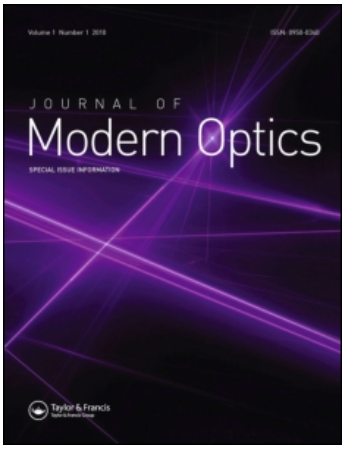

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Nonlinear optical properties of mercury dithizonate in a polymer film

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Abstract. The absorption spectra of *trans* and *cis* isomers of mercury dithizonate in a doped poly(methyl methacrylate) film are measured, and the optical properties of the two isomers are analysed. The properties indicate that different isomers of mercury dithizonate can convert into each other when irradiated by light of appropriate wavelength. With the *Z*-scan method, the nonlinear optical properties of mercury dithizonate are investigated, and experimental data on the nonlinear refractive index and the change in refractive index are obtained. The changes in refractive index as a function of wavelength are obtained by the Kramers–Kronig transformation.

1. Introduction

The photochromism of mercury dithizonate was discovered by Irving *et al.* [1] and Webb *et al.* [2] respectively in the 1950s. By the investigation of the mechanism of photochromism, Meriwether *et al.* [3] proposed that the photochromism process was the isomerization reaction in the molecules of mercury dithizonate, which included two processes: hydrogen N–N transfer and *cis–trans* isomerization of the C–H double bond. Wu *et al.* [4] investigated the dynamics of mercury dithizonate in macromolecules and found that the breakdown processes of the S–Hg bond and photon transfer were the keys to photochromism, while isomerization seldom occurred. Wang and Wu [5] explored the return process of mercury dithizonate in a polymer and concluded that the photochromic mechanics was a bimolecular process, that is transfer of hydrogen between molecules, instead of the transfer process of hydrogen in one molecule. Mercury dithizonate has both photochromic properties in a wide range of wavelengths and significant nonlinear optical properties. The latter feature will be discussed in this paper.

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2. The molecular structure and the absorption spectra of two isomers of mercury dithizonate

The structure and isomers of mercury dithizonate are shown in figure 1. The preparation of mercury dithizonate polymer film is as follows: mercury dithizonate and poly(methyl methacrylate) (PMMA) dissolved in chloroform respectively, a solution of mercury dithizonate (10^{-4} mol l^{-1}) and a solution of PMMA (5 wt%) are mixed together completely, then the mixed solution is spread on a clean glass plate uniformly and dried at room temperature for 24 h [5]. The thickness of the film is about 40 μm, and the concentration of mercury dithizonate in PMMA medium is 5.89×10^{-3} mol l^{-1}, which is measured by the standard working curve method.

The absorption spectrum of the mercury dithizonate polymer film is measured in the dark, then the mercury dithizonate polymer film is irradiated using a He–Cd laser (443 nm, 5 mW cm^{-2}) for about 10 s; as a result, most of the mercury dithizonate molecules isomerize from *trans* to *cis* and the colour of the sample turns from light brown to blue; immediately, the absorption spectrum of the sample was measured. Curves 1 and 2 in figure 2 are the absorption spectra of the *trans* to *cis* isomers respectively of mercury dithizonate. The absorption spectra indicate that mercury dithizonate has two absorption peaks located at 490 nm and 630 nm respectively. After irradiation using the He–Cd laser (443 nm), mercury dithizonate molecules isomerize from *trans* to *cis* and the number of *trans* molecules is reduced; as a result, the absorption peak at 490 nm increases. Accordingly, the contribution of *trans* molecules to the absorption spectrum decreases, and the absorption peak corresponding to the *trans* isomer decreases too. On the contrary, the number of

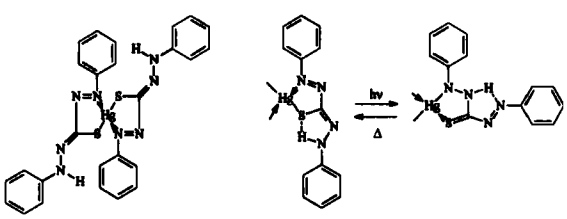

Figure 1. (*a*) Molecular structure and (*b*) isomers of mercury dithizonate.

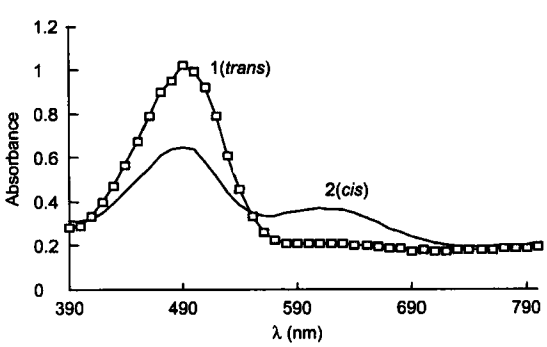

Figure 2. Absorption spectra of the *trans* and *cis* isomers of mercury dithizonate in a doped PMMA film.

the *cis* molecules increases, and the contribution of the *cis* molecules to the absorption spectrum increases, so the corresponding absorption peak becomes higher. Comparing curve 1 with curve 2, we can conclude that the absorption peaks at 490 nm and 630 nm refer to the *trans* isomer and *cis* isomer respectively.

After irradiation with a He–Cd laser beam, the sample of mercury dithizonate remains blue for a couple of days. This property indicates that the mercury dithizonate polymer film can be used as an optical storage material. On irradiation using a He–Ne laser ($\lambda = 633$ nm), the *cis* isomer isomerizes to the *trans* isomer, so the blue colour of the sample disappears and the film returns to the original brown colour. This means that the information stored in the sample can be erased. So the mercury dithizonate polymer film can be used as an erasable optical storage medium.

3. Experiment

The Z-scan method described by M. Sheik–Bahae *et al.* [6] in 1989 is a simple and sensitive technique for determining the intensity-dependent refraction index n_2 of cubic nonlinear optical materials. In the experimental set-up shown in figure 3, a Gaussian beam focuses on the thin sample and undergoes phase and amplitude distortions during propagation. An aperture and a photodetector D_2 are centred at the beam and located in the far field to record the power passing the aperture. The photodetector D_1 is used to detect part of the incident power and to eliminate the effect of the fluctuation of incident power on measured results. Because of the lens effect caused by nonlinear refraction, the beam transmitting the sample will diverge for negative nonlinear materials and will focus for positive nonlinear materials. When the sample is scanned around the waist of the focused beam along the z axis, the measured transmitted power will change with the distance that the sample is from the waist position. A typical peak–valley transmittance curve is obtained and then the nonlinear refractive index can be inferred.

The refractive index of nonlinear optical materials can be written as

$$n = n_0 + \Delta n, \tag{1}$$

where n is the total refractive index, n_0 is the linear refractive index, Δn is the change in refractive index that can be written as

$$\Delta n = n_2 I, \tag{2}$$

where n_2 is the intensity dependent index of refraction, and I is the intensity of the Gaussian beam inside the film:

$$I = \frac{2P}{\pi\omega^2}, \tag{3}$$

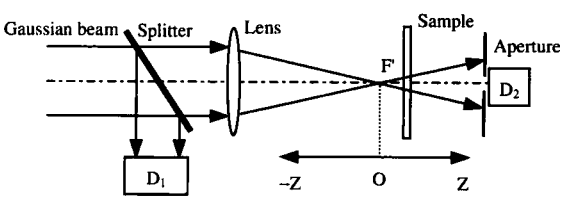

Figure 3. Schematic diagram of the Z-scan method.

where ω is the waist radius of the incident beam inside the film and P is the power of the Gaussian beam.

Let z_0 be the diffraction length, L the thickness of the sample and λ the free space wavelength of the beam. If $z_0 = \pi\omega^2/\lambda > L$, the sample can be considered as a thin medium. In our experiment, the condition $z_0 > L$ is satisfied. For a thin medium, the phase shift $\Delta\Phi_0$ on axis can be calculated from

$$|\Delta\Phi_0| = \frac{\Delta T_{P-V}}{0.406(1-s)^{0.25}}, \text{ for } |\Delta\Phi_0| \leq \pi, \tag{4}$$

where ΔT_{P-V} is the normalized transmittance difference between maximum transmittance and minimum transmittance, and $s = P_a/P_0$ is the linear transmittance (here P_a and P_0 are the measured powers using a closed aperture and an open aperture respectively). The phase shift $\Delta\Phi_0$ can be calculated from

$$\Delta\Phi_0 = \frac{2\pi}{\lambda}\Delta n L_{eff} = \frac{2\pi}{\lambda} n_2 I L_{eff}, \tag{5}$$

where L_{eff} is the effective thickness of the sample expressed as

$$L_{eff} = \frac{1-\exp(-\alpha L)}{\alpha}, \tag{6}$$

where α is the effective absorption coefficient. Using equations (1)–(6) and the Z-scan data, we can calculate the refractive index change Δn of an optical nonlinear medium, and the effective nonlinear index can also be easily obtained.

Using a He–Ne laser ($\lambda = 633$ nm) as a probe beam, the measured results of the Z scan are shown in figure 4. The data in figures 4(a) and 4(b) are the measured results using a closed aperture and and open aperture respectively. The curves in figures 4(a) and 4(c) are normalized to the value when the sample is located in the focus position. In order to eliminate the effect of intensity-dependent transmittance of the sample on the measured results, the data in figure 4(a) are divided by the corresponding data in figure 4(b) and the corrected data are shown in figure 4(c). From figure 4(c), we got $\Delta T_{P-V} = 0.2$. Since $L = 40\,\mu$m, $P = 4$ mW, $s = 0.5$, $\omega = 0.037$ mm and $\alpha = 12.2\,\text{mm}^{-1}$, we obtained $\Delta n = -0.0011$ and $n_2 = -6.04 \times 10^{-10}\,\text{m}^2\,\text{W}^{-1}$.

Similarly, for the probe beam with $\lambda = 535$ nm, the results of the Z scan using a closed aperture and open aperture, and the corrected results are shown in figure 5. From figure 5(c), we obtained $\Delta T_{P-V} = 0.7$. Using $L = 40\,\mu$m, $P = 3$ mW, $s = 0.5$, $\omega = 0.06$ mm and $\alpha = 12.5\,\text{mm}^{-1}$, we found that $\Delta n = -0.0034$ and $n_2 = -7.06 \times 10^{-9}\,\text{m}^2\,\text{W}^{-1}$.

4. The Kramers–Kronig transformation

An optical material may have an obvious nonlinear optical effect in some wavelength ranges; however, the effect may be weak in other range. Hence, it is necessary to determine the wavelength-dependent characteristics of mercury dithizonate. Because of the limitation of the wavelengths of available lasers, it is difficult to obtain the changes in refractive index of the sample at various wavelengths by the Z-scan method. For this reason, we apply the Kramers–Kronig transformation to calculate the changes in refractive index of the sample at various wavelengths from the absorption spectra of the *trans* isomer and the *cis*

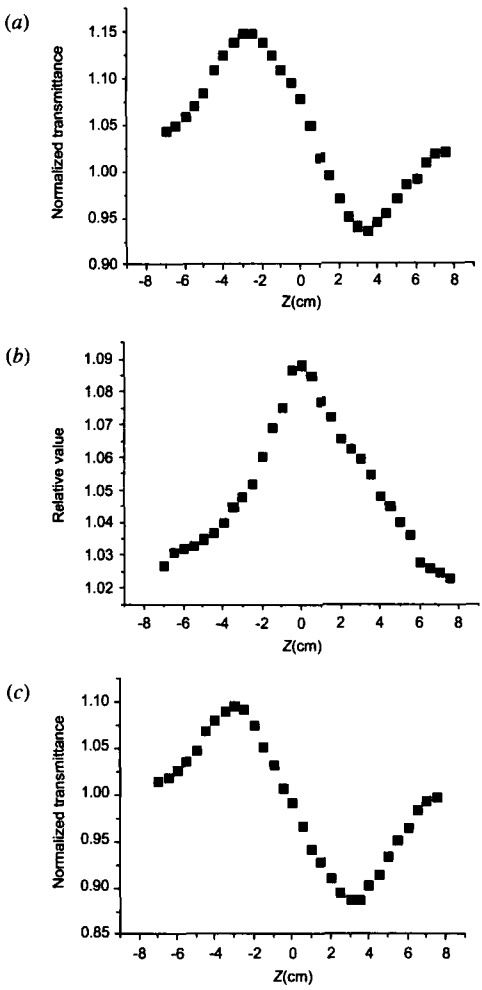

Figure 4. Normalized Z-scan transmittance of the mercury dithizonate film using the 633 nm laser: (*a*) closed-aperture Z scan; (*b*) open-aperture Z scan; (*c*) divided Z scan (obtained from dividing the closed aperture normalized Z scan by the open-aperture normalized Z scan).

isomer of the sample. So, the optimally operating wavelength of mercury dithizonate can be found.

According to the Kramers–Kronig relation, the change $\Delta n(\lambda)$ in the refractive index as a fuction of wavelength can be calculated from

$$\Delta n(\lambda) = \frac{2.3026}{2\pi^2 L} \mathrm{PV} \int_0^\infty \frac{A_1(\lambda') - A_2(\lambda')}{(1 - \lambda'^2/\lambda^2)} \, \mathrm{d}\lambda', \tag{7}$$

where PV represents the principal value of the Cauchy integral, and $A_1(\lambda)$ and $A_2(\lambda)$ are the absorbances of the *trans* isomer and *cis* isomers respectively of the sample. Using equation (7) and the data in figure 2, the changes Δn in refractive index of the sample as a function of wavelength shown in figure 6 are the differences between the refractive indices of the *cis* and the *trans* isomers of the sample. Apparently, the change in refractive index, which has two peaks located

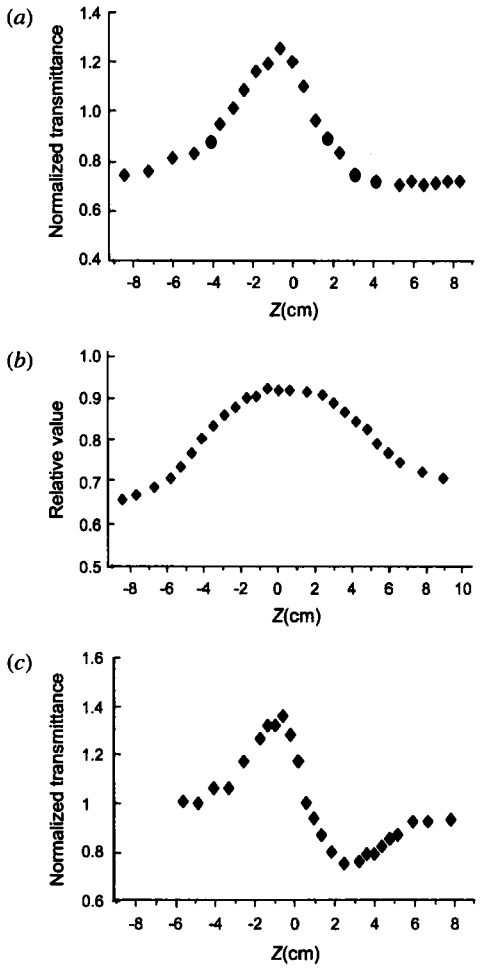

Figure 5. Normalized Z-scan transmittance of the mercury dithizonate film using the 535 nm laser: (*a*) closed-aperture Z scan; (*b*) open-aperture Z scan; (*c*) divided Z scan (obtained from dividing the closed-aperture normalized Z scan by the open-aperture normalized Z scan).

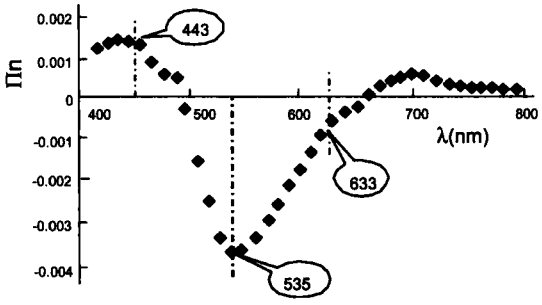

Figure 6. The change Δn in refractive index as a function of wavelength of the sample.

at 433 nm and 535 nm, but almost no change at 490 nm and 650 nm, depends on the wavelength sensitively. The nonlinear effect is most obvious for a laser wavelength of 535 nm and it is negative.

5. Conclusions

The nonlinear optical properties of mercury dithizonate in a doped PMMA film were measured and the refractive index change and the intensity-dependent index of refraction are obtained by the Z-scan method at wavelengths of 633 nm and 535 nm respectively. The results indicate that mercury dithizonate has a larger optical nonlinearity and wide responsive bandwidth:

(1) n_2 in mercury dithizonate has been determined to be in the range from 10^{-10} to $10^{-9}\,m^2\,W^{-1}$, while other nonlinear materials such as the poly(phenylacetylene) and poly (p-methoxyphenylacetylene) have $n_2 = 6 \times 10^{-22}\,m^2\,W^{-1}$ and $n_2 = 1.1 \times 10^{-21}\,m^2\,W^{-1}$, respectively [7]; the averaged n_2 values for crystals $LiNbO_3$: MgO and KT_iOPO_4 are $2.0 \times 10^{-19}\,m^2\,W^{-1}$ and $1.2 \times 10^{-19}\,m^2\,W^{-1}$, respectively [8]; for eosin in a polymer film, $n_2 = 5.58 \times 10^{-16}\,m^2\,W^{-1}$ [9].

(2) For instance, the absorption spectrum of azobenzene-doped PMMA ranges from 380 to 400 nm [10]; the absorption spectrum of methyl red dye-doped PMMA film is from 400 to 550 nm [11]. Comparatively, the absorption spectra of mercury dithizonate ranges from 390 to 690 nm, so that almost the whole range of visible light can change the optical nonlinearity of mercury dithizonate.

According to the absorption spectra of mercury dithizonate, the relationship between the change in refractive index and wavelength is obtained by means of the Kramers–Kronig transformation, and the optimum operating wavelength range is determined.

Acknowledgment

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