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Femtosecond Z-scan Measurement of the Third Order Nonlinear Optical Coefficient of CuPc Thin Film

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The third order nonlinear refractive index and absorption coefficient of copper-phthalocyanine (CuPc) thin film were measured by Z-scan method in ultrafast time regime. By changing pulse separation, we found that the nonlinear absorption behavior is different for the different pulse repetition rate. At 4MHz, the film exhibits RSA (reverse saturable absorption), while at 800kHz and 400kHz it shows SA (saturable absorption). Also the nonlinear refractive index is found to be different at 4MHz and other repetition rates.

Keywords Z-scan, CuPc, third order nonlinear coefficient

INTRODUCTION

CuPc possesses a highly conjugated two-dimensional π electron system and an exceptional chemical and thermal stability.[1] These make CuPc a strong candidate for the third-order nonlinear optical

material. To measure directly the sign and the size of the real and the imaginary parts of electronic $\chi^{(3)}$, we used the Z-scan technique in femto second time region.

EXPERIMENTAL

The Z-scan measurement was performed at 750nm with 150fs pulses from Ti:sapphire laser system. The pulse duration was measured by an autocorrelator. Pulse repetition rates were changed by a pulse selector, 400kHz, 800kHz, and 4MHz. The CuPc thin film was prepared by a vacuum evaporation at 10^{-6} Torr pressure. Thickness of the thin film measured by an alpha step profiler was 100nm. The linear absorption spectra of the CuPc thin film showed a strong absorption peak at 750nm (Q-band). To obtain the nonlinear absorption coefficient, the CuPc thin film was Z-scanned with the open aperture. To calculate the value of the nonlinear refractive index, the sample was Z-scanned with a closed aperture and the detected transmission data were divided by the open aperture data.

RESULTS AND DISCUSSION

The normalized transmittance without the aperture is

$$T(z) = 1 + \frac{\beta I_0(t) L_{eff}}{3\left(1 + \frac{z^2}{z_0^2}\right)} \qquad (1)$$

where $I_0(t)$ is the on-axis instantaneous intensity at focus (z=0). L_{eff} is effective sample thickness. The experimental result as a function of z at 800kHz repetition rate is shown in Figure 1(a). It is symmetric with respect to the focus where it has maximum transmission, thus SA is observed. β is determined from the result of curve fitting open aperture transmission. In our experiment, as $I_0(t)$ is 6.0 GW/cm^2, the β at 800kHz and 400kHz pulse repetition rate are -2.2×10^{-8} m/W and

-2.8×10^{-8} m/W. But at 4MHz, the sign is positive and the magnitude is much larger than the others. The experiment result at 4MHz is shown in Figure 1(b). It shows minimum value at focus, thus RSA is observed

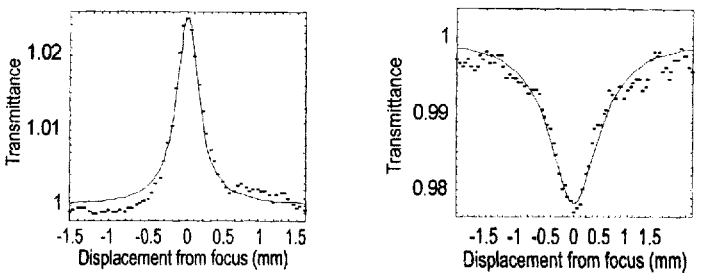

FIGURE 1 Open aperture experiment result (a) at 800kHz pulse repetition rate (b) at 4MHz pulse repetition rate

The energy level diagram of CuPc is shown in Figure 2. It consists of five levels showing the possibility of intersystem crossing.[1][2] At high repetition rate of 4MHz, the electrons in the ground state are initially excited to the vibrational manifold of S_1 at 750nm. During short pulse duration of 150fs, the electrons are less likely excited to the high-lying upper singlet states than to the low-lying triplet state, because the absorption cross-section of the $S_1 \rightarrow S_n$ transition of CuPc is usually much smaller than the $T_1 \rightarrow T_n$ transition.[2] The intersystem crossing to the lowest excited triplet state occurs during or after a laser pulse and then the electrons rapidly relax to the T_1. If the second pulse arrives within the lifetime of T_1 state, longer than 0.25 μs, it can lead to the triplet excited-state absorption. Therefore the open aperture Z-scan transmission is reduced and exhibits RSA behavior. On the other hand, at the low repetition rates, the electrons in T_1 have enough time to get down to the singlet ground state before the next pulse comes in. At these repetition rates, there is no excited-state absorption, which means that it exhibits a normal SA behavior. This is a very interesting result.

Only through a change in the pulse repetition rates at the same wavelength, the nonlinear absorption behaviors of CuPc film can be reversed. From this measurement, the triplet state lifetime of the CuPc thin film employed in this experiment is estimated to be between 0.25μs and 1.25μs. For the closed aperture Z-scan, the CuPc film has the peak-valley profile. It means that the sample has a self defocusing effect at 750nm.

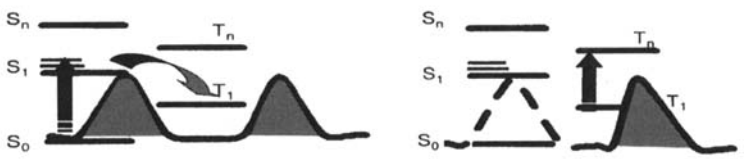

FIGURE 2 Energy level of CuPc (a) Electrons are excited by the first pulse to S_1 state, and then they go to directly T_1 state (b) the second pulse arrives, electrons in the T_1 are excited to T_n state by the 2nd pulse

And there is also a small difference between the results of 4MHz and the other pulses. At 4MHz, γ is -1.6×10^{-14} m^2/W, at 400kHz -1.1×10^{-14} m^2/W, and at 800kHz -1.2×10^{-14} m^2/W. The difference suggests that the accumulative thermal effect by increasing nonlinear absorption might affect the nonlinear refractive coefficient γ [3].

Acknowledgements

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