

Experimental investigation of the thermo-optical nonlinearity of solutions of synthesized rare-earth complexes

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The large nonlinearities of the solutions of a new type of rare-earth complexes $R_E(TTA)_4:HP$, synthesized by ourselves, are experimentally demonstrated. The critical powers for the self-trapping of a laser beam in the solutions were measured. The dependence of the self-trapping critical powers on the absorptivity of the solutions and the type of solute complexes was found. The analysis for the experimental results shows that the effects of self-focusing and self-trapping of light in the solutions are not due to the change of molecular local density but the thermo-optical nonlinearities of the dissolved molecules themselves.

1. Introduction

The excellent nonlinear optical properties of artificial synthesized organic materials have recently been receiving increased attention [1]. It is significant to test the optical nonlinearities of new synthesized materials before they are made into solid crystals. In accordance with the symmetric analysis of the tetra(2-thenoyl-trifluoroacetone) mono piperidine complexes of lanthanide trivalent ions synthesized in the Institute of Molecular Science of Shanxi University [2], we predicted that they might possess large optical nonlinearities. Their acetonitrile and alcohol solutions were employed as the nonlinear media to observe the self-focusing and self-trapping of laser beams in our experiments. The self-focusing and self-trapping effects of light in a 10 mm-long solution cell were clearly observed and recorded. The self-trapping critical powers of the beam were of the order of 10 mW and dependent on the type of complexes and absorptivity of solutions. The calculated nonlinear refractive indices n_2 of the solutions were of the order of $10^{-11} \text{ m}^2 \text{ W}^{-1}$ which were about 10^5 times that of CS_2 . The medium's response time was about $400 \mu\text{s}$. We considered that the reason for self-focusing and self-trapping in the solutions should be attributed to thermo-optical nonlinearities of the solute complexes, i.e. the complexes in the solutions have a positive temperature coefficient of refractive index $dn/dT > 0$ and so the heating of the

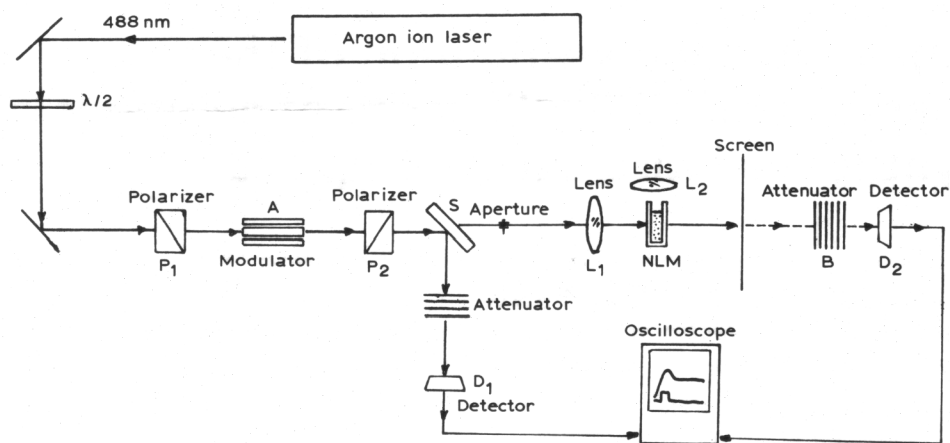


Figure 1 Experimental setup.

medium by a laser beam results in induced positive lens effects [3]. An electronic nonlinearity of the complexes was not found in our experiments.

2. Preparation of samples

The acetonitrile and alcohol solutions of the complexes $R_E(TTA)_4:HP$ (R_E represents the rare-earth elements in the complexes) were chemically prepared and their concentrations were accurately known. The sizes of the complexes in the solutions are ~ 1.9 nm. All samples were preserved in hermetic containers during the experiments to protect them from vaporization.

3. Experimental setup

The basic experimental setup was sketched in Fig. 1. A linearly polarized c.w. TEM_{00} argon laser was used as the light source, the output beam diameter ($1/e$) and divergence for the 488 nm laser line were 1.61 mm and 0.47 mrad. The input powers were controlled and scanned by a rotatable half-wave plate and electro-optical modulator (A) placed between two crossed polarizers P1 and P2. The beam splitter (S) divided the laser beam into two parts. The weaker part was directed to the detector D_1 to monitor the input power while most was focused into a 10 mm long hermetic solution-filled cell NLM by a positive lens L1 with a focal length of 45 mm. The diameter of the beam incident upon L1 was ~ 2.4 mm. The sample cell could be moved forward and backward freely in order to adjust the position of the focal point of the beam within it. The beam patterns at the output face of the sample cell were projected onto an observation screen S, 500 mm from the focal point of the laser beam and were recorded by a camera. To measure and monitor the transmitted laser powers through the cell NLM and the response time of the nonlinear medium, the screen was replaced by the detector D_2 with the attenuator B and the photo-current signals were displayed on an oscilloscope.

4. Experimental results

A TEM_{00} 488 nm c.w. laser beam was focused near the centre of the sample cell filled by the acetonitrile solutions of $R_E(TTA)_4:HP$ complexes. Under low input powers, we observed the unperturbed diffracted Gaussian beam trajectory and a large ~ 35 mm diameter light spot

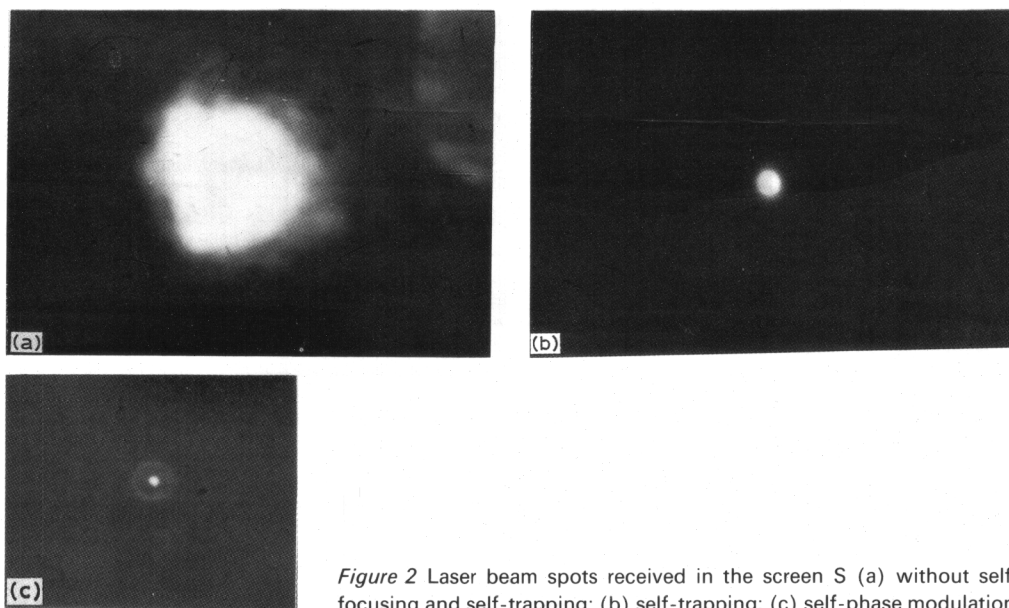


Figure 2 Laser beam spots received in the screen S (a) without self-focusing and self-trapping; (b) self-trapping; (c) self-phase modulation.

was received at the screen as shown in Fig. 2a. By slowly rotating the half-wave plate and gradually increasing the input powers, the beam shrank because of the onset of self-focusing and finally propagated as a self-trapped filament. The changing process of the beam trajectory from spreading to filament could be monitored through the magnifier L2. The long self-trapped filament propagated in the solution without significant beam spreading for a distance of ~ 5 mm which was 25 times the confocal distance of the laser beam. The self-trapped filament transmitted through the back face of the cell spread weakly, the diameter of the filament spot at the screen S was ~ 3 mm which was about 12 times less than the original laser spot (Fig. 2b). If, after the beam self-trapping, the input powers were continuously increased, the typical ring pattern of beam self-phase modulation appeared at the screen (Fig. 2c). The ring is due to the aberrations of the self-focusing beam, i.e. the peripheral rays cross the axis of beam [3].

For quantitatively comparing the intensities of the output beams with and without self-trapping, we replaced the observation screen by a 3 mm diameter aperture which let the self-trapped beam entirely pass through but blocked most of the power of the rest of the beam except its central portion. Figure 3a and b show the input (lower) and output (upper) waveforms obtained at 13 mW input power for the sample cell filled with the (a) pure acetonitrile and (b) Nd(TTA)₄:HP acetonitrile solution. The beam self-trapping occurred in the case of (b) but did not in the case of (a), therefore the transmitted intensity shown in (b) was ~ 9 times higher than that in (a). This observation was in good agreement with the calculated results for the Gaussian distribution of the laser beam intensity. The input powers at the moment at which the transmitted beam entirely passed through the 3 mm diameter aperture were taken as the critical powers of the solutions for beam self-trapping.

The critical powers were dependent on the types of the rare-earth elements in the complexes and especially on the concentrations of the solutions. The experimentally measured critical powers, P_c , and the absorption coefficients, α , for the acetonitrile solutions of various $R_E(\text{TTA})_4$:HP complexes with the same concentration ($\rho = 0.06 \text{ mol l}^{-1}$) are

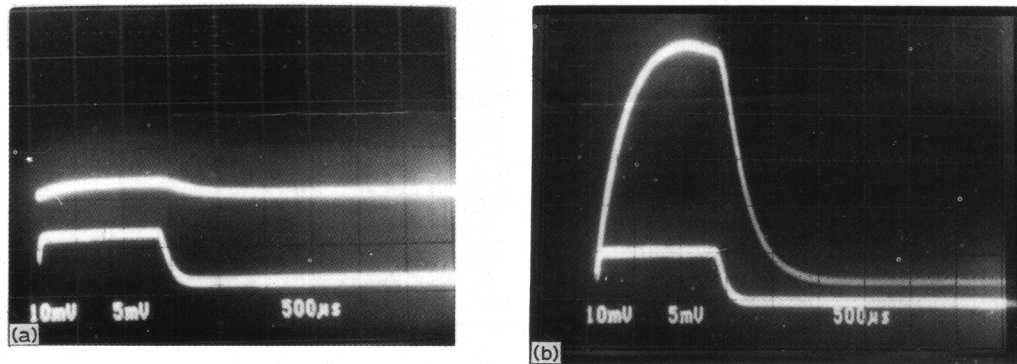


Figure 3 The input (lower curves) and output (upper curves) waveforms (a) without self-focusing and self-trapping (b) self-trapping.

given in Table I. We roughly calculated their nonlinear coefficients n_2 from the following relation [4]:

$$P_c = \frac{1.86c\lambda^2}{16\pi^2 n_2} \quad (1)$$

where P_c is the measured critical power for self-trapping, c the speed of light in vacuum and λ the laser wavelength. The concentration dependences of the self-trapping critical powers for the acetonitrile solutions of $\text{Nd}(\text{TTA})_4:\text{HP}$ are shown in Fig. 4. The experimental results show that the critical powers for all types of $R_E(\text{TTA})_4:\text{HP}$ solution always monotonously decrease in a similar manner to the curve of Fig. 4 as the concentrations of the solution were increased. Table II shows n_2 and $n_2/\rho\alpha$ for the acetonitrile solutions of $\text{Nd}(\text{TTA})_4:\text{HP}$ with different concentrations of ρ ($\rho\alpha$ indicates the absorption of the solutions).

By comparing the input (rectangular) and the output (with the inclined rising edge) waveforms (see Fig. 5), we found that the response time of the solution was about $400\ \mu\text{s}$.

For separating the electronic and thermal-optical nonlinearity we illuminated the solutions of complexes with a single laser pulse taken by a chopper to avoid thermo-relaxation. The chopper is a homemade electro-optical switch which consists of an electro-optical crystal (LiNbO_3) placed between two orthogonal polarizers. The switch is controlled by the pulse voltages applied to the crystal. The widths of pulses provided by a high voltage pulse generator can be changed from $100\ \mu\text{s}$ to $10\ \text{ns}$. The critical powers significantly increase as the width of optical pulses is decreased. When the width of the pulse was less than $100\ \text{ns}$ no self-defocusing was observed until $3\ \text{W}$ input power.

TABLE I $\rho = 60\ \text{mol m}^{-3}$

| | R_E | | | |
|--|-------|-------|-------|-------|
| | Nd | Er | Sm | Tm |
| $P_c (\pm 3\ \text{mW})$ | 13 | 24 | 38 | 170 |
| $n_2 (10^{-11}\ \text{m}^2\ \text{W}^{-1})$ | 3.364 | 1.824 | 1.151 | 0.258 |
| $\alpha (\text{cm}^{-1})$ | 0.40 | 0.29 | 0.17 | 0.05 |
| $n_2/\alpha\rho (10^{-14}\ \text{m}^6\ \text{W}^{-1}\ \text{mol})$ | 1.401 | 1.048 | 1.128 | 0.869 |

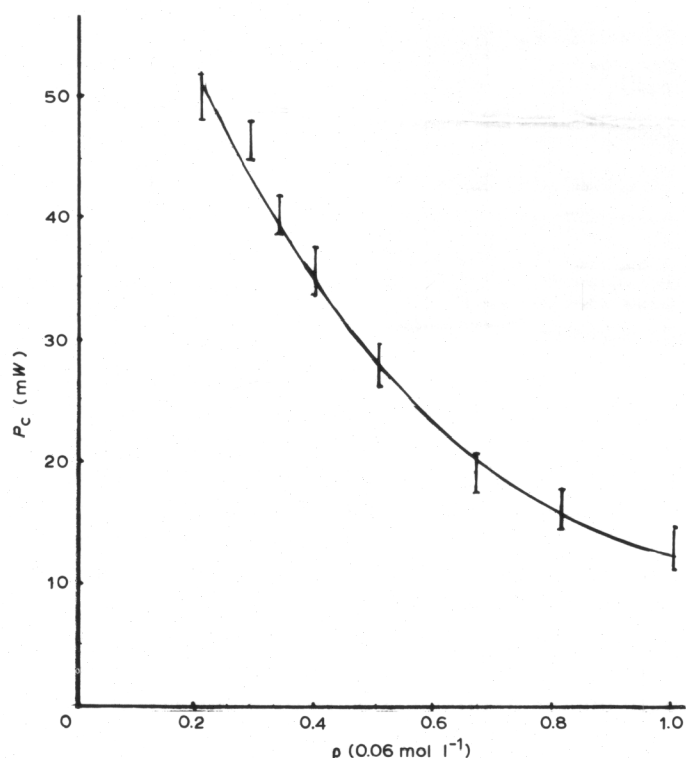


Figure 4 The concentration dependence of the critical powers for Nd(TTA)₄:HP acetonitrile solutions.

5. Discussion

The continuous-wave self-focusing and self-trapping of light in artificial Kerr media has been studied by several authors [4–6]. In these experiments the liquid suspensions of submicrometre dielectric particles were used as the nonlinear media. The laser fields in the media provided light-pressure forces that pull the higher-refractive-index particles into regions of high optical intensity [4, 6]. Consequently an increased local refractive index results so that a Gaussian laser beam in the medium would induce a positive lens effect and result in beam self-trapping. If the reason for self-focusing in our experiments was also the light pressure forces, the self-trapping critical powers should not depend on the chemical compositions of solutes but just on their sizes and weights. Theoretical analyses have indicated that the sizes and weights of various complexes in the R_E(TTA)₄:HP series have no significant difference [2]. However, we found that their beam trapping critical powers are quite different (see Table I). Thus the origin of the observed nonlinearity cannot be attributed to molecular orientational diffusion.

Indeed, the effect of a laser beam on particles with sizes less than 0.1 μm is more akin to

TABLE II Nd(TTA)₄:HP, $\alpha = 0.4 \text{ cm}^{-1}$

| | | | | | | | | |
|--|------|------|------|------|------|------|------|------|
| $P_c (\pm 3 \text{ mW})$ | 50 | 46 | 40 | 35 | 28 | 19 | 16 | 13 |
| $n_2 (10^{-11} \text{ m}^2 \text{ W}^{-1})$ | 0.88 | 0.95 | 1.10 | 1.25 | 1.56 | 2.31 | 2.73 | 3.36 |
| $\rho (\text{mol m}^{-3})$ | 13 | 17 | 20 | 23 | 30 | 39 | 48 | 60 |
| $n_2/\alpha\rho (10^{-14} \text{ m}^6 \text{ W}^{-1} \text{ mol})$ | 1.69 | 1.40 | 1.38 | 1.36 | 1.30 | 1.48 | 1.42 | 1.40 |

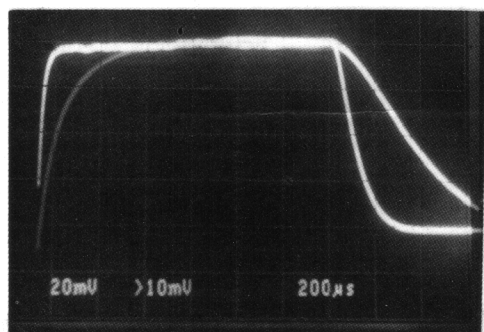


Figure 5 Input waveform with rectangular modulation and output waveform with inclined rising edge.

an effect on atoms, and the light forces on atoms are large only in the vicinity of a resonance transition frequency [8]. In our experiment, however, we use the 488 nm line of an argon laser which is far from the resonant frequency of the atoms. Thereby, the effects of light pressure on the molecular complexes of about 1.9 nm-size in the solutions can be ignored. In addition, the measured nonlinear response time of the solutions is about $400 \mu\text{s}$ which is much faster (about 10^3 times) than that of the liquid suspensions (about 1 s) [9]. Therefore, the nonlinear mechanism should be different. The response time of $400 \mu\text{s}$ is in the expected range for a thermo-optical nonlinearity. There is a possibility that the composition and concentration dependence of the nonlinearity can be explained in terms of the difference in linear absorption of the solutions. The refractive index change Δn arising from heating of the medium through optical absorption is expressed as [10, 11]

$$\Delta n = \Delta T \frac{dn}{dT} \quad (2)$$

where ΔT is the temperature variation on the cross-section of the laser beam. This depends upon the absorption of the medium which is determined by the product $\rho\alpha$ of the absorption coefficient α and the concentration ρ of the solutions, and the transverse distribution of the laser beam intensity. dn/dT is the temperature coefficient of the refractive index which directly depends upon the nonlinear coefficient n_2 of the media, and dn/dT is positive for beam self-focusing and self-trapping. $n_2/\alpha\rho$ can be considered as a performance parameter to compare the nonlinearity of variant materials. Tables I and II show that $n_2/\alpha\rho$ are different for the solutions of different complexes, but almost the same (to our experimental accuracy) for the solutions of the same complex $[\text{ND}(\text{TTA})_4:\text{HP}]$ with different concentrations. Therefore $n_2/\alpha\rho$ can characterize the nonlinearity of the solution complexes. The larger the $n_2/\alpha\rho$ is, the higher the nonlinearity.

We consider that the thermal-optical nonlinearity of the solutions should be attributed to the dissolved molecules in the solutions. In order to exclude the influence of the solvents, we experimented with the alcohol solutions of the $\text{R}_E(\text{TTA})_4:\text{HP}$ series complexes. The beam self-trapping was observed under the same levels of the critical power as long as the concentration of the solutions were the same as their acetonitrile solutions. In other respects, no beam self-focusing and self-trapping were found in the pure alcohol and acetonitrile up to the input power of 500 mW. As is well-known, the alcohol is a self-defocusing medium with $dn/dT < 0$ [3], but its $\text{R}_E(\text{TTA})_4:\text{HP}$ solutions showed strong self-focusing effects at low input power, it means that the complexes in alcohol have the positive temperature coefficient of refractive index and its absolute value is much higher than those of alcohol.

Unfortunately fast electronic nonlinearity of the complexes has not been found in our experiments. But we cannot come to the conclusion that these rare-earth complexes have

essentially no electronic component of the nonlinearity because the numbers of the complex molecules in the solutions were quite low and the input powers were not high enough. We can only note that the thermal-optical nonlinearity plays a dominant role in our self-defocusing experiments for the solutions of the complexes. For checking the electronic nonlinearity of the material, the experiments must be done with the powder or crystal of the complexes.

6. Conclusion

In conclusion, we have observed laser beam self-focusing and self-trapping phenomena in solutions of new synthesized rare-earth complexes. The critical powers for beam self-trapping are evidently dependent on the types of the rare-earth elements in the complexes and the concentrations of the solutions. The nonlinear refractive index n_2 of these media are much larger than that of CS_2 . The nonlinearities of the solutions arise from the thermo-optical nonlinear properties of the complexes in the solutions. Therefore, the experimental results show that the new synthesized $\text{R}_E(\text{TTA})_4:\text{HP}$ complexes might at least become a type of promising organic thermo-optical nonlinear material. It should be mentioned that the measurement of the critical power of the beam self-trapping, and hence the evaluation of the optical nonlinearity coefficients n_2 , are not very precise, but the relative errors of measurements are tolerable ($\pm 3 \text{ mW}$). Therefore, the order of the obtained nonlinearity coefficients and their composition and concentration dependence are valid.

References

1. D. J. WILLIAMS (ed), Nonlinear Optical Properties of Organic and Polymetric Materials, American Chemical Society Symposium.
2. YANG PIN and WANG YUEKUI, *Scientia Sinica B* **30** (1982) 907.
3. S. A. AKHAMANOV, et al. *IEEE J. Quantum Electron.* **QE-4** (1968) 568.
4. A. ASHKIN et al. *Opt. Lett.* **7** (1982) 276.
5. J. H. MERBURGER, *Prog. Quantum. Electron.* **4** (1975) 35.
6. F. W. DUBBY and J. R. WHINNERY, *Appl. Phys. Lett.* **13** (1968) 284.
7. P. W. SMITH, et al. *Opt. Lett.* **6** (1980) 284.
8. A. ASHKIN, *Science* **210** 4474 (1980) 1081.
9. P. W. SMITH, *Opt. Lett.* **10** (1984) 131.
10. J. C. KHOO, *Appl. Phys. Lett.* **41** (1982) 909.
11. M. SHEIK-BAHAE et al. *Opt. Lett.* **14** (1989) 955.