Multidimensional Spectroscopic Studies of Photosynthetic Reaction Centers

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We describe two-dimensional electronic spectroscopy studies of the primary processes of energy transfer and charge separation in photosynthetic reaction centers. We compare the observation of coherent dynamics in reaction centers with control studies in monomer pigments. To probe charge separation in reaction centers, we combine two-dimensional electronic and Stark spectroscopies.

The primary events in photosynthesis involve the harvesting of light energy by photosynthetic antennae and the ultrafast transfer of the excitation to reaction centers which rapidly transform it into stable charge separation. In the photosystem II reaction center (PSII RC) of higher plants, the predominant pigment is Chlorophyll a (Chl a) while in bacterial reaction centers (BRC) of purple photosynthetic bacteria it is bacteriochlorophyll a (BChl a). The PSII RC and BRC possess similar structures, exhibiting two-fold symmetry with electron transfer occurring along a single branch. The first reports of coherent dynamics in photosynthetic systems were made by Vos et al. in the BRC[1]. More recently, coherent processes in photosynthetic systems have received considerable attention following their observation in the FMO complex[2] by two-dimensional electronic spectroscopy (2DES). An ongoing challenge is to understand the physical origin and functional significance of the observed coherent dynamics[3]. Coherent dynamics were recently reported in 2DES studies of the PSII RC as well[4]. 2DES provides rich information about coherent dynamics and their physical origin[5]. We present comparative 2DES studies of the PSII RC and BRCs, and their monomer pigments Chl a and BChl a. By comparing the frequencies and distributions of the coherent dynamics in the monomers and RCs we motivate the assignment of the physical origin of the coherences. By better understanding the spectroscopic signatures of coherence we aim to gain insight into the possible functional significance of the coherences in RCs.

A key challenge for understanding photosynthetic charge separation is identifying the charge transfer states. Linear Stark spectroscopy has proven to be a valuable tool for uncovering charge-transfer states in photosynthetic RCs [2, 3] and other systems [1]. We demonstrate 2D electronic Stark spectroscopy (2DESS) to enable sensitive, high time-resolution detection of charge transfer states and their role in charge separation in photosynthetic RCs.

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