Theory of relaxation dynamics within carotenoids via high frequency stretching modes

VYTAUTAS BALEVICIUS, DARIUS ABRAMAVICIUS, Vilnius University — Carotenoids are ubiquitous natural pigment molecules acting as light harvesters in the blue-green region of the spectrum, and at the same time ensuring the photoprotection against excessive light by quenching the triplet state of chlorophylls and singlet oxygen. However, their photophysics is still not fully understood, because the absorption takes place not into the optically dark lowest excited state $S_1$, but to the short-lived higher-lying state $S_2$. This leads to complicated intramolecular energy redistribution schemes within carotenoids. From the transient absorption experiments it is known that the $S_1$ state is populated shortly after the excitation of the $S_2$ state (on the time-scale of tens of femtoseconds). The corresponding excited state absorption signal is blue-shifting and narrowing at early times, which is attributed to the vibrational cooling of the $S_1$ state. We apply the secular density matrix theory to take into account both the internal conversion from the $S_2$ into the $S_1$ state and the subsequent relaxation within the manifold of high-frequency vibrational states corresponding to the carbon-carbon stretching modes (C-C and C=C). It allows us to obtain relevant pump-probe spectra in the time range from femto- to picoseconds.

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