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Theory of Ultrafast Exciton Motion in Photosynthetic Antenna Systems

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To investigate ultrafast exciton motion, exciton relaxation and related nonlinear optical spectra of photosynthetic antenna systems the dissipative multi-exciton theory is utilized. This type of approach accounts for optically induced transitions to the band of delocaliced single-exciton and two-exciton states as well as takes notice of the coupling to the vibrations of the protein matrix. Different applications are mentioned with emphasis on the Fenna Matthews Olson (FMO) photosynthetic antenna complex of Chlorobium Tepidum.

Keywords: photosynthetic antennae; excitons in molecular systems; density matrix theory

1. INTRODUCTION

Antenna systems are found in photosynthetic membranes of bacteria and higher plants cells. Their task is to increase the light–absorption cross section of the photosynthetic reaction center where the charge separation process takes place as the initial step of light–driven chemical synthesis. Photosynthetic antenna systems are huge pigment protein complexes containing different Chlorophyll (Chl) or Bacteriochlorophyll (BChl) species as functional chromophores. The pigments are arranged in a particular spatial order, and resulting from this a characteristic energy spectrum of the antenna complex is formed.

Using optical spectroscopy and some information on the molecular structure a lot of ideas on the functionality of these antenna systems have been developed during the last two decades (see[1]). Meanwhile, structural data

with a resolution of some Angstroem are available for a selected number of antenna systems[2,3,4]. This makes it possible to establish a relation between the spatial arrangement of the pigments in the antenna complex and its functionality.

Some functional important events, i.e. the first steps of excitation energy (exciton) motion and exciton relaxation proceed in the subpicosecond time-domain. It is a topic of femtosecond spectroscopy to collect data on these ultrafast processes. To achieve a proper understanding of the measured behavior theoretical models have to be build up, and simulations valid on this subpicosecond time-scale must be carried out.

2. MODELS AND SIMULATION TECHNIQUE

In recent years a number of models and simulation techniques have been developed which are general and flexible enough to explain the femtosecond spectroscopic data from a unique theoretical point of view (see[5]). Of central interest is the interplay of Coulomb interaction, leading to the formation of delocaliced exciton states, and of static as well as dynamic disorder. For that end, a general model can be established including the vibrational Hamiltonian $H_{ma}(q)$ for the various pigments (counted by m) and valid for some selected electronic states $|\varphi_a>$ ($a = S_0, S_1, S_{n>1}$). In order to allow for the formation of delocaliced exciton states the Coulomb interaction among different pigments is considered, usually in the approximation of the dipole-dipole coupling J_{mn}. The influence of the vibrational modes q (dynamic disorder of the protein) can be accounted for in a perturbation scheme, or for some selected modes in an exact manner. Finally, the coupling to the ultrashort laser pulse has to be included. This can be done in a known perturbation scheme of nonlinear optics ($\chi^{(3)}$-approach) or in an exact manner. The use of such not too difficult models is strictly desirable to achieve a description of the quantum dynamics including the light-induced formation of coherence phenomena and their respective decay.

The density matrix technique is applied as the basic theoretical tool to describe coherent exciton motion, exciton dissipation, vibrational coherencies and the coupling to ultrafast light-pulses. Clearly, the basics of the dissipative quantum dynamics of excitons in organics are well established. But, the simulation of ultrafast spectroscopic experiments on photosyn-

thetic antenna systems desires a number of extensions to the standard approach.

The extensions concern the inclusion of two and three exciton manifolds allowing to account for the simultaneous presence of two, three (or more) excitations in the single pigment protein complex. Besides, higher excited singlet states of the single Chl are introduced (S_n-states). Both extension of standard exciton theory are necessary to describe optical excitation at higher intensity as done in various experiments. To consider the complex protein structure and its hierarchy of dynamic phenomena one can introduce normal-mode vibrations of the protein in combination with static disorder. The latter is taken into account via configuration averaging done after the simulation of the time dependent phenomena, whereas the normal-modes of the protein lead to exciton-vibration coupling. Here, the concept of the protein spectral density $J(\omega)$ plays the key role in characterizing excitation energy dissipation. Models which go beyond this concept and allow to describe coherent vibrations of the protein environment (nuclear coherencies) have been already discussed[6,7,8]. Combining this with radiationless transitions within a single Chl or between different molecules, internal conversion processes can be included and a microscopic description of exciton annihilation is achieved[8].

3. RESULTS

The explained theoretical concepts have been used to study ultrafast exciton motion in the Fenna Mathew Olson (FMO) complex of green bacteria[2], in the Light Harvesting Complex II (LH II) of purple bacteria[3], and in the Light Harvesting Complex of the photosystem II of higher plants (LHC II)[4]. All these complexes are known with a spatial resolution of about 3 Ångstroem. In our first studies we concentrated on the LHC II which could be successfully described within a Chl*a*-Chl*b* dimer model including a single active vibrational mode per pigment. Such a model is justified by the strong Chl*a*-Chl*b* coupling. Vibrational coherencies have been studied and the observed dependence of the spectra on the pump-field intensity could be explained[6,7,8].

Changing to the description of pigment oligomers with some ten of Chls or BChls the quantum dynamics of a single mode per pigment cannot be

simulated. For these systems the *dissipative multi-exciton theory* has been used. Within this approach one starts with a set of pure electronic degrees of freedom (forming the excitonic spectra) and couples these to the protein vibrations which act as the dissipative environment. As long as the exciton vibrational coupling is weak or of intermediate strength this would be a good approach. Just in the LH II and the FMO complex the conditions are of such a type. Both systems have been studied extensively (see[5] and[9], respectively). In the case of the FMO complex[9] it was possible to combine simulations in the frequency domain and in the time domain. Since the excitation energies of the BChls are not so precisely know CW-absorption has been fitted including homogeneous and inhomogeneous broadening. To get the homogeneous broadening, the shape of the spectral density of protein vibrations and the type of vibrations (local vibrations or delocalized ones) have been determined separately.

Therefore, a particular *ansatz* for the spectral density $J_{mn}(\omega)$ (coupling strength weighted density of oscillator states) has been taken. Since for $m \neq n$ J_{mn} gives the strength different pigments (positioned at m and n) are correlated by delocalized normal-mode vibrations of the protein, we assume $J_{mn} = \exp(-R_{mn}/R_c) \times J_{pig}$, where R_{mn} denotes the inter-pigment distance and J_{pig} is the single-pigment spectral density. The correlation radius R_c as well as the cut-off frequency of J_{pig} have been determined by an optimization procedure. As a result, an extension of the vibrations over the whole complex came out and the spectral density could be identified to extend up to 40 cm^{-1}. Furthermore, the inhomogeneous broadening has been optimized too. The obtained parameters gave an overall good agreement with the differential absorption $\Delta\alpha$ (absorption of the probe beam in the presence of the pump beam minus absorption in the absence of the pump beam) measured in[10].

The gain of information within a pump-probe configuration is increased if measurements with polarized light are carried out. Usually, one determines the transient anisotropy defined as $(\Delta\alpha_{\|} - \Delta\alpha_{\perp})/(\Delta\alpha_{\|} + 2\Delta\alpha_{\perp})$. Here, $\Delta\alpha_{\|}$ ($\Delta\alpha_{\perp}$) denotes the differential absorption for parallel (perpendicular) polarized pump and probe pulses.

In Fig. 1 the calculated anisotropy is shown for the pump as well as the probe wavelength taken at 621 nm, where optical transitions to the low-lying single-exciton states occur. All parameters have been taken from

the calculations on linear absorption spectra and pump–probe spectra (for details see[9]). The results are in agreement with the experiment of *Savhikin et al.*[11] on the FMO complex of *Chlorobium Tepidum*. Since not any additional parameter has been introduce the reproduction of the transient anisotropy data gives a nice proof for the consistence of the used model. It is not only valid for a single type of experiments but for a broader class.

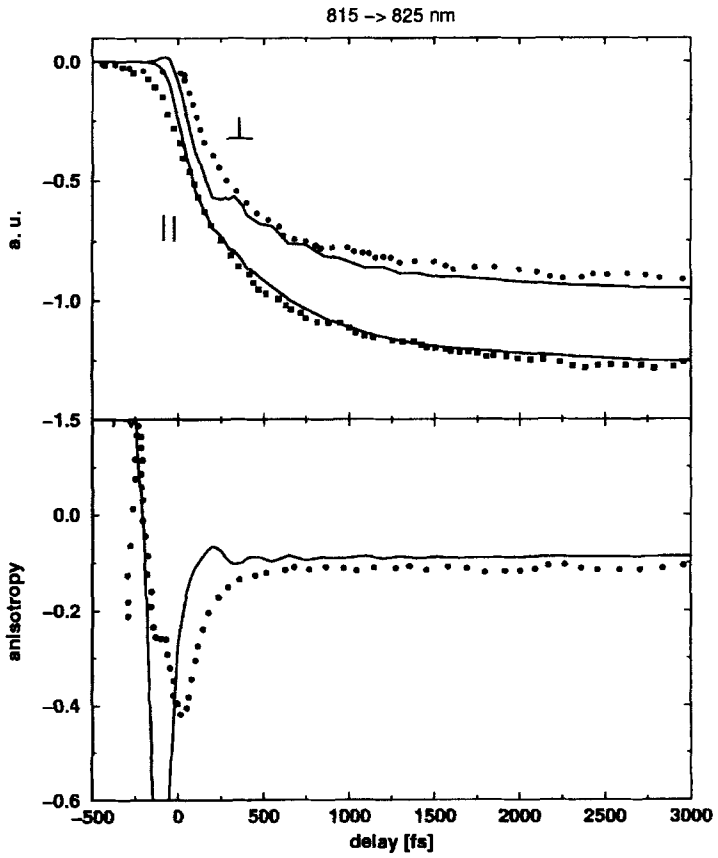

FIGURE 1 Two-color anisotropy with pump-wavelength at 815 nm and probe wavelength at 825 nm (T=19 K). Upper part: $\Delta\alpha_{||}$ and $\Delta\alpha_{\perp}$. Lower part: transient anisotropy. (Full lines: theoretical results. Experimental data from[11].)

4. CONCLUSIONS

Using the dissipative multi–exciton theory a number of different experiments on antenna systems could be described comprising ultrafast time–domain as well as frequency–domain measurements. It has to be considered as a main result of our studies that a common description of such diverse experiments on a highly structured biological systems is possible within a single model of intermediate complexity. Hence we may conclude that models describing the pigments as electronic two or three level systems and considering dynamic disorders within a perturbational treatment using the protein spectral density are of broad importance for a deeper understanding of some early events in photosynthesis. This conclusion could be already confirmed by recent calculations on the LHC II.

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