

Highly Nonthermal Intramolecular Energy Distribution in Isolated Infrared Multiphoton Excited CF_2Cl_2 Molecules

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When a polyatomic molecule with a strong vibrational absorption band is irradiated with an intense resonant infrared laser pulse it can absorb many (10 to 40) infrared photons.¹ If some initial energy deposition is 'localized'—preferably in one vibrational mode or in a subset of modes—it may become possible to induce 'mode-selective' reactions by infrared multiphoton excitation. The intramolecular dynamics of infrared multiphoton excited molecules has been studied by a variety of spectroscopic techniques.² One of these techniques is spontaneous Raman spectroscopy. In the past five years this technique has been successfully applied to monitor the vibrational energy in infrared multiphoton excited molecules.^{3,4}

In this work we present experimental results of recent time-resolved spontaneous Raman experiments on collisionless infrared multiphoton excited CF_2Cl_2 molecules. The experiments show that the intramolecular energy distribution is highly nonthermal, and that a large part of the vibrational energy remains localized in the pump mode for a period of time long compared to the mean free time of the molecules.

The experimental procedure is described in detail in previous papers.⁵ Briefly, a 15 ns CO_2 -laser pulse excites the 919 cm^{-1} band of the CF_2Cl_2 molecules. After a short time delay a second 20 ns laser pulse from a frequency-doubled ruby laser probes the excited molecules. Raman scattered light is analyzed with a double monochromator and a high-gain photomultiplier. The time delay between the two laser pulses can be varied from 10 ns to 10 μs . The present measurements were carried out at a pressure of 400 Pa.

Fig. 1 shows the anti-Stokes spectrum of the multiphoton excited CF_2Cl_2 . Signals from three Raman active modes, at 664 , 919 and 1082 cm^{-1} are visible. The room temperature Stokes side of the Raman spectrum is shown in the same graph. At room temperature the intensity of the anti-Stokes peaks is too small to be measured at a pressure of 400 Pa. The intensity of the Raman peaks is a measure of the vibrational energy in each of the Raman-active modes.⁴ Therefore, by measuring the time dependence of the anti-Stokes intensity, one can study the evolution of the vibrational energy distribution in multiphoton excited molecules.

The time dependence of the anti-Stokes Raman signals is shown in Fig. 2. The signals are normalized with their corresponding room temperature Stokes counterparts to correct for the different Raman cross sections. The rise time of the signals corresponds to the pulse duration of the laser pulses. The decay of the signals is due to a combination of collisional vibrational relaxation and diffusion of the excited molecules out of the excitation region. By comparing the intensity of the signals one can determine the distribution of energy in the vibrational modes. Fig. 3 shows the normalized intensity distribution 100 ns after excitation.

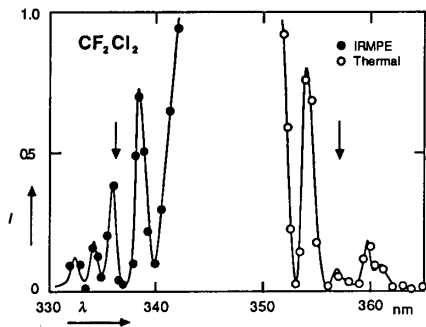


Fig. 1. Raman spectrum of infrared multiphoton excited CF_2Cl_2 at 400 Pa. The arrows show the position of the pump line.

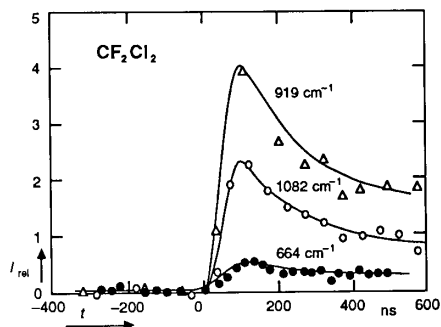


Fig. 2. Intensity of the normalized anti-Stokes signals as a function of the time delay between pump and probe pulse for CF_2Cl_2 .

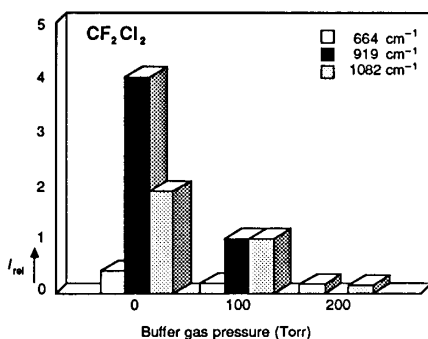


Fig. 3. Normalized anti-Stokes intensities for 3 modes of CF_2Cl_2 at 2 J/cm^2 for different N_2 buffer gas pressures.

From this graph it is clear that most of the excitation energy remains in the pump mode at 919 cm^{-1} for collisionless excitation without buffer gas. As an increasing amount of N_2 buffer gas is added the distribution tends toward thermal equilibrium, but the overall signal strengths decrease because of vibration-translation relaxation.

Summarizing, we present here time-resolved spontaneous Raman scattering measurements of infrared multiphoton excited CF_2Cl_2 at low pressure. The results show a highly nonthermal energy distribution among different modes, which persists even on time scales long compared to the mean free time of the molecules. A more detailed discussion of these results will be published elsewhere.⁶ This work was supported by the Army Research Office and the Joint Services Electronics Program under contracts with Harvard University.⁷

References

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