The Influence of a Static Magnetic Field on the Optical Properties of Chiral Molecules

G. Wagnière
Institute of Physical Chemistry, University of Zurich, Switzerland

Z. Naturforsch. 39a, 254–261 (1984); received October 19, 1983

A static magnetic field parallel to the direction of propagation of an incident light beam causes a small shift in the value of the refractive index and, correspondingly, of the absorption coefficient of a chiral molecule. This shift is opposite for enantiomers. However, it occurs for arbitrarily polarized light and is therefore not a circular differential effect.

1. Introduction

We have recently shown [1] that a static magnetic field parallel to the direction of propagation of an incident light beam causes a small shift in the value of the absorption coefficient of a chiral molecule. This shift, in contrast to natural CD and to magnetooptical rotatory dispersion, MORD, is not a circular differential effect: It therefore also occurs with linearly or arbitrarily polarized light. However, for enantiomers, the sign of the shift is opposite. This effect, which for the sake of brevity we shall call MIAD (for magnetic field-induced absorption difference), is some orders of magnitude smaller than MCD. It should nonetheless be observable by modern phase-sensitive means of detection. Furthermore, it may have played a role in inducing the photoenrichment of a given enantiomer in the course of molecular evolution [2].

To MIAD, which manifests itself inside of absorption bands in chiral media, there corresponds a dispersion effect which we will call MIDD (for magnetic field-induced dispersion difference). This effect was predicted already over 20 years ago by Groenewege [3] in a paper on Faraday dispersion. As, however, Groenewege was mainly interested in magnetic optical rotatory dispersion, MORD, in nonchiral media, he does not seem to have pursued the study of MIDD further.

The aim of the present paper is to give a comprehensive survey of MIDD and MIAD, to show how these phenomena are related to ORD and CD on one hand, to MORD and MCD on the other, as well as to other optical effects of higher order. In particular, we shall also study the behavior of molecular states which are degenerate to zeroth order and are split by the magnetic field and we shall consider the influence of damping on lineshapes. As in previous investigations, we work within the frame of semiclassical radiation theory. The interaction of the molecule under consideration with the radiation field is expanded into a multipole series [4–6].

2. Nondegenerate molecular states. MIDD

To classify optical phenomena, the use of simple graphs is most convenient [1, 7, 8]. Graphs 1a, b in Figure 1 represent the contribution to the electric polarization induced in the molecule due to the electric dipole–electric field interaction [7]. Keeping with previous notation [8], we designate this contribution as $\mathbf{p}^{(1)}(\pm \omega, \pm \omega)$. This is the term responsible for ordinary Rayleigh scattering. Graphs 2a, b stand for the contribution to the electric polarization induced by the magnetic dipole–magnetic field interaction which we write as $\mathbf{p}^{(1)}(\pm \omega, \mp \omega(M))$, and similarly, graphs 3a, b describe the polarization terms arising from the electric quadrupole–electric field gradient interaction, $\mathbf{p}^{(1)}(\pm \omega, \mp \omega(Q))$. Graphs 2a, b and 3a, b thus represent terms responsible for optical rotatory dispersion. It must be added that $\mathbf{p}^{(1)}(\pm \omega, \mp \omega(Q))$ vanishes upon isotropic averaging [4]. This, however, does in no way imply that higher-order effects in which the electric quadrupole–electric field gradient interaction plays
of which there are 6 permutations [7]. However, instead of taking into account the influence of the static field in the frame of time-dependent perturbation theory, we prefer to assume that time-independent perturbation theory is here applicable. Introducing first-order corrections into (1) and keeping only terms linear in $H_0$, leads us to

$$p^{(1)}(+\omega; -\omega(M); H_0)$$

$$= \frac{1}{\hbar^2} \sum_k \sum_f \left[ \frac{\omega_{ka} \langle a \cdot m \cdot H_0 k \rangle \langle f | m | k \rangle \langle k | m \cdot H_0 a \rangle}{\omega_{ka} (\omega_{ka} - \omega^2)} + \frac{\langle a \cdot m \cdot H_0 k \rangle \langle f | m | k \rangle \langle k | m \cdot H_0 a \rangle}{\omega_{fa} (\omega_{fa} + \omega^2)} + 6 \text{ additional similar terms} \right].$$

(2)

After isotropic averaging, and assuming that the molecular wavefunctions are real, which we may do in the absence of degeneracies, we obtain

$$p^{(1)}(+\omega; -\omega(M); H_0) = \frac{1}{\hbar^2} \sum_k \sum_f \left[ \frac{\omega_{ka} \langle a \cdot m \cdot H_0 k \rangle \langle f | m | k \rangle \langle k | m \cdot H_0 a \rangle}{\omega_{ka} (\omega_{ka} - \omega^2)} + \frac{\langle a \cdot m \cdot H_0 k \rangle \langle f | m | k \rangle \langle k | m \cdot H_0 a \rangle}{\omega_{fa} (\omega_{fa} + \omega^2)} + 3 \text{ additional similar terms} \right] (H_\times H_0).$$

(3)

After some straightforward algebraic manipulations we then find

$$p^{(1)}(+\omega; -\omega(M); H_0) = \chi^{(1)}(+\omega; -\omega(M); H_0) (H_\times H_0)$$

$$= \frac{1}{\hbar^2} \sum_k \sum_f \left[ \frac{\omega_{ka} \langle a \cdot m \cdot H_0 k \rangle \langle f | m | k \rangle \langle k | m \cdot H_0 a \rangle}{\omega_{ka} (\omega_{ka} - \omega^2)} - \frac{\langle a \cdot m \cdot H_0 k \rangle \langle f | m | k \rangle \langle k | m \cdot H_0 a \rangle}{\omega_{fa} (\omega_{fa} + \omega^2)} - \frac{\omega_{ka}^2}{\omega_{ka} (\omega_{ka} - \omega^2)} (H_\times H_0).$$

(4)

Taking into account some differences in notation, this result may be compared to the quantity $\delta H \times H'$ in expressions (37) and (38) of Groenewege's paper [3]. As Groenewege noted, the tensor $\delta$, or correspondingly $\chi^{(1)}(+\omega; -\omega(M); H_0)$, is odd with respect to parity. It only fails to vanish in optically active media and it has the opposite sign for enantiomers. Using the notation and the definitions of
[8], we obtain for the field part of expression (4) in the case of left circularly polarized incident light
\[ H_x H_0 = \frac{e H_0}{2} (+ ii - j), \]
and for right circularly polarized incident light
\[ H_x H_0 = \frac{e H_0}{2} (+ ii + j). \]

Both for left and right c.p. light the vector \( H_x H_0 \) has the same sign and phase as the electric field vector \( E_\perp \), implying that we have no circular differential effect [8]. The effect occurs also with linearly polarized incident light or, in general, with arbitrarily polarized light, provided that the direction of propagation is not perpendicular to the static magnetic field.

By solving Maxwell’s equations, Groenewege [3] showed that the quantity \( \delta \) indeed makes a small contribution to the ordinary index of refraction. A crude estimate shows, however, that for a field strength of 10 T, or \( 10^5 \) Gauss, the quantity \( H_0 \chi^{(1)}(+ \omega i - \omega) H_0 \), or \( H_0 \delta \), is of the order of \( 10^{-6} \) times \( \chi^{(1)}(+ \omega i - \omega) \), or \( \chi \), resulting in a change in the refractive index which is hard to detect, though not unmeasurable. As we shall subsequently see, however, it appears that the search for this phenomenon should be more rewarding inside absorption bands.

The terms pertaining to the electric quadrupole—electric field gradient interaction must also be taken into consideration (Graph 5 in Figure 1). They are obtained from expressions (1) and (2) by replacing the operator \( - m \cdot H_\perp \) with \( - Q \cdot V E_\perp \). Subsequent isotropic averaging of the corresponding fourth-rank tensor leads to
\[
\chi^{(1)}(+ \omega i - \omega) Q H_0 \cdot V E_\perp. \tag{6}
\]

We forego giving this expression here in explicit detail, as it does not convey any basically new aspect to the phenomenon under discussion. It merely adds an increment to the MIDD effect.

3. Nondegenerate molecular states. MIAD

In [1] we have considered the various contributions to the transition probability per unit time from a nondegenerate ground state \( a \) to a nondegenerate excited state \( b \). We have derived both the magnetic dipole—magnetic field and the electric quadrupole—electric field gradient contributions to MIAD. We here merely state expression (3) of [1], in a slightly modified notation and form, suited to our present investigation (see also (43)):
\[
\frac{2}{3h^2} \text{Re} \left[ \sum_{n \neq b} \omega_{n b} \left( \langle n, \mu, a \rangle \cdot \langle a, m, b \rangle \times \langle b, m, n \rangle \right) + \sum_{n \neq a} \omega_{n b} \left( \langle b, \mu, n \rangle \cdot \langle a, m, b \rangle \times \langle n, m, a \rangle \right) \right] \times g(\omega_{ka}, \omega) (E_\perp \cdot H_\perp \times H_0). \tag{7}
\]

Introducing the explicit expressions for the field vectors, one finds, both for left and right c.p. light
\[
E_\perp \cdot H_\perp \times H_0 = e^2 H_0/2. \tag{8}
\]

We shall, in the following, concentrate on the study of degenerate transitions which get split by the applied static magnetic field \( H_0 \). We shall explicitly consider the influence of damping, so as to be able to go from dispersion to absorption in a continuous way and to be in a position to study lineshapes.

4. Degenerate excited molecular states. MORD and MCD

As preparation for the following section and for the sake of a comparison, we rederive the \( A \)-terms of MORD and MCD [9, 10], introducing damping as described by Ward [7] or by Loudon [11].

As, in the following, we will very carefully have to sort out real and imaginary contributions to the molecular susceptibility, we consider the full expression for the induced, time-dependent polarization, namely [8]
\[
p^{(1)}(\omega i - \omega) = p^{(1)}(\omega i - \omega) \exp (-i \omega t) + p^{(1)}(-\omega i + \omega) \exp (+i \omega t). \tag{9}
\]

In general we have
\[
p^{(1)}(\omega i - \omega) = \frac{1}{h t} \sum_k \left[ \langle a, \mu, k \rangle \langle k, \mu, E_\perp, a \rangle \omega_{ka} - \omega - i \Gamma_{ka} \right.
\frac{\langle k, \mu, a \rangle}{\omega_{ka} + \omega + i \Gamma_{ka}} \left. \right], \tag{10a}
\]
and similarly

$$p^{(1)}(-\omega_0 + \omega) = \frac{1}{\hbar} \sum_k \left[ \frac{\langle a | \mu | k \rangle \langle k | \mu \cdot E_+ | a \rangle}{\omega_{ka} + \omega - i \Gamma_{ka}} + \frac{\langle a | \mu | E_+ | k \rangle \langle k | \mu \cdot a \rangle}{\omega_{ka} - \omega + i \Gamma_{ka}} \right].$$

(10b)

We now assume that above the ground state \( a \) we have two degenerate states \( b_- \) and \( b_+ \) which get split by the magnetic field. We further assume that the frequency of the radiation \( \omega \) to be so close to the resonance frequency of the transitions \( a \rightarrow b_- \) and \( a \rightarrow b_+ \), and the splitting between \( b_- \) and \( b_+ \) to be relatively so small, that the influence of other states \( k \neq a, b_\pm \) may be ignored.

We write

$$\omega_{b_-, a} = \omega_0 - \Delta \equiv \omega_-,$$

$$\omega_{b_+, a} = \omega_0 + \Delta \equiv \omega_+,$$

where

$$\Delta = \hbar^{-1} \langle b_+ | -m \cdot H_0 | b_+ \rangle = -\hbar^{-1} \langle b_- | -m \cdot H_0 | b_- \rangle,$$

(12)

and is positive. Furthermore, we assume that

$$\Gamma_{b_-, a} = \Gamma_{b_+, a} \equiv \Gamma.$$

(13)

The contribution of the transition \( a \rightarrow b_- \) to \( p^{(1)}(+\omega_0 - \omega) \) is then found from (10a) to be

$$h^{-1} \text{Re} \left( \langle a | \mu | b_- \rangle \langle b_- | \mu | a \rangle \right) \cdot E_- \left[ f_1(\omega_-, \omega) + ig_1(\omega_-, \omega) \right] + h^{-1} i \text{Im} \left( \langle a | \mu | b_- \rangle \langle b_- | \mu | a \rangle \right) \cdot E_- \left[ f_2(\omega_-, \omega) + ig_2(\omega_-, \omega) \right].$$

(14)

It must be emphasized that the function \( b_- \) is complex and that we have \( b_- = b_+^* \).

The quantity \( \langle a | \mu | b_- \rangle \langle b_- | \mu | a \rangle \cdot E_- \) thus is a complex tensor product, dotted to the right into the complex vector \( E_- \). The lineshape functions explicitly read (in this respect our notation here differs somewhat from that of [1]):

$$f_1(\omega_-, \omega) = \text{Re} \left( (\omega_- - \omega - i \Gamma)^{-1} + (\omega_- + \omega + i \Gamma)^{-1} \right),$$

$$f_2(\omega_-, \omega) = \text{Re} \left( (\omega_- - \omega - i \Gamma)^{-1} - (\omega_- + \omega + i \Gamma)^{-1} \right),$$

$$g_1(\omega_-, \omega) = \text{Im} \left( (\omega_- - \omega - i \Gamma)^{-1} + (\omega_- + \omega + i \Gamma)^{-1} \right),$$

$$g_2(\omega_-, \omega) = \text{Im} \left( (\omega_- - \omega - i \Gamma)^{-1} - (\omega_- + \omega + i \Gamma)^{-1} \right).$$

(15a)–(16b)

From (10b) we similarly obtain for the contribution of the transition \( a \rightarrow b_+ \) to \( p^{(1)}(-\omega_0 + \omega) \):

$$h^{-1} \text{Re} \left( \langle a | \mu | b_+ \rangle \langle b_+ | \mu | a \rangle \right) \cdot E_+ \left[ f_1(\omega_-, \omega) - ig_1(\omega_-, \omega) \right],$$

$$+ h^{-1} i \text{Im} \left( \langle a | \mu | b_+ \rangle \langle b_+ | \mu | a \rangle \right) \cdot E_+ \left[ f_2(\omega_-, \omega) + ig_2(\omega_-, \omega) \right].$$

(17)

We now Taylor-expand the lineshape functions (15a)–(16b) to first order with respect to the center of gravity of the band, \( \omega_0 = (\omega_+ + \omega_-)/2 \). For this to be meaningful, we must assume that the half-width of a given line is much larger than the Zeeman-splitting, \( \Gamma \gg \Delta \). We write

$$f_1(\omega_-, \omega) = f_1(\omega_0, \omega) - \Delta \cdot f_1'(\omega_0, \omega) + \ldots,$$

(18)

where

$$f_1'(\omega_0, \omega) \equiv \left( \frac{\partial f_1(\omega_-, \omega)}{\partial \omega_-} \right)_{\Delta = 0}.$$

(19)

The functions \( g_1(\omega_-, \omega), f_2(\omega_-, \omega) \) and \( g_2(\omega_-, \omega) \) are similarly expanded. Introducing these expressions into (14) and (17), we keep the terms linear in \( \Delta \). Then we make use of equation (12) and isotropically average the third-rank tensors that we so obtain. It is seen that the terms containing the factor
Re(\langle a | \mu | b_+ \rangle \langle b_- | \mu | a \rangle) average to zero. One then finds
\[ p^{(1)}(\omega; \omega; H_0; t)_{a \rightarrow b_-} = - \frac{1}{6\hbar^2} \langle b_- | m | b_- \rangle \]
\[ \cdot \text{Im} \langle a | \mu | b_+ \rangle \times \langle b_- | \mu | a \rangle \]
\[ \times \left[ i \left( [E_+ \times H_0] \exp (-i\omega t) \right. \right. \]
\[ - i(E_+ \times H_0) \exp (+i\omega t) f'_2(\omega_0, \omega) \]
\[ + \left. \left. i \left( E_+ \times H_0 \right) \exp (-i\omega t) \right. \right. \]
\[ + i(E_+ \times H_0) \exp (+i\omega t) \right] \right] \left[ E_- \exp (-i\omega t) + E_+ \exp (+i\omega t) \right], \]
(20)
For \( p^{(1)}(\omega; \omega; H_0; t)_{a \rightarrow b_-} \) we obtain the same expression as (20), but with \( b_- \) replaced by \( b_+ \). As now
\[ \langle b_- | m | b_+ \rangle \cdot \text{Im} \langle a | \mu | b_+ \rangle \times \langle b_- | \mu | a \rangle \]
\[ = \langle b_- | m | b_+ \rangle \cdot \text{Im} \langle a | \mu | b_+ \rangle \times \langle b_- | \mu | a \rangle, \]
(21)
we have
\[ p^{(1)}(\omega; \omega; H_0; t)_{a \rightarrow b_-} = p^{(1)}(\omega; \omega; H_0; t)_{a \rightarrow b_+}, \]
and consequently
\[ p^{(1)}(\omega; \omega; H_0; t)_{a \rightarrow b_-} = p^{(1)}(\omega; \omega; H_0; t)_{a \rightarrow b_+} + \]
\[ + 2p^{(1)}(\omega; \omega; H_0; t)_{a \rightarrow b_-}. \]
(23)
For left c.p. light, we find from (5a):
\[ E_- \times H_0 = (+i) H_0 E_-, \quad E_+ \times H_0 = (-i) H_0 E_+. \]
(24)
Then, from (20) and (23) follows
\[ p^{(1)}(\omega; \omega; H_0; t)_L = + \frac{H_0}{3\hbar^2} \langle b_- | m | b_- \rangle \]
\[ \cdot \text{Im} \langle a | \mu | b_+ \rangle \times \langle b_- | \mu | a \rangle \]
\[ \times \left[ f'_2(\omega_0, \omega) [E_+ \exp (-i\omega t) + E_- \exp (+i\omega t)] \right. \]
\[ + \left. i g'_2(\omega_0, \omega) [E_+ \exp (-i\omega t) - E_- \exp (+i\omega t)] \right], \]
(25)
Similarly, for right c.p. light we obtain:
\[ E_- \times H_0 = (-i) H_0 E_-, \quad E_+ \times H_0 = (+i) H_0 E_+. \]
(26)
Based on a general definition of the complex susceptibility:
\[ p = (\chi' + i\chi'') E_+ \exp (-i\omega t) \]
\[ + (\chi' - i\chi'') E_- \exp (+i\omega t) \]
\[ = \chi' E_- \exp (-i\omega t) + E_+ \exp (+i\omega t) \]
\[ + i\chi'' [E_- \exp (-i\omega t) - E_+ \exp (+i\omega t)], \]
(27)
it is then easy to identify the quantities \( \chi^{(1)\nu}(\omega; \omega; H_0) \) and \( \chi^{(1)\nu}(\omega; \omega; H_0) \) from expression (25).

5. Degenerate excited states. MIDD and MIAD

We now return to our topic of direct concern. In expressions (10a) and (10b) the operators \( \mu \cdot E_- \) and \( \mu \cdot E_+ \) are replaced by \( m \cdot H_- \) and \( m \cdot H_+ \), respectively. In analogy to (14), the contribution of the transition \( a \rightarrow b_- \) to \( p^{(1)}(\omega; -\omega; \omega; M) \) is then found to be
\[ h^{-1} \text{Re} \langle a | \mu | b_- \rangle \langle b_- | m | a \rangle \]
\[ \cdot H_- [f_1(\omega_-, \omega) + ig_1(\omega_-, \omega)] \]
\[ + h^{-1} i \text{Im} \langle a | \mu | b_- \rangle \langle b_- | m | a \rangle \]
\[ \cdot H_- [f_2(\omega_-, \omega) + ig_2(\omega_-, \omega)], \]
(31)
and in analogy to (17), the contribution of this same transition to \( p^{(1)}(-\omega; \omega + \omega; M) \) is
\[ h^{-1} \text{Re} \langle a | \mu | b_- \rangle \langle b_- | m | a \rangle \]
\[ \cdot H_- [f_1(\omega_-, \omega) - ig_1(\omega_-, \omega)] \]
\[ + h^{-1} i \text{Im} \langle a | \mu | b_- \rangle \langle b_- | m | a \rangle \]
\[ \cdot H_- [-f_2(\omega_-, \omega) + ig_2(\omega_-, \omega)]. \]
(32)

G. Wagnière • The Optical Properties of Chiral Molecules

Indeed we find
\[ \chi^{(1)\nu}(\omega; \omega; H_0)_L = \frac{H_0}{3\hbar^2} \langle b_- | m | b_- \rangle \]
\[ \cdot \text{Im} \langle a | \mu | b_+ \rangle \times \langle b_- | \mu | a \rangle \]
\[ \cdot g'_2(\omega_0, \omega). \]
(28)
Based on (20), (26) and (27), we notice that in the case of right c.p. light \( \chi^{(1)\nu}(\omega; \omega; H_0) \) has the opposite sign. Thus we may write
\[ \chi^{(1)\nu}(\omega; \omega; H_0)_R = - \chi^{(1)\nu}(\omega; \omega; H_0)_L. \]
(29)
The corresponding contribution to the Einstein coefficient is obtained from the general relation
\[ B(a \rightarrow b; \omega; H_0)_L = \frac{4\pi}{h} \chi^{(1)\nu}(\omega; \omega; H_0)_L. \]
(30)
As may be seen from (15b) and (16b), the lineshapes functions \( g_1(\omega_0, \omega) \) and \( g_2(\omega_0, \omega) \) approach each other in the limit \( \Gamma < \omega_0, \omega \approx \omega_0 \). Their first derivative change sign at (or near) \( \omega_0 \). These derivative functions thus represent bisignate signals. The absolute sign of these functions for given value of \( \omega \) depends on whether one has differentiated with respect to \( \omega_0 \), as in (19), or with respect to \( \omega \). Care must therefore be taken to specify this exactly. \( g'_2(\omega_0, \omega) \) as defined here is positive for \( \omega < \omega_0 \), negative for \( \omega > \omega_0 \). This completes for our purposes the derivation of the MCD A-term [9, 10, 12].
Upon Taylor-expansion of the lineshape functions, keeping only the terms linear in $H_0$ and isotropic averaging, we obtain, in analogy to (20):

$$p^{(1)}(\omega; \omega (M); H_0; t)_{a \to b_+} = -\frac{1}{6\hbar^2} \langle b_+ | m | b_+ \rangle \cdot \text{Re} \langle a | \mu | b_- \rangle \times \langle b_- | m | a \rangle \times \left[ \langle [H_+ \times H_0] \exp (-i\omega t) + (H_+ \times H_0) \exp (+i\omega t) \rangle \right. $$

$$+ \left. \langle [H_+ \times H_0] \exp (-i\omega t) - (H_+ \times H_0) \exp (+i\omega t) \rangle \right] g_1(\omega_0, \omega).$$

This then leads, for

$$p^{(1)}(\omega; \omega (M); H_0; t)_{a \to b_-} = P^{(1)}(\omega; \omega (M); H_0; t)_{a \to b_+} + P^{(1)}(\omega; \omega (M); H_0; t)_{a \to b_-}$$

to the following resulting expression:

$$p^{(1)}(\omega; \omega (M); H_0; t)_{a \to b_-} = -\frac{1}{3\hbar^2} \langle b_- | m | b_- \rangle \cdot \text{Re} \langle a | \mu | b_- \rangle \times \langle b_- | m | a \rangle \times \left[ \langle [H_+ \times H_0] \exp (-i\omega t) + (H_+ \times H_0) \exp (+i\omega t) \rangle \right. $$

$$+ \left. \langle [H_+ \times H_0] \exp (-i\omega t) - (H_+ \times H_0) \exp (+i\omega t) \rangle \right] g_1(\omega_0, \omega).$$

Making use of (5a) and the complex conjugate thereof, we find, for left as well as for right c.p. light:

$$p^{(1)}(\omega; \omega (M); H_0; t)_{a \to b_-} = -\frac{H_0}{3\hbar^2} \langle b_- | m | b_- \rangle \cdot \text{Re} \langle \langle a | \mu | b_- \rangle \times \langle b_- | m | a \rangle \rangle$$

$$\times \left[ f'_1(\omega_0, \omega)[E_+ \exp (-i\omega t) + E_+ \exp (+i\omega t)] \right. $$

$$+ \left. ig'_1(\omega_0, \omega)[E_- \exp (-i\omega t) - E_- \exp (+i\omega t)] \right].$$

This allows one to identify

$$\chi^{(1)}(\omega; \omega (M); H_0) = -\frac{H_0}{3\hbar^2} \langle b_- | m | b_- \rangle \cdot \text{Re} \langle \langle a | \mu | b_- \rangle \times \langle b_- | m | a \rangle \rangle g'_1(\omega_0, \omega).$$

For the contribution to the transition probability per unit time, we have, in the notation of [1]:

$$w(a \to b; II; H_0) = w(a \to b_+; \omega (M); H_0) + w(a \to b_+; \omega (M); H_0)$$

$$= B(a \to b; \omega (M); H_0) g(\omega).$$

$g(\omega)$ designates the energy density of the radiation field per unit of angular velocity. From (5a, b) one finds it to be equal to $c^2(\omega)/4\pi$.

In analogy to (30), we also obtain

$$B(a \to b; \omega (M); H_0) = -\frac{4\pi H_0}{3\hbar^3} \langle b | m | b \rangle$$

$$\cdot \text{Re} \langle \langle a | \mu | b \rangle \times \langle b | m | a \rangle \rangle g'_1(\omega_0, \omega),$$

where $b$ stands either for $b_-$ or $b_+$. $g'_1(\omega_0, \omega)$ is the derivative of $g_1(\omega_0, \omega)$ with respect to $\omega_0$ and represents a bisignate signal.

The effect here predicted occurs for arbitrarily polarized light propagating parallel to the static magnetic field. The expressions (38) and (41) vanish for molecules with rotation-reflection axes.

As in Sect. 2, we omit to explicitly deduce the expression which gives the contribution of the electric quadrupole–electric field gradient interaction to the effect considered.

6. Degenerate ground state

If we have a degenerate, magnetic field-split ground state, we obtain in MCD both an $A$-term and, because of the difference in population, a $C$-term [9, 10]. For MIAW the situation is analogous. Instead of calculating the real and imaginary part of the susceptibility, as in the previous section, we concentrate on the region of absorption and deduce
the corresponding terms from the “golden rule” expression for the transition probability per unit time, as in [1]. The ground state wavefunctions, in the basis of which the operator $-\mathbf{m} \cdot \mathbf{H}$ is diagonal, are designated by $a_-$ and $a_+. N_{a_-}$ and $N_{a_+}$ are the number of molecules per cm$^3$ in substates $a_-$ and $a_+$, respectively. We then have

$$N_{a_-} w(a_- \rightarrow b; \Pi)$$

$$= \frac{2N_{a_-}}{\hbar^2} \langle \mathbf{b} \cdot \mathbf{E}_- a_- \rangle \langle a_- | \mathbf{m} \cdot \mathbf{H}_+ | b \rangle$$

$$+ \frac{2N_{a_-}}{\hbar^2} \langle \mathbf{b} \cdot \mathbf{E}_- a_- \rangle \langle a_- | \mathbf{m} \cdot \mathbf{H}_+ | b \rangle g \left( \omega_-, \omega \right),$$

where $\omega_- \equiv \omega_{a_-}$. An analogous expression is written for $N_{a_+} w(a_+ \rightarrow b; \Pi)$. In the limit $\Gamma \rightarrow 0$ we have

$$g \left( \omega_-, \omega \right) = \pi \delta (\omega_- - \omega) = \frac{1}{2} \delta (v_- - v),$$

and a similar relation for $g \left( \omega_+, \omega \right)$.

We define

$$N = 2 \tilde{N}_a = N_{a_-} + N_{a_+},$$

and assume a Boltzmann distribution, giving approximately, for $h \Lambda \ll kT$:

$$N_{a_-} = \tilde{N}_a \left( 1 + \frac{h \Lambda}{kT} \right), \quad N_{a_+} = \tilde{N}_a \left( 1 - \frac{h \Lambda}{kT} \right).$$

After introducing (45) into the expressions for the transition rates, Taylor-expanding the functions $g \left( \omega_-, \omega \right)$ and $g \left( \omega_+, \omega \right)$ with respect to $\omega_0$, keeping only terms linear in $H_0$ and isotropic averaging, we finally obtain

$$N \cdot w (a_+ \rightarrow b; \Pi)$$

$$= \tilde{N}_a w(a_+ \rightarrow b; \Pi; H_0) + \tilde{N}_a w(a_- \rightarrow b; \Pi; H_0)$$

$$= \frac{4N_{a_-}}{\hbar^2} \text{Re} \left[ \left( \langle \mathbf{b} \cdot \mathbf{E}_- a_- \rangle \cdot \langle a_- | \mathbf{m} | b \rangle \right) \times \langle a_- | \mathbf{m} | a_- \rangle \right] \langle E_- \cdot H_+ \times H_0 \rangle$$

$$\times \left[ \frac{1}{kT} g \left( \omega_0, \omega \right) + \frac{1}{\hbar} g' \left( \omega_0, \omega \right) \right].$$

In (46) the function $a_-$ may equivalently be replaced by $a_+$. Making use of (8), and taking into account that $\langle a_- | \mathbf{m} | a_- \rangle$ is real, we may write

$$N \cdot w (a_+ \rightarrow b; \Pi)$$

$$= \frac{2N_{a_-}}{\hbar^2} \varepsilon H_0 \langle a_- | \mathbf{m} | a_- \rangle$$

$$\cdot \text{Re} \left[ \langle \mathbf{a}_- \cdot \mathbf{b} \rangle \times \langle \mathbf{b} \cdot \mathbf{a}_- \rangle \right]$$

$$\times \left[ \frac{1}{kT} g \left( \omega_0, \omega \right) + \frac{1}{\hbar} g' \left( \omega_0, \omega \right) \right].$$

With $\varepsilon ^2 (\omega) = 4\pi q (\omega)$ we finally get

$$B (a \rightarrow b; \omega (M); H_0) = \frac{4\pi H_0}{3\hbar^2} \langle a | \mathbf{m} | a \rangle$$

$$\cdot \text{Re} \left( \langle \mathbf{a}_- \cdot \mathbf{b} \rangle \times \langle \mathbf{b} \cdot \mathbf{a}_- \rangle \right)$$

$$\times \left[ \frac{1}{kT} g \left( \omega_0, \omega \right) + \frac{1}{\hbar} g' \left( \omega_0, \omega \right) \right],$$

where $a$ stands either for $a_-$ or $a_+$. The temperature-dependent term bears an analogy to the MCD C-term [9, 10, 12]. The explicit form of $g \left( \omega_0, \omega \right)$ is here not specified; but obviously the temperature-dependent signal has a monosignate lineshape, while the second term, or A-term, is bisignate. Here, as in the foregoing, the derivative $g' \left( \omega_0, \omega \right)$ is understood to be taken with respect to $\omega_0$.

7. Conclusions

We have theoretically investigated a magneto-optical effect which only occurs in chiral molecules. An applied static magnetic field induces a difference in refractive index and, correspondingly, absorption coefficient between enantiomers for arbitrarily polarized light, provided the light propagates parallel or antiparallel to the static magnetic field. If the relative direction of propagation with respect to the static magnetic field is reversed, the effect changes sign.

We have called this phenomenon magnetic field-induced dispersion difference, MIDD, or magnetic field-induced absorption difference, MIAD, respectively. The order of magnitude of the signals to be expected is small. It should be of the order of $(e\hbar/2mc)/e\alpha_0$ times smaller than that of corresponding MORD or MCD signals. With a static magnetic field of the order of 5T, the signals should be measurable with the help of phase-sensitive detection devices.

The interest of MIDD and MIAD does not lie in any foreseeable practical application. However, it may possibly be of some significance from the point of view of molecular evolution. It may suggest a mechanism hitherto uninvestigated by which, starting from a racemic mixture, the photoenrichment of one enantiomer with respect to the other is initiated [2].
In the present paper, we have focussed our attention mainly on degenerate transitions which get split by the magnetic field. We have discussed the lineshapes to be expected. They show an analogy to the A- and C-terms of MORD and MCD [9, 10, 12]. It must, however, once more be stressed that MIDD and MIAD are not circular differential effects. Indeed, there does exist a magnetic field-induced circular differential effect of higher order which only occurs in chiral molecules, namely the quadratic Faraday effect [13]. This phenomenon should, however, be even smaller than MIDD or MIAD at magnetic field strengths accessible in the laboratory.

Acknowledgements

The author thanks Mr. A. Meier and Mr. H. Wagner for discussions on the projected measurement of MIAD. Financial support from the Swiss National Science Foundation (Project number 2.891-0.80) is gratefully acknowledged. After completing this manuscript the author has been informed of some similar work carried out by L. D. Barron and J. Vrbancich on “magnetochiral birefringence and dichroism” in Molecular Physics in press. The author thanks Professor Barron from the University of Glasgow for an exchange of correspondence on this topic.