

Raman optical activity by coherent anti-Stokes Raman scattering spectral interferometry

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Abstract: We demonstrate a method to measure Raman optical activity (ROA) by using coherent anti-Stokes Raman scattering (CARS) spectral interferometry. An extremely weak chirality-induced CARS field is amplified through the interference with a strong CARS field generated from an external reference and is extracted by the Fourier transformation. In this interferometric coherent Raman optical activity (iCROA), both the sign and the magnitude of optical active non-resonant background susceptibility can be directly determined. Measurement of a CARS-ROA spectrum with less artifact is obtained because a broad offset artifact due to optical rotatory dispersion is clearly distinguished in iCROA.

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References and links

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14. Although the LO term should be written as $E_2^{LO}(\omega)e^{-i\omega\tau}\cos\theta$ in a precise sense, $\cos\theta$ can be approximated by 1 because θ changes between -0.125° and 0.125° in this study.

1. Introduction

Raman optical activity (ROA) provides a powerful method to characterize chiral molecules [1, 2]. Thanks to its high sensitivity to three-dimensional molecular structure, ROA spectroscopy has been widely used to investigate the configurations of biological molecules such as proteins and DNAs [3, 4, 5]. Conventionally, ROA spectrum is observed as a difference between Raman spectra of right- and left-circularly polarized incident and/or scattered light. Extremely small signal intensity of the ROA signal in comparison with its parent Raman scattering (the achiral background) has made it difficult to perform time-resolved ROA measurements, which have potential to unveil structural evolution of biological molecules during biochemical reactions. In order to overcome this difficulty, we have recently developed an ROA measurement system with the small achiral background by using coherent anti-Stokes Raman scattering (CARS-ROA) [6].

Chirality-induced CARS is generated as an electromagnetic field polarized perpendicular to the polarizations of the incident fields, which are parallel to each other. To amplify the exceptionally weak chirality-induced CARS signal, the polarization-resolved heterodyne-detected CARS scheme was employed in our previous study [6]. In this scheme, the polarizer for the generated CARS radiation was slightly tilted from the perpendicular configuration so that the strong achiral CARS signal was introduced as a local oscillator (LO). The obtained spectral intensity was then proportional to $|\sin\theta\chi_{1111} + \cos\theta\chi_{2111}|^2$, where χ was the third-order optical susceptibility tensor and θ represented the analyzer angle from the perpendicular configuration [6]. By taking difference between CARS spectra at $\theta = \pm\theta_1$, the homodyne terms were canceled out and only the heterodyne term was obtained. The heterodyne term was proportional to χ_{2111} and enabled us to retrieve both the amplitudes and the phases of the chiral signal. Although the contrast ratio of the chiral signal to the achiral background was considerably improved in CARS-ROA in comparison with spontaneous ROA, it was not still easy to obtain an artifact-free CARS-ROA spectrum because residuals of the homodyne term after the spectral subtraction sometimes gave rise to artificial peaks in a CARS-ROA spectrum. Moreover, it has remained unclear in the previous paper how large the optically active non-resonant part of the susceptibility χ_{2111}^{NR} contributed to the CARS-ROA spectrum [6]. It was mainly because the previous method was less sensitive to the optically active nonresonant background.

In this study, we report an interferometric coherent Raman optical activity (iCROA) technique using an external LO. By introducing the external LO, only the heterodyne terms can be extracted by Fourier transform spectral interferometry (FTSI) [7]. FTSI is used to obtain both the amplitude and phase of the generated electric signals in CARS [8, 9], sum frequency generation [10, 11], vibrational/electronic optical activity free induction decay [12, 13]. In iCROA, the chiral signal from a sample is combined with the CARS radiation generated in the LO arm with the time difference τ . The heterodyne terms between the signals from the sample and the reference can then be extracted by Fourier transformation (FT) because fringes with the frequency of $1/\tau$ are incorporated only in the heterodyne terms. By using this scheme, we show that a CARS-ROA spectrum can be obtained free from the achiral background of the sample, that the amount of χ_{2111}^{NR} is evaluated and shown to be pure imaginary for (-)- β -pinene, and that

artificial signals due to optical rotatory dispersion (ORD) of chiral samples are experimentally distinguished.

2. Experimental

The schematic diagram of our iCROA setup is shown in Fig. 1. The light source is a 1064 nm microchip laser (Hamamatsu, L11435) with a repetition rate of 25 kHz, a pulse width of 400 ps and output power of 20 μJ . The pump and Stokes pulses are narrow-band fundamental and broadband white-light continuum (from 1100 nm to >1300 nm) generated by a 2.5-m long photonic crystal fiber (SC-5.0-1040, NKT Photonics), respectively. Incident pulses are divided into two, namely the sample arm and the LO arm, by a half wave plate and polarized beam splitter. Optical configuration of the sample arm is the same as the reported one [6]. The polarizations of pump and Stokes pulses are set parallel to each other by the Glan-Taylor prism placed before the sample. Generated chirality-induced CARS field whose polarization is near perpendicular to the incident polarization is selected by the second Glan-Taylor prism (Fig. 2). In the LO arm, CARS field from the reference (water in the present setup) is generated without polarizers and combined with the CARS from the sample with the optical delay of τ . It should be noted that although the polarizations of the incident beams in the two arms are perpendicular after the PBS, the polarizations of the chirality-induced CARS from the sample and the achiral CARS field from the reference are almost parallel and interfere with each other. The reflected and transmitted beams of the BS are dispersed by a polychromator (LS785, Princeton Instruments) and then focused onto the different columns of the CCD camera (PIXIS 100BR eXcelon, Princeton Instruments). The incident energies are 8 μJ (pump in the sample arm), 0.4 μJ (Stokes in the sample arm), 1.5 μJ (pump in the reference arm), and 0.07 μJ (Stokes in the reference arm) at the sample. In order to evaluate our iCROA method, we performed proof-of-principle experiments on liquid (-)- β -pinene. Liquid (-)- β -pinene was purchased from Aldrich and used as received. The sample was set in a quartz cell with a path length of 1.0 mm.

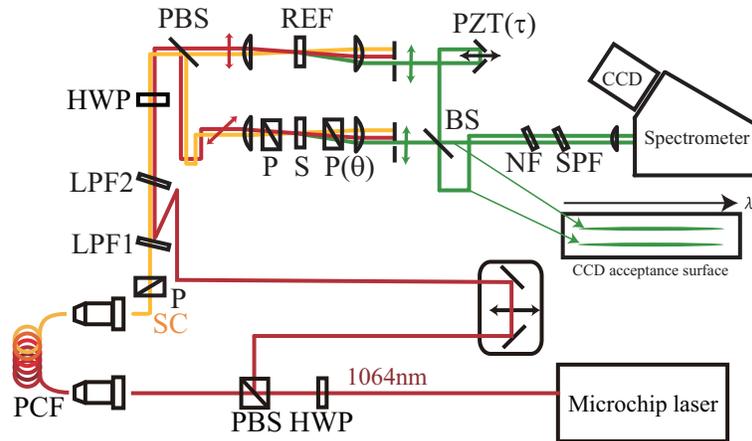


Fig. 1. Experimental setup. PCF: photonic crystal fiber, PBS: polarized beam splitter, HWP: half wave plate, P: polarizer, LPF1: long pass filter (cutoff @ 1064 nm), LPF2: long pass filter (cutoff @ 1050 nm), REF: reference (water), S: sample ((-)- β -pinene, BS: beam splitter, PZT(τ): piezo stage for optical delay $\tau = \tau_0 + \tau_1 n$, NF: notch filter (1064 nm), SPF: short pass filter (cutoff @ 1050 nm).

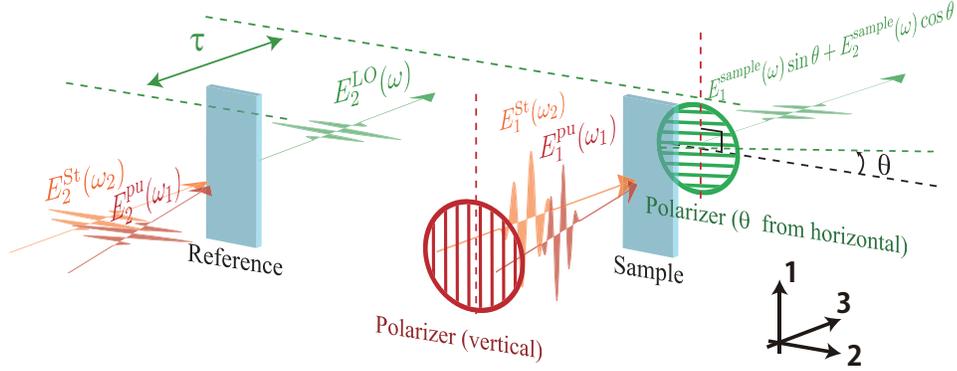


Fig. 2. Schematic diagram of experimental configuration around the sample and the reference.

3. Basic theory

In the polarization configuration depicted in Fig. 2, the total electric field in the frequency domain is expressed as a sum of CARS fields generated from the reference and the sample [14]:

$$\begin{aligned}
 E(\omega, \theta) &= E_1^{\text{sample}}(\omega) \sin \theta + E_2^{\text{sample}}(\omega) \cos \theta + E_2^{\text{LO}}(\omega) e^{-i\omega\tau} \\
 &= [A(\chi_{1111}^{\text{sample}}(\omega) \sin \theta + \chi_{2111}^{\text{sample}}(\omega) \cos \theta) + B\chi_{1111}^{\text{LO}} e^{-i\omega\tau}] E_1^{\text{pu}}(\omega_1) E_1^{\text{pu}}(\omega_1) E_1^{\text{St}*}(\omega_2),
 \end{aligned} \tag{1}$$

where ω , ω_1 , ω_2 represent the angular frequencies of the CARS, pump and Stokes pulses, which satisfy $\omega = 2\omega_1 - \omega_2$, A and B are real positive constants, τ is the time delay between the LO and the CARS field from the sample and the subscripts of E represent the direction of the polarization (in Cartesian coordinates, see Fig. 2).

The observed CARS intensity is formulated as the absolute square of the electromagnetic field as

$$\begin{aligned}
 I(\omega, \theta) &= |E_1^{\text{sample}}(\omega) \sin \theta + E_2^{\text{sample}}(\omega) \cos \theta + E_2^{\text{LO}}(\omega) e^{-i\omega\tau}|^2 \\
 &\propto A^2 |\chi_{1111}^{\text{sample}}(\omega)|^2 \sin^2 \theta + A^2 |\chi_{2111}^{\text{sample}}(\omega)|^2 \cos^2 \theta + B^2 |\chi_{1111}^{\text{LO}}|^2 \\
 &\quad + A^2 \sin \theta \cos \theta \text{Re}[\chi_{1111}^{\text{sample}}(\omega) \chi_{2111}^{\text{sample}*}(\omega)] \\
 &\quad + AB \sin \theta \text{Re}[\chi_{1111}^{\text{sample}}(\omega) \chi_{1111}^{\text{LO}*} \exp(i\omega\tau)] \\
 &\quad + AB \cos \theta \text{Re}[\chi_{2111}^{\text{sample}}(\omega) \chi_{1111}^{\text{LO}*} \exp(i\omega\tau)].
 \end{aligned} \tag{2}$$

In the previous CARS-ROA study without the external LO [6], the fourth term of Eq. (2) has been observed as a chirality sensitive term. The observed raw spectra were mainly dominated by the achiral background $|\chi_{1111}^{\text{sample}}(\omega)|^2$. Thus it has been needed to take difference between spectra at $\theta = \pm\theta_1$ to obtain a CARS-ROA spectrum. In this study, fairly strong external LO is introduced ($A \ll B$) and the raw spectra are dominated by $|\chi_{1111}^{\text{LO}}|^2$, which does not have vibrational peaks.

We extracted the last two terms of Eq. (2) by following three procedures:

1. Obtaining both signals transmitted and reflected by the beam splitter and taking difference spectrum between them.

2. Modulating the time difference as $\tau = \tau_0 + \tau_1 n$ (n represents the data number) by moving the piezo stage and performing Fourier transformation to extract only the modulated components.
3. Extracting $t = \tau_0$ component by multiplying window function by the time domain interferogram (FTSI [7]).

By the above procedures, only the positive time delay components of the Eq. (2):

$$S(\omega, \theta) = \sin \theta \chi_{1111}^{\text{sample}}(\omega) \exp(i\omega \tau_0) + \cos \theta \chi_{2111}^{\text{sample}}(\omega) \exp(i\omega \tau_0) \quad (3)$$

are extracted.

4. Results and discussion

In order to extract the heterodyne term, 20 spectra with different time delay τ were measured. Then the extracted spectra of the heterodyne term were averaged over 150 times to increase the signal to noise ratio. With 4.8 s exposure time of a single raw spectrum, the total collection time to obtain the final spectrum $S(\omega, \theta)$ was 4.2 h for one polarizer angle θ . The magnitudes of the extracted heterodyne terms at $\theta = 0.000^\circ$ and $\theta = -0.125^\circ$ are shown in Fig. 3(a). At $\theta = -0.125^\circ$, the achiral homodyne CARS line shape is observed. The spectral profile of the achiral CARS is formulated by

$$\begin{aligned} |\chi_{1111}| &= \left(\left| \chi_{1111}^{\text{NR}} + \frac{A}{\Omega - \omega_R - i\Gamma} \right|^2 \right)^{\frac{1}{2}} \\ &= \left((\chi_{1111}^{\text{NR}})^2 + \frac{2\chi_{1111}^{\text{NR}}A(\Omega - \omega_R)}{(\Omega - \omega_R)^2 + \Gamma^2} + \frac{A^2}{(\Omega - \omega_R)^2 + \Gamma^2} \right)^{\frac{1}{2}}, \end{aligned} \quad (4)$$

where A , Ω , and Γ are the amplitude, the frequency, and the damping constant of the Raman active vibrational mode, respectively, $\omega_R = \omega - \omega_1$ is Raman shift. The dispersive line shape of the spectrum is due to the second term in the square root and the phases of all the peaks are the same because A is positive for all the bands. In $|S(\omega, 0.000^\circ)|$ spectrum, four peaks at 640 cm^{-1} , 717 cm^{-1} , 767 cm^{-1} , 855 cm^{-1} are clearly observed. These peaks have also the dispersive line shape but the phases of each peak are not monosignate. Namely, the phases of $717, 855 \text{ cm}^{-1}$ are the same as the phases of the achiral CARS spectrum and the phases of the other peaks are opposite. The spectrum at $\theta = 0.000^\circ$ is formulated as

$$|\chi_{2111}| = \left(|\chi_{2111}^{\text{NR}}|^2 + \frac{\text{Im}(\chi_{2111}^{\text{NR}})\Delta A(\Omega - \omega_R)}{(\Omega - \omega_R)^2 + \Gamma^2} + \frac{\Delta^2 A^2/4}{(\Omega - \omega_R)^2 + \Gamma^2} \right)^{\frac{1}{2}}, \quad (5)$$

where, Δ is the circular intensity difference measured in forward-scattered spontaneous ROA studies [1, 2]. In Eq. (5), χ_{2111}^{NR} is assumed to be pure imaginary, which is experimentally verified below. The different phases of each peak of $|S(\omega, 0.000^\circ)|$ are explained by the fact that the signs of Δ are different in general for different peaks.

The real and imaginary parts of the extracted $S(\omega, \theta)$ spectra of (-)- β -pinene at $\theta = -0.125^\circ, 0.000^\circ$, and 0.125° are shown in Fig. 3(b). The interference fringes of Fig. 3(b) are due to the time delay τ_0 ($\simeq 1.8 \text{ ps}$ in this study). The fringes of the spectra at $\theta = \pm 0.125^\circ$ are obviously in anti-phase. It is because the first term of Eq. (3) is dominant in $S(\omega, \pm 0.125^\circ)$ and is odd function of θ . The oscillation feature is also found in the $S(\omega, 0.000^\circ)$ spectrum. The phase of $S(\omega, 0.000^\circ)$ in the spectral range without vibrational peaks is different by $\mp \pi/2$ from those of $S(\omega, \pm 0.125^\circ)$. Considering the fact that χ_{1111}^{NR} is real, it can be concluded that χ_{2111}^{NR} is pure imaginary. The value of χ_{2111}^{NR} relative to χ_{1111}^{NR} is calculated as $\chi_{2111}^{\text{NR}} \simeq$

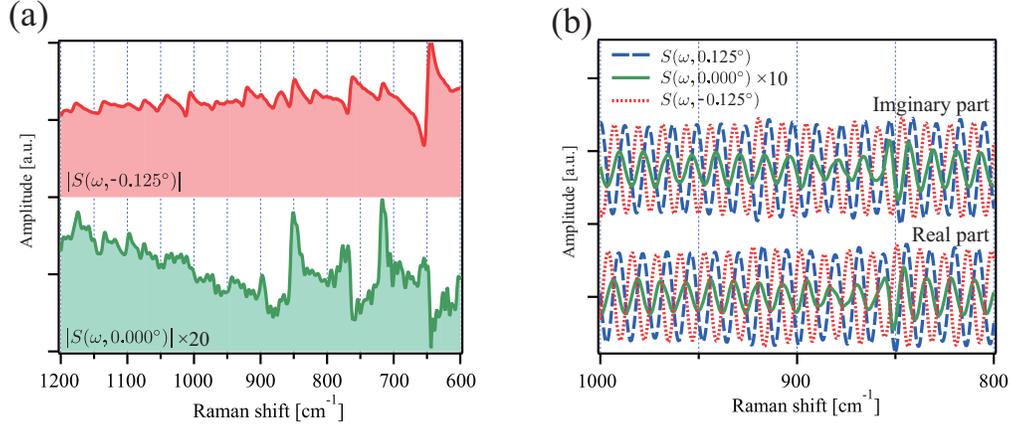


Fig. 3. (a): $|S(\omega, \theta)|$ spectra of (-)- β -pinene at $\theta = -0.125^\circ$ (top, red) and 0.000° (bottom, green). (b) Imaginary (top) and real (bottom) parts of $S(\omega, \theta)$ spectra of (-)- β -pinene at $\theta = -0.125^\circ$ (red dotted line), 0.000° (green solid line) and 0.125° (blue dashed line).

$-9 \times 10^{-5} \times \chi_{1111}^{\text{NR}} i$ by taking the average value of $\sin(0.125^\circ)S(\omega, 0.000^\circ)/S(\omega, 0.125^\circ)$ over the frequency range without vibrational peaks. This result is consistent with our previous estimation ($|\text{Im}(\chi_{2111}^{\text{NR}}/\chi_{1111}^{\text{NR}})| < 4 \times 10^{-4}$) in the supporting information of ref. [6]. The capability to detect the sign and absolute magnitude of this term provides a possibility to investigate the excited electronic states by iCROA. It should be noted that the optically active non-resonant background is definitely distinguishable from the achiral non-resonant background due to experimental imperfections such as non-zero extinction ratio of the analyzer. It is because $\pi/2$ phase difference of the non-resonant background cannot be explained only by the first term of Eq. (3).

The CARS-ROA spectrum is obtained as [6]

$$\text{Re}(\chi_{1111}^* \chi_{2111}) = \sum_{i=1}^n \frac{(\Delta_i \chi_{1111}^{\text{NR}} + \text{Im}(\chi_{2111}^{\text{NR}})) A_i \Gamma_i}{(\Omega_i - \omega_R)^2 + \Gamma_i^2}. \quad (6)$$

If ORD of the sample is negligible in the whole spectral range, CARS-ROA can be obtained as $\text{Re}[S(\omega, 0.000^\circ)S^*(\omega, 0.125^\circ)] \propto \text{Re}(\chi_{1111}^* \chi_{2111})$. If this is not the case, $\text{Re}[S(\omega, 0.000^\circ)S^*(\omega, 0.125^\circ)]$ spectrum includes not only CARS-ROA but also the achiral CARS components;

$$\begin{aligned} \text{Re}[S(\omega, 0.000^\circ)S^*(\omega, 0.125^\circ)] &\simeq \text{Re}[\sin(0.125^\circ)\chi_{1111}e^{i\omega\tau}(\chi_{2111}^* + \sin\alpha(\omega)\chi_{1111}^*)e^{-i\omega\tau}] \\ &\propto \text{Re}(\chi_{1111}^* \chi_{2111}) + \sin\alpha(\omega)|\chi_{1111}|^2, \end{aligned} \quad (7)$$

where $\alpha(\omega)$ represents the ORD. It should be noted that $\alpha(\omega)$ represents the ORD both of the Stokes and of the CARS radiation. The CARS-ROA spectrum of (-)- β -pinene is shown in the top of Fig. 4. A broad offset due to the second term of Eq. (7) is observed in the whole spectral range. The offset can be canceled by subtracting the achiral contribution with an appropriate coefficient $c(\omega)$ as

$$\begin{aligned} S'(\omega, 0.000^\circ) &= S(\omega, 0.000^\circ) - c(\omega)S(\omega, 0.125^\circ) \\ &\propto \chi_{2111} \exp(i\omega\tau). \end{aligned} \quad (8)$$

The coefficient is assumed to be a spline function and determined by fitting so that the phase of $S'(\omega, 0.000^\circ)/S(\omega, 0.125^\circ)$ is equal to $-\pi/2$ in the range without vibrational peaks. After the compensation, the CARS-ROA spectrum is calculated as $\text{Re}[S'(\omega, 0.000^\circ)S^*(\omega, 0.125^\circ)]$, which is shown in the bottom of Fig. 4. The broad offset due to the ORD is substantially reduced by using the phase information of the non-resonant background signal.

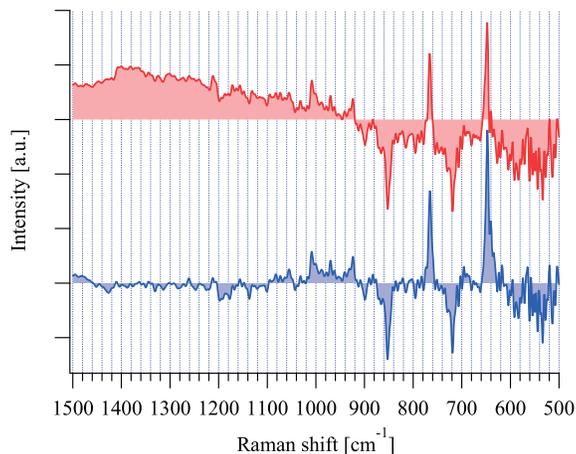


Fig. 4. CARS-ROA spectra of (-)- β -pinene before (top) and after (bottom) the compensation to cancel the achiral contribution. The top spectrum is calculated as $\text{Re}[S(\omega, 0.000^\circ)S^*(\omega, 0.125^\circ)]$ and the bottom one is calculated as $\text{Re}[S'(\omega, 0.000^\circ)S^*(\omega, 0.125^\circ)]$.

5. Conclusion

We have developed a novel CARS-ROA measurement method with CARS spectral interferometry, iCROA. Only the heterodyne terms between the CARS fields from the sample and the reference are selectively extracted by the analyses. The non-resonant background susceptibility is shown to be pure imaginary and the sign and the magnitude is also determined for (-)- β -pinene. The artifact due to the ORD of the chiral sample is reduced by exploiting the phase sensitivity of iCROA.

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