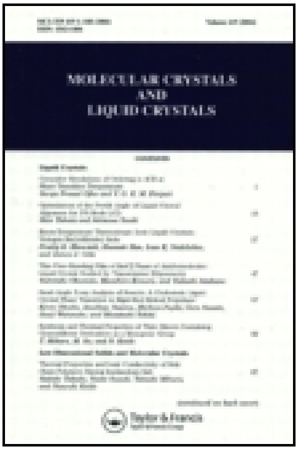

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R. W. Munn [a]

[a] Department of Chemistry, and Centre for Electronic Materials, UMIST, Manchester, M60 1QD, United Kingdom

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THEORY OF OPTICAL PROPERTIES OF CRYSTALS OF CHIRAL MOLECULES

R.W. MUNN
Department of Chemistry and Centre for Electronic Materials, UMIST, Manchester M60 1QD, United Kingdom

Abstract An improved theory of the optical properties of crystals of chiral molecules is developed. It incorporates molecular chirality via the response coefficients used in treating molecular optical activity and lattice chirality via lattice sums used in treating crystal spatial dispersion. Excitons in crystals of enantiomeric molecules should exhibit different Davydov splittings.

1. INTRODUCTION

Treatments of optical activity have tended to concentrate on the effect either of molecular chirality or of crystal chirality. For isotropic solutions only the former contributes to optical activity, and for atomic crystals only the latter contributes (to a good first approximation). However, for crystals of chiral molecules both molecular and crystal chirality must contribute to optical activity. This raises questions as to how these contributions combine: for example, what is the effect of a left-handed helical arrangements of right-handed helical molecules, can crystal optical activity be analysed to deduce molecular optical activity, and how do crystals of enantiomeric molecules differ?

The theory of molecular optical activity is well established,[1,2] and that of crystal optical activity has been re-examined thoroughly quite recently.[3,4] A general theory covering optical activity of molecular crystals is available,[5] but is rather formidable in appearance and is not related in the most obvious way to the molecular theory. Hence the present paper describes work on developing a theory of optical properties, including optical activity, of crystals of chiral molecules. The treatment is designed to be obviously compatible with treatments of molecular optical activity and with previous work on optical and dielectric properties of molecular crystals.[6] Particular attention is paid to the effect of molecular chirality on the crystal exciton frequencies.

2. METHOD

Consider first the molecular optical activity. In a wave description this arises from oscillating multipole moments that are induced by an incident light beam and then re-radiate the light. For ordinary optics it suffices to consider the molecular electric dipole moment $\boldsymbol{p}$ induced by an electric field $\boldsymbol{F}$ through the molecular polarizability α. For optical activity, it is necessary to consider additional contributions that reflect the molecular chirality. These can all be expressed in terms of response to the electric field gradient $\boldsymbol{F}'$; the combination of $\boldsymbol{F}$ and $\boldsymbol{F}'$ at a molecule can probe the molecular chirality in a way that $\boldsymbol{F}$ alone cannot.

Hence p is augmented by a contribution induced by $\boldsymbol{F}'$ through the field-gradient polarizability Λ. This immediately means that it no longer suffices to consider the electric dipole moment alone, for the same quantity Λ also governs the electric quadrupole moment q induced by the electric field $\boldsymbol{F}$, which must therefore be included in the treatment for consistency. Furthermore, through a Maxwell equation the presence of $\boldsymbol{F}'$ implies the presence of a time-varying magnetic induction $\boldsymbol{B}$. This can induce a contribution to $\boldsymbol{p}$ in its own right through the imaginary part of the magnetic induction polarizability G'. This in turn means that it no longer suffices to consider electric multipole moments alone, for the same quantity G' also governs the magnetic dipole moment $\boldsymbol{m}$, induced by the electric field $\boldsymbol{F}$ which must be included for consistency. The magnetic induction also induces a contribution to $\boldsymbol{m}$ through the magnetizability κ, but since this does not contribute to the optical activity and changes the refractive indices by typically only parts per million, it is ignored here.

The electromagnetic waves that a medium can sustain are deduced by solving the Maxwell equations with the aid of microscopic or macroscopic constitutive equations relating the response of the medium to the fields. Substituting an assumed wave solution yields a set of homogeneous equations, usually in terms of the electric field, and the usual condition for non-trivial solutions yields the propagation characteristics of the waves. For non-magnetic non-chiral media, this procedure works via the electric displacement and the electric polarization, treated as the electric dipole moment density. For the more complicated media considered here, two changes are necessary.[2] First, the electric polarization must be augmented by a term arising from the divergence of the electric quadrupole moment density.[1] Second, the quantity corresponding to the electric displacement must be augmented by a term arising from the curl of the magnetic dipole moment density.[2]

The result of these changes is that the polarization in the usual treatment is replaced by the density of effective dipole moments $\boldsymbol{r}$ given by

$$r_\alpha = \alpha_{\alpha\beta} F_\beta + \gamma_{\alpha\beta\gamma} F'_{\beta\gamma} , \tag{1}$$

where the coefficient of the field gradient is

$$\gamma_{\alpha\beta\gamma} = [\Lambda_{\alpha\beta\gamma} - \Lambda_{\gamma\beta\alpha}] - (1/\omega)[G'_{\alpha\delta}\varepsilon_{\delta\beta\gamma} - G'_{\gamma\delta}\varepsilon_{\delta\beta\alpha}] , \tag{2}$$

with ω the angular frequency of the wave. In terms of the quantity ζ' previously used to characterize molecular optical activity[2] this coefficient corresponds to $-(c/\omega)\zeta'_{\alpha\beta\gamma}$. This combination of Λ and G' yields a quantity independent of the choice of molecular origin, unlike the individual coefficients.[1,2]

The quantity γ (or ζ) leads directly to the molecular optical activity in a dilute gas. With interactions between molecules negligible, $\boldsymbol{F}$ can be taken as the macroscopic electric field $\boldsymbol{E}$ of the light wave and $\boldsymbol{F}'$ as its gradient $\boldsymbol{E}'$. However, in a crystal or other condensed phase the interactions between molecules cause the local polarizing field $\boldsymbol{F}$ to differ from $\boldsymbol{E}$ and $\boldsymbol{F}'$ from $\boldsymbol{E}'$. It is then necessary to relate the local field to the macroscopic field in order to obtain the crystal optical properties.

The local field and field gradient differ from the macroscopic field and field gradient through the contributions of the molecular charge distributions. These are described by the effective electric dipole moments $\boldsymbol{r}$ and effective electric quadrupole moments s given by

$$s_{\alpha\beta} = F_\gamma \gamma_{\gamma\alpha\beta} . \tag{3}$$

These effective moments act as sources for fields outside the molecules arising from their internal charge and current distributions. With the molecules in the unit cell labelled k one obtains for the local field

$$\boldsymbol{F}(k;y) = \boldsymbol{E}(y) + \sum_{k'} [\boldsymbol{L}(kk';y)\cdot\boldsymbol{r}(k') + \boldsymbol{M}(kk';y):\boldsymbol{s}(k')] / \varepsilon_0 v , \tag{4}$$

and for its gradient

$$F'(k;y) = E'(y) + \sum_{k'} [M(kk';y)\cdot r(k') + N(kk';y):s(k')] / \varepsilon_0 v . \quad (5)$$

where $L(y)$, $M(y)$ and $N(y)$ are lattice dipole, quadrupole and octupole sums modulated at the wavevector y of the light wave. Equations (4) and (5) can be solved with equations (1) and (3) to express the local electric field and its gradient and the effective dipole and quadrupole moments in terms of the macroscopic electric field and its gradient, the coefficients being combinations of the molecular response functions and the lattice sums.

For the optical properties one needs the effective polarization $\boldsymbol{R}$, which is the density of the effective electric dipole moments $\boldsymbol{r}$, expressed in terms of $\boldsymbol{E}$ and $\boldsymbol{E}'$, i.e.

$$\boldsymbol{R} = (1/v)\sum_k \boldsymbol{r}(k) = \varepsilon_0(\boldsymbol{\chi}^0\cdot\boldsymbol{E} + \boldsymbol{\Gamma}:\boldsymbol{E}') . \quad (6)$$

Here χ^0 is the usual electric susceptibility tensor as $y \to 0$ and Γ is the optical activity tensor. There are two contributions to Γ: one (denoted Γ_0) is the direct response to E', and the other (denoted χ') comes from the wavevector derivative of the response to $\boldsymbol{E}$, since the product $\boldsymbol{E}\,y$ is equivalent to E' in a wave. The latter term is the contribution from spatial dispersion, which is the only contribution if the molecules are not optically active ($\gamma = 0$).

The detailed results for the crystal optical response coefficients are as follows.[7] The susceptibility takes the form

$$\boldsymbol{\chi}^0 = \sum_{kk'} (\boldsymbol{B}^{-1} - \boldsymbol{L})^{-1}_{kk'} \equiv \sum_{kk'} \boldsymbol{\chi}^0_{kk'} , \quad (7)$$

where $\boldsymbol{L}$ is the $y \to 0$ limit of $\boldsymbol{L}(y)$. This expression is of the usual form,[6] except that the quantity $\boldsymbol{B}$ replaces the polarizability. It is given by

$$\boldsymbol{B}_{kk'} = \sum_{KK'} \boldsymbol{S}_{kK}\cdot\boldsymbol{A}_{KK'}\cdot\tilde{\boldsymbol{S}}_{K'k'} \quad (8)$$

$$\boldsymbol{S}_{kK} = (\boldsymbol{I} - \boldsymbol{g}:\boldsymbol{M})^{-1}_{kK} \quad (9)$$

$$\boldsymbol{A}_{KK'} = \boldsymbol{a}_K\,\delta_{KK'} + \boldsymbol{g}_K:\boldsymbol{N}_{KK'}:\tilde{\boldsymbol{g}}_{K'} , \quad (10)$$

where the tilde denotes the transpose; $\boldsymbol{I}$ is a unit matrix, $\boldsymbol{a} = \alpha/\varepsilon_0 v$ and $\boldsymbol{g} = \gamma/\varepsilon_0 v$, and $\boldsymbol{M}$ and $\boldsymbol{N}$ are the $y \to 0$ limits of $M(y)$ and $N(y)$.

The first part of the optical activity tensor is given by

$$\boldsymbol{\Gamma}_0 = \sum_{kk'k''} (\boldsymbol{I} - \boldsymbol{B}\cdot\boldsymbol{L})^{-1}_{kk'}\cdot\boldsymbol{S}_{k'k''}\cdot\boldsymbol{g}_{k''} \ . \tag{11}$$

It is clearly zero if $\boldsymbol{g}$ (or γ) is zero, and reduces to $\boldsymbol{g}$ when interactions are negligible so that the lattice sums are zero. The second part of the optical activity tensor is more complicated:

$$\begin{aligned}\boldsymbol{\chi}' = \sum_{kk'}\sum_{KK'} \boldsymbol{\chi}^0_{kK}\cdot(\boldsymbol{L}' + \boldsymbol{B}^{-1}\cdot\boldsymbol{S}\cdot\boldsymbol{g}:\boldsymbol{M}' + \boldsymbol{M}':\tilde{\boldsymbol{g}}\cdot\tilde{\boldsymbol{S}}\cdot\boldsymbol{B}^{-1} \\ + \boldsymbol{B}^{-1}\cdot\boldsymbol{S}\cdot\boldsymbol{g}:\boldsymbol{N}':\tilde{\boldsymbol{g}}\cdot\tilde{\boldsymbol{S}}\cdot\boldsymbol{B}^{-1})_{KK'}\cdot\boldsymbol{\chi}^0_{K'k'} \ .\end{aligned} \tag{12}$$

Here the primed quantities are the wavevector derivatives of the corresponding lattice sums, evaluated in the limit $y \rightarrow 0$, and so this part is seen to arise solely from the lattice. These results are compatible with those obtained previously.[4,5]

3. DISCUSSION

The results embodied in equations (7) - (12) achieve the objectives set out in the Introduction: they are consistent with accepted treatments of molecular optical activity,[1,2] as already indicated, and can also be reconciled with previous work in molecular crystals.[5] These equations contain much information that remains to be examined in detail for specific crystals. Numerical calculations for atomic crystals[4] prove well able to reproduce experimental optical activity results, and some effects of lattice symmetry have been examined.[5] Here attention is focused on the effect on the linear susceptibility of generalizing the molecular response.

In the usual treatment, the susceptibility is determined by the effective molecular polarizability α in the crystal environment. This differs from the free-molecule polarizability α_0 because of short-range effects such as orbital confinement. Introducing the generalized field-gradient polarizability leads to an effective polarizability $\boldsymbol{A}$ that is nonlocal[8] (i.e. that relates the induced dipole moment at molecule k to the local field not only at that molecule but also at other molecules k'), which is further modified to $\boldsymbol{B}$.

Of course, the polarizability is frequency dependent. Resonances in α_0 occur at the free-molecule absorption frequencies, while those in α can be regarded as occurring at the site-shifted exciton frequencies.[9] Those in χ^0 are split by inequivalent interactions $L_{kk'}$ for $k \neq k'$, and this yields the Davydov splitting.[6,9] In the present treatment, α is modified to A and thence to $\boldsymbol{B}$, so that the exciton frequencies are also modified. Suppose that the only significant frequency dependence is that of the polarizability. Near an absorption frequency ω_0 of A we have $A \sim D / (\omega^2 - \omega_0^2)$, where $\boldsymbol{D}$ does not depend on frequency. Substituting in equations (7) - (10) then yields

$$\boldsymbol{\chi}^0 = \sum_{kk'} [(\omega_0^2 - \omega^2 - \boldsymbol{H}\cdot\boldsymbol{L})^{-1}\cdot\boldsymbol{H}]_{kk'} , \tag{13}$$

$$\boldsymbol{H}^{-1} = \boldsymbol{D}^{-1} - \boldsymbol{M}:\tilde{\boldsymbol{g}}\cdot\boldsymbol{D}^{-1} - \boldsymbol{D}^{-1}\cdot\boldsymbol{g}:\boldsymbol{M} + \boldsymbol{M}:\tilde{\boldsymbol{g}}\cdot\boldsymbol{D}^{-1}\cdot\boldsymbol{g}:\boldsymbol{M} , \tag{14}$$

so that the Davydov splitting is modified because $\boldsymbol{D}$ is modified to $\boldsymbol{H}$ through the terms in $\boldsymbol{g}$. Consider now crystals of two enantiomers. The enantiomers have opposite signs for $\boldsymbol{g}$ and hence the terms linear in $\boldsymbol{g}$ and $\tilde{\boldsymbol{g}}$ have opposite effects on $\boldsymbol{H}$, provided that the enantiomeric crystal structures yield essentially the same lattice sums $\boldsymbol{M}$. Thus crystals of two enantiomers should have different Davydov splittings, which can be regarded as a form of circular dichroism. Numerical calculations are required to estimate the difference and the conditions under which it may be detected.

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