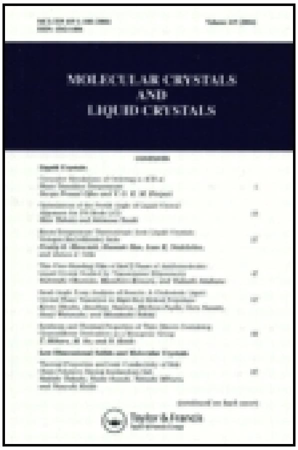

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Hyperpolarizability of Organic Compounds at the Excited State Estimated by Nano-second Hyper-Rayleigh Scattering Method under Excitation

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Hyperpolarizability of Organic Compounds at the Excited State Estimated by Nano-second Hyper-Rayleigh Scattering Method under Excitation

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Optical enhancement and control of the nonlinear optical (NLO) properties of organic compounds can be expected at the excited state because of changes in dipole moments and oscillator strength caused by electron density distribution different from that at the ground state. We constructed a novel measurement system of hyperpolarizability β at the excited state of molecules in solutions. The system was based on nanosecond Hyper-Rayleigh Scattering (HRS) method with CW laser excitation. In the HRS technique, a chromophore solution was irradiated by YAG laser beam of various intensities (frequency ω), and the scattered photons at 2ω were detected. The HRS intensity was proportional to the square of the incident laser intensity. The increase of HRS intensity for *p*-nitroaniline was observed in methanol solutions upon excitation with CW Ar laser at 457.9 nm. The β- value at the excited state was estimated.

Keywords: hyperpolarizability, excited state, hyper-Rayleigh scattering

INTRODUCTION

Future generations of optoelectronic devices for telecommunication, information storage, optical switching, and signal processing are predicated to a large degree on the development of materials with exceptional nonlinear optical (NLO) responses. Toward this end, considerable efforts have been made to design and develop chromophores with large hyperpolarizabilities β. It is also possible to modulate[1] or enhance NLO responses by photo-excitation. Recently the hyper-Rayleigh scattering (HRS) method has been widely used to determine β-values in solutions[2]. In order to evaluate the β-values at the excited state and thus to get information on the molecular design, we have constructed a HRS system with CW or pulsed laser excitation. In this paper, results with CW laser excitation are presented.

EXPERIMENTAL

A layout of the present excited HRS system is shown in Fig.1. The incident (probe) light, Q-switched pulsed Nd:YAG laser at 1064 nm, was split into two parts. The probe light was brought focus into both cells (5 cm) filled with organic compound solution via plano-convex lens. CW Ar laser at 457.9 nm was introduced to one cell as the excitation light. The intensity of the probe beam was changed with neutral density (ND) filters[3]. The scattered light was collected by a condenser system. The collected signal was detected by a photomultiplier tube (PMT) through a sharp bandpass filter set at 2ω or a monochromator. All experiments were carried out at room temperature. *p*-nitroaniline (*p*NA) was dissolved in methanol (MeOH)

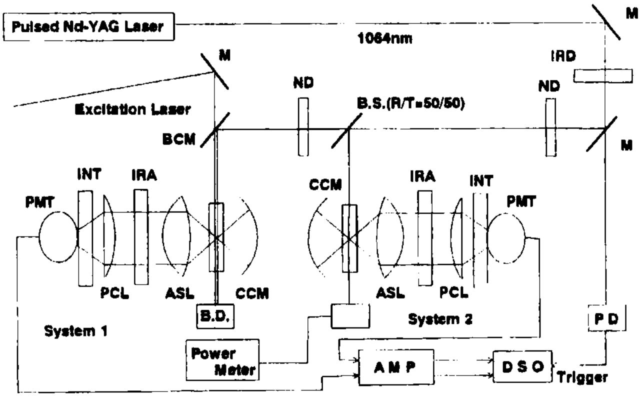

FIGURE 1 Experimental setup of a dual HRS measurement system at the ground and the excited state in solution.

at different concentrations and filtered through a 0.1 μm membrane filter to remove dusts.

RESULTS AND DISCUSSION

Using a monochromator and the fundamental of YAG laser as the probe, it was confirmed that no signals were observed except at 532 nm. This scattered light (532 nm) was caused by the second order nonlinear optical effect. The intensity of the second harmonic light ($I_{2\omega}$) is proportional to the number of scattering centers (N), the square of the hyperpolarizability (β^2) and the square of the intensity of the probe light (I_ω^2). The accuracy of our HRS system at the ground state was confirmed by the fact that the estimated β-value of *p*NA correspond well with the value by EFISH[4].

Scattered light intensity at 532 nm from *p*NA increased upon excitation as shown in Fig.2, which shows temporal HRS signal profiles with and without excitation light. The base line was increased by ca.7 % upon CW Ar laser excitation at 26 mW due probably to fluorescence and/or Raman scattering. It was already corrected in this figure. The increase of HRS intensity was 18% at 26 mW and increased with excitation power. The increase of HRS signals were exclusively attributed to the increased β at the excited state of chromophore from following results. First, Raman scattering and fluorescence at the 532 nm with CW laser excitation at 457.9 nm did not contribute to the temporal signals. Second, fluorescence induced by sum

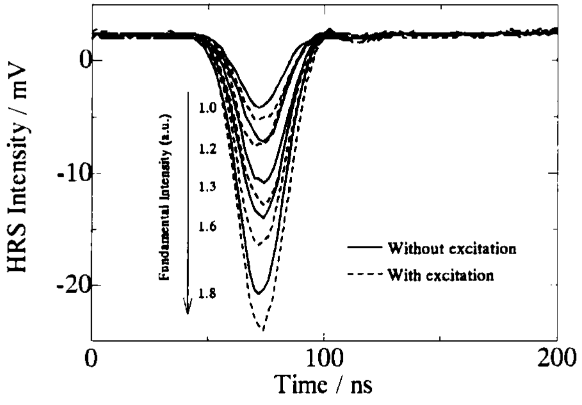

FIGURE 2 Temporal HRS signal profiles with and without excitation at 457.9 nm for different probe intensities for *p*NA in methanol solutions.

frequency caused by pulsed probe (1064 nm) and CW excitation (457.9 nm) can be excluded because no signal was observed at 320 nm. The HRS intensity ratio at the excited state and the ground state can be expressed by

$$\frac{S_{2\omega}(ex)}{S_{2\omega}(0)} = \frac{N_s\beta_s^2+(N_0-N_{ex})\beta_0^2+N_{ex}\beta_{ex}^2}{N_s\beta_s^2+N_0\beta_0^2}$$

where $S_{2\omega}$ is HRS intensity, β_{ex} and β_0 are β-value at the excited and the ground state, respectively. N_0 and N_{ex} are the initial number density and that of the excited state, respectively. The ratio of number densities, N_{ex}/N_0, can be estimated by the excitation laser power and the lifetime of the excited state assuming a steady state between the excited and the ground state. The value of $\beta_{pNA,ex}$ was thus estimated as 4.2×10^{-27} esu. The enhancement of β at the excited state was about 120 times. According to CNDO/S calculations, the enhancement of β was 11 to 32 times for the excited state *p*NA [5]. Several factors such as increased dipole moment or resonance effect at the excited state can contribute to the observed enhancement. The observed enhancement factor might also include possible contribution of thermal effect.

CONCLUSION

We constructed a new HRS measurement system to evaluate hyperpolarizability at the excited state. We showed the β-value of *p*NA actually increased upon CW laser excitation. Further HRS experiments including pulsed laser excitation will open a new field of excited second order nonlinear optics.

Acknowledgments

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References

[1.] T. Nagamura, H. Sakaguchi, and T. Matsuo, *Thin Solid Films*, **210/211**, 160 (1992).
[2.] K. Clays and A. Persoons, *Phys. Rev. Lett.*, **66**(23), 2980 (1991).
[3.] A. Harada, M. Takasaka, and T. Nagamura, *Bull. Res. Inst. Elec. Shizuoka Univ.*, **31**, 15 (1996).
[4.] M. Stahelin, D. M. Burland, and J. E. Rice, *Chem. Phys. Lett.*, **191**, 245 (1992)
[5.] R. Sen, D. Majumdar, S. P. Bhattacharyya, and S. N. Bhattacharyya, *J. Phys. Chem.*, **97**, 7491 (1993).