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All-optical switching and nonlinear optical properties of HBT in ethanol solution*

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This paper demonstrates an all-optical switching model system comprising a single pulsed pump beam at 355 nm and a CW He–Ne signal beam at 632.8 nm with 2-(2′-hydroxyphenyl)benzothiazole (HBT) in ethanol solution. The origins of the optical switching effect were discussed. By the study of nonlinear optical properties for HBT in ethanol solvent, this paper verified that the excited-state intramolecular proton transfer (ESIPT) effect of HBT and the thermal effect of solvent worked on quite different time scales and together induced the change of the refractive index of HBT solution, leading to the signal beam deflection. The results indicated that the HBT molecule could be an excellent candidate for high-speed and high-sensitive optical switching devices.

Keywords: all-optical switching, 2-(2′-hydroxyphenyl) benzothiazole, ESIPT, nonlinear optical properties

PACC: 4260K, 7820, 4265

1. Introduction

Switch is the basic building block of information processing systems. High-speed and high-sensitive optical switching devices play an important role in optical information processing, optical computation and optical communication.[1−3] The key element in an all-optical switching is the material which exhibits large nonlinear optical response. Many materials for optical switching devices have been reported, including inorganic and semiconductor materials, multiple quantum wells, liquid crystals and so on.[4−9] However, few researches are focused on organic-molecule-based devices with excited-state intramolecular proton transfer (ESIPT) effect. Recently, our group have reported the optical switching effect of some organic molecules with ESIPT effect and obtained some significant results.[10,11]

2-(2′-hydroxyphenyl)benzothiazole (HBT) is a typical compound possessing ESIPT effect and is perhaps the simplest compound which offers tantalizing possibilities of optical processing at a molecular level.[12] On the one hand, HBT exhibits high quantum efficiency, large absorption cross-section and stability against environmental perturbations.[13−17] On the other hand, the ESIPT can result in the population and relaxation of several temporal electronic states, causing a change in the nonlinear refractive index of the HBT molecule, and time-resolved studies have shown that this process is ultrafast, less than a few picoseconds or even on the subpicosecond time scale.[13,14,17] Therefore, the HBT molecule with ESIPT effect may be an excellent nonlinear optical material for various types of photo-electronic devices.

In this paper, we demonstrate a simple all-optical switching model system with HBT solution for the first time. A single pulsed pump beam at 355 nm modulated the transmission signal of a low-power CW He–Ne signal beam at 632.8 nm. Experimental results and theoretical calculations show that the ESIPT effect of HBT and the thermal effect of solvent worked on quite different time scales and together affected the optical switching characteristics. Furthermore, we also determine the nonlinear refractive index n_2 by using the Z-scan technique. By means of the study on nonlinear optical properties of HBT solution, we verified that the origin of the nonlinear refractive index is mainly attributed to the ESIPT effect of the HBT

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molecule.

2. Experiment

HBT was purchased from Acros Co. and further purified by re-crystallization with methanol before use. Ethanol of spectra-grade served as solvent, and the concentration of HBT solution was 2×10^{-2} mol/L.

The experimental setup for observing the optical switching effect of HBT solution is shown in Fig.1. The 355 nm pump beam is the third-harmonic generation of a mode-locked Nd:YAG laser (YG901C, Quantel Co.), which generates 35 ps laser pulses operating at 10 Hz repetition rate. An electronically controlled shutter is used to ensure that only one laser pulse of pump beam arrives at a 1 mm thick quartz cell with HBT solution every two seconds. The signal beam, from a 20 mW CW 632.8 nm He–Ne laser, intersects with the pump beam in the sample cell, and is monitored by a photomultiplier tube (PMT) connected with a digital oscilloscope (TSD3052B, Tektronix). To ensure maximum overlap of the pump beam with the signal beam inside the sample cell, the intersecting angle of the two beams should be as small as possible, which is important for the precision measurement of beam-spot size. All the measurements of photoelectric signal from the signal beam and PMT are performed in a shielded room.

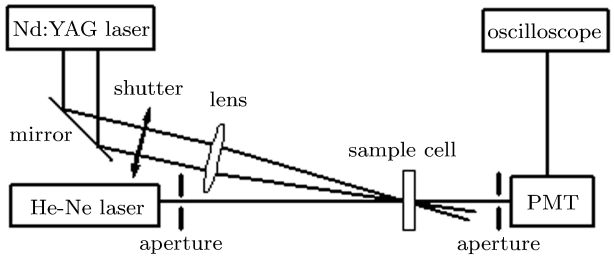


Fig.1. Experimental setup of all-optical switching of HBT solution.

3. Results and discussion

3.1. All-optical switching effect of HBT solution

Figures 2(a) and 2(b) show the typical oscilloscope pictures for 1 mm and 0.5 mm beam-spot radii sizes respectively. When the pump beam is shut off by the shutter, the signal beam can pass through the sample cell and the aperture, and then is received by the PMT. Here, the oscilloscope shows a high horizontal electrical signal (switch 'on' state). Once the shutter is opened and the pump laser beam irradiates the HBT solution, the signal beam deflects from its original route inside the sample cell and propagates away from the aperture before the PMT. As a result, the high horizontal electrical signal on the screen of the oscilloscope falls off suddenly (switch 'off' state), that is to say the signal beam is switched off temporarily. Later, when the pump beam is shut off again by the shutter, the HBT solution gradually recoveries to its original state and the He–Ne signal beam can pass through the aperture again. The signal on the screen of the oscilloscope returns to the original level.

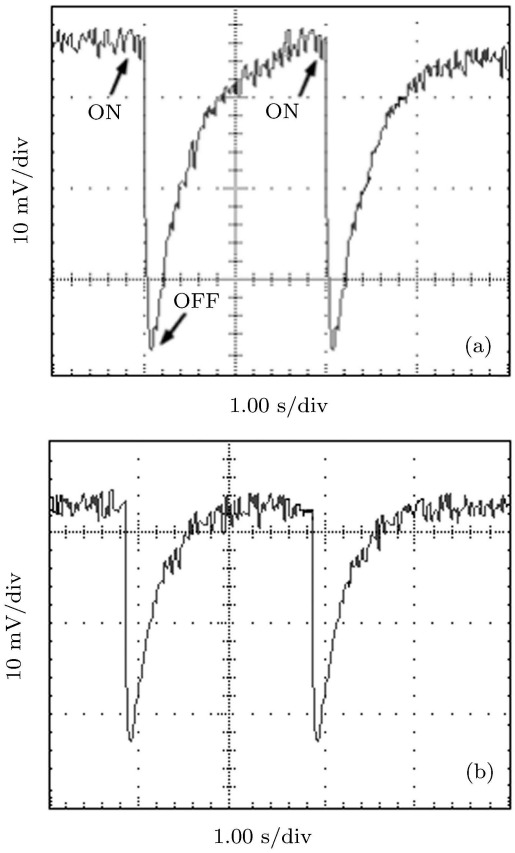


Fig.2. Optical switching signal of HBT in ethanol solvent. (a) $w_0 = 1$ mm; (b) $w_0 = 0.5$ mm.

The origin of the optical switching effect of HBT in ethanol solvent is mainly due to the change of the refractive index of HBT solution, which leads to the deflection of the signal beam. There might be two main reasons why the refractive index of HBT solution was changed. One reason is the ESIPT effect of HBT. Because HBT is a typical compound exhibiting ESIPT effect, and exists largely in the structure of enol (N) under the normal condition. Excitation of the enol

form N to its first singlet excited state gives rise to an enol form N* which turns into an excited state T* of the keto form via an intramolecular proton transfer. Following deactivation to the keto ground state T, an inverted proton transfer (IPT) leads back to the starting form N.[16,17] This process is illustrated in Fig.3 with a simple four energy-level scheme. In short, the enol form can turn into the keto form under the irradiation of the UV pump beam, which results in the population and relaxation of several electronic states. Thus, the nonlinear refractive index of the HBT molecule would be changed.

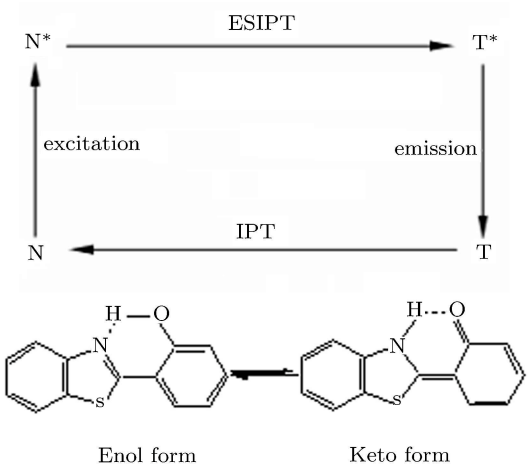


Fig.3. Excited-state intramolecular proton transfer process in a four-level scheme for HBT.

The other reason is the thermal effect of HBT solution as a result of the irradiation of the 355 nm pump beam. Because the thermal diffusion generates the thermal-lens effect, which produces a negative nonlinear refractive index and can also change the refractive index of the HBT solution.

It is conceivable that the start-up (from 'on' state to 'off' state) of the optical switching effect should rest with the one with the fastest response time in the all factors. Previous work has shown that the switch-off duration of the optical switching effect is about the picosecond time scale,[10,11] which is very close to the response time of ESIPT.[13,14] As for the rise time of the thermal-lens effect $t_{\rm rise}$, it is given by[18,19]

$$t_{\rm rise} = \omega_0/v_{\rm s}\,, \tag{1}$$

where ω_0 is the beam-spot radii size and $v_{\rm s}$ is the acoustic velocity in the solution. We can assume that the thermal property of HBT solution is governed by the ethanol solvent. In our experiments, $\omega_0 = 0.5$ and 1 mm, $v_{\rm s} = 1161.8$ m/s, so the rise time for thermal lens effect is about 0.43 μs and 0.86 μs respectively, which are far slower than the response time of the ESIPT effect of HBT. Therefore, the optical switching effect of HBT solution originates from the ESIPT effect of HBT in the beginning.

The recovery (from 'off' state to next 'on' state) of the optical switching effect should lie on the one that has the slowest recovery time in all factors. The duration of the IPT process $t_{\rm IPT}$ is about on nanosecond time scale.[13,14,17] Then, the thermal-relaxation time of HBT solution can be estimated from the relation[20]

$$t_{\rm relax} = \omega_0^2 \rho C_{\rm p}/4\kappa\,, \tag{2}$$

where ρ is the liquid density, $C_{\rm p}$ is the specific heat at constant pressure and κ is the thermal conductivity. Some physical parameters of ethanol used in the calculation and the corresponding results are listed in Table 1. The calculated thermal-relaxation time $t_{\rm relax}$ is about 2.59 and 0.65 s, which is much larger than the $t_{\rm IPT}$ time of the IPT process. Compared with the optical switching signal curve in Fig.2, the theoretical calculations are in approximate agreement with the experimental results. It shows that the recovery of optical switching effect is determined by the thermal-relaxation of the HBT solution in the end. This is why the signal does not return immediately to the original level and a 'tail' phenomenon appears in the all-optical switching signal curve after the pump beam pulse dies away. The slow increasing 'tail' is mainly attributed to the thermal-contribution mechanism.

Table 1. Physical parameters of ethanol and the corresponding calculated $t_{\rm relax}$ values.

Quantity	ρ/(g/m^3)	$C_{\rm p}$/(J/g·K)	κ/(W/m·K)	$t_{\rm relax}$/s ($\omega_0 = 1$ mm)	$t_{\rm relax}$/(s) ($\omega_0 = 0.5$mm)
Value	7.89×105	2.38	0.181	2.59	0.65

According to the discussion and the theoretically calculated results in the above, the condition

$$t_{\rm ESIPT}({\rm ps}) < t_{\rm IPT}({\rm ns}) < t_{\rm rise}(\mu{\rm s}) < t_{\rm relax}({\rm s}) \tag{3}$$

is satisfied. So the fast ESIPT dynamics is totally obscured by the slow thermal effect dynamics. As a result, the ESIPT and the thermal effect together induced the refractive index variation and dominated

the optical switch 'off' and 'on' respectively. In this case, it is necessary for us to investigate the nonlinear refractive index of HBT solution, and then take measures to weaken the 'tail' of the optical switching.

3.2. The nonlinear refractive index measurement

The nonlinear refractive index n_2 of HBT solution was determined by using the Z-scan technique.[10,11] Fig.4 shows the Z-scan experimental result. The scatter points represent experimental data, and the solid curve is theoretical fitting one. The curve shows a symmetric valley–peak configuration, which means that the nonlinear refractive index n_2 of HBT solution is positive. The normalized transmittance of the fitted curve is given by[18]

$$T(z) = 1 + \frac{4\langle\Delta\Phi_0(t)\rangle x}{(x^2+9)(x^2+1)} + \frac{\langle\Delta\Phi_0(t)\rangle^2}{(x^2+9)} + \cdots, \quad (4)$$

with

$$\Delta\Phi_0(t) = kn_2 I_0 L_{\text{eff}}, \quad (5)$$

where $x = z/z_0$ ($z_0 = \pi\omega_0^2/\lambda$ is the Rayleigh diffraction length), $\langle\Delta\Phi_0(t)\rangle$ represents the time-averaged on-axis phase shift at focus, k is the wave vector, n_2 (SI) is the nonlinear refractive index, I_0 is the on-axis excitation intensity in the focus plane and $L_{\text{eff}} = [1-\exp(-\alpha L)]/\alpha$, where α is the linear absorption coefficient. Transforming Eq.(6), we can write the nonlinear refractive index n_2 as

$$n_2 = \frac{\sqrt{2}\langle\Delta\Phi_0(t)\rangle}{kI_0 L_{\text{eff}}}. \quad (6)$$

In this equation, except for the value of $\langle\Delta\Phi_0(t)\rangle$, the other parameters can be easily obtained.

Equation (4) is used to fit numerically the Z-scan curve to determine the value of $\langle\Delta\Phi_0(t)\rangle$, and then calculate the corresponding n_2 based on Eq.(5) at the given I_0. The fourth and higher terms on the right-hand side of Eq.(4) are neglected in the process because the absolute value of phase shift is at focus $|\langle\Delta\Phi_0(t)\rangle| \leq 1$.[21,22] Compiling a program with MatLab to calculate the $\langle\Delta\Phi_0(t)\rangle$ value, we can easily obtain the n_2 value according to Eq.(6). As a result, the nonlinear refractive index n_2 is about $(4.74 \pm 0.2) \times 10^{-18}$ m^2/W. The main reason of uncertainty in the value of n_2 is the fluctuation of the irradiance. In order to reduce the error, all Z-scan measured data are average values of the 20 pulses. The relative error is only about 4%. So the Z-scan data have a high reliability and repeatability.

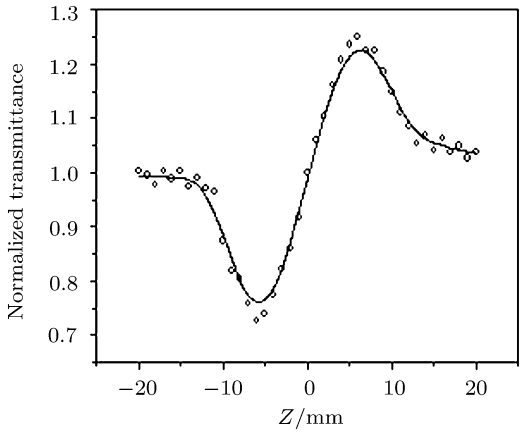


Fig.4. Z-scan curve of HBT solution. The scatter points represent experimental data, and solid curve is theoretical fitting curve.

In order to inspect the contribution of the solvent to the nonlinear refractive index of the HBT solution, we used pure ethanol as the sample and measured the nonlinear refractive index under the same condition. The experimental result shows that the n_2 value of the ethanol is much less than that of HBT solution, so the contribution of the ethanol to n_2 of the HBT solution can be ignored. Therefore, we conclude that the principal origin of the nonlinear refractive index of HBT solution is the ESIPT effect of HBT under the pump beam. In other words, it is ESIPT effect of HBT that starts up the optical switching effect.

We have analysed the origin of the nonlinear refractive index and the key factors influencing the optical switching effect of HBT solution in the above. Then, how can we effectively weaken the 'tail' phenomenon of the optical switching? As the expressions shown in Eqs.(2) and (3), the recovery time of the optical switching effect is dominated by the thermal-relaxation time, and the latter is only related to the beam-spot size ω_0 for the given solvent. Therefore, the way by reducing the beam-spot size can markedly shorten the thermal-relaxation time, which has been shown to be in good agreement with our experimental results. A similar experimental result was obtained by Karlheinz Strobl and Golub.[20] They fabricated an all-optical switching device by using the thermal nonlinearity of an absorbing liquid and obtained a very short thermal-relaxation time, which was about 80 μs, when the beam-spot size $\omega_0 \approx 5$ μm. Consequently, it appears possible that complete optical switching at low power and short switching time ($\sim$ ms- even μs-

scale) can be achieved, when the beam-spot size decreases from mm-scale to μm-scale in our experiment, on which a particular and thorough investigation is in process.

4. Conclusion

In summary, we have shown a simple all-optical switching model system with HBT solution. The optical switching effect originates from the refractive index change of HBT solution. The primary origin of the nonlinear refractive index of HBT solution is the ESIPT effect of HBT molecule under the ultraviolet pump beam. The recovery time of the optical switching effect is dominated by the thermal effect of HBT solution. Reducing the signal beam waist radius is a viable means of accelerating the recovery of the optical switching effect. Therefore, the HBT molecule with the ESIPT effect could be an excellent candidate for high-speed and high-sensitive optical switching devices.

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