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Solvation dynamics of p-methoxy-p'-cyanodiphenylacetylene was investigated by observing time-resolved fluorescence anisotropy and dynamic Stokes shift. The time-resolved anisotropy and Stokes shift were measured in the picosecond time region in n-butanol. Fluorescence spectra of p-methoxy-p'-cyanodiphenylacetylene exhibited a large Stokes shift, depending on the solvent polarity. The observed time-resolved anisotropy and Stokes shift were simultaneously analyzed with the theory based on continuum model, described in the preceding paper, by a simulation procedure of non-linear least square's method. The both decays satisfactorily fit with the theory. Obtained dipole moment in the excited state was 14 (D). The dipole moment in the ground state was negligibly small.

Keywords: simultaneous simulation ; time-resolved anisotropy and Stokes shift ; p-methoxy -p'-cyanodiphenylacetylene

INTRODUCTION

The dynamics of polar solvation is important in relation to many problems, such as electron transfer processes, chemical reactions, and liquid structures. The measurements of dynamic solvation by means of ultrafast spectroscopy may provide an information on microscopic feature of interaction between polar solute and solvents, rotational motion of solute, and solvent relaxation. A

number of experimental works have been reported on the dynamic Stokes shift [1-4]. On the other hand, as indicated by the many works [5-8], the time-resolved fluorescence anisotropy is an alternative useful technique to measure the solvation dynamics. Solute molecules used for the experiments of dynamic Stokes shift and anisotropy decay have been rather complicated aromatic molecules, like coumarine derivatives or other aromatic dyes, which may not be ideal for the test of the theoretical models on the solvation dynamics by these experiments.

p-Methoxy-p'-cyanodiphenylacetylene (MCDA) is a rod-like molecule and is expected to have large dipole moment. Directions of dipole moments in the excited and ground states, and transition moments of MCDA, are all considered to be along long axis of this molecule. In the present work we have simultaneously analyzed the observed time-resolved fluorescence anisotropy and Stokes shift of MCDA in n-butanol with the equations obtained in the preceded work[9] with continuum model.

METHOD OF EXPERIMENTS

Materials

MCDA was synthesized as described elsewhere [10]. It was purified in acetonitrile-water mixed solvent (1:1) with a HPLC (JASCO, Japan). Organic solvents used for the measurements were all ultrapure spectroscopic grade (Nacarai Tesque, Kyoto).

Measurements

Time-resolved fluorescence anisotropy and dynamic Stokes shift were measured by single photon timing spectroscopy [11]. A second harmonics (315 nm, pulse width ca. 10 ps) of a synchronously pumped, cavity-dumped rhodamine 6G dye laser (Coherent Antares 86 S and 702) was used for the excitation pulse.

The fluorescence anisotropy decay were obtained by parallel and perpendicular polarization conditions with respect to the pump pulse by using a film polarizer (Polaroid, HNP'B). A wedge depolarizer was inserted

between the analyzing polarizer and a monochrometer.

Time-resolved fluorescence spectra were constructed from the observed decay curves at 400 different wavelengths. The spectra were corrected for the wavelength-dependent sensitivity of the detector system with a standard halogen lamp. Dynamic Stokes shifts were calculated by a set of the time-resolved fluorescence spectra.

METHOD OF ANALYSIS

Molecular shape of MCDA was reasonably assumed to be a prolonged spheroid. Long axis of MCDA was taken to be z-axis. Direction of dipole moment in the excited state was assumed to be along z-axis. It was also assumed that transition moment of emission of MCDA was along z-axis. Parameters necessary for the calculation of anisotropy decay are an angle between transition moment of absorption and z-axis, θ_a, static dielectric constant, ε_0, optical dielectric constant, ε_∞, dielectric constant of cavity, ε_c, dipole moment of excited state, μ_e, dielectric relaxation time of solvent, τ, solvent viscosity, η, spheroid molecular size of solute, 2a along z-axis and 2b along x- or y-axes, according to the preceded work [9]. Empirical expressions of temperature-dependence for ε_0, ε_∞ and τ of n-butanol are given by Castner et al [1].

Most of the parameters used for the analyses of anisotropy decays were in common with the analyses of Stokes shift, except for θ_a. An additional parameter, μ_g, dipole moment of the ground state, was necessary for the Stokes shift. The best-fit procedure was made by varying μ_e, μ_g, ε_c and θ_a, so as to obtain the minimum value of χ_T^2, by means of a non-linear least square's method based on the Marquardt algorithm.

$$\chi_T^2 = \chi_A^2 + \chi_E^2 \tag{1}$$

where χ_A^2 is chi-square between the observed and the calculated values of

anisotropy, χ^2_E a chi-square between the observed and calculated energy shift expressed in units of eV.

RESULTS

Electronic Spectra of MCDA

Absorption band of MCDA in n-hexane around 370 nm of the peak wavelength was structured while it was diffused in acetonitrile. The band peak itself did not shift at all when solvent was changed from n-hexane to

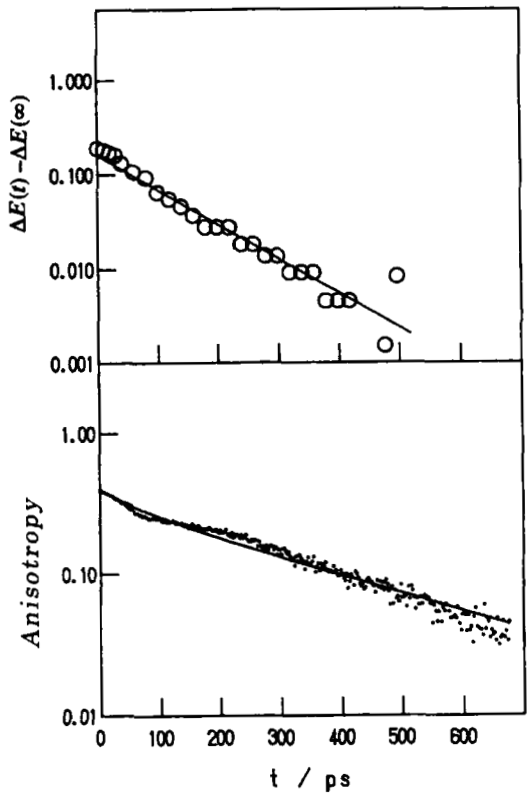

FIGURE 1 Time-dependent Stokes shift and Anisotropy of MCDA in n-butanol

acetonitlile. Fluorescence spectra of MCDA in n-hexane also exhibited structured band at 334nm of maximum wavelength. It shifted toward longer wavelength at 418 nm, and emission band became structureless in acetonitrile. In n-butanol the maximum wavelength of emission was 403 nm.

Stokes Shift and Anisotropy

Fig. 1 shows $\triangle E(t) - \triangle E(\infty)$ in eV unit and anisotropy of MCDA in n-butanol at 22 ℃. Both decays were simulated at once by varying μ_e, μ_g, ε_c and θ_a at several sets of a and b. The obtained parameters and physical constants used for the calculations are listed in Table I. Rotational diffusion coefficient of MCDA was evaluated from these sets of a and b by slip model. When it was evaluated by stick model, the fitting was very poor. The calculated decays of Stokes shift and anisotropy at the best fit were indicated by solid curves. In all cases examined μ_g was always very small, compared with the magnitude of μ_e which was about 14 D. The magnitude of μ_e did not much change with the molecular size of MCDA or rotational diffusion coefficient.

TABLE I Simultaneous Simulation of Fluorescence Anisotropy and Stokes Shift of MCDA in n-Butanol at 22 ℃ a).

μ_e (D)	μ_g (D)	ε_c	θ_a (degree)	a (nm)	b (nm)
13.5	0.0	2.4	17	0.78	0.26
13.9	0.0	2.4	21	0.80	0.26
14.1	0.0	2.5	23	0.82	0.26
13.7	0.0	2.8	22	0.82	0.24
13.0	0.0	2.7	18	0.78	0.24
13.1	0.0	2.3	13	0.76	0.26

a) The quantities of μ_e, μ_g, ε_c and θ_a were analyzed at several set of a and b. The constants of n-butanol, τ = 573 ps, ε_0 = 17.6 and ε_∞=3.4, according to Castner et al. [1] and η = 2.78 cP were used for the simulation.

DISCUSSION

Molecular structure of MCDA seems to be much simple compared to aromatic dyes which were frequently used for the studies of dynamic solvation. Directions of transition moment of emission and dipole moments are considered to be all along long axis of MCDA.

The observed time-dependent energy shift and anisotropy of MCDA in n-butanol were analyzed with the equations obtained in the preceded work [9]. In these equations dielectric friction in polar solvent was introduced through rotational motion of solute molecules with non-Markov process, according to the framework of Nee and Zwanzig [12]. Although the limitations of their theoretical treatments for the dielectric friction have been frequently discussed [13-16], in the present work both decays of the energy shift and anisotropy were able to be reproduced in the time range longer than 10 ps by our theoretical equations [9] with common parameters.

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