

Theoretical Investigation of the Electronic Asymmetry of the Special Pair Cation Radical in the Photosynthetic Type-II Reaction Center

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The electronic asymmetry of the special pair cation radical in the photosynthetic reaction center (RC) was studied, using quantum chemical calculations with a polarizable continuum model and a point charge model as the protein environment. The calculated spin density distribution between the halves of the special pair from *Rhodobacter (Rb.) sphaeroides* agreed qualitatively well with the experimental value due to the protein polarity effect. The differences in the specific orientations of the ester carbonyl groups of the phytyl groups, as well as the methyl ester groups, are one of the origins of the electronic asymmetry.

The generality of the specific orientations was confirmed with fourteen X-ray structures of a variety of type-II RCs. The interactions between the methyl ester and phytyl groups and the surrounding amino acids were investigated by structural and sequence alignments. The alignments revealed that specific van der Waals contacts and polar interactions are conserved among the type-II RCs, with a few exceptions, suggesting that the orientations of these groups are controlled by the specific interactions between them as the evolutionary consequence. The calculated spin density distributions of special pair cation radical from anoxygenic bacteria of *Rb. sphaeroides* and *Rhodospseudomonas viridis* RCs and from oxygenic photosystem II RC (Cyanobacteria) of *Thermosynechococcus elongatus* were always localized in the L-side halves of special pair cation radical, qualitatively reproducing the experimental results. The difference in the orientation of the phytyl group, which is controlled by the protein environment, is the common feature among type-II RCs to determine the electronic asymmetry.

Proceedings of The Joint 2nd Pacific Rim International
Conference on Protein Science and 4th Asian-Oceania
Human Proteome Organization, Cairns- Australia, 22-26
June 2008