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Intensity relation between IR–UV doubly resonant sum-frequency spectra and antisymmetric resonant vibrational Raman scattering of chiral solutions

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Abstract

This Letter studies intensity relation between IR–UV doubly resonant sum-frequency vibrational spectra (DR-SFVS) and antisymmetric resonant vibrational Raman scattering, and gives an approximate expression of their intensity ratio. Based on the intensity ratio expression and the related experimental data of IR and antisymmetric resonant vibrational Raman spectra, hypothetical DR-SFVS of ferrocytochrome *c* has been sketched. The experimental investigation on IR–visible DR-SFVS of ferrocytochrome *c* may be a test of the related theory.

1. Introduction

Antisymmetric matter tensor is important in connection with antisymmetric light scattering and optical activity [1,2], and recently has attracted new interest [3–17]. Optical sum-frequency generation (SFG) of chiral solution as a novel spectroscopic tool to probe molecular chirality is currently being developed [6–13] and reviewed in [14–17]. In SFG vibrational spectroscopy, IR–UV doubly resonant sum-frequency vibrational spectra (DR-SFVS) have the unusually strong resonant enhancement and can significantly improve sensitivity of chiral spectroscopy [9]. However, to the best of our knowledge so far, only DR-SFVS of 1,1′-bi-2-naphthol (BN) solution [9] has been experimentally demonstrated in the literature of DR-SFVS of chiral solutions. This fact may indicate a limitation from the time-reversal and spatial symmetry selection rules [18,19]. In addition to BN, more chiral solutions should be further investigated by DR-SFVS.

It was proposed [10] that the strength of the chiral vibrational peaks in IR–UV DR-SFVS from isotropic chiral liquids is proportional to the square of the corresponding antisymmetric Raman element. Recently, we have measured UV near-resonance Raman spectra of BN solutions and discussed the relation between DR-SFVS and antisymmetric Raman tensors of BN molecules [20]. From point of view of antisymmetric resonant Raman (RR) scattering, ferrocytochrome *c* might be an ideal candidate for IR–UV DR-SFVS measurement and for the comparative study with resonant Raman spectra. Antisymmetric vibrational Raman scatterings were first observed in the resonance Raman spectra of ferrocytochrome *c* and their relative magnitudes were definitely determined by Nestor and Spiro [21] and Peticolas and co-workers [22]. Since then, ferrocytochrome *c* has been a well-known prototype compound with prominent antisymmetric Raman scattering intensity. Ferrocytochrome *c* is a vital component of every cell, and plays a crucial role of the transport of electrons in the respiratory chains and in photosynthetic cell [23]. Recently, second-harmonic generation-circular dichroism (SHG-CD) has been used, together with a surface-enhanced resonance Raman spectra, to monitor the oxidation state of ferrocytochrome *c* absorbed on model membrane surface and

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SFG-CD was shown to be a particularly sensitive probe of the redox state of the heme group [24].

This Letter studies intensity relation between IR–UV DR-SFVS of chiral solutions and antisymmetric resonant vibrational Raman spectra in Sections 2.1 and 2.2, and gives their intensity ratio expression in Section 2.3. Based on the intensity ratio expression and the related experimental data of IR and RR spectra, hypothetical DR-SFVS of ferrocytochrome *c* has been proposed in Section 3. The experimental investigation on IR–UV DR-SFVS of ferrocytochrome *c* may be a test of the related theory.

2. Theory

2.1. IR–UV DR-SFVS intensity

In electric-dipole approximation the IR–UV DR-SFVS output intensity from a chiral solution is given by [14,15]

$$I(\nu=\nu_1+\nu_2)\propto|\chi^{(2)}_{\mathrm{B}}(\nu,\nu_2)|^2 I_1(\nu_1)I_2(\nu_2), \tag{1}$$

where $I_1(\nu_1)$ and $I_2(\nu_2)$ are the UV beam intensity at the frequency ν_1 and the IR beam intensity at the frequency ν_2, respectively. $\chi^{(2)}_{\mathrm{B}}(\nu,\nu_2)$ is the bulk nonlinear susceptibility and expressed by the first hyperpolarizability $\alpha^{(2)}_{\rho\sigma\kappa}$ [9,15]

$$\chi^{(2)}_{\mathrm{B}}(\nu,\nu_2)=\frac{N_{\mathrm{B}}}{6\varepsilon_0}\sum_{\rho,\sigma,\kappa}\alpha^{(2)}_{\rho\sigma\kappa}\varepsilon_{\rho\sigma\kappa}, \tag{2}$$

where $\varepsilon_{\rho\sigma\kappa}$ are the Levi–Citita symbols. ρ, σ, κ are three different molecular coordinates. Local field corrections have been ignored in Eq. (2). In IR–UV DR-SFVS, the first hyperpolarizability $\alpha^{(2)}_{\rho\sigma\kappa}$ can be expressed into the direct product of the IR transition moment and the resonant antisymmetric anti-Stokes Raman polarizability $\alpha^{\mathrm{ant}}_{\rho\sigma}$ [9,17]

$$\begin{aligned}\alpha^{(2)}_{\rho\sigma\kappa}(\nu,\nu_2)=2\mu_\kappa\alpha^{\mathrm{ant}}_{\rho\sigma}=2\left[\frac{1}{h}\frac{\langle Gg'|\hat{\mu}_\kappa|Gg\rangle}{(\nu_2-\nu_{Gg',Gg}+\mathrm{i}\Gamma_{gg'})}\right]\\ \times\frac{1}{2h}\left[\frac{\langle Gg|\hat{\mu}_\rho|Mm\rangle\langle Mm|\hat{\mu}_\sigma|Gg'\rangle}{\nu-\nu_{Mm,Gg}+\mathrm{i}\Gamma_{Mm}}\right.\\ \left.-\frac{\langle Gg|\hat{\mu}_\sigma|Mm\rangle\langle Mm|\hat{\mu}_\rho|Gg'\rangle}{\nu+\nu_{Mm,Gg'}+\mathrm{i}\Gamma_{Mm}}\right],\end{aligned} \tag{3}$$

where G, M are the ground electronic state and resonant excited state, respectively. g, g′ and m are the vibrational states in G and in M state, respectively. Antisymmetric anti-Stokes transition polarizability $\alpha^{\mathrm{ant}}_{\rho\sigma}$ is defined by

$$\alpha^{\mathrm{ant}}_{\rho\sigma}=\frac{1}{2}[(\alpha_{\rho\sigma})_{Gg,Gg'}-(\alpha_{\sigma\rho})_{Gg,Gg'}], \tag{4}$$

where the resonant anti-Stokes transition polarizability $\alpha_{\rho\sigma}$ is expressed by neglecting its nonresonant part

$$(\alpha_{\rho\sigma})_{Gg,Gg'}=\frac{1}{h}\frac{\langle Gg|\hat{\mu}_\rho|Mm\rangle\langle Mm|\hat{\mu}_\sigma|Gg'\rangle}{\nu-\nu_{Mm,Gg}+\mathrm{i}\Gamma_{Mm}}. \tag{5}$$

By use of Eq. (3), Eq. (2) becomes

$$\chi^{(2)}_{\mathrm{B}}(\nu,\nu_2)=\frac{N_{\mathrm{B}}}{3\varepsilon_0}\sum_{\rho,\sigma,\kappa}\mu_\kappa\alpha^{\mathrm{ant}}_{\rho\sigma}\varepsilon_{\rho\sigma\kappa}. \tag{2′}$$

2.2. Selection rules of IR–UV DR-SFVS

While the selection rules for IR–visible SF vibration spectra of a molecule at surfaces and interfaces are reasonably well established and reviewed in [16,17], the related selection rules for DR-SFVS of chiral solutions need to be further examined. Based on spatial symmetry arguments of a molecule, Eqs. (1)–(3) can give the following necessary conditions for non-zero $\chi^{(2)}_{\mathrm{B}}(\nu,\nu_2)$ of chiral solution: (i) In the electric-dipole approximation (no magnetic or electronic-quadrupolar contributions), DR-SFVS can be generated in a liquid of molecules only if the molecules are of chirality, thus, they possess no center of symmetry, no symmetric plane, and no rotation-reflection axes [25]. (ii) The vibrational modes in DR-SFVS spectra have to be active both in IR absorption and in corresponding anitsymmetric Raman scattering. Based on the conditions (i) and (ii) and according to the Raman tensor patterns in [26] and character tables for point groups in [27], chiral molecules with IR–UV DR-SFVS have to belong to certain point groups with limited vibrational modes as listed in Table 1. In addition to the spatial symmetry, time-reversal arguments are important to be explored and applied to new aspects of molecular behavior [3]. Particularly, the time-reversal selection rule for resonant antisymmetric vibrational Raman scattering of even-electron molecules was discussed in [18,19].

It is noteworthy that the spatial and time-reversal symmetry selection rules for only electronically resonant sum-frequency spectroscopy (SFS) (with single resonance at the sum-frequency) in chiral solutions are less restrictive than those for IR–UV DR-SFVS. For single resonance enhancement at the sum-frequency, the first hyperpolarizability tensor $\alpha^{(2)}_{\rho\sigma\kappa}$ is given by the direct product of the electronic transition moment and the two-photon absorption (TPA) polarizability tensor [17]. TPA polarizability tensor has similar symmetric properties and expressions to electronic Raman scattering tensor [28]. It is known [29] that there is a fundamental difference between vibrational Raman scattering and electronic Raman scattering in that the latter may be controlled by an asymmetric tensor which includes antisymmetric components, even under non-resonance conditions. The consequence of this is that electronic Raman selection rules are less restrictive than those operative in vibrational Raman spectroscopy. So electronically resonant SFG in chiral solutions arise from couples with the asymmetry in the TPA polarizability tensor [28] and may be readily measured.

2.3. Approximation expression of the intensity ratio

Although the first hyperpolarizability $\alpha^{(2)}_{\rho\sigma\kappa}$ can be expressed into the direct product of the IR transition moment and the resonant antisymmetric anti-Stokes Raman transition polarizability, $|\chi^{(2)}_{\mathrm{B}}(\nu,\nu_2)|^2$ and DR-SFVS output intensity from a chiral solution are not simply proportional to the product of IR and antisymmetric