

Nonthermal Intramolecular Vibrational Energy Distribution in Infrared-Multiphoton-Excited CF₂Cl₂

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The intramolecular vibrational energy distribution of infrared-multiphoton-excited CF₂Cl₂ molecules is studied with time-resolved spontaneous Raman scattering. The time evolution of the signals from three vibrational modes is studied up to 600 ns after excitation, and in the presence of N₂ buffer gas. Following collisionless infrared multiphoton excitation a nonthermal distribution of vibrational energy is observed. This nonequilibrium distribution persists up to high levels of vibrational excitation, with at least 10000 cm⁻¹ in three out of the nine vibrational modes.

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In 1973 it was discovered that isolated molecules in the ground electronic state can be dissociated by a short, intense pulse from a CO₂ laser.¹ Since then, the absorption of large numbers of monochromatic infrared photons by single molecules has been studied extensively.²⁻⁷ Because of the selectivity of vibrational excitation, infrared multiphoton excitation has received much attention. Initially it was hoped that a "bond-selective" or "mode-selective" photochemistry based on infrared multiphoton excitation could be developed.⁸

Information on the intramolecular vibrational energy distribution in infrared-multiphoton-excited molecules has been obtained experimentally in a number of ways.⁹⁻¹⁶ It was shown that the infrared-multiphoton-dissociation branching ratios and the energy distributions of the dissociation fragments are consistent^{5,16} with Rice-Ramsberger-Kassel-Marcus theory.¹⁷ This means that when molecules are excited above or close to the dissociation threshold, equilibration of the intramolecular vibrational energy distribution occurs. Whether this holds true for highly excited molecules below the dissociation threshold remains an open question. Spontaneous Raman scattering was used to study various infrared-multiphoton-excited molecules, and the results provided information on the vibrational energy distribution after excitation.^{11,12,14,18} This paper presents time-resolved Raman-scattering measurements on infrared-multiphoton-excited CF₂Cl₂, a molecule which allows direct comparison of the Raman signal intensities of different modes after excitation. Since the Raman signal intensity is directly proportional to the energy in the mode, the results provide direct information on the intramolecular vibrational energy distribution of CF₂Cl₂ at various levels of excitation. The present experimental data fill the gap in the transition regime between the well-known low-excitation (single vibrational mode) and high-excitation (dissociation) regions.

In simple harmonic approximation, the total, spectrally integrated, intensity of the Raman signal of a particular vibrational mode is proportional to the average ener-

gy in that mode, $\langle E_{\text{total}} \rangle$. This follows from the fact that the transition probability is proportional to the vibrational quantum number n .¹⁸ For an anti-Stokes transition $n \rightarrow n-1$, with transition probability $W_{n \rightarrow n-1}$, one therefore obtains for the total anti-Stokes Raman signal intensity

$$I_{\text{total}}^{\text{AS}} = \sum_{n=0}^{\infty} P_n W_{n \rightarrow n-1} = a \sum_{n=0}^{\infty} P_n n, \quad (1)$$

where P_n is the population of vibrational state n , and a a mode-dependent quantity related to the Raman-scattering cross section. To eliminate the proportionality constant a , the anti-Stokes signal is normalized with the corresponding Stokes signal at room temperature, I_0^{S} . The resulting normalized anti-Stokes signal, I_{norm} , is therefore proportional to the average energy in that mode,

$$I_{\text{norm}} \equiv \frac{I_{\text{total}}^{\text{AS}}}{I_0^{\text{S}}} = b^{-1} \sum_{n=0}^{\infty} P_n n = b^{-1} \frac{\langle E_{\text{total}} \rangle}{h\nu}, \quad (2)$$

with

$$b \equiv \sum_{n=0}^{\infty} P_n^0 (n+1), \quad (3)$$

where P_n^0 is the population distribution at room temperature, h Planck's constant, and ν the frequency of the mode. If, as is usually the case, the energy of vibrational quanta is much larger than kT at room temperature, the Boltzmann factor $e^{-h\nu/kT}$ is small, and $b \approx 1$. Under these conditions I_{norm} is a *direct* measure of the average number, $\langle n \rangle = \langle E_{\text{total}} \rangle / h\nu$, of vibrational quanta in each vibrational mode. This allows one to compare the average energy from mode to mode after excitation of the molecules and determine the vibrational energy distribution.

The experimental setup^{18,19} consists of a low-pressure gas cell, an infrared pump laser, and an ultraviolet probe laser. To isolate intramolecular from (collisional) intermolecular effects, the signals are measured at pressures low enough to ensure that no significant collisional relax-

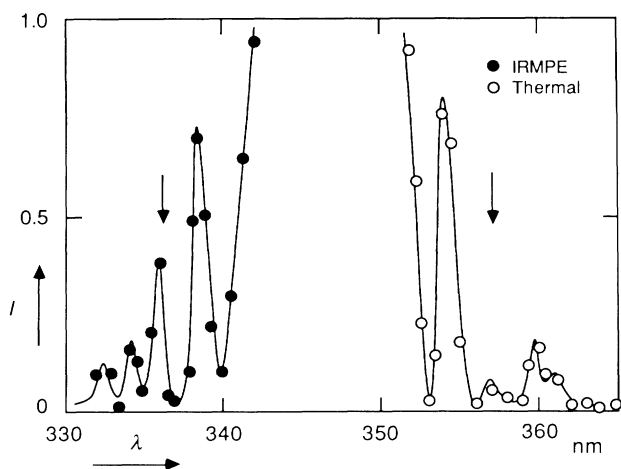


FIG. 1. Raman spectrum of CF_2Cl_2 , with (filled circles) and without (open circles) infrared multiphoton excitation.

ation of vibrational energy occurs on the time scale of the excitation. The infrared radiation is generated by a high-power, short-pulse, tunable CO_2 laser.^{20,21} The infrared pulses of 15 ns duration have a maximum energy of 200 mJ at the $P(32)$ line of the $10.6\text{-}\mu\text{m}$ branch. A 30-ns frequency-doubled ruby laser pulse of 3 mJ serves as Raman probe. The Raman signals are detected with a low-resolution (1.5 nm) double monochromator and a high-gain fast photomultiplier tube. A complete description of the experimental setup can be found in previous papers.^{18,19}

The experimental results on CF_2Cl_2 presented here were obtained at a pressure of 400 Pa (3 Torr). The reported purity of the commercially obtained gas is better than 99.995%. Of the nine vibrational modes of CF_2Cl_2 ,^{22,23} three, at 667, 923, and 1098 cm^{-1} , are accessible to our apparatus. The CCl_2 asymmetric stretch mode at 923 cm^{-1} is resonant with the $10.6\text{-}\mu\text{m}$ $P(32)$ line of the CO_2 laser. Since this mode is both Raman and infrared active, one can directly monitor the excitation in the pumped mode.

The Raman spectrum of CF_2Cl_2 , obtained with and without infrared multiphoton excitation, is shown in Fig. 1. The large central peak in the spectrum corresponds to Rayleigh scattering. Because of the low population of excited levels at room temperature, only Stokes signals can be detected in the absence of infrared pumping. These room-temperature data are shown in the right-hand side of the graph; the corresponding anti-Stokes spectrum has been omitted. After the excitation, large anti-Stokes signals appear. The Stokes and anti-Stokes peaks at 356.5 and 336 nm (see arrows) correspond to the 923-cm^{-1} pump mode. One can obtain an indication of the average excitation in each mode by comparing the intensities of the anti-Stokes peaks with the intensities of the corresponding Stokes peaks in this

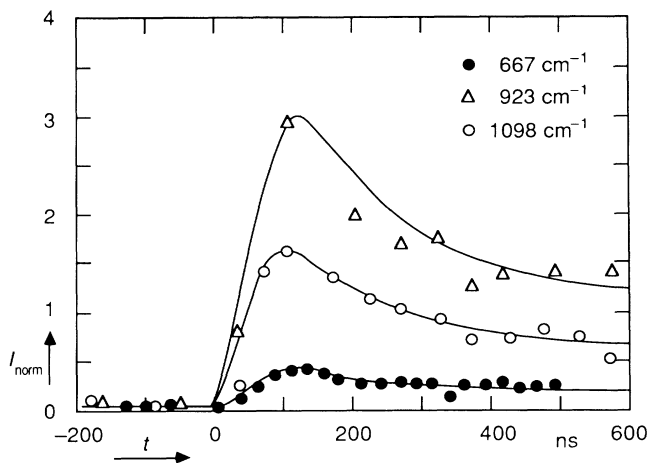


FIG. 2. Normalized anti-Stokes signals as functions of the time delay between pump and probe pulse.

graph, as in Eq. (2). From such a simple comparison, it becomes immediately clear that the pump mode is much more highly excited than the other modes.

Figure 2 shows the normalized anti-Stokes signal from Eq. (2), I_{norm} , versus the time delay between pump and probe pulses at an average fluence of $1.8 \times 10^4\text{ J/m}^2$. For $t < 0$, the molecules are probed before the excitation, i.e., at room temperature. The rise time of all three vibrational modes is limited by the 30-ns instrumental time resolution, which in turn is determined by the temporal width of the laser pulses. The decay of the signals is most likely due to the collisional transfer of energy to other initially "cold" vibrational modes. Such a collisional relaxation should result in a growth of energy content of the initially unexcited modes. Because it is not possible to observe all nine vibrational modes, however, this could not be verified.

For an equilibrium distribution of energy among the

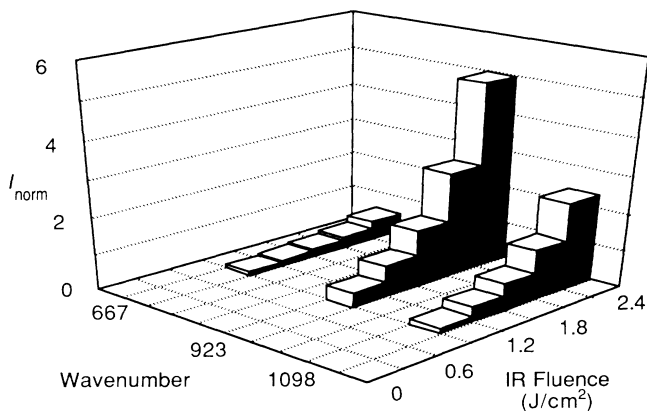


FIG. 3. Infrared fluence dependence of the normalized anti-Stokes signals for CF_2Cl_2 at 400 Pa.

vibrational modes, the intensities of the normalized signals are given by

$$I_{\text{norm}} = (e^{hv/kT} - 1)^{-1}. \quad (4)$$

Figure 2, however, shows that after excitation the signal intensities cannot be described by Eq. (4) for any temperature T . The normalized intensity of the pumped vibrational mode at 923 cm^{-1} is considerably higher than the corresponding intensities of the other two modes.

Figure 3 shows the normalized anti-Stokes signals as functions of infrared fluence. The normalized intensity ratios as well as values of $\langle E_{\text{total}} \rangle$ for each mode obtained from Eq. (2) are displayed in Table I. The normalized anti-Stokes intensities of all three modes increase exponentially with increasing fluence, with the pumped mode at 923 cm^{-1} containing the largest amount of energy for all infrared fluences. The ratios of normalized anti-Stokes signals clearly indicate a nonequilibrium intramolecular vibrational energy distribution among the three observed vibrational modes. As the fluence is increased from $(1.8 \text{ to } 2.4) \times 10^4 \text{ J/m}^2$, the energy in the pumped mode triples and the total vibrational energy in the three probed modes is at least 10000 cm^{-1} , yet the nonequilibrium ratio of intensities remains unchanged. This implies that the observed nonequilibrium distribution *cannot* be the result of averaging a "hot" equilibrium ensemble and a "cold" bottlenecked¹² ensemble. If that were the case, the intensity ratios in Table I would change as the fraction of molecules in the hot ensemble increases with increasing fluence. Since more than one mode is highly excited, the behavior is distinctly different from the low-excitation behavior. On the other hand, the nonthermal distribution at this relatively high excitation contrasts with the well established equilibrium distribution of vibrational energy in the infrared multiphoton dissociation of CF_2Cl_2 molecules.^{5,16} It is therefore interesting to compare the 10000 cm^{-1} of internal energy in the three probed modes with the 24000-cm^{-1} (74

kcal/mol) thermal dissociation energy of CF_2Cl_2 . At the highest fluence used, two of the probed modes contain about twice the energy that would result from a statistical distribution of the 24000-cm^{-1} dissociation energy over all the modes. One must therefore conclude that reported equilibration of vibrational energy occurs only at still higher fluences, when the energy in the pumped mode is well above its thermal-dissociation value. It is not possible, however, to probe the molecules at higher excitation because of laser-induced fluorescence from dissociation fragments.

Collisions relax the nonequilibrium intramolecular vibrational energy distribution of the excited molecules, and the normalized anti-Stokes signals should therefore approach their thermal equilibrium values as collisions occur. Unfortunately it is not possible to draw any quantitative conclusions from the decay of the anti-Stokes signals in Fig. 2, because the signals drop below the noise level before equilibrium is reached. The relaxation rate was therefore increased by addition of N_2 buffer gas. Figure 4 shows the normalized anti-Stokes signals at various buffer-gas pressures. The same graph also shows the equilibrium values of the Raman signals, calculated under the assumption of the same amount of total internal energy in the three modes as in the left graph. The observed signals decrease quickly with increasing buffer-gas pressure, but at the same time the differences between them become smaller. Within the experimental accuracy, equilibrium is reached between the 923- and 1098-cm^{-1} modes at 13 kPa buffer-gas pressure. At 26 kPa, equilibrium between the 667- and 1098-cm^{-1} modes is also established. Because of the small Raman

TABLE I. Average vibrational energy and relative intensity ratio for three Raman-active modes of CF_2Cl_2 , at 667, 923, and 1098 cm^{-1} , after infrared multiphoton excitation. The top row gives the (calculated) room-temperature equilibrium values.

F (10^4 J/m^2)	p_{N_2} (kPa)	I_{rel} ratio	E_{667} (cm^{-1})	E_{923} (cm^{-1})	E_{1098} (cm^{-1})
0	...	3.4:1:0.45	28	11	6
1.2	...	0.21:1:0.23	70	480	130
1.5	...	0.15:1:0.41	120	1140	560
1.8	...	0.12:1:0.48	180	2160	1240
2.1	...	0.10:1:0.48	280	3800	2190
2.4	...	0.10:1:0.48	440	6300	3620
2.1	13	0.20:1:1	130	920	1100
2.1	26	0.17: ... :0.15	110	<450	160

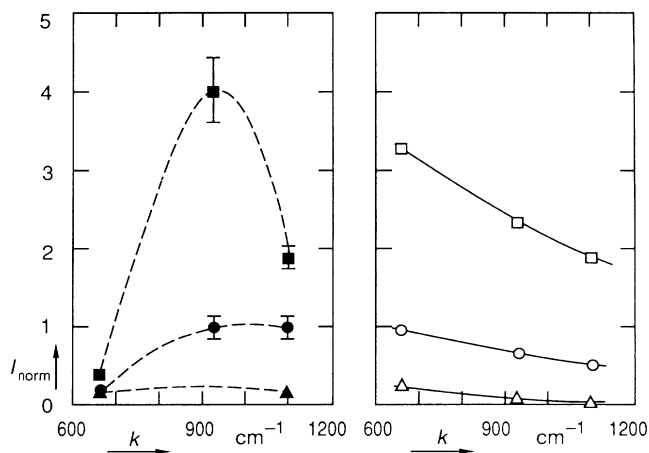


FIG. 4. Comparison of the observed normalized anti-Stokes signals with calculated equilibrium values. On the left, signals after infrared multiphoton excitation for three different N_2 buffer-gas pressures: 0 Pa (squares), 13 kPa (circles), and 26 kPa (triangles). On the right, calculated equilibrium values at three different temperatures: 3900 K (squares), 1500 K (circles), and 600 K (triangles).

cross section of the 923-cm^{-1} mode, data are not available for this mode at 26 kPa buffer-gas pressure. At this pressure the vibrational energy of the highly excited CF_2Cl_2 is rapidly transferred to the buffer gas, and the anti-Stokes signal of the 923-cm^{-1} pump mode drops below the noise level. A comparison with the calculated equilibrium values on the other side of the graph shows that as the buffer-gas pressure is increased, the intramolecular vibrational energy distribution tends to equilibrate.

In conclusion, we have employed time-resolved spontaneous Raman scattering to study the infrared multiphoton excitation of CF_2Cl_2 . The observed anti-Stokes signals show a nonthermal energy distribution among the observed Raman-active modes of infrared-multiphoton-excited CF_2Cl_2 which tends toward equilibrium as an increasing amount of buffer gas is added. Even though at high excitation two of the observed modes already contain about twice their "statistical share" of the dissociation energy, the distribution of energy is still far from the well established equilibrium at dissociation.

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¹N. R. Isenor, V. Merchant, R. S. Hallsworth, and M. C. Richardson, *Can. J. Phys.* **51**, 1281 (1973).

²V. B. Bagratashvili, V. S. Letokhov, A. A. Makarov, and E. A. Ryabov, *Multiple Photon Infrared Laser Photophysics and Photochemistry* (Harwood Academic, New York, 1985).

³N. Bloembergen and E. Yablonovitch, *Phys. Today* **31**, No. 5, 23 (1978).

⁴C. D. Cantrell, S. M. Freund, and J. L. Lyman, in *Laser Handbook*, edited by M. L. Stitch (North-Holland, Amsterdam, 1979), Vol. 3.

⁵P. A. Schultz, Aa. S. Sudbø, D. J. Krajnovitch, H. S. Kwok, Y. R. Shen, and Y. T. Lee, *Annu. Rev. Phys. Chem.* **30**, 379 (1979).

⁶W. Fuss and K. L. Kompa, *Prog. Quantum Electron.* **7**, 117 (1981).

⁷D. S. King, in *Dynamics of the Excited State*, edited by K. P. Lawley (Wiley, New York, 1982).

⁸V. S. Letokhov, *Phys. Today* **33**, No. 11, 34 (1980).

⁹D. S. Frankel and T. J. Manuccia, *Chem. Phys. Lett.* **54**, 451 (1978).

¹⁰J. G. Black, P. Kolodner, M. J. Schultz, E. Yablonovitch, and N. Bloembergen, *Phys. Rev. A* **19**, 704 (1979).

¹¹V. B. Bagratashvili, Yu. G. Vainer, V. S. Dolzhikov, S. F. Kol'yakov, A. A. Makarov, L. P. Malyavkin, E. A. Ryabov, E. G. Sil'kis, and V. D. Titov, *Appl. Phys.* **22**, 101 (1980).

¹²V. B. Bagratashvili, Yu. G. Vainer, V. S. Dolzhikov, S. F. Kol'yakov, V. S. Letokhov, A. A. Makarov, L. P. Malyavkin, E. A. Ryabov, E. G. Sil'kis, and V. D. Titov, *Zh. Eksp. Teor. Fiz.* **80**, 1008 (1981) [*Sov. Phys. JETP* **53**, 512 (1981)].

¹³R. C. Sharp, E. Yablonovitch, and N. Bloembergen, *J. Chem. Phys.* **74**, 5357 (1981).

¹⁴E. Mazur, I. Burak, and N. Bloembergen, *Chem. Phys. Lett.* **105**, 258 (1984).

¹⁵Yu. S. Dolzhikov, V. S. Letokhov, A. A. Makarov, A. L. Malinovsky, and E. A. Ryabov, *Chem. Phys. Lett.* **124**, 304 (1986).

¹⁶D. S. King and J. C. Stephenson, *Chem. Phys. Lett.* **51**, 48 (1977).

¹⁷P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley-Interscience, New York, 1972).

¹⁸Jyhpyng Wang, Kuei-Hsien Chen, and Eric Mazur, *Phys. Rev. A* **34**, 3892 (1986).

¹⁹Eric Mazur, *Rev. Sci. Instrum.* **57**, 2507 (1986).

²⁰E. Yablonovitch and J. Goldhar, *Appl. Phys. Lett.* **25**, 580 (1974).

²¹H. S. Kowk and E. Yablonovitch, *Opt. Commun.* **21**, 252 (1977).

²²Charles A. Bradley, Jr., *Phys. Rev.* **40**, 908 (1932).

²³T. Shimanouchi, *J. Phys. Chem. Ref. Data* **6**, 993 (1977).