

Ultrafast Interaction of Dark and Bright Electronic States in Open-Chain Carotenoids Investigated by Pump-DFWM

T. Miki¹, T. Buckup¹, M. Marek¹, R. J. Cogdell² and M. Motzkus¹

¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

²Institute of Biomedicine & Life Science, University of Glasgow, G12 8QQ Glasgow, Lanark, Scotland

Authors e-mail address: tiago.buckup@pci.uni-heidelberg.de, marcus.motzkus@pci.uni-heidelberg.de

Abstract: Coupling between dark and bright electronic states in carotenoids was observed in the ultrafast evolution of vibrational coherence and in the non-oscillatory signal of pump-DFWM. Coupling efficiency depends on the number of conjugated double bonds.

OCIS codes: (300.6230) Spectroscopy, coherent anti-Stokes Raman scattering; (300.6500) Spectroscopy, time-resolved

1. Introduction

The ultrafast femtochemistry of carotenoids is governed by the interaction between electronic excited states. The two important functions of carotenoids, namely light harvesting and photo-protection, has been explained by the relaxation dynamics within a few hundred femtoseconds from the lowest optically allowed excited state S_2 to the optically dark state S_1 [1-3]. Extending this picture, some additional dark states (generally called S_x) and their interaction with S_2 state have been also suggested to play a major role in the ultrafast deactivation of carotenoids and its properties [4-6]. Here, we investigate the interaction between such dark and bright electronic excited states of open chain carotenoids, particularly its dependence on the number of conjugated double bonds (N). We focus on the ultrafast wave packet motion on the modified potential surface by the interaction between bright and dark electronic states. In this regard, pump-degenerate four-wave mixing (pump-DFWM) is applied to a series of carotenoids with different number of conjugated double bonds $N = 9, 10, 11$ and 13 (neurosporene, spheroidene, lycopene and spirilloxanthin, respectively).

2. Experimental

Pump-DFWM measurements were carried out by using the experimental setup which has been described in detail previously [7]. All pulses were generated using non-collinear optical parametric amplifiers (nc-OPA). The Initial Pump pulse (IP) (18 fs) was resonant with the S_0 - S_2 absorption. All three DFWM pulses were originated from a second nc-OPA (15 fs). DFWM spectrum was resonant only with the excited state absorption (ESA). The IP pulse was sent to a delay line (delay T) while two DFWM pulses were further delayed via piezo stages (τ_{12} and τ_{23}). DFWM beams were configured in a folded boxcar geometry producing a spatially separate, background-free signal. Recrystallized carotenoids were dissolved in THF and circulated in a 450 μm flow cell during the measurements.

3. Results and Discussion

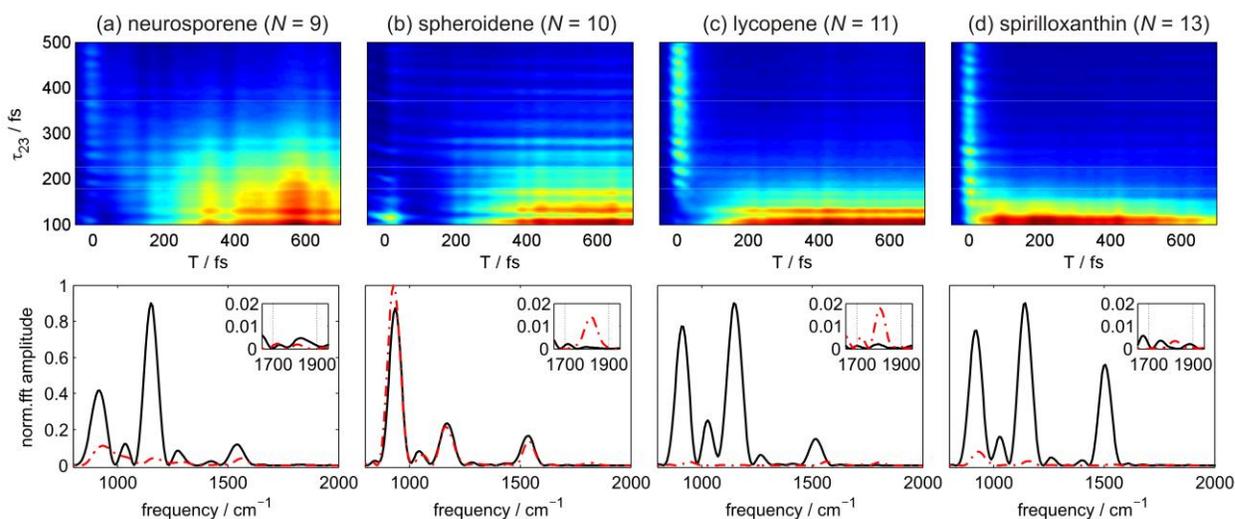


Fig. 1. 2D-Plots of the pump-DFWM transients in the probe delay τ_{23} against the initial pump delay T of the four different carotenoids (top). FFT power spectra of coherent signals at $T = 10$ fs (black solid line) and at 700 fs (red broken line) by frequency axis (bottom). Detection wavelengths were chosen to maximize contribution from C-C and C=C modes. Mode at 1800 cm^{-1} is weak at selected detection wavelengths.

The pump-DFWM transient 2D signals of the four carotenoids show similar features (Fig. 1, top). Strong non-oscillatory signal at late T-delays ($\sim T > 200$ fs) dephases fast and its dephase time constant scales with the lifetime of S_1 -state. Further non-oscillatory contribution at early T-delays ($\sim T < 50$ fs) is related to the formation of a hot- S_0 signal via stimulated emission pumping (SEP) directly after excitation of the S_2 with the IP. This signal raises slowly along τ_{23} delay for all carotenoids except for spheroidene ($N=10$). In spheroidene, such a SEP signal can be detected already at very early τ_{23} delay times. Numerical simulation of the whole 2D signal of pump-DFWM shows the SEP pathway does not occur directly from the S_2 state for spheroidene, but from an additional excited state (S_x), which is populated within 10-20 fs after the Franck-Condon region [8,9].

The 2D signals also display a strong oscillatory contribution (Fig. 1, bottom). After FFT, several vibrational modes can be clearly identified at 915 cm^{-1} (solvent), 1030 cm^{-1} (methyl rocking mode), 1150 cm^{-1} (C-C stretching modes) as well as 1550 cm^{-1} (C=C stretching mode). Here, the amplitude ratio between C-C and C=C modes is similar for all measurements except, again, for spheroidene. Spheroidene's spectrum additionally differs from the other ones by showing asymmetric satellites, which are visible only at early T delays and vanish completely for later T. The satellites stem from interferences between the coherences of the SEP and the ESA signal and further corroborates the existence of an additional dark (S_x) state being populated at early T delays in spheroidene [8,9].

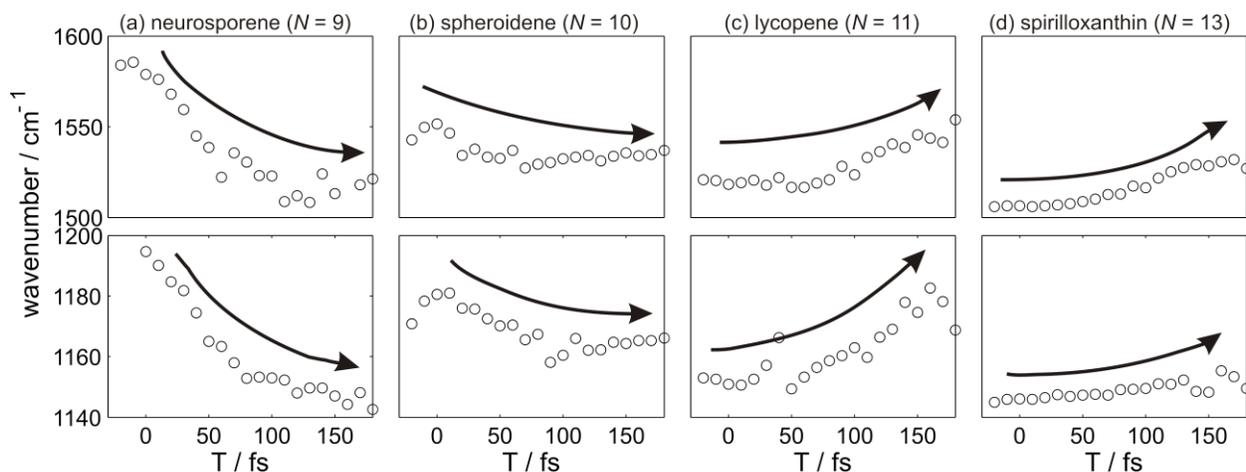


Fig. 2. The vibrational frequency evolution of C-C and C=C modes.

The evolution of the vibrational frequency in the T-delay reveals additional interactions between dark and bright states. Such an evolution of C-C (1150 cm^{-1}) and C=C (1545 cm^{-1}) stretching modes are shown in figure 2. While for longer carotenoids ($N=11$ and 13), the vibrational frequency increases as the system follows the S_2 - S_1 relaxation, for shorter carotenoids ($N=9$ and 10), the frequency decreases. In general, in an anharmonic potential the vibrational frequency increases as the system relaxes towards lower levels. Our results indicate that short carotenoids display strongly distorted potentials when compared to longer carotenoid. The magnitude of this anharmonicity can be explained by the efficient coupling between S_2 and a dark S_x state (in this case a B_u type), which stabilizes the higher energy levels of the C-C and C=C vibrational modes at early delay times ($T < 50$ fs) [10]. For longer carotenoids, this dark state is energetically shifted in respect to the S_2 , decreasing the interaction and leading to harmonic potential surface.

4. Conclusion

Pump-DFWM gives direct experimental evidence of the interaction between dark states with the S_2 electronic state. This interaction is highly dependent on the length of the carotenoid due to the energy shift between the electronic states, leading to different degrees of anharmonicity in electronic excited states.

5. References

- [1] H. A. Frank, R. J. Cogdell, *Photochem. Photobiol.* **63**, 257 (1996)
- [2] T. Polívka, V. Sundström, *Chem. Rev.*, **104**, 20211 (2004)
- [3] A. P. Shreve, J. K. Trautman, T. G. Owens, A. C. Albrecht, *Chem. Phys. Lett.*, **178**, 89 (1991)
- [4] G. Cerullo, D. Polli, G. Lanzani, S. De Silvestri, H. Hashimoto, R. J. Cogdell, *SCIENCE*, **298**, 2395 (2002)
- [5] H. Nagae, Y. Kakitani, Y. Koyama, *Chemical Physics Letters*, **474**, 342 (2009)
- [6] E. Ostroumov, M. G. Müller, C. M. Marian, M. Kleinschmidt, A. R. Holzwarth, *Phys. Rev. Lett.*, **103**, 108302 (2009)
- [7] J. Hauer, T. Buckup, and M. Motzkus, *J. Phys. Chem. A*, **111**, 10517 (2007)
- [8] M. S. Marek, T. Buckup, R. J. Cogdell and M. Motzkus *J. Phys. Chem.*, **139** (7), 074202 (2013)
- [9] T. Buckup and M. Motzkus *Annu. Rev. Phys. Chem.*, **65**, 39 (2014)
- [10] Y. Koyama, Y. Kakitani, T. Miki, R. Christiana and H. Nagae, *Int. J. Mol. Sci.* **11**(4), 1888 (2010)