COHERENT POLARIZATION SPECTROSCOPY OF TWO-PHOTON ABSORPTION

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Vol. 35, No. 1, pp. 42-51, 1980.

UDC 537.874; 535.36

A polarization scheme for four-photon spectrscopy of two-quantum transitions in isotropic media and cubic crystals is presented; a new way of measuring the scattering cross section in two-photon absorption is demonstrated. Irreducible tensor groups are used in averaging the components of the tensor for the molecular resonant hyperpolarizability, and a relationship is established for the invariants of the molecular tensor for two-photon polarizability and the nonzero components of the tensor for the third-order macroscopic susceptibility. Theoretical estimates and experimental results are presented for the polarization dispersion of the signal in various organic liquids. Similar estimates have been made for GaP and ZnSe crystals.

INTRODUCTION

Nonlinear four-photon spectroscopy arose comparatively recently, but the abundance and variety of information it provides has caused rapid development. The most promising and thoroughly examined form of four-photon spectroscopy involves induced Raman scattering IRS [1, 2]. In IRS one examines the dispersion of the nonlinear cubic susceptibility $\chi^{(3)}_{ijkl}$, which describes the generation of radiation of frequency $\omega_a=\omega\pm(\omega_1-\omega_2)$ (here ω_1 and ω_2 are the frequencies of the biharmonic pumping, while ω is the test-wave frequency) in the case where $\omega_1-\omega_2$ is close to a molecular vibration frequency. One can logically consider the same process for the mixing of three waves when $\omega_1+\omega_2$ is in resonance with an electronic transition in the medium, which is a case of resonance involving two-photon absorption TPA. The four-photon scheme proposed first in [3] can be used to determine the TPA parameters [4, 5]. Coherent four-photon processes may be used instead of ordinary methods involving recording the actual absorption [6] to overcome various difficulties that arise in the latter case on account of the spatial and time inhomogeneities of the radiation, the presence of competing first-order cascade processes, etc. [1]. In four-photon spectroscopy it has recently been shown for IRS [7-9] that the most convenient method which is also of elevated accuracy, is polarization four-photon spectroscopy, which deals with the polarization dispersion for the signal at frequency $\omega_a=\omega+(\omega_1-\omega_2)$ when one or both of the pumping frequencies is swept.

Here we consider a scheme for such spectroscopy for two-photon absorption resonances. It is shown that a wave of frequency ω_a linearly polarized far from TPA resonance (the radiations at ω_1, ω_2, and ω are linearly polarized) becomes elliptically polarized near the TPA resonance. The polarization parameters show

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that the dispersion in the ellipticity (the frequency dependence of the ratio of the semiaxes of the ellipse) is uniquely determined by the dispersion of the imaginary part of the cubic susceptibility, and therefore it is directly related to the TPA cross-section. The dispersion in the orientation of the major axis of the ellipse is governed by the dispersion of the real component of the cubic susceptibility.

1. NONLINEAR MEDIUM POLARIZATION

1. Cubic Susceptibility Tensor in TPA. The induced nonlinear polarization in the medium can be put as

$$P_i^{(3)}(\omega_a) = \mathscr{D}\chi_{ijkl}^{(3)}(\omega_a;\ \omega,\ \omega_1,\ -\omega_2)\, E_j E_k^{(1)} E_l^{(2)*}, \tag{1}$$

where $\mathbf{E}$, $\mathbf{E}^{(1)}$, $\mathbf{E}^{(2)}$ are the interacting waves, $\mathscr{D}=6$ if there is no frequency degeneracy, and $\mathscr{D}=3$ if $\omega = \omega_1$. We determine the coefficient for nonlinear coupling in the four-wave interaction λ by means of

$$\lambda(\omega_a;\ \omega,\ \omega_1,\ -\omega_2) = \\ = \chi_{ijkl}^{(3)}(\omega_a;\ \omega,\ \omega_1,\ -\omega_2)\, e_{ai}^* e_j e_{1k} e_{2l}^* = \frac{\mathbf{P}^{(3)}(\omega_a)\,\mathbf{e}_a^*}{\mathscr{D}\, E E^{(1)} E^{(2)*}}. \tag{2}$$

We consider the resonance in two-photon absorption ($\omega+\omega_1 \simeq \Omega_E^*$, where Ω_E is the frequency of the electronic transition in the medium) and represent λ as the sum of resonant and nonresonant parts:

$$\lambda = \lambda_R + \lambda_{NR}. \tag{3}$$

(If at the same time $\omega_1 - \omega_2$ is close to a molecular vibration frequency, then there may be a contribution to the nonlinear polarization at frequency $\omega_a = \omega+\omega_1-\omega_2$ from the analogous process of coherent anti-Stokes scattering. Also, there may be interference from the two processes [10]. Here however we are interested only in the resonances in two-photon absorption; the polarization characteristics of coherent anti-Stokes scattering have been studied in [7-9].)

We represent the cubic-susceptibility tensor in analogous form:

$$\chi_{ijkl}^{(3)} = \chi_{ijkl}^{(3)R} + \chi_{ijkl}^{(3)NR}. \tag{4}$$

We use the result of [11] to find λ_R, which was derived from perturbation theory in the dipole approximation:

$$\lambda_R = \frac{NL^4}{24\hbar^3}\,\frac{1}{\Omega_{ln}-\omega-\omega_1+i\Gamma_E}\times \\ \times \sum_{\text{выр.}n,l} \rho_{nn}^{(0)} \sum_{m,k} \left\{ \frac{(\mathbf{p}_{nm}\mathbf{e}_a^*)(\mathbf{p}_{ml}\mathbf{e}_2^*)(\mathbf{p}_{lk}\mathbf{e})(\mathbf{p}_{kn}\mathbf{e}_1)}{(\Omega_{mn}-\omega_a)(\Omega_{kn}-\omega_2)} + \right. \\ + \frac{(\mathbf{p}_{mn}\mathbf{e}_a^*)(\mathbf{p}_{ml}\mathbf{e}_2^*)(\mathbf{p}_{lk}\mathbf{e})(\mathbf{p}_{kn}\mathbf{e}_1)}{(\Omega_{mn}-\omega_2)(\Omega_{kn}-\omega_1)} + \frac{(\mathbf{p}_{ml}\mathbf{e}_a^*)(\mathbf{p}_{mn}\mathbf{e}_2^*)(\mathbf{p}_{lk}\mathbf{e})(\mathbf{p}_{kn}\mathbf{e}_1)}{(\Omega_{mn}-\omega_2)(\Omega_{kn}-\omega_1)} + \\ \left. + \frac{(\mathbf{p}_{ml}\mathbf{e}_a^*)(\mathbf{p}_{mn}\mathbf{e}_2^*)(\mathbf{p}_{lk}\mathbf{e}_1)(\mathbf{p}_{nn}\mathbf{e})}{(\Omega_{mn}-\omega_2)(\Omega_{kn}-\omega_1)} \right\}. \tag{5}$$

Here $p_{mn}=\langle m|\mathbf{p}|n\rangle$ is the matrix element for the dipole moment, Ω_{mn} is the frequency of the transition between states m and n, $\Omega_{ln}=\Omega_E$, the summation is carried over the intermediate virtual states, Γ_E is the half-width of the absorption line, and L is the Lorentz factor. It is convenient to introduce the TPA tensor α in accordance with the formula

$$\alpha_{ij}(\omega, \omega_1) = \frac{1}{\hbar}\sum_b \left[\frac{(p_i)_{nb}(p_j)_{bl}}{\Omega_{mn}-\omega} + \frac{(p_j)_{nb}(p_i)_{bl}}{\Omega_{mn}-\omega_1}\right]. \tag{6}$$

This enables us to put λ_R as

$$\lambda_R = \frac{N_n L^4}{24\hbar}\sum_{\text{de}\ .n,l} \frac{\alpha_{ij}(\omega, \omega_1)\,\alpha_{jk}(\omega_2, \omega_a)}{\Omega_{nl}-\omega-\omega_1+i\Gamma_E}\, e^*_{ai}\, e^*_{2l}\, e_j e_{1k}. \tag{7}$$

Here $N_n = N\rho^{(0)}_{nn}$.

2. **Isotropic Media: Averaging Over Molecular Orientations.** We perform the summation in (7) for an isotropic medium by means of Rak algebra [12, 13]. For this purpose we need to write the tensor α_{ij} in the irreducible representation. By analogy with IRS [14, 15] we get as a result of averaging that

$$\begin{gathered}\lambda_R = \frac{N_n L^{4\prime}}{24\hbar}\,\frac{1}{\Omega_{\bar{l}n}-\omega-\omega_1+i\Gamma_E}\sum_{M_l M_n}\sum_{\substack{KQ\\ K'Q'}}[(-1)^{Q+Q'}\begin{pmatrix}M_n & K & J_l\\ J_n & Q & M_l\end{pmatrix}\times \\ \times\,\tilde{\alpha}^{(K')*}(\mathbf{e}^*_a\times\mathbf{e}^*_2)^{(K)}_{-Q}\begin{pmatrix}M^l & K' & J_n\\ J_l & Q' & M_n\end{pmatrix}\alpha^{(K')}(\mathbf{e}\times\mathbf{e}_1)^{(K')}_{-Q'}, \\ \bar{n} = (nv_n\, J_n),\end{gathered} \tag{8}$$

where n is the quantum number that enumerates the electronic states and v_n and J_n are the vibrational and rotational quantum numbers.

The following expression is readily seen to be correct:

$$\sum_{M_l M_n}\begin{pmatrix}M_n & K & J_l\\ J_n & Q & M_l\end{pmatrix}\begin{pmatrix}M_l & K' & J_n\\ J_l & Q' & M_n\end{pmatrix} = \frac{1}{[K^2]}\,\delta_{QQ'}\,\delta_{KK'}\,(-1)^{K-Q};\ [K^2]=2K+1. \tag{9}$$

This gives us that

$$\lambda_R = \frac{N_n L^4}{24\hbar}\,\frac{1}{\Omega_{\bar{l}n}-\omega-\omega_1+i\Gamma_E}\sum_K \frac{\tilde{\alpha}^{(K)*}\alpha^{(K)}}{[K^2]}\,\theta^{(K)}, \tag{10}$$

where

$$\theta^{(K)} = (-1)^K(\mathbf{e}^*_a\times\mathbf{e}^*_2)^{(K)}(\mathbf{e}\times\mathbf{e}_1)^{(K)}. \tag{11}$$

We expand the tensor factors in (11) and transfer from the circular components e_q $(q=0, \pm1)$ of the polarization vectors to the cartesian ones e_k $(k=x, y, z)$ to get the polarization dependence of the nonlinear coupling coefficients in

explicit form:

$$\theta^{(0)} = \frac{1}{3}\,(\mathbf{e}_a^* \mathbf{e}_2^*)\,(\mathbf{e}\,\mathbf{e}_1); \tag{12}$$

$$\theta^{(1)} = \frac{1}{2}\,[(\mathbf{e}_a^* \mathbf{e}_1)\,(\mathbf{e}_2\mathbf{e}) - (\mathbf{e}_a^*\mathbf{e})\,(\mathbf{e}_2^*\mathbf{e}_1)]; \tag{13}$$

$$\theta^{(2)} = -\frac{1}{3}\,(\mathbf{e}_a^* \mathbf{e}_2^*)\,(\mathbf{e}\,\mathbf{e}_2) + \frac{1}{2}\,(\mathbf{e}_a^* \mathbf{e})\,(\mathbf{e}_2^* \mathbf{e}_1) + \frac{1}{2}\,(\mathbf{e}_a^* \mathbf{e}_1)\,(\mathbf{e}_2^* \mathbf{e}). \tag{14}$$

Here $(\mathbf{e}_i\mathbf{e}_k) = (\mathbf{e}_i)_x(\mathbf{e}_k)_x + (\mathbf{e}_i)_y(\mathbf{e}_k)_y + (\mathbf{e}_i)_z(\mathbf{e}_k)_z$ is the ordinary scalar product of the vectors $\mathbf{e}_i$ and $\mathbf{e}_k$.

From (12)-(14) we can represent (2) as

$$\frac{\mathbf{P}_R^{(3)}(\omega_a)}{EE^{(1)}\,E^{(2)*}} = \gamma_0\,\mathbf{P}_{\text{is}} + \gamma_1\,\mathbf{P}_{\text{ant}} + \gamma_2\,\mathbf{P}_{\text{anis}}, \tag{15}$$

where

$$\gamma_k = \tilde{\alpha}^{(K)*}\,\alpha^{(K)};$$

$$\mathbf{P}_{\text{is}} = \frac{\mathscr{D}}{3}\,\mathbf{e}_2^*\,(\mathbf{e}\mathbf{e}_1); \tag{16}$$

$$\mathbf{P}_{\text{ant}} = \frac{\mathscr{D}}{2}\,[\mathbf{e}_1\,(\mathbf{e}_2^*\mathbf{e}) - \mathbf{e}\,(\mathbf{e}_2^*\,\mathbf{e}_1)]; \tag{17}$$

$$\mathbf{P}_{\text{anis}} = -\frac{\mathscr{D}}{3}\,\mathbf{e}_2^*(\mathbf{e}\,\mathbf{e}_1) + \frac{\mathscr{D}}{2}\,\mathbf{e}\,(\mathbf{e}_2^*\mathbf{e}_1) + \frac{\mathscr{D}}{2}\,\mathbf{e}_1\,(\mathbf{e}_2^*\mathbf{e}). \tag{18}$$

In an isotropic medium, only 21 out of the 81 components of the nonlinear-susceptibility tensor $\chi^{(3)}_{ijkl}$ are nonzero on account of symmetry requirements, and only the components $\chi^{(3)}_{1212}$, $\chi^{(3)}_{1221}$, $\chi^{(3)}_{1122}$ are independent. Now for these we find from (10)-(15) that

$$\chi^{(3)R}_{1221}(\omega_a;\ \omega,\ \omega_1,\ -\omega_2) = \frac{N_n^- L^4}{24\hbar}\,\frac{1}{\Omega - \omega - \omega_1 + i\Gamma_E}\left(\frac{1}{3}\,\gamma_0 - \frac{1}{3}\,\gamma_2\right); \tag{19}$$

$$\chi^{(3)R}_{1212}(\omega_a;\ \omega,\ \omega_1,\ -\omega_2) = \frac{N_n^- L^4}{24\hbar}\,\frac{1}{\Omega - \omega - \omega_1 + i\Gamma_E}\left(\frac{1}{2}\,\gamma_1 + \frac{1}{2}\,\gamma_2\right); \tag{20}$$

$$\chi^{(3)R}_{1122}(\omega_a;\ \omega,\ \omega_1,\ -\omega_2) = \frac{N_n^- L^4}{24\hbar}\,\frac{1}{\Omega - \omega - \omega_1 + i\Gamma_E}\left(-\frac{1}{2}\,\gamma_1 + \frac{1}{2}\,\gamma_2\right). \tag{21}$$

Here

$$\chi^{(3)}_{1221} + \chi^{(3)}_{1212} + \chi^{(3)}_{1122} = \chi^{(3)}_{1111}. \tag{22}$$

Note that $\gamma_1 = 0$ in the case of frequency degeneracy ($\omega = \omega_1$) and the resonant processes are characterized by only two invariants: γ_0 and γ_2.

We determine the parameters ρ_1 and ρ_2:

$$\rho_1 = \frac{\chi^{(3)R}_{1122}}{\chi^{(3)R}_{1111}}, \quad \rho_2 = \frac{\chi^{(3)R}_{1212}}{\chi^{(3)R}_{1111}}. \tag{23}$$

These are used to put the nonlinear-polarization vector as

$$\frac{\mathbf{P}^{(3)}(\omega_a)}{EE^{(1)}E^{(2)*}} = \chi^{(3)NR}_{1111}\mathbf{p}_{NR} + \chi^{(3)R}_{1111}\mathbf{p}_R, \tag{24}$$

where

$$\mathbf{p}_{NR} = \frac{\mathscr{D}}{3}[\mathbf{e}(\mathbf{e}_1\mathbf{e}_2^*) + \mathbf{e}_1(\mathbf{e}\mathbf{e}_2^*) + \mathbf{e}_2^*(\mathbf{e}\mathbf{e}_1)], \tag{25}$$

$$\mathbf{p}_R = \mathscr{D}(1-\rho_1-\rho_2)\mathbf{e}_2^*(\mathbf{e}\mathbf{e}_1) + \mathscr{D}\rho_1\mathbf{e}(\mathbf{e}_1\mathbf{e}_2^*) + \mathscr{D}\rho_2\mathbf{e}_1(\mathbf{e}\mathbf{e}_2^*). \tag{26}$$

Expressions (19)-(21) provide a relation between the polarization parameter ρ_1 and the molecular invariants γ_0 and γ_2 for an isotropic medium:

$$\rho_1 = \frac{\chi^{(3)R}_{1122}}{\chi^{(3)R}_{1111}} = \frac{3\gamma_2}{2\gamma_0 + 4\gamma_2}.$$

The maximum value $\rho_1 = 3/4$ is attained for $\gamma_0 = 0$, while the minimal value $\rho_1 = 0$ is attained for $\gamma_2 = 0$. Therefore, the parameter ρ_1 introduced in (23) plays a part in describing the coherent four-photon process $\omega_a = \omega + \omega_1 - \omega_2$ near the TPA resonance the same as the degree of depolarization $\bar{\rho}$ for the Raman line in describing the analogous four-photon process near a Raman resonance [1].

Formulas (10), (12)-(14), (19)-(21), and (24) describe completely the state of polarization and frequency dependence of the nonlinear source $\mathbf{p}^{(3)}(\omega_a)$ near a single resonance in two-photon absorption in an isotropic medium.

3. **Cubic Crystals: Polarization Dispersion.** A cubic crystal having a fourth-order axis (classes 43m, 432, m3m) differs from an isotropic medium only in that the isotropic condition (22) is not met. We introduce the additional parameter

$$\rho_3 = \frac{\chi^{(3)R}_{1221}}{\chi^{(3)R}_{1111}}. \tag{27}$$

Then (25) and (26) may be modified in application to a crystal of cubic symmetry:

$$\mathbf{p}_{NR} = \mathscr{D}[(1-3\tau)(\mathbf{e}\times\mathbf{e}_1\times\mathbf{e}_2^*) + \tau(\mathbf{e}(\mathbf{e}_1\mathbf{e}_2^*) + \mathbf{e}_1(\mathbf{e}\mathbf{e}_2^*) + \mathbf{e}_2^*(\mathbf{e}\mathbf{e}_1))]^*; \tag{28}$$

$$\mathbf{p}_R = \mathscr{D}[(1-\rho_1-\rho_2-\rho_3)(\mathbf{e}\times\mathbf{e}_1\times\mathbf{e}_2^*) + \rho_1\mathbf{e}(\mathbf{e}_1\mathbf{e}_2^*) + \rho_2\mathbf{e}_1(\mathbf{e}\mathbf{e}_2^*) + \rho_3\mathbf{e}_2^*(\mathbf{e}\mathbf{e}_1)], \tag{29}$$

where

* $(\mathbf{e}\times\mathbf{e}_1\times\mathbf{e}_2^*) = (e_x e_{1x} e_{2x}^* e_y e_{1y} e_{2y}^*, \; e_z e_{1z} e_{2z}^*)$.

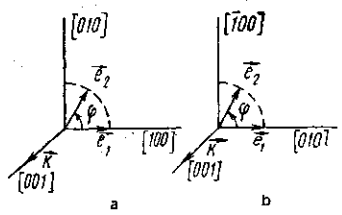

Fig. 1

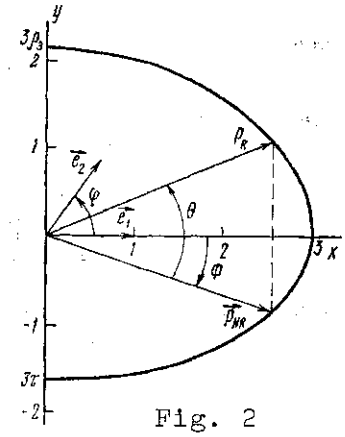

Fig. 2

Fig. 1. Mutual disposition of the polarization vectors for the interacting waves for collinear propagation in a crystal along the [001] axis: a) vector e_1 oriented along the [100] axis; b) vector e_1 oriented along the [010] axis.

Fig. 2. Orientations of p_R and p_{NR}, components of the polarization vector for the nonlinear source $P^{(3)}(\omega_R)$

$$\tau = \frac{\chi_{1122}^{(3)NR}}{\chi_{1111}^{(3)NR}}. \tag{30}$$

It is readily seen that the contributions from the various components of the nonlinear-susceptibility tensor to the nonlinear source of (2) are substantially dependent on the wave propagation directions and on the orientations of the polarization vectors. This can be used to determine the signs and magnitudes of the individual components of the $\chi_{ijkl}^{(3)}$ tensor. As an example we consider two cases shown in Fig. 1 for collinear propagation of all waves with frequency degeneracy ($\omega = \omega_1$) for $\varphi = (\widehat{e_1, e_2})$.

1. Propagation along the [001] axis, vector e_1 along the [100] axis. Contributions to the signal come from $\chi_{1111}^{(3)NR}$, $\chi_{1122}^{(3)NR}$, $\chi_{1111}^{(3)R}$, $\chi_{1221}^{(3)R}$.

From (28) and (29) we readily get the dependence of the angles $\Phi = (\widehat{e_1, p_{NR}})$ and $\theta = (\widehat{p_{NR}, p_R})$ on the depolarization parameters, τ, and the angle between the polarization vectors of the pumping waves:

$$\operatorname{tg}\Phi = \tau \operatorname{tg}\varphi; \tag{31}$$

$$\operatorname{tg}\theta = \frac{(\rho_3 - \tau)\operatorname{tg}\varphi}{1 + \rho_3\tau \operatorname{tg}^2\varphi}. \tag{32}$$

The mutual disposition of the vectors p_{NR} and p_R for this case is shown graphically in Fig. 2 for $\varphi = 45°$, $\tau = -1/2$, $\rho_3 = 3/4$; it is clear that θ differs from zero for $\rho_3 \neq \tau$ and the signal becomes elliptically polarized. Here there is a new feature relative to the situation in [7]. If $\tau < 0$, p_{NR} goes over to the

fourth quadrant. A similar possibility exists for $\mathbf{p}_R$ when there is an appropriate relation between ρ_3, τ, and φ. Figure 2 and (32) show that the angle θ between $\mathbf{p}_{NR}$ and $\mathbf{p}_R$ is $\pi/2$ for $\rho_3\tau\,\mathrm{tg}^2\varphi=-1$ and the ellipticity of the signal is maximal at ω_a. As was mentioned in the introduction, the polarization parameters of the signal show dispersion on sweeping $2\omega_1$ over the two-photon absorption region, namely the inclination ψ of the major semiaxis of the ellipse and the ellipticity χ($\mathrm{tg}\,\chi=b/a$, where b is the minor semiaxis and a is the major one). By analogy with [8, 9] we get expressions for ψ and χ for the case of precise two-photon resonance

$$\mathrm{tg}\,2\psi=\frac{\sigma^2[1+(\rho_3\,\mathrm{tg}\,\varphi)^2]\sin 2\theta}{[1+(\tau\,\mathrm{tg}\,\varphi)^2]+\sigma^2[1+(\rho_3\,\mathrm{tg}\,\varphi^2)]\cos 2\theta}, \tag{33}$$

$$\sin 2\chi=\frac{2\sigma\sqrt{[1+(\tau\,\mathrm{tg}\,\varphi)^2][1+(\rho_3\,\mathrm{tg}\,\varphi)^2]}\,\sin\theta}{[1+(\tau\,\mathrm{tg}\,\varphi)^2]+\sigma^2[1+(\rho_3\,\mathrm{tg}\,\varphi)^2]}, \tag{34}$$

where

$$\sigma=\frac{\bar{\chi}^{(3)R}_{1111}}{\chi^{(3)NR}_{1111}}.$$

Measurement of ψ and χ for a given φ enables one to determine two of the three parameters ρ_3, σ, and τ.

2. Propagation along the [001] axis, vector $\mathbf{e}_1$ along the [010] axis. Contributions to the nonlinear source come only from the components

$$\chi^{(3)NR}_{1122},\ \chi^{(3)R}_{1122},\ \chi^{(3)R}_{1221}.$$

For Φ and θ we have

$$\mathrm{tg}\,\Phi=\frac{1}{3}\,\mathrm{tg}\,\varphi; \tag{35}$$

$$\mathrm{tg}\,\theta=\frac{2(\rho_3-\rho_1)\,\mathrm{tg}\,\varphi}{3(2\rho_1+\rho_3)+\rho_3\,\mathrm{tg}^2\varphi}. \tag{36}$$

The inclination of the major semiaxis and the ellipticity for exact resonance are given by

$$\mathrm{tg}\,2\psi=\frac{\alpha^2\sin 2\theta}{1+\alpha^2\cos 2\theta}; \tag{37}$$

$$\sin 2\chi=\frac{2\alpha\sin\theta}{1+\alpha^2}, \tag{38}$$

where

$$\alpha=\frac{\sigma}{\tau}\sqrt{\frac{(\rho_3\,\mathrm{tg}\,\varphi)^2+(2\rho_1+\rho_3)^2}{\mathrm{tg}^2\varphi+9}}. \tag{39}$$

If φ, ψ, and χ are known from experiment, one can obtain the values of $\rho_1\sigma/\tau$

$\rho_3\sigma/\tau$, i.e.,

$$\chi^{(3)R}_{1122}/\chi^{(3)NR}_{1122} \text{ и } \chi^{(3)R}_{1221}/\chi^{(3)NR}_{1122}.$$

Naturally, everything said here for cubic crystals can be applied directly to an isotropic medium if (22) is written for the components of the $\chi^{(3)}_{ijkl}$ tensor and we put correspondingly

$$\rho_3 = 1 - (\rho_1 + \rho_2), \ \tau = 1/3.$$

2. TWO-PHOTON ABSORPTION CROSS SECTION IN TERMS OF THE CUBIC-SUSCEPTIBILITY TENSOR

The two-photon absorption cross section δ is proportional to the imaginary part of the cubic susceptibility [1]; the polarization dependence of ordinary TPA for complete frequency degeneracy ($\omega = \omega_1 = \omega_2$) gives us the relationship for this case as

$$\delta(\mathbf{e}_1, \mathbf{e}_1) = \frac{2\hbar\omega_1^2}{Nc^2n^2} \operatorname{Im} \lambda_R(\omega_1; \omega_1, \omega_1, -\omega_1). \tag{40}$$

The imaginary part of the nonlinear-coupling coefficient in the nondegenerate case is determined by the two TPA cross sections:

$$\delta(\mathbf{e}, \mathbf{e}_1)\,\delta(\mathbf{e}_2^*, \mathbf{e}_a^*) = \frac{16\hbar^2\omega\omega_1\omega_2\omega_a}{N^2c^4nn_1n_2n_a} (\operatorname{Im} \lambda_R(\omega_a; \omega, \omega_1, -\omega_2))^2. \tag{41}$$

It follows from (40) and (41) that measurements on the components of the $\chi^{(3)}_{ijkl}$ tensor give exhaustive information on TPA; in particular, the components of this tensor can be used for an isotropic medium to express the commonly used polarization parameter Ω. The expression [6] is $\Omega = \delta(1)/\delta(0)$, where $\delta(1)$ is the cross section of TPA for circularly polarized pumping waves and $\delta(0)$ is the cross section for linear polarization (we envisage the case of freqeuncy degeneracy). Then (40) gives $\Omega = \operatorname{Im}\lambda_R(1)/\operatorname{Im}\lambda_R(0)$ when the arguments 1 and 0 have the meaning as for δ. We use (24) and (26) the nonlinear-coupling coefficient for the imaginary:

$$\begin{aligned} \operatorname{Im} \lambda_R(\omega_1; \omega_1, \omega_1, -\omega_1) &= \operatorname{Im}(\chi^{(3)R}_{1111}(\omega_1; \omega_1, \omega_1 - \omega_1)) \times \\ &\times [2\rho_1(\mathbf{e}_1\mathbf{e}_1^*)(\mathbf{e}_1\mathbf{e}_1^*) + (1 - 2\rho_1)(\mathbf{e}_1^*\mathbf{e}_1^*)(\mathbf{e}_1\mathbf{e}_1)]. \end{aligned} \tag{42}$$

We have $(\mathbf{e}_1\mathbf{e}_1) = 1$, for type 0 polarization, while $(\mathbf{e}_1\mathbf{e}_1) = 0$, $(\mathbf{e}_1\mathbf{e}_1^*) = 1$ for type 1 polarization; finally, from (42) we have

$$\Omega = 2\rho_1. \tag{43}$$

3. NUMERICAL ESTIMATES AND EXPERIMENTS

The applicability of the above procedure for recording TPA spectra is dependent primarily on the error in measuring the parameters of the elliptical polarization; in particular, the scheme is inapplicable when the limit of detection

for the ellipsometer system exceeds the maximum ellipticity in the signal. The latter in turn is shown by (36)-(39) to be determined by the product $(\chi^{(3)R}_{1111}/\chi^{(3)NR}_{1111})$ $(1-3\rho_3)$ for an isotropic medium, so a situation unfavorable to measurement may occur for $\chi^{(3)R}_{1111}/\chi^{(3)NR}_{1111} \ll 1$, and $3\rho_3 \simeq 1$.

1. **Isotropic Media.** We have estimated the ellipticity at ω_a for solutions of rhodamine 6G and rhodamine B in ethanol (concentration 2×10^{-3} M) for $2\omega_1 \simeq$ $\simeq 18{,}800$ cm^{-1} (transition between the A_1 and B_2 states, $\rho_3 = -1/2$) and for $2\omega_1 \simeq$ $\simeq 28{,}800$ cm^{-1} (transition $A_1 \rightarrow A_1$, $\rho_3 = 1/3$). We used (37) and (38) for the experimental data of [16].

The estimates showed that the two-photon susceptibility is small for $A_1 \rightarrow B_2$ transitions, so the signal is almost linearly polarized; the susceptibility is larger by an order of magnitude for $A_1 \rightarrow A_1$ transitions, $\rho_3 = 1/3$, so this transition is also virtually unrepresented in the polarization spectrum.

Transstilbene has high electronic and two-photon susceptibilities; the values given are [4, 17] $\chi^{(3)NR}_{1111} = 1{,}3 \cdot 10^{-12}$ electrostatic CGS units and $\chi^{(3)R}_{1111} = 10 \cdot 10^{-12}$ in the same units, i.e., $\rho_3 = 1/2$ and $\varphi = 70°$ we have $\psi \simeq 7°$, $b/a = 0{,}10$.

2. **Cubic Crystals.** The estimates for these crystals were made for the interaction geometry shown in Fig. 1b.

We see from (36)-(39) that the signal ellipticity in that case is dependent only on two parameters:

$$\frac{\rho_1\sigma}{\tau} = \frac{\chi^{(3)R}_{1122}}{\chi^{(3)NR}_{1122}} \text{ and } \frac{\rho_3\sigma}{\tau} = \frac{\chi^{(3)R}_{1221}}{\chi^{(3)NR}_{1122}}. \tag{44}$$

The quantity $\rho_1\sigma/\tau$ can be estimated for example by the method of Coulomb anharmonicity [18]; also, reliable experimental evidence is available [19, 20] for $\chi^{(3)R}_{1122}$. Indirect evidence indicates that the parameter $\rho_3\sigma/\tau$ can be taken as 1. Table 1 gives results for GaP and ZnSe crystals at $\lambda = 0.69$ μm. It is clear that the state of polarization of the signal changes substantially in the presence of two-photon absorption for these crystals.

3. **Experiment.** We have performed experiments on coherent polarization spectrscopy in two-photon absorption for various isotropic liquids.

Table 1

Crystal	$\chi^{(3)R}_{1122}/\chi^{(3)NR}_{1122}$	$\chi^{(3)R}_{1221}/\chi^{(3)NR}_{1122}$	θ	ψ	b/a
GaP	5*	1	−32°	−28°	0,17
ZnSe	2**	1	−14°	9°	0,11

* $\chi^{(3)NR}_{1122} = 3 \cdot 10^{-10}$ cm^3/erg; $\chi^{(3)R}_{1122} = 1{,}6 \cdot 10^{-9}$ cm^3/erg — calculated by the Coulomb-anharmonicity method [18]. $\chi^{(3)R}_{1122} = 2 \cdot 10^{-9}$ cm^3/erg; experiment [19].

** $\chi^{(3)NR}_{1122} = 1{,}2 \cdot 10^{-10}$ cm^3/erg; $\chi^{(3)R}_{1122} = 2{,}8 \cdot 10^{-10}$ cm^3/erg — calculated by the Coulomb-anharmonicity method [18]. $\chi^{(3)R}_{1122} \doteq 2 \cdot 10^{-10}$ cm^3/erg — from experiment [20].

Table 2

Compound	λ_1^*, μm	λ_2^*, μm	$\varphi = e_1 \wedge e_2$, deg	Φ, deg		$\chi^{(3)}_{1122}/\chi^{(3)***}_{1221}$
				theory**	experiment	
Toluene	0,532	0,565—0,579	45	18,4	18	1,0
Chlorobenzene	0,532	0,565—0,579	70	42,5	44	0,9
Benzene	0,532	0,569—0,577	69	41	45	0,8
Benzene	0,572—0,577	0,532	69,5	41,7	40	1,1
Phenanthrene (liquid state)	0,532	0,567	70	42,5	42,7	1,0
Naphthalene (liquid state)	0,532	0,567	69	41	39	1,1

* $\lambda_{1,2} = 2\pi c/\omega_{1,2}$; $\omega_a = 2\omega_1 - \omega_2$.

** From (35).

*** If the Kleinman relations are met $\chi^{(3)}_{1122}/\chi^{(3)}_{1221} = 1$.

The apparatus was similar to that shown in Fig. 3 of [9]. Table 2 gives the results. The basic result was that Kleinman's relations were not obeyed for substances such as benzene, chlorbenzene, and naphthalene (in the liquid state). For toluene and phenanthrene (in the liquid state) there were no observed deviations from the Kleinman relations. The pumping frequencies ω_1 and ω_2 were far from the one-photon absorption resonancies, so the deviations from the Kleinman relations must be due only to two-quantum resonances, namely of Raman type at frequency ω_1 and ω_2 and of two-photon type (at frequency $2\omega_1$). The experiments were performed with values of $\omega_1 - \omega_2$ differing widely from molecular vibration frequencies. The upper limit to the vibrational contribution to Φ_{exp} for benzene was not more than 1.5°; for the other liquids it was substantially less than 0.5°.

This indicates that two-photon absorption is responsible for the deviation from the Kleinman relations.

Raman scattering makes a comparatively large contribution to Φ_{exp} for benzene, and for this we obtained relations between the nonresonance susceptibility $\chi^{(3)NR}_{1111}$ and the components $\chi^{(3)R}_{1221}$, $\chi^{(3)R}_{1111}$ responsible for the two-photon absorption:

$$\chi^{(3)R}_{1221} - 0{,}38\,\chi^{(3)R}_{1111} = 0{,}028\,\chi^{(3)NR}_{1111} \text{ for } 2\omega_1 \simeq 37\,600 \text{ cm}^{-1},$$

$$\chi^{(3)R}_{1221} - 0{,}32\,\chi^{(3)R}_{1111} = 0{,}035\,\chi^{(3)NR}_{1111} \text{ for } 2\omega_1 \simeq 34\,800 \text{ cm}^{-1}.$$

An error level of ±1° is readily attained in measuring ψ and χ; this results in an error of ±15% for

$$\chi^{(3)R}_{1122}/\chi^{(3)NR}_{1111} \text{ and } \pm 25\,\% \text{ for } \chi^{(3)R}_{1221}/\chi^{(3)NR}_{1111}.$$

The results may be summarized as follows. A new polarization scheme has been proposed for four-photon spectroscopy of two-quantum transitions in isotropic media and cubic crystals. As in the case of coherent ellipsometry in Raman scattering, the scheme is insensitive to fluctuations in the intensities of the exciting waves and to inhomogeneities in the cross section. This is an

essential difference from the methods normally used in TPA spectroscopy, where real two-quantum transitions are recorded [21, 22, 23].

The estimates show that the most promising application of the polarization scheme is to the measurement of TPA spectra for transparent semiconductors. An experiment on coherent polarization spectroscopy shows that two-photon absorption occurs in various organic liquids, and this has enabled us to determine the ratio of the corresponding components of the cubic-susceptibility tensor. Considerable interest also attaches to TPA spectra applied to localized states in solids, including color centers, electronic states of atoms and ions present in trace amounts, exciton states, and so on, especially at low temperatures, when the corresponding resonances are much narrower.

The authors are indebted to S.A. Akhmanov and N.A. Bez'yazychnyi for their interest in this work.

REFERENCES

1. S. A. Akhmanov and N. I. Koroteev, Usp. Fiz. Nauk, vol. 123, p. 350, 1977.
2. M. Maier, Appl. Phys., vol. 11, p. 209, 1976; W. M. Tolles, J. W. Nibler, J. R. McDonald, and A. B. Harvey, Appl. Spectr., vol. 31, no. 4, p. 253, 1977.
3. M. D. Levenson and N. Bloembergen , Phys. Rev., vol. B10, p. 4447, 1974.
4. R. J. M. Anderson, G. R. Holton, and W. M. McClain, J. Chem. Phys., vol. 66, p. 3832, 1977.
5. R. T. Lynch, Jr. and H. J. Lotem, J. Chem. Phys., vol. 66, p. 1905, 1977.
6. V. I. Bredikhin, M. D. Galanin, and V. N. Genkin, Usp. Fiz. Nauk, vol. 110, p. 3, 1973.
7. A. F. Bunkin, S. G. Ivanov, and N. I. Koroteev, DAN SSSR, vol. 233, p. 333, 1977.
8. S. A. Akhmanov, A. F. Bunkin, S. G. Ivanov, and N. I. Koroteev, Pis'ma v ZhETF, vol. 25, p. 444, 1977.
9. S. A. Akhmanov, A. F. Bunkin, S. G. Ivanov, and N. I. Koroteev, ZhETF, vol. 74, p. 1272, 1978.
10. R. T. Lynch, Jr., S. D. Kramer, H. Lotem, and N. Bloembergen, Opt. Comm., vol. 16, p. 372, 1976.
11. J. A. Armstrong, N. Bloembergen, J. Ducning, and P. S. Pershan, Phys. Rev., vol. 127, p. 1918, 1962.
12. A. Edmonds, Angular Momentum in Quantum Mechanics, New York, 1959.
13. U. Fano and G. Racah, Irreducible Tensorial Sets, Academic Press, New York, 1956.
14. M. A. Yuratich and D. C. Hanna, J. Phys., vol. B9, p. 729, 1976; Opt. Comm., vol. 18, p. 134, 1976; Mol. Phys., vol. 33, p. 671, 1977.
15. L. S. Aslanyan and N. I. Koroteev, Kvant. Elektronika, vol. 6, p. 942, 1979.
16. J. P. Hermann and J. Ducning, Opt. Comm., vol. 6, p. 101, 1972.
17. J. L. Oudar, J. Chem. Phys., vol. 67, p. 446, 1977.
18. L. B. Meisner and N. G. Khadzhiiski, Kvant. Elektronika, vol. 6, p. 345, 1979.
19. I. M. Catalano, A. Cingolani, and A. Minafra, Solid St. Comm., vol. 16, p. 417, 1975.
20. V. V. Arsen'ev, V. S. Dneprovskii, D. M. Klyshko, and A. N. Penin, ZhETF, vol. 56, p. 760, 1969.
21. P. R. Monson and W. M. McClain, J. Chem. Phys., vol. 53, p. 29, 1970.
22. W. M. McClain, J. Chem. Phys, vol. 55, p. 2789, 1971.
23. V. Bosl, H. T. Neusser, and F. W. Schlag, J. Chem. Phys., vol. 15, p. 167, 1976.

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