"Early events of energy relaxation dynamics in carotenoids in solution and inside light-harvesting complexes"

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Carotenoids are ubiquitous pigments in photosynthetic organisms, performing the essential functions of photoprotection and light harvesting. They protect the photosynthetic apparatus by quenching both triplet excited (bacterio)chlorophyll ((B)Chl) and singlet oxygen. In addition, they serve as accessory light-harvesting pigments: light absorbed by carotenoids in the blue, green and yellow regions of the spectrum is transferred to (B)Chl, thereby making it available to drive photosynthesis. Traditionally, excited states dynamics in carotenoids has been described in terms of two low-lying excited singlet states called S_1 and S_2. The transition from S_0 ($1^1A_g^-$) to S_1 ($2^1A_g^-$) is one-photon forbidden for reasons of symmetry, so that the one-photon-allowed optical transition goes from S_0 to S_2 ($1^1B_u^+$). After photoexcitation, S_2 undergoes a rapid internal conversion (IC) process to S_1, completed in a few hundreds fs. An additional IC process from S_1 back to S_0 occurs on the ps timescale. Study of the IC process in carotenoids is a prerequisite for the understanding of the primary events in photosynthesis, .

In this work, we study the $S_2 \rightarrow S_1$ IC dynamics in carotenoids with conjugation length (number of conjugated double bonds) *n* ranging from *n*=5 to *n*=15, both in solution and inside the light harvesting complex 2 (LH2) of purple photosynthetic bacteria. To this purpose, we use a specially developed spectroscopic system combining very high temporal resolution (pulse width less than 20 fs) and broad spectral tunability, from the visible to the near-infrared wavelength range. This allows us to simultaneously probe the dynamics of S_2 and S_1 states and thus to obtain a complete picture of the IC process. The main results of these studies are the detection of an intermediate state mediating the $S_2 \rightarrow S_1$ IC process and the direct measurement of the energy transfer efficiency to the BChl.