P–E1–13

RELAXATION OF THE TRIPLET STATE OF P680 IN PHOTOSYSTEM II

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Purpose: Characterisation of the spin-polarised triplet state ^{3}P680, which results from charge recombination in Photosystem II in plants. The main issues are the localisation of this state on one or more Chl *a* molecules and the orientation of these molecules in the photosynthetic membrane.

Methods: Pulsed and cw EPR techniques are used in combination with flash excitation of Photosystem II. Experiments are performed in various preparations. Relaxation is studied by analysis of the kinetics of the EPR signals and the nuclear modulation on these signals.

Results: Relaxation of this recombination triplet state is enhanced by interactions with the protein environment. EPR spectrum and kinetics can be explained by dimeric models.

Conclusions: The photochemically active Chl *a* molecules in Photosystem II derive their special properties from the interaction with the protein rather than from an unusual molecular structure.

P–E1–14

SPECTROSCOPIC INVESTIGATION OF THE REACTION CENTER OF THE GREEN-SULFUR BACTERIA *CHLOROBIUM LIMICOLA*

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Purpose: To investigate the nature of the special pair and the intrinsic antenna pigments of different, low-BChla, preparations of the Reaction Center of photosynthetic green-sulphur bacteria.

Methods: Circular Dichroism and Linear Dichroism measurements, Stark spectroscopy, Triplet minus Singlet delta absorption spectroscopy to probe the spatial organization and mutual interactions of the pigments.

Results: LD and Stark measurements show the heterogeneity of the P840 band: (at least) two different pigment pools. The red most absorbing pool is probably an excitation energy trap as revealed by T-S delta absorption measurements. CD and Stark measurements indicate that the arrangement of the intrinsic antenna pigments is like FMO The homodimeric nature of this Reaction Center is reflected in the difference dipole moment of the P840 band.

Conclusions: All preparations are capable of primary charge transfer but show a different degree of association of antenna pigments. The P840 band is heterogeneous. There is a possible role of mixed in Charge Transfer states in electron transfer from P840 to Chl670. There is a possible symmetry breaking by internal antenna pigments

P–E1–15

THE ORIGIN OF "g=4.1" EPR SIGNALS FROM AN S_2-STATE OF PHOTOSYNTHETIC WATER SPLITTING ENZYME AND THE STRUCTURAL INFORMATION INVOLVED

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In plant photosystem II, tetranuclear Mn clusters are involved as an active site of the water splitting enzyme. Their one-electron oxidation state, S_2, in the enzymatic Kok:s cycle exhibits two kinds of EPR signals at low temperatures, called "multiline" and "g=4". The facts that the multiline signal arises from an S=1/2 ground state of Mn(3,4,4,4) tetramer whose excited state lies ca. 30 cm^{-1} above it have been used to obtain valuable structural information on the Mn(3,4,4,4) exchange interactions. Here, by thorough computer simulations of a variety of g=4 signals observed (the g=4 signal exhibits 600-700 G wide near Gaussian line shape without hyperfine structure in normal samples but at least 16 resolved hyperfine lines in NH_3-treated samples), it will be shown that the g=4 signal arises from the middle Kramers doublet of the S=5/2 Mn(3,4,4,4) tetramer, not S=3/2 and not Mn(3,4,3,3) oxidation state. Furthermore, by exact computational work, it will be demonstrated that, when the Mn cluster is assumed to contain a di(μ-oxo) bridged $Mn_a(3)$ –$Mn_b(4)$ bond as an origin of a strong antiferromagnetic exchange interaction, J_{ab} (≈ 200-300 cm^{-1}), (an important result from EPR and EXAFS studies), an exchange interaction parallel to it, i.e. J_{cd}, must be most probably ferromagnetic, indicating that the other pair of $Mn_c(4)$ and $Mn_d(4)$ ions must be bonded more than 2.85 Å apart, an estimate from an empirical relation between a Mn(4)-Mn(4) distance and the exchange interaction derived from model binuclear Mn complexes. These results suggest that the Mn clusters in the S_2 state must be in general inhomogeneous depending upon the sample treatment, taking at least two EPR-susceptible forms, an S=1/2 form and an S=5/2 form. It should be noted that these forms must be close in energy, so that these forms may be in thermal equilibrium even at room temperatures.

P–E1–16

EFFECT OF BACKGROUND ILLUMINATION ON THE $P^+Q_A^-$ RECOMBINATION IN MEMBRANE BOUND REACTION CENTERS OF *RHODOBACTER SPHAEROIDES*.

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Purpose: To investigate conformational changes associated with the formation of the charge separated state $P^+Q_A^-$ in photosynthetic bacterial reaction centers (RCs).

Methods: For RCs cooled down in the dark the $P^+Q_A^-$ recombination rate (k_r) is studied as a function of background illumination intensity between 77 K and room temperature. The true value k_r in the presence of background illumination follows from the measurement of the fraction of open RCs and the observed rate of recombination.

Results: At 77 K k_r is constant as a function of background illumination intensity. At room temperature k_r decreases upon increasing light intensity.

Conclusions: At room temperature the RCs perform a conformational change upon charge separation, which relaxes on a time scale slower than the charge recombination.