

Probing magnetochirality

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Abstract. Magnetochiral anisotropy refers to the phenomenon that when light is passed through a chiral medium placed in an external magnetic field, the refractive index, or equivalently, the absorption encountered by the light differs depending on whether it travels parallel or antiparallel to the magnetic field. It is a very small effect, the change in refractive index because of this effect alone being of the order of 10^{-11} . This effect has recently been measured in an active ring laser interferometer in which the detection scheme convincingly eliminates the contributions from natural optical activity, the Faraday effect and other stray anisotropies in the system. The phenomenon is important in the context of fundamental interactions between light and matter and the governing symmetry principles, and also in biochemistry as one possible explanation for the homochirality of life.

Keywords. Magnetochirality; optical activity; active interferometry; ring laser.

PACS Nos 33.15.Bh; 33.55.Fi; 78.20.Ls

1. Introduction

What is magnetochirality? If a linearly polarized light is passed through a chiral medium (i.e., a medium lacking mirror symmetry), the plane of polarization of the light gets rotated, and this is the familiar *natural optical activity*. The same effect is observed if light is passed through any non-chiral medium in the presence of a magnetic field, and this is called the *magnetic optical activity* or the *Faraday effect*. The strong phenomenological resemblance between the two effects has prompted numerous studies in search of a link between the two, starting with the work of Pasteur. The physical origins of the two kinds of optical activity are completely different: natural optical activity occurs because of nonlocal optical response in chiral media, whereas the magnetic optical activity occurs in all media because of the breaking of time-reversal symmetry by a magnetic field. When both symmetries are broken simultaneously in chiral media in the presence of a magnetic field collinear with the direction of propagation of light, a cross-effect becomes possible: the refractive index (or equivalently, the absorption) that the light encounters will differ depending on whether it travels parallel or antiparallel to the magnetic field. This is *magnetochirality*, called magnetochiral birefringence in refraction, and magnetochiral dichroism in absorption or emission. Magnetochiral anisotropy has opposite sign for the two enantiomers (mirror images) of the chiral medium, and depends on the relative orientation of the light field wave-vector \vec{k} and the magnetic field \vec{B} . However, it is independent of the state of polarization of light. As the name implies, magnetochirality occurs in a chiral medium in

the presence of a magnetic field, and can be thought of as either the magnetically induced change of natural optical activity or the difference in magnetic optical activity of the two enantiomers of a chiral medium.

Investigation of this effect acquires significance in the context of fundamental interactions between light and matter because of the governing symmetry principles. Also, the chemistry of life is homochiral: it is based almost exclusively on L-amino acids and D-sugars [1]. Biological molecules are capable of discriminating between enantiomers which is vital for living systems. Magnetochirality provides a possible explanation for the homochirality of life, i.e., the origin of handedness in nature.

An implicit prediction of such an effect was made by Groenewege in 1962 [2], and there were some preliminary investigations in crystals by Portigal and Burstein in 1971 [3], and by Markelov *et al* in 1977 [4]. The effect was predicted for molecules by Baranova, Bogdanov and Zel'dovich in 1977 [5], and a simple microscopic model for the effect was provided by Baranova and Zel'dovich in 1979 [6]. Magnetochirality in absorption was predicted by Wagnière and Meier in 1982 [7]. An elegant molecular theory for the magnetochiral anisotropy was formulated by Barron and Vrbancich in 1984 [8]. For any quantitative prediction, however, this theory requires complete knowledge of all molecular transition moments involved, and hence can not be easily used for comparison with experimental results. For quantitative comparisons, the model of Baranova and Zel'dovich [6] comes more handy though it is not very rigorous, as we will see below.

The first observation of magnetochiral dichroism (i.e., in absorption or emission) was reported by Rikken and Raupach in 1997 [9]. In 2000, Rikken and Raupach [10] were able to demonstrate magnetochiral enantioselective photochemistry for the first time, by applying a static magnetic field to bias a chemical process in favour of one of two mirror-image products. They used the chiral Cr(III)tris-oxalato complex which is unstable in solution and spontaneously dissociates and re-associates producing equal concentrations of right- and left-handed enantiomers at equilibrium. This dissociation is accelerated by the absorption of light. In their experiment, in the presence of an unpolarized laser beam traveling parallel to a static magnetic field, a small excess of one enantiomer was produced and maintained. Reversing the magnetic field direction resulted in an equal concentration of mirror-image enantiomer.

For magnetochiral birefringence, the first experiments for the detection of the change in the refractive index were performed by Wagnière and co-workers [11] using a passive interferometer. These measurements are not very convincing as the reported experimental values are about two orders of magnitude larger than the theoretical predictions of Baranova and Zel'dovich [6]. The experimental difficulty lies in eliminating the effects of all other anisotropies in the system which would be much larger than that of the magnetochiral anisotropy and hence mask the weak signal. In a carefully devised experiment using an active interferometer, we have recently measured magnetochiral birefringence for two different chiral compounds [12] and the results are in agreement with the theory.

2. Understanding magnetochiral anisotropy

The broad features of the magnetochiral effect can be understood by considering the multipole-series interaction Hamiltonian of the molecular system coupled to the electromagnetic ($\vec{E}(t), \vec{B}(t)$) fields:

$$H_{\text{int}} = -\vec{\mu} \cdot \vec{E}(t) - \vec{m} \cdot \vec{B}(t) - \vec{Q} : \nabla \vec{E}(t) + \dots, \quad (1)$$

where $\vec{\mu}$ and \vec{m} are the induced electric and magnetic dipole moments, \vec{Q} is the induced electric quadrupole moment, etc. For the case of ordinary refraction and absorption, the electric dipole term dominates (the long-wavelength approximation). Rayleigh scattering has products of the kind $\mu\mu$. For natural optical activity, the susceptibility has products of electric dipole transition moments which are parity-odd polar vectors, and magnetic dipole transition moments which are parity-even axial vectors. Hence the natural optical activity tensor involving products of the kind μm is parity-odd, i.e., it occurs only in a non-centrosymmetric medium, and thus in fluids the molecules have to be chiral. Magnetic optical activity or the Faraday effect has products of the kind $\mu\mu m$ which is even with respect to parity, and thus it occurs in all materials. Any effect involving an odd number of magnetic dipole and/or electric quadrupole interactions will be a circular-differential effect, i.e., it will depend on the state of polarization of the electromagnetic wave. Magnetochirality arises through the combination of a magnetic dipole interaction with a static magnetic field and a magnetic dipole, or an electric quadrupole interaction with the radiation, involving products of the kind $\mu m m$ which is parity-odd. Thus it occurs in chiral media in the presence of a magnetic field.

We now briefly outline the interpretation of the magnetochiral effect as given in [6]. For non-magnetic materials, the propagation of light is governed by the relative dielectric tensor ϵ . The magnetochiral effect can thus be deduced from an expansion of ϵ to first order in \vec{k} and \vec{B} . When considering chiral liquids in magnetic fields parallel to the wave-vector of incident light, the relative dielectric constants ϵ_- and ϵ_+ for right- and left-circularly polarized light, respectively, can be written as

$$\epsilon_{\pm}(\omega, \vec{k}, \vec{B}) = \epsilon(\omega) \pm a_F(\omega) B \pm a_{OA}(\omega) k + a_{MC}(\omega) (\vec{B} \cdot \vec{k}), \quad (2)$$

where ω is the optical frequency, a_F and a_{OA} characterize the magnetic optical activity and the natural optical activity, respectively. The fourth term, a_{MC} , describes the magnetochiral anisotropy of the sample. The a 's are real functions in the absence of absorption, otherwise, the real and imaginary parts are connected by the Kramers–Kronig relations. Magnetochirality is a scalar non-reciprocal effect, which changes sign with the handedness of the chiral molecules. Also, in a chiral medium subjected to a longitudinal magnetic field two counter-propagating light waves (of any polarization) experience different refractive indices. The difference in refractive index Δn for the two cases with \vec{B} and \vec{k} parallel and antiparallel, respectively, can be evaluated for magnetochiral birefringence alone, by avoiding absorption for large detunings from the absorption bands of the medium. Such a pure birefringence measurement is free from any cascading effects (mixing of natural and magnetic optical activities) proportional to $(\vec{B} \cdot \vec{k})$ [6,13]. Δn can be approximated as [6]

$$\Delta n = n(\vec{B} \uparrow \vec{k}) - n(\vec{B} \updownarrow \vec{k}) \approx \frac{|e|}{2m\sqrt{\epsilon(\omega)}} (\vec{B} \cdot \vec{k}) \frac{\partial a_{OA}}{\partial \omega}, \quad (3)$$

where e and m are the charge and the mass of an electron, and $(\vec{B} \uparrow \vec{k})$ and $(\vec{B} \updownarrow \vec{k})$ denote parallel and antiparallel \vec{B} and \vec{k} , respectively. Note that eq. (3) is only approximate – it takes into account the contribution of only magnetic dipole interactions through the dispersion of a_{OA} , and since a_{OA} does not have a contribution due to electric quadrupole

interactions, Δn in eq. (3) does not include electric quadrupolar contributions, though they are of the same order of perturbation as the magnetic dipolar terms [8,6]. For the organic liquid of limonene with an enantiomeric purity of 100% and for ordinary magnetic fields, such as $B = 1.3$ kG, one expects a difference of refractive index, $\Delta n = 2 \times 10^{-11}$ at a wavelength $\lambda = 470$ nm and at room temperature. It corresponds to a difference in phase, $\Delta\phi = k \Delta n L = 2.6 \times 10^{-6}$ rad for an interaction length $L = 1$ cm. Experimentally the challenge was to measure this tiny phase-difference accurately and reliably.

3. Experimental set-up and results

In order to detect the phase difference, the magnetic optical activity, i.e., the Faraday effect, and the natural optical activity had to be carefully compensated to zero. An active interferometer in the form of a ring laser was specially designed to detect the magneto-chiral birefringence of an intracavity sample. The active medium consisted of a commercial dc-excited discharge tube filled with argon gas (transition at $\lambda = 488$ nm). The quartz Brewster windows closing the discharge tube imposed linear polarization of light, canceling any possible polarization-induced non-reciprocal systematic effects. Two curved mirrors (radius of curvature 6 m) and two plane mirrors formed the ring cavity whose perimeter was servo-controlled by locking a resonance frequency of the cavity to the optical frequency of a stabilized 633 nm He-Ne laser beam injected inside the cavity. An étalon ensured a single longitudinal mode for the two counter-propagating – clockwise (cw) and counterclockwise (ccw) – waves at frequencies ν_{cw} and ν_{ccw} , respectively. Two identical fused silica cells of length $L = 1$ cm were inserted inside the cavity, one cell filled with one chiral species and the other one with its enantiomer. The use of the cw and ccw traveling waves of a ring laser ensured that the two beams shared the same path, thus avoiding beam alignment problems. The use of paired cells canceled out the influence of natural and magnetic optical activities. After traveling through the opposite-chirality samples in the two cells, the cw and ccw waves did not experience any net rotation of the plane of polarization due to natural optical activity. Two identical Ni-Fe-B permanent magnets were set in front of the two cells. They induced opposite longitudinal magnetic fields in the optical paths inside the cells. Therefore, the magnetic optical activity, or Faraday rotation, was also canceled after propagation through the two cells. However, the contributions of the magneto-chiral effects of the two cells to the overall non-reciprocity added up.

The difference in the refractive index Δn experienced by the two counter-propagating waves inside the samples resulted in a difference in their oscillation frequencies. To measure the beat-note frequency $\nu_{cw} - \nu_{ccw}$, the output beams were recombined and sent to a photodiode. The flow of the ionized gas towards the cathode inside the tube induced a relatively large Fresnel drag-type optical bias, $\Delta\nu_0 = 30$ kHz. This large bias was located well outside the lock-in region of the laser gyro, allowed one to measure easily the few hundred Hz variations of the beat-note frequency expected for intracavity magneto-chiral birefringence, and placed the measurement at frequencies higher than most of the technical noises of the experiment. Variations smaller than 100 Hz over one minute were actually measured.

An independent calibration of the interferometer was carried out by setting the entire apparatus in a rocking motion and then matching the resultant beat-note frequency with that expected from the Sagnac effect in the ring cavity [14].

In the sample of pure limonene, the change in refractive index Δn was measured to be $(10 \pm 1.6) \times 10^{-11}$ at 488 nm with a magnetic field of 1.3 kG. This value is in agreement with earlier theoretical predictions [6] based on the contribution of magnetic dipole interactions to Δn . For the second sample of an amino-acid proline (5.4 M in H₂O; pH = 7.4; $T = 21^\circ\text{C}$), the experimental value was $\Delta n = (6.5 \pm 1.4) \times 10^{-11}$, which was again in agreement with the rough theoretical estimate from [6].

4. Summary

Through the example of observation of magnetochiral birefringence, the effectiveness of the method of active interferometry in precision measurement of phase has been highlighted. The observed new magnitudes of this fundamental effect should stimulate further theoretical studies of magnetochiral anisotropies. Magnetochiral interaction is important in chemistry and biology for its potential implications in symmetry breaking between left- and right-handed biomolecules. It is worth noting that parity violation in chiral systems has recently been investigated by high-resolution laser spectroscopy [15] and Mössbauer spectroscopy [16].

It is expected that when light of arbitrary polarization interacts with a chiral polarizable medium, a static magnetic field will be induced. Existence of this *inverse* magnetochiral birefringence, which is again independent of the state of polarization of the incident radiation and changes sign with enantiomers, is yet to be experimentally confirmed.

The study of nonlinear optics with chiral molecules is now well on its way. The second-order process of surface second-harmonic generation is a very sensitive probe of the chirality of molecules deposited on a substrate and thus brings out the role of the electric and magnetic dipolar contributions in the field-matter interactions [17]. It will be interesting to explore the third-order nonlinear response in chiral molecules introducing nonlocal effects with magnetic-dipolar or electric-quadrupolar terms in the field-matter interaction Hamiltonian, and some studies on third-order circular dichroism have already been reported in the literature [18].

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