Study of two xanthene dyes using spectrally resolved three-pulse photon echo spectroscopy

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Comparative study of the molecular dynamics of two xanthene dye derivatives (Rhodamine-6G and Fluorescein-548) is reported using spectrally resolved three-pulse photon echo spectroscopy. An appreciable change in the coherence and population dynamics was observed between the two xanthene derivatives due to the presence of different functional groups. Solution of Rhodamine-6G in methanol behaves in a more coherent fashion compared to that of Fluorescein-548 dye.

The femtosecond nonlinear spectroscopy is widely used to determine various nonlinear responses that reflect the dynamics of intra or intermolecular vibrations[1–8]. The vibrational dynamics in electronic ground state can be determined by time-resolved infrared spectroscopy[5,6]. This technique, however, cannot be applied for studying complex molecular systems or for the study of electronic state dynamics[5,6]. Other nonlinear spectroscopic techniques, such as transient absorption and pump-probe spectroscopy also face the same difficulty of interpreting the data at very short timescales because of the coherence spike resulting from the overlap of pulses[9]. Similar problems also exist in time-resolved photon echo peak shift technique in which the correlation function has masked the initial time behaviour by the rapid free induction decay of the inhomogeneously broadened ensembles[2]. The fast dynamical processes during the pulse overlap timescale make it difficult to select the single band from its congested spectrum and also to study its molecular dynamics[10].

The use of multiple laser pulses increases the capability of ultrafast nonlinear spectroscopy for studying the molecular dynamics on very short timescales[2,7,8,11–14]. The interaction of multiple femtosecond pulses in a sequential manner induces nonlinear polarization in the sample and creates coherence and population in different states[10]. These multiple laser pulses can manipulate and probe the coherence and population dynamics, which is dependent on the molecular structure, electronic vibrational coupling mechanism and environmental effect[10]. The measurement of nonlinear polarization induced in the sample by the interaction of multiple laser pulses can give detailed information about the dephasing time, population relaxation time and the inhomogeneous broadening in the spectrum[1,15,16]. In this context, we present here the study of two xanthene dyes using spectrally resolved three-pulse photon echo (SRPE) spectroscopy.

Method

The experimental set-up consists of a commercial Ti : sapphire KM labs oscillator which is used as seed laser for amplification. This seed pulse is amplified by multi-pass amplifier (ODIN, Quantronix Corp., USA). The Nd : YAG pump laser operating at 1 kHz (Corona, Coherent Inc., USA) is used to pump the seed pulses generated by the KM labs oscillator. The amplified laser system generates 40 fs pulses at central wavelength of 806 nm with a repetition rate of 1 kHz. The amplified laser pulses are further amplified using commercial computer-controlled travelling-wave optical parametric amplifier (TOPAS, Light-Conversion Ltd, USA). This optical parametric amplifier (OPA) generates 50 fs pulses of tunable wavelength with 1 kHz repetition rate which covers the whole visible region. The out beam coming from OPA was split into three beams of nearly equal intensity using 70 : 30 and 50 : 50 thin ultrafast beam splitters and suitable optics. These three laser beams were sent through variable delay lines consisting of retro-reflectors and motorized translation stages for creating the delay between the pulses. Finally the laser beams were focused on the flowing sample using achromatic lens of 20 cm focal length in boxcar geometry. Rhodamine-6G and Fluorescein-548 were purchased from Sigma Aldrich and dissolved in methanol to result in a solution of 10^{-4} molar concentration for the experiments. The centre wavelength of the laser pulses coming from OPA (TOPAS) was tuned to 530 nm for Rhodamine-6G and at 510 nm for collecting the data for Fluorescein-548. Rhodamine-6G has its S_1 absorption peak at 528 nm whereas Fluorescein-548 has its absorption peak at 500 nm.

Results and discussion

Measurement of photon echo spectra as a function of coherence time (t_{12}) and wavelength detected by the spectrometer, provides information about coherence and population dynamics. It also provides information about the dephasing time of inhomogeneous broadening.

Coherence and population dynamics of Rhodamine-6G

We scanned the coherence time at different fixed population times for our data collection. Figure 1 shows the SRPE spectra for Rhodamine-6G at the centre wavelength of 530 nm, plotted against coherence time for various fixed population times. In Figure 1 *a*, at zero population time (t_{23}), the spectra exhibit long trailing part and quantum beat oscillations, resulting from vibrational coherences generated by the short laser pulses towards the positive coherence time. This long trailing part shows that Rhodamine-6G is a highly coherent dye. A slight tilt is also observed in Figure 1 *a* and *b*, which shows that for positive coherence, the spectra are red-shifted and for negative coherence time, they are blue-shifted. This indicates the inhomogeneous broadening in the spectra. For positive coherence time (t_{12}), contribution of photon echo-like signal is more in the spectra, whereas for negative t_{12}, the contribution of Free Induction Decay-like

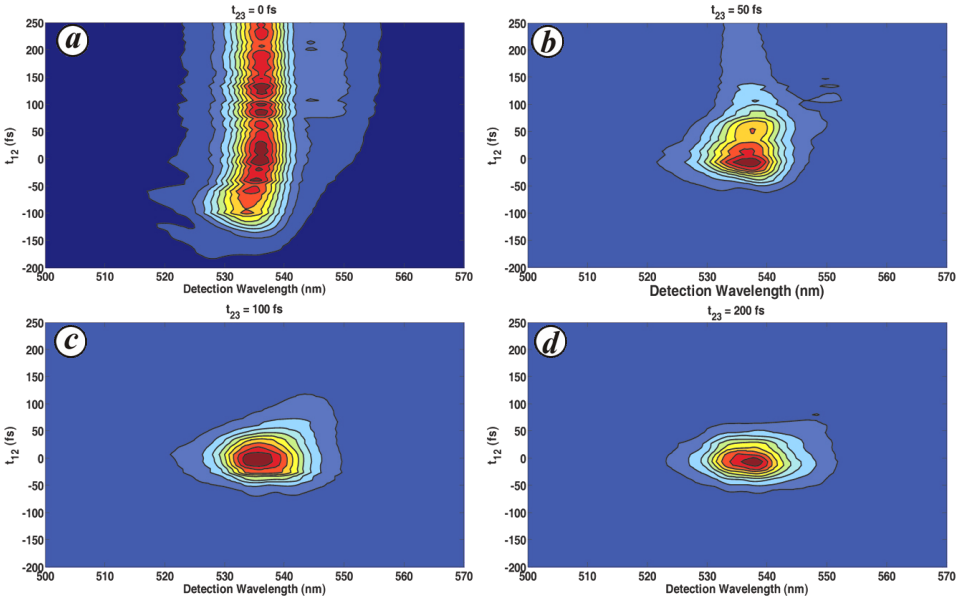

Figure 1. Spectrally resolved photon echo plots for Rhodamine-6G in methanol taken while scanning the coherence time (t_{12}) for various fixed population times (t_{23}) of (***a***) 0 fs; (***b***) 50 fs; (***c***) 100 fs; (***d***) 200 fs.

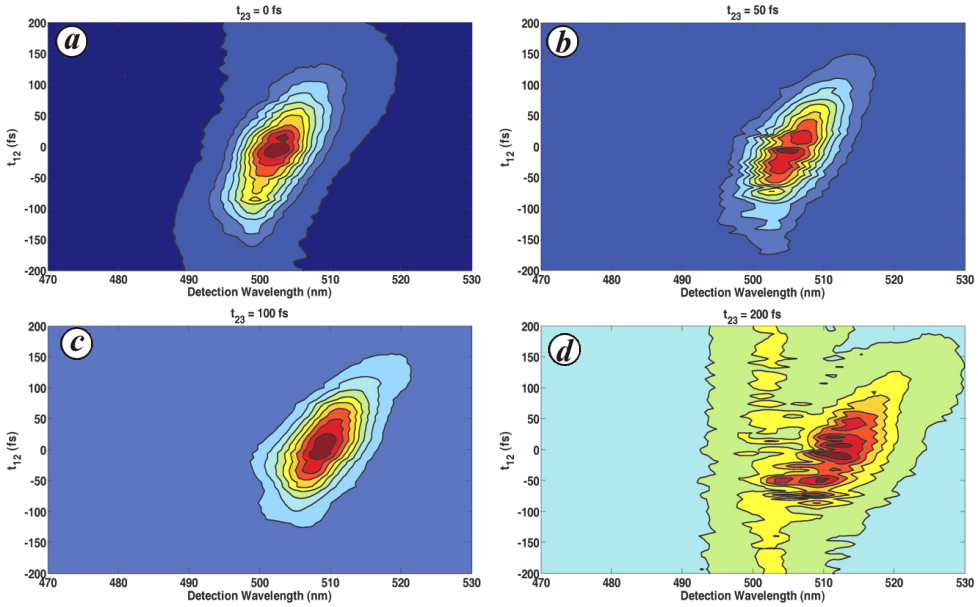

Figure 2. Spectrally resolved photon echo plots for Fluorescein-548 dye in methanol taken while scanning the coherence time (t_{12}) for various fixed population times (t_{23}) of (***a***) 0 fs; (***b***) 50 fs; (***c***) 100 fs; (***d***) 200 fs.

signal is more in the spectra. At 50 fs population time, the long trailing part reduces to 150 fs and the spectra start becoming symmetrical with respect to zero coherence time. The signal intensity is also centred near about zero coherence time, as shown in Figure 1 *b*. A very small wavelength shift is observed as we increase the fixed population time from 0 to 50 fs timescale. The wavelength and temporal shift in the spectra occurs due to inhomogeneous broadening[1], and the wavelength shifts in the spectra occur due to the transfer of the optical coherence from the initially excited transition[15]. This indicates the population relaxation dynamics of Rhodamine-6G in methanol solvent. In Figure 1 *c* at 100 fs population time, the spectra become symmetrical with respect to zero coherence time and extend up to 100 fs timescale. The signal maxima are also centred at zero coherence time and no wavelength shift is observed as we increase the fixed

population time from 50 to 100 fs timescale. This indicates that the spectral diffusion process occurs in ~100 fs timescale for Rhodamine-6G in methanol.

Coherence and population dynamics of Fluorescein-548

In Fluorescein-548, the photon echo spectra were scanned from –200 to 200 fs for varying coherence times at different fixed population times of 0, 50, 100 and 200 fs. The central wavelength of laser pulses is tuned to 500 nm for excitation throughout the experiment. The contour plots of photon echo spectra for Fluorescein-548 are shown in Figure 2. At zero population time (t_{23}), as shown in Figure 2 *a*, a peak appears at around $t_{23} = 0$ fs and is centred at 503 nm. The contours in Figure 2 *a–d* show that the photon echo spectra are blue-shifted at negative coherence times and red-shifted at positive population times. This indicates the inhomogeneous broadening in the spectra. At $t_{23} = 50$ fs, the spectra are red-shifted from 500 to 505 nm. At $t_{23} = 100$ fs, the spectra shift from 505 to near 510 nm, and the signal intensity is maximum at 0 fs coherence time. This continuous shift in spectra indicates population relaxation dynamics. The blue-shift of photon echo spectra, during the negative coherence time and red-shift during the positive coherence time are seen till 200 fs timescale, although the signal intensity has almost decayed. This is due to the occurrence of inhomogeneous broadening at a longer timescale. This indicates that the spectral diffusion process occurs at more than 200 fs timescale for Fluorescein-548.

Conclusion

Our experimental result shows an appreciable change in coherence and population dynamics of two xanthene derivatives due the presence the *o*-carboxyphenyl group in the fluorescein molecule, which forms intermolecular hydrogen bonds with the solvent as well as with the other fluorescein molecules. This results into a large inhomogeneous broadening in the photon echo spectra. The presence of some other electronegative functional groups on the Fluorescein molecule can further increase the probability of hydrogen bond formation, which may contribute to the large inhomogeneous broadening seen in the spectra. However, in the case of Rhodamine-6G, presence of the ester group prevents the formation of hydrogen bonding, which results in a small inhomogeneous broadening in comparison to fluorescein. The long trailing part in the contour plot for Rhodamine-6G, at zero delay, shows that it is a highly coherent dye compared to Fluroscein-548, in which no trailing part is observed in the spectrum. Experimental observations also indicate that the interaction of methanol is much stronger with Fluorescein compared to that of Rhodamine-6G.

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