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Limitation of Absorbance Measurement by Using Photoacoustic Method

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The solute dependence of the photoacoustic (PA) signal intensity has been examined. The results show that the PA signal intensity depends not only on the released energy, but also on the nature of the solute. This means that the absorbance of an unknown sample cannot be precisely measured by comparing the PA signal intensity with that of a standard solution containing a different solute.

Photothermal techniques, such as thermal lens (TL)[2,3] and photoacoustic (PA),[4–6] have been utilized for the sensitive detection of weak absorptions. In order to obtain absorptivity in a quantitative manner, the light energy absorbed by a solution should be obtained from the signal intensity. However, since the TL and PA signal intensities depend on the various physical properties of the solution (vide infra) and experimental conditions, it is extremely difficult, if not impossible, to determine the absorbed energy from the signal intensity. In view of this difficulty, one usually tries to estimate the absorbed energy by comparing the signal intensity with that of a standard sample of known absorbance.[4–15] This comparison method is based on the theoretical expectation[4–8] that, provided that the proper correction for the energy loss due to radiative emission and photochemical reaction is made, the signal intensity should be proportional only to the absorbed energy in the series of experimental data obtained with the same experimental setup. In particular, since the signal intensity of the sample is compared with that of the standard solution, which usually contains a different solute, the signal intensity should not depend on the nature of the solute if the released energy is identical.

Even though this comparison method is frequently used in both the PA and TL methods,[4–15] we found in a previous study that the absorbance of a sample cannot be precisely measured, at least by the TL method.[1] This result was based on the fact that the TL signal intensity depends not only on the releasing energy but also on the nature of the solute. Namely, the assumption which is essential for the capability of the quantitative measurement has been revealed to be invalid. We have suggested that the solute dependence of the TL signal comes from the vibrational mode dependence of the vibration to the translation energy transfer rate.[1]

As an extension of this TL experiment, we attempted in the present work to study the PA signal and its correlation with the TL signal by using a simultaneous PA and TL measuring system. As described in detail below, we found that the PA signal intensity also depends on the solute. This means that the PA signal intensity of a solution cannot be calibrated by using a standard sample solution containing a different solute.

Experimental

The apparatus of the TL experiment described previously[1] was modified so as to perform simultaneous measurements of both the TL and PA signals (Fig. 1). For the PA detector, a piezoelectric transducer (PZT) of a lead zirconate-lead titanate cylinder (Tohoku Kinzoku Co. N-6) poled axially was used. It was mounted inside a metal case, essentially the same as designed by Patel and Tam.[17] The transducer was directly attached to the wall of the square cell from the outside with a thin vacuum grease layer to facilitate acoustic coupling. The signal from the transducer was amplified by a wide-band preamplifier (PAR, Model 115) with a voltage gain of 10. The signal from the amplifier was fed into a transient digitizer (Iwatsu Co., DM901) and averaged by a microcomputer (NEC, PC-9801). For the excitation light source, a nitrogen laser (Molectron UV-24) was used. The laser power was 3 μJ/pulse. In the case of 400-nm excitation, a dye laser (Molectron, DLII-14P) pumped by the nitrogen laser was used for the light source. The laser beam, focused using a 20-cm focal-length lens, passed through the sample cell at the distance 5 mm from the PA detector. Since the PA signal intensity slightly depended on the volume of the sample in the cell, we use a fixed volume (3.5 cm^3) of the sample for the measurement.

Chemicals and purification procedures were the same as previously reported.[1] The concentrations of the sample solutions were adjusted so that the absorbance at 337.1 nm

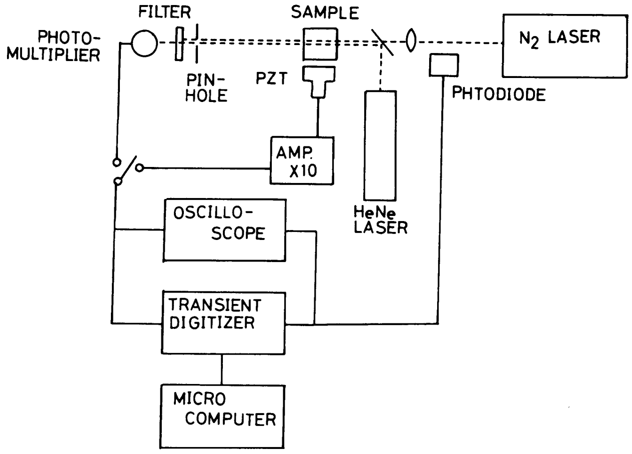

Fig. 1. Block diagram of the experimental setup for thermal lens and photoacoustic measurement in simultaneously.

was 0.1±0.01. Therefore, the concentration of each solution varied, depending on the molar extinction coefficient at 337.1 nm.

Method

If the assumptions described below are satisfied, the electronic signal from a PZT is given by[8,9]

$$I_{\mathrm{PA}} = K\frac{v^2\beta}{C_{\mathrm{P}}}(1 - 10^{-A})H, \qquad (1)$$

where K is a constant that depends on the geometrical parameters as well as on the response properties of the PZT, but not on the nature of the solute. Further, C_{p}, β, A, and v denote the molar heat capacity at constant pressure, the thermal expansion coefficient, the absorbance of the sample, and acoustic velocity, respectively. The factor $(1-10^{-A})H$ represents the releasing energy from the sample as the radiationless transition. H is expressed by[1]

$$H = H_0\left(1 - \frac{E_{\mathrm{s}}}{E_{\mathrm{ex}}}\phi_{\mathrm{f}} - \frac{\Delta H}{E_{\mathrm{ex}}}\phi_{\mathrm{reac}}\right), \qquad (2)$$

where E_{ex}, E_{s}, and H_0 are the photon energy of the pulsed laser, the photon energy of the fluorescence, and the laser power which is used to excite the solute, respectively. Further, ϕ_{f} is the quantum yield of the fluorescence and ϕ_{reac} is a quantum yield of the photochemical reaction. The quantity ΔH is the enthalpy difference between the reactant and the product. For air-saturated samples, any radiative decay due to phosphorescence can be neglected.

The assumptions which were used to derive Eq. 1 are as follows:[8,9]

(a) A thin cylindrical excitation (week absorption of the sample),
(b) $w^2/D \gg t_{\mathrm{a}}$, (3)
(c) $t_{\mathrm{a}} \gg t_{\mathrm{p}}$, (4)

and

(d) $t_{\mathrm{a}} \gg t_{\mathrm{nr}}$. (5)

Here t_{p}, t_{nr}, and t_{a} are the pulse length of the excitation laser, the relaxation time from the excited state, and an acoustic transit time to travel across the laser illuminated region in the sample, respectively. Further, D and w are the thermal diffusion coefficient and the laser spot size, respectively.

The PA signal intensity should be solute independent as long as Eq. 1 is valid, since Eq. 1 was derived from thermodynamic equations, in which there are no solute dependent factors. Previously, investigators have taken it for granted that Eq. 1 is valid for many molecules under real experimental conditions. Our goal in this study was to check whether or not Eq. 1 is valid under our experimental condition. We define the corrected signal intensity as

$$S_{\mathrm{PA}} = I_{\mathrm{PA}}/(1 - 10^{-A})H = K\frac{v^2\beta}{C_{\mathrm{p}}}. \qquad (6)$$

If the thermal properties (β, C_{v}, v) of a solution are essentially identical to those of the solvent, S_{PA} should not depend on the solutes as long as Eq. 1 is valid. We measured S_{PA} for many organic solutes in the same solvent (benzene).

The TL signal intensity (I_{TL}) and the corrected intensity (S_{TL}), defined previously,[1] are given here again for convenience:

$$I_{\mathrm{TL}} = \frac{I(t{=}0) - I(t{=}\infty)}{I(t{=}0)} \qquad (7)$$

and

$$S_{\mathrm{TL}} = I_{\mathrm{TL}}/(1 - 10^{-A})H, \qquad (8)$$

where $I(t{=}0)$ and $I(t{=}\infty)$ are the intensity of the cw monitoring laser just after the solute is excited by the pulsed laser and that after the sufficiently long time compared with the heat diffusion time in the solution, respectively.

Results

A typical PA siganl is shown in Fig. 2. There is no detectable signal from the pure solvent; we therefore conclude that there is no signal from the wall of the cell or due to scattered light. The peak height of the first minimum in the PA signal is an arbitrary measure of the amplitude of the signal (I_{PA})(Fig. 2), because the first maximum peak is easily disturbed by the electric noise coming from the excitation laser. The relative I_{PA}

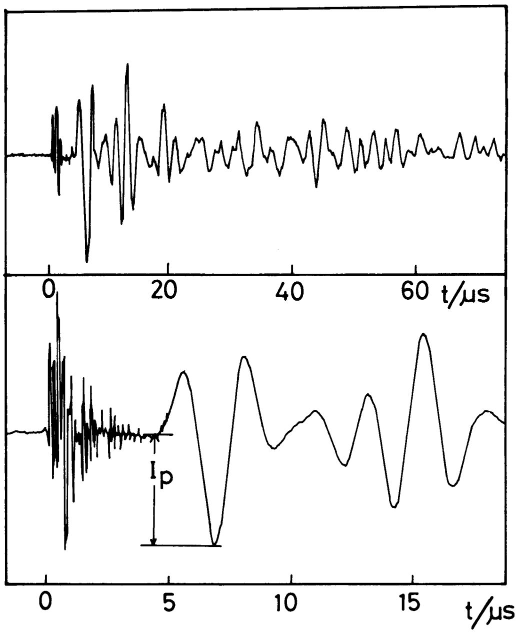

Fig. 2. Single pulse trace of the PA signal. The signal intensity (I_{PA}) which we measured is also represented.

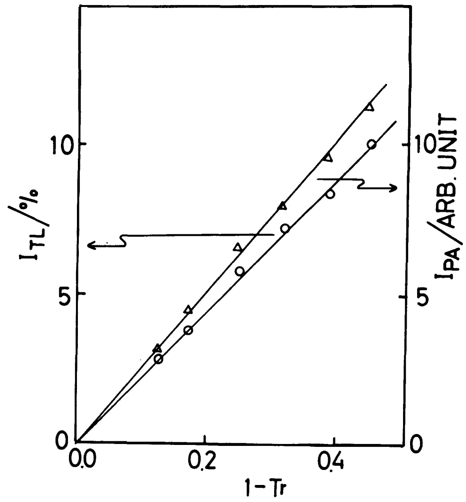

Fig. 3. Plot of the thermal lens and photoacoustic signal intensity vs. $(1-T_r)$, where T_r is the transmittance of the benzophenone in benzene at 337.1 nm.

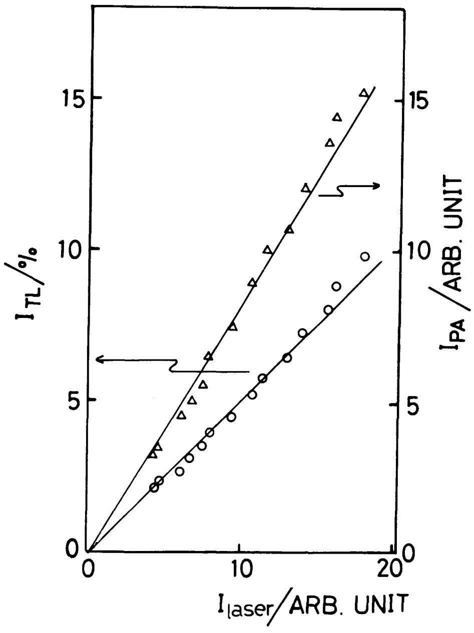

Fig. 4. Plot of the thermal lens and photoacoustic signal intensity vs. the excitation laser power for benzophenone in benzene.

Table 1. The Corrected TL (S_{TL}) and PA (S_{PA}) Signal Intensity for Various Solutes in Benzene
S_{PA} and S_{TL} of benzophenone is set to be 1.00.

Solute	S_{PA}	S_{TL}
Benzophenone	1.00	1.00
Anthracene	0.98	1.10
Phenanthrene	1.00	1.03
Stilbene	0.92	0.65
9,10-Dibromoanthracene	0.83	0.92
9,10-Anthraquinone	0.83	0.73
Fluorenone	0.79	0.90
Biacetyl	0.83	0.99
Tetrachloro-*p*-benzoquinone	0.62	0.83
1,2-Naphthoquinone	0.81	0.83
1,4-Naphthoquinone	0.97	0.83
Benzil	0.85	0.83
1-Amino-9,10-anthraquinone	0.76	0.75
9,10-Phenanthraquinone	0.70	0.83
Quinoxaline	0.68	0.82
Phthalazine	0.88	0.76
Quinoline	0.81	0.81
Isoquinoline	1.00	0.89
Phenazine	0.81	0.91
9,10-Diazaphenanthrene	0.96	0.89
Azobenzene	0.85	0.60
3,3′-Dimethylazobenzene	0.81	0.59
p-Nitrophenol	1.00	0.84
p-Nitroaniline	0.96	0.69
o-Nitroaniline	0.86	0.61
Nitrodiphenylamine	0.97	0.70

values were reproducible within 5%.

First, we checked the linerity of our system for the PA and TL measurements. Figure 3 shows the signal intensity of PA and TL against $(1-10^{-A})$. The linear dependence of the PA and TL signal intensities on the laser power is shown in Fig. 4. Within the range of concentrations and laser powers which we used there was no saturation effect. These results rationalize the validity of Eq. 6.

Table 1 summarizes the relative PA (S^{r}_{PA}) and TL(S^{r}_{TL}) signal intensities observed for various solutes in benzene. The signal intensity of benzophenone is set to be 1.00; that is,

$$S^{r}_{PA} = S_{PA}(\text{sample})/S_{PA}(\text{benzophenone})$$

and

$$S^{r}_{TL} = S_{TL}(\text{sample})/S_{TL}(\text{benzophenone}).$$

The correction parameters for fluorescence and photochemical reactions are the same as those listed previously.[1]

Discussion

The Validity of Eq. 1. According to Eq. 1, the PA signal intensity should be proportional to the releasing energy. Further, if the releasing energy, experimental configuration and thermal properties (β, v, C_p) are identical, the PA signal intensity should be identical. The results listed in Table 1 are, however, inconsistent with this prediction.

Before we doubt the validity of Eq. 1, we should check the solute dependence of the factors which affect the signal intensity. We will first check the thermal properties of the solutions. In dilute solutions, as in this case, the thermal properties of the solution are considered to be almost identical to those of the pure solvent. Actually, we have already confirmed that the thermal properties which affect the TL signal intensity (thermal diffusivity, thermal conductivity and dn/dT; where n and T denote the refractive index and temperature, respectively) are almost identical to those

Table 2. The PA Signal Intensity (I_{PA}) of Mixed Solutions to Examine the Solute Effect on the Thermal Properties of the Solvent
The excitation wavelength is 400.0 nm. I_{PA} of 9,10-dibromoanthracene (DBA) is set to be 1.00 as reference.

	I_{PA}
9,10-Dibromoanthracene (DBA)	1.00
DBA+anthracene	0.95
DBA+benzophenone	0.99
DBA+quinoxaline	0.95
DBA+stilbene	0.98

of the pure solvent.[1] Here, we examine whether the thermal properites which affect the PA signal (β, v, C_p) are similarly identical to those of a pure solvent.

The principle is as follows: If the thermal properties of a solution are different from those of a pure solvent upon adding a solute (solute A), the PA signal intensity which comes from another solute (solute B) with solute A should be different from that of solute B without solute A. We used 9,10-dibromoanthracene (DBA) as solute B. We choose benzophenone, stilbene, quinoxaline, and anthracence for solute A. A dye laser at 400 nm was used to excite only solute B, not solute A. Note that only DBA possesses an absorption band at 400 nm. We prepared two kinds of solutions. One solution contained only solute B, whose absorbance at 400 nm was adjusted to 0.1. The other solution contained solute B of the same concentration as solute A, whose absorbance at 337.1 nm was adjusted to 0.1, identical to the previous experiment (Table 1). If the PA signal intensity of the solution contained both A and B is different from that of the solution contained only solute B, it means that solute A changes the thermal properties of the solution from those of a pure solvent. The observed S_{PA}, summarized in Table 2, does not depend on whether or not solute A is contained within the experimental error. This result shows that the thermal properties which affect the PA signal intensity are almost identical to those of a pure solvent. Therefore, the solute dependence (Table 1) cannot be explained by the solute effect on the thermal properties of the solvent.

Other trivial factors, such as multiphoton and/or transient absorption and scattering processes, can be neglected under our conditions, as confirmed previously.[1]

The S_{TL} values listed in Table 1 are almost identical to the values reported in Ref. 1. In that paper, we conclude that the dissipation of thermal energy as pressure waves does not play an important role in the solute dependence of the TL signal intensity. If the thermal energy dissipation as pressure waves is the origin of the solute dependence of the TL signal, a solute which gives a small S_{TL} should give a large S_{PA}. However, such a negative correlation was not found, as shown in Fig. 5. This result supports the previous conclusion.[1]

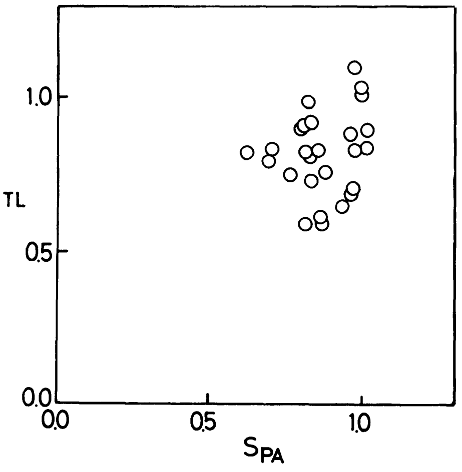

Fig. 5. Plot of the corrected TL (S_{TL}) vs. PA (S_{PA}) signal intensity for various solutions listed in Table 1.

The Origin of the Solute Dependence. According to the above discussion, the solute dependence of S_{PA} means that Eq. 1 does not hold under our experimental conditions. In this section, we discuss the origin of the solute dependence by checking the assumptions on which Eq. 1 is based.

Under our experimental conditions, the first (a thin cylindrical excitation), the second (Eq. 3) and the third (Eq. 4) assumptions were considered to be adequate on the basis of parameters $w \approx 1$ mm, $D \approx 10^{-3}\,\mathrm{cm^2\,s^{-1}}$, $t_a \approx 4\times10^{-7}$ s, and $t_p \approx 1\times10^{-8}$ s. Furthermore, these conditions should not depend on the nature of the solute, as considered in the previous section (Table 2). Therefore, the solute dependence is not due to a violation of these conditions. The factor t_{nr} of Eq. 5 represents the relaxation time of the energy transfer from the electronic energy of the solute to the translational energy of the solvent. If t_{nr} is longer than 500 ns, this quantity can be measured from the rise time of the TL signal and the adequacy of the fourth condition checked. Unfortunately, we found that the rise times of the TL signal of these solutions which we investigated are determined by the time constant of the TL signal (500 ns) in our experimental apparatus. We can therefore only say that t_{nr} is shorter than 500 ns. Although we cannot conclude the invalidity of the fourth condition exclusively, we may suggest that the remaining condition, i.e. the fourth condition (Eq. 5), could be the reason for the solute dependence; namely, the fourth condition does not hold for some solutes. The experimental support for this assumption is now in progress.

The observed solute dependence of the PA signal intensity means that the quantitative measurement by the PA method using a reference solute is not precious. In order to measure the absorbance precisely, the solute of the reference sample should be the same solute as the sample, or the solute-dependent factor should be corrected before the PA signal intensity is compared. For practical purposes, we suggest that the signal intensity of the PA signal should be expressed empirically be

$$I_{\mathrm{PA}} = K'\frac{v^2\beta}{C_{\mathrm{p}}}(1 - 10^{-A})H, \tag{9}$$

where K' depends on the nature of the solute.

Conclusion

Our experimental results show that not only the TL signal but also the PA signal intensity depends on the solute, even if the releasing energy and the experimental configuration are identical. This fact means that absorbance measurements by the TL and PA method are not precious unless the signal intensity is calibrated using the same solute.

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