SOVIET PHYSICS JETP VOLUME 26, NUMBER 1 JANUARY, 1968

THREE-PROTON SCATTERING OF LIGHT IN AN ISOTROPIC MEDIUM

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Submitted January 24, 1967

Zh. Eksp. Teor. Fiz. **53**, 244–253 (July, 1967)

A general phenomenological theory of three-photon scattering of light in an isotropic medium in the transparency region is developed. The theory is similar to that of two-photon scattering presented in[9]. The formulas describe, in particular, the angular dependence of the scattering intensity, the degree of depolarization, etc. The number of independent parameters of the medium cancels out and all formulas are significantly simpler in the special case when the scattering tensor possesses Kleinman symmetry properties. This case is analyzed in detail. A quantum treatment of scattering in gases is also presented. It is shown that the tensor responsible for three-photon scattering can be transformed in the adiabatic approximation; the treatment is similar to that in the polarizability theory as applied to two-photon scattering, etc. The frequency dependence of the scattering intensity is briefly considered.

THE use of lasers as radiation sources has made it possible to observe, among other new phenomena, also three photon scattering (TS) of light[1]. From the quantum point of view, this effect can be treated as the vanishing of two photons of a primary beam of frequency ω when the radiation interacts with matter, and creation of one photon of frequency 2ω or $2\omega \pm \omega_m$ (ω_m—one of the natural frequencies of the particles of the medium). This process is described by the nonlinear terms of the electric dipole moment of the molecule, which is induced by the external field. Although terms of this type have been under consideration for quite a long time[2–8], many questions in the theory of three-photon scattering have not yet been answered. The earlier investigations were devoted essentially to different aspects of the quantum theory in the noninteracting-molecule approximation. At the same time, there is still no general phenomenological theory of this effect. Such a theory is of interest since, on the one hand, many properties of TS, and primarily its angular dependence, can be successfully described even at this level, and on the other hand, the theory indicates the quantities that must be additionally calculated in quantum theory in order to obtain a complete description. Such a combination of the phenomenological and quantum approaches appears to be the most rational.

We have therefore developed a phenomenological theory of spontaneous TS in an isotropic (nonmagnetic) medium in the transparency region (Sec. 1). The model followed was the theory of ordinary two-photon scattering, an exposition of which is given in[9]. Section 2 contains a quantum analysis of the scattering in the particular case of gases.

1. PHENOMENOLOGICAL THEORY OF THREE-PHOTON SCATTERING OF LIGHT IN AN ISOTROPIC MEDIUM

As explained in[9], in an phenomenological description of the scattering effect it is necessary to use equations that are "intermediate" between the microscopic and macroscopic Maxwell's equations: It is necessary to average over physically infinitesimally small volumes, but not average in time over the particle motion. The field values pertaining to the scattered wave, for which the first averaging is carried out, will be marked by primes, for example, $\mathbf{D}' = \mathbf{E}' + 4\pi\mathbf{P}'$. With this

$$P_i' = \alpha'\hat{E}_i' + \chi_{ik}E_k + \chi_{ijk}E_jE_k + \ldots, \tag{1}$$

with summation over repeated indices implied throughout. The field of the exciting wave is assumed to have the form $\mathbf{E} = \mathbf{E}_0 \exp[i(\mathbf{k}\cdot\mathbf{r} - \omega t)]$. The first term of (1) describes the effective propagation of the scattered waves in the medium; it must be taken to mean the sum of terms pertaining to scattered waves, with appropriate polarizabilities α'. The second and third terms are responsible for the occurrence of scattered radiation with frequencies $\omega + \omega_m$ and $2\omega \pm \omega_m$ respectively (as a particular case we can have $\omega_m = 0$). The quantities χ_{ij} and χ_{ik} are proportional to $\exp[\mp i\omega_m t]$ and are random functions of the coordinates, but their tensor character does not contradict, of course, the isotropy of the medium, which appears only following the complete averaging. We note that the tensor χ_{ijk} can be regarded as symmetrical in the second and third indices.

Scattering with frequencies $\omega \pm \omega_m$ was analyzed by Landau and Lifshitz[9]; we shall consider here scattering at the frequency $\omega' = 2\omega \pm \omega_m$. For this frequency, omitting the term (1) and going over to the induction, we have

$$D_i' = \varepsilon' E_i' + 4\pi\chi_{ijk}E_jE_k.$$

The quantity to be determined is the field of the scattered wave at the large distance R from the scattering region of the body. It can be obtained in the same manner as in[9], and we shall therefore write out the result immediately:*

$$\mathbf{E}' = -\frac{e^{ik'R}}{\varepsilon' R}[\mathbf{k}'[\mathbf{k}'\mathbf{G}]], \quad k' = \frac{\omega'}{c}\sqrt{\varepsilon'} \quad \mathbf{k}' \| \mathbf{R};$$

$$\mathbf{G} = \tilde{\mathbf{P}}'(\mathbf{k}') = \int \tilde{\mathbf{P}}'(\mathbf{r})e^{-i\mathbf{k}'\mathbf{r}}dv = \int (\chi E_0^2)e^{-i\mathbf{q}\mathbf{r}}dv,$$

$$\mathbf{q} = \mathbf{k}' - 2\mathbf{k}.$$

Here $\mathbf{P}'(\mathbf{r}) = (\chi E^2)$ is a vector with component $\chi_{ijk}E_jE_k$.

To find the intensity of the scattered wave at the observation point it is necessary to form the tensor[9,10] $I_{ij} = \langle E_i'^* E_j \rangle$; the symbol $\langle \ldots \rangle$ denotes averaging over the motion of the particles of the medium. We choose the z axis parallel to $\mathbf{k}'$, and designate the components in the xy plane by the Greek letters α and β. Then

$$I_{\alpha\beta} = A\langle G_\alpha^* G_\beta \rangle, \quad A = k'^4 / R^2\varepsilon'^2, \tag{2}$$

$$\langle G_i^* G_j \rangle = \int\int \langle \tilde{P}_i'^*(\mathbf{r}_1)\tilde{P}_j'(\mathbf{r}_2)\rangle e^{-i\mathbf{k}'(\mathbf{r}_1-\mathbf{r}_2)}dv_1dv_2. \tag{3}$$

As in[9], we assume that the correlations in the motion of the particles of the medium extend only to distances on the order of intermolecular, so that (3) can be reduced to the form

$$\begin{gathered}\langle G_i^* G_j \rangle = VE_{0l}^* E_{0m}^* E_{0n}E_{0s}f_{ilm,jns}, \\ f_{ilm,jns} = \int \langle \chi_{ilm}^*(\mathbf{r}_1)\chi_{jns}(\mathbf{r}_2)\rangle dv.\end{gathered} \tag{4}$$

The integration in (4) is over the coordinate $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, on which the integrand depends after the averaging[1)]; V is the scattering volume.

The tensor $f_{ilm,jns}$, which is symmetrical in the indices l and m and also in n and s, should already reflect the macroscopic symmetry of the medium.

The most general form of such a tensor in an isotropic medium is[1]

$$\begin{aligned} f_{ilm,jns} = {} & {}^1\!/_2 a(\delta_{ij}\delta_{ln}\delta_{ms} + \delta_{ij}\delta_{ls}\delta_{mn}) + b\delta_{ij}\delta_{lm}\delta_{ns} \\ & + {}^1\!/_4 c(\delta_{im}\delta_{ln}\delta_{js} + \delta_{il}\delta_{mn}\delta_{js} + \delta_{il}\delta_{ms}\delta_{jn} + \delta_{im}\delta_{ls}\delta_{jn}) \\ & + {}^1\!/_4 d(\delta_{in}\delta_{lj}\delta_{ms} + \delta_{in}\delta_{ls}\delta_{mj} + \delta_{is}\delta_{lj}\delta_{mn} + \delta_{is}\delta_{ln}\delta_{mj}) \\ & + {}^1\!/_2 g(\delta_{il}\delta_{mj}\delta_{ns} + \delta_{im}\delta_{lj}\delta_{ns}) + {}^1\!/_2 g^*(\delta_{in}\delta_{lm}\delta_{js} \\ & + \delta_{is}\delta_{lm}\delta_{jn}), \end{aligned} \tag{5}$$

where a, b, c, d, g, and g* are scalar quantities that depend on ω and ω', and the first four of them are real.

Taking (5) into account, we can reduce $I_{\alpha\beta}$ [Eq. (2)] to the form

$$\begin{aligned} I_{\alpha\beta} = {} & AV[\delta_{\alpha\beta}(a|\mathbf{E}_0|^4 + b|\mathbf{E}_0^2|^2) + (cE_{0\alpha}^* E_{0\beta} \\ & + dE_{0\alpha}E_{0\beta}^*)|\mathbf{E}_0|^2 + gE_{0\alpha}^* E_{0\beta}^* \mathbf{E}_0^2 + g^* E_{0\alpha}E_{0\beta}\mathbf{E}_0^{*2}]. \end{aligned} \tag{6}$$

Formula (6) is the sought-for general expression for the TS intensity. Further concretization depends on the state of the polarization of the exciting radiation.

Let us consider first the case of linearly polarized light. The quantity $\mathbf{E}_0 = E_0\mathbf{e}$, with $e = 1$, can then be regarded as real. We choose the x axis in the plane containing $\mathbf{e}$ and $\mathbf{k}'$, and denote by ϑ the angle between $\mathbf{e}$ and $\mathbf{k}'$. Then, as can be readily verified,

$$\begin{gathered} I_{xx} = AVE_0^4(a' + c'\sin^2\vartheta), \quad I_{yy} = AVE_0^4 a', \quad I_{xy} = 0, \\ a' = a + b, \quad c' = c + d + 2\operatorname{Re} g. \end{gathered} \tag{7}$$

The total intensity of the TS of polarized light is proportional to the quantity

$$\begin{gathered} I_n = I_{xx} + I_{yy} = I_n(90^\circ)\left(1 - \frac{1-\rho_n}{1+\rho_n}\cos^2\vartheta\right), \\ \rho_n = \frac{I_{yy}}{I_{xx}(90^\circ)} = \frac{a'}{a'+c'}, \quad I_n(90^\circ) = AVE_0^4(2a' + c'). \end{gathered} \tag{8}$$

Let us consider further the case of natural exciting radiation. Now E_0 can be represented in the form[10] $\mathbf{E}_0 = \mathbf{u}e^{i\alpha} + \mathbf{v}e^{i\beta}$, where $\mathbf{u}$ and $\mathbf{v}$ are mutually perpendicular real vectors of equal length, and α and β are real phase factors which are independent random quantities in time or over an ensemble. It is accordingly necessary to average additionally over the ensemble (or over the observation times if the source is an ergodic system); we designate it by a superior bar. As a result we get

$$\begin{gathered} \overline{E_{0\alpha}E_{0\beta}}^* = {}^1\!/_2|\mathbf{E}_0|^2(\delta_{\alpha\beta} - s_\alpha s_\beta), \quad \overline{|\mathbf{E}_0^2|^2} = {}^1\!/_2|\mathbf{E}_0|^4, \\ \overline{E_{0\alpha}E_{0\beta}\mathbf{E}_0^{*2}} = {}^1\!/_4|\mathbf{E}_0|^4(\delta_{\alpha\beta} - s_\alpha s_\beta), \\ |\mathbf{E}_0|^2 = 2u^2, \quad \mathbf{s} = \mathbf{k}/k. \end{gathered} \tag{9}$$

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*$[\mathbf{k}'[\mathbf{k}'\mathbf{G}] \equiv \mathbf{k}' \times [\mathbf{k}' \times \mathbf{G}]$.

[1)] When long-range correlations are taken into account, $f_{ilm,jns}$ should be replaced by the Fourier component of the quantity $\langle\chi_{ilm}^*(\mathbf{r}_1)\chi_{jns}(\mathbf{r}_2)\rangle$ the Fourier-transformation argument being q. Appropriate Fourier components replace also the parameters a, b, ... which enter in (5) and below.

Taking (9) into account we get

$$I_{\alpha\beta} = AV|\mathbf{E}_0|^4(\delta_{\alpha\beta}a'' - s_\alpha s_\beta c''),$$
$$a'' = {}^1/_2(2a + b + c + d + \operatorname{Re} g),$$
$$c'' = {}^1/_2(c + d + \operatorname{Re} g). \tag{10}$$

This time we choose the x axis in the plane of the vectors k and k′ and denote by θ the angle between these vectors. Then

$$I_{xx} = I_\parallel = AV|E_0|^4(a'' - c''\sin^2\theta),$$
$$I_{yy} = I_\perp = AV|E_0|^4 a'', \quad I_{xy} = 0,$$
$$I = I_\perp + I_\parallel = I(90^\circ)\left(1 + \frac{1-\rho}{1+\rho}\cos^2\theta\right),$$
$$\rho = \frac{I_\parallel(90^\circ)}{I_\perp}, \quad I(90^\circ) = AV|E_0|^4(2a'' - c''). \tag{11}$$

As seen from (8) and (11), the intensity of the scattering can be expressed in both cases in terms of two experimentally observed quantities: the intensity and degree of depolarization for the case of perpendicular observation. I is expressed here in terms of the given quantities in the same manner as in two-photon scattering[11,12]. There exist, however, also essential differences from the latter case. First, in the general case, it is impossible to indicate the connection between the quantities ρ and ρ_n, whereas for two-photon scattering such a connection exists in the form[12] $\rho = 2\rho_n/(1 + \rho_n)$. Second, the connection between the quantities a′ and c′ on the one hand and a″ and c″ on the other with the microscopic parameters is different than for the corresponding quantities in two-photon scattering, and therefore the limits of variation of the quantities ρ and ρ_n also turn out to be different.

In the transparency region, we can use additionally, Kleinman's approximate symmetry properties[13,14], according to which the tensor χ_{ijk} should be regarded as symmetrical in all the indices[2]. Then, as can be readily verified, $a = d/2$, $b = c/4 = g/2 = g^*/2$, and only two parameters of theory are left, a and b, making it possible to obtain a number of additional relations. Above all, $a' = a + b$, $c' = 2a + ab$, and $a'' = 2a + 7b/2$ and $c'' = a + 3b$, hence

$$\rho_n = \frac{a+b}{3(a+3b)}, \quad \rho = \frac{2a+b}{4a+7b}, \quad \rho = \frac{15\rho_n - 1}{15\rho_n + 3}. \tag{12}$$

We see that a definite connection is established between the quantities ρ and ρ_n. Further, choosing in (4) and (5) different concrete values of the indices, it is easy to obtain for the quantities a and b the following inequalities[3]:

$$\int \langle \chi^*_{xyz}(\mathbf{r}_1)\chi_{xyz}(\mathbf{r}_2)\rangle\, dv = a/2 \geqslant 0, \quad a \geqslant 0;$$
$$\int \langle \chi^*_{xxx}(\mathbf{r}_1)\chi_{xxx}(\mathbf{r}_2)\rangle\, dv = 3a + 9b \geqslant 0, \quad b \geqslant -a/3. \tag{13}$$

From this and from (12) it follows that the quantities ρ are bounded by the following limits[4]:

$$ {}^1/_9 \leqslant \rho_n < \infty, \quad {}^1/_7 \leqslant \rho < 1. \tag{14}$$

Let us assume now that the exciting radiation consists of two waves of different frequencies and different wave vectors

$$\mathbf{E} = \mathbf{E}_1 + \mathbf{E}_2 = \mathbf{E}_{10}e^{i(\mathbf{k}_1\mathbf{r} - \omega_1 t)} + \mathbf{E}_{20}e^{i(\mathbf{k}_2\mathbf{r} - \omega_2 t)}$$

and scattering is observed with frequency $\omega' = \omega_1 + \omega_2 \pm \omega_m$. The analysis of this case as a whole is similar to the proceding one, but a number of complications arise. First, it is necessary to take into account the fact that the corresponding tensor χ_{ijk} does not have in the general case symmetry with respect to permutation of the indices. Therefore all fifteen terms must enter into the expression (5) for $f_{ilm,jns}$ with different coefficients a_i. If we number them in the same sequence as in (5), then we can only state that $a_7 = a_5^*$, $a_{10} = a_9^*$, $a_{14} = a_{13}^*$, $a_{15} = a_{12}^*$, and the remaining a_i are real.

Calculation of the quantities $I_{\alpha\beta} = A\langle G_\alpha^* G_\beta\rangle = AVE_{10l}E_{20m}E_{10n}E_{20s}f_{\alpha lm,\beta ns}$ leads to the following result:

$$\begin{aligned} I_{\alpha\beta} = AV\{&\delta_{\alpha\beta}[a_1|\mathbf{E}_{10}|^2|\mathbf{E}_{20}|^2 + a_2|(\mathbf{E}_{10}\mathbf{E}_{20}^*)|^2 \\ &+ a_3|(\mathbf{E}_{10}\mathbf{E}_{20})|^2] + a_4E_{20\alpha}^*E_{20\beta}|\mathbf{E}_{10}|^2 \\ &+ a_5E_{10\alpha}^*E_{20\beta}(\mathbf{E}_{10}\mathbf{E}_{20}^*) + a_6E_{10\alpha}^*E_{10\beta}|\mathbf{E}_{20}|^2 \\ &+ a_5^*E_{20\alpha}^*E_{10\beta}^*(\mathbf{E}_{10}^*\mathbf{E}_{20}) + a_8E_{10\alpha}E_{10\beta}^*|\mathbf{E}_{20}|^2 \\ &+ a_9E_{10\alpha}E_{20\beta}^*(\mathbf{E}_{10}^*\mathbf{E}_{20}) + a_9^*E_{20\alpha}E_{10\beta}^*(\mathbf{E}_{10}\mathbf{E}_{20}^*) \\ &+ a_{11}E_{20\alpha}E_{20\beta}^*|\mathbf{E}_{10}|^2 + a_{12}E_{10\alpha}^*E_{20\beta}^*(\mathbf{E}_{10}\mathbf{E}_{20}) \\ &+ a_{13}E_{20\alpha}^*E_{10\beta}^*(\mathbf{E}_{10}\mathbf{E}_{20}) + a_{13}^*E_{10\alpha}E_{20\beta}(\mathbf{E}_{10}^*\mathbf{E}_{20}^*) \\ &+ a_{12}^*E_{20\alpha}E_{10\beta}(\mathbf{E}_{10}^*\mathbf{E}_{20}^*)\}. \end{aligned} \tag{15}$$

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[2] These properties, strictly speaking, were established for the tensor of the nonlinear dielectric constant, but in the transparency region it was analogously [14] possible to introduce into consideration the part of the free energy responsible for the scattering with frequency ω', and to establish by similar reasoning the symmetry with respect to all indices also for our tensor χ_{ijk} which describes processes such as Raman scattering.

[3] In (13) there is no summation over the indices x, y, and z. It is easy to verify that the integrals in their left sides are positive by using considerations similar to those used in [9], Sec. 93, in the investigation of similar integrals. The choice of other combinations of indices does not yield any new results.

[4] When the properties of the scattering medium are more concrete specified, the intervals of variation of the quantities ρ and ρ_n may become still narrower, as can be seen from [7], where scattering of freely rotating molecules by a gas is considered.

Let us consider again the particular case when both waves are linearly polarized, so that $\mathbf{E}_{10} = E_{10}\mathbf{e}_1$, $\mathbf{E}_{20} = E_{20}\mathbf{e}_2$, and $e_{1,2} = 1$. For this case, (15) takes the form

$$I_{\alpha\beta} = AVE_{10}^2E_{20}^2\{\delta_{\alpha\beta}[a + b(\mathbf{e}_1\mathbf{e}_2)^2] + ce_{1\alpha}e_{1\beta} + de_{2\alpha}e_{2\beta} + (ge_{1\alpha}e_{2\beta} + g^*e_{2\alpha}e_{1\beta})(\mathbf{e}_1\mathbf{e}_2)\},$$
$$a = a_1, \quad b = a_2 + a_3, \quad c = a_6 + a_8, \quad d = a_4 + a_{11},$$
$$g = a_5 + a_9 + a_{12} + a_{13}^*. \tag{16}$$

Formula (16) solves the problem. The reduction of the two-dimensional tensor $I_{\alpha\beta}$ to the principal axes and the determination of its principal values, which are proportional to the intensities of the mutually-perpendicular polarized components, entails no difficulty.

In the transparency region we can neglect the dependence of the quantities a_i on the frequencies $\omega_{1,2}$ and ω', since, just as in the case when $\omega' = 2\omega \pm \omega_m$, symmetry conditions of the Kleinman type arise, according to which the tensor χ_{ijk} is symmetrical with respect to all the indices. With this, $a_1 = a_2 = a_8 = a_9 = a_9^* = a_{11} = a$, $a_3 = a_4 = a_5^* = a_6 = a_{12} = a_{12}^* = a_{13} = a_{13}^* = f$, and $b = c = d = a + f$, $g = a + 3f$. Further

$$I_{\alpha\beta} = AVE_{10}^2E_{20}^2a\{\delta_{\alpha\beta}[1 + (1+\eta)(\mathbf{e}_1\mathbf{e}_2)^2] + (1+\eta)(e_{1\alpha}e_{1\beta} + e_{2\alpha}e_{2\beta}) + (1+3\eta)(\mathbf{e}_1\mathbf{e}_2)(e_{1\alpha}e_{2\beta} + e_{2\alpha}e_{1\beta})\}, \quad \eta = f/a. \tag{17}$$

We see that, just as in the preceding case, the scattering intensity is determined only by two constants, a and η. Let us consider also the particular case when the three vectors $\mathbf{e}_1$, $\mathbf{e}_2$ and $\mathbf{k}'$ lie in one plane, which can be chosen to be the xz plane. Denoting by $\vartheta_{1,2}$ the angles between $\mathbf{e}_{1,2}$ and $\mathbf{k}'$ and putting $\vartheta = \vartheta_1 - \vartheta_2$, we get

$$I_{xx} = AVE_{10}^2E_{20}^2a[1 + (1+\eta)(\cos^2\vartheta + \sin^2\vartheta_1 + \sin^2\vartheta_2) + 2(1+3\eta)\cos\vartheta\sin\vartheta_1\sin\vartheta_2],$$
$$I_{yy} = AVE_{10}^2E_{20}^2a[1 + (1+\eta)\cos^2\vartheta], \quad I_{xy} = 0. \tag{18}$$

We now assume that the excitation is made by natural radiation, so that we can put

$$\mathbf{E}_{1,20} = \mathbf{u}_{1,2}e^{i\alpha_{1,2}} + \mathbf{v}_{1,2}e^{i\beta_{1,2}}$$

$(\mathbf{u}_1, \mathbf{v}_1)$ and $(\mathbf{u}_2, \mathbf{v}_2)$ are two pairs of real vectors of equal length, which are arbitrarily located in planes perpendicular to $\mathbf{k}_1$ and $\mathbf{k}_2$ and are mutually orthogonal; $\alpha_{1,2}$ and $\beta_{1,2}$ are random functions. We choose the vectors $\mathbf{u}_{1,2}$ perpendicular to the plane σ of the vectors $\mathbf{k}_{1,2}$, and the vectors $\mathbf{v}_{1,2}$ to lie in this plane, so that $\mathbf{u}_1 \parallel \mathbf{u}_2$ and $\mathbf{v}_1 \cdot \mathbf{v}_2 = v_1v_2\cos\varphi = u_1u_2\cos\varphi$, where φ is the angle between the vectors $k_{1,2}$. To go over to the observable quantities, it is necessary, in analogy with (9), to average additionally over the ensemble (or over the observation times) fourth-order combinations of the components of $\mathbf{E}_{1,20}$ which enter in (18). The averaging yields

$$\overline{|(\mathbf{E}_{10}\mathbf{E}_{20}^*)|^2} = \overline{|(\mathbf{E}_{10}\mathbf{E}_{20})|^2} = (\mathbf{u}_1\mathbf{u}_2)^2 + (\mathbf{v}_1\mathbf{v}_2)^2 = 2u_1^2u_2^2\cos^2(\varphi/2),$$
$$\overline{E_{10\alpha}\;E_{10\beta}|\mathbf{E}_{20}|^2} = 2u_1^2u_2^2(\delta_{\alpha\beta} - s_{1\alpha}s_{1\beta}),$$
$$\overline{E_{10\alpha}^*E_{20\beta}(\mathbf{E}_{10}\mathbf{E}_{20}^*)} = u_1^2u_2^2(\xi_\alpha\xi_\beta + \xi_{1\alpha}\xi_{2\beta}\cos\varphi),$$
$$|\mathbf{E}_{1,20}|^2 = 2u_{1,2}^2, \qquad \mathbf{s}_{1,2} = \mathbf{k}_{1.2}/k_{1.2}, \qquad \xi = \mathbf{u}_{1.2}/u_{1.2},$$
$$\xi_{1,2} = \mathbf{v}_{1.2}/v_{1.2}$$

and similarly for other quantities of the same type as those written out. As a result we get

$$I_{\alpha\beta} = AV|\mathbf{E}_{10}|^2|\mathbf{E}_{20}|^2\Big[\delta_{\alpha\beta}\Big(a + b\cos^2\frac{\varphi}{2}\Big) + \frac{c}{2}(\delta_{\alpha\beta} - s_{1\alpha}s_{1\beta}) + \frac{d}{2}(\delta_{\alpha\beta} - s_{2\alpha}s_{2\beta}) + \frac{\sigma}{4}(\xi_\alpha\xi_\beta + \xi_{1\alpha}\xi_{2\beta}\cos\varphi) + \frac{g^*}{4}(\xi_\alpha\xi_\beta + \xi_{2\alpha}\xi_{1\beta}\cos\varphi)\Big]. \tag{19}$$

In the Kleinman approximation, expression (19) goes over into

$$I_{\alpha\beta} = AV|E_{10}|^2|E_{20}|^2a\Big\{\delta_{\alpha\beta}\Big(1 + \frac{1+\eta}{2}\cos^2\frac{\varphi}{2}\Big) + \frac{1+\eta}{2}(2\delta_{\alpha\beta} - s_{1\alpha}s_{1\beta} - s_{2\alpha}s_{2\beta}) + \frac{1+3\eta}{4}[2\xi_\alpha\xi_\beta + (\xi_{1\alpha}\xi_{2\beta} + \xi_{2\alpha}\xi_{1\beta})\cos\varphi]\Big\}.$$

In the particular case when the vector $\mathbf{k}'$ is located in the plane σ, which can be chosen as the xz plane, we have

$$I_{xx} = AV|\mathbf{E}_{10}|^2|\mathbf{E}_{20}|^2\frac{a}{2}\Big\{2 + (1+\eta)\Big[\cos^2\theta_1 + \cos^2(\theta_1 - \varphi) + \cos^2\frac{\varphi}{2}\Big] + (1+3\eta)\cos\theta_1\cos(\theta_1 - \varphi)\cos\varphi\Big\},$$
$$I_{yy} = AV|\mathbf{E}_{10}|^2|\mathbf{E}_{20}|^2\frac{a}{2}(1+\eta)\Big(5 + \cos^2\frac{\varphi}{2}\Big), \quad I_{xy} = 0, \tag{20}$$

where θ_1 is the angle between $\mathbf{k}'$ and $\mathbf{k}_1$. The angles θ_1 and φ must be taken with equal signs if they are reckoned from $\mathbf{k}_1$ in the same direction.

It can be verified that expressions (17) go over into (7) in the particular case when $\mathbf{e}_1 \parallel \mathbf{e}_2$, and Eqs. (20) go over into (10) when $\varphi = 0$, as should be the case. The case $\omega' = \omega_1 - \omega_2 \pm \omega_m$ is treated in exactly the same manner. Finally, we note also that, in accordance with (2), the quantities $I_{\alpha\beta}$ are in all cases proportional to ω'^4.

2. CASE OF GAS

In order to illustrate the connection between the phenomenological theory and the microscopic theory, let us consider the case of a gas. As is clear from the foregoing, in the microscopic theory it is sufficient to find the quantity $f_{ilm,jns}$ [Eq. (4)] or the related quantity $M_{ij}(\mathbf{r}_1 - \mathbf{r}_2) = \langle \widetilde{P}_i'^*(\mathbf{r}_1)\widetilde{P}_j'^*(\mathbf{r}_2)\rangle$. The method of finding it is in principle the same for two- and three-photon scattering. For simplicity we shall first discuss two-photon scattering $\omega' = \omega \pm \omega_m$.

In the quantum-mechanical analysis, it is necessary to replace the quantity $\mathbf{P}'(\mathbf{r})$ by the operator of the specific dipole moment averaged over the physically infinitesimally small volume $\Delta v(\mathbf{r})$ near the point $\mathbf{r}$ (see[9]). This operator is of the form

$$\mathbf{P}(\mathbf{r}) = \sum_{\nu} \mathbf{p}_\nu D(\mathbf{r} - \mathbf{R}^\nu);$$

$\mathbf{p}_\nu$ and $\mathbf{R}^\nu$ are the dipole-moment operator and the radius vector of the center of mass of the ν-th molecule; the function $D(\mathbf{r})$ is equal to $(\Delta v)^{-1}$ if the end of the vector $\mathbf{r}$ lies within the volume $\Delta v(0)$, and vanishes otherwise; the summation over ν is performed for all the gas molecules. The quantity $\widetilde{\mathbf{P}}'^*(\mathbf{r})$ must be replaced by $\mathbf{P}^+(\mathbf{r}) = \mathbf{P}(\mathbf{r})$. It is thus necessary to calculate the quantum-mechanical mean of the operator $L^{ij} = P_i(\mathbf{r}_1)P_j(\mathbf{r}_2)$. The results will describe the processes of scattering of different types and frequencies, and is therefore necessary to pick out from it the terms corresponding to the required frequency ω'.

Using the completeness property of the system of the wave functions of the gas perturbed by the field $(0, F)$ (the index 0 pertains to the initial state), we can easily verify that

$$L_{00}{}^{ij} = \sum_{\widetilde{F}} P_{i,0F}(\mathbf{r}_1)P_{j,F0}(\mathbf{r}_2) = \frac{1}{V^2}\sum_{\nu f \mathbf{k}_f} p_{\nu,i;\,0f}\,p_{\nu,j;\,f0}\,e^{i(\mathbf{k}_{f0}-\mathbf{k})(\mathbf{r}_1-\mathbf{r}_2)}. \tag{21}$$

Here V is the volume of the region occupied by the gas; $(0, f)$ is the aggregate of the perturbed states of an isolated molecule located at the origin; $\mathbf{k}_{f0} = \mathbf{k}_f - \mathbf{k}_0$, the quantities $\mathbf{k}_0$ and $\mathbf{k}_f$ being the quasimomenta of the molecule in the states $(0, f)$. The summation over $\mathbf{k}_f$ can be replaced by integration, thereby introducing $V\delta(\mathbf{r}_1 - \mathbf{r}_2)$. The quantities $\mathbf{p}_{\nu,0f}$ actually do not depend on ν. Each of them contains terms with a time dependence of the type $\exp(i\omega' t) = \exp[i(\omega - \omega_{f0})t]$[1,2], responsible for the scattering with the given frequency ω'. We denote the coefficient of such an exponential by $p'_{i,0f}$. On going from $L_{00}{}^{ij}$ to $M_{ij}(\mathbf{r}_1 - \mathbf{r}_2)$, it is necessary to retain only the term with the required f. In the case of vibrational transitions with registration of integral scattering-line intensities, it is necessary to sum over all the rotational components. It is more convenient, however, to regard the relatively-slowly-varying rotational variables as classical parameters from the very outset, and then summation over ν in (21) reduces to averaging over all the orientations of the molecule. In addition, it is necessary to average over the initial states, which we shall arbitrarily denote with the aid of $\hat{g}_0$. As a result we have

$$M_{ij}(\mathbf{r}_1 - \mathbf{r}_2) = N\hat{g}_0\langle p'_{i,0f}p'_{j,f0}\rangle_{\text{rot}}\ \delta(\mathbf{r}_1 - \mathbf{r}_2), \tag{22}$$

where N is the molecule concentration.

The final formula (22) of course remains in force also for TS, if we replace the quantities p'_{0f} by those coefficients in the terms of $\mathbf{p}_{0f}$ which have the time dependence $\exp[i(\omega_1 + \omega_2 - \omega_{f0})t]$, which appear when $\mathbf{p}_{0f}$ is calculated in second order of perturbation theory. The quantities $\mathbf{p}'_{0f}$ and $\mathbf{p}'_{f0}$ can be represented in the form[6,7] $p'_{j,f0} = \alpha^{f0}{}_{jns}E_{10n}E_{20s}$ and $p'_{i,0f} = \alpha_{ilm}{}^{f0*}E^*{}_{10l}E^*{}_{20m}$, and therefore we obtain for $f_{ilm,jns}$ [Eq. (4)] and for the analogous quantity $f_{il,jn}$ characterizing two-photon scattering, the following intuitively clear result

$$f_{ilm,jns} = N\hat{g}_0\langle \alpha_{ilm}^{f0*}\alpha_{jns}^{f0}\rangle_{\text{rot}},$$

$$f_{il,jn} = N\hat{g}_0\langle \alpha_{il}^{f0*}\alpha_{jn}^{f0}\rangle_{\text{rot}}. \tag{23}$$

The tensor $\alpha_{ijk}{}^{f0}$ is best called the tensor of three-photon Raman scattering (or Rayleigh scattering when $f = 0$). In the theory of two-photon Raman scattering extensive use is made of the polarizability-theory approximation[11,12], in which the corresponding tensor $\alpha_{ij}{}^{f0}$ is represented in the form of an expansion (we omit the indices f0)

$$\alpha_{ij} = \Big[\alpha_{ij}{}^0 + \sum_{\mu}\alpha_{ij,\mu}^{(1)}(Q_\mu - Q_\mu{}^0) + \ldots\Big]_{v'v}, \tag{24}$$

where Q_μ and $Q_\mu{}^0$ are respectively the normal coordinate of the vibrations of the nuclei and its equilibrium value in the electronic ground state, and $[\ldots]_{v'v}$ denotes the matrix element of the wave functions of the vibrational motion in the initial and final states of the molecule. The proof of the possibility of introducing the tensor (24) was considered in a number of papers[11,12,15,16].

It is of interest to obtain an expansion of the type (24) for the tensor α_{ijk}. This can be done in the adiabatic approximation, using the explicity expression obtained in[6] for α_{ijk}, as well as a method similar to that described in[17]. Without writing out the rather complicated relations, we shall illustrate this by using as an example the following term:

$$\beta_{\alpha\beta\gamma} = \frac{1}{\hbar^2} \sum_{lj} \frac{p_{\alpha,0l} p_{\beta,lj} p_{\gamma,jf}}{(\omega_{l0} - \omega)(\omega_{j0} - 2\omega)} \tag{25}$$

which enters as a component part of α in the case when $\omega' = 2\omega - \omega_{f0}$[6]. The quantities $p_{\alpha,0l}$, $p_{\beta,lj}$, and $p_{\gamma,jf}$ are the matrix elements of the components of the dipole moment of the molecule, calculated from the unperturbed wave function; $\omega_{l0} = \omega_l - \omega_0$ and $\hbar\omega_l$ are the energy levels of the isolated molecules. We separate the vibrational and electronic quantum numbers, so that the initial and final states are $(0v)$ and $(0v')$, and the intermediate states are (lv_l) and (jv_j); the summation in (25) should be over l, j, v_l, and v_j. The matrix elements in (25) can be represented in the form $(p_\alpha{}^{0l})_{vv_l}$ etc., where $p_\alpha{}^{0l}$ are the matrix elements of the electronic parts of the wave functions. Using the fact that the functions of the states $(0v)$ and $(0v')$ decrease rapidly with increasing distance between Q_μ and Q_μ^0, we can expand $p_\alpha{}^{0l}$ in powers of $Q_\mu - Q_\mu^0$, and expand the frequency factors

$$(\omega_{v_l v}^{l0} - \omega)^{-1} = (\omega_{l0}' - \omega)^{-1}(1 + \xi)^{-1}$$

in powers of

$$\xi = (\omega_{v_l v}^{l0} - \omega_{l0}')/(\omega_{l0}' - \omega),$$

where ω'_{l0} is the frequency of the Franck-Condon transition $0 \rightarrow l$ at $Q_\mu = Q_\mu^0$. Using the completeness property of the system of the eigenfunctions of the operator of the nuclear-motion energy in the l-th electronic state, in perfect analogy with the procedure used in[17], we can prove that

$$\beta_{\alpha\beta\gamma} = [\beta_{\alpha\beta\gamma}^{(0)} + \beta_{\alpha\beta\gamma}^{(1)}(Q - Q_0) + \ldots]_{v'v} \tag{26}$$

(we leave out, for simplicity, the summation over μ), where

$$\beta_{\alpha\beta\gamma}^{(0)} = \frac{1}{\hbar^2} \sum_{lj} \frac{A_{\alpha\beta\gamma}^{lj}}{(\omega_{l0}' - \omega)(\omega_{j0}' - 2\omega)}$$

$$\beta_{\alpha\beta\gamma}^{(1)} = \frac{1}{\hbar^2} \sum_{lj} \left\{ \frac{B_{\alpha\beta\gamma}^{lj}}{(\omega_{l0}' - \omega)(\omega_{j0}' - 2\omega)} \right.$$

$$- \frac{A_{\alpha\beta\gamma}^{lj}}{(\omega_{l0}' - \omega)(\omega_{j0}' - 2\omega)} \cdot \left[\frac{1}{\omega_{l0}' - \omega} \left(\frac{\partial \omega_{l0}'(Q)}{\partial Q} \right)_{Q_0} \right.$$

$$\left. \left. + \frac{1}{\omega_{j0}' - 2\omega} \left(\frac{\partial \omega_{j0}'(Q)}{\partial Q} \right)_{Q_0} \right] \right\},$$

$$A_{\alpha\beta\gamma}^{lj} = (p_\alpha{}^{0l} p_\beta{}^{lj} p_\gamma{}^{j0})_{Q_0},$$

$$B_{\alpha\beta\gamma} = \left(\frac{\partial p_\alpha{}^{0l}}{\partial Q} p_\beta{}^{lj} p_\gamma{}^{j0} + p_\alpha{}^{0l} \frac{\partial p_\beta{}^{lj}}{\partial Q} p_\gamma{}^{j0} + p_\alpha{}^{0l} p_\beta{}^{lj} \frac{\partial p_\gamma{}^{j0}}{\partial Q} \right)_{Q_0} \tag{27}$$

$\omega_{l0}'(Q)$ is the frequency of the Franck-Condon transition for arbitrary Q. When $v' = v$ (Rayleigh case) it is necessary to take in (26) the first term, when $v' = v \pm 1$ the second term, etc.

The expression (27) for $\beta_{\alpha\beta\gamma}^{(1)}$, is obtained, strictly speaking, in the following fashion: the first term in the curly brackets corresponds to the term with ξ raised to the zero power and to allowance for the dependence of the product of the matrix elements $p_\alpha^{0l} p_\beta^{lj} p_\gamma^{j0}$ on Q in the linear approximation. The second term corresponds to terms linear in ξ, in which the matrix elements p_α^{0l} etc. are already taken with $Q = Q_0$. In these terms, as can be seen from (25), there appear in the numerators the quantities

$$T_{v'v} = \sum \langle v' | v_l \rangle \hbar (\omega_{v_l v}^{l0} - \omega_{l0}') \langle v_l | v \rangle,$$

which, by virtue of the completeness of the system of functions $\{v_l\}$ in Q-space, can be transformed for $v' = v \pm 1$ into

$$T_{v'v} = \sum_{v_l v_l'} \langle v' | v_l \rangle \langle v_l | H^l(Q) - A_v{}^l | v_l' \rangle \langle v_l' | v \rangle = \langle v' | H^l(Q)$$

$$- A_v{}^l | v \rangle = \langle v' | H^0(Q) + V^{l0}(Q) | v \rangle = \langle v' | V^{l0}(Q) | v \rangle$$

$$= \hbar \left(\frac{\partial \omega_{l0}'(Q)}{\partial Q} \right)_{Q_0} (Q - Q_0)_{v'v}.$$

Here H^0 and $H^l = H^0 + V^l - V^0 = H^0 + V^{l0}$ are the operators of nuclear-motion energy in the initial and l-th electronic states, V^0 and V^l are the corresponding potential energies, and the quantities $A_v{}^l$ do not depend on Q and therefore $\langle v' | A_v{}^l | v \rangle = 0$. When the foregoing is taken into account, the structure of both terms $\beta_{\alpha\beta\gamma}^{(1)}$ becomes clear.

The remaining terms α_{ijk} can be transformed similarly. The resultant formulas not only demonstrate the possibility of a changeover to polarizability theory, but also facilitate the problem of investigating the tensor α in different concrete cases, since summation over virtual vibrational sublevels is eliminated; they also make it possible to assess the frequency dependence of the scattering intensity, especially if the number of actual electronic states is not too large. Just as in two-photon scattering[11,12,17,18], it is possible to distinguish between two frequency regions. In the first region, ω or 2ω is close to the actual electronic absorption band l_0, whereas the other bands are quite remote from either ω or 2ω. In this region, the main contribution to α is made by the term β [Eq. (27)], and dominating in β is the second term, which contains a stronger frequency dependence and the large factor $(\partial\omega l_0 0(Q)/\partial Q)_{Q_0}$, due to the virtual transitions on the steep wall of the potential curve of the electronic state l_0 (cf. estimates given in [12,18]). The frequency dependence of the scattering intensity corresponds approximately to[5)] $I \sim \omega^{14}(\omega l_0 0' - \omega)^{-4}$ or $I \sim \omega^{14}(\omega l_0 0' - 2\omega)^{-4}$. The second frequency region corresponds to the case when $2\omega \ll \omega' l_0$ for all the actual electronic transitions (it is called the Placzek region in the theory of two-photon scattering). The vibrational structure of the electronic states l and j, together with the second term of (27), cease to be important in this case. The dispersion of the first term of β can also be neglected, and $I \sim \omega^{14}$. The Kleinman symmetry conditions referred to above are valid precisely in this frequency region. A more detailed discussion of the problem of the frequency dependence is outside the scope of our present problem.

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Translated by J. G. Adashko
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[5)] We do not discuss here the question of the possible change in the form in which the tensors α and β are rewritten on the basis of the sum rules.