



The chiral specificity of sum-frequency generation in solutions

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Abstract

Sum-frequency generation in isotropic media is in the electric-dipole approximation the only symmetry allowed for chiral systems. We demonstrate that the sum-frequency intensity from an optically active liquid depends quadratically on the difference in concentration of the two enantiomers. The dominant contribution to the signal is found to be due to the chirality specific electric-dipolar three-wave mixing nonlinearity. Selecting the polarization of all fields allows the chiral electric-dipolar contributions to the bulk sum-frequency signal to be discerned from any achiral magnetic-dipolar and electric-quadrupolar contributions. © 2002 Published by Elsevier Science B.V.

1. Introduction

The specificity and function of biological molecules can often be traced to their chirality. A well established optical probe of chirality is optical activity, which is based on the different response of chiral media to left and right circularly polarized light [1]. It may be observed through optical rotation, circular dichroism, or Rayleigh and Raman optical activity. These optical activity phenomena require electric-dipolar as well as magnetic-dipolar or electric-quadrupolar interactions of the medium with the electromagnetic fields.

A purely electric-dipolar process in nonlinear optics can, however, also be a probe of chirality as has been demonstrated by Hicks and coworkers [2,3] who report large circular intensity differences

in surface-second-harmonic generation from a chiral monolayer of 1,1'-bi-2-naphthol (BN). Nonlinear surface spectroscopies, however, require knowledge of the orientational distribution of molecules at the surface to be unambiguous probes of chirality [4].

An electric-dipolar nonlinear susceptibility may also be chirality-specific in an isotropic medium should it concern coherent nonlinear-optical sum- or difference-frequency generation (SFG, DFG) [5]. These second-order processes involve the simultaneous interaction of three electric fields (two incident and one signal) and are thus mediated by a parity-odd material response, a response tensor containing the product of three electric-dipole transition moment operators. It follows that for any medium to exhibit a coherent second-order nonlinear optical response it needs to be non-centrosymmetric on a macroscopic scale. A *chiral* liquid, gas or amorphous solid satisfies this requirement and may thus give rise to sum- or

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difference-frequency generation through a non-vanishing isotropic average of the corresponding second-order susceptibility tensor [6].

There have been two reports of sum-frequency signals from aqueous solutions of arabinose [7,8], but they are at odds with a recent combined theoretical and experimental study that fails to detect sum-frequency from optically active solutions of arabinose [9]. Belkin et al. [10] also fail to observe any SFG from arabinose solutions, however they report partially electronically resonant visible–visible SFG in 0.55 M solutions of BN in tetrahydrofuran (THF) [10], and vibrationally resonant infrared–visible SFG in limonene [11]. In a dilution study in which the handedness of the solution is not changed, Shen and coworkers measure a quadratic dependence of the sum-frequency signal on the concentration of BN [10] and thus confirm the bulk-origin of the observed coherent SFG from chiral BN solutions. In this Letter we show how such a bulk (visible–visible) sum-frequency signal (BN in THF) is an unambiguous probe of chirality and report its quadratic dependence on the difference in (fractional) concentration of the enantiomers. We thus directly measure the chirality of an optically active solution [1,12].

We also report the results of a polarization study that lends further credence to the finding that the dominant contribution to the sum-frequency signal is from the chiral bulk electric-dipolar second-order nonlinear susceptibility and not from achiral higher-order multipolar bulk contributions. Nevertheless, we show that selecting the polarization of all three fields allows for the unambiguous identification of the chiral contributions to the sum-frequency signal.

2. The isotropic second-order susceptibility

The induced polarization oscillating at the sum-frequency $\omega_S = \omega_1 + \omega_2$ is in the electric-dipole approximation given by

$$P_\alpha^{(2)}(\omega_S) = \epsilon_0 \chi_{\alpha\beta\gamma}^{(2)} E_\beta(\omega_1) E_\gamma(\omega_2) + \dots, \quad (1)$$

where $E_\beta(\omega_1)$ and $E_\gamma(\omega_2)$ are monochromatic fields whose frequency components are ω_1 and ω_2 , respectively. Higher-order multipolar contributions

are discussed subsequently. For an isotropic medium such as a liquid,

$$\chi_{\alpha\beta\gamma}^{(2)} = \epsilon_{\alpha\beta\gamma} \chi^{(2)}, \quad (2)$$

where $\epsilon_{\alpha\beta\gamma}$ is the unit skew-symmetric tensor. The pseudoscalar $\chi^{(2)}$ is the isotropic component of the second-order nonlinear susceptibility tensor $\chi_{\alpha\beta\gamma}^{(2)}$. $\chi^{(2)}$ is in turn related to the completely antisymmetric component of the first hyperpolarizability tensor¹,

$$\chi^{(2)} = \sum_i \frac{N_i}{6\epsilon_0} (\beta_{i,xyz} - \beta_{i,xzy} + \beta_{i,yzx} - \beta_{i,yxz} + \beta_{i,zxy} - \beta_{i,zyx}) \equiv \sum_i \frac{N_i}{\epsilon_0} \bar{\beta}_i, \quad (3)$$

where the summation is over all orientationally averaged molecular species, and where the i th species is present in number density N_i . The term in parentheses in Eq. (3) vanishes for any molecules that possess reflection planes, a center of inversion, and rotation–reflection axes, and thus $\bar{\beta}_i$ is only non-zero for chiral molecules. It is of opposite sign for the enantiomers of a chiral molecule.

For a solution that contains only two optically active molecular species, namely the R- and S-enantiomers of a chiral molecule, we may write Eq. (3) as

$$\chi^{(2)} = \frac{(N_R - N_S)}{\epsilon_0} \bar{\beta}_R = \frac{1000N_A}{\epsilon_0} ([R] - [S]) \bar{\beta}_R, \quad (4)$$

where N_A is Avogadro's number, $\bar{\beta}_R$ is the $\bar{\beta}$ of the R-enantiomer, and where the square brackets denote a concentration in mol/l. It is seen that $\chi^{(2)}$ is zero for a solution containing an equal number of enantiomers (i.e. a racemate). Since the intensity at the sum-frequency is proportional to the square modulus of the induced polarization at the sum-frequency, it follows that a homodyne sum-frequency signal depends quadratically on the difference in concentration of the two enantiomers. Thus, SFG from a solution depends quadratically on the product of enantiomeric excess with total

¹ We note that in some quantum-chemical calculations the hyperpolarizability contains a divisor of 2! in the expression for the macroscopic susceptibility in Eq. (3). This factor is properly absent in the time-ordered density matrix approach.

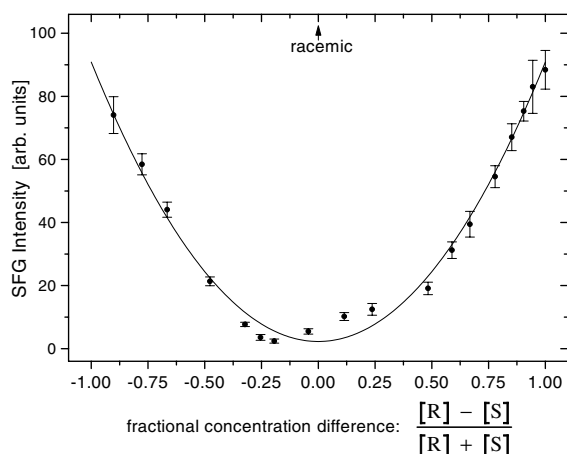


Fig. 1. Dependence of a bulk sum-frequency signal on the difference in concentrations of the R and S enantiomers of 1,1'-bi-2-naphthol (BN) in tetrahydrofuran. The BN concentration is ~ 0.5 M throughout. The solid line is a quadratic function fitted to the data. The input fields are *P*-polarized and the *S*- and *P*-polarized signal field (no analyzer) is detected. The vertical error bars are a measure of the pulse-to-pulse fluctuations of the laser. The errors in determining the fractional concentration difference of the solution are due to uncertainties in pipetting small volumes ($\sim \mu\text{l}$). These errors are largest for the measurements where the fractional concentration difference is within -0.25 and $+0.25$ where they are estimated to be $\sim \pm 0.12$.

enantiomeric concentration². A sum-frequency experiment therefore measures the chirality of a solution and not its handedness [12]. This is demonstrated in Fig. 1 where a quadratic dependence of a SFG signal on the difference in (fractional) concentration of the R-(+)-BN and S-(-)-BN enantiomers is shown. The data are collected in a continuous titration of two ~ 0.5 M solutions of R-(+)-BN and S-(-)-BN in THF and the sum-frequency is observed at 266 nm using the fundamental (800 nm) and harmonic (400 nm) pulses from a Ti:sapphire regenerative amplifier (Clark/MXR) with a repetition rate of 1 kHz and a pulse duration of ~ 160 fs. We estimate that at the sum-frequency 266 nm $|\bar{\beta}(\omega + 2\omega)|$ is ≈ 40 a.u. ($e^3 a_0^3 / E_h^2$). This is in keeping with the many order

of magnitude amplification of $\bar{\beta}$ through resonances as predicted by theory [6] and quantum-chemical computations [9,13,14].

As stated, a purely electric-dipolar bulk response must vanish for a racemic mixture. Higher-order multipolar contributions to the sum-frequency will, however, continue to contribute even when the solution is a racemate. Within the uncertainties of our measurements we estimate that the achiral contribution to the signal are at least ~ 50 times weaker compared to the chiral (electric-dipolar) bulk sum-frequency contribution. As we shall see, these findings are supported by a study of SFG as a function of the polarization of the input fields.

3. Sum-frequency generation beyond the electric-dipole approximation

In the electric dipole approximation (EDA) the spatial variation of the electric field is taken to be constant over the polarizable unit. In the case of a plane monochromatic wave with wave-vector k_x the EDA corresponds to taking

$$e^{ik_x r_x} = 1 + ik_x r_x + \dots \simeq 1. \quad (5)$$

Keeping higher-order terms in $e^{ik_x r_x}$ leads to higher-order multipolar contributions to the interaction Hamiltonian [15] and the polarizabilities [16,17]. In particular, the first-order correction term beyond the EDA, given by $ik_x r_x$, is required to describe processes mediated by a magnetic-dipole or an electric-quadrupole. When considering nonlinear processes that involve several field-actions, we assume the lowest-order correction to the EDA where only one of the fields is taken beyond the EDA. As is well known, transition moments that include the $ik_x r_x$ correction term will be diminished by roughly the ratio of a molecular dimension to the wavelength of light, which, for optical fields and typical molecular sizes, is small and $\approx 10^{-3}$. Nevertheless, magnetic-dipolar and electric-quadrupolar interactions can be of considerable interest in nonlinear spectroscopies, especially when an optical process is symmetry forbidden within the EDA. Such is the case for SFG from achiral isotropic media. For a chiral

² The enantiomeric excess, e.e., is defined as

$$\text{e.e.} = \frac{[R] - [S]}{[R] + [S]}.$$

solution this means that the normally achiral but highly concentrated solvent can give rise to SFG (as well as the more dilute chiral solute).

As already remarked, in the electric-dipole approximation a three-wave mixing process has its molecular basis in the parity-odd first hyperpolarizability, a tensor of the third rank. The corresponding macroscopic susceptibility is related to the hyperpolarizabilities of the constituent molecules by an orientational average that involves three direction cosines each linking the local molecular Cartesian space of the transition electric-dipole moments to the laboratory Cartesian space, which contains the polarization-vectors of the three fields. At the level of the EDA the wave-vectors play no role in this average. However, when the $ik_x r_x$ correction is considered for any one of the three fields, then one additional direction cosine arises (linking wave-vector k_x to the position operator r_x in the molecular frame). Thus one important consequence of including the $ik_x r_x$ correction is that the first hyperpolarizability now contains a field-dependent quantity that is not a tensor property of the medium alone [18]. This correction to the hyperpolarizability and its corresponding susceptibility therefore transform as a parity-even fourth-rank tensor with the condition that the wave-vector is orthogonal to the polarization-vector of the corresponding field (as is required for transverse waves). This switch from third to fourth rank causes survival of a new set of tensor elements under rotational averaging over an isotropic molecular ensemble. A second consequence of the $ik_x r_x$ term is that the matrix element that is taken beyond the EDA now contains an operator that is quadratic in r_x (scaled by $i|k_x|$) instead of the electric-dipole transition moment which is linear in r_x .

We now show how simple polarization experiments provide an easy means to fully discriminate between chirality specific SFG derived at the EDA (and mediated by a third rank susceptibility) and SFG that exists for all isotropic media (and which is mediated by a fourth rank tensor).

We consider two incident electromagnetic waves that may give rise to a sum-frequency (or difference-frequency) wave in an isotropic medium. The subsequent discussion is in terms of S

and P polarized fields. Momentum conservation in an isotropic medium requires that the wave-vectors of all three waves lie in a common plane, and we denote any vector lying in this plane by P . (A collinear geometry can not give rise to SFG in an isotropic medium.) A vector perpendicular to that plane has a unique direction and is designated by S .

From Eq. (2) it is seen that the chirality-specific isotropic component of the second-order susceptibility contains an anti-symmetric combination of all rank three tensor elements in which each of the Cartesian indices appears only once (i.e. the six permutations of the 'XYZ' components). These anti-symmetric tensor components can only be probed in a non-collinear geometry and require two fields to be P -polarized and one field to lie along S . Chirality based SFG in the EDA is hence unique to the PPS , PSP , and SPP polarization combinations of the three waves.

On the other hand, the susceptibility giving rise to achiral SFG – within the $ik_x r_x$ correction – transforms as a fourth-rank tensor. There are three rotationally invariant tensor components at this rank, and they each consist of linear combinations of tensor elements for which *none contains the same Cartesian index an odd number of times* [1]. Due to the wave-vector dependence of this tensor, one of its components is always along P ; and since S is along the same direction for all waves, it follows that achiral SFG may only be observed if there are an even number of S polarized fields. Hence, a non-collinear geometry is required to probe this susceptibility tensor, and only when all three fields are either P -polarized, or when two are S -polarized and the third is P -polarized is it ensured that any Cartesian index appears an even number of times. Thus achiral SFG can only be seen in the SSP , SPS , PSS and PPP polarizations. No bulk SFG of any origin should be seen when all three waves are S -polarized (SSS). These conclusions are summarized in Table 1.

We note that the above results for the bulk differ from second-order nonlinear optical studies of surfaces (second-order processes are allowed in the EDA at an interface due to the broken inversion symmetry) where it is not possible to distin-

Table 1

The polarization combinations that in isotropic media allow bulk SFG (DFG) signals with chiral origin to be distinguished from those that have an achiral origin (see also [11])

Polarizations	Chiral	Achiral
<i>PPP</i>	0	Yes
<i>PPS, PSP, SPP</i>	Yes	0
<i>SSP, SPS, PSS</i>	0	Yes
<i>SSS</i>	0	0

guish higher-order multipolar contributions from the purely electric-dipolar signal [19].

In the SFG experiment with ~ 0.5 M solutions of optically active BN in THF, reported in Fig. 2, the polarization of each of the two incident fields is independently varied from *S* to *P* in 4° increments, and the unpolarized signal (both *S* and *P*) is detected. Given the above conclusions, it follows that any sum-frequency that arises when both incident beams are *S* polarized can only have an achiral origin. The SFG strength in a *SS* experiment thus provides a semi-quantitative measure of the purely magnetic-dipolar and electric-quadrupolar sources to the SFG intensity (as do the signal levels in Fig. 1 when the solution is racemic). For any other

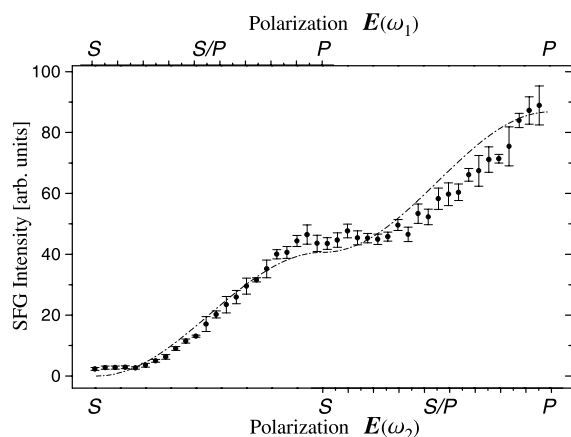


Fig. 2. Bulk sum-frequency signal as a function of the polarizations of the incident fields. The polarization of each of the incident waves is rotated one at a time such that the polarization-vectors of the incident fields are changed from *SS* (for the 800, and 400 nm waves, respectively) to *PS*, and then to *PP*. For lack of a polarizer at 266 nm, both the *S* and *P*-polarized sum-frequency signal is detected from ~ 0.5 M solution of R-(+)-1,1'-bi-2-naphthol in THF. The line is a fit from theory assuming only chiral contributions to the sum-frequency signal.

(not *SS*) polarization state of the incident fields both sources of SFG can contribute to the signal. However, if both fields have a definite polarization state, then the chiral and achiral sum-frequency fields will have orthogonal polarizations and cannot interfere (as seen in Table 1). Should any of the incident beams be of a mixed polarization state (partially *S* and *P*), then the signal may contain a cross term. An interference term between chiral and achiral contributions to the sum-frequency intensity has been observed by Belkin et al. [11]. Should the phase of the chiral and achiral SFG susceptibilities be known from computation, then such a cross term could in principle be used to determine the handedness of the solution. Alternatively, the application of an additional static electric-field to a SFG experiment in a chiral liquid can give rise to an interference term linear in the dc-field that would also allow the determination of the handedness (absolute conformation of the optical isomer) of the solution [20].

The achiral contributions to the sum-frequency signal in Fig. 2 are judged to be small compared to the chirality based SFG in the EDA, as a theoretical fit, that only assumes the presence of chirality based SFG, is seen to follow the observed sum-frequency data quite well. Belkin et al. [10] note the absence of any SFG above the noise using *SPS* and *PPP* beam polarizations in their experiments on chiral BN solutions. Measurements using the chirality-specific *PPS*, *PSP* and *SPP* polarizations give, in the absence of any achiral contributions to the sum-frequency, the identical results to those that do not analyze the signal polarization. Complete three-field polarization experiments are being developed.

4. Conclusions

We show that the origin of sum-frequency generation (mixing of the fundamental at 800 nm with its harmonic to generate the third-harmonic) from optically active solutions of 1,1'-bi-2-naphthol in tetrahydrofuran is the chirality-specific electric-dipolar three-wave-mixing nonlinearity. The signal depends quadratically on the concentration difference of the R and S enantiomers. In

going beyond the electric-dipole approximation sum-frequency generation is symmetry allowed for all media, i.e. even for centrosymmetric isotropic systems (such as any liquid). However, for certain polarization combinations only the purely electric-dipolar contributions are allowed, such that sum- and difference frequency generation can be a truly background-free chiral nonlinear spectroscopy.

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