and \( 2\text{CH}_4(\nu_2) \) have
been neglected. The relaxation is monitored by observing total fluorescence from the $v_4$ mode and also the hot fluorescence transmitted through a gas filter. Initially there is one quantum of $v_4$ excitation per photon absorbed and all of the fluorescence is hot. After $V + V$ equilibration, conversion of $v_2$ quanta to $v_4$ and sharing of the excitation among molecules yields 1.64 quanta of "cold" excitation, fundamental fluorescence. Total $v_4$ fluorescence increases monotonically toward this limit. The hot $v_4$ fluorescence, Fig. 6, increases or decreases initially depending on whether $k_{17} - k_{18} - k_{19}$ is positive or negative. The small initial increase and plateau of hot $v_4$ fluorescence shows that $k_{17}$ is slightly larger than $k_{18} + k_{19}$. As $v_2 + v_4$ equilibrates with $2v_4$ at a ratio of 1/3, hot $v_4$ fluorescence decays at a rate of

$$0.75 k_{20} + 0.25(k_{18} + k_{19}) = 0.6 \pm 0.2 \mu \text{sec}^{-1} \text{Torr}^{-1}.$$  

The rate constants for intermolecular transfer of bending quanta $k_{20}$ and $k_{18} + k_{19}$ should be of approximately the same order of magnitude and thus $k_{20} \approx 0.6 \mu \text{sec}^{-1} \text{Torr}^{-1}$. From the initial shape of the hot fluorescence curve and from the approximate equalities deduced above we may conclude that

$$k_{17} = 1 \pm 0.5 \mu \text{sec}^{-1} \text{Torr}^{-1}.$$
E. Summary of rates

Table I gives approximate rates for the various types of V → V energy transfer processes which occur in pure CH$_4$. All of the rates fall in the range of roughly 0.1 to 1 μsec$^{-1}$ Torr$^{-1}$, or (0.3 to 3) x 10$^{-11}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$, corresponding to probabilities per gas kinetic collision between 10$^{-2}$ and 10$^{-1}$. The scaling factor appropriate for first order perturbations of harmonic oscillators is listed for each measured rate or type of rate. If these V → V transfer rates scale in this way, then the rates for the process involving transitions between levels ν = 0 and ν = 1 may be found by dividing the reported rate by the factor n. The fastest rate is for transfer of energy within a single molecule between the symmetric and asymmetric stretching modes. The analogous processes for bending vibrations, intramolecular conversion between ν$_2$ and ν$_4$ excitation, is also fast. The stretch-to-bend transfers are dominated by intramolecular conversion of ν$_3$ primarily to 2ν$_4$ and ν$_2$ + ν$_4$. In any case ν$_2$ + ν$_4$ and 2ν$_4$ are rapidly equilibrated. Presumably 2ν$_2$ also equilibrates rapidly with these levels by this rapid intramolecular interconversion of ν$_2$ and ν$_4$ quanta. For the stretch-to-bend relaxation of ν$_3$ it has been observed previously that rare gases are comparably effective to methane itself as energy transfer collision partners. This should be true for all of the intramolecular transfer processes. The intermolecular V → V transfers are slower than the intramolecular ones even
though they involve smaller changes in total vibrational energy. The rates for transfer of a bending or a stretching quantum from one molecule to another are listed at the bottom of Table I.

Recently de Vasconcelos and de Vries\textsuperscript{7} have reported spectrophonc relaxation measurements on CH\textsubscript{4} and CD\textsubscript{4} in which both $v_3$ and $v_4$ excitation were used. Their data are completely consistent with the laser fluorescence data presented here and in previous works.\textsuperscript{3, 4} They observed relaxation times for overall $V + T, R$ relaxation analyzed by a two-state model of $1.63 \pm 0.02$ \(\mu\text{s}ec\ \text{atm}\) for $v_4$ excitation and $1.41 \mu\text{s}ec\ \text{atm}$ for $v_3$ excitation. When $v_3$ is excited, $V \rightarrow V$ equilibration produces an equilibrated mixture of $v_2$ and $v_4$ excitation on a timescale two orders of magnitude faster than detectable by acoustic response. The 3019 cm\textsuperscript{-1} $v_3$ quantum is transferred to an excitation of $2[(0.82 \times 1306) + (0.18 \times 1533)] = 2694$ cm\textsuperscript{-1}. Thus the $V \rightarrow V$ transfer energy discrepancies are deposited instantly as translation-rotation energy and $2694/3019 = 0.89$ of the energy is transferred at the $V + T, R$ rate. It is for this reason that the ratio of observed relaxation times $\tau_{v_3}/\tau_{v_4} = 0.87 \pm 0.02$. The relaxation mechanism from which de Vasconcelos and de Vries derive a $V \rightarrow V$ transfer rate of $0.003 \mu\text{s}ec^{-1} \text{Torr}^{-1}$ is incorrect.

In conclusion, approximate values are found for the different types of $V + V$ energy transfer processes which relax the higher vibrational levels of methane. In systems which
are only partially relaxed the relative speed of intramolecular processes vs intermolecular ones will tend to keep the excitation energy concentrated in the molecule excited. Thus in experiments such as those of Ehrlich\textsuperscript{16} or Yates\textsuperscript{17} and their collaborators on gas-surface interactions the population of CH\textsubscript{4}(2\nu\textsubscript{4}) will be more important than the production of 2CH\textsubscript{4}(\nu\textsubscript{4}) following \nu\textsubscript{3} excitation. To the extent that intramolecular transfers are faster than intermolecular ones, laser-induced chemical reactions of small molecules may be favored by keeping the total energy of a molecule above threshold while energy is transferred to the most effective modes for reactions.

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TABLE I. Rates of collisional V → V energy transfer in CH₄ at 294 K.

<table>
<thead>
<tr>
<th>Processes predominantly intramolecular</th>
<th>$n^a$</th>
<th>$(pt)^{-1}$</th>
<th>$k \times 10^{11}$</th>
<th>$p^b$</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>(μsec⁻¹ Torr⁻¹)</td>
<td>(cm³ molec⁻¹ sec⁻¹)</td>
<td></td>
</tr>
<tr>
<td>$ν₃ + ν₁$</td>
<td>1</td>
<td>$k_1 = 1.2 \pm 0.3$</td>
<td>3.6</td>
<td>0.09</td>
</tr>
<tr>
<td>$ν₂ + ν₄ \leftrightarrow 2ν₄$</td>
<td>2</td>
<td>$k_{17} = 1 \pm 0.5$</td>
<td>3</td>
<td>0.08</td>
</tr>
<tr>
<td>$ν₃ \rightarrow 2ν₉$</td>
<td>1</td>
<td>$k_9 = 0.28 \pm 0.06$</td>
<td>0.8</td>
<td>0.022</td>
</tr>
<tr>
<td>$2ν₃ \rightarrow ν₃ + 2ν₉$</td>
<td>2</td>
<td>$k_{12} + k_{13} = 0.6 \pm 0.2$</td>
<td>1.8</td>
<td>0.05</td>
</tr>
<tr>
<td>$ν₃ + ν₄ \rightarrow 3ν₉$</td>
<td>1-2</td>
<td>$k_8 = 0.7 \pm 0.2$</td>
<td>2.1</td>
<td>0.05</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Intermolecular single quantum transfer</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$ν₄$</td>
<td>2</td>
<td>$k_{20} = 0.6 \pm 0.2$</td>
<td>1.8</td>
<td>0.05</td>
</tr>
<tr>
<td>stretch</td>
<td>2</td>
<td>$k_{11} + 2k_{14} = 0.25 \pm 0.15$</td>
<td>0.8</td>
<td>0.02</td>
</tr>
<tr>
<td>bend and stretch</td>
<td>1</td>
<td>$k_2 = 0.2 \pm 0.1$</td>
<td>0.6</td>
<td>0.02</td>
</tr>
</tbody>
</table>

a. Normalization factor for first order perturbation of harmonic oscillators
b. Probability per gas kinetic collision, $(ptZ)^{-1}$, Ref. 4.
Figure 1. Energy levels of CH$_4$ with laser excitation (→) and some fluorescence (↔) transitions indicated.

Figure 2. Decay of $v_3$ fluorescence following overtone and combination level excitation. Reciprocal lifetime versus pressure for the fall of hot $v_3$ fluorescence, $\tau_t = 1.2 \pm 0.3$ μsec Torr (open symbols) and for the fall of fundamental $v_3$ fluorescence, $\tau_t = 3.3 \pm 0.7$ μsec Torr (solid symbols): 
$\Delta$, $\triangle$ excitation of $2v_3$; $\bigcirc$, $\bigdot$ excitation of $v_3 + v_4$; $\square$, $\blacksquare$ excitation of $v_1 + v_4$.

Figure 3. $V + V$ transfer $v_3 \leftrightarrow v_4$. Reciprocal lifetime versus pressure for the rise of hot $\bigcirc$, total $\blacktriangle$, and fundamental $\square v_3$ fluorescence exciting the combination band $v_1 + v_4$. The slope drawn is 1.8 μsec$^{-1}$ Torr$^{-1}$.

Figure 4. Stretch-to-bend relaxation. Reciprocal lifetime versus pressure for the fall of total $v_3$ fluorescence: $\bigcirc$ excitation of P(9) of the fundamental $v_3$; $\blacktriangle$ excitation of P(8) ($v_3$) in $^{13}$CH$_4$ (sample 10% $^{12}$CH$_4$ and 90% $^{13}$CH$_4$); $\bigdot$ excitation of P(6) of the fundamental $v_3$; $\blacktriangle$ excitation of P(5) $v_3$ in $^{13}$CH$_4$. The decay time for CH$_4$ is $3.2 \pm 0.6$ μsec Torr and for $^{13}$CH$_4$ $3.5 \pm 0.6$ μsec Torr.

Figure 5. $V + V$ transfer among bending levels. Reciprocal lifetime vs pressure for: rise of total ($\bigcirc$) and hot ($\bigodot$) $v_4$
fluorescence after $v_3$ Q-branch excitation; and fall of hot $v_4$ fluorescence after $v_2 + v_4$ excitation. The slopes are 0.31 and 0.55 $\mu$sec$^{-1}$ Torr$^{-1}$.

Figure 6. Hot $v_4$ fluorescence intensity vs time following $v_2 + v_4$ excitation at 1.11 Torr. Beyond 2 $\mu$sec the decay time is 1.5 $\mu$sec. The electronics response time has been increased to 0.3 $\mu$sec. S/N is the lowest of all data used in this work.