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Toward Chiral Sum-Frequency Spectroscopy

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Abstract: Chiral sum-frequency (SF) spectroscopy that measures both the real and the imaginary components of the SF spectral response was demonstrated for the first time. It was based on interference of the SF signal with a dispersionless SF reference. Solutions of 1,1′-bi-2-naphthol (BN) were used as model systems, and their chiral SF spectra over the first exciton-split transitions were obtained. Chiral spectra are useful for determination of absolute configuration and conformation of chiral molecules.

Introduction

Optical techniques that distinguish liquids made of molecules of opposite handedness, such as circular dichroism (CD) and optical rotatory dispersion (ORD), have long been important tools in chemistry and biology. Besides being able to differentiate molecules with different chiralities, these techniques are also able to produce chiral spectra that can provide information on molecular structure and conformation. Recently, second-order nonlinear optical processes, second-harmonic generation (SHG) and sum-frequency generation (SFG), have been developed as alternative tools to probe the molecular chirality of monolayers,[1−7] liquids,[8−12] and films.[13−15] Different from CD and ORD, where the chiral response originates from the product of the electric and magnetic dipole transition elements, SHG and SFG originate from pure electric-dipole transition moments. Hence, they have higher sensitivity that allows measurements of optically active (but not chiral) spectra from monolayers and thin films.[16]

To selectively probe the optically active response of a chiral medium, one would choose specific input/output polarization combinations in SHG or SFG.[1,8] The output is then proportional to $|\chi^{(2)}_{\text{chiral}}|^2$, where $\chi^{(2)}_{\text{chiral}}$ is the chiral nonlinear susceptibility that has opposite signs for left-handed and right-handed enantiomers and vanishes for achiral media.[17] Thus the measurement yields only optical activity but not chirality. To distinguish the two enantiomers, interference schemes incorporating some achiral coefficient in the response have been devised.[2,3,6,12] The output is now proportional to $|\chi^{(2)}_{\text{chiral}} + \delta_{\text{achiral}}|^2$, where δ_{achiral} is the incorporated achiral nonlinear response from the medium. This output is clearly different for the two enantiomers. However, such interference measurements cannot produce a chiral spectrum for the medium, i.e., $\chi^{(2)}_{\text{chiral}}(\omega)$, since $\delta_{\text{achiral}}(\omega)$ also carries the spectral response of the medium. Like the CD spectrum, the chiral SHG or SFG spectrum is nevertheless important because it can provide not only the chirality but also information on the chiral structure and conformation of molecules. To obtain a chiral SHG or SFG spectrum with the interference method, we must replace $\delta_{\text{achiral}}(\omega)$ by a dispersionless quantity. In this article, we describe a general scheme in which we use an external reference to produce a dispersionless parameter to replace $\delta_{\text{achiral}}(\omega)$ in the interference that then allows us to deduce the chiral spectrum of $\chi^{(2)}_{\text{chiral}}(\omega)$. We applied this scheme to (*S*)-(−)-1,1′-bi-2-naphthol (S-BN) and (*R*)-(+)-1,1′-bi-2-naphthol (R-BN) solutions and obtained their chiral SFG spectra.

Sum-Frequency Generation from Chiral Liquids

The basic theory for SFG has been described elsewhere.[18] Briefly, when two electromagnetic waves with frequencies ω_1 and ω_2 interact in a medium, a nonlinear polarization $\vec{P}^{(2)}(\omega_s = \omega_1 + \omega_2) = \vec{\vec{\chi}}^{(2)}:\vec{E}_1(\omega_1)\vec{E}_2(\omega_2)$ can be induced, where $\vec{\vec{\chi}}^{(2)}$ is the nonlinear susceptibility of the medium, and $\vec{E}_1$ and $\vec{E}_2$ are the input optical fields. Under the electric-dipole approximation, $\vec{\vec{\chi}}^{(2)}$ is nonzero only if the medium has no inversion symmetry. This is the case of chiral liquids with a net chirality.

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[16] Optical activities usually refer to effects that show whether a system is chiral but cannot distinguish the enantiomers (mirror-image chiral systems). Effects that can distinguish the enantiomers are referred to as “chiral”.
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The isotropy symmetry of a chiral liquid requires that the electric-dipole-allowed nonvanishing $\overleftrightarrow{\chi}^{(2)}$ elements all have the same magnitude and are related by

$$\chi^{(2)}_{xyz} = -\chi^{(2)}_{yxz} = \chi^{(2)}_{yzx} = -\chi^{(2)}_{zyx} = \chi^{(2)}_{zxy} = -\chi^{(2)}_{xzy} \equiv \chi^{(2)}_{\mathrm{chiral}} \quad (1)$$

Here, x, y, and z refer to the Cartesian laboratory coordinates, and $\chi^{(2)}_{\mathrm{chiral}}$ is of opposite signs for the two enantiomeric solutions and zero for a racemic mixture. The nonlinear susceptibility $\chi^{(2)}_{\mathrm{chiral}}$ is resonantly enhanced if any one of the three frequencies, ω_1, ω_2, and ω_s, is resonant with a molecular transition, thus generating a chiral spectrum. For single resonances, $\chi^{(2)}_{\mathrm{chiral}}$ can be written as

$$\chi^{(2)}_{\mathrm{chiral}} = \sum_n \frac{A_n}{\omega - \omega_n + i\Gamma_n} + \chi^{(2)}_{\mathrm{chiral,NR}} \quad (2)$$

Here A_n, ω_n, and Γ_n denote the amplitude, resonant frequency, and damping constant for the nth transition, and $\chi^{(2)}_{\mathrm{chiral,NR}}$ describes the nonresonant contribution. Both chiral electronic and chiral vibrational spectra of $\chi^{(2)}_{\mathrm{chiral}}$ for chiral liquids can be obtained from SF spectroscopic measurements.

In conventional SFG experiments, the output signal is proportional to $|\hat{e}_S \langle\vec{P}^{(2)}(\omega_S)|^2 \propto |\hat{e}_S \langle\overleftrightarrow{\chi}^{(2)}:\hat{e}_1\hat{e}_2|^2$, where $\hat{e}_i$ is the unit polarization vector of the ω_i wave. For chiral liquids, one can use polarization combination SPP (with $\hat{e}_S$, $\hat{e}_1$, and $\hat{e}_2$ corresponding to S-, P-, and P-polarized, respectively), PSP, or PPS to probe $\chi^{(2)}_{\mathrm{chiral}}$, resulting in a SF output signal of[8]

$$S_{\mathrm{SF}} = C|\chi^{(2)}_{\mathrm{chiral,eff}}|^2$$
$$\chi^{(2)}_{\mathrm{chiral,eff}} \equiv F\chi^{(2)}_{\mathrm{chiral}} l_{\mathrm{c}} \quad (3)$$

where C is a constant determined by the experimental geometry and input beam characteristics, F is the product of Fresnel coefficients for input and output fields, and l_{c} is the coherence length. The measurement allows the determination of only $|\chi^{(2)}_{\mathrm{chiral}}|$ but not the phase of $\chi^{(2)}_{\mathrm{chiral}}$. It tells whether the sample is chiral but not its handedness. The corresponding spectrum is therefore an optically active SFG (OA-SFG) spectrum and not a chiral SFG spectrum.

This lack of phase information on $\chi^{(2)}_{\mathrm{chiral}}$ also makes it difficult to determine the relative signs (more generally, phases) of the amplitudes (A_n in eq 2) of different modes in a spectrum. This is illustrated in Figure 1 showing the OA-SFG spectra of solutions of (*S*)-(−)-1,1′-bi-2-naphthol (S-BN) and (*R*)-(+)-1,1′-bi-2-naphthol (R-BN) in tetrahydrofuran with ω_s covering the frequency range of the first two excitonic transitions of BN.[6] As expected, the spectra from S- and R-BN are identical. To deduce molecular structural information from the spectra, one would fit the spectra using eqs 2 and 3. However, the fit may not be unique, especially with respect to the signs of A_n's. As shown in Figure 1, two curves with different parameter sets, one having the same sign and the other having opposite signs for A_n's of the two excitonic transitions, fit the experimental spectra almost equally well. The relative sign of A_n is important, as it is directly related to the molecular configuration.

Chiral Sum-Frequency Spectroscopy

Interference schemes of SHG and SFG have been devised to differentiate enantiomers. In all cases, an achiral contribution is introduced into the SHG/SFG to interfere with the chiral contribution. This can be achieved by adjusting the polarization of one of the input/output waves[2,3,6] or by including a dc electric-field-induced achiral $\overleftrightarrow{\chi}^{(2)}$ component.[12] Denoting the achiral contribution as $c\chi^{(2)}_{\mathrm{achiral}}$ with c being a constant, we can arrange to have two overall SF signals S^{+}_{SF} and S^{-}_{SF},

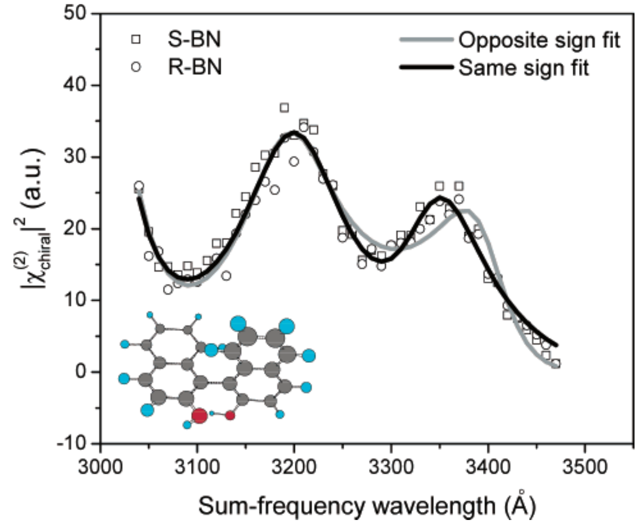

Figure 1. $|\chi^{(2)}_{\mathrm{chiral}}|^2$ versus sum-frequency wavelength from solutions of S- and R-BN. Black and gray curves are fits to the data points using eqs 2 and 3 with A_n's of the two transitions having the same and opposite signs, respectively. The polarization combination used was SPP. The molecular structure of BN is depicted in the inset.

$$S^{\pm}_{\mathrm{SF}} \propto |\chi^{(2)}_{\mathrm{chiral}} \pm c\chi^{(2)}_{\mathrm{achiral}}|^2$$

and their difference,

$$S^{+}_{\mathrm{SF}} - S^{-}_{\mathrm{SF}} \propto 4\mathrm{Re}(\chi^{(2)}_{\mathrm{chiral}}\chi^{(2)*}_{\mathrm{achiral}})$$

For R- and S-enantiomers, $(\chi^{(2)}_{\mathrm{chiral}})_{\mathrm{R}} = -(\chi^{(2)}_{\mathrm{chiral}})_{\mathrm{S}}$, whereas $(\chi^{(2)}_{\mathrm{achiral}})_{\mathrm{R}} = (\chi^{(2)}_{\mathrm{achiral}})_{\mathrm{S}}$. Therefore, the two enantiomers can be distinguished from their respective spectra of S^{+}_{SF} , S^{-}_{SF}, or $S^{+}_{\mathrm{SF}} - S^{-}_{\mathrm{SF}}$.

However, because $\chi^{(2)}_{\mathrm{achiral}}$ of the medium is often resonantly enhanced at the same set of transitions as $\chi^{(2)}_{\mathrm{chiral}}$, $S^{\pm}_{\mathrm{SF}}$ and $S^{+}_{\mathrm{SF}} - S^{-}_{\mathrm{SF}}$ are convoluted spectra of $\chi^{(2)}_{\mathrm{chiral}}$ and $\chi^{(2)}_{\mathrm{achiral}}$. Without knowing the complex $\chi^{(2)}_{\mathrm{achiral}}$ beforehand, the complex values of $\chi^{(2)}_{\mathrm{chiral}}$ cannot be determined. Therefore, these interference schemes cannot yield chiral SF spectra analogous to those by CD and ORD that have been used to deduce the absolute configuration of chiral molecules.

It is obvious that, in order to obtain a chiral SF spectrum, we must interfere $\chi^{(2)}_{\mathrm{chiral}}$ with a dispersionless $\chi^{(2)}_{\mathrm{achiral}}$. This means that we have to use $\chi^{(2)}_{\mathrm{achiral}}$ from an external reference. Here, we demonstrate the scheme using a quartz crystal in contact with the chiral liquids as the reference to supply such a $\chi^{(2)}_{\mathrm{achiral}}$, using an experimental arrangement similar to that of the recently developed phase-sensitive surface SFG spectroscopy.[19]

In this scheme, the liquid is sandwiched between an ordinary fused silica window and a crystalline quartz plate. The input

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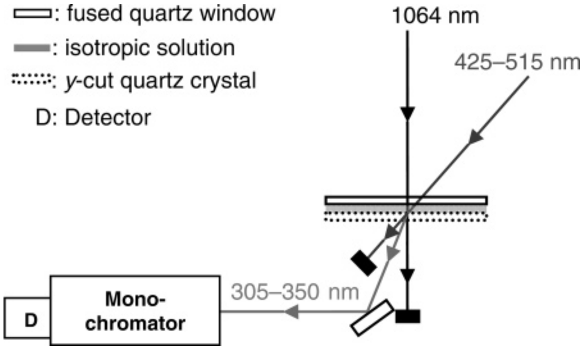

Figure 2. Schematic of the experimental setup. Input beams were overlapped at the liquid interface with the bottom window, and the SF signal was detected in the transmission direction. The polarization combination of the beams was SPP.

beams are overlapped at the liquid−quartz interface, so that the generated sum-frequency signal is given by

$$S_{\mathrm{SF}} = C|\chi^{(2)}_{\mathrm{chiral,eff}} + \chi^{(2)}_{\mathrm{Quartz,eff}}|^2$$

where $\chi^{(2)}_{\mathrm{Quartz,eff}}$ denotes the contribution from the quartz crystal and can be approximated as dispersionless with only a real component in the frequency range of our interest. By properly orienting the crystal azimuthally, $\chi^{(2)}_{\mathrm{Quartz,eff}}$ can be adjusted to equal to zero or $\pm\kappa$, with κ being a real number. We can then measure separately

$$S^0_{\mathrm{SF}} = C|\chi^{(2)}_{\mathrm{chiral,eff}}|^2$$

$$S^{\pm}_{\mathrm{SF}} = C|\chi^{(2)}_{\mathrm{chiral,eff}} \pm \kappa|^2$$

as well as $S^{\mathrm{Q}}_{\mathrm{SF}} = C|\chi^{(2)}_{\mathrm{Quartz,eff}}|^2 = C|\kappa|^2$ from the quartz crystal alone by replacing the chiral liquid with an achiral racemic mixture. Alternatively, S^0_{SF} can be measured by replacing the quartz plate with a fused silica window. We then find, with eq 3,[20]

$$\mathrm{Re}(\chi^{(2)}_{\mathrm{chiral}}) = \frac{S^{+}_{\mathrm{SF}} - S^{-}_{\mathrm{SF}}}{4Fl_c S^{\mathrm{Q}}_{\mathrm{SF}}}\chi^{(2)}_{\mathrm{Quartz,eff}} = \frac{S^{+}_{\mathrm{SF}} - S^{0}_{\mathrm{SF}} - S^{\mathrm{Q}}_{\mathrm{SF}}}{2Fl_c S^{\mathrm{Q}}_{\mathrm{SF}}}\chi^{(2)}_{\mathrm{Quartz,eff}} \tag{4}$$

$$|\mathrm{Im}(\chi^{(2)}_{\mathrm{chiral}})| = [|\chi^{(2)}_{\mathrm{chiral}}|^2 - |\mathrm{Re}(\chi^{(2)}_{\mathrm{chiral}})|^2]^{1/2} \tag{5}$$

Equation 5 indicates that the sign of $\mathrm{Im}(\chi^{(2)}_{\mathrm{chiral}})$ cannot be determined. However, for systems with simple spectral features such as BN, it can be deduced from the dispersion of $\mathrm{Re}(\chi^{(2)}_{\mathrm{chiral}})$ around resonances. For more complicated spectra with multiple overlapping resonances, a simultaneous fit on S^0_{SF} and $\mathrm{Re}(\chi^{(2)}_{\mathrm{chiral}})$ gives the transition amplitudes, from which the sign of $\mathrm{Im}(\chi^{(2)}_{\mathrm{chiral}})$ could be determined unambiguously.

Experimental Arrangement and Materials

As a demonstration, we measured the chiral electronic SFG spectra from S- and R-BN solutions. The experimental arrangement is schematically shown in Figure 2. A tunable visible beam generated by a homemade OPG/OPA pumped by a Nd:YAG laser (PY61C-20, Continuum Inc.) and the 1064 nm beam directly from the laser were overlapped at the interface of the liquid and the bottom window of the liquid cell. The visible beam was tuned from 425 to 515 nm so that the SF output has a wavelength between 304 and 347 nm, in resonance with the first two excitonic transitions of BN. The laser pulse width was around 20 ps, and the energies per pulse were ~2.0 mJ and ~300 μJ for the 1064 nm and the visible beams, respectively. Incident angles are 0° and 45° for the 1064 nm and the visible beams, respectively. The input beams were set to be P-polarized, and the S-polarized SF signal was detected in the transmission direction after spatial and spectral filtering.

A fused silica window was used as the bottom window to obtain the OA-SFG spectra S^0_{SF} from S- and R-BN solutions. To measure the interfered spectrum S^{+}_{SF} , a *y*-cut α-quartz crystal plate was used as the bottom window. Taking advantage of the anisotropy of quartz crystal, we could azimuthally orient it to obtain a value of $\chi^{(2)}_{\mathrm{Quartz,eff}}$ variable from positive to negative so that it can interfere effectively with $\chi^{(2)}_{\mathrm{chiral}}$ from the solution. The SF signal from the quartz crystal alone, $S^{\mathrm{Q}}_{\mathrm{SF}}$, was measured with the racemic mixture solution in contact with the quartz crystal.

S-BN, R-BN, and tetrahydrofuran were purchased from Sigma-Aldrich and used as received. S-BN and R-BN solutions were prepared by dissolving BN samples in tetrahydrofuran. The concentration of BN solutions varied between 0.3 and 0.5 M. All the spectra were normalized by the concentration. The racemic mixture was prepared by dissolving equal amounts of S-BN and R-BN.

Our measurements reported here were carried out with 600 shots per data point, yielding $S/N \leq 1$ for $|\chi^{(2)}_{\mathrm{chiral}}/\Delta k| \leq 1 \times 10^{-21}$ m^2/V, which is the sensitivity limit of our chiral detection. For BN, it corresponds to a concentration of ~0.02 M if only the sum frequency is at resonance in this spectral range. Other chiral molecules, such as amino acids, have a $|\chi^{(2)}_{\mathrm{chiral}}/\Delta k|$ a few times weaker than that of BN. The sensitivity can be improved if the wave vector mismatch Δk can be reduced.

Result and Discussion

The measured S^{+}_{SF} , S^{0}_{SF}, and $S^{\mathrm{Q}}_{\mathrm{SF}}$ spectra allowed the deduction of $\mathrm{Re}(\chi^{(2)}_{\mathrm{chiral}})$ and $\mathrm{Im}(\chi^{(2)}_{\mathrm{chiral}})$ for S- and R-BN, as presented in Figure 3. As expected, both the real and the imaginary components of $\chi^{(2)}_{\mathrm{chiral}}$ have opposite signs for R- and S-BN. The spectra in Figure 3 are the first chiral sum frequency spectra ever reported. The spectra were fitted by eq 2 with two resonant peaks at 320 nm and 340 nm, arising from transitions between the ground state and the first pair of exciton-split excited states of BN.[6] Unlike the OA-SFG spectra in Figure 1, they clearly show that the amplitudes of the exciton-split peaks have opposite signs.

It is well-known in CD that pairs of exciton-split transitions in chiral molecules consisting of two identical chromophores give rise to a bisignate CD spectrum with peaks showing consecutive positive and negative Cotton effects. The locations of the peak and the trough have been used to derive the absolute configuration and conformation of many organic compounds.[21] Although the structural parameters that produce the linear and the nonlinear chiral responses are different,[22] a theory for SFG

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(20) Here we neglect the imaginary part of the refractive index of the chiral liquid, because that of the samples used in our experiment is on the order of 0.01.

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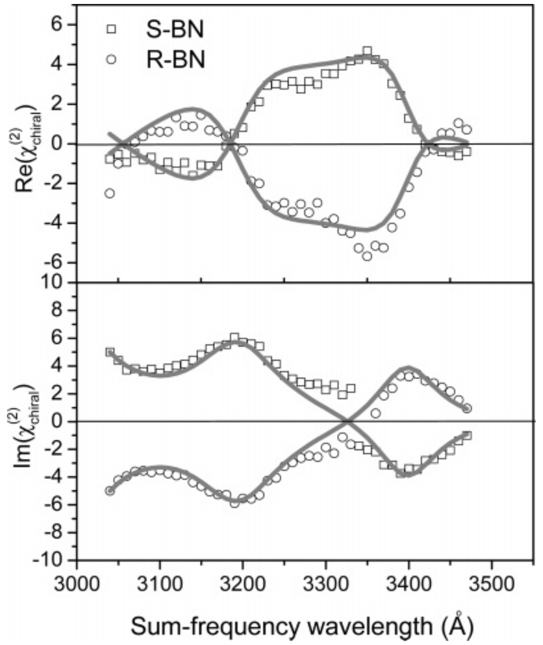

Figure 3. Spectra of real and imaginary components of $\chi^{(2)}_{\text{chiral}}$ over the first two exciton-split transitions of S-BN and R-BN. The curves are fits to the data with eq 2 using the same set of parameters that yields the gray curve for $|\chi^{(2)}_{\text{chiral}}|^2$ in Figure 1.

based on a coupled-oscillator model predicted that pairs of exciton-split peaks should also exhibit the bisignate feature in $\chi^{(2)}_{\text{chiral}}$,[23] which was indeed observed as shown in Figure 3.

In the above analysis, the signs of Re($\chi^{(2)}_{\text{chiral}}$) and Im($\chi^{(2)}_{\text{chiral}}$) are defined with respect to that of $\chi^{(2)}_{\text{Quartz,eff}}$ in eq 4, which is taken as negative. However, in practice, the sign of $\chi^{(2)}_{\text{Quartz,eff}}$ itself is difficult to define. For the same piece of quartz crystal, flipping the crystal upside down makes $\chi^{(2)}_{\text{Quartz,eff}}$ change sign, and so does rotating the crystal by selected angles. Instead of setting the absolute sign of $\chi^{(2)}_{\text{Quartz,eff}}$ by painstakingly defining the orientation of a reference quartz crystal so that different research groups can follow, we propose to use the signs of $\chi^{(2)}_{\text{chiral}}$ of S- and R-BN as the references, against which the sign of $\chi^{(2)}$ of a reference quartz crystal or other dispersionless reference media can be calibrated. We can then determine configurations of other chiral molecules by measuring their chiral SFG spectra with their signs relative to those of BN.[24]

We note in passing that SHG, a special case of SFG, was first employed to probe chiral surfaces by Hicks and co-workers.[1−5] A major difference between SHG and SFG is that SHG is still forbidden in isotropic chiral liquids. In anisotropic chiral systems, SHG is allowed, but the signal depends on both the chirality and the orientation of chiral molecules. A mixed polarization scheme was also used by Hicks and co-workers to distinguish S- and R-enantiomers in SHG,[2,3] but as we discussed earlier, it cannot produce chiral spectra analogous to those of CD and ORD for the enantiomers.

The chiral SFG spectroscopic method described here is generally applicable to all chiral media and can also be used to obtain chiral SF vibrational spectra. In principle, the achiral reference response in the interference is not necessarily dispersionless if the dispersion of its complex $\chi^{(2)}$ is known or measurable, but this is often not easy. The interference method can be viewed as a heterodyne technique: the sensitivity of the $\chi^{(2)}_{\text{chiral}}$ measurement can be significantly enhanced through interference of $\chi^{(2)}_{\text{chiral}}$ with a strong $\chi^{(2)}_{\text{Quartz,eff}}$, as can be seen from comparison of $S^{+}_{\text{SF}} - S^{0}_{\text{SF}} - S^{\text{Q}}_{\text{SF}}$ with S^{0}_{SF}.

Conclusion

We have described an interference technique that allows measurement of true chiral SF spectra, i.e., spectra of both real and imaginary components of the second-order nonlinear chiral response $\chi^{(2)}_{\text{chiral}}$, analogous to ORD and CD in linear optical measurements. To demonstrate the technique, we used chiral S-BN and R-BN solutions as model systems and obtained the first chiral sum-frequency spectra. Having an intrinsically high sensitivity, this chiral SFG spectroscopy could become a powerful analytical tool for studying molecular chirality.

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(24) The signs of $\chi^{(2)}_{\text{chiral}}$ near resonances are directly related, through transition amplitudes, to the chirality of the BN molecules and, more generally, dimer-like chiral molecules. See ref 21 for similar approaches in CD.