Following a brief outline of the development of ideas about light harvesting and the photosynthetic unit, the mechanism of light capture and transfer in purple photosynthetic bacteria is discussed. The structure of the LH2 antenna complex is described and the theoretical issues it raises discussed. Femtosecond fluorescence depolarization and photon echo studies of both LH1 and LH2 are then presented. The fluorescence depolarization data are interpreted as implying that the elementary energy transfer step takes \( \sim 100 \) fs and occurs with retention of vibrational phase for at least two vibrational modes. The photon echo results reveal that the electron–phonon coupling is quite weak in LH1 and LH2. We propose that energy transfer is manifest in these data via its ability to disable rephasing of the inhomogeneous ensemble. This ansatz leads to energy transfer timescales that are consistent with the fluorescence data and suggests that the excitation rapidly becomes localized on 3 to 4 molecules.

I. Introduction

The primary steps of photosynthesis involve two ultrafast processes — energy and electron transfer. Electron transfer proceeds in specialized pigment–protein complexes called reaction centers. Purple bacteria, heliobacteria, and green sulfur bacteria possess a single reaction center, whereas cyanobacteria and plants have two types of reaction centers called PSI and PSII, respectively. A plausible evolutionary model for the development of modern photosynthetic organisms proposes that the ancestral photosynthetic organism (which was anoxygenic) led to two lines of development [1]. One line, the iron–sulfur (FeS) line gives rise to heliobacteria and green sulfur bacteria, while the other, the pheophytin-quinone (Pheo-Q) line, gives rise to the purple bacteria. Fusion of these two lines then leads to organisms with two reaction centers — PSI arising from the FeS line and PSII from the Pheo-Q line.

Even in bright sunlight the rate of photosynthesis would be limited by the rate of excitation of the reaction center if these complexes were the sole constituents of the photosynthetic apparatus. Instead, photosynthetic organisms have developed antenna systems with which to ‘harvest’ sunlight and transport it to the reaction center with very high quantum efficiency (typically \( \sim 90\% \)). In this introduction we aim to give a brief account of how ideas about light-harvesting have developed in parallel with improvements in ultrafast spectroscopy. In subsequent sections we outline theoretical
models and issues relating to efficient light-harvesting. We then describe the structures of several antenna systems as a prelude to a description of our experimental studies of the energy transfer via fluorescence, pump–probe, and photon echo spectroscopy. The paper concludes with a summary of the overall picture that has thus far emerged.

1.1 Development of light harvesting models

Fluorescence was regarded as a very mysterious phenomenon when it was first studied, for example, by Hershel [2]. Stokes greatly clarified the situation in a detailed series of studies in 1852 [3]. Amongst the systems he studied were the photosynthetic pigments (extract of leaves), in which he observed the familiar red fluorescence of chlorophyll. He showed that fluorescence was a short-lived phenomenon, although it took until the 1920's before the Kerr effect was exploited to show that fluorescence lifetimes were typically on the nanosecond timescale [4]. Stokes further showed the fluorescence was depolarized, and that the shape of the fluorescence spectrum of a pure pigment is independent of excitation wavelength and is shifted (the Stokes shift) beyond the longest wavelength of the absorption spectrum.

In a remarkable series of experiments published in 1883 [5] Englemann recorded the action spectrum for oxygen production by photosynthetic filamentous algae. He dispersed the solar spectrum along a filament and observed by light scattering where oxygen-loving bacteria congregated. In this way, Englemann was able to show that absorption by chlorophyll (and carotenoids) was required for photosynthesis. The seminal experiments of Emerson and Arnold in 1932 [6] led to the concept of the photosynthetic unit with separate light harvesting and photochemical functions, although as we will see, this implication was not immediately apparent to these authors.

Emerson and Arnold used state-of-the-art 10 µs flashes to saturate photosynthesis, the short duration being required to ensure that each reaction center was excited only once per flash. They obtained a 100–200 s⁻¹-cyci rate, a number of great significance, since if photosynthesis were initiated by a single (pair) of chlorophyll molecules, even in bright sunlight the maximum rate of excitation would be about 1 s⁻¹. Emerson and Arnold determined the number of chlorophyll molecules required to generate a molecule of oxygen and were apparently startled by their result: “We can give no adequate explanation of our ratio of 2480 molecules of chlorophyll per molecule of CO₂ [or O₂ evolved] per flash.” They further remarked “Perhaps the quantum efficiency is very low or most of the chlorophyll is not absorbing the light?” At the end of the same paragraph, they point out that not all the chlorophyll molecules need to be excited to explain their result, and they make the remark...“We need only suppose that for every 2480 molecules of chlorophyll, there is present in the cell one unit capable of reducing one molecule of CO₂ each time it is suitably activated by light.” [6]. By unit, Emerson and Arnold presumably meant an enzyme, not an antenna/reaction center complex. Several explanations for these results were put forward, and the resolution was not aided by the confusion over how many photons are required to generate an O₂ molecule. Using the
now accepted value of about 8 [7], we see that Emerson and Arnold’s value leads to a total of 300 chlorophylls per O₂. The hypothesis of the photosynthetic unit containing a large light harvesting antenna seems to have originated with Gaffron and Wohl in 1936 [8], although these authors thought that several thousand molecules were involved.

In 1944 Lewis and Kashia published their findings on the triplet state, clarifying the photophysical picture significantly [9]. Förster, in 1947, was the first to discuss quantitatively the process by which light energy absorbed by an arbitrary chlorophyll molecule was transferred by inductive resonance via other chlorophyll molecules to a reaction center present in small concentration [10]. Unfortunately, he used the solution value of the chlorophyll fluorescence yield to calculate the efficiency of the transfer process and calculated that typically 10,000 excitation jumps occurred. In 1951, Franck used a fluorescence yield value that was much too small and arrived at a maximum of 10 jumps [11], a value that would not be functionally significant. He took the much longer lifetime of the triplet state as compared to the excited singlet state to imply that it was the energy stored in the triplet state which was used in the photochemical reaction. In 1955 Calvin argued that light simply ionized chlorophyll and that holes and electrons were somehow separated, perhaps by a carotenoid [12]. Light harvesting was clearly not a completely accepted concept at this stage.

However, in 1952, in his thesis [13] Duysens proposed an essentially correct form for the photosynthetic unit with a reaction center present in low concentration and connected to about 200 antenna molecules. Using a correct quantum yield he estimated 750 jumps via the Förster mechanism for the singlet excitation and by 1964 using lattice models arrived at the timescale of a single jump as being $10^{-10}$ s [14]. Once the antenna size was clarified it was natural to propose ways in which the antenna might be organized to focus the excitation. Duysens realized that the multiple spectral forms found, for example, in photosynthetic purple bacteria could be arranged in a ‘funnel’ (Fig. X.1) and showed that bacteriochlorophyll molecules (BChl) absorbing at 800, 850, and 890 nm (B800, B850, B890) were coupled by ~100% efficient energy transfer. He made the remarkably prescient remark that “B800, B850, B890 may be due to association of different cell constituents with a BChl molecule or to different types of binding of the BChl molecules or to polymers of BChl.” [13,14].

The timescale proposed by Duysens was completely out of reach as flash photolysis (1949) was improved from ms to μs resolution [15]. It took until 1957 before time resolution in the ns range was available and Brody in the USA [16] and Terenin in Russia [17] made the first direct measurements of chloroplast fluorescence lifetimes. Meanwhile, an apparently serious problem with an antenna based on singlet energy migration had emerged. In 1950, Watson and Livingston pointed out that the fluorescence yield of a 0.1 M solution of chlorophyll (the concentration in the chloroplast) is unmeasurably small [18]. This phenomenon, concentration quenching, involves excitation migration to a pair of molecules closer than a critical distance (~10 Å in random solution [19]) followed by very rapid radiationless decay to the ground state (internal conversion). Clearly, photosynthetic antennas must exercise some degree of control over the spacing of the chlorophyll molecules or the “trapping” process.
must be faster than the radiationless decay. An additional problem was defined by Claes in 1954 who showed that chlorella mutants lacking carotenoids were damaged by light [20]. By 1959 Livingston had shown that carotenoids quench triplet chlorophylls [21].

The development of mode-locked lasers (1966), coupled with the knowledge that the primary electron donor in the purple bacterial reaction center is a dimer (the special pair; Norris and Katz (1971) [22]) soon led (1975) to the first efforts to measure the primary charge separation timescale by Parson and Windsor [23] and Rentzepis and Dutton [24]. The currently accepted value of 3 ps was established by Martin and Migus in 1986 [25]. Finally, in 1984 Michel and Diesenhofer determined the X-ray crystal structure of the reaction center from *Rps. viridis* [26], confirming the special pair nature of the donor and the composition of the electron transfer chain.

The seminal achievement of the reaction center structure was followed by remarkable success in obtaining the structure of the LH2 antenna complex (B800–B850) of *Rps. acidophila* by Cogdell, Isaacs, and coworkers [27]. At much lower resolution, the structure of the core antenna complex (LH1) has also been determined [28]. More recently, a second LH2 structure, that of *Rsp. molischianum*, has been solved by Michel, Schulten, and coworkers [29]. These structures enable us to see how many of the questions raised above are answered by nature and have stimulated a flurry of ultrafast
spectroscopic investigations, greatly aided by the happy coincidence of the titanium sapphire lasing spectrum [30] with the absorption spectra of the purple bacterial antenna components. The situation with plant antenna systems has also dramatically changed with somewhat lower resolution structures now available for LHCII (the most important antenna complex in plants) [31] and for PSI [32].

In the following section we briefly discuss the structure of LH2 [27] and the bacterial photosynthetic unit to see how the functional system solves the problems described above.

Fig. X.2. A model for the light harvesting and trapping machinery in the photosynthetic membrane of a purple bacterium. The view is along the membrane plane, and only the bacteriochlorophyll pigments are shown. The LH2 and reaction center structures are based on crystallography. The LH1 structure is modelled using the size of the reaction center protein (not shown) and the αβ unit of the LH2 structure.

2. The structure of LH2 from purple bacteria [ ].

Fig. X.2 shows the proposed arrangement of the photosynthetic apparatus in purple bacteria, based on the structures of LH2 and LH1 [27–28]. The reaction center (only prosthetic groups shown) is believed to sit inside the LH1 protein — a large ring containing 24 BChl molecules absorbing at 875 nm (B875). Touching the edge of the LH1 ring are several LH2 proteins containing (in Rps. acidophila) nine B800 BChls and 18 B850 BChls. The structure of LH2 in Rps. acidophila is known to 2.5 Å resolution [27] and is based on a ring of nine pairs of α and β apoproteins enclosing a cylinder. The cluster of 18 B850 molecules has the ring planes oriented perpendicular to the membrane surface and is formed from nine B850 pairs with each pair ligated to histidine residues on adjacent α and β apoproteins. A second LH2 structure recently solved, Rsp. molischianum, is very similar to that of Rps. acidophila, but now the rings
of B800 and B850 contain 8 and 16 molecules, respectively [29]. The absorption energies of the BChl are the result of both pigment–pigment and pigment–protein interactions. Clearly, the arrangement depicted in Fig. X.2 contains a funnel-like energy cascade and should be extremely efficient at moving energy in two dimensions without requiring specific orientational docking of the LH2 proteins with LH1. Further note that the rate limiting step in this process is the final energy transfer from the B875 molecules in LH1 to the special pair of the reaction center. (The distance from B875 to P is larger than B875–B875 or B875–B850, etc.) This timescale is ~35 ps [33], whereas, as we will demonstrate below, the timescale of energy transfer within the rings of B850 and B875 is on the order of 100 fs. Thus, a large timescale separation exists between excitation motion in the rings and the final trapping event. A side view of a small portion of the B850 ring of LH2 shows why this is (Fig. X.3). The electron clouds of

Fig. X.3. The B850 pigments in the LH2 complex from Rps. acidophila. The BChl pigments are in van der Waals contact. The rings show alternating spacings: within an α–β protomer (defined as a radially associated pair) C(2)–C(2) distance 3.89 Å, C(3)–C(3) distance 4.03 Å. Between BChl of adjacent protomers C(12)–C(12) 3.61 Å, and C(13)–C(13) 3.89 Å. See ref. 34.

successive pairs of B850 molecules overlap, while the separation between adjacent members of two such ‘pairs’ is only very slightly larger. For example, the Mg–Mg separation within a single αβ pair is 9.6 Å while it is 8.9 Å between adjacent protomer Mg atoms. (The distance from the B875 ring to the special pair is approximately 40 Å.) Such an arrangement of chromophores cannot be regarded as a ring of monomeric molecules, although this description probably applies well to the B800 ring in which the BChls are separated by 22 Å (center to center). Rather, the B850 ring must be considered a strongly coupled aggregate in which the balance of delocalizing and localizing influences on the electronic excitation must be carefully considered. We return to this point in the following section.
The structure of LH1 is based on the same principles, but this complex lacks the monomeric BChls, containing a single ring of B875 molecules, presumably in a very similar arrangement to B850, although the current structural information [28] is of insufficient resolution (8.5 Å) to directly confirm this. The LH1 ring in the membrane is believed to be positioned at the same height as the special pair of the reaction center, facilitating the final energy transfer step.

Fig. X.4. The base unit of the LH2 complex. The fully-resolved rhodopin glucoside (RG) molecule touches the B850 pigments.
The final structural aspect we wish to emphasize is the positioning of the carotenoid (CAR) molecules. Fig. X.4 shows the arrangement of the BChls and carotenoids in _Rps. acidophila_. All-trans carotenoids play several important roles in photosynthesis. For example, they protect the photosynthetic apparatus from damage by singlet molecular oxygen, through rapid BChl→CAR triplet–triplet energy transfer. The carotenoid triplet lies at too low an energy (unlike BChl) to allow promotion of triplet (ground state) oxygen to its excited singlet state. As Fig. X.4 shows, each B800 molecule and each B850 αβ ‘pair’ is in van der Waals contact with the carotenoid molecule. (A second CAR is also present, but only one third of it is resolved. CAR2 appears to make van der Waals contact with the same BChl of the B850 dimer.)

The carotenoids also play a role in light harvesting in the blue–green portion of the spectrum [35–37]. As the lowest excited state of the carotenoids is optically forbidden, any energy transfer via this state must involve orbital overlap between donor and acceptor. The S₂ CAR state is strongly allowed and may transfer via a Coulombic mechanism to the Q₁ state of the BChls.

3. Theoretical issues

The structural information given above immediately raises a number of conceptual issues in the description of the purple bacterial antenna system: How delocalized are the electronic states of the B850 and B875 rings? And how long does this delocalization persist? What is the mechanism of the various energy transfer steps, namely, B800–B800, B800–B850, B850–B850, B850–B875, B875–B875, B875–P (the special pair), CAR S₂–B875/B850/B800 (Q₂). CAR S₁–B875/B850/B800 (Q₁). Are vibrational relaxation and dephasing fast or slow compared to the elementary energy transfer steps? What are the magnitude and timescales of the coupling of the electronic excitations to the nuclear degrees of freedom of protein and chromophores? What is the extent of and influence of energetic and structural disorder in these highly symmetric systems? Is the degree of delocalization strongly temperature dependent?

Formulating answers to these questions requires a synergistic application of spectroscopy, electronic structure calculations, and theoretical modeling, combined with atomic resolution structural information. At this stage, it is probably fair to say that broad agreement exists only for the mechanism of the long range energy transfer steps (i.e., B800–B800, B800–B850, B850–B875, and B875–P). The Förster dipole–dipole mechanism is capable of explaining the timescales for these steps and even the variation of the rate with changing spectral overlap in the case of B800–B850 where mutants have been used to shift the spectra of the B850 molecules [38].

The issue of delocalization of the electronic states of B850 and B875 is far more complex and currently contentious. It has been discussed from a theoretical perspective by Novoderezhkin and Razjivin [39]. Circular dichroism (CD) data have been interpreted as implying complete delocalization around the entire B850 ring [44]. However, we do not believe that CD data are capable of providing this conclusion. We consider that CD
merely reflects the presence of inter-pigment interaction. It does not imply that this interaction is sufficiently strong to overcome the localizing effects of temperature, disorder, and vibrational and protein dynamics. Several groups have studied pump-probe spectra of B850 and B875 [41-43]. Kennis and coworkers initially interpreted their data as implying delocalization over the complete ring of B850 [41] but more recently have revised their estimate to 4 ± 2 molecules [44]. Pullerits et al. [42] also found 4 ± 2 from modeling absorption difference spectra in LH2 of Rb. sphaeroides. Interestingly, this same group found a negligible influence of temperature on the delocalization length. Chachisvilis [45] has performed detailed simulations of transient absorption spectra for LH1 and LH2 as a function of temperature. Diagonal disorder is included in these calculations, and a delocalization length of 4 at 4 K and 3 at 280 K was found for B875.

In our own studies of this issue we have used several approaches. First, we performed calculations of the inverse participation ratio (i.e., the number of molecules over which the excitation is delocalized) using a circularly symmetric exciton model with diagonal disorder. Coupling strengths of 280 cm⁻¹ and 110 cm⁻¹ were taken for the intra- and inter-dimer and various levels of diagonal (i.e., site energy) disorder were investigated following the methods of Fidder et al [46]. In a homogeneous, two-level system composed of say, 18 chromophores with circular symmetry, a band of 18 levels labeled k = 0, ± 1, ± 2, ± 3, ± 4, ± 5, ± 6, ± 7, ± 8, 9 is formed. Oscillator strength is concentrated in just two (degenerate) levels, k = ± 1, in the homogeneous system. However, diagonal (and off diagonal) disorder will distribute oscillator strength over all the levels. As Fig. X.5 shows, a 200 cm⁻¹ (FWHM) Gaussian distribution of site energies produces an absorption spectrum of similar width to the actual one, even without the inclusion of vibronic structure. In particular, the calculated width of the k = 0 level, shown with a dashed line in the figure, is in good agreement with the width of the k = 0 level observed in low temperature hole burning spectroscopy [47]. The figure also shows the localization parameter, L(E).

For B850, L(E) can range from a value of 1/18 for a fully delocalized state, through 0.5 for dimer, to a value of 1.0 for a state localized on a single BChl molecule. For states with significant oscillator strength, using the above parameters, L(E) corresponds to delocalization of ~5 pigments. This model does not include phonon or off-diagonal disorder, both of which will increase the degree of localization.

Disorder is also manifest in our fluorescence depolarization measurements [48,49], as well as in wavelength resolved pump-probe data [43]. For depolarization within a homogeneous symmetric ring system, the final value of the anisotropy, after orientational randomization in the ring plane should be 0.1, independent of detection wavelength. The anisotropy, except perhaps at very short times, should decay exponentially. Neither feature is precisely confirmed in fluorescence depolarization studies of B850 and B875 [48,49]. The fluorescence anisotropy decays, in both cases, from an initial value near 0.4 to a final value that is a little less than 0.1 and dependent on detection wavelength. In addition to a major component of ~50 fs (LH2, B850) and ~110 fs (LH1, B875) a longer component of ~500 fs is observed. Both of these findings
Fig. X.5. Results of exciton calculations on B850, including energetic (diagonal) disorder. The calculation assumed an intra-dimer coupling of 230 cm⁻¹ and inter-dimer coupling of 110 cm⁻¹, along with a 200 cm⁻¹ FWHM distribution of site energies. The top frame shows the number of pigments over which the excited state is delocalized, as a function of wavelength. The bottom frame shows the simulated absorption spectrum. The inset shows the absorption due to high-lying exciton states of the aggregate. These states overlap with B800 emission and may play a role in mediating energy transfer from B800 to B850.
can be readily reproduced by incorporating a modest distribution of site energies into a hopping model for the energy transfer. Spectral selection in detection influences the long-time value of the anisotropy, while slow energy transfer steps involving outlying (low energy) members of the distribution give the slow tail to the decay.

The initial value of the absorption anisotropy has been discussed extensively in the context of delocalization [50–52]. In principle, initial anisotropies significantly different than 0.4 can be obtained for aggregates of strongly coupled molecules [51]. In practice, interpretation of absorption anisotropies can be difficult, since for multistate systems, if the pump–probe signal is a sum of individual contributions, the anisotropy is an average. For two contributions, the pump–probe signal is $S_{pp} = \alpha I_A + \beta I_B$ and the anisotropy is $\Gamma_{pp} = (\alpha/(\alpha+\beta)) \Gamma_A + (\beta/(\alpha+\beta)) \Gamma_B$. In the presence of both positive and negative signals (e.g., bleaching, stimulated emission, excited state absorption, product absorption), the pump–probe anisotropy can take on any value, $-\infty < \Gamma_{pp} < \infty$ [53]. Furthermore, since the operations of convolution and division do not commute, the significance of the directly constructed anisotropy, $R(t)$

\[
R(t) = \frac{I_\perp(t) - I_\parallel(t)}{I_\parallel(t) + 2I_\perp(t)}
\]

(X.1)

at times when the pump and probe pulses overlap is not straightforward. In addition, inclusion of contributions from terms involving improperly ordered diagrams of the electric field interactions can, for multilevel systems, significantly alter the initial value of the anisotropy [54]. Fluorescence depolarization measurements, on the other hand, isolate the dynamics of the excited state and are significantly more straightforward to interpret although the complication of convolution remains.

The degree of delocalization has also been addressed by measurements of superradiance [55]. At room temperature in both LH1 and LH2 the observed dipole strength corresponds to 2–3 BChl monomers. Interestingly, the dipole strength is quite insensitive to temperature down to 4 K in LH2, but increases substantially in LH1.

Our own experimental approach to this problem has been to use photon echo spectroscopy, in particular the three pulse echo peak shift technique [56,57], to determine the strength of electron–phonon coupling, the relative magnitudes of the dynamic and static components, and the timescale of the dynamical contribution. Before describing these experiments, we first turn to a discussion of our fluorescence depolarization data.
4. Femtosecond spectroscopy

We have already briefly alluded to our fluorescence depolarization data. Fig. X.6 shows the anisotropy decay for LH1 [48]. The fitted initial value is very close to 0.4. (Note

![Graphs showing fluorescence and anisotropy decay over time](image)

**Fig. X.6.** Polarized femtosecond emission from LH1 complexes of *Rb. sphaeroides*. Top frame shows fluorescence polarized parallel (top) and perpendicular (bottom) to the excitation beam. The bottom frame shows the anisotropy constructed from the data. Both frames also show, in solid lines, the fit to the data. The excitation was at 860 nm, fluorescence detected at 943 nm.
that for the reasons given above, simple inspection of the quantity $R(t)$ cannot be used to discern this fact.) The decay is clearly biphasic, the fit reveals exponential components of 110 fs and 440 fs along with a finite long-time value with an anisotropy of 0.06. The anisotropy decay is quite smooth (i.e., no obvious oscillations are present) despite their obvious presence in the individual parallel, perpendicular, and magic angle curves.

![Graph 1](Image)

**Fig. X.7.** Isotropic emission from the LH1 complex. Oscillations corresponding to 105 cm$^{-1}$ and 20 cm$^{-1}$ frequencies are evident in the residuals from exponential fits to the data (top frame). Fits including the oscillatory components give damping times of ~400 fs and ~2 ps for the high and low frequency modes, respectively.
Fig. X.7 shows magic angle data for LH1 with a fit including two damped cosine functions with frequencies of 110 cm\(^{-1}\) (damping time ~500 fs) and ~20 cm\(^{-1}\) (damping time ~2 ps) [48]. It is clear that these oscillations arise from excited state wavepacket motion. As discussed in the previous section, while perhaps definitive evidence has not yet been provided, most analyses of the degree of delocalization (including our photon echo studies, *vide infra*) suggest that excitation is localized on a small number (2–4) of BChl molecules. Accordingly, we have taken as a zeroth order model for transfer between B875 molecules (as well as B850 molecules) at room temperature, one in which the basic unit is viewed as a dimer. We then calculate energy transfer based on the Förster model, i.e., as stochastic hopping between dimers [58]. Once a small distribution of individual site energies is introduced, this model can explain many features of the experimental results. Without adjusting the Förster parameters or the structural data [28], an energy transfer timescale very similar to the experimental one is observed. For LH1, the mean hopping time is approximately 80 fs, and with just 250 cm\(^{-1}\) of inhomogeneity, 30% of the anisotropy decay becomes slow (500 fs). The asymptotic value of the anisotropy depends on the detection wavelength (spectral filter effect) and is qualitatively consistent with experiment.

If 80 fs, indeed, represents the typical energy transfer timescale, the observation of vibrational beats persisting for much longer than this immediately raises interesting questions. We, in collaboration with Jean, have approached this issue via multilevel Redfield theory [59–61]. This density matrix approach, in addition to the usual population and dephasing terms considered in two-level Bloch-type models, also retains both one and two phonon coherence transfer terms (i.e., vibrational superpositions involving levels \(i\) and \(j\) can be converted to superpositions of levels \(j\) and \(k\) (one phonon) or \(k\) and \(l\) (2 phonon)). The theory has been discussed elsewhere in detail and here we give a brief summary of the conclusions. Initial vibrational coherence, created by the optical absorption process, can be transferred to a product in a nonadiabatic process. Indeed, vibrational coherence can be created in the product even if none exists in the reactant, provided the reactive event is fast enough. Vibrational coherence is not necessarily destroyed by energy relaxation, and in multilevel systems very substantial amounts of vibrational energy can be dissipated with retention of memory of the nuclear coordinates. Attempts to destroy coherence in model calculations by increasing the pure dephasing rate are not necessarily effective because the coherence transfer rate is also increased through the relationships of the different elements of the Redfield tensor.

Very recently, Jean has addressed the issue of coherence transfer in the antenna directly by modeling energy transfer between two dimers [62]. Each dimer, in his model, has a single (common) vibrational mode that is significantly displaced in the excited state. His calculations show that initially created coherence can be transferred effectively to the dimer that was initially in its ground state. In principle, such coherence transfer can be repeated multiple times until the wavepacket has had time to sample the entire vibrational coordinate. If a single energy transfer step, or a sequence of \(N\) such steps occurs on this timescale, the stochastic nature of the energy transfer time will mean that at this point energy transfer will be occurring from all possible values of the nuclear
coordinate with roughly equal probability and the coherence will be lost. From this perspective, then, lower frequency modes can survive more hops than higher frequency modes and there is at least a hint that this is observed in the data of Fig. X.7.

Vibrational wavepackets, though clearly observable in pump–probe data, are substantially less prominent in LH2 than LH1. Our fluorescence data for LH2 do not show any obvious signs of wavepacket motion. The fluorescence depolarization for B850 in LH2 is even faster (~50 fs) than for B875 [49]. We do not attribute this to a faster intrinsic rate of energy transfer, but simply to a smaller ring size (vide supra) so that the angle change per hop is larger in LH2 than in LH1.

We now wish to return to the issue of delocalization. The issue is a complex one: not simply are the magnitudes of the electronic coupling strength, the strength of coupling to the nuclear degrees of freedom (Stokes shift), and the disorder (both diagonal and off-diagonal) critical, but the timescales of the Stokes shift and inter-exciton relaxation will also play vital roles in determining how much and how long the excitation is delocalized. At present, we do not believe that either all of the above quantities are sufficiently well determined, or that there exists a sufficiently general theory to provide a definitive answer to the question of the timescale and extent of delocalization. Extensive, high-level quantum chemical calculations are necessary to establish the magnitude and mechanism of the electronic coupling. We have begun such calculations for the system of carotenoid–BChl dimer [63]. In parallel, we have carried out photon echo studies of LH1 and LH2 [64,65] in an attempt to determine the magnitude and timescale of the Stokes shift and the degree of diagonal disorder. The technique we have used, the three pulse echo peak shift method, has recently been developed extensively for studies of non-interacting chromophores in fluid and solid solutions [56,57,66]. In order to provide context for the results we will present, we briefly outline what the technique measures and how it is carried out. Detailed descriptions are given elsewhere [56].

Consider an isolated chromophore, i, in a solid matrix such as a polymer glass or a protein. The transition frequency between ground and excited electronic states can be written as

\[ \omega_i^j(t) = \langle \omega_{eg} \rangle + \Delta \omega(t) + \epsilon_i \]  \hspace{1cm} (X.2)

where \( \langle \omega_{eg} \rangle \) is the average transition frequency of the whole ensemble, \( \Delta \omega(t) \) is a fluctuating term representing the modulation of the transition frequency by the nuclear degrees of freedom (both intramolecular and intermolecular) and \( \epsilon_i \) is the offset of the individual transition frequency from the mean. Thus, the width of the distribution \( f(\epsilon) \) is the inhomogeneous width or diagonal disorder. The correlation function describing the fluctuations

\[ M(t) = \frac{\langle \Delta \omega(t) \Delta \omega(0) \rangle}{\langle \Delta \omega^2 \rangle} \]  \hspace{1cm} (X.3)
can be Fourier transformed to give the spectral density, \( \rho(\omega) \) describing the energy gap fluctuations [67]. A unified description of linear and nonlinear spectroscopies, and dynamical phenomena such as electron transfer, can be given in terms of the spectral density [68].

We now briefly digress to describe the peak shift measurement. This method is a form of 3-pulse stimulated echo in which the two, time-reversed, phase matched echoes at \(-k_1 + k_2 + k_3\) and \(-k_1 - k_2 + k_3\) are simultaneously measured for different, fixed values of the second time period, which we call the population period, \( T \) (see Fig. X.8). The simultaneous measurement of the two signals enables the position of the peak of the echo signal (as a function \( \tau \), the first time variable) with respect to the time origin (\( \tau = 0 \)) to be determined very precisely. Typically, our experimentally determined precision

![Diagram](image)

**Fig. X.8.** Pulse sequence and phase matching diagram for the 3 pulse echo. The three pulses, incident on the sample with wavevectors \( k_1 \), \( k_2 \) and \( k_3 \) generate two mirror image echo signals in the phase matched directions \( k_1 - k_2 + k_3 \) and \(-k_1 + k_2 + k_3\), as indicated in the diagram by the open circles. The experimentally controllable center-to-center temporal delays between \( k_1 \) and \( k_2 \) and between \( k_1 \) and \( k_3 \) are \( \tau \) and \( T \), respectively. These two delays are sometimes referred to as the coherence and population times. For the purposes of calculation, \( t_1 \), \( t_2 \), and \( t_3 \) denote field-matter interaction points, while \( t'_1 \), \( t'_2 \), and \( t'_3 \) refer to delays between interaction points. \( P^{(3)}(t') \) is the third order polarization generated by the three interactions at \( t'_1 \), \( t'_2 \), and \( t'_3 \).
for the "peak shift," \( \tau^* \), which is defined as half the separation of the two echo signals is \( \pm 300 \) as. The peak shift is now determined as a function of the population period, \( T \), and the resulting \( \tau^*(T) \) vs \( T \) plot represents our source of information regarding the spectral dynamics.

For isolated chromophores we have shown that at longer times than the bath correlation time, \( \tau^*(T) \) directly represents the transition frequency correlation function, \( M(t) \) [57]. The short time behavior of \( M(t) \) must be obtained by fitting the peak shift to model functions and properly taking account of electric field envelopes of the three pulses. Furthermore, a non-zero long-time value indicates definitively the presence of static (on the timescale of the measurement) inhomogeneity.

The peak shift method has been successfully applied to studies of solvation dynamics in polar liquids [56] and the temperature dependent dephasing of a chromophore in a polymer glass between 30 K and 300 K [66]. In such systems, the technique is capable of determining the overall strength of coupling to nuclear degrees of freedom and the magnitude of the inhomogeneous contribution to the spectral broadening, in addition to the full range of dynamical timescales. A determination of such qualities for LH1 and LH2 would greatly aid in modeling the electronic states and dynamics in these systems. There are presently, however, a number of complications in interpreting peak shift measurements on such systems. The development of appropriate theoretical models for interpreting echo measurements on reactive systems has lagged slightly behind the experimental capabilities. Development of a theory for energy transfer systems is underway, but not yet complete. For the present we will use a simple extension of the isolated molecule formalism to interpret the peak shift data for LH1 and LH2.

Fig. X.9 compares peak shift data for LH1 with similar data taken for the dye IR144 dissolved in the polymer glass PMMA at 300 K [62]. Several interesting points of comparison emerge directly from the \( \tau^*(T) \) vs \( T \) plots of Fig. X.9. First, the initial value of the peak shift is inversely related to the overall coupling of the electronic transition to the nuclear degrees of freedom. It is also somewhat sensitive to pulse duration [56] which is a little longer for the LH1 data than for IR144, but this effect is quite small, and it is apparent that the overall coupling of the electronic and nuclear degrees of freedom (both intra- and intermolecular) is weak in the light harvesting complex. This is also clear in the vibrational beats readily apparent in the IR144 data (e.g., at 200 fs), but much less prominent in LH1. Second, the long-time value of the peak shift of LH1 is much smaller than that of the dilute chromophore in the glass. In fact, a plot of \( \tau^*(T) \) vs \( \log T \) reveals a slow (12 ps) component in the LH1 data, taking \( \tau^* \) to zero on the \(-10 \) ps timescale. Similar data are obtained for LH2, although in this case the vibrational beats are even less prominent than in LH1.

Since it is certainly clear that LH1 and LH2 contain a distribution of site energies, we propose that the energy transfer process itself is reflected in the peak shift measurement by its ability to disable rephasing of the nonlinear polarization. In other words, the stochastic jumping between different members of the \( f(\varepsilon) \) distribution destroys the memory of the transition frequency and thus prevents the third pulse from
Fig. X.9. Peak shifts of LH1 (squares) and IR144 in PMMA (circles). The peak shift in fs is plotted against time. The LH1 peak shift is of larger initial magnitude and continues to decay at long times. This effect is due to energy transfer. The IR144/PMMA peakshift, in contrast, shows a constant offset which may be interpreted as static inhomogeneity.

rephasing the ensemble. In this model, the energy transfer timescale should contribute directly to the peak shift. If we assume that a single hop disables rephasing, we can interpret the timescales of ~90 fs for LH1 and ~130 fs for LH2 as the hopping contribution to M(t), consistent with the timescales inferred from our modeling of the fluorescence anisotropy data [48,49]. The slow component in the peak shift (~12.5 ps in LH1) then reflects very slow energy transfer involving molecules in the tail of the inhomogeneous distribution, in an analogous manner to their role in the final value of the fluorescence anisotropy and the non-exponentiality of the anisotropy decay (vide supra). If such an assignment is made, then the remainder of the peak shift can be analyzed according to the methods developed for isolated chromophores. This leads to estimates for the magnitude and timescale of the Stokes shift (≈2λ) for LH1, 2λ = 195 cm⁻¹ with a timescale of 40–50 fs and LH2 2λ = 130 cm⁻¹ with the same timescale. We
can then estimate the magnitude of the inhomogeneous broadening at room temperature to be \( \sim 500 \, \text{cm}^{-1} \) for LH1 and \( \sim 400 \, \text{cm}^{-1} \) for LH2.

There are a number of serious approximations in this analysis. First, the exciton structure discussed earlier has been neglected. Relaxation between exciton components and the contribution of the exciton band to the overall spectral width are both ignored. This may well mean that the inhomogeneous widths quoted above are overestimates. Second, the energy transfer is treated as a weak perturbation on the system. This may not be correct, and for strong coupling cases, the nonlinear polarization must be calculated in an eigenstate representation rather than the implicit site representation that we have used so far. Incorporation of these effects and others such as the coupling of the solvation dynamics and the energy transfer must await theoretical developments.

For the present, what can be done is a comparison of the parameters listed above with the model calculations of Leegwater [69]. This author, using a Green's function approach, has modeled the simultaneous influence of homogeneous (i.e., fast) and inhomogeneous (i.e., diagonal disorder) broadening on the number of molecules coherently excited in circular aggregates such as LH1 and LH2. His starting point is to build the rings from dimers so that LH1 is modeled as \( N=16 \), i.e., 16 dimers. If we assume the electronic coupling is \( \sim 250 \, \text{cm}^{-1} \), consistent with the hopping timescale, then the parameters of our echo measurements imply that for LH1 the inverse participation ratio corresponds to 3–4 molecules. The exciton in this parameter range is largely dynamically localized. Although it is encouraging that this estimate of the delocalization corresponds quite well with that of a number of other groups, based on different techniques [42–44], it must be admitted that the final word has not yet been obtained. Electronic structure calculations and theoretical developments are required to spur further experimental studies and sharpen our grasp on the influence of intra and intermolecular interactions, disorder and coupling strength, and type (i.e. \( R^{-6} \) vs \( \exp(-\alpha R) \)) on the energy transfer dynamics.

5. Summary

The overall scheme of bacterial light harvesting and the timescales are now clear. Developing microscop[ic] models for the energy transfer dynamics with the B875 and B850 rings of LH1 and LH2 is driving developments in the theory of condensed phase quantum dynamics, maintaining the active feedback between the biological aspects of photosynthesis and molecular spectroscopy that has been in operation for at least 150 years. Repeating the current level of success with plant photosystems [31,32] and understanding the sophisticated regulation mechanisms at work in plants should keep this symbiotic relationship flourishing for many more years.
6. Acknowledgments

This work was supported by the National Science Foundation and in part by the Donors to the Petroleum Research Fund administered by the American Chemical Society. We thank our coworkers Stephen Bradforth, Marilena Ricci, Taiha Joo, Jae-Young Yu, Frank van Mourik, and S. N. Dikshit for their invaluable contributions to this work and James Longworth for much advice on the historical aspects of light harvesting.
6. References