# Signatures of charge separation in the reaction center of PSII revealed by 2D electronic spectroscopy

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Charge separation in the Photosystem II (PSII) reaction center (RC) was studied with 2D electronic spectroscopy at ambient conditions. Primary charge separation and associated timescale (1.5 ps) are identified by comparison of measured and calculated 2D decay-associated-spectra (2DDAS). For the modelling, we applied a tight-binding Hamiltonian.

PSII RC is a unique biological system that converts sunlight energy into chemical energy by water splitting. The structure of the PSII RC [1] shows two symmetric branches containing 8 pigments each. It provides a very important model for the study of natural charge separation and charge transfer and has been extensively studied experimentally and theoretically. The charge separation processes in the PSII RC have been extensively investigated in the past by means of time-resolved spectroscopies; however, the 2D electronic spectroscopy was applied only recently (at 77 K [2] and at room temperature [3]). These studies were focused on the energy transfer processes and coherent oscillations arising in the series of 2D-spectra measured at different waiting times.

We performed an extended 2D electronic spectroscopy study of the PSII RC at ambient temperature combined with theoretical modelling. This approach allowed identification of the primary charge separation process in the RC and the corresponding timescale, as well as resolving energy transfer pathways. An excellent agreement was achieved between the measured and simulated 2D spectra (Fig. 1) and 2DDAS without involving any long-lived oscillations in the model to enhance charge separation [3] in the PSII RC.

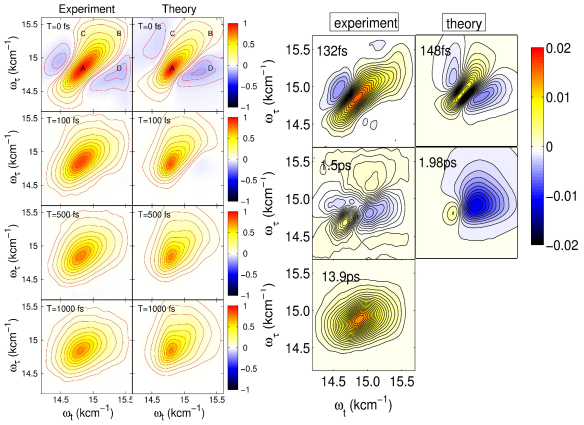


**Fig. 1.** Left: measured 2D spectra at different waiting times (as indicated) in comparison with the simulated one. Right: comparison of 2DDAS retrieved from the experiment and from the simulations.

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