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Femtosecond Transient Grating Studies of Electron Transfer in Porphyrin and Chlorophyll Donor-Acceptor Molecules

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Time-resolved transient grating experiments are performed on artificial photosynthetic systems. Relative donor and acceptor orientation and solvation effects of charge transfer are discussed.

DISCLAIMER

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I. Introduction

Transient grating experiments have been utilized to study a variety of condensed phase phenomena. Most of these studies are performed on transparent media, resulting in non-resonant probing of the material response of the system. Such experiments include the study of orientational dynamics in liquids, acoustic and optical phonon dynamics as they relate to phase transitions in solid state media, optical Kerr effects, intramolecular vibrations, etc. In its simplest form, the technique requires two beams to be temporally and spatially overlapped in the sample. An interference pattern is created, which modulates the real part of the index of refraction through the third order susceptibility ($\chi^{(3)}$). A phase grating results, through which a variably delayed probe beam incident on the sample may diffract and provide temporal information about the material response.

Resonant transient grating experiments are also frequently utilized to perform studies on a variety of photophysical and photochemical processes. They include electron transport in semiconductors, energy transfer, and simple chemical reactions. An absorption (amplitude) grating modulates the imaginary part of the susceptibility tensor. Such chemical systems are generally carefully chosen to avoid interference from non-resonant phase gratings or multiple absorptions. Interference between the phase and amplitude gratings can complicate the time-dependent results and obscure the phenomena of interest. However, the exploitation of the polarization selective nature of transient grating experiments that was first done by Etchepare et al. and further enhanced by Deeg and Fayer has resulted in a leap in the ability to probe the desired phenomena of interest (1,2). It was shown that the different elements of the nonlinear susceptibility tensor possess different polarization characteristics and can be individually probed through prudent choices for the input and detection polarizations. Etchepare et al. first showed how to eliminate the nuclear and optical Kerr effect in CS_2 (1). Deeg and Fayer were the first to utilize this technique with an absorption contribution to the diffracted signal and to show that the anisotropy of the excited state grating can be utilized to provide valuable information about the relation between the excitation transition dipole and the probed transition dipole (2).

II. Experimental

In addition to the polarization characteristics of the transient grating technique, it is also a background free experiment, enabling higher sensitivity than with pump-probe experiments. The greater sensitivity enables one to utilize lower excitation intensities and

avoid higher order effects that sometimes plague pump-probe experiments. In our experiments, we utilize a femtosecond dye laser system that has been described in detail previously (3). The output is 75 fsec pulses amplified at 1 kHz at 585 nm up to 20 uJ. The white light that is utilized for the variably delayed probe is generated through focussing into a rotating quartz block and the scattered light is detected with a PMT.

III. Results

The goal of this report is to lay the groundwork for transient grating studies of electron transfer in artificial photosynthetic systems. Such systems include simple donor-acceptor molecules where the donor, typically a chlorophyll or porphyrin, is rigidly attached to an easily reduced species such as napthoquinone or benzoquinone. Over the last few years, we have made significant progress in the synthesis of acceptor molecules which have well defined absorption bands upon reduction which are well removed from the excited and cationic states of porphyrins and chlorophylls. They also possess large molar extinction coefficients (100,000 M^{-1} cm^{-1}) that dominate the spectra and also have well defined polarization characteristics. These traits are ideal for polarization sensitive transient grating experiments which will enable accurate determination of the angle of the transition dipole between the initial excitation and the acceptor probe, dynamic solvation effects on the charge separated species, and any time dependent rotation of the chromophores relative to each other (i.e. twisted intramolecular charge transfer states), etc.

An example of the type of molecule that we utilize for these experiments is shown in Figure 1. It consists of a free base porphyrin (HP) donor and a pyromellitic diimide (PI) acceptor directly bonded to the porphyrin ring. When PI is reduced, a large absorption band at 710 nm results. Utilizing a polarization sensitive transient grating experiment to diffract at 710 nm can give us information about the time dependent orientation of PI relative to the porphyrin by probing the anisotropy of the absorption grating. For such, an experiment to be succesful, electron transfer must occur on a time scale that is faster than the rotational diffusion of the molecule or all polarization information is lost. Here, electron transfer occurs in 16 ps in benzonitrile and the rotational diffusion time of the molecule is approximately 200 ps. Figure 2 shows the results of the transient grating experiment both with no polarization selectivity and with polarization selection for elimination of contributions from the fully charge separated species. In the latter case, the time dependent change in the anisotropy of the absorption grating is probed. The technique is also utilized to probe solvent interactions with the charge separated species. In addition to studying charge transfer compounds, results

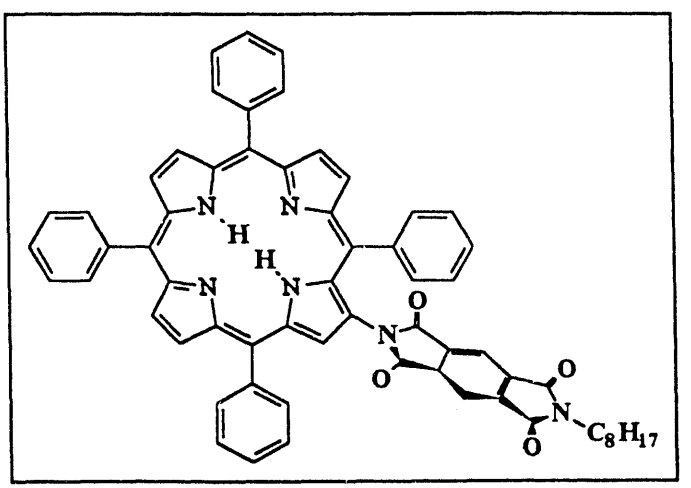

Figure 1: The porphyrin-pyromellitic (HP-PI) molecule.

from probing the excited states of chlorophyll a and bacteriochlorophyll are also presented.

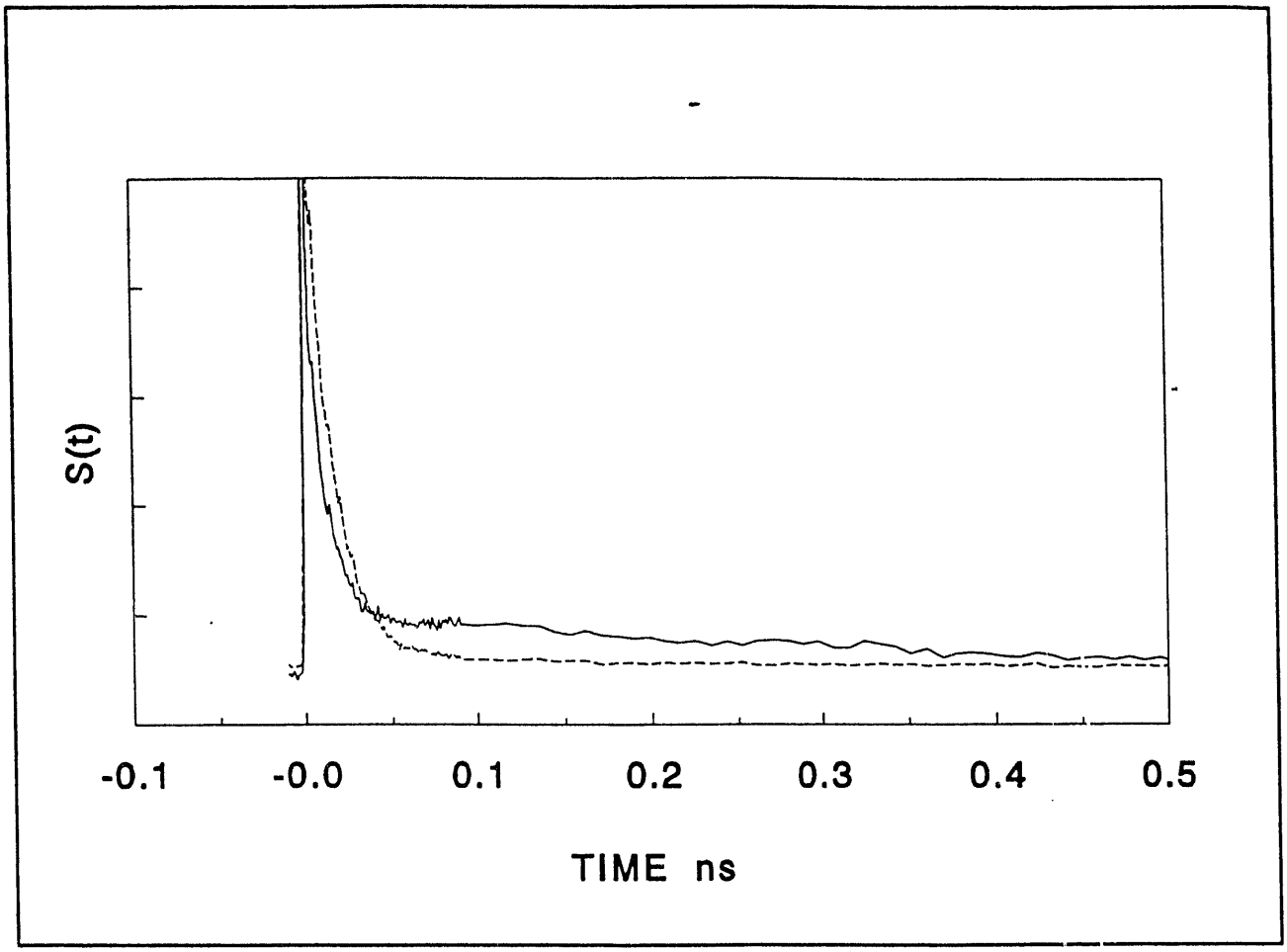

Figure 2: The transient grating results from HP-PI in benzonitrile at 710 nm with no (—) polarization selectivity and with the reduced PI species elimiinated (- - -) from the detected signal.

iV. References

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