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Intrinsic Photophysics of Light-harvesting Charge-tagged Chlorophyll *a* and *b* Pigments

Elisabeth Gruber, Christina Kjær, Steen Brøndsted Nielsen and Lars H. Andersen*

Abstract: Chlorophylls *a* and *b* (Chl*a/b*) are responsible for light-harvesting by photosynthetic proteins in plants. They display broad absorption in the visible region with multiple bands, due to the asymmetry of the macrocycle and strong vibronic coupling. Their photophysics relies on the microenvironment, with regard to transition energies as well as quenching of triplet states. Here we firmly establish the splitting of the Q and Soret bands into *x* and *y* polarized bands for the isolated molecules in vacuo, and resolve vibronic features. Storage-ring experiments reveal that dissociation of photoexcited charge-tagged complexes occurs over several milliseconds, but with two different time constants. A fast decay is ascribed to dissociation after internal conversion and a slow decay to the population of a triplet state that acts as a bottleneck. Support for the latter is provided by pump-probe experiments, where a second laser pulse probes the long-lived triplet state.

Photosynthesis is the key process which provides chemical energy for almost all life on Earth. The light-harvesting process starts with the absorption of photons in pigment-protein antenna complexes, followed by rapid and highly efficient transport of the excitation energy to a reaction center where charge separation occurs. The high efficiency of light-to-charge conversion of >95% relies on efficient energy transfer, which competes with excited-state relaxation mechanisms.^[1] Besides the importance of the spatial organization of pigments in photosynthetic protein complexes on the ultrafast energy transfer, the impact of quantum coherence on promoting the efficiency and directionality of the energy transport has attracted a great deal of attention in the last decade.^[2–5]

One of the most well-known and abundant pigments in photosystems is chlorophyll (Chl). Chls belong to the porphyrin (or reduced porphyrin; chlorin) family and have a characteristic macrocyclic ring with a magnesium ion at the center (see Fig. 1). Several chemical variations of Chl are found in plants, algae and bacteria with different spectroscopic properties.^[6] In nature, Chls are embedded in protein pockets, and pigment-pigment as well as pigment-protein interactions tune the photophysics. UV/Vis spectra of porphyrins typically display absorption in two regions, the intense band at higher energy, the so-called Soret band or B band (380–420 nm), and the weaker Q band (500–800 nm). The transitions are understood on the basis of Gouterman's four-orbital model.^[7]

The sensitivity of Chl's photophysical properties to its surrounding molecular environment makes it difficult to disentangle which aspects of its spectroscopic properties are intrinsic and which are due to neighbouring interactions. To obtain the intrinsic properties, the molecule has to be studied isolated in the gas phase. After the absorption spectrum of the bare Chl is established, perturbations can be included by complexation of the

Figure 1. Structure of Chl*a/b* and of the charge tag used.

the pigment with various adducts to study the effect of individual interactions.^[8–10]

The first gas-phase absorption measurements of Chl revealed a significant blueshift of the Q as well as the Soret band compared to Chl-containing proteins, which emphasized the strong effect of the microenvironment on the overall transition energies.^[11–13] The binding of a negatively charged axial ligand to the Mg²⁺ center^[14] as well as excitonic coupling between two Chl molecules^[15] produce large color shifts and can to some extent account for the strong spectral variation between bare Chls and pigment-proteins. Photodissociation action spectra of metalated Chl*a* have shown that spectral features within the Soret band markedly depend on the identity of the cation, whereas fluorescence spectra show only small dependences. Replacing the metal ion with a proton switches the fluorescence off.^[16]

In this contribution we have examined the intrinsic photophysical properties of Chl*a* and Chl*b* by using the electrostatic ion storage ring ELISA^[17] at Aarhus University (see Fig. 2 and SI for experimental details). The storage ring technique, applicable to ions, was used before to study the photodissociation of deprotonated Chl*a* and Chl*b*.^[18] The deprotonation strongly perturbs the electronic system, and the absorption spectrum differs from those of neutral Chls. To study the intrinsic photophysical properties of the neutral form, we used the charge-tag approach (see Fig. 1), examined before in single-pass experiments^[12,13]. Therein Chl*a* was tagged with quaternary ammonium ions with differences in their size. The action spectra of the complexes between Chl*a* and the various tags have shown negligible dependence on the nature of the tag, indicating that the charge is located far from the π -electron cloud of the porphyrin ring and has minimal influence on the excitation energy of Chl. Density Functional Theory (DFT) calculations supported the conclusion that the charge tag causes only minor perturbations of the Chl system. The advantage of the ion storage ring technique in comparison to single-pass experiments is that we can study

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photodissociation over a time window of several ms, in comparison to ~ 20 μ s only.

It is known for Chls (and other porphyrins) that after excitation into the lowest singlet excited state Q_y , an efficient intersystem crossing generates the T_1 state in competition with radiative and nonradiative decay to the singlet ground state.^[6,19,20] The lifetime of the triplet state depends strongly on the microenvironment, and the state is easily quenched by efficient energy transfer to surrounding molecular oxygen under aerobic conditions.^[20,21] In photosynthetic systems of higher plants the triplet state of Chl safely dissipates the excess energy to carotenoid and the generation of harmful singlet oxygen is avoided.^[22,23] Here, we have examined the triplet quantum yield and triplet lifetime in absence of any quencher molecules.

Figure 3a shows the action spectra measured for excitation wavelengths in the range 220–700 nm, which covers both the Q ($S_0 \rightarrow S_1$) and the Soret ($S_0 \rightarrow S_2$) band of both complexes. The Q band of Chlb is blueshifted relative to that of Chla, and the opposite is the case for the Soret band. This color fine-tuning of the absorption spectra is an intrinsic effect induced by the replacement of a methyl group in Chla with a formyl group in Chlb (see Fig. 1).^[13] As Chla and Chlb are asymmetric, excitations along the x and y axes are not equivalent, which results in a splitting of the bands into x and y components, see Fig. 3. The splitting between B_x and B_y is 0.30 eV for Chla and 0.17 eV for Chlb. The splitting between Q_x and Q_y is 0.29 eV for Chla and 0.37 eV for Chlb (see Figure 3b and Table 1), in reasonable agreement with theoretical predictions of 0.43 eV for Chla and 0.35 eV for Chlb, respectively.^[24] The absorption bands at higher energies are attributed to vibronic transitions with values of vibrational frequencies between 1100–1300 cm^{-1} for Chla which may be due to a breathing mode of the entire ring known to lie around 1200 cm^{-1} for Chla.^[24] Action spectroscopy of cold complexes (ion trap cooled to 100 K) shows a blueshift of the maximum of the Q band of 20 meV (see Fig. 3c). This shift is explained by the occupation of higher vibrational levels of the electronic ground state at 300 K compared to 100 K (hot bands). Furthermore, the bands for the cold molecules appear more distinct.

The absorption spectra were obtained by measuring delayed photofragmentation at times down to about a quarter of a revolution time (~ 30 μ s) and up to tens of ms after laser excitation. Photoexcitation leads to one relevant fragmentation channel, the separation of the chlorophyll and the charge tag.^[12,13]

Table 1. Energy band maxima in eV extracted from Fig. 3 a. The corresponding absorption wavelengths in nm are provided in brackets. Comparison with data from earlier measurements and DFT calculations are found in the SI.

Chla-1 ⁺		Chlb-1 ⁺	
Q band	Soret band	Q band	Soret band
1.94 (639)	3.08 (403)	1.97 (629)	2.88 (431)
2.07 (599)	3.38 (367)	2.09 (593)	3.05 (407)
2.23 (556)		2.34 (530)	
2.38 (521)		2.60 (477)	

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Figure 4. Fragmentation yield as a function of laser pulse energy for the delayed as well as prompt action for two different wavelengths, 395 nm (left) and 640 nm (right). The solid lines are fits through the data points using the Poisson distribution with $n=1$ in the case of delayed action and $n=2$ in the case of prompt action. Thus n indicates the number of photons needed to cause dissociation in the given time windows.

Laser pulse energy dependence measurements show that the absorption of a single photon is enough to induce dissociation (see Fig. 4). The prompt signal, detected on the SED, as a function of the laser pulse energy revealed that in this case fragmentation is caused by sequential multiphoton absorption. The Poisson distribution with $n=2$ nicely fits the prompt data. This result is in agreement with observations obtained by single-pass experiments where the time window for sampling dissociation was limited to about 20 μ s, and the fragmentation was assigned to the absorption of more than one photon.^[12,13] In this single-pass experiment Q_y is found at 629 nm, slightly blueshifted in comparison to the present results (see Table 1). This is caused by the finite (prompt) time window in the single-pass experiment,^[12] which emphasizes signal in the blue part of the spectrum, associated with fast action, thereby distorting the absorption profile slightly.

In Fig. 5a, the time-resolved fragmentation yield of photoexcited charge-tagged Chla is plotted for two excitation energies (more time spectra at various excitation energies are found in the SI). The curve obtained at 640 nm shows the fragmentation after photoexcitation into S_1 , the curve at 410 nm after photoexcitation into S_2 . It is noticed that the decays do not follow a simple exponential or a power law. The latter may be expected for isolated systems with a broad energy distribution.^[25,26] To fit the decay spectra we used a rate model (rate equation and fitting parameters are found in the SI), visualized in Fig. 5b. After photoexcitation into S_n , two competing relaxation branches lead into the vibrationally excited ground state S_0^* from where statistical dissociation with a rate constant k may occur. One branch describes the relaxation $S_2 \rightarrow S_1 \rightarrow S_0^*$ by internal conversion (IC) and intramolecular vibrational energy redistribution (IVR). These processes are normally fast and occur on a sub-ps to ns timescale. The second branch describes intersystem crossing (ISC) into the lowest-lying triplet state and from there ISC back to S_0^* ($S_1 \rightarrow T_1 \rightarrow S_0^*$). For this branch the bottleneck is the triplet-to-singlet conversion rate constant k_{TS} , which depends on the overlap of the nuclear wave functions and the spin-orbit coupling. We cannot exclude that the charge tag may slightly affect the singlet-triplet mixing. From the model we determined a triplet quantum yield of 0.7–0.8. Similar high triplet quantum yields were reported for Chla/b^[27] and for BChl in solution phase^[28], and for porphyrin cations in the gas phase.^[19] The triplet lifetime, $1/k_{TS}$, lies between 2.5 and 5.8 ms, depending on the excitation energy. Several ms-long lifetimes of the triplet-excited states were reported for porphyrin cations in the gas

phase.^[29] The population of the triplet state is easily quenched by efficient energy transfer to surrounding molecular oxygen under aerobic conditions.^[6,20] The high triplet quantum yield and long lifetime of the isolated species clearly emphasize the importance of quenching mechanisms in plants.

The dissociation rate constant k is strongly dependent on the excitation energy and was used to estimate the activation energy E_a of the statistical fragmentation into the neutral chromophore and the charge-tag by assuming an Arrhenius-type decay (see Fig. 5d). The preexponential factor A is correlated with the mode of the decay, and T is the temperature of the molecules. The initial internal temperature and the corresponding internal energy of the chromophores are determined by the temperature of the ion trap. The internal energy at a given temperature was calculated as the weighted sum over all normal modes, calculated with the PM3 semi-empirical method with Gaussian03.^[30] At room temperature, the total vibrational energy is about 2 eV distributed over 456 vibrational modes. The average energy per mode is about 35 cm^{-1} . After being injected into the storage ring, the molecules are no longer in equilibrium with a heat bath but described as microcanonical ensembles. The absorption of n photons increases the internal energy by $\Delta E = nhc/\lambda$ which corresponds to an increase of the microcanonical temperature of the molecules of $\Delta T_m = \Delta E/C_m$ with C_m being the microcanonical heat capacity. Figure 5c shows the internal-energy distribution of the molecules leaving the ion trap at room temperature, before and after the absorption of 640-nm and 360-nm photons. The microcanonical temperatures T_m were calculated directly from the level-density, obtained by the Beyer-Swinehart algorithm together with the calculated vibrational frequencies (calculated internal energy, microcanonical temperature, and heat capacity for different excitation wavelengths are listed in Table 3 in the SI). Figure 5d shows the Arrhenius plot for the charge-tagged Chla by using the obtained values for k and T_m at different excitation wavelengths. From the linear fit we extracted an activation energy of 0.9 ± 0.2 eV, in reasonable agreement with theoretical predictions of 1.35 eV^[12], and a preexponential factor of $3 \cdot 10^{13} \text{ s}^{-1}$ with an uncertainty of ± 2 in the exponent. The replacement of T_m by the effective temperature $T^* = T_m - E_a/2C$ (with the second term being the heat bath correction^[26]) yields a preexponential factor of $1 \cdot 10^{14} \text{ s}^{-1}$.

To probe the long-lived triplet state we performed pump-probe experiments on a μ s to ms timescale.^[31] The ions were first excited by a ns-pump pulse at 420 nm and after 260 μ s (2 revolutions later) photoexcited by the probe pulse with wavelengths between 630 and 850 nm. The action spectrum (Fig. 6) shows the yield of photoneutrals as a function of the probe wavelength. These photoneutrals are induced either by excitation of the 420-nm photoexcited ions or by excitation of ions in the ground state which were not photoexcited before by the pump beam. The intense band with the maximum at 640 nm corresponds to the ground state absorption. The red shoulder of the main peak is induced by the absorption of vibrationally hot anions after ICs from S_2 to S_0^* . The absorption bands with maxima at 685 nm and 756 nm may be due to triplet-triplet absorption. To see if we also get some contribution from the 'hot' ground state in this wavelength-regime, we carried out a separate experiment, where we photoexcited the ion bunch right after the injection into the storage ring. Here, the fragmentation is already particularly high due to the decay of vibrationally hot molecules, which are formed due to collisions with residual gas during the transfer from the trap to the ring. For these 'hot' molecules we registered no signal above ~ 670 nm, and we therefore conclude that the two absorption bands observed in the pump-probe experiment arise from triplet absorption. The triplet absorption observed here is within the expected absorption region for chlorophylls excited to triplet states.^[6,20,32] In condensed phase, triplet-triplet absorption was reported in the near-infrared regime by performing flash absorption spectroscopy with an absorption band around 760 nm and a very broad band around 1100 nm.^[32] In more recent investigations, triplet-triplet absorption by Chla in various solvents was shown in triplet-minus-singlet

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Figure 5. a Time-resolved fragmentation after photoexcitation at 640 nm and 410 nm. The solid lines are fitted curves from the rate model sketched in b. Two competing relaxation branches lead into the vibrationally excited ground state from where statistical dissociation may occur (rate constant k). The yellow branch describes fast electronic de-excitation by internal conversion (IC) and intramolecular vibrational redistribution (IVR). The green branch describes intersystem crossing (ISC) into the lowest-lying triplet state. The triplet-to-singlet conversion rate constant is described by k_{TS} . c Illustration of the internal energy distribution of an ensemble of molecules leaving the ion trap at room temperature, before and after the absorption of a 640-nm (1.94-eV) and 360-nm (3.44-eV) photon. On the upper x-axis the corresponding microcanonical temperature T_m is given. d Arrhenius plot for the charge-tagged Chla molecule. A linear fit gives an activation energy of $E_a = 0.9$ eV and a preexponential factor of $A = 3 \cdot 10^{13} s^{-1}$. The red data points show the Arrhenius plot under consideration of the finite heat-bath correction yielding $A = 1 \cdot 10^{14} s^{-1}$ by assuming $E_a = 0.9$ eV (for more details see text).

(T-S) transient absorption spectra and evolution-associated difference spectra (EADS) between 700 and 800 nm^[6,20]. Moreover, the absorption profile (see Fig. 6) supports the suggestion of triplet-triplet absorption as the energy differences between the two bands is similar to the one observed between $Q_{x/y}$ and higher vibrational states for the ground-state molecules.

In summary, we have performed action spectroscopy of charge-tagged Chla and Chlb isolated in *vacuo* to study their intrinsic photophysical properties. High quality absorption spectra reveal the splitting of the Q and the Soret bands into distinct x and y components. The energy gap between Q_x - Q_y and B_x - B_y was found to be ~ 0.3 eV in the case of Chla, and similar values were determined for Chlb (~ 0.2 eV for Q_x - Q_y and ~ 0.4 eV for B_x - B_y). We modeled the photofragmentation of charge-tagged Chla by considering both, the thermally induced dissociation after rapid electronic de-excitation, and the thermally induced decay proceeding via a triplet-state intermediate. The population of the intermediate triplet state was supported by performing ns-pump-probe measurements on a μs to ms timescale. The measured decay of several μs was ascribed to thermally induced fragmentation after internal conversion, which is strongly dependent on the excitation energy. The activation energy of the ground state fragmentation was found to be ~ 0.9 eV. The slow decay of several ms was ascribed to the population of a triplet state with a high quantum yield of 0.7-0.8. We have shown that time-resolved action spectroscopy is an appropriate setup to study the intrinsic photophysics of Chls. This may serve to benchmark high-level calculations of excited-state energies, as well as to follow the excited-state kinetics in absence of quenching molecules.

Figure 6. Normalized yield of fragments due to the pump laser pulse (420 nm, indicated by the blue arrow in the schematic) as a function of the probe wavelength (630-850 nm, indicated by the red arrow). The second laser pulse was fired 260 μs after the pump pulse and probes the hot electronic ground state or the triplet state (red data points). The hot band contribution is seen in the red shoulder of the main peak, while the two peaks with maxima at 685 nm and 756 nm may be due to triplet-triplet absorption. For comparison the ground-state absorption profile is shown (black data points). The lines through the data points are fitted by sums of Gaussians.

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Experimental Section

Experimental details are reported in the Supporting Information

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Keywords: action spectroscopy • chlorophyll • chromophore
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The intrinsic photophysics of chlorophyll *a* and *b*, the light-harvesting pigments in photosynthetic proteins in plants, have been studied from gas-phase action spectroscopy. We have firmly established the splitting of the Q and Soret bands into *x* and *y* polarized components and found dissociation occurring on long time scales due to the population of triplet states after photoexcitation.

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