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Development of ultrafast Electronic-Raman 2D spectroscopy

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14. ABSTRACT
The PI has had good success at accomplishing their research objectives for this grant. They were able to combining the pulse shaper assisted 2D spectroscopic method and FSRS to create 2DER spectroscopy that follows the dynamics of vibrational Raman modes of chromophores and correlates them to the initial electronic excitation wavelength. This grant provided financial support for a postdoc on the program. Two peer reviewed papers were a direct result of this grant award. Additionally, the PI was able to present this work at several optics conferences.

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Abstract

We have demonstrated a new nonlinear optical spectroscopic technique: Ultrafast Two Dimensional Electronic-Raman spectroscopy (2DER), which is capable of measuring the correlation between excited electronic states and their vibrational Raman spectral signature. In this technique, each of the multiple excited electronic transitions in a complex system can be correlated with its low vibrational frequency (Raman) spectrum. The 2DER spectrum presents the initial actinic excitation wavelength with nanometer spectral resolution in the first axis, and the detected stimulated Raman spectra in the second axis. This work has been published in a leading journal in optics: *Optics Letters* **43**, 939 (2018). With this technique, we will be able to obtain an unprecedented picture of how the transient structure mediates the functions and properties of important biological and chemical systems. We present preliminary results on the application of 2DER on characterization of the dark state of photosynthetic accessory pigment β-carotene.

Introduction

Recent advances in coherent two-dimensional (2D) optical spectroscopy have substantially extended the spectral correlation range of optical spectroscopies. Femtosecond time-resolved 2D correlation spectra with excitation and detection windows from ultraviolet (UV) to mid-infrared (MIR) wavelengths have been implemented [1-3]. This broad spectral range has enabled the direct visualization of correlations for various ultrafast processes previously inaccessible to one-dimensional optical methods. However, the combination of correlation wavelengths accessible in most current coherent multidimensional spectroscopies excites and probes similar degrees of freedom.

For example, 2D infrared spectroscopy (2DIR) correlates vibrational couplings in order to resolve molecular structures and dynamics of chemical and biological complexes [4-6], while 2D electronic spectroscopy (2DES) correlates electronic states to elucidate energy transfer dynamics of biological systems [7, 8]. In contrast, the correlation between initial electronic excitation and ultrafast structural changes in chromophores is only in the nascent stage of development, due to challenges in implementing multiple femtosecond phase-locked excitation pulses in combination with broadband probes over different spectral regions. These recent developments include 2D electronic-vibrational spectroscopy [9] and 2D vibrational-electronic spectroscopy [10]. The ability to correlate the initial excitation of electronic states to the evolution of vibrational modes is important to explain dynamics not described in the framework of the Born-Oppenheimer approximation, such as the nonradiative transfer pathways between electronic states [11].

Compared to ultrafast electronic and IR spectroscopy, femtosecond stimulated Raman spectroscopy (FSRS) is a complementary technique that has the ability to interrogate ultrafast biological processes with high spectral resolution, by measuring narrow linewidth vibrational spectra in the time domain with femtosecond resolution [12, 13]. To obtain a FSRS spectrum, after initial electronic excitation from a visible broadband ultrafast actinic pump pulse, a picosecond Raman pulse and a femtosecond supercontinuum probe pulse stimulate the scattering of the molecular vibrational modes, and the resultant Raman scattering provides better signal intensity with greatly improved time resolution compared to traditional time-resolved spontaneous Raman spectroscopy [14]. While offering excellent temporal and vibrational spectral resolution to study excited-state structural dynamics, FSRS reports with limited electronic spectral resolution due to the broad electronic spectral line shape.

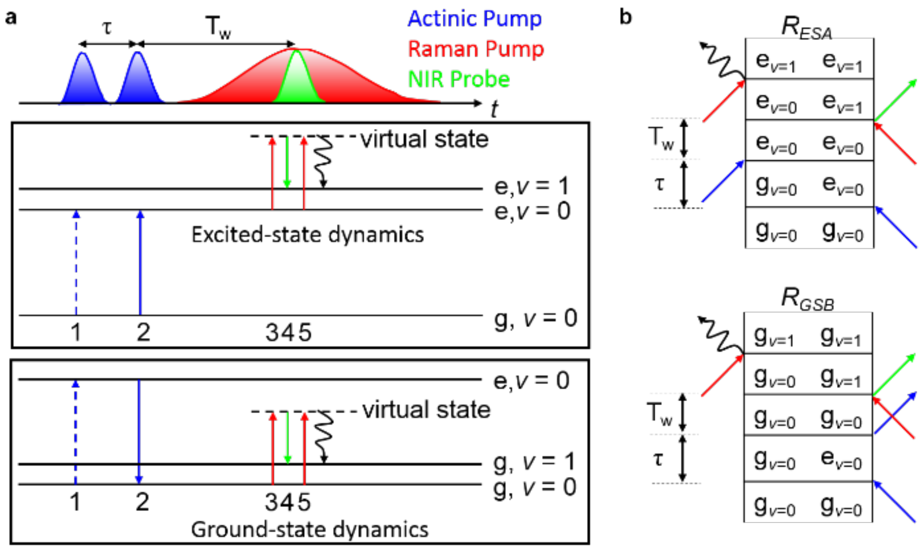

Fig. 1. Simplified schematic of two-dimensional electronic-Raman spectroscopy (2DER). (a) Energy ladder diagram of a three-level system and the 2DER pulse timing. The first excitation pulse (1) promotes the system to be in superposition between the ground state (g) and excited state (e). Dephasing of the electronic coherence is measured by step-wise increment (τ) of the second excitation pulse (2), and the second interaction populates the system to the excited/ground state. After a waiting time (Tw), near-infrared (NIR) probe (3) and Raman (4) pulses create a vibrational coherence on the excited/ground state. Additional interaction with the long-duration NIR probe (5) results in the emission of a photon during the vibrational free-induction decay in the direction of the NIR probe beam and is self-heterodyne detected. (b) Double-sided Feynman diagram describing the 2DER processes of the excited state (top) and ground state (bottom) manifolds.

Here, we employ multidimensional spectroscopy techniques in combination with FSRS to achieve frequency-resolved actinic excitation, which allows us to correlate the photoinitiated electronic excited state with the subsequent evolution of the nuclear vibrational modes. As a result of this combination, we obtain two-dimensional electronic-Raman (2DER) spectra with narrow-linewidth vibrational bands, nanometer electronic excitation resolution and femtosecond time resolution. Figure 1a illustrates the pulse interaction scheme of 2DER. An interaction with the first visible actinic pump pulse creates a coherent superposition between the ground state and the excited electronic state. The second interaction with a second visible actinic pump pulse (at a delay τ after the first pulse) converts the system from a coherence to a population state. After a waiting time T_w, the Raman pump and probe pulses interrogate the vibrational state of the system, and the resultant signal is emitted. In a pump-probe geometry, the signal travels in the same direction as the probe pulse and is self-heterodyne detected. Figure 1b describes the 2DER experiment under the framework of the diagrammatic perturbation theory used in nonlinear optical spectroscopy [15]. At a particular waiting time T_w, the experiment is repeated over a series of actinic pump delays τ. By Fourier transforming over τ, the spectrum of the excitation frequency can be resolved to obtain a two-dimensional spectrum that correlates the electronic excitation energy levels with the Raman vibrational modes. Previous study followed a similar approach by combining 2DES with a FSRS probe [16], but did not observe any T_w-dependent spectral shifts in the electronic excitation wavelength and vibrational Raman modes. As a high-resolution correlation technique, 2DER can elucidate the interaction pathways of various electronic states by obtaining spectral dynamics of Raman fingerprints without sacrificing time or spectral resolution. We demonstrate the capabilities of 2DER in the study of energy transfer processes by resolving the pathway of excited-state relaxation dynamics for β-carotene, a photosynthetic pigment that has an electronically dark state (S_1 band) which undergoes vibrational cooling on an ultrafast timescale [14].

Method

In our experimental setup (Fig. 2), a home-built noncollinear optical parametric amplifier (NOPA) was pumped by 40 fs pulses at 800 nm from a regenerative amplifier (Legend Elite, Coherent). The NOPA converted 19 mW of the fundamental pump pulses into 3 mW visible actinic pump pulses centered at 500 nm, corresponding to the S2 absorption band of β-carotene. The actinic pump beam was coupled into an acousto-optic programmable dispersive filter (AOPDF) pulse shaper (Dazzler, Fastlite) which compresses the pulses to ~50 fs, with bandwidth from 10-16 nm at full-width half-maximum (FWHM) and pulse energy of 500 µJ. The compressed actinic pump was modulated by the pulse shaper to obtain two 250 µJ pulses centered at 500 nm wavelength with controllable time delay τ from 0 to 160 fs in 4 fs steps, and relative phases of 0 and π. The actinic pump pulses were then directed to the sample using a 650 nm long-pass dichroic mirror (DMLP650, Thorlabs). A linear positioning stage (LS-110, PI) was used to control the waiting time Tw of the actinic pump pulses with femtosecond precision. Part of the fundamental pump beam from the amplifier was sent to a 4-f grating filter that consist a pair of ruled diffraction gratings (1200 lines/mm) and a pair of f = -250 mm concave mirrors. The Raman pump pulse was generated by spectrally filtering the pump beam to a narrow band spectral profile centered at 791 nm with a bandwidth of 1 nm at FWHM, and pulse energy of 1 µJ.

Fig. 2. Schematic of the 2DER setup. From the output of the NOPA, the pulse shaper creates two actinic pump pulses with variable delays and relative phases. The two collinearly aligned actinic and Raman pump pulses together with the NIR region of a white-light continuum are focused on the same spot of the sample in a pump-probe geometry.

The Raman pump beam was directed to the sample through the 650 nm long-pass dichroic mirror collinearly with the actinic excitation beam. A small amount of fundamental light was focused with a f = 50 mm convex lens into a 2 mm thick sapphire plate to generate a white light continuum which was collimated by a f = -50 mm silver parabolic mirror. The white light continuum was spectrally filtered by an 850 nm long-pass filter (FELH0850, Thorlabs) to obtain only the NIR wavelength region for the probe, with pulse energy of 30 nJ. Using a translation stage, the Raman pump beam was adjusted to be temporally overlapped with the probe beam to enable stimulated Raman scattering. All three pump and probe beams were focused onto the sample in the 200 µm pathlength flow cell that is mounted onto a motorized rotation stage (PRM1Z8, Thorlabs), at the same spot with a f = -150 mm silver parabolic mirror in a pump-probe geometry. Estimated spot sizes of the actinic pump, Raman pump and Raman probe on the sample are 90 µm, 70 µm and 60 µm, respectively. The signal is emitted in the same direction as the probe beam, which is collimated by an identical silver parabolic mirror. The signal and probe beams were focused with a f = 50 mm convex lens into an imaging spectrograph (ARC-SP-2356, Princeton Instruments) and detected with a digital charge-coupled device (CCD) camera (PIX100F, Princeton Instruments).

The ability to control the relative phases of the actinic pump pulses with the pulse shaper allows phase-cycling to be implemented to filter away unwanted lower-order signals, and enables data to be collected in a rotating frame [17, 18]. The reference wavelength was set at 530 nm to collect the data in a partial rotating frame, resulting in a Nyquist sampling limit of 12 fs. These phase-cycling and reference frequency procedures are similar to the procedures for a pulse shaper assisted 2DES experiment [17]. The actinic pump beam and Raman pump beam were chopped at a frequency of 250 Hz and 500 Hz, respectively, to produce pulse sequence that yielded different spectra [19]. The digital CCD camera acquired spectral images of the transmitted probe beam at a frame rate of 1 kHz, which matches the repetition rate of the laser in our experiment. To acquire a single 2DER spectrum with the above parameters without averaging, 328 frames are required. Typically, ~12,000 spectra were recorded to generate an averaged 2DER spectrum at one waiting time Tw. Recorded raw FSRS spectra at all actinic pump delays τ and relative phases were fitted with a broad baseline obtained from spline interpolation of points between Raman peaks and with straight lines under the peaks to remove the background present from transient absorption of β-carotene at 791 nm [20]

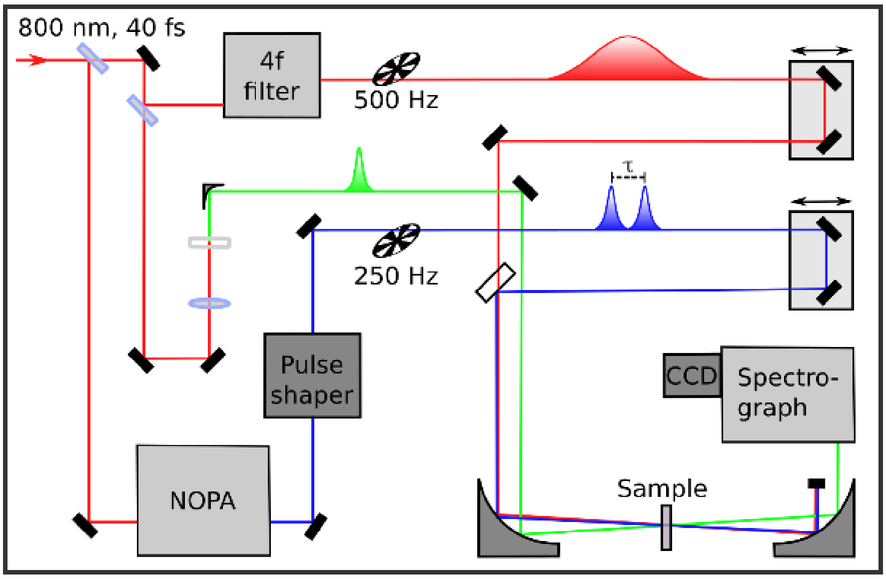

Figure 2. Schematic of the 2DER setup. From the output of the NOPA, the pulse shaper creates two actinic pump pulses with variable delays and relative phases. The two collinearly aligned actinic and Raman pump pulses together with the NIR region of a white-light continuum are focused on the same spot of the sample in a pump-probe geometry.

In 2DER measurements, the vibrational Raman modes of β-carotene molecules were driven in and out of resonance as the time separation τ between the two actinic pump pulses increased, while non-resonant Raman signal such as solvent peaks led to non-responsive changes. Therefore, measuring the rise and fall of the Raman bands as τ changes remove contributions from solvent peaks, allowing the identification of transient Raman peaks without having to examine the difference in the signal obtained from the FSRS spectrum of β-carotene and pure solvent. Transient stimulated Raman signals were phase-cycled to remove unwanted lower-order signals [17, 18]. The phase-cycled data were Fourier transformed along the pump delay τ axis to yield a 2DER spectrum.

Results

We performed 2DER spectroscopy to examine β-carotene (Sigma-Aldridge) that was dissolved in cyclohexane solvent (OD500nm = 0.3). Several distinct stimulated Raman bands in the FSRS spectrum were observed with high contrast after removal of the broad background with the vibrational bands at 1005 cm-1, 1156 cm-1, 1523 cm-1 and 1770 cm-1 to 1800 cm-1 corresponding to methyl rock, symmetric C−C stretch, terminal C=C stretch and central C=C stretch [20], respectively.

To present both the electronic and Raman vibrational spectral information of all measured vibrational frequencies, we plotted the excitation wavelength for each transient stimulated Raman frequency, and used colored contours to denote the measured stimulated Raman intensity of each vibrational mode (Fig. 3a).

In the time-resolved 2DER spectra (Figs. 3a-c), the negative peaks are due to prominent ground state bleach (GSB) signals from S0→S2 population transfer [21]. Positive peaks at the same excitation wavelength are from excited state absorption (ESA) signals of the S1 state and imply a S2→S1 population transfer pathway. High electronic excitation spectral resolution was achieved for the transient vibrational Raman modes, including ground-state bleaches of methyl rock, C−C stretch, symmetric C=C stretch, and excited-state absorption of central C=C stretching mode. Furthermore, we were able to observe relaxation dynamics of β-carotene with femtosecond temporal resolution. The narrowing and upshift of the S1 C=C peak from 1770 cm-1 to 1800 cm-1 (horizontal dotted lines in Fig. 3d) is consistent with previous studies [14] and has been assigned to a vibrational cooling process. As a consistency check, we integrated the 2DER spectrum over the actinic pump axis and retrieve a transient spectrum similar to that obtained from the difference between the FSRS and ground-state Raman spectra. The strength of 2DER spectroscopy lies in its ability to resolve the excitation degree of freedom. This capability is illustrated in our observation of the S1 ESA linewidth broadening towards shorter actinic pump wavelengths as waiting time Tw increases (vertical dotted lines in Fig. 4d). This linewidth broadening may be related to the coupling of vibronic levels in the S2 and S1 states [22] and work is currently being undertaken to clarify the details. From the 2DER spectra in Figure 4, it can also be seen that different electronic states represented by different narrow Raman bands were also well resolved from each other. In comparison, 2DES achieves a lower resolution when only electronic transitions are probed, as different electronic transitions have broad overlapping line shapes [23, 24].

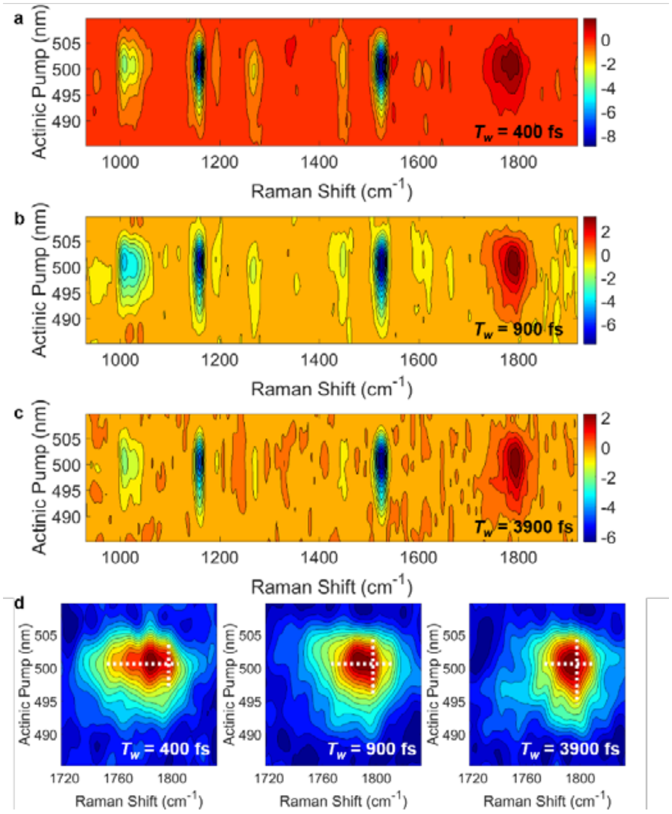

Fig. 3. 2DER resolves initial electronic excitation wavelengths in time-resolved FSRS to correlate electronic transitions with vibrational Raman frequencies of β-carotene. (a-c) Absorptive 2DER spectra of β-carotene taken at different waiting times Tw (bottom right). Peaks with negative amplitude at 1005 cm-1, 1156 cm-1, and 1523 cm-1 are due to GSB signals, while peaks with positive amplitude from 1770 cm-1 to 1800 cm-1 are due to excited state signals. Fourier transform of the 2D signal in Fig. 3c along the actinic pump delay τ is shown in a. (d) Close-up of the S1 ESA 2DER spectral shape in a-c. Full width at half maximum (FWHM) of the 2DER spectra for actinic pump at 500 nm and Raman shift at 1798 cm-1 are plotted in horizontal and vertical dotted lines, respectively. Spectral FWHM along the vibrational Raman axis narrows from 53 cm-1 (left) to 46 cm-1 (center) to 36 cm-1 (right). Spectral FWHM along the actinic pump axis broadens from 6.5 nm (left) to 8.5 nm (center) to 9.7 nm (right).

Discussions and Conclusions

By combining the pulse shaper assisted 2D spectroscopic method and FSRS, we have achieved 2DER spectroscopy that follows the dynamics of vibrational Raman modes of chromophores and correlates them to the initial electronic excitation wavelength. Two-dimensional electronic-vibrational spectroscopy [9] and two-dimensional vibrational-electronic spectroscopy [10] have generally low time resolution (~200 fs) that is limited by the narrow IR spectral bandwidth (~200 cm^{-1}), and it is challenging to access a wide infrared spectral range. Although a wide spectral detection range has been reported using an octave-spanning broadband MIR probe pulse [25], the stimulated Raman-based system we reported here is simpler to implement in a straightforward adaptation of a pump-probe geometry 2DES experiment [17, 26] by adding a narrowband Raman pump that can be obtained with a grating or narrowband filter. With our setup, a 2DER spectrum and a 2DES spectrum with NIR probe can be simultaneously obtained by chopping the Raman pump beam.

Our 2DER results exemplify the sensitivity and spectral resolution of 2DER, enabling the characterization of energy relaxation pathways and other spectral dynamics that are obscure to other methods. The application of 2DER to natural and artificial photosynthetic light-harvesting complexes is particularly useful because the elucidation of energy transfer pathways often requires knowledge of molecular structure of the chromophores and their relative orientations. A combination of 2DER with plasmonic materials designed to enhance Raman scattering can further expand the applicability of 2DER and poses exciting prospects.

Future outlook

Carotenoid plays crucial roles in light-harvesting and photo-protection during photosynthesis [27,28]. In plants, carotenoids are essential for the absorption of light in the wavelength regions that is inaccessible to chlorophylls, increasing spectral cross-section, driving photosynthesis. Despite its importance, our understanding of carotenoid excited-state manifold remains incomplete. Transient absorption spectroscopy has described carotenoids by a three-level system , in which the light is absorbed by the S_2 state before rapidly decaying in a few hundreds of femtoseconds to the “dark” S_1 state, which then decays back to the grounds state (S_0) on the picosecond time scale [29]. The S_0 to S_1 state transition is symmetry forbidden [30]. However, it remains unclear about the presence of additional intermediate electronic state involved in the relaxation process [31]. These intermediate electronic states were predicted to be dark states between S_2 and S_1 states, although previous works have reported a transition dipole moment for the intermediate electronic state [32,33]. Hence, the challenge of resolving the energetic organization of the electronic states in carotenoids requires spectroscopic tools with both high temporal and frequency resolution. We have acquired some preliminary results as reported in the earlier parts of this report. Our immediate plan is to deploy the new 2DER technique to resolve this long standing puzzle in carotenoid studies.

Achievements

The grant has provided manpower support for a year for one Postdoctoral Fellow, Dr. Zhengyang Zhang.

The results achieved from this research project has been published in a leading journal of optics: ‘Two-dimensional electronic-Raman spectroscopy’, *Optics Letters* **43**, 939 (2018).

We also used the setup to study the dynamics of phycocyanobilin in a glass forming liquid. This is published in ‘Glass formation of a DMSO–water mixture probed with a photosynthetic pigment’, *Phys. Chem. Chem. Phys.* **20**, 17552-17556 (2018).

An invited presentation entitled “Two-Dimensional Electronic-Raman Spectroscopy“ will also be presented at the leading conference for Raman spectroscopy, 26th International Conference on Raman Spectroscopy, 26th-31st June 2018. Jeju, South Korea. http://www.icors2018.org/invited.php

Presentations of the work have also been made at the

1. Contributed talk: The 6th Asian Spectroscopy Conference (ASC6), 1-4 Sep. 2017, National Tsing Hua University, Hsinchu, Taiwan
2. Poster: The 9th International Conference on Coherent Multidimensional Spectroscopy (CMDS2018), 25-29 June 2018, Seoul, S. Korea

References

1. Jonas, D. M., Two-dimensional femtosecond spectroscopy. Annu. Rev. Phys. Chem. 2003, 54, 425-63.
2. Mukamel, S., Multidimensional Femtosecond Correlation Spectroscopies of Electronic and Vibrational Excitations. Annu. Rev. Phys. Chem. 2000, 51, 691-729.
3. Cho, M., Coherent Two-Dimensional Optical Spectroscopy. Chem. Rev. 2008, 108, 1331-1418.
4. Zheng, J.; Kwak, K.; Fayer, M. D., Ultrafast 2D IR Vibrational Echo Spectroscopy. Acc. Chem. Res. 2007, 40, 75-83.
5. Hamm, P.; Helbing, J.; Bredenbeck, J., Two-dimensional infrared spectroscopy of photoswitchable peptides. Annu. Rev. Phys. Chem. 2008, 59, 291-317.
6. Ghosh, A.; Ostrander, J. S.; Zanni, M. T., Watching Proteins Wiggle: Mapping Structures with Two-Dimensional Infrared Spectroscopy. Chem. Rev. 2017, 117, 10726-10759.
7. Schlau-Cohen, G. S.; Ishizaki, A.; Calhoun, T. R.; Ginsberg, N. S.; Ballottari, M.; Bassi, R.; Fleming, G. R., Elucidation of the timescales and origins of quantum electronic coherence in LHCII. Nat. Chem. 2012, 4 (5), 389-95.
8. Ostroumov, E. E.; Mulvaney, R. M.; Cogdell, R. J.; Scholes, G. D., Broadband 2D electronic spectroscopy reveals a carotenoid dark state in purple bacteria. Science 2013, 340 (6128), 52-6.
9. Oliver, T. A.; Lewis, N. H.; Fleming, G. R., Correlating the motion of electrons and nuclei with two-dimensional electronic-vibrational spectroscopy. Proc. Natl. Acad. Sci. U.S.A. 2014, 111 (28), 10061-6.
10. Courtney, T. L.; Fox, Z. W.; Slenkamp, K. M.; Khalil, M., Two-dimensional vibrational-electronic spectroscopy. J. Chem. Phys. 2015, 143 (15), 154201.
11. Kühl, A.; Domcke, W., Multilevel Redfield description of the dissipative dynamics at conical intersections. J. Chem. Phys. 2002, 116 (1), 263.
12. Kukura, P.; McCamant, D. W.; Mathies, R. A., Femtosecond Stimulated Raman Spectroscopy. Annu. Rev. Phys. Chem. 2007, 58, 461-88.
13. Dietze, D. R.; Mathies, R. A., Femtosecond Stimulated Raman Spectroscopy. Chem. Phys. Chem. 2016, 17 (9), 1224-51.
14. McCamant, D. W.; Kukura, P.; Mathies, R. A., Femtosecond Time-Resolved Stimulated Raman Spectroscopy: Application to the Ultrafast internal Conversion in b-carotene. J. Phys. Chem. A 2003, 107, 8208-8214.
15. Mukamel, S., Principles of Nonlinear Optics and Spectroscopy. Oxford University Press: New York, 1995.
16. Wilcox, D. E.; Ogilvie, J. P., Two-dimensional electronic femtosecond stimulated Raman spectroscopy. EPJ Web Conf. 2013, 41.
17. Zhang, Z.; Wells, K. L.; Hyland, E. W. J.; Tan, H.-S., Phase-cycling schemes for pump–probe beam geometry two-dimensional electronic spectroscopy. Chem. Phys. Lett. 2012, 550, 156-161.
18. Tan, H.-S., Theory and Phase Cycling Scheme Selection Principles of Collinear Phase Coherent Multi-dimensional Optical Spectroscopy. J. Chem. Phys. 2008, 129, 124501.
19. Laimgruber, S.; Schachenmayr, H.; Schmidt, B.; Zinth, W.; Gilch, P., A femtosecond stimulated raman spectrograph for the near ultraviolet. Appl. Phys. B 2006, 85 (4), 557-564.
20. Quick, M.; Kasper, M. A.; Richter, C.; Mahrwald, R.; Dobryakov, A. L.; Kovalenko, S. A.; Ernsting, N. P., b-Carotene Revisited by Transient Absorption and Stimulated Raman Spectroscopy. Chem. Phys. Chem. 2015, 16 (18), 3824-35.
21. Kukura, P.; McCamant, D. W.; Mathies, R. A., Femtosecond Time-Resolved Stimulated Raman Spectroscopy of the S2 (1Bu+) Excited State of b-Carotene. J. Phys. Chem. A 2004, 108, 5921-5925.
22. Takaya, T.; Iwata, K., Relaxation Mechanism of b-carotene from S2 (1Bu+) State to S1 (2Ag-) State: Femtosecond Time-Resolved Near-IR Absorption and Stimulated Resonance Raman Studies in 900-1550 nm Region. J. Phys. Chem. A 2014, 118 (23), 4071-8.
23. Christensson, N.; Milota, F.; Nemeth, A.; Sperling, J.; Kauffmann, H. F.; Pullerits, T.; Hauer, J., Two-Dimensional Electronic Spectroscopy of b-Carotene. J. Phys. Chem. B 2009, 113, 16409–16419.
24. Calhoun, T. R.; Davis, J. A.; Graham, M. W.; Fleming, G. R., The separation of overlapping transitions in b-carotene with broadband 2D electronic spectroscopy. Chem. Phys. Lett. 2012, 523, 1-5.
25. Gaynor, J. D.; Courtney, T. L.; Balasubramanian, M.; Khalil, M., Fourier transform two-dimensional electronic-vibrational spectroscopy using an octave-spanning mid-IR probe. Opt. Lett. 2016, 41 (12), 2895-8.
26. Myers, J. A.; Lewis, K. L. M.; Tekavec, P. A.; Ogilvie, J. P., Two-color two-dimensional Fourier transform electronic spectroscopy with a pulse-shaper. Opt. Express 2008, 16, 17420-17428.

27 Frank, H. A.; Cogdell, R. J., Carotenoids in Photosynthesis. *J. Photochem. Photobiol.* 1996, *63*, 257-264.

28. Polívka, T.; Sundström, V., Ultrafast Dynamics of Carotenoid Excited States-From Solution to Natural and Artificial Systems. *Chem. Rev.* 2004, *104*, 2021–2071.
29. Perez Lustres, J. L.; Dobryakov, A. L.; Holzwarth, A.; Veiga, M., $S_2 \rightarrow S_1$ internal conversion in b-carotene: strong vibronic coupling from amplitude oscillations of transient absorption bands. *Angew. Chem. Int. Ed. Engl.* 2007, *46* (20), 3758-61.
30. Polívka, T.; Herek, J. L.; Zigmantas, D.; Akerlund, H.; Sundström, V., Direct observation of the (forbidden) S_1 state in carotenoids. *Proc. Natl. Acad. Sci. U.S.A.* 1999, *96*, 4914-4917.
31. Polívka, T.; Sundström, V., Dark excited states of carotenoids: Consensus and controversy. *Chem. Phys. Lett.* 2009, *477* (1-3), 1-11.
32. Ostroumov, E.; Muller, M. G.; Marian, C. M.; Kleinschmidt, M.; Holzwarth, A. R., Electronic coherence provides a direct proof for energy-level crossing in photoexcited lutein and *b*-carotene. *Phys. Rev. Lett.* 2009, *103* (10), 108302.
33. Ostroumov, E. E.; Mulvaney, R. M.; Cogdell, R. J.; Scholes, G. D., Broadband 2D Electronic Spectroscopy Reveals a Carotenoid Dark State in Purple Bacteria. *Science* 2013, *340*, 52-56.