Coherence Shift Mechanism Explains Long-Lived Beatings in Bacterial Reaction Centers.

D. Paleček[1]*, P. Edlund[2], S. Westenhoff [2] and D. Zigmantas[1]
[1]Department of Chemical Physics, Lund University, P.O. Box 124, 221 00 Lund, Sweden
[3]Department of Chemistry, University of Gothenburg, Medicinaregatan 9C, 40530 Gothenburg, Sweden
**david@stanka.de*

We experimentally identified a new photophysical mechanism of coherence shift from the excited to ground electronic state, occurring during energy transfer process. It provides a clear explanation for the picosecond lifetimes of the coherences in the reaction centers.

In the number of two-dimensional electronic spectroscopy (2DES) studies, beatings in photosynthetic systems have been interpreted in terms of excitonic coherences and observation of coherent energy transfer has been claimed [1,2]. However ongoing controversy persists regarding interpretation of these signals. We used polarization-controlled 2DES and Fourier analysis to uncover a new coherence shift mechanism in purple bacteria *Rhodobacter sphaeroides* at 77 K, which explains in detail the appearance of the long-lived beatings.
In our earlier report, we showed spectroscopic signatures in bacterial reaction centers that pointed to the electronic origin of the coherences [3]. However the lifetime of these coherences is tenfold longer than the lifetimes of the participating excited states, which is unsettling. Recently, interplay between vibrational and electronic degrees of freedom (vibronic mixing), was proposed to be important for the interpretation of the quantum beats in 2DES [4,5]. However, none of these provide full explanation of our observations. Improved experiments and complex Fourier analysis allowed us to identify a new photophysical mechanism that we term “Energy transfer induced coherence shift” (ETICS). During ETICS, coherence, initiated in the excited state, is shifted to the ground electronic state during the energy transfer step [6]. Taking into account ETICS pathways resolves the disturbing mismatch of the lifetimes and provides explanation of the oscillation maps for all-parallel and cross-polarized measurements (Fig. 1), including the amplitude cancellation on the diagonal.

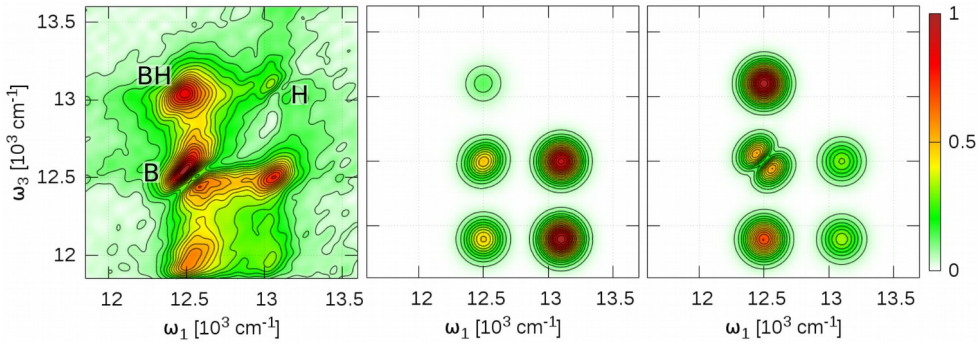

Fig. 1. All-parallel oscillation map at 560 cm^{-1}. Left: experimental oscillation map of rephasing real 2D signal, center: modeled pattern expected from normal stimulated emission and ground state bleach contributions, right: modeled interference between ground state bleach and ETICS signals reproducing cancellation on the diagonal.

ETICS process only requires fast energy transfer and relatively weak vibronic coupling. As these conditions are satisfied in multiple light-harvesting complexes and reaction centers, ETICS mechanism could play an important role in the coherent dynamics in these systems.

[1] H. Lee et al., Science **316**, 1462 (2007).
[2] G. S. Engel et al., Nature **446**, 782-786 (2007).
[3] S. Westenhoff et al., J. Am. Chem. Soc. **134**, 16484-16487 (2012).
[4] N. Christensson et al., J. Phys. Chem. B **116**, 7449-7454 (2012).
[5] V. Tiwari et al., Proc. Natl. Acad. Sci. U.S.A. **110**, 1203-1208 (2013).
[6] T. Mančal *et al*., Can. J. Chem., **92,** 135 (2014).