Time-dependent wave packet averaged vibrational frequencies from femtosecond stimulated Raman spectra

Wu, Yue-Chao; Zhao, Bin; Lee, Soo-Ying

2016

Wu, Y.-C., Zhao, B., & Lee, S. Y. (2016). Time-dependent wave packet averaged vibrational frequencies from femtosecond stimulated Raman spectra. *The Journal of Chemical Physics*, 144(5), 054104-.

<https://hdl.handle.net/10356/86606>

<https://doi.org/10.1063/1.4941057>

© 2016 AIP Publishing LLC. This paper was published in *The Journal of Chemical Physics* and is made available as an electronic reprint (preprint) with permission of AIP Publishing LLC. The published version is available at: [<http://dx.doi.org/10.1063/1.4941057>]. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper is prohibited and is subject to penalties under law.

Downloaded on 26 Apr 2023 19:46:13 SGT

Time-dependent wave packet averaged vibrational frequencies from femtosecond stimulated Raman spectra

Yue-Chao Wu, Bin Zhao, and Soo-Y. Lee^{a)}

*Division of Physics & Applied Physics, and Division of Chemistry & Biological Chemistry,
School of Physical & Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore*

(Received 16 November 2015; accepted 19 January 2016; published online 2 February 2016)

Femtosecond stimulated Raman spectroscopy (FSRS) on the Stokes side arises from a third order polarization, $P^{(3)}(t)$, which is given by an overlap of a first order wave packet, $|\Psi_2^{(1)}(pu, t)\rangle$, prepared by a narrow band (ps) Raman pump pulse, $E_{pu}(t)$, on the upper electronic e_2 potential energy surface (PES), with a second order wave packet, $\langle\Psi_1^{(2)}(pr^*, pu, t)|$, that is prepared on the lower electronic e_1 PES by a broadband (fs) probe pulse, $E_{pr}(t)$, acting on the first-order wave packet. In off-resonant FSRS, $|\Psi_2^{(1)}(pu, t)\rangle$ resembles the zeroth order wave packet $|\Psi_1^{(0)}(t)\rangle$ on the lower PES spatially, but with a force on $|\Psi_2^{(1)}(pu, t)\rangle$ along the coordinates of the reporter modes due to displacements in the equilibrium position, so that $\langle\Psi_1^{(2)}(pr^*, pu, t)|$ will oscillate along those coordinates thus giving rise to similar oscillations in $P^{(3)}(t)$ with the frequencies of the reporter modes. So, by recovering $P^{(3)}(t)$ from the FSRS spectrum, we are able to deduce information on the time-dependent quantum-mechanical wave packet averaged frequencies, $\bar{\omega}_j(t)$, of the reporter modes j along the trajectory of $|\Psi_1^{(0)}(t)\rangle$. The observable FSRS Raman gain is related to the imaginary part of $P^{(3)}(\omega)$. The imaginary and real parts of $P^{(3)}(\omega)$ are related by the Kramers-Kronig relation. Hence, from the FSRS Raman gain, we can obtain the complex $P^{(3)}(\omega)$, whose Fourier transform then gives us the complex $P^{(3)}(t)$ to analyze for $\bar{\omega}_j(t)$. We apply the theory, first, to a two-dimensional model system with one conformational mode of low frequency and one reporter vibrational mode of higher frequency with good results, and then we apply it to the time-resolved FSRS spectra of the *cis-trans* isomerization of retinal in rhodopsin [P. Kukura *et al.*, *Science* **310**, 1006 (2005)]. We obtain the vibrational frequency up-shift time constants for the C₁₂-H wagging mode at 216 fs and for the C₁₀-H wagging mode at 161 fs which are larger than for the C₁₁-H wagging mode at 127 fs, i.e., the C₁₁-H wagging mode arrives at its final frequency while the C₁₂-H and C₁₀-H wagging modes are still up-shifting to their final values, agreeing with the findings of Yan *et al.* [*Biochemistry* **43**, 10867 (2004)]. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4941057>]

I. INTRODUCTION

Spectroscopy can be described in either the time or frequency domains, and in principle they carry the same amount of information and are related by a Fourier transform.¹ 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 finite spectral and temporal resolutions, and the choice between the two domains is usually determined by the complexity of the system. Small and simple systems may be appropriately described in the frequency domain, while the time domain description is preferred for large and complex systems. The time-dependent picture for applications in spectroscopy has been formulated with an intuitive representation by wave packets,^{2,3} and Raman spectroscopy has been effectively described in terms of wave packet theory.^{4–8}

Recently, time-resolved femtosecond stimulated Raman spectroscopy (FSRS), or 2D-FSRS, with the delay time

between actinic pump and probe pulses in one dimension and the dispersed FSRS spectrum in the other dimension, has been developed to study structural changes in ultrafast photophysical and photochemical processes.^{9–23} In 2D-FSRS, a femtosecond off-resonant impulsive or resonant actinic pump pulse initializes the dynamics by preparing a coherent wave packet on either the ground^{16,24} or excited¹⁴ electronic state, respectively. The subsequent dynamics are then monitored 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 appears to offer simultaneous high temporal and spectral resolutions for vibrational modes. The temporal resolution is determined by the ultrashort fs impulsive/actinic pump and probe pulses, and the spectral resolution is due to the vibrational free induction decay which is determined by the vibrational dephasing and the decay of the ps Raman pump pulse.^{15,17} Since the temporal and spectral resolutions are independently determined by different pulses and the vibrational dynamics, they are not related by a Fourier transform and so the Heisenberg time-energy uncertainty principle does not apply.

^{a)} Author to whom correspondence should be addressed. Electronic mail: sooying@ntu.edu.sg

Temporal and spectral resolutions in the traditional pump-probe experiments have been discussed for integrated and dispersed detection schemes.^{25,26} The integrated signal is recorded as the time-integrated signal intensity within the probe pulse duration as a function of pump-probe delay time. 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 the probe pulse is broad and 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 the polarization decay time or free induction decay (FID) time, rather than the probe pulse duration.²⁵

This issue has been discussed in some detail by different groups in the context of FSRS.^{27,28} Mukamel and Biggs²⁷ was of the view that FSRS may not be able to reveal “real-time” dynamics at the time of the probe pulse, even though it uses an ultrashort probe pulse to stimulate the Raman process. By noting that FSRS gain is obtained as the ratio of dispersed signals in the probe pulse direction for Raman pump-on and pump-off minus one, it is explained in analogy to pump-probe experiments that the observed spectra are generated in a much longer time period after the probe pulse and so the peak positions of the FSRS gain will not give a high resolution snapshot of the vibrational frequencies at the time of the probe pulse. We wish to show that a high resolution snapshot of the (quantum mechanical wave packet averaged) vibrational frequencies is in fact contained in the time-dependent third-order polarization, $P^{(3)}(t)$, and not in the FSRS spectra, and we can invert the latter to obtain $P^{(3)}(t)$.

In the quantum theory for FSRS, it has been shown that, in the rotating wave approximation, the Raman gain spectrum is described by eight Feynman dual time-line diagrams, which can be grouped under 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).^{29,30} 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 can be intermediate state population in the HL terms.²⁹ When the Raman pump and probe pulses are off-resonant, it has been shown that (a) the SRS(II) and IRS(II) processes give rise to broad featureless spectra, determined by the spectrum of the ultrashort probe pulse, and they cancel each other out on summation, (b) the SRS(I) spectrum accounts for the Stokes lines, and (c) the IRS(I) spectrum accounts for the anti-Stokes lines. The width of the Stokes and anti-Stokes lines is largely determined by the vibrational dephasing time and the decay of the Raman pump pulse. We will be dealing with off-resonant Stokes FSRS and so our focus is on the SRS(I) term.

In Sec. II, we present the theory for off-resonant FSRS and show how to invert the FSRS signal to obtain the third-order polarization. A two-dimensional model potential with a low-frequency conformational mode and a high-frequency reporter mode, and how wave packets are propagated in the adiabatic approximation are described in Sec. III. The calculated results

and discussion on high-time and high-frequency resolution in off-resonant FSRS signals for: (a) the two-dimensional model potential and (b) Kukura *et al.*'s¹⁵ observed time-resolved femtosecond stimulated Raman spectra from 200 fs to 2 ps of reactive rhodopsin in the hydrogen-out-of-plane (HOOP) region are presented in Sec. IV. We conclude in Sec. V.

II. THEORY

The pulse sequence for FSRS is shown in Fig. 1(a), illustrated with three electronic states (g , e_1 , and e_2) and each has a two-dimensional potential energy surface with a low frequency conformational mode Q and a high frequency reporter mode q , with the contour potential energy surfaces for e_1 and e_2 shown in Fig. 1(b). There is a displacement along the reporter mode q between the e_1 and e_2 potential energy surfaces to give a Raman signal. A fs actinic pump pulse, with electric field $E_{Apu}(t)$ and wavevector $\mathbf{k}_1$, sends a wave packet from the ground electronic state, g , to an excited electronic state e_1 to initiate a reaction. We will designate the wave packet prepared on e_1 as a zeroth order wave packet $|\Psi_1^{(0)}(t)\rangle$.

FIG. 1. Two-dimensional (2D) model potential energy surfaces (PESs) with one low frequency conformational mode Q and another high frequency (reporter) vibrational mode q for femtosecond stimulated Raman spectroscopy. (a) Cut of the PESs along the conformational coordinate Q , where the ground electronic state, g , PES is given by the black dotted line, the first excited electronic state, e_1 , PES is given by the blue solid curve, and the second excited electronic state, e_2 , PES is given by the red dash line. The green curve represents the initial wave packet. (b) Contour plot of the 2D PESs with blue solid curve for the e_1 PES and red dash curve for the e_2 PES, and the initial wave packet is shown in green. The energy unit in both plots is in $\hbar\omega_0$. The two excited PESs have a large energy gap of $\epsilon \hbar\omega_0$, and a relative displacement along the reporter coordinate. The initial wave packet on the e_1 PES is created by an impulsive actinic pump pulse acting on the lowest eigenstate of the g PES, and as it evolves it is monitored by femtosecond stimulated Raman spectroscopy.

The latter evolves on the potential energy surface of e_1 , slowly along the conformational coordinate Q , as shown in Fig. 1(b). The dynamics on the e_1 potential energy surface is monitored by off-resonant FSRS with a pair of narrowband (ps) Raman pump pulse, $\{E_{pu}(t), \mathbf{k}_2\}$, and broadband (fs) probe pulse, $\{E_{pr}(t), \mathbf{k}_3\}$. The probe pulse which stimulates the Raman scattering is delayed by a time T from the actinic pump pulse. The FSRS Raman gain is measured along $\mathbf{k}_3$ as the ratio of the intensity of pump-on divided by pump-off minus one.¹⁷

It has been shown^{29,30} that off-resonant Stokes FSRS can be described by a third order polarization with just the SRS(I) term,

$$P^{(3)}(t) = \langle \Psi_1^{(2)}(pr, pu, t) | \mu_{21} | \Psi_2^{(1)}(pu, t) \rangle, \quad (1)$$

which is an overlap between a first-order wave packet prepared on e_2 by the Raman pump pulse,

$$\begin{aligned} |\Psi_2^{(1)}(pu, t)\rangle &= \frac{i}{\hbar} \int_0^t \exp(-i\hat{H}_2(t-t')/\hbar) \\ &\times E_{pu}(t') \mu_{21} |\Psi_1^{(0)}(t')\rangle dt', \end{aligned} \quad (2)$$

and a second-order wave packet that is prepared on e_1 by the fs probe pulse acting on this first-order wave packet,

$$\begin{aligned} |\Psi_1^{(2)}(pr, pu, t)\rangle &= \frac{i}{\hbar} \int_0^t \exp(-i\hat{H}_1(t-t')/\hbar) \\ &\times E_{pr}(t') \mu_{12} |\Psi_2^{(1)}(pu, t')\rangle dt'. \end{aligned} \quad (3)$$

In the equations, μ_{ji} denotes the transition dipole moment from electronic state i to electronic state j ; $\hat{H}_i$ denotes the vibrational Hamiltonian for electronic state i ; $E_{pu}(t)$ and $E_{pr}(t)$ denote the laser fields for the Raman pump and probe pulse, respectively, which may be taken to have a Gaussian envelope,

$$E_{s=pu,pr}(t) = \mathcal{E}_{s=pu,pr} \exp\left(-2 \ln 2 \frac{t^2}{\delta_s^2}\right) \cos(\omega_s t + \varphi_s), \quad (4)$$

where $\mathcal{E}_s$ is a constant field amplitude; δ_s is the full width at half maximum (FWHM); and ω_s, φ_s are the pulse central frequency and phase, respectively. The time-dependent wave packets are functions of the conformational coordinate Q and reporter vibrational coordinate q . Each (harmonic) reporter mode frequency, $\omega(Q)$, could depend on Q . Clearly, $P^{(3)}(t)$ is initiated with the arrival of the probe pulse and it decays with vibrational dephasing on e_1 as well as with the fall-off in the Raman pump pulse. In general, the quantum-mechanical expression for the third-order polarization, Eq. (1), for FSRS from a *non-stationary vibrational state*, as is the case in this work, cannot be written simply as a product of the derivative of the classical polarizability and a time-dependent vibrational amplitude.³¹

In off-resonant FSRS, the wave packets $\Psi_1^{(0)}(t)$ and $\Psi_2^{(1)}(t)$ mirror each other in spatial distribution, as $\Psi_1^{(0)}(t)$ that is brought up from e_1 to e_2 at each instant of time by the Raman pump to create $\Psi_2^{(1)}(t)$ exists for a vanishingly short period of time due to the off-resonance condition. The ultrashort probe pulse stimulation brings $\Psi_2^{(1)}(T)$ down to the e_1 surface to create $\Psi_1^{(2)}(t)$, and because of the force of the displaced potential energy surfaces, $\Psi_1^{(2)}(t)$ makes small oscillations along the reporter mode coordinate q as it moves along

the conformational coordinate Q . So, the oscillations in $P^{(3)}(t)$ will give the time-dependent wave packet averaged vibrational frequencies of the reporter modes especially at times close to the probe pulse stimulation before the wave packet $\Psi_1^{(2)}(t)$ spreads, when $P^{(3)}(t)$ is recovered from the observed Raman gain spectrum.

We look at the conventional four-wave mixing FSRS experiment where the FSRS Raman gain, $\Delta I_{RG}(\omega)$, is given by the ratio of the dispersed signals in the probe pulse direction for Raman pump-on and pump-off minus one. The Raman gain (RG) cross section, $\sigma_{RG}(\omega)$, which is directly proportional to $\Delta I_{RG}(\omega)$, is given by

$$\begin{aligned} \sigma_{RG}(\omega) &= C' \Delta I_{RG}(\omega) / |E_{pr}(\omega)|^2 \\ &= C \omega \text{Im} \left\{ P^{(3)}(\omega) / E_{pr}(\omega) \right\}, \end{aligned} \quad (5)$$

where C' and C are collections of constants, and $P^{(3)}(\omega)$ and $E_{pr}(\omega)$ are Fourier transforms of the corresponding time-dependent functions. We can define the linear response susceptibility,

$$\chi(\omega) = P^{(3)}(\omega) / E_{pr}(\omega) = \chi_1(\omega) + i \chi_2(\omega), \quad (6)$$

where the real and imaginary parts satisfy the Kramers-Kronig relation,³²

$$\begin{aligned} \chi_1(\omega) &= \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\omega' \chi_2(\omega')}{\omega'^2 - \omega^2} d\omega' \\ &= \text{Re} \{ P_{SRS(I)}^{(3)}(\omega) / E_{pr}(\omega) \}, \end{aligned} \quad (7)$$

with $\mathcal{P}$ denoting the Cauchy principal value. So, from the observable Raman gain cross section, we have $\chi_2(\omega)$, and we use the Kramers-Kronig relation, Eq. (7), to calculate $\chi_1(\omega)$, and then $P^{(3)}(\omega)$, Eq. (6), followed by the time-dependent third-order polarization by an inverse Fourier transform,

$$P^{(3)}(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty e^{-i\omega t} P^{(3)}(\omega) d\omega. \quad (8)$$

The reconstruction of the third-order polarization $P^{(3)}(t)$ from the observable FSRS spectrum is based on exact mathematical relations given by Eqs. (5)–(8) which are independent of the spectral width of the Raman pump and the temporal width of the probe pulse.

For off-resonant Stokes FSRS, it can be shown^{27,28,33} that if the probe pulse is nearly impulsive, as is the case with the experiments, then the third-order polarization for a single reporter mode is given by

$$\begin{aligned} P^{(3)}(t) &\approx \mathcal{A} \exp\left(-2 \ln 2 \frac{(t-T)^2}{\delta_{pu}^2}\right) \\ &\times \exp\left(-i\omega_{pu}(t-T) + i \int_T^t \bar{\omega}(\tau) d\tau - \gamma(t-T)\right), \end{aligned} \quad (9)$$

where $\mathcal{A}$ is a collection of constants, δ_{pu} is the full width at half maximum (FWHM), ω_{pu} is the central frequency of the Raman pump pulse, and γ is the dephasing rate of the reporter mode; and the time-dependent wave packet averaged frequency $\bar{\omega}(t)$ of the reporter mode is given by

$$\bar{\omega}(t) = \langle \Psi_1^{(0)}(t) | \omega(Q) | \Psi_1^{(0)}(t) \rangle, \quad (10)$$

where $\omega(Q)$ is the frequency of the reporter mode which may depend on the conformational coordinate Q . The FSRS spectrum is taken relative to the position of the Rayleigh line, and so the rapidly oscillating term $\exp(-i\omega_{pu}(t-T))$ in Eq. (9) at the Rayleigh frequency can be omitted, and the third-order polarization takes on a simpler form,

$$P^{(3)}(t) \approx A(t) \exp\left(i \int_T^t \bar{\omega}(\tau) d\tau\right) = A(t) \exp(i\phi(t)), \quad (11)$$

where the envelope $A(t)$ is given by

$$A(t) = \mathcal{A} \exp\left(-2 \ln 2 \frac{(t-T)^2}{\delta_{pu}^2} - \gamma(t-T)\right). \quad (12)$$

The envelope of the finite duration Raman pump, which need not be monochromatic, appears in Eqs. (9) and (11). Here, the probe pulse has to be sufficiently impulsive, as a fraction of the vibrational period of the reporter mode, so that the second order wave packet $\Psi_1^{(2)}(t)$ resembles $\Psi_2^{(1)}(t)$ or $\Psi_1^{(0)}(t)$ except that it receives a kick along the reporter mode due to the displaced potentials between e_1 and e_2 . A longer probe pulse would lead to a more smeared out wave packet in $\Psi_1^{(2)}(t)$ along the reporter mode and the simple form for the phase in Eqs. (9) and (11) may get less accurate.

III. MODEL POTENTIALS AND WAVE PACKET PROPAGATION

The molecular Hamiltonian for our three electronic states (g, e_1, e_2) model, shown in Fig. 1, is given by

$$\hat{H} = |g\rangle \hat{H}_g \langle g| + |e_1\rangle \hat{H}_{e_1} \langle e_1| + |e_2\rangle \hat{H}_{e_2} \langle e_2|, \quad (13)$$

where each two-dimensional (2D) vibrational Hamiltonian $\hat{H}_j$ has a conformational mode (c) with coordinate Q and a harmonic vibrational reporter mode (r) with coordinate q ,

$$\hat{H}_j = \hat{h}_{c,j} + \hat{h}_{r,j}, \quad (14)$$

where

$$\hat{h}_{c,j} = \beta \hbar \omega_0 \left\{ -\frac{1}{2} \frac{\partial^2}{\partial Q^2} + \frac{1}{\beta} v_j(Q) \right\}, \quad (15)$$

$$\hat{h}_{r,j} = \hbar \omega_Q \left\{ -\frac{1}{2} \frac{\partial^2}{\partial q^2} + \frac{1}{2} (q - q_{j,0})^2 \right\}. \quad (16)$$

In Eq. (15), β is a small constant which ensures a slow motion in the conformational mode relative to a fast motion in the reporter mode, and ω_0 is the reporter vibrational frequency at $Q = 0$. The potentials for the conformational mode, in units of $\hbar \omega_0$, are similar to those used by Cina and Kovac,³⁴

$$v_g(Q) = k \left\{ \frac{4}{5} + \frac{4}{3\sqrt{5}} Q - Q^2 + \frac{5}{6} Q^4 \right\}, \quad (17)$$

$$v_{e_1}(Q) = k \left\{ \frac{4}{5} - \frac{4}{3\sqrt{5}} Q - Q^2 + \frac{5}{6} Q^4 \right\}, \quad (18)$$

$$v_{e_2}(Q) = v_{e_1}(Q) + \varepsilon, \quad (19)$$

where k is a constant. The energy gap between the two excited state potentials is given by $\varepsilon \hbar \omega_0$. Since we are dealing with off-resonant FSRS, a different potential energy shape for e_2 will not affect the results, as the wave packet $\Psi_2^{(1)}(t)$ exists for

a vanishingly short period of time due to the off-resonance condition and will be largely independent of the potential energy shape for e_2 . In Eq. (16), the reporter mode frequency is dependent on the conformational coordinate,

$$\omega_Q = \omega_0 |1 - \lambda Q^2|, \quad (20)$$

where λ is a constant. The equilibrium positions for the reporter mode harmonic oscillators are chosen to be independent of Q ,

$$q_{g,0} = q_{e_1,0} = 0, \quad (21)$$

$$q_{e_2,0} = q_0, \quad (22)$$

where the finite displacement q_0 between the e_2 and e_1 potentials gives rise to the reporter mode FSRS signal. The potential energy surfaces in units of $\hbar \omega_0$ are shown in Fig. 1 with $k = 3$ and $\lambda = 0.09$. The purpose of the ground state potential g is just to provide an initial wave packet for the actinic pulse (taken to be a δ -function here) to initiate a reaction on e_1 .

There are numerical procedures^{35,36} to solve the low dimensional time-dependent Schrödinger equation exactly for the wave packet motion,

$$i\hbar \frac{\partial}{\partial t} |\Psi_j\rangle = \hat{H}_j |\Psi_j\rangle. \quad (23)$$

However, they can be slow and time consuming. A faster and equally accurate procedure for the potentials here is to use the adiabatic approximation with separation of motion of the high frequency reporter mode from the low frequency conformational mode, just like for an electronic-vibrational adiabatic separation of motion. The wave packet can be written as

$$|\Psi_j(q, Q, t)\rangle = \sum_{n_j} C_{n_j} |n_j\rangle |\psi_{n_j}(Q, t)\rangle, \quad (24)$$

where C_{n_j} is a complex number which is determined by the known initial wave packet, $|n_j\rangle$ is a harmonic oscillator eigenfunction of the reporter mode with eigenenergy $(n_j + \frac{1}{2})\hbar \omega_Q$, and $|\psi_{n_j}(Q, t)\rangle$ represents the wave packet for the conformational motion. The Hamiltonian for wave packet propagation can then be expressed as

$$\hat{H}_j = \hat{h}_{c,j} + \sum_{n_j} |n_j\rangle \left\{ (n_j + \frac{1}{2})\hbar \omega_Q - i\gamma_{n_j} \right\} \langle n_j|, \quad (25)$$

where we have added a dephasing term with vibrational dephasing rate γ_{n_j} in the reporter mode which includes both the finite lifetime and pure dephasing.

IV. RESULTS AND DISCUSSION

We first look at recovering the time-dependent wave packet averaged vibrational frequency of the reporter mode from the calculated FSRS spectra of the 2D model above. Then, we recover the time-dependent vibrational frequencies of the HOOP modes from the experimental time-resolved FSRS spectra of rhodopsin.

TABLE I. Parameters for two-dimensional potential model.

	β	λ	ω_0	k	q_0	ϵ	γ_{01}	$\gamma_{n1}(n > 0)$	γ_{n2}	δ_{pu}	ω_{pu}	φ_{pu}	δ_{pr}	ω_{pr}	φ_{pr}
(a)	3×10^{-4}														
(b)	2×10^{-5}	0.09	10^3 cm^{-1}	3	0.70	20	0	50 cm^{-1}	100 cm^{-1}	1 ps	$12\omega_0$	0	10 fs	$11\omega_0$	0

A. Frequency recovery from FSRS spectra of 2D model

The parameters for the 2D potentials and the FSRS pulses are given in Table I. Calculations were made for two values of β , where the lower value corresponds to a slower motion of the wave packet along the conformational mode. The frequency of the conformational mode is very much smaller than the reporter vibrational mode. We have set $\omega_0/2\pi c = 1000 \text{ cm}^{-1}$ for the reporter mode at $Q = 0$ and this sets the time scale for the dynamics.

The ground vibrational state of the ground electronic state, g , surface is instantaneously placed on the e_1 surface at time $t = 0$ by a δ -function actinic pump pulse. The wave packet evolves and the FSRS spectrum is calculated at various time delays T between the fs probe pulse and the actinic pump pulse.

In Fig. 2 we show how the time-dependent wave packet averaged vibrational frequency of the reporter mode is recovered from the Raman gain spectrum. The calculated Raman gain spectrum for the fast conformational mode case, $\beta = 3 \times 10^{-4}$, for a time delay $T = 0.6 \text{ ps}$ is shown in Fig. 2(a). Using Eqs. (5) and (6), we obtain the imaginary part of the susceptibility $\chi_2(\omega)$ shown in Fig. 2(b). The Kramers-Kronig relation, Eq. (7), is used to calculate the real part of the susceptibility $\chi_1(\omega)$ shown in Fig. 2(c). An inverse Fourier transform of the product of the susceptibility and the probe spectrum gives the time-dependent third order polarization shown in Fig. 2(d), with the real part in blue and the imaginary part in red and begins with the arrival of the probe pulse at about 0.6 ps. The envelope $A(t) = |P^{(3)}(t)|$ is shown in Fig. 2(e), and the complex oscillatory function $\exp(i \int_T^t \bar{\omega}(\tau) d\tau)$ of $P^{(3)}(t)$ is shown in Fig. 2(f), from which the phase $\phi(t)$ is extracted and shown in Fig. 2(g).

FIG. 2. Flow chart for recovering the time-dependent wave packet averaged vibrational frequency from the FSRS spectrum: (a) Raman gain spectrum, $\Delta I_{RG}(\omega)$, calculated for a delay time of 0.6 ps for the fast conformational motion with the potentials in Fig. 1. (b) Imaginary part of the susceptibility, $\chi_2(\omega)$, calculated from $\Delta I_{RG}(\omega)$. (c) Real part of the susceptibility, $\chi_1(\omega)$, calculated by Kramers-Kronig relation from $\chi_2(\omega)$. (d) Time-dependent third order polarization $P^{(3)}(t)$ by inverse Fourier transform of the susceptibility $\chi(\omega)$ where the red and blue traces denote the real and imaginary parts, respectively, and begins with the arrival of the probe pulse at about 0.6 ps. (e) Envelope $A(t)$ of $P^{(3)}(t)$. (f) Sinusoidal oscillations of $P^{(3)}(t)$ after removing $A(t)$. (g) Time-dependent phase, $\phi(t)$, of the polarization. (h) Recovered time-dependent wave packet averaged vibrational frequency, $\bar{\omega}(t)$, starting at about 0.6 ps, calculated by the derivative of phase $\phi(t)$ (blue line), as compared with the actual $\bar{\omega}(t)$ calculated from the zeroth-order wave packet evolving on the e_1 PES (black line).

The derivative $d\phi/dt$ gives the time-dependent vibrational frequency shown by the solid blue line in Fig. 2(g) and compared with the time-dependent wave packet averaged vibrational frequency $\bar{\omega}(t)$ calculated by Eq. (10) with the zeroth-order wave packet and shown by the thin solid line in Fig. 2(h). The agreement is good before the first and second order wave packets spread too much after the arrival of the probe pulse. One can qualitatively explain why $\bar{\omega}(t)$ recovered from the FSRS spectrum, which arises from the overlap of $\Psi_2^{(1)}(t)$ with $\Psi_1^{(2)}(t)$, may deviate from $\bar{\omega}(t)$ calculated by Eq. (10) using just $\Psi_1^{(0)}(t)$, at longer times, as being due to the difference in the spread of the wave packets $\Psi_2^{(1)}(t)$ and $\Psi_1^{(2)}(t)$ over time. This spread would depend on the initial conditions of the wave packets, the extent of the wave packet distribution, and the form of primarily the e_1 potential energy surface.

The calculated Raman gain spectra for the fast conformational mode case, $\beta = 3 \times 10^{-4}$, for time delays from $T = 0.3$ – 1.3 ps, in steps of 100 fs are shown in Fig. 3(a). Following the procedure just described, the recovered real part of the time-dependent third-order polarizations is shown in Fig. 3(b), and the recovered time-dependent vibrational frequencies are shown by the thick lines in Fig. 3(c), in

good agreement with the time-dependent zeroth-order wave packet averaged vibrational frequency $\bar{\omega}(t)$ shown by the thin line over several cycles of motion along the conformational coordinate. The important point is that we can recover the time-dependent wave packet averaged vibrational frequency of the reporter mode from the Raman gain spectrum. Clearly, there is temporal resolution for the vibrational dynamics after the fs probe pulse. In Fig. 3(a), each solid dot gives the zeroth-order wave packet averaged vibrational frequency of the reporter mode at the peak of the probe pulse which can differ significantly from the peak position of the Raman gain spectrum. By taking the average of the recovered frequency in Fig. 3(c) over the decaying pump pulse envelope and dephasing time, we obtain the crosses in Fig. 3(a) which match the peak positions of the Raman gain spectra. It reflects the fact that the Raman gain spectrum depends on the entire trajectory of the frequency $\bar{\omega}(\tau)$ from the stimulation time T onwards. So, the high frequency resolution is contained in the time-dependent third-order polarization and not in the peak position of the Raman gain spectrum.

In Fig. 4, we show similar calculations for the slow conformation mode case with $\beta = 2 \times 10^{-5}$, for time delays

FIG. 3. Recovering the time-dependent wave packet averaged vibrational frequency for the case of fast conformational motion where $\beta = 3.0 \times 10^{-4}$: (a) Calculated FSRS spectra for different time delays from 0.3 ps to 1.3 ps. Each solid circular dot is placed at the time-dependent wave packet averaged vibrational frequency at the time of arrival of the probe pulse, and each cross is placed at the pump pulse averaged time-dependent vibrational frequency after the arrival of the probe pulse. (b) Real part of the recovered time-dependent polarization $P^{(3)}(t)$ for the corresponding spectra. (c) Recovered time-dependent wave packet averaged vibrational frequencies, $\bar{\omega}(t)$, (colored lines) from the various time-delayed polarizations in (b) compared with the actual $\bar{\omega}(t)$ (black line). The more rapid spread of the second-order wave packet created by the probe pulse in this fast conformational motion means that the recovered $\bar{\omega}(t)$ tends to be good for times nearer the probe pulse than further away.

FIG. 4. Similar to Fig. 3 but with slow conformational motion where $\beta = 2.0 \times 10^{-5}$. The recovered $\bar{\omega}(t)$ in (c) is very much better than for the fast conformational motion case as the second-order wave packet created by the probe pulse spreads slowly. The solid circular dots and crosses are also in better agreement with the peaks of the FSRS spectra shown in (a).

from $T = 1.2$ – 5.4 ps, in steps of 200 fs. The wave packet moves slowly along the conformation mode Q , and the results will be more classical-like. Here, the agreement between the recovered time-dependent vibrational frequencies and the time-dependent zeroth-order wave packet averaged vibrational frequency $\bar{\omega}(t)$ is even better than for the fast conformation mode case, as shown in Fig. 4(c), because the wave packets have remained somewhat localized over the duration of the pump pulse. Similarly the dots and crosses in Fig. 4(a) are closer to each other and to the peak position of each Raman gain spectrum.

B. Frequency recovery from FSRS spectra of isomerization of retinal in rhodopsin

We have applied the theory to recover the time-dependent vibrational frequencies of the four modes directly involved in the light-induced 11-*cis* to all-*trans* isomerization of retinal in rhodopsin. Kukura *et al.*¹⁴ had previously given a molecular depiction of the rhodopsin retinal structure and we follow the labelling of C_{10} , C_{11} , and C_{12} there. The experimental time-resolved FSRS spectra of the HOOP region of the isomerizing retinal from 200 fs to 2 ps are shown in Fig. 5(a) as solid lines. The tails of each spectrum have been smoothed as shown by the dash lines. Each FSRS spectrum is divided into three regions as shown in Fig. 5(b): (i) concerted HOOP mode

FIG. 5. (a) Experimental rhodopsin HOOP mode time-resolved FSRS spectra of Kukura *et al.*¹⁴ at time delays from 200 fs to 2 ps, shown as solid line with smoothing of the tails shown as red dash lines. (b) Partitioning of each FSRS spectrum into 3 regions corresponding to: (i) Concerted HOOP mode in blue (right), (ii) C_{11} –H wagging mode in green (middle), and (iii) C_{10} –H and C_{12} –H wagging modes where the two frequencies are close together in red (left), for frequency recovery.

FIG. 6. Concerted HOOP mode: (a) Time-resolved FSRS spectra. (b) Recovered real part of the time-dependent third-order polarization. (c) Recovered $\bar{\omega}(t)$ is shown as red solid squares and is nearly constant at $959 \pm 3 \text{ cm}^{-1}$ (red line).

in blue (right) which are Lorentzian-like, (ii) $\text{C}_{11}\text{-H}$ wagging mode in green (middle) where the spectra are dispersive for delay times between 200 and 300 fs, and Lorentzian-like thereafter, and (iii) $\text{C}_{10}\text{-H}$ and $\text{C}_{12}\text{-H}$ wagging modes where the two frequencies are close together in red (left) where the spectra arises from the superposition of the polarization from the two modes.

The time-resolved FSRS spectra for the concerted HOOP mode from 200 fs to 2 ps are shown in Fig. 6(a). The real part of the recovered time-dependent third-order polarizations is shown in Fig. 6(b), and we obtain the wave packet averaged frequency from each of them at a point close to the arrival time of the respective probe pulses and shown as red square dots in Fig. 6(c). Clearly, the frequency of this mode is nearly

FIG. 7. Similar to Fig. 6, but for the $\text{C}_{11}\text{-H}$ wagging mode: (a) Time-resolved FSRS spectra. (b) Recovered real part of the time-dependent third-order polarization. (c) Recovered $\bar{\omega}(t)$ are shown as red solid squares with the best fit based on Eq. (26) given by the red line.

FIG. 8. (a) Overlapping time-resolved FSRS spectra for C₁₀-H and C₁₂-H wagging modes. (b) Recovered real part of the time-dependent third-order polarization with the removal of an exponential decay for a dephasing time constant of 620 fs. The envelope of the third-order polarization gives the beating of the two modes. (c) Recovered $\bar{\omega}(t)$ are shown as solid squares—red for the C₁₀-H wag and blue for the C₁₂-H wag, with the best fit based on Eq. (26) given by the solid lines.

constant with time and shown by a straight line fit at 959 cm⁻¹. The envelopes of the polarizations give a dephasing time of about 620 fs.

In Fig. 7(a), we show the time-resolved FSRS spectra for the C₁₁-H wagging mode from 200 fs to 2 ps, with the real part of the recovered time-dependent third-order polarizations shown in Fig. 7(b) and the wave packet averaged frequencies shown as red square dots in Fig. 7(c). From the recovered third-order polarizations in Fig. 7(b), we can infer that the quality of the experimental FSRS signal for this mode in Fig. 7(a) at short delay times of 200–250 fs is not so good, as gauged from the envelope of the third-order polarization which does not follow the shape of the decay as given by Eq. (12). However, the third-order polarizations for delay times of about 300 fs onwards appear to be good, and so we use them to obtain the frequency points in Fig. 7(c). The envelope of the time-dependent third-order polarization gives a dephasing time of about 620 fs, and this asymptotic final value of the frequency is $\bar{\omega}_f = 915.0$ cm⁻¹. This leaves just two parameters in the frequency expression,

$$\bar{\omega}(t) = \bar{\omega}_f - (\bar{\omega}_f - \bar{\omega}_{t=200}) \times \exp(-(t - 200)/\Gamma), \quad t \geq 200 \text{ fs}, \quad (26)$$

where $\bar{\omega}_{t=200}$ is the wave packet averaged frequency at 200 fs, and Γ is the frequency upshift constant, to be determined by a least square fit curve and we obtained $\bar{\omega}_{t=200} = 875.0$ cm⁻¹ and $\Gamma = 127$ fs.

The C₁₀-H and C₁₂-H wagging modes have frequencies that are close together, which makes it impossible to separate the spectra as shown in Fig. 8(a). The recovered time-dependent third-order polarizations will show a superposition of the two modes. After peeling away the dephasing time of

620 fs, each of the real part of the time-dependent third-order polarizations in Fig. 8(b) has an envelope that shows the beat between the two frequencies, and we can also obtain the average frequency of the two modes from the fast oscillations. Thus we can obtain the frequencies for the two modes and these are shown by the red square dots for the C₁₀-H wagging mode and by the blue square dots for the C₁₂-H wagging mode in Fig. 8(c). The parameters for the best fit lines using Eq. (26) are given in Table II together with those of the C₁₁-H wagging mode.

Kukura *et al.*,¹⁴ McCamant,²⁸ and Mukamel and Biggs²⁷ had all assumed a common frequency up-shifting time constant for all three wagging modes in their simulations of the spectra. However, there is no reason for this assumption to be true since the environment for all three modes are different. We are able to avoid this assumption as we make a direct inversion of the FSRS spectra and not a simulation of the spectra, and so we are able to obtain three different up-shifting time constants. The vibrational frequency upshift time constants Γ for the C₁₂-H wagging mode at 216 fs and for the C₁₀-H wagging mode at 161 fs are larger than for the C₁₁-H wagging mode at 127 fs. These results are consistent with the DFT calculations of Yan *et al.*³⁷ who found that the

TABLE II. Initial and final vibrational frequencies and frequency upshift constant of rhodopsin HOOP modes.

	$\bar{\omega}_{t=200}$ (cm ⁻¹)	$\bar{\omega}_f$ (cm ⁻¹)	Γ (fs)
C ₁₀ -H	798.1	867.0	161
C ₁₁ -H	875.0	915.0	127
C ₁₂ -H	782.8	847.0	216

FIG. 9. Comparison of the direct recovery of the time-dependent vibrational frequencies from the experimental spectra (red solid square dots) as described in this work for the C_{12} -H, C_{10} -H, and C_{11} -H wagging modes with the time-dependent vibrational frequencies used in simulations of the FSRs spectra by Kukura *et al.*¹⁴ (open circles), Mukamel and Biggs²⁷ (half-solid circles), and McCamant²⁸ (solid circles).

upshifting time constant for C_{11} -H should be much smaller than for C_{10} -H and C_{12} -H.

Figure 9 compares the direct recovery of the time-dependent vibrational frequencies from the experimental spectra (red solid square dots) as described in this work for the C_{12} -H, C_{10} -H, and C_{11} -H wagging modes with the time-dependent vibrational frequencies used in simulations of the FSRs spectra by Kukura *et al.*¹⁴ (open circles), Mukamel and Biggs²⁷ (half-solid circles), and McCamant²⁸ (solid circles). It had been pointed out by McCamant²⁸ that Kukura *et al.*¹⁴ had used an incorrect equation for the time dependence of the frequency shifts, resulting in a much larger value for the up-shifting time constant Γ . Therefore, in Fig. 9, we see Kukura *et al.*'s results deviating significantly from the rest for all three wagging modes.

V. CONCLUSION

Off-resonant femtosecond stimulated Raman spectroscopy is well suited to monitor the dynamics of a reactive process because the first-order wave packet prepared by the Raman pump pulse resembles the zeroth-order wave packet of the reactive process, and the second-order wave packet created by the ultrashort probe pulse acting on the first-order wave packet has oscillations along the reporter modes due to the displacement of the potential energy surfaces involved along those modes. The high time-resolution arises from the use of an ultrashort actinic pump pulse that initiates the reaction and an ultrashort probe pulse, after a time delay T , that initiates the time-dependent third-order polarization, $P^{(3)}(t)$, giving rise to the Raman signal. The high resolution snapshot of the (quantum mechanical wave packet averaged) vibrational frequencies is contained in $P^{(3)}(t)$ and not in the peak positions of the FSRs spectra. By the use of

the Kramers-Kronig relation, we can recover $P^{(3)}(t)$ from the observed femtosecond stimulated Raman spectra. If the FSRs spectrum can be separated into contributions from individual modes, this direct method for frequency recovery is straightforward to apply. Even for overlapping Raman spectra where two modes are close in frequency, as in the case of the C_{10} -H and C_{12} -H wagging modes in rhodopsin, we can use the beats in $P^{(3)}(t)$ after peeling away the dephasing time to obtain the frequency difference of the two modes and to determine the average time-dependent frequencies from the oscillations in the polarization. If there are three or more modes with overlapping Raman spectra, then we may need to use the conventional method^{14,27,28} to perform simulations of the Raman spectra with functional forms and adjustable parameters for the time-dependent frequencies.

ACKNOWLEDGMENTS

This work was supported by a Nanyang Technological University research Grant No. M4080467 and a Ministry of Education, Singapore, research Grant No. MOE2011-T2-2-087.

¹D. J. Tannor, *Introduction to Quantum Mechanics—A Time-Dependent Perspective* (University Science Books, Sausalito, California, 2006).

²E. J. Heller, *J. Chem. Phys.* **62**, 1544 (1975).

³E. J. Heller, *Acc. Chem. Res.* **14**, 368 (1981).

⁴E. J. Heller, *J. Chem. Phys.* **68**, 2066 (1978).

⁵S. Y. Lee and E. J. Heller, *J. Chem. Phys.* **71**, 4777 (1979).

⁶E. J. Heller, R. L. Sundberg, and D. Tannor, *J. Phys. Chem.* **86**, 1822 (1982).

⁷D. Imre, J. L. Kinsey, A. Sinha, and J. Krenos, *J. Phys. Chem.* **88**, 3956 (1984).

⁸B. R. Johnson, C. Kittrell, P. B. Kelly, and J. L. Kinsey, *J. Phys. Chem.* **100**, 7743 (1996).

⁹D. W. McCamant, P. Kukura, and R. A. Mathies, *Appl. Spectrosc.* **57**, 1317 (2003).

¹⁰P. Kukura, D. W. McCamant, P. H. Davis, and R. A. Mathies, *Chem. Phys. Lett.* **382**, 81 (2003).

- ¹¹D. W. McCamant, P. Kukura, S. W. Yoon, and R. A. Mathies, *Rev. Sci. Instrum.* **75**, 4971 (2004).
- ¹²P. Kukura, D. W. McCamant, and R. A. Mathies, *J. Phys. Chem. A* **108**, 5921 (2004).
- ¹³D. W. McCamant, P. Kukura, and R. A. Mathies, *J. Phys. Chem. B* **109**, 10449 (2005).
- ¹⁴P. Kukura, D. McCamant, S. Yoon, D. Wandschneider, and R. A. Mathies, *Science* **310**, 1006 (2005).
- ¹⁵P. Kukura, S. Yoon, and R. A. Mathies, *Anal. Chem.* **78**, 5952 (2006).
- ¹⁶P. Kukura, R. Frontiera, and R. A. Mathies, *Phys. Rev. Lett.* **96**, 238303 (2006).
- ¹⁷P. Kukura, D. W. McCamant, and R. A. Mathies, *Annu. Rev. Phys. Chem.* **58**, 461 (2007).
- ¹⁸C. Fang, R. R. Frontiera, R. Tran, and R. A. Mathies, *Nature* **462**, 200 (2009).
- ¹⁹R. R. Frontiera, C. Fang, J. Dasgupta, and R. A. Mathies, *Phys. Chem. Chem. Phys.* **14**, 405 (2012).
- ²⁰M. Yoshizawa, Y. Hattori, and T. Kobayashi, *Phys. Rev. B* **49**, 13259 (1994).
- ²¹M. Yoshizawa, H. Aoki, and H. Hashimoto, *Phys. Rev. B* **63**, 180301(R) (2001).
- ²²A. Weigel and N. P. Ernsting, *J. Phys. Chem. B* **114**, 7879 (2010).
- ²³K. E. Brown, B. S. Veldkamp, D. T. Co, and M. R. Wasielewski, *J. Phys. Chem. Lett.* **3**, 2362 (2012).
- ²⁴B. Zhao, Z. Sun, and S.-Y. Lee, *J. Chem. Phys.* **134**, 024307 (2011).
- ²⁵G. Stock and W. Domcke, *Phys. Rev. A* **45**, 3032 (1992).
- ²⁶L. Seidner, G. Stock, and W. Domcke, *J. Chem. Phys.* **103**, 3998 (1995).
- ²⁷S. Mukamel and J. D. Biggs, *J. Chem. Phys.* **134**, 161101 (2011).
- ²⁸D. W. McCamant, *J. Phys. Chem. B* **115**, 9299 (2011).
- ²⁹Z. Sun, J. Lu, D. H. Zhang, and S. Y. Lee, *J. Chem. Phys.* **128**, 144114 (2008).
- ³⁰B. Zhao, K. Niu, X. Li, and S.-Y. Lee, *Sci. China: Chem.* **54**, 1989 (2011).
- ³¹S. Y. Lee, D. Zhang, D. W. McCamant, P. Kukura, and R. A. Mathies, *J. Chem. Phys.* **121**, 3632 (2004).
- ³²S. Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, New York, 1995).
- ³³X. Qiu, X. Li, K. Niu, and S. Y. Lee, *J. Raman Spectrosc.* **42**, 563 (2011).
- ³⁴J. A. Cina and P. A. Kovac, *J. Phys. Chem. A* **117**, 6084 (2013).
- ³⁵R. Kosloff, *J. Phys. Chem.* **92**, 2087 (1988).
- ³⁶J. C. Light and T. Carrington, Jr., *Adv. Chem. Phys.* **114**, 263 (2000).
- ³⁷E. C. Y. Yan, Z. Ganim, M. A. Kazmi, B. S. W. Chang, T. P. Sakmar, and R. A. Mathies, *Biochemistry* **43**, 10867 (2004).