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VIBRATIONAL RELAXATION OF THE $2\nu_5$ OVERTONE OF $CDCl_3$ HIGHLY EXCITED BY A TEA CO_2 LASER

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A homemade TEA CO_2 laser tuned to the 10P(48) line, 10.91 μm, was used to excite the ν_4 mode of $CDCl_3$ (914 cm^{-1}). The IR fluorescence signal from the $CDCl_3$ $2\nu_5$ overtone band (1492 cm^{-1}) was isolated by means of a gaseous filter. The temporal variation of this fluorescence emission was studied as a function of the laser fluence. Under high excitation conditions, non-linear effects become obvious, and measured rate constants greater than predicted from linear kinetic rate equations have been found.

KEY WORDS: Vibrational Relaxation, IR Fluorescence, Laser.

1. INTRODUCTION

A good understanding of the collisional effects observed in the IR multiple-photon excitation processes (IRMPE) of $CDCl_3$[1,2] needs a good knowledge of the vibrational energy transfer processes which occur in this gas upon molecular collisions. In a preceding paper,[3] we have presented the results of a study of these relaxation processes performed by exciting the ν_4 state of the C–D bending mode by pulses delivered by a TEA CO_2 laser operating in the 10P(48) line. By monitoring the laser-induced fluorescence emitted in the $2\nu_5$ overtone of the C–Cl_3 stretching mode, we have shown that, subsequent to pumping the ν_4 state, a very fast equilibrium of

the population of this state with the ν_5 state population occurs through a very fast $\nu_4 \leftrightarrow \nu_5$ Coriolis-assisted intermode transfer process, at a rate $\geq 10^6$ s^{-1} Torr^{-1}. Then the vibrational energy spills over at a slower rate (7.1×10^3 s^{-1} Torr^{-1}) from ν_4 and ν_5 to ν_2 via a $(\nu_4, \nu_5) \rightarrow \nu_2$ intermode transfer. At last, it relaxes to a thermodynamic equilibrium at a rate of 111 s^{-1} Torr^{-1} via far-from-resonance intermode transfer and V-T, R deexcitation processes.

In this work, the rate constants have been determined under low excitation conditions so that the linearity of the rate equations may be assumed. But in the IRMPE, the laser excitation is much higher; the deviations of populations are no longer small with respect to the thermodynamic equilibrium populations and non-linear effects in the relaxation become obvious. Therefore, it was interesting to perform measurements under the same high excitation conditions as those encountered in the IRMPE, and to determine the evolution of the rate constants as a function of the laser fluence. The results of this study are given in the present paper.

II. EXPERIMENTAL PROCEDURE

The experimental set-up has been described in detail previously[3] (Fig. 1). A homemade TEA CO_2 multimode laser tuned to the P(48) line, (10.91 μm), was used

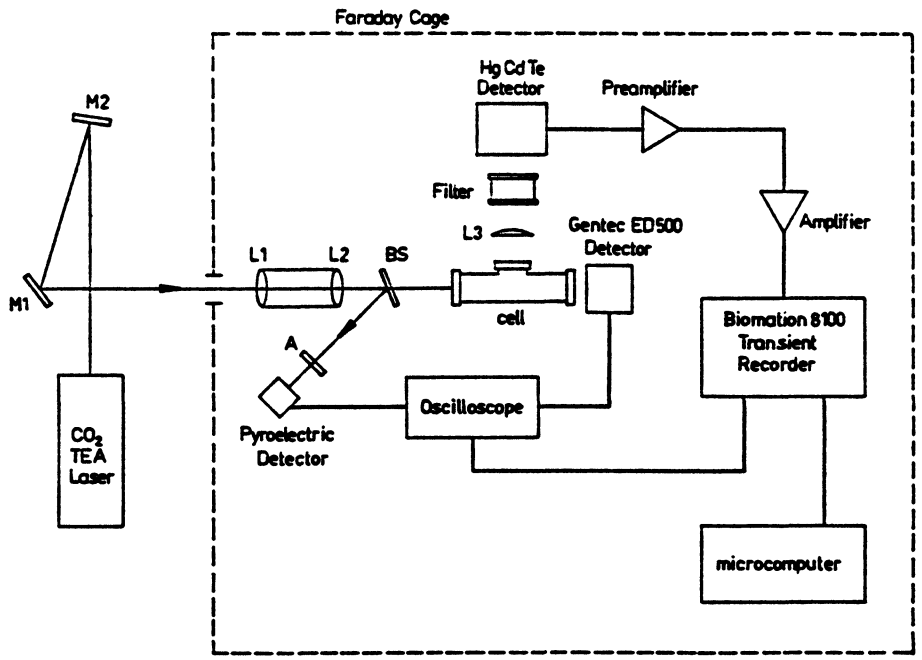

Figure 1 Experimental set-up for laser induced fluorescence measurements. M_1, M_2: mirrors, L_1, L_2, L_3: lenses, A: CaF_2 attenuators.

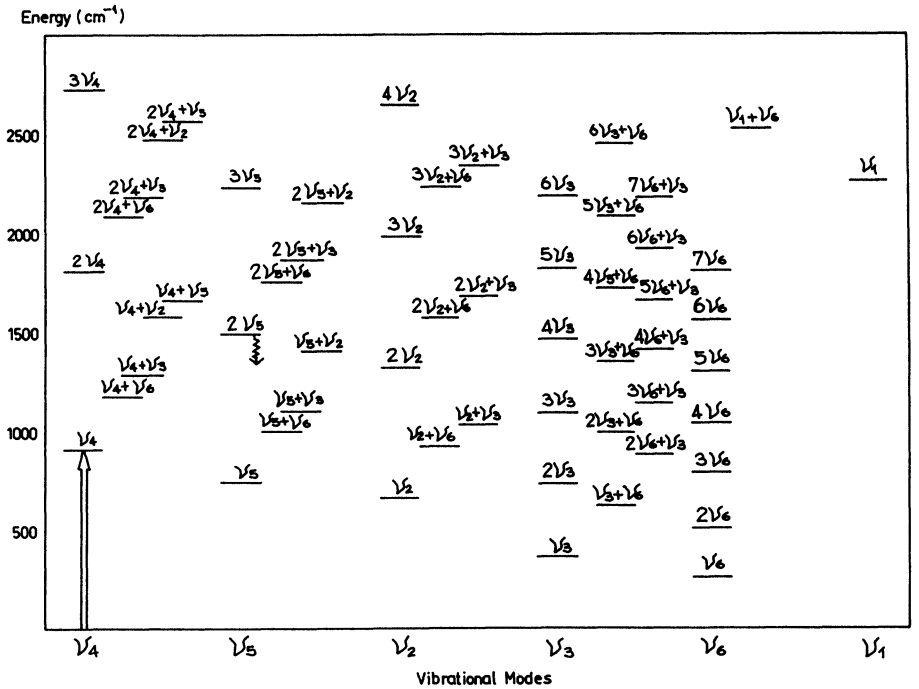

Figure 2 Energy level diagram of $CDCl_3$ for energies up to 2750 cm^{-1}. The solid line indicates the CO_2 laser pumping of the ν_4 mode. The wavy line indicates the fluorescence observed at 6.7 μm following laser excitation.

to excite the C–D bending mode ν_4 of $CDCl_3$, (914 cm^{-1}) as shown in the energy level diagram[4] in Fig. 2. The laser pulse energy at this line was typically 1.2 J/pulse with He and 600 mJ/pulse without He at 0.3 Hz. Pulse-to-pulse variations in the laser output was within 10%. The laser pulse consisted of a 90 ns FWHM spike followed by a 200 ns tail, measured with a photon-drag detector. No difference in the pulse form and length was found with and without He, so that the variations in the laser fluence correspond to the same variations in the laser peak intensity. The beam was collimated by a system of mirrors and lenses to an area of 0.2 cm^2. CaF_2 flats were used to vary the irradiation fluence from 1.5 to 4.5 J/cm^2.

The fluorescence emitted in the $2\nu_5$ vibrational band at 6.7 μm was isolated by a gas filter consisting of a mixture of 400 Torr of vinylfluoride, 200 Torr of C_2F_4 and 100 Torr of Freon 11, as shown in [3], then was detected by an HgCdTe detector.

The signal was digitized with a Biomation 8100 transient recorder, averaged with a microcomputer, then transferred to an IBM PC AT for subsequent analysis. The response time of the detection system was 1.5 μsec. The reflection of the laser beam at a NaCl beam-splitter was used as a trigger pulse of the signal processing system.

III. RESULTS AND DATA ANALYSIS

A typical 6.7 μm fluorescence signal characterizing the V–V energy redistribution processes after irradiating 7 Torr of $CDCl_3$ with a laser fluence of 2.5 J/cm^2 is shown in Fig. 3. As can be seen, it consisted of a very rapid rise to its peak, followed by a somewhat rapid decay to about half of the peak amplitude in about 20 μsec. Two much slower decays of about 10 msec characterized the return to the initial baseline.

The fluorescence signals were described as a sum of exponential functions by a non-linear least-squares regression method based on the Marquardt algorithm to obtain the measured rate constants and the initial intensities.

The risetime was limited by the response time of the detection system in the $CDCl_3$ pressure range of 2–20 Torr where sufficient signal intensity could be obtained to allow accurate measurement after excitation with laser fluences in the range 1.5–4.5 J/cm^2. A lower limit of ~1 μsec^{-1} Torr^{-1} was therefore set for this process.

Fig. 4 shows the pressure dependence of the fast decay rate for two different irradiation fluences. From a least squares fit of the slopes, rate constants of 40.8 ± 2.0 and 181.2 ± 8.6 msec^{-1} Torr^{-1} were obtained for irradiation with 2.5 and 4.5 J/cm^2, respectively. These values are 2.5 times and 11 times larger than that obtained with an irradiation fluence of 1.5 J/cm^2, i.e. 16.3 ± 1.3 msec^{-1} Torr^{-1}.

The faster of the two slow decays corresponds to a competion between far-from-resonance intermode transfer processes from the ν_5 and ν_2 modes to the ν_3 and ν_6 modes and, V–T/R energy transfer processes[3]. Rate constants of 0.251 ± 0.044 and 0.412 ± 0.031 msec^{-1} Torr^{-1} were obtained for irradiation with 2.5 and 4.5 J/cm^2, respectively. These values are larger than the 0.111 ± 0.015 msec^{-1} Torr^{-1} obtained with an irradiation fluence of 1.5 J/cm^2. The slowest decay corresponds to thermal diffusivity to the walls of the cell.[5]

The initial fluorescence intensities were obtained from the extrapolation to the time origin of the least squares results of the fast decay curves. Fig. 5 shows the pressure dependence of the initial fluorescence intensity for different irradiation fluences: under low excitation conditions, this intensity increases linearly versus gas pressure, while under high excitation conditions, the dependence of the intensity upon gas pressure is non-linear.

As in the low fluence experiments, the fast decays were measured in mixtures of $CDCl_3$ with Argon and rate constants of 41.3 ± 13.4 and 187.1 ± 14.5 ms^{-1} Torr^{-1} were obtained in good agreement within experimental error with the values in neat $CDCl_3$.

IV. DISCUSSION

A variety of intermode vibrational energy redistribution processes take place following CO_2 laser excitation of the $CDCl_3$ ν_4 mode.

As discussed in [3], the rise of the fluorescence intensity observed for the $2\nu_5$ overtone band is certainly due to a $\nu_4 \leftrightarrow \nu_5$ intermode transfer process:

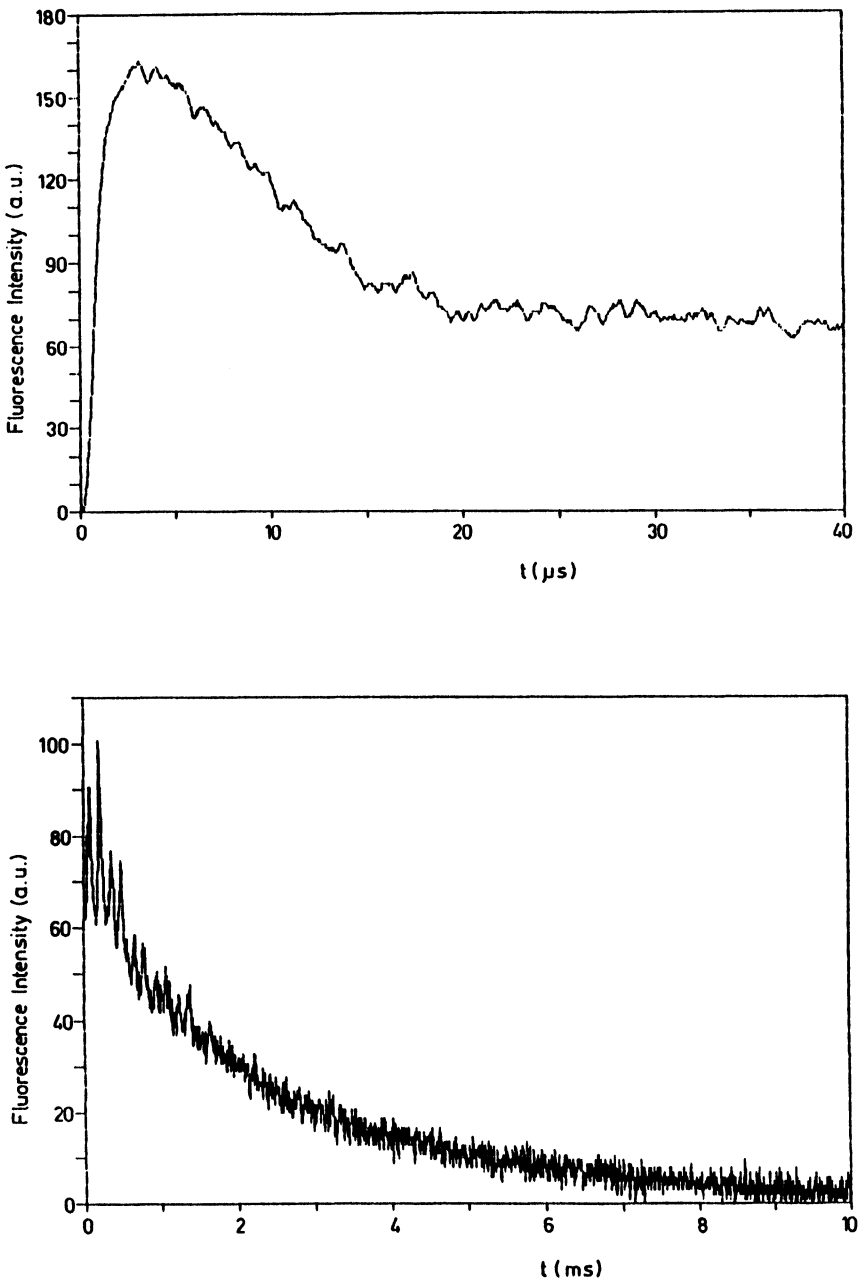

Figure 3 Fluorescence signal from the $2\nu_5$ overtone after irradiation of 7 Torr of $CDCl_3$ with a laser fluence of 2.5 J/cm^2. a) Rise and fast decay measured at a sample rate of 0.02 μs, (40 μs full scale). b) Slow decay measured at a sample rate 5 μs, (10 ms full scale).

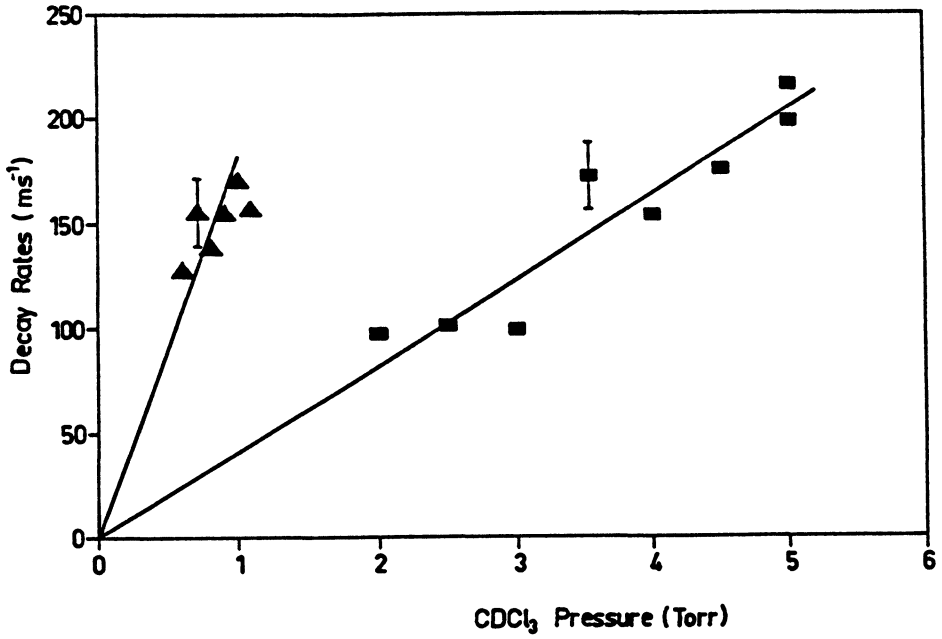

Figure 4 Pressure dependence of the fast decay rates for the different irradiation fluences: (■) 2.5 J/cm^2 and (▲) 4.5 J/cm^2.

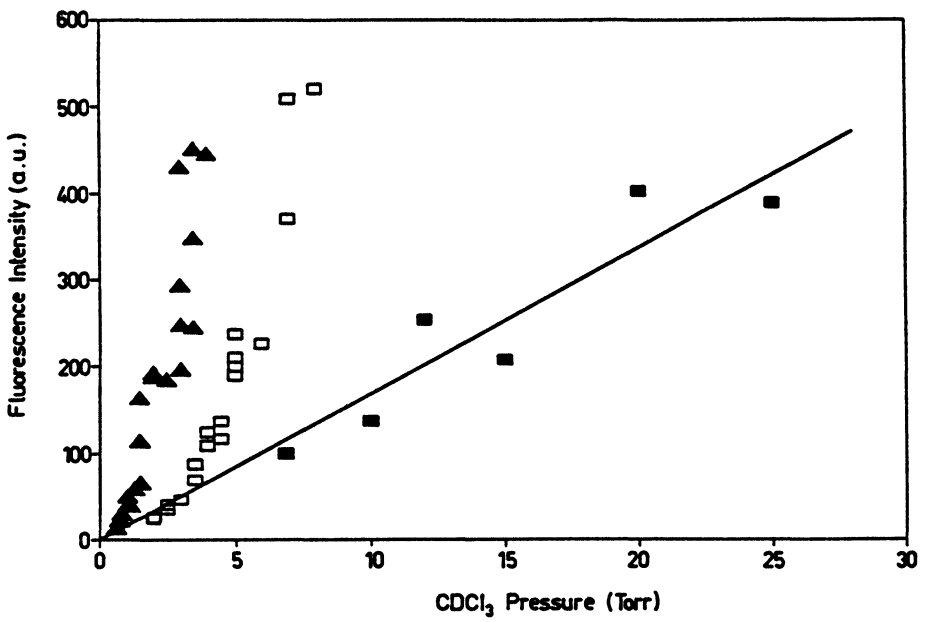

Figure 5 Pressure dependence of the initial fluorescence intensity for the different irradiation fluences: (■) 1.5 J/cm^2, (□) 2.5 J/cm^2 and (▲) 4.5 J/cm^2.

$$CDCl_3(\nu_4) + CDCl_3(0) = CDCl_3(0) + CDCl_3(\nu_5) + 168\ cm^{-1} \quad (1)$$

followed by a ladder-climbing process:

$$CDCl_3(\nu_5) + CDCl_3(\nu_5) = CDCl_3(2\nu_5) + CDCl_3(0) + \sim 0\ cm^{-1} \quad (2)$$

The $2\nu_5$ fluorescence risetime is about 1 μsec^{-1} for 1 Torr, so that the two processes must be very fast. This is effectively expected for the process (2), considering on one hand the near-resonance of the energy transfer and on the other hand the rather large value of the transition dipole moment corresponding to the ν_5 transition (0.28 Debye). The large efficiency of the far-from-resonance $\nu_4 \leftrightarrow \nu_5$ intermode transfer is probably due to a Coriolis-coupling existing between the ν_4 and the ν_5 states.[6]

Following the fast rise, the slower $2\nu_5$ fluorescence decay reflects the population loss of the ν_5 state as a result of intermode transfer processes, the most probable one being the transfer to the ν_2 mode:

$$CDCl_3(\nu_5) + CDCl_3(0) = CDCl_3(\nu_2) + CDCl_3(0) + 86\ cm^{-1} \quad (3)$$

the equilibration of population between the ν_4 and ν_5 modes being maintained at each time during the flow of population to the ν_2 mode.

The $2\nu_5$ fluorescence risetime being found two orders of magnitude smaller than the decay time, and considering that in the ν_5 mode the states higher than $2\nu_5$ are weakly populated, the time variation of the $2\nu_5$ population during the relaxation may be described by the process (2). From the corresponding bimolecular kinetic equation and with the mathematical approximations made in [3], the population deviation of $2\nu_5$ is given by[7]

$$\Delta N_{2\nu 5} = N_0^{-1}\ (2N^0_{\nu_5}\ \Delta N_{\nu_5} + \Delta N_{\nu_5}{}^2) \quad (4)$$

with $N_0 = N_0^0$, N_i^0 being the equilibrium population of state i.

In the low excitation limit where $2N^0_{\nu 5} >> \Delta N_{\nu 5}$, this population deviation can be approximated by[8]

$$\Delta N_{2\nu 5} = 2(N^0_{\nu 5}/N_0)\ \Delta N_{\nu 5} = 0.11\ \Delta N_{\nu 5} \quad (5)$$

Eq. (5) shows that the population deviation of the $2\nu_5$ overtone will depend linearly on the population deviation of the ν_5 state. It also means that the $2\nu_5$ population will decay at the same rate as that of the ν_5 state through which it is filled.[8,9]

Above this low excitation limit, $\Delta N_{\nu 5}$ will no longer be negligible compared to $N^0_{\nu 5}$ and the $2\nu_5$ population deviation will depend upon the square of the ν_5 population deviation. Then, as the laser excitation increases, the $2\nu_5$ population will decay with a rate constant which increases up to twice that of the ν_5 population according to eq. (4) in the limit where $\Delta N_{2\nu 5} \simeq N_0^{-1}\ \Delta N^2_{\nu 5}$. But this limit must be considered as a crude approximation; indeed, under high excitation conditions, the vibrational temperature in the mode ν_5 can become very elevated and the populations of states higher than $2\nu_5$ relatively great. The time variation of the $2\nu_5$ population cannot be described anymore only by the process (2), but also ladder-climbing processes such as:

$$CDCl_3(\nu_5) + CDCl_3(2\nu_5) = CDCl_3(3\nu_5) + CDCl_3(0) \quad (6)$$

or

$$CDCl_3(2\nu_5) + CDCl_3(2\nu_5) = CDCl_3(3\nu_5) + CDCl_3(\nu_5) \quad (7)$$

must be taken into consideration. In the present experiment the decay rate is found to increase with the laser fluence by a factor which can become much larger than 2, and which rises up to 11 for a laser fluence of 4.5 J/cm^2.

At high excitation levels, the relaxation mechanism may also become more complex. The increase of population in the upper vibrational states of the ν_4 and the ν_5 modes may open alternative relaxation channels. Then the intermode energy transfer from ν_4 and ν_5 modes to ν_2 or other modes may occur not only through process (3) but also through processes involving overtone states, which may be very efficient if these overtone states are coupled by a Coriolis or Fermi interaction. The lack of data on the spectroscopy of $CDCl_3$ does not allow any further identification of such probable pathways. Then, the decay rate constant for the $2\nu_5$ population can become much greater than twice that of the ν_5 state. This means that, in the high excitation regime, the $2\nu_5$ overtone fluorescence decay will no longer monitor the population loss of the ν_5 mode.

The final relaxation to the Boltzmann equilibrium occurs, too, at faster rates than in the low excitation regime. As in the intermode energy transfer from the ν_4 and ν_5 modes to ν_2, alternative relaxation channels involving overtone states may be opened in the intermode energy transfer from the ν_5 and ν_2 modes to the ν_3 and ν_6 modes. On the other hand, the V-T/R deexcitation rates have been shown to increase with increasing vibrational energy.[11]

V. CONCLUSIONS

The $2\nu_5$ overtone fluorescence of $CDCl_3$ has been measured under strong irradiation conditions of the ν_4 mode with a TEA CO_2 laser. The fast decay rates observed were compared with those obtained under low fluence irradiation.

At low laser fluence, (1.5 J/cm^2), the rate constants measured described a linear relaxation process which reflected the loss of population from the ν_5 to the ν_2 mode through a non-resonant collisional process.

Under strong irradiation conditions, the relaxation process became more complex and fluorescence decay rates faster by a factor 2.5–11 than in the low excitation regime were obtained. Therefore, for these excitation conditions, the $2\nu_5$ fluorescence decay no longer describes the relaxation of the ν_5 mode. Direct intermode as well as non-linear relaxation of the $2\nu_5$ overtone must be considered in addition under these conditions.

Relaxation to the thermodynamic equilibrium will be enhanced too probably due to non-linear relaxation pathways from the ν_5 and ν_2 modes to the ν_3 and ν_6 modes and faster V-T/R relaxation rates with increasing fluence.

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