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Femtosecond-time-resolved highly selective molecular-vibration excitation using a novel vibrationally synchronized pumping technique with frequency difference resonance

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Abstract

Selective stimulated Raman scattering using a single-color femtosecond N -pulse train of finite pulse duration leads to a low excitation efficiency in the high frequency region. This low efficiency of Raman mode excitation is due to spectral modulation which stems from the finite duration of the pulses in each train. To overcome the low efficiency of excitation in the high frequency region, a vibrationally synchronized pumping technique with frequency difference resonance is proposed. In this technique, both the pulse-repetition rate and the center frequency difference of carrier-phase-locked two-color beams consisting of a femtosecond N -pulse train are chosen to be resonant with the frequency of a specific vibrational or rotational mode of interest. In addition, a formula describing the optimum pulse number N for efficient selective excitation is derived. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The recent development of the ultrafast technology has enabled us to generate optical pulses whose duration is shorter than the molecular vi-

bration or rotation period. Typical values of the vibrational or rotational period corresponding to the Stokes shift in many Raman scattering media are of the order of 10^{-13} – 10^{-14} s. This means that with the use of laser pulses whose duration ~ 10 – 100 fs, many Raman modes can be excited in a time-resolved stimulated Raman scattering (SRS) experiment simultaneously [1–3], but not

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selectively. On the other hand, selective excitation of a specific Raman mode or quantum control of molecular motion with a high time resolution has been carried out using femtosecond shaped optical pulse sequences (consisting of N -pulse trains) whose repetition rate are equal to their vibrational or rotational frequency [4,5]. In addition, an analysis of this selective excitation with the N -pulse train has been done only under the assumption that each constituent pulse is a δ -function in time [6,7]. However, a more realistic analysis of the selective excitation with the N -pulse train consisting of pulses with a finite duration is essential for proper analysis of experimental results.

In this paper, we show that the practical analysis of selective excitation of molecular vibration or rotation using an N -pulse train with finite pulse duration leads to a low selectivity or efficiency due to the envelope spectral modulation arising from the finite pulse duration. In order to overcome this problem we propose an ultrafast vibrationally synchronized pumping technique with frequency difference resonance where not only the pulse repetition rate (T^{-1}) but also the center frequency difference ($(\omega_1 - \omega_2)/2\pi$) between carrier phase-locked two-color femtosecond-pulse-train beams are tuned to the corresponding resonance frequency ($\omega_{R,int}/2\pi$) of a specific vibrational or rotational mode. With this detailed analysis that accounts for the finite pulse duration, it is demonstrated that this novel technique allows efficient selective excitation.

2. Proposal and fundamental analysis for a femtosecond vibrationally synchronized pumping technique with frequency difference resonance

2.1. Proposal

Here we propose a vibrationally synchronized pumping technique with frequency difference resonance for efficient selective molecular vibrational or rotational excitation that can be applied up to the high frequency region. The basic concept of the vibrationally synchronized pumping technique with frequency difference resonance is that both the center frequency difference and the repetition rates of two-color N -pulse train beams can be simultaneously tuned to the resonance of a specific molecular vibrational or rotational frequency of interest. For example, this vibrationally synchronized pumping technique with frequency difference resonance can be implemented as shown in Fig. 1. After the amplified femtosecond optical pulses are spectrally broadened by self-phase or induced-phase modulation [8–10], they are guided into a two-dimensional (2D) pulse shaper consisting of a $4f$ -system in which a 2D spatial light amplitude- and phase-modulator are located in the Fourier-plane. By use of this 2D-pulse shaper, simultaneous two-color pulse shaping is carried out with an arbitrary center frequency (wavelength) selection (ω_1 and ω_2) and with arbitrary control of the pulse intervals T (pulse repetition rates: T^{-1}). Thus we generate two-color shaped N -pulse train beams whose center frequen-

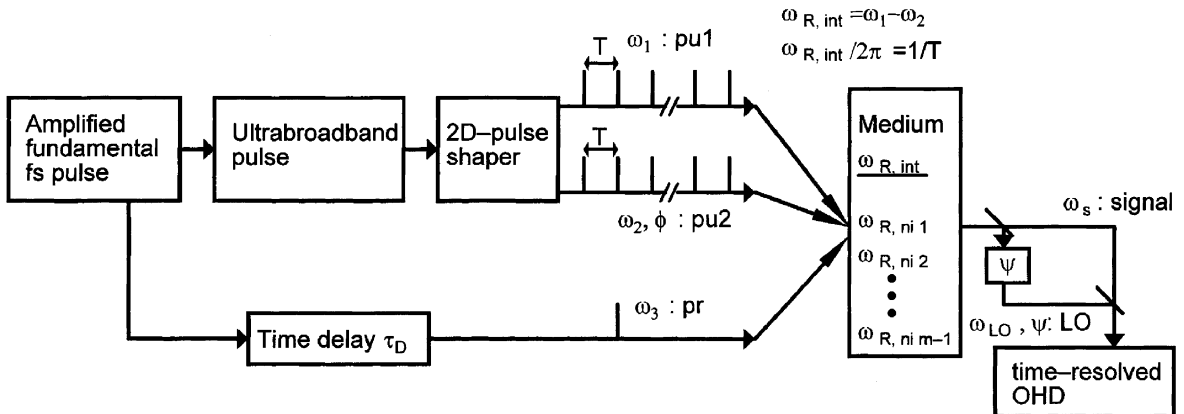


Fig. 1. Schematic diagram of the vibrationally synchronized pumping technique with frequency difference resonance.

cies are ω_1 and ω_2 , with the same repetition rates T^{-1} as the pump beams (pump1 and pump2) which are focused into the medium under study. When we adjust the center frequency difference of these beams $\omega_1 - \omega_2$ to a specific molecular vibrational or rotational frequency of interest $\omega_{R,int}$ and the pulse repetition rates T^{-1} to $\omega_{R,int}/2\pi$, we can achieve vibrationally synchronized pumping excitation with frequency difference resonance. In this vibrationally synchronized pumping technique with frequency difference resonance, the *pulse-repetition-rate synchronization with vibration* leads to selective excitation and the *center-frequency difference resonance* brings Raman-signal enhancement of the selective excitation. That is, the $\omega_{R,int}$ -vibrational or rotational mode is selectively excited with a relatively high signal intensity. When the probe pulse having time delay τ_D between the pump1 and pump2 is also focused into the medium, we can observe behavior characteristic of temporally SRS of a selected Raman mode. A local oscillator pulse LO, derived from a portion of the signal before detection, is used for optical heterodyne detection (OHD). We term ϕ the relative phase of the pump2 with respect to the pump1 or probe and ψ the phase of the local oscillator with respect to the probe. The phase difference between the pump1 and the probe is arbitrary. When one adjusts ϕ and ψ to the appropriate values, the real and imaginary parts of the Raman response can be obtained.

2.2. Fundamental analysis

Fundamental analysis of selective excitation using an N -pulse train with finite duration in the two-color pump case as well as the one-color pump case is described in Appendix A. From Appendix A, the optical-heterodyne-detected coherent Raman scattering signal is expressed by

$$\begin{aligned}
 S_{\text{hetero}}(\mathbf{k}_s, \tau_D) \propto & \\
 & -2\omega_s \text{Im} \left[\int_{-\infty}^{\infty} dt |\bar{E}_{\text{pr}}(t - \tau_D)|^2 \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} \right. \\
 & \times \mathcal{F} \left\{ \bar{E}_{\text{pu1}}(t) \bar{E}_{\text{pu2}}^*(t) \right\} \times \mathcal{F} \left\{ \exp[i(\omega_1 - \omega_2)t] u(t) \right. \\
 & \left. \left. \times \sum_j r_j(t) \right\} \exp[i(\phi + \psi)] \right]. \quad (1)
 \end{aligned}$$

Here, $u(t)$ is the unit step function, represented by

$$u(t) = \begin{cases} 0, & \text{if } t < 0, \\ 1, & \text{if } t \geq 0. \end{cases} \quad (2)$$

In the case where pump1 and pump2 have the same pulse-train envelopes and $T_0 \ll T$, as shown in Fig. 2(a), the factor $\mathcal{F} \{ \bar{E}_{\text{pu1}}(t) \bar{E}_{\text{pu2}}^*(t) \}$ in Eq. (1) has the form $\sin(N\omega T/2) e^{-i(N-1)\omega T/2} \mathcal{F} \{ |F(t/T_0)|^2 \} / W \sin(\omega T/2)$ (see Appendix B). From this, it should be noted that, because of the finite pulse duration, the spectrum of an N -pulse train is modulated by a factor $\mathcal{F} \{ |F(t/T_0)|^2 \}$. This corresponds to the spectrum of the constituent pulse, unlike in the delta-function pulse train case. The

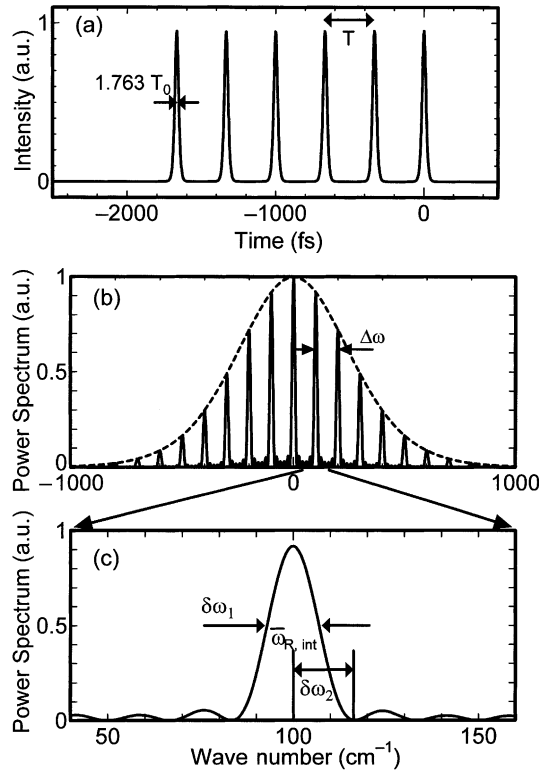


Fig. 2. (a) An example of an N -pulse train ($F(t/T_0) = \text{sech}(t/T_0)$, $t_p = 1.763T_0 = 30$ fs, $N = 6$ and $T = 333.56$ fs). (b) Its spectrum is represented by the solid line. The dashed line corresponds to a spectrum of a $t_p = 30$ fs single pulse. The wave number 0 cm^{-1} corresponds to the center wavelength. (c) The spectral peak around $T^{-1} = 100 \text{ cm}^{-1}$ is magnified. The full width at half maximum $\delta\omega_1$ of the peak approximately equals $\delta\omega_2$, which is the difference between the peak and the first adjacent zero point.

conventional analysis using an infinitesimal duration is impractical because it could excite a mode strongly in an arbitrarily high vibrational frequency region. As an example, in our analysis here, we consider $F(t/T_0)$ as a hyperbolic secant function. Then

$$\begin{aligned} C(\omega) &\equiv \mathcal{F}\left\{|F(t/T_0)|^2\right\} = \mathcal{F}\left\{\operatorname{sech}^2(t/T_0)\right\} \\ &= \pi\omega T_0^2 \operatorname{cosech}(\pi\omega T_0/2), \end{aligned} \quad (3)$$

as shown in Fig. 2(b). Since spectral filtering for selective excitation at $\omega_{\text{R,int}}$ is done by the peak of $\omega = \omega_{\text{R,int}} = 2\pi/T$, the stimulated Raman signal for N -pulse train beams with finite duration is reduced by a factor of $C(\omega_{\text{R,int}})/C(\omega = 0)$ compared to that for delta-function N -pulse train beams. For the example described in Section 4 ($\omega_{\text{R,int}}/2\pi = 448.2 \text{ cm}^{-1}$ and $T_0 = 30/1.763 = 17.0 \text{ fs}$), the analysis using the N -pulse train with the infinitesimal duration overestimates the power spectrum of the coherent Raman scattering signal excited selectively at $\omega_{\text{R,int}}/2\pi = 448.2 \text{ cm}^{-1}$ by about a factor of five compared to our analysis using the N -pulse train with finite duration. Thus the analysis using the N -pulse train with the finite duration is essential for an accurate interpretation of the experimental results.

3. Optimum pulse number of an N -pulse train

For a practical consideration of the selective excitation using an N -pulse train with finite duration, the condition that the total energy of the N -pulse train is constant should be considered. SRS is a third-order non-linear process governed by the pulse peak intensities. Thus, under the constant total-energy condition, it is important to derive the formula that determines the minimum pulse number for efficient selective excitation in both cases of one- and two-color N -pulse train beams. Fig. 2(c) shows the magnification of the first positive frequency (or negative-frequency) sub-spectrum of $\mathcal{F}\{\bar{E}_{\text{pu1}}(t)\bar{E}_{\text{pu2}}^*(t)\}$ at $\omega = \pm 2\pi/T$, which is used for conventional selective excitation. From equation in Appendix B, the shape of this sub-spectrum is expressed mainly through the factor $\sin(N\omega T/2)/W \sin(\omega T/2)$. Adjacent spectral zero

points are at $\omega = 2\pi(1 \pm 1/N)/T$. Approximating the shape around the first positive frequency sub-spectrum to that of an isosceles triangle, we can evaluate the full width at half maximum (FWHM; $\delta\omega_1$) of the first positive frequency (or negative-frequency) sub-spectrum to be $2\pi/NT$, which is equal to half of the base width $\delta\omega_2$ of the triangle. Considering that only the Raman spectral component almost within the FWHM of the first positive frequency (or negative-frequency) sub-spectrum can be excited effectively, we find that the condition for efficient selective excitation is that the FWHM should be smaller than the minimum interval $(\Delta\omega_{\text{R}})_{\text{min}}$ of the intervals between the Raman line $\omega_{\text{R,int}}$ of interest and the lines $\omega_{\text{R,ni},j}$ ($j = 1, \dots, m - 1$) of no interest. That is,

$$N \gtrsim \frac{2\pi}{(\Delta\omega_{\text{R}})_{\text{min}} T}. \quad (4)$$

This is the criterion for the optimum pulse number N for efficient selective excitation using an N -pulse train. It should be noted that the optimum pulse number does not depend on the shape of each pulse that constitutes the N -pulse train, because the width of the first positive frequency (or negative-frequency) sub-spectrum is determined by the factor $\sin(N\omega T/2)/W \sin(\omega T/2)$.

4. Efficient selective excitation by the vibrationally synchronized pumping technique with frequency difference resonance

As mentioned above, the spectral modulation of $\mathcal{F}\{\bar{E}_{\text{pu1}}(t)\bar{E}_{\text{pu2}}^*(t)\}$ in Eq. (1) leads to a low selective-excitation efficiency of a specific Raman mode in the high frequency region in the case of $\omega_1 - \omega_2 = 0$. In order to avoid this low selective-excitation efficiency, due to the factor $\mathcal{F}\{\bar{E}_{\text{pu1}}(t) \times \bar{E}_{\text{pu2}}^*(t)\}$, we take notice of another factor of $\mathcal{F}\{\exp[i(\omega_1 - \omega_2)t]u(t) \sum_j r_j(t)\}$ in Eq. (1). While the spectral modulation due to $\mathcal{F}\{\bar{E}_{\text{pu1}}(t)\bar{E}_{\text{pu2}}^*(t)\}$ decreases the spectral amplitude at $\omega = \omega_{\text{R,int}}$, especially in the high frequency region, the spectral amplitude at $\omega = 0$ is not modulated even in the finite duration case. Moreover, shifting the Raman spectrum is possible with a factor $\exp[i(\omega_1 - \omega_2)t]$

in $\mathcal{F}\{\exp[i(\omega_1 - \omega_2)t]u(t)\sum_j r_j(t)\}$ by varying the $\omega_1 - \omega_2$ value. When we adjust $\omega_1 - \omega_2 = \omega_{R,int}$, we can shift the Raman spectrum by $-\omega_{R,int}$, thus we can use the un-modulated spectral component at $\omega = 0$ of the N -pulse train for selective Raman-mode excitation. That is, to greatly improve on the low efficiency of selective excitation in the high frequency region, we employ the vibrationally synchronized pumping technique with frequency difference resonance. We use two-color N -pulse train beams with a frequency difference of $\omega_1 - \omega_2$ which corresponds to the Raman frequency $\omega_{R,int}$ and for which the pulse interval T satisfies $\omega_{R,int} = 2\pi/T$. These two-color N -pulse train beams, as well as one-color N -pulse train beams, can selectively excite the specific Raman mode of $\omega_{R,int}$. Moreover, when adjusting the center frequencies of the two-color beams that satisfy $\omega_1 - \omega_2 = \omega_{R,int}$, we can shift the spectrum of the Raman response effectively to make them resonant with the central spectral peak of the N -pulse trains. Thus, we can perform efficient selective excitation even in the high frequency region, with complicated Raman lines, using two-color N -pulse train beams.

As an example, we investigate the efficient selective excitation of tetrachloroethylene that has Raman modes at 236.6, 346.5, 448.2 and 511.9 cm^{-1} in the high frequency region [11], as shown in Fig. 3(a). Here, we consider the selective excitation of the 448.2 cm^{-1} Raman line. The pulse interval T for selective excitation at 448.2 cm^{-1} is 74.4 fs, and the minimum frequency interval $(\Delta\omega)_{\min}/2\pi$ is 63.7 cm^{-1} . To avoid a decrease in power of each constituent pulse for selective excitation under the condition that the total energy of the N -pulse train is constant, N should be at least 7 to satisfy the inequality (4).

The power spectrum of Eq. (B.4) in the case where $\bar{E}_{\text{pu1}}(t) = \bar{E}_{\text{pu2}}(t)$, $F(t/T_0) = \text{sech}(t/T_0)$, $N = 7$, $T = 74.4$ fs and every pulse duration $t_p = 2T_0 \ln(1 + \sqrt{2}) = 30$ fs ($T_0 = 17.0$ fs) for selective excitation at 448.2 cm^{-1} is shown in Fig. 3(b). The height of the first peak at the positive or negative frequency ($\omega/2\pi = \pm 448.2$ cm^{-1}) is much lower than that of the peak at the center of $\omega = 0$ cm^{-1} .

As a measure of the selectivity and efficiency of excitation, we define a factor η_S , such that

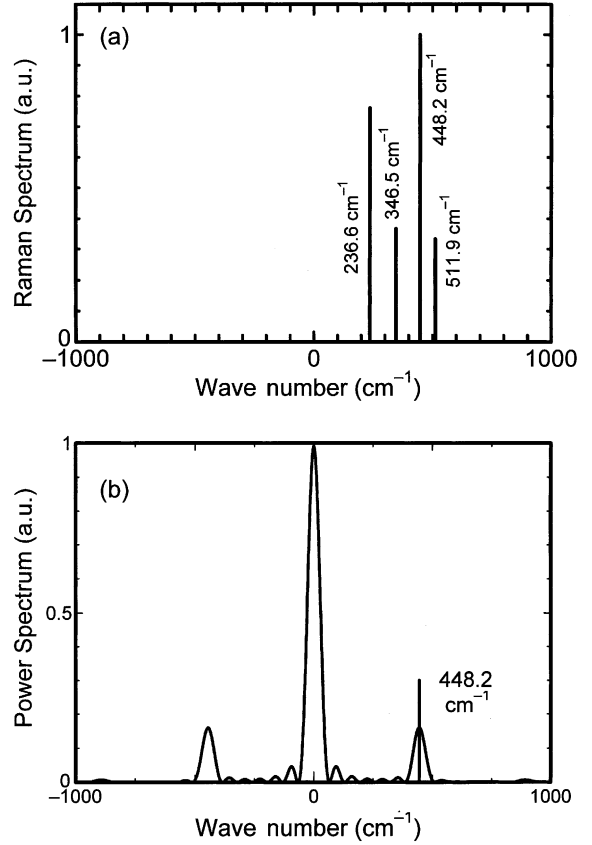


Fig. 3. (a) Raman spectrum of tetrachloroethylene. (b) The spectrum of an $N = 7$ pulse train for selective excitation at 448.2 cm^{-1} mode. The wave number 0 cm^{-1} corresponds to the center wavelength.

$$\eta_S = \left| \frac{\tilde{S}_{\text{hetero}}(\mathbf{k}_s, \omega_{R,int})}{\tilde{S}_{\text{hetero}}(\mathbf{k}_s, \omega_{R,ini}^{\max})} \right|^2. \quad (5)$$

The ratio of the power spectrum $|\tilde{S}_{\text{hetero}}(\mathbf{k}_s, \omega_{R,int})|^2$ of the SRS signal $\tilde{S}_{\text{hetero}}(\mathbf{k}_s, \omega)$ at the specific frequency of interest $\omega_{R,int}$ to $|\tilde{S}_{\text{hetero}}(\mathbf{k}_s, \omega_{R,ini}^{\max})|^2$ at another Raman frequency $\omega_{R,ini}^{\max}$ that maximizes the spectral intensity among the Raman frequencies $\omega_{R,ni,j}$ ($j = 1, \dots, m - 1$; $\tilde{S}_{\text{hetero}}(\mathbf{k}_s, \omega)$ is the Fourier transform of $S_{\text{hetero}}(\mathbf{k}_s, \tau_D)$). In Section 4, the efficient selective excitation by the vibrationally synchronized pumping technique with frequency difference resonance will be discussed together with the η_S values. Fig. 4 shows the calculated coherent Raman scattering signals as a

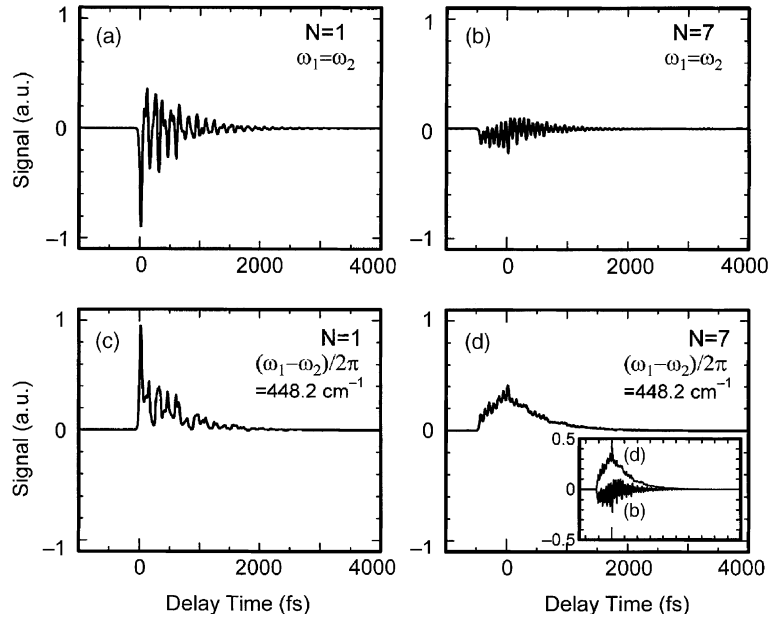


Fig. 4. Temporal profiles of heterodyne-detected coherent Raman scattering signals with pump pulses of (a) $\omega_1 - \omega_2 = 0$ and $N = 1$, (b) $\omega_1 - \omega_2 = 0$ and $N = 7$, (c) $(\omega_1 - \omega_2)/2\pi = 448.2 \text{ cm}^{-1}$ and $N = 1$, and (d) $(\omega_1 - \omega_2)/2\pi = 448.2 \text{ cm}^{-1}$ and $N = 7$. The comparison of the signals in the (b) and (d) cases is shown in the inset.

function of delay time in the OHD scheme for four cases ((a) $N = 1$, $\omega_1 = \omega_2$, (b) $N = 7$, $\omega_1 = \omega_2$, (c) $N = 1$, $(\omega_1 - \omega_2)/2\pi = 448.2 \text{ cm}^{-1}$ and (d) $N = 7$, $(\omega_1 - \omega_2)/2\pi = 448.2 \text{ cm}^{-1}$), on the assumption that the damping rates γ of all Raman modes in Eq. (4) are all 20 cm^{-1} . To obtain maximum signal intensities in the OHD scheme, we set the $\phi + \psi$ values to $\pi/2$ and 0 for the $\omega_1 - \omega_2 = 0$ and 448.2 cm^{-1} cases, respectively. In the $N = 1$ (Fig. 4(a) and (c)) cases, it is found that the signals exhibit combined oscillation of more than one frequency. In the $N = 7$ and $\omega_1 - \omega_2 = 0$ case (Fig. 4(b)), it is seen that the signal oscillates with a specific frequency at $\omega_{R,int}$ but the signal oscillating at $\omega_{R,int}$ is weak. In the $N = 7$ and $(\omega_1 - \omega_2)/2\pi = 448.2 \text{ cm}^{-1}$ (Fig. 4(d)), it is seen that the signal is dominated by a non-oscillating component. This non-oscillating part corresponds to the selectively-excited mode of interest owing to the frequency shift of $(\omega_1 - \omega_2)/2\pi = 448.2 \text{ cm}^{-1}$. By considering the integral of the non-oscillating with respect to the time delay, the selectively excited Raman signal at $\omega_{R,int} = 448.2 \text{ cm}^{-1}$ mode is

found to be comparatively large. (See the inset of Fig. 4(d).) To further clarify the selectivity of the excitation, the corresponding power spectra are shown in Fig. 5. Signal intensities when $\omega_1 - \omega_2 = 0$ (Fig. 5(a) and (b)) are low owing to the spectrum modulation factor $\mathcal{F}\{|F(t/T_0)|^2\}$ in Eq. (1). On the other hand, signal intensities when $(\omega_1 - \omega_2)/2\pi = 448.2 \text{ cm}^{-1}$ (Fig. 5(c) and (d)) are much more enhanced than those when $\omega_1 - \omega_2 = 0$. For Fig. 5(c) and (d), the horizontal axis represents wave number corresponding to $[\omega - (\omega_1 - \omega_2)]/2\pi$. Thus, the peak at 0 cm^{-1} corresponds to the vibrational mode of 448.2 cm^{-1} . That is, by adjusting $(\omega_1 - \omega_2)/2\pi$ to the mode frequency $\omega_{R,int}/2\pi$ of interest, we can effectively shift the Raman mode frequencies by $-(\omega_1 - \omega_2)/2\pi$ so that the only the signal intensity of interest is strengthened. As a result we can achieve much more efficient excitation at $\omega = 0 \text{ cm}^{-1}$. In addition, the $N = 7$ pulse train enables the further selective excitation of only the 448.2 cm^{-1} mode (Fig. 5(d)), while the $N = 1$ pulse excites all the Raman modes simultaneously (Fig. 5(c)). The quantitative comparison

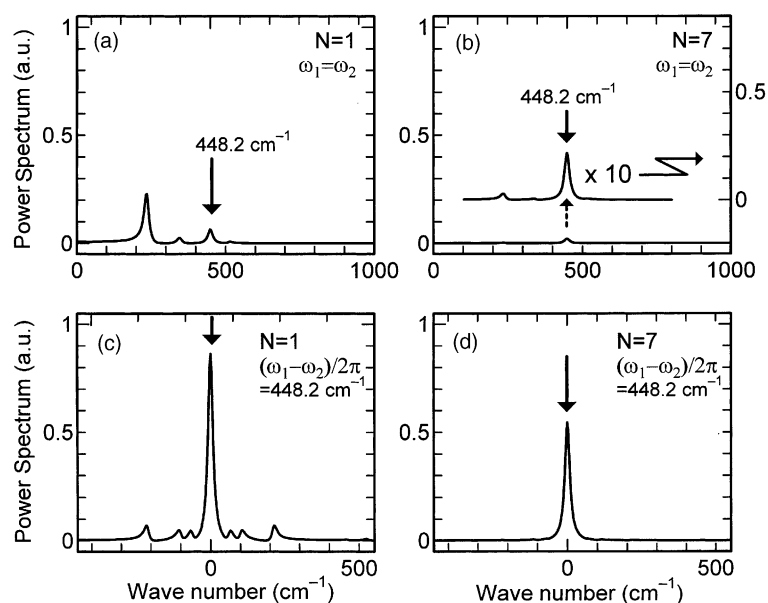


Fig. 5. Power spectra of heterodyne-detected coherent Raman scattering signals with pump pulses of (a) $\omega_1 - \omega_2 = 0$ and $N = 1$, (b) $\omega_1 - \omega_2 = 0$ and $N = 7$, (c) $(\omega_1 - \omega_2)/2\pi = 448.2 \text{ cm}^{-1}$ and $N = 1$, and (d) $(\omega_1 - \omega_2)/2\pi = 448.2 \text{ cm}^{-1}$ and $N = 7$. The selectivity is determined by η_S , which is defined by Eq. (5). This is evaluated to be (a) 0.285, (b) 7.35, (c) 12.2 and (d) 199.

of the selection factor η_S defined by Eq. (5) makes it clear that the η_S values are 0.285, 7.35, 12.2 and 199 for Fig. 5(a)–(d), respectively. Thus, it is found that, even in the high frequency region, efficient selective excitation can be made with two-color synchronized shaped- N -pulse train beams whose frequency difference is adjusted to the phonon mode frequency of interest (Fig. 5(d)). The calculated results show that this vibrationally synchronized pumping technique with frequency difference resonance (Fig. 5(d)) has the advantage of exhibiting an enhancement factor about 20 times larger in the power spectrum of Raman signal for selective excitation than the conventional one-color pulse shaping technique (Fig. 5(b)).

5. Conclusions

We have analyzed the SRS signal using N -pulse trains with finite duration. It was found that spectral modulation due to the finite duration of the constituent pulse causes low efficiency of selective excitation in the high vibrational frequency

region. To greatly improve on this low efficiency in the high frequency region, the vibrationally synchronized pumping technique with frequency difference resonance is proposed, in which both the pulse-repetition rate and the center-frequency difference of the two-color N -pulse train beams are made resonant with the frequency of the specific vibrational or rotational mode of interest. From the experimental point of view, under the condition that the total pulse energy is constant, the formula describing the optimum pulse number for effective selective excitation has been derived. As an example, we have calculated the SRS signal of tetrachloroethylene for (a) single pulses ($N = 1$, $\omega_1 - \omega_2 = 0$) case, (b) single pulses with frequency difference resonance ($N = 1$, $\omega_1 - \omega_2 = \omega_{R,int}$) case, (c) single frequency N -pulse trains (only repetition rate resonance: $N = 7$, $\omega_1 - \omega_2 = 0$) case and (d) N -pulse trains with repetition-rate and frequency difference resonances (vibrationally synchronized pumping technique with frequency difference resonance: $N = 7$, $\omega_1 - \omega_2 = \omega_{R,int}$) case. In the vibrationally synchronized pumping case with frequency difference resonance (d), a specific

vibration mode is selectively excited with a ~ 20 times larger power spectrum than in the repetition-rate resonance case (b). Thus, it is shown that this vibrationally synchronized pumping technique with frequency difference resonance for selective excitation is useful in the high frequency region as well as in the low frequency region.

Appendix A. Fundamental analysis of selective Raman-mode excitation

In order to clarify the advantage of the selective excitation using two-color pulse trains, we first describe the analysis of selective excitation by an N -pulse train with finite duration including two-color pump case as well as one-color pump case here. Consider a thin medium interacting with an external electric field:

$$E(\mathbf{r}, t) = E_{\text{pu}}(\mathbf{r}, t) + E_{\text{pr}}(\mathbf{r}, t), \quad (\text{A.1})$$

$$E_{\text{pu}}(\mathbf{r}, t) = \frac{1}{2}\bar{E}_{\text{pu1}}(t) \exp[i(\mathbf{k}_1 \cdot \mathbf{r} - \omega_1 t)] + \frac{1}{2}\bar{E}_{\text{pu2}}(t) \exp[i(\mathbf{k}_2 \cdot \mathbf{r} - \omega_2 t - \phi)] + \text{c.c.}, \quad (\text{A.2})$$

$$E_{\text{pr}}(\mathbf{r}, t) = \frac{1}{2}\bar{E}_{\text{pr}}(t - \tau_D) \exp[i(\mathbf{k}_3 \cdot \mathbf{r} - \omega_3 t)] + \text{c.c.}, \quad (\text{A.3})$$

$$E_{\text{LO}}(\mathbf{r}, t) = \frac{1}{2}\bar{E}_{\text{LO}}(t - \tau_D) \exp[i(\mathbf{k}_s \cdot \mathbf{r} - \omega_{\text{LO}} t - \psi)] + \text{c.c.} \quad (\text{A.4})$$

Here, $\bar{E}_{\text{pu1}}(t)$, $\bar{E}_{\text{pu2}}(t)$, $\bar{E}_{\text{pr}}(t)$ and \bar{E}_{LO} denote the temporal envelopes of pump1, pump2, probe and local oscillator pulses with different center frequencies ω_j ($j = 1, 2, 3$ or LO), respectively. The probe pulse is delayed by the time interval τ_D with respect to pump1 and pump2.

Pump1 and pump2 interfere in the medium, creating a transient grating with a wave vector $\mathbf{k}_1 - \mathbf{k}_2$. The probe beam then is Bragg-diffracted by this grating, resulting in the scattered beam in the $\mathbf{k}_s = \mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3$ direction. The center frequency of the scattered signal is $\omega_s = \omega_1 - \omega_2 + \omega_3$. An experimental setup of the box-CARS geometry for coherent Raman scattering is one of the cases of this configuration. In addition to these three pulses, a fourth pulse that can be used as a local oscillator for OHD is included here [12–14].

We here focus on Raman processes, with off-resonant electronic-state excitation such that

$$\begin{aligned} \omega_{\text{eg}} \pm \omega_1 &\gg 1/t_{\text{p},1}, \\ \omega_{\text{eg}} \pm \omega_2 &\gg 1/t_{\text{p},2}, \\ \omega_{\text{eg}} \pm \omega_3 &\gg 1/t_{\text{p},3}, \end{aligned} \quad (\text{A.5})$$

where $\hbar\omega_{\text{eg}}$ is the energy difference between the electronic excited and ground states, and $t_{\text{p},i}$ ($i = 1, 2, 3$) is the pulse duration of pump1, pump2 and the probe pulses, respectively. In this case, the optical-heterodyne-detected coherent Raman scattering signal in the \mathbf{k}_s -direction is given by

$$\begin{aligned} S_{\text{hetero}}(\mathbf{k}_s, \tau_D) &\propto \\ &- 2\omega_s \text{Im} \left\{ \int_{-\infty}^{\infty} dt |\bar{E}_{\text{pr}}(t - \tau_D)|^2 \int_0^{\infty} d\tau \bar{E}_{\text{pu1}}(t - \tau) \right. \\ &\times \bar{E}_{\text{pu2}}^*(t - \tau) \exp[i(\omega_1 - \omega_2)\tau] \sum_j r_j(\tau) \\ &\left. \times \exp[i(\phi + \psi)] \right\}, \end{aligned} \quad (\text{A.6})$$

integrated over all times t , on the assumption that $\bar{E}_{\text{LO}}(t) \propto \exp[i(\mathbf{k}_s \cdot \mathbf{r} - \omega_s t)]$. $r_j(t)$ is the Raman response of the medium exhibiting the j th vibrational mode ($j = 1, \dots, m$), expressed by

$$r_j(t) = A_j \exp(-\gamma_j t/2) \sin(\bar{\omega}_{\text{R},j} t), \quad (\text{A.7})$$

$$\bar{\omega}_{\text{R},j} = \sqrt{\omega_{\text{R},j}^2 - (\gamma_j/2)^2}, \quad (\text{A.8})$$

where A_j , γ_j and $\omega_{\text{R},j}$ are the relative strength, the damping rate and the natural vibrational frequency of the j th mode, respectively. In accordance with the philosophy of selective excitation, m modes are classified into a mode of interest ($\omega_{\text{R,int}}$) and $m - 1$ modes of no particular interest ($\omega_{\text{R,ni1}}, \dots, \omega_{\text{R,ni}(m-1)}$), hereafter. We do not include the electronic response function here.

Defining the Fourier transform of a function $f(t)$ as

$$\mathcal{F}\{f(t)\} = \int_{-\infty}^{\infty} dt e^{i\omega t} f(t), \quad (\text{A.9})$$

we can rewrite Eq. (A.6) as Eq. (1).

Appendix B. Mode selection

The coherent Raman scattering signal produced by the vibrationally synchronized pumping technique with frequency difference resonance is analyzed by describing the profiles of the pump pulses, using a shaped-pulse train in the form

$$\begin{aligned}\bar{E}_{\text{pu1}}(t) &= \bar{E}_{\text{pu2}}(t) \\ &= \sum_{n=1}^N F([t + (n-1)T]/T_0)/\sqrt{W},\end{aligned}\quad (\text{B.1})$$

$$W = \int_{-\infty}^{\infty} dt \left| \sum_{n=1}^N F([t + (n-1)T]/T_0) \right|^2, \quad (\text{B.2})$$

where $F(t/T_0)$ denotes the profile of each constituent pulse composing an N -pulse train with the constituent-pulse duration parameter T_0 , and T is the time interval between pulses, as shown by Fig. 2(a). Considering practical cases for selective excitation using pulse trains, the electric field is normalized by \sqrt{W} under the condition that the total pulse energy is constant. In the case where $T_0 < T$,

$$\begin{aligned}\bar{E}_{\text{pu1}}(t)\bar{E}_{\text{pu2}}^*(t) &\simeq \\ &\left\{ \sum_{n=1}^N |F([t + (n-1)T]/T_0)|^2 \right. \\ &+ \sum_{n=1}^{N-1} F([t + (n-1)T]/t_0)F^*([t + nT]/t_0) \\ &+ \sum_{n=2}^N F([t + (n-1)T]/t_0) \\ &\left. \times F^*([t + (n-2)T]/t_0) \right\} / W.\end{aligned}\quad (\text{B.3})$$

When $T_0 \ll T$, the second and the third terms in Eq. (B.3) can be neglected. Thus, the Fourier transform of the first term in Eq. (B.3) is

$$\begin{aligned}\mathcal{F}\left\{\bar{E}_{\text{pu1}}(t)\bar{E}_{\text{pu2}}^*(t)\right\} &\simeq \\ &\frac{1}{W} \frac{\sin(N\omega T/2)}{\sin(\omega T/2)} e^{-i(N-1)\omega T/2} \mathcal{F}\left\{|F(t/T_0)|^2\right\}.\end{aligned}\quad (\text{B.4})$$

The spectrum of Eq. (B.4) is almost discretized with the frequency spacing $\Delta\omega = 2\pi/T$, determined by the time interval T of the N -pulse train. This discretization enables us to excite coherent phonons selectively, that is, to excite only a specific vibrational mode. This is in stark contrast to the single-pulse (non-pulse train; $N = 1$) case where many Raman modes are excited simultaneously. This selective excitation can be explained through Eq. (1): among the Raman modes represented by $r_j(t)$, only a specific vibrational mode $\bar{\omega}_{\text{R,int}}$ is filtered by the spectrum $\mathcal{F}\{\bar{E}_{\text{pu1}}(t)\bar{E}_{\text{pu2}}^*(t)\}$, when $m\Delta\omega = \bar{\omega}_{\text{R,int}}$ (m : integer) in Eq. (A.8).

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