

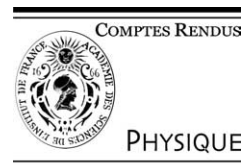


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Experimental evidence of magneto-chiral interaction in Pasteur's tartrates

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Abstract

We have isolated the magneto-chiral refraction in Pasteur's tartrates and deduced the associated magneto-chiral absorption. The presence of a strong peak at 235 nm in the magneto-chiral absorption spectrum of tartrates shows that Pasteur's first attempt to induce chirality with a magnetic field could perhaps have succeeded, provided that a UV source was simultaneously used. **To cite this article:** T. Ruchon et al., C. R. Physique 5 (2004).

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Résumé

Démonstration expérimentale de l'existence de l'interaction magnéto-chirale dans les tartrates de Pasteur. Nous avons isolé l'interaction magnéto-chirale en réfraction dans les tartrates étudiés par Pasteur, et en avons déduit l'absorption magnéto-chirale. La présence d'un pic important à 235 nm dans le spectre d'absorption magnéto-chirale montre que les tentatives de Pasteur pour induire de la chiralité à partir d'un champ magnétique auraient peut-être pu aboutir s'il avait utilisé simultanément une source UV. **Pour citer cet article :** T. Ruchon et al., C. R. Physique 5 (2004).

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Mots-clés : Tartrates de Pasteur ; Interaction magnéto-chirale ; Absorption magnéto-chirale

1. Introduction

About 150 years ago, Pasteur discovered that the chemistry of life shows a preference for molecules with a particular handedness [1,2]. He then tried to carry out experiments aimed at the discovery of an asymmetric physical force that could account for the origin of biological homochirality [3]. In particular, he attempted to induce handedness: (i) by performing reactions in a centrifuge; and (ii) by growing his famous tartrate crystals in a magnetic field. Both attempts failed. Curiously, concerning Pasteur's first attempt, it has been recently shown that by stirring solutions of achiral porphyrins, one can induce

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chiral symmetry breaking in the resulting mesophases [4]. Regarding the second attempt, all the attempts using only magnetic fields have given rise to unsuccessful tests and controversies [5]. Indeed, as stated by Kelvin [6], who introduced the word chirality into science, “the magnetic rotation alone has neither left-handed nor right-handed quality”. Lately, de Gennes has demonstrated that even the superposition of a magnetic field and an electric field suggested by Curie [7] does not allow asymmetrical reactions, unless maybe if the final state is not at thermodynamic equilibrium [8]. Nonetheless, it was predicted twenty years ago that light would be absorbed slightly differently by chiral molecules if the beam travels parallel or antiparallel to an applied magnetic field [9]. The application of symmetry arguments to the hyperpolarizability tensors shows that this fundamental interaction, christened ‘magneto-chiral dichroism’: (i) is supported only by chiral molecules; (ii) occurs for either unpolarized or polarized light [10]. This effect has been recently observed and has been used to preferentially photo-destroy one of the two enantiomers of a racemic medium [11], without using any circularly-polarized light [5]. Furthermore, the corresponding magneto-chiral birefringence, which was predicted for molecules in the late seventies [12], has also recently been observed in both passive and active interferometers [13,14]. This effect consists of a difference Δn between the refractive indices experienced by two counterpropagating waves upon propagation through a chiral medium subjected to a static longitudinal magnetic field. For liquids exhibiting fairly large optical activity, such as for example pure limonene or proline (4 M in H_2O), the difference Δn was shown to be in the range of 10^{-10} [14]. The sensitivity and the precision of the Sagnac-type active laser thus allows us to wonder if any magneto-chiral effect really exists in Pasteur’s tartrates.

2. The experimental setup and results

Our experimental setup, similar to that used in [14], is briefly schematized in Fig. 1. It consists of an *active* interferometer based on a home-made monomode ring laser. The cavity is made of four mirrors M_i ($i = 1, \dots, 4$). A discharge tube provides gain at the wavelength $\lambda = 488$ nm on the Ar^+ laser transition. The quartz windows closing the discharge tube impose linear polarization of light inside the cavity. The magneto-chiral birefringence of intracavity samples is deduced from the beat note $\Delta\nu = \nu_{cw} - \nu_{ccw}$ between the two frequencies of the clockwise (cw) and counterclockwise (ccw) counterpropagating oscillating waves probing the samples. Here, in order to increase the sensitivity, we have lowered the technical noises by improving the mechanical stability, by isolating the experiment from acoustic vibrations, and by circumventing thermal drifts. It then allows us to average successive measurements (up to fifteen) and to expect a sensitivity on Δn better than 10^{-12} . The flow of the ionized gas inside the tube induces a Fresnel drag-type optical bias ν_0 between the cw and ccw propagating beams. ν_0 is equal to 30 kHz. The beat frequency $\Delta\nu$ is used as a differential probe of small Sagnac-type effects like the expected magneto-chiral birefringence of the tartrates. Let us insert two paired 1 cm-long cells, each containing one tartrate enantiomer, inside the ring cavity. The solutions consist in saturated solutions of calcium tartrates (5.7 M in H_2O). The cells are submitted to opposite magnetic fields B . It follows that, after having travelled through both cells, the two counterpropagating waves experience no rotation of the plane of polarization due to natural and magnetic optical activity. Shielding the discharge tube from external magnetic fields with a mumetal plate avoids any magnetically-induced variations of ν_0 . We have experimentally checked that the beat frequency

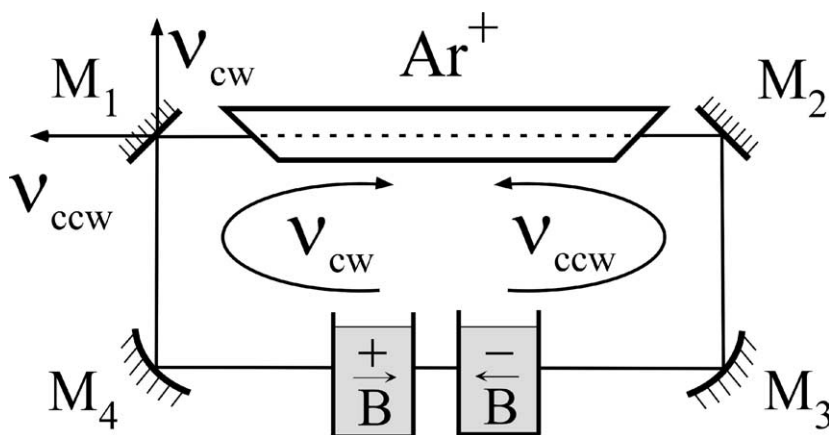


Fig. 1. Scheme of the Ar^+ ring laser interferometer. Two counter-oscillating waves at frequencies ν_{ccw} and ν_{cw} probe the intracavity cells filled with D-(+) and L-(-) calcium tartrates. Two permanent magnets induce opposite magnetic fields of amplitude B inside the cells.

Fig. 1. Principe de l'interféromètre laser en anneau à Ar^+ . Deux ondes contrapropagatives de fréquences ν_{ccw} et ν_{cw} sondent les cellules intracavitaires remplies de tartrates de calcium D-(+) et L-(-). Deux aimants permanents induisent des champs magnétiques opposés d'amplitude B dans les cellules.

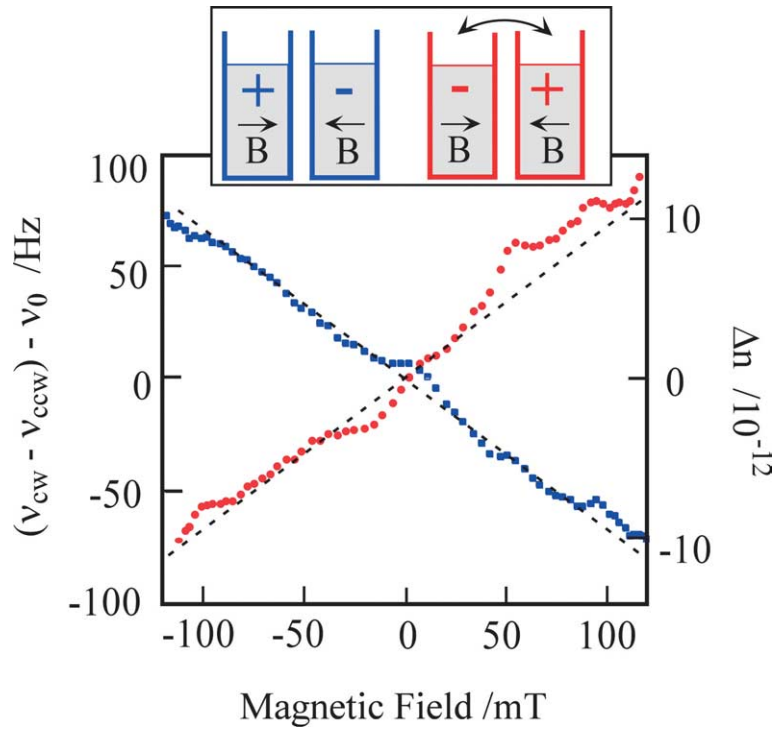


Fig. 2. Magneto-chiral birefringence of calcium tartrates as function of the longitudinal magnetic field. Dots: experimental values, dashed lines: linear fits. The interchange of the liquids leads to the reversed sign for the magneto-chiral birefringence as expected by the theory. The difference of indices for calcium tartrate (5.7 M in H₂O) are in the range of 10⁻¹¹.

Fig. 2. Biréfringence magnéto-chirale du tartrate de calcium en fonction du champ magnétique longitudinal. Points : valeurs expérimentales, lignes pointillées : régressions linéaires. Le signal change de signe quand on permute les deux liquides, en accord avec la théorie. La différence des indices pour les solutions de tartrate de calcium (5.7 M in H₂O) est dans la gamme des 10⁻¹¹.

does not vary as a function of B when both cells are filled with achiral liquids. The Faraday rotation value is measured to be 35' for each 1 cm long cell submitted to a longitudinal magnetic field B of 130 mT, and the optical activity is measured to be 1.7 degrees for 1 cm. With these values, one may expect a signal of the order of 10⁻¹¹ [12], that is roughly ten times smaller than the one measured previously for studied molecules [14]. Symmetry arguments indicate that Δn is proportional to the scalar product **B** · **k**, where **k** is the wavevector of unpolarized or polarized light. The results are shown in Fig. 2. A linear fit of the data leads to Δn = 10⁻¹⁰ T⁻¹ with a correlation coefficient greater than 0.99. This corresponds to an error of ±30 Hz/T on Δν and ±5 × 10⁻¹² T⁻¹ on Δn. These results are typical of diamagnetic molecules with the expected small values for the magneto-chiral birefringences. Interchanging the liquid samples in the cells leads to the opposite sign, in agreement with the fact that Δn is proportional to the enantiomeric purity C of the sample. C is equal to +1 (respectively -1) for pure (D-(+)) (respectively pure (L-(-)) tartrate and C is equal to zero for a racemic mixture. Furthermore, at 488 nm, the absorption can be neglected, thus circumventing any cascade mechanisms due to residual absorption that otherwise could alter the results [12]. So, the magneto-chiral birefringence is thus really observable in Pasteur's tartrates.

Since the magneto-chiral interaction exists in refraction in Pasteur's tartrates, one expects the effect necessarily to occur also in absorption. It corresponds to the term proportional to the scalar product **B** · **k** in the imaginary part of the optical index. We first estimate the size of the absorption effect. We define the absorptive magneto-chiral factor A_{MC} as

$$A_{MC} = 2 \frac{\alpha_D(\mathbf{B} \uparrow \uparrow \mathbf{k}) - \alpha_L(\mathbf{B} \uparrow \uparrow \mathbf{k})}{\alpha_D(\mathbf{B} \uparrow \uparrow \mathbf{k}) + \alpha_L(\mathbf{B} \uparrow \uparrow \mathbf{k})} \tag{1}$$

α is the optical extinction coefficient. D and L refer to D-tartrates and L-tartrates respectively. Here, **B** ↑ ↑ **k** denotes parallel vectors. For antiparallel vectors, one gets A_{MC}(**B** ↑ ↓ **k**) = -A_{MC}(**B** ↑ ↑ **k**). From the standard Becquerel model, extended to treat the magneto-chiral interaction, one finds that

$$A_{MC} = \frac{|e|B}{2\pi mc\alpha_M} \frac{\partial(\lambda^2 \Delta\alpha_M)}{\partial\lambda} \tag{2}$$

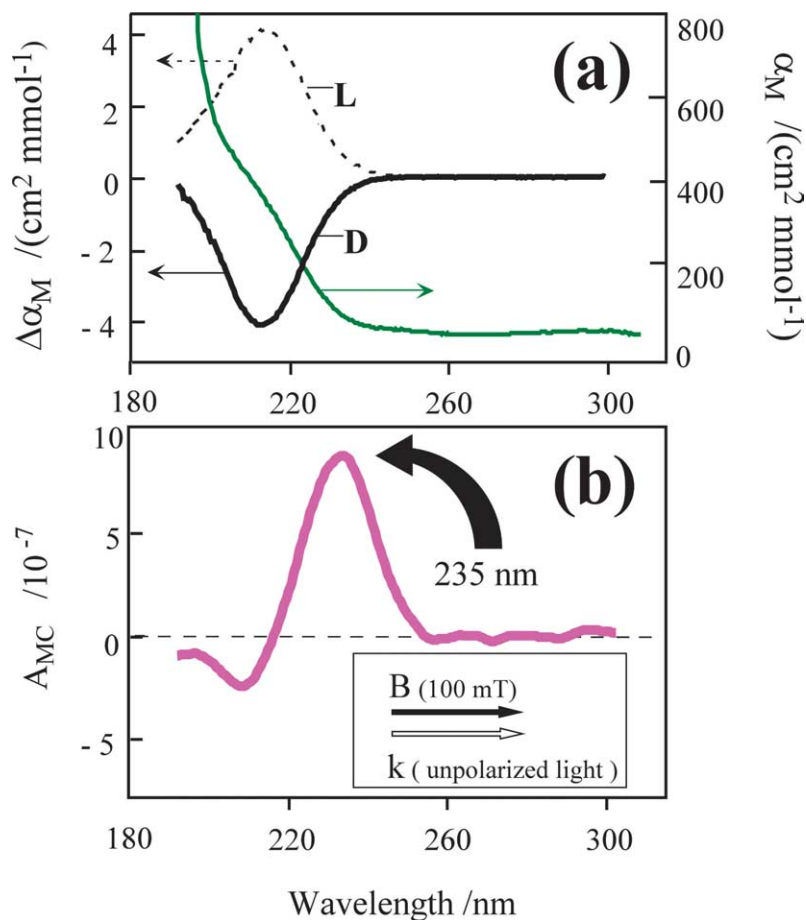


Fig. 3. (a) UV absorption spectrum α_M (green line) and circular dichroism spectrum $\Delta\alpha_M$ for calcium tartrate solutions (1.3×10^{-4} M in H_2O). Solid line: D-tartrate, dashed line: L-tartrate. (b) Deduced value of the absorptive magnetochiral anisotropy factor in tartrates for $B = 100$ mT and for \mathbf{B} and \mathbf{k} vectors parallel.

Fig. 3. (a) Coefficient d'extinction molaire α_M (vert) et de dichroïsme circulaire molaire $\Delta\alpha_M$ de solutions de tartrates de calcium (1.3×10^{-4} M in H_2O). Ligne pleine : D-tartrate, ligne pointillée : L-tartrate. (b) Valeur déduite de l'anisotropie magnétochirale en absorption dans les tartrates pour $B = 100$ mT et pour \mathbf{B} et \mathbf{k} parallèles.

where c is the speed of light, m and e are the mass and the charge of an electron. The molar extinction coefficient α_M and the molar circular dichroism $\Delta\alpha_M$ are recorded with a spectrometer and a circular dichroism spectropolarimeter respectively, both being purged with nitrogen [15]. Fig. 3(a) shows the tartrate's deep-UV spectra. The circular dichroism spectrum is seen to possess a maximum in the region of about 210 nm due to the $n-\pi^*$ transition in the carboxylic group [16]. Based on this data and using Eq. (2), we calculate the absorptive magnetochiral factor for the tartrate, assuming a magnetic field $B = 100$ mT. We find that A_{MC} presents a pronounced peak at 235 nm, as shown on Fig. 3(b). It corresponds to $A_{MC} = 8 \times 10^{-7}$. This peak could potentially enable one to induce selective nucleation of tartrate solutions with natural light in the presence of magnetic field. Pasteur's first attempt to induce chirality with a magnetic field could thus have succeeded, provided that a light source was simultaneously used.

3. Conclusion

In conclusion, we have demonstrated that a magnetochiral interaction occurs in refraction in tartrate and have deduced the existence of the associate effect in absorption. Curiously, because of the strong peak at 235 nm, the tartrates, which have played such a key role in the historical development of this field, appear to be particularly good candidates for observing light-assisted magnetically controlled chirality.

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