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**Femtosecond Heterodyne Transient Grating Studies of Nonradiative Decay in $\beta$-Carotene and Peridinin: Contributions of Dark Intermediates and Double Quantum Coherences** SOUMEN GHOSH, JEROME ROSCIOLI, Michigan State Univ, HARRY FRANK, University of Connecticut, WARREN BECK, Michigan State Univ — Femtosecond transient grating spectroscopy with optical heterodyne detection was employed to characterize the ultrafast events in the nonradiative decay of $\beta$-carotene and peridinin in solution from the $S_2$ state. The contribution of double-quantum coherences to the time evolution of the third order signal was probed by scanning the interpulse delay between the first two pulses in the transient grating or stimulated photon-echo sequence. The results show that the double-quantum coherence pathways contribute significantly to the transient grating signal only at negative population delays, which is consistent with the requirements determined from double-sided Feynman diagrams when the third order signal is detected in the $-k_1+k_2+k_3$ direction. Response function calculations support the conclusion that the ultrafast (<20 fs) decay that contributes to the third order signal at positive population delays arises from an kinetic intermediate, which has been previously assigned to the $S_x$ state. We suggest that this intermediate arises not from a discrete electronic state but rather from a twisted conformation of the conjugated polyene. This proposal has significant implications with respect to the energy transfer function of carotenoids in photosynthesis.

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