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Second-Harmonic Generated by Self-Squeezed Light in Isotropic Medium. The Role of Light Intensity-Dependent Effects and Molecular-Statistical Structure*

S. Kielich, R. Tanaś, and R. Zawodny

Nonlinear Optics Division, Institute of Physics, A. Mickiewicz University, PL-60-780 Poznań, Poland

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Abstract. An isotropic medium with electrically removed centre of symmetry in which a fundamental wave at frequency ω generates the second harmonic at 2ω is considered. The two waves give rise to self-acting effects modifying the refractive indices at ω and/or 2ω (self-induced ellipse rotation, optical Kerr effect). For this physical situation, an effective interaction Hamiltonian is introduced involving nonlinear coupling parameters, discussed versus the dc electric field and temperature as well as the density, concentration and molecular structure of the medium. The solutions of the respective quantum equations for the field operators at ω and 2ω permit, in particular, the calculation of the variances for a novel process of second-harmonic generation by light, self-squeezed in an isotropic medium. It is shown that squeezing in the out-of-phase component of the second harmonic beam follows, with some delay, after self-squeezing in the in-phase component of the fundamental beam.

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The pioneering observations of the second harmonic of laser light in quartz crystal (with no centre of symmetry) by Franken et al. [1] started the epoch-making evolution of non-linear optics [2]. In the quantum picture we deal here with a nonlinear elementary process in which two photons are annihilated and one photon with doubled frequency is created in the direction of light propagation. Intense laser light is the cause of many nonlinear optical effects; here, we restrict ourselves to mentioning the optical Kerr effect [3] and self-induced ellipse rotation [4] (strictly speaking, elliptical birefringence [5]). In optically active bodies, moreover intensity-dependent optical activity is induced [6]. Mayer [7] succeeded in demonstrating the occurrence of second-harmonic generation in gases, the dipolar molecules of which undergo reorientation in the dc electric field [8].

In recent years, nonlinear optical processes have been shown to play a quite exceptionally great role in the generation of squeezed states of the electromagnetic field, which are manifestations of the quantum nature of light. Among the numerous nonlinear processes hitherto discussed, we shall direct our attention to squeezing as it occurs in second-harmonic generation [9–14] and to self-squeezing in nonlinear light propagation [15]. Recently, several authors have announced observations of squeezing in different nonlinear processes [16–19], in particular Kimble and Hall [20] in interacavity harmonic conversion.

In the present paper we consider the situation when an intense light wave of fundamental frequency ω is incident on an isotropic medium in a weak dc electric field leading to generation of the second harmonic and to decay of the latter into the fundamental wave. In the

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medium, simultaneously, self-induced effects take place modifying nonlinearly its refractive indices at ω and/or 2ω and causing optical birefringence (optical Kerr effect) at the frequencies ω and 2ω. We derive classical as well as quantum equations for the (slowly variable) amplitudes of the electric fields in the processes under consideration. In fact, in these complex processes we are dealing with an entirely new phenomenon, residing in generation of the second harmonic by the self-squeezed light arising in the isotropic medium. In addition, it presents a manifestation of interaction between squeezed light and matter; it is highly promising with a view to applications in practice, e.g., in molecular optical engineering. With this in mind we shall concentrate on the nonlinear coupling parameters occurring in the equations of motion, parameters dependent on the dc electric field strength as well as the statistical-molecular structure of the medium and its density, concentration and temperature. The numerical values of these nonlinear coupling parameters can be determined from measurements of the respective intensity-dependent variations of the refractive indices or dc-field-induced second-harmonic generation. All the above enumerated external and internal factors enable us to control the efficiency of quantum field generation in isotropic media.

1. Classical Phenomenological Approach

We assume the electric vector $\mathbf{E}(\mathbf{r}, t)$ at the time-space point $(\mathbf{r}, t)$ to be the superposition of two fields, with the fundamental frequency ω and the second-harmonic frequency 2ω, respectively (with the third harmonic being neglected)

$$\mathbf{E}(\mathbf{r},t)=\mathbf{E}^{+}(\omega)\mathrm{e}^{\mathrm{i}(\mathbf{k}_{\omega}\cdot\mathbf{r}-\omega t)} + \mathbf{E}^{+}(2\omega)\mathrm{e}^{\mathrm{i}(\mathbf{k}_{2\omega}\cdot\mathbf{r}-2\omega t)}+\text{c.c.}, \tag{1}$$

where $\mathbf{k}_{\omega}$ and $\mathbf{k}_{2\omega}$ are the respective wave vectors.

Our interest bears on the nonlinear interaction of the field (1) and the medium. Classically, it can be expressed by the time-averaged free energy [2];

$$\begin{aligned} F_{NL}=&-\chi_{ijk}(-2\omega,\omega,\omega)\\ &\times E_i^{-}(2\omega)E_j^{+}(\omega)E_k^{+}(\omega)\mathrm{e}^{\mathrm{i}\Delta\mathbf{k}\cdot\mathbf{r}}+\text{c.c.}\\ &-\tfrac{3}{4}[\chi_{ijkl}(-\omega,-\omega,\omega,\omega)\\ &\times E_i^{-}(\omega)E_j^{-}(\omega)E_k^{+}(\omega)E_l^{+}(\omega)+\text{c.c.}]\\ &-3[\chi_{ijkl}(-\omega,-2\omega,\omega,2\omega)\\ &\times E_i^{-}(\omega)E_j^{-}(2\omega)E_k^{+}(\omega)E_l^{+}(2\omega)+\text{c.c.}]\\ &-\tfrac{3}{4}[\chi_{ijkl}(-2\omega,-2\omega,2\omega,2\omega)\\ &\times E_i^{-}(2\omega)E_j^{-}(2\omega)E_k^{+}(2\omega)E_l^{+}(2\omega)+\text{c.c.}], \end{aligned} \tag{2}$$

with

$$\Delta\mathbf{k}=2\mathbf{k}_{\omega}-\mathbf{k}_{2\omega}, \tag{3}$$

and the numerical factors resulting from frequency degeneracy [5] as well as the Einstein summation convention over recurring indices $i, j, k, l = x, y, z$ taken into account.

In the phenomenological approach, (1) provides the starting point for calculating the vector components of nonlinear polarisation at the frequency $\Omega=\omega$ or 2ω:

$$P_i^{\pm}(\Omega)_{NL}=-\frac{\partial F_{NL}}{\partial E_i^{\mp}(\Omega)}. \tag{4}$$

By (2 and 4), we get for the nonlinear polarisation at ω

$$\begin{aligned} P_i^{+}(\omega)_{NL}=&2\chi_{ijk}(-\omega,-\omega,2\omega)\\ &\times E_j^{-}(\omega)E_k^{+}(2\omega)\mathrm{e}^{-\mathrm{i}\Delta\mathbf{k}\cdot\mathbf{r}}\\ &+3\chi_{ijkl}(-\omega,-\omega,\omega,\omega)E_j^{-}(\omega)E_k^{+}(\omega)E_l^{+}(\omega)\\ &+6\chi_{ijkl}(-\omega,-2\omega,\omega,2\omega)E_j^{-}(2\omega)E_k^{+}(\omega)E_l^{+}(2\omega). \end{aligned} \tag{5}$$

Above, the third-rank tensor $\chi_{ijk}(-\omega,-\omega,2\omega)$ defines the second-order nonlinear susceptibility, related with a process which is the inverse of second-harmonic generation: it consists in the reconversion of part of the second harmonic at 2ω back into the fundamental nonlinear wave ω. The fourth-rank tensor $\chi_{ijkl}(-\omega, -\omega, \omega, \omega)$ determines the third-order nonlinear electric susceptibility, related with the self-induced intensity-dependent refractive index at ω [3–6]. Similarly, the nonlinear susceptibility tensor $\chi_{ijkl}(-\omega, -2\omega, \omega, 2\omega)$ determines the optical Kerr effect at ω [3] produced by the intensity of the second harmonic $|E^{-}(2\omega)|^2$.

With regard to (2 and 4) we obtain, for the nonlinear polarisation at 2ω,

$$\begin{aligned} P_i^{+}(2\omega)_{NL}=&\chi_{ijk}(-2\omega,\omega,\omega)\\ &\times E_j^{+}(\omega)E_k^{+}(\omega)\mathrm{e}^{\mathrm{i}\Delta\mathbf{k}\cdot\mathbf{r}}\\ &+6\chi_{ijkl}(-2\omega,-\omega,2\omega,\omega)\\ &\times E_j^{-}(\omega)E_k^{+}(2\omega)E_l^{+}(\omega)\\ &+3\chi_{ijkl}(-2\omega,-2\omega,2\omega,2\omega)\\ &\times E_j^{-}(2\omega)E_k^{+}(2\omega)E_l^{+}(2\omega), \end{aligned} \tag{6}$$

where the third-rank tensor $\chi_{ijk}(-2\omega, \omega, \omega)$ is that of the second-order nonlinear susceptibility responsible for second-harmonic generation [1], whereas

$\chi_{ijkl}(-2\omega, -\omega, 2\omega, \omega)$ describes the nonlinear variations of the refractive index at 2ω [21] due to the intensity $|E^-(\omega)|^2$. Similarly, the nonlinear susceptibility tensor $\chi_{ijkl}(-2\omega, -2\omega, 2\omega, 2\omega)$ describes the self-induced intensity-dependent refractive index at 2ω.

The effects represented by (5 and 6) correspond to nonresonant nondissipative processes, related with the real part of the respective nonlinear susceptibility. Here, the following permutation symmetry relations are fulfilled [2]

$$\begin{aligned}
&\chi^*_{ijkl}(-\omega, -2\omega, \omega, 2\omega) = \chi_{lkji}(-2\omega, -\omega, 2\omega, \omega),\\
&\chi^*_{ijkl}(-\omega, -2\omega, \omega, 2\omega) = \chi_{klij}(-\omega, -2\omega, \omega, 2\omega),\\
&\chi^*_{ijkl}(-\omega, -\omega, \omega, \omega) = \chi_{klij}(-\omega, -\omega, \omega, \omega),\\
&\chi^*_{ijk}(-\omega, -\omega, 2\omega) = \chi_{kij}(-2\omega, \omega, \omega).
\end{aligned} \tag{7}$$

Our interest bears on isotropic centrosymmetric media. In the electric-dipole approximation, their χ_{ijk}-components vanish, and second-harmonic generation is forbidden. An externally applied dc electric field destroys the centre of symmetry and the medium is then endowed with the symmetry C_{∞_v} so that it becomes capable of generating the second harmonic. As long as the dc electric field E^0_y is weak (it is assumed to act along the y-axis of the laboratory coordinate system xyz) we are justified in writing [8]

$$\begin{aligned}
\chi^{2\omega}_{ijk}(\mathbf{E}^0) &= \chi^{2\omega}_{ijk}(0) + \chi^{2\omega}_{xxyy}\delta_{ij}E^0_k\\
&+ \chi^{2\omega}_{xyxy}\delta_{ik}E^0_j + \chi^{2\omega}_{yxxy}\delta_{jk}E^0_i,
\end{aligned} \tag{8}$$

(with the notation $\chi^{2\omega}_{ijk} = \chi_{ijk}(-2\omega, \omega, \omega)$), where the components $\chi^{2\omega}_{ijk}(0)$ in the absence of the dc field are related with negligible multipolar contributions only [2, 22] which, in the case of our geometry of observation and for isotropic media, vanish since the second harmonic propagates along the z axis in the propagation direction of the fundamental wave. More generally, however, it can be shown that if the light beam of frequency ω propagates along the z axis of the laboratory coordinates x, y, z not coinciding with the crystallographical set of coordinates X, Y, Z, generation of the second harmonic can occur in certain crystals of the regular symmetry class even in the absence of a dc electric field. Specifically, in the symmetry classes 23, $\bar{4}3\,\mathrm{m}$ and $\bar{4}3\,\underline{\mathrm{m}}$, the following components [23] in laboratory coordinates are nonzero:

$$\begin{aligned}
&\chi^{2\omega}_{yxx}(0) = \chi^{2\omega}_{xxy}(0) = -\sin 2\Theta \cos 2\varphi \chi^{2\omega}_{XYZ}(0),\\
&\chi^{2\omega}_{xxx}(0) = 3\cos^2\Theta \sin\Theta \sin 2\varphi \chi^{2\omega}_{XYZ}(0),\\
&\chi^{2\omega}_{xyy}(0) = \chi^{2\omega}_{yyx}(0) = \sin\Theta \sin 2\varphi \chi^{2\omega}_{XYZ}(0),
\end{aligned} \tag{8a}$$

and we note that they are determined by one component from the crystallographical set of coordinates $\chi^{2\omega}_{XYZ}$ only.

In (8) the components $\chi^{2\omega}_{xxyy}$, $\chi^{2\omega}_{xyxy}$, $\chi^{2\omega}_{yxxy}$ are expressed, in accordance with classical electrodynamics and statistics, by the electro-optical molecular parameters, e.g., the electric-dipole moment as well as the first- and second-order hyperpolarizabilities [7, 8] (next subsect.).

For an isotropic medium in the absence of natural gyration we can write the tensor of third-order nonlinear susceptibility as follows [24]:

$$\begin{aligned}
\chi_{ijkl} &= \chi_{xxyy}\delta_{ij}\delta_{kl} + \chi_{xyxy}\delta_{ik}\delta_{jl}\\
&+ \chi_{xyyx}\delta_{il}\delta_{jk}.
\end{aligned} \tag{9}$$

The nonlinear susceptibility tensor $\chi_{ijkl}(-\omega, -\omega, \omega, \omega)$ is symmetric in the pairs of indices ij and kl, so that the 3 components of (9) reduce to 2 mutually independent ones, χ_{xxyy} and $\chi_{xyxy} = \chi_{xyyx}$. The tensor $\chi_{ijkl}(-2\omega, -\omega, 2\omega, \omega)$ is not symmetric, so that $\chi_{xxyy} \neq \chi_{xyxy} \neq \chi_{xyyx}$. It has been shown recently that, in the case of molecular substances, the symmetry relation of Kleinman is not fulfilled generally for the tensor χ_{ijkl} [25–28].

We shall now write the electric field (1) in spherical representation. For the right- and left-polarized wave, propagating along the z axis (and on applying the angular momentum convention) we now have

$$E^+_\pm(\mathbf{r}, t) = \tfrac{1}{2}\sqrt{2}[E^+_x(z, t) \mp \mathrm{i}E^+_y(z, t)]. \tag{10}$$

By (8–10), in spherical representation, we obtain the averaged free energy (2) of the isotropic medium:

$$\begin{aligned}
F_{NL} = &-\tfrac{1}{2}\{g^\omega_1[E^-_+(\omega)^2 E^+_+(\omega)^2\\
&+ E^-_-(\omega)^2 E^+_-(\omega)^2]\\
&+ 4g^\omega_2 E^-_+(\omega)E^-_-(\omega)E^+_+(\omega)E^+_-(\omega)\\
&+ g^{2\omega}_1[E^-_+(2\omega)^2 E^+_+(2\omega)^2\\
&+ E^-_-(2\omega)^2 E^+_-(2\omega)^2]\\
&+ 4g^{2\omega}_2 E^-_+(2\omega)E^-_-(2\omega)E^+_+(2\omega)E^+_-(2\omega)\}\\
&- i\{g^{2\omega}_3[E^-_+(2\omega)E^+_+(\omega)^2\\
&- E^-_-(2\omega)E^+_-(\omega)^2]\\
&- 2g^{2\omega}_4[E^-_+(2\omega)\\
&- E^-_-(2\omega)]E^+_+(\omega)E^+_-(\omega)\}\mathrm{e}^{\mathrm{i}\Delta\mathbf{k}\cdot\mathbf{r}} + \text{c.c.}\\
&- g^{2\omega}_5[E^-_+(2\omega)E^-_-(\omega)E^+_+(\omega)E^+_-(2\omega)\\
&+ E^-_-(2\omega)E^-_+(\omega)E^+_-(\omega)E^+_+(2\omega)]\\
&- g^{2\omega}_6[E^-_+(2\omega)E^-_-(\omega)E^+_-(\omega)E^+_+(2\omega)\\
&+ E^-_-(2\omega)E^-_+(\omega)E^+_+(\omega)E^+_-(2\omega)]\\
&- g^{2\omega}_7[E^-_+(2\omega)E^-_+(\omega)E^+_+(\omega)E^+_+(2\omega)\\
&+ E^-_-(2\omega)E^-_-(\omega)E^+_-(\omega)E^+_-(2\omega)],
\end{aligned} \tag{11}$$

where we have the nonlinear coupling parameters

$$g_1^{\Omega}=6\chi_{xyxy}(-\Omega,-\Omega,\Omega,\Omega),$$
$$g_2^{\Omega}=3[\chi_{xxyy}(-\Omega,-\Omega,\Omega,\Omega)+\chi_{xyxy}(-\Omega,-\Omega,\Omega,\Omega)],$$
$$g_3^{2\omega}=\frac{2}{\sqrt{2}}\chi_{xxyy}(-2\omega,\omega,\omega,0)E_y^0,$$
$$g_4^{2\omega}=\frac{1}{\sqrt{2}}[\chi_{xxyy}(-2\omega,\omega,\omega,0)+\chi_{yxxy}(-2\omega,\omega,\omega,0)]E_y^0,$$
$$g_5^{2\omega}=3[\chi_{xxyy}(-2\omega,-\omega,\omega,2\omega)+\chi_{xyxy}(-2\omega,-\omega,\omega,2\omega)],$$
$$g_6^{2\omega}=3[\chi_{xxyy}(-2\omega,-\omega,\omega,2\omega)+\chi_{xyyx}(-2\omega,-\omega,\omega,2\omega)],$$
$$g_7^{2\omega}=3[\chi_{xyxy}(-2\omega,-\omega,\omega,2\omega)+\chi_{xyyx}(-2\omega,-\omega,\omega,2\omega)]. \quad (12)$$

Applying (4 and 11), we obtain the nonlinear polarisations in spherical representation:

$$\begin{aligned}P_{\pm}^{+}(\omega)_{NL}=&\{g_1^{\omega}|E_{\pm}^{-}(\omega)|^2+2g_2^{\omega}|E_{\mp}^{-}(\omega)|^2\}E_{\pm}^{+}(\omega)\\&-2i\{\pm g_3^{-2\omega}E_{\pm}^{+}(2\omega)E_{-}^{-}(\omega)\\&-g_4^{-2\omega}[E_{+}^{+}(2\omega)\\&-E_{-}^{+}(2\omega)]E_{\mp}^{-}(\omega)\}e^{-i\Delta\mathbf{k}\cdot\mathbf{r}}\\&+g_5^{2\omega}E_{-}^{-}(2\omega)E_{-}^{+}(\omega)E_{+}^{+}(2\omega)\\&+\{g_6^{2\omega}|E_{\mp}^{-}(2\omega)|^2\\&+g_7^{2\omega}|E_{\pm}^{-}(2\omega)|^2\}E_{\pm}^{+}(\omega), \quad (13)\end{aligned}$$

$$\begin{aligned}P_{\pm}^{+}(2\omega)_{NL}=&\{g_1^{2\omega}|E_{\pm}^{-}(2\omega)|^2+2g_2^{2\omega}|E_{\mp}^{-}(2\omega)|^2\}E_{\pm}^{+}(2\omega)\\&+i\{\pm g_3^{2\omega}E_{\pm}^{+}(\omega)^2\\&\mp 2g_4^{2\omega}E_{+}^{+}(\omega)E_{-}^{+}(\omega)\}e^{i\Delta\mathbf{k}\cdot\mathbf{r}}\\&+g_5^{2\omega}E_{-}^{-}(\omega)E_{+}^{+}(\omega)E_{-}^{+}(2\omega)\\&+\{g_6^{2\omega}|E_{\mp}^{-}(\omega)|^2\\&+g_7^{2\omega}|E_{\pm}^{-}(\omega)|^2\}E_{\pm}^{+}(2\omega). \quad (14)\end{aligned}$$

Once the Fourier components of (13 and 14) are available, we are in a position to determine the slowly varying spatial behaviour of the field amplitudes (1) as the waves propagate through the isotropic medium. In the case under consideration we make use of the well known wave equation of Maxwell [2]. For the electric field amplitudes, we obtain

$$\frac{dE_{\pm}^{+}(\omega)}{dz}=i\frac{2\pi\omega^2}{c^2k_{\omega}}P_{\pm}^{+}(\omega)_{NL}, \quad (15)$$

$$\frac{dE_{\pm}^{+}(2\omega)}{dz}=i\frac{2\pi(2\omega)^2}{c^2k_{2\omega}}P_{\pm}^{+}(2\omega)_{NL}. \quad (16)$$

On restricting ourselves in (13, 14) to the terms related with the self-induced intensity-dependent effect at $\Omega=\omega$ or 2ω we get, with (15, 16) (on neglecting interferences)

$$\frac{dE_{\pm}^{+}(\Omega)}{dz}=i\frac{2\pi\Omega^2}{c^2k_{\Omega}}[g_1^{\Omega}|E_{\pm}^{-}(\Omega)|^2+2g_2^{\Omega}|E_{\mp}^{-}(\Omega)|^2]E_{\pm}^{+}(\Omega). \quad (17)$$

Since $|E_{\pm}^{-}(\Omega)|^2$ does not depend on z because $(d/dz)|E_{\pm}^{-}(\Omega)|^2=0$, (17) in our case possesses the well known exponential solution [29]

$$E_{\pm}^{+}(\Omega,z)=\exp(i\Phi_{\pm}z)E_{\pm}^{+}(\Omega,0), \quad (18)$$

where

$$\Phi_{\pm}=\frac{2\pi\Omega}{n_{\Omega}c}[g_1^{\Omega}|E_{\pm}^{-}(\Omega)|^2+2g_2^{\Omega}|E_{\mp}^{-}(\Omega)|^2], \quad (19)$$

determines the light intensity phase shifts of the field amplitude.

The set of (13–16) is accessible to solution by perturbative methods only.

On having recourse to the well known relation between the refractive index and the nonlinear polarisation of the isotropic medium $n\delta n_{\pm}E_{\pm}(\mathbf{r},t)=2\pi P_{\pm}(\mathbf{r},t)^{NL}$ and applying (13, 14), we obtain the nonlinear variations for the right- and left-polarized wave at ω and 2ω

$$\delta n_{\pm}(\omega)=\frac{2\pi}{n_{\omega}}[g_1^{\omega}|E_{\pm}^{-}(\omega)|^2+2g_2^{\omega}|E_{\mp}^{-}(\omega)|^2+g_6^{2\omega}|E_{\mp}^{-}(2\omega)|^2+g_7^{2\omega}|E_{\pm}^{-}(2\omega)|^2], \quad (20)$$

$$\delta n_{\pm}(2\omega)=\frac{2\pi}{n_{2\omega}}[g_1^{2\omega}|E_{\pm}^{-}(2\omega)|^2+2g_2^{2\omega}|E_{\mp}^{-}(2\omega)|^2+g_6^{2\omega}|E_{\mp}^{-}(\omega)|^2+g_7^{2\omega}|E_{\pm}^{-}(\omega)|^2]. \quad (21)$$

Measurements of these variations of the refractive indices lead us directly to the numerical values of the nonlinear coupling parameters g_1, g_2, g_6, and g_7.

Equation (20) gives us the difference between the two indices at ω (elliptic birefringence [5])

$$\begin{aligned}\delta n_{+}(\omega)-\delta n_{-}(\omega)=&\frac{6\pi}{n_{\omega}}\{2\chi_{xxyy}(-\omega,-\omega,\omega,\omega)[|E_{-}^{-}(\omega)|^2\\&-|E_{+}^{-}(\omega)|^2]+[\chi_{xxyy}(-\omega,-2\omega,\omega,2\omega)\\&-\chi_{xyyx}(-\omega,-2\omega,\omega,2\omega)][|E_{-}^{-}(2\omega)|^2\\&-|E_{+}^{-}(2\omega)|^2]\}, \quad (22)\end{aligned}$$

where the first term describes the well known effect of Maker et al. [4], consisting in self-rotation of the polarization ellipse due to the intensity of elliptically polarized light at ω. The second term accounts for the

additional anisotropy in nonlinear susceptibility due to the intensity of the second harmonic at 2ω – a novel effect, reminiscent of the optical Kerr effect for circularly polarized light [30] (e.g., right handed $E_- = 0$).

Similarly, with (21), we get for the optical rotation at 2ω

$$\delta n_+(2\omega) - \delta n_-(2\omega) = \frac{6\pi}{n_{2\omega}} \{[\chi_{xxyy}(-2\omega, -\omega, \omega, 2\omega) - \chi_{xyyx}(-2\omega, -\omega, \omega, 2\omega)][|E^-(\omega)|^2 - |E^-_+(\omega)|^2] + 2\chi_{xxyy}(-2\omega, -2\omega, 2\omega, 2\omega)[|E^-(2\omega)|^2 - |E^-_+(2\omega)|^2]\}. \quad (23)$$

Here, we come upon a new effect, hitherto not studied experimentally.

2. The Nonlinear Coupling Parameters Versus the Number Density, Concentration, Temperature and DC Electric Field

The nonlinear coupling parameters (12) are expressed by way of the respective tensor components of the nonlinear susceptibilities; the latter reflect the molecular structure of the medium in accordance with the manner in which they depend on the frequency of the electric field. In the case of isotropic media the most highly structure-sensitive nonlinear susceptibility is that given by the phenomenological relation (8), and we shall accordingly start by discussing it first, on the classical level.

For simplicity, we begin by assuming that the isotropic medium is sufficiently rarefied to be free of intermolecular interactions, as it is the case in gases. On denoting by $\varrho = N/V$ the number density of molecules, we may express the tensor of macroscopic second-order nonlinear susceptibility in the form of the following expansion in the presence of a not excessively intense dc electric field [on denoting $\chi(-2\omega, \omega, \omega)$ by $\chi^{2\omega}$] [8]

$$\chi^{2\omega}_{ijk}(\mathbf{E}^0) = \varrho \int \{\beta^{2\omega}_{ijk} + \gamma^{2\omega}_{ijkl} E^0_l + \ldots\} f(\boldsymbol{\Omega}, \mathbf{E}^0) d\boldsymbol{\Omega}, \quad (24)$$

where $f(\boldsymbol{\Omega}, \mathbf{E}^0)$ is a statistical function describing the distribution of molecules in the medium having the orientation $\boldsymbol{\Omega}$ with respect to the direction of the external field $\mathbf{E}^0$. Integration in (24) extends over all possible orientations of the molecules in the body angle element $d\boldsymbol{\Omega}$, with $\boldsymbol{\Omega}$ the set of Euler angles.

In (24), the third-rank tensor β_{ijk} determines the nonlinear molecular polarizability of the second order (first-order hyperpolarizability). The variation of the latter caused by the dc field E^0 is described by the fourth-rank tensor γ_{ijkl} of third-order nonlinear molecular polarizability (second-order hyperpolarizability).

If the molecules possess a permanent electric dipole moment $\boldsymbol{\mu}$, the Boltzmann-Debye distribution function, in a linear approximation in $\mathbf{E}^0$, becomes

$$f(\boldsymbol{\Omega}, \mathbf{E}^0) = f(\boldsymbol{\Omega}) \left(1 + \frac{\mu_i E^0_i}{kT}\right), \quad (25)$$

where $f(\boldsymbol{\Omega})$ is the distribution function in the absence of external fields, when the orientation of the molecules of the medium is completely random.

With regard to (24, 25), we have

$$\chi^{2\omega}_{ijk}(\mathbf{E}^0) = \varrho \left(\langle \gamma^{2\omega}_{ijkl} \rangle_{\boldsymbol{\Omega}} + \frac{1}{kT} \langle \beta^{2\omega}_{ijk} \mu_l \rangle_{\boldsymbol{\Omega}}\right) E^0_l, \quad (26)$$

since in optically inactive media the term $\langle \beta^{2\omega}_{ijk} \rangle_{\boldsymbol{\Omega}}$ vanishes on averaging over all possible molecular orientations $\boldsymbol{\Omega}$ as denoted by the symbol $\langle\ \rangle_{\boldsymbol{\Omega}}$.

The molecular tensors of (26), given in the laboratory system of coordinates x, y, z (Latin indices i, j, k, l), have to be transformed to molecular coordinates 1, 2, 3 (Greek indices $\alpha, \beta, \gamma, \delta$) in accordance with the relation $\mu_i = R_{i\alpha}\mu_\alpha$, etc., where the $R_{i\alpha}$'s are rotational transformation coefficients connecting the two coordinate systems x, y, z and 1, 2, 3. As a result, we get

$$\chi^{2\omega}_{ijk}(\mathbf{E}^0) = \varrho \left(\gamma^{2\omega}_{\alpha\beta\gamma\delta} + \frac{1}{kT} \beta^{2\omega}_{\alpha\beta\gamma} \mu_\delta\right) \langle R_{i\alpha} R_{j\beta} R_{k\gamma} R_{l\delta} \rangle_{\boldsymbol{\Omega}} E^0_l. \quad (26a)$$

The general formula for unweighted rotational averaging $\langle R_{i\alpha} R_{j\beta} R_{k\gamma} R_{l\delta} \rangle_{\boldsymbol{\Omega}}$ is well known [31]. Hence, we arrive quite generally at (8) with the tensor components of third-order nonlinear susceptibility [8]

$$\chi^{2\omega}_{xxyy} = \chi^{2\omega}_{xyxy} = \frac{\varrho}{30}\left[3\gamma^{2\omega}_{\alpha\alpha\beta\beta} - \gamma^{2\omega}_{\alpha\beta\beta\alpha} + \frac{1}{kT}(3\beta^{2\omega}_{\alpha\alpha\beta}\mu_\beta - \beta^{2\omega}_{\alpha\beta\beta}\mu_\alpha)\right],$$

$$\chi^{2\omega}_{yxxy} = \frac{\varrho}{15}\left[2\gamma^{2\omega}_{\alpha\beta\beta\alpha} - \gamma^{2\omega}_{\alpha\alpha\beta\beta} + \frac{1}{kT}(2\beta^{2\omega}_{\alpha\beta\beta}\mu_\alpha - \beta^{2\omega}_{\alpha\alpha\beta}\mu_\beta)\right]. \quad (27)$$

Thus, in the molecular-statistical approach, the macroscopic susceptibility tensor components (8) given by the expressions (27) originate in two microscopic processes: (i) the one (temperature-independent terms) consists in direct nonlinear electronic Lorentz-Voigt polarisation, common to all molecular symmetries including atoms in their ground state, and (ii) the other (temperature-dependent terms) consisting in reorientation of the permanent electric dipoles in the dc electric field as described by the theory of Langevin and Debye.

In the absence of electronic dispersion, the hyperpolarizability tensors $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ are completely symmetric; by (27), we obtain the symmetry relation of Bloembergen [24]

$$\chi^{2\omega}_{xxyy}=\chi^{2\omega}_{xyxy}=\chi^{2\omega}_{yxxy}=\tfrac{1}{3}\chi^{2\omega}_{yyyy}, \tag{28}$$

where

$$\chi^{2\omega}_{yyyy}=\frac{\varrho}{5}\left(\gamma^{2\omega}_{\alpha\alpha\beta\beta}+\frac{1}{kT}\beta^{2\omega}_{\alpha\alpha\beta}\mu_\beta\right). \tag{29}$$

In applications to different point group symmetries, it is convenient to have recourse to the irreducible representation of the tensors $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ [30, 32–34]. In particular, a completely symmetric tensor β_{ijk} can be represented in the form of two irreducible tensors of weights 1 and 3 (a vector and a septor [32])

$$\beta_{ijk}=\beta^{(1)}_{ijk}+\beta^{(3)}_{ijk}. \tag{30}$$

For a dipolar molecule with axial symmetry defined by a unit vector **s** along the 3-axis ($\mu_i=\mu_3 s_i$), we have [30]

$$\beta^{(1)}_{ijk}=\tfrac{1}{3}\beta_{(1)}(\delta_{ij}s_k+\delta_{jk}s_i+\delta_{ki}s_j), \tag{30a}$$

$$\beta^{(3)}_{ijk}=\tfrac{1}{2}\beta_{(3)}[5s_is_js_k-(\delta_{ij}s_k+\delta_{jk}s_i+\delta_{ki}s_j)], \tag{30b}$$

where we have denoted the irreducible molecular hyperpolarizabilities by

$$\beta_{(1)}=\tfrac{3}{5}(\beta_{333}+2\beta_{113}),\quad \beta_{(3)}=\tfrac{2}{5}(\beta_{333}-3\beta_{113}).$$

In this case (29) simplifies to

$$\chi^{2\omega}_{yyyy}=\varrho\left(\gamma^{2\omega}_{(0)}+\frac{\mu_3\beta^{2\omega}_{(1)}}{3kT}\right), \tag{29a}$$

with

$$\gamma_{(0)}=\gamma_{\alpha\alpha\beta\beta}/5=(3\gamma_{3333}+12\gamma_{3311}+8\gamma_{1111})/15.$$

Thus, in the case under consideration, the technique of dc-field-induced second-harmonic generation enables us to determine the rotational invariant $\gamma^{2\omega}_{(0)}$ of the tensor $\gamma^{2\omega}_{\alpha\beta\gamma\delta}$ and the irreducible weight 1 component $\beta^{2\omega}_{(1)}$ of the tensor $\beta^{2\omega}_{\alpha\beta\gamma}$. In this way, the parameters $\gamma^{2\omega}_{(0)}$ and $\beta^{2\omega}_{(1)}$ have been determined for many different molecules of gases and liquids [35–42].

In a strong field $\mathbf{E}^0$ the relations (28, 29) are not fulfilled; restricting ourselves to the term in the first hyperpolarizability [8, 28, 33], we now have

$$\begin{aligned}\chi^{2\omega}_{xxy}(E^0_y)&=\chi^{2\omega}_{xyx}(E^0_y)=\chi^{2\omega}_{yxx}(E^0_y)\\&=\varrho[\tfrac{1}{3}\beta^{2\omega}_{(1)}\langle P_1(\cos\Theta)\rangle_{E^0_y}\\&\quad-\tfrac{1}{2}\beta^{2\omega}_{(3)}\langle P_3(\cos\Theta)\rangle_{E^0_y}],\end{aligned} \tag{28a}$$

$$\begin{aligned}\chi^{2\omega}_{yyy}(E^0_y)&=\varrho[\beta^{2\omega}_{(1)}\langle P_1(\cos\Theta)\rangle_{E^0_y}\\&\quad+\beta^{2\omega}_{(3)}\langle P_3(\cos\Theta)\rangle_{E^0_y}],\end{aligned} \tag{29b}$$

with the Boltzmann-distribution-averaged Legendre polynomials

$$\langle P_1(\cos\Theta)\rangle_{E^0_y}=L_1(p),$$

$$\langle P_3(\cos\Theta)\rangle_{E^0_y}=\tfrac{1}{2}[5L_3(p)-3L_1(p)],$$

$L_1(p)$ and $L_3(p)$ being Langevin functions of the dipole reorientation parameter $p=\mu_3E^0_y/kT$ [8, 30].

Thus, in the present case, we are able to determine the values of the two irreducible molecular hyperpolarizabilities $\beta^{2\omega}_{(1)}$ and $\beta^{2\omega}_{(3)}$ of the tensor (30).

The technique of hyper-Rayleigh scattering [30] also permits the determination of the irreducible 1 and 3 weight component of the tensor (30) and the irreducible components of the tensor $\gamma^{2\omega}_{\alpha\beta\gamma\delta}$ of weights 2 and 4.

In condensed liquids and gases, as the result of various molecular correlations and molecular electric field fluctuations, the nonlinear susceptibilities (27, 29) become functions of higher powers of the density and (in mixtures) the concentrations as well as various molecular parameters and the macroscopic field [24, 40, 44, 45]. In Kirkwood's semi-macroscopic approach [45], we can express the effective nonlinear susceptibility of a dense medium in the following form

$$\chi^{2\omega}_{yyyy}=f_{2\omega}f^2_\omega f_0\Gamma^{2\omega}_m, \tag{31}$$

where $f_{2\omega}$, f_ω, f_0 are shape parameters of the macroscopic field existing in the sample evaluated at the frequencies 2ω, ω, and 0 (e.g., by methods involving the local Lorentz or Onsager field [2, 30, 43]).

In (31), we have introduced the following molecular hyperpolarizability parameter of the mixture:

$$\begin{aligned}\Gamma^{2\omega}_m&=\varrho\sum_i x_i\Gamma^{2\omega}_i+\varrho^2\sum_{ij}x_ix_j\Gamma^{2\omega}_{ij}\\&\quad+\varrho^3\sum_{ijk}x_ix_jx_k\Gamma^{2\omega}_{ijk}+\ldots\end{aligned} \tag{32}$$

with x_i denoting the molar fraction of the i-th component of the mixture, and $N_i=Nx_i$ – the number of molecules of the i-th species.

$\Gamma^{2\omega}_i$ is the parameter of nonlinear hyperpolarizability of an isolated i-th molecule in the absence of molecular correlations; its form is given by (29). Thus, the first term of (32) expresses the additivity principle for the nonlinear susceptibilities of the ideal components of a mixture. The other terms of (32) describe divergences of the nonlinear susceptibility from the additivity principle due to different radial and angular correlations between molecules of the same or different species (specific models have been discussed in [45]).

Various factors and molecular models can raise or lower the value of the effective nonlinear susceptibility (31) and thus can lead to greater or smaller values of the parameters of nonlinear coupling (12).

Our preceding discussion concerned the case of a weak dc electric field with the linear equation (8) valid.

In a sufficiently strong field reorientation of the molecules (particularly macromolecules) can become considerable causing the molecular system as a whole to behave like a uniaxial crystal [8] (electric saturation). In this case the nonlinear coupling parameters can attain high values and are accessible to control by varying the intensity of the dc electric field. In certain model situations, multipolar electric and magnetic contributions [2, 22, 43, 46] to the first component of (8) can play an essential role.

The other nonlinear coupling parameters (12), related with self-action light intensity, are dependent on electronic and molecular-statistical mechanisms such as intervene in the optical Kerr effect [30, 47].

3. Quantum Description

The central problem in the quantum approach to the statistics of nonlinear processes resides in our knowledge of the analytical form of the Hamiltonian of interaction H_I between the material system (described by fermions) and the field of radiation (described by bosons). Although the determination of the interaction Hamiltonian on the microscopic level is possible for simple systems [48–50], one is in practice very often forced to use a semi-classical Hamiltonian [51], or an effective interaction Hamiltonian [52] constructed with the time-averaged free energy of the system (2) where the electric fields are now dealt with as quantum boson operators:

$$\hat{E}_{\pm}^{+}(\omega)=\mathrm{i}\left(\frac{2\pi\hbar\omega}{n_{\omega}^{2}V}\right)^{1/2}a_{\pm},$$

$$\hat{E}_{\pm}^{+}(2\omega)=\mathrm{i}\left(\frac{2\pi\hbar 2\omega}{n_{2\omega}^{2}V}\right)^{1/2}b_{\pm}, \tag{33}$$

with commutation rules

$$[a_i,a_j^{+}]=[b_i,b_j^{+}]=\delta_{ij},$$
$$[a_i,b_j]=[a_i,b_j^{+}]=0,\quad i,j=+\text{ or }-. \tag{34}$$

Taking into consideration that [52] $H_I=\int F dV$, we obtain by (11, 33) for the effective Hamiltonian of nonlinear interaction

$$\begin{aligned}H_I^{NL}=&-\frac{\hbar}{2}[\tilde{g}_1^{\omega}(a_+^{+2}a_+^2+a_-^{+2}a_-^2)+4\tilde{g}_2^{\omega}a_+^{+}a_-^{+}a_+a_-\\&+\tilde{g}_1^{2\omega}(b_+^{+2}b_+^2+b_-^{+2}b_-^2)\\&+4\tilde{g}_2^{2\omega}b_+^{+}b_-^{+}b_+b_-]\\&-\hbar[\tilde{g}_3^{2\omega}(b_-^{+}a_-^2-b_+^{+}a_+^2)\\&+2\tilde{g}_4^{2\omega}(b_+^{+}-b_-^{+})a_+a_-]\mathrm{e}^{\mathrm{i}\Delta\mathbf{k}\cdot\mathbf{r}}+\text{H.C.}\\&-\hbar[\tilde{g}_5^{2\omega}(b_+^{+}a_-^{+}a_+b_-+b_-^{+}a_+^{+}a_-b_+)\\&+\tilde{g}_6^{2\omega}(b_+^{+}a_-^{+}a_-b_++b_-^{+}a_+^{+}a_+b_-)\\&+\tilde{g}_7^{2\omega}(b_+^{+}a_+^{+}a_+b_++b_-^{+}a_-^{+}a_-b_-)],\end{aligned} \tag{35}$$

where we have denoted the nonlinear coupling parameters by

$$\tilde{g}_p^{\Omega}=\frac{V}{\hbar}\left(\frac{2\pi\hbar\Omega}{n_{\Omega}^2V}\right)^2 g_p^{\Omega},$$
$$\tilde{g}_q^{2\omega}=\frac{V}{\hbar}\left(\frac{2\pi\hbar 2\omega}{n_{2\omega}^2V}\right)^{1/2} g_q^{2\omega}\left(\frac{2\pi\hbar\omega}{n_{\omega}^2V}\right),$$
$$\tilde{g}_s^{2\omega}=\frac{V}{\hbar}\left(\frac{2\pi\hbar 2\omega}{n_{2\omega}^2V}\right)\left(\frac{2\pi\hbar\omega}{n_{\omega}^2V}\right) g_s^{2\omega}, \tag{36}$$

with $p=1, 2$, $q=3, 4$, and $s=5, 6, 7$.

In order that our further procedure shall be in agreement with the classical treatment involving (15, 16) we go over from the Heisenberg equations of motion for the time-evolution of the field operators to spatial propagation equations [53] which, in our case, for the operator $A(z)$, take the form

$$\frac{dA(z)}{dz}=-\frac{\mathrm{i}n_{\omega}}{\hbar c}[A(z),H_I^{NL}]. \tag{37}$$

With (35, 37), we obtain the following equations of motion for the field operators of the fundamental and second-harmonic wave:

$$\begin{aligned}\frac{da_{\pm}(z)}{dz}=&\mathrm{i}\frac{n_{\omega}}{c}(\tilde{g}_1^{\omega}a_{\pm}^{+}a_{\pm}+2\tilde{g}_2^{\omega}a_{\mp}^{+}a_{\mp})a_{\pm}\\&+\mathrm{i}2\frac{n_{\omega}}{c}[\mp\tilde{g}_3^{-2\omega}b_{\pm}a_{\pm}^{+}\\&+\tilde{g}_4^{-2\omega}(b_+-b_-)a_{\mp}^{+}]\mathrm{e}^{-\mathrm{i}\Delta\mathbf{k}\cdot\mathbf{r}}\\&+\mathrm{i}\frac{n_{\omega}}{c}\{\tilde{g}_5^{2\omega}b_{\mp}^{+}a_{\mp}b_{\pm}\\&+(\tilde{g}_6^{2\omega}b_{\pm}^{+}b_{\mp}+\tilde{g}_7^{2\omega}b_{\pm}^{+}b_{\pm})a_{\pm}\},\end{aligned} \tag{38}$$

$$\begin{aligned}\frac{db_{\pm}(z)}{dz}=&\mathrm{i}\frac{n_{2\omega}}{c}(\tilde{g}_1^{2\omega}b_{\pm}^{+}b_{\pm}+2\tilde{g}_2^{2\omega}b_{\mp}^{+}b_{\mp})b_{\pm}\\&+\mathrm{i}\frac{n_{2\omega}}{c}(\mp\tilde{g}_3^{2\omega}a_{\pm}^2\pm 2\tilde{g}_4^{2\omega}a_+a_-)\mathrm{e}^{\mathrm{i}\Delta\mathbf{k}\cdot\mathbf{r}}\\&+\mathrm{i}\frac{n_{2\omega}}{c}[\tilde{g}_5^{2\omega}a_{\mp}^{+}a_{\pm}b_{\mp}\\&+(\tilde{g}_6^{2\omega}a_{\mp}^{+}a_{\mp}+\tilde{g}_7^{2\omega}a_{\pm}^{+}a_{\pm})b_{\pm}].\end{aligned} \tag{39}$$

On neglecting in (38) interference related with the second harmonic, we obtain a formal solution in the form of the translation operator

$$a_{\pm}(z)=\exp\{\mathrm{i}z[\varepsilon_{\omega}a_{\pm}^{+}(0)a_{\pm}(0)+\delta_{\omega}a_{\mp}^{+}(0)a_{\mp}(0)]\}a_{\pm}(0), \tag{40}$$

where we have made use of the notation

$$\varepsilon_{\omega}=\frac{n_{\omega}}{c}\tilde{g}_1^{\omega},\quad \delta_{\omega}=2\frac{n_{\omega}}{c}\tilde{g}_2^{\omega}. \tag{41}$$

The solution in the form (40) has been obtained by Ritze [54] for photon antibunching, and by Tanaś and Kielich [15] for light self-squeezing. Similar solutions have been obtained by others [53, 55–57] for a variety of nonlinear optical processes. A solution analogous to (40) is obtained from (39) for the second harmonic (if present) in the absence of interference with the fundamental wave.

In the general case when coupling between the fundamental beam and the second-harmonic beam is taken into account, both (38) and (39) should be solved simultaneously. This is, however, a very difficult task to perform, and some approximations are needed. There are a number of terms in (38, 39) all of which can contribute to the solution. As an example of an approximate solution of (38, 39) we will calculate the normally ordered variances of the second-harmonic field generated by the self-squeezed light of the fundamental beam. To this end we assume that the main process is that of self-interaction of the fundamental beam in the nonlinear medium. The latter is described by the coupling constants $\tilde{g}_1^{\omega}$ and $\tilde{g}_2^{\omega}$. If all other coupling constants are smaller than $\tilde{g}_1^{\omega}$ and $\tilde{g}_2^{\omega}$ we can take advantage of the solution (40) and apply it as the zero-order solution in solving (39) for the second-harmonic field perturbatively. Eq. (39) can be integrated formally, giving

$$b_{\pm}(z)=b_{\pm}(0)\mp \mathrm{i}\frac{n_{2\omega}}{c}\int_0^z dz'\,\mathrm{e}^{\mathrm{i}\Delta k z'}\{\tilde{g}_3^{2\omega}a_{\pm}^2(z') -2\tilde{g}_4^{2\omega}a_+(z')a_-(z')\}, \tag{42}$$

where we have dropped all terms with integrations containing the second-harmonic operators $b_{\pm}(z)$. The contributions from these terms would appear as higher-order in the coupling constants were the second-harmonic field taken as initially (i.e., for $z=0$) in the vacuum state $b_{\pm}(0)|0\rangle=0$.

Thus, they can be omitted. Moreover, we assume that the fundamental beam is initially in a coherent state with right circular polarization, i.e. $a_+(0)|\alpha_+\rangle=\alpha_+|\alpha_+\rangle$. This assumption eliminates also the term proportional to $\tilde{g}_4^{2\omega}$. On these assumptions, the problem becomes more transparent and allows for relatively simple formulas describing the quantum fluctuations in the second-harmonic beam.

On insertion of (40) into (42) and using the commutation rules (34) we obtain the following expression for the normally ordered variances of the second-harmonic field

$$\begin{aligned}
&\pm\langle{:}[\Delta(b_+(z)\pm b_+^{+}(z))]^2{:}\rangle\\
&=\pm\langle{:}[b_+(z)\pm b_+^{+}(z)]^2{:}\rangle\mp\langle b_+(z)\pm b_+^{+}(z)\rangle^2\\
&=-2\kappa^2\int_0^z dz'\int_0^z dz''\{\pm\alpha_+^4\exp\{[\cos 2\varepsilon_{\omega}(z'+z'')\\
&\quad -1]|\alpha_+|^2\}\cos\{(\Delta k+\varepsilon_{\omega})(z'+z'')+4\varepsilon_{\omega}z''\\
&\quad +|\alpha_+|^2\sin 2\varepsilon_{\omega}(z'+z'')\}\\
&\quad \mp\alpha_+^4\exp\{[\cos 2\varepsilon_{\omega}z'+\cos 2\varepsilon_{\omega}z''-2]|\alpha_+|^2\}\\
&\quad \times\cos\{(\Delta k+\varepsilon_{\omega})(z'+z'')\\
&\quad +|\alpha_+|^2(\sin 2\varepsilon_{\omega}z'+\sin 2\varepsilon_{\omega}z'')\}\\
&\quad -|\alpha_+|^4\exp\{[\cos 2\varepsilon_{\omega}(z'-z'')-1]|\alpha_+|^2\}\\
&\quad \times\cos\{(\Delta k+\varepsilon_{\omega})(z'-z'')+|\alpha_+|^2\sin 2\varepsilon_{\omega}(z'-z'')\}\\
&\quad +|\alpha_+|^4\exp\{[\cos 2\varepsilon_{\omega}z'+\cos 2\varepsilon_{\omega}z''-2]|\alpha_+|^2\}\\
&\quad \times\cos\{(\Delta k+\varepsilon_{\omega})(z'-z'')\\
&\quad +|\alpha_+|^2(\sin 2\varepsilon_{\omega}z'-\sin 2\varepsilon_{\omega}z'')\}\},
\end{aligned} \tag{43}$$

where we have used the notation

$$\kappa=\frac{n_{2\omega}}{c}\tilde{g}_3^{2\omega}. \tag{44}$$

The upper (lower) sign applies to the in-phase (out-of-phase) component of the second-harmonic field. A field is said to be in a squeezed state if one of its variances becomes negative. The expression (43) is still quite complicated because the integrations cannot be performed analytically. However, in real physical situations the nonlinear parameter ε_{ω} is very small and we have $\varepsilon_{\omega}z\ll 1$, allowing us to expand the integrand into a power series and retain only the leading terms with respect to this small parameter, terms containing $\varepsilon_{\omega}z|\alpha_+|^2$ with values of the order of unity for $|\alpha_+|^2\gg 1$. Assuming, moreover, the phase of the incoming field as zero ($\alpha_+=|\alpha_+|$) and that the linear phase matching conditions are met (i.e., $\Delta k=0$), we have

$$\begin{aligned}
&\pm\langle{:}[\Delta(b_+(z)\pm b_+^{+}(z))]^2{:}\rangle\\
&=\frac{2\eta}{\beta^2}\{\pm[2\cos\beta-1-\cos 2\beta\\
&\quad -\beta(\sin 2\beta-\sin\beta)]\\
&\quad +(\cos\beta-1+\beta\sin\beta)^2\},
\end{aligned} \tag{45}$$

where $\beta=2\varepsilon_{\omega}z|\alpha_+|^2$, and we have introduced the power conversion ratio

$$\eta=\frac{2\kappa^2|\alpha_+|^4z^2}{|\alpha_+|^2}\approx\frac{I(2\omega)}{I_0(\omega)}, \tag{46}$$

describing the fraction of the initial power transferred into the second harmonic.

The expression (45) is already simple enough and easy to evaluate numerically. In Fig. 1 the normally ordered variance of the out-of-phase component of the second-harmonic field is plotted against $\varepsilon_{\omega}z|\alpha_+|^2$ and compared to the variance of the in-phase component of

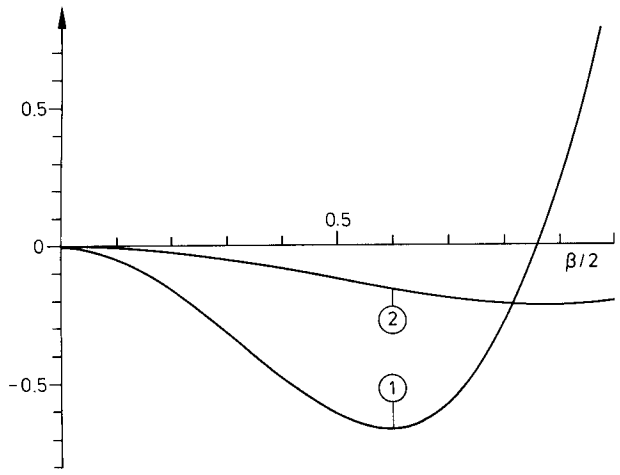

Fig. 1. Plot of the normally ordered variance of the in-phase component of the fundamental beam (curve 1) and the out-of-phase component of the second-harmonic beam (curve 2) against $\beta/2=\varepsilon_\omega z|\alpha_+|^2$

the fundamental beam [15]. One notes that squeezing in the out-of-phase component of the second-harmonic field (negative values of curve 2) is correlated to the self-squeezing of the in-phase component of the fundamental field (negative values of curve 1). For small values of β both curves take on negative values. However, the maximum of squeezing in the second-harmonic field (minimum of curve 2) occurs for positive values of curve 1 (no squeezing in the fundamental field). One can say that when the second harmonic is generated by the self-squeezed light, squeezing from the in-phase component of the fundamental beam is transferred in some sense into the out-of-phase component of the second-harmonic beam. The correlation of squeezing in the two beams is not so strong as in the case of third-harmonic generation [58]. The value of squeezing in the second harmonic is proportional to the conversion ratio η. We have to bear in mind, however, that (45) has been obtained under the assumption that there was no coupling of the second harmonic back into the fundamental beam, and our approximation breaks down if η becomes large. We should also emphasize that the mechanism of producing squeezed states in the second harmonic generated in isotropic media as considered in this paper is quite different from the mechanism considered earlier [12, 13, 23].

4. Conclusion

We have considered the process of second-harmonic generation in isotropic media by self-squeezed light. We have introduced an effective interaction Hamiltonian describing the processes related to the propagation of the strong optical field in the nonlinear medium and generation of the second harmonic in such a medium. The nonlinear coupling constants have been derived explicitly including their statistical molecular contents. Second-harmonic generation in an isotropic medium subjected to a dc electric field is considered. Classical as well as quantum equations describing the field evolution in the nonlinear medium have been derived. A new mechanism leading to squeezing of quantum fluctuations in the second-harmonic field has been discussed. Some correlation between squeezing in the second-harmonic beam and self-squeezing in the fundamental beam has been shown to exist, although the squeezing in the second harmonic does not follow exactly that in the fundamental field. The maximum of squeezing in the second harmonic appears already for positive values of the normally ordered variance of the fundamental field. Thus squeezing in the second-harmonic field is delayed with respect to self-squeezing in the fundamental field.

We should also emphasize that, to obtain considerable squeezing in the second harmonic by way of the mechanism discussed here, it is essential to make the linear mismatch much smaller than $2\varepsilon_\omega z|\alpha_+|^2$. The squeezing is proportional to the conversion ratio η, as given by (45, 46). Thus, the squeezing increases with increasing conversion ratio. One should bear in mind, however, that for higher-conversion ratios the approximation used breaks down and (38, 39) have to be solved without the perturbative expansion used above. This is, however, a rather difficult task to perform. On neglecting the nonlinear propagation effects leading to self-squeezing and on solving (38, 39) perturbatively, one arrives at the results already obtained for squeezing in harmonics generation [13]. The latter mechanism is of higher order ($\sim\kappa^4$) in the coupling constant κ than that discussed in this paper ($\sim\kappa^2$). So the new mechanism due to the nonlinear propagation effect should be predominant whenever κ is small.

Finally, we would like to make the following terminological remark: Tanaś and Kielich [15] referred to squeezing due to nonlinear propagation of strong laser light in a Kerr medium as the "self-squeezing effect" and refer to the states of the field as "self-squeezed states". Recently, Kitagawa and Yamamoto [56] have discussed the properties of the states that are created due to self-phase-modulation in the Kerr medium, according to their interaction Hamiltonian $a^{+2}a^2$, and have obtained the quasiprobability density for such states showing that it has a "crescent" shape (which differs essentially from the ellipse that is obtained for ordinary squeezed states). In fact, the "crescent" squeezing of Kitagawa and Yamamoto [56] is exactly the same as the "self-squeezing" of Tanaś and Kielich [15] in the one-mode case.

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