

Supplemental Material for “**Sum-frequency vibrational spectroscopy of limonene chiral liquids due to the nonadiabatic effect**”

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## 1. The chiral nonlinear susceptibility

The chiral nonlinear susceptibility  $\chi_{chiral}^{(2)}(\omega, \omega_2)$  is written into<sup>2,16</sup>

$$\begin{aligned}\chi_{chiral}^{(2)}(\omega, \omega_2) &= \frac{1}{6\epsilon_0} N_B L(\omega)L(\omega_1)L(\omega_2) \cdot \sum_{ijk} p_{ijk} \alpha_{ijk}^{(2)} \\ &= \frac{1}{\epsilon_0} N_B L(\omega)L(\omega_1)L(\omega_2) \frac{\alpha_{xyz}^{(2)} - \alpha_{yxz}^{(2)} + \alpha_{zxy}^{(2)} - \alpha_{xzy}^{(2)} + \alpha_{yzx}^{(2)} - \alpha_{zyx}^{(2)}}{6},\end{aligned}\quad (s1)$$

where x, y and z refer to the molecular Cartesian coordinates. The hyperpolarizability

$\alpha_{ijk}^{(2)}$  is given by

$$\alpha_{ijk}^{(2)} = \frac{\langle g,1 | \mu_k | g,0 \rangle}{\hbar(\omega_2 - \omega_{(g,1)(g,0)} + i\Gamma_{(g,1)(g,0)})} \cdot M_{ij}.\quad (s2)$$

Here the anti-Stokes Raman tensor  $M_{ij}$  is written as

$$M_{ij} = \frac{1}{\hbar} \sum_{n,\delta} \left[ \frac{\langle g,0 | \mu_i | n,\delta \rangle \langle n,\delta | \mu_j | g,1 \rangle}{\omega - \omega_{(n,\delta)(g,0)} + i\Gamma_{(n,\delta)(g,0)}} - \frac{\langle g,0 | \mu_j | n,\delta \rangle \langle n,\delta | \mu_i | g,1 \rangle}{\omega - \omega_{(g,1)(n,\delta)} + i\Gamma_{(g,1)(n,\delta)}} \right].\quad (s3)$$

The definition of the symbols can be found in our text. Thus Eq. (s1) can be written

into:

$$\begin{aligned}\chi_{chiral}^{(2)}(\omega, \omega_2) &= \frac{1}{\epsilon_0} \frac{N_B L(\omega)L(\omega_1)L(\omega_2)}{\hbar(\omega_2 - \omega_{(g,1)(g,0)} + i\Gamma_{(g,1)(g,0)})} \times \\ &\frac{\langle g,1 | \mu_z | g,0 \rangle (M_{xy} - M_{yx}) + \langle g,1 | \mu_y | g,0 \rangle (M_{zx} - M_{xz}) + \langle g,1 | \mu_x | g,0 \rangle (M_{yz} - M_{zy})}{6}\end{aligned}\quad (s4)$$

$M_{ij}$  can be the sum of A and B terms:

$$M_{ij} = A_{ij} + B_{ij}.\quad (s5)$$

The expression of  $A_{ij}$  is<sup>2,16</sup>

$$\begin{aligned}A_{ij} &= \frac{1}{\hbar} \sum_{n \neq g} \left[ \left( \frac{\mu_i^{ng} \mu_j^{ng} \omega_{(n,1)(n,0)} \langle 0_g | 1_n \rangle}{(\omega - \omega_{(n,0)(g,0)} + i\Gamma_{(n,0)(g,0)}) (\omega - \omega_{(n,1)(g,0)} + i\Gamma_{(n,1)(g,0)})} \right) \right. \\ &\left. + \left( \frac{\mu_i^{ng} \mu_j^{ng} \omega_{(n,1)(n,0)} \langle 0_g | 1_n \rangle}{(\omega - \omega_{(g,1)(n,0)} + i\Gamma_{(g,1)(n,0)}) (\omega - \omega_{(g,1)(n,1)} + i\Gamma_{(g,1)(n,1)})} \right) \right].\end{aligned}\quad (s6)$$

From the above equation, we find that  $A_{ij}$  is symmetric and  $A_{ij} = A_{ji}$ , i.e.,  $A_{xy} = A_{yx}$ ,

$A_{zx} = A_{xz}$  and  $A_{zy} = A_{yz}$ . Substituting  $A_{ij}$  into Eq.(s4), we found that

$$\chi_{chiral}^{(2)}(\omega, \omega_2) = \frac{1}{\epsilon_0} \frac{N_B L(\omega) L(\omega_1) L(\omega_2)}{\mathbf{h}(\omega_2 - \omega_{(g,1)(g,0)} + i\Gamma_{(g,1)(g,0)})} \times \frac{\langle g,1 | \mu_z | g,0 \rangle (A_{xy} - A_{yx}) + \langle g,1 | \mu_y | g,0 \rangle (A_{zx} - A_{xz}) + \langle g,1 | \mu_x | g,0 \rangle (A_{yz} - A_{zy})}{6}. \quad (s7)$$

Due to the expressions  $A_{xy} - A_{yx} = 0$ ,  $A_{zx} - A_{xz} = 0$  and  $A_{yz} - A_{zy} = 0$ , Eq. (s7)

is zero.  $A_{ij}$  is symmetric and it has no influence on the chiral SFVS. Just as we know,

only the antisymmetric anti-Stokes Raman tensor contributes to the bulk chiral SFVS.

The expression of  $B_{ij}$  is<sup>2,16</sup>

$$B_{ij} = B_{ij}^s + B_{ij}^a. \quad (s8)$$

Where the symmetric part  $B_{ij}^s$  is<sup>16</sup>

$$B_{ij}^s = \frac{1}{2\mathbf{h}^2} \sum_{n \neq g} \sum_{s < n, \neq g} V_{sn} \langle 0 | Q | 1 \rangle \left[ \left( \frac{1}{(\omega - \omega_{(n,1)(g,0)} + i\Gamma_{(n,1)(g,0)}) (\omega - \omega_{(s,0)(g,0)} + i\Gamma_{(s,0)(g,0)})} - \frac{1}{(\omega - \omega_{(n,0)(g,0)} + i\Gamma_{(n,0)(g,0)}) (\omega - \omega_{(s,1)(g,0)} + i\Gamma_{(s,1)(g,0)})} \right) - \left( \frac{1}{(\omega - \omega_{(g,1)(n,1)} + i\Gamma_{(g,1)(n,1)}) (\omega - \omega_{(g,1)(s,0)} + i\Gamma_{(g,1)(s,0)})} - \frac{1}{(\omega - \omega_{(g,1)(n,0)} + i\Gamma_{(g,1)(n,0)}) (\omega - \omega_{(g,1)(s,1)} + i\Gamma_{(g,1)(s,1)})} \right) \right] (\mu_i^{ng} \mu_j^{sg} + \mu_j^{ng} \mu_i^{sg}) \quad (s9)$$

From Eq.(s9), we discover that  $B_{ij}^s$  is symmetric and  $B_{ij}^s = B_{ji}^s$ . Similar to the

discussion for  $A_{ij}$ , we can find that the symmetric part  $B_{ij}^s$  has no contribution to chiral

nonlinear susceptibility.

The anti-symmetric part  $B_{ij}^a$  is<sup>16</sup>

$$\begin{aligned}
B_{ij}^a = & \frac{-1}{2\hbar^2} \sum_{n \neq g} \sum_{s < n, \neq g} V_{sn} \langle 0 | Q | 1 \rangle \left[ \frac{1}{(\omega - \omega_{(n,1)(g,0)} + i\Gamma_{(n,1)(g,0)}) (\omega - \omega_{(s,0)(g,0)} + i\Gamma_{(s,0)(g,0)})} \right. \\
& - \frac{1}{(\omega - \omega_{(n,0)(g,0)} + i\Gamma_{(n,0)(g,0)}) (\omega - \omega_{(s,1)(g,0)} + i\Gamma_{(s,1)(g,0)})} \\
& - \frac{1}{(\omega - \omega_{(g,1)(n,1)} + i\Gamma_{(g,1)(n,1)}) (\omega - \omega_{(g,1)(s,0)} + i\Gamma_{(g,1)(s,0)})} \\
& \left. - \frac{1}{(\omega - \omega_{(g,1)(n,0)} + i\Gamma_{(g,1)(n,0)}) (\omega - \omega_{(g,1)(s,1)} + i\Gamma_{(g,1)(s,1)})} \right] (\mu_i^{ng} \mu_j^{sg} - \mu_j^{ng} \mu_i^{sg})
\end{aligned} \quad . \quad (s10)$$

Where  $B_{ij}^a$  is not symmetric and  $B_{ij}^a \neq B_{ji}^a$ . Thus the anti-symmetric part  $B_{ij}^a$  has influence on the chiral nonlinear susceptibility.

## 2. Fermi resonance and SFVS

From Ref. [s1], we know that when the UV/visible light is off electronic resonance and the IR light is close to the vibrational resonance, the molecular hyperpolarizability can be written into

$$\alpha_{\xi\eta\zeta}^{(2)} = \frac{1}{\hbar} \langle Gg | \mu_\zeta | Nn \rangle \langle Nn | \alpha_{\xi\eta} | Gg \rangle \frac{1}{\omega_2 - \omega_q + i\Gamma_q} . \quad (s11)$$

Where  $\mu_\zeta$  is the dipole moment,  $\alpha_{\xi\eta}$  is the polarizability, and the vibrational wavefunctions due to the Femi resonance are

$$\begin{aligned}
n^+ &= |1_t 0_s\rangle - \frac{iV}{\omega_1 - 2\omega_2} |0_t 2_s\rangle, \\
n^- &= |0_t 2_s\rangle - \frac{iV}{\omega_1 - 2\omega_2} |1_t 0_s\rangle.
\end{aligned} \quad (s12)$$

From the above functions, we find that the intensities from the Femi resonance is inversely proportional to the frequency difference between the double frequency  $2\omega_2$  of the C-H bending and the C-H stretching vibrational frequency  $\omega_1$ . Only the frequency difference that is small has important influence on vibrational wavefunctions and the

corresponding SFVS intensities. From Ref. [s1], the frequencies  $\omega^\pm$  under the influence of the Femi resonance for  $n^+$  and  $n^-$  are respectively

$$\omega^\pm = \frac{\omega_1 + 2\omega_2}{2} \pm \sqrt{\left(\frac{\omega_1 - 2\omega_2}{2}\right)^2 + V^2}. \quad (\text{s13})$$

Where  $V$  is the off-diagonal element (the detailed definition can be found in Ref. [s1]).

The frequencies are shifted due to the Femi resonance. However, when  $V$  is small, the frequencies  $\omega^\pm$  can be reduced to<sup>s1</sup>

$$\begin{aligned} \omega^+ &= \omega_1, \\ \omega^- &= 2\omega_2. \end{aligned} \quad (\text{s14})$$

Thus the Femi resonance shifts the frequencies that are small when off-diagonal element  $V$  is not large.

From Ref. [23], there is the SFVS at methanol/vapor interface where there are SFVS peaks due to the Femi resonance, Generally, the SFVS intensity from  $\text{CH}_3$  symmetric stretching vibration are much stronger than that from the  $\text{CH}_3$  anti-symmetric vibration. However, due to the Femi resonance, the SFVS intensity from the  $\text{CH}_3$ -Femi can be compared with the symmetric one. Hence, the Femi resonance can enhance the SFVS intensity. In our manuscript, the SFVS intensity weaker than experiment. If the Femi resonance is taken into account, the SFVS intensity may become larger and agree well with experiment.

### 3. Rotational invariants for Raman

Rotational invariants for Raman is defined in Ref. [30]. The Raman scattering cross section is<sup>30</sup>

$$\frac{d\sigma}{d\Omega} = \left[ \frac{2\pi(v_0 - v_t)}{c} \right]^4 \frac{1}{30[1 - \exp(hcv_t / k_B T)]} (10\Sigma^0 + 5\Sigma^1 + 7\Sigma^2), \quad (\text{s15})$$

Where  $c$  is light speed,  $k_B$  is the Boltzmann constant and  $T$  is temperature. For randomly oriented scattering systems, the differential scattering cross-sections for the scattered light polarized parallel to the polarization of the input light and the other polarized perpendicular to it are respectively

$$\left( \frac{d\sigma}{d\Omega} \right)_{para} = \left[ \frac{2\pi(v_0 - v_t)}{c} \right]^4 \frac{1}{30[1 - \exp(hcv_t / k_B T)]} (10\Sigma^0 + 4\Sigma^2), \quad (\text{s16})$$

$$\left( \frac{d\sigma}{d\Omega} \right)_{perp} = \left[ \frac{2\pi(v_0 - v_t)}{c} \right]^4 \frac{1}{30[1 - \exp(hcv_t / k_B T)]} (5\Sigma^1 + 3\Sigma^2), \quad (\text{s17})$$

where  $v_t$  is the vibrational frequency for the  $t$  mode,  $\Sigma^0$ ,  $\Sigma^1$  and  $\Sigma^2$  are isotropic, antisymmetric and anisotropic rotational invariants, respectively<sup>30</sup>

$$\Sigma^0 = \frac{1}{3} |\alpha_{xx} + \alpha_{yy} + \alpha_{zz}|^2,$$

$$\Sigma^1 = \frac{1}{2} (|\alpha_{xy} - \alpha_{yx}|^2 + |\alpha_{xz} - \alpha_{zx}|^2 + |\alpha_{yz} - \alpha_{zy}|^2),$$

$$\Sigma^2 = \frac{1}{2} (|\alpha_{xy} + \alpha_{yx}|^2 + |\alpha_{xz} + \alpha_{zx}|^2 + |\alpha_{yz} + \alpha_{zy}|^2) + \frac{1}{3} (|\alpha_{xx} - \alpha_{yy}|^2 + |\alpha_{xx} - \alpha_{zz}|^2 + |\alpha_{yy} - \alpha_{zz}|^2). \quad (\text{s18})$$

Where  $\alpha_{ij}$  ( $i, j = x, y, z$ ) is Raman polarizability. The depolarization ratio can be the ratio of the perpendicular scattering cross-section to the parallel one<sup>30</sup>

$$\rho = \frac{5\Sigma^1 + 3\Sigma^2}{10\Sigma^0 + 4\Sigma^2}. \quad (\text{s19})$$

The isotropic and anisotropic rotational invariants are symmetric, which do not contribute to the bulk SFVS, however, the antisymmetric rotational invariant is asymmetric and affects the bulk SFVS of the chiral molecules. In our case, the isotropic and anisotropic rotational invariants are mainly from the Franck-Condon term and the

Herzberg-Teller term, which is much larger than the antisymmetric rotational invariant due to the nonadiabatic effect. And the antisymmetric rotational invariant is very sensitive to the light frequency and decreases rapidly when the light frequency is far away from resonance (see Figure 3).

s1 T. Ishiyama, V. V. Sokolov and A. Morita, *J. Chem. Phys.*, 2011, **134**, 024509.