

Articles

Investigation of Molecular Coupling Effects on Photothermal Properties of Polar Solutions by Thermal Lens

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Photothermal properties depend on the characteristics of energy transfer processes in solution. In this study, a time-resolved single beam thermal lens experiment in various solvents is employed to investigate the energy coupling effects which govern the energy transfer processes. Interestingly, it is observed that the behaviour of the photothermal propagation in solution depends on the property of solution and the concentration of solute in a single beam thermal lens configuration. These characteristics lead us to consider the solute-solvent coupling effects as well as the solvent-solvent interactions.

Introduction

The effect of thermal lens was first observed by Gordon *et al.* in 1964.¹ Thereafter, this method has been little developed until early 1980's.² But, now the thermal lens studies have extended into a large number of fields, for example, calorimetry, absorption spectroscopy, energy transfer kinetics, transport phenomena, photochemistry.³ The thermal lens method monitors the heat generation and propagation occurred during the nonradiative relaxation processes of photo-excited molecules. Thus, the thermal lens method can be used as a complimentary tool to the other well-established spectroscopic methods such as fluorescence spectroscopy.⁴ When the sample is irradiated by the laser light of Gaussian TEM₀₀ mode, the Gaussian shaped temperature variation in space, associated with the absorption of radiation, induces the refractive index change. That is, a lens-like optical element is formed in the sample.⁵ The optical configurations for the thermal lens experiments can be divided into the two; the single- and the dual-beam configurations. In the single-beam configuration, a single laser beam both creates and probes the thermal lens in the sample. The dual-beam configuration utilizes two lasers; one beam, absorbed by the sample, forms the lens while the second beam probes the sample for the presence of the lens.⁶ In this study, we use the time-resolved single-beam thermal lens method. In this configuration, the lens effect builds up with time and reaches the steady state, following the equation below.⁷

$$f(t) = f_{\infty} [1 + t_c/2t] \quad (1)$$

Here, $f(t)$ is the time dependent focal length, changing with the characteristic thermal time constant (t_c) which depends on the properties of molecular systems. f_{∞} is the constant focal length at the infinite time. The thermal time constant value, t_c , shows the relationship of $t_c = \omega_0^2 \rho C_p / (4\kappa)$. In this equation, ω_0 is the minimum radius of the focused laser beam, ρ is the density of the solvent, C_p is the isobaric heat

capacity of the solvent, and κ is the thermal conductivity of the solvent.

As stated above, the t_c value includes many important information needed to understand the molecular system. This important characteristic thermal lens time constant can be obtained by fitting the thermal lens signal to the following equation.⁸

$$I(t) = I_0 + \Delta I \cdot \exp(-t/t_c) \quad (2)$$

In equation (2), I_0 represents the background intensity and ΔI indicates the loss in the intensity after the thermal lens reaches its steady state. Therefore the t_c value, which we measure in this study, can be represented as the formation time of the steady-state thermal lens.

In many experiments, the thermal lens signals have been interpreted only as solvent properties, particularly, in the single beam configuration.^{1,5,7,8} However, the signal obtained in this experiment shows the different single or double exponential behaviour, even in the single beam configuration. It suggests us to consider that there could be two mechanisms which induce the different types of thermal lens effects. To understand the single or double exponential pattern of the thermal lens signals, we performed the thermal lens experiments with various molecular systems, by changing the solvent and the concentration of the solute. Based on the experimental results, we discuss these behaviours in terms of the translational and vibrational energy transfer among the solvent molecules and, also, the energy coupling effects between the solute and the solvent molecules.

Experimental

The laser used in this experiment is a He-Ne laser (Meredith Instruments) operating at 632.8 nm with the power of 5 mW. The laser was modulated through a 30 Hz chopper (Stanford Research Systems, model SR540) and then, focused with a convex lens of 5 cm focal length. The laser beam was focused within a 10 mm pathlength cuvette containing

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the sample. The exact position of the sample cuvette on the laser beam was optimized for the maximum thermal lens effect. The diverging laser beam, due to the thermal lens effect, passed through an iris (diameter of 1.0 mm) which was placed approximately 1 meter away from the sample cuvette. After the iris, a fast silicon photodiode (Newport 818-bb-20) was used to detect the signal. The output of the photodiode was collected with the 500 MHz digital storage scope (Hewlett Packard, 54520A). The signals were averaged, 1200 times, in this scope and analyzed with an iterative least square fitting method in the PC. The solute was chosen as acid blue 25 (Aldrich company) because of its absorption spectrum peaked at 630 nm. The recrystallized acid blue 25 was used in the experiment. Acetone (duksan, special grade), ethanol (duksan, special grade), water (deionized) were used as the solvents for the preparations of the solutions. For each solvent, we prepared five solutions of the different concentrations: 5.0×10^{-5} M, 3.5×10^{-5} M, 2.0×10^{-5} M, 1.0×10^{-5} M, 5.0×10^{-6} M. We also used the FT-IR (Nicolet, Magma IR550 series II) and the UV-VIS (Shimadzu, UV-160A) spectrometers to obtain the information on the vibrational structures and the ground state solvent-solute energy coupling, respectively. Since the t_c values are very sensitive to the experimental configuration, we didn't move any component in the configuration once the measurement had started. Even for the different samples, the careful measurements were done just by changing the samples with a micropipette, without touching the sample cuvette. The whole experiments continued without intermission in order to avoid any possible changes in the experimental conditions.

Results and Discussion

Typical thermal lens signals are presented in Figure 1. The overall decrease in the signal amplitude represents the t_c value and the sharp rise at the end of the signal is due to the disappearance of the thermal lens effect. This sharp rise occurs at the end since the chopper starts to close, causing the weak intensity of the excitation beam. The weak intensity of the excitation beam causes the shallow profile of the refractive index gradient, inducing no more diverging beam profile. This sharp rise is just an interesting artifact in the signal and it doesn't include any meaningful results.

In the fitting process, the following equation was used to obtain the characteristic thermal time constants (t_{c1} , t_{c2}).

$$I(t) = I_0 + \Delta I_1 \cdot \exp(-t/t_{c1}) + \Delta I_2 \cdot \exp(-t/t_{c2}) \quad (3)$$

As mentioned previously, I_0 is the background intensity, ΔI_1 and ΔI_2 are the losses in the intensity of each exponential component for two different steady states of the thermal lens. The thermal time constants, t_{c1} and t_{c2} , represent the characteristic times of thermal lens formation.

From the results of fitting the data with equation (3), we found that the signals for water solvent were fitted to a single exponential function. But, for the acetone and the ethanol, the signals were better fitted to a double exponential function. These characteristics of the exponential behaviours are shown in Figure 1. Therefore, we classify the signal into the fast component and the slow component.

First of all, consider the case of water solvent. As shown

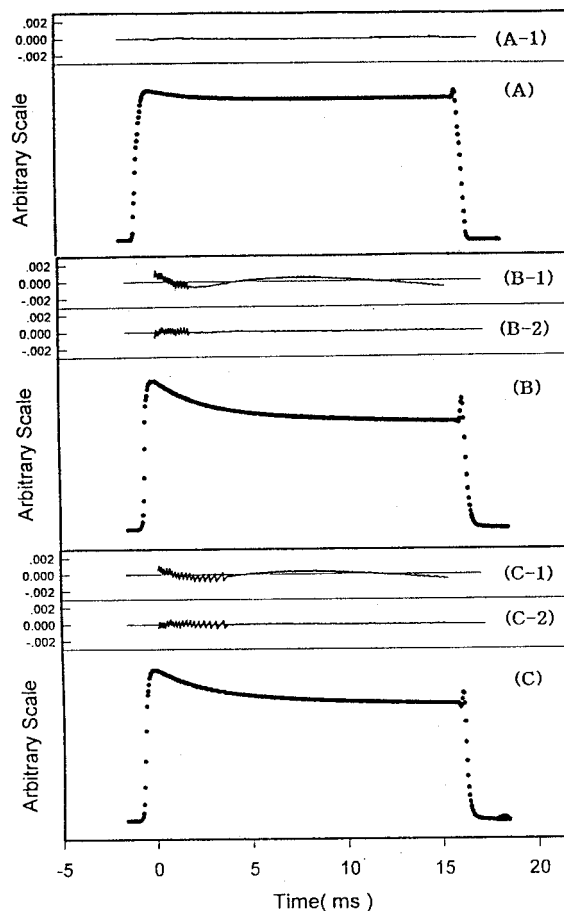


Figure 1. Typical thermal lens signals for acid blue 25 in three solvents; (A) water, (B) acetone, (C) ethanol. (A-1): residuals of single exponential fitting, (B-1): residuals of single exponential fitting, (B-2): residuals of double exponential fitting, (C-1): residuals of single exponential fitting, (C-2): residuals of double exponential fitting.

in Figure 2, at the lowest concentration, the t_c value for the water is very similar to the fast t_{c1} values for the other solvents. It implies that the t_c values of this component are only dependent on the solute, not on the solvents. Since the solute doesn't change the density of the solvent, it can be considered that the refractive index gradient is almost not affected by the solvent density but mostly affected by the solute temperature. When the chopped CW excitation beam is irradiated onto the sample, the electronically and vibrationally higher states are more populated than they are without the irradiation. As shown in Figure 2. (c), the thermal lens signal of the water solution rises in the range of 1.54-2.90 microseconds, depending upon the concentration of the solute. The temperature of the solute molecules reaches at an equilibrated state in this time range, as the heat generated from the high vibrational states in the electronically excited and the relaxed electronic ground states becomes an equilibrium with the heat dissipation through nearby solvent molecules. Since the laser intensity profile is the TEM₀₀ mode and spatially Gaussian shape, the Gaussian temperature gradient made by the equilibrated hot solutes is instan-

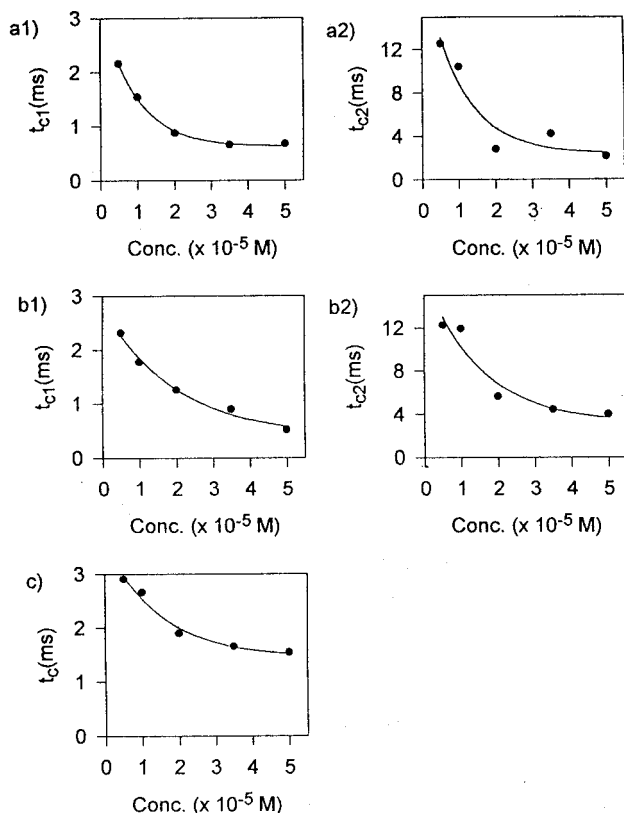


Figure 2. The variations of the t_c values in each solvents as a function of the concentration; a1) the fast t_c values in acetone, a2) the slow t_c values in acetone, b1) the fast t_c values in ethanol, b2) the slow t_c values in ethanol, c) the t_c values in water.

tly spatially formed. Therefore this temperature gradient is responsible for the fast lens effect which appears in the water solvent system.^{9,10,11} When the concentration dependence of solute on the thermal lens effect is considered, the fast t_c values become even faster as the concentration of the solute increases. The extent of this decrease of the t_c values in water solution is less than that in the other solvents.

As mentioned briefly, the above two phenomena have the close relationship to the energy dissipation mechanism and the energy coupling efficiency of the solute with the solvent. In the first phenomenon, the plausible reason why the thermal lens effects in the water solutions show only the fast t_c values, implying that this fast lens effects are mainly contributed by the solute molecules only (not by the solvent molecules), can be suggested as the following; after the excitation of the solutes by photons, the excitation electronic energy is initially converted to the vibrational energy of the solute ground state as well as the excited state.¹² Thereafter the vibrational energy of the solute is transferred to the vibrational modes of the solvent. This energy is dissipated by the vibrational-vibrational (V-V) energy transfer among the solvents very rapidly.^{12,13} During this process, the vibrational-translational (V-T) energy transfer between the solvents also occur.^{12,14} The V-T energy transfer is much faster in the molecule having more number of the low-frequency vibrational modes.^{12,15} Using the FT-IR, we obtained the vibrational spectra of three solvents. Among the three solvents, water has

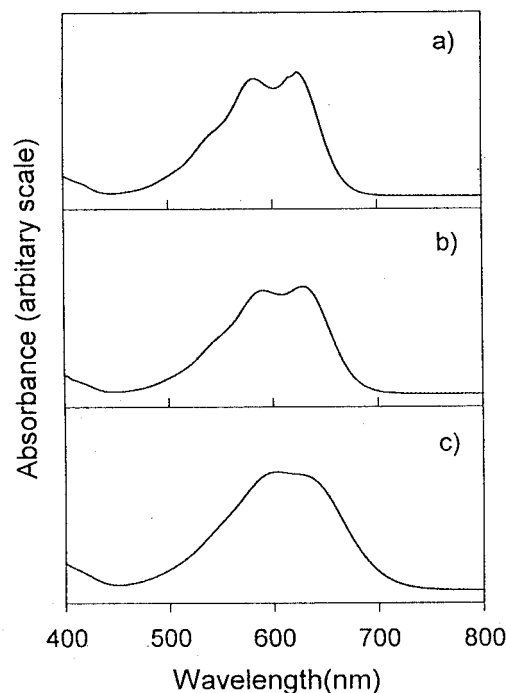


Figure 3. The UV-VIS absorption spectra of the acid blue 25 at 1.0×10^{-4} M in a) acetone, b) ethanol, c) water.

Table 1. The overall amplitude of the thermal lens effect in each solvent

| | Solvent | | | |
|--------------|------------------------|----------------------|-------|------|
| | Acetone ^a | Ethanol ^a | Water | |
| $\Delta I/I$ | 5.0×10^{-6} M | 30.7 | 25.6 | 1.92 |
| $\times 100$ | 1.0×10^{-5} M | 77.1 | 65.4 | 2.60 |
| (%) | 2.0×10^{-5} M | 89.2 | 84.9 | 4.00 |
| | 3.5×10^{-5} M | 90.3 | 88.3 | 5.35 |
| | 5.0×10^{-5} M | 88.0 | 95.8 | 6.28 |

^aThe numbers in the columns are the summed amplitude values of the fast and the slow components

the largest number of the low-frequency vibrational modes, suggesting that the V-T energy transfer in the water solvent molecules is faster than the others. The translational modes make the largest contribution to the thermal lens.¹⁶ In the water solution, a lot of energy flows into the translational modes due to this low frequency vibrational mode characteristics and the good coupling efficiency between the solute and water solvent as shown in Figure 3 where the absorption spectrum in water solution has the structureless band, on the other hand the other solvent systems shows the rovibrational substructure in the electronic absorption band, indicating better coupling efficiency in the water system than the others. So, the component caused by the solvent diffusion process due to the V-T energy transfer of the water solvent may be formed very rapidly. This component was not experimentally detected because of much faster time scale than our time resolution. However, instead, we observed that the amplitudes of thermal lens effect in the water system is not

so large as those in the other solvents as shown in Table 1. This is because of more efficient energy coupling of the solute with the solvent and the better V-T energy transfer processes as stated before. The V-V energy transfer rate is very fast in all the solvents, so the cross section (*i.e.* the energy coupling of the solute with the solvent) plays an important role in the energy dissipation. In the water solution, which has larger cross section (*i.e.* more efficient energy coupling of the solute) and better V-T energy transfer processes, the energy dissipation reaches the equilibrium faster. Therefore, the amplitude of the thermal lens effect in the water solution is much smaller than those in the other solvents. Consequently, the slow component corresponding to the density gradient caused by the solvent diffusion process, which is shown in the acetone and the ethanol solvent, is not detected in the water solvent, leading the signal to be a single exponential behaviour. In the second phenomenon, as the solute concentration increases, the rate of decrease of the t_c value in water solvent is less than those in the other solvents. It suggests the following situation. Because of more efficient energy coupling between the solute and the water solvent than the others as shown in Figure 3, a solute makes a whole system with more neighboring solvation shell. Thus the heating process becomes less efficient due to the larger heat capacity, *i.e.*, the thermal lens is formed relatively slowly compared to the others.

Next, consider the cases of the acetone and the ethanol solvents. In these cases, we obtained the fast t_{c1} values which are similar to the t_c value of the water solvent at the lowest concentration, as well as the slow t_{c2} components. As the solute concentration increases, the fast t_{c1} values decrease more rapidly than t_c values in the water solvent.

These experimental results can be interpreted in the same analogy with the case of the water solvent. Firstly, the fast t_c value corresponds to the thermal lens caused by the temperature gradient of the solutes and the slow t_c value corresponds to the thermal lens caused by the density gradient of the solvent molecules due to the V-V energy transfer and V-T energy transfer processes among the solvent molecules. In contrast with the water solvent, the slow component was observed since the V-T energy transfer was expected to occur slower in the acetone and the ethanol solvents. Secondly, as shown in Figure 3, the energy coupling of the solute with the solvent is less efficient than the water case. Thus the solute can't form an efficient system with the solvation shell as much as the water system does. Therefore the formation rate of the equilibrated solute temperature becomes greater than that in the water as the solute concentration increases, resulting that the thermal lens caused by the temperature gradient of the solutes reaches at the steady-state more rapidly.

Conclusions

In the single beam thermal lens experiments, the thermal

lens effect has normally been treated with the properties of solvent and considered in order to obtain the information on the thermodynamic properties (C_p , k , etc.) of the solvent molecular system using the equations stated previously in this paper. However, in some cases, such information can't be simply obtained due to the solute contributions to the thermal lens effect. This study reveals that the solute-solvent coupling dynamics should be carefully considered for the time-resolved single beam thermal lens effects, as well as the solvent-solvent interactions. Such observed phenomena during this study are treated in the macroscopic point since the time constants obtained from the experiments are only the averaged values before the equilibrium. Therefore, in order to get more microscopic views of these coupling dynamics, picosecond two color thermal lens studies are underway in this laboratory with a series of solute molecules.

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