New Electro-Optic Effect: Sum-Frequency Generation from Optically Active Liquids in the Presence of a dc Electric Field

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We report the observation of sum-frequency signals that depend linearly on an applied electrostatic field and that change sign with the handedness of an optically active solute. This recently predicted chiral electro-optic effect exists in the electric-dipole approximation. The static electric field gives rise to an electric-field-induced sum-frequency signal (an achiral third-order process) that interferes with the chirality-specific sum-frequency at second order. The cross-terms linear in the electrostatic field constitute the effect and may be used to determine the absolute sign of second- and third-order nonlinear-optical susceptibilities in isotropic media.

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Most biological molecules are chiral [1], i.e., have a nonsuperimposable mirror image. In many respects, the two mirror image forms (enantiomers) of a chiral molecule have identical physical properties. Optical activity is often the only practical means to distinguish between enantiomers in solution. Conventional optical activity phenomena, such as optical rotation and circular dichroism, are based on the interference of radiation from induced oscillating electric and magnetic dipoles (and electric quadrupoles), and arise from a differential response to left and right circularly polarized light [2].

Remarkably, a purely electric-dipolar nonlinear-optical process can also be a probe of chirality [3]. Two optical fields of different frequency can coherently mix in an isotropic medium to generate light at their sum (or difference) frequency if the medium is optically active, i.e., a nonracemic solution of chiral molecules [3]. The signal itself is then a probe of molecular chirality: It is the intrinsic broken symmetry of the chiral molecules that causes a nonracemic liquid to be noncentrosymmetric and, hence, allows for an electric-dipolar second-order nonlinear-optical process in an isotropic medium.

The sum-frequency intensity is in general, however, not sensitive to the sign of the underlying property tensor, and thus does not readily distinguish between enantiomers. In this Letter, we report the observation of a recently predicted chiral electro-optic effect [4] that arises when a static electric field is applied to coherent sum- or difference-frequency generation in an optically active liquid. The static field does not change the phase matching conditions, but it gives rise to an electric-field-induced contribution to the signal. The beat between chirality-sensitive sum-frequency generation (a second-order process) and achiral electric-field-induced sum-frequency generation (a third-order process) yields a contribution to the intensity that is linear in the static electric field and that changes sign with the enantiomer [4,5]. The effect can give the absolute sign of the isotropic part of the sum-frequency hyperpolarizability (if the sign of the achiral third-order property is known) and, hence, makes it possible to determine the handedness of chiral molecules in solution via an electric-dipolar optical process.

Sum-frequency generation (SFG) from chiral liquids has recently been reexamined [6] and has been observed experimentally [7–9]. The molecular response to two optical fields $E_\beta(\omega_1)$ and $E_\gamma(\omega_2)$ [and a static field $E_\delta(0)$] at the sum-frequency $\omega_3 = \omega_1 + \omega_2$ can be written in terms of an induced oscillating dipole moment

$$\begin{aligned}\mu_\alpha(\omega_3) = {}& \tfrac{1}{2}\beta_{\alpha\beta\gamma}(\omega_3 = \omega_1 + \omega_2)E_\beta(\omega_1)E_\gamma(\omega_2) \\ & + \tfrac{1}{2}\gamma_{\alpha\beta\gamma\delta}(\omega_3 = \omega_1 + \omega_2 + 0) \\ & \times E_\beta(\omega_1)E_\gamma(\omega_2)E_\delta(0),\end{aligned} \tag{1}$$

where $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ are the first and the second hyperpolarizabilities, respectively. The macroscopic response is given by an appropriate spatial average. Here we consider an isotropic medium in the presence of a static electric field $E_\delta(0)$. A Boltzmann average yields the induced macroscopic polarization at the sum frequency [4,5]:

$$P_\alpha(\omega_3) = \epsilon_0 E_\beta(\omega_1)E_\gamma(\omega_2)\Big[\underbrace{\epsilon_{\alpha\beta\gamma}\chi^{(2)}}_{\text{chiral}} + \underbrace{3(\chi_1^{(3)}\delta_{\alpha\beta}\delta_{\gamma\delta} + \chi_2^{(3)}\delta_{\alpha\gamma}\delta_{\beta\delta} + \chi_3^{(3)}\delta_{\alpha\delta}\delta_{\beta\gamma})\mathrm{E}_\delta(0)}_{\text{achiral}}\Big], \tag{2}$$

where $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita tensor and $\delta_{\alpha\beta}$ the Kronecker delta. $\chi^{(2)}$ is, as we will show, the completely antisymmetric chirally sensitive isotropic component of the second-order susceptibility, and $\chi_i^{(3)}$ with $i = 1$, 2, or 3 are the achiral isotropic components of the third-order susceptibility. The intensity at the sum frequency is proportional to $|P_\alpha(\omega_3)|^2$ and so contains — besides a contribution independent of the static field, and one that is quadratic in the static field — cross terms that are linear in the static field and linear in $\chi^{(2)}$:

$$\mathrm{SFG}(E) \propto \mathrm{Re}[\chi^{(2)}(\chi_i^{(3)})^*]E(0)I(\omega_1)I(\omega_2), \tag{3}$$

where I are the respective incident intensities, Re is the real part, and the star indicates a complex conjugate. We have denoted the contribution to the intensity at the sum-frequency that is linear in the static field by SFG(E).

$\chi^{(2)}$ is proportional to the isotropic component of the first hyperpolarizability and is given by

$$\chi^{(2)} = \sum_m \frac{N_m}{12\,\epsilon_0}(\beta_{m,xyz} - \beta_{m,xzy} + \beta_{m,yzx} - \beta_{m,yxz} + \beta_{m,zxy} - \beta_{m,zyx}), \tag{4}$$

where the summation is over all molecular species, and where the mth species has a first hyperpolarizability tensor $\beta_{m,\alpha\beta\gamma}$ and is present in number density N_m. It is seen that $\chi^{(2)}$ vanishes for any molecular species that possesses a mirror plane, a center of inversion, or a rotation-reflection axis; thus, $\chi^{(2)}$ is only nonzero for chiral systems and changes sign as the handedness of the optically active liquid changes. The contribution to the intensity linear in $E(0)$ may therefore reveal the sign of the pseudoscalar $\chi^{(2)}$. It can be used to determine the absolute configuration of the chiral molecules in the optically active liquid.

$\chi_1^{(3)}$, $\chi_2^{(3)}$, and $\chi_3^{(3)}$ are given in terms of scalar combinations of the second hyperpolarizability tensor components by [4]

$$\begin{aligned}\chi_1^{(3)} &= \sum_m \frac{N_m}{180\epsilon_0}[+4\gamma_{m,\alpha\alpha\beta\beta} - \gamma_{m,\alpha\beta\alpha\beta} - \gamma_{m,\alpha\beta\beta\alpha}],\\ \chi_2^{(3)} &= \sum_m \frac{N_m}{180\epsilon_0}[-\gamma_{m,\alpha\alpha\beta\beta} + 4\gamma_{m,\alpha\beta\alpha\beta} - \gamma_{m,\alpha\beta\beta\alpha}],\\ \chi_3^{(3)} &= \sum_m \frac{N_m}{180\epsilon_0}[-\gamma_{m,\alpha\alpha\beta\beta} - \gamma_{m,\alpha\beta\alpha\beta} + 4\gamma_{m,\alpha\beta\beta\alpha}].\end{aligned} \tag{5}$$

Should the duration of the static applied field be longer than the rotational time of the molecules in solution, then there are additional temperature-dependent terms of the form $\beta_{m,\alpha\alpha\beta}(\omega_3 = \omega_1 + \omega_2)\,\mu_{m,\beta}^{(0)}/(kT)$ for molecular species m with a permanent dipole moment $\mu_{m,\beta}^{(0)}$ [4]. At ambient conditions, the temperature-dependent contributions may dominate for dipolar molecules and be of either sign. Both $\gamma_{\alpha\alpha\beta\beta}$ and $\beta_{\alpha\alpha\beta}\,\mu_\beta^{(0)}$ are unchanged under mirror symmetry operation and so it follows that the $\chi_i^{(3)}$ exist for achiral molecules (e.g., an achiral solvent) and are necessarily the same for both enantiomers of a chiral molecule.

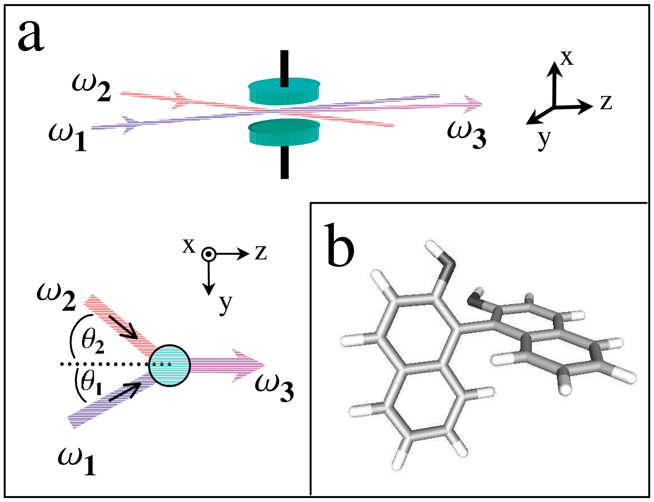

FIG. 1 (color online). (a) Beam geometry and choice of axes. The optical beams lie in the y, z plane, and the static field is S polarized along x. The incident beam at ω_1 makes an angle of θ_1 with the sum-frequency beam at ω_3, and similarly for ω_2. (The cuvette with the optically active liquid is not shown.) (b) Structure of R-(+)-1, 1′-bi-2-naphthol ($C_{20}H_{14}O_2$).

We observe the chiral electro-optic effect in an experimental arrangement schematically depicted in Fig. 1(a). From the antisymmetry of the Levi-Civita tensor in Eq. (2), it follows that the optical fields need to have components that are mutually orthogonal such that they span the x, y, and z axes of a Cartesian frame. Hence, sum-frequency generation from isotropic media requires that one optical field be S polarized and the remaining two be P polarized. Further, the static electric field has to be S polarized for it to give rise to an electric-field-induced contribution to the sum-frequency signal.

We use the ~775 nm fundamental wavelength of a Ti:sapphire regenerative amplifier (Clark-MXR CPA-2010) along with its second harmonic at 388 nm to generate sum-frequency signals at 258 nm. The pulse duration is ~150 fs and the repetition rate is 1 kHz. The experiments are conducted at peak intensities between 10 and 50 GW/cm^2. We detect ~1000 counts per second and, accounting for the detection efficiency, we estimate that there are several hundred sum-frequency photons per pulse. A custom-built high-voltage power supply provides 3.5 to 10 kV peak to peak modulated at 500 Hz. The applied field is essentially static for a liquid and $\chi_i^{(3)}$ for 1, 1′-bi-2-naphthol (BN), and tetrahydrofuran (THF) will thus have both a purely electronic as well as a temperature-dependent orientational contribution. The modulation of the applied electric field permits phase-sensitive detection.

Unlike collinear electric-field-induced second-harmonic generation [10], the noncollinear SFG beam geometry [6] allows the use of fully immersed electrodes. These are suspended in a standard quartz optical cuvette and spaced ~2 mm apart.

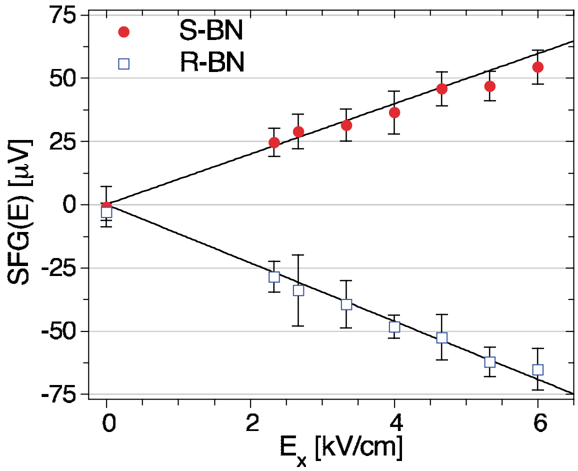

FIG. 2 (color online). SFG(E) signals from ~0.5M solutions of S-(−)- and R-(+)-1, 1′-bi-2-naphthol, respectively, measured at different strengths (estimated) of the applied electric field. The solid lines are linear functions fitted to the data.

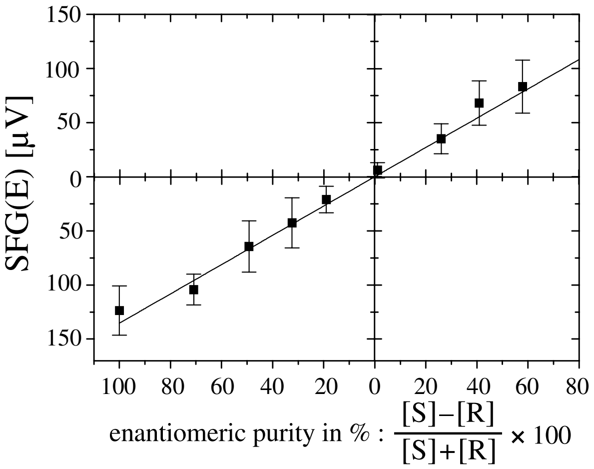

FIG. 3. SFG(E) signals measured as a function of the fractional concentration difference of R-(+)- and S-(−)-1, 1′-bi-2-naphthol in THF. The solid line is a linear function fitted to the data.

We observe the chiral electro-optic effect in optically active solutions prepared from R-(+)- or S-(−)-1, 1′-bi-2-naphthol (R-BN and S-BN) [see Fig. 1(b)] which are dissolved in the achiral solvent THF. In Fig. 2, we show that the signals are of opposite sign for the R and S enantiomers of BN and that they vary linearly with the strength of the applied low-frequency field. The small difference in absolute strength of the respective signals is attributed to small differences in the electrode spacings and/or the concentrations. The SFG(E) signals change sign if the direction of the static field is reversed.

For fixed beam polarizations, direction, and strength of the static field, we also observe a linear dependence of the chiral electro-optic effect on the enantiomeric concentration difference of the optically active solution, as seen in Fig. 3. Starting with a 0.56M solution of R-(+)-1, 1′-bi-2-naphthol in THF, the handedness of the 0.56M solution is gradually changed by the addition of a solution of S-(−)-1, 1′-bi-2-naphthol in THF. The SFG(E) signal correspondingly changes sign. It is zero for the racemic mixture.

To describe the polarization dependence of the sum-frequency signals, we now consider the axis system and beam geometry depicted in Fig. 1(a). For simplicity, we ignore the small rotation of the plane of polarization in the chiral liquid due to optical activity (<0.5°), and we note that a static electric field cannot contribute linearly to optical rotation in a fluid.

From Eq. (2) and the requirement for a transverse wave at the sum frequency, it follows that a PPS combination of polarizations (listed throughout this Letter in the order of the optical fields at ω_3, ω_1, and ω_2) gives rise to an SFG(E) signal of the form

$$\mathrm{SFG}(E)_{PPS} = (+)\eta\,\mathrm{Re}[\chi^{(2)}(\chi_1^{(3)})^*]\sin(2\theta_1)E_x(0),$$

where θ_1 is the angle the incident beam at ω_1 makes with respect to the sum-frequency beam, and where we have subsumed the incident intensities and any numerical factors common to all SFG(E) intensities in the positive multiplier η. Similarly, PSP polarizations give rise to

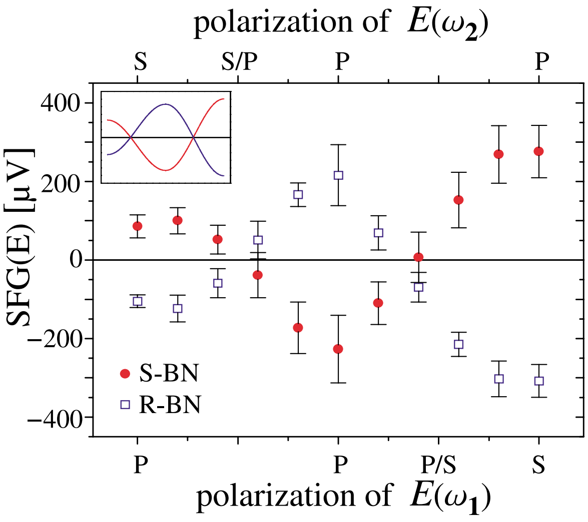

FIG. 4 (color online). Sum-frequency generation signals from optically active ~0.5M solutions of S-(−)- and R-(+)-BN in THF observed for different beam polarizations. The polarization state of the ω_1 beam is shown on the lower axis and that of the ω_2 beam on the upper axis. First, $E(\omega_1)$ is kept P polarized while the polarization of $E(\omega_2)$ is changed from S to P in 18° increments. Subsequently, $E(\omega_2)$ remains P polarized while the polarization of the ω_1 beam is changed from P to S. When both the incident optical fields at ω_1 and ω_2 are P polarized, then the ω_3 beam is S polarized. Mixed input polarizations (S and P) give rise to a P-polarized signal. The static electric field E_x is ~2 kV/cm. The expected trend of the signals is shown by a model calculation depicted in the inset.

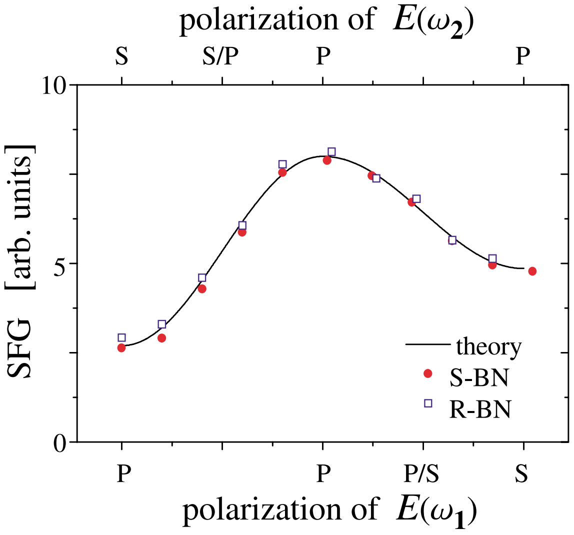

FIG. 5 (color online). The SFG intensity in the absence of a static electric field is shown as a function of the input beam polarizations (see caption of Fig. 4 for details). The solid line is a fit from theory. The contribution quadratic in the static field is below the sensitivity of the experiment.

$$\mathrm{SFG}(E)_{PSP} = (+)\eta\, \mathrm{Re}[\chi^{(2)}(\chi_2^{(3)})^*]\sin(2\theta_2)E_x(0),$$

and SPP polarizations probe

$$\mathrm{SFG}(E)_{SPP} = (-)\eta\, \mathrm{Re}[\chi^{(2)}(\chi_3^{(3)})^*]\sin[2(\theta_1 + \theta_2)]E_x(0).$$

Since $\chi_i^{(3)}$ are the same for the R and S enantiomers while the $\chi^{(2)}$ change sign, solutions of R-BN and S-BN with equal concentration will have equal but opposite SFG(E) intensities in the same field $E_x(0)$, and this can be seen in Fig. 4. Further, the change of sign in going from PPS to SPP polarizations and similarly from SPP to PSP suggests that $\chi_1^{(3)}$, $\chi_2^{(3)}$, and $\chi_3^{(3)}$ have the same sign for BN $[2(\theta_1 + \theta_2) < \pi]$. The three polarization states PPS, PSP, and SPP permit the observation of the three isotropic third-order susceptibilities, $\chi_i^{(3)}$. For a static field of ~2.5 kV/cm, the SFG(E) signals are, depending on beam polarizations, ~5% to 20% of the SFG signals in the absence of a dc electric field shown in Fig. 5. Nonlinear-optical susceptibilities of different order may thus be measured under identical optical field conditions without the need for an external reference, as the $\chi^{(2)}$ will act as an internal standard. The relative strength of $\chi_1^{(3)}$, $\chi_2^{(3)}$, and $\chi_3^{(3)}$ may in turn yield information about specific hyperpolarizability tensor components entering the third-order susceptibility. Such an analysis is, however, chromophore specific and will not be discussed further here. Finally, Fig. 5 confirms that SFG signals independent of E do not distinguish between enantiomers.

For a dc electric field along $+x$ [see Fig. 1(a)], we measure a positive SFG$(E)_{PSP}$ intensity for S-BN. In the case of the resonant signals from R-BN and S-BN, where the complex nature of the response tensors needs to be considered, and in the absence of any measurable $\chi_i^{(3)}$ contribution from the achiral solvent, the determination of the absolute configuration of the chiral molecules will require quantum chemical computations for both $\chi^{(2)}$ and $\chi_i^{(3)}$. However, the contribution from an achiral solvent should make it possible to determine the absolute sign of both the second- and third-order susceptibilities for both optical isomers of a chiral molecule [4].

In summary, we have observed the linear effect of a static electric field on the sum-frequency generation intensity from optically active liquids. The reported electro-optic effect arises in the electric-dipole approximation and changes sign with the enantiomer and upon reversing the direction of the static electric field. The effect may be used to determine the absolute sign of the second-order and third-order nonlinear-optical susceptibilities. Should the achiral solvent give rise to an appreciable electric-field-induced sum-frequency signal, then the effect could be used to amplify weak sum-frequency signals from optically active solutions.

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