Laser Original

Determination of Second Molecular Hyperpolarizability γ of Thiaheterohelicene by Degenerate Four-Wave Mixing Method

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Degenerate four-wave mixing method was employed to determine second molecular hyperpolarizabilities γ of a series of thiahetero [N] helicenes ($N=3, 5, 7$) and their methyl derivatives. γ values were calculated from the measured bulk susceptibility $\chi^{(3)}$ of benzene solution. It was found that γ increases by about one order of magnitude with the addition of one benzothiophene unit. The largest value of γ was about hundred times larger than that of carbon disulfide. The comparison of the optical absorption spectra measured before and after laser irradiation indicated that two chemical processes induced by photon absorption were involved.

Key Words: Degenerate four-wave mixing, Molecular hyperpolarizability, Helicene.

1. Introduction

Recently, there has been growing interest in the nonlinear optical properties of organic molecules because of the expectation of high density and fast optical information processing. The year 1982 was a epoch in nonlinear optical properties of organic and polymeric materials. At that time, ACS organized a symposium on them¹⁾. The developments, thereafter, were compiled by Chemla and Zyss²⁾ at 1987. Our interest is in third order optical processes which are related to the optical phase conjugation and optical bistability, rather than the second-order process where the frequency conversion is a main target. At the present stage, it is well recognized that the delocalization and correlation of π electrons are playing a main role to

enhance the molecular hyperpolarizability. In the early study, Rustagi and Ducuing³⁾ used free electron model to predict that γ increases by 5th power of molecular unit. McIntire and Hamerka⁴⁾ predicted 5.257th power law based on the simple Hückel approximation. de Melo and Silbey^{5,6)} used PPP/CHF method to predict 4.25th power law. On the other hand, Heflin, Wong, Zamani-Khanmini, and Garito⁷⁾ pointed out the importance of the electron correlation effect on γ values, and showed the 4.6th power law, using CNDO/CI and time dependent perturbation methods. Concerning the discussions cited above, thiaheterohelicenes are of particular interest because of their highly delocalized π electron system consisting of alternatively condensed benzene and thiophene nucleus as shown in an illustration of Fig. 1. The purpose

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Fig. 3 Three dimensional streak image of probe pulse and phase-conjugated signal (left peak) and intensities of pulses after integration along time axis (right peak).

Fig. 4 Temporal behaviors of probe pulse and phase-conjugated signal from thiahetero³⁾ helicene solution.

Fig. 5 Temporal behaviors of probe pulse and phase-conjugated signal from thiahetero⁷⁾ helicene solution.

Table I Molecular second hyperpolarizabilities of helicenes.

Compound	γ value (a. u.)
Benzene	2.4×10^4
Carbon disulfide	1.8×10^5
Thiahetero [3] helicene	1.7×10^5
Thiahetero [5] helicene	3.2×10^6
Thiahetero [7] helicene	1.3×10^7
2-methylthiahetero [3] helicene	1.4×10^5
2-methylthiahetero [5] helicene	9.1×10^5

Fig. 6 Semi-log plot of γ values of helicenes versus number of benzothiophene units.

mined by plotting the reflectivity versus the pump intensity. The second molecular hyperpolarizabilities were calculated with the local field correction. The measurement was performed on a series of thiahetero [N] helicenes ($N=3, 5, 7$) and their methyl derivative, and the results are summarized in Table I. The plot of dependence of γ on the number of benzothiophene units is illustrated in Fig. 6. The optical absorption spectra were measured before and after laser irradiation which is reproduced in Fig. 7 to examine the possibility of photochemical process, although helicenes are transparent at the

Fig. 7 Optical absorption spectra of thiahetero⁽⁵⁾ helicene before (solid line) and after (dashed line) DFWM measurement.

employed wave length.

Thiaheterohelicenes and their derivatives were synthesized by the method reported previously⁹⁾.

3. Molecular Hyperpolarizability of Thiaheterohelicene

As described above, the second hyperpolarizabilities of thiaheterohelicenes were determined by using the data of carbon disulfide as a reference whose γ was determined by plotting the reflectivity R of the phase conjugate signal versus the pump intensity using the relation¹⁰⁾

$$R^{1/2} = 24 \pi^3 \chi^{(3)} (I_1 I_2)^{1/2} / l c n^2, \quad (1)$$

where I_1 and I_2 are pump intensities, while l , c and n are interaction length, the velocity of

light, and refractive index, respectively. From $\chi^{(3)}$, we determined γ by using the equation

$$\chi^{(3)} = fN\gamma \quad (2)$$

where N is the number of molecules and we used the local field correction f as follows.

$$f = \left(\frac{n^2 + 2}{3} \right)^4 \quad (3)$$

The γ values of the helicenes were determined using Eqs. (2) and (3), where we used the refractive index of benzene as the solution was dilute enough, that is, typically 0.2 w%. As summarized in Table II, γ values of the helicenes increased by the increased number of benzothiophene units. The largest γ examined in the present study was that of thiahetero⁷⁾ helicene which is about one hundred times larger than that of carbon disulfide which is the well-known compound which has large γ . This fairly large γ is of interest as a promising molecule for the third-order nonlinear optical processes. The dependence of γ on the number of benzothiophene units is shown in Fig. 6, which indicates that γ increases by 2.8 th power on the number of the units. This observation indicates that the delocalization of π electron plays a main role to increase the γ values of helicenes. This statement arose from our *ab initio* molecular orbital calculation in which we indicated that inclusion of diffuse functions enhances γ by an order of magnitude whereas the electron correlation was found to enhance it just around by the factor two¹¹⁾.

4. Discussions

As shown in Fig. 4, the phase-conjugated signal from the thiahetero³⁾ helicene solution responds fast within the time scale of around nano second compared to the probe pulse. This clearly indicates that the thermal mechanism is not

involved in determining $\chi^{(3)}$ of the solution. This is reasonable as the helicene solution is transparent at the examined wave length. On the other hand, the phase-conjugate signal from thiahetero⁷⁾ helicene responds rather slowly as shown in Fig. 5. This slow response may arise from two possible mechanisms. One is the slow molecular reorientation of thiaheterohetero⁷⁾ helicene which has a large molecular diameter. The other is the thermal effect induced by two-photon absorption which must produce thermal grating, which is known to produce slow response. At the present stage, we can not determine which mechanism is playing a dominant role. A pico second study is under progress to clarify this point.

Optical absorption spectra were examined before and after the laser irradiation, and the result is shown in Fig. 7. This measurement was motivated by the observation that the high laser light scattering was found to disturb the DFWM measurement. As shown in Fig. 7, the peak of the spectra indicated by an arrow was significantly decreased by the irradiation of laser pulses. As the helicene solution is transparent at the examined wavelength, two-photon absorption must induce some kind of photochemical process as the energy of the laser pulse was strong enough, that is, 20 milli joules. However, details of this photochemistry remain to be clarified.

2-methyl derivatives of helicenes were examined in the belief that the solubility, which is important when we hope to use helicenes as nonlinear optical device, can be enhanced by the addition of alkyl group. In the present study, we found that the solubility of helicenes increases by introducing methyl group in benzene. None the less, our attempt to dope helicenes in polymers is not successful at the present study. We found that the solubility of

helicenes in polystyrene was good, but the optical homogeneity was not good enough resulting in high light scattering which disturbed the DFWM measurement. We found that PMMA is a nice matrix because of good optical quality, but the solubility was so poor that we could not measure $\chi^{(3)}$ for the polymer film. An effort is under progress to introduce long alkyl chain to enhance the solubility of helicene in polymers. We are also seeking a possibility to dope helicenes in inorganic glasses which have low melting temperature. If these attempts are successful, we will not only determine the purely electronic γ values by the elimination of the contribution of molecular orientation, but also obtain solid state optical material for practical application in the nonlinear optics.

5. Concluding Remarks

We found large γ value of thiahetero⁷⁾ helicene which is one hundred times larger than that of carbon disulfide. These values are promising for us to use the helicenes as nonlinear optical material as the γ deemed to come mainly from electronic origin, although the contribution from the molecular reorientation and/or thermal grating can not completely be eliminated. Even if we take into account the molecular reorientation effect, the γ values of

helicenes are fairly large as the molecular reorientation plays significant role in the case of carbon disulfide.

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