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Chapter 9

Optical Response of a Chiral Liquid

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The optical properties of a molecule can be analyzed in terms of the oscillations in the charge and current density induced by the electromagnetic field associated with the optical wave. The induced electric and magnetic moments are related to the optical field through molecular property tensors. We discuss the symmetry of these response tensors and show that the first hyperpolarizability, like the optical rotation tensor, has an isotropic component and is chirally sensitive. The first hyperpolarizability may give rise to second-harmonic generation, sum- and difference-frequency generation, and the Pockels effect. We show that second-harmonic generation and the Pockels effect vanish for any liquid. Sum- and difference-frequency generation are symmetry allowed in chiral liquids, and may give rise to a novel linear electro-optic effect. This effect arises from the interference of the first hyperpolarizability $\beta_{\alpha\beta\gamma}$ with an electric field-induced hyperpolarizability $\gamma_{\alpha\beta\gamma\delta} F_\delta$, where F_δ is a component of an electrostatic field.

Optical response tensors

Optical fields that are incident upon a molecule induce time-varying molecular moments which themselves radiate. The interaction of the electromagnetic field and an uncharged molecule is formally described by the multipolar interaction Hamiltonian, H_I:

$$\hat{H}_I(t) = -\hat{\mu}_\alpha E_\alpha(t) - \frac{1}{3}\hat{\Theta}_{\alpha\beta}E_{\alpha\beta}(t) - \hat{m}_\alpha B_\alpha + \dots \tag{1}$$

where $E_{\alpha\beta} = \nabla_\alpha E_\beta$.

The molecular dipole moment, electric quadrupole moment and magnetic dipole moment operators are respectively defined by

$$\hat{\mu}_\alpha = \sum_i e_i r_{i_\alpha} \tag{2}$$

$$\hat{\Theta}_{\alpha\beta} = \frac{1}{2}\sum_i e_i(3r_{i_\alpha}r_{i_\beta} - r_i^2\,\delta_{\alpha\beta}) \tag{3}$$

$$\hat{m}_\alpha = \sum_i \frac{e_i}{2m_i}\,(l_{i_\alpha} + g_i\,s_{i_\alpha}) \quad . \tag{4}$$

Note that the electric quadrupole moment is symmetric in α and β and traceless.

Most linear optical phenomena such as refraction, absorption of light, Rayleigh and Raman scattering can be interpreted through the oscillating induced dipole moment linear in the electric field [1] :

$$\Delta\mu_\alpha = \alpha_{\alpha\beta}\,E_\beta + \alpha'_{\alpha\beta}\,\dot{E}_\beta/\omega \tag{5}$$

where $E_\beta = E_\beta^{(0)}\cos(\omega t - k_\gamma r_\gamma)$. $\alpha_{\alpha\beta}$ is the symmetric polarizability tensor and $\alpha'_{\alpha\beta}$ is the antisymmetric polarizability tensor. Summation over repeated tensor suffices is implied.

In order to describe the optical properties of chiral molecules it becomes necessary to consider response tensors other than the electric-dipole polarizability.

More generally the molecular moments linear in the periodic electromagnetic field are [1, 2, 3]:

$$\Delta\mu_\alpha = \alpha_{\alpha\beta}\, E_\beta + \frac{1}{\omega}\,\alpha'_{\alpha\beta}\,\dot{E}_\beta + G_{\alpha\beta}\, B_\beta + \frac{1}{\omega}\, G'_{\alpha\beta}\,\dot{B}_\beta + \frac{1}{3}\, A_{\alpha,\beta\gamma}\, E_{\beta\gamma} + \frac{1}{3\,\omega}\, A'_{\alpha,\beta\gamma}\,\dot{E}_{\beta\gamma} + \ldots \qquad (6a)$$

$$\Delta m_\alpha = \chi_{\alpha\beta}\, B_\beta + \frac{1}{\omega}\,\chi'_{\alpha\beta}\,\dot{B}_\beta + G_{\beta\alpha}\, E_\beta - \frac{1}{\omega}\, G'_{\beta\alpha}\,\dot{E}_\beta + \frac{1}{3}\, D_{\alpha,\beta\gamma}\, E_{\beta\gamma} + \frac{1}{3\,\omega}\, D'_{\alpha,\beta\gamma}\,\dot{E}_{\beta\gamma} + \ldots \qquad (6b)$$

$$\Delta\Theta_{\alpha\beta} = A_{\gamma,\alpha\beta}\, E_\gamma - \frac{1}{\omega}\, A'_{\gamma,\alpha\beta}\,\dot{E}_\gamma + C_{\alpha\beta,\gamma\delta}\, E_{\gamma\delta} + \frac{1}{\omega}\, C'_{\alpha\beta,\gamma\delta}\,\dot{E}_{\gamma\delta} + D_{\gamma,\alpha\beta}\, B_\gamma - \frac{1}{\omega}\, D'_{\gamma,\alpha\beta}\,\dot{B}_\gamma + \ldots \qquad (6c)$$

Higher powers of the fields or the simultaneous interaction of several electromagnetic fields give rise to a nonlinear optical response. The dipole oscillating at the sum-frequency $\omega_3 = \omega_1 + \omega_2$ induced by linearly polarized beams $E_{1_\beta} = E_{1_\beta}^{(0)} \cos \omega_1 t$ and $E_{2_\gamma} = E_{2_\gamma}^{(0)} \cos \omega_2 t$ is

$$\Delta\mu_\alpha(-\omega_3;\omega_1,\omega_2) = \frac{1}{2}\,\beta_{\alpha\beta\gamma}\, E_{1_\beta}^{(0)}\, E_{2_\gamma}^{(0)} \cos(\,\omega_1 + \omega_2\,)\, t \qquad (7)$$

where the incident optical fields are $E_{1_\beta}(\omega_1)$ and $E_{2_\gamma}(\omega_2)$, and where we have limited our analysis to electric dipolar interactions. Only the time-even first hyperpolarizability is considered.

In order to describe the optical properties of a liquid, we now need to average the response tensors in Eqns (6) and (7) over the orientational distribution of the ensemble of molecules.

Isotropic tensors

A vector transforms as D_1 and therefore has no isotropic component. A second rank tensor (e.g. the polarizability) transforms as $D_1 \otimes D_1 = D_0 + D_1 + D_2$, where the tensor's isotropic part transforms as D_0, its antisymmetric part as D_1 and its traceless symmetric part as D_2. Similarly, a third and fourth rank tensor transform as $D_1 \otimes D_1 \otimes D_1 = D_0 + 3D_1 + 2D_2 + D_3$ and $D_1 \otimes D_1 \otimes D_1 \otimes D_1 = 3D_0 + 6D_1 + 6D_2 + 3D_3 + D_4$, respectively, so there is one isotropic tensor of the third rank and three independent isotropic tensors of the fourth rank. In an isotropic medium, such as a fluid or a gas, a Cartesian property tensor $< \mathbf{X} >$ may thus be replaced by [4]

$$\begin{aligned}
< X_{\alpha\beta} > &= \overline{X}_a \; \delta_{\alpha\beta} && \text{(8a)}\\
< X_{\alpha\beta\gamma} > &= \overline{X}_b \; \epsilon_{\alpha\beta\gamma} && \text{(8b)}\\
< X_{\alpha\beta\gamma\delta} > &= \overline{X}_{c1} \; \delta_{\alpha\beta}\delta_{\gamma\delta} + \overline{X}_{c2} \; \delta_{\alpha\gamma}\delta_{\beta\delta} + \overline{X}_{c3} \; \delta_{\alpha\delta}\delta_{\beta\gamma} && \text{(8c)}
\end{aligned}$$

with

$$\begin{aligned}
\overline{X}_a &= \frac{1}{3} X_{\alpha\beta} \; \delta_{\alpha\beta} = \frac{1}{3} X_{\alpha\alpha} && \text{(9a)}\\
\overline{X}_b &= \frac{1}{6} X_{\alpha\beta\gamma} \; \epsilon_{\alpha\beta\gamma} && \text{(9b)}\\
\overline{X}_{c1} &= \frac{1}{30} \left[4X_{\alpha\alpha\beta\beta} - X_{\alpha\beta\alpha\beta} - X_{\alpha\beta\beta\alpha}\right] && \text{(9c)}\\
\overline{X}_{c2} &= \frac{1}{30} \left[-X_{\alpha\alpha\beta\beta} + 4X_{\alpha\beta\alpha\beta} - X_{\alpha\beta\beta\alpha}\right] && \text{(9d)}\\
\overline{X}_{c3} &= \frac{1}{30} \left[-X_{\alpha\alpha\beta\beta} - X_{\alpha\beta\alpha\beta} + 4X_{\alpha\beta\beta\alpha}\right] && \text{(9e)}
\end{aligned}$$

where $\delta_{\alpha\beta}$ is the Kronecker delta and $\epsilon_{\alpha\beta\gamma}$ is the unit skew-symmetric (Levi-Civita) tensor.

The polarizability and the first hyperpolarizability are second and third rank tensors respectively and have the following isotropic components:

$$\begin{aligned}
< \alpha_{\alpha\beta} > &= \overline{\alpha} \; \delta_{\alpha\beta}\\
\overline{\alpha} &= \frac{1}{3} \; \alpha_{\alpha\alpha} = \frac{1}{3} \left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)\\
< \beta_{\alpha\beta\gamma} > &= \overline{\beta} \; \epsilon_{\alpha\beta\gamma}\\
\overline{\beta} &= \frac{1}{6} \; \epsilon_{\alpha\beta\gamma} \; \beta_{\alpha\beta\gamma}\\
&= \frac{1}{6} \left(\beta_{xyz} - \beta_{xzy} + \beta_{yzx} - \beta_{yxz} + \beta_{zxy} - \beta_{zyx}\right) && \text{(10)}
\end{aligned}$$

Note that the isotropic component of a third rank tensor is completely anti-symmetric. As the dipole-quadrupole polarizability $A_{\alpha,\beta\gamma}$ is symmetric in its last two indices, it follows that it does not have an isotropic part (see Table 2).

Symmetry

We consider the symmetry operations of time reversal and parity in order to identify those optical property tensors that may give rise to a chirally sensitive response in a liquid. Parity inverts all coordinates and hence the electric field and the electric dipole are odd under parity whereas the magnetic field is even. Time-reversal inverts the direction of momenta and spins but leaves charges invariant. It follows that an electric field is symmetric under time-reversal, whereas a magnetic field and a magnetic dipole are time-antisymmetric. Table 1 shows the effect of $\hat{P}$ and $\hat{T}$ on various properties and fields.

Table 1: Symmetry of various molecular property tensors and external fields under parity ($\hat{\mathrm{P}}$) and time reversal ($\hat{\mathrm{T}}$).

external field or property		$\hat{P}$	$\hat{T}$
$\mathbf{E}$	electric field	−	+
$\dot{\mathbf{E}}$	time derivative of electric field	−	−
μ	electric dipole moment	−	+
Θ	electric quadrupole moment	+	+
$\mathbf{B}$	magnetic field	+	−
$\dot{\mathbf{B}}$	time derivative of magnetic field	+	+
m	magnetic dipole moment	+	−

The behaviour of the property tensors under time reversal and space inversion (see Table 2) can be inferred from Eqns (6) and (7) with the help of Table 1; e.g. the parity-even, time-odd magnetic dipole m induced by a parity-odd, time-odd time derivative of the electric field $\dot{\mathbf{E}}$ requires a parity-odd, time-even molecular response, here the optical rotation tensor, $G'_{\beta\alpha}$.

A molecule that is distinct from its mirror image is considered to be chiral [5]. Parity interconverts a chiral molecule into its mirror image. A chirally sensitive response thus requires a parity-odd property tensor; and since the isotropic part of any tensor is a scalar it follows that pseudoscalars (independent of the choice of coordinate axes, and of opposite sign for enantiomers) are associated with chirally

Table 2: Behaviour of various molecular response tensors under space inversion (parity, $\hat{P}$) and time reversal ($\hat{T}$).

response tensor		operators	$\hat{P}$	$\hat{T}$	isotropic part	chirally sensitive
$\alpha_{\alpha\beta}$	symmetric polarizability	$\hat{\mu}\hat{\mu}$	+	+	$\surd$	
$\alpha'_{\alpha\beta}$	antisymmetric polarizability	i $\hat{\mu}\hat{\mu}$	+	−	$\surd$	
$G'_{\alpha\beta}$	optical rotation tensor	i $\hat{m}\hat{\mu}$	−	+	$\surd$	$\surd$
$A_{\alpha,\beta\gamma}$	dipole-quadrupole polarizability	$\hat{\mu}\hat{\Theta}$	−	+		
$C_{\alpha\beta,\gamma\delta}$	quadrupole polarizability	$\hat{\Theta}\hat{\Theta}$	+	+	$\surd$	
$\chi_{\alpha\beta}$	$= \chi^{dia.}_{\alpha\beta} + \chi^{para.}_{\alpha\beta}$ magnetizability	$\hat{m}\hat{m}$	+	+	$\surd$	
$\alpha'_{\alpha\beta\gamma}$	Faraday rotation	i $\hat{\mu}\hat{\mu}\hat{m}$	+	+	$\surd$	
$G'_{\alpha\beta\gamma}$	electric field on opt. rotation tensor	i $\hat{m}\hat{\mu}\hat{\mu}$	+	+	$\surd$	
$\beta_{\alpha\beta\gamma}$	first hyperpolarizability	$\hat{\mu}\hat{\mu}\hat{\mu}$	−	+	$\surd$	$\surd$
$\gamma_{\alpha\beta\gamma\delta}$	second hyperpolarizability	$\hat{\mu}\hat{\mu}\hat{\mu}\hat{\mu}$	+	+	$\surd$	

sensitive observables. Further, as a stationary fluid medium in the absence of an external magnetic field is invariant under time-reversal, we seek a time-even (and parity-odd) response tensor that has a non-vanishing isotropic part. We refer to Barron [3, 6] for a more complete account of the symmetry properties of optical activity phenomena.

In Table 2 it is seen that the optical rotation tensor $G'_{\beta\alpha}$ and the first hyperpolarizability $\beta_{\alpha\beta\gamma}$ are both odd under parity and even under time reversal. As required, the isotropic parts associated with $G'_{\beta\alpha}$ and $\beta_{\alpha\beta\gamma}$ are therefore time-even pseudoscalars. For a review of the optical activity phenomena associated with the optical rotation tensor, and in particluar vibrational and Raman optical activity, we refer to the references [3, 7, 8]. Henceforth, we will concetrate on $\overline{\beta}$ and discuss the nonlinear optical effects it may give rise to in a chiral liquid.

Sum-over-states expression of the isotropic part of the first hyperpolarizability

Second-harmonic generation (SHG) $2\omega = \omega + \omega$, sum-frequency generation (SFG) $\omega_3 = \omega_1 + \omega_2$, and difference-frequency generation (DFG) $\omega_3 = \omega_1 - \omega_2$ and the Pockels effect $\omega = \omega + 0$, are all described by the first hyperpolarizability $\beta_{\alpha\beta\gamma}$. Time-dependent perturbation theory may be used to obtain a sum-over-states expression for $\beta_{\alpha\beta\gamma}$. The isotropic component $\overline{\beta}$ of the sum-frequency hyperpolarizability is given by [9]:

$$\overline{\beta}(-\omega_3;\omega_1,\omega_2) = \frac{1}{6\,\hbar^2}\sum_{kj}\left(\boldsymbol{\mu}_{gk}\cdot\left[\boldsymbol{\mu}_{kj}\times\boldsymbol{\mu}_{jg}\right]\right)$$
$$\times\{\ (\tilde{\omega}_{kg}-\omega_3)^{-1}\left((\tilde{\omega}_{jg}-\omega_2)^{-1}-(\tilde{\omega}_{jg}-\omega_1)^{-1}\right)$$
$$+(\tilde{\omega}^*_{kg}+\omega_1)^{-1}\left((\tilde{\omega}^*_{jg}+\omega_3)^{-1}-(\tilde{\omega}_{jg}-\omega_2)^{-1}\right)$$
$$+(\tilde{\omega}^*_{kg}+\omega_2)^{-1}\left((\tilde{\omega}_{jg}-\omega_1)^{-1}-(\tilde{\omega}^*_{jg}+\omega_3)^{-1}\right)\} \qquad (11)$$

The summation is over all excited states k and j, and the electric-dipole transition matrix element $\langle g|\hat{\boldsymbol{\mu}}|k\rangle \equiv \boldsymbol{\mu}_{gk}$. By allowing the transition frequency to be the complex quantity $\tilde{\omega}_{kg} \equiv \omega_{kg} - (\mathrm{i}/2)\,\Gamma_{kg}$, where ω_{kg} is the real transition frequency and Γ_{kg} the width at half the maximum height of the linear absorption spectral line from the ground state g to the the upper level k. Eqn. (11) is valid near resonance. The corresponding expression for DFG follows with the substitutions $\omega_2 \to -\omega_2$. The pseudoscalar $\overline{\beta}$ changes sign with the enantiomer and consequently averages to zero in the bulk of a racemic mixture (and in any achiral liquid). It may be seen that $\overline{\beta}$ vanishes for second-harmonic generation.

We now consider electro-optic effects in chiral liquids. The sum-over-states expression for the isotropic part of the Pockels tensor is [10]:

$$\overline{\beta}(-\omega;\omega,0) = \frac{1}{6\,\hbar^2}\sum_{kj}\left(\boldsymbol{\mu}_{gk}\cdot\left[\boldsymbol{\mu}_{kj}\times\boldsymbol{\mu}_{jg}\right]\right)$$
$$\times\{\ (\tilde{\omega}_{kg}-\omega)^{-1}\left(\omega_{jg}^{-1}-(\tilde{\omega}_{jg}-\omega)^{-1}\right)$$
$$+(\tilde{\omega}^*_{kg}+\omega)^{-1}\left((\tilde{\omega}^*_{jg}+\omega)^{-1}-\omega_{jg}^{-1}\right)$$
$$+(\omega_{kg}^{-1}\left((\tilde{\omega}_{jg}-\omega)^{-1}-(\tilde{\omega}^*_{jg}+\omega)^{-1}\right)\} \qquad (12)$$

The terms in brackets {} in Eqn (12) are symmetric in k and j, and for real wavefunctions (as is appropriate in the absence of an external magnetic field) the triple vector product of transition dipole matrix elements is anti-symmetric, and hence the isotropic part of the Pockels tensor is zero. Eqn (12) may be deduced from Eqn (11) by setting an optical frequency *and* the associated complex damping term to zero [10]. This does not seem to have been appreciated in a number of recent publications [11-16]. Inconsistencies in the signs of the damping terms in sum-over-states expressions cause the Pockels tensor to have a non-vanishing isotropic component. We refer to reference [10] for a more detailed discussion.

In summary, the first hyperpolarizability has a nonvanishing isotropic component in a chiral liquid for sum- and difference-frequency generation, and this is discussed further in [17]. Second-harmonic generation and the Pockels effect are forbidden by symmetry in any liquid.

In the next section we show that the Pockels effect (linear change of the refractive index due to a static electric field) is also absent when the chiral liquid is dipolar and the interaction between the permanent molecular dipole moment and the electrostatic field is considered.

Orientational averages in the presence of a static field

If a molecule possesses a permanent electric dipole moment $\boldsymbol{\mu}^{(0)}$, then a static electric field, $\mathbf{F}$, will exert a torque on the molecules, such that they orient. The orientational average of a perturbed molecular tensor component $\mathbf{X}$ in space-fixed axes in the presence of a static electric field can be found by taking a classical Boltzmann average [3, 18]:

$$< \mathbf{X}(\Omega) >_{\mathbf{F}} = \frac{\int \mathbf{X}(\Omega)\, e^{-V(\Omega,\mathbf{F})/kT}\, d\Omega}{\int e^{-V(\Omega,\mathbf{F})/kT}\, d\Omega} \qquad (13)$$

The potential energy V is a function of the static field and the molecule's orientation Ω in the field:

$$V(\Omega, \mathbf{F}) = V(\Omega) - \mu_\alpha^{(0)} F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}^{(0)} F_\alpha F_\beta - \ldots \qquad (14)$$

where $\alpha_{\alpha\beta}^{(0)}$ is the static polarizability. Assuming that the sample is initially randomly oriented, and that $V(\Omega, \mathbf{F}) - V(\Omega) \ll kT$ we use the expansion

$$\begin{aligned} < \mathbf{X}(\Omega) >_{\mathbf{F}} \;=\; & < \mathbf{X}(\Omega) > + \frac{F_\alpha}{kT} < \mathbf{X}(\Omega)\mu_\alpha^{(0)} > \qquad (15) \\ & + \frac{F_\alpha F_\beta}{k^2T^2}\left[\frac{1}{2} < \mathbf{X}(\Omega)\mu_\alpha^{(0)}\mu_\beta^{(0)} > - \frac{1}{2} < \mathbf{X}(\Omega) >< \mu_\alpha^{(0)}\mu_\beta^{(0)} > \right. \\ & \left. + \frac{kT}{2}\left\{< \mathbf{X}(\Omega)\alpha_{\alpha\beta}^{(0)} > - < \mathbf{X}(\Omega) >< \alpha_{\alpha\beta}^{(0)} >\right\}\right] + \ldots \end{aligned}$$

where the brackets $< \ldots >$ denote an isotropic average. If the duration of the applied static field is long compared to a molecular rotational time, the tensors $X_{\alpha\beta\gamma}$ and $X_{\alpha\beta\gamma\delta}$ in (8) should include linear terms $X_{\alpha\beta}\mu_\gamma^{(0)}/(kT)$ and $X_{\alpha\beta\gamma}\mu_\delta^{(0)}/(kT)$ respectively.

Considering the polarizability perturbed by the electrostatic field in Eqn (15), it is seen that the static field F_γ does not make a linear contribution to the hyperpolarizability $\beta_{\alpha\beta\gamma}(-\omega;\omega,0)$, since the isotropic part of $\alpha_{\alpha\beta}(-\omega;\omega)\mu_\gamma^{(0)}/(kT)$

vanishes, and $\alpha'_{\alpha\beta}(-\omega;\omega)\mu_\gamma^{(0)}/(kT)$ is zero in a liquid in the absence of a magnetic field.

However, an electrostatic field may have a linear effect on the intensity of a sum-frequency signal in a chiral liquid which is discussed next.

A linear electro-optic effect in chiral liquids

We consider a coherent sum-frequency generation process in a chiral liquid in an electrostatic field. We include the second hyperpolarizability in the expression for the induced dipole oscillating at $\omega_3 = \omega_1 + \omega_2$ (see Eqn 7) and obtain

$$\begin{aligned} \Delta\mu_\alpha(-\omega_3;\omega_1,\omega_2,0) &= \\ & \frac{1}{2}\,\beta_{\alpha\beta\gamma}(-\omega_3;\omega_1,\omega_2)\,E_{1_\beta}^{(0)}\,E_{2_\gamma}^{(0)}\,\cos\left(\omega_1+\omega_2\right)t \qquad (16) \\ & +\frac{1}{3}\,\gamma_{\alpha\beta\gamma\delta}(-\omega_3;\omega_1,\omega_2,0)\,E_{1_\beta}^{(0)}\,E_{2_\gamma}^{(0)}\,F_\delta\,\cos\left(\omega_1+\omega_2\right)t \end{aligned}$$

where we only consider the time-even hyperpolarizabilities. The second hyperpolarizability $\gamma_{\alpha\beta\gamma\delta}$ describes the response to third order in the applied fields and exists for all matter, even a spherical atom.

The scattering power at the sum-frequency is proportional to the square of the induced dipole moment $|\Delta\mu_\alpha|^2$ and consists of terms quadratic in the applied optical fields, one of which is linear in the applied static or low-frequency field, F [19]. The term linear in the electrostatic field arises from interference of the sum-frequency generator $\beta_{\alpha\beta\gamma}(-\omega_3;\omega_1,\omega_2)$ and the electric-field-induced sum-frequency generator $\gamma_{\alpha\beta\gamma\delta}(-\omega_3;\omega_1,\omega_2,0)\,F_\delta$ [19]. Their contributions to the scattering power can be distinguished.

If 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 polarized in the yz plane, then the amplitude of the induced-dipole along x oscillating at the sum-frequency is

$$|\Delta\mu_x|^2 = \left|\frac{1}{2}\overline{\beta}\,E_{1_y}\,E_{2_z} + \frac{1}{3}\overline{\gamma}_3\,E_{1_y}\,E_{2_y}\,F_x\right|^2 \quad , \qquad (17)$$

where the electrostatic field is taken along x. For an order-of-magnitude estimate we neglect the intensity component quadratic in the d.c. field and determine a fraction of the total signal that is linear in the d.c. field of

$$\frac{4\,|\overline{\gamma}_3\,F_x|}{3\,|\overline{\beta}|} \sim 10^{-2} \tag{18}$$

where we have taken $|\overline{\beta}|$ (at transparent frequencies) to be $\sim$ 0.03 au [20], $|\overline{\gamma}|$ to be $\sim$ 100 au, and $F_x \sim 2 \times 10^{-6}$ au $\approx 10^6$ V/m.

Conclusions

Symmetry arguments show that parity odd, time even molecular property tensors that have nonvanishing isotropic parts may give rise to chirally sensitive signals in liquids. Such tensors are the optical rotation tensor $G'_{\alpha\beta}$ in linear optics and the electric-dipolar first hyperpolarizability $\beta_{\alpha\beta\gamma}$ in nonlinear optics. Optical rotation, vibrational and Raman optical activity are all described by $G'_{\alpha\beta}$ (and its interference with the linear polarizability $\alpha_{\alpha\beta}$). Comparatively little is however known about the nonlinear optical phenomena in isotropic chiral media, such as sum- and difference-frequency generation [20]. It is expected that the hyperpolarizability $\overline{\beta}$ will be more sensitive than $\overline{\alpha}$ to environmental influences in the liquid [21].

The signal from a sum-frequency generation process in a chiral liquid in the presence of a static electric field is predicted to include an intensity component linear in the static field. Observation of the effect will require an appreciable isotropic component of the first hyperpolarizability.

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