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Study of excited state processes by using dynamic gratings in the frequency domain

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Abstract

Ultrafast relaxation of excited states in a system with three energy levels has been investigated theoretically and experimentally by using laser frequency-domain techniques. The picosecond process of electron transfer in binary molecules of porphyrin–porphyrin or porphyrin–phthalocyanine was studied and is discussed here.

1. Introduction

The laser frequency technique of nondegenerate four-wave mixing (NDFWM) is a promising method for investigating ultrafast optical relaxation processes [1]. It is well known that ultrafast processes in the time domain correspond to a broad frequency distribution in the frequency domain. Therefore, ultrafast relaxation processes can be more conveniently studied in the frequency domain than in the time domain. No special ultrashort pulsed laser and streak camera is required in the laser frequency method and a nanosecond pulsed laser or even a continuous wave laser can be used.

The photo-induced charge transfer in covalently bound porphyrin–porphyrin or porphyrin–phthalocyanine and their derivatives was demonstrated by transient absorption [2, 3]. Our investigations [4, 5] reveal that these materials exhibit strong optical nonlinearity which allows us to use the nonlinear optical means of NDFWM to analyze their relaxation processes. In the present paper, we present results of experiments and theoretical calculations of their excited state relaxations, with three-energy-level model systems based on the transient grating, with emphasis on picosecond processes for photo-induced charge transfer.

2. Basic description

The transient grating for analyzing ultrafast relaxation processes is based on the interaction between the external laser light field and the excited states of solids. The transient grating is formed by interference of two coherent light pulses, which are incident on the nonlinear medium. Under resonant or band-to-band excitation, the population in the excited state is modulated and consequently a grating can be produced in the medium. The decay of the formed grating is due physically to the population relaxation. The third light pulse is used to probe the time dependence of this grating. The diffracted signal from the probe pulse, as a function of frequency shift, represents the population

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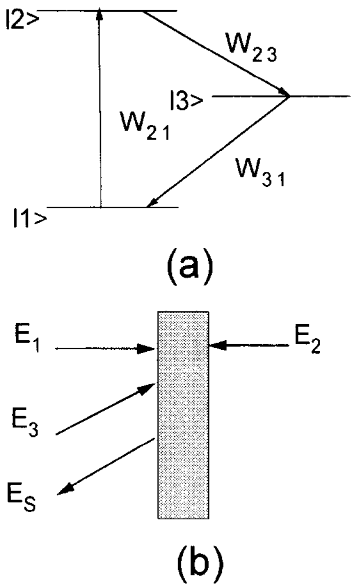

Fig. 1. Schematic diagram for the energy levels of the system and the interaction pathway of the four-wave mixing. (a) The three-energy level model for binary molecules with charge transfer. (b) Geometry for NDFWM. S: sample, E_1 and E_2 are the forward and backward pumping light fields, E_3 the probe light, and E_S the conjugate signal field.

relaxation. The schematic diagram for the energy levels and the configuration of NDFWM is shown in Fig. 1.

With short-duration excitation the population ΔN in the excited state $|2\rangle$ is given by

$$\Delta N \propto A\mathrm{e}^{-W_2 t},$$

where $W_2 = W_{21} + W_{23}$ and A is a constant.

(1) *Modulation field*: The population in $|2\rangle$ is modulated by the transient grating formed by the light fields propagating $\boldsymbol{K}_3$ and $\boldsymbol{K}_1$, as shown in Fig. 1(b). The modulated optical intensity $I(\boldsymbol{r}, t)$ is expressed as

$$I(\boldsymbol{r}, t) \propto |\boldsymbol{E}_1 + \boldsymbol{E}_3|^2 \propto 1 + \beta\{\exp[\mathrm{i}(\delta t - \boldsymbol{q}\cdot\boldsymbol{r})] + \exp[-\mathrm{i}(\delta t - \boldsymbol{q}\cdot\boldsymbol{r})]\},$$

where

$$\boldsymbol{E}_j(\boldsymbol{r}, t) = \boldsymbol{E}_j \exp[\mathrm{i}(\omega_j t - \boldsymbol{K}_j\cdot\boldsymbol{r})],$$

$$\delta = \omega_3 - \omega_1,$$

$$\boldsymbol{q} = \boldsymbol{K}_3 - \boldsymbol{K}_1.$$

(2) *Population modulation by the modulation field*: In the presence of the external light field the population of the excited state $|2\rangle$ is also modulated in terms of the modulation intensity:

$$L(\Delta N_{\mathrm{ex}}) \propto L(\Delta N) L(I(\boldsymbol{r}, t)),$$

where L denotes the Laplace operator.

(3) *Detection of the population grating*: The probe light field applied to detect the grating evolution is

$$\boldsymbol{E}_2(\boldsymbol{r}, t, \boldsymbol{K}_2) = \boldsymbol{E}_2 \exp[\mathrm{i}(\omega t - \boldsymbol{K}_2\cdot\boldsymbol{r})],$$

where $\omega \equiv \omega_1$. The signal field $\boldsymbol{E}(\boldsymbol{K}, t)$ from the probe field diffracted by the grating in the direction $\boldsymbol{K}$ is given by

$$\boldsymbol{E}(\boldsymbol{K}, t) = \int \Delta N_{\mathrm{ex}}\cdot\boldsymbol{E}_2(\boldsymbol{r}, t, \boldsymbol{K}_2)\cdot\mathrm{e}^{\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{r}}\,\mathrm{d}\boldsymbol{r}.$$

Thus one obtains

$$\boldsymbol{E}(\boldsymbol{K}, t) \propto \frac{A}{W_2}\mathrm{e}^{\mathrm{i}\omega t}\delta(\boldsymbol{K} - \boldsymbol{K}_2) + \frac{\beta|E_2|}{W_2 + \mathrm{i}\delta}\mathrm{e}^{\mathrm{i}(\omega-\delta)t}\delta(\boldsymbol{K} - \boldsymbol{K}_2 - \boldsymbol{q}) + \frac{\beta|E_2|}{W_2 - \mathrm{i}\delta}\mathrm{e}^{\mathrm{i}(\omega+\delta)t}\delta(\boldsymbol{K} - \boldsymbol{K}_2 + \boldsymbol{q}).$$

The first term represents the transmission of the probe light field in the direction $\boldsymbol{K} = \boldsymbol{K}_2$.

(4) *Analysis of the excited state relaxation in the NDFWM configuration*: The third term in the above formula stands for the diffracted signal field from the probe light in the direction $\boldsymbol{K} = -\boldsymbol{K}_3$ which is detected in our experimental configuration. One has the component of the signal in the direction $\boldsymbol{K} = -\boldsymbol{K}_3$:

$$\boldsymbol{E}(-\boldsymbol{K}_3, t) = \frac{\beta E_2}{W_2 - \mathrm{i}\delta}\mathrm{e}^{\mathrm{i}(\omega+\delta)t}.$$

As a result, the corresponding signal intensity is

$$I_{\mathrm{S}}(-\boldsymbol{K}_3) \propto |\boldsymbol{E}(-\boldsymbol{K}_3, t)|^2,$$

i.e.

$$I_{\mathrm{S}}(-\boldsymbol{K}_3) \propto \frac{1}{W_2^2 + \delta^2}.$$

Using the above relation to fit the signal intensity of the conjugated reflection of the probe light as a function of frequency detuning in NDFWM, one obtains the relaxation rate of the excited state including the photo-induced charge transfer rate.

3. Results and discussion

The phase conjugation setup of NDFWM is shown in Fig. 1. 532 nm light from the second harmonic of a *Q*-switched Nd:YAG laser with a pulse duration of 10 ns and a repetition rate of 15 Hz is split into two beams which pump two identical dye lasers. The weaker dye beam is used as a probe beam and the other stronger dye beam is subsequently split into two equally intense beams used as the forward and backward counter-propagating pump light. The probe light is incident at a small angle with respect to the forward pump beam. The two pump beams and the probe beam are incident on exactly the same spot of the 2 mm quartz cuvette. Three polarizers are used to change the polarization configuration of the light fields. An optical delay line is used to ensure the temporal overlap of the three light pulses in the sample. The phase conjugate signal propagates in a counter direction to the probe beam and a fraction of the signal is reflected to a spectrometer. The signals are finally recorded and processed by a microcomputer.

Samples studied were free-base tetratolyl porphyrin dimers (TTP–TTP) and covalently linked tetratolyl porphyrin and phthalocyanine (TTP–O–Pc). These materials were dissolved in the solvent of N,N-dimethyl formamide at a concentration of 10^{-4} M. Typical absorption bands for TTP are centered at 410, 470, 500, 550, and 590 nm. The center wavelength of the dye lasers in the NDFWM is tuned to the absorption peak of 550 nm where the molecules under study are resonantly excited to produce the population grating.

The excitation and recombination processes can be understood with a simplified energy level configuration, with a ground state $|1\rangle$, an excited state $|2\rangle$, and an excited electron transfer state $|3\rangle$. The binary molecules are resonantly excited to the excited state $|2\rangle$ from the ground state $|1\rangle$, and then the electrons of the excited state de-excite: (1) by the electron recombination $|2\rangle \rightarrow |1\rangle$ which gives rise to luminescence with a lifetime of several ns, and (2) the electron is transferred to the electron transfer state by the process $|2\rangle \rightarrow |3\rangle$ estimated to be in the picosecond regime [6, 7]. Therefore, the fast decay process of the electron transfer can be deduced from the relationship of $I_S(-\boldsymbol{K}_3)$ and δ. The experimental result of the signal intensity of NDFWM as a function of frequency distribution for TTP–TTP is presented in Fig. 2. The charge transfer time constant is derived to be 6 ps from the fit of the experimental data in Fig. 2 and similarly 18 ps for TTP–O–Pc.

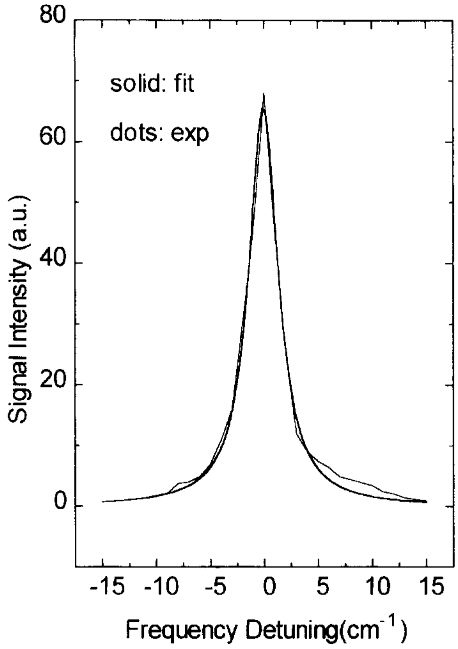

Fig. 2. Signal intensity of NDFWM as a function of frequency detuning in TTP–TTP.

In the theoretical fitting of the experimental data, effects arising from nonlinear processes and from absorption–section variation due to laser-frequency detuning on the profiles of the NDFWM signal intensity are taken into account. The signal field $E_S(\delta)$ is separated into its real $R(\delta)$ and imaginary $I(\delta)$ parts:

$$E_S(\delta) = R(\delta) + iI(\delta).$$

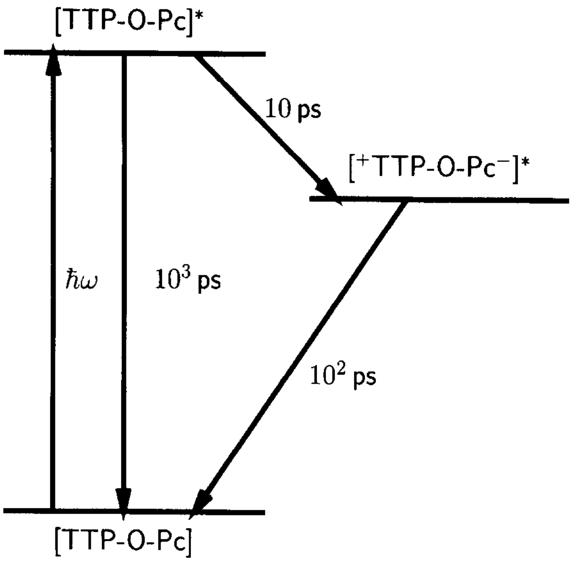

Fig. 3. Energy level diagram showing the excitation and recombination processes in TTP–O–Pc.

The signal intensity $I_S(\delta)$ is

$$I_S(\delta) = R^2(\delta) + I^2(\delta).$$

The fitting function $F(\delta)$ is taken as

$$F(\delta) = [R(\delta) + C_1]^2 + [I(\delta) + C_2]^2.$$

C_1 and C_2 are additional fitting parameters introduced to allow for the effects of nonresonant nonlinearity and absorption cross-section variations on the theoretical fitting. When C_1 and C_2 are zero, $F(\delta)$ exactly equals $I_S(\delta)$. The best-fit results of Fig. 2 are obtained for the values $C_1 = 0.012$ and $C_2 = 0.010$, which indicate that the influence of nonresonant nonlinearity and the absorption cross-section change are quite small and the best-fit results are quite reliable.

New optical features in binary molecules have been observed because of the electron transfer. The increase of absorption with increase of excitation density is known as inverse saturation absorption. The inverse saturation absorption found for TPP and Pc can be explained by the triplet state being a mesostate with a longer lifetime. Electrons are first excited from the ground state to the singlet excited state, and then rapidly decay to the excited triplet state (mesostate). Under high-intensity excitation, electrons can be further excited from the mesostate to the higher excited triplet state by absorbing incident photons. These transitions from the mesostate to the higher excited states lead to an increase in the absorption with increase of the excitation intensity.

The inverse saturation taking place in TTP or Pc does not occur for the binary molecules TTP–O–Pc or TTP–TTP. The excitation and recombination processes in TTP–O–Pc are illustrated in Fig. 3. In this figure ($^+$TTP–O–Pc$^-$)* stands for the excited state of the electron transfer with a lifetime of about 10^2 ps (measured by the pump-and-probe technique), which is not able to be considered as a mesostate. Electrons remain only a very short time on the ($^+$TTP–O–Pc$^-$)* as they annihilate nonradiatively very rapidly. Therefore, inverse saturation absorption for TTP–O–Pc is not observed.

The photo-induced electron transfer brings about an enhancement of the optical nonlinearity. The third-order nonlinear susceptibility $\chi^{(3)}$ for TTP–O–Pc is 6×10^{-10} esu, which is about three orders of magnitude larger than those of TTP, Pc, or systems of mixed TTP and Pc. When the covalent bond chain changes from TTP–O–Pc to TTP–O–$(CH_2)_5$–O–Pc, $\chi^{(3)}$ increases to 8.5×10^{-9} esu. As the covalent chain increases its length, the effective photo-induced polarization increases and leads to the enhancement of the optical nonlinearity.

In summary, the laser-frequency method can be applied to investigate excited state relaxations over picosecond or subpicosecond time scales. The electron transfer rate is inversely proportional to the chain length. The photo-induced electron transfer in binary molecules leads to an enhancement of the optical nonlinearity.

Acknowledgements

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