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Dependence of line shapes in femtosecond broadband stimulated Raman spectroscopy on pump-probe time delay

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Abstract

The effect of the time delay between the picosecond Raman pump and the femtosecond Stokes probe pulse on the Raman gain line shape in femtosecond broadband stimulated Raman spectroscopy (FSRS) is presented. Experimental data are obtained for cyclohexane to investigate the dependence of the FSRS line shape on this time delay. Theoretical simulations of the line shapes as a function of the time delay using the coupled wave theory agree well with experimental data, recovering broad line shapes at positive time delays and narrower bands with small Raman loss side wings at negative time delays. The analysis yields the lower bounds of the vibrational dephasing times of 2.0 ps and 0.65 ps for the 802 and 1027 cm^{-1} modes for cyclohexane, respectively. The theoretical description and simulation using the coupled wave theory are also consistent with the observed Raman gain intensity profile over time delay, reaching the maximum at a slightly negative time delay (~ -21 ps), and show that the coupled wave theory is a good model for describing FSRS.

I. INTRODUCTION

Femtosecond broadband stimulated Raman spectroscopy (FSRS) is a powerful technique that reveals vibrational structural information of stationary, transient, or excited states.¹⁻⁶ A narrow bandwidth picosecond Raman pump pulse and a broadband femtosecond Stokes-Raman probe pulse acting simultaneously on the sample produce a high resolution Raman gain spectrum with high efficiency and speed, free from fluorescence background interference.^{2,3} Combined with another ultrafast laser pulse that prepares the molecules in an electronic excited state, time-resolved FSRS can be used to explore the evolution of the vibrational structure of transient species with both high temporal (<100 fs) and spectral (~ 10 cm^{-1}) resolution, overcoming the pulse duration/bandwidth transform limit in conventional time-resolved Raman spectroscopy. The electronic excited state dynamics of polyenes and of biological pigments have thus far been studied using time-resolved FSRS.^{1,4,5,7-12}

Despite its ever increasing applications, theoretical understanding of the FSRS experiment has been formalized only recently. Early classical and quantum theories for stimulated Raman scattering were developed for cw fields, and clearly had to be modified and extended to pulsed fields. Lee *et al.*⁶ developed semiclassical coupled wave and quantum mechanical approaches

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for FSRS for the case where the Raman pump and Stokes probe pulse maxima are coincident, and showed the correspondence between the two approaches under the following principal assumptions: (a) the Raman pump frequency is off-resonant with any excited electronic state, and (b) the molecule undergoes a fundamental Stokes–Raman transition. Figure 1 illustrates the quantum-mechanical description of FSRS using the energy ladder, bra–ket time evolution diagram of Lee and Albrecht,¹³ from which we can draw the correspondence with the coupled wave theory. The first two dashed arrows correspond to bra side interaction with the Raman pump E_p^* and Stokes probe E_s fields which excite the system from an initial ground vibrational Liouville state $|0\rangle\langle 0|$ to the state $|0\rangle\langle 1|$ where there is one vibrational quantum in the bra, creating a coherent vibration in the system. The coherent vibration as a function of time $Q^*(t)$ is described by a forced, damped oscillator decaying with a characteristic vibrational dephasing time T_2 in the coupled wave theory. In the Placzek polarizability model, the change in polarization in FSRS arises from the interaction of $Q^*(t)$ with the long Raman pump field E_p designated by the solid arrow acting on the ket side of the system in the density matrix. The change in polarization in the medium then radiates coherently, giving the stimulated Raman line as described by Maxwell's equation for the electric field, and leaves the system in the $|1\rangle\langle 1|$ state. Energy conservation and phase matching conditions require that the radiation copropagate with the Stokes probe beam with a frequency ω_s .

The spectral line shapes reflect the intramolecular and intermolecular processes in a medium. Therefore, detailed analysis of the line shape of Raman spectra, in the context of an appropriate theoretical treatment, can provide insight on the spectroscopic and dynamic processes occurring in the medium. The line shapes of four-wave mixing spectra such as coherent anti-Stokes Raman spectra (CARS) and inverse Raman spectra, for example, have been successfully analyzed using nonlinear third-order susceptibility described within the framework of quantum statistical density matrix formalism.^{13,14}

In this paper, we explore experimentally the change of the FSRS line shapes as a function of time delay between the Raman pump and Stokes probe. We extend the coupled wave theory to include a time delay between the two pulses and elucidate the experimental results in the light of the theory. In Sec. II, we derive the coupled wave theory for FSRS including a variable time delay between the Raman pump and Stokes probe pulses. The experimental setup is presented in Sec. III and measurements on the dependence of the line shape of FSRS spectra with time delay for cyclohexane in the ground electronic state are presented in Sec. IV. The ability of the coupled wave theory to account for the experimental observations and the analysis of the FSRS line shape for vibrational dephasing time is also presented in Sec. IV.

II. THEORY

The theory of stimulated Raman scattering, using both the classical and quantum-mechanical approaches, has been presented by many authors with varying degrees of success.^{15–25} The most successful has been the semiclassical description in terms of a coupling between the light waves and the molecular vibrations.^{20–23,25} However, these theories at some stage make the assumption of coincident cw fields to simplify the derivations. It was necessary to extend the coupled wave theory to include pulsed fields in order to describe FSRS.

In an earlier paper,⁶ we presented the semiclassical coupled wave theory of FSRS with zero time delay between the Raman pump and Stokes probe pulses, and showed its correspondence with the quantum-mechanical theory. Here we extend the coupled wave theory for FSRS to the situation, where there may be a time delay between the two pulses and obtain expressions for the Raman gain profile that can be used to simulate experimental measurements of FSRS line shapes.

The medium is taken to be a collection of oscillators with vibrational coordinate Q , and we focus on just one vibrational mode of angular frequency ω_0 . The classical theory for the optical field-medium interaction together with the Placzek model for the polarization of the oscillator gives the equation of motion for the vibration Q ,

$$\frac{d^2 Q}{dt^2} + 2\gamma \frac{dQ}{dt} + \omega_0^2 Q = \alpha_0' |E(z, t)|^2, \quad (1)$$

where α_0' is the first-order derivative of the polarizability with respect to Q evaluated at the equilibrium configuration, $E(z, t)$ is the linearly polarized electric field propagating along the z axis, and $2\gamma dQ/dt$ is a phenomenological damping term for the vibration which decays as $e^{-\gamma t}$. The damping constant γ would typically be given by $\gamma = T_Q^{-1} + T_{\text{pop}}^{-1}$ where T_Q is the vibrational dephasing time and T_{pop} is the lifetime of the transient species bearing the vibration. The reacting medium modifies the optical field in a nonlinear way described by the Maxwell equation, and again using the Placzek model for the polarization, we have

$$\frac{\partial^2 E(z, t)}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2 E(z, t)}{\partial t^2} \approx \frac{4\pi}{c^2} N \alpha_0' \frac{\partial^2 [QE(z, t)]}{\partial t^2}, \quad (2)$$

where N is the number of oscillators per unit volume. Equations (1) and (2) are the central equations that can be used to describe stimulated Raman scattering. We first solve for $Q(t)$ using Eq. (1) and the result is then used in the Maxwell equation (2) to solve for the output field $E(z, t)$.

The total field in FSRS is a sum of a Raman pump field and a Stokes probe field,

$$E(z, t) = E_p(z, t) + E_s(z, t), \quad (3)$$

and we shall take the Stokes probe maximum to arrive at time t_D relative to the Raman pump maximum, with Gaussian pulse envelopes as follows:

$$E_p(z, t) = E_p^0 e^{-\left(t+t_D-z/c\right)^2/2\tau_p^2} e^{-i\omega_p(t+t_D-z/c)}, \quad (4)$$

$$E_s(z, t) = E_s^0 e^{-(t-z/c)^2/2\tau_s^2} e^{-i\omega_s(t-z/c)}, \quad (5)$$

and whose spectra (given by the Fourier transform $\int_{-\infty}^{\infty} dt e^{i\omega t}$) are

$$E_p(z, \omega) = E_p^0 \sqrt{2\pi\tau_p} e^{-\left(\omega-\omega_p\right)^2\tau_p^2/2} e^{-i\omega(-t_D+z/c)}, \quad (6)$$

$$E_s(z, \omega) = E_s^0 \sqrt{2\pi\tau_s} e^{-\left(\omega-\omega_s\right)^2\tau_s^2/2} e^{i\omega z/c}. \quad (7)$$

In the FSRS experiments of Mathies and co-workers¹⁻⁵ the pump field $E_p(z, t)$ is a ~ 800 nm long pulse ($\tau_p \sim 1-3$ ps) of narrow bandwidth ($\sim 5-15$ cm⁻¹), while the Stokes probe field $E_s(z, t)$ is a 830–950 nm short continuum pulse ($\tau_s \sim 30-50$ fs) covering stimulated Raman shifts of 500–2300 cm⁻¹. The picosecond pump pulse can sometimes be very long compared to the vibrations which have periods of 15–70 fs (500–2300 cm⁻¹) and the vibrational dephasing time, in which case it can even be taken to be monochromatic, but we do not need to assume this here.

Now, $|E(z,t)|^2$ has four components, but only the component $E_p(z, t)E_s^*(z, t)$ possesses the right frequency $\sim e^{-i(\omega_p - \omega_s)t}$ to exert a resonant forcing term on the vibration $Q \sim e^{-i\omega_0 t}$, with the equation of motion for the vibration given by

$$\frac{d^2 Q}{dt^2} + 2\gamma \frac{dQ}{dt} + \omega_0^2 Q = a_0' E_p E_s^* \quad (8)$$

Using Eqs. (4) and (5) in Eq. (8), and defining $t' = t - z/c$, we obtain

$$\frac{d^2 Q}{dt^2} + 2\gamma \frac{dQ}{dt} + \omega_0^2 Q = E_p^0 E_s^{0*} a_0' e^{-t'^2/2\tau_s^2 - i(\omega_p - \omega_s)t'} e^{-i\omega_p t_D - t_D^2/2\tau_p^2}, \quad (9)$$

where we have used the value of the Gaussian envelope for the long Raman pump pulse at the ultrashort Stokes probe maximum ($t'=0$). Clearly, a coherent vibration Q is impulsively induced in the medium due to the coupled fields acting for a duration corresponding to that of the ultrashort Stokes probe pulse ($\tau_s \sim 30$ fs) centered at time t_D relative to the maximum of the Raman pump pulse.

The solution to Eq. (9) comprises a homogeneous solution and a particular solution. As shown previously,⁶ the homogeneous solution can be ignored because of its random phase; leaving only the particular solution. To solve Eq. (9) for the particular solution $Q_p(z, t)$, we take a Fourier transform $\int_{-\infty}^{\infty} dt e^{i\omega t}$ (note that it is with respect to t and not t') and integrate by parts to remove the derivatives in t to yield the solution in frequency space,

$$Q_p(z, \omega) = \frac{f(\omega) e^{i\omega z/c - i\omega_p t_D - t_D^2/2\tau_p^2}}{\omega_0^2 - \omega^2 - i2\gamma\omega}, \quad (10)$$

with $f(\omega)$ given by

$$\begin{aligned} f(\omega) &= \int_{-\infty}^{\infty} E_p^0 E_s^{0*} a_0' e^{-t'^2/2\tau_s^2 - i(\omega_p - \omega_s)t'} e^{i\omega t'} dt' \\ &= E_p^0 E_s^{0*} a_0' \sqrt{2\pi\tau_s} e^{-(\omega - \omega_p + \omega_s)^2 \tau_s^2 / 2}. \end{aligned} \quad (11)$$

Now, $f(\omega)$ is a Gaussian distribution in ω centered at $(\omega_p - \omega_s)$, as broad as the Stokes probe spectrum, which means that the distribution of $Q_p(z, \omega)$ is determined by the energy denominator in Eq. (10), leading to a narrow bandwidth real dispersive-like term of width 2γ and an imaginary Lorentzian-like term of width γ , centered about $\omega \approx \omega_0$.

By choosing the complex conjugate of the forcing term on the right of Eq. (8), we have another solution for $Q_p(z, t)$, which we designate as $Q_p^*(z, t)$, and later on we will need $Q_p^*(z, \omega)$, the Fourier transform of $Q_p^*(z, t)$,

$$Q_p^*(z, \omega) = \frac{E_p^{0*} E_s^0 a_0' \sqrt{2\pi\tau_s} e^{-(\omega + \omega_p - \omega_s)^2 \tau_s^2 / 2} e^{i\omega z/c + i\omega_p t_D - t_D^2/2\tau_p^2}}{\omega_0^2 - \omega^2 - i2\gamma\omega}, \quad (12)$$

where the Gaussian numerator is broad and centered at $(\omega_s - \omega_p) < 0$, and again the shape of $Q_p^*(z, \omega)$ is determined by the energy denominator, giving rise to narrow bandwidth real and imaginary parts which are similar to those of $Q_p(z, \omega)$, but are now centered about $\omega \approx -\omega_0$. We can then make the approximation

$$Q_p^*(z, \omega) \approx \frac{E_p^{0*} E_s^0 a_0' \sqrt{2\pi} \tau_s e^{-\left(\omega_p - \omega_s - \omega_0\right)^2 \tau_s^2 / 2} e^{i\omega z / c + i\omega_p t_D - t_D^2 / 2 \tau_p^2}}{2 \omega_0 (\omega + \omega_0 + i \gamma)}. \quad (13)$$

Turning now to the Maxwell equation (2), where the polarization is given in the Placzek model by $P(z, t) = a_0' Q(z, t) E(z, t)$, and considering the output Stokes probe field and the particular solution for $Q(z, t)$, we would choose the inhomogeneous term on the right to fall within the frequency range of the Stokes field, thus obtaining

$$\frac{\partial^2 E_s(z, t)}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2 E_s(z, t)}{\partial t^2} \approx \frac{4\pi}{c^2} N a_0' \frac{\partial^2 [Q_p^*(z, t) E_p(z, t)]}{\partial t^2}. \quad (14)$$

Effectively, the polarization is proportional to the product of the vibration $Q_p^*(z, t)$ set up by the impulsive coupled fields at delay time t_D , relative to the Raman pump maximum, and the Raman pump field $E_p(z, t)$. So, on the basis of causality, we would expect the impulsively generated vibration to interact with more of the Raman pump field for more negative time delays (Stokes probe *before* Raman pump maximum), which means that the line shape of the stimulated Raman band will be narrower for more negative time delays and broader for more positive time delays (Stokes probe *after* Raman pump maximum). We shall see later that this is borne out in the simulations.

To solve Eq. (14), we take a Fourier transform $\int_{-\infty}^{\infty} dt e^{i\omega t}$ to give

$$\frac{\partial^2 E_s(z, \omega)}{\partial z^2} + \frac{\omega^2}{c^2} E_s(z, \omega) \approx -\frac{4\pi\omega^2}{c^2} N a_0' \text{FT}\{Q_p^*(z, t) \otimes E_p(z, t)\}, \quad (15)$$

where $\text{FT}\{\dots\}$ denotes taking the Fourier transform, and

$$\text{FT}\{Q_p^*(z, t) E_p(z, t)\} = (2\pi)^{-1} Q_p^*(z, \omega) \otimes E_p(z, \omega), \quad (16)$$

where the right-hand side is a convolution of $Q_p^*(z, \omega)$ of width 2γ centered at $-\omega_0$, with a narrow pump spectrum $E_p(z, \omega)$, of width τ_p^{-1} centered at ω_p , and the output is significant only for ω in the neighborhood $\omega \approx \omega_p - \omega_0$. Using Eqs. (6) and (13), we obtain

$$\begin{aligned} Q_p^*(z, \omega) \otimes E_p(z, \omega) &= \int_{-\infty}^{\infty} Q_p^*(z, \tilde{\omega}) E_p(z, \omega - \tilde{\omega}) d\tilde{\omega} \\ &= \int_{-\infty}^{\infty} \frac{E_p^{0*} E_s^0 a_0' \sqrt{2\pi} \tau_s (2\omega_0)^{-1} e^{-\left(\omega_p - \omega_s - \omega_0\right)^2 \tau_s^2 / 2} e^{i\omega z / c + i\omega_p t_D - t_D^2 / 2 \tau_p^2}}{(\tilde{\omega} + \omega_0 + i \gamma)} \\ &\quad \times E_p^0 \sqrt{2\pi} \tau_p e^{-\left(\omega - \tilde{\omega} - \omega_p\right)^2 \tau_p^2 / 2} e^{i(\omega - \tilde{\omega})(-t_D + z/c)} d\tilde{\omega} \\ &= a_0' \pi \tau_s \tau_p \omega_0^{-1} e^{-\left(\omega_p - \omega_s - \omega_0\right)^2 \tau_s^2 / 2} \left\{ \int_{-\infty}^{\infty} \frac{e^{-\left(\omega - \tilde{\omega} - \omega_p\right)^2 \tau_p^2 / 2} e^{i(\omega - \tilde{\omega})(-t_D + z/c)}}{(\tilde{\omega} + \omega_0 + i \gamma)} d\tilde{\omega} \right\} \\ &\quad \times E_p^{0*} E_s^0 e^{i\omega z / c} e^{-t_D^2 / 2 \tau_p^2}, \end{aligned} \quad (17)$$

and the result shows a wave vector dependence $e^{i\omega z/c}$, with $\omega \approx \omega_p - \omega_0$, which falls within the continuum Stokes probe beam, with a $|E_p^0|^2 |E_s^0|^2$ dependence on the field amplitudes which is associated with stimulated Raman scattering. We can also approximate Eq. (17) as

$$Q_p^*(z, \omega) \otimes E_p(z, \omega) \approx a_0' \sqrt{\pi/2} \tau_p \omega_0^{-1} e^{-t_D^2/2 \tau_p^2} g(\omega, t_D) |E_p^0|^2 E_s^{\text{free}}(z, \omega), \quad (18)$$

where $E_s^{\text{free}}(z, \omega)$ is the free Stokes probe spectrum given by Eq. (7) and

$$g(\omega, t_D) \equiv \int_{-\infty}^{\infty} \frac{e^{-\left(\tilde{\omega} - \omega_p\right)^2 \tau_p^2 / 2 - i\left(\tilde{\omega} - \omega_p\right) t_D}}{\left(\tilde{\omega} + \omega_0 + i\gamma\right)} d\tilde{\omega}. \quad (19)$$

By using the integral representation

$$\left(\tilde{\omega} + \omega_0 + i\gamma\right)^{-1} = -i \int_0^{\infty} e^{i\left(\tilde{\omega} + \omega_0 + i\gamma\right)t} dt, \quad (20)$$

and performing the integral over $\tilde{\omega}$, we can convert the convolution integral in Eq. (19) to the following half-Fourier transform:

$$g(\omega, t_D) = -i \sqrt{2\pi} \tau_p^{-1} \int_0^{\infty} e^{i\left(\omega + \omega_0 - \omega_p\right)t} e^{-\left(t + t_D\right)^2 / 2 \tau_p^2 - \gamma t} dt. \quad (21)$$

It can be shown that $|g(\omega, t_D)|$ peaks at $\omega \approx \omega_p - \omega_0$ with width governed by τ_p^{-1} and γ , or the larger of the two if one is dominant.

Returning to Eq. (15), the Maxwell equation for the Stokes probe beam is thus given by

$$\begin{aligned} \frac{\partial^2 E_s(z, \omega)}{\partial z^2} + \frac{\omega^2}{c^2} E_s(z, \omega) &\approx -\frac{\omega^2}{c^2} \sqrt{2\pi} N |E_p^0|^2 (a_0')^2 \omega_0^{-1} \tau_p e^{-t_D^2/2 \tau_p^2} g(\omega, t_D) \times E_s^{\text{free}}(z, \omega) \\ &\equiv -\frac{\omega^2}{c^2} 4\pi \chi_R(\omega, t_D) |E_p^0|^2 E_s^{\text{free}}(z, \omega), \end{aligned} \quad (22)$$

where we have defined the Raman susceptibility $\chi_R(\omega, t_D)$ as

$$\chi_R(\omega, t_D) \equiv N (a_0')^2 (2\omega_0)^{-1} (2\pi)^{-1/2} \tau_p e^{-t_D^2/2 \tau_p^2} g(\omega, t_D). \quad (23)$$

Outside the narrow region of the stimulated Raman line at $\omega \approx \omega_p - \omega_0$, the right-hand side of Eq. (22) is effectively zero, and we solve a homogeneous equation

$$\frac{\partial^2 E_s(z, \omega)}{\partial z^2} + \frac{\omega^2}{c^2} E_s(z, \omega) = 0, \quad (24)$$

whose solution is given by the free Stokes probe spectrum $E_s^{\text{free}}(z, \omega)$ as in Eq. (7). The solution to Eq. (22) can then be shown by substitution to be

$$E_s(z, \omega) = \left\{ 1 + i 2\pi \chi_R(\omega, t_D) |E_p^0|^2 \frac{\omega z}{c} \right\} E_s^{\text{free}}(z, \omega). \quad (25)$$

FSRS measures the Raman gain, i.e., transmittance, by a heterodyne technique, given by the ratio of the intensity of the Stokes probe spectrum with and without the presence of the Raman pump,

$$G_R(\omega, t_D) = \frac{|E_S(z, \omega)|^2}{|E_S^{\text{free}}(z, \omega)|^2} = \left| 1 + i2\pi\chi_R(\omega, t_D) |E_P^0|^2 \frac{\omega z}{c} \right|^2 \equiv [1 + A(\omega, t_D)]^2 + [B(\omega, t_D)]^2, \quad (26)$$

where

$$A(\omega, t_D) = \kappa e^{-t_D^2/2\tau_P^2} \omega \int_0^\infty \cos[(\omega + \omega_0 - \omega_P)t] \times e^{-(t+t_D)^2/2\tau_P^2 - \gamma t} dt, \quad (27)$$

$$B(\omega, t_D) = \kappa e^{-t_D^2/2\tau_P^2} \omega \int_0^\infty \sin[(\omega + \omega_0 - \omega_P)t] \times e^{-(t+t_D)^2/2\tau_P^2 - \gamma t} dt, \quad (28)$$

and κ is a collection of constants that can be taken as a parameter to fit the experimental data. The Raman gain $G_R(\omega, t_D)$, Eq. (26), is nearly an even function in ω about $(\omega_P - \omega_0)$ and can be easily evaluated numerically to generate a line shape for any given pulse delay t_D .

For small gain, we can approximate Eq. (26) as

$$G_R(\omega, t_D) = \left| 1 + i2\pi\chi_R(\omega, t_D) |E_P^0|^2 \frac{\omega z}{c} \right|^2 \approx e^{-4\pi\text{Im}(\chi_R(\omega, t_D)) |E_P^0|^2 \omega z / c}. \quad (29)$$

We can then define a Raman optical density as

$$D_R(\omega, t_D) \equiv \ln G_R(\omega, t_D) \approx -4\pi\text{Im}(\chi_R(\omega, t_D)) |E_P^0|^2 \omega z / c, \quad (30)$$

and using the definition of $\chi_R(\omega, t_D)$ in Eq. (23) we obtain a result that is rather similar to absorbance measurements where the optical density is linearly proportional to the concentration N of the scattering species and the cell length z , but in FSRS it is also proportional to the intensity $|E_P^0|^2$ of the Raman pump field.

The coupled wave theory for FSRS can be illustrated by examining the time and frequency response of the system to the Raman pump and Stokes probe pulses, using the case where there is zero time delay between the pulses ($t_D=0$) as shown in Fig. 2. The Raman pump field, Eq. (4), is a narrow bandwidth ~ 2 ps pulse centered at ~ 800 nm. Figure 2(a) illustrates the Raman pump field $E_P(z=0, t)$ and its spectral intensity $I_P(\omega) \equiv |E_P(\omega)|^2$. Similarly, the ~ 20 fs broadband Stokes probe field, Eq. (5), and its spectral intensity are shown in Fig. 2(b). When the two pulses are overlapped at the sample, they drive Raman active molecular vibrations at the beat frequency between the pulses as described by Eq. (9). The particular solution, in the frequency domain, $Q(z, \omega)$ is given by Eqs. (10) and (11). By choosing $\gamma/\pi c \approx 15 \text{ cm}^{-1}$, the spectral intensity $I_Q(\omega) \equiv |Q(z=0, \omega)|^2$ is plotted on the right of Fig. 2(c), with the inverse transform of $Q(z=0, \omega)$ shown on the left having a characteristic dephasing time of ~ 700 fs. In the Placzek model, the total sample polarization is given by

$$P_{\text{Total}}(t) = a \cdot E_p(t) = [a_0 + a_0' Q(t)] E_p(t);$$

it follows the Raman pump field before the arrival of the Stokes probe field, but after the impulsive excitation of the material the polarization is modulated at the vibration frequency as shown in Fig. 2(d) on the left. In frequency space, $P_{\text{Total}}(\omega)$ is dominated by the Raman pump Fourier component, but has a Stokes shifted sideband at $\omega = \omega_p - \omega_0$; the spectral intensity $I_{\text{Total}}^P(\omega) \equiv |P_{\text{Total}}(\omega)|^2$ is shown in Fig. 2(d) on the right. Only the sideband Fourier component of the polarization that falls within the Stokes probe spectrum enters into the Maxwell equation (15) in frequency space and contributes to the Raman gain. There is, of course, another weaker (due to Boltzmann population considerations) sideband at $\omega_p + \omega_0$ for excitation from the ground electronic state, but it is not measured in the FSRs configuration used here. The solution of the Maxwell equation is the heterodyne result given by Eq. (25), which has two components: the broadband free Stokes probe spectrum, and on top of it a narrow bandwidth stimulated Raman spectrum peaking at $\omega \approx \omega_p - \omega_0$. The heterodyne spectral intensity is shown on the right of Fig. (2e), and the inverse Fourier transform (IFT) of the component field spectra, shown on the left of Fig. (2e), are the free Stokes probe field $E_s^{\text{free}}(t)$ and the stimulated Raman field $E_{\text{SR}}(t) \propto \text{IFT}\{\omega \chi_R(\omega, t_D = 0) E_s^{\text{free}}(\omega)\}$. The latter appears with the impulsive excitation of the system, as required by causality. The line width of the stimulated Raman spectrum will be largely determined by the vibrational dephasing time T_2 if the Raman pump pulse is much longer than T_2 , as in the example here. However, if the duration of the Raman pump is shorter than T_2 , then the convolution of the vibrational amplitude spectrum with the Raman pump spectrum will lead to a further broadening of the stimulated Raman line than that predicted by T_2 alone. The instrumental resolution is a further source of line broadening.

III. EXPERIMENTAL APPROACH

The dependence of cyclohexane FSRs line shapes on time delay between the Raman pump and Stokes probe pulses was determined experimentally and simulated using the coupled wave theory described in the preceding section. The experimental setup for FSRs has been described in detail elsewhere,^{1,3} so only an outline related to the current experiment is presented here. Two pulses—Raman pump and Stokes probe—are used to produce femtosecond stimulated Raman spectra. A regeneratively amplified Ti:Sapphire oscillator produces 1 kHz, 750 μJ pulses at 800 nm. Part of the amplifier output beam produces a continuum in a 3 mm thick sapphire plate which is compressed in a prism compressor to give 30 fs long, broadband Stokes probe pulses that span from 830 to 960 nm. A circularly variable neutral density filter in the beam path is used to adjust the power of the Stokes probe beam up to 6.1 nJ/pulse.

The Raman pump pulses ($\lambda = 794$ nm) are produced by passing the remainder of the amplifier output through a pair of narrow band pass filters or a spectral grating filter.^{26,27} Adjusting the slit width of the grating filter changes the pulse width from ~ 2 to ~ 6 ps. The pulse width of the Raman pump is measured using the optical Kerr effect cross correlation technique^{28,29} in cyclohexane. Figure 3 presents a cross correlation in cyclohexane between the Raman pump generated with a ~ 120 μm slit width and 30 fs FWHM Stokes probe. Since the pulse width of the Stokes probe is much shorter than that of the Raman pump, it is assumed that the cross correlation reflects the pulse width of the Raman pump which fits to a Gaussian function with 2.7 ps FWHM. The power of the Raman pump at the sample is maintained at 480 μJ /pulse and the polarization is set parallel to the Stokes probe for the experiment. The Raman pump beam is collinearly combined with the Stokes probe beam after a delay stage and focused onto the sample in a 1 cm cuvette. A fraction of the Stokes probe beam is split off before the sample and used as a reference. After passing through the sample, the Raman pump beam is blocked

by a long-pass filter and the transmitted broadband Stokes probe beam, combined with the reference beam, is collected, dispersed in a spectrograph, and imaged onto a dual photodiode array detector. The linear dispersion of the spectrograph is $0.08 \text{ cm}^{-1}/\mu\text{m}$. The observed linewidths were not broadened by the instrumental resolution since the observed bandwidth was independent of slit width.

The time delay t_D between the two pulses in the experiment is defined as illustrated in Fig. 4. When $t_D > 0$, the maximum of Raman pump arrives at the sample prior to the Stokes probe. Therefore, the electric field envelopes of the $\sim$ picosecond Raman pump pulse and the ultrashort Raman probe pulse ($\sim 30 \text{ fs}$) will appear at the sample as in Fig. 4(b), where time progresses from left to right in the time coordinate.

Raman gain spectra are obtained by turning the Raman pump pulses on and off successively using an electronic shutter and calculating the Raman pump-induced amplification in the probe spectra with respect to the spectra in the absence of the Raman pump: Raman Gain,

$$G_R = \frac{[(\text{probe} - \text{bkgnd}) \div (\text{ref} - \text{bkgnd})]_{\text{Raman Pump On}}}{[(\text{probe} - \text{bkgnd}) \div (\text{ref} - \text{bkgnd})]_{\text{Raman Pump Off}}} \quad (31)$$

Each final spectrum presented is an average of 50 spectra, each of which is obtained using 70 ms exposure time, corresponding to 8 s of total acquisition time.

IV. RESULTS AND DISCUSSION

The FSRS spectra of cyclohexane at selected time delays are presented in Fig. 5(a). The three peaks in the spectra are assigned to symmetric C–C stretch ($A_{1g}, 802 \text{ cm}^{-1}$), doubly degenerate C–C stretch ($E_g, 1027 \text{ cm}^{-1}$), and CH_2 rock ($A_{1g}, 1157 \text{ cm}^{-1}$) of cyclohexane. The change in the line shape with time delay is most apparent for the intense 802 cm^{-1} peak. The spectral line broadens with increasing positive time delays. As the time delay t_D decreases in the negative direction, the peak becomes narrower and the line shape develops small Raman loss side wings. The two-dimensional contour plot of the Raman gain spectra in Fig. 5(b) clearly indicates that the loss intensity features appear in the wings of the band at time delays from -2 ps to -4 ps for the 802 cm^{-1} mode.³⁰ Furthermore the maximum of the Raman gain appears at $t_D \approx -1 \text{ ps}$, in contrast to physical intuition which suggests that the maximum gain occur at $t_D = 0 \text{ ps}$ when the largest temporal overlap between the Raman pump and Stokes probe pulse envelopes is achieved. The change in the line shape with time delay of the weaker vibrational bands ($1027, 1157$, and 1266 cm^{-1}) has a similar pattern to that of the 802 cm^{-1} band. All the line shape features, including the broadening with more positive time delays and the narrowing with more negative time delays, remain the same as we decrease the power of the Raman probe laser, indicating that these features are not due to a nonlinear effect of the Raman probe field.

The coupled wave theory described in the preceding section can be used to model these experimental observations (Fig. 6). Assuming that only the vibrational dephasing contributes to the line broadening, we fit our experimental Raman gain spectra using Eq. (26), $\ln [G_R(\omega, t_D)]$, with the vibrational dephasing time γ as a fitting parameter. As γ decreases (thus, vibrational dephasing time increases), the linewidth of the spectrum decreases and the Raman loss side wings at negative time delays become more pronounced. The simulation using γ^{-1} of $2.0 \pm 0.2 \text{ ps}$ for the 802 cm^{-1} mode and $0.65 \pm 0.02 \text{ ps}$ for the 1027 cm^{-1} gives the best agreement with the experimental spectra. Figure 6 shows that the simulation reproduces all the line shape features and trends.³¹

The vibrational dephasing time of the totally symmetric 802 cm^{-1} band has been derived from the isotropic spontaneous Raman linewidth, which are assumed to be homogeneous. Tanabe^{32,33} obtained the linewidth of $1.6 \pm 0.1 \text{ cm}^{-1}$, corresponding to a $6.6 \pm 0.4 \text{ ps}$ vibrational

dephasing time. The Fourier transform of the isotropic scattering intensity gives the vibrational correlation function from which vibrational dephasing times of 4.9 ± 0.3 ps and 4.7 ± 0.5 ps have been determined.^{34,35} For the 1027 cm^{-1} band, Arndt and McClung³⁶ reported 0.9 ps for the vibrational relaxation time. The difference between the dephasing time from our FSRS experiment and those from the isotropic Raman linewidth suggests that the FSRS gain spectra include other line broadening contributions such as orientation relaxation and inhomogeneous broadening, making the effective vibrational dephasing time shorter and providing a lower bound for the vibrational dephasing time. From the relation $1/\tau = 1/T_2 + 1/\tau_R$, where τ is the effective relaxation time and τ_R is the reorientational relaxation time ($1\text{--}1.5$ ps for cyclohexane),^{32,35,37-40} we obtain $\tau = 1.2$ ps which is closer to our observed relaxation time. A full theoretical treatment that properly considers the tensorial nature of the Raman polarizability, extending the earlier limited treatment by Laubereau and Kaiser,²² might better explain the differences between the measured relaxation times but is beyond the scope of the current work. Experimental separation of the vibrational and rotational contributions to the spectra in FSRS might be possible by including another coupling picosecond pulse and choosing different combinations of polarizations for each Raman pump pulse as demonstrated in time-resolved coherent Stokes and anti-Stokes Raman spectroscopy.^{22,41-44}

Figure 7 presents a contour plot providing an overall comparison of the theory with experiment for FSRS line shapes as a function of time delay and Raman shift for the 802 and 1027 cm^{-1} modes. There is a striking resemblance between simulation and experiment showing that the coupled wave theory is a good model for describing the physics of FSRS. We observed similar line shape patterns and agreement with theory for the spectra obtained with different Raman pump pulse widths (FWHM = 0.44 , 4.5 , and 5.5 ps).

A comparison of the experimental and theoretical results for the Raman gain intensity profile as a function of time delay for the 802 and 1027 cm^{-1} modes is shown in Fig. 8. The doubly degenerate vibrational mode (1027 cm^{-1}) has a broader bandwidth and reaches the maximum Raman gain at a slightly earlier time delay (-0.7 ps) than the totally symmetric 802 cm^{-1} mode (-1 ps). The theoretical gain profile obtained from the simulation used in Fig. 7 agrees well with the experimental results. The coupled wave theory sheds light on why the maximum gain appears at a negative time delay rather than at $t_D = 0$: The polarization that radiates as stimulated Raman is dependent on the product of the coherent vibration $Q^*(z, t)$ and the Raman pump field $E_p(z, t)$, as in Eq. (14). Although the largest coherent vibration is induced in the sample when the maxima of the Raman pump and Stokes probe are coincident ($t_D = 0$), the coherent vibration interacts with the Raman pump field for a longer period of time at more negative time delays. Due to these two competing factors, the maximum gain appears at slightly negative time delay.

V. CONCLUSIONS

We have presented the coupled wave theory of FSRS which considers the time delay t_D between the maxima of the Raman pump and Stokes probe fields. Experimental data on the dependence of the FSRS line shape on the time delay for the two most prominent modes of cyclohexane, 802 and 1027 cm^{-1} , in the ground electronic state have been obtained and analyzed with the coupled wave theory. The theoretical simulations provide a good fit to the experimental line shapes, recovering broad linewidths at positive time delays and narrower linewidths with small Raman loss features on the wings at negative time delays. From the fit, we have determined the lower bounds for the vibrational dephasing time of the 802 and the 1027 cm^{-1} modes to be 2.0 and 0.65 ps, respectively. Theoretical prediction of the Raman gain intensity profile with time delay also agrees well with experimental observation, peaking at a slightly negative time delay.

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30. The Raman loss features at negative time delay are not evident for other modes due to their small intensities or larger γ although the broadening at positive time delay and narrowing at negative time delay are clearly observed. The Raman gain/loss is determined largely by term $A(\omega, t_D)$ in Eq. (27), which is an overlap of the oscillatory $\cos[(\omega + \omega_0 - \omega_p)t]$ term, which has higher frequency oscillations for a larger mismatch of ω with $\omega_p - \omega_0$, and a shifted Gaussian with peak at $t = -t_D$ and width determined by τ_p . Raman loss occurs when the shifted Gaussian sits across a largely negative portion of the $\cos[(\omega + \omega_0 - \omega_p)t]$ term.
31. The line shape becomes a doublet at long positive time delays. We could not reproduce this bifurcation of the peak using the coupled wave theory. The Raman pump pulse in the tail beyond 2 ps is not exactly Gaussian, as shown in Fig. 3 where it is seen to tail off followed by another small hump. The apparent split in the line shape for $t_D > 2$ ps could be due to this non-Gaussian tail.

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FIG. 1.

FSRS wave mixing energy level diagram in Liouville space. The dashed arrow corresponds to bra side interaction with the Raman pump E_p^* and Stokes probe E_s fields, producing a coherent vibration $Q^*(t)$ that decays with the vibrational dephasing time T_2 . The system changes from the Liouville state $|0\rangle\langle 0|$ to the state $|0\rangle\langle 1|$. In the Placzek polarizability model, the change in polarization arises from the interaction of $Q^*(t)$ with the long Raman pump field E_p , designated by a solid arrow acting on the ket side of the system. The induced polarization then radiates coherently at $(\omega_s, \vec{k}_s)$, giving rise to the stimulated Raman line, and the system changes from the Liouville state $|0\rangle\langle 1|$ to a final state $|1\rangle\langle 1|$. The wavy arrow designates the output stimulated Raman radiation which propagates with the frequency ω and the wave vector $\vec{k}$.

FIG. 2.

Coupled time-dependent electric fields and polarization with corresponding frequency spectra relevant for FSRS. The Raman pump and Stokes probe pulses and the response of the sample for $t_D=0$ are illustrated in the time domain (left panel) and in its Fourier-transformed frequency domain (right panel). (a) Raman pump field $E_p(t)$ from Eq. (4) with 2 ps pulse width and center frequency at ~ 800 nm. (b) Stokes broadband probe field $E_s(t)$ from Eq. (5) with 20 fs pulse width. (c) Coherent vibrational amplitude $Q(t)$ induced by the coupling of the Raman pump pulse and Stokes probe pulse in the material. By choosing a 700 fs vibrational dephasing time T_2 , the spectral intensity $I_Q(\omega)$ given by Eq. (10) and (11), has $2\gamma=15$ cm^{-1} FWHM. (d) The total sample polarization $P_{\text{Total}}(t)$ in the Placzek model is given by $P_{\text{Total}}(t)=Q(t)E_p(t)$. The vibrational amplitude thus generates new frequency components in the fields by modulating the polarization of the material via the coordinate dependent polarizability $Q(t)E_p(t)$. (e) The net FSRS signal can be derived from the wave equation and is shown here as the heterodyned signal arising from the free Stokes probe field $E_s^{\text{free}}(t)$ plus the field generated by the system polarization $E_{\text{SR}}(t)$.

FIG. 3.

Cross correlation of Raman pump and Stokes probe using cyclohexane. The cross correlation (circles) reveals the shape of the Raman pump pulse which is fit to a Gaussian function (solid line) with FWHM of 2.7 ps. The 30 fs FWHM Stokes probe pulse is shown for comparison.

FIG. 4.

(a) Schematic of FSRS setup in the space domain. The pulse envelope represents a snapshot of the pulse in space at a fixed time. When $t_D > 0$, the maximum of the 1–3 ps Raman pump pulse arrives at the sample prior to the 30 fs broadband continuum probe pulse by ct_D where c is the speed of light. (b) Electric field envelope for Raman pump and Stokes probe at the sample in the time domain when $t_D > 0$. Time progresses from left to right.

FIG. 5.

(a) FSR spectra of cyclohexane at selected time delays t_D between Raman pump and Stokes probe. The spectra are vertically offset for display. Raman gain G_R is defined by Eq. (31) and we used $\ln(G_R)$ for the plot. Typical Raman gain for the 802 cm^{-1} band of cyclohexane in the experiment was 1.53 at $t_D=0$. (b) Contour plot of the Raman gain spectra of cyclohexane. The spectra have been taken with time steps of 100 fs from -3 ps to 3 ps, and 200 fs elsewhere. Gray scale becomes darker as the intensity of the FSR spectra increases. Negative (Raman loss) intensity is designated by the dotted contours.

FIG. 6.

Comparison of experimental Raman gain spectra line shapes at selected time delays with theory. Simulated spectra using Eq. (26) are illustrated with thick solid lines and the experimentally observed spectra are presented with thin lines. The theoretical calculations give the best agreement with the vibrational dephasing time γ^{-1} of 2.0 ps for the 802 cm^{-1} mode and 0.65 ps for the 1027 cm^{-1} mode. The intensities of the simulated spectra have been scaled to match those of the experimental spectra.

FIG. 7.

Contour plot of the Raman gain spectra of cyclohexane as a function of time delay t_D : (a) experimental spectra, (b) simulated spectra. Same gray scale has been used in (a) and (b) and the spectra are scaled to the same maximum intensity. Black represents the highest intensity. Negative intensities are designated by dotted lines.

FIG. 8. Peak intensity of the 802 and 1027 cm^{-1} bands of cyclohexane as a function of time delay t_D between Raman pump and Raman probe. Thin lines (solid and dashed) plot the peak heights of the two experimental bands as a function of t_D and thick lines (solid and dot-dashed) plot the peak heights of the simulated spectra using the coupled wave theory.