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Magnetic-dipole nonlinearities in chiral materials

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Abstract

We propose a new measurement procedure to study the role of magnetic-dipole contributions to the second-order nonlinearity in chiral materials. The procedure is based on the measurement of the ellipticity of the second-harmonic light generated in the chiral material. A better insight in the magnetic-dipole nonlinearities of materials could eventually lead to the observation of new phenomena in the field of photochemistry and photophysics. © 2001 Published by Elsevier Science B.V.

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1. Introduction

Chiral molecules show extremely interesting second-order nonlinear optical (NLO) properties. For example, the NLO properties of chiral molecules and polymers can be significantly enhanced by optimizing magnetic-dipole contributions to the nonlinearity, in addition to the usual electric-dipole contributions [1]. Furthermore, the symmetry properties of magnetic-dipole interactions are different from those of electric-dipole interactions. As a consequence, they can support electric-dipole forbidden second-order NLO processes in highly symmetric media [2]. Hence, the importance of magnetic interactions in chiral media could therefore provide a new approach to the development of second-order NLO materials. In general, a careful study of magnetic-dipole nonlinearities in chiral materials could lead to a variety of new optical phenomena and applications, such as selective photodestruction of enantiomers through a NLO interaction, or probing the enantiomeric excess in surfaces and membranes. For this reason, measurement techniques that specifically probe magnetic contributions to the nonlinearity are needed. Recently, evidence of magnetic-dipole contributions to the nonlinearity of chiral thin films has been obtained from second-harmonic generation (SHG) experiments: a detailed study of the dependence of the s- and p-polarized SHG signals on the polarization of the fundamental beam revealed strong (i.e. comparable to the electric-dipole contributions) magnetic-dipole contributions [3,4]. In this paper, we propose a new measurement procedure based on the detection of elliptically polarized second-harmonic light that can be used to study the role of magnetic contributions in chiral materials.

2. Theory and discussion

All optical phenomena are governed by the Maxwell equations [5]:

$$\nabla \times \boldsymbol{E} = -\frac{1}{c}\frac{\partial \boldsymbol{B}}{\partial t} \tag{1}$$

$$\nabla \times \boldsymbol{H} = \frac{1}{c}\frac{\partial \boldsymbol{D}}{\partial t} + \frac{4\pi}{c}\boldsymbol{J} \tag{2}$$

$$\nabla \cdot \boldsymbol{D} = 4\pi \boldsymbol{\rho} \tag{3}$$

$$\nabla \cdot \boldsymbol{B} = 0 \tag{4}$$

where $\boldsymbol{J}$ and $\boldsymbol{\rho}$ are the current and charge densities, $\boldsymbol{E}$ the electric field, $\boldsymbol{D}$ the electric displacement, $\boldsymbol{H}$ the magnetic field and $\boldsymbol{B}$ the magnetic induction. $\boldsymbol{E}$ and $\boldsymbol{D}$, and $\boldsymbol{H}$ and $\boldsymbol{B}$ are connected through the constitutive relations

$$\boldsymbol{D} = \boldsymbol{E} + 4\pi\boldsymbol{P} - 4\pi\nabla \cdot \boldsymbol{Q} \tag{5}$$

$$\boldsymbol{B} = \boldsymbol{H} + 4\pi\boldsymbol{M} \tag{6}$$

where $\boldsymbol{P}$, $\boldsymbol{Q}$ and $\boldsymbol{M}$ are the electric polarization, the electric quadrupolarization and the magnetization, respectively.

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Using these relations and Maxwell equations (1) and (2), we obtain

$$\nabla \times \boldsymbol{B} = \frac{4\pi}{c}\boldsymbol{J} + \frac{1}{c}\frac{\partial}{\partial t} \times \left(\boldsymbol{E} + 4\pi \boldsymbol{P} - \nabla \cdot \boldsymbol{Q} + 4\pi c \int (\nabla \times \boldsymbol{M})\partial t\right) = \frac{4\pi}{c}\boldsymbol{J} + \frac{1}{c}\frac{\partial}{\partial t}(\boldsymbol{E} + 4\pi \boldsymbol{P}_{\mathrm{eff}}) \quad (7)$$

where $\boldsymbol{P}_{\mathrm{eff}}$ is the only time-varying source term [6].

Furthermore, the effective polarization can be divided into a linear and nonlinear contribution. In the remainder of this paper we will focus on the nonlinear contribution and more in particular the effective polarization $\boldsymbol{P}_{\mathrm{eff}}(2\omega)$ at the second-harmonic frequency. At this point, we would also like to note that we will explicitly consider only electric-dipole and magnetic-dipole contributions to the nonlinearity. One reason for this is that the magnetic-dipole interaction is actually somewhat stronger than the quadrupole interaction [7]. Furthermore, the importance of magnetic contributions in chiral media is well established [8], and one can argue that chirality favors the magnetic interactions. Furthermore, the general symmetry properties of magnetic-dipole and electric quadrupole interactions are very similar in second-order nonlinear optics, and experimental separation between the two is difficult [2,9,10]. Hence, the quadrupole interaction is implicitly included in the magnetic-dipole interaction, which simplifies our discussion considerably. Under those conditions, the effective nonlinear polarization $\boldsymbol{P}_{\mathrm{eff}}(2\omega)$ is given by

$$\boldsymbol{P}_{\mathrm{eff}}(2\omega) = \boldsymbol{P}(2\omega) + \frac{c}{\mathrm{i}2\omega}\nabla \times \boldsymbol{M}(2\omega) \quad (8)$$

The components of $\boldsymbol{P}(2\omega)$ and $\boldsymbol{M}(2\omega)$ are up to first-order in the magnetic-dipole interaction, defined as [1]

$$P_i(2\omega) = \sum_{j,k} \left\lfloor \chi_{ijk}^{\mathrm{eee}} E_j(\omega)E_k(\omega) + \chi_{ijk}^{\mathrm{eem}} E_j(\omega)B_k(\omega) \right\rfloor \quad (9)$$

$$M_i(2\omega) = \sum_{j,k} \chi_{ijk}^{\mathrm{mee}} E_j(\omega)E_k(\omega) \quad (10)$$

where the subscripts refer to Cartesian coordinates in the laboratory (macroscopic) frame. The superscripts in the susceptibility components of the tensors, χ associate the respective subscripts with electric-dipole (e) or magnetic-dipole (m) interactions. Both nonlinear polarization and magnetization act as sources of SHG. The number of nonvanishing susceptibility components depends on the symmetry of the materials system.

Now let us consider a particular configuration that is experimentally accessible. We take a chiral medium with net orientation along the z-direction and with a laser beam propagating along the x-direction (Fig. 1). The laser beam is polarized along the z-direction. The symmetry of the medium is C_∞. For such a system there are four independent components of the χ^{eee} and χ^{mee} tensors and seven independent components for the χ^{eem} tensor. All the nonvanshing components are summarized in Table 1. Components that are nonvanishing only for chiral samples are designated as chiral components, the other is referred to as achiral. The components of the electric and magnetic fields are $\boldsymbol{E}(\omega) = \boldsymbol{E}(0, 0, E_z)$ and $\boldsymbol{B}(\omega) = \boldsymbol{B}(0, B_y, 0)$ and the nonvanishing polarization and magnetization components that are able to radiate are

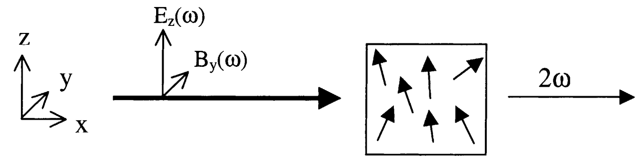

Fig. 1. A fundamental laser beam at frequency ω is incident on a chiral oriented medium (C_∞ symmetry). Second-harmonic light is generated in the transmitted direction.

$$P_z(2\omega) = \chi_{zzz}^{\mathrm{eee}} E_z(\omega)E_z(\omega),$$
$$P_y(2\omega) = \chi_{yzy}^{\mathrm{eem}} E_z(\omega)B_y(\omega),$$
$$M_z(2\omega) = \chi_{zzz}^{\mathrm{mee}} E_z(\omega)E_z(\omega) \quad (11)$$

Hence, by using the relation (1), the effective polarization becomes

$$\boldsymbol{P}_{\mathrm{eff}}(2\omega) = \chi_{zzz}^{\mathrm{eee}} E_z(\omega)E_z(\omega)z + (\chi_{yzy}^{\mathrm{eem}} + \chi_{zzz}^{\mathrm{mee}})E_z(\omega)E_z(\omega)y \quad (12)$$

This expression can now be used to phenomenologically describe the second-harmonic response of the chiral medium depicted in Fig. 1. For lossless materials (off-resonance excitation), the components of χ^{eem} and χ^{mee} have been shown theoretically to be imaginary, while the components of χ^{eee} are essentially real [11,12]. This 90° phase difference can in principle be exploited to discriminate between the magnetic- and electric-dipole contributions. In general however (i.e. closer to resonance), there will be an arbitrary phase difference between both contributions. Hence, if we

Table 1
Nonvanishing components of the tensors χ^{eee}, χ^{eem} and χ^{mee} for the experimental configuration shown in Fig. 1. Components that are nonvanishing only for chiral samples are designated as chiral, the other components are referred to as achiral

Tensor	Achiral components	Chiral components
χ^{eee}	zzz $zxx = zyy$ $xxz = xzx = yyz = yzy$	$xyz = xzy = -yxz = -yzx$
χ^{eem}	$xyz = -yxz$ $zxy = -zyx$ $xzy = -yzx$	zzz $zxx = zyy$ $xxz = yyz$ $xzx = yzy$
χ^{mee}	$xyz = xzy = -yxz = -yzx$	zzz $zxx = zyy$ $xxz = xzx = yyz = yzy$

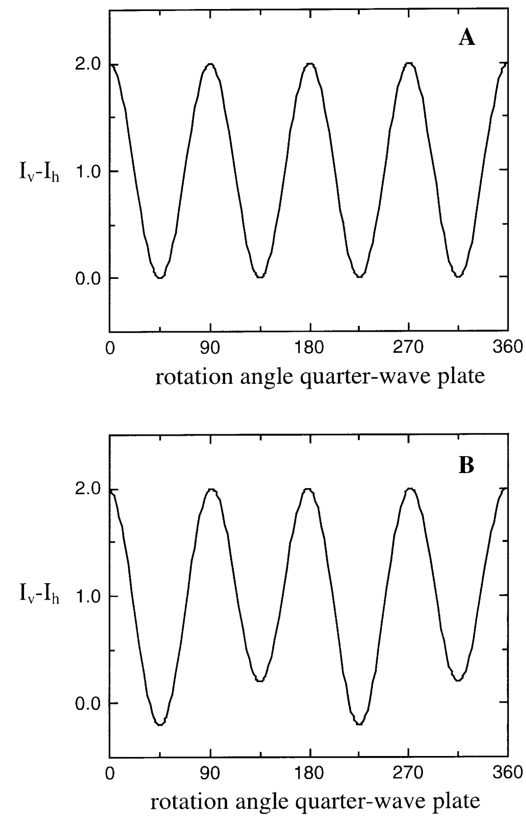

Fig. 2. Vertically polarized SH intensity minus the horizontally polarized SH intensity vs. the rotation angle of the quarter-wave plate. Plot A represents the effect of the wave-plate on linearly polarized second-harmonic radiation; plot B illustrates the effect of the wave-plate on elliptically polarized SH-light.

take a closer look at Eq. (12), it is a clear that there will generally be a phase difference between the z- and y-component of the effective polarization. The effective polarization will generate two second-harmonic fields, one z-component $E_z(2\omega)$ and one y-component $E_y(2\omega)$ that differ in phase, and thus give rise to elliptically polarized SH-light. Hence, the presence of ellipticity in the second-harmonic light is clear evidence of the presence of magnetic-dipole contributions to the nonlinearity. Moreover, the combination $\chi_{yzy}^{\rm eem} + \chi_{zzz}^{\rm mee}$ in Eq. (12) only exists in chiral samples and the presence of elliptically polarized light is therefore also an indication for the presence of chirality in the material system.

From a practical point of view, the ellipticity can be determined by modulating the second-harmonic light continuously by a rotating quarter-wave plate and detecting the vertical and horizontal components of the modulated SH-light simultaneously. This procedure results in two polarization patterns for the second-harmonic light. By calculating the action of a quarter-wave plate on the elliptically polarized second-harmonic, these two polarization patterns can be fitted and analyzed.

A simulation of the effect of a quarter-wave plate on the polarization of the second-harmonic light is shown in Fig. 2, where we plotted the difference between the vertically and horizontally polarized second-harmonic intensities vs. the rotation angle of the quarter-wave plate. Plot A represents the effect of the wave-plate on linearly polarized second-harmonic radiation, while plot B illustrates the effect of the wave-plate on elliptically polarized SH-light. Important is the extreme sensitivity of the polarization pattern to even the slightest amount of ellipticity in the SH-light: in the presence of elliptically polarized light, the polarization pattern becomes strongly asymmetric with respect to the 180° rotation angle of the quarter-wave plate. For example, in curve B we took $E_y/E_z = 0.05$ (which corresponds to $(\chi_{yzy}^{\rm eem} + \chi_{zzz}^{\rm mee})/\chi_{zzz}^{\rm eee} = 0.05$) and a phase-difference of 90° between both components. Hence, we believe that the proposed measurement procedure can be useful in the detection of the presence of even small magnetic-dipole contributions to the nonlinearity.

3. Conclusions

We have described a new measurement procedure, based on SHG, to access the role of magnetic-dipole contributions to the nonlinearity of chiral materials. The procedure is based on the detection of elliptically polarized second-harmonic light.

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