CHIRALITY OF FIELD INDUCED NATURAL AND MAGNETIC OPTICAL ACTIVITY

M.W. EVANS [1]

Bourne Laboratory, Department of Chemistry, Royal Holloway and Bedford New College, University of London, Egham, Surrey TW20 0EW, UK

Received 11 September 1989; revised manuscript received 1 November 1989; accepted for publication 16 March 1990
Communicated by A.R. Bishop

The symmetry and chirality of field induced natural and magnetic optical activity are investigated with Barron's definition of chirality and the third principle of group theoretical statistical mechanics (g.t.s.m.). The results for several different external field symmetries are given for the point group $R_h(3)$ of achiral ensembles and for R(3) of chiral ensembles. The distinction is made between natural and magnetic optical rotation/dichroism and the field symmetries necessary for these to appear are defined in both point groups. The analysis resolves some recent literature confusion and suggests new field induced dichroic phenomena.

1. Introduction

This communication aims to define the tensor symmetries required for the appearance of dichroism in chiral and achiral molecular ensembles. Dichroism accompanies optical activity through the Kramers–Kronig relation, and causes birefringence. The distinction between natural and magnetic optical activity was first made by Kelvin, and Barron [1–3] has recently expressed this difference in terms of the parity reversal operator

$$\hat{P}: \quad (\boldsymbol{r},\boldsymbol{p}) \to (-\boldsymbol{r}, -\boldsymbol{p}) \tag{1}$$

and the time reversal operator

$$\hat{T}: \quad (\boldsymbol{r},\boldsymbol{p}) \to (\boldsymbol{r}, -\boldsymbol{p}) \,. \tag{2}$$

Here $\boldsymbol{r}$ denotes position and $\boldsymbol{p}$ denotes momentum, as usual. Barron defines a natural, or truly chiral, symmetry as being positive to $\hat{T}$ and negative to $\hat{P}$. This symmetry may be that of a force field, or that of a chiral molecular or crystalline structure, of a chiral mesophase and so forth. There is no distinction made between a chiral effect and a chiral structure in this context, and by implication, none between the symmetries of cause and effect. Magnetic optical activity/circular dichroism is caused according to Barron through Faraday's effect by an achiral magnetic field, which is positive to $\hat{P}$ and negative to $\hat{T}$, and produces therefore an achiral effect.

The symmetry of cause and effect is the same, an achiral magnetic field produces an achiral response, magnetic circular dichroism. A chiral field symmetry on the other hand produces chiral response [4–9]. Symmetry is defined in this communication through the appropriate point group of the ensemble. If the latter consists of achiral molecules this is $R_h(3)$, the point group of all rotations and reflections [10]; if the molecules of the ensemble are chiral, the point group is R(3), the group of all rotations. Field symmetries may be defined precisely in either point group through its irreducible representations (D symmetries).

The combination of D, $\hat{P}$, and $\hat{T}$ symmetries for either point group is sufficient to show whether a given field symmetry (or combined symmetry) produces dichroism/optical activity/birefringence, and whether this is natural (truly chiral) or magnetic (Faraday) optical activity.

2. Basic symmetry definitions

In considering the interaction of electric, mag-

[1] Present address: Theory Center, Cornell University, Ithaca, NY, USA.

netic, and electro-magnetic force fields with molecular ensembles the fundamental vector symmetries are taken to be those of the electric field ($\boldsymbol{E}$), magnetic field ($\boldsymbol{B}$) and Maxwell's (classical, non-relativistic) wave-vector ($\boldsymbol{k}$). The latter is also known as the propagation vector. Their $\hat{P}$, $\hat{T}$ and D symmetries used in this Letter are defined in table 1.

Table 1 shows for example that the static (intrinsically time independent) electric field of force, $\boldsymbol{E}$, is a time-even polar vector, negative (ungerade) to $\hat{P}$. The D symmetry [11–13] (irreducible representation) of $\boldsymbol{E}$ in the point group $R_h(3)$ is $D_u^{(1)}$ and in R(3) it is $D^{(1)}$. $\boldsymbol{E}$ produces a response in achiral ensembles whose symmetry is $D_u^{(1)}$, and a response in chiral ensembles whose symmetry is $D^{(1)}$. A simple example is polarisation, which is a non-vanishing ensemble average over the molecular dipole moment, $\langle\boldsymbol{\mu}\rangle$. The magnetic field of force is an axial vector (gerade) which is negative to $\hat{T}$. These define the symmetry of $\boldsymbol{k}$ through one part of the Maxwell equations,

$$\Gamma(\boldsymbol{B})=\Gamma(\boldsymbol{k}\times\boldsymbol{E}) . \tag{3}$$

Note that $\boldsymbol{k}$ is not a field of force. The tabulated symmetries of $\boldsymbol{B}$ and $\boldsymbol{E}$ come from their fundamental definitions through the scalar (ϕ) and vector ($\boldsymbol{A}$) potentials.

Maxwell's equations show that the $\hat{T}$ symmetries of $\boldsymbol{B}$ and $\boldsymbol{E}$ must be opposite. The symmetries of $\boldsymbol{E}$, $\boldsymbol{B}$, and $\boldsymbol{k}$ given in table 1 are self-consistent within the framework of Maxwell's field equations. These contain the well known phase factor $\omega t-\boldsymbol{k}\cdot\boldsymbol{r}$, which is an exponent and therefore a scalar, + to $\hat{P}$. Since $\boldsymbol{r}$ is − to $\hat{P}$, $\boldsymbol{k}$ must also be − to $\hat{P}$ to obtain a scalar from $\boldsymbol{k}\cdot\boldsymbol{r}$. The $\hat{T}$ symmetry of ωt is − because frequency (a number) is not reversed by motion reversal. In this respect the scalar symbol ω, denoting angular frequency, must be carefully distinguished from the vector $\boldsymbol{\omega}$, denoting angular velocity. The latter is − to $\hat{T}$. Position $\boldsymbol{r}$ is + to $\hat{T}$ and the overall

Table 1
Fundamental symmetry definitions.

Field	$\hat{P}$	$\hat{T}$	$R_h(3)$	R(3)
$\boldsymbol{E}$	−	+	$D_u^{(1)}$	$D^{(1)}$
$\boldsymbol{B}$	+	−	$D_g^{(1)}$	$D^{(1)}$
$\boldsymbol{k}$	−	−	$D_u^{(1)}$	$D^{(1)}$

$\hat{T}$ symmetry of $\boldsymbol{k}\cdot\boldsymbol{r}$ and ωt must be the same, so that $\boldsymbol{k}$ must be − to $\hat{T}$. This symmetry of $\boldsymbol{k}$ is the same as used by Barron [1–3].

These careful definitions are necessary because of the ambiguities of Maxwell's theory, discussed, for example, by Landau and Lifshitz [14].

Subtle and profound problems emerge when an attempt is made to compare $\boldsymbol{k}$ with the photon momentum ($\boldsymbol{p}$) of quantum mechanics. These may well be at the root of the different conclusions of this Letter and the recent work of Ross et al. [15], suggesting that the definition and experimental observation of chiral effects are fundamentally important to any attempt to resolve these ambiguities.

The relation is the superficially simple

$$\boldsymbol{p}=\frac{h}{2\pi}\boldsymbol{k}, \tag{4}$$

where h is Planck's constant from de Broglie's particle/wave duality. Here $\boldsymbol{p}$ is the photon momentum. This has no classical meaning because $\boldsymbol{p}$ is massless, travelling always at c, the speed of light, and classically, Planck's constant vanishes. The $\hat{T}$ symmetry of $\boldsymbol{p}$ is not obvious. It depends, for example through the uncertainty relation

$$\delta\boldsymbol{p}\cdot\delta\boldsymbol{x}\gtrsim\frac{h}{4\pi}, \tag{5}$$

on that of Planck's constant itself. The energy/frequency relation

$$E=h\nu \tag{6}$$

suggests that h is + to $\hat{T}$, because E and ν are both positive to $\hat{T}$, frequency being a number, and energy a scalar, both quantities being unaffected by motion reversal. However, if $\boldsymbol{k}$ is − and h + to $\hat{T}$, $\boldsymbol{p}$ must be − to $\hat{T}$ from eq. (4). If however, $\boldsymbol{p}$ is − to $\hat{T}$ the uncertainty relation (eq. (5)) implies that the quantity $\boldsymbol{x}$ (position) must be − to $\hat{T}$, a result which contradicts the fundamental (classical) definition (2) of the operator $\hat{T}$. *These ambiguities arise because $\hat{T}$ in quantum mechanics is ill-defined* [1–3]. Also the O(4, 1) invariant relativistic quantity in de Broglie's theory is the *square* of the phase $\omega t-\boldsymbol{k}\cdot\boldsymbol{r}$, and the energy of photons is given by

$$E=(m^2c^4+p^2c^2)^{1/2} . \tag{7}$$

This means that if the phase factor is either + or −

to $\hat{T}$, the relativistic invariant is always + to $\hat{T}$. Similarly if $\boldsymbol{p}$ is either + or − to $\hat{T}$ the energy is always + to $\hat{T}$.

The ambiguities do not end here, for if we examine the units of Planck's constant (J s), they are those of energy multiplied by time, leading to the superficial conclusion that h has − $\hat{T}$ symmetry, i.e. is a pseudo-scalar. However, this immediately contradicts the energy/frequency relation. In order to recover an E + to $\hat{T}$ we would need a frequency, ν, − to $\hat{T}$. Since frequency denotes the number of events per unit time, it does not change with motion reversal.

Finally, if $\boldsymbol{k}$ is thought of as a unit vector in the direction of travel of a light beam, then motion reversal due to the classical $\hat{T}$ operator reverses the direction of the vector $\boldsymbol{k}$, whose $\hat{T}$ symmetry is therefore negative, as in table 1.

3. Combined symmetries of tensor products

The fundamentals of table 1 are sufficient to resolve old and recent literature controversies and suggest new effects.

Define the combined D symmetry of a tensor product such as $\boldsymbol{EB}$ as the product of their individual symmetry representations in the appropriate point group. Thus

$$\mathrm{R}_h(3):\quad \Gamma(\boldsymbol{EB})=\Gamma(\boldsymbol{E})\Gamma(\boldsymbol{B})$$
$$=\mathrm{D}_u^{(0)}+\mathrm{D}_u^{(1)}+\mathrm{D}_u^{(2)}, \tag{8}$$

$$\mathrm{R}(3):\quad \Gamma(\boldsymbol{EB})=\Gamma(\boldsymbol{E})\Gamma(\boldsymbol{B})$$
$$=\mathrm{D}^{(0)}+\mathrm{D}^{(1)}+\mathrm{D}^{(2)} \tag{9}$$

through the Clebsch–Gordan theorem. Similarly, the combined $\hat{P}$ and $\hat{T}$ symmetries are the products of individual $\hat{P}$ and $\hat{T}$ symmetries. Proceeding in this way, table 2 defines combined symmetries for several field combinations (tensor products) of interest.

From fundamentals the first rank tensor has three scalar components in the three dimensional laboratory frame (X, Y, Z); the second rank tensor (e.g. $\boldsymbol{EB}$) has nine components, and is a three by three matrix; and the third rank tensor ($\boldsymbol{EBk}$) has 27 scalar components. Note that the tensors in table 2 are all force fields or products thereof. $\boldsymbol{EBk}$ falls into this category because $\boldsymbol{Ek}$ has the units of $\boldsymbol{B}$, a force field.

In classical electromagnetic field theory, rank 0 natural optical rotation is the rotation of plane polarised radiation in a chiral ensemble. The rotation changes sign between enantiomers (for chiral ensembles), and is a pseudo-scalar quantity negative to $\hat{P}$ and positive to $\hat{T}$. The symmetry signature of natural optical rotation is therefore recognisable through the presence of $\mathrm{D}^{(0)}(+)$ in R(3). (Its equivalent in $\mathrm{R}_h(3)$ is $\mathrm{D}_u^{(0)}$.) The equivalent signatures for magnetic optical activity are $\mathrm{D}^{(1)}(-)$ and $\mathrm{D}_g^{(1)}(-)$ respectively. (The quantities in brackets denote the $\hat{T}$ symmetry.) The signatures of natural optical activity of all ranks are chiral and those of magnetic optical activity achiral. Optical activity/dichroism of either type occur whenever the combined field symmetries contain these signatures. Table 3 is a summary of dichroic/optically active effects expected from the combined field symmetries of table 2.

4. Discussion

Table 3 gives the relation between combined field

Table 2
Some combined field symmetries.

Tensor	$\hat{P}$	$\hat{T}$	$\mathrm{R}_h(3)$	R(3)
$\boldsymbol{E}$	−	+	$\mathrm{D}_u^{(1)}$	$\mathrm{D}^{(1)}$
$\boldsymbol{Ek}$	+	−	$\mathrm{D}_g^{(0)}+\mathrm{D}_g^{(1)}+\mathrm{D}_g^{(2)}$	$\mathrm{D}^{(0)}+\mathrm{D}^{(1)}+\mathrm{D}^{(2)}$
$\boldsymbol{Bk}$	−	+	$\mathrm{D}_u^{(0)}+\mathrm{D}_u^{(1)}+\mathrm{D}_u^{(2)}$	$\mathrm{D}^{(0)}+\mathrm{D}^{(1)}+\mathrm{D}^{(2)}$
$\boldsymbol{B}$	+	−	$\mathrm{D}_g^{(1)}$	$\mathrm{D}^{(1)}$
$\boldsymbol{EE}$	+	+	$\mathrm{D}_g^{(0)}+\mathrm{D}_g^{(1)}+\mathrm{D}_g^{(2)}$	$\mathrm{D}^{(0)}+\mathrm{D}^{(1)}+\mathrm{D}^{(2)}$
$\boldsymbol{BB}$	+	+	$\mathrm{D}_g^{(0)}+\mathrm{D}_g^{(1)}+\mathrm{D}_g^{(2)}$	$\mathrm{D}^{(0)}+\mathrm{D}^{(1)}+\mathrm{D}^{(2)}$
$\boldsymbol{EB}$	−	−	$\mathrm{D}_u^{(0)}+\mathrm{D}_u^{(1)}+\mathrm{D}_u^{(2)}$	$\mathrm{D}^{(0)}+\mathrm{D}^{(1)}+\mathrm{D}^{(2)}$
$\boldsymbol{EBk}$	+	+	$\mathrm{D}_g^{(0)}+3\mathrm{D}_g^{(1)}+2\mathrm{D}_g^{(2)}+\mathrm{D}_g^{(3)}$	$\mathrm{D}^{(0)}+3\mathrm{D}^{(1)}+2\mathrm{D}^{(2)}+\mathrm{D}^{(3)}$

Table 3
Summary of field induced optical activity/dichroism.

Tensor	Occurrence of signature			
	$D_u^{(0)}(+)$	$D_g^{(1)}(-)$	$D^{(0)}(+)$	$D^{(1)}(-)$
E	no	no	no	no
Ek	no	yes	no	yes
Bk	yes	no	yes	no
B	no	yes	no	yes
EE	no	no	yes	no
BB	no	no	yes	no
EB	no	no	no	yes
EBk	no	no	yes	no

symmetry and the production of natural or magnetic dichroism either in achiral or chiral ensembles. We compare these results with those of other workers.

4.1. Symmetry *E*

The achiral electric field produces no dichroism of any kind. This agrees with Ross et al. [15].

4.2. Combined symmetry *Ek*

The achiral cross (rank 1) product $\boldsymbol{k}\times\boldsymbol{E}=+\boldsymbol{B}$ produces magnetic circular dichroism in both chiral and achiral ensembles, the overall $\hat{T}$ symmetry of which is negative, not positive as indicated by Ross et al. [15]. The latter oppositely define $\boldsymbol{k}$ as being positive to $\hat{T}$ and $\hat{P}$.

4.3. Combined symmetry *Bk*

Table 3 shows that the chiral dot (rank 0) product $\boldsymbol{B}\cdot\boldsymbol{k}$ produces natural (truly chiral) dichroism in chiral and achiral ensembles. This is the magneto-chiral effect of Wagnière and Meier [16–18], and Barron and Vrbancich [19], whose symmetry has been discussed by Evans [20]. Ross et al. are led to classify this as achiral because of their opposite $\boldsymbol{k}$ definition. The product $\boldsymbol{B}\cdot\boldsymbol{k}$ in the magneto-chiral effect must be generated by a combination of a magnetic field and an unpolarised laser. In electromagnetic radiation $\boldsymbol{B}\cdot\boldsymbol{k}$ vanishes. However, the rank 1 product $\boldsymbol{B}\times\boldsymbol{k}$ does not, and by Barron's definition this is chiral. The complete symmetry of the tensor ***Bk*** is given in table 2, all three D components of which are chiral. Ross et al. do not refer to the literature on the forward [16–20] or inverse [21,22] magneto-chiral effect.

4.4. Symmetry *B*

The achiral magnetic field produces magnetic circular dichroism, the Faraday effect, in both achiral and chiral ensembles.

4.5. Combined symmetry *EE*

This is an achiral combined field symmetry in the point group $R_h(3)$ which is, however, overall positive to time reversal. Its signature in the point group R(3) does not refer to parity reversal (table 2), and contains $D^{(0)}(+)$, which is imparted by g.t.s.m's principle three [4–9] to the chiral molecular ensemble as natural optical activity. The Kerr effect is characterised by $D^{(0)}(+)+D^{(2)}(+)$ from ***EE*** in R(3), and is therefore accompanied in chiral ensembles only by natural (chiral) dichroism at ranks 0 and 2.

Electrostriction is characterised by $D^{(0)}(+)$ in R(3) and is similarly accompanied by natural optical activity at rank 0. The field $\boldsymbol{E}\times\boldsymbol{E}^*$ may be generated [20] in a laser, where $\boldsymbol{E}^*$ is the complex conjugate of $\boldsymbol{E}$. This is an achiral pseudovector positive to T, not negative to $\hat{T}$ as in a magnetic field. It generates the inverse Faraday effect in both achiral and chiral ensembles which by principle three must include the overall symmetry $\boldsymbol{E}\times\boldsymbol{E}^*$. This is a type of magnetization generated by a quantity ~~positive~~ to $\hat{T}$, ~~not negative~~ as produced by $\boldsymbol{B}$. The latter is also capable of generating rank 1 natural optical activity/dichroism in chiral ensembles only. This seems to be a new effect.

Ross et al. [15] also define the combined $\hat{P}$ and $\hat{T}$ symmetries of ***EE*** as being both positive and the field ***EE*** as achiral, in agreement with our analysis. This is because $\boldsymbol{k}$ does not enter into consideration in this case.

4.6. Combined symmetry *BB*

The considerations are similar to those for ***EE***, here we have the Cotton–Mouton effect, magnetostriction, and the field $\boldsymbol{B}\times\boldsymbol{B}^*$ generated in a laser. The field ***BB*** is achiral, again in agreement with Ross et al.

4.7. Combined symmetry ***EB***

This is an achiral field symmetry negative to both $\hat{P}$ and $\hat{T}$. Here we are in disagreement with Ross et al. [15], who classify the field as chiral due to their opposite definition of ***k***. By Barron's definition [1] it cannot produce truly chiral optical activity/dichroism, either in chiral or achiral ensembles, because it is negative to $\hat{T}$. Confusion about the chiral effect of ***EB*** has been reviewed by Barron [1]. We argue here that because ***EB*** is negative to both $\hat{T}$ and $\hat{P}$ it can produce neither natural nor magnetic optical activity in achiral ensembles (such as water). The controversy and confusion, going back to Pierre Curie [1] could surely be settled by a very simple experiment, that of measuring the effect of an additional static electric field on magnetic circular dichroism in Faraday's magnetic field experiment. In achiral ensembles the observed optical rotation in the latter should not be directly or linearly affected by ***E***. Table 3 shows that ***EB*** can produce magnetic optical activity/dichroism in chiral ensembles only, so that an additional ***E*** in Faraday's experiment will appear to linearly enhance the optical rotation in this case due to additional magnetic optical activity from the combined symmetry ***EB***. This effect should not occur in achiral ensembles. In this context the inverse magneto-chiral effect [21] is caused by the time-odd, parity-odd field pseudo-vector $\boldsymbol{E}\times\boldsymbol{B}^*$, and in chiral ensembles this should also produce magnetic optical activity/dichroism.

4.8. Combined symmetry ***EBk***

This is an achiral combined field symmetry positive both to $\hat{P}$ and $\hat{T}$. Here we are fortuitously in agreement with Ross et al., as regards chirality, but in disagreement as regards combined parity reversal (their "joint field parity") and combined time reversal symmetry, again due to their opposite ***k*** definition. The combined field symmetry may produce natural optical activity and dichroism to rank 0, 1, 2 and 3 in chiral ensembles only.

5. Conclusions

Classical definitions of the $\hat{T}$ and $\hat{P}$ symmetries of ***E***, ***B***, and ***k*** lead to a classification of observable optical rotation effects, both natural and magnetic. Some of the predictions made differ from those of Ross et al. [15] due to the profound difficulties which are encountered in the quantum mechanical definition of the operator $\hat{T}$, and therefore in the $\hat{T}$ symmetry of photon momentum. The present treatment is classical, relying on the propagation vector ***k***, argued as being − both to $\hat{P}$ and $\hat{T}$. Experimental consequences of this classical definition have been discussed and compared with those of Ross et al. (photon momentum definition). Such observations could lead to profound consequences at the boundary between classical and quantum electrodynamics.

Acknowledgement

The Academic Board of Royal Holloway and Bedford New College is thanked for the award of a Honorary Research Fellowship and Professor L.D. Barron for correspondence.

References

[1] L.D. Barron, Chem. Soc. Rev. 15 (1986) 189.
[2] L.D. Barron, Biosystems 20 (1987) 7.
[3] L.D. Barron, Chem. Phys. Lett. 123 (1986) 423.
[4] M.W. Evans, Chem. Phys. 128 (1988) 413.
[5] M.W. Evans, Chem. Phys. 132 (1989) 1.
[6] M.W. Evans, Phys. Rev. A 39 (1989) 6041.
[7] M.W. Evans, Phys. Lett. A 134 (1989) 409.
[8] M.W. Evans, Molecular diffusion, simulation and symmetry (Oxford Univ. Press, Oxford, 1990).
[9] M.W. Evans and D.M. Heyes, Mol. Phys. 65 (1988) 1441.
[10] L.D. Barron, Molecular light scattering and optical activity (Cambridge Univ. Press, Cambridge, 1982).
[11] D.H. Whiffen, Mol. Phys. 63 (1988) 1053.
[12] R.L. Flurry Jr., Symmetry groups, theory and chemical applications (Prentice-Hall, Englewood Cliffs, 1980).
[13] F.A. Cotton, Chemical applications of group theory (Wiley/Interscience, New York, 1963).
[14] L.D. Landau and E.M. Lifshitz, The classical theory of fields (Pergamon, Oxford, 1960).
[15] H.J. Ross, B.S. Sherborne and G.E. Stedman, J. Phys. B 22 (1989) 459.
[16] G. Wagnière and A. Meier, Chem. Phys. Lett. 93 (1982) 78.
[17] G. Wagnière, Z. Naturforsch. 39a (1984) 254.
[18] G. Wagnière and A. Meier, Experientia 39 (1983) 1090.
[19] L.B. Barron and J. Vrbancich, Mol. Phys. 51 (1984) 715.
[20] M.W. Evans, Chem. Phys. Lett. 152 (1988) 33.
[21] G. Wagnière, Phys. Rev. A, in press.
[22] M.W. Evans, Chem. Phys., submitted.