
Magneto-chiral Effect in H_h and V_h Components of Rayleigh Light Scattering by Diamagnetic Molecular Systems

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A static magnetic field \mathbf{B}^0 , acting on a chiral liquid perpendicular to the propagation direction of an optical beam, is shown to induce a magneto-chiral change of Rayleigh light scattering which is different in sign for the light scattered parallel and antiparallel to \mathbf{B}^0 . It is related to the electric dipole and magnetic dipole or/and electric quadrupole moments induced simultaneously in a chiral molecule by electric dipole interaction with electromagnetic radiation. For diamagnetic molecules the effect is described by linear and nonlinear polarizabilities, responsible also for circular birefringence (natural optical activity and the Faraday effect) as well as axial (magneto-chiral) birefringence.

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1. Introduction

Chirality is a very important structural feature of some molecules which distinguishes them from others and allows the appearance of phenomena, which are forbidden for achiral molecules [1–3]. In the absence of external fields molecular chiral media show natural optical activity, and, moreover, the effect known as Rayleigh and Raman optical activity in light scattering [4–8]. Both effects are circular differential. In isotropic media (e.g., liquids) natural optical activity is related

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to electric dipole and magnetic dipole interaction of molecules of the medium with electromagnetic wave, while in scattering effects electric quadrupole interaction can contribute as well.

In a chiral medium exposed to strong external fields we can observe a variation of effects related to its natural optical activity as well as investigate new phenomena which reveal nonlinear electro-magneto-optical properties of chiral molecules. Thus the impact of a strong static magnetic field \mathbf{B}^0 on the chiral molecular system can induce a change of circular birefringence [10–13] and circular dichroism [12] proportional to $(B^0)^2$ which has the same symmetry classification as natural optical activity: parity-odd ($P-$) and time-even ($T+$), and can be separated experimentally from the Faraday effect [13]. On the other hand, in an optically active isotropic medium a static magnetic field directed along the propagation direction of a light beam of any polarization induces a linear change in the refractive index [14–17] as well as in the absorption coefficient [16–18], which are not circular differential effects, leading to magnetochiral birefringence and magnetochiral dichroism [19, 20]. Both effects have been measured: magnetochiral dichroism in emission — using a modulated magnetic field and phase-sensitive detection [21], and magnetochiral birefringence — by the interferometric measurement in a static magnetic field of 5 T [22]. The molecular theory of magnetochiral birefringence and dichroism has been extended to the case of additional external high electric [23, 24] or optical [25] fields for media composed of diamagnetic as well as paramagnetic chiral molecules [26]. Both effects have been considered also in connection with parity violation in atoms [27] and, recently, the relation of the magnetochiral effect to other optical and magneto-optical phenomena has been discussed [28].

Magnetochiral birefringence is an axial birefringence following from the difference $n^{\uparrow\uparrow} - n^{\uparrow\downarrow}$ between the refractive indices for unpolarized probe light propagating parallel ($n^{\uparrow\uparrow}$) and antiparallel ($n^{\uparrow\downarrow}$) to the direction of the static magnetic field \mathbf{B}^0 . It is characterized by molecular polarizabilities describing the linear influence of the field \mathbf{B}^0 on: (i) the electric dipole polarizabilities ${}^e\alpha^m$ and ${}^e\alpha^q$ related to magnetic dipole and electric quadrupole interaction of the molecules with electromagnetic wave, respectively, (ii) the magnetic dipole polarizability ${}^m\alpha^e$ and the electric quadrupole polarizability ${}^q\alpha^e$ related to electric dipole interaction with light. However, only the real part of the polarizabilities ${}^e\alpha^m$ and ${}^m\alpha^e$, and the imaginary part of ${}^e\alpha^q$ and ${}^q\alpha^e$ contribute to the magnetochiral birefringence [17, 20].

Similarly to natural optical activity, which appears in light scattering at right angles as Rayleigh and Raman optical activity, magnetochiral birefringence also has its equivalent in light scattering with the same polarizabilities involved as in the magnetochiral effect. Since magnetochiral birefringence is an axial birefringence, then the magnetochiral effect in light scattering (we can call it the magnetochiral Rayleigh and Raman light scattering) appears as an axial differen-

tial effect, contrary to Rayleigh and Raman optical activity as well as magnetic Rayleigh and Raman optical activity [1, 29–32], which are circular differential. This difference between magnetic Rayleigh/Raman optical activity and magnetochiral Rayleigh/Raman light scattering implies the need for a different experimental configuration for measurement of these effects:

(i) magnetic Rayleigh/Raman optical activity is observed at right angles to the propagation direction of a circularly polarized (CP) light beam propagating parallel to a DC magnetic field, as the difference $I^+ - I^-$ of the light scattering intensity for right (+) and left (–) CP probe wave;

(ii) magnetochiral Rayleigh/Raman light scattering can be observed at right angles to the propagation direction of light propagating perpendicularly to a DC magnetic field, as the difference of the light scattering intensity $I^{\uparrow\uparrow} - I^{\uparrow\downarrow}$ for light scattered parallel ($\uparrow\uparrow$) and antiparallel ($\uparrow\downarrow$) to the magnetic field.

In the present paper we show that such an axial differential effect in light scattering can exist even for isotropic media composed of diamagnetic chiral molecules and can be observed as an axial differential effect of H_h and V_h components of anisotropic Rayleigh light scattering. The magnetochiral effect in other experimental configurations of light scattering for diamagnetic as well as paramagnetic molecular systems will be discussed in a separate paper.

2. Intensity of magnetochiral Rayleigh light scattering

We shall consider a transparent isotropic medium composed of diamagnetic chiral molecules subjected to the action of a static homogeneous magnetic field $\mathbf{B}^0 = jB_y^0$, directed along the Y axis of the laboratory frame of coordinates $\{X, Y, Z\}$ (Fig. 1) in which a linearly (horizontally) polarized light beam of circular frequency ω with the electric field

$$E_y(z, t) = \frac{1}{2} E_y(\omega) \exp \left[-i\omega \left(t - \frac{z}{c} \right) \right] + \text{c.c.}, \quad (1)$$

a magnetic induction $B_x(z, t)$ and an intensity I_h propagates in the z direction, c is the velocity of light in vacuum. The amplitude $E_y(\omega)$ is assumed to be small compared to the strength of the molecular field.

Multipole interactions of the electromagnetic wave (1) with the medium molecule lead to light scattering. The scattered light intensity I^s with the electric field \mathbf{E}^s having the polarization of the unit vector \mathbf{e}^s ,

$$I^s = \frac{\epsilon_0 c}{2} \langle |\mathbf{E}^s \cdot \mathbf{e}^{s*}|^2 \rangle \quad (2)$$

depends on the induced multipole moments, i.e., the electric dipole moment $\boldsymbol{\mu}(\omega)$, the magnetic dipole moment $\mathbf{m}(\omega)$, and the electric quadrupole moment $\mathbf{q}(\omega)$ vibrating at a frequency ω (other higher multipole moments can be neglected) as well as on the scattering angle [6]; the brackets $\langle \dots \rangle$ stands for statistical averaging over all possible orientation of the molecules.

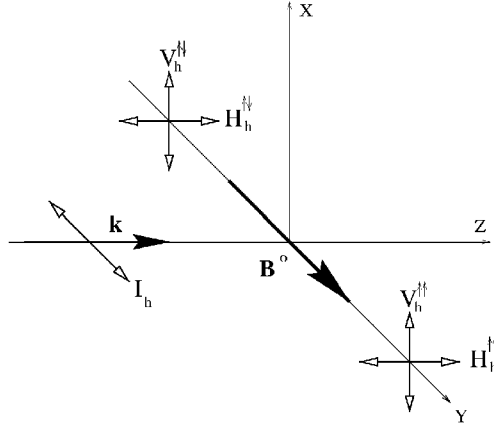


Fig. 1. Scattering configuration as analyzed in the present work.

In the present paper we are concerned with the light scattered in the direction parallel and antiparallel to the DC field \mathbf{B}^0 and the two components of light intensity, H_h and V_h , scattered by a unit volume of the medium are discussed. The indices in Krishnan's symbols H_h and V_h denote the polarization status of the incident beam (h — for horizontal), and the capital letter stands for the orientation of the polarizer before the detector of the scattered light (H — for horizontal, V — for vertical).

Denoting the intensities H_h and V_h of the scattered light propagating parallel ($\uparrow\uparrow$) or antiparallel ($\uparrow\downarrow$) to the direction of \mathbf{B}^0 by $H_h^{\uparrow\uparrow}$, $V_h^{\uparrow\uparrow}$ and $H_h^{\uparrow\downarrow}$, $V_h^{\uparrow\downarrow}$, respectively, the magnetochiral effect in anisotropic light scattering measured at a distance R from the scattering center is described by the following equations:

$$\begin{aligned} \Delta H_h = H_h^{\uparrow\uparrow} - H_h^{\uparrow\downarrow} = K_1 \langle & 2[\mu_z(\omega, \mathbf{B}^0)m_x^*(\omega, \mathbf{B}^0) + \mu_z^*(\omega, \mathbf{B}^0)m_x(\omega, \mathbf{B}^0)] \\ & + i\omega[\mu_z(\omega, \mathbf{B}^0)q_{zy}^*(\omega, \mathbf{B}^0) - \mu_z^*(\omega, \mathbf{B}^0)q_{zy}(\omega, \mathbf{B}^0)] \rangle \end{aligned} \quad (3)$$

and

$$\begin{aligned} \Delta V_h = V_h^{\uparrow\uparrow} - V_h^{\uparrow\downarrow} = K_1 \langle & -2[\mu_x(\omega, \mathbf{B}^0)m_z^*(\omega, \mathbf{B}^0) + \mu_x^*(\omega, \mathbf{B}^0)m_z(\omega, \mathbf{B}^0)] \\ & + i\omega[\mu_x(\omega, \mathbf{B}^0)q_{xy}^*(\omega, \mathbf{B}^0) - \mu_x^*(\omega, \mathbf{B}^0)q_{xy}(\omega, \mathbf{B}^0)] \rangle, \end{aligned} \quad (4)$$

where $K_1 = \rho\omega^4/32\pi^2\epsilon_0c^4R^2$, ρ is the number density of the chiral molecules and the asterisk represents the complex conjugate. Restricting our consideration to the linear influence of the static field \mathbf{B}^0 we have

$$\begin{aligned} \mu_i(\omega, \mathbf{B}^0) = & {}^e\alpha^e{}_{ij}(-\omega; \omega)E_j(\omega) + {}^e\alpha^m{}_{ij}(-\omega; \omega)B_j(\omega) \\ & + \frac{1}{2}{}^e\alpha^q{}_{ijk}(-\omega; \omega)\nabla_j E_k(\omega) + {}^e\alpha^{em}{}_{ijk}(-\omega; \omega, 0)E_j(\omega)B_k^0 \\ & + {}^e\alpha^{mm}{}_{ijk}(-\omega; \omega, 0)B_j(\omega)B_k^0 + \frac{1}{2}{}^e\alpha^{qm}{}_{ikl}(-\omega; \omega, 0)\nabla_j E_k(\omega)B_l^0, \end{aligned} \quad (5)$$

$$m_i(\omega, \mathbf{B}^0) = {}^m\alpha_{ij}^e(-\omega; \omega)E_j(\omega) + {}^m\alpha_{ijk}^{em}(-\omega; \omega, 0)E_j(\omega)B_k^0, \quad (6)$$

$$q_{ij}(\omega, \mathbf{B}^0) = {}^q\alpha_{(ij)k}^e(-\omega; \omega)E_k(\omega) + {}^q\alpha_{(ij)kl}^{em}(-\omega; \omega, 0)E_k(\omega)B_l^0, \quad (7)$$

where the superscripts e, m, and q on the right-hand side of the symbol α (representing molecular polarizabilities) are related to electric dipole (e), magnetic dipole (m) and electric quadrupole (q) interactions with the radiation inducing electric dipole, magnetic dipole and electric quadrupole moments denoted by the superscripts e, m, and q, respectively, on the left-hand side of the symbol α .

In a general case each polarizability tensor α may be split into [6, 32, 33]

$$\alpha = \beta + i\gamma, \quad (8)$$

where, in the absence of damping, the tensors β and γ are real.

Applying Eq. (8) to all polarizabilities in (5–7) (now we use the concise notation ${}^e\beta^e(\omega)$, ${}^e\gamma^m(\omega)$, ${}^m\gamma^e(\omega)$, ${}^e\beta^q(\omega)$ and ${}^q\beta^e(\omega)$ instead of ${}^e\beta^e(-\omega; \omega)$, ${}^e\gamma^m(-\omega; \omega)$, ${}^m\gamma^e(-\omega; \omega)$, ${}^e\beta^q(-\omega; \omega)$ and ${}^q\beta^e(-\omega; \omega)$ for unperturbed linear polarizabilities as well as ${}^e\gamma^{em}(\omega)$, ${}^e\beta^{mm}(\omega)$, ${}^m\beta^{em}(\omega)$, ${}^q\gamma^{em}(\omega)$ and ${}^e\gamma^{qm}(\omega)$ instead of perturbed polarizability tensors ${}^e\gamma^{em}(-\omega; \omega, 0)$, ${}^e\beta^{mm}(-\omega; \omega, 0)$, ${}^m\beta^{em}(-\omega; \omega, 0)$, ${}^q\gamma^{em}(-\omega; \omega, 0)$ and ${}^e\gamma^{qm}(-\omega; \omega, 0)$, respectively) we have that for non-magnetic molecules the tensors

$$\begin{aligned} {}^e\beta_{\alpha\beta}^e(\omega), {}^e\gamma_{\alpha\beta}^m(\omega) &= -{}^m\gamma_{\beta\alpha}^e(\omega), {}^e\beta_{\alpha(\beta\gamma)}^q(\omega) = {}^q\beta_{(\beta\gamma)\alpha}^e(\omega), {}^e\gamma_{[\alpha\beta]\gamma}^{em}(\omega), \\ {}^e\beta_{\alpha\beta\gamma}^{mm}(\omega) &= {}^m\beta_{\beta\alpha\gamma}^{em}(\omega), {}^e\gamma_{\alpha(\beta\gamma)\delta}^{qm}(\omega) = -{}^q\gamma_{(\beta\gamma)\alpha\delta}^{em}(\omega) \end{aligned} \quad (9)$$

are non-zero, whereas the others vanish [17]. The indices whose transposition changes the sign of the respective components of the multipolar polarizabilities are indicated by rectangular brackets, whereas the round parentheses denote the indices whose transposition does not change the sign. The formulas for the tensors in Eq. (9) have been given in [6, 29, 30] in terms of a sum over all excited states.

The statistical averages in Eqs. (3) and (4) with respect to (5–9), which is equivalent to the space average of five- and six-rank tensors [34], show that for the configuration presented in Fig. 1 the magnetochiral Rayleigh light scattering is the same for H_h and V_h intensity components and for diamagnetic molecules

$$\Delta H_h = \Delta V_h = (A^m + \omega A^q)K I_h B_y^0. \quad (10)$$

The first molecular constant in the above equation

$$A^m = A_1^m + A_2^m \quad (11)$$

with

$$A_1^m = 14\varepsilon_{\alpha\beta\gamma} \{ {}^m\gamma_{\alpha\beta}^e(\omega) {}^e\gamma_{[\gamma\delta]}^{em}(\omega) - {}^m\gamma_{\alpha\delta}^e(\omega) [{}^e\gamma_{[\beta\gamma]\delta}^{em}(\omega) + {}^e\gamma_{[\beta\delta]\gamma}^{em}(\omega)] \} \quad (12)$$

and

$$A_2^m = 14\varepsilon_{\alpha\beta\gamma} {}^e\beta_{(\alpha\delta)}^e(\omega) [{}^m\beta_{\beta\gamma\delta}^{em}(\omega) + {}^m\beta_{\beta\delta\gamma}^{em}(\omega)] \quad (13)$$

describes magnetochiral light scattering due to vibration of electric dipole and magnetic dipole moments induced simultaneously in the molecule by electric dipole interaction with the incident light and perturbed by the static field \mathbf{B}^0 : A_1^m — for the perturbed electric dipole moment, A_2^m — for the perturbed magnetic dipole moment; $\varepsilon_{\alpha\beta\gamma}$ is the Levi–Civita third-rank antisymmetric unit tensor.

The second molecular constant

$$A^q = A_1^q + A_2^q \quad (14)$$

with

$$A_1^q = 7[{}^q\beta_{(\alpha\beta)\beta}^e(\omega) {}^e\gamma_{[\gamma\alpha]\gamma}^{\text{em}}(\omega) + {}^q\beta_{(\alpha\beta)\gamma}^e(\omega) {}^e\gamma_{[\gamma\alpha]\beta}^{\text{em}}(\omega)] \quad (15)$$

and

$$A_2^q = {}^e\beta_{(\alpha\beta)}^e(\omega)[5 {}^q\gamma_{(\alpha\beta)\gamma\gamma}^{\text{em}}(\omega) + 3 {}^q\gamma_{(\alpha\gamma)\beta\gamma}^{\text{em}}(\omega) + 3 {}^q\gamma_{(\alpha\gamma)\gamma\beta}^{\text{em}}(\omega) - 2 {}^q\gamma_{(\gamma\gamma)\alpha\beta}^{\text{em}}(\omega)] - {}^e\beta_{(\alpha\alpha)}^e(\omega)[{}^q\gamma_{(\beta\beta)\gamma\gamma}^{\text{em}}(\omega) + 2 {}^q\gamma_{(\beta\gamma)\beta\gamma}^{\text{em}}(\omega)] \quad (16)$$

describes the light scattering related to the vibration of electric dipole and electric quadrupole moments induced simultaneously in a molecule of the medium by electric dipole interaction with the incident light and perturbed by the static magnetic field \mathbf{B}^0 (A_1^q or A_2^q , respectively, for perturbed electric dipole or electric quadrupole moments). The constant K in Eq. (10) has the form

$$K = \frac{2K_1}{105\epsilon_0 c} = \frac{\rho\omega^4}{1680\pi^2\epsilon_0^2 c^5 R^2}. \quad (17)$$

It is convenient to introduce a dimensionless value of magnetochiral light scattering which for both components H_h and V_h of the scattered light is defined as

$$\delta H_h = \frac{H_h^{\uparrow\uparrow} - H_h^{\uparrow\downarrow}}{H_h^{\uparrow\uparrow} + H_h^{\uparrow\downarrow}} \quad (18)$$

and

$$\delta V_h = \frac{V_h^{\uparrow\uparrow} - V_h^{\uparrow\downarrow}}{V_h^{\uparrow\uparrow} + V_h^{\uparrow\downarrow}}. \quad (19)$$

The main contribution to the denominators in Eqs. (18) and (19) is related to electric dipole type of light scattering

$$H_h^{\uparrow\uparrow} + H_h^{\uparrow\downarrow} = V_h^{\uparrow\uparrow} + V_h^{\uparrow\downarrow} = \frac{\rho\omega^4 I_h}{240\pi^2\epsilon_0^2 c^4 R^2} \times [3 {}^e\beta_{\alpha\beta}^e(\omega) {}^e\beta_{\alpha\beta}^e(\omega) - {}^e\beta_{\alpha\alpha}^e(\omega) {}^e\beta_{\beta\beta}^e(\omega)]. \quad (20)$$

In the above equation the quadratic contribution caused by the external field \mathbf{B}^0 is neglected because it is much smaller than the expression (20).

We can introduce here a dimensionless parameter of the linear optical anisotropy $\kappa(\omega)$ [35]:

$$\kappa^2(\omega) = \frac{3 {}^e\beta_{\alpha\beta}^e(\omega) {}^e\beta_{\alpha\beta}^e(\omega) - {}^e\beta_{\alpha\alpha}^e(\omega) {}^e\beta_{\beta\beta}^e(\omega)}{18\beta^2(\omega)} \quad (21)$$

with $\beta(\omega) = \frac{1}{3} {}^e\beta_{\alpha\alpha}^e(\omega)$ being the mean value of the linear polarizability ${}^e\beta^e(\omega)$. Then expressions (18) and (19) can be written as

$$\delta H_h = \delta V_h = \frac{(A^m + \omega A^q) B_y^0}{126c\beta^2(\omega)\kappa^2(\omega)}. \quad (22)$$

As only diagonal components of the tensor ${}^e\beta_{\alpha\beta}^e(\omega)$ are non-zero for diamagnetic chiral molecules, the anisotropy $\kappa^2(\omega)$ has the form

$$\kappa^2(\omega) = \frac{[{}^e\beta_{11}^e(\omega) - {}^e\beta_{22}^e(\omega)]^2 + [{}^e\beta_{22}^e(\omega) - {}^e\beta_{33}^e(\omega)]^2 + [{}^e\beta_{33}^e(\omega) - {}^e\beta_{11}^e(\omega)]^2}{18\beta^2(\omega)}. \quad (23)$$

3. The influence of molecular symmetry on magnetochiral light scattering

Diamagnetic chiral molecules belong to the point group symmetries D_2 (222), C_3 (3), C_4 (4), C_6 (6), C_∞ (∞), D_3 (32), D_4 (422), D_6 (622), T (23), O (432), Y and K . Since the relations between non-zero components of the polar tensors ${}^e\beta^e(\omega)$, ${}^m\beta^{em}(\omega)$, and ${}^q\beta^e(\omega)$ as well as those of the axial tensors ${}^m\gamma^e(\omega)$, ${}^e\gamma^{em}(\omega)$, and ${}^q\gamma^{em}(\omega)$ are available for all point group symmetries [1, 17], we are in a position to determine the molecular constants A^m and A^q for all above symmetries. Thus, for molecules having the symmetry D_2

$$A_1^m = 14\{[{}^m\gamma_{22}^e(\omega) - {}^m\gamma_{11}^e(\omega)][{}^e\gamma_{231}^{em}(\omega) + {}^e\gamma_{123}^{em}(\omega) - 2{}^e\gamma_{312}^{em}(\omega)] + [{}^m\gamma_{33}^e(\omega) - {}^m\gamma_{11}^e(\omega)][{}^e\gamma_{312}^{em}(\omega) + {}^e\gamma_{231}^{em}(\omega) - 2{}^e\gamma_{123}^{em}(\omega)]\}, \quad (24)$$

$$A_2^m = 14\{[{}^e\beta_{22}^e(\omega) - {}^e\beta_{11}^e(\omega)][{}^m\beta_{312}^{em}(\omega) + {}^m\beta_{321}^{em}(\omega)] + [{}^e\beta_{33}^e(\omega) - {}^e\beta_{22}^e(\omega)][{}^m\beta_{123}^{em}(\omega) + {}^m\beta_{132}^{em}(\omega)] + [{}^e\beta_{11}^e(\omega) - {}^e\beta_{33}^e(\omega)][{}^m\beta_{213}^{em}(\omega) + {}^m\beta_{231}^{em}(\omega)]\}, \quad (25)$$

$$A_1^q = 7\{[{}^q\beta_{123}^e(\omega) - {}^q\beta_{231}^e(\omega)]{}^e\gamma_{312}^{\text{em}}(\omega) + [{}^q\beta_{231}^e(\omega) - {}^q\beta_{312}^e(\omega)]{}^e\gamma_{123}^{\text{em}}(\omega) + [{}^q\beta_{312}^e(\omega) - {}^q\beta_{123}^e(\omega)]{}^e\gamma_{231}^{\text{em}}(\omega)\}, \quad (26)$$

$$A_2^q = {}^e\delta_1^e(\omega)\{6{}^q\gamma_{3333}^{\text{em}}(\omega) - 3[{}^q\gamma_{2222}^{\text{em}}(\omega) + {}^q\gamma_{1111}^{\text{em}}(\omega) + {}^q\gamma_{1133}^{\text{em}}(\omega) + {}^q\gamma_{2233}^{\text{em}}(\omega)] + 4[{}^q\gamma_{3311}^{\text{em}}(\omega) + {}^q\gamma_{3322}^{\text{em}}(\omega)] - 2[{}^q\gamma_{1221}^{\text{em}}(\omega) + {}^q\gamma_{2112}^{\text{em}}(\omega) - {}^q\gamma_{1122}^{\text{em}}(\omega) - {}^q\gamma_{2211}^{\text{em}}(\omega) + {}^q\gamma_{1331}^{\text{em}}(\omega) + {}^q\gamma_{3113}^{\text{em}}(\omega) + {}^q\gamma_{2332}^{\text{em}}(\omega) + {}^q\gamma_{3223}^{\text{em}}(\omega)]\} + {}^e\delta_2^e(\omega)\{9[{}^q\gamma_{1111}^{\text{em}}(\omega) - {}^q\gamma_{2222}^{\text{em}}(\omega)] + 7[{}^q\gamma_{1122}^{\text{em}}(\omega) - {}^q\gamma_{2211}^{\text{em}}(\omega)] + 5[{}^q\gamma_{1133}^{\text{em}}(\omega) - {}^q\gamma_{2233}^{\text{em}}(\omega)] + 3[{}^q\gamma_{3113}^{\text{em}}(\omega) - {}^q\gamma_{3223}^{\text{em}}(\omega)] + 3[{}^q\gamma_{1331}^{\text{em}}(\omega) - {}^q\gamma_{2332}^{\text{em}}(\omega)] + 2[{}^q\gamma_{3322}^{\text{em}}(\omega) - {}^q\gamma_{3311}^{\text{em}}(\omega)]\} \quad (27)$$

with the anisotropies ${}^e\delta_1^e(\omega)$ and ${}^e\delta_2^e(\omega)$ of the linear polarizability ${}^e\beta^e(\omega)$

$${}^e\delta_1^e(\omega) = {}^e\beta_{33}^e(\omega) - \frac{1}{2}[{}^e\beta_{11}^e(\omega) + {}^e\beta_{22}^e(\omega)], \quad (28)$$

$${}^e\delta_2^e(\omega) = \frac{1}{2}[{}^e\beta_{11}^e(\omega) - {}^e\beta_{22}^e(\omega)]. \quad (29)$$

For chiral molecules with the point group symmetries C_3 , C_4 , C_6 , and C_∞

$$A_1^m = 28{}^m\delta^e(\omega)[{}^e\gamma_{312}^{\text{em}}(\omega) - {}^e\gamma_{123}^{\text{em}}(\omega)] + 5{}^m\gamma_{12}^e(\omega){}^e\gamma_{311}^{\text{em}}(\omega), \quad (30)$$

$$A_2^m = 28{}^e\delta^e(\omega)[{}^m\beta_{123}^{\text{em}}(\omega) - {}^m\beta_{231}^{\text{em}}(\omega)], \quad (31)$$

$$A_1^q = 14\{[{}^q\beta_{113}^e(\omega) - 3{}^q\beta_{311}^e(\omega) - {}^q\beta_{333}^e(\omega)]{}^e\gamma_{311}^{\text{em}}(\omega) + {}^q\beta_{231}^e(\omega)[{}^e\gamma_{123}^{\text{em}}(\omega) - {}^e\gamma_{312}^{\text{em}}(\omega)]\}, \quad (32)$$

$$A_2^q = 2{}^e\delta^e(\omega)[3{}^q\gamma_{3333}^{\text{em}}(\omega) - 3{}^q\gamma_{1111}^{\text{em}}(\omega) + 4{}^q\gamma_{3311}^{\text{em}}(\omega) - {}^q\gamma_{1133}^{\text{em}}(\omega) - {}^q\gamma_{1122}^{\text{em}}(\omega) - 2{}^q\gamma_{1221}^{\text{em}}(\omega) + {}^q\gamma_{1331}^{\text{em}}(\omega) + {}^q\gamma_{3113}^{\text{em}}(\omega)], \quad (33)$$

where

$${}^e\delta^e(\omega) = {}^e\beta_{33}^e(\omega) - {}^e\beta_{11}^e(\omega), \quad (34)$$

$${}^m\delta^e(\omega) = {}^m\gamma_{33}^e(\omega) - {}^m\gamma_{11}^e(\omega) \quad (35)$$

are the anisotropies of the polarizabilities ${}^e\beta^e(\omega)$ and ${}^m\gamma^e(\omega)$ for the molecules

with the above symmetries; for molecules having the symmetries D_3 , D_4 , and D_6

$$A_1^m = 28^m \delta^e(\omega) [{}^e\gamma_{312}^{em}(\omega) - {}^e\gamma_{123}^{em}(\omega)], \quad (36)$$

$$A_2^m = 28^e \delta^e(\omega) [{}^m\beta_{123}^{em}(\omega) - {}^m\beta_{231}^{em}(\omega)], \quad (37)$$

$$A_1^q = 14^q \beta_{231}^e(\omega) [{}^e\gamma_{123}^{em}(\omega) - {}^e\gamma_{312}^{em}(\omega)], \quad (38)$$

$$A_2^q = 2^e \delta^e(\omega) [3^q \gamma_{3333}^{em}(\omega) - 4^q \gamma_{1111}^{em}(\omega) + 4^q \gamma_{3311}^{em}(\omega) - 3^q \gamma_{1133}^{em}(\omega) + {}^q\gamma_{1331}^{em}(\omega) + {}^q\gamma_{3113}^{em}(\omega)]. \quad (39)$$

For the remaining point groups of chiral molecules (T , O , Y , and K) all parameters A_1^m , A_2^m , A_1^q , and A_2^q are equal to zero.

4. Discussion

It is worth emphasizing the physical mechanism of magnetochiral light scattering considered in this paper: only the electric dipole and magnetic dipole or/and the electric quadrupole moments induced simultaneously in the molecule by only the electric dipole interaction with the incident light are responsible for the effect discussed (Eq. (10)). On the other hand, the electric dipole moments induced by magnetic dipole and electric quadrupole interactions with the light do not contribute to the effect in spite of the fact that the polarizabilities mediating these interactions are in simple relations to the polarizabilities describing the phenomenon under consideration (see Eq. (9)).

Experimental results show that magnetic dipole interactions can be responsible for some nonlinear optical effects like nonlinear optical activity observed in second harmonic generation [36, 37] and the occurrence of a second harmonic signal [38]. However, contributions due to electric quadrupole interactions with radiation are related to the same order of perturbation calculus as magnetic dipole interactions and they may be, in general, of the same order of magnitude in some optical effects [39] or, even, the electric quadrupole interactions can dominate as in the residual second harmonic signal [40].

To estimate the magnitude of the effect discussed let us consider, as an example, the contribution related to the constant A_1^m and A_1^q . For molecules possessing the symmetries D_3 , D_4 , and D_6 , for which the expressions describing the scattering effect have the simplest form, we get

$$\delta H_h(A_1^m) = \delta V_h(A_1^m) = \frac{2^m \delta^e ({}^e\gamma_{312}^{em} - {}^e\gamma_{123}^{em}) B_y^0}{c({}^e\delta^e)^2}, \quad (40)$$

$$\delta H_h(A_1^q) = \delta V_h(A_1^q) = \frac{\omega^q \beta_{231}^e ({}^e\gamma_{123}^{em} - {}^e\gamma_{312}^{em}) B_y^0}{c({}^e\delta^e)^2}, \quad (41)$$

where, for the sake of simplicity, we omitted the frequency symbol ω in all tensor components writing, e.g., ${}^e\gamma_{123}^{\text{em}}$ instead of ${}^e\gamma_{123}^{\text{em}}(\omega)$, and so on.

To estimate roughly the magnetochiral effect given by Eq. (40) we can assume that the anisotropy ${}^m\delta^e$ is of the same order of magnitude as ${}^m\gamma^e$, the mean value of the polarizability ${}^m\gamma^e$ (that is usually valid for anisotropic chiral molecules except for those with ${}^m\gamma_{11}^e \approx {}^m\gamma_{22}^e \approx {}^m\gamma_{33}^e$), which is related to the specific rotation $[\varphi]$ of liquid [39, 41]

$${}^m\delta^e \approx {}^m\gamma^e = \frac{\epsilon_0 \lambda c}{2\pi\rho} [\varphi], \quad (42)$$

where $[\varphi]$ is given in radians per meter measured for wavelength λ of the probe light beam. Taking $[\varphi] = 10 \text{ rad m}^{-1}$, $\rho = 2 \times 10^{27} \text{ m}^{-3}$ and $\lambda = 500 \text{ nm}$ we get ${}^m\delta^e \approx 1 \times 10^{-36} \text{ J m}^3 \text{ V}^{-2} \text{ s}^{-1}$.

Similarly, the order of magnitude of the anisotropy ${}^e\delta^{\text{em}} = {}^e\gamma_{312}^{\text{em}} - {}^e\gamma_{123}^{\text{em}}$ can be obtained assuming ${}^e\delta^{\text{em}} \approx {}^e\gamma^{\text{em}}$ — the mean value of the polarizability ${}^e\gamma^{\text{em}}$. Then we have [12, 42]

$${}^e\delta^{\text{em}} \approx {}^e\gamma^{\text{em}} = \frac{n\lambda\epsilon_0}{\pi\rho} V, \quad (43)$$

where V is the Verdet constant given in SI units (radians per meter and Tesla), n — is the refractive index for the wavelength λ . Taking $V = 10 \text{ rad m}^{-1} \text{ T}^{-1}$ (for many liquids the Verdet constant has that value [13, 43]), $\rho = 2 \times 10^{27} \text{ m}^{-3}$, $n = 1.5$ and $\lambda = 500 \text{ nm}$ we get ${}^e\delta^{\text{em}} \approx 10^{-44} \text{ J m}^4 \text{ V}^{-3} \text{ s}^{-1}$.

For the above values of ${}^m\delta^e$, ${}^e\delta^{\text{em}}$, and ${}^e\delta^e \approx 10^{40} \text{ J m}^2 \text{ V}^{-2}$ [44] we have

$$\delta H_{\text{h}}(A_1^{\text{m}}) = \delta V_{\text{h}}(A_1^{\text{m}}) \approx 10^{-8} [\text{T}^{-1}] B_y^0, \quad (44)$$

where B_y^0 is in Tesla (T).

To estimate $\delta H_{\text{h}}(A_1^{\text{q}})$ and $\delta V_{\text{h}}(A_1^{\text{q}})$ (Eq. (41)) we assume (as a conservative estimate) the quadrupole–dipole polarizability ${}^q\beta^e \approx 10^{-50} \text{ C}^2 \text{ m}^3 \text{ J}^{-1}$ (a magnitude $10^{-49} \text{ C}^2 \text{ m}^3 \text{ J}^{-1}$ is typical of the ${}^q\beta_{333}^e$ linear molecules [45]) and we obtain

$$\delta H_{\text{h}}(A_1^{\text{q}}) = \delta V_{\text{h}}(A_1^{\text{q}}) \approx 10^{-7} [\text{T}^{-1}] B_y^0. \quad (45)$$

The above rough estimations show that the magnetochiral effect in Rayleigh light scattering is rather small but it seems to be measurable by photon counting methods [46]. For some chiral molecules the anisotropies ${}^m\delta^e$ and ${}^e\delta^{\text{em}}$ as well as the polarizability ${}^q\beta^e$ can be greater than the values assumed in our estimation leading to an appropriate larger effect. It is also expected that magnetochiral Rayleigh light scattering should be larger in some systems of paramagnetic chiral molecules. However, this aspect of our investigation will be discussed in a separate paper.

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