

VIBRATIONAL RELAXATION OF THE $2\nu_5$ OVERTONE OF CDCl_3 FOLLOWING TEA CO_2 LASER EXCITATION OF THE ν_4 MODE

M. A. VAZQUEZ^{a)}, M. L. AZCÁRATE^{b)}, E. J. QUEL, L. DOYENNETTE^{c)},
C. RINALDI^{d)}, J. C. FERRERO^{d)}

a) *Student of Licenciatura en Ciencias Físicas. Fac. Cs. Ex. y Nat. Universidad de Buenos Aires. ARGENTINA*

b) *Research career of CONICET. ARGENTINA*

c) *Laboratoire de Physique Moléculaire et Applications. CNRS. Université Pierre et Marie Curie. Paris. FRANCE*

d) *INFIQC, Departamento de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Sucursal 16, C.C. 61, 5016 Córdoba, ARGENTINA*

and

CEILAP (CITEFA-CONICET)

Zufriategui 4380, (1603) Villa Martelli, Bs. As., ARGENTINA

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The time variation of the $2\nu_5$ fluorescence intensity was measured in CDCl_3 excited in the ν_4 C–D bending mode by a TEA CO_2 laser operating on the 10P(48) line. A fast rise of the fluorescence, with a time constant $\leq 1 \mu\text{s Torr}$, was first observed, showing that a fast equilibration of population occurs between the ν_4 and ν_5 modes through a $\nu_4 \leftrightarrow \nu_5$ Coriolis-assisted intermode transfer and a $\nu_5 \leftrightarrow 2\nu_5$ near-resonant ladder-climbing process. Then a first fast fluorescence decay was observed and attributed to a $(\nu_4, \nu_5) \rightarrow \nu_2$ intermode transfer with a rate constant of $(7.10 \pm 1.13) \text{ ms}^{-1} \text{ Torr}^{-1}$. At last, a much slower decay, with a rate constant of $0.111 \pm 0.015 \text{ ms}^{-1} \text{ Torr}^{-1}$, results from the less efficient intermode transfer and V–T,R deexcitation processes involving the ν_3 and ν_6 states, and which compete to relax the gas to a thermodynamic equilibrium.

KEY WORDS: Vibrational Relaxation, IR Fluorescence, Laser.

I. INTRODUCTION

The IR multiple-photon excitation processes (IRMPE) induced by an intense IR laser source in small polyatomic molecules are restricted by rotational and anharmonic bottlenecks at the first stage of excitation.¹ Consequently, the dissociation efficiency is lowered. Information on the energy-transfer mechanisms in collisional processes of vibrationally excited molecules is of great interest to understand the dynamics of

II. EXPERIMENTAL PROCEDURE

The experimental set-up is shown in Figure 2. A homemade TEA CO_2 multimode laser tuned to the P(48) line, ($10.91 \mu\text{m}$), was used as radiation source. The laser frequency was verified with a CO_2 spectrum analyzer (Optical Engineering). The laser pulses consisted of a 90 ns FWHM spike followed by a 250 ns tail as measured with a photon-drag detector. The laser output energy was attenuated with CaF_2 flats in order to obtain a laser-induced fluorescence intensity just high enough to perform rate measurements in conditions where the rate equations can be linearized. The pumping energy, measured with a pyroelectric detector GENTEC ED500 was always $\leq 1.5 \text{ J/cm}^2$. The gas sample was irradiated in a pyrex cell, (2.85 cm diameter and 15.35 cm long), sealed with NaCl windows. Sample pressures were measured with an MKS Baratron capacitance manometer. CDCl_3 (99.8% D) was purchased from Merck and used without purification except outgasing of non-condensable gases at 77 K.

The IR fluorescence emitted by the gas was focused through a 2 cm focal length lens into a liquid Nitrogen cooled photoconductive HgCdTe detector, Judson Infrared J15-D12, at right angles to the laser propagation direction. The CDCl_3 fluorescence emitted in the CDCl_3 $2\nu_5$ overtone band at $6.7 \mu\text{m}$ was isolated by a gas filter placed between the collecting lens and the detector. The gas filter consisted of a 2.5 cm

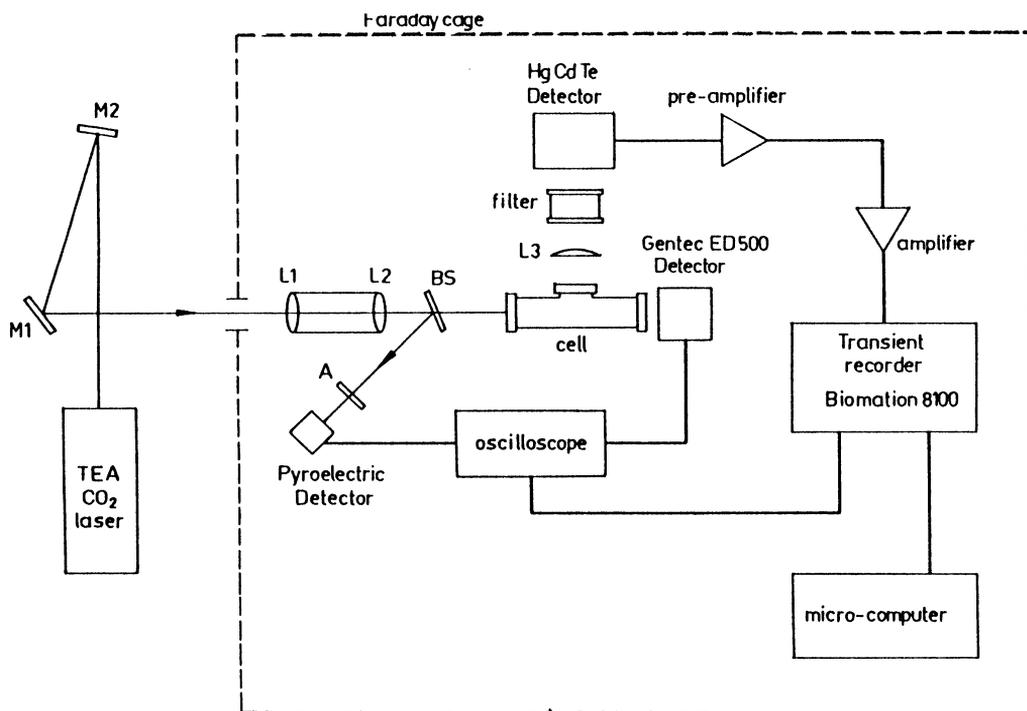


Figure 2 Experimental set-up for laser induced fluorescence measurements. M_1 , M_2 : mirrors, L_1 , L_2 , L_3 : lenses, A : CaF_2 attenuators.

diameter, 5.5 cm long pyrex cell filled with a mixture of 400 Torr of vinylfluoride, 200 Torr of C₂F₄ and 100 Torr of Freon 11. The fluorescence signal was preamplified with a matched amplifier, amplified with a Tektronix AM502 amplifier, digitized with a Biomation 8100 transient recorder, averaged with an Apple II microcomputer and finally transferred to an IBM PC AT for subsequent analysis. The response time of the detection system was 1.5 μ sec. The reflection of the laser beam on a NaCl beam-splitter was used as a trigger pulse of the signal processing system.

III. RESULTS AND DATA ANALYSIS

A typical 6.7 μ m laser induced fluorescence signal, obtained by pumping 7 Torr of CDCl₃ with the 10P(48) CO₂ laser line is shown in Figure 3. As can be seen, the fluorescence intensity rises very rapidly to its peak, then decays first somewhat rapidly to about half of the peak amplitude in about 20 μ s and then much more slowly in about 10 ms to the initial baseline. Oscillations are observed on the slow decaying signal, as can be seen in Figure 3b. They are caused by a laser-induced acoustic disturbance propagating inside the sample cell, as first observed in SF₆ by Bates *et al.*,⁶ and then in many other gases.

The fluorescence signals were fitted to a sum of exponential functions by a non-linear least-squares regression method based on the Marquardt algorithm to obtain relaxation rates and initial intensities.

The numerical fit of the risetime was always found to be about 0.6 μ s in the pressure range 2–20 Torr where sufficient signal intensity could be obtained to allow accurate measurement. This risetime was limited by the response time of the detection system thus setting a lower limit of about 0.8 μ s⁻¹ Torr⁻¹ for the rate constant of this process.

Decay rates increasing linearly with gas pressure were deduced from the fast and slow fluorescence intensity decays. Another much slower decay rate, varying linearly with 1/pressure and, consequently attributed to the thermal diffusivity to the walls of the cell,⁷ was also deduced from the slow fluorescence intensity decay. Rate constants equal to 16.3 \pm 1.3 ms⁻¹ Torr⁻¹ and to 0.111 \pm 0.015 ms⁻¹ Torr⁻¹ were successively deduced from measurements.

These rates were also measured in mixtures of CDCl₃ with Argon and rate constants of 18.1 \pm 4.9 ms⁻¹ Torr⁻¹ and 0.089 \pm 0.01 ms⁻¹ Torr⁻¹ were obtained in good agreement within experimental error with those in neat CDCl₃.

IV. DISCUSSION

Following the pumping of CDCl₃ in a rovibrational level of ν_4 by the 10P(48) CO₂ laser line, a very fast equilibration of populations first occurs among all the rovibrational levels in the ν_4 state upon rotational energy transfer processes. We shall then consider as instantaneous the rotational relaxation, the rates of which are generally in 10⁷–10⁸ s⁻¹ Torr⁻¹, compared to the vibrational energy transfers.

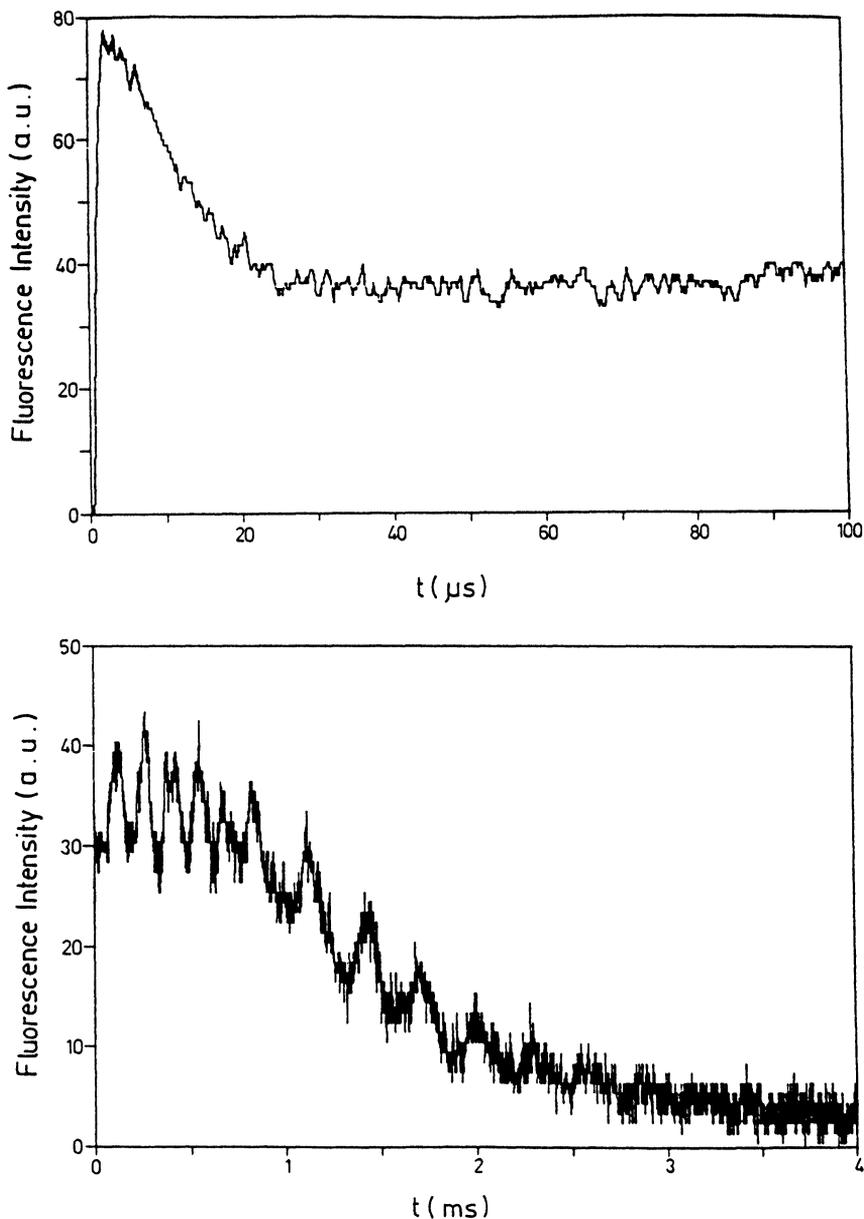
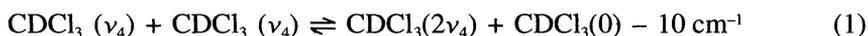
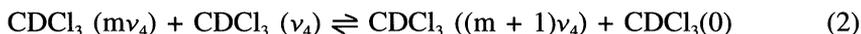


Figure 3 Fluorescence signal from the $2\nu_5$ overtone after irradiation of 7 Torr of CDCl_3 with a laser fluence of 1.5 J/cm^2 . a) Rise and fast decay measured at a sample rate of $0.05 \mu\text{s}$, ($100 \mu\text{s}$ full scale). b) Slow decays measured at a sample rate $2 \mu\text{s}$, (4 ms full scale).

The excitation energy would first flow rapidly from ν_4 to all the vibrational states of the ν_4 mode through ladder climbing processes such as:

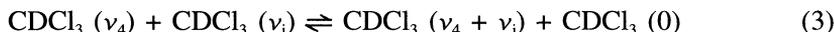


and more generally:

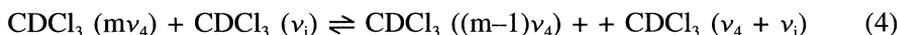


These processes are very fast because they are near-resonant and the two colliding molecules are undergoing $\Delta\nu_4 = 1$ transitions characterized by high transition dipole moments (0.21 Debye for the ν_4 transition).⁸

It is also the case for the near-resonant processes:

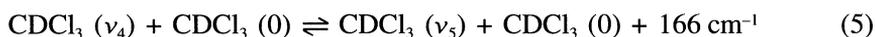


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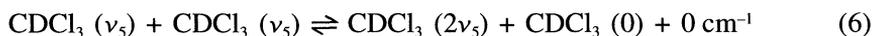


These processes, involving ν_i states with low energies ($i = 2, 3, 5, 6$) and consequently with relatively large populations, would be efficient to populate the $(\nu_4 + \nu_i)$ combination states, and upper $(m\nu_4 + n\nu_i)$ states.

The fast rise of the fluorescence intensity observed for the $2\nu_5$ overtone band is certainly first due to an intermode transfer from ν_4 to ν_5 :



Then to a ladder-climbing process analogous to the process (1):



The process (6) is certainly as fast as process (1), the ν_5 transition dipole moment being of 0.28 Debye.⁸ In principle it should be faster than the process (5) which is a non-resonant process, and which consequently would determine the risetime of the $2\nu_5$ fluorescence intensity. But this risetime is found to be about $1 \mu\text{s}$ for 1 Torr, a time constant which shows that the process (5), although non-resonant, is very efficient. This is certainly due to Coriolis interaction which couples the two states ν_4 and ν_5 .⁹ Indeed such a coupling, which causes a mixing of rovibrational wave functions of two states, enhances the efficiency of an intermode transfer occurring between the two states, as it has been observed in many gases such as D_2CO and HDCO ,¹⁰ CD_3H ,¹¹ CD_3Cl ¹² or O_3 .¹³

The $2\nu_5$ state may also be populated through other processes such as the near-resonant processes:



But such a process involving multiquantum transitions are generally of low efficiency. A fast equilibration of population would also occur between the ν_5 state and all the vibrational states in the ν_5 mode and the combination states $(m\nu_5 + n\nu_i)$ with $i = 2, 3, 6$, through near-resonant processes analogous to (2)–(4).

Since the rise of the $2\nu_5$ fluorescence intensity has been found to be two orders of magnitude faster than its first decay, the time variation of the $2\nu_5$ population during the relaxation may be described only by the process (6)¹⁴ from which the following bimolecular equation is deduced:

$$dN_{2\nu_5}/dt = k_u N_{\nu_5} N_{\nu_5} - k_d N_{2\nu_5} N_0 \quad (8)$$

where N_i is the population density in molecules/cm³ of the vibrational state i . At the equilibrium, populations are given by:

$$N_{\nu_5}^2 = N_{2\nu_5} N_0 \quad (9)$$

considering that for a nearly resonant process, one has $k_u \approx k_d$. The population of each state i being the sum of an equilibrium population N_i^0 and of a time dependent population deviation ΔN_i ,

$$N_i = N_i^0 + \Delta N_i \quad (10)$$

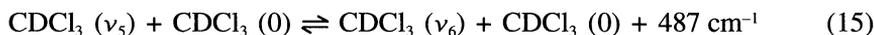
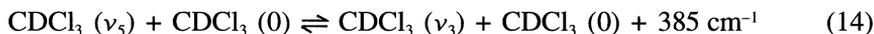
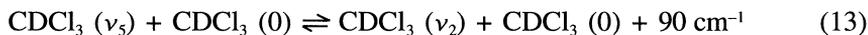
the population deviation of $2\nu_5$ is given by

$$\Delta N_{2\nu_5} = N_0^{-1} (2\nu_{\nu_5}^0 \Delta N_{\nu_5} + \Delta N_{\nu_5}^2) \quad (11)$$

with $N_0 = N_0^0$. In the low excitation limit where $2N_{\nu_5}^0 \gg \Delta N_{\nu_5}$, this population deviation will be given by

$$\Delta N_{2\nu_5} = 2(N_{\nu_5}^0/N_0) \Delta N_{\nu_5} = 0.11 \Delta N_{\nu_5} \quad (12)$$

Since the $2\nu_5$ state population is much smaller than that of the ν_5 state, the $2\nu_5$ overtone fluorescence intensity decay will reflect the population loss of the ν_5 state through which it is filled.¹⁴⁻¹⁷ The dynamic equilibrium established between the C-Cl₃ stretching fundamental and the first overtone will be maintained while the ν_5 state excess population due to vibrational excitation begins to flow to other modes through slower processes such as:



If the $\nu_4 \leftrightarrow \nu_5$ intermode transfer process (5) is very fast, as expected, the equilibration of populations between the ν_4 and ν_5 modes would be maintained at each time during the flow of population to the ν_2 , ν_3 and ν_6 modes.

Only one fast decay is observed after the initial rise of the fluorescence intensity. Because of the smaller energy gap involved in process (13) and the larger ν_2 dipole transition moment compared to ν_3 and ν_6 ,⁸ the fast decay would be due only to the process (13). The approximate time to equilibrate ν_5 and ν_2 is found to be 100 μs^{-1} at 1 Torr. When the equilibrium is established, the excess of population in the ν_5 mode will have decreased to a value $\Delta N_{\nu_5}^{\text{eq}}$. The amplitude of the fast fluorescence decay falls to about half of its peak value before V-T/R energy transfer sets in. The ratio $\Delta N_{2\nu_5}^{\text{eq}}/\Delta N_{\nu_5}^0$ is ≈ 0.5 , $\Delta N_{2\nu_5}^0$ being the population of the $2\nu_5$ overtone at the maximum of the fluorescence intensity, i.e., when the V-V equilibrium between the ν_5 and $2\nu_5$ states is established, and before the ν_5 state begins to fill the ν_2 mode. Since the populations of the ν_5 and $2\nu_5$ states may be considered as permanently equilibrated, $\Delta N_{\nu_5}^{\text{eq}}/\Delta N_{\nu_5}^0 = \Delta N_{2\nu_5}^{\text{eq}}/\Delta N_{2\nu_5}^0 \approx 0.5$, and thus the ν_5 mode transfers half of its excitation population to the ν_2 mode through the process (13).

The bimolecular kinetic equation corresponding to process (13) is:

$$dN_{\nu_3}/dt = k_{25}N_{\nu_2}N_0 - k_{52}N_{\nu_5}N_0 \quad (16)$$

where N_i is the population density in molecules/cm³ of the state i . Expanding the total population of each state i as in (10), eq. (16) becomes

$$d\Delta N_{\nu_3}/dt = K_{25}\Delta N_{\nu_2} - K_{52}\Delta N_{\nu_5} \quad (17)$$

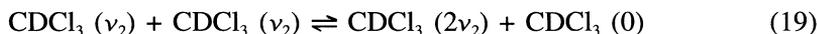
with $K_{ij} = k_{ij}N_0$. The initial conditions being $\Delta N_{\nu_5} = \Delta N_{\nu_5}^0$ and $\Delta N_{\nu_2} = 0$ for $t = 0$, and the conservation of the quanta number requiring $\Delta N_{\nu_5} + \Delta N_{\nu_2} = \Delta N_{\nu_5}^0$, the solution of (17) is:

$$\Delta N_{\nu_5}(t) = \left(\Delta N_{\nu_5}^0 - \frac{k_{25}\Delta N_{\nu_5}^0}{k_{25} + k_{52}} \right) e^{-(k_{52} + k_{25})t} + \frac{k_{25}\Delta N_{\nu_5}^0}{k_{25} + k_{52}} \quad (18)$$

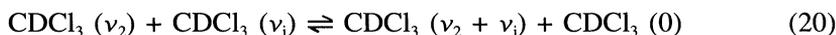
which yields the rate constant $k_{52} = 7.10 \pm 1.13 \text{ ms}^{-1} \text{ Torr}^{-1}$.

In fact the vibrational energy flows from ν_4 and ν_5 to ν_2 : indeed ν_4 and ν_5 are coupled by a very fast intermode transfer, as previously discussed, so that they can be considered as permanently in equilibrium with each other during the much slower transfer to ν_2 . Therefore, the two states may be considered as one state (ν_4, ν_5) and ν_5 would be replaced by (ν_4, ν_5) in the equations (16)–(18).

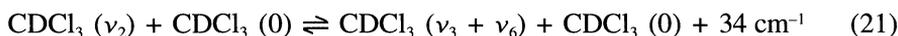
The filling of the ν_2 state due to the $\nu_5 \leftrightarrow \nu_2$ intermode transfer would induce that of all the vibrational states in the ν_2 mode through near-resonant ladder climbing processes such as:



and the filling of the combination states ($\nu_2 + \nu_i$), and then of upper ($m\nu_2 + n\nu_i$) states, through processes such as:

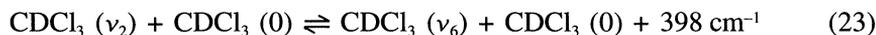
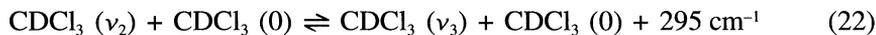


Another near-resonant energy transfer process may be considered:



but this process involving a two quanta transition is probably not very efficient. More generally, in the present kinetic scheme, processes involving multiquanta transitions have been disregarded, including near-resonant ones.

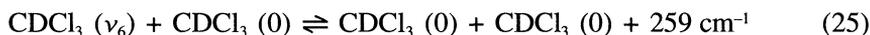
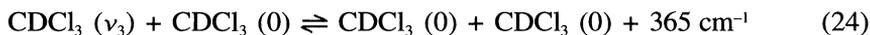
Then, the excited vibrational states relax slowly to a Boltzmannian equilibrium at a rate of $111 \pm 0.015 \text{ s}^{-1} \text{ Torr}^{-1}$ through a variety of processes. First the vibrational energy would be transferred from the ν_5 mode to the ν_3 and ν_6 modes through far-from-resonance intermode transfer processes (14) and (15) and also from the ν_2 mode to these same modes through processes:



These intermode transfer processes (14), (15), (22) and (23) are far-from-resonance and, furthermore, the ν_3 and ν_6 transitions are characterized by weak dipole moments,

as it can be deduced from the weakness of the ν_3 and ν_6 absorption band intensity.⁸ Therefore they are expected to be slow.

At last, the V-T/R deexcitation processes would occur essentially through the deexcitation of the lowest energy states ν_3 and ν_6 .¹⁷



Other V-T/R deexcitation processes may be considered but the processes (24) and (25) which require the release of a minimum amount of vibrational energy into translational and rotational energy might be the most efficient ones. The energy gaps involved in these processes are relatively close to those involved in the previous intermode transfer processes (14), (15), (22) and (23). Therefore, all these processes would compete for the relaxation of the ν_4 , ν_5 and ν_2 modes to a thermodynamic equilibrium, and would be responsible of the slow decay observed in the experiments for the $2\nu_5$ fluorescence intensity.

V. CONCLUSIONS

Relaxation constants were deduced from the time variation of the $2\nu_5$ overtone fluorescence intensity emitted by CDCl_3 excited to the ν_4 C-D bending mode by a TEA CO_2 laser operating in the 10P(48) line. The measurements were performed at the lowest laser fluence for which appreciable fluorescence intensity was obtained ($1,5 \text{ J/cm}^2$). The fluorescence intensity risetime, found to be $\geq 1.2 \text{ ms Torr}$ shows that a fast equilibration of population occurs from the ν_4 to the ν_5 mode. The most probable processes responsible of that equilibration are a $\nu_4 \rightarrow \nu_5$ intermode transfer process followed by a $\nu_5 \rightarrow 2\nu_5$ ladder-climbing process. Although the $\nu_4 \rightarrow \nu_5$ intermode transfer is non-resonant, its particularly large efficiency is certainly due to the existence of a Coriolis interaction coupling the ν_4 and ν_5 states. Indeed the effect of such interaction is to enhance the efficiency of an energy exchange between two states.

Other measurements of these rate constants have also been performed by using high CO_2 laser fluences and will be given in a next paper.

Moreover, for a thorough understanding of the vibrational relaxation occurring in CDCl_3 , we plan to perform other measurements by observing the time variation of the fluorescence emitted in other vibrational bands.

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References

1. Letokhov. "Non-Linear Laser Chemistry", ed. F. P. Schafer. Springer-Verlag, Berlin. (1983)
2. Flynn. "Chemical and Biochemical Applications of Lasers", Vol. 1, ed. C. Bradley Moore. Academic Press, New York, 163 (1974).
3. M. L. Azcárate, E. J. Quel, B. Toselli, J. C. Ferrero, E. H. Staricco. *J. Phys. Chem.*, **92**, 403–408 (1988).
4. M. L. Azcárate, E. J. Quel. *J. Phys. Chem.*, **93**, 697–702 (1989).
5. García, R. Escribano, G. del Rio, J. M. Orza. *Anal. Quim.*, **71**, 745 (1975).
6. Bates, G. W. Flynn, J. T. Knudtson and A. M. Ronn. *J. Chem. Phys.*, **53**, 3621 (1970).
7. Bates, Jr., J. T. Knudtson, G. W. Flynn, A. M. Ronn. *J. Chem. Phys.*, **57**, 4172 (1972).
8. Calculated from data from K. Kim, W. T. King. *J. Chem. Phys.*, **80**, 978 (1984).
9. Escribano private communication.
10. Haub and B. J. Orr. *J. Chem. Phys.*, **86**, 3380 (1987).
11. F. Menard-Bourcin and L. Doyennette. *J. Chem. Phys.*, **88**, 5506 (1988).
12. L. Doyennette and F. Menard-Bourcin. *J. Chem. Phys.*, **89**, 5578 (1988).
13. L. Doyennette, J. Menard and F. Menard-Bourcin. *Chem. Phys. Letters*, **170**, 197 (1990).
14. H. Castelton, G. Flynn. *J. Chem. Phys.*, **67**, 3133 (1977).
15. Sheorey, G. Flynn. *J. Chem. Phys.*, **72**, 1175 (1980).
16. Fujimoto, E. Weitz. *Chem. Phys.*, **27**, 65 (1978).
17. S. Sheorey, R. C. Slater, G. W. Flynn. *J. Chem. Phys.*, **68**, 1058 (1978).