Coherent ellipsometry of Raman scattering of light

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(Submitted April 7, 1977)
Pis'ma Zh. Eksp. Teor. Fiz. **25**, No. 9, 444–449 (5 May 1977)

A new method of coherent four-photon spectroscopy is proposed and realized. It is based on registration of the dispersion of the parameters of the elliptic polarization of the anti-Stokes signal at the frequency $\omega_a = 2\omega_1 - \omega_2$ as $\omega_1 - \omega_2$ is scanned. The data obtained by this method on the dispersion $\chi^{(3)}(\omega_a;\omega_1,\omega_1-\omega_2)$ have exceedingly high accuracy, due to the fact that the fluctuations of the registered quantities are not connected with fluctuations of the intensities of the pump waves ω_1 and ω_2, but are determined only by the lattice-polarization fluctuations, which are quite small. The fine structure of the inhomogeneously broadened Raman scattering line of HNO_3 is registered; a noticeable dispersion of the nonresonant component of $\chi^{(3)}$ is observed in a number of liquids.

PACS numbers: 07.60.Fs, 78.30.Cp, 78.20.Dj, 42.65.Cq

1. The present article deals with a discussion of a new method of nonlinear polarization spectroscopy of Raman-active transitions in an isotropic medium. The method consists of measuring the dispersions of the parameters of the elliptic polarization of the anti-Stokes signal at a frequency $\omega_a = 2\omega_1 - \omega_2$ as the pump-frequency difference $\omega_1 - \omega_2$ is scanned near the frequency Ω of the chosen transition. The use of this method makes it possible to measure the dispersion of the cubic susceptibility of the medium $\chi^{(3)}_{ijkl}(\omega_a;\omega_1,\omega_1,-\omega_2)$ accurate to 10^{-3}—10^{-4} of the absolute value, something unattainable in other methods, as well as to resolve the inhomogeneous structure of the bands produced by lines of different symmetry, and to measure with high accuracy the degree of depolarization of the Raman-scattering (RS) lines. We present below the theory of the method and describe experiments that confirm its capabilities.

2. One of the most promising methods of nonlinear molecular spectroscopy is nonlinear four-photon spectroscopy, which has been named, applied to transitions that manifest themselves in RS, active RS spectroscopy[1] (the acronym CARS and the designations three- and four-wave displacement spectroscopy are also used[2–5]). However, in all the studies reported to date, the dispersion of the intensity of the anti-Stokes signal was registered. Notwithstanding the appreciable superiority in signal levels over spontaneous RS spectroscopy, the capabilities of such an "amplitude" spectroscopy are limited (strong fluctuations and the presence of a high nondispersive pedestal hinder the measurement of weak lines and of the fine structure[1,3,4,6]). The polarization method described below, called coherent RS ellipsometry, makes it possible to overcome completely the shortcomings of the "amplitude" variants of CARS, while maintaining a high level of the registered signal.

3. The proposed method is based on the fact that, owing to difference between the requirements imposed by molecular and macroscopic symmetry on the components of the tensors $\chi^{(3)R}_{ijkl}(\omega_a;\omega_1,\omega_1,-\omega_2)$ and $\chi^{(3)NR}_{ijkl}(\omega_a;\omega_1,\omega_1,-\omega_2)$

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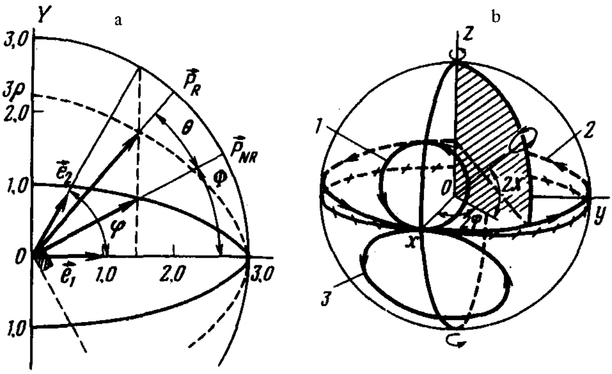

FIG. 1. a) Relative placement of the pump-wave polarization unit vectors $(\mathbf{e}_1, \mathbf{e}_2)$, and of the resonant Raman $(\mathbf{P}_R)$ and nonresonant $(\mathbf{P}_{NR})$ components of the linear source $P^{(3)}(\omega_a)$. All the vectors lie in a plane perpendicular to the direction of the collinear propagation of the pump waves. The resonant component $\mathbf{P}_R$ corresponds to a fully depolarized RS line ($\rho = 3/4$). b) Geometric representation, with the aid of a Poincare sphere, of the polarization state of the coherent anti-Stokes signal: 1—$\alpha \sin\theta = 0.3$; 2—$\alpha \sin\theta = 10$; 3—$\alpha \sin\theta = 0.6$. In the case when the Kleinman conditions are satisfied we have $\alpha \sin\theta = (3\chi_{1111}^{(3)R}/2\chi_{1111}^{(3)NR})[(3\rho - 1)\sin 2\phi/(8\cos^2\phi + 1)]$. The arrows show the direction of variation of the state of polarization when $\Delta = (\omega_1 - \omega_2 - \Omega)/\Gamma$ is increased from $-\infty$ to $+\infty$.

(they correspond to the resonant Raman and to the nonresonant electronic contributions to the total nonlinearity of the medium, respectively: $\chi_{ijkl}^{(3)} = \chi_{ijkl}^{(3)R} + \chi_{ijkl}^{(3)NR}$), the polarization states $\mathbf{P}_R$ and $\mathbf{P}_{NR}$ of the resonant and nonresonant components of the nonlinear source are generally speaking likewise different $P_i^{(3)}(\omega_a) = 3\chi_{ijkl}^{(3)}(\omega_a; \omega_1, \omega_1, -\omega_2) \times E_j^{(1)} E_k^{(1)} E_l^{(2)*}$. There is this, in particular, which explains the dispersion of the plane of polarizatization of the CARS signal.[2]

In the case of an isotropic medium we can write (see, e.g., [6]):

$$\mathbf{P}^{(3)}(\omega_a) = (\chi_{1111}^{(3)NR}\,\mathbf{P}_{NR} + \chi_{1111}^{(3)R}(\Delta)\mathbf{P}_R)(E^{(1)})^2 E^{(2)*}. \tag{1}$$

Here $\mathbf{E}^{(1,2)} = \mathbf{e}_{1,2} E^{(1,2)}$ are the amplitudes of the linearly polarized pump waves; $(\mathbf{e}_1, \mathbf{e}_1) = (\mathbf{e}_2, \mathbf{e}_2) = 1$,

$$\mathbf{P}_{NR} = 3[(2\chi_{1122}^{(3)NR}/\chi_{1111}^{(3)NR})\mathbf{e}_1(\mathbf{e}_1, \mathbf{e}_2) + (\chi_{1221}^{(3)NR}/\chi_{1111}^{(3)NR})\mathbf{e}_2], \tag{2}$$

$$\mathbf{P}_R = 3(1 - \rho)\mathbf{e}_1(\mathbf{e}_1, \mathbf{e}_2) + 3\rho\mathbf{e}_2 \tag{3}$$

$\rho = \overline{\chi}_{1221}^{(3)R}/\overline{\chi}_{1111}^{(3)R}$ is the degree of polarization of the investigated RS line;

$$\chi_{1111}^{(3)R}(\Delta) = \chi_{1111}^{(3)R}(\omega_a; \omega_1, \omega_1, -\omega_2) \approx \overline{\chi}_{1111}^{(3)R}/(-i - \Delta);$$

$$\Delta = (\omega_1 - \omega_2 - \Omega)/\Gamma;$$

Γ is the halfwidth of the RS line (see Fig. 1a).

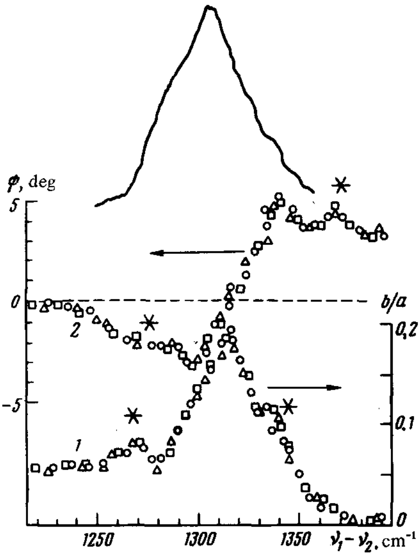

FIG. 2. Dispersion of the parameters of the elliptic polarization of the anti-Stokes signal from concentrated nitric acid. The symbols ○, △, □ make the experimental points obtained in different measurement runs. Upper curve—spectrum of spontaneous RS obtained with a DFS-24 spectrometer with excitation by the 5145 Å line of an argon laser; $\phi = 70°$.

We note immediately that Eqs. (1)—(3) imply independence of the polarization of the nonlinear source $P^{(3)}(\omega_a)$ of the pump-wave amplitude. At $\rho \neq \chi_{1221}^{(3)NR}/\chi_{1111}^{(3)NR}$, $\phi \neq 0, \pi/2$ the angle θ between $\mathbf{P}_R$ and $\mathbf{P}_{NR}$ (Fig. 1a) differs from zero, and the wave of the anti-Stokes signal is elliptically polarized. We introduce the following notation: b and a are respectively the minor and major semiaxes of the polarization ellipse, ψ is the angle of inclination of the major semiaxis of the ellipse, reckoned from a direction that makes an angle $\Phi = \tan^{-1}(\frac{1}{3}\tan\phi)$ with the direction of $\mathbf{e}_1$—this is precisely the angle between the vector $\mathbf{P}_{NR}$ and $\mathbf{e}_1$, if the Kleinman conditions[7] for the components $\chi_{ijkl}^{(3)NR}$ are exactly satisfied: $\chi_{1221}^{(3)NR} = \chi_{1122}^{(3)NR} = \frac{1}{3}\chi_{1111}^{(3)NR}$ [otherwise the angle Φ' between $\mathbf{P}_{NR}$ and $\mathbf{e}_1$ can be calculated from the formula $\Phi' = \arctan[(\chi_{1221}^{(3)NR}/\chi_{1111}^{(3)NR})\tan\phi]$ (cf. also[2])], and $\chi = \tan^{-1}(b/a)$. In the case of a solitary RS line the following relations can be obtained with the aid of (1)—(3):

$$\mathrm{tg}\,2\psi = -2a\sin\theta\,(\Delta - a\cos\theta)/[(\Delta - a\cos\theta)^2 + 1 - a^2\sin^2\theta], \tag{4}$$

$$\sin 2\chi = 2a\sin\theta/[(\Delta - a\cos\theta)^2 + 1 + a^2\sin^2\theta]. \tag{5}$$

Here

$$a = (\bar{\chi}_{1111}^{(3)R}/\chi_{1111}^{(3)NR})|\mathbf{P}_R|/|\mathbf{P}_{NR}|.$$

It is convenient to represent the elliptically-polarized waves by using a Poincare sphere[8] (see Fig. 1b). Equations (4) and (5) define on this sphere a circle with a center at a point have a "latitude" $2\chi_0 = \arcsin[\alpha\sin\theta/\sqrt{1+\alpha^2\sin^2\theta}]$ and a "longitude" $2\psi_0 = 0$. Values $\chi < 0$ are ascribed to an ellipse with left-hand rotation. It is seen from (4) and (5), in particular, that at $\mathrm{Max}[\chi_{1111}^{(3)}(\Delta)| \ll |\chi_{1111}^{(3)NR}|$, the values of ψ and χ are small, with $\psi \sim \mathrm{Re}\chi_{1111}^{(3)R}(\Delta)$; and $\chi \sim \mathrm{Im}\chi_{1111}^{(3)R}(\Delta)$.

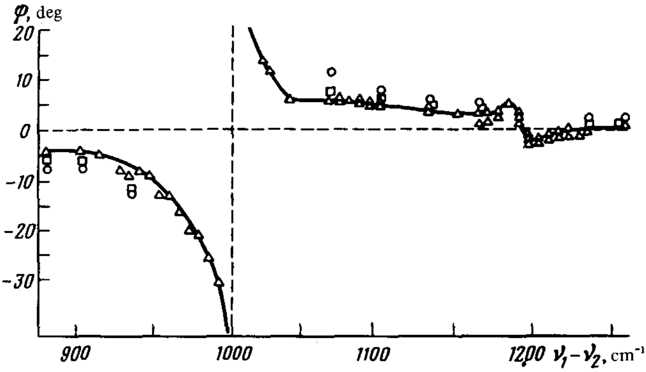

FIG. 3. Dispersion of the inclination angle ψ of the major axis of the polarization ellipse of an anti-Stokes signal from benzene: △—experimental points obtained at $\phi = 45°$ (see Fig. 1a); □—the same at $\phi = 60°$, ○—at $\phi = 70°$. At $(\omega_1 - \omega_2)/2\pi c > 1000\ \mathrm{cm}^{-1}$ the angles marked are $\psi + 180°$.

4. The results of experiments performed by the method of coherent RS ellipsometry are shown in Figs. 2 and 3. As the pair of pump waves we used the second harmonics of an Nd:YAG laser and of a tunable laser based on a solution of rhodamine-6G in ethanol; the powers of both lines were 30—50 kW, and the line widths were less than 0.5 cm^{-1}. The elliptically polarized light was analyzed with the aid of a rotary calcite compensator.

The capabilities of the method are particularly clearly illustrated by the results of an experiment on the resolution of the RS line in concentrated nitric acid (HNO_3) with a central frequency $\Omega/2\pi c = 1304\ \mathrm{cm}^{-1}$ (Fig. 2). We recall that we are dealing here with a very broad line ($2\Gamma/2\pi c \approx 57\ \mathrm{cm}^{-1}$), which makes a small contribution to $\chi^{(3)}$.

This circumstance notwithstanding, it is possible to measure the contours of $\psi(\omega_1 - \omega_2)$ and $(b/a)(\omega_1 - \omega_2)$ with a large degree or reproducibility. The results have made it possible to determine the integral parameters of these lines: $\rho = 0.08$ (this quantity, to our knowledge, was not determined in spontaneous RS) and $\chi_{1111}^{(3)R}/\chi_{1111}^{(3)NR} = 0.32$ (a parameter that cannot be determined with the aid of spontaneous RS). The fine structure of the polarization spectra is clearly observed (and marked by asterisks). Since this structure is not present in the spontaneous spectrum, one can speak of resolution of superimposed lines of different symmetry. (The results here correspond qualitatively to the experimental data on SRS[9]).

Measurements performed in benzene by this procedure (Fig. 3) have revealed new singularities of the dispersion of $\chi^{(3)}$, not heretofore noted. From the position of the wing of the dispersion curve $\psi(\omega_1 - \omega_2)$ on the left of the 992 cm^{-1} line we have obtained $\chi_{1111}^{(3)NR}/\chi_{1221}^{(3)NR} = 2.7 \pm 0.1$ (this practically coincides with the data of[2]). However, from the position of the high-frequency wing of the same curve $[(\omega_1 - \omega_2)/2\pi c \gtrsim 1250\ \mathrm{cm}^{-1}]$ it is seen that the ratio of the components is altered: $\chi_{1111}^{(3)NR}/\chi_{1221}^{(3)NR} = 3.3 \pm 0.1$. The "step" between the wings has a maximum value $\sim 8.5°$ at $\phi = 70°$.

5. Measurements performed by the same procedure in mesitylene have revealed the presence of a similar "step" between the wings $\psi(\omega_1-\omega_2)$ on opposite sides of the fully-symmetrical line with frequency $\Omega/2\pi c=999$ cm^{-1}. Its maximum value, however, was less than $\sim 3°$. It cannot be ascertained at present whether this effect is due only to the nonresonant ionic contribution to $\chi_{ijkl}^{(3)NR}$, or whether resonant two-quantum electronic transitions are important here.

We note that within the framework of coherent RS ellipsometry it becomes possible to control the value of the contribution of one RS line or another to the course of the dispersion of the ellipticity parameters of the signal by varying the angle ϕ.

6. Particularly promising is the use of coherent ellipsometry in the case of CARS in the field of a cw laser,[10] where one can make full use of the well developed methods of traditional ellipsometry, with its outstandingly high accuracy (see[11]). Great interest attaches to the possibility, uncovered by coherence ellipsometry, of developing a new approach to the measurement of the relaxation time of RS-active oscillations on the basis of registration of the change of the polarization state of a coherently-scattered signal as the durations of the pulses at frequencies ω_1 and ω_2 are varied.

The authors thank I. A. Yakovlev for supplying the compensator and for a discussion of the ellipsometry methods.

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