

Observation of resonant interference of nonlinear optical susceptibilities of molecules in a solution

A. F. Bunkin, S. G. Ivanov, and N. I. Koroteev

Moscow State University

(Submitted September 9, 1976)

Pis'ma Zh. Eksp. Teor. Fiz. **24**, No. 8, 468-472 (20 October 1976)

We consider a resonant modification of the method of coherent active Raman-scattering spectroscopy (ARSS), when the Raman and single-photon electron resonances are localized on different molecules of the solution. A coherent "subtraction" of the nondispersive pedestal is observed in the spectrum of the coherently scattered light. The complex value of the resonant nonlinear susceptibility of the rhodamine-6G molecules has been measured.

PACS numbers: 32.20.Dr, 33.40.Jq

1. We develop in this paper a new approach to the problem of resonant inelastic scattering of light, a method closely related with that of coherent active Raman-scattering spectroscopy (ARSS).^[1] In contrast to the latter, however, in this variant it becomes possible to eliminate almost completely the coherent background against which the scattering lines are observed in ARSS, as well as to observe the characteristic interference effects in the spectra of the scattered radiation. This is accomplished by using double optical resonance in a specially prepared mixture of molecules of two sorts. The molecules of one component of the mixture have a resonance of the Raman type, which is investigated in scattering (frequency Ω_R), while the molecules of the other kind have a single-photon electron resonance (frequency Ω_E). Coherently scattered

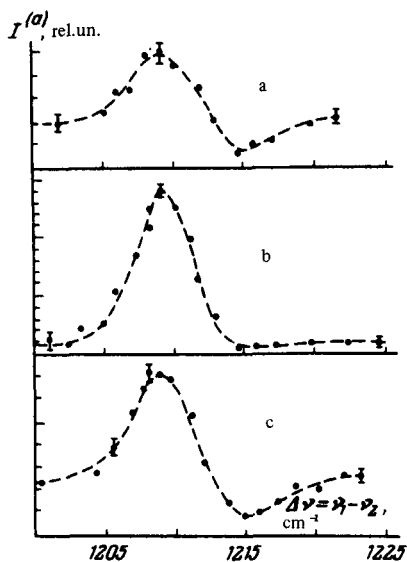


FIG. 1. Deformation of the active spectra of toluene (line $\nu_R = 1209 \text{ cm}^{-1}$) when an absorbing additive is mixed-in; a—pure toluene, b—toluene with rhodamine-6G, $N_2 = 0.46 \times 10^{16} \text{ cm}^{-3}$; c—toluene with rhodamine-6G; $N_2 = 1.7 \times 10^{16} \text{ cm}^{-3}$.

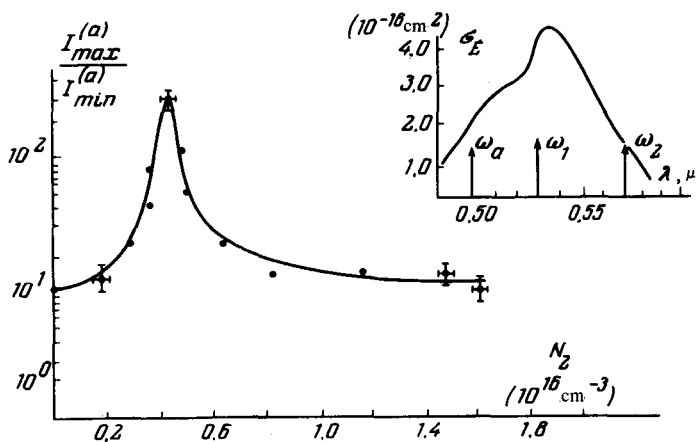


FIG. 2. Dependence of the contrast of the active spectrum of toluene, $k = I_{\max}^{(a)}/I_{\min}^{(a)}$, of the RS line $\nu_R = 1209 \text{ cm}^{-1}$, on the concentration N_2 of the rhodamine-6G molecules. On the upper right is shown the contour of the absorption line of the rhodamine-6G molecule in toluene and the relative positions of the pump line and the line of the coherently scattered anti-Stokes signal.

radiation is observed with frequency $\omega_a = 2\omega_1 - \omega_2$, where $\omega_1 \approx \Omega_E$ is the fixed frequency of the laser and ω_2 is the dye laser frequency and is tunable in the region of the Raman resonance $\omega_1 - \omega_2 \approx \Omega_R$. Owing to the coherence of the scattering, the contributions from the different mixture components do not add up, but interfere and lead to a spectrum deformation typical of resonant Raman scattering.

It is also of interest to employ this modification of the ARSS to measure the complex value of the resonant nonlinear susceptibility of the absorbing component.

The questions touched upon in this communication are particularly timely in view of the fact that the ARSS method has recently been gaining wide use both to measure nonlinear optical susceptibilities^[1-3] and for analytic purposes.^[6,7]

The experiment was performed with toluene ($\text{C}_6\text{H}_5\text{CH}_3$), the active spectrum of which is well known.^[1] We chose for the measurement a relatively weak RS line with $\Omega_R/2\pi c = 1209 \text{ cm}^{-1}$. We measured the intensity of the second harmonic (SH) of a YAG:Nd³ laser (frequency ω_1) scattered into the anti-Stokes region (frequency ω_a) at $\omega_1 - \omega_2 = \Omega_R$. The source of the pump wave with tunable frequency ω_2 was a laser with a solution of rhodamine 6G in ethanol, excited by part of the second harmonic of the driving laser. The width of the tunable line was about 1 \AA , and this determined the spectral resolution.

We were interested primarily in how addition of a dye that absorbs the second harmonic changes the contrast of the "active" RS spectrum of toluene, obtained by scanning ω_2 , i. e., in the ratio of the maximum anti-Stokes signal $I_{\max}^{(a)}$ to the minimum value $I_{\min}^{(a)}$:

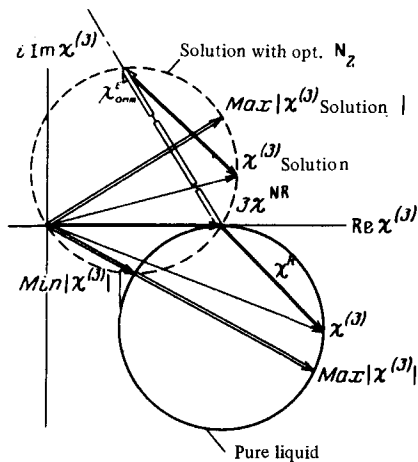


FIG. 3. Diagram showing, on the complex plane, the different contributions made to the total nonlinearity of $\chi_{1111}^{(3)}$ of the solution. When the dye is added, the circle representing the geometric locus of $\chi_{1111}^{(3)}$ of the solution is translated along the dash-dot line (χ_{1111}^E). The plot of $k(N_2)$ has only one maximum.

$$k = I_{\max}^{(a)} / I_{\min}^{(a)} = \max |\chi_{1111}^{(3)}(\omega_a')|^2 / \min |\chi_{1111}^{(3)}(\omega_q'')|^2.$$

The character of the deformation of the active RS spectrum of toluene when rhodamine-6G is dissolved in it is seen from Fig. 1. Figure 2 shows the experimental dependence of the contrast k on the density N_2 of the dye molecules. It is clearly seen that at $N_2 \approx 0.45 \times 10^{16} \text{ cm}^{-3}$ the contrast of the active spectrum increases by more than one order of magnitude. This increase can be interpreted as a coherent "subtraction" of the nondispersive component χ_{1111}^{NR} of the toluene on account of the nonlinear susceptibility of the dye χ_{1111}^E .

3. The foregoing can be illustrated with a simple model of a medium made up of non-interacting molecules of two sorts, one of which has only a resonance of the Raman type, $\omega_1 - \omega_2 \approx \Omega_R$, and the other only single-photon resonance, $\omega_1 = \Omega_E$. The cubic nonlinear susceptibility of such a medium is of the form^[2,3]

$$\chi_{1111}^{(3)}(\omega_a = 2\omega_1 - \omega_2) = 3\chi_{1111}^{NR} + \frac{\bar{\chi}_{1111}^R}{i - \Delta} + \chi_{1111}^{E'} - i\chi_{1111}^{E''}. \quad (1)$$

Here $\Delta = (\omega_1 - \omega_2 - \Omega_R) / \Gamma_R$ is the deviation from the center of the Raman resonance and its half width is

$$\Gamma_R, \bar{\chi}_{1111}^R = (N_1 c^4 / \hbar \omega_2^4 \Gamma_R) (d\sigma / d\omega),$$

where N_1 is the density of the RS-active molecules, $d\sigma / d\omega$ is the cross section of the spontaneous (Stokes) RS; $\chi_{1111}^{E'}$ and $\chi_{1111}^{E''}$ are proportional to N_2 and are the real and imaginary parts of the resonant contribution of the absorbing component to the total optical nonlinearity of the mixture, and are connected by a relation of the Kramers-Kronig type.^[8]

Figure 3 shows a plot of the nonlinearity $\chi_{1111}^{(3)}$ on the complex plane. When ω_2 is scanned, the end point of the complex vector $\chi_{1111}^{(3)}$ of the pure liquid

traces the solid circle. Addition of the dye translates the circle as a unit by an amount equal to the complex vector χ_{1111}^E . The length of the translated vector is proportional to the dye concentration N_2 . The dashed circle corresponds to the optimally chosen concentration, for in this case $k \rightarrow \infty$. In the general case the contrast of the "active" spectrum of the medium, which has a susceptibility of the form (1), is given by the expression

$$k = \max |\chi_{1111}^{(3)}(\omega_a')|^2 / \min |\chi_{1111}^{(3)}(\omega_a'')|^2 = \left(\frac{1 + \delta}{1 - \delta} \right)^2, \quad (2)$$

where

$$\delta = (\bar{\chi}_{1111}^R / 2) / \sqrt{(\chi_{1111}^{E''} + \bar{\chi}_{1111}^R / 2)^2 + (3\chi_{1111}^{NR} + \chi_{1111}^{E'})^2}. \quad (3)$$

It is clear that $k \rightarrow \infty$ at $\delta = 1$, or, equivalently, when

$$-\bar{\chi}_{1111}^R \chi_{1111}^{E''} = (\chi_{1111}^{E''})^2 + (\chi_{1111}^{E'} + 3\chi_{1111}^{NR})^2. \quad (4)$$

This condition can be satisfied by selecting the concentration N_2 of the molecules of the absorbing component of the mixture if $\bar{\chi}_{1111}^R \chi_{1111}^{E''} \leq 0$; in the opposite case k is maximal when δ is maximal, and the latter can again be accomplished by choosing N_2 .

From the results of our measurements we established with the aid of the diagram of Fig. 3 that at $N_2 = 0.45 \times 10^{16} \text{ cm}^{-3}$, we have $|\chi_{1111}^E| = 3\chi_{1111}^{NR} = 4.5 \times 10^{-14} \text{ cm}^3/\text{erg}$ (the value of χ_{1111}^{NR} was taken from [1] with allowance for the frequency degeneracy).

From this we can estimate the resonant hyperpolarizability of the rhodamine-6G molecule:

$$|\langle \gamma_{1111}^E \rangle| = \frac{|\chi_{1111}^E|}{L^4 \cdot N_2} = \frac{4.5 \cdot 10^{-14} \text{ cm}^6}{4 \cdot 0.45 \cdot 10^{16} \text{ erg}} \cdot 2.5 \cdot 10^{-30} \text{ cm}^6/\text{erg}.$$

Here $L = (n^2 + 2)/3$ is the Lorentz factor of the internal field. In this case $\langle \chi_{1111}^{E''} \rangle / \langle \chi_{1111}^{E'} \rangle = 2.2$ and $\langle \chi_{1111}^{E'} \rangle, \langle \chi_{1111}^{E''} \rangle < 0$.

4. In conclusion, we emphasize once more that in the contrast of the case of spontaneous RS, in ARSS, owing to the coherence of the scattering process, the contributions to the scattered signal from the various mixture components do not add up, but interfere. The cancellation of the nonresonant electronic susceptibility of an RS-active liquid or gas, χ^{NR} , can be attained either by adding to it a resonant absorber, or by mixing it with a substance that has a real component of $\chi^{E'}$ with $\chi^{E''} = 0$.

The latter can be cyanine dyes with an absorption band in the 1- μ region, in which the real electronic cubic susceptibility is negative. [9]

The authors thank S. A. Akhmanov for useful discussions and support.

¹S. A. Akhmanov and N. I. Koroteev, Zh. Eksp. Teor. Fiz. 67, 1306 (1974) [Sov. Phys. JETP 40, 650 (1975)].

²S. A. Akhmanov, Lecture at E. Fermi International School of Physics, Varenna, Italy, 1975.

- ³N. I. Koroteev, *Kvantovaya Elektron*, **3**, 755 (1976) [*Sov. J. Quant. Electron.* **6**, 411 (1976)].
- ⁴M. D. Levenson and N. Bloembergen, *Phys. Rev.* **B10**, 4447 (1974).
- ⁵R. T. Lynch, S. D. Kramer, H. Lotem, and N. Bloembergen, *Opt. Commun.* **16**, 372 (1976).
- ⁶F. Moya, S. A. J. Druet, and J.-P. E. Taran, *Opt. Commun.* **13**, 169 (1975).
- ⁷J. W. Nilber, J. R. McDonald, and A. B. Harvey, Report on Ninth Intern. Conf. on Quant. Electr., Amsterdam, 1976; *Opt. Commun.* **18**, 133 (1976).
- ⁸N. Bloembergen, *Nonlinear Optics*, Benjamin, 1965 [Russ. transl., Mir, 1966, p. 89].
- ⁹J. P. Herrmann, *Opt. Commun.* **12**, 102 (1974).