

Raman spectroscopy of infrared multiphoton excited molecules

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Anti-Stokes signals from various modes of isolated, infrared multiphoton excited SF₆ and C₂H₄F₂ molecules are measured as a function of pressure, infrared fluence and wavelength. This allows to verify whether intramolecular equilibrium of vibrational energy is established after infrared multiphoton excitation in isolated molecules.

A question in the field of infrared multiphoton excitation on which much effort has been focusing recently is how, under collisionless conditions, vibrational energy is distributed among the different modes of isolated infrared multiphoton excited molecules.¹ In recent experiments we have been using time-resolved spontaneous Raman spectroscopy in low pressure samples as a tool to study the intramolecular vibrational energy distribution in isolated infrared multiphoton excited molecules. Several authors have proposed that the ensemble of modes in highly vibrationally excited molecules can be described statistically.²⁻³ A statistical description implies an equipartitioning of energy among the various molecular modes. The aim of our current research is to determine experimentally whether such an approach is justified.

Measurements were carried out on SF₆ and C₂H₄F₂. In both cases it is observed that part of the excitation energy is distributed to Raman active modes. The total amount of energy in the Raman active mode can be determined by measuring the intensity of the Raman signals. Quantitative measurements of the Raman signals have been carried out as a function of time, gas pressure, infrared excitation energy, pulse duration and frequency.

Fig. 1 shows the increase in anti-Stokes Raman intensity for one of the four accessible Raman active lines of C₂H₄F₂. Without excitation no anti-Stokes signal could be observed. This is due to the fact that at room temperature less than 2% of the molecules are in excited states. After multiphoton excitation the energy in the Raman mode is changed as can be seen from the increase in anti-Stokes intensity. At a fluence of 1.5 J/cm² all of a sudden broadband fluorescence obscures the Raman scattering. This broadband fluorescence is due to electronic excitation by the probing

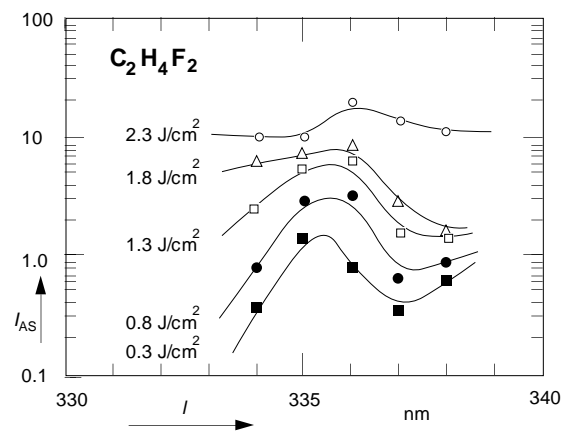


Fig. 1. Anti-Stokes spectrum for one of the Raman active lines of C₂H₄F₂ at a shift of 863 cm⁻¹ for different infrared excitation fluences. The increase in intensity at the right is due to Rayleigh scattering. Above 1.5 J/cm² broadband fluorescence obscures the Raman scattering.

ultraviolet pulse of either highly excited $C_2H_4F_2$ or its dissociation fragments.

After measuring the energy in the Raman modes, one can compare this energy with the energy in other Raman active modes and with the total energy absorbed by the molecule as a whole (known from photoacoustic measurements).⁴ In Fig. 2 the energy in the Raman active mode of multiphoton excited SF_6 is compared to the average energy (in units of infrared photons) absorbed per molecule, assuming equipartitioning of energy among the different modes. The results show a remarkable agreement. For $C_2H_4F_2$, on the other hand, the energy stored in the various Raman active modes after the infrared multiphoton excitation does not correspond to a 'common temperature.' The energy in one mode (at a Raman shift of 3000 cm^{-1}), namely, does not change within the experimental accuracy, while the other modes do exhibit changes.

In conclusion, we report here on detailed quantitative measurements of the intramolecular vibrational energy distributions in infrared multiphoton excited molecules. It is found that although intramolecular equilibrium is reached in infrared multiphoton excited SF_6 , this is not necessarily true for infrared multiphoton excited molecules in general.

- 1 See, e.g., the following publications and references therein: V.N. Bagratashvili, V.S. Letokhov, A.A. Makarov, E.A. Ryabov, Multiple Photon Infrared Laser Photophysics and Photochemistry (Harwood Academic Publishers, New York, 1985); W. Fuss and K. L. Kompa, Prog. Quant. Electr. 7, 117 (1981); D.S. King, Dynamics of the Excited State, Ed. K. P. Lawley (Wiley, New York, 1982);
- 2 N. Bloembergen and E. Yablonovitch, Physics Today 5, 23 (1978)
- 3 H.W. Galbraith and J.R. Ackerhalt, in Laser induced Chemical Processes, Ed. J.I. Steinfeld (Plenum, New York, 1981)
- 4 J.G. Black, P. Kolodner, M.J. Schultz, E. Yablonovitch, and N. Bloembergen, Phys. Rev. A19, 704 (1979)

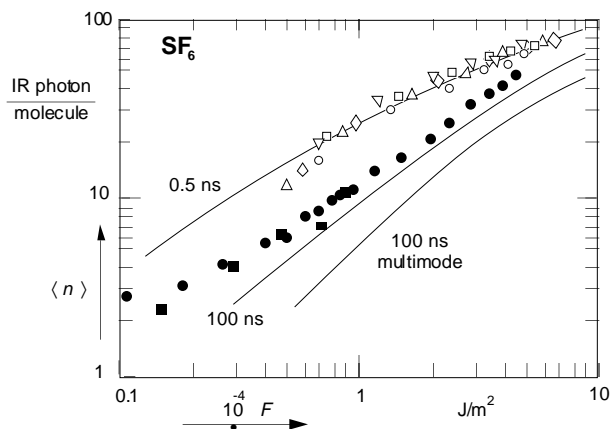


Fig. 2. Average number of infrared photons absorbed per molecule as a function of infrared fluence. The data points shown were obtained from the present Raman measurements, assuming thermal equilibrium between all vibrational modes immediately after the infrared multiphoton excitation. The solid lines are the average number of infrared photons obtained from previously reported photoacoustic measurements. The results show a remarkable agreement.