CHAPTER 1

WAVE PACKET ANALYSIS OF FEMTOSECOND STIMULATED RAMAN SPECTROSCOPY

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Femtosecond stimulated Raman spectroscopy (FSRS) is described here by both the classical coupled wave approach and by the quantum theory with wave packet analysis. The classical coupled wave approach is restricted to off-resonance FSRS, but the quantum theory also applies to the resonance regime. The quantum theory describes FSRS by the third-order polarization with eight perturbative terms which are pictured with Feynman dual time-line diagrams as well as the complementary four-wave mixing energy level diagrams. The eight terms can be placed into four sets — SRS(I), SRS(II), IRS(I), IRS(II) — where SRS stands for stimulated Raman scattering and IRS stands for inverse Raman scattering. In the SRS(I) set, there are three terms which are similar to the resonance Raman scattering and hot luminescence terms in spontaneous Raman scattering. The remaining five terms in SRS(II), IRS(I) and IRS(II) entail “absorption” of the probe pulse, and these are absent in spontaneous Raman scattering because of the vacuum probe field but they are present in FSRS. The SRS(I) set accounts for the sharp Stokes Raman lines while the IRS(I) term accounts for the sharp anti-Stokes Raman lines in the FSRS spectrum. We illustrate the theory with calculations on (a) the resonance FSRS of Rhodamine 6G and (b) the FSRS from a coherent vibrational state prepared by an impulsive pump pulse in CDC13. The calculated results compare well with experiment, and it is shown that in the case of FSRS on CDC13 there is a cascade effect involving two molecules that makes a dominant contribution to the FSRS spectra.

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1. Introduction

Femtosecond stimulated Raman spectroscopy (FSRS) with femtosecond time resolution and high vibrational spectral resolution has been developed to study time-resolved structural changes in ultrafast photophysical and photochemical processes. In a time-resolved FSRS experiment, shown schematically in Fig. 1, three pulses are used: A ~ 50 fs actinic pump pulse to excite the molecule to an upper electronic state, followed by stimulated Raman spectroscopy with an overlapping pair of ps Raman pump pulse, a ~ 15 fs continuum probe pulse, and heterodyne detection of the FSRS spectrum is made in the probe pulse direction. It is possible to acquire spectra with time resolution of ~ 50 fs in the time delay between the actinic pump and probe pulses, and spectral resolution of < 10 cm\(^{-1}\) due largely to the ps Raman pump pulse. Other advantages of FSRS are rapid data acquisition, Raman spectra unaffected by background fluorescence, and vibrational spectrum acquisition in the range of 600–2500 cm\(^{-1}\). FSRS has been used to study numerous systems, including vibrational relaxation and internal conversion in β-carotene and diphenyloctatetraene, excited state structural dynamics of the photoisomerization of the retinal chromophore in bacteriorhodopsin and rhodopsin, anharmonic coupling in CDCl\(_3\), resonance Raman scattering from Rhodamine 6G (R6G) which is a highly fluorescent compound, and excited state isomerization in phytochrome.

The theory of both spontaneous and stimulated Raman spectroscopy traces back to the beginnings of quantum theory, and encompasses...
both classical\textsuperscript{17} and quantum\textsuperscript{18–23} approaches. The quantum-mechanical, sum-over-states Kramers-Heisenberg-Dirac quantum scattering theory is a time-independent approach that can account for both spontaneous and stimulated Raman scattering from a stationary vibrational state with delta-function bandwidth cw radiation. With the advent of resonance Raman spectroscopy, the equivalent time-dependent wave packet approach provided an advantageous description physically and computationally.\textsuperscript{24, 25} With intense lasers, stimulated Raman spectroscopy was possible, and Shen and Bloembergen\textsuperscript{26, 27} have provided a semiclassical coupled-wave description of stimulated Raman scattering with cw radiation.

In this chapter, we discuss both the coupled wave and the quantum theory of FSRS where neither the Raman pump nor the probe pulse are cw with delta function bandwidth. The coupled wave theory provides a useful classical physical description of FSRS in the off-resonance scattering regime, and the quantum theory of FSRS applies also to the resonance regime. The quantum theory of FSRS is applied: (a) to calculate resonance FSRS spectra of R6G as a function of the Raman pump wavelengths, and (b) to calculate the time-dependent 2D FSRS spectra of an initially prepared coherent state (moving wave packet) of CDCl\textsubscript{3}, which turns out to have a dominant cascade effect involving two molecules, and to compare them with recent experimental results.\textsuperscript{8, 13, 14}

2. Theory

In FSRS, the narrow bandwidth ps Raman pump pulse may be taken to be cw to a good approximation, but the continuum fs Stokes probe pulse, which is almost a delta function pulse, clearly cannot be. So, the existing classical and quantum theories for stimulated Raman scattering which are geared towards cw Raman pump and probe pulses need to be reexamined and modified to apply to FSRS. Here, we review both the classical coupled wave and the quantum theory of FSRS.

2.1. Coupled wave theory of FSRS and its limitations

The physical picture of light interacting with a medium is the following: The medium is taken to be a collection of oscillators with vibrational coordinate $Q$, say, and we focus on just one vibrational mode of frequency $\omega_0$. An
intense time-dependent electric field $E(z, t)$, which could be a sum of fields, here taken to be linearly polarized and propagating along the $z$ axis, induces a nonlinear response in the medium, described by the polarization $P(z, t)$ as a function of the electric field $E(z, t)$ which gives the constitutive equation. The reacting medium then modifies the electric fields in a nonlinear way as they propagate through the medium, a process described by Maxwell equations.

Using the Placzek model\(^{17}\) for the polarization of the oscillators, $P(z, t) = \alpha \cdot E(z, t)$, where $\alpha$ is the polarizability (a molecular property), the Lagrangian for the electric fields coupled to the oscillators, and the Lagrange equation of motion, we obtain the equation of motion for the coherent vibration $Q$,\(^{28, 29}\)

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

Here $\alpha_0'$ is the first-order derivative of the polarizability with respect to $Q$ evaluated at the equilibrium configuration, and $2\gamma dQ/dt$ is a phenomenological damping term for the vibration which decays as $e^{-\gamma t}$.

The Maxwell equation for the modified electric fields is given by,\(^{28, 29}\)

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

where $N$ is the number of oscillators per unit volume. Eqs. (1) and (2) are the central equations that can be used to describe FSRS by the classical coupled wave theory.

The total field in FSRS is a sum of a Raman pump (pu) field and a Stokes probe (pr) field, here taken to propagate in the same direction,

$$E(z, t) = E_{pu}(z, t) + E_{pr}(z, t), \quad (3)$$

and we shall take the Stokes probe pulse envelope maximum to arrive at time $t_d$ delayed from the Raman pump pulse envelope maximum, with Gaussian pulse envelopes as follows:

$$E_{pu}(z, t) = E_{pu}^0 e^{-(t+t_d-z/c)^2/2\tau_{pu}^2} e^{-i\omega_{pu}(t+t_d-z/c)}, \quad (4)$$

$$E_{pr}(z, t) = E_{pr}^0 e^{-(t-z/c)^2/2\tau_{pr}^2} e^{-i\omega_{pr}(t-z/c)}. \quad (5)$$
The corresponding spectra, given by the Fourier transform, are

\[ E_{pu}(z, \omega) = E_{pu}^0 \sqrt{2\pi} \tau_{pu} e^{-(\omega-\omega_{pu})^2/2\tau_{pu}^2} e^{i\omega(t_d+z/c)}, \]  

\[ E_{pr}(z, \omega) = E_{pr}^0 \sqrt{2\pi} \tau_{pr} e^{-(\omega-\omega_{pr})^2/2\tau_{pr}^2} e^{i\omega z/c}. \]

In the FSRS experiments of Mathies et al.\(^1\)\(^-\)\(^4\)\(^,\)\(^3\(^0\) the Raman pump field \( E_{pu}(t) \) is a \( \sim 800 \) nm, narrow bandwidth (\( \sim 5\)–15 cm\(^{-1}\)), long pulse (\( \tau_{pu} \sim 1\)–3 ps), while the Stokes probe field \( E_{pr}(t) \) is a \( \sim 830\)–950 nm, continuum, short pulse (\( \tau_{pr} \sim 30\)–50 fs) covering stimulated Raman Stokes shifts of \( \sim 500\)–2300 cm\(^{-1}\). The ps Raman pump field and its spectral intensity are illustrated in Fig. 2a, and the fs Stokes probe field and its spectral intensity are illustrated in Fig. 2b.

Using Eq. (3), \( |E(z, t)|^2 \) on the right-hand side in Eq. (1) has four components. One component \( E_{pu}^* E_{pr} \) has the right frequency \( \sim e^{i(\omega_{pu}-\omega_{pr})t} \) to exert a resonant forcing term on the vibrational term \( Q \sim e^{i\omega_0 t} \), which will come into play in Eq. (2), with equation of motion for the vibration now given by

\[ \frac{d^2Q}{dt^2} + 2\gamma \frac{dQ}{dt} + \omega_0^2 Q = \alpha_0' E_{pu}^* E_{pr}. \]  

The solution to Eq. (8) comprises a homogeneous solution and a particular solution, and it has been shown that the homogeneous solution can be ignored because of its random phase.\(^2\(^8\) The particular solution can be obtained in the frequency domain and can be shown to be given by,\(^2\(^9\)

\[ Q_p(z, \omega) = g(\omega) e^{i\omega z/c+i\omega_{pu} t_d-\omega_0^2/2\tau_{pu}^2}/(\omega_0^2 - \omega^2 - i2\gamma\omega), \]

with \( g(\omega) \) given by

\[ g(\omega) = \frac{E_{pu}^0 E_{pr}^0 \alpha_0' \sqrt{2\pi} \tau_{pr} e^{-(\omega+\omega_{pu}-\omega_{pr})^2/2\tau_{pr}^2}}{\omega_0^2 - \omega^2 - i2\gamma\omega}. \]

The inverse Fourier transform of Eq. (9) gives \( Q_p(z, t) \). Clearly, \( g(\omega) \) is a Gaussian distribution in \( \omega \) centered at \(-\omega_{pu}\) and is as broad as the Stokes probe spectrum, which means that the distribution of \( Q_p(z, \omega) \) is determined by the sharp energy denominator in Eq. (9), leading to a narrow bandwidth real dispersive term of width \( 2\gamma \) and an imaginary Lorentzian term of width \( \gamma \), both centered about \( \omega \approx -\omega_0 \), and \( |Q_p(z, \omega)|^2 \) appears...
Fig. 2. Time and frequency domain FSRS related components. (a) The ps Raman pump field and its spectral intensity. (b) The fs Raman probe field and its spectral intensity. (c) Coherent vibrational amplitude $Q_p(t)$ with 700 fs dephasing time and the corresponding spectral intensity. (d) The total sample polarization in the Placzek model and the spectral intensity. (e) The associated component fields $E_{pr}(t)$ and $E_{SR}(t)$ and the heterodyne signal, $I_{het}(\omega)$.
Lorentzian of width $\sim 2\gamma$. A much smaller, narrow band about $\omega \approx \omega_0$ is ignored. Both $Re [Q_p(t)]$ and $I_{Q_p}(\omega) = |Q_p(\omega)|^2$ are illustrated in Fig. 2c. The total sample polarization in the Placzek model is given by, $P_{\text{Total}}(t) \approx \omega_0 + Q'_0(t)|E_{pu}(t)|$, where $\alpha_0$ and $\alpha'_0$ are constants, and is illustrated in Fig. 2d with its spectral intensity $I_{P_{\text{Total}}}(\omega)$ showing narrow bands at the Raman pump frequency $\omega_{pu}$ as well as at $\omega_{pu} - \omega_0$ due to the modulation in $P_{\text{Total}}(t)$ with the arrival of the Stokes probe pulse stimulating the coherent vibration.

Turning now to the Maxwell equation, Eq. (2), and using $Q = Q_p(z, t)$ and $E(z, t) = E_{pu}(z, t)$ on the right-hand side, we have,

$$\frac{\partial^2 E(z, t)}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2 E(z, t)}{\partial t^2} \approx \frac{4\pi}{c^2} N\alpha'_0 \frac{\partial^2}{\partial t^2} [Q_p(z, t)E_{pu}(z, t)].$$

(11)

This equation describes the stimulated Raman scattering output within the spectrum of the Stokes probe field, as the product $Q_p(z, t)E_{pu}(z, t) \sim |E_0^{pu}|^2 e^{-i(\omega_{pu} - \omega_0)t}$. Equation (11) is best solved in the frequency domain, and the heterodyne solution in the probe pulse direction has been shown to be,$^{29}$

$$E_{\text{het}}(z, \omega) \approx \{1 + i2\pi \chi_R(\omega, t_d)|E_{pu}^0|^2 \omega z/c\} E_{pr}(z, \omega)
= E_{pr}(z, \omega) + E_{SR}(z, \omega),$$

(12)

where the first term is the probe pulse spectrum that comes from the homogeneous solution and the second term is the particular solution giving the stimulated Raman spectrum, and we have defined the Raman susceptibility $\chi_R(\omega, t_d)$ as

$$\chi_R(\omega, t_d) = N(\alpha'_0)^2 (2\omega_0)^{-1/2} \tau_{pu}^{-1/2} G(\omega, t_d),$$

(13)

where

$$G(\omega, t_d) = -i\sqrt{2\pi} \tau_{pu}^{-1} \int_0^\infty e^{i(\omega + \omega_0 - \omega_{pu})t - (t + td)^2/2\tau_{pu}^2 - \gamma t} dt.$$  

(14)

It can be shown that $|G(\omega, t_d)|$ peaks at $\omega \approx \omega_{pu} - \omega_0$, with width governed by $\tau_{pu}^{-1}$ and $\gamma$, or the larger of the two if one is dominant and it is usually $\gamma$ from the coherent vibration, so that we see a narrow bandwidth gain signal at $\omega_{pu} - \omega_0$ sitting atop the broad Stokes probe pulse spectrum in the heterodyne signal $|E_{\text{het}}(z, \omega)|^2 \equiv I_{\text{het}}(\omega)$. The inverse Fourier transform
of $E_{het}(z, \omega)$ in Eq. (12) gives the Stokes probe field, $E_{pr}(z, t)$, and the stimulated Raman field, $E_{SR}(z, t)$, in the probe pulse direction. Clearly, the stimulated Raman field is initiated only in the presence of the (ultrashort) probe pulse and it decays on the timescale of the coherent vibration. The heterodyne signal, $I_{het}(\omega)$, and the associated component fields $E_{pr}(t)$ and $E_{SR}(t)$ are illustrated in Fig. 2e.

The coupled wave theory thus provides a useful physical picture of the FSRS process. It shows that the FSRS spectrum can have: (a) high frequency resolution governed by the narrow linewidth of the Raman pump field and/or the coherent vibration, and (b) high time resolution as the stimulated Raman field is initiated only in the presence of the ultrashort probe pulse. There’s no contradiction with the Heisenberg uncertainty principle as the frequency resolution and time resolution involve different pulses. The drawbacks of the coupled wave theory are: (a) it uses the Placzek polarizability theory which is restricted to off-resonance Raman scattering whereas experiments with FSRS have been carried out in both the off-resonance and resonance regimes,\textsuperscript{13,14} and (b) it cannot correctly explain the observation of strong anti-Stokes lines in FSRS even in the off-resonance regime. These drawbacks can only be overcome with the quantum theory of FSRS.

2.2. Quantum theory of FSRS

FSRS can be applied to a molecule initially in a stationary vibrational state or to a moving wave packet. We consider the general case of a moving wave packet $|\psi_1(Q, t)\rangle$ which has been prepared on an (excited) electronic state $e_1$, perhaps by an ultrashort fs actinic (resonant) pump pulse acting on a molecule which was initially in, say, the $v=0$ vibrational state on the ground electronic state surface $e_0$, as shown in Fig. 3. A moving wave packet could also be prepared on the ground electronic state surface by an impulsive off-resonant pump pulse. Here, we assume that the moving wave packet is on the $e_1$ surface, which after a time delay $t_D$ can be interrogated by FSRS using a picosecond Raman pump pulse coupled with a femtosecond probe pulse. The time delay $t_D$ here is measured between the two ultrashort pulses. The FSRS process is mediated by another electronic state, shown to be $e_2$ state in Fig. 3, but could also be the $e_0$ state, or both, depending
Wave Packet Analysis of FSRS

Fig. 3. Femtosecond stimulated Raman scattering from a moving wave packet. The molecule is initially in, say, the \( v = 0 \) state on the ground state \( e_0 \) surface. An ultrashort actinic pump pulse\(^1\) comes along and prepares the molecule as a moving wave packet on the excited state \( e_1 \) surface. A picosecond Raman pump pulse\(^2\) coupled with a femtosecond probe pulse\(^3\) interrogates the moving wave packet, mediated by a higher excited state \( e_2 \), at various times, \( t_D \), through stimulated Raman scattering as measured in the gain or loss of the probe spectrum. Reproduced with permission from J. Chem. Phys. 128, 144114 (2008).

If the actinic pump pulse and the Raman pump and probe pulses overlap significantly, then we would need a fifth-order polarization \( P_{pr}^{(5)}(t) \) to describe the stimulated Raman scattering starting from the ground electronic state \( e_0 \). Here, we assume that the actinic pump acts on the molecule first to prepare a coherent state, followed by FSRS with a pair of Raman pump and probe pulses, as is the case in FSRS experiments,\(^9\) and a third-order polarization \( P_{pr}^{(3)}(t) \) suffices to describe the FSRS.

We focus on the two Born-Oppenheimer \( e_1 \) and \( e_2 \) electronic states and their associated vibrational manifolds, and we can write the density on the wavelengths of the Raman pump and probe pulses and the relative energies of the potential energy surfaces (PESs) as FSRS is enhanced by resonance. The FSRS spectrum is obtained by heterodyne detection along the probe pulse direction.
matrix as,
\[ \rho(t) = \sum_{a,b=1}^{2} |e_a\rangle \rho_{ab}(Q,t) \langle e_b|, \] (15)
where Q denotes the nuclear coordinates and \( \rho_{ab}(Q,t) \) is the vibrational density matrix associated with electronic states \( |e_a\rangle \) and \( |e_b\rangle \) simultaneously. The actinic pump pulse prepares a pure vibrational wave packet on electronic state \( e_1 \), described by the density matrix,
\[ \rho^{(0)}_{11}(t) = |\psi_1(Q,t)\rangle \langle \psi_1(Q,t)|. \] (16)
By turning on the Raman pump and probe pulses, the density matrix evolves according to the quantum Liouville equation,
\[ \frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [H_0 + \mathcal{V}(t), \rho(t)] - \Gamma \rho(t), \] (17)
with
\[ H_0 = |e_1\rangle h_1(Q) \langle e_1| + |e_2\rangle h_2(Q) \langle e_2|, \]
\[ \mathcal{V}(t) = -\mu(Q) \cdot E(R,t), \]
\[ \mu(Q) = |e_2\rangle \mu_{21}(Q) \langle e_1| + c.c., \]
\[ E(R,t) = \epsilon_{pu} E_{pu}(t-t_D) \exp(i k_{pu} \cdot R) + \epsilon_{pr} E_{pr}(t-t_D) \exp(i k_{pr} \cdot R) = E_{pu}(t-t_D) + E_{pr}(t-t_D). \] (18)
\( \mu_{ab}(Q) \) is the coordinate-dependent transition dipole between electronic states \( e_a \) and \( e_b \), and \( E_{pu}(t-t_D) \) and \( E_{pr}(t-t_D) \), both peaked at \( t_D \), i.e. without a time delay between them, are the Raman pump and probe fields which propagate in space \( R \) (which can be taken to be a constant in the long wavelength approximation) with wave vectors \( k_{pu} \) and \( k_{pr} \), and polarizations \( \epsilon_{pu} \) and \( \epsilon_{pr} \), respectively. The Raman pump and probe pulses are commonly taken to be similar to Eqs. (4) and (5) with a Gaussian envelope and setting \( t_d = 0 \) and \( z = 0 \). We could easily include a time delay \( t_d \) between the Raman pump and probe pulses, but that would make the notation rather cumbersome and so we have left it out. We assume that \( E_{pu}(t-t_D) \) and \( E_{pr}(t-t_D) \) appear after the ultrashort actinic pump pulse
which peaks at $t = 0$ has passed, and $t_D$ is interpreted as the time delay between the ultrashort actinic pump and probe pulses. For simplicity, we will assume parallel polarizations $\varepsilon_{pu} = \varepsilon_{pr}$ and write $\mu_{ab} = \mu_{ab} \cdot \varepsilon_{pr}$; and $\Gamma$ is the relaxation superoperator which describes vibronic dephasing and relaxation effects, with matrix elements $\gamma_{ab}$.

We have to take into account the fact that the pump and probe pulses can lead to “excitation” or “de-excitation” on either the bra or ket interaction. Raman scattering from a moving wave packet is described by the third-order polarization,

$$p^{(3)}(t) = \text{Tr}\{\mu^2_{21}\rho^{(3)}(t)\},$$  

where the perturbative response of the density matrix to third order, $\rho^{(3)}(t)$, is obtained by integrating Eq. (17). Now, we define $t_a$ as the time after the actinic pump pulse has passed, but before the Raman pump and probe pulses appear, and the molecule is prepared in a non-stationary state $|\psi_1(Q, t_a)\rangle$ on electronic state $e_1$. We assume for simplicity that the relaxation constants $\gamma_{ab}$ are given by the simple form,

$$\gamma_{ab} = (\gamma_a + \gamma_b)/2.$$  

It can then be shown that the third-order difference polarization in the probe direction $k_{pr}$ between having the Raman pump on versus off, but with the probe on in both situations, $P^{(3)}_{\text{diff}}(k_{pr}; t) = P^{(3)}_{\text{pump on}}(k_{pr}; t) - P^{(3)}_{\text{pump off}}(k_{pr}; t)$, has eight terms, which can be grouped into four sets as follows:

**Stimulated Raman Scattering, SRS(I)**

$$P^{(3)}_{\text{RIS(1)}}(t; t_D) = e^{ik_{pr} \cdot R} \left( \frac{i}{\hbar} \right)^3 \int_{t_a}^{t} \int_{t_a}^{t_1} \int_{t_a}^{t_2} \int_{t_a}^{t_3} E_{pu}(t_1 - t_D)$$

$$\times E_{pr}(t_2 - t_D) E_{pu}(t_3 - t_D) \langle \psi_1(Q, t_a) | e^{(i\hbar_1 - \gamma_1/2)(t_3 - t_a)/\hbar}$$

$$\times \mu_{21}^{\ast} e^{(i\hbar_2 - \gamma_2/2)(t_2 - t_1)/\hbar} \mu_{21} e^{(i\hbar_1 - \gamma_1/2)(t_2 - t_1)/\hbar}$$

$$\times \mu_{21}^{\ast} e^{(-i\hbar_2 - \gamma_2/2)(t_1 - t_a)/\hbar} \mu_{21} e^{(-i\hbar_1 - \gamma_1/2)(t_1 - t_a)/\hbar}$$

$$\times |\psi_1(Q, t_a)\rangle,$$  

(21)
\[
P^{(3)}_{\text{HL(I)}}(t; t_D) = e^{i \mathbf{k}_{pr} \cdot \mathbf{R}} \left( \frac{i}{\hbar} \right)^3 \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3 E_{pr}(t_1 - t_D) \\
\times E_{pu}(t_2 - t_D) E_{pu}(t_3 - t_D) \langle \psi_1(\mathbf{Q}, t_0) | e^{i(h_1 - \gamma_1/2)(t_3 - t_0)/\hbar} \rangle \\
\times \mu_{21}^* e^{(i\hbar_2 - \gamma_2/2)(t_1 - t_3)/\hbar} \mu_{21} e^{(i\hbar_1 - \gamma_1/2)(t_2 - t_0)/\hbar} \\
\times \langle \psi_1(\mathbf{Q}, t_0) \rangle.
\]

(22)

\[
P^{(3)}_{\text{HL(II)}}(t; t_D) = e^{i \mathbf{k}_{pr} \cdot \mathbf{R}} \left( \frac{i}{\hbar} \right)^3 \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3 E_{pr}(t_1 - t_D) \\
\times E_{pu}(t_2 - t_D) E_{pu}(t_3 - t_D) \langle \psi_1(\mathbf{Q}, t_0) | e^{i(h_1 - \gamma_1/2)(t_3 - t_0)/\hbar} \rangle \\
\times \mu_{21}^* e^{(i\hbar_2 - \gamma_2/2)(t_1 - t_3)/\hbar} \mu_{21} e^{(i\hbar_1 - \gamma_1/2)(t_2 - t_0)/\hbar} \\
\times \langle \psi_1(\mathbf{Q}, t_0) \rangle.
\]

(23)

**Stimulated Raman Scattering, SRS(II)**

\[
P^{(3)}_{\text{RRS(II)}}(t; t_D) = e^{i \mathbf{k}_{pr} \cdot \mathbf{R}} \left( \frac{i}{\hbar} \right)^3 \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3 E_{pr}(t_1 - t_D) \\
\times E_{pu}(t_2 - t_D) E_{pu}(t_3 - t_D) \langle \psi_1(\mathbf{Q}, t_0) | e^{i(h_1 - \gamma_1/2)(t_3 - t_0)/\hbar} \rangle \\
\times \mu_{21}^* e^{(i\hbar_2 - \gamma_2/2)(t_1 - t_3)/\hbar} \mu_{21} e^{(i\hbar_1 - \gamma_1/2)(t_2 - t_0)/\hbar} \\
\times \langle \psi_1(\mathbf{Q}, t_0) \rangle.
\]

(24)

\[
P^{(3)}_{\text{HL(III)}}(t; t_D) = e^{i \mathbf{k}_{pr} \cdot \mathbf{R}} \left( \frac{i}{\hbar} \right)^3 \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3 E_{pr}(t_1 - t_D) \\
\times E_{pu}(t_2 - t_D) E_{pu}(t_3 - t_D) \langle \psi_1(\mathbf{Q}, t_0) | e^{i(h_1 - \gamma_1/2)(t_3 - t_0)/\hbar} \rangle \\
\times \mu_{21}^* e^{(i\hbar_2 - \gamma_2/2)(t_1 - t_3)/\hbar} \mu_{21} e^{(i\hbar_1 - \gamma_1/2)(t_2 - t_0)/\hbar} \\
\times \langle \psi_1(\mathbf{Q}, t_0) \rangle.
\]

(25)
Inverse Raman Scattering, IRS(I)

\[
P^{(3)}_{\text{IRS(I)}}(t'; t_D) = e^{i \mathbf{k}_{pu} \cdot \mathbf{R} \left( \frac{i}{\hbar} \right)^3} \int_{t_a}^{t_f} dt_1 \int_{t_a}^{t_1} dt_2 \int_{t_a}^{t_2} dt_3 E_{pu}(t_1 - t_D) \\
\times E_{pu}^{*}(t_2 - t_D) E_{pu}(t_3 - t_D) \langle \psi_1(\mathbf{Q}, t_0) | e^{i(h_2 - \gamma_2/2)(t_{1-2})/\hbar} \\
\times \mu_{21} \psi_1(t_1 - t_{1-2})/\hbar \mu_{21} e^{i(h_1 - \gamma_1/2)(t_{1-2})/\hbar} \\
\times \mu_{21} e^{-(i\hbar_2 - \gamma_2/2)(t_{2-3})/\hbar} \mu_{21} e^{-(i\hbar_1 - \gamma_1/2)(t_{3-0})/\hbar} \\
\times |\psi_1(\mathbf{Q}, t_0)\rangle. \tag{26}
\]

Inverse Raman Scattering, IRS(II)

\[
P^{(3)}_{\text{IRS(II)}}(t'; t_D) = e^{i \mathbf{k}_{pu} \cdot \mathbf{R} \left( \frac{i}{\hbar} \right)^3} \int_{t_a}^{t_f} dt_1 \int_{t_a}^{t_1} dt_2 \int_{t_a}^{t_2} dt_3 E_{pu}(t_1 - t_D) \\
\times E_{pu}^{*}(t_2 - t_D) E_{pu}(t_3 - t_D) \langle \psi_1(\mathbf{Q}, t_0) | e^{i(h_2 - \gamma_2/2)(t_{1-2})/\hbar} \\
\times \mu_{21} \psi_1(t_1 - t_{1-2})/\hbar \mu_{21} e^{i(h_1 - \gamma_1/2)(t_{1-2})/\hbar} \\
\times \mu_{21} e^{-(i\hbar_2 - \gamma_2/2)(t_{2-3})/\hbar} \mu_{21} e^{-(i\hbar_1 - \gamma_1/2)(t_{3-0})/\hbar} \\
\times |\psi_1(\mathbf{Q}, t_0)\rangle. \tag{27}
\]

We can draw Feynman dual time-line diagrams, Fig. 4, to depict the eight terms, and these diagrams provide a useful time-frame wave packet propagation viewpoint. Each diagram has two time-lines for ket and bra propagation, with time increasing from bottom to top, and there are three field interactions denoted by arrows. An arrow pointing into the time-line denotes absorption with a transition from a lower to a higher electronic state, while an arrow pointing away from the time-line denotes emission.
Fig. 4. Feynman dual time-line diagrams for SRS(I), SRS(II), IRS(I) and IRS(II) processes describing FSRS.

with a transition from a higher to a lower electronic state. Arrows that point to the right correspond to the fields $E_{pu/pr}(t)$, while the arrow that points to the left is $E_{pu}^*(t)$. We have drawn the diagrams to show that the wave vectors for the two pump interactions cancel, leaving a resultant polarization
Wave Packet Analysis of FSRS

in the probe pulse direction. The abbreviation \textit{coh.} stands for coherence, and \textit{pop.} stands for population. The vibrational coherence and population on the excited electronic state $e_2$ are shown shaded, while those on the $e_1$ state are not. We have used the term coherence when the first two electric field interactions leave a resultant wave vector $k_{pr} - k_{pu}$ even though the Liouville state has the bra and ket vectors in the same electronic state, while population is used when there is a zero resultant wave vector. Finally, at time $t$ we overlap the bra and ket states mediated by the transition dipole moment $\mu_{12}$, denoted by the dashed line, to give the third-order polarization.

The SRS(I) set has $E_{pu}^*, E_{pu}$ fields acting on the right (bra) time-line and $E_{pu}$ acting on the left (ket) time-line, while the SRS(II) set has $E_{pu}^*, E_{pu}$ fields acting on the bra time-line and $E_{pr}$ acting on the ket time-line. Each of the SRS(I) and SRS(II) sets has three diagrams which differ by the time ordering of the field interaction on the ket time-line. One of the diagrams is labeled as resonance Raman scattering, RRS, where there is no intermediate $|\textit{ket}\rangle\langle\textit{bra}|$ in electronic state $e_2$, and another two are labeled as hot luminescence, HL, where there is intermediate $|\textit{ket}\rangle\langle\textit{bra}|$ in electronic state $e_2$, shown shaded. The IRS(I) diagram has $E_{pr}, E_{pu}^*, E_{pu}$ fields acting on the ket time-line, while the IRS(II) diagram has $E_{pu}, E_{pu}^*$, and $E_{pr}$ fields also acting on the ket time-line.

If in the Feynman diagrams in Fig. 4 we look at the interaction time-points and view each as either absorption or emission without being concerned with the form or type of pulses, then topologically RRS(I) and RRS(II) are similar, and Mukamel\textsuperscript{33} describes them with a four-time correlation function $R_3(t, t_1, t_2, t_3)$. Similarly, HL(I) and HL(III) are similar and described by $R_2(t, t_1, t_2, t_3)$; HL(II) and HL(IV) are similar and described by $R_1(t, t_1, t_2, t_3)$; and IRS(I) and IRS(II) are similar and described by $R_4(t, t_1, t_2, t_3)$. The actual pulses can then be incorporated into the time integrations and this may facilitate computation of each of the terms, but physically we find it more meaningful to group them as shown in Fig. 4.

In SRS(I), the probe pulse stimulates emission from $e_2$ to $e_1$, while in SRS(II), IRS(I) and IRS(II) the probe pulse leads to absorption from $e_1$ to $e_2$. Now, for spontaneous Raman scattering the probe pulse would be the vacuum field, which cannot give rise to absorption from $e_1$ to $e_2$, and so the SRS(II), IRS(I) and IRS(II) processes would be forbidden, leaving
just the SRS(I) process, whose three terms — RRS(I), HL(I) and HL(II) — are precisely those described by Shen.\(^{21}\) For stimulated Raman scattering, however, where it is also possible to absorb from the probe pulse, we have to include all eight diagrams.

Yoshizawa et al.\(^{34,35}\) had used a simple three-state model, where \(a, b, c\) represent three vibrational states, with \(a\) and \(c\) on one electronic state and \(b\) is on an excited electronic state to describe FSRS. They showed that if \(N(t)\) is the population of the transient state \(a\) at time \(t\), then the third order polarization for FSRS is given by

\[
P^{(3)}(t) = \left(\frac{i\mu}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 N(t_3) \\
\times \tilde{E}_{pu}(t_3) e^{i(\omega_{pu} - \omega_{ba})t_3} e^{-\gamma_{ba}(t_2 - t_3)} \\
\times \tilde{E}_{pu}(t_2) e^{-i(\omega_{pu} - \omega_{bc})t_2} e^{-\gamma_{bc}(t_1 - t_2)} \\
\times \tilde{E}_{pu}(t_1) e^{-i(\omega_{pu} - \omega_{ba})t_1} e^{-\gamma_{ba}(t - t_1)} e^{-i\omega_{bc}t},
\]

where \(\mu\) is the transition dipole moment, \(\omega_{\alpha\beta}\) and \(\gamma_{\alpha\beta}\) denote the transition frequency and the dipole decay between the \(\alpha\) and \(\beta\) states respectively. By writing the electric fields of the Raman pump and probe pulses as \(\tilde{E}_{pu}(t) = \tilde{E}_{pu}(t)e^{-i\omega_{pu}t}\) and \(\tilde{E}_{pr}(t) = \tilde{E}_{pr}(t)e^{-i\omega_{pr}t}\), respectively, it can be shown\(^{36}\) that Eq. (29) corresponds to the RRS(I) term in Eq. (21), when we use a three-state model. It can also be deduced from the sequence of the electric fields and the change in state, \(a, c \leftrightarrow b\), induced by each electric field interaction. The other seven terms that also contribute to FSRS have thus been neglected. This can be shown to be fine\(^{31}\) so long as one is looking at off-resonant Stokes side FSRS spectrum in which case the RRS(I) term is the main contributor. It has also been shown\(^{28}\) that the coupled wave theory of FSRS is derivable from the RRS(I) term for off-resonance stimulated Raman scattering and for the fundamental Stokes transition.

Looking at the Feynman diagrams in Fig. 4, it is possible and useful to write the third order polarizations as overlaps between wave packets evolving on the bra and ket time-lines. For SRS(I) and SRS(II), it is an overlap between a second-order bra wave packet with a first-order ket wave packet, while for IRS(I) and IRS(II) it is an overlap between a zeroth-order
bra wave packet with a third-order ket wave packet,

\[
P^{(3)}_{\text{SRS(I)}}(t) = \langle \psi^{(2)}_1(Q, -k_{pr}, k_{pu}; t) | \mu_{21}^* | \psi^{(1)}_2(Q, k_{pu}; t) \rangle, \tag{30}
\]

\[
P^{(3)}_{\text{SRS(B)}}(t) = \langle \psi^{(2)}_1(Q, -k_{pu}, k_{pu}; t) | \mu_{21}^* | \psi^{(1)}_2(Q, k_{pr}; t) \rangle, \tag{31}
\]

\[
P^{(3)}_{\text{IRS(I)}}(t) = \langle \psi^{(1)}_1(Q, t) | \mu_{21}^* | \psi^{(3)}_2(Q, k_{pu}, -k_{pu}, k_{pu}; t) \rangle, \tag{32}
\]

\[
P^{(3)}_{\text{IRS(B)}}(t) = \langle \psi^{(1)}_1(Q, t) | \mu_{21}^* | \psi^{(3)}_2(Q, k_{pr}, -k_{pu}, k_{pu}; t) \rangle. \tag{33}
\]

Here, for \( P^{(3)}_{\text{SRS(I)}}(t) \), we have the wave packets

\[
| \psi^{(1)}_2(Q, k_{pu}; t) \rangle = e^{ik_{pu} \cdot R} \left( \frac{i}{\hbar} \right) \int_0^{t-t_D} d\tau E_{pu}(t - \tau) e^{i\hbar\gamma/2}(t - \tau - \tau_D)/\hbar | \psi^{(1)}_1(Q, t_a) \rangle,
\]

\[
\langle \psi^{(2)}_1(Q, -k_{pr}, k_{pu}; t) | = e^{i(k_{pr} - k_{pu}) \cdot R} \left( \frac{i}{\hbar} \right)^2 \int_0^{t-t_D} d\tau \int_0^{t-t_D - \tau} d\tau' \times E_{pr}(t - \tau - \tau_D) E_{pu}(t - \tau' - \tau_D) \times \langle \psi^{(1)}_1(Q, t_a) | e^{i(h\gamma/2)(t - \tau' - \tau_D)/\hbar} \mu_{21}^* \times e^{i(h\gamma/2)\tau'/\hbar} \mu_{21} e^{i(h\gamma/2)\tau/\hbar}, \tag{34}
\]

and by appropriate change of fields, we can write down similar expressions for \( | \psi^{(1)}_2(Q, k_{pu}; t) \rangle \) and \( \langle \psi^{(2)}_1(Q, -k_{pu}, k_{pu}; t) | \) which appear in \( P^{(3)}_{\text{SRS(B)}}(t) \).

For \( P^{(3)}_{\text{IRS(I)}}(t) \), the wave packets are

\[
\langle \psi^{(1)}_1(Q, t) | = \langle \psi^{(1)}_1(Q, t_a) | e^{(i(h\gamma/2)(t - t_D))/\hbar}, \tag{36}
\]

\[
| \psi^{(3)}_2(Q, k_{pu}, -k_{pu}, k_{pr}; t) \rangle = e^{ik_{pr} \cdot R} \left( \frac{i}{\hbar} \right)^3 \int_0^{t} dt_3 \int_0^{t_1} dt_2 \int_0^{t_2} dt_1 \times E_{pu}(t_1 - t_D) E_{pu}(t_2 - t_D) E_{pr}(t_3 - t_D) \times e^{i(-h\gamma/2)(t_3 - t_D)/\hbar} \mu_{21} e^{i(-h\gamma/2)(t_1 - t_2)/\hbar} \times \mu_{21}^* e^{i(-h\gamma/2)(t_2 - t_3)/\hbar} \times \mu_{21} e^{i(h\gamma/2)(t_3 - t_D)/\hbar} | \psi^{(1)}_1(Q, t_a) \rangle. \tag{37}
\]
and by an appropriate change of fields in Eq. (37), we can write down a similar expression for $|\psi_2^{(3)}(\mathbf{Q}, \mathbf{k}_{pr}, -\mathbf{k}_{pu}, \mathbf{k}_{pu}; t)\rangle$ which appear in $P_{IRS(1)}^{(3)}(t)$.

The total third-order difference polarization that radiates in the $\mathbf{k}_{pr}$ direction is then given by

$$P_{\text{diff}}^{(3)}(t) = P_{\text{pump on}}^{(3)}(\mathbf{k}_{pr}; t) - P_{\text{pump off}}^{(3)}(\mathbf{k}_{pr}; t)$$

$$= P_{\text{SRS(I)}}^{(3)}(t) + P_{\text{SRS(II)}}^{(3)}(t) + P_{\text{IRS(I)}}^{(3)}(t) + P_{\text{IRS(II)}}^{(3)}(t).$$

(38)

The (experimental) Raman gain (RG) spectrum in the direction of the probe pulse is defined as the ratio of the probe spectrum with and without the Raman pump. If we subtract 1 from this ratio, we have the Raman gain cross section which is given by

$$\sigma_{\text{RG}}(\omega) = - \frac{4\pi}{3\epsilon_0 c n} \omega \text{Im} \left\{ \frac{P_{\text{diff}}^{(3)}(\omega)}{E_{pr}(\omega)} \right\},$$

(39)

where $\epsilon_0$ is the vacuum permittivity, $c$ is the speed of light; $n$ is the refractive index; $P_{\text{diff}}^{(3)}(\omega)$ is the Fourier transform of the difference polarization

$$P_{\text{diff}}^{(3)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} P_{\text{diff}}^{(3)}(t) dt,$$

(40)

and $E_{pr}(\omega)$, the spectrum of the incoming probe pulse, is given by

$$E_{pr}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} E_{pr}(t) dt.$$

(41)

3. Applications, Results and Discussion

3.1. Analytic results for FSRS from a stationary state with polyatomic harmonic potentials

Using Eqs. (30–33), FSRS can be calculated for arbitrary adiabatic PESs by propagating wave packets on the bra and ket time-lines. However, for large molecules, propagating wave packets can be time consuming and costly. For many large molecules, we can represent their potential surfaces by multidimensional separable displaced harmonic oscillators, and it is possible to derive analytic expressions to calculate the FSRS spectrum from a stationary state.
In an $N$-dimensional separable system, the initial wave packet is a product of one-dimensional wave packets

$$|\psi_1(Q, 0)\rangle = \prod_{r=1}^{N} |\psi_{1r}(Q_r, 0)\rangle,$$  \hspace{1cm} (42)

and the Hamiltonians are sums of one-dimensional Hamiltonians

$$h_1 = \sum_{r=1}^{N} h_{1r}, \hspace{1cm} (43)$$

$$h_2 = \sum_{r=1}^{N} h_{2r} + E_{21}, \hspace{1cm} (44)$$

where $h_{1r}$ and $h_{2r}$ are one-dimensional Hamiltonians in mode $Q_r$, and $E_{21}$ is the energy gap between the minima of the two multidimensional PESs. The propagators are then products of one-dimensional propagators.

The third-order polarization terms in the $k_{pr}$ direction, assuming constant transition dipole moment $\mu_{12}$ and leaving out the $e^{i k_{pr} \cdot R}$ term, can be written as\(^{31}\)

$$P_{\text{SRS(II)}}^{(3)}(t) = \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_1$$

$$\times e^{-\gamma_1 t_3 / 2\hbar - \gamma_2 (t_2 - t_3) / 2\hbar - \gamma_1 (t - t_2) / 2\hbar} e^{i E_{21} (t_2 - t_3) / \hbar} E_{pr}(t_2; T_{pr}) e^{-i E_{21} (t - t_1) / \hbar}$$

$$\times E_{pu}(t_1; T_{pu}) |\mu_{12}|^4 \prod_r S_r(t, t_1, t_2, t_3), \hspace{1cm} (45)$$

$$P_{\text{SRS(II)}}^{(3)}(t) = \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_1$$

$$\times e^{-\gamma_1 t_3 / 2\hbar - \gamma_2 (t_2 - t_3) / 2\hbar - \gamma_1 (t - t_2) / 2\hbar} e^{i E_{21} (t_2 - t_3) / \hbar} E_{pu}(t_2; T_{pu})$$

$$\times e^{-i E_{21} (t - t_1) / \hbar} E_{pr}(t_1; T_{pr}) |\mu_{12}|^4 \prod_r S_r(t, t_1, t_2, t_3), \hspace{1cm} (46)$$

$$P_{\text{IRS(II)}}^{(3)}(t) = \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3$$

$$\times e^{-\gamma_1 t_1 / 2\hbar - \gamma_2 (t_2 - t_1) / 2\hbar - \gamma_1 (t_1 - t_2) / 2\hbar} e^{i E_{21} (t_2 - t_1) / \hbar} E_{pu}(t_2; T_{pu})$$

$$\times e^{-i E_{21} (t_1 - t_2) / \hbar} E_{pr}(t_1; T_{pr}) |\mu_{12}|^4 \prod_r S_r(t, t_1, t_2, t_3).$$
Assuming (a) taken out and placed in the time-dependent pre-factor in Eqs. (45–48).

Complete basis set harmonic oscillators are displaced in coordinate $\mathbf{r}$ between the excited and ground state potentials. Note that the displaced for a pair of displaced harmonic oscillators without frequency changes

The four-time correlation functions can be computed analytically for a pair of displaced harmonic oscillators without frequency changes between the excited and ground state potentials. Note that the displaced harmonic oscillators are displaced in coordinate $\mathbf{Q}$ only, as the displacement in energy $E_{21}$ of the multidimensional potentials has been taken out and placed in the time-dependent pre-factor in Eqs. (45–48). Assuming (a) $|\psi_{1r}^{(0)}(\mathbf{Q}, 0)\rangle$ is the ground vibrational state, $|\psi_{1r}^{(0)}(\mathbf{Q}, 0)\rangle = |\psi_{1r0}(\mathbf{Q})\rangle$, with $h_{1r}|\psi_{1r0}(\mathbf{Q})\rangle = E_{1r0}|\psi_{1r0}(\mathbf{Q})\rangle$, and (b) inserting a complete basis set $\sum_{r'}|\psi_{1r'}(\mathbf{Q})\rangle\langle \psi_{1r'}(\mathbf{Q})|$, where $h_{1r}|\psi_{1r'}(\mathbf{Q})\rangle = E_{1r'}|\psi_{1r'}(\mathbf{Q})\rangle$, in the middle, we obtain for each mode

$$S_r(t_1, t_2, t_3) = \langle \psi_{1r}^{(0)}(\mathbf{Q}, 0)\rangle e^{i\hbar t_{13}/\hbar} e^{i\hbar t_{12}/\hbar} \times e^{i\hbar t_{12}/\hbar} e^{-i\hbar t_{12}/\hbar} \times e^{-i\hbar t_{12}/\hbar} |\psi_{1r}^{(0)}(\mathbf{Q}, 0)\rangle,$$
Wave Packet Analysis of FSRS

\begin{equation}
I_r(t, t_1, t_2, t_3) = e^{-iE_{1r0}(t_3-t)/\hbar}
\times \sum_{\nu'} \langle \psi_{1r0}(Q_r) | e^{iE_{1\nu'}(t_1-t_3)/\hbar} | \psi_{1\nu'}(Q_r) \rangle
\times e^{-iE_{1\nu'}(t_1-t)/\hbar}
\times \langle \psi_{1\nu'}(Q_r) | e^{i2\omega(t_2-t_3)/\hbar} | \psi_{1r0}(Q_r) \rangle.
\end{equation}

(52)

Now, each of the correlation functions are of the form \( \langle \psi_n | e^{-i2\omega/\hbar} | \psi_0 \rangle \equiv \langle \psi_n | \psi_0(t) \rangle \) or its complex conjugate, with analytic result given by

\begin{equation}
\langle \psi_n | \psi_0(t) \rangle = \exp\left\{-\left(\frac{\Delta^2}{2}\right)[1 - \exp(-i\omega t) - i\omega t/2]\right\}
\times \left(\frac{1}{n!}\right)^n \frac{1}{(2\pi)^{1/2}} [1 - \exp(-i\omega t)]^n.
\end{equation}

(53)

where \( \Delta \) is the excited state mode displacement relative to the ground state and \( \omega \) is the mode frequency.

All the third-order polarizations are zero before the arrival of the probe pulse, i.e. they begin when there is coupling between the Raman pump and probe pulses acting on the molecule. Furthermore, \( P^{(3)}_{\mathrm{SRS(I)}}(t) \) and \( P^{(3)}_{\mathrm{IRS(I)}}(t) \) lasts as long as the (ps) Raman pump pulse or the decay time of the vibrational coherence, giving rise to sharp spectral lines with nearly the Raman pump bandwidth, while \( P^{(3)}_{\mathrm{SRS(II)}}(t) \) and \( P^{(3)}_{\mathrm{IRS(II)}}(t) \) rises and falls according to the dynamics on the excited state surface induced by the ultrashort probe pulse, giving rise to broad featureless spectra when the dynamics is of short time, in the order of fs, as in the FSRS of R6G below. The polarizations \( P^{(3)}_{\mathrm{SRS(I)}}(t) \) and \( P^{(3)}_{\mathrm{IRS(I)}}(t) \) in the frequency domain can have the fingerprint of the Rayleigh, fundamentals, overtones, and the mixed mode transitions.

In the condensed phase, one needs to take into account inhomogeneous broadening due to variations in the local environment of the molecule by using a Gaussian distribution of zero-zero energies,

\begin{equation}
G(E_{21}) = \exp \left[ -\frac{(E_{21} - \bar{E}_{21})^2}{2\sigma^2} \right].
\end{equation}

(54)
where $\bar{E}_{21}$ is the average zero-zero energy, and $\theta$ is the standard deviation in the broadening. $G(t)$ is the Fourier transform of the inhomogeneous distribution function

$$G(t) = \int_0^\infty dE_{21} e^{-iE_{21}t/\hbar} G(E_{21}).$$

(55)

It can then be shown that by including inhomogeneous broadening, the FSRS third-order polarization terms take the form

$$P_{\text{SRS(I)}}^{(3)}(t) = \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_1$$

$$\times e^{-\gamma_1 t_3/2h - \gamma_2 (t_2 - t_3)/2h - \gamma_2 (t_1 - t_2)/2h - \gamma_1 (t - t_2)/2h}$$

$$\times E_{\text{pu}}^{a}(t_3; T_{\text{pu}}) E_{\text{pu}}(t_2; T_{\text{pu}}) E_{\text{pu}}(t_1; T_{\text{pu}}) G(t - t_1 - t_2 + t_3)$$

$$\times |\mu_{12}|^4 \prod_r S_r(t, t_1, t_2, t_3),$$

(56)

$$P_{\text{SRS(II)}}^{(3)}(t)$$

$$= \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_1$$

$$\times e^{-\gamma_1 t_3/2h - \gamma_2 (t_2 - t_3)/2h - \gamma_2 (t_1 - t_2)/2h - \gamma_1 (t - t_2)/2h}$$

$$\times E_{\text{pu}}^{a}(t_3; T_{\text{pu}}) E_{\text{pu}}(t_2; T_{\text{pu}}) E_{\text{pr}}(t_1; T_{\text{pr}}) G(t - t_1 - t_2 + t_3)$$

$$\times |\mu_{12}|^4 \prod_r S_r(t, t_1, t_2, t_3),$$

(57)

$$P_{\text{IRS(I)}}^{(3)}(t) = \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3$$

$$\times e^{-\gamma_1 t_2/2h - \gamma_2 (t_1 - t_2)/2h - \gamma_2 (t_1 - t_2)/2h - \gamma_1 t_3/2h}$$

$$\times E_{\text{pu}}(t_1; T_{\text{pu}}) E_{\text{pu}}^{a}(t_2; T_{\text{pu}}) E_{\text{pr}}(t_3; T_{\text{pr}})$$

$$\times G(t - t_1 + t_2 - t_3) |\mu_{12}|^4 \prod_r I_r(t, t_1, t_2, t_3),$$

(58)

$$P_{\text{IRS(II)}}^{(3)}(t)$$

$$= \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3$$

$$\times e^{-\gamma_1 t_2/2h - \gamma_2 (t_1 - t_2)/2h - \gamma_2 (t_1 - t_2)/2h - \gamma_1 t_3/2h}$$

$$\times E_{\text{pu}}(t_1; T_{\text{pu}}) E_{\text{pu}}^{a}(t_2; T_{\text{pu}}) E_{\text{pr}}(t_3; T_{\text{pr}})$$

$$\times G(t - t_1 + t_2 - t_3) |\mu_{12}|^4 \prod_r I_r(t, t_1, t_2, t_3),$$
Wave Packet Analysis of FSRS

\[ \times E_{pr}(t_1; T_{pr})E_{pu}^*(t_2; T_{pu})E_{pu}(t_3; T_{pu}) \]
\[ \times G(t - t_1 + t_2 - t_3)| \mu_{12}|^4 \prod_r I_r(t, t_1, t_2, t_3). \]  

(59)

All the integrands in Eqs. (56–59) are of analytic form. However, the numerical integration for the multiple integrals may be very time consuming when the Raman pump pulse is about a picosecond in duration and when the inhomogeneous broadening constant \( \theta \) is large, of the order of a few hundred cm\(^{-1}\).

While the Feynman diagrams (Fig. 4) provide a useful time-frame viewpoint, it is also useful to look at four-wave mixing energy level diagrams (FWMEL) to provide an energy-frame viewpoint of FSRS from a stationary state. The FWMEL diagrams corresponding to each of the Feynman diagrams are shown in Fig. 5. Time increases from left to right in each diagram. The interaction on the bra is denoted by a dashed arrow and on the ket by a solid arrow. The narrow bandwidth Raman pump and the broadband (grey energy bar) probe pulse are shown. The final wavy line denotes closure between the bra and the ket to give the third-order polarization. It is easy to see from the wavy line closure between bra and ket of well-defined energies that the RRS(I) term gives rise to sharp Stokes and Rayleigh gain lines with energy transferred from the Raman pump to the probe pulse. For HL(I) (or HL(II), one pump interaction on the bra (or ket)) at \( t_3 \) and another on the ket (or bra) at \( t_2 \) can prepare a population on \( e_2 \) which is then stimulated by the probe at \( t_1 \) to emit. The population on \( e_2 \), however, is going to be very small off-resonance and so the HL(I) and HL(II) contribution to the FSRS spectrum will be small compared to the RRS(I) term. Even on resonance, the correlation function from the overlap between the amplitude on \( e_2 \) and the final state on \( e_1 \) is usually short-lived particularly for incommensurate frequency oscillators and so the contribution to the FSRS spectrum from HL(I) and HL(II) is usually broad. In the case of the RRS(II), HL(III) and HL(IV) terms, the wavy line closure is between a continuum of ket states due to the probe excitation with a bra of well-defined energy, thus they give rise to broad spectra. The IRS(I) term is like the RRS(I) term, but it gives rise to sharp anti-Stokes and Rayleigh loss lines with energy transferred from the probe to the Raman.
Fig. 5. Four-wave mixing energy level diagrams corresponding to the Feynman diagrams of Fig. 4.

pump. Finally, the IRS(II) term is like the RRS(II), HL(III) and HL(IV) terms and gives rise to a broad spectrum.

3.2. Application to FSRS of Rhodamine 6G

Recently, the highly fluorescent molecule Rhodamine 6G (R6G) has been studied by femtosecond stimulated Raman spectroscopy (FSRS) to acquire and quantify its resonance Raman (RR) cross section on the Stokes side even in the presence of strong fluorescence at 532-nm and 555-nm Raman pump.14 FSRS on both the Stokes and anti-Stokes side have also been
Wave Packet Analysis of FSRS

Table 1. Potential parameters for R6G.14

| Frequency $\omega_r$, cm$^{-1}$ | Displacement $|\Delta r|$ |
|-------------------------------|-------------------|
| 300                          | 0.24              |
| 375                          | 0.46              |
| 518                          | 0.17              |
| 604                          | 0.42              |
| 761                          | 0.29              |
| 917                          | 0.14              |
| 1116                         | 0.15              |
| 1172                         | 0.24              |
| 1303                         | 0.28              |
| 1356                         | 0.34              |
| 1504                         | 0.32              |
| 1571                         | 0.27              |
| 1647                         | 0.30              |

collected over a wide range of excitation wavelengths, 540–580 nm, as well as for various pump-probe delays at 540-nm Raman pump.13 Here, we apply the FSRS theory above to calculate FSRS spectra of R6G from its ground vibrational state with ps Raman pump and fs probe pulses to compare with the experimental results of Shim et al.14 and Frontiera et al.13

Shim et al.14 have determined the excited state displacements of each of the 13 modes of R6G using experimental Raman intensities. The signs of the displacements could not be determined, but they are not important because in the harmonic model the dynamics depend only on $|\Delta r|^2$. Table 1 gives the frequencies and modulus of the displacements of the 13 modes used in all our FSRS calculations below. We assume that R6G is initially in the ground vibrational state in all our calculations below. By a fit of the absorption spectrum of R6G,13,14 we have obtained the average zero-zero energy $\bar{E}_{21} = 18850$ cm$^{-1}$, the homogeneous damping constant on the excited electronic state $\gamma_2 = 340$ cm$^{-1}$, and the inhomogeneous damping constant $\theta = 300$ cm$^{-1}$.13 The absorption maximum of R6G is at (about) 528 nm. The homogeneous damping constant on the ground electronic state, $\gamma_1$, is set at 0 cm$^{-1}$. In the calculations, we have used the same carrier wavelengths for the Raman pump and probe pulses, i.e. we have
set $\omega_{pu} = \omega_{pr}$, but it is not important so long as the broadband probe spectrum can span the range of FSRS anti-Stokes and Stokes bands. We have used Gaussian pulses characterized by $\tau$, the full-width at half-maximum (FWHM), with $\tau_{pu} = 600$ fs with linewidth of $35 \text{ cm}^{-1}$ which gives sharp Stokes and anti-Stokes lines, similar to those seen in the FSRS experiments on R6G, and $\tau_{pr} = 10$ fs which provides a broad window, spanning about $4000 \text{ cm}^{-1}$, to stimulate Raman scattering across both the anti-Stokes and Stokes bands.

Off-resonance Stokes and anti-Stokes FSRS (cross section) spectra of transparent liquids such as a mixture of cyclohexane and chloroform show an inversion symmetry of the Stokes and anti-Stokes lines about the centre (Rayleigh line position), with Raman gain on the Stokes side and a Raman loss on the anti-Stokes side. It was also observed that the anti-Stokes bands are equal in magnitude and linewidth to the corresponding Stokes bands, for any wavenumber, independent of the probe pulse shape and intensity; this is because it is a cross section described by Eq. (39) where the probe field amplitude cancels out in the numerator and denominator. The strong and inverted anti-Stokes bands in FSRS are from the ground vibrational state and makes them very different in origin from spontaneous Raman scattering where the anti-Stokes bands come from Boltzmann population of excited vibrational states. The explanation for the off-resonance FSRS spectra has been given earlier: the Stokes band is due to the SRS(I) process where a Raman pump photon is converted to a probe photon (of lower energy) and the molecule is excited by one vibrational quantum in the ground electronic state; the anti-Stokes band is due to the IRS(I) process where a probe photon (of higher energy than the Raman pump) from the broad probe spectrum is converted to a pump photon and the molecule is also excited by one vibrational quantum. In transparent liquids, the excited states are very high in energy relative to the ground electronic state minimum, in the far UV, and even a visible 550-nm Raman pump would be very far off-resonance with the excited electronic state. In the case of colored dyes like R6G, the excited electronic states can be reached with visible light.

In Fig. 6, we show the calculated FSRS spectra of R6G with excitation wavelengths of 600–1200 nm where the cross section drops about 400-fold on the Stokes side between 600 nm and 1200 nm excitation. The tail end of the absorption can be reached by the 600-nm Raman pump and
Fig. 6. Calculated FSRS spectra of R6G with excitation wavelengths of 600–1200 nm; the cross section drops about 400-fold on the Stokes side between 600 nm and 1200 nm excitation. At 600-nm excitation which is near resonance, there is a clear asymmetry between the Stokes and anti-Stokes bands. From 800–1200 nm, we have off-resonance FSRS and the inversion symmetry of the lines appear. Reproduced with permission from J. Chem. Phys. 131, 054311 (2009).

there’s a clear asymmetry between the Stokes and anti-Stokes bands. From 800–1200 nm, we have off-resonance FSRS and the inversion symmetry of the lines appear. However, the anti-Stokes bands are about twice as intense as the Stokes bands, but they have the same linewidths due to the 600-fs Raman pump. The reason is because the anti-Stokes bands are due to the IRS(I) process where the broadband probe pulse can get closer to resonance with the excited electronic state compared to the narrow bandwidth Raman pump in the SRS(I) process that accounts for the Stokes bands. So, only when the excited electronic states are very high up in energy and in far off-resonance FSRS can we expect to see near perfect inversion symmetry between the cross section of the Stokes and anti-Stokes bands as in the case of transparent liquids like cyclohexane and chloroform.

Frontiera et al.\textsuperscript{13} have obtained the resonance FSRS spectra of R6G as a function of excitation wavelengths through the red side of the absorption maximum, from 540–580 nm, and both the anti-Stokes, Fig. 7c, and Stokes, Fig. 7d, bands were recorded. The 1020 cm\textsuperscript{-1} CO stretch of methanol,
Fig. 7. Resonance FSRS spectra of R6G as a function of excitation wavelengths. (a) Calculated resonance FSRS anti-Stokes bands of R6G at excitation wavelengths from 540–580 nm. (b) Similar to (a), but for Stokes bands. (c) Experimental FSRS results from Frontiera et al. for the anti-Stokes bands. (d) Same as for (c), but for the Stokes bands. The off-resonance FSRS of the CO stretch of the solvent methanol at 1020 cm$^{-1}$ is marked with asterisks, showing anti-Stokes loss and Stokes gain. Reproduced with permission from J. Chem. Phys. 131, 054311 (2009).
shown by an asterisk, appears clearly as a Raman loss on the anti-Stokes spectra and as a Raman gain on the Stokes spectra for all excitation wavelengths which are far off-resonance with respect to the methanol high energy excited states. The corresponding calculated results for the resonance FSRS spectra of R6G are shown in Figs. 7a and 7b for the anti-Stokes and Stokes bands, respectively. The intensity of the anti-Stokes bands are much stronger than the Stokes bands; the frequencies of the bands are the same on both sides, but the band shapes clearly do not exhibit any symmetry about the Rayleigh 0 cm$^{-1}$ position, unlike in the far off-resonance regime. There is generally good agreement in the trend of the baselines between the calculated and the experimental spectra. The contribution of the four nonlinear processes — SRS(I), SRS(II), IRS(I), IRS(II) — to the calculated resonance FSRS spectra of R6G in Figs. 7a and 7b, are shown in Fig. 8. The baselines seen in the FSRS anti-Stokes and Stokes spectra in Fig. 7 arise, to a large extent, from the sum of the featureless, broad spectra due to SRS(II) and IRS(II) processes shown in Fig. 8, with the SRS(II) process being the larger contributor as the excitation wavelength is tuned closer to the absorption maximum. The broad SRS(II) and IRS(II) spectra arise from the short-time overlap between a ket vector prepared on the excited state $e_2$ surface by the ultrashort probe pulse and an effectively stationary state bra vector in $e_1$, for reasons the same as in the short-time autocorrelation function for the photoabsorption of R6G.

The shape of the experimental Stokes bands at 604 and 761 cm$^{-1}$ in Fig. 7d may appear ambiguous as to whether or not they may be evolving from positive to dispersive lineshape as the excitation wavelength is tuned towards the absorption maximum, from 580 nm to 540 nm. The Stokes bands come from the SRS(I) process, as shown in Fig. 8, and the calculations show that they are in fact all positive Raman gain features. It is the addition of the sloping baselines coupled with the instrumental resolution that may give the illusion of dispersive lineshapes. The anti-Stokes bands in Fig. 7c may appear to have a more complicated structure. They arise from the IRS(I) process as shown by calculations in Fig. 8, where the broadband probe pulse initiates the Raman process as seen in Fig. 4. The bands start off negative, when the probe wavelength is off-resonance, becomes dispersive, then positive, then oppositely phased dispersive, and then negative again as the excitation wavelength nears the absorption maximum. These changes
Fig. 8. The SRS(I), SRS(II), IRS(I) and IRS(II) components of the calculated resonance FSRS of R6G at excitation wavelengths from 540–580 nm for both the anti-Stokes and Stokes bands in Figs. 7a and 7b. The SRS(II) and IRS(II) terms contribute to the broad baselines in the FSRS spectra; the IRS(I) term accounts for the sharp anti-Stokes bands; and the SRS(I) term accounts for the sharp Stokes bands. Reproduced with permission from J. Chem. Phys. 131, 054311 (2009).

in the lineshapes were also observed by Frontiera et al.\textsuperscript{13} in the experiment, as shown in Fig. 7c.

Frontiera et al.\textsuperscript{13} have also acquired the resonance FSRS spectra of R6G as a function of the Raman pump-probe delay from $-533$ to 400 fs, at 540 nm excitation. A negative time delay means that the 10 fs probe pulse arrives before the 600-fs Raman pump maximum, and a positive time delay means that it arrives after. The experimental results for the anti-Stokes side are shown in Fig. 9c and for the Stokes side in Fig. 9d. The dispersive
Wave Packet Analysis of FSRS

bands on the anti-Stokes side at 604 and 761 cm$^{-1}$ for the 0 fs delay seem to resemble more the experimental resonance FSRS spectrum taken at 550 nm excitation shown in Fig. 7c. Thus, we have calculated the corresponding resonance FSRS spectra in Figs. 9a and 9b using a 550 nm excitation instead. Generally, the trend in the calculated results are in good agreement with experiments. The linewidths of both the anti-Stokes and Stokes bands become broader as the time delay is increased. The reason is because of the shorter time that the final pump field has to interact with the coherent Liouville vibrational state on $e_1$, prepared by an initial pump-probe or probe-pump interaction, as shown in the IRS(I) diagram for anti-Stokes bands and RRS(I) diagram (in the SRS(I) set) for the Stokes bands in Fig. 4, which in turn shortens the time-scale of the temporal third-order polarization that begins when the probe is on, and by Fourier transform it gives a broader linewidth. Overall, more negative time delays, where the fs probe pulse precedes the ps Raman pump pulse maximum, give sharper Stokes and anti-Stokes lines with reduced baselines in the FSRS spectra, but also some reduction in the intensity; positive time delays should be avoided.

3.3. Application to the FSRS from a coherent vibrational state of CDCl$_3$

In a 2D-FSRS experiment of the type that has been used to study chloroform$^8,42$ and acetonitrile,$^{43}$ the 1D-FSRS is applied after an off-resonant fs impulsive pump (Ipu) pulse, with field $E_{Ipu}(t, T_{Ipu})$, has prepared a coherent vibrational state, i.e. a moving wave packet, on the ground electronic state by a second-order process on the ket or bra wavefunction. The observable is the difference in the Raman gain spectra with and without the Ipu pulse as a function of the time delay between the fs Ipu and fs pr pulses, and our 2D-FSRS here has one dimension as the frequency of the FSRS spectra and another as the time delay. One can take a Fourier transform of the spectra as a function of time delay and turn the time delay dimension to frequency too, as is done in Mehlenbacher et al.,$^{42}$ but it carries the same information. Our focus here is in explaining the off-resonance 2D-FSRS of CDCl$_3$ in the experiment of Kukura et al.,$^8$ whose difference (Stokes) Raman gain spectra at various time delays show a high frequency C-D symmetric stretch
Fig. 9. Resonance FSRS spectra of R6G as a function of Raman pump-probe delay. A positive time delay means that the 600-fs Raman pump maximum arrives before the 10-fs probe pulse. (a) Calculated resonance FSRS anti-Stokes bands of R6G at excitation wavelength of 550 nm with pump-probe time delays from $-533$ to $+400$ fs. (b) Similar to (a) but for the Stokes bands. (c) Experimental FSRS results from Frontiera et al. for the anti-Stokes bands at excitation wavelength of 540 nm. (d) Same as for (c), but for the Stokes bands. The line at 1020 cm$^{-1}$ is due to the CO stretch of the solvent methanol. Reproduced with permission from J. Chem. Phys. 131, 054311 (2009).
Wave Packet Analysis of FSRS

band at 2255 cm\(^{-1}\), denoted by \(\omega_{CD}\), and sidebands that are displaced to the left and right of it by 262 and 365 cm\(^{-1}\), corresponding to the C-Cl \(E\) and \(A_1\) bends, respectively, and denoted by \(\omega_{E/A_1}\). The \(Ipu\) pulse can only create vibrational coherence in the low frequency \(\omega_{E/A_1}\) bends, and the central frequency of the broadband (pr) pulse is red-shifted from the narrow bandwidth \(pu\) which on “emission” can span the vibrational levels on the ground PES with frequencies \(\omega_{CD}\) and \(\omega_{CD} \pm \omega_{E/A_1}\). When the \(Ipu\) pulse acts first, followed by FSRS with \(pu\) and \(pr\) pulses acting on the same molecule, we have a direct fifth-order process. On the other hand, the \(pu\) pulse which largely follows the \(Ipu\) pulse can act together on a molecule (A) to produce new CARS and CSRS fields in the \(pu\) direction. These new fields can then participate in the FSRS process on another molecule B together with the \(pu\) and \(pr\) pulses, and we call it a cascade process. The direct fifth-order and cascade process are shown schematically in Fig. 10.44

3.3.1. Direct fifth-order process

The Feynman dual time-line diagrams for the evolution of the ket and \(bra\) wave packet in Liouville space, describing the difference Raman gain

Fig. 10. Schematic of direct fifth-order process with impulsive pump followed by FSRS with Raman pump and probe pulses all acting on molecule A versus a cascade process where the impulsive pump and Raman pump pulses first act on molecule A to produce new CARS and CSRS fields along the Raman pump direction which then participate in FSRS with the Raman pump and probe pulses on molecule B. Reproduced with permission from J. Chem. Phys. (in press, 2011).44
spectra in the probe pulse direction with and without Ipu, in the direct fifth-order process on one molecule are given in Figs. 11a and 11b. The convention for the Feynman diagrams is the same as described for Fig. 4. The three different fields, $E_{Ipu}$, $E_{pu}$ and $E_{pr}$, are drawn to point in three different directions. We have drawn the diagrams to show that the wave vectors for the two impulsive pump interactions cancel and the two Raman pump interactions cancel, leaving a resultant polarization in the probe pulse direction. The dashed line connecting the ket and bra at time $t$ denotes the final collapse of polarization to produce the detected signal. In the experiments on chloroform, all the pulses — Ipu, pu, and pr — are off-resonance. The Ipu pulse prepares a time-dependent coherent state (a second-order wave packet that can also be calculated nonperturbatively) in the low frequency C-Cl bends on the ground electronic state $e_1$. This is shown as two interactions by the Ipu pulse on the ket or bra side in Fig. 11a or 11b at times $t_5$ and $t_4$. The off-resonance FSRS for the Stokes side spectrum which is given by the SRS(I) process is then grafted on,
after the interactions with $I_{pu}$. Only the (main) $RRS(I)$ term in $SRS(I)$ is shown in both figures, with the understanding that $t_1$ can be permuted to come before $t_2$ or $t_3$, i.e. to include the (smaller) $HL(I)$ and $HL(II)$ terms of $SRS(I)$ in this off-resonance $FSRS$. The time variables in all our integrals are actual interaction times with the electric fields along the ket or bra time-lines, and they are useful when considering wave packet propagation with finite pulses along these time-lines. In response theories, it is the time difference between pulse interactions on either the ket or bra time-lines, and they are useful when considering wave packet propagation with finite pulses along these time-lines. In response theories, it is the time difference between pulse interactions on either the ket or bra time-lines that is commonly used, which can facilitate making approximations under ultrashort pulses or ultrafast electronic dephasing times or classical nuclear dynamics. We take CDCl$_3$ to have a $Q_{CD}$ stretch and two low frequency C-Cl bends $Q_{A_1}$ and $Q_{E}$, and the fifth-order polarizations can be directly written down from the Feynman diagrams,

$$P_{2D-FSRS^{(-)}}^{(S)}(t) = e^{ik_pR} \left( \frac{i}{\hbar} \right)^5 \int_{t_0}^{t_1} dt_1 \int_{t_0}^{t_2} dt_2 \int_{t_0}^{t_3} dt_3 \int_{t_0}^{t_4} dt_4 \int_{t_0}^{t_5} dt_5$$

$$\times E_{pu}(t_1; T_{pu}) E_{pr}(t_2; T_{pr}) E_{pu}^*(t_3; T_{pu}) E_{pu}^*(t_4; T_{pu})$$

$$\times E_{pu}(t_5; T_{pu})(\psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_{E}, t_a))$$

$$\times e^{(i\hbar_1-\gamma_1/2)(t_3-t_0)/\hbar} \mu_{21} e^{i(\hbar_2-\gamma_2/2)(t_2-t_1)/\hbar}$$

$$\times \mu_{21} e^{i(-\hbar_1-\gamma_1/2)(t_1-t_0)/\hbar} \mu_{21} e^{i(-\hbar_2-\gamma_2/2)(t_4-t_3)/\hbar}$$

$$\times e^{i(-\hbar_1-\gamma_1/2)(t_5-t_a)/\hbar} |\psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_{E}, t_a)\rangle.$$  \hspace{1cm} (60)$$

$$P_{2D-FSRS^{(+)}}^{(S)}(t) = e^{ik_pR} \left( \frac{i}{\hbar} \right)^5 \int_{t_0}^{t_1} dt_1 \int_{t_0}^{t_2} dt_2 \int_{t_0}^{t_3} dt_3 \int_{t_0}^{t_4} dt_4 \int_{t_0}^{t_5} dt_5$$

$$\times E_{pu}(t_1; T_{pu}) E_{pr}(t_2; T_{pr}) E_{pu}^*(t_3; T_{pu}) E_{pu}^*(t_4; T_{pu})$$

$$\times E_{pu}(t_5; T_{pu})(\psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_{E}, t_a))$$

$$\times e^{(i\hbar_1-\gamma_1/2)(t_3-t_0)/\hbar} \mu_{21} e^{i(\hbar_2-\gamma_2/2)(t_2-t_1)/\hbar}$$

$$\times \mu_{21} e^{i(-\hbar_1-\gamma_1/2)(t_1-t_0)/\hbar} \mu_{21} e^{i(-\hbar_2-\gamma_2/2)(t_4-t_3)/\hbar}$$

$$\times e^{i(-\hbar_1-\gamma_1/2)(t_5-t_a)/\hbar} |\psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_{E}, t_a)\rangle.$$  \hspace{1cm} (61)
Here, $|\psi^{(0)}_1(\mathbf{Q}_{\text{CD}}, \mathbf{Q}_{\text{A}_1}, \mathbf{Q}_{\text{E}}, t_0)\rangle$ is the initial wave packet on the ground electronic PES, and $t_0$ is a time before the Ipu pulse appears. FSRS$^{(-)}$ and FSRS$^{(+)}$ refer to the left and right sidebands relative to the C-D stretch, respectively, and both diagrams also account for the fundamental C-D stretch, as shown by the wave mixing energy level (WMEL) diagrams in Mehlenbacher et al.\textsuperscript{42} We have assumed a two electronic state system $e_i$, $i = 1, 2$ where the vibrational Hamiltonian on electronic state $e_i$ is denoted by $h_i$ with homogeneous damping constants $\gamma_i$, and $\mu_{12}$ as vibrational coordinate dependent transition dipole moments.

### 3.3.2. Cascade processes

In the 2D-FSRS experiment on chloroform,\textsuperscript{8, 45} the pu pulse which largely follows the Ipu pulse can both act on molecule A in the first step of the cascade process to produce new third-order CARS (coherent anti-Stokes Raman Spectroscopy) and CSRS (coherent Stokes Raman spectroscopy) fields in the direction of the pu pulse. It is not essential for the Ipu and pu pulses to overlap. So long as the vibrational coherence in the ground electronic state created by the Ipu pulse is maintained when the pu pulse acts on the molecule, the CARS and CSRS fields will be produced. The Feynman diagrams to describe the CARS process are shown on the left of Figs. 12a and 13a, which are complex conjugates of each other, and for the CSRS process in Figs. 12b and 13b, also complex conjugates of each other. In both Figs. 12 and 13, the CARS and CSRS fields in (a) and (b), respectively, propagates from molecule A to participate in the FSRS process on molecule B. The 30 fs (full width at half maximum (FWHM) of $E_{Ipu}^2$) impulsive pump has a bandwidth of about 360 cm$^{-1}$ and can only excite the low frequency C-Cl symmetric ($A_1$) and asymmetric ($E$) bends, but not the C-D stretch. The two interactions with the Ipu pulse first create a time-dependent (second-order) coherent wave packet in the C-Cl bends on the ground electronic state $e_1$ on either the ket or bra side of the dual time-line diagram, and after a third interaction with pu on either the same or opposite side and with the collapse of the third-order polarization, the CARS or CSRS field, respectively, is produced. Using WMEL diagrams,\textsuperscript{42} it is straightforward to show that the CARS field has three frequency components: one at the Raman pump frequency, $\omega_{Ipu}$, and two others at
Fig. 12. Feynman dual time-line diagrams for the parallel cascade process. Reproduced with permission from *J. Chem. Phys.* (in press, 2011).\(^\text{44}\)

Fig. 13. Feynman dual time-line diagrams for the sequential cascade process. Reproduced with permission from *J. Chem. Phys.* (in press, 2011).\(^\text{44}\)
\( \omega_{pu} + \omega_{E/A_1} \); while the CSRS field also has three frequency components: one at the Raman pump frequency, \( \omega_{pu} \), and two others at \( \omega_{pu} - \omega_{E/A_1} \).

From the Feynman diagram on the left of Fig. 12a for the CARS process, the time-dependent third-order polarization \( P_{CARS}^{(3)}(\tau) \) that radiates along the pu direction is given by,

\[
P_{CARS}^{(3)}(\tau) = e^{\text{ik}_{pu}R} \left( \frac{i}{\hbar} \right)^3 \int_{\tau}^{\tau'} d\tau_1 \int_{\tau_1}^{\tau'} d\tau_2 \int_{\tau_2}^{\tau'} d\tau_3 E_{pu}(\tau'; T_{pu})
\]

\[
\times E_{pu}^*(\tau'_1; T_{pu}) E_{pu}(\tau'_2; T_{pu}) (\psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_{E}, t_0))
\]

\[
\times e^{i\hbar_1 - \gamma_1/2)(\tau-\tau_0)/\hbar} \mu_{21}^* e^{-i\hbar_2 - \gamma_2/2)(\tau-\tau')/\hbar} \mu_{21}
\]

\[
\times e^{-i\hbar_1 - \gamma_1/2)(\tau'_1-\tau'_2)/\hbar} \mu_{21}^* e^{-i\hbar_2 - \gamma_2/2)(\tau'_2-\tau'_3)/\hbar} \mu_{21}
\]

\[
\times e^{-i\hbar_1 - \gamma_1/2)(\tau'_3-\tau'_0)/\hbar} |\psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_{E}, t_0)\rangle. \quad (62)
\]

In the left dual time-line diagram of Fig. 13a, we have the complex conjugate of the CARS process. Similarly, from the Feynman diagram on the left of Fig. 12b for the CSRS process, the time-dependent third-order polarization \( P_{CSRS}^{(3)}(\tau) \) that radiates along the pu direction is given by,

\[
P_{CSRS}^{(3)}(\tau) = e^{\text{ik}_{pu}R} \left( \frac{i}{\hbar} \right)^3 \int_{\tau}^{\tau'} d\tau_1 \int_{\tau_1}^{\tau'} d\tau_2 \int_{\tau_2}^{\tau'} d\tau' E_{pu}(\tau'; T_{pu})
\]

\[
\times E_{pu}^*(\tau'_1; T_{pu}) E_{pu}(\tau'_2; T_{pu}) (\psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_{E}, t_0))
\]

\[
\times e^{i\hbar_1 - \gamma_1/2)(\tau-\tau_0)/\hbar} \mu_{21}^* e^{-i\hbar_2 - \gamma_2/2)(\tau-\tau')/\hbar} \mu_{21}
\]

\[
\times e^{i\hbar_1 - \gamma_1/2)(\tau'-\tau_0)/\hbar} \mu_{21}^* e^{-i\hbar_2 - \gamma_2/2)(\tau'-\tau'_0)/\hbar} \mu_{21}
\]

\[
\times e^{i\hbar_1 - \gamma_1/2)(\tau'_0-\tau'_1)/\hbar} \mu_{21}^* e^{-i\hbar_2 - \gamma_2/2)(\tau'_1-\tau_0)/\hbar} \mu_{21}
\]

\[
\times e^{-i\hbar_1 - \gamma_1/2)(\tau'_0-\tau'_1)/\hbar} |\psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_{E}, t_0)\rangle. \quad (63)
\]

In the left dual time-line diagram of Fig. 13b, we have the complex conjugate of the CSRS process.

The relationship between the electric field and the polarization in the time domain is given by,\(^{38}\)

\[
E_{CARS/CSRS}^{(3)}(t) = -N \frac{2\pi i}{ne_0} \frac{\partial P_{CARS/CSRS}^{(3)}(t)}{\partial t}. \quad (64)
\]
where \( N \) is the number density of molecules, \( l \) is the sample path length, \( n \) is the refractive index, \( c \) is the speed of light, and \( \varepsilon_0 \) is the vacuum permittivity, and in the frequency domain it is given by the Fourier transform with the result,

\[
E^{(3)}_{\text{CARS/CSRS}}(\omega) = iN \frac{2\pi l \omega}{nc \varepsilon_0} P^{(3)}_{\text{CARS/CSRS}}(\omega).
\]  

(65)

As the new fields \( E^{(3)}_{\text{CARS/CSRS}}(t) \) are propagating along the pu direction through the sample, an off-resonant third-order FSRS with pu and pr pulses, described by the SRS(I) process, may be taking place on another molecule B from its ground vibrational state, and the CARS/CSRS field may be inserted in place of the pu in two different ways. It can be inserted on the ket side as the third interaction in a RRS(I) diagram, as shown in Figs. 12a and 12b on the right diagram, which we term parallel pCARS-FSRS and pCSRS-FSRS, respectively. Alternatively, it can be inserted on the bra side as the first interaction in a RRS(I) diagram, as shown in Figs. 13a and 13b on the right diagram, which we term sequential sCARS-FSRS and sCSRS-FSRS, respectively. The four terms shown in Figs. 12 and 13 would describe the off-resonant difference cascade Raman gain spectra with Ipu and without Ipu as a function of the time delay between the fs Ipu and pr pulses giving us 2D-FSRS.

With the Feynman dual time-line diagrams in Figs. 12 and 13, we can write down the corresponding polarizations:

(i) The pCARS-FSRS process is given by Fig. 12a, and the fifth-order polarization in the probe direction, which generates bands at frequencies \( \omega_{pu} - \omega_{CD} \) and \( \omega_{pu} - (\omega_{CD} \pm \omega_{E/A}) \), that can be shown by a WMEL diagram,\(^42\) is given by,

\[
P^{(5)}_{\text{pCARS-FSRS}}(t) = e^{i\mathbf{k}_{pu} \cdot \mathbf{R}} \left( \frac{i}{\hbar} \right)^3 \int_{\tau_a}^{\tau_1} d\tau_1 \int_{\tau_a}^{\tau_1} d\tau_2 \int_{\tau_a}^{\tau_1} d\tau \ E^{(3)}_{\text{CARS}}(\tau)
\times E_{pu}(\tau_1; T_{pu}) E^{*}_{pu}(\tau_2; T_{pu}) \langle \psi_1(0)(Q_{CD}, Q_{A_1}, Q_E, \tau_a)|
\times e^{(i\hbar_1 - \gamma_1/2)(\tau_2 - \tau_a)/\hbar} \mu_{21} e^{(i\hbar_2 - \gamma_2/2)(\tau_1 - \tau_2)/\hbar} \mu_{21}
\times e^{(i\hbar_1 - \gamma_1/2)(\tau - \tau_a)/\hbar} \mu_{21} e^{(-i\hbar_2 - \gamma_2/2)(\tau - \tau)/\hbar} \mu_{21}
\times e^{(-i\hbar_1 - \gamma_1/2)(\tau_a - \tau)/\hbar} |\psi_1(0)(Q_{CD}, Q_{A_1}, Q_E, \tau_a)\rangle.
\]

(66)
(ii) The pCSRS-FSRS process is given by Fig. 12b, and the fifth-order polarization in the probe direction which generates bands at frequencies \(\omega_{pu} - \omega_{CD} \) and \(\omega_{pu} - (\omega_{CD} + \omega_{E/A_1})\), is given by,

\[
P_{pCSRS-FSRS}^{(5)}(t) = e^{i k_{pr} \cdot \mathbf{R}} \left( \frac{i}{\hbar} \right)^3 \int_{t_a}^{t} \int_{t_a}^{t} \int_{t_a}^{t} dt_1 dt_2 dt_3 \ E_{pCSRS}^{(3)}(\tau) \\
\times E_{pr}^{\ast}(\tau_1; T_{pr}) E_{pu}^{\ast}(\tau_2; T_{pu}) (\varphi_1^{(0)}(Q_{CD}. Q_{A_1}, Q_{E}. t_a)) | \\
\times e^{(i h_1 - \gamma_1/2)(\tau_2 - t_a)/\hbar} | (t_1 - \tau)/\hbar | \mu_{21} e^{(i h_2 - \gamma_2/2)(\tau_1 - \tau)/\hbar} | \\
\times e^{(i h_1 - \gamma_1/2)(\tau_2 - t_a)/\hbar} | (t_2 - \tau)/\hbar | \mu_{21} e^{(i h_2 - \gamma_2/2)(\tau_1 - \tau)/\hbar} | \\
\times e^{(i h_1 - \gamma_1/2)(\tau_2 - t_a)/\hbar} | (t_3 - \tau)/\hbar | \mu_{21} e^{(i h_2 - \gamma_2/2)(\tau_1 - \tau)/\hbar} .
\] (67)

(iii) The sCARS-FSRS process is given by Fig. 13a, and the fifth-order polarization in the probe direction which generates bands at frequencies \(\omega_{pu} - \omega_{CD} \) and \(\omega_{pu} - (\omega_{CD} + \omega_{E/A_1})\) is given by,

\[
P_{sCARS-FSRS}^{(5)}(t) = e^{i k_{pr} \cdot \mathbf{R}} \left( \frac{i}{\hbar} \right)^3 \int_{t_a}^{t} \int_{t_a}^{t} \int_{t_a}^{t} dt_1 dt_2 dt_3 \ E_{pCSRS}^{(3)}(\tau) \\
\times E_{pr}^{\ast}(\tau_1; T_{pr}) E_{pu}^{\ast}(\tau_2; T_{pu}) (\varphi_1^{(0)}(Q_{CD}. Q_{A_1}, Q_{E}. t_a)) | \\
\times e^{(i h_1 - \gamma_1/2)(\tau_2 - t_a)/\hbar} | (t_1 - \tau)/\hbar | \mu_{21} e^{(i h_2 - \gamma_2/2)(\tau_1 - \tau)/\hbar} | \\
\times e^{(i h_1 - \gamma_1/2)(\tau_2 - t_a)/\hbar} | (t_2 - \tau)/\hbar | \mu_{21} e^{(i h_2 - \gamma_2/2)(\tau_1 - \tau)/\hbar} | \\
\times e^{(i h_1 - \gamma_1/2)(\tau_2 - t_a)/\hbar} | (t_3 - \tau)/\hbar | \mu_{21} e^{(i h_2 - \gamma_2/2)(\tau_1 - \tau)/\hbar} .
\] (68)

(iv) Finally, the sCSRS-FSRS process is given by Fig. 13b, and the fifth-order polarization in the probe direction which generates bands at frequencies \(\omega_{pu} - \omega_{CD} \) and \(\omega_{pu} - (\omega_{CD} + \omega_{E/A_1})\) is given by,

\[
P_{sCSRS-FSRS}^{(5)}(t) = e^{i k_{pr} \cdot \mathbf{R}} \left( \frac{i}{\hbar} \right)^3 \int_{t_a}^{t} \int_{t_a}^{t} \int_{t_a}^{t} dt_1 dt_2 dt_3 \ E_{pCSRS}^{(3)}(\tau) \\
\times E_{pr}^{\ast}(\tau_1; T_{pr}) E_{pu}^{\ast}(\tau_2; T_{pu}) (\varphi_1^{(0)}(Q_{CD}. Q_{A_1}, Q_{E}. t_a)) | \\
\times e^{(i h_1 - \gamma_1/2)(\tau_2 - t_a)/\hbar} | (t_1 - \tau)/\hbar | \mu_{21} e^{(i h_2 - \gamma_2/2)(\tau_1 - \tau)/\hbar} | \\
\times e^{(i h_1 - \gamma_1/2)(\tau_2 - t_a)/\hbar} | (t_2 - \tau)/\hbar | \mu_{21} e^{(i h_2 - \gamma_2/2)(\tau_1 - \tau)/\hbar} | \\
\times e^{(i h_1 - \gamma_1/2)(\tau_2 - t_a)/\hbar} | (t_3 - \tau)/\hbar | \mu_{21} e^{(i h_2 - \gamma_2/2)(\tau_1 - \tau)/\hbar} .
\] (69)
Writing the fifth-order polarizations describing the difference Raman gain spectra by each process generally as $P_{\text{FSRS}}^{(5)}(t)$, the Fourier transform gives,

$$
P_{\text{FSRS}}^{(5)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} P_{\text{FSRS}}^{(5)}(t) \, dt, \quad (70)
$$

and the corresponding differential signal field in the pr direction is,

$$
E_{\text{FSRS}}^{(5)}(\omega) = iN \frac{2\pi\omega}{n(\omega)c} P_{\text{FSRS}}^{(5)}(\omega). \quad (71)
$$

With this, we can calculate the difference Raman gain spectra with heterodyne detection and normalized with respect to the pr spectrum in logarithm units ($-\Delta \text{OD}$) as,

$$
I_{\text{FSRS}}(\omega) \approx \frac{\text{Re}(E_{\text{pr}}^{*}(\omega) \cdot E_{\text{FSRS}}^{(5)}(\omega))}{2.303|E_{\text{pr}}(\omega)|^2}, \quad (72)
$$

where $E_{\text{pr}}(\omega)$ is the spectrum of the pr pulse, and it is assumed that $E_{\text{FSRS}}^{(5)} \ll E_{\text{pr}}$.

### 3.3.3. Direct fifth-order and cascade results of CDCl$_3$

The \textit{ab initio} 3D PES of the ground electronic state of CDCl$_3$ which includes the C-D stretch, C-Cl $A_1$ bend, and one of the degenerate C-Cl $E$ bend modes was calculated using density functional theory at the B3LYP level with the 6-311++(3df, 2pd) basis. The parameters for the PES are summarized in Table 2. It has harmonic terms and three cubic anharmonic terms, $Q_{\text{CD}}^3 Q_{A_1}$, $Q_{E}^3 Q_{CD}$ and $Q_{E}^3 Q_{CD}$, with coefficients $3 \times 10^{-3}$, $1.8 \times 10^{-4}$ and $1.6 \times 10^{-4}$ a.u., respectively. The excited electronic state PES is taken to be 3D harmonic oscillators with the same quadratic coefficients as the ground electronic state PES, and the energy gap is set to be 5 eV at the ground equilibrium configuration. Duschinsky rotation in the excited electronic state is neglected. The dimensionless displacements of the excited electronic state PES for the symmetric C-D stretch and C-Cl $A_1$ bend are set to be 0.1 relative to the ground electronic state PES. Neither the magnitude of the energy gap nor the normal mode displacements affect the FSRS lineshapes for off-resonance FSRS. For the asymmetric C-Cl $E$ bend mode, the equilibrium displacement in the excited state is zero for
Table 2. Parameters for Quantum models of 3D potential energy surface for C-D stretch and C-Cl bends.

<table>
<thead>
<tr>
<th></th>
<th>C-D stretch</th>
<th>C-Cl A₁ bend</th>
<th>C-Cl E bend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground/Excited (cm⁻¹)</td>
<td>2338</td>
<td>363</td>
<td>258</td>
</tr>
<tr>
<td>Displacement (Dimensionless)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Reduced mass (amu)</td>
<td>2.32</td>
<td>20.86</td>
<td>25.93</td>
</tr>
<tr>
<td>Anharmonicity (a.u.)</td>
<td>Q₂CDQA₁, 3 × 10⁻³</td>
<td>Q₂₁QE, 1.8 × 10⁻⁴</td>
<td>Q₀₂QE, 1.6 × 10⁻⁴</td>
</tr>
<tr>
<td>Transition dipole moment (a.u.)</td>
<td>μ₁₂ = μ₀₁₂ + C₀QCD + C₁QA₁ + C₂QE</td>
<td>μ₀₁₂ = 0.310, C₀ = −0.268</td>
<td>C₁ = −0.057, C₂ = −0.040</td>
</tr>
</tbody>
</table>

Symmetry reason. The coordinate-dependent transition dipole moment is given by,

$$\mu_{12} = \mu_{12}^0 + C_0 Q_{CD} + C_1 Q_{A1} + C_2 Q_E,$$

where the parameters are given in Table 2. The value for $\mu_{12}^0$ was obtained from the \textit{ab initio} calculation, and the dependence on $Q_E$ makes it possible to observe a Raman gain in that asymmetric mode too. The relative values of $C_i$ were determined from the Raman cross sections given by Mehlenbacher \textit{et al.}, where for off-resonance Raman scattering, if the transition dipole moment is $\mu_{12}^0 + C \cdot Q$, the Raman cross sections are proportional to $C^2 / \omega$, where $\omega$ is the mode frequency. In the quantum model, the Raman scattering arises from a combination of the coordinate dependence in the transition dipole moment and the mode displacements between the ground and excited state PESs, whereas in the classical model it depends on $\alpha'$, the derivative of the molecular polarizability with respect to the displacement along the vibrational mode. We have used experimental parameters for the sample as follows: number density $N = 7.5 \times 10^{21}$ ml⁻¹, sample path length $l = 1$ mm and refractive index $n = 1.49$. The three pulses are assumed to be in the same polarization direction, and have the form,

$$E(t, T) = E_0 g(t, T)e^{-i\omega t},$$

where $E_0$ is the field amplitude, $T$ is the time when the pulse envelope is maximum, $\omega$ is the central frequency, and the Gaussian envelope $g(t, T)$
Wave Packet Analysis of FSRS

Table 3. Parameters for the laser pulses.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>T (fs)</th>
<th>τ (fs)</th>
<th>Intensity (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impulsive pump</td>
<td>800</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>Raman pump</td>
<td>800</td>
<td>1000</td>
<td>1 × 10¹⁰</td>
</tr>
<tr>
<td>Probe</td>
<td>930</td>
<td>Td</td>
<td>8</td>
</tr>
</tbody>
</table>

The central wavelength of each pulse is given by $2\pi c/\omega$. The parameters for the three pulses — impulsive pump, Raman pump and probe — are given in Table 3. As all the processes are off-resonance, we have set the homogeneous damping constants $\gamma_i$ to zero.

We have calculated the difference Raman gain spectra with and without the Ipu pulse for the direct fifth-order process of CDCl₃ using the sum of Eqs. (60)–(61), and Eqs. (70)–(72), for delay times $T_d$ of 700–790 fs between the Ipu and pr pulses. These are shown in Fig. 14. The inversion symmetry of the sidebands of the C-Cl $A_1$ bend, which are displaced to the left and right from the central C-D stretch by 363 cm⁻¹, can clearly be seen. They arise from the symmetry that allowed for the anharmonic coupling term $Q_{CD}^2 Q_{A_1}$. The small peaks at 2045 cm⁻¹ and 2560 cm⁻¹ are the sidebands of the C-Cl $E$ bend which are very weak compared to the C-Cl $A_1$ bend, contrary to what has been observed experimentally,⁸ where both the C-Cl $A_1$ and $E$ bend sidebands are of about the same intensity. Sun et al.⁴⁶ had to introduce an additional anharmonic coupling term $Q_{CD}^2 Q_{E}$, which is symmetry forbidden in the $ab$ initio calculation, in order to see stronger sidebands in the C-Cl $E$ bend. This is already a hint that the direct fifth-order process may not be the main one to account for the difference Raman gain spectra in CDCl₃.

In the first step of the cascade fifth-order processes, the Ipu pulse followed by the pu pulse acting on a CDCl₃ molecule can produce two new fields, CARS and CSRS, traveling along the Raman pump direction,
Fig. 14. Difference Raman gain spectra for the direct fifth-order process with the anharmonic potential for CDCl3. Reproduced with permission from J. Chem. Phys. (in press, 2011).44

as shown in Figs. 12 and 13. We have calculated the CARS and CSRS fields using Eqs. (62)–(65) on the anharmonic potential of CDCl3. The absolute values of the CARS and CSRS fields in frequency space are shown in Figs. 15a and 15b, respectively. Our convention, following the experiment,8 is that frequencies are taken relative to \( \omega_{pu} \), and the Stokes side is plotted as positive frequencies while the anti-Stokes side is plotted as negative frequencies. Panel (a) shows the CARS fields in the Raman pump direction with a strong frequency component at \( \omega_{pu} \) which we have centered at 0 cm\(^{-1}\), and the inset in the range −400 to −200 cm\(^{-1}\) shows two weak frequency components at \( \omega_{pu} + \omega_{E/A_1} \), i.e. at about −258 cm\(^{-1}\) and −363 cm\(^{-1}\) in the plot. Panel (b) shows the corresponding CSRS fields in the Raman pump direction with a strong frequency component at \( \omega_{pu} \) and the inset in the range 200 to 400 cm\(^{-1}\) shows two weak frequency components at \( \omega_{pu} - \omega_{E/A_1} \), i.e. at about 258 cm\(^{-1}\) and 363 cm\(^{-1}\). The
real and imaginary parts of the CARS and CSRS fields in the range \(-400\) to \(400\) cm\(^{-1}\), plotted in Fig. 15c–h clearly show that the CARS and CSRS fields are \(180^\circ\) out of phase with each other, and this property later accounts for the inversion symmetry in the difference Raman gain spectra in CDCl\(_3\) about the C-D stretch frequency.

In Fig. 16a we reproduce the experimental results of Kukura et al.\(^8\) for the experimental difference Raman gain spectra with time delays of 777–867 fs between the Ipu and pr pulses. The experimental results do not show the band at \(\omega_{\text{CD}}\). We should note that the experimental time delay measurement may have a displacement to it, as the result for the 777 fs time delay in Kukura et al.\(^8\) is similar to the 700 fs time delay reported in Frontiera et al.,\(^47\) and here we have chosen to start all our calculations at 700 fs. The difference Raman gain spectra for the four cascade processes in CDCl\(_3\) shown in Figs. 12 and 13 were calculated with Eqs. (66)–(72) at time delays of 700–790 fs between the Ipu and pr pulses, on both the anharmonic and harmonic ground state potentials of CDCl\(_3\) and plotted in Figs. 16b and 16c, respectively. There is good agreement between the calculated, Fig. 16b for the anharmonic potential, and the experimental results, Fig. 16a, on the change in lineshape of the sidebands with time delay. The inversion symmetry of the Raman sidebands about \(\omega_{\text{CD}}\) is seen for all delay times and is due to the \(180^\circ\) phase difference between the CARS and CSRS fields giving rise to the sidebands. The lineshape of each sideband changes in phase from positive Lorentzian to dispersive, to negative Lorentzian, to negative dispersive, and back to positive Lorentzian with the periodicity of the sideband frequency. It can be shown\(^44\) that the phase of each sideband follows the motion of the time-dependent second-order coherent wave packet on the ground PES of molecule A prepared by the Ipu pulse, with dispersive lineshape when the wave packet has maximum momentum and Lorentzian lineshape at the turning point along the mode.

The intensity of the difference Raman gain spectra by the cascade process is about one order of magnitude larger than by the direct fifth-order process shown in Fig. 14. In Fig. 16c, we have plotted the corresponding results with the 3D harmonic potential by dropping all the cubic anharmonic terms. Comparing the results in panels (b) and (c), the anharmonic terms have no observable effect on the phase and intensity of the difference Raman gain spectra. The only effect of the anharmonicities is in the shift of the spectra
Fig. 15. CARS and CSRS fields in the frequency domain relative to the Raman pump frequency for the impulsive pump and Raman pump pulses acting on CDCl₃. (a) Absolute value of CARS field, and insets magnified 75 times on both sides of the Raman pump frequency to show the CARS fields in the range $-400$ to $-200\,\text{cm}^{-1}$. (b) Absolute value of CSRS field, and insets magnified 75 times on both sides of the Raman pump frequency to show the CSRS fields in the range 200 to 400 $\text{cm}^{-1}$. (c) Real part of the CARS and CSRS fields in the frequency range $-400$ to $-200\,\text{cm}^{-1}$ showing the 180° phase difference. (d) Same as (c) but for the frequency range $-200$ to 200 $\text{cm}^{-1}$. (e) Same as (c) but for the frequency range 200 to 400 $\text{cm}^{-1}$. (f) Similar to (c) but for the imaginary part of the CARS and CSRS fields showing the 180° phase difference. (g) Same as (f) but for the frequency range $-200$ to 200 $\text{cm}^{-1}$. (h) Same as (f) but for the frequency range 200 to 400 $\text{cm}^{-1}$. Reproduced with permission from J. Chem. Phys. (in press, 2011).
Fig. 16. (a) Experimental results of Kukura et al. for the difference Raman gain spectra of CDCl\textsubscript{3} with time delays from 777–867 fs. (b) Sum of the four cascade fifth-order processes with the anharmonic ground PES for CDCl\textsubscript{3} with time delays from 700–790 fs. (c) Same as (b) but with the harmonic ground PES for CDCl\textsubscript{3}. Reproduced with permission from J. Chem. Phys. (in press, 2011).

To the red by about 35 cm\textsuperscript{−1} from the harmonic frequencies. So, clearly the FSRS from the coherent vibrational state of CDCl\textsubscript{3} does not provide a direct observation of the anharmonic coupling because of the strong cascade effect.

4. Conclusion and outlook

Femtosecond stimulated Raman spectroscopy (FSRS) has been described by both the classical coupled wave approach and the quantum theory with wave packet analysis. The classical coupled wave approach uses the Placzek polarizability and thus is necessarily restricted to off-resonance FSRS, but the quantum theory also applies to the resonance regime. The quantum theory describes FSRS by the third-order polarization with eight perturbative terms which can be pictured with Feynman dual time-line diagrams as well as the complementary four-wave mixing energy level diagrams, giving us two equivalent points of view — one for the time-frame wave packet analysis and another for the FSRS energy spectra. The eight terms can be placed into four sets — SRS(I), SRS(II), IRS(I), IRS(II).
In the SRS(I) set, there are three terms which entail “absorption” of the Raman pump pulse and “stimulated emission” by the probe pulse — they are similar to the resonance Raman scattering and hot luminescence terms in spontaneous Raman scattering where the probe pulse is the vacuum field. The remaining five terms in SRS(II), IRS(I) and IRS(II) entail “absorption” of the probe pulse and “stimulated emission” by the Raman pump pulse, and these are absent in spontaneous Raman scattering because of the vacuum probe field, but they are present in FSRS because the molecule does not distinguish between the pulses for “absorption” and “stimulated emission”. The SRS(I) set accounts for the sharp Stokes Raman lines while the IRS(I) term accounts for the sharp anti-Stokes Raman lines in the FSRS spectrum. The classical coupled wave approach comes from the resonance Raman scattering term in the SRS(I) set with the assumption of off-resonance Raman scattering and a fundamental Stokes transition, and cannot account for the strong anti-Stokes lines in FSRS. We illustrated the theory with calculations on (a) the resonance FSRS of R6G and (b) the FSRS from a coherent vibrational state prepared by an impulsive pump pulse in CDCl₃. The calculated results compared well with experiment, and it is shown that in the case of FSRS on CDCl₃ there is a cascade effect that makes a dominant contribution to the FSRS spectra and the observed sidebands are not due to anharmonic coupling on the ground state surface.

The perturbative wave packet analysis above can be generalized to treat various nonlinear spectroscopies, such as polarization response spectroscopy (PORS)⁴⁸,⁴⁹ and resonant pump third-order Raman spectroscopy (RaPTORS).⁵⁰–⁵² PORS is rather similar to 2D FSRS. In the 2D FSRS on CDCl₃, we had an impulsive Raman pump pulse followed by a FSRS process using a set of two other pulses — a Raman pump pulse and a probe pulse. In PORS, a pair of actinic pump pulses — \( E_1(k_1, t) \) and \( E_2(k_2, t) \) — take the place of the impulsive Raman pump pulse; another pair of time delayed pulses — \( E_3(k_3, t) \) and \( E_4(k_4, t) \) — take the place of the Raman pump pulse; and finally a fifth further time-delayed pulse, \( E_5(k, t) \), takes the place of the probe pulse. Field pair 1, 2 is about 100 fs, field pair 3, 4 is about 700 fs, and field 5 is 100–200 fs FWHM — rather similar to the pulses used in 2D-FSRS. The PORS signal is emitted in the phase-matched direction \( k_s = -k_1 + k_2 - k_3 + k_4 + k_5 \) and heterodyne detected. In 2D FSRS, all the pulses act on the solute. However, in PORS the field pair 1,
Wave Packet Analysis of FSRS

2 is resonant with the solute excited electronic state to initiate a reaction, followed by off-resonant pulses 3, 4, and 5 to probe the solvent dynamics. One can draw Feynman dual time-line diagrams, like Fig. 11, to describe the PORS processes and write down the corresponding expressions for the fifth-order polarizations. Moran et al.\textsuperscript{48} have shown that there are eight such diagrams. Using off-resonant pulses 3, 4 and 5 to probe the solvent dynamics means that we can revert to polarizability theory, similar to the classical coupled wave theory to analyze the experimental results.

We have presented the perturbative approach to FSRS which works well for weak fields and isolated PESs, and provides us with an intuitive understanding of the FSRS process. For strong fields and for cases where there are potential surface crossings, as in a full spectroscopic probing of cis-trans photoisomerization processes in the excited state,\textsuperscript{12, 15} one has to use non-perturbation theory.\textsuperscript{53, 54} Much work remains open in this area.

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References

Wave Packet Analysis of FSRS