Theoretical investigations and simulations of femtosecond stimulated Raman spectroscopy and coherent anti-stokes Raman spectroscopy

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**THEORETICAL INVESTIGATIONS AND
SIMULATIONS OF FEMTOSECOND STIMULATED
RAMAN SPECTROSCOPY AND COHERENT
ANTI-STOKES RAMAN SPECTROSCOPY**

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Summary

Femtosecond stimulated Raman spectroscopy (FSRS) is a novel technique that possesses many advantages: simultaneous high temporal and spectral resolutions, free of fluorescence background, high signal-to-noise ratio, wide vibrational spectrum range and rapid data acquisition. Together with coherent anti-Stokes Raman spectroscopy (CARS), they are widely employed to study the molecular structure and chemical reaction dynamics of physical and biological processes that occur on the ultrafast femtosecond time scale. The research in this thesis aims to provide a quantum mechanical investigation of FSRS and CARS. A multidimensional separable displaced harmonic oscillators model is used to derive analytical expressions for the third-order polarization and FSRS intensities are calculated to compare with experiments.

FSRS simulated with a delta function probe pulse in rhodamine 6G (R6G) from the ground vibrational state has been investigated by the perturbative quantum wave packet theory. By using the delta function probe pulse, the four-time correlation function in the third-order polarization reduces to a three-time correlation function which saves computation time. The analytic third-order polarization expressions can be written down for each term from the eight Feynman dual time line diagrams. Six effective terms $RRS(I)$, $HL(I)+HL(II)$, $RRS(II)$, $HL(III)+HL(IV)$, $IRS(I)$, and $IRS(II)$ are calculated and the results 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. Using the $SRS(I)$ term, we showed that the FSRS vibrational linewidth gets narrower

as the Raman pump pulse duration and/or the vibrational dephasing time is lengthened; the homogeneous and inhomogeneous damping constants do not affect the vibrational linewidth; the homogeneous damping constant affects the width and structure of the Raman excitation profile (REP) of a vibrational line where a smaller homogeneous damping constant can lead to a narrower REP with vibrational structures that do not correspond to any of the harmonic frequencies used in the calculation.

Simulation of the inverse Raman scattering (IRS) process on crystal violet (CV) with the same perturbative quantum wave packet theory is carried out. Calculations with separable multidimensional harmonic oscillators model are made to compare with the absorption and resonant ultrafast Raman loss spectroscopy (URLS) experiments on CV. Both IRS and URLS show the Raman loss and dispersive line shapes on anti-Stokes bands, which could be accounted for by the IRS(I) term of FSRS using our quantum theory. The change in phase of the line shapes with Raman pump wavelength is well reproduced. It is shown that the line shapes change from negative dispersive to Lorentzian, to dispersive, and then to negative Lorentzian as the Raman pump excitation is tuned from the red tail of the absorption spectrum to near the absorption maximum. Increasing the Raman pump bandwidth or decreasing the Raman vibrational dephasing time broadens the IRS bands. The well-known expression for $\chi_{IRS}^{(3)}$ is derived from multi-mode third-order susceptibility for IRS with the limit of monochromatic Raman pump and probe pulses, which is used to explain the mode dependent phase changes as a function of Raman pump excitation in the URLS of CV.

Twenty four Feynman dual time line and four wave mixing energy level diagrams are first presented to depict CARS from the ground electronic state. Calculations are made on toluene for off-resonance CARS and R6G for resonance CARS for each of the twenty four terms that contributes to the third-order polarization of CARS. By interpreting the line-shape and relative intensity of each term, we find that the traditional CARS term with pump, Stokes and probe interactions all on the ket time line is the dominant term in both off-resonance and resonance CARS.

Introduction

1.1 Background and Motivation

1.1.1 Femtosecond stimulated Raman spectroscopy (FSRS)

Typically, chemical bond breaking, forming and geometry rearrangement during chemical reactions take place in the femtosecond time scale. To observe and reveal the dynamics of structural evolution in physical, chemical, and biological processes, an ultrashort laser pulse with duration shorter than characteristic molecular vibrational period is essential. 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. 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. Linear transient infrared (IR) probing techniques have been generally limited to 200 fs time resolution in a narrow (200 cm^{-1}) spectral region. 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. Thus, achieving both high time and high spectral resolution is impossible in traditional spontaneous Raman spectroscopy using a single pulse. Recently, a novel time-resolved femtosecond stimulated Raman spectroscopy (FSRS) has been developed to study structural changes in ultrafast

photophysical and photochemical processes with fs time resolution and high vibrational spectral resolution. With FSRS one can achieve less than 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.

Yoshizawa *et al* [1] first reported FSRS in 1994 to get Raman spectrum with temporal resolution of 300 fs using three pulses of femtosecond durations. By using a narrow band Raman pump and two ultrashort probe pulses with a time delay [2], a Raman spectrum with both high temporal resolution (250 fs) and spectral resolution (25 cm^{-1}) was obtained. Meanwhile, the same technique was proposed by Mathies' *et al.*, and was named "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].

Time-resolved or 2D-FSRS is a resonant/off-resonant optical nonlinear vibrational spectroscopy technique in mixed time and frequency domain, using self-heterodyne and dispersed detection schemes. The idea behind this novel technique is shown schematically in Fig. 1.1. The molecule is initially in, say, the $v = 0$ vibrational state on the ground electronic state e_0 surface. An ultrashort fs actinic pump pulse ① first prepares a wave packet that then evolves on the excited electronic state e_1 surface. A picosecond Raman pump pulse ② coupled with a femtosecond probe pulse ③ interrogates the evolving wave packet, mediated by a higher excited electronic state e_2 , at various delay times, T , through stimulated Raman scattering as measured by the gain or loss of the probe spectrum. The delay time T is one dimension and the frequency of the FSRS spectrum at each time T is the second dimension in 2D-FSRS. If there is no actinic pump pulse, as in FSRS from a stationary state, we call it 1D-FSRS.

The geometry for the implementation of time-resolved FSRS could be drawn like a BOXCARS arrangement as shown in Fig. 1.2, or the 3 pulses could all propagate in a plane at different angles, but intersecting at the sample. The actinic fs pump pulse has wavevector $\mathbf{k}_{ac}$ and arrives first at sample. This is followed by a pair of ps Raman pump pulse with wavevector $\mathbf{k}_{pu}$ and a fs probe pulse with wavevector $\mathbf{k}_{pr}$, which are delayed from the actinic pump pulse by a time T . Heterodyne detection of the spectra, with and without the Raman pump on, and with and

Figure 1.1: Femtosecond stimulated Raman scattering from an evolving wave packet on an excited electronic state that is initially prepared by an actinic pump pulse.

without the actinic pump on, is made in the phase-matching probe pulse direction $\mathbf{k}_{pr}$ which are then used to calculate the FSRS spectra.

Figure 1.2: Geometry of time-resolved FSRS experiment.

It is possible to acquire spectra with time resolution of ~ 50 fs in the time delay between the actinic pump and probe pulses, and spectral resolution of < 10 cm^{-1} due largely to the ps Raman pump pulse [11, 12]. Other advantages of FSRS are rapid data acquisition, Raman spectra unaffected by background fluorescence, and vibrational spectrum acquisition in the range of 600-2500 cm^{-1} . FSRS has been used to study numerous systems, including vibrational relaxation

and internal conversion in β -carotene [8] and diphenyloctatetraene [6], excited state structural dynamics of the photoisomerization of the retinal chromophore in bacteriorhodopsin [9, 15] and rhodopsin [10], anharmonic coupling in CDCl_3 [17], resonance Raman scattering from Rhodamine 6G (R6G) which is a highly fluorescent compound [14, 13], and excited state isomerization in phytochrome [18].

1.1.2 Ultrafast Raman Loss Spectroscopy (URLS)

Ultrafast Raman loss spectroscopy (URLS) is a nonlinear technique which can be described as inverse Raman scattering (IRS). URLS has the advantages of rapid data acquisition, high signal to noise ratio, natural fluorescence rejection and experimental ease [19, 20, 21].

URLS involves the observation of IRS signal utilizing a picoseconds (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 - FSRS when there is no actinic pump pulse (1D-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]. URLS obtain loss signals only on the blue side with respect to the wavelength of the ps pulse. While, 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. 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 Raman spectrum free of fluorescence background 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, 22, 23, 24].

1.1.3 Coherent anti-Stokes Raman spectroscopy (CARS)

Ever since coherent anti-Stokes Raman scattering (CARS) was first proposed by Terhune and Marker [25, 26] in 1960s, various theoretical and experimental investigations have been performed in physical, chemical, and biological areas [27, 28]. Similar to Raman spectroscopy, CARS is a powerful technique for detecting vibrational features, measuring temperature as well as deriving images of chemical and biological samples [29, 30, 31]. CARS is generated by three electric fields: a pump pulse with frequency ω_{pu} , a Stokes pulse with frequency ω_{st} , and a probe pulse with frequency ω_{pr} interacting with matter, and it is detected in the $\mathbf{k}_{CARS} = \mathbf{k}_{pu} - \mathbf{k}_{st} + \mathbf{k}_{pr}$ phase matching direction.

Following the development of ultrashort laser techniques, femtosecond laser pulses with high repetition rate and broadband play an important role in CARS experiments for both small and large molecules [32, 33, 34, 35, 36]. CARS had been used to investigate the molecular dynamics on the excited and ground state potential energy surfaces of iodine and bromine in the gas phase [37, 38]. Time-resolved (tr), electronically resonant CARS could prepare and interrogate vibronic coherences of molecular iodine in matrix Ar [39]. Heid *et al.* [40] investigated the ground electronic state vibrational dynamics of porphyrin molecules in solution using CARS and provided a discussion of the expected signals on a theoretical basis by using the CARS third-order non-linear polarization. Knopp *et al.* [41] showed that the technique of femtosecond tr CARS spectroscopy provided a powerful tool for the investigation of collision-induced linewidths and the validation of rotational energy transfer models. The polarization beat spectroscopy of I₂-Xe complex in solid krypton was studied by Kiviniemi *et al.* [42] using the tr CARS technique. Tran *et al.* [43] carried out measurements and modeling of femtosecond tr CARS signal in H₂-N₂ mixtures at low densities. Pure rotational tr CARS using picosecond duration laser pulses has been used for gas thermometry of N₂ [44]. Begley *et al.* [45] proposed that CARS is also useful for investigating biological compounds where background fluorescence is a problem for conventional spontaneous Raman studies. Prince *et al.* [46] carried out both tr fs CARS and fs/ps CARS experiments on toluene and Rhodamine 6G (R6G) and introduced a phenomenological analysis of the toluene off-resonance CARS. In the phenomenological analysis, the relevant response function is assumed to be a summation of each Raman active vibrational level which is assigned a central frequency

and homogeneously broadened lifetime [46, 47]. However, a derivation of the phenomenological result from a quantum approach for the polarization has been lacking.

Shen *et al.* [48] and Tolles *et al.* [49] have reviewed the theory of CARS using a time-independent method and the approximation of cw or delta-function pulses. In addition, Kuehner *et al.* [50] have developed a time-independent perturbation theory for three-laser electronic-resonance-enhanced CARS spectroscopy of nitric oxide. Besides the time-independent method, Tannor *et al.* [51] proposed a time-dependent approach with finite pulses for CARS and the method was applied to investigate quantum beats and IVR process related to CARS. Time-dependent wave packet calculations were also applied to analyze tr fs CARS experiments on gas-phase iodine molecules [52].

Time resolved (tr) fs CARS, shown in Fig. 1.3 in a BOXCAR arrangement, involves three broadband (fs) input pulses: a pump pulse (pu) with frequency ω_{pu} , a Stokes pulse (st) with frequency ω_{st} , and a probe pulse (pr) with frequency ω_{pr} [46]. The pump and Stokes pulses are temporally coincident at the sample, and prepare coherence on the ground electronic state, while the probe pulse acts after a delay time. The tr fs CARS is homodyne detected in the $\mathbf{k}_{\text{CARS}} = \mathbf{k}_{\text{pu}} - \mathbf{k}_{\text{st}} + \mathbf{k}_{\text{pr}}$ phase matching direction. When the probe pulse full width at half maximum (FWHM) becomes less than 20 cm^{-1} , about 1 ps or more, the spectrum is called fs/ps CARS. In the CARS experiments performed by Prince *et al.* [46], the wavelengths of the pump and Stokes pulses are around 530 nm and the probe pulse wavelength is 800 nm. The central frequency difference between pump and Stokes pulses provides a window for the Raman active modes of the ground electronic state, but with broadband pulses, that frequency difference is not even necessary. The probe pulse, which is off-resonance with the zero-zero transition between ground and excited electronic states, acts on the coherence produced by the pump and Stokes pulses to generate the third-order polarization.

For CARS, there are several ways to choose the pulses. In Chapter 4, we adopted the CARS geometry from H. U. Stauffer's group [46] as shown in Fig. 1.3, and our calculation is based on their experimental parameters. We use two fs pulses, pump and Stokes, to prepare coherence in the sample, and then probe by a ps probe pulse, so that we could obtain CARS with vibrational peaks. Tahara *et al.* [53] have proposed a time-frequency two-dimensional multiplex CARS,

Figure 1.3: Geometry of a tr fs CARS experiment. The fs pump and fs Stokes pulses are temporally coincident at the sample followed by a fs probe pulse that is delayed by time T . The observation of the tr fs CARS spectrum is made in the phase matching direction: $\mathbf{k}_{\text{CARS}} = \mathbf{k}_{\text{pu}} - \mathbf{k}_{\text{st}} + \mathbf{k}_{\text{pr}}$.

where they used a fs pump pulse for photoexcitation, a nanosecond pulse plus a broadband pulse for the CARS probing. The multiplex detection in the frequency domain is achieved by using a broadband pulse and a spectrograph. The time resolution is determined by the duration of the fs pump pulse and the time resolution of the detection system. The selection of pulses is similar to Stauffer's work.

1.2 Theories

1.2.1 Diagrammatic perturbation theory for FSRS ¹

The theory of both spontaneous and stimulated Raman spectroscopy traces back to the beginnings of quantum theory [55], and encompasses both classical [56] and quantum [57, 58, 59, 60, 61, 62] approaches. The quantum-mechanical, sum-over-states Kramers-Heisenberg-Dirac quantum scattering theory is a time-independent approach that can account for both spontaneous and stimulated Raman scattering from a stationary vibrational state with monochromatic cw radiation. With the advent of resonance Raman spectroscopy, the equivalent time-dependent wave packet approach provided an advantageous description physically and computationally [63, 64]

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With intense lasers, stimulated Raman spectroscopy was possible, and Shen and Bloembergen [65, 66] have provided a semiclassical coupled-wave description of stimulated Raman scattering with cw radiation. Recently, we have provided a quantum perturbative theory to describe stimulated Raman scattering with finite Raman pump and probe pulses which applies to 1D- and 2D-FSRS [67, 23, 68, 69, 22, 70, 71, 24].

The total Hamiltonian for a molecule interacting with an external electric field, $\mathbf{E}(\mathbf{r}, t)$, is given by

$$H_{\text{T}} = H + H_{\text{int}} , \quad (1.1)$$

where H is the material Hamiltonian in the absence of the external field, and H_{int} is the matter-field interaction. In the electric dipole and long wavelength approximation, the latter is given by

$$H_{\text{int}} = -\mu E(t) , \quad (1.2)$$

where μ is the molecular dipole projected onto the electric field.

The density matrix of the system, $\rho(t)$, satisfies the Liouville equation

$$d\rho(t)/dt = -i/\hbar[H, \rho(t)] - i/\hbar[H_{\text{int}}, \rho(t)] . \quad (1.3)$$

This equation can be solved perturbatively, by expanding the time dependent density matrix $\rho(t)$ in powers of the electric field

$$\rho(t) = \rho^{(0)}(t) + \rho^{(1)}(t) + \rho^{(2)}(t) + \dots , \quad (1.4)$$

where $\rho^{(n)}$ denotes the n th order contribution in the electric field and $\rho^{(0)}(t) = \rho(-\infty)$.

The time-dependent polarization $P(t)$, is given by the expectation value of the dipole operator μ

$$P(t) = \text{Tr}[\mu\rho(t)] . \quad (1.5)$$

Substituting Eq. (1.4) into Eq. (1.5), the perturbative expansion of the polarization in powers of the electric field is given by

$$P(t) = P^{(1)}(t) + P^{(2)}(t) + P^{(3)}(t) + \dots , \quad (1.6)$$

with

$$P^{(n)}(t) = \text{Tr}[\mu\rho^{(n)}(t)] . \quad (1.7)$$

In particular, the third-order polarization $P^{(3)}(t)$ is given by

$$P^{(3)}(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 S^{(3)}(t_1, t_2, t_3) E(t_1) E(t_2) E(t_3) , \quad (1.8)$$

where the third-order nonlinear response function, $S^{(3)}(t_1, t_2, t_3)$, can be expressed as [72, 73]

$$S^{(3)}(t_1, t_2, t_3) = \left(\frac{i}{\hbar}\right)^3 \text{Tr}[\mu \mathcal{G}(t - t_1) \mathcal{V} \mathcal{G}(t_1 - t_2) \mathcal{V} \mathcal{G}(t_2 - t_3) \mathcal{V} \rho(-\infty)] . \quad (1.9)$$

Here, $\mathcal{G}(t)$ is the time evolution operator (Green function) in the absence of the external field, defined by its action on an arbitrary dynamical variable A as

$$\mathcal{G}(t)A = \exp(-iHt)A\exp(iHt) , \quad (1.10)$$

and the commutation operator $\mathcal{V}$ is defined by

$$\mathcal{V}A = [\mu, A] . \quad (1.11)$$

In FSRS, there are three different fields, E_{pu} , E_{pu}^* and E_{pr} , with wavevectors $\mathbf{k}_{pu}$, $-\mathbf{k}_{pu}$ and $\mathbf{k}_{pr}$, respectively, interacting with the molecule, which is assumed to have just two electronic states e_1 and e_2 , and the molecule is initially in e_1 . The wavevectors for E_{pu} and E_{pu}^* point in opposite directions and so cancel out, leaving an output polarization propagating, under phase matching condition, in the $\mathbf{k}_{pr}$ direction with heterodyne detection. We can use Feynman dual time line diagrams, shown in Fig. 1.4, for ket and bra evolution with interactions from the three fields, to depict the numerous terms which contribute to the nonlinear response function and hence to the output polarization. In our Feynman dual time line diagrams, 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. We have used the direction of the arrows to denote the direction of propagation of the pump and probe pulses, which has not been done before, and we can see the arrows for the pump pulse in FSRS cancel each other and leaving the third-order polarization in the probe pulse direction. That is to say, arrows that point to the right correspond to the fields $E_{pu/pr}(t)$, while the arrow that points to the left is $E_{pu}^*(t)$. The wave vectors for the two pump interactions cancel, giving rise to an output third-order polarization, $P^{(3)}(t)$, in the phase matched probe pulse direction.

Figure 1.4: Eight basic Feynman dual time-line diagrams. Each diagram has $3!$ permutations of the fields, giving a total of 48 possible diagrams. 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. Time increases from the bottom to the top of the timelines. The interaction times on the ket or bra are labeled as t_1 , t_2 and t_3 . The closure between the bra and ket at time t is mediated by the transition dipole moment μ_{12} .

The commutation operator $\mathcal{V}$ in Eq. (1.11) leads to the four possibilities, as shown in Fig. 1.4: (I) three field interactions on the ket, (II) three field interactions on the bra, (III) one field interaction on the ket and two field interactions on the bra, and (IV) two field interactions on the ket and one field interaction on the bra. In (III), three different diagrams are possible due to the time ordering of the ket interaction relative to the bra interactions. Similarly for (IV). Since the three fields are distinguishable, the permutation of the fields lead to $3!$ possibilities for each diagram, making a total of 48 diagrams in all.

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. This means that many of the 48 diagrams have off-resonant transitions that involve emission from e_1 or absorption from e_2 states, and they can be neglected, leaving just 8 resonant diagrams, shown in Fig. 1.5, which are classified into inverse Raman scattering (IRS) and stimulated Raman scattering (SRS). Corresponding to Fig. 1.4, there are only two resonant possibilities in the permutation of $3!$ in diagram (I), which are labeled as Inverse Raman Scattering, IRS(I) and IRS(II), because all three field-matter interactions are on the ket wave function with “absorption” of the probe, which is the inverse of spontaneous Raman scattering which would have “emission” in the observed (probe) direction. For diagram (II), there is no resonant possibility. So is diagram (IV). There are a total of 18 diagrams for permutations of the fields with diagram (III), and 6 of them are resonant. We label them Stimulated Raman Scattering, SRS(I) and SRS(II), because they have two field-matter interactions on the bra (or ket) and one field-matter interaction on the ket (or bra), just as in the description of spontaneous Raman scattering as a nonlinear spectroscopy. The SRS(I) set has three diagrams: RRS(I), HL(I) and HL(II), with different time ordering of E_{pu} acting on the ket. Here RRS denotes resonance Raman scattering, and HL denotes hot luminescence. The HL terms have population created on e_2 by the pump pulse, shown shaded, which can then be stimulated to emit with E_{pr} . The SRS(II) set is similar with three diagrams, but with “absorption” of the probe pulse on the ket [23]. The SRS(I) set applies also to spontaneous Raman scattering and they are similar to the RRS(I), HL(I) and HL(II) terms in Y. R. Shen’s paper but with the vacuum field in place of the probe field [60]. The other sets - SRS(II), IRS(I), and IRS(II) - have a probe field which is

Figure 1.5: Resonant Feynman dual time-line diagrams for IRS(I), IRS(II), SRS(I), and SRS(II) processes describing FSRs. The abbreviations “coh.” stands for coherence and “pop.” stands for population shown shaded.

“absorbed” in each of the processes, and so they are irrelevant for spontaneous Raman scattering.

It is generally true that for any third-order polarization with three pulse interactions for a two-electronic state system, that there are 48 Feynman dual time-line diagrams, and 8 of these diagrams will be resonant. In the case of coherent anti-Stokes Raman spectroscopy (CARS), with a proper choice of frequencies for the pump (pu), Stokes (st) and probe (pr) pulses, with wavevectors $\mathbf{k}_{pu}$, $\mathbf{k}_{st}$ and $\mathbf{k}_{pr}$, respectively, and using the BOXCARS geometry with observation along $\mathbf{k}_{CARS} = \mathbf{k}_{pu} - \mathbf{k}_{st} + \mathbf{k}_{pr}$, it may even be possible to reduce the 8 resonant diagrams down to just one most resonant diagram, which is the typical CARS diagram [46, 72]. It will be illustrated in the following section.

The Feynman dual time line diagrams provide the time-frame view. The 8 resonant diagrams for FSRS in Fig. 1.5, can also be viewed in the energy-frame using the four-wave mixing energy level (FWMEL) diagrams, shown in Fig. 1.6. In each diagram, time increases from left to right. The interaction on the bra is denoted by a dashed arrow and on the ket by a solid arrow. The narrow bandwidth Raman pump and the broadband (grey energy bar) probe pulse are shown. The final wavy line denotes closure between the bra and the ket to give the third-order polarization. It is easy to see from the wavy line closure between bra and ket of well-defined energies that the SRS(I) set of terms gives rise to sharp Stokes and Rayleigh gain lines with energy transferred from the Raman pump to the probe pulse. In the case of the SRS(II) set, the wavy line closure is between a broad band of ket states due to the probe excitation with a bra of well-defined energy and so they give rise to broad spectra. The IRS(I) term is like the RRS(I) term, but it gives rise to sharp anti-Stokes and Rayleigh lines with energy “absorbed” from the probe. Finally, the IRS(II) term is like RRS(II), and gives rise to a broad spectrum.

From the Feynman diagrams in Fig. 1.5, we can write the third-order polarizations as overlaps between wave packets evolving on the bra and ket time lines. For SRS(I) and SRS(II) it is an overlap between a second-order bra wave packet with a first-order ket wave packet, while for IRS(I) and IRS(II) it is an overlap between a zeroth-order bra wave packet with a third-order ket wave packet,

$$P_{\text{SRS(I)}}^{(3)}(t) = \langle \psi_1^{(2)}(\mathbf{Q}, -\mathbf{k}_{pr}, \mathbf{k}_{pu}; t) | \mu_{21}^* | \psi_2^{(1)}(\mathbf{Q}, \mathbf{k}_{pu}; t) \rangle , \quad (1.12)$$

$$P_{\text{SRS(II)}}^{(3)}(t) = \langle \psi_1^{(2)}(\mathbf{Q}, -\mathbf{k}_{pu}, \mathbf{k}_{pu}; t) | \mu_{21}^* | \psi_2^{(1)}(\mathbf{Q}, \mathbf{k}_{pr}; t) \rangle , \quad (1.13)$$

Figure 1.6: Four-wave mixing energy level diagrams corresponding to the Feynman diagrams of Fig. 1.5. 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.

$$P_{\text{IRS(I)}}^{(3)}(t) = \langle \psi_1(\mathbf{Q}, t) | \mu_{21}^* | \psi_2^{(3)}(\mathbf{Q}, \mathbf{k}_{pu}, -\mathbf{k}_{pr}, \mathbf{k}_{pr}; t) \rangle , \quad (1.14)$$

$$P_{\text{IRS(II)}}^{(3)}(t) = \langle \psi_1(\mathbf{Q}, t) | \mu_{21}^* | \psi_2^{(3)}(\mathbf{Q}, \mathbf{k}_{pr}, -\mathbf{k}_{pu}, \mathbf{k}_{pu}; t) \rangle . \quad (1.15)$$

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

$$\begin{aligned} |\psi_2^{(1)}(\mathbf{Q}, \mathbf{k}_{pu}; t)\rangle &= e^{i\mathbf{k}_{pu} \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right) \int_0^t dt_1 E_{pu}(t_1) e^{(-ih_2 - \gamma_2/2)(t-t_1)/\hbar} \\ &\times \mu_{21} e^{(-ih_1 - \gamma_1/2)t_1/\hbar} |\psi_1(\mathbf{Q})\rangle , \end{aligned} \quad (1.16)$$

$$\begin{aligned} \langle \psi_1^{(2)}(\mathbf{Q}, -\mathbf{k}_{pr}, \mathbf{k}_{pu}; t) | &= e^{i(\mathbf{k}_{pr} - \mathbf{k}_{pu}) \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right)^2 \int_0^t dt_2 \int_0^{t_2} dt_3 \\ &\times E_{pr}(t_2) E_{pu}^*(t_3) \\ &\times \langle \psi_1(\mathbf{Q}) | e^{(ih_1 - \gamma_1/2)t_3/\hbar} \mu_{21}^* \\ &\times e^{(ih_2 - \gamma_2/2)(t_2 - t_3)/\hbar} \mu_{21} e^{(ih_1 - \gamma_1/2)(t - t_2)/\hbar} , \end{aligned} \quad (1.17)$$

and by appropriate change of fields, we can write down similar expressions for $|\psi_2^{(1)}(\mathbf{Q}, \mathbf{k}_{pr}; t)\rangle$

and $\langle \psi_1^{(2)}(\mathbf{Q}, -\mathbf{k}_{pu}, \mathbf{k}_{pr}; t) |$ which appear in $P_{\text{SRS(II)}}^{(3)}(t)$. For $P_{\text{IRS(I)}}^{(3)}(t)$, the wave packets are

$$\langle \psi_1(\mathbf{Q}, t) | = \langle \psi_1(\mathbf{Q}) | e^{(ih_1 - \gamma_1/2)t/\hbar} , \quad (1.18)$$

$$\begin{aligned} |\psi_2^{(3)}(\mathbf{Q}, \mathbf{k}_{pu}, -\mathbf{k}_{pu}, \mathbf{k}_{pr}; t)\rangle &= e^{i\mathbf{k}_{pr} \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \\ &\times E_{pu}(t_1) E_{pu}^*(t_2) E_{pr}(t_3) \\ &\times e^{(-ih_2 - \gamma_2/2)(t-t_1)/\hbar} \mu_{21} e^{(-ih_1 - \gamma_1/2)(t_1 - t_2)/\hbar} \\ &\times \mu_{21}^* e^{(-ih_2 - \gamma_2/2)(t_2 - t_3)/\hbar} \\ &\times \mu_{21} e^{(-ih_1 - \gamma_1/2)t_3/\hbar} |\psi_1(\mathbf{Q})\rangle , \end{aligned} \quad (1.19)$$

and by an appropriate change of fields in Eq. (1.19), we can write down a similar expression for

$|\psi_2^{(3)}(\mathbf{Q}, \mathbf{k}_{pr}, -\mathbf{k}_{pu}, \mathbf{k}_{pu}; t)\rangle$ which appear in $P_{\text{IRS(II)}}^{(3)}(t)$.

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

$$\begin{aligned} P_{\text{diff}}^{(3)}(t) &= P_{\text{pump on}}^{(3)}(\mathbf{k}_{pr}; t) - P_{\text{pump off}}^{(3)}(\mathbf{k}_{pr}; t) \\ &= P_{\text{SRS(I)}}^{(3)}(t) + P_{\text{SRS(II)}}^{(3)}(t) + P_{\text{IRS(I)}}^{(3)}(t) + P_{\text{IRS(II)}}^{(3)}(t) . \end{aligned} \quad (1.20)$$

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 [74, 75, 76, 77]

$$\sigma_{\text{RG}}(\omega) = -\frac{4\pi}{3\epsilon_0 c n} \omega \text{Im} \left\{ P_{\text{diff}}^{(3)}(\omega) / E_{\text{pr}}(\omega) \right\} , \quad (1.21)$$

where ϵ_0 is the vacuum permittivity, c is the speed of light; n is the refractive index; $P_{\text{diff}}^{(3)}(\omega)$ is the Fourier transform of the difference polarization

$$P_{\text{diff}}^{(3)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} P_{\text{diff}}^{(3)}(t) dt , \quad (1.22)$$

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

$$E_{\text{pr}}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} E_{\text{pr}}(t) dt . \quad (1.23)$$

Generally, the perturbation theory above for FSRS applies for weak fields, and for the experiments thus far, including those described below, it has worked well. In strong fields, we would have to consider all higher odd-order (fifth, seventh, etc.) polarizations along the probe pulse direction, which requires either summing up the perturbative contributions, hopefully, in decreasing order of contribution but with many more Feynman dual time-line diagrams to deal with, or solving the Liouville equation, Eq. (1.3), nonperturbatively. Both are a challenge for simulating nonlinear spectroscopy with strong fields, and it is beyond the current scope of work.

1.2.2 Diagrammatic perturbation theory for CARS ²

In diagrammatic perturbation theory, CARS, with three color fields or pulses - pump (pu), Stokes (st) and probe (pr) - acting on an initial pure state $|\psi_1^{(0)}\rangle\langle\psi_1^{(0)}|$, is represented by eight “basic” Feynman dual time-line (FDTL) diagrams in Liouville space with ket and bra evolution. These eight diagrams are as follows: (a) three field interactions on the ket, (b) three field interactions on the bra, (c) two field interactions on the ket and one field interaction on the bra, but the time ordering of the latter relative to the former leads to three diagrams, and (d) one field interaction on the ket and two field interactions on the bra, and again the time ordering leads to three diagrams. For each basic diagram, the 3! permutation of the three fields leads to another six diagrams, making a total of 48 diagrams.

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In the rotating wave approximation, the most resonant diagrams satisfy the condition that the first interaction on the ket or bra time-line is an absorption from e_1 to e_2 , followed by a stimulated emission from e_2 to e_1 , and then an absorption again, if relevant. Coupled with the phase matching condition for CARS, $\mathbf{k}_{\text{CARS}} = \mathbf{k}_{\text{pu}} - \mathbf{k}_{\text{st}} + \mathbf{k}_{\text{pr}}$, there are only four “basic” FDTL diagrams remaining, as shown in Fig. 1.7. The pure state $|\psi_1^{(0)}\rangle$ could either be a stationary state or an evolving wave packet prepared earlier by an actinic pump pulse. Set I has one diagram with three field interactions on the ket, and set II has one field interaction on the ket and two on the bra, with three time orderings for the ket interaction leading to three diagrams. The molecule interacts with the laser fields from t_3 to t in time order. The arrows pointing into the time-line denote absorption from e_1 to e_2 , while the arrows pointing away from the time-line denote stimulated emission from e_2 to e_1 . Arrows that point to the right have wave vectors $+\mathbf{k}$ and those that point to the left have $-\mathbf{k}$. Each of the diagrams has a resultant wave vector $\mathbf{k}_{\text{CARS}}$.

For each diagram, we can interchange $\mathbf{k}_{\text{pu}}$ and $\mathbf{k}_{\text{pr}}$ since their wave vectors point in the same direction. However, for the CARS experiments that we are describing here, the probe pulse is very much to the red of the pump and Stokes pulses, and the four diagrams shown are the most resonant ones. This can be seen more clearly in the four-wave mixing energy level (FWMEL) diagrams in Fig. 1.8 where the diagrams are in one-to-one correspondence with the FDTL diagrams in Fig. 1.7. Here, time increases from left to right in each diagram, and $v = 0, 1$ represent the vibrational levels. The interaction on the bra is denoted by a dash arrow and on the ket by a solid arrow. The pump, Stokes and probe pulses are shown. In diagram I, the pump pulse leads to excitation while Stokes pulse leads to deexcitation and the frequency difference between pump and Stokes pulses covers the fundamental vibrational transitions in the ground electronic state. Diagram I is clearly more resonant than diagrams II (a)-(c).

The FDTL diagrams and the FWMEL diagrams are complementary to each other. They are like time-frame and energy-frame viewpoints. From the FDTL diagrams, one can conveniently write down the expressions for the third-order polarizations. On the other hand, the FWMEL diagrams help to better see which terms are more resonant in the rotating wave approximation and can make a larger contribution to the third-order polarization.

As the probe pulse is applied after the pump and Stokes pulses have prepared the coherences

Figure 1.7: Four basic Feynman dual time-line diagrams of CARS that satisfy the resonant rotating wave approximation and the phase matching condition for CARS: (I) three ket interactions, (II) one ket and two bra interactions. Being resonant terms, the first interaction on either time-lines is an absorption (arrow pointing into the time-line), followed by an emission (arrow pointing away from the time-line), and then an absorption, if relevant. The pump and the probe fields can be interchanged while retaining the phase matching condition. These diagrams facilitate writing down the time-dependent third-order polarizations.

Figure 1.8: Basic four-wave mixing energy level diagrams corresponding to the Feynman dual time-line diagrams in Figure 1.7. Time increases from left to right in each diagram, and $v = 0, 1$ represent the ground electronic state vibrational levels. The interaction on the bra is denoted by a dash arrow and on the ket by a solid arrow. These diagrams give the energy-frame viewpoint and help us visualize the resonant terms.

in the molecule and is off-resonance with the zero-zero energy transition between the ground and excited electronic states, the CARS spectrum for each mode should have the width of the probe pulse. It is typically broad when the probe pulse is of fs duration, and narrow when it is of ps duration. Moreover, the line shape of multi-mode tr fs CARS will depend on the relationship between the width of the probe spectrum and the energy spacing between vibrational modes, i.e., one can see the quantum beats in the tr fs CARS spectrum when the probe spectrum is broader than the mode energy spacings. In fs/ps CARS, the ps probe spectrum is narrower than the mode spacings, and so the vibrational spectrum for fs/ps CARS will not change with delay time beyond about about 2 ps.

The third-order polarization for diagram I is given by [22, 68]

$$\begin{aligned}
P_I^{(3)}(t) &= \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \\
&\times e^{-\gamma_2(t-t_1)/2\hbar - \gamma_1(t_1-t_2)/2\hbar - (t_1-t_2)/T_2 - \gamma_2(t_2-t_3)/2\hbar - \gamma_1(t+t_3)/2\hbar} \\
&\times E_{pr}(t_1) E_{st}^*(t_2) E_{pu}(t_3) I(t, t_1, t_2, t_3) ,
\end{aligned} \tag{1.24}$$

where $\{\gamma_i, i = 1, 2\}$ are the lifetime of the respective electronic states, which give rise to homogeneous broadening. T_2 is the vibrational dephasing time, which is the decay time of the vibrational coherences prepared by pump and Stokes pulses in the e_1 state. $E_{pr}(t)$, $E_{st}^*(t)$ and $E_{pu}(t)$ represent the electric fields for the probe, Stokes and pump pulses, respectively. The four-time correlation function, $I(t, t_1, t_2, t_3)$, is given by [22]

$$\begin{aligned}
I(t, t_1, t_2, t_3) &= G(t - t_1 + t_2 - t_3) \langle \psi_1^{(0)}(\mathbf{Q}, 0) | e^{i\mathbf{h}_1 t/\hbar} \mu_{12} e^{-i\mathbf{h}_2(t-t_1)/\hbar} \mu_{21} \\
&\times e^{-i\mathbf{h}_1(t_1-t_2)/\hbar} \mu_{12} e^{-i\mathbf{h}_2(t_2-t_3)/\hbar} \mu_{21} e^{-i\mathbf{h}_1 t_3/\hbar} | \psi_1^{(0)}(\mathbf{Q}, 0) \rangle ,
\end{aligned} \tag{1.25}$$

where μ_{12} and μ_{21} represent the transition dipole moment; $\mathbf{h}_1$ and $\mathbf{h}_2$ denote the multi-mode Hamiltonian for the e_1 and e_2 electronic states, respectively; $|\psi_1^{(0)}(\mathbf{Q}, 0)\rangle$ is a stationary vibrational state or a wave packet prepared earlier by an actinic pump pulse in the e_1 state; and $G(t)$ is an inhomogeneous broadening term which is the Fourier transformation (FT) of the inhomogeneous distribution function

$$G(t) = \int_0^\infty dE_{21} e^{-iE_{21}t/\hbar} G(E_{21}) , \tag{1.26}$$

and

$$G(E_{21}) = \frac{\exp \left[-\frac{(E_{21} - \bar{E}_{21})^2}{2\theta^2} \right]}{\theta(2\pi)^{1/2}}, \quad (1.27)$$

where $\bar{E}_{21}$ is the energy gap between the minima of the two multidimensional potential energy surfaces and θ is the standard deviation in the inhomogeneous broadening.

1.3 Separable Displaced Harmonic Oscillator Model

Our time-dependent quantum wave packet theory is applicable for any form of potential energy surfaces. A three-state model has been used on FSRS [68]. 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. In general, more realistic 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 multi-dimensions to represent the ground and excited potential energy surfaces of polyatomic molecules with variable displacements in the modes, with relative rotation of the vibrational coordinates (Duschinsky effect), and coordinate dependent transition dipole moment. The third-order polarizations can then be written as triple time integrals over four-time correlation functions, and the analytic expressions could be obtained with homogeneous and inhomogeneous damping taken into account. Heller *et al.* have presented the time-dependent theory for multi-dimensional displaced harmonic oscillators with and without Dushinsky rotation for spontaneous Raman scattering [79].

For the problems in the thesis, we are mostly dealing with short-time dynamics on the excited state potential and only the region of the excited state potential in the Franck-Condon region is important, so we can represent it with a multi-dimensional separable displaced harmonic oscillator. We have successfully applied the perturbative wave packet theory to the FSRS

of Rhodamine 6G (R6G) and crystal violet (CV) and to the CARS of toluene and R6G using separable multi-dimensional harmonic oscillator model. 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 [70]. However, for a situation like photoisomerization on the excited state potential or where there is curve crossing with conical intersections, then the harmonic oscillator model could be inadequate and more realistic potentials need to be used. Zhao *et al.* have added the anharmonic terms to the harmonic model to solve the mode coupling potential energy of CDCl_3 [71].

In our calculations below we consider two Born-Oppenheimer electronic states e_1 and e_2 and their associated vibrational manifolds. We will assume that the Hamiltonians h_1 and h_2 are for a set of displaced, separable, multi-dimensional harmonic oscillators. In an N -dimensional separable system, the vibrational Hamiltonians on e_1 and e_2 are sums of one-dimensional displaced harmonic oscillator Hamiltonians. The propagators are then products of one-dimensional propagators. We will explain detailedly in Chapter 2.

1.4 Outline of Dissertation

This thesis presents the quantum mechanical wave packet perturbation theory of femtosecond stimulated Raman spectroscopy (FSRS) and coherent anti-Stokes Raman spectroscopy (CARS). The calculations have been carried out using multidimensional separable displaced harmonic oscillators model to simulate the FSRS of Rhodamine 6G (R6G) and crystal violet (CV) and the CARS of toluene and R6G.

In chapter 2, the FSRS simulated with a delta function probe pulse in rhodamine 6G (R6G) from the ground vibrational state has been investigated by the perturbative quantum wave packet theory. The expressions of all the eight processes for the FSRS third-order polarizations with both homogeneous damping and inhomogeneous broadening are presented. 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]. It is possible to simulate the FSRS process with a delta-function probe pulse, because the probe pulse initiates the third-order polarization and the duration of the probe pulse is short relative to the vibrational period. By adopting the multidimensional displaced harmonic oscillator model, the four nonlinear processes of FSRS could be written as triple time integrals over four-time correlation functions which have analytic results for any number of dimensions [22]. 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, especially for large polyatomic molecules with many vibrational modes.

Chapter 3 describes the simulation of the inverse Raman scattering (IRS) on crystal violet (CV) with the same quantum wave perturbation packet theory. Calculations with separable multidimensional harmonic oscillators model are made to compare with the absorption and resonant ultrafast Raman loss spectroscopy (URLS) experiments [21] on CV. Both IRS and URLS shows the Raman loss and dispersive line shapes on anti-Stokes bands, which could be accounted for by the IRS(I) term of FSRS with our quantum theory. The effects of Raman pump pulse temporal width and the Raman transition damping time to the IRS spectrum are studied. Moreover, 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.

Twenty four Feynman dual time line and four wave mixing energy level diagrams are presented in Chapter 4 to depict CARS from the ground electronic state. Calculations are made on toluene for off-resonance CARS and R6G for resonance CARS for each of the twenty four terms that contributes to the third-order polarization of CARS. The line-shape and relative intensity of each term are interpreted for both off-resonance CARS and resonance CARS on toluene and R6G, respectively.

Finally, a brief conclusion highlights the central results and the prospects for future work are presented in Chapter 5.

Broadband Stimulated Raman Scattering With A Picosecond Raman Pump and A Delta Function Probe Pulse ¹

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 (super-continuum) 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**:

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2.1 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, 80, 81] 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 [55], tracing back to the beginnings of quantum theory, and both classical [56] and quantum [57, 58] 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 [63, 64]. With intense lasers, stimulated Raman spectroscopy was possible, and Shen and Bloembergen [65, 66] 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 [82]. Later, it was found that the coupled-wave approach is valid only for off-resonance FSRS and works only for the Stokes bands [67]. 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 [23]. 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 [23, 68, 69, 22]. The quantum wave packet theory can be extended as two third-order processes to cover the recently observed cascading Raman signals in FSRS [83].

The quantum theory of stimulated Raman scattering [23] 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 [22]. 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.

2.2 Theory

2.2.1 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

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}[\mathcal{H}_0 + \mathcal{V}(t), \rho(t)] - \Gamma \rho(t) , \quad (2.1)$$

with

$$\begin{aligned} \mathcal{H}_0 &= |e_1\rangle \mathbf{h}_1(\mathbf{Q}) \langle e_1| + |e_2\rangle \mathbf{h}_2(\mathbf{Q}) \langle e_2| , \\ \mathcal{V}(t) &= -\boldsymbol{\mu}(\mathbf{Q}) \cdot \mathbf{E}(\mathbf{R}, t) , \\ \boldsymbol{\mu}(\mathbf{Q}) &= |e_2\rangle \boldsymbol{\mu}_{21}(\mathbf{Q}) \langle e_1| + \text{c.c.} , \\ \mathbf{E}(\mathbf{R}, t) &= \boldsymbol{\varepsilon}_{pu} E_{pu}(t; T_{pu}) \exp(i\mathbf{k}_{pu} \cdot \mathbf{R}) + \boldsymbol{\varepsilon}_{pr} E_{pr}(t; T_{pr}) \exp(i\mathbf{k}_{pr} \cdot \mathbf{R}) + \text{c.c.} \\ &\equiv \mathbf{E}_{pu}(t; T_{pu}) + \mathbf{E}_{pr}(t; T_{pr}) + \text{c.c.} . \end{aligned} \quad (2.2)$$

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

$$\rho(t) = \sum_{a,b=1}^2 |e_a\rangle \rho_{ab}(\mathbf{Q}, t) \langle e_b| , \quad (2.3)$$

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. (2.1) 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

$$E_{pr}(t; T_{pr}) = E_{0,pr} \delta(t - T_{pr}) , \quad (2.4)$$

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

$$E_{pu}(t; T_{pu}) = E_{0,pu} g_{pu}(t; T_{pu}) e^{-i\omega_{pu}t} , \quad (2.5)$$

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

$$g_{pu}(t; T_{pu}) = \exp\left(-2 \ln 2 \frac{(t - T_{pu})^2}{\Delta_{pu}^2}\right) , \quad (2.6)$$

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.

Figure 2.1: 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} .

2.1. 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) [23]. 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 [60]. So, stimulated Raman scattering

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 2.2: Four-wave mixing energy level diagrams corresponding to the Feynman diagrams in Fig. 2.1. 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. 2.2. 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

$$\begin{aligned}
P_{\text{diff}}^{(3)}(t) &= P_{\text{pump+probe}}^{(3)}(t; \mathbf{k}_{pr}) - P_{\text{probe only}}^{(3)}(t; \mathbf{k}_{pr}) \\
&= P_{\text{RRS(I)}}^{(3)}(t; \mathbf{k}_{pr}) + P_{\text{HL(I)+HL(II)}}^{(3)}(t; \mathbf{k}_{pr}) \\
&\quad + P_{\text{RRS(II)}}^{(3)}(t; \mathbf{k}_{pr}) + P_{\text{HL(III)+HL(IV)}}^{(3)}(t; \mathbf{k}_{pr}) \\
&\quad + P_{\text{IRS(I)}}^{(3)}(t; \mathbf{k}_{pr}) + P_{\text{IRS(II)}}^{(3)}(t; \mathbf{k}_{pr}) , \tag{2.7}
\end{aligned}$$

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 [74, 75, 76, 77]

$$\sigma_{RG}(\omega) = -\frac{4\pi}{3\epsilon_0 c n} \omega \text{Im} \left\{ P_{\text{diff}}^{(3)}(\omega) / E_{pr}(\omega) \right\} , \tag{2.8}$$

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

$$E_{pr}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} E_{pr}(t) dt , \tag{2.9}$$

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

$$P_{diff}^{(3)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} P_{diff}^{(3)}(t) dt . \quad (2.10)$$

2.2.2 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,

$$\mathbf{h}_1 = \sum_{r=1}^N h_{1r} , \quad (2.11)$$

$$\mathbf{h}_2 = \sum_{r=1}^N h_{2r} + E_{21} , \quad (2.12)$$

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 ,

$$|\psi_1(\mathbf{Q}, t=0)\rangle = \prod_r |\psi_{1r0}(Q_r)\rangle . \quad (2.13)$$

With a delta function probe pulse, Eq.(2.4), the third-order polarization for RRS(I) can be written as

$$\begin{aligned} P_{RRS(I)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_{T_{pr}}^t dt_1 \int_0^{T_{pr}} dt_2 \\ &\times e^{-\gamma_1 t_2/2\hbar - \gamma_2(T_{pr}-t_2)/2\hbar - \gamma_1(t-T_{pr})/2\hbar - \gamma_2(t-t_1)/2\hbar - \gamma_1 t_1/2\hbar} \\ &\times E_{pu}^*(t_2; T_{pu}) e^{iE_{21}(T_{pr}-t_2)/\hbar} e^{-iE_{21}(t-t_1)/\hbar} E_{pu}(t_1; T_{pu}) \\ &\times \prod_r S_{1,r}(t, t_1, t_2; T_{pr}, T_2) , \end{aligned} \quad (2.14)$$

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

$$\begin{aligned} S_{1,r}(t, t_1, t_2; T_{pr}, T_2) &= \mu^4 e^{-iE_{1r0}(t_1-t_2)/\hbar} \\ &\times \sum_{v'} \langle \psi_{1r0}(Q_r) | e^{ih_{2r}(T_{pr}-t_2)/\hbar} | \psi_{1rv'}(Q_r) \rangle e^{iE_{1rv'}(t-T_{pr})/\hbar} \\ &\times \langle \psi_{1rv'}(Q_r) | e^{-ih_{2r}(t-t_1)/\hbar} | \psi_{1r0}(Q_r) \rangle \\ &\times \left\{ \delta_{0v'} + e^{-(t_1-T_{pr})/T_2} (1 - \delta_{0v'}) \right\} , \end{aligned} \quad (2.15)$$

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,

$$\begin{aligned}
P_{HL(I)+HL(II)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_0^{T_{pr}} dt_1 \int_0^{T_{pr}} dt_2 \\
&\times e^{-\gamma_1 t_2 / 2\hbar - \gamma_2 (T_{pr} - t_2) / 2\hbar - \gamma_1 (t - T_{pr}) / 2\hbar - \gamma_2 (t - t_1) / 2\hbar - \gamma_1 t_1 / 2\hbar} \\
&\times E_{pu}^*(t_2; T_{pu}) e^{iE_{21}(T_{pr} - t_2) / \hbar} e^{-iE_{21}(t - t_1) / \hbar} E_{pu}(t_1; T_{pu}) \\
&\times \prod_r S_{1', r}(t, t_1, t_2; T_{pr}) , \tag{2.16}
\end{aligned}$$

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. (2.15),

$$\begin{aligned}
S_{1', r}(t, t_1, t_2; T_{pr}) &= \mu^4 e^{-iE_{1r0}(t_1 - t_2) / \hbar} \\
&\times \sum_{v'} \langle \psi_{1r0}(Q_r) | e^{ih_{2r}(T_{pr} - t_2) / \hbar} | \psi_{1rv'}(Q_r) \rangle e^{iE_{1rv'}(t - T_{pr}) / \hbar} \\
&\times \langle \psi_{1rv'}(Q_r) | e^{-ih_{2r}(t - t_1) / \hbar} | \psi_{1r0}(Q_r) \rangle . \tag{2.17}
\end{aligned}$$

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

$$\begin{aligned}
P_{RRS(II)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_0^{T_{pr}} dt_1 \int_0^{t_1} dt_2 \\
&\times e^{-\gamma_1 t_2 / 2\hbar - \gamma_2 (t_1 - t_2) / 2\hbar - \gamma_1 (t - t_1) / 2\hbar - \gamma_2 (t - T_{pr}) / 2\hbar - \gamma_1 T_{pr} / 2\hbar} \\
&\times E_{pu}^*(t_2; T_{pu}) e^{iE_{21}(t_1 - t_2) / \hbar} E_{pu}(t_1; T_{pu}) e^{-iE_{21}(t - T_{pr}) / \hbar} \\
&\times \prod_r S_{2, r}(t, t_1, t_2; T_{pr}) , \tag{2.18}
\end{aligned}$$

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

$$\begin{aligned}
S_{2, r}(t, t_1, t_2; T_{pr}) &= \mu^4 e^{-iE_{1r0}(T_{pr} - t_2) / \hbar} \\
&\times \sum_{v'} \langle \psi_{1r0}(Q_r) | e^{ih_{2r}(t_1 - t_2) / \hbar} | \psi_{1rv'}(Q_r) \rangle e^{iE_{1rv'}(t - t_1) / \hbar} \\
&\times \langle \psi_{1rv'}(Q_r) | e^{-ih_{2r}(t - T_{pr}) / \hbar} | \psi_{1r0}(Q_r) \rangle . \tag{2.19}
\end{aligned}$$

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,

$$\begin{aligned}
P_{HL(III)+HL(IV)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_{T_{pr}}^t dt_1 \int_0^{t_1} dt_2 \\
&\times e^{-\gamma_1 t_2 / 2\hbar - \gamma_2 (t_1 - t_2) / 2\hbar - \gamma_1 (t - t_1) / 2\hbar - \gamma_2 (t - T_{pr}) / 2\hbar - \gamma_1 T_{pr} / 2\hbar} \\
&\times E_{pu}^*(t_2; T_{pu}) e^{iE_{21}(t_1 - t_2) / \hbar} E_{pu}(t_1; T_{pu}) e^{-iE_{21}(t - T_{pr}) / \hbar} \\
&\times \prod_r S_{2,r}(t, t_1, t_2; T_{pr}) .
\end{aligned} \tag{2.20}$$

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

$$\begin{aligned}
P_{IRS(I)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_{T_{pr}}^t dt_1 \int_{T_{pr}}^{t_1} dt_2 \\
&\times e^{-\gamma_2 (t - t_1) / 2\hbar - \gamma_1 (t_1 - t_2) / 2\hbar - \gamma_2 (t_2 - T_{pr}) / 2\hbar - \gamma_1 T_{pr} / 2\hbar} \\
&\times e^{-iE_{21}(t - t_1) / \hbar} E_{pu}(t_1; T_{pu}) E_{pu}^*(t_2; T_{pu}) e^{-iE_{21}(t_2 - T_{pr}) / \hbar} \\
&\times \prod_r I_{1,r}(t, t_1, t_2; T_{pr}, T_2) ,
\end{aligned} \tag{2.21}$$

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

$$\begin{aligned}
I_{1,r}(t, t_1, t_2; T_{pr}, T_2) &= \mu^4 e^{-iE_{1r0}(T_{pr} - t) / \hbar} \\
&\times \sum_{v'} \langle \psi_{1r0}(Q_r) | e^{-ih_{2r}(t - t_1) / \hbar} | \psi_{1rv'}(Q_r) \rangle e^{-iE_{1rv'}(t_1 - t_2) / \hbar} \\
&\times \langle \psi_{1rv'}(Q_r) | e^{-ih_{2r}(t_2 - T_{pr}) / \hbar} | \psi_{1r0}(Q_r) \rangle \\
&\times \left\{ \delta_{0v'} + e^{-(t_1 - t_2) / T_2} (1 - \delta_{0v'}) \right\} ,
\end{aligned} \tag{2.22}$$

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

$$\begin{aligned}
P_{IRS(II)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_0^{T_{pr}} dt_1 \int_0^{t_1} dt_2 \\
&\times e^{-\gamma_2 (t - T_{pr}) / 2\hbar - \gamma_1 (T_{pr} - t_1) / 2\hbar - \gamma_2 (t_1 - t_2) / 2\hbar - \gamma_1 t_2 / 2\hbar} \\
&\times e^{-iE_{21}(t - T_{pr}) / \hbar} E_{pu}^*(t_1; T_{pu}) e^{-iE_{21}(t_1 - t_2) / \hbar} E_{pu}(t_2; T_{pu}) \\
&\times \prod_r I_{2,r}(t, t_1, t_2; T_{pr}) ,
\end{aligned} \tag{2.23}$$

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

$$\begin{aligned}
I_{2, r}(t, t_1, t_2; T_{pr}) &= \mu^4 e^{-iE_{1r0}(t_2-t)/\hbar} \\
&\times \sum_{v'} \langle \psi_{1r0}(Q_r) | e^{-ih_{2r}(t-T_{pr})/\hbar} | \psi_{1rv'}(Q_r) \rangle e^{-iE_{1rv'}(T_{pr}-t_1)/\hbar} \\
&\times \langle \psi_{1rv'}(Q_r) | e^{-ih_{2r}(t_1-t_2)/\hbar} | \psi_{1r0}(Q_r) \rangle ,
\end{aligned} \tag{2.24}$$

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.(2.15, 2.19, 2.22, and 2.24). 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

$$\langle \psi_n | e^{-ih_2 t/\hbar} | \psi_0 \rangle \equiv \langle \psi_n | \psi_0(t) \rangle \tag{2.25}$$

$$\begin{aligned}
\langle \psi_n | \psi_0(t) \rangle &= \exp\{-(\Delta^2/2)[1 - \exp(-i\omega t)] - i\omega t/2\} \\
&\times \frac{(-1)^n \Delta^n}{(2^n n!)^{1/2}} [1 - e^{(-i\omega t)}]^n ,
\end{aligned} \tag{2.26}$$

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

2.2.3 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

$$G(t) = \int_0^\infty dE_{21} e^{-iE_{21}t/\hbar} G(E_{21}) , \tag{2.27}$$

where

$$G(E_{21}) = \frac{\exp\left[-\frac{(E_{21}-\bar{E}_{21})^2}{2\theta^2}\right]}{\theta(2\pi)^{1/2}} , \tag{2.28}$$

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. 2.27 and 2.28. 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 [84, 85, 86, 22] that the FSRs third-order polarization terms with inhomogeneous broadening are given by,

$$\begin{aligned}
P_{RRS(I)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_{T_{pr}}^t dt_1 \int_0^{T_{pr}} dt_2 \\
&\times e^{-\gamma_1 t_2 / 2\hbar - \gamma_2 (T_{pr} - t_2) / 2\hbar - \gamma_1 (t - T_{pr}) / 2\hbar - \gamma_2 (t - t_1) / 2\hbar - \gamma_1 t_1 / 2\hbar} \\
&\times E_{pu}^*(t_2; T_{pu}) E_{pu}(t_1; T_{pu}) G(t - t_1 - T_{pr} + t_2) \\
&\times \prod_r S_{1, r}(t, t_1, t_2; T_{pr}, T_2) , \tag{2.29}
\end{aligned}$$

$$\begin{aligned}
P_{HL(I)+HL(II)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_0^{T_{pr}} dt_1 \int_0^{T_{pr}} dt_2 \\
&\times e^{-\gamma_1 t_2 / 2\hbar - \gamma_2 (T_{pr} - t_2) / 2\hbar - \gamma_1 (t - T_{pr}) / 2\hbar - \gamma_2 (t - t_1) / 2\hbar - \gamma_1 t_1 / 2\hbar} \\
&\times E_{pu}^*(t_2; T_{pu}) E_{pu}(t_1; T_{pu}) G(t - t_1 - T_{pr} + t_2) \\
&\times \prod_r S_{1', r}(t, t_1, t_2; T_{pr}) , \tag{2.30}
\end{aligned}$$

$$\begin{aligned}
P_{RRS(II)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_0^{T_{pr}} dt_1 \int_0^{t_1} dt_2 \\
&\times e^{-\gamma_1 t_2 / 2\hbar - \gamma_2 (t_1 - t_2) / 2\hbar - \gamma_1 (t - t_1) / 2\hbar - \gamma_2 (t - T_{pr}) / 2\hbar - \gamma_1 T_{pr} / 2\hbar} \\
&\times E_{pu}^*(t_2; T_{pu}) E_{pu}(t_1; T_{pu}) G(t - T_{pr} - t_1 + t_2) \\
&\times \prod_r S_{2, r}(t, t_1, t_2; T_{pr}) , \tag{2.31}
\end{aligned}$$

$$\begin{aligned}
P_{HL(III)+HL(IV)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_{T_{pr}}^t dt_1 \int_0^{t_1} dt_2 \\
&\times e^{-\gamma_1 t_2 / 2\hbar - \gamma_2 (t_1 - t_2) / 2\hbar - \gamma_1 (t - t_1) / 2\hbar - \gamma_2 (t - T_{pr}) / 2\hbar - \gamma_1 T_{pr} / 2\hbar} \\
&\times E_{pu}^*(t_2; T_{pu}) E_{pu}(t_1; T_{pu}) G(t - T_{pr} - t_1 + t_2) \\
&\times \prod_r S_{2, r}(t, t_1, t_2; T_{pr}) . \tag{2.32}
\end{aligned}$$

$$\begin{aligned}
P_{IRS(I)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_{T_{pr}}^t dt_1 \int_{T_{pr}}^{t_1} dt_2 \\
&\times e^{-\gamma_2(t-t_1)/2\hbar - \gamma_1(t_1-t_2)/2\hbar - \gamma_2(t_2-T_{pr})/2\hbar - \gamma_1 T_{pr}/2\hbar} \\
&\times E_{pu}(t_1; T_{pu}) E_{pu}^*(t_2; T_{pu}) G(t - t_1 + t_2 - T_{pr}) \\
&\times \prod_r I_{1, r}(t, t_1, t_2; T_{pr}, T_2) , \tag{2.33}
\end{aligned}$$

$$\begin{aligned}
P_{IRS(II)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_0^{T_{pr}} dt_1 \int_0^{t_1} dt_2 \\
&\times e^{-\gamma_2(t-T_{pr})/2\hbar - \gamma_1(T_{pr}-t_1)/2\hbar - \gamma_2(t_1-t_2)/2\hbar - \gamma_1 t_2/2\hbar} \\
&\times E_{pu}^*(t_1; T_{pu}) E_{pu}(t_2; T_{pu}) G(t - T_{pr} + t_1 - t_2) \\
&\times \prod_r I_{2, r}(t, t_1, t_2; T_{pr}) . \tag{2.34}
\end{aligned}$$

All the integrands in Eqs.(2.29- 2.34) 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.

2.2.4 Mukamel's three-state model for off-resonant FSRS

Mukamel's 3-state model for off-resonant FSRS [87] with vibrational states $|a\rangle$ and $|c\rangle$ on the lower electronic state and a single vibrational state $|b\rangle$ on the upper electronic state, as shown in Fig. 2.3, can be derived from Eqs. (2.14) and (2.16). Mukamel's assumptions are as follows: (a) Off-resonant FSRS and only Stokes lines are considered. Hence only the SRS(I) term, which is the sum of RRS(I), HL(I) and HL(II) terms, needs to be considered. (b) Separable modes, and so only one mode is considered. (c) Raman pump pulse is monochromatic ($E_{Rpu}(t) = E_{0,Rpu} \exp(-i\omega_{Rpu}t)$) and probe pulse is impulsive ($E_{pr}(t) = E_{0,pr} \delta(t - T)$). (d) The frequency ω_{ca} is time-dependent but the rate of change is adiabatic. The molecule that begins in state $|a\rangle$ will remain in state $|a\rangle$ throughout the FSRS process.

The molecule is initially prepared by actinic pump pulse in a vibrational state $|a\rangle$, as shown in Fig. 2.3. Subsequently, a monochromatic Raman pump pulse excites the system to a virtual state that is off-resonant with the vibrational level $|b\rangle$ in a higher excited electronic state, while a third delta function pulse centered at T stimulates the Raman signal, and the Raman process takes the molecule back to another vibrational level $|c\rangle$ in the same electronic state with $|a\rangle$.

Figure 2.3: Schematic energy level diagram of time-resolved FSRS process. An ultrashort actinic pulse sends the molecule from the ground state g to a vibrational state a on excited electronic state. A monochromatic Raman pump pulse excites the system to a virtual state that is off-resonant with the vibrational level b in a higher excited electronic state, while a third delta function pulse centered at T stimulates the Raman signal, and the Raman process takes the molecule back to another vibrational level c in the same electronic state with a .

With Mukamel's assumption that Raman probe pulse is impulsive ($E_{pr}(t) = E_{0,pr}\delta(t - T_p)$), the third-order polarization for RRS(I) can be obtained from Eq. (2.14) for a single mode as,

$$\begin{aligned}
P_{RRS(I)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_T^t dt_1 \int_0^T dt_2 \\
&\times e^{-\gamma_1 t_2 / 2\hbar - \gamma_2 (T - t_2) / 2\hbar - \gamma_1 (t - T) / 2\hbar - \gamma_2 (t - t_1) / 2\hbar - \gamma_1 t_1 / 2\hbar} \\
&\times E_{Rpu}^*(t_2) E_{Rpu}(t_1) S_1(t, t_1, t_2; T) ,
\end{aligned} \tag{2.35}$$

where the three-time correlation function $S_1(t, t_1, t_2; T)$ is defined as

$$\begin{aligned}
S_1(t, t_1, t_2; T) &= |\mu_{ab}|^2 |\mu_{cb}|^2 \langle a | e^{ih_1 t_2} | b \rangle \langle b | e^{ih_2 (T - t_2)} | c \rangle \\
&\times \langle c | e^{ih_1 (t - T)} e^{-ih_2 (t - t_1)} | b \rangle \langle b | e^{-ih_1 t_1} | a \rangle \\
&= |\mu_{ab}|^2 |\mu_{cb}|^2 e^{i\omega_a t_2} e^{i\omega_b (T - t_2)} e^{i\omega_c (t - T)} e^{-i\omega_b (t - t_1)} e^{-i\omega_a t_1} .
\end{aligned} \tag{2.36}$$

Similarly, the summation of the third-order polarization for HL(I) and HL(II) for a single mode which differs from RRS(I) by changing the limit of integral of t_1 can be derived from Eq. (2.16) as,

$$\begin{aligned}
P_{HL(I)+HL(II)}^{(3)}(t; \mathbf{k}_{pr}) &= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_0^T dt_1 \int_0^T dt_2 \\
&\times e^{-\gamma_1 t_2 / 2\hbar - \gamma_2 (T - t_2) / 2\hbar - \gamma_1 (t - T) / 2\hbar - \gamma_2 (t - t_1) / 2\hbar - \gamma_1 t_1 / 2\hbar} \\
&\times E_{Rpu}^*(t_2) E_{Rpu}(t_1) S_1(t, t_1, t_2; T) .
\end{aligned} \tag{2.37}$$

The expression for the third-order polarization for SRS(I) is given by,

$$\begin{aligned}
P_{SRS(I)}^{(3)}(t; \mathbf{k}_{pr}) &= P_{RRS(I)}^{(3)}(t; \mathbf{k}_{pr}) + P_{HL(I)+HL(II)}^{(3)}(t; \mathbf{k}_{pr}) \\
&= E_{0,pr} \left(\frac{i}{\hbar} \right)^3 \int_0^t dt_1 \int_0^T dt_2 \\
&\times e^{-\gamma_1 t_2 / 2\hbar - \gamma_2 (T - t_2) / 2\hbar - \gamma_1 (t - T) / 2\hbar - \gamma_2 (t - t_1) / 2\hbar - \gamma_1 t_1 / 2\hbar} \\
&\times E_{Rpu}^*(t_2) E_{Rpu}(t_1) S_1(t, t_1, t_2; T) ,
\end{aligned} \tag{2.38}$$

With Mukamel's assumption that Raman pump pulse is monochromatic

$$E_{Rpu}(t) = E_{0,Rpu} \exp(-i\omega_{Rpu} t) , \tag{2.39}$$

Eq. 2.38 then gives,

$$\begin{aligned}
P_{SRS(I)}^{(3)}(t;T) &= \left(\frac{i}{\hbar}\right)^3 |E_{0,Rpu}|^2 E_{0,pr} |\mu_{ab}|^2 |\mu_{cb}|^2 \int_0^t dt_1 \int_0^T dt_2 \\
&\quad \times e^{-\gamma_1 t_2 / 2\hbar - \gamma_2 (T-t_2) / 2\hbar - \gamma_1 (t-T) / 2\hbar - \gamma_2 (t-t_1) / 2\hbar - \gamma_1 t_1 / 2\hbar} \\
&\quad \times e^{i\omega_a t_2} e^{i\omega_b (T-t_2)} e^{i\omega_c (t-T)} e^{-i\omega_b (t-t_1)} e^{-i\omega_a t_1} e^{i\omega_{Rpu} t_2} e^{-i\omega_{Rpu} t_1} \\
&= \left(\frac{i}{\hbar}\right)^3 |E_{0,Rpu}|^2 E_{0,pr} |\mu_{ab}|^2 |\mu_{cb}|^2 \frac{1}{i(\omega_{Rpu} - \omega_{ba}) + \gamma_2} \frac{1}{-i(\omega_{Rpu} - \omega_{ba}) + \gamma_2} \\
&\quad \times e^{-i(\omega_{Rpu} - \omega_{ca})t - \gamma_1 t} e^{i(\omega_{Rpu} - \omega_{ca})T + \gamma_1 T} \\
&= \left(\frac{i}{\hbar}\right)^3 |E_{0,Rpu}|^2 E_{0,pr} \frac{|\mu_{ab}|^2 |\mu_{cb}|^2}{(\omega_{Rpu} - \omega_{ba})^2} \\
&\quad \times e^{-i\omega_{Rpu} (t-T)} e^{i\omega_{ca} (t-T)} e^{-\gamma_1 (t-T)}, \tag{2.40}
\end{aligned}$$

where γ_2 has been set to zero as we are considering off-resonance FSRs where only very short time dynamics on the upper electronic state is important, and we have dropped the $\mathbf{k}_{pr}$ in the argument for the polarization, with the understanding that it is for observation in the $\mathbf{k}_{pr}$ direction.

With Mukamel's assumption that the frequency of ω_{ca} is time-dependent but the rate of change is adiabatic, the molecule is always in state $|a\rangle$ throughout the FSRs process. The hamiltonian $h_1(t)$ is time-dependent and the evolution of wave function $|a(t)\rangle$ on e_1 is expressed as

$$|a(t)\rangle = e^{-i \int_0^t d\tau h_1(\tau)/\hbar} |a(0)\rangle. \tag{2.41}$$

The SRS(I) third-order polarization now is expressed in the form as

$$\begin{aligned}
P_{SRS(I)}^{(3)}(t;T) &= \left(\frac{i}{\hbar}\right)^3 |E_{0,Rpu}|^2 E_{0,pr} |\mu_{ab}|^2 |\mu_{cb}|^2 \int_0^t dt_1 \int_0^T dt_3 \\
&\quad \times e^{i \int_0^{t_3} d\tau \omega_a(\tau)} e^{i\omega_{Rpu} t_3} e^{i\omega_b (T-t_3) - \gamma_2 (T-t_3)} e^{i \int_T^t d\tau \omega_c(\tau) - \gamma_1 (t-T)} \\
&\quad \times e^{-i\omega_b (t-t_1) - \gamma_2 (t-t_1)} e^{-i\omega_{Rpu} t_1} e^{-i \int_0^{t_1} d\tau \omega_a(\tau)} \\
&= \left(\frac{i}{\hbar}\right)^3 |E_{0,Rpu}|^2 E_{0,pr} \frac{|\mu_{ab}|^2 |\mu_{cb}|^2}{(\omega_{Rpu} - \omega_{ba})^2} \\
&\quad \times e^{-i\omega_{Rpu} (t-T)} e^{i \int_T^t d\tau \omega_{ca}(\tau)} e^{-\gamma_1 (t-T)}, \tag{2.42}
\end{aligned}$$

Eq. 2.42 is precisely Mukamel's three-state expression for the polarization of the off resonance FSRs Stokes line [87].

2.3 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 2.1. 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.* [22] used the potential parameters in Table 2.1 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 [88].

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. 2.2, and can be calculated with the relevant polarization terms Eqs.(2.14) and (2.16) for homogeneous broadening, and Eqs.(2.29) and (2.30) when inhomogeneous broadening is included. We used harmonic potentials for R6G with the parameters in Table 2.1 from Shim *et al.* [13] to calculate the effect of various parameters on this FSRS Stokes spectrum described by the SRS(I) term.

Table 2.1: 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

Figure 2.4 shows the calculations for the effect of the variation in the Raman pump pulse 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 2.5 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 2.6 shows the calculations for the effect of the variation in the homogeneous damping

Figure 2.4: 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 $T_2 = \infty$

Figure 2.5: 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 2.6: 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, $\Delta_{pu} = 750 \text{ fs}$, $T_2 = 1600 \text{ fs}$ and $\theta = 0 \text{ cm}^{-1}$.

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. 2.7, 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 [89, 90].

Figure 2.7: 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. 2.6.

Figure 2.8 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, Δ_{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 2.8, 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. 2.27), and the weight for each energy level is smaller, resulting in lower intensity for the overall spectra. In the thesis, we applied the quantum wave packet method to FSRS and CARS. The aim is to investigate the applicability and significance of the time dependent wave packet theory for FSRS and CARS spectroscopy, and to carry out simulations to understand the basic physics. The electronic dephasing time and inhomogeneous width do not affect the line shape of spectra but only the width of the spectral lines, and for the experiments that we analyzed the changes in width are negligible. So we can approximate the electronic dephasing and inhomogeneous width as a constant.

Figure 2.8: 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} .

Figure 2.9 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

Figure 2.9: (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 2.1. Combination bands occur at &, $370 + 375$ cm⁻¹ and #, $375 + 604$ cm⁻¹, which can also be made out in the experimental results.

a well-resolved spectrum in Fig. 2.9(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. 2.9(b). The experimental spectrum in Fig. 2.9(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. 2.9(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 2.1. 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. 2.9(a) may be broader than the calculated spectrum in Fig. 2.9(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. 2.9(c), and the stick spectrum, Fig. 2.9(b), from experiment is good for almost all the vibrational lines.

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.(2.29- 2.32) and shown in Fig. 2.10. In the calculations, we used $\Delta_{pu} = 750$ fs, $T_2 = 1600$ fs, $\gamma_2 = 340$ cm⁻¹, and $\theta = 300$ 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 give the SRS(II) spectra in Fig. 2.11. 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.(2.33- 2.34). 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.

Figure 2.10: 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 (2.29- 2.32) with $\Delta_{pu} = 750$ fs, $T_2 = 1600$ fs, $\gamma_2 = 340$ cm⁻¹, $\theta = 300$ cm⁻¹.

Figure 2.11: The SRS(I) spectra obtained by adding up RRS(I) and HL(I) + HL(II) spectra in Fig. 2.10, 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.(2.33- 2.34) with $\Delta_{pu} = 750$ fs, $T_2 = 1600$ fs, $\gamma_2 = 340 \text{ cm}^{-1}$, $\theta = 300 \text{ cm}^{-1}$.

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. 2.12(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 the Raman pump excitation wavelengths decrease. It is possible that the collection times or the number of shots taken were reduced 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. 2.11 after scaling by the C-O line intensity are shown in Fig. 2.12(b); they account for the origin of the loss, gain or dispersive character of each of the observed vibrational lines seen in Fig. 2.12(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. 2.2 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. 2.12(c) which compares rather well with the experimental results in Fig. 2.12(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. 2.12, the experimental and calculated results for the R6G Stokes FSRS spectra are shown in Fig. 2.13. The experimental R6G Stokes FSRS spectra of Frontiera *et al.* [14] as a

Figure 2.12: 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. 2.11, 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 2.13: (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. 2.11, 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).

function of the Raman pump excitation wavelength are shown in Fig. 2.13(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. 2.11. The calculated SRS(I) spectra on the Stokes side from Fig. 2.11 are scaled by the C-O line intensity and shown in Fig. 2.13(b); they show that the observed vibrational lines in Fig. 2.13(a) should all have Lorentzian character. Adding in the baseline due to the SRS(II) and IRS(II) terms, we obtain Fig. 2.13(c) which compares rather well with the experimental results in Fig. 2.13(a).

2.4 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 Stokes spectrum which comes from the SRS(I) (=RRS(I)+HL(I)+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 ¹

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.

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3.1 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. 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 [91], 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, fluorescent compounds, and low pressure gases [92, 93, 94, 95, 96, 97].

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 [19, 20, 21]. 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, 22, 23, 24].

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 [82, 67, 23, 69, 22, 24]. 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 [22]. 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.* [21] 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. 3.2, 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. 3.3, 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. 3.4.

3.2 Theory of IRS with finite pulses

The Feynman dual time-line diagram for IRS is shown in Fig. 3.1(a). It has three field interactions on the ket at times t_3 , t_2 and t_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. 3.1(a), arrows that point to the right are the fields $E_{pr/pu}(t)$ with wave vectors $\mathbf{k}_{pr/pu}$ interacting with the molecule at times $t_{3/2}$, while the arrow that points to the left is $E_{pu}^*(t)$ interacting at time t_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 τ_3 , τ_2 and τ_1 , which are used in the

time integrations below, are $\tau_3 = t_2 - t_3$, $\tau_2 = t_1 - t_2$ and $\tau_1 = t - t_1$.

Figure 3.1: (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. 3.1(b), and for the Rayleigh line in Fig. 3.1(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 t_2 and t_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. 3.1(b), and Rayleigh, Fig. 3.1(c), lines. URLS is concerned only with the fundamental anti-Stokes lines.

It is straightforward to translate from Fig. 3.1(a) to the mathematical expression for the third-order polarization [22]. 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,

$$\begin{aligned}
P_{IRS}^{(3)}(t) = & \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \\
& \times e^{-\gamma_g t/2\hbar - \gamma_e(t-t_1)/2\hbar - \gamma_d(t_1-t_2)/\hbar - \gamma_g(t_1-t_2)/2\hbar - \gamma_e(t_2-t_3)/2\hbar - \gamma_g t_3/2\hbar} \\
& \times E_{pu}(t_1) E_{pu}^*(t_2) E_{pr}(t_3) G(t-t_1+t_2-t_3) I(t, t_1, t_2, t_3) .
\end{aligned} \tag{3.1}$$

The four-time correlation function $I(t, t_1, t_2, t_3)$ is defined as

$$\begin{aligned}
I(t, t_1, t_2, t_3) = & \langle \psi_{g0}(\mathbf{Q}) | e^{i\mathbf{h}_g t/\hbar} \mu_{ge} e^{-i\mathbf{h}_e(t-t_1)/\hbar} \\
& \times \mu_{eg} e^{-i\mathbf{h}_g(t_1-t_2)/\hbar} \mu_{ge} e^{-i\mathbf{h}_e(t_2-t_3)/\hbar} \\
& \times \mu_{eg} e^{-i\mathbf{h}_g t_3/\hbar} | \psi_{g0}(\mathbf{Q}) \rangle ,
\end{aligned} \tag{3.2}$$

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 $G(E)$

$$G(t) = \int_0^\infty dE_{eg} e^{-iE_{eg}t/\hbar} G(E_{eg}) , \tag{3.3}$$

and

$$G(E_{eg}) = \frac{\exp\left[-\frac{(E_{eg}-\bar{E}_{eg})^2}{2\theta^2}\right]}{\theta(2\pi)^{1/2}} , \tag{3.4}$$

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. $E_{pu/pr}(t)$ in Eq.(3.1) are the Raman pump/probe electric fields; $\gamma_{g/e}$ are the lifetime of the respective electronic states, which give rise to homogeneous broadening; and γ_d is the vibrational dephasing time for the coherent vibrational state between times t_2 and t_1 .

The Raman gain (RG) spectrum in the direction of the probe pulse, $\mathbf{k}_{pr}$, can be shown to be given by [74, 75, 76],

$$\Delta I_{RG}(\omega) = \frac{8\pi^2 l C}{3n} \omega \operatorname{Im}\{E_{pr}^*(\omega) P_{IRS}^{(3)}(\omega)\} , \quad (3.5)$$

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,

$$E_{pr}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} E_{pr}(t) dt , \quad (3.6)$$

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

$$P_{IRS}^{(3)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} P_{IRS}^{(3)}(t) dt . \quad (3.7)$$

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

$$\mathbf{h}_g = \sum_{r=1}^N h_{gr} , \quad (3.8)$$

$$\mathbf{h}_e = \sum_{r=1}^N h_{er} + E_{eg} , \quad (3.9)$$

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

$$|\psi_{g0}(\mathbf{Q})\rangle = \prod_{r=1}^N |\psi_{g0_r}(Q_r)\rangle , \quad (3.10)$$

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

$$\begin{aligned} I(t, \tau_1, t_2, t_3) &= |\mu|^4 e^{-iE_{eg}(\tau_1 + \tau_3)/\hbar} \\ &\times \prod_{r=1}^N e^{i\omega_r(\tau_1 + \tau_2 + \tau_3)/2} \\ &\times \sum_{n_r} e^{-i\omega_r(n_r + \frac{1}{2})\tau_2} \\ &\times \langle \psi_{g0_r}(Q_r) | e^{-ih_{er}\tau_1/\hbar} | \psi_{gn_r}(Q_r) \rangle \\ &\times \langle \psi_{gn_r}(Q_r) | e^{-ih_{er}\tau_3/\hbar} | \psi_{g0_r}(Q_r) \rangle , \end{aligned} \quad (3.11)$$

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. (3.11) for each mode is of the form $\langle \psi_{g n_r} | e^{-i h_{er} t / \hbar} | \psi_{g 0_r} \rangle \equiv \langle \psi_{g n_r} | \psi_{g 0_r}(t) \rangle$ or its complex conjugate, and in the harmonic oscillator approximation, we obtain analytic results given by [98]

$$\begin{aligned} \langle \psi_{g n_r} | \psi_{g 0_r}(t) \rangle &= \exp\{-(\Delta_r^2/2)[1 - \exp(-i\omega_r t)] - i\omega_r t/2\} \\ &\times \frac{(-1)^{n_r} \Delta_r^{n_r}}{(2^{n_r} n_r!)^{1/2}} [1 - \exp(-i\omega_r t)]^{n_r}, \end{aligned} \quad (3.12)$$

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. (3.1), and the Raman gain, Eq. (3.5).

3.3 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 broadband probe pulse that extends to the blue of the Raman pump, with heterodyne detection along the probe pulse direction [21]. 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.

3.3.1 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 [64]

$$I_k/I_{k'} = \Omega_k^3 \Delta_k^2 / \Omega_{k'}^3 \Delta_{k'}^2, \quad (3.13)$$

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 [99], 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 [21]. 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 3.1 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 3.1: 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 [21] is shown in Fig. 3.2 (dash - dot line). We have calculated (solid line) the absorption spectrum of CV [86, 22], 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. 3.2, 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 3.2: The measured absorption spectrum of crystal violet from Umapathy and coworkers [21] (dash-dot line) in ethanol. The calculated absorption spectrum (solid line) using the potential parameters in Table 3.1 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.

3.3.2 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

$$E_{pu/pr}(t; T_{pu/pr}) = E_{0,pu/pr} g_{pu/pr}(t) e^{-i\omega_{pu/pr}t}, \quad (3.14)$$

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

$$g_{pu/pr}(t) = \exp\left(-2 \ln 2 \frac{t^2}{\Delta_{pu/pr}^2}\right), \quad (3.15)$$

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 [21], and are indicated by arrows in Fig. 3.2. The URLS anti-Stokes bands for CV from -1000 cm^{-1} to -1700 cm^{-1} are reproduced in Fig. 3.3(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 [100, 101], 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. 3.3(b). For the calculations, we have used the mode frequencies 1177 cm^{-1} and 1618 cm^{-1} obtained by Kelley *et al.* [99] 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 3.3: (a) Experimental URLS results for crystal violet (CV) of Umapathy and coworkers [21] 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 3.4: 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} .

Figure 3.4 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 3.5 shows the calculations for the effect of the variation in the 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 3.5: 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} .

3.3.3 Third-order susceptibility for IRS with monochromatic pulses

Monochromatic Raman pump and probe pulses are written as

$$E_{pu/pr}(t) = E_{0,pu/pr} e^{-i\omega_{pu/pr}t}, \quad (3.16)$$

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 time duration variables: τ_1 , τ_2 , and τ_3 . If inhomogeneous broadening is neglected, i.e. setting $G(\tau_1 + \tau_3) = 1$, 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.

(3.1), becomes

$$\begin{aligned}
P_{IRS}^{(3)}(t) &= \left(\frac{i}{\hbar}\right)^3 E_{0,pu}^2 E_{0,pr} e^{-i\omega_{pr}t} \int_0^t d\tau_2 e^{-\gamma_d \tau_2 / \hbar - i(\omega_{pu} - \omega_{pr})\tau_2 - i\omega_R \tau_2} \\
&\times \int_0^t d\tau_1 e^{-\gamma_e \tau_1 / 2\hbar + i\omega_{pr}\tau_1 + iE_{g0}\tau_1 / \hbar} \langle \psi_{g0}(\mathbf{Q}) | \mu_{ge} e^{-i\mathbf{h}_e \tau_1 / \hbar} \mu_{eg} | \psi_{g0'1R}(\mathbf{Q}) \rangle \\
&\times \int_0^t d\tau_3 e^{-\gamma_e \tau_3 / 2\hbar + i\omega_{pr}\tau_3 + iE_{g0}\tau_3 / \hbar} \langle \psi_{g0'1R}(\mathbf{Q}) | \mu_{ge} e^{-i\mathbf{h}_e \tau_3 / \hbar} \mu_{eg} | \psi_{g0}(\mathbf{Q}) \rangle \quad (3.17)
\end{aligned}$$

Noting that the integrals over τ_1 and τ_3 are identical, because $\mathbf{h}_e$ is Hermitian, and using the definition of the third-order susceptibility, we obtain,

$$\begin{aligned}
\chi_{IRS}^{(3)} &\equiv \lim_{t \rightarrow \infty} \frac{P_{IRS}^{(3)}(t)}{E_{pr}(t)} \\
&= E_{0,pu}^2 \frac{1}{\hbar\omega_R + \hbar(\omega_{pu} - \omega_{pr}) - i\gamma_d} \\
&\times \left\{ \frac{i}{\hbar} \int_0^\infty dt e^{i(E_{g0} + \hbar\omega_{pr})t / \hbar - \gamma_e t / 2\hbar} \langle \psi_{g0'1R}(\mathbf{Q}) | \mu_{ge} e^{-i\mathbf{h}_e t / \hbar} \mu_{eg} | \psi_{g0}(\mathbf{Q}) \rangle \right\}^2 \quad (3.18)
\end{aligned}$$

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 [63]. It corresponds physically with Fig. 3.1(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 t_3 , t_2 and t_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. (3.18),

$$\begin{aligned}
\chi_{IRS}^{(3)} &= E_{0,pu}^2 \frac{1}{\hbar\omega_R + \hbar(\omega_{pu} - \omega_{pr}) - i\gamma_d} \\
&\times \left(\sum_v \frac{\langle \psi_{g1}(Q) | \psi_{ev}(Q) \rangle \langle \psi_{ev}(Q) | \psi_{g0}(Q) \rangle}{\hbar\omega_{ev,g0} - \hbar\omega_{pr} - i\gamma_e/2} \right)^2, \quad (3.19)
\end{aligned}$$

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 (3.19) corresponds to the well-known third-order susceptibility for inverse Raman scattering, e.g. Eq.(4) of Tasumi and co-workers [102]. The observed IRS signal is directly proportional to the imaginary component of $\chi_{IRS}^{(3)}$. Thus, Eqs. (3.1), (3.5)-(3.7) describe IRS with finite Raman pump and probe pulses, while Eqs. (3.18) and (3.19) are for monochromatic pulses.

Tasumi and co-workers [102] have used the imaginary part of Eq. (3.18) 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 URLS of CV, the probe laser frequency (see Fig. 3.1(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. 3.2 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. 3.3(a) or 3.3(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 [21]. 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 [102].

3.4 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 [21].

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.

3.5 Acknowledgement

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What Are the Line Shapes and Relative Intensities of the Twenty Four Spectral Groups to Describe Coherent Anti-Stokes Raman Spectroscopy?

Twenty four spectral groups expressed in separable harmonic oscillators model are involved in coherent anti-Stokes Raman spectroscopy (CARS) from a pure state. The vibrational features can be detected in four groups, while line shapes of all the other twenty groups are featureless for both toluene and rhodamine 6G. Our calculation shows that pump pulse excitation, Stokes pulse deexcitation and probe pulse excitation process is dominant. Besides this, the CARS from excited electronic state for a moving wave packet is also discussed.

4.1 Introduction

Physical, chemical, and biological processes and reactions occur on the ultrafast time-scale and coherent anti-Stokes Raman spectroscopy (CARS) is one of the techniques developed to study such systems. CARS can be used in many fields, such as detecting vibrational features, measuring

temperature as well as deriving images of chemical and biological samples [29, 30, 31]. Three electric fields, Raman pump (pu), Stokes (st), and probe pulses (pr) are involved in CARS which is detected in $\mathbf{k}_{\text{pu}} - \mathbf{k}_{\text{st}} + \mathbf{k}_{\text{pr}}$ direction [46].

Coherent anti-Stokes Raman scattering (CARS) was first proposed by Terhune and Marker [25, 26] in 1960s and various theoretical and experimental investigations have been performed in physical, chemical, and biological areas [27, 28]. Following the development of ultrashort laser techniques, femtosecond laser pulses with high repetition rate and broadband play an important role in CARS experiments for both small and large molecules [32, 33, 34, 35, 36]. CARS had been used to investigate the molecular dynamics on the excited and ground state potential energy surfaces of iodine and bromine in the gas phase [37, 38]. Similar to Raman spectroscopy, CARS is a powerful technique for detecting vibrational features, measuring temperature as well as deriving images of chemical and biological samples. However, CARS is not free of nonresonant background contribution [103]. In order to obtain CARS from excited electronic states, we need to get a deep insight in the contributions of CARS.

Niu *et al.* have carried out a derivation of the phenomenological result from a quantum approach for CARS polarization [78]. There are 48 terms contributing to the third-order polarization for CARS in diagrammatic form. Only one dominant resonant term with pump pulse excitation, Stokes pulse deexcitation and probe pulse excitation is used to investigate time-resolved fs CARS and fs/ps CARS for toluene and R6G. However, one may expect to investigate the line shape of the other terms and their contributions to the total CARS signal.

In this paper, we first present the forty eight terms in third-order polarization for CARS in Feynman dual time line and four-wave mixing energy level diagrams, and they fall into four groups: (A) three field interactions on the ket, with 6 diagrams from the permutation of the three fields, (B) two field interactions on the ket and one field interaction on the bra, with 6 representative diagrams from the permutation of the three fields, and for each representative term there are three different time orderings of the field interaction on the bra relative to the two field interactions on the ket, giving a total of 18 diagrams, (C) one field interaction on the ket and two field interactions on the bra, again giving rise to 6 representative diagrams from the permutations of the three fields, and for each representative term there are three different time orderings of

the field interaction on the ket relative to the two field interactions on the bra, giving a total of 18 diagrams, and (D) three field interactions on the bra, with 6 diagrams from the permutation of the three fields. Each of the diagrams in Groups A and D, and each of the representative diagrams in Groups B and C with time orderings of the bra or ket interactions ignored, gives rise to a third-order polarization term, and so there are 6 polarization terms for each group, giving a total of twenty four polarization terms. The Feynman diagram is used to facilitate writing down the third order polarization and in interpreting the dynamics in nonlinear spectroscopy, especially for perturbative theory [104, 105, 82]. By introducing both Feynman dual time line diagram and energy level diagram, one can get the expressions of third order polarizations for nonlinear spectroscopy and understand the physics associated with the expression more easily and profoundly [23, 70]. Next, we describe the molecule by multidimensional separable harmonic potential surfaces with Frank-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. Calculations are made with the theoretical expressions for the twenty four terms and obtain the intensities and line-shapes of their contributions to CARS from a stationary vibrational state. It is shown that in fs/ps CARS, where we use a fs Raman pump pulse, a fs Stokes pulse and a ps probe pulse, sharp vibrational features can be detected in four of the polarization terms where the Raman pump and Stokes pulses can create a vibrational coherence, while the line-shapes of the other twenty terms are broad and featureless for both off-resonance CARS in toluene and resonance CARS in rhodamine 6G. The traditional CARS term, with the Raman pump, Stokes and probe fields, in that order, interacting on the ket, is the dominant term, with intensity at least two orders of magnitude larger than the other terms.

4.2 Theory

Coherent anti-Stokes Raman spectroscopy (CARS), using three color pulses - pump (pu), Stokes (st) and probe (pr) - acting on an initial pure state $|\psi_1^{(0)}\rangle\langle\psi_1^{(0)}|$ is described by forty eight terms in third-order perturbation theory. The pure state $|\psi_1^{(0)}\rangle$ can either be a stationary state or an evolving wave packet prepared earlier by an actinic pump pulse on an excited electronic state. In Liouville space with ket and bra evolution, the forty eight terms can be represented by Feynman

dual time-line (FDTL) diagrams or four-wave mixing energy level (FWMEL) diagrams [22], as shown in the left and right, respectively, in the first column of Table 4.1. The molecule interacts with the laser field from t_3 to t in time order. In the FDTL diagrams, the arrows pointing into the time-line denote absorption from e_1 to e_2 , while the arrows pointing away from the time-line denote stimulated emission from e_2 to e_1 . For the corresponding FWMEL diagrams, the bra interaction is denoted by a dash arrow and the ket interaction by a solid arrow. The FDTL diagrams and the FWMEL diagrams are complementary to each other, giving the time-frame and energy-frame viewpoints, respectively, of the CARS processes. Using the FDTL diagrams, we can conveniently write down the expressions for the third-order polarizations, while the FWMEL diagrams help us to better see which terms are more resonant in the rotating wave approximation and can make a larger contribution to the third-order polarization.

In Table 4.1, the forty-eight diagrams or terms fall into four groups. Group A diagrams have three field interactions on the ket, with 6 diagrams, Aa to Af, from the permutation of the three fields. Group B diagrams have two field interactions on the ket and one field interaction on the bra, with 6 representative diagrams, Ba to Bf, from the permutation of the three fields, and for each representative diagram there are three different time orderings of the field interaction on the bra relative to the two field interactions on the ket, giving a total of 18 diagrams. Group C diagrams have one field interaction on the ket and two field interactions on the bra, again giving rise to 6 representative diagrams, Ca to Cf, from the permutations of the three fields, and for each representative term there are three different time orderings of the field interaction on the ket relative to the two field interactions on the bra, giving a total of 18 diagrams. Finally, Group D diagrams have three field interactions on the bra, with 6 diagrams, Da to Df, from the permutation of the three fields.

Table 4.1: Feynman dual time-line (FDTL) diagram (first column, left) and four-wave mixing energy level (FWMEL) diagram (first column, right) for CARS process. Pump, Stokes, and probe pulses are illustrated by blue, green, and red arrows, respectively. An arrow pointing into the time-line in a FDTL diagram denotes an excitation process, while an arrow pointing away from the time-line denotes a deexcitation process. In the FWMEL diagrams, ket and bra interactions are represented by solid and dash arrows, respectively. The coherence status for the $v=0$ and 1 vibrational levels and resonance condition for electronic states are shown in the second and third columns, respectively. The relative intensities from each term for toluene (off-resonance CARS) and R6G (resonance CARS) are given in the fourth and fifth columns, respectively. The intensity for off-resonance CARS is much weaker than for resonance CARS.

Diagrams A	Coherence	Resonance	Rel. Intensity	
			Toluene /8.12x10 ⁻⁷	R6G
a	Y- ket	YYY	1.00	1.00
b	Y- ket	NYN	0.0172	3.06x10 ⁻⁷
c	N	YYY	1.23x10 ⁻⁹	8.33x10 ⁻¹²
d	N	YNN	1.94x10 ⁻¹⁰	1.67x10 ⁻⁹
e	N	NYN	6.74x10 ⁻¹¹	1.24x10 ⁻¹⁴
f	N	YNN	6.07x10 ⁻¹¹	4.45x10 ⁻¹³

Diagrams B	Coherence	Resonance	Rel. Intensity	
			Toluene /8.12x10 ⁻⁷	R6G
a	Y- ket	YYN	0.0693	1.25x10 ⁻³
b	Y- ket	NYN	1.19x10 ⁻³	3.57x10 ⁻¹⁰
c	N	YNY	4.31x10 ⁻¹⁰	1.40x10 ⁻⁶
d	N	YNY	1.35x10 ⁻¹⁰	2.90x10 ⁻¹⁰
e	N	YYN	5.37x10 ⁻¹¹	4.35x10 ⁻¹⁵
f	N	NYN	2.95x10 ⁻¹²	6.83x10 ⁻¹⁸

Diagrams C	Coherence	Resonance	Rel. Intensity	
			Toluene /8.12x10 ⁻⁷	R6G
a	N	YYY	3.06x10 ⁻⁸	4.16x10 ⁻⁸
b	N	YYY	1.81x10 ⁻⁸	6.53x10 ⁻⁵
c	N	NY Y	6.01x10 ⁻¹⁰	3.18x10 ⁻¹⁴
d	N	NY Y	5.62x10 ⁻¹⁰	1.01x10 ⁻¹⁰
e	N	NNN	2.02x10 ⁻¹³	6.76x10 ⁻¹⁹
f	N	NNN	1.29x10 ⁻¹³	3.15x10 ⁻¹⁹

Diagrams D	Coherence	Resonance	Rel. Intensity	
			Toluene /8.12x10 ⁻⁷	R6G
a	N	YYN	2.28x10 ⁻⁹	9.18x10 ⁻¹¹
b	N	YYN	4.24x10 ⁻¹⁰	3.01x10 ⁻¹¹
c	N	NYN	4.49x10 ⁻¹¹	7.60x10 ⁻¹⁷
d	N	NYN	1.32x10 ⁻¹¹	6.08x10 ⁻¹⁷
e	N	NNY	2.75x10 ⁻¹³	1.08x10 ⁻¹⁸
f	N	NNY	1.75x10 ⁻¹³	5.01x10 ⁻¹⁹

Each of the diagrams in Groups A and D gives rise to a polarization term. In the absence of vibrational dephasing, the time ordering of the bra and ket interactions relative to the ket and bra interactions for each of the representative diagrams in Groups B and C, respectively, is not important, and each of the representative diagrams in Groups B and C gives rise to a third-order polarization term. So, in total we have twenty four polarization terms. From the Feynman dual time-line diagrams, one can conveniently write down the expressions for the third-order polarizations.

The polarizations for the twenty four terms can be expressed by the overlap of wave packets on the bra and ket side when vibrational dephasing time is not taken into account [23, 22]. The third order polarizations for diagrams Aa, Dc and Ca, Bb are given by

$$\begin{aligned}
P_{Aa}^{(3)}(t) &= \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \\
&\quad \times e^{-\gamma_2(t-t_1)/2\hbar - \gamma_1(t_1-t_2)/2\hbar - \gamma_2(t_2-t_3)/2\hbar - \gamma_1(t+t_3)/2\hbar} \\
&\quad \times E_{pr}(t_1) E_{st}^*(t_2) E_{pu}(t_3) I(t, t_1, t_2, t_3) \\
&= -P_{Dc}^{(3)}(t)^* ,
\end{aligned} \tag{4.1}$$

and

$$\begin{aligned}
P_{Ca}^{(3)}(t) &= \left(\frac{i}{\hbar}\right)^3 \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau \\
&\quad \times e^{-\gamma_1\tau_2/2\hbar - \gamma_2(\tau_1-\tau_2)/2\hbar - \gamma_1(t-\tau_1)/2\hbar - \gamma_2(t-\tau)/2\hbar - \gamma_1\tau/2\hbar} \\
&\quad \times E_{st}^*(\tau_2) E_{pu}(\tau_1) E_{pr}(\tau) S(t, \tau_1, \tau_2, \tau) \\
&= -P_{Bb}^{(3)}(t)^* ,
\end{aligned} \tag{4.2}$$

where the four-time correlation functions, $I(t, t_1, t_2, t_3)$ and $S(t, \tau_1, \tau_2, \tau)$, can be expressed as [22]

$$\begin{aligned}
I(t, t_1, t_2, t_3) &= \langle \psi_1^{(0)}(\mathbf{Q}, 0) | e^{i\mathbf{h}_1 t/\hbar} \mu_{12} e^{-i\mathbf{h}_2(t-t_1)/\hbar} \mu_{21} e^{-i\mathbf{h}_1(t_1-t_2)/\hbar} \\
&\quad \times \mu_{12} e^{-i\mathbf{h}_2(t_2-t_3)/\hbar} \mu_{21} e^{-i\mathbf{h}_1 t_3/\hbar} | \psi_1^{(0)}(\mathbf{Q}, 0) \rangle ,
\end{aligned} \tag{4.3}$$

$$\begin{aligned}
S(t, \tau_1, \tau_2, \tau) &= \langle \psi_1^{(0)}(\mathbf{Q}, 0) | e^{i\mathbf{h}_{1r}\tau_2/\hbar} \mu_{12} e^{i\mathbf{h}_{2r}(\tau_1-\tau_2)/\hbar} \mu_{21} e^{i\mathbf{h}_{1r}(t-\tau_1)/\hbar} \\
&\quad \times \mu_{12} e^{-i\mathbf{h}_{2r}(t-\tau)/\hbar} \mu_{21} e^{-i\mathbf{h}_{1r}\tau/\hbar} | \psi_1^{(0)}(\mathbf{Q}_r, 0) \rangle .
\end{aligned} \tag{4.4}$$

By using the appropriate pulse sequence, the third order polarizations for the other terms in Groups A and D, or Groups B and C, can be written down in a similar manner as Eq. (4.1) and Eq. (4.2).

The separable, displaced harmonic oscillators model has previously been used to obtain analytic expressions for the four-time correlation functions from an initial ground vibrational state [106, 22, 70]. Only a brief outline of the pertinent equations is given here. In an N -dimensional separable system, the Hamiltonians are sums of one-dimensional Hamiltonians

$$\mathbf{h}_1 = \sum_{r=1}^N h_{1r} , \quad (4.5)$$

$$\mathbf{h}_2 = \sum_{r=1}^N h_{2r} + \bar{E}_{21} , \quad (4.6)$$

where h_{1r} and h_{2r} are one-dimensional Hamiltonians in mode q_r . The propagators are then products of one-dimensional propagators. The wave packet is a product of one-dimensional wave packets

$$|\psi_1^{(0)}(\mathbf{Q}, 0)\rangle = \prod_{r=1}^N |\psi_{1r}^{(0)}(q_r, 0)\rangle , \quad (4.7)$$

The four-time correlation function in Eq. (4.3) becomes [22]

$$I(t, t_1, t_2, t_3) = G(t - t_1 + t_2 - t_3) |\mu_{21}|^4 \prod_r I_r(t, t_1, t_2, t_3) . \quad (4.8)$$

where $G(t)$, a Gaussian distribution of zero-zero energies, is the inhomogeneous broadening representing variations in the local environment of molecule [84, 86, 105].

$$G(t) = \int_0^\infty dE_{21} e^{-iE_{21}t/\hbar} G(E_{21}) , \quad (4.9)$$

and

$$G(E_{21}) = \frac{\exp\left[-\frac{(E_{21} - \bar{E}_{21})^2}{2\theta^2}\right]}{\theta(2\pi)^{1/2}} , \quad (4.10)$$

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

For each mode, the four-time correlation function is given by

$$\begin{aligned} I_r(t, t_1, t_2, t_3) &= \langle \psi_{1r}^{(0)}(q_r, 0) | e^{ih_{1r}t/\hbar} e^{-ih_{2r}(t-t_1)/\hbar} e^{-ih_{1r}(t_1-t_2)/\hbar} \\ &\quad \times e^{-ih_{2r}(t_2-t_3)/\hbar} e^{-ih_{1r}t_3/\hbar} | \psi_{1r}^{(0)}(q_r, 0) \rangle , \end{aligned} \quad (4.11)$$

where $h_{2r}(t)$ is the one-dimensional Hamiltonian in mode q_r of the excited electronic state e_2 . Assuming that $|\psi_{1r}^{(0)}(q_r, 0)\rangle$ is the ground vibrational state $|\psi_{1r0}(q_r)\rangle$, and inserting a complete

vibrational basis set, $\sum_{v'} |\psi_{1rv'}(q_r)\rangle \langle \psi_{1rv'}(q_r)|$, of e_1 into Eq. (4.11), we obtain

$$\begin{aligned} I_r(t, t_1, t_2, t_3) &= e^{-iE_{1r0}(t_3-t)/\hbar} \sum_{v'} \langle \psi_{1r0}(q_r) | e^{-ih_{2r}(t-t_1)/\hbar} | \psi_{1rv'}(q_r) \rangle \\ &\times e^{-iE_{1rv'}(t_1-t_2)/\hbar} \langle \psi_{1rv'}(q_r) | e^{-ih_{2r}(t_2-t_3)/\hbar} | \psi_{1r0}(q_r) \rangle , \end{aligned} \quad (4.12)$$

where $E_{1rv'}$ is the eigenenergy of $|\psi_{1rv'}(q_r)\rangle$. Now, each of the correlation functions in Eq. (4.12) is of the form $\langle \psi_n | e^{-ih_2t/\hbar} | \psi_0 \rangle \equiv \langle \psi_n | \psi_0(t) \rangle$ or its complex conjugate, with analytic result given by [106]

$$\begin{aligned} \langle \psi_n | \psi_0(t) \rangle &= \exp\{-(\Delta^2/2)[1 - \exp(-i\omega t)] - i\omega t/2\} \\ &\times \frac{(-1)^n \Delta^n}{(2^n n!)^{1/2}} [1 - \exp(-i\omega t)]^n , \end{aligned} \quad (4.13)$$

where Δ is the excited state mode displacement relative to the ground state and ω is the mode frequency. The integrand in Eq. (4.1) is then of analytic form which facilitates the calculation of the third-order polarization. The spectral intensity is proportional to squared magnitude of the third-order polarization [46, 72], and the spectra in the frequency domain are given by the FT of the time domain polarization.

Similarly, the four-time correlation function, $S(t, \tau_1, \tau_2, \tau)$, in Eq. (4.4) is given by

$$S(t, \tau_1, \tau_2, \tau) = G(t - \tau - \tau_1 + \tau_2) |\mu_{21}|^4 \prod_r S_r(t, \tau_1, \tau_2, \tau) , \quad (4.14)$$

and

$$\begin{aligned} S_r(t, \tau_1, \tau_2, \tau) &= \langle \psi_{1r}^{(0)}(q_r, 0) | e^{ih_{1r}\tau_2/\hbar} \mu_{12} e^{ih_{2r}(\tau_1-\tau_2)/\hbar} \mu_{21} e^{ih_{1r}(t-\tau_1)/\hbar} \\ &\times \mu_{12} e^{-ih_{2r}(t-\tau)/\hbar} \mu_{21} e^{-ih_{1r}\tau/\hbar} | \psi_{1r}^{(0)}(q_r, 0) \rangle . \end{aligned} \quad (4.15)$$

With homodyne detection, the CARS intensity and spectral intensity for each of the 24 terms are defined respectively as [72]

$$\mathcal{I}_{\text{CARS}}(\omega) = |P_S^{(3)}(\omega)|^2 = \left| \sum_{\eta} P_{\eta}^{(3)}(\omega) \right|^2 , \quad (4.16)$$

$$\mathcal{I}_{\eta}(\omega) = |P_{\eta}^{(3)}(\omega)|^2 , \quad (4.17)$$

where $P_S^{(3)}(\omega)$ and $P_{\eta}^{(3)}(\omega)$ are the Fourier transform of the summation of time domain polarizations of the twenty four terms and the corresponding term η ($\eta = \text{Aa}, \text{Ab}, \dots, \text{Df}$), respectively.

Table 4.2: Laser pulse parameters for CARS on toluene

	Wavelength (nm)	Linewidth (cm^{-1})
pump pulse	517	250
Stokes pulse	547.34	300
probe pulse	800	16

4.3 Results and Discussion

The twenty four terms of CARS without Rayleigh line in Table 4.1 are investigated using toluene and R6G with potential energy and laser pulse parameters listed from Tables 4.2 to 4.5, respectively. For toluene, the Raman pump and Stokes pulses are off-resonant with the zero-zero transition between the ground and excited electronic states. The twenty four terms for fs/ps CARS are illustrated in Fig. 4.1. Each row in Fig. 4.1 is arranged in one to one correspondence with the diagram terms in Table 4.1. The intensity for each terms is normalized according to the peak intensity in between 400 and 2000 cm^{-1} , where the effective spectral range is determined by the frequency difference and pulse linewidths of the pump and Stokes pulses. Also, the peak intensity for terms Aa is chosen as 1.0 and the peak intensity for the other terms can be multiplied by a factor illustrated in the corresponding figure. For example, with respect to term Aa, the peak intensity of term Ab and Bb should be 1.72×10^{-2} and 1.19×10^{-3} , respectively.

In the *fs/ps* CARS calculation, we chose the delay time between Raman pump and Stokes pulses is 0 *fs*, while the probe delay time to be the minimum of the integrated CARS signal at 1930 *fs* to minimize any non-resonant contribution. Furthermore, the intensities among the three pulses are identical. The square of polarization in frequency domain (SPF) for term Aa is illustrated in Fig. 4.1 Aa. In term Aa, the difference between pump and Stokes pulses provides a window for the modes of the ground electronic state and coherence between modes are detected by the narrow bandwidth probe pulse. Therefore, one can see the mode frequencies of the ground electronic state in Fig. 4.1 Aa. In Fig. 4.1 Ab, the window of the ground electronic state vibrational mode is provided by deexcitation Stokes pulse and excitation pump pulse whose SPF should be smaller than that of the Aa term. In Fig. 4.1 Ac, the probe pulse leads to excitation and Stokes pulse leads to deexcitation. Then, the third order process is realized by the pump

Table 4.3: Potential parameters of toluene [22]. Energy gap between ground and excited electronic is 37225 cm^{-1} . Homogeneous and inhomogeneous broadenings are 197 cm^{-1} and 0, respectively.

Frequency	Displacement
$\Omega_r, \text{ cm}^{-1}$	$ \Delta_r $
521.70	1.00
786.50	1.07
1003.6	1.19
1030.6	0.54
1211.4	0.35
1605.1	0.14
3057.1	0.12

pulse. However, only virtual vibrational states are reached by the laser pulses, which results in a featureless spectrum whose line-shape should resemble the spectrum of the pump pulse. The peak position of the spectrum is at $\omega_{pu} - \omega_{st}$, about 1072 cm^{-1} . In Fig. 4.1 Ad, the pump pulse leads to excitation from ground to excited electronic state (ES). Then the wave packet in ES is transferred (in an off-resonant way) to the ground electronic state (GS) by an excitation process of the probe pulse. Finally, the wave packet is transferred (again in an off-resonant way) GS to ES by deexcitation by the Stokes pulse. As the wave packet deexcited from GS to ES is smaller than that of the excitation process, the peak intensity of SPF for term Ad is smaller than that for term Ac. Since no real vibrational states are matched in the process of Ad, the line-shape of SPF is featureless with a Gaussian line-shape. In Table 4.1, the first order wavepacket in e_2 for Ae should be smaller than that of Ad. The other processes for both Ad and Ae are off-resonant processes. Thus, the peak intensity for Ad is larger than for Ae. The first order wave packet in e_2 for Ad should be stronger than that for Af. The following two processes for Ad and Af are all off-resonance according to the 0-0 transition between e_2 and e_1 . Therefore, the SPF intensity for Fig. 4.1 Ad is stronger than that for Fig. 4.1 Af.

Figure 4.1: Twenty four polarization terms of fs/ps CARS of toluene.

In Table 4.1 Group B, one can find the energy difference between pump and Stokes pulses matching the first two vibrational levels of toluene. As the first transition in Ba is an excitation process from e_1 to e_2 as compared to a deexcitation process from e_1 to e_2 for Bb, the peak intensity of SPF of Fig. 4.1 Ba is larger than that of Fig. 4.1 Bb. Similar to the relationship of the peak intensities of SPF between Figs. 4.1 Ad and Af, the intensity for Fig. 4.1 Bc should be stronger than that for Fig. 4.1 Bd. The first order wave packet in Be is stronger than that of Bf, which leads to a stronger SPF intensity for Fig. 4.1 Be than that for Fig. 4.1 Bf.

Group C illustrated in Table 4.1 represents diagrams with one ket interaction and two bra interactions. The most resonant term in Group C should be Ca and Cb. As the energy difference between pump and Stokes pulses is about 1000cm^{-1} , the peak value of SPF of Ca should be stronger than that of Cb, and it is similar for the relationship between Cc and Cd. As the first order wave packet for the bra side in Ce is larger than that of Cf, the peak intensity of SPF of Ce is stronger than that of Cf. For the last group D, all interactions are on the ket side of the FWME/FDTL diagrams and each diagram is just a complex conjugate of the corresponding diagram in Group C, due to the ket side interaction in the latter being transferred to the bra side for Group D. The order of the peak intensity of SPF in Group D can be interpreted in similar manner as in Group C.

It is shown that in Fig. 4.1, terms Aa, Ab, Ba, and Bb with identical sharp anti-Stokes lines give the vibrational features of the ground electronic state of toluene, while the line-shape of SPF of other processes are broad and featureless with Gaussian line-shape. The vibrational features of the ground electronic state in the CARS spectra can only be seen when the third probe pulse acts on the coherence produced by the pump and Stokes pulses in the molecule. The central frequency difference between the pump and Stokes pulses provides a window for the Raman active modes of the ground electronic state, but with sufficiently broadband pulses that frequency difference is not necessary. As the probe pulse is off-resonance with the zero-zero energy transition between the ground and excited electronic states, the CARS spectrum for each mode should have the width of the probe pulse. It is typically broad when the probe pulse is of fs duration, and narrow when it is of ps duration. Thus in fs/ps CARS, only terms Aa, Ab, Ba, and Bb reflect the vibrational features of ground electronic state with sharp anti-Stokes lines. The intensities of

Table 4.4: Laser pulse parameters for CARS on R6G.

	Wavelength (nm)	Linewidth (cm^{-1})
pump pulse	509	500
Stokes pulse	548	275
probe pulse	800	15

SPF of terms Ab, Ba and Bb are smaller than that of Aa owing to the deexcitation from e_1 to e_2 by the Stokes pulse in Ab and by the probe pulse in Ba and Bb. The spectra of the other terms without coherence are featureless and they generally peak at about 1072 cm^{-1} anti-Stokes shift.

With the aid of Fig. 4.2, one can reveal the relationship of calculated twenty four CARS terms for R6G. The peak value of the spectra are indicated in each inset. Decoherence life time for e_1 is set to infinity in the theoretical investigations. The laser pulse and potential parameters are collected in Tables 4.4 and 4.5 [13], while the central time for pump, Stokes, and probe pulses are identical to the investigation of toluene. Both the wavelengths of pump and Stokes pulses are near the absorption maximum of R6G. Therefore, Fig. 4.2 is resonant CARS for the twenty four terms. Similar to the spectra in toluene, the major mode peaks within the pump-Stokes frequency difference range can be seen in Fig. 4.2 Aa, Ab, Ba, Bb. The width of each anti-Stokes line in Fig. 4.2 Aa, Ab, Ba, Bb is around 16 cm^{-1} which is the linewidth of the probe pulse. The intensity for term Aa is much stronger than the other terms due to the resonance transition between e_1 and e_2 induced by pump and Stokes pulses. In Table 4.1 Ab, the Stokes pulse interaction is off-resonance, and in Ba the probe pulse interaction is off-resonance, while in Bb both the Stokes and probe pulses are off-resonance. Hence their intensities in Fig. 4.2 Ab, Ba, and Bb are much lower than Aa. The remaining terms in Fig. 4.2 are all broad, featureless and weak due to the lack of coherence and with one or more pulse interactions being off-resonance.

Table 4.5: Potential parameters for R6G [13] . Energy gap between ground and excited electronic is 18850 cm^{-1} . Homogeneous and inhomogeneous broadenings are 340 and 300 cm^{-1} , respectively.

Frequency	Displacement
$\Omega_r, \text{ cm}^{-1}$	$ \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

Figure 4.2: Twenty four polarization terms of fs/ps CARS of R6G.

In Figs. 4.3 (a) and (b), we compare the spectra for Aa (dashed line) and summation of the polarizations of all terms (solid line) for toluene and R6G respectively. The line-shape and intensity of the CARS spectra for toluene/R6G are very well given by the dominant and traditional CARS term Aa. Thus, one may investigate the CARS spectra from ground electronic state by calculating the spectra of just term Aa rather than calculating all the polarizations of the twenty four terms which saves time and money.

4.4 Conclusion

The separable, displaced harmonic oscillators model was introduced to investigate the twenty four polarization terms for CARS from the ground electronic state. The line-shape and relative intensity of each term were calculated and well interpreted according to the Feynman dual time line and four wave mixing energy level diagrams. The results showed that the traditional CARS term Aa is the dominant term in both off-resonance and resonance CARS.

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Figure 4.3: (Solid line) fs/ps CARS vs. (dashed line) SPF of term Aa for (a) toluene and (b) R6G.

Conclusion and Prospects

5.1 Conclusion

Quantum mechanical wave packet simulations of femtosecond stimulated Raman spectroscopy (FSRS) and coherent anti-Stokes Raman spectroscopy (CARS) had been carried out using third-order perturbative method. We used multidimensional separable displaced harmonic oscillators model to derive analytical expressions for the third-order polarization and FSRS intensities were calculated to compare with experiments.

FSRS simulated with a delta function probe pulse in rhodamine 6G (R6G) from the ground vibrational state had been investigated by the perturbative quantum wave packet theory. By using the delta function probe pulse, the four-time correlation function in the third-order polarization reduced to a three-time correlation function which saved computation time. The analytic third-order polarization expressions could be written down for each term from the eight Feynman dual time line diagrams. Six effective terms RRS(I), HL(I)+HL(II), RRS(II), HL(III)+HL(IV), IRS(I), and IRS(II) were calculated and the results were consistent with experiments. It was shown that the RRS(I) term is responsible for the Stokes lines while the IRS(I) term accounts for the anti-Stokes lines. Using the SRS(I) term, we showed that the FSRS vibrational linewidth gets narrower as the Raman pump pulse duration and/or the vibrational dephasing time is lengthened; the homogeneous and inhomogeneous damping constants do not affect the vibrational linewidth; 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 vibrational structures that do not correspond to any of the harmonic frequencies used in the calculation.

The same perturbative quantum wave packet theory was applied to simulate the inverse Raman scattering (IRS) of crystal violet (CV). The calculated results agreed well with the experimental URS results as a function of the resonance Raman pump excitation [21]. It was shown that the line-shapes change from negative dispersive to Lorentzian, to dispersive, and then to negative Lorentzian as the Raman pump excitation is tuned from the red tail of the absorption spectrum to near the absorption maximum. Increasing the Raman pump bandwidth or decreasing the Raman vibrational dephasing time, broadened the IRS bands. The well-known expression for $\chi_{IRS}^{(3)}$ was derived from multi-mode third-order susceptibility for IRS with the limit of monochromatic Raman pump and probe pulses in one-dimension.

Twenty four Feynman dual time line and four wave mixing energy level diagrams were used to depict CARS from the ground electronic state. Calculations were made on toluene for off-resonance CARS and R6G for resonance CARS for each of the twenty four terms that contributes to the third-order polarization of CARS. By interpreting the line-shape and relative intensity of each term, we found that the traditional CARS term with pump, Stokes and probe interactions all on the ket time line is the dominant term in both off-resonance and resonance CARS.

5.2 Prospects

Femtosecond stimulated Raman spectroscopy (FSRS) and coherent anti-Stokes Raman scattering (CARS) have been investigated with quantum mechanical methods. We have successfully applied the perturbative wave packet theory to the FSRS of Rhodamine 6G (R6G) and crystal violet (CV) and to the CARS of toluene and R6G. For FSRS in the thesis, we did calculations to simulate experiments which do not use an actinic pump, i.e. FSRS process starts from a stationary state. However, the theory also applies to FSRS from a moving wave packet prepared by an actinic pump pulse, and such calculations have been carried out in the group earlier by Sun *et al.* [67]. If the actinic pump and FSRS pulses overlap, we will need to treat the FSRS as a fifth order process - second order in the actinic pump with wave vectors cancelling each other, and third order

in the FSRS Raman pump and probe, with heterodyne detection in the probe pulse direction. There will be more than eight Feynman diagrams to describe the overlapping actinic pump-FSRS process, due to many possible time orderings of the pulses. This is left for future work when such experiments are also being carried out.

Generally, the perturbation theory above is used for weak fields, and for the experiments thus far, it has worked quite well. However if strong fields are used, we would have to consider all higher odd-order (fifth, seventh, etc.) polarizations along the signal direction. It requires summing up the perturbative contributions, hopefully, in decreasing order of contribution, and it needs to deal with many more Feynman dual time-line diagrams. An alternative method would be the nonperturbative (NP) method. All the contributing terms which are calculated separately in perturbative method, will be included. The NP method can deal with overlapping pulses automatically, without the need to consider time ordering of pulses in overlapping regions as in the perturbative method, and it also enables the treatment of non-Condon effects and dissipation at the duration of pulses [107]. However, a NP calculation will produce an overall polarization of all the contributing directions, which are easily distinguished by the directions of the emitted radiation both in experiments and perturbative calculations. We need to take an extra step to extract the orientation resolved signals in NP calculation, for example, by performing a discrete Fourier transform of the underlying Liouville equation with respect to the phase of involved pulses.

We can adopt the time dependent wave packet theory to investigate other spectroscopies, such as 2D-IR photo-echo spectroscopy (2D-IR) and polarizability response spectroscopy (PORS). 2D-IR recently has gained much popularity and application involving three infrared excitation pulses with heterodyne detection [108, 109, 110, 111]. In 2D-IR, the wave packet on a single electronic state can be treated with the same numerical method, but the light-matter interaction has to be modified. Dynamics in various systems, such as chemical exchange process in solvent-solute complex, intramolecular interaction, transition-state geometries and interfacial dynamics of a catalytic monolayer, could be revealed by the numerical investigation of various 2D-IR experiments. Solvent motion is very important to chemical reactions in solutions. PORS is a novel fifth-order nonlinear spectroscopy which is intended to provide a direct view of solvent

motion in the vicinity of the solute over the course of a reaction [112, 113]. The process is essentially a sequence of two events: an electronically resonant pulse first initiates a reaction in a solute to create ground and excited state wave packets; the nonequilibrium solvent structure surrounding the excited system relaxes in the reaction time which is detected by Raman probe. PORS can, in principle, measure the same polarization response as the FSRS with resonant actinic pump pulse, but the probe pulse used is off-resonant with the solute electronic states as the focus is on enhancing the solvent response. Hence, we are able to adopt similar theories and methods to investigate PORS. All these are possible new work for the future.

List of Publications

1. 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
2. Xueqiong Qiu, Xiuting Li, Kai Niu, and Soo-Y Lee, “Inverse Raman Bands in Ultrafast Raman Loss Spectroscopy”, J. Chem. Phys. 2011, **135**, 164502
3. Bin Zhao, Kai Niu, Xiuting Li and Soo-Y. Lee, “Simple Aspects of Femtosecond Stimulated Raman Spectroscopy”, Science China Chemistry 2011, **54**, 1989 (invited)
4. Xiuting Li, Kai Niu, and Soo-Y. Lee, “What are the line shapes and relative intensities of the twenty four spectral groups to describe coherent anti-Stokes Raman spectroscopy? ”, manuscript in preparation.

Bibliography

- [1] M. Yoshizawa, Y. Hattori, and T. Kobayashi. Femtosecond time-resolved Raman gain spectroscopy in polydiacetylene. *Phys. Rev. B*, 49:13259, 1994.
- [2] M. Yoshizawa and M. Kurosawa. Femtosecond time-resolved Raman spectroscopy using stimulating Raman scattering. *Phys. Rev. A*, 61:013808, 1999.
- [3] D. W. McCamant. *Femtosecond stimulated Raman spectroscopy of ultrafast biophysical reaction dynamics*. PhD thesis, University of California, Berkeley, 2004.
- [4] D. W. McCamant, P. Kukura, and R. A. Mathies. Femtosecond broadband stimulated Raman : A new approach for high-performance vibrational spectroscopy. *Appl. Spectrosc.*, 57:1317, 2003.
- [5] D. W. McCamant, P. Kukura, and R. A. Mathies. Femtosecond time-resolved stimulated raman spectroscopy : Application to the ultrafast internal conversion in β - carotene. *J. Phys. Chem. A*, 107:8208, 2003.
- [6] P. Kukura, D. W. McCamant, P. H. Davis, and R. A. Mathies. Vibrational structure of the S_2 ($1B_u$) excited state of diphenylacetylene observed by femtosecond stimulated Raman spectroscopy. *Chem. Phys. Lett.*, 382:81, 2003.

- [7] D. W. McCamant, P. Kukura, S. W. Yoon, and R. A. Mathies. Femtosecond broadband stimulated Raman spectroscopy: Apparatus and methods. *Rev. Sci. Instr.*, 75:4971, 2004.
- [8] P. Kukura, D. W. McCamant, and R. A. Mathies. Femtosecond time-resolved stimulated Raman spectroscopy of the $S_2(1B_u^+)$ excited state of beta carotene. *J. Phys. Chem. A*, 108:5921, 2004.
- [9] D. W. McCamant, P. Kukura, and R. A. Mathies. Femtosecond stimulated Raman study of excited-state evolution in bacteriorhodopsin. *J. Phys. Chem. B*, 109:10449, 2005.
- [10] P. Kukura, D. W. McCamant, S. W. Yoon, D. B. Wandschneider, and R. A. Mathies. Structural observation of the primary isomerization in vision with femtosecond-stimulated Raman. *Science*, 310:1006, 2005.
- [11] P. Kukura, S. Yoon, and R. A. Mathies. Femtosecond stimulated Raman spectroscopy. *Anal. Chem.*, 78:5952, 2006.
- [12] P. Kukura, D. W. McCamant, and R. A. Mathies. Femtosecond stimulated Raman spectroscopy. *Ann. Rev. Phys. Chem.*, 58:461, 2007.
- [13] S. Shim, C. M. Stuart, and R. A. Mathies. Resonance Raman cross-sections and vibronic analysis of Rhodamine 6G. *ChemPhysChem*, 9:697, 2008.
- [14] R. R. Frontiera, S. Shim, and R. A. Mathies. Origin of negative and dispersive features in anti-Stokes and resonance FSRS. *J. Chem. Phys.*, 129:064507, 2008.
- [15] S. Shim, J. Dasgupta, and R. A. Mathies. Femtosecond time-resolved stimulated Raman reveals the birth of bacteriorhodopsin’s J and K intermediates. *J. Am. Chem. Soc.*, 131:7592, 2009.
- [16] C. Fang, R. R. Frontiera, R. Tran, Y. Prior, and R. A. Mathies. Mapping GFP structure evolution during proton transfer with femtosecond Raman spectroscopy. *Nature*, 462:200, 2009.
- [17] P. Kukura, R. Frontiera, and R. A. Mathies. Direct observation of anharmonic coupling in the time domain with femtosecond stimulated Raman scattering. *Phys. Rev. Lett.*, 96:238303, 2006.

- [18] J. Dasgupta, R. R. Frontiera, K. C. Taylor, J. C. Lagarias, and R. A. Mathies. Ultrafast excited-state isomerization in phytochrome revealed by femtosecond stimulated Raman spectroscopy. *Proc. Natl. Acad. Sci. US*, 106:1784, 2009.
- [19] S. Umapathy, A. Lakshmanna, and B. Mallick. Ultrafast Raman loss spectroscopy. *J. Raman Spectrosc.*, 40:235–237, 2009.
- [20] A. Lakshmanna, B. Mallick, and S. Umapathy. Ultrafast Raman loss spectroscopy: a new approach to vibrational structure determination. *Current Science*, 97:210–216, 2009.
- [21] S. Umapathy, B. Mallick, and A. Lakshmanna. Mode-dependent dispersion in Raman line shapes: Observation and implications from ultrafast Raman loss spectroscopy. *J. Chem. Phys.*, 133:024505, 2010.
- [22] K. Niu, S. L. Cong, and S. Y. Lee. Femtosecond stimulated Raman scattering for polyatomics with harmonic potentials: Application to Rhodamine 6G. *J. Chem. Phys.*, 131:054311, 2009.
- [23] Z. Sun, J. Lu, D. H. Zhang, and S. Y. Lee. Quantum theory of femtosecond time-resolved stimulated Raman scattering. *J. Chem. Phys.*, 128:144114, 2008.
- [24] X. Q. Qiu, X. T. Li, K. Niu, and S. Y. Lee. Femtosecond stimulated Raman spectroscopy modeled with a delta probe pulse: application to Rhodamine 6G. *J. Raman Spectrosc.*, 42:563, 2011.
- [25] R. W. Terhune. Coherent anti-Stokes Raman spectroscopy. *Bull. Am. Phys. Soc.*, 8:359, 1963.
- [26] P. D. Maker and R. W. Terhune. Study of optical effects due to an induced polarization third order in the electric field strength. *Phys. Rev.*, 148(2):990, 1966.
- [27] M. Müller and A. Zumbusch. Coherent anti-Stokes Raman scattering microscopy. *ChemPhysChem*, 8:2156, 2007.
- [28] S. Roy, G. R. Gord, and A. K. Patnaik. Recent advances in coherent anti-Stokes Raman scattering spectroscopy: Fundamental developments and applications in reacting flows. *Prog. Energ. Combust.*, 36:280, 2010.

- [29] R. D. Hancock, F. R. Schauer, R. P. Lucht, and R. L. Farrow. Dual-pump coherent anti-Stokes Raman scattering measurements of nitrogen and oxygen in a laminar jet diffusion flame. *Appl. Opt.*, 36:3217, 1997.
- [30] A. Zumbusch, G. R. Holtom, and X. Sunney. Three-dimensional vibrational imaging by coherent anti-Stokes Raman scattering. *Phys. Rev. Lett.*, 82:4142, 1999.
- [31] T. R. Meyer, S. Roy, and J. R. Gord. Improving signal-to-interference ratio in rich hydrocarbon-air flames using picosecond coherent anti-Stokes Raman scattering. *Appl. Spectrosc.*, 61:1135, 2007.
- [32] A. C. Eckbreth. *Laser diagnostics for combustion temperature and species*. Gordon and Breach, Amsterdam, 1996.
- [33] R. P. Lucht, S. Roy, T. R. Meyer, and J. R. Gord. Femtosecond coherent anti-Stokes Raman scattering measurement of gas temperatures from frequency-spread dephasing of the Raman coherence. *Appl. Phys. Lett.*, 89:251112, 2006.
- [34] J. R. Gord, T. R. Meyer, and S. Roy. Applications of ultrafast lasers for optical measurements in combustng flows. *Ann. Rev. Anal. Chem.*, 1:663, 2008.
- [35] N. Dudovich, D. Oron, and Y. Silberberg. Single-pulse coherently controlled nonlinear Raman spectroscopy and microscopy. *Nature*, 418:512, 2002.
- [36] D. Oron, N. Dudovich, and Y. Silberberg. Femtosecond phase-and-polarization control for background-free coherent anti-Stokes Raman spectroscopy. *Phys. Rev. Lett.*, 90:213902, 2003.
- [37] M. Schmitt, G. Knopp, A. Materny, and W. Kiefer. Femtosecond time-resolved coherent anti-Stokes Raman scattering for the simultaneous study of ultrafast ground and excited state dynamics: iodine vapour. *Chem. Phys. Lett.*, 270(1):9, 1997.
- [38] M. Schmitt, G. Knopp, A. Materny, and W. Kiefer. The application of femtosecond time-resolved coherent anti-Stokes Raman scattering for the investigation of ground and excited state molecular dynamics of molecules in the gas phase. *J. Phys. Chem. A*, 102(23):4059–4065, 1998.

- [39] M. Karavitis, R. Zadoyan, and V. Ara Apkarian. Time resolved coherent anti-Stokes Raman scattering of I_2 isolated in matrix argon: Vibrational dynamics on the ground electronic state. *J. Chem. Phys.*, 114:4131, 2001.
- [40] M. Heid, S. Schlücker, U. Schmitt, T. Chen, R. Schweitzer-Stenner, V. Engel, and W. Kiefer. Two-dimensional probing of ground-state vibrational dynamics in porphyrin molecules by fs-CARS. *J. Raman Spectrosc.*, 32:771, 2001.
- [41] G. Knopp, P. Radi, M. Tulej, T. Gerber, and P. Beaud. Collision induced rotational energy transfer probed by time-resolved coherent anti-Stokes Raman scattering. *J. Chem. Phys.*, 118:8223, 2003.
- [42] T. Kiviniemi, T. Kiljunen, and M. Pettersson. Femtosecond coherent anti-Stokes Raman-scattering polarization beat spectroscopy of I-Xe complex in solid krypton. *J. Chem. Phys.*, 125:164302, 2006.
- [43] H. Tran, F. Chaussard, N. Le Cong, B. Lavorel, O. Faucher, and P. Joubert. Femtosecond time resolved coherent anti-Stokes Raman spectroscopy of H-N mixtures in the Dicke regime: Experiments and modeling of velocity effects. *J. Chem. Phys.*, 131:174310, 2009.
- [44] T. Seeger, J. Kiefer, A. Leipertz, B. D. Patterson, C. J. Kliewer, and T. B. Settersten. Picosecond time-resolved pure-rotational coherent anti-Stokes Raman spectroscopy for N_2 thermometry. *Opt. Lett.*, 34:3755, 2009.
- [45] R. F. Begley, A. B. Harvey, and R. L. Byer. Coherent anti-Stokes Raman spectroscopy. *Appl. Phys. Lett.*, 25:387, 1974.
- [46] B. D. Prince, A. Chakraborty, B. M. Prince, and H. U. Stauffer. Development of simultaneous frequency-and time-resolved coherent anti-Stokes Raman scattering for ultrafast detection of molecular raman spectra. *J. Chem. Phys.*, 125:044502, 2006.
- [47] D. D. Dlott. in *Laser Spectroscopy of Solids II*, volume p. 167. Springer-Verlag, Berlin, 1988.
- [48] Y. R. Shen. Recent advances in nonlinear optics. *Rev. Mod. Phys.*, 48:1, 1976.

- [49] W. M. Tolles, J. W. Nibler, J. R. McDonald, and A. B. Harvey. A review of the theory and application of coherent anti-Stokes Raman spectroscopy (CARS). *Appl. Spectrosc.*, 31:253, 1977.
- [50] J. P. Kuehner, Sameer V. Naik, W. D. Kulatilaka, N. Chai, N. M. Laurendeau, R. P. Lucht, M. O. Scully, S. Roy, A. K. Patnaik, and J. R. Gord. Perturbative theory and modeling of electronic-resonance-enhanced coherent anti-Stokes Raman scattering spectroscopy of nitric oxide. *J. Chem. Phys.*, 128:174308, 2008.
- [51] D. J. Tannor, S. A. Rice, and P. M. Weber. Picosecond CARS as a probe of ground electronic state intramolecular vibrational redistribution. *J. Chem. Phys.*, 83:6185, 1985.
- [52] S. Meyer and V. Engel. Femtosecond time-resolved CARS and DFWM spectroscopy on gas-phase I_2 : a wave-packet description. *J. Raman Spectrosc.*, 31(1-2):33–39, 2000.
- [53] T. Tahara and H. Hamaguchi. Construction of a time-frequency two-dimensional multiplex coherent anti-Stokes Raman scattering spectrometer having 15 ps time resolution. *Rev. Sci. Instr.*, 65:3332, 1994.
- [54] B. Zhao, K. Niu, X. T. Li, and S. Y. Lee. Simple aspects of femtosecond stimulated Raman spectroscopy. *Sci China Chem*, 54:1989, 2011.
- [55] D. A. Long. *The Raman Effect. A Unified Treatment of the Theory of Raman Scattering by Molecules*. John Wiley Sons, Chichester, 2002.
- [56] 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.
- [57] H. A. Kramers and W. Heisenberg. Über die streuung von strahlung durch atome. *Z. Phys.*, 31:681, 1925.
- [58] P. A. M. Dirac. The quantum theory of dispersion. *Proc. Roy. Soc.*, 114:710, 1927.
- [59] A. C. Albrecht. On the theory of Raman intensities. *J. Chem. Phys.*, 34:1476, 1961.

- [60] Y. R. Shen. Distinction between resonance Raman scattering and hot luminescence. *Phys. Rev. B*, 9:622, 1974.
- [61] Y. Fujimura, H. Kono, T. Nakajima, and S. H. Lin. A theoretical study of resonance Raman scattering from molecules. III. resonance Raman scattering and resonance fluorescence. *J. Chem. Phys.*, 75:99, 1981.
- [62] D. Lee and A. C. Albrecht. A unified view of Raman, resonance Raman, and fluorescence spectroscopy and their analogues in two-photon absorption. In R. J. H. Clark, Robin Jon Hawes Clark, and R. E. Hester, editors, *Advances in Infrared and Raman Spectroscopy*, volume 12, pages 179—213. Wiley Heyden, London, 1985.
- [63] S. Y. Lee and E. J. Heller. Time-dependent theory of Raman scattering. *J. Chem. Phys.*, 71:4777, 1979.
- [64] E. J. Heller, R. L. Sundberg, and D. Tannor. Simple aspects of Raman scattering. *J. Phys. Chem.*, 86:1822, 1982.
- [65] N. Bloembergen and Y. R. Shen. Coupling between vibrations and light waves in Raman laser media. *Phys. Rev. Lett.*, 12:504, 1964.
- [66] Y. R. Shen and N. Bloembergen. Theory of stimulated Brillouin and Raman scattering. *Phys. Rev.*, 137:A1787, 1965.
- [67] Z. Sun, Z. Jin, J. Lu, D. H. Zhang, and S. Y. Lee. Wave packet theory of dynamic stimulated Raman spectra in femtosecond pump-probe spectroscopy. *J. Chem. Phys.*, 126:174104, 2007.
- [68] Z. Sun, X. Q. Qiu, J. Lu, D. H. Zhang, and S. Y. Lee. Three-state model for femtosecond broadband stimulated Raman scattering. *J. Raman Spectrosc.*, 39:1568, 2008.
- [69] Z. Sun, B. Fu, D. H. Zhang, and S. Y. Lee. Theoretical investigation of the direct observation of anharmonic coupling in CDCl_3 in the time domain with FSRS. *J. Chem. Phys.*, 130:044312, 2009.

- [70] K. Niu, B. Zhao, Z. G. Sun, and S. Y. Lee. Analysis of femtosecond stimulated Raman spectroscopy of excited-state evolution in bacteriorhodopsin. *J. Chem. Phys.*, 132:084510, 2010.
- [71] B. Zhao, Z. G. Sun, and S. Y. Lee. Quantum theory of time-resolved femtosecond stimulated Raman spectroscopy: Direct versus cascade processes and application to CDCl_3 . *J. Chem. Phys.*, 134:024307, 2011.
- [72] S. Mukamel. *Principles of Nonlinear Optical Spectroscopy*. Oxford University Press, New York, 1995.
- [73] Y. J. Yan, L. E. Fried, and S. Mukamel. Ultrafast pump-probe spectroscopy: Femtosecond dynamics in Liouville space. *J. Phys. Chem.*, 93:8149, 1989.
- [74] G. Stock and W. Domcke. Detection of ultrafast molecular-excited-state dynamics with time- and frequency-resolved pump-probe spectroscopy. *Phys. Rev. A*, 45:3032, 1992.
- [75] S. Y. Lee. in *Femtosecond Chemistry*, volume 1, Chap. 7, p. 273. VCH, Weinheim, 1995.
- [76] W. T. Pollard and R. A. Mathies. Analysis of femtosecond dynamic absorption spectra of nonstationary states. *Ann. Rev. Phys. Chem.*, 43:497, 1992.
- [77] L. Seidner, G. Stock, and W. Domcke. Nonperturbative approach to femtosecond spectroscopy: General theory and application to multidimensional nonadiabatic photoisomerization processes. *J. Chem. Phys.*, 103:3998, 1995.
- [78] K. Niu and S. Y. Lee. Analysis of time resolved femtosecond and femtosecond/picosecond coherent anti-Stokes Raman spectroscopy: Application to toluene and rhodamine 6G. *J. Chem. Phys.*, 136:064504, 2012.
- [79] E. J. Heller and D. J. Tannor. Polyatomic Raman scattering for general harmonic potentials. *J. Chem. Phys.*, 77:202, 1982.
- [80] M. Yoshizawa, H. Aoki, and H. Hashimoto. Vibrational relaxation of the $2A_g^-$ excited state in all-*trans*- β -carotene obtained by femtosecond time-resolved Raman spectroscopy. *Phys. Rev. B*, 63:180301(R), 2001.

- [81] M. Yoshizawa, H. Aoki, and H. Hashimoto. Femtosecond time-resolved Raman signals on ultrafast dynamics in all-*trans*- β -carotene. *Bull. Chem. Soc. Jpn.*, 75:949, 2002.
- [82] S. Y. Lee, D. H. Zhang, D. W. McCamant, P. Kukura, and R. A. Mathies. Theory of femtosecond stimulated Raman spectroscopy. *J. Chem. Phys.*, 121:3632, 2004.
- [83] K. C. Wilson, B. Lyons, R. Mehlenbacher, R. Sabatini, and D. W. McCamant. Two-dimensional femtosecond stimulated Raman spectroscopy: Observation of cascading Raman signals in acetonitrile. *J. Chem. Phys.*, 131:214502, 2009.
- [84] A. B. Myers, R. A. Harris, and R. A. Mathies. Resonance Raman excitation profiles of bacteriorhodopsin. *J. Chem. Phys.*, 79:603, 1983.
- [85] W. T. Pollard, S. L. Dexheimer, Q. Wang, L. A. Peteaunu, C. V. Shank, and R. A. Mathies. Theory of dynamic absorption spectroscopy of nonstationary states. *J. Phys. Chem.*, 96:6147, 1992.
- [86] 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.
- [87] S. Mukamel and J. D. Biggs. Communication: Comment on the effective temporal and spectral resolution of impulsive stimulated Raman signals. *J. Chem. Phys.*, 134:161101, 2011.
- [88] S. W. Yoon, D. W. McCamant, P. Kukura, R. A. Mathies, D. H. Zhang, and S. Y. Lee. Dependence of line shapes in femtosecond broadband stimulated Raman spectroscopy on pump-probe time delay. *J. Chem. Phys.*, 122:024505, 2005.
- [89] L. Tutt, D. Tannor, J. Schindler, E. J. Heller, and J. I. Zink. Missing mode effect. *J. Phys. Chem.*, 87:3017, 1983.
- [90] S. Y. Lee and H. Y. Chang. Missing mode effect in REP. *J. Chem. Phys.*, 100:4056, 1994.
- [91] W. J. Jones and B. P. Stoicheff. Inverse Raman spectra: Induced absorption at optical frequencies. *Phys. Rev. Lett.*, 13:657, 1964.

- [92] A. Lau, W. Werncke, M. Pfeiffer, K. Lenz, and H. J. Weigmann. Inverse Raman scattering. *Sov. J. Quantum Electron.*, 6:402, 1976.
- [93] I.I. Kondilenko, N. E. Kornienko, V. I. MalyT, and G. V. Ponezha. Some regularities in the spectra of inverse Raman scattering. *Sov. J. Quantum Electron.*, 11:1494, 1981.
- [94] L. A. Rahn and R. E. Palmer. Studies of nitrogen self-broadening at high temperature with inverse Raman spectroscopy. *J. Opt. Soc. Am. B*, 3:1164, 1986.
- [95] T. Ishihara and T. Goto. Resonant inverse Raman scattering in red-HgI₂. *Opt. Commun.*, 59:357, 1986.
- [96] W. J. Jones. Picosecond inverse Raman spectroscopy of liquid crystals. *J. Mol. Struct.*, 404:129, 1997.
- [97] D. R. Solli, P. Koonath, and B. Jalali. Inverse Raman scattering in silicon: A free-carrier enhanced effect. *Phys. Rev. A*, 79:053853, 2009.
- [98] D. J. Tannor and E. J. Heller. Polyatomic Raman scattering for general harmonic potentials. *J. Chem. Phys.*, 77:202, 1982.
- [99] A. M. Kelley, L. C. T. Shoute, M. Blanchard-Desce, G. P. Bartholomew, and G. C. Bazan. Resonance Raman , hyper-Raman , and hyper-Rayleigh depolarization ratios and symmetry breaking in solution. *Molecular Physics*, 104:1239, 2006.
- [100] L. Angeloni, G. Smulevich, and M. P. Marzocchi. Resonance Raman spectrum of crystal violet. *J. Raman Spectrosc.*, 8:305, 1979.
- [101] E. J. Liang, X. L. Ye, and W. Kiefer. Surface-enhanced Raman spectroscopy of crystal violet in the presence of halide and halate ions with near-infrared wavelength excitation. *J. Phys. Chem. A*, 101:7330, 1997.
- [102] M. Takayanagi, H. Hamaguchi, and M. Tasumi. Probe-frequency dependence of the resonant inverse Raman band shape. *J. Chem. Phys.*, 89:3945, 1988.
- [103] E. Ploetz, S. Laimgruber, S. Berner, W. Zinth, and P. Gilch. Femtosecond stimulated Raman microscopy. *Appl. Phys. B.: Lasers Opt.*, 87:389, 2007.

- [104] R. P. Feynman. Space-time approach to quantum electrodynamics. *Phys. Rev.*, 76:769, 1949.
- [105] W. T. Pollard, S. L. Dexheimer, Q. Wang, L. A. Peteaunu, C. V. Shank, and R. A. Mathies. Theory of dynamic absorption spectroscopy of nonstationary states. *J. Phys. Chem.*, 96:6147, 1992.
- [106] D. J. Tannor and E. J. Heller. Polyatomic Raman scattering for general harmonic potentials. *J. Chem. Phys.*, 77:202, 1982.
- [107] T. Mančal, A. V. Pislakov, and G. R. Fleming. Two-dimensional optical three-pulse photon echo spectroscopy. I. nonperturbative approach to the calculation of spectra. *J. Chem. Phys.*, 124:234504, 2006.
- [108] D. D. Klott. Ultrafast chemical exchange seen with 2D vibrational echoes. *Science*, 309:1333, 2005.
- [109] J. F. Cahoon, K. R. Sawyer, J. P. Schlegel, and C. B. Harris. Determining transition-state geometries in liquids using 2D-IR. *Science*, 319:1820, 2007.
- [110] J. Zheng, K. Kwak, J. Asbury, X. Chen, I. R. Piletic, and M. D. Fayer. Ultrafast dynamics of solute-solvent complexation observed at thermal equilibrium in real time. *Science*, 309:1338, 2005.
- [111] Daniel E. Rosenfeld, Zolt Gengeliczki, Brian J. Smith, T. D. P. Stack, and M. D. Fayer. Structural dynamics of a catalytic monolayer probed by ultrafast 2D IR vibrational echoes. *Science*, 334:634, 2011.
- [112] A. M. Moran, S. Park, and N. F. Scherer. Polarizability response spectroscopy: Formalism and simulation of ultrafast dynamics in solvation. *Chem. Phys.*, 341:344, 2007.
- [113] A. M. Moran, R. A. Nome, and N. F. Scherer. Field resolved measurement of reaction-induced spectral densities by polarizability response spectroscopy. *J. Chem. Phys.*, 127:184505, 2007.

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