The theory and experiment of solute migration caused by excited state absorptions*

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Nonsymmetrical transition from reverse-saturable absorption (RSA) to saturable absorption (SA) caused by excited state absorption induced mass transport of the CuPcTs dissolved in dimethyl sulfoxide is observed in an open aperture Z-scan experiment with a 21-ps laser pulse. The nonsymmetrical transition from RSA to SA is ascribed neither to saturation of excited state absorption nor to thermal induced mass transport, the so-called Soret effect. In our consideration, strong nonlinear absorption causes the rapid accumulation of the non-uniform kinetic energy of the solute molecules. The non-uniform kinetic field in turn causes the migration of the solute molecules. Additionally, an energy-gradient-induced mass transport theory is presented to interpret the experimental results, and the theoretical calculations are also taken to fit our experimental results.

Keywords: solute migration, excited state absorption, energy-gradient

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1. Introduction

Nonlinear optical properties of materials have been widely used in optical switching and information storage. Excited state absorption which can cause large nonlinearities has been widely investigated in metalloporphyrin.[1−4] In recent years, metallophthalocyanines have attracted much interest for large reverse-saturable absorption (RSA) coefficents ascribed to the highly π-conjugated system.[5−9] The mass transport of AlClPc solution induced by optical excitation was first reported by Wei *et al.*[10] They did Z-scan experiments for different pulse energies at different repetition rates. The accumulative effect of mass transport and the diffusion back of the solute molecules were well observed in their experiments. In our Z-scan experiment, transition from RSA to SA which is mostly ascribed to the reduction of density of the solute molecules is observed. In the present paper, an energy transport theory model is proposed and a correlative numerical calculation is carried out to interpret the experimental results. The Soret effect, thermoinduced mass transport, is distinguished from excited state absorption induced mass migration following giant laser pulse excitation.

2. Experiment

The Z-scan technique (Fig. 1) is a simple but sensitive technique for measuring the nonlinear absorption and refraction of materials. It has been described in detail by Shake-Bahae *et al.*[11] Briefly, the beam splitter BS1 splits and directs a small portion of the incident beam to the detector D1, which monitors the fluctuation of the incident pulse energy. The rest of the pulse is tightly focused by a lens and transmits through the sample at various positions (Z) relative to the beam waist at $Z = 0$. We normalize the value of D2, which monitors the transmitted energy, by the

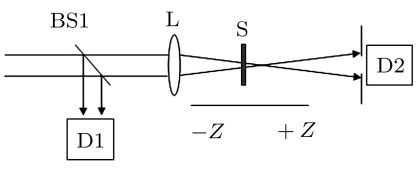


Fig. 1. Experimental scheme of Z-scan. BS, beam splitter; L, lens; S, sample; D1 and D2, detectors.

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corresponding value obtained in the linear regime (at the starting Z), thereby yielding the normalized transmitted energy (NT).

The pulse used in this study is generated by using a Q-switched model-locked Nd:YAG laser. The laser is frequency doubled with an output wavelength of 532 nm and operated at 10 Hz in the TEM_{00} mode with a full width of 21 ps at half maximum intensity at a focus spot of 21 μm in size. The data are recorded as the sample position is increased or reduced along the Z axis in steps of 3 mm. The experiments are performed with the pulse energies 1.00 μJ, and 7.28 μJ at room temperature on CuPcTs dissolved in dimethyl sulfoxide (DMSO) solution with a concentration of 1.6×10^{23} m^{-3} in a 2-mm wide cell.

The results obtained from the Z-scan experiment of pulse energy of 1.00 μJ with an open aperture are shown in Fig. 2 by empty circles. The curve exhibits strong RSA, and with the pulse energy increasing to 7.28 μJ the RSA-to-SA transition occurs as shown below in Fig. 4 by empty circles. Note that the Z-scan curve is asymmetric, and the excited state absorption saturation induced RSA-to-SA transition is symmetric. We consider that the strong excited state absorptions cause the density of the solute molecules at the centre of the laser beam to reduce. The density of the solute molecules in turn induces the increase in transmittance. For the cumulative migration of solute molecules, the Z-scan exhibits asymmetry. We will interpret our experiments in detail in the following section.

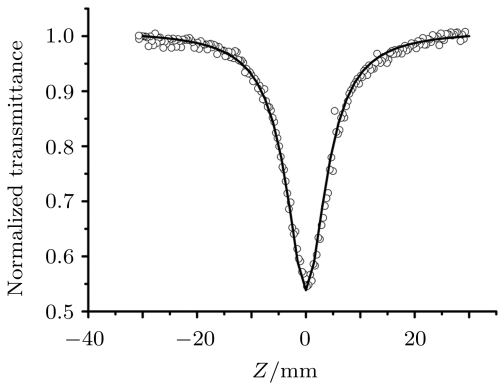


Fig. 2. Z-scan measured curves with pulse energy 1.00 μJ. The empty circles denote the experimental results. The solid line refers to the theoretical fit line for the pure three-level model.

3. Theoretical model

It is appropriate to use the five-energy-band model (Fig. 3) for CuPcTs in our experiment.

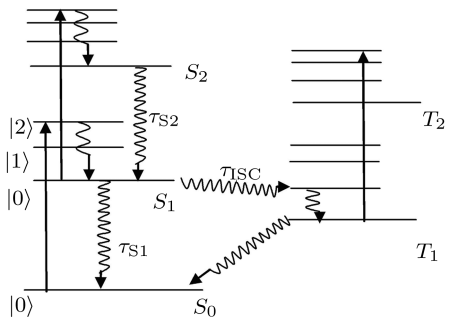


Fig. 3. Diagram of the five-energy-band model showing optical excitation (upward-pointing arrows) and relaxation (wiggly lines).

We interpret optical excitation and its associated population redistribution among various energy bands. Each energy band, including the associated zero-point level $|0\rangle$ and vibronic level $|\nu \neq 0\rangle$, is conventionally named $S_{\rm i}$ for the singlet manifold and $T_{\rm i}$ for the triple manifold. The equation governing the intensity attenuation with the penetration z' into the sample can be written as

$$\frac{{\rm d}I}{{\rm d}z'} = -\alpha I = -[\sigma_{\rm aS0} N_{\rm S0}(t) + \sigma_{\rm aS1} N_{\rm S1}(t)]I, \quad (1)$$

where I is the intensity and $\sigma_{\rm a}$ denotes the absorption cross section of the states specified by the subscripts. In Eq. (1) we neglect the absorption of the triple manifold because $\tau_{\rm isc}$ can be regarded as infinitely long compared with the width of the pulse. Also we neglect the attenuation of the population of the S_1 state, because $\tau_{\rm S1}$ is of the order of ns. The population-change rate equations are

$$\frac{{\rm d}N_{\rm S0}(t)}{{\rm d}t} = -\frac{\sigma_{\rm aS0} N_{\rm S0}(t) I}{\hbar\omega}, \quad (2)$$

$$\frac{{\rm d}N_{\rm S1}}{{\rm d}t} = \frac{\sigma_{\rm aS0} N_{\rm S0}(t) I}{\hbar\omega} - \frac{\sigma_{\rm aS1} N_{\rm S1}(t) I}{\hbar\omega} + \frac{N_{\rm S2}}{\tau_{\rm S2}}, \quad (3)$$

$$\frac{{\rm d}N_{\rm S2}}{{\rm d}t} = \frac{\sigma_{\rm aS1} N_{\rm S1}(t) I}{\hbar\omega} - \frac{N_{\rm S2}}{\tau_{\rm S2}}, \quad (4)$$

where N denotes the population of states specified by the subscripts. The RSA due to the excited state absorption (ESA) with $\sigma_{\rm aS0} < \sigma_{\rm aS1}$ means that the nonlinear absorption coefficient α increases with the increase of incident fluence. In the case where $\sigma_{\rm aS0} < \sigma_{\rm aS1}$ and the lifetime of the S_2 state ($\tau_{\rm S2}$) is nonvanishing, when the incident fluence reaches a threshold, the population of the S_1 state will decrease with the increase of the incident fluence, so the absorption coefficient α decreases with the increase of the incident fluence, and the RSA-to-SA transition takes place. As shown in Fig. 2, the NT curve exhibits RSA when using an energy of 1.00 μJ, while when using an energy

of 7.28 μJ the NT curve exhibits the RSA-to-SA transition shown in Fig. 4. Note that the plain RSA-to-SA transition described above is a symmetrical curve while the curve in Fig. 4 is asymmetrical because of the cumulative migration of the solute molecules induced by the giant laser pulse. For the small input pulse energy 1.00 μJ there is no mass transport for the weakly excited solute molecules, induced by the input laser pulse. With Eqs. (1)–(4), we simulate our experiments. Using $\sigma_{\rm aS0} = 7.1 \times 10^{-22}$ m^2, $\sigma_{\rm aS1} = 8.0 \times 10^{-21}$ m^2, and $\tau_{S2} = 250$ fs, the best fittings are obtained as shown by solid lines in Fig. 2.

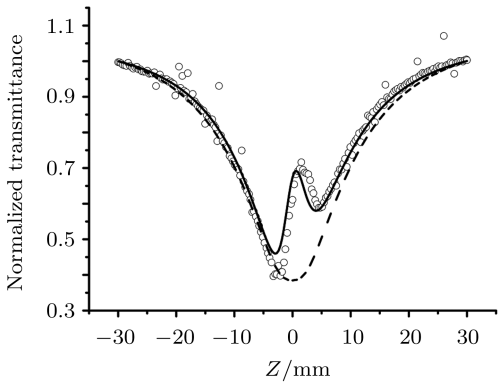


Fig. 4. Z-scan measured curves with a pulse energy of 7.28 μJ. The empty circles denote experimental results, the solid line represents the theoretical fit line considering mass transport, and the dash line refers to the theoretical line considering the Soret effect.

The CuPcTs molecules pumped by a laser pulse at 532 nm in picoseconds are promoted into the vibronic level of the S_1 or S_2 state. Accompanied by these excitations, fast decays: $|v\rangle\, S_1 - |0\rangle\, S_1$; $|v\rangle\, S_2 - |0\rangle\, S_2$; $|0\rangle\, S_2 - |0\rangle\, S_1$ take place compared with the laser pulse width 21 ps. The intra-molecular processes and other transitions among the singlet states are not of concern because of their low rates. The energy dissolved from the fast decays is converted into the CuPcTs molecules' own energy in a time of the order of subpicoseconds. The energy converting process occurs long before the subsequent energy dissipation into the solvent since the correlative local thermoequilibrium time $\tau_{\rm thermo}$ is on the order of 200 ps.[12] The energy of the CuPcTs molecules comprises various molecule motions: vibrations, librations, and the centre-of-mass oscillation. So, the excitation of the laser pulse will engender a non-uniform kinetic energy field. The non-uniform velocity field of the solute molecules is established. The distribution of the velocity field mimics the Gaussian pulse profile as well. The non-uniform velocity field will inevitably cause migration of the molecules. It is just like a bomb exploding. Meanwhile, we try to interpret the migration of the solute molecule by using the energy transport theory. We consider that energy is transported in solution in two different ways: (a) solute molecules with high kinetic energy transport the energy to the solvent molecules by colliding with the surrounding molecules; (b) the migration of the solute molecules from the centre of the laser beam to the edge. The kinetic energy density of the solute molecules, ψ, is equal to $N \times \varphi$, where N denotes the density of solute molecules, φ refers to the kinetic energy of a single solute molecule. Accompanied by the solute molecule migration from the centre of the beam to the edge, the number of centre solute molecules, which is directly related to the kinetic energy, decreases while on the edge the kinetic energy increases with the number of the solute molecules increasing. The non-uniform kinetic energy field causes the migration of the solute molecules; on the other hand the migration reduces the non-uniformity of the kinetic energy field.

In the process of the migration, the solute molecules collide with the solvent molecules, thereby reducing the non-uniformity of the kinetic energy field. The migration process is sustained until the kinetic energy field becomes uniform. In general, process (a) always exists, while in special conditions the migration of solute molecules takes place. A detailed discussion will be given below.

Under the excitation of 21-ps laser pulse the solute molecules absorb the laser energy, so the kinetic energy increases. However, the kinetic energy of solute molecules will also dissipate by collision. There exists a competition between the accumulation of kinetic energy and the dissipation of the energy. Because the width of the pulse is 21 ps, which is much shorter than the local thermoequilibrium time $\tau_{\rm thermo}$, we neglect the dissipation of the kinetic energy. Most of the energy released by the fast decays is converted into the solute molecules' own energy. The pulse with an energy of 7.28 μJ causes rapid accumulation of the kinetic energy. The non-uniform kinetic energy causes the migration of the solute molecules. The accumulated mass transport causes the skewed 'w' shape of the Z-scan curve as shown in Fig. 4. For a small pulse energy, the kinetic energy is not as strong as that in the case without mass transport, and the Z-scan curves are shown in Fig. 2.

The thermodiffusion in liquid mixture (known as the Soret effect[13−16]) seems to be the cause of the mi-

gration. We perform Z-scan experiments with a pulse width of 4 ns at different pulse energies, of which the highest energy is 31.00 μJ; there is no mass migration. When considering the ns laser pulse, the rate of the accumulation of the kinetic energy is low because the pulse width is much longer than $\tau_{\rm thermo}$, and we cannot neglect the dissipation of the kinetic energy. The accumulation of kinetic energy is not strong enough to cause the migration of the solute molecule. Apparently, the solute molecules have absorbed more energy in the 4-ns Z-scan experiment than in the 21-ps Z-scan experiment, and more heat is generated in 4-ns Z-scan experiments, but no mass migration is observed in the 4-ns Z-scan experiment. With the help of a thermally induced mass transport model, the numerical calculation for the 7.28 μJ 21-ps Z-scan experiment is also performed to fit to our experimental results. The equation of thermodiffusion can be written as[13]

$$\frac{\partial c}{\partial t} - D\Delta c = D_{\rm T}{\rm div}[c(1-c){\rm grad}\, T]. \tag{5}$$

In the case where the value of c varies smoothly, Eq. (5) is simplified into

$$\frac{\partial c}{\partial t} - D\Delta c = D_{\rm T}c(1-c)\Delta T, \tag{6}$$

where D is the mass diffusion constant; parameter $D_{\rm T}$ is the coefficient of thermodiffusion; and c denotes the concentration of solute molecules, and it is defined as the ratio of the number of inclusions per unit volume to the total density of particles.

Assuming that the absorbed energy is totally converted into thermal energy, the equation of thermodiffusion associated with the absorbed energy can be written as

$$\frac{\partial T}{\partial t} - \chi\nabla^2 T = \frac{(\sigma_{\rm aS0}N_{\rm S0} + \sigma_{\rm aS1}N_{\rm S1})I}{\rho C_{\rm P}}, \tag{7}$$

where ρ is the density of the solvent; $C_{\rm P}$ denotes the isobaric specific heat of the solvent.

Given the input pulses and the concentration of the solution, using Eqs. (1)–(7) we numerically simulate the results of the Z-scan experiment. The parameters we used are: $\rho = 1.0 \times 10^3 {\rm kg}\cdot{\rm m}^{-3}$; $C_{\rm P} = 1.9 \times 10^3 {\rm J}\cdot{\rm kg}^{-1}\cdot{\rm K}^{-1}$; $D = 0.6 \times 10^{-10}{\rm m}^2\cdot{\rm s}^{-1}$; $\chi = 1.0 \times 10^{-7}{\rm m}^2\cdot{\rm s}^{-1}$; $D_{\rm T} = 1.0 \times 10^{-10}{\rm m}^2\cdot{\rm s}^{-1}\cdot{\rm K}^{-1}$. The coefficient $D_{\rm T}$ we used is in the large number case. The theoretical curve is shown in Fig. 4 as the dash line. The result indicates that the thermally induced mass transport model is not appropriate to the explanation of our experimental results.

Although the driving force of the mass transport is not clear, the result of the migration leads the energy to be uniform. So we assume that the Laplacian of the kinetic energy density ψ causing the migration of the molecules is like Fick's law, and we give the equation

$$\frac{\partial N_{\rm S0}}{\partial t} = -D_\psi \nabla^2 \psi, \tag{8}$$

where D_ψ denotes the coefficient of the mass transport and varies with ψ. The kinetic energy density ψ is directly associated with the escaping velocity of the solute molecule which is related to the diffusion coefficient D_ψ. For simplicity, we assume the value of D_ψ to be a constant in our simulations. The gradient of the kinetic energy originates from different absorptions at different positions in the sample. For the used Gaussian profile beam, the distribution of absorbed energy mimics the Gaussian profile. The width of the pulse is 21 μm, so the absorbed energy density at position $r = 21$ μm is about $1/{\rm e}^2$ times the absorbed energy density at position $r = 0$. The absorbed energy density changes fast as the value of r increases. However, for the variation of absorbed energy density along the Z axes, the gradient is mostly attributed to nonlinear absorption of the sample. Indeed, this gradient is very small; as can be seen from Fig. 4, the absorbed pulse energy is about 0.7 times the input pulse energy at position $Z = 0$. The length of the sample is 2 mm. The variation of the absorbed energy is very slow, and so is the gradient. Summing up the above, the gradient of the kinetic energy density along the Z axis is much smaller than that in the transverse direction. Thus, in our Z-scan experiment we neglect the migration of solute molecules along the Z axis, and the operator ∇^2 approximates to ∇_r^2. The kinetic energy is

$$\psi = \eta\phi_{\rm a}, \tag{9}$$

where $\phi_{\rm a}$ denotes the absorbed energy density, η refers to the converting efficiency. We substitute Eq. (8) with Eq. (9); Eq. (8) can be written as

$$\frac{\partial N_{\rm S0}}{\partial t} = -D'_\psi \nabla_r^2 \phi_{\rm a}, \tag{10}$$

where D'_ψ is defined as

$$D'_\psi = \eta D_\psi. \tag{11}$$

The equation of absorbed energy density can be written as:

$$\phi_{\rm a} = \int_{-\infty}^{+\infty} I(\sigma_{\rm aS0}N_{\rm S0} + \sigma_{\rm aS1}N_{\rm S1})\,{\rm d}t. \tag{12}$$

Accompanied by mass transport, collisions between molecules and solvent molecules take place, so

$\phi_{\rm a}$ will attenuate. For simplicity, we consider the attenuation associated with thermodiffusion, and the value of $\phi_{\rm a}$ is given by

$$\frac{{\rm d}\phi_{\rm a}}{{\rm d}t} = -\frac{\phi_{\rm a}}{\tau_{\rm thermo}}. \tag{13}$$

The inverse diffusion of the solute molecules should be taken into account, and the correlation equation is

$$\frac{\partial N_{\rm S0}}{\partial t} = -D\nabla_r^2 N_{\rm S0}. \tag{14}$$

Considering the mass transport, given the input pulse energy, concentration of the solution and the corresponding coefficient, using Eqs. (1)–(4) and (10)–(14) we numerically simulate our experiments. All of the pulses which are determined by the repetition rate of the laser and the velocity of the platform should be taken into account because the mass migration is an accumulation effect. Each pulse does not experience the mass transport induced by itself but suffers the perturbation of the former pulses. The interval time 0.1 s is long enough so that we assume that all molecules return to the ground state S_0 and the temperature gradient has dissipated, because the thermodiffusion time is of the order of ms.[12] However, 0.1 s is not long enough for the molecules blown away to return because the mass diffusion time is on the order of 0.3 s, like the diffusion time of AlClPc dissolved in methanol.[10] That is, each pulse encounters fresh molecules but the distribution of the concentration of the solution has changed by pre-pulses. For a pulse, the population density $N_{\rm S0}$ is given by calculating the perturbation of the solute molecules excited by the pre-pulse. Using Eqs. (1)–(4) and (12) we calculate the value of $\phi_{\rm a}$. Then we integrate Eq. (10) with the help of Eq. (13) by using the upper limit 10 ns which indicates that the mass transport is accomplished on the ns time scale, and this will be approved in further work. Using the value of $N_{\rm S0}$ which is derived from Eq. (10) as the initial condition of Eq. (14), we integrate Eq. (14) by using the upper limit of the interval pulse time 0.1 s. The derived value of $N_{\rm S0}$ serves as the initial condition for the next pulse. By doing so iterately, we derive different values of $N_{\rm S0}$ (see Fig. 5) for each pulse with the respect to the different Z positions. The concentration of the solution in the centre of the beam is obviously lower than the equilibrium concentration, while near the centre the concentration is higher than the equilibrium concentration. Note that the change of $N_{\rm S0}$ with r reveals the conservation of the population. Using the initial concentration: $N_{\rm S0} = 1.6 \times 10^{23}$ m^{-3}, $N_{\rm S1} = 0$, $N_{\rm S2} = 0$, $\sigma_{\rm aS0} = 7.1 \times 10^{-22}$ m^2, $\sigma_{\rm aS1} = 8.0 \times 10^{-21}$ m^2, $\tau_{\rm S2} = 250$ fs, $D = 6 \times 10^{-11}$ m$^2 \cdot$s^{-1}, and $D_\psi = 4.4 \times 10^{15}$ m$^2 \cdot$J$^{-1} \cdot$s^{-1} the theoretical fit is carried out, and the results are shown in Figs. 4 and 6 with the solid line.

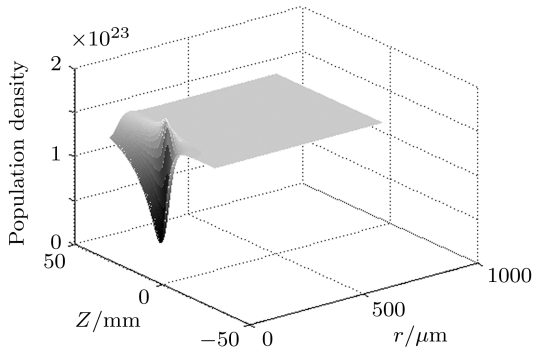


Fig. 5. Population density of the solution versus r and Z.

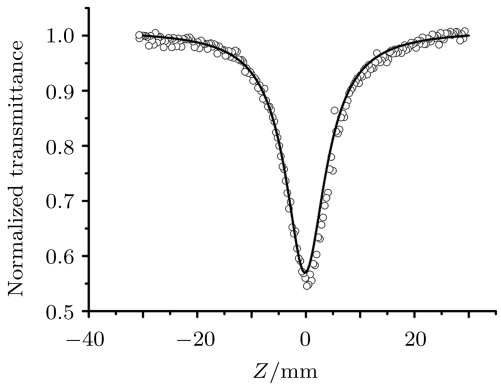


Fig. 6. Z-scan measured curves with a pulse energy of 1.00 μJ. The empty circles denote experimental results, the solid line refers to theoretical fit line considering mass transport.

There are some discrepancies between the theoretical lines and the experimental lines as shown in Fig. 4. The constant approximation of D_ψ is the problem. As mentioned above, the escaping velocity of the solute molecules is related to D_ψ. When the sample moves towards position $Z = 0$, the escaping velocity of the solute molecules becomes larger, and so does D_ψ. In our approximation, the value D_ψ is overestimated at large $|Z|$ positions, while underestimated at small $|Z|$ positions.

4. Conclusions

An energy transport theory is proposed to explain the nonsymmetrical RSA-to-SA transition of the

CuPcTs/DMSO in an open aperture Z-scan experiment with 21-ps laser pulse. Experimental results and theoretical calculations are taken to prove that excited state absorption induced mass transport is a phenomenon different from thermoinduced mass diffusion.

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