

Experimental Evidence of Third-Order Nonlinear Dichroism in a Liquid of Chiral Molecules

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We present experimental evidence of the existence of a nonlinear circular dichroism in a liquid of chiral molecules. This effect is demonstrated by a light-induced circular dichroism on two enantiomeric RuTB [ruthenium(II) tris(bipyridyl)] samples after a careful analysis of the impact of the third-order nonlinear response on the optical activity of the system. These experimental results are in good agreement with a previous theoretical investigation.

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Chiral molecules, which exist under two mirror-image enantiomeric forms, play a very important role in most biochemical processes, and the physicochemistry of such molecules is the subject of many theoretical and experimental investigations. Among them, optics has always had a prevalent position, as optical rotation and circular dichroism (difference of absorption of left or right circularly polarized light: CD) are well known to be sensitive probes of chirality. On the other hand, nonlinear optics has appeared only for a few years in the investigation of chiral molecules. Nonlinear optics can provide a lot of information due to the higher number of parameters accessible in such experiments compared to linear optics, and this has been successfully demonstrated in second-order experiments: surface second harmonic generation has proved to be a very sensitive probe of the chirality of molecules deposited on a substrate and to bring valuable information such as the role of the electric and magnetic dipolar contributions in the electromagnetic interactions [1–3]. Third-order effects have, however, not been used to the same extent. Intensity-dependent optical rotation has been predicted [4,5] and experimentally observed [6,7]. However, optical rotation is not very selective and CD is usually preferred to obtain information about the molecular structures. Third-order effects in the CD have never been studied. A few attempts to measure time-resolved circular dichroism spectra have been shown to give information about the excited states of the molecules [8,9], but these experiments, carried out with intense lasers which excite almost all the molecules, are very far from the third-order perturbative approach we are interested in. In a recent paper [10], we investigated theoretically the third-order nonlinear response of a liquid of chiral molecules and, introducing nonlocal effects such as magnetic-dipolar or electric-quadrupolar terms in the field-matter interaction Hamiltonian, we demonstrated that one expects to observe a chirality-related nonlinear response which describes a change of the CD induced by the light [nonlinear circular dichroism (NLCD)]. Furthermore, utilizing model two- or three-level systems, we were able to compare such NLCD to the (nonchiral) absorption saturation effect.

In this Letter, we want to bring experimental evidence of NLCD. The simplest manifestation of this effect is obtained in a one-beam experiment: monitoring the transmission and the circular dichroism of a nonracemic sample as a function of the intensity of the light beam, one expects to observe a change in the circular dichroism, as well as in the absorption. At this order of perturbation, one can describe the evolution of the intensity I along the z direction by

$$\frac{\partial I}{\partial z} = -(\alpha + \beta I)I, \quad (1)$$

where α is the linear absorption and β accounts for the nonlinear response. This formulation allows a direct comparison with [10] as αI and βI^2 correspond to the linear and nonlinear energy transfers between the molecules and the light. In the case of chiral molecules, both the linear and nonlinear absorptions are expected to be different for left and right circularly polarized light and we write

$$\alpha = \alpha_0 \pm \Delta\alpha, \quad (2)$$

$$\beta = \beta_0 \pm \Delta\beta, \quad (3)$$

the “plus” (“minus”) sign corresponding to the left (right) polarization. $\Delta\alpha$ is directly related to the CD and $\Delta\beta$ corresponds to the NLCD, i.e., to the change of β with the handedness of the light polarization. It is this quantity that we want to evidence experimentally.

The experiment is carried out with a ruthenium(II) tris(bipyridyl) salt (RuTB) under its two pure enantiomeric (Δ and Λ) forms. This molecule has been thoroughly studied and presents an absorption band in the 400–500 nm range corresponding to a metal-ligand charge transfer transition which displays a clear and strong CD structure (Fig. 1). Furthermore, the excited state is known to be long lived (600 ns [11]), without noticeable absorption [12] or CD [13] and our experimental results on the absorption saturation confirm that the excited state is well behaved, without any intraband relaxation or transfer. RuTB is therefore quite close to an ideal molecule featuring a unique optical transition with optical activity when probed in the visible. To benefit from this without

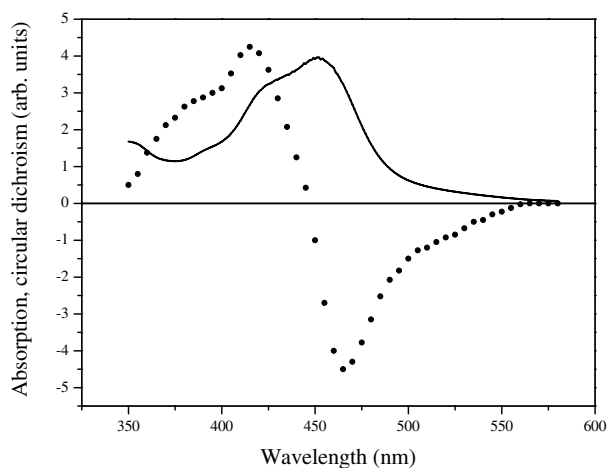


FIG. 1. Absorption and circular dichroism spectra (in arbitrary units) of the Δ -RuTB samples.

any interference from upper-lying transitions, we choose to study nonlinear absorption and CD at the wavelength of 470 nm where the CD amplitude is maximum. We use a solution ($1.7 \times 10^{-3} M$) in ethanol for both enantiomers corresponding to an absorption coefficient of $\alpha L = 5.6$. In order to have noticeable effects and to avoid thermal problems, we use a 3 mm thick circulating cell. The light source consists of 180 fs pulses at a repetition rate of 1 kHz. The maximum pulse energy is less than 1 μJ , ensuring that no thermal effects can affect the experiments. This light source is derived from an amplified Ti:sapphire laser utilizing several steps of optical parametric amplification. To access the CD, the light polarization is modulated from left to right circular by a transverse Pockels cell. A quarter-wave voltage (± 410 V at 470 nm) is applied at 80 Hz, allowing us to use lock-in detection techniques. The measurement setup is twofold. First, a photomultiplier tube measures the transmission of the light through the cell. This directly gives the saturation of the absorption, independently of any chirality-related effect. This signal is then sent to a lock-in amplifier which measures the modulated part of the signal. From both signals, one can deduce the CD.

It is essential for all these CD measurements that the circular polarizations be well controlled. Extreme care is brought to this point throughout the experimental procedure. After alignment and adjustment of the voltage, the Pockels cell is equivalent to a $\lambda/4$ plate to within 4% with a high degree of symmetry between the positive and negative voltages. The focusing lens (focal length = 250 mm) as well as the cell or the filters are carefully aligned so as to preserve the state of polarization. The cell is a homemade, strain-free one to minimize birefringence problems and all the measurements are carried out with the same one. To check the whole setup, we perform the experiment with a racemic mixture of our molecules in which case no noticeable signal can be measured with the lock-in amplifier.

When increasing the intensity of the laser, spurious effects can appear due to induced birefringence or op-

tical artifacts. They have been thoroughly studied for pump-probe experiments in Refs. [14,15]. However, in a one-beam experiment, such effects can be ruled out for different reasons. First of all, a careful investigation of the tensor properties shows that all these effects are the same for left or right circularly polarized beams and should not appear when measuring the CD [16]. On the other hand, we have checked experimentally that no modulated signal exists for the racemic mixture, even at high intensity and, as a further proof, we will see that the results have opposite signs for the two enantiomers, revealing confidently their chiral origin.

Prior to the intensity-dependent CD investigation, it is worthwhile checking that the nonlinear effects we induce in the liquid are not too strong and can be described in terms of third-order effects. This is easily checked by plotting the normalized transmittance of the sample as a function of the pulse energy (Fig. 2): this gives a straight line as expected. Deviation from this linear dependence occurs only for pulse energies larger than 1 μJ . These numbers are consistent with the known absorption cross section of RuTB (5.4×10^{-17} cm²) and the molecule density.

Resolution of Eq. (1) for a Gaussian beam can be found in [17] and yields for the normalized transmittance

$$\frac{T}{T_0} = 1 - r \frac{\beta_0}{\alpha_0} I, \quad (4)$$

where the coefficient r takes the geometrical and reflectivity factors into account. Note that for our samples, we observe a saturation of the absorption which corresponds to a negative β . To access the intensity-dependent CD, one must calculate the ratio of the lock-in amplifier output and of the photomultiplier tube one, after properly taking into account the calibration factor of the lock-in amplifier (1.1 for a square modulated signal). Deriving the expressions of these outputs from Eq. (4) and defining

$$\frac{\Delta\beta}{\beta_0} = K \frac{\Delta\alpha}{\alpha_0}, \quad (5)$$

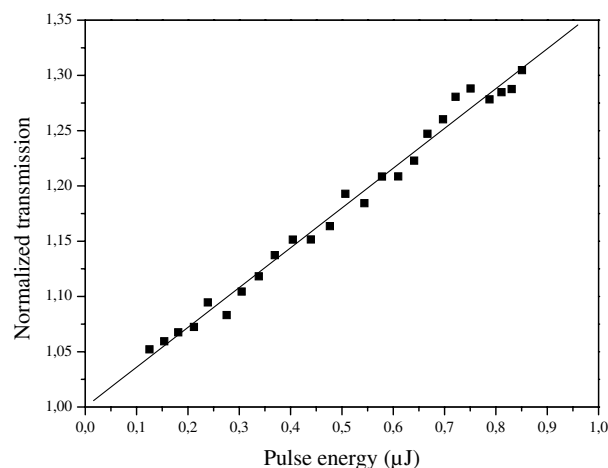


FIG. 2. Normalized transmission as a function of the pulse energy.

one can express the intensity-dependent $CD(I)$ as a function of the low intensity CD :

$$CD(I) = CD \left[1 - r \frac{\beta_0}{\alpha_0} I \frac{1 - K}{\alpha_0 L} \right]. \quad (6)$$

This equation deserves some comments. As expected, one gets the linear CD at low intensity and $CD(I)$ is a linear function of I for not too large intensities. This intensity dependence is, however, not a proof of the existence of NLCD. Indeed, one can see that, if $K = 0$, i.e., without NLCD, the signal nonetheless varies with the laser intensity. Indeed, the saturation effect scales as β/α [see Eq. (4)]. With α being different for the two circular polarizations, the saturation is also different, yielding an intensity-dependent signal, even if β does not change with the light handedness. Observation of an intensity-dependent signal is therefore not sufficient to ascertain the existence of NLCD. However, in the case of NLCD, the factor K is expected to be positive and larger than 1 (see below [10]) which means that there is a change in the sign of the slope of $CD(I)$. In other words, in the absence of NLCD, the absolute value of $CD(I)$ must increase with the intensity, while it must decrease when NLCD is present.

Let us come now to the experimental results. In Fig. 3, we have plotted $CD(I)$ normalized to the linear absorption. If we consider the intensity dependence, it clearly appears that the absolute value of $CD(I)$ decreases with I , indicating the presence of NLCD in our samples. Note that the curves are symmetrical for the two enantiomers, ruling out previously mentioned artifactual results. Interpolating at a null intensity, we get a value of $\pm 7 \times 10^{-4}$ for the two enantiomers corresponding to the usual CD effect. A careful analysis of our polarizations shows that the Δ (Λ) enantiomer absorbs preferentially the right (left) circular light at 470 nm as expected. Let us be more quantitative. Plugging the $r\beta_0/\alpha_0$ value obtained from Fig. 2 in Eq. (6), we obtain from Fig. 3 $K = 4.0 \pm 0.5$, a defi-

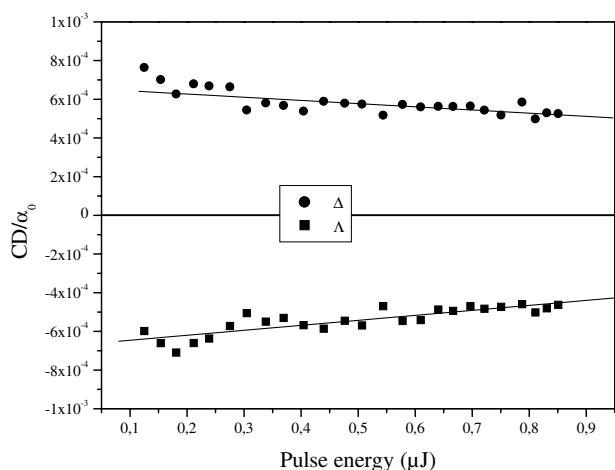


FIG. 3. Circular dichroism normalized to the linear absorption as a function of the pulse energy for the two enantiomers (Δ and Λ).

nately nonzero value. To the best of our knowledge, such a third-order effect in the CD has never been observed.

We can now proceed to a more precise comparison of these results with the theoretical expectations. As already stated, RuTB is close to an ideal chiral molecule with only one optical transition. As a fundamental sum rule forbids a two-level system to be optically active [10], we describe this molecule by a three-level system such as the one depicted in the inset in Fig. 4 where two almost degenerated transitions are involved with opposite optical activities. This description corresponds very well to the excitonic coupling responsible for the chirality of such transition metal complexes. An experimental signature of these two transitions is provided in the CD spectrum: one of the transitions gives the positive part of the curve, whereas the other one gives the negative part. Theoretical calculations have been made for such three-level systems in [10] and it ensues that, as far as the third-order response is concerned, they are mainly equivalent to two independent two-level systems $|0\rangle \rightarrow |\alpha\rangle$ and $|0\rangle \rightarrow |\beta\rangle$. For each two-level system characterized by its frequency detuning Δ between the transition and the photon frequencies, its transition dipole moment μ , its rotational strength R , its lifetime T_1 , and its linewidth Γ , one gets

$$\alpha + \beta I = \frac{4\pi\omega}{3\hbar} \frac{|\mu|^2}{nc} \frac{\Gamma}{\Delta^2 + \Gamma^2} \times \left[1 - \frac{8}{15\hbar^2} \frac{|\mu|^2}{nc} \frac{T_1\Gamma}{\Delta^2 + \Gamma^2} I \right] \quad (7)$$

and

$$\Delta\alpha + \Delta\beta I = \frac{16\pi\omega}{3\hbar} \frac{R}{nc} \frac{\Gamma}{\Delta^2 + \Gamma^2} \times \left[1 - \frac{16}{15\hbar^2} \frac{|\mu|^2}{nc} \frac{T_1\Gamma}{\Delta^2 + \Gamma^2} I \right] \quad (8)$$

from which one immediately obtains

$$K = 2. \quad (9)$$

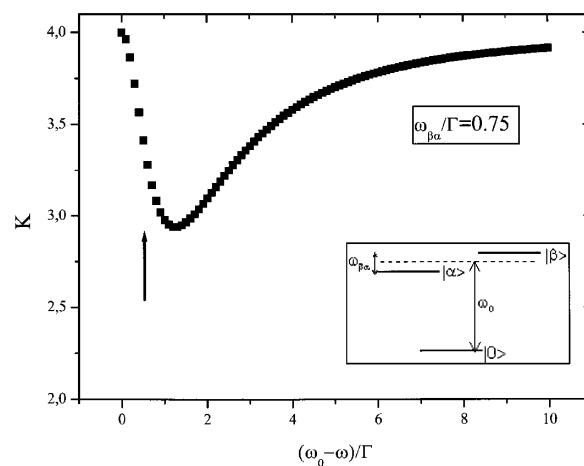


FIG. 4. Parameter K as a function of the laser detuning (see text). Inset: Schematic representation of the three-level system describing a chiral molecule.

For three-level systems, one must take into account the contributions of the two two-level systems which must be added for the absorption and subtracted for the CD. Defining $\Omega = (\omega_0 - \omega)/\Gamma$ and $\delta = \omega_{\beta\alpha}/2\Gamma$ (cf. inset in Fig. 4), one calculates after some algebra

$$K = \frac{4}{1 + \left(\frac{2\delta\Omega}{\Omega^2 + \delta^2 + 1}\right)^2}. \quad (10)$$

A numerical plot of this ratio is displayed in Fig. 4 for $\delta = 0.75$ which is close to the experimental data. The ratio K takes values between 2.9 and 4 and, when $\Omega = \delta$, which corresponds to the experimental case where the photon energy is in exact resonance with one of the transitions (marked by an arrow in Fig. 4), one gets $K = 3.1$. This value is in correct agreement with the experimental value. Perfect agreement should, however, not be sought as a description of the absorption profile in a liquid by Lorentzians may not be very adequate. The main point is nevertheless that for a unique transition K is expected to be around 2, whereas it is expected to be close to 4 when two almost degenerate transitions are considered. We have clear evidence that experimentally the latter case is correct. This sensitivity to the fine structure of the transitions, which is very important as far as chirality is concerned, brings further evidence that the phenomenon we observe is a pure chiroptical effect.

In summary, we have presented in this Letter an experimental evidence of the existence of a nonlinear circular dichroism in a liquid of chiral molecules. This effect is demonstrated by a light-induced CD on two enantiomeric RuTB samples after a careful analysis of the impact of the nonlinear response on the chiral response of the system. These experimental results are in good agreement with a previous theoretical investigation about NLCD [10]. In particular, the measured ratio K , close to 4, shows that such experiments are very sensitive to the fine structure of the transitions, revealing the nonlocal character of the interactions taking place in these processes. Further experiments aiming at studying the frequency dependence of the ratio K are expected to sharpen this analysis. As a conclusion, let us point out that this feature allows one to separate chirality-related phenomena from others and that utilization of such light-induced phenomena in pump-probe ex-

periments should lead to a new valuable technique to study the dynamics of chirality-related processes.

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