Exciton Dynamics in LH1 and LH2 of *Rhodopseudomonas Acidophila* and *Rhodobium Marinum* Probed with Accumulated Photon Echo and Pump−Probe Measurements

Stefania S. Lampoura,*,†,‡ Rienk van Grondelle,† Ivo H. M. van Stokkum,† Richard J. Cogdell,§ Douwe A. Wiersma,‡ and Koos Duppen‡

Department of Physics and Astronomy, Vrije Universiteit, De Boelelaan 1081, 1081 HV, Amsterdam, The Netherlands, Ultrafast Laser and Spectroscopy Laboratory, Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands, and Institute of Biomedical and Life Sciences, Division of Biochemistry and Molecular Biology, University of Glasgow, Glasgow G12 8QQ, UK

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Exciton dynamics in the B850 and B875 bands of isolated complexes of *Rhodopseudomonas acidophila* (strain 10 050 and 7050) and in the B875 band of isolated complexes of *Rhodobium marinum* were investigated by means of accumulated photon echo and pump−probe techniques at different temperatures and wavelengths. For all three systems, the optical dephasing time T_2 was found to be very similar: at 4.2 K, T_2 is 116 and 106 ps for the B850 and B875 bands of *Rhodopseudomonas acidophila*, respectively, and 93 ps for the B875 band of *Rhodobium marinum*. The rapid dephasing, which displays glassy character, is a consequence of the strong pigment−protein interactions that arise through the rather short distances in these complexes. The observed dephasing time at the red edge of the B850 band of *Rhodopseudomonas acidophila* at 4.2 K reveals the existence of spectral diffusion in this system. From the wavelength dependence of the pump−probe signal in the B875 LH1 band of *Rhodopseudomonas acidophila* at 3 K it is concluded that energy transfer between energetically inequivalent LH1 rings occurs on a time scale of several tens picoseconds, while energy trapping takes place in about 250 ps.

Introduction

The fundamental processes in photosynthesis, underlying the conversion of solar energy into a useful chemical energy, have been extensively studied in many ways. Optical spectroscopic methods have proven to be a powerful tool in these efforts.[1−8] In photosynthesis, two ultrafast events play a decisive role: excitation energy transfer in the light harvesting antenna followed by charge separation in the reaction center (RC).[1,9,10] In most photosynthetic purple bacteria, the antenna system that transfers energy to the RC is composed of two different light harvesting complexes, a core complex surrounding the reaction center, LH1, and a more peripheral complex, LH2.

Recently, the structure of the peripheral light harvesting antenna complex, LH2 of *Rps. acidophila*[11] was resolved to 2.5 Å resolution, by means of X-ray diffraction. This high-resolution crystal structure revealed a densely packed bacteriochlorophyll−protein system. Sandwiched between two concentric cylinders of protein subunits in LH2, there are two parallel rings of Bchl-*a* molecules, which give rise to absorption bands at 800 nm (B800 band) and 850 nm (B850 band), respectively. The B800 band originates from 9 monomeric Bchl-*a* molecules with their chlorin planes parallel to the membrane surface, whereas the B850 band contains 18 strongly interacting Bchl-*a* molecules with their chlorin planes perpendicular to the membrane surface.[11] The close distance of about 9 Å between neighboring B850 Bchl-*a* molecules leads to large interaction energies of about 250−300 cm^{-1}, whereas the much larger distance of 21 Å between adjacent molecules in the B800 band leads to weaker interaction energies of about 20 cm^{-1} [12−14]. The second light harvesting antenna, the core antenna LH1 which surrounds the reaction center, is proposed to consist of 32 Bchl-*a* molecules, arranged in a circular configuration.[15] This complex gives rise to an absorption band at 875 nm (B875 band).

The large interaction energies between nearest neighbor molecules in the B850 and B875 bands lead to a delocalization of the excitation with an extent that is limited by static and dynamic disorder. Despite the various experimental and theoretical methods that have been applied in order to establish how many Bchl-*a* molecules (N_{del}) are involved in the delocalized states, no consensus on this point has been reached: N_{del} for the B850 and B875 bands at room temperature have been estimated to range from one dimmer to the whole ring.[16−26] Another issue that is still under investigation is the role of the protein structures in controlling the Bchl-*a* exciton state dynamics. Experiments in which the hydrogen bonding pattern of the Bchl-*a*'s was selectively perturbed by genetic engineering,[27] demonstrated that, besides excitonic effects, the strong protein−pigment interactions also contribute significantly to the red shift of the Q_y band of the LH2 complex. Stark spectroscopy[5] has been used to verify this influence of the protein environment on the absorption spectrum of the LH2 B850 band.

The dynamics of a chromophore, embedded in a host material, are reflected by the homogeneous line width (Γ_{hom}) of the absorption or emission spectrum. However, obtaining information about the dynamics from the line shape of the absorption

* To whom correspondence should be addressed. Tel: +31−20−4447935. Fax: +31−20−4447899. E-mail: lampoura@nat.vu.nl.
† Department of Physics and Astronomy, Vrije Universiteit.
‡ Ultrafast Laser and Spectroscopy Laboratory, Materials Science Center, University of Groningen.
§ Institute of Biomedical and Life Sciences, Division of Biochemistry and Molecular Biology, University of Glasgow.

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or emission spectrum is not straightforward. The ensemble of chromophores, which contribute to these spectra, are subject to a distribution of electrostatic interactions with the surroundings, giving rise to a distribution of transition frequencies which is called inhomogeneous broadening. Optical line narrowing techniques have to be used to extract the homogeneous line width from an inhomogeneously broadened transition. Two main categories of techniques are widely used for this purpose. First, frequency domain spectroscopies such as fluorescence line narrowing and hole burning[22,28] and second, time domain methods such as photon echoes and pump−probe techniques.[29] Spectral hole burning (HB) gives Γ_{hom} directly, whereas in photon echo (PE) spectroscopy, the optical dephasing time (T_2) is determined. These two parameters are often related by the expression $\Gamma_{hom}=1/(\pi c T_2)$.[29] This relation is expected to hold in cases where the system shows no spectral diffusion. Spectral diffusion originates from structural fluctuations of the surrounding matrix of the chromophore system, which occur on time scales slower than T_2 but comparable to or faster than the measuring time of the frequency domain methods, employed to determine Γ_{hom}. As a result, the value of Γ_{hom} becomes explicitly dependent on the measuring time.

In the accumulated photon echo (APE) technique, the signal results from a population grating in the electronic ground state that is built up over some hundreds of excitation pulse pairs.[30] This signal coincides with the single shot one color pump−probe signal, but under favorable conditions the APE signal is significantly enhanced due to the accumulation effect. The APE signal decays as e^{-2t/T_2}, thus providing information about the dephasing time T_2. When spectral diffusion occurs on time scales faster than the accumulation time, the measured T_2 is affected accordingly.

The APE technique is very useful for the study of the photosynthetic antenna systems for the following reasons: First, it allows detection of echoes that are generated with very low intensity pulses, thus avoiding photodamage of the system, and second, it is sensitive to the transition from the ground state to the one-exciton band only, without any contributions from transitions to higher exciton bands.[31] A necessary requirement for the generation of an efficient accumulated photon echo signal is the presence of a bottleneck state in the population decay process from the excited state. This is usually a triplet state that is long-lived compared to the 10.6 ns round trip time of the laser. In case of inefficient accumulation of the grating, a significant amplitude due to the one color pump−probe (PP) signal is present in the observed APE signals, as will be explained in detail in the "Results" section.

The first accumulated photon echo (APE) measurements on photosynthetic materials were performed on the reaction center of *Rhodobacter sphaeroides* by Meech et al.[4] Over the past few years, numerous photon echo[3,32,33] and hole-burning[34−36] studies have been performed on the B800, B850, and B875 absorption bands of light harvesting complexes. A recent HB study on the B850 band of LH2 from *Rps. acidophila*[2] showed that narrow holes could only be burnt at the red edge of this band. The average width of the zero phonon holes throughout the absorption spectrum was 120 ± 10 cm^{-1} at 4.2 K, but at the red edge a hole width of 0.86 cm^{-1} was observed. This corresponds to a dephasing time of 24.5 ps which was attributed to the lowest exciton level of the B850 band.

In this paper, we present a study of the optical dephasing behavior of the B850 and B875 bands in LH2 and LH1+RC, respectively, of *Rps. acidophila* and of the B875 band in LH1 of *Rd. marinum*. APE experiments were performed as a function of temperature over the wavelength range of 872−930 nm. The results on the B850 band of LH2 are compared with the HB experiments by Small and co-workers.[2] It is concluded that pure dephasing exists in LH2 even at a temperature as low as 4.2 K and that spectral diffusion occurs as well. The dephasing of the excitation in all antenna complexes at low temperatures is shown to occur through the coupling of the Bchl-*a* chromophores to the surroundings, which can be modeled as "glassy" two-level systems. The dynamics at 4.2 K are caused by strong Bchl-*a*-protein interactions. The observed wavelength dependence of the APE signals in the B875 band of *Rps. acidophila* is attributed to energy transfer between energetically inequivalent LH1 rings.

Materials and Methods

The B800−B850 (LH2) and B875 (LH1+RC) pigment−protein complexes of *Rps. acidophila* (strain 10 050 and strain 7050) and the B875 (LH1) of *Rd. marinum* were isolated and purified as described elsewhere.[37,38] The isolated antenna complexes were dissolved in buffer solution (Tris HCl 50 mM, pH8, 0.01% v/v LDAO) and both *Rps. acidophila* and *Rd. marinum* solutions were diluted with a glycerol/water mixture (1/1.5−2, v/v) which produced a clear glass sample at low temperature. Addition of 0.2% of the detergent lauryldimethylamine *N*-oxide (LDAO) led to a significant improvement of the diluted sample stability. The optical density was set to 1.2 at the maximum of absorption for the B850 band in a 1 mm cuvette and for the B875 bands in a 3 mm cuvette at cryogenic temperatures. Oxygen was removed from the samples with the "pump-freeze and thaw" technique. The samples were rapidly frozen by immersing them in a cryostat at 100 K and subsequently cooled slowly to 1.5 K.

Accumulated photon echo (APE) measurements were performed as described previously.[30] An Innova 99 mode-locked argon-ion laser, operating at 400 mW and generating pulses of 100 ps at a repetition rate of 94 MHz, was used to synchronously pump a dye laser. Styryl 9M and Styryl 13 in a 5/1 mixture of ethylene glycol and propylene carbonate were used as the lasing medium so that we could cover the whole wavelength region from 850 to 930 nm. The measurements of the wavelength dependencies of the dephasing times were performed using both transform limited pulses and stochastic excitation.[39] For the transform limited pulses, two plate Lyot filters were used as a wavelength tuning element and pulses of 8−12 cm^{-1} spectral width were produced. For the stochastic excitation, a 5 μm pellicle was used as a wavelength-tuning element and pulses of 50−100 cm^{-1} spectral width were produced. The coherent part of the autocorrelation of 0.4 ps, as measured in a KDP crystal, gives an indication of the time resolution of this technique.

The power in the two beams for both the wavelength and temperature-dependent measurements was set to 50 μW in most cases, to avoid photodamage of the sample. A 16 cm focal length lens was used to combine the two beams in the sample. A double modulation scheme was used for AM-radio sideband detection of the photon echoes to increase the signal-to-noise ratio.[40]

Pump−probe (PP) signals were measured with the same setup, but now with a travelling wave modulator (TWM) in the excitation beam. The TWM destroys the phase between consecutive excitation pulses and therefore does not allow for the accumulation of the ground-state population grating, necessary for the generation of the APE signal.[41] As a result, in the presence of the TWM only the PP signal is recorded.

Absorption spectra were obtained using an optical multichannel analyzer.

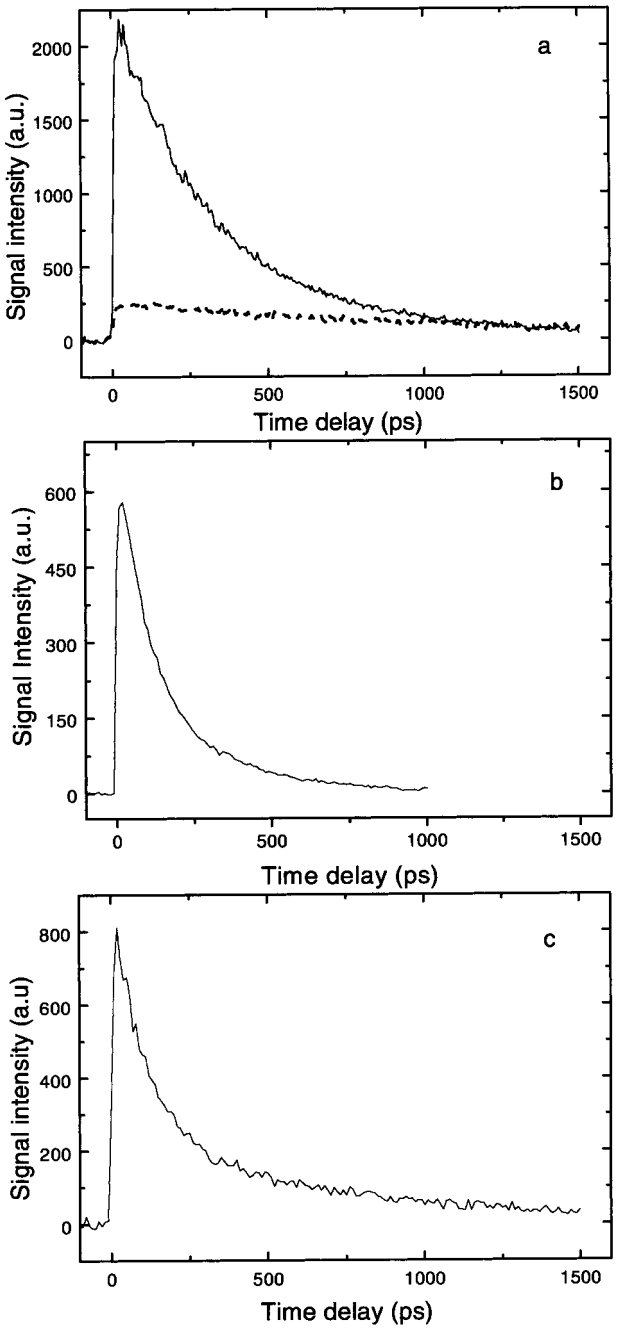

Figure 1. (a) APE signal (solid line) for stochastic excitation at 883 nm of the B850 band of *Rps. acidophila* at 1.5 K. Biexponential decay with 300 ps and 1 ns decay constant is observed. The incoherent PP background signal (dotted line) decays with a single exponent of 1 ns. (b) Typical APE signal for stochastic excitation at 3 K at 924 nm of the B875 band of *Rps. acidophila*. (c) Typical APE signal for stochastic excitation at 4 K and at 910 nm of the B875 band of *Rd. marinum*.

Results

i) Accumulated Photon Echo Signals. Figure 1a shows the APE and the PP signal intensities of the B850 band of the LH2 complex from *Rps. acidophila* at 1.5 K for stochastic excitation at 883 nm, and Figure 1, parts b and c, shows the corresponding typical APE signals of the B875 band of *Rps. acidophila* and *Rd. marinum* for stochastic excitation at 924 and 910 nm, respectively. All three of the APE signals exhibit a characteristic decay consisting of at least two exponential decay components, irrespective of whether stochastic excitation or transform-limited pulses were used.

In the case of stochastic excitation of the B850 band at 883 nm, (Figure 1a), the APE signal can be very well fitted with a biexponential decay function. The fast 300 ps component is the pure APE signal that disappears with $T_2/2$. The slow 1 ns long component is due to incoherent PP background, which arises from the rather inefficient accumulation of the grating, as will be explained in detail later on. Subsequently, by placing a travelling wave modulator (TWM) in the excitation beam, the pure PP signal was measured, which decays with the population lifetime T_1. The dephasing time T_2 and the population lifetime T_1 are, in the absence of spectral diffusion, related via:

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*} \tag{1}$$

where T_2^* is called the pure dephasing time.

From Figure 1a, in which both the APE and the incoherent PP signal intensities are plotted against the delay time for the B850 band of *Rps. acidophila*, it is evident that the fast component in the APE signal is due to dephasing, whereas the slow component is caused by population dynamics. This conclusion is supported by three observations: First, the slow component in the APE signal is identical to the 1 ns decay time, obtained from single exponential fitting of the PP data. This value agrees well with the excited state population lifetime as reported previously in the literature.[42] Second, consistent with expectation, the pure echo signal is observed to vanish when the temperature is raised, whereas the slow decay component in the APE signal was found to be largely independent of temperature. Third, the slow decay signal was found to change sign for excitation wavelengths to the blue of the absorption maximum, exactly where the PP signal is expected to show induced absorption from the one- to the two-exciton band.[18,43,44]

As mentioned in the "Introduction", a necessary requirement for efficient accumulated photon echo signal is the presence of a bottleneck state, which is usually a triplet state that is long-lived compared to the 10.6 ns round trip time of the laser. However, if the triplet population is transferred to another molecule, the grating is eliminated because the originally excited molecules return to their ground state. In such circumstances, the efficiency of the accumulation is determined by both the intersystem crossing yield and the energy transfer time from the initially excited molecule to the second one. In photosynthetic antenna complexes, the time during which accumulation of the grating takes place, is mainly limited by energy transfer from the Bchl-*a* triplet state to the carotenoid. This energy transfer time is about 700 ns for the B850 band at 4 K for LH2 of *Rps. acidophila*.[45] This leads to rather inefficient accumulation of the grating, and therefore small APE signals. Because the repetition rate of our laser system is 94 MHz, only 66 pulse pairs can contribute to the accumulation of the grating and as a consequence the signals clearly display an incoherent PP background signal. Nevertheless, they are strong enough to determine the dephasing time in the temperature range 2−9 K, whereas at the same time, the PP background provides information about T_1.

Earlier APE measurements on photosynthetic complexes have been performed on isolated RC of *Rb. sphaeroides*,[4] *Rb. sphaeroides* mutants (*R26* and *(M)Y210W*),[46] and *FMO* complexes.[33] Recently, the B800 band of two mutant LH2 complexes from *Rb. sphaeroides* and the B777 subparticle of the LH1-complex of *Rs. rubrum*[32] were studied with this method. In all of these species, the determination of T_2 was feasible at temperatures above 10 K, in some cases even up to 50 K. The lifetime of the bottleneck state of these species varies between

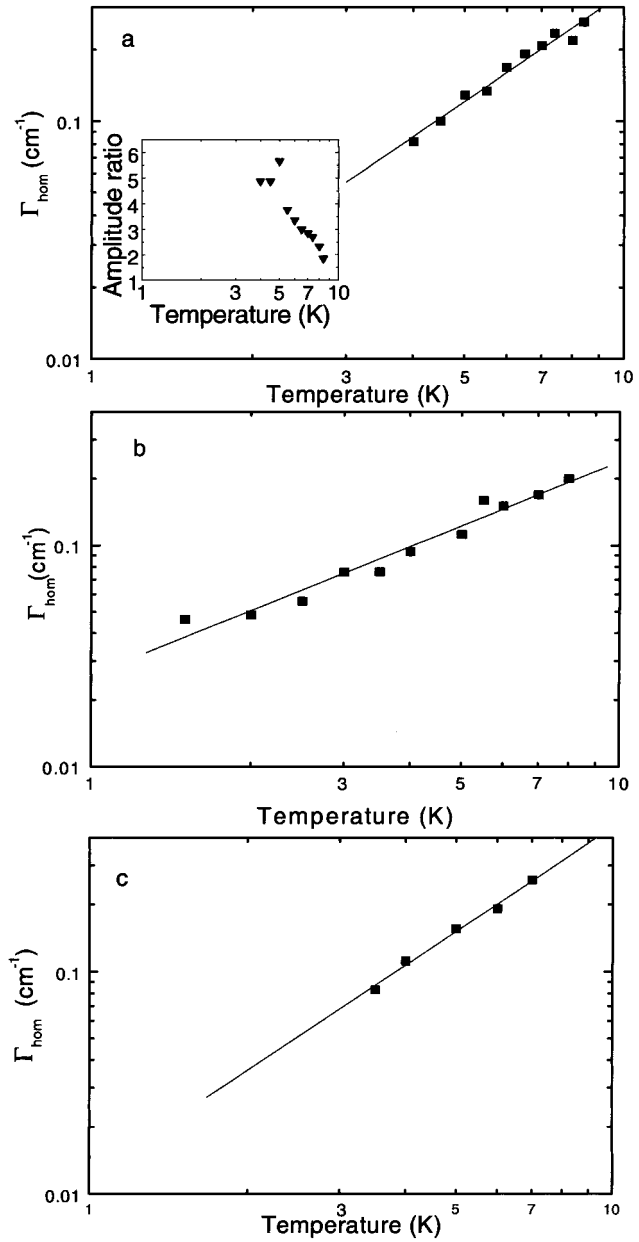

Figure 2. (a) Temperature dependence of Γ_{hom} for excitation at 885 nm of the B850 band of *Rps. acidophila*, Inset: Temperature dependence of the amplitude ratio of the pure APE to PP signals. The line gives the power law fit with $\alpha = 1.3 \pm 0.3$. (b) Temperature dependence of Γ_{hom} for excitation at 924 nm of the B875 band of *Rps. acidophila*. The line gives the power law fit with $\alpha = 1.3 \pm 0.3$. (c) Temperature dependence of Γ_{hom} for excitation at 910 nm of the B875 band of *Rd. marinum*. The line gives the power law fit with $\alpha = 1.3 \pm 0.3$.

1 ms and 40 ms at 4 K. This is so long that efficient accumulation of the population grating occurs and strong APE signals are observed.

Strikingly, in the APE measurements on LH1+RC "core complexes" from *Rps. acidophila*, as displayed in Figure 1b, we detect an APE signal even though the excitation should be rapidly trapped by the primary donor of the reaction center. The formation of an APE signal with a significant amplitude demonstrates that energy trapping of the excitation from the antenna to the reaction center is not very efficient at 3 K, in agreement with previously reported Bchl-*a* fluorescence measurements.[47]

ii) Dephasing and Population Dynamics. In Figure 2 , the temperature dependencies of the homogeneous line widths of the B850 band of LH2 of *Rps. acidophila* at 885 nm (a), and of the B875 bands of LH1 of *Rps. acidophila* at 924 nm (b) and *Rd. marinum* at 910 nm (c) are plotted. These data were extracted from APE measurements. In the inset of Figure 2a, the amplitude ratio of the pure APE to the PP signal is plotted as a function of temperature. It is clear that the echo signal is dominant at lower temperatures, whereas the pump−probe signal becomes dominant at temperatures higher than 9 K.

As mentioned in the "Introduction", the dephasing time T_2 corresponds via the relation $\Gamma_{hom}=1/\pi c T_2$ to the homogeneous line width Γ_{hom}. For all systems, the homogeneous line width was found to increase rapidly with increasing temperature. Above 9 K, the incoherent PP background severely hampers accurate determination of T_2. In all cases, the temperature dependence of Γ_{hom} up to 9 K could be fitted with the power law T^{α} with α equal to 1.3 ± 0.3. This behavior is well-known for chromophores in amorphous hosts, in which the dephasing is assumed to occur by coupling the energy levels of the chromophore to a distribution of two level systems (TLS) of the hosts.[28,48] The TLS consists of different conformational sub-states and the phonon assisted flipping between these sub-states results, in this case, to a fluctuation of the Bchl-*a* transition frequency. In literature,[28,48] the exponent for chromophores in glasses was consistently found to have the value of 1.3 ± 0.1.

To be able to compare our results below with existing hole burning data and APE experiments on the B800 band, we will discuss the dynamics specifically for the temperature of 4.2 K. We find a striking similarity between the dephasing dynamics of all measured bands. The dephasing times of 116 and 106 ps for the LH2 B850 and the LH1 B875 bands of *Rps. acidophila*, respectively, and 93 ps for the LH1 B875 band of *Rd. marinum* are so close to each other that this suggests a common mechanism for these dynamics, originating from the structural similarity of LH2 and LH1 of *Rps. acidophila* and a close resemblance of the core antennas of *Rd. marinum* and *Rps. acidophila.*

Hole burning studies[2] (HB) performed on the B850 band of LH2 of *Rps. acidophila*, have reported significantly shorter dephasing times at 4.2 K (almost by a factor of 5) compared to the ones described above. The measured homogeneous line widths, using HB, correspond to an optical dephasing time of approximately 24.5 ps at 885 nm and 100 fs at other excitation wavelengths.

The discrepancy between the HB and APE results for the dephasing time at 885 nm might be due to a number of reasons. The different time scales of these experiments (6 orders of magnitude) may give rise to a substantially larger contribution of spectral diffusion to the HB results compared to those of the APE results. Spectral diffusion of Bchl-*a* molecules can occur through structural fluctuations of the protein and/or the glycerol-water glass, resulting in a time scale dependence of the observed homogeneous line width.[25,49] Spectral diffusion has been also suggested to be induced from energy transfer.[50] Similar discrepancies in dephasing time between APE and hole burning were observed for Fenna−Matthews−Olson (FMO) complexes,[33] whereas for the B820 subunit of the LH1 complex from *Rs. rubrum*, it was explicitly shown that the observed holewidths depended on the time between burning and probing the hole.[51]

Singlet−triplet annihilation and local heating effects have also been proposed as a possible reason for the discrepancy between the APE and HB results because in HB experiments typically higher laser power densities are used.[33] In Figure 3 we show

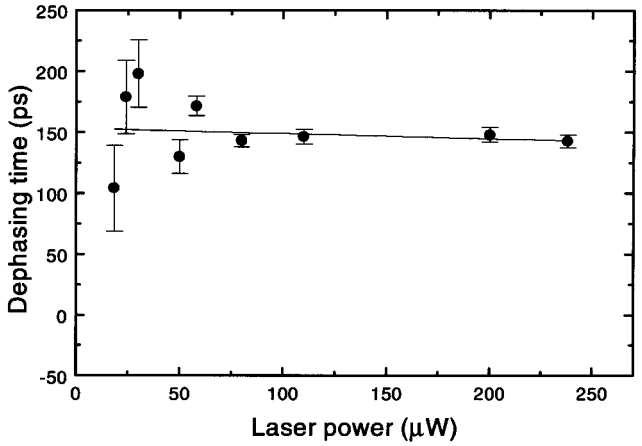

Figure 3. Intensity dependence of T_2 for excitation at 885 nm of the B850 band of *Rps. acidophila* at 4 K. The relative uncertainty in the data is indicated with error bars. The line is the least-squares fit of the data (appropriately weighted) and the slope parameter of the weighted fit is -0.04 ± 0.05, thus, the slope of the least squares fit is practically zero.

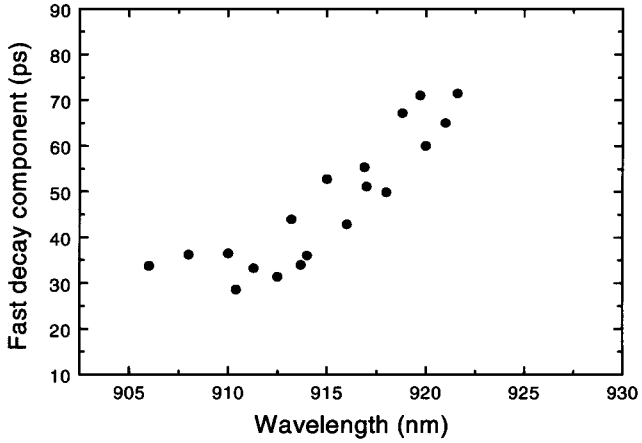

Figure 4. Wavelength dependence of the fast decay component of the PP signal for excitation in the B875 band of *Rps. acidophila* at 3 K.

the intensity dependence of the APE experiment on LH2 of *Rps. acidophila* at 885 nm. It is clear that, for excitation at 885 nm at 4 K, T_2 is essentially constant over the whole excitation energy range from 20 to 230 μW. This indicates that singlet−triplet annihilation or local heating in the sample does not play a role in the experiments reported here.

The PP signal of the B875 band of *Rps. acidophila* contains a fast decay component of the order of tens of ps, which also shows up in the APE experiments, even up to 80 K where the pure echo signal disappears. As shown in Figure 4 for wavelengths between 905 and 922 nm, this population decay time is wavelength dependent. The general trend of longer decay at longer wavelengths might be explained by exciton relaxation because it is known that excitation of an LH2 or LH1 ring in higher exciton states results in ultrafast relaxation to the lower exciton states.[44,52−54] However, this relaxation process occurs at room temperature in about 150 fs,[44,53] which is too fast to play a role here. We therefore propose that the fast PP decay component reflects energy transfer between energetically inequivalent rings. This suggestion was recently also put forward to explain the dynamics at the red edge of the B850 band of LH2, where fs pump−probe experiments showed decay components of 0.8−150 ps[52,55] and 0.6−19.5 ps,[54] in addition to ultrafast fs relaxation. These ps decays were attributed to either energy transfer between energetically inequivalent rings[52] or to polaron formation within the LH2 ring.[54]

Discussion

When the average energetic position of the lowest exciton state in LH2 is taken to be 885 nm, we can calculate the pure dephasing time at 4.2 K from our experimental results at this wavelength to be $T_2^* = 130$ ps (see eq 1). This short dephasing time, even at such low temperatures, indicates that there is strong coupling between the Bchl-*a* chromophores, the protein structure and possibly the glass. The observed $T^{1.3}$ temperature dependence seems to point to more or less conventional glass dynamics. However, it should be mentioned that the dephasing times of isolated systems, embedded in amorphous hosts, are usually 2 orders of magnitude longer[56,57] than the times found in this paper for both LH2 and LH1. Evidently, the strong and specific chromophore-protein coupling determines T_2^* to a large extent, and causes modulation of the transition frequency even at temperatures as low as a few Kelvin.

The protein medium surrounds the Bchl-*a* pigments of LH2 and LH1 with distances on the order of 3 Å.[58] They are large systems that prevent a strong direct coupling of the Bchl-*a* molecules with the glass in which the pigment−proteins are embedded. Proteins are a unique state of matter, which display both glassy and crystalline properties.[59] In general, they are crystalline in the sense that every atom is at a more or less fixed position in space, but glassy in the sense that they exhibit structural heterogeneity and low temperature dynamics. Unlike in perfectly ordered crystalline materials, the potential energy surfaces of both proteins and glasses possess a large degree of complexity, due to the high dimensionality of coordinate space. In such complicated situations, the optical dynamics are often modeled by thermally activated barrier crossing in a distribution of two-level systems. The $T^{1.3}$ temperature power law dependence, observed both for LH2 and LH1, directly follows from this glassy two-level model. The same power law dependence has also been reported in hole burning studies[2] on LH2 from *Rps. acidophila* and also for Bchl-*a* molecules in triethylamine glasses.[35]

Recently, APE measurements were performed on the B800 band in mutant LH2 complexes, that were modified in such a way that the transfer of the excitation energy from the B800 to the B850 band was inhibited.[32] The observed T_2^* of approximately 300 ps at 4 K is considerably longer than the dephasing times reported here for the B850 and B875 bands. It was attributed to the dephasing of single Bchl-*a* molecules. The weaker pigment−pigment coupling in B800 in the mutant LH2 complexes (due to the larger Bchl-*a*−Bchl-*a* distances) is actually expected to yield shorter dephasing times. The reason is that by excitonic coupling, the interaction with phonons and low-frequency vibrations is reduced. For example, exciton transitions in TDBC aggregates have a dephasing time that is at least a factor of 2 longer than TDBC single molecules under the same circumstances.[60] The fact that the single molecule dephasing in the B800 band of LH2 is longer than the excitonic dephasing in the B850 band of LH2 and the B875 band of LH1 points to much stronger intrinsic coupling with phonons and low-frequency vibrations in the latter two systems.[61] This can be rationalized from the stronger pigment−protein interactions that arise due to the shorter distances.[58] Note that the excitonic character of the pigments is also reduced by this interaction.

The population lifetimes, as measured by PP and the long tail of the APE, were 1 ns for the LH2 B850 band of *Rps acidophila* and 750 ps for the LH1 B875 band of *Rd. marinum.*

No wavelength dependence was observed. The wavelength dependence of the fast component in the population lifetime experiments on the LH1 B875 band of *Rps. acidophila* was treated in the previous section (see Figure 4). It is most probably due to energy transfer among energetically inequivalent LH1 complexes. The longer, wavelength independent component of about 250 ps is not so easy to interpret. In *Rps. acidophila*, the physical association of the LH1 and the reaction center is so strong that LH1 cannot be separated from the RC without losing its spectral properties. Therefore, the sample of *Rps. acidophila* contains LH1 in contact with the RC complex. The spectrum consists of a single band peaking at 885 nm, which means that the antenna absorbs in the same wavelength region as the primary donor of the reaction center.

The energy transfer time of the excitation to open reaction centers at room temperature has been established to be 35−60 ps,[1,62] whereas the trapping of the excitation energy by closed reaction centers occurs by a factor three to five times slower.[1] Both the energy transfer and the energy trapping times for the reaction center have been reported to decrease at lower temperatures.[47,63−65] The samples used in the APE measurements had open reaction centers at room temperature when not pumped by light. However, all the APE experiments were performed at low temperatures with unflowed samples and a laser pulse repetition rate of 94 MHz at 50 μW. Under these conditions, most of the reaction centers were probably closed and unable to perform light driven charge separation. Thus, the 246 ps decay component for excitation in the B875 band of *Rps. acidophila* probably represents the energy trapping time of the excitation by closed reaction centers.

Conclusions

In this paper, we have studied the exciton dynamics in LH2 and LH1 of *Rps. acidophila* and in LH1 of *Rd. marinum* at low temperatures and at different excitation wavelengths. We have shown that optical dephasing of the B850 and B875 bands at low temperatures (from 2 to 9 K) occurs via strong coupling of the Bchl-*a* chromophores in these complexes to the surrounding protein structure. The dynamics can be modeled in terms of "glassy" two-level systems.

The dephasing times at 4.2 K were: 116 ps for excitation in the B850 band of *Rps. acidophila*, and 106 and 93 ps for excitation in the B875 band of the LH1 complex from *Rps. acidophila* and *Rd. marinum* respectively. The dephasing time of 116 ps for excitation at 885 nm in the B850 band of LH2 of *Rps. acidophila* is almost a factor of 5 longer than the dephasing time obtained with hole-burning measurements.[2] This discrepancy is probably a consequence of spectral diffusion in this system. From a comparison of the pure dephasing dynamics of the LH2 B850 and B800 bands, it was concluded that the protein−pigment interactions are much stronger for the Bchl-*a* molecules in the B850 band.

Finally, the wavelength dependence of the fast component in the pump−probe signal of the B875 band of the LH1 complex from *Rps. acidophila* at 3 K was attributed to energy transfer between energetically inequivalent LH1 rings. The decay ranges from 34 ps for excitation near the maximum of the absorption band to 71 ps for excitation at the red side of the absorption band. The longer component in the pump−probe decay is due to energy trapping of the excitation of LH1 by closed reaction centers.

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