Light-Induced Electron Spin Qubit Pair States in Type I and Type II Photosynthetic Reaction Centers

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Photosynthetic Reaction Center (RC) proteins are complex yet well-defined and tunable systems, which can serve as ideal model systems for investigating spin dynamics and coherences, since long-lived electron spin entanglement - manifested as light-induced spin-correlated radical pairs (SCRPs) - can easily be generated and observed. Since discovery of SCRPs in our group in the 1980s, they have been extensively used to enhance our understanding of structure-function relationships in photosynthetic RC proteins. More recently, SCRPs have also been utilized as tools for quantum sensing where they act as electron spin-based quantum bit (qubit) pairs. Decoherence poses a significant challenge in realizing practical applications of electron spin qubits. Despite their importance, critical aspects like coherence spatial lengths, lifetime, decoherence mechanisms, and their interaction with the local and global protein structure, remain poorly understood, limiting our understanding of decoherence. Our work utilizes both experimental and theoretical strategies, including deuteration, biochemical modification of photosynthetic RCs, advanced EPR techniques, and semiclassical, atomistic modeling to describe decoherence processes in Photosystem I and type II photosynthetic RCs of purple bacteria. In particular, high-frequency electron paramagnetic resonance (EPR) spectroscopy operating at 130 GHz and 4.6 T was used to study coherence times through the decay of two-pulse electron spin echo signals and Rabi oscillations at various temperatures. The coherence times show only minimal dependence on biological species, deuteration, biochemical treatment, and paramagnetic species. To interpret these observations, we carried out large scale simulations of spin dynamics utilizing existing RC crystal structures. Comparison with the experiments shows that “classical” nuclear spin diffusion and instantaneous diffusion mechanisms alone cannot explain the observed decoherence times. We suggest that the low-temperature dynamics of methyl and amino groups surrounding the unpaired electron spin centers are the main factor governing loss of coherence in photosynthetic RCs. Understanding the intricate dynamics can enhance our knowledge of photosynthetic processes and their potential applications in achieving more efficient solar energy conversion.