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2012

Niu, K., & Lee, S. Y. (2012). Analysis of time resolved femtosecond and femtosecond/picosecond coherent anti-Stokes Raman spectroscopy : application to toluene and Rhodamine 6G. *The Journal of Chemical Physics*, 136(6).

<https://hdl.handle.net/10356/95210>

<https://doi.org/10.1063/1.3682470>

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Citation: *J. Chem. Phys.* **136**, 064504 (2012); doi: 10.1063/1.3682470

View online: <http://dx.doi.org/10.1063/1.3682470>

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Analysis of time resolved femtosecond and femtosecond/picosecond coherent anti-Stokes Raman spectroscopy: Application to toluene and Rhodamine 6G

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(Received 10 September 2011; accepted 19 January 2012; published online 8 February 2012)

The third-order polarization for coherent anti-Stokes Raman scattering (CARS) from a pure state is described by 48 terms in perturbation theory, but only 4 terms satisfy the rotating wave approximation. They are represented by Feynman dual time-line diagrams and four-wave mixing energy level diagrams. In time-resolved (tr) fs and fs/ps CARS from the ground vibrational state, one resonant diagram, which is the typical CARS term, with three field interactions—pump, Stokes, followed by probe—on the ket is dominant. Using the separable, displaced harmonic oscillators approximation, an analytic result is obtained for the four-time correlation function in the CARS third-order polarization. Dlott's phenomenological expression for off-resonance CARS from the ground vibrational state is derived using a three-state model. We calculated the tr fs and fs/ps CARS for toluene and Rhodamine 6G (R6G), initially in the ground vibrational state, to compare with experimental results. The observed vibrational features and major peaks for both tr fs and fs/ps CARS, from off-resonance (for toluene) to resonance (for R6G) pump wavelengths, can be well reproduced by the calculations. The connections between fs/ps CARS, fs stimulated Raman spectroscopy, and impulsive stimulated scattering for toluene and R6G are discussed. © 2012 American Institute of Physics. [doi:10.1063/1.3682470]

I. INTRODUCTION

Ever since coherent anti-Stokes Raman scattering (CARS) was first proposed by Terhune and Maker^{1,2} in 1960s, various theoretical and experimental investigations have been performed in physical, chemical, and biological areas.^{3,4} Similar to Raman spectroscopy, CARS is a powerful technique for detecting vibrational features, measuring temperature as well as deriving images of chemical and biological samples.^{5–7} CARS is generated by three electric fields: a pump pulse with frequency ω_{pu} , a Stokes pulse with frequency ω_{st} , and a probe pulse with frequency ω_{pr} interacting with matter, and it is detected in the $\mathbf{k}_{CARS} = \mathbf{k}_{pu} - \mathbf{k}_{st} + \mathbf{k}_{pr}$ phase matching direction.

Following the development of ultrashort laser techniques, femtosecond laser pulses with high repetition rate and broadband play an important role in CARS experiments for both small and large molecules.^{8–12} CARS had been used to investigate the molecular dynamics on the excited and ground state potential energy surfaces of iodine and bromine in the gas phase.^{13,14} Time-resolved (tr), electronically resonant CARS could prepare and interrogate vibronic coherences of molecular iodine in matrix Ar.¹⁵ Heid *et al.*¹⁶ investigated the ground electronic state vibrational dynamics of porphyrin molecules in solution using CARS and provided a discussion of the expected signals on a theoretical basis by using the CARS third-order non-linear polarization. Knopp *et al.*¹⁷ showed

that the technique of femtosecond tr CARS spectroscopy provided a powerful tool for the investigation of collision-induced linewidths and the validation of rotational energy transfer models. The polarization beat spectroscopy of I₂–Xe complex in solid krypton was studied by Kiviniemi *et al.*¹⁸ using the tr CARS technique. Tran *et al.*¹⁹ carried out measurements and modeling of femtosecond tr CARS signal in H₂–N₂ mixtures at low densities. Pure rotational tr CARS using picosecond duration laser pulses has been used for gas thermometry of N₂.²⁰ Begley *et al.*²¹ proposed that CARS is also useful for investigating biological compounds where background fluorescence is a problem for conventional spontaneous Raman studies. Prince *et al.*²² carried out both tr fs CARS and fs/ps CARS experiments on toluene and Rhodamine 6G (R6G) and introduced a phenomenological analysis of the toluene off-resonance CARS. In the phenomenological analysis, the relevant response function is assumed to be a summation of each Raman active vibrational level which is assigned a central frequency and homogeneously broadened lifetime.^{22,23} However, a derivation of the phenomenological result from a quantum approach for the polarization has been lacking.

Shen²⁴ and Tolles *et al.*²⁵ have reviewed the theory of CARS using a time-independent method and the approximation of cw or delta-function pulses. In addition, Kuehner *et al.*²⁶ have developed a time-independent perturbation theory for three-laser electronic-resonance-enhanced CARS spectroscopy of nitric oxide. Besides the time-independent method, Tannor *et al.*²⁷ proposed a time-dependent approach with finite pulses for CARS and the method was applied to

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FIG. 1. Geometry of a tr fs CARS experiment. The fs pump and fs Stokes pulses are temporally coincident at the sample followed by a fs probe pulse that is delayed by time T . The observation of the tr fs CARS spectrum is made in the phase matching direction: $\mathbf{k}_{\text{CARS}} = \mathbf{k}_{\text{pu}} - \mathbf{k}_{\text{st}} + \mathbf{k}_{\text{pr}}$.

investigate quantum beats and intramolecular vibrational redistribution (IVR) process related to CARS. Time-dependent wave packet calculations were also applied to analyze tr fs CARS experiments on gas-phase iodine molecules.²⁸

Time resolved (tr) fs CARS, shown in Fig. 1 in a BOXCARS arrangement, involves three broadband (fs) input pulses: a pump pulse (pu) with frequency ω_{pu} , a Stokes pulse (st) with frequency ω_{st} , and a probe pulse (pr) with frequency ω_{pr} .²² The pump and Stokes pulses are temporally coincident at the sample, and prepare coherence on the ground electronic state, while the probe pulse acts after a delay time. The tr fs CARS is homodyne detected in the $\mathbf{k}_{\text{CARS}} = \mathbf{k}_{\text{pu}} - \mathbf{k}_{\text{st}} + \mathbf{k}_{\text{pr}}$ phase matching direction. When the probe pulse full width at half maximum (FWHM) becomes less than 20 cm^{-1} , about 1 ps or more, the spectrum is called fs/ps CARS. In the CARS experiments performed by Prince *et al.*,²² the wavelengths of the pump and Stokes pulses are around 530 nm and the probe pulse wavelength is 800 nm. The central frequency difference between pump and Stokes pulses provides a window for the Raman active modes of the ground electronic state, but with broadband pulses, that frequency difference is not even necessary. The probe pulse, which is off-resonance with the zero-zero transition between ground and excited electronic states, acts on the coherence produced by the pump and Stokes pulses to generate the third-order polarization.

Besides CARS, femtosecond stimulated Raman spectroscopy (FSRS) (Refs. 29 and 30) and impulsive stimulated scattering (ISS) (Refs. 31 and 32) are also powerful tools in four wave mixing spectroscopy. FSRS uses a simultaneous pair of narrow band Raman pump pulse and a broadband stimulating probe pulse to interrogate the sample with heterodyne detection in the probe pulse direction. Time resolved FSRS, where FSRS is preceded by an impulsive or actinic pump pulse, can provide both high time and high frequency resolution, based on different pulses and thus not circumventing the Heisenberg uncertainty principle.^{29,33,34} FSRS can be applied to highly fluorescent molecules like Rhodamine 6G,³⁰ to monitor the dynamics of cis-trans photoisomerization process,³⁵ and to image molecules.³⁶ In ISS, two temporally short “excitation” (fs) pulses of identical wavelength and different wave vectors are overlapped spatially and temporally in a sample to generate the vibrational coherences followed by interrogation with a probe pulse.^{31,32} CARS is synonymous with ISS when the parameters for Stokes and pump

pulses are identical except for the pulse directions. Similar to CARS, time resolved spectroscopy exists in ISS.³⁷ Though the names and optical processes and applications are different for CARS, FSRS, and ISS, the commonality among them is the coherences produced by the first two pulses which are subsequently probed by the third pulse. Therefore, one may be interested in the connection between the three nonlinear processes.

In Sec. II, we describe the terms that contribute to the third-order polarization for CARS in diagrammatic form. The dominant “resonant” diagram is used to investigate tr fs CARS and fs/ps CARS for toluene and R6G. Dlott’s phenomenological expression³⁸ for the off-resonance CARS third-order polarization is derived using a quantum three-state model. The calculated results and the connection between fs/ps CARS, FSRS, and ISS for toluene and R6G are presented in Sec. III. We conclude in Sec. IV.

II. THEORY

A. Diagrammatic perturbation theory for CARS

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

In the rotating wave approximation, the most resonant diagrams satisfy the condition that the first interaction on the ket or bra time-line is an absorption from e_1 to e_2 , followed by a stimulated emission from e_2 to e_1 , and then an absorption again, if relevant. Coupled with the phase matching condition for CARS, $\mathbf{k}_{\text{CARS}} = \mathbf{k}_{\text{pu}} - \mathbf{k}_{\text{st}} + \mathbf{k}_{\text{pr}}$, there are only four “basic” FDTL diagrams remaining, as shown in Fig. 2. The pure state $|\psi_1^{(0)}\rangle$ could either be a stationary state or an evolving wave packet prepared earlier by an actinic pump pulse. Set I has one diagram with three field interactions on the ket, and set II has one field interaction on the ket and two on the bra, with three time orderings for the ket interaction leading to three diagrams. The molecule interacts with the laser fields from t_3 to t in time order. The arrows pointing into the time-line denote absorption from e_1 to e_2 , while the arrows pointing away from the time-line denote stimulated emission from e_2 to e_1 . Arrows that point to the right have wave vectors $+\mathbf{k}$ and those that point to the left have $-\mathbf{k}$. Each of the diagrams has a resultant wave vector $\mathbf{k}_{\text{CARS}}$.

For each diagram, we can interchange the fields E_{pu} and E_{pr} , while conserving the phase matching condition. However, for the CARS experiments that we are describing here, the probe pulse is very much to the red of the pump and Stokes

FIG. 2. Four basic Feynman dual time-line diagrams of CARS that satisfy the resonant rotating wave approximation and the phase matching condition for CARS: (I) three ket interactions and (II) one ket and two bra interactions. Being resonant terms, the first interaction on either time-lines is an absorption (arrow pointing into the time-line), followed by an emission (arrow pointing away from the time-line), and then an absorption, if relevant. The pump and the probe fields can be interchanged while retaining the phase matching condition. These diagrams facilitate writing down the time-dependent third-order polarizations.

pulses, and the four diagrams shown are the most resonant ones. This can be seen more clearly in the four-wave mixing energy level (FWMEL) diagrams in Fig. 3 where the diagrams are in one-to-one correspondence with the FDTL diagrams in Fig. 2. Here, time increases from left to right in each diagram, and $v = 0, 1$ represent the vibrational levels. The interaction on the bra is denoted by a dashed arrow and on the ket by a solid arrow. The pump, Stokes, and probe pulses are shown. In diagram I of Fig. 3, the pump pulse leads to excitation while Stokes pulse leads to de-excitation and the frequency difference between pump and Stokes pulses covers the fundamental vibrational transitions in the ground electronic state. Diagram I of Fig. 3 is clearly more resonant than diagrams II(a)–II(c) of Fig. 3.

FIG. 3. Basic four-wave mixing energy level diagrams corresponding to the Feynman dual time-line diagrams in Figure 2. Time increases from left to right in each diagram, and $v = 0, 1$ represent the ground electronic state vibrational levels. The interaction on the bra is denoted by a dashed arrow and on the ket by a solid arrow. These diagrams give the energy-frame viewpoint and help us visualize the resonant terms.

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

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

The third-order polarization for diagram I of Fig. 3 is given by^{34,39}

$$P_I^{(3)}(t) = \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \times e^{-\gamma_2(t-t_1)/2\hbar - \gamma_1(t_1-t_2)/2\hbar - (t_1-t_2)/T_2 - \gamma_2(t_2-t_3)/2\hbar - \gamma_1(t+t_3)/2\hbar} \times E_{pr}(t_1)E_{st}^*(t_2)E_{pu}(t_3)I(t, t_1, t_2, t_3), \quad (1)$$

where $\{\gamma_i, i = 1, 2\}$ are the homogeneous linewidths for the respective electronic states. T_2 is the decoherence lifetime, which is the decay time of the vibrational coherences prepared by pump and Stokes pulses in the e_1 state. $E_{pr}(t)$, $E_{st}^*(t)$, and $E_{pu}(t)$ represent the electric fields for the probe, Stokes and pump pulses, respectively. The four-time correlation function, $I(t, t_1, t_2, t_3)$, is given by³⁴

$$I(t, t_1, t_2, t_3) = G(t - t_1 + t_2 - t_3) \langle \psi_1^{(0)}(\mathbf{Q}, 0) | e^{i\mathbf{h}_1 t/\hbar} \mu_{12} e^{-i\mathbf{h}_2(t-t_1)/\hbar} \mu_{21} \times e^{-i\mathbf{h}_1(t_1-t_2)/\hbar} \mu_{12} e^{-i\mathbf{h}_2(t_2-t_3)/\hbar} \mu_{21} e^{-i\mathbf{h}_1 t_3/\hbar} | \psi_1^{(0)}(\mathbf{Q}, 0) \rangle, \quad (2)$$

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

$$G(t) = \int_0^\infty dE_{21} e^{-iE_{21}t/\hbar} G(E_{21}), \quad (3)$$

$$G(E_{21}) = \frac{\exp\left[-\frac{(E_{21}-\bar{E}_{21})^2}{2\theta^2}\right]}{\theta(2\pi)^{1/2}}, \quad (4)$$

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

B. Separable, displaced harmonic oscillators model

The separable, displaced harmonic oscillators model has previously been described.^{34,40,41} Only a brief description is presented here. In an N -dimensional separable system, the Hamiltonians are sums of one-dimensional Hamiltonians

$$\mathbf{h}_1 = \sum_{r=1}^N h_{1r}, \quad (5)$$

$$\mathbf{h}_2 = \sum_{r=1}^N h_{2r} + \bar{E}_{21}, \quad (6)$$

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

$$|\psi_1^{(0)}(\mathbf{Q}, 0)\rangle = \prod_{r=1}^N |\psi_{1r}^{(0)}(q_r, 0)\rangle. \quad (7)$$

The four-time correlation function in Eq. (2) becomes³⁴

$$I(t, t_1, t_2, t_3) = G(t - t_1 + t_2 - t_3) |\mu_{21}|^4 \prod_r I_r(t, t_1, t_2, t_3). \quad (8)$$

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

$$I_r(t, t_1, t_2, t_3) = \langle \psi_{1r}^{(0)}(q_r, 0) | e^{ih_{1r}t/\hbar} e^{-ih_{2r}(t-t_1)/\hbar} e^{-ih_{1r}(t_1-t_2)/\hbar} \\ \times e^{-ih_{2r}(t_2-t_3)/\hbar} e^{-ih_{1r}t_3/\hbar} | \psi_{1r}^{(0)}(q_r, 0) \rangle, \quad (9)$$

where $h_{2r}(t)$ is the one-dimensional Hamiltonian in mode q_r of the excited electronic state e_2 . Assuming that $|\psi_{1r}^{(0)}(q_r, 0)\rangle$ is the ground vibrational state $|\psi_{1r0}(q_r)\rangle$, and inserting a complete vibrational basis set, $\sum_{v'} |\psi_{1rv'}(q_r)\rangle \langle \psi_{1rv'}(q_r)|$, of e_1 into Eq. (9), we obtain

$$I_r(t, t_1, t_2, t_3) = e^{-iE_{1r0}(t_3-t)/\hbar} \sum_{v'} \langle \psi_{1r0}(q_r) | e^{-ih_{2r}(t-t_1)/\hbar} | \psi_{1rv'}(q_r) \rangle \\ \times e^{-iE_{1rv'}(t_1-t_2)/\hbar} \langle \psi_{1rv'}(q_r) | e^{-ih_{2r}(t_2-t_3)/\hbar} | \psi_{1r0}(q_r) \rangle, \quad (10)$$

where $E_{1rv'}$ is the eigenenergy of $|\psi_{1rv'}(q_r)\rangle$. Now, each of the correlation functions in Eq. (10) is of the form $\langle \psi_n | e^{-ih_2t/\hbar} | \psi_0 \rangle \equiv \langle \psi_n | \psi_0(t) \rangle$ or its complex conjugate, with analytic result given by⁴⁰

$$\langle \psi_n | \psi_0(t) \rangle = \exp\{-(\Delta^2/2)[1 - \exp(-i\omega t)] - i\omega t/2\} \\ \times \frac{(-1)^n \Delta^n}{(2^n n!)^{1/2}} [1 - \exp(-i\omega t)]^n, \quad (11)$$

where Δ is the excited state mode displacement relative to the ground state and ω is the mode frequency. The integrand

in Eq. (1) is then of analytic form which facilitates the calculation of the third-order polarization. The spectral intensity is proportional to squared magnitude of the third-order polarization,^{22,42} and the spectra in the frequency domain are given by the FT of the time domain polarization.

The CARS intensity, including the instrument response, is defined as

$$\mathcal{I}_{\text{CARS}}(\omega) = \int_{-\infty}^{\infty} d\omega_1 R(\omega - \omega_1) |P_1^{(3)}(\omega_1)|^2, \quad (12)$$

where $P_1^{(3)}(\omega)$ represents the FT of the time domain polarization. $R(\omega)$ denotes the Gaussian spectrometer response which can be expressed as

$$R(\omega) = \exp\left(-4 \ln 2 \frac{\omega^2}{\Delta_{\text{inf}}^2}\right). \quad (13)$$

Here, Δ_{inf} is the FWHM of the instrument response function.

In the calculations, the electric fields are given by

$$E_j(t) = E_{0,j} \exp\left[-2 \ln 2 \frac{(t - T_j)^2}{\Delta_j^2}\right] \\ \times \exp[-i\omega_j(t - T_j)]; \quad j = \text{pu, st, pr}, \quad (14)$$

where the laser pulse is centered at T_j , with amplitude $E_{0,j}$ and linewidth Δ_j . The experimental delay time is given by $T_{\text{pr}} - T_{\text{st}}$. The delay time between pump and Stokes pulses is zero. The carrier wavelengths of the pulses are given by $2\pi c/\omega_j$.

C. Three-state model for CARS and Dlott's phenomenological result

Here, we show that Dlott's phenomenological result³⁸ for the CARS third-order polarization can be derived from a three-state model, where the lower two vibrational states belong to the ground electronic state, e_1 , and the third vibrational state belongs to an excited electronic state, e_2 , with Hamiltonians and wave functions given by

$$h_{1r} |\psi_{1r0}\rangle = E_{1r} |\psi_{1r0}\rangle, \\ h_{1r} |\psi_{1r1}\rangle = (E_{1r} + \hbar\omega_r) |\psi_{1r1}\rangle, \\ h_{2r} |\psi_{2r}\rangle = E_{2r} |\psi_{2r}\rangle, \quad (15)$$

where $E_{1r} = E_{2r}$ based on our definition of the vibrational Hamiltonians in Eq. (6). The four-time correlation function, Eq. (10), then yields

$$I_r(t, t_1, t_2, t_3) = A_{0r} + A_{1r} e^{-i\omega_r(t_1-t_2)}, \quad (16)$$

where ω_r denotes the frequency for the r th mode, and A_{0r}, A_{1r} are the intensities for Rayleigh and fundamental Raman terms of mode r ,

$$A_{0r} = |\langle \psi_{1r0} | \psi_{2r} \rangle|^4 \\ A_{1r} = |\langle \psi_{1r0} | \psi_{2r} \rangle|^2 |\langle \psi_{2r} | \psi_{1r1} \rangle|^2. \quad (17)$$

Substituting Eq. (16) into Eq. (8) and removing Rayleigh, Raman overtones, and the mixed mode transitions, the

four-time correlation function for the fundamental becomes

$$\begin{aligned}
 I(t, t_1, t_2, t_3) &= G(t - t_1 + t_2 - t_3) |\mu_{21}|^4 \sum_r A_{1r} \\
 &\times \prod_{r' \neq r} A_{0r'} e^{-i\omega_r(t_1 - t_2)} \\
 &= G(t - t_1 + t_2 - t_3) |\mu_{21}|^4 \sum_r A_r e^{-i\omega_r(t_1 - t_2)},
 \end{aligned} \quad (18)$$

where

$$A_r = A_{1r} \prod_{r' \neq r} A_{0r'}. \quad (19)$$

Dlott's phenomenological expression³⁸ for the CARS third-order polarization can be derived from the three-state model as follows. The inhomogeneous broadening is ignored for simplicity. The ground state homogeneous linewidth γ_1 is chosen to be zero. We assume the Condon approximation, and $|\mu_{21}|$ is set to 1 here. Using Eqs. (1), (8) and (18), the fundamental CARS term can be written as

$$\begin{aligned}
 P_1^{(3)}(t) &= \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \\
 &\times e^{-(\gamma_2/2 + i\bar{E}_{21})(t-t_1)/\hbar - (t_1 - t_2)/T_2 - (\gamma_2/2 + i\bar{E}_{21})(t_2 - t_3)/\hbar} \\
 &\times E_{pr}(t_1) E_{st}^*(t_2) E_{pu}(t_3) \sum_r A_r e^{-i\omega_r(t_1 - t_2)}. \quad (20)
 \end{aligned}$$

As the purpose of the pump and Stokes pulses is to provide window for the probe pulse, $E_{pu}(t)$ and $E_{st}(t)$ are assumed to be delta function pulses, while $E_{pr}(t)$ is approximated as a monochromatic continuous wave. The center times for pump and Stokes pulses are chosen as 0 for convenience. By using $\int_0^t dt' \delta(t') e^{i\alpha t'} = 1$ and $\int_0^t dt' e^{i\alpha t'} = 1/\alpha(e^{i\alpha t} - 1)$, Eq. (20) gives

$$P_1^{(3)}(t) = \left(\frac{i}{\hbar}\right)^3 \sum_r A'_r [e^{-\frac{t}{T_2} - i(\omega_{pr} + \omega_r)t} - e^{-(\gamma_2/2 + i\bar{E}_{21})t/\hbar}], \quad (21)$$

where

$$A'_r = \frac{A_r}{(\gamma_2/2 + i\bar{E}_{21})/\hbar - 1/T_2 - i(\omega_{pr} + \omega_r)}. \quad (22)$$

In Eq. (21), the first term on the right in the square brackets is the anti-Stokes side spectra shifted from the probe frequency by ω_r , which is Dlott's phenomenological expression for CARS.³⁸ The anti-Stokes shift of the second term in the square brackets relative to ω_{pr} is $\bar{E}_{21}/\hbar - \omega_{pr}$, which is out of range of the observed CARS spectrum. In order to obtain $P_1^{(3)}(0) = 0$, this second term should be included in Dlott's phenomenological expression.³⁸

D. Third-order polarization for inverse Raman scattering in FSRS

In FSRS, the anti-Stokes side spectrum is mainly determined by the inverse Raman scattering (I) process (IRS(I)),

whose third-order polarization is given by^{33,34}

$$\begin{aligned}
 P_{\text{IRS(I)}}^{(3)}(t) &= \left(\frac{i}{\hbar}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \\
 &\times e^{-\gamma_2(t-t_1)/2\hbar - \gamma_1(t_1-t_2)/2\hbar - (t_1-t_2)/T_2 - \gamma_2(t_2-t_3)/2\hbar - \gamma_1(t+t_3)/2\hbar} \\
 &\times E_{pu}(t_1) E_{pu}^*(t_2) E_{pr}(t_3) G(t - t_1 + t_2 - t_3) \\
 &\times |\mu_{12}|^4 \prod_r I_r(t, t_1, t_2, t_3). \quad (23)
 \end{aligned}$$

The Raman gain (RG) spectrum on the anti-Stokes side due to IRS(I) is given by⁴³⁻⁴⁶

$$\sigma_{\text{RG}}(\omega) = -\frac{4\pi}{3\epsilon_0 c n} \omega \text{Im} \{ P_{\text{IRS(I)}}^{(3)}(\omega) / E_{pr}(\omega) \}, \quad (24)$$

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

$$E_{pr}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} E_{pr}(t) dt, \quad (25)$$

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

$$P_{\text{IRS(I)}}^{(3)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} P_{\text{IRS(I)}}^{(3)}(t) dt. \quad (26)$$

III. RESULTS AND DISCUSSIONS

A. Non-resonant CARS on toluene

The theory is first applied to the non-resonant CARS on toluene, initially in the ground vibrational state. We only consider the S_0 to S_1 states of toluene. The transition dipole moment between S_0 and S_1 is usually stronger than between S_0 and S_2 or higher excited electronic states, for symmetry reasons. These higher excited electronic states are also higher up in energy, and so they contribute less to the Raman scattering amplitude because of the energy mismatch in the energy denominator. Hence, it is a good approximation to consider just S_0 and S_1 for off-resonance Raman scattering in toluene. The quality of the agreement between calculations (with just S_0 and S_1) and experiment for non-resonant tr fs CARS and fs/ps CARS of toluene below also supports it.

The vibrational mode frequencies and relative Raman intensities for toluene were obtained from the McCreery group.⁴⁷ In the harmonic approximation, assuming no Duschinsky rotation and no change in a normal mode frequency between ground and excited electronic states, the ratio of Raman intensities $I^k/I^{k'}$ between modes k and k' is related to ratio of frequencies and displacements by the Savin formula⁴⁸

$$I^k/I^{k'} = \Omega_k^3 \Delta_k^2 / (\Omega_{k'}^3 \Delta_{k'}^2), \quad (27)$$

where Ω_k is the frequency and Δ_k is the displacement of equilibrium positions between the ground and excited electronic states of the k th mode. The toluene displacements

FIG. 4. Experimental (dashed line) and calculated (solid line) absorption spectra of toluene. (Experimental absorption data for toluene were adapted from Ref. 51.)

were first calculated relative to Δ_3 using Eq. (27). $\bar{E}_{21}$, γ_2 , θ , and Δ_3 were then adjusted to fit the absorption spectrum of toluene.⁴⁹ The experimental absorption spectrum of toluene dissolved in cyclohexane was obtained from the PhotochemCAD package.^{50,51} The absorption spectrum was calculated using the procedure described in Refs. 34 and 52 and shown in Fig. 4. The best fit mode displacements are listed in Table I with an average zero-zero energy $\bar{E}_{21} = 37\,225\text{ cm}^{-1}$, a homogeneous damping constant $\gamma_2 = 197\text{ cm}^{-1}$, and an inhomogeneous damping constant $\theta = 0$. The major peaks and the width of the absorption spectrum are rather well reproduced. The differences between the experimental and calculated results could be due to modes not accounted for and to anharmonicity effects.⁴⁹

Prince *et al.*²² applied tr fs CARS and fs/ps CARS techniques to toluene in the ground vibrational state. The pulse parameters of the pump, Stokes and probe pulses are given in Table II. The pump and Stokes pulses are temporally overlapped to create coherences in the sample which are then interrogated with a time delayed probe pulse. The experimental²² spectrally dispersed tr fs CARS signal as a function of the probe delay for toluene is shown in Fig. 5(b). The spectrally integrated tr fs CARS signal as a function of the probe delay is shown in Fig. 5(a), with its FT shown in the inset. The FT of the frequency slices of the tr fs CARS signal denoted by (i), (ii), and (iii) at frequencies of 1227, 991, and 791 cm^{-1} , respectively, are shown in Fig. 5(c). The corresponding calculated results are shown in Figs. 5(d) and 5(f). In the calculations, we used a decoherence lifetime of 5 ps as can be gauged from the decay of the tr fs CARS spectrum, and the zero-zero transition energy and the homogeneous damping

TABLE I. Harmonic potential parameters of toluene.

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

TABLE II. Laser pulse parameters for CARS on toluene.

Pulse	Wavelength (nm)	Linewidth (cm^{-1})
Pump	517	250
Stokes	547.34	300
Probe	800	350 (tr fs CARS) 16 (fs/ps CARS)

constant are chosen as 37 225 and 197 cm^{-1} , respectively. The major peaks and coherence period seen in the experimental results, Figs. 5(a) and 5(b), can be well reproduced by the calculations in Figs. 5(d) and 5(e), respectively. In Fig. 5(f), we have calculated the FT of the tr fs CARS signal in Fig. 5(e), and presented it as a contour plot. The frequency slices correspond well to those from the experiment in Fig. 5(c).

The FT of the spectrally integrated tr fs CARS signal for the experimental and calculated results is illustrated in the insets in Figs. 5(a) and 5(d), respectively. The major oscillation period is about 1700 fs, which is due to the coherence between the 1003.6 and 1030.6 cm^{-1} modes. Minor oscillations can also be seen clearly in each inset. The calculated results in Fig. 5(d) inset show five peaks at 27, 180.8, 207.8, 217.1, and 244.1 cm^{-1} , which can be attributed to the coherences between the following pairs of modes: (1003.6, 1030.6), (1030.6, 1211.4), (1003.6, 1211.4), (786.5, 1003.6), and (786.5, 1030.6) cm^{-1} . One can barely observe the small humps at 180.8, 207.8, and 244.1 cm^{-1} in Fig. 5(a) inset besides the major peaks at 27 and 217.1 cm^{-1} . The reason is because the experimental results in Fig. 5(b) show a decoherence lifetime much shorter than 5 ps around 1200 cm^{-1} . The short decoherence lifetime leads to the weak intensities in the 180.8 and 207.8 cm^{-1} beats which come from the (1030.6, 1211.4), (1003.6, 1211.4) cm^{-1} coherences in the experimental results. The beats can be seen more clearly in the FT of tr fs CARS shown in Figs. 5(c) and 5(f).

The spectrally dispersed tr fs CARS signal as a function of the probe delay time of toluene, without the instrument response function, calculated by phenomenological approach versus the quantum results are illustrated in Figs. 6(a) and 6(b), respectively. The CARS intensities were calculated using Eq. (12), where the polarizations are given by Eq. (1) and Eq. (20) for the quantum and phenomenological approach, respectively. From Eq. (17), the parameters A_r in Eq. (20) would be given by the relative intensities of the fundamental Raman bands in toluene.⁴⁷ The relative values for $|A_1|$ to $|A_7|$ are 10, 39, 100, 23, 16, 6, and 30, respectively. The other parameters in the calculation are identical to those used in Fig. 5(e). The oscillations and peak positions are reproduced well in the phenomenological result, Fig. 6(a), and it is nearly identical to the quantum result in Fig. 6(b) in both the oscillation period and peak positions. This can be interpreted as follows. For toluene, the energy gap between ground and excited states is very high compared with the wavelengths of the laser pulses. Thus, the wave packet lifetime in the excited state is short, and so the effect of the excited state structure on the spectra is not very important. However, for resonance CARS, such as on R6G below, the phenomenological result is no longer valid and one has to resort to the quantum approach.

FIG. 5. Time-resolved (tr) fs CARS of toluene. (a) Spectrally integrated tr fs CARS, in (b), from toluene as a function of the probe delay, with Fourier transform (FT) in the inset. (b) Spectrally dispersed tr fs CARS from toluene as a function of the probe delay. (c) The FT of the tr fs CARS in (b) at anti-Stokes shifts of 791, 991, and 1227 cm^{-1} . Diagrams (d), (e), and (f) are the calculated results corresponding to diagrams (a), (b), and (c). In (f), we have the contour plot for the FT of the calculated tr fs CARS in (e). The dashed horizontal lines in (f) gives the FT at frequencies of 791, 991, and 1227 cm^{-1} to compare with the corresponding spectra in (c), and they show good agreement. (Experimental data (a), (b), and (c) are reprinted with permission from B. D. Prince, A. Chakraborty, B. M. Prince, and H. U. Stauffer, J. Chem. Phys. **125**, 044502 (2006). Copyright 2006, American Institute of Physics.)

The experimental fs/ps CARS result for toluene is shown in Fig. 7(a),²² and the calculated results are shown in Fig. 7(b). We chose the probe time delay for both the experimental and calculated results to be the minimum of the integrated CARS signal at 1.93 ps to minimize any non-resonant contribution. The potential parameters and lifetimes used were the same as for the tr fs CARS calculations. We normalized the spectrum in Fig. 7(b) to the intensity of the 1003.6 cm^{-1} mode. The dashed line shows that the calculated fs/ps CARS spectrum with probe pulse linewidth of 16 cm^{-1} , while the fs/ps CARS spectrum with an additional 14 cm^{-1} instrument response is shown by the solid line. The peak positions and relative intensities of the experimental data are well reproduced by the calculation.

B. CARS on R6G

As CARS does not create a population on the excited electronic state e_2 , it is free from background fluorescence, and highly fluorescent molecules like R6G can be investigated using CARS. Prince *et al.*²² carried out tr fs CARS and fs/ps CARS studies on R6G in the ground vibrational state. In the experiment, the pump pulse, centered at 509 nm (FWHM 500 cm^{-1}), is on resonance with the electronic transition, the

Stokes pulse was centered at 556 nm (FWHM 275 cm^{-1}), and the probe pulse wavelength was chosen to be 800 nm for both tr fs CARS and fs/ps CARS. For fs/ps CARS the linewidth of the probe pulse is reduced to 15 cm^{-1} .

The experimental spectrally dispersed tr fs CARS signal from R6G in methanol is illustrated in Fig. 8(a).²² It evolves periodically in the time domain, corresponding to the coherence between modes. Removal of the exponentially decaying baseline signal from the tr CARS signal and then taking the FT leads to Fig. 8(b) where some of the mode frequencies and beats can be seen clearly, but the small intensity vibrational modes are still ambiguous. Very clear information of the mode frequencies and the CARS intensities of R6G are obtained in the fs/ps CARS signal in Fig. 8(c).

The tr fs CARS and fs/ps CARS signals were calculated using the harmonic potential parameters derived earlier by Shim *et al.*,³⁰ and summarized in Table III, together with an average zero-zero energy $\bar{E}_{21} = 18850 \text{ cm}^{-1}$, a homogeneous damping constant $\gamma_2 = 340 \text{ cm}^{-1}$, an inhomogeneous damping constant $\theta = 300 \text{ cm}^{-1}$,³⁴ and a decoherence lifetime $T_2 = 500 \text{ fs}$ as can be gauged from the decay of the experimental tr fs CARS spectrum in Fig. 8(a). The pump, Stokes and probe pulse parameters are given in Table IV. The calculated tr fs CARS signal using a Gaussian probe pulse, FT of

FIG. 6. Calculated off-resonance tr fs CARS of toluene without the instrument response function for (a) Dlott's phenomenological, and (b) quantum results.

the tr fs CARS signal with the exponentially decaying baseline signal removed, and the fs/ps CARS signal are shown in Figs. 8(d) to 8(f), respectively. Comparing Figs. 8(a) and 8(d), the oscillations and the peak intensities are qualitatively reproduced. The major beat frequencies in Fig. 8(b) are also seen in Fig. 8(e). Very good agreement is seen in the fs/ps CARS spectrum between Figs. 8(c) and 8(f).

The line shape of the tr fs CARS signal, however, is dependent on the line shape of the probe pulse. The probe pulse in the experiment deviates from a Gaussian. The insertion of a slit gives an output probe pulse that has a spectral profile given by the product of a Gaussian (350 cm^{-1} or 15 cm^{-1} FWHM for tr fs CARS or fs/ps CARS, respectively) and a

FIG. 7. The fs/ps CARS spectrum of toluene. (a) Experimental fs/ps CARS. (Reprinted with permission from B. D. Prince, A. Chakraborty, B. M. Prince, and H. U. Stauffer, *J. Chem. Phys.* **125**, 044502 (2006). Copyright 2006, American Institute of Physics.) (b) Calculated fs/ps CARS without (dashed line) and with instrument response function (solid line).

TABLE III. Harmonic potential parameters for R6G.³⁰

Frequency $\Omega_r\text{ (cm}^{-1}\text{)}$	Displacement $ \Delta_r $
300	0.24
375	0.46
518	0.17
604	0.42
761	0.29
917	0.14
1116	0.15
1172	0.24
1303	0.28
1356	0.34
1504	0.32
1571	0.27
1647	0.30

square wave (350 cm^{-1} or 15 cm^{-1} wide) which then interacts with the sample. In the time domain, by Fourier transform, this output probe pulse is therefore given by the convolution of a Gaussian with a sinc (GCS) pulse. In the experiments of Prince *et al.*,²² the FWHM of the GCS pulse in the frequency domain is 350 and 15 cm^{-1} for tr fs CARS and fs/ps CARS, respectively, which is thus largely determined by the square wave spectrum. In Figs. 8(g) to 8(i), we show the calculated results with a GCS probe pulse, corresponding to Figs. 8(a) to 8(c). Now, the agreement between the experimental and calculated results for the tr fs CARS and its FT, which shows the beat frequencies, has improved considerably. The fs/ps CARS spectrum in Fig. 8(i) is almost identical to Fig. 8(f), because in both cases, the ps probe pulse spectrum is much narrower than the spacings between mode frequencies.

By FT of the tr fs CARS signal, shown in Figs. 8(b), 8(e), and 8(h), one can see the coherence between modes more clearly. For example, the peak around 1500 cm^{-1} anti-Stokes shift has beat frequencies at $\sim 70\text{ cm}^{-1}$ and at $\sim 150\text{ cm}^{-1}$, and the peak around 1350 cm^{-1} anti-Stokes shift has a $\sim 50\text{ cm}^{-1}$ beat frequency, which are due to the coherences between the following pairs of modes: (1509, 1575), (1356, 1509), and (1303, 1356) cm^{-1} , respectively. As at least six modes and many coherences between modes are involved in the tr fs CARS signal of R6G, one should read the mode information from the tr fs CARS signal and its FT carefully. The fs/ps CARS signal shown in Figs. 8(c), 8(f), and 8(i) provides an alternative means to determine the vibrational modes for the highly fluorescent molecule R6G. The calculations agree well with the experimental data. Peaks can be seen for each vibrational mode and the major peaks are at 1356 and 1504 cm^{-1} for both the experimental and calculated data. The

TABLE IV. Laser pulse parameters for CARS on R6G.

Pulse	Wavelength (nm)	Linewidth (cm^{-1})
Pump	509	500
Stokes	548	275
Probe	800	350 (tr fs CARS) 15 (fs/ps CARS)

FIG. 8. (a) Experimental spectrally dispersed tr fs CARS of R6G in methanol. (b) FT of the spectrally dispersed tr fs CARS shown as a contour plot. (c) Experimental fs/ps CARS spectrum of R6G in methanol. The calculated results using a Gaussian probe pulse corresponding to (a), (b), and (c) are given in (d) with 350 cm^{-1} FWHM Gaussian, (e) FT of (d), and (f) with 15 cm^{-1} FWHM Gaussian, respectively. The calculated results using a Gaussian convoluted with sinc (GCS) probe pulse are given in (g) with 350 cm^{-1} FWHM GCS, (h) FT of (g), and (i) with 15 cm^{-1} FWHM GCS, respectively. (Experimental data (a), (b), and (c) are reprinted with permission from B. D. Prince, A. Chakraborty, B. M. Prince, and H. U. Stauffer, *J. Chem. Phys.* **125**, 044502 (2006). Copyright 2006, American Institute of Physics.)

width for the experimental peaks are slightly broader than that of the calculated results, which may be due to the instrument response and the effect of the solvent. The linewidth of the probe pulse in the fs/ps CARS is 15 cm^{-1} and the decoherence broadening plays an important role for the linewidth of the peaks. Hence, the fs/ps CARS signal with the Gaussian probe pulse in Fig. 8(f) is identical to that with the GCS probe pulse in Fig. 8(i).

C. Relationship among CARS, FSRS, and ISS

Many experimental and theoretical investigations have been carried out with CARS, FSRS, and ISS. They are all described by the third-order polarization, so we would expect some connection between CARS, FSRS, and ISS. When the pump and Stokes pulses have identical line shapes, then iden-

tical CARS and ISS spectra will result. Therefore, we will just compare the CARS and FSRS spectra.

In FSRS, the broadband probe allows vibrational spectrum in the range of $200\text{--}2500\text{ cm}^{-1}$ to be determined.^{29,30} In CARS, the effective spectral range is determined by the frequency difference and pulse linewidths of the pump and Stokes pulses. So, while vibrational features within a 800 cm^{-1} window can be determined by fs/ps CARS,²² the spectral range can be extended by using broadband pump and Stokes pulses. Here, we wish to first discuss the relationship between FSRS and CARS.

We consider off-resonance FSRS and CARS on toluene in the ground vibrational state. In FSRS, it is the IRS(I),³³ term that contributes to the anti-Stokes spectrum, and it has a Feynman dual time-line diagram with a probe-pump-pump interaction on the ket time-line, like diagram I in Fig. 2 for

CARS. In the IRS(I) calculation using Eq. (24),³⁴ the delay time between the pump and probe pulses and FWHM of the probe pulse were 0 fs and 10 fs, respectively. The linewidth for the pump pulse is 16 cm^{-1} , and the wavelength for both pump and probe pulses is 800 nm. In the fs/ps CARS calculation, the FWHM for both coincident pump and Stokes pulses are 10 fs, and no instrument response function is taken into account. The other parameters are identical to those used in the calculation of the fs/ps CARS signal for toluene in Fig. 7(b). The spectral range is broad enough for determining the vibrational features of toluene in both FSRS and fs/ps CARS. We note that the CARS intensity, being homodyne detected, is proportional to the square of the third-order polarization spectrum, Eq. (12), while the FSRS intensity, being heterodyne detected, is linearly related.³³ Hence, to compare the two, the off-resonance (square-root) fs/ps CARS and (negative, since it is a loss) IRS(I) signals for toluene are displayed in Fig. 9(a). The line shapes are nearly identical, but the calculations show that the dispersed -IRS(I) signal is about 200 times stronger than CARS here, due to the coincident pump and probe pulses in IRS(I) versus a time delay of about 2 ps between the pump-Stokes and probe pulses in CARS. Besides this, the intensity given by the square root of CARS, $\sqrt{I_{\text{CARS}}}$, is proportional to $E_{0,\text{pu}}E_{0,\text{st}}E_{0,\text{pr}}$, while the intensity of IRS(I) process, $I_{\text{IRS(I)}}$, is proportional to $E_{0,m}^2$.^{29,34} Hence, $I_{\text{IRS(I)}}$ should be stronger than $\sqrt{I_{\text{CARS}}}$ for weak fields. In the IRS(I) process, the vibrational features fall within the range given roughly by half the width of the broadband probe pulse, while for fs/ps CARS it is roughly half the width of the broadband pump or Stokes pulse. Therefore, similar vibrational features of the ground electronic state can be obtained by both IRS(I) and fs/ps CARS.

The comparison of the (square-root) fs/ps CARS and -IRS(I) signals for R6G, initially in the ground vibrational

state, are shown in Fig. 9(b). In the fs/ps CARS calculation, the off-resonance 800 nm final probe pulse interaction reaches a virtual state of R6G. So, we chose an off-resonance IRS(I) situation where we used 1200 nm pump and probe pulses, and the other pulse parameters were identical to those used in Fig. 9(a). In the fs/ps CARS calculation, the FWHM for both pump and Stokes pulses were chosen to be 10 fs and no instrument response function was included. The other parameters were identical to the fs/ps CARS of R6G in Fig. 8(f). A wide frequency window is open to detect the vibrational levels of the ground electronic state by the broadband pulses in both CARS and -IRS(I), and the anti-Stokes shifts of the peaks are identical in Fig. 9(b) for both spectra. Due to the resonant pump and Stokes pulses for the CARS process, the peak intensities for the respective vibrational modes shown by CARS and -IRS(I) are slightly different, but the off-resonance -IRS(I) signal is still about 10 times stronger than resonance CARS due to the same reason attributed to the pulses as for toluene.

IV. CONCLUSION

We have shown that diagrammatic perturbation theory in Liouville space is useful to describe many nonlinear third-order spectroscopies, including tr fs and fs/ps CARS, FSRS, and ISS. We can use either the time-frame Feynman dual time-line diagram for ket and bra evolution which is useful in writing down the third-order polarization directly, or the energy-frame four-wave mixing energy level diagram which is useful in visualizing resonances. The CARS process with three different pulse interactions is described by 48 diagrams in perturbation theory, but most of the diagrams contribute little to the CARS amplitude due to off-resonant intermediate states brought about by one or more pulse interactions. The single most resonant term in CARS, with pump absorption-Stokes emission-probe absorption on the ket time-line, is used to simulate the tr fs CARS and fs/ps CARS experiments of Prince *et al.*²² for toluene and R6G from the ground vibrational state. We show that the third-order polarization for CARS with finite pulses can be easily calculated using the separable, displaced harmonic oscillators approximation for the ground and excited state potential energy surfaces. The parameters for the harmonic oscillators can be deduced from absorption and Raman scattering data. The calculated results agreed well with the experimental results for tr fs CARS and fs/ps CARS of toluene with off-resonance pump, and R6G with resonance pump. In tr fs CARS, the spectral line shape varies with the shape of the probe pulse spectrum, as seen in the case of R6G. We derived Dlott's phenomenological expression³⁸ for the CARS polarization using a three-state model and the phenomenological result agrees with the quantum result for off-resonance tr fs CARS of toluene. The vibrational features of molecules in the ground electronic state can be detected by fs/ps CARS, IRS(I) of FSRS, and ISS, which are shown to be related to each other. The relation between off-resonant fs/ps CARS and -IRS(I) of FSRS was illustrated by calculations on toluene and R6G.

FIG. 9. Relation between the square root of the fs/ps CARS spectrum (solid line) versus -IRS(I) spectrum (circles) for (a) toluene, and (b) R6G.

ACKNOWLEDGMENTS

This work was supported by a Ministry of Education, Singapore, research grant.

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