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Nuclear dynamics in electronic ground and excited states probed by spectrally resolved four wave mixing

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Time-resolved ground-state bleach and excited-state stimulated emission spectra have been measured for indocyanine green dissolved in methanol by employing spectrally resolved four wave mixing (SRFWM). The separation of the SRFWM signals into the ground-state bleach and excited-state stimulated emission contributions allows observation of intramolecular vibrational wave packet motions and intermolecular solvation dynamics upon impulsive excitation, while the molecule resides either in the ground or in the excited state. Frequencies of the indocyanine green intramolecular vibrational modes in the ground and excited states are practically the same. Vibrational dephasing times in the excited state range from a few hundred fs to ~ 2 ps, and they are consistently shorter than those in the ground state. When excitation frequency is centered near the 0-0 transition, center frequencies of the stimulated emission redshift due to solvation of the excited state in nonequilibrium solvent configuration, whereas those of the ground-state bleach blueshift due to equilibrium fluctuation of the solvent molecules around the chromophore in the ground state. At early times, the solvation function obtained from the time-resolved ground-state bleach spectra is slower than the solvation function obtained from the time-resolved excited-state stimulated emission spectra. © 2002 American Institute of Physics. [DOI: 10.1063/1.1479345]

I. INTRODUCTION

When a molecule is promoted to an electronic excited state impulsively, i.e., the excitation pulse duration is shorter than a vibrational period, a nuclear wave packet is created in the excited-state potential surface.¹⁻⁷ Measurement of the time-dependent transition frequency between the ground and the excited states gives direct information on nuclear dynamics, which includes both intermolecular solvation dynamics and intramolecular vibrational wave packet motion, while the molecule stays in the excited state. Time-resolved spontaneous fluorescence with enough time resolution corresponds to this type of measurement. In the meantime, the excitation leaves a hole in the ground-state absorption spectrum. Intramolecular and intermolecular nuclear dynamics in the ground-state surface manifest themselves in the time-resolved spectra of the hole. Transient hole burning (THB),⁸ which measures the ground-state bleach contribution in a transient absorption (TA) spectrum, corresponds to this type of measurement.

According to the classical Franck principle,⁹ immediately after the excitation by pump pulses, center frequencies of the ground-state bleach (GB) and excited-state stimulated emission (ESE) contributions in a TA spectrum would be the same. As intermolecular dynamics involving solvent molecules (solvation) and chromophore intramolecular nuclear dynamics proceed, frequencies of the two components shift to their equilibrium counterparts, i.e., stationary absorption and fluorescence spectra, respectively. In a typical TA measurement of a dye molecule in polar liquid, initial spectral

dynamics are ultrafast due to initial rupture of the wave packet formed by constructive interference of many intramolecular vibrational modes and inertial solvation dynamics occurring on a 100 fs time scale.^{10,11} In solutions showing large reorganization energy (Stokes shift), TA spectra may be separated into the GB and ESE components some time after the excitation by using a continuum probe pulse.¹²⁻¹⁴ In this case, intramolecular and intermolecular nuclear dynamics can be measured independently while a molecule stays in either the electronic ground or excited state.

In resonant third-order nonlinear spectroscopies, such as TA, transient grating (TG), and photon echoes, there exists an ambiguity in the origin of an oscillation in signal traces. This arises because a third-order nonlinear response function consists of ground-state as well as excited-state pathways.^{6,7,15} Assignment of an oscillation to a vibrational mode in either electronic state is usually made through probe wavelength dependence, its dephasing time, and/or dependence on pulse chirps.¹⁶⁻²² This is a particularly important issue in the study of photochemical reactions involving an excited electronic state such as isomerization of rhodopsin²³ and primary charge separation in photosynthetic apparatus.¹⁶ If the separation of a TA spectrum into GB and ESE contributions can be achieved, an unambiguous assignment can be made, which will greatly facilitate the interpretation. In addition, vibrational spectrum of a molecule in an electronic excited state, especially in a low-frequency region, can be obtained, which is otherwise difficult to acquire.

Solvation dynamics in liquids has been studied extensively over the last decade. Dynamics of solvation can be characterized via the solvent response function,

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$$S(t) = \frac{\omega(t) - \omega(\infty)}{\omega(0) - \omega(\infty)},$$

where $\omega(0)$, $\omega(t)$, and $\omega(\infty)$ are the average frequencies of the emission spectra at times 0, t , and infinity, respectively. Majority of the $S(t)$ reported to date have been obtained by employing either time-resolved spontaneous fluorescence or stimulated emission in TA. The solvation dynamics can also be obtained from THB.^{24–26} However, there is one important distinction between the $S(t)$ obtained from time-resolved Stokes shift of the excited state and that obtained from THB: in a time-resolved Stokes shift measurement, solvent molecules respond to the nonequilibrium charge distribution of the chromophore in an excited state, whereas the change of the ground-state bleach spectra in THB represents fluctuation of the solvent molecules around the chromophore in equilibrium ground state. Within the linear solvent response regime, however, the two are the same. In theoretical studies of solvation dynamics, equilibrium simulations are also frequently employed instead of calculating nonequilibrium response functions.²⁷ Separation of time-resolved TA spectra into GB and ESE contributions will thus provide an opportunity to examine the validity of the linearity of solvation dynamics in liquids.²⁵

In this work, we report sub-20 fs time-resolved transient spectra measurements of a cyanine dye, indocyanine green (ICG), dissolved in methanol by employing spectrally resolved four wave mixing (SRFWM). ICG, an infrared laser dye, is widely applied in medical diagnosis.²⁸ In our previous report of the SRFWM of 3,3'-diethylthiatricarbocyanine iodide (DTTCI) in methanol,²⁹ feasibility of obtaining high quality frequency-time-resolved spectrogram was demonstrated, although the ground-state bleach spectra and the stimulated emission spectra were not resolved due to a small Stokes shift. For ICG in methanol, however, transient spectrum at each time can be separated into GB and ESE contributions. The separation allows observation of the nuclear motions in each electronic state independently, which will provide detailed information on intramolecular as well as intermolecular nuclear dynamics in each electronic state.

II. EXPERIMENT

Light source was a home-built cavity-dumped Kerr lens mode-locked Ti:sapphire laser generating 18 fs pulses centered around 800 nm. Repetition rate and energy of the pulses were adjusted to 150 kHz and 3 nJ, respectively, to avoid power-induced artifacts, including photoisomerization.

Optical layout and details of the SRFWM measurements have been described previously.²⁹ SRFWM is essentially the same as the three-pulse TG measurement. In SRFWM, the TG signal is spectrally dispersed to record a spectrum at each time delay T . The laser output was split into three roughly equal energy pulses, and passed through delay stages. Pulses 1 and 2 overlap in time at the sample, while pulse 3 was delayed by T from the pulses 1 and 2. The three beams were focused in a geometry that satisfies the Bragg diffraction condition. The third-order nonlinear signal into $-\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ phase matching direction, where \mathbf{k}_i are the wave vectors of the pulses 1–3, was spatially filtered and directed to a

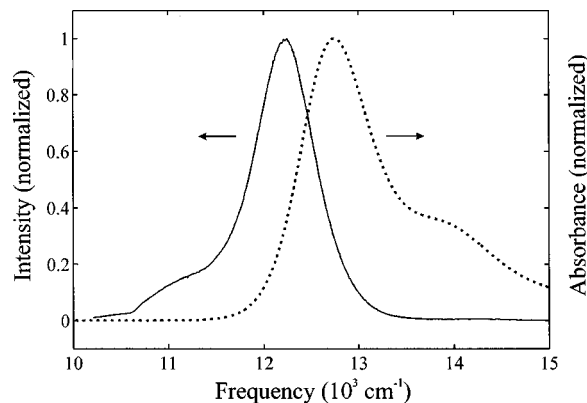


FIG. 1. Stationary absorption (dotted line) and emission (solid line) spectra of indocyanine green in methanol.

spectrograph equipped with a CCD array detector. Spectra of the third-order nonlinear signal and the probe pulse (\mathbf{k}_3) were measured simultaneously by using a two-leg fiber. All three input beams are polarized parallel with each other. Background noise was negligible compared to the SRFWM signal at large T (> 1 ns).

ICG (product name IR125) from Exciton Co. was used as received. Methanol solution of ICG was prepared by the highest-grade solvent from Aldrich, and the solution was flown through a 100 μ path length flow cell. All measurements were performed at ambient temperature ($22 \pm 1^\circ \text{C}$).

III. RESULTS

Infrared laser dyes employed frequently in the study of solvation dynamics are usually large and flexible with a possibility of conformational inhomogeneity. For example, DTTCI dissolved in methanol shows large inhomogeneity persistent over several nanoseconds, as revealed by 3-pulse stimulated photon echo peak shifts (3PEPS) measurements.³⁰ Conformational isomerism was alluded to the inhomogeneity. Figure 1 shows absorption and stationary fluorescence spectra of ICG in methanol. The two are in mirror symmetry with the Stokes shift of 490 cm^{-1} . The symmetry may indicate similar vibrational spectra in the ground and excited states with rigid molecular structures.³¹ 3PEPS measurement of ICG (see below) shows minimal inhomogeneity indicating that the line broadening is mostly due to vibronic structures and solvent-solute interactions, not due to the conformational inhomogeneity. A shoulder separated by 940 cm^{-1} from the main peak is apparent in the absorption spectrum as well as in the emission spectrum. The 940 cm^{-1} mode is found in the time-resolved measurements in this study and in Raman spectra reported by Ashworth *et al.*³¹ and by Kagan and McCreery.³² In addition, infrared laser dyes show generally lower photostability and thermal stability compared to visible laser dyes. ICG, however, shows very high photostability and thermal stability in organic solvents,^{33,34} which makes it suitable as a fluorescence probe molecule.

Representative SRFWM signals for several T values together with two-Gaussian function fits are shown in Fig. 2. The raw data were normalized by the probe pulse spectrum, which was acquired simultaneously with the data. It is evi-

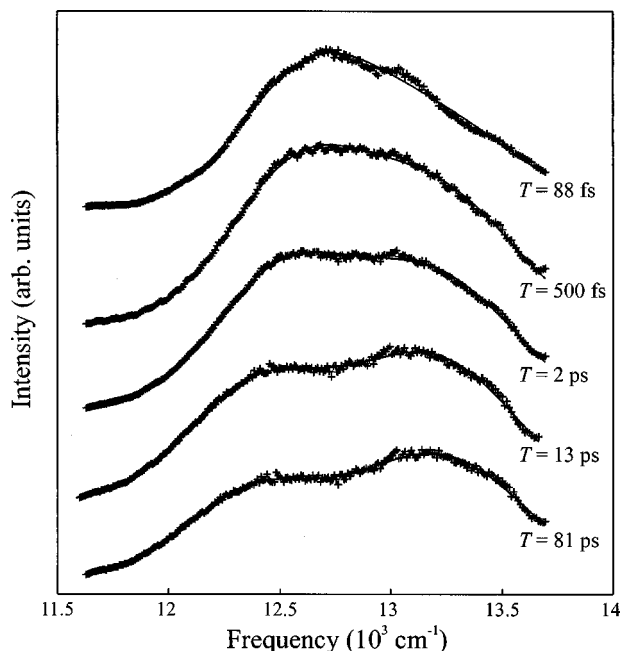


FIG. 2. Representative SRFWM signals for several T values. Solid lines are two-Gaussian fits.

dent that the SRFWM spectra consist of two components at large T . For $T < 80$ fs, fitting of the SRFWM signals to two separate Gaussian functions cannot be attained reliably due to insufficient separation of the GB and ESE contributions. A log-normal function has been used frequently to fit emission spectra in time-resolved fluorescence³⁵ and TA experiments¹² to account for the asymmetry of line shapes. We have also tried two log-normal functions to fit the SRFWM data, one each for the GB and ESE contributions. Slightly better fits were obtained for large T , although the Gaussian fits were somewhat more reliable for small T . Experimental results described below are practically the same for the two different fits, and the Gaussian fit results will be used hereafter.

The SRFWM signal at large T (80 ps) is similar to a sum of the stationary absorption and fluorescence spectra, although they are shifted to higher frequencies. The discrepancy is partly due to the systematic errors in the measurement such as detector sensitivity and fitting procedure of the signal to two-Gaussian functions. The normalization of the SRFWM signals by probe spectrum may contribute significantly due to the limited bandwidth of the probe pulse. The discrepancy is also due to the inhomogeneity, which comprises ca. 10% of the total reorganization energy at ~ 1 ns as measured by 3PEPS (see below). Center frequencies of the SRFWM spectra change slightly as the excitation frequency is varied because of the inhomogeneity of the system.

Third-order nonlinear signals have a contribution from excited state absorption (ESA). If ESA from S_1 exists in the spectral region of interest, it will significantly affect the SRFWM spectra and undermine the validity of the separation of the SRFWM spectra into GB and ESE contributions. An ESA component in a TA gives negative contribution (increased optical density) to the signal, whereas GB and ESE components give positive contribution. TA spectra of ICG shows no negative component over the spectral region of

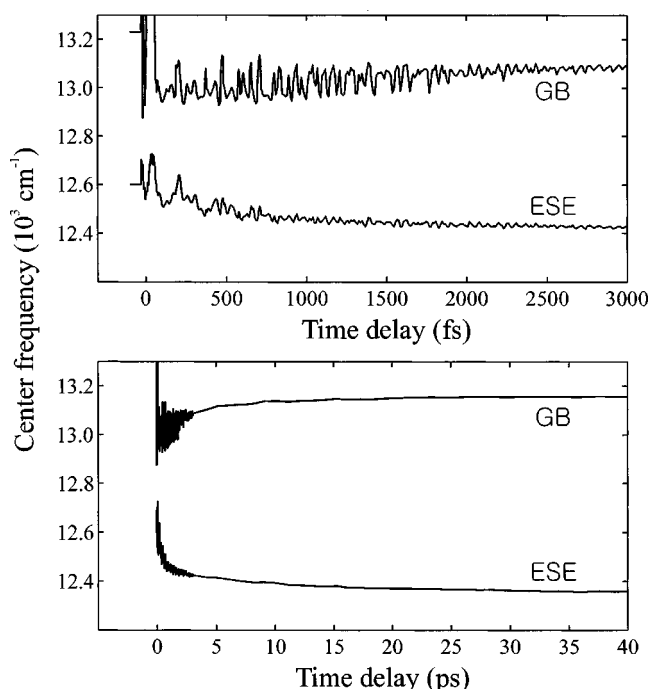


FIG. 3. Center frequencies as a function of time delay T for the ground-state bleach and excited state stimulated emission contributions of the SRFWM of indocyanine green in methanol shown in two different time scales.

interest, and the spectra is close to a sum of the GB and ESE. Based on these observations, it is concluded that contribution of ESA from S_1 in the SRFWM signals is negligible.

Center frequencies of the GB and ESE components from the two-Gaussian fits are shown in Fig. 3 as a function of time delay, T . Although widths of the spectra should give similar information on nuclear dynamics, we limit ourselves to the center frequencies in this article because description using center frequencies will be more intuitive. Immediately apparent is the large amplitude oscillations in the GB and ESE center frequencies, which correspond to the intramolecular vibrational wave-packet dynamics in the ground- and excited-state potential surfaces, respectively. Thus, the separation provides an opportunity to observe the wave-packet motions in each electronic state independently, which will give frequencies, dephasing times, and phase information of the vibrations. To proceed, exponential contributions were first subtracted, and the remaining oscillatory portions were Fourier-transformed to give the power spectra shown in Fig. 4. Frequencies and dephasing times were obtained by linear prediction singular value decomposition (LPSVD) method^{36,37} with the help of the Fourier transform. The results are summarized in Table I.

Table I indicates that frequencies of a vibrational mode in the ground and excited states are the same within experimental uncertainty except the 146 cm^{-1} mode, which appears at 138 cm^{-1} in the excited state. Nevertheless, it is not certain whether the difference is significant, since frequency uncertainty of the $146(138)\text{ cm}^{-1}$ mode is considerably larger than those of other modes because of its short dephasing times and low frequencies. In addition, small intensity of the 146 cm^{-1} mode in the GB data makes accurate frequency determination difficult. The fact that the vibrational

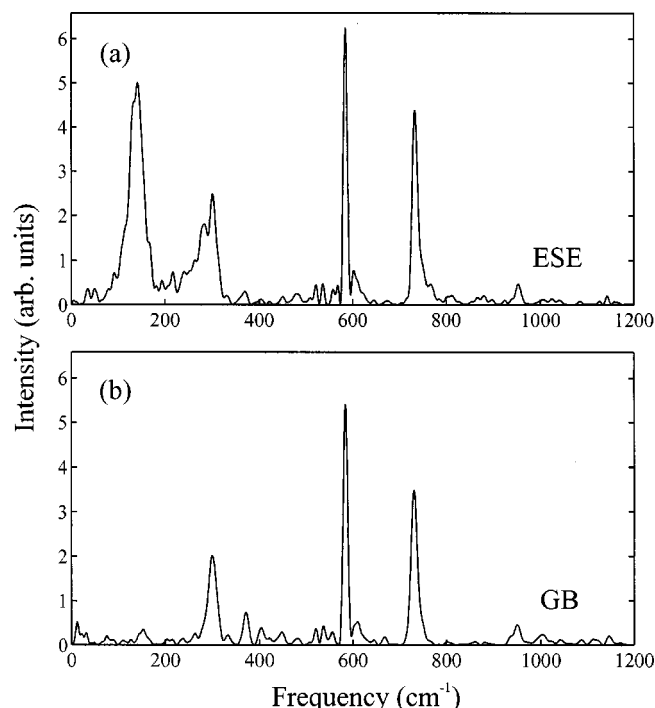


FIG. 4. Fourier power spectra of the oscillatory components in the center frequencies of the ESE (a) and GB (b) contributions of the SRFWM of indocyanine green in methanol shown in Fig. 3.

structures of the two electronic states are the same is consistent with the mirror symmetry between the absorption and emission spectra of ICG in methanol. In terms of vibrational dephasing times, they are consistently shorter in the excited state, which conforms to the general notion that vibrational dephasing rate in an electronic excited state is faster than that in the ground state.³⁸

In addition to the oscillations due to intramolecular vibrations, the center frequencies shift to their equilibrium counterparts exponentially on a longer time scale. Because the center frequency of the excitation pulse is located near the center of the stationary absorption and emission maxima, the center frequencies of the ESE component redshift, whereas those of the GB component blueshift. The redshift of the ESE contribution originates from the solvation of ICG molecules in the excited state, that is, the dynamics of solvent molecules in nonequilibrium configuration due to abrupt

TABLE II. Time constants of the exponential contributions in the center frequencies of the GB components of the SRFWM, center frequencies of the ESE of the SRFWM, TG, and 3PEPS.

	τ_1 (fs)	τ_2 (ps)	τ_3 (ps)
SRFWM, ESE	400	5.0	20
SRFWM, GB	...	2.7	16
3PEPS	250	1.9	16
TG	330	4.3	40

excitation of the chromophore, whereas the blueshift of the GB component reflects equilibrium solvent fluctuation around the chromophore in the ground state. The center frequencies versus T are fitted to a sum of exponential functions along with the damped sinusoids determined above. Two (GB) or three (ESE) exponentials adequately describe the data, and the results are summarized in Table II. It is well known that time constants in a multiexponential fit are strongly correlated.³⁰ Therefore, the time constants should be considered as an approximate time scale of the dynamics.

Since the GB and ESE contributions have been measured separately, it would be sensible to compare the results with the ordinary third-order time domain techniques. For this purpose, TA, TG, and 3PEPS measurements of ICG in methanol have been performed. All these measurements share the same third-order nonlinear response function, which includes both the ground- and excited-state pathways. Consequently, similar information on intramolecular and intermolecular nuclear dynamics may be obtained, although the ground- and excited-state contributions cannot be separated. Unique in a 3PEPS measurement is its background free nature, that is, peak shifts are zero when all nuclear dynamics are completed.³⁹ In TA and TG, nuclear dynamics comprises only part of the signal with the major component being lifetime decay. Figure 5 shows the TG and 3PEPS measurements of ICG in methanol. The TA signal (not shown) is similar to the TG. Note that there exists a small residual peak shift at long times (>100 ps) in the 3PEPS, which manifests inhomogeneous broadening on the time scale of SRFWM measurements (<100 ps).⁴⁰ The inhomogeneity is, however, much smaller than that of DTTCl dissolved in methanol. The TG and 3PEPS data are analyzed in a manner similar to the analyses of the center frequencies of

TABLE I. Frequencies (ω) and dephasing times (T_{2v}) of the oscillatory components in the center frequencies of the GB components of the SRFWM, center frequencies of the ESE of the SRFWM, TG, and 3PEPS obtained by linear prediction singular value decomposition method.

SRFWM							
GB		ESE		TG		3PEPS	
ω (cm ⁻¹)	T_{2v} (fs)	ω (cm ⁻¹)	T_{2v} (fs)	ω (cm ⁻¹)	T_{2v} (fs)	ω (cm ⁻¹)	T_{2v} (fs)
146	550	138	320	140	420	137	210
298	2800	297	420	297	620	298	500
				423	250	428	220
584	3100	584	1800	587	400	582	470
733	2100	734	1200	731	530	729	750
952	1400	954	710	949	330

^aAbsent due to insufficient time resolution.

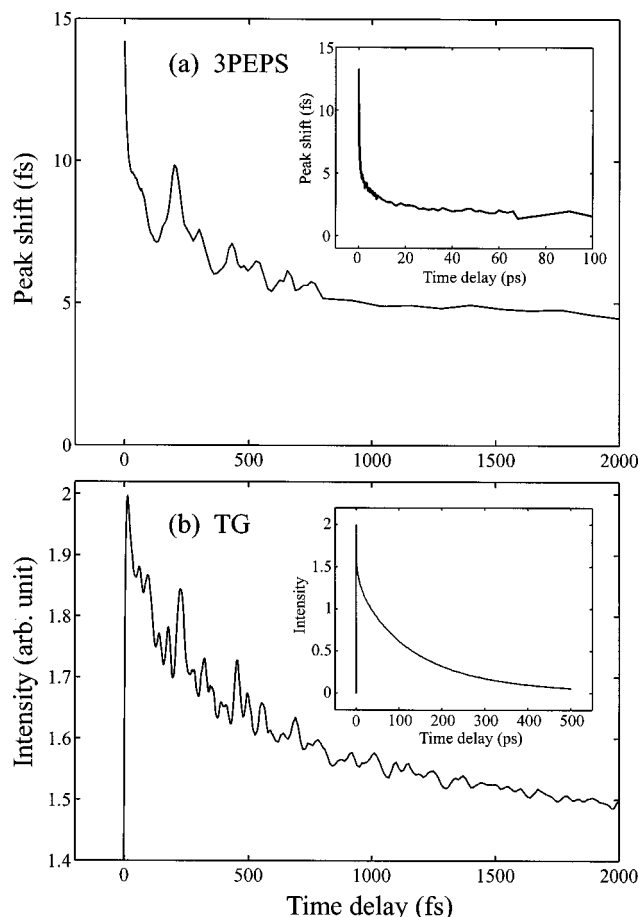


FIG. 5. 3PEPS (a) and TG (b) of indocyanine green in methanol. Insets show data in larger time scales.

the SRFWM. Fourier transforms of the oscillatory portions are shown in Fig. 6. Oscillation frequencies and decay time constants obtained from LPSVD fits are also listed in Table I.

All the oscillation frequencies found in the SRFWM are present in TG and 3PEPS. They were also observed in the Raman spectrum of ICG reported previously,^{31,32} where only the ground-state vibrations should appear. In addition to the oscillation frequencies observed in the SRFWM, a 423 cm^{-1} (428 cm^{-1}) mode is also observed in TG (3PEPS), which shows very short decay time constant. The same mode at 420 cm^{-1} was observed in transient birefringence measurements by Kleiman *et al.*²⁰ The 420 cm^{-1} mode was assigned to a vibration arising from the excited state based on its short dephasing time and dependence on pulse chirp.²⁰ It is not clear why the mode is absent in SRFWM but appears in other third-order measurements.

Table I indicates that the vibrational dephasing times observed in the TG are generally shorter than those in the SRFWM. Surprisingly, they are even shorter than the vibrational dephasing times from the ESE contributions of the SRFWM for high frequency ($>500\text{ cm}^{-1}$) modes. We speculate that in TG and 3PEPS, destructive interference between the two oscillations of a single vibrational mode, one each from each electronic state with perhaps slightly different frequencies, may lead for the oscillations to dephase faster.

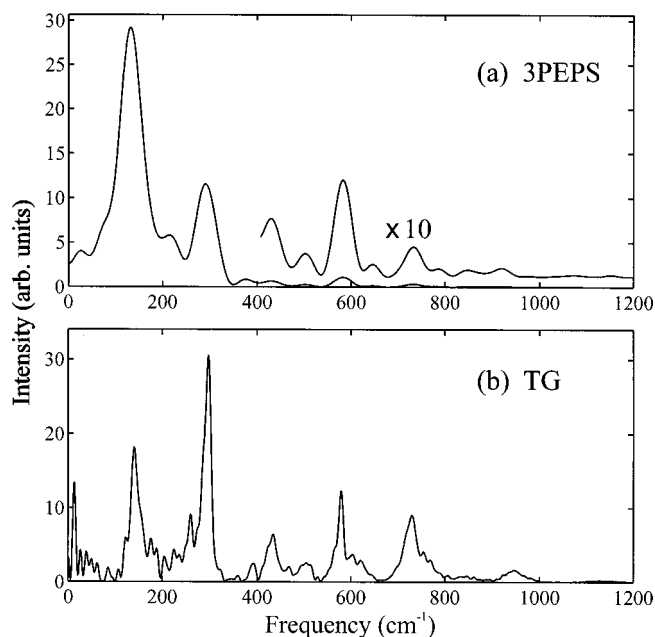


FIG. 6. Fourier power spectra of the oscillatory components of the 3PEPS (a) and TG (b).

It has been established from theory and experiment that exponential contributions in TA, TG, and 3PEPS represent solvation dynamics.^{39,41–46} Three exponentials describe the exponential contributions in TG and 3PEPS adequately, and the results are summarized in Table II. The 160 ps decay component apparent in the TG signal as shown in Fig. 5 arises from the excited-state lifetime and reorientational diffusion of ICG in methanol.⁴⁷ Time constants from the 3PEPS are 250 fs, 1.9 ps, and 16 ps. These values are qualitatively similar to the solvation dynamics of other dye molecules in methanol.^{30,35,39,45,48,49} Time constants from the TG agree qualitatively, although they are slower than those in the 3PEPS. This is caused in part by the interference from reorientational diffusion and lifetime decay contributions in TG. The exponential contributions extracted from each measurement are compared graphically in Fig. 7. It is interesting to

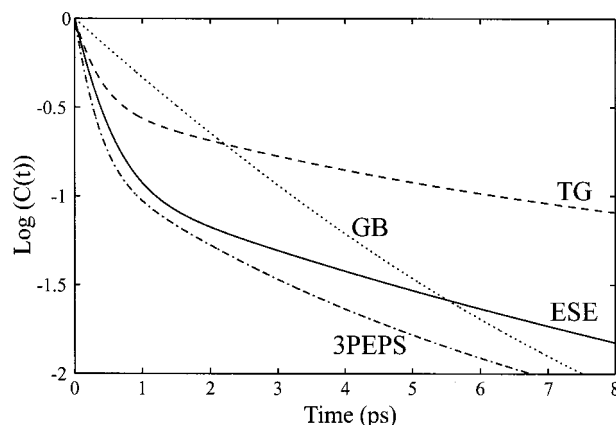


FIG. 7. Comparison of the exponential contributions in the ESE of the SRFWM (solid line), GB of the SRFWM (dotted line), 3PEPS (dash-dotted line), and TG (dashed line).

note that the ~ 300 fs component present in the ESE of the SRFWM, 3PEPS, and TG (and TA) is absent in the GB of the SRFWM.

IV. DISCUSSION

Frequency-time-resolved spectra, particularly in a form of frequency-resolved TA, is frequently employed in a study exploiting femtosecond pulses. GB, ESE, and ESA contributions may be identified in such a measurement, and dynamical information can be obtained from each component. Ernsting and co-workers employed frequency-resolved continuum probe TA to measure time-resolved Stokes shift of the ESE component to study solvation dynamics of a styryl dye in liquids^{12,13} and 2-amino-7-nitro-fluorene in acetonitrile and chloroform.¹⁴ The ESE contribution was separated from the TA spectra by assuming that the GB contribution is invariant in time. Oscillation of the ESE center frequency due to wave-packet motion was not observed, although pulse duration was short enough to excite impulsively. Palit *et al.* used continuum probe TA to measure the ESE component to study solvation dynamics of LDS-821 in liquids.⁵⁰ Kinoshita *et al.* observed solvent relaxation by THB of dyes in solution on tens of ps time resolution.⁵¹ Berg and co-workers have employed THB to study solvation dynamics for a system where vibronic bands are spectrally well resolved.^{25,26} Longer pump pulses (narrow spectral width) in the range of a few hundred fs to several ps were used to maintain spectral selectivity. Time-resolved GB and ESE contributions were measured to study solvation dynamics and to test the linearity of solvation.²⁵

In the present study, frequency-time-resolved spectra after impulsive excitation have been recorded by employing SRFWM. The spectra have been analyzed in terms of GB and ESE contributions. It was demonstrated that the SRFWM spectra can be separated into the GB and ESE contributions for $T > 100$ fs and that their center frequencies can be determined precisely from the two-Gaussian fit. This was made possible by the fact that initial spectral relaxation due to intramolecular and intermolecular nuclear dynamics are ultrafast. For the gas phase, the separation of the signal into the ground- and excited-state contributions must be straightforward, as demonstrated by Lozovoy *et al.* in a SRFWM measurement of I_2 in gas phase.⁵² The separation into GB and ESE components may be achieved more readily for a system with large Stokes shift. For DTTCl in methanol employed previously for an SRFWM measurement,²⁹ separation into GB and ESE components could not be attained, although Stokes shifts of DTTCl and ICG in methanol are about equal. This apparent contradiction can be accounted for by the large inhomogeneity of DTTCl in methanol. 3PEPS of DTTCl in methanol revealed large inhomogeneity, nearly 50% of the total Stokes shift, whereas 3PEPS of ICG in methanol (Fig. 5) showed much smaller inhomogeneity. That is, a fraction of the solvent-induced Stokes shift in methanol is much larger for ICG than DTTCl.

A. Intramolecular wave packet dynamics

Although vibrational frequencies of ICG in the ground and excited states are nearly the same, some of their intensi-

ties are quite different. The most prominent distinction between the GB and the ESE spectra shown in Fig. 4 is the disparity of the intensities of the 138 cm^{-1} (146 cm^{-1} in GB) mode. It is tempting to assign the 138 cm^{-1} oscillation as a vibration present exclusively in the excited state. However, the mode appears consistently in the GB spectra in repeated measurements. The disparity in amplitudes can be accounted for by considering the formation of wave packets in the ground and excited surfaces. Creation of the wave packets by impulsive excitation and their propagation have been investigated theoretically and experimentally.^{2,3,16,21,22,53,54} In resonant third-order nonlinear spectroscopies, two field-matter interactions are required to create an excited-state population and wave packets. During the time interval between the two field-matter interactions, the material system is in electronic coherence state. Time delay between the two field-matter interactions is not required to create a wave packet in the excited state. Wave packets in the ground state are created by impulsive stimulated Raman process, and the electronic coherence created by the first field-matter interaction needs to evolve for finite time before it makes a Raman transition back to the ground state to form a wave packet in the ground-state surface.² Consequently, the wave packets in the ground and excited state show different behavior on pulse duration.^{3,16,53,54} In the limit of delta function pump pulses, wave packets in the excited state are created exclusively. A similar argument, but in the frequency domain, can also be used to lead to the same results on the wave packet formation.³ A wave packet in the ground state is formed most favorably for a pulse duration equal to roughly a quarter of a vibrational period.³ Since the pulse duration in the experiment was 18 fs, much shorter than the period (242 fs) of the 138 cm^{-1} mode, formation of the wave packet in the ground state will be attenuated. This also explains somewhat smaller intensity of the 300 cm^{-1} mode in the GB spectrum than that in the ESE spectrum. Since both GB and ESE contribute to the third-order polarization, the 138 cm^{-1} mode appears in the TG and 3PEPS. It can be said that the 138 cm^{-1} oscillation in the TG signal is originated from the excited state, not because the vibrational mode is absent in the ground state, but because the wave packet was not created due to the short pulse duration.

Table I shows that vibrational dephasing times in the ground state are generally longer than those in the excited state. Vibrational dephasing times in the ground state can be measured easily from the linewidth of infrared or Raman spectra, and they usually fall in the range of 1–10 ps.⁵⁵ Vibrational dephasing times in the excited state of a molecule in liquid, however, are not easy to measure. In frequency domain, transient Raman spectroscopy is usually employed for that purpose. In a transient Raman, time resolution is determined by the pulse duration, but spectral resolution, which carries dephasing information, is determined by the inverse of the pulse duration. Therefore, moderately long pulses (~ 2 ps) are usually considered to be the optimum pulse duration to maintain both time and frequency resolution.^{56–59} Third-order time-domain measurements also provide vibrational dephasing times, although definite assignment to either electronic state cannot be made in most

cases. An oscillation with short decay time is usually assigned to a vibration in the excited state.^{17,20} Time-domain measurements are advantageous in that both time and frequency resolutions can be kept high. However, extremely short pulses must be used to study high-frequency vibrations.

It is interesting to note that vibrational dephasing times, T_{2v} , in electronic excited states observed from time-domain measurements are usually within a few hundred fs,^{17,20} whereas frequency domain measurements, such as transient Raman spectroscopy, usually show longer T_{2v} (narrow vibrational Raman lines) in excited states.^{56–60} For the molecule ICG employed in this study, T_{2v} in the excited state are comparable to those in the ground state, except the 298 cm⁻¹ mode, which shows much shorter T_{2v} in the excited state. In addition, T_{2v} obtained from TG and 3PEPS are significantly shorter than the GB contributions of the SRFWM, and they are even shorter than those in the ESE contributions. It is to be noted that this is not due to the quadrature detection nature of the TG and 3PEPS measurements; it is well known that TG and 3PEPS directly reflect intramolecular and intermolecular dynamics of a system,³⁹ although a decay time constant in a TG signal due to excited-state lifetime is one-half of the actual lifetime. It is speculated that the shorter dephasing times observed in the usual third-order time domain measurements is due to the destructive interference with nearby vibrational modes especially with that in different electronic states.

B. Solvation dynamics

Solvation dynamics can be studied by various time-domain techniques such as time-resolved Stokes shift measurement using fluorescence up conversion, TA, TG, 3PEPS, and spectrally dispersed transient absorption. The solvation dynamics of a dye molecule in methanol has been studied extensively, and it is now well known that the solvation dynamics of methanol has a series of time scales ranging from 100 fs to tens of ps.^{30,35,39,45,48–50,61} The fastest time scale observed in this work is considerably slower than 100 fs, a typical value found in the literature.^{35,39} In solvation dynamics studies employing large and flexible infrared laser dyes such as DTTCl, somewhat longer time scales have been observed.^{30,50} In the current TA, TG, 3PEPS, and ESE of the SRFWM measurements of ICG in methanol, similar time scales as in DTTCl have been observed. The slow down of the solvation dynamics in these large probe molecules are in accord with the molecular dynamics simulation studies by Ladanyi and Maroncelli.⁶² In a molecular dynamics simulation of a benzene like solute in acetonitrile, it was found that the most critical attribute of a probe molecule on the solvation dynamics is their charge distribution; initial solvation time increases from 120 to 180 fs as the charge distribution in benzene changes from monopolar to octupolar.⁶² For the large probe molecules such as DTTCl and ICG, with minimal dipole moment change upon electronic transition, charge distribution will be highly multipolar, and the solvation will become slower compared to smaller molecules such as coumarins, which also show large dipole moment change upon electronic transition.

As pointed out, there is an important distinction between the solvation dynamics measured by GB and ESE components. In contrast to the nonequilibrium solvation of the excited state created suddenly, the solvation dynamics obtained from the GB component is due to the equilibrium thermal fluctuation of the solvent molecules around the chromophore in the ground state. In the linear solvation regime, where the solvent coordinates are coupled with the solute electronic transition energy linearly, the two are identical. Most of the theoretical and experimental works rely on this linearity. The issue of nonlinear response in solvation has been discussed by several authors.^{25,27,63–69} The solvation nonlinearity is usually attributed to the saturation of a dipolar liquid by the solute dipole. Kumar and Maroncelli²⁷ have reported that linear response approximation is valid in the dipolar solvation of coumarin 153 in acetonitrile and methanol, although some deviation from linearity has been found in the ionic solvation of methanol.

Separation of the transient spectra into the GB and ESE components offers an opportunity to test the linearity of the solvation dynamics. Since the Stokes shift of ICG in methanol is smaller than that of coumarin 153, the current solute–solvent is expected to follow the linearity of solvation more rigorously. However, Table II (Fig. 7) shows that the initial rate of solvation measured by ESE of the SRFWM, TG, and 3PEPS is about the same, whereas the initial solvation rate measured by GB of the SRFWM is significantly slower. Although there may be some artifacts in the fitting of the center frequencies to a sum of exponentials, inspection of Fig. 3 certainly shows that the initial rate of frequency shift in the GB spectra is slower than that of the ESE spectra. This may suggest that the nonequilibrium solvation of the excited state is faster than the equilibrium fluctuation of the ground state for this chromophore/solvent system. For the ICG/methanol system with minor dipole moment change upon electronic transition, dipolar saturation is not expected to be the cause of the observed nonlinearity. The time scales and amplitudes of solvation dynamics is completely determined by the solvation spectrum, which is a product of the “bare spectral density” of the solvent and the coupling strengths between the solvent normal modes and the transition energy of the solute. We speculate that there may be some specific interactions between the solute and solvent in this associative solvent to give different coupling strengths to make the solvation spectrum distinct for the ground and excited states.

V. CONCLUSION

In this work, we have presented detailed frequency-time-resolved spectra of a dye molecule in methanol at room temperature following impulsive excitation using sub-20 fs pulses. The particular system studied is typical of a chromophore in a polar liquid, where stationary absorption spectrum shows a single featureless broad band. The transient spectra were successfully separated into the ground-state bleach and excited-state stimulated emission components, and the center frequencies of each component were measured with a few cm⁻¹ precision as a function of time delay. The separation into GB and ESE and the high precision in the center frequency measurement allow observation of the in-

tramolecular vibrational wave packet dynamics in the ground- and the excited-state potential surfaces independently through the time-dependent shift of the center frequencies of the GB and ESE components. The ambiguity in the assignment of an oscillation to either the ground or the excited electronic states, which exists in all third-order nonlinear time-domain measurement, can be resolved unambiguously. In addition, the solvation function can be obtained from the dynamics of the ground-state hole and from the usual time-resolved Stokes shift of the excited-state stimulated emission. It was observed that the solvation function obtained from the ground state is slower.

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