Studies of Photochemically Induced Dynamic Nuclear Polarization in Photosynthetic Bacterial Reaction Centers: Wavelength and Time Dependence

Solid-state NMR spectra of quinone-reduced photosynthetic bacterial reaction centers (RCs) and chromatophores exhibit certain strongly enhanced lines under illumination, a result of photochemically induced dynamic nuclear polarization (photo-CIDNP). These signals can be assigned to bacteriochlorophyll and bacteriopheophytin chromophores, and certain adjacent residues in the RC. This technique offers a new method to investigate photosynthetic electronic transactions while retaining the NMR advantages of narrow linewidths and site-specific resolution.

This enhancement is thought to be an effect of hyperfine couplings during the lifetime of an electronic biradical. Although the singlet and triplet states are far too short-lived to be directly detectable via NMR, the resulting nuclear polarization is long lived and readily observed. The enhancement of pheophytin cannot be strictly explained by the Radical Pair Mechanism (RPM) common to solution experiments. An additional proposal, the Three Spin Mechanism (TSM), may explain these results. Nuclei in the donor and acceptor both affect S—T_0 mixing rates, and this hyperfine coupling can drive transitions between nuclear spin levels once spin sorting has occured, producing NMR observable populations.

Pulsed laser illumination at 532 nm was used as the basis for time resolved photo-CIDNP experiments, a technique not previously published for solid-state photosynthetic systems. These experiments revealed different polarization decay times for different ^{15}N

sites within the bacteriochlorophyll dimer, an observation not predicted by earlier theories. Polarization on the N-I and N-III nuclei may be the result of indirect spin transfer, rather than the direct polarization previously anticipated. The photosynthetic process, CIDNP mechanisms, and other possible explanations for this differential decay are discussed.

Studies were also made on enhancement and electron transport effects using broadband illumination across selected wavelength ranges and near-continuous monochromatic laser illumination. The results of these experiments are discussed in the context of the visible absorption spectrum of the RC.