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Theoretical investigation of quadrupole contributions to surface sum-frequency vibrational spectroscopy

Ren-hui Zheng,^{*a} Wen-mei Wei^b and Qiang Shi^a

We study the effect of electric transition quadrupole moments on surface sum-frequency vibrational spectroscopy (SFVS). The SSP, PPP and SPS effective sum-frequency susceptibilities are derived from the nonzero macroscopic susceptibility tensors and related to molecular quadrupole polarizabilities. Using time-dependent density functional theory, we calculate the quadrupole susceptibilities of R-limonene liquids for the first time. The results indicate that quadrupole contributions have a significant influence on SFVS transmitted signals in the SPS polarization combination. We also suggest that the SPS spectra may be used as a general technique for detecting electric transition quadrupole moments.

Received 17th November 2014,
Accepted 26th February 2015

DOI: 10.1039/c4cp05347h

www.rsc.org/pccp

1. Introduction

Sum-frequency vibrational spectroscopy (SFVS) is an important technique to study the molecular orientation, structure, and dynamics on surfaces and at interfaces,^{1–5} as well as the chiral structure in solutions or liquids.^{6–8} For achiral molecules, the bulk system is isotropic and SFVS cannot be observed. However, SFVS has also been detected in liquids or solutions for chiral molecules by applying incident lights with mutually perpendicular polarization, where the SFVS signal is related to the antisymmetric Raman polarizabilities.^{7,9} On the surface where the centrosymmetry is broken, SFVS can be used to study both achiral and chiral molecules.

Surface SFVS is similar to optical second harmonic generation (SHG). Generally, it is believed that surface SFVS and SHG are dominated by contributions from electric transition dipole moments. However, the understanding has been changed since Terhune, Maker, and Savage observed SHG for the crystal calcite with a center of inversion when a dc electric field is applied.¹⁰ They found that the SHG signal exists even at zero applied field, which indicated that the process may involve electric-quadrupole contributions. Thereafter, theoretical and experimental studies have been performed to investigate the electric-quadrupole contributions to both bulk and surface nonlinear spectroscopy.^{11–22}

In 1986 and 1987, Guyot-Sionnest *et al.*^{14,15} studied SHG at the fused-quartz interface and found that the electric transition quadrupole moment contributions from field discontinuity dominate the surface SHG. In 2000, Wei *et al.*¹⁶ investigated bulk contributions for the SFVS of an octadecyltrichlorosilane monolayer and a polyethylene film with transmission and reflection geometries, and the experimental results revealed that SFVS from the bulk contributions is only important for the transmission geometry. The reason is that the susceptibility of SFVS from the bulk contributions is proportional to the coherence length, which is much larger in the transmission geometry.⁷ In 2002, Held *et al.*¹⁷ presented a study of SFVS at the decane and glass interface from the bulk contributions using reflection and transmission geometries. And the experimental results showed that the bulk contributions from SPS and PSS combination are almost the same, however, those from SSP combination are negligible. In 2004, Hayashi *et al.*¹⁸ derived the theoretical expressions of SFVS from the quadrupole contributions, and Morita²⁰ also gave theoretical expressions for the electric transition quadrupole moment contributions to SFVS. In 2011, Yamaguchi *et al.*²¹ conducted the study on the quadrupole contributions to vibrationally and electronically nonresonant sum-frequency generation (SFG) at several air-liquid interfaces and discovered that the nonresonant nonlinear susceptibility with a negative sign has quadrupole contributions from the bulk and interface, which indicates that the sign of susceptibility is not related to the molecular alignment at interfaces. In 2013, Shiratori *et al.*²² calculated the nonlinear susceptibility at water interfaces applying molecular dynamics simulations by taking the dipole and quadrupole contributions into account and found that the nonresonant SHG is dominantly from quadrupole contributions.²²

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It is currently still difficult to quantitatively describe the contributions of the electric quadrupole moments to the surface SFVS, as one cannot yet obtain the individual contributions from electric dipole, electric quadrupole, and magnetic dipole moments to the overall SFVS signals from experimental studies alone. Different from the electric dipole polarizabilities which are zero in the isotropic bulk system, the quadrupole polarizabilities are non-zero in the bulk system. In SFVS studies, the thickness of the surface for dipole contributions and that of the bulk for quadrupole contributions are different. And their ratio is $\lambda/2\pi d$, where d is the thickness of the surface, and λ is the light wavelength.¹⁴ Then if we assume that the surface thickness is 1 nm and the wavelength is 532 nm, the above ratio is about 84. The thickness effect can enhance the quadrupole contributions by two orders of magnitude. By the rough estimation, the quadrupole polarizability is about two orders of magnitude smaller than electric dipole polarizability (see Theory section). Thus the quadrupole polarizability contributions from the bulk may be comparable to the electric dipole polarizability contributions from the surface, and may have an observable impact on the surface SFVS.

Ab initio calculations now provide a powerful tool to obtain the wavefunctions or electronic densities of the ground and excited states. Theoretically, this allows us to calculate all interesting physical quantities to obtain the SFVS signals. Several groups have calculated the contributions of electric transition dipole moments to SFVS. However, only a few computational studies have been performed on quadrupole polarizabilities of SFVS using the static electric field approximation.²² In this paper, we start from the relation between the macroscopic susceptibility tensors and the microscopic molecular polarizabilities from quadrupole contributions and perform frequency-dependent quadrupole calculations of R-limonene molecules using density functional theory (DFT) and time-dependent density functional theory (TDDFT) for the first time. The calculated quadrupole contributions to the SFVS signals are then compared with the experimental surface SFVS achiral signals.

II. Theory

SFVS is a second-order nonlinear optical process resulting from the nonlinear polarization of the media at frequency $\omega_s = \omega_1 + \omega_2$ by the two input light field \vec{E}_1 and \vec{E}_2 at frequencies ω_1 and ω_2 , respectively. We use the multipole expansion for the nonlinear polarization including contributions from the electric-quadrupole polarization $\vec{Q}^{(2)}$, electric-dipole polarization $\vec{P}^{(2)}$, and magnetization $\vec{M}^{(2)}$.^{7,23}

$$\begin{aligned}\vec{P}_{\text{eff}}^{(2)}(\omega_s) &= \vec{P}^{(2)}(\omega_s) - \vec{\nabla} \cdot \vec{Q}^{(2)}(\omega_s) + \frac{i}{\omega_s} \vec{\nabla} \times \vec{M}^{(2)}(\omega_s), \\ \vec{P}^{(2)}(\omega_s) &= \epsilon_0 \vec{\chi}_{eee}^{(2)} : \vec{E}_1 \vec{E}_2 + \epsilon_0 \vec{\chi}_{eqe}^{(2)} : \vec{E}_1 \vec{k}_1 \vec{E}_2 + \epsilon_0 \vec{\chi}_{eeq}^{(2)} : \vec{E}_1 \vec{E}_2 \vec{k}_2 \\ &\quad + \epsilon_0 \vec{\chi}_{eme}^{(2)} : \left(\frac{\vec{k}_1}{\omega_1} \times \vec{E}_1 \right) \vec{E}_2 + \epsilon_0 \vec{\chi}_{eem}^{(2)} : \vec{E}_1 \left(\frac{\vec{k}_2}{\omega_2} \times \vec{E}_2 \right), \\ \vec{Q}^{(2)}(\omega_s) &= \epsilon_0 \vec{\chi}_{qee}^{(2)} : \vec{E}_1 \vec{E}_2, \\ \vec{M}^{(2)}(\omega_s) &= \omega_s \epsilon_0 \vec{\chi}_{mee}^{(2)} : \vec{E}_1 \vec{E}_2,\end{aligned}\quad (1)$$

Here \vec{k}_1 and \vec{k}_2 are the wavevectors of the light fields \vec{E}_1 and \vec{E}_2 , respectively; $\vec{\chi}_{abc}^{(2)}$ is the second-order nonlinear media susceptibility tensor with the indices referring to the electric-quadrupole (q), electric-dipole (e), or magnetic-dipole (m) contributions, respectively.

In Fig. 1, we show the molecular structure of R-limonene and experimental arrangement for SFVS.^{7,23} There are three types of electric-quadrupole susceptibilities: $\vec{\chi}_{qee}^{(2)}$, $\vec{\chi}_{eqe}^{(2)}$ and $\vec{\chi}_{eeq}^{(2)}$. The relation between the macroscopic susceptibility $\vec{\chi}_{ijab}^{(2)} = \vec{\chi}_{qee}^{(2)}(\chi_{ijab}^{Q1} = \chi_{eqe}^{(2)}, \chi_{ijab}^{Q2} = \chi_{eeq}^{(2)})$, where the subscripts i, j, a , and b refer to X, Y, and Z components in the lab coordinate. The microscopic (molecular) polarizability is through the Euler transformation from the laboratory coordinate to the molecular coordinate and the orientational average over the

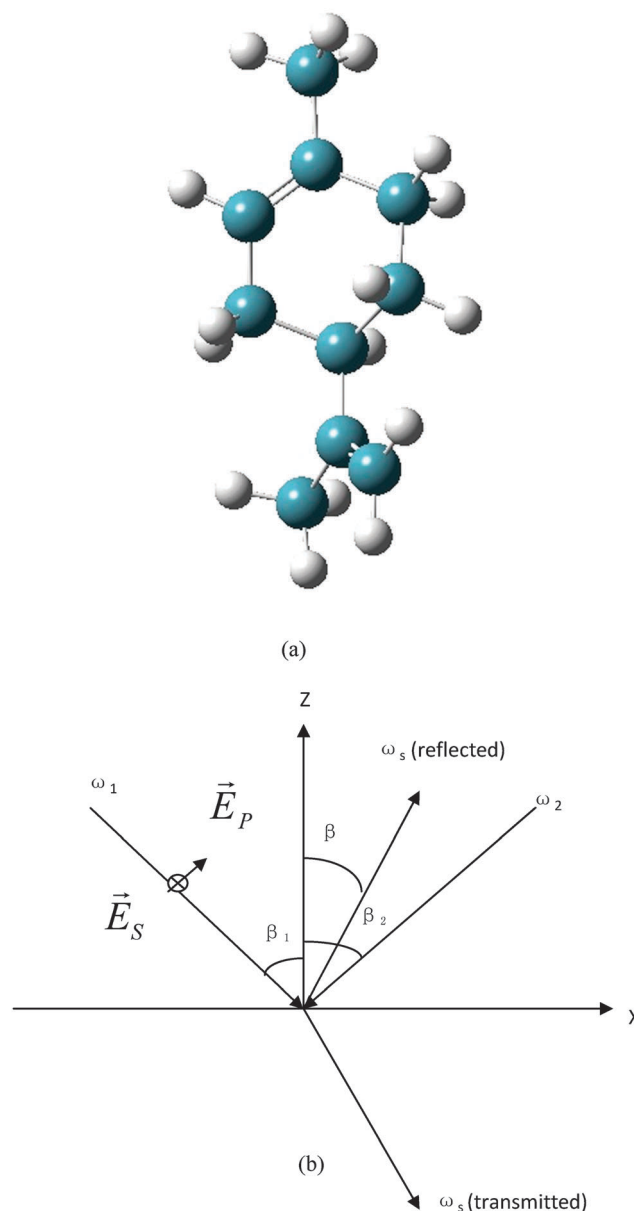


Fig. 1 (a) Molecular structure of R-limonene and (b) beam geometry for the SFVS experiment.

Euler rotation matrix. Only the components that appear even times can be non-zero after the orientational average. For example, χ_{YZYZ}^{Q1} , χ_{ZYXX}^{Q1} and χ_{YZZX}^{Q1} are zero, and χ_{YZYZ}^{Q1} , χ_{ZYXX}^{Q1} and χ_{ZZZZ}^{Q1} are non-zero. Thus, the polarization combination of SPP (electric field directions of the sum-frequency, UV/visible, IR lights \hat{e}_s , \hat{e}_1 and \hat{e}_2 are S, P, P polarized, respectively), PSP, or PPS cannot detect the electric-quadrupole susceptibility in the bulk system because there is only one Y component produced by the S polarization. Only the SSP, SPS, PSS and PPP polarization combinations can detect nonzero electric-quadrupole susceptibility.

For an isotropic liquid, the effective susceptibility χ_{eff}^{Q1} is related to nonzero macroscopic susceptibility tensors in transmission:¹⁷

$$\begin{aligned}\chi_{\text{eff}}^{Q1, \text{SSP}} &= -L_{YY}(\omega)L_{QYZ}(\omega_1)L_{ZZ}(\omega_2)\cos\beta_1\sin\beta_2\chi_{YZYZ}^{Q1} \\ &\quad - L_{YY}(\omega)L_{QYZ}(\omega_1)L_{XX}(\omega_2)\sin\beta_1\cos\beta_2\chi_{ZYXX}^{Q1}, \\ \chi_{\text{eff}}^{Q1, \text{PPP}} &= -L_{ZZ}(\omega)L_{QZZ}(\omega_1)L_{ZZ}(\omega_2)\sin\beta\sin\beta_1\cos\beta_1\sin\beta_2\chi_{ZZZZ}^{Q1} \\ &\quad - L_{ZZ}(\omega)L_{QZZ}(\omega_1)L_{XX}(\omega_2)\sin\beta\sin^2\beta_1\cos\beta_2\chi_{ZZXX}^{Q1} \\ &\quad + L_{ZZ}(\omega)L_{QXX}(\omega_1)L_{XX}(\omega_2)\sin\beta\cos^2\beta_1\cos\beta_2\chi_{ZZXX}^{Q1} \\ &\quad + L_{ZZ}(\omega)L_{QXX}(\omega_1)L_{ZZ}(\omega_2)\sin\beta\sin\beta_1\cos\beta_1\sin\beta_2\chi_{ZZXX}^{Q1} \\ &\quad + L_{XX}(\omega)L_{QZZ}(\omega_1)L_{XX}(\omega_2)\cos\beta\sin\beta_1\cos\beta_1\sin\beta_2\chi_{XXZZ}^{Q1} \\ &\quad + L_{XX}(\omega)L_{QZZ}(\omega_1)L_{ZZ}(\omega_2)\cos\beta\sin^2\beta_1\sin\beta_2\chi_{XXZZ}^{Q1} \\ &\quad - L_{XX}(\omega)L_{QXX}(\omega_1)L_{ZZ}(\omega_2)\cos\beta\cos^2\beta_1\sin\beta_2\chi_{XXZZ}^{Q1} \\ &\quad - L_{XX}(\omega)L_{QXX}(\omega_1)L_{XX}(\omega_2)\cos\beta\sin\beta_1\cos\beta_1\sin\beta_2\chi_{XXXX}^{Q1},\end{aligned}\quad (2)$$

$$\begin{aligned}\chi_{\text{eff}}^{Q1, \text{SPS}} &= -L_{YY}(\omega)L_{QZZ}(\omega_1)L_{YY}(\omega_2)\sin\beta_1\cos\beta_1\chi_{YZYZ}^{Q1} \\ &\quad + L_{YY}(\omega)L_{QXX}(\omega_1)L_{YY}(\omega_2)\sin\beta_1\cos\beta_1\chi_{ZYXX}^{Q1}.\end{aligned}$$

Here, L is the Fresnel coefficient by the bulk refractive index, and β is the incident or the transmitted angle. From the following derivation, we know that $\chi_{YZYZ}^{Q1} = \chi_{ZYXX}^{Q1}$ in the bulk system. Hence the $\chi_{\text{eff}}^{Q1, \text{SPS}}$ term does not contribute to the SPS effective susceptibility if we do not take the difference between quadrupole Fresnel coefficients $L_{QZZ}(\omega_1)$ and $L_{QXX}(\omega_1)$ into account. The effect that $\chi_{\text{eff}}^{Q1, \text{SPS}}$ is close to zero has an important impact on the SPS quadrupole signal.

The formulae for effective sum-frequency susceptibilities χ_{eff}^{Qs} , χ_{eff}^{Q1} and χ_{eff}^{Q2} in the transmission and reflection arrangements can be written in a similar way, and the details are not presented here.

By isotropic average, the macroscopic susceptibility tensors can be related to the microscopic molecular polarizabilities:

$$\begin{aligned}\chi_{YZYZ}^{Q1} &= \frac{1}{10}(\alpha_{jxyx}^{Q1} + \alpha_{xxxy}^{Q1} + \alpha_{yyzz}^{Q1} + \alpha_{zyzy}^{Q1} + \alpha_{zxzx}^{Q1} + \alpha_{xxzz}^{Q1}) \\ &\quad + \frac{1}{15}(\alpha_{xxxx}^{Q1} + \alpha_{yyyy}^{Q1} + \alpha_{zzzz}^{Q1}) \\ &\quad - \frac{1}{30}(\alpha_{jxxy}^{Q1} + \alpha_{jxyx}^{Q1} + \alpha_{jyzy}^{Q1} + \alpha_{jzyy}^{Q1} + \alpha_{jxzx}^{Q1} + \alpha_{jzxx}^{Q1}),\end{aligned}\quad (3)$$

$$\begin{aligned}\chi_{ZZXX}^{Q1} &= -\frac{1}{15}(\alpha_{jxyx}^{Q1} + \alpha_{xxxy}^{Q1} + \alpha_{yyzz}^{Q1} + \alpha_{zyzy}^{Q1} + \alpha_{zxzx}^{Q1} + \alpha_{xxzz}^{Q1}) \\ &\quad + \frac{1}{15}(\alpha_{xxxx}^{Q1} + \alpha_{yyyy}^{Q1} + \alpha_{zzzz}^{Q1}) \\ &\quad + \frac{2}{15}(\alpha_{jxxy}^{Q1} + \alpha_{jxyx}^{Q1} + \alpha_{jyzy}^{Q1} + \alpha_{jzyy}^{Q1} + \alpha_{jxzx}^{Q1} + \alpha_{jzxx}^{Q1}),\end{aligned}\quad (4)$$

$$\begin{aligned}\chi_{ZZZZ}^{Q1} &= \frac{2}{15}(\alpha_{jxyx}^{Q1} + \alpha_{xxxy}^{Q1} + \alpha_{yyzz}^{Q1} + \alpha_{zyzy}^{Q1} + \alpha_{zxzx}^{Q1} + \alpha_{xxzz}^{Q1}) \\ &\quad + \frac{1}{5}(\alpha_{xxxx}^{Q1} + \alpha_{yyyy}^{Q1} + \alpha_{zzzz}^{Q1}) \\ &\quad + \frac{1}{15}(\alpha_{jxxy}^{Q1} + \alpha_{jxyx}^{Q1} + \alpha_{jyzy}^{Q1} + \alpha_{jzyy}^{Q1} + \alpha_{jxzx}^{Q1} + \alpha_{jzxx}^{Q1}).\end{aligned}\quad (5)$$

The following relation holds: $\chi_{YZYZ}^{Q1} = \chi_{ZYXX}^{Q1} = \chi_{ZZXX}^{Q1} = \chi_{ZZXX}^{Q1} = \chi_{XXZZ}^{Q1}$, $\chi_{ZZXX}^{Q1} = \chi_{XXZZ}^{Q1} = \chi_{ZZXX}^{Q1} = \chi_{ZYXX}^{Q1} = \chi_{ZYXX}^{Q1}$, $\chi_{ZZXX}^{Q1} = \chi_{XXZZ}^{Q1}$ for the macroscopic susceptibility tensors. Using eqn (3)–(5), we can also see that $\chi_{ZZZZ}^{Q1} = 2\chi_{YZYZ}^{Q1} + \chi_{ZZXX}^{Q1}$, hence there are two independent macroscopic susceptibility tensors. Similarly, we can write down the macroscopic expressions for χ^{Qs} and χ^{Q2} , which are not shown here for simplicity. The following relation holds for χ^{Qs} and χ^{Q2} : $\chi_{ZZXX}^{Qs} = \chi_{XXZZ}^{Qs} = \chi_{ZZXX}^{Qs} = \chi_{ZYXX}^{Qs} = \chi_{ZYXX}^{Qs} = \chi_{ZYXX}^{Qs} = \chi_{ZYXX}^{Qs}$, $\chi_{ZZXX}^{Qs} = \chi_{XXZZ}^{Qs} = \chi_{ZZXX}^{Qs} = \chi_{ZYXX}^{Qs} = \chi_{ZYXX}^{Qs} = \chi_{ZYXX}^{Qs} = \chi_{ZYXX}^{Qs}$, $\chi_{ZZXX}^{Q2} = \chi_{XXZZ}^{Q2} = \chi_{ZZXX}^{Q2} = \chi_{ZYXX}^{Q2} = \chi_{ZYXX}^{Q2} = \chi_{ZYXX}^{Q2} = \chi_{ZYXX}^{Q2}$.

In SFVS, when the IR light ν_2 is resonant to a vibrational mode, the resonant parts of the molecular polarizabilities $\alpha_{\sigma\rho\kappa\gamma}$ can be calculated¹⁸

$$\begin{aligned}\alpha_{\sigma\rho\kappa\gamma}^{Q1}(\nu_s, \nu_2) &= \frac{1}{h^2} \frac{\langle Gg' | \mu_\gamma | Gg \rangle}{(\nu_2 - \nu_{Gg', Gg} + i\Gamma_{gg'})} \\ &\quad \times \sum_{N, n} \left[\frac{\langle Gg | \mu_\sigma | Nn \rangle \langle Nn | q_{\rho\kappa} | Gg' \rangle}{(\nu_s - \nu_{Nn, Gg} + i\Gamma_{Nn})} \right. \\ &\quad \left. - \frac{\langle Gg | q_{\rho\kappa} | Nn \rangle \langle Nn | \mu_\sigma | Gg' \rangle}{(\nu_{Nn, Gg'} + \nu_s + i\Gamma_{Nn})} \right],\end{aligned}\quad (6)$$

where h is the Planck constant, μ_σ and μ_γ are the molecular dipole operators, $q_{\rho\kappa}$ is the quadrupole operator, G represents the ground electronic state and N is the excited state, g , g' and n are the vibrational levels, $\nu_{Nn, Gg}$ and $\nu_{Nn, Gg'}$ represent the frequency differences between the indicated vibronic levels and Γ_{Nn} is the damping parameter of the N th vibronic state. In SFVS off electronic resonance, the sum-frequency ν_s is non-resonant, thus Γ_{Nn} and the frequency differences between the vibrational states in eqn (6) can be neglected. Under the Born-Oppenheimer approximation and using $\sum_n |n\rangle\langle n| = 1$, eqn (6) is rewritten into

$$\begin{aligned}\alpha_{\sigma\rho\kappa\gamma}^{Q1}(\nu_s, \nu_2) &= \frac{1}{h^2} \frac{\langle Gg' | \mu_\gamma | Gg \rangle}{(\nu_{Gg', Gg} - \nu_2 - i\Gamma_{gg'})} \\ &\quad \times \sum_N \left[\frac{\langle g | \langle G | \mu_\sigma | N \rangle \langle N | q_{\rho\kappa} | G \rangle | g' \rangle}{(\nu_{NG} - \nu_s)} \right. \\ &\quad \left. + \frac{\langle g | \langle G | q_{\rho\kappa} | N \rangle \langle N | \mu_\sigma | G \rangle | g' \rangle}{(\nu_{NG} + \nu_s)} \right],\end{aligned}\quad (7)$$

where ν_{NG} is the energy difference between the indicated electronic states.

In the above equation, $|g\rangle = |0\rangle$ is the ground vibrational state and $|g'\rangle = |1\rangle$ is the first excited vibrational state for the ground electronic state. When $|G\rangle$ and $|N\rangle$ are non-degenerate states, eqn (7) can be written as

$$\alpha_{\sigma\rho\kappa\gamma}^{Q1}(\nu_s, \nu_2) = \frac{1}{4\pi^2\hbar\nu_t} \frac{\partial\langle G|\mu_\gamma|G\rangle/\partial Q_t}{(\nu_t - \nu_2 - i\Gamma_{gg'})} \times \sum_N \nu_{NG} \left[\frac{(\partial\langle G|\mu_\sigma|G\rangle/\partial Q_t)\langle N|q_{\rho\kappa}|G\rangle + \langle G|\mu_\sigma|N\rangle(\partial\langle N|q_{\rho\kappa}|G\rangle/\partial Q_t)}{(\nu_{NG}^2 - \nu_s^2)} \right], \quad (8)$$

where Q_t is the normal coordinate for the t vibrational mode.

Similarly, we obtain the expressions for the molecular polarizabilities $\alpha_{\sigma\rho\kappa\gamma}^{Qs}$ and $\alpha_{\sigma\rho\kappa\gamma}^{Q2}$

$$\alpha_{\sigma\rho\kappa\gamma}^{Qs}(\nu_s, \nu_2) = \frac{1}{4\pi^2\hbar\nu_t} \frac{\partial\langle G|\mu_\gamma|G\rangle/\partial Q_t}{(\nu_t - \nu_2 - i\Gamma_{gg'})} \times \sum_N \nu_{NG} \left[\frac{(\partial\langle G|q_{\sigma\rho}|N\rangle/\partial Q_t)\langle N|\mu_\kappa|G\rangle + \langle G|q_{\sigma\rho}|N\rangle(\partial\langle N|\mu_\kappa|G\rangle/\partial Q_t)}{(\nu_{NG}^2 - \nu_s^2)} \right], \quad (9)$$

$$\alpha_{\sigma\rho\kappa\gamma}^{Q2}(\nu_s, \nu_2) = \frac{1}{4\pi^2\hbar\nu_t} \frac{\partial\langle G|q_{\kappa\gamma}|G\rangle/\partial Q_t}{(\nu_t - \nu_2 - i\Gamma_{gg'})} \times \sum_N \nu_{NG} \left[\frac{(\partial\langle G|\mu_\sigma|N\rangle/\partial Q_t)\langle N|\mu_\rho|G\rangle + \langle G|\mu_\sigma|N\rangle(\partial\langle N|\mu_\rho|G\rangle/\partial Q_t)}{(\nu_{NG}^2 - \nu_s^2)} \right]. \quad (10)$$

Comparing eqn (9) with eqn (8), we find that $\alpha_{\sigma\rho\kappa\gamma}^{Q1}(\nu_s, \nu_2) = \alpha_{\rho\kappa\sigma\gamma}^{Qs}(\nu_s, \nu_2)$. Thus we can obtain the following relations

$$\chi_{YZYZ}^{Q1} = \chi_{YZYZ}^{Qs}, \quad \chi_{ZXZX}^{Q1} = \chi_{ZXZX}^{Qs}, \quad \chi_{ZZZZ}^{Q1} = \chi_{ZZZZ}^{Qs}. \quad (11)$$

These relations indicate that the corresponding effective susceptibility from the UV/visible and sum-frequency signals is of the same order of magnitude since the difference of wave numbers between the two signals is small. According to ref. 17, we obtain the total susceptibility:

$$\chi_{\text{tot}} = \chi_{\text{eff}}^{Q1}k_1 + \chi_{\text{eff}}^{Q2}k_2 - \chi_{\text{eff}}^{Qs}k_s, \quad (12)$$

which includes all the contributions from the three lights. Note that in eqn (12), the total susceptibility not included the bulk density N_b , thus the square of the total susceptibility is in the unit of $(\text{m}^4 \text{V}^{-1})^2$. If the bulk density is included, it has a unit of $\text{m}^2 \text{V}^{-2}$. We find that our formulas are similar to eqn (5c)–(5f) in ref. 22. In ref. 22, molecular dynamics simulation is applied to calculate quadrupole contributions. The quadrupole susceptibilities are written into a sum of quadrupole hyperpolarizabilities of constituent molecules, and the hyperpolarizabilities are from their second derivatives with respect to the electric field. And the dipole–dipole interactions are used to consider the molecular couplings. Here we apply quantum computation to compute the quadrupole hyperpolarizabilities and the molecules are studied in gas phase because the molecular couplings of our computational molecules are weak. Both of us discover that the nonresonant quadrupole contributions are important.

III. Results and discussion

We then compute the SFVS off electronic resonance for R-limonene chiral liquids from the quadrupole contributions and compare the quadrupole results to the experimental surface SFVS signals. Using B3LYP/6-311++G** with the Gaussian 03 software,²⁴ we first optimize the molecular structure and obtain the vibrational frequencies, molecular orbital coefficients

and the quadrupole matrix in atomic orbitals. The vibrational frequencies are scaled by a factor of 0.9614. Next, based on the optimized structure of the ground state, we calculate the excited states applying time-dependent density functional theory (TDDFT) and get the configuration interaction (CI) coefficients and the electric transition dipole moments from the excited states to the

ground state. Using the quadrupole matrix, molecular orbital and CI coefficients, we compute the electric transition quadrupole moments between the excited and ground states. Derivatives of

dipole and quadrupole moments with respect to the normal coordinates are calculated using the numerical difference. In the numerical difference, the displacement of the normal coordinate is taken to be $0.01 \text{ amu}^{1/2} \text{ \AA}$. The Fresnel coefficients are taken to be 2.2.²³ We take the angles of the two input lights β_1 and β_2 both as 45 degrees.^{7,23} According to ref. 7, the directions of the sum-frequency (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. According to the requirement, the output angle of the sum-frequency β is 30.8 degrees.

Using eqn (8)–(10), (3)–(5) and (2), we calculate the quadrupole contributions to the SFVS, including all terms in eqn (12). The quadrupole SSP, PPP and SPS spectra are plotted in Fig. 2. In ref. 7, Belkin *et al.* have presented the absolute and relative intensities of the chiral SFVS and only relative intensities of achiral SFVS. We know from ref. 7 and 23 that the chiral susceptibility $|\chi_{\text{chiral}}^{\text{bulk}}/N_b|^2$ for R-limonene can be $1.2 \times 10^{-83} (\text{m}^4 \text{V}^{-1})^2$, and the ratio of surface sum-frequency intensities of SSP, PPP, and SPS spectra to that of the chiral spectra is 0.08, 0.13, and 0.04, respectively (Fig. 2 in ref. 7). From Fig. 2, our calculation shows that the strengths of quadrupole SSP, PPP and SPS signals are 1.0×10^{-85} , 4.8×10^{-86} , and $5.0 \times 10^{-85} (\text{m}^4 \text{V}^{-1})^2$, respectively. So the quadrupole SSP and PPP signals are two orders of magnitude smaller than chiral SFVS and one order of magnitude smaller than the corresponding surface SSP and PPP spectra. Quantum computations and molecular dynamics simulations indicate that the electric transition dipole moments dominate the surface SSP and PPP signals.²⁵ Note that the quadrupole SSP and PPP lineshapes are a little different from the experimental ones. However, the quadrupole SPS signal is more intense and only one order of magnitude smaller than chiral SFVS, and is of the same order of magnitude of the corresponding SPS signal in the surface SFVS experiment.⁷ The calculated quadrupole SPS spectra are also compared with the experimental surface SFVS in Fig. 2(c). The experimental SPS spectra⁷ have two intense peaks with frequencies of 2837 and 2950 cm^{-1} , and the corresponding

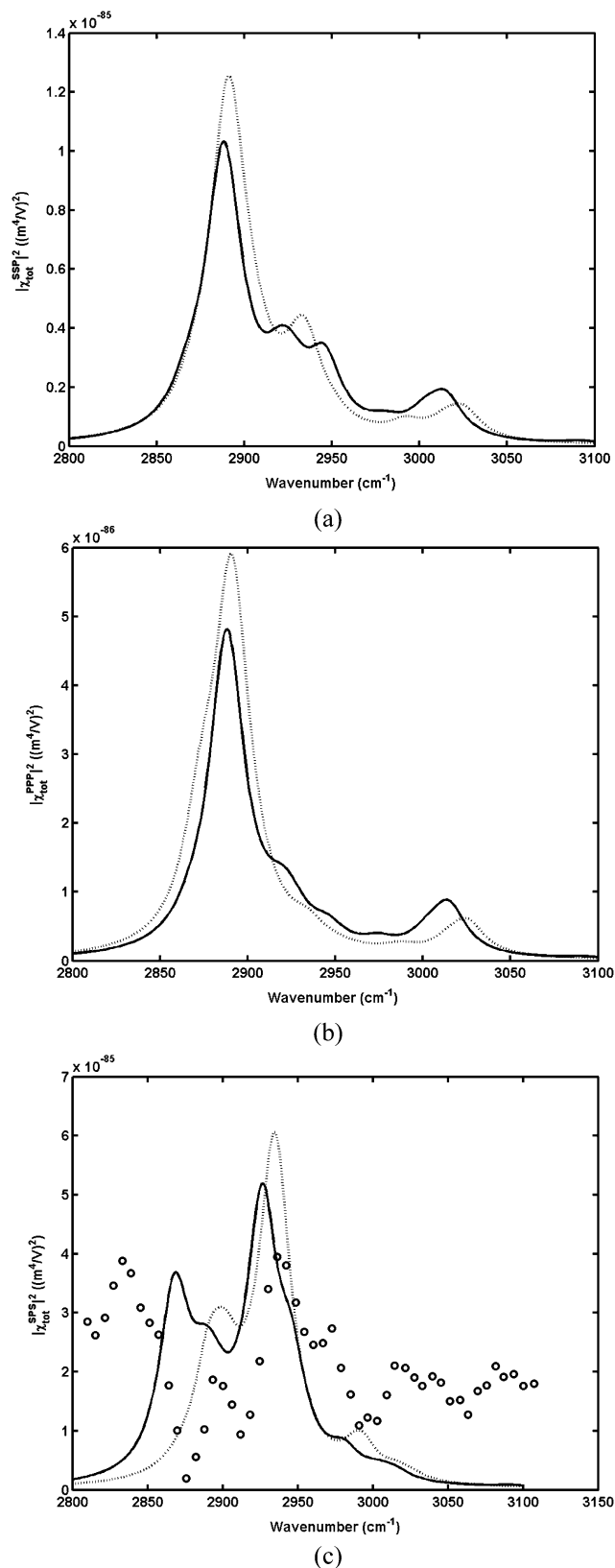


Fig. 2 The calculated total effective quadrupole susceptibilities (a) $|\chi_{\text{tot}}^{\text{SSP}}|^2$, (b) $|\chi_{\text{tot}}^{\text{PPP}}|^2$ and (c) $|\chi_{\text{tot}}^{\text{SPS}}|^2$ by TDDFT/B3LYP/6-311++G** (solid line) and TDDFT/B3LYP/Aug-cc-pVDZ (dotted line) and the experimental SPS data (open circles) from ref. 7.

calculated peaks are 2874 and 2927 cm^{-1} , respectively. The difference of vibrational frequencies may result from the inaccuracy of the quantum chemistry calculations. Furthermore the molecule is in the gas phase in our computation, however, the experiment is done in the liquid phase. The solvent effect may have a little influence on the vibrational frequencies. And the anharmonicity may also impact on the vibrational frequencies. Modern functional instead of B3LYP may improve our results. In order to study the influence of basis sets on SFVS, we also apply the dunning basis sets TDDFT//B3LYP/Aug-cc-pVDZ and TDDFT//B3LYP/cc-pVTZ to compute SFVS. The SSP and PPP spectra by TDDFT//B3LYP/Aug-cc-pVDZ and TDDFT//B3LYP/6-311++G** are similar in SFVS vibrational frequencies and intensities (see Fig. 2(a) and (b)). The SPS intensities by TDDFT//B3LYP/Aug-cc-pVDZ are reasonable and in good agreement with the experimental results,⁷ however, the frequencies are not better than those by TDDFT//B3LYP/6-311++G** (see Fig. 2(c)). The B3LYP/cc-pVTZ method is also used to compare the vibrational frequencies, and the frequencies are not better than those by the above two basis sets. Hence the results are not shown here. Fig. 2(c) shows that quadrupole contributions have an important influence on the SPS spectroscopy in transmission. Indeed, Belkin *et al.* have pointed out that the achiral SPS spectrum was hardly observable in reflection.⁷ The difference between the transmission and reflection SFVS signals indicates that the surface signals from electric dipole moments are much smaller than quadrupole contributions.

Now we discuss the reason why the quadrupole SSP and PPP signals $\chi_{\text{tot}}^{\text{SSP}}$ and $\chi_{\text{tot}}^{\text{PPP}}$ are small. In the experimental arrangement, $\chi_{\text{eff}}^{\text{O1,SSP}} = -L\chi_{\text{YZYZ}}^{\text{O1}}$ and $\chi_{\text{eff}}^{\text{Os,SSP}} = -L\frac{\sin\beta + \cos\beta}{\sqrt{2}}\chi_{\text{YZYZ}}^{\text{O1}} = 0.97L\chi_{\text{YZYZ}}^{\text{O1}}$, thus $\chi_{\text{tot}}^{\text{SSP}} \approx (k_s - k_i)L\chi_{\text{YZYZ}}^{\text{O1}}$, where the UV/visible and sum-frequency terms cancel each other out and result in a small signal. Similarly, $\chi_{\text{eff}}^{\text{O1,PPP}} = -L\frac{\sin\beta + \cos\beta}{\sqrt{2}}\chi_{\text{YZYZ}}^{\text{O1}} = -0.97L\chi_{\text{YZYZ}}^{\text{O1}}$, and $\chi_{\text{eff}}^{\text{Os,PPP}} = -2\sin\beta\cos\beta L\chi_{\text{YZYZ}}^{\text{O1}} = -0.88L\chi_{\text{YZYZ}}^{\text{O1}}$. So, the UV/visible and sum-frequency terms also cancel each other out for the PPP polarization combination. For the SPS combination, $\chi_{\text{eff}}^{\text{O1,SPS}}$ is zero and $\chi_{\text{eff}}^{\text{Os,SPS}}$ is nonzero, thus they do not cancel each other out and the total signal is large. We further note that the electric dipole SPS susceptibility is related to the nondiagonal components of Raman transition polarizability and the electric dipole SSP and PPP susceptibilities are from diagonal components. Since the nondiagonal components are generally smaller than diagonal ones and the distribution of R-limonene at interfaces makes the SPS signal small,²⁵ the electric dipole SPS susceptibility is small and it is hard to detect the surface electric dipole SPS signal.²⁵ If the quadrupole contributions from the bulk system are large compared with the electric dipole SPS susceptibility from the surface, the SPS polarized combination may provide a novel method for studying the electric transition quadrupole moments.

IV. Conclusions

In this work, we have addressed an important and long-standing problem in the area of surface sum-frequency vibrational

spectroscopy: the contributions of electric transition quadrupole moments to the SFVS signals. Since the quadrupole signals can have a bulk origin, understanding such contributions could be critical in explaining the experimental findings, yet quantitative characterization of these effects is scarce. Here we present the expressions of the molecular polarizabilities from the contribution of quadrupole moments to the sum-frequency vibrational spectroscopy. The relations between the effective susceptibilities, macroscopic susceptibilities and molecular polarizabilities have been derived. Using time-dependent density functional theory, we calculate the quadrupole SFVS in transmission for R-limonene molecules for the first time. The calculated results indicate that quadrupole contributions are one order of magnitude smaller than the experimental surface SFVS signals in SSP and PPP polarization combinations, but have a significant influence on the achiral SFVS signal in the SPS polarization combination. The SPS combination may provide a new way to investigate the molecular electric transition quadrupole moments.

Acknowledgements

This work is supported by National Natural Science Foundation (NNSF) of China (Grant No. 21103003, 21290194), the 973 program (Grant No. 2011CB808502, 2013CB933501), the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB12020300).

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