

Vibrational relaxation in highly excited SF₆ and SiF₄ molecules

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Coherent anti-Stokes Raman spectroscopy has been used to study collision processes and to determine the rate of transfer of vibrational energy in SF₆ and SiF₄ molecules excited by the IR field from a CO₂ laser. The mechanism for the fast intermode energy exchange, which results from the effect of highly excited states, is discussed.

The collisional redistribution of vibrational energy in polyatomic molecules is customarily broken up¹ into a stage of $V-V$ exchange, i.e., a quiresonant exchange of energy within a single vibrational mode, and $V-V'$ exchange, which results in an exchange of energy between different vibrational modes of the molecules.

In Ref. 2 we developed and described an effective method for studying the vibrational relaxation of molecules through a multiphoton excitation of the molecules in an IR laser field and by probing the vibrational states by means of coherent anti-Stokes Raman scattering (CARS). We used this procedure to measure the rate constants of the $V-V$ exchange for the ν_3 mode of SF₆ molecules.

In this letter we report a study of intermode collisional $V-V'$ energy exchange in SF₆ and SiF₄ molecules excited highly by IR light. In the results we see several common threads, whose interpretation goes beyond the scope of the usual understanding.

1. From the transformation of the CARS spectra (Fig. 1, a and b) recorded for SF₆ and SiF₄ molecules when the probing is delayed $\tau > 500$ ns with respect to the excitation (at a gas pressure of 0.3 Torr and a temperature $T = 150$ K) we see that in addition to the filling of the $1\nu_3$, $2\nu_3$, and $3\nu_3$ states in the field, there are some other lines, which result from the filling of discrete states of the ν_4 mode in the course of collisions.

The distribution of the populations of the $1\nu_4$, $2\nu_4$, and $3\nu_4$ levels reconstructed from the spectra is a Boltzmann distribution with a vibrational temperature determined by the intensity of the exciting field and the delay time τ .

2. Analysis of the time evolution of the temperature of the ν_4 mode and of its arrival at a quasisteady value (Fig. 2 for SiF₄ molecule) shows that an increase in the energy density of the IR field from 0.4 to 1.2 J/cm² ($\nu_{\text{exc}} = 1028$ cm⁻¹) leads to an increase in the rate of filling of the vibrational states of the ν_4 molecule from $5.0(12) \times 10^6$ s⁻¹·Torr⁻¹ to $1.2(4) \times 10^7$ s⁻¹·Torr⁻¹ in the case of the SiF₄ molecules, while for the SF₆ molecules an increase in the energy density to 0.4 J/cm² ($\nu_{\text{exc}} = 944.4$ cm⁻¹) leads to an increase in this rate to $1.0(3) \times 10^7$ s⁻¹·Torr⁻¹ (the characteristic rate of gas-kinetics collisions).

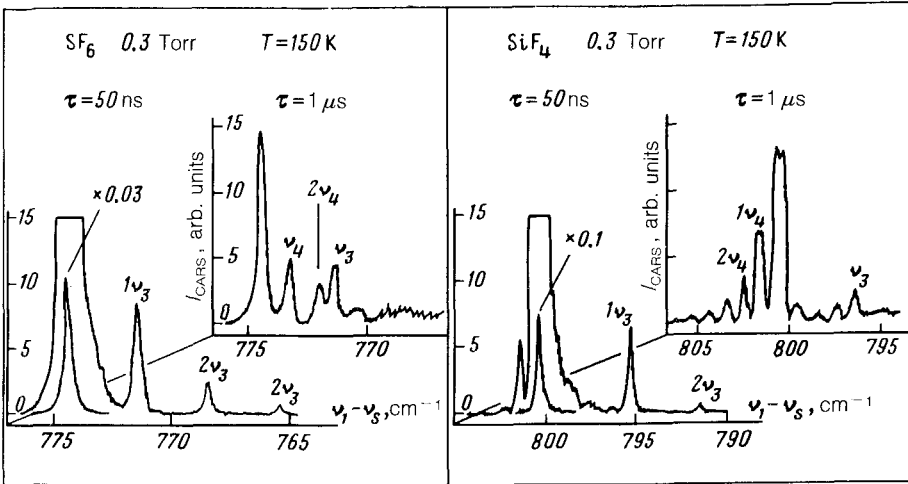


FIG. 1. Transformation of the SF₆ and SiF₄ spectra over time. The SF₆ was excited by a 40-ns pulse from a CO₂ laser at the frequency 944.2 cm⁻¹ with Φ_{CO₂} = 0.3 J/cm²; the SiF₄ was excited at the frequency 1024 cm⁻¹ at Φ_{CO₂} = 1.2 J/cm².

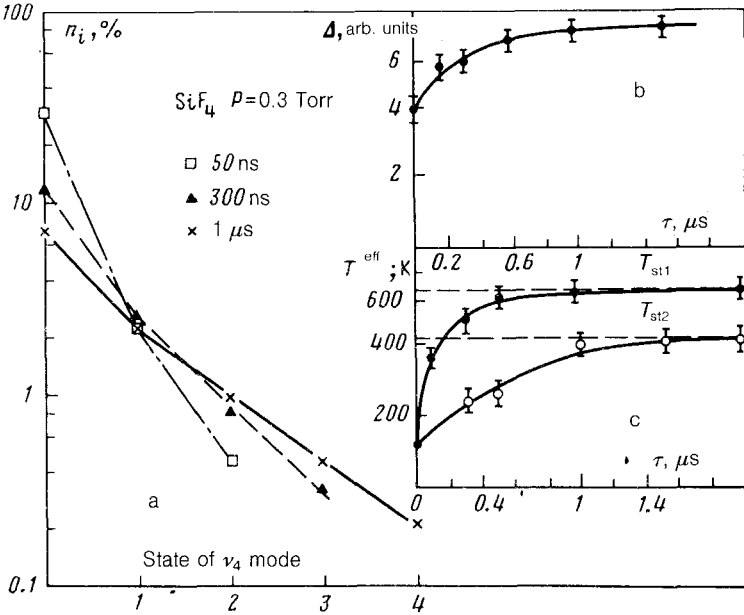


FIG. 2. a: Distribution of the populations of the sublevels of the ν_4 mode ($\Phi_{CO_2} = 1.2 \text{ J/cm}^2$). b: Time evolution of the half-width of the fundamental transition band, Δ . c: Time evolution of the temperature (T^{eff}) of the ν_4 mode (T_{st1} corresponds to $\Phi_{CO_2} = 1.2 \text{ J/cm}^2$, and T_{st2} corresponds to $\Phi_{CO_2} = 0.4 \text{ J/cm}^2$).

3. The broadening of the $0-\nu_1$ transition lines found experimentally is evidence that energy is also transferred to discrete levels of low-frequency modes, ν_6 in the SF_6 molecule and ν_2 in the SiF_4 molecule. The typical rates involved here are those found for the ν_4 mode.

The reason for the observed rapid collisional filling of the vibrational states of the ν_4 and ν_6 modes of SF_6 and the ν_4 and ν_2 modes of SiF_4 may be either a resonance of the states ν_3 and $\nu_4 + \nu_6$ in SF_6 and of ν_3 and $2\nu_4 + \nu_2$ in SiF_4 (the energy defect between these states is 14 cm^{-1} in SF_6 and 10 cm^{-1} in SiF_4) or a vibrational exchange between molecules excited into a quasicontinuum with molecules in low-lying discrete vibrational states. A characteristic feature of this exchange is its resonant nature, i.e., the ability of molecules in randomized states of the quasicontinuum to undergo a collisional exchange of a vibrational quantum of any mode. In an effort to test these suggestions, we selected excitation conditions for SF_6 molecules which resulted in an effective filling of states of the quasicontinuum, while the populations at the discrete levels of the excited mode remained below the sensitivity of the apparatus. The CARS spectra recorded at a gas pressure of 0.1 Torr and a delay time $\tau = 300 \text{ ns}$ are evidence that there is no significant filling of the low-lying discrete vibrational states. When gaseous $^{32}\text{SF}_6$ in a 1:10 mixture with $^{34}\text{SF}_6$ was excited under similar conditions, at a total pressure of 0.1 Torr, with the same delay times, the CARS spectra clearly reveal lines responsible for transitions from low-lying excited vibrational states of the ν_3 and ν_4 modes. This fact is convincing evidence of an effective vibrational exchange between the deliberately prepared ensembles of $^{32}\text{SF}_6$ molecules in highly excited vibrational states and unexcited $^{34}\text{SF}_6$ molecules in the vibrational ground state.

The behavior of the CARS spectra over long delay times $1 < \tau < 10 \mu\text{s}$ reflects a

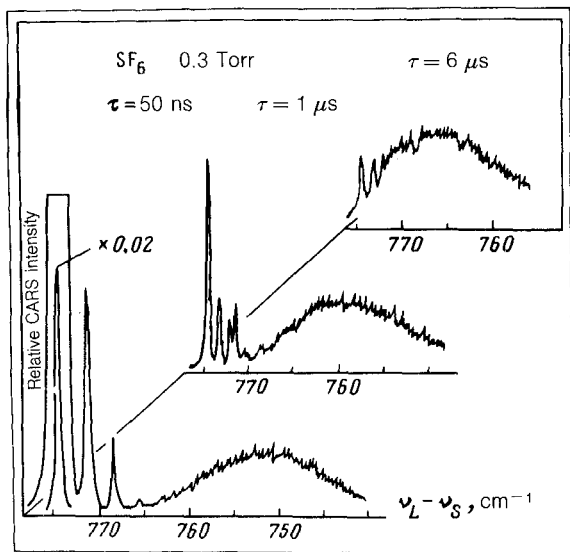


FIG. 3. CARS spectra of SF_6 excited at the frequency 944.2 cm^{-1} at $\Phi_{\text{CO}_2} = 0.4 \text{ J/cm}^2$.

redistribution of the absorbed energy in the system of vibrational states of all the modes of the molecules. Since there are many such states, the lines corresponding to transitions from them overlap markedly and form a structureless spectrum with a maximum shifted from the line of the $0-\nu_1$ transition by an amount equal to an anharmonic frequency deviation determined by the amount of energy in the vibrational degrees of freedom. The transformation of this spectrum over time and its arrival at a steady shape in a time $\sim 6 \mu\text{s}$ (Fig. 3) make it possible to determine the relaxation rate of a common vibrational temperature in the system of vibrational states of the modes: $2.5 \times 10^6 \text{ s}^{-1} \cdot \text{Torr}^{-1}$.

In summary, this study yields a picture of the collisional redistribution of vibrational energy of polyatomic molecules excited into the vibrational quasicontinuum. A distinctive feature of this process and of the establishment of a common vibrational temperature of the molecules is the high rate of collisional energy transfer, which is a consequence of the resonant nature of the collisional exchange of the quanta of arbitrary modes along a chain: (molecule in a discrete state of mode i)—(molecule in the quasicontinuum)—(molecule in a discrete state of mode j). We observe a high rate of relaxation to a complete vibrational equilibrium ($2.5 \times 10^6 \text{ s}^{-1} \cdot \text{Torr}^{-1}$) in the presence of leading channels for vibrational exchange (the ν_3 and ν_4 modes).

¹B. F. Gordiets, A. I. Osipov, and L. A. Shelepin, *Kineticheskie protsessy v gazakh i molekulyarnye lazery* (Kinetic Processes in Gases and Molecular Lasers), Nauka, Moscow, 1980, p. 512.

²A. M. Prokhorov (editor), *Spektroskopiya kogerentnogo antistoksova rasseyaniya sveta molekulyarnykh gazov* (Coherent Anti-Stokes Light-Scattering Spectroscopy of Molecular Gases, Vol. 2, Proceedings of the Institute of General Physics), 1986, pp. 64–149.

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