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Contributions of transient absorption and population lens in thermal lens spectroscopy

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Abstract; Contaminations of the population lens and transient absorption in the observed thermal lens signal sometimes cause a misinterpretation of the signal. Recently, we have developed several methods to evaluate the relative contributions of these components in the observed thermal lens signal. These methods with recent results are summarized, and merits and limitations of each method are discussed.

1. Introduction

In the thermal lens (TL) method, a variation of probe beam light *density* caused by a non-uniformly spatial shaped excitation beam is detected through a pinhole. Usually the observed TL signal is assumed to be composed of the thermal effect due to the radiationless transition from the photoexcited state[1]. Since the signal intensity is proportional to the amount of heat as long as the above assumption is correct and the experimental conditions are adequate, it has been used as a sensitive and fast response thermometer to trace the dynamics of metastable states [2,3] or chemical reactions [4]. From the time profile or the signal intensity, the quantum yield, the energy of the excited states, reaction enthalpy and so on can be determined.

However, there are expected to be several origins apart from the heating effect that could change the refractive index of the solution after photoexcitation. For example, the different *optical properties* between the original state and the metastable state or reaction products will vary the refractive index of the solution and it may contribute to the observed TL signal. Also if the metastable state absorbs the probe light, the absorption (transient absorption (TA)) varies the probe light *intensity* and the variation will contaminate the observed TL signal. (Hereafter, we use a notation of "TL_{ex} signal" as the variation of the probe light intensity detected under a normal TL experiment; namely, the probe light *intensity* is detected through the pinhole. The TL_{ex} signal may contain other contributions besides the pure TL signal.) Previously we have shown that the refractive index change due to the different optical properties indeed affects the time profile of the TL_{ex} signal and we have referred to that refractive index lens as the population lens (PL) [5]. This work clearly shows that it is important to evaluate such possible contaminations (PL and TA) in order to use the TL method as one of the calorimetric methods. Here we

intend to show several methods to evaluate the PL and TA in the TL_{ex} signal and discuss the merits and limitations. We have chosen the lowest excited triplet (T_1) state of several organic compounds as examples of the metastable states for our demonstrations.

The TL_{ex} signal was observed by using a dual beam (pump/probe) configuration setup, which has been described elsewhere in detail [5-7].

2. Contribution of transient absorption

If the T_1 - T_n absorption of the probe beam occurs from the metastable T_1 state, it decreases the probe light *intensity*. Although the origin of the TA signal is obviously different from that of the TL or PL, both of which appear as the variation of the probe beam *density*, the change of the probe light intensity is detected through the pinhole as well as the TL signal and it is rather difficult to separate out or evaluate the contribution of TA from the time resolved TL signal quantitatively. One of the reasons of the difficulty comes from the fact that a very small central area in the probe beam is monitored in the TL_{ex} experiment, so that the quantitative measurement of the pure TA intensity using only that area is very difficult, if not impossible. Also the fact that the decay rate constant of the TA should be the same as the rise time constant of the TL signal (*vide infra*) makes the separation difficult. Naturally, the different origins of the TA and TL may be used to evaluate the TA contribution. For example, if the TL_{ex} signal is detected as a change of the beam spot size by using an imaging detector [8], the contribution of TA in the whole probe beam may be calculated from the integrated probe beam intensity. Then the TA intensity at the central part can be calculated by using the radial profile of the excitation beam. However applicability of this method is limited by the slow time response of the detector. Here we show two methods to evaluate the TA contribution with the pinhole and a simple photodetector system.

2.1 Coincident focal point method

One way to measure the pure TA intensity in the TL_{ex} signal is achieved by eliminating the TL signal under the TL experimental conditions. This disappearing condition is fulfilled by adjusting the probe beam waist against that of the excitation beam. It is known that the TL effect is sensitive to the location of the probe beam waist with respect to the excitation beam waist [8]. When the focal point of the probe beam coincides with that of the excitation beam, the lens signal (TL and PL) will disappear and only the TA signal is detected. After the measurement of the time profile of TA ($U_{TA}(t)$) under this condition, the TA contribution can be subtracted from the observed TL_{ex} signal with a different focal point position of the probe beam.

This method has been used to show the existence of PL in the time resolved TL_{ex} signal after the photoexcitation of C_{60} (a member of fullerenes) for the first time [5]. Although this method can be used generally, relatively fine adjustment of the probe and excitation beams is required. Therefore we think that it is not convenient to be used for routine work.

2.2 The Concave - Convex Lens (CCL) method

The TA effect and the refractive index lens effect could be distinguished by using different probe beam optical paths in the two cases; the TA effect does not change the optical path, while the PL

or TL effects do. In the concave-convex lens (CCL) method, the probe beam is collimated at the TL region of the sample [6,10] and then the beam is expanded with a concave or with a convex lens before the pinhole-detector system (Fig.1). When the probe beam is expanded by the concave lens, the beam intensity through the pinhole should decrease by the TL effect as well as by TA. On the other hand, when the beam is expanded by the convex

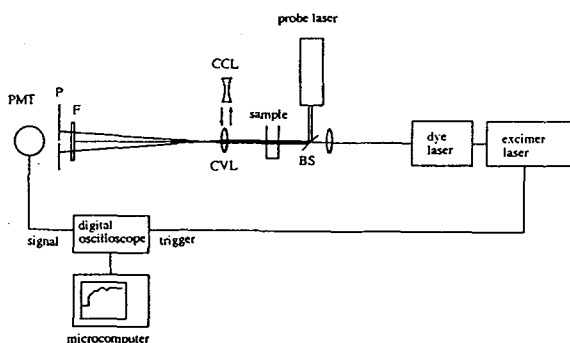


Fig.1 Experimental setup for the CCL method. Notations; BS; beam splitter, F; filter, P; pinhole, PMT; photomultiplier.

lens, the expanded beam due to the TL effect is focused at a farther position from the sample than the unperturbed beam. Then the probe beam intensity through the pinhole increases due to the TL effect, while the TA contribution decreases the light intensity. By comparing these signals, the contribution of TA can be evaluated.

According to the theory of the ray optics [11], when a lens with a focal length, f , is used for the expansion, the observed signal $U(t)$ is expressed by [6]

$$U(t) = Af\Delta n(t) - U_{TA}(t) \quad (1)$$

where A is a constant and $\Delta n(t)$ is the refractive index variation of the solution due to the TL and/or PL. Further, the focal length, f , is defined to be negative or positive in the cases of the concave or convex lens, respectively. When one uses the lenses with the same focal length ($f_{CC} = -f_{CV}$), the simple average of two signals measured with the concave ($U_{CC}(t)$) and with the convex ($U_{CV}(t)$) lenses will give $U_{TA}(t)$.

$$U_{TA}(t) = -(U_{CC}(t) + U_{CV}(t))/2 \quad (2)$$

Applicability of this method has been demonstrated by using samples of quinoxaline and C₆₀ [6]. The S₁ - T₁ intersystem crossing of the two samples takes place very efficiently after the photoexcitation to the excited singlet state. The triplet-triplet (T-T) absorption of quinoxaline at 633 nm has been known to be weak [12], while the T-T absorption spectrum of C₆₀ is located near that wavelength and the absorbance is relatively large [13].

The time dependence of the pure TL signal in the quinoxaline case has been studied. Since the time profile of the pure TL signal reflects the heat releasing process and the decay rate constant from the excited singlet state is much faster than the time resolution of the TL signal, the heat accompanied by the decay of the S₁ state appears as the fast rise with a time constant limited by the instrumental response. On the other hand, decay from the T₁ state can be slower than the time resolution and the TL signal rise with the same rate constant of the decay process. The total (U_{TOT}^{TL}) and slow (U_{SLOW}^{TL}) rising signal intensities are expressed by [3]

$$U_{SLOW}^{TL}/U_{TOT}^{TL} = \phi_{isc}(h\nu_{ex} - \phi_f E_f)/E_T \quad (3)$$

where ϕ_{isc} and ϕ_f are, respectively, the quantum yields of the triplet formation and the fluorescence, E_T the energies of the T_1 state, E_f average photon energy of the fluorescence, $h\nu_{ex}$ photon energy of the excitation.

The TL_{ex} signal after photoexcitation of quinoxaline appears as the decrease of probe light with the concave lens for expansion. The time profile consists of fast and slow rising components, which reflect the heat releasing processes of quinoxaline as explained above. When the convex lens is used for expansion, the TL_{ex} signal shows the increase of the probe beam intensity as predicted by eq.(1) with $U_{TA} \ll A_f \Delta n(t)$. The important point is that U_{SLOW}/U_{TOT} of the observed signal is essentially the same as in the convex lens case. This fact and eq.(1) indicate that the TA contribution is negligible in the TL_{ex} signal, which is consistent with the T-T absorption studies of quinoxaline [12]. On the other hand, there is a difference in the time profiles of the TL_{ex} signals after the excitation of C_{60} with the convex lens and with the concave lens. The slow rising component in the signal with the concave lens is much smaller than that with the convex lens, although the time constants of the slow rising signals are similar to each other. The different U_{SLOW}/U_{TOT} is due to the contribution of the TA in the early time region.

From both signals and eq.(2), U_{TA} in the TL_{ex} signal can be reasonably evaluated. These results show that this method is reliable and convenient for many experiments.

3. Contribution of population lens

Since the PL signal appears as a result of the probe beam expansion due to the non-uniform distribution of the refractive index in solution, the separation of PL from the pure TL signal is expected to be more difficult. However there are several ways to evaluate the relative contribution in the TL_{ex} signal.

3.1 Probe wavelength dependence

The refractive index variation due to the TL effect is essentially independent of the probe wavelength, while that due to PL is not. The relationship between the absorption spectrum and the dispersion of the concomitant refractive index change (Δn_{PL}) is given by eq.(4) [14] and depicted in Fig.2-a .

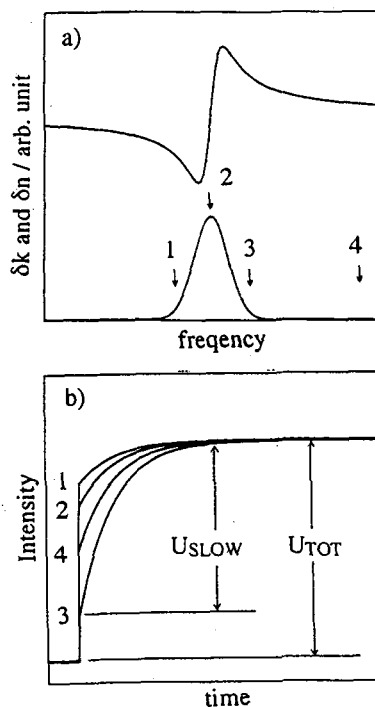


Fig.2 (a) Absorption spectrum (lower curve) and dispersion curve of the concomitant refractive index (upper curve). (b) Expected time resolved TL_{ex} signals probed at various frequencies indicated in (a). A time profile of the pure TL signal is curve 4. TA and/or negative Δn_{PL} contributions make the slow rising component smaller (curves 1 and 2), while positive Δn_{PL} makes it larger (curve 3). The intensities of the total (U_{TOT}) and slow rising component (U_{SLOW}) are shown in the curve 3 as an example.

$$\Delta n_{PL} = \sum C_i (\omega_0^2 - \omega_i^2) / \{ (\omega_0^2 - \omega_i^2)^2 + \gamma_i^2 \omega_i^2 \} \quad (4)$$

where ω_i and γ_i are the frequency at the absorption maximum and the linewidth of the i -th band, respectively. If the excited triplet state is the only metastable state as we assume here and the absorption spectra from the ground and the T_1 states have been known completely, the contribution of PL could be quantitatively calculated from eq.(4). This expectation is demonstrated as follows.

If the TL_{EX} signal is composed of only the pure TL signal, the time profile is expressed by eq.(3). On the other hand, if PL contaminates the TL_{EX} signal, U_{SLOW}/U_{TOT} deviates from the expected value from eq.(3) even after removing the TA contribution. Since the PL contribution should disappear after the excited state has relaxed, U_{TOT} should be composed of the pure TL signal.

$$U_{SLOW}/U_{TOT} = (U_{SLOW}^{TL} + U_{PL})/U_{TOT}^{TL} \quad (5)$$

In this equation, U_{PL} depends on the probe wavelength as predicted by eq.(4), while U_{SLOW}^{TL} does not. Therefore the time profile, especially U_{SLOW}/U_{TOT} , should depend on the probe wavelength. Expected time profiles of the TL_{EX} signal at various probe wavelengths are shown in Fig.2-b.

We have measured U_{SLOW}/U_{TOT} of anthracene in benzene at various probe wavelengths using an Ar ion laser [6] and the values are plotted in Fig.3-a with a reported T-T absorption spectrum [15]. The value decreases with probing at longer wavelength. U_{PL} is obtained from the time dependence of the signal and the literature value $\phi_{isc}=0.70$ [16]. The U_{PL}/U_{TL} values are plotted on Fig.3-b. U_{PL} is also calculated from the reported absorption spectra. The probe wavelength dependence agrees fairly well with the experimental values. This method will give U_{PL} hidden in the TL_{EX} signal from the absorption spectra, which are much easier to measure. However, if all absorption bands including far UV region are not known, a possibility of an offset in the calculated U_{PL} cannot be excluded completely.

3.2 Solvent dependence

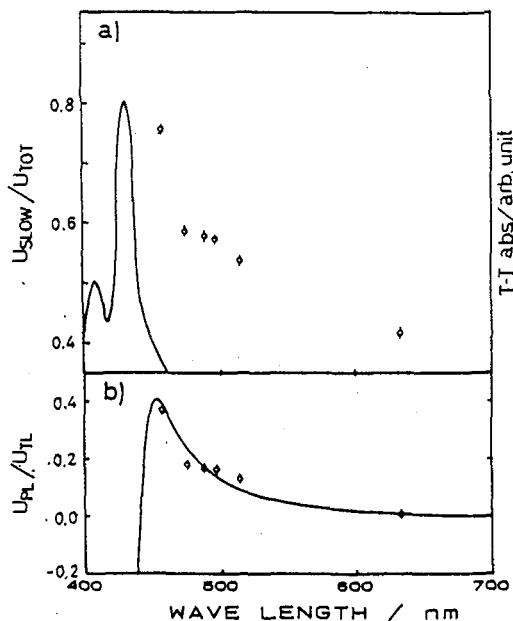


Fig.3 (a) Probe wavelength dependence of U_{SLOW}/U_{TOT} in the observed TL_{EX} signals of anthracene in benzene and a reported T-T absorption spectrum. (b) Relative contribution of PL in the pure TL signal (U_{PL}/U_{TL}) and a theoretically calculated probe wavelength dependence of U_{PL}/U_{TL} from the ground state absorption and the T-T absorption spectra.

Generally, not all of the absorption spectra from the ground and the T_1 states of many compounds have been reported. In such cases, the contribution of PL should be determined experimentally not from absorption spectra and eq.(4). Alternatively, we might use a different effect of thermal properties of the medium to PL and TL. The TL signal intensity depends on the thermal properties of the medium as

$$U_{TL} = A'H(dn/dT) / \rho C_p = A''S C^{ex} \quad (6)$$

where S is defined by ρC_p and C^{ex} is the concentration of the excited state, which should be proportional to the thermal energy, H , from the excited state. Combining eq.(3) and (6), one can obtain U_{SLOW}/U_{TOT} as

$$U_{SLOW}/U_{TOT} = U_{SLOW}^{TL}/U_{TOT}^{TL} + D \Delta n_{PL}/Sn \quad (7)$$

where D is a proportionality constant. Since the first term in eq.(7) is determined solely by the photophysical properties of the solute, it is the second term that affects the thermal properties of the medium. Therefore when U_{SLOW}/U_{TOT} is measured by changing S , the plot of U_{SLOW}/U_{TOT} against $1/Sn$ should give a straight line with an intercept of $U_{SLOW}^{TL}/U_{TOT}^{TL}$. This idea is demonstrated in the case of anthracene by changing the solvents (a series of alkanes [6]). Fig.4 shows the plot of the U_{SLOW}/U_{TOT} value probed at 458 nm against C/Sn . The contribution of TA is eliminated by the CCL method. Since at this probe wavelength, even a small peak shift of the T-T absorption band affects Δn_{PL} , the variation of Δn_{PL} due to that solvent effect should be taken into consideration by a parameter C , which is calculated from eq.(4). The plot shows a straight

line as expected. The intercept (0.4) gives $\phi_{isc}=0.70$, which agrees well with the previously determined value. This method should work well when the absorption band is not located near the probe wavelength. When that is the case, a small shift of the absorption band due to the solvent effect will seriously change Δn_{PL} and this method cannot be applied.

3.3 Rise profile

In many organic solvents, the origin of the TL signal is the refractive index variation due to the volume expansion of the medium, which is induced by heat. The volume expansion does not take place immediately after the heat release. Therefore there is a finite rise time, which is determined by the acoustic transit time (around 100 ns under normal TL experimental conditions). On the other hand, PL is created whenever the metastable state is created and the rise time is determined by the creation rate of the metastable state, which could be an order of 10 ns or less for many compounds. On the basis of

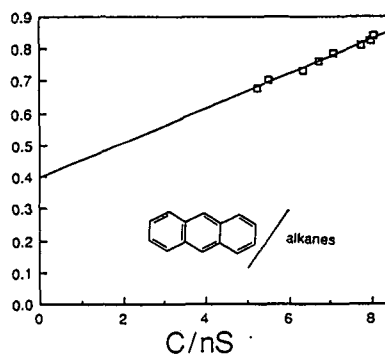


Fig.4 Plot of U_{SLOW}/U_{TOT} after the photoexcitation of anthracene in a series of alkanes probed at 458 nm. The straight line is calculated by the least square method.

these facts, it is expected that the PL contribution can be separated from the pure TL signal by analyzing the rise profile of the TL_{ex} signal.

Fig.5-a shows the time profile of the TL_{ex} signal after the photoexcitation of 9,10-diazaphenanthrene (DAP) in benzene. It is already known that DAP possesses very short lived S_1 and T_1 states and the heat releasing rate is considered to be instantaneous. Therefore we can safely neglect the contribution of PL, TA, and the slow heat releasing processes. The TL signal gradually appears after the photoexcitation, it reaches a maximum, then it decreases to take a plateau. The time profile is very similar to that reported by Bailey et al. in the gas phase with a fast relaxation time [17]. Indeed, we find this time profile can be fitted well by a theoretical calculation from the Navier-Stokes equation and the energy transport equation [18]. Fig.5-b depicts the rise profile of the TL_{ex} signal of C_{60} in benzene after subtracting the TA contribution by the CCL method.

It is clear that there is a fast rising component in the

signal. The time profile can be fitted well by the superposition of the TL signal, which has the same time dependence as in the 9,10-diazaphenanthrene case and a single exponential function of PL.

$$\Delta n_{PL}(t) = \Delta n_0 \exp(-kt) \quad (8)$$

The decay rate constant, k , represents the decay rate constant of the T_1 state of C_{60} . The fit agrees well with the observed signal and the contribution of PL can be determined quantitatively. The Contribution of PL can be measured from a single experiment by using this method and it does not require any information on the absorption spectra.

4. Conclusion

For the quantitative application of the TL method to investigate the excited state dynamics and chemical reactions, it is important to ensure that the observed signal is truly a pure TL signal. If the TL signal is contaminated, the time profile as well as the signal intensity no longer reflects the heating effect by the photoexcited molecules or chemical reactions. There are several origins except the TL signal to give a TL like signal, such as the transient absorption, the population lens and do on. Problems are how to detect such an "impure signal" (of course, the impure signal itself could be important for another application) and how to quantitatively evaluate it. In this paper, we present several new methods to evaluate the TA and PL contributions in the observed TL_{ex} signal. We have demonstrated the

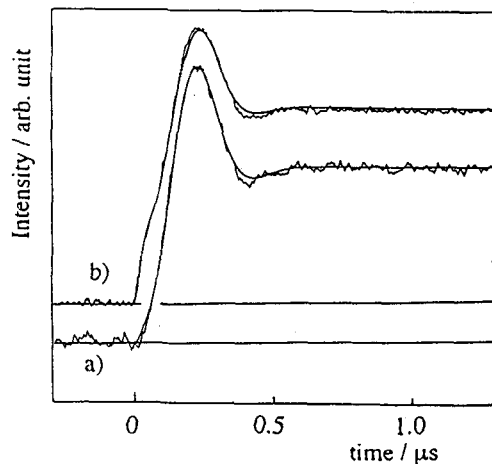


Fig.5 Rise time profiles of the TL_{ex} signals after the photoexcitation of DAP (a) and C_{60} (b) in benzene. The smooth curves are best fitted theoretically calculated curves with only the pure TL contribution for (a) and a superposition of the TL and PL contributions for (b).

applicability of these methods by taking examples of the T_1 state as the metastable state. Most of them except the rise time profile analysis method can be applicable to the steady state (cw) TL experiment.

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