Excited States of the Chromophores of the Photosynthetic Reaction Center from *Rhodopseudomonas viridis* A QM/MM Study That Includes MM Polarization

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Abstract We present a Hybrid Quantum Mechanical/Molecular Mechanical (QM/MM) model for microscopic solvation effects that includes polarizability in the MM region (QM/MMpol). QM/MMpol treatment of both ground and excited states are presented in the formalism. We present QM/MMpol analysis of the ground and electronic excited states of the bacteriochlorophyll *b* dimer (P) of the photosynthetic reaction center (RC) of *Rps. viridis* (Figure 1) using the INDO/S method. We treat P and five adjacent amino acid side chains quantum mechanically, and the remainder of the protein, cofactors, and waters of crystallization with polarizable MM (325 QM atoms embedded in the field of 20158 polarizable MM atoms). While dimer formation alone is enough to account for the majority of the monomer BChlb to P red-shift of the lowest electronic excited state of P (Q_{y1}), we demonstrate that explicit treatment of the protein is required to properly interpret the experimental Stark effect data that describe the charge transfer asymmetry of Q_{y1}. The static-charge potential from the MM model of the RC alone causes Q_{y1} to have significantly better agreement with the Stark effect results than isolated P. However, consideration of the protein polarization potential is further required to obtain more complete agreement with Stark effect experiments. Thus we calculate a Q_{y1} transition energy at 10826 cm^{-1} with a ground to excited state change in dipole moment of 4.8 D; an absorption Stark effect angle of 43^o; a net shift of 0.15 electrons from the L-subunit to the M-subunit of P; and a linear dichroism angle (between the transition moment of Q_{y1} and the pseudo-C_2 axis of the RC) of 81^o. These results are in good agreement with experiment. Interestingly, we find that net CT increase is greater for Q_{y1} than for the second excited state of P (Q_{y2}), a result that we anticipated in an early model dimer study. We will also present results of calculations of vertical charge transfer states between the chromophores of the RC and discuss the role of instantaneous solvent polarization on these states.

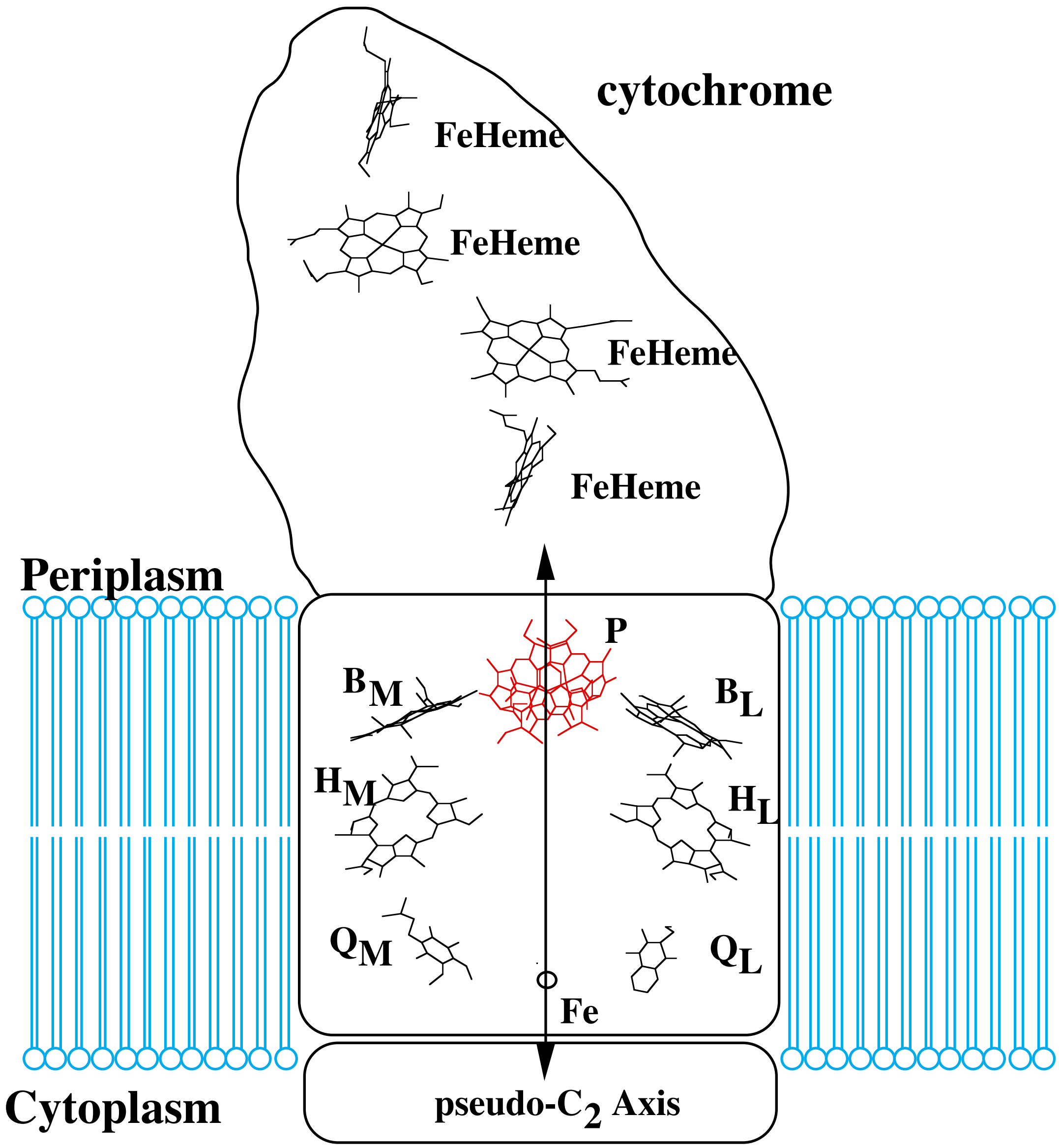

Figure 1. The photosynthetic reaction center from *Rps. viridis* .The lipid bilayer membrane and proteins C (cytochrome), L, M, and H are shown schematically. The abbreviations are: P, the bacteriochlorophyll *b* (BChl*b*) dimer; B_L,B_M, the auxiliary BChl*b* pigments of the L and M branches, respectively; H_L,H_M, the bacteriopheophytin *b* (BPhe*b*) pigments of the L and M branches respectively; Q_L,Q_M, the menaquinone and ubiquinone, respectively; and Fe, the non-heme iron atom. Also shown are the four Fe-hemes contained in the cytochrome protein. The phytyl tails of the BChl*b* and BPhe*b* and the isoprene tail of the menaquinone (Q_L) have been truncated for clarity. The pseudo-C_2 symmetry axis of the RC is also shown.