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Photosynthetic light-harvesting

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Abstract: The peripheral light-harvesting complex of the photosynthetic bacterium *Rhodopseudomonas acidophila* (LH2) absorbs solar photons and transfers the electronic excitation to the reaction center, to drive a charge separation. In LH2 the bacteriochlorophyll molecules are arranged in a highly symmetric ring and the average distance between the pigments is 1 nm or less and, as a consequence, the electronic interaction between the pigments is strong (> 100 cm^{-1}). Therefore, the excitation transport in these photosynthetic light-harvesting systems can not be described by a simple Förster type transfer mechanism, but new or other transfer mechanisms may be operative, for instance a mechanism in which the excitation is to some extent delocalized. Crucial parameters are the strength of the electronic coupling, the amount of energetic disorder and/or heterogeneity and the nature and strength of the interactions of the pigments with the protein.

Introduction:

In photosynthesis light is absorbed by the light-harvesting antenna and the excitation is transported to a reaction center (RC) where a charge separation is iniated. The photosynthetic apparatus that performs this function consists of a membrane-associated network of photosynthetic pigment-proteins[1]. About 10 years ago the structure of the bacterial RC was resolved by Michel and Deisenhofer[2], and this discovery has led to a deep understanding of charge separation. Recently, the structure of two light harvesting complexes has been resolved and it is expected that, during the next decade, these discoveries will also lead to new insights into the process of excitation energy transfer .

Structure and Spectroscopy of LH1/2.

Recently the 2.5 Å structure of the peripheral light-harvesting complex (LH2) of *Rps. acidophila* was discovered [3,4]. A schematic view of the organization of the pigments is shown in fig. 1. The structure of LH2 is highly symmetric and consists of 2 concentric rings of each 9 transmembrane helices with the BChl *a* molecules sandwiched between them. A ring of 9 pairs of BChls, each pair liganded to highly conserved histidine residues in the two subunits, corresponds to the 850 nm absorption band. The B850 BChls in the ring are at a distance of 0.9 nm and consequently the electronic coupling within a pair and beween BChls on adjacent subunits is very similar. The B800 pigments are oriented with their tetra-pyrole ring slightly tilted away from the plane of the membrane. Because of the strong homology of the α and β protein sequences between different species and between the core complex LH1 and the peripheral complex LH2, all these complexes are likely to have a similar organization[5,6] . Using the LH2 structure of *Rps. acidophila* as a reference the structure of the LH2 complex of *Rsp. molischianum* was solved and found to be a ring with an eight-fold rotational symmetry[7]. In this structure the B800's were found to be 90 degrees rotated relative to

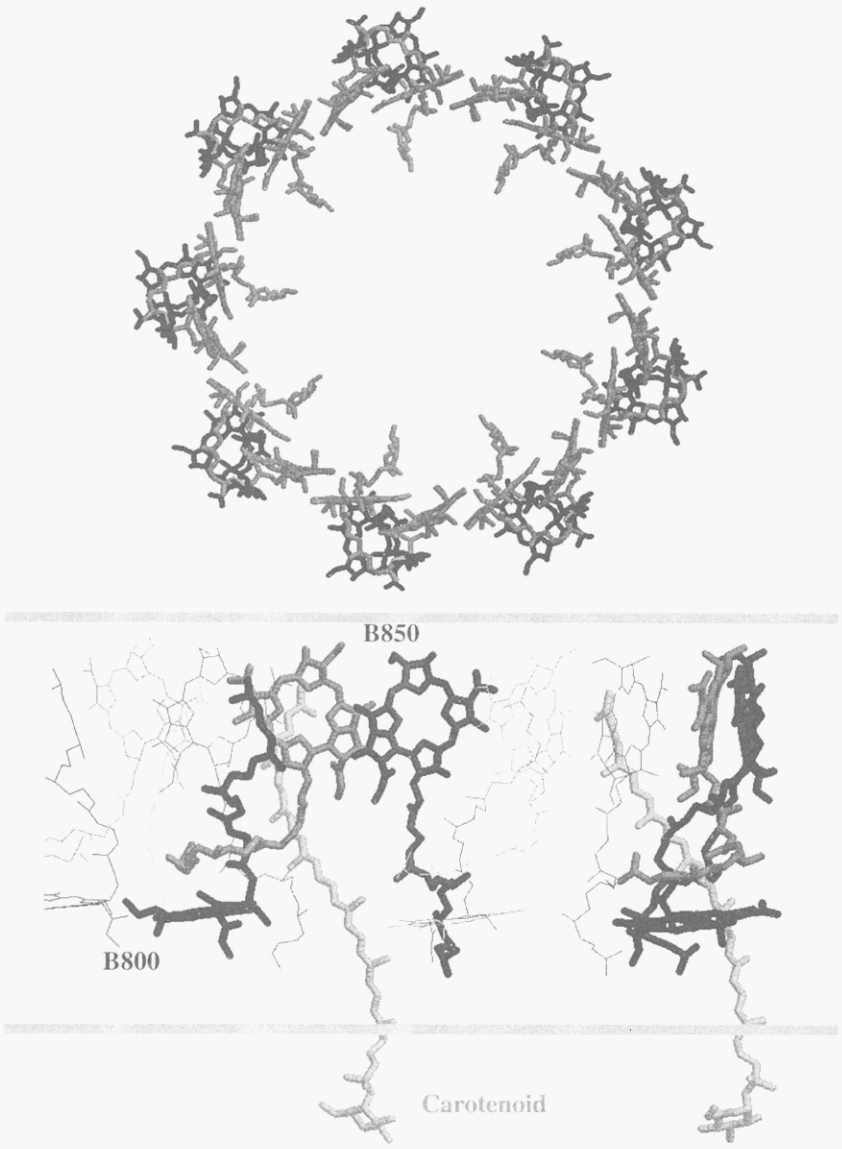

Fig. 1: Top (A) and side (B) view of the Bchl-*a* and carotenoid molecules in the LH2 complex of *Rps. acidophila*[3,4] . The B800 molecules (black) have the porphyrin macrocycles parallel to the membrane plane, whereas the B850 molecules (grey) have their macrocycles perpendicular to the membrane plane. The side view picture highlights the pigments in two αβ-pairs, one pair viewed onto the macrocycle plane of the B850s and the second pair is rotated over about 90°. The long molecule (light grey), shown only in the side view, is a carotenoid molecule, which spans the entire membrane. The approximate membrane position is indicated by two horizontal lines. This figure was created using RasMol 2.4.

Rps. acidophila and tilted about 35 degrees away from the membrane plane. Also LH1 is a ring with an analogous subunit and pigment arrangement[8]. In LH1 the ring contains 16 subunits and the inner diameter is large enough to encompass the RC. In this structure the distance between the BChls in the LH1 ring and the special pair of the RC is 4 nm.

The size of the interaction energy V governs the rate of energy transfer between the pigments and the excitonic nature of the spectrum. V is determined by the coulombic interaction of all the charges of the pigments and their surroundings and contains both resonance and exchange terms and for LH2 estimates for

V range from 230-700 cm^{-1} for the intradimer coupling and between 100 and 500 cm^{-1} for the interdimer coupling in the B850 ring[9-12] . For the LH1 ring a similar spread is obtained. For B820, the LH1 dimeric subunit, the intradimer coupling is estimated[13] to be 230 cm^{-1} .

The spectral properties of individual pigments are strongly determined by more subtle interactions with the surrounding protein. The transition frequency of each pigment is sensitive to changes of fluctuations in the direct environment. Fluctuations on a fast time scale lead to "homogeneous broadening" of the optical transition, slow fluctuations or static disorder lead to "inhomogeneous broadening". For LH1/2 widths of the inhomogeneous distribution function (IDF) between150 and 400 cm^{-1} have been estimated[11,13-21] ; estimates for the width of the homogeneous broadening yield about 150-250 cm^{-1}.

Various groups have performed exciton calculations on ring-like structures ignoring spectral inhomogeneity[9,11,22,23]. These calculations implicitly assume that the excitation is fully delocalized over the LH1/2 ring. In that case the only transitions that acquire significant dipole strength are two degenerate and mutually perpendicular transitions in the plane of the ring and a third component polarized perpendicular to it. For LH1/2 the latter component is to the red of the two strong transitions and gains some oscillator strength because the B850/875 dipoles are not perfectly in plane. For LH2 this transition would carry an dipole strength of less than 2% of the total.

Inclusion of inhomogeneous broadening into the exciton calculations, for instance introduced by assuming that the site energies are taken randomly from an IDF, has effect on both the relative magnitude and the polarisation of the exciton bands[19,24,25]. A remarkable effect is that "forbidden" exciton bands may become partially "allowed" in the presence of disorder. Also orthogonally polarized "pure" exciton transitions are no longer orthogonal in the presence of disorder. Furthermore, inhomogeneous broadening leads to localization since due to the distribution in site energies, the relative participation of each of the locally excited state wavefunctions is now weighted with the energy mismatch. A calculation (Monshouwer et al., submitted) demonstrates that with a ratio of V over σ_{inhom} of about 1 the average dipole strength of the emitting state is about 3 monomeric units. To illustrate how energetic disorder leads to localization we have plotted in fig. 2 the averaged amplitude of the wavefunction of the exciton states, weighted with the dipole strength as a function of the amount of inhomogeneity. Fig. 2 shows that even for moderate inhomogeneity the exciton states are localized on only a few pigments, consistent with the experimental results.

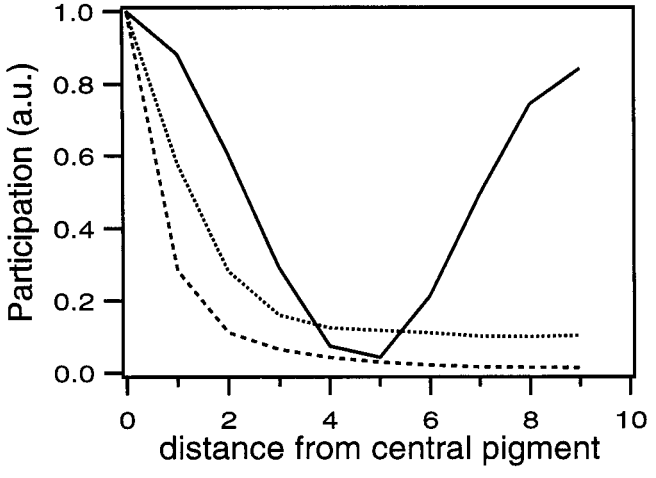

fig 2: Shape of the delocalisation of the exciton for different amounts of inhomogeneity. Shown is the average contribution of pigment i to exciton state k, $|c_{ik}|^2$ as a function of the distance of this pigment to the centre of weight of the exciton distribution. The distributions shown are normalised to 1 for the central pigment, and weighed with the dipole strength of the exciton transition. $|\mu_k|^2$. The solid line is for $\sigma/V=0$, dotted is $\sigma/V=1$ and dashed is $\sigma/V=3$.

If the interaction between the two pigments in a subunit of LH1/2 is much stronger than that between pigments on different subunits, we have the "weakly coupled dimer" model. This model was used by Scherz

et al. to explain the CD and OD spectra of LH 2 of *Rb. sphaeroides*[26] and subsequently by others to explain various different steady-state and time-resolved measurements on LH1 and LH2[10,15-17,19-21,23,27]. The spectroscopic properties of this dimer are often based on the B820-subunit of LH1. Spectroscopically this subunit behaves as an excitonically coupled dimer. Taking σ_{inhom}=250 cm^{-1} and V=230 cm^{-1} between the monomers describes the spectroscopic properties of this subunit[19,25,28]. For the validity of the weakly coupled dimer model, an estimate for the coupling between the subunits in the ring is needed. Experiments[15,17] for LH1 suggest inter-dimer coupling of less than 50-100 cm^{-1}, corresponding to a 200 fs hopping time of the excitation between adjacent dimers. From the Mg-Mg distances and using the dipole - dipole approximation, an intra- vs interdimer ration in coupling of about $(9.7Å/8.7Å)^3 \approx 1.4$ can be calculated for LH2. However, as stated above, with these short distances the dipole-dipole approximation is probably not valid. It is argued by Jimenez et al. that for molecules of the dimer being in Van der Waals contact exchange coupling is important[10]. The exponential fall off of the exchange coupling can significantly enlarge the difference between inter- and intra-dimer coupling. This yields for the interdimer coupling a value of about 100 cm^{-1}.

Excitation transfer:

Singlet-singlet annihilation experiments have conclusively demonstrated that excitation transfer in bacterial light-harvesting antenna occurs on a subpicosecond time scale[1,29-31]. Recent pump-probe[12,15,16,18,32-35] and spontaneous emission measurements[10,17] employing 100 fs Ti:Sapphire laser pulses demonstrated that spectral relaxation and depolarization take place within a picosecond after excitation. In LH1 of *Rs. rubrum* Visser et al.[15] measured a 12 nm redshift of the zero-crossing of the transient difference spectrum characterized by a single exponential decay time of 325 fs. It was proposed that the observed shift is due to a thermal redistribution of the excitations within the inhomogeneously broadened absorption band. Assuming that the antenna can be modelled as a cluster of weakly coupled dimers, these authors conclude that for LH1 σ_{inhom}=400 cm^{-1} and they estimate an average single site lifetime of 50-70 fs. At low temperature, using the same model, but explicitly accounting for the temperature dependence of a single-site absorption spectrum an inhomogeneous broadening of 250 cm^{-1} and a single site lifetime of about 100-150 fs have been estimated[16]. For LH2 the kinetics measured close to the zero-crossing in the transient difference spectrum following excitation in the blue part of the band also showed the redshift of the zero-crossing with a quasi-single exponential time constant of about 150-200 fs [34].

Fleming and coworkers used a similar model to explain the spontaneous emission of LH1 and LH2 of *Rb. sphaeroides* [10,17]. In both systems they find a bi-exponential anisotropy decay of the fluorescence with components of approximately 100 fs and 400 fs for LH1 and a somewhat faster decay for LH2. To explain the bi-exponentiality, they also assume a spectral inhomogeneity for LH1 and LH2. For LH1 excitation transfer is modelled by a ring of 16 weakly coupled dimers, with an inhomogeneous broadening of 250 cm^{-1} and a single site lifetime of 50 -100 fs, very similar to the estimate of Visser et al for *Rs. rubrum* [15]. For LH2, using again σ_{inhom}=250 cm^{-1}, the single site lifetime was found to be somewhat shorter [18]. An alternative explanation for the spectral shift is given by Kennis et al. [35]. They propose that light absorption by LH2 excites a strongly allowed and delocalized exciton state and the observed spectral relaxation is due to equilibration among the exciton levels of the aggregate.

In an attempt to understand the nature of the excitation transport Pullerits et al.[36] compared the anisotropy and population decay for LH2 of *Rb. sphaeroides* in a one colour pump probe experiment. Note that the depolarization of the fluorescence or bleaching signal is not only determined by the hopping time of the

excitation, but also by the difference in orientation between the initially excited and the subsequently probed state. When the angle between the neighbouring pigments is small, the anisotropy decay is much slower than the hopping time [12,17] and from numerical simulations based on the LH2 structure, and assuming complete localization a ratio of 3 between anistropic and isotropic decay rates is expected. However, in the red part of the band they find an anisotropy decay of 130 fs vs. an isotropic decay of 70 fs and consequently it is concluded that the excitation must be (partly) delocalized. To estimate the degree of localisation models that explicitly account for the (partial) coherence of the excitation transfer must be developed.

Already early quantum yield measurements of the B800 fluorescence showed picosecond energy transfer from B800 to B850 at low temperature [37]. Later picosecond absorption[38-40] and spectral hole-burning experiments[1,14,41-44]gave a 2.2-2.5 ps energy transfer at liquid helium temperature, suggesting a B800-B850 distance of about 1.7 nm[44], close to the value obtained from the structure. With increasing temperature the rate of transfer speeds up, to about 1.1 ps at 77K [40]and to 0.6-0.7 ps at room temperature [32,40,45]. The moderate increase of the rate with temperature can be explained within the Förster model for energy transfer, assuming that the overlap between the B800 emission and a broad vibrational profile of B850 is responsible for the transfer[18,33,37,41,44]. The observation that mutants with blue-shifted B850-profiles show slower B800->B850 energy transfer[33,44] could consistently be explained within the Förster model. Polarized fluorescence experiments on the weak B800 fluorescence also indicated energy transfer among the B800 pigments in LH2 and a transfer time of less than a picosecond was estimated[46]. This implies a B800-B800 distance of about 2 nm, close to the value found in the LH2 structure. Later spectral hole-burning[18,42] and time-resolved pump-probe[32,40] measurements clearly demonstrated downhill energy transfer within the B800-band, followed by energy transfer to B850. Fig 3 shows the result of an experiment in which in LH2 of *Rb. sphaeroides* B800 is excited in the blue wing and the transient absorption signal is probed in the red wing of the B800 absorption band. The signal exhibits a clear rise with a time-constant of 440 fs followed by a 1.2 ps decay due to B800->B850 energy transfer. A simple calculation assuming realistic values for the B800 emission and absorption properties shows that these rates are fully consistent with the structural parameters[40].

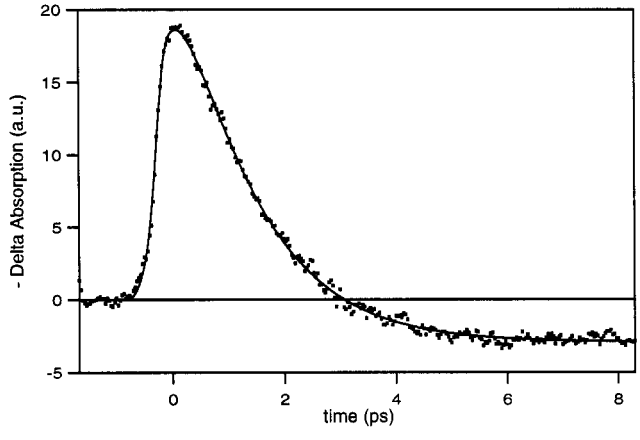

Fig. 3 : Two colour pump probe measurement in the B800 band of *Rb. sphaeroides* at 77K. Excitation was at 791 nm, detection at 810 nm. The solid line is a fit with a rise of 440 fs, reflecting downhill energy transfer among B800's, and a 1.26 ps decay due to B800 -> B850 transfer.

Coherent oscillations in photosynthetic antenna systems.

Following the observation of coherent nuclear motions in reaction centres of photosynthetic bacteria upon excitation with a short laser pulse[47] several reports have appeared of similar phenomena in bacterial antenna systems[17,48,49]. Chachisvilis et al.[48] found oscillations with a dominating frequency of approximately 100

cm^{-1} in LH1 and LH2 of *Rb. sphaeroides* and in LH1 of *Rs. rubrum*. From the wavelength dependence of the phase they conclude that these oscillations are predominantly due to wavepacket motion in the excited state. Oscillations with comparable frequency have been observed by Bradforth et al.[17] in the spontaneous emission of LH1 of *Rb. sphaeroides* using fluorescence upconversion. Recently, Monshouwer et al.[34] observed a similar oscillatory pattern in pump-probe experiments in *Rps. viridis*. A typical example of such an experiment is presented in Fig. 4. For bacterial reaction centres the Fourier spectrum of the oscillatory part of the kinetics has been correlated with the low-frequency resonance Raman spectrum[50] and the enhanced modes have been interpreted as characteristic for the special pair. Also for bacterial light-harvesting systems these pronounced low frequency vibrations may reflect the primarily dimeric nature of the elementary unit, although their origin is still under debate. Nevertheless, their presence reflects the fact that vibrational dephasing is far from complete on the timescale of excitation energy transfer and this fact should be taken into account in a proper description of the energy transfer process in photosynthesis.

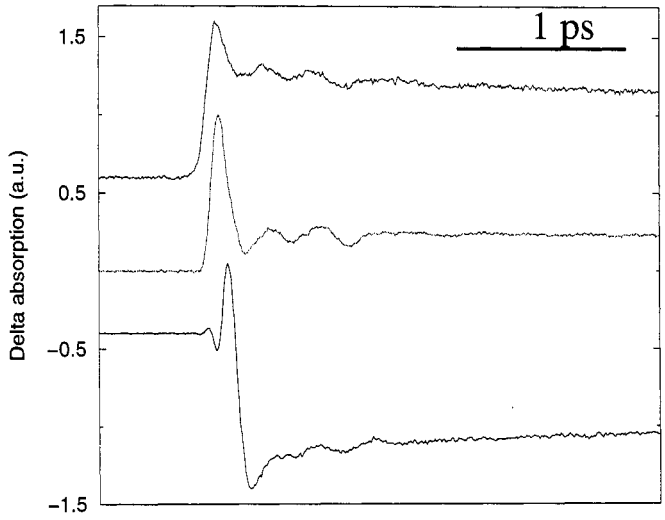

Fig. 4 Room temperature pump probe measurements on the core antenna of *Rps. viridis*. Excitation was at 1030 nm, detection at 960 nm (top), 990 nm (middle) and 1050 nm (bottom). The power spectrum of the residual of these traces showed a clear peak at 110 cm^{-1} due to oscillations.

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References:

1. Van Grondelle, R.; Dekker, J. P.; Gillbro, T and Sundström, V.; *Biochim. Biophys. Acta*, **1994**, 1187, 1.

2. Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R. and Michel, H.; *Nature*, **1985**, 318, 618.
3. McDermott, G.; Prince, S.M.; Freer, A.A.; Hawthornthwaite-Lawless, A.M.; Papiz, M.Z.; Cogdell, R.J. and Isaacs, N.W.; *Nature,* **1995**, 374 ,517.
4. Freer,A.; Prince,S.; Sauer,K.; Papiz,M.; Hawthornthwaite-Lawless,A.; MacDermott, G.; Cogdell, R.J. and Isaacs, N.; *Structure*, **1996**, 4, 449.
5. Zuber, H. and Brunisholz, R.A.; in: *Chlorophylls;* Scheer, H., Ed., CRC Press: Boca Raton, Florida, 1991, p 627.
6. Olsen, J. D. and Hunter, C. N. *Photochem. Photobiol*, **1994**, 60, 521.
7. Kroepke, J.; Xiche, H.; Muenke, C.; Schulten, K. and Michel, H.; *Structure*, **1996**, 4, 581.
8. Karrasch, S.; Bullough, P.A. and Ghosh, R.; *EMBO J.* **1995**, 14-4,631.
9. Sauer, K., Cogdell, R. J., Prince, S.. M., Freer, A., Isaacs, N. W. and Scheer, H. *Photochem. Photobiol,* **1996**, 64, 564.
10. Jimenez, R.; Dikshit, S.N.; Bradforth, S.E. and Fleming, G.R.; *J. Phys. Chem.* **1996,** 100, 6825.
11. Novoderezhkin, V.I. and Razjivin, A.P.; *FEBS lett.*, **1993**, 330, 5.
12. Pullerits, T.; Chachisvilis, M. and Sundström, V.; *J. Phys. Chem.* **1996**, 100, 10787.
13. Van Mourik, F.; Van der Oord, K. J.; Visscher, K. J.; Parkes-Loach, P. S.; Loach, P. A.; Visschers, R. W. and Van Grondelle, R; *Biochim. Biophys. Acta,* **1991**, 1059, 111.
14. Reddy, N.R.S.; Picorel, R. and Small, G.J.; *J. Phys. Chem.* **1992**, 96, 6458.
15. Visser, H.M.; Somsen, O.J.G.; van Mourik, F.; Lin, S.; van Stokkum, I.H.M. and van Grondelle, R. ; *Biophys. J.* **1995**, 69,1083.
16. [Visser, H.M.; Somsen, O.J.G.; van Mourik, F. and van Grondelle, R. ; *J. Phys Chem.* **1996**, in press.
17. Bradforth, S.E.; Jimenez, R.; van Mourik, F.; van Grondelle, R. and Fleming, G.R. ; *J. Phys. Chem.* **1995**, 99, 16179.
18. Wu, H.-M.; Savikhin, S.; Reddy, N. R. S.; Jankowiak, R.; Cogdell, R. J.; Struve, W. S. and Small, G. J.; *J. Phys. Chem.* **1996**, 100, 12022.
19. Koolhaas, M.H.C.; van Mourik, F.; van der Zwan, G. and van Grondelle, R.; *J. of Luminescence* **1994**, 60&61, 515.
20. Pullerits, T.; Visser., K. J.; Hess, S.; Sundström, V.; Freiberg, A.; Timpmann, K. and van Grondelle, R.; *Biophys. J.* **1994**, 66, 236.
21. Pullerits, T.; van Mourik, F.; Monshouwer, R.; Visschers, R.W. and van Grondelle, R.; *J. of Luminescence* **1994**, 58,168.
22. Sturgis, J.N. and Robert, B.; *Photochem. Photobiol.* **1996**, in press.
23. Van Mourik, F.; Visschers, R.W.; Chang, M.C.; Cogdell, R.J.; Sundström, V. and van Grondelle, R. in: *Molecular Biology of Membrane-Bound Complexes in Phototrophic Bacteria*, Drews, G. and Dawes, E.A. Eds., Plenum Press: New York, 1990, p. 345.
24. Fidder, J.R.E.; Knoester, J. and Wiersma, D.A. ; *J. Phys. Chem.* **1991**, 95, 7880.
25. Van Mourik, F.; Visschers, R.W. and van Grondelle, R. ; *Chem. Phys. Lett.* **1992**, 193,1.
26. Scherz, A. and Parson, W.W.; *Photosyn. Res.* **1986**, 9, 21.
27. Van Mourik, F. *PhD Thesis*, Vrije Universiteit, Amsterdam, The Netherlands, 1993.
28. Pullerits, T.; Monshouwer, R.; van Mourik, F. and van Grondelle, R.; *Chem. Phys.* **1995**, 194, 395.
29. Valkunas, L.; Trinkunas, G.; Liuolia, V. and van Grondelle, R.; *Biophys. J.* **1995**, 69, 1117.
30. Bakker, J.G.C.; den Hollander, W. Th. F. and van Grondelle, R. ; *Biochim. Biophys. Acta* **1983**, 725, 508.
31. Van Grondelle, R; *Biochim. Biophys. Acta* **1985**, 811, 147.
32. Hess, S.; Feldchtein, F.; Babin, A.; Nurgaleev, I.; Pullerits, T.; Sergeev, A. and Sundström, V.; *Chem. Phys. Lett.* **1993**, 216-3,247.
33. Hess, S.; Visscher, K.J.; Pullerits, T.; Sundström, V.; Fowler, G.J.S. and Hunter, C.N. *Biochemistry* **1994**, 33, 8300.
34. Monshouwer, R. and Van Grondelle, R.; *Biochim. Biophys. Acta* **1996**, 1275, 70.
35. Kennis, J.T.M.; Streltsov, A.M.; Aartsma, T.J.; Nozawa, T. and Amesz, J.; *J. Phys.*

Chem. **1996**, 100, 2438.
36. Pullerits, T.; Chachisvilis, M. and Sundström, V. in: *Photosynthesis: from Light to Biosphere*, Mathis, P. Ed., Kluwer Academic Publishers: Dordrecht, 1995, Vol. 1, p. 107.
37. Van Grondelle R.; Kramer, H.J.M. and Rijgersberg, C.P., *Biochim. Biophys. Acta* **1982**, 682, 208.
38. Sundström, V.; van Grondelle, R.; Bergström, H., Åkesson, E. and Gillbro, T.; *Biochim. Biophys. Acta* **1986**, 851, 431.
39. Van Grondelle, R.; Bergström, H.; Sundström, V. and Gillbro, T.; *Biochim. Biophys. Acta.***1987**, 894, 313.
40. Monshouwer, R.; Ortiz de Zarate, I.; van Mourik, F. and van Grondelle, R.; *Chem. Phys. Lett.* **1995**, 246, 341.
41. Van der Laan, H.; Schmidt, Th.; Visschers, R.W.; Visscher, K.J.; van Grondelle, R. and Völker, S. ; *Chem. Phys. Lett.* **1990**, 170, 231.
42. De Caro, C.; Visschers, R.W.; van Grondelle, R. and Völker, S. ; *J. Phys. Chem.* **1994**, 98, 10584.
43. Reddy, N. R. S.; Small, G. J.; Seibert, M. and Picorel, R. ; *Chem. Phys. Lett.* **1991**, 181, 391.
44. Van der Laan, H.; De Caro, C.; Schmidt, Th.; Visschers, R.W.; van Grondelle, R.; Fowler, G.J.S.; Hunter, C.N. and Völker, S.; *Chem. Phys. lett.***1993**, 212, 569.
45. Shreve, A.P.; Trautman, J.K.; Frank, H.A., Owens, T.G. and Albrecht, A.C.; *Biochim. Biophys. Acta.* **1991**, 1058, 280.
46. Kramer, H.J.M.; van Grondelle, R.; Hunter, C.N.; Westerhuis, W.H.J. and Amesz, J.; *Biochim. Biophys. Acta*, **1984**, 765, 156.
47. Vos, M.H.; Jones, M.R.; Hunter, C.N.; Breton, J. and Martin, J.; *Proc. Natl. Acad. Sci. USA* **1994**, 91, 12701.
48. Chachisvilis, M.; Fidder, H.; Pullerits, T. and Sundström, V.; *J. of Raman Spectroscopy* **1995**, 26, 513.
49. Bradforth, S.E.; Jimenez, R.; Dikshit, S. N. and Fleming, G .R. in: *Photosynthesis: from Light to Biosphere,* Mathis, P., Ed., Kluwer academic publishers: Dordrecht, 1995, Vol.1, p. 23.
50. Cherepy, N. J.; Shreve, A. P.; Moore, L. J.; Franzen, S.; Boxer, S. and Mathies, R. A.; *J. Phys. Chem.* **1994**, 98, 6023.