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

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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 magneto circular dichroism, MCD, 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].

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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 $\boldsymbol{p}^{(1)}(\pm\omega; \mp\omega)$. 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 $\boldsymbol{p}^{(1)}(\pm\omega; \mp\omega(M))$, and similarly, graphs 3a, b describe the polarization terms arising from the electric quadrupole–electric field gradient interaction, $\boldsymbol{p}^{(1)}(\pm\omega; \mp\omega(Q))$. Graphs 2a, b and 3a, b thus represent terms responsible for optical rotatory dispersion. It must be added that $\boldsymbol{p}^{(1)}(\pm\omega; \mp\omega(Q))$ 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

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a role similarly average to zero [1, 8]. Written out explicitly we have

$$\boldsymbol{p}^{(1)}(+\omega; -\omega(M)) = \frac{1}{\hbar}\sum_k \left[\frac{\langle a|\boldsymbol{\mu}|k\rangle\langle k|\boldsymbol{m}\cdot\boldsymbol{H}_-|a\rangle}{\omega_{ka}-\omega} + \frac{\langle a|\boldsymbol{m}\cdot\boldsymbol{H}_-|k\rangle\langle k|\boldsymbol{\mu}|a\rangle}{\omega_{ka}+\omega} \right], \quad (1)$$

where $\boldsymbol{\mu}$ and $\boldsymbol{m}$ are the electric and magnetic dipole operator, respectively. Expression (1) only fails to vanish in optically active molecules. We now assume the molecular eigenstates to be perturbed by a static magnetic field $\boldsymbol{H}_0 = H_0\boldsymbol{k}$. This situation may be represented by the generalized graph 4 in Fig. 1,

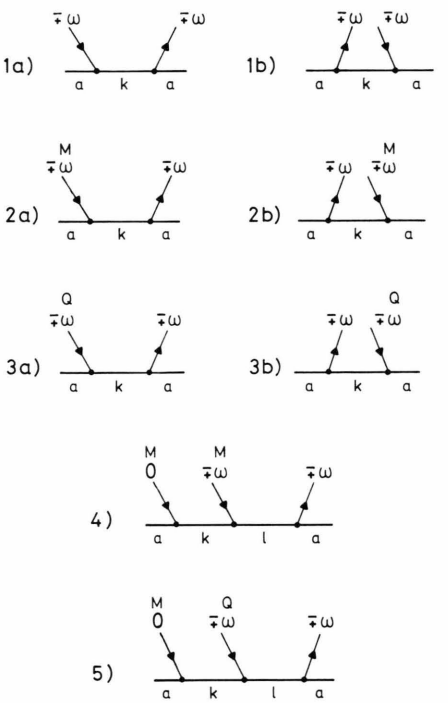

Fig. 1. Graphs [7] representing contributions to the radiation field-induced electric polarization: 1a, b) the first-order electric dipole contribution, responsible for ordinary Rayleigh scattering; 2a, b) the first-order magnetic dipole contribution, responsible for ORD; 3a, b) the electric quadrupole contribution, also contributing to ORD; 4) the generalized graph for the magnetic dipole contribution to MIDD (see text); 5) the generalized graph for the electric quadrupole contribution to MIDD. The vertex designated by M and $\omega = 0$ represents the static magnetic field. A similar graph representation for MIAD (see text) is given in [1].

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

$$\boldsymbol{p}^{(1)}(+\omega; -\omega(M); H_0) = \frac{1}{\hbar^2}\sum_k\sum_l \left[\frac{\langle a|\boldsymbol{m}\cdot\boldsymbol{H}_0|l\rangle\langle l|\boldsymbol{\mu}|k\rangle\langle k|\boldsymbol{m}\cdot\boldsymbol{H}_-|a\rangle}{\omega_{la}(\omega_{ka}-\omega)} + \frac{\langle a|\boldsymbol{m}\cdot\boldsymbol{H}_-|k\rangle\langle k|\boldsymbol{\mu}|l\rangle\langle l|\boldsymbol{m}\cdot\boldsymbol{H}_0|a\rangle}{\omega_{la}(\omega_{ka}+\omega)} + 6 \text{ additional similar terms} \right]. \quad (2)$$

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

$$\boldsymbol{p}^{(1)}(+\omega; -\omega(M); H_0) = \frac{1}{3\hbar^2}\sum_k\sum_l \left[\frac{\omega_{ka}\langle a|\boldsymbol{m}|l\rangle\cdot\langle l|\boldsymbol{\mu}|k\rangle\times\langle k|\boldsymbol{m}|a\rangle}{\omega_{la}(\omega_{ka}^2-\omega^2)} + 3 \text{ additional similar terms} \right](\boldsymbol{H}_-\times\boldsymbol{H}_0). \quad (3)$$

After some straightforward algebraic manipulations we then find

$$\boldsymbol{p}^{(1)}(+\omega; -\omega(M); H_0) = \chi^{(1)}(+\omega; -\omega(M); H_0)\,(\boldsymbol{H}_-\times\boldsymbol{H}_0) = -\frac{1}{3\hbar^2}\sum_k\sum_l \left[\langle a|\boldsymbol{m}|k\rangle\cdot\langle k|\boldsymbol{\mu}|l\rangle\times\langle l|\boldsymbol{m}|a\rangle \cdot\frac{\omega_{ka}}{\omega_{la}(\omega_{ka}^2-\omega^2)} - \langle a|\boldsymbol{m}|k\rangle\cdot\langle k|\boldsymbol{m}|l\rangle\times\langle l|\boldsymbol{\mu}|a\rangle \cdot\frac{\omega^2(\omega_{ka}+\omega_{la})}{\omega_{ka}(\omega_{ka}^2-\omega^2)\,(\omega_{la}^2-\omega^2)} \right](\boldsymbol{H}_-\times\boldsymbol{H}_0). \quad (4)$$

Taking into account some differences in notation, this result may be compared to the quantity $\delta\boldsymbol{H}\times\boldsymbol{H}'$ in expressions (37) and (38) of Groenewege's paper [3]. As Groenewege noted, the tensor δ, 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

$$\boldsymbol{H}_- \times \boldsymbol{H}_0 = \frac{\varepsilon H_0}{2}(+i\boldsymbol{i}-\boldsymbol{j}), \quad \boldsymbol{E}_- = \frac{\varepsilon}{2}(+i\boldsymbol{i}-\boldsymbol{j}), \quad (5a)$$

and for right circularly polarized incident light

$$\boldsymbol{H}_- \times \boldsymbol{H}_0 = \frac{\varepsilon H_0}{2}(+i\boldsymbol{i}+\boldsymbol{j}), \quad \boldsymbol{E}_- = \frac{\varepsilon}{2}(+i\boldsymbol{i}+\boldsymbol{j}). \quad (5b)$$

Both for left and right c. p. light the vector $\boldsymbol{H}_- \times \boldsymbol{H}_0$ has the *same sign and phase* as the electric field vector $\boldsymbol{E}_-$, 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 δ 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 $H_0\chi^{(1)}(+\omega; -\omega(M); H_0)$, or $H'\delta$, is of the order of 10^{-6} times $\chi^{(1)}(+\omega; -\omega)$, or α, 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 $-\boldsymbol{m}\cdot\boldsymbol{H}_-$ with $-Q{:}\nabla\boldsymbol{E}_-$. Subsequent isotropic averaging of the corresponding fourth-rank tensor leads to

$$\boldsymbol{p}^{(1)}(+\omega; -\omega(Q); H_0) \\ \chi^{(1)}(+\omega; -\omega(Q); H_0)\,(\boldsymbol{H}_0\cdot\nabla)\,\boldsymbol{E}_-. \quad (6)$$

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)):

$$w(a\to b; \mathrm{II}; H_0) \\ = \frac{2}{3\hbar^3}\mathrm{Re}\Big[\sum_{n\neq b}\omega_{nb}^{-1}\left(\langle n|\boldsymbol{\mu}|a\rangle\cdot\langle a|\boldsymbol{m}|b\rangle\times\langle b|\boldsymbol{m}|n\rangle\right. \\ \left.+\langle b|\boldsymbol{\mu}|a\rangle\cdot\langle a|\boldsymbol{m}|n\rangle\times\langle n|\boldsymbol{m}|b\rangle\right) \\ +\sum_{n\neq a}\omega_{na}^{-1}\left(\langle b|\boldsymbol{\mu}|n\rangle\cdot\langle a|\boldsymbol{m}|b\rangle\times\langle n|\boldsymbol{m}|a\rangle\right. \\ \left.+\langle b|\boldsymbol{\mu}|a\rangle\cdot\langle n|\boldsymbol{m}|b\rangle\times\langle a|\boldsymbol{m}|n\rangle\right)\Big] \\ \times g(\omega_{ba},\omega)\,(\boldsymbol{E}_-\cdot\boldsymbol{H}_+\times\boldsymbol{H}_0)\,. \quad (7)$$

Introducing the explicit expressions for the field vectors, one finds, *both for left and right c.p. light*

$$\boldsymbol{E}_-\cdot\boldsymbol{H}_+\times\boldsymbol{H}_0 = \varepsilon^2 H_0/2\,. \quad (8)$$

We shall, in the following, concentrate on the study of degenerate transitions which get split by the applied static magnetic field $\boldsymbol{H}_0$. 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]

$$\boldsymbol{p}^{(1)}(\omega;\omega;t) = \boldsymbol{p}^{(1)}(+\omega;-\omega)\exp(-i\omega t) \\ +\boldsymbol{p}^{(1)}(-\omega;+\omega)\exp(+i\omega t)\,. \quad (9)$$

In general we have

$$\boldsymbol{p}^{(1)}(+\omega;-\omega) = \frac{1}{\hbar}\sum_k\left[\frac{\langle a|\boldsymbol{\mu}|k\rangle\langle k|\boldsymbol{\mu}\cdot\boldsymbol{E}_-|a\rangle}{\omega_{ka}-\omega-i\Gamma_{ka}}\right. \\ \left.+\frac{\langle a|\boldsymbol{\mu}\cdot\boldsymbol{E}_-|k\rangle\langle k|\boldsymbol{\mu}|a\rangle}{\omega_{ka}+\omega+i\Gamma_{ka}}\right], \quad (10a)$$

and similarly

$$\boldsymbol{p}^{(1)}(-\omega;+\omega)=\frac{1}{\hbar}\sum_k\left[\frac{\langle a|\boldsymbol{\mu}|k\rangle\langle k|\boldsymbol{\mu}\cdot\boldsymbol{E}_+|a\rangle}{\omega_{ka}+\omega-i\Gamma_{ka}}+\frac{\langle a|\boldsymbol{\mu}\cdot\boldsymbol{E}_+|k\rangle\langle k|\boldsymbol{\mu}|a\rangle}{\omega_{ka}-\omega+i\Gamma_{ka}}\right]. \quad (10\,b)$$

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 the frequency of the radiation ω to be so close to the resonance frequency of the transitions $a\to b_-$ and $a\to b_+$, 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

$$\omega_{b_-a}=\omega_0-\Delta\equiv\omega_-\,, \quad (11\,a)$$

$$\omega_{b_+a}=\omega_0+\Delta\equiv\omega_+\,, \quad (11\,b)$$

where

$$\Delta=\hbar^{-1}\langle b_+|-\boldsymbol{m}\cdot\boldsymbol{H}_0|b_+\rangle=-\hbar^{-1}\langle b_-|-\boldsymbol{m}\cdot\boldsymbol{H}_0|b_-\rangle\,, \quad (12)$$

and is positive. Furthermore, we assume that

$$\Gamma_{b_-a}=\Gamma_{b_+a}\equiv\Gamma\,. \quad (13)$$

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

$$\hbar^{-1}\,\mathrm{Re}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\langle b_-|\boldsymbol{\mu}|a\rangle)\cdot\boldsymbol{E}_-[f_1(\omega_-,\omega)+ig_1(\omega_-,\omega)]+\hbar^{-1}i\,\mathrm{Im}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\langle b_-|\boldsymbol{\mu}|a_-\rangle)\cdot\boldsymbol{E}_-[f_2(\omega_-,\omega)+ig_2(\omega_-,\omega)]\,. \quad (14)$$

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

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

$$f_1(\omega_-,\omega)=\mathrm{Re}[(\omega_--\omega-i\Gamma)^{-1}+(\omega_-+\omega+i\Gamma)^{-1}]=\frac{2\omega_-(\omega_-^2+\Gamma^2-\omega^2)}{(\omega_-^2+\Gamma^2-\omega^2)^2+4\omega^2\Gamma^2}\,, \quad (15\,a)$$

$$g_1(\omega_-,\omega)=\mathrm{Im}[(\omega_--\omega-i\Gamma)^{-1}+(\omega_-+\omega+i\Gamma)^{-1}]=\frac{4\omega_-\omega\Gamma}{(\omega_-^2+\Gamma^2-\omega^2)^2+4\omega^2\Gamma^2}\,, \quad (15\,b)$$

$$f_2(\omega_-,\omega)=\mathrm{Re}[(\omega_--\omega-i\Gamma)^{-1}-(\omega_-+\omega+i\Gamma)^{-1}]=\frac{2\omega\,(\omega_-^2-\Gamma^2-\omega^2)}{(\omega_-^2+\Gamma^2-\omega^2)^2+4\omega^2\Gamma^2}\,, \quad (16\,a)$$

$$g_2(\omega_-,\omega)=\mathrm{Im}[(\omega_--\omega-i\Gamma)^{-1}-(\omega_-+\omega+i\Gamma)^{-1}]=\frac{2\Gamma\,(\omega_-^2+\Gamma^2+\omega^2)}{(\omega_-^2+\Gamma^2-\omega^2)^2+4\omega^2\Gamma^2}\,. \quad (16\,b)$$

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

$$\hbar^{-1}\,\mathrm{Re}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\langle b_-|\boldsymbol{\mu}|a\rangle)\cdot\boldsymbol{E}_+[f_1(\omega_-,\omega)-ig_1(\omega_-,\omega)]+\hbar^{-1}i\,\mathrm{Im}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\langle b_-|\boldsymbol{\mu}|a\rangle)\cdot\boldsymbol{E}_+[-f_2(\omega_-,\omega)+ig_2(\omega_-,\omega)]\,. \quad (17)$$

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

$$f_1(\omega_-,\omega)=f_1(\omega_0,\omega)-\Delta\cdot f_1'(\omega_0,\omega)+\ldots\,, \quad (18)$$

where

$$f_1'(\omega_0,\omega)\equiv\left(\frac{\partial f_1(\omega_-,\omega)}{\partial\omega_-}\right)_{\Delta=0}. \quad (19)$$

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 Δ. 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

$\mathrm{Re}(\langle a|\boldsymbol{\mu}|b_-\rangle\langle b_-|\boldsymbol{\mu}|a\rangle)$ average to zero. One then finds

$$\begin{aligned}\boldsymbol{p}^{(1)}(\omega;\omega;H_0;t)_{a\to b_-} &= -\frac{1}{6\hbar^2}\langle b_-|\boldsymbol{m}|b_-\rangle \\ &\cdot \mathrm{Im}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\times\langle b_-|\boldsymbol{\mu}|a\rangle) \\ &\times\{[i(\boldsymbol{E}_-\times\boldsymbol{H}_0)\exp(-i\omega t) \\ &\quad - i(\boldsymbol{E}_+\times\boldsymbol{H}_0)\exp(+i\omega t)]f_2'(\omega_0,\omega) \\ &\quad + [i(\boldsymbol{E}_-\times\boldsymbol{H}_0)\exp(-i\omega t) \\ &\quad + i(\boldsymbol{E}_+\times\boldsymbol{H}_0)\exp(+i\omega t)]ig_2'(\omega_0,\omega)\}\,. \end{aligned} \tag{20}$$

For $\boldsymbol{p}^{(1)}(\omega;\omega;H_0;t)_{a\to b_+}$ we obtain the same expression as (20), but with b_- replaced by b_+. As now

$$\begin{aligned}&\langle b_+|\boldsymbol{m}|b_+\rangle\cdot\mathrm{Im}\,(\langle a|\boldsymbol{\mu}|b_+\rangle\times\langle b_+|\boldsymbol{\mu}|a\rangle) \\ &=\langle b_-|\boldsymbol{m}|b_-\rangle\cdot\mathrm{Im}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\times\langle b_-|\boldsymbol{\mu}|a\rangle)\,, \end{aligned} \tag{21}$$

we have

$$\boldsymbol{p}^{(1)}(\omega;\omega;H_0;t)_{a\to b_-} = \boldsymbol{p}^{(1)}(\omega;\omega;H_0;t)_{a\to b_+}\,, \tag{22}$$

and consequently

$$\begin{aligned}&\boldsymbol{p}^{(1)}(\omega;\omega;H_0;t) \\ &\quad = \boldsymbol{p}^{(1)}(\omega;\omega;H_0;t)_{a\to b_-} + \\ &\boldsymbol{p}^{(1)}(\omega;\omega;H_0;t)_{a\to b_+} \\ &\quad = 2\,\boldsymbol{p}^{(1)}(\omega;\omega;H_0;t)_{a\to b_-}\,. \end{aligned} \tag{23}$$

For *left* c. p. light, we find from (5a):

$$\boldsymbol{E}_-\times\boldsymbol{H}_0 = (+i)\,H_0\boldsymbol{E}_-,\quad \boldsymbol{E}_+\times\boldsymbol{H}_0 = (-i)\,H_0\boldsymbol{E}_+\,. \tag{24}$$

Then, from (20) and (23) follows

$$\begin{aligned}&\boldsymbol{p}^{(1)}(\omega;\omega;H_0;t)_{\mathrm{L}} = +\frac{H_0}{3\hbar^2}\langle b_-|\boldsymbol{m}|b_-\rangle \\ &\cdot\mathrm{Im}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\times b_-|\boldsymbol{\mu}|a\rangle) \\ &\times\{f_2'(\omega_0,\omega)\,[\boldsymbol{E}_-\exp(-i\omega t)+\boldsymbol{E}_+\exp(+i\omega t)] \\ &+ ig_2'(\omega_0,\omega)\,[\boldsymbol{E}_-\exp(-i\omega t)-\boldsymbol{E}_+\exp(+i\omega t)]\}\,. \end{aligned} \tag{25}$$

Similarly, for *right* c. p. light we obtain:

$$\boldsymbol{E}_-\times\boldsymbol{H}_0 = (-i)\,H_0\boldsymbol{E}_-,\quad \boldsymbol{E}_+\times\boldsymbol{H}_0 = (+i)\,H_0\boldsymbol{E}_+\,. \tag{26}$$

Based on a general definition of the complex susceptibility:

$$\begin{aligned}\boldsymbol{p} &= (\chi'+i\chi'')\,\boldsymbol{E}_-\exp(-i\omega t) \\ &\quad + (\chi'-i\chi'')\,\boldsymbol{E}_+\exp(+i\omega t) \\ &= \chi'[\boldsymbol{E}_-\exp(-i\omega t)+\boldsymbol{E}_+\exp(+i\omega t)] \\ &\quad + i\chi''[\boldsymbol{E}_-\exp(-i\omega t)-\boldsymbol{E}_+\exp(+i\omega t)]\,, \end{aligned} \tag{27}$$

it is then easy to identify the quantities $\chi^{(1)\prime}(\omega;\omega;H_0)$ and $\chi^{(1)\prime\prime}(\omega;\omega;H_0)$ from expression (25).

Indeed we find

$$\begin{aligned}\chi^{(1)''}(\omega;\omega;H_0)_{\mathrm{L}} &= \frac{H_0}{3\hbar^2}\langle b_-|\boldsymbol{m}|b_-\rangle \\ &\cdot\mathrm{Im}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\times\langle b_-|\boldsymbol{\mu}|a\rangle)\,g_2'(\omega_0,\omega)\,. \end{aligned} \tag{28}$$

Based on (20), (26) and (27), we notice that in the case of *right* c.p. light $\chi^{(1)''}(\omega;\omega;H_0)$ has the opposite sign. Thus we may write

$$\chi^{(1)''}(\omega;\omega;H_0)_{\mathrm{R}} = -\chi^{(1)''}(\omega;\omega;H_0)_{\mathrm{L}}\,. \tag{29}$$

The corresponding contribution to the Einstein coefficient is obtained from the general relation

$$B(a\to b;\omega;H_0)_{\substack{\mathrm{L}\\\mathrm{R}}} = \frac{4\pi}{\hbar}\chi^{(1)''}(\omega;\omega;H_0)_{\substack{\mathrm{L}\\\mathrm{R}}}\,. \tag{30}$$

As may be seen from (15b) and (16b), the lineshape functions $g_1(\omega_0,\omega)$ and $g_2(\omega_0,\omega)$ approach each other in the limit $\Gamma\ll\omega_0$, $\omega\approx\omega_0$. Their first derivative change sign at (or near) ω_0. These derivative functions thus represent bisignate signals. The absolute sign of these functions for given value of ω depends on whether one has differentiated with respect to ω_0, as in (19), or with respect to ω. Care must therefore be taken to specify this exactly. $g_2'(\omega_0,\omega)$ as defined here is positive for $\omega\gg\omega_0$, negative for $\omega\ll\omega_0$. This completes for our purposes the derivation of the MCD A-term [9, 10, 12].

5. Degenerate excited states. MIDD and MIAD

We now return to our topic of direct concern. In expressions (10a) and (10b) the operators $\boldsymbol{\mu}\cdot\boldsymbol{E}_-$ and $\boldsymbol{\mu}\cdot\boldsymbol{E}_+$ are replaced by $\boldsymbol{m}\cdot\boldsymbol{H}_-$ and $\boldsymbol{m}\cdot\boldsymbol{H}_+$, respectively. In analogy to (14), the contribution of the transition $a\to b_-$ to $\boldsymbol{p}^{(1)}(+\omega;-\omega\,(M))$ is then found to be

$$\begin{aligned}&\hbar^{-1}\,\mathrm{Re}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\langle b_-|\boldsymbol{m}|a\rangle) \\ &\qquad\cdot\boldsymbol{H}_-[f_1(\omega_-,\omega)+ig_1(\omega_-,\omega)] \\ &+\hbar^{-1}\,i\,\mathrm{Im}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\langle b_-|\boldsymbol{m}|a\rangle) \\ &\qquad\cdot\boldsymbol{H}_-[f_2(\omega_-,\omega)+ig_2(\omega_-,\omega)], \end{aligned} \tag{31}$$

and in analogy to (17), the contribution of this same transition to $\boldsymbol{p}^{(1)}(-\omega;+\omega\,(M))$ is

$$\begin{aligned}&\hbar^{-1}\,\mathrm{Re}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\langle b_-|\boldsymbol{m}|a\rangle) \\ &\qquad\cdot\boldsymbol{H}_+[f_1(\omega_-,\omega)-ig_1(\omega_-,\omega)] \\ &+\hbar^{-1}\,i\,\mathrm{Im}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\langle b_-|\boldsymbol{m}|a\rangle) \\ &\qquad\cdot\boldsymbol{H}_+[-f_2(\omega_-,\omega)+ig_2(\omega_-,\omega)]. \end{aligned} \tag{32}$$

Upon Taylor-expansion of the lineshape functions, keeping only the terms linear in H_0 and isotropic averaging, we obtain, in analogy to (20):

$$\begin{aligned}
&\boldsymbol{p}^{(1)}(\omega;\omega(M);H_0;t)_{a\to b_-}\\
&=-\frac{1}{6\hbar^2}\langle b_-|\boldsymbol{m}|b_-\rangle\cdot\mathrm{Re}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\times\langle b_-|\boldsymbol{m}|a\rangle)\\
&\quad\times\{[(\boldsymbol{H}_-\times\boldsymbol{H}_0)\exp(-i\omega t)\\
&\qquad+(\boldsymbol{H}_+\times\boldsymbol{H}_0)\exp(+i\omega t)]f_1'(\omega_0,\omega)\\
&\qquad+[(\boldsymbol{H}_-\times\boldsymbol{H}_0)\exp(-i\omega t)\\
&\qquad-(\boldsymbol{H}_+\times\boldsymbol{H}_0)\exp(+i\omega t)]\,i\,g_1'(\omega_0,\omega)\}\\
&\quad-\frac{1}{6\hbar^2}\langle b_-|\boldsymbol{m}|b_-\rangle\cdot\mathrm{Im}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\times\langle b_-|\boldsymbol{m}|a\rangle)\\
&\quad\times\{[i\,(\boldsymbol{H}_-\times\boldsymbol{H}_0)\exp(-i\omega t)\\
&\qquad-i\,(\boldsymbol{H}_+\times\boldsymbol{H}_0)\exp(+i\omega t)]f_2'(\omega_0,\omega)\\
&\qquad+[i\,(\boldsymbol{H}_-\times\boldsymbol{H}_0)\exp(-i\omega t)\\
&\qquad+i\,(\boldsymbol{H}_+\times\boldsymbol{H}_0)\exp(+i\omega t)]\,i\,g_2'(\omega_0,\omega)\}\,. \qquad (33)
\end{aligned}$$

To obtain $\boldsymbol{p}^{(1)}(\omega;\omega(M);H_0;t)_{a\to b_+}$, we replace in expression (33) the function b_- by b_+. We then find

$$\begin{aligned}
&\langle b_+|\boldsymbol{m}|b_+\rangle\cdot\mathrm{Re}\,(\langle a|\boldsymbol{\mu}|b_+\rangle\times\langle b_+|\boldsymbol{m}|a\rangle)\\
&=\langle b_-|\boldsymbol{m}|b_-\rangle\cdot\mathrm{Re}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\times\langle b_-|\boldsymbol{m}|a\rangle)\,, \qquad (34\,\mathrm{a})
\end{aligned}$$

on the other hand

$$\begin{aligned}
&\langle b_+|\boldsymbol{m}|b_+\rangle\cdot\mathrm{Im}\,(\langle a|\boldsymbol{\mu}|b_+\rangle\times\langle b_+|\boldsymbol{m}|a\rangle)\\
&=-\langle b_-|\boldsymbol{m}|b_-\rangle\cdot\mathrm{Im}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\times\langle b_-|\boldsymbol{m}|a\rangle)\,. \qquad (34\,\mathrm{b})
\end{aligned}$$

This then leads, for

$$\begin{aligned}
&\boldsymbol{p}^{(1)}(\omega;\omega(M);H_0;t) \qquad (35)\\
&=\boldsymbol{p}^{(1)}(\omega;\omega(M);H_0;t)_{a\to b_-}+\boldsymbol{p}^{(1)}(\omega;\omega(M);H_0;t)_{a\to b_+}
\end{aligned}$$

to the following resulting expression:

$$\begin{aligned}
&\boldsymbol{p}^{(1)}(\omega;\omega(M);H_0;t)\\
&=-\frac{1}{3\hbar^2}\langle b_-|\boldsymbol{m}|b_-\rangle\cdot\mathrm{Re}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\times\langle b_-|\boldsymbol{m}|a\rangle)\\
&\quad\times\{[(\boldsymbol{H}_-\times\boldsymbol{H}_0)\exp(-i\omega t)\\
&\qquad+(\boldsymbol{H}_+\times\boldsymbol{H}_0)\exp(+i\omega t)]f_1'(\omega_0;\omega)\\
&\qquad+[(\boldsymbol{H}_-\times\boldsymbol{H}_0)\exp(-i\omega t)\\
&\qquad-(\boldsymbol{H}_+\times\boldsymbol{H}_0)\exp(+i\omega t)]\,i\,g_1'(\omega_0,\omega)\}. \qquad (36)
\end{aligned}$$

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

$$\begin{aligned}
&\boldsymbol{p}^{(1)}(\omega;\omega(M);H_0;t)\\
&=-\frac{H_0}{3\hbar^2}\langle b_-|\boldsymbol{m}|b_-\rangle\cdot\mathrm{Re}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\times\langle b_-|\boldsymbol{m}|a\rangle)\\
&\quad\times\{f_1'(\omega_0,\omega)[\boldsymbol{E}_-\exp(-i\omega t)+\boldsymbol{E}_+\exp(+i\omega t)] \qquad (37)\\
&\qquad+i\,g_1'(\omega_0,\omega)[\boldsymbol{E}_-\exp(-i\omega t)-\boldsymbol{E}_+\exp(+i\omega t)]\}\,.
\end{aligned}$$

This allows one to identify

$$\begin{aligned}
&\chi^{(1)\prime\prime}(\omega;\omega(M);H_0)=-\frac{H_0}{3\hbar^2}\langle b_-|\boldsymbol{m}|b_-\rangle\\
&\qquad\cdot\mathrm{Re}\,(\langle a|\boldsymbol{\mu}|b_-\rangle\times\langle b_-|\boldsymbol{m}|a\rangle)\,g_1'(\omega_0,\omega)\,. \qquad (38)
\end{aligned}$$

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

$$\begin{aligned}
&w(a\to b;\mathrm{II};H_0)\\
&=w(a\to b_-;\omega(M);H_0)+w(a\to b_+;\omega(M);H_0)\\
&=B(a\to b;\omega(M);H_0)\,\varrho(\omega)\,. \qquad (40)
\end{aligned}$$

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

In analogy to (30), we also obtain

$$\begin{aligned}
&B(a\to b;\omega(M);H_0)=-\frac{4\pi H_0}{3\hbar^3}\langle b|\boldsymbol{m}|b\rangle\\
&\qquad\cdot\mathrm{Re}\,(\langle a|\boldsymbol{\mu}|b\rangle\times\langle b|\boldsymbol{m}|a\rangle)\,g_1'(\omega_0,\omega)\,, \qquad (41)
\end{aligned}$$

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 ω_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 MIAD 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 $-\boldsymbol{m}\cdot\boldsymbol{H}$ 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

$$N_{a_-} w(a_- \to b; \mathrm{II}) = \frac{2N_{a_-}}{\hbar^2}(\langle b|\boldsymbol{\mu}\cdot\boldsymbol{E}_-|a_-\rangle\langle a_-|\boldsymbol{m}\cdot\boldsymbol{H}_+|b\rangle + \langle b|\boldsymbol{m}\cdot\boldsymbol{H}_-|a_-\rangle\langle a_-|\boldsymbol{\mu}\cdot\boldsymbol{E}_+|b\rangle)\, g(\omega_-, \omega)\,, \quad (42)$$

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

$$g(\omega_-, \omega) = \pi\delta(\omega_- - \omega) = \tfrac{1}{2}\delta(\nu_- - \nu)\,, \quad (43)$$

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

We define

$$N = 2\bar{N}_a = N_{a_-} + N_{a_+}\,, \quad (44)$$

and assume a Boltzmann distribution, giving approximately, for $\hbar\Delta \ll kT$:

$$N_{a-} = \bar{N}_a\left(1 + \frac{\hbar\Delta}{kT}\right), \quad N_{a+} = \bar{N}_a\left(1 - \frac{\hbar\Delta}{kT}\right).$$

After introducing (45) into the expressions for the transition rates, Taylor-expanding the functions $g(\omega_-, \omega)$ and $g(\omega_+, \omega)$ with respect to ω_0, keeping only terms linear in H_0 and isotropic averaging, we finally obtain

$$N\cdot w(a \to b; \mathrm{II}) = \bar{N}_a[w(a_- \to b; \mathrm{II}; H_0) + w(a_+ \to b; \mathrm{II}; H_0)] = \frac{4\bar{N}_a}{3\hbar^2}\,\mathrm{Re}\,[(\langle b|\boldsymbol{\mu}|a_-\rangle\cdot\langle a_-|\boldsymbol{m}|b\rangle \times\langle a_-|\boldsymbol{m}|a_-\rangle)\,(\boldsymbol{E}_-\cdot\boldsymbol{H}_+\times\boldsymbol{H}_0)] \times\left[\frac{1}{kT}g(\omega_0, \omega) + \frac{1}{\hbar}g'(\omega_0, \omega)\right]. \quad (46)$$

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

$$N\cdot w(a \to b; \mathrm{II}) = \frac{2\bar{N}_a\varepsilon^2 H_0}{3\hbar^2}\langle a_-|\boldsymbol{m}|a_-\rangle \cdot\mathrm{Re}\,(\langle a_-|\boldsymbol{\mu}|b\rangle\times\langle b|\boldsymbol{m}|a_-\rangle) \times\left[\frac{1}{kT}g(\omega_0, \omega) + \frac{1}{\hbar}g'(\omega_0, \omega)\right]. \quad (47)$$

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

$$B(a \to b; \omega(M); H_0) = \frac{4\pi H_0}{3\hbar^2}\langle a|\boldsymbol{m}|a\rangle \cdot\mathrm{Re}\,(\langle a|\boldsymbol{\mu}|b\rangle\times\langle b|\boldsymbol{m}|a\rangle) \times\left[\frac{1}{kT}g(\omega_0, \omega) + \frac{1}{\hbar}g'(\omega_0, \omega)\right], \quad (48)$$

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 $g(\omega_0, \omega)$ 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 $g'(\omega_0, \omega)$ is understood to be taken with respect to ω_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 $(e\hbar/2mc)/ea_0$ times smaller than that of corresponding MORD or MCD signals. With a static magnetic field of the order of 5 T, 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.

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