Direct observation of short-lived excited electronic states with multidimensional light-matter interaction using 1+3 pulses

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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. 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 their properties.

Since traditional pump-probe transient absorption experiments fail to give an unambiguous picture of the dynamics in such complex molecules, we have developed and applied different strategies to extract more explicit information from the light-matter interaction. In particular we investigated the interaction between such dark and bright electronic excited states of open chain carotenoids with a specifically designed sequence of one pump and three probe pulses. This pump-degenerate four-wave mixing (pump-DFWM) technique, as a variant of multidimensional spectroscopy, allows to identifying the very short lived dynamics of the dark states. The approach is extended to a series of carotenoids with N = 9, 10, 11 and 13 (neurosporene, spheroidene, lycopene and spirilloxanthin) where the ultrafast wave packet motion on the potential surface is modified by the systematically tuned interaction between bright and dark electronic states.

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