

# Comparison of Coherent Oscillations in 2DES studies of Bacterial Reaction Centers and Bacteriochlorophyll a

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We use two-dimensional electronic spectroscopy to study the coherent dynamics of photosynthetic Bacterial Reaction Centers (BRC) and monomeric Bacteriochlorophyll a (BChl a), the most abundant pigment in BRCs. We find several coherent modes common to both systems and consider the origin of the coherent dynamics.

The Bacterial Reaction Center (BRC) serves as an important model system for understanding photosynthetic charge separation. Within the BRC, four BChl a and two bacteriopheophytin a (BPheo a) pigments are arranged along two symmetric branches. Within the Q<sub>y</sub> region, the BRC contains three well-separated absorptions, denoted P, B and H for the strongly-coupled “special pair” BChl a, the monomeric BChl a and the BPheo a. The BRC has been extensively studied using ultrafast pump-probe spectroscopy; a pump-probe study by Vos, et al was notably the first to observe coherent oscillatory dynamics in photosynthetic pigment-protein complexes [1]. Coherent dynamics have since been observed using two-dimensional electronic spectroscopy (2DES) in the FMO complex [2] and as well as many other systems. 2DES is particularly suited for characterizing coherent dynamics: the two dimensional distribution of coherent signals can provide insight into the physical origin of the coherences [3,4]. Here we present a comparative 2DES study of the *Rh. sphaeroides* WM250V mutant BRC, which lacks the active-branch quinone, side by side with 2DES of monomeric BChl a in solution. Both systems exhibit many prominent coherent modes (Figure 1), several of which are common to both systems. By comparing the frequencies and distributions of the coherent dynamics in BChl a and the BRC we motivate the assignment of the physical origin of the coherences in BRCs.

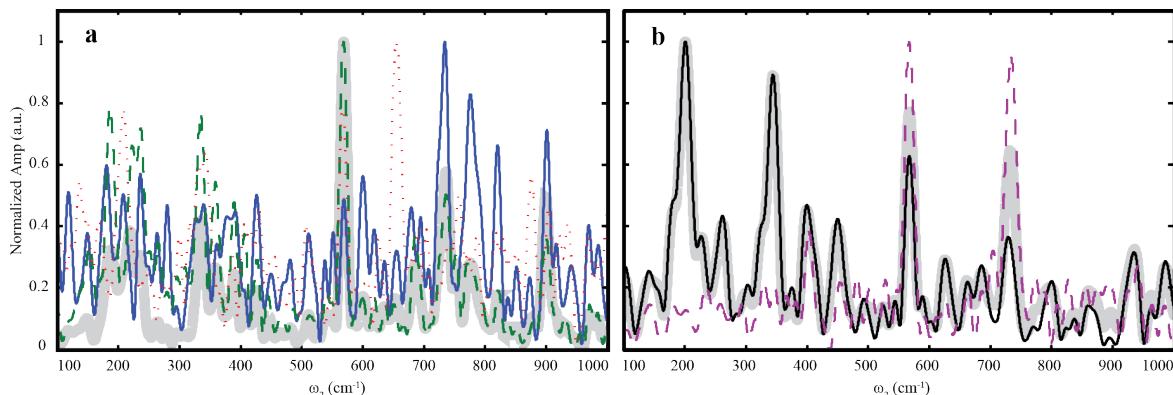


Fig.1 (a) Normalized Frobenius Spectra of WM250V BRC and (b) BChl a. Frobenius spectrum of the full 2D spectrum shown by thick grey lines. (a) Windows around the diagonal peak of the BChl a special pair P shown by blue line (solid, thin), BChl a peak B in green line (dashed), and Bacteriopheophytin a H in red line (dotted). (b) Windows around the Q<sub>v</sub> peak shown by black line (solid), and cross peak by purple line (dashed).

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- [3] V. Butkus, *et al*, Chem Phys Lett **545**, 40-43 (2012).
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