

Transient Non-Equilibrium Ground State Signals in 2D Spectra due to Energy Transfer

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Spectral features of energy transferring photosynthetic pigments are studied theoretically. We identify electronic ground state signals due to non-equilibrium state of nuclear vibrations resulting from de-excitation of pigments as the excitation passes through. We find characteristic long lived signals with unusual amplitude dependences on energy transfer rates and energetic disorder.

Energy transfer in photosynthetic pigments in nature predominantly occurs in a single exciton regime. In this regime, most of the nuclear motion on the photosynthetic pigments proceeds on the electronic ground state potential energy surfaces (PES). During the energy transfer process, molecules losing their excitation return to the electronic ground states, but the state of the nuclei exhibits transient traces of the evolution on the excited state PES. In a simplified picture, when the excitation leaves certain spectral region, the corresponding excited state absorption (ESA) and stimulated emission (SE) signals disappear, and the static ground state bleach (GSB) signal is compensated by the de-excited wavepacket. The compensation, however, is not perfect until the de-excited wavepacket equilibrates [1]. In the case of some intramolecular vibrational modes coupled to the electronic transition, the signal mismatch can survive for extended periods of time, while exhibiting patterns which cannot be explained by the ordinary ESA-SE-GSB picture (Fig. 1(middle)). The ground state signatures exhibit both coherent [2,3] and incoherent contributions, and their amplitudes behave differently from the excited state transient features with respect to energy transfer rates and the amount of electronic disorder in the system [1].

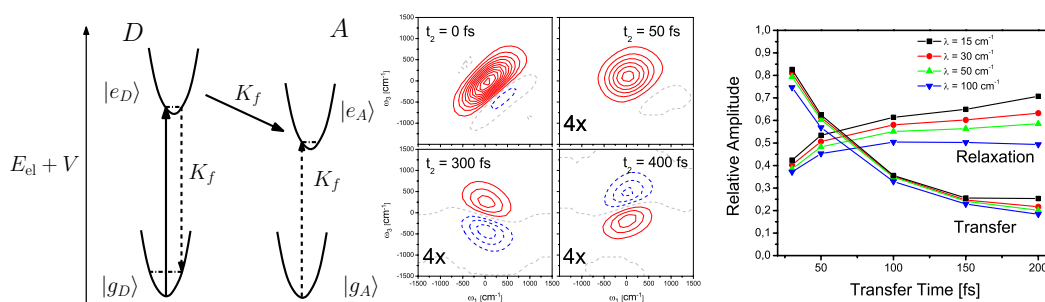


Fig.1 (left) Energy level and PES scheme of energy transfer between localized sites. Resonance excitation energy transfer is inevitably connected with exciting non-equilibrium vibrational wavepacket on both the acceptor and the donor molecules. (middle) The signal resulting from the non-equilibrium ground state wavepacket competes with the normal ground state bleach signal and decreases the total signal (cf. signals at $t_2 = 0$ and $t_2 = 50$ fs). Cancellation of the two ground state contributions is incomplete resulting in a net signal ($t_2 = 300$ fs and $t_2 = 400$ fs) until the transfer induced wavepacket reaches equilibrium. (right) Amplitude of the excited state acceptor signal decreases with increasing transfer time. On the donor, the amplitude remains largely unaffected by the transfer time. There is a pronounced dependence of the donor signal amplitude on the bath reorganization energy.

[1] T. Mančal *et al.*, *Can. J. Chem.*, **92**, 135 (2014).

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[3] D. Paleček *et al.*, manuscript in preparation