Frequency Mixing of Laser Waves in Electrically Polarised Media

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The non-linear susceptibility tensor $\chi_{ijk}(-\omega_3,\omega_1,\omega_2,\mathbf{E}^0)$ is discussed for optical mixing due to electrically induced processes of non-linear electronic distortion and statistical fluctuation, reorientation and relaxation of permanent and induced molecular electric multipoles, for isotropic optically active and inactive bodies in particular. Suggestions are made for the observation of wave mixing and second harmonic generation in new experimental set-ups devised to permit determinations of the non-zero independent elements of 4, 5 and 6 rank tensors of non-linear susceptibilities and to yield more information on the microstructure of substances and their electro-optical properties.

1. Introduction

DC electric-field-induced second harmonic generation (SHG) has been obtained in calcite [1, 2], TGS crystal in the paraelectric phase [3], as well as in molecular substances [4]. Such bodies naturally possess a centre of symmetry, and are in principle able to yield only SHG of the quadrupolar type, of rather low intensity. An externally applied DC electric field $\mathbf{E}^0$ removes the centre of symmetry thus causing a rise in SHG intensity. The electric anisotropy induced in isotropic bodies depends, in addition to the strength of the field $\mathbf{E}^0$, on its spatial inhomogeneities. Although the non-linearities induced in a medium by the gradient (or higher spatial inhomogeneities) of $\mathbf{E}^0$ are generally insignificant, experimental conditions of observation can often be arranged so that the anisotropy due to the uniform field shall not intervene directly [5]. Also, it has to be kept in mind that the action of a uniform electric field is differently apparent in isotropic optically inactive bodies and in those that are optically active, as the latter have the property of generating summation frequencies [6, 7].

This paper is intended as a discussion of the mutual interaction of two laser waves propagating in a medium acted on by a strong DC electric field (or by an alternating electric field), taking into consideration the spatial inhomogeneities (gradients of various order) of the applied field. The problem is considered with sufficient generality to permit a formulation of new feasible experimental situations in which matter is subject to non-linear cross-variations dependent of the strength of the applied DC electric field and electromagnetic fields concomitantly. A phenomenological description of these processes is given together with their microscopic interpretation on a classical level, bringing to the fore their more important distortional and statistical-fluctuational mechanisms.

2. Optical Polarisation of the Second Order in the Presence of a DC Electric Field

Two electromagnetic waves E^{ω_1} and E^{ω_2} oscillating at frequencies ω_1 and ω_2 induce in the medium a polarisation of the second order at the frequency $\omega_3 = \omega_1 + \omega_2$ [8]:

$$P_i(\omega_3) = \chi_{ijk}^{\omega_3} E_j^{\omega_1} E_k^{\omega_2} , \qquad (1)$$

where $\chi_{ijk}^{\omega_3} = \chi_{ijk}(-\omega_3, \omega_1, \omega_2)$, is the tensor of second-order non-linear susceptibility with non-zero components only in bodies without a centre of inversion.

When a DC electric field $\mathbf{E}^0$ acts on the medium, the polarisation (1) becomes a function of $\mathbf{E}^0$ and if non-linearity is moderate, one can write the expansion:

$$\chi_{ijk}^{\omega_3}(\mathbf{E}^0) = \chi_{ijk}^{\omega_3}(0) + \chi_{ijkl}^{\omega_3}E_l^0 + \chi_{ijklm}^{\omega_3}E_l^0E_m^0 + \eta_{ijklm}^{\omega_3}E_{lm}^0 + \chi_{ijklmn}^{\omega_3}E_l^0E_m^0E_n^0 + \eta_{ijklmn}^{\omega_3}E_l^0E_{mn}^0 + \mathscr{H}_{ijklmn}^{\omega_3}E_{lmn}^0 + \ldots, \quad (2)$$

$\chi_{ijk}^{\omega_3}(0)$ being the susceptibility tensor at $\mathbf{E}^0 = 0$ and the other tensors defining its successive non-linear variations due to the DC field strength E^0, the field gradient $E_{ij}^0 = \nabla_i E_j^0$, the gradient of the field gradient $E_{ijk} = \nabla_i \nabla_j E_k^0$, and so forth.

Resorting to the semi-macroscopic method [9], one can represent the phenomenological expansion (2), which is applicable to arbitrary media, in a form rendering apparent the microstructure of the medium (of volume V) as well as its thermodynamic state. We shall now discuss, one by one, the terms of the expansion (2).

2.1. The Linear Variations Induced by a Uniform DC Electric Field

These are described by the tensor of rank 4:

$$V\chi_{ijkl}^{\omega_3} = \{\langle C_{mnop}^{\omega_3}\rangle + \beta\langle B_{mno}^{\omega_3}M_p\rangle\}L_{mi}^{\omega_3}L_{nj}^{\omega_1}L_{ok}^{\omega_2}L_{pl}^0, \quad (3)$$

where $\beta = 1/kT$ and the brackets $\langle\ \rangle$ stand for statistical averaging in the absence of external fields; in the case of a spherical specimen of electric permittivity tensor ε_{ij} immersed in an isotropic medium of dielectric constant ε_e we have

$$L_{ij}^{\omega_1} = \frac{\varepsilon_{ij}^{\omega_1} + 2\varepsilon_e\delta_{ij}}{3\varepsilon_e}, \text{ etc}. \quad (4)$$

If the specimen is isotropic and the induced anisotropy small, one has $\varepsilon_{ij} = \varepsilon\delta_{ij}$ (where δ_{ij} is Kronecker's unit symmetric tensor), and equation 4 yields:

$$L_{ij}^{\omega_1} = \frac{\varepsilon^{\omega_1} + 2\varepsilon_e}{3\varepsilon_e}\delta_{ij} = L^{\omega_1}\delta_{ij}. \quad (4a)$$

M_i is the electric dipole moment of the medium in the absence of external fields; $B_{ijk}^{\omega_3}$ and $C_{ijkl}^{\omega_3}$ are tensors of its optical non-linear polarisability [9]. The first right hand term of equation 3 depends only weakly on the density and temperature of the medium and accounts chiefly for the mechanism of non-linear electronic polarisability of the third order (spatial redistribution of the atoms, molecules or ions is quite unimportant, making up 10% at the most). The second term of equation 3 depends directly on temperature; it is related not only with the distortional process, which gives rise to electronic polarisability of the second order, but moreover with the statistical process consisting of reorientation of permanent electric dipoles (if present) in the DC electric field [4] or of reorientation of induced dipoles whose existence is due to fluctuational microscopic fields of the electric multipoles of closest neighbours [9].

2.2. Quadratic Variations in a DC Electric Field

These are accounted for by the susceptibility tensor of rank 5:

$$2V\chi_{ijklm}^{\omega_3} = \{\langle D_{nopqr}^{\omega_3} + 2\beta\langle C_{nopq}^{\omega_3}M_r\rangle + \beta\langle \Delta B_{nop}\Delta A_{qr}\rangle + \beta^2\langle \Delta B_{nop}^{\omega_3}\Delta(M_qM_r)\rangle\}L_{ni}^{\omega_3}L_{oj}^{\omega_1}L_{pk}^{\omega_2}L_{ql}^0L_{rm}^0. \quad (5)$$

The first term expresses essentially the distortional process of non-linear electronic polarisability. The subsequent, temperature-dependent terms stand in relation with statistical fluctuations of the non-linear second-order polarisability $\Delta B_{ijk}^{\omega_3}$ as well as fluctuations of the linear polarisability ΔA_{kl} and of the squared dipole moment $\Delta(M_kM_l)$. In the microscopic picture, these terms give the mechanism of reorientation of the electric molecular dipoles and of the molecular electric polarisability ellipsoids.

2.3. The Gradient of the DC Electric Field

This causes variations of the optical susceptibility described by the tensor

$$3\,V\eta^{\omega_3}_{ijklm} = \{\langle G^{\omega_3}_{ijklm}\rangle + \beta\langle B^{\omega_3}_{ijk}Q_{lm}\rangle\}L^{\omega_3}L^{\omega_1}L^{\omega_2}L^{0}_{G} \tag{6}$$

involving, beside macroscopic parameters of the uniform electric field (4a), a parameter of the field gradient (on neglecting anisotropy of the dielectric constant):

$$L^{0}_{G} = \frac{2\varepsilon + 3\varepsilon_e}{5\varepsilon_e}\,. \tag{7}$$

Equation 6 contains, in addition to the first term accounting for the distortional effect, a temperature-dependent term related moreover with the statistical effect of reorientation of electric quadrupoles by the DC electric field gradient (Q_{ij} is the electric quadrupole moment tensor of the medium).

2.4. Higher Non-linearities

These are defined by tensors of higher rank (upward of the fifth). The tensors, when written out explicitly, are rather involved in form, and we refrain from adducing them here. The respective terms become relevant at sufficiently high field strengths E^0 causing strong non-linear electric distortion of the electronic shells of the microsystems (atoms, molecules, ions, macromolecules) and a considerable degree of reorientation of the latter with a tendency to complete alignment of all the microsystems into the direction of the electric field vector which can lead to electric saturation. These processes have been discussed by us elsewhere [10, 11], and we shall not consider them further now.

3. Discussion and Final Remarks

Light generation at doubled frequency or summation frequency in the presence of a DC electric field is of particular importance in isotropic bodies which, naturally, are unable to produce these phenomena in the electric dipole approximation. For isotropic optically inactive bodies, the expansion (2) yields in a linear approximation [10]:

$$\chi^{\omega_3}_{ijk}(\mathbf{E}^0) = \chi^{\omega_3}_{xxyy}\delta_{ij}E^0_k + \chi^{\omega_3}_{xyxy}\delta_{ik}E^0_j + \chi^{\omega_3}_{yxxy}\,\delta_{jk}E^0_i \quad . \tag{8}$$

In various particular cases, well-defined symmetry relations [10, 11] exist between the three mutually independent components which satisfying the relation [12]: $\chi_{xxyy}+\chi_{xyxy}+\chi_{yxxy} = \chi_{yyyy}$. A glance at the form of equation 8 shows immediately that optical polarisation components (1) exist when the waves are incident perpendicular to the direction of the DC electric field; this, in fact, was the situation in Mayer's experiments [4] on molecular substances.

Giordmaine [6] was able to show that, in isotropic bodies, the asymmetric part of the tensor $\chi^{\omega_3}_{ijk}$ has non-zero elements so that sum frequency generation can take place in the absence of an external field [7]. In this case, the tensor $\chi^{\omega_3}_{ijk}$ depends quadratically on the DC uniform electric field strength (the third term of the expansion (2)) and this dependence is described by a fifth-rank tensor of the form of equation 5 whose non-zero elements are accessible to experimental determination by wave mixing. One is easily convinced of this on considering the simple situation when two laser beams propagate in the yz-plane at acute angles θ_1 and θ_2 to the z-axis intersecting one another (fig. 1). If the wave conveying the field E^{ω_1} is linearly polarised with electric oscillations perpendicular to the yz-plane (thus parallel to the x-axis) and if the other wave E^{ω_2} oscillates in the propagation plane yz, the following polarisation components (1) will be non-zero:

$$P_y(\omega_3) = \chi^{\omega_3}_{yxz}E^{\omega_1}_x E^{\omega_2}_z\,,$$
$$P_z(\omega_3) = \chi^{\omega_3}_{zxy}E^{\omega_1}_x E^{\omega_2}_y\,, \tag{9}$$

permitting the calculation of the resultant polarisation transverse to the propagation vector $\mathbf{k}_3 = \mathbf{k}_1 + \mathbf{k}_2$ [7].

If the DC electric field is uniform and acts along the y-axis (fig. 1a), the tensor elements $\chi_{ijk}^{\omega_3}$ of equation 9 are subject to the following quadratic variations (see Appendix):

$$\delta\chi_{yxz}^{\omega_3} = \chi_{yxzyy}^{\omega_3} E_y^0 E_y^0 ,$$
$$\delta\chi_{zxy}^{\omega_3} = \chi_{zxyyy}^{\omega_3} E_y^0 E_y^0 , \tag{10}$$

and we get, in the absence of optical dispersion,

$$\chi_{zxyyy}^{\omega_3} = -\chi_{yxzyy}^{\omega_3} . \tag{10a}$$

If the waves propagate in the presence of a field gradient, as shown in fig. 1b, where $E_{xx}^0 = - E_{yy}^0$, we obtain instead of (10), on neglecting dispersion,

$$\delta\chi_{zxy}^{\omega_3} = -\delta\chi_{yxz}^{\omega_3} = \eta_{zxyyy}^{\omega_3} E_{yy}^0 . \tag{11}$$

Quite similarly, proceeding from equations 1 and 2, one can analyse various experimental wave mixing situations involving yet other configurations between the DC electric field vector, the propagation directions of the waves, and the oscillation directions of their electric fields, leading to the determination of the other non-zero elements of the tensors (5) and (6).

A closer analysis based on equations 1 and 2 shows that wave generation and mixing processes are accompanied by self-induction of optical birefringence in the medium, with optical axis parallel to the electric vector oscillations in the case of linearly polarised waves, and parallel to the propagation direction in that of circularly polarised or unpolarised waves. In isotropic optically inactive bodies, self-induced optical birefringence accompanies SHG only if a weak DC electric field is operative [11]. On the other hand, in isotropic optically active ones, ware mixing processes [7] are accompanied by self-induced optical anisotropies even in the absence of a DC electric field, in accordance with the equation:

$$2\chi_{ijk}^{\omega_3}(I_1, I_2) = \chi_{ijklm}^{\omega_3}(E_l^{\omega_1} E_m^{-\omega_1} + E_l^{\omega_2} E_m^{-\omega_2}) + \ldots . \tag{12}$$

Quite obviously, the optical anisotropies due to beams of intensities I_1 and I_2 arise by processes of non-linear distortion, optical reorientation of molecular polarisability ellipsoids, and molecular correlations and redistribution [9, 11].

The expressions (3), (5) and (6) provide a basis for studies, in isotropic (optically active and inactive) bodies, of not only the distortional effects consisting of non-linear distortion of electron shells by the simultaneous action of electromagnetic fields and a DC electric field, but moreover of the statistical-fluctuational processes related with the electric properties of the microsystems. This information is indeed available because each of the macroscopic tensors M_i, Q_{ij}, A_{ij} ..... can be expressed in terms of properties of the individual microsystems; thus e.g. the total electric dipole moment in the absence of external fields in general can be expressed as follows for a medium consisting of N microsystems [9].

$$M_i = \sum_{p=1}^{N} \{\mu_i^{(p)} + \alpha_{ij}^{(p)} F_j^{(p)} + \tfrac{1}{2}\beta_{ijk}^{(p)} F_j^{(p)} F_k^{(p)} + \tfrac{1}{6}\gamma_{ijkl}^{(p)} F_j^{(p)} F_k^{(p)} F_l^{(p)} + \ldots\} \tag{13}$$

with $\mu_i^{(p)}$ the dipole moment of the pth microsystem, $\alpha_{ij}^{(p)}$ the tensor of its linear electric polarisability, $\beta_{ijk}^{(p)}$, $\gamma_{ijkl}^{(p)}$ etc. tensors of its non-linear electric polarisability and $F_i^{(p)}$ the electric field effectively acting on it owing to the presence of the electric multipoles of the surrounding N-1 microsystems [13]. The electric polarisability tensor of the medium is

$$A_{ij} = \sum_{p=1}^{N} \{\alpha_{ij}^{(p)} + \beta_{ijk}^{(p)} F_k^{(p)} + \tfrac{1}{2}\gamma_{ijkl}^{(p)} F_k^{(p)} F_l^{(p)} + \ldots\} . \tag{14}$$

Expansions similar to that of equations 13 and 14 can be written for the other, already mentioned, tensors of higher rank [13].

In sufficiently dense substances, microscopic electric fields exist even in the absence of an external field; accordingly, their fluctuations give rise to a number of statistical processes, which can variously modify the non-linear optical processes studied here. Insight into the part played by them with regard to non-linear processes of electronic distortion should be available from a closer investigation of processes of wave generation and mixing as a function of temperature, pressure and concentration.

Moreover, equations 3, 5 and 6 permit studies of the relations existing between the macroscopic symmetry of bodies and the symmetries of their microsystems. This is all the more feasible as at present we know methods for determining the non-zero components of some of the higher-rank tensors intervening here (up to rank 5 and 6 inclusive) for all point groups of microsystems [14] as well as for all crystallographical classes [15]. In particular the tensor $\chi_{ijklm}^{\omega_3}$, which has 243 components, reduces the number of its non-zero components to 60 in the case of the regular (cubic) system; 20 of them are mutually independent for class 23, 10 of them for classes 432 and $\bar{4}3$m, and 6 for an isotropic optically active body (see Appendix). A further reduction in number of independent tensor components results by Kleinman's symmetry conjecture [8]. Tables of components of the tensors of rank 5 and 6 occurring in the expansion (2) prepared at this Institute and covering all crystallographical classes will be published separately [16].

By applying an alternating electric field of oscillation frequency well below the optical range (in place of a DC field), one will obtain the possibility of studying the contribution to wave mixing from processes of Debye molecular relaxation [9].

We hope that the preceding analysis (it was not our intention to deal more closely with the technicalities) may have shown convincingly that experimenters have here at their disposal new possibilities of investigating the DC electric field induced generation of double, sum and difference frequencies with the aim of determining tensor elements not only of rank 4 but also of ranks 5 and 6 describing non-linear processes of higher orders. The non-linear processes suggested here can be advantageously studied in macromolecular and colloid solutions [11], liquid crystals [17], weakly non-linear crystals [18], as well as various other unbounded random media [19].

Appendix

For isotropic optically active bodies we have by equation 1 three polarisation components in the presence of a DC electric field:

$$P_x(\omega_3, \mathbf{E}^0) = \chi_{xyz}^{\omega_3}(\mathbf{E}^0)E_y^{\omega_1}E_z^{\omega_2} + \chi_{xzy}^{\omega_3}(\mathbf{E}^0)E_z^{\omega_1}E_y^{\omega_2},$$
$$P_y(\omega_3, \mathbf{E}^0) = \chi_{yxz}^{\omega_3}(\mathbf{E}^0)E_x^{\omega_1}E_z^{\omega_2} + \chi_{yzx}^{\omega_3}(\mathbf{E}^0)E_z^{\omega_1}E_x^{\omega_2},$$
$$P_z(\omega_3, \mathbf{E}^0) = \chi_{zxy}^{\omega_3}(\mathbf{E}^0)E_x^{\omega_1}E_y^{\omega_2} + \chi_{zyx}^{\omega_3}(\mathbf{E}^0)E_y^{\omega_1}E_x^{\omega_2}.$$

In the absence of an electric field we have [6]

$$\chi_{xyz}^{\omega_3} = \chi_{yzx}^{\omega_3} = \chi_{zxy}^{\omega_3} = -\chi_{xzy}^{\omega_3} = -\chi_{yxz}^{\omega_3} = -\chi_{zyx}^{\omega_3},$$

whereas in the presence of the gradient of a DC electric field we have:

$$\chi_{xyz}^{\omega_3}(\nabla\mathbf{E}^0) = A_1^{\omega_3}E_{xx}^0 - A_2^{\omega_3}E_{yy}^0 + A_3^{\omega_3}E_{zz}^0,$$
$$\chi_{xzy}^{\omega_3}(\nabla\mathbf{E}^0) = -A_1^{\omega_3}E_{xx}^0 + A_2^{\omega_3}E_{zz}^0 - A_3^{\omega_3}E_{yy}^0,$$
$$\chi_{yxz}^{\omega_3}(\nabla\mathbf{E}^0) = A_1^{\omega_3}E_{yy}^0 + A_2^{\omega_3}E_{xx}^0 - A_3^{\omega_3}E_{zz}^0,$$
$$\chi_{yzx}^{\omega_3}(\nabla\mathbf{E}^0) = A_1^{\omega_3}E_{yy}^0 - A_2^{\omega_3}E_{zz}^0 + A_3^{\omega_3}E_{xx}^0,$$
$$\chi_{zxy}^{\omega_3}(\nabla\mathbf{E}^0) = A_1^{\omega_3}E_{zz}^0 - A_2^{\omega_3}E_{xx}^0 + A_3^{\omega_3}E_{yy}^0,$$
$$\chi_{zyx}^{\omega_3}(\nabla\mathbf{E}^0) = -A_1^{\omega_3}E_{zz}^0 + A_2^{\omega_3}E_{yy}^0 - A_3^{\omega_3}E_{xx}^0,$$

where the constants A_1, A_2, A_3 are given in terms of the appropriate tensor components (6). The preceding expressions remain unchanged in form on expressing the constants A_1, A_2, A_3

in terms of relevant tensor components (5), and the field gradient components $E^0_{xx}, \ldots$ in terms of the respective squared components of the uniform field $E^0_x E^0_x, \ldots$.

For the case of an isotropic body, the non-zero elements of tensors of higher ranks can be found by the method of statistical averaging with equal probability over all possible orientations of the co-ordinate axes [14, 20]. This procedure leads to the following expression for the elements of an arbitrary tensor of rank 5

$$\chi_{ijklm} = \chi_1^{(5)}\varepsilon_{ijk}\delta_{lm} + \chi_2^{(5)}\varepsilon_{ijl}\delta_{km} + \chi_3^{(5)}\varepsilon_{ijm}\delta_{kl} + \chi_4^{(5)}\varepsilon_{ikl}\delta_{jm} + \chi_5^{(5)}\varepsilon_{ikm}\delta_{jl} + \chi_6^{(5)}\varepsilon_{ilm}\delta_{jk} + \chi_7^{(5)}\varepsilon_{jkl}\delta_{im} + \chi_8^{(5)}\varepsilon_{jkm}\delta_{il} + \chi_9^{(5)}\varepsilon_{jlm}\delta_{ik} + \chi_{10}^{(5)}\varepsilon_{klm}\delta_{ij} ,$$

where the constants $\chi_1^{(5)}, \ldots, \chi_{10}^{(5)}$ are defined in a manner to form an orthonormal set of six linearly independent invariants [14, 20]. (It may be worth a reminder that ε_{ijk} is the Levi-Cività antisymmetric unit tensor; its elements equal 1 for different indices i, j, k following one another in cyclic order, or are equal to -1 if the indices i, j, k occur in anticyclic order, say i, k, j, or become 0 if any two indices are the same, e.g. for i, i, k.)

Similarly, in the general case, an arbitrary isotropic tensor of rank 6 can be written in the form

$$\chi_{ijklmn} = \sum_{s=1}^{s=15} \chi_s^{(6)}\delta_{ij}\delta_{kl}\delta_{mn} ,$$

where summation extends over the 15 independent tensor elements $\chi_1^{(6)}, \ldots \chi_{15}^{(6)}$ which result on performing the complete set of permutations of the indices i, j, k, l, m, n in the product $\delta_{ij}\delta_{kl}\delta_{mn}$ of unit tensors [20].

A reduction in number of the 15 constants $\chi_1^{(6)}, \ldots \chi_{15}^{(6)}$ will result in various cases from the type of symmetry of the tensor χ_{ijklmn}; when the latter is totally symmetric (symmetric in all 6 indices) this reduction can lead to two constants, or even to one [21] (on neglecting electronic dispersion and absorption).

The preceding considerations show that it is feasible to choose the geometrical conditions (as done with regard to other materials in the absence of an electric field [7, 18]) in a manner to be able to observe wave mixing processes (transverse polarisation component) in the presence of a uniform field or field gradient (see fig. 1).

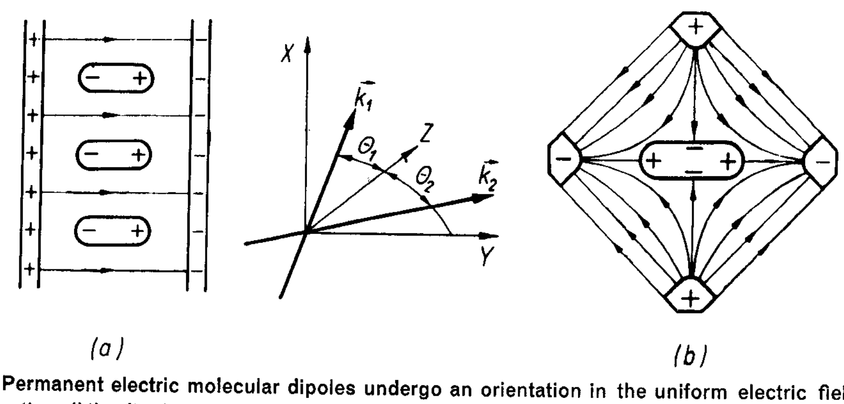

Figure 1 (a) Permanent electric molecular dipoles undergo an orientation in the uniform electric field $\mathbf{E}^0$; at electric saturation all the dipoles of the medium are aligned along the lines of force of the field (y-axis). (b) Permanent electric molecular quadrupoles undergo an orientation by the electric field gradient $E^0_{xx} = -E^0_{yy}$ produced in the medium by a four-wire capacitor (the conducting wires run parallel to the z-axis, which is the axis of the capacitor).

The propagation directions $\mathbf{k}_1$ and $\mathbf{k}_2$ of the two mutually intersecting laser beams lie in the yz-plane. The directions in which their electric vectors $\mathbf{E}^{\omega_1}$ and $\mathbf{E}^{\omega_2}$ oscillate are not visualised. The preceding experimental set-up is intended as one example resulting from the general theory. Hinging on various possible requirements, as they may occur to the experimenter, configurations of $\mathbf{E}^0$, $\mathbf{k}_1$, $\mathbf{k}_2$ $\mathbf{E}^{\omega_1}$ and $\mathbf{E}^{\omega_2}$ can suggest themselves for consideration as promising. However, it was not our aim to give these technicalities a closer treatment here.

References

1. R. W. TERHUNE, P. D. MAKER, and C. M. SAVAGE, *Phys. Rev. Letts.* **8** (1962) 404-406.
2. J. E. BJORKHOLM and A. E. SIEGMAN, *Phys. Rev.* **154** (1967) 851-860.
3. V. S. SUVOROV and A. S. SONIN, *Zh. Eksperim. i Teor. Fiz.* **54** (1968) 1044-1050.
4. G. MAYER, *C.R. Acad. Sci. Paris* **267B** (1968) 54-57; G. HAUCHECORNE, F. KERHERVÉ, and G. MAYER, *J. Physique, Paris* **31** (1970), in press.
5. S. KIELICH, *Physica* **29** (1963) 938-947; *Acta Phys. Polon.* **30** (1966) 851-876.
6. J. A. GIORDMAINE, *Phys. Rev.* **138** (1965) A 1599-1606.
7. P. M. RENTZEPIS, J. A. GIORDMAINE, and K. W. WECHT, *Phys. Rev. Letts.* **16** (1966) 792-794; J. A. GIORDMAINE and P. M. RENTZEPIS, *J. Chimie Physique* (1967) 215-221.
8. N. BLOEMBERGEN, "Nonlinear Optics" (W. A. Benjamin, New York, 1965).
9. S. KIELICH, *Acta Phys. Polon.* **A37** (1970) 205-219.
10. *Idem, IEEE J. Quantum Electr.* **QE-5** (1969) 562-568.
11. *Idem, Opto-electronics* **2** (1970) 5-20.
12. P. N. BUTCHER, "Nonlinear Optical Phenomena" (Columbus, Ohio State University Press, 1965).
13. S. KIELICH, *J. Chem. Phys.* **46** (1967) 4090-4099; *J. Physique* **29** (1968) 619-630 and references therein.
14. L. L. BOYLE, *Int. J. Quantum Chem.* **3** (1969) 231-243; **4** (1970) 413-425.
15. F. G. FUMI, *Nuovo Cimento* **9** (1952) 739-756; R. FIESCHI and F. G. FUMI, *ibid* **10** (1953) 865-882.
16. T. BANCEWICZ, S. KIELICH, Z. OŻGO, W. PIECZYŃSKI, and R. ZAWODNY, *Bull. Soc. Amis. Lettres Poznań, Sér. B* **22** (1969/70, in press).
17. L. S. GOLDBERG and J. M. SCHNUR, *Radio and Electronic Engineer* **39** (1970) 279-285.
18. M. TAKATSUJI, *Japan J. Appl. Phys.* **5** (1966) 389-400.
19. I. FREUND and I. KOPF, *Phys. Rev. Letts.* **24** (1970) 1017-1021.
20. S. KIELICH, *Acta Phys. Polonica* **20** (1961) 433-445; **31** (1967) 929-953; *Bull. Soc. Amis. Sci. Lettres Poznań, Sér B* **21** (1968/69) 47-55.
21. *Idem, Bull. Soc. Amis. Sci. Lettres Poznań, Sér B* **16** (1960/61) 69-80.