

Almost all life on Earth depends on the products of photosynthesis — the biochemical process whereby solar energy is stored as chemical-rich compounds. The energy of captured photons is transferred through a network of pigment-protein complexes towards the reaction center. The reaction center is responsible for trans-membrane charge separation, which generates a proton motive force which drives all subsequent biochemical reactions. The ultrafast (femtosecond) nature of the primary processes in photosynthesis is the main reason for its astonishing efficiency. On this timescale, quantum effects start to play a role and can appear in measured spectra as oscillations. It has been hypothesized that these are evidence of wave-like energy transfer.

To unveil the fundamental principals of ultrafast excitation energy transfer in both natural and artificial light-harvesting systems, advanced spectroscopy techniques have been utilized. Coherent two-dimensional electronic spectroscopy is a state of the art technique which allows the most complete spectroscopic and temporal information to be extracted from the system under study. This technique has allowed us to identify a new photophysical process where the coherence of the initially excited state is shifted to the ground state upon an energy transfer step. Coherence dynamics caused by this process bear most of the signatures of pure electronic coherences, and can therefore be easily mistaken for coherent energy transfer. Our results imply that the wave-like energy transfer hypothesis should be reconsidered and tested against coherence shift mechanisms. Furthermore, we have demonstrated that the mixing between vibrational and electronic motions seem to be a general phenomenon in light-harvesting systems.