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New non-linear circular birefringence effects of the electromagnetic field

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The polarization, $\boldsymbol{P}$, due to an electromagnetic field is expanded in powers of its electronic ($\boldsymbol{E}$) and magnetic ($\boldsymbol{B}$) components, and the Maxwell equations solved for new circular birefringence (CB) effects. At zeroth order there is a circular birefringence dependent on the anisotropy of the molecular polarisability. This is + to parity reversal P and occurs in achiral media. At first order the CB is proportional, in chiral media, to the product of $\boldsymbol{E}$ and the anisotropy of the electric hyperpolarisability tensor $\boldsymbol{\beta}_1^*$. This CB is − to P and changes sign between enantiomers. There is a similar term proportional to $\boldsymbol{B}$ and the anisotropy of the $\boldsymbol{\beta}_4^*$ tensor. Finally there are terms in $\boldsymbol{E}$ which are P positive and occur in achiral media.

1. Introduction

Circular birefringence is usually the name given to the rotation of plane polarised electromagnetic radiation. It is well known to occur in a chiral ensemble, in which parity (P) inversion generates the opposite enantiomer [1–4], or in the Faraday effect [5], where a static magnetic field is applied to a chiral or achiral ensemble. Other, less well known, effects of this nature are the inverse Faraday effect [6], where magnetisation is induced by the electromagnetic field, the magneto-chiral effect [7–14], which is usually described as electric polarisation due to a collinear, unpolarised, laser and a static magnetic field, and the "inverse magneto-chiral effect" [15] and spin-chiral dichroism [16]. Recently, these effects have been explained systematically in terms of an expansion [17–20] of the induced electric and magnetic dipole moments in terms of $\boldsymbol{E}$ and $\boldsymbol{B}$, the electric and magnetic components of the electromagnetic field. The symmetry framework used in this classification scheme anticipates the existence of several new circular birefringence (CB) phenomena. This Letter solves the Maxwell equations for these CB effects, and provides simple and exact expressions for the birefringence and optical rotation angle at zeroth and first order in $\boldsymbol{E}$ and $\boldsymbol{B}$. These equations link the CB directly to new complex molecular property tensors and can be used to derive these experimentally. They therefore provide new information on fundamental molecular electric/magnetic properties.

2. The polarisation and magnetization due to a laser field

Application of the Helman/Feynman theorem and a double Taylor expansion leads [17–20] to the following expressions for the polarisation ($\boldsymbol{P}$) and magnetization ($\boldsymbol{M}$) due to an electromagnetic field. To second order:

$$\boldsymbol{P}=N(\alpha^*_{1ij}E_j+\alpha^*_{2ij}B_j+\beta^*_{1ijk}E_jE_k+\beta^*_{2ijk}E_jB_k$$
$$+\beta^*_{3ijk}B_jE_k+\beta^*_{4ijk}B_jB_k)+\ \dots\,(\mathrm{o}(E^3,B^3))\,, \qquad (1)$$

$$\boldsymbol{M}=N(q^*_{1ij}B_j+a^*_{2ij}E_j+b^*_{1ijk}B_jB_k+b^*_{2ijk}B_jE_k$$
$$+b^*_{3ijk}E_jB_k+b^*_{4ijk}E_jE_k)+\dots\,(\mathrm{o}(E^3,B^3))\,. \qquad (2)$$

Here the quantities with an asterisk are complex molecular property tensors and the products are in general the vector parts of complete tensor products with powers of $\boldsymbol{E}$ and $\boldsymbol{B}$. The latter are also complex quantities from Maxwell's equations. A symmetry anal-

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ysis [17–20] shows that molecular property tensors must be P (parity) negative or positive. The former exist [17–20] in chiral ensembles only. This Letter solves the Maxwell equations for the circular birefringence $(n'_L - n'_R)$ in terms of these molecular property tensors, providing simple new equations which can be used experimentally. Here n'_R is, as usual, the refractive index in a right circularly polarised laser field and n'_L its left counterpart. We have

$$\theta = \frac{l\omega}{2c}(n'_L - n'_R) \tag{3}$$

for the angle of rotation in terms of the sample length (l) and the angular frequency (ω), with c as the speed of light.

3. Solving the Maxwell equations

The Maxwell equations are solved in the excellent approximation $\boldsymbol{M} \ll \boldsymbol{P}$, using $\boldsymbol{J} = \boldsymbol{0}$, where $\boldsymbol{J}$ is the current density. Writing ϵ_0 and μ_0 respectively for the vacuum permittivity and permeability (S.I. units), the Maxwell equations provide

$$\nabla \times \boldsymbol{B} = \mu_0 \frac{\partial}{\partial t}(\epsilon_0 \boldsymbol{E} + \boldsymbol{P}) . \tag{4}$$

Using eq. (1) for $\boldsymbol{P}$ and the fundamental relations

$$\nabla^2 \boldsymbol{B} = -k^2 \boldsymbol{B} , \quad \ddot{\boldsymbol{B}} = -\omega^2 \boldsymbol{B} , \tag{5}$$

reduces eq. (3) to the form

$$\begin{aligned} -k'^2_{L,R}(\boldsymbol{j} \pm \mathrm{i}\boldsymbol{i}) &= -\mu_0 \epsilon_0 \omega^2 (\boldsymbol{j} \pm \mathrm{i}\boldsymbol{i}) \\ &- \mu_0 N \nabla \times (\alpha^*_{2ij} \dot{B}_j) - \mu_0 N \nabla \times (\alpha^*_{1ij} \dot{E}_j) \\ &- \mu_0 N \nabla \times \left(\frac{\partial}{\partial t} (\beta^*_{4ijk} B_j B_k) \right) \ldots . \end{aligned} \tag{6}$$

Here the superscripts R and L denote right or left circularly polarised, as usual, and $\boldsymbol{k}'$ is the wave-vector. The vectors $\boldsymbol{i}$ and $\boldsymbol{j}$ are unit vectors in X and Y of the laboratory frame, and i denotes the root of minus one. The complex quantities with asterisks are written as the sums of real and imaginary parts, for example

$$\alpha^*_{1ij} = \alpha'_{1ij} + \mathrm{i}\alpha''_{1ij} . \tag{7}$$

The $\boldsymbol{\alpha}^*$ tensors are second rank, and the $\boldsymbol{\beta}^*$ tensors are third rank. The vector product of $\boldsymbol{\alpha}^*_1$ and $\boldsymbol{j} \pm \mathrm{i}\boldsymbol{i})$ is therefore

$$\begin{aligned} &\mathrm{Vector}(\boldsymbol{\alpha}^*_1(\boldsymbol{j} \pm \mathrm{i}\boldsymbol{i})) \\ &\quad = (\alpha^*_{1XY} \pm \alpha^*_{1XXi})\boldsymbol{i} + (\alpha^*_{1YY} \pm \alpha^*_{1YXi})\boldsymbol{j} \\ &\quad + (\alpha^*_{1ZY} \pm \alpha^*_{1ZXi})\boldsymbol{k} \end{aligned} \tag{8}$$

and the vector part of a tensor product such as $\beta^*_{4ijk} B_j B_k$ is

$$\beta^*_{4ijk} B_j B_k = (C^*_X \boldsymbol{i} + C^*_Y \boldsymbol{j} + C^*_Z \boldsymbol{k})\, \mathrm{e}^{2\phi \mathrm{i}} , \tag{9}$$

$$\begin{aligned} C^*_X &= \beta^*_{4XXX} B_X B_X + \beta^*_{4XXY} B_X B_Y + \beta^*_{4XYX} B_Y B_X \\ &+ \beta^*_{4XYY} B_Y B_Y , \\ C^*_Y &= \beta^*_{4YXX} B_X B_X + \beta^*_{4YXY} B_X B_Y + \beta^*_{4YYX} B_Y B_X \\ &+ \beta^*_{4YYY} B_Y B_Y , \\ C^*_Z &= \beta_{4ZXX} B_X B_X + \beta^*_{4ZXY} B_X B_Y + \beta^*_{4ZYX} B_Y B_X \\ &+ \beta^*_{4ZYY} B_Y B_Y . \end{aligned}$$

Using the fundamental relation

$$k'_{L,R} = \frac{\omega}{c} n'_{L,R} \tag{10}$$

between the wave vector and the refractive index, and comparing $\boldsymbol{j}$ and $\boldsymbol{i}$ coefficients provides the following fundamental relations.

4. Circular birefringence to zeroth order in $\boldsymbol{E}$ and $\boldsymbol{B}$

Leaving out, for the moment, beta tensor terms, using

$$\epsilon_0 \mu_0 = 1/c^2 \tag{11}$$

and comparing $\boldsymbol{j}$ coefficients gives

$$\begin{aligned} n'^2_L &= 1 + \frac{N}{\epsilon_0}(\alpha''_{1XX} - \alpha'_{1XY}) \\ &+ \frac{N}{\epsilon_0 c}(\alpha'_{2XX} + \alpha''_{2XY}) n'_L , \end{aligned} \tag{12}$$

$$\begin{aligned} n'^2_R &= 1 + \frac{N}{\epsilon_0}(\alpha''_{1XX} + \alpha'_{1XY}) \\ &+ \frac{N}{\epsilon_0 c}(\alpha''_{2XY} - \alpha'_{2XX}) n'_R , \end{aligned} \tag{13}$$

which are equations quadratic in the real part of the refractive index (n'). These equations give the exact result

$$n'_\mathrm{L}-n'_\mathrm{R}=\frac{N\alpha'_{2XX}}{\epsilon_0 c}-\frac{2N\alpha'_{1XY}}{n'_\mathrm{L}+n'_\mathrm{R}} \tag{14}$$

for the CB and the angle of rotation. To zeroth order in $\boldsymbol{E}$ and $\boldsymbol{B}$, therefore, the CB and angle of rotation are related to the components α'_{2XX} and α'_{1XY} of the molecular property tensors α^*_{2ij} and α^*_{1ij}. These are respectively − and + to P [17–20]. The tensor component α'_{2XX} changes sign, therefore, between enantiomers, and the component α'_{1XY} does not. The former is an expression of what is usually known as CB. The latter, which is provided directly by the Maxwell equations, is a new type of birefringence which does *not* change sign between enantiomers. It relates the anisotropy of the molecular polarisability (α'_{1XY}) directly to the angle of rotation, and can be isolated using a weak probe laser (where the beta tensor terms are negligible) by comparing the angles of rotation of opposite enantiomers. *Its presence means that θ for one enantiomer is not the same in general, as that of the opposite.* (Note that this is not the minute difference caused by enantiomeric energy inequivalence [21] from P violation. It is due to anisotropy of polarisability.)

5. First order (beta tensor effects)

The four complex beta tensors β^*_{1ijk} to β^*_{4ijk} in eq. (1) mediate the influence of the complex tensor products ***EE***, ***EB***, ***BE***, and ***BB*** respectively on the electric polarisation ***P***. The polarisation due to $\beta^*_{4ijk}B_jB_k$, for example, leads to a kind of magneto-chiral CB due purely to electromagnetic radiation. (This is different from the literature magneto-chiral effect.) Symmetry analysis [17–20] shows that β^*_{1ijk} and β^*_{4ijk} are − to P, and β^*_{2ijk} and β^*_{3ijk} are + to P. The former two can exist therefore only in chiral ensembles, and the latter two exist in both chiral and achiral ensembles. The solution of the Maxwell equations is illustrated for $\beta^*_{4ijk}B_jB_k$. For the tensor product of right c.p. fields

$$\nabla\times\frac{\partial}{\partial t}\left(\beta^*_{4ijk}B_j^{(\mathrm{R})}B_k^{(\mathrm{R})}\right)$$
$$=4k'_\mathrm{R}\omega C_X^{*\mathrm{RR}}\,\mathrm{e}^{2\mathrm{i}\phi_\mathrm{R}}\boldsymbol{j}+\dots, \tag{15}$$

where

$$C_X^{*\mathrm{RR}}=B_0^2\{(\beta'_{4XYY}-\beta'_{4XXX})+(\beta''_{4XXY}+\beta''_{4XYX})$$
$$+\mathrm{i}[(\beta''_{4XYY}-\beta''_{4XXX})-(\beta'_{4XXY}+\beta'_{4XYX})]\} \tag{16}$$

and for the product of left c.p. fields

$$\nabla\times\frac{\partial}{\partial t}\left(\beta^*_{4ijk}B_j^{(\mathrm{L})}B_k^{(\mathrm{L})}\right)$$
$$=4k'_\mathrm{L}\omega C_X^{*\mathrm{LL}}\,\mathrm{e}^{2\mathrm{i}\phi_\mathrm{L}}\boldsymbol{j}+\dots, \tag{17}$$

where

$$C_X^{*\mathrm{LL}}=B_0^2\{(\beta'_{4XYY}-\beta'_{4XXX})-(\beta''_{4XXY}+\beta''_{4XYX})$$
$$+\mathrm{i}[(\beta''_{4XYY}-\beta''_{4XXX})+(\beta'_{4XXY}+\beta'_{4XYX})]\}\,. \tag{18}$$

The last term on the r.h.s. of eq. (6) can therefore be written as

$$-[4k'_{\mathrm{L,R}}\omega C_X^{*\mathrm{LL,RR}}\exp(\mathrm{i}\phi_{\mathrm{L,R}}/2)$$
$$\times B_0\exp(\mathrm{i}\phi_{\mathrm{L,R}}/2)]\boldsymbol{j}/B_0^2+\dots\,. \tag{19}$$

Taking the time average [22], using the relations

$$\langle\mathrm{Re}\,\boldsymbol{A}\,\mathrm{Re}\,\boldsymbol{B}\rangle_\mathrm{time}=\tfrac{1}{2}\mathrm{Re}(\boldsymbol{A}\boldsymbol{B}^\mathrm{conjugate})\,,$$
$$\boldsymbol{A}\equiv\boldsymbol{A}_0\mathrm{e}^{\mathrm{i}\phi/2}\,,\quad\boldsymbol{B}\equiv\boldsymbol{B}_0\mathrm{e}^{\mathrm{i}\phi/2}\,, \tag{20}$$

finally gives

$$(n'_\mathrm{R}-n'_\mathrm{L})_4=\frac{2NB_0}{\epsilon_0 c}(\beta''_{4XXY}+\beta''_{4XYX})\,. \tag{21}$$

An entirely analogous calculation for the β^*_{1ijk} tensor term gives

$$(n'_\mathrm{L}-n'_\mathrm{R})=\frac{2NE_0^2}{\epsilon_0 cB_0}(\beta''_{1XXY}+\beta''_{1XYX})\,. \tag{22}$$

6. Discussion

Eqs. (21) and (22) give the CB expected from scalar components of β^*_{4ijk} and β^*_{1ijk}, and in both cases the analogous θ's change sign between enantiomers. The β_4 effect can be isolated by plotting θ_4 against the intensity B_0 and taking the slope. The θ_1 effect is isolated by plotting θ_1 against E_0^2/B_0. The slope changes sign in the opposite enantiomer. The CB from β^*_{2ijk} and β^*_{3ijk} can be derived in the same way:

$$(n'_{\rm R}-n'_{\rm L})_2=(n'_{\rm R}-n'_{\rm L})_3 = \frac{2E_0N}{\epsilon_0 c}\,(\beta''_{2XXX}-\beta''_{2XYY}) \tag{23}$$

and does *not* change sign between enantiomers, because β^*_{2ijk} and β^*_{3ijk} are + to P. The β_2 and β_3 effects should also be observable in achiral media, and are proportional to $\boldsymbol{E}_0$.

Figs. 1 and 2 illustrate the geometry of these new non-linear effects, showing that the plane of polarisation of an intense laser beam passing through the sample is rotated about the Z axis of the laboratory frame, the axis of propagation of the laser beam.

Physically, these non-linear effects show an optical rotatory dispersion, being proportional to the angular frequency of the laser beam through eq. (3). The hyperpolarisability elements appearing in eqs. (21)–(23) are supported by various crystal structures as discussed by Shen in table 2.1 of ref. [23]. This table lists all the elements of molecular hyperpolarisability which survive ensemble averaging in the thirty-two crystalline point groups. Note carefully that the hyperpolarisability elements of eqs. (21)–(23) do *not* survive ensemble averaging in an isotropic molecular liquid, which supports only totally antisymmetric elements [2], but may do so in liquid crystals and other anisotropic media. Similarly, the element α'_{1XY} of the molecular polarisability which appears in eq. (14), and which mediates first order optical rotatory dispersion in achiral ensembles, survives ensemble averaging in most of the crystal point groups listed by Shen in table 2.1 of ref. [23], so that this new first order effect can be observed in a low symmetry achiral crystal point group such as monoclinic or orthorhombic. It may also be observable in some smectic or nematic liquid crystals [24]. This effect does not depend on the electric or magnetic field strength, in contrast to the second-order effects of eqs. (21)–(23).

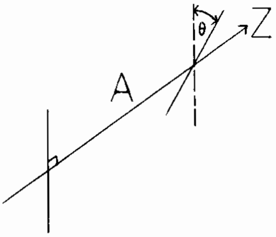

Fig. 1. Geometry of the new non-linear optical rotatory dispersion effect for achiral molecular crystal samples (A).

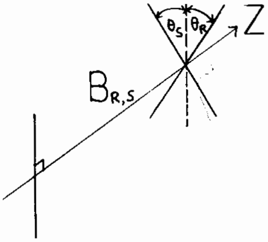

Fig. 2. As for fig. 1, geometry for chiral molecular crystal samples (B), showing that the angle of rotation is reversed from one enantiomer to the other (R to S).

Observation of these new optical rotatory dispersion effects provides information on the ensemble average over the mediating molecular property tensor elements appearing in eqs. (14) and (21)–(23), and the technique is especially valuable for the determination of molecular hyperpolarisability tensor elements, about which little is known experimentally.

7. Conclusion

We have isolated five new CB effects which can be investigated experimentally to give new molecular property tensors. Simple expressions are given relating the angle of rotation of CB to the relevant scalar components of the tensors.

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