Intra- and Intermode Vibrational Energy Flow in CH$_3$F Excited by Irradiation with an Intense CO$_2$ Laser: A Non-Linear Vibrational Relaxation

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The vibrational relaxation mechanism of CH$_3$F whose $v_3$ mode is excited by a transversely excited atmospheric (TEA) CO$_2$ laser-pulse has been discussed on the basis of observation of the laser-induced fluorescence (LIF) of the $v_3$ overtones and of the C–H stretching modes and kinetic analyses. The time-evolved LIF in the 3-$\mu$m region was found to be dependent significantly on the laser fluence; at a low fluence (<0.01 J cm$^{-2}$), the emission intensity increased almost exponentially with a rate similar to the one determined in the experiment with a Q-switched laser, while at a higher fluence (>0.1 J cm$^{-2}$) the emission rose much faster to form a peak which decayed quickly before a second broad peak appeared. In the wavelength-resolved fluorescence measurement, it was found that the kinetics of population in the $v_4$ level were similar to those in the $3v_3$ level, while those in the $v_1$, $2v_5$, $v_2 + v_5$ and $2v_2$ levels behaved in a way different from those in the $v_4$ level. These observations lead to the conclusion that the laser energy poured into the $v_3$ mode flows to the $v_4$ level directly through $3v_3$ as well as by the successive inter- and intramode V–V energy transfers, i.e., $v_3 \rightarrow v_6 \rightarrow v_2$, $v_3 \rightarrow 2(v_2, v_5) \rightarrow v_1 \rightarrow v_4$. A model calculation of the relaxation kinetics, including the direct V–V energy transfer between two $3v_3$ and $v_4$ levels, could reproduce the 3-$\mu$m emission data. Another significant finding is a non-exponential depopulation in the $2v_3$ level, the $v_4$, $v_1$ and other vibrational levels in the 3-$\mu$m region in the final stage of the relaxation. The deactivation rate is larger for a higher level and is a decreasing function of time and is much larger than the V–T/R energy transfer rate determined in the

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experiment of weak laser excitation. This may be attributed primarily to the successive intermode V–V energy transfers from the 3ν₃ to the ν₄, ν₁, 2ν₅, . . . levels which lie between the 2ν₃ and 3ν₃ levels. This process may be repeated if the intramode V–V energy transfer from the 2ν₃ to the 3ν₃ level occurs. The deactivation mechanism found in this experiment is called 'catastrophic cyclic path' which is effective until the relative population distribution in relevant levels between 2ν₃ and 3ν₃ becomes that in equilibrium at the translational temperature of the CH₃F gas.

KEY WORDS: Vibrational relaxation; IR laser-induced fluorescence; vibrational energy transfer; CH₃F, vibrational relaxation of.

INTRODUCTION

In dealing with the mechanism of vibrational energy flow in polyatomic molecules whose specific vibrational mode is excited by laser irradiation, it has become the general consensus that the intramode vibration-to-vibration (V–V) energy transfer dominates the intermode V–V so that a local vibrational quasiequilibrium distribution is attained within the laser-pumped vibrational mode prior to establishment of the steady-state distribution among all modes, and that in the final stage of the relaxation, the vibration-to-translation/rotation (V–T/R) energy transfer occurs from modes having low fundamental frequencies. The former studies on the vibrational relaxation of a number of small polyatomic molecules support this mechanism and are reviewed in detail by Flynn¹.

Of the polyatomic molecules, CH₃F has been investigated the most intensively for its vibrational relaxation. Since the ν₃ C–F stretching mode of CH₃F has the lowest vibrational frequency resonant to the CO₂ laser line and the V–T/R relaxation is relatively slow, a large part of the energy pumped into the ν₃ mode by the CO₂ laser irradiation is stored within various vibrational modes for a relatively long period. This implies that under a quasiequilibrium condition, a population distribution with a high vibrational temperature is realized in each mode, and CH₃F could thus be one of the polyatomic molecules which are adequate for more detailed investigation of their intra- and inter-mode energy transfer mechanism on the basis of observations of laser-induced fluorescence (LIF).

According to the aforementioned general principle of vibrational relaxation, the CH₃F molecules which have absorbed CO₂ laser photons in the ν₃ mode transfer their energies to the ν₄ mode through the following pathway (see Figure 1):
Figure 1  Vibrational energy level diagram of CH$_3$F in which each level represents its degeneracy, and energy transfer reaction is shown by an arrow. In the present model, $v_1$, $2v_5$ and $v_2 + v_5$ are represented by $v_{125}$. $\rightarrow$: intramode V–V; $\leftrightarrow$: intermode V–V; $\longleftrightarrow$: V–T/R energy transfer.

\[ v_3 \rightarrow v_6 \rightarrow v_2, \quad v_5 \rightarrow 2v_2, \quad 2v_5 \rightarrow v_1 \rightarrow v_4 \quad (1) \]

This mechanism was proved by Sheorey and Flynn$^2$ and Apkarian and Weitz$^3$ in the LIF measurement of CH$_3$F excited by a Q-switched CO$_2$ laser. Contrary to this, another pathway, which includes the intramode V–V ladder climbing within the $v_3$ mode and the near-resonant intermode V–V energy transfer between $3v_3$ and $v_4$:

\[ v_3 \rightarrow 2v_3 \rightarrow 3v_3 \rightarrow v_4 \rightarrow v_1 \rightarrow 2v_2, \quad v_2 + v_5, \quad 2v_5 \quad (2) \]

has been proposed based on high-resolution spectroscopic data; this indicates that a number of rotational levels of the $3v_3$ state are strongly Coriolis coupled with those of the $v_4$ state$^4$. The main reason for preference of the pathway in Eqn (1) rather than that in Eqn (2) is that the populations in the bending overtones, $2v_2$ and $2v_5$, are much larger than those in the $3v_3$ level and, moreover, that bending overtones and C–H stretching modes are coupled with each other by Fermi as well as Coriolis interaction$^5,6$. In the pathway of Eqn (1), the population rate in the $v_4$ level should not depend on the average number of CO$_2$ laser
The present authors proposed the pathway in Eqn (2) as a mechanism to explain the aforementioned phenomenon found in the 3-μm emission induced by irradiation of CH₃F with a TEA CO₂ laser. However, Forber et al.⁹ opted for Eqn (1) as a dominant energy flow mechanism on the basis of the measurement of the vibrational temperature for each mode of ¹³CH₃F excited by a TEA CO₂ laser. More recently, Apkarian et al.¹⁰ carried out a model calculation of coupled rate equations which were formulated based on Eqn (1) as well as Eqn (2) to conclude that the direct V–V transfer from 3ν₃ to ν₁/ν₄ could not occur even under a strong laser excitation condition, since the vibrational heat capacity of the ν₁, ν₄, 2ν₂, ν₂ + ν₅, 2ν₅ levels was too large to fill them from 3ν₃.

If the observed increase of the population rate in the ν₁, ν₄ levels of CH₃F molecules whose ν₃ mode is excited by a strong CO₂ laser is attributed to the existence of the pathway in Eqn (2) as well as Eqn (1), the intermode V–V energy transfer from the 3ν₃ to the ν₄ level must be extraordinarily efficient. According to the established view¹ of the collision probability of V–V energy transfer rates, its rate may not be large unless both the energy non-resonance, which must be transferred to/from translation/rotation, and the change in the number of vibrational quanta are minimized. Therefore, it would be of fundamental importance to clarify the mechanism of the intermode energy flow in CH₃F molecules whose specific mode is excited by a strong CO₂ laser.

In this paper, we report the measurements of the wavelength-resolved infrared (IR) fluorescence from CH₃F whose ν₃ mode is excited by irradiation with a TEA CO₂ laser and the kinetic analysis of the relaxation process. The main purpose of this study is to test
whether the kinetics of the population in each vibrational level is
dependent or not on an initial amount of the laser energy which is
poured into the $\nu_3$ mode of CH$_3$F and to seek a more general
vibrational energy flow mechanism which is applicable irrespective of
the extent of laser irradiation.

EXPERIMENTAL

The $\nu_3$ mode of CH$_3$F in a gas cell was excited by irradiation with the
9.4-$\mu$m P(20) line of a TEA CO$_2$ laser (Lumonics, TE-102-2). The
laser pulse energy was adjusted in the range of 0.7–0.01 J by placing an
appropriate number of polyethylene films (0.01 mm in thickness) in
the pathway of the laser beam as an attenuator. The laser energy and
the pulse shape were measured by a calorimeter (Gentec, Ed-500) and
by a photon-drag detector (Rofin, 7400), respectively. The pulse was
composed of a spike of 200-nm FWHM and a tail of 1.5 $\mu$s duration
down the laser medium was a mixture of He : CO$_2$ : N$_2$ = 3 : 1 : 0.4 and
the pulse repetition frequency was 2.5 Hz. The cross-section of the
laser beam was reduced to the size of $9.5 \times 6.5$ mm by use of a ZnSe
condenser lens, so that the laser fluence was increased up to 1 J cm$^{-2}$.

The laser intensity was not completely homogeneous throughout the
cross-section. In fact, the fluence distribution across the beam cross-
section was determined by probing energy of the laser beam which
passed through a pin-hole of 1 mm inner diameter by a pyroelectric
energy meter. The result of this measurement indicates that it is a good
approximation to assume the above size of the cross-section for
homogeneous intensity of the laser beam.

Two types of gas cell were employed. The first one was designed
according to the proposal of Manuccia and Frankel$^{11}$, and was
employed for measurement of the dispersed LIF spectrum. The
second was one for observing a time-evolved IR fluorescence at a fixed
wavelength. Both systems were composed of a Pyrex glass cell (10 cm
i.d. and 30 cm in length) which includes two mirror systems: one for
multiple reflection of the incident laser beam and the other for
collection of the induced IR fluorescence. The latter mirror system was
of the Welsh type$^{12}$. In the first arrangement of the cell, five plane
mirrors were placed inside the cell as a pentagonal column whose
internal surfaces enabled the incident laser beam to traverse a long
distance when the incident direction of the beam was slightly tilted from one perpendicular to the column axis. In this experiment, the incident laser beam reflected on the internal mirrors 24 times, its pathlength being about 1.5 m; at the end of the beam's traverse the laser intensity was attenuated to about one-half of the original value. Since this attenuation was unfavorable for quantitative discussion of the fluorescence data, a second arrangement of the mirror system was employed; the laser beam was reflected only three times by two parallel plane mirrors placed 12 cm apart from each other, so that the attenuation of the laser intensity was less than 10%. The LIF collected by the Welsh mirror system was taken to a monochromator ($f = 3.4$) with a 4-$\mu$m blazed grating of 300 groove mm$^{-1}$ or to band pass filters for 3 and 5-$\mu$m regions before illuminating an InSb photovoltaic detector (Fujitsu, IV200). The signal was initially treated by a current preamplifier (PAR, 181) whose frequency response was d.c. to 0.67 MHz ($-3$ dB), and this output was amplified by an amplifier (Brookdeal, 9454) with a bandwidth of 0.1 Hz–3 MHz ($-3$ dB). The final signal was digitized and accumulated by a data processor (Iwasaki, SM 1300). Normally, 1024 or 2048 data were averaged to improve the $S/N$ ratio. The time response function of the detector system was determined to be about 3 $\mu$s by use of a GaAs IR emission diode which was pulsed by an electric square wave. Calibration of the sensitivity of the monochromator, including the detecting system, was made by a spectral measurement of the radiation from a homemade black body furnace. The discharge noise of the TEA CO$_2$ laser was employed as a trigger pulse for timing the signal processing system; the time between the trigger and the CO$_2$ laser pulse was determined to be 1.5–0.5 $\mu$s by monitoring the laser pulse by the photon-drag detector. The fluctuation of this delay time was disregarded because of the relatively long response time of the detector. Special attention was paid to reducing the discharge noise of the TEA CO$_2$ laser which interfered significantly with the signal processing. The entire laser apparatus was covered by copper plates of 0.3 mm in thickness, and the LIF measurement system, including the monochromator, the detector and the current preamplifier, was also shielded by copper plates.

The sample gas of CH$_3$F was a commercial gas (PCR) with a nominal purity of 97–98%, and was employed after repeated solidification at liquid N$_2$ temperature. According to the mass spectroscopic analysis, the impurity content was less than 0.4%. The pressure of the sample
gas in the cell was measured with a capacitance manometer (MKS Baratron, 210).

The average number of CO$_2$ laser photons which were absorbed by one CH$_3$F molecule was determined by the absorption measurement; the attenuation of the laser beam through traversing a cell of 1 m in length containing CH$_3$F was determined by the energy measurement of the laser pulse.

RESULTS AND DISCUSSION

Undispersed LIF at 3μm

The observed temporal behavior of the 3-μm emission from CH$_3$F whose $v_3$ mode is excited by irradiation with a TEA CO$_2$ laser, 9.4-μm P(20) line, is shown in Figure 2 as a function of the laser energy fluence. The data taken at a low fluence and reproduced in Figure 2(a) shows that the emission rises almost exponentially to a plateau, although a large discharge noise of the laser makes it difficult to trace the initial rise of the emission accurately. Disregarding the noise, it is seen that the rise rate is in the same order of magnitude as the one reported on the excitation by a Q-switched CO$_2$ laser (cf. Figure 6(b) of Ref. 2). In contrast to this, as shown in Figure 2(b), increasing the fluence of the laser, the emission rises much faster to form a peak which is followed by a second broad peak. This observation is analogous to that found by Sheorey and Flynn$^2$ under focused irradiation with a Q-switched CO$_2$ laser (cf. Figure 6(a) of Ref. 2). In the data of Figure 2(c) which has been observed at the highest fluence of this experiment, the emission forms a clear peak in the initial stage, while the second broad peak in Figure 2(b) changes to a shoulder of the initial peak.

The results shown in Figure 2 imply that we may not apply the energy flow mechanism of Eqn (1) to interpret the observed dependence of the 3-μm emission of the laser fluence. According to the mechanism of Eqn (1), the vibrational relaxation proceeds towards a quasiequilibrium state, in which the population distribution in each mode is of the Boltzmann type. Therefore, populations in respective levels except those of the laser-pumped mode may not exceed the magnitudes defined by the quasiequilibrium condition. For example, populations in the $v_1$ and $v_4$ levels grow after the pulsed excitation of the $v_3$ mode and approach the steady-state values with a rate defined by
Figure 2  Time-evolved LIF taken through the 3-μm bandpass filter as a function of the energy fluence of the TEA CO₂ laser at 0.5 Torr of CH₃F pressure. A spike signal at t = 0 is due to the discharge noise of the laser.

combination of the intra- and intermode V–V energy transfer rates and, thus, the rate must be much less dependent on the laser fluence than the observed one.

It has been suggested by Sheorey and Flynn² that a rapid accumulation of population in the v₁ + v₃ or v₄ + v₃ level through the resonant process:

\[
\text{CH}_3\text{F}(v_1) + \text{CH}_3\text{F}(v_3) \rightarrow \text{CH}_3\text{F}(v_1 + v_3) + \text{CH}_3\text{F}(0)
\]  (3)

results in an initial rapid rise of the emission due to the transition v₁ + v₃ → v₃. However, the population in the v₁ or v₄ level is limited to the amount in equilibrium at room temperature, so that it would be difficult to explain the significant increase of the fluorescence intensity just after the excitation with a high laser fluence. Moreover, even if Eqn (3) contributes to the initial rapid rise of the 3-μm emission, the emission intensity must exceed the initial value in the later stage since populations in the v₁ and v₄ levels should grow due to the mechanism of
Eqn (1). This expectation was not realized in the present experiment using strong laser excitation.

The observed phenomenon on the ν3 emission of CH3F excited by the TEA CO2 laser may not be attributed to a multiple photon absorption. The 3-μm emission of CH3F was induced by irradiation with only two CO2 laser lines, i.e. the 9.4-μm P(20) and the 10.2-μm R(20) lines. Of these lines, the latter induced the emission with its intensity being 1/100 that of the former. It is well known that the frequency of the 9.4-μm P(20) line is near-resonant to the qQK(12)(K = 1, 2) ν = 0 → 1 transition of the ν3 mode13. Thus, the linear resonant absorption in the ν3 mode must be the major factor which determines the initial condition of the laser excitation.

Dispersed fluorescence spectra of ν3 overtone and C—H stretching bands

Figure 3 shows the time-resolved fluorescence spectra of the ν3 overtone band taken at intervals of 0.01 μm. Since the wavelength resolution of the monochromator is not sufficient to separate each vibration-rotation line, the observed spectra of the ν3 = 2 → 0, 3 → 2 and 4 → 2 transitions of the ν3 overtone overlap with each other. The intensity of the spectral line for the vibration-rotation transition ν′J′K′ → ν″J″K″ of a symmetric top molecule is described as

\[
I_{\nu'J'K'\rightarrow\nu''J''K''} = C_{\text{em}}(\omega_{\nu'J'K'})^4 S_{J'K'}^{J''K''} (g_{J'K'} g_{J''K''}/2J' + 1) g_{J'K'}^2 \frac{\exp[-hcF(J'K')/kT_R]}{Q_R} |M_{\nu'}|^2 N_{\nu'}
\]

(4)

where the notations are defined as follows:

- \(C_{\text{em}}\), a constant (= 64 ω^4c/3);
- \(\omega_{\nu'J'K'}\), wavenumber of the \(\nu'J'K' \rightarrow \nu''J''K''\) transition \(= F(J'K') - F(J''K'') + G(\nu') - G(\nu'')\);
- \(S_{J'K'}^{J''K''}\), angular part of the dipole moment matrix element;
- \(M_{\nu'}\), vibrational contribution to the dipole matrix element;
- \(T_R\) and \(Q_R\), rotational temperature and rotational partition function, respectively;
- \(g_{J'K'}\) and \(g_{J''K''}\), degeneracy of the \(J'K'\) state and spin degeneracy, respectively;
- \(N_{\nu'}\), population density in \(\nu'\) level of the relevant vibrational mode.
Figure 3  Dispersed time-resolved fluorescence spectra of the ν₃ overtone band of CH₃F at 0.5 Torr excited by 9.4-µm P(20) CO₂ laser line with the fluence of 0.52 J cm⁻². The spectra taken at the delay times of 2.0, 4.0, 10.2 and 102 µs are shown in frames (a)–(d), respectively. The calculated contributions of respective vibrational transitions of ν₃ = 2→0, 3→1 and 4→2 are given in (e) in which each rotational line is shown in only for 2→0 band.

Equation (43) can be reformed by introducing a function \( U(ν'J'K') \) as:

\[
I_{ν'J'K'}^{νJK} = u(ν'J'K')(|M_ν'|^2N_ν')
\]  

(5)

If the monochromator which is set at a wavenumber \( ω_i \) has a spectral slit function \( f(ω_i, ω) \), the observed emission intensity at this wavenumber is described as:

\[
I(ω_i) = \sum_{ν'} \sum_{J'K'} u(ν'J'K')f(ω_i, ω)ν'J'K'\nu(ν')\nu(ν')(|M_ν'|^2N_ν')
\]

\[
= \sum_{ν'} U(ν', ω_i)(|M_ν'|^2N_ν').
\]  

(6)
Thus, by defining \( u(v'J'K') \) for vibrational transition from the \( v' \) level, the population multiplied by the dipole transition matrix element can be determined from the observed emission spectrum. The function \( U(v', \omega_i) \) in the present experimental condition is given in Figure 3(e) in which bars indicate the relative magnitude of \( \Sigma_K u(v'J'K') \) for \( v' = 2 \rightarrow 0 \) transition of the \( v_3 \) mode. In Figure 3 the calculated spectrum is also given assuming relative values for \( |M_{v'}|^2 N_{v'} \) from which the spectrum best fitted to the observed one is obtained. The relative fluorescence intensity from each of the \( 2v_3, 3v_3 \) and \( 4v_3 \) levels is determined to be \( 1:0.4:0.02, 1:0.80:0.10, 1:0.80:0.10 \), and \( 1:0.50:0.02 \) for respective delay times of \( 2.0, 4.0, 10.2 \) and \( 102 \mu s \) after irradiation with the laser pulse. It is seen from Figure 3 that the populations in higher levels increase in the later stage indicating the ‘up-the-ladder’ intramode \( V-V \) energy transfer pumping. Since the spectrum calculated by Eqn (6) agrees very well with the observed \( v_3 \) overtone emission spectrum, in the later experiments, the emissions at three wavelengths are selected for determination of the relative populations in the \( 2v_3, 3v_3 \) and \( 4v_3 \) levels, i.e. the relative fluorescence intensities \( I_2, I_3 \) and \( I_4 \) from respective vibrational levels of \( v_3 = 2, 3 \) and \( 4 \) in the \( v_3 \) mode are determined as follows:

\[
I_2 = I_{4.76}/U(2, 4.76), \tag{7a}
\]

\[
I_3 = [I_{4.84} - U(2, 4.84)I_2]/U(3, 4.84), \tag{7b}
\]

\[
I_4 = [I_{4.92} - U(2, 4.92)I_2 - U(3, 4.92)I_3]/U(4, 4.92), \tag{7c}
\]

where the observed fluorescence intensities at \( 4.76, 4.84 \) and \( 4.92 \mu m \) are denoted as \( I_{4.76}, I_{4.84} \) and \( I_{4.92} \), respectively.

The time-resolved fluorescence spectrum of the \( \text{C—H} \) stretching bands taken at the interval of \( 0.01 \mu m \) in the region from \( 3.19 \) to \( 3.59 \mu m \) is shown in Figure 4. The spectral analysis of the band is very complicated, since the emission is composed of a number of vibrational transitions, which densely overlap with each other. In Figure 4(d), the calculated spectrum for each vibrational transition is given on the basis of the data reported by Gigure and Overend\(^{14} \). Recently, Graner and coworkers\(^{5,6} \) have reported a new set for the assignment: \( v_1, 2v_2, 2v_5^0 \) for \( A_1 \) symmetry and \( v_4, v_2 + v_5, 2v_5^2 \) for \( E \) symmetry. According to their analysis, these vibrational states form a group of Fermi-coupled states in each symmetry and moreover, there are many Coriolis-coupled rotational levels belonging to different vibrational
Figure 4 Dispersed fluorescence spectra of CH$_3$F in the 3-$\mu$m region under the same conditions as those given in Figure 3. Frames (a)–(c) are the spectra taken at the delay times of 2.8, 6.4 and 300 $\mu$s, respectively. In (d), the contributions of respective vibrational transitions are given.

states. Therefore, it is difficult to estimate the extent of the contribution of respective vibrational states to the observed fluorescence spectrum. Nevertheless, in a shorter wavelength region, the $v_4$ vibration band is isolated from other bands due to relatively weak Fermi coupling with $v_1$ vibration. Thus, it can be stated that the population rate in the $v_4$ level in the early stage of the relaxation is larger than that in the $v_1$, $2v_5$, . . . levels. In Figure 4 the observed spectral intensities in the wavelength range 3.2–3.3 $\mu$m are also found to be larger than those of the calculation. This might be attributable to a perturbation due to Coriolis coupling between the 3$v_3$ and $v_4$ state which has been pointed out already by Graner and Guelachvili$^5$.

The time-evolved emissions of the $v_3$ overtone and those in the 3-$\mu$m region observed through the monochromator are shown in Figure 5. The emission data at the three wavelengths in Figure 5(a), (b) and (c) may yield the relative values for the populations in the 2$v_3$, 3$v_3$ and 4$v_3$
states, respectively, on the basis of Eqns (7a)–(7c). The $2\nu_3$ population increases quickly to a peak which decays with an initial large rate. The population in the $3\nu_3$ level behaves in a way similar to that in the $2\nu_3$ level. The time-evolved emissions at 3.29, 3.43 and 3.52 $\mu$m are also shown in Figure 5(d)–(f). Referring to the spectrum given in Figure 4, the emission at the shortest wavelength can be interpreted as the contribution of population in the $\nu_4$ level, while the data at the other two wavelengths are due to the densely overlapped emission bands from the $\nu_1$, $2\nu_5$, $\nu_2 + \nu_5$ and $2\nu_2$ level. The emission at 3.29 $\mu$m rises quickly to form a peak in the early stages of relaxation. This behavior is common to that observed in the $\nu_3$ overtone. Emission in the longer wavelength region rises slightly after increase of the emission intensity at a shorter wavelength, reaching an almost constant intensity, although it does not form a clear peak. This finding implies that the kinetics for the $\nu_4$ population are different from those of the other levels; $\nu_1$, $2\nu_5$, $\nu_2 + \nu_5$ and $2\nu_2$. These data will be discussed by comparison with the computer modelling of the relaxation kinetics.
Average number of photons absorbed per CH₃F molecule

The average number of laser photons absorbed per CH₃F molecule, ⟨n⟩, has been determined from observation of the intensity attenuation of the laser beam which passes through the CH₃F gas in a cell 1 m in length. Figure 6 indicates that ⟨n⟩ is dependent on the laser fluence as well as on the pressure. The value of ⟨n⟩ is defined by:

\[ ⟨n⟩ = \int [σ(t)/nhcω]N^0 - N^1 dt, \tag{8} \]

where N is the number density of CH₃F, and N⁰ and N¹ are those in the ground and excited levels, respectively, which may interact with the laser field, I(t) is the laser intensity at time t, σ is the absorption cross section, and ω is the laser frequency. Using the reported values of the absorption cross-section and the rotational relaxation rate constant assuming that the qQ₁(12) and qQ₂(12) transitions to be resonant with the CO₂ laser line, it was impossible to reproduce the data given in Figure 6 based on Eqn (8) combined with the kinetic scheme described later. This is probably due to the power broadening of spectral lines and the collision-assisted multiple photon absorption. A value of ⟨n⟩ exceeding 0.5 at higher fluences is attributable to the fact that CH₃F excited to the v₃ level makes collisional–rotational transitions to levels

![Figure 6](image-url)
which enable \( \text{CH}_3\text{F} \) to absorb another photon to attain the \( 2\nu_3 \) level during the laser pulse. This has been demonstrated in the \( \text{CO}_2 \) laser irradiation of the \( \text{CH}_3\text{F}/\text{Ar} \) mixture\(^\text{16}\).

Table I  Frequency difference in MHz of the rotation–vibration transitions of the \( \nu_3 \) mode from the laser line, 9.4 \( \mu \)m \( P(20) \)^a.

| \( K \) | \( ^aP_K(1) \) | \( ^aQ_K(11) \) | \( ^aQ_K(12) \) | \( ^aQ_K(13) \) | \( ^aR_K(8) \) | \( ^aR_K(20) \) | \( ^aR_K(35) \) |
|---|---|---|---|---|---|---|---|
| 0 | 1587 | 1726 | 3632 | -7047 |
| 1 | 8070 | -28.8 | -8786 | 1745 | 3641 | -7070 |
| 2 | 8152 | 43.8 | -8724 | 1830 | 3669 | -7100 |
| 3 | 8295 | 171 | -8615 | 1972 | 3715 | -7166 |
| 4 | 8508 | 360 | -8450 | 2170 | 3779 | -7259 |
| 5 | 8801 | 625 | -8217 | 2426 | 3861 | -7378 |
| 6 | 9192 | 980 | -7900 | 2738 | 3962 | -7524 |
| 7 | 9700 | 1445 | -7480 | 3107 | 4081 | -7696 |
| 8 | 2043 | -6935 | 3533 | 4218 | -7894 |
| 9 | 2799 | -6238 | 4373 | -8119 |

\(^a\) The laser frequency \( \nu_L \) is 31,383,905.6 MHz determined by Chang\(^\text{13}\), and the rotation–vibration transition frequencies are obtained based on the molecular constants given by Freund et al.\(^\text{18}\).

The pressure dependence of \( \langle n \rangle \) is attributable to the collision broadening of the absorption spectral line and also to the collision-induced rotational transitions which suppress saturation of the stimulated transitions. As shown in Table I, the laser line of 9.4 \( \mu \)m \( P(20) \) is near resonant to a number of transitions of \( \nu_3 = 0 \rightarrow 1, 1 \rightarrow 2, 2 \rightarrow 3 \) etc., in which \( \nu_3 \) denotes the vibrational quantum number of the \( \nu_3 \) mode. The absorption cross-section of the \( \nu \)th vibration–rotation transition in those listed in Table I is defined as follows, taking the collision broadening and the power broadening as well as the Doppler effect into account:

\[
\sigma_i(\nu, I) = \int_{-\infty}^{+\infty} \frac{S_i \gamma_p}{\pi} \frac{1}{(\nu_i - \nu')^2 + \gamma_p^2 + \chi^2} f^D(\nu', \nu_i) d\nu',
\]

where \( \nu_i \) is the frequency of the \( \nu \)th line, \( \gamma_p \), the collision frequency, \( \chi \), the Rabi frequency, \( f_D(\nu', \nu_i) \), the Doppler line profile, and

\[
S_i = (8\pi^3 v_i / 3hc) |M_{ii}|^2.
\]
in which $|M_i|$ is the transition dipole moment. This value is described by the vibrational and rotational contributions:

$$|M_i|^2 = |M|^2 S_i. \quad (11)$$

The value of $|M|^2$ for the $\nu_3 = 0 \rightarrow 1$ transition of CH$_3$F was determined by Saeki et al. to be $0.1953 \pm 0.07$.

Owing to multimode oscillation of the present TEA CO$_2$ laser, the laser pulse is composed of a number of lines whose frequency distributes over a range as wide as 1 GHz. Assuming the Lorentz function to describe the frequency distribution of the CO$_2$ laser line, the effective absorption cross section due to the $i$th transition of CH$_3$F for the laser line is defined as:

$$\sigma_i(\tilde{v}_L) = \int \sigma_i(v) g(v) dv / \int g(v) dv \quad (12)$$

where $\tilde{v}_L$ is the mean frequency of the laser line. The average number of photons absorbed per CH$_3$F molecule may be calculated by the equation:

$$\langle n \rangle = \sum_i \left[ \sigma_i(\tilde{v}_L) I(t) / N h \tilde{v}_L \right] (N^i_{\text{lower}} - N^i_{\text{upper}}) dt \quad (13)$$

where $N^i_{\text{lower}}$ and $N^i_{\text{lower}}$ are the number densities of CH$_3$F molecules in the lower and upper levels of the $i$th transition, respectively, and $N$ is the total number density of CH$_3$F. The summation in Eqn (13) must be made on respective transitions of the $\nu_3$ vibration listed in Table I, and $N^i$ values are the solution of the coupled rate equations that describe the stimulated transitions and the rotational and vibrational energy transfer collisions. If these rate equations are formulated for each population in respective levels of $J, K$ states relating to the stimulated transition induced by laser irradiation, the number of coupled rate equations to be solved is very large, and it becomes physically unrealistic. Thus, we define a parameter which represents an average absorption cross-section for the $\nu_3 = \nu'' \rightarrow \nu'$ transition as follows:

$$\sigma_{\nu''} = \sum_i \sigma_i(\tilde{v}_L) f_i / \sum_i f_i, \quad (14)$$

where $f_i$ is the fraction of population in the lower rotational level of the vibrational state $\nu''$ for the $i$th transition. Assuming the average effective
(apparent) cross-section defined above, the kinetic equation is formulated to describe the laser-induced stimulated transitions and the collisional rotation as well as vibration transfer processes. It is assumed that a fraction of the population in the \( v' \) states possesses the absorption cross section of Eqn (12) and this fraction is a function of the laser fluence:

\[
    f = f_0 + aI(t), \quad \text{for } v_3 = 0
\]
\[
    f = aI(t) \quad \text{for } v_3 = 1 \text{ and } 2 \tag{15}
\]

where \( f_0 \) is estimated to be 0.042 assuming the thermal rotational equilibrium distribution at room temperature, and \( I(t) \) is the laser power at time \( t \), and a coefficient \( a \) is selected so that the calculated value of \( \langle n \rangle \) fits with the observed values given in Figure 6. If the fraction \( f \) introduced in Eqn (14) is a certain constant value independent of the laser power, the calculated result of \( \langle n \rangle \) may not reproduce the experimental data which is a function of the laser fluence as well as the \( \text{CH}_3\text{F} \) pressure. Thus, the laser stimulation scheme presented above is adopted to model the excitation and relation kinetics of laser-irradiated \( \text{CH}_3\text{F} \) molecules.

**Excitation and relaxation kinetics**

Simultaneous differential equations are formulated to describe the excitation and relaxation kinetics of \( \text{CH}_3\text{F} \) whose \( v_3 \) mode is excited by irradiation with the 9.4-\( \mu \text{m} \) P(20) line of the TEA \( \text{CO}_2 \) laser pulse. The vibrational levels taken into consideration are summarized in Table II. For convenience, one vibrational level which represents both the \( v_2 \) and \( v_5 \) levels is assumed by introducing the increased degeneracy and is designated \( v_{25} \)—the energy level is the average of \( v_2 \) and \( v_5 \) weighted by their degeneracies. A similar treatment was taken for levels in the \( \text{C—H} \) stretching region. Referring to the emission spectrum given in Figure 4, it is seen that one cannot discriminate respective contributions of the \( v_1, 2v_2, v_2 + v_5 \), and \( 2v_5 \) levels to the observed emission spectrum. Moreover, according to the high resolution spectroscopic studies, these vibrational states couple strongly with each other by Coriolis and Fermi interactions\(^5\).\(^6\). Therefore, five vibrational states are presented by one state \( v_{125} \) whose degeneracy is seven in the present model. The vibrational frequencies listed in Table II are taken
from Freund et al.\textsuperscript{18} for $v_3$, Gigure and Overend\textsuperscript{14} for $v_1$ and $v_4$ and Shimanouchi\textsuperscript{19} for the others.

**Table II** Vibrational energy levels of CH$_3$F taken into account in the kinetic model calculation.

| Level number | Level       | Energy (cm$^{-1}$) | Degeneracy |
|--------------|-------------|--------------------|------------|
| 1            | $v_3$       | 1049               | 1          |
| 2            | $v_6$       | 1182               | 2          |
| 3            | $v_{25}$\textsuperscript{a} | 1466               | 3          |
| 4            | $2v_3$      | 2081               | 1          |
| 5            | $v_3 + v_6$ | 2230               | 2          |
| 6            | $2v_6$      | 2348               | 3          |
| 7            | $v_3 + v_{25}$ | 2515              | 3          |
| 8            | $v_6 + v_{25}$ | 2634              | 6          |
| 9            | $v_{125}$\textsuperscript{b} | 2914              | 7          |
| 10           | $v_4$       | 3009               | 2          |
| 11           | $3v_3$      | 3098               | 1          |
| 12           | $v_3 + v_{125}$ | 3963              | 7          |
| 13           | $v_3 + v_4$ | 4058               | 2          |
| 14           | $4v_3$      | 4099               | 1          |
| 0            | 0           | 0                  | 1          |

\textsuperscript{a} $v_2(A_1)$ 1464, $v_5(E)$ 1467 cm$^{-1}$.

\textsuperscript{b} $v_1(A_1)$ 2966, $2v_2(A_1)$ 2926, $2v_5(A_1)$ 2863, $v_2 + v_5(E)$ 2927, $2v_5(E)$ 2922 cm$^{-1}$.

In Table III, the energy transfer processes taken into consideration are summarized together with the non-resonant energy $\Delta E$, and the rate constant assigned to each process. The energy transfer process may be categorized into three groups: intermolecular intramode V–V energy transfer, intra- or intermolecular intermode V–V, and V–T/R energy transfer. Of intramode V–V energy transfers, the energy transfer from $v_{25}$ to $2v_5$ is the assumed to occur through the intermediate state of $v_2 + v_5$, since the $2v_5$ level is Fermi coupled and greatly shifted. The intermode V–V energy transfers considered here are all involved in the relaxation mechanism proposed by Sheorey and Flynn\textsuperscript{2} and also by Apkarian and Weitz\textsuperscript{3}, except for process [18] (in Table III) which is the direct energy transfer between $3v_3$ and $v_4$. This latter process is assumed to occur collisionally and will be discussed later. V–T/R energy transfer is assumed to occur from $v_3$ and $v_6$ modes. Most of the rate constants for the energy transfer processes [1]–[23] are taken from the papers of Sheorey and Flynn\textsuperscript{2} and Apkarian and Weitz\textsuperscript{3}. However, there remain many unknown rate constants that must have been
Table III  Energy transfer processes assumed in the kinetic model calculation.

| Process | \( \Delta E (\text{cm}^{-1}) \) | Rate constant \( (\text{s}^{-1} \text{Torr}^{-1}) \) |
|---------|-------------------------------|-------------------------------------------|
| **Intramode V-V energy transfer** | | |
| [1] \((v_3) + (v_3) \rightarrow (2v_3) + (0)\) | +17 | \(k_{a3} = 2.4 \times 10^6 \) \(^b\) |
| [2] \((2v_3) + (v_3) \rightarrow (3v_3) + (0)\) | +32 | \(k_{a33} = 3.7 \times 10^6 \) \(^d\) |
| [3] \((3v_3) + (v_3) \rightarrow (4v_3) + (0)\) | +48 | \(k_{a333} = 4.9 \times 10^6 \) \(^d\) |
| [4] \((v_6) + (v_6) \rightarrow (2v_6) + (0)\) | +16 | \(k_{a6} = 1 \times 10^6 \) |
| [5] \((v_{25}) + (v_{25}) \rightarrow (v_{125}) + (0)\) | 0 | \(k_{a25} = 1.6 \times 10^6 \) \(^c\) |
| [6] \((v_3) + (v_6) \rightarrow (v_3 + v_6) + (0)\) | +1 | \(k_{a36} = 1 \times 10^6 \) \(^f\) |
| [7] \((v_3) + (v_{25}) \rightarrow (v_3 + v_{25}) + (0)\) | 0 | \(k_{a23} = 1 \times 10^6 \) \(^f\) |
| [8] \((v_6) + (v_{125}) \rightarrow (v_3 + v_{125}) + (0)\) | 0 | \(k_{a13} = 1 \times 10^6 \) \(^f\) |
| [9] \((v_6) + (v_{25}) \rightarrow (v_6 + v_{25}) + (0)\) | +14 | \(k_{a26} = 1 \times 10^6 \) \(^f\) |
| [10] \((v_3) + (v_4) \rightarrow (v_3 + v_4) + (0)\) | 0 | \(k_{a34} = 1 \times 10^6 \) \(^f\) |
| **Intermode V-V energy transfer** | | |
| [11] \((v_3) + M \rightarrow (v_6) + M\) | -133 | \(k_{3,6} = 2.9 \times 10^5 \) \(^b\) |
| [12] \((v_3) + M \rightarrow (v_{25}) + M\) | -284 | \(k_{3,25} = 7.0 \times 10^4 \) \(^b\) |
| [13] \((2v_3) + M \rightarrow (v_3 + v_6) + M\) | -149 | \(k_{33,36} = 5.8 \times 10^4 \) \(^d\) |
| [14] \((v_3 + v_6) + M \rightarrow (2v_3) + M\) | -118 | \(k_{36,66} = 5.8 \times 10^4 \) \(^d\) |
| [15] \((2v_6) + M \rightarrow (v_6 + v_{25}) + M\) | -286 | \(k_{66,26} = 1.4 \times 10^5 \) \(^d\) |
| [16] \((v_6 + v_{25}) + M \rightarrow (v_3 + v_{125}) + M\) | -280 | \(k_{61,26} = 1.4 \times 10^5 \) \(^d\) |
| [17] \((v_3 + v_6) + M \rightarrow (v_3 + v_{25}) + M\) | -285 | \(k_{36,23} = 7.0 \times 10^4 \) \(^e\) |
| [18] \((v_3 + v_{25}) + M \rightarrow (v_6 + v_{25}) + M\) | -119 | \(k_{23,26} = 2.9 \times 10^4 \) \(^e\) |
| [19] \((3v_3) + M \rightarrow (v_3) + M\) | +89 | \(k_{33,4} = 5 \times 10^4 \) \(^f\) |
| [20] \((v_{125}) + M \rightarrow (v_4) + M\) | +95 | \(k_{1,4} = 1 \times 10^6 \) \(^f\) |
| **V-T/R energy transfer** | | |
| [21] \((nv_3) + M \rightarrow (n - 1) v_3) + M\) | +1049 | \(k_{3} = 3.7 \times 10^2\) \(^g\) |
| [22] \((nv_6) + M \rightarrow (n - 1) v_6) + M\) | +1182 | \(k_{6} = 8.7 \times 10^2\) \(^h\) |

\(^{a}\) \(\text{CH}_3\text{F}\) in \(v_i\) level is denoted as \((v_i)\), while \(\text{CH}_3\text{F}\) in the ground state as \((0)\) and \(\text{CH}_3\text{F}\) as a third body collider as \(M\).

\(^{b}\) Determined by Sheorey and Flynn\(^2\).

\(^{c}\) Determined by Apkarian and Weitz\(^3\).

\(^{d}\) Estimated from the data of Sheorey and Flynn\(^2\) based on the Landau–Teller rule.

\(^{e}\) Estimated from the data of Sheorey and Flynn\(^2\).

\(^{f}\) Assumed value.

\(^{g}\) Determined by Weitz and Flynn\(^23\); here the ratio of \(k_\alpha\) to \(k_\beta\) is assumed as the one calculated by the SSH theory.

\(^{h}\) Assuming the detailed balancing rule, the rate constant for the backward reaction is defined as \(k_{di}\) for \(k_{ui}\), \(k_{ji}\) for \(k_{ui}\), and \(k_{abi}\) for \(k_{ui}\).

Estimated on a reasonable basis. Regarding the intramode V-V energy transfers, the rate constants for \(2v_3 \rightarrow 3v_3\) and \(3v_3 \rightarrow 4v_3\) are estimated from that for \(v_3 \rightarrow 2v_3\) determined by Sheorey and Flynn\(^2\) assuming the Landau–Teller rule, where the effect of the non-resonance on the rate constant is disregarded, so that possibly the rate constants are slightly
overestimated. For the other intramode V–V energy transfer rates, the value of \(1 \times 10^6 \text{s}^{-1} \text{Torr}^{-1}\) is assumed for the first step of the "up-the-ladder" process, since the rates for these V–V energy transfers must be close to the one for \(v_{25} \rightarrow v_2 + v_5\) which has been determined by Apkarian and Weitz\(^3\) or to another intramode V–V energy transfer rate which is of the order of \(10^6 \text{s}^{-1} \text{Torr}^{-1}\). As for the intermode V–V energy transfers, based on the data of Sheorey and Flynn\(^2\) for \(v_3 \rightarrow v_6\) and \(v_6 \rightarrow v_{25}\), the other V–V energy transfer rates through the combination levels such as \(2v_3 \rightarrow v_3 + v_6\), \(v_3 + v_6 \rightarrow 2v_6\) etc. are also estimated by the Landau–Teller rule. For the intermode V–V energy transfers of \(3v_3 \leftrightarrow v_4\) and \(v_4 \leftrightarrow v_{125}\), the values listed in Table III are adopted in the trial calculation. The effect of the direct energy transfer from \(3v_3\) to \(v_4\) and other states on the entire relaxation is one of the major subjects of this paper, so that the adequacy of these rate constants will be discussed later.

Taking the energy transfer processes [1]–[21] into account, the kinetic equations are formulated to describe the time-dependent population in each vibrational level among 14 levels in the course of the relaxation which starts by laser excitation of the \(v_3\) mode at the time origin. In the equations, the number density in \(i\)th level is denoted as \(N_i\) in which the level number \(i\) is defined in Table I except in \(i = 0\) which means the ground state. The total number density of CH\(_3\)F is defined as \(N = \sum N_i\).

For the excitation process, it is assumed that a fraction of \(N_i(i = 0, 4, \text{or} 11)\) may interact with the laser radiation field of 9.4-\(\mu\)m P(20) line, and that the average absorption cross section \(\sigma_j\) is common for the transition from the \(jv_3\) state to the \((j + 1)v_3\). If the parameter \(f_j\) is introduced as an equilibrium fraction of populations in these rotational levels of the relevant vibrational state, the rate equation for the population, \(N_{i j}^{v_j}\), in the rotational levels of the \(i\)th state which makes a stimulated transition to or from the \(k\)th state is formulated as follows:

\[
\frac{dN_{i j}^{v_j}}{dt} = -(\sigma_j I/h\nu)(N_{i j}^{v_j} - n_{v_j}') + \{-k_{\text{rot}}N_{i j}^{v_j}N + [f_j(1 - f_j)]k_{\text{rot}}(N_i - N_{i j}^{v_j})\} + f_jR_i, \quad (16)
\]

where \(j = 1, 2\) and 3 corresponds to the transitions of \(i = 0 \rightarrow 1, 1 \rightarrow 4\) and \(4 \rightarrow 11\), respectively, and \(k_{\text{rot}}\) is the rate constant of transitions from rotational levels interacting with the laser photon field to the other rotational levels, and is assumed to be a common value of
1.25 × 10^8 s^{-1} Torr^{-1} for all rotational levels, and $R_i$ is the overall rate of the collisional vibrational transition to the $i$th state from the other vibrational states, i.e.:

$$R_0 = (-k_{d3}N_4N_0 + k_{u3}N_1N_1) + (-k_{d33}N_{11}N_0 + k_{u33}N_4N_1)$$
$$+ (-k_{d333}N_{14}N_0 + k_{u333}N_{11}N_1) + (-k_{d6}N_6N_0 + k_{u6}N_2N_2)$$
$$+ (-k_{d25}N_9N_0 + k_{u25}N_3N_3) + (-k_{d13}N_{14}N_0 + k_{u13}N_9N_1)$$
$$+ (-k_{d34}N_{13}N_0 + k_{u34}N_{10}N_1) + (-k_{d36}N_{5}N_0 + k_{u36}N_2N_1)$$
$$+ (-k_{d26}N_8N_0 + k_{u26}N_3N_2) + (-k_{d23}N_7N_0 + k_{u23}N_3N_1)$$
$$+ (-k_{ib3}N_0N + k_{ib3}N_1N) + (-k_{ib6}N_0N + k_{ib6}N_2N)$$

(17)

$$R_1 = 2(-k_{u3}N_1N_1 + k_{d3}N_4N_0) + (-k_{u33}N_{11}N_1 + k_{d33}N_{14}N_0)$$
$$+ (-k_{u333}N_{11}N_1 + k_{d333}N_{14}N_0) + (-k_{u16}N_9N_1 + k_{d13}N_{12}N_0)$$
$$+ (-k_{u34}N_{10}N_1 + k_{d34}N_{13}N_0) + (-k_{u36}N_{5}N_1 + k_{d36}N_2N_0)$$
$$+ (-k_{u23}N_3N_1 + k_{d23}N_7N_0) + (-k_{3,6}N_1N + k_{6,3}N_2N)$$
$$+ (-k_{ib3}N_1N + k_{ib3}N_0N) + (2k_{ib3}N_4N - 2k_{ib3}N_1N)$$
$$+ (-k_{ib6}N_3N + k_{ib6}N_1N)$$

(18)

$$R_2 = (-k_{d3}N_4N_0 + k_{u3}N_1N_1) + (-k_{u33}N_{41}N_1 + k_{d33}N_{11}N_0)$$
$$+ (-k_{3,36}N_{41}N_0 + k_{36,33}N_5N) + (-2k_{ib3}N_4N + 2k_{ib3}N_1N)$$
$$+ (3k_{ib3}N_11N - 3k_{ib6}N_1N)$$

(19)

$$R_{11} = (-k_{d34}N_{13}N_0 + k_{u34}N_{10}N_1) + (-3k_{ib3}N_{11}N + 3k_{ib3}N_4N)$$

(20)

The kinetic equations for respective vibrational levels are formulated according to the mechanism described in Table III as follows:

$$dN_1/dt = (\sigma_1/\hbar\nu)(N_0^1 - N_1^1) - (\sigma_2/\hbar\nu)(N_0^2 - N_1^2) + R_1$$

(21)

$$dN_2/dt = 2(-k_{u6}N_2N_2 + k_{d6}N_{6}N_0) + (-k_{u36}N_1N_2 + k_{d36}N_2N_0)$$
$$+ (-k_{u26}N_2N_3 + k_{d26}N_8N_0) + (-k_{6,3}N_2N + k_{3,6}N_1N)$$
$$+ (-k_{6,2}N_2N + k_{2,6}N_3N) + (-k_{6}N_2N + k_{b6}N_0N)$$
$$+ (k_{ib3}N_5N - k_{ib3}N_2N) + (2k_{ib6}N_6N - 2k_{ib6}N_2N)$$

(22)

$$dN_3/dt = 2(-k_{u2}N_3N_3 + k_{d2}N_9N_0) + (-k_{u23}N_1N_3 + k_{d23}N_7N_0)$$
$$+ (-k_{u26}N_2N_3 + k_{d26}N_8N_0) + (-k_{2,6}N_3N + k_{6,2}N_2N)$$
$$+ (k_{ib3}N_7N - k_{ib3}N_3N) + (k_{ib6}N_8N - k_{ib6}N_3N)$$

(23)

$$dN_4/dt = (\sigma_2/\hbar\nu)(N_0^4 - N_0^3) - (\sigma_3/\hbar\nu)(N_0^4 - N_1^4) + R_4$$

(24)

$$dN_5/dt = (-k_{d3}N_5N_0 + k_{u36}N_2N_1) + (-k_{36,33}N_5N + k_{33,36}N_4N)$$
$$+ (-k_{36,23}N_5N + k_{23,36}N_7N) + (-k_{36,66}N_5N + k_{66,36}N_6N)$$
$$+ (-k_{ib3}N_5N + k_{ib3}N_2N) + (-k_{ib6}N_5N + k_{ib6}N_1N)$$

(25)

$$dN_6/dt = (-k_{d6}N_6N_0 + k_{u6}N_2N_2) + (-k_{66,36}N_6N + k_{36,66}N_5N)$$
$$+ (-k_{66,26}N_6N + k_{26,66}N_8N) + (-2k_{ib6}N_6N + 2k_{ib6}N_2N)$$

(26)
\[
dN_7/dt = (-k_{d23} N_7 N_0 + k_{u23} N_3 N_1) + (-k_{23,36} N_7 N_k + k_{36,23} N_5 N) \\
+ (-k_{23,26} N_7 N + k_{26,23} N_8 N) + (-k_{t3} N_7 N + k_{tb3} N_3 N) \\
\text{ (27)}
\]

\[
dN_8/dt = (-k_{d26} N_8 N_0 + k_{u26} N_2 N_3) + (-k_{26,1} N_8 N_k + k_{1,26} N_9 N) \\
+ (-k_{26,23} N_8 N + k_{23,26} N_7 N) + (-k_{26,66} N_8 N_k + k_{66,26} N_6 N) \\
+ (-k_{t6} N_8 N + k_{tb6} N_3 N) \\
\text{ (28)}
\]

\[
dN_9/dt = (k_{u25} N_3 N_3 - k_{d25} N_9 N) + (-k_{u13} N_9 N_k + k_{d13} N_12 N) \\
+ (k_{26,1} N_8 N - k_{1,26} N_9 N) + (-k_{1,4} N_9 N + k_{4,1} N_10 N) \\
+ (k_{t3} N_12 N - k_{tb3} N_9 N) \\
\text{ (29)}
\]

\[
dN_{10}/dt = (k_{u34} N_10 N_1 + k_{d34} N_13 N_0) + (-k_{4,333} N_{10} N + k_{333,4} N_{11} N) \\
+ (-k_{4,1} N_{10} N + k_{1,4} N_9 N) + (k_{t3} N_{13} N - k_{tib3} N_9 N) \\
\text{ (30)}
\]

\[
dN_{11}/dt = (\sigma_3 I/h\nu)(N_{11}^3 - N_{11}^l) + R_{11} \\
\text{ (31)}
\]

\[
dN_{12}/dt = (-k_{d13} N_{12} N_0 + k_{u13} N_9 N_1) + (-k_{t3} N_{12} N + k_{tb3} N_9 N) \\
\text{ (32)}
\]

\[
dN_{13}/dt = (-k_{d34} N_{13} N_0 + k_{u34} N_{10} N_1) + (-k_{t3} N_{13} N + k_{tb3} N_{10} N) \\
\text{ (33)}
\]

\[
dN_{14}/dt = (-k_{d333} N_{14} N_0 + k_{u333} N_{11} N_1) + (-4k_{t3} N_{14} N + 4k_{tb3} N_{11} N) \\
\text{ (34)}
\]

The number density of the ground state may be derived by the relation

\[
N_0 = N - \sum_{i=1}^{14} N_i. \\
\text{ (35)}
\]

These coupled differential Eqns (16), (21)–(34) were solved numerically by a Runge–Kutta–Gill method with the initial condition that the population distribution in respective vibrational levels at \( t = 0 \) is assumed to be in equilibrium at 295 K.

**Comparison of kinetic calculation with LIF data**

In Figure 7, the calculated fractional population changes in the \( 2\nu_3 \) and \( 3\nu_3 \) levels induced by laser irradiation are shown together with the observed overtone emission from each state. Here, the observed emission intensities from \( 2\nu_3 \) at the laser fluence of 0.7 J cm\(^{-2}\) are plotted so as to fit with the calculated ones in the later stage of relaxation. Thus, we may discuss the emission intensities from the \( 3\nu_3 \) level relative to those from \( 2\nu_3 \), and also the emission under a high
Figure 7 Observed and calculated fractional population changes in 2ν3 and 3ν3 levels of CH3F at 0.5 Torr. The calculation was carried out based on the kinetic scheme described in Table III. The relative population is given by the 3ν3 or 2ν3 emission intensity. (a) and (b) 2ν3 emission in excitation with fluence of 0.7 (○) and 0.097 J cm⁻² (△), respectively; (c) and (d) 3ν3 emission with 0.7 (△) and 0.097 J cm⁻² (×), respectively. The observed 2ν3 emission intensities are plotted in accord with the calculated values 10–40 μs after the laser pulse.

fluence irradiation relative to those under a low fluence. Due to the relatively slow response of the IR light detecting system, the emission intensities were found to increase with a rate smaller than that calculated. However, the observed relative intensities and the decay rates of the 2ν3 emission are in good agreement with the calculated fractional population change in 2ν3 level based on the model including the direct 3ν3 $\rightarrow\nu_4$ V–V energy transfer. The observed population change in 3ν3, which is defined as an emission intensity from the 3ν3 level relative to that from 2ν3, is larger by a factor of 1.5 than the calculated population change. Nevertheless, it may be stated that the
present kinetic model calculation could reproduce the population kinetics determined by the LIF emission measurement.

Referring to the spectral analysis of the 3-μm emission band shown in Figure 4(d), the emission at the shortest wavelength 3.28 μm in this experiment is attributable to the ν₄ population, while the emission in the longer wavelength region, e.g. 3.52 μm is contributed from mainly 2ν₂, ν₂ + ν₅ and ν₅. Figure 8 shows the emission data together with the calculated results. Here, the observed ν₄ emission intensities at a later stage of the relaxation under the laser fluence of 0.7 J cm⁻² are plotted to fit with the calculated ν₄ population. The ν₄ emission at 3.29 μm

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**Figure 8** Observed and calculated fractional population changes in ν₄ and ν₁₂₅ levels of CH₂F at 0.5 Torr. (a) and (b) ν₁₂₅ emission at 3.52 μm in excitation with fluence of 0.7 (Δ) and 0.097 J cm⁻² (×), respectively; (c) and (d) ν₄ emission at 3.29 μm in excitation with 0.7 (○) and 0.097 J cm⁻² (+), respectively. The ν₁₂₅ and ν₄ emission intensities at the fluence of 0.7 J cm⁻² are plotted in accord with calculated values 10–40 μs after the laser pulse.
forms a peak at an initial stage which is reproduced in the calculation in spite of some disagreement in the increasing rate. This latter fact is probably due to insufficient response of the present IR light detecting system. The calculated $v_4$ population in laser irradiation with a lower fluence, 0.097 J cm$^{-2}$, is almost in agreement with the observed emission intensity, although its relative magnitude is too small by a factor of 1.5. This implies that the kinetic model given in Table III may predict the dependence of the $v_4$ emission on the irradiated laser fluence. The emission at 3.52 μm does not show a clear peak after the initial rapid rise, and it keeps almost a constant magnitude during several tens of microseconds. This observation is consistent with the present kinetic model, if it is admitted that the $v_1$, 2$v_5$ and $v_2 + v_5$ levels contribute to the 3.52-μm emission.

Of the rate constants assigned to energy transfer processes listed in Table III, the magnitudes of $k_{333,4}$ and $k_{1,4}$ are most ambiguous. The energy transfer between $v_1$ and $v_4$ must be very efficient, because some rotational levels of these vibrational states are coupled with each other due to Coriolis forces and furthermore large dipole matrices are expected because of the intense absorption of the $v_1$ and $v_4$ bands. Therefore, a large value, $1 \times 10^6$ s$^{-1}$ Torr$^{-1}$, is assumed for a temporal value of $k_{1,4}$. The kinetic calculation was made assuming various values for $k_{333,4}$ in the range of $1 \times 10^5$–$1 \times 10^6$ s$^{-1}$ Torr$^{-1}$. Comparison of the calculated time-evolved populations with the observed emissions from 2$v_3$, 3$v_3$, $v_4$ and $v_1/2v_2/v_2 + v_5/2v_5$ leads to the conclusion that $k_{333,4}$ must be between $5 \times 10^5$ and $1 \times 10^6$ s$^{-1}$ Torr$^{-1}$. Similarly, $k_{1,4}$ was changed by a factor of five assuming the fixed value for $k_{333,4}$ of $5 \times 10^5$ s$^{-1}$ Torr$^{-1}$. However the calculated time-evolved populations in relevant vibrational states were found to be relatively insensitive to the magnitude of this rate constant. Thus, it was concluded that the set of rate constants given in Table III was satisfactory for quantitative discussion on the relaxation mechanism.

In Figure 9, the experimental decay data of emissions from the 2$v_3$, 3$v_3$ and $v_4$ levels in the final stage of the relaxation are presented. The intensities of the 2$v_3$ and $v_4$ emission are normalized in a way similar to that shown in Figures 7 and 8, so that one may discuss the population changes in 3$v_3$ relative to 2$v_3$ and also those of $v_{125}$ to $v_4$ using the calculated results given in Figure 9 as absolute values of the population changes in the respective states. Good agreement is seen between the observed emission decays and the kinetic model calculation in the later
Figure 9  Observed and calculated fractional population changes in (a) $2v_3$ (o), (b) $v_{125}$ (x), (c) $3v_3$ (a), and (d) $v_4$ (+) in the later stage of the relaxation of CH$_3$F excited with fluence of 0.7 J cm$^{-2}$ (see Figures 7 and 8).

stage of relaxation. Clearly, the observed decay of populations in the $2v_3$, $3v_3$ and $v_4$ states is much faster than the V–T/R transfer, and is not simply exponential; the decay rate is reduced gradually in the later stage and the decay of the $2v_3$ emission is slower than those in the other higher states, $v_{125}$, $v_4$ and $3v_3$. These observations are reproduced well by the present kinetic model calculation.

Relaxation kinetic scheme with versus without $3v_3 \leftrightarrow v_4$ V–V energy transfer

The kinetic rate Eqns (16), (21–34), which are formulated based on the energy transfer processes given in Table III, are solved numerically for two cases: under the initial conditions of weak and strong laser
excitation. Figures 10(a) and (b) show the calculated population changes in respective vibrational levels after the laser pulse excitation with the fluence of 0.001 J cm\(^{-2}\). The calculation was made on the basis of the kinetic mechanism with or without the \(3\nu_3 \leftrightarrow \nu_4\) V–V energy transfer. In the initial stage of relaxation, as shown in Figure 10(a), rapid increase of the populations in the \(\nu_3\), \(2\nu_3\), \(3\nu_3\) levels occurs indicating the laser excitation to these levels and the efficient intra-mode V–V energy transfers within the \(\nu_3\) mode. In the next stage, intermode V–V energy transfers from \(\nu_3\) to the other modes occur resulting in rapid reduction of populations in the \(\nu_3\) mode and increase of populations in the other states. In the case of the weak laser excitation, the \(3\nu_3 \leftrightarrow \nu_4\) V–V energy transfer may not affect the

![Figure 10 (a)](image-url)  
*Figure 10 (a) Calculated fractional population changes in respective levels of CH\(_2\)F irradiated with the CO\(_2\) laser pulse at the fluence of 0.001 J cm\(^{-2}\). The curves marked with symbols show the results obtained based on the kinetic scheme without the \(3\nu_3 \leftrightarrow \nu_4\) V–V energy transfer, while those without symbols show the results with the above V–V energy transfer.*
relaxation kinetics. In two mechanisms with and without the V–V energy transfer, the $\nu_4$, $\nu_1$, and other nearby states are populated with almost the same rate. Population in $\nu_4$ is slightly accelerated by inclusion of the $3\nu_3 \leftrightarrow \nu_4$ V–V energy transfer, but the major part of the population is caused by the energy flow mechanism in Eqn (1). In the later stage of the relaxation, the calculations based on either mechanism result in the same population kinetics at the respective levels. The population in each level is reduced exponentially with the common rate, which is defined from the V–T/R energy transfer rates of $\nu_3$ and $\nu_6$ modes. Thus, in weak laser excitation of $\nu_3$ mode, the vibrational energy flow from $\nu_3$ to $\nu_4$ and $\nu_1$ and other nearby levels occurs mainly through Eqn (1) and the contribution of Eqn (2) is relatively small.

In the case of strong laser excitation, a large energy is poured into the $\nu_3$ mode, and the vibrational energy flow scheme from $\nu_3$ to $\nu_4$, $\nu_1$,
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and other levels is dependent significantly upon whether the kinetic model includes the $3\nu_3 \leftrightarrow \nu_4$ energy transfer or not. Without the V–V energy transfer, the population kinetics are essentially the same as those given in Figure 10(a). The vibrational energy flows from $\nu_3$ to $\nu_2$, $\nu_5$ through $\nu_6$ and finally to $\nu_1$ and $\nu_4$ keeping the quasiequilibrium population distribution within each vibrational mode. In the later stage of the relaxation, as shown in Figure 10(d), populations in respective levels decrease exponentially against time with the V–T/R energy transfer rate. Contrary to this, if the $3\nu_3 \leftrightarrow \nu_4$ V–V energy transfer is included in the kinetic mechanism, the population kinetics for respective levels differ significantly from those predicted based on the mechanism without the $3\nu_3 \leftrightarrow \nu_4$ V–V energy transfer. The

![Graph](image)

**Figure 10 (c)** Calculated fractional population changes in respective levels of CH₃F irradiated with the CO₂ laser at the fluence of 1 J cm⁻². The curves marked with various symbols show the values calculated based on the kinetic scheme without the $3\nu_3 \leftrightarrow \nu_4$ V–V energy transfer, while the curves without symbols show those based on the scheme without the above V–V energy transfer.
population in the $v_4$ level is accelerated greatly due to the direct energy flow from $3v_3$ just after the laser excitation to reach a maximum. Then, the $v_4$ population is reduced due to the intermode V–V energy transfer to $v_1, 2v_5, v_2 + v_3$ and other nearby levels and also to $v_6, v_2$ and $v_5$ modes via the $3v_3$ level since the excess energy accumulated in the $v_3$ mode in the initial stage must be transferred to other levels. As already demonstrated in Figure 8, the observed emission data from $v_4$ are in good agreement with the present model calculation.

Another significant finding in the kinetic model, including the $3v_3 \leftrightarrow v_4$ V–V energy transfer, is that the vibrational quasiequilibrium population distribution may not be realized even in the final stage of the relaxation. In Figure 10(d), the population in each level decays in a non-exponential manner and the population ratio of certain levels is not constant during the course of the relaxation. On the contrary, in the case of weak laser excitation, as shown in Figure 10(b),
the population distribution in the respective levels is in equilibrium at a single vibrational temperature in the final stage of relaxation; populations in all levels decay with the same rate, the V–T/R rate. Referring to Figure 10(d), it is seen that the non-exponential population decay is more significant in higher levels, $v_3 + v_4, v_3 + v_{125}, v_4, 3v_3, \ldots$, and the populations in lower levels are reduced almost exponentially although the rate is larger than the V–T/R rate.

This non-exponential population decay is caused by the existence of the $3v_3 \leftrightarrow v_4$ V–V energy transfer. When this process is very efficient, a series of intermode V–V energy transfers occurs from $3v_3$ to $2v_3$ (see Figure 1) connecting levels which are located in between the two levels. This energy flow must occur if the relative population distribution in these levels exceeds the thermal one at room temperature, since the non-resonant energy of a V–V energy transfer process is transferred to/from translation and/or rotation whose energy distribution is in equilibrium at room temperature. After the successive intermode V–V energy transfers from the $3v_3$ to the $2v_3$ level, one quantum of the $v_3$ vibration is transferred to translation and/or rotation. Further $v_3$ quanta are lost if the intramode V–V pumping occurs within the $v_3$ mode such as $2v_3 + v_3 \rightarrow 3v_3 + 0$. The overall process is that proposed by Mandich and Flynn\textsuperscript{20} for the vibrational relaxation of N\textsubscript{2}O and named a "catastrophic cyclic path". Since the cyclic path includes the intramode V–V energy transfer whose rate is a non-linear function with respect to the number density in a $v_3$-excited level, the population decay in each relevant level must be dependent on the extent of the excitation and be non-exponential against time. The decay rate is much larger than that of the V–T/R energy transfer which is a linear process.

The Coriolis interaction of high rotational levels of the $3v_3$, level with those of the $v_4$ level has been pointed out by Graner\textsuperscript{4}, who suggested an efficient energy transfer between $3v_3$ and $v_4$ through Coriolis-coupled rotational levels. Later, his group carried out the intensive analysis of the high resolution spectrum in the 3-μm region, $v_4(E), v_1(A), 2v_2(A), 2v_5(A_1 + E), v_2 + v_5(E)$\textsuperscript{5,6}. According to their analysis, $3v_3$, which lies 90 cm\textsuperscript{-1} higher than $v_4$, interacts with $v_4$ leading to localized level crossing due to Coriolis coupling. Since the $v_2$ and $v_5$ fundametals are only 8.4 cm\textsuperscript{-1} apart, their overtone levels are coupled by a strong Coriolis interaction and, thus, the same Coriolis coupling must be significant in $2v_2$ with $v_2 + v_5$ and in $v_2 + v_5$ with $2v_5$. Furthermore, a
strong Fermi resonance is found in the $v_1$ band since two parallel bands of equal intensity exist; the overtone level involved in the coupling is $2v_2$ or $2v_5$. The $v_4$ band is relatively separate although a Fermi resonance between $v_4$ and $2v_5$ must be taken into account. Thus, in the present kinetic model, only three levels, $3v_3$, $v_4$ and $v_{125}$, are introduced for the levels in the C—H stretching vibration region.

The conclusion derived in the former experiment$^{8,16}$ was criticized by Apkarian et al.$^{10}$ According to their numerical solution of rate equations, which are formulated for seven excited vibrational levels, $v_3$, $v_6$, $v_2/v_5$, $2v_3$, $2(v_2/v_5)$, $v_1/v_4$, and $3v_3$, under the initial condition of 40% CH$_3$F being in the $v_3$ level and the remaining fraction in the ground level, the $v_1/v_4$ level is populated quickly to reach a peak, while $2(v_2/v_5)$ is not, even if the $3v_3 \leftrightarrow v_1/v_4$ direct V—V energy transfer is included in the kinetic scheme. They attributed this to a small vibrational heat capacity of the $3v_3$ level relative to that of the $v_1/v_4$ and $2(v_2/v_5)$ levels, and suggested that a pathway from $2v_3$ to $2(v_2/v_5)$ via $v_x(v_3 + v_6, 2v_6, v_3 + v_2/v_5$, etc.) contributed significantly to the population of the levels in the C—H stretching region. Their calculation was extended to the CH$_3$F/Ar mixture, in which we demonstrated very efficient excitation of $v_4$, $v_1$ and other nearby levels in strong laser excitation$^{16}$, and claimed that their model could not reproduce the rapid accumulation of population in these levels. Thus, they concluded that the $3v_3 \leftrightarrow v_4$ direct V—V energy transfer could not contribute largely to the entire relaxation in strong laser excitation of CH$_3$F at a low pressure (0.5 Torr) or in a mixture with Ar at a higher pressure (70 Torr).

The present kinetic model is essentially similar to the one adopted by Apkarian et al.$^{10}$, although seven excited levels in their model are replaced by 14 levels which include $v_x$ in their notation. The rate equations describing the initial stimulation processes are not included in their model, but, instead, an initial excitation condition is assumed which is almost in accord with the present average number of photons absorbed at a fluence of 0.5 J cm$^{-2}$ (see Figure 6). The only essential difference in the present calculation from that of Apkarian et al. is that their adopted rate constant for the $v_1/v_4 \leftrightarrow 2(v_2/v_5)$ V—V energy transfer is much smaller than that for the $v_4 \leftrightarrow v_{125}$ given in Table III. However, this value is possibly larger than those accepted normally because of a very strong interaction between the relevant levels that has been proved by high resolution IR spectroscopy$^{5,6}$. For the kinetic
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in the CH$_3$F/Ar mixture, Apkarian et al. assumed the absorbed photon number per CH$_3$F molecule to be 0.40 or 0.44. However, this number has been measured to be as large as 6 in the mixture of 0.12 Torr CH$_3$F and 120 Torr Ar at the laser fluence of 1 J cm$^{-2}$. Therefore, the assumed extent of their excitation is very much underestimated, and may not be the basis for discussion of the role of the $3\nu_3 \leftrightarrow \nu_4$ V–V energy transfer in the relaxation. For the excitation and relaxation kinetics of CH$_3$F or other molecules in a dense third body medium will be reported elsewhere.

In the present kinetic calculation simulating the experimental data, it has been concluded that a cyclic series of the V–V energy transfers $2\nu_3 \leftrightarrow \nu_x \leftrightarrow 2\nu_5/\nu_2 + \nu_3/2\nu_2/\nu_1 \leftrightarrow \nu_4 \leftrightarrow 3\nu_3 \leftrightarrow 2\nu_3$ plays a significant role in the relaxation of CH$_3$F whose $\nu_3$ mode is highly excited. The conclusion derived by Apkarian et al.\textsuperscript{10} that the $3\nu_3$ level may not contribute significantly to the filling of $2(\nu_3/\nu_5)$ in either the low or high excitation regime is not consistent with the present finding of non-exponential decay of populations in higher vibrational levels in the final stage of relaxation. As shown in Figure 10(c) and (d), this phenomenon could not be explained by the mechanism without the $3\nu_3 \leftrightarrow \nu_4$ V–V energy transfer process.

The non-linear type relaxation found in the present experiment was also reported in the LIF kinetic studies\textsuperscript{21} of COF$_2$ whose $\nu_2$ mode is excited by an intense CO$_2$ laser. In weak laser excitation of COF$_2$, which was carried out by Castleton and Flynn\textsuperscript{22}, the LIF at 5 $\mu$m rose rapidly by the $\nu_2 \leftrightarrow 2\nu_2$ intramode ladder climbing to reach a peak, which decayed biexponentially; the fast decay was assigned to V–V energy transfers from $\nu_1$, $\nu_2$ to the other modes, while the final decay was due to the V–T/R process. Contrary to this, in strong laser excitation, the 5- $\mu$m LIF of the final stage of the relaxation decayed non-exponentially; the rate defined from the decay slope became smaller in the later stage of relaxation. This observation is common to the present finding on $\nu_3$-excited CH$_3$F by the TEA CO$_2$ laser, and might be caused by a mechanism similar to that proposed in this experiment.

Dependence on laser fluence

In the experiment of Sheorey and Flynn\textsuperscript{2}, CH$_3$F was excited by a Q-switched CO$_2$ laser with energy of about 1 mJ, and the induced 3-$\mu$m
emission was found to increase almost exponentially after the laser pulse (see Figure 6(b) of Ref. 2). This observation is consistent with the energy flow pathway in Eqn (1): \( v_3 \rightarrow v_6 \rightarrow v_2/v_5 \rightarrow 2(v_2/v_5) \rightarrow v_1 \rightarrow v_4 \). The present experiment of strong laser excitation indicates that the mechanism in Eqn (1) must be supplemented by taking into consideration the intermode V–V energy transfers such as \( 3v_3 \leftrightarrow v_4 \). The kinetic model thus postulated should be applicable to more general cases in the wide range of the extent of laser excitation.

In order to test the applicability of the present kinetic model, the 3-\( \mu \)m LIF was observed as a function of the laser fluence and compared with kinetic calculations. As shown in Figure 11, at the laser fluence of

![Graph of observed and calculated time-evolved 3-\( \mu \)m emissions in CHF at 0.5 Torr as a function of the laser fluence together with the results calculated based on the scheme given in Table III with the rate constant of the 3\( v_3 \leftrightarrow v_4 \) V–V energy transfer of 0(1), \( 1 \times 10^5(2), 3 \times 10^5(3), 5 \times 10^5(4), 7 \times 10^5(5) \) and \( 1 \times 10^6 \) s\(^{-1}\) Torr\(^{-1}\)(6). The laser fluence is 0.011(a), 0.04(b) and 0.46 J cm\(^{-2}\)(c).
0.46 J cm\(^{-2}\), the emission intensity increased rapidly to form a peak in the initial stage, while at 0.011 J cm\(^{-2}\) its increase is much slower showing an exponential growth. The numerical solutions of the kinetic Eqns (16), (21–34) are also presented. The calculation was made by use of the rate constants listed in Table III except \(k_{333,4}\), several values of which were assumed to optimize the simulation. The relative intensities of the 3-\(\mu\)m emission are given as a sum of populations in \(v_4\), \(v_1\) and other relevant levels with weights which are taken from relative absorption band intensities\(^{14}\).

As pointed out previously, in the mechanism without the \(3v_3 \leftrightarrow v_4\) V–V energy transfer, the 3-\(\mu\)m emission intensity increases after an induction period which is almost independent of the laser fluence. Thus, to simulate the dependence of the 3-\(\mu\)m emission intensity on the laser fluence, it is inevitable to introduce the \(3v_3 \leftrightarrow v_4\) V–V energy transfer in the mechanism. If the value of \(k_{333,4}\) is assumed to be \(5 \times 10^5\) s\(^{-1}\) Torr\(^{-1}\), the present kinetic model may reproduce the observed 3-\(\mu\)m emission of CH\(_3\)F laser excited with the fluence in the range of 0.01–0.5 J cm\(^2\).

**CONCLUSION**

When CH\(_3\)F is excited in its \(v_3\) mode by irradiation with an intense CO\(_2\) laser pulse, the energy flow pathway from \(v_3\) to \(v_4\), \(v_1\) and other nearby levels has been proved to be the pathway in Eqn (1) combined with that in Eqn (2); the former is generally accepted in weak laser excitation,

\[
v_3 \rightarrow v_6 \rightarrow v_2, \quad v_5 \rightarrow 2v_5, \quad v_2 + v_5, \quad 2v_2 \rightarrow v_1 \rightarrow v_4
\]  

(1)

and the latter involves the intermode V–V energy transfer from the high overtone level, \(3v_3\) to \(v_4\), which is Coriolis coupled:

\[
v_3 \rightarrow 2v_3 \rightarrow 3v_3 \rightarrow v_4 \rightarrow v_1 \rightarrow 2v_2, \quad v_2 + v_5, \quad 2v_5
\]  

(2)

The relaxation mechanism of CH\(_3\)F in strong laser excitation is characterized by the above intermode V–V energy transfer.

In the initial stage of the relaxation of \(v_3\)-excited CH\(_3\)F by strong laser irradiation, \(v_4\), \(v_1\) and other nearby levels are populated rapidly to reach a peak, which decays to a second broad maximum or to a plateau depending on the excitation condition. In the final stage of the relaxation, a quasiequilibrium vibrational distribution may not be
established, since a non-linear type relaxation, which is composed of the successive V-V energy transfers from $3\nu_3$ to $2\nu_3$ through $\nu_4$, $\nu_1$, and other closely lying levels, is much more efficient for transferring the vibrational energy to the translation and/or rotation than the V-T/R energy transfer from modes having low vibrational frequencies.

The present kinetic mechanism of non-linear type relaxation could be generalized for the intermode vibrational energy flow of polyatomic molecules whose single mode is excited by strong laser irradiation. Intermode V-V energy transfers from high overtone levels of a laser-excited mode to singly excited levels of other modes play a significant role in causing non-linear relaxation kinetics which are quite different from those normally accepted under low excitation conditions.

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