

## The Third-Order Nonlinear Optical Susceptibilities of Long-Chained Organic Molecules

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The third-order nonlinear optical susceptibilities of  $\beta$ -carotene, retinal and retinol have been measured using self-induced ellipse rotation and dc-Kerr effects. The strengths of  $\chi_{1221}(-\omega, \omega, -\omega, \omega)$  and  $\chi_{1221}(-\omega, \omega, 0, 0)$  measured by the two different methods are not different each other significantly. And it is observed that the strength of the third order nonlinear optical susceptibility is relatively insensitive to the conformational difference between retinal and retinol. It is also demonstrated that the third order nonlinear optical susceptibility of long-chained organic molecules is dependent upon the number of the double-bonds.

### I. INTRODUCTION

It is well known that the nonlinearity of the optical media can be induced deliberately by the polarized intense laser beam or dc-electric field. The optical nonlinearities of thin films and conjugated polymers have been measured using four wave mixing and third harmonic generation.<sup>[1]</sup> The third order nonlinear optical susceptibilities, especially  $\chi_{1221}(-\omega, \omega, -\omega, \omega)$ , of liquid,<sup>[2]</sup> glasses and cubic crystals<sup>[3]</sup> have been measured using the self-induced ellipse rotation (SIER). The self-induced ellipse rotation results from the self-induced circular birefringence which rotates the polarization ellipse of the pump beam. The dc-Kerr effect is due to the alignment of molecules in the presence of the dc-electric field. The medium responses optically as an uniaxial crystal where the electric field defines the optic axis. The induced third order nonlinear optical susceptibility  $\chi_{1221}(-\omega, \omega, 0, 0)$  can be measured by dc-Kerr effect.

Polymers with delocalized  $\pi$ -electrons are currently

of considerable interest due to their potential applications such as optical switches and other nonlinear optical devices.<sup>[4]</sup> Theoretical calculations showed that the large optical nonlinearities in organic molecules such as cyanines and polyenes are due to broad delocalization of the  $\pi$  electrons over the molecular chain.<sup>[5]</sup>

In this paper, we report the measurement of the third order nonlinear optical susceptibilities,  $\chi_{1221}(-\omega, \omega, -\omega, \omega)$  and  $\chi_{1221}(-\omega, \omega, 0, 0)$  of  $\beta$ -carotene, retinal and retinal and retinol and demonstrate that the number of conjugated double-bonds affects the third order nonlinear optical susceptibilities.

### II. THEORETICAL BACKGROUND

#### A. Experimental Samples

$\beta$ -carotene ( $C_{40}H_{56}$ ), retinal ( $C_{20}H_{28}O$ ) and retinol ( $C_{20}H_{30}O$ ) are long-chained organic molecules and their molecular structures are shown in Fig. 1. They have 11, 6, and 5 double bonds, respectively.

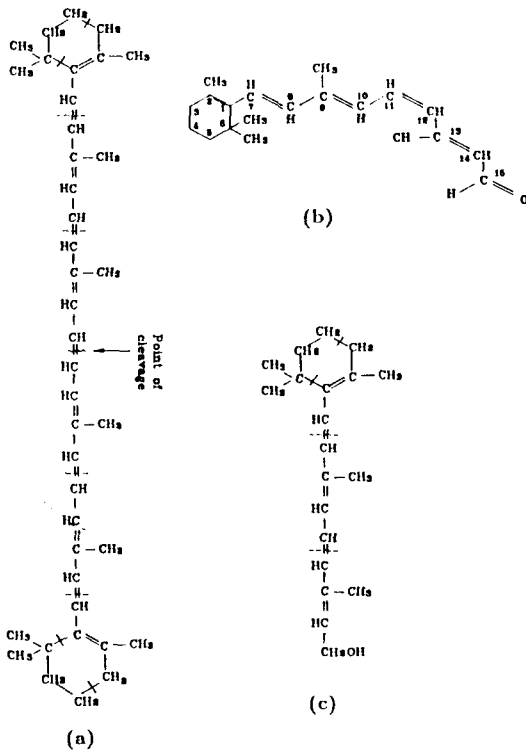


Fig. 1. Molecular structures of  $\beta$ -carotene, (a), retinal (b) and retinol (c).

$\beta$ -carotene can be obtained from carrots, sweet potatoes, and other yellow vegetables and vitamin  $A_1$  or retinol can be formed by cleavage of  $\beta$ -carotene as shown in Fig. 1. Retinal is an oxidized form of retinol and is the active component bound to an opsin in the visual cycle. It is related with a function of sensing low intensity light. The polarizability of  $\beta$ -carotene is expected to be largest among these samples due to its nearly linear structure and many double bonds. The electrons at the double bonds can move easily along the direction of molecules. However, the polarizabilities of retinal and retinol are difficult to compare at once due to their structural differences. Retinal is in the cis form at the 11th carbon atom while retinol is in the trans form. Retinal has an additional double bond between the last carbon and the terminal oxygen which has large electronegativity. A simple free electron model.<sup>[5]</sup> where  $\pi$ -electrons are assumed to move in a

periodic potential, may be used to estimate the low-frequency polarizability. However, the theoretical calculation of optical nonlinearities requires more realistic models. For example, electrons may be assumed to move in the periodic anharmonic potentials. The  $\pi$ -electrons are relatively free compared to the  $\sigma$ -electrons and optical nonlinearities will be due to these  $\pi$ -electrons moving around the anharmonic potential well. The magnitudes of nonlinear optical susceptibilities may depend on the geometry of organic molecules (cis- and trans-form), but they will largely depend on the number of the double bonds.

### B. Self-Induced Ellipse Rotation

The nonlinear optical susceptibility tensor is real in transparent media and the self-induced ellipse rotation (SIER) can be observed where the self-induced circular dichorism is absent. The rotational angle of polarization ellipse by the elliptically polarized beam is given by<sup>[2,3]</sup>

$$\theta = (\omega/2c)(\delta n_+ - \delta n_-)l = \frac{48\pi^2}{n^2c^2} \omega I_0 P \chi_{1221}(-\omega, \omega, -\omega, \omega) \quad (1)$$

where  $l$  is the length of the optical medium,  $P$  is the polarization factor given by  $P = (|E_-|^2 - |E_+|^2)/|E|^2$ ,  $I_0$  is the intensity of pump beam and  $n$  is the linear refractive index. The ratio of intensity of  $p$ -polarized wave to that of  $s$ -polarized beam at the analyzer is given by<sup>[6]</sup>

$$\gamma = \frac{I_s}{I_p} = \frac{\cos^2 \alpha \sin^2(\alpha - \theta) + \sin^2 \alpha \cos^2(\alpha - \theta)}{\cos^2 \alpha \cos^2(\alpha - \theta) + \sin^2 \alpha \sin^2(\alpha - \theta)} \quad (2)$$

where  $\alpha$  is the angle between the linear polarizer and the optic axis of  $\lambda/4$  plate. The intensity ratio  $\gamma$  can be measured and  $\chi_{1221}^{(3)}$  can be calculated from Eqs. (1) and (2).

### C. DC-Kerr Effects

The induced birefringence at  $\omega$  due to static electric field  $E(0)$  can be described in the following:

$$\Delta n = \delta n_{\parallel} - \delta n_{\perp} = (2\pi/n) 48 \chi_{1221}^{(3)}(-\omega, \omega, 0, 0) E^2 = K \lambda E^2 \quad (3)$$

where  $\delta n_{\parallel}$  and  $\delta n_{\perp}$  are the changes of the refractive indices for the beams polarized parallel and perpendicular to the direction of applied dc-electric field.  $K$  is the static Kerr constant.  $n$  is the refractive index at the angular frequency  $\omega$ ,  $E$  is the dc-electric field and  $\lambda$  is the wavelength. The phase difference of the beams with polarizations parallel and perpendicular to the direction of applied dc-field is given by

$$\delta = (2\pi/\lambda)\Delta n l, \tag{4}$$

where  $l$  is the cell length.

When the polarization axis of analyzer are perpendicular to the polarization direction of input laser beam, the signal intensity from the analyzer is zero in the absence of dc-electric field, while it is given by

$$I = I_0 \sin^2(\delta/2) \tag{5}$$

with the application of dc-electric field. The phase difference  $\delta$  can be measured by using a calibrated photodiode or by rotating the analyzer by angle  $\beta$  in the absence of dc-electric field to make the beam intensity equal to that given by Eq. (5). The angle  $\beta$  is equal to  $\delta/2$  in this case and the Kerr constant can be calculated from Eqs. (3) and (4).

### III. EXPERIMENTAL RESULTS AND DISCUSSIONS

#### A. Self-Induced Ellipse Rotation

The experimental setup for self-induced ellipse rotation is shown in Fig. 2. A Q-switched Nd:YAG laser (Spectra Physics DCR-2) of peak power 35 MW/cm<sup>2</sup>, pulsewidth 8.5 ns was used. The length

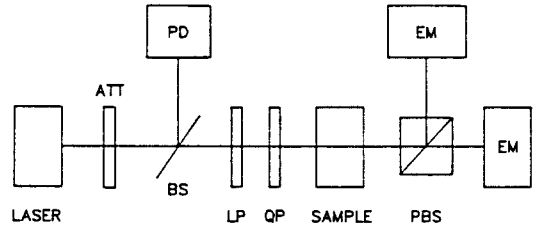


Fig. 2. Experimental arrangement for self-induced ellipse rotation.

ATT: attenuator, BS: beam splitter, LP: linear polarizer, QP: quarter-wave plate, PBS: polarizing beam splitter, EM: energy/power meter, PD: photodiode.

of the cell was 15 cm. An aperture of diameter 3 mm was used to select the center portion of the radial profile of incident laser pulse. The fast axis of a quarter wave plate was rotated by  $\alpha$  relative to the axis of linear polarizer to produce an elliptically polarized laser beam. The axis of analyzer was parallel to that of linear polarizer. The polarization factor  $P$  is given by

$$P = 2 \sin\alpha \cos\alpha \tag{6}$$

From the measurements of the transmitted intensity ratio  $\gamma(\theta)$ , one can deduce the rotational angle of polarization ellipse  $\theta$  in Equation (1). Then the third-order optical susceptibility can be obtained by measurements of  $\gamma(\theta)$  through relationship between Equations (1), (2) and (6).

The peak value of the transmitted intensity ratio of  $s$ - and  $p$ - polarized components  $\gamma = I_s/I_p$  at the analyzer was measured with a power/energy meter (Scientech 362). From the ratio ( $\gamma = I_s/I_p$ ) for saturated  $\beta$ -carotene, unsaturated retinal and retinol in

Table 1. The third order nonlinear optical susceptibilities of  $\beta$ -carotene, retinal and retinol.

Sample	$\beta$ -Carotene	Retinal	Retinol
Number of double bond (SIER)	11	6	5
$\chi^{(3)}_{1221}(-\omega, \omega, \omega, -\omega)$ (cm <sup>3</sup> /erg)	$(3.2 \pm 0.2) \times 10^{-13}$	$(2.6 \pm 0.2) \times 10^{-13}$	$(2.2 \pm 0.3) \times 10^{-13}$
(DC-Kerr Effect)			
$\chi^{(3)}_{1221}(-\omega, \omega, 0, 0)$ (cm <sup>3</sup> /erg)	$(3.3 \pm 0.2) \times 10^{-13}$	$(2.8 \pm 0.3) \times 10^{-13}$	$(2.4 \pm 0.3) \times 10^{-13}$

$\text{CS}_2$ , the third-order optical susceptibility is accordingly obtained.  $\beta$ -carotene of  $7.6 \times 10^{-3} \text{g}$  was dissolved in 15 ml  $\text{CS}_2$  (mole concentration  $\approx 1.0 \times 10^{-3}$ ). Retinal and retinol of  $4.0 \times 10^{-3} \text{g}$  were also dissolved respectively in 15 ml  $\text{CS}_2$  (mole concentration  $\approx 1.0 \times 10^{-3}$ ). The contribution of  $\text{CS}_2$  to the optical susceptibilities was subtracted from the each data to obtain the third-order nonlinear optical susceptibilities  $\chi_{1221}(-\omega, \omega, -\omega, \omega)$  of  $\beta$ -carotene, retinal and retinol. The results are listed in Table 1.

### B. DC-Kerr Effects

Fig. 3 shows the experimental setup for the measurement of the dc-Kerr constant. The dc-electric field was applied up to 3 KV/mm. The axis of the analyzer was perpendicular to that of the linear polarizer and the direction of applied electric field was at 45 degree with respect to the axis of the linear polarizer. A He-Ne laser with power of 20 mW was used as a probe beam. The signal beam intensity was measured with a calibrated large-area photodiode and an oscilloscope. From the measured phase differences  $\delta$ , the third order nonlinear optical susceptibilities  $\chi_{1221}(-\omega, \omega, 0, 0)$  of  $\beta$ -carotene, retinal, and retinol are deduced. The contributions of  $\text{CS}_2$  are also subtracted. The results of  $\chi_{1221}(-\omega, \omega, 0, 0)$  of  $\beta$ -carotene, retinal and retinol are shown in Table 1.

We have used saturated  $\beta$ -carotene, but unsaturated retinal and retinol in  $\text{CS}_2$ . But previous measurement showed that the molten and saturated media exhibit the same nonlinear optical susceptibilities.<sup>[7]</sup>

The value of the nonlinear susceptibility between  $\chi_{1221}(-\omega, \omega, -\omega, \omega)$  from the self-induced ellipse rotation and  $\chi_{1221}(-\omega, \omega, 0, 0)$  from the dc-Kerr effect do not differ each other significantly as

shown in Table 1. Furthermore, the nonlinear susceptibility is relatively insensitive to the conformational difference as shown in the case of retinal and retinol.

Our data shows that the strength of the third order optical susceptibility increases roughly with the increase of the number of double-bonds. The  $\beta$ -carotene with 11 double bonds has the largest value among the three samples. Even though the strength difference between retinal and retinol is not so big, the relative magnitudes between them could be sufficient to indicate the dependency of the strength to the number of double-bonds, regarding to the important contribution of the delocalized  $\pi$ -electron to the susceptibility and insensitiveness of the experimental results to the conformational difference between them. But it might need further detailed investigation to clarify above discussion in the samples which have similar number of double-bonds but have different conformation.

## IV. CONCLUSIONS

We have measured the third order nonlinear optical susceptibilities of  $\beta$ -carotene, retinal, and retinol by self-induced ellipse rotation and dc-Kerr effects. The nonlinear susceptibilities obtained from dc-Kerr effects do not differ significantly from that of the self-induced ellipse rotation effects and it is insensitive to the conformational difference. The large optical susceptibility of  $\beta$ -carotene compared to those of retinal and retinol has been ascribed to the large number of double bonds of  $\beta$ -carotene.

It might be an important and interesting research subject to investigate relationship between nonlinear susceptibility and visual cycles of the sample. But it also might be very difficult investigation, because the visual cycles usually involved fast dynamics such as fast conformational changes.

## ACKNOWLEDGEMENT

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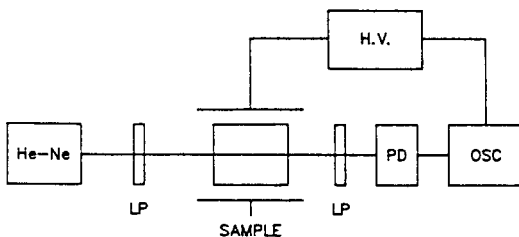


Fig. 3. Experimental arrangement for dc-Kerr effect. LP: linear polarizer, PD: photodiode, OSC: oscilloscope, H.V.: high voltage power supply.

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