

Vibrational relaxation rate of SF₆ molecules excited in an intense IR laser field

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The characteristic times and collision cross sections have been measured for the resonant intramode (the ν_3 mode) vv exchange and the nonresonant intermode vv' exchange of vibrational energy in SF₆ molecules vibrationally excited in an IR laser field. The measurements were taken by coherent anti-Stokes Raman spectroscopy. The cross section for the resonant vv exchange is considerably larger than the cross section for gas kinetic collisions and increases linearly with the vibrational excitation level of the molecules.

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1. The collisional relaxation of vibration energy plays an important role in research on the excitation of the high-lying vibrational levels of polyatomic molecules. The vibrational relaxation of polyatomic molecules is generally broken up into the relatively fast process of vv relaxation, i.e., the relaxation to an equilibrium within the individual modes, and the vv' relaxation, i.e., the relaxation to an equilibrium between different vibrational degrees of freedom of the molecule.¹ While vv' relaxation of polyatomic molecules has been studied quite thoroughly during both single-photon^{2,3} and many-photon^{4,5} vibrational excitation, we do not yet have a clear picture of the rates of the resonant intramode vv exchange in polyatomic molecules. The reason for this situation is the difficulty in directly observing a redistribution of the populations of the vibrational levels of a mode by the conventional methods.

Coherent anti-Stokes Raman spectroscopy (CARS) of vibrationally excited molecules opens up some new opportunities for studying vibrational relaxation.^{6–8}

We have previously reported⁸ direct observation by the CARS method of the filling of high-lying vibrational levels of the SF₆ molecule in an IR laser field. In the present letter we report measurements of the rates of vv and vv' relaxation of SF₆ excited in an IR laser field.

2. The experimental apparatus is the same as that described in Ref. 8, aside from modifications to improve the time resolution. The pulse from the CO₂ laser exciting the SF₆ molecules was shortened to 40 ns, and the sensitivity of the CARS spectrometer was improved to the point at which the SF₆ spectra could be detected at pressures down to 0.01 Torr. It thus became possible to study relaxation processes with characteristic times as short as $p\tau \sim 1$ ns·Torr.

3. Figure 1 shows the CARS spectra of the ν_1 mode of gaseous SF₆, excited through the ν_3 mode, for three values of the time delay between the exciting pulse from the CO₂ laser and the probing pulses from the CARS spectrometer. The equidistant

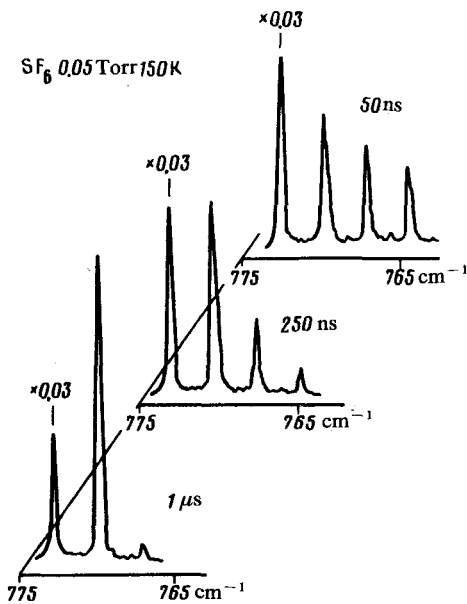


FIG. 1. CARS spectra of the SF₆ molecule in the case of a short delay between excitation and probing.

peaks in this spectrum correspond to scattering from the ground state and three excited states of the ν_3 mode ($0, \nu_3, 2\nu_3$, and $3\nu_3$). The frequencies of these peaks are shifted from that of the ground peak, $\nu_1 = 774.5 \text{ cm}^{-1}$, by $x_{13}, 2x_{13}$, and $3x_{13}$, respectively, where $x_{13} = -2.99 \text{ cm}^{-1}$ (Ref. 8) is the intermode anharmonicity constant of the ν_1 and ν_3 modes.

Figure 2 shows the distribution of molecules among the levels of the ν_3 mode found from these spectra. The populations were calculated by the $N = (A_v/g_v A)^{1/2}$ procedure used in Ref. 8, where A_v is the height of a scattering peak of the excited gas, $g_v = [(v+1)(v+2)/2]$ is the degeneracy of the vibrational levels, and A is the height of the scattering peak of the unexcited gas. Analysis of the curves in Fig. 2 shows that at an SF₆ pressure $p = 0.05$ Torr the redistribution of the populations of the various states of the ν_3 mode is essentially completed by a probing time $\tau = 1 \mu\text{s}$, and the distribution which is established can be approximated well as a Boltzmann distribution with an energy $\bar{v} = \frac{3}{\exp(h\nu/kT) - 1} \approx 0.8 \text{ kV/molecule}$ in the ν_3 mode. From an analysis of how well the level populations are approximated by the values corresponding to a Boltzmann distribution we determined the characteristic relaxation times. These times depend strongly on the index of the excited level. Corresponding measurements carried out at three SF₆ pressures ($p = 0.05, 0.1$, and 0.2 Torr) (Fig. 3) and with an admixture of a buffer gas (Xe) showed that the characteristic times for the relaxation to the equilibrium populations decrease in proportion to the SF₆ pressure but are independent of the Xe pressure. In terms of the SF₆ pressure, these times are $31 \pm 3 \text{ ns}\cdot\text{Torr}$ for the ν_3 level, $17 \pm 4 \text{ ns}\cdot\text{Torr}$ for the $2\nu_3$ level, and $10 \pm 5 \text{ ns}\cdot\text{Torr}$ for the $3\nu_3$ level ($T = 150 \text{ K}$).¹⁾

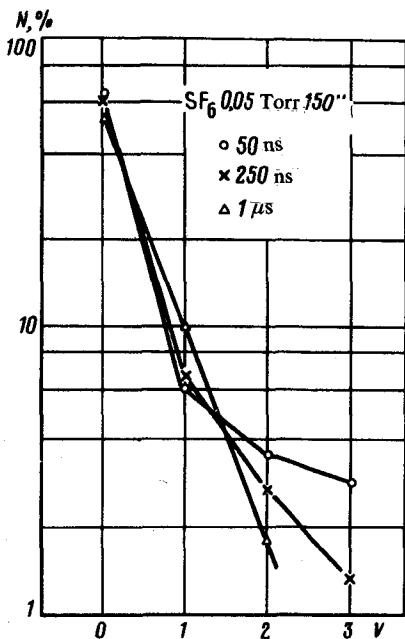


FIG. 2. Distribution of the vibrational populations of excited SF_6 .

A study of the conversion of the spectra at much longer delay times (Fig. 4) revealed the appearance of additional peaks, associated with the collisional transfer of energy from the ν_3 mode to other modes of the molecule. By measuring the frequency positions of these peaks and comparing the results with the anharmonicity constants from Ref. 9 ($x_{14} = -1.1 \text{ cm}^{-1}$), we can explain the appearance of these new peaks in

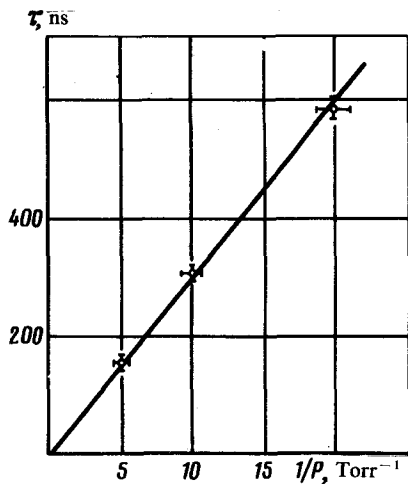


FIG. 3. Time required for relaxation to the equilibrium populations vs the density of SF_6 molecules.

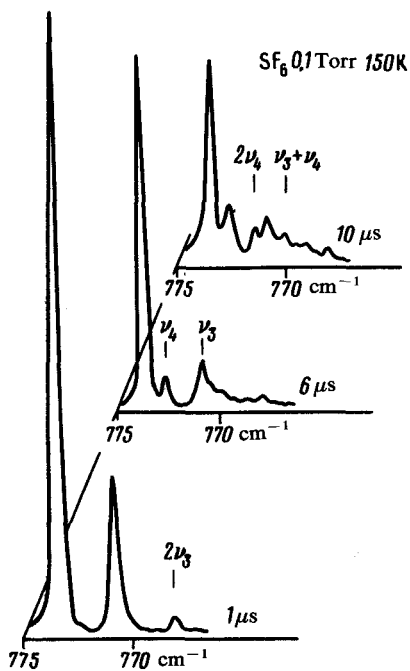


FIG. 4. CARS spectra of the SF_6 molecule for a long delay between the excitation and the probing.

terms of a collisional filling of ν_4 , $2\nu_4$, and $\nu_3 + \nu_4$ levels. The characteristic time for this transfer, estimated from the rate at which the ν_4 peak appears, is 700 ns-Torr ($T = 150$ K). The ν_3 peak disappears at the same rate.

4. These results demonstrate an exceedingly high rate of resonant $\nu\nu$ exchange in the ν_3 mode of the SF_6 molecule. The collision cross sections $\sigma = (\tau_{\nu\nu}/4n)(\pi m/kT)^{1/2}$ introduced phenomenologically to correspond to the measured relaxation times of the ν_3 , $2\nu_3$, and $3\nu_3$ levels are 240, 440, and 750 \AA^2 , respectively, considerably larger than the gas dynamic collision cross section $\sigma_g = 70 \text{\AA}^2$. This result is evidence of a long-range nature of the interaction of the colliding molecules; the most probable mechanism for this interaction is a resonant dipole-dipole mechanism in this case.^{10,11}

Another important fact is that the measured time for the $\nu\nu$ exchange of the ν_3 level corresponds well to the rotational-relaxation time of SF_6 : $\tau_{RR} = 35$ ns-Torr, measured in Refs. 12 and 13 by a double IR resonance method, i.e., during vibrational excitation of the ν_3 state. This agreement suggests that a resonant $\nu\nu$ exchange accompanied by a simultaneous change in the rotational number is the primary mechanism for the rotational relaxation in this case. As a further argument we might cite the circumstance that the cross section for the rotational relaxation of SF_6 , $\sigma_{RR} = 59 \text{\AA}^2$, in the vibrational ground state of SF_6 (measured in Ref. 14 by an NMR method) is significantly smaller, even in comparison with the gas kinetic cross section.

The experimental increase in the relaxation rate with increasing excitation level is important for reaching an understanding of the mechanism by which the high-lying

vibrational levels of polyatomic molecules are excited. This result agrees well with the model of single-quantum resonant $\nu\nu$ exchange. This model predicts that the relaxation rate will increase not only with increasing index of the vibrational level but also with increasing average vibrational energy in the mode, $\bar{\nu}$, i.e., with increasing vibrational temperature. The $\nu\nu$ exchange in the region of the high-lying vibrational states $\nu, \bar{\nu} = 5$, can explain the relaxation observed in SF₆ in Refs. 15 and 16 with a characteristic time $\tau \approx 2$ ns·Torr. The existence of such short relaxation processes requires a re-examination of the possibility of collisions in several experiments on the multiphoton excitation of polyatomic molecules.

This model would also require re-examining the condition for the existence of a "cold" ensemble of molecules,¹⁷ i.e., an ensemble of molecules which have remained in the vibrational ground state because the excitation was not resonant. When we take into account the dependence of the rate of $\nu\nu$ exchange on the average excitation level of the mode, $\bar{\nu}$, we should write this condition as $\tau_p < \tau_{\nu\nu}/p\bar{\nu}$, where τ_p is the length of the exciting pulse, and p is the gas pressure.

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¹⁾These times can be converted into the rate constants of the elementary $\nu\nu$ processes through detailed kinetic calculations.

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