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# IR-Luminescence of $\text{CF}_2\text{Cl}_2$ Molecules in Multiple-Photon Excitation with $\text{CO}_2$ -Laser Radiation

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We studied the IR luminescence spectra of vibrationally excited  $\text{CF}_2\text{Cl}_2$  molecules resulting from excitation of the  $\nu_1$  ( $1098\text{ cm}^{-1}$ ) and  $\nu_8$  ( $922\text{ cm}^{-1}$ ) modes with a pulsed  $\text{CO}_2$  laser. The nonequilibrium spectra obtained under pumping conditions where their equilibrium counterparts coincide (the number of the photons absorbed per molecule being the same) were found to differ considerably. We suppose that this difference is due to different types of vibrational distribution formed as a result of the IR laser pumping. When pumping the  $\nu_1$  mode, excitation of the *R*-branch occurs, resulting in the molecules "sticking" on the lower vibrational levels, whereas in the case of the  $\nu_8$  mode, it is the *P*-branch that gets excited so that the molecules become easy to raise to high-lying vibrational levels.

**KEY WORDS:** Luminescence, multiple photon,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CO}_2$  laser.

## INTRODUCTION

At the present time, multiple-photon excitation (MPE) with IR-laser radiation is a universal means of preparing vibrationally excited molecules and is being widely used both to effect isotope-selective multiple-photon dissociation (MPD) of molecules and to produce radicals.<sup>1,2</sup> The form of energy distribution among vibrational states established in the course of MPE with IR-laser radiation remains one

of the main questions. The vibrational energy distribution in the MPE of various molecules was studied by a variety of techniques: UV-probing,<sup>3,4</sup> MPE of vibrationally excited molecules (two-frequency excitation),<sup>5,6</sup> IR-luminescence,<sup>7</sup> spontaneous Raman scattering (SRS),<sup>8,9</sup> and coherent anti-Stokes Raman scattering.<sup>10-12</sup> As a result of these works, the form of energy distribution among vibrational states in MPE with IR-laser radiation was established for a series of molecules. In many cases (e.g.,  $\text{CF}_2\text{HCl}$ ,<sup>13</sup>  $\text{CF}_3\text{Br}$ ,<sup>14</sup>  $\text{SF}_6$ ,<sup>7,8</sup>) this distribution was demonstrated to be of a complex, inhomogeneous character. Qualitatively, one of the most important results of these investigations boils down to the fact that the initially suggested division of molecules into two ensembles—"cold" (unexcited molecules) and "hot" (highly excited molecules)<sup>15,16</sup>—has been supplemented with an intermediate group of molecules "stuck" on the lower vibrational levels. Of course, such a division into molecular ensembles is rather arbitrary, but useful for a number of applications. For some molecules (e.g.,  $\text{CF}_2\text{HCl}$ ,  $\text{CCl}_2\text{HF}$ ) the "sticking" on the lower levels is so great that only a small fraction of molecules get excited to high-lying states, this leading to a relatively low MPD yield.<sup>13,17</sup> As a result, despite the considerable success achieved in recent years in the studies of vibrationally excited molecules, the mechanisms responsible for the establishment of vibrational energy distribution in the course of MPE are not quite understood and require further investigations.

In this paper, we report on our research into the MPE of  $\text{CF}_2\text{Cl}_2$ , based on the IR-luminescence spectra of the vibrationally excited molecules, the pumped molecular mode being either  $\nu_1$  or  $\nu_8$ . We compared the vibrational energy distributions formed upon excitation of the  $\nu_1$  and  $\nu_8$  modes with a  $\text{CO}_2$ -laser radiation. The IR-luminescence spectra were compared at one and the same absorbed energy. The spectra resulting from the excitation of the  $\nu_1$  and  $\nu_8$  modes of the  $\text{CF}_2\text{Cl}_2$  molecule with the  $\text{CO}_2$ -laser radiation were demonstrated to be essentially different, this being due to the different forms of the ensuing vibrational energy distributions. We also studied the effect of buffer gas on the IR-luminescence spectra.

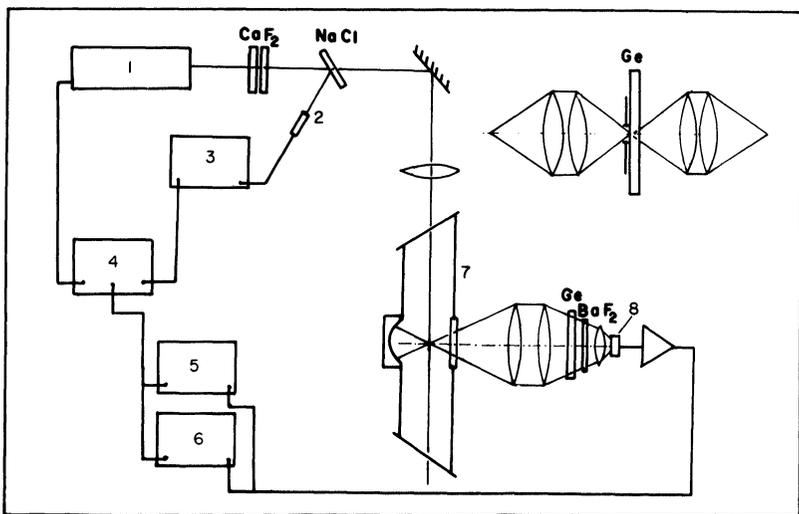
## EXPERIMENTAL

In our experiment, we analysed the spectra of IR luminescence

induced in the  $\text{CF}_2\text{Cl}_2$  molecule with a  $\text{CO}_2$ -laser radiation. The analysis was performed with a view to comparing the vibrational energy distributions  $f(E_{v,j})$  formed when exciting this molecule within the different absorption bands corresponding to the modes  $\nu_1 = 1098 \text{ cm}^{-1}$  and  $\nu_8 = 922 \text{ cm}^{-1}$ . The comparison was made by observing the IR-luminescence spectrum in the  $\nu_1$  mode absorption band with the absorbed energies being the same.

The experimental set-up is illustrated in Figure 1. Radiation from a pulsed transversely-excited  $\text{CO}_2$  laser was collimated by means of a NaCl lens with a focal length of  $f = 1 \text{ m}$  and then directed into the sample gas cell. The  $\text{CO}_2$ -laser pulse had a typical shape: a peak 100 ns wide and a "tail" of about 500 ns (FWHM). The pulse energy on the 10P(40) and 9R(38)  $\text{CO}_2$ -laser lines used in the experiment was 0.2 J.

To observe IR luminescence, the sample gas cell 500 mm in length and 20 mm in inside diameter and equipped with NaCl windows set at the Brewster angles was provided with a 30-mm-dia. side port of  $\text{BaF}_2$



**Figure 1** Schematic of experimental set-up. 1—pulsed  $\text{CO}_2$  laser; 2—calorimeter; 3, 5—digital voltmeters; 4—pulsed generator; 6—oscilloscope; 7—sample gas cell; 8—IR detector (GeHg). The inset in the right top corner shows the optical IR-luminescence collection arrangement used in conjunction with the ring filter.

at the centre. In order to improve the IR-luminescence collection efficiency as much as possible, a gold-coated spherical mirror ( $R = 10$  mm) was installed opposite to the side port.

IR luminescence was registered by means of a liquid-helium-cooled GeHg detector. The detector was  $2 \times 6$  mm<sup>2</sup> in effective area and 2 mm in thickness. Its dark resistance was around 2 M $\Omega$ . The load resistor used ( $\approx 11$  k $\Omega$ ) provided for a speed of response of about 1.5  $\mu$ s. The signal from the photodetector was fed to a multiplier arranged on the nitrogen jacket of the helium cryostat, amplified by a low-noise amplifier with a gain of around 500, and then processed with a suitable system.

The spectral analysis of the IR-luminescence radiation was performed by means of two types of IR filter. (1) A ring interference filter tunable over the range 800–1350 cm<sup>-1</sup> (see reference 18). The maximum-transmission wavelength  $\lambda_m$  was determined by the filter region selected and the bandwidth  $\Delta\lambda$ , by the width of the respective section isolated by means of a slit. The slit used in the experiment was 3 mm wide, this corresponding to a bandwidth of  $\Delta\lambda \approx 30$  cm<sup>-1</sup> in a region of  $\lambda_m \approx 1000$  cm<sup>-1</sup>. (2) Narrow interference filters with a fixed bandwidth ( $\Delta\lambda \approx 10$  cm<sup>-1</sup>). The particular arrangement of the optical system for collecting luminescence radiation and focusing it onto the GeHg photodetector was chosen to suit the filter used (see Figure 1). The ring filter was used in conjunction with a four-lens optical system (60-mm-dia. NaCl lenses,  $f = 100$  mm) (see Figure 1) which made it possible to minimize the loss of luminescence caused by the narrow slit.

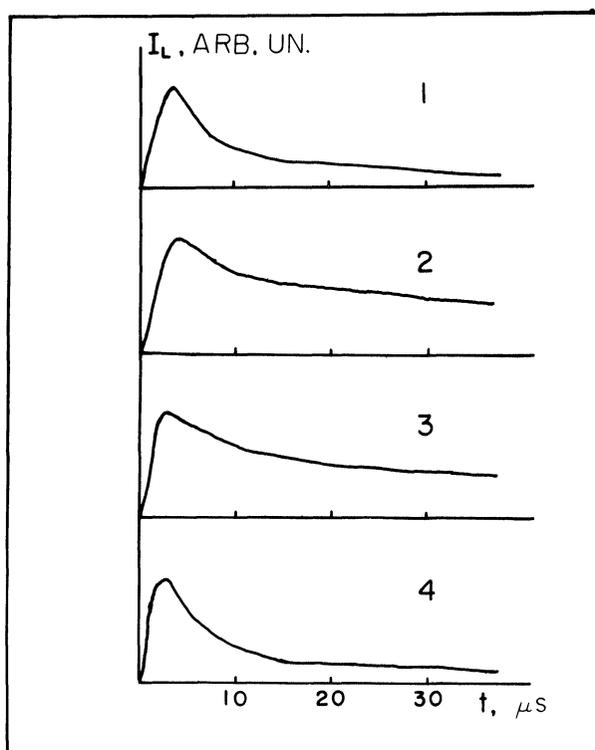
When using narrow-band, wide-aperture filters, the luminescence radiation was focused onto the photodetector by means of two similar NaCl lenses. In both cases, a short-focus BaF<sub>2</sub> lens (dia. 25 mm,  $f = 25$  mm) was set inside the cryostat 12 mm distant from the photodetector, which made it possible to reduce somewhat the image of the luminescent region and thus increase the fluorescence radiation density incident upon the detector.

Falling within the CO<sub>2</sub>-laser bandwidth are two strong IR-absorption bands of CF<sub>2</sub>Cl<sub>2</sub>. The least-energy mode  $\nu_8 = 922$  cm<sup>-1</sup> corresponds to the torsional vibrations of the CF<sub>2</sub> group. It manifests itself in the form of a doublet because of the Fermi resonance with the low-lying modes<sup>19</sup>. The mode  $\nu_1 = 1098$  cm<sup>-1</sup> corresponds to the vibrations of the C–F bond. Close in frequency to this mode is the

mode  $\nu_6 = 1160 \text{ cm}^{-1}$  associated with the antisymmetric stretching vibrations of the C-Cl bond.

## EXPERIMENTAL RESULTS

Figure 2 shows typical IR-luminescence pulses from  $\text{CF}_2\text{Cl}_2$  obtained under various conditions of excitation with a  $\text{CO}_2$ -laser radiation (see caption to the figure). In all cases, the character of the temporal

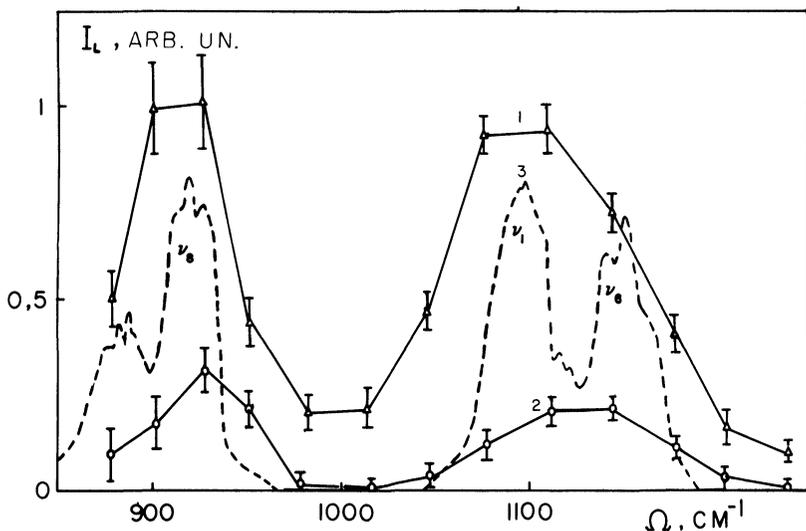


**Figure 2** Typical IR-luminescence pulses obtained at a  $\text{CF}_2\text{Cl}_2$  gas pressure of 1 Torr (*1, 2, 3*) and in a mixture of 1 Torr  $\text{CF}_2\text{Cl}_2$  + 5 Torr Kr (*4*) using wide-aperture narrow-band filters. *1, 2*—comparison between luminescence pulses obtained when exciting the  $\nu_1$  mode (frequency  $1089 \text{ cm}^{-1}$ , R(38)  $\text{CO}_2$ -laser line) and registering luminescence at  $990 \text{ cm}^{-1}$  and  $1064 \text{ cm}^{-1}$ , respectively; *3, 4*—effect of buffer gas on luminescence pulses when exciting the  $\nu_8$  mode (frequency  $925 \text{ cm}^{-1}$ , P(40)  $\text{CO}_2$ -laser line) and registering luminescence at  $1064 \text{ cm}^{-1}$ .

behaviour of luminescence is approximately the same and reduces to a relatively fast rise ( $\tau_1 \approx 1.5 \mu\text{s}$  FWHM), followed by a fast fall ( $\tau_2 \approx 5 \mu\text{s}$ ) to some equilibrium value which varies but slightly with time ( $\tau_3 \approx 10^3 \mu\text{s}$ ). The observed decay of IR-luminescence is caused mainly by the following processes: (1) Vibrational–vibrational ( $V$ – $V$ ) exchange. This process has a characteristic time of the order of a few  $\mu\text{s}$  · Torr and leads to the establishment of equilibrium among vibrational degrees of freedom; (2) Vibrational–translational ( $V$ – $T$ ) relaxation with a characteristic time of around  $50 \mu\text{s}$  Torr<sup>19</sup>. This process will lead to a decrease in the vibrational temperature; (3) Diffusion of the excited molecules from the observation region in about  $10^3 \mu\text{s}$  ( $p = 1$  Torr) will reduce the concentration of the excited molecules in this region and hence will also lead to the decay of luminescence. Addition of a buffer gas increases the heat capacity of the system, which results in a reduced amplitude of the luminescence pulse “tail” (cf. pulses 3 and 4).

Measuring the luminescence pulses at the moments their amplitudes were a maximum yielded nonequilibrium IR-luminescence spectra. Measuring the pulse amplitudes approximately  $20 \mu\text{s}$  after the  $\text{CO}_2$ -laser pulses made it possible to obtain equilibrium spectra and then find the necessary conditions of excitation in the  $\nu_1$  and  $\nu_8$  bands by comparing these spectra. For instance, the identity of equilibrium spectra resulting from excitation in different bands points to the quality of the energies absorbed by the molecules from the laser field.

Figure 3 shows the IR-luminescence spectrum obtained when exciting the  $\nu_8$  mode of the  $\text{CF}_2\text{Cl}_2$  molecule at a frequency of  $\nu = 925 \text{ cm}^{-1}$  [P(40)  $\text{CO}_2$ -laser line]. Curve 1 corresponds to the maxima of the luminescence pulses and represents a nonequilibrium spectrum. Curve 2 was obtained by measuring the luminescence pulse amplitudes  $20 \mu\text{s}$  after the  $\text{CO}_2$ -laser pulses and corresponds to a vibrationally-equilibrium spectrum. The spectra were taken with the ring interference filter. The laser fluence in the sample gas cell was around  $1.5 \text{ J/cm}^2$ , about six quanta per molecule being in this case absorbed in the irradiated volume. The figure also presents the linear IR-absorption bands corresponding to the  $\nu_1$ ,  $\nu_6$  and  $\nu_8$  modes of the  $\text{CF}_2\text{Cl}_2$  molecule. As can be seen, the observed luminescence spectra correlate well with the respective bands in the linear IR-absorption spectrum. The equilibrium spectrum has a lower integral intensity, and its maximum is shifted towards the high-frequency side, which is explained by the



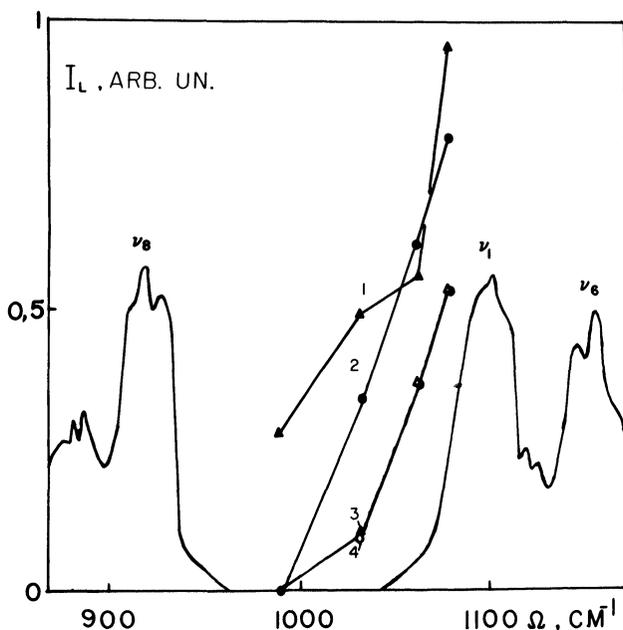
**Figure 3** IR-luminescence spectrum of  $\text{CF}_2\text{Cl}_2$  obtained with the ring filter when exciting the  $\nu_8$  mode [frequency  $925\text{ cm}^{-1}$ , P(40)  $\text{CO}_2$ -laser line]. Gas pressure 1 Torr.  $\text{CO}_2$ -laser fluence around  $1.5\text{ J/cm}^2$ , which corresponds to an average number of absorbed quanta per molecule of  $\langle n \rangle \approx 6$ . Curve 1—spectrum obtained from IR-luminescence pulse maxima, curve 2—spectrum obtained from IR-luminescence pulse “tails.” Shown for comparison is also the IR-absorption spectrum of  $\text{CF}_2\text{Cl}_2$  (curve 3).

average vibrational energy store in the modes  $\nu_1$  and  $\nu_6$  of interest decreasing as a result of  $V$ - $V'$  exchange in the course of establishment of equilibrium.

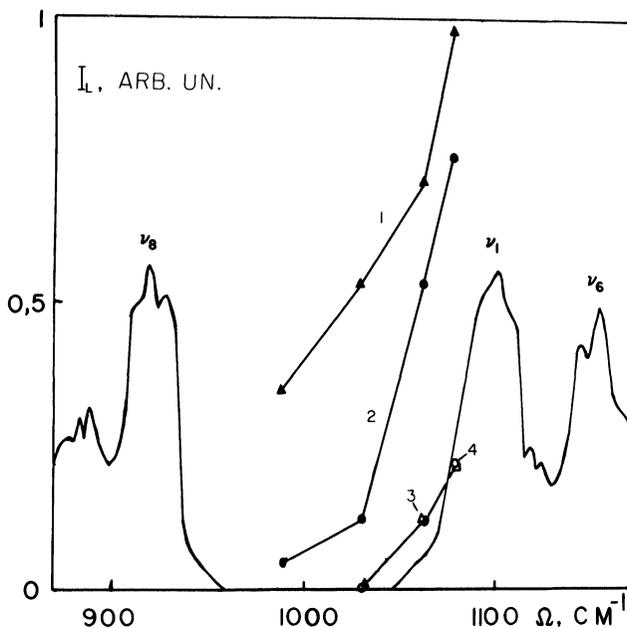
The long-wavelength tails of these spectra (in the range  $950$ – $1100\text{ cm}^{-1}$ ) are of the greatest interest, since it is exactly these tails that are associated with the high-lying vibrational states of the  $\text{CF}_2\text{Cl}_2$  molecule becoming populated as a result of excitation with laser radiation. The IR-luminescence spectra in this region were analysed by means of wide-aperture interference filters with a fixed bandwidth. The registered signal was in this case considerably increased (by about 5 times), which made it possible to study the far wings of the spectra and compare them more accurately when exciting the different modes ( $\nu_1$  or  $\nu_8$ ) of the  $\text{CF}_2\text{Cl}_2$  molecule.

Figure 4 presents the long-wavelength wings of the IR-luminescence spectra obtained when exciting the modes  $\nu_1$  [ $\nu_{\text{las}} = 1089\text{ cm}^{-1}$ , R(38)  $\text{CO}_2$ -laser line] and  $\nu_8$  [ $\nu_{\text{las}} = 925\text{ cm}^{-1}$ , P(40)  $\text{CO}_2$ -laser line] (curves 1

and 2, respectively) of the  $\text{CF}_2\text{Cl}_2$  molecule. The laser fluences for the nonequilibrium spectra 1 and 2 were selected from the condition of equality of the absorbed energies so as to make the respective equilibrium spectra sections (curves 3 and 4) coincide. It can be seen from the figure that with the absorbed energies being equal, i.e., with the equilibrium IR-luminescence spectra being identical, the non-equilibrium spectra obtained when exciting the modes  $\nu_1$  and  $\nu_8$  are essentially different. Addition of a buffer gas (Kr) makes this difference still greater. Such a comparison of spectra in conditions where 5 Torr of Kr was added to 1 Torr of  $\text{CF}_2\text{Cl}_2$  in the cell is illustrated in Figure 5. When exciting the  $\nu_8$  mode, the long-wavelength wing of the spectrum varies relatively weakly, whereas the respective wing obtained when exciting the  $\nu_1$  mode becomes much more intense.



**Figure 4** IR-luminescence spectra obtained with narrow-band wide-aperture filters when exciting the modes  $\nu_1$  [curves 1, 3, frequency  $1089\text{ cm}^{-1}$ , R(38)  $\text{CO}_2$ -laser line] and  $\nu_8$  [curves 2, 4, frequency  $925\text{ cm}^{-1}$ , P(40)  $\text{CO}_2$ -laser line]. Curves 1, 2 correspond to nonequilibrium spectra at the luminescence pulse maxima; curves 3, 4 correspond to equilibrium spectra (denoted  $\Delta$  and  $\circ$ ).  $\text{CF}_2\text{Cl}_2$  gas pressure 1 Torr. Laser fluence  $1.34\text{ J/cm}^2$  when exciting  $\nu_1$  mode and  $1.5\text{ J/cm}^2$  when exciting  $\nu_8$  mode, which corresponds to an average number of absorbed quanta per molecule of  $\langle n \rangle \approx 6$ .



**Figure 5** IR-luminescence spectra obtained with narrow-band wide-aperture filters when exciting modes  $\nu_1$  (curves 1, 3) and  $\nu_8$  (curves 2, 4). Mixture 1 Torr CF<sub>2</sub>Cl<sub>2</sub> + 5 Torr Kr. Laser fluence 1.24 J/cm<sup>2</sup> when exciting  $\nu_1$  mode and 2.23 J/cm<sup>2</sup> when exciting  $\nu_8$  mode, which corresponds to an average number of absorbed quanta per molecule of  $\langle n \rangle \approx 14$ . Other conditions and designations same as in Figure 4.

## DISCUSSION OF THE RESULTS

The radiation density  $W(\nu)$  emitted by vibrationally excited molecules per unit time per unit frequency interval is given by the expression

$$W(\nu) = \sum_{\nu, J} A_{\nu' J' \leftarrow \nu J} N f(E_{\nu J}) h \nu_{\nu' J' \leftarrow \nu J} \quad (1)$$

Summation here is extended over all the dipole-allowed transitions  $\langle \nu', J' | \leftarrow \langle \nu, J |$ , i.e.,  $\nu' = \nu - 1$ ,  $J' = J$ ,  $J \pm 1$ ;  $N$  is the molecular density,  $f_{\nu' J' \leftarrow \nu J}$  the vibrational-rotational distribution function,  $\nu_{\nu' J' \leftarrow \nu J}$  the frequency of the transition  $\langle \nu', J' | \leftarrow \langle \nu, J |$ , and  $A_{\nu' J' \leftarrow \nu J}$  the Einstein coefficient for spontaneous emission:

$$A_{\nu' J' \leftarrow \nu J} = [(64\pi^4)/(3hc^3)] \nu_{\nu' J' \leftarrow \nu J}^3 [S(\nu' J' \leftarrow \nu J)/g_{\nu J}] \quad (2)$$

where  $S(\nu' J' \leftarrow \nu J)$  is the line strength and  $g_{\nu J}$  the degeneracy of the

initial state  $\langle \nu J \rangle$ . Using Eq. (1), one can, in principle, find the vibrational energy distribution function of the molecules. This problem was analysed for SF<sub>6</sub> in Reference 21. But it is possible only where the spectroscopic constants describing the luminescence band under analysis are well known. For the CF<sub>2</sub>Cl<sub>2</sub> molecule, such constants are unknown. In the present work, therefore, we restricted ourselves to comparison between luminescence spectra obtained when exciting the modes  $\nu_1$  and  $\nu_8$ . This comparison has shown the luminescence spectra to be essentially different, this being due to the difference between the vibrational energy distribution functions  $f(E_{\nu,J})$  (as to the  $\nu_1$  mode) formed when exciting the modes  $\nu_1$  and  $\nu_8$  of this molecule.

The difference between the vibrational energy distributions can be due to two causes: (1) excitation of different modes ( $\nu_1$  or  $\nu_8$ ) of CF<sub>2</sub>Cl<sub>2</sub> and (2) excitation of different branches in these modes (P-branch of mode  $\nu_1$  or R-branch of mode  $\nu_8$ ). The limited CO<sub>2</sub>-laser tuning range made it impossible for us to differentiate between these causes.

But how can different vibrational energy distributions be formed? The mechanism responsible for the formation of the different distributions  $f(E_{\nu,J})$  is apparently related to the "sticking" of molecules on the lower energy levels in the course of MPE. In that case, as has been demonstrated for CF<sub>2</sub>HCl<sup>13</sup> and CCl<sub>2</sub>HF,<sup>22</sup> the molecules are distributed mainly over the lower vibrational levels so that only a small fraction of them are on the high-lying levels corresponding to the vibrational quasicontinuum (QC). Now, if such a "sticking" occurs in the course of MPE in the  $\nu_8$  mode and is absent when exciting the  $\nu_1$  mode, the ensuing vibrational energy distributions will be essentially different.<sup>22</sup> In the former case, the high-lying vibrational states are populated comparatively small, whereas in the latter their population is much larger. Inasmuch as the "sticking" is caused by the molecule falling out of resonance with a series of successive vibrational transitions,<sup>23</sup> it should be expected that excitation of the molecule in the R-branch would contribute to this.

Let us now consider how the addition of a buffer gas will affect the IR-luminescence spectra obtained when exciting the different modes ( $\nu_1$  or  $\nu_8$ ) of the CF<sub>2</sub>Cl<sub>2</sub> molecule. Adding the buffer gas increases the fraction of molecules in the quasicontinuum. Indeed, let only some fraction  $q$  of the molecules interact effectively with the laser field. Then, in the absence of collisions, a fraction of these molecules,  $f_0$ , is raised to the quasicontinuum:<sup>13</sup>

$$f_0 = q[1 - \exp(-w\tau_p)] \quad (3)$$

In collisional conditions at a sufficiently high buffer gas pressure, this fraction  $f_{pr}$  is determined by the expression

$$f_{pr} = 1 - \exp(-qw\tau_p) \quad (4)$$

where  $w$  is the rate of molecular excitation to the quasicontinuum and  $\tau_p$  the laser pulse width. Consider two extreme cases where the rate of excitation of the molecules to the quasicontinuum is high,  $qw\tau_p \gg 1$ , and low,  $qw\tau_p \ll 1$ . The latter condition means that at some stage of excitation there occurs a sharp reduction in the absorption cross section. In the former case, comparing Eqs. (3) and (4), it can be readily seen that  $f_{pr} \approx f_0/q$ , i.e., addition of the buffer gas will lead to an increase in the fraction of the highly excited molecules, giving rise to an enhancement of the long-wavelength wing of the IR-luminescence spectrum. In the latter case,  $f_{pr} \approx f_0$ , i.e., the buffer gas affects but slightly the fraction of molecules raised to the quasicontinuum. For this reason, one should not expect any strong changes in the low-frequency wing of the spectrum in the latter case.

Both the above situations are apparently realized in our experiment and explain the difference observed between the spectra obtained when exciting the different modes ( $\nu_1$  or  $\nu_8$ ) of CF<sub>2</sub>Cl<sub>2</sub>. In the MPE of the P-branch of the  $\nu_1$  mode, the induced excitation rate is high enough, the "sticking" is absent, and the effect of the buffer gas on the long-wavelength wing of the IR-luminescence spectrum is substantial. When exciting in the R-branch of the  $\nu_8$  mode, the excitation rate  $w$  drops drastically at some stage so that the "sticking" of the molecules on the lower vibrational levels is observed and, as a result, the influence of the buffer gas on the spectrum is weak. A similar situation can, for example, be realized when exciting the P- and R-branches of one and the same mode.

## CONCLUSION

Our experimental results have shown that excitation of the modes  $\nu_1$  and  $\nu_8$  of the CF<sub>2</sub>Cl<sub>2</sub> molecule gives rise to essentially different IR-luminescence spectra, the absorbed energies being the same. The difference between the spectra becomes more pronounced when a buffer gas is added. The observed difference is explained by different

vibrational energy distributions (as to the  $\nu_1$  mode) formed when exciting the P- and R-branches of the  $\nu_1$  and  $\nu_8$  modes of the  $\text{CF}_2\text{Cl}_2$  molecule. In the work reported,<sup>24</sup> they observed a qualitative difference in ArF-laser dissociation kinetics between the  $\text{CF}_2\text{Cl}_2$  molecules having their  $\nu_1$  and  $\nu_8$  modes preliminarily excited with a  $\text{CO}_2$ -laser radiation. To our view, this difference may also be due to essentially different vibrational energy distributions formed when exciting the P-branch of the  $\nu_1$  mode and the R-branch of the  $\nu_8$  mode of  $\text{CF}_2\text{Cl}_2$ .

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