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A Time-Resolved Photoacoustic Method with Pulsed Laser Excitation in the Condensed Phase: The Relation between Signal Intensity and Decay-Rate Constant

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The photoacoustic signal magnitude in the condensed phase with a piezoelectric transducer and a pulsed laser is theoretically calculated for various quantum yield of the triplet formation (ϕ_{isc}) and decay rate constants from the triplet state. The results show that the ϕ_{isc} value and the triplet lifetime can be determined from the PA signal intensity.

Photothermal methods, such as the photoacoustic (PA) and thermal lens (TL) methods, are suitable for sensitively detecting nonradiative transition. The time resolution of the TL method is usually short, of an order of submicroseconds. By using this advantage, the TL method has been used to separate the nonradiative decay processes of a microsecond order and those of nanosecond order by the time-resolved manner.[1—11] In view of this good time-resolution, this method has subsequently been successfully applied to the determination of the triplet lifetime,[1,3] the quantum yield of the triplet formation (ϕ_{isc}),[1,3] the enthalpy difference between reactant and product,[2] and so on.

Contrary to the TL method, the time response of the PA signal with a microphone and mechanically modulated excitation light is rather slow.[12—15] Therefore, the time resolved study with the PA method has been done by measuring the dependence of the amplitude or the phase shift of the PA signal on the modulation frequency.[16—18] However, for the PA method with a piezoelectric transducer (PZT) and pulsed laser light, even these indirect time-resolved methods have never been applied. Recently, though, Beck et al. have developed a time-resolved PA method with a microsecond time-resolution by using a PZT and pulsed laser light.[19,20] They estimated the nonradiative decay rate by analyzing the waveform of the PA signal. They intended, however, to analyze the signal in the gas phase, in which the main deactivation process is slow. The lifetime of the excited state should be comparable to, or longer than, the acoustic transit time, $\tau_a = R/v_a$, where R is the beam radius of the excitation laser and where v_a is the velocity of sound in that medium. Usually, the acoustic transit time in an experimental setup is of a microsecond order. In a condensed phase, on the other hand, there are usually two kinds of pathways for nonradiative decay. One is much shorter than the transit time under ususal experimental conditions (less than a nanosecond order), while the other is rather long (longer than a microsecond order). For instance, the T_1–S_0 intersystem crossing (isc) is included in the latter processes, while vibrational relaxation and internal conversion are included in the former processes. In such a case, since the waveform of PA signal depends on ϕ_{isc} and the decay rate constant of the slow process in a complicated manner, the analysis of the waveform becomes difficult. Moreover, the waveform easily suffers from the time response of the instruments used for the measurement.

Beside the analysis of the waveform, the PA signal magnitude may be expected to give information on the decay-rate constant (Fig. 4 of Ref. 19). However, the relation between the PA signal intensity obtained by using a PZT and the decay rate constant is not clear. So far, the contribution to the PA signal intensity from the slow decay process has been neglected, and the PA signal intensity has been analyzed by considering only the contribution from the fast decay processes (vide infra).[21] The quantum yield of the triplet formation has been measured under this assumption.[21] There are no theoretical grounds, however, for answering the question; how long should the triplet lifetime be in order to satisfy the above assumption?

In this paper, we will focus our attention on the relation between the PA signal intensity obtained by using a PZT after pulsed laser excitation and the decay rate constant when there are two kinds of heating processes. As will be described below, we find a simple correlation between the PA signal intensity and the decay-rate constant of the slow decay process. By using this correlation, we show that the quantum yield of the triplet formation and the triplet lifetime can be determined from the PA signal intensity. Finally, we will discuss the solute dependence of the PA signal under the air-saturated condition reported previously.[22]

Experimental

The experimental setup for the PA detection is essentially the same as that reported previously.[22] The system is, however, modified to measure simultaneously the lifetime of the triplet state by a flash photolysis method (Fig. 1). A nitrogen laser (Molectron UV-400) (ca. 10 μJ/pulse) was used for excitation. The laser-beam diameter was 2 mmϕ. The signals from a PZT for the PA measurement and those from a photomultiplier (Hamamatsu R928) for the flash-photolysis measurement were fed into a transient memory (Iwatsu

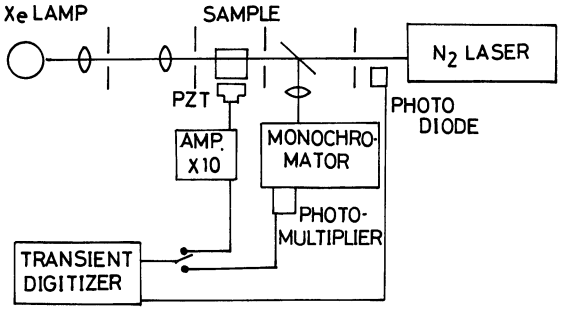

Fig. 1. Experimental setup for the simultaneous measurement of PA and transient absorption.

DM-901) and averaged up to 100 times in order to improve the S/N ratio. For monitoring the transient absorption of quinoxaline in benzene, light from an Xe lamp (Ushio 500 W) was made collinear with the nitrogen laser beam. The detection wavelength was 420 nm.

Quninoxaline purchased from the Wako Co. was purified by vacuum sublimation. The absorbance of the sample solution at 337.1 nm was adjusted to 0.1.

Theoretical

The PA signal intensity is calculated on the basis of the formalism of Lai and Young.[23] When the thermal diffusion and the effect of electrostriction are neglected, the excess pressure P, which is proportional to the PA signal, is expressed as:

$$P = K\frac{\partial \Phi}{\partial t} \tag{1}$$

where $K=\alpha\beta/C_p$, with α being the optical absorption coefficient; β, the volume expansivity, and C_p, the molar heat capacity at a constant pressure. Further, Φ is the velocity potential and is given by the solution of Eq. 2:

$$\left(\frac{1}{v_a}\frac{\partial^2}{\partial t^2} - \nabla^2\right)\Phi = I, \tag{2}$$

and:

$$I = Ef(t)\,g(r),$$

where r denotes the two-dimensional displacement transverse to the axis of the beam, where E is the total energy released from the excited solute, where $f(t)$ is the temporal profile of the deactivation process, and where $g(r)$ is the radial profile of the excited solute in the solution.

When reflection can be ignored, Eq. 2 can be solved as Eq. 3 in an infinite medium with outgoing wave conditions at infinity.

$$\Phi(t,r) = K\int_{-\infty}^{t}(t-t')^{-1/2}\hat{f}(t')\,\mathrm{d}t' \tag{3}$$

where $\hat{f}(t)$ is an effective temporal profile,

$$\hat{f}(t) = \int_{-\infty}^{t} f\left(t+\frac{r'}{v_a}\right)g(r')\,\mathrm{d}r' \tag{4}$$

and where:

$$K = (2\pi\sqrt{2}\,)E\sqrt{v_a/r}.$$

The PA signal intensity is numerically calculated by using Eqs. 1—4.

For the radial profile, we use the Gaussian radial distribution:

$$g(r) = \frac{1}{\sqrt{2\pi R^2}}\exp\left(-\left(\frac{r^2}{2R^2}\right)\right), \tag{5}$$

where R is the beam radius. For the temporal profile of the deactivation processes, a biexponential decay is assumed.

$$f(t) = A_f k_f \exp(-k_f t) + A_s k_s \exp(-k_s t), \tag{6}$$

where k_f and k_s represent the rate constants of the fast decay processes (e.g., vibrational relaxation, S_1–T_1 isc, and S_1–S_0 internal conversion) and a slow decay process (T_1–S_0 isc), respectively. The pre-exponential factors, A_f and A_s, represent the heat contribution from the fast and slow decay components, respectively. The sum of the pre-exponential factors is defined to be unity, so that $f(t)$ is normalized in such a way that:

$$\int f(t)\mathrm{d}t = 1.$$

The quantum yield of the triplet formation is represented by:

$$\phi_{\mathrm{isc}} = A_s(E_{\mathrm{ex}} - \phi_f E_f)/E_T$$

where E_{ex}, E_f, and E_T represent the photon energy of the excitation laser, that of the fluorescence, and the energy of the T_1 state, respectively. Further, ϕ_f means the quantum yield of the fluoresence. The decay-rate constant, k_f, is set so to as be sufficiently larger than $1/\tau_a$ (τ_a=1.6 μs) and of the same order as τ_p (=10 ns), which is the width of the Gaussian temporal profile of the exitation laser pulse. The value of k_f is fixed throughout this calculation. Since the time dependence of nonradiative decay follows that of the excitation laser pulse under the condition of $k_f \gg 1/\tau_a$, the variation in k_f under the condition $k_f \gg 1/\tau_a$ does not affect the calculated result. The slow decay-rate constant, k_s varies over the range of $0.05 < k_s\tau_a < 20$.

Results and Discussion

Result of the Calculation. The time-dependence of the PA signal, as calculated by using Eqs. 1—6, is shown in Fig. 2. The peak height from the bottom to the peak is taken to be the PA signal magnitude. In

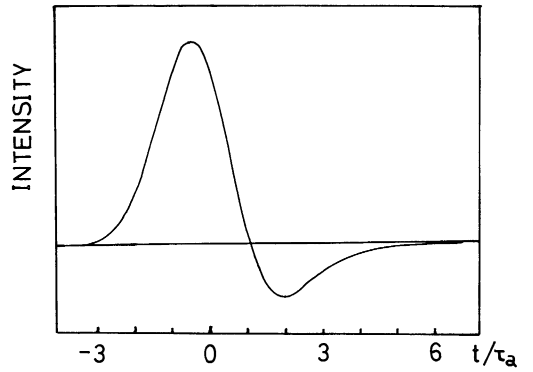

Fig. 2. Typical time dependence of the calculated PA signal by using Eqs. 1—6 with $A_s/A_f=1.0$ and $K_s\tau_a=10$.

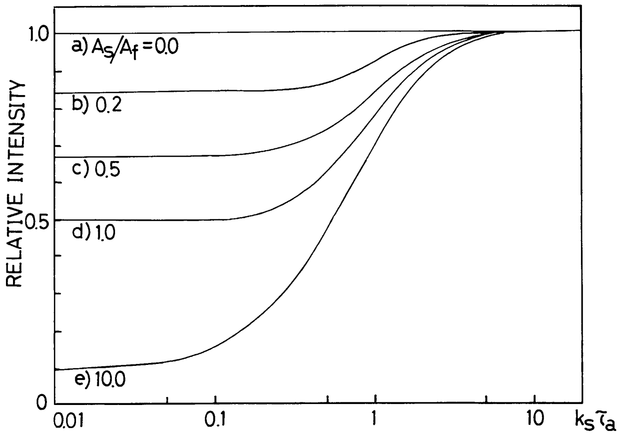

Fig. 3. Plot of the calculated PA signal intensity vs. decay rate constant of the slow decay process ($k_s\tau_a$). (a) $A_s/A_f=0.0$, (b) $A_s/A_f=0.2$, (c) $A_s/A_f=0.5$, (d) $A_s/A_f=1.0$, and (e) $A_s/A_f=10.0$.

Fig. 3, the PA signal intensity for various k_s and A_s/A_f values is shown. The results show that the signal intensity varies smoothly with the variation in the k_s and A_s/A_f values. The signal intensity remains constant until $k_s\tau_a$ becomes smaller than 5.0; then, it decreases with the decrease in $k_s\tau_a$. The signal intensity again takes a plateau value in $k_s\tau_a<0.1$. The plateau value in the small range of A_s/A_f is the same as the signal intensity (I_p) calculated by neglecting the contribution of the slow decay process:

$$I_p = I_p^0 \left(1-\frac{\phi_{isc}E_T}{E_{ex}}\right) \qquad (7)$$

where I_p^0 is the PA signal intensity with $A_s/A_f=0$, where E_T is the energy of the triplet state, and where E_{ex} is the photon energy of the excitation laser. The $\phi_{isc}E_T/E_{ex}$ factor represents the heat contribution from the triplet state. However, the signal intensity at $k_s\tau_a>0.2$ differs from the value calculated by using Eq. 7 (the plateau value of the signal intensity in $k_s\tau_a<0.1$). Especially for large A_s/A_f values, the deviation becomes large. For example, in the case of $A_s/A_f=10.0$, the signal intensities calculated from Eqs. 1—6 and those calculated from Eq. 7 are not the same values in the range of $k_s\tau_a>0.05$. If τ_a is 1.6 μs (the transit time under our experimental conditions), the contribution of the slow decay process cannot be neglected unless $k_s<3.1\times10^4$ s^{-1}.

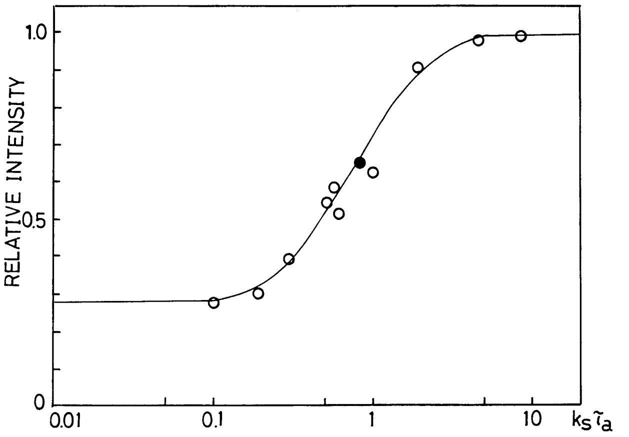

Fig. 4. Experimentally obtained PA signal intensity of quinoxaline in benzene vs. the triplet lifetime (open circules). The data point at air saturated condition is indicated by a closed circle. The calculated curve with $A_s/A_f=2.5$ is also shown.

Comparison with Experimental Results. The quantum yield of the triplet formation of quinoxaline is unity, and the phosphorescence from the T_1 state can be neglected in a benzene solution at room temperature. Oxygen efficiently quenches the T_1 state of quinoxaline. After the laser excitation to the higher vibrational level of the S_1 state, the fast nonradiative decay processes (vibrational relaxation to the zero vibrational level of the S_1 state, S_1–T_1 isc, and vibrational relaxation to the T_1 state) occur within a nanosecond time scale, followed by the slow nonradiative decay process (T_1–S_0 isc). In order to compare the theoretical results with the experimental results, we measured the PA signal intensity as a function of the lifetime of the T_1 state of quinoxaline in benzene. The lifetime of the T_1 state was varied by bubbling in a mixed gas of oxygen and nitrogen. The experimental results are shown in Fig. 4. The experimental data could be fitted well by using Eqs. 1—6 with $A_s/A_f=2.5$ ($\phi_{isc}=1.0$).

The method of obtaining ϕ_{isc} and k_s is summarized as follows. First, the PA signal intensities under the condition of a very fast triplet decay ($k_s>5/\tau_a$) and of the sufficiently slow triplet decay ($k_s<0.05/\tau_a$) should be measured. From the ratio of the intensities, the value of ϕ_{isc} can be determined. Once the value of ϕ_{isc} is determined, the triplet lifetime (k_s) can be estimated from the signal intensity. Even if the signal inensities of $k_s > 5/\tau_a$ and $k_s < 0.05/\tau_a$ cannot be measured for some reason, still ϕ_{isc} can be determined by fitting the variation in the signal intensities at various decay rates to Eqs. 1—6 (Fig. 3).

Under our experimental conditions, the upper limit of the time resolution was ca. $2 \times 10^6\ s^{-1}$, which was determined by the transit time and the response of our PZT. Recently, Tam et al.[24] and Heihoff et al.[25] have reported a PA method with a very fast time response (ca. 10 ns). If such a detection system with a smaller beam radius is used, the upper limit of the time resolution becomes much larger.

Quantitative Measurement by the PA Method. Our results (Fig. 3) show that the PA signal intensity is sensitive to the nonradiative decay rate constant within $0.1 < k_s\tau_a < 2.0$. We should emphasize that even the signal intensity at $k_s \sim 2/\tau_a$ is only slightly different from that in $k_s > 10/\tau_a$ for large ϕ_{isc} values. This means that we should be much more careful in the quantitative measurement of the PA signal. Frequently, the quantum yield of luminescene, the absorptivity of a solution, and the enthalpy difference between reactants and products are determined by comparing the PA signal intensities of samples with those of standard solutions.[26—34] However, the decay rate constant of the nonradiative transition has scarcely been taken into account in the interpretation of the signal intensity.

Previously, we have reported that the PA signal intensity depends on the nature of the solute.[22] At that time, we found that the signal intensity of quinoxaline was much smaller than those of other solutes under air-saturated conditions. In this work, we note that the lifetime of the triplet state of quinoxaline under air-saturated conditions is indeed shorter than those of τ_a, but it is not sufficiently shorter than τ_a; that is, k_s is not as large as $k_s\tau_a > 10.0$ (Fig. 4). This means that the PA signal intensity of quinoxaline under air-saturated conditions should be smaller than that of other solute which releases heat energy promptly ($k_s > 10/\tau_a$). The expected small signal intensity of quinoxaline agrees with the reported solute dependence of the PA signal reported previously.[22] That is, different PA signal intensities due to different decay-rate constants among the various solutes can be one of the reasons for the solute-dependent PA-signal intensity.

Conclusion

The PA signal intensities for various values of ϕ_{isc} and triplet lifetimes were calculated numerically. The results showed that the signal intensity depends on these quantities sensitively in the range of $0.1 < k_s\tau_a < 2$. This means that the triplet lifetimes and ϕ_{isc} values can be measured from the PA signal intensity. Under our experimental conditions, the upper limit of the time resolution is ca. $2 \times 10^6\ s^{-1}$, which is determined by the transit time and the response of our PZT.

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