Sum-Frequency Vibrational Spectroscopy on Chiral Liquids: A Novel Technique to Probe Molecular Chirality

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Optical activity in sum-frequency vibrational spectra has been observed for the first time in chiral liquids. The electric-dipole allowed chiral element of the nonlinear susceptibility appears to be 3 orders of magnitude smaller than typical allowed achiral elements. This is partly because the observed chirality requires a breakdown of the Born-Oppenheimer approximation.

Chiral molecules play an important role in molecular science including biology and medicine [1]. Optical circular birefringence (CB), circular dichroism (CD), and Raman optical activity (ROA) are the usual techniques used to probe molecular chirality [2]. Recently, nonlinear optical studies of chiral molecules have attracted a great deal of attention. Hicks and co-workers first demonstrated the existence of optical activity in second-harmonic generation (SHG) from a surface monolayer of chiral molecules [3]. Persoons and co-workers also studied SHG from chiral surfaces, monolayers, and films [4]. The main interest in SHG as a chirality probe lies in the fact that the optical coefficients for CB, CD, and ROA are electric-dipole forbidden, while the surface nonlinearity for optically active SHG is electric-dipole allowed.

It seems natural to extend SHG studies of chirality to sum-frequency generation (SFG). With tunable infrared sources, SFG can be used as a vibrational spectroscopic tool [5] and therefore can be a much more powerful probe than SHG. It would allow probing of chirality in vibrational modes associated with selected atomic groups within a chiral molecule.

Like SHG, SFG is electric-dipole allowed at a liquid surface, but, unlike SHG, the chiral components of SFG are also electric-dipole allowed by symmetry in a liquid bulk [6]. Then, as Giordmaine suggested in 1965 [6],

the optically active SFG from the bulk of a chiral liquid would be easily observable. Rentzepis *et al.* did report the observation of the effect in 1966 [7], but their results have not yet been definitely confirmed [8].

In this paper we report the first measurement of optically active SFG vibrational spectra from a number of chiral liquids. We demonstrate the applicability of SFG as a vibrational spectroscopic tool to study chirality, and also confirm experimentally the existence of electric-dipole allowed SFG from the bulk of chiral liquids. We have found that, although the optically active SFG signal enhanced by vibrational resonances is readily detectable, its strength is rather weak, corresponding to a nonlinearity 3 orders smaller than the typical electric-dipole allowed nonlinearity. We understand that this is because the Born-Oppenheimer (adiabatic) approximation is not strictly valid and the chirality in an inherently achiral atomic group, such as CH_2 or CH, is present only because of *perturbation* from the chiral molecular structure. In our case, the chiral SFG signal is observable in transmission owing to the relatively long coherence length of the interaction, but it is too weak to be observed in reflection or from a surface monolayer.

Consider two input waves $\vec{E}_1$ and $\vec{E}_2$ at frequencies ω_1 (visible) and ω_2 (infrared) with wave vectors $\vec{k}_1$ and $\vec{k}_2$, respectively, interacting in a medium. The effective nonlinear polarization induced can be written in the form [9]

$$
\begin{aligned}
\vec{P}_{\text{eff}}^{(2)}(\omega) &= \vec{P}^{(2)}(\omega) - \vec{\nabla} \cdot \overleftrightarrow{Q}^{(2)}(\omega) + \frac{i}{\omega}\vec{\nabla} \times \vec{M}^{(2)}(\omega) + \dots, \\
\vec{P}^{(2)}(\omega) &= \epsilon_0 \overleftrightarrow{\chi}^{eee} : \vec{E}_1\vec{E}_2 + \epsilon_0 \overleftrightarrow{\chi}^{eqe} : \vec{k}_1\vec{E}_1\vec{E}_2 + \epsilon_0 \overleftrightarrow{\chi}^{eeq} : \vec{k}_2\vec{E}_1\vec{E}_2 + \epsilon_0 \overleftrightarrow{\chi}^{eme} : (\vec{k}_1 \times \vec{E}_1)\vec{E}_2 \\
&\quad + \epsilon_0 \overleftrightarrow{\chi}^{eem} : \vec{E}_1(\vec{k}_2 \times \vec{E}_2), \\
\overleftrightarrow{Q}^{(2)}(\omega) &= \epsilon_0 \overleftrightarrow{\chi}^{qee} : \vec{E}_1\vec{E}_2, \\
\vec{M}^{(2)}(\omega) &= \omega\,\epsilon_0 \overleftrightarrow{\chi}^{mee} : \vec{E}_1\vec{E}_2,
\end{aligned}
\tag{1}
$$

where $\omega = \omega_1 + \omega_2$, $\vec{P}^{(2)}$, $\overleftrightarrow{Q}^{(2)}$, and $\vec{M}^{(2)}$ denote the electric-dipole polarization, electric-quadrupole polarization, and magnetization, respectively, and $\overleftrightarrow{\chi}$'s are the second-order nonlinear susceptibilities.

In an achiral liquid, symmetry arguments yield $\overleftrightarrow{\chi}^{eee} = 0$, and the only nonvanishing elements stem from electric-quadrupole and magnetic-dipole allowed $\overleftrightarrow{\chi}_{QM}$ (we shall use $\overleftrightarrow{\chi}_{QM}$ to represent $\overleftrightarrow{\chi}^{eqe}$, $\overleftrightarrow{\chi}^{eme}$, etc.) [10]. In a chiral

liquid, however, $\chi_{ijk}^{eee} = \chi_{\text{chiral}} \cdot e_{ijk}$, where e_{ijk} is the Levi-Civita symbol, does not vanish. There exist no chiral elements (i.e., the elements that are different for different enantiomers) in $\overleftrightarrow{\chi}_{QM}$. If χ_{chiral} were of the same order of magnitude as a typical electric-dipole allowed element of $\overleftrightarrow{\chi}^{(2)}$, e.g., that of quartz, we would expect to observe optically active SFG easily.

In terms of the nonlinear polarizability elements $\alpha_{\xi\eta\zeta}^{(2)}$ of a molecule, we have [6]

$$\chi_{\text{chiral}} = \frac{1}{\epsilon_0} NL(\omega)L(\omega_1)L(\omega_2) \cdot \alpha_{\text{chiral}}, \qquad (2)$$

where

$$\alpha_{\text{chiral}} \equiv \frac{\alpha_{\xi\eta\zeta}^{(2)} - \alpha_{\xi\zeta\eta}^{(2)} + \alpha_{\zeta\xi\eta}^{(2)} - \alpha_{\zeta\eta\xi}^{(2)} + \alpha_{\eta\zeta\xi}^{(2)} - \alpha_{\eta\xi\zeta}^{(2)}}{6}.$$

Here ξ, η, and ζ are three different molecular coordinates, N is the number of molecules per unit volume, and $L(\omega_i) = \frac{\epsilon(\omega_i)+2}{3}$ is the Lorentz local-field correction factor at ω_i with $\epsilon(\omega_i)$ being the dielectric constant at ω_i. If ω_2 is near a vibrational resonance, then the resonant part of $\overleftrightarrow{\alpha}^{(2)}$ can be expressed as [11]

$$(\alpha_q^{(2)})_{\xi\eta\zeta} = \frac{1}{2\omega_q} \frac{\partial\alpha_{\xi\eta}}{\partial Q_q} \frac{\partial\mu_\zeta}{\partial Q_q} \frac{1}{\omega_2 - \omega_q + i\Gamma_q}, \qquad (3)$$

where ω_q is the resonance frequency, Q_q is the normal coordinate, $\frac{\partial\alpha_{\xi\eta}}{\partial Q_q}$ is the Raman polarizability element, and μ_ζ is the dipole moment along ζ for the qth vibrational mode. It was shown in Ref. [12] that, for ω_1 and ω far from resonance (as in our experiment), the antisymmetric Raman components are appreciable only when the adiabatic approximation for electron-vibrational coupling breaks down, but still only $\sim 10^{-2}$ times as large as the symmetric components of $\frac{\partial\alpha_{\xi\eta}}{\partial Q_q}$. We therefore expect α_{chiral} to be no more than $\sim 10^{-2}$ times the typical achiral element of $\overleftrightarrow{\alpha}^{(2)}$, or electric-dipole allowed χ_{chiral} to be about the same as the elements of $\overleftrightarrow{\chi}_{QM}$.

The SFG signal with the $(\hat{e}, \hat{e}_1, \hat{e}_2)$ input/output polarization combinations is generally given by [5]

$$I(\omega) = \frac{\omega^2}{8\epsilon_0 c^3 \cos^2(\beta)} |\chi_{\text{eff}}^{(2)}|^2 I_1(\omega_1) I_2(\omega_2),$$

$$\chi_{\text{eff}}^{(2)} = [\overleftrightarrow{F}(\omega) \cdot \hat{e}] \cdot \overleftrightarrow{\chi}_T^{(2)} : [\overleftrightarrow{F}(\omega_1) \cdot \hat{e}_1][\overleftrightarrow{F}(\omega_2) \cdot \hat{e}_2],$$

$$\overleftrightarrow{\chi}_T^{(2)} = \overleftrightarrow{\chi}_S^{(2)} + \overleftrightarrow{\chi}_B^{(2)}/\Delta k_z,$$

$$\Delta k_z = k_z - k_{1z} - k_{2z}, \qquad (4)$$

where $\omega = \omega_1 + \omega_2$ and $\vec{k}$ are the frequency and the wave vector of sum-frequency (SF) beam, $I_i(\omega_i)$ is the beam intensity at ω_i, β is the exit angle of the SF beam in air, $\overleftrightarrow{F}(\omega_i)$ is the tensorial Fresnel transmission factor at ω_i at the interface, $\overleftrightarrow{\chi}_S^{(2)}$ is the surface nonlinear susceptibility, $\overleftrightarrow{\chi}_B^{(2)} \equiv \vec{P}_{\text{eff}}^{(2)}/(\vec{E}_1\vec{E}_2)$ is the bulk nonlinear susceptibility $\{[\chi_B^{(2)}]_{ijk}(i \neq j \neq k) = \chi_{\text{chiral}} \cdot e_{ijk}$ is responsible for the optically active SFG$\}$, $l_{\text{coh}} \equiv 1/|\Delta k_z|$ is the coherence

length of the interaction, and $\hat{z}$ is along the surface normal. Equation (4) is valid for SFG in both transmission and reflection, but l_{coh} is about 20 times larger for transmission than for reflection. Therefore the contribution from $\overleftrightarrow{\chi}_B^{(2)}$ to the SFG signal is much weaker in reflection [~ 400 times weaker than in transmission if the contribution from $\overleftrightarrow{\chi}_S^{(2)}$ is negligible]. Both $\overleftrightarrow{\chi}_S^{(2)}$ and $\overleftrightarrow{\chi}_B^{(2)}$ can be decomposed into a resonant part and a nonresonant background. We can write, in general,

$$\begin{aligned} \overleftrightarrow{\chi}_S^{(2)} &= \overleftrightarrow{\chi}_S^{NR} + \overleftrightarrow{\chi}_S^{R}, \\ \overleftrightarrow{\chi}_B^{(2)} &= \overleftrightarrow{\chi}_B^{NR} + \overleftrightarrow{\chi}_B^{R}, \end{aligned} \qquad (5)$$

with $\overleftrightarrow{\chi}_{S,B}^{R} = \sum_q \frac{(\overleftrightarrow{A}_q)_{S,B}}{\omega_1 - \omega_q + i\Gamma_q}$. With this expression for $\overleftrightarrow{\chi}_S^{(2)}$ and $\overleftrightarrow{\chi}_B^{(2)}$, Eq. (4) describes the SFG vibrational spectrum.

To access χ_{chiral} of a chiral liquid by SFG, we must have components of $\vec{E}(\omega_1)$, $\vec{E}(\omega_2)$, and $\vec{P}_{\text{eff}}^{(2)}(\omega)$ mutually perpendicular to each other. This is achieved by overlapping the two input beams at an angle at the entrance to the liquid and having an input/output polarization combination of SPP ($\hat{e}$, $\hat{e}_1$, and $\hat{e}_2$ being S, P, and P polarized, respectively), PSP, or PPS. In such a geometry, no achiral component of $\overleftrightarrow{\chi}_T^{(2)}$ contributes to the SFG output. The achiral elements can be accessed separately by the SSP, SPS, and PPP polarization combinations.

Our experimental arrangement, shown schematically in Fig. 1(a), is similar to the one described in [10]. The two input beams, one fixed at 0.532 μm and the other tunable in the infrared between 3.6 and 3.2 μm (2800–3100 cm^{-1}), were generated by a mode-locked Nd:YAG laser system. They both had a pulse width of ~ 25 psec and a repetition rate of 10 Hz. Their pulse intensities were 800 and 200 μJ per pulse, respectively. The two beams overlapped at 90° over an area of 2.5×10^{-3} cm^2 on the sample. The SF output was detected by a gated detector system. The directions of SF output in both transmission and reflection were determined by the requirement $k_{1x} + k_{2x} = k_x$, with $\hat{x}$ being along the surface. Tuning the infrared input over vibrational resonances of the sample yields the SFG vibrational spectrum. The samples we studied were chiral liquids in an optical cell with fused quartz windows. The cell thickness of 0.5 mm was much larger than l_{coh}. We shall focus our discussion on limonene [Fig. 1(b)].
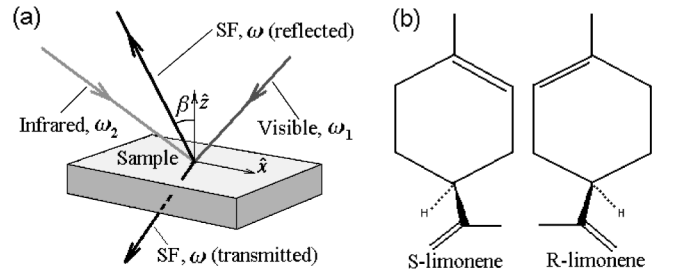

FIG. 1. (a) Experimental setup. (b) Molecular structure of S- and R-limonene.

Figure 2 displays the SFG spectra in the CH stretch region for the two enantiomers of limonene and their racemic mixture obtained in transmission with *SPP*, *PSP*, *SSP*, *PPP*, and *SPS* polarization combinations. The spectra were normalized with respect to a reference crystalline quartz plate. The "achiral" *SSP*, *PPP*, and *SPS* spectra come only from the achiral elements of $\overleftrightarrow{\chi}_T^{(2)}$ in Eq. (4), whereas the "chiral" *SPP* and *PSP* spectra originate only from the chiral elements. They are clearly very different, indicating that the vibrational modes with strong chirality are not necessarily the dominant modes in achiral SFG spectra.

The spectra in Fig. 2 provide the following information. (i) The achiral SFG spectra for the two limonene enantiomers and the racemic mixture appear to be the same. The chiral SFG spectra for the two enantiomers are also identical, and, for the racemic mixture, no chiral SFG signal can be detected. This clearly indicates that we have observed optically active SFG and the associated vibrational spectrum for chiral limonene. (ii) The peaks in the chiral spectra are ~25 times stronger than the ones in the achiral *SPS* spectrum. As will be discussed later, the *SPS* spectrum is dominated by bulk contribution from the electric-dipole forbidden $\overleftrightarrow{\chi}_{QM}$. From the chiral and achiral spectra and Eq. (4), we estimated χ_{chiral} and the elements of $\overleftrightarrow{\chi}_{QM}$ and found that they have comparable magnitudes, as was predicted. (iii) The chiral spectra yield $|\chi_{\text{chiral}}(\omega_1)|^2$, which is shown in Fig. 3. Fitting $|\chi_{\text{chiral}}(\omega_1)|^2$ by Eqs. (4) and (5) allows us to deduce the characteristic parameters for each vibrational mode. They are shown in Table I. We assigned the observed resonances in the chiral spectra as follows [13]: symmetric CH_2 stretch at 2839 cm^{-1}, symmetric CH_3 stretch at

2879 cm^{-1}, CH stretch at 2905 cm^{-1}, antisymmetric CH_2 stretch at 2936 cm^{-1}, and a very weak symmetric stretch of the C=C double bonded CH_2 group at 2990 cm^{-1} (not shown in the table). (iv) The values of $|\alpha_{\text{chiral}}|$ at resonance deduced from $|\chi_{\text{chiral}}|$ for different modes using Eq. (2) are also listed in Table I. They are more than 3 orders of magnitude smaller than the typical resonant value of $\sim 2 \times 10^{-50} \frac{\text{m}^3\text{C}}{\text{V}^2}$ of an achiral element of $\overleftrightarrow{\alpha}^{(2)}$ for a CH_x stretch vibration [14]. The result supports our theoretical prediction discussed earlier.

As a chiral response, χ_{chiral} should change sign for the two enantiomers [6]. This can be checked by using *PMP* input/output polarization combinations, where *M* ("mixed") refers to a linear polarization of the visible beam at $\pm 45°$ from its plane of incidence. From Eq. (4), we then have

$$(\chi_{\text{eff}}^{(2)})_{\pm} = \frac{1}{\sqrt{2}}[(\chi_{\text{eff}}^{(2)})_{PSP} \pm (\chi_{\text{eff}}^{(2)})_{PPP}]. \qquad (6)$$

Therefore, the SFG output proportional to $|(\chi_{\text{eff}}^{(2)})_{\pm}|^2$ should display interference between the chiral and achiral contributions so that the spectra of $|(\chi_{\text{eff}}^{(2)})_{+}|^2$ and $|(\chi_{\text{eff}}^{(2)})_{-}|^2$ are different.

Figure 4 shows that this is indeed the case for both enantiomers of limonene. With

$$|(\chi_{\text{eff}}^{(2)})_{+}|^2 - |(\chi_{\text{eff}}^{(2)})_{-}|^2 = (\chi_{\text{eff}}^{(2)})_{PSP}(\chi_{\text{eff}}^{(2)})_{PPP}^* \\ + (\chi_{\text{eff}}^{(2)})_{PSP}^*(\chi_{\text{eff}}^{(2)})_{PPP}, \qquad (7)$$

we notice that, since $(\chi_{\text{eff}}^{(2)})_{PSP} \propto \chi_{\text{chiral}}$ changes sign when *R*-limonene is switched to *S*-limonene, the difference spectrum must be inverted, as actually seen in Fig. 4(c). Note that the peak strength in the difference spectra depends on the product of the chiral and achiral strengths at the same frequency.

We also measured SFG in reflection from the limonene liquids (limonene/quartz interface). No chiral signal could be distinguished from noise. The achiral *SPS* spectrum was also hardly observable. Since l_{coh} is ~20 times less for SFG in reflection than in transmission, we can conclude, following Eq. (4), that the *SPS* spectrum from transmission is dominated by the bulk contribution through $\overleftrightarrow{\chi}_{QM}$.
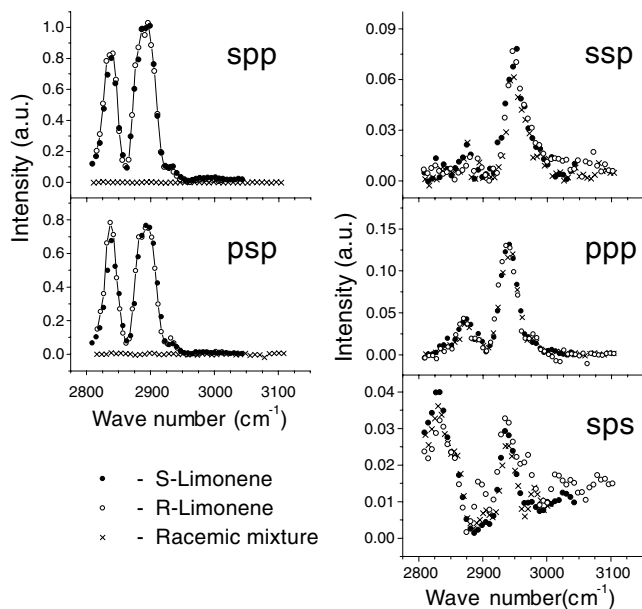
FIG. 2. SFG spectra of limonene samples in transmission in *SPP*, *PSP* (chiral spectra), *SSP*, *SPS*, and *PPP* (achiral spectra) polarization combinations.
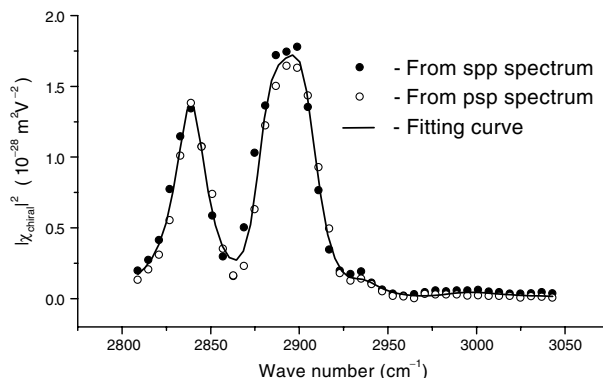
FIG. 3. Measured spectral dependence of $|\chi_{\text{chiral}}|^2$.

TABLE I.   Molecular vibrational modes and their chiral nonlinear amplitudes obtained from fitting SFG spectra with chiral polarization combinations.

q	$\omega_q/2\pi c$	$\Gamma_q/2\pi c$	$A_q/2\pi c$	$\|(\alpha_{\text{chiral}})_q\|$
CH_2^{sym}	2839 cm^{-1}	11 cm^{-1}	13×10^{-12} V^{-1}	1.3×10^{-53} $\frac{\text{m}^3\text{C}}{\text{V}^2}$
CH_3^{sym}	2879 cm^{-1}	12 cm^{-1}	11×10^{-12} V^{-1}	1.0×10^{-53} $\frac{\text{m}^3\text{C}}{\text{V}^2}$
CH	2905 cm^{-1}	13 cm^{-1}	-16×10^{-12} V^{-1}	1.3×10^{-53} $\frac{\text{m}^3\text{C}}{\text{V}^2}$
CH_2^{asym}	2936 cm^{-1}	11 cm^{-1}	2.1×10^{-12} V^{-1}	0.2×10^{-53} $\frac{\text{m}^3\text{C}}{\text{V}^2}$

We can also conclude from the absence of chiral spectra in reflection that the contribution from $\overleftrightarrow{\chi}_S^{(2)}$ to the chiral SFG signal observed in transmission is negligible (if any).

In conclusion, we observed, for the first time, optical activity in the SFG vibrational spectra of chiral liquids and thus proved the applicability of SFG as a vibrational spectroscopic tool to study chirality. The characteristic features appear as expected, but the chiral nonlinear polarizability element, which is electric-dipole allowed, is found to be about 3 orders of magnitude smaller than a typical achiral component. This can be understood from the fact that the observed effect requires a breakdown of the Born-Oppenheimer approximation to induce an antisymmetric component in the Raman polarizability associated with the vibrational resonances. That chirality is induced in inherently achiral atomic groups by perturbation results in further reduction. While the work reported here is focused on limonene, we have obtained similar results from other chiral liquids: carvone, menthylacetate, and 2-butanol.

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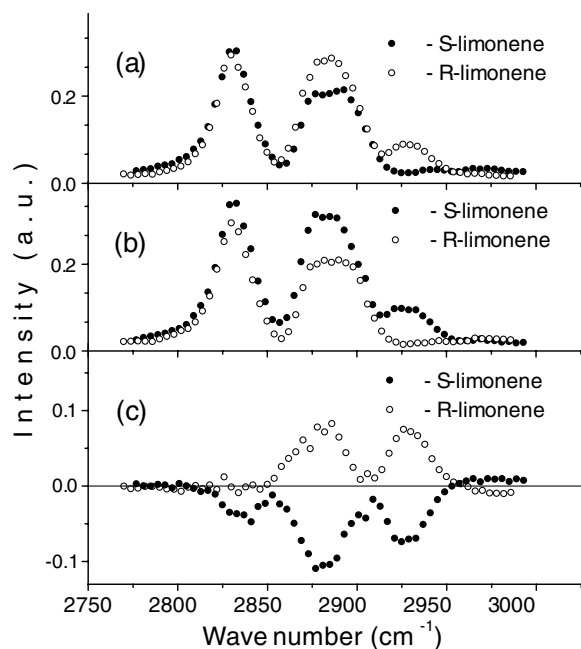
FIG. 4.   Spectra of *S*- and *R*-limonene in mixed polarization combinations: (a) $|(\chi_{\text{eff}}^{(2)})_+|^2$, (b) $|(\chi_{\text{eff}}^{(2)})_-|^2$, and (c) $|(\chi_{\text{eff}}^{(2)})_+|^2 - |(\chi_{\text{eff}}^{(2)})_-|^2$.