

# Direct CARS observation of vibrational states of the SF<sub>6</sub> molecule excited by a resonant IR field

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The coherent anti-Stokes Raman spectra have been measured for the gas SF<sub>6</sub> excited in an IR laser field. Some spectral structure has been observed which results from the filling of vibrational levels of the  $\nu_3$  mode. The vibrational-energy distribution functions have been studied for various excitation conditions.

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1. One of the most important questions for reaching an understanding of the mechanism for the stepwise excitation of molecules in an intense IR laser beam is the distribution of the energy absorbed by the molecules in the various vibrational levels and in the various degrees of freedom. It is well known that the method of coherent anti-Stokes Raman spectroscopy (CARS) can be used to study the distribution of molecules in vibrational levels.<sup>1</sup> The CARS method has a fundamental advantage over the method of spontaneous Raman spectroscopy,<sup>2</sup> which has been used previously to study the vibrational excitation of SF<sub>6</sub>, in its high spectral resolution, which is set by the linewidths of the laser sources for the CARS spectrometer.

In this method, the Raman-active mode  $\nu_1$  of the SF<sub>6</sub> molecules which are excited in a pulsed laser beam tuned to resonance with the IR-active mode  $\nu_3$  is probed with a pulsed CARS spectrometer. The excitation of the molecules leads to additional lines in the CARS spectrum. These additional lines are shifted by an amount  $x_{1i}\nu_i$  from the frequency  $\nu_1$  of the line corresponding to scattering by the unexcited gas from the vibrational ground state ( $x_{1i}$  is the constant of the intermode anharmonicity of the  $i$ th excited mode of the molecule with mode  $\nu_1$ , and  $\nu_i$  is the number of quanta in the  $i$ th mode).

By studying the structure of the CARS spectrum of molecules excited in an IR laser beam we can determine the distribution of the absorbed energy in the vibrational levels and in the degrees of freedom. Furthermore, by varying the delay of the probing pulses with respect to the time of excitation we can study the relaxation kinetics.

2. In the present experiments we used a pulsed CARS spectrometer<sup>1</sup> with a spectral resolution of 0.2 cm<sup>-1</sup> and a repetitively pulsed CO<sub>2</sub> laser which can be tuned over its output lines. The energy in the 100-ns output pulse from this laser can be varied up to 0.3 J at a repetition frequency of 12.5 Hz. The pulse length of the lasers of the CARS spectrometer is 10 ns; these lasers are synchronized with the pulse from the CO<sub>2</sub> laser within 30 ns, and this time determines the time resolution of the apparatus. The SF<sub>6</sub> is excited by the CO<sub>2</sub> laser at the frequency 947.8 cm<sup>-1</sup> in a waveguide cell 5 mm in diameter and 10 cm long, cooled to 150 K. The CARS probing is carried out in the transverse direction through a small aperture in the waveguide.

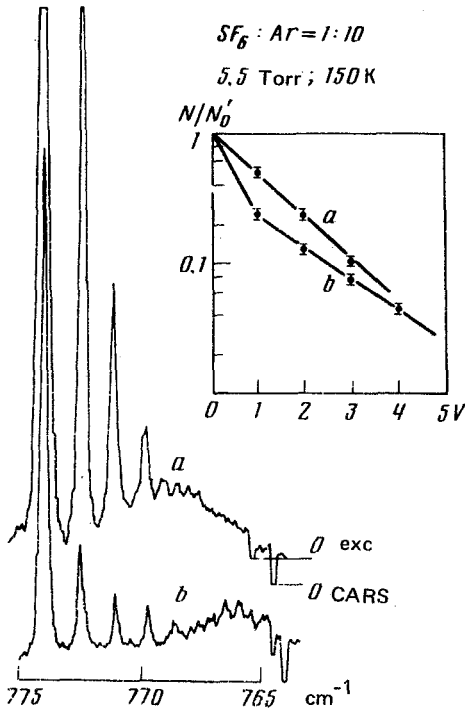


FIG. 1. CARS spectrum of the gas  $SF_6$ , excited in an IR laser beam.  $\Phi = 0.05$  and  $0.28 \text{ J/cm}^2$ ;  $\tau_d = 100 \text{ ns}$ . Distribution of the molecules in the levels of the  $\nu_3$  mode.

3. Figure 1 shows the CARS spectra of  $SF_6$  recorded at two different energy densities ( $\Phi$ ) of the  $CO_2$  laser and at the delay time of  $\tau_d = 100 \text{ ns}$ . We can clearly see lines which correspond to scattering by the transitions  $\nu \nu_3 \rightarrow \nu \nu_3 \rightarrow \nu_1$  ( $\nu = 1, 2, 3, 4$ ); these lines are shifted by an amount  $\nu x_{13} + \nu^2 x_{133}$  with respect to the frequency of the fundamental peak (0),  $\nu_1$  ( $774.5 \text{ cm}^{-1}$ ). From these spectra we find the anharmonicity constant  $x_{13}$  to be  $-2.99 \pm 0.03 \text{ cm}^{-1}$ , in good agreement with the value  $x_{13} = -2.93 \text{ cm}^{-1}$  measured in Ref. 3. These spectra also yield a value for the higher-order constant  $x_{133}$ :  $x_{133} \approx 0.02 \text{ cm}^{-1}$ .

Intensification of the exciting field causes a substantial redistribution of the intensity among the peaks. The inset in the upper part of Fig. 1 shows distributions of the level populations  $\nu \nu_3$  constructed from these spectra. For this plot it was assumed that the peak heights  $A_\nu$  are proportional to  $N^2 g_\nu$ , where  $g_\nu = (\nu + 1)(\nu + 2)/2$  is the degeneracy of the initial levels for the  $\nu_3$  mode. Strictly speaking, this calculation should be corrected for a possible partial overlap of the rotational components of the transitions being probed; it is difficult to take such an overlap into account because of the complicated nature of the anharmonic and Coriolis splitting of the vibrational levels. The fact that  $\ln[N(\nu)/N(0)]$  is a linear function of  $\nu$  is evidence that the level populations of the  $\nu_3$  mode have a Boltzmann distribution apparently because of the extremely rapid collisional  $\nu-\nu$  relaxation of  $SF_6$  molecules with respect to the  $\nu_3$  mode.<sup>4</sup> The vibrational tempera-

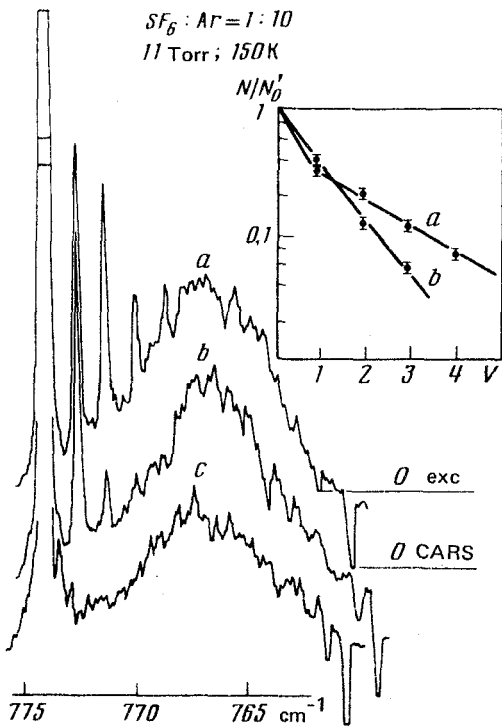


FIG. 2. CARS spectra of the gas  $\text{SF}_6$  excited in an IR laser beam for various delay times. a— $\tau_d = 100$  ns; b—200 ns; c—2  $\mu\text{s}$ .  $\Phi = 0.2 \text{ J/cm}^2$ .

tures determined for the  $\nu_3$  mode from the slopes of the lines are 1900 K (a) and 2700 K (b); these values correspond to average energies  $\nu_3 = \bar{\nu} = 3/e(h\nu/kT) - 1$  of 3 and 4.6 quanta/molecule in the  $\nu_3$  mode. In addition to the narrow peaks, the spectra have a broad, rounded maximum with a poorly resolved structure. This maximum is apparently a consequence of an energy redistribution and a filling of the levels of other modes of  $\text{SF}_6$ . As the excitation intensity is raised, this maximum shifts toward longer wavelengths, and the CARS signal integrated over the spectrum decreases. Ambartsumyan *et al.*<sup>5</sup> have also observed a decrease in the scattering signal integrated over the spectrum in  $\text{SF}_6$ ; they attributed it to an increase in the homogeneous width of transitions in the quasicontinuum. We believe that the basic reason for this effect is a rapid increase in the degeneracy  $g_\nu$  of the levels populated by the laser beam or through an energy transfer during collisions.

Evidence that a collisional transfer of vibrational energy ( $\nu-\nu'$  relaxation) makes a definite contribution to the shaping of the distribution of  $\text{SF}_6$  molecules in vibrational levels comes from the important change in the CARS spectrum with increasing delay of the probing with respect of the exciting pulse (Fig. 2). An increase in  $\tau_d$  to 200 ns, for example, substantially reduces the temperature of the  $\nu_3$  mode, and at  $\tau_d = 2 \mu\text{s}$  the peaks of the  $\nu_3$  mode disappear almost completely, and peaks of the  $\nu_6$  mode appear in the spectrum. The fact that  $\nu-\nu'$  relaxation can be reliably detected in the time range  $\sim 100$  ns at an  $\text{SF}_6$  pressure of 1 Torr is evidence of a significant acceleration of  $\nu-\nu'$  relaxation with increasing vibrational excitation.

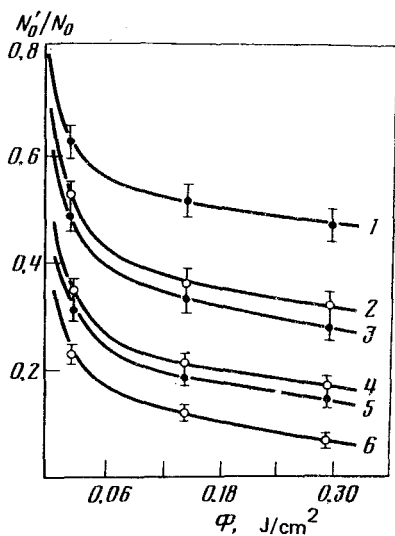


FIG. 3. Dependence of the fraction of molecules remaining in the ground state on the energy density of the IR radiation. 1,3,5-SF<sub>6</sub> pressure of 1 Torr; 2,4,6-1:10 SF<sub>6</sub>:Ar mixture, P<sub>Σ</sub> = 11 Torr; 1,2-τ<sub>d</sub> = 100 ns; 3,4-200 ns; 5,6-2 μs.

Figure 3 shows how the fraction ( $q$ ) of molecules remaining in the ground state ( $\nu=0$ ) depends on the energy density of the exciting pulse as a buffer gas is added and as the delay  $\tau_d$  is varied. The fraction  $q$  is determined from the change in the height  $A_0$  of the fundamental peak in the scattering spectrum upon excitation ( $q + N'_0/N_0$ ). Analysis of these curves shows that the fraction of unexcited molecules falls off with increasing excitation intensity and when a buffer gas is added; this decrease is caused by the rotational relaxation during the excitation pulse.<sup>6</sup> The substantial decrease in  $q$  with increasing  $\tau_d$  is evidently due to the attainment of an equilibrium distribution in the vibrational degrees of freedom through collisional  $\nu-\nu'$  relaxation.

Measurements of the fraction of molecules which are excited ( $1-q$ ) and comparison of this fraction with the total population of the levels of the  $\nu_3$  mode,  $\sum_{\nu} N(\nu)g_{\nu}$  (found from the spectra in Figs. 1 and 2), allow us to use the ratio  $\Sigma/(1-q)$  to determine that fraction of the excitation energy which goes into the  $\nu_3$  mode. Estimates show that for the spectra in Fig. 1 this ratio is approximately unity, while for the spectrum of Fig. 2 recorded with a delay  $\tau_d = 200$  ns it is  $\sim 0.6$ . These estimates show that up to the excitation level  $\bar{\nu} = 4.6$  most of the absorbed energy goes into the  $\nu_3$  mode, and the primary pathway for thermalization of the vibrational energy is  $\nu-\nu'$  relaxation. The rate of this relaxation increases with the excitation level of the molecules<sup>4</sup> and is significantly higher than the value measured in Ref. 7 during single-photon excitation of SF<sub>6</sub> ( $\tau_{\nu\nu'} = 1.5$  μs Torr).

Consequently, in order to determine the excitation level at which there is a purely radiative or intramolecular thermalization of the vibrational energy, it is necessary to substantially reduce the SF<sub>6</sub> pressure, in order to completely eliminate the effects of relaxation processes.

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