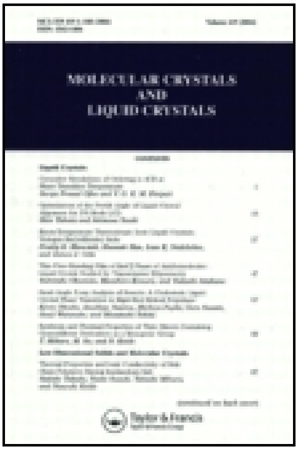

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Femtosecond Hyper-Rayleigh Scattering Measurement System for Organic Dyes in Solutions at the Excited State

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Femtosecond Hyper-Rayleigh Scattering Measurement System for Organic Dyes in Solutions at the Excited State

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Nonlinear optical properties can be enhanced at the excited state due to changes of electronic distribution. Femtosecond (fs) hyper-Rayleigh scattering measurement systems were constructed in order to quantitatively evaluate hyperpolarizability both at the ground and the excited states in solutions. Excitation of nitrostyrylpyridinium or crystal violet at 400 nm or 550 nm by fs laser resulted in one-photon or two-photon fluorescence at the wavelength to probe the HRS signals.

Keywords: hyperpolarizability; excited state hyper-Rayleigh scattering; femtosecond laser excitation; crystal violet; two-photon fluorescence

INTRODUCTION

Nonlinear optical responses are very important to achieve, for example, wavelength conversion, electro-optical or all-optical control of the refractive index, and all-optical logic. One of the main problems is that nonlinear optical (NLO) coefficients are very small, which requires high power laser. Many efforts havebeen made to increase the NLO coeeficients by "chemical" approaches such as increasing dipole moment, extents of electronic distribution, and molecular orientation. We have been making "physical" approaches to modulate or enhance the second and the third order nonlinear optical properties by changing the electronic state or the extent of electronic distribution upon photoexcitation [1-4]. Degenerate four wave mixing (DFWM) signal intensity of poly(3-dodecylthiophene) (PDT) in chloroform increased by more than three orders upon excitation by femtosecond (fs) laser at 400 nm [1,2]. Excitonic states produced in one-dimensional chain backbone of a conjugated polymer like PDT upon photoexcitation most probably contributed the observed enhancement [1,2].

In order to quantitatively evaluate the second NLO coefficient, hyperpolarizability at the excited state in solutions, we constructed excited-state hyper-Rayleigh scattering (HRS) measurement systems. We also observed similar enhancement of the second order optical nonlinearity upon photoexcitation [3,4]. The enhancement factor for *p*-nitroaniline (pNA) was about 60 at the instance of ns laser excitation.

In the present paper, we will report the construction of excited HRS measurements with fs laser in order to quantitatively the b-value at the excited state of molecules in solutions. The ground state fs HRS was demonstrated to have advantages such as high peak powers and high S/N ratio as compared with the nanosecond HRS [5].

EXPERIMENTAL

The fs HRS measurement system at the ground state was first constructed using regeneratively amplified fs pulses at 800 nm, 1 kHz repetition as a probe with powers less than 1 mW. After confirming its performance, we constructed two systems for the fs HRS measurement at the excited state of molecules in solutions. One system schematically shown in FIGURE 1 used the fundamental output of a regenerative amplifier (10 Hz) at 800 nm as a probe and the second harmonics of a home-made optical parametric amplifier (OPA) output at 1100 nm as a pump pulse. The power of the probe was controlled by a fs half-wave plate and a polarizer with an optical delay. The signal at 400 nm was collected by lenses through band-pass filters and was detected by a photomultiplier through an optical fiber. In the other fs HRS system, the second harmonics of 800 nm amplified fs pulses (10 Hz) was used as the probe and the second harmonics of OPA at 1100 nm was used as the pump through the fs half-wave plate and the polarizer.

Samples used for the present study include crystal violet (CV), 1-methyl-4-(4-nitrostyryl)pyridinium chlodide (NSPCl), and 1-hexadecyl-4-(4-nitrostyryl)pyridiniumbromide (NSPBr) in methanol.

RESULTS AND DISCUSSION

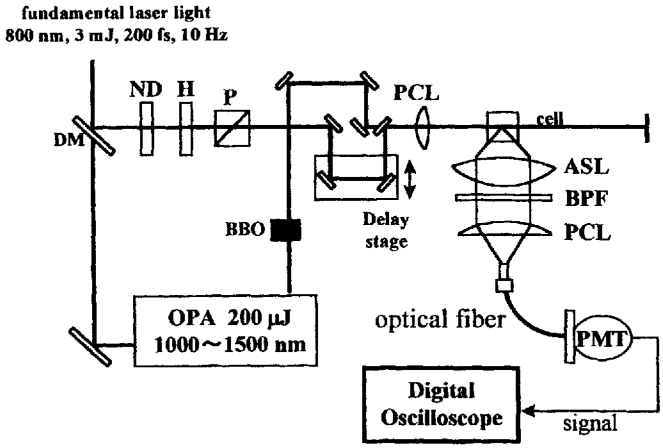

FIGURE 1 Schematic represdentation of fs HRS measurement system upon the excitation with the second harmonics of OPA.

The hyperporalizability of CV was evaluated to be 3.3 x 10^{-28} esu, which corrresponded with previous results by non-amplified femtosecond laser [5]. The present fs HRS system using the regenerative amplifier at 1 kHz was thus proved to work well.

The transient bleaching was observed for CV in methanol as shown in FIGURE 2 upon excitation with fs laser at 550 nm, which indicated the formation of the excited state. The signal observed at 400 nm was quadratically increased with the fundamental intensity up to 10 mJ/pulse in a similar manner as above. Before making the excited fs HRS measurements of CV, it was checked that no signals were observed for methanol alone with using both pump and probe laser pulses. FIGURE 3 shows the temporal signals observed at 400 nm for CV in methanol excited at 550 nm without using the probe. It was decreased partly or completely by using short-cut filters L-39 (>365 nm) and Y-44 (> 400 nm). It was thus attributed to two-photon fluorescence from CV, which made very difficult to observe the HRS signal with excitatin at 550 nm.

We then selected NSPCl or NSPBr in methanol as samples with small absorption at 400 nm and very weak fluorescence to make excited HRS measurements with 400 nm pump and 1100 nm probe as shown in FIGURE 2. Transient signals were observed at 550 nm upon excitation

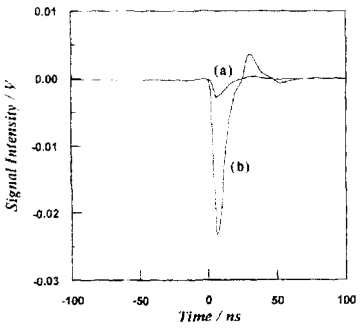

FIGURE 2 Temporal profiles at 590 nm for CV in methanol (a) without and (b) with fs laser excitation at 550 nm.

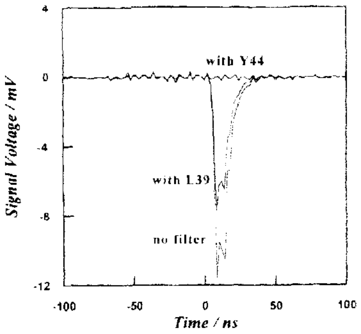

FIGURE 3 Temporal profiles at 400 nm for CV in methanol with and without short-cut filters upon excitation at 550 nm.

of NSPCl or NSPBr at 400 nm, which did not increase much by using the probe pulse at 1100 nm. These signals also disappeared with a short-cut filter R-60 (> 580 nm). It was thus attributed to one-photon fluorescence from NSPCl or NSPBr. From these results it turns out to be very difficult to observe excited HRS signals without fluorescence.

CONCLUSION

New systems were constructed to observe HRS signals at the ground and the excited states of molecules in solutions. The present study will contribute a great deal to evaluate materials for molecular photonics.

Acknowledgments

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