



Three pulse echo peak shift measurements on the B820 subunit of LH1 of *Rhodospirillum rubrum*

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Abstract

Three pulse photon echo peak shift measurements (3PEPS) of the detergent isolated B820 subunit of the light harvesting complex of *Rhodospirillum rubrum* are presented and compared with 3PEPS data for the LH1 complex of *Rhodobacter sphaeroides*. The comparison suggests that the 90 fs component of LH1 3PEPS is indeed the energy transfer component. The striking similarity between 3PEPS of LH1 and B820 subunit also suggests that excitation is delocalized over only a dimer unit. © 1997 Elsevier Science B.V.

1. Introduction

In recent years considerable progress has been made towards a determination of the molecular structure and the layout of the photosynthetic apparatus of purple bacteria. Using X-ray diffraction techniques, the structures of the reaction center (RC) [1] and the light-harvesting 2 complex (LH2) [2] have been determined at atomic resolution (≤ 2.6 Å) while a lower resolution study of the light harvesting 1 complex (LH1) [3] confirms its similarity in overall design to LH2, in that both are highly symmetrical ring structures composed of repeating units of $\alpha\beta$ pairs of transmembrane polypeptides. It is believed

that the reaction center sits inside the LH1 ring and that multiple copies of LH2, perhaps up to 8, surround LH1 to give the entire photosynthetic unit. This arrangement corresponds to a funnel for the excitation energy as LH2 contains bacteriochlorophyll molecules (BChl) absorbing at 800 nm (B800) and 850 nm (B850) whereas the BChl in LH1 absorbs at 875 nm (B875).

Since the discovery of the beautifully symmetric ring of 18 B850 molecules in LH2 of *Rhodospseudomonas acidophila* [2] and 16 B850 molecules in LH2 of *Rhodospirillum molischianum* [4], and the strong evidence that LH1 is comprised of a similar but larger ring of 32 B875 molecules, the mechanism and timescale of energy transfer in such a symmetric and strongly coupled aggregate has been the object of intense study. LH1 and LH2 have been studied with a variety of time-resolved spectroscopic techniques [5–8] (for an overview of earlier work, see for instance, the 1994 review by Van Grondelle et

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al.) Fluorescence depolarization studies of LH1 and LH2 were carried out by Bradforth et al. [5] and Jimenez et al. [6]. The depolarization decayed on several timescales in both cases and this was interpreted as reflecting hopping among an inhomogeneous distribution of site energies located within each ring structure [5]. In order to quantitatively model the data an inhomogeneous width of $\sim 500 \text{ cm}^{-1}$ (FWHM) was required for LH1 and hopping was assumed to be between dimers [5]. The average hopping times resulting from this model are on the order of 100 fs. Pump-probe experiments have also been employed extensively to study the energy migration [9–11]. Visser et al. [7,8] studied the equilibration of the transient spectrum LH1 of *Rb. sphaeroides* and *Rhodospirillum rubrum*. Their results could be explained by a very similar model to that used for the fluorescence depolarization, and a ratio of homogeneous/inhomogeneous width of 0.6 was obtained [5].

The extent of excitonic delocalization in B850 and B875 has been very extensively debated [5,6,12–18]. Key quantities are the electronic coupling between BChls, the electron–phonon coupling (reorganization energy and timescale) the temperature, and the diagonal (site energy) and off-diagonal (coupling) disorder. In an attempt to provide experimental characterization of the electron–phonon coupling and the magnitude of the inhomogeneous broadening, Jimenez et al. carried out three pulse photon echo peak shift (3PEPS) [12] measurements on LH1 and LH2 [12]. In a system with dilute non-interacting chromophores the 3PEPS measurement is particularly well suited to characterizing the system-bath coupling and the inhomogeneous broadening [19–21]. In particular, for a dilute chromophore the presence of a nonzero time independent peak shift ($\tau^*(T)$) value at large values of the population period T is a definitive sign of broadening that is static on the experimental timescale [19]. The initial value of the peak shift $\tau^*(0)$ is sensitive to the total reorganization energy, while the timescales in the decay of $\tau^*(T)$ to its long-time ($\tau^*(T \rightarrow \infty)$) value reflect the timescales of the coupling of the electronic transition to the nuclear degrees of freedom [19].

A striking result of the 3PEPS data on LH1 and LH2 is that $\tau^*(T)$ decays to zero at long times.

Jimenez et al. proposed that, rather than indicating a system with a very small distribution of site energies, this resulted from the loss of rephasing capability as a result of energy transfer [12]. In effect, the energy transfer process ‘‘averages’’ over the inhomogeneous distribution. In this scenario they argued that the energy transfer timescale should be directly observable in the $\tau^*(T)$ vs. T data and that the amplitude (coupling strength) of this contribution should equal the width of the inhomogeneous distribution. Analyzing the 3PEPS data on this basis gave an energy transfer timescale and inhomogeneous width in reasonable accord with the fluorescence results [5,6]. The analysis was originally based on a plausible argument, but more recently Cho has shown, for a well-defined model, that the energy transfer rate appears directly in the expression for the peak shift [22].

The B820 subunit [23–25] of LH1 allows us to address those issues in greater detail. The subunit can be reversibly re-associated to the B875 (LH1) complex [26,27]. B820 consists of one α and one β transmembrane polypeptide and two BChl-*a* molecules [23]. Thus, energy transfer will not occur outside the dimer pair, and if the electronic states of LH1 involve many more than two molecules, the optical properties of the two samples might be expected to differ significantly.

In this letter, three-pulse photon echo peak shift (3PEPS) measurements on the B820 subunit of *Rhodospirillum rubrum* are presented. By comparing our data with the peak shift measurements of LH1 by Jimenez et al. [12], we confirm that energy transfer is observed in the peak shift data for LH1. In addition, the comparison suggests that the elementary unit of LH1 can be considered to be a *single* dimer subunit.

2. Experimental

2.1. Material

The B820 subunit was dissociated from the LH1 complex of *Rhodospirillum rubrum* following the preparation procedure of Miller et al. [23]. The B820 subunit absorption spectrum is shown in Fig. 1. A total of 3 ml of B820 subunit sample was circulated through a 200 μm quartz flow cell (Starna) pumped

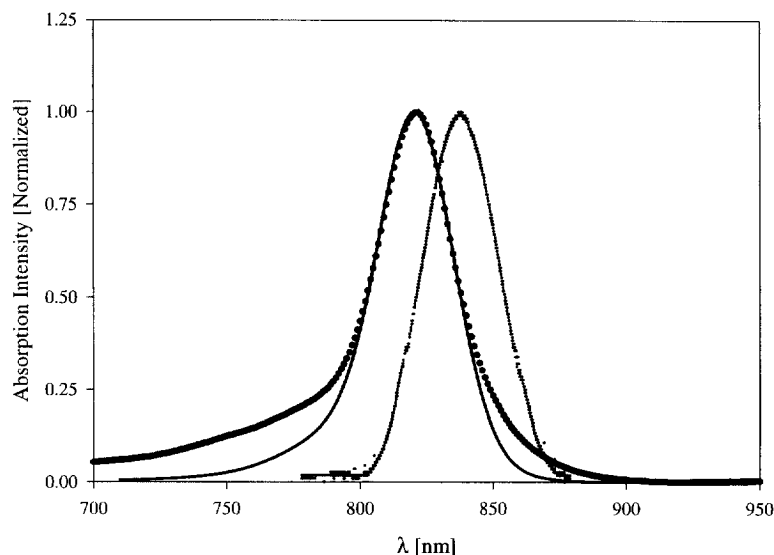


Fig. 1. The absorption spectrum of the B820 subunit dissociated from LH1 of *Rhodospirillum rubrum* by n-octyl- β -D-glycopyranoside (OG) (solid circles). Simulated absorption spectrum using the parameters to simulate 3PEPS (solid line). The dotted curve is the spectrum of the laser pulses. See the text in Section 3 for details of parameters used.

by a peristaltic pump. Due to the high reactivity of the sample with oxygen, the sample cell and the tubing were sealed under a nitrogen environment.

2.2. Three pulse photon echo measurements

The three pulse photon echo experimental optical arrangements are similar to that used by Jimenez et al. [12]. A cavity-dumped Ti:Sapphire laser mode-locked at 837 nm was used. At this wavelength, the laser generates 37 fs FWHM pulses. The repetition rate was set to 250 KHz for most of the data collection. A lower repetition rate was also used to check for thermal effects, but none were observed. A maximum energy of 570 pJ/pulse was used. Experiments were also performed with a pulse energy of 120 pJ/pulse and no difference in the form of the echo signals was observed.

3. Results and discussion

Fig. 2 shows a plot of the peak shift vs. population time ($\tau^*(T)$ vs. T) for B820 (squares) (this work) and for the LH1 from Ref. [12] (circles). The two curves are strikingly different. After ~ 200 fs

the B820 peak shift remains almost constant up to 100 ps, while the LH1 data decay on two very different timescales and have almost decayed to zero by 10 ps. (The long time-constant is ~ 12 ps [12]). Thus, B820 shows clear evidence of significant inhomogeneous broadening. In addition, the initial value of the peak shift is significantly larger for B820. In order to understand these differences we first turn to a brief discussion of spectral broadening and dynamics.

The electronic transition frequency of an individual chromophore, in general, can be decomposed into three terms [19] as shown in Eq. (1).

$$\omega_i(t) = \langle \omega \rangle + \delta \omega_i(t) + \epsilon_i. \quad (1)$$

Here $\omega_i(t)$ is the time dependent transition frequency of molecule i , $\langle \omega \rangle$ is the mean transition frequency, $\delta \omega_i(t)$ is the dynamical fluctuation term, and ϵ_i is the static off-set from the mean transition frequency. For a system consisting of non-interacting chromophores (i.e., with no energy transfer) the dynamical contributions to the echo signal are contained in $M(t) = \langle \delta \omega(t) \delta \omega(0) \rangle$ [28], and the static term will produce rephasing in photon echo measurements. As noted earlier, existence of static inhomogeneity results in a non-zero value of the peak shift

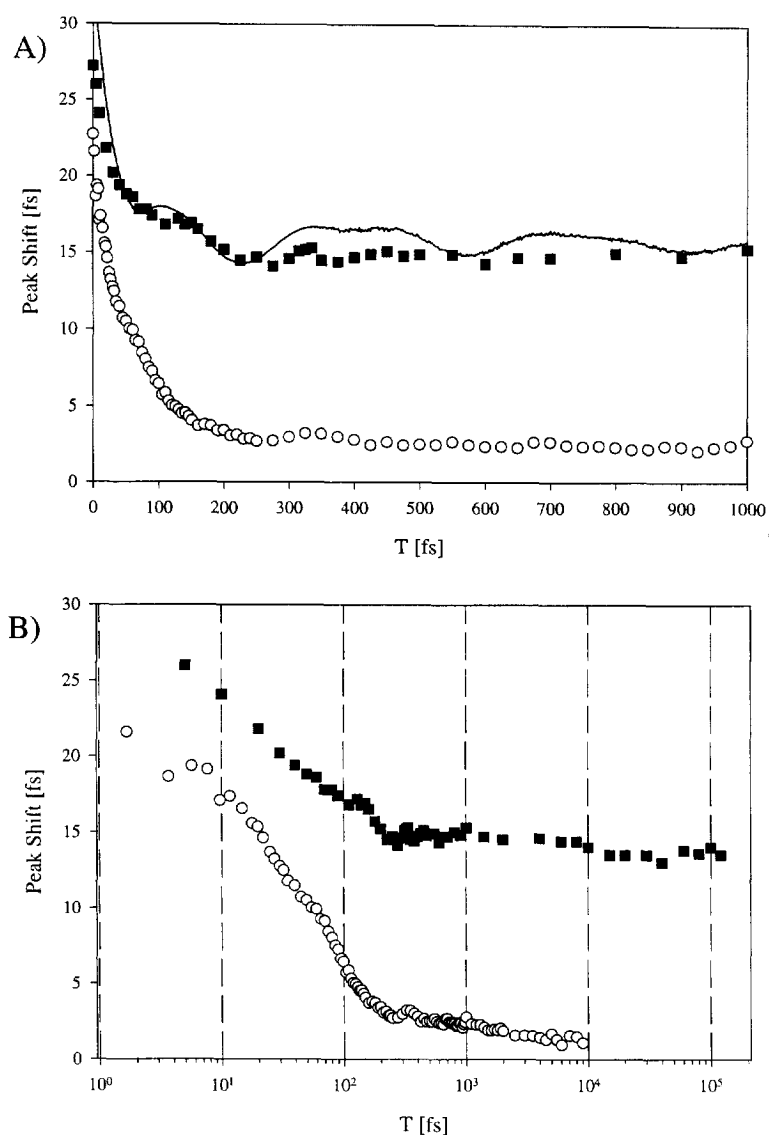


Fig. 2. (a) 3PEPS measurements of LH1 of *Rb. sphaeroides* (open circles) and the B820 subunit from LH1 of *Rs. rubrum* (solid squares). The solid line is a simulation of the B820 subunit using parameters taken from a fit to the LH1 data [12] (see the text for details). The population time (T) ranges from 0 ps to 1 ps. (b) The same experimental data as in (a), with the population time plotted on a log-scale. T now runs from 0 ps to 140 ps.

for large values of the population time. When transfer occurs, however, the excitation energy should be tracked instead of the molecule that was originally excited. The result of tracking the excitation energy is that the memory of the static off-set information is lost as excitation energy is transferred from one chromophore to another. One can visualize this by sitting on the excitation. The excitation originally on

site i migrates to site j , and as a result there is a sudden change in local environment of the excitation, i.e., the static off-set is now different. From this perspective, the transition frequency is now written as

$$\omega_k(t) = \langle \omega \rangle + \delta \omega_k(t) + \epsilon_k(t), \quad (2)$$

where the subscript k represents the k th excitation rather than the k th chromophore, and the static offset has become a time dependent quantity. In this case, the correlation function $M(t)$ contains contributions from both $\langle \delta\omega(t)\delta\omega(0) \rangle$ and $\langle \epsilon(t)\epsilon(0) \rangle$. Assuming that these two correlation functions are not coupled

$$M(t) \equiv \langle (\omega(t) - \langle \omega \rangle)(\omega(0) - \langle \omega \rangle) \rangle \\ = \langle \delta\omega(t)\delta\omega(0) \rangle + \langle \epsilon(t)\epsilon(0) \rangle. \quad (3)$$

According to Eq. (3), the inhomogeneity correlation function contributes to the decay of photon echo signals, as well as to the photon echo peak shift. If a stochastic energy hopping process is assumed, an exponential form results for the inhomogeneity correlation function [12]. Other functional forms for the energy transfer process will produce similar results provided they have the same correlation time. However, in the simplest limit where the system loses coherence after one ‘‘hop’’ onto an adjacent site, this is an exact model, and the pair-wise hopping rate is twice the correlation time used for the energy transfer term.

Jimenez et al. [12] modeled $M(t)$ as

$$M(t) = a_G^2 \exp\left[-(t/\tau_G)^2\right] + a_{\text{exp}}^2 \exp(-t/\tau_{\text{exp}}) \\ + \sum_i a_{o,i}^2 \exp(-t/\tau_{o,i}) \cos(\omega_{o,i}t + \phi_{o,i}) \\ + \Delta_{\text{in}}^2 \exp(-t/\tau_{\text{ET}}). \quad (4)$$

Here, the a are the coupling strengths, the τ are correlation times, the ω are vibrational frequencies, the ϕ the phase shifts, Δ_{in} is the standard deviation of the inhomogeneity, i.e., the distribution of ϵ_i values, and τ_{ET} is the time scale associated with the energy transfer process. The subscript ‘‘G’’ denotes a Gaussian process, ‘‘exp’’ denotes an exponential process, and ‘‘o’’ denotes a damped oscillatory process. A fit of the LH1 data required one 60 fs Gaussian mode, one 12.5 ps exponential mode, one 90 fs exponential mode which was associated with energy transfer process, and four damped oscillatory modes [12]. The absence of energy transfer in the B820 subunit suggests that we attempt to model B820 with the same parameters but with $\tau_{\text{ET}} = \infty$. This approach retains the coupling strength of the 90 fs component as the standard deviation of the static inhomogeneity of the system, following Jimenez et

al.’s suggestion that entire inhomogeneous distribution of site energies is sampled. Thus, if the exciton–phonon coupling is the same for LH1 and the B820 subunit, and if the excitonic states of LH1 and the B820 subunit have similar size, $M(t)$ for the B820 subunit can be modeled as

$$M(t) = a_G^2 \exp\left[-(t/\tau_G)^2\right] + a_{\text{exp}}^2 \exp(-t/\tau_{\text{exp}}) \\ + \sum_i a_{o,i}^2 \exp(-t/\tau_{o,i}) \cos(\omega_{o,i}t + \phi_{o,i}) \\ + \Delta_{\text{in}}^2, \quad (5)$$

where the parameters are shown in Table 1. Three pulse photon echo peak shifts are simulated using the $M(t)$ in Eq. (5) and including all possible electronic pathways in a two-level system [28,29].

The solid line in Fig. 2 shows the result of this calculation for B820 using the identical parameters used to fit LH1 [12]. No adjustment of any parameter was made. Both the large long time value of the peak shift ($\tau^*(T \rightarrow \infty)$) and the increased initial value ($\tau^*(0)$) over that in LH1 are reproduced qualitatively. The increase in $\tau^*(0)$ reflects the absence of the energy transfer process in the loss of phase memory in B820, since the magnitude of $\tau^*(0)$ results from the magnitude of the dynamical broadening processes, and the ratio of dynamic to static broadening processes [30]. An experimental observation of this effect in a dye/PMMA system was given by Nagasawa et al. [20] where the initial peak shift increases from 13 fs at 294 K to 17 fs at 32 K. This

Table 1
Parameters^a used for simulating peak shift measurements of the B820 subunit of *Rs. rubrum*

	a cm ⁻¹	τ fs	ν cm ⁻¹	τ_{damp} fs	ϕ rad
Gaussian	100	60	–	–	–
exponential	85	12500	–	–	–
oscillation 1	45	–	110	700	–2.1
oscillation 2	45	–	190	400	0
oscillation 3	170	–	560	70	–0.2
oscillation 4	120	–	750	50	0
inhomogeneity	160	–	–	–	–

^aThe parameters are taken from Ref. [12] except for the energy transfer process term. See Eq. (5) for the model $M(t)$ associated with the above parameters. The a value in ‘‘inhomogeneity’’ row corresponds to Δ_{in} in Eq. (5).

increase comes from a decrease in the coupling strength of dynamic processes as a result of the lower population of excited phonon modes at low temperature. In the case of the B820 subunit, the total coupling strength of the dynamical processes is smaller than in LH1 because of the absence of the energy transfer process.

In addition, the LH1-based calculation predicts all time scales quite well. The vibrational beats in the B820 subunit are slightly less pronounced than those in the calculated curve. This may result from the different bandwidths and center frequencies of the excitation pulses with respect to the absorption maxima in the two experiments. In addition, the energy transfer term probably decreases the accuracy with which the coupling strengths and the correlation times of vibrational modes can be estimated in the LH1 data. Nevertheless, the good agreement between the simulated echo signal and the peak shift measurements of the B820 subunit strongly suggests that the energy transfer process has been captured correctly in the LH1 simulation of Jimenez et al., and that the exciton–phonon coupling is very similar in LH1 and the B820 subunit.

In order to address this latter point definitively, it is necessary to consider the nonlinear response of aggregates at a more sophisticated level than the two-level approach used above. Meier et al. [17] have described the behavior of the photon echo for interacting chromophores in terms of excitonic states. The line broadening function, $g(t)$, which controls the molecular response has prefactors related to inverse participation ratios of the chromophores in the presence of excitonic interactions. These prefactors are always less than one and become smaller as the excitonic length grows, so they effectively reduce the coupling strengths of dynamical processes. Thus, the effective coupling strengths will be similar for LH1 and the B820 subunit only if the excitonic lengths of both systems are similar. The B820 peak shift data cannot be reproduced by a simulation using the fitting parameters for the LH1 peak shift data if the excitonic lengths are different. If the excitonic length in LH1 is greater than that of the B820 subunit, the B820 experimental peak shifts should be smaller than the simulated peak shifts. However, the agreement of calculated and measured peak shifts shown in Fig. 2a suggests that the *excitonic length of the*

LH1 is roughly two BChl-a molecules, since if it were significantly larger, the simulated B820 curve would lie significantly above the data at all times. The blue shift which occurs when LH1 dissociates to B820 subunits is not due to breaking of excitonic interactions among dimers, but must be caused by changes in local environment [31–34].

The calculated linear absorption spectrum, constructed from the same $M(t)$ used for the B820 subunit 3PEPS calculations with a minor correction which sets all phases of vibrational modes to zero, agrees well with the measured absorption spectrum except in the wings, where it deviates significantly, as shown in Fig. 1. The B820 sample has a small amount of free BChl-a molecules which absorb around 777 nm and aggregated species which absorb light around 870 nm. We believe that these free and aggregated species are responsible for the additional intensity in the wings of the experimental absorption spectrum. The existence of these species is evident from the B820 subunit absorption spectrum taken at low temperatures by Visschers et al. [35].

The inhomogeneous linewidth of 377 cm^{-1} (FWHM), $= \Delta_{\text{inh}}/(8 \ln 2)$, used in the simulation of the peak shift and the absorption spectrum is significantly smaller than the value of 530 cm^{-1} estimated by Jimenez et al. [12]. The difference comes from the definition of homogeneous linewidth used by Jimenez et al. In order to estimate the inhomogeneous linewidth for the LH1, Jimenez et al. used only the Gaussian process in Eq. (4) as the homogeneous linewidth, and defined the rest of the line broadening in the room temperature absorption spectrum to be inhomogeneous broadening. This approach neglects the broadening from the vibrational motions and the 12.5 ps exponential decay in $M(t)$, and thus corresponds to an effective upper limit of the inhomogeneous linewidth for the LH1.

The inhomogeneous linewidth has an important influence on the degree of excitonic delocalization [12,15,18]. Recently, Monshouwer et al. [18] measured the temperature dependence of the superradiance of the B820 subunit, LH1 and LH2. This was modeled using estimates of the interaction energy between monomeric Bchl-a (200 cm^{-1}), and the inhomogeneous linewidth ($> 200 \text{ cm}^{-1}$ FWHM) of LH1. From these quantities, the excitation length was determined to be 2–3 pigments in LH1. The

inhomogeneous width determined in this paper (377 cm^{-1}) is somewhat larger than assumed by Monshouer et al. and suggests an excitation length of roughly two BChl in LH1, although we note that the definition of delocalization length depends on the quantity being measured [17].

In summary, an energy transfer term can be identified in three pulse photon echo peak shift measurements of aggregates such as LH1 and LH2. The coupling strength of the energy transfer term is given by the standard deviation of inhomogeneous width of the system. Our simulation of B820 peak shift measurements using LH1 peak shift parameters with this assumption and the energy transfer rate set to zero suggests that in the context of stimulated photon echoes the dimer model of LH1 appears to provide an excellent representation as previously suggested by Bradforth et al. [5] and Monshouer et al. [18] and that the exciton–phonon coupling is very similar in the subunit and the intact antenna.

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