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Inter- and Intramolecular Vibrational Distribution in IR Multiple Photon Excitation: CF₂Cl₂ Molecule

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Vibrational energy distribution of IR MP-excited CF₂Cl₂ is studied when pumping molecules through ν_1 and ν_8 modes. In both cases the intermolecular distribution is found to be in a state of nonequilibrium consisting of ensembles of “hot” and “cold” molecules. The structure of the “cold” ensemble is different when ν_1 and ν_8 modes are pumped. Statistical intramolecular energy distribution caused by stochastization of vibrational motion is found for “hot” molecules. The estimated value of stochastization onset energy equals $E_{th} \leq 7800 \text{ cm}^{-1}$.

KEY WORDS Infrared; multiple photon; CF₂Cl₂; stochastization.

INTRODUCTION

Numerous investigations of IR multiple photon excitation (MPE) (see review in References 1 and 2) led to a considerable progress in the understanding of this effect. At the same time, there remained a whole series of unsolved problems which are, at present, the subject of intense studies. One is the question of the form of vibrational energy distribution produced in the course of IR MPE. Speaking of the energy distribution, one can single out two of its aspects—intermolecular distribution and intramolecular distribution. What is meant in the

former case is the distribution of the absorbed energy among the different molecules in the sample gas, and in the latter, the distribution of the energy among the different modes of the isolated molecule itself.

Knowledge of the form of intermolecular energy distribution is exceptionally important for an adequate description of the IR MPE process proper, and for the study of the subsequent reactions of the excited molecules. As concerns the intramolecular distribution, its study is of special significance, insofar as it yields information on the character of vibrational motion in a highly excited molecule (stochastization of motion,¹⁻³ intramolecular energy redistribution, interaction of normal modes, etc.).

A large number of spectroscopic investigation techniques were proposed to solve the above range of problems (see review in References 1 and 2). One of the most promising techniques is based on the use of the spontaneous Raman scattering.⁴ Even in the first experiments on the Raman scattering probing of the SF₆ and CF₃I molecules,^{4,5} it was demonstrated that the IR MPE process gives rise to a nonequilibrium bimodal intermolecular energy distribution in which two molecular ensembles can be singled out. The upper, "hot" ensemble consists of highly excited molecules with the absorbed energy being distributed among all the molecular modes in a statistically equilibrium manner. The lower, "cold" ensemble is constituted by unexcited or weakly excited molecules. Such distribution parameters were determined as the average energy $\bar{\epsilon}^*$ and the fraction q of the upper-ensemble molecules. The experiments performed have made it possible to establish that the equilibrium excitation of all the modes in the upper molecular ensemble is a result of the stochastization of vibrational motion and occurs only when the total molecular energy exceeds some limiting value referred to as the stochastization onset E_{thr} .

Subsequent experiments with the CF₂HCl⁶ and CF₃Br^{7,8} molecules allowed the picture of energy distribution arising in the course of MPE to be verified. It was demonstrated in particular that in the lower molecular ensemble, the energy of the resonant mode being pumped may perceptibly exceed that of other modes having their temperature at the initial, room value. This energy excess is due to molecules remaining on the lower resonance mode levels below the stochastization onset. A similar inference was drawn earlier for SF₆ in Refer-

ence 9 on the basis of experiments on its coherent anti-Stokes Raman spectroscopy probing.

The use of the spontaneous Raman scattering probing technique made it possible to determine the position of the stochastization onset in all the above molecules. Depending on the molecular species, it lies within the range 4000–8000 cm⁻¹. To reveal the mechanism of stochastization requires systematic measurements of E_{thr} for different molecules. Besides, it is of interest to find out how excitation conditions influence the character of vibrational energy distribution, particularly the ratio between the energies absorbed in the upper and lower molecular ensembles, and how this ratio depends on the method of depositing energy in the molecule. The presence in CF₂Cl₂ of two IR active modes (ν_1 and ν_8) the frequencies of which fall within the CO₂-laser bandwidth makes this molecule a convenient subject of such inquiries.

The MP excitation and dissociation of CF₂Cl₂ were studied earlier in a great number of works (see review in References 1 and 2 and also works reported in References 10–13 and references in them). In particular, to explain their experiments on IR–UV excitation reported in References 11 and 12, they put forward a suggestion that excitations of the ν_1 and ν_8 modes give rise to qualitatively different characters of energy distribution, the absorbed energy in the latter case being assumed to remain localized in this mode. A similar conclusion was drawn on the basis of IR–UV ionization experiments in the work reported in Reference 13 where they argued that no stochastization was present when acting on the ν_8 mode.

Our experiments on the spontaneous Raman scattering probing of MP excited CF₂Cl₂ molecules enabled us to obtain direct information on the character of the vibrational energy distribution formed. The results of these experiments are presented below.

EXPERIMENTAL METHOD AND SET-UP

Research into the vibrational energy distribution parameters by the spontaneous Raman scattering technique relies on a certain relationship between the average number of quanta in some or other mode, and the integral spontaneous Raman scattering intensity taken

over the spectral region corresponding to the mode being probed. Specifically, the spontaneous Raman scattering signal for fundamental transitions is proportional to the average energy in a given mode and is independent of the molecular energy distribution function. That this is true was demonstrated in the works reported in References 4–6. In our subsequent works,^{7,8} the spontaneous Raman scattering probing technique was extended to cover transitions in overtones and combined bands, which enabled us to obtain a more detailed information about the character of energy distribution. Information on the form of the energy distribution function can also be obtained from the spontaneous Raman scattering spectra of the molecules under excitation.^{5,6,8}

Our experimental set-up was described in detail in the work reported in Reference 6. The molecules under study were excited by TEA CO₂ laser pulses 25–30 ns (FWHM) in duration. Probing was effected by means of the second harmonic output from an Nd:YAG laser with a pulse duration of 8 ns. The instability of the delay time τ_d between the exciting and probing pulses did not exceed 20 ns, this value determining also the minimum τ_d .

Spontaneous Raman scattering signals were registered by two methods: as an integral value over the desired spectral region using a photomultiplier and with a high resolution using a multichannel system, a photon counting mode being realized in both cases.

The CF₂Cl₂ molecule belongs to the C_{2v} or C_s symmetry group, depending on which chlorine isotope enters into its composition, and has nine normal vibrations. As mentioned earlier, two of these vibrations— ν_1 (1100 cm⁻¹) related mainly to the stretching of the C–F bond and ν_8 (922 cm⁻¹) associated with the stretching of the C–Cl bond—have their frequencies falling within the CO₂ laser bandwidth. All the nine modes are active in spontaneous Raman scattering. In addition, two overtones— $2\nu_5$ (640 cm⁻¹) and $2\nu_6$ (2320 cm⁻¹)—can also be seen in the spontaneous Raman scattering spectrum.

When exciting the molecules through the ν_1 mode, irradiation was carried out on the 9R(30) line ($\Omega_{\text{CO}_2} = 1084.6 \text{ cm}^{-1}$) and when acting on the ν_8 mode, the molecules were irradiated on the 10P(34) line ($\Omega_{\text{CO}_2} = 931 \text{ cm}^{-1}$). Realized in the first case was a long-wavelength detuning and in the second, a short-wavelength detuning from the respective linear absorption band. The exciting laser fluence in both cases was varied in the range 0.075–1 J/cm². It follows from our

measurements that in these conditions the molecular dissociation is insignificant and can be disregarded.

Preliminarily we performed experiments to establish collisionless excitation conditions. For this purpose, we measured the gas pressure dependence of the anti-Stokes Raman scattering signal in the ν_2 mode (667.2 cm^{-1}) at the minimum delay time. The measurements were taken at two laser fluence values— 0.2 and 1 J/cm^2 —on the 9R(30) line. As can be seen from Figure 1, departure from linear dependence is in both cases observed at pressures $p \geq 2$ Torr, i.e., the rise of the average energy in the ν_2 mode due to collisions starts at $p\tau_d \geq 50$ Torr. At lower pressures, collisions can be neglected. For this reason, most of the subsequent experiments were carried out at $p = 0.75$ Torr.

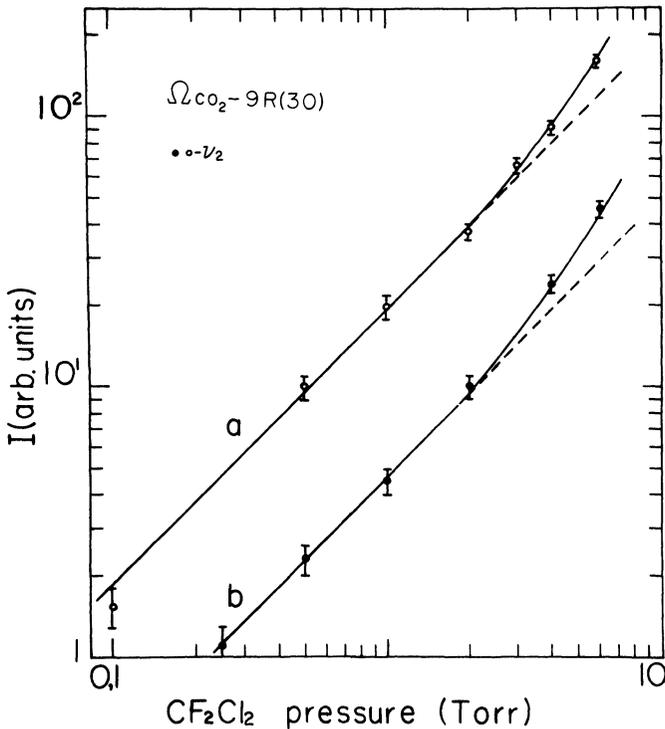


Figure 1 "Instantaneous" integral signal I (ν_2 mode) as a function of CF_2Cl_2 gas pressure for two CO_2 laser fluence values: (a) $\Phi = 1 \text{ J/cm}^2$ and (b) $\Phi = 0.2 \text{ J/cm}^2$. Pumped mode— ν_1 .

EXPERIMENTAL RESULTS

I. When acting on the ν_1 mode, we performed the anti-Stokes Raman spectroscopy of eight modes (except for $\nu_6 = 1160 \text{ cm}^{-1}$). As in the case of the experiments with other molecules,⁴⁻⁸ the response to excitation of all the modes appeared at minimum delay times between the exciting and probing pulses. Figure 2 shows the average energies $\bar{\epsilon}_i$ in the different modes (the total value being given for the group of modes ν_3, ν_7, ν_9) as a function of IR fluence. The method of determining the absolute values of $\bar{\epsilon}_i$ has been described in Reference 6. As can be seen, increasing the fluence Φ causes $\bar{\epsilon}_i$ to grow monotonically in all the modes.

Measurements show that in this case, as in the case of experiments with other molecules, a nonequilibrium intermolecular energy distribution is established. This is borne out by the following facts. First, the appearance in the "instantaneous" Stokes spectrum of the ν_2 mode (667.2 cm^{-1}), like with the molecules SF_6 ⁵ and CF_2HCl ⁶, of a wide band on the "red" side of the line corresponding to the unexcited molecules. Secondly, the character of energy redistribution among the different modes as the delay time τ_d is increased and an equilibrium distribution is established as a result of collisions. Thus (see Figure 2), it can be seen that the energy store of the modes ν_1 and ν_2 decreases, while that of the group of modes ν_3, ν_7, ν_9 remains unchanged. The probing of the ν_8 mode also points to energy outflow from this mode. At $\Phi = 0.4 \text{ J/cm}^2$ the decrease is $\Delta\bar{\epsilon}_8 \approx 55 \text{ cm}^{-1}$. Similar measurements carried out for the lowest-frequency modes ν_5 (322 cm^{-1}) and ν_4 (261.5 cm^{-1}) have shown their energy to rise. At $\Phi = 0.35 \text{ J/cm}^2$ the increase for ν_4 is $\Delta\epsilon_4 = 40 \text{ cm}^{-1}$ (at $\bar{\epsilon}_4 (\tau_d \leq 20 \text{ ns}) = 160 \text{ cm}^{-1}$).

The inference as to the character of the intermolecular energy distribution in this case (i.e., whether there are molecules having only their lower resonance mode levels excited) can be drawn by comparing the "instantaneous" values of $\bar{\epsilon}_i$ in the modes ν_1 and ν_8 . The comparatively small difference in frequency (170 cm^{-1}) between these modes results in their heat capacities being close over a fairly broad temperature range. Therefore, in the absence of molecules with excited lower levels of the mode ν_1 being pumped, the average energies $\bar{\epsilon}_i$ in these modes will differ very slightly, even if the intermolecular energy distribution is nonequilibrium. As seen from Figure 2, $\bar{\epsilon}_1$ and $\bar{\epsilon}_8$ over the entire laser fluence range coincide accurate to within the measure-

ment error, which points to the absence of any energy excess in the resonant mode ν_1 .

Thus, the fact that all the molecular modes are being excited and no energy excess is present in the mode being pumped allows one to draw an unambiguous conclusion about the form of the nonequilibrium intermolecular energy distribution. The distribution is constituted by two molecular ensembles. As in the case of the molecules studied earlier, the upper ensemble is formed by molecules featuring an equilibrium excitation of all their modes. The lower consists of molecules that have not interacted with the radiation. Proceeding from this conclusion, we can determine such distribution parameters as the

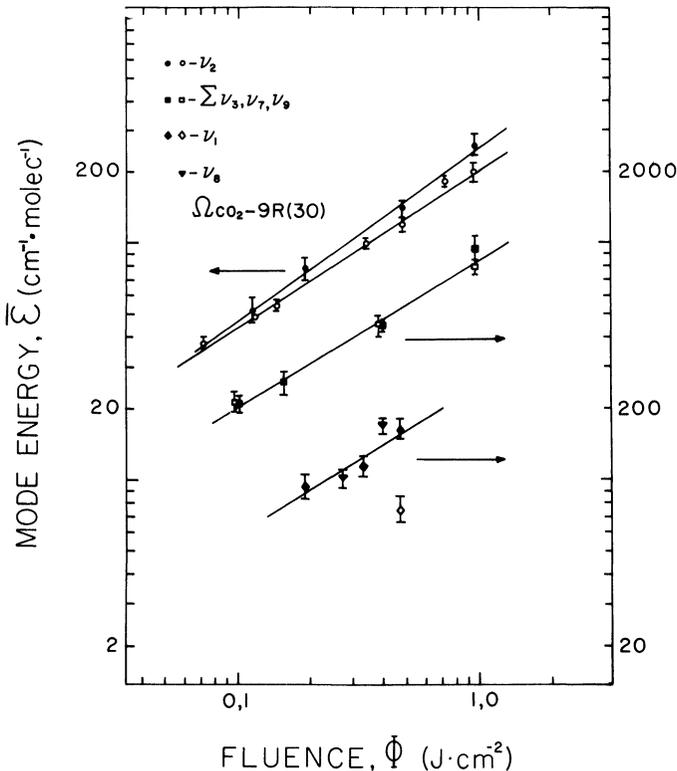


Figure 2 Average energies $\bar{\epsilon}_i$ in modes ν_1 , ν_2 , and ν_8 and also in group of modes ν_3 , ν_7 , ν_9 as a function of CO₂ laser pulse fluence Φ . Pumped mode— ν_1 (solid symbols — $\tau_d \leq 20$ ns; open symbols — $\tau_d = 4 \mu\text{s}$).

fraction q and the average energy $\bar{\epsilon}^*$ of the molecules in the upper ensemble. The procedure is based, as in References 5 and 6, on measuring the total absorbed energy per molecule, $\bar{\epsilon}^s$, and the fraction $1 - q$ of the molecules not involved in the process of excitation. The quantity $\bar{\epsilon}^s$ can be found from measurements of the average energy $\bar{\epsilon}_i$ in any of the modes being probed at the moment vibrational equilibrium has already set in as a result of the $V-V'$ relaxation but the loss of energy to other degrees of freedom is as yet insignificant. In our experiments, these measurements were taken at $\tau_d = 4 \mu s$. That vibrational equilibrium did, in fact, set in this case is confirmed by Figure 3 which presents the values of T_i obtained on the basis of

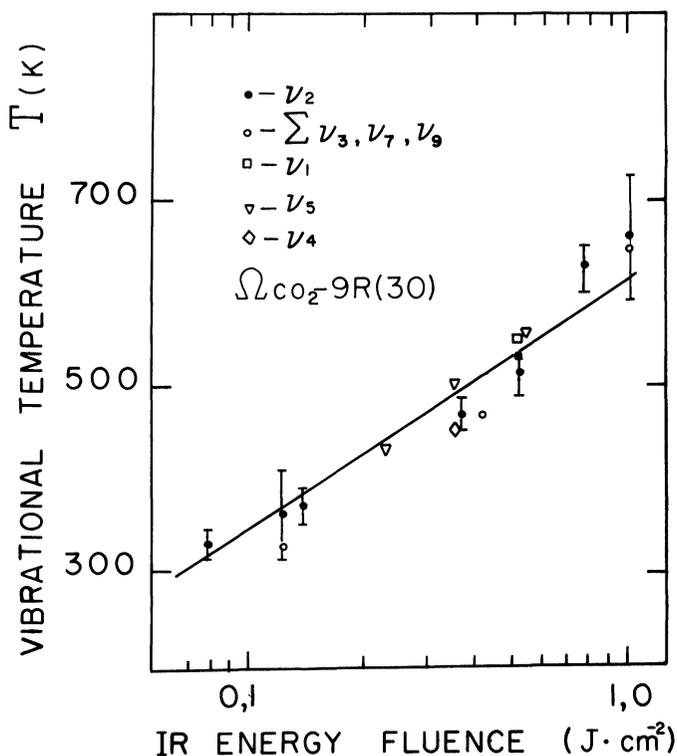


Figure 3 Final vibrational temperature in different modes (after establishment of vibrational equilibrium) as a function of CO₂ laser pulse fluence Φ . Pumped mode— ν_1 .

measurements of $\bar{\epsilon}_i$ at $\tau_d = 4 \mu\text{s}$. As can be seen, at $p\tau_d = 3 \mu\text{s Torr}$ the temperatures in the different modes coincide accurate to within the measurement error. That no energy is transferred during this time to other degrees of freedom is confirmed by the fact that the total energies in all the modes measured immediately after excitation and after the lapse of the time $\tau_d = 4 \mu\text{s}$ coincide accurate enough.

The dynamics of the collisional vibrational energy redistribution process was studied by monitoring the ν_1 mode. Measurements showed that this process obeyed an exponential law with the constant $p\tau = 1.1 \pm 0.4 \mu\text{s Torr}$.

The fraction of molecules that had not interacted with the radiation was determined by the Stokes Raman scattering spectra in the ν_2 mode. The integral intensity of the ν_2 mode peak was measured for each fixed value of the laser fluence Φ , the domain of integration being selected so as to exclude from it as far as possible any signals from excited molecules. The relative reduction of this integral directly yields the quantity q —the fraction of the “hot” molecules. The results of these measurements are shown in Figure 4 (bottom curve). Assuming that the rest of the molecules have the average energy $\bar{\epsilon}^0$ corresponding to the room temperature T_0 , we may write down the following expression for the total molecular energy $\bar{\epsilon}^s$.

$$\bar{\epsilon}^s = q\bar{\epsilon}^* + (1 - q)\bar{\epsilon}^0 \quad (1)$$

From this equation it is not very difficult to find $\bar{\epsilon}^*$ —the average energy of the “hot” molecules. The laser fluence dependence of this quantity is also presented in Figure 4 (top curve).

It follows from the results presented in Figure 4 that, as with a large number of other molecules (see References 1 and 2), the rise of absorption in the sample gas with increasing laser fluence Φ at a not very high excitation level $\bar{\epsilon}^*$ is due mainly to the increase in the fraction q of the excited molecules. The average energy $\bar{\epsilon}^*$ of these molecules rises much slower. The results obtained also make it possible to estimate the upper limit E_{thr} above which there occurs an equilibrium excitation of all the molecular modes. The minimum value of $\bar{\epsilon}^*$ reached by us amounts to around 7800 cm^{-1} . This yields $E_{thr} \leq 7800 \text{ cm}^{-1}$.

The correctness of our inference about the character of vibrational energy distribution and determination of the parameters $\bar{\epsilon}^*$ and q can be checked by calculating the average energy in any mode for the

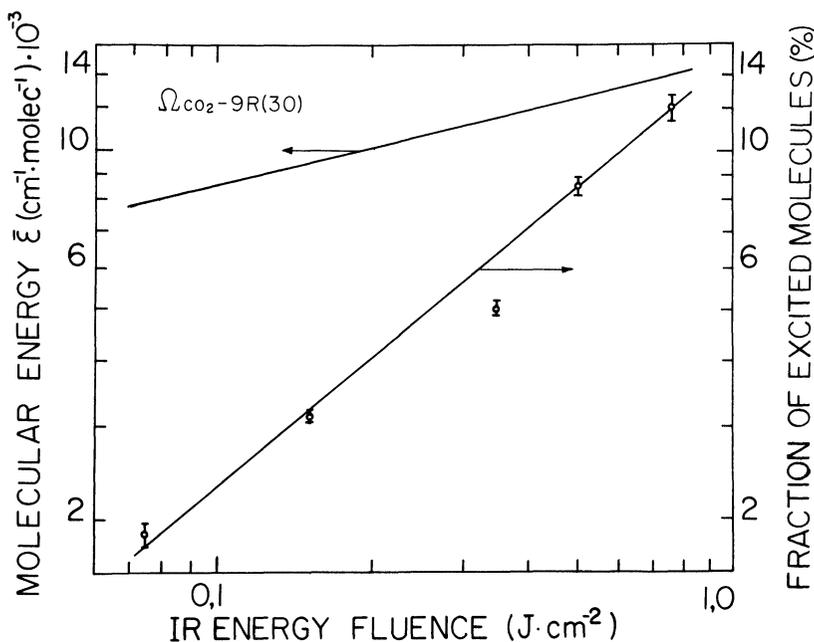


Figure 4 Fraction q of "hot" ensemble molecules (bottom curve) and their average energy $\bar{\epsilon}^*$ (top curve) as a function of CO_2 laser pulse fluence Φ . Pumped mode— ν_1 .

values of these parameters found. By analogy with Eq. (1), we may write down the following expression for some mode ν_i :

$$\bar{\epsilon}_i = q\bar{\epsilon}_i^* + (1 - q)\bar{\epsilon}_i^0 \quad (2)$$

where $\bar{\epsilon}_i^0$ and $\bar{\epsilon}_i^*$ are the average energy in the chosen mode at room temperature and in the "hot" ensemble, respectively. The results of such calculations for some modes at $\Phi = 0.35 \text{ J/cm}^2$ are given in Table 1. As can be seen, the calculated and experimentally measured values of $\bar{\epsilon}_i$ agree well enough. The spontaneous Raman scattering probing of the $2\nu_6$ overtone, followed by the processing of the results by a method similar to the one described in [References 7 and 8], showed a qualitative agreement with the results presented. Thus, at $\Phi = 0.5 \text{ J/cm}^2$ we got $\bar{\epsilon}^* = 16,900 \pm 3300 \text{ cm}^{-1}$ and $q = (7 \pm 1.3)\%$.

Table 1 Experimental and calculated values of the average energy $\bar{\epsilon}_i$ in different modes of CF₂Cl₂.

Energy	Mode			
	ν_2 (667.2 cm ⁻¹)	ν_5 (322 cm ⁻¹)	ν_8 (922 cm ⁻¹)	$\Sigma(\nu_3, \nu_7, \nu_9)$
Calculation $\bar{\epsilon}_i$ (cm ⁻¹)	103.5	167	82	414
Experiment $\bar{\epsilon}_i$ (cm ⁻¹)	115 ± 10	185 ± 25	100 ± 10	400 ± 40

II. When acting on the ν_8 mode, we carried out the anti-Stokes Raman spectroscopy of the modes ν_2 , ν_1 and ν_8 and of the group of modes ν_3 , ν_7 and ν_9 (see Figure 5). As with the action on the ν_1 mode, the response to excitation from *all* the modes was observed at minimum τ_d , which points to a collisionless mechanism of the absorbed energy transfer to the nonresonance modes. In the “instantaneous” Stokes Raman spectrum of the ν_2 mode, there was also observed the appearance of a wide “hump” on the “red” side of the line corresponding to the “cold” molecules.

But despite the fact that the general pictures in these cases coincide, there are some differences. Thus, it is seen that now, in contrast to what occurs when acting on the ν_1 mode, the energy stored in the ν_2 mode and in the group of modes ν_3 , ν_7 , ν_9 grows higher as τ_d is increased. Besides, the “instantaneous” value of the average energy in the mode ν_8 is appreciably higher than in the now reference mode ν_1 over the entire range of laser fluences Φ . An excess of energy in the IR MP-pumped ν_8 mode of CF₂Cl₂ relative to the other Raman-active modes was also detected in Reference 15. Both these facts point to differences in the character of the energy distribution formed in the course of IR MPE. A similar picture (outflow of energy from high-frequency modes and its inflow to low-frequency ones) was earlier observed by us in experiments with CF₂HCl.⁶ As in that case, the energy excess should be related to the presence of a group of molecules in which the absorbed energy remained localized on the lower resonance mode levels of the lower ensemble. In experiments with the CF₃Br molecule,⁸ the existence of such molecules was confirmed by direct spectral measurements. In the case of the CF₂Cl₂ molecule, the

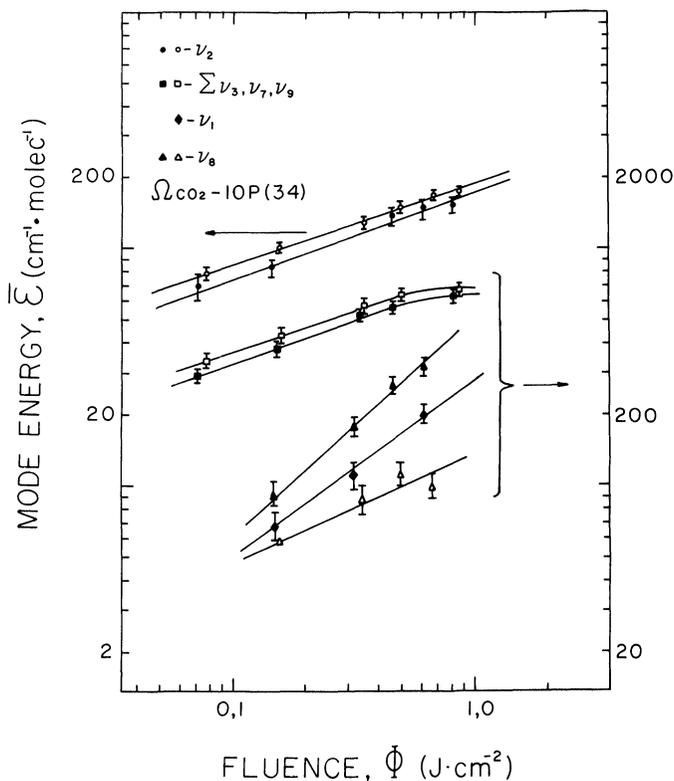


Figure 5 Average energies ν_i in modes ν_1 , ν_2 and ν_8 and also in group of modes ν_3 , ν_7 , ν_9 as a function of CO_2 laser pulse fluence Φ . Pumped mode— ν_8 (solid symbols — $\tau_d \leq 20$ ns; open symbols — $\tau_d = \mu\text{s}$).

interpretation of spectral measurements is difficult to make because of the lack of data on the intermode anharmonicities. For the same reason, we failed to determine such energy distribution function parameters as $\bar{\epsilon}^*$ and q , it being impossible to account correctly for the contribution to the observed spectrum from the molecules “stuck” on the discrete resonance mode levels. As in the case of action on the ν_1 mode, we found the vibrational temperature $T_i(\Phi)$ in the different modes in $4 \mu\text{s}$'s time after excitation. The dependence $T(\Phi)$ thus obtained was used to calculate $\bar{\epsilon}^s$. The values of the average energy $\bar{\epsilon}^s$

in the case of MP excitation of the mode ν_8 were found to be approximately the same as in the case of excitation of the mode ν_1 .

DISCUSSION OF THE RESULTS

One result common to both cases of MP excitation of the molecules—excitation through the ν_1 mode and that through the ν_8 mode—is the appearance of the response to the action of IR radiation from all the modes on a time scale of $(2 \text{ to } 3) \times 10^{-8}$ s, which means that the transfer of excitation to nonresonant modes occurs even during the CO₂ laser pulse. At gas pressures ≤ 1 Torr such a redistribution of the absorbed energy cannot be explained by the $V-V'$ exchange processes the time of which, according to our measurements for this and other molecules,^{5,6,8} is much longer. We believe that, as with other molecules, the redistribution of energy among other modes takes place as a result of stochastization of vibrational motion in the molecules whose total energy exceeds some critical value referred to as the stochastization onset. For the CF₂Cl₂ molecule, the level of this onset, as follows from Figure 4, does not exceed $E_{thr} \leq 7800 \text{ cm}^{-1}$. This estimate was obtained when exciting the molecules through the ν_1 mode. But the nonresonant modes also get excited when depositing energy into the molecules through the ν_8 mode. This gives reason to believe that stochastization occurs in this case as well. According to the existing theoretical notions¹⁴, the presence of a stochastization onset is decisively governed by the properties of the molecule itself and does not depend on the method of depositing energy in it. We therefore believe that when exciting the molecules through the ν_8 mode the value of the stochastization onset E_{thr} is also close to the above estimate.

As regards the intermolecular energy distribution in the case of MPE of CF₂Cl₂, it turns out to be as essentially nonequilibrium as with the CF₃I, SF₆, CF₂HCl, and CF₃Br molecules. The experimental results obtained allow us to conclude that when exciting CF₂Cl₂ through both the ν_1 and ν_8 modes there are formed, as in the case of the above-mentioned molecules, two molecular ensembles (Figure 6). At the same time, the qualitative energy distribution pictures in these cases feature essential differences. If the upper ensembles are in both cases formed by molecules with $E > E_{thr}$ and having an equilibrium intramolecular energy distribution, the structures of the lower ensembles differ greatly.

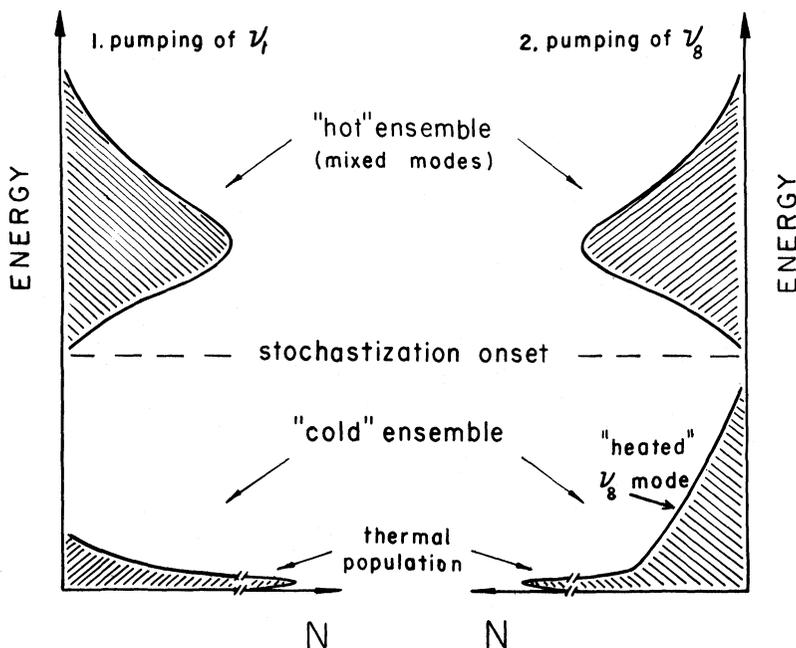


Figure 6 Vibrational energy distribution in IR MP excited CF_2CL_2 .

When exciting the ν_1 mode, there is no excess energy in this mode, and for this reason, the lower ensemble in this case consists of unexcited "cold" molecules with the vibrational temperature in all modes having the initial or close to the initial value.

When exciting the ν_8 mode, the energy distribution picture is more complex. The energy excess in this mode indicates that the lower ensemble contains, in addition to the "cold" molecules, also molecules with excited resonant mode. Thus, at $\Phi = 0.7 \text{ J/cm}^2$, the average energy $\bar{\epsilon}_8$ in the resonance mode is equal to 340 cm^{-1} , whereas that in the reference mode ν_1 is $\bar{\epsilon}_1 = 200 \text{ cm}^{-1}$. So, the energy excess in the ν_8 mode, which is due to the excitation of this mode in the lower ensemble, is $\delta\epsilon_8 \approx 140 \text{ cm}^{-1}$.

With account being taken of the initial thermal excitation, this means that about 10% of the absorbed energy remains localized in the resonant mode. This energy is distributed among the ν_8 mode levels up to $E_{thr} \leq 7800 \text{ cm}^{-1}$. Such an excitation of the mode can materially

influence the subsequent excitation of these molecules by visible or UV light, provided that this mode manifests itself in the respective transitions. This apparently can explain the differences in the results of UV excitation of the CF₂Cl₂ molecules preliminarily MP excited through the ν_1 or ν_8 mode.^{11,13} At the same time, as follows from our direct measurements, complete localization of the absorbed energy in the ν_8 mode is out of the question.

The lack of adequate theory of MP excitation of molecules in the lower level system makes it difficult to interpret qualitatively the results obtained. We believe that the different energy distributions are formed not as a result of molecular excitation through different modes, but rather are due to the different positions of the exciting radiation relative to the linear absorption spectrum of the modes being excited.

Unfortunately, the CO₂ laser tuning range does not allow this hypothesis to be checked for the CF₂Cl₂ molecule. The answer to this question can be provided by experiments with more convenient molecules which can be excited within the limits of a single band at different senses and magnitudes of the detuning of the exciting radiation frequency with respect to the linear absorption band center of the IR active mode.

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