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Energy flow in photosynthetic light harvesting: spectroscopy and control

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1. INTRODUCTION

The function of a light-harvesting antenna complex is to harvest sunlight and, through a series of energy transfer steps both within and between complexes, to make the energy available to the reaction centre, where it is used to fuel the primary dark reactions of photosynthesis. Harvested excitation energy from the absorption of blue-green light in carotenoids undergoes ultrafast partitioning between excitation energy transfer (EET) to bacteriochlorophyll (BChl) and losses by internal conversion (IC) within the carotenoid (Car) [1]. The classical scheme of the energy flow (Fig. 1) describes the carotenoid IC as a sequential process from the absorbing Car S_2 state, $1B_u^+$ in the idealised C_{2h} symmetry, to the lower-lying Car S_1 ($2A_g^-$) state and further on to the ground state Car S_0 ($1A_g^-$). The EET channel takes roughly half of the excitation energy directly from Car S_2 to the BChls, which ultimately resides in the lowest-lying singlet state of the complex, BChl B850 Q_y. Recently we reported feedback-optimised coherent control of the energy flow pathways in the antenna complex LH2 of *Rps. acidophila* [2]. By excitation of Car S_0-S_2 with shaped femtosecond pulses, the ratio IC/EET was changed by ~35% as compared to excitation with transform-limited pulses.

Here we present additional data in order to extract a characteristic 'control' frequency and establish a detailed picture of the laser-chromophore interaction and the ensuing dynamics. This work demonstrates the use of coherent control as a valuable tool for the spectroscopy of complex molecules.

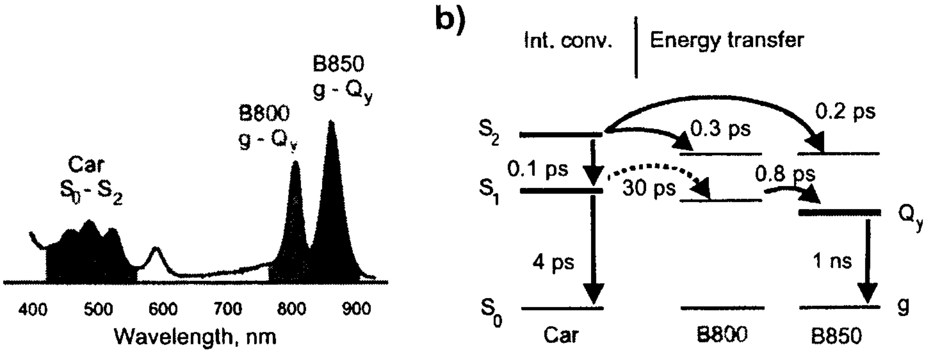

Fig. 1. Light harvesting complex LH2 from Rps. acidophila. a) Absorption spectrum. b) Standard model of the energy flow rates upon excitation of Car S_2 [3].

2. SPECTROSCOPY BY COHERENT CONTROL

As described previously [2], we excite selectively the Car S_0-S_2 absorption (Fig. 1a) with pulses at 525nm that have passed through a 4-f-shaper. We detect the transient absorption simultaneously at 580nm (Car S_1-S_n) for the IC channel and at 880nm (BChl B850 g-Q_y) for the EET channel (Figs. 1b and 2a). The excitation pulses have 30fs transform limited duration as long as the shaper is inactive and the signals in the IC and EET channels are measured at an excitation intensity of 8×10^{14} photons/cm^2. The signal of IC is quantified by integrating the transient at 580nm across 5-20ps probe delay. The signal of EET is quantified by averaging the asymptotic absorption at 880nm at 20ps delay. An optimisation of the pulse shape for maximal ratio IC/EET naturally converges to a solution of multipulse excitations [2].

The multipulse excitation is generated by a modulation of the spectral phases,

$$\Phi(\omega) = a\sin\left(b(\omega-\omega_0)+c\right), \tag{1}$$

with period $2\pi/b$, modulation depth a, and phase c relative to the center of the spectrum ω_0. Fourier transformation of Eq. (1) shows that the higher the value of a, where 0 a π, the more intensity is found in replica pulses of an equispaced multipulse sequence with $\Delta\tau = b$ (Fig. 2a). Parameter c controls the relative carrier phases between successive pulses of the sequence.

The optimal parameters for maximal IC/EET converge reproducibly in successive optimisation runs. Most importantly, we find that the optimal value of the periodic modulation is $2\pi/v_{light}b$=160±25cm^{-1} (Fig. 2b). The control of IC/EET is best if the modulation is as deep as possible, with a=π, generating ~8 subpulses. Previously we have shown that also parameter c, and thus the relative carrier phase, has a decisive influence on the control effect [2].

The mechanism of control with multipulse excitation is likely due to dynamics of the carotenoid donor. The presumably incoherent EET process [1] would not support the observed dependence on the carrier phase via the parameter c. Furthermore, the control effect does not suffer from annihilation at higher excitation intensities [2], as would be characteristic for the delocalised excitons in the B850 ring [1]. However, it is well known that femtosecond pulses populate higher ground state vibrational levels by impulsive Raman scattering (IRS) [4], and that the periodic phase modulation (Eq. 1) makes IRS selective for specific vibrations

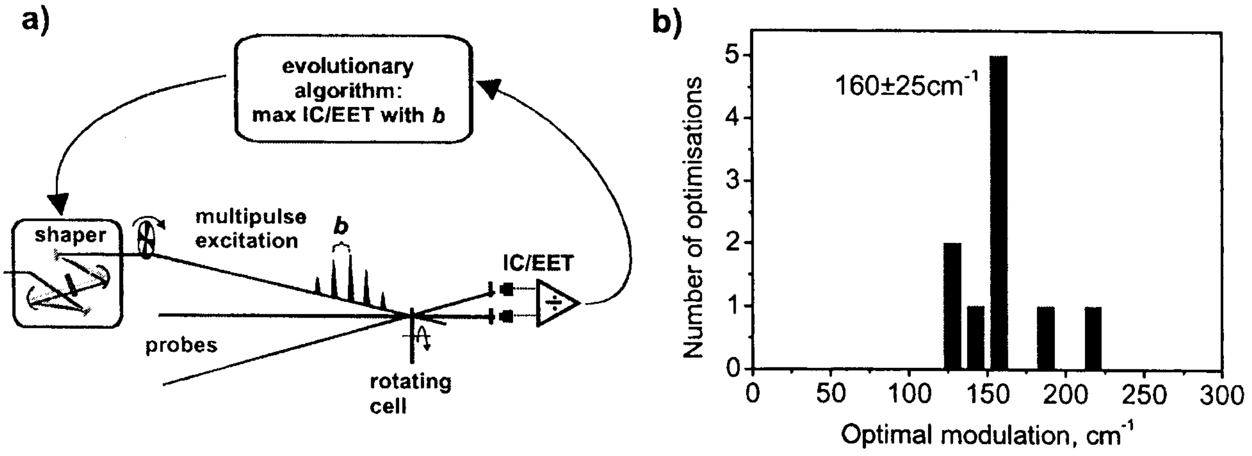

Fig. 2. Optimisation of internal conversion with multipulse excitation. a) Experimental setup: Coherent multipulse sequences are generated by periodic modulation of the spectral phases. The multipulse spacing b is optimised for maximal ratio IC/EET by an evolutionary algorithm. b) Histogram of optimal modulation $2\pi/v_{light}b$ (i.e. multipulse separation) by successive optimisations.

[5, 6]. The selectivity of Raman excitation can be derived in three simple equations: The Raman excitation P of a mode of energy Ω_R is given by

$$P(\Omega_R) \propto \left| \int d\omega E(\omega) E^*(\omega - \Omega_R) \right|^2 , \tag{2}$$

with the electric field $E(\omega) = A(\omega)\exp\{i\Phi(\omega)\}$. Each Raman frequency pair contributes the phase term $\Phi(\omega) - \Phi(\omega - \Omega_R)$. Interference is constructive, if for the entire spectrum holds:

$$\Phi(\omega) = \Phi(\omega - \Omega_R) . \tag{3}$$

The periodic modulation Eq. (1) selects a Raman level Ω_R^{res}, (m an integer number):

$$\Omega_R^{res} = m \frac{2\pi}{b} . \tag{4}$$

The multipulse laser field generated by Eq. (1) is thus synchronised to the vibrational wave packet in a specific coordinate. Here the experiments on LH2 finds $2\pi/v_{light}b$ =160±25cm^{-1} (Fig. 2b) as effective mode for maximal IC/EET. In the carotenoid, this low frequency mode can be identified with a b_u mode that induces an angle alternation or bending of the CCC backbone [7]. Excursion along such an asymmetric coordinate is necessary to couple Car S_2 and S_1 or, more specifically, to reach a point where the C_{2h} symmetry is broken such that the electronic surfaces of S_2 and S_1 can cross via a conical intersection [7]. Selective IRS of the coupling b_u mode facilitates IC and is thus responsible for the control of the energy flow ratio IC/EET. If IC is faster, EET is less efficient, as we have demonstrated in the transients after optimally shaped multipulse excitation [2]. The influence of the carrier phase parameter c [2] is attributed to vibrational wavepacket interference [8], but not yet fully understood.

We have thus identified a mechanistic picture of the IC dynamics and their control that allows attribution of the measured optimal modulation to a specific mode. However, the mechanism is based on the assumption that IRS is relevant in carotenoids. In the following experiment we strive to directly detect that assumed hot ground state by the corresponding redshifted ground-state Car S_0-S_2 absorption.

3. DETECTION OF THE HOT GROUND STATE

We studied lycopene in solution, which has a conjugation system identical to that of rhodopin glucoside (the native carotenoid of *Rps. acidophila)* yet is less susceptible to degradation. The experimental approach is different from above, since now unshaped, i.e. transform-limited pulses (30fs duration) excite the Car S_0-S_2 (v=0-v'=0) transition at 505nm. As measured by its fluorescence, the S_2 state lives 100-200 fs in carotenoids with conjugation length N=11 in solution [1]. At a delay of T=50fs, another transform-limited pulse, now at 795nm (110fs duration), depletes the population in the Car S_2 state by pumping its near-infrared absorption band (Fig. 3a). Every state that is populated by IC from the initially absorbing Car S_2 state should now show less population, but not the hypothetical hot ground state populated by IRS. Indeed, the absorption signal on the low-frequency side of cold ground state absorption (~530 nm) is exempt from depletion (Fig. 3b) and can thus be identified with the anticipated

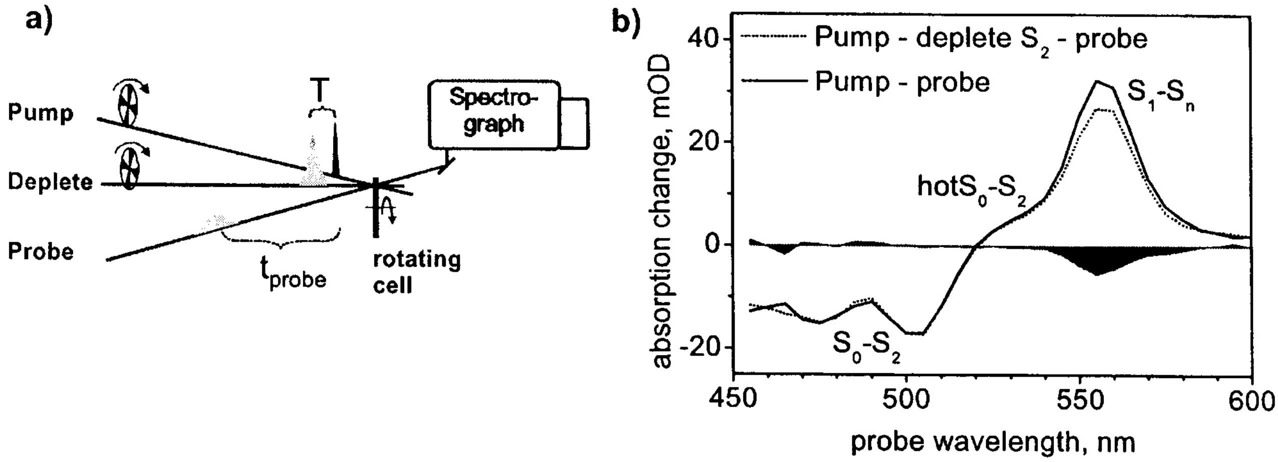

Fig. 3. Pump-deplete-probe spectroscopy on lycopene in hexane. a) Experimental setup: After excitation and depletion of Car S_2 with a delay of T=50fs, a white-light probe pulse at delay t_{probe}=2ps measures the transient absorption spectrum. b) Spectra without (solid curve) and with depletion pulse (dotted) and their difference (shaded area). Only the Car S_1 state is depleted; the ground state bleach (S_0-S_2) and positive absorption feature on its low energy side (hotS_0-S_2) are unaffected.

hot ground state [10]. This result strongly supports the proposed mechanism of coherent control via selective IRS. Further support comes from similar studies in a series of carotenoids with N=11-19, in which the positive transient absorption signal to the red side of the ground state bleach shows a constant lifetime of 6.2±0.4 ps [9]. We attribute this time constant to ground state vibrational relaxation.

4. CONCLUSION

Excitation of Car S_2 in LH2 with optimally shaped multipulse sequences allowed extraction of a characteristic molecular vibration of 160±25cm^{-1}, attributed to an asymmetric b_u coordinate that facilitates the internal conversion pathway [7]. The mechanism of preparation is explained by the well established concept of coherently controlled impulsive Raman scattering [5, 6]. To corroborate this model, we identified the transient absorption signal of the hot ground state [10] that is created by impulsive Raman scattering [4]. To that aim we have again gone beyond pump-probe spectroscopy by introducing pump-deplete-probe spectroscopy [9]. Coherent control is thus employed as a spectroscopic tool to measure the frequency of the promoting mode of IC in a biological molecule.

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