Quantum mechanical investigation of femtosecond stimulated Raman spectroscopy

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TECHNOLOGICAL
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**QUANTUM MECHANICAL INVESTIGATION OF
FEMTOSECOND STIMULATED RAMAN SPECTROSCOPY**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2012

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FEMTOSECOND STIMULATED RAMAN SPECTROSCOPY**

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Abstract

Femtosecond Stimulated Raman Spectroscopy (FSRS) is a novel spectroscopy that offers simultaneous high temporal and spectral resolutions, and it also bears many other advantages, such as fluorescence background free, high signal-to-noise ratio, wide vibrational spectrum range, and rapid data acquisition. The research works in this thesis aim to provide a quantum mechanical investigation on FSRS and try to elucidate the underlying quantum mechanical processes for the first 500 fs photoisomerization dynamics in the excited state of bacteriorhodopsin, and for the side bands with inverse symmetry around the CD stretch frequency of CDCl_3 molecule from the direct fifth and cascade processes in time-resolved FSRS. The issue of simultaneous high temporal and spectral resolutions obtained by FSRS is investigated from a quantum mechanical point of view, and the temporal resolution is revealed by the polarization from the inverse Fourier transform of the Stokes line.

In the quantum mechanical investigation of the first 500 fs photoisomerization dynamics in the excited state of bacteriorhodopsin, we use four-wave mixing energy level diagrams to describe the FSRS processes, and a 29-mode separable harmonic oscillator model for BR_{568} in the calculations. From the calculation results, we find that FSRS of BR_{568} effectively occurs between the ground vibrational state of S_1 and high energy vibrational states on BR (S_0), and only the ground vibrational state of each of the observed 800-1800 cm^{-1} modes of S_1 is involved in the process. The FSRS dispersive lines are shown to be due to the inverse Raman scattering (IRS) term with $|0\rangle\langle 1|$ vibrational coherence on the S_1 surface, and are not due to Raman Initiated by Nonlinear Emission (RINE) with vibrational coherence on the S_0 surface. Our calculations show that the RINE process gives rise to broad featureless spectra.

We use a quantum mechanical wave packet treatment to investigate the 2D-FSRS of CDCl_3 molecule, where a vibrational coherence is initiated with an impulsive Raman pump. It is found that the experimentally observed side bands may come from two processes, which can occur concurrently but with different intensities: a direct fifth-order process taking place on one molecule, and a cascade process comprising two third-order processes on two different molecules. Our quantum mechanical calculation shows that the observed side bands are from

the cascade process with stronger intensity, and the appearance of side bands are due to the CARS and CSRS fields produced in the first step of the cascade process. The coherent line shapes of the side bands are correlated with the momentum of the wave packet prepared on the ground state surface by the impulsive pump along the sideband normal coordinate, and the inversion symmetry of the side bands about the C-D stretch frequency is due to the 180° phase difference between the CARS and CSRS fields that produced the left and right sidebands.

In the elucidation of simultaneous high temporal and spectral resolutions of FSRS, we use both three-state model and wave packet method to investigate FSRS spectra of the vibrational modes with time-dependent frequency. The adiabatic theorem supports the validity of three-state model for the vibrational modes with time-dependent frequency. The wave packet method is more general in treating real initial wave packet and pulses with finite duration. The results obtained by the two methods agree well with each other for off-resonance FSRS spectra of the vibrational mode with time-dependent frequency. The high temporal resolution of FSRS is demonstrated by revealing the time-dependent vibrational frequency from the inverse Fourier transform of the Stokes lines. It is also found by the wave packet method that off-resonance FSRS can't distinguish between coherence and no coherence in the initial wave packet from the line shape and position of the Stokes lines.

Introduction

1.1 Motivation of Femtosecond Stimulated Raman Spectroscopy (FSRS)

1.1.1 Motivation

Though remarkably detailed information about the static molecular structures of both reactant and product has been provided by a variety of microscopic and spectroscopic techniques, little insight into the actual atomic motions involved in chemical reaction has been obtained in ‘real-time’ until the first revolutionary experimental observation of femtosecond pump-and-probe transition state spectroscopy in ICN [1] and NaI [2]. Typically, chemical bond breaking, forming and geometry rearrangement during chemical reactions take place in the time scale of femtosecond, and thus femtochemistry gains its name for this research field. In femtochemistry the concept of coherence plays a decisive role in elucidation of dynamical structure evolution. The preparation and detection of coherence are essential to observing and revealing dynamics of structural evolution [3]. Preparation of coherence is always achieved by an ultrashort laser pulse with a duration shorter than the characteristic molecular vibrational period, and then the coherent molecular wave packet moves along the reaction coordinate from the reactant region to the product region, transversing intermediate transition states. For the detection of coherence, a variety of methods have been implemented in laboratories around the world: laser-induced fluorescence, laser multiphoton ionization, mass spectroscopy, coulomb explosion, electron diffraction, photoelectron spectroscopy, transient absorption and nonlinear spectroscopies [4, 5], which make use of the correlation of time with frequency, mass, velocity or orientation during dynamic processes.

As a direct consequence of the availability of various ultrashort laser pulses, spectroscopy

based detection techniques have gained much popularity, and better time-resolution can be achieved compared to other detection schemes. Spectroscopy based detection techniques also have the capability to study other ultrafast processes besides reaction dynamics, such as molecular cluster formation, solvation dynamics, electron and proton transfer. Optical transient absorption or stimulated emission in commonly implemented pump-probe scheme with both ultrashort optical pulses are the most straightforward techniques [6, 7]. However, the transient electronic spectra obtained provide limited structural information, especially for large polyatomic molecules. Vibrational spectroscopy, on the other hand, is the preferred and indispensable tool for molecular structure determination, due to its close relationship to intermolecular and intramolecular nuclear motion [8]. Recently, time-resolved two-dimensional infrared (2D-IR) vibrational echo spectroscopy [9], with three infrared excitation pulses and without the need for an optical trigger, has been invented to investigate various ultrafast dynamics within a ground electronic state, including peptides [10], transition-state geometries [11], ultrafast chemical exchange in formation and dissociation of solute-solvent complexes [12, 13, 14, 15, 16, 17], biomolecule structure and function [18], interfacial dynamics and structure of a catalytic monolayer [19] and still more processes.

However, like in 2D-IR, most molecular structures obtained are largely restricted to the ground electronic state, and relatively little information has been revealed about excited state molecular structures, which is partly due to the short lifetime of the excited electronic states (usually < 50 fs) as well as the complexity of the spectra. To reveal dynamical information of an excited electronic state requires femtosecond time-resolved vibrational spectroscopy, in which an ultrashort optical pulse triggers dynamics on an excited electronic state and the subsequent dynamics is probed by ultrashort IR/optical pulses. One of them is the linear transient infrared (IR) absorption (transient optical-pump/IR-probe) spectroscopy [20, 21]. The challenge of this method in a biological application is the problem of intense absorption from water and protein environment. Nevertheless, transient IR absorption enjoys successful application in the study of solid-state ultrafast processes [22, 23].

A versatile and robust alternative is offered by time-resolved Raman spectroscopy [24, 25], which avoids the problem of transient IR absorption in biological applications. Resonant Raman scattering (RRS) is capable of revealing information about excited electronic state, but it is intrinsically a spontaneous Raman (SR) method and temporal resolution is limited to 1-2 picoseconds. It should also be noted that SR scattering is a weak effect and it is easily overwhelmed by background signals. On the other hand, time-resolved (TR) femtosecond

(fs) four wave mixing (FWM) spectroscopy is an imperative tool to reveal dynamic information on different potential energy surfaces by various degrees of freedom, such as timing, polarization, laser wavelength and probe window bandwidth [26]. TR coherent anti-Stokes Raman scattering (CARS) was first applied by Leonhardt *et al.* to study high-frequency quantum beats, and fs time resolution was achieved [27]. It was shown that TR fs-CARS is capable of observing dynamics of both ground and excited electronic states in gas phase iodine [28]. Various improvements on conventional TR fs-CARS have been implemented. fs/ps CARS obtains better frequency resolution by replacing the third broadband pulse with a narrowband picosecond pulse [29]. Electronic resonance enhanced (ERE) CARS has recently been applied to study solvent effects on CV670 [30]. However CARS based techniques cannot avoid the drawback of a large inherent non-resonant background. Other techniques of TR fs-FWM are TR degenerate FWM (DFWM) [31] and coherent Stokes Raman scattering (CSRS).

Recently, a novel TR fs-FWM spectroscopy - 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 [32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42].

1.1.2 Introduction to FSRS ¹

Time-resolved or 2D-FSRS is a resonant/off-resonant optical nonlinear vibrational spectroscopy technique in mixed time and frequency domains, 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 is shown in Fig. 1.2. The

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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.

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 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 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. Fig. 1.2 looks like a BOXCARS arrangement, but the box is not quite complete. One could have (homodyne or heterodyne) detection along $\mathbf{k}_{ac} - \mathbf{k}_{pr} + \mathbf{k}_{pu}$, which is along the direction from the sample to the fourth vertex on the right output box in Fig. 1.2, to complete the BOXCARS arrangement, but this is not the case for FSRS where the detection is along $\mathbf{k}_{pr}$.

Figure 1.2: Geometry of time-resolved FSRS experiment.

It is possible to acquire spectra with a time resolution of ~ 50 fs in the time delay between the actinic pump and probe pulses, and a spectral resolution of < 10 cm^{-1} due largely to the ps Raman pump pulse [38, 40]. Other advantages of FSRS are rapid data acquisition, Raman spectra unaffected by background fluorescence, high signal-to-noise ratio, and wide 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[35] and diphenyloctatetraene [33], excited state structural dynamics of the photoisomerization of the retinal chromophore in bacteriorhodopsin[36, 44] and rhodopsin [37], anharmonic coupling in CDCl_3 [39], resonance Raman scattering from Rhodamine 6G (R6G) which is a highly fluorescent compound [45, 46], and excited state isomerization in phytochrome [47].

The theory of both spontaneous and stimulated Raman spectroscopy traces back to the beginnings of quantum theory [48], and encompasses both classical [49] and quantum [50, 51, 52, 53, 54, 55] 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 [56, 57]. With intense lasers, stimulated Raman spectroscopy was possible, and Shen and Bloembergen [58, 59] 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 [60, 61, 62, 63, 64, 65, 66, 67].

1.2 Outline of dissertation

In chapter 2, most of the fundamental theories related to FSRS are explained, and followed by numerical methods that are used to simulate quantum mechanical processes in FSRS. In the theory part, we firstly present time-dependent Schrödinger equation, which is the crucial equation that governs the evolution of quantum states. Then we describe the perturbative approaches to simulate FSRS. We first explain the general idea behind perturbative approach, and use three diagrammatic perturbative methods to describe the third-order nonlinear processes in FSRS, Feynman dual time-line diagram, four-wave mixing energy level diagram and closed time loop diagram. We conclude the theory part with

the novelty of FSRS that provides simultaneous high temporal and spectral resolutions. In the numerical methods part, we start with Gaussian quadrature, and then describe three representations, VBR, FBR and DVR, and the relation between them. In numerically solving the time-dependent Schrödinger equation, using an efficient and accurate propagation method is highly important, and we describe the most general short time propagator - split operator method. Finally, we explain how to evaluate third-order nonlinear polarization of FSRS process.

In chapter 3, we present the numerical study for the first 500 fs photoisomerization dynamics in the excited state of bacteriorhodopsin, BR^* (S_1), created by a prior 500 nm, 35 fs actinic pump pulse. We use four-wave mixing energy level diagrams to describe the FSRS processes, and a 29-mode separable harmonic oscillator model for BR_{568} in the calculations. The calculations show that FSRS of BR_{568} effectively occurs from the ground vibrational state of each of the observed 800-1800 cm^{-1} modes of S_1 . The lifetime on S_1 determines the linewidth and decay of the dispersive lines, and is estimated to be ~ 600 fs, comparable to the stimulated emission decay time. The FSRS dipole couplings are from the ground vibrational state of S_1 to high energy vibrational states on BR (S_0), and we place a fast decay lifetime of ~ 100 fs on S_0 which can be attributed to the correlation function from the many unobserved low frequency modes. The FSRS dispersive lines are shown to be due to the inverse Raman scattering (IRS) term with $|0\rangle\langle 1|$ vibrational coherence on the S_1 surface, and are not due to RINE with vibrational coherence on the S_0 surface. Our calculations show that the RINE process gives rise to broad featureless spectra.

In chapter 4, we present a quantum mechanical wave packet treatment of time-resolved FSRS, or two-dimensional (2D) FSRS, where a vibrational coherence is initiated with an impulsive Raman pump which is subsequently probed by FSRS. In this 2D-FSRS, two processes can occur concurrently but with different intensities: a direct fifth-order process taking place on one molecule, and a cascade process comprising two third-order processes on two different molecules. The cascade process comprises a parallel and a sequential cascade. Quantum mechanical calculation shows that: (a) the cascade process is stronger than the direct fifth-order process by one order of magnitude, (b) the sidebands assigned to C-Cl E and A_1 bends, observed on both sides of the Stokes C-D stretch frequency, are not due to anharmonic coupling between the C-D stretch and the C-Cl bends, but are instead due to the CARS and CSRS fields produced in the first step of the cascade process, (c) for each delay time between the fs impulsive pump and FSRS probe pulses, the line shape of

the sidebands show an inversion symmetry about the C-D stretch frequency, and this is due to the 180° phase difference between the CARS and CSRS fields that produced the left and right sidebands, and (d) for each sideband, the line shape changes from positive Lorentzian to dispersive to negative Lorentzian then to negative dispersive and back to positive Lorentzian with the period of the bending vibration, and it is correlated with the momentum of the wave packet prepared on the ground state surface by the impulsive pump along the sideband normal coordinate.

In chapter 5, we discuss the high temporal and high spectral resolution in off-resonance FSRS. The high temporal resolution is provided by the inverse Fourier transform of the Stokes line to yield the time-dependent polarization and then to extract ‘real-time’ frequency, and the high spectral resolution is provided by the sharp, narrow lines in the FSRS spectra. Time resolution is better revealed in the time domain. The information in the frequency domain is related to the counterpart in time domain by a Fourier transform. We also found that off-resonance FSRS cannot distinguish between coherence and no coherence in the initial wave packet, because they both give the same line shape and position of the Stokes lines.

Theories and Numerical Methods

2.1 Theories

In quantum mechanics, the complete information about a certain physical quantum system is embodied in the wave function $|\psi\rangle$, which is an abstract symbol and can be represented in a complex vector space (Hilbert space). An observable, on the other hand, is represented by an operator. Operator acts on a state to produce another state or an overlap of states.

2.1.1 Time-dependent Schrödinger equation

Evolution of the quantum system is governed by the quantum mechanical equation of motion – time-dependent Schrödinger equation (TDSE),

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle, \quad (2.1)$$

in which $\hat{H}$ is a system Hamiltonian operator. It can be either time-dependent (TD) or time-independent (TI). If $\hat{H}$ is time-independent, Eqn. (2.1) can be solved like a normal linear first-order ordinary differential equation to the form,

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar} \hat{H}(t-t_0)} |\psi(t_0)\rangle \quad (2.2)$$

where the propagator $\hat{U}(t, t_0) = e^{-\frac{i}{\hbar} \hat{H}(t-t_0)}$ is a function of $\hat{H}$ operator, and in principle it can be understood as a Taylor series expansion in powers of $\hat{H}$,

$$e^{-\frac{i}{\hbar} \hat{H}(t-t_0)} = I - \left[\frac{i}{\hbar} \hat{H}(t-t_0) \right] + \frac{1}{2!} \left[\frac{i}{\hbar} \hat{H}(t-t_0) \right]^2 - \dots \quad (2.3)$$

however, in practice a general function of operator should be evaluated in the following manner [68, 69],

$$f(\hat{A}) = \sum_i |\alpha_i\rangle f(a_i) \langle \alpha_i| \quad (2.4)$$

where a_i 's and $|\alpha_i\rangle$'s are the eigenvalues and eigenvectors of the operator $\hat{A}$, respectively. This indicates that if a function of operator is evaluated in its eigenfunction basis, it is replaced by the much easier evaluation of the function of a scalar.

If $\hat{H}(t)$ is TD, specifically if $\hat{H}(t)$ includes a field-matter interaction Hamiltonian term $\hat{V}_{int}(t)$, the propagator has a complicated form and it is calculated order by order, [68]

$$\hat{U}(t, t_0) = 1 + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \dots \int_{t_0}^{\tau_1} d\tau_1 \hat{H}(t_n) \hat{H}(t_{n-1}) \dots \hat{H}(t_1). \quad (2.5)$$

If the Hamiltonians commute at different times, $[\hat{H}(\tau_1), \hat{H}(\tau_2)] = 0$, above formidable expression for $\hat{U}(t, t_0)$ can be simplified

$$\hat{U}(t, t_0) = \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau \hat{H}(\tau) \right]. \quad (2.6)$$

or else a time ordering operator $\hat{\mathbf{T}}$ has to be applied in front,

$$\hat{U}(t, t_0) = \hat{\mathbf{T}} \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau \hat{H}(\tau) \right]. \quad (2.7)$$

In the following part of this chapter, operators will no longer be denoted with a hat on top, if there is no misunderstanding.

2.1.2 Perturbation theory

Problems in quantum mechanics are seldom solved exactly for either TI or TD Hamiltonians. Perturbation method is one of the most widely used approximation methods, where the total Hamiltonian is partitioned into two parts,

$$H = H_0 + V_p \quad (2.8)$$

where H_0 is the TI unperturbed molecular Hamiltonian, and V_p is the perturbation. V_p in our case is the field-matter interaction Hamiltonian V_{int} ,

$$V_{int}(\mathbf{R}, t) = -\boldsymbol{\mu}(\mathbf{R}) \cdot \mathbf{E}(t) \quad (2.9)$$

For simplicity, we consider a molecular system involving two electronic states, which are coupled by V_{int} . The molecular wavefunction is written in the form,

$$\Psi(\mathbf{R}) = \psi_1(\mathbf{R})|1\rangle + \psi_2(\mathbf{R})|2\rangle \quad (2.10)$$

where the distinction between adiabatic and diabatic electronic representation is suppressed, $|1\rangle$ and $|2\rangle$ are the two electronic basis functions, $\psi_1(\mathbf{R})$ and $\psi_2(\mathbf{R})$ are the nuclear wavefunction on the two electronics states. The Hamiltonian is written as,

$$\begin{aligned} H = & (T_N + V_1)|1\rangle\langle 1| + (T_N + V_2)|2\rangle\langle 2| \\ & + V_{int}(|2\rangle\langle 1| + |1\rangle\langle 2|) \end{aligned} \quad (2.11)$$

Now the TDSE can be written in a matrix form in the electronic basis,

$$i\hbar \frac{\partial}{\partial t} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = \begin{bmatrix} T_N + V_1 & V_{int} \\ V_{int} & T_N + V_2 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} \quad (2.12)$$

$$\begin{aligned} &= \begin{bmatrix} h_1 & V_{int} \\ V_{int} & h_2 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} \\ &= \begin{bmatrix} h_1 & 0 \\ 0 & h_2 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} + \begin{bmatrix} 0 & V_{int} \\ V_{int} & 0 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} \end{aligned} \quad (2.13)$$

where $H_0 = \begin{bmatrix} h_1 & 0 \\ 0 & h_2 \end{bmatrix}$ is the TI unperturbed molecular Hamiltonian, and $V_p = \begin{bmatrix} 0 & V_{int} \\ V_{int} & 0 \end{bmatrix}$ is the perturbation, which is assumed to be small enough to use perturbation method. A parameter λ is introduced to organize terms in same orders of perturbation,

$$H = H_0 + \lambda V_{int} \quad (2.14)$$

Wave function is expanded in a power series of λ ,

$$\begin{bmatrix} \psi_1(t) \\ \psi_2(t) \end{bmatrix} = \begin{bmatrix} \psi_1^{(0)}(t) \\ \psi_2^{(0)}(t) \end{bmatrix} + \lambda \begin{bmatrix} \psi_1^{(1)}(t) \\ \psi_2^{(1)}(t) \end{bmatrix} + \lambda^2 \begin{bmatrix} \psi_1^{(2)}(t) \\ \psi_2^{(2)}(t) \end{bmatrix} + \dots \quad (2.15)$$

By substituting Eqns. (2.14) and (2.15) into the TDSE and collecting terms with same

powers of λ , we can obtain

$$i\hbar \frac{\partial}{\partial t} \begin{bmatrix} \psi_1^{(0)}(t) \\ \psi_2^{(0)}(t) \end{bmatrix} = \begin{bmatrix} h_1 & 0 \\ 0 & h_2 \end{bmatrix} \begin{bmatrix} \psi_1^{(0)}(t) \\ \psi_2^{(0)}(t) \end{bmatrix} \quad (2.16)$$

$$i\hbar \frac{\partial}{\partial t} \begin{bmatrix} \psi_1^{(1)}(t) \\ \psi_2^{(1)}(t) \end{bmatrix} = \begin{bmatrix} h_1 & 0 \\ 0 & h_2 \end{bmatrix} \begin{bmatrix} \psi_1^{(1)}(t) \\ \psi_2^{(1)}(t) \end{bmatrix} + \begin{bmatrix} 0 & V_{int} \\ V_{int} & 0 \end{bmatrix} \begin{bmatrix} \psi_1^{(0)}(t) \\ \psi_2^{(0)}(t) \end{bmatrix} \quad (2.17)$$

$$i\hbar \frac{\partial}{\partial t} \begin{bmatrix} \psi_1^{(2)}(t) \\ \psi_2^{(2)}(t) \end{bmatrix} = \begin{bmatrix} h_1 & 0 \\ 0 & h_2 \end{bmatrix} \begin{bmatrix} \psi_1^{(2)}(t) \\ \psi_2^{(2)}(t) \end{bmatrix} + \begin{bmatrix} 0 & V_{int} \\ V_{int} & 0 \end{bmatrix} \begin{bmatrix} \psi_1^{(1)}(t) \\ \psi_2^{(1)}(t) \end{bmatrix} \quad (2.18)$$

Eqn. (2.16) is simply the unperturbed TDSE. If the initial wave function at t_0 is given as,

$$\begin{bmatrix} \psi_1(t_0) \\ \psi_2(t_0) \end{bmatrix} = \begin{bmatrix} \psi_1^{(0)}(t_0) \\ \psi_2^{(0)}(t_0) \end{bmatrix} \quad (2.19)$$

one can solve Eqns. (2.16)-(2.18) order by order. Solutions to the zeroth-order wavefunctions are straightforward,

$$\psi_1^{(0)}(t) = e^{-\frac{i}{\hbar}h_1(t-t_0)}\psi_1^{(0)}(t_0) \quad (2.20)$$

$$\psi_2^{(0)}(t) = e^{-\frac{i}{\hbar}h_2(t-t_0)}\psi_2^{(0)}(t_0) \quad (2.21)$$

After substituting zeroth-order solution into Eqn. (2.17), it becomes simply a linear first-order ordinary differential equation, and solutions are found to be,

$$\psi_1^{(1)}(t) = -\frac{i}{\hbar} \int_{t_0}^t dt' e^{-\frac{i}{\hbar}h_1(t-t')} V_{int} e^{-\frac{i}{\hbar}h_2(t'-t_0)} \psi_2^{(0)}(t_0) \quad (2.22)$$

$$\psi_2^{(1)}(t) = -\frac{i}{\hbar} \int_{t_0}^t dt' e^{-\frac{i}{\hbar}h_2(t-t')} V_{int} e^{-\frac{i}{\hbar}h_1(t'-t_0)} \psi_1^{(0)}(t_0) \quad (2.23)$$

Similarly Eqn. (2.18) is solved to be,

$$\psi_1^{(2)}(t) = \left(-\frac{i}{\hbar^2}\right)^2 \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' e^{-\frac{i}{\hbar}h_1(t-t')} V_{int} e^{-\frac{i}{\hbar}h_2(t'-t'')} V_{int} e^{-\frac{i}{\hbar}h_1(t''-t_0)} \psi_1^{(0)}(t_0) \quad (2.24)$$

$$\psi_2^{(2)}(t) = \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' e^{-\frac{i}{\hbar}h_2(t-t')} V_{int} e^{-\frac{i}{\hbar}h_1(t'-t'')} V_{int} e^{-\frac{i}{\hbar}h_2(t''-t_0)} \psi_2^{(0)}(t_0) \quad (2.25)$$

Normally only the first electronic state is populated at the initial time t_0 , then it can be

found that odd-th and even-th order corrections to $\psi_1(t)$ and $\psi_2(t)$ are zero, respectively. Generalization to more than two electronic states is obvious.

2.1.3 Diagrammatic perturbation theory for FSRs ¹

Recalling the definition of Hamiltonian for a molecule interacting with an external electric field,

$$H = H_0 + V_{int} \quad (2.26)$$

where H_0 is the TI unperturbed molecular Hamiltonian in the absence of the external field, and V_{int} is the matter-field interaction,

$$V_{int} = -\boldsymbol{\mu} \cdot \mathbf{E}(t) = -\mu E(t) \quad (2.27)$$

where μ is the molecular dipole projected onto the polarization direction of electric field.

By solving the TDSE for the wave function as shown in section 2.1.2, the overall electric polarization $\mathbf{P}(t)$ is given as the quantum mechanical expectation value of the dipole operator,

$$\mathbf{P}(t) = \langle \Psi(t) | \boldsymbol{\mu} | \Psi(t) \rangle \quad (2.28)$$

Within electric dipole approximation, the electric polarization $\mathbf{P}(t)$ completely describes the response of the molecular system to electric fields.

The perturbative expansion of the polarization in powers of the electric field can be given by,

$$\mathbf{P}(t) = \mathbf{P}^{(1)}(t) + \mathbf{P}^{(3)}(t) + \mathbf{P}^{(5)}(t) + \dots \quad (2.29)$$

where even-order polarizations usually vanish due to symmetry consideration. Polarization for each odd-order is given as

$$\mathbf{P}^{(2N+1)}(t) = 2\Re \sum_{n=0}^N \langle \Psi^{2(N-n)}(t) | \psi_1 \rangle \boldsymbol{\mu}_{12} \langle \psi_2 | \Psi^{(2n+1)}(t) \rangle \quad (2.30)$$

for wave-function formalism.

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

$$\mathbf{P}^{(3)}(t) = [\langle \Psi^{(2)}(\mathbf{t}) | \psi_1 \rangle \boldsymbol{\mu}_{12} \langle \psi_2 | \Psi^{(1)}(\mathbf{t}) \rangle + \langle \Psi^{(0)}(\mathbf{t}) | \psi_1 \rangle \boldsymbol{\mu}_{12} \langle \psi_2 | \Psi^{(3)}(\mathbf{t}) \rangle] + c.c \quad (2.31)$$

The electric polarization $\mathbf{P}(t)$ can also be given in the more general density-matrix formalism, where individual phenomenological relaxation constants for the population and coherence can be well described for finite temperature effects.

The density matrix of the system, $\rho(t)$, is defined as,

$$\rho(t) = |\Psi(t)\rangle \langle \Psi(t)| \quad (2.32)$$

and it satisfies the Liouville equation

$$d\rho(t)/dt = -i[H, \rho(t)]/\hbar - i[V_{int}, \rho(t)]/\hbar . \quad (2.33)$$

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

$$\rho(t) = \rho^{(0)}(t) + \rho^{(1)}(t) + \rho^{(2)}(t) + \dots \quad (2.34)$$

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

The time-dependent overall polarization $\mathbf{P}(t)$, is given by the expectation value of the dipole operator $\boldsymbol{\mu}$

$$\mathbf{P}(t) = \text{Tr}[\boldsymbol{\mu}\rho(t)] . \quad (2.35)$$

In density-matrix formalism, polarization can also perturbatively expand in powers of the electric field as in Eqn. (2.29), and odd-order polarization is given as

$$\mathbf{P}^{(2N+1)}(t) = \text{Tr}[\boldsymbol{\mu}\rho^{(2N+1)}(t)] . \quad (2.36)$$

for density-matrix formalism.

In particular, the third-order polarization $P^{(3)}(t)$ (for simplicity vector notation of polarization is suppressed from now on) is given by,

$$P^{(3)}(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 S^{(3)}(t_1, t_2, t_3) E(t_1) E(t_2) E(t_3) , \quad (2.37)$$

where the third-order nonlinear response function, $S^{(3)}(t_1, t_2, t_3)$, can be expressed as [68, 70]

$$S^{(3)}(t_1, t_2, t_3) = \left(\frac{i}{\hbar}\right)^3 \text{Tr}[\mu \mathcal{G}(t - t_1) \mathcal{V} \mathcal{G}(t_1 - t_2) \mathcal{V} \mathcal{G}(t_2 - t_3) \mathcal{V} \rho(-\infty)] . \quad (2.38)$$

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

$$\mathcal{G}(t)A = \exp(-iHt)A\exp(iHt) , \quad (2.39)$$

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

$$\mathcal{V}A = [\mu, A] . \quad (2.40)$$

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. One can use Feynman dual time line diagrams, shown in Fig. 2.1, 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. 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.

Eqn. (2.31) in wave-function formalism reveals four possibilities to arrive at the third-order polarization of FSRS, as shown in Fig. 2.1: (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. These can also be shown in density-matrix formalism by the commutation operator $\mathcal{V}$ in Eqn. (2.38).

An arrow pointing into the time-line denotes absorption with a transition from a lower to

Figure 2.1: Eight basic Feynman dual time-line diagrams. Each diagram has $3!$ permutations of the fields, giving a total of 48 possible diagrams.

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 diagrams which are shown in Fig. 2.2 which are grouped into four sets: IRS(I), IRS(II), SRS(I) and SRS(II), where IRS refers to inverse Raman scattering and SRS refers to stimulated Raman scattering [61]. 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 [53]. The HL terms have population created on e_2 by the pump pulse, 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. Spontaneous Raman scattering is described wholly by the SRS(I) set of diagrams, with a vacuum field for E_{pr} [53]. The other five diagrams - IRS(I), IRS(II), and the SRS(II) set - have “absorption” from the probe field, which is a vacuum field in spontaneous Raman scattering, and so are not allowed there.

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 [29, 68].

The Feynman dual time line diagrams provide the time-frame view. The 8 resonant diagrams for FSRS in Fig. 2.2, can also be viewed in the energy-frame using the four-wave mixing energy level (FWMEL) diagrams, shown in Fig. 2.3. 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

Figure 2.2: Resonant Feynman dual time-line diagrams for IRS(I), IRS(II), SRS(I), and SRS(II) processes describing FSRs.

Figure 2.3: Four-wave mixing energy level diagrams corresponding to the Feynman diagrams of Fig. 2.2.

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.

Closed time path loop (CTPL) diagrams, shown in Fig. 2.4, have been introduced by Mukamel *et al.* [71], particularly as a short-hand notation to collapse the SRS(I) and SRS(II) set of diagrams into just one diagram each, by neglecting dephasing between the ket and the bra or absorbing it in the lifetimes of the electronic states. In earlier wave packet simulation of FSRS [60, 61, 63, 66], researchers had already adopted the CTPL approach to calculate SRS(I) and SRS(II) as a single term each, by propagating wave packets on the ket and bra time lines separately where only the interactions in either the bra or ket side are time ordered, but not between them.

From the Feynman diagrams in Fig. 2.2 and Eqn. (2.31), it is more convenient to write the third-order polarizations as overlaps between wave packets evolving on the bra and ket time lines. For SRS(I) and SRS(II) it is an overlap between a second-order bra wave packet with a first-order ket wave packet, while for IRS(I) and IRS(II) it is an overlap between a zeroth-order bra wave packet with a third-order ket wave packet,

$$P_{\text{SRS(I)}}^{(3)}(t) = \langle \psi_1^{(2)}(\mathbf{Q}, -\mathbf{k}_{pr}, \mathbf{k}_{pu}; t) | \mu_{21}^* | \psi_2^{(1)}(\mathbf{Q}, \mathbf{k}_{pu}; t) \rangle, \quad (2.41)$$

Figure 2.4: Mukamel's closed time loop diagrams for (a) IRS(I), (b) IRS(II), (c) SRS(I), and (d) SRS(II).

$$P_{\text{SRS}(\text{II})}^{(3)}(t) = \langle \psi_1^{(2)}(\mathbf{Q}, -\mathbf{k}_{pu}, \mathbf{k}_{pu}; t) | \mu_{21}^* | \psi_2^{(1)}(\mathbf{Q}, \mathbf{k}_{pr}; t) \rangle , \quad (2.42)$$

$$P_{\text{IRS}(\text{I})}^{(3)}(t) = \langle \psi_1(\mathbf{Q}, t) | \mu_{21}^* | \psi_2^{(3)}(\mathbf{Q}, \mathbf{k}_{pu}, -\mathbf{k}_{pu}, \mathbf{k}_{pr}; t) \rangle , \quad (2.43)$$

$$P_{\text{IRS}(\text{II})}^{(3)}(t) = \langle \psi_1(\mathbf{Q}, t) | \mu_{21}^* | \psi_2^{(3)}(\mathbf{Q}, \mathbf{k}_{pr}, -\mathbf{k}_{pu}, \mathbf{k}_{pu}; t) \rangle . \quad (2.44)$$

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

$$\begin{aligned} |\psi_2^{(1)}(\mathbf{Q}, \mathbf{k}_{pu}; t)\rangle &= e^{i\mathbf{k}_{pu} \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right) \int_0^t dt_1 E_{pu}(t_1) e^{(-ih_2 - \gamma_2/2)(t-t_1)/\hbar} \\ &\quad \times \mu_{21} e^{(-ih_1 - \gamma_1/2)t_1/\hbar} |\psi_1(\mathbf{Q})\rangle , \end{aligned} \quad (2.45)$$

$$\begin{aligned} \langle \psi_1^{(2)}(\mathbf{Q}, -\mathbf{k}_{pr}, \mathbf{k}_{pu}; t) | &= e^{i(\mathbf{k}_{pr} - \mathbf{k}_{pu}) \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right)^2 \int_0^t dt_2 \int_0^{t_2} dt_3 \\ &\quad \times E_{pr}(t_2) E_{pu}^*(t_3) \\ &\quad \times \langle \psi_1(\mathbf{Q}) | e^{(ih_1 - \gamma_1/2)t_3/\hbar} \mu_{21}^* \\ &\quad \times e^{(ih_2 - \gamma_2/2)(t_2 - t_3)/\hbar} \mu_{21} e^{(ih_1 - \gamma_1/2)(t - t_2)/\hbar} , \end{aligned} \quad (2.46)$$

and by appropriate change of fields, we can write down similar expressions for $|\psi_2^{(1)}(\mathbf{Q}, \mathbf{k}_{pr}; t)\rangle$ and $\langle \psi_1^{(2)}(\mathbf{Q}, -\mathbf{k}_{pu}, \mathbf{k}_{pu}; t) |$ which appear in $P_{\text{SRS}(\text{II})}^{(3)}(t)$. For $P_{\text{IRS}(\text{I})}^{(3)}(t)$, the wave packets are

$$\langle \psi_1(\mathbf{Q}, t) | = \langle \psi_1(\mathbf{Q}) | e^{(ih_1 - \gamma_1/2)t/\hbar} , \quad (2.47)$$

$$\begin{aligned} |\psi_2^{(3)}(\mathbf{Q}, \mathbf{k}_{pu}, -\mathbf{k}_{pu}, \mathbf{k}_{pr}; t)\rangle &= e^{i\mathbf{k}_{pr} \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \\ &\quad \times E_{pu}(t_1) E_{pu}^*(t_2) E_{pr}(t_3) \\ &\quad \times e^{(-ih_2 - \gamma_2/2)(t-t_1)/\hbar} \mu_{21} e^{(-ih_1 - \gamma_1/2)(t_1 - t_2)/\hbar} \\ &\quad \times \mu_{21}^* e^{(-ih_2 - \gamma_2/2)(t_2 - t_3)/\hbar} \\ &\quad \times \mu_{21} e^{(-ih_1 - \gamma_1/2)t_3/\hbar} |\psi_1(\mathbf{Q})\rangle , \end{aligned} \quad (2.48)$$

and by an appropriate change of fields in Eqn. (2.48), 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 $P_{\text{IRS}(\text{II})}^{(3)}(t)$.

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

by

$$\begin{aligned} P_{\text{diff}}^{(3)}(t) &= P_{\text{pump on}}^{(3)}(\mathbf{k}_{pr}; t) - P_{\text{pump off}}^{(3)}(\mathbf{k}_{pr}; t) \\ &= P_{\text{SRS(I)}}^{(3)}(t) + P_{\text{SRS(II)}}^{(3)}(t) + P_{\text{IRS(I)}}^{(3)}(t) + P_{\text{IRS(II)}}^{(3)}(t) . \end{aligned} \quad (2.49)$$

The intensity of the (experimental) Raman gain (RG) spectrum in the direction of the probe pulse can be shown as [7, 72, 73, 74],

$$\Delta I_{RG}(\omega) = -\frac{8\pi^2 l C}{3n} \omega \text{Im} \left\{ P_{\text{diff}}^{(3)}(\omega) \cdot E_{pr}^*(\omega) \right\} , \quad (2.50)$$

where l is the cell length, C is the number of molecules per unit volume; n is the refractive index; $P_{\text{diff}}^{(3)}(\omega)$ is the Fourier transform of the difference polarization

$$P_{\text{diff}}^{(3)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} P_{\text{diff}}^{(3)}(t) dt , \quad (2.51)$$

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

$$E_{pr}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} E_{pr}(t) dt . \quad (2.52)$$

2.1.4 Novelty of FSRS: simultaneous high temporal and spectral resolutions ¹

Simultaneous high temporal and spectral resolutions may suggest circumventing the Heisenberg uncertainty principle. However, what we really mean is the time resolution in the time delay T between fs actinic pump and the fs probe, and the frequency resolution in the FSRS spectra taken at the time delay T . Since the two are not Fourier transform pairs, the issue of circumventing the Heisenberg uncertainty principle does not arise.

This seeming paradox had been discussed by Domcke *et al.* in 1992 for the traditional pump-probe spectroscopy with ultrashort pulsed lasers [75], and Mukamel *et al.* have recently reanalyzed this issue in the context of FSRS [76]. In integrated measurement, observed spectrum is generated during the probe-matter interaction time, and the spectrum possesses a high temporal resolution, which is given by the duration of ultrashort probe pulse. Spectral resolution of integrated spectrum is bad, because it is Fourier transform

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limited with respect to probe pulse duration. In contrast, the duration of dispersed spectrum measurement is determined by the decay time of probe pulse induced polarization, which is not correlated with the pump-probe delay time, and simultaneous high temporal and spectral resolutions are achievable. However, a dispersed spectrum does not represent a true ‘real-time’ measurement, as the spectrum is not generated at the duration of the probe, but at the polarization decay time, which is usually much longer than the probe pulse. The simultaneous high temporal and spectral resolutions of time-resolved FSRS can be understood in an analogue to pump-probe spectroscopy with the combination of the Raman pump and the probe as probing method.

Consider the idea behind the time and frequency resolved FSRS shown in Fig. 1.1, but illustrated with two-dimensional potential energy surfaces with a large amplitude reaction coordinate in one dimension and an oscillator in the other dimension with frequencies that change from ω_i in the reactant region to ω_f in the product region, as shown in Figs. 2.5 and 2.6, and this could represent a photoisomerization reaction. The wave packet picture for the third-order polarization of the SRS(I) and IRS(I) processes, described by Eqns. (2.41) and (2.43), are shown in Figs. 2.5 (a) and (b), respectively. Similarly, the SRS(II) and IRS(II) processes, described by Eqns. (2.42) and (2.44), are shown in Figs. 2.6 (a) and (b), respectively. In both sets of figures, the actinic pump is assumed to be temporally separated from the subsequent ps Raman pump and fs probe pulses for FSRS to monitor the evolving wave packet on the e_1 surface. The actinic pump pulse, $E_{ac}(t)$, almost instantaneously prepares ket (red) and bra (grey) wave packets, from the ground vibrational state of e_0 , on the excited electronic state e_1 surface, which are denoted as $|\psi_1^{(0)}(0)\rangle$ and $\langle\psi_1^{(0)}(0)|$, respectively. The ket and bra wave packets evolve along the reaction coordinate on the e_1 surface as $|\psi_1^{(0)}(t)\rangle$ and $\langle\psi_1^{(0)}(t)|$, respectively.

In SRS(I), Fig. 2.5 (a), the evolving bra at time t_3 , $\langle\psi_1^{(0)}(t_3)|$, is acted on by the Raman pump pulse $E_{pu}^*(t_3)$ which sends it to the excited electronic state e_2 , creating a piece of the wave packet $\langle\psi_2^{(1)}(t_3)|$ there. It then evolves on the e_2 surface till time t_2 , within range of the fs probe pulse which is delayed from the actinic pump by a time T , as $\langle\psi_2^{(1)}(t_2)|$. If the pump pulse is off-resonant with e_2 , which is a typical FSRS arrangement, then the evolving $\langle\psi_2^{(1)}(t_3 \rightarrow t_2)|$ resembles $\langle\psi_1^{(0)}(t_3 \rightarrow t_2)|$ [77]. The fs probe pulse then almost instantaneously images $\langle\psi_2^{(1)}(t_2)|$ down to the e_1 surface which then evolves as $\langle\psi_1^{(2)}(t_2 \rightarrow t)|$. In the meantime, the Raman pump pulse, $E_{pu}(t_1)$, sends pieces of the ket, $|\psi_1^{(0)}(t_1)\rangle$, up to the e_2 surface, and it evolves as $|\psi_2^{(1)}(t_1 \rightarrow t)\rangle$. The third-order polarization $P_{\text{SRS(I)}}^{(3)}(t; T)$ is

Figure 2.5: Wave packet picture for (a) SRS(I) and (b) IRS(I).

Figure 2.6: Wave packet picture for (a) SRS(II) and (b) IRS(II).

given by the overlap of the bra on e_1 , $\langle \psi_1^{(2)}(t) |$, and the ket on e_2 , $|\psi_2^{(1)}(t)\rangle$. Since $\langle \psi_1^{(2)}(t) |$ exists only after the probe pulse acts on the molecule, it follows that $P_{\text{SRS(I)}}^{(3)}(t)$ begins only when there is coupling between the Raman pump and probe pulses acting simultaneously on the molecule, i.e. from around the delay time T onwards. The time-dependent $P_{\text{SRS(I)}}^{(3)}(t; T)$ and its frequency-dependent $P_{\text{SRS(I)}}^{(3)}(\omega; T)$ which contributes to the FSRS signal are Fourier-transform pairs, Eqn. (5.37), governed by the Heisenberg uncertainty principle. Clearly, $P_{\text{SRS(I)}}^{(3)}(t; T)$ has a duration at most half as long as the ps Raman pump pulse since the fs probe pulse acts about mid-way through the Raman pump pulse. It could be further shortened by the decay time of the vibrational coherence on e_1 as present in $\langle \psi_1^{(2)}(t_2 \rightarrow t) |$, the change in the frequency of the oscillator with time, and inhomogeneous broadening from the environment, giving rise to possibly sharp spectral lines that is not narrower than the Raman pump bandwidth. When there is high frequency resolution in $P_{\text{SRS(I)}}^{(3)}(\omega; T)$, it means that $P_{\text{SRS(I)}}^{(3)}(t; T)$ has one or more recurrences in the wave packet overlap, consistent with the Heisenberg uncertainty principle, which in turn means that the wave packet $|\psi_1^{(0)}(t)\rangle$ has sampled a fair portion of the e_1 surface in time, and one can say that there is poor time resolution on the wave packet.

However, the delay time T between the fs actinic pump and fs probe pulse can be rather well defined, i.e. with high time resolution, and we can take SRS(I) spectra as a function of the delay time T , given by $P_{\text{SRS(I)}}^{(3)}(\omega; T)$. The delay time T affects the amplitude and phase of $P_{\text{SRS(I)}}^{(3)}(t; T)$, especially at early times t when the fs probe pulse interacts, and this affects the SRS(I) line shape given by $P_{\text{SRS(I)}}^{(3)}(\omega; T)$. If instead of a large amplitude reaction coordinate, we had a harmonic oscillator of similar frequency as the other oscillator, then one can see periodicity in $P_{\text{SRS(I)}}^{(3)}(t; T)$ as a function of the delay time T , and hence a similar periodicity in the SRS(I) signal $P_{\text{SRS(I)}}^{(3)}(\omega; T)$ and line shapes, like that of the moving wave packet on e_1 . However, having high time resolution in the delay time T is not the same as attaining high time resolution on the moving wave packet $|\psi_1^{(0)}(t)\rangle$ on the e_1 surface in the sense of being able to take snapshots of the evolving wave packet. Hence, one can say that the SRS(I) process affords high time resolution in the delay time T between the fs actinic pump and the fs probe pulse, and high frequency resolution (with lines as narrow as the ps Raman pump bandwidth) in the SRS(I) spectrum at each delay time T , but the latter gives the impression that there is poor time resolution on the moving wave packet in the e_1 electronic state being investigated. However, we show in Chapter 5 that the third-order time-dependent polarization, which can be recovered by an inverse Fourier transform of the

FSRS spectrum, contains information about the time dependent frequency of the reporter modes sampled by the moving wave packet.

A similar picture emerges from the IRS(I) process in Fig. 2.5 (b). Here, the fs probe, $E_{pr}(t_3)$, and the ps Raman pump, $E_{pu}^*(t_2)$ creates an instantaneous ket on the e_1 surface which then evolves as $|\psi_1^{(2)}(t_2 \rightarrow t_1)\rangle$ before being acted on by the Raman pump pulse, $E_{pu}(t_1)$. A third-order ket wave packet is created on e_2 which evolves as $|\psi_2^{(3)}(t_1 \rightarrow t)\rangle$. The third-order polarization $P_{IRS(I)}^{(3)}(t; T)$ is given by the overlap of the zeroth-order bra on e_1 , $\langle\psi_1^{(0)}(t)|$, and the third-order ket on e_2 , $|\psi_2^{(3)}(t)\rangle$. Similar to the SRS(I) process, $P_{IRS(I)}^{(3)}(t; T)$ lasts at most half as long as the ps Raman pump pulse, and its Fourier transform $P_{IRS(I)}^{(3)}(\omega; T)$ gives rise to possibly sharp spectral lines that is not narrower than the Raman pump bandwidth.

A different picture emerges from the SRS(II) and IRS(II) processes shown in Fig. 2.6. In SRS(II), Fig. 2.6 (a), the off-resonant fs probe pulse, $E_{pr}(t_1)$, almost instantaneously images the zeroth-order ket $|\psi_1^{(0)}(t_1)\rangle$ onto the electronic state e_2 to give a short-lived wave packet which evolves as $|\psi_2^{(1)}(t_1 \rightarrow t)\rangle$. The third-order polarization $P_{SRS(II)}^{(3)}(t; T)$ is given by the overlap of the bra, $\langle\psi_1^{(2)}(t)|$, prepared earlier by the two pump field interactions, and the short-lived ket $|\psi_2^{(1)}(t_1 \rightarrow t)\rangle$. So, $P_{SRS(II)}^{(3)}(t; T)$, is as short-lived as the fs probe pulse and so it gives rise to a broad SRS(II) spectrum, $P_{SRS(II)}^{(3)}(\omega; T)$. Here, one has high time resolution in the time delay T , and also high time resolution in capturing the moving wave packet $|\psi_1^{(0)}(t)\rangle$ on the e_1 surface, but it leads to a broad, low resolution spectrum $P_{SRS(II)}^{(3)}(\omega; T)$. The same conclusion is reached for the IRS(II) process in Fig. 2.6 (b). The third-order polarization $P_{IRS(II)}^{(3)}(t; T)$ is again as short-lived as the fs probe pulse, has high time-resolution in capturing the moving wave packet $|\psi_1^{(2)}(t)\rangle$, but gives rise to a broad spectrum $P_{IRS(II)}^{(3)}(\omega; T)$.

The FSRS spectrum is the sum of the SRS(I), IRS(I), SRS(II) and IRS(II) processes. The SRS(I) spectrum can give sharp lines on the Stokes side relative to the Raman pump frequency; the IRS(I) spectrum can give sharp lines on the anti-Stokes side; and both the SRS(II) and IRS(II) spectra give a broad baseline.

2.2 Numerical Methods

Numerical simulation nowadays has become the third approach in scientific research realm besides experimental and theoretical means, and by using a computer it can represent and emulate a physical system or process which is either too expensive to carry out an

experiment or too complex to theoretically arrive at an analytic expression. Particularly in femto-chemistry and quantum dynamics, experimental results normally require numerical calculations for a better understanding and interpretation.

In this thesis, we used various numerical methods to solve the time-dependent Schrödinger equation for nuclear dynamics, which is a linear first-order ordinary differential equation. The procedure usually includes following steps,

- (1) A proper coordinate system is chosen to conveniently describe the problem.
- (2) Available *ab initio* or model potential energy surface is provided.
- (3) Adequate and efficient bases for each dimension are appropriately chosen to represent system Hamiltonian, wave functions and other analysis operators. Bases are always optimally chosen to possess the same symmetry properties and boundary conditions as the problem itself.
- (4) Appropriate initial wave functions in a variety of specific quantum states are prepared.
- (5) Approximate propagation methods with given accuracy are used to track the evolution of wave functions under the influence of system Hamiltonian.
- (6) Analysis operators are applied to extract desired information contained in the wave functions.

2.2.1 Gaussian quadrature

Numerical quadrature is the numerical approximation of definite integrals, replacing the integral by a weighted sum of integrand values at finite discrete points,

$$\int_a^b f(x)dx = \sum_{\alpha=1}^N \omega_{\alpha} f(x_{\alpha}). \quad (2.53)$$

where ω_{α} 's are weights and x_{α} 's are quadrature points. Newton-Cotes quadrature is the simplest quadrature rule, with equally spaced quadrature points and properly evaluated weights. Among all the quadrature rules, Gaussian quadrature has the highest numerical accuracy for a fix number of nodes, in which both the weights and quadrature points are optimally chosen to make the quadrature rule accurate for polynomials with degrees no larger than $2N - 1$. In principle, weights and quadrature points can be calculated by solving a system of $2N$ nonlinear equations, each of which is the equality between quadrature and integral results of all the polynomials with degrees from zero to $2N - 1$. However such equations are not straightforward to solve due to its nonlinear nature, and alternatively

classical orthogonal polynomials are used to determine quadrature points as the zeros of the corresponding orthogonal polynomial with degree of N . Then weights are determined by solving a system of N linear equations straightforwardly [78].

In a numerical calculation, Gaussian quadrature weights and points are usually tabulated in advance with various orders and types, and they are stored in a specific subroutine, which can be called when needed, without computing or knowing about the actual values. Some of the Gaussian quadrature rules are tabulated in [79]. If no tabulated values are available, there is an efficient way to compute Gaussian quadrature weights and points by solving the coordinate matrix eigenvalue problem in classical orthogonal polynomial basis. Gaussian quadrature points can be shown as the zeros of polynomial P_N by using the three-term recursion relations of classical orthogonal polynomials,

$$P_j(x) = (a_j x + b_j)P_{j-1}(x) - c_j P_{j-2}(x), \quad j = 1, 2, \dots, N \quad (2.54)$$

and all the relations can be written as

$$x \begin{bmatrix} P_0(x) \\ P_1(x) \\ \vdots \\ P_{N-1}(x) \end{bmatrix} = \begin{bmatrix} -b_1/a_1 & 1/a_1 & & \\ c_2/a_2 & -b_2/a_2 & \ddots & \\ & \ddots & \ddots & 1/a_{N-1} \\ & & c_N/a_N & -b_n/a_n \end{bmatrix} \begin{bmatrix} P_0(x) \\ P_1(x) \\ \vdots \\ P_{N-1}(x) \end{bmatrix} + \begin{bmatrix} 0 \\ \vdots \\ 0 \\ P_N(x)/a_N \end{bmatrix} \quad (2.55)$$

In matrix form,

$$x\mathbf{P}(x) = \mathbf{T}\mathbf{P}(x) + (1/a_N)P_N(x)\mathbf{e}_N \quad (2.56)$$

where $\mathbf{T}$ is the tridiagonal matrix, $\mathbf{P}(x) = [P_0(x), P_1(x), \dots, P_{N-1}(x)]^T$ and $\mathbf{e}_N = [0, 0, \dots, 0, 1]^T$.

For classical orthogonal polynomials, matrix $\mathbf{T}$ is symmetric or can be transformed to symmetric form by diagonal similarity transformation. It is clear that if $P_N(x_\alpha) = 0$, x_α 's will be the eigenvalues of $\mathbf{T}$, $x_\alpha \mathbf{P}(x_\alpha) = \mathbf{T}\mathbf{P}(x_\alpha)$. This is the relation between Gaussian quadrature and coordinate matrix diagonalization, and it was independently discovered by Dickinson *et al.* [80] in 1968 and Golub *et al.* [81] in 1969.

Gaussian quadrature rules are derived only for some specific intervals, and thus any general quadrature on intervals $[a, b]$ must be transformed to the standard interval $[u, v]$. Following is one of the simple linear transformation,

$$t = \frac{(b-a)x + av - bu}{v-u} \quad (2.57)$$

which preserves the degree of the quadrature rule. Then the integral on the interval $[a, b]$ can be evaluated,

$$\begin{aligned}\int_a^b f(t)dt &= \frac{b-a}{v-u} \int_u^v f\left(\frac{(b-a)x + av - bu}{v-u}\right)dx \\ &\approx \frac{b-a}{v-u} \sum_{\alpha=1}^N \omega_{\alpha} f\left(\frac{(b-a)x_{\alpha} + av - bu}{v-u}\right)\end{aligned}\quad (2.58)$$

2.2.2 Representations

Wave functions and the operators can be described in different representations. For example, in coordinate space, $|\psi(\mathbf{r})\rangle$ denotes the probability amplitude to find a quantum particle at position $\mathbf{r}$, and in momentum space, $|\psi(\mathbf{p})\rangle$ denotes the probability amplitude to find a quantum particle with momentum $\mathbf{p}$, and in energy space, $|\psi(E)\rangle$ denotes the probability amplitude to find the particle with an energy of E . In the first two spaces, the coordinate and momentum of the particle are continuous, however if the particle is trapped in a potential well, the allowed energy of the particle is then a discrete series of numbers $E_0, E_1, E_2, \text{etc.}$ $|\psi(\mathbf{r})\rangle$, $|\psi(\mathbf{p})\rangle$ and $|\psi(E)\rangle$ describe the same quantum state and they are equivalent to each other. It is the representations where they are defined that are different, i.e. coordinate representation, momentum representation and energy representation, respectively.

In a representation, bases are used to describe wave functions and operators. Usually a set of basis $|\phi_i\rangle$'s are chosen to be the normalized eigenvectors of a certain operator A . Hilbert space is of infinite dimension, but in numerical calculation basis are truncated at a finite dimension to make a reduced Hilbert space, in which wave functions and operators can be evaluated to be vectors and matrices.

Nowadays DVR has become the most prevalent and highly accurate representation for its intuitive and simple characters: wave functions and potential energy operators are represented by their values at a set of grid points, and kinetic energy operators are first easily evaluated in FBR and transformed to DVR by DVR-FBR transformation matrix. DVR is shown to be equivalent to FBR with an unitary transformation. Potential energy operators in DVR and FBR are approximated to the accurate ones of VBR in a reduced Hilbert space, but kinetic energy operators are all evaluated exactly in the three representations.

2.2.2.1 Variational Basis Representation (VBR)

For a one-dimensional problem, orthonormalized $|\phi_i\rangle_{i=1}^{\infty}$ are chosen as a complete square-integrable basis set. In a numerical implementation, this infinite basis set is truncated by the projector operator,

$$\hat{P} = \sum_{i=1}^N |\phi_i\rangle\langle\phi_i|, \quad (2.59)$$

to be $|\phi_i\rangle_{i=1}^N$ as the reduced Hilbert space. This truncation results in the first source of numerical error.

The elements of the $N \times N$ matrix of first and second derivative operators $\mathbf{D}^{(1)}$ and $\mathbf{D}^{(2)}$ are supposed to have analytical expressions,

$$D_{jk}^{(1)} = \langle\phi_j|d/dx|\phi_k\rangle \quad (2.60)$$

$$D_{jk}^{(2)} = \langle\phi_j|d^2/dx^2|\phi_k\rangle \quad (2.61)$$

This is always guaranteed by properly choosing classical orthogonal polynomials according to the form of kinetic energy operator. Using these two derivative relation of the orthogonal basis functions, truncated kinetic energy operator T_N can be calculated exactly. In some other cases, the orthonormalized basis $|\phi_i\rangle_{i=1}^N$ are chosen to be eigenfunctions of a model Hamiltonian $H_0 = T + V_0$, and H_0 matrix is diagonal in this basis.

The elements of the $N \times N$ matrix of coordinate operator $\mathbf{Q}$ also possess analytic expression for classical orthogonal polynomials, as stated by the three-term recursion relations.

$$Q_{jk} = \langle\phi_j|\hat{x}|\phi_k\rangle \quad (2.62)$$

Evaluation of (residual) potential energy matrix,

$$V_{jk}^{VBR} = \langle\phi_j|\hat{V}|\phi_k\rangle, \quad (2.63)$$

is performed by exact numerical integration and is in general non-trivial. This is the variational basis representation (VBR). The name VBR is designated to note the fact that eigenvalues obtained by N function representation of H matrix are the variational upper bounds to the true eigenvalues of H [82].

2.2.2.2 Finite Basis Representation (FBR)

In Finite Basis Representation (FBR), evaluation of potential energy matrix is simplified and it is approximated by either Gaussian quadrature obtained by basis functions,

$$V_{jk}^{FBR} = \sum_{\alpha} \omega_{\alpha} \phi_j^*(x_{\alpha}) V(x_{\alpha}) \phi_k(x_{\alpha}) \quad (2.64)$$

or by a function of matrix representation of the coordinate operator $\mathbf{Q}$ [83],

$$\mathbf{V}^{FBR} = V(\mathbf{Q}). \quad (2.65)$$

The former is named as quadrature FBR and the latter product FBR. In cases where no Gaussian quadrature is available for the basis functions used, such as eigenfunctions of a model Hamiltonian, only product FBR can be used to evaluate potential matrix in FBR. If classical orthogonal polynomials are used as basis functions, the two FBR are identical. The second source of numerical error is introduced by simplifying the evaluation of potential energy matrix in the above methods, and they are named as quadrature error and product approximation error, respectively.

V^{FBR} would be the same as V^{VBR} if the basis set chosen were complete (no truncation were used). Quadrature error is from the limited Gaussian quadrature accuracy with degree no larger than $2N - 1$, and product approximation error can be disclosed by evaluating matrix element of $V = x^2$,

$$[V(\mathbf{Q})]_{ij} = [\mathbf{Q}\mathbf{Q}]_{ij} = \sum_{n=1}^{\infty} Q_{in} Q_{nj} \quad (2.66)$$

and note that summation is from one to infinite.

2.2.2.3 Discrete Variable Representation (DVR)

Evaluation of potential energy matrix in FBR is not yet the most efficient method. Discrete Variable Representation (DVR) greatly simplifies the evaluation of potential energy matrix by the value of potential at DVR points and no integral or quadrature are required. This was first introduced by Harris *et al.* [84] in the calculation of potential energy matrix elements with transformation theory.

For classical orthogonal polynomial bases, the associated Gaussian quadrature rules provide quadrature points (x_{α}) and weights ω_{α} . The orthonormality relations of classical

orthogonal polynomials $P_i(x)$ with weight function $\omega(x)$ are

$$\begin{aligned}\delta_{ij} &= \int_a^b \omega(x) P_i(x) P_j(x) dx \\ &= \sum_{\alpha=1}^N \omega_{\alpha} P_i(x_{\alpha}) P_j(x_{\alpha})\end{aligned}\tag{2.67}$$

if a new basis $\phi_i(x)$ is defined with the relation to $P_i(x)$ as

$$\phi_i(x) = \sqrt{\omega(x)} P_i(x)\tag{2.68}$$

this orthonormality relations are now in the form

$$\begin{aligned}\delta_{ij} &= \int_a^b \phi_i^*(x) \phi_j(x) dx \\ &= \sum_{\alpha=1}^N \frac{\omega_{\alpha}}{\omega(x_{\alpha})} \phi_i^*(x_{\alpha}) \phi_j(x_{\alpha})\end{aligned}\tag{2.69}$$

and the matrix elements of coordinate operator $\hat{x}$ are given by

$$\begin{aligned}Q_{jk} &= \int_a^b \phi_i^*(x) x \phi_j(x) dx \\ &= \sum_{\alpha=1}^N \frac{\omega_{\alpha}}{\omega(x_{\alpha})} \phi_i^*(x_{\alpha}) x_{\alpha} \phi_j(x_{\alpha})\end{aligned}\tag{2.70}$$

As Gaussian quadrature is exact for degree no larger than $2N - 1$ and basis functions $\phi_i(x)$'s contain powers of x only from 0 to $N - 1$, both orthonormality relation and $\mathbf{Q}$ matrix are exactly evaluated.

If one defines a matrix $\mathbf{U}$ with its elements as

$$U_{\alpha i} = \sqrt{\frac{\omega_{\alpha}}{\omega(x_{\alpha})}} \phi_i(x_{\alpha}),\tag{2.71}$$

above two relation can be written in matrix form as

$$\mathbf{I} = \mathbf{U}^{\dagger} \mathbf{U}\tag{2.72}$$

$$\mathbf{Q} = \mathbf{U}^{\dagger} \mathbf{X}^{DVR} \mathbf{U}\tag{2.73}$$

where $\mathbf{X}^{DVR}$ is the diagonal matrix of $\hat{x}$ operator in DVR with the diagonal elements as the quadrature points. These points are named as DVR points in DVR. From Eqn. (2.73), $\mathbf{U}$ is actually the transformation matrix between DVR and FBR.

Using unitary property of $\mathbf{U}$ matrix (shown in Eqn. (2.72)), we multiply $\mathbf{U}$ from left and $\mathbf{U}^\dagger$ from right on both sides of Eqn. (2.73),

$$\mathbf{U}\mathbf{Q}\mathbf{U}^\dagger = \mathbf{X}^{DVR} \quad (2.74)$$

which means that matrix $\mathbf{U}^\dagger$ diagonalizes the coordinate matrix $\mathbf{Q}$.

Eqns. (2.71) and (2.74) reveal two methods to generate transformation matrix between DVR and FBR. First, it can be generated from the evaluation of classical orthogonal polynomials at quadrature points via Eqn. (2.71). The other method is to diagonalize coordinate matrix. Gaussian quadrature points are the eigenvalues, and transformation matrix is related to eigenvectors. The second method is often preferred for its simplicity that no explicit quadrature points and weights are required. Furthermore, for a general basis, such as eigenfunctions of a model Hamiltonian (Potential Optimized DVR), no Gaussian quadrature (points and weights) is available and only the diagonalization method can generate transformation matrix between DVR and FBR, following the procedure provided by Harris *et al.* [84]

Basis functions $\theta_\alpha(x)$ in DVR can be generated from Eqn. (2.74) by multiplying transforming matrix $\mathbf{U}^\dagger$ on $\phi_i(x)$ from right side,

$$\theta_\alpha(x) = \sum_i^N U_{\alpha i}^* \phi_i(x). \quad (2.75)$$

Thus obtained DVR basis functions $\theta_\alpha(x)$'s localize at DVR points x_α 's, with a nonzero value at the corresponding DVR point but a null value at the other DVR points. With such property of DVR basis functions, wave function is not represented by its overlaps with basis functions, but rather simply by its values on DVR points. This feature makes DVR a pointwise representation.

In DVR, potential energy matrix now can be evaluated as

$$V_{\alpha\beta}^{DVR} = \langle \theta_\alpha | \hat{V} | \theta_\beta \rangle = V(x_\alpha) \delta_{\alpha\beta}. \quad (2.76)$$

The last equality is from the delta-function property of DVR basis functions. By noting $\mathbf{X}^{DVR}$ is diagonal, above potential energy matrix can be written as

$$\mathbf{V}^{DVR} = \mathbf{V}(\mathbf{X}^{DVR}) \quad (2.77)$$

If above equation is transformed to FBR by $\mathbf{U}$ matrix, it can be shown that quadrature FBR and product approximation FBR are the same for classical orthogonal polynomial basis.

The most significant advantage of DVR among all its virtues is the ease of Hamiltonian matrix calculation by avoiding integral evaluation. Kinetic energy matrix $\mathbf{T}^{DVR}$ in DVR is non-diagonal and is always first calculated in FBR as $\mathbf{T}^{FBR}$ and then transformed to DVR by transform matrix $\mathbf{U}$,

$$\mathbf{T}^{DVR} = \mathbf{U}\mathbf{T}^{FBR}\mathbf{U}^\dagger \quad (2.78)$$

If $\mathbf{T}^{DVR}$ is evaluated in such a manner, no explicit reference to the underlying basis set is required in following wave function propagation step [85].

$$\mathbf{H}^{DVR} = \mathbf{T}^{DVR} + \mathbf{V}^{DVR} = \mathbf{U}\mathbf{T}^{FBR}\mathbf{U}^\dagger + \mathbf{V}^{DVR} \quad (2.79)$$

DVR is especially useful in a multidimensional problem. Preparation of full Hamiltonian matrix can be avoided if an appropriate orthogonal coordinate system is chosen for Hamiltonian operator. Potential energy matrix is always diagonal in DVR, and kinetic energy matrix can be separately evaluated from the one-dimensional kinetic energy terms for each dimension. This will result in a very sparse Hamiltonian, which can save much computational time and storage.

2.2.3 Propagation method

One possible way to solve the TDSE is to evaluate the unitary propagator $U(t, t_0)$ in the H eigenfunction basis, where $U(t, t_0)$ can be evaluated just like a function of scalar (eigenvalues of H). However, solving the eigenvalue problem of Hamiltonian matrix is not only non-trivial but also expensive. It requires both constructing and diagonalizing the full Hamiltonian matrix, and the latter scales as N^3 . The limitation of this method has already come to the surface from a polyatomic problem with only four atoms, where the full Hamiltonian matrix is difficult to fit in the memory of one or more moderate computers and the scaling rule of N^3 demands a formidable computational time. In addition, the computation of all eigenfunctions and eigenvalues of a Hamiltonian is not necessary, and it is considered as a waste of time, as normally only a certain eigenvalues within a predefined range are needed. Nevertheless, iterative diagonalization [86, 87, 88] has been brought forward to work in this direction.

TD method possesses many advantages over the TI one. In TD method, an initially chosen wave packet is propagated under the operation of system Hamiltonian by the unitary propagator $U(t, t_0) = e^{-\frac{i}{\hbar}H(t-t_0)}$. Normally, the propagator $U(t, t_0)$ is approximated by various schemes [89, 90, 91], including split operator (SO) method [92, 93, 94], Chebyshev polynomial (CHP) expansion [95], Faber polynomial (FP) expansion [96, 97], short iterative Lanczos (SIL) propagation method [98], Crank-Nicholson (CN) second-order differencing [99, 100, 101], symplectic (SY) method [102, 103] and Multi-Configuration Time-Dependent Hartree (MCTDH) Method [104, 105, 106, 107, 108]. To propagate a wave packet with a TD Hamiltonian $H(t)$, it requires using those short time propagation methods, SO, SIL, CN, SY or MCTDH, in which the total time period $t - t_0$ is divided into small time intervals $\Delta t = (t - t_0)/N$ and the Hamiltonian over each small time interval is assumed to have effectively no variation, and then the propagator can be described as product of short time propagators,

$$U(t, t_0) = \prod_{n=1}^N e^{-\frac{i}{\hbar}H(n\Delta t+t_0)\Delta t} \quad (2.80)$$

It should be noted here that this discrete product is an approximate method, and it is accurate only if the time interval is chosen small enough.

One of the most commonly used propagation methods will be briefly described in the following parts. SO method is one of the simplest propagation methods and it requires the separation of kinetic and potential energy parts in the Hamiltonian.

2.2.3.1 Split Operator method

Split operator (SO) method [92] gains the popularity for its simplicity, robustness and flexibility in treating TD or TI Hamiltonian system. Due to its unitary nature, SO method is stable and always conserves the norm of wave packet, regardless the size of time interval used to propagate the wave packet. SO method is efficient and no extra storage of the whole wave packet is needed during propagation, especially when DVR is used and kinetic energy operator is sparse.

The strategy of SO method is to separately propagate the kinetic and potential energy parts in the representations where they are in the diagonal forms. The simplest SO method is the second-order one, which can be expressed in a symmetric form to acquire accuracy of second order,

$$S_2(\Delta t) = e^{-i\hat{T}\Delta t/(2\hbar)} e^{-i\hat{V}\Delta t/\hbar} e^{-i\hat{T}\Delta t/(2\hbar)} + O(\Delta t^3) \quad (2.81)$$

or

$$S_2(\Delta t) = e^{-i\hat{V}\Delta t/(2\hbar)} e^{-i\hat{T}\Delta t/\hbar} e^{-i\hat{V}\Delta t/(2\hbar)} + O(\Delta t^3) \quad (2.82)$$

where $\hat{T}$ and $\hat{V}$ are kinetic and potential energy operators, respectively. The leading error $O(\Delta t^3)$ of second-order SO method is proportional to $[T, V]$, which can be shown by comparing Taylor expansion series of $S_2(\Delta t)$ and $e^{-i(\hat{T}+\hat{V})\Delta t/\hbar}$. Operators like $e^{-i\hat{V}\Delta t/\hbar}$ are easily calculated in DVR by direct multiplication, and operator like $e^{-i\hat{T}\Delta t/\hbar}$ are calculated by $Ze^{-i\hat{T}\Delta t/\hbar}Z^\dagger$, in the procedure that the wave packet is first transformed to the representation where kinetic energy operator is diagonal and then transformed back to DVR after the multiplication of $e^{-i\hat{T}\Delta t/\hbar}$. Normally, if Fourier, sine or cosine basis is used, a fast algorithm is available to efficiently transform between DVR and FBR [109, 110, 111]. For some other bases, $Ze^{-i\hat{T}\Delta t/\hbar}Z^\dagger$ can be multiplied together in advance and only one matrix-vector operation is needed during propagation.

There are also higher-order SO method with higher accuracy [93], but the formula would become a bit complex. Normally second-order SO method is sufficient for most of the problems, as converged results with predefined accuracy can always be obtained by continuously reducing time intervals. However, when treating problems that require long propagation time, such as long life-time resonance states in reactive scattering, accumulated error in each time interval would introduce abnormal signals in the final results. In such case, it would not be a wise decision to reduce the time interval further to arrive at a converged result, because the total number of time intervals would be too large and it would cost too much time. Alternatively, higher-order SO method with higher accuracy would be the candidate to treat such problems, and Sun *et al.* have recently intensively discussed higher-order SO method in reactive scattering problems [94].

2.2.4 Numerical method for the evaluation of third-order polarization

Third-order polarization in Eqns. (2.41)-(2.44) are calculated by the overlaps of bra and ket sides wave packets, which can be obtained by first-order perturbation theory order by order. For $P_{\text{SRSI}}^{(3)}(t)$, the first-order wave packet $|\psi_2^{(1)}(t)\rangle$ on ket side is rewritten to be,

$$|\psi_2^{(1)}(t)\rangle = \frac{i}{\hbar} \int_0^t dt_1 E_{pu}(t_1) e^{-ih_2(t-t_1)/\hbar} \mu_{21} e^{-ih_1 t_1/\hbar} |\psi_1(0)\rangle \quad (2.83)$$

where the coordinate dependence of the wave packet is suppressed, and damping factor is omitted here and will be treated later. If the total period of t is broken into N small time

intervals $\Delta t = t/N$ and let $t_n = n\Delta t$, the first-order wave packet can be written as a sum of all the integral in the interval Δt ,

$$\begin{aligned} |\psi_2^{(1)}(t)\rangle &= \frac{i}{\hbar} \sum_{n=0}^{N-1} \int_{t_n}^{t_n+\Delta t} dt_1 E_{pu}(t_1) e^{-ih_2(t-t_1)/\hbar} \mu_{21} e^{-ih_1 t_1/\hbar} |\psi_1(0)\rangle \\ &\approx \frac{i\Delta t}{\hbar} \sum_{n=0}^{N-1} e^{-ih_2(t-t_n-\Delta t/2)/\hbar} E_{pu}(t_n + \Delta t/2) \mu_{21} |\psi_1(t_n + \Delta t/2)\rangle \end{aligned} \quad (2.84)$$

where the integral within each time interval is replaced by the simplest mid-point rule, which is of first-order accuracy. Iteratively, the first-order wave packet at each time grid can be solved as

$$\begin{aligned} |\psi_2^{(1)}(t_n + \Delta t)\rangle &= e^{-ih_2(\Delta t)/\hbar} |\psi_2^{(1)}(t_n)\rangle \\ &\quad + \frac{i\Delta t}{\hbar} e^{-ih_2(\Delta t/2)/\hbar} E_{pu}(t_n + \Delta t/2) \mu_{21} |\psi_1(t_n + \Delta t/2)\rangle \end{aligned} \quad (2.85)$$

For the sake of computation efficiency, the evaluation of integrant at the end of the interval, rather than the middle is used,

$$\begin{aligned} |\psi_2^{(1)}(t_n + \Delta t)\rangle &= e^{-ih_2(\Delta t)/\hbar} |\psi_2^{(1)}(t_n)\rangle \\ &\quad + \frac{i\Delta t}{\hbar} E_{pu}(t_n + \Delta t) \mu_{21} |\psi_1(t_n + \Delta t)\rangle \end{aligned} \quad (2.86)$$

The damping factor is omitted in writing Eqn. (2.83), and it can be easily considered. As the damping factor always comes with the Hamiltonian, one can add in the damping effect by simply multiplying $e^{-\frac{\gamma_i}{2}\Delta t}$ with the propagated wave packet after it is propagated.

From Eqn. (2.18), it can be seen that the second-order wave packet $\langle\psi_1^{(2)}(t)|$ on the bra side can also be obtained by first-order perturbation theory from the first-order wave packet $\langle\psi_2^{(1)}(t)|$ on the bra side. First $\langle\psi_2^{(1)}(t)|$ can be obtained exactly the same as $|\psi_2^{(1)}(t)\rangle$, and then $\langle\psi_1^{(2)}(t)|$ can iteratively solved to be,

$$\begin{aligned} \langle\psi_1^{(2)}(t_n + \Delta t)| &= e^{ih_2(\Delta t)/\hbar} \langle\psi_1^{(2)}(t_n)| \\ &\quad + \frac{i\Delta t}{\hbar} E_{pr}(t_n + \Delta t) \mu_{12} \langle\psi_2^{(1)}(t_n + \Delta t)| \end{aligned} \quad (2.87)$$

After having obtained the wave packets on both ket and bra sides, $P_{\text{SRSI}}^{(3)}(t_n)$ can be easily

evaluated to be

$$P_{\text{SRSI}}^{(3)}(t_n) = \langle \psi_1^{(2)}(t_n) | \mu_{12}^* | \psi_2^{(1)}(t_n) \rangle \quad (2.88)$$

Similarly, the other three terms can be evaluated.

Analysis of Femtosecond Stimulated Raman Spectroscopy of Excited-State Evolution in Bacteriorhodopsin¹

3.1 Introduction

The photophysics and photochemistry of retinal proteins, which are important photosynthetic systems, have been studied extensively in a quest to understand the molecular mechanism by which visible light is initially stored with accompanying structural changes in the retinal chromophore and how this energy is used by the protein for a specific function while returning the retinal chromophore to its original state [44, 112, 113, 114, 115]. Bacteriorhodopsin (BR), for example, is a protein found in the purple membrane of *Halobacterium salinarum*, which functions as a light activated proton pump. Upon absorption of a visible photon, the all-trans retinal chromophore in BR is instantaneously excited to BR* in the Franck-Condon region, often labelled as H, and in ~ 200 fs the excited state wave packet moves to an intermediate I₄₆₀, then to a J₆₂₅ intermediate in ~ 500 fs, and subsequently to the fully isomerized 13-cis retinal K₆₁₀ product in ~ 3 ps (Figure 5.1) [44, 113]. Further changes in the μ s and ms time regime then lead to a transport of a proton out of the cell and the regeneration of all-trans retinal [116]. The ultrafast primary events in the temporal and structural changes in BR upon light absorption have to be studied with femtosecond transient electronic and vibrational spectroscopies.

Femtosecond stimulated Raman spectroscopy (FSRS) with femtosecond time resolution

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Figure 3.1: Schematic diagram of the photoisomerization process of bacteriorhodopsin (BR) and the FSRS experiment. An ultrashort actinic pump pulse prepares a wave packet on BR*, and as the wave packet moves from the Franck-Condon region to other parts of the excited state surface and finally to the isomerized K product it is investigated with a pair of ps Raman pump and fs probe pulses.

and high vibrational spectral resolution has been developed to study time-resolved structural changes in ultrafast photophysical and photochemical processes [32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42]. In the time-resolved experiments, three pulses are used: A <50 fs actinic pump pulse to excite the molecule to an upper electronic state, followed by stimulated Raman spectroscopy with an overlapping pair of ps Raman pump pulse and a ~ 15 fs continuum probe pulse. 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 to the ps Raman pump pulse [38, 40]. 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 [35] and diphenyloctatetraene [33], excited state structural dynamics of the photoisomerization of the retinal chromophore in bacteriorhodopsin [36, 44] and rhodopsin [37], direct observation of anharmonic coupling in CDCl_3 [39], and excited state isomerization in phytochrome [47].

Lee and co-workers [61, 62] have developed the quantum theory for FSRS from both a stationary state and a moving wave packet prepared by an actinic pump pulse or by impulsive Raman scattering. It was shown that the FSRS spectrum in the probe pulse direction can be described by eight Feynman dual time-line diagrams and fall into four groups which are labelled as stimulated Raman scattering (SRS) or inverse Raman scattering (IRS) - SRS(I), SRS(II), IRS(I), IRS(II) [61]. In particular, SRS(I) has three Feynman diagrams corresponding to resonance Raman scattering (RRS) with no intermediate state population, and hot luminescence (HL) where intermediate population is possible in the excited state, similar to those described by Shen [53] for spontaneous Raman scattering where the probe is now the vacuum field. For the other terms, SRS(II) also has three diagrams, while IRS(I) and IRS(II) have one each, where the role of the probe pulse is reversed from that for SRS(I). The quantum theory of FSRS has been used to successfully explain the inversion symmetry in the FSRS Stokes and anti-Stokes spectrum [61, 62], to simulate off-resonance and resonance FSRS spectra of rhodamine 6G in comparison with experiment [64], and to simulate how FSRS can provide direct observation of anharmonic coupling in CDCl_3 [63].

Recently, McCamant *et al.* [36] used FSRS to study the photoisomerization dynamics in the excited state of bacteriorhodopsin. A mixture of ground state BR and excited state BR^* was prepared by an actinic pump and both the FSRS of BR and BR^* were recorded. The FSRS (Stokes) spectrum of ground state BR showed the expected Lorentzian lines at

vibrational frequencies from 750-1700 cm^{-1} due to the SRS(I) process, but the FSRS spectra of the mixture of BR and BR* for actinic pump-probe delay times from 0-500 fs displayed dispersive looking lines at slightly downshifted ($\sim 1\text{-}5 \text{ cm}^{-1}$) vibrational frequencies [36]. The dispersive lines in the FSRS spectra of BR* were revealed by subtracting the baseline which could be caused by Raman pump induced bleach of the stimulated emission band and 0.91 times the FSRS spectrum of ground state BR. A “Raman Initiated by Nonlinear Emission” (RINE) mechanism was postulated to account for the dispersive lines [36]. In RINE, ground state vibrational coherence was first generated by a set of dipole couplings due to the Raman pump and probe fields acting on the ket and bra from the excited state surface, labelled as nonlinear emission, followed by Raman-like dipole couplings. Two four-wave mixing energy level diagrams together with the rules of Lee and Albrecht [55] which were meant for continuous wave interactions gave an expression for RINE that yielded dispersive lines. By removing the term that gave rise to dispersion, reconstructed spectra with Lorentzian line shapes were obtained which decayed with a 260-fs time constant. The decay was attributed to the dynamical motion of the excited state wave packet along the many low-frequency modes from the Franck-Condon region (H) to the photochemically active I₄₆₀ region.

Here, we present the theory of FSRS of BR* in section 3.2 We argue that the actinic pump energy, although on resonance with BR*, is not too high in the experiment of McCamant *et al.* [36] and so each molecule would only have a few modes, typically the low frequency ones, excited while most modes are in the ground vibrational state. Over a large collection of molecules, the FSRS of BR* which detects individual vibrational modes appears to be taking place effectively from the $v = 0$ state of each observed mode on the S₁ surface. We use four-wave mixing energy level diagrams, and there are eight of them which can be grouped as SRS(I), SRS(II), IRS(I), IRS(II), to describe FSRS from BR*. It is then possible to identify the diagrams pertaining to RINE and others that are related to it. In section 3.3, we show how the experimental results are analyzed for the FSRS contribution from BR* only, and present calculations using the 29-mode model of Myers *et al.* [117] for the ground and excited state surfaces of BR. We are able to show that the dispersive line shapes arise from the inverse Raman scattering IRS(I) term, and not from RINE. We conclude in section 3.4.

3.2 Theory

Myers *et al.* [117] have calculated the 29-mode harmonic ground and excited state surface parameters (Table 3.1) for BR in the Franck-Condon region, from observed Raman spectra, with a zero-zero energy of $17,000\text{ cm}^{-1}$. For each mode, it is assumed that the frequency in the ground and excited electronic state is the same. This should be quite a good assumption since we are dealing with vibrations in the range of $800\text{--}1700\text{ cm}^{-1}$ in the FSRS experiment, and these correspond to hydrogen out-of-plane (HOOP) wags, C-C stretches, CCH in-plane rocks, and combination C=C stretches where sigma bonds predominate, in a $\pi \rightarrow \pi^*$ transition with photoisomerization along a low frequency reaction coordinate of about 50 cm^{-1} [118, 119].

The 500 nm, 35 fs, actinic pump (ac) used in the BR experiment delivers photons largely in the energy range $20,000 \pm 500\text{ cm}^{-1}$. Since the zero-zero energy between S_1 and S_0 is $17,000\text{ cm}^{-1}$, it means that vibrational states between $2,500$ and $3,500\text{ cm}^{-1}$ above the zero point energy of S_1 will have amplitude with the actinic pump. Using the 29 modes in Table 3.1, it can be shown that there are 105,095 vibrational states within that energy range. When we analyze the quantum numbers of all these states, we find that $> 95\%$ of the states are in the $v = 0$ state for modes of frequencies $> 1200\text{ cm}^{-1}$, $> 90\%$ are in $v = 0$ for modes of frequencies $900\text{--}1200\text{ cm}^{-1}$, and $> 85\%$ are in $v = 0$ for modes of frequencies $800\text{--}900\text{ cm}^{-1}$. Since the FSRS spectra are taken in the frequency range of $800\text{--}1800\text{ cm}^{-1}$, the net result is that we are observing FSRS largely from $v = 0$ for each of the modes. We do not need to invoke intramolecular vibrational relaxation (IVR) down to the ground vibrational state $(0, 0, \dots, 0)$ on BR^* at all which nevertheless does take place, and in BR^* it is thought to be an ultrafast process as observed in the $< 30\text{ fs}$ growth in the red-shifted stimulated emission band [113]. The FSRS that follows the actinic pump uses a 809 nm, 3.5 ps, Raman pump (pu) and a (840-960 nm) ultrashort probe pulse (pr) with energies that fall within a strong stimulated emission band from BR^* (S_1) to BR (S_0) [113], and so we can use just these two surfaces in the FSRS calculations. The Raman pump and probe pulses couple S_1 to short-lived vibrational states on S_0 which will be explained below. Only the Stokes spectrum relative to the Raman pump frequency is measured in the probe pulse direction.

The theory of FSRS from the ground state surface has been given earlier in terms of eight Feynman dual time-line diagrams [61, 64]. Here, we use the familiar four-wave mixing energy level (FWMEL) diagrams of Lee and Albrecht [55] to describe FSRS from the excited state surface applicable to BR^* . The eight diagrams contributing to FSRS [61, 64], grouped

Table 3.1: Excited state parameters for BR₅₆₈

Vibrations	Frequency $\omega_r, \text{ cm}^{-1}$	Displacement $ \Delta_r $
CCC torsions and bends	187	0.85
	266	0.46
	284	0.23
	402	0.29
	452	0.18
	497	0.14
	529	0.12
	557	0.18
HOOP wags	830	0.16
	843	0.13
	882	0.19
	959	0.15
	1008	0.42
C-C stretches	1170	0.42
	1201	0.38
	1215	0.28
	1253	0.17
CCH in plane rocks	1273	0.20
	1304	0.14
	1321	0.17
	1333	0.08
	1349	0.20
	1379	0.09
	1448	0.13
	1457	0.13
C=C stretches	1527	0.70
	1580	0.15
	1600	0.13
	1640	0.21

as stimulated Raman scattering - SRS(I) and SRS(II) - and inverse Raman scattering - IRS(I) and IRS(II) - are shown in Fig. 3.2. For each diagram, time progresses from left to right; a solid arrow denotes interaction on the ket, a dash arrow denotes interaction on the bra, and the wavy line at time t denotes closure between bra and ket to give the third-order polarization. The grey bar indicates the broadband probe or broadband polarization, if it's on the wavy line. Looking at the end of wavy line representing closure for the third-order polarization, it can be seen that the three diagrams for SRS(I) - RRS(I), HL(I) and HL(II) - are not resonant with any final vibrational state on S_1 on the Stokes side of the Raman pump and so we would expect the SRS(I) spectrum to be broad and lacking in any vibrational features. In the three diagrams for SRS(II) - RRS(II), HL(III) and HL(IV) - the Raman pump takes the molecule to assumed short-lived vibrational states relatively high in energy on S_0 , and the end of the probe arrow will also engage similar short-lived vibrational states on S_0 on the Stokes side, and the wavy line closure will be broadband. The same applies for IRS(II). These relatively high energy states of S_0 have many populated low frequency modes not in the observed range of 800-1800 cm^{-1} that can take the amplitude of the wave packet coming from S_1 away from the Franck-Condon region quickly, and the correlation function for these low frequency modes is accounted for by a relatively small γ_0^{-1} with fast decay, which indirectly makes the vibrational states for the observed modes appear short-lived [57, 120]. Thus SRS(II) and IRS(II) would give smooth spectra lacking in vibrational features. On the other hand, the diagram for IRS(I) shows resonance for the third-order polarization and coherence between $v = 0$ and $v = 1$ states on S_1 for each mode, and so we can expect to see vibrational lines for the modes of S_1 in the IRS(I) spectrum.

The RINE (Raman induced nonlinear emission) mechanism is described by McCamant *et al.* with a one-dimensional model [36]. It assumes that the actinic pump prepares a stationary state $|n\rangle$ on S_1 , and a CW Raman pump matches the energy gap between $|n\rangle$ on S_1 and another vibrational state $|n'\rangle$ on S_0 , followed by a CW probe that takes $\langle n|$ on S_1 to $\langle n' + 1|$ on S_0 thus creating a vibrational coherence $|n'\rangle\langle n' + 1|$ on S_0 . These assumptions are not really consistent with the FSRS experiment that uses a ps Raman pump and a fs probe, but nevertheless RINE as described can be represented by the HL(III) and HL(IV) diagrams where instead of short-lived states for the higher energy levels on S_0 we have long-lived real states, with a $|n'\rangle\langle n' + 1|$ vibrational coherence created on S_0 between times (τ_2, τ_1) by the Raman pump acting on the ket and the probe field acting on the bra for HL(III), and a reversal of time ordering for HL(IV), in an emission-like process. This is the

Figure 3.2: Four-wave mixing energy ladder (FWMEL) diagrams for the 8 terms in FSRS relevant to the BR experiment, after an actinic (ac) pump prepares a wave packet on S_1 . Time increases from left to right. Solid arrows correspond to ket interaction, and dashed arrows for the bra. The Raman pump (pu) is to the blue of the probe (pr) pulse. SRS(I) comprises three diagrams: RRS(I), HL(I) and HL(II), with the bra interaction by the Raman pump at times τ , τ_1 , and τ_2 , respectively. For HL(I) and HL(II), there can be intermediate population on S_0 between (τ_1, τ) . Similarly, SRS(II) has three diagrams where the bra interaction is by the probe pulse. IRS(I) and IRS(II) have one diagram each, where all the interactions with the Raman pump and probe pulses are on the bra.

“nonlinear emission”, and it is followed by Raman-like dipole couplings where the Raman pump takes the ket $|n'\rangle$ on S_0 to S_1 and a dipole coupling closure between the ket now on S_1 and the bra $\langle n' + 1|$ on S_0 with resultant polarization in the probe direction. Of significance are the dipole couplings between a vibrational state $|n\rangle$ on S_1 and a pair of vibrational states $|n'\rangle$ and $|n' + 1\rangle$ on S_0 by the Raman pump and probe pulses, respectively, which are seen in the HL(III) and HL(IV) diagrams, but they are also present in the RRS(II) and IRS(II) diagrams. The RRS(II), HL(III) and HL(IV) diagrams are related and differ in only whether the probe field interaction on the bra comes after, in between, or before the two Raman pump field interactions on the ket, respectively, and hence they are grouped under the SRS(II) process. The IRS(II) diagram has been described as nonlinear emission elsewhere [119]. All these diagrams can have the same spectral pattern.

The Raman gain cross section for FSRS is given by [64],

$$\sigma_{RG}(\omega) = -\frac{4\pi}{3\epsilon_0 c n} \omega \text{Im} \left\{ P_{diff}^{(3)}(\omega) / E_{pr}(\omega) \right\} , \quad (3.1)$$

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

$$E_{pr}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} E_{pr}(t) dt , \quad (3.2)$$

$P_{diff}^{(3)}(\omega)$ is the Fourier transform of the difference polarization with and without the Raman pump that radiates in the probe pulse direction

$$P_{diff}^{(3)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} P_{diff}^{(3)}(t) dt , \quad (3.3)$$

and the difference third-order polarization is given by

$$\begin{aligned} P_{diff}^{(3)}(t) &= P_{\text{pump on}}^{(3)}(t) - P_{\text{pump off}}^{(3)}(t) \\ &= P_{SRS(I)}^{(3)}(t) + P_{SRS(II)}^{(3)}(t) + P_{IRS(I)}^{(3)}(t) + P_{IRS(II)}^{(3)}(t) . \end{aligned} \quad (3.4)$$

We have an N -dimensional separable system. The Hamiltonians for S_1 and S_0 are sums of one-dimensional Hamiltonians

$$\mathbf{h}_1 = \sum_{r=1}^N h_{1r} + E_{10} , \quad (3.5)$$

$$\mathbf{h}_0 = \sum_{r=1}^N h_{0r} , \quad (3.6)$$

where h_{1r} and h_{0r} are one-dimensional Hamiltonians in mode Q_r on S_1 and S_0 , and E_{10} is the energy gap between the minima of the two multidimensional potential energy surfaces. The initial wave packet is a product of one-dimensional wavefunction in each mode r on the S_1 surface, which in the case of BR* are all ground vibrational wavefunctions,

$$|\psi_1(\mathbf{Q}, 0)\rangle = \prod_{r=1}^N |\psi_{1r0}(Q_r, 0)\rangle . \quad (3.7)$$

We assume that the phenomenological damping matrix can be written as $\gamma_{ij} = \frac{1}{2}(\gamma_i + \gamma_j)$, where γ_i is the inverse lifetime on electronic state i , and constant transition dipole moment μ_{10} (Condon approximation) [53, 119]. The respective third-order polarizations can then be read off the diagrams in the usual manner [64],

$$\begin{aligned} P_{SRS(I)}^{(3)}(t) &= \left(\frac{i}{\hbar}\right)^3 \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau \\ &\times e^{-\gamma_1 \tau / 2\hbar - \gamma_0(t-\tau)/2\hbar - \gamma_1(t-\tau_1)/2\hbar - \gamma_0(\tau_1-\tau_2)/2\hbar - \gamma_1 \tau_2 / 2\hbar} \\ &\times e^{iE_{10}\tau/\hbar} E_{pu}(\tau; T_{pu}) e^{-iE_{10}(t-\tau_1)/\hbar} E_{pr}(\tau_1; T_{pr}) E_{pu}^*(\tau_2; T_{pu}) e^{-iE_{10}\tau_2/\hbar} \\ &\times |\mu_{10}|^4 \prod_r S_r(t, \tau_1, \tau_2, \tau) , \end{aligned} \quad (3.8)$$

$$\begin{aligned} P_{SRS(II)}^{(3)}(t) &= \left(\frac{i}{\hbar}\right)^3 \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau \\ &\times e^{-\gamma_1 \tau / 2\hbar - \gamma_0(t-\tau)/2\hbar - \gamma_1(t-\tau_1)/2\hbar - \gamma_0(\tau_1-\tau_2)/2\hbar - \gamma_1 \tau_2 / 2\hbar} \\ &\times e^{iE_{10}\tau/\hbar} E_{pr}(\tau; T_{pr}) e^{-iE_{10}(t-\tau_1)/\hbar} E_{pu}(\tau_1; T_{pu}) E_{pu}^*(\tau_2; T_{pu}) e^{-iE_{10}\tau_2/\hbar} \\ &\times |\mu_{10}|^4 \prod_r S_r(t, \tau_1, \tau_2, \tau) , \end{aligned} \quad (3.9)$$

$$\begin{aligned} P_{IRS(I)}^{(3)}(t) &= \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \\ &\times e^{-\gamma_1 t_3 / 2\hbar - \gamma_0(t_2-t_3)/2\hbar - \gamma_1(t_1-t_2)/2\hbar - (t_1-t_2)/T_2 - \gamma_0(t-t_1)/2\hbar - \gamma_1 t / 2\hbar} \\ &\times e^{iE_{10}t_3/\hbar} E_{pr}(t_3; T_{pr}) E_{pu}^*(t_2; T_{pu}) e^{iE_{10}(t_1-t_2)/\hbar} E_{pu}(t_1; T_{pu}) e^{-iE_{10}t/\hbar} \\ &\times |\mu_{10}|^4 \prod_r I_r(t, t_1, t_2, t_3) , \end{aligned} \quad (3.10)$$

and

$$\begin{aligned}
P_{IRS(II)}^{(3)}(t) &= \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \\
&\times e^{-\gamma_1 t_3/2\hbar - \gamma_0(t_2-t_3)/2\hbar - \gamma_1(t_1-t_2)/2\hbar - \gamma_0(t-t_1)/2\hbar - \gamma_1 t/2\hbar} \\
&\times e^{iE_{10}t_3/\hbar} E_{pu}(t_3; T_{pu}) E_{pu}^*(t_2; T_{pu}) e^{iE_{10}(t_1-t_2)/\hbar} E_{pr}(t_1; T_{pr}) e^{-iE_{10}t/\hbar} \\
&\times |\mu_{10}|^4 \prod_r I_r(t, t_1, t_2, t_3) .
\end{aligned} \tag{3.11}$$

Only the IRS(I) diagram shows vibrational coherence on S_1 ; so, in Eq.(3.10), in addition to the electronic lifetimes γ_i , we have added a vibrational coherence $|0\rangle\langle 1|$ dephasing time T_2 in BR^* for evolution between (t_2, t_1) , assuming that it's the same for all modes. The Raman pump (pu) or probe (pr) pulse (electric field) is commonly taken to be of the form

$$E_{pu/pr}(t; T_{pu/pr}) = E_{0,pu/pr} g_{pu/pr}(t; T_{pu/pr}) e^{-i\omega_{pu/pr}t} , \tag{3.12}$$

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

$$g_{pu/pr}(t; T_{pu/pr}) = \exp\left(-2 \ln 2 \frac{(t - T_{pu/pr})^2}{\Delta_{pu/pr}^2}\right) , \tag{3.13}$$

giving a laser pulse centered at $T_{pu/pr}$, with intensity proportional to $|g_{pu/pr}(t; T_{pu/pr})|^2$ with full-width at half maximum (FWHM) of $\Delta_{pu/pr}$. For each mode r , the four-time correlation functions are defined as

$$\begin{aligned}
S_r(t, \tau_1, \tau_2, \tau) &= \langle \psi_{1r0}(Q_r, 0) | e^{ih_{1r}\tau/\hbar} e^{ih_{0r}(t-\tau)/\hbar} \\
&\times e^{-ih_{1r}(t-\tau_1)/\hbar} e^{-ih_{0r}(\tau_1-\tau_2)/\hbar} e^{-ih_{1r}\tau_2/\hbar} | \psi_{1r0}(Q_r, 0) \rangle ,
\end{aligned} \tag{3.14}$$

and

$$\begin{aligned}
I_r(t, t_1, t_2, t_3) &= \langle \psi_{1r0}(Q_r, 0) | e^{ih_{1r}t_3/\hbar} e^{ih_{0r}(t_2-t_3)/\hbar} \\
&\times e^{ih_{1r}(t_1-t_2)/\hbar} e^{ih_{0r}(t-t_1)/\hbar} e^{-ih_{1r}t/\hbar} | \psi_{1r0}(Q_r, 0) \rangle .
\end{aligned} \tag{3.15}$$

The correlation functions can be computed analytically for a pair of displaced harmonic oscillators without frequency changes between the excited and ground state potentials [64].

3.3 Experimental Results, Calculations and Discussion

3.3.1 Experimental Results

Figure 3.3: FSRs Raman gain spectra of a mixture of BR and BR* for various time delays between actinic pump and probe pulses with ninth-order polynomial baselines drawn in. The FSRs Raman gain spectrum of the ground state BR is also shown.

The experimental results have been obtained by McCamant *et al.* [36] where an actinic pump pulse (500 nm, 35 fs) first prepares a mixture of BR ($\sim 91\%$) and BR* ($\sim 9\%$) followed by FSRs with a (809 nm, 3.5 ps) Raman pump and a (840-960 nm) ultrashort probe pulse. The Raman gain spectrum for the mixture of BR and BR* is given by the ratio of the Raman pump-on probe spectrum over the Raman pump-off probe spectrum. The Raman gain spectra for various delay times between the actinic pump and probe pulses are shown in Fig. 3.3, together with the Raman gain spectrum of the BR ground state. We then fitted a ninth-order polynomial baseline to each of the spectra and subtracted it from its baseline. For delay times of 40 fs and greater, we also subtracted 0.91 times the ground state spectrum following the prescription of McCamant *et al.* [36], while for the delay time of 0 fs we subtracted 0.955 times the ground state spectrum because the BR* population would only be half of the peak value. The net result is the Raman gain spectra for BR* only, without the baselines, and these are shown in Fig. 3.4. Dispersive lines for about 8 to 9 vibrational modes can be seen clearly, with intensities more or less proportional to $\omega_r^3 \Delta_r^2$,

just as for the usual Raman intensities. The linewidths stay nearly the same for all time delays, and the intensity of the lines were deduced to decay with a time constant of ~ 260 fs based on the RINE model [36].

Figure 3.4: FSRs Raman gain spectra for BR* only (vertically offset) without the baselines at various time delays between actinic pump and probe pulses. These are obtained by subtracting the baselines followed by subtracting 0.91 times the ground state spectrum for delay times of 40 fs and greater, while for the delay time of 0 fs we subtracted 0.955 times the ground state spectrum because the BR* population would only be half of the peak value.

3.3.2 Calculations and Discussion

We first calculated the Raman gain spectrum for the ground state BR using the potential parameters in Table 3.1 with zero-zero energy $17,000 \text{ cm}^{-1}$, (809 nm, 3.5 ps) Raman pump, and a (900 nm, 10 fs) probe pulse. It is off-resonance FSRs, and the principal contribution is from the RRS(I) term [61, 64]. In principle, we don't need to use all 29 modes in Table 3.1, but only those in the range of 800-1700 cm^{-1} relevant to the experiment; nevertheless, we have included them all in the calculations and the results are the same. The shape of the ultrashort probe pulse is not critical so long as its spectrum spans the range 840-960 nm for observing the FSRs spectrum. As in the experiment, the probe precedes the Raman pump by 1 ps. The method for calculating the FSRs for polyatomics with harmonic potentials from the ground vibrational state is described in Niu *et al.* [64]. In this case, it's off-resonance FSRs where the contribution is wholly from the RRS(I) term with vibrational coherence $|0\rangle\langle 1|$ on S_0 and associated vibrational dephasing time T_2 that affects the linewidths. Since it's FSRs from the stationary ground vibrational state, we set $\gamma_0 = 0$, and for off-resonance

FSRS the wave packet dynamics on the excited state S_1 is short-lived by the uncertainty principle and so γ_1 is less important and we can set $\gamma_1 = 0$ [56, 57]. We chose T_2 on S_0 to be 600 fs to give linewidths comparable to the experimental results [36], as shown in Fig. 3.5. A longer dephasing time T_2 , which is homogeneous damping, together with inhomogeneous damping due to fluctuations in the energy difference between the zero-point energy of e_0 and e_1 electronic states (energy gap E_{10}) can also give similar broadening in the spectral lines, and absolute resonance Raman intensities would be needed to distinguish between homogeneous and inhomogeneous broadening [117]. There's generally excellent agreement between the calculated and experimental results which shows that the separable harmonic model is applicable and the harmonic potential parameters are good. However, some lower intensity lines like the 1272 cm^{-1} line appear weaker and the 1640 cm^{-1} line appear stronger in the calculated results compared to the experiment. This may mean that the excited state displacements in Table 3.1 or the transition dipole moments for these modes need to be adjusted. The strengths of these lines, although of lower intensity, also show in the calculated FSRS Raman gain for BR^* below.

Figure 3.5: Experimental and calculated results with the 29-mode model for the FSRS Raman gain of ground state BR. The calculated results is with the RRS(I) term as this is off-resonance FSRS and we used a vibrational coherence dephasing time T_2 on S_0 of 600 fs.

The 500 nm, 35 fs, actinic pump prepares population on BR^* followed by FSRS with a pair of Raman pump and probe pulses as described above. The population prepared on BR^* would reach a peak by about 40 fs, and at 0 fs time delay between the actinic pump and probe, only half of the peak population is prepared. This accounts for why the Raman gain in Fig. 3.4 for 0 fs delay is only about half that for 40 fs delay. As explained in the theory above, the FSRS of BR^* largely takes place from the ground vibrational state of each mode

and so we could calculate it effectively from the multidimensional ground vibrational state of S_1 . The calculations on FSRs from BR^* were made with Eqs. (3.1-3.15) above. We have chosen $\gamma_0^{-1} = 100$ fs to reflect the short lifetime in this relatively high-lying energy region of S_0 reached by the Raman pump/probe from S_1 , where the available phase space is larger and the potential is anharmonic. The decay factor can be attributed to the many low frequency modes outside the observed range of $800\text{-}1800\text{ cm}^{-1}$ that can take the amplitude of the wave packet coming from S_1 away from the Franck-Condon region quickly, and the correlation function from these low frequency modes has a fast decay. A longer lifetime in this high-lying energy region of S_0 would lead to resolved vibrational states and noisy lines in the FSRs spectra from SRS(II) and IRS(II) processes as shown below, unlike the relatively smooth spectra observed in the experiment. The lifetime γ_1^{-1} of S_1 was chosen to be 600 fs and the vibrational dephasing time T_2 on S_1 was taken to be infinite, to simulate the observed linewidths, but a longer lifetime γ_1^{-1} and a shorter T_2 for S_1 could give similar linewidths. It's reasonable for γ_1^{-1} , where we are starting with the lower vibrational states on S_1 , to be larger than γ_0^{-1} , where we have dipole couplings with the more numerous and higher vibrational states of S_0 in the FSRs of BR^* . The calculated results for SRS(I), SRS(II) and IRS(II) for time delays between actinic pump and probe of 0-500 fs are shown in Fig. 3.6, and they are all broad and without vibrational features which can be explained with the FWME diagrams in Fig. 3.2 where the wavy line closure for the polarization is broad. The SRS(I) lines are flat, and the SRS(II) and IRS(II) lines are decreasing in magnitude in the Stokes range of $800\text{-}1800\text{ cm}^{-1}$ due to the probe interaction getting further away from resonance with S_0 as the Stokes frequency increases, as shown in Fig. 3.2, and they tend to the zero baseline from the negative and positive side, respectively, with 180° phase difference. All these spectra contribute only to the Raman gain baseline. However, the IRS(I) spectra, shown in Fig. 3.7, show a striking resemblance in the dispersive lines, in the linewidths, frequencies and relative intensities, to the experimental results shown in Fig. 3.4. The IRS(I) process with its dispersive lines of the correct phase, with a negative dip on the low frequency side and rising sharply to a positive peak followed by a return to the baseline, from the vibrational coherence $|0\rangle\langle 1|$ on S_1 is dominant for all delay times. All the observed modes are well reproduced, and it shows that RINE, included in SRS(II), is not the explanation, but rather it is inverse Raman scattering given by IRS(I) that gives rise to the dispersive lines. Dispersive lineshapes have been observed before in resonant inverse Raman scattering of rhodamine 640 with cw lasers [121].

Figure 3.6: Calculated results (vertically offset) for SRS(I), SRS(II) and IRS(II) in the Raman gain of BR^* for time delays between actinic pump and probe of 0-500 fs. Lifetimes used are $\gamma_0^{-1} = 100$ fs, $\gamma_1^{-1} = 600$ fs, and T_2 on S_1 at infinity.

Figure 3.7: Calculated results (vertically offset) for IRS(I), in the Raman gain of BR^* for time delays between actinic pump and probe of 0-500 fs. Lifetimes used are $\gamma_0^{-1} = 100$ fs, $\gamma_1^{-1} = 600$ fs, and T_2 on S_1 at infinity. The dispersive line shapes resemble the experimental results shown in Fig. 3.4.

The ~ 600 fs lifetime on S_1 here is comparable to the stimulated emission decay time, but it is longer than the rapid 260 fs decay estimated by McCamant *et al.* [36] from reconstructed RINE peak areas. Our model here is different from the RINE model. A shorter lifetime γ_1^{-1} on S_1 would lead to broader dispersive lines for each of the modes and nearby lines would coalesce. The effect of the lifetime γ_1^{-1} of S_1 and the dephasing time T_2 on the linewidths in the FSR spectra will be discussed further below. Shorter lifetimes for γ_0^{-1} gave identical results, and we will also discuss longer lifetimes below.

We would expect the RINE spectra, which are included in SRS(II), to show vibrational structures when the lifetime γ_0^{-1} is increased, so that the short-lived states reached by the Raman pump/probe may turn into longer-lived states and it would be possible to create a vibrational coherence on S_0 . In Fig. 3.8 we show the results for time delay of 100 fs and γ_0^{-1} ranging from 50-600 fs, while keeping $\gamma_1^{-1} = 600$ fs and T_2 at infinity. Indeed, vibrational structures begin to appear in the spectra for $\gamma_0^{-1} \geq 200$ fs in SRS(II) and IRS(II), and they are made up of fundamentals and combination bands especially with the lower frequency modes. The dispersive lines in the IRS(I) spectra, however, remain at well defined frequencies of BR^* due to the ever present $|0\rangle\langle 1|$ vibrational coherence on S_1 for each mode. It can also be seen that the width of the dispersive lines in IRS(I) is rather independent of the lifetime γ_0^{-1} on S_0 . The observed FSR spectra would be the sum of SRS(I), SRS(II), IRS(I) and IRS(II), and since the baselines of the observed spectra are

relatively smooth, we can rule out larger values for $\gamma_0^{-1} \geq 200$ fs because they can lead to a noisy SRS(II) component due to many possible vibrational resonances and a noisy baseline.

Figure 3.8: Calculated results (vertically offset) for SRS(I), SRS(II), IRS(I) and IRS(II) in the Raman gain of BR* at a time delay of 100 fs with $\gamma_1^{-1} = 600$ fs, T_2 on S_1 at infinity, and for γ_0^{-1} ranging from 50-600 fs.

The width of the dispersive lines in IRS(I) depends on both the lifetime γ_1^{-1} on S_1 as well as the $|0\rangle\langle 1|$ vibrational dephasing time T_2 . In Fig. 3.9, we show the IRS(I) results for time delay of 100 fs, $\gamma_1^{-1} = 600$ fs, $\gamma_0^{-1} = 100$ fs and T_2 ranging from 250-infinity fs. In Fig. 3.10, we show the IRS(I) results for time delay of 100 fs, $\gamma_0^{-1} = 100$ fs, T_2 at infinity, and γ_1^{-1} ranging from 100-800 fs. Clearly, as T_2 or γ_1^{-1} decreases, the dispersive linewidths get broader. A decay time constant of $\gamma_1^{-1} = 600$ fs on S_1 , or a longer γ_1^{-1} plus a finite vibrational dephasing time T_2 of the order of a ps would also give dispersive linewidths that compare well with experiment.

3.4 Conclusion

FSRS of BR* prepared by a 500 nm, 35 fs actinic pump pulse effectively takes place from the $v = 0$ state of each of the modes in the observed Stokes range of 800-1800 cm^{-1} on

Figure 3.9: Calculated results (vertically offset) for IRS(I) in the Raman gain of BR* at a time delay of 100 fs with $\gamma_0^{-1} = 100$ fs, $\gamma_1^{-1} = 600$ fs and T_2 on S_1 ranging from 250-infinity fs.

Figure 3.10: Calculated results (vertically offset) for IRS(I) in the Raman gain of BR* at a time delay of 100 fs with $\gamma_0^{-1} = 100$ fs, T_2 on S_1 at infinity, and γ_1^{-1} ranging from 100-800 fs.

S_1 . Four-wave mixing energy level diagrams are used to describe the FSRS process, and the eight diagrams can be grouped into SRS(I), SRS(II), IRS(I) and IRS(II). It is shown that RINE is equivalent to HL(III)+HL(IV) which is a subset of SRS(II). Calculations with the 29-mode model for BR show that the dispersive lines observed in the FSRS of BR* come from inverse Raman scattering, IRS(I), with $|0\rangle\langle 1|$ vibrational coherence on the S_1 surface, and are not due to RINE with vibrational coherence on the S_0 surface. In our model, the dipole couplings are from S_1 to short-lived states, ~ 100 fs, on the S_0 surface, where the decay can be attributed to the correlation function from the many low frequency modes on S_0 and S_1 outside the observed range of $800\text{-}1800\text{ cm}^{-1}$ in the FSRS experiment. The decay time constant γ_1^{-1} on S_1 is estimated to be ~ 600 fs which is comparable to the stimulated emission decay time. A shorter γ_1^{-1} of 260 fs estimated by McCamant *et al.* [36] with the RINE model would lead to broader dispersive lines and nearby lines would coalesce contrary to the sharp dispersive lines observed in the experiment. We have explained the origin of the dispersive lines. However, the time-resolved FSRS experiment with a 500 nm, 35 fs actinic pump pulse with observation of the Stokes spectra in the $800\text{-}1800\text{ cm}^{-1}$ range is unable to provide direct observation of the dynamics of BR* that may be happening along the low frequency modes and is not present in the current dispersive lines.

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Quantum Theory of time-resolved Femtosecond Stimulated Raman Spectroscopy: Direct versus Cascade processes and application to CDCl_3 ¹

4.1 Introduction

Using femtosecond (fs) pulses and pump-probe techniques, it is possible to prepare and monitor coherent vibrational wave packets in the ground and excited electronic states of polyatomic molecules [122, 123]. In the usual pump-probe scheme, an impulsive or actinic fs pump pulse that is significantly shorter than the period of a vibrationally active mode of a molecule first produces a localized vibrational wave packet which is nonstationary in either the ground or excited electronic state or both, and the dynamic wave packet is monitored, for example, with a fs probe pulse in absorption or emission [7, 112, 119]. The dynamic wave packet may also be probed by femtosecond stimulated Raman spectroscopy (FSRS) which uses a simultaneous pair of picosecond (ps) Raman pump and fs probe pulses to give time-resolved FSRS spectra [40, 124, 125]. This time-resolved FSRS technique affords both high temporal resolution, given by the delay time between the fs impulsive/actinic pump pulse and the fs probe pulse, as well as high spectral resolution due to the ps Raman pump pulse [38, 40, 60, 61], thus overcoming the limitations of conventional time-resolved spontaneous

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Raman spectroscopy that uses a single Raman pump pulse. (Time-resolved) FSRS has been developed into a powerful technique that can reveal vibrational structural information of both stationary and transient states [39, 40, 44, 47, 124, 125, 126, 127, 128]. Other multidimensional Raman scattering spectroscopies based on femtosecond (delta-function) pulses have also been proposed for their ability to sensitively and selectively reveal the vibrational anharmonic coupling strengths, to study the relative strength of homogeneous and inhomogeneous line broadening, and to determine the Duschinsky terms in the Taylor series of the molecular polarizability [68, 129, 130, 131, 132, 133, 134, 135, 136, 137].

Recently, Kukura *et al.* [39] used an impulsive pump pulse to initiate a vibrational wave packet in the C-Cl bends of CDCl_3 on the ground electronic state potential which was probed after various time delays by Stokes FSRS on the C-D stretch leading to 2D FSRS spectra, in an attempt to make direct observation of anharmonic coupling between the C-D stretch and the C-Cl bends as a function of the time delay. This technique has similarities to fifth-order Raman photon echo techniques using five pulses that creates intermolecular vibrational coherence in a sample and the desired fifth-order polarization is detected in a direction different from the applied fields [135]. In the 2D FSRS spectra of CDCl_3 , sidebands were observed on both sides of the Stokes C-D stretch band at 2255 cm^{-1} plus or minus the C-Cl E and A_1 bend frequencies of 262 and 365 cm^{-1} , respectively. The sidebands showed inversion symmetry about the C-D stretch band, and the lineshape of each sideband changed in phase from positive Lorentzian to dispersive, to negative Lorentzian, to negative dispersive, and back to positive Lorentzian with the periodicity of the C-Cl bending frequency. Kukura *et al.* [39] assumed that the C-D stretch is anharmonically coupled to both the C-Cl bends, and used a semiclassical coupled-wave approach and a 1D oscillator model for the C-D stretch whose frequency is modulated in time by the C-Cl bends to simulate the general features of the experimental results. However, the symmetric C-D stretch frequency cannot be modulated by the asymmetric C-Cl E bend, and the 1D model therefore cannot account for the latter sideband. Subsequently, Sun *et al.* used a quantum mechanical direct fifth-order process with *ab initio* anharmonic potential energy surface (PES) for the three modes of CDCl_3 to simulate the time-resolved FSRS spectra [63]. The cubic anharmonic coupling term $Q_{A_1}Q_{CD}^2$ between the C-D stretch and the C-Cl A_1 bend coordinates in the *ab initio* PES meant that the C-D stretch frequency is modulated by the C-Cl A_1 bend and explained the presence of the C-Cl A_1 sidebands as well as the inversion symmetry. However, a similar coupling term $Q_EQ_{CD}^2$ between the C-D stretch and the C-Cl E bend is symmetry forbidden

and so the latter sidebands would be absent. Sun *et al.* [63] had to artificially introduce such a term to account for the C-Cl *E* sidebands, with the argument that it could be allowed by the asymmetric environment of surrounding molecules in order to see more intense C-Cl *E* sidebands in the calculations.

It has been found by Wright *et al.* [138] and by Albrecht *et al.* [130, 139] that with the same phase-matching condition, a cascade process can also occur that may overwhelm the direct fifth-order coherent light scattering. Fleming *et al.* [140, 141, 142] have shown experimentally that cascade signals did dominate the fifth-order signal in 2D Raman scattering spectroscopy of CS₂ and CHCl₃, using five pulses that come in two pairs with a time delay between them followed by a fifth probe pulse to stimulate the Raman scattering. More recently, using three pulses where the impulsive pump and Raman pump pulses act as a pair each followed by the third probe pulse and so is equivalent to Fleming’s five-pulse experiment, Mehlenbacher *et al.* [143] showed that the direct fifth-order signal that arises from the three pulses acting on one CDCl₃ molecule is contaminated by cascade processes comprising two third-order processes on two different molecules. Using a 50:50 mixture of CDCl₃ and CHCl₃, they found equivalent intensity signals of low frequency CDCl₃ modes as sidebands of the C-D stretch of CDCl₃ and the C-H stretch of CHCl₃. These can only be explained by the dominant cascade processes.

Theoretically, Mehlenbacher *et al.* [143] used the coupled-wave classical polarizability treatment [126] to describe the 2D FSRS spectra for both the direct fifth-order process and the cascade processes. It has been shown earlier [126] that this classical treatment is valid only for off-resonance FSRS spectra, and fortunately the 2D FSRS spectra for CDCl₃ had been obtained under off-resonance conditions. Mehlenbacher *et al.* [143] showed by calculation that the cascade signals are at least one order of magnitude larger than the direct fifth-order FSRS signals. The coupled-wave classical approach, however, leads to cumbersome expressions and will be invalid in the pre-resonance and resonance regimes. In theoretical studies of nonlinear spectroscopies, including multidimensional Raman scattering spectroscopies, the nonlinear response theory [68] has been widely used. In principle, it leads to unified expressions for describing all kinds of nonlinear optical process which differ by either temporal sequences of laser pulses or their frequencies and directions, and specific models for matter can be introduced to calculate the required polarization. However, in applications, approximations such as ultrashort and delta function pulses, ultrafast electronic dephasing, and classical Franck-Condon approximations are commonly made

[70, 132, 137, 140, 144, 145]. Our approach below is essentially nonlinear response theory which we implement by the wave packet approach and using finite pulses similar to those in the experiments. It is valid for all excitation energy regimes - resonance and off-resonance. We can include as many details as possible, such as *ab initio* potential energy surfaces, transition dipole moments, and any shape and sequence of the applied laser pulses which may lead to distinct spectra. Therefore, the combination of nonlinear response theory with the time-dependent wave packet method is able to provide a more realistic account of the probed molecular dynamics.

Time-dependent wave packet methods provide a physically intuitive understanding as well as being simple and effective for calculating molecular spectra [56, 119, 120, 146]. Accurate and efficient numerical methods for time-dependent wave packet propagation have been developed and used in many areas of quantum dynamics and spectroscopy [83, 147]. In our previous work using the time-dependent quantum wave packet model and Feynman dual time-line diagrams, the quantum theory for the third-order FSRS process has been presented [60, 61]. Recently, the results from a resonance FSRS experimental investigation of rhodamine 6G met with our theoretical predictions very well [45, 61, 64]. In this chapter, we identify the relevant off-resonance FSRS terms, and multi-dimensional wave packet models are applied to simulate and interpret the FSRS difference spectra for pumped minus unpumped CDCl_3 [39, 148], where an off-resonance impulsive pump initiates a dynamic wave packet on the ground potential energy surface by a Raman process which is subsequently probed by FSRS. We investigate the correlation between the temporal phase of the sidebands in the FSRS difference spectra and the momentum of the probed wave packet, as well as understand the origin of the inversion symmetry of the sidebands for the C-Cl E and A_1 bends about the central C-D Stokes stretch based on the dominant cascade process.

In section 4.2, we first summarize the results for 1D-FSRS and then present the quantum wave packet analysis of 2D-FSRS. This is done with the aid of Feynman dual time-line diagrams for the evolution of the ket and bra wave packets in Liouville space to describe the difference Raman gain spectra in the probe pulse direction. Both the direct fifth-order process and the cascade processes are described quantum-mechanically, and expressions for calculating the (fifth-order) polarizations are derived. The first principles wave packet calculation, different from the classical coupled-wave polarizability theory [126, 143], for the 2D-FSRS of CDCl_3 is described in section 4.3. Calculations are made for both the *ab initio* anharmonic ground state potential of CDCl_3 as well as for the harmonic potential by

discarding the anharmonic terms. The calculated results are compared with experiment. All the features of the experimental[39] 2D-FSRS spectra of CDCl_3 are shown to be accounted for by the cascade process where the anharmonic coupling between the C-D stretch and the C-Cl bends is not responsible for the sidebands. We conclude in section 4.4.

4.2 Quantum theory of 2D-FSRS experiment

A 1D-FSRS experiment is carried out with a pair of ps Raman pump (Rpu) and fs probe (pr) pulses, with fields $E_{Rpu}(t, T_{Rpu})$ and $E_{pr}(t, T_{pr})$ where the pulse envelopes have peak intensities at T_{Rpu} and T_{pr} , respectively, with heterodyne detection in the probe pulse direction. The Raman gain spectrum can be defined as the log of the ratio of the signal intensity in the probe pulse direction with and without the Raman pump pulse [143]. In the quantum theory for FSRS, the Raman gain spectrum has been shown to be given by eight Feynman dual time-line diagrams which can be grouped under four processes - two are classified as stimulated Raman scattering, SRS(I), SRS(II), and two others as inverse Raman scattering, IRS(I) and IRS(II) [61, 64, 65]. It was further shown that each of the SRS process has three terms with one resonance Raman scattering (RRS) term and two hot luminescence (HL) terms, where in RRS there's no intermediate population of the excited electronic state whereas there is intermediate population in the HL terms [61]. When the Raman pump and probe pulses are off-resonance, it has been shown that (a) the SRS(II) and IRS(II) spectra cancel out, (b) the SRS(I) spectrum accounts for the Stokes lines, and (c) the IRS(I) spectrum accounts for the anti-Stokes lines [61, 64].

In a 2D-FSRS experiment of the type that has been used to study chloroform [39, 143] and acetonitrile [149], the 1D-FSRS is preceded by an off-resonant fs impulsive pump (Ipu) pulse, with field $E_{Ipu}(t, T_{Ipu})$, which prepares a wave packet on the ground electronic state by an impulsive stimulated Raman process. The observable is the difference in the Raman gain spectra with and without the Ipu pulse as a function of the time delay between the fs Ipu and fs pr pulses, and our 2D-FSRS here has one dimension as the frequency of the FSRS spectra and another as the time delay. One can take a Fourier transform of the spectra as a function of time delay and turn the time delay dimension to frequency too, as is done in Mehlenbacher *et al.*[143], but it carries the same information. Our focus in this chapter is in explaining the off-resonance 2D-FSRS of deuterated chloroform in the experiment of Kukura *et al.* [39], whose difference (Stokes) Raman gain spectra at various time delays show a high frequency C-D symmetric stretch band at 2255 cm^{-1} , denoted by ω_{CD} , and sidebands that

are displaced to the left and right of it by 262 and 365 cm^{-1} , corresponding to the C-Cl E and A_1 bends, respectively, and denoted by ω_{E/A_1} . The Ipu pulse can only create vibrational coherence in the low frequency ω_{E/A_1} bends, and the central frequency of the broadband pr pulse is red-shifted from the narrow bandwidth Rpu which on “emission” can span the vibrational levels on the ground potential energy surface (PES) with frequencies ω_{CD} and $\omega_{CD} + \omega_{E/A_1}$. When the Ipu pulse acts first followed by FSRS with Rpu and pr pulses acting on the same molecule, we call it a direct fifth-order process. On the other hand, the Rpu pulse which largely follows the Ipu pulse can both act together on a molecule (A) to produce new CARS and CSRS fields in the Rpu direction. These new fields can then participate in the FSRS process on another molecule B together with the Rpu and pr pulses, leading to a cascade process. The direct fifth-order and cascade processes are shown schematically in Fig. 4.1.

Figure 4.1: Schematic of direct fifth-order process with impulsive pump followed by FSRS with Raman pump and probe pulses all acting on molecule A versus a cascade process where the impulsive pump and Raman pump pulses first act on molecule A to produce new CARS and CSRS fields along the Raman pump direction which then participate in FSRS with the Raman pump and probe pulses on molecule B.

4.2.1 Direct fifth-order process

The Feynman dual time-line diagrams for the evolution of the ket and bra wave packet in Liouville space, describing the difference Raman gain spectra in the probe pulse direction with and without Ipu, in the direct fifth-order process on one molecule are given in Fig. 4.2(a) and (b). For each diagram, time progresses vertically from bottom to top. 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 is consistent with convention [68]. The three different fields, E_{Ipu} , E_{Rpu} and E_{pr} , are drawn to point in three different directions. We have drawn the diagrams to show that the wave vectors for the two impulsive pump interactions cancel and the two Raman pump interactions cancel, leaving a resultant polarization in the probe pulse direction. The dash line connecting the ket and bra at time t denotes the final collapse of polarization to produce the detected signal. In the experiments on chloroform [39, 143], all the pulses - Ipu, Rpu, and pr - are off-resonance. The Ipu pulse prepares a time-dependent coherent state (a second-order wave packet that can also be calculated nonperturbatively) in the low frequency C-Cl bends on the ground electronic state e_1 . This is shown as two interactions by the Ipu pulse on the ket or bra side in Fig. 4.2(a) or (b) at times t_5 and t_4 . The off-resonance FSRS for the Stokes side spectrum which is given by the SRS(I) process is then grafted on, after the interactions with Ipu. Only the (main) RRS(I) term in SRS(I) is shown in both figures, with the understanding that t_1 can be permuted to come before t_2 or t_3 , i.e. to include the (smaller) HL(I) and HL(II) terms of SRS(I) in this off-resonance FSRS [61]. The time variables in all our integrals are actual interaction times with the electric fields along the ket or bra time-lines, and they are useful when considering wave packet propagation with finite pulses along these time-lines. In response theories, it is the time difference between pulse interactions on either the ket or bra time-lines that is commonly used, which can facilitate making approximations under ultrashort pulses or ultrafast electronic dephasing times or classical nuclear dynamics [68, 70].

The fifth-order polarizations can be directly written from the diagrams in Fig. 4.2(a) or (b), where we assume that the molecule is deuterated chloroform with the Q_{CD} stretch and two low frequency C-Cl bends Q_{A_1} and Q_E [39], and they are given by,

$$\begin{aligned}
P_{2D-FSRS(-)}^{(5)}(t) = & e^{i\mathbf{k}_{pr} \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right)^5 \int_{t_a}^t dt_1 \int_{t_a}^{t_1} dt_4 \int_{t_a}^{t_4} dt_5 \int_{t_a}^t dt_2 \int_{t_a}^{t_2} dt_3 \\
& E_{Rpu}(t_1; T_{Rpu}) E_{pr}(t_2; T_{pr}) E_{Rpu}^*(t_3; T_{Rpu}) \\
& \times E_{Ipu}^*(t_4; T_{Ipu}) E_{Ipu}(t_5; T_{Ipu}) \langle \psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_E, t_a) | \\
& \times e^{(i\mathbf{h}_1 - \gamma_1/2)(t_3 - t_a)/\hbar} \mu_{21}^* e^{(i\mathbf{h}_2 - \gamma_2/2)(t_2 - t_3)/\hbar} \\
& \times \mu_{21} e^{(i\mathbf{h}_1 - \gamma_1/2)(t - t_2)/\hbar} \mu_{21}^* e^{(-i\mathbf{h}_2 - \gamma_2/2)(t - t_1)/\hbar} \\
& \times \mu_{21} e^{(-i\mathbf{h}_1 - \gamma_1/2)(t_1 - t_4)/\hbar} \mu_{21}^* e^{(-i\mathbf{h}_2 - \gamma_2/2)(t_4 - t_5)/\hbar} \\
& \times \mu_{21} e^{(-i\mathbf{h}_1 - \gamma_1/2)(t_5 - t_a)/\hbar} | \psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_E, t_a) \rangle , \quad (4.1)
\end{aligned}$$

(a) Fifth-order 2D FSRS⁽⁻⁾

(b) Fifth-order 2D FSRS⁽⁺⁾

Figure 4.2: Feynman dual time-line diagram for direct fifth-order process.

and

$$\begin{aligned}
P_{2D-FSRS^{(+)}}^{(5)}(t) = & e^{i\mathbf{k}_{pr} \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right)^5 \int_{t_a}^t dt_1 \int_{t_a}^t dt_2 \int_{t_a}^{t_2} dt_3 \int_{t_a}^{t_3} dt_4 \int_{t_a}^{t_4} dt_5 \\
& E_{Rpu}(t_1; T_{Rpu}) E_{pr}(t_2; T_{pr}) E_{Rpu}^*(t_3; T_{Rpu}) \\
& \times E_{Ipu}(t_4; T_{Ipu}) E_{Ipu}^*(t_5; T_{Ipu}) \langle \psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_E, t_a) | \\
& \times e^{(i\mathbf{h}_1 - \gamma_1/2)(t_5 - t_a)/\hbar} \mu_{21}^* e^{(i\mathbf{h}_2 - \gamma_2/2)(t_4 - t_5)/\hbar} \\
& \times \mu_{21} e^{(i\mathbf{h}_1 - \gamma_1/2)(t_3 - t_4)/\hbar} \mu_{21}^* e^{(i\mathbf{h}_2 - \gamma_2/2)(t_2 - t_3)/\hbar} \\
& \times \mu_{21} e^{(i\mathbf{h}_1 - \gamma_1/2)(t - t_2)/\hbar} \mu_{21}^* e^{(-i\mathbf{h}_2 - \gamma_2/2)(t - t_1)/\hbar} \\
& \times \mu_{21} e^{(-i\mathbf{h}_1 - \gamma_1/2)(t_1 - t_a)/\hbar} | \psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_E, t_a) \rangle . \quad (4.2)
\end{aligned}$$

$FSRS^{(-)}$ and $FSRS^{(+)}$ refer to the left and right sidebands relative to the C-D stretch, respectively, and both diagrams also account for the fundamental C-D stretch, as shown by the wave mixing energy level (WMEL) diagrams in Mehlenbacher *et al.* [143] Here, we have assumed a two electronic state system e_i , $i = 1, 2$ with the molecule initially in the ground vibrational state $|\psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_E, t_a)\rangle$ of e_1 , where t_a is an initial time before the arrival of the Ipu pulse, the vibrational Hamiltonian on electronic state e_i is denoted by $\mathbf{h}_i$ with homogeneous damping constant γ_i , and μ_{12} are vibrational coordinate dependent transition dipole moments.

4.2.2 Cascade process

In the 2D-FSRS experiment on chloroform [39, 143], the Rpu pulse which largely follows the Ipu pulse can both act on molecule A in the first step of the cascade process to produce new third-order CARS (coherent anti-Stokes Raman Spectroscopy) and CSRS (coherent Stokes Raman spectroscopy) fields in the direction of the Rpu pulse. It is of course not essential for the Ipu and Rpu pulses to overlap, but it is necessary for the vibrational coherence in the ground electronic state created by the Ipu pulse to be maintained when the Rpu pulse acts on the molecule in order to produce the CARS and CSRS fields. The Feynman diagrams to describe the CARS process are shown on the left of Figs. 4.3(a) and 4.4(a), which are complex conjugates of each other, and for the CSRS process in Figs. 4.3(b) and 4.4(b), also complex conjugates of each other. In both Figs 4.3 and 4.4, the CARS and CSRS fields in (a) and (b), respectively, propagate from molecule A to participate in the FSRS process on molecule B. The 30 fs (FWHM of E_{Ipu}^2) impulsive pump has a bandwidth of about 360 cm^{-1} and can only excite the low frequency C-Cl symmetric (A_1) and asymmetric

(E) bends, but not the C-D stretch. The two interactions with the Ipu pulse first create a time-dependent (second-order) coherent wave packet in the C-Cl bends on the ground electronic state e_1 on either the ket or bra side of the dual time-line diagram, and after a third interaction with Rpu on either the same or opposite side and with the collapse of the third-order polarization, the CARS or CSRS field, respectively, is produced. Using WMEL diagrams [143], it is straightforward to show that the CARS field has three frequency components: one at the Raman pump frequency, ω_{Rpu} , and two others at $\omega_{Rpu} + \omega_{E/A_1}$; while the CSRS field also has three frequency components: one at the Raman pump frequency, ω_{Rpu} , and two others at $\omega_{Rpu} - \omega_{E/A_1}$.

Figure 4.3: Feynman dual time-line diagram for parallel cascade process.

From the Feynman diagram on the left of Fig. 4.3(a) for the CARS process, the time-dependent third-order polarization $P_{CARS}^{(3)}(\tau)$ that radiates along the Rpu direction is given by,

$$\begin{aligned}
 P_{CARS}^{(3)}(\tau) &= e^{i\mathbf{k}_{Rpu} \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right)^3 \int_{t_a}^{\tau} dt'_1 \int_{t_a}^{t'_1} dt'_2 \int_{t_a}^{t'_2} dt'_3 \\
 &\quad \times E_{Rpu}(t'_1; T_{Rpu}) E_{Ipu}^*(t'_2; T_{Ipu}) E_{Ipu}(t'_3; T_{Ipu}) \\
 &\quad \times \langle \psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_E, t_a) | e^{(i\hbar_1 - \gamma_1/2)(\tau - t_a)/\hbar} \mu_{21}^* \\
 &\quad \times e^{(-i\hbar_2 - \gamma_2/2)(\tau - t'_1)/\hbar} \mu_{21} e^{(-i\hbar_1 - \gamma_1/2)(t'_1 - t'_2)/\hbar} \\
 &\quad \times \mu_{21}^* e^{(-i\hbar_2 - \gamma_2/2)(t'_2 - t'_3)/\hbar} \mu_{21} e^{(-i\hbar_1 - \gamma_1/2)(t'_3 - t_a)/\hbar} \\
 &\quad \times | \psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_E, t_a) \rangle . \tag{4.3}
 \end{aligned}$$

Figure 4.4: Feynman dual time-line diagram for sequential cascade process.

In the left dual time-line diagram of Fig. 4.4(a), we have the complex conjugate of the CARS process. Similarly, from the Feynman diagram on the left of Fig. 4.3(b) for the CSRS process, the time-dependent third-order polarization $P_{CSRS}^{(3)}(\tau)$ that radiates along the Rpu direction is given by,

$$\begin{aligned}
 P_{CSRS}^{(3)}(\tau) &= e^{i\mathbf{k}_{Rpu} \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right)^3 \int_{t_a}^{\tau} d\tau'_1 \int_{t_a}^{\tau'_1} d\tau'_2 \int_{t_a}^{\tau} d\tau' \\
 &\quad \times E_{Rpu}(\tau'; T_{Rpu}) E_{Ipu}(\tau'_1; T_{Ipu}) E_{Ipu}^*(\tau'_2; T_{Ipu}) \\
 &\quad \times \langle \psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_E, t_a) | e^{(i\mathbf{h}_1 - \gamma_1/2)(\tau'_2 - t_a)/\hbar} \mu_{21}^* \\
 &\quad \times e^{(i\mathbf{h}_2 - \gamma_2/2)(\tau'_1 - \tau'_2)/\hbar} \mu_{21} e^{(i\mathbf{h}_1 - \gamma_1/2)(\tau - \tau'_1)/\hbar} \\
 &\quad \times \mu_{21}^* e^{(-i\mathbf{h}_2 - \gamma_2/2)(\tau - \tau')/\hbar} \mu_{21} e^{(-i\mathbf{h}_1 - \gamma_1/2)(\tau' - t_a)/\hbar} \\
 &\quad \times | \psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_E, t_a) \rangle .
 \end{aligned} \tag{4.4}$$

In the left dual time-line diagram of Fig. 4.4(b), we have the complex conjugate of the CSRS process.

The relationship between the electric field and the polarization in the time domain is

given by [72],

$$E_{CARS/CSRS}^{(3)}(t) = -N \frac{2\pi l}{nc\epsilon_0} \frac{\partial P_{CARS/CSRS}^{(3)}(t)}{\partial t}, \quad (4.5)$$

where N is the number density of molecules, l is the sample path length, n is the refractive index, c is the speed of light, and ϵ_0 is the vacuum permittivity, and in the frequency domain it is given by the Fourier transform with the result,

$$E_{CARS/CSRS}^{(3)}(\omega) = iN \frac{2\pi l\omega}{nc\epsilon_0} P_{CARS/CSRS}^{(3)}(\omega). \quad (4.6)$$

While the new fields $E_{CARS/CSRS}^{(3)}(t)$ are propagating along the Rpu direction through the sample, an off-resonant third-order FSRS with Rpu and pr pulses, described by the SRS(I) process, may be taking place on another molecule B, and the CARS/CSRS field may be inserted in place of Rpu in two different ways. It can be inserted on the ket side, as shown in Figs. 4.3(a) and (b) on the right diagram, which we term parallel (p) CARS-FSRS and CSRS-FSRS, respectively. Alternatively, it can be inserted on the bra side as the first interaction, as shown in Figs. 4.4(a) and (b) on the right diagram, which we term sequential (s) CARS-FSRS and CSRS-FSRS, respectively. The four terms shown in Figs. 4.3 and 4.4 would describe the off-resonant difference cascade Raman gain spectra with Ipu and without Ipu as a function of the time delay between the fs Ipu and pr pulses in 2D-FSRS.

With the Feynman dual time-line diagrams in Figs. 4.3 and 4.4, we can write down the corresponding polarizations:

(i) The pCARS-FSRS process is given by Fig. 4.3 (a), and the fifth-order polarization in the probe direction is given by,

$$\begin{aligned} P_{pCARS-FSRS}^{(5)}(t) &= e^{i\mathbf{k}_{pr} \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right)^3 \int_{t_a}^t d\tau_1 \int_{t_a}^{\tau_1} d\tau_2 \int_{t_a}^{\tau_2} d\tau \\ &\times E_{CARS}^{(3)}(\tau) E_{pr}(\tau_1; T_{pr}) E_{Rpu}^*(\tau_2; T_{Rpu}) \\ &\times \langle \psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_E, t_a) | e^{(i\hbar_1 - \gamma_1/2)(\tau_2 - t_a)/\hbar} \mu_{21}^* \\ &\times e^{(i\hbar_2 - \gamma_2/2)(\tau_1 - \tau_2)/\hbar} \mu_{21} e^{(i\hbar_1 - \gamma_1/2)(t - \tau_1)/\hbar} \mu_{21}^* \\ &\times e^{(-i\hbar_2 - \gamma_2/2)(t - \tau)/\hbar} \mu_{21} e^{(-i\hbar_1 - \gamma_1/2)(\tau - t_a)/\hbar} \\ &\times | \psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_E, t_a) \rangle. \end{aligned} \quad (4.7)$$

This generates bands at frequencies $\omega_{Rpu} - \omega_{CD}$ and $\omega_{Rpu} - (\omega_{CD} \pm \omega_{E/A_1})$, as verified by calculations below. The band at frequency $\omega_{FSRS} = \omega_{Rpu} - (\omega_{CD} - \omega_{E/A_1})$ is explained by the WMEL diagram in Fig. 4 (a) of Mehlenbacher *et al.* [143], where $\omega_{CARS} = \omega_{Rpu} + \omega_{E/A_1}$

is produced by molecule A, and the pr pulse on molecule B FSRS ends in the state (0, 1). However, because of the broadband Ipu and pr pulses, there are three other similar WMEL diagrams: (1) $\omega_{CARS} = \omega_{Rpu} + \omega_{E/A_1}$ is produced by molecule A, and the pr pulse on molecule B FSRS can end in the state (1,1), which leads to $\omega_{FSRS} = \omega_{Rpu} - \omega_{CD}$; (2) the second Ipu pulse interaction on molecule A ends in state (0,0) giving $\omega_{CARS} = \omega_{Rpu}$ (we have chosen to use ω_{CARS} here instead of $\omega_{Rayleigh}$ for convenience), and the pr pulse on molecule B FSRS ends in the state (0, 1), which leads to $\omega_{FSRS} = \omega_{Rpu} - \omega_{CD}$; and (3) $\omega_{CARS} = \omega_{Rpu}$ is produced by molecule A, and the pr pulse on molecule B FSRS ends in the state (1,1), which leads to $\omega_{FSRS} = \omega_{Rpu} - (\omega_{CD} + \omega_{E/A_1})$. The wave packet calculation can give us the relative intensities of the bands.

(ii) The pCSRS-FSRS process is given by Fig. 4.3 (b), and the fifth-order polarization in the probe direction is given by,

$$\begin{aligned}
P_{pCSRS-FSRS}^{(5)}(t) = & e^{i\mathbf{k}_{pr} \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right)^3 \int_{t_a}^t d\tau_1 \int_{t_a}^{\tau_1} d\tau_2 \int_{t_a}^{\tau_2} d\tau \\
& \times E_{CSRS}^{(3)}(\tau) E_{pr}(\tau_1; T_{pr}) E_{Rpu}^*(\tau_2; T_{Rpu}) \\
& \times \langle \psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_E, t_a) | e^{(i\hbar_1 - \gamma_1/2)(\tau_2 - t_a)/\hbar} \mu_{21}^* \\
& \times e^{(i\hbar_2 - \gamma_2/2)(\tau_1 - \tau_2)/\hbar} \mu_{21} e^{(i\hbar_1 - \gamma_1/2)(t - \tau_1)/\hbar} \mu_{21}^* \\
& \times e^{(-i\hbar_2 - \gamma_2/2)(t - \tau)/\hbar} \mu_{21} e^{(-i\hbar_1 - \gamma_1/2)(\tau - t_a)/\hbar} \\
& \times | \psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_E, t_a) \rangle .
\end{aligned} \tag{4.8}$$

This generates bands at frequencies $\omega_{Rpu} - \omega_{CD}$ and $\omega_{Rpu} - (\omega_{CD} + \omega_{E/A_1})$ and $\omega_{Rpu} - (\omega_{CD} + 2\omega_{E/A_1})$. The band at the latter frequency is weak and not observed in the FSRS of CDCl_3 . The band at frequency $\omega_{FSRS} = \omega_{Rpu} - (\omega_{CD} + \omega_{E/A_1})$ has been explained by the WMEL diagram in Fig. 4 (b) of Mehlenbacher *et al.* [143], where $\omega_{CSRS} = \omega_{Rpu} - \omega_{E/A_1}$ is produced by molecule A, and the pr pulse on molecule B FSRS ends in the state (0, 1). Three other diagrams due to the broadband Ipu and pr pulses, as in the case of pCARS-FSRS above, produce bands at $\omega_{Rpu} - (\omega_{CD} + 2\omega_{E/A_1})$, $\omega_{Rpu} - \omega_{CD}$, and $\omega_{Rpu} - (\omega_{CD} + \omega_{E/A_1})$, respectively.

(iii) The sCARS-FSRS process is given by Fig. 4.4 (a), and the fifth-order polarization in the probe direction which generates bands at frequencies $\omega_{Rpu} - \omega_{CD}$ and $\omega_{Rpu} - (\omega_{CD} + \omega_{E/A_1})$

is given by,

$$\begin{aligned}
P_{sCARS-FSRS}^{(5)}(t) &= e^{i\mathbf{k}_{pr} \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right)^3 \int_{t_a}^t d\tau_1 \int_{t_a}^{\tau_1} d\tau_2 \int_{t_a}^t d\tau \\
&\times E_{Rpu}(\tau, T_{Rpu}) E_{pr}(\tau_1; T_{pr}) E_{CARS}^{(3)*}(\tau_2) \\
&\times \langle \psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_E, t_a) | e^{(i\mathbf{h}_1 - \gamma_1/2)(\tau_2 - t_a)/\hbar} \mu_{21}^* \\
&\times e^{(i\mathbf{h}_2 - \gamma_2/2)(\tau_1 - \tau_2)/\hbar} \mu_{21} e^{(i\mathbf{h}_1 - \gamma_1/2)(t - \tau_1)/\hbar} \mu_{21}^* \\
&\times e^{(-i\mathbf{h}_2 - \gamma_2/2)(t - \tau)/\hbar} \mu_{21} e^{(-i\mathbf{h}_1 - \gamma_1/2)(\tau - t_a)/\hbar} \\
&\times | \psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_E, t_a) \rangle . \tag{4.9}
\end{aligned}$$

(iv) Finally, the sCSRS-FSRS process is given by Fig. 4.4 (b), and the fifth-order polarization in the probe direction which generates bands at frequencies $\omega_{Rpu} - \omega_{CD}$ and $\omega_{Rpu} - (\omega_{CD} + \omega_{E/A_1})$ is given by,

$$\begin{aligned}
P_{sCSRS-FSRS}^{(5)}(t) &= e^{i\mathbf{k}_{pr} \cdot \mathbf{R}} \left(\frac{i}{\hbar} \right)^3 \int_{t_a}^t d\tau_1 \int_{t_a}^{\tau_1} d\tau_2 \int_{t_a}^t d\tau \\
&\times E_{Rpu}(\tau, T_{Rpu}) E_{pr}(\tau_1; T_{pr}) E_{CSRS}^{(3)*}(\tau_2) \\
&\times \langle \psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_E, t_a) | e^{(i\mathbf{h}_1 - \gamma_1/2)(\tau_2 - t_a)/\hbar} \mu_{21}^* \\
&\times e^{(i\mathbf{h}_2 - \gamma_2/2)(\tau_1 - \tau_2)/\hbar} \mu_{21} e^{(i\mathbf{h}_1 - \gamma_1/2)(t - \tau_1)/\hbar} \mu_{21}^* \\
&\times e^{(-i\mathbf{h}_2 - \gamma_2/2)(t - \tau)/\hbar} \mu_{21} e^{(-i\mathbf{h}_1 - \gamma_1/2)(\tau - t_a)/\hbar} \\
&\times | \psi_1^{(0)}(Q_{CD}, Q_{A_1}, Q_E, t_a) \rangle . \tag{4.10}
\end{aligned}$$

With the fifth-order polarizations above describing the difference Raman gain spectra by each process, which we write generally as $P_{FSRS}^{(5)}(t)$, the Fourier transform gives,

$$P_{FSRS}^{(5)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} P_{FSRS}^{(5)}(t) dt, \tag{4.11}$$

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

$$E_{FSRS}^{(5)}(\omega) = iN \frac{2\pi l \omega}{n(\omega)c} P_{FSRS}^{(5)}(\omega). \tag{4.12}$$

With this, we can calculate the difference Raman gain spectra with heterodyne detection and normalized with respect to the pr spectrum in logarithm units ($-\Delta OD$) as [143],

$$I_{FSRS}(\omega) \approx \frac{Re(E_{pr}^*(\omega) \cdot E_{FSRS}^{(5)}(\omega))}{2.303 |E_{pr}(\omega)|^2}, \tag{4.13}$$

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

4.3 Models, Results and Discussion

4.3.1 *Ab initio* potential energy surface (PES) and parameters for CDCl_3

The *ab initio* 3D potential energy surface (PES) of the ground electronic state of CDCl_3 which includes the C-D stretch, C-Cl A_1 bend, and one of the degenerate C-Cl E bend modes had been calculated earlier using density functional theory at the B3LYP level with the 6-311++(3df, 2pd) basis [63]. Mehlenbacher *et al.* [143] had used the same density functional and basis set to calculate the anharmonicity in the ground electronic state of CDCl_3 . The parameters for the PES are summarized in Table 4.1. It has harmonic terms and only three cubic anharmonic terms, $Q_{A_1}Q_{CD}^2$, $Q_{CD}Q_{A_1}^2$ and $Q_{CD}Q_E^2$, with coefficients 3×10^{-3} , 1.8×10^{-4} and 1.6×10^{-4} a.u., respectively. The excited electronic state PES for both the harmonic and anharmonic 3D models is taken to be 3D harmonic oscillators with the same quadratic coefficients as the ground electronic state PES, and the energy gap is set to be 5 eV at the ground equilibrium configuration. Duschinsky rotation in the excited electronic state is neglected. The dimensionless displacements of the excited electronic state PES for the symmetric C-D stretch and C-Cl A_1 bend are set to be 0.1 relative to the ground electronic state PES. Neither the magnitude of the energy gap nor the normal mode displacements affect the FSRS lineshapes for off-resonance FSRS. For the asymmetric C-Cl E bend mode, the equilibrium displacement in the excited state is zero for symmetry reason. The coordinate dependent transition dipole moment is given by,

$$\mu_{12} = \mu_{12}^0 + C_0 Q_{CD} + C_1 Q_{A_1} + C_2 Q_E, \quad (4.14)$$

where the parameters are given in Table 4.1. The value for μ_{12}^0 was obtained from the *ab initio* calculation. The dependence on Q_E makes it possible to observe a Raman gain in that mode. The relative values of C_i were determined from the Raman cross sections given by Mehlenbacher *et al.* [143], where for off-resonance Raman scattering, if the transition dipole moment is $\mu_{12}^0 + C \cdot Q$, then the off-resonant Raman cross sections are proportional to C^2/ω , where ω is the frequency of the mode. In our quantum model, the Raman scattering arises from a combination of the coordinate dependence in the transition dipole moment and the mode displacements between the ground and excited state PES, whereas in the classical model it depends on α' , the derivative of the molecular polarizability with respect

to the displacement along the vibrational mode. We have used experimental parameters for the sample as follows: number density $N = 7.5 \times 10^{21} \text{ ml}^{-1}$, sample path length $l = 1 \text{ mm}$ and refractive index $n = 1.49$. The three pulses are assumed to be in the same polarization direction, and have the form,

$$E(t, T) = E_0 g(t, T) e^{-i\omega t}, \quad (4.15)$$

where E_0 is the field amplitude, T is the time when the pulse envelope is maximum, ω is the central frequency, and the Gaussian envelope $g(t, T)$ has the form,

$$g(t, T) = \exp\left(-2 \ln 2 \frac{(t - T)^2}{\Delta^2}\right), \quad (4.16)$$

giving a laser pulse intensity proportional to $|g(t, T)|^2$ with full width at half maximum (FWHM) of Δ . The central wavelength of each pulse is given by $2\pi c/\omega$. The parameters for the three pulses - impulsive pump, Raman pump and probe - are given in Table 4.2. As all the processes are off-resonance, we have set the homogeneous damping constants γ_i to zero.

Table 4.1: Parameters for 3D potential energy surfaces for CDCl_3			
	C-D stretch	C-Cl A_1 bend	C-Cl E bend
Ground/Excited (cm^{-1})	2338	363	258
Displacement(Dimensionless)	0.1	0.1	0.0
Reduced mass (amu)	2.32	20.86	25.93
Anharmonicity (a.u.)			
$3 \times 10^{-3} Q_{CD}^2 Q_{A_1} + 1.8 \times 10^{-4} Q_{A_1}^2 Q_{CD} + 1.6 \times 10^{-4} Q_E^2 Q_{CD}$			
Transition dipole moment(a.u.)			
$\mu_{12} = \mu_{12}^0 + C_0 Q_{CD} + C_1 Q_{A_1} + C_2 Q_E$			
$\mu_{12}^0 = 0.310, C_0 = -0.268, C_1 = -0.057, C_2 = -0.040$			

Table 4.2: Parameters for the three pulses				
	Wavelength (nm)	T (fs)	τ (fs)	Intensity (W/cm^2)
Impulsive pump	800	0	30	1×10^{12}
Raman pump	800	T_d	1000	1×10^{10}
Probe	930	T_d	8	1×10^{10}

4.3.2 Results and Discussion

We have calculated the difference Raman gain spectra with and without the Ipu pulse for the direct fifth-order process of CDCl_3 using the sum of Eqs. (4.1)-(4.2), and Eqs.

(4.11)-(4.13), for delay times of 700-790 fs between the Ipu and pr pulses. These are shown in Fig. 4.7 (b). The inversion symmetry of the sidebands of the C-Cl A_1 bend, which are displaced to the left and right from the central C-D stretch by 363 cm^{-1} , can clearly be seen. They arise from the symmetry allowed anharmonic coupling term $Q_{A_1}Q_{CD}^2$. The small peaks at 2045 cm^{-1} and 2560 cm^{-1} are the sidebands of the C-Cl E bend which are very weak compared to the C-Cl A_1 bend, contrary to what has been observed experimentally [39], shown in Fig. 4.7 (a), where both the C-Cl A_1 and E bend sidebands are of about the same intensity. Sun *et al.* [63] had to introduce an additional anharmonic coupling term $Q_EQ_{CD}^2$, which is symmetry forbidden in the *ab initio* calculation, in order to see stronger sidebands in the C-Cl E bend. This is already a hint that the direct fifth-order process may not be the main one to account for the difference Raman gain spectra in CDCl_3 .

In the first step of the cascade fifth-order processes, the Ipu pulse followed by the Rpu pulse acting on a CDCl_3 molecule can produce two new fields, CARS and CSRS, traveling along the Raman pump direction, as shown in Figs. 4.3 and 4.4. We have calculated the CARS and CSRS fields using Eqs. (4.3)-(4.6) on the anharmonic potential of CDCl_3 . The absolute values of the CARS and CSRS fields in frequency space are shown in Fig. 4.5 (a) and (b), respectively. Our convention, following the experiment [39], is that frequencies are taken relative to ω_{Rpu} , and the Stokes side is plotted as positive frequencies while the anti-Stokes side is plotted as negative frequencies. Panel (a) shows the CARS fields in the Raman pump direction with a strong frequency component at ω_{Rpu} which we have centered at 0 cm^{-1} , and the inset in the range -400 to -200 cm^{-1} shows two weak frequency components at $\omega_{Rpu} + \omega_{E/A_1}$, i.e. at about -258 cm^{-1} and -363 cm^{-1} in the plot. Panel (b) shows the corresponding CSRS fields in the Raman pump direction with a strong frequency component at ω_{Rpu} and the inset in the range 200 to 400 cm^{-1} shows two weak frequency components at $\omega_{Rpu} - \omega_{E/A_1}$, i.e. at about 258 cm^{-1} and 363 cm^{-1} . The real and imaginary parts of the CARS and CSRS fields in the range -400 to 400 cm^{-1} , plotted in Fig. 4.5 (c)-(h) clearly show that the CARS and CSRS fields are 180° out of phase with each other, and this property later accounts for the inversion symmetry in the difference Raman gain spectra in CDCl_3 about the C-D stretch frequency.

Next, the difference Raman gain spectra for the four cascade processes in CDCl_3 shown in Figs. 4.3 and 4.4 were calculated with Eqs. (4.7)-(4.13) at a time delay of 700 fs between the Ipu and pr pulses, on the anharmonic potential of CDCl_3 . In Fig. 4.6 (a) we show the sum of the parallel processes pCARS-FSRS and pCSRS-FSRS as a solid line, and the

Figure 4.5: CARS and CSRS fields in the frequency domain relative to the Raman pump frequency for the impulsive pump and Raman pump pulses acting on CDCl_3 . (a) Absolute value of CARS field, and insets magnified 75 times on both sides of the Raman pump frequency to show the CARS fields in the range -400 to -200 cm^{-1} . (b) Absolute value of CSRS field, and insets magnified 75 times on both sides of the Raman pump frequency to show the CSRS fields in the range 200 to 400 cm^{-1} . (c) Real part of the CARS and CSRS fields in the frequency range -400 to -200 cm^{-1} showing the 180° phase difference. (d) Same as (c) but for the frequency range -200 to 200 cm^{-1} . (e) Same as (c) but for the frequency range 200 to 400 cm^{-1} . (f) Similar to (c) but for the imaginary part of the CARS and CSRS fields showing the 180° phase difference. (g) Same as (f) but for the frequency range -200 to 200 cm^{-1} . (h) Same as (f) but for the frequency range 200 to 400 cm^{-1} .

sum of the sequential processes sCARS-FSRS and sCSRS-FSRS as a dash line. Clearly, we can see bands at ω_{CD} and $\omega_{CD} \pm \omega_{E/A_1}$ for the parallel processes, and bands at ω_{CD} and $\omega_{CD} + \omega_{A_1}$ for the sequential processes. For the latter, the band at $\omega_{CD} + \omega_E$ is too weak to be seen. Cancellation occurs when we sum the parallel and sequential processes in Fig. 4.6 (a), and the result is the difference Raman gain spectrum shown in Fig. 4.6 (b). The inversion symmetry of the sidebands about ω_{CD} can clearly be seen.

In Fig. 4.7 (a) we reproduce the experimental results of Kukura *et al.* [39] for the experimental difference Raman gain spectra with time delays of 777-867 fs between the Ipu and pr pulses. We should note that the experimental time delay measurement may have a displacement to it, as the result for the 777 fs time delay in Kukura *et al.* [39] is similar to the 700 fs time delay reported in Frontiera *et al.* [148], and we have chosen to start all our calculations at 700 fs. The experimental results do not show the band at ω_{CD} . Similar to Fig. 4.6 (b), we have calculated the difference Raman gain spectra on the anharmonic potential of CDCl_3 with time delays of 700-790 fs and plotted them in Fig. 4.7 (c) to compare with the experimental results. The correspondence between the calculated and experimental results on the change in lineshape of the sidebands with time delay is very good. The inversion symmetry of the Raman gain spectrum about ω_{CD} is seen for all delay times, and the lineshape of each sideband changes in phase from positive Lorentzian to dispersive, to negative Lorentzian, to negative dispersive, and back to positive Lorentzian with the periodicity of the sideband frequency. The intensity of the difference Raman gain spectra by the cascade process is about one order of magnitude larger than by the direct fifth-order process shown in Fig. 4.7 (b), using the parameters in our calculations. In Fig. 4.7 (d), we have plotted the corresponding results with the 3D harmonic potential by dropping all the cubic anharmonic terms. Comparing the results in panels (c) and (d), the anharmonic terms have no observable effect on the phase and intensity of the difference Raman gain spectra. The only effect of the anharmonicities is in the shift of the spectra to the red by about 35 cm^{-1} from the harmonic frequencies.

The phase of the sidebands in the temporal evolution of the cascade difference Raman gain spectra follows the motion of the time-dependent (second-order) coherent wave packet on the ground PES of molecule A prepared by the Ipu pulse where the information is transmitted through the CARS and CSRS fields which participate in the FSRS on molecule B. In Fig. 4.8 (a) we show the temporal variation of the mean position of the C-Cl A_1 bend in the second-order coherent wave packet created by the impulsive pump pulse on the

Figure 4.6: Difference Raman gain spectra for cascade processes at a delay time of 700 fs calculated with the anharmonic ground PES for CDCl_3 . (a) Sum of pCARS-FSRS and pCSRS-FSRS contributions (solid line); sum of sCARS-FSRS and sCSRS-FSRS contributions (dash line). (b) Difference Raman gain spectrum as a sum of the parallel and sequential processes in (a). The inversion symmetry in the lineshape of the sidebands about ω_{CD} can be seen.

Figure 4.7: (a) Experimental results of Kukura *et al.*[39] for the difference Raman gain spectra of CDCl_3 with time delays from 777-867 fs. (b) Difference Raman gain spectra for the direct fifth-order process with the anharmonic ground PES for CDCl_3 with time delays from 700-790 fs (c) Sum of the four cascade fifth-order processes with the anharmonic ground PES for CDCl_3 with time delays from 700-790 fs. (d) Same as (c) but with the harmonic ground PES for CDCl_3 .

anharmonic ground PES of molecule A calculated by the method given in Sun *et al.* [63], and in panel (b) we have the temporal variation of the cascade difference Raman gain spectra with the C-Cl A_1 bend highlighted. When the wave packet is at a turning point with zero momentum, the lineshape of the spectra is either a positive or negative Lorentzian, and when the wave packet is at the mid-point with maximum momentum the lineshape of the spectra will be either positive or negative dispersive. The phase of the sideband clearly follows the wave packet motion in the C-Cl A_1 bend. In Fig. 4.9 we have the corresponding results for the C-Cl E bend, where again we see similar correspondence between the lineshape of the C-Cl E bend and the momentum of the wave packet along that mode. The direct fifth-order difference Raman gain spectra also has a similar correspondence between the lineshape of the sidebands and the second-order coherent wave packet prepared by the Ipu pulse as shown in the work of Sun *et al.* [63].

The cascade and fifth-order processes are governed by different factors: (1) There are eight dipole interactions in the cascade process and only six dipole interactions in the direct fifth-order process. Molecules with smaller transition dipole moments are likely to show a relatively stronger direct fifth-order signal. (2) The cascade intensity is proportional to l^2 while the direct fifth-order intensity is proportional to l , the cell path length, which indicates that a thinner sample length can increase the relative ratio of direct to cascade signal. (3) The cascade intensity is proportional to N^2 while the direct fifth-order intensity is proportional to N , the number density of molecules. Diluting the sample can increase the relative ratio of direct to cascade signal. (4) Both the cascade and the direct fifth-order signals have the same dependence on the intensity of Ipu, Rpu and pr pulses, so changing any of the three fields will not affect the relative ratio of the two signals. (5) The energy mismatches between the wave packets created by the pulse interactions with the molecule(s) and the excited electronic state energy in the Franck-Condon region would appear as energy denominators three times for the direct fifth-order signal and four times for the cascade signal; so a larger off-resonance energy mismatch would favor the direct fifth-order signal. The results of the quantum wave packet analysis and the classical coupled-wave polarizability treatment [143] are in agreement and show unequivocally that the cascade intensity is stronger than the direct fifth-order intensity in explaining the difference temporal Raman gain spectra in CDCl_3 .

Some proposed experimental methodologies to detect the direct fifth-order signal and suppress the signal from third-order cascades include maximizing the phase-matching con-

Figure 4.8: Correlation between the wave packet motion initiated by the impulsive pump pulse along the C-Cl A_1 bend and the phase of the corresponding sideband in the difference cascade Raman gain spectra (shown boxed) as a function of time delay. (a) The time variation of mean position of the second-order coherent wave packet along the C-Cl A_1 bend created by the impulsive pump pulse on the ground PES of CDCl_3 . (b) The temporal evolution of the difference cascade Raman gain spectra from 692 to 784 fs in steps of 1/8 period of the C-Cl A_1 bend. The (left) sideband changes lineshape from positive Lorentzian to dispersive, to negative Lorentzian, to negative dispersive, and back to positive Lorentzian with the period of the sideband.

Figure 4.9: Same as for Fig. 9, but for the C-Cl *E* bend. (a) The time variation of mean position of the second-order coherent wave packet along the C-Cl *E* bend created by the impulsive pump pulse on the ground PES of CDCl_3 . (b) The temporal evolution of the difference cascade Raman gain spectra from 711 to 839 fs in steps of $1/8$ period of the C-Cl *E* bend. The (left) sideband changes lineshape from positive Lorentzian to dispersive, to negative Lorentzian, to negative dispersive, and back to positive Lorentzian with the period of the sideband.

dition only for the fifth-order signal, using diffractive optics that can generate the beam pattern for the phase-matched fifth-order signal, heterodyne detection, and varying the polarization and phase of the laser pulses [141, 142, 150, 151, 152, 153, 154]. A situation where the fifth-order signal is dominant is by tuning the impulsive pump pulse to be on resonance with an excited electronic state and to create vibrational coherence there which can then be monitored by femtosecond stimulated Raman spectroscopy using the Raman pump and probe pulses. McCamant *et al.* have used this method to study the excited state evolution in bacteriorhodopsin [36], while Fang *et al.* have used it to study the structural evolution of the green fluorescent protein (GFP) during the proton transfer process [127]. However, cascades are unavoidable when studying vibrational coherence in the ground electronic state with 2D Raman techniques.

4.4 Conclusion

The impulsive pump and the Raman pump pulses acting on a molecule can produce new CARS and CSRS fields in the Raman pump pulse direction, and these new fields can then participate in a FSRS process in a second molecule together with the Raman pump and probe pulses with the final FSRS signal in the probe pulse direction. There are four kinds of such cascade processes: parallel and sequential CARS-FSRS and CSRS-FSRS. The intermediate CARS and CSRS fields and the difference Raman gain spectra have been calculated for CDCl_3 with off-resonance impulsive pump pulse and off-resonance FSRS with Raman pump and probe pulses, consistent with the experiment of Kukura *et al.* [39] The lineshape of the left and right sidebands from the fundamental C-D stretch frequency, assigned to the C-Cl A_1 and E bends, are shown to arise from the cascade processes. The temporal evolution of sidebands are correlated to the motion of the second-order wave packet created by impulsive pump pulse on the ground electronic state PES. The inversion symmetry of the sidebands relative to the C-D stretch frequency arises from the 180° phase difference between the CARS and CSRS fields produced in the first step of the cascade process on molecule A which then participates in the FSRS process in molecule B. The anharmonic vibrational coupling terms in CDCl_3 do not affect the lineshape of the sidebands which is largely governed by the harmonic terms in the cascade process, but they do shift the frequencies of the bands due to the anharmonicity. The alternative mechanism for the 2D FSRS of CDCl_3 is the direct fifth-order process on one molecule, but it is shown that sideband for the asymmetric C-Cl E bend would be very weak. Moreover, the cascade process

gives one order of magnitude more intense lines than the direct fifth-order process in CDCl_3 .

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Temporal and Spectral Resolutions of Femtosecond Stimulated Raman Spectroscopy¹

5.1 Introduction

With the advent of ultrashort laser technique, time-resolved femtosecond spectroscopy has become an imperative tool to reveal dynamic information about molecules, for example, femtosecond stimulated Raman spectroscopy (FSRS), using various properties of the pulses, such as timing, polarization, laser wavelength and probe window bandwidth. Various aspects of the spectra then provide insights into underlying physical and chemical processes, for example,

- (1) narrow peak position reveals vibrational frequency (spectral resolution);
- (2) intensity decay and line width reveal population relaxation time (temporal resolution);
- (3) inversion of the sharp Stokes line of a vibrational mode with time-dependent frequency in FSRS to get the time-dependent polarization, can reveal ‘real-time’ frequency change (simultaneous spectral and temporal resolutions).

Spectroscopy can be described in both time and frequency domains, and in principle they carry the same amount of information and are related by a Fourier transform [68]. However, in practice, one of the two domains may be advantageous over the other for a particular system. Realistic spectroscopy with finite duration pulses are characterized by a finite spectral and temporal resolutions, and the choice between the two domains is

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usually determined by the complexity of the systems. Small and simple systems may be most appropriate for a description in the frequency domain, and time domain description is preferred for large and complex systems. The time-dependent picture for applications in spectroscopy has been reformulated with intuitive representation of wave packet [120, 155], and dynamical Raman spectroscopy has been described in terms of wave packet theory [56, 57, 156, 157, 158].

Recently, time-resolved femtosecond stimulated Raman spectroscopy (FSRS), or 2D-FSRS, has been developed to study structural changes in ultrafast photophysical and photochemical processes [32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42]. In 2D-FSRS, a femtosecond off-resonant impulsive or resonant actinic pump pulse initializes the dynamics by preparing a coherent moving wave packet on either the ground or excited electronic state, respectively. The subsequent dynamics are then detected by a FSRS process with a pair of Raman pump and probe pulses. 2D-FSRS operates in the mixed frequency and time domain, and it offers simultaneous high temporal and spectral resolutions for a certain vibrational mode. The temporal resolution is from the time delay between the actinic/impulsive pump and probe pulses, and the spectral resolution is due largely to the picosecond Raman pump pulse [38, 40].

Temporal and spectral resolutions in the traditional pump-probe experiment have been discussed for integrated and dispersed detection schemes [73, 74]. Integrated signal is recorded as the time-integrated signal intensity within probe duration as a function of pump-probe delay time, and the frequency resolution is obtained from the carrier frequency of probe pulse. Using an ultrashort probe pulse, one is able to obtain a high temporal resolution, but the corresponding spectral resolution is poor, as the spectrum of broadband probe pulse has little dependence on the carrier frequency. On the other hand, in dispersed spectroscopy, the signal fields are dispersed with a spectrometer, and in theory it is operated as a Fourier transform of the signal fields. The spectral resolution of dispersed spectroscopy is determined by the duration of polarization decay time or free-induced decay (FID) time, rather than probe pulse duration [73].

This issue has recently been discussed in some detail in different groups in the context of FSRS [76, 159]. Mukamel *et al* [76] is of the view that FSRS may not be able to reveal ‘real-time’ dynamics at the duration of probe pulse, even though it uses an ultrashort probe pulse to stimulate the Raman process. By noting that spectra of FSRS are obtained as the difference of dispersed probe pulse with and without Raman pump pulse, it is ex-

plained in analogy to pump-probe experiments that the observed spectra are generated in a much longer period after probe pulse. However, with time delays between ultra short actinic/impulsive and probe pulses, we show below that high temporal resolution from the peak time difference of actinic/impulsive pump and probe can be achieved in time-resolved FSRS, which is not correlated with the polarization decay time. For a mode with time-dependent frequency, we will show that the ‘real-time’ frequency can be obtained from the inverse Fourier transform of the Stokes line, and the use of ultrashort probe pulse is essential in two facets: on one hand, ultra short probe pulse is required to mark the start of Stokes polarization as inverted from Stokes line, and on the other hand, the inverted Stokes polarization is the cross-correlation between the real Stokes polarization and the probe pulse, which requires the probe pulse shorter than the vibrational period to be able to deduce the third-order Stokes polarization that is obtained by the inversion process.

In the quantum theory for FSRS, it has been shown that the Raman gain spectrum is described by eight Feynman dual time-line diagrams, which fall into four processes - two are denoted as stimulated Raman scattering, SRS(I), SRS(II), and the other two as inverse Raman scattering, IRS(I) and IRS(II) [43, 61]. It was further shown that each of the SRS process has three terms with one resonance Raman scattering (RRS) term and two hot luminescence (HL) terms, where in RRS there is no intermediate population of the excited electronic state whereas there is intermediate population in the HL terms [61]. When the Raman pump and probe pulses are off-resonance, it has been shown for spectra from an initial stationary vibrational state that (a) the SRS(II) and IRS(II) present broad featureless spectra, determined by the spectrum of ultra short probe pulse, and they cancel out with each other, (b) the SRS(I) spectrum accounts for the sharp Stokes lines, and (c) the IRS(I) spectrum accounts for the sharp anti-Stokes lines. The width of the Stokes and anti-Stokes lines are largely determined by the narrow bandwidth of Raman pump pulse.

In contrast to FSRS from a stationary vibrational state, FSRS spectra of a coherent moving wave packet show Stokes and anti-Stokes lines in both SRS(I) and IRS(I) processes [61]. The line shape of individual Stokes and anti-Stokes spectra in SRS(I) or IRS(I) changes from positive Lorentzian to dispersive, to negative Lorentzian, to negative dispersive, and back to positive Lorentzian with the period of the vibrational mode of initial wave packet. However, the coherent line shape evolution is lost when SRS(I) and IRS(I) are summed together, with positive Lorentzian on Stokes side and negative Lorentzian on anti-Stokes side at all delay times. Only the modulation of spectra intensity is observed, which is

correlated to the position of wave packet. When wave packet moves to the coordinate region with smaller detuning, relatively stronger spectra lines are observed than the spectra at the coordinate region with larger detuning.

The theory for solving time-dependent Schrödinger equation with both time-independent and time-dependent Hamiltonian is provided in section 5.2.1 to explain the theoretical models for FSRS with constant vibrational frequency in section 5.2.2 and time-dependent vibrational frequency in section 5.2.4. The adiabatic theorem is used to explain the validity of three-state model for a vibrational mode with time-dependent frequency in section 5.2.3. The expressions for FSRS cross section and spectral inversion are provided in section 5.2.5. In the results and discussion part, SRS(I) and IRS(I) spectra obtained from analytic expressions are presented for the three-state model with constant vibrational frequency in section 5.3.1. In section 5.3.2, validity of three-state model for a vibrational mode with time-dependent frequency is supported by a model calculation. In section 5.3.3, the underlying physical process for SRS(I) is demonstrated from a wave packet perspective, and results obtained with the wave packet method are compared with those obtained with the three-state model. In section 5.3.4, high temporal resolution is revealed by third-order Stokes polarization of the SRS(I) process. Finally, we point out in section 5.3.5 that off-resonance FSRS cannot distinguish between coherence and no coherence in the initial wave packet from the line shapes and position of the Stokes lines.

5.2 Theory

5.2.1 Time-dependent Schrödinger equation

Generally the time-dependent Schrödinger equation with a time-independent Hamiltonian can be solved like a normal linear first-order ordinary differential equation to the form,

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}\hat{H}\cdot(t-t_0)}|\psi(t_0)\rangle \quad (5.1)$$

where the propagator $\hat{U}(t, t_0) = e^{-\frac{i}{\hbar}\hat{H}\cdot(t-t_0)}$ is a function of $\hat{H}$ operator, and this governs the evolution of the quantum system.

However if the Hamiltonian $\hat{H}(t)$ is time-dependent, the propagator has a complicated form and it is calculated order by order [68],

$$\hat{U}(t, t_0) = 1 + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \dots \int_{t_0}^{\tau_2} d\tau_1 \hat{H}(\tau_n) \hat{H}(\tau_{n-1}) \dots \hat{H}(\tau_1). \quad (5.2)$$

If the Hamiltonians at different times commute, $[\hat{H}(\tau_1), \hat{H}(\tau_2)] = 0$, above formidable expression for $\hat{U}(t, t_0)$ can be simplified

$$\hat{U}(t, t_0) = \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau \hat{H}(\tau) \right]. \quad (5.3)$$

or else a time ordering operator $\hat{\mathbf{T}}$ has to be applied in front,

$$\hat{U}(t, t_0) = \hat{\mathbf{T}} \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau \hat{H}(\tau) \right]. \quad (5.4)$$

5.2.2 Theoretical models for FSRS with constant vibrational frequency

ω_{ca}

Figure 5.1: Schematic of time-resolved FSRS with the dynamics prepared by an actinic pump pulse on the first excited electronic state e_1 . Energy levels of three-state and four-state models are indicated by a,b,c,d.

In time-resolved FSRS, the initial wave packet $|\psi_i(0)\rangle$ is prepared by impulsive or actinic pump pulse on either ground or excited electronic state, respectively. Schematic of the former is shown in Fig. 5.1. The initial wave packet $|\psi_i(0)\rangle$ prepared by broadband impulsive/actinic pump is a coherent moving wave packet, and it can be expanded in the

basis set of vibrational eigenfunctions,

$$|\psi_i(0)\rangle = \sum_{\alpha} c_{\alpha}(0)|\alpha\rangle \quad (5.5)$$

where $|\alpha\rangle$'s are the vibrational eigenfunctions of the corresponding electronic state, and $c_{\alpha}(0)$ are expansion coefficients.

In perturbation theory, the third-order polarizations corresponding to SRS(I) and IRS(I) processes are given by following expressions [61],

$$\begin{aligned} P_{SRS(I)}^{(3)}(t) &= \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \\ &\times \langle \psi_i(0) | e^{ih_1(t_3-0)/\hbar} \mu^* E_{Rpu}^*(t_3) e^{ih_2(t_2-t_3)/\hbar - \gamma_2(t_2-t_3)} \\ &\times \mu E_{pr}(t_2) e^{ih_1(t-t_2)/\hbar - \gamma_1(t-t_2)} \mu^* e^{-ih_2(t-t_1)/\hbar - \gamma_2(t-t_1)} \\ &\times \mu E_{Rpu}(t_1) e^{-ih_1(t_1-0)/\hbar} | \psi_i(0) \rangle \end{aligned} \quad (5.6)$$

$$\begin{aligned} P_{IRS(I)}^{(3)}(t) &= \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \\ &\times \langle \psi_i(0) | e^{ih_1(t-0)/\hbar} \mu^* e^{-ih_2(t-t_1)/\hbar - \gamma_2(t-t_1)} \\ &\times \mu E_{Rpu}(t_1) e^{-ih_1(t_1-t_2)/\hbar - \gamma_1(t_1-t_2)} \mu^* E_{Rpu}^*(t_2) \\ &\times e^{-ih_2(t_2-t_3)/\hbar - \gamma_2(t_2-t_3)} \mu E_{pr}(t_3) e^{-ih_1(t_3-0)/\hbar} | \psi_i(0) \rangle \end{aligned} \quad (5.7)$$

where h_1 and h_2 are the two Hamiltonians of two electronic states e_1 and e_2 , respectively, γ_1 and γ_2 are phenomenological relaxation constants, $E_{Rpu}(t)$ and $E_{pr}(t)$ are the electric fields of Raman pump and probe pulses, respectively. With wave packet method, Eqns. (5.6) and (5.7) can be treated with arbitrary form of initial wave packet $|\psi_i(0)\rangle$ and finite laser pulses on either model or *ab initio* potential energy surface from a time-dependent perspective. Propagation of wave packet is carried out with accurate numerical method, and the laser-matter interaction is performed perturbatively order by order.

For the sake of clarity and simplicity, we consider a general initial wave packet, which is the superposition of two vibrational states,

$$|\psi_i(0)\rangle = c_a(0)|a\rangle + c_c(0)|c\rangle \quad (5.8)$$

where we denote a as the ground vibrational level, c and d the first and second excited vibrational levels, respectively, as indicated in Fig. 5.1. If this initial wave packet in Eqn.

(5.8) is substituted into Eqn. (5.6), the third-order polarization is written into a sum of four individual polarizations from different density matrix elements,

$$\begin{aligned}
P_{SRS(I)}^{(3)}(t) &= \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^t dt_2 \int_0^{t_2} dt_3 \\
&\times (c_a^*(0)\langle a| + c_c^*(0)\langle c|) e^{ih_1 t_3/\hbar} \mu^* E_{Rpu}^*(t_3) e^{ih_2(t_2-t_3)/\hbar - \gamma_2(t_2-t_3)} \\
&\times \mu E_{pr}(t_2) e^{ih_1(t-t_2)/\hbar - \gamma_1(t-t_2)} \mu^* e^{-ih_2(t-t_1)/\hbar - \gamma_2(t-t_1)} \\
&\times \mu E_{Rpu}(t_1) e^{-ih_1 t_1/\hbar} (c_a(0)|a\rangle + c_c(0)|c\rangle) \\
&= \rho_{aa} P_{aa,SRS(I)}^{(3)}(t) + \rho_{cc} P_{cc,SRS(I)}^{(3)}(t) + \rho_{ac} P_{ac,SRS(I)}^{(3)}(t) + \rho_{ca} P_{ca,SRS(I)}^{(3)}(t)
\end{aligned} \tag{5.9}$$

where ρ_{aa} , ρ_{cc} , ρ_{ac} and ρ_{ca} are the density matrix elements, and $P_{aa,SRS(I)}^{(3)}(t)$, $P_{cc,SRS(I)}^{(3)}(t)$, $P_{ac,SRS(I)}^{(3)}(t)$ and $P_{ca,SRS(I)}^{(3)}(t)$ are the corresponding third-order polarizations for SRS(I) process.

$P_{aa,SRS(I)}^{(3)}(t)$ corresponds to the case with stationary initial state, where only the ground vibrational state is populated,

$$\begin{aligned}
P_{aa,SRS(I)}^{(3)}(t) &= \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^t dt_2 \int_0^{t_2} dt_3 \\
&\times \langle a| e^{ih_1 t_3/\hbar} \mu^* E_{Rpu}^*(t_3) e^{ih_2(t_2-t_3)/\hbar - \gamma_2(t_2-t_3)} \\
&\times \mu E_{pr}(t_2) e^{ih_1(t-t_2)/\hbar - \gamma_1(t-t_2)} \mu^* e^{-ih_2(t-t_1)/\hbar - \gamma_2(t-t_1)} \\
&\times \mu E_{Rpu}(t_1) e^{-ih_1 t_1/\hbar} |a\rangle
\end{aligned} \tag{5.10}$$

If a complete basis set $\sum_\alpha |\alpha\rangle\langle\alpha|$ of eigenfunctions of e_1 electronic state is inserted into Eqn. (5.10),

$$\begin{aligned}
P_{aa,SRS(I)}^{(3)}(t) &= \left(\frac{i}{\hbar}\right)^3 \sum_\alpha \int_0^t dt_2 \int_0^{t_2} dt_3 \langle a| e^{ih_1 t_3/\hbar} \mu^* E_{Rpu}^*(t_3) \\
&\times e^{ih_2(t_2-t_3)/\hbar - \gamma_2(t_2-t_3)} \mu E_{pr}(t_2) e^{ih_1(t-t_2)/\hbar - \gamma_1(t-t_2)} |\alpha\rangle \\
&\times \int_0^t dt_1 \langle \alpha| \mu^* e^{-ih_2(t-t_1)/\hbar - \gamma_2(t-t_1)} \\
&\times \mu E_{Rpu}(t_1) e^{-ih_1 t_1/\hbar} |a\rangle
\end{aligned} \tag{5.11}$$

$$= \sum_\alpha \langle \psi_1^{(2)}(t) | \alpha \rangle \langle \alpha | \psi_2^{(1)}(t) \rangle \tag{5.12}$$

where the cases when $|\alpha\rangle$ equal $|a\rangle$ and $|c\rangle$ correspond to Rayleigh and Stokes lines, respec-

tively, and the second- and first order-wave packets are defined as

$$\begin{aligned} \langle \psi_1^{(2)}(t) | &= \left(\frac{i}{\hbar} \right)^2 \int_0^t dt_2 \int_0^{t_2} dt_3 \langle a | e^{ih_1 t_3 / \hbar} \mu^* E_{Rpu}^*(t_3) \\ &\times e^{ih_2(t_2-t_3)/\hbar - \gamma_2(t_2-t_3)} \mu E_{pr}(t_2) e^{ih_1(t-t_2)/\hbar - \gamma_1(t-t_2)} \end{aligned} \quad (5.13)$$

$$\begin{aligned} | \psi_2^{(1)}(t) \rangle &= \left(\frac{i}{\hbar} \right) \int_0^t dt_1 \mu^* e^{-ih_2(t-t_1)/\hbar - \gamma_2(t-t_1)} \\ &\times \mu E_{Rpu}(t_1) e^{-ih_1 t_1 / \hbar} | a \rangle \end{aligned} \quad (5.14)$$

If we assume that Raman pump pulse is monochromatic ($E_{Rpu}(t) = E_{Rpu} \exp(-i\omega_{Rpu}t)$) and probe pulse is impulsive ($E_{pr}(t) = E_{pr} \delta(t - T)$), Eqn. (5.11) can be simplified as

$$\begin{aligned} P_{aa, SRS(I)}^{(3)}(t, T) &= \left(\frac{i}{\hbar} \right)^3 \sum_{\alpha} E_{Rpu}^2 E_{pr} \\ &\times \int_0^T dt_3 \langle a | e^{ih_1 t_3 / \hbar} \mu^* e^{i\omega_{Rpu} t_3} \\ &\times e^{ih_2(T-t_3)/\hbar - \gamma_2(T-t_3)} \mu e^{ih_1(t-T)/\hbar - \gamma_1(t-T)} | \alpha \rangle \\ &\times \int_0^t dt_1 \langle \alpha | \mu^* e^{-ih_2(t-t_1)/\hbar - \gamma_2(t-t_1)} \\ &\times \mu e^{-i\omega_{Rpu} t_1} e^{-ih_1 t_1 / \hbar} | a \rangle \end{aligned} \quad (5.15)$$

where the third-order polarization is written as a product of two integral overlaps of bra and ket, and they are similar to time-dependent expression of cw Raman spectroscopy [56, 160].

The three-state model has been proposed to explain off-resonance FSRS from a stationary state $|a\rangle$ with fixed vibrational frequency ω_{ca} , and sharp Lorentzian line shape of Stokes gain and anti-Stokes loss is obtained [62]. In three-state model, the excited electronic state e_2 is represented by a single level b , as shown in Fig. 5.1. By inserting $|b\rangle\langle b|$ into the two overlaps in Eqn. (5.15),

$$\begin{aligned} P_{aa, SRS(I)}^{(3)}(t, T) &= \left(\frac{i}{\hbar} \right)^3 \sum_{\alpha} E_{Rpu}^2 E_{pr} \\ &\times \int_0^T dt_3 \langle a | e^{ih_1 t_3 / \hbar} \mu^* e^{i\omega_{Rpu} t_3} | b \rangle \\ &\times \langle b | e^{ih_2(T-t_3)/\hbar - \gamma_2(T-t_3)} \mu e^{ih_1(t-t_2)/\hbar - \gamma_1(t-T)} | \alpha \rangle \\ &\times \int_0^t dt_1 \langle \alpha | \mu^* e^{-ih_2(t-t_1)/\hbar - \gamma_2(t-t_1)} | b \rangle \\ &\times \langle b | \mu e^{-i\omega_{Rpu} t_1} e^{-ih_1 t_1 / \hbar} | a \rangle \end{aligned} \quad (5.16)$$

It has been shown that the cases where $|\alpha\rangle$ is substituted by $|a\rangle$ and $|c\rangle$ correspond to sharp Rayleigh gain and Stokes gain, respectively. Note that $|a\rangle$, $|c\rangle$ are eigenfunctions of h_1 , and

$|b\rangle$ is eigenfunction of h_2 , so we can operate h_1 and h_2 on their corresponding eigenfunctions, and after integration we will obtain the analytic expression for Rayleigh and Stokes lines as follows,

$$\begin{aligned}
P_{aa,SRS(I)}^{(3)}(t, T) = & \left(\frac{i}{\hbar}\right)^3 |E_{Rpu}|^2 E_{pr} \frac{|\mu_{ba}|^4}{(\omega_{Rpu} - \omega_{ba})^2} \\
& \times e^{-i\omega_{Rpu}t - \gamma_1 t} e^{i\omega_{Rpu}T + \gamma_1 T} \\
& + \left(\frac{i}{\hbar}\right)^3 |E_{Rpu}|^2 E_{pr} \frac{|\mu_{ba}|^2 |\mu_{bc}|^2}{(\omega_{Rpu} - \omega_{ba})^2} \\
& \times e^{-i(\omega_{Rpu} - \omega_{ca})t - \gamma_1 t} e^{i(\omega_{Rpu} - \omega_{ca})T + \gamma_1 T}
\end{aligned} \tag{5.17}$$

where the other unimportant terms after integration have been omitted for the sake of clarity, γ_2 is assumed to be zero, $\mu_{bi} = \langle b|\mu|i\rangle$ is the expectation value of the electric transition dipole moment between the b and i -th vibrational state on e_1 electronic states, respectively, where $i = a, c$. If Condon approximation is used, μ_{bi} will reduce to the product of a Franck-Condon factor and a constant electronic transition dipole moment. $\omega_{ij} = \omega_i - \omega_j$, and ω_i and ω_j are related to the eigenvalues of h_1 and h_2 . The first term of Eqn. (5.17) is responsible for Rayleigh line, and second term for Stokes line. Similarly, analytic expressions for Rayleigh and anti-Stokes lines from IRS(I) process can be obtained as follows,

$$\begin{aligned}
P_{aa,IRS(I)}^{(3)}(t, T) = & \left(\frac{i}{\hbar}\right)^3 |E_{Rpu}|^2 E_{pr} \frac{|\mu_{ba}|^4}{[i(\omega_{Rpu} - \omega_{ba}) + \gamma_1]^2} \\
& \times e^{-i\omega_{Rpu}t - \gamma_1 t} e^{i\omega_{Rpu}T + \gamma_1 T} \\
& + \left(\frac{i}{\hbar}\right)^3 |E_{Rpu}|^2 E_{pr} \frac{|\mu_{ba}|^2 |\mu_{bc}|^2}{[i(\omega_{Rpu} - \omega_{bc}) + \gamma_1]^2} \\
& \times e^{-i(\omega_{Rpu} + \omega_{ca})t - \gamma_1 t} e^{i(\omega_{Rpu} + \omega_{ca})T + \gamma_1 T}
\end{aligned} \tag{5.18}$$

The first term of Eqn. (5.18) is responsible for Rayleigh line, and second term for anti-Stokes line.

Treating the Raman pump as a continuous wave is a good approximation, as the experimental Raman pump pulse is of $\sim 10 \text{ cm}^{-1}$ bandwidth. Treating the probe pulse as a delta pulse overestimates the bandwidth of the experimental probe pulse, which is of tens of femtosecond duration. A finite probe pulse has limited bandwidth and it cannot reach all the vibrational states that bear significant Franck-Condon factors with the initial vibrational states.

5.2.3 Adiabatic theorem

The simplest quantum model that accounts for frequency change during a chemical process is of two dimensions. The first dimension is the reaction coordinate, and the second dimension is the reporter mode, which changes in vibrational frequency $\omega_{ca}(t)$ when the wave packet moves along the reaction coordinate.

For FSRS spectra from a vibrational mode with time-dependent frequency, the evolution of wave packet on e_1 has to be expressed with an integral form as indicated in Eqn. (5.4), and it can be expressed in the following form,

$$|\psi_i(t)\rangle = e^{-i \int_0^t d\tau h_1(\tau)/\hbar} |\psi_i(0)\rangle \quad (5.19)$$

where the time ordering operator is omitted and the propagation can be treated properly by short time propagator in the numerical calculation.

According to adiabatic theorem [161, 162], the initial wave packet adiabatically remains in the ground vibrational state of a harmonic oscillator with a time-dependent frequency if the frequency gradually changes in an adiabatic way. The wave packet propagated by Eqn. (5.19) can be expanded in the instantaneous eigenfunction basis set $\{|\alpha(t)\rangle\}$,

$$|\psi_i(t)\rangle = \sum_{\alpha} c_{\alpha}(t) |\alpha(t)\rangle e^{i\theta_{\alpha}(t)} \quad (5.20)$$

where

$$\theta_{\alpha}(t) = -\frac{1}{\hbar} \int_0^t E_{\alpha}(t') dt' \quad (5.21)$$

is the dynamics phase factor, and it can be included in the expansion coefficients $c_{\alpha}(t)$.

The expansion coefficients $c_{\beta}(t)$ satisfy following relation [161],

$$\dot{c}_{\beta}(t) = -c_{\beta} \langle \psi_{\beta} | \dot{\psi}_{\beta} \rangle - \sum_{\alpha \neq \beta} c_{\alpha} \frac{\langle \psi_{\beta} | \dot{H} | \psi_{\alpha} \rangle}{E_{\alpha} - E_{\beta}} e^{(-i/\hbar) \int_0^t [E_{\alpha}(t') - E_{\beta}(t')] dt'} \quad (5.22)$$

which is exact. If adiabatic approximation is used, the second term of above equation can be omitted for an adiabatically changing hamiltonian H . For the wave packet initially in the ground vibrational state,

$$c_{\alpha}(0) = \begin{cases} 1, & \alpha = 0 \\ 0, & \alpha \neq 0 \end{cases}. \quad (5.23)$$

it will remain in the ground vibrational state of the time-dependent Hamiltonian, and it is expressed as

$$|\psi_i(t)\rangle = c_0(t)|0(t)\rangle e^{i\theta_0(t)} \quad (5.24)$$

Beyond the adiabatic approximation, the other expansion coefficients $c_\beta(t)$'s need to be calculated. For $\beta \neq 0$,

$$\dot{c}_\beta(t) = -c_0 \frac{\langle \psi_\beta(t) | \dot{H} | \psi_0 \rangle}{E_0 - E_\beta(t)} e^{(-i/\hbar) \int_0^t [E_0(t') - E_\beta(t')] dt'} \quad (5.25)$$

The Hamiltonian for a harmonics oscillator with time-dependent vibrational frequency is given to be

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m x^2 \omega^2(t), \quad (5.26)$$

and if the time-dependent frequency is in the following form

$$\omega(t) = \begin{cases} \omega^{\text{final}} + e^{-t/t'} (\omega^{\text{initial}} - \omega^{\text{final}}), & t \geq 0 \\ \omega^{\text{initial}}, & t < 0 \end{cases}. \quad (5.27)$$

the derivative of H will be in the form,

$$\dot{H} = m x^2 \omega(t) \left[\frac{e^{-t/t'}}{t'} (\omega^{\text{final}} - \omega^{\text{initial}}) \right] \quad (5.28)$$

From the selection rule determined by $\langle \psi_m | \dot{H} | \psi_0 \rangle$, it is found that only the expansion coefficients $c_2(t)$ can have non-zero amplitude,

$$\begin{aligned} \langle \psi_2 | x^2 | \psi_0 \rangle &= \langle \psi_2 | \frac{\hbar}{2m\omega(t)} [(a_+)^2 + a_+ a_- + a_- a_+ + (a_-)^2] | \psi_0 \rangle \\ &= \frac{\hbar}{2m\omega(t)} \langle \psi_2 | (a_+)^2 | \psi_0 \rangle \\ &= \frac{\sqrt{2}\hbar}{2m\omega(t)} \end{aligned} \quad (5.29)$$

Note that $E_0 - E_2 = -2\hbar\omega^{\text{initial}}$ and $E_0(t) - E_2(t) = -2\hbar\omega(t)$, then

$$\dot{c}_2(t) = \frac{\sqrt{2}}{4\omega^{\text{initial}}} \cdot \frac{\omega^{\text{final}} - \omega^{\text{initial}}}{t'} \cdot e^{-t/t'} \cdot e^{2i \int_0^t \omega(t) dt} \quad (5.30)$$

which needs to be numerically integrated due to the complicated expression of $e^{2i \int_0^t \omega(t) dt}$, and the value of $c_2(t)$ will be shown to have a negligible value.

5.2.4 Expression for the third-order polarization of a vibrational mode with time-dependent frequency ω_{ca}

As shown by adiabatic theorem that initial ground vibrational remains to be the ground vibrational state even though the vibrational frequency varies with time, three-state model is valid to describe FSRS process for a displaced harmonic oscillator model with a time-dependent vibrational frequency. The operation of Hamiltonian on the time-dependent eigenstate results in a time-dependent energy, and it can be analytically integrated. If assuming h_2 is time-independent, SRS(I) polarization for ρ_{aa} of three-state model now is expressed into the form ,

$$\begin{aligned}
P_{aa, SRS(I)}^{(3)}(t, T) &= \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \\
&\times \langle a | e^{i \int_0^{t_3} d\tau_3 h_1(\tau_3)/\hbar} \mu^* E_{Rpu}^*(t_3) e^{ih_2(t_2-t_3)/\hbar - \gamma_2(t_2-t_3)} \\
&\times \mu E_{pr}(t_2; T) e^{i \int_{t_2}^t d\tau_2 h_1(\tau_2)/\hbar - \gamma_1(t-t_2)} \mu^* e^{-ih_2(t-t_1)/\hbar - \gamma_2(t-t_1)} \\
&\times \mu E_{Rpu}(t_1) e^{-i \int_0^{t_1} d\tau_1 h_1(\tau_1)/\hbar} |a\rangle \\
&\approx \left(\frac{i}{\hbar}\right)^3 |E_{Rpu}|^2 E_{pr} \frac{|\mu_{ba}|^2 |\mu_{bc}|^2}{(\omega_{Rpu} - \omega_{ba})^2} \\
&\times e^{-i\omega_{Rpu}(t-T)} e^{-\gamma_1(t-T)} e^{i \int_T^t d\tau \omega_{ca}(\tau)}
\end{aligned} \tag{5.31}$$

where only the term for Stokes line is present, ω_{ba} in the denominator is approximated as a constant, because the variation of $h_1(t)$ is negligible compared with the energy gap between e_1 and e_2 . If there are N modes, with no coupling between the modes, then the total polarization is given by the sum of the polarizations of the modes,

$$\begin{aligned}
P_{aa, SRS(I)}^{(3)}(t, T) &\approx \left(\frac{i}{\hbar}\right)^3 |E_{Rpu}|^2 E_{pr} \frac{|\mu_{ba}|^2 |\mu_{bc}|^2}{(\omega_{Rpu} - \omega_{ba})^2} \\
&\times e^{-i\omega_{Rpu}(t-T)} e^{-\gamma_1(t-T)} \sum_{j=1}^N e^{i \int_T^t d\tau \omega_{j, ca}(\tau)}
\end{aligned} \tag{5.32}$$

The wave packet method can also be implemented to calculate the third-order polarization of the vibrational mode with time-dependent frequency. The expression for third-order polarization of SRS(I) process with time-dependent vibrational frequency are the same as described by Eqn. (5.6), except that the propagation of wave packets on e_1 is performed by

a time-dependent Hamiltonian $h_1(t)$,

$$\begin{aligned}
P_{aa,SR(SI)}^{(3)}(t, T) = & \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^t dt_2 \int_0^{t_2} dt_3 \\
& \times \langle \psi_i(0) | e^{i \int_0^{t_3} d\tau_3 h_1(\tau_3)/\hbar} \mu^* E_{Rpu}^*(t_3) e^{ih_2(t_2-t_3)/\hbar - \gamma_2(t_2-t_3)} \\
& \times \mu E_{pr}(t_2; T) e^{i \int_{t_2}^t d\tau_2 h_1(\tau_2)/\hbar - \gamma_1(t-t_2)} \mu^* e^{-ih_2(t-t_1)/\hbar - \gamma_2(t-t_1)} \\
& \times \mu E_{Rpu}(t_1) e^{-i \int_0^{t_1} d\tau_1 h_1(\tau_1)/\hbar} | \psi_i(0) \rangle
\end{aligned} \tag{5.33}$$

in which the propagation of wave packet can be accurately implemented by various short-time integrators, such as split operator [92, 93, 94], short iterative Lanczos [98], and multi-configuration time-dependent Hartree (MCTDH) [104, 105, 106, 107, 108]. Similarly, the total polarization of a multi-mode problem for off-resonance Stokes FSRS can also be treated with the wave packet method as a direct sum of the individual polarization from each mode,¹

$$\begin{aligned}
P_{aa,SR(SI)}^{(3)}(t, T) \approx & \sum_{j=1}^N \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^t dt_2 \int_0^{t_2} dt_3 \\
& \times \langle \psi_{j,i}(0) | e^{i \int_0^{t_3} d\tau_3 h_{j,1}(\tau_3)/\hbar} \mu^* E_{Rpu}^*(t_3) e^{ih_{j,2}(t_2-t_3)/\hbar - \gamma_2(t_2-t_3)} \\
& \times \mu E_{pr}(t_2; T) e^{i \int_{t_2}^t d\tau_2 h_{j,1}(\tau_2)/\hbar - \gamma_1(t-t_2)} \mu^* e^{-ih_{j,2}(t-t_1)/\hbar - \gamma_2(t-t_1)} \\
& \times \mu E_{Rpu}(t_1) e^{-i \int_0^{t_1} d\tau_1 h_{j,1}(\tau_1)/\hbar} | \psi_{j,i}(0) \rangle
\end{aligned} \tag{5.34}$$

For the simplest case with coherence in the initial wave packet, as described by Eqn. (5.8), only the wave packet method can properly treat coherence in off-resonance FSRS, and the IRS(I) process will also contribute on the Stokes side. The expression for the IRS(I) process can be similarly obtained by replacing the propagation of wave packet on e_1 by a time-dependent Hamiltonian $h_1(t)$ in Eqn. (5.7).

5.2.5 Expression for FSRS cross section and spectral inversion

The total third-order difference polarization that radiates in the $\mathbf{k}_{pr}$ direction is given by following expression [61],

$$\begin{aligned}
P_{\text{diff}}^{(3)}(t) &= P_{\text{pump on}}^{(3)}(\mathbf{k}_{pr}; t) - P_{\text{pump off}}^{(3)}(\mathbf{k}_{pr}; t) \\
&= P_{SR(SI)}^{(3)}(t) + P_{SR(II)}^{(3)}(t) + P_{IRS(I)}^{(3)}(t) + P_{IRS(II)}^{(3)}(t) .
\end{aligned} \tag{5.35}$$

¹A full quantum calculation with a direct-product form for the wave packet of the multi-dimensional model will be implemented in the future.

It should be noted that each of the four processes consists of its individual density matrix elements. In off-resonance FSRS, SRS(II) and IRS(II) merely present broad featureless spectra, which are determined by the spectrum of ultra short probe pulse and they cancel out with each other. We only focus on SRS(I) and IRS(I) processes henceforth.

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

$$\sigma_{RG}(\omega) = -\frac{4\pi}{3\epsilon_0 cn} \omega \text{Im} \left\{ P_{diff}^{(3)}(\omega) / E_{pr}(\omega) \right\} , \quad (5.36)$$

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

$$P_{diff}^{(3)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} P_{diff}^{(3)}(t) dt , \quad (5.37)$$

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

$$E_{pr}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} E_{pr}(t) dt . \quad (5.38)$$

We then define

$$\chi_2(\omega) \equiv \text{Im} \left\{ P_{diff}^{(3)}(\omega) / E_{pr}(\omega) \right\} = -\frac{3\epsilon_0 cn}{4\pi\omega} \sigma_{RG}(\omega) \quad (5.39)$$

which can be calculated from the observed Raman gain cross section, as the value of ω can be read along the axis, and other constants are known. The real part $\chi_1(\omega) \equiv \text{Re} \left\{ P_{diff}^{(3)}(\omega) / E_{pr}(\omega) \right\}$ can be obtained through Kramers-Kronig relation,

$$\chi_1(\omega) = \frac{2}{\pi} \mathcal{P} \int_0^{\infty} \frac{s \chi_2(s)}{s^2 - \omega^2} ds, \quad (5.40)$$

where $\mathcal{P}$ denotes the Cauchy principal value. The third-order polarization $P_{diff}^{(3)}(\omega)$ can be obtained as

$$P_{diff}^{(3)}(\omega) = [\chi_1(\omega) + i\chi_2(\omega)] \cdot E_{pr}(\omega) \quad (5.41)$$

where the probe spectrum $E_{pr}(\omega)$ can be calculated according to Eqn. (5.38) and the peak time T of the probe pulse is experimentally determined. After an inverse Fourier transform,

the original third-order polarization $P_{diff}^{(3)}(t)$ is recovered,

$$P_{diff}^{(3)}(t) = \int_{-\infty}^{\infty} e^{-i\omega t} P_{diff}^{(3)}(\omega) d\omega . \quad (5.42)$$

5.3 Results and discussions

5.3.1 FSRS spectra of three-state model with constant vibrational frequency ω_{ca}

Figure 5.2: FSRS spectra of three-state model. (a) SRS(I) and IRS(I) spectra of three-state model, (b) Sum of SRS(I) and IRS(I) spectra

FSRS spectra has been calculated with finite Raman pump and probe pulses in the three-state model [62], and Stokes gain and anti-Stokes loss in off-resonance FSRS are obtained. With cw Raman pump and delta probe pulses, we have derived analytic expressions for both SRS(I) and IRS(I) processes in the three-state model, as shown by Eqns. (5.17) and (5.18). In this model, the vibrational frequency of electronic state e_1 and e_2 are both 750 cm^{-1} , but they are displaced by two dimensionless units, energy gap is set to be 2.5 eV, the phenomenological damping constant $\gamma^{-1} = 620$ fs. FSRS spectra from the analytic expressions are shown in Fig. 5.2. In panel (a), there are Rayleigh and Stokes lines in SRS(I) process, and Rayleigh and anti-Stokes lines in IRS(I) process. Rayleigh lines have similar intensities as Stokes and anti-Stokes lines, which is different from wave packet results with exact wave packet propagation on e_2 . The sum of SRS(I) and IRS(I) processes in

panel (b) shows the cancellation of Rayleigh line, which can be clearly understood from the analytic expressions in Eqns. (5.17) and (5.18). The two terms responsible for Rayleigh lines have exactly the same t -dependent and T -dependent components, but they differ at the denominators of the fraction numbers. If γ_1 is set to be zero, the Rayleigh lines will have same intensity but opposite signs. The imperfect cancellation of Rayleigh lines in the SRS(I) and IRS(I) processes is due to the finite lifetime γ_1 .

5.3.2 Validity of three-state model for a vibrational mode with time-dependent frequency

Figure 5.3: Modulus square of c_2 obtained by (a) wave packet method and (b) numerical integration of Eqn. (5.30)

It has been explained that the initial wave packet of ground vibrational state stays as the ground vibrational state $|a\rangle$ of a time-dependent harmonic oscillator, if the frequency changes adiabatically [161, 162]. Here a one dimensional displaced harmonic oscillator model is used to calculate the expansion coefficients c_α in Eqn. (5.20) with wave packet method, and the results obtained by integrating Eqn. (5.30) are compared. In this model, the vibrational frequency of electronic state e_1 changes from 750 cm^{-1} to 867 cm^{-1} as described by Eqn. 5.27 ($t'=300 \text{ fs}$). Due to the selection rule, only the $v = 2$ vibrational state can acquire amplitude, and the modulus square of $v = 2$, $|c_2|^2$, is compared in Fig. 5.3. The

two results agree with each other well, and the final population of $v = 2$ vibrational state has a negligible value of about 5×10^{-7} . If the frequency changes slowly with $t'=5$ ps, a smaller $|c_2|^2$ of about 1.5×10^{-9} is obtained. This supports the validity of Mukamel's *et al*'s three-state model [76] for a vibrational mode with time-dependent frequency, where the molecules effectively remains in the $v = 0$ state throughout.

5.3.3 FSRS spectra of three-state model and wave packet method with time-dependent vibrational frequency ω_{ca}

The underlying physical process for SRS(I) at a delay time of 200 fs is demonstrated in detail in Fig. 5.4 from a wave packet perspective with the displaced harmonic oscillator model where the vibrational frequency of electronic state e_1 changes from 750 cm^{-1} to 867 cm^{-1} as described by Eqn. 5.27 ($t'=300$ fs), and the vibrational frequency of e_2 is 750 cm^{-1} , it is displaced by two dimensionless units, energy gap is set to be 2.5 eV. The parameters for Raman pump and probe pulses are listed in Table 5.1, and these parameters are used throughout this chapter. In panel (a), the zeroth-order wave packet $\psi_1^{(0)}(t)$ on e_1 remains in the ground vibrational state of the time-dependent potential. In panel (b), the first-order wave packet $\psi_2^{(1)}(t)$ excited by the off-resonance Raman pump to e_2 follows the profile of the Raman pump pulse. The second-order wave packet $\psi_1^{(2)}(t)$ de-excited by the probe pulse from e_2 to e_1 is shown in panel (c), and the oscillating feature of wave packet motion is observed. Even though wave packet $\psi_2^{(1)}(t)$ has a limited lifetime on e_2 , it acquires a momentum kick from the slope of e_2 in the Franck-Condon region before de-excited by broadband probe pulse, and multiple vibrational states are excited coherently. Projection of $\psi_1^{(2)}(t)$ on the time-dependent eigenstate $|1(t)\rangle$ is shown in panel (d). The real part of SRS(I) Stokes polarization $\langle \psi_1^{(2)}(t) | 1(t) \rangle \langle 1(t) | \psi_2^{(1)}(t) \rangle$, with the high frequency oscillation component $e^{-i\omega_{Rpu}(t-T)}$ divided out, is shown in panel (e) as the product of two overlaps, $\langle \psi_1^{(2)}(t) | 1(t) \rangle$ and $\langle 1(t) | \psi_2^{(1)}(t) \rangle$, which is responsible for Stokes line. The imaginary part of the SRS(I) Stokes polarization is the same as the real part, except a phase shift of $\pi/2$, and in the following discussion only the real part of polarization will be shown. The lifetime of the long lived polarization is determined by Raman pump pulse and phenomenological damping constant γ_1 , and the SRS(I) spectrum has sharp vibrational lines.

However, during the lifetime of the polarization after the probe pulse has acted, $\psi_1^{(2)}(t)$ samples the (time-dependent) harmonic oscillator frequency on e_1 , as shown in panel (f). Hence the peak position of the SRS(I) line is an average frequency on e_1 rather than the

Figure 5.4: Demonstration of SRS(I) process at delay time of 200 fs from a wave packet perspective. (a) Initial wave packet $\psi_i(t)$ on e_1 , and we name it the zeroth-order wave packet $\psi_1^{(0)}(t)$; (b) first-order wave packet $\psi_2^{(1)}(t)$ excited by off-resonance Raman pump pulse on e_2 ; (c) second-order wave packet $\psi_1^{(2)}(t)$ de-excited by probe pulse back to e_1 ; (d) projection of $\psi_1^{(2)}(t)$ on the first excited vibrational state of e_1 . The modulus values of the wave packet are shown in (a)-(d); (e) real part of third-order Stokes polarization of SRS(I) process $\langle \psi_1^{(2)}(t) | 1(t) \rangle \langle 1(t) | \psi_2^{(1)}(t) \rangle$ from the ground vibrational state of displaced harmonic oscillator with time-dependent frequency; (f) time-dependent vibrational frequency with dots representing instantaneous frequency obtained from the Stokes polarization in (e).

Table 5.1: Pulses parameters

	Duration (fs)	Central frequency (eV)
Raman pump	3000	1.6
Probe	10	1.6

frequency of the harmonic oscillator at the time of the probe pulse which is being sampled, and therefore a precise time resolution of the frequency of the harmonic oscillator on e_1 is not possible to be obtained from the peak position. Fortunately, panel (e) of Fig. 5.4 suggests one way to reveal instantaneous vibrational frequency from the intervals of adjacent crests in the real part of Stokes polarization with the rapidly oscillating $e^{-i\omega_{Rpu}(t-T)}$ divided out. As indicated by Eqn. (5.31), after the division of $e^{-i\omega_{Rpu}(t-T)}$, the Stokes polarization oscillates with the instantaneous vibrational frequency $\omega_{ca}(t)$, and the average frequency of one period can be evaluated as

$$\omega_{ca}(t) = \frac{1}{\Delta t \cdot c} \quad (5.43)$$

where Δt is the interval between two adjacent crests and c is the speed of light. After measuring all the intervals of adjacent crests, instantaneous vibration frequencies at the middle of two crests can be computed with Eqn. (5.43), and they are marked as dots in panel (f). The dots agree with the time-dependent frequency curve.

The spectra obtained by three-state model and wave packet method are compared in Fig. 5.5 for the one dimensional displaced harmonic oscillator model with fast ($t'=300$ fs) frequency change. The time-dependent vibrational frequency is displayed in panel (a), and it can be seen that the frequency rapidly changes from the initial value of 750 cm^{-1} to near 867 cm^{-1} within 1 ps. The third-order polarizations in (b) by the three-state model and (d) by wave packet method agree well with each other, and the same are for SRS(I) spectra in (c) and (e), respectively. During the lifetime of the polarization at early delay time of 200 fs, the vibrational frequency changes rapidly, and the FSRS spectrum at 200 fs shows a dispersive line shape. At a later delay time, for example, 1000 fs, the frequency almost reaches the final value, and the spectrum is almost a Lorentzian. Similarly, observations are made for the one dimensional displaced harmonic oscillator model with slow ($t'=5$ ps) frequency change in Fig. 5.6.

Table 5.2: The four selected modes in rhodopsin

	mode 1	mode 2	mode 3	mode 4
$\omega_{\text{initial}}(\text{cm}^{-1})$	750	770	820	959
$\omega_{\text{final}}(\text{cm}^{-1})$	867	851	915	959

Figure 5.5: Illustration of the one dimensional displaced harmonic oscillator model with fast ($t'=300\text{fs}$) frequency change. (a) time dependent vibrational frequency; third-order Stokes polarization of SRS(I) process $\langle\psi_1^{(2)}(t)|1(t)\rangle\langle 1(t)|\psi_2^{(1)}(t)\rangle$ for (b) three-state model and (d) wave packet method at different delay times; corresponding SRS(I) spectra for (c) three-state model and (e) wave packet method at different delay times

Figure 5.6: Illustration of the one dimensional displaced harmonic oscillator model with slow ($t'=5$ ps) frequency change. (a) time dependent vibrational frequency; third-order Stokes polarization of SRS(I) process $\langle \psi_1^{(2)}(t) | 1(t) \rangle \langle 1(t) | \psi_2^{(1)}(t) \rangle$ for (b) three-state model and (d) wave packet method at different delay times; corresponding SRS(I) spectra for (c) three-state model and (e) wave packet method at different delay times

Figure 5.7: Time-resolved femtosecond stimulated Raman spectra of the isomerization process in rhodopsin after passing through conical intersection. (a) Experimental results [37]; Simulation results obtained from (b) three-state model and (c) wave packet method for time-dependent vibrational modes in rhodopsin

A three-state model with four separable modes, with a time-dependent vibrational frequency, has been used to simulate the time-resolved FSRS experimental spectra in the panel (a) of Fig. 5.7, for the wave packet after passing through the conical intersection in the isomerization process in rhodopsin [76], and the result is shown in panel (b) of Fig. 5.7, calculated with Eqn. (5.32). Four representative vibrational modes are selected to simulate the spectra, the parameters for each mode are listed in Table 5.2, and the vibrational frequencies change with time according to Eqn. (5.27), in which $t'=300$ fs. The phenomenological relaxation constants γ_1^{-1} is 620 fs. The same results are also obtained by wave packet method with finite Raman pump and probe pulses, shown in panel (c) of Fig. 5.7, calculated with Eqn. (5.34). The results obtained by three-state model and wave packet method both agree with the experimental results in panel (a).

5.3.4 Temporal resolution revealed by third-order Stokes polarization of SRS(I) process $\langle \psi_1^{(2)}(t) | 1(t) \rangle \langle 1(t) | \psi_2^{(1)}(t) \rangle$ with a one-dimensional displaced harmonic oscillator model

5.3.4.1 Forward calculation

Figure 5.8: Time-resolved instantaneous vibrational frequency as scattered dots on time-dependent vibrational frequency curve for (a) slowly changing vibrational frequency and (c) fast changing vibrational frequency; real part of Stokes polarizations calculated from $\langle \psi_1^{(2)}(t) | 1(t) \rangle \langle 1(t) | \psi_2^{(1)}(t) \rangle$ by wave packet method for (b) slowly changing vibrational frequency and (d) fast changing vibrational frequency.

As has been shown in panel (f) of Fig. 5.4, instantaneous vibrational frequency can be

revealed by the intervals of adjacent crests in the real part of third-order Stokes polarization. The full recover of instantaneous vibrational frequencies as scattered dots on the time-dependent frequency curves are shown in panel (a) and (c) of Fig. 5.8 for slowly and fast changing vibrational frequency, respectively. The third-order Stokes polarization has a limited lifetime, caused both by the finite duration of Raman pump and phenomenological relaxation constant γ_1^{-1} , and multiple polarizations are needed to recover the instantaneous frequency at the whole time range. For the case with slowly changing vibrational frequency, ten polarizations are used at the time increment of 1200 fs in panel (b), and for the case with fast changing vibrational frequency, only four polarizations are required with time increment of 600 fs in panel (d). In both cases, the scattered dots of instantaneous frequencies agree well with the time-dependent curves at all delay times.

5.3.4.2 Recovering of the polarizations by inverse Fourier transform of the FSRS spectra

Figure 5.9: Time-resolved instantaneous vibrational frequency as scattered dots on time-dependent vibrational frequency curve for (a) slowly changing vibrational frequency and (c) fast changing vibrational frequency; real part of the polarization by inverse Fourier transform of the Stokes spectra by wave packet method for (b) slowly changing vibrational frequency and (d) fast changing vibrational frequency.

The third-order polarizations with continuous information on the instantaneous frequencies are not observables in experiment. The theory in Section 5.2.5 shows how to invert the observed Stokes spectral line to its corresponding Stokes polarization. The procedure for recovering the Stokes polarization is as follows:

Figure 5.10: Real part of the polarization by inverse Fourier transform of the Stokes spectra of rhodopsin with four modes at a delay time of 200 fs

- (1) take the spectrum of a Stokes line about its peak frequency;
- (2) remove any base line in the spectrum;
- (3) define $\chi_2(\omega) = \text{Im} \left\{ P_{diff}^{(3)}(\omega)/E_{pr}(\omega) \right\}$, and it is related to the Raman gain cross section $\sigma_{RG}(\omega)$, referring to Eqn. (5.39);
- (4) use Kramers-Kronig relation to retrieve $\chi_1(\omega) = \text{Re} \left\{ P_{diff}^{(3)}(\omega)/E_{pr}(\omega) \right\}$, referring to Eqn. (5.40);
- (5) after combining the real part $\chi_1(\omega)$ and imaginary part $\chi_2(\omega)$, $P_{diff}^{(3)}(\omega)$ is obtained by multiplying the probe pulse spectrum $E_{pr}(\omega)$, referring to Eqn. (5.41);
- (6) perform inverse Fourier transform and obtain the recovered polarization $P_{diff}^{(3)}(t)$, as indicated by Eqn. (5.42) and shown in panel (b) and (d) of Fig. 5.9 for slow and fast changing frequency, respectively;
- (7) instantaneous vibrational frequencies are revealed by the intervals of adjacent crests in the recovered polarizations, as shown by scattered dots on the time-dependent frequency curve in panel (a) and (c) of Fig. 5.9 for slow and fast changing frequency, respectively.

It should be noted that in step (5) the probe pulse with various delay times determines the time axis for each scattered dots on the time-dependent frequency curve.

In principle, the four-mode Stokes lines in the isomerization process of rhodopsin can also been treated by the above procedure, and the real part of the recovered third-order Stokes

Figure 5.11: Calculated results by wave packet method for the individual polarization and Stokes line for each mode as well as the sum of them at a delay time of 200 fs: (a) and (b) for mode 1; (c) and (d) for mode 2; (e) and (f) for mode 3; (g) and (h) for mode 4; (i) and (j) for the sum.

polarization is shown in Fig. 5.10. The recovered polarization for this four-mode case is difficult to analyze, and it is not possible to read out the ‘real-time’ frequency change from the time intervals of adjacent crests. This is due to a superposition of the four modes with Stokes lines that overlap, as demonstrated in Fig. 5.11, and the recovered Stokes polarization is the sum of the individual Stokes polarization of each modes. A straightforward method to reveal the frequency change is to fit the observed spectra by finding a suitable model for the form of time-dependent frequencies, or else the complexity caused by the overlap of the four-mode Stokes lines should be reduced by two possible methods: (1) separate out the polarizations for each mode from the recovered Stokes polarization; (2) separate the individual mode contribution to the Stokes spectra and then take the above procedure for each mode.

5.3.5 Coherence in a displaced harmonic oscillator model with time-dependent vibrational frequency

The wave packet method can be used to study coherence in the initial wave packet for the one dimensional displaced harmonic oscillator model with time-dependent vibrational frequency. With proper propagation of a wave packet on e_2 , the effect of all the vibrational levels of e_2 is automatically taken into consideration. For an initial coherent moving wave packet consisting of the first two vibrational states, there would be four density matrix elements that contribute to SRS(I) process as shown in Eqn. (5.9), and similarly there are four that contribute to IRS(I) process. In wave packet method, the four contributions from different density matrix elements are treated as a whole, and they are generally described by Eqns. (5.6) and (5.7). For the displaced harmonic oscillator model with time-dependent vibrational frequency, the propagation of wave packets on e_1 is performed by a time-dependent Hamiltonian $h_1(t)$, which is accurately implemented by the short-time integrator of split operator method.

The calculated spectra of SRS(I), IRS(I) and sum of the two by wave packet method are shown in Fig. 5.12, with the initial wave packet consisting of two vibrational states of equal amplitude. The expansion coefficients of c_a and c_c can be varied to other values, but it will only affect the relative intensity. In Fig. 5.12, the vibrational frequency changes from 750 cm^{-1} to 867 cm^{-1} as described by Eqn. 5.27, and $t'=300\text{ fs}$ (fast). Various dispersive line shapes for both SRS(I) and IRS(I) spectra are seen in panel (a) and (b), respectively. The calculated SRS(I) and IRS(I) spectra are not observables separately, but the sum which

Figure 5.12: Wave packet results from a coherent moving wave packet on a PES with fast changing vibrational frequency. (a) SRS(I) spectra with all the four density matrix components summed together; (b) the same as (a) but for IRS(I); (c) the sum of SRS(I) and IRS(I) at different delay times

gives the FSRS intensity is an observable. The dispersive line shapes in SRS(I) and IRS(I) cancel each other in FSRS spectra as the sum of the two, shown in panel (c), except for a slight dispersive line shape at early delay times, where the vibrational frequency changes rapidly. It is found that the FSRS spectra with coherence in the initial wave packet have the same line shape as panel (e) of Fig. 5.5, but the intensity of the Lorentzian lines varies at different delay times more for the FSRS spectra from a coherent initial wave packet.

Similarly, the spectra of the same coherent initial wave packet of the one dimensional displaced harmonic oscillator model with $t'=5$ ps (slow) are shown in Fig. 5.13, and the coherent line shape changing in SRS(I) and IRS(I) processes cancel each other, and only Lorentzian line shape is observed in FSRS as the sum of SRS(I) and IRS(I) processes. Compared with panel (e) of Fig. 5.6, it seems that off-resonance FSRS cannot distinguish stationary from coherent states in the initial wave packet by the line shape. Resonance FSRS may be able to distinguish the two cases.

The isomerization process in rhodopsin is also treated with coherence in the initial wave packet. The same four dimensional model is used, but the initial wave packet consists of the ground and first excited vibrational states of equal amplitude for each mode. The calculated SRS(I) and IRS(I) spectra in panels (a) and (b), respectively, of Fig. 5.14 are not observables even though the line shapes of some lines have a pattern in changing from Lorentzian to dispersive to negative Lorentzian to negative dispersive etc. with delay time. However, the

Figure 5.13: Wave packet results from a coherent moving wave packet on a PES with slowly changing vibrational frequency. (a) SRS(I) spectra with all the four density matrix components summed together; (b) the same as (a) but for IRS(I); (c) the sum of SRS(I) and IRS(I) at different delay times

Figure 5.14: Wave packet results from a coherent moving wave packet after passing through the conical intersection in the isomerization process in rhodopsin. (a) SRS(I) spectra with all the four density matrix components summed together; (b) the same as (a) but for IRS(I); (c) the sum of SRS(I) and IRS(I) at different delay times

sum of SRS(I) and IRS(I) processes, which is the observable FSRS spectrum, in panel (c) of Fig. 5.14, shows spectra similar to the no coherence case in the panel (c) of Fig. 5.7.

5.4 Conclusion

Off-resonance FSRS can give high temporal and high spectral resolutions where the high temporal resolution of the second-order wave packet from the Raman pump - probe interactions moving on the lower electronic state potential is seen in the third-order time-dependent polarization, and the high spectral resolution is seen in the FSRS spectra. Mukamel *et al* made an error by looking for high temporal resolution in the FSRS spectra. The FSRS spectrum is related to the time-dependent third-order polarization by an inverse Fourier transform. The high temporal resolution is contained in the time-dependent third-order polarization.

Off-resonance FSRS cannot distinguish between coherence and no coherence in the initial wave packet, because they both give the same line shape and position of the Stokes lines. It is nicely illustrated with the data on rhodopsin. It may be possible to distinguish it in the resonance FSRS Stokes line, but this is left for future work.

Conclusions and Prospects

6.1 Conclusions

A novel spectroscopy, Femtosecond Stimulated Raman spectroscopy (FSRS), has been investigated with quantum mechanical methods for the first 500 fs photoisomerization dynamics in the excited state of bacteriorhodopsin, BR^* (S_1), and for the direct fifth and cascade processes in 2D-FSRS of $CDCl_3$ molecule. The simultaneous high temporal and spectral resolutions of FSRS has been explained.

The first 500 fs dynamics in the photoisomerization process of the excited state of BR^* (S_1), has been investigated by quantum mechanical approach, and we find that the FSRS process occurs between the ground vibrational state of S_1 and the high energy vibrational states on BR (S_0), and only the ground vibrational state of each of the observed 800-1800 cm^{-1} modes of S_1 is effectively excited by the actinic pump pulse. The FSRS dispersive lines are attributed to the inverse Raman scattering (IRS) term with $|0\rangle\langle 1|$ vibrational coherence on the S_1 surface, rather than the RINE with vibrational coherence on the S_0 surface.

The side bands around CD stretch observed in $CDCl_3$ molecule in 2D-FSRS has been studied quantum mechanically. It is found that two processes can occur concurrently but with different intensities: a direct fifth-order process taking place on one molecule, and a cascade process comprising two third-order processes on two different molecules, and according to our calculation results, the stronger cascade signal is dominant in the experimental spectra. We also find that the appearance of side bands is due to the CARS and CSRS fields produced in the first step of the cascade process, and the inverse symmetry of line shape between the left and right side bands around CD stretch is due to the 180° phase difference between the CARS and CSRS fields that produced the left and right sidebands, respectively. The coherent line shape changing of side bands is correlated with the momen-

tum of the wave packet prepared on the ground state surface by the impulsive pump along the sideband normal coordinate.

The issue of simultaneous high temporal and spectral resolutions in FSRS has been explained by both three-state model and wave packet method. We find that temporal resolution is better revealed in the time domain. The information in frequency domain is related to the counterpart in time domain with a Fourier transform. The simultaneous high temporal and spectral resolutions of FSRS have been revealed by inverting the sharp Stokes line to recover the polarization, and the high temporal resolution is obtained by the intervals of adjacent crests in the Stokes polarization. We also find by wave packet method that off-resonance FSRS cannot distinguish between coherence and no coherence in the initial wave packet, because the FSRS spectra obtained from the initial wave packet with and without coherence give the same line shape and position of the Stokes lines.

6.2 Prospects

Within the theoretical frame for FSRS, we are able to extend the quantum mechanical investigation to nonperturbative treatment of FSRS, especially the cis-trans photoisomerization process in the excited electronic state through a multi-dimensional conical intersection. The strong internal coupling and light-matter coupling in rhodopsin [6, 37, 163] and bacteriorhodopsin [36, 44, 112] requires the nonperturbative approach, in which the two couplings are dealt equally as the off diagonal element in the electronic basis. Besides, the highly efficient Multi-Configuration Time-Dependent Hartree (MCTDH) method [104, 105, 106, 107, 108] is tailored for multi-dimensional problems. Consequently, a multi-dimensional model, with many vibrational modes coupled to the reaction coordinate, can be treated nonperturbatively using MCTDH method. Some work has been done in the spectroscopy field with MCTDH method, but they are all limited to the linear spectroscopy, including the resonant Raman spectrum of CH_3I [164], absorption spectra of ammonia [165], infrared spectra of water dimer [166, 167, 168, 169] and photo electron spectra of key five-membered heterocycles [170], photodetachment spectroscopy of phenide anion [171]. It would be straightforward to extent MCTDH method to the nonlinear regime to study some complex systems, which is beyond the capability of standard method. With little difference, we can use the same theory for FSRS to study a much more complex system with the wave packet propagated by MCTDH method.

Besides FSRS, we are able to adopt the similar theories and methods to investigate

heterodyne detected 2D-IR photo-echo spectroscopy with three infrared excitation pulses, which recently has gained much popularity and application [9, 11, 12, 19]. In 2D-IR, wave packet on a single electronic state can be treated with the same numerical method, but the interaction of light-matter has to be modified. Numerical investigation of various 2D-IR experiments can be carried out in revealing 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. The interaction of excited solute with solvent molecules in polarizability response spectroscopy (PORS) [172, 173] can be similarly studied.

The polarization-dependence of spectroscopy is used to reveal information about symmetry of vibrational modes, such as depolarization ratio. Polarization dependent FSRS spectra were observed in CDCl_3 signals, where the intensity of asymmetric E bend mode depends on the polarization direction of impulsive pump pulse but symmetric A_1 bend mode doesn't [148]. To investigate polarization dependence of FSRS, each element of the macroscopic susceptibility tensor in laboratory frame (XYZ) needs to be expressed in terms of the microscopic hyperpolarizability tensor in molecule frame (xyz). As the contribution of hyperpolarizability from each molecule to macroscopic susceptibility depends on the orientation of the molecule in laboratory frame, orientational average of the contribution from all the molecules in a unit volume should be carried out with direction cosines. It should also be noted that the third-order polarizability is related to two linear polarizability. Molecule alignment and orientation may also be studied in the same theoretical frame [174].

Attosecond atomic/molecular electron dynamics can also be investigated with wave packet method [175]. Attosecond photoelectron spectroscopy (APS) with attosecond XUV field reveals from electron wave-packet dynamics the stepwise behavior of optical field ionization by a strong linearly polarized IR field [176]. The dynamics of photoelectron wave packet, excited by resonant single-photon, can be steered by light in the attosecond time scale [177]. Attosecond pump probe wave packet simulation of low-lying excited states of the helium atom has also been carried out [178]. Valence-electron wave packets has been observed with attosecond laser fields [179, 180]. Besides in atoms, electron wave packet in molecules can also be studied by APS, and angular momentum distribution of photoelectrons produced by sub-fs XUV pulse has been simulated to reveal intramolecular electronic motion by collecting photoelectrons in two opposite directions along the molecular axis aligned with the light fields [181]. The effects of attosecond electronic motion on chemical reaction

can be revealed by electron wave packet theory, which works in the regime beyond the Born-Oppenheimer approximation. The influence of electron motion on nuclear dynamics in photo-dissociation of D_2 has been studied with electron wave packet method [182, 183].

List of Publications

- (1) Kai Niu, Bin Zhao, Zhigang Sun and Soo-Y. Lee, “Analysis of femtosecond stimulated Raman spectroscopy of excited-state evolution in bacteriorhodopsin”, *Journal of Chemical Physics* **132**, 084510 (2010).
- (2) Bin Zhao, Zhigang Sun and Soo-Y. Lee, “Quantum Theory of time-resolved Femtosecond Stimulated Raman Spectroscopy: Direct versus Cascade processes and application to CDCl_3 ”, *Journal of Chemical Physics* **134**, 024307 (2011).
- (3) Kai Niu, Bin Zhao, Zhigang Sun and Soo-Y. Lee. “Wave Packet Analysis of Femtosecond Stimulated Raman Spectroscopy”, *Advances in Multi-Photon Processes and Spectroscopy*, Volume 20, 1 (2011) (invited).
- (4) Bin Zhao, Kai Niu, Xiuting Li and Soo-Y. Lee, “Simple Aspects of Femtosecond Stimulated Raman Spectroscopy”, *Science China Chemistry* **54**, 1989 (2011) (invited)
- (5) Bin Zhao, Zhigang Sun, and Soo-Y. Lee, “Temporal and Spectral Resolutions of Femtosecond Stimulated Raman Spectroscopy”, in preparation.

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