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Study on the Photolysis Quantum Yield of Diphenyl Disulfide by the Transient Grating Method

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Transient grating (TG) spectroscopy, photoaccoustic spectroscopy, and transient adsorption spectroscopy have been applied to studying the nongeminate recombination of photodissociated diphenyl disulfide (DPDS) in liquids. The photolysis quantum yield can be easily determined by an analysis of the time profile of the thermal grating signal, if the contribution of the population grating can be neglected. The quantum yield of the photodissociation for DPDS in isooctane has been determined to be 0.43±0.02, which coincides with the values evaluated from the acoustic strength in the TG signal and the acoustic intensity in an ordinary photoacoustic measurement. This result is compared with a pico-second transient absorption measurement (T. W. Scott and S. N. Liu, *J. Phys. Chem.*, **93**, 1393 (1989)).

The photodissociation and recombination reaction in a dense fluid is one of the simplest reactions which reflects various interesting aspects of the dynamic and static effects of the environment on chemical reactions: e.g., the collisional deactivation and recombination of the molecules on a dissociative potential surface before complete dissociation (the primary geminate recombination), the diffusive effect on the recombination of the produced geminate pair (the secondary geminate recombination) and of the nongeminate pair, and the collisional vibrational deactivation of the recombined pair of the molecule, and so on.(1) These solvent effects are often referred to as the cage effect. The photolysis quantum yield, defined as the fraction of pairs of free radicals produced by photodissociation, is strongly connected with the solvent cage effect mentioned above. This can be simply seen by an intuitive idea that the stronger solvent cage traps more geminate pairs (a higher quantum yield of the primary geminate recombination) and leads to a higher probability of collisional stabilization of the encounter complex in competition with back diffusion into free radicals (a higher quantum yield of secondary geminate recombination). As a result, the photolysis quantum yield decreases along with increasing the solvent viscosity, which is often considered to be an index of the strength of the solvent cage.

In general, it is difficult to carry out a quantitative experiment to obtain the photolysis quantum yield by adsorption and fluorescence measurements. In principle, the photolysis quantum yield can be determined by transient adsorption spectroscopy with a nanosecond time resolution by analyzing the absorption of the transient species using a simple relation with a few observable quantities, such as the laser-pulse intensity absorbed in a sample and the nongeminate recombination rate constant.(2) This procedure requires "the number of laser photons absorbed in the sample" at high precision. Femto- and pico-second transient absorption spectroscopy have also been extensively utilized to pursue the photodissociation of I_2 and several polyatomic molecules.(1) In this time range, however, the vibrational relaxation of the recombined pair, and/or energy dissipation of the hot geminate pair, brings about some ambiguity in assigning the transient adsorption and a quantitative estimation of the dissociated molecules.

Photothermal methods, such as using thermal lens, photoacoustic, and photothermal grating methods, have great advantage in measuring nonradiative processes in chemical reactions.(3) These methods detect the heat dissipated by photochemical processes, and can effectively determine the quantum yield of the nonradiative process. Especially the photothermal grating method has a great advantage in its time resolution.(4) The time resolution of photothermal grating spectroscopy is limited by either the laser pulse duration or the time required for a sound wave to traverse the grating fringe distance, whichever is longer. Since the velocity of sound in a liquid is ordinarily on the order of $1000\ \mathrm{ms}^{-1}$, it is quite easy to obtain nanosecond time resolution by making the grating fringe as narrow as on the order of 1 μm. Recently, photothermal grating spectroscopy with nanosecond time resolution has been applied for the determination of the quantum yield of triplet formation by Terazima and Hirota,(5) and the quantum yield of the photodissociation of I_2 by Zhu and Harris.(6) In these experiments, the signal due to the photothermal grating consists of two components; a fast component which rises within the laser pulse duration, and a slow component which rises after the fast component. Each component decays with the thermal diffusion process. The fast component corresponds to exothermic processes with shorter relaxation times than the pump laser pulse duration, such as the excess energy relaxation of the singlet state, or the primary and secondary geminate recombination processes. We use the term "fast heat" for this type of heat.

The slowly rising photothermal grating signals correspond to an exothermic process with a slower relaxation time than the pump pulse duration, such as decay of the triplet state or nongeminate recombination of the dissociated iodine atom. We use the term "slow heat" for this type of heat. In the case of the decay of the triplet state, the released heat can be described by separate spatial and temporal terms, since the process obeys first-order decay. On the other hand, nongeminate recombination shows second-order kinetics where these terms can no longer be separated without a more complicated analysis.[6)]

In this study we have applied the transient grating (TG) method to measurements of the photolysis quantum yield (ϕ_d) of diphenyl disulfide (DPDS) in liquid solvents. The photodissociation dynamics of disulfide compounds has been studied by several authors using a transient absorption spectroscopy from the micro-second to pico-second time regime.[7—23)] DPDS is well known to undergo photolysis of the S–S bond by UV excitation, forming phenylsulfanyl radicals (PS•), which recombines to reproduce the parent molecule with a quantum yield of almost unity. It is an interesting issue as to how the polyatomic nature of DPDS affects the solvent dependence of the photolysis quantum yield. We have determined ϕ_d of DPDS in a variety of solvents by measuring the TG rise signal. Here, we propose a simplified analysis procedure to the theory proposed by Zhu and Harris,[6)] the result of which has been verified by the results of two other different experiments: a measurement of the intensity of the acoustic signal in the TG signal,[24)] and a measurement of the intensity of an ordinary photoacoustic (PA) signal.[25)] Both in PA and TG acoustic measurements, we can determine the photolysis quantum yield by the sound strength produced by expansion of the solution by fast heat. In these two measurements, however, we need a reference sample to convert the sound strength to the heat dissipated by the fast process. We consider that the TG method is of great advantage concerning the point that we can determine the photolysis quantum yield without any reference sample. It should be noted that we use the term "transient grating method" instead of "photothermal grating spectroscopy", since not only the thermal grating, but also the population grating (i.e. the grating due to the change of the refractive index and the absorption coefficient by the change of the population of the parent molecule and the transient chemical species), can contribute to the signals in some cases, which brings about some difficulty in determining the thermal contribution. The PA measurement has a merit concerning this point since the signal is not disturbed by a change of the optical properties of the produced radicals. By comparing the results obtained by using these three methods, we can accurately determine the photolysis quantum yield.

Theory

We briefly give an outline of the theory to determine the photolysis quantum yield (ϕ_d) by the TG signal based on a discussion given by Zhu and Harris. We use almost the same notations as given in Ref. 6. We consider the reaction scheme depicted as in Scheme 1, which is quite similar to Fig. 1(b) in Ref. 6, except for the molecule under consideration. Under the assumption that the nonradiative quantum yield is nearly unity and that k', k_1, and k_2 are quite faster than the pulse duration, the total heat emitted by these fast processes (Q_f) can be expressed as

$$Q_f = Q_0[1-\exp(-I/I_{sat})], \tag{1}$$

where $Q_0 = [C][E_{ex} - \Delta H\phi_d]/\phi_d$, $[C]$ is the bulk concentration of the parent molecule, E_{ex} the excitation pulse energy, ΔH the enthalpy of the recombination of the radicals, I the laser power of the excitation pulse, and I_{sat} the saturation intensity given by $(\sigma t_0\phi_d)^{-1}$, where σ is the absorption cross section and t_0 is the pulse duration.

The rate of the heat released by the nongeminate recombination, i.e., the slow heat component, can be given by

$$\frac{dQ_s(t)}{dt} = \frac{\Delta H k_r[R]_0^2}{[1+2k_r[R]_0 t]^2}, \tag{2}$$

where k_r is the rate constant for the nongeminate recombination and $[R]_0$ is the concentration of the free radicals produced by the photoexcitation, given by

$$[R]_0 = 2[C][1-\exp(-I/I_{sat})]. \tag{3}$$

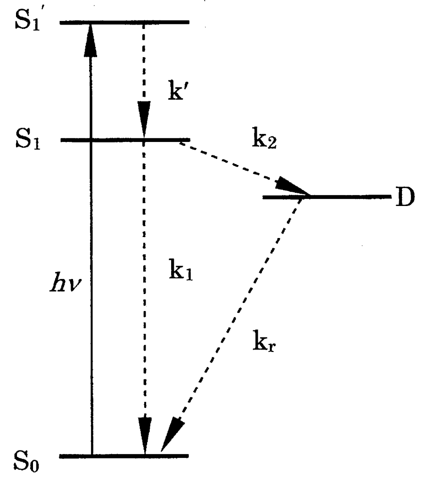
We assume that the pulse duration can be expressed like a δ-function.

In the grating experiment, the sample is excited by crossing two laser pulses with an angle θ as follows:

$$I(x) = I_0[1+\cos(qx)], \tag{4}$$

where $q = (4\pi n_0/\lambda_e)\sin(\theta/2)$, λ_e is the wavelength of the excitation pulse and n_0 is the average refractive index of the media. According to an analysis by Zhu and Harris, the diffraction efficiency (η) at the Bragg angle for the first harmonic grating is given by

$$\eta \propto [Ag_1(t) * \exp(-D_{th}q^2t) + B\exp(-D_{th}q^2t)]^2, \tag{5}$$



Scheme 1. Four-level kinetic model for the photo-dissociation and recombination process.

where $A=\Delta H[C]/\rho C_p$, $B=Q_{\mathrm{f1}}/\rho C_p$, and D_{th} is the thermal diffusivity given by $\Lambda/\rho C_p$, where Λ is the thermal conductivity, ρ is the density, and C_p is the isobaric heat capacity, respectively. The product$*$ denotes the convolution integral. The value of Q_{f1} is given by $Q_0 d_1(a)$, where $d_1(a)=2\exp(-a)I_1(a)$, $a=I_0/I_{\mathrm{sat}}$, and I_1 is the first modified Bessel function with an imaginary argument, respectively. The first term in the brackets in Eq. 5 is the contribution of the slow heat released by the nongeminate recombination, and the second term is that of the fast heat yielded by the photodissociation and geminate recombination. The function $g_1(t)$ is defined as

$$g_1(t)=\frac{2q}{\pi}\int_0^{\pi/q}\frac{k_{\max}[1-\exp(-I(x)/I_{\mathrm{sat}})]^2}{\{1+k_{\max}[1-\exp(-I(x)/I_{\mathrm{sat}})]t\}^2}\cos(qx)\mathrm{d}x, \quad (6)$$

where $k_{\max}=4k_{\mathrm{r}}[C]$.

It should be noted that, in the analysis by Zhu and Harris, A and $k_{\max}$ are independent of the laser power. They determined ϕ_{d} for iodine from I_{sat} estimated by the power dependence of B, and ΔH from the ratio between A and B. In this procedure, however, detailed knowledge of the excitation beam profile is required, and the alignment must be kept rigorously the same during the measurement of several data. To make the analysis much simpler, we have made the following assumptions:

(1) The laser power is much weaker than the saturation strength, i.e., $I<<I_{\mathrm{sat}}$.

(2) The efficiency of the grating is mainly determined by the peak-null difference of the refractive index and the absorption coefficient, themselves.

Under these assumptions, the intensity of the TG signal can be expressed as follows:[4)]

$$I_{\mathrm{TG}}\propto(\Delta n)^2+(\Delta k)^2, \quad (7)$$

where Δn is the peak-null difference of the refractive index, and Δk is the peak-null difference of the absorption coefficient. Δn is given by

$$\Delta n(t)\propto\left[Q_{\mathrm{f}}'\exp(-D_{\mathrm{th}}q^2t)+\frac{\mathrm{d}Q_{\mathrm{S}}'(t)}{\mathrm{d}t}*\exp(-D_{\mathrm{th}}q^2t)\right] + a(\Delta n_{\mathrm{P}}/2+\Delta n_{\mathrm{R}})N_{\mathrm{R}}(t), \quad (8)$$

where a is a constant. The first two terms in the brackets correspond to the fast and slow parts of the heat, which are given by

$$Q_{\mathrm{f}}'=[C]_0[E_{\mathrm{ex}}-\Delta H\phi_{\mathrm{d}}]/\phi_{\mathrm{d}}, \quad (9)$$

$$Q_{\mathrm{S}}'(t)=Q_{\mathrm{S}}'\frac{k_{\max}'t}{1+k_{\max}'t}, \quad (10)$$

where $[C]_0\equiv(2I_0/I_{\mathrm{sat}})[C]$ $(=[\mathrm{R}]_0/2)$ is the number of parent molecules which dissociate to radicals, $Q_{\mathrm{S}}'\equiv\Delta H[C]_0$, and $k_{\max}'\equiv4k_{\mathrm{r}}[C]_0$. The value of $[C]_0$ is given by expanding Eq. 3 to the linear term of I_0/I_{sat}. We have added the last term in Eq. 8 which corresponds to the population grating due to a refractive index change resulting from a decrease in the parent molecule (Δn_{P}) and an increase in the radical molecule (Δn_{R}), respectively. The function $N_{\mathrm{R}}(t)$ corresponds to the population decay of the radical, given by

$$N_{\mathrm{R}}(t)=\frac{2[C]_0}{1+k_{\max}'t}. \quad (11)$$

In the above expressions, we have neglected the mass diffusion of molecules through the grating lattice, as well as the term due to volume gratings.[26)] The term due to the absorption coefficient in Eq. 7 consists of only the absorption term due to the population grating as

$$\Delta k(t)\propto(\Delta k_{\mathrm{P}}/2+\Delta k_{\mathrm{R}})N_{\mathrm{R}}(t), \quad (12)$$

where Δk_{P} and Δk_{R} are the peak-null difference of the absorption coefficient of parent and radicals.

Using the parameters given by above expressions, we can determine the photolysis quantum yield by

$$\phi_{\mathrm{d}}=\frac{E_{\mathrm{ex}}}{\Delta H}\frac{Q_{\mathrm{S}}'}{Q_{\mathrm{S}}'+Q_{\mathrm{f}}'}. \quad (13)$$

This is the final expression for the photolysis quantum yield. The value of ϕ_{d} is determined from Q_{S}' and Q_{f}' obtained by a simulation of the TG rise signal by Eq. 7 together with Eqs. 8 and 12 if ΔH is known. Assumption (1) is easily accomplished by reducing the laser power for excitation. Assumption (2) was also ascertained by comparing the numerical simulations between Eqs. 6 and 10, although the simplified procedure very slightly overestimates the decay rate of the slow heat. The simplified procedure used here is much easier to apply than a rigorous simulation of the signal.

To discuss the validity of Eq. 13 further, we compare the result with other experimental results by the PA and the TG acoustic signals. In the PA measurement, we measure the strength of sound by the expansion of the media due to the heat released by the nonradiative process. In the system under consideration, the fast heat process is much shorter than the acoustic transit time to travel the laser-illuminated region of the sample (t_{a}, typically 1 μs), and t_{a} is much longer than the pulse duration (t_0). If the beam profile is well characterized, the first-peak intensity from the acoustic signal (I_{PA}) is given by[25)]

$$I_{\mathrm{PA}}\propto\frac{v^2\alpha}{C_p}(1-10^{-\mathrm{OD}})H, \quad (14)$$

where α, OD, and v are the thermal expansion coefficient, the absorbance of the sample, and the sound velocity, respectively. The factor $(1-10^{-\mathrm{OD}})H$ represents the releasing energy due to the fast heat process, and H is given by

$$H=H_0\left(1-\frac{\Delta H}{E_{\mathrm{ex}}}\phi_{\mathrm{d}}\right), \quad (15)$$

where H_0 denotes the laser power used for the excitation. To determine ϕ_{d}, we must evaluate the system response by doing an experiment under the same conditions on a sample which does not show any slow response, i.e., $\phi_{\mathrm{d}}=0$. The photolysis quantum yield is then given by

$$\phi_{\mathrm{d}}=\left(1-\frac{I_{\mathrm{PA}}}{I_{\mathrm{PA}}^{\mathrm{R}}}\right)\frac{E_{\mathrm{ex}}}{\Delta H}, \quad (16)$$

where $I_{\mathrm{PA}}^{\mathrm{R}}$ is the photoacoustic intensity of the reference sample of the same absorbance at the excitation wavelength.

A similar acoustic signal can be observed in the initial part of the TG signal, if the acoustic transit time over the grating lattice, given by $(vq)^{-1}$, is sufficiently longer than the pulse duration. In our experiment, this time could typically be around 100 ns by making q as small as possible. In this timescale, the decay of the TG signal due to thermal diffusion and the slow rise of the signal due to recombination can be neglected, and the acoustic oscillation in the absence of the population signal can be detected as

$$I_{\mathrm{TG}}(t)^{1/2} \propto I_{\mathrm{AC}}[1-\exp(-t/\tau_{\mathrm{AC}})\cos(t/vq)], \qquad (17)$$

where τ_{AC} is the acoustic damping constant specific to the solvent. The value of I_{AC} is dependent on the reaction system in a similar manner as in the PA measurement, and the photolysis quantum yield is given by

$$\phi_{\mathrm{d}} = \left(1-\frac{I_{\mathrm{AC}}}{I_{\mathrm{AC}}^{\mathrm{R}}}\right)\frac{E_{\mathrm{ex}}}{\Delta H}, \qquad (18)$$

where $I_{\mathrm{AC}}^{\mathrm{R}}$ is the acoustic intensity of the reference sample. In Eq. 17, we have neglected the pulse-shaping effect on the TG acoustic signal. In a real experiment, the excitation pulse has a certain duration, not like a delta-function. If the pulse duration is comparable, or not so short, compared with $(vq)^{-1}$, the acoustic strength is reduced by the pulse-shaping effect.[27] However, the reduction in the acoustic strength is not dependent on the quantity of the thermal energy, and we can obtain the relative acoustic strength by the following equation:

$$\frac{I_{\mathrm{AC}}}{I_{\mathrm{AC}}^{\mathrm{R}}} = \frac{I_{\mathrm{TG}}(t)^{1/2}}{I_{\mathrm{TG}}^{\mathrm{R}}(t)^{1/2}}. \qquad (19)$$

Experimental

The experimental setups of the TG, the PA, and the transient absorption measurement were the same as those reported previously.[5,25,28] We explain them briefly below.

In the TG measurement, an excimer laser (Lumonics Hyper 400) (λ_{ex}=308 nm) was used for the excitation beam. The excitation laser power for the TG measurement was typically 1 μJ/pulse. After crossing two pump beams from the excimer laser in a sample solution, the time dependence of the grating probed by a He–Ne laser (λ_{pr}=633 nm) was monitored with a photomultiplier (Hamamatsu R928). The spot size of the pump beam was about 1 mm in diameter. After the signal was fed into a digital oscilloscope, the data were transferred to a computer for averaging and signal processing. The repetition rate of the excitation pulse was typically 5 Hz. As a reference sample, nitrobenzene (NB) was used. Since the lifetimes of the excited states of nitrobenzene are less than 1 ns,[29] and the radiative transition and photochemical reaction are negligible, all of the photon energy absorbed by nitrobenzene should be promptly released as heat.

In the PA measurement, a piezoelectric transducer (PZT) of a lead zirconatelead titanate cylinder (Tohoku Kinzoku, Co. N-6) poled axially was used for a PA detector. 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 signals from a PZT were fed into the same oscilloscope as that for TG measurements.

The transient absorption (TA) was measured by a standard 90°-angle with the pump (excimer laser) and the probe light. A Xe flash lamp (Eagle Technology YXP-150RE) was used as a source of the probe light. The timing between the pump and probe light was tuned by a decay generator (EG&G, 9650), and the transient absorption was monitored by a photomultiplier tude (Hamamatsu Photonics R446) attached to a spectrometer (Engis Model 600 or Shimadzu SPG-100).

DPDS (Nacalai Tesque) was recrystallized twice from a diethyl ether solution. Nitrobenzene (Nacalai Tesque), hexane, isooctane (2,2,4-trimethylpentane) (Nacalai Tesque, spectroscopic grade), and dodecane (Nacalai Tesque, >99%) were used without further purification. All measurements were performed at room temperature.

Results and Discussion

The TA spectrum of isooctane solution of DPDS excited at 308 nm and 300 ns after laser excitation is shown in Fig. 1. The spectrum is quite similar to that observed in a cyclohexane solution, and is assigned to the phenylsulfanyl radical (PS•).[19] It has been reported that there is a possibility to make an aggregate of DPDS with PS• at higher DPDS concentrations[30] (e.g. above 5×10^{-2} mol dm^{-3} in decalin[13]). We therefore carried out transient absorption measurements at a sample concentration of about 1.5×10^{-4} mol dm^{-3}. As shown in Fig. 1, the absorption band is far from the TG probe laser wavelength (633 nm), and we assumed that the contribution of the population grating is small.

A typical TG signal for DPDS in isooctane is shown in Fig. 2 together with the TG signal for NB in isooctane at the same optical density at 308 nm as the solution of DPDS under the same experimental conditions (hereafter we simply mention the reference for the solution of NB at the same optical density at 308 nm under the same optical alignment). The TG signal for DPDS has an instantaneous rise with the pulse duration and a subsequent slow rise. The former represents the fast heat due to possible nonradiative decays of excited states of DPDS and the geminate recombination, and the latter represents the nongeminate recombination, respectively.

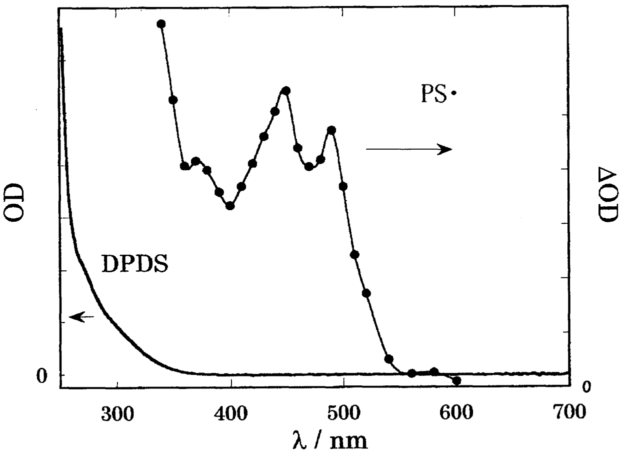


Fig. 1. The absorption spectrum (the solid line) of DPDS in isooctane and the transient absorption spectrum (the solid line with closed circles) of DPDS in isooctane at 3 μs after the excitation at 308 nm at room temperature.

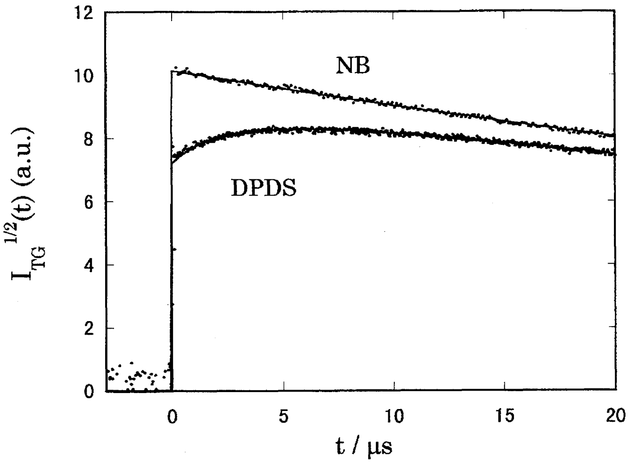


Fig. 2. The time profiles of the TG signals of DPDS and NB in isooctane obtained under the same condition (the closed circles). The best fits by Eq. 7 with Eq. 8 are also shown (solid lines).

As shown in Fig. 2, the TG signal of the reference decays exponentially, indicating that only fast heat is involved. The solid lines in the figure show the least-squares fits to the data by Eq. 7 with Eq. 8. In the simulation we neglected the population grating terms. The TG signal for the solution of NB was fit under the condition $Q'_S=0$. In fitting the TG signal for the solution of DPDS, the value of D_{th} was fixed to the value obtained by the fit for the signal of the reference. As shown in the figure, Eq. 8 works well to simulate the TG signals. A trial inclusion of the population grating signal in the spectral simulation did not improve the quality of the fitting.

To make sure of the validity of the spectral simulation, we first measured the q-dependence of the TG signal. In our simplified simulation procedure, the value of q appears only in the decay constant of the thermal grating (Eq. 8), although a rigorous expression has the integration of the signal with respect to the grating fringe (Eq. 6). In Fig. 3(a), we have plotted the ratio of Q'_S to Q'_f versus q estimated from the thermal diffusion constant obtained by the TG signal of the reference. In this measurement, the concentration of DPDS was adjusted to 1.4 mM to make the optical density at 308 nm be 1.5 using a 1 cm quartz cell. The result shows that the ratio is almost constant irrespective of q.

The next point under question is the effect of saturation on the ratio of Q'_S to Q'_f. To test this point, we measured the power and the concentration dependence of the TG signal. Figures 3(b) and 3(c) show the laser-power dependence and concentration dependence of Q'_S/Q'_f. In both measurements the optical density at 308 nm was between 0.7 and 1.5 of 1 cm optical path length. In both cases, we obtained a constant value of the ratio within the experimental errors. This is in contrast to the result of I_2 by Zhu and Harris. This can be ascribed to the difference of the laser intensity and the saturation intensity of the sample, and not to the error caused by discussing the signal only with the peak-null difference, since there is no meaningful q-dependence of the ratio and the total heat is well conserved, as discussed in the following.

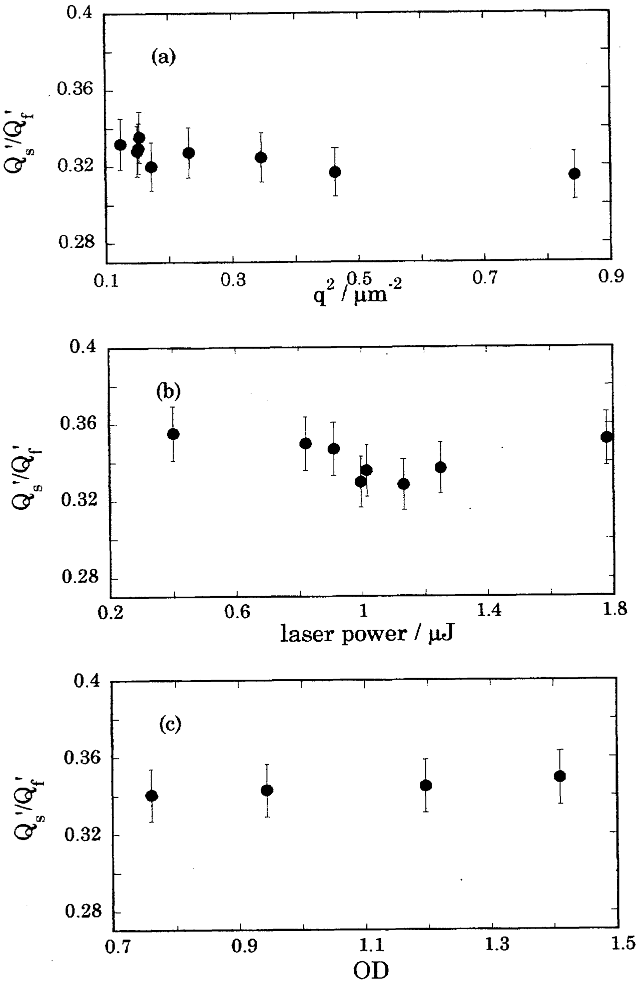


Fig. 3. (a) The plot of Q'_S/Q'_f obtained by the simulation of the TG signal of DPDS in isooctane against q^2. (b) The same plot of Q'_S/Q'_f against the laser power. (c) The same plot of Q'_S/Q'_f against the optical density of the solution at 308 nm using the quartz cell with 1 cm path length.

To make sure that the quantum yield of the nonradiative process is unity and Eq. 7 is valid, we compared the total heat emitted by the solution of DPDS with that of the reference solution; i.e., the sum of the fast and slow heats from DPDS should coincide with the fast heat from the reference. Figure 4 shows the sum of Q'_f and Q'_S (Q'_{tot}) for the solution of DPDS versus Q'_f from the reference. In this figure, we include both results of the laser-power dependence and the concentration dependence. The best fit of the slope is almost unity (1.05±0.03).

By averaging all values of Q'_S/Q'_f obtained by the q-dependence, the concentration dependence, and the power dependence, we obtained 0.34±0.02 for the ratio. By using the literature value of ΔH for the association of phenylsulfanyl radical (55 kcal mol^{-1}),[31] we obtain ϕ_d as 0.43±0.02 by Eq. 13. Using this value of ϕ_d, we can calculate the saturation intensity to be 2.2×10^{25} photons cm^{-2} s^{-1} by the value of the molal extinction coefficient (1.1×10^3 mol^{-1} dm^3 cm^{-1}) at 308 nm and the pulse duration of the excimer laser (ca. 25 ns). This is much larger than the laser-power intensity under

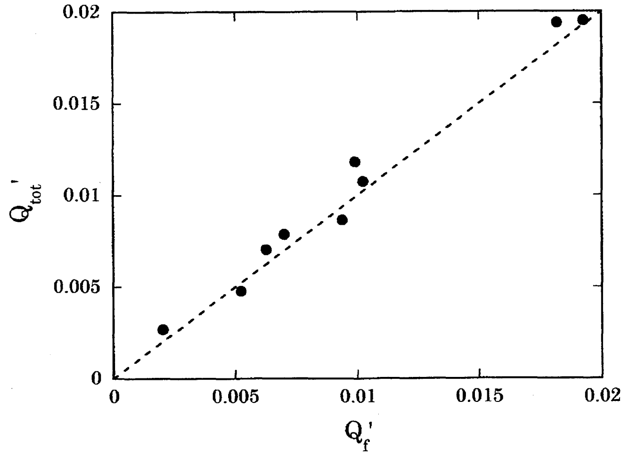


Fig. 4. The plot of the total heat (Q_{tot}') for the isooctane solution of DPDS against the fast heat from the reference solution (NB in isooctane).

operation (less than 1.3 μJ or 5.1×10^{21} photons cm^{-2} s^{-1} using the beam diameter as 1 mm), which verifies assumption (1).

To make a further verification, we compared the result with those of other experiments, TG acoustic and PA measurements. In both experiments, we obtained the relative strength of the fast heat component to the total heat by comparing the acoustic strength with that of the reference system. Figure 5(a) shows the TG acoustic signal for DPDS in isooctane with OD=1.0 at 308 nm using a 1 cm quartz cell, together with the signal from the reference. The acoustic intensity of DPDS is much reduced compared with that of the reference, which results from the nonzero value of ϕ_d. The broken line in the figure is the result of a simulation using Eq. 19, where I_{AC}/I_{AC}^R is an adjustable parameter. The simulation works fairly well. Figure 5(b) shows the intensity of the TG acoustic signals for DPDS in isooctane compared to that of the reference at several concentrations from OD=0.77 to 1.5. The plot gives a straight line with a slope of 0.76±0.01, which corresponds to Q_f'/Q_{tot}'. We also compared the PA intensity of DPDS in isooctane to that of the reference in an ordinary PA experiment. The results showed almost a linear correlation, as in the case of the TG acoustic measurement; the slope is 0.78±0.04, which is almost the same as the value obtained from the TG acoustic signal. Using Eqs. 16 and 18, we can obtain ϕ_d as 0.41±0.02 and 0.37±0.07, respectively, assuming ΔH=55 kcal mol^{-1}. These values coincide well with the value from the TG measurement, and ensure the validity of Eq. 7.

In our experiments, the photolysis quantum yield of DPDS in an isooctane solution was studied by three different methods; we obtained the value of ϕ_d as 0.42±0.03 by averaging the results from two different TG measurements.[32] Let us compare our result with those reported previously by other groups. The PA measurement had been performed previously by Griller et al., giving a value of 0.18±0.1,[33] which is smaller than our estimation. They used the same reaction enthalpy as we used. The reason for the difference is not clear, but one possible origin is the difference in the excitation pulse energy; they used a nitrogen laser (337.1 nm) as an excitation source, and the excess energy for the dissociation is by about 8 kcal mol^{-1} smaller than our case. In the case of the photodissociation of iodine, a significant excess energy dependence of the photolysis quantum yield has been reported,[34] although the excess energy dependence of ϕ_d for DPDS has not yet been demonstrate. This point should be clarified in the future.

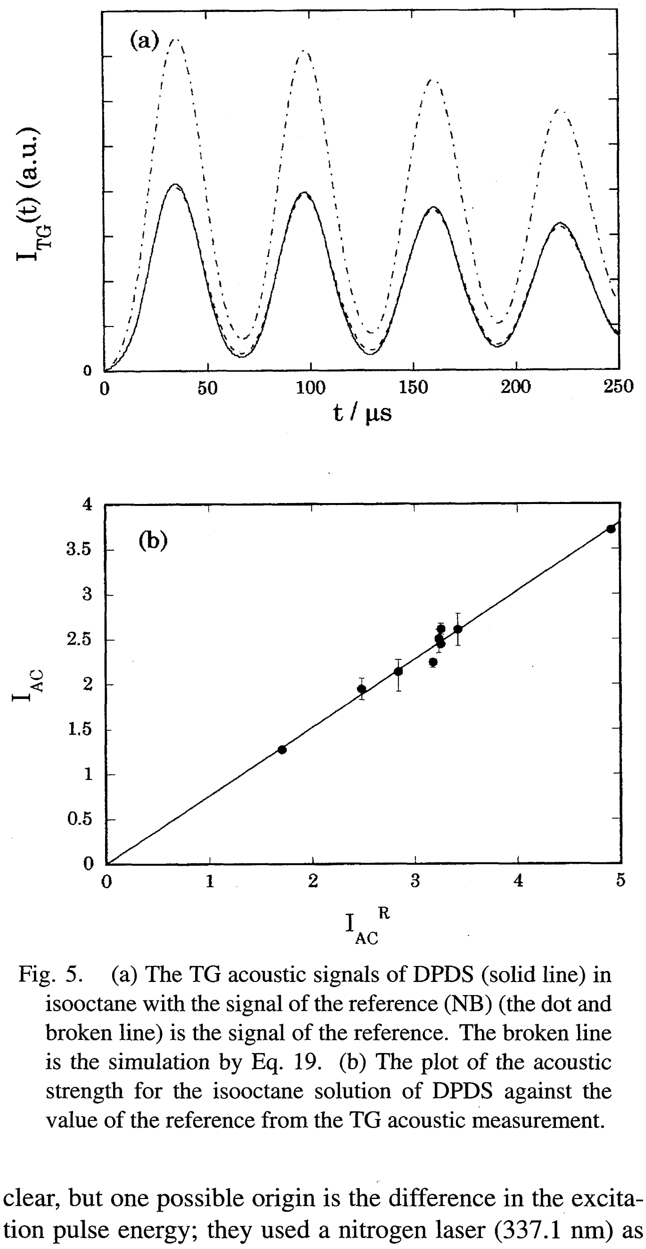


Fig. 5. (a) The TG acoustic signals of DPDS (solid line) in isooctane with the signal of the reference (NB) (the dot and broken line) is the signal of the reference. The broken line is the simulation by Eq. 19. (b) The plot of the acoustic strength for the isooctane solution of DPDS against the value of the reference from the TG acoustic measurement.

Scott and Liu have performed transient adsorption measurements at pico-second time resolution.[13] They found that the transient adsorption signal shows an initial fast decay due to the secondary geminate recombination of PS•; also, the signal was fitted by the solution of the Brownian diffusion model for the survival probability of PS•.[35] If all molecules which adsorb excitation photons undergo dissociation to make geminate pairs, ϕ_d can be calculated from the survival probability for a long time after secondary geminate recombination. According to their result, ϕ_d are estimated to be 0.66 for a hexane solution and 0.40 for a dodecane solution at 278 K with an excitation wavelength at 355 nm. We carried out a TG measurement on both solutions at room temperature, and obtained values of 0.48 ± 0.02 for a hexane solution and 0.34 ± 0.02 for a dodecane solution, which are relatively smaller than their value. One possibility to create this difference is that the value of ΔH used here is incorrect. The value of ΔH as 55 kcal mol^{-1} is estimated in the gaseous phase, and solvation may cause a different value of ΔH in hexane. If we calculate ΔH from our result of Q'_f/Q'_{tot} assuming $\phi_d = 0.66$ for a hexane solution, ΔH should be 41 kcal mol^{-1} in hexane. This means a solvation energy of 14 kcal mol^{-1}, which appears to be unreasonably large for a nonpolar system. Although the solvent-dependent reaction enthalpy may modify our result, the difference is too large to be ascribed to a solvent effect on ΔH.

Another probable reason of the difference is that the contributions of the primary geminate recombination and/or the fast non-radiative process from the excited state to the ground state of DPDS have been dropped in the TA measurement. In this case, their result is the ratio of the photolysis quantum yield to the sum of the quantum yields of the secondary geminate recombination and the photodissociation, and could be an overestimate of ϕ_d. For example, it has been reported that the relative contribution of the primary geminate recombination of I_2 amounts to 70% of the secondary geminate recombination.[36] Although we do not know the potential surfaces of the excited state of DPDS and dynamic in the very fast time scale on these surfaces, it seems certain that the contribution of fast nonradiative processes other than the secondary geminate recombination reduces the value presented by Scott and Liu. It is also noted that the shape of the transient absorption spectrum has been reported to be time-dependent in cyclohexane due to energy relaxation and/or the formation/dissociation of a geminate pair.[19] This kind of behavior also causes ambiguity in determining the escape probability from the TA measurement.

Summary

We have performed TG, TG acoustic, and PA measurements on the system of photodissociation and recombination processes of diphenyl disulfide. We have demonstrated that a simplified analysis to that given by Zhu and Harris works well under the condition that the saturation effect can be neglected. The TG rise analysis is the most efficient way to determine the photolysis quantum yield, because we need no reference sample. The photolysis quantum yield obtained from three different methods coincides with one another. We also compared our results with those reported previously, and discussed the possible causes of the discrepancy. By the TG method developed here, we are now studying the solvent effect on the photolysis quantum yield in a wide density region of a fluid from gaseous-like to liquid-like densities, so-called in supercritical fluids, together with the solvent effect on the non-geminate recombination rate. The results in liquid solvents presented here will be discussed in relation with the results in supercritical fluids in the near future.

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