Active spectroscopy of Raman scattering of light in the continuous regime; possibility of ultrahigh resolution spectroscopy of Raman transition

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The active-spectroscopy method was used to obtain the Raman-scattering spectrum of liquefied N_2 in the vicinity of the 2326 cm^{-1} line. We measured the magnitude and sign of the relative contributions of the nuclear and electronic subsystems to the nuclear polarizability: $\chi^R/\chi^{NR} = +200 \pm 40$.

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1. We report in this article the results of an experiment in which we obtain, for the first time, the Raman scattering spectrum from molecules of a liquid (liquefied N_2) by the active-spectroscopy method (ASRS) with the aid of cw lasers.

The results have enabled us to determine the absolute magnitude and the sign of the ratio of the contributions of the nuclear and electronic subsystems to the optical cubic susceptibility $\chi^{(3)}$. It is specially noted that the active spectroscopy using narrow-band tunable cw lasers can become a unique method for ultrahigh resolution of Raman transitions. The anti-Stokes scattering signal obtained with the aid of ASRS can exceed the spontaneous-scattering signal of the same beam in the Stokes region even at moderate pump-beam powers, so that it becomes possible to measure the RS spectra of luminescent and colored media in a spectral range that is almost free of background illumination, at a registered-signal level not lower than the level in the standard scheme of Stokes spontaneous RS.

2. The ASRS method using tunable lasers has recently been excessively used to measure Raman transitions in molecules of gases, liquids, and solids, and also for analytic purposes.[1–5] In practice, however, all the experiments were performed using high-power pulsed tunable lasers. Active Raman spectroscopy in the field of cw lasers is in essence a new trend. We know of only one recent study,[6] in which an ASRS signal was registered in the continuous regime in gaseous CH_4, a cell filled with which was placed inside a tunable-laser resonator. Owing to the weakness of the signal, however, the parameters of the RS lines were not measured.

To measure the dispersion of the nonlinearity of $\chi^{(3)}$ near the vibrational transition $\Omega_R/2\pi c = 2326$ cm^{-1} of liquid nitrogen, we registered the anti-Stokes component (frequency ω_a) for the scattering of the radiation of the argon laser (ω_1) by coherent molecular vibrations of N_2 molecules, set in phase by the beats of the pump waves: $\omega_a = \omega_1 + (\omega_1 - \omega_2) = 2\omega_1 - \omega_2$ with ω_2 varied, and $\omega_1 - \omega_2 \approx \Omega_R$. This four-photon process is described by the susceptibility

$$\chi^{(3)} = 3\chi^{NR} + \chi^R;$$
$$\chi^R = \bar{\chi}^R/(i - \Delta); \quad \Delta = [(\omega_1 - \omega_2) - \Omega_R]/\Gamma_R \tag{1}$$

is the frequency deviation from the center of the line, Γ_R is the half-width of the RS line, $\bar{\chi}^R = (2c^4N/\omega_2^4\hbar\Gamma_R)(d\sigma/do)$, $d\sigma/do$ is the cross section for spontaneous Stokes RS, and N is the molecule number density. Measurement of the signal power P_a at the frequency $\omega_a = 2\omega_1 - \omega_2$ at resonance ($\Delta = 0$) and far from resonance ($\Delta \gg 1$) makes it possible to determine the ratio

$$\left|\frac{\bar{\chi}^R}{3\chi^{NR}}\right| = \left[\frac{P_a(\Delta = 0)}{P_a(\Delta \neq 0)}\right]^{1/2}, \tag{2}$$

and measurement of the position of the point of mutual cancellation of the electronic and ionic contribution to $\chi^{(3)}$ makes it possible to determine the sign of this ratio

$$\mathrm{sign}\, \bar{\chi}^R/3\chi^{NR} = \mathrm{sign}\,(\nu_{max} - \nu_{min}), \tag{3}$$

where ν_{max} and ν_{min} are the positions of the maximum and minimum of $|\chi^{(3)}|^2$ respectively. In addition[2,7]:

$$|\nu_{max} - \nu_{min}| = \Gamma_R \left|\frac{\bar{\chi}^R}{3\chi^{NR}}\right|^2. \tag{4}$$

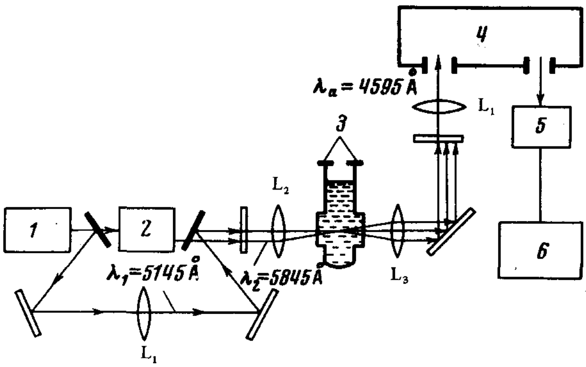

FIG. 1. Diagram of experimental ASRS setup in the continuous regime.

4. The experimental setup is shown in Fig. 1. The driving ionized-argon laser (1) delivered a power $P_1 = 2$ W in the line $\lambda_1 = 5145$ Å. The power of the tunable line of laser (2) (solution of rhodamine-6g in ethanol) was $P_2 \approx 150$ mW, and the line width was 0.6 cm^{-1}. The achromatic objective L_2 focused the pump beams into a cell with liquid N_2 (3); the length $b \approx 300\ \mu$ of the beam neck at the focus was smaller than the coherent-interaction length $l_{coh} = \pi/\Delta k$, $\Delta k = k_a - (2k_1 - k_2)$ is the wave detuning ($l_{coh} \approx 500\ \mu$). Under these conditions, the signal power P_a is independent of the degree of focusing of the beams

$$P_a = \frac{\lambda_1^4 N^2}{\pi^2 c^2 \hbar^2 (\Gamma_R)^2} P_1^2 P_2 \left(\frac{d\sigma}{do}\right) \tag{5}$$

The strongest signal at the frequency ω_a was obtained at an angle setting $\alpha = 2°30'$ between the pump beams (outside the cell) (see Fig. 2). The power P_a of the anti-Stokes ASRS signal was 1.5 times larger than the power of the spontaneous RS Stokes signal of the same beam gathered with lens L_3 from a solid angle 0.2 sr (outside the cell). Calculation of this quantity by means of formula (5) yields $P^{(\mathrm{ASRS})}/P^{(\mathrm{spont})}_{\mathrm{Stokes}} = 2$ at $P_1 = 400$ mW and $P_2 = 70$ mW. However, even in the case of collinear propagation of the pump beams ($\alpha = 0$) the signal power P_a

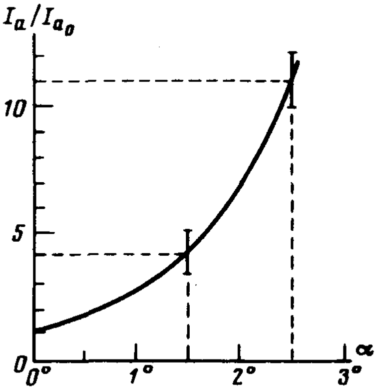

FIG. 2. Dependence of the power of ASRS signal on the angle α between pump beams (outside the cell).

was only one order of magnitude smaller than in the direction of the exact sychronism. The anti-Stokes radiation produced in this case a cone with apex angle of approximately 3°. Thus, when rigidly focused beams are used, there is no need to worry about the preliminary splitting of the angles between the pump beams, and a collinear scheme can be used. The loss in the signal magnitude is not very significant in this case.

5. Figure 3 shows the spectrum of the ASRS signal (solid line), obtained by scanning the monochromator [see (4) on Fig. 1] with the aid of a photomultiplier

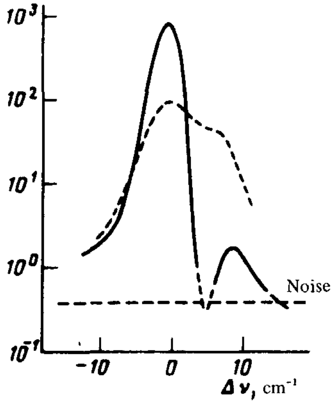

FIG. 3. Spectrum of ASRS signal (solid line) at the oscillation $\Omega_R/2\pi c = 2326$ cm^{-1} of liquefied N_2, obtained by scanning the monochromator. The dashed line shows the spectrum of the tunable pump component; $\Delta\nu = (\omega_1 - \omega_2)/2\pi c$. The noise level is due to the dark current of the photomultiplier.

(5) and an automatic recorder (6). The dashed line in this figure shows the spectrum of the tunable laser participating in the excitation of the "active" spectrum. The spectral width of the monochromator slit was 2 cm^{-1}. The reduction of the "active" spectrum by the ASRS method with broadband excitation[7] and with allowance for the width of the spontaneous Raman-scattering line $2\Gamma_R/2\pi c = 0.067$ cm^{-1} leads to the estimate

$$\bar{\chi}^R/3\chi^{NR}_{1111} = +190 \pm 40. \tag{6}$$

Estimates by formula (2) yields

$$|\bar{\chi}^R/3\chi^{NR}_{1111}| = 200 \pm 40. \tag{7}$$

6. Thus, it has been experimentally demonstrated that when a relatively broadband tunable cw laser is used it is possible to measure the parameters of the Raman transition of liquid molecules by the ASRS method. The use of single-frequency continuous lasers, together with the substantial improvement in the resolution, determined by the laser line width, increases even more the level of the resonant signal: calculation shows that in this case the anti-Stokes ASRS signal exceeds the level of the spontaneous Stokes RS even at pump-line powers $P_1 = 45$ mW and $P_2 = 7.5$ mW. This circumstance turns out to be exceedingly valuable in measurements by the ASRS lines of Raman scattering of strongly luminescent and colored media, which produce strong illumination in the Stokes region.

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