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**Nonlinear optical activity in chiral molecules:
surface second harmonic generation
and nonlinear circular dichroism**

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Abstract Nonlinear optical activity in chiral molecules is investigated. We first examine the importance of the nonlocality of the light–matter interaction in optical activity and extend this concept to second-order (surface second harmonic generation) and third-order (nonlinear circular dichroism) nonlinear optical phenomena. Microscopic models are also discussed. Various phenomena derived from these considerations are demonstrated experimentally with specially-synthesized chiral molecules. *To cite this article: F. Hache et al., C. R. Physique 3 (2002) 429–437.* © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

chiral molecules / nonlinear optical activity

**Activité optique non linéaire des molécules chirales : génération de
second harmonique en surface et dichroïsme circulaire non linéaire**

Résumé Nous analysons en détail l'activité optique non linéaire des molécules chirales. La non-localité de l'interaction lumière–matière qui est à l'origine de l'activité optique est étendue aux effets d'optique non linéaire du second ordre (génération de second harmonique en surface) et du troisième ordre (dichroïsme circulaire non linéaire). Nous discutons également des modélisations microscopiques de l'activité optique. Différents phénomènes qui découlent de ces considérations sont ensuite démontrés expérimentalement sur des molécules chirales spécialement synthétisées. *Pour citer cet article : F. Hache et al., C. R. Physique 3 (2002) 429–437.* © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

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1. Introduction

Chiral molecules, which exist under two non-mirror-symmetrical forms (called ‘enantiomers’), are of paramount importance in biology and chemistry, as most of the molecules in living organisms are chiral and exist preferentially under a definite enantiomer. Despite their huge similarity, the two enantiomers can have radically different properties when involved in a biochemical reaction. This explains the interest of a great deal of scientists for this intriguing molecular feature. Physicists have studied these chiral molecules for a long time, and among the physical techniques, optical properties have always been of paramount importance. These properties, cast under the generic name of ‘natural optical activity’ have been known for over a century [1,2]. They are two-fold: the rotation of the polarization of a linearly-polarized light going through an enantiomerically-pure solution and the circular dichroism (CD), which consists in a difference in absorption depending on the handedness of the (circular) polarization of the light. On the other hand, nonlinear optics, which is known to bring a host of new phenomena inducing new investigative techniques, have not been much considered for chiral molecules. In this paper, we present several aspects of this ‘nonlinear optical activity’. In Section 2, we introduce the concept of ‘nonlocality’ in the light–matter interaction which is fundamental to the understanding of the origin of the optical activity and then discuss the extension of nonlocality towards nonlinear optics. Second- and third-order effects, which give rise to very different effects, are analyzed in detail. Model calculations describing the linear and nonlinear optical activity of chiral molecules are also introduced. Sections 3 and 4 are then devoted to a few experimental evidences of this nonlinear optical activity, illustrating the potentiality of these techniques to get new ways of investigation of the chemical physics of chiral molecules.

2. Nonlinear optical activity

2.1. Generalities – linear response

The difference between two enantiomers of a given chiral molecule clearly lies in the spatial arrangement of the atoms in the molecule. Optical activity, which is the signature of this difference, must also rely on this feature. One therefore understands that the so-called electric-dipolar approximation, most often utilized in the description of the light–matter interaction, is not sufficient to account for the optical activity. Indeed, in this approximation, the electromagnetic field of the light is spatially uniform over all the extension of the molecule. It seems to be justified as soon as the molecule under study is small compared to the wavelength. However, it clearly does not allow one to distinguish between two mirror-symmetrical arrangements of the atoms in the molecule and thus to describe the optical activity. It is therefore necessary to overcome this approximation when one deals with chiral molecules – explaining why the optical activity is so weak in most samples. As a result, one must consider that the light is a propagating wave and that the electromagnetic field is not exactly the same for all the atoms of the molecule. This feature can be traced back to the nonlocality of the light–matter interaction, which expresses the fact that the response at one point of the molecule not only depends on the electromagnetic field at this same point, but is influenced by the field all around it [3]. A simple way to account for this nonlocality to first order is to use the multipolar expansion and to introduce the magnetic dipolar and the electric quadrupolar terms beside the usual electric dipolar one. The light–matter interaction Hamiltonian thus can be written:

$$H_{\text{int}} = -\mathbf{P} \cdot \mathbf{E} - \mathbf{M} \cdot \mathbf{B} - \mathbf{Q} : \nabla \mathbf{E} \quad (1)$$

where \mathbf{P} , \mathbf{M} , \mathbf{Q} are the electric polarization, the magnetization and the electric quadrupolarization, respectively. Nonlocality appears in the occurrence of the magnetic field and of the gradient of the electric field. To describe the interaction of light with an ensemble of molecules, one must introduce its polarization, defined as the average density of the light induced-dipole moments. This polarization allows one to get all the relevant information such as the index of refraction or the absorption of the sample. Introduction

of the nonlocality at this stage implies that one considers not only the electric dipolar effects, but also the magnetic dipolar and the electric quadrupolar effects. This introduction is two-fold: one must consider three contributions \mathbf{P} , \mathbf{M} , \mathbf{Q} , but one must also consider the magnetic and electric field gradient contributions to the electric polarization. Other contributions (such as the effect of the magnetic field on the magnetization) are of higher order in the multipole expansion and are neglected. It is possible to cast all these contributions in a reduced number of components by working with the effective polarization [4]:

$$\mathbf{P}_{\text{eff}} = \mathbf{P} + \frac{i}{\omega} \nabla \times \mathbf{M} - \nabla \cdot \mathbf{Q}, \quad (2)$$

and introducing the ‘local’ and ‘nonlocal’ susceptibility tensors. For the linear response, one has:

$$\mathbf{P}_{\text{eff}}^{(1)} = \varepsilon_0 \chi^{(1)ee} \mathbf{E} + \varepsilon_0 \chi^{(1)e\nabla e} \nabla \mathbf{E}, \quad (3)$$

where the local susceptibility $\chi^{(1)ee}$ is a rank-2 tensor whereas the nonlocal one $\chi^{(1)e\nabla e}$ is a rank-3 tensor. The antisymmetric part of this latter leads to magnetic dipolar effects and symmetric part to electric quadrupolar ones. Such an expression will be extended to the optical nonlinear response later on. The rank of the tensor is very important to sort out the symmetry properties. For example, considering the linear response of an isotropic liquid, the rank-3 tensors vanish unless the medium is non centrosymmetric. We recover the fact that only liquids of *chiral* molecules, which are intrinsically non centrosymmetric, display optical activity. Note, however, that in crystals, one can have optical activity even for achiral molecules if the crystal is not centrosymmetric [3].

2.2. Second-order nonlinear response

Let us proceed now to second-order nonlinear optics and consider the second harmonic generation (SHG) from a fundamental beam at ω . The relevant nonlinear polarization can be expressed:

$$\mathbf{P}_{\text{eff}}^{(2)}(2\omega) = \varepsilon_0 \chi^{(2)eee} \mathbf{E}(\omega) \mathbf{E}(\omega) + \varepsilon_0 \chi^{(2)ee\nabla e} \mathbf{E}(\omega) \nabla \mathbf{E}(\omega). \quad (4)$$

The rank of the local tensor is now 3 whereas the nonlocal one is 4. One therefore sees that the symmetry rules will be reversed compared to the linear case: in an isotropic liquid, the local terms only exist for chiral molecules whereas the nonlocal ones always contribute. Electric contribution to SHG therefore only exist in principle for a liquid of chiral molecules. However, the degeneracy of the frequencies precludes such effect and one can show that only nondegenerate sum frequency is possible in such a liquid [5]. Experimental demonstration have been given recently [6].

Second-order nonlinear optics is in fact much more powerful when working with surface SHG [7,8]. This experiment consists in sending a fundamental beam on a layer of molecules deposited on a substrate or on top of a liquid and to measure the reflected harmonic beam. Such a technique has been widely utilized in the past for nonchiral samples [9]. For a few years, application of this technique to chiral molecules has proved to be very instructive [7,8]. In such an experiment, the symmetry of the sample is C_∞ , in which case both local and nonlocal tensors have nonzero components for chiral as well as achiral samples. This intricacy of all the susceptibility components is fortunately lifted when one plays around with the polarizations of the fundamental and harmonic beams, as explained now.

Polarizations of the light beams can be decomposed in s or p , depending on the orientation of the electric field compared to the surface under study. Introducing six new coefficients, we can write the generated second harmonic electric field as a function of the incoming fundamental one as [8]

$$E_{s,p}(2\omega) = f_{s,p} E_p^2(\omega) + g_{s,p} E_s^2(\omega) + h_{s,p} E_p(\omega) E_s(\omega). \quad (5)$$

This expansion has the advantage that it separates the chiral and the achiral contributions: f_p , g_p and h_s only involve achiral components whereas f_s , g_s and h_p only chiral ones. On the other hand, each coefficient mixes local and nonlocal contributions. However, due to the presence of a magnetic dipole or an electric quadrupole moment transition instead of an electric dipole one in the expression of the nonlocal susceptibilities, local and nonlocal contributions experience a phase difference of $\pi/2$. Measuring the above coefficients and their relative phase therefore allows to separate the *achiral/chiral* components as well as the *local/nonlocal* ones. Such experiments are presented in Section 3. In connection with the model calculation to be presented next, they have proved to be a very sensitive probe of the microscopic origin of the optical activity in chiral molecules.

2.3. Third-order nonlinear response

We can extend the formalism to third-order nonlinear optics. We will be interested here only in the optical Kerr effect in an isotropic liquid as it gives birth to new spectroscopic techniques. In particular, it includes the pump-probe experiments where a first intense beam (ω_2) excites a sample which is probed by a second weak beam (ω_1). The effective polarization describing such effect is

$$\begin{aligned} P_{\text{eff}}^{(3)}(\omega_1) = & \varepsilon_0 \chi^{(3)eeee} \mathbf{E}(\omega_1) \mathbf{E}^*(\omega_2) \mathbf{E}(\omega_2) + \varepsilon_0 \chi^{(3)eee\nabla e} \mathbf{E}(\omega_1) \mathbf{E}^*(\omega_2) \nabla \mathbf{E}(\omega_2) \\ & + \varepsilon_0 \chi^{(3)ee\nabla ee} \mathbf{E}(\omega_1) \nabla \mathbf{E}^*(\omega_2) \mathbf{E}(\omega_2) + \varepsilon_0 \chi^{(3)e\nabla eee} \nabla \mathbf{E}(\omega_1) \mathbf{E}^*(\omega_2) \mathbf{E}(\omega_2). \end{aligned}$$

The ranks of the local and nonlocal tensors are 4 and 5, respectively, and we recover the same symmetry properties as for the linear case: only liquids of *chiral* molecules will display a nonlinear optical activity. Here again, such a nonlinear optical activity can be observed in achiral noncentrosymmetric crystals [3]. The nonlocal contributions give birth to several new nonlinear effects. Their real parts induce a nonlinear optical rotation of a linearly polarized beam whereas their imaginary parts induce a nonlinear circular dichroism (NLCD). In this paper, we concentrate on this latter effect as it allows us to develop new time-resolved techniques to study chiral molecules. Several configurations allow us to observe this NLCD. The simplest one is to measure the CD of a sample as a function of the intensity of the laser beam and to observe for example a saturation of the CD [10]. The other possibility is to carry out a pump-probe experiment and to measure not only the absorption but also the CD, to observe a pump-induced CD [11]. Both experiments are similar to usual absorption measurements. The difference is that, focussing on the optical activity instead of on the absorption, one accesses quite different information. To understand this, it is worthwhile examining the microscopic origin of the optical activity in chiral molecules and developing simple models that can describe it.

2.4. Origin of the optical activity – microscopic models

The origin of the optical activity can be deduced from Eq. (3). Deriving the expression of $\chi^{(1)e\nabla e}$ from quantum mechanics, one gets that the relevant parameter describing the optical activity is the Rosenfeld rotational strength $R = \text{Im} \mu \cdot \mathbf{m}$, where μ and \mathbf{m} are the electric and magnetic dipole moments, respectively [5]. A first origin arises directly from this formula. If an optical transition has an electric and a magnetic character together (with non perpendicular transition moments), R will be nonzero and some optical activity occurs. This is clearly the case for a helical molecule. Such a molecule can be readily described by a model where an electron is harmonically bound onto a helix (one-electron or Kauzmann model [12]). This primary origin is, however, not at all the whole story. Indeed, if one considers a large molecule consisting of several atomic groups separated in space, one must calculate R by taking into account the interaction between the groups. Tinoco has made such a calculation [13] and it appears that even in the absence of any magnetic-dipole allowed transition, it is possible to have an optical activity due to the coupling of two electric-dipole allowed transitions, on the condition that the two transition moments be non coplanar. This corresponds, for example, to the case of excitonic coupling [14]. This mechanism is also very simply modelled with the Kuhn model consisting of two noncoplanar harmonic oscillators in

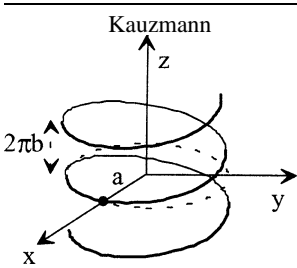
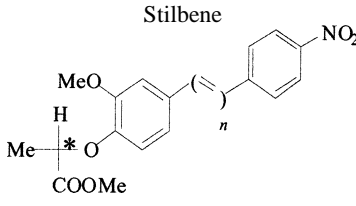
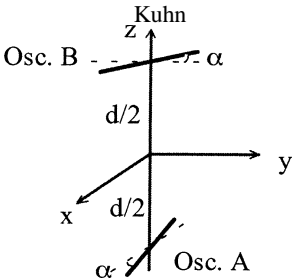
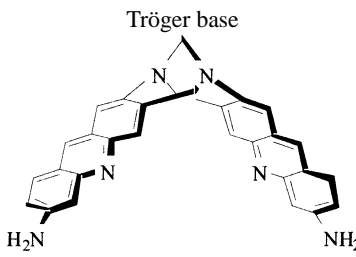
interaction. Note that in general a third mechanism can induce optical activity, namely the coupling in the molecule between an electric dipole moment and a magnetic one. This latter case is, however, more difficult to model.

Concentrating on the Kauzmann and Kuhn models, we want now to extend them to our nonlinear experiments. Indeed, the above models deal with harmonic oscillators and therefore do not allow us to obtain a nonlinear response. The simplest way to access a nonlinear response is to allow the oscillators to be anharmonic. Each oscillator excited with a monochromatic wave will generate a nonlinear dipole and this nonlinearity will affect not only the local response but also the nonlocal one, that is to say, the optical activity. The nonlinear optical activity of a given molecule then needs to be averaged over the distribution to access the total nonlinear polarization and be able to analyze real experiments.

We have performed this nonlinear calculation for the two models going to second- and third-order effects [15]. In this calculation, it is possible to consider precisely the contributions of the magnetic dipole moments as well as of the electric quadrupole moments. It appears that even though both contributions exist in the nonlinear response, they are indistinguishable in an experiment, justifying the customary practice of mixing both contributions in an effective magnetic contribution. Third-order effects in an isotropic liquid of such chiral molecules are found to be similar for the two models. This means that such odd-order nonlinear experiments do not allow one to gain information on the microscopic origin of the optical activity. Such is not the case for surface SHG experiments. We derived for both models the second harmonic electric field radiated from an isotropic surface of chiral molecule, reproducing exactly the conditions of real-life experiments [15]. The results are summarized in Table 1: we obtain strikingly different results for the two models. In the Kauzmann model, the chiral components are only of magnetic origin whereas in the

Table 1. Comparison of the model calculations with experiments. The experiments with a chiral stilbene, exemplifying the Kauzmann model, only give a CD-SHG signal as expected; those with a chiral Tröger base, exemplifying the Kuhn model, give CD, LD and ORD-SHG signals.

Tableau 1. Comparaison des modèles et des expériences. Avec le stilbène chiral, correspondant au modèle de Kauzmann, on n'observe que du signal en CD-SHG ; avec la base de Tröger chirale, correspondant au modèle de Kuhn, on observe du signal en CD, LD et ORD-SHG.

Model	Example	Relevant parameters	Expected effects
 <p>Kauzmann</p>	 <p>Stilbene</p>	f_p, g_p and h_s (achiral) = electric dipolar f_s, g_s and h_p (chiral) = magnetic dipolar	CD-SHG
 <p>Kuhn</p>	 <p>Tröger base</p>	f_g, g_p and h_s (achiral) = electric quadrupolar + magnetic dipolar + electric dipolar f_s, g_s and h_p (chiral) = electric dipolar	CD-SHG + LD, ORD-SHG

Kuhn model, they are of electric origin. These features reflect in very strongly different effects in surface SHG experiments, as described in Section 3. This proves that these experiments are very sensitive to the conformation of the molecules and give a new technique to gain information on the microscopic origin of the optical activity.

In spite of the lack of discrimination between the two models in third-order experiments, these calculations are nevertheless instructive to the understanding of the potentialities of such a technique for resolving temporally some conformational changes in chiral molecules. Considering, for example, a molecule pertaining to the Kuhn model, one obtains that the CD directly depends on geometrical factors such as the distance between the two oscillators or their relative orientation. Should the pump beam induce a change in one of these parameters, the CD would strongly reflect this change. One can therefore understand the principle of time-resolved CD experiments in which a pump beam is used to trigger a conformational change in the molecule. This change produces a modification of the CD which is measured with the probe. Varying the time delay between the two pulses allows one to gain information on the dynamics of these conformational changes, which are generally not accessible in a usual (absorption-based) pump-probe experiment.

3. Surface second harmonic generation

In order to illustrate second-order nonlinear optical activity, we present here experimental results that we have obtained in a surface SHG experiment [16]. The experiment is carried out with a 82 MHz titanium:sapphire laser delivering pulses tunable around 800 nm. This laser beam is sent on an isotropic layer of chiral molecules deposited on a glass substrate. The polarization of this fundamental beam is carefully controlled with a Glan prism and a Babinet–Soleil compensator. The harmonic beam reflected by the sample is then measured after polarization analysis with a very sensitive detection system based on a lock-in detection and a photon-counting photomultiplier tube. Three kinds of experiments which are sensitive to the chirality of the molecules can be performed. First, the SHG signal polarization is analyzed for a *p*-polarized fundamental beam (ORD-SHG). Any rotation of the former is characteristic of chiral molecules. Then we record the *s*- or *p*-polarized SHG signal when continuously rotating the Babinet–Soleil compensator adjusted to a half or quarter waveplate, respectively. Any difference for a $\pm 45^\circ$ linear or left or right circular polarization is also characteristic of chirality; it is called linear or circular difference, respectively (LD-SHG or CD-SHG).

By implementing the above-mentioned model calculations in these experiments, one obtains that, in the Kauzmann model, only CD-SHG will give a nonzero signal, whereas all three experiments (ORD, LD, CD-SHG) contribute a nonzero signal for the Kuhn case. To check that point, we synthesized two kinds of chiral molecules. For both molecules, a two-photon resonance was used to increase the SHG signal. First of all, we studied a chiral stilbene (cf. the first line of Table 1) which exemplifies a one-electron chirality pertaining to the Kauzmann model. Indeed, the asymmetric carbon indicated by a star induces a twist in the otherwise linear motion of the π electrons, rendering their path slightly helical. Experimental results are shown in Fig. 1. This figure corresponds to a CD-SHG experiment and one clearly sees that the SHG signal is different for a right or left circularly polarized fundamental beam. Other experiments (ORD and LD-SHG) did not give any chiral signature. This is in perfect agreement with the theoretical expectations. Secondly, we studied a Tröger base (cf. the second line of Table 1) which is composed of two identical parts arranged in a noncoplanar manner. The optical activity of this molecule comes from an excitonic coupling and is well described by the Kuhn model. In that case, we obtain a chiral signature for the three experiments as expected from the calculations. This is illustrated in Fig. 2 where the ORD-SHG results are displayed. One observes a rotation of the polarization of the harmonic beam as strong as 64° when exciting on the chromophore resonance. Note that for these experiments, we studied both enantiomers and that we could check that all the chiral signals reversed when going from one enantiomer to the other one, as expected from symmetry considerations.

Figure 1. CD-SHG experiment in a chiral stilbene: *s*-polarized SHG signal as a function of the angle of the Babinet–Soleil compensator adjusted to be a quarter-waveplate for the fundamental beam. The curved arrows on top correspond to right and left circular polarizations.

Figure 1. *Expérience de CD-SHG dans un stilbène chiral : signal SHG polarisé s en fonction de l'angle du compensateur de Babinet–Soleil ajusté comme lame quart d'onde pour le fondamental. Les flèches courbes au-dessus de l'image correspondent à des polarisations circulaires droite et gauche.*

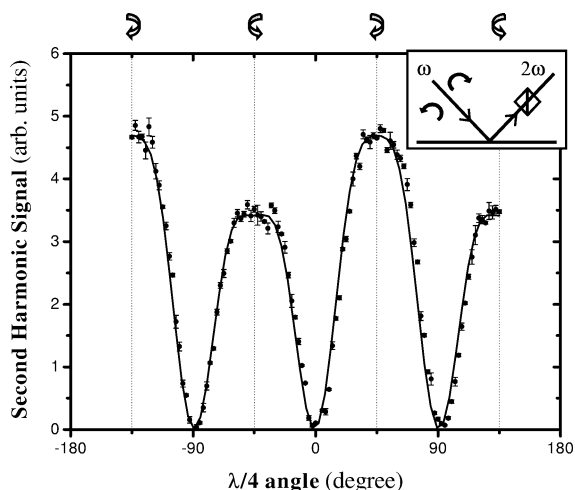
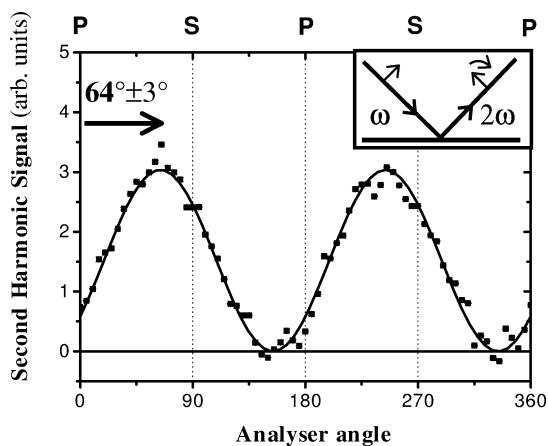


Figure 2. ORD-SHG experiment in a chiral Tröger base: SHG signal as a function of the analyzer angle. A rotation of 64° of the harmonic polarization is observed.

Figure 2. *Expérience de ORD-SHG dans une base de Tröger chirale : signal SHG en fonction de l'angle de l'analyseur. Une rotation de la polarisation du faisceau harmonique de 64° est observée.*



These experiments show that surface SHG is a very sensitive probe not only of chirality, but also of the microscopic origin of the optical activity in chiral molecules.

4. Nonlinear circular dichroism

We want in this section to present experimental evidence of nonlinear circular dichroism in experiments such as described above: a one-beam experiment (observation of a saturation of the CD [10]) and a pump-probe one (observation of a pump-induced CD [11]). To have a clear demonstration of these effects, we studied a ruthenium(II) tris(bipyridyl) salt (see inset of Fig. 4) in solution in ethanol ($1.5 \cdot 10^{-3}$ M). This molecule was chosen as it possesses several advantages that make it close to a model system for this problem: it has a nice isolated absorption structure accompanied by a strong bisignate CD structure around 450 nm (corresponding to a metal-to-ligand charge transfer) and it behaves very closely to a two-level system as far as nonlinear absorption is concerned. Furthermore, the excited state has a long lifetime (600 ns) and no complicated relaxation that could perturb the measurements occurs on the picosecond timescale of our experiments. Furthermore, we have synthesized and isolated the two enantiomers (Δ and Λ) and we have been able in all experiments to check the symmetry between both.

The light source is derived from a 1 kHz amplified titanium:sapphire laser and after several stages of parametric amplification, we get 250 fs pulses tunable around 450 nm. To access the CD, we modulate the

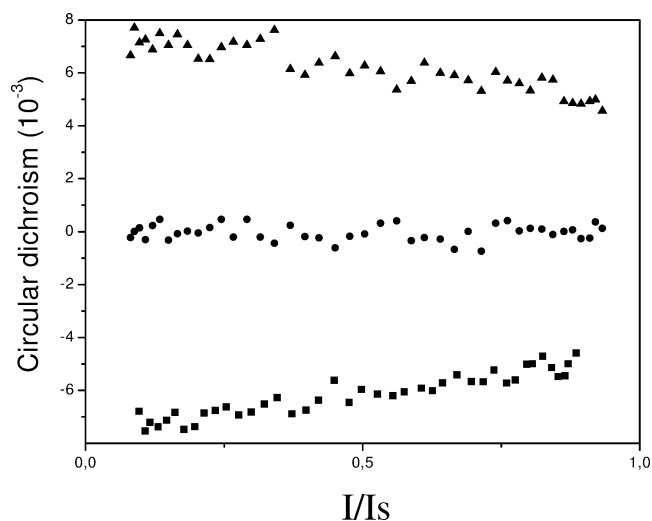


Figure 3. Circular dichroism (normalized to the absorption) as a function of the pump intensity (normalized to the saturation intensity). Squares: racemic mixture; triangles (respectively circles): Δ (respectively Λ) enantiomer. The pump and the probe wavelengths are 470 nm.

Figure 3. *Dichroïsme circulaire (normalisé à l'absorption) en fonction de l'intensité de la pompe (normalisée à l'intensité de saturation). Les longueurs d'onde de la pompe et de la sonde sont égales à 470 nm. Carrés : mélange racémique; triangles (respectivement cercles) : énantiomère Δ (respectivement Λ).*

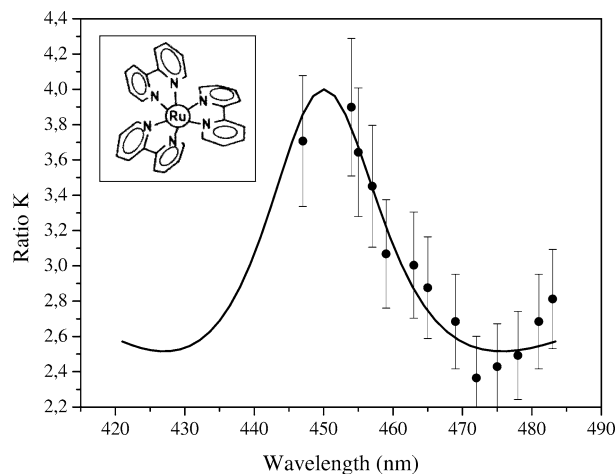


Figure 4. Parameter K describing the nonlinear circular dichroism (see text) as a function of the laser wavelength. The solid line is calculated from a two two-level system model. The inset displays the structure of the ruthenium tris(bipyridyl) salt used in the experiments.

Figure 4. *Paramètre K correspondant au dichroïsme circulaire non linéaire (voir le texte) en fonction de la longueur d'onde du laser. La courbe en trait plein est calculée à partir d'un modèle de deux systèmes à deux niveaux. L'encart montre la structure du sel de ruthénium tris(bipyridyl) utilisé pour ces expériences.*

polarization of the laser beam from a right to a left circular beam with a longitudinal Pockels cell and detect the subsequent intensity modulation with a lock-in amplifier. The experiments then consist in measuring this CD as a function either of the beam intensity (saturation of the CD) or as a function of the pump intensity (pump-probe experiment). In both cases, we clearly observe the NLCD. An illustration is given in Fig. 3 where the probe CD is plotted as a function of the pump intensity for a fixed delay of 1 ps between the two pulses. The three curves correspond to the two enantiomers and the racemic mixture (equal mixing of the two enantiomers). The perfect symmetry between the Λ - and the Δ -curves and the null effect for the racemic clearly show that we definitely measure a nonlinear optical activity effect free of artefacts.

As explained above, the ruthenium salt is very close to a two-level system. In fact, to describe not only the absorption but also the CD, it is necessary to introduce a pair of such two-level systems (optical activity comes from an excitonic coupling in this molecule and the Kuhn model applies [14]). In this oversimplified case of a pair of two-level systems, it is possible to calculate the nonlinear optical activity and to compare with the experiments. Such a comparison is displayed in Fig. 4 for the one-beam experiment. The parameter K , which is plotted as a function of the wavelength, is a measure of the NLCD. It is more precisely the ratio (NLCD/CD)/(nonlinear absorption/absorption), independent of the sample concentration or of the light intensity. The agreement is quite correct. The shape of the curve is perfectly reproduced

without adjustable parameter but we had to multiply the calculated value by 0.6 to match the experimental ones. Similar agreement is obtained in the pump-probe experiments.

Before concluding this section, we would like to comment further on the pump-probe experiments. Indeed, pump-probe experiments are of paramount importance to access dynamic information on an ultrashort timescale. In our experiments, we do have a subpicosecond resolution, but as explained before, nothing happens in the ruthenium sample on this timescale. This time resolution is nevertheless the biggest advantage of this new technique. Indeed, as already mentioned, by measuring the evolution of the CD after a change triggered by the pump, one can access the evolution of the conformation of the molecules. Such an approach should be of great interest, especially for biomolecules for which the conformation plays a dominant role in biochemical reactions.

5. Conclusions

In this paper, we have summarized several aspects of an emerging field, namely the nonlinear optical activity. We have first introduced the effects of the nonlocality in the light–matter interaction and examined the implications in second- and third-order nonlinear optics. Second-order phenomena are somewhat more complex, but they give birth to a great sensitivity to the microscopic origin of the optical activity in surface SHG experiments. On the other hand, third-order nonlinear optical activity opens up a new field of investigation by allowing the measurement of time-resolved circular dichroism in a liquid of chiral molecules. Experimental demonstrations of both kinds of effects have been presented on specially synthesized molecules. There is no doubt now that the fundamental mechanisms of these new effects are fairly well understood and we can hope that applications to the study of molecules – and especially of biomolecules – will bring new interesting findings.

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