

Linear electro-optic effect in optically active liquids

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Abstract

A linear effect of an electrostatic field \mathbf{F} on the intensity of sum- and difference-frequency generation in a chiral liquid is predicted. It arises in the electric dipole approximation. The effect changes sign with the enantiomer and on reversing the direction of the electrostatic field. The sum-frequency generator $\chi_{\alpha\beta\gamma}^{(2)}(-\omega_3; \omega_1, \omega_2)$, where $\omega_3 = \omega_1 + \omega_2$, and the electric field-induced sum-frequency generator $\chi_{\alpha\beta\gamma\delta}^{(3)}(-\omega_3; \omega_1, \omega_2, 0)F_\delta$ interfere and their contributions to the scattering power can be distinguished. Encouraging predictions are given for a typical experimental arrangement. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Crystals may exhibit linear electro-optical properties, but isotropic systems such as liquids and gases generally show quadratic effects of an electric field on their linear and non-linear optical properties. However, there is an electro-optic effect in an isotropic system which has a component of the scattering power proportional to the applied electrostatic field: a change of the order of a few parts in a million was measured in the depolarized intensity scattered by gaseous methyl chloride linear on applying an electrostatic field, and the effect changes sign on reversing the static field, or the direction of scattering or the circularity of the light [1,2]. The differential scattering of circularly polarized light in a static field results from interference of electric and magnetic dipole scattering and is expected to be exhibited by all matter [2]. The effect should show itself in reflection from a polarized surface [3].

The effect we discuss in this Letter can be understood within the electric dipole approximation and will depend on the symmetry properties of the material. The induced non-linear polarization oscillating at the sum-frequency $\omega_3 = \omega_1 + \omega_2$ consists of terms quadratic in the applied optical fields, one of which is linear in the applied static or low-frequency field, \mathbf{F} ,

$$P_\alpha(\omega_3) = \varepsilon_0 K^{(2)}(-\omega_3; \omega_1, \omega_2) \chi_{\alpha\beta\gamma}^{(2)}(-\omega_3; \omega_1, \omega_2) E_\beta(\omega_1) E_\gamma(\omega_2) + \varepsilon_0 K^{(3)}(-\omega_3; \omega_1, \omega_2, 0) \\ \times \chi_{\alpha\beta\gamma\delta}^{(3)}(-\omega_3; \omega_1, \omega_2, 0) E_\beta(\omega_1) E_\gamma(\omega_2) F_\delta + \dots \quad (1)$$

where ε_0 is the permittivity of free space and where the $K^{(n)}$ are numerical factors chosen such that all

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susceptibilities $\chi_{\alpha\beta\dots\epsilon}^{(n)}$ of order n converge to the same static limit [4]. The tensors $\chi_{\alpha\beta\gamma}^{(2)}$ and $\chi_{\alpha\beta\gamma\delta}^{(3)}$ are the second- and third-order non-linear optical susceptibilities, respectively. Expressions similar to Eq. (1) for second-harmonic (SHG) or difference-frequency (DFG) generation are simply obtained by the respective transformations $\omega_2 \rightarrow \omega_1$ or $\omega_2 \rightarrow -\omega_2$, throughout. The intensity is proportional to the square of the polarization and it follows from Eq. (1) that should both $\chi_{\alpha\beta\gamma}^{(2)}$ and $\chi_{\alpha\beta\gamma\delta}^{(3)}$ be non-zero, then there will be an interference term, linear in \mathbf{F} .

Symmetry arguments show that the second-order non-linear susceptibility describing SHG vanishes in an isotropic system, such as a gas or a liquid, ² unlike the sum-frequency generation (SFG) and DFG susceptibility which has an isotropic component for optically active media [6]. The third-order susceptibility describing electric field-induced SHG (ESHG), electric field-induced SFG (ESFG), and electric field-induced DFG (EDFG) is present in all systems. Rentzepis et al. [7] measured coherent SFG from arabinose solutions and we base our estimates for the magnitude of the predicted effect on an adaptation of their experimental arrangement.

A linear electro-optical effect in anisotropic and non-centrosymmetric systems (many crystals) is the well known Pockels effect [8]. For small electrostatic fields the optical dielectric tensor, $\epsilon_{\alpha\beta}(\omega, \mathbf{F})$, may be expanded in a power series in \mathbf{F} [9]:

$$\epsilon_{\alpha\beta}(\omega, \mathbf{F}) = \epsilon_{\alpha\beta}^{(1)}(\omega) + 2 \epsilon_{\alpha\beta\gamma}^{(2)}(\omega) F_\gamma + 3 \epsilon_{\alpha\beta\gamma\delta}^{(3)}(\omega) F_\gamma F_\delta + \dots \quad (2)$$

Similarly the dipole moment per unit volume, $P_\alpha(\omega)$, can be expressed as a power series in the static electric field:

$$P_\alpha(\omega) = \epsilon_0 \left[\chi_{\alpha\beta}^{(1)}(-\omega; \omega) + 2 \chi_{\alpha\beta\gamma}^{(2)}(-\omega; \omega, 0) F_\gamma + 3 \chi_{\alpha\beta\gamma\delta}^{(3)}(-\omega; \omega, 0, 0) F_\gamma F_\delta + \dots \right] E_\beta(\omega). \quad (3)$$

Substituting Eq. (2) into

$$P_\alpha = \epsilon_0 \left[\epsilon_{\alpha\beta}(\omega, \mathbf{F}) - \delta_{\alpha\beta} \right] E_\beta, \quad (4)$$

where $\delta_{\alpha\beta}$ is Kronecker's delta, allows one to identify the successive contributions to the optical dielectric tensor [9]:

$$\begin{aligned} \epsilon_{\alpha\beta}^{(1)}(\omega) &= \delta_{\alpha\beta} + \chi_{\alpha\beta}^{(1)}(-\omega; \omega); \\ \epsilon_{\alpha\beta\gamma}^{(2)}(\omega) &= \chi_{\alpha\beta\gamma}^{(2)}(-\omega; \omega, 0); \\ \epsilon_{\alpha\beta\gamma\delta}^{(3)}(\omega) &= \chi_{\alpha\beta\gamma\delta}^{(3)}(-\omega; \omega, 0, 0). \end{aligned} \quad (5)$$

The second-order optical dielectric tensor $\epsilon_{\alpha\beta\gamma}^{(2)}(\omega)$, and hence the change in the refractive index, will be proportional to the applied dc field strength, giving the Pockels effect. Although, a field of 1000 kV/m induces only a small change Δn in the refractive index, typically of the order of 10^{-5} , it can cause a considerable phase shift $\Delta n l \omega/c$ of more than $\pi/2$ for a visible beam over a path length l of 1 cm. The quadratic electro-optical or Kerr effect exists for all systems, but is not considered in this Letter.

The linear electro-optic effect proposed in this Letter is only present in media lacking inversion symmetry, as second-order non-linear optical processes in centrosymmetric systems are forbidden under the electric-dipole approximation. Its observation in anisotropic systems may be complicated by the concomitant Pockels effect.

² Second-harmonic generation is possible for five-wave mixing via a fourth-order non-linearity $\chi_{\alpha\beta\gamma\delta\epsilon}^{(4)}(-2\omega; \omega, \omega, \omega, -\omega)$ in an optically active solution and has been observed by Shkurinov et al. [5].

This suggests ESFG and EDFG experiments in non-centrosymmetric isotropic media, namely optically active fluids.

2. Theoretical background

We consider plane monochromatic fields of the form

$$\mathbf{E}(\omega) = \frac{1}{2} \left[\mathbf{E}^\omega e^{i\mathbf{k}_\omega \cdot \mathbf{r}} + (\mathbf{E}^\omega)^* e^{-i\mathbf{k}_\omega \cdot \mathbf{r}} \right], \quad (6)$$

here expressed as a Fourier transform. The fields can easily be extended to include more than one frequency component.

The molecular dipole moment and the macroscopic polarization can be expanded in terms of a power series in the applied electric field [10]. The ξ -component of the dipole moment of the molecule oscillating at ω_σ is then given by

$$\begin{aligned} \mu_\xi^{\omega_\sigma} = & \alpha_{\xi\eta}(-\omega_\sigma; \omega_1) E_\eta^{\omega_1} + \frac{1}{2} K^{(2)}(-\omega_\sigma; \omega_1, \omega_2) \beta_{\xi\eta\nu}(-\omega_\sigma; \omega_1, \omega_2) E_\eta^{\omega_1} E_\nu^{\omega_2} \\ & + \frac{1}{6} K^{(3)}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) \gamma_{\xi\eta\nu\varrho}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) E_\eta^{\omega_1} E_\nu^{\omega_2} E_\varrho^{\omega_3} + \dots, \end{aligned} \quad (7)$$

where summation over repeated suffices is implied and $\alpha_{\xi\eta}$ is the molecular polarizability tensor, $\beta_{\xi\eta\nu}$ the first, and $\gamma_{\xi\eta\nu\varrho}$ the second, hyperpolarizability tensors.

The macroscopic susceptibility $\chi_{\alpha\beta\dots\varepsilon}^{(n)}$ can be related to the n th molecular hyperpolarizability tensor, $\gamma_{\xi\eta\dots\zeta}^{(n)}$, through a coordinate transformation from molecule-fixed axes to the frame of the incident radiation averaged over the molecular orientational distribution, denoted below by the angular brackets,

$$\chi_{\alpha\beta\dots\varepsilon}^{(n)}(-\omega_\sigma; \omega_1, \dots, \omega_n) = \frac{\mathcal{N} \gamma_{\xi\eta\dots\zeta}^{(n)}(-\omega_\sigma; \omega_1, \dots, \omega_n)}{n! \varepsilon_0} \langle a_{\xi\alpha} a_{\eta\beta} \dots a_{\zeta\varepsilon} \rangle, \quad (8)$$

where $a_{\xi\alpha}$ are direction cosines and \mathcal{N} is the number density of molecules.

$$K^{(2)} = \begin{cases} \frac{1}{2} & \text{for SHG; } \omega_\sigma = 2\omega_1(\text{SHG}), \\ 1 & \text{for SFG or DFG; } \omega_\sigma = \omega_1 \pm \omega_2(\text{SFG,DFG}), \end{cases} \quad (9)$$

$$K^{(3)} = \begin{cases} \frac{3}{2} & \text{for dc field-induced SHG; } \omega_\sigma = 2\omega_1 + 0(\text{ESHG}), \\ 3 & \text{for dc field-induced SFG or DFG; } \omega_\sigma = \omega_1 \pm \omega_2 + 0(\text{ESFG,EDFG}). \end{cases} \quad (10)$$

In condensed systems the field at a molecule will be different from the applied macroscopic field due to induced dipole–dipole interactions of the surrounding molecules. In the Lorentz model the n th-order non-linear susceptibility ($n = 2, 3, \dots$) is multiplied by $n + 1$ local field correction factors, one for each frequency component $\omega_\sigma, \omega_1, \dots, \omega_n$ [9]:

$$\chi_{\alpha\beta\dots\varepsilon}^{(n)}(-\omega_\sigma; \omega_1, \dots, \omega_n) = \left[\frac{\varepsilon^{(1)}(\omega_\sigma) + 2}{3} \right] \left[\frac{\varepsilon^{(1)}(\omega_1) + 2}{3} \right] \dots \left[\frac{\varepsilon^{(1)}(\omega_n) + 2}{3} \right]. \quad (11)$$

Perturbation theory can be used to obtain general sum-over-states expressions for the n th-order hyperpolarizability, $\gamma_{\xi\eta\cdots\zeta}^{(n)}$ [11]:

$$\gamma_{\xi\eta\cdots\zeta}^{(n)}(-\omega_\sigma; \omega_1, \dots, \omega_n) = \frac{1}{\hbar^n} \mathbf{S}_T \sum_{a_1} \sum_{a_2} \cdots \sum_{a_n} \frac{\langle g | \hat{\mu}_\xi | a_1 \rangle \langle a_1 | \hat{\mu}_\eta | a_2 \rangle \cdots \langle a_n | \hat{\mu}_\zeta | g \rangle}{(\omega_{a_1g} - \omega_\sigma) (\omega_{a_2g} - \omega_\sigma + \omega_1) \cdots (\omega_{a_ng} - \omega_n)} \quad (12)$$

where g is the ground vibronic state and the summations $\sum_{a_1} \sum_{a_2} \cdots$ are over all possible internal quantum states of the fixed molecule. The total symmetrization operator \mathbf{S}_T implies that the expression which follows is to be summed over all $(n+1)!$ terms obtained by permuting pairs of dipole operators $\hat{\mu}$ and corresponding optical frequencies ω , i.e. the pairs $(\hat{\mu}_\xi, -\omega_\sigma)$, $(\hat{\mu}_\eta, \omega_1)$, \dots , $(\hat{\mu}_\zeta, \omega_n)$. For dipolar molecules the dipole operators are replaced by fluctuation dipole operators $\bar{\mu}$, introduced by Brueckner [12],

$$\bar{\mu} \equiv \hat{\mu} - \langle g | \hat{\mu} | g \rangle. \quad (13)$$

The first hyperpolarizability $\beta_{\xi\eta\nu}$ and the second hyperpolarizability $\gamma_{\xi\eta\nu\zeta}$ correspond to $\gamma_{\xi\eta\nu}^{(2)}$ and $\gamma_{\xi\eta\nu\zeta}^{(3)}$, respectively, in Eq. (12). The sum-over-states expressions are valid for off-resonance conditions. Since we consider chiral molecules, $\beta_{\xi\eta\nu}$ and $\gamma_{\xi\eta\nu\zeta}$ may have all their tensor components (27 and 81, respectively) independent.

3. A review of coherent SFG in optically active liquids

For chiral molecules the SFG non-linear susceptibility tensor $\chi_{\alpha\beta\gamma}^{(2)}(-(\omega_1 + \omega_2); \omega_1, \omega_2)$ has an isotropic component

$$\chi_{\alpha\beta\gamma}^{(2)} = \chi^{(2)} \varepsilon_{\alpha\beta\gamma}, \quad (14)$$

where $\chi^{(2)}$ is a pseudoscalar,

$$\chi^{(2)} = \frac{\mathcal{N}}{2 \varepsilon_0} \frac{1}{6} \varepsilon_{\xi\eta\nu} \beta_{\xi\eta\nu}, \quad (15)$$

and $\varepsilon_{\alpha\beta\gamma}$ is the unit skew-symmetric tensor. Rentzepis et al. observed SFG from a 694.3 nm beam of a ruby laser and its harmonic in optically active 2.46 M d- and l-arabinose aqueous solutions and measured a $|\chi^{(2)}|$ of 7.5×10^{-14} m/V [7]. Three-wave mixing in optically active aqueous solutions of arabinose and of α -cyclodextrin at 1064 and 355 nm was later reported by Shkurinov and coworkers [5].

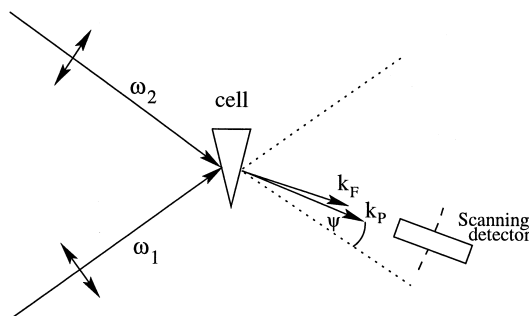


Fig. 1. Experimental arrangement similar to the one used by Rentzepis et al. [7] in the detection of a three-wave mixing process in optically active arabinose solutions. The liquid sample is in a prismatic cell.

The polarization at the sum-frequency is given by

$$P_{\alpha}^{\omega_1+\omega_2} = \varepsilon_0 \chi^{(2)} \varepsilon_{\alpha\beta\gamma} E_{\beta}^{\omega_1} E_{\gamma}^{\omega_2}, \quad (16)$$

where $E_{\beta}^{\omega_1}$ and $E_{\gamma}^{\omega_2}$ are the optical fields at angular frequencies ω_1 and ω_2 , respectively. Eq. (16) suggests an experimental arrangement, shown in Fig. 1, where the input beams are crossed and have orthogonal electric field vector components.

The pseudoscalar $\chi^{(2)}$ changes sign with the enantiomer. It follows that there will be no signal for a racemic mixture. The scattering power at the sum-frequency is proportional to the square of the polarization, $|P_{\alpha}^{\omega_1+\omega_2}|^2$, and thus the experiment [7] does not distinguish between optical isomers.

Two sum-frequency waves ($\omega_3 = \omega_1 + \omega_2$) are generated at the non-linear boundary [13]. One wave, the *free wave*, is the solution to the harmonic wave equation and has wavevector magnitude $k_F = n_3 \omega_3/c$, where n_3 is the refractive index at ω_3 . The other wave, the *polarization wave*, is a particular solution to the anharmonic wave equation and has wavevector $\mathbf{k}_p = \mathbf{k}_1 + \mathbf{k}_2$, sometimes termed the non-linear source-, bound- or forced-wave. The use of a prismatic sample cell eliminates the possibility of interference between the polarization- and the free-wave as the sum-frequency beams are refracted differently. The directions and emission angles (ψ) of the two waves are determined by the boundary conditions at the prism surfaces [14].

4. Intensity component linear in the static field

We now consider coherent three-wave mixing in an optically active fluid in an electrostatic field \mathbf{F} . The polarization oscillating at the sum-frequency now includes an additional term and is given by

$$P_{\alpha}^{\omega_1+\omega_2} = \varepsilon_0 \left[3 \left(\chi_1^{(3)} \delta_{\alpha\beta} \delta_{\gamma\delta} + \chi_2^{(3)} \delta_{\alpha\gamma} \delta_{\beta\delta} + \chi_3^{(3)} \delta_{\alpha\delta} \delta_{\beta\gamma} \right) E_{\beta}^{\omega_1} E_{\gamma}^{\omega_2} F_{\delta} + \chi^{(2)} \varepsilon_{\alpha\beta\gamma} E_{\beta}^{\omega_1} E_{\gamma}^{\omega_2} \right] \quad (17)$$

where $E_{\beta}^{\omega_1}, E_{\gamma}^{\omega_2}$ are the optical and F_{δ} is the static or low-frequency field. There are three independent isotropic tensors of the fourth rank [15]; for molecules with no permanent dipole moment the corresponding scalar third-order susceptibilities in Eq. (17) are

$$\begin{aligned} \chi_1^{(3)} &= \frac{\mathcal{N}}{180\varepsilon_0} \left[4\gamma_{\xi\xi\eta\eta} - \gamma_{\xi\eta\xi\eta} - \gamma_{\xi\eta\eta\xi} \right], \\ \chi_2^{(3)} &= \frac{\mathcal{N}}{180\varepsilon_0} \left[-\gamma_{\xi\xi\eta\eta} + 4\gamma_{\xi\eta\xi\eta} - \gamma_{\xi\eta\eta\xi} \right], \\ \chi_3^{(3)} &= \frac{\mathcal{N}}{180\varepsilon_0} \left[-\gamma_{\xi\xi\eta\eta} - \gamma_{\xi\eta\xi\eta} + 4\gamma_{\xi\eta\eta\xi} \right]. \end{aligned} \quad (18)$$

For dipolar gaseous molecules the $\gamma_{\xi\eta\nu\zeta}$ has to be replaced by $\gamma_{\xi\eta\nu\zeta} + \beta_{\xi\eta\nu} \mu_{\zeta}^{(0)}/(kT)$ [16].

Should the experimental arrangement, i.e. the beam directions and polarizations, be chiral, then the magnitude of the induced dipole and hence the intensity will include a term linear in the static field.

We now consider an explicit example and define our axis system for the beams *inside* the liquid cell, as seen in Fig. 2. For simplicity we ignore the rotation of the plane of polarization in the chiral liquid due to optical activity and assume that the light is linearly polarized. The angles and polarizations of the input beams outside the prismatic sample can be deduced from Snell's law and are not markedly different as a detailed analysis by Giordmaine and Rentzepis confirms [17]. The input beams define the yz plane and we choose the ω_1 beam to travel along the z direction and have its electric field vector oscillating along y and the ω_2 beam to be plane

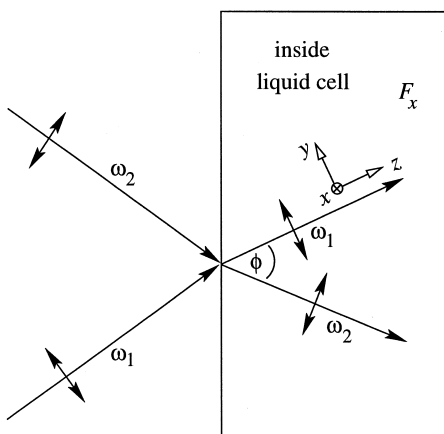


Fig. 2. Axis system defined for beam geometry inside the liquid cell. The static or low-frequency field points along the x axis.

polarized in the yz plane. The components $E_y^{\omega_2}$ and $E_z^{\omega_2}$ are determined by the angle ϕ the ω_1 beam makes with the ω_2 beam (see Fig. 2),

$$E_y^{\omega_2} = E^{\omega_2} \cos \phi \quad \text{and} \quad E_z^{\omega_2} = E^{\omega_2} \sin \phi. \quad (19)$$

In the experimental arrangement used by Rentzepis et al. [7] $\phi \approx 35^\circ$ for 2.46 M d- and l-arabinose solutions.

We choose the dc field across the prismatic cell to point along the x axis. The square of the polarization at the sum-frequency, $P_x^{\omega_1+\omega_2}$, in Eq. (17) takes the form

$$\begin{aligned} |P_x^{\omega_1+\omega_2}|^2 = \varepsilon_0^2 & \left[9 |\chi_3^{(3)}|^2 |E_y^{\omega_1}|^2 |E_y^{\omega_2}|^2 |F_x|^2 + |\chi^{(2)}|^2 |E_y^{\omega_1}|^2 |E_z^{\omega_2}|^2 \right. \\ & \left. + \frac{3}{2} \left(\chi_3^{(3)} (\chi^{(2)})^* |E_y^{\omega_1}|^2 |E^{\omega_2}|^2 \sin 2\phi F_x + \text{c.c.} \right) \right]. \quad (20) \end{aligned}$$

It is possible to observe the other isotropic fourth-rank tensors, or combinations thereof, using different beam polarizations. Since $\chi_1^{(3)}$, $\chi_2^{(3)}$ and $\chi_3^{(3)}$ are the same for d- and l-enantiomers while the $\chi^{(2)}$ are equal but opposite, Eq. (20) indicates that d and l samples will have different ESFG intensities in the same field F_x . The three contributions to the intensity at the the sum-frequency could be measured separately by modulating F_x and using phase-sensitive detection.

Absolute signs of non-linear susceptibilities are generally difficult to determine experimentally. However, this experiment makes it possible to determine the absolute sign of $\chi^{(2)}$ and $\chi_3^{(3)}$ for both optical isomers of a chiral compound in an achiral solvent. There is a contribution to $\chi_3^{(3)}$ from the achiral solvent and from the chiral solute

$$\chi_3^{(3)} = \chi_{\text{solvent}}^{(3)} + \chi_{\text{solute}}^{(3)}(\rho), \quad (21)$$

where we suppose that a value for $\chi_{\text{solvent}}^{(3)}$, possibly water, can be obtained computationally. Both $\chi^{(2)}(\rho)$ and $\chi_{\text{solute}}^{(3)}(\rho)$ are functions of the chiral solute's concentration ρ . The achiral solvent makes no contribution to $\chi^{(2)}$ except through weak intermolecular interactions [18]. Taking the susceptibilities as real we obtain from Eq. (20)

$$\begin{aligned} |P_x^{\omega_1+\omega_2}|^2 = \varepsilon_0^2 & \left[|\chi^{(2)}(\rho)|^2 |E_y^{\omega_1}|^2 |E_z^{\omega_2}|^2 + 9 |\chi_{\text{solvent}}^{(3)}|^2 |E_y^{\omega_1}|^2 |E_y^{\omega_2}|^2 |F_x|^2 \right. \\ & + 9 |\chi_{\text{solute}}^{(3)}(\rho)|^2 |E_y^{\omega_1}|^2 |E_y^{\omega_2}|^2 |F_x|^2 + 18 \chi_{\text{solvent}}^{(3)} \chi_{\text{solute}}^{(3)}(\rho) |E_y^{\omega_1}|^2 |E_y^{\omega_2}|^2 |F_x|^2 \\ & \left. + 3 \chi_{\text{solvent}}^{(3)} \chi^{(2)}(\rho) |E_y^{\omega_1}|^2 |E^{\omega_2}|^2 \sin 2\phi F_x + 3 \chi_{\text{solute}}^{(3)}(\rho) \chi^{(2)}(\rho) |E_y^{\omega_1}|^2 |E^{\omega_2}|^2 \sin 2\phi F_x \right], \end{aligned}$$

where the last two terms are linear in the applied field. These could be isolated by modulating F_x and using phase-sensitive detection. Measurements of the contribution to the sum-frequency intensity linear in F_x for different concentrations determine the sign and the magnitude of $\chi_{\text{solute}}^{(3)}(\rho)$ and $\chi^{(2)}(\rho)$ for one optical isomer, since $\chi_{\text{solvent}}^{(3)}$ is presumed to be known from computations.

5. Estimate of the magnitude of the effect

The peak power of the wave at the sum-frequency, \mathcal{P}_{ω_3} , can be estimated approximately assuming all beams have the same cross-sectional area A :

$$\mathcal{P}_{\omega_3} = I_{\omega_3} A \approx \frac{\omega_3^2}{8 n_3 \varepsilon_0 c} |P_x^{\omega_1 + \omega_2}|^2 A L^2, \quad (22)$$

where L is the length the beams interact along the phase-matched direction. We have used

$$I_{\omega_i} = \frac{1}{2} n_i c \varepsilon_0 |\mathbf{E}^{\omega_i}|^2.$$

We assume that all beams are far from resonance and hence take both susceptibilities as real. Substitution of Eq. (20) into (23) yields

$$\mathcal{P}_{\omega_3} \approx \frac{\omega_3^2 \mathcal{P}_{\omega_1} \mathcal{P}_{\omega_2} L^2}{2 n_1 n_2 n_3 \varepsilon_0 c^3 A} \left[9 |\chi_3^{(3)}|^2 \cos^2 \phi |F_x|^2 + |\chi^{(2)}|^2 \sin^2 \phi + 3 \chi_3^{(3)} \chi^{(2)} \sin 2\phi F_x \right]. \quad (23)$$

For an order-of-magnitude estimate we neglect the intensity component quadratic in the dc field and determine a fraction of the total signal which is linear in the dc field of

$$\frac{|\chi_3^{(3)} F_x|}{|\chi^{(2)}|} > 10^{-5}, \quad (24)$$

where we have used the second-hyperpolarizability for third-harmonic generation of ethanol as a lower limit for $\chi_3^{(3)}$ ($\approx 10^{-24} \text{ m}^2/\text{V}^2$) [19] and used Rentzepis' measured value for d- and l-arabinose of $|\chi^{(2)}| \approx 7.5 \times 10^{-14} \text{ m/V}$ [7] and a static field strength of $\geq 1000 \text{ kV/m}$. We obtain a conservative estimate of $\sim 10^5$ photons per pulse of which about 10 photons would be due to the component linear in the dc field, using typical numbers from Rentzepis' original ruby laser experiment [7]; estimates of the power of the input beams are $\mathcal{P}_{\omega_1} = 5 \text{ MW}$ at 694.3 nm and $\mathcal{P}_{\omega_2} = 10 \text{ kW}$ at 347.2 nm, with pulse durations of 20 ns. The beam cross-section is $A \approx 5.5 \times 10^{-6} \text{ m}^2$. We take L as the coherence length $l_c \approx 2 \text{ }\mu\text{m}$. Photon numbers would be considerably higher with modern laser systems.

6. Conclusions

We predict a new electro-optical effect that is linear in an electrostatic field in isotropic chiral media. It involves SFG or DFG and exists in the electric dipole approximation. It arises from the interference of an electric field-induced third-order non-linear susceptibility with the second-order non-linear susceptibility. Symmetry arguments suggest that this effect occurs for electric field-induced SHG in anisotropic media. However, care has to be taken to distinguish it from the Pockels effect. An order-of-magnitude analysis shows that in an isotropic chiral fluid the electro-optical effect is at least one part in 10^5 of the total scattering at the sum-frequency. The d- and l-enantiomers of the chiral solute can be distinguished by their respective ESFG intensities. Modulation of the static field combined with phase-sensitive detection for different concentrations of the optically active solute allows one to determine the absolute sign of $\chi^{(2)}$ and $\chi^{(3)}$ for both optical isomers.

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