

New non-linear optical effects: application of group theoretical statistical mechanics

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Abstract—The interaction of intense electromagnetic radiation with molecular matter is considered in terms of group theoretical statistical mechanics (gtsm). Field induced dipole moments are expanded in a double Taylor series in powers of the electric and magnetic field components multiplied by complex molecular property tensors (susceptibilities). The third principle of gtsm leads to several new non-linear optical effects, together with a symmetry classification of known effects. One new effect is detailed in terms of the Maxwell equation, and an estimate made of its order of magnitude.

INTRODUCTION

GROUP theoretical statistical mechanics (gtsm) applies group theory to statistical mechanics, and rests on three principles [1–5]. The first is the Neumann/Curie principle restated in terms of contemporary group theory; the second principle applies this to the molecule fixed frame, using molecular point group theory; and the third deals with the effect of applied fields. Although firmly rooted in well-known point group theory, gtsm used in combination with computer simulation has recently produced several useful insights. They have defined the role of asymmetric cross correlation functions (ccfs) in microrheology [6–8]; anticipated shear induced depolarized light scattering [9]; thermal conductivity due to combined shear and elongational flow [10]; the nature of ccfs in liquid crystals [11, 12]; and have been applied [13] to molecule fixed ccfs from a variety of computer simulations of the dynamics of molecules [14–16].

In this paper the third principle is used to anticipate and classify new non-linear birefringence phenomena produced by the interaction of intense electromagnetic radiation with molecular ensembles. The field induced electric and magnetic dipole moments are expanded in terms of molecular property tensors such as the polarizability and hyperpolarizability multiplied term by term into appropriate field tensors. The third principle of gtsm in this case asserts that the symmetry of the complete product of field tensor and molecular property tensor is imparted in general to new ensemble average. The symmetry of any one of these averages is part of this complete product. Thus, the symmetry of an induced molecular electric dipole moment, for example, is produced by the polar vector part of the complete product of molecular polarizability and electric field (E_i); hyperpolarizability and $E_i E_j$ tensor and so on. Systematic application of the third principle allows a classification of the various birefringence phenomena produced by the electric and magnetic components of the electromagnetic field. These include the non-linear Faraday effect, the inverse Faraday effect [17], magneto-chiral birefringence [18–20], (the Wagnière/Meier effect), its inverse (the Wagnière effect [21]), electric and magnetic rectification [22], and several new higher order effects given here for the first time. Barron's rule [23] is used to classify the chirality of the effect in each case.

2. THE THREE PRINCIPLES

Principle 1. The Neumann/Curie Principle

The thermodynamic ensemble average $\langle A_i B_j C_k \dots \rangle$ over the product $A_i B_j C_k \dots$ exists in frame (X, Y, Z) if the product of symmetry representations $\Gamma(A_i) \Gamma(B_j) \Gamma(C_k) \dots$ contains at least once the totally symmetric representation (tsr) of the point group $R_h(3)$ of achiral ensembles or $R(3)$ of chiral ensembles.

Principle 2

This ensemble average exists in the molecule fixed frame (x, y, z) if the product of symmetry representations in the molecular point group contains that point group's tsr at least once.

Principle 3

If an external field of force is applied to a molecular ensemble, new ensemble averages are formed which include the symmetry of the applied field.

3. SOME BACKGROUND SYMMETRY CONCEPTS

In order to apply these three principles it is necessary to define the point group symmetry of molecular ensembles, those of molecular dynamical variables in these ensembles, and finally the symmetry of applied fields in terms of the irreducible representations of these point groups. In this context the point group of achiral molecules is distinguished carefully from that of chiral (optically active) molecules.

The point group $R_h(3)$ is the group of all rotations and reflections of an isotropic ensemble of achiral molecules. The point group $R(3)$ is that of all possible rotations in an ensemble of structurally chiral molecules. Reflection in this case is not a valid symmetry operation because it generates a different molecule, the opposite enantiomer.

It is well known from standard point group theory that all valid symmetry operations of a point group can be expressed in terms of irreducible representations. For the groups $R_h(3)$ and $R(3)$ these are the well known D representations [1–12] of the Clebsch–Gordan Theorem. In $R_h(3)$ they are

$$\begin{aligned} D_g^{(0)}, D_g^{(1)}, \dots, D_g^{(n)}; \\ \text{tsr} = D_g^{(0)}; \\ D_u^{(0)}, D_u^{(1)}, \dots, D_u^{(n)}, \end{aligned}$$

respectively, even (g) and odd (u) to the parity inversion operator P , which inverts coordinates in the laboratory frame,

$$P: (X, Y, Z) \rightarrow (-X, -Y, -Z).$$

The superscripts denote the order of spherical harmonics. Accordingly, the symmetry representation of the ensemble (Gaussian, or thermodynamic) *average* over a scale quantity such as mass in $R_h(3)$ is $D_g^{(0)}$. By principle 1, this quantity does not vanish after ensemble averaging. In contrast, the irreducible representation of a polar vector as molecular center of mass velocity, v , is $D_u^{(1)}$, signifying that velocity is negative to P in $R_h(3)$ and is a rank one cartesian tensor. By principle 1, the ensemble average over v , denoted by $\langle v \rangle$, vanishes for all t . Similarly, the irreducible representation of an axial vector such as molecular angular velocity, Ω , is $D_g^{(1)}$, and the ensemble average $\langle \Omega \rangle$ vanishes by principle 1.

In order to apply principle 1 systematically to more complicated ensemble averages, such as time correlation functions, we need the Clebsch–Gordan Theorem

$$\begin{aligned} D^{(n)}D^{(m)} &= D^{(n+m)} + D^{(n+m-1)} + \dots + D^{|n-m|} \\ \mathbf{g} \times \mathbf{g} &= \mathbf{u} \times \mathbf{u} = \mathbf{g} \\ \mathbf{g} \times \mathbf{u} &= \mathbf{u} \times \mathbf{g} = \mathbf{u} \end{aligned} \quad (1)$$

which multiplies irreducible representations of either $R_h(3)$ or $R(3)$. (In the latter omit the subscripts when multiplying.) A good example is the problem of whether the time

correlation function $\langle v_i(t)\Omega_j(0) \rangle$ between v_i and Ω_j exists in either point group, i.e. in an achiral or chiral ensemble. Principle 1 provides an immediate solution, as follows, which is not obvious from the equations of motion in standard statistical mechanics. The symmetry representations of the time correlation function in the two point groups are

$$R_h(3): \Gamma(\langle v_i(t)\Omega_j(0) \rangle) = D_u^{(1)}D_g^{(1)} = D_u^{(0)} + D_u^{(1)} + D_u^{(2)} \quad (2)$$

and

$$R(3): \Gamma(\langle v_i(t)\Omega_j(0) \rangle) = D^{(1)}D^{(1)} = D^{(0)} + D^{(1)} + D^{(2)}. \quad (3)$$

Applying principle 1, we see that the autocorrelation function vanishes in $R_h(3)$, but may exist in $R(3)$. We can proceed in this way to work out by symmetry whether a complicated ensemble average may or may not exist in either point group, without immediate recourse to computation. Principle 2 allows a similar analysis in the molecule fixed (x, y, z) , and shows [13] that in this frame a correlation function such as $\langle v_i(t)\Omega_j(0) \rangle$ may exist, even when the molecular framework is achiral. Using these principles in combination with computer simulation allows a detailed appreciation of molecular dynamical processes in ensembles of molecules.

In order to apply principle 3, we need the D representations of applied force fields, together with the latter's motion reversal symmetry. We also need to know how the fields interact with the ensemble, expressed succinctly by the interaction Hamiltonian. In this context, the motion reversal symmetry operator, T , reverses momenta but does not affect coordinates. Thus, the T symmetry of a static electric field (E_{i0}) is positive and that of a static magnetic field (B_{i0}) is negative. In this context, "static" implies "intrinsically time invariant", so that the time derivatives vanish;

$$\frac{dE_{i0}}{dt} = \frac{dB_{i0}}{dt} = 0. \quad (4)$$

If these derivatives exist, the fields are defined as intrinsically time dependent, so that their motion reversal symmetry may be either positive or negative. For example, the T symmetry of a cosinusoidal electric field is

$$E_i(t) = E_{i0} \cos(\omega t); E_i(-t) = E_{i0} \cos(-\omega t) E_i(t) = E_i(-t) \quad (5)$$

which is positive, but it is negative for a sinusoidal field

$$E_i(t) = E_{i0} \sin(\omega t); E_i(-t) = E_{i0} \sin(-\omega t) E_i(t) = -E_i(-t). \quad (6)$$

Opposite symmetries are obtained for time dependent magnetic fields. For the electromagnetic fields discussed in this paper, both their electric and magnetic components are complex, one part being cosinusoidal and the other sinusoidal, so that the overall T symmetries of both the electric and magnetic parts are mixed, denoted (\pm) for the electric part and (\mp) for the magnetic part.

4. PARITY AND REVERSALITY OF THE COMPLETE EXPERIMENT

In addition to applying the three principles it is necessary to consider the P and T symmetries of the complete experiment, following the well known Wigner principle first proposed in 1927 in the context of quantum mechanics [24]. The Wigner principle is described fully in the literature, for example Ref. [23], and states essentially that if P or T are applied to the observables, fields, and molecules of an experiment, then in both cases these must be relatively equivalent in the P or T inverted experiment. The principle can be used to show [23], for example, that a static electric field cannot cause optical

rotation, in contrast to a static magnetic field, essentially because when T is applied to such an experiment, the field, observables and ensemble are not relatively equivalent in the motion reversed experiment. Later in this article, the Wigner principle is applied to one of the new effects allowed by gtsm.

5. TENSOR SYMMETRIES

In what follows, frequent use is made of tensor notation, in which summation is implied, as usual, over repeated indices. In this context, the tensor symmetry of a correlation function such as that between linear and angular velocities of a diffusing molecule is, from the Clebsch–Gordan Theorem;

$$\begin{aligned} R_h(3): D_u^{(0)} + D_u^{(1)} + D_u^{(2)} \\ R(3): D^{(0)} + D^{(1)} + D^{(2)}, \end{aligned}$$

a sum of three parts. This sum is an expression of the fact that the second rank tensor

$$A_{ij} \equiv \langle v_i(t) \Omega_j(0) \rangle \quad (7)$$

is, in general, the sum

$$A_{ij} = \frac{1}{3}A\delta_{ij} + C_k + S_{ij} \quad (8)$$

whose trace, $A/3$, is denoted by $D_u^{(0)}$ in $R_h(3)$ or by $D^{(0)}$ in $R(3)$. Here δ_{ij} is the Kronecke delta. The antisymmetric part is

$$C_k = \frac{1}{2}\epsilon_{ijk}B_{ij} = \frac{1}{2}(A_{ij} - A_{ji}) \quad (9)$$

equivalent to a pseudovector (or axial vector) through the tensor relation

$$C_k = \epsilon_{ijk}B_{ij} \quad (10)$$

where ϵ_{ijk} is the totally antisymmetric third rank tensor, whose only non-vanishing elements are

$$\begin{aligned} \epsilon_{xyz} = \epsilon_{zxy} = \epsilon_{yxz} = 1 \\ \epsilon_{xzy} = \epsilon_{yxx} = \epsilon_{zyx} = -1. \end{aligned} \quad (11)$$

This is also known as the Levi–Civita symbol. The antisymmetric part of the tensor is denoted $D_u^{(1)}$ in $R_h(3)$ or $D^{(1)}$ in $R(3)$. The third part is the irreducible, traceless, symmetric, second rank tensor

$$S_{ij} = \frac{1}{2}(A_{ij} + A_{ji}) - \frac{A}{3}\delta_{ij} \quad (12)$$

which is denoted $D_u^{(2)}$ in $R_h(3)$ or $D^{(2)}$ in $R(3)$. The quantities A , C_k and S_{ij} form spherical tensors of rank 0, 1 and 2, respectively, which transform as the spherical harmonics Y_L^M for $L=0, 1$, and 2.

6. FIELD INDUCED ELECTRIC AND MAGNETIC DIPOLE MOMENTS

The energy of each molecule of an ensemble is assumed to change by

$$\Delta H = -\mu_i E_i - m_i B_i \quad (13)$$

when treated with a strong electromagnetic field propagating in Z . Here, μ_i is the total molecular electric dipole moment; m_i its (classical) magnetic counterpart; E_i the electric field and B_i the magnetic field components. These electromagnetic components are complex in general and defined according to IUPAC convention, with right or left circular polarity. The total electric and magnetic dipole moments are each sums of permanent and field induced components. For each molecule of the ensemble the Hellman/Feynman Theorem gives

$$\frac{\partial En}{\partial E_i} \equiv \left\langle \frac{\partial H}{\partial E_i} \right\rangle = -\langle \mu_i \rangle; \quad \frac{\partial En}{\partial B_i} \equiv \left\langle \frac{\partial H}{\partial B_i} \right\rangle = -\langle m_i \rangle \quad (14)$$

from the Hamiltonian [Eqn (13)]. A double Taylor expansion then results in

$$\begin{aligned} En(E_i, B_i) = & En_{0,0} + E_i \left(\frac{\partial En}{\partial E_i} \right)_{0,0} + B_i \left(\frac{\partial En}{\partial B_i} \right)_{0,0} \\ & + \frac{1}{2!} \left[E_i E_j \left(\frac{\partial^2 En}{\partial E_i \partial E_j} \right)_{0,0} + E_i B_j \left(\frac{\partial^2 En}{\partial E_i \partial B_j} \right)_{0,0} \right. \\ & \left. + B_i E_j \left(\frac{\partial^2 En}{\partial B_i \partial E_j} \right)_{0,0} + B_i B_j \left(\frac{\partial^2 En}{\partial B_i \partial B_j} \right)_{0,0} \right] + \dots \end{aligned} \quad (15)$$

Applying Eqn (14) gives the following series expansions for the electric and magnetic dipole moments of each molecule in terms of products of field tensors and susceptibility tensors

$$\begin{aligned} \mu_i = & \mu_{0i} + \alpha_{1ij} E_j + \alpha_{2ij} B_j + \frac{1}{2!} \left[\beta_{1ijk} E_j E_k + \beta_{2ijk} E_j B_k + \beta_{3ijk} B_j E_k + \beta_{4ijk} B_j B_k \right] \\ & + \frac{1}{3!} \left[\gamma_{1ijkl} E_j E_k E_l + \gamma_{2ijkl} E_j E_k B_l + \dots + \gamma_{8ijkl} B_j B_k B_l \right] + \frac{1}{4!} [\dots] + \dots \end{aligned} \quad (16)$$

$$\begin{aligned} m_i = & m_{0i} + a_{1ij} B_j + a_{2ij} E_j + \frac{1}{2!} \left[b_{1ijk} B_j B_k + b_{2ijk} B_j E_k + b_{3ijk} E_j B_k + b_{4ijk} E_j E_k \right] \\ & + \frac{1}{3!} \left[g_{1ijkl} B_j B_k B_l + \dots + g_{8ijkl} E_j E_k E_l \right] + \dots \end{aligned} \quad (17)$$

The susceptibility tensors are identified as follows, and their symmetry properties tabulated in Table 1 in terms of time reversal (T) and parity reversal (P) symmetry, and the irreducible (D) representations [1–5] of point group theory.

$$\begin{aligned} \mu_{0i} & \equiv - \left(\frac{\partial En}{\partial E_i} \right)_{00}; \quad \alpha_{1ij} \equiv - \left(\frac{\partial^2 En}{\partial E_i \partial E_j} \right)_{00}; \\ \alpha_{2ij} & \equiv - \left(\frac{\partial^2 En}{\partial E_i \partial B_j} \right); \dots; \quad m_{0i} \equiv - \left(\frac{\partial En}{\partial B_i} \right)_{00}; \dots \\ \mathbf{E}_-^{(L)} & = E_0(\mathbf{i} + \mathbf{j})e^{-i\theta_L}; \quad \mathbf{E}_-^{(R)} = E_0(\mathbf{i} - \mathbf{j})e^{-i\theta_R}; \\ \mathbf{E}_+^{(L)} & = E_0(\mathbf{i} - \mathbf{j})e^{i\theta_L}; \quad \mathbf{E}_+^{(R)} = E_0(\mathbf{i} + \mathbf{j})e^{i\theta_R}; \\ \mathbf{B}_-^{(L)} & = B_0(\mathbf{j} - \mathbf{i})e^{-i\theta_L}; \quad \mathbf{B}_-^{(R)} = B_0(\mathbf{j} + \mathbf{i})e^{-i\theta_R}; \\ \mathbf{B}_+^{(L)} & = B_0(\mathbf{j} + \mathbf{i})e^{i\theta_L}; \quad \mathbf{B}_+^{(R)} = B_0(\mathbf{j} - \mathbf{i})e^{i\theta_R}; \\ \theta_L & = \omega t - \mathbf{K}_L \cdot \mathbf{r}; \quad \theta_R = \omega t - \mathbf{K}_R \cdot \mathbf{r} \end{aligned}$$

Here the superscripts (L) and (R) denote left and right circularly, polarised, respectively; and the plus or minus subscripts denote complex conjugate sum and difference frequencies which appear in non-linear optical phenomena [18–21]. The phases θ are in IUPAC convention, the other symbols being defined conventionally.

7. APPLICATION OF GTSM

gtsm is used here to argue for the existence of various new non-linear birefringence phenomena, which in some instances are accompanied by optical rotation and dichroism. In so doing, thermodynamic ensemble averages must be taken over the quantities in Eqns (4) and (5), applying the third principle [1–5] term by term. To do this, the irreducible representations [1–5] of each susceptibility and field tensor quantity are defined in the appropriate ensemble point group: 1) $R_h(3)$ for ensembles of structurally achiral molecules; 2) $R(3)$ for chiral ensembles. Some of these are given in Table 1 for $R_h(3)$. For the equivalents in $R(3)$ remove the subscripts (g or u). The P and T symmetries of the field tensors are, respectively, the products of individual field components, E and B , defined through the fundamental scalar (ϕ) and vector (A) potentials

$$E = -\partial A/\partial t - \nabla\phi; \quad B = \nabla \times A \quad (18)$$

from which E is $-$ to P and \pm to T ; and B is $+$ to P and \mp to T .

In Table 1, the T representations are given in brackets. The symmetry representation of the complete product of field and susceptibility is the product of D , P and T representations, worked out [1–5] with the Clebsch–Gordan Theorem. The number of times $D_u^{(1)}(\pm)$ appears in each field-susceptibility product signifies the number of independent induced dipole components generated by the complete product. Thus, on the right hand side of Eqn (16) there is one independent type of induced dipole component at zero'th order in the field (i.e. μ_{0i}); three at first order (there are three occurrences of $D_u^{(1)}(\pm)$ in each of the complete products $\alpha_{1ij}E_j$ and $\alpha_{2ij}B_j$); fifteen independent types in each of the four second order field tensors; and no less than 91 different types at third order for each of the eight different field tensors in the double Taylor expansion.

These results come directly out of the third principle, which in this context asserts that the symmetry of the ensemble average over the observable on the left hand side of Eqn (4) is obtained from the appropriate $D_u^{(1)}(\pm)$ types in the ensemble averages over the complete products term by term on the right hand side. Each type signifies a different effect. References to types (effects) recorded in the literature are made in the following discussion. gtsm in this context shows without further analysis that only a few out of the rich variety of effects possible have been named or recorded in the literature.

This analysis can be repeated for Eqn (5) (the induced magnetic dipole moment); and for other observables, such as Barron's signature of natural optical activity [23], $D_u^{(0)}(+)$. This occurs in the susceptibilities marked with an asterisk in Table 1, i.e. in those which are $-$ to P . According to principle 1 of gtsm (the Neumann/Curie principle [1–5], the ensemble averages over these susceptibilities vanish in $R_h(3)$ because they do not contain its totally symmetric irreducible representation, $D_g^{(0)}$. They exist, however, in $R(3)$ of chiral ensembles, giving rise to: (a) optical rotation and dichroism; (b) contributions to induced electric and magnetic dipole moments which accompany (a). This is because Barron's signature in $R(3)$ is the totally symmetric irreducible representation itself, $D^{(0)}$.

8. DISCUSSION

Only a few of the possibilities from the gtsm symmetry analysis seem to be known, or clearly named, in the literature. Table 2 is a summary of these. They are named with

Table 1. $R_h(3)$ irreducible representations of susceptibility and field tensors of Eqn (16); electric dipole

Field	Susceptibility	
	$\mu_{0i};$	$D_u^{(1)}(\pm)$
$E_i; D_u^{(1)}(\pm)$	$\alpha_{ij};$	$D_g^{(0)} + D_g^{(1)} + D_g^{(2)}(+)$
$B_j; D_g^{(1)}(\mp)$	$\alpha_{2ij};^*$	$D_u^{(0)} + D_u^{(1)} + D_u^{(2)}(-)$
$E_i E_j; D_g^{(0)} + D_g^{(1)} + D_g^{(2)}(+)$	$\beta_{1ijk};^*$	$D_u^{(0)} + 3D_u^{(1)} + 2D_u^{(2)} + D_u^{(3)}(\pm)$
$E_i B_j; D_u^{(0)} + D_u^{(1)} + D_u^{(2)}(-)$	$\beta_{2ijk};$	$D_g^{(0)} + 3D_g^{(1)} + 2D_g^{(2)} + D_g^{(3)}(\mp)$
$B_i E_j; D_u^{(0)} + D_u^{(1)} + D_u^{(2)}(-)$	$\beta_{3ijk};$	$D_g^{(0)} + 3D_g^{(1)} + 2D_g^{(2)} + D_g^{(3)}(\mp)$
$B_i B_j; D_g^{(0)} + D_g^{(1)} + D_g^{(2)}(+)$	$\beta_{4ijk};^*$	$D_u^{(0)} + 3D_u^{(1)} + 2D_u^{(2)} + D_u^{(3)}(\pm)$
$E_i E_j E_k; D_u^{(0)} + 3D_u^{(1)} + 2D_u^{(2)} + D_u^{(3)}(\pm)$	$\gamma_{1ijk};$	$3D_g^{(0)} + 6D_g^{(1)} + 6D_g^{(2)} + 3D_g^{(3)} + D_g^{(4)}(+)$
$E_i E_j B_k; D_g^{(0)} + 3D_g^{(1)} + 2D_g^{(2)} + D_g^{(3)}(\mp)$	$\gamma_{2ijk};^*$	$3D_u^{(0)} + 6D_u^{(1)} + 6D_u^{(2)} + 3D_u^{(3)} + D_u^{(4)}(-)$
\vdots	\vdots	\vdots
$B_i B_j B_k; D_g^{(0)} + 3D_g^{(1)} + 2D_g^{(2)} + D_g^{(3)}(\mp)$	$\gamma_{8ijkl};^*$	$3D_u^{(0)} + 6D_u^{(1)} + 6D_u^{(2)} + 3D_u^{(3)} + D_u^{(4)}(-)$

* Contains the pseudo-scalar representation in $R_h(3)$.

references, if recorded, suggested names are given in inverted commas if they seem not to be in the literature. (1) The first order optical Kerr effect [25]. (2) Electro-optical rotation [25]. (3) "First order magneto-optic birefringence". (4) "First order magneto-optic circular dichroism". (5) "Second order electro-optic birefringence". (6) Magneto-chiral birefringence [18–20], the Wagnière/Meier effect. (7) Inverse Faraday effect [17]. (8) Inverse magneto-chiral birefringence [21] (the Wagnière effect). (9) "Second order electro-optic circular dichroism". (10) "Second order magneto-optic birefringence".

Column 2 of Table 2 denotes that this list is by no means exhaustive. The listed first order effects, for example, all come from the scalar or pseudoscalar parts of the various susceptibility tensors. There are in general three types, or components, to each first order effect. In the optical Kerr effect (effect 1), the quantum mechanical representation in column 3 corresponds to a part of the classical complete product of column 2, in this case the $D_g^{(0)}$ part of α_{ij} multiplied in to the $D_u^{(1)}$ representation of $E_{\pm}^{L,R}$. In general, both the susceptibility and field tensors are complex, and this allows other effects to occur, which seem to be largely unrecorded in the literature. In particular, each of effects 1–4 is accompanied by two others, from the $D_g^{(1)}$ and $D_g^{(2)}$ parts of the susceptibility multiplied by the $D_u^{(1)}$ part of the field. Using the Clebsch–Gordan theorem, both types of D multiplication can result in the required symmetry of the real observable, i.e. an induced electric or magnetic dipole moment. At second order there are already no less than 15 types, so that 5 to 10 are each only one out of 15 different effects allowed by gtsm. The

Table 2. Some effects from gtsm to first and second order in E and/or B

Effect	Part of	Quantum Rep. [21]
First Order		
1	$\alpha_{ij} E_j$	$(\mu, \mu'_i) E_j$
2*	$\alpha_{2ij} B_j$	$(\mu, m_j) B_j$
3	$a_{ij} B_j$	$(m, m'_i) B_j$
4*	$a_{2ij} E_j$	$(m_i, \mu_i) E_j$
Second Order		
5	$(\beta_{2ijk} E_j B_k + \beta_{3ijk} B_j E_k)$	$(\mu \cdot \mu' \times m') (iE_- \times B_+)$
6*	$(\beta_{4ijk} B_j B_k)$	$(\mu \cdot m' \times m'') (B_- \times B_+)$
7	$(b_{4ijk} E_j E_k)$	$(m' \cdot \mu \times \mu') (iE_- \times E_+)$
8*	$(b_{2ijk} B_j E_k + b_{3ijk} E_j B_k)$	$(m \cdot \mu' \times m'') (E_- \times B_+)$
9*	$(\beta_{1ijk} E_j E_k)$	$(\mu \cdot \mu' \times \mu'') (E_- \times E_+)$
10	$(b_{1ijk} B_j B_k)$	$(m \cdot m' \times m'') (B_- \times B_+)$

* Denotes dichroic effect, producing optical rotation; E_i and B_i , in general, denote $E_{\pm}^{L,R}$ and $B_{\pm}^{L,R}$.

dichroic effects are marked with an asterisk in Table 2. They are simply defined by the occurrence of $D_u^{(0)}$ in the susceptibility tensor. There is no need to make a further distinction [23] between “natural” or “magnetic” optical activity. Columns 2 and 3 match the symmetries, furthermore, of the isotropically averaged quantum matrix elements introduced by Wagnière [21] with those of the appropriate parts of the classical susceptibility tensors. In general, each field representation E_i and B_i in Table 2 can be (R) or (L), and a sum (+) or difference (−) frequency. This allows for a great deal of latitude in the experimental investigation of these effects as functions of E_i and B_i , their products, field strengths, polarizations and sum and difference frequencies. Finally, all these ensemble effects can be computer simulated using the appropriate torques [26–31] and frame transformations. Magnitudes of effects 6 and 8 have been estimated in the literature [21, 32] and experimental investigation of effect 6 is in its final stages [33]. The inverse Faraday effect was first confirmed experimentally in the mid sixties [34]. There has been one, preliminary, computer simulation of effect 1 [28].

In order to illustrate how a symmetry predicted non-linear optical effect is treated analytically and experimentally, we solve the Maxwell equation for axial birefringence [18] due to electric and magnetic rectification measured with a co-linear pump and probe laser system. By switching the intense pump laser from right to left circular polarization, the unpolarized probe picks up a change in refractive index caused by symmetry allowed perturbations caused by electric and magnetic rectification [21] in the pump laser. This change in refractive index provides new information on the mediating molecular property tensors, which are in general complex and frequency dependent [23].

Electric rectification is described by the field product [21];

$$(\boldsymbol{\mu} \cdot \boldsymbol{\mu}' \times \boldsymbol{\mu}'')(\mathbf{E}_- \times \mathbf{E}_+). \quad (19)$$

The vector product here is between complex conjugates of right and left circularly polarized electric components of the electromagnetic field. Thus

$$\mathbf{E}_+^{(L)} \times \mathbf{E}_-^{(L)} = -\mathbf{E}_+^{(R)} \times \mathbf{E}_-^{(R)} = 2iE_0^2 \mathbf{k} \quad (20)$$

which removes the time and wave vector dependence (phase) of the electromagnetic field, and which is, in general, complex. The effect 9 of Table 2 depends after isotropic averaging [21, 23] on this product. There is also a real product

$$i\mathbf{E}_+^{(L)} \times \mathbf{E}_-^{(L)} = -i\mathbf{E}_+^{(R)} \times \mathbf{E}_-^{(R)} = -2E_0^2 \mathbf{k}. \quad (21)$$

There are magnetic equivalents (effects 6 and 10). All four effects cause axial birefringence of the type first proposed by WAGNIÈRE and MEIER [18] for static magnetic fields (an effect now known as “magneto-chiral birefringence”). Restricting consideration for the moment to electric rectification, we seek a way of observing this with a pump probe laser system, which is a standard experimental set up in non-linear optics. This is achieved through the Voigt Born perturbations

$$\alpha_{1ij} = (\alpha_{1ij})_0 \pm 2\alpha_{1ijz} E_{0z}^2 i \quad (22)$$

and

$$\alpha_{2ij} = (\alpha_{2ij})_0 \pm 2\alpha_{2ijz} E_{0z}^2 i \quad (23)$$

as the polarization of the pump laser is switched from left to right. The theory of axial birefringence [32] uses the standard expansion

$$\boldsymbol{\mu}_i = \alpha_{1ij} E_j + \alpha_{2ij} B_j + \frac{1}{3} A_{ijk} \nabla_j E_k + \dots \quad (24)$$

of the electric dipole moment, which incorporates the electric field gradient $\nabla_j E_k$ premultiplied by the electric dipole/electric quadrupole tensor A_{ijk} . Essentially speaking,

the inclusion of the term $\frac{1}{3}A_{ijk}\nabla_j E_k$ removes the problem of origin dependence [23] in the molecular property tensor definitions. We therefore add the Voigt Born perturbation;

$$A_{ijk} = (A_{ijk})_0 \pm 2A_{ijkz}E_{0z}^2. \quad (25)$$

Finally, the usual theory of axial birefringence includes magnetization to the first term only of Eqn (17);

$$m_i = \alpha_{2ji}^{\text{conj}} E_j + \dots \quad (26)$$

With these definitions, and applying the standard theory [23], we obtain, after some calculation, the axial birefringence [32];

$$\langle n'_{\parallel R} - n'_{\parallel L} \rangle_1 = 2\mu_0 c N E_{0z}^2 [\langle \alpha''_{2xyz} \rangle + \langle \alpha''_{2yxz} \rangle - \frac{\omega}{3} (\langle A'_{xxzz} \rangle + \langle A'_{yyzz} \rangle)] + \dots \quad (27)$$

Axial birefringence due to electric rectification (of the type that generates the second order effect (9) is therefore mediated by these scalar elements of three and four rank molecular property tensors, the only elements to survive ensemble averaging. This birefringence is easily measurable with an unpolarized probe laser in the same (Z) axis as a powerful pump laser, whose circular polarization is switched from right to left with a device such as a piezzo-optic modulator [35]. The birefringence varies with the frequency of the probe, and is essentially a new type of spectrum.

Similarly, there is axial birefringence due to the field product [Eqn (21)], given after standard calculation by

$$\langle n'_{\parallel R} - n'_{\parallel L} \rangle_a = 2\mu_0 c N E_{0z}^2 [\langle \alpha'_{2xyz} \rangle + \langle \alpha'_{2yxz} \rangle - \frac{\omega}{3} (\langle A''_{xxzz} \rangle + \langle A''_{yyzz} \rangle)] + \dots \quad (28)$$

i.e. by the real as opposed to imaginary parts of the mediating tensor components. In general, both effects are present simultaneously, but both are proportional to E_{0z}^2 and therefore are distinguishable from other non-linear effects. They are expected to completely dominate the accompanying magnetic effects.

An order of magnitude estimate of the effect can be made by writing Eqn. (2), for example, as

$$\langle n'_{\parallel R} - n'_{\parallel L} \rangle_2 \doteq 2\mu_0 c N E_{0z}^2 \alpha'_{2xy} L_a + \dots \quad (29)$$

where L_2 is the second order Kielich function [28] which mediates the orientating effect of the pump laser, which sets up a potential energy of the form

$$-\alpha_{ij} E_{0i} E_{0j}$$

with the molecular polarizability. The torque set up by this effect is computer simulated in Ref. [28]. The Kielich function goes to unity as $E_0 \rightarrow \infty$. We set this conservatively at 0.01. The other quantities in Eqn (29) are as follows;

$$\mu_0 = 4\pi \times 10^{-7} \text{Js}^2\text{C}^{-2}\text{m}^{-1}; \quad c = 3 \times 10^8 \text{ms}^{-1}; \quad \text{and } N = 6 \times 10^{26} \text{m}^{-3};$$

and for α'_{2xy} we use a conservative order of magnitude of $10^{-36} \text{A}^2\text{J}^{-1}\text{m}^3\text{s}$. This leaves the electric field strength of the pump laser. HUTCHINSON [36] estimates that this can reach about 10^9V m^{-1} in a small, commercially available, Q switched and focussed Nd: YAG

laser. For $L_2 = 0.01$, the birefringence from Eqn [29] is

$$\langle n'_{\uparrow R} - n'_{\uparrow L} \rangle \doteq 144\pi \times 10^{-11} E_{0z}^2 + \dots \quad (30)$$

and for a conservative value of E_{0z} of 1000 V m^{-1} , this is about 0.01. Clearly, in a focussed and Q switched Nd:YAG laser, the effect can be orders of magnitude larger, and the Kielich function, L_2 , can be saturated, i.e. reach 1.0.

Finally, application of the Wigner theorem [23, 24] to the pump/probe configuration just described is as follows. Application of the motion reversal operator, T , reverses the direction of the propagation vector, \mathbf{K} , of both lasers, while leaving the sense of circular polarization unchanged. The relative configuration of these variables, and of the observable, axial birefringence, is unchanged. Similarly the T operator leaves molecular structure unchanged. Therefore the experiment conserves reversality of the complete experiment. The application of the P operator reverses the propagation vector of both the pump and probe lasers, and also reverses the sense of circular polarization, so the axial birefringence changes sign. P has no effect, however, on the structure of an achiral molecule, and in consequence the experiment violates parity in an achiral ensemble. It conserves parity in a chiral ensemble, however, because P in this case generates the opposite enantiomer. The P reversed complete experiment is therefore relatively the same as the original experiment in a chiral ensemble only. In other words there will be no effect in an achiral ensemble, in which all elements of the mediating tensor components in Eqn (27) will vanish.

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