

Coherent active Raman spectroscopy of polyatomic molecules during many-photon excitation

R. V. Ambartsumyan, S. A. Akhmanov, A. M. Brodnikovskii, S. M. Gladkov, A. V. Evseev, V. N. Zadkov, M. G. Karimov, N. I. Koroteev, and A. A. Puretskii

M. V. Lomonosov Moscow State University; Institute of Spectroscopy, Academy of Sciences of the USSR

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Coherent active Raman spectra have been measured for vibrationally excited SF₆ molecules. The homogeneous broadening of the transitions in the vibrational quasicontinuum is evaluated.

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1. In this letter we are reporting the first use of coherent active Raman spectroscopy (CARS)¹ to study the population distribution among vibrational levels and the characteristics of the vibrational quasicontinuum of SF₆ molecules excited by resonant IR light in a many-photon process. The results can be used to study the population shifts during the collisionless excitation and subsequent vibrational relaxation of the molecules, to find the boundary of the vibrational quasicontinuum, and to evaluate the homogeneous broadening of the transitions in this quasicontinuum.

2. Progress toward an understanding of the physics of the many-photon excitation of molecules will lean heavily on the development of suitable methods for probing the fast collisionless-excitation processes and effective methods for the spectroscopy of highly excited states (see the review by Bagratashvili²). Some interesting data on the inter- and intra-molecular distribution of the excitation energy in SF₆ and CF₃I molecules have been obtained by spontaneous-Raman spectroscopy by Bagratashvili.³ We have previously pointed out¹ the advantages of the active version of Raman spectroscopy for studying many-photon excitation: It has a high spectral resolution and a high sensitivity; it can yield information on the distribution of the molecules among energy states; it can simultaneously yield information on the spectroscopic parameters of these states; etc. In the version of CARS which we used in the present experiments, we measured the dispersion of the intensity (I_a) of the anti-Stokes signal at the frequency $\omega_a = 2\omega_1 - \omega_2$ (ω_1 and ω_2 are the frequencies of the biharmonic pump; $\omega_1 - \omega_2 \approx \Omega$). The intensity I_a is proportional to $|\chi^{(3)}(\omega_1 - \omega_2)|^2$, where the cubic susceptibility of the excited multilevel molecule is

$$\chi^{(3)}(\omega_1 - \omega_2) \propto \sum_{\{v, J\}} \left(\frac{d\sigma}{d\omega} \right)_{\{v, J\}} \frac{\Delta N_{\{v, J\}}}{\Omega_{\{v, J\}}} (\omega_1 - \omega_2) - i\Gamma_{\{v, J\}} \Gamma^{-1}, \quad (1)$$

Contributing to expression (1) are transitions which begin from all the populated vibrational-rotational states $\{v, J\}$, with frequencies $\Omega_{\{v, J\}}$ and Raman cross sec-

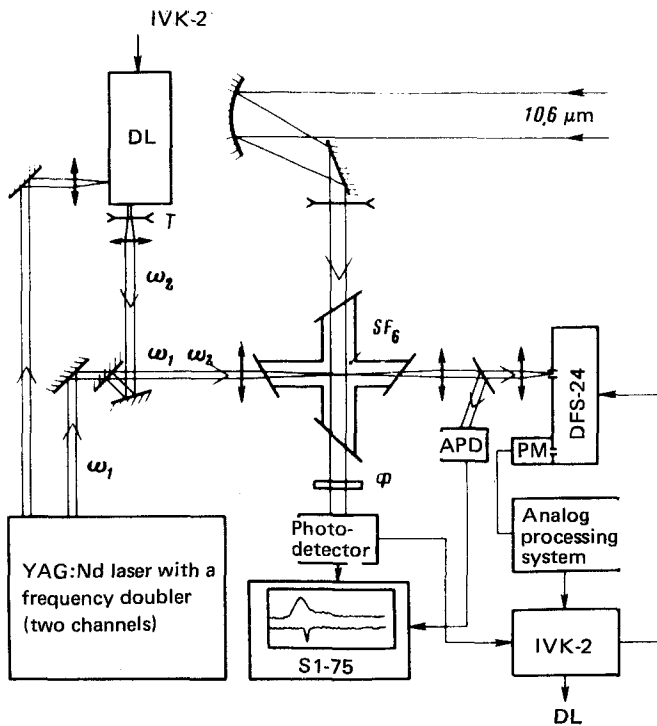


FIG. 1. Schematic diagram of the experimental apparatus. The gaseous SF_6 , contained in a cross-shaped cell at $T \approx 300$ K and at a pressure in the range $p = 2\text{--}10$ Torr, is excited by the pulse from a CO_2 laser in a volume with dimensions $20 \times 5 \times 3$ mm. The gas is probed in the transverse direction by collinear focused beams at the second harmonic from a YAG:Nd laser ($\lambda_1 = 2\pi c/\omega_1 = 532$ nm) and a dye laser (DL; $\lambda_2 = 2\pi c/\omega_2 \approx 555$ nm). The dimensions of the probing region are $2 \times 0.03 \times 0.03$ mm. T —Telescope; F —filter; APD—avalanche photodiode; S1-75—oscilloscope.

tions $(d\sigma/d\omega)_{\{v,j\}}$; here $\Delta N_{\{v,j\}}$ is a function which describes the distribution of the population differences. We measured the dispersion of $I_a = I_a(\omega_1 - \omega_2)$ at various delays of the probing signals with respect to the pulse from the CO_2 laser so that we could follow the various stages of the many-photon excitation.

3. The experimental apparatus is shown schematically in Fig. 1. The SF_6 pressure was varied from 2 to 10 Torr. The SF_6 molecules were excited by the beam from a CO_2 laser at the frequency 947.7 cm^{-1} (the ν_3 mode was excited). The length of the excitation pulse at half-maximum was 150 ns, and its energy was varied up to 0.5 J. The Raman-active mode ν_1 was probed in a CARS arrangement. For this probing we used the second harmonic from a YAG:Nd laser ($\lambda_1 = 532$ nm) and the beam from a dye laser (with a wavelength tunable near $\lambda_2 \approx 555$ nm). The length of the probing pulses was $\tau_p \approx 20$ ns. The spectral resolution was no worse than 0.5 cm^{-1} . An IVK-2 data acquisition and processing complex controlled the tuning of the frequency of the dye laser (λ_2), the monochromator, and all the data acquisition and processing.

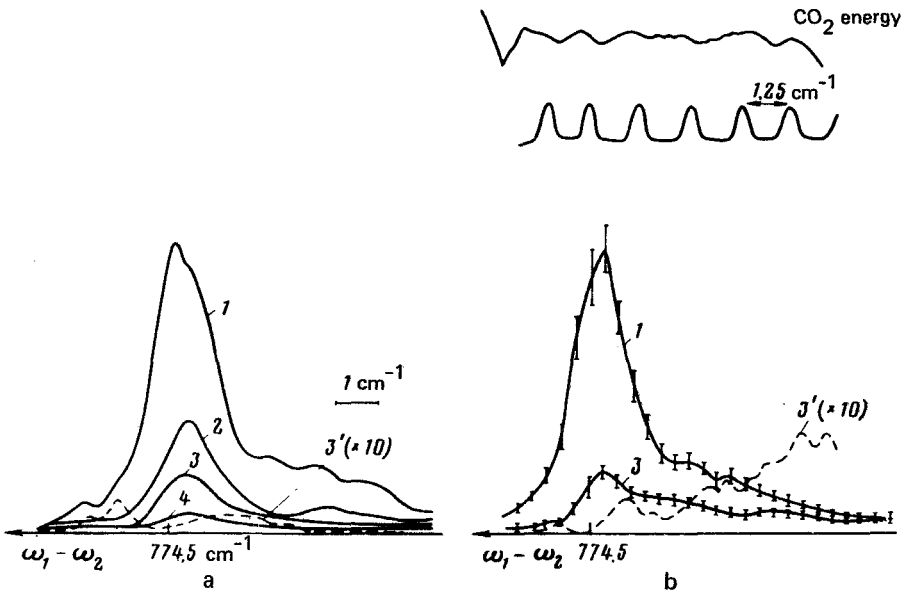


FIG. 2. Coherent anti-Stokes scattering spectra for the scattering of light in the ν_1 mode of the SF_6 molecules during many-photon IR excitation of the ν_3 mode. $T \approx 300$ K; $p = 5$ Torr. a: The delay between the excitation and probing pulses is $\tau = 30 \pm 10$ ns. Spectrum 1—The total energy density (or dose) of IR light, Φ , is 0; 2—0.15 J/cm²; 3—0.73 J/cm²; 4—1.5 J/cm². b: The delay is $\tau = 3 \mu\text{s}$. 1— $\Phi = 0$ ("cold" molecules); 3— $\Phi = 0.73$ J/cm²; 3'—(in both parts of the figure, and these curves are magnified by a factor of ten) correspond to only the excited molecules. These spectra were found from spectra 3 by subtracting the spectrum of "cold" molecules. (Because of the rotational relaxation, all the molecules in the zone irradiated by the IR laser should be involved in the many-photon excitation in the present experiments because of rotational relaxation.⁴ The residual signal at ~ 774 cm⁻¹ is therefore caused by molecules which have been illuminated only slightly by the edge of the IR beam.) All the spectra were plotted by the IVK-2 complex. Shown in Fig. 2b along with the CARS spectra are wavelength markers of the tunable laser (the ring of the Fabry-Perot measuring interferometer, with a base line of 1.25 cm⁻¹) and the energy of the excitation pulse from the CO₂ laser. The dispersions of the intensity of the anti-Stokes signal calculated by the IVK-2 complex are also shown.

4. Figure 2 shows the "active" spectra measured at various intensities of the IR excitation and at a pressure of 5 Torr. The delay for the curves in Fig. 2a is $\tau = 30 \pm 10$ ns, which corresponds to excitation and probing which are essentially collisionless with respect to V - V exchange. As the energy density Φ of the CO₂ laser is raised, we see a rapid decrease in the integrated intensity of the CARS signal:

$$J_a = \int I_a d\omega_a \int | \chi^{(3)} |^2 d\omega_a \rightarrow 0. \quad (2)$$

The cubic susceptibility of the highly excited molecules decreases rapidly, but the spectral line retains the same shape. Figure 2b shows spectra for a delay $\tau \approx 3 \mu\text{s}$, which is longer than the scale time for collisional V - V exchange. In this case we see definite changes in the shape of the spectrum. There is a difference in the shape of the lines (see the dashed curves, which were found by subtracting the contribution of the unexcited molecules in Figs. 2a and 2b), which is evidence of a difference in

the distribution laws $w(N_{\nu, J})$ for the "collisional" and "collisionless" cases. The distribution is narrower in the collisionless case.

5. The weakening of the coherent anti-Stokes signal in the frequency region corresponding to scattering from unexcited molecules is caused by an emptying of the ground and low-lying vibrational states, which are populated at $T \approx 300$ K. In contrast, the signal from the molecules excited by the many-photon process is extremely weak. This signal lies on the low-frequency side of the band at ~ 774 cm^{-1} (unexcited molecules). A possible reason for this result is, according to (1), an increase in the homogeneous width of the transitions in the quasicontinuum, Γ , since $|\chi^{(3)}|^2$ is proportional to $1/\Gamma^2$, and \mathcal{S}_a is proportional to $1/\Gamma$. We carried out a quantitative calculation, working from the known anharmonicity constants,⁵ for a Boltzmann population distribution. The results of these calculations reveal a very strong

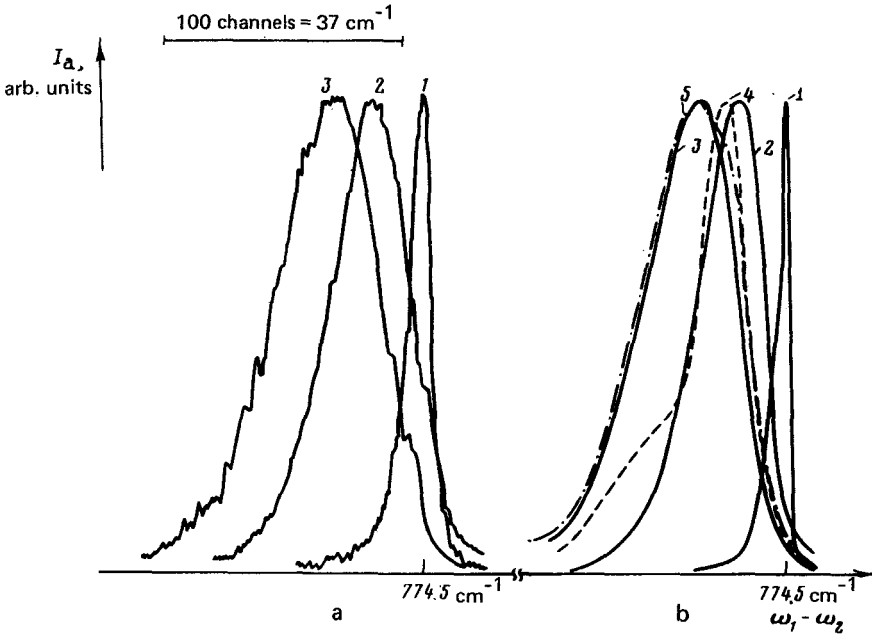


FIG. 3. Coherent anti-Stokes scattering spectra for scattering of light in the ν_1 mode by thermally heated gaseous SF_6 at various temperatures. The gas density is $N_0 = 3.4 \times 10^{18} \text{ cm}^{-3}$. (a) Experimental results. 1— $T=300$ K; 2— $T=870$ K; 3— $T=1000$ K. The curves are normalized to the same spectral maximum. These curves were obtained by a multichannel optical analyzer during wide-band excitation of the CARS spectra (see Chapter VI in Ref. 1). The spectral width of the instrumental function is 1.8 cm^{-1} (five channels of the multichannel optical analyzer). (b) Results of a numerical simulation of the CARS spectra. 1— $T=300$ K; 2— $T=720$ K; 3, 4, 5— $T=1000$ K. In the calculation of spectra 1–3, the homogeneous width $\Gamma_{\nu, J}$ for all the transitions was assumed to be independent of the index of the initial level, $\{\nu, J\}$, and equal to the line width of the tunable laser: $\Gamma_{\nu, J}/2\pi c = \text{const} = 0, 2 \text{ cm}^{-1}$. In the calculation of spectrum 4, the width $\Gamma_{\nu, J}$ was taken to be a step function; specifically, it was assumed that this function rises abruptly from 0.2 to 5 cm^{-1} when the energy of the initial state of the transition $(\nu_1, J_1; \nu_2, J_2, \dots, \nu_6, J_6) \rightarrow (\nu_1 + 1, J_1; \nu_2, J_2, \dots, \nu_6, J_6)$ exceeds $E_{\text{vib}} = 5000 \text{ cm}^{-1}$. Spectrum 5 was calculated in a similar way, but the height of the "step", $\Gamma_{\nu, J}/2\pi c$, was less (the change was from 0.2 to 1 cm^{-1}), and the step occurred at $E_{\text{vib}} = 4000 \text{ cm}^{-1}$.

dependence of the shape of the signal of the line width Γ in the quasicontinuum. We can therefore find an extremely accurate value for Γ by comparing the calculated and experimental results. To evaluate Γ in the SF_6 quasicontinuum, we measured the spectra of equilibrium, thermally excited SF_6 over the temperature range 300–1000 K (the average energies \bar{E} varied from 590 to 6500 cm^{-1} , i.e., to a point actually above the quasicontinuum boundary, according to Ref. 3).

The calculated spectra are shown in Fig. 3b. A comparison of the calculated and experimental results shows that the homogeneous broadening Γ in the vibrational-energy range $E_{\text{vib}} \leq 6000 \text{ cm}^{-1}$ does not exceed $\Gamma/2\pi c \approx 1 \text{ cm}^{-1}$ for SF_6 . The error in this estimate is no greater than 1 cm^{-1} and thus much smaller than those of other methods. With data on the spectral characteristics of the excited states, we could also find the distribution law $w(N_{|v,r|})$ from experimental data like those in Fig. 2.

In summary, active spectroscopy may become a common method for studying the population distribution functions during many-photon excitation of molecules⁶ and for spectroscopy of the vibrational quasicontinuum.

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