

# Parametric scattering of light by molecules and in crystals without a symmetry center

N. B. Baranova and B. Ya. Zel'dovich

*P. N. Lebedev Physics Institute, USSR Academy of Sciences*  
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Scattering of light due to spontaneous decay of the incident photon of frequency  $\omega_0$  into a pair of photons of such frequencies  $\omega_1$  and  $\omega_2$  such that  $\omega_1 + \omega_2 = \omega_0$  is considered for molecules without a symmetry center. The main contribution to the cross section for gases or liquids with freely oriented molecules is made by quanta with  $\omega_1 \approx \omega_2 \approx \omega_0/2$ . The transition from freely orienting molecules to noncentral-symmetric crystals is considered. In this case the process goes over into the familiar phenomenon of parametric scattering in a crystal. For allowed synchronism the total cross section per molecule increases by approximately  $N\lambda^3$  times, where  $N$  is the density of molecules in the crystal. Parametric scattering from the crystal boundaries in the absence of synchronism is discussed.

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## 1. INTRODUCTION

Parametric scattering in a crystal without central symmetry, i. e., the decay of a quantum of frequency  $\omega_0$  into quanta with frequencies  $\omega_1$  and  $\omega_2$  such that  $\omega_0 = \omega_1 + \omega_2$  was predicted theoretically and observed experimentally about ten years ago<sup>[1]</sup> and has been used since to investigate nonlinear and dispersion properties of crystals. This process is the spontaneous analog of parametric generation of light and is essentially connected with two factors: 1) the macroscopic quadratic polarizability of the medium  $\chi_{ijk}$  and 2) the synchronism condition  $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_0$ , which determines the high directivity of the scattered quanta along the incident radiation. Both factors are essential also for the generation of the second harmonic of light in crystals or for frequency mixing.

For isotropic media such as gases or liquids, the macroscopic quadratic nonlinearity is equal to zero,  $\chi_{ijk} = 0$ . At the same time, it is possible to realize in such media (see<sup>[2]</sup>) the so called hyper-scattering process, i. e., incoherent generation of the second harmonic of the light by non-centrally-symmetrical freely-orienting molecules (by the quadratic nonlinearity  $\beta_{ijk}$  of the individual molecule). In this case only the intensities of the harmonics emitted by individual molecules are additive, while the small shifts of the frequency  $\Omega$  in the relation  $\omega_0 - \Omega = 2\omega_1$  characterize the vibrational, rotational, or translational motion of the molecule.

In this paper we discuss light scattering which is also due to the optical nonlinearity  $\beta_{ijk}$  of an individual molecule, namely, the spontaneous decay  $\hbar\omega_0 \rightarrow \hbar\omega_1 + \hbar\omega_2$ , which we show below to be parametric scattering (abbreviated PS) of light. The PS probability, just as the probability of parametric scattering in a crystal (PSC) is linear in the intensity  $I$  of the incident radiation, in contrast to hyperscattering, the probability of which depends quadratically on  $I$ .

In Appendix 3 are given illustrative estimates of the PS, PSC, and hyperscattering cross sections, which require no calculations whatever and which lead to a better understanding of the transition from the PS by an isolated molecule to PS in a crystal.

## 2. PARAMETRIC SCATTERING OF LIGHT BY MOLECULES

The Hamiltonian of the free-photon interaction of a real electric field  $\mathcal{E}(\mathbf{r}, t)$  of a light wave with a molecule without symmetry center is determined in the dipole approximation by the hyperpolarizability tensor  $\beta_{ijk}$  and can be arbitrarily written in the form (cf. <sup>[3, 4]</sup>)

$$H_{int} = -\frac{1}{2}\beta_{ijk}\mathcal{E}_i\mathcal{E}_j\mathcal{E}_k \quad (1a)$$

The real value of the nonlinear dipole moment is defined here by

$$(d_{real})_i = \beta_{ijk}\mathcal{E}_j\mathcal{E}_k \quad (1b)$$

In optics it is customary to use for the calculations the complex amplitudes of the field  $\mathbf{E}$ , of the dipole moment  $\mathbf{d}$ , etc., which are connected with the real quantities as follows:

$$A_{real}(t) = \frac{1}{2}[A(\omega)e^{-i\omega t} + A^*(\omega)e^{i\omega t}] \quad (2)$$

The complex amplitude of the dipole moment describing parametric scattering is then equal to

$$d_i(\omega) = \frac{1}{2}\beta_{ijk}[E_j(\omega_0)E_k^*(\omega_2) + E_j^*(\omega_2)E_k(\omega_0)] \\ = \beta_{ijk}E_j(\omega_0)E_k^*(\omega_2), \quad (3a)$$

and for the hyperscattering process (second harmonic generation) we have

$$d_i(2\omega) = \frac{1}{2}\beta_{ijk}E_j(\omega)E_k(\omega). \quad (3b)$$

In (1), (3a), and (3b) we have neglected the frequency dispersion of the tensor  $\beta$ ; therefore all these formulas contain one and the same real tensor  $\beta_{ijk}$ , which is fully symmetrical in all the indices.

The differential cross section for the scattering of a wave of frequency  $\omega_0$  and a unit polarization vector  $\mathbf{e}_0$  by a pair of quanta with frequencies  $\omega_1$  and  $\omega_2$ , wave vectors  $\mathbf{k}_1$  and  $\mathbf{k}_2$ , and polarizations  $\mathbf{e}_1$  and  $\mathbf{e}_2$  is obtained with the aid of the standard first-order perturbation-theory formulas, and its value for the Hamiltonian (1) is

$$\frac{d\sigma}{d\omega_1 d\omega_2} = \frac{\hbar}{\pi^2} \frac{n_1 n_2}{n_0} \frac{\omega_0 \omega_1^3 \omega_2^3}{c^7} |e_{\alpha i} \beta_{ijk} e_{ij}^* e_{\alpha k}|^2 \delta(\omega_0 - \omega_1 - \omega_2). \quad (4)$$

Here  $n_1 = n(\omega_1)$ ,  $n_2 = n(\omega_2)$ , and  $n_0 = n(\omega_0)$  are the refractive indices of the medium at the corresponding frequencies.

For freely orienting molecules, the quadratic combination of the tensor components in the form  $\beta_{ijk} \beta_{lmn}$  should be averaged over the orientations. The corresponding expression for the correlator  $\langle \beta_{ijk} \beta_{lmn} \rangle$  is given in Appendix 1 and is determined by only two scalar parameters, namely by the sum  $B^2$  of the squares of all the components and by the dimensionless parameter  $\xi$ :

$$B^2 = \langle \beta_{ijk} \beta_{ijk} \rangle, \quad \xi = \langle \beta_{ijk} \beta_{kij} \rangle / B^2. \quad (5)$$

Since the parameters  $B^2$  and  $\xi$  are scalar, it is convenient to calculate them in a coordinate system that is rigidly connected with the molecule axes.

If the cross section (4) is summed over the polarizations of one of the quanta and integrated over the angles and frequencies of this quantum, then we obtain for the cross section for the appearance of quanta with frequency  $\omega_1$  and polarization  $e_1$  in the solid angle  $d\Omega_1$  in the PS process

$$\frac{d\sigma}{d\Omega_1 d\omega_1} = \frac{8\hbar}{3\pi} \frac{n_1 n_2}{n_0} \frac{\omega_0 \omega_1^3 (\omega_0 - \omega_1)^3}{c^7} \times B^2 \left\{ \frac{1}{9} \xi |e_{\alpha i} e_{\alpha i}|^2 + \frac{1}{10} \left( 1 - \frac{\xi}{3} \right) \left( 1 + |e_{\alpha i} e_{\alpha i}|^2 - \frac{2}{3} |e_{\alpha i} e_{\alpha i}|^2 \right) \right\}. \quad (6)$$

The cross sections (4) and (6) are symmetrical with respect to  $\omega_1 \rightleftharpoons \omega_2$  and have a rather sharp maximum at  $\omega_1 = \omega_2 = \omega_0/2$ . The cross sections (4) and (6) have no dependence on the scattering angles themselves, and for the cross section (6) the dependence on the polarizations reduces to two well-known types of scattering, namely scalar and symmetrical zero-trace scattering.

The total scattering cross section  $\sigma_{PS}$  is defined as the ratio of the total scattered power to the power density in the incident wave. This yields

$$\sigma_{PS} = \frac{1}{\hbar \omega_0} \sum_{\alpha i} \int \hbar \omega_1 \frac{d\sigma}{d\Omega_1 d\omega_1} d\Omega_1 d\omega_1 = \frac{1}{2} \sum_{\alpha i} \int \frac{d\sigma}{d\Omega_1 d\omega_1} d\Omega_1 d\omega_1 \approx 2.167 \frac{n^2(\omega_0/2)}{n(\omega_0)} \hbar c \left( \frac{\omega_0}{2c} \right)^8 B^2. \quad (7)$$

In the derivation of (7) we have replaced the true variation of the refractive index  $n(\omega_1)$  by its value  $n(\omega_0/2)$ , since the main contribution to  $\sigma_{PS}$  is made by quanta with  $\omega_1 \approx \omega_0/2$ . The number 2.167 stands for the rational fraction  $2^{11} \cdot 3^{-3} \cdot 5^{-1} \cdot 7^{-1}$ . It is interesting to note the very strong ( $\propto \omega_0^8$ ) dependence of the cross section  $\sigma_{PS}$  on the frequency. Taking into account the actually existing small dispersion of the tensor  $\beta$ , the cross section  $\sigma_{PS}$  in the visible region of the spectrum should increase with increasing frequency even somewhat more rapidly.

In the integration of (4) and (6) over the frequencies it is necessary to exclude the opacity regions at the frequencies  $\omega_1$  and  $\omega_2$ , where the parametric scattering

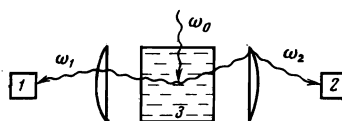


FIG. 1. Correlation experiments aimed at separating parametric scattering against a background of other types of scattering: 1, 2—photon counters, 3—investigated substance;  $\omega_0$  denotes the incident photon and  $\omega_1$  and  $\omega_2$  the pair of produced photons.

proper is already difficult to distinguish from the usual Raman scattering, etc. We note also that the value of  $\sigma_{PS}$  from (7) turns out to be independent of the parameter  $\xi$  and is determined only by the sum of the squares of the components of the tensor,  $B^2 = \beta_{ijk} \beta_{ijk}$ .

The order of magnitude of the tensor  $\beta_{ijk}$  for a noncentrally-symmetrical molecule far from the absorption bands can be estimated at  $\beta \sim \alpha/E_{at}$ , where  $\alpha \sim 10^{-23} \text{ cm}^3$  is the linear polarizability and  $E_{at} \sim 3 \times 10^6 \text{ cgs esu} \approx 10^9 \text{ C/cm}$  is the characteristic intensity of the field acting in the atom or molecule on the optical electron. In this case  $\beta \sim 3 \cdot 10^{-30} \text{ cgs esu}$ ; assuming  $B^2 \sim 3\beta^2 \sim 3 \cdot 10^{-59} (\text{cgs esu})^2$ , we obtain for the wavelength  $\lambda_0 = 0.35 \mu$  the value  $\sigma_{PS} \sim 10^{-35} \text{ cm}^2$ . If the molecules form a liquid, then we can estimate the density at  $N \sim 10^{22} \text{ cm}^{-3}$ . The extinction coefficient in this case is  $R = N\sigma \sim 10^{-13} \text{ cm}^{-1}$ , i.e.,  $10^{-13}$  incident quanta are scattered by one centimeter of the medium.

Let us discuss the possibility of observing parametric scattering of light by molecules. At a constant incident-radiation intensity  $I_0 \sim 10^{17} \text{ qu/sec}$  ( $P_0 \sim 0.03 \text{ W}$ ), the number of scattered quanta from one centimeter of path is  $2I_0 N\sigma L \sim 2 \cdot 10^4 \text{ qu/sec}$ . Assuming that the recording photoreceiver has a photocathode quantum efficiency  $\eta \sim 0.05$  and covers a fraction  $\sim 2 \times 10^{-2}$  of the total solid angle  $4\pi$ , we obtain for the counting rate  $i \sim 20 \text{ counts/sec}$ . The registration of this intensity by itself is perfectly feasible by photomultipliers cooled to  $t^\circ \sim -20 \text{ }^\circ\text{C}$ . Furthermore, the experiment does not call for monochromaticity and high directivity of the radiation, and therefore it is possible to use an incoherent source of ultraviolet radiation such as a mercury lamp.

A serious difficulty in the registration may be caused by the background of other types of scattering, luminescence from impurities, etc. It is possible to get rid of this background in part by means of spectral filters. The clearest proof of the observation of just parametric scattering would be the observation of the correlation  $\langle n_1 n_2 \rangle$  of the counts of the two counters 1 and 2 of Fig. 1. This correlation was discussed first in<sup>[5]</sup> and is due to the decay of the incident photon into just quantum pairs. A more detailed discussion of the correlation of the photocounts is given in Appendix 2.

The calculation of hyperscattering, i.e., of the intensity of radiation at the frequency  $\sim 2\omega_1$  when the incident radiation has a frequency  $\omega_1$  and a field amplitude  $E_1 = e_1 |E_1|$ , yields for the process the cross section

$$\sigma_{\text{hyp}} = \sigma_2 \frac{cn}{8\pi} |\mathbf{E}|^2, \quad \sigma_2 = \frac{(8\pi)^2}{12c} \frac{n_0}{n_1^2} \left( \frac{2\omega_1}{c} \right)^4 B^2 \left\{ \frac{3-\xi}{15} + |e_{\alpha\beta}|^2 \frac{2\xi-1}{15} \right\}. \quad (8)$$

Thus, the cross section for PS by molecules and the cross section of hyperscattering turn out to be uniquely connected with each other, since they are expressed in terms of the same constants.

In liquids, owing to the difference between acting field and the macroscopic field, the effective value of  $\beta_{ijk}$  is generally speaking different from the value of  $\beta_{ijk}$  in vacuum. In addition, owing to a certain correlation between the orientations of the neighboring molecules, the product  $N\sigma \sim N\beta^2$  in the coefficient of extinction of the PS should be taken to mean

$$N\beta^2 \rightarrow \int d^3\mathbf{r} \langle \delta\chi(0) \delta\chi(\mathbf{r}) \rangle, \quad (9a)$$

just as in the extinction coefficient for Rayleigh scattering we have

$$N\alpha^2 \rightarrow \frac{1}{(4\pi)^2} \int d^3\mathbf{r} \langle \delta\epsilon(0) \delta\epsilon(\mathbf{r}) \rangle. \quad (9b)$$

Here  $\delta\chi$  is the fluctuation of the macroscopic nonlinear polarizability,  $\alpha$  is the linear polarizability of the molecule,  $\delta\epsilon$  is the fluctuation of the dielectric constant, and  $N$  is the number of molecules per unit volume. It is easily seen, however, that the connection between the PS and hyperscattering cross sections remains unchanged, since both quantities are proportional to the right-hand side of (9a).

### 3. TRANSITION TO PARAMETRIC SCATTERING IN A CRYSTAL

The problem of parametric scattering in a plane layer of a non-centrally-symmetrical crystal of thickness  $L$  was considered numerous times in the literature (see, e.g., [3-6]). The simplest to obtain is the expression for the doubly differential (with respect to  $\mathbf{k}_1$  and  $\mathbf{k}_2$ ) scattering intensity

$$dI = 2^2 \chi^2 \hbar c I_0 \frac{\omega_0}{n_0 n_1^2 n_2^2} |\mathbf{k}_1| |\mathbf{k}_2| \frac{\sin^2[(\mathbf{k}_0 - \mathbf{k}_1 - \mathbf{k}_2)_z L/2]}{(\mathbf{k}_0 - \mathbf{k}_1 - \mathbf{k}_2)_z^2} \times \delta(\omega_0 - \omega_1 - \omega_2) \delta^{(2)}[(\mathbf{k}_0 - \mathbf{k}_1 - \mathbf{k}_2)_\perp] d\mathbf{k}_1 d\mathbf{k}_2. \quad (10)$$

Here  $I_0$  [erg/sec] is the power of the incident beam;  $\omega_0$ ,  $\omega_1$ ,  $\omega_2$ ,  $\mathbf{k}_0$ ,  $\mathbf{k}_1$ ,  $\mathbf{k}_2$ ,  $\mathbf{e}_0$ ,  $\mathbf{e}_1$ , and  $\mathbf{e}_2$  are the frequencies, wave vectors, and unit vectors of the polarization of the incident and two scattered waves, respectively;  $n_0$ ,  $n_1$ , and  $n_2$  are the refractive indices at the frequencies  $\omega_0$ ,  $\omega_1$ , and  $\omega_2$ . The  $z$  axis, along which the wave vector  $\mathbf{k}_0$  is directed, is perpendicular to the scattering layer, and  $L$  is the thickness of the layer along the  $z$  axis, while the layer is assumed to be infinite along the axes  $x$  and  $y$ . The subscripts  $z$  and  $\perp$  denote the projections of the detuning vector on the  $z$  axis and a plane perpendicular to it, respectively, and  $\chi^2 = |\chi_{ijk} e_{0i}^* e_{1j}^* e_{2k}^*|^2$ . We shall henceforth disregard the dependence of  $\chi^2$  on the polarization and take  $\chi^2$  to mean a certain averaged value.

In this section we discuss the behavior of the inte-

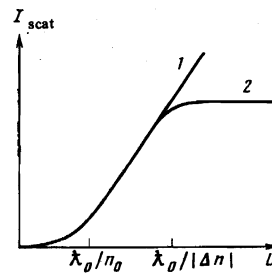


FIG. 2. Dependence of the total intensity of the photons parametrically scattered in a crystal layer on the layer thickness  $L$ . The branch 1 of the curve corresponds to exchange PSC in the case of allowed synchronism,  $\Delta n = n(\omega_0) - n(\omega_0/2) < 0$ . The branch 2 of the curve describes PSC of the layer surfaces in the case of forbidden synchronism,  $\Delta n > 0$ .

grated (over all angles and frequencies) scattering intensity in a layer for a normally incident wave with frequency  $\omega_0$ , when the thickness of this layer is varied from  $L \ll \lambda_0/n_0$  to  $L \rightarrow \infty$ . To obtain explicit expressions for the integrated quantities we assume the following simplified model of the medium. We assume that with respect to the linear optical properties the medium at the frequencies  $\omega_1$  and  $\omega_2$  of the scattered field can be regarded as isotropic and non-dispersive, with a refractive index  $n_1$ , while at the frequency  $\omega_0$  the medium has a refractive index  $n_0$ , with  $|\Delta n| = |n_0 - n_1| \ll n_0 \sim 1$ . We neglect also the dependence of the quadratic polarizability  $\chi$  on the frequencies. We note that the qualitative character of the dependence of the scattering intensity on the layer thickness  $L$ , which is discussed is discussed below, is preserved also if these assumptions are not made. The dependence of the integrated intensity of parametric scattering in a crystal (PSC) on the thickness is given by a plot of the type shown in Fig. 2.

On the segment  $0 \leq L \leq \lambda_0/n_0$ , the intensity increases like the square of  $L$ . Integration of (10) yields an order of magnitude

$$I_{\text{scat}} \approx 3.37\pi \frac{\hbar c}{n_0} \left( \frac{\omega_0}{c} \right)^6 L^2 \chi_{ijk}^2 I_0. \quad (11)$$

The angular distribution of the scattered photons is in this case approximately isotropic, although there is a small spike near the direction in the plane of the layer  $\theta = \pi/2$ . This isotropy is due to the fact that at  $L \ll \lambda_0/n_0$  the conservation law need be satisfied only for the transverse components of the momentum.

On the segment  $\lambda_0/n_0 \leq L \leq \lambda_0/|\Delta n|$ , the intensity increases linearly with  $L$ ; from (10) we obtain, in order of magnitude,

$$I_{\text{scat}} \approx 2.12\pi^2 \frac{\hbar c}{n_0 n_1} \left( \frac{\omega_0}{c} \right)^5 L \chi_{ijk}^2 I_0. \quad (12)$$

The angular distribution of the scattered photons narrows down with increasing  $L$  like  $\Delta\theta \sim (\lambda_0/L)^{1/2}$  around the direction of propagation of the incident wave, and at  $L \sim \lambda_0/|\Delta n|$  it amounts to  $\Delta\theta \sim |\Delta n|^{1/2}$ .

The subsequent behavior of the scattering intensity depends on the sign of  $\Delta n = n_0 - n_1$ . If  $n_0 < n_1$ , then it is

possible to satisfy the synchronization conditions  $\omega_0 = \omega_1 + \omega_2$  and  $\mathbf{k}_0 = \mathbf{k}_1 + \mathbf{k}_2$  at certain scattering angles  $\theta_1$  and  $\theta_2$ ; in particular, if  $\omega_1 \approx \omega_2 \approx \omega_0/2$ , then  $\theta_1 \sim \theta_2 \sim |\Delta n|^{1/2}$ . In this case the linear growth of the scattered intensity continues with the same slope up to  $L \rightarrow \infty$ , and the angular width of the scattered radiation is  $\Delta\theta \sim |\Delta n|^{1/2}$ .

We consider now the case  $n_0 > n_1$  (this is precisely the relation typical of waves of one and the same type if there are no absorption bands in the interval between  $\omega_0/2$  and  $\omega_0$ ). The synchronism conditions cannot be satisfied in this case for any pair of directions or of frequencies of the scattered photons 1 and 2. The integration of (10) yields for this case, in order of magnitude,

$$I_{\text{scat}} \approx 2.12\pi \frac{\hbar c}{n_1 n_0 \Delta n} \left(\frac{\omega_0}{c}\right)^4 \chi_{ijk}^2 l_0. \quad (13)$$

Thus, at  $n_0 > n_1$ , i. e., in the absence of synchronism, the scattering intensity is independent of  $L$ . This is as if the input and output surface layers of thickness  $\sim \lambda/\Delta n$  of our crystal, the total thickness of which is  $L$ , were to scatter in accordance with the law (12). The main fraction of the photons scattered in the surface layers of the crystal has a smooth angular distribution with  $\Delta\theta \sim (\Delta n)^{1/2}$  near the propagation direction of the incident wave. This "surface" scattering is close in its character to the so called "background" scattering considered by Kleinman.<sup>[4]</sup>

We note that surface parametric scattering of this type is essentially connected with the jump-like change of  $\chi(\mathbf{r})$  on the crystal boundary. One can imagine a model of the medium, in which  $\chi(z)$  and  $\varepsilon(z)$  vary smoothly over distances  $\Delta z \gg \lambda_0/|\Delta n|$ . For this model, parametric scattering in the case of allowed synchronism will be of the volume type, as before, i. e., the scattering intensity will be determined by expression (12), and in the case of forbidden synchronisms, the scattering becomes of the surface type, but with an intensity much less than given by (13).

The growth of the scattering intensity  $\sim L$  for allowed synchronism can be interpreted in terms of a constant cross section per unit volume (i. e., extinction coefficient  $R$ ). Dividing  $R$  by the number of molecules per unit volume  $N$ , we obtain for the cross section of parametric scattering of light in the crystal, per molecule

$$\sigma_{\text{PSC}} \sim \left(\frac{\chi}{N}\right)^2 \hbar c \left(\frac{\omega_0}{2c}\right)^4 N \lambda_0^3. \quad (14)$$

For the purpose of comparison with the cross section for PS by randomly oriented molecules (with formula (7)) we assume that  $\chi \sim N\beta$ , where  $\beta$  is the hyperpolarizability of one molecule. It follows that from (14) and (7) that

$$\sigma_{\text{PSC}} \sim \sigma_{\text{PS}} N \lambda_0^3. \quad (15)$$

This means that the unification of the molecules in a crystal with fixation of the orientation leads (if synchronism is allowed) to an increase of the cross section per molecule by a factor  $N \lambda_0^3$ . On the other hand, if the crystal dimensions  $l$  satisfy the inequality  $l \lesssim \lambda_0/$

$|\Delta n|$ , then relation (15) is satisfied independently of the sign of  $\Delta n$ . The last circumstance uncovers a possibility for observing PS by powders of non-central-symmetry crystals (cf. the powder method<sup>[7]</sup> for measuring  $\chi$  in a non-central-symmetry crystal for the generation of the second harmonic of light).

In conclusion, the authors thank D. N. Klyshko for useful discussions.

## APPENDIX 1: CORRELATOR OF THE TENSOR $\beta_{ijk}$

For an isotropic medium, the general form of the correlator for a tensor  $\beta_{ijk}$  which is fully symmetrical in all the indices is described by two parameters,  $C^{(1)}$  and  $C^{(3)}$ , in accordance with the two irreducible representations of such a tensor—of rank 1 and 3:

$$\langle \beta_{ijk} \beta_{lmn} \rangle = C^{(1)} T_{ijk|lmn}^{(1)} + C^{(3)} T_{ijk|lmn}^{(3)}; \quad (1.1)$$

$$T_{ijk|lmn}^{(1)} = \delta_{ij} \delta_{kl} \delta_{mn} + \delta_{im} \delta_{jk} \delta_{ln} + \delta_{in} \delta_{jk} \delta_{lm} + \delta_{jl} \delta_{ik} \delta_{mn} + \delta_{jm} \delta_{ik} \delta_{ln} + \delta_{jn} \delta_{ik} \delta_{lm} + \delta_{kl} \delta_{ij} \delta_{mn} + \delta_{km} \delta_{ij} \delta_{ln} + \delta_{kn} \delta_{ij} \delta_{lm}, \quad (1.2)$$

$$T_{ijk|lmn}^{(3)} = \delta_{ij} \delta_{jm} \delta_{kn} + \delta_{ji} \delta_{im} \delta_{kn} + \delta_{kl} \delta_{jm} \delta_{in} + \delta_{il} \delta_{km} \delta_{jn} + \delta_{im} \delta_{jn} \delta_{kl} + \delta_{km} \delta_{jl} \delta_{in} - 2/3 T_{ijk|lmn}^{(1)},$$

$$C^{(1)} = 1/75 \langle \beta_{ijk} \beta_{jkl} \rangle, \quad C^{(3)} = 1/42 \langle \beta_{ijk} \beta_{ijk} \rangle - 3/5 \langle \beta_{ijk} \beta_{jkl} \rangle.$$

## APPENDIX 2: STATISTICS OF THE PHOTOCOUNTS IN PARAMETRIC SCATTERING

To describe the photon-counting experiments schematically illustrated in Fig. 1, it is convenient to introduce a generating function  $Q(\lambda_1, \lambda_2)$  for the photocounts  $n_1$  and  $n_2$  in the elementary observation act

$$Q(\lambda_1, \lambda_2) = \langle (1 - \lambda_1)^{n_1} (1 - \lambda_2)^{n_2} \rangle, \quad (2.1)$$

where the angle brackets denote averaging over the ensemble of all possible fluctuations that occur in the system. We then obtain for  $Q(\lambda_1, \lambda_2)$  (cf. [5, 6])

$$Q(\lambda_1, \lambda_2) = \exp \{ -\lambda_1 \langle n_1 \rangle - \lambda_2 \langle n_2 \rangle + 1/2 \lambda_1^2 A_{11} + 1/2 \lambda_2^2 A_{22} + \lambda_1 \lambda_2 A_{12} \}. \quad (2.2)$$

In this formula,  $\langle n_{1,2} \rangle$  are the average numbers of the counts during the time of the elementary observation act:

$$\langle n_{1,2} \rangle = \tau_0 \left[ i_{1,2} + I_0 N L \sum_{\mathbf{n}} \int \frac{d\sigma}{d\omega d\omega'} \eta_{1,2}(\mathbf{n}, \omega, \mathbf{e}) d\omega d\omega' \right]. \quad (2.3)$$

Here  $i_{1,2}$  is the background current (counts/sec), including the dark current of the photomultiplier and the current from the background illumination;  $\eta_k(\mathbf{n}, \omega, \mathbf{e})$  denotes the quantum efficiency of the registration, by the  $k$ -th counter of the photons of frequency  $\omega$  and polarization  $\mathbf{e}$  in the propagation direction  $\mathbf{n}$ . The parameters  $A_{ik}$  (at  $i, k = 1, 2$ ) are equal to

$$A_{ik} = \tau_0 I_0 N L \sum_{\mathbf{e}_1} \sum_{\mathbf{e}_2} \int \frac{d\sigma}{d\omega_1 d\omega_2} \times \eta_i(\omega_1, \mathbf{n}_1, \mathbf{e}_1) \eta_k(\omega_2, \mathbf{n}_2, \mathbf{e}_2) d\omega_1 d\omega_2 d\omega_2. \quad (2.4)$$

The correlation of the photocounts  $n_1$  and  $n_2$  is given by the expressions

$$\langle n_1 n_2 \rangle = \langle n_1 \rangle \langle n_2 \rangle + A_{12}, \quad \langle n_i^2 \rangle = \langle n_i \rangle^2 + \langle n_i \rangle + A_{11},$$

$$\langle n_2^2 \rangle = \langle n_2 \rangle^2 + \langle n_2 \rangle + A_{22}. \quad (2.5)$$

We note that the second and third terms in (2.5) are proportional to  $\tau_0$  (and not  $\tau_0^2$  as the first), and describe the effective production of quantum pairs. At a sufficiently short time of the elementary observation act,  $\tau_0 \sim 10^{-8}$  sec, corresponding to the time resolution of high-sensitivity photomultipliers, the correlation  $A_{12}$  can apparently be registered even at a relatively intense background illumination. Thus, an estimate obtained by the methods of [8] yields the necessary accumulation time (at  $\langle n_1 \rangle = \langle n_2 \rangle$ ):

$$T \sim \tau_0 M^2 \langle n_1 \rangle^2 / A^2, \quad (2.6)$$

where  $M$  is the required signal/noise ratio after averaging the results ( $T/\tau_0$ ) of the elementary experiments. For the example discussed in the text, at  $\tau_0 \sim 10^{-8}$  sec, we obtain  $A_{12} \sim 10^{-10}$ . Assuming  $M \sim 3$  and a dark (or extraneous illumination) current  $i_0 \sim 3 \times 10^3$  counts/sec, we obtain  $T \sim 10^4$  sec (approximately 3 hours). This time is acceptable for observations by the photon-counting method (see the discussion in [8]).

### APPENDIX 3: ESTIMATES OF THE CROSS SECTIONS FOR MOLECULAR SCATTERING OF LIGHT

In this appendix we present rough estimates of the PS, PSC, and hyperscattering cross sections. To compare these processes with ordinary types of light scattering, it is appropriate to reproduce here also the well known estimates for the latter. The cross section for Rayleigh scattering in a gas is determined by the intensity  $I \approx (\dot{d})^2 n c^{-3}$  of the radiation of a dipole  $\mathbf{d} = \alpha \mathbf{E}$ , induced in a medium with a refractive index  $n$  by an incident wave of amplitude  $\mathbf{E}$  in a molecule with polarizability  $\alpha$ . Assuming  $\ddot{d} \sim \omega_0^2 d$ , where  $\omega_0$  is the frequency of the incident light, and dividing the radiative intensity  $I$  (erg/sec) by the powder density  $c n_0 |\mathbf{E}|^2 / 8\pi$ , in the incident wave, we obtain the scattering cross section ( $\text{cm}^2$ ), which, apart from a factor on the order of unity, is given by [1]

$$\sigma_{\text{Rayleigh}} \approx (\omega_0/c)^4 \alpha^2. \quad (3.1)$$

The polarizability  $\alpha$  of a molecule with moderate dimensions in the visible region of the spectrum (far from strong absorption bands) can be estimated as the cube of the Bohr radius  $a_0$ , or somewhat larger:  $\alpha \sim (1-10)a_0^3$ ; at  $\lambda = 0.5 \mu$  and  $\alpha \sim 10^{-23} \text{ cm}^3$  we have  $\sigma_{\text{Rayleigh}} \sim 10^{-25} \text{ cm}^2$ .

The scattering or extinction coefficient  $R$  [ $\text{cm}^{-1}$ ] for a gas is obtained by multiplying  $\sigma$  by the density  $N$  [ $\text{cm}^{-3}$ ],  $R = N\sigma$ . For liquids,  $N \sim 10^{22} \text{ cm}^{-3}$ , in which case  $R \sim 10^{-4} \text{ cm}^{-1}$ . Strictly speaking, in a liquid, the scattering cross section per molecule is determined only as  $\sigma = R/N$ , and is itself a function of the density and temperature (thus, for scalar type of scattering we have  $R \propto (\partial \epsilon / \partial \rho)^2 (\delta \rho)^2$ , where  $\delta \rho$  is the density fluctuation and  $\epsilon$  is the permittivity). Therefore at low temperature the cross section per molecule can be much lower than (3.1), and near phase-transition points it can be much larger than (3.1); these differences are connected with the correlation of the positions of the various molecules.

For non-extremal conditions, the estimate (3.1) exaggerates a scattering cross section of the scalar type by an approximate factor  $(v_s - v_T)^2$ , where  $v_s$  is the speed of sound in the condensed medium and  $v_T$  is the thermal velocity of the molecules making up this medium. However, for not too large molecules at room temperature, this factor decreases the true cross section in comparison with (3.1) by only one or two orders of magnitude.

The estimate (3.1) is quite suitable for scattering by orientation fluctuations of optically anisotropic molecules, since the orientation of the different molecules is weakly correlated even in liquids (but not in liquid crystals). The quantity  $\alpha^2$  in (3.1) must in this case be replaced by the square of the anisotropic (zero-trace) part of the polarizability  $\tilde{\alpha}_{ijk} = \alpha_{ijk} - \frac{1}{3} \delta_{ijk} \alpha_{ii}$ ; for typical molecules we have  $\tilde{\alpha}_{ijk}^2 \sim (0.5 - 0.1) \alpha^2$ .

The cross section for the vibrational Raman scattering  $\sigma_{\text{vib}}$  is also given by the estimate (3.1), with the substitution  $\alpha^2 \rightarrow (\partial \alpha / \partial q)^2 \langle \delta q^2 \rangle$ , where at not too high temperatures, i.e., at  $kT \ll \hbar \Omega_{\text{vib}}$ ,  $\langle \delta q^2 \rangle$  is the mean square of the zero-point fluctuations of the vibrational coordinates. Estimating

$$\frac{\partial \alpha}{\partial q} \sim (1-0.1) \frac{\alpha}{a_0} \quad \langle \delta q^2 \rangle \sim a_0^2 (m/M)^{1/2},$$

where  $m$  is the electron mass and  $M$  is the "mass" of the molecular vibrations, we obtain

$$\sigma_{\text{vib}} \sim (1-10^{-2}) \left( \frac{m}{M} \right)^{1/2} \sigma_{\text{Rayleigh}} \sim (10^{-2} - 10^{-5}) \sigma_{\text{Rayleigh}}$$

which yield, with the same wavelength of the incident light,  $\sigma_{\text{vib}} \sim 10^{-27} - 10^{-30} \text{ cm}^2$ ; the dependence on the frequency of the incident light  $(\omega_0 - \Omega)^4$  is practically the same as for Rayleigh scattering, since  $\Omega \ll \omega_0$ .

The fact that the molecule has no symmetry center allows it to have a quadratic polarizability  $\beta_{ijk}$ , so that the dipole moment of the molecule at high intensity of the incident radiation of frequency  $\omega_0$  acquires an additional term of the type  $d_i = \beta_{ijk} E_j E_k$ . The intensities of the photons of frequency  $2\omega_0$  emitted by different freely oriented molecules are additive. Division of the radiation power  $(\dot{d})^2 n c^{-3}$  by the flux density yields the hyperscattering cross section

$$\sigma_{\text{hyp}} (\text{cm}^2) = \sigma_z \frac{c n_0}{8\pi} |E|^2; \quad \sigma_z \sim \frac{8\pi}{c n_0} \beta^2 \left( \frac{2\omega_0}{c} \right)^4. \quad (3.2a)$$

In the visible range, far from resonances, we can assume for  $\beta$  the estimate  $\beta \sim \alpha E_{\text{at}}^{-1} \sim a_0^3 E_{\text{at}}^{-1}$ , where  $E_{\text{at}} \sim (10^6 - 10^7) \text{ cgs esu}$  is the intensity of the intra-atomic field,  $E_{\text{at}} \sim e/a_0^2$ . In this case

$$\sigma_z \sim 16 \sigma_{\text{Rayleigh}} \frac{8\pi}{c n_0 E_{\text{at}}^2} \sim (10^{-41} - 10^{-43}) \frac{\text{cm}^4}{\text{W}} \quad (3.2b)$$

Parametric scattering of light by molecules is analogous to a considerable degree to Raman scattering, with the substitution  $(\partial \alpha / \partial q) \delta q \rightarrow \beta \delta E$ , where  $\delta E$  are the vacuum fluctuations of the electromagnetic fields. If the

incident photon decays in the course of the Stoke's Raman scattering into a scattered photon and a molecular phonon, then in PS the incident photon decays into two photons. The value  $\langle \delta E^2 \rangle$ , which depends on the frequency interval in which we are considering the fluctuations  $\delta E$ , can be easily estimated. We assume a frequency interval  $0 < \omega \lesssim \omega_1 \approx \omega_0/2$  and stipulate that in the volume  $\sim \lambda_1^3 = (c/\omega_1)^3$  the energy  $\lambda_1^3 \delta E^2 n / 8\pi$  be equal to  $\hbar\omega_1/2$ , whence

$$(\delta E_{vac})^2 \sim \frac{4\pi}{n} \hbar c \left( \frac{\omega_1}{c} \right)^4 \sim (10^9 \text{ cgs esu})^2 \sim \left( 3 \cdot 10^4 \frac{\text{V}}{\text{cm}} \right)^2;$$

The last figure is given for  $\lambda_1 = 0.7 \mu$ . Thus, the PS cross section turns out to be proportional to  $\omega_0^8$ :

$$\sigma_{PS} \sim \beta^2 \left( \frac{\omega_0}{2c} \right)^8 \frac{4\pi}{n} \hbar c \sim \sigma_{\text{Rayleigh}} \frac{(\delta E_{vac})^2}{E_{at}^2} \sim \sigma_2 \frac{cn}{8\pi} (\delta E_{vac})^2 \quad (3.3)$$

and numerically we have  $\sigma_{PS} \sim 10^{-36} - 10^{-34} \text{ cm}^2$  for  $\lambda_0 = 0.35 \mu$ . The dimensionless factor  $(\delta E_{vac})^2/E_{at}^2$  can be written symbolically in the form  $(\omega_1/\omega_{at})^4 (e^2/\hbar c)^3$ , where  $e$  is the electron charge,  $e^2/\hbar c = 1/137$  and  $\omega_{at} \sim Ry/\hbar$  is the characteristic frequency of the ultraviolet absorption bands of the molecules.

The unification of  $K$  of equally oriented molecules into one microcrystal with dimensions smaller than the wavelength  $\lambda$  leads to an increase of the PS cross section (just as in the case of Rayleigh scattering):  $\beta^2 \rightarrow K^2 \beta^2$ , so that the PS cross section per molecule increases by a factor  $K$ . This increase exhibits saturation when the dimensions of the crystallite become comparable with  $\lambda$ .

The intensity of the parametric scattering in a crystal (PSC) can be very roughly estimated by recognizing that the vacuum fluctuations of the electromagnetic field, at the same instant of time, are correlated over a distance  $\lesssim \lambda_2 \approx 2\lambda_0$ . The independent scattering elements can then be taken to be the volumes  $\sim \lambda_2^3$ . Their hyperpolarizability is  $\beta \approx \chi \lambda_2^3$ , where  $\chi$  is the macroscopic quadratic polarizability of the crystal. As a result we find that the PSC cross section per molecule is equal to

$$\sigma_{PSC} = R_{PSC} N^{-1} \sim \frac{8\pi \hbar c}{N} \chi^2 \left( \frac{\omega_0}{2c} \right)^8 \quad (3.4)$$

and  $\sigma_{PSC} \sim 10^{30} - 10^{32} \text{ cm}^2$  for  $\lambda_0 = 0.5 \mu$ . Thus, if we assume  $\chi \sim N\beta$ , then

$$\sigma_{PSC}/\sigma_{PS} \sim N\lambda^3, \quad (3.5)$$

which corresponds to saturation of both of the cross sections for PS by the crystallite at dimensions  $\sim \lambda$ .

The foregoing estimate of the PSC is very crude; a substantial role in the formation of the PSC is played by

the fact that at unequal times the correlation of the scattering perturbations—vacuum fluctuations of the fields—propagates with the speed of light over a distance much larger than  $\lambda$ . Therefore the interference of the fields scattered by different volume elements greatly narrows down the angular distribution; the PSC is directed mainly forward as a result of the synchronism conditions  $\mathbf{k}_0 = \mathbf{k}_1 + \mathbf{k}_2$ . A detailed analysis of PSC (see<sup>[3-6]</sup> and Sec. 3 of the present paper) shows that the estimate (3.4) is meaningful only for the case when the synchronism condition is satisfied. It is easy to verify that the decrease of the total solid angle from  $4\pi$  to the value  $\Delta\Omega \sim \Delta\theta^2 \sim |\Delta n|$  and the corresponding decrease of the mean squared value  $\langle E_{vac}^2 \rangle$  are compensated by an increase, by the same factor, of the transverse dimension of the fluctuation coherence. The fact that the scattering through the indicated small angles is formed precisely by such large (with respect to the transverse dimension) region is just a manifestation of the effect of enhancement due to a large number of particles. We find thus that when account is taken of the synchronism condition, the PSC cross section per molecule amounts to  $\sigma_{PSC} \sim \sigma_{PS} N \lambda^3$ . On the other hand, if the synchronism condition cannot be satisfied (because the refractive index  $n(\omega_0)$  is larger than the refractive indices  $(n(\omega_1)$  and  $n(\omega_2))$  at all admissible  $\omega_1$  and  $\omega_2$ ), then only molecules of the surface layers of the crystals produce scattering (with cross section (3.4)). From the uncertainty relation it follows that the thickness of these layers is  $\Delta L \sim (\Delta k)^{-1} \sim \lambda(n_0 - n_1)^{-1}$ , which agrees with the result obtained in Sec. 3.

<sup>1)</sup>This quantity characterizes more readily the cross section  $d\sigma/d\Omega$  per unit solid angle; incidentally, according to our terminology  $4\pi$  is a factor on the order of unity.

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