Theoretical studies and model calculations of femtosecond stimulated Raman spectroscopy

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**THEORETICAL STUDIES AND MODEL
CALCULATIONS OF FEMTOSECOND
STIMULATED RAMAN SPECTROSCOPY**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES
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CALCULATIONS OF FEMTOSECOND STIMULATED
RAMAN SPECTROSCOPY**

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2012

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Summary

Femtosecond stimulated Raman spectroscopy(FSRS) is a recently developed technique that possesses many advantages, such as fluorescence background free, high signal-to-noise ratio, high frequency and high time resolution, and rapid data acquisition. It has been widely used to study the molecular structure and chemical reaction dynamics of physical and biological processes that occur on the ultrafast femtosecond time scale. This thesis aims to present theoretical descriptions of FSRS and study the features of FSRS. Three-state model and displaced harmonic oscillator model were proposed to study FSRS. Two molecules were studied using displaced harmonic oscillator model: FSRS of Rhodamine 6G (R6G) using a delta probe pulse and inverse Raman bands of crystal violet (CV).

A full quantum-mechanical description of FSRS for a three-state model was proposed. A completed series of expressions of third-order polarizations were obtained to represent all the Stokes, Rayleigh, and anti-Stokes lines. Our study showed that eight terms contribute to the FSRS, and we grouped them in four groups, which correspond to four nonlinear processes - stimulated Raman scattering (SRS(I) and SRS(II)) and inverse Raman scattering (IRS(I) and IRS(II)). The contributions of the four nonlinear processes to the FSRS spectra were described.

In order to get analytical expressions for the FSRS spectra, a displaced harmonic oscillator model was proposed, where the molecules were described by separable multidimensional harmonic potential surfaces with Franck-Condon displacements in the modes. Using this model, the

analytical expressions of third-order polarizations were obtained in the form of triple integrals over four-time correlation functions. These expressions could be further simplified by simulating FSRS with a delta function probe pulse. The four-time correlation function in the third-order polarization then reduces to a three-time correlation function which saves computation time.

The analytical expressions for the FSRS were applied to two fluorescence materials - Rhodamine 6G (R6G) and crystal violet (CV) - and compared to the experimental results. The comparison of calculated results with experimental results provided good test of our theory and helped to understand all the features of FSRS. The FSRS spectra of Rhodamine 6G (R6G) for various pump wavelengths and using a delta probe pulse were calculated. The effect of the Raman pump pulse temporal width, the vibrational dephasing time, the homogeneous damping constant, and the inhomogeneous damping constant on FSRS line shapes were studied.

Dispersive and negative line shapes in Raman spectra have been investigated, and these unconventional line shapes were not explained clearly before. The complicated line shapes appears on anti-Stokes band which comes from the IRS(I) term. The ultrafast Raman loss spectroscopy (URLS), which is accounted for by IRS(I), of CV was calculated. The change in phase of the line shapes with Raman pump wavelength was very well reproduced. In the limit of monochromatic Raman pump and probe pulses, we obtained the third-order susceptibility and recovered the well-known expression for the third-order susceptibility, $\chi_{IRS}^{(3)}$, for IRS. It was used to explain the mode dependent phase changes as a function of Raman pump excitation in the URLS of CV.

List of Publications

1. Z. Sun, Xue Q. Qiu, J. Lu, Dong H. Zhang and Soo-Y. Lee, “Three-state model for femtosecond broadband stimulated Raman scattering”, J. Raman Spectrosc. 2008; **39**: 1568 - 1577
2. Xueqiong Qiu, Xiuting Li, Kai Niu and Soo-Y. Lee, “Femtosecond stimulated Raman spectroscopy modeled with a delta probe pulse: application to rhodamine 6G”, J. Raman Spectrosc. 2011, **42**: 563 - 575
3. Xueqiong Qiu, Xiuting Li, Kai Niu, and Soo-Y Lee, “Inverse Raman Bands in Ultrafast Raman Loss Spectroscopy”, submitted to J. Chem. Phys. 2011, **135**: 164502

Introduction to Femtosecond Stimulated Raman Spectroscopy

1.1 Motivation

The availability of femtosecond pulses and pump-probe techniques have made it possible to directly prepare and monitor coherent vibrational wave packets in the ground and excited electronic states of polyatomic molecules. The dynamic wave packet can be monitored, for example, with a femtosecond probe pulse in absorption or emission, or using a simultaneous pair of picosecond pump and femtosecond probe pulses in stimulated Raman scattering, which is a more recently developed technique, termed as “Femtosecond stimulated Raman spectroscopy (FSRS)”. Femtosecond stimulated Raman spectroscopy was first reported in 1994 by Yoshizawa *et. al* [1] to get Raman spectrum with temporal resolution of 300 fs using three pulses of femtosecond durations. And later Raman spectrum with both high temporal resolution (250 fs) and spectral resolution (25 cm^{-1}) was obtained using a narrow band Raman pump and two femtosecond ultrashort probe pulses with a time delay [2]. At the same time, the same technique was proposed by Richard A Mathies’ *et. al*, and was named as “FSRS” [3]. From then on, FSRS was developed and widely used in studying chemical reaction dynamics and physical and biological processes systems [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16].

Although time-resolved vibrational spectroscopy has advanced toward the femtosecond time

domain, there is a fundamental uncertainty principle limitation of the pulse duration/bandwidth transform limit when a single pulse is used for probing as in spontaneous Raman scattering. Direct IR probing techniques have been generally limited to 200 fs time resolution in a narrow (200 cm^{-1}) spectral region. [17, 18, 19, 20, 21, 22, 23, 24] Alternatively, a full vibrational spectrum over a 3000 cm^{-1} window can be obtained by using spontaneous Raman spectroscopy, but pulse duration longer than 0.7 ps is necessary to achieve acceptable spectral resolution. [25, 26, 27] Thus, achieving both high time and high spectral resolution is impossible in traditional spontaneous Raman spectroscopy using a single pulse. On the other hand, with FSRS one can achieve < 100 fs time resolution as well as capture a high-resolution vibrational spectrum over a wide spectral window. Additional benefits of FSRS are that the amplification process is self-phase matched and the detection of the coherent and intense probe beam is unaffected by any spontaneous fluorescence at the sample.

A typical FSRS experiment can be explained with the potential energy surface diagram in Figure. 1.1. A femtosecond actinic pump pulse ① prepares the molecule in a non-stationary state, a dynamic wave packet $|\psi(t)\rangle$, on the excited state surface. A delayed pair of narrow bandwidth picosecond Raman pump pulse ② and a broadband femtosecond Raman probe pulse ③ acting on the sample produces a high resolution stimulated Raman gain spectrum in the direction of the probe pulse with high efficiency and speed, free from fluorescence background interference. The time delay t_D between the fs actinic and fs probe pulses can be resolved to < 100 fs, while the spectral resolution of the Raman gain profile is limited by the narrow-bandwidth Raman pump, the natural vibrational linewidth of the sample, and the resolution of the spectrograph, which in total can be about 10 cm^{-1} . So, the FSRS technique can afford both high temporal resolution and high spectral resolution, thus overcoming the limitations of conventional time-resolved Raman spectroscopy using a single ultrashort Raman pump pulse [12].

As the experimental application of FSRS grows rapidly, the theoretical study of this technique becomes important as well. Our group previously attempted to explain FSRS using both coupled wave description and quantum theory using perturbation theory. In order to understand experimental results and reveal the features of FSRS, we will use perturbative wave packet approaches with reasonable potential energy surfaces to model and calculate FSRS processes in molecules.

Figure 1.1: Femtosecond stimulated Raman scattering from a moving wave packet. The molecule is initially in, say, the $v = 0$ state on the ground state surface e_0 . An ultrashort actinic pump pulse ① comes along and prepares the molecule as a moving wave packet on the excited state surface e_1 . 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.

New characteristics of FSRS may be foreseen through our calculations.

1.2 Theoretical development of stimulated Raman spectroscopy

The theory of spontaneous and stimulated Raman spectroscopy has been studied intensively using both classical [28] and quantum [29, 30, 31, 32, 33, 34, 35, 36] approaches. For the spontaneous Raman scattering, a time-independent approach, the quantum mechanical sum-over-states Kramers-Heisenberg-Dirac scattering theory and the equivalent time-dependent wave packet approach were proposed. The latter provided a more advantageous description physically and computationally over the sum-over-states approach for polyatomics [37, 38]. For stimulated Raman scattering, Shen and Bloembergen [39, 40] have provided a semiclassical coupled-wave description with CW light. To describe FSRS, we have extended the semi-classical coupled-wave description of SRS from CW radiation to pulsed radiation by approximating the narrow-bandwidth Raman pump pulse to be CW [41]. It has been shown by coupled-wave theory that there is a gain in both the Stokes line and the anti-Stokes line, while the latter is contrary to experimental results [42, 12, 14]. Later, quantum wave packet theory was used to explain FSRS. In the first attempt [43], a density matrix approach was used and the relevant third-order polarization in the direction of the probe pulse was derived. It was shown then that FSRS is given by three terms - resonance Raman scattering (RRS) and the hot luminescence (HL(I) and HL(II)). On closer examination of the theory then, there was an implicit assumption made that the Raman pump pulse leads to excitation (absorption), while the probe pulse leads to de-excitation (emission). In reality, however, the molecule does not discriminate between the two pulses. Thus rather than three, there are eight terms in perturbation theory necessary to account for SRS [44]. The quantum wave packet theory of FSRS promises to be able to account for all features of the FSRS spectra.

1.2.1 Quantum wave packet within perturbation theory

We consider two Born-Oppenheimer electronic states e_1 and e_2 and their associated vibrational manifolds. By turning on the Raman pump and probe pulses, the density matrix evolves according to the quantum Liouville equation

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}[\mathcal{H}_0 + \mathcal{V}(t), \rho(t)] - \Gamma \rho(t) , \quad (1.1)$$

with

$$\begin{aligned} \mathcal{H}_0 &= |e_1\rangle \mathbf{h}_1(\mathbf{Q}) \langle e_1| + |e_2\rangle \mathbf{h}_2(\mathbf{Q}) \langle e_2| , \\ \mathcal{V}(t) &= -\boldsymbol{\mu}(\mathbf{Q}) \cdot \mathbf{E}(\mathbf{R}, t) , \\ \boldsymbol{\mu}(\mathbf{Q}) &= |e_2\rangle \boldsymbol{\mu}_{21}(\mathbf{Q}) \langle e_1| + \text{c.c.} , \\ \mathbf{E}(\mathbf{R}, t) &= \boldsymbol{\varepsilon}_{pu} E_{pu}(t; t_{pu}) \exp(i\mathbf{k}_{pu} \cdot \mathbf{R}) + \boldsymbol{\varepsilon}_{pr} E_{pr}(t; t_{pr}) \exp(i\mathbf{k}_{pr} \cdot \mathbf{R}) \\ &\equiv \mathbf{E}_{pu}(t; t_{pu}) + \mathbf{E}_{pr}(t; t_{pr}) . \end{aligned} \quad (1.2)$$

The theory is applicable for any form of potential energy surfaces. The relaxation superoperator that describes vibronic dephasing and relaxation effects is denoted by Γ . The transition dipole moment between electronic states e_a and e_b , which may be coordinate-dependent, is denoted by $\boldsymbol{\mu}_{ab}(\mathbf{Q})$, and $\mathbf{E}_{pu}(t; t_{pu})$ and $\mathbf{E}_{pr}(t; t_{pr})$, are the Raman pump and probe fields, peaked at times t_{pu} and t_{pr} , and which propagate in space $\mathbf{R}$ (which can be taken to be a constant in the long wavelength approximation) with wave vectors $\mathbf{k}_{pu}$ and $\mathbf{k}_{pr}$, and have polarizations $\boldsymbol{\varepsilon}_{pu}$ and $\boldsymbol{\varepsilon}_{pr}$, respectively.

The molecule is assumed to be initially in the ground vibrational state on electronic state e_1 , described by the density matrix

$$\rho_{11}^{(0)}(0) = |\psi_1^{(0)}(\mathbf{Q}, 0)\rangle \langle \psi_1^{(0)}(\mathbf{Q}, 0)| . \quad (1.3)$$

The ansatz for the density matrix can be written as

$$\rho(t) = \sum_{a,b=1}^2 |e_a\rangle \rho_{ab}(\mathbf{Q}, t) \langle e_b| , \quad (1.4)$$

where $\mathbf{Q}$ denotes the multidimensional normal coordinates and $\rho_{ab}(\mathbf{Q}, t)$ is the vibrational density matrix associated with electronic states $|e_a\rangle$ and $|e_b\rangle$ simultaneously. This can be solved order by order with diagrammatic perturbation theory - either dual time-line Feynman diagrams or

four wave mixing energy level (FWMEL) diagrams - and the appropriate third order polarization $P^{(3)}(t) = \text{Tr}\{\mu\rho^{(3)}(t)\}$ can be written down.

1.2.2 Feynman and ladder diagrams

Perturbation calculations can be facilitated with the help of diagrams. Diagrammatic perturbation theory is a simplified way to keep track of the contributions to a particular nonlinear signal. It allows us to interpret the microscopic origin of a signal with a particular frequency and wavevector of detection, given the specifics of the quantum system we are studying and the details of the incident radiation. It provides a shorthand form of the correlation functions contributing to a particular nonlinear signal and allows us to keep track of the contributions of the incident fields to the frequency and wavevector of the nonlinear polarization. Simple diagrams could be used to represent the evolution of the density matrix ρ . From a diagram, one can immediately determine its signal frequency and wavevector and write down a correlation function directly by assigning a factor for each interaction, a factor for each time evolution, and the final trace.

Feynman and ladder diagrams are commonly used tools for perturbation theory. Both types of diagrams show an explicit series of absorption or emission events induced by the fields, and symbolize the coherence or population state in which the density matrix evolves during a time interval. The signal emission, is represented by wavy line connecting dipole coupled states.

Feynman diagram is a simple way of tracking coherences in different time periods, and for noting absorption and emission events. A typical Feynman diagram is shown in Fig. 1.2(a). E_1 , E_2 , etc. are light fields, a , b , c , $d...$ are the electronic states, $\hat{G}(\tau)$ are the propagation under the Hamiltonian H_0 of the material system between interactions. The rules of drawing a Feynman diagram are as follows: (1) Double line represents ket and bra side of ρ . (2) Time-evolution is upward. (3) Lines intersecting diagram represent field interaction. (4) System evolves freely under H_0 between interactions, and density matrix element for that period is often explicitly written.

Ladder diagrams are helpful for describing multistate systems and/or with multiple frequencies; however, it is difficult to immediately see the state of the system during a given time interval.

A typical ladder diagram is shown in Fig. 1.2(b). The rules of drawing a ladder diagram are as follows: (1) Multiple states are arranged vertically by energy. (2) Time propagates to the right. (3) Arrows connecting levels indicate resonant interactions. (4) Free propagation under H_0 between interactions.

The representation of Feynman and ladder diagrams for light-matter interactions is shown in Fig. 1.3. They are described as follows: Each light-matter interaction acts on one side of ρ , either through absorption or stimulated emission. For Feynman diagrams absorption is designated through an inward pointing arrow, whereas emission is an outward pointing arrow. Action on the left line is action on the ket, whereas the right line is on the bra. For ladder diagrams, absorption is an upward arrow and emission is downward. A solid line is used to indicate action on the ket, whereas a dotted line is action on the bra. Each interaction adds a dipole matrix element μ_{ij} that describes the interaction amplitude and any orientational effects. Each interaction adds input electric field factors to the polarization, which are used to describe the frequency and wavevector of the radiated signal. Action on the bra is the complex conjugate of ket and absorption is complex conjugate of stimulated emission. The action of the final dipole operator must return to a diagonal element to contribute to the signal.

1.2.3 Third-order polarization and FSRS

It is easy to find the complete set of diagrams for a perturbation process of a given order. For example, there are eight basic diagrams for a third-order process [45], the permutation of three different pulses results in a complete set of 48 diagrams. In FSRS, two coherent optical fields - a narrow bandwidth Raman pump pulse with wave vector $\mathbf{k}_{pu}$ and an ultrashort continuum probe pulse with wave vector $\mathbf{k}_{pr}$ - are incident on a sample with molecular vibrations, and stimulated Raman spectra from the pump-induced gain appear in the probe spectrum. The process is accounted for by a sum of time-dependent third-order polarizations in the direction of the probe pulse $(+\mathbf{k}_{pu} - \mathbf{k}_{pu} + \mathbf{k}_{pr})$. The two color permutation and the final signal direction determine that FSRS can be represented by eight Feynman dual time-line diagrams, with ket evolution on the left and bra evolution on the right, as shown in Fig. 1.4. E_{pu} and E_{pu}^* represent pump pulses, while E_{pr} represent probe pulses. An arrow pointing into the timeline denotes absorption,

Figure 1.2: A typical Feynman diagram (a) and ladder diagram (b). E_1 , E_2 , etc. are light fields, a , b , c , d ... are the electronic states, $\hat{G}(\tau)$ are the propagation under the Hamiltonian H_0 of the material system between interactions.

<i>Interaction</i>	<i>Diagrammatic Representation</i>	contribution to $\mathbf{k}_{sig}$ & ω_{sig}
<u>KET SIDE</u>		
Absorption		$+\mathbf{k}_n \quad +\omega_n$
Stimulated Emission		$-\mathbf{k}_n \quad -\omega_n$
<u>BRA SIDE</u>		
Absorption		$-\mathbf{k}_n \quad -\omega_n$
Stimulated Emission		$+\mathbf{k}_n \quad +\omega_n$
<u>CLOSURE BETWEEN BRA & KET</u> (Final trace, convention: ket side)		

Figure 1.3: The representation of Feynman and ladder diagrams for different light-matter interactions.

whereas an arrow pointing away from the timeline denotes emission. The eight contributing processes are labelled as resonance Raman scattering (RRS(I) and RRS(II)), hot luminescence (HL(I), HL(II), HL(III) and HL(IV)) and inverse Raman scattering (IRS(I) and IRS(II)). In the absence of vibrational dephasing, the resonance Raman scattering and hot luminescence terms were grouped as stimulated Raman scattering (SRS(I) and SRS(II)) where SRS(I) comprised RRS(I), HL(I) and HL(II), while SRS(II) comprised RRS(II), HL(III) and HL(IV), and it was possible to express them as overlaps of evolving bra and ket wave packets.

Looking at the three diagrams for SRS(I) in Fig. 1.4, the pump interaction on the ket line to the left can occur at any time independent of the two interactions - pump followed by probe - on the bra line to the right. The third-order polarization for SRS(I) is given by the overlap of wave packets, one on the bra side and another on the ket side,

$$P_{\text{SRS(I)}}^{(3)}(t; \mathbf{k}_{pr}) = \langle \psi_1^{(2)}(\mathbf{Q}, t; -\mathbf{k}_{pr}, \mathbf{k}_{pu}) | \mu_{12} | \psi_2^{(1)}(\mathbf{Q}, t; \mathbf{k}_{pu}) \rangle . \quad (1.5)$$

Here, $|\psi_2^{(1)}(\mathbf{Q}, t; \mathbf{k}_{pu})\rangle$ is the first order wave packet prepared by the Raman pump pulse on the (upper) electronic state e_2 ,

$$|\psi_2^{(1)}(\mathbf{Q}, t; \mathbf{k}_{pu})\rangle = e^{i\mathbf{k}_{pu} \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right) \int_0^t d\tau e^{(-i\mathbf{h}_2 - \gamma_2/2)(t-\tau)/\hbar} \mu_{21} E_{pu}(\tau; t_{pu}) e^{(-i\mathbf{h}_1 - \gamma_1/2)\tau/\hbar} |\psi_1^{(0)}(\mathbf{Q}, 0)\rangle , \quad (1.6)$$

where $\psi_1^{(0)}(\mathbf{Q}, 0)$ is the initial wave packet on electronic state e_1 , t_{pu} is the peak position of the Raman pump pulse envelope, $\{\gamma_i, i = 1, 2\}$ are the homogeneous line-widths for the respective electronic states, and $\langle \psi_1^{(2)}(\mathbf{Q}, t; \mathbf{k}_{pu}, -\mathbf{k}_{pr}) |$ is a second order wave packet prepared by the Raman pump followed by the probe pulse on electronic state e_1 ,

$$\begin{aligned} \langle \psi_1^{(2)}(\mathbf{Q}, t; -\mathbf{k}_{pr}, \mathbf{k}_{pu}) | &= e^{i(\mathbf{k}_{pr} - \mathbf{k}_{pu}) \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right)^2 \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \\ &\times \langle \psi_1^{(0)}(\mathbf{Q}, 0) | e^{(i\mathbf{h}_1 - \gamma_1/2)\tau_1/\hbar} \mu_{12} E_{pu}^*(\tau_1; t_{pu}) e^{(i\mathbf{h}_2 - \gamma_2/2)(\tau_2 - \tau_1)/\hbar} \\ &\times \mu_{21} E_{pr}(\tau_2; t_{pr}) e^{(i\mathbf{h}_1 - \gamma_1/2)(t - \tau_2)/\hbar} \\ &= e^{i(\mathbf{k}_{pr} - \mathbf{k}_{pu}) \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right) \int_0^t d\tau_2 \langle \psi_2^{(1)}(\mathbf{Q}, \tau_2) | \\ &\times \mu_{21} E_{pr}(\tau_2; t_{pr}) e^{(i\mathbf{h}_1 - \gamma_1/2)(t - \tau_2)/\hbar} , \end{aligned} \quad (1.7)$$

It can similarly be shown that,

$$P_{\text{SRS(II)}}^{(3)}(t; \mathbf{k}_{pr}) = \langle \psi_1^{(2)}(\mathbf{Q}, t; -\mathbf{k}_{pu}, \mathbf{k}_{pu}) | \mu_{12} | \psi_2^{(1)}(\mathbf{Q}, t; \mathbf{k}_{pr}) \rangle , \quad (1.8)$$

Figure 1.4: Eight Feynman dual time line diagrams for the four nonlinear processes: femtosecond stimulated Raman scattering (SRS(I)), SRS(II), inverse Raman scattering (IRS(I)) and IRS(II), with ket evolution on the left and bra evolution on the right. Small arrows represent pump pulses, while big arrows represent probe pulses. An inward pointing arrow designate absorption, whereas outward pointing arrow designate emission.

which differs from SRS(I) by a pump-pump interaction for the second-order wave packet on the bra side and a probe interaction for the first-order wave packet on the ket side. The inverse Raman scattering terms,

$$P_{\text{IRS(I)}}^{(3)}(t; \mathbf{k}_{pr}) = \langle \psi_1^{(0)}(\mathbf{Q}, t) | \mu_{12} | \psi_2^{(3)}(\mathbf{Q}, t; \mathbf{k}_{pu}, -\mathbf{k}_{pu}, \mathbf{k}_{pr}) \rangle , \quad (1.9)$$

$$P_{\text{IRS(II)}}^{(3)}(t; \mathbf{k}_{pr}) = \langle \psi_1^{(0)}(\mathbf{Q}, t) | \mu_{12} | \psi_2^{(3)}(\mathbf{Q}, t; \mathbf{k}_{pr}, -\mathbf{k}_{pu}, \mathbf{k}_{pu}) \rangle , \quad (1.10)$$

have a third-order wave packet on the ket side, with IRS(I) having the probe interaction before the two pump interactions, and vice versa for IRS(II), where

$$\langle \psi_1^{(0)}(\mathbf{Q}, t) | = \langle \psi_1^{(0)}(\mathbf{Q}, 0) | e^{(i\mathbf{h}_1 - \gamma_1/2)t/\hbar} , \quad (1.11)$$

and

$$\begin{aligned} |\psi_2^{(3)}(\mathbf{Q}, t; \mathbf{k}_{pu}, -\mathbf{k}_{pu}, \mathbf{k}_{pr})\rangle &= e^{i\mathbf{k}_{pr} \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 e^{(-i\mathbf{h}_2 - \gamma_2/2)(t-t_1)/\hbar} \\ &\quad \times \mu_{21} E_{pu}(t_1; t_{pu}) e^{(-i\mathbf{h}_1 - \gamma_1/2)(t_1-t_2)/\hbar} \\ &\quad \times \mu_{12} E_{pu}^*(t_2; t_{pu}) e^{(-i\mathbf{h}_2 - \gamma_2/2)(t_2-t_3)/\hbar} \\ &\quad \times \mu_{21} E_{pr}(t_3; t_{pr}) e^{(-i\mathbf{h}_1 - \gamma_1/2)(t_3)/\hbar} |\psi_1^{(0)}(\mathbf{Q}, 0)\rangle , \end{aligned} \quad (1.12)$$

and

$$\begin{aligned} |\psi_2^{(3)}(\mathbf{Q}, t; \mathbf{k}_{pr}, -\mathbf{k}_{pu}, \mathbf{k}_{pu})\rangle &= e^{i\mathbf{k}_{pr} \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 e^{(-i\mathbf{h}_2 - \gamma_2/2)(t-t_1)/\hbar} \\ &\quad \times \mu_{21} E_{pr}(t_1; t_{pu}) e^{(-i\mathbf{h}_1 - \gamma_1/2)(t_1-t_2)/\hbar} \\ &\quad \times \mu_{12} E_{pu}^*(t_2; t_{pu}) e^{(-i\mathbf{h}_2 - \gamma_2/2)(t_2-t_3)/\hbar} \\ &\quad \times \mu_{21} E_{pu}(t_3; t_{pr}) e^{(-i\mathbf{h}_1 - \gamma_1/2)(t_3)/\hbar} |\psi_1^{(0)}(\mathbf{Q}, 0)\rangle . \end{aligned} \quad (1.13)$$

The total third-order difference polarization that radiates in the $\mathbf{k}_{pr}$ direction between having the Raman pump on versus off, but with the probe on in both situations, $P_{\text{diff}}^{(3)}(t) = P_{\text{pump on}}^{(3)}(t; \mathbf{k}_{pr}) - P_{\text{pump off}}^{(3)}(t; \mathbf{k}_{pr})$ is then given by

$$P_{\text{diff}}^{(3)}(t) = P_{\text{SRS(I)}}^{(3)}(t; \mathbf{k}_{pr}) + P_{\text{SRS(II)}}^{(3)}(t; \mathbf{k}_{pr}) + P_{\text{IRS(I)}}^{(3)}(t; \mathbf{k}_{pr}) + P_{\text{IRS(II)}}^{(3)}(t; \mathbf{k}_{pr}) . \quad (1.14)$$

The Raman gain (RG) spectrum in the direction of the probe pulse, $\mathbf{k}_{pr}$, can be shown [46, 47, 48, 49] to be given by,

$$\Delta I_{\text{RG}}(\omega) = -\frac{8\pi^2 l C}{3n} \omega \text{Im} \left\{ E_{pr}^*(\omega) P_{\text{diff}}^{(3)}(\omega) \right\} \quad (1.15)$$

where l is the cell length, C is the number of molecules per unit volume; n is the refractive index; $E_{pr}(\omega)$, the spectrum of the incoming probe pulse is given by,

$$E_{pr}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} E_{pr}(t) dt \quad (1.16)$$

and $P_{\text{diff}}^{(3)}(\omega)$ is the Fourier transform of the difference polarization,

$$P_{\text{diff}}^{(3)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} P_{\text{diff}}^{(3)}(t) dt . \quad (1.17)$$

1.3 Outline

FSRS is governed essentially by four nonlinear processes: SRS(I), SRS(II), IRS(I) and IRS(II). Theoretically, the contribution and lineshapes from each component can be studied separately, but the experimental result is the sum of the four terms. Our calculated results showed that for off-resonance FSRS, the sum of the SRS(II) and IRS(II) terms accounts for the broad baseline, the SRS(I) term accounts for the sharp Stokes and Rayleigh bands, and the IRS(I) term accounts for the sharp anti-Stokes and Rayleigh bands. For resonance FSRS, the line shapes on the anti-Stokes side can be complex, but the lineshapes on the Stokes side are Lorentzian-like. The FSRS lineshapes depend on the Raman pump pulse temporal width, the vibrational dephasing time, the homogeneous damping, the inhomogeneous damping, and the instrumental resolution.

Yoshizawa *et.al.* [42] had used a three-state model to describe FSRS from a transient state, and they had written down the third-order polarization for describing FSRS. However, it was shown that the expression they wrote down was just one of the eight terms given by our perturbation theory [44]. In chapter 2, we present a full quantum-mechanical description of FSRS for a three-state model. The perturbative approach via density matrix theory and the third-order polarization is used to describe FSRS. All terms in perturbation theory are included. Calculations of FSRS for various Raman pump and probe pulses and for off-resonance and resonance scattering are considered.

The expressions for the third-order polarizations could be written by the evolving bra and ket wave packets from the eight Feynman dual time-line diagrams as stated before in our quantum theory. The theory is applicable for any form of potential energy surfaces. To adopt the

displaced harmonic oscillator model in multi-dimensions to represent the ground and excited potential energy surfaces, the four nonlinear processes can be written as triple time integrals over four-time correlation functions which have analytic results for any number of dimensions. [50] However, computing the four-time correlation functions was very time consuming, especially for large polyatomic molecules with many vibrational modes. In FSRS, the probe pulse initiating the third-order polarization and vibrational coherence is typically of very short femtosecond duration, so it should be possible to approximate it by a delta function pulse. By using a delta function probe pulse, the third-order polarizations could be simplified to two time integrals over three-time correlation functions. This will reduce the computation time considerably and allows us to compute all the eight processes separately as well as take into account explicit vibrational dephasing. The expressions for the third-order polarizations of all the eight processes are presented in Chapter 3, where both homogeneous damping and inhomogeneous broadening are considered. Calculations are made to see how the Raman pump pulse temporal width, the vibrational dephasing time, and the homogeneous and inhomogeneous damping constants affect the FSRS spectrum. Simulations are also made to compare with the experimental FSRS results on rhodamine 6G (R6G) [14, 13].

The basic model presented in Chapter 1 doesn't specify the potential energy surfaces (PES) for the ground or excited state. In Chapter 2, the 'three state model' is the simplest model where we used two vibrational levels, a and c, of the Raman transition for the ground electronic state and a single vibrational level b for the excited electronic state. In Chapter 3, the PES for both ground and excited states are taken to be harmonic oscillators, where the energy levels are given by $E_n = h\nu(n+1/2)$ where $n=1, 2, 3, \dots$ and ν is the mode frequency.

One of the advantages of FSRS over traditional spectroscopy techniques is that FSRS provides fluorescence background free anti-Stokes bands. During the FSRS study for fluorescence materials, Raman loss and dispersive line shapes were observed on anti-Stokes bands [14, 50]. It has been shown by our quantum theory that the IRS(I) term accounts for the anti-Stokes FSRS. So it is necessary to study the inverse Raman scattering process deeply. Umapathy and co-workers [51] collected resonance inverse Raman spectrum of crystal violet (CV) by ultrafast Raman loss spectroscopy(URLS), which is analogous to anti-Stokes bands, utilizing a picosecond

Raman pump and a femtosecond pulse. They scanned across a broad range of excitation wavelengths that span on the red side of the absorption maximum and found that the inverse Raman line shapes were Raman pump frequency dependent. In Chapter 4, we review the third-order polarization for IRS process in diagrammatic form and write the expressions for the third-order polarizations from the diagram. Analytic expression for the four-time correlation function in the time-dependent third-order polarization was written with describing the molecule CV by separable multidimensional harmonic potential surfaces with Franck-Condon displacements in the modes. Calculations are made and the results are compared with the absorption and on resonant URLS experiments on CV. The effects of Raman pump pulse temporal width and the Raman transition damping time to the IRS spectrum are also studied. The analytical expression for third-order susceptibility for IRS is derived to understand the mode dependent phase changes as a function of Raman pump in the URLS of CV.

Finally, I summarize the main features of FSRS and conclude with a discussion of the current state of the theories and models and prospects for future work is given.

Three-State Model For Femtosecond Broadband Stimulated Raman Scattering

2.1 Abstract

Stimulated Raman scattering (SRS) is analyzed with a three-state model. Using a diagrammatic density-matrix formalism, SRS by Raman pump pulse and probe pulse, with observation along the probe direction, is described principally by eight terms. The eight terms can be grouped into four sets, which are labeled as SRS or IRS (inverse Raman scattering): SRS(I), SRS(II), IRS(I), and IRS(II). Specializing to the case of femtosecond SRS (FSRS) by a picosecond (ps) Raman pump pulse and a femtosecond (fs) probe pulse, the spectra for the four sets of terms under off-resonance and resonance conditions were calculated. The results obtained can explain the FSRS experimental observations from a (decaying) stationary vibrational state, such as (1) high wavenumber resolution (determined by the narrow bandwidth Raman pump pulse) and high time resolution (determined by the fs probe pulse), (2) Stokes gain vs anti-Stokes loss in off-resonance FSRS, and (3) dispersive lineshapes in resonance FSRS.

2.2 Introduction

Recently, femtosecond (broadband) stimulated Raman spectroscopy (FSRS), using a picosecond (ps) Raman pump and a femtosecond (fs) probe pulse, has been developed as a powerful technique that can reveal vibrational structural information of stationary or transient excited states [1, 2, 52, 42, 53, 54, 4, 6, 5, 7, 41, 8, 55, 10, 9, 56, 57, 58, 59, 12]. In time-resolved FSRS, three optical pulses are used, as shown in Fig. 2.1. An ultrashort actinic pump pulse acting on the ground vibronic state g prepares an excited vibronic state e , which undergoes a rapid conversion to a transient vibronic state a . Subsequently, a picosecond Raman pump pulse and femtosecond probe pulse interrogates the transient state a , and the Raman process may take the molecule back to state a or to another vibrational level c in the same transient electronic state. In a three-state model, the Raman scattering is mediated via another vibrational level b in a higher excited electronic state. The time delay t_D between the fs actinic and femosecond probe pulses can be resolved to <100 fs, while the spectral resolution of the Raman gain (RG) profile is limited by the narrow-bandwidth Raman pump, the natural vibrational linewidth of the sample, and the resolution of the spectrograph, which in total can be ~ 10 cm^{-1} . So, the FSRS technique can afford both high temporal resolution as well as high spectral resolution, thus overcoming the limitations of conventional time-resolved Raman spectroscopy using a single ultrashort Raman pump pulse [12]. The technique has been applied to study the photoexcited dynamics of many molecules, including carotenoids [42, 53, 8], dyes [2], transition-metal complexes [59], and rhodopsin [10].

Figure 2.1: Schematic energy level diagram of time-resolved femtosecond stimulated Raman spectroscopy. An ultrashort, broadband actinic pulse sends the molecule from the ground to an initial photoexcited state, which rapidly converts to a transient state a . A narrow-bandwidth Raman pump pulse and broadband probe pulse at a time delay t_D then acts on state a , and the Raman signal along the probe pulse direction, with and without the Raman pump on, is collected. States a and c can be taken to be on one electronic state, and state b is on a higher electronic state.

The theory of Raman spectroscopy has a long history [60], encompassing both classical [28] and quantum [35, 36] approaches tracing back to the beginnings of quantum theory. The quantum-mechanical Kramers - Heisenberg - Dirac quantum scattering theory can account for both spontaneous and stimulated Raman scattering (SRS) from a stationary vibrational state with narrow bandwidth continuous wave (CW) radiation, and typically a sum-over-states, time-independent approach is used. Shen and Bloembergen [39, 40] have provided a semiclassical coupled-wave description of SRS with CW radiation. While the narrow-bandwidth Raman pump pulse in FSRS can, to a good approximation, be taken to be CW, the continuum femtosecond Stokes probe pulse clearly is not. The coupled-wave theory of SRS has been extended to FSRS, where it has been shown that there is a gain in the Stokes line that has a width that is determined by the narrow

bandwidth of the picosecond Raman pump pulse and the decay constant of the molecular vibration, which can be just tens of wavenumbers, and does not depend on the broadband femtosecond probe pulse [6, 41]. It also predicts a gain in the anti-Stokes line, which is contrary to experimental results [42]. The coupled-wave approach has been shown to rest on several assumptions, of which the main ones are off-resonance Raman scattering and a fundamental Raman transition from the $v = 0$ state. So, clearly, a quantum theory is needed as FSRs is a quantum phenomenon and both off-resonance and resonance conditions have to be treated in one formulation.

In a first attempt at the quantum theory for FSRs [43], a density matrix approach was used and the relevant third-order polarization in the direction of the probe pulse was derived. It was shown then that FSRs is given by three terms - one for RRS(I) and the other two for hot luminescence (HL(I) and HL(II)) - which can be represented by Feynman dual time-line diagrams, one line for the time- evolution of the ket vector and another for the bra vector. By assuming stationary-state Raman scattering, and replacing the probe pulse with the vacuum field, then the three terms reduce to similar three terms discussed by Shen [61] for spontaneous Raman scattering from a stationary state with CW Raman pump excitation using a three-state model. On closer examination of this first attempt, there was an implicit assumption made that the Raman pump pulse leads to excitation (absorption), while the probe pulse leads to de-excitation (emission). The three terms then naturally correlate with the spontaneous Raman scattering case, where the probe pulse is now the vacuum field which can only lead to de-excitation. In reality, however, the molecule does not discriminate between the two pulses and so can be excited or de-excited by either the Raman pump or probe pulses in stimulated Raman scattering.

Yoshizawa et al. [2, 42, 53] have used a three-state model to describe FSRs from a transient state, where a and c are on one electronic state and b is on an excited electronic state. They showed that if $N(t) = N_0 e^{-t/T_N}$ is the population of the transient state a at time t , then the third-order polarization for FSRs is given by

$$\begin{aligned}
P^{(3)}(t) = & \left(\frac{i\mu}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 N(t_3) \\
& \times \tilde{E}_R^*(t_3) e^{i(\omega_R - \omega_{ba})t_3} e^{-(T_{ba}^{-1} + T_N^{-1})(t_2 - t_3)} \\
& \times \tilde{E}_S^*(t_2) e^{-i(\omega_S - \omega_{bc})t_2} e^{-(T_{ca}^{-1} + T_N^{-1})(t_1 - t_2)} \\
& \times \tilde{E}_R^*(t_1) e^{-i(\omega_R - \omega_{ba})t_1} e^{-(T_{bc}^{-1} + T_N^{-1})(t - t_2)} e^{-i\omega_{bc}t}, \tag{2.1}
\end{aligned}$$

where μ is the dipole moment, $\omega_{\alpha\beta}$ and $T_{\alpha\beta}$ denote the transition wavenumber and the dipole decay between the α and β states, respectively, and we have written the electric fields of the Raman pump and probe pulses as $E_R(t) = \tilde{E}_R(t)e^{-i\omega_R t}$ and $E_S(t) = \tilde{E}_S(t)e^{-i\omega_S t}$, respectively. It can be shown that Eqn (2.1) corresponds to the RRS(I) term in SRS, which 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. If we consider the Raman pump pulse is an exponential decay on both sides of the delay time, t_d , and the probe pulse is a delta function, it was shown that the Raman signal is a Lorentzian with width given by $(\gamma_R + T_{ca}^{-1} + T_N^{-1})$ i.e. the width of the Raman pump pulse and the molecular decay times. The result is not expected to be valid for resonance FSRS, and even off-resonance FSRS has more terms than RRS(I).

In this chapter, we present a full quantum-mechanical description of SRS for a three-state model. We allow both the Raman pump and probe pulses to cause excitation or de-excitation of the molecule. This relaxed assumption is necessary, as the Raman pump and probe pulses are acting simultaneously on the molecule in the FSRS experiments, and the molecule does not distinguish between the two pulses. Below, the perturbative approach via density matrix theory and the third-order polarization is used to describe SRS for any duration Raman pump and probe pulses, with observation along the probe pulse direction. All terms in perturbation theory are included. Calculations of FSRS for various Raman pump and probe pulses and for off-resonance and resonance scattering are considered then. We conclude in the final section.

2.3 Theory

Our focus is on the SRS by a pair of Raman pump and probe pulses on the transient state a. The equation of motion for the density matrix operator ρ is

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}[\mathcal{H}_0 + \mathcal{V}(t), \rho(t)] - \Gamma\rho(t), \quad (2.2)$$

with

$$\mathcal{V}(t) = -\mu \cdot \mathbf{E}(\mathbf{R}, t), \quad (2.3)$$

$$\mathbf{E}(\mathbf{R}, t) = \varepsilon_R E_R(t) e^{(-i\omega_R t + i\mathbf{k}_R \cdot \mathbf{R})} + \varepsilon_S E_S(t) e^{(-i\omega_S t + i\mathbf{k}_S \cdot \mathbf{R})} \quad (2.4)$$

where Γ is the relaxation superoperator that describes vibronic dephasing and relaxation effects, with matrix elements $T_{ij}^{-1} = T_{ji}^{-1} = (T_i^{-1} + T_j^{-1})/2$; $\boldsymbol{\mu}$ is the transition dipole between electronic states; $E_R(t)$ and $E_S(t)$ are the (real) envelope of the Raman pump and probe fields, and the fields propagate in space $\mathbf{R}$ (which can be taken to be a constant in the long wavelength approximation) with wave vectors $\mathbf{k}_R$ and $\mathbf{k}_S$, and polarizations $\boldsymbol{\varepsilon}_R$ and $\boldsymbol{\varepsilon}_S$, respectively. Henceforth, we shall write $\boldsymbol{\mu} \cdot \boldsymbol{\varepsilon} = \mu$, and take it to be a constant.

We can expand ρ into a series of ascending orders, in powers of $\mathbf{E}$, $\rho = \rho^{(0)} + \rho^{(1)} + \rho^{(2)} + \rho^{(3)} + \dots$, and each term can be derived successively by an iterative solution of Eqn (2.2). In Raman scattering, the intensity is determined by the third-order polarization

$$P^{(3)}(t) = Tr\{\mu^* \cdot \rho^{(3)}(t)\} + c.c.. \quad (2.5)$$

Using the diagrammatic technique for the density matrix or third-order polarization, e.g. Yee and Gustafson [62], and following the convention of Shen [45], there are 8 basic dual time-line Feynman diagrams, out of a total of 24 diagrams for a two-color system of Raman pump and probe pulses, that have the output Raman signal in the probe pulse direction, and these are shown in Fig. 2.2. The eight terms have been grouped into four sets which are labeled as SRS and inverse Raman scattering (IRS): SRS(I), SRS(II), IRS(I), and IRS(II). In each diagram, the left line is for the ket evolution, while the right line is for the bra evolution. Although the dual time-line Feynman diagrams are typically for CW excitation [45], there is no restriction to extend them to pulse excitation.

The theory is applicable to SRS with any duration of Raman pump and probe pulses, but with observation in the probe pulse direction. It can be modified for other SRS such as coherent anti-Stokes Raman scattering (CARS) and coherent Stokes Raman scattering (CSRS) [63]. In FSRS, the picosecond Raman pump pulse has a narrow bandwidth, while the femtosecond probe pulse has a much broader bandwidth. We can also assign the vibrational states, (a, b , or c), on the time lines after each interaction between the pulse and the molecule. The diagrams make it easy to write the expressions for the third-order polarization.

We assume that the transient state a decays as $N(t) = N_0 e^{-t/T_a}$, $t \geq 0$. Reading the diagrams from bottom up in Fig. 2.2, we are able to write the third-order polarizations for Raman scattering from an initial state a to a final state a or c , with net polarization in the direction of the probe

Figure 2.2: Feynman dual time-line diagrams to depict the third-order polarization for stimulated Raman scattering in a three-state (a , c , b) system. The left time line depicts ket evolution, and the right time line depicts bra evolution. The molecule begins in the Louville state $|a\rangle\langle a|$, and interaction with the Raman pump pulse, ω_R , or probe pulse, ω_S , turns state $|a\rangle$ (or $\langle a|$) into state $|b\rangle$ (or $\langle b|$). The molecule finally ends in the Louville state $|a\rangle\langle a|$ or $|c\rangle\langle c|$. The diagrams fall under four nonlinear processes: stimulated Raman scattering, SRS(I) and SRS(II), and inverse Raman scattering, IRS(I) and IRS(II). Each of the SRS(I) and SRS(II) processes has three diagrams, one is labeled as resonance Raman scattering, RRS, where there is no intermediate population in state b , and another two are labeled as hot luminescence, HL, where there is intermediate population in state b . In SRS(II), IRS(I), and IRS(II), the probe pulse leads to excitation, and these terms are not allowed in spontaneous Raman scattering, but permitted in SRS.

pulse $\mathbf{k}_s$, for all the terms.

Stimulated Raman Scattering, SRS(I_{aa}). Sharp Rayleigh gain.

This process is represented by the three terms in the first row of Fig.2.2, where the molecule begins and ends in state a . The terminology that we use - RRS, where there is no population of the intermediate state b , and HL, where there is population of state b - follows that of Shen [61] for spontaneous Raman scattering, but with the understanding that the probe field for SRS takes the place of the vacuum field in spontaneous Raman. Since the probe field is much stronger than the vacuum field, the stimulated Raman process overwhelms the spontaneous one. The Raman pump pulse has a narrow bandwidth and it takes the molecule to a virtual state (or state b) of well-defined energy. The probe pulse stimulates emission from this virtual state to the final state a , thus giving a sharp Rayleigh gain at ω_R . In RRS(I_{aa}), which is the first term, the density matrix changes as $|a\rangle\langle a| \rightarrow |a\rangle\langle b| \rightarrow |a\rangle\langle a| \rightarrow |b\rangle\langle a| \rightarrow |a\rangle\langle a|$, and the diagonal third-order polarization is given by,

$$\begin{aligned}
P_{RRS(I_{aa})}^{(3)}(t) = & \left(\frac{i\mu}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 N(t_3) \\
& \times E_R^*(t_3) e^{i(\omega_R - \omega_{ba})t_3} e^{-T_{ba}^{-1}(t_2 - t_3)} \\
& \times E_S(t_2) e^{-i(\omega_S - \omega_{ba})t_2} e^{-T_{aa}^{-1}(t_1 - t_2)} \\
& \times E_R(t_1) e^{-i(\omega_R - \omega_{ba})t_1} e^{-T_{ab}^{-1}(t - t_1)} e^{-i\omega_{ba}t} + c.c.
\end{aligned} \tag{2.6}$$

The integrand can be read in relation to the first diagram in the first row of Fig. 2.2 as follows: At time t_3 , the molecule has population $N(t_3)$ in state $|a\rangle\langle a|$. The bra side is acted on by the Raman pump pulse in absorption and a transition may be made to a state $\langle b|$, giving rise to the factor $E_R^*(t_3)e^{i(\omega_R - \omega_{ba})t_3}$. The molecule is now in state $|a\rangle\langle b|$, which evolves to time t_2 with a decay factor $e^{-T_{ba}^{-1}(t_2 - t_3)}$. At time t_2 , the bra side is acted on by the probe pulse in emission and a transition is made to state $\langle a|$, giving rise to the factor $E_S(t_2)e^{-i(\omega_S - \omega_{ba})t_2}$. The molecule is now in state $|a\rangle\langle a|$, which evolves to time t_1 with a decay factor $e^{-T_{aa}^{-1}(t_1 - t_2)}$. At time t_1 , the ket side is acted on by the Raman pump pulse in absorption and a transition is made to state $\langle b|$, giving rise to the factor $E_R(t_1)e^{-i(\omega_R - \omega_{ba})t_1}$. The molecule is now in state $|b\rangle\langle a|$, which evolves to time t with a decay factor $e^{-T_{ab}^{-1}(t - t_1)}$. At time t , the ket $|b\rangle$ makes a transition to state $|a\rangle$

in closure, which introduces the factor $e^{-i\omega_{ba}t}$. Other third-order polarization terms below can similarly be read off the dual time-line diagrams.

In HL(I_{aa}), the second term, the density matrix changes as $|a\rangle\langle a| \rightarrow |a\rangle\langle b| \rightarrow |b\rangle\langle b| \rightarrow |b\rangle\langle a| \rightarrow |a\rangle\langle a|$, and the third-order polarization is given by,

$$\begin{aligned}
P_{HL(I_{aa})}^{(3)}(t) &= \left(\frac{i\mu}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 N(t_3) \\
&\quad \times E_R^*(t_3) e^{i(\omega_R - \omega_{ba})t_3} e^{-T_{ba}^{-1}(t_2 - t_3)} \\
&\quad \times E_R(t_2) e^{-i(\omega_R - \omega_{ba})t_2} e^{-T_{bb}^{-1}(t_1 - t_2)} \\
&\quad \times E_S(t_1) e^{-i(\omega_S - \omega_{ba})t_1} e^{-T_{ab}^{-1}(t - t_1)} e^{-i\omega_{ba}t} + c.c.
\end{aligned} \tag{2.7}$$

In HL(II_{aa}), the third term, the density matrix, changes as $|a\rangle\langle a| \rightarrow |b\rangle\langle a| \rightarrow |b\rangle\langle b| \rightarrow |b\rangle\langle a| \rightarrow |a\rangle\langle a|$, and the third-order polarization is given by,

$$\begin{aligned}
P_{HL(II_{aa})}^{(3)}(t) &= \left(\frac{i\mu}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 N(t_3) \\
&\quad \times E_R(t_3) e^{-i(\omega_R - \omega_{ba})t_3} e^{-T_{ab}^{-1}(t_2 - t_3)} \\
&\quad \times E_R^*(t_2) e^{i(\omega_R - \omega_{ba})t_2} e^{-T_{bb}^{-1}(t_1 - t_2)} \\
&\quad \times E_S(t_1) e^{-i(\omega_S - \omega_{ba})t_1} e^{-T_{ab}^{-1}(t - t_1)} e^{-i\omega_{ba}t} + c.c.
\end{aligned} \tag{2.8}$$

The sum of these three polarizations gives,

$$P_{SRS(I_{aa})}^{(3)}(t) = P_{RRS(I_{aa})}^{(3)}(t) + P_{HL(I_{aa})}^{(3)}(t) + P_{HL(II_{aa})}^{(3)}(t). \tag{2.9}$$

Stimulated Raman Scattering, SRS(I_{ca}). Sharp Stokes gain.

This process is also represented by the three terms in the first row of Fig.2.2, where the molecule begins in state a and now ends in state c . Similar to SRS(I_{aa}), the probe pulse stimulates emission from a virtual state (or state b) of well-defined energy to the final state c , thus giving a sharp Stokes gain at $\omega_R - \omega_{ca}$. In RRS(I_{ca}), the density matrix changes as $|a\rangle\langle a| \rightarrow |a\rangle\langle b| \rightarrow |a\rangle\langle c| \rightarrow |b\rangle\langle c| \rightarrow |c\rangle\langle c|$, and the third-order polarization is given by,

$$\begin{aligned}
P_{RRS(I_{ca})}^{(3)}(t) &= \left(\frac{i\mu}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 N(t_3) \\
&\quad \times E_R^*(t_3) e^{i(\omega_R - \omega_{ba})t_3} e^{-T_{ba}^{-1}(t_2 - t_3)} \\
&\quad \times E_S(t_2) e^{-i(\omega_S - \omega_{bc})t_2} e^{-T_{ca}^{-1}(t_1 - t_2)} \\
&\quad \times E_R(t_1) e^{-i(\omega_R - \omega_{ba})t_1} e^{-T_{cb}^{-1}(t - t_1)} e^{-i\omega_{bc}t} + c.c.
\end{aligned} \tag{2.10}$$

This $\text{SRS}(I_{ca})$ term is similar to Eqn.(2.1), except for the decay terms with T_N^{-1} , and it is the only term that Yoshizawa et al. [42, 53] considered in describing time-resolved SRS. Clearly, there are other terms corresponding to the other seven diagrams in Fig. 2.2, as well as the $\text{RRS}(I_{aa})$ term, that have to be taken into account to explain the total SRS in the probe pulse direction.

In $\text{HL}(I_{ca})$, the density matrix changes as $|a\rangle\langle a| \rightarrow |a\rangle\langle b| \rightarrow |b\rangle\langle b| \rightarrow |b\rangle\langle c| \rightarrow |c\rangle\langle c|$, and the third-order polarization is given by,

$$\begin{aligned}
P_{HL(I_{ca})}^{(3)}(t) &= \left(\frac{i\mu}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 N(t_3) \\
&\times E_R^*(t_3) e^{i(\omega_R - \omega_{ba})t_3} e^{-T_{ba}^{-1}(t_2 - t_3)} \\
&\times E_R(t_2) e^{-i(\omega_R - \omega_{ba})t_2} e^{-T_{bb}^{-1}(t_1 - t_2)} \\
&\times E_S(t_1) e^{-i(\omega_S - \omega_{bc})t_1} e^{-T_{cb}^{-1}(t - t_1)} e^{-i\omega_{bc}t} + c.c. .
\end{aligned} \tag{2.11}$$

In $\text{HL}(II_{ca})$, the density matrix changes as $|a\rangle\langle a| \rightarrow |b\rangle\langle a| \rightarrow |b\rangle\langle b| \rightarrow |b\rangle\langle c| \rightarrow |c\rangle\langle c|$, and the third-order polarization is given by,

$$\begin{aligned}
P_{HL(II_{ca})}^{(3)}(t) &= \left(\frac{i\mu}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 N(t_3) \\
&\times E_R(t_3) e^{-i(\omega_R - \omega_{ba})t_3} e^{-T_{ab}^{-1}(t_2 - t_3)} \\
&\times E_R^*(t_2) e^{i(\omega_R - \omega_{ba})t_2} e^{-T_{bb}^{-1}(t_1 - t_2)} \\
&\times E_S(t_1) e^{-i(\omega_S - \omega_{bc})t_1} e^{-T_{cb}^{-1}(t - t_1)} e^{-i\omega_{bc}t} + c.c. .
\end{aligned} \tag{2.12}$$

The sum of these three polarizations gives,

$$P_{SRS(I_{ca})}^{(3)}(t) = P_{RRS(I_{ca})}^{(3)}(t) + P_{HL(I_{ca})}^{(3)}(t) + P_{HL(II_{ca})}^{(3)}(t). \tag{2.13}$$

Thus the third-order polarization for the SRS(I) process is given by,

$$P_{SRS(I)}^{(3)}(t) = P_{SRS(I_{aa})}^{(3)}(t) + P_{SRS(I_{ca})}^{(3)}(t). \tag{2.14}$$

Stimulated Raman Scattering, SRS(II, $a \rightarrow a$). Broad Rayleigh gain.

This process is represented by the three terms in the second row of Fig. 2.2, where the molecule begins and ends in state a . It is similar to SRS(I), except for the interchange of ω_R and ω_S between the ket and the bra time lines, and the signal will show a gain. On the bra side, two Raman pump interactions, of relatively well defined energy, brings the molecule from state a to a virtual state (or state b) and back to a . On the ket side, the probe excitation, which can take

place over the broad probe spectrum, takes the molecule from state a to a virtual state (or state b) followed by closure to bring it back to state a . The result is a broad Rayleigh gain centered at ω_S .

In RRS(II), the density matrix changes as $|a\rangle\langle a| \rightarrow |a\rangle\langle b| \rightarrow |a\rangle\langle a| \rightarrow |b\rangle\langle a| \rightarrow |a\rangle\langle a|$, and the third-order polarization is given by,

$$\begin{aligned}
P_{RRS(II)}^{(3)}(t) = & \left(\frac{i\mu}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 N(t_3) \\
& \times E_R^*(t_3) e^{i(\omega_R - \omega_{ba})t_3} e^{-T_{ba}^{-1}(t_2 - t_3)} \\
& \times E_R(t_2) e^{-i(\omega_R - \omega_{ba})t_2} e^{-T_{aa}^{-1}(t_1 - t_2)} \\
& \times E_S(t_1) e^{-i(\omega_S - \omega_{ba})t_1} e^{-T_{ab}^{-1}(t - t_1)} e^{-i\omega_{ba}t} + c.c. . \quad (2.15)
\end{aligned}$$

In HL(III), the density matrix changes as $|a\rangle\langle a| \rightarrow |a\rangle\langle b| \rightarrow |b\rangle\langle b| \rightarrow |b\rangle\langle a| \rightarrow |a\rangle\langle a|$, and the third-order polarization is given by,

$$\begin{aligned}
P_{HL(III)}^{(3)}(t) = & \left(\frac{i\mu}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 N(t_3) \\
& \times E_R^*(t_3) e^{i(\omega_R - \omega_{ba})t_3} e^{-T_{ba}^{-1}(t_2 - t_3)} \\
& \times E_S(t_2) e^{-i(\omega_S - \omega_{ba})t_2} e^{-T_{bb}^{-1}(t_1 - t_2)} \\
& \times E_R(t_1) e^{-i(\omega_R - \omega_{ba})t_1} e^{-T_{ab}^{-1}(t - t_1)} e^{-i\omega_{ba}t} + c.c. . \quad (2.16)
\end{aligned}$$

In HL(IV), the density matrix changes as $|a\rangle\langle a| \rightarrow |b\rangle\langle a| \rightarrow |b\rangle\langle b| \rightarrow |b\rangle\langle a| \rightarrow |a\rangle\langle a|$, and the third-order polarization is given by,

$$\begin{aligned}
P_{HL(IV)}^{(3)}(t) = & \left(\frac{i\mu}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 N(t_3) \\
& \times E_S(t_3) e^{-i(\omega_S - \omega_{ba})t_3} e^{-T_{ab}^{-1}(t_2 - t_3)} \\
& \times E_R^*(t_2) e^{i(\omega_R - \omega_{ba})t_2} e^{-T_{bb}^{-1}(t_1 - t_2)} \\
& \times E_R(t_1) e^{-i(\omega_R - \omega_{ba})t_1} e^{-T_{ab}^{-1}(t - t_1)} e^{-i\omega_{ba}t} + c.c. . \quad (2.17)
\end{aligned}$$

Thus the third-order polarization for the SRS(II) process is given by,

$$P_{SRS(II)}^{(3)}(t) = P_{RRS(II)}^{(3)}(t) + P_{HL(III)}^{(3)}(t) + P_{HL(IV)}^{(3)}(t) . \quad (2.18)$$

Inverse Raman Scattering, IRS(I_{aa}, $a \rightarrow a$ via $|a\rangle\langle a|$). Sharp Rayleigh loss.

This process is given by the left diagram in the third row of Fig. 2.2, where the molecule begins

and ends in state a via the density matrix $|a\rangle\langle a|$. On the bra side, there is no change. On the ket side, the broadband probe pulse prepares a broad range of virtual states (which may include state b), and it is followed by a narrow-bandwidth Raman pump interaction that sends the molecule to state a . In so doing, only a narrow band of the probe spectrum corresponding to the Raman pump spectrum is involved. This is then followed by another narrow-bandwidth Raman pump interaction that sends the molecule to a virtual state (or state b) of well-defined energy. Closure brings the molecule back to state a . The result is a sharp Rayleigh loss at ω_R .

In $\text{IRS}(\text{I}_{aa})$, the density matrix changes as $|a\rangle\langle a| \rightarrow |b\rangle\langle a| \rightarrow |a\rangle\langle a| \rightarrow |b\rangle\langle a| \rightarrow |a\rangle\langle a|$, and the third-order polarization is given by,

$$\begin{aligned}
P_{\text{IRS}(\text{I}_{aa})}^{(3)}(t) &= \left(\frac{i\mu}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 N(t_3) \\
&\quad \times E_S(t_3) e^{-i(\omega_S - \omega_{ba})t_3} e^{-T_{ab}^{-1}(t_2 - t_3)} \\
&\quad \times E_R^*(t_2) e^{i(\omega_R - \omega_{ba})t_2} e^{-T_{aa}^{-1}(t_1 - t_2)} \\
&\quad \times E_R(t_1) e^{-i(\omega_R - \omega_{ba})t_1} e^{-T_{ab}^{-1}(t - t_1)} e^{-i\omega_{ba}t} + c.c. . \quad (2.19)
\end{aligned}$$

Inverse Raman Scattering, $\text{IRS}(\text{I}_{ca}, a \rightarrow a$ via $|c\rangle\langle a|$). Sharp anti-Stokes loss.

This process is also given by the left diagram in the third row of Fig. 2.2, where the molecule begins and ends in state a via the density matrix $|c\rangle\langle a|$. It differs from the IRS term, $\text{IRS}(\text{I}_{aa})$ - the first narrow-bandwidth Raman pump interaction after the probe interaction now sends the molecule to state c , and the narrow band of the probe spectrum involved in the first excitation has the anti-Stokes wavenumber $\omega_R + \omega_{ca}$, resulting in a sharp anti-Stokes loss at that frequency.

In $\text{IRS}(\text{I}_{ca})$, the density matrix changes as $|a\rangle\langle a| \rightarrow |b\rangle\langle a| \rightarrow |c\rangle\langle a| \rightarrow |b\rangle\langle a| \rightarrow |a\rangle\langle a|$, and the third-order polarization is given by,

$$\begin{aligned}
P_{\text{IRS}(\text{I}_{ca})}^{(3)}(t) &= \left(\frac{i\mu}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 N(t_3) \\
&\quad \times E_S(t_3) e^{-i(\omega_S - \omega_{ba})t_3} e^{-T_{ab}^{-1}(t_2 - t_3)} \\
&\quad \times E_R^*(t_2) e^{i(\omega_R - \omega_{bc})t_2} e^{-T_{ac}^{-1}(t_1 - t_2)} \\
&\quad \times E_R(t_1) e^{-i(\omega_R - \omega_{bc})t_1} e^{-T_{ab}^{-1}(t - t_1)} e^{-i\omega_{bc}t} + c.c. . \quad (2.20)
\end{aligned}$$

Thus the third-order polarization for the $\text{IRS}(\text{I})$ process is given by,

$$P_{\text{IRS}(\text{I})}^{(3)}(t) = P_{\text{IRS}(\text{I}_{aa})}^{(3)}(t) + P_{\text{IRS}(\text{I}_{ca})}^{(3)}(t) . \quad (2.21)$$

This process is given by the right diagram in the third row of Fig. 2.2, where the molecule begins and ends in state a . It is similar to IRS(I), except for the interchange of ω_R and ω_S between the first and third bra interactions, and the signal will show a loss. The first two Raman pump interactions are sharp in energy and takes the molecule from state a to a virtual state (or state b) and back to state a . This is followed by the broadband probe interaction that takes it to a virtual state (which may include state b). Closure brings it back to state a from any energy within the broad probe spectrum. It results in a broad Rayleigh loss centered at ω_S .

In IRS(II), the density matrix changes as $|a\rangle\langle a| \rightarrow |b\rangle\langle a| \rightarrow |a\rangle\langle a| \rightarrow |b\rangle\langle a| \rightarrow |a\rangle\langle a|$, and the third-order polarization is given by,

$$\begin{aligned}
 P_{IRS(II)}^{(3)}(t) = & \left(\frac{i\mu}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 N(t_3) \\
 & \times E_R(t_3) e^{-i(\omega_R - \omega_{ba})t_3} e^{-T_{ab}^{-1}(t_2 - t_3)} \\
 & \times E_R^*(t_2) e^{i(\omega_R - \omega_{ba})t_2} e^{-T_{aa}^{-1}(t_1 - t_2)} \\
 & \times E_S(t_1) e^{-i(\omega_S - \omega_{ba})t_1} e^{-T_{ab}^{-1}(t - t_1)} e^{-i\omega_{ba}t} + c.c. .
 \end{aligned} \tag{2.22}$$

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

$$\begin{aligned}
 P_{diff}^{(3)}(t) = & P_{pump}^{(3)}(\mathbf{k}_S, t) - P_{pump}^{(3)}(\mathbf{k}_S, t) \\
 = & P_{SRS(I)}^{(3)}(t) + P_{SRS(II)}^{(3)}(t) + P_{IRS(I)}^{(3)}(t) + P_{IRS(II)}^{(3)}(t) .
 \end{aligned} \tag{2.23}$$

The RG spectrum in the direction of the probe pulse, $\mathbf{k}_S$, can be shown [46, 47, 48] to be given by,

$$\Delta I_{RG}(\omega) = \frac{8\pi^2 l C}{3n} \omega \text{Im} E_S^*(\omega) P_{diff}^{(3)}(\omega) \tag{2.24}$$

where l is the cell length, C is the number of molecules per unit volume; n is the refractive index; $E_S(\omega)$, the spectrum of the incoming probe pulse is given by,

$$E_S(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} E_S(t) e^{-i\omega_S t} dt \tag{2.25}$$

and $P_{diff}^{(3)}(\omega)$ is the Fourier transform of the difference polarization,

$$P_{diff}^{(3)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} P_{diff}^{(3)}(t) dt . \tag{2.26}$$

2.4 Results and Discussion

The three states, a , c and b have energies given by $\omega_a = 0 \text{ cm}^{-1}$, $\omega_c = 500 \text{ cm}^{-1}$ and $\omega_b = 2000 \text{ cm}^{-1}$. We take the real Raman pump or probe electric field to have the form,

$$E_{R/S}(t - t_D) = E_{0,R/S} G_{R/S}(t - t_D) \quad (2.27)$$

where $E_{0,R/S}$ is a constant, and the Gaussian envelope $G_{R/S}(t - t_D)$, centered at t_D , has the form,

$$G_{R/S}(t - t_D) = \exp\left(-2\ln 2 \frac{(t - t_D)^2}{\Delta^2}\right) \quad (2.28)$$

giving a laser pulse intensity proportional to $|G_{R/S}(t - t_D)|^2$ with full width at half-maximum (FWHM) of Δ . The central wavelengths of the Raman pump and probe pulses are given by $2\pi c/\omega_{R/S}$. It is generally not possible to obtain analytic expressions for all the third-order polarizations, but the three time integrals can be easily calculated by straightforward numerical integration.

We first look at FSRS from a (decaying) state a . The narrow bandwidth Raman pump pulse has 500 fs FWHM and 600 nm central wavelength, and the broadband probe pulse has 10 fs FWHM and 620 nm central wavelength, whose energies are below the absorption band to state b . In this off-resonance situation, any amplitude on state b will be short lived by virtue of the Heisenberg uncertainty principle, and we can use $T_b = \infty$ fs for the state b lifetime. We chose two sets of decay times for states a and c , $T_a = T_c = \infty$ and 111 fs, and calculated the FSRS spectrum at a time delay t_D of 1100 fs from the start of the exponential decay of state a .

The Raman gain spectra for the four nonlinear processes, SRS(I), SRS(II), IRS(I) and IRS(II), are shown in the upper half, and the sum to give the FSRS spectrum is in the lower half of Fig. 2.3. The wavenumber axis is the Raman shift taken relative to the central energy of the Raman pump pulse. We begin with the left column of Fig. 2.3, where $T_a = T_c = \infty$ fs. In the SRS(I) spectrum, the sharp Rayleigh gain at ω_R due to SRS(I $_{aa}$), and the sharp Stokes gain at $\omega_R - \omega_{ca}$ due to SRS(I $_{ca}$) can be clearly seen. The width of these sharp lines follows the narrow bandwidth of the Raman pump pulse. The SRS(II) spectrum shows a broad Rayleigh gain, as wide as the probe spectrum which has a width of about $1,500 \text{ cm}^{-1}$, at ω_S . In the IRS(I) spectrum, the sharp Rayleigh loss at ω_R due to IRS(I $_{aa}$), and the sharp anti-Stokes loss at $\omega_R + \omega_{ca}$ due to IRS(I $_{ca}$)

can be clearly seen. Again, the width of these sharp lines follows the narrow bandwidth of the Raman pump pulse. The IRS(II) spectrum shows a broad Rayleigh loss, again as wide as the probe spectrum, at ω_S , and is a reflection of the SRS(II) spectrum.

In summing to give the FSRS spectrum in the lower half of Fig. 2.3, SRS(II) and IRS(II) spectra would cancel each other; so the FSRS signal depends on the SRS(I) and IRS(I) spectra. The Rayleigh components SRS(I_{aa}) and IRS(I_{aa}) nearly cancel each other, and the FSRS signal shows just a Raman gain on the Stokes side due to SRS(I_{ca}), and a Raman loss on the anti-Stokes side due to IRS(I_{ca}). Previous theories [2, 42, 43] based on RRS(I_{ca}), Eq.(2.10), or SRS(I_{ca}), Eq.(2.13), alone could not account for the observed Raman loss on the anti-Stokes side[42], as well as the absence of a Rayleigh line in FSRS. In spontaneous Raman scattering from the $v = 0$ state, the anti-Stokes transition is forbidden because there is no vibrational state below it. In FSRS, however, the anti-Stokes line comes from the IRS(I_{ca}) term which is absent in spontaneous Raman scattering. The intensity of the Stokes line is stronger than the anti-Stokes line because the central wavenumber of the Gaussian probe pulse is centered at the Stokes frequency. The calculations were made with Eq. (2.24) where the spectrum is not normalized by dividing the Raman pump-on signal by the Raman pump-off signal. If it had been normalized by dividing by the probe spectrum and minus 1, then the Stokes and anti-Stokes lines would show the same intensity.

Comparing the left and right columns of Fig. 2.3, increasing $T_a = T_c$, (a) increases the width of the FSRS line beyond that determined by the narrow bandwidth of the Raman pump pulse for $T_a = \infty$ fs, and (b) decreases the intensity of the FSRS signal in proportion to the exponential decay, e^{-t_D/T_a} , of state a .

Figure 2.4 differs from Fig. 2.3 in the use of a broader-bandwidth Raman pump pulse of 50 fs FWHM. All other parameters are kept the same. Clearly, comparing the first column in Figs. 2.3 and 2.4, the bandwidth of the FSRS lines increases with the bandwidth of the Raman pump pulse, which has broadened from about 30 cm⁻¹, for a Raman pump pulse of 500 fs FWHM in Fig. 2.3 to about 300 cm⁻¹ for a Raman pump pulse of 50 fs FWHM in Fig. 2.4.

The comparison of the results in Figs. 2.3 and 2.4 showed that a longer Raman pump pulse will lead to higher spectral resolution, consistent with the Heisenberg uncertainty principle. The

Figure 2.3: Off-resonance FSRS on a (decaying) stationary state a . The energies are $\omega_a = 0$ cm^{-1} , $\omega_c = 500$ cm^{-1} , and $\omega_b = 20\,000$ cm^{-1} . The Raman pump pulse is 600 nm, 500 fs FWHM, and the probe pulse is 620 nm, 10 fs FWHM. On the left, the decay constants are $T_a = T_c = \infty$ fs; on the right, they are $T_a = T_c = 111$ fs. In both cases, $T_b = \infty$ fs. The components, SRS(I), SRS(II), IRS(I), and IRS(II), are shown on the upper half diagram, and the sum to give the FSRS spectrum is shown in the lower half diagram.

spectral resolution of the observed Raman gain profile, however, is determined by the sum of the narrow-bandwidth Raman pump, the natural vibrational line width of the sample, and the resolution of the spectrograph, which in total can be as low as 10 cm^{-1} , if we choose a Raman pump pulse of a few ps duration.

Figure 2.4: Off-resonance FSRS on a (decaying) stationary state a . Same as Fig. 2.3, but with a broader-bandwidth Raman pump pulse of 50 fs FWHM.

Figure 2.5 differs from Fig. 2.3 in the use of a narrower-bandwidth probe pulse of 100 fs FWHM. All other parameters are kept the same. Now, the anti-Stokes line is absent because the narrow bandwidth (about 150 cm^{-1}) probe pulse, as seen in the SRS(II) and IRS(II) spectra, is restricted to the region of the Stokes line at 500 cm^{-1} . The bandwidth of the Stokes line is again determined by the bandwidth of the Raman pump pulse.

The resonance FSRS from state a with $T_a = T_b = T_c = 222 \text{ fs}$, at a delay time of 1100 fs, is shown in Fig. 2.6. The central wavenumber of the Raman pump pulse of 500 fs FWHM is scanned from 500 cm^{-1} below state b to 500 cm^{-1} above it. The central wavenumber of the probe pulse of 10 fs FWHM is kept at 500 cm^{-1} to the red side of the Raman pump pulse. The FSRS spectra are plotted at intervals of 100 cm^{-1} of the central wavenumber of the Raman pump pulse. When it is exactly on-resonance with state b , the FSRS spectrum shows strong Lorentzian Rayleigh and Stokes lines. But slightly away from resonance, the FSRS spectrum becomes dispersive. The FSRS spectra are taken relative to the central wavenumber of the Raman pump pulse, which is increasing in energy from bottom to top in Fig. 2.6. The main line in the FSRS spectra that shifts to the red with increasing wavenumber of the Raman pump corresponds to transition from state b to state a . From Fig. 2.3 and 2.4, it can be seen that the linewidth is affected by

Figure 2.5: Off-resonance FSRS on a (decaying) stationary state a. Same as Fig. 2.3, but with a narrower-bandwidth probe pulse of 100 fs FWHM.

both the Raman pump duration and the dephasing time. With the same pump pulse duration, a longer dephasing time of levels a and c will result in narrower linewidth. So in Fig. 2.6, the linewidth is broader than in Figs. 2.3 - 2.5.

In a real experiment, a more realistic set of potential energy surfaces need to be used. the electronic structure of a system is much more complicated than three-state model structure. The transition frequency of the excited electronic state could be obtained from the absorption spectrum. By scanning the Raman pump frequency across the absorption band, the on-resonance FSRS spectra could be obtained, but in such a situation a more realistic excited state potential energy surface is required, and the transition frequency should be in this region. Specifically for a molecule with a featureless bell-shaped absorption spectrum, the energy difference between the ground and excited state levels ω_{ba} can be taken to corresponds to the maximum of the absorption spectrum, for off-resonance FSRS.

The components of the FSRS spectra - SRS(I), SRS(II), IRS(I) and IRS(II) - for Fig. 2.6 are shown in Fig. 2.7. As seen in Fig. 2.7, on exact resonance with state b, the SRS(I) spectrum, which is the sum of three terms-RRS(I), HL(I) and HL(II), is the strongest. In this situation,

Figure 2.6: Resonance FSRS on a (decaying) stationary state a . The decay constants are $T_a = T_c = 222$ fs. The central wavenumber of the Raman pump pulse of 500 fs FWHM is scanned from 500 cm^{-1} below state b to 500 cm^{-1} above it. The central wavenumber of the probe pulse of 10 fs FWHM is kept at 500 cm^{-1} to the red side of the Raman pump pulse. The FSRS spectra are plotted at intervals of 100 cm^{-1} .

Figure 2.7: The components - SRS(I), SRS(II), IRS(I) and IRS(II) - of the FSRS spectra in Fig. 2.6.

the HL(I) (or HL(II)) terms with one pump interaction on the bra (or ket) and another on the ket (or bra) prepares a population on the excited state b , as shown by the grey hatched areas in Fig.2.2, which is then stimulated by the probe to emit with a sharp Stokes and Rayleigh line in the FSRS spectrum. Away from state b , the SRS(II) spectrum with dispersive lineshape is strongest, because at least the broadband probe pulse on the ket side can be on resonance with state b as seen in the second row of Fig.2.2.

2.5 Conclusion

A complete perturbation theory with a three-state model has been presented for the new experimental technique of femtosecond stimulated Raman scattering (FSRS). The FSRS spectrum in the k_{pr} direction is shown to be governed essentially by four nonlinear processes: $\text{SRS(I)} = \text{SRS(I}_{aa}) + \text{SRS(I}_{ca})$, SRS(II) , $\text{IRS(I)} = \text{IRS(I}_{aa}) + \text{IRS(I}_{ca})$ and IRS(II) . All these terms contribute to FSRS, but in different ways. For off-resonance scattering, the RRS(I) term gives rise to sharp Stokes and Rayleigh gain lines with energy transferred from the Raman pump to the probe, while the IRS(I) term gives rise to sharp anti-Stokes and Rayleigh loss lines with energy transferred from the probe to the Raman pump. In the case of HL(I) (or HL(II)), one pump interaction on the bra (or ket) and another on the ket (or bra) prepares a short-lived population

on excited state, which is then stimulated by the probe to emit and so the FSRS spectrum for HL(I) and HL(II) is broad. As for the other terms - RRS(II), HL(III), HL(IV) and IRS(II) - the closure is between a ket of continuum probe excitation with a bra of well-defined energy and so they give rise to broad spectra. So for the experimentalist, the most important terms in off-resonance FSRS are RRS(I) and IRS(I). For resonance FSRS, the three-state model is less useful and we would need a more realistic set of ground and excited state potential energy surfaces, and these are used in subsequent chapters. The results obtained with the three-state model can explain the FSRS experimental observations from a (decaying) stationary vibrational state, such as (a) high wavenumber resolution (determined by the narrow bandwidth Raman pump pulse) and high time resolution (determined by the femtosecond probe pulse), (b) Stokes gain versus anti-Stokes loss in off-resonance FSRS. Future work will have to consider proper potential energy surfaces for the a, c and b states. It will then be possible to also look at FSRS from a moving wavepacket on the potential energy surface that contains the a, c states.

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Broadband stimulated Raman scattering with a picosecond Raman pump and a delta function probe pulse

3.1 Abstract

Femtosecond stimulated Raman spectroscopy (FSRS) typically uses a picosecond Raman pump and a ~ 10 fs probe pulse. Such an ultrashort probe pulse is akin to a delta function (supercontinuum) pulse and the expressions for the third-order polarization simplifies with a reduction in the four-time correlation function to a three-time correlation function. Assuming multi-mode harmonic potentials for the ground and excited states of the molecule, we obtain analytic expressions for the three-time correlation functions that facilitate the computation of the third-order polarizations for resonance Raman scattering, hot luminescence, and inverse Raman scattering terms which contribute to the FSRS spectra from the ground vibrational state. The effect of Raman pump pulse temporal width, the vibrational dephasing time, the homogeneous damping constant, and the inhomogeneous damping constant on the Raman Stokes spectrum are also more readily studied. The resonance FSRS spectra of rhodamine 6G from the ground vibrational state with various resonance excitation wavelengths were calculated using a delta probe and shown to

account well for the recent experimental results of Frontiera *et al.*, *J. Chem. Phys.* 2008; **129**: 064507 for both the Stokes and anti-Stokes bands, as well as of Shim *et al.*, *ChemPhysChem*. 2008; **9**: 697.

3.2 Introduction

Femtosecond stimulated Raman spectroscopy (FSRS), using a combination of a narrow-bandwidth picosecond Raman pump pulse overlapping with a broadband probe pulse of the order of ten femtosecond to produce Raman resonances shifted from the Raman pump wavelength on the broad probe spectrum, has been developed extensively by the Mathies group. [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16] As an analytical resonance Raman technique, it has been shown to produce high signal-to-noise spectra, free from background fluorescence, with very short acquisition times. [4, 11] When it is preceded by an ultrafast femtosecond actinic pump pulse to initiate the dynamics either on the excited or ground state surface, FSRS promises to be a powerful tool to push the time resolution of Raman spectroscopy into the femtosecond regime, giving FSRS spectra with both high time and high frequency resolution. It opens up Raman spectroscopy to study chemical reaction dynamics and physical and biological processes that occur on the ultrafast femtosecond time scale. The high time resolution comes from the time delay between the femtosecond actinic pump and probe pulses, while the high spectral resolution arises from the narrow-bandwidth Raman pump, and these are independent quantities not governed by the uncertainty principle. It is possible to push the time - frequency product $\Delta t \Delta \nu$ to $< 500 \text{ fs cm}^{-1}$. Earlier experiments in the same direction by Kobayashi and Yoshizawa *et al.* [1, 2, 52, 42, 53, 54] used $\sim 650 \text{ fs}$ Raman pump and $\sim 300 \text{ fs}$ probe pulses, resulting in poorer time resolution and with $\Delta t \Delta \nu > 6000 \text{ fs cm}^{-1}$.

The theory of spontaneous Raman spectroscopy has a long history [60], tracing back to the beginnings of quantum theory, and both classical [28] and quantum [35, 36] approaches have been proposed. The quantum-mechanical sum-over-states Kramers-Heisenberg-Dirac scattering theory is a time-independent approach that accounts for spontaneous Raman scattering from a stationary vibrational state with incident CW light of a fixed wavelength. With the advent of resonance Raman spectroscopy in the seventies and the interest in excited state dynamics, the equivalent

time-dependent wave packet approach provided a more advantageous description physically and computationally over the horrendous sum-over-states approach for polyatomics [37, 38]. With intense lasers, stimulated Raman spectroscopy was possible, and Shen and Bloembergen [39, 40] have provided a semiclassical coupled-wave description of stimulated Raman scattering with CW light. An attempt was made to extend the coupled-wave approach to FSRS where the narrow bandwidth Raman pump pulse can, to a good approximation, be taken to be CW, but the continuum femtosecond Stokes probe pulse clearly isn't [41]. Later, it was found that the coupled-wave approach is valid only for off-resonance FSRS and works only for the Stokes bands [43]. It predicts a Raman gain in both the Stokes and anti-Stokes bands, and the latter turns out to be incorrect even for off-resonance FSRS [14]. Both spontaneous and stimulated Raman scattering are described by third-order polarizations as a response of the molecule to the Raman pump and probe pulses. For spontaneous Raman scattering, the probe pulse is just the vacuum field which cannot lead to excitation. We now have a quantum wave packet theory of stimulated Raman scattering, including FSRS, from a stationary state or a moving wave packet prepared by an actinic pump pulse [44]. It applies to both off-resonance as well as resonance with an excited electronic state, and spontaneous Raman scattering is a subset of the theory. It promises to be able to account for all features of the FSRS spectra covering both Stokes and anti-Stokes bands [44, 64, 65, 50]. The quantum wave packet theory can be extended as two third-order processes to cover the recently observed cascading Raman signals in FSRS [66].

The quantum theory of stimulated Raman scattering [44] was shown to have eight contributing processes which were labelled as resonance Raman scattering (RRS(I) and RRS(II)), hot luminescence (HL(I), HL(II), HL(III) and HL(IV)) and inverse Raman scattering (IRS(I) and IRS(II)). In the absence of vibrational dephasing, the resonance Raman scattering and hot luminescence terms were grouped as stimulated Raman scattering (SRS(I) and SRS(II)) where SRS(I) comprised RRS(I), HL(I) and HL(II), while SRS(II) comprised RRS(II), HL(III) and HL(IV), and it was possible to express them as overlaps of evolving bra and ket wave packets. Each process is given by a third-order polarization which can be written as triple time integrals over four-time correlation functions, and the latter have analytic results for the separable, displaced harmonic oscillator model in any number of dimensions [50]. However, computing the four-time

correlation functions was very time consuming, especially for large polyatomic molecules with many vibrational modes. Moreover, we could compute only with the absence of explicit vibrational dephasing, and assumed that it was included with the lifetime of each electronic state. In FSRS, the probe pulse initiating the third-order polarization and vibrational coherence is typically of very short femtosecond duration, and so it should be possible to approximate it by a delta function pulse. This will then remove one time integral from the polarization and we have a reduced three-time correlation function which will reduce the computation time considerably and allows us to compute all the eight processes separately as well as take into account explicit vibrational dephasing.

In this chapter, we review the third-order polarizations for FSRS in diagrammatic form where we present both the Feynman dual time-line diagrams as well as the corresponding four-wave mixing energy level (FWMEL) diagrams for the eight processes. The advantage of the Feynman diagrams which comes from perturbation theory is that they facilitate writing down the third-order polarization expressions directly, while the FWMEL diagrams provides a physical way to view resonances and understand the vibrational structures as well as the broad baseline in a FSRS spectrum. By using a delta function probe pulse, the third-order polarizations are now given by two time integrals over three-time correlation functions. Using separable multidimensional harmonic potential surfaces with Franck-Condon displacements in the modes, we can obtain analytic expressions for the three-time correlation functions. Expressions for both homogeneous damping and inhomogeneous broadening are given. Calculations are made to see how the Raman pump pulse temporal width, the vibrational dephasing time, and the homogeneous and inhomogeneous damping constants affect the FSRS spectrum. Calculations are also made to compare with results from recent FSRS experiments [14, 13] on the fluorescent dye, rhodamine 6G (R6G) where the Raman pump pulse is about 750 fs long and the probe pulse is about 10 fs which can be approximated by a delta function pulse. The calculations and experiments cover both Stokes and anti-Stokes bands, and span the resonance FSRS regime, and so provides a good test of the theory too.

3.3 Theory

3.3.1 Third-order polarization and FSRS

We consider two Born-Oppenheimer electronic states e_1 and e_2 and their associated vibrational manifolds. By turning on the Raman pump and probe pulses, the density matrix evolves according to the quantum Liouville equation

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}[\mathcal{H}_0 + \mathcal{V}(t), \rho(t)] - \Gamma \rho(t) , \quad (3.1)$$

with

$$\begin{aligned} \mathcal{H}_0 &= |e_1\rangle \mathbf{h}_1(\mathbf{Q}) \langle e_1| + |e_2\rangle \mathbf{h}_2(\mathbf{Q}) \langle e_2| , \\ \mathcal{V}(t) &= -\boldsymbol{\mu}(\mathbf{Q}) \cdot \mathbf{E}(\mathbf{R}, t) , \\ \boldsymbol{\mu}(\mathbf{Q}) &= |e_2\rangle \boldsymbol{\mu}_{21}(\mathbf{Q}) \langle e_1| + \text{c.c.} , \\ \mathbf{E}(\mathbf{R}, t) &= \boldsymbol{\varepsilon}_{pu} E_{pu}(t; T_{pu}) \exp(i\mathbf{k}_{pu} \cdot \mathbf{R}) + \boldsymbol{\varepsilon}_{pr} E_{pr}(t; T_{pr}) \exp(i\mathbf{k}_{pr} \cdot \mathbf{R}) + \text{c.c.} \\ &\equiv \mathbf{E}_{pu}(t; T_{pu}) + \mathbf{E}_{pr}(t; T_{pr}) + \text{c.c.} . \end{aligned} \quad (3.2)$$

The theory is applicable for any form of potential energy surfaces, but for our calculations below we will assume that the Hamiltonians $\mathbf{h}_1(\mathbf{Q})$ and $\mathbf{h}_2(\mathbf{Q})$ are for a set of displaced, separable, multidimensional harmonic oscillators. The relaxation superoperator for homogeneous broadening is denoted by Γ , whose constant matrix elements γ_{ab} , would depend on the associated vibrational states in e_a and e_b . Here, we set $\gamma_{12} = \gamma_{21} = (\gamma_1 + \gamma_2)/2$, $\gamma_{22} = \gamma_2$ regardless of whether there's population or coherence on e_2 , and $\gamma_{11} = \gamma_1$ if there's population on e_1 , but $\gamma_{11} = 1/T_2$ when there's coherence on e_1 with T_2 as the dephasing time. The transition dipole moment between electronic states e_a and e_b , which may be coordinate-dependent, is denoted by $\boldsymbol{\mu}_{ab}(\mathbf{Q})$, and $\mathbf{E}_{pu}(t; T_{pu})$ and $\mathbf{E}_{pr}(t; T_{pr})$, are the Raman pump and probe fields, peaked at times T_{pu} and T_{pr} , and which propagate in space $\mathbf{R}$ (which can be taken to be a constant at the molecule in the long wavelength approximation) with wave vectors $\mathbf{k}_{pu}$ and $\mathbf{k}_{pr}$, and have polarizations $\boldsymbol{\varepsilon}_{pu}$ and $\boldsymbol{\varepsilon}_{pr}$, respectively. For simplicity, we will assume parallel polarizations $\boldsymbol{\varepsilon}_{pu} = \boldsymbol{\varepsilon}_{pr}$ and write $\mu_{ab} = \boldsymbol{\mu}_{ab} \cdot \boldsymbol{\varepsilon}_{pr}$.

The ansatz for the density matrix can be written as

$$\rho(t) = \sum_{a,b=1}^2 |e_a\rangle \rho_{ab}(\mathbf{Q}, t) \langle e_b| , \quad (3.3)$$

where $\mathbf{Q}$ denotes the multidimensional normal coordinates and $\rho_{ab}(\mathbf{Q}, t)$ is the vibrational density matrix associated with electronic states $|e_a\rangle$ and $|e_b\rangle$ simultaneously. In the weak field limit, we can solve Eq.(3.1) order by order with perturbation theory and the terms can be represented by diagrams - either dual time-line Feynman diagrams or four wave mixing energy level (FWMEL) diagrams. The Feynman diagrams are useful for writing down the expression for the third order polarization $P^{(3)}(t) = Tr\{\mu\rho^{(3)}(t)\}$, while the FWMEL diagrams are useful in understanding the structure of the vibrational lines in the spectra.

In FSRS, two weak coherent optical fields - a narrow bandwidth Raman pump pulse $E_{pu}(t; T_{pu})$ of about a picosecond and an ultrashort continuum probe pulse $E_{pr}(t; T_{pr})$ of ~ 10 femtoseconds - are incident on a sample with molecular vibrations, and stimulated Raman spectra from the pump-induced gain appear in the probe spectrum. The fs probe (pr) pulse is taken to be a delta function

$$E_{pr}(t; T_{pr}) = E_{0,pr} \delta(t - T_{pr}) , \quad (3.4)$$

where $E_{0,pu}$ is a constant. It reduces the time integrals for the polarization by one and so saves computation time. The Raman pump (pu) pulse is commonly taken to be of the form

$$E_{pu}(t; T_{pu}) = E_{0,pu} g_{pu}(t; T_{pu}) e^{-i\omega_{pu}t} , \quad (3.5)$$

where $E_{0,pu}$ is a constant, and the Gaussian pulse envelope $g_{pu}(t; T_{pu})$ is given by

$$g_{pu}(t; T_{pu}) = \exp\left(-2 \ln 2 \frac{(t - T_{pu})^2}{\Delta_{pu}^2}\right) , \quad (3.6)$$

giving a laser pulse centered at T_{pu} , with intensity proportional to $|g_{pu}(t; T_{pu})|^2$ with full-width at half maximum (FWHM) of Δ_{pu} . Using different values of T_{pu} and T_{pr} allow us to see the effect of time delays between Raman pump and probe pulses on the FSRS spectra. The carrier wavelength of the Raman pump is given by $2\pi c/\omega_{pu}$, and this can be varied for off-resonance and resonance FSRS spectra.

The FSRS spectra (Raman pump-probe minus probe only) and associated polarization in the direction of the probe pulse is described by eight Feynman diagrams which are shown in Fig.

3.1. Each diagram has 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 with a transition from a higher to a lower electronic state. Arrows that point to the right correspond to the fields $E_{pu/pr}(t)$ with wavevectors $\mathbf{k}_{pu/pr}$, while the arrow that points to the left is $E_{pu}^*(t)$ with wavevector $-\mathbf{k}_{pu}$. We have drawn the diagrams to show that the wave vectors for the two pump interactions cancel, leaving a resultant polarization in the probe pulse direction. The ground electronic vibrational dephasing time is denoted by T_2 . At time t we overlap the bra and ket states mediated by the transition dipole moment μ_{12} , denoted by the dashed line, to give the third-order polarization. In the conventional diagrams, this would be represented by a dashed or wavy arrow interaction pointing to the left on the ket time-line at time t , but it would imply that the final Liouville state is in e_1 . This would be fine for off-resonance FSRS where the molecule begins in e_1 and ends in e_1 , but for resonance FSRS the final state could be in e_2 and so a dashed line as shown connecting the ket and bra vectors at time t which leaves open whether the final dashed arrow interaction at time t is on the ket or bra time-line is preferred, for the final Liouville state to be in e_1 or e_2 , respectively.

The eight diagrams have previously been grouped under four nonlinear processes: stimulated Raman scattering, SRS(I) and SRS(II), and inverse Raman scattering, IRS(I) and IRS(II) [44]. Each of SRS(I) and SRS(II) processes has three diagrams, one is labelled as resonance Raman scattering, RRS(I) or RRS(II), where there is no intermediate population of electronic state e_2 , and another two are labelled as hot luminescence, HL(I) and HL(II) or HL(III) and HL(IV), where intermediate population of electronic state e_2 is possible. In the case of SRS(I), the three diagrams differ from each other by the interaction time of the Raman pump on the ket, while for SRS(II) it is the interaction time of the probe pulse on the ket. 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 . In 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 diagrams - RRS(I), HL(I) and HL(II) - are precisely those described by Shen [61]. So, stimulated Raman scattering

Figure 3.1: Feynman dual time-line diagrams for SRS(I) (comprising RRS(I), HL(I), HL(II)), SRS(II) (comprising RRS(II), HL(III), HL(IV)), IRS(I) and IRS(II) processes describing FSRs. E_{pu} , E_{pr} denote Raman pump and probe fields. The wave vectors for the Raman pump pulse interactions cancel, leaving a third-order polarization along the probe pulse wave vector. The interaction times on the ket or bra for the Raman pump are labeled as t_1 and t_2 , and for the probe it is at T_{pr} . The vibrational dephasing time on e_1 is denoted by T_2 . The closure between the bra and ket at time t is mediated by the transition dipole moment μ_{12} .

differs from spontaneous Raman scattering in having five additional diagrams: RRS(II), HL(III), HL(IV), IRS(I) and IRS(II) where the probe pulse can lead to absorption.

Figure 3.2: Four-wave mixing energy level diagrams corresponding to the Feynman diagrams in Fig. 3.1. Time increases from left to right. Dashed arrows are interactions on the bra, and solid arrows are for interactions on the ket. The grey energy bar on the probe indicates that it is broadband. The final wavy line denotes closure between the bra and ket to give the third-order polarization.

The corresponding four-wave mixing energy level (FWMEL) diagrams are shown in Fig. 3.2. Here, 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 in off-resonance scattering, the RRS(I) term gives rise to sharp Stokes and Rayleigh gain lines with energy transferred from the Raman pump to the probe, while the IRS(I) term gives rise to sharp anti-Stokes and Rayleigh loss lines with energy transferred from the probe to the Raman pump. For resonance scattering, the lineshapes on the anti-Stokes side can be complex. In the case of HL(I) (or HL(II)), one pump interaction on the bra (or ket) at t_2 and another on the ket (or bra) at t_1 prepares a short-lived population on e_2 which is then stimulated by the probe at T_{pr} to emit and so the FSRS spectrum for HL(I) and HL(II) is broad. As for the other terms - RRS(II), HL(III), HL(IV) and IRS(II) - the wavy line closure is between a continuum of ket states due to the probe excitation with a bra of well-defined energy and so they give rise to broad spectra.

In FSRS, the difference third-order polarization with and without the Raman pump pulse and that radiates in the $\mathbf{k}_{pr}$ direction is measured and it is given by

$$\begin{aligned}
P_{\text{diff}}^{(3)}(t) &= P_{\text{pump+probe}}^{(3)}(t; \mathbf{k}_{pr}) - P_{\text{probe only}}^{(3)}(t; \mathbf{k}_{pr}) \\
&= P_{\text{RRS(I)}}^{(3)}(t; \mathbf{k}_{pr}) + P_{\text{HL(I)+HL(II)}}^{(3)}(t; \mathbf{k}_{pr}) \\
&\quad + P_{\text{RRS(II)}}^{(3)}(t; \mathbf{k}_{pr}) + P_{\text{HL(III)+HL(IV)}}^{(3)}(t; \mathbf{k}_{pr}) \\
&\quad + P_{\text{IRS(I)}}^{(3)}(t; \mathbf{k}_{pr}) + P_{\text{IRS(II)}}^{(3)}(t; \mathbf{k}_{pr}) ,
\end{aligned} \tag{3.7}$$

where we have chosen to group HL(I)+HL(II) and HL(III)+HL(IV), because of the similarity in the processes. We show below that it is possible to calculate the six polarizations: $P_{\text{RRS(I)}}^{(3)}(t; \mathbf{k}_{pr})$, $P_{\text{HL(I)+HL(II)}}^{(3)}(t; \mathbf{k}_{pr})$, $P_{\text{RRS(II)}}^{(3)}(t; \mathbf{k}_{pr})$, $P_{\text{HL(III)+HL(IV)}}^{(3)}(t; \mathbf{k}_{pr})$, $P_{\text{IRS(I)}}^{(3)}(t; \mathbf{k}_{pr})$, and $P_{\text{IRS(II)}}^{(3)}(t; \mathbf{k}_{pr})$, separately, and to obtain their individual contribution to the FSRS spectrum.

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 [5, 4, 7, 12, 11]. If we subtract

1 from this ratio, then we have the Raman gain cross section which is given by [46, 47, 48, 49]

$$\sigma_{RG}(\omega) = -\frac{4\pi}{3\epsilon_0 c n} \omega \text{Im} \left\{ P_{\text{diff}}^{(3)}(\omega) / E_{pr}(\omega) \right\} , \quad (3.8)$$

where ϵ_0 is the vacuum permittivity, c is the speed of light; n is the refractive index; $E_{pr}(\omega)$, the spectrum of the incoming probe pulse is given by

$$E_{pr}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} E_{pr}(t) dt , \quad (3.9)$$

and $P_{\text{diff}}^{(3)}(\omega)$ is the Fourier transform of the difference polarization

$$P_{\text{diff}}^{(3)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} P_{\text{diff}}^{(3)}(t) dt . \quad (3.10)$$

3.3.2 Separable displaced harmonic oscillators

In an N -dimensional separable system, the vibrational Hamiltonians on e_1 and e_2 are sums of one-dimensional Hamiltonians,

$$\mathbf{h}_1 = \sum_{r=1}^N h_{1r} , \quad (3.11)$$

$$\mathbf{h}_2 = \sum_{r=1}^N h_{2r} + E_{21} , \quad (3.12)$$

where h_{1r} and h_{2r} can be one-dimensional displaced harmonic oscillator Hamiltonians for vibrational coordinate Q_r , and E_{21} is the energy gap between the minima of the two multidimensional potential energy surfaces. The propagators are then products of one-dimensional propagators. The molecule is assumed to be initially in the ground vibrational state of electronic state e_1 ,

$$|\psi_1(\mathbf{Q}, t=0)\rangle = \prod_r |\psi_{1r0}(Q_r)\rangle . \quad (3.13)$$

With a delta function probe pulse, Eq.(3.4), the third-order polarization for RRS(I) can be written as

$$\begin{aligned} P_{RRS(I)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_{T_{pr}}^t dt_1 \int_0^{T_{pr}} dt_2 \\ &\times e^{-\gamma_1 t_2 / 2\hbar - \gamma_2 (T_{pr} - t_2) / 2\hbar - \gamma_1 (t - T_{pr}) / 2\hbar - \gamma_2 (t - t_1) / 2\hbar - \gamma_1 t_1 / 2\hbar} \\ &\times E_{pu}^*(t_2; T_{pu}) e^{iE_{21}(T_{pr} - t_2) / \hbar} e^{-iE_{21}(t - t_1) / \hbar} E_{pu}(t_1; T_{pu}) \\ &\times \prod_r S_{1,r}(t, t_1, t_2; T_{pr}, T_2) , \end{aligned} \quad (3.14)$$

where for each mode r , the three-time correlation function $S_{1, r}(t, t_1, t_2; T_{pr}, T_2)$ is defined as

$$\begin{aligned}
S_{1, r}(t, t_1, t_2; T_{pr}, T_2) &= \mu^4 e^{-iE_{1r0}(t_1-t_2)/\hbar} \\
&\times \sum_{v'} \langle \psi_{1r0}(Q_r) | e^{ih_{2r}(T_{pr}-t_2)/\hbar} | \psi_{1rv'}(Q_r) \rangle e^{iE_{1rv'}(t-T_{pr})/\hbar} \\
&\times \langle \psi_{1rv'}(Q_r) | e^{-ih_{2r}(t-t_1)/\hbar} | \psi_{1r0}(Q_r) \rangle \\
&\times \left\{ \delta_{0v'} + e^{-(t_1-T_{pr})/T_2} (1 - \delta_{0v'}) \right\}, \tag{3.15}
\end{aligned}$$

where $\delta_{0v'}$ is the Kronecker delta, and T_2 is the ground electronic state vibrational dephasing time which operates when $v' \neq 0$.

Similarly, the sum of the third-order polarization for HL(I) and HL(II) can be written as,

$$\begin{aligned}
P_{HL(I)+HL(II)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_0^{T_{pr}} dt_1 \int_0^{T_{pr}} dt_2 \\
&\times e^{-\gamma_1 t_2/2\hbar - \gamma_2(T_{pr}-t_2)/2\hbar - \gamma_1(t-T_{pr})/2\hbar - \gamma_2(t-t_1)/2\hbar - \gamma_1 t_1/2\hbar} \\
&\times E_{pu}^*(t_2; T_{pu}) e^{iE_{21}(T_{pr}-t_2)/\hbar} e^{-iE_{21}(t-t_1)/\hbar} E_{pu}(t_1; T_{pu}) \\
&\times \prod_r S_{1', r}(t, t_1, t_2; T_{pr}), \tag{3.16}
\end{aligned}$$

where the ground electronic vibrational dephasing is absent, and the three-time correlation function $S_{1', r}(t, t_1, t_2; T_{pr})$ is defined similar to Eq.(3.15),

$$\begin{aligned}
S_{1', r}(t, t_1, t_2; T_{pr}) &= \mu^4 e^{-iE_{1r0}(t_1-t_2)/\hbar} \\
&\times \sum_{v'} \langle \psi_{1r0}(Q_r) | e^{ih_{2r}(T_{pr}-t_2)/\hbar} | \psi_{1rv'}(Q_r) \rangle e^{iE_{1rv'}(t-T_{pr})/\hbar} \\
&\times \langle \psi_{1rv'}(Q_r) | e^{-ih_{2r}(t-t_1)/\hbar} | \psi_{1r0}(Q_r) \rangle. \tag{3.17}
\end{aligned}$$

The third-order polarization for RRS(II) can be written as

$$\begin{aligned}
P_{RRS(II)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_0^{T_{pr}} dt_1 \int_0^{t_1} dt_2 \\
&\times e^{-\gamma_1 t_2/2\hbar - \gamma_2(t_1-t_2)/2\hbar - \gamma_1(t-t_1)/2\hbar - \gamma_2(t-T_{pr})/2\hbar - \gamma_1 T_{pr}/2\hbar} \\
&\times E_{pu}^*(t_2; T_{pu}) e^{iE_{21}(t_1-t_2)/\hbar} E_{pu}(t_1; T_{pu}) e^{-iE_{21}(t-T_{pr})/\hbar} \\
&\times \prod_r S_{2, r}(t, t_1, t_2; T_{pr}), \tag{3.18}
\end{aligned}$$

where for each mode r , the three-time correlation function $S_{2, r}(t, t_1, t_2; T_{pr})$ is defined as

$$\begin{aligned}
S_{2, r}(t, t_1, t_2; T_{pr}) &= \mu^4 e^{-iE_{1r0}(T_{pr}-t_2)/\hbar} \\
&\times \sum_{v'} \langle \psi_{1r0}(Q_r) | e^{ih_{2r}(t_1-t_2)/\hbar} | \psi_{1rv'}(Q_r) \rangle e^{iE_{1rv'}(t-t_1)/\hbar} \\
&\times \langle \psi_{1rv'}(Q_r) | e^{-ih_{2r}(t-T_{pr})/\hbar} | \psi_{1r0}(Q_r) \rangle. \tag{3.19}
\end{aligned}$$

There is no ground electronic vibrational dephasing as the Raman pump is of narrow bandwidth such that between t_1 and T_{pr} the molecule remains in the ground vibrational state.

The sum of the third-order polarization for HL(III) and HL(IV) is given by,

$$\begin{aligned}
P_{HL(III)+HL(IV)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_{T_{pr}}^t dt_1 \int_0^{t_1} dt_2 \\
&\times e^{-\gamma_1 t_2 / 2\hbar - \gamma_2 (t_1 - t_2) / 2\hbar - \gamma_1 (t - t_1) / 2\hbar - \gamma_2 (t - T_{pr}) / 2\hbar - \gamma_1 T_{pr} / 2\hbar} \\
&\times E_{pu}^*(t_2; T_{pu}) e^{iE_{21}(t_1 - t_2) / \hbar} E_{pu}(t_1; T_{pu}) e^{-iE_{21}(t - T_{pr}) / \hbar} \\
&\times \prod_r S_{2,r}(t, t_1, t_2; T_{pr}) .
\end{aligned} \tag{3.20}$$

Here, the excited electronic vibrational dephasing is assumed to be included in the excited state lifetime γ_2^{-1} , especially when the dynamics on the excited state surface is short-lived as in the case of rhodamine 6G below.

The third-order polarization for IRS(I) can be written as

$$\begin{aligned}
P_{IRS(I)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_{T_{pr}}^t dt_1 \int_{T_{pr}}^{t_1} dt_2 \\
&\times e^{-\gamma_2 (t - t_1) / 2\hbar - \gamma_1 (t_1 - t_2) / 2\hbar - \gamma_2 (t_2 - T_{pr}) / 2\hbar - \gamma_1 T_{pr} / 2\hbar} \\
&\times e^{-iE_{21}(t - t_1) / \hbar} E_{pu}(t_1; T_{pu}) E_{pu}^*(t_2; T_{pu}) e^{-iE_{21}(t_2 - T_{pr}) / \hbar} \\
&\times \prod_r I_{1,r}(t, t_1, t_2; T_{pr}, T_2) ,
\end{aligned} \tag{3.21}$$

where the three-time correlation function $I_{1,r}(t, t_1, t_2; T_{pr}, T_2)$ is defined as

$$\begin{aligned}
I_{1,r}(t, t_1, t_2; T_{pr}, T_2) &= \mu^4 e^{-iE_{1r0}(T_{pr} - t) / \hbar} \\
&\times \sum_{v'} \langle \psi_{1r0}(Q_r) | e^{-ih_{2r}(t - t_1) / \hbar} | \psi_{1rv'}(Q_r) \rangle e^{-iE_{1rv'}(t_1 - t_2) / \hbar} \\
&\times \langle \psi_{1rv'}(Q_r) | e^{-ih_{2r}(t_2 - T_{pr}) / \hbar} | \psi_{1r0}(Q_r) \rangle \\
&\times \left\{ \delta_{0v'} + e^{-(t_1 - t_2) / T_2} (1 - \delta_{0v'}) \right\} ,
\end{aligned} \tag{3.22}$$

where T_2 is the vibrational dephasing time that operates between t_2 and t_1 when $v' \neq 0$.

Similarly, the third-order polarization for IRS(II) can be written as

$$\begin{aligned}
P_{IRS(II)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_0^{T_{pr}} dt_1 \int_0^{t_1} dt_2 \\
&\times e^{-\gamma_2 (t - T_{pr}) / 2\hbar - \gamma_1 (T_{pr} - t_1) / 2\hbar - \gamma_2 (t_1 - t_2) / 2\hbar - \gamma_1 t_2 / 2\hbar} \\
&\times e^{-iE_{21}(t - T_{pr}) / \hbar} E_{pu}^*(t_1; T_{pu}) e^{-iE_{21}(t_1 - t_2) / \hbar} E_{pu}(t_2; T_{pu}) \\
&\times \prod_r I_{2,r}(t, t_1, t_2; T_{pr}) ,
\end{aligned} \tag{3.23}$$

where the three-time correlation function $I_{2, r}(t, t_1, t_2; T_{pr})$ is defined as

$$\begin{aligned}
I_{2, r}(t, t_1, t_2; T_{pr}) &= \mu^4 e^{-iE_{1r0}(t_2-t)/\hbar} \\
&\times \sum_{v'} \langle \psi_{1r0}(Q_r) | e^{-ih_{2r}(t-T_{pr})/\hbar} | \psi_{1rv'}(Q_r) \rangle e^{-iE_{1rv'}(T_{pr}-t_1)/\hbar} \\
&\times \langle \psi_{1rv'}(Q_r) | e^{-ih_{2r}(t_1-t_2)/\hbar} | \psi_{1r0}(Q_r) \rangle, \tag{3.24}
\end{aligned}$$

and the ground electronic vibrational dephasing is absent here because of the narrow bandwidth Raman pump.

It is straightforward to evaluate the overlap matrices in the three-time correlation functions, Eqs.(3.15, 3.19, 3.22, and 3.24). For each mode, leaving out the subscript r , the overlap matrix for vibrational states $|\psi_n\rangle$ and $|\psi_0\rangle$ on the electronic ground state is given by

$$\langle \psi_n | e^{-ih_2 t/\hbar} | \psi_0 \rangle \equiv \langle \psi_n | \psi_0(t) \rangle \tag{3.25}$$

$$\begin{aligned}
\langle \psi_n | \psi_0(t) \rangle &= \exp\{-(\Delta^2/2)[1 - \exp(-i\omega t)] - i\omega t/2\} \\
&\times \frac{(-1)^n \Delta^n}{(2^n n!)^{1/2}} [1 - e^{(-i\omega t)}]^n, \tag{3.26}
\end{aligned}$$

where Δ is the mode displacement in the excited electronic state and ω is the mode frequency.

3.3.3 Inhomogeneous broadening

In our calculations below, we also take into account inhomogeneous broadening due to variations in the local environment of the molecule by using a Gaussian distribution of zero-zero energies. We define $G(t)$ as the Fourier transform of the inhomogeneous distribution function

$$G(t) = \int_0^\infty dE_{21} e^{-iE_{21}t/\hbar} G(E_{21}) \tag{3.27}$$

where

$$G(E_{21}) = \frac{\exp\left[-\frac{(E_{21}-\bar{E}_{21})^2}{2\theta^2}\right]}{\theta(2\pi)^{1/2}}, \tag{3.28}$$

and $\bar{E}_{21}$ is the average zero-zero energy, and θ is the standard deviation in the broadening.

We introduced the inhomogeneous broadening term $G(t)$ to describe the zero-zero energy variations due to the local environment of the molecule. We used a Gaussian distribution to describe the zero-zero energy, E_{21} , between the ground and excited potential energy surfaces, with distribution function given by Eqs. 3.27 and 3.28. So, in the time integral expressions

of $P^{(3)}(t)$, the terms with E_{21} are replaced with $G(t)$ functions. For every E_{21} , the same set of Feynman diagrams prevail and there is no change to the time propagation interval.

It can then be shown [67, 68, 69, 50] that the FSRS third-order polarization terms with inhomogeneous broadening are given by,

$$\begin{aligned}
P_{RRS(I)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_{T_{pr}}^t dt_1 \int_0^{T_{pr}} dt_2 \\
&\times e^{-\gamma_1 t_2 / 2\hbar - \gamma_2 (T_{pr} - t_2) / 2\hbar - \gamma_1 (t - T_{pr}) / 2\hbar - \gamma_2 (t - t_1) / 2\hbar - \gamma_1 t_1 / 2\hbar} \\
&\times E_{pu}^*(t_2; T_{pu}) e^{iE_{21}(T_{pr} - t_2) / \hbar} e^{-iE_{21}(t - t_1) / \hbar} E_{pu}(t_1; T_{pu}) G(t - t_1 - T_{pr} + t_2) \\
&\times \prod_r S_{1, r}(t, t_1, t_2; T_{pr}, T_2) , \tag{3.29}
\end{aligned}$$

$$\begin{aligned}
P_{HL(I)+HL(II)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_0^{T_{pr}} dt_1 \int_0^{T_{pr}} dt_2 \\
&\times e^{-\gamma_1 t_2 / 2\hbar - \gamma_2 (T_{pr} - t_2) / 2\hbar - \gamma_1 (t - T_{pr}) / 2\hbar - \gamma_2 (t - t_1) / 2\hbar - \gamma_1 t_1 / 2\hbar} \\
&\times E_{pu}^*(t_2; T_{pu}) e^{iE_{21}(T_{pr} - t_2) / \hbar} e^{-iE_{21}(t - t_1) / \hbar} E_{pu}(t_1; T_{pu}) G(t - t_1 - T_{pr} + t_2) \\
&\times \prod_r S_{1', r}(t, t_1, t_2; T_{pr}) , \tag{3.30}
\end{aligned}$$

$$\begin{aligned}
P_{RRS(II)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_0^{T_{pr}} dt_1 \int_0^{t_1} dt_2 \\
&\times e^{-\gamma_1 t_2 / 2\hbar - \gamma_2 (t_1 - t_2) / 2\hbar - \gamma_1 (t - t_1) / 2\hbar - \gamma_2 (t - T_{pr}) / 2\hbar - \gamma_1 T_{pr} / 2\hbar} \\
&\times E_{pu}^*(t_2; T_{pu}) e^{iE_{21}(t_1 - t_2) / \hbar} E_{pu}(t_1; T_{pu}) e^{-iE_{21}(t - T_{pr}) / \hbar} G(t - T_{pr} - t_1 + t_2) \\
&\times \prod_r S_{2, r}(t, t_1, t_2; T_{pr}) , \tag{3.31}
\end{aligned}$$

$$\begin{aligned}
P_{HL(III)+HL(IV)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_{T_{pr}}^t dt_1 \int_0^{t_1} dt_2 \\
&\times e^{-\gamma_1 t_2 / 2\hbar - \gamma_2 (t_1 - t_2) / 2\hbar - \gamma_1 (t - t_1) / 2\hbar - \gamma_2 (t - T_{pr}) / 2\hbar - \gamma_1 T_{pr} / 2\hbar} \\
&\times E_{pu}^*(t_2; T_{pu}) e^{iE_{21}(t_1 - t_2) / \hbar} E_{pu}(t_1; T_{pu}) e^{-iE_{21}(t - T_{pr}) / \hbar} G(t - T_{pr} - t_1 + t_2) \\
&\times \prod_r S_{2, r}(t, t_1, t_2; T_{pr}) . \tag{3.32}
\end{aligned}$$

$$P_{IRS(I)}^{(3)}(t; \mathbf{k}_{pr}) = E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_{T_{pr}}^t dt_1 \int_{T_{pr}}^{t_1} dt_2$$

$$\begin{aligned}
& \times e^{-\gamma_2(t-t_1)/2\hbar - \gamma_1(t_1-t_2)/2\hbar - \gamma_2(t_2-T_{pr})/2\hbar - \gamma_1 T_{pr}/2\hbar} \\
& \times e^{-iE_{21}(t-t_1)/\hbar} E_{pu}(t_1; T_{pu}) E_{pu}^*(t_2; T_{pu}) e^{-iE_{21}(t_2-T_{pr})/\hbar} G(t-t_1+t_2-T_{pr}) \\
& \times \prod_r I_{1,r}(t, t_1, t_2; T_{pr}, T_2) , \tag{3.33}
\end{aligned}$$

$$\begin{aligned}
P_{IRS(II)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_0^{T_{pr}} dt_1 \int_0^{t_1} dt_2 \\
& \times e^{-\gamma_2(t-T_{pr})/2\hbar - \gamma_1(T_{pr}-t_1)/2\hbar - \gamma_2(t_1-t_2)/2\hbar - \gamma_1 t_2/2\hbar} \\
& \times e^{-iE_{21}(t-T_{pr})/\hbar} E_{pu}^*(t_1; T_{pu}) e^{-iE_{21}(t_1-t_2)/\hbar} E_{pu}(t_2; T_{pu}) G(t-T_{pr}+t_1-t_2) \\
& \times \prod_r I_{2,r}(t, t_1, t_2; T_{pr}) . \tag{3.34}
\end{aligned}$$

All the integrands in Eqs.(3.29- 3.34) are of analytic form in the polyatomic harmonic oscillator model. However, the numerical integration for the multiple integrals can be time consuming when the Raman pump pulse is about a picosecond in duration and when the inhomogeneous broadening constant θ is large, of the order of a few hundred cm^{-1} , but the reduction of the four-time correlation functions for finite probe pulse to three-time correlation functions for a delta function probe pulse saves computation time considerably with comparable results. The theory can be generalized to FSRS from a moving wave packet which is prepared by a preceding actinic pump pulse, and also for non-separable Hamiltonians, but analytic expressions are no longer possible and the wave packet propagation and correlation functions can be computationally demanding and feasible only for a small number of dimensions.

The homogeneous damping constant γ_1 in the ground electronic state e_1 , especially when dealing with low lying vibrational levels as is the case in the application below, can be set to zero, i.e. a long lifetime for the wave packet or wavefunction on the ground state surface. The other critical parameters that may have an effect on the FSRS spectra are: the Raman pump pulse temporal width Δ_{pu} , the vibrational dephasing time T_2 , the homogeneous damping constant γ_2 in the excited electronic state e_2 , and the inhomogeneous damping constant θ . We examine how these parameters affect the FSRS spectra for rhodamine 6G (R6G) below.

3.4 Results and Discussion

Shim *et al.* [13] have obtained the absorption spectrum of R6G in MeOH:H₂O as well as the broadband stimulated Raman Stokes spectrum at 532 nm excitation with a 750 ps Raman pump pulse. It would not be possible to obtain the Raman Stokes spectrum with spontaneous resonance Raman scattering as it would be masked by strong fluorescence. From the resonance Raman cross-sections of R6G and assuming the harmonic oscillator model, the excited state displacements of 13 modes were determined and they are reproduced in Table 3.1. Frontiera *et al.* [14] also collected the absorption spectrum of R6G in methanol which is slightly narrower than that of Shim *et al.* [13]. Niu *et al.* [50] used the potential parameters in Table 3.1 and obtained a best fit of both absorption spectra with homogeneous damping constant for the excited state $\gamma_2 = 340 \text{ cm}^{-1}$, inhomogeneous damping constant $\theta = 300 \text{ cm}^{-1}$, and an average zero-zero energy $\bar{E}_{21} = 18850 \text{ cm}^{-1}$. Frontiera *et al.* [14] acquired the resonance FSRS spectra of R6G as a function of excitation wavelengths from 540-580 nm, which lie on the red side of the absorption maximum. The temporal duration of the Raman pump was up to 800 fs. Both Stokes and anti-Stokes spectra were obtained with $T_{pu} = T_{pr}$, i.e. zero pump-probe time delay. FSRS spectra at 540 nm excitation and various pump-probe time delays were also obtained for R6G. The spectra showed that the vibrational lines sharpen when T_{pr} precedes T_{pu} and broadens otherwise, and this is simply due to the temporal duration of the third order polarization which begins at T_{pr} and so is longer when T_{pr} precedes T_{pu} . Dependence of line shapes in femtosecond broadband stimulated Raman spectroscopy on pump-probe time delay also been studied by semiclassical model. [56]

The FSRS Stokes spectrum of R6G obtained by Shim *et al.* [13] at 532 nm excitation showed well resolved vibrational lines after subtraction of the broad baseline. This Stokes spectrum without the broad baseline can be described by the SRS(I) (= RRS(I)+HL(I)+HL(II)) set of terms in Fig. 3.2, and can be calculated with the relevant polarization terms Eqs.(3.14) and (3.16) for homogeneous broadening, and Eqs.(3.29) and (3.30) when inhomogeneous broadening is included. We used harmonic potentials for R6G with the parameters in Table 3.1 from Shim *et al.* [13] to calculate the effect of various parameters on this FSRS Stokes spectrum described by the SRS(I) term.

Figure 3.3 shows the calculations for the effect of the variation in the Raman pump pulse

Table 3.1: Potential parameters for rhodamine 6G from Shim et al. [13]

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

temporal width Δ_{pu} from 250-1250 fs on the FSRS Stokes spectrum at 532 nm excitation. Here, $\gamma_2 = 340 \text{ cm}^{-1}$, $\theta = 0 \text{ cm}^{-1}$, and $T_2 = \infty$. As the temporal width of the Raman pump pulse gets longer, the vibrational linewidth gets narrower, with an expected transform relationship between them.

Figure 3.4 shows the calculations for the effect of the variation in the vibrational dephasing time T_2 from 200-infinity fs on the FSRS Stokes spectrum at 532 nm excitation. Here, $\Delta_{pu} = 750 \text{ fs}$, $\gamma_2 = 340 \text{ cm}^{-1}$, and $\theta = 0 \text{ cm}^{-1}$. As the dephasing time gets longer, the vibrational linewidth gets narrower, with the total linewidth coming from both the dephasing time and the Raman pump pulse temporal width. The transform relation also applies to the dephasing time alone and the associated linewidth component.

Figure 3.5 shows the calculations for the effect of the variation in the homogeneous damping constant γ_2 in the excited electronic state e_2 from 240-540 cm^{-1} on the FSRS Stokes spectrum.

For each γ_2 , we have calculated the FSRS Stokes spectra for Raman pump excitation from 490-550 nm. Here, $\Delta_{pu} = 750$ fs, $T_2 = 1600$ fs, and $\theta = 0$ cm⁻¹. Clearly, γ_2 has no effect on the vibrational linewidth, but it affects the Raman excitation profile (REP) - the variation of Raman intensity with excitation wavelength - for a vibrational line. In Fig. 3.6, we plot the REPs of the 604 cm⁻¹ line for the four values of γ_2 from 240-540 cm⁻¹. Generally, the width of the REP increases with an increase in γ_2 because the latter means a shorter lifetime for the wave packet on the excited state surface which in turn gives a shorter duration correlation function and the transform relation then leads to a broader REP. For small γ_2 , i.e. longer lifetime on the excited state surface, however, we can see vibrational structure in the REP with a frequency interval of about 550 cm⁻¹. This is related to the well-known missing mode effect seen in absorption and REP of polyatomic molecules [70, 71].

Figure 3.7 shows the calculations for the effect of the variation in the inhomogeneous damping constant θ from 0 to 500 cm⁻¹ on the FSRS Stokes spectrum at 532-nm excitation. Here, $\Delta_{pu} = 750$ fs, $T_2 = 1600$ fs and $\gamma_2 = 340$ cm⁻¹. Clearly, θ has no effect on the vibrational line width of the Stokes spectrum. From Figure 3.7, we can see that as θ increase the intensity becomes weaker, because a larger θ means a wider distribution of zero-zero energy E_{21} (refer to Eq. 3.27), and the weight for each energy level is smaller, resulting in lower intensity for the overall spectra.

Figure 3.8 compares the calculated and the experimental FSRS Stokes spectrum of R6G obtained by Shim *et al.*[13] at 532 nm excitation. It would not have been possible to obtain such a well-resolved spectrum in Fig. 3.8(a) by spontaneous resonance Raman spectroscopy because of strong fluorescence. The Raman cross sections from the integrated areas of the bands in Fig. 8(a) are shown as a stick spectrum in Fig. 3.8(b). The experimental spectrum in Fig. 3.8(a) has had the baseline subtracted out, and so would be accounted for by the SRS(I) term. The calculated SRS(I) spectrum is shown in Fig. 3.8(c), with $\Delta_{pu} = 750$ fs, $T_2 = 1600$ fs, $\gamma_2 = 340$ cm⁻¹, $\theta = 300$ cm⁻¹, and using the harmonic oscillator potential parameters for R6G in Table 3.1. A couple of weak combination bands in the calculated results can also be made out in the experimental results. The linewidths from the experimental spectrum in Fig. 3.8(a) may be broader than the calculated spectrum in Fig. 3.8(c) for some lines due to additional damping factors and instrumental response which are not included in the theory. In general, the agreement between

theory, Fig. 3.8(c), and the stick spectrum, Fig. 3.8(b), from experiment is good for almost all the vibrational lines.

Figure 3.3: FSRS Stokes spectra at 532-nm excitation as a function of the Raman pump pulse temporal width Δ_{pu} from 250 to 1250 fs. Here, $\gamma_2 = 340 \text{ cm}^{-1}$, $\theta = 300 \text{ cm}^{-1}$ and $T_2 = \infty$

The contributions of the RRS(I), HL(I)+HL(II), RRS(II), and HL(III)+HL(IV) terms to the R6G FSRS spectra at excitations from 540-580 nm are calculated using the polarizations given by Eqs.(3.29- 3.32) and shown in Fig. 3.9. In the calculations, we used $\Delta_{pu} = 750 \text{ fs}$, $T_2 = 1600 \text{ fs}$, $\gamma_2 = 340 \text{ cm}^{-1}$, and $\theta = 300 \text{ cm}^{-1}$. Only the RRS(I) spectra show sharp vibrational lines at the mode frequencies on the Stokes side, with Raman gain arising from a transfer of energy from the Raman pump to the probe pulse. All the other terms - HL(I)+HL(II), RRS(II), and HL(III)+HL(IV) - are broad and without vibrational structure, due to short time dynamics on the excited state e_2 surface, and they would contribute to the baseline of the overall FSRS spectra. If γ_2 was smaller, allowing for longer time dynamics on the e_2 surface, we would be able to see vibrational structures of the e_2 surface in these terms. We added up RRS(I) and HL(I)+HL(II) spectra to give the SRS(I) spectra, and RRS(II) and HL(III)+HL(IV) spectra to

Figure 3.4: FSRs Stokes spectra at 532-nm excitation as a function of the vibrational dephasing time T_2 from 200 to infinity fs. Here, $\Delta_{pu} = 750 \text{ fs}$, $\gamma_2 = 340 \text{ cm}^{-1}$ and $\theta = 0 \text{ cm}^{-1}$.

Figure 3.5: FSRs Stokes spectra at 532-nm excitation as a function of the homogeneous damping constant γ_2 in the excited electronic state e_2 from 240 to 540 cm^{-1} . Here, $\Delta_{pu} = 750$ fs, $T_2 = 1600$ fs and $\theta = 0$ cm^{-1} .

Figure 3.6: Raman excitation profiles (REPs) of the 604 cm^{-1} line for the four values of γ_2 from 240 to 540 cm^{-1} in Fig. 3.5.

give the SRS(II) spectra in Fig. 3.10. The latter figure also shows the contributions of the IRS(I) and IRS(II) terms to the FSRS spectra at excitations from 540-580 nm, using the polarizations given by Eqs. (3.33- 3.34). Clearly, the SRS(I) term shows sharp Stokes gain lines, while the IRS(I) term shows sharp anti-Stokes lines which may be loss, gain or dispersive in character. The SRS(II) and IRS(II) terms are smooth and can contribute only to the baselines of the FSRS spectra.

The SRS(I), SRS(II), IRS(I) and IRS(II) spectra are added up to give the overall R6G FSRS spectra at excitation wavelengths from 540-580 nm. The anti-Stokes FSRS spectra are interesting as they can be of much stronger intensity compared to the Stokes FSRS spectra, and this is not seen in normal Raman scattering where the relationship between the two is governed by the Boltzmann distribution with the anti-Stokes spectra being very much weaker than the Stokes spectra. In Fig. 3.11(a) we show the experimental R6G anti-Stokes FSRS spectra of Frontiera *et al.* [14] as a function of the Raman pump excitation wavelength. The peaks marked with stars are the C-O solvent lines. The peak areas of the far off-resonance C-O solvent line decrease as

Figure 3.7: FSRs Stokes spectra at 532-nm excitation as a function of the inhomogeneous damping constant θ from 0 to 500 cm^{-1} . Here, $\Delta_{pu} = 750$ fs, $T_2 = 1600$ fs and $\gamma_2 = 340$ cm^{-1} .

the Raman pump excitation wavelengths decrease. It is possible that the collection times or the number of shots taken were reduces as the excitation wavelengths in the experiment approached resonance. Another explanation is that the Raman pump is getting absorbed by the sample when the excitation frequency is getting closer to absorption maximum, so the average Raman pump power interacting with the sample is less than the incident power. We have scaled our calculated FSRs spectra by the peak areas of the C-O solvent lines accordingly to compare with experiment. The calculated IRS(I) spectra on the anti-Stokes side from Fig. 3.10 1after scaling by the C-O line intensity are shown in Fig. 3.11(b); they account for the origin of the loss, gain or dispersive character of each of the observed vibrational lines seen in Fig. 3.11(a) very well. It is observed that the higher frequency vibrational lines are stronger than the lower frequency lines, and this can be explained by the IRS(I) diagram in Fig. 3.2 where the broadband probe pulse covers the absorption range followed by the Raman pump (pu^*) which is able to de-excite more intensely from closer to the absorption maximum for the higher frequency lines. By adding in the baseline

due to the SRS(II) and IRS(II) terms, we obtain Fig. 3.11(c) which compares rather well with the experimental results in Fig. 3.11(a), realizing that other processes may also contribute to the latter baselines. For example, the lineshapes of the 604 cm^{-1} and the 761 cm^{-1} bands change from dispersive to positive peaks, then to oppositely phased dispersive as the pump wavelength is tuned towards the absorption maximum from 580 nm to 540 nm, in both the experimental and calculated results.

Similar to Fig. 3.11, the experimental and calculated results for the R6G Stokes FSRS spectra are shown in Fig. 3.12. The experimental R6G Stokes FSRS spectra of Frontiera *et al.* [14] as a function of the Raman pump excitation wavelength are shown in Fig. 3.12(a). Again the collection times for the various experimental spectra differed as judged by the peak area of the C-O solvent line. The vibrational lines in these Stokes spectra are broader than those observed by Shim *et al.* [13] at 532 nm excitation, and could be due to instrumental sensitivity and resolution as the intensity of the Stokes lines decreases rather rapidly when the Raman pump wavelength is tuned away from the absorption maximum as seen in the calculated SRS(I) spectra on the Stokes side in Fig. 3.10. The calculated SRS(I) spectra on the Stokes side from Fig. 3.10 are scaled by the C-O line intensity and shown in Fig. 3.12(b); they show that the observed vibrational lines in Fig. 3.12(a) should all have Lorentzian character. Adding in the baseline due to the SRS(II) and IRS(II) terms, we obtain Fig. 3.12(c) which compares rather well with the experimental results in Fig. 3.12(a).

3.5 Conclusion

Femtosecond stimulated Raman scattering (FSRS) can be simulated with a delta function probe pulse. The four-time correlation function in the third-order polarization then reduces to a three-time correlation function which saves computation time. Analytic expressions can be derived for the three-time correlation function using the displaced harmonic oscillator model. We apply it to calculate effectively six terms - RRS(I), HL(I)+HL(II), RRS(II), HL(III)+HL(IV), IRS(I), and IRS(II) - that contribute to FSRS in rhodamine 6G (R6G) from the ground vibrational state. We look at the effect of the Raman pump pulse temporal width, the vibrational dephasing time, the homogeneous damping constant, and the inhomogeneous damping constant on the Raman

Figure 3.8: (a) FSRs Stokes spectrum of R6G obtained by Shim et al. [13] at 532-nm excitation. The C-O stretch of the solvent methanol is shown. (b) Raman cross section from integrated areas of the bands in (a). (c) Calculated SRS(I) spectrum with $\Delta_{pu} = 750$ fs, $T_2 = 1600$ fs, $\gamma_2 = 340$ cm⁻¹, $\theta = 300$ cm⁻¹, and the harmonic oscillator potential parameters for R6G in Table 3.1. Combination bands occur at $\&$, $370 + 375$ cm⁻¹ and $\#$, $375 + 604$ cm⁻¹, which can also be made out in the experimental results.

Figure 3.9: Contributions of the RRS(I), HL(I) + HL(II), RRS(II), and HL(III) + HL(IV) terms to the FSRs spectra at excitations from 540 to 580 nm calculated using the polarizations given by Eqns (3.29- 3.32) with $\Delta_{pu} = 750$ fs, $T_2 = 1600$ fs, $\gamma_2 = 340$ cm⁻¹, $\theta = 300$ cm⁻¹.

Figure 3.10: The SRS(I) spectra obtained by adding up RRS(I) and HL(I) + HL(II) spectra in Fig. 3.9, and the SRS(II) spectra obtained by adding up the RRS(II) and HL(III) + HL(IV) spectra. Contributions of the IRS(I) and IRS(II) terms to the FSRS spectra at excitations from 540 to 580 nm are calculated using the polarizations given by Eqns.(3.33- 3.34) with $\Delta_{pu} = 750$ fs, $T_2 = 1600$ fs, $\gamma_2 = 340 \text{ cm}^{-1}$, $\theta = 300 \text{ cm}^{-1}$.

Figure 3.11: a) Experimental FSRS anti-Stokes spectra as a function of the Raman pump wavelength from 540 to 580 nm of Frontiera et al. [14] (b) Calculated IRS(I) spectra on the anti-Stokes side from Fig. 3.10, but scaled based on the peak areas of the C-O solvent line in the experiment which reflect the different data collection times for the various Raman pump wavelengths. (c) Resultant FSRS spectra with the baselines due to the SRS(II) and IRS(II) terms added to the IRS(I) spectra in (b).

Figure 3.12: (a) Experimental FSRS Stokes spectra as a function of the Raman pump wavelength from 540 to 580 nm of Frontiera et al. [14] (b) Calculated SRS(I) spectra on the Stokes side from Fig. 3.10, but scaled on the basis of the peak areas of the C-O solvent line in the experiment which reflect the different data collection times for the various Raman pump wavelengths. (c) Resultant FSRS spectra with the baselines due to the SRS(II) and IRS(II) terms added to the SRS(I) spectra in (b).

Stokes spectrum which comes from the $\text{SRS(I)} (= \text{RRS(I)} + \text{HL(I)} + \text{HL(II)})$ term. The vibrational linewidth gets narrower as the Raman pump pulse duration and/or the vibrational dephasing time is lengthened due to the transform relation. The homogeneous and inhomogeneous damping constants do not affect the vibrational linewidth. However, the homogeneous damping constant affects the width and structure of the Raman excitation profile (REP) of a vibrational line where a smaller homogenous damping constant can lead to a narrower REP with missing mode structures due to the wave packet being able to remain longer on the excited state surface with a return overlap in the correlation function. Calculations with the harmonic model for R6G gave results that are consistent with experiments. It is shown that the RRS(I) term is responsible for the Stokes lines while the IRS(I) term accounts for the anti-Stokes lines, and the full FSRS spectra observed for R6G for various Raman pump wavelengths can be accounted for rather well in both the lineshapes and the relative intensity of the vibrational lines by the theory.

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Inverse Raman Bands in Ultrafast Raman Loss Spectroscopy

4.1 Abstract

Ultrafast Raman loss spectroscopy (URLS) is equivalent to anti-Stokes femtosecond stimulated Raman spectroscopy (FSRS), using a broadband probe pulse that extends to the blue of the narrow bandwidth Raman pump, and can be described as inverse Raman scattering (IRS). Using the Feynman dual time-line diagram, the third-order polarization for IRS with finite pulses can be written down in terms of a four-time correlation function. An analytic expression is obtained for the latter in the harmonic approximation which facilitates computation. We simulated the URLS of crystal violet (CV) for various resonance Raman pump excitation wavelengths using the IRS polarization expression with finite pulses. The calculated results agreed well with the experimental results of S.Umapathy *et al.*, *J. Chem. Phys.* **133**, 024505 (2010). In the limit of monochromatic Raman pump and probe pulses, we obtain the third-order susceptibility for multi-modes, and for a single mode we recover the well-known expression for the third-order susceptibility, $\chi_{IRS}^{(3)}$, for IRS. The latter is used to understand the mode dependent phase changes as a function of Raman pump excitation in the URLS of CV.

4.2 Introduction

Normal Raman scattering gives rise to weak signals which can often be enhanced by a factor of $10^4 - 10^6$ by the resonance Raman technique. However, in the case of fluorescent molecules or in the presence of fluorescent impurities, the strong fluorescence signal can overwhelm the resonance Raman signal [72, 73, 74, 75, 76, 77, 78]. Fluorescence appears on the red side of the Raman excitation wavelength, and fluorescence rejection requires a technique that records spectra on the blue side of the Raman excitation wavelength. One such technique is inverse Raman spectroscopy (IRS), which was first reported by Jones and Stoicheff [79], where a molecular medium is irradiated simultaneously by an intense monochromatic light at frequency ν_L and by a “continuum” in the region of the anti-Stokes line, and absorption (Raman loss) occurs from the “continuum” at the anti-Stokes frequency $\nu_L + \nu_M$, where ν_M is a Raman frequency of the medium. There are many advantages of IRS compared to other spectroscopic techniques. The position of the IRS spectrum in the anti-Stokes region makes the spectrum free from interference by normal fluorescence which lies in the Stokes region. The use of an ultrashort continuum pulse allows IRS to be used to study ultrafast processes. It extends the application of Raman spectroscopy to unstable species, fluorescing compounds, and low pressure gases [80, 81, 82, 83, 84, 85].

Ultrafast Raman loss spectroscopy (URLS) is a recently developed method in IRS with advantages of rapid data acquisition, high signal to noise ratio, natural fluorescence rejection and experimental ease [86, 87, 51]. URLS involves the observation of IRS signal utilizing a picosecond (ps) narrow-bandwidth Raman pump pulse and a femtosecond (fs) broadband probe pulse to the blue of the Raman pump wavelength. Both the pulses are spatially and temporally overlapped at the sample, leading to the generation of loss signal on the blue side with respect to the wavelength of the ps pulse. The URLS spectrum is obtained by either subtracting or taking the ratio of the probe signals with Raman pump on versus without.

The experimental design of URLS is similar to that of an earlier reported technique - femtosecond stimulated Raman spectroscopy (FSRS), which has been widely used to study the molecular structure and chemical reaction dynamics of physical and biological processes that occur on the ultrafast femtosecond time scale [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16]. In FSRS, a narrow-bandwidth ps Raman pump pulse overlaps with a broadband fs probe pulse to produce

Raman resonances shifted from the Raman pump wavelength on the broad probe spectrum. Unlike URLS, which obtain signals only on blue side of the fs continuum, FSRS produces signals on both blue (anti-Stokes) and red (Stokes) sides shifted from the ps Raman pump wavelength on the broad fs probe spectrum. URLS is actually a subset of FSRS. FSRS has been shown to produce fluorescence background free Raman spectrum with high signal-to-noise ratio, high frequency and high time resolution, and rapid data acquisition [4, 11]. Strong inverse Raman bands can be observed by using Raman pump and probe pulses of identical or similar carrier wavelengths [14, 50, 44, 88].

The theory of FSRS has been intensively studied and a quantum wave packet theory of FSRS has been presented. The theory is able to account for all features of the FSRS spectra which are consistent with experimental observations [41, 43, 44, 65, 50, 88]. The quantum theory showed that the FSRS is governed by four nonlinear processes: stimulated Raman scattering (SRS(I) and SRS(II)) and inverse Raman scattering (IRS(I) and IRS(II)). These four processes could be expressed as overlaps of evolving bra and ket wave packets which are given by third-order polarizations. To adopt the displaced harmonic oscillator model in multi-dimensions to represent the ground and excited potential energy surfaces, the four nonlinear processes can be written as triple time integrals over four-time correlation functions which have analytic results for any number of dimensions [50]. The four nonlinear processes accounted for various contributions to the FSRS spectra. The sum of the SRS(II) and IRS(II) terms gives rise to the broad baseline of each FSRS spectra, the SRS(I) term accounts for the sharp Stokes bands, and the IRS(I) term accounts for the sharp anti-Stokes bands. URLS should thus be described by the IRS(I) term.

Using URLS, Umapathy *et al.* [51] collected the stimulated anti-Stokes resonance Raman spectra of crystal violet (CV). A broad range of excitation wavelengths that span the red side of the absorption maximum was used, and it was observed that the phase of the inverse Raman line shapes was Raman pump frequency dependent. The most notable changes were observed for two modes, 1172 and 1620 cm^{-1} . The purpose of this work is to compare the theoretical calculations of IRS(I) (denoted as IRS henceforth) on CV with the URLS experimental results and to study the Raman pump frequency dependent inverse Raman line shapes. In Sec. 4.3, we review the third-order polarization for the IRS process in diagrammatic form where both the Feynman dual

time-line diagram as well as the corresponding four-wave mixing energy level (FWMEL) diagrams are presented. We show how to write the expression for the third-order polarization in terms of the evolving bra and ket wave packets from the diagram. Next, we describe the molecule by separable multidimensional harmonic potential surfaces with Franck-Condon displacements in the modes, which allows us to write analytic expressions for the four-time correlation functions in the time-dependent third-order polarizations. The expressions include homogeneous damping and inhomogeneous broadening. In Sec. 4.4, calculations are made with the quantum theoretical expressions of IRS and the results are compared with the absorption and resonance URLS spectra of CV, where the Raman pump pulse is about 1 ps and the probe pulse is about 10 fs. The effects of the Raman pump pulse temporal width and the Raman transition dephasing constant on the IRS spectrum are also studied. Finally, we show how to derive the expression for the third-order susceptibility of IRS in the limit of monochromatic Raman pump and probe pulses for multi-modes as well as for the commonly seen analytic expression for a single mode. The latter is used to understand the mode dependent phase changes as a function of Raman pump wavelength in the URLS of CV. We conclude in Sec. 4.5.

4.3 Theory of IRS with finite pulses

The Feynman dual time-line diagram for IRS is shown in Fig. 4.1(a). It has three field interactions on the ket at times τ_3 , τ_2 and τ_1 , 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 with a transition from a higher to a lower electronic state. In Fig. 4.1(a), arrows that point to the right are the fields $E_{pr/pu}(\tau)$ with wave vectors $\mathbf{k}_{pr/pu}$ interacting with the molecule at times $\tau_{3/2}$, while the arrow that points to the left is $E_{pu}^*(\tau)$ interacting at time τ_1 , with wave vector $-\mathbf{k}_{pu}$. It can be seen that the wave vectors for the two pump interactions cancel, leaving a resultant polarization in the probe pulse direction. The abbreviation “coh.” stands for vibrational coherence when the probe followed by the Raman pump interactions leave the molecule with different vibrational states for the ket and bra in the ground electronic state, with a resultant wave vector $\mathbf{k}_{pr} - \mathbf{k}_{pu}$. At time t we overlap the bra and ket states mediated by the transition dipole moment μ_{ge} , denoted by the dashed line, to give the

third-order polarization. The definition of the time intervals t_3 , t_2 and t_1 , which are used in the time integrations below, are $t_3 = \tau_2 - \tau_3$, $t_2 = \tau_1 - \tau_2$ and $t_1 = t - \tau_1$.

Figure 4.1: (a) Feynman dual time-line diagram for the IRS process. The wave vectors for the Raman pump pulse interactions cancel, leaving a third-order polarization along the probe pulse wave vector. The abbreviation coh. stands for coherence. (b) Four-wave mixing energy level diagram corresponding to the Feynman dual time-line diagram, (a), for fundamental IRS. Time increases from left to right. The solid arrows indicate ket interactions. The grey energy bar on the probe pulse indicates that it is broadband. The final wavy line denotes closure between the bra and ket, mediated by the transition dipole moment, to give the third-order polarization. (c) Same as (b), but for Rayleigh IRS.

The corresponding four-wave mixing energy level diagram (FWMEL), for the anti-Stokes fundamental, is shown in Fig. 4.1(b), and for the Rayleigh line in Fig. 4.1(c). Here, time increases from left to right with the same definition as in the Feynman diagram. All the interactions are on the ket and are denoted by solid arrows. The narrow bandwidth Raman pump and the broadband (grey energy bar) probe pulses are shown. The final wavy line denotes closure, mediated by the transition dipole moment μ_{ge} , between an evolving ket on the excited electronic state and the ground vibrational state bra to give the third-order polarization. The broadband probe followed by the two narrow bandwidth Raman pump interactions at times τ_2 and τ_1 lead to a third-order evolving ket with well defined energy on the excited electronic state, and the wavy line closure leads to IRS with sharp anti-Stokes, Fig. 4.1(b), and Rayleigh, Fig. 4.1(c), lines. URLS

is concerned only with the fundamental anti-Stokes lines.

It is straightforward to translate from Fig. 4.1(a) to the mathematical expression for the third-order polarization. [50] The time-dependent third-order polarization for IRS in the probe direction $\mathbf{k}_{pr}$ is given by the overlap a third-order wave packet on the ket side and a ground vibrational state on the bra side, mediated by a transition dipole moment μ_{ge} , taking into consideration inhomogeneous broadening, denoted by $G(t)$, and integrating over the three interaction times,

$$\begin{aligned}
P_{IRS}^{(3)}(t) = & \left(\frac{i}{\hbar}\right)^3 \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \\
& \times e^{-\gamma_g t/2\hbar - \gamma_e(t-\tau_1)/2\hbar - \gamma_d(\tau_1-\tau_2)/\hbar - \gamma_g(\tau_1-\tau_2)/2\hbar - \gamma_e(\tau_2-\tau_3)/2\hbar - \gamma_g\tau_3/2\hbar} \\
& \times E_{pu}(\tau_1)E_{pu}^*(\tau_2)E_{pr}(\tau_3)G(t-\tau_1+\tau_2-\tau_3)I(t, \tau_1, \tau_2, \tau_3) .
\end{aligned} \tag{4.1}$$

The four-time correlation function $I(t, \tau_1, \tau_2, \tau_3)$ is defined as

$$\begin{aligned}
I(t, \tau_1, \tau_2, \tau_3) = & \langle \psi_{g0}(\mathbf{Q}) | e^{i\mathbf{h}_g t/\hbar} \mu_{ge} e^{-i\mathbf{h}_e(t-\tau_1)/\hbar} \\
& \times \mu_{eg} e^{-i\mathbf{h}_g(\tau_1-\tau_2)/\hbar} \mu_{ge} e^{-i\mathbf{h}_e(\tau_2-\tau_3)/\hbar} \\
& \times \mu_{eg} e^{-i\mathbf{h}_g\tau_3/\hbar} | \psi_{g0}(\mathbf{Q}) \rangle
\end{aligned} \tag{4.2}$$

where $\mathbf{Q}$ is the multidimensional vibrational coordinate; $|\psi_{g0}(\mathbf{Q})\rangle$ is the initial ground vibrational state on the ground electronic state $|g\rangle$; and $\mathbf{h}_g$ and $\mathbf{h}_e$ are multidimensional vibrational Hamiltonians in the ground and excited electronic states. $G(t)$ is the Fourier transform of the inhomogeneous distribution function $G(E)$

$$G(t) = \int_0^\infty dE_{eg} e^{-iE_{eg}t/\hbar} G(E_{eg}) , \tag{4.3}$$

and

$$G(E_{eg}) = \frac{\exp\left[-\frac{(E_{eg}-\bar{E}_{eg})^2}{2\theta^2}\right]}{\theta(2\pi)^{1/2}} , \tag{4.4}$$

where E_{eg} is the zero-zero energy gap between the minima of the excited and ground multidimensional potential energy surfaces; $\bar{E}_{eg}$ is the average zero-zero energy; and θ is the standard deviation of the broadening. $E_{pu/pr}(\tau)$ in Eq.(4.1) are the Raman pump/probe electric fields; $\gamma_{g/e}$ are the homogeneous linewidths for the respective electronic states; and γ_d is the Raman vibrational dephasing time for the coherent vibrational state between times τ_2 and τ_1 .

The Raman gain (RG) spectrum in the direction of the probe pulse, $\mathbf{k}_{pr}$, can be shown to be given by [46, 47, 48],

$$\Delta I_{RG}(\omega) = \frac{8\pi^2 l C}{3n} \omega \operatorname{Im}\{E_{pr}^*(\omega) P_{IRS}^{(3)}(\omega)\} \quad (4.5)$$

where l is the cell length, C is the number of molecules per unit volume; n is the refractive index; $E_{pr}(\omega)$, the spectrum of the incoming probe pulse is given by,

$$E_{pr}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} E_{pr}(t) dt \quad (4.6)$$

and $P_{IRS}^{(3)}(\omega)$ is the Fourier transform of the difference polarization,

$$P_{IRS}^{(3)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} P_{IRS}^{(3)}(t) dt \quad (4.7)$$

In a N -dimensional separable system, the Hamiltonians are sums of one-dimensional Hamiltonians,

$$\mathbf{h}_g = \sum_{r=1}^N h_{gr} , \quad (4.8)$$

$$\mathbf{h}_e = \sum_{r=1}^N h_{er} + E_{eg} , \quad (4.9)$$

and the wave packet is a product of one-dimensional wave packets,

$$|\psi_{g0}(\mathbf{Q})\rangle = \prod_{r=1}^N |\psi_{g0_r}(Q_r)\rangle , \quad (4.10)$$

where h_{gr} and h_{er} are one-dimensional displaced harmonic oscillator Hamiltonians in mode Q_r , and E_{eg} is the energy gap between the minima of the two multidimensional potential energy surfaces. The propagators are then products of one-dimensional propagators.

Assuming that $\mu_{ge} = \mu_{eg} = \mu$ and inserting a complete basis set $\sum_{n_r} |\psi_{gn_r}(Q_r)\rangle \langle \psi_{gn_r}(Q_r)|$ for h_{gr} . The N -dimensional four-time correlation function in terms of the time intervals becomes

$$\begin{aligned} I(t, \tau_1, \tau_2, \tau_3) &= |\mu|^4 e^{-iE_{eg}(t_1+t_3)/\hbar} \\ &\times \prod_{r=1}^N e^{i\omega_r(t_1+t_2+t_3)/2} \\ &\times \sum_{n_r} e^{-i\omega_r(n_r+\frac{1}{2})t_2} \\ &\times \langle \psi_{g0_r}(Q_r) | e^{-ih_{er}t_1/\hbar} | \psi_{gn_r}(Q_r) \rangle \\ &\times \langle \psi_{gn_r}(Q_r) | e^{-ih_{er}t_3/\hbar} | \psi_{g0_r}(Q_r) \rangle , \end{aligned} \quad (4.11)$$

where the $|\psi_{g0_r}(Q_r)\rangle$ is the ground vibrational state, with $h_{g0_r}|\psi_{g0_r}(Q_r)\rangle = E_{g0_r}|\psi_{g0_r}(Q_r)\rangle = \hbar\omega_r/2|\psi_{g0_r}(Q_r)\rangle$, and ω_r is the mode r frequency.

Now, the correlation function in Eq. (4.11) for each mode is of the form $\langle \psi_{gn_r} | e^{-i\hbar_{er}t/\hbar} | \psi_{g0_r} \rangle \equiv \langle \psi_{gn_r} | \psi_{g0_r}(t) \rangle$ or its complex conjugate, and in the harmonic oscillator approximation, we obtain analytic results given by [89]

$$\begin{aligned} \langle \psi_{gn_r} | \psi_{g0_r}(t) \rangle &= \exp\{-(\Delta_r^2/2)[1 - \exp(-i\omega_r t)] - i\omega_r t/2\} \\ &\times \frac{(-1)^{n_r} \Delta_r^{n_r}}{(2^{n_r} n_r!)^{1/2}} [1 - \exp(-i\omega_r t)]^{n_r}, \end{aligned} \quad (4.12)$$

where Δ_r is the excited electronic state mode displacement relative to the ground electronic state. This facilitates computation of the third-order polarization, Eq. (4.1), and the Raman gain, Eq. (4.5).

4.4 Results and Discussion

Recently, the fluorescent material crystal violet (CV) was studied by ultrafast Raman loss spectroscopy (URLS) using a narrow band picosecond Raman pump pulse and a femtosecond broad-band probe pulse that extends to the blue of the Raman pump, with heterodyne detection along the probe pulse direction [51]. The experimental geometry is identical to femtosecond stimulated Raman spectroscopy [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16]. The anti-Stokes Raman gain spectra for URLS of CV were recorded with different Raman pump excitation energies that ranged from the red of the absorption spectrum to nearly the absorption maximum. The experimental results showed that the line shape for a mode changes in phase continuously from Lorentzian to dispersive and then to negative Lorentzian as the excitation energy is tuned from the tail of the absorption spectrum towards the absorption maximum. The phase change for different modes is asynchronous.

4.4.1 Harmonic potentials for Crystal Violet

In order to calculate IRS of CV, the normal mode frequencies and normal mode displacements must first be obtained. In the harmonic approximation, assuming no Duschinsky rotation and no change in normal mode frequencies, the relative spontaneous Raman intensities $I_k/I_{k'}$ between modes k and k' can be expressed by the Savin Formula as [38]

$$I_k/I_{k'} = \Omega_k^3 \Delta_k^2 / \Omega_{k'}^3 \Delta_{k'}^2 \quad (4.13)$$

where Ω_k is the frequency of k th mode and Δ_k is the Franck-Condon displacement of the k th mode. The Raman intensities and frequencies can be read off the spontaneous Raman spectrum of CV [90], and the relative intensities would then give the relative mode displacements. The absolute displacements together with values for E_{eg} , γ_2 , and θ , were obtained by fitting the absorption spectrum of CV in 0.1 mM ethanol [51]. The signs of the mode displacements could not be determined, but they are not important because in the harmonic model the dynamics depend only on Δ_r^2 . Table 4.1 gives the frequencies and modulus of the displacements of the 5 modes in the range of 1000 to 1700 cm^{-1} . We assume that CV is initially in the ground vibrational state in all our calculations below.

Table 4.1: Potential parameters for crystal violet

Frequency ω_r/cm^{-1}	Displacement $ \Delta_r $
1177	0.52
1306	0.28
1363	0.51
1540	0.31
1618	0.49

The absorption spectrum of CV in 0.1 mM ethanol solution [51] is shown in Fig. 4.2 (dash - dot line). We have calculated (solid line) the absorption spectrum of CV [69, 50], giving an average zero-zero energy $\bar{E}_{eg} = 16950 \text{ cm}^{-1}$, a homogeneous damping constant on the excited electronic state $\gamma_e = 200 \text{ cm}^{-1}$, and an inhomogeneous damping constant $\theta = 450 \text{ cm}^{-1}$. The homogeneous damping constant on the ground electronic state, γ_g , is set at 0 cm^{-1} . These parameters were used in all our IRS calculations below. The featureless absorption spectrum, typical for most large molecules, of full-width at half height of about 2000 cm^{-1} , arises from the Fourier transform of a short-time autocorrelation function of width about 10 fs due to the homogeneous and inhomogeneous damping together with the incommensurate frequencies and various displacements of the 5 modes. The absorption maximum of the calculated and experimental spectra is similar, at about 590 nm. The red of the absorption maximum is fitted very

well, but the blue side in the range 17000-21000 cm^{-1} shows some differences due to absorption to higher excited electronic states. The difference between the experimental absorption spectrum and the calculated spectrum is shown by the dotted line in Fig. 4.2, which lie to the blue of the absorption maximum. Fortunately, the URLS spectra for CV were taken with Raman pump wavelengths that are to the red of the absorption maximum, and so the higher excited electronic states will not contribute to the IRS calculation and a two-electronic state model suffices.

Figure 4.2: The measured absorption spectrum of crystal violet from Umapathy and coworkers [51] (dash-dot line) in ethanol. The calculated absorption spectrum (solid line) using the potential parameters in Table 4.1 together with an average zero-zero energy, $E_{eg} = 16950 \text{ cm}^{-1}$, a homogeneous damping constant on the excited electronic state, $\gamma_e = 200 \text{ cm}^{-1}$, and an inhomogeneous damping constant, $\theta = 450 \text{ cm}^{-1}$, gives a good fit of the measured absorption spectrum to the red of the absorption maximum. The difference (dotted line) between the measured and the calculated absorption spectra is attributed to higher excited electronic states. The Raman pump wavelengths for the URLS of CV are shown as arrows at: (a) 609 nm, (b) 613 nm, (c) 630 nm, (d) 637 nm, (e) 640 nm, (f) 645 nm, (g) 650 nm, (h) 654 nm, (i) 662 nm, (j) 666 nm.

4.4.2 Simulating the URLS of Crystal Violet as IRS

The Raman pump and probe pulses were taken to have a Gaussian envelope and of the form

$$E_{pu/pr}(t; T_{pu/pr}) = E_{0,pu/pr} g_{pu/pr}(t) e^{-i\omega_{pu/pr}t}, \quad (4.14)$$

where $E_{0,pu/pr}$ is a constant, and the Gaussian pulse envelope $g_{pu/pr}(t)$ is given by

$$g_{pu/pr}(t) = \exp\left(-2 \ln 2 \frac{t^2}{\Delta_{pu/pr}^2}\right), \quad (4.15)$$

giving a laser pulse centered at $t = 0$, with intensity proportional to $|g_{pu/pr}(t)|^2$ with full-width at half maximum (FWHM) of $\Delta_{pu/pr}$. The carrier wavelengths of the Raman pump and probe pulses are given by $2\pi c/\omega_{pu/pr}$, and these can be varied for off-resonance and resonance URLS spectra.

In the calculations, we have used the same carrier wavelengths for the Raman pump and probe pulses, $\omega_{pu} = \omega_{pr}$, but it is not important so long as the broadband probe spectrum can span the range of anti-Stokes bands in URLS. We have used $\Delta_{pu} = 1$ ps, similar to that used in the CV URLS experiment, and $\Delta_{pr} = 10$ fs which provides a broad window, spanning about 4000 cm^{-1} , which can stimulate Raman scattering across both the anti-Stokes and Stokes bands relative to ω_{pu} .

The Raman pump wavelengths used in the URLS of CV were (a) 609 nm, (b) 613 nm, (c) 630 nm, (d) 637 nm, (e) 640 nm, (f) 645 nm, (g) 650 nm, (h) 654 nm, (i) 662 nm, (j) 666 nm [51], and are indicated by arrows in Fig. 4.2. The URLS anti-Stokes bands for CV from -1000 cm^{-1} to -1700 cm^{-1} are reproduced in Fig. 4.3(a). Two distinct bands at -1620 cm^{-1} , assigned as ring C-C/C=C stretching where the bond order is 1.5, and -1172 cm^{-1} , assigned as in-plane ring C-H bend [91, 92], can clearly be seen. The line shape of the -1620 cm^{-1} mode changes from positive Lorentian at 666 nm excitation to negative Lorentzian at 609 nm through a dispersive form at 637-640 nm. The change in phase is slightly displaced for the -1172 cm^{-1} mode, as it evolves from oppositely phased dispersive form at 666 nm excitation to positive Lorentzian at about 640-645 nm to dispersive form at 630 nm to negative Lorentzian at 609 nm. The corresponding calculated results using the theory above for IRS are shown in Fig. 4.3(b). For the calculations, we have used the mode frequencies 1177 cm^{-1} and 1618 cm^{-1} obtained by Kelley *et al.*[90] which were used to deduce the excited and ground electronic state mode displacements, but the slight difference

in frequencies is not critical to the results. The change in phase of the line shapes with Raman pump wavelength for both modes is very well reproduced using the multidimensional harmonic model, and they are asynchronous.

Figure 4.3: (a) Experimental URLS results for crystal violet (CV) of Umapathy and coworkers [51] show the variation of the line shapes of the -1620 and -1172 cm^{-1} modes as a function of the Raman pump wavelengths from 609 to 666 nm (a-j). (b) Calculated IRS spectra of CV at Raman pump wavelengths from 609 to 666 nm (a-j). The good agreement in the change in phase of the experimental URLS bands and the calculated IRS bands as a function of the Raman pump wavelength can clearly be seen.

Figure 4.4 shows the calculations for the effect of the variation in the Raman pump pulse temporal width Δ_{pu} from 500 fs to 1500 fs on the IRS spectrum at 630-nm excitation. Here, $\Delta_{pr} = 10$ fs, $\gamma_e = 200$ cm^{-1} , $\gamma_d = 0$ cm^{-1} , and $\theta = 450$ cm^{-1} . As the temporal width of the Raman pump pulse gets longer, the IRS vibrational line width gets narrower, with an expected transform relationship between them.

Figure 4.5 shows the calculations for the effect of the variation in the Raman vibrational dephasing time γ_d from 20 cm^{-1} to 0 cm^{-1} on the IRS spectrum at 630 nm excitation. Here,

$\Delta_{pu} = 1$ ps, $\Delta_{pr} = 10$ fs, $\gamma_e = 200$ cm $^{-1}$, and $\theta = 450$ cm $^{-1}$. As the Raman vibrational dephasing time gets longer, the IRS vibrational line width gets narrower, with the total line width coming from both the Raman vibrational dephasing time and the Raman pump pulse temporal width. The transform relation also applies to the vibrational dephasing time alone and the associated line width component.

Figure 4.4: IRS spectra at 630 nm Raman pump excitation as a function of the Raman pump pulse temporal width Δ_{pu} from 500 fs to 1500 fs. Here, $\Delta_{pr} = 10$ fs, $\gamma_e = 200$ cm $^{-1}$, $\gamma_d = 0$ cm $^{-1}$, and $\theta = 450$ cm $^{-1}$.

4.4.3 Third-order susceptibility for IRS with monochromatic pulses

Monochromatic Raman pump and probe pulses are written as

$$E_{pu/pr}(t) = E_{0,pu/pr} e^{-i\omega_{pu/pr}t} \quad (4.16)$$

where $E_{0,pu/pr}$ is a constant, and the wavelengths of the Raman pump and probe pulses are given by $2\pi c/\omega_{pu/pr}$. The homogeneous damping constant γ_g in the ground electronic state $|g\rangle$, especially when dealing with low-lying vibrational levels, can be set to zero, i.e. a long lifetime for the wave packet or wave function on the ground state surface. Here, we will use the

Figure 4.5: IRS spectra at 630 nm Raman pump excitation as a function of the Raman vibrational dephasing time γ_d from 20 cm^{-1} to 0 cm^{-1} . Here, $\Delta_{pu} = 1$ ps, $\Delta_{pr} = 10$ fs, $\gamma_e = 200$ cm^{-1} , and $\theta = 450$ cm^{-1} .

time duration variables: t_1 , t_2 , and t_3 . If inhomogeneous broadening is neglected, i.e. setting $G(t_1 + t_3) = 1$, and assuming a Raman transition for mode R from $(0_1, 0_2, \dots, 0_R, \dots, 0_N) \equiv \mathbf{0}$ to $(0_1, 0_2, \dots, 1_R, \dots, 0_N) \equiv \mathbf{0}'1_R$ vibrational states, then the third-order polarization for IRS, Eq. (4.1), becomes

$$\begin{aligned}
 P_{IRS}^{(3)}(t) &= \left(\frac{i}{\hbar}\right)^3 E_{0,pu}^2 E_{0,pr} e^{-i\omega_{pr}t} \int_0^t dt_2 e^{-\gamma_d t_2 / \hbar - i(\omega_{pu} - \omega_{pr})t_2 - i\omega_R t_2} \\
 &\times \int_0^t dt_1 e^{-\gamma_e t_1 / 2\hbar + i\omega_{pr} t_1 + iE_{g0} t_1 / \hbar} \langle \psi_{g\mathbf{0}}(\mathbf{Q}) | \mu_{ge} e^{-i\mathbf{h}_e t_1 / \hbar} \mu_{eg} | \psi_{g\mathbf{0}'1_R}(\mathbf{Q}) \rangle \\
 &\times \int_0^t dt_3 e^{-\gamma_e t_3 / 2\hbar + i\omega_{pr} t_3 + iE_{g0} t_3 / \hbar} \langle \psi_{g\mathbf{0}'1_R}(\mathbf{Q}) | \mu_{ge} e^{-i\mathbf{h}_e t_3 / \hbar} \mu_{eg} | \psi_{g\mathbf{0}}(\mathbf{Q}) \rangle. \quad (4.17)
 \end{aligned}$$

Noting that the integrals over t_1 and t_3 are identical, because $\mathbf{h}_e$ is Hermitian, and using the definition of the third-order susceptibility, we obtain,

$$\begin{aligned}
 \chi_{IRS}^{(3)} &\equiv \lim_{t \rightarrow \infty} \frac{P_{IRS}^{(3)}(t)}{E_{pr}(t)} \\
 &= E_{0,pu}^2 \frac{1}{\hbar\omega_R + \hbar(\omega_{pu} - \omega_{pr}) - i\gamma_d} \\
 &\times \left\{ \frac{i}{\hbar} \int_0^\infty dt e^{i(E_{g0} + \hbar\omega_{pr})t/\hbar - \gamma_e t/2\hbar} \langle \psi_{g\mathbf{0}'1_R}(\mathbf{Q}) | \mu_{ge} e^{-i\mathbf{h}_e t/\hbar} \mu_{eg} | \psi_{g\mathbf{0}}(\mathbf{Q}) \rangle \right\}^2. \quad (4.18)
 \end{aligned}$$

It says that the third-order susceptibility for IRS is a product of a resolvent function, whose real part is dispersive and the imaginary part is a Lorentzian depicting energy conservation, and the square of the Raman amplitude. [37] It corresponds physically with Fig. 4.1(b), where vibrational resonance for IRS is achieved with $\hbar\omega_R = \hbar(\omega_{pr} - \omega_{pu})$, and the two Raman amplitudes arise from Raman interactions at τ_3 , τ_2 and τ_1 , t .

For a single mode, inserting a complete basis set $\sum_v |\psi_{ev}(Q)\rangle\langle\psi_{ev}(Q)|$ for $\mathbf{h}_e$, we obtain from Eq. (4.18),

$$\begin{aligned} \chi_{IRS}^{(3)} = & E_{0,pu}^2 \frac{1}{\hbar\omega_R + \hbar(\omega_{pu} - \omega_{pr}) - i\gamma_d} \\ & \times \left(\sum_v \frac{\langle\psi_{g1}(Q)|\psi_{ev}(Q)\rangle\langle\psi_{ev}(Q)|\psi_{g0}(Q)\rangle}{\hbar\omega_{ev,g0} - \hbar\omega_{pr} - i\gamma_e/2} \right)^2 \end{aligned} \quad (4.19)$$

where $\hbar\omega_{ev,g0} = E_{ev} - E_{g0}$; E_{ev} is the energy of the v th vibrational level of the excited state potential relative to the ground potential energy surface minimum, and E_{g0} is the energy of the ground vibrational level of the ground state potential. Equation (4.19) corresponds to the well-known third-order susceptibility for inverse Raman scattering, e.g. Eq.(4) of Tasumi and co-workers [93]. The observed IRS signal is directly proportional to the imaginary component of $\chi_{IRS}^{(3)}$. Thus, Eqs. (4.1), (4.5)-(4.7) describe IRS with finite Raman pump and probe pulses, while Eqs. (4.18) and (4.19) are for monochromatic pulses.

Tasumi and co-workers [93] have used the imaginary part of Eq. (4.18) to simulate the IRS band of rhodamine 640 at 1647 cm^{-1} as a function of the probe laser frequency. It was observed that: (a) the band shape is dispersive when the probe laser frequency is to the red of the absorption maximum, (b) it changes continuously to a negative Lorentzian as the probe laser frequency increases to around the absorption maximum, (c) with further increase in the probe laser frequency to the blue of the absorption maximum, the band shape then becomes a negative dispersion, and (d) as the probe laser frequency is increased further to the blue of the absorption maximum, the band shape becomes Lorentzian. In the case of URS of CV, the probe laser frequency (see Fig. 4.1(b)) is equivalent to the narrow band Raman pump laser frequency ω_{pu} plus the vibrational frequency ω_R , and the excitation frequencies as shown in Fig. 4.2 are all to the red of the absorption maximum. Similar to the IRS of rhodamine 640, we clearly see the lineshape signatures of (a) and (b), see Fig. 4.3(a) or 4.3(b), when $\omega_{pu} + \omega_R$ is to the red of the

absorption maximum and near the absorption maximum for CV, respectively, for both the 1172 cm^{-1} and 1620 cm^{-1} modes [51]. By extension, we also see the Lorentzian line shape preceding the dispersive line shape when $\omega_{pu} + \omega_R$ is at the red tail of the CV absorption spectrum for the 1620 cm^{-1} mode, and we also see negative dispersion preceding the Lorentzian for the 1172 cm^{-1} mode. The change in line shapes for different modes are continuous but asynchronous with Raman pump excitation frequency because of differences in frequency and displacement. The advantage of URLS or FSRS, where a broadband probe is used, is that one can obtain the IRS bands at one go rather than having to use a scanning monochromatic Raman pump (or probe) lasers as in a conventional IRS experiment [93].

4.5 Conclusion

We have shown that ultrafast Raman loss spectroscopy (URLS) is accounted for by inverse Raman scattering (IRS), and the use of a broadband probe pulse allows us to capture the IRS bands at one go. The third-order polarization for IRS with finite pulses can be written down with the aid of the Feynman dual time-line diagram for process. An analytic expression for the four-time correlation function in the third-order polarization expression can be derived assuming multidimensional harmonic potentials for the ground and excited electronic states of a molecule. We used the harmonic model to simulate the IRS of crystal violet and the calculated results agree with the experimental URLS results as a function of the resonance Raman pump excitation [51]. Lineshapes that change continuously from negative dispersive to Lorentzian, to dispersive, and then to negative Lorentzian can be seen as the Raman pump excitation is tuned from the red tail of the absorption spectrum to near the absorption maximum in both the experimental and calculated results. Increasing the Raman pump bandwidth or decreasing the Raman vibrational dephasing time, broadens the IRS bands. The multi-mode third-order susceptibility for IRS can be derived in the limit of monochromatic Raman pump and probe pulses, and in one-dimension it reduces to the well-known expression for $\chi_{IRS}^{(3)}$. The latter can be used to understand the change in lineshape as a function of the resonance Raman pump excitation.

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Conclusion and Prospects

5.1 Conclusion

This thesis presented the quantum-mechanical description and model calculation of femtosecond stimulated Raman spectroscopy. Two models were adopted for deriving analytical expressions for the third-order polarization and explaining the FSRS experimental observations, i.e. three-state model and separable displaced harmonic oscillators model. The theory was applied to simulate the FSRS of Rhodamine 6G and crystal violet. The contribution of the four nonlinear processes to FSRS was discussed. All features of FSRS were represented through the simulations. The effects of the Raman pump pulse temporal width, the vibrational dephasing time, the homogeneous damping constant, and the inhomogeneous damping constant on FSRS line shapes were studied.

Our theoretical study shows that FSRS is governed by four nonlinear processes: stimulated Raman scattering (SRS(I) and SRS(II)) and inverse Raman scattering (IRS(I) and IRS(II)). These four processes could be expressed as overlaps of evolving bra and ket wave packets. Each process is given by a third-order polarization with the mathematical expressions translated from Feynman diagrams. In three-state model approximation, the third-order polarizations been read off the dual time-line diagrams are expressed as triple time integrals, and can be calculated numerically. The results obtained with the three-state model can explain the FSRS experimental observations from a (decaying) stationary vibrational state. However it is not good enough for simulating molecules. Proper potential energy surfaces for the three states should be considered. Evolving

wave packets could be solved order by order, but there is a constraint in computational storage and time that limits it to small molecules described by a low number of vibrational modes. However, polyatomic molecules have $3N-6$ vibrational modes, where N is the number of atoms, and ten or more modes often feature in the vibrational spectra. It is useful and common to adopt the displaced harmonic oscillator model in multidimensions to represent the ground and excited potential energy surfaces of polyatomic molecules. Then, the third-order polarizations can be written as triple time integrals over four-time correlation functions, and the analytic expressions could be obtained, meanwhile, homogeneous and inhomogeneous damping could be taken into account. This separable displaced harmonic oscillators model was successfully applied to the FSRS simulations of Rhodamine 6G and crystal violet. The calculations, either in the three-state model or in separable harmonic oscillators model, showed that the four nonlinear processes accounted for various contributions to the FSRS spectra. The sum of the SRS(II) and IRS(II) terms accounted for the broad baseline of each FSRS spectra, the SRS(I) term accounted for the sharp Stokes bands of positive Lorentzian shape, and the IRS(I) term accounted for the sharp anti-Stokes bands of line shapes with complicated features.

Many features of FSRS has been shown theoretically and they are consistent with experimental results. (1) Narrow-band Raman pump gives high frequency resolution and broadband probe straddles both the Stokes and anti-Stokes sides. (2) For off-resonance, Stokes and anti-Stokes FSRS spectra show an inversion symmetry about the center with Raman Gain on the Stokes side and a Raman loss on the anti-Stokes side. The anti-Stokes side of the FSRS spectrum equal (can even be larger) in magnitude and width to the Stokes side features with identical or similar wavelength for Raman pump and probe. (3) While on resonance, the anti-Stokes FSRS signal has complicated features, change from negative signals to positive through dispersive form as the Raman pump pulse excitation wavelength is scanned through the electronic spectral profile of a molecular system. (4) The vibrational linewidth gets narrower as the Raman pump pulse duration and/or the vibrational dephasing time is lengthened. (5) The homogeneous and inhomogeneous damping constants do not affect the vibrational linewidth. However, it affects the width and structure of the Raman excitation profile (REP) of a vibrational line where a smaller homogenous damping constant can lead to a narrower REP with missing mode structures.

5.2 Prospects

The time dependent wave packet method provides a physically intuitive picture for FSRS as well as being simple and effective in calculations. Diagrammatic perturbation technique was very helpful in tracking the contributions to FSRS and obtain third-order polarizations. These method and technique could be modified for other stimulated Raman scattering processes, such as widely used techniques coherent anti-Stokes Raman scattering (CARS) and coherent Stokes Raman scattering (CSRS). Even higher order Raman scattering could be represented theoretically. One interesting work is to study the novel fifth-order spectroscopy polarizability response spectroscopy (PORS), which is a new class of coherent Raman spectroscopies intended to provide a direct view of solvent motion in the vicinity of the solute over the course of a reaction.

The perturbative wave packet approaches using separable harmonic oscillators model has been successfully applied to R6G and CV. This model overcomes the difficulty of multi-mode-calculations of large molecules due to the computational barrier on propagating multi-dimensional wave packet. It will be useful in large molecules studies. With reasonable potential energy surfaces, it is possible to calculate the various nonlinear ultrafast spectroscopic processes in more complicated photochemical and photobiological systems, such as FSRS of bacteriorhodopsin.

The current work deals with the observation of FSRS from ground vibrational state. It will also be possible to look at FSRS from a moving wavepacket created by an actinic pulse on the excited potential energy surface. Time resolved spectrum could be considered by varying time delays between the Raman pump and probe pulses, or between the actinic and probe pulses. The temporal evolution of wave packet and line shapes of vibrational spectrum could be investigated with variation of the delay time and molecular dynamics information could be obtained.

Chapter 6

Appendix

6.1 Codes for chapter 2

The following main program and subroutines of integration were provided by Dr. Sun Zhigang.

6.1.1 Main Program

```
program main
implicit real*8 (a-h,o-z)

complex*16 wi,tmp,tmp1,tmp2,tmp3
allocatable:: tt(:),fsrc(:),rmp1(:),rmp2(:)
complex*16, allocatable:: p(:),cmp1(:),cmp2(:)
dimension nd(3)

cm2au=4.55635d-6
au2fs=2.41888435d-2
pi=dacos(-1.d0)
wi=(0.d0,1.d0)

open(18,file='input')
```

```

!-----
! read parameters
!-----

read(18,*)nprint,N,dt,ncase,nout

print*,nprint,N,dt,ncase,nout

read(18,*)Taa,Tbb,Tcc

read(18,*)eba,eca

read(18,*)td,wid_R,wid_S,w_R,w_S,nws


print*, 'time step number:',N

print*, 'time step:',dt

print*, 'energy spacing:'

print*, 'ba=',eba,'ca=',eca

print*, 'lifetimes: Taa,Tbb,Tcc'

write(*, "(6E14.8)")Taa,Tbb,Tcc

print*, 'central times of pulses:',td

print*, 'pulses FWHM:',wid_R,wid_S

print*, 'pulses frequency:',w_R


pi2=2.d0*pi

!-----
! unit conversion
!-----

eba=eba*cm2au

eca=eca*cm2au

ebc=eba-eca

dt=dt/au2fs

td=td/au2fs

wid_R=wid_R/au2fs

```

```

wid_S=wid_S/au2fs

w_R=w_R*cm2au

if(nws.eq,0)then

w_S=w_R-500.d0*cm2au

else

w_s=w_s*cm2au

endif

Taa=Taa*cm2au/pi2

Tbb=Tbb*cm2au/pi2

Tcc=Tcc*cm2au/pi2

Tab=(Taa+Tbb)*0.5d0

Tba=Tab

Tcb=(Tcc+Tbb)*0.5d0

Tbc=Tcb

Tac=(Taa+Tcc)*0.5d0

Tca=Tac

print*, 'lifetimes:  Tab,Tba,Tbc,Tcb,Tac,Tca'

write(*, "(6E14.8)")Tab,Tba,Tbc,Tcb,Tac,Tca


E0=1.D-6


allocate(p(N),tt(N),cmp1(N),cmp2(N),rmpr(N),fsrsc(4*N),stat=ierr)


fac1=-2.d0*dlog(2.d0)

do i=1,N

cmp1(i)=0.d0;cmp2(i)=0.d0

t=(i-0.5d0)*dt

tt(i)=t

ER1=E0*dexp(fac1*(t-td)**2/wid_R**2)

```

```

rmpr(i)=ER1

ES2=E0*dexp(fac1*(t-td)**2/wid_S**2)

rmpr(i)=ES2

enddo

p=0.d0

fac=3.0d0

N0=N

!_____

! third-order polarization calculation

!_____

if(ncase.eq.1)then
print*, 'RRS(I) calculation!'
nd=5;nd(1)=0

call terms(p,cmp1,cmp2,Taa,Tba,Taa,Tab,dt,eba,eba,eba,eba,N, rmpr,rmps,rmpr,w_r,w_s,w_r,tt,nd)

open(15,file='RRS1')

elseif(ncase.eq.2)then
print*, 'HL(I) calculation!'
nd=5;nd(1)=0

call terms(p,cmp1,cmp2,Taa,Tba,Tbb,Tab,dt,eba,eba,eba,eba,N, rmpr,rmpr,rmps,w_r,w_r,w_s,tt,nd)

open(15,file='HL1')

elseif(ncase.eq.3)then
print*, 'HL(II) calculation!'
nd=5;nd(2)=0

call terms(p,cmp1,cmp2,Taa,Tab,Tbb,Tab,dt,eba,eba,eba,eba,N, rmpr,rmpr,rmps,w_r,w_r,w_s,tt,nd)

open(15,file='HL2')

elseif(ncase.eq.4)then
print*, 'RRS(Ip) calculation!'
nd=5;nd(1)=0

```

```

call terms(p,cmp1,cmp2,Taa,Tba,Tca,Tcb,dt,eba,ebc,eba,ebc,N, rmpr,rmps,rmpr,w_r,w_s,w_r,tt,nd)

open(15,file='RRS1p')

elseif(ncase.eq.5)then

print*, 'HL(Ip) calculation!'

nd=5;nd(1)=0

call terms(p,cmp1,cmp2,Taa,Tba,Tbb,Tcb,dt,eba,eba,ebc,ebc,N, rmpr,rmpr,rmps,w_r,w_r,w_s,tt,nd)

open(15,file='HL1p')

elseif(ncase.eq.6)then

print*, 'HL(IIp) calculation!'

nd=5;nd(2)=0

call terms(p,cmp1,cmp2,Taa,Tab,Tbb,Tcb,dt,eba,eba,ebc,ebc,N, rmpr,rmpr,rmps,w_r,w_r,w_s,tt,nd)

open(15,file='HL2p')

elseif(ncase.eq.7)then

print*, 'RRS(II) calculation!'

nd=5;nd(1)=0

call terms(p,cmp1,cmp2,Taa,Tba,Taa,Tab,dt,eba,eba,eba,eba,N, rmpr,rmpr,rmps,w_r,w_r,w_s,tt,nd)

open(15,file='RRS2')

elseif(ncase.eq.8)then

print*, 'HL(III) calculation!'

nd=5;nd(1)=0

call terms(p,cmp1,cmp2,Taa,Tba,Tbb,Tab,dt,eba,eba,eba,eba,N, rmpr,rmps,rmpr,w_r,w_s,w_r,tt,nd)

open(15,file='HL3')

elseif(ncase.eq.9)then

print*, 'HL(IV) calculation!'

nd=5;nd(2)=0

call terms(p,cmp1,cmp2,Taa,Tab,Tbb,Tab,dt,eba,eba,eba,eba,N, rmps,rmpr,rmpr,w_s,w_r,w_r,tt,nd)

open(15,file='HL4')

elseif(ncase.eq.10)then

print*, 'IRS(I) calculation!'

```

```

nd=5;nd(2)=0

call terms(p,cmp1,cmp2,Taa,Tab,Taa,Tab,dt,eba,eba,eba,eba,N, rmpr,rmpr,rmpr,w_s,w_r,w_r,tt,nd)

open(15,file='IRS1')

elseif(ncase.eq.11)then

print*, 'IRS(Ip) calculation!'

nd=5;nd(2)=0

call terms(p,cmp1,cmp2,Taa,Tab,Tac,Tab,dt,eba,eba,eba,eba,N, rmpr,rmpr,rmpr,w_s,w_r,w_r,tt,nd)

open(15,file='IRS1p')

elseif(ncase.eq.12)then

print*, 'IRS(II) calculation!'

nd=5;nd(2)=0

call terms(p,cmp1,cmp2,Taa,Tab,Taa,Tab,dt,eba,eba,eba,eba,N, rmpr,rmpr,rmpr,w_r,w_r,w_s,tt,nd)

open(15,file='IRS2')

endif


do i=1,N0

write(13,*)(i-0.5d0)*dt*au2fs,cdabs(p(i))

enddo


!-----
! calculate FSRS
!-----

fsrsc=0.d0


do i=1,N0

fsrsc(i*2-1)=imag(p(i))

fsrsc(i*2)=0.d0

enddo

```

```

call fft(fsrtc(1),fsrtc(2),N0*2,N0*2,N0*2,2)

do i=1,N0

p(i)=dcmplx(fsrtc(i*2-1),fsrtc(2*i))

enddo


do i=1,N0

t=(i-0.5d0)*dt

fsrtc(i*2-1)=real(rmps(i)*cdexp(-wi*w_S*t))

fsrtc(i*2)=imag(rmps(i)*cdexp(-wi*w_S*t))

enddo


call fft(fsrtc(1),fsrtc(2),N0*2,N0*2,N0*2,2)


do i=1,N0

write(14,*)(i-0.5d0)*dt*au2fs,fsrtc(i*2-1)

enddo


do i=1,N0

omega=(i-1.d0)*2*pi/cm2au/(dt*N0*2)

ctmp=fsrtc(2*i-1)-wi*fsrtc(2*i)

ctmp=ctmp*p(i)

if(omega.le.3.d4)write(nout,*)omega,-omega*imag(ctmp), -omega*real(ctmp)

enddo

end

```


6.1.2 Subroutines

!-----

! subroutines of ingetration

!-----

subroutine term(p,cmp1,cmp2,cmp3,Tn,dt,omega,N, nprint,wd,td,tt,nff)

implicit real*8 (a-h,o-z)

complex*16 cmp1(1),cmp2(1),cmp3(1),p(1), ctmp1,ctmp2,ctmp3,WI,cfac,csum

real*8 wd(3),tt(1)

WI=(0.d0,1.d0)

N0=N/nff

dt0=dt*nff

do i=1,N0

if(mod(i,nprint).eq.0)write(*,"(' steps done:',I4)")i

csum=0.d0

t=(i-0.5d0)*dt0

cfac=cdexp(-t*omega*wi)*dexp(-t*Tn)

do 402 j=1,nff*i-1

ctmp1=cmp1(j)*cfac

if(dabs(tt(j)-td).ge.wd(1))goto 402

do 401 k=1,j-1

ctmp2=cmp2(k)

if(dabs(tt(k)-td).ge.wd(2))goto 401

do 400 L=1,k-1

ctmp3=cmp3(L)

```

if(dabs(tt(L)-td).ge.wd(3))goto 400

csum=csum+ctmp1*ctmp2*ctmp3

400 continue

401 continue

402 continue

p(i)=csum

enddo

return

end

subroutine terms(p,c1,c2,T1,T2,T3,T4,dt,e1,e2,e3,e4,N, rmpa,rmpb,rmpc,wo1,wo2,wo3,tt,nd)

implicit real*8 (a-h,o-z)

dimension nd(1),rmpa(1),rmpb(1),rmpc(1),tt(1),wd(1)

complex*16 wi,ctmp,ctmp2,c1(1),c2(1),p(1)

complex*16, allocatable:: cmp1(:),cmp2(:),cmp3(:)

allocatable:: rmp1(:),rmp2(:),rmp3(:)

allocate(cmp1(N),cmp2(N),cmp3(N),rmp1(N),rmp2(N),rmp3(N),STAT=IERR)

wi=(0.d0,1.d0)

do i=1,n

cmp1(i)=cdexp(-wi*(wo1-e1)*tt(i))*dexp(-T1*tt(i))

if(nd(1).eq.0)cmp1(i)=dconjg(cmp1(i))

rmp1(i)=dexp(-T2*tt(i))

cmp2(i)=cdexp(-wi*(wo2-e2)*tt(i))

if(nd(2).eq.0)cmp2(i)=dconjg(cmp2(i))

rmp2(i)=dexp(-T3*tt(i))

```

```

cmp3(i)=cdexp(-wi*(wo3-e3)*tt(i))
if(nd(3).eq.0)cmp3(i)=dconjg(cmp3(i))
rmp3(i)=dexp(-T4*tt(i))
enddo

do i=1,n
do j=1,i-1
ctmp=rmpa(j)*cmp1(j)*rmp1(i-j)
c1(i)=c1(i)+ctmp
enddo
enddo

do i=1,n
do j=1,i-1
ctmp=c1(j)*rmpb(j)*cmp2(j)*rmp1(i-j)
c2(i)=c2(i)+ctmp
enddo
enddo

do i=1,n
t=tt(i)
ctmp2=cdexp(-e4*wi*t)
do j=1,i-1
ctmp=c2(j)*rmpe(j)*cmp3(j)*rmp3(i-j)*ctmp2
p(i)=p(i)+ctmp
enddo
enddo

return

```

end

```
!_____
! subroutine of Fast Fourier Transform
!_____
```

The subroutine of fft.f used in the main program is provided by Richard. C. singleton and the whole code could be gotten from the website: <http://www.netlib.org/go/fft.f>

6.2 Codes for chapter 3

The following main program and subroutines were written by Qiu Xueqing and Li Xiuting refer to the codes for chapter 4.

6.2.1 Main Program

```
program main

use mdl,only:fc12,en,fcfnew,mTTau,mTau12

use mdl,only:ne21tau, pe21taup, nr1t, pr1tau, nr2tau, pe10tau, ne10eta, pe2taup, peleta, ne2tau,
pnpitaup, npn1tau, peiw, neiw, omegaS0, iwS0

use mdl,only:disp01

implicit real*8 (a-h,o-z)

allocatable:: RQ(:),V1(:),V2(:),V3(:),DIPOLE(:,,:),EINT(:)

allocatable:: dpulse(:,,:),FABS(:,,:)

real*8,allocatable::nrgy(:,,:)

complex*16:: ataup,ataup1,aeta,aeta1

real*8:: aeta2

complex*16,allocatable:: w1(:,,:),w2(:,,:),w3(:,,:),cwk(:),eintc(:)

real*8,allocatable::fcf12(:,::,::),m411(:),ert2n(:),ert2p(:)

complex*16,allocatable::m7(:),m4(:),m17(:),m41(:),pulse(:,,:), cpulse(:,::)
```

```

real*8 wPes(40)

double precision :: mu(10), lambda

dimension Ep(10),omega(10),T0(10),delta(10),lambda(10), phi(10),phsder(10),npsudd(10)

complex*16 WI,ctemp,ctemp1,ctemp2,ctemp3,dtau

common /constants/ eV,cm2au,amu2au,au2m,pc,ph,au2fs,au2j,au2co,dielec,em,pi,WI

character*4 ch,ItoC

character*2 cht,ItoCt,chtt,prox

character*30 tbgn,tend

character*14 chrMd

integer*8 planf(10),planb(10),plansp

complex*16,allocatable:: corr(:),corr1(:),corr3(:),fcf3(:) ,fcf4(:),corr4(:)

complex*16,allocatable:: corr01(:,:),corr11(:,:),corr30(:,:), m40(:,:),m70(:,:),tQ(:) !fcf3(:)

complex*16:: ataup10(250)

integer span(2,3),nttl(3)

allocatable:: fsrsc(:),thetai(:)

complex*16,allocatable::er2E21p(:), dexexp(:,:), dexexn(:,:), exdp(:,:),exdn(:,:),ex_p(:,:),ex_n(:,:),mexp(:,:),
mexn(:,:), er2E21n(:), inho(:), eE21p(:)

dimension R1(10),R2(10),NR(10),qscal(10),qzero(10),IVB(10)

dimension dispi(50)

complex*16 ::eye=dcmplx(0.d0,1.d0)

integer N(3),MS

integer a(18)

data a/0,1,2,3,4,8,10,16,32,64,72,128,256,512,518,1024,2048,4096/

!_____

! read parameters

!_____

read*, nchirp,nprint,nstep,dt

read*, NDM,norder,norder1 !,(NR(i),i=1,NDM)

```

```

read*, npulse,(T0(i),i=1,npulse)

read*, (delta(i),i=1,npulse)

read*, ntype_Ep,(Ep(i),i=1,npulse)

read*, ntype_pulse,(lambda(i),i=1,npulse)

read*, (phi(i),i=1,npulse)

read*, (phsder(i),i=1,npulse)

read*, iwp,npes,ntype,ntheory

read*, (npsudd(i),i=1,npulse)

read*, Glife1,Glife2,Glife3,theta

read*, ttout1,ttout2,nread

read*,(wPes(i),i=1,NDM)

read*,(dispi(i),i=1,NDM)

read*,e21

read*,e21ave

read*,T2


print*, ' mode w delta'

do i=1,NDM

print*,i,wPes(i),dispi(i)

enddo

if(theta==0.d0)norder=1

if(norder<300) then

print*, 'norder should not be more than 300'

stop

endif

print*, 'Expand the inhomogeneous broadening to',norder,'.'

print*, 'Glife3 and theta are', Glife3,theta

if(norder1<0.or. (norder1<norder))then

norder1=99

```

```

print*, 'Sum all corr30.'

else

print*, 'Calculate the fft of corr', norder1

endif

prox=ItoCt(abs(norder1))

prox=ItoCt(abs(norder))

write(*, '(1X,I4, ' multi-dimensional FSRs calculation!')') NDM

print*, 'the number of pulses used:', npulse

print*, 'the peak time of the pulse (fs):'

print*, (T0(i), i=1, npulse)

print*, 'the wavelength of the pulse (nm):'

print*, (lambda(i), i=1, npulse)

print*, 'the FWHM of the pulse (fs):'

print*, (delta(i), i=1, npulse)

allocate(pulse(nstep, npulse), cpulse(nstep, npulse), dpulse(nstep, npulse))

nffac=4

nc=nstep*nffac

allocate(corr(nc), fsrsc(nc*2))

!_____

! unit conversion

!_____

eV=27.2114d0

cm2au=4.55635d-6

amu2au=1822.888d0

au2m=0.5291771d-10

pc=2.99792458d8

```

```

ph=6.626075540d-34

au2fs=2.41888435d-2

au2j=4.3597482d-18

au2co=1.602177d-19

dielec=8.8542d-12

em=9.1093897d-31

pi=dacos(-1.d0)

WI=(0.d0,1.d0)


MS=INT(ABS(e21-e21ave))

if(e21-e21ave<0.1d0)then

MS=MS+1

print*, 'For delay time<0, 1fs is added to identify.'

endif


print*, 'e21ave,e21: ',e21ave,e21 !/cm

e21ave=e21ave*cm2au

e21=e21*cm2au

wPes=wPes*cm2au

print*, 'T2:'

print*, T2

T2=T2/au2fs


print*, 'lifetime of ground state:'

print*, Glife1

Glife1=Glife1*cm2au

print*, 'lifetime of first excited state:'

print*, Glife2

Glife2=Glife2*cm2au

```



```

print*, 'lifetime of second excited state:'

print*, Glife3

Glife3=Glife3*cm2au

print*, 'Inhomogeneous broadening:'

print*, theta

theta =theta*cm2au


ttout1=ttout1/au2fs

ttout2=ttout2/au2fs


dt=dt/au2fs

ttime=nstep*dt


print*

print*, 'time step', dt, 'time iterations number', nstep

if(ttime-T0(2).lt.delta(2)*5)then

print*, ' be careful, ttime less raman pulse 5 FWHM!'

endif


if(n_type_Ep==0)then

APU=1.D12;APR=1.D12

else

APU=4.D-2;APR=1.D-2

endif

if(ntheory.eq.0)then

print*, 'perturbation theory calculation!'

if(n_type.eq.0)then

print*, 'RRS(I) calculation'

elseif(n_type.eq.1)then

```

```

print*, 'HL(I) calculation'

elseif(ntype.eq.2)then

print*, 'HL(II) calculation'

elseif(ntype.eq.3)then

print*, 'RRS(II) calculation'

elseif(ntype.eq.4)then

print*, 'HL(III) calculation'

elseif(ntype.eq.5)then

print*, 'HL(IV) calculation'

elseif(ntype.eq.6)then

print*, 'IRS(I) calculation'

elseif(ntype.eq.7)then

print*, 'IRS(II) calculation'

elseif(ntype.eq.8)then

print*, 'absorp calculation'

elseif(ntype.eq.9)then

print*, 'emission calculation'

elseif(ntype.eq.10)then

print*, 'HL(I+II) calculation'

elseif(ntype.eq.11)then

print*, 'SRS(I) calculation'

elseif(ntype.eq.12)then

print*, 'SRS(II) calculation'

elseif(ntype.eq.13)then

print*, 'HL(III+IV) calculation'

endif

print*, 'the phase of the pulse:'

print*, (phi(i), i=1, npulse)

else

```

```

stop 'something wrong with ntheory!'

endif

!_____

! parameters of pulse into atomic units

!_____

do i=1,npulse

delta(i)=delta(i)/au2fs

phsder(i)=phsder(i)/au2fs**2

T0(i)=T0(i)/au2fs

phi(i)=phi(i)*pi

if(n_type_pulse.eq.0)then

omega(i)=(pc/lambda(i))*ph*1.0d9/au2j

omega1=(pc/lambda(i))*ph*1.0d9/au2j

else

omega(i)=lambda(i)/eV

endif

if(n_type_Ep.eq.0)then

temp=dsqrt(2.d0*Ep(i)/(dielec*pc))

Ep(i)=temp*au2m*au2co/au2j

else

Ep(i)=Ep(i)/eV

endif

enddo

print*, 'the peak time of the pulse (a.u.):'

print*,(T0(i),i=1,npulse)

print*, 'the peak intensities of the pulse (a.u.):'

print*,(Ep(i),i=1,npulse)

print*, 'the wavelength of the pulse (eV):'

```

```

print*,(omega(i)*eV,i=1,npulse)

print*, 'the FWHM of the pulse (a.u.):'

print*,(delta(i),i=1,npulse)


T0(3)=T0(3)+T0(2)

N(3)=T0(3)/dt

print*, 'N(3)=', N(3)

ch=ItoC(abs(MS))

print*,ch

cht=ItoCt(abs(notype))

chtt=ItoCt(abs(ntheory))


!-----
! initialize the corr array for fsrs calculation
!-----

do i=1,nc
corr(i)=(0.d0,0.d0)

fsrsc(2*i-1)=0.d0

fsrsc(2*i)=0.d0

enddo


!-----
! define the shape of the pulse
!-----

if(nchirp.eq.0)then

call pulsedf(nstep,pulse,cpulse,Ep,delta,T0,omega,dt,npulse,phi)

else

print*, 'chirped pulse sub used!'

call pulsedfch(nstep,pulse,Ep,delta,T0,omega,dt,npulse,phi,phsder)

```

```

endif

!_____

! define detla pulse

!_____

call pulse_delta(nstep,dpulse,Ep,T0,dt,npulse,npsudd)


do i=1,nstep,4

write(102,'(14F18.10)')(i-0.5d0)*dt*au2fs,pulse(i,2),cpulse(i,2),pulse(i,3),cdabs(pulse(i,3)), dpulse(i,3)

enddo

print*, 'dpulse(N(3)+1,3)',dpulse(N(3)+1,3)


!_____

! initialize matrix

!_____

print*, 'initialize matrix '

allocate(er2E21p(0:nstep), dexexp(0:nstep,NDM), dexexn(0:nstep,NDM), expdp(0:nstep,NDM),
exdn(0:nstep,NDM), ex_p(0:nstep,NDM), ex_n(0:nstep,NDM), mexp(0:nstep,NDM), mexn(0:nstep,NDM),
er2E21n(0:nstep), inho(0:nstep), tQ(0:nstep), eE21p(0:nstep), ert2n(0:nstep), ert2p(0:nstep) )

allocate(corr01(norder,nstep), corr11(norder,nstep), corr30(norder,nstep), m40(norder,0:nstep),
m70(norder,0:nstep))


do j=1,ndm

if(ntype/=8)then

do i=0,nstep

tt=i*dt

ert2n(i)=dexp(-tt/T2)

ert2p(i)=dexp(tt/T2)

er2E21p(i)=cdexp((-Glif3/2+eye*e21)*tt) !-0.5d0*(tt*theta)**2)


```

```

er2E21n(i)=cdexp((-Glif3/2-eye*e21)*tt) !-0.5d0*(tt*theta)**2)

eE21p(i)=cdexp(eye*(e21)*tt)

tQ(i)=tt*theta

ex_p(i,j)=cdexp(eye*wPes(j)*tt)

ex_n(i,j)=1.d0/ex_p(i,j)

mexp(i,j)=-1.d0+ex_p(i,j)

mexn(i,j)=-1.d0+ex_n(i,j)

exdp(i,j)=cdexp(0.5d0*dispi(j)**2*mexp(i,j))

exdn(i,j)=cdexp(0.5d0*dispi(j)**2*mexn(i,j))

dexexp(i,j)=dispi(j)/dsqrt(2.d0)*exdp(i,j)

dexexn(i,j)=dispi(j)/dsqrt(2.d0)*exdn(i,j)

enddo

else !ntype absorption

do i=0,nstep

tt=i*dt

er2E21n(i)=cdexp((-Glif3/2-eye*e21)*tt)

exdn(i,j)=cdexp(0.5d0*dispi(j)**2*(-1.d0+cdexp(-eye*tt*wPes(j))))

er2E21p(i)=dexp(-0.5d0*(tt*theta)**2) !/dsqrt(2*pi)

enddo

endif !ntype

enddo

ncaseStep=1e2

!_____

! main propagation iteration

!_____

if(ntheory.eq.0)then ! perturbation theory calculation output

open(50,file=cht//'corr'//ch)

```

```

else ! non-perturbation theory calculation output

open(50,file=chtt//'corr'//ch)

endif

nbgn=1;nfml=nstep

do i=1,nstep

if(dabs(i*dt-T0(3));5.d0*delta(3))exit

enddo

nbgn=i

do i=nbgn,nstep

if(dabs(i*dt-T0(3));5.d0*delta(3))exit

enddo

nfml=i-1

print*, 'probe begin and final: ',nbgn,nfml

print*, 'probe begin and final: ',nbgn*dt*au2fs,nfml*dt*au2fs

select case(ntype)

!_____

! calculate RRS(I)

!_____

case(0) !RRSI

allocate(m4(0:nstep),m41(0:nstep),m7(0:nstep),m17(0:nstep),m411(0:nstep))

allocate(corr1(nstep),corr3(nstep))

do iii=1,18

ii=a(iii)

do i=0,nstep

m4(i)=1.d0

```

```

m41(i)=1.d0

m7(i)=1.d0

m17(i)=1.d0

m411(i)=1.d0

enddo

write(chrMd,200)ii+8192

print*, chrMd


do kk=0,nstep

do jj=1,NDM

if(chrMd(14-jj+1:14-jj+1)=='1')then

aeta=-dexexp(kk,jj)*mexn(kk,jj)

ataup=-dexexn(kk,jj)*mexp(kk,jj)

ataup1=ex_p(kk,jj)*ert2n(kk)

aeta1=ex_n(kk,jj)!*ert2p(kk)

aeta2=ert2p(kk)

else !0

ataup=exdn(kk,jj)

aeta=exdp(kk,jj)

aeta1=1.d0

ataup1=1.d0

aeta2=1.d0

endif

m7(kk)=m7(kk)*ataup !exdn(kk,jj) !ataup !1007

m4(kk)=m4(kk)*aeta !400

m41(kk)=m41(kk)*aeta1 !

m17(kk)=m17(kk)*ataup1

m411(kk)=m411(kk)*aeta2

enddo !jj

```



```
enddo !kk
```

```
do i=0,nstep
```

```
m41(i)=m41(i)*dconjg(pulse(i,2))
```

```
m17(i)=m17(i)*pulse(i,2)
```

```
m7(i)=m7(i)*er2E21n(i)
```

```
m4(i)=m4(i)*er2E21p(i)
```

```
factor1=1.d0
```

```
do j=1,norder
```

```
factor1=factor1*dsqrt(dble(j))
```

```
m40(j,i)=m4(i)*tQ(i)**j/factor1
```

```
m70(j,i)=m7(i)*tQ(i)**j/factor1
```

```
enddo !j
```

```
enddoli
```

```
do i=N(3)+1,nstep
```

```
ataup=0.d0
```

```
do j=N(3)+1,i-1
```

```
ataup=ataup+m7(i-j)*m17(j)
```

```
enddo
```

```
corr(i)=ataup ! *eE21p(i)
```

```
enddo !i
```

```
ataup=0.d0
```

```
do i=1,N(3)
```

```
ataup=ataup+m4(N(3)+1-i)*m41(i)*m411(N(3)+1)
```

```
enddo
```

```

do i=N(3)+1,nstep

corr(i)=-eye*ataup*corr(i)*dpulse((N(3)+1),3)

enddo


do i=N(3)+1,nstep

corr3(i)=corr3(i)+corr(i)

corr30(:,i)=corr30(:,i)+corr01(:,i)

enddo

print*,ii, ' '

enddo !iii


!_____

! calculate HLI+HLII

!_____

case(10) !HL1+2

allocate(m4(0:nstep),m41(0:nstep),m7(0:nstep),m17(0:nstep))

allocate(corr1(nstep),corr3(nstep))

do iii=1,18

ii=a(iii)


do i=0,nstep

m4(i)=1.d0

m41(i)=1.d0

m7(i)=1.d0

m17(i)=1.d0

enddo

write(chrMd,200)ii+8192

print*, chrMd

```

```

do kk=0,nstep

do jj=1,NDM

if(chrMd(14-jj+1:14-jj+1)=='1')then

aeta=-dexexp(kk,jj)*mexn(kk,jj)

ataup=-dexexn(kk,jj)*mexp(kk,jj)

ataup1=ex_p(kk,jj)

aeta1=ex_n(kk,jj)

else !0

ataup=exdn(kk,jj)

aeta=exdp(kk,jj)

aeta1=1.d0

ataup1=1.d0

endif

m7(kk)=m7(kk)*ataup !exdn(kk,jj) !ataup !1007

m4(kk)=m4(kk)*aeta !400

m41(kk)=m41(kk)*aeta1 !

m17(kk)=m17(kk)*ataup1

enddo !jj

enddo !kk

```

```

do i=0,nstep

m41(i)=m41(i)*dconjg(pulse(i,2))

m17(i)=m17(i)*pulse(i,2)

m7(i)=m7(i)*er2E21n(i)

m4(i)=m4(i)*er2E21p(i)

factor1=1.d0

do j=1,norder

factor1=factor1*dsqrt(dble(j))

m40(j,i)=m4(i)*tQ(i)**j/factor1

```

```

m70(j,i)=m7(i)*tQ(i)**j/factor1

enddo !j

enddo!i


do i=N(3)+1,nstep

ataup=0.d0

do j=1,N(3)

ataup=ataup+m7(i-j)*m17(j)

enddo

corr(i)=ataup ! *eE21p(i)

enddo !i


ataup=0.d0

do i=1,N(3)

ataup=ataup+m4(N(3)+1-i)*m41(i)

enddo


do i=N(3)+1,nstep

corr(i)=-eye*ataup*corr(i)*dpulse(N(3)+1,3) !*cpulse(N(3)+1,3)

enddo


do i=N(3)+1,nstep

corr3(i)=corr3(i)+corr(i)

corr30(:,i)=corr30(:,i)+corr01(:,i)

enddo

print*,ii,' '

enddo !iii

!_____

```

```

! calculate SRS(I)

!_____

case(11) !SRSI

allocate(m4(0:nstep),m41(0:nstep),m7(0:nstep),m17(0:nstep))

allocate(corr1(nstep),corr3(nstep))

do iii=1,18

ii=a(iii)


do i=0,nstep

m4(i)=1.d0

m41(i)=1.d0

m7(i)=1.d0

m17(i)=1.d0

enddo

write(chrMd,200)ii+8192

print*, chrMd


do kk=0,nstep

do jj=1,NDM

if(chrMd(14-jj+1:14-jj+1)=='1')then

aeta=-dexexp(kk,jj)*mexn(kk,jj)

ataup=-dexexn(kk,jj)*mexp(kk,jj)

ataup1=ex_p(kk,jj)

aeta1=ex_n(kk,jj)

else !0

ataup=exdn(kk,jj)

aeta=exdp(kk,jj)

aeta1=1.d0

ataup1=1.d0

```

```

endif

m7(kk)=m7(kk)*ataup !exdn(kk,jj) !ataup !1007

m4(kk)=m4(kk)*aeta !400

m41(kk)=m41(kk)*aeta1 !

m17(kk)=m17(kk)*ataup1

enddo !jj

enddo !kk

```

```

do i=0,nstep

m41(i)=m41(i)*dconjg(pulse(i,2))

m17(i)=m17(i)*pulse(i,2)

m7(i)=m7(i)*er2E21n(i)

m4(i)=m4(i)*er2E21p(i)

```

```

factor1=1.d0

do j=1,norder

factor1=factor1*dsqrt(dble(j))

m40(j,i)=m4(i)*tQ(i)**j/factor1

m70(j,i)=m7(i)*tQ(i)**j/factor1

enddo !j

enddo!i

```

```

do i=N(3)+1,nstep

ataup=0.d0

do j=1,i-1

ataup=ataup+m7(i-j)*m17(j)

enddo

corr(i)=ataup ! *eE21p(i)

enddo !i

```

```

print*, 'm4 '

ataup=0.d0

do i=1,N(3)

ataup=ataup+m4(N(3)+1-i)*m41(i)

enddo


do i=N(3)+1,nstep

corr(i)=-eye*ataup*corr(i)*dpulse(N(3)+1,3) !*cpulse(N(3)+1,3)

enddo


do i=N(3)+1,nstep

corr3(i)=corr3(i)+corr(i)

corr30(:,i)=corr30(:,i)+corr01(:,i)

enddo

print*,ii, ' '

enddo !iii


!_____

! calculate SRS(II)

!_____

case(12)!SRSII

allocate(m4(0:nstep),m41(0:nstep),m7(0:nstep),m17(0:nstep))

allocate(corr1(nstep),corr3(nstep))

do iii=1,18

ii=a(iii)


do i=0,nstep

m4(i)=1.d0

m41(i)=1.d0

```

```

m7(i)=1.d0

m17(i)=1.d0

enddo

write(chrMd,200)ii+8192


do kk=0,nstep

do jj=1,NDM

if(chrMd(14-jj+1:14-jj+1)=='1')then

aeta=-dexexp(kk,jj)*mexn(kk,jj)

ataup=-dexexn(kk,jj)*mexp(kk,jj)

ataup1=ex_p(kk,jj)

aeta1=ex_n(kk,jj)

else !0

ataup=exdn(kk,jj)

aeta=exdp(kk,jj)

aeta1=1.d0

ataup1=1.d0

endif

m7(kk)=m7(kk)*ataup !exdn(kk,jj) !ataup !1007

m4(kk)=m4(kk)*aeta !400

m41(kk)=m41(kk)*aeta1 !

m17(kk)=m17(kk)*ataup1

enddo !jj

enddo !kk


do i=0,nstep

m41(i)=m41(i)*dconjg(pulse(i,2))

m17(i)=m17(i)

m7(i)=m7(i)*er2E21n(i)

```



```

m4(i)=m4(i)*er2E21p(i)

factor1=1.d0

do j=1,norder

factor1=factor1*dsqrt(dble(j))

enddo !j

enddo!i


do i=1,nstep

ataup=0.d0

do j=1,i-1

ataup=ataup+m4(i-j)*m41(j)

enddo

corr1(i)=ataup

enddo


do j=N(3)+1,nstep

ataup=0.d0

do i=1,j-1

ataup=ataup+corr1(i)*m7(j-N(3)-1)*m17(N(3)+1)*pulse(i,2)

enddo

corr(j)=-eye*ataup*dpulse(N(3)+1,3) !*cpulse(N(3)+1,3)

enddo !j


do i=N(3)+1,nstep

corr3(i)=corr3(i)+corr(i)

enddo

print*,ii, ' '

enddo !iii

```

```

!_____

! calculate RRS(II)

!_____

case(3)!RRSII

allocate(m4(0:nstep),m41(0:nstep),m7(0:nstep),m17(0:nstep))

allocate(corr1(nstep),corr3(nstep))

do iii=1,18

ii=a(iii)


do i=0,nstep

m4(i)=1.d0

m41(i)=1.d0

m7(i)=1.d0

m17(i)=1.d0

enddo

write(chrMd,200)ii+8192


do kk=0,nstep

do jj=1,NDM

if(chrMd(14-jj+1:14-jj+1)=='1')then

aeta=-dexexp(kk,jj)*mexn(kk,jj)

ataup=-dexexn(kk,jj)*mexp(kk,jj)

ataup1=ex_p(kk,jj)

aeta1=ex_n(kk,jj)

else !0

ataup=exdn(kk,jj)

aeta=exdp(kk,jj)

aeta1=1.d0

ataup1=1.d0

```

```

endif

m7(kk)=m7(kk)*ataup !exdn(kk,jj) !ataup !1007

m4(kk)=m4(kk)*aeta !400

m41(kk)=m41(kk)*aeta1 !

m17(kk)=m17(kk)*ataup1

enddo !jj

enddo !kk

```

```

do i=0,nstep

m41(i)=m41(i)*dconjg(pulse(i,2))

m17(i)=m17(i)

m7(i)=m7(i)*er2E21n(i)

m4(i)=m4(i)*er2E21p(i)

factor1=1.d0

do j=1,norder

factor1=factor1*dsqrt(dble(j))

enddo !j

enddo!i

```

```

do i=1,nstep

ataup=0.d0

do j=1,i-1

ataup=ataup+m4(i-j)*m41(j)

enddo

corr1(i)=ataup

enddo

```

```

do j=N(3)+1,nstep

ataup=0.d0

```

```

do i=1,N(3)

ataup=ataup+corr1(i)*m7(j-N(3)-1)*m17(N(3)+1)*pulse(i,2)

enddo

corr(j)=-eye*ataup*dpulse(N(3)+1,3) !*cpulse(N(3)+1,3)

enddo !j


do i=N(3)+1,nstep

corr3(i)=corr3(i)+corr(i)

enddo

print*,ii,' '

enddo !iii


!_____

! calculate HLIII+HLIV

!_____

case(13)!HLIII+HLIV

allocate(m4(0:nstep),m41(0:nstep),m7(0:nstep),m17(0:nstep))

allocate(corr1(nstep),corr3(nstep))

do iii=1,18

ii=a(iii)


do i=0,nstep

m4(i)=1.d0

m41(i)=1.d0

m7(i)=1.d0

m17(i)=1.d0

enddo

write(chrMd,200)ii+8192

```

```

do kk=0,nstep

do jj=1,NDM

if(chrMd(14-jj+1:14-jj+1)=='1')then

aeta=-dexexp(kk,jj)*mexn(kk,jj)

ataup=-dexexn(kk,jj)*mexp(kk,jj)

ataup1=ex_p(kk,jj)

aeta1=ex_n(kk,jj)

else !0

ataup=exdn(kk,jj)

aeta=exdp(kk,jj)

aeta1=1.d0

ataup1=1.d0

endif

m7(kk)=m7(kk)*ataup !exdn(kk,jj) !ataup !1007

m4(kk)=m4(kk)*aeta !400

m41(kk)=m41(kk)*aeta1 !

m17(kk)=m17(kk)*ataup1

enddo !jj

enddo !kk


do i=0,nstep

m41(i)=m41(i)*dconjg(pulse(i,2))

m17(i)=m17(i)

m7(i)=m7(i)*er2E21n(i)

m4(i)=m4(i)*er2E21p(i)

factor1=1.d0

do j=1,norder

factor1=factor1*dsqrt(dble(j))

enddo !j

```

```

enddo!i

do i=1,nstep
    ataup=0.d0
    do j=1,i-1
        ataup=ataup+m4(i-j)*m41(j)
    enddo
    corr1(i)=ataup
enddo

do j=N(3)+1,nstep
    ataup=0.d0
    do i=N(3)+1,j-1
        ataup=ataup+corr1(i)*m7(j-N(3)-1)*m17(N(3)+1)*pulse(i,2)
    enddo
    corr(j)=-eye*ataup*dpulse(N(3)+1,3) !*cpulse(N(3)+1,3)
enddo !j

do i=N(3)+1,nstep
    corr3(i)=corr3(i)+corr(i)
enddo

print*,ii,' '
enddo !iii

!_____
! calculate IRS(I)
!_____

case(6)!IRSI

```

```

allocate(m4(0:nstep),m41(0:nstep),m7(0:nstep),m17(0:nstep),m411(0:nstep))

allocate(corr1(nstep),corr3(nstep))

do iii=1,18

ii=a(iii)


do i=0,nstep

m4(i)=1.d0

m41(i)=1.d0

m7(i)=1.d0

m17(i)=1.d0

m411(i)=1.d0

enddo

write(chrMd,200)ii+8192


do kk=0,nstep

do jj=1,NDM

if(chrMd(14-jj+1:14-jj+1)=='1')then

aeta=-dexexn(kk,jj)*mexp(kk,jj)

ataup= dexexn(kk,jj)*mexn(kk,jj)

ataup1=ex_p(kk,jj)*ert2p(kk)

aeta1=ex_n(kk,jj)

aeta2=ert2n(kk)

else !0

ataup=exdn(kk,jj) !1007

aeta=exdn(kk,jj) !400

aeta1=1.d0

ataup1=1.d0

aeta2=1.d0

endif

```

```

m7(kk)=m7(kk)*ataup !exdn(kk,jj) !ataup !1007

m4(kk)=m4(kk)*aeta !400

m41(kk)=m41(kk)*aeta1 !

m411(kk)=m411(kk)*aeta2 !T2

m17(kk)=m17(kk)*ataup1

enddo !jj

enddo !kk


do i=0,nstep

m17(i)=m17(i)*dconjg(pulse(i,2))

m7(i)=m7(i)*er2E21n(i)

m4(i)=m4(i)*er2E21n(i)

factor1=1.d0

do j=1,norder

factor1=factor1*dsqrt(dble(j))

ataup=(eye*tQ(i))**j

m40(j,i)=m4(i)*ataup /factor1

m70(j,i)=m7(i)*ataup/factor1

enddo !j

enddo!i


do i=1,nstep

ataup=0.d0

ataup10(1:norder)=0.d0

do j=N(3)+1,i-1

ataup=ataup+m7(j-N(3)-1)*m17(j)

ataup10(1:norder)=ataup10(1:norder)+m70(:,j-N(3)-1)*m17(j)

enddo

corr1(i)=ataup !*m411(i)

```



```

corr11(:,i)=ataup10(1:norder)

enddo

do i=N(3)+1,nstep

ataup=0.d0

ataup10(1:norder)=0.d0

do j=N(3)+1,i-1

ataup=ataup+corr1(j)*m4(i-j)*pulse(j,2) !*m411(j) !i*er2E21n(i-j)

ataup10(1:norder)=ataup10(1:norder)+corr11(:,j)*m40(:,i-j)*pulse(j,2)

enddo

corr(i)=-eye*ataup*m41(i)*dpulse(N(3)+1,3) !*cpulse(N(3)+1,3)

corr01(:,i)=-eye*ataup10(1:norder)*m41(i)*pulse(N(3)+1,3)

enddo

do i=N(3)+1,nstep

corr3(i)=corr3(i)+corr(i)

corr30(:,i)=corr30(:,i)+corr01(:,i)

enddo

print*,ii, ' '

enddo !iii

!_____

! calculate IRS(II)

!_____

case(7) !IRSII

allocate(m4(0:nstep),m41(0:nstep),m7(0:nstep),m17(0:nstep))

```

```

allocate(corr1(nstep),corr3(nstep))

do iii=1,18

ii=a(iii)


do i=0,nstep

m4(i)=1.d0

m41(i)=1.d0

m7(i)=1.d0

m17(i)=1.d0

enddo

write(chrMd,200)ii+8192


do kk=0,nstep

do jj=1,NDM

if(chrMd(14-jj+1:14-jj+1)=='1')then

aeta=-dexexn(kk,jj)*mexp(kk,jj)

ataup= dexexn(kk,jj)*mexn(kk,jj)

ataup1=ex_p(kk,jj)

aeta1=ex_n(kk,jj)

else !0

ataup=exdn(kk,jj)

aeta=exdn(kk,jj)

aeta1=1.d0

ataup1=1.d0

endif

m7(kk)=m7(kk)*ataup !exdn(kk,jj) !ataup !1007

m4(kk)=m4(kk)*aeta !400

m41(kk)=m41(kk)*aeta1 !

m17(kk)=m17(kk)*ataup1

```

```

enddo !jj

enddo !kk


do i=0,nstep

m17(i)=m17(i)*dconjg(pulse(i,2))

m7(i)=m7(i)*er2E21n(i)

m4(i)=m4(i)*er2E21n(i)

factor1=1.d0

do j=1,norder

factor1=factor1*dsqrt(dble(j))

ataup=(eye*tQ(i))**j

m40(j,i)=m4(i)*ataup/factor1

m70(j,i)=m7(i)*ataup/factor1

enddo !j

enddo!i


do i=1,nstep

ataup=0.d0

ataup10(1:norder)=0.d0

do j=1,i-1

ataup=ataup+m7(i-j)*pulse(j,2) ! ipulse(i,2)

ataup10(1:norder)=ataup10(1:norder)+m70(:,i-j)*pulse(j,2)

enddo

corr(i)=ataup*m17(i)

corr01(:,i)=ataup10(1:norder)*m17(i)

enddo

```

```

    ataup=0.d0

    ataup10(1:norder)=0.d0

    do j=1,N(3)

    ataup=ataup+corr(j)

    ataup10(1:norder)=ataup10(1:norder)+corr01(:,j)

    enddo

    do i=N(3)+1,nstep

    corr(i)=-eye*ataup*m4(i-N(3)-1)*m41(i)*dpulse(N(3)+1,3) !*cpulse(N(3)+1,3)

    enddo

    do i=N(3)+1,nstep

    corr3(i)=corr3(i)+corr(i)

    corr30(:,i)=corr30(:,i)+corr01(:,i)

    enddo

    print*,ii, ' '

    enddo !iii

!-----
! calculate absorption
!-----

case(8) !absorption

allocate(m7(0:nstep),m17(0:nstep))

allocate(corr1(nstep),corr3(nstep))

do ii=0,0,2**NDM-1

    do i=0,nstep

    m7(i)=1.d0

    m17(i)=1.d0

```

```

enddo

write(chrMd,200)ii+8192


do kk=0,nstep

do jj=1,NDM

ataup=exdn(kk,jj)

m7(kk)=m7(kk)*ataup !exdn(kk,jj) !ataup !1007

enddo !jj

enddo !kk


do i=0,nstep

m7(i)=m7(i)*er2E21n(i)*er2E21p(i)

enddo!i


do i=1,nstep

ataup=0.d0

do j=1,i-1

ataup=ataup+m7(i-j)*pulse(j,3) ! ipulse(i,2)

enddo

corr(i)=ataup*eye*dt*2.d0

enddo

do j=1,nstep,ncaseStep

ataup=corr(j)

if(cdabs(ataup)>1.d-50)then

write(50,100)j*dt*au2fs,cdabs(ataup),dreal(ataup),dimag(ataup)

else

write(50,100)j*dt*au2fs,0.d0,0.d0,0.d0 !cdabs(ataup),dreal(ataup)

endif

enddo !j

```

```

if(mod(ii,ncaseStep)==0)print*,ii,' '
enddo !ii

goto 400

case default

print*, 'wrong in ncase'

stop

endselect


do j=1,nstep

corr(j)=corr3(j)*dt**3

write(50,100)j*dt*au2fs,dreal(corr(j)),dimag(corr(j))

enddo


400 continue

open(88,file=cht//fsrs//ch//'_.'/prox)

open(89,file=cht//fs//ch )

do i=1,nstep

fsrsc(2*i-1)=dreal(corr(i))*2

fsrsc(2*i)=0.d0 ! dimag(corr(i))

enddo


call fft(fsrsc(1),fsrsc(2),nc,nc,nc,2)

do i=1,nc

corr(i)=dcmplx(fsrsc(2*i-1),fsrsc(2*i))

enddo


do i=1,nc

fsrsc(2*i-1)=0.d0

fsrsc(2*i)=0.d0

enddo

```

```

do i=1,nstep

fsrsc(2*i-1)=dpulse(i,3) !*(e21-omega(2))

enddo

call fft(fsrsc(1),fsrsc(2),nc,nc,nc,2)

if(ntype/=8)then

Ezero=omega(2)

Erange=4000.D0*cm2au

print*, ctempe

do i=1,nc

otemp=2.d0*pi*(i-1)/(dt*nc)

if(otemp.le.Ezero+Erange.and.otemp.ge.Ezero-Erange)then

ctemp=fsrsc(2*i-1)+WI*fsrsc(2*i)

aotemp=(otemp-Ezero)/cm2au

write(88,'(14E26.10)')(aotemp), -imag(corr(i)*dconjg(ctemp))*otemp, -imag(corr(i))*otemp,
-imag(corr(i)/ctemp)*otemp, -real(corr(i)*ctemp)*otemp, cdabs(ctemp),dreal(corr(i)), dimag(corr(i))
,cdabs(corr(i))

write(89,'(14E26.10)') -imag(corr(i)/ctemp)*otemp

endif

enddo

else lntype

Ezero=omega(3)

Erange=4000.D0*cm2au

do i=1,nc

otemp=2.d0*pi*(i-1)/(dt*nc)

if(otemp.le.Ezero+Erange.and.otemp.ge.Ezero-Erange)then

ctemp=fsrsc(2*i-1)+WI*fsrsc(2*i)

aotemp=otemp/cm2au

```

```

write(88,'(14E26.10)')(aotemp),imag(corr(i)*dconj(ctemp))*otemp,imag(corr(i)/ctemp)*otemp,-
real(corr(i)*ctemp)*otemp ,cdabs(ctemp),cdabs(otemp*corr(i)/ctemp)

endif

enddo

endif

close(88)

close(89)

100 format(524E26.10)

200 format(b14)

end

```

6.2.2 Subroutines

```

!_____

! define the chirped pulse

!_____

subroutine pulsedfch(nstep,pulse,Ep,delta,T0,omega,dt,npulse,phi,phsder)

implicit real*8 (a-h,o-z)

dimension pulse(npulse,1),ep(1),delta(1),T0(1),omega(1)

dimension phi(1),phsder(1),deltap(npulse), phi0(npulse),alpha(npulse),delta1(npulse)

complex*16 ctmp,WI

au2fs=2.41888435d-2

WI=(0.d0,1.d0)

do i=1,npulse

delta1(i)=delta(i)/dsqrt(4.d0*dlog(2.d0)) ! from FWHM trans into delta

Deltap(i)=delta1(i)*dsqrt(1.d0+(2.d0*phsder(i)/delta1(i)**2)**2)

```



```

alpha(i)=2.d0*phsder(i)/(delta1(i)**4+(2.d0*phsder(i))**2)

phi0(i)=datan(-alpha(i)*deltap(i)**2)*0.5d0

enddo


tmp=au2fs*dsqrt(4.d0*dlog(2.d0))

print*, 'chirped pulse used in fs'

print*, (delta1(i)*tmp, i=1, npulse)

print*, (deltap(i)*tmp, i=1, npulse)

print*, 'chirped rate'

print*, (alpha(i), i=1, npulse)

print*, 'uniformal phase shift, phi0='

print*, (phi0(i), i=1, npulse)


do j=1, npulse

do i=1, nstep

t=(i-0.5d0)*dt

pulse(j,i)=0.d0

if(dabs(t-T0(j)).lt.deltap(j)*5.d0)then

ctmp=ep(j)*dsqrt(delta1(j)/deltap(j))*dexp(-(t-T0(j))**2/deltap(j)**2)*cdexp(-WI*alpha(j)*(t-
T0(j))**2) *cdexp(-WI*(omega(j)*(t-T0(j))+phi(j)+phi0(j)))

pulse(j,i)=0.5D0*(ctmp+dconjg(ctmp))

endif

enddo

enddo

return

end

!_____

! define the pulse of delta shape

```

```

!-----

subroutine pulse_delta(nstep,pulse,Ep,T0,dt, npulse,npsudd)

implicit real*8 (a-h,o-z)

dimension pulse(nstep,1),Ep(1),T0(1),npsudd(1)

do i=1,npulse

if(npsudd(i).ne.0)print*, i,'th pulse has delta shape'

enddo

do i=1,npulse

init=0

if(npsudd(i).ne.0)then

do j=1,nstep

temp=(j-0.5d0)*dt

pulse(j,i)=0.d0

if(temp.ge.T0(i).and.init.eq.0)then

pulse(j,i)=Ep(i)

init=1

endif

enddo

endif

enddo

return

end

!-----

! define the Gaussian pulses

!-----

subroutine pulsedf(nstep,pulse,Ep, delta,T0,omega,dt,npulse,phi)

implicit real*8 (a-h,o-z)

dimension pulse(nstep,1),ep(1),delta(1),T0(1),omega(1)

```

```

dimension phi(1),delta_tmp(npulse)

complex*16 WI,pulsec(npulse,1),ctmp

pi=dacos(-1.d0)

WI=(0.d0,1.d0)

fsc=pi-2.d0*dasin(0.5d0**0.25)

nshape=0

if(nshape==0)then ! pulse of gaussian function

print*, 'Gaussian pulse used!'

nfwhmc=1

if(nfwhmc==0)then

print*, 'FWHM of E, but not E*E!'

Efactor=4.d0

else

print*, 'FWHM of E*E, but not E!'

Efactor=2.d0

endif

do j=1,npulse

do i=1,nstep

pulse(i,j)=0.d0

t=(i)*dt

if(dabs(t-T0(j)).lt.delta(j)*5.d0)then

ctmp=ep(j)*dexp(-Efactor*dlog(2.d0)*(t-T0(j))*(t-T0(j))/delta(j)/delta(j))*cdexp(-WI*(omega(j)*(t-
T0(j))+phi(j)))

pulse(i,j)=0.5D0*(ctmp+dconjg(ctmp))

endif

enddo

enddo

elseif(nshape==1)then !pulse of sin2 function

print*, 'sin2 shape laser pulse used!'

```

```

do i=1,npulse

delta_tmp(i)=delta(i)*pi/fsc

enddo

do j=1,npulse

do i=1,nstep

pulse(i,j)=0.d0

t=(i-0.5d0)*dt

if((t-T0(j)).le.0.5d0*delta_tmp(j).and.(t-T0(j)).ge.-0.5d0*delta_tmp(j))then

ctmp=ep(j)*dsin(pi*((t-T0(j))/delta_tmp(j)+0.5d0))**2*cdexp(-WI*(omega(j)*(t-T0(j))+phi(j)))

pulse(i,j)=0.5D0*(ctmp+dconjg(ctmp))

endif

enddo

enddo

endif !end pulse shape choice

return

end

```

6.3 Codes for chapter 4

The following main program and subroutines were provided by Dr. Niu Kai. In the work of chapter 4, IRS(I) and absorption spectra were calculated by using this code.

6.3.1 Main Program

```

program main

use mdl,only:fc12,en,fcfnew,mTTau,mTau12

use mdl,only:ne21tau,pe21taup,nr1t,pr1tau, nr2tau, pe10tau, ne10eta, pe2taup, pe1eta, ne2tau,npnitaup,

npnitaup, peiw,neiw, omegaS0, iwS0

use mdl,only:disp01

```

```

implicit real*8 (a-h,o-z)

allocatable:: RQ(:),V1(:),V2(:),V3(:),DIPOLE(:,,:),EINT(:)

allocatable:: pulse(:,,:),FABS(:,,:)

real*8,allocatable::nrgy(:,)

complex*16:: ataup,ataup1,aeta,aeta1

real*8:: aeta2

complex*16,allocatable:: w1(:,,:),w2(:,,:),w3(:,,:),cwkc(:),eintc(:)

real*8,allocatable::fcf12(:,::,:),m411(:),ertdn(:),ertdp(:)

complex*16,allocatable::m7(:),m4(:),m17(:),m41(:)

real*8 wPes(40)

double precision :: mu(10), lambda

dimension Ep(10),omega(10),T0(10),delta(10),lambda(10),phi(10),phsder(10),npsudd(10)

complex*16 WI,ctemp,ctemp1,ctemp2,ctemp3,dtau

common /constants/ eV,cm2au,amu2au,au2m,pc,ph,au2fs, au2j,au2co,dielec,em,pi,WI

character*4 ch,ItoC

character*2 cht,ItoCt,cht,prox

character*30 tbgn,tend

character*14 chrMd

integer*8 planf(10),planb(10),plansp

complex*16,allocatable:: corr(:),corr1(:),corr3(:),fcf3(:),fcf4(:),corr4(:)

complex*16,allocatable:: corr01(:,,:),corr11(:,,:),corr30(:,,:),m40(:,,:),m70(:,,:),tQ(:) !fcf3(:)

complex*16:: ataup10(250)

integer span(2,3),nttl(3)

allocatable:: fsrc(:),thetai(:)

complex*16,allocatable::er2E21p(:),dexexp(:,,:),dexexn(:,,:),exdp(:,,:), exdn(:,,:), ex_p(:,,:),ex_n(:,,:),

mexp(:,,:), mexn(:,,:), er2E21n(:), inho(:), eE21p(:)

dimension R1(10),R2(10),NR(10),qscal(10),qzero(10),IVB(10)

dimension dispi(50)

```

```

complex*16 ::eye=dcmplx(0.d0,1.d0)

integer a(6)

data a/0,1,2,4,8,16/

!_____

! read parameters

!_____

read*, nchirp,nprint,nstep,dt

read*, NDM,norder,norder1 !,(NR(i),i=1,NDM)

read*, npulse,(T0(i),i=1,npulse)

read*, (delta(i),i=1,npulse)

read*, ntype.Ep,(Ep(i),i=1,npulse)

read*, ntype.pulse,(lambda(i),i=1,npulse) !case ntype=0 w/cm2 1 ev

read*, (phi(i),i=1,npulse)

read*, (phsder(i),i=1,npulse) !chirp

read*, iwp,npes,ntype,ntheory liwp=0 to calculate initial w.f. //ntheory=1 non-pertubative

read*, (npsudd(i),i=1,npulse) ! delta pulse

read*, Glife1,Glife2,Glife3,theta

read*, ttout1,ttout2,nread

read*,(wPes(i),i=1,NDM)

read*,(dispi(i),i=1,NDM)

read*,e21

read*,Td

print*, ' mode w delta'

do i=1,NDM

print*,i,wPes(i),dispi(i)

enddo

if(theta==0.d0)norder=1

if(norder<300) then

```

```

print*, 'norder should not be more than 300'

stop

endif

print*, 'Expand the inhomogeneous broadening to', norder, '.'

print*, 'Glif3 and theta are', Glif3, theta

if(norder1; 0.or. (norder1; norder)) then

norder1=99

print*, 'Sum all corr30.'

else

print*, 'Calculate the fft of corr', norder1

endif

prox=ItoCt(abs(norder1))

prox=ItoCt(abs(norder))


write(*, "(1X,I4, ' multi-dimensional FSRS calculation!')") NDM

print*, 'the number of pulses used:', npulse

print*, 'the peak time of the pulse (fs):'

print*, (T0(i), i=1, npulse)

print*, 'the wavelength of the pulse (nm):'

print*, (lambda(i), i=1, npulse)

print*, 'the FWHM of the pulse (fs):'

print*, (delta(i), i=1, npulse)


allocate(pulse(nstep, npulse))

nffac=4

nc=nstep*nffac

allocate(corr(nc), fsrsc(nc*2))


!_____

```

```

! unit conversion

!_____

eV=27.2114d0

cm2au=4.55635d-6

amu2au=1822.888d0

au2m=0.5291771d-10

pc=2.99792458d8

ph=6.626075540d-34

au2fs=2.41888435d-2

au2j=4.3597482d-18

au2co=1.602177d-19

dielec=8.8542d-12

em=9.1093897d-31

pi=dacos(-1.d0)

WI=(0.d0,1.d0)

e21=e21*cm2au

print*, 'e21: ', e21 ! /cm2au

wPes=wPes*cm2au

print*, 'Td:'

print*, Td

Td=Td*cm2au


MS=INT(DABS(theta)+.1d0)

print*, 'lifetime of ground state:'

print*, Glife1

Glife1=Glife1*cm2au

print*, 'lifetime of first excited state:'

print*, Glife2

```



```

Glife2=Glife2*cm2au

print*, 'lifetime of second excited state:'

print*, Glife3

Glife3=Glife3*cm2au

print*, 'Inhomogeneous broadening:'

print*, theta

theta =theta*cm2au


ttout1=ttout1/au2fs

ttout2=ttout2/au2fs


dt=dt/au2fs

ttime=nstep*dt


print*, 'time step', dt, 'time iterations number', nstep

if(ttime-T0(2).lt.delta(2)*5)then

print*, ' be careful, ttime less raman pulse 5 FWHM!'

endif


if(n_type_Ep==0)then

APU=1.D12;APR=1.D12

else

APU=4.D-2;APR=1.D-2

endif

if(ntheory.eq.0)then ! perturbation theory calculation

print*, 'perturbation theory calculation!'

if(n_type.eq.0)then

print*, 'SRS(I) calculation'

elseif(n_type.eq.1)then

```

```

print*, 'SRS(II) calculation'

elseif(ntype.eq.2)then

print*, 'IRS(I) calculation'

elseif(ntype.eq.3)then

print*, 'IRS(II) calculation'

elseif(ntype.eq.8)then

print*, 'absorp calculation'

elseif(ntype.eq.9)then

print*, 'emission calculation'

endif

print*, 'the phase of the pulse:'

print*, (phi(i), i=1, npulse)

else

stop 'something wrong with ntheory!'

endif

!-----
! parameters of pulse into atomic units
!-----

do i=1, npulse

delta(i)=delta(i)/au2fs

phsder(i)=phsder(i)/au2fs**2

T0(i)=T0(i)/au2fs

phi(i)=phi(i)*pi

if(ntype_pulse.eq.0)then

omega(i)=(pc/lambda(i))*ph*1.0d9/au2j

omega1=(pc/lambda(i))*ph*1.0d9/au2j

else

omega(i)=lambda(i)/eV

```

```

endif

if(ntype_Ep.eq.0)then

temp=dsqrt(2.d0*Ep(i)/(dielec*pc))

Ep(i)=temp*au2m*au2co/au2j

else

Ep(i)=Ep(i)/eV

endif

enddo

print*

print*, 'the peak time of the pulse (a.u.):'

print*,(T0(i),i=1,npulse)

print*, 'the peak intensities of the pulse (a.u.):'

print*,(Ep(i),i=1,npulse)

print*, 'the wavelength of the pulse (eV):'

print*,(omega(i)*eV,i=1,npulse)

print*, 'the FWHM of the pulse (a.u.):'

print*,(delta(i),i=1,npulse)


MS=INT(DABS(T0(3))*au2fs+.1d0)

if(T0(3)>0.1d0)then

MS=MS+1

print*, 'For delay time>0, 1fs is added to identify.'

endif

T0(3)=T0(3)+T0(2)

ch=ItoC(abs(MS))

cht=ItoCt(abs(ntype))

chtt=ItoCt(abs(ntheory))

!_____

```

```

! initialize the corr array for fsrs calculation

!-----

do i=1,nc

corr(i)=(0.d0,0.d0)

fsrsc(2*i-1)=0.d0

fsrsc(2*i)=0.d0

enddo


!-----

! define the shape of the pulse

!-----

if(nchirp.eq.0)then

call pulsedf(nstep,pulse,Ep, delta,T0,omega,dt,npulse,phi)

else

print*, 'chirped pulse sub used!'

call pulsedfch(nstep,pulse,Ep, delta,T0,omega,dt,npulse,phi,phsder)

endif


!-----

! define detla pulse

!-----

call pulse_delta(nstep,pulse,Ep,T0,dt,npulse,npsudd)

do i=1,nstep,4

write(102,'(4F18.10)')(i-0.5d0)*dt*au2fs,pulse(i,1), pulse(i,2),pulse(i,3)

enddo


!-----

! initialize matrix

!-----

```

```

print*, 'initialize matrix '

allocate(er2E21p(0:nstep),dexexp(0:nstep,NDM), dexexn(0:nstep,NDM), exdp(0:nstep,NDM),
exdn(0:nstep,NDM), ex_p(0:nstep,NDM), ex_n(0:nstep,NDM), mexp(0:nstep,NDM), mexn(0:nstep,NDM),
er2E21n(0:nstep), inho(0:nstep),tQ(0:nstep), eE21p(0:nstep), ertdn(0:nstep),ertdp(0:nstep) )

allocate(corr01(norder,nstep), corr11(norder,nstep), corr30(norder,nstep) ,m40(norder,0:nstep),
m70(norder,0:nstep))

do j=1,ndm

if(notype/=8)then

do i=0,nstep

tt=i*dt

ertdn(i)=dexp(-tt*Td)

ertdp(i)=dexp(tt*Td)

er2E21p(i)=cdexp((-Glif3/2+eye*e21)*tt-0.5d0*(tt*theta)**2)

er2E21n(i)=cdexp((-Glif3/2-eye*e21)*tt-0.5d0*(tt*theta)**2)

eE21p(i)=cdexp(eye*(e21)*tt)

tQ(i)=tt*theta

ex_p(i,j)=cdexp(eye*wPes(j)*tt)

ex_n(i,j)=1.d0/ex_p(i,j)

mexp(i,j)=-1.d0+ex_p(i,j)

mexn(i,j)=-1.d0+ex_n(i,j)

exdp(i,j)=cdexp(0.5d0*dispi(j)**2*mexp(i,j))

exdn(i,j)=cdexp(0.5d0*dispi(j)**2*mexn(i,j))

dexexp(i,j)=dispi(j)/dsqrt(2.d0)*exdp(i,j)

dexexn(i,j)=dispi(j)/dsqrt(2.d0)*exdn(i,j)

enddo

else lntype absorption

do i=0,nstep

```

```

tt=i*dt

er2E21n(i)=cdexp((-Glif3/2-eye*e21)*tt)

exdn(i,j)=cdexp(0.5d0*dispi(j)**2*(-1.d0+cdexp(-eye*tt*wPes(j))))

er2E21p(i)=dexp(-0.5d0*(tt*theta)**2)/dsqrt(2*pi)

enddo

endif !ntype

enddo

ncaseStep=1e2

!_____

! main propagation iteration

!_____

if(ntheory.eq.0)then ! perturbation theory calculation output
open(50,file=cht//'corr'//ch)

else ! non-perturbation theory calculation output
open(50,file=chtt//'corr'//ch)

endif

nbgn=1;nfnl=nstep

do i=1,nstep

if(dabs(i*dt-T0(3))>5.d0*delta(3))exit

enddo

nbgn=i

do i=nbgn,nstep

if(dabs(i*dt-T0(3))>5.d0*delta(3))exit

enddo

nfnl=i-1

print*, 'probe begin and final: ',nbgn,nfnl

print*, 'probe begin and final: ',nbgn*dt*au2fs,nfnl*dt*au2fs

```

```

select case(ntype)

!_____

! calculate SRS(I)

!_____

case(0)

allocate(m4(0:nstep),m41(0:nstep),m7(0:nstep),m17(0:nstep))

allocate(corr1(nstep),corr3(nstep))

do iii=1,6

ii=a(iii)


do i=0,nstep

m4(i)=1.d0

m41(i)=1.d0

m7(i)=1.d0

m17(i)=1.d0

enddo

write(chrMd,200)ii+8192


do kk=0,nstep

do jj=1,NDM

if(chrMd(14-jj+1:14-jj+1)=='1')then

aeta=-dexexp(kk,jj)*mexn(kk,jj)

ataup=-dexexn(kk,jj)*mexp(kk,jj)

ataup1=ex_p(kk,jj)

aeta1=ex_n(kk,jj)

else !0

ataup=exdn(kk,jj)

aeta=exdp(kk,jj)

```

```

aeta1=1.d0

ataup1=1.d0

endif

m7(kk)=m7(kk)*ataup !exdn(kk,jj) !ataup !1007

m4(kk)=m4(kk)*aeta !400

m41(kk)=m41(kk)*aeta1 !

m17(kk)=m17(kk)*ataup1

enddo !jj

enddo !kk


do i=0,nstep

m41(i)=m41(i)*pulse(i,2)

m17(i)=m17(i)*pulse(i,2)

m7(i)=m7(i)*er2E21n(i)

m4(i)=m4(i)*er2E21p(i)


factor1=1.d0

do j=1,norder

factor1=factor1*dsqrt(dble(j))

m40(j,i)=m4(i)*tQ(i)**j/factor1

m70(j,i)=m7(i)*tQ(i)**j/factor1

enddo !j

enddo!i

do i=nbgn,nstep

ataup=0.d0

ataup10(1:norder)=0.d0

do j=1,i-1

ataup=ataup+m7(i-j)*m17(j)

ataup10(1:norder)=ataup10(1:norder)+m70(:,i-j)*m17(j)

```



```

enddo

corr(i)=ataup ! *eE21p(i)

corr01(:,i)=ataup10(1:norder) !*eE21p(i)

enddo !i


do i=1,nfnl

ataup=0.d0

ataup10(1:norder)=0.d0

do j=1,i-1

ataup=ataup+m4(i-j)*m41(j)*pulse(i,3)

ataup10(1:norder)=ataup10(1:norder)+m40(:,i-j)*m41(j)*pulse(i,3)

enddo

corr1(i)=ataup

corr11(:,i)=ataup10(1:norder)

enddo !i


do j=nbg,nstep

if(ji=nfnl)then

ataup=0.d0;

ataup10(1:norder)=0.d0

do i=nbg,j-1

ataup=ataup+corr1(i)

ataup10(1:norder)=ataup10(1:norder)+corr11(:,i)

enddo

endif

corr(j)=-eye*ataup*corr(j)

corr01(:,j)=-eye*ataup10(1:norder)*corr01(:,j)

enddo !j

```

```

do i=nbg,nstep

corr3(i)=corr3(i)+corr(i)

corr30(:,i)=corr30(:,i)+corr01(:,i)

enddo

print*,ii,' '

enddo !ii

!_____

! calculate SRS(II)

!_____

case(1)

allocate(m4(0:nstep),m41(0:nstep),m7(0:nstep),m17(0:nstep))

allocate(corr1(nstep),corr3(nstep))

do iii=1,6

ii=a(iii)

do i=0,nstep

m4(i)=1.d0

m41(i)=1.d0

m7(i)=1.d0

m17(i)=1.d0

enddo

write(chrMd,200)ii+8192

do kk=0,nstep

do jj=1,NDM

if(chrMd(14-jj+1:14-jj+1)=='1')then

aeta=-dexexp(kk,jj)*mexn(kk,jj)

ataup=-dexexn(kk,jj)*mexp(kk,jj)


```

```

    ataup1=ex_p(kk,jj)

    aeta1=ex_n(kk,jj)

    else !0

    ataup=exdn(kk,jj)

    aeta=exdp(kk,jj)

    aeta1=1.d0

    ataup1=1.d0

    endif

    m7(kk)=m7(kk)*ataup !exdn(kk,jj) !ataup !1007

    m4(kk)=m4(kk)*aeta !400

    m41(kk)=m41(kk)*aeta1 !

    m17(kk)=m17(kk)*ataup1

    enddo !jj

    enddo !kk


do i=0,nstep

    m41(i)=m41(i)*pulse(i,2)

    m17(i)=m17(i)*pulse(i,3)

    m7(i)=m7(i)*er2E21n(i)

    m4(i)=m4(i)*er2E21p(i)

    factor1=1.d0

    do j=1,norder

        factor1=factor1*dsqrt(dble(j))

        m40(j,i)=m4(i)*tQ(i)**j/factor1

        m70(j,i)=m7(i)*tQ(i)**j/factor1

    enddo !j

    enddo!i


do i=nbg,nstep

```

```

    ataup=0.d0

    ataup10(1:norder)=0.d0

    nfnl1=nfnl-1

    if(ijnfnl)nfnl1=i-1

    do j=nbg,nfnl1 !i-1

    ataup=ataup+m7(i-j)*m17(j)

    ataup10(1:norder)=ataup10(1:norder)+m70(:,i-j)*m17(j)

    enddo

    corr(i)=ataup

    corr01(:,i)=ataup10(1:norder)

    enddo


do i=1,nstep

    ataup10(1:norder)=0.d0

    ataup=0.d0

    do j=1,i-1

    ataup10(1:norder)=ataup10(1:norder)+m40(:,i-j)*m41(j)*pulse(i,2)

    ataup=ataup+m4(i-j)*m41(j)*pulse(i,2)

    enddo

    corr1(i)=ataup

    corr11(:,i)=ataup10(1:norder)

    enddo


do j=nbg,nstep

    ataup=0.d0

    ataup10(1:norder)=0.d0

    do i=1,j-1

    ataup=ataup+corr1(i) !*pulse(i,2)

    ataup10(1:norder)=ataup10(1:norder)+corr11(:,i)

```

```

enddo

corr(j)=-eye*ataup*corr(j)

corr01(:,j)=-eye*ataup10(1:norder)*corr01(:,j)

enddo !j

do i=nbg,nstep

corr3(i)=corr3(i)+corr(i)

corr30(:,i)=corr30(:,i)+corr01(:,i)

enddo

print*,ii,' '

enddo !ii

!_____

! calculate IRS(I)

!_____

case(2)

allocate(m4(0:nstep),m41(0:nstep),m7(0:nstep),m17(0:nstep),m411(0:nstep))

allocate(corr1(nstep),corr3(nstep))

do iii=1,6

ii=a(iii)

do i=0,nstep

m4(i)=1.d0

m41(i)=1.d0

m7(i)=1.d0

m17(i)=1.d0

m411(i)=1.d0

enddo

write(chrMd,200)ii+8192

```

```

do kk=0,nstep

do jj=1,NDM

if(chrMd(14-jj+1:14-jj+1)=='1')then

aeta=-dexexn(kk,jj)*mexp(kk,jj)

ataup= dexexn(kk,jj)*mexn(kk,jj)

ataup1=ex_p(kk,jj)*ertdp(kk)

aeta1=ex_n(kk,jj)*ertdn(kk)

! aeta2=ertdn(kk) !*ex_n(kk,jj)

else !0

ataup=exdn(kk,jj) !1007

aeta=exdn(kk,jj) !400

aeta1=1.d0

ataup1=1.d0

aeta2=1.d0

endif

m7(kk)=m7(kk)*ataup !exdn(kk,jj) !ataup !1007

m4(kk)=m4(kk)*aeta !400

m41(kk)=m41(kk)*aeta1 !

!m411(kk)=m411(kk)*aeta2 !T2

m17(kk)=m17(kk)*ataup1

enddo !jj

enddo !kk

```

```

do i=0,nstep

m17(i)=m17(i)*pulse(i,2)

m7(i)=m7(i)*er2E21n(i)

m4(i)=m4(i)*er2E21n(i)

factor1=1.d0

do j=1,norder

```

```

factor1=factor1*dsqrt(dble(j))

ataup=(eye*tQ(i))**j

m40(j,i)=m4(i)*ataup /factor1

m70(j,i)=m7(i)*ataup/factor1

enddo !j

enddoli

do i=nbg,nstep

ataup=0.d0

ataup10(1:norder)=0.d0

nfnl=nfnl-1

if(i>nfnl)nfnl=i-1

do j=nbg,nfnl

ataup=ataup+m7(i-j)*pulse(j,3) !*m17(i) ! ipulse(i,2)

ataup10(1:norder)=ataup10(1:norder)+m70(:,i-j)*pulse(j,3)

enddo

corr(i)=ataup *m17(i)

corr01(:,i)=ataup10(1:norder)*m17(i)

enddo

do i=nbg,nstep

ataup=0.d0

ataup10(1:norder)=0.d0

do j=nbg,i-1

ataup=ataup+corr(j)

ataup10(1:norder)=ataup10(1:norder)+corr01(:,j)

enddo

corr1(i)=ataup

corr11(:,i)=ataup10(1:norder)

```

```

enddo

do i=nbg,nstep

  ataup=0.d0

  ataup10(1:norder)=0.d0

  do j=nbg,i-1

    ataup=ataup+corr1(j)*m4(i-j)*pulse(j,2) !i*er2E21n(i-j)

    ataup10(1:norder)=ataup10(1:norder)+corr11(:,j)*m40(:,i-j)*pulse(j,2)

  enddo

  corr(i)=-eye*ataup*m41(i)

  corr01(:,i)=-eye*ataup10(1:norder)*m41(i)

enddo


do i=nbg,nstep

  corr3(i)=corr3(i)+corr(i)

  corr30(:,i)=corr30(:,i)+corr01(:,i)

enddo

print*,ii,' '

enddo !ii


!_____

! calculate IRS(II)

!_____

case(3)

allocate(m4(0:nstep),m41(0:nstep),m7(0:nstep),m17(0:nstep))

allocate(corr1(nstep),corr3(nstep))

do iii=1,6

  ii=a(iii)

do i=0,nstep

```



```

m4(i)=1.d0

m41(i)=1.d0

m7(i)=1.d0

m17(i)=1.d0

enddo

write(chrMd,200)ii+8192


do kk=0,nstep

do jj=1,NDM

if(chrMd(14-jj+1:14-jj+1)=='1')then

aeta=-dexexn(kk,jj)*mexp(kk,jj)

ataup= dexexn(kk,jj)*mexn(kk,jj)

ataup1=ex_p(kk,jj)

aeta1=ex_n(kk,jj)

else !0

ataup=exdn(kk,jj)

aeta=exdn(kk,jj)

aeta1=1.d0

ataup1=1.d0

endif

m7(kk)=m7(kk)*ataup !exdn(kk,jj) !ataup !1007

m4(kk)=m4(kk)*aeta !400

m41(kk)=m41(kk)*aeta1 !

m17(kk)=m17(kk)*ataup1

enddo !jj

enddo !kk


do i=0,nstep

m17(i)=m17(i)*pulse(i,2)

```

```

m7(i)=m7(i)*er2E21n(i)

m4(i)=m4(i)*er2E21n(i)

factor1=1.d0

do j=1,norder

factor1=factor1*dsqrt(dble(j))

ataup=(eye*tQ(i))**j

m40(j,i)=m4(i)*ataup/factor1

m70(j,i)=m7(i)*ataup/factor1

enddo !j

enddoli

do i=1,nstep

ataup=0.d0

ataup10(1:norder)=0.d0

do j=1,i-1

ataup=ataup+m7(i-j)*pulse(j,2) ! ipulse(i,2)

ataup10(1:norder)=ataup10(1:norder)+m70(:,i-j)*pulse(j,2)

enddo

corr(i)=ataup *m17(i)

corr01(:,i)=ataup10(1:norder)*m17(i)

enddo

do i=nbgn,nfnl

ataup=0.d0

ataup10(1:norder)=0.d0

do j=1,i-1

ataup=ataup+corr(j)

ataup10(1:norder)=ataup10(1:norder)+corr01(:,j)

enddo

corr1(i)=ataup

corr11(:,i)=ataup10(1:norder)

```

```

enddo

do i=nbg,nstep

    ataup=0.d0

    ataup10(1:norder)=0.d0

    nfnl1=nfnl-1

    if(i>nfnl)nfnl1=i-1

    do j=nbg,nfnl1 !i-1

        ataup=ataup+corr1(j)*m4(i-j)*pulse(j,3) !i*er2E21n(i-j)

        ataup10(1:norder)=ataup10(1:norder)+corr1(:,j)*m40(:,i-j)*pulse(j,3)

    enddo

    corr(i)=-eye*ataup*m41(i)

    corr01(:,i)=-eye*ataup10(1:norder)*m41(i)

enddo


do i=nbg,nstep

    corr3(i)=corr3(i)+corr(i)

    corr30(:,i)=corr30(:,i)+corr01(:,i)

enddo

print*,ii,' '

enddo !ii


!-----
! calculate absorption
!-----

case(8)

allocate(m7(0:nstep),m17(0:nstep))

allocate(corr1(nstep),corr3(nstep))

do ii=0,0,2**NDM-1

```

```

do i=0,nstep

m7(i)=1.d0

m17(i)=1.d0

enddo

write(chrMd,200)ii+8192


do kk=0,nstep

do jj=1,NDM

ataup=exdn(kk,jj)

m7(kk)=m7(kk)*ataup !exdn(kk,jj) !ataup !1007

enddo !jj

enddo !kk


do i=0,nstep

m7(i)=m7(i)*er2E21n(i)*er2E21p(i)

enddo!i


do i=1,nstep

ataup=0.d0

do j=1,i-1

ataup=ataup+m7(i-j)*pulse(j,3) ! ipulse(i,2)

enddo

corr(i)=ataup*eye*dt*2.d0

enddo

do j=1,nstep,ncaseStep

ataup=corr(j)

if(cdabs(ataup)>1.d-50)then

write(50,100)j*dt*au2fs,cdabs(ataup),dreal(ataup),dimag(ataup)

```

```

else

write(50,100)j*dt*au2fs,0.d0,0.d0,0.d0 !cdabs(ataup),dreal(ataup)

endif

enddo !j

if(mod(ii,ncaseStep)==0)print*,ii,' '

enddo !ii

goto 400

case default

print*, 'wrong in ncase'

stop

endselect

do j=1,nstep

corr(j)=corr3(j)*dt**3

corr30(:,j)=corr30(:,j)*dt**3

enddo

do j=1,nstep,ncaseStep

ataup=corr(j)

ataup10(1:norder)=corr30(:,j)

if(theta==0.d0)ataup10(norder)=ataup

if(cdabs(ataup10(1))>1.d-90)then

write(50,100)j*dt*au2fs,cdabs(ataup),cdabs(ataup10(1:norder))

else

write(50,100)j*dt*au2fs,0.d0,(0.d0,k=1,norder) !abs(ataup),dreal(ataup)

endif

enddo !j

select case(norder1)

case(0)

```

```

case(99)

do j=1,nstep

corr(j)=corr(j)+sum(corr30(:,j))

enddo

case default

do j=1,nstep

corr(j)=(corr30(norder1,j))

enddo

endselect

400 continue

open(88,file=cht//'fsrs'//ch//'_ '//prox)

do i=1,nstep

fsrsc(2*i-1)=dreal(corr(i)) *2

fsrsc(2*i)=0.d0 ! dimag(corr(i))

enddo


call fft(fsrsc(1),fsrsc(2),nc,nc,nc,2)

do i=1,nc

corr(i)=dcmplx(fsrsc(2*i-1),fsrsc(2*i))

enddo


do i=1,nc

fsrsc(2*i-1)=0.d0

fsrsc(2*i)=0.d0

enddo

do i=1,nstep

fsrsc(2*i-1)=pulse(i,3) !*(e21-omega(2))

```

```

enddo

call fft(fsrtc(1),fsrtc(2),nc,nc,nc,2)

if(ntype/=8)then

Ezero=omega(2)

Erangle=4000.D0*cm2au

do i=1,nc

otemp=2.d0*pi*(i-1)/(dt*nc)

if(otemp.le.Ezero+Erangle.and.otemp.ge.Ezero-Erangle)then

ctemp=fsrtc(2*i-1)+WI*fsrtc(2*i)

aotemp=(otemp-Ezero)/cm2au

write(88,'(14E26.10)')(aotemp), -imag(corr(i)*dconjg(ctemp))*otemp, -imag(corr(i)/ctemp)*otemp,-
real(corr(i)*ctemp)*otemp ,cdabs(ctemp),dreal(corr(i)),dimag(corr(i)),cdabs(corr(i))

endif

enddo

else !ntype

Ezero=omega(3)

Erangle=4000.D0*cm2au

do i=1,nc

otemp=2.d0*pi*(i-1)/(dt*nc)

if(otemp.le.Ezero+Erangle.and.otemp.ge.Ezero-Erangle)then

ctemp=fsrtc(2*i-1)+WI*fsrtc(2*i)

aotemp=otemp/cm2au

write(88,'(14E26.10)')(aotemp), imag(corr(i)*dconjg(ctemp))*otemp, imag(corr(i)/ctemp)*otemp,-
real(corr(i)*ctemp)*otemp,cdabs(ctemp),cdabs(otemp*corr(i)/ctemp)

endif

enddo

endif

```

```
close(88)
```

```
100 format(524E26.10)
```

```
200 format(b14)
```

```
end
```

6.3.2 Subroutines

The subroutines for pulse definition and fast Fourier transform called in the main program are the same as for chapter 2 and 3.

Bibliography

- [1] M. Yoshizawa, Y. Hattori, and T. Kobayashi. *Phys. Rev. B*, 49:13259, 1994.
- [2] M. Yoshizawa and M. Kurosawa. *Phys. Rev. A*, 61:013808, 1999.
- [3] David William McCamant. *Femtosecond stimulated Raman spectroscopy of ultrafast biochemical reaction dynamics*. PhD thesis, University of California, Berkeley, 2004.
- [4] D. W. McCamant, P. Kukura, and R. A. Mathies. *Appl. Spectrosc.*, 57:1317, 2003.
- [5] D. W. McCamant, P. Kukura, and R. A. Mathies. *J. Phys. Chem. A*, 107:8208, 2003.
- [6] P. Kukura, D. W. McCamant, P. H. Davis, and R. A. Mathies. *Chem. Phys. Lett.*, 382:81, 2003.
- [7] D. W. McCamant, P. Kukura, S. W. Yoon, and R. A. Mathies. *Rev. Sci. Instr.*, 75:4971, 2004.
- [8] P. Kukura, D. W. McCamant, and R. A. Mathies. *J. Phys. Chem. A*, 108:5921, 2004.
- [9] D. W. McCamant, P. Kukura, and R. A. Mathies. *J. Phys. Chem. B*, 109:10449, 2005.
- [10] P. Kukura, D.W. McCamant, S.W. Yoon, D.B. Wandschneider, and R. A. Mathies. *Science*, 310:1006, 2005.
- [11] P. Kukura, S. Yoon, and R. A. Mathies. *Anal. Chem.*, 78:5952, 2006.

- [12] P. Kukura, D. W. McCamant, and R. A. Mathies. *Ann. Rev. Phys. Chem.*, 58:461, 2007.
- [13] S. Shim, C. M. Stuart, and R. A. Mathies. *ChemPhysChem*, 9:697, 2008.
- [14] R. R. Frontiera, S. Shim, and R. A. Mathies. *J. Chem. Phys.*, 129:064507, 2008.
- [15] S. Shim, J. Dasgupta, and R. A. Mathies. *J. Am. Chem. Soc.*, 131:7592, 2009.
- [16] C.Fang, R.R.Frontiera, R.Tran, Y.Prior, and R.A.Mathies. *nature*, 462:200, 2009.
- [17] T. Lian, S. E. Bromberg, M. C. Asplund, H. Yang, and C. B. Harris. *J. Phys. Chem.*, 100:11 994–12 001, 1996.
- [18] I. V. Rubtsov, T. Zhang, H. Nakajima, S. Aono, G. I. Rubtsov, S. Kumazaki, and K. Yoshihara. *J. Am. Chem. Soc.*, 123:056–063, 2001.
- [19] R. Diller, S. Maiti, G. C. Walker, B. R. Cowen, R. Pippenger, R. A Bogomolni, and R. M. Hochstrasser. *Chem. Phys. Lett.*, 241:109–115, 1995.
- [20] N. G. Hirendra, V. Sandep, and T. J. Nibberig Erik. *J. Phys. Chem. A*, 115:664–670, 2011.
- [21] Y. Ming, S. Lukasz, T. J. Nibbering Jens, D. an dErik, and Thomas E. *J. Phys. Chem. A*, 114:12195–12201, 2010.
- [22] T. S. Preston, K. P. Christine, T. K. Kenneth, Y. Haw, and B. H. Charles. *J. Am. Chem. Soc.*, 123:2255–2264, 2001.
- [23] R. Matteo, H. Ann-Kathrin, Erik. T. J. Nibbering, and F. Henk. *J. Am. Chem. Soc.*, 125:3028–3034, 2003.
- [24] C. A. Matthew, T. S. Preston, S. Y. Jake, J. W. Mattew, K. P. Christine, Y. Haw, T. K. Kenneth, F. Heinz, Robert G. B., and B. H. Charles. *J. Am. Chem. Soc.*, 124:10605–10612, 2002.
- [25] J. E. Kim, D. W. MacCamat, L. Zhu, and R. A. Mathies. *J. Phys. Chem. B*, 105:1240–1294, 2001.
- [26] S. C. Hayes, M. J. Philpott, and P. J. Reid. *J. Chem. Phys.*, 109:2596–2599, 1998.
- [27] S. Franzen, B. Bohn, C. Poyart, and J. L. Martin. *Biochemistry*, 34:1224–1237, 1995.

- [28] G. Placzek. In E. Marx, editor, *Handbuch der Radiologie*, volume 6, pages 205. English Translation by Ann Werbin, UCRL Trans-526(L). Akademische Verlagsgesellschaft, Leipzig, 1934.
- [29] Mukamel Shaul. *Principles of Nonlinear Optical Spectroscopy*. Oxford University Press, New York, 1995.
- [30] S. Mukamel and Y. J. Yan. in *Recent Trends in Raman Spectroscopy: Raman Spectroscopy and Four Wave Mixing; A Probe for Solvation Dynamics*. World Scientific, Singapore, 1989.
- [31] S. Mukamel. *J. Chem. Phys.*, 82:5398–5408, 1985.
- [32] R. F. Loring and S. Mukamel. *J. Chem. Phys.*, 83:2116–2128, 1985.
- [33] Y. J. Yan and S. Mukamel. *J. Chem. Phys.*, 86:6085–6107, 1987.
- [34] S. Mukamel. *Adv. Chem. Phys.*, 70 Part I:165–230, 1988.
- [35] H. A. Kramers and W. Heisenberg. *Z. Phys.*, 31:681, 1925.
- [36] P. A. M. Dirac. *Proc. Roy. Soc.*, 114:710, 1927.
- [37] S. Y. Lee and E. J. Heller. *J. Chem. Phys.*, 71:4777, 1979.
- [38] E. J. Heller, R. L. Sundberg, and D. Tannor. *J. Phys. Chem.*, 86:1822, 1982.
- [39] N. Bloembergen and Y. R. Shen. *Phys. Rev. Lett.*, 12:504, 1964.
- [40] Y. R. Shen and N. Bloembergen. *Phys. Rev.*, 137:A1787, 1965.
- [41] S. Y. Lee, D. H. Zhang, D. W. McCamant, P. Kukura, and R. A. Mathies. *J. Chem. Phys.*, 121:3632, 2004.
- [42] M. Yoshizawa, H. Aoki, and H. Hashimoto. *Bull. Chem. Soc. Jpn.*, 75:949, 2002.
- [43] Z. Sun, Z. Jin, J. Lu, D. H. Zhang, and S. Y. Lee. *J. Chem. Phys.*, 126:174104, 2007.
- [44] Z. Sun, J. Lu, D. H. Zhang, and S. Y. Lee. *J. Chem. Phys.*, 128:144114, 2008.
- [45] Y. R. Shen. *The principle of nonlinear optics*. Wiley, New York, 1984.
- [46] G. Stock and W. Domcke. *Phys. Rev. A*, 45:3032, 1992.

- [47] S. Y. Lee. *in Femtosecond Chemistry*, volume 1, Chap. 7, p. 273. VCH, Weinheim, 1995.
- [48] W. T. Pollard and R. A. Mathies. *Ann. Rev. Phys. Chem.*, 43:497, 1992.
- [49] L. Seidner, G. Stock, and W. Domcke. *J. Chem. Phys.*, 103:3998, 1995.
- [50] K. Niu, S. Cong, and S. Y. Lee. *J. Chem. Phys.*, 131:054311, 2009.
- [51] S. Umapathy, B. Mallick, and A. Lakshmanan. *J. Chem. Phys.*, 133:024505, 2010.
- [52] M. Yoshizawa, H. Aoki, and H. Hashimoto. *Phys. Rev. B*, 63:180301(R), 2001.
- [53] M. Yoshizawa and H. Hashimoto. *Proc. SPIE-Int. Soc. Opt. Eng.*, 5212:13, 2003.
- [54] M. Yoshizawa, H. Aoki, M. Ue, and H. Hashimoto. *Phys. Rev. B*, 67:174302, 2003.
- [55] H. Hashimoto, K. Yanagi, M. Yoshizawa, D. Polli, G. Cerullo, G. Lanzani, S. De Silvestri, A. T. Gardiner, and R. J. Cogdell. *Arch. Biochem. Biophys.*, 430:61, 2004.
- [56] S. W. Yoon, D. W. McCamant, P. Kukura, R. A. Mathies, D. H. Zhang, and S. Y. Lee. *J. Chem. Phys.*, 122:024505, 2005.
- [57] P. Kukura, SW Yoon, and RA Mathies. *Anal. Chem.*, 78:952, 2006.
- [58] P. Kukura, R. Frontiera, and R. A. Mathies. *Phys. Rev. Lett.*, 96:238303, 2006.
- [59] S. W. Yoon, P. Kukura, C. M. Stuart, and R. A. Mathies. *Mol. Phys.*, 104:1275, 2006.
- [60] D. A. Long. *The Raman Effect. A Unified Treatment of the Theory of Raman Scattering by Molecules*. John Wiley Sons, Chichester, 2002.
- [61] Y. R. Shen. *Phys. Rev. B*, 9:622, 1974.
- [62] TK Yee and TK. Gustafson. *Phys. Rev. A*, 18:1597, 1978.
- [63] Kiefer W. *Nonlinear Raman Spectroscopy and its Chemical Applications*. Holland, 1984.
- [64] Z. Sun, X. Q. Qiu, J. Lu, D. H. Zhang, and S. Y. Lee. *J. Raman Spectrosc.*, 39:1568, 2008.
- [65] Z. Sun, B. Fu, D. H. Zhang, and S. Y. Lee. *J. Chem. Phys.*, 130:044312, 2009.
- [66] Kristina C. Wilson, Brendon Lyons, Randy Mehlenbacher, Randy Sabatini, and David W. McCamant. *J. Chem. Phys.*, 131:214502, 2009.

- [67] A. B. Myers, R. A. Harris, and R. A. Mathies. *J. Chem. Phys.*, 79:603, 1983.
- [68] W. T. Pollard, S. L. Dexheimer, Q. Wang, L. A. Peteaunu, C. V. Shank, and R. A. Mathies. *J. Phys. Chem.*, 96:6147, 1992.
- [69] A. B. Myers and R. A. Mathies. in *Biological Applications of Raman Spectroscopy: Resonance Raman Spectra of Polyenes and Aromatics*, volume 2, p. 1-58. John Wiley & Sons, New York, 1987.
- [70] L. Tutt, D. Tannor, J. Schindler, E. J. Heller, and J. I. Zink. *J. Phys. Chem.*, 87:3017, 1983.
- [71] S. Y. Lee and H. Y. Chang. *J. Chem. Phys.*, 100:4056, 1994.
- [72] G. B. Hurst and J. C. Wright. *J. Chem. Phys.*, 97:3940, 1992.
- [73] S. H. Lee, D. C. Nguyen, and J. C. Wright. *Appl. Spectros.*, 37:472, 1983.
- [74] J. C. Wright. *Appl. Spectrosc.*, 34:151, 1980.
- [75] Jason C. Kirkwood and A. C. Albrecht. *Journal of Raman Spectroscopy*, 31:107–124, 2000.
- [76] Darin J. Ulness Michael J. Stimson and A. C. Albrecht. *Journal of Raman Spectroscopy*, 28:579–587, 1998.
- [77] Duckhwan Lee S. A. Schaertel and A. C. Albrecht. *Journal of Raman Spectroscopy*, 26:889–899, 1995.
- [78] S. A. Schaertel and A. C. Albrecht. *Journal of Raman Spectroscopy*, 25:545–555, 1994.
- [79] W. J. Jones and B. P. Stoicheff. *Phys. Rev. Lett.*, 13:657, 1964.
- [80] A. Lau, W. Werncke, and K. Lenz M. Pfeiffer, and H. J. Weigmann. *Sov. J. Quantum Electron.*, 6:402, 1976.
- [81] I.I. Kondilenko, N. E. Kornienko, V. I. MalyT, and G. V. Ponezha. *Sov. J. Quantum Electron.*, 11:1494, 1981.
- [82] L. A. Rahn and R. E. Palmer. *J. Opt. Soc. Am. B*, 3:1164, 1986.
- [83] Teruya Ishihara and Takenari Goto. *Opt. Commun.*, 59:357, 1986.

- [84] W. Jeremy Jones. *J. Mol. Struct.*, 404:129, 1997.
- [85] D. R. Solli, P. Koonath, and B. Jalali. *Phys. Rev. A*, 79:053853, 2009.
- [86] Siva Umapathy, Adithya Lakshmanan, and Babita Mallick. *J. Raman Spectrosc.*, 40:235–237, 2009.
- [87] A. Lakshmanan, B. Mallick, and S. Umapathy. *Curr. Sci.*, 97:210–216, 2009.
- [88] Xueqiong Qiu, Xiuting Li, Kai Niu, and Soo-Y. Lee. *J. Raman Spectrosc.*, 42:563, 2011.
- [89] D. J. Tannor and E. J. Heller. *J. Chem. Phys.*, 77:202, 1982.
- [90] A. M. Kelley, L. C. T. Shoute, M. Blanchard-Desce, G. P. Bartholomew, and G. C. Bazan. *Mol. Phys.*, 104:1239, 2006.
- [91] L. Angeloni, G. Smulevich, and M. P. Marzocchi. *J. Raman Spectrosc.*, 8:305, 1979.
- [92] E. J. Liang, X. L. Ye, and W. Kiefer. *J. Phys. Chem. A*, 101:7330, 1997.
- [93] M. Takayanagi, H. Hamaguchi, and M. Tasumi. *J. Chem. Phys.*, 89:3945, 1988.