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Coherent Picosecond Exciton Dynamics in a Photosynthetic Reaction Center

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Supporting Information

ABSTRACT: Photosynthetic reaction centers convert sunlight into a transmembrane electrochemical potential difference, providing chemical energy to almost all life on earth. Light energy is efficiently transferred through chromophore cofactors to the sites, where charge separation occurs. We applied two-dimensional electronic spectroscopy to assess the role of coherences in the photoresponse of the bacterial reaction center of *Rhodobacter sphaeroides*. By controlling the polarization of the laser beams, we were able to assign unambiguously the oscillatory dynamics to electronic (intermolecular) coherences. The data show that these coherences are sustained for more than 1 ps, indicating that the protein coherently retains some excitation energy on this time scale. Our finding provides a mechanism for effective delocalization of the excitations on the picosecond time scale by electronic coherence, setting the stage for efficient charge separation.

Photosynthesis provides energy to most life on earth by conversion of sunlight into chemical energy. The light is absorbed by pigment-rich antenna proteins and transferred to reaction-center proteins, where charge separation occurs. All photosynthetic reaction centers contain a conserved functional core, which in this study is represented by the reaction center of the purple bacteria *Rhodobacter sphaeroides* (RC_{sph}). The RC_{sph} comprises, among other cofactors, four bacteriochlorophylls and two bacteriopheophytins. These chromophores form an assembly (see Figure 1a) and give rise to three distinctive absorption bands peaking at 760, 805, and 860 nm, respectively (Figure 1b, red line). We use H, B, and P to denote the excitonic states that give rise to these bands and whose major contributions are from the bacteriopheophytins, the accessory bacteriochlorophylls, and the dimeric bacteriochlorophylls (spatial pair), respectively. It is generally accepted that the photoexcitations are transferred from H over B to P within 200 fs.[1] Subsequently, charge separation occurs within a few picoseconds.[2]

To elucidate further the photoresponse of photosynthetic reaction centers, it is important to assess the role of quantum coherences (superpositions) between the excited states. This has been made possible by the advent of two-dimensional (2D) optical spectroscopy in the visible spectral range.[3,4] Excited-state coherences, which were first studied in photosynthetic antenna proteins, have been shown to live for several hundred femtoseconds in complexes from bacteria,[5,6] higher plants,[7] and marine algae.[8] The implications of these findings for the photophysical function of the proteins are today vividly debated. Some theoretical studies suggest that coherent, wavelike motion of the excitations may be responsible for the high quantum yield of excitation energy transfer among the antenna pigments,[9,10] but the mechanism causing the long-lived

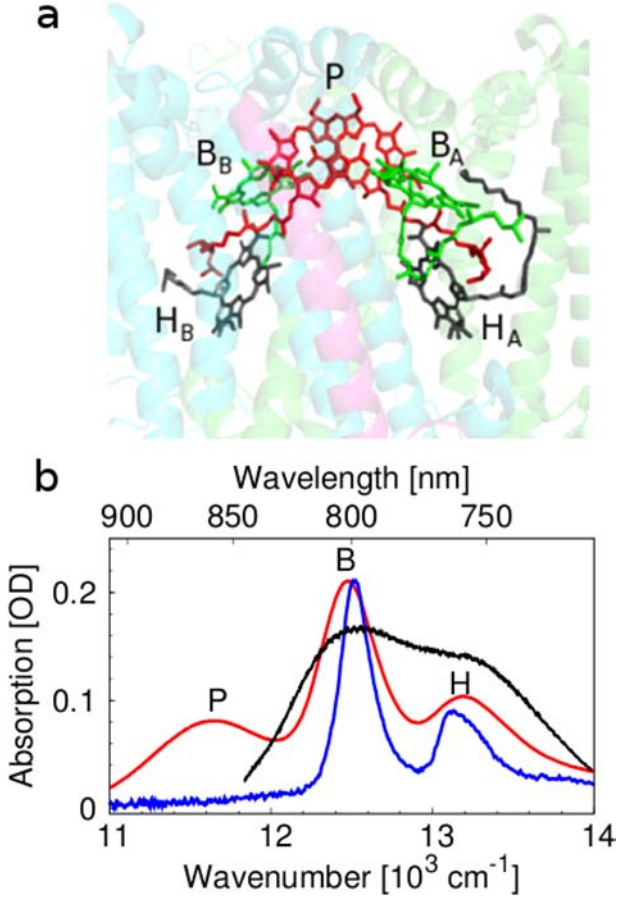

Figure 1. Structure and absorption spectra of RC_{sph}. (a) Molecular arrangement of H, B, and P (see text for abbreviations) in the RC_{sph} binding pocket. (b) Linear absorption spectra of RC_{sph} at 294 K (red) and RC_{sph} with oxidized P at 80 K (blue) and the laser spectrum (black).

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quantum coherences is not well understood at present.[11−16] For reaction-center proteins, information on quantum-coherence dynamics is sparse. In the reaction center of photosystem II, electronic coherences could not be assigned unambiguously by 2D electronic spectroscopy.[17] For RC_{sph}, a two-color photon echo experiment indicated a decay time of 440 fs for the coherent interaction between the B and H excitons at 77 K,[18] but direct observation of the electronic coherence by oscillatory dynamics has remained elusive. It is therefore highly desirable to assess directly the electronic coherences in reaction-center proteins.

In this work, we used 2D electronic spectroscopy to probe simultaneously the population and coherence dynamics of excitations in detergent-solubilized RC_{sph} with a chemically oxidized P at 80 K. The absorption spectrum of this sample is shown by the blue line in Figure 1b. The chemical modification blocks the charge transfer and strongly reduces the absorption strength of P but leaves B, H, and the energy transfer to P unaffected.[19,20] A typical 2D spectroscopy map at a waiting time t_2 = 40 fs is shown in Figure 2a. The B and H bands are clearly visible on the diagonal, as is the cross-peak below the diagonal (marked "HB"). The corresponding upper cross-peak is masked by the negative excited-state absorption signal from B.

The 2D spectroscopy experiment can probe the evolution of populations, vibrational (intramolecular) coherences, or electronic (intermolecular) coherences as a function of t_2. Population dynamics gives rise to smoothly evolving signals, whereas coherences are observed as oscillatory signals. Typically, this leads to convoluted traces where vibrational and electronic coherences as well as population dynamics contribute, making assignments difficult. An example is shown in Figure 2b, where the t_2 dependencies of the diagonal H and B peaks and the lower HB cross-peak (under all-parallel polarization conditions) reveal a decay of populations overlaid with small oscillatory signals.

To identify coherences with electronic character, we used a special combination of linearly polarized pulses that dramatically suppresses all of the signals except the oscillating intermolecular ones.[7] This strategy was borrowed from 2D IR spectroscopy, where a number of polarization schemes are used to suppress or enhance certain pathways.[21,22] In our configuration, the polarization orientation of pulses 1 to 4 was set to $\pi/4$, $-\pi/4$, $\pi/2$, and 0, respectively. This selects, after orientational averaging, only those interaction pathways that evolve during t_2 as a superposition of two excited states with different transition dipole moment orientations, which we term "intermolecular" or "electronic" coherences in the remainder of the manuscript. The configuration strongly suppresses the population dynamics contributions and the coherences between vibrational states, which are termed "intramolecular" or "vibrational" coherences, because populations and vibrational coherences are prepared by the transitions with parallel dipole moments. Taking into account all of the experimental considerations in the measurements discussed here, we estimate the suppression ratio of the population dynamics and vibrational coherences to be ∼85 in the ($\pi/4$, $-\pi/4$, $\pi/2$, 0) polarization configuration relative to the all-parallel configuration.

The effectiveness of this acquisition strategy is documented in Figure 2b, where the t_2 dependences of the HB cross-peak for the ($\pi/4$, $-\pi/4$, $\pi/2$, 0) and all-parallel polarization configurations are shown as magenta and green traces, respectively. Clearly, population dynamics are suppressed in

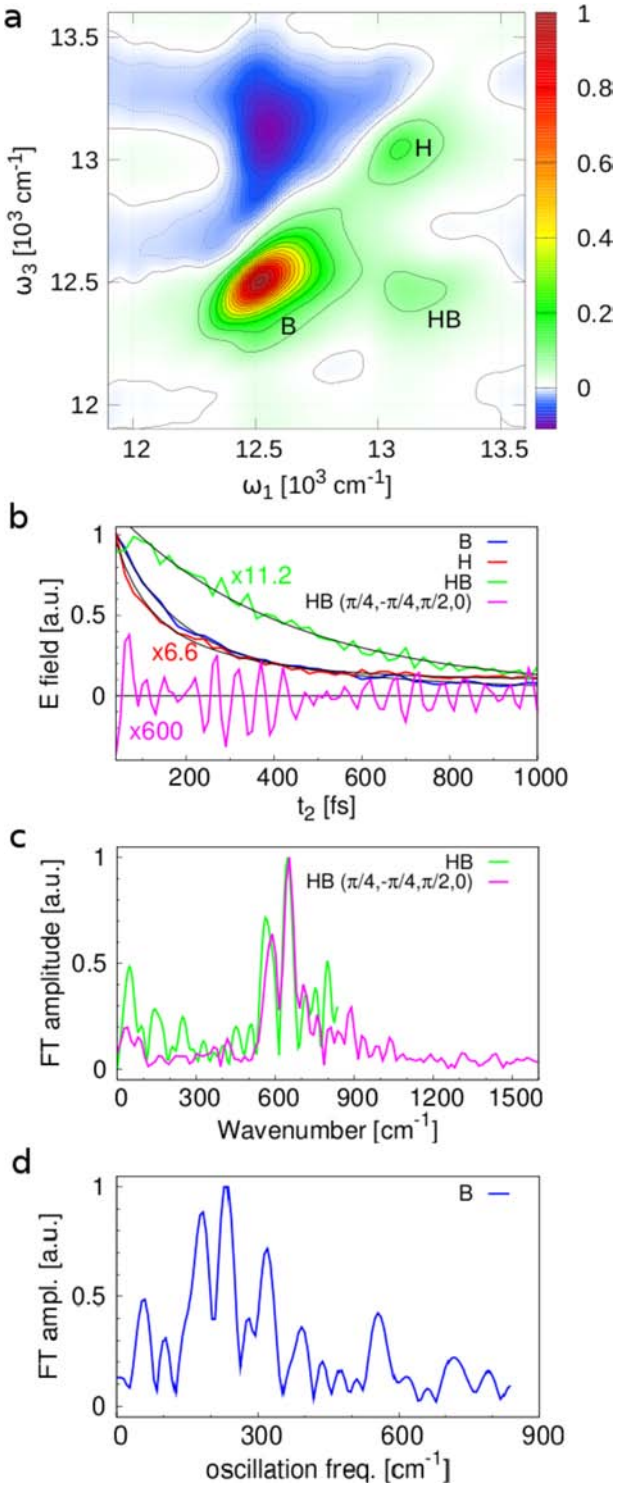

Figure 2. 2D absorption spectroscopy of oxidized RC_{sph} at 80 K. (a) Representative 2D spectrum at a waiting time t_2 = 40 fs. ω_1 and ω_3 are the Fourier transform frequencies corresponding to the coherence and detection times t_1 and t_3, respectively. (b) Intensities of the diagonal peaks H and B and the cross-peak HB as functions of t_2. The gray lines are fits of multiexponential decay functions to the data. The effective decay times calculated from the two major decay rates are 94 and 151 fs for H and B, respectively. (c) Fourier spectra of the t_2 dependence of the lower cross-peak HB for the all-parallel and ($\pi/4$, $-\pi/4$, $\pi/2$, 0) polarization conditions. (d) Fourier spectrum of the t_2 dependence of the diagonal peak B. In all of the panels, unless indicated otherwise in the figure legend, the beams were polarized in parallel.

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case of the $(\pi/4, -\pi/4, \pi/2, 0)$ configuration and an offset-free oscillating signal is observed. This signal must be from a coherence that involves two excited states with different transition dipole orientations, and we therefore assign it to coherences with electronic character. Furthermore, the Fourier transforms of these kinetic traces (Figure 2c) reveal 645 cm^{-1} as the major frequency component for both the $(\pi/4, -\pi/4, \pi/2, 0)$ and all-parallel polarization conditions. This frequency corresponds exactly to the difference between the transition energies of B and H, further strengthening our assignment.

Figure 2d shows the Fourier transform amplitude of the oscillatory signals in the decay of the diagonal peak B measured with all-parallel pulse polarizations. Oscillations are observed at 90, 190, 220, 310, 390, and 710 cm^{-1}. All of these modes have vibrational origin, as they match quite well the published resonance Raman frequencies of B.[23] The peak at 575 cm^{-1} is observed in all of the measurements presented in Figure 2c,d and is thus likely of mixed vibrational and electronic origin.[12] A more detailed analysis of these vibrational coherences will be presented in a forthcoming publication.

In summary this analysis shows that the t_2 dependence of the lower cross-peak HB measured with the $(\pi/4, -\pi/4, \pi/2, 0)$ polarization conditions is a direct and clean signature of coherence beatings between H and B with electronic character. Remarkably, this coherence lives significantly longer than the 1 ps time window probed here (Figure 2b, magenta trace), and its lifetime exceeds the previously reported value of 440 fs based on the two-color photon echo experiment.[18,24] Figure 2b also illustrates that in contrast to the long-lived coherence between H and B, most of the populations on H and B decay with effective time constants of ∼94 and ∼151 fs, respectively, in agreement with previous reports.[20] Clearly, the observed coherence between H and B has a much longer decay time than the population dynamics of H and B.

This finding is unexpected. When the total molecular system dynamics is considered in terms of population relaxation rates (γ_H and γ_B) and coherence dephasing rates, the total HB coherence dephasing rate is given by

$$\Gamma_{BH} = \frac{1}{2}(\gamma_H + \gamma_B) + \Gamma_{BH}^{pure} \quad (1)$$

where Γ_{BH}^{pure} is the pure electronic dephasing rate of the electronic coherence between H and B. From this argument, it follows that the observed long-lived coherence between H and B cannot survive without corresponding excitation populations on H and B. We note that this statement reflects a very general property of the reduced density matrix of molecular aggregates, σ_{ij}, where off-diagonal and diagonal elements represent coherences and populations, respectively, on sites i and j. By definition,

$$\sqrt{\sigma_{ii}\sigma_{jj}} \geq |\sigma_{ij}| \quad (2)$$

further demonstrating that coherences cannot exist without corresponding populations.[25]

Indeed, close inspection of the population decays (Figure 2b; also see Figure 2 in ref 20) reveals small but long-lived (more than 1 ps) population components on both H and B. This behavior is surprising because the driving force for excitation energy transfer from H to B and P vastly exceeds the available thermal energy. Within the framework of incoherent excitation energy transfer, Boltzmann statistics would therefore predict negligible back-transfer from P to H and B, and the populations of H and B should decay to zero within the time window probed. This shows that excitation energy transfer to P is incomplete. Taken together with our finding of the long-lived coherences between H and B, we conclude that the reaction center coherently retains some excitation energy in higher-energy chromophores on a picosecond time scale.

For molecular aggregates in the weak or intermediate coupling regime, electronic coherence effectively delocalizes excitations over one or several chromophores, whereas dephasing leads to localization of the energy. This is exemplified in multichromophoric light-harvesting proteins, where long-lived electronic coherences have previously been observed.[5−8] In contrast to the findings for antenna proteins, we have found in the present work that electronic coherences apparently outlive the majority of the excitation populations and that this leads to incomplete energy transfer. We therefore suggest that the reaction center protein uses long-lived electronic coherences to delocalize excitation energy over H, B, and likely P on picosecond time scales. This mechanism is in agreement with efficient charge generation in wild-type RC_{sph} because intermolecular excited-state delocalization benefits efficient charge transfer.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and the protocol for the overproduction and purification of RC_{sph}. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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