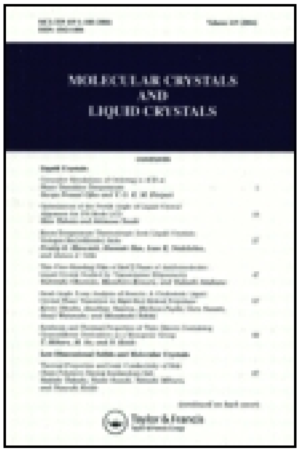

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PHOTOREACTIVE DISORDERED SYSTEMS STUDIED BY PERMANENT AND TRANSIENT HOLE-BURNING

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Abstract Permanent and transient hole-burning experiments carried out on various types of amorphous systems at temperatures between 0.3 and 20 K are presented. Optical dephasing on organic molecules in glasses and polymers measured on different time scales are discussed in relation to spectral diffusion processes and compared to the literature. The pure dephasing time appears to be proportional to the excited state lifetime of the guest. Organic molecules adsorbed on the surface of porous silica glass show that their homogeneous linewidth is an order of magnitude larger than in polymers and glasses in the bulk, but follows the same temperature dependence. Hole-burning results on bacteriochlorophyll in various disordered hosts are compared to those on a isolated light-harvesting photosynthetic pigment-protein complex (B800-850). From the holewidth in the latter the energy transfer rate between aggregated bacteriochlorophyll pigments is determined and compared to time-resolved spectroscopy results in the literature.

INTRODUCTION

Spectral line shapes of guest ions and molecules in amorphous solids at low temperature are usually determined by structural disorder, which gives rise to broad inhomogeneous linewidths of the order of a few hundred cm^{-1}. In order to get information on dynamical interactions, like relaxation processes of the excited state of the guest, it is necessary to know the homogeneous linewidth, Γ_{hom}, which is given by the effective optical dephasing time, T_2:

$$\Gamma_{hom} = (\pi T_2)^{-1} = (2\pi T_1)^{-1} + (\pi T_2^*)^{-1}$$

where T_1 is the excited state lifetime, and T_2^* is the pure dephasing time determined by thermally induced fluctuations of the optical transition frequency (e.g. phonon scattering). Since the homogeneous line is hidden under the inhomogeneously broadened absorption band, Γ_{hom} cannot be obtained by conventional spectroscopy, and time- and frequency- domain laser techniques are used to overcome this problem. Spectral hole-burning (HB) belongs to the latter category. The unknown quantity Γ_{hom} is then given, under certain conditions, by half the holewidth, $\frac{1}{2}\Gamma_{hole}$. The high optical resolution that can be obtained with this technique makes HB a powerful tool for spectroscopy in the MHz-regime.

In the present paper optical dephasing results on organic molecules in disordered hosts at temperature between 0.3 and 20 K obtained by permanent (PHB) and transient (THB) hole-burning will be discussed in relation to spectral diffusion processes. Then, HB experiments on a mixed organic-inorganic system will be presented, which were carried out with the purpose to test models for optical dephasing in glasses. Finally, HB results on bacteriochlorophyll in various glassy hosts will be compared with those on a photosynthetic antenna complex.

THE INFLUENCE OF THE EXPERIMENTAL TIME SCALE ON OPTICAL DEPHASING: IN SEARCH OF SPECTRAL DIFFUSION

PHB experiments performed in our group on the $S_1 \leftarrow S_0$ 0-0 transition of various organic molecules in a large variety of glasses and polymers between 0.3 and 20 K have shown that the value of $\Gamma_{hom} = \frac{1}{2}\Gamma_{hole}$ (at very low burning fluences) extrapolates to the fluorescence lifetime-limited value, $\Gamma_0 \simeq (2\pi T_1)^{-1}$, when $T \rightarrow 0$, and $\Gamma_{hom} - \Gamma_0 \propto T^{1.3}$, independent of the hole-burning mechanism[1,2,3]. A $T^{1.3}$-dependence has subsequently also been reported by other groups for many organic amorphous systems and even for chromophore-protein complexes, at least in a restricted temperature range (see references in [3]).

It has been argued that linewidths obtained by permanent hole-burning do not yield the homogeneous linewidth, but only reflect the presence of slow relaxation processes in the glass. The reasoning was based on contradictory results obtained for the value of Γ_{hom} by PHB and photon echoes[4]. Because glasses have a very broad distribution of relaxation rates, and these two techniques measure on different time scales they may yield different information on dynamical processes. So far there has not been an unambiguous demonstration of spectral diffusion on a time scale between that of photon echoes and PHB (picoseconds to minutes).

Porphins in polyethylene: permanent and transient hole burning

We have performed transient hole-burning (THB) experiments on free-base porphin (H_2P) in polyethylene (PE) with a time resolution of 5 ms in order to check the influence of the time scale on the value of Γ_{hom} [5]. THB takes place in this system because population is transferred from the ground state, by irradiation with a narrow-band laser into the first excited singlet state, to the metastable triplet state. The latter has a lifetime of about 6 ms at 1.2 K, and determines the decay time of the hole. Simultaneously, permanent holes (PHB) are created as a result of phototautomerism of the inner hydrogens in H_2P. In order to separate these two types of holes experimentally, we have very slowly scanned the frequency of the burning pulse (0.1 MHz/ms) as compared to the frequency of the probe pulse (≈ 50 MHz/ms). In this way a new hole at a different frequency is burnt after each burn-delay-probe cycle[5].

Our THB-results for H_2P in PE have been plotted on the lowest curve of fig.1 (open circles) in a log (Γ_{hom}-Γ_0) versus log T form. They are identical to those previously obtained by PHB on a time scale of minutes[2] (closed circles , no error bars shown), between 0.3 and 4.2 K. These results, together with the observation that holes probed in fluorescence excitation do not broaden as a function of time after burning between a few seconds and many hours[2,3], suggest that spectral diffusion does not take place over a time span of seven orders of magnitude (from 10^{-3} to 10^4 s), at least for the system H_2P in PE.

In fig.1 (two upper curves) we have also plotted our THB-results for two metal porphins, ZnP and MgP in PE, between 0.3 and 4.2 K, measured on a millisecond time scale. These systems do not undergo PHB. As for H_2P, Γ_{hom} extrapolates to $\Gamma_0 \simeq (2\pi T_1)^{-1}$ when $T \to 0$ ($\Gamma_0 \simeq$ 95 MHz for ZnP, and $\Gamma_0 \simeq$ 14 MHz for MgP, not shown in the figure), and $\Gamma_{hom}-\Gamma_0 \propto T^{1.3}$. The values of $\Gamma_{hom}-\Gamma_0$ in ZnP are about 10 times larger than in H_2P, whereas for MgP they are about a factor 1.5 larger, which suggets that the pure dephasing time T_2^* may be correlated with the fluorescence lifetime T_1.

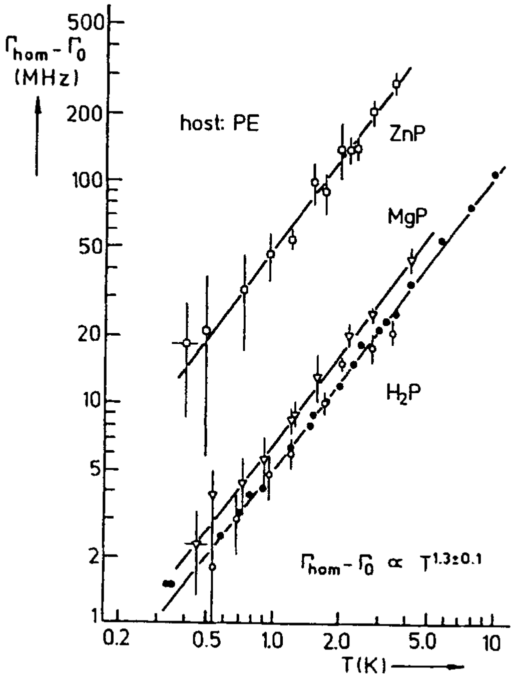

FIGURE 1 Log ($\Gamma_{hom}-\Gamma_0$) versus log T for zinc porphin, magnesium porphin and free-base porphin in polyethylene. Open dots: THB data, black dots: PHB data. Notice that $\Gamma_{hom}-\Gamma_0 \propto T^{1.3}$.

In fig.2 we have plotted T_2^* versus T_1 for various porphin molecules: those discussed above, and the free-bases phthalocyanine (H_2Pc) [6], chlorin (H_2Ch), and octaethylporphin (OEP) [7], whose values of $\Gamma_{hom}-\Gamma_0$ were obtained by PHB. The data fall on a straight line. This linear relationship is consistent with the observed Lorentzian line shape for Γ_{hom}. The results indicate that spectral diffusion processes are *not* occuring in these amorphous systems. It should be mentioned that T_1 in porphins is mainly determined by nonradiative decay.

We have found a similar relation for guest molecules in polymethylmethacrylate (PMMA): the neutral molecules H_2P, H_2Ch and dimethyl-s-tetrazine (DMST) have the same value of $(\Gamma_{hom}-\Gamma_0)/\Gamma_0$ at a given temperature, whereas ionic dyes seem to have a different value.

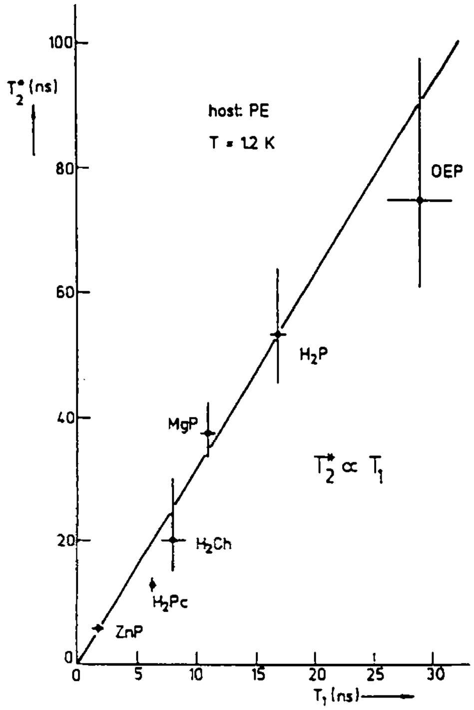

FIGURE 2 Pure dephasing time T_2^* as a function of the fluorescence lifetime T_1 for various porphin molecules in polyethylene at 1.2 K. OEP:octaethylporphin, H_2P:free-base porphin, MgP: magnesium porphin, H_2Ch:chlorin, H_2Pc:phthalocyanine, ZnP:zinc porhin.

We are currently investigating the validity of these findings for other disordered systems.

Octaethylporphin in polymers: comparison of Γ_{hom} with the literature.

After a thorough PHB and THB study of the unsubstituted H_2P molecule, we have started to look at the influence on the dephasing of a variation of substituent groups in porphin molecules[7]. The results of PHB experiments on octaethylporphin (OEP) in PE, PMMA and polystyrene (PS) are presented in fig.3 in a log (Γ_{hom}-Γ_0) versus log T form and compared with PHB-results of H_2P in the same three hosts[2,3]. In all cases, $\Gamma_{hom}-\Gamma_0 \propto T^{1.3}$ and $\Gamma_{hom} \to \Gamma_0 = (2\pi T_1)^{-1}$ when $T \to 0$. Notice that the value of $\Gamma_{hom}-\Gamma_0$ increases for polymers with larger sidegroups[3]. Contrary to our expectations, we have observed that for a given

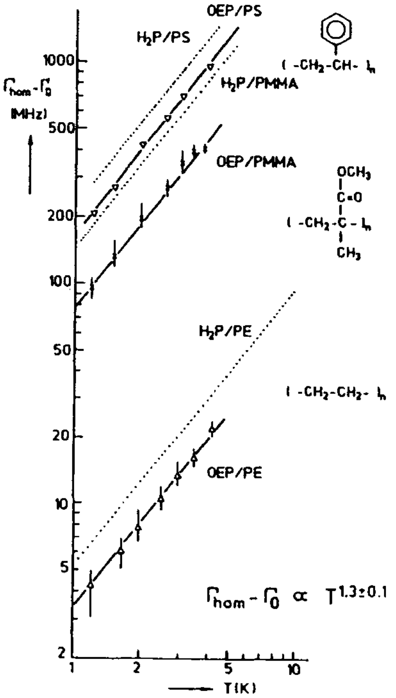

FIGURE 3 Log-log of Γ_{hom}-Γ_0 versus T for OEP and H_2P in polystyrene (PS), polymethylmethacrylate (PMMA) and polyethylene (PE).

polymer, Γ_{hom}-Γ_0 is smaller for the substituted OEP than for the unsubstituted H_2P [7]. Thus, the outer ethyl-groups do not seem to contribute to a stronger guest-host coupling. Apparently, the larger T_1-value of OEP (≈29 ns) as compared to that of H_2P (≈17 ns) contributes to a longer dephasing time T_2^*, as discussed above. Optical dephasing on other substituted porphins with different fluorescence lifetimes are presently under study.

We have extended the PHB-experiments on OEP in PS up to 12 K, and have compared the results with those reported in the literature for the same system[7]. Fig.4 shows that our data follow Γ_{hom}-$\Gamma_0 \propto T^{1.3}$ over a whole decade in T (1.2-12 K). PHB-results from the literature[8] have a similar $T^{1.2-1.3}$ dependence between 0.3 and 1.5 K, but their values of Γ_{hom}-Γ_0 are larger than ours (see fig.4).

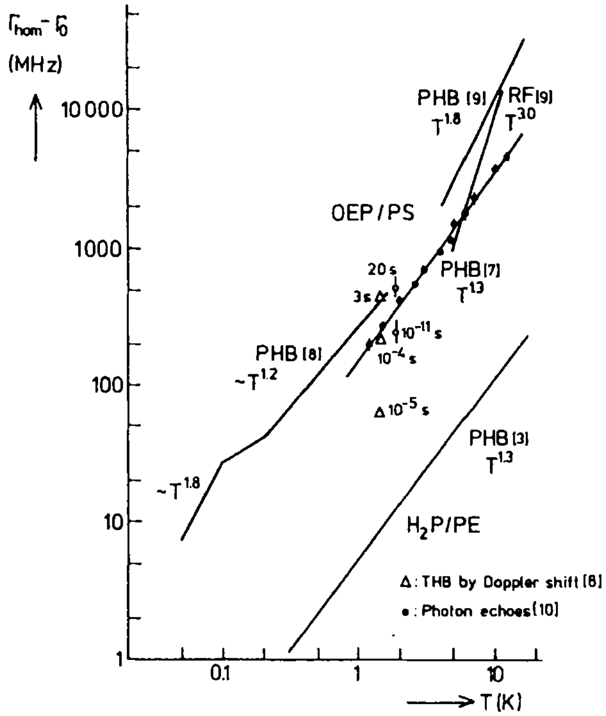

FIGURE 4 Log-log of $\Gamma_{hom}-\Gamma_0$ versus T for OEP and H_2P in PS between 1.2 and 12 K. Data are compared to the literature (see text).

However, below 0.1 K [8] and between 4 and 16 K [9], their data deviate from this power law. Resonance fluorescence experiments (in a time scale of 10^{-8} s) by the same group[9] yielded linewidths that were smaller than their holewidths, with a $T^{3.0}$ dependence between 5 and 11 K. The difference in the data was attributed to spectral diffusion[9]. It is interesting to notice that at 5 K our PHB-data coincide with the resonance fluorescence data of ref.9, but are a factor of 2 smaller than their hole-burning data. From these results we have concluded that the holewidths of ref.9 are probably broadened by too high burning fluences.

Notice further in fig.4 that the THB-values for $\Gamma_{hom}-\Gamma_0$ at 1.45 K obtained from Doppler shift[8] in 10^{-4}s are very similar to our PHB-values measured on a time scale of minutes, which is a strong indication that spectral diffusion does *not* take place in a time scale longer then 10^{-4}s. However, holes measured by the same technique in 10^{-5}s were reported to be much narrower[8] (see fig.4). In this context, it seems contradictory that recent two-pulse photon echo experiments[10] (time scale ≈ 10^{-11}s) at 1.9 K yield values for $\Gamma_{hom}-\Gamma_0$ that lie above the Doppler shift point of 10^{-5}s. The difference between T_2-values obtained by two-pulse photon echoes and photochemically accummulated photon echoes (time scale ≈ 20 s) was attributed in ref.10 to spectral diffusion[10]. Obviously, more work is needed to solve the controversial issue of time scales in amorphous systems.

OPTICAL DEPHASING OF ORGANIC MOLECULES ADSORBED ON THE SURFACE OF POROUS SILICA

We have carried out PHB-experiments on mixed organic-inorganic systems[11] with the purpose to test the general validity of the $T^{1.3}$ dependence of $\Gamma_{hom}-\Gamma_0$ found for pure organic amorphous systems[1-3]. The results on the $S_1 \leftarrow S_0$ 0-0 transition of resorufin *adsorbed* on porous silica (Vycor glass, pore diameter ≈60Å) between 0.3 and 4.2 K, and DMST on Vycor glass at 1.2 K, yield a value of Γ_{hom} which is one order of magnitude larger than in polymers[3,11]. When $T \rightarrow 0$, Γ_{hom} however extrapolates to the fluorescence lifetime-limited value of resorufin, $\Gamma_0 = (2\pi T_1)^{-1}$, but at 0.3 K it is still far from this value. In order to reach Γ_0, temperatures down to at least 0.05 K would be necessary. As in pure organic glassy systems, $\Gamma_{hom}-\Gamma_0 \propto T^{1.3}$. This is shown in the log-log plot of $\Gamma_{hom}-\Gamma_0$ versus T of fig.5 for the samples mentioned above.

Since optical dephasing experiments on chlorin and oxazine-4 perchlorate embedded in the *bulk* of amorphous silica[12] (prepared by the sol-gel method) between 1.7 and 5.7 K have shown homogeneous linewidths very similar to those observed in pure organic glassy systems, it has been concluded that the geometric structure of the environment of the guest seems to be more important in the determination of the linewidth than the chemical composition of the amorphous host[12]. The substantially broader homogeneous linewidths obtained for molecules adsorbed on the *surface* of porous silica are probably due to a higher degree of freedom of the guest, as compared to molecules incorporated in the *bulk* of the host[11].

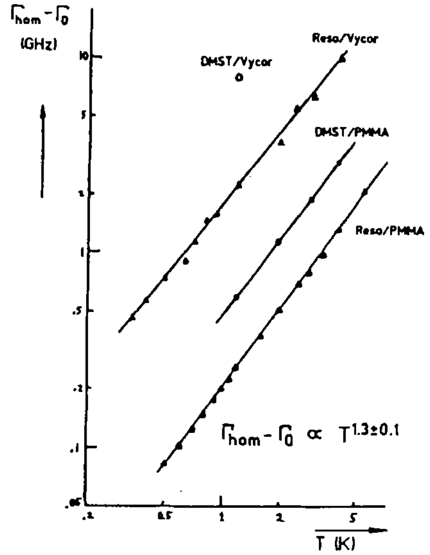

FIGURE 5 Log-log of Γ_{hom}-Γ_0 versus T for resorufin adsorbed on the surface of porous silica (Vycor glass) between 0.3 and 4.2 K, and for DMST adsorbed on Vycor at 1.2 K [3]. The values of Γ_{hom}-Γ_0 are about a factor of 10 larger than in the bulk of PMMA. All samples follow Γ_{hom}-$\Gamma_0 \propto T^{1.3}$.

We have further observed that holes burnt in resorufin adsorbed on the surface of Vycor glass at 1.2 K do not broaden as a function of time after burning, when measured on a time scale of minutes to hours and probed by fluorescence excitation[11]. This indicates that long-time spectral diffusion processes do *not* seem to occur for organic molecules *on the surface* of porous silica, as long as the molecules are in thermal contact with liquid helium.

In order to check whether the guest-host interaction is long- or short-range, we have compared holewidths in two Vycor samples, a "wet" and a "dry" one, doped with resorufin. The "wet" sample was a piece of porous Vycor glass soaked with resorufin dissolved in ethanol, and cooled to liquid He temperature. The "dry" sample, which is the one dicussed in the other parts of this section, was obtained from the "wet" sample by allowing the ethanol to evaporate in an oven. As a result, resorufin was adsorbed on the surface of the pores. The "wet" sample yielded the same holewidths as resorufin in ethanol (see fig.6 left). In the "dry" sample, however, the holes are much broader (see

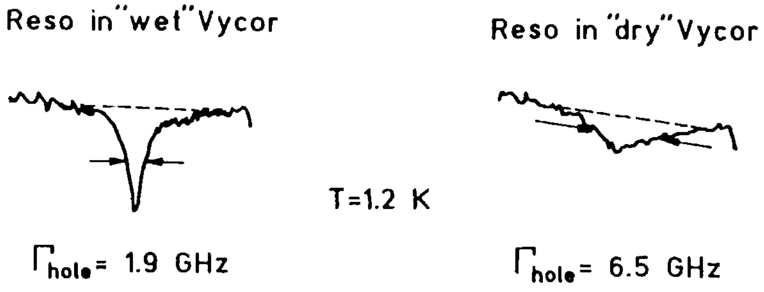

FIGURE 6 Holes burnt into a "wet" sample of resorufin in ethanol in porous glass (left), and into a "dry" sample of resorufin adsorbed on the surface of porous glass (right), at λ = 585 nm with burning fluence Pt = 15 mJ/cm^2. The holewidths do not represent the homogeneous linewidth because they are power broadened.

fig.6 right). From these results we conclude, as previously for semicrystalline polymers and other mixed inorganic-organic systems[3], that hole-burning probes the direct environment of the guest molecule, which in this case is confined to the pore radius of 30Å.

From a combination of site-selection spectroscopy and hole-burning experiments at 1.2 K we have further determined that not only the inhomogeneous and homogeneous linewidths of the 0-0 transition, but also those of the 580 cm^{-1} vibration of resorufin in Vycor glass are broader than in ethanol. By assuming that the contribution to optical dephasing in vibronic lines at 1.2 K is of the same order as in the 0-0 transition, we have obtained a value for the vibrational relaxation time of resorufin adsorbed on the *surface* of Vycor glass of about 1-2 ps, which is a factor of 4 to 6 faster than in the *bulk* of ethanol. These results suggest that very low frequency modes are present on the surface that couple very efficiently to the excited guest molecule, enhancing relaxation and dephasing processes.

PHOTOSYNTHETIC SYSTEMS AND MODEL COMPOUNDS

In order to get a better understanding of the dynamical behaviour of guest-host interactions in model systems and complex photo-synthetic compounds, we have carried out PHB experiments on bacteriochlorophyll in various glassy hosts, and on the isolated pigment-protein complex B800-850 of the light harvesting antenna of the purple bacteria Rhodobacter sphaeroides.

Bacteriochlorophyll in glasses: influences of the host on the holewidth

PHB-experiments have been performed on the Q_y 0-0 transition of bacteriochlorophyll-a (BChl-a) in the hosts triethylamine (TEA), water with 1% and 10% detergent lauryldimethylamine N-oxide (LDAO), and buffer:glycerol (1:1) solution with 0.5% LDAO between 1.2 and 4.2 K [13]. A diode laser (bandwidth ≈ 100 MHz) was used to burn and probe the holes at ~780 nm. The buffer solution was similar to that in photosynthetic antenna complexes and reaction centers.

In fig. 7a the absorption spectrum of BChl-a in a buffer:glycerol (1:1) solution with 0.5% LDAO at room temperature is given. Fig. 7b shows two holes for BChl-a in TEA (top) and BChl-a in the buffer solution (bottom). Notice that the holewidth for BChl-a in TEA at 4.2 K is about 610 MHz broad, a value which is comparable to those obtained for free-base porphin in alcoholic glasses and polymers[1-3]. However, the holewidths of BChl-a in a buffer:glycerol (1:1) solution with 0.5% LDAO at 4.2 K, $\Gamma_{hole} \approx 8 \pm 4$ GHz, are one order of magnitude larger. On the other hand, BChl-a in water with 1% LDAO yields holewidths of about 2.2 ± 0.7 GHz at 1.2 K, and 11 ± 2 GHz at 4.2 K, from which one obtains again a $T^{1.3}$-dependence of Γ_{hom}, as in other organic glassy systems.

Holes burnt into BChl-a in water with 10% LDAO at 1.2 K, $\Gamma_{hole} \approx 1.0 \pm 0.3$ GHz, seem to be somewhat narrower than in 1% LDAO. We are currently investigating the influence of various hosts and the amount of detergent on the homogenous linewidth of BChl-a.

Energy transfer in a photosynthetic antenna complex

Light harvesting antenna pigment-protein complexes of purple bacteria capture and transfer the energy of light to the photochemically active reaction centers in a very efficient way[14]. In Rhodobacter sphaeroides the antenna is mainly composed of two different pigment-protein complexes, called B800-850 and B875 in accordance with their absorption frequencies in the near infrared region. These complexes have been isolated with the purpose to study energy transfer processes, avoiding

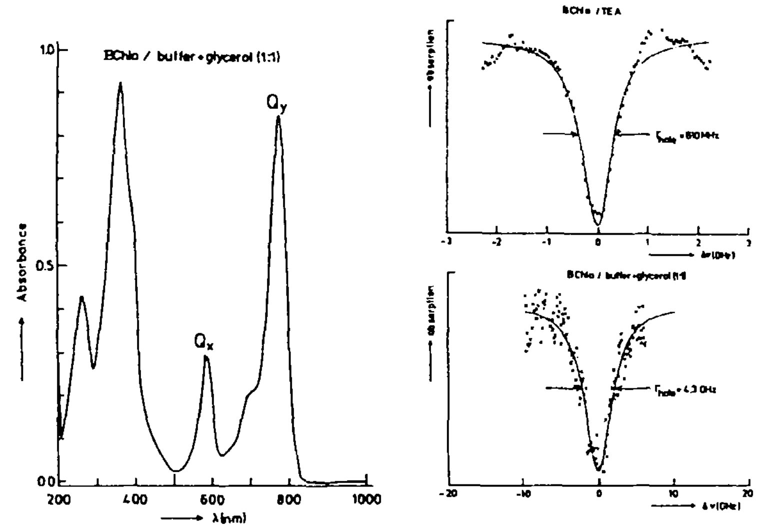

FIGURE 7 Left: Absorption spectrum of BChl-a in buffer:glycerol (1:1) with 0.5% LDAO at room temperature. Right: Holes burnt in BChl-a in TEA (top) and BChl-a in buffer:glycerol (1:1) with 0.5% LDAO (bottom) at 780 nm, at 4.2 K. The holewidths are not corrected for laser bandwidth (≈ 100 MHz).

in this way the complicated dynamics that takes place in intact membrane preparations[15]. The B800-850 complex consists of aggregates of basic units which contain four BChl 850, two BChl 800 and three carotenoid molecules in an α,β polypeptide dimer[14]. The absorption spectrum of B800-850 in 0.1% LDAO is given fig. 8a (taken from ref. 15).

We have burnt holes in the 800 nm band of this pigment-protein complex between 1.2 and 4.2 K with a CW dye laser (dye Styryl 8, bandwidth ≈ 1 cm^{-1})[16]. The holewidths, Γ_{hole} ≈ 160±30 GHz, are about two orders of magnitude larger than in monomeric BChl-a in a glassy host. We have neither observed a dependence of the holewidth on excitation wavelength between 790 and 802 nm, nor a dependence on temperature between 1.2 and 4.2 K. If we assume that the homogeneous linewidth here is entirely determined by population decay, $\Gamma_{hom} = \Gamma_0 = (2\pi T_1)^{-1}$, we obtain, after deconvolution of the laser, a value for $T_1 = 2.2 \pm 0.4$ ps [16]. This value is in good agreement with the values obtained by picosecond absorption recovery measurements[14]

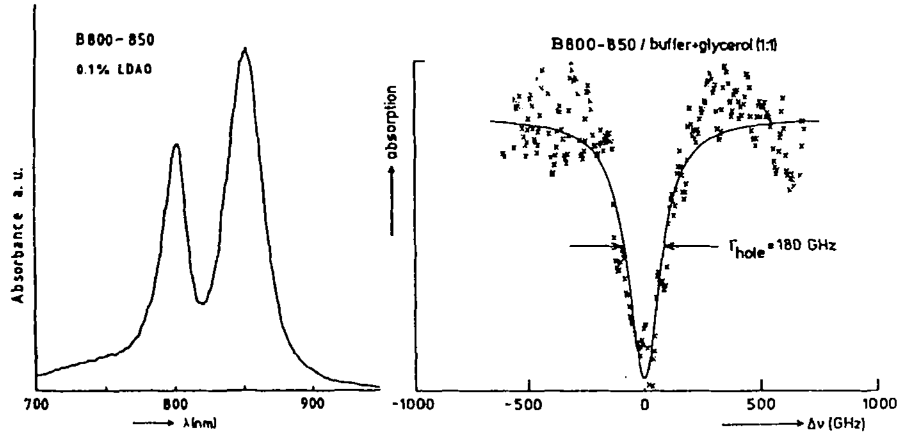

FIGURE 8 Left: Absorption spectrum of the isolated B800-850 pigment-protein complex. Right: Hole burnt into the 800 nm band at 4.2 K. The holewidth is not corrected for laser bandwidth (≈ 35 GHz).

(1 ps at 77 K), and femtosecond pump-probe experiments[17] (2.5 ps at room temperature), which have been attributed to the energy transfer rate from BChl 800 to BChl 850 molecules.

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