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Diffusion of Organic Molecules in the Excited Triplet States Detected by the Transient Grating with a High Wavenumber

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Diffusion constants of organic molecules in the excited triplet states are measured in solution by using the transient grating technique with a high wavenumber, which is about 1 order of magnitude larger than that commonly used so far. Using this high wavenumber grating system under two different experimental conditions, we can detect the diffusion process of molecules in the T_1 states as long as the lifetime is longer than 300 ns. Contrary to the previously observed slow diffusion of many transient radicals, diffusion coefficients (D) of all molecules in the T_1 states of this study (benzophenone, 4,4′-dimethylbenzophenone, phenazine, anthracene, fluorenone, 2-nitrofluorenone, benzil, 1-nitronaphthalene, C_{60}, and Michler's ketone) are close to those in the ground state but most of them (except C_{60}) are slightly ($\leq$5−10%) but certainly larger than D in the ground states. D of C_{60} in the T_1 state is found to be the same as that in the ground state.

1. Introduction

Translational diffusion of molecules, in particular unstable chemically reactive molecules or molecules in excited states in solution is of importance in many respects; it controls the rates of chemical reactions, rates of energy transfer, or even the fate of intermediate species.[1−3] Hence the diffusion coefficients (D) of chemically intermediate species and the excited-state molecules are essential for understanding any chemical reactions, energy transfer processes, or electron transfer. However, despite the importance, data of D of excited molecules are very limited. In many cases, D of an unstable molecule or a molecule in an excited state is assumed to be the same as D of the stable molecule with a similar shape and size or D of the molecule in the ground state.

In contrast to this usual assumption, in a series of our previous papers, we have demonstrated that D of photochemically intermediate radicals are generally smaller than those of the closed shell molecules with similar shapes and sizes by using the transient grating (TG) method.[4−13] The smaller D are interpreted in terms of stronger attractive intermolecular interactions between the radicals and the solvents. From these findings, it may be expected that the diffusion process of an electronically excited molecule is also altered from that molecule in the ground state. If this is the case, this difference should be considered in the analysis of the energy transfer or of the excited-state quenching process. Since the motion is influenced by the intermolecular interaction,[14,15] we may not be able to just guess D of the excited molecules from reported D of stable molecules in the ground states. Furthermore, a question whether D depends on the electronic state or not has been a long standing unsolved interesting problem in physical chemistry. In this paper, we tried to answer these questions by measuring D of many organic molecules in the excited triplet states and comparing them with those in the ground states.

An experimental difficulty of the measurement of D of molecules in excited states with short lifetimes comes from a relatively long period required for the diffusion measurement. Despite this difficulty, there have been several reports on D in the excited states or unstable species in solution. Noyes measured D of chemically reactive molecules by the "photochemical space intermittency".[16,17] In this method, the excitation light intensity is spatially modulated by an optical mask and the product concentration under the steady-state illumination was analyzed by using D as one of the fitting parameters. Ern, Avakin, and Merrifield have used a similar technique of a spatially inhomogeneous excited light, which was created by placing a ruling between a light source and sample, and the delayed fluorescence intensity was detected to measure the diffusion constant of triplet exciton in anthracene crystals.[18,19] As the exciton spreads out due to the diffusion from the light illuminated region to the dark region, the total delayed fluorescence intensity decreases with increasing D. By monitoring the intensity at various spacings of the ruling, D can be calculated. This method was also applied to the measurement of D of anthracene in the lowest excited triplet (T_1) state in solution by Burkhurt.[20] Later, Nickel and co-workers used this method to reexamine D of anthracene and pyrene in the T_1 states and also extended the technique to use an interference pattern of the light intensity between two excitation beams.[21,22] These methods are certainly useful but only applicable to molecules that exhibit P type delayed fluorescence. On the other hand, since the TG technique can detect the refractive index change by the presence of the excited state, there is essentially no limitation for the target molecules.

There are two factors, however, that make the application of the TG method to the detection of the diffusion of excited molecules in solution very difficult. First, as will be described in the next section in detail, the decay of the TG signal is mainly governed by two processes: diffusion and relaxation from the excited state. Hence, if the lifetime of the excited state is much shorter than the smearing-out time of the grating by the diffusion process, the dynamics of such a TG signal is almost solely determined by the deactivation process and the diffusion constant cannot be obtained from the TG signal. For example, the lifetime of the excited state, even that of the T_1 state under the oxygen-eliminated condition (k_T^{-1}), could be much shorter than the diffusion process in solution for a usual TG experimental setup. Typically, since the range of the wavenumber of

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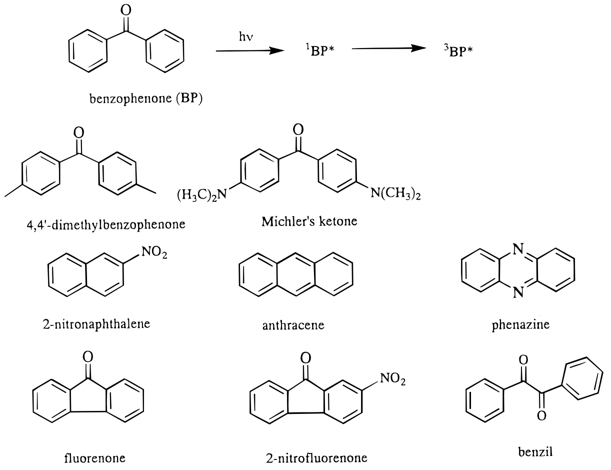
SCHEME 1



the TG setup is 0.2×10^6 m^{-1} < q < 2×10^6 m^{-1}, a range of the decay rate constant due to the diffusion is 4×10 s^{-1} < Dq^2 < 4×10^3 s^{-1} using a typical D ($\sim 10^{-9}$ m^2 s^{-1}). On the other hand, the decay rate constant of the T$_1$ state of many organic molecules in solution at room temperature could be 10^4-10^5 s^{-1}. Therefore, the decay of the TG signal is predominantly determined by the relaxation process. Second, if the thermal diffusion time, which is typically in a range of a few microsecond to a few hundreds of microseconds under the usual setup, is comparable to or longer than the lifetime of the excited state, the strong thermal grating signal frequently masks the grating signal due to the chemical species (species grating). Hence, observation of the species grating becomes difficult and so the measurement of D, too. (These difficulties can be avoided by using a molecule with a long-lived T$_1$ state or in a case that the thermal grating signal intensity is sufficiently weak such as in a solid matrix. Indeed, D of hematoporphyrin was reported before because the triplet lifetime is sufficiently longer than the TG decay time.[23] The exciton diffusion of the anthracene crystal was also measured by the TG technique.[24])

In this study, we modify our transient grating setup to achieve a high grating wavenumber ($q \sim (1.4-1.5) \times 10^7$ m^{-1}) to make the diffusion process dominant compared with the relaxation rate of the T$_1$ state and also to make the decay rate of the thermal grating signal much faster than the decay rate of the species grating signal. We successfully detect the TG signals that represent the diffusion processes of many organic molecules in the T$_1$ states (Scheme 1). By measurements under two different experimental conditions, we can determine D of molecules in the T$_1$ states, most of them for the first time. The results indicate that D of all molecules in the T$_1$ states (except C$_{60}$) we studied here are close to but slightly ($\leq 5-10\%$) larger than those in the ground state.

2. Method and Analysis

A sinusoidal modulation of a light intensity is produced by the interference of two light waves. Simply, by assuming that directions of the polarizations are parallel to each other and that the amplitudes of the two fields are equal, the optical interference pattern is described as[25]

$$I(x) = 2I_0[1 + \cos(2\pi x/\Lambda)] \tag{1}$$

where I_0 is the intensity in each beam and x is the coordinate transverse to the average direction of the excitation beams. The fringe spacing, Λ, is given by

$$\Lambda = \lambda_{\text{ex}}/2 \sin(\theta/2) \tag{2}$$

where θ is the angle between the two beams and λ_{ex} denotes the wavelength of the excitation. The photoexcitation of the sample creates the sinusoidal modulation in the refractive index and the absorbance caused by factors discussed below. The grating is monitored by the diffraction of a continuous wave (cw) probe beam that is brought in at an appropriate angle to satisfy the phase matching condition (the Bragg condition). Under a weak diffraction condition, the TG signal intensity (I_{TG}) is proportional to the square of the variations in the refractive index (δn) and absorption (δk),[25]

$$I_{\text{TG}} \cong \alpha(\delta n)^2 + \beta(\delta k)^2 \tag{3}$$

where α and β are constants. The first term describes the effect of the refractive index change (the phase grating), and the second term results from the absorption change (the amplitude grating).

Whenever the excited state relaxes, the excess energy flows into the kinetic energy as heat, which creates the thermal grating. The temporal dependence of this contribution can be written as

$$\delta n_{\text{th}} = \delta n_{\text{th}}{}^0 \exp(-D_{\text{th}} q^2 t) \tag{4}$$

where D_{th} is the thermal diffusivity of the medium and $\delta n_{\text{th}}{}^0$ is the initial refractive index caused by the heating.

In a bright region of the grating pattern, the molecules are excited and the T$_1$ state is created by the successive intersystem crossing. In the dark region, only the ground-state molecules exist. Since the TG signal intensity should reflect the spatial modulation of the chemical species, the intensity becomes weaker as the reactant and the product become uniform in the grating region, which is accomplished by the translational diffusion or back-relaxation to the ground state (rate constant; k_{T}). Solving the diffusion equations, one obtains the time developments of the refractive index ($\delta n_{\text{s}}(t)$) and absorption changes ($\delta k_{\text{s}}(t)$) due to chemical species (species grating) as[13]

$$\delta n_{\text{s}}(t) = \delta n_1 \exp(-D_{\text{S}_0} q^2 t) + \delta n_2 \exp(-(D_{\text{T}} q^2 + k_{\text{T}})t)$$

$$\delta k_{\text{s}}(t) = \delta k_2 \exp(-(D_{\text{T}} q^2 + k_{\text{T}})\text{t}) \tag{5}$$

The preexponential factors are given by

$$\delta n_1 = -\,\delta n_{\text{S0}}(D_{\text{T}} - D_{\text{S}_0})q^2/\{(D_{\text{T}} - D_{\text{S}_0})q^2 + k_{\text{T}}\} \tag{6a}$$

$$\delta n_2 = \delta n_{\text{T}} - \delta n_{\text{S0}} k_{\text{T}}/\{(D_{\text{T}} - D_{\text{S}_0})q^2 + k_{\text{T}}\} \tag{6b}$$

$$\delta k_2 = \delta k_{\text{T}}/\{(D_{\text{T}} - D_{\text{S}_0})q^2 + k_{\text{T}}\} \tag{6c}$$

where D_{T} and D_{S_0} are the diffusion constants of the molecule in the T$_1$ and the S$_0$ states, respectively. δn_{S_0} and δn_{T} are the refractive index changes due to the presence of the T$_1$ and the S$_0$ states at $t = 0$, respectively. Here we use a fact that there is no absorption at the probe wavelength from the ground state for the molecules we studied here (except C$_{60}$). Therefore, the temporal profile of the TG signal may be written as

$$I_{\text{TG}}(t) = \alpha(\delta n_{\text{th}}{}^0 \exp(-D_{\text{th}} q^2 t) + \delta n_1 \exp(-D_{\text{S}_0} q^2 t) + \delta n_2 \exp(-(D_{\text{T}} q^2 + k_{\text{T}})))^2 + \beta(\delta k_2 \exp(-(D_{\text{T}} q^2 + k_{\text{T}})t))^2 \tag{7}$$

The decay rate of the T_1 state (k_T) was measured by the transient absorption (TA) technique simultaneously. Usually, in determining the diffusion constants, we plot the decay rate constants of the grating signal against q^2, and D of the transient species and that of the original species are calculated from the slopes. However, we cannot change q over a wide region in the present case, because we have to satisfy a condition of $D_Tq^2 \geq k_T$ (or $D_Tq^2 \sim k_T$), and also $D_{th}q^2 > D_Tq^2 + k_T$. Therefore, we calculate D_T from the decay rate constant of the TG signal and k_T.

We used two different conditions for the measurements of the TG signal. First, the sample solution was well deoxygenated by nitrogen bubbling to lengthen the lifetime of the T_1 state sufficiently. When k_T is comparable to or smaller than $|D_T - D_{S_0}|q^2$ (long T_1 lifetime condition), the δn_1 term as well as the δn_2 term in eq 6 may not be neglected, and the observed species grating signal may be fitted by a biexponential function. Under the other condition we used, we partially deoxygenated the sample solution to make the triplet lifetime rather short, for example around 500−800 ns. In this case, k_T could be much larger than $|D_T - D_{S_0}|q^2$, but still this T_1 lifetime is long enough to separate the species grating signal from the thermal part (short T_1 lifetime condition). (For relatively small molecules in nonviscous solutions, D is on the order of 10^{-9} m^2 s^{-1}. If the difference of D_T and D_{S_0} is, for example, 10%, $\{|D_T - D_{S_0}|q^2\}^{-1}$ under the present experimental condition of q is about 50 μs, which is sufficiently longer than $k_T{}^{-1}$.) Under this $k_T \gg |D_T - D_{S_0}|q^2$ condition, the observed species grating signal after the complete decay of the thermal grating signal may be simplified as

$$I_{TG} \cong \{\alpha(\delta n_2)^2 + \beta(\delta k_2)^2\} \exp(-2(D_Tq^2 + k_T)t) \tag{8}$$

Therefore, the species grating signal can be fitted by a single exponential function, and D_T can be calculated from the decay rate constant and k_T. As shown later, the measurements under these two different conditions provide valuable information for the analysis of the TG signal.

3. Experimental Section

The experimental setup of the TG measurement is similar to that reported previously.[4−13] The third harmonics of a Nd:YAG laser (Spectra Physics, GCR170) was split into two with a nearly equal intensity by a beam splitter and crossed at a sample to create the transient grating (Figure 1). The excitation beams were not tightly focused on the sample to avoid any multiphoton process or higher order reaction (spot size ∼ 1 mm o.d.). The high-q grating is achieved by crossing two excitation beams at a large angle (about 50°). Each excitation beam was focused by a separated lens (focus length = 20 cm). A He−Ne laser was used for the probe beam, which was sent to the grating region at about ∼50° from the normal to the sample surface. Under this condition, the signal light appears at ∼50° from the normal to the sample surface. If we used a normal flat cell, at this large incidence angle, the reflection on the cell window became large, which weakened the signal intensity. To minimize the reflection on the cell surface, a triangular quartz cell was used. The signal was detected by a photomultiplier (Hamamatsu R928) and averaged by a digital oscilloscope (Tektronix 2430A) and a microcomputer. The wavenumber of the grating was determined from the decay rate of the species grating signal observed after the photoexcitation of Methyl Red in benzene and known decay rate constant ($q^2 = (2.15-2.3) \times 10^{14}$ m^{-2}).[13]

For measuring the transient absorption (TA) signal, the He−Ne laser (633 nm) or another He−Ne laser for green light (543.5 nm) was used for the probe light. The light intensity after passing through the excitation region was monitored by a photomultiplier tube and averaged by the digital oscilloscope.

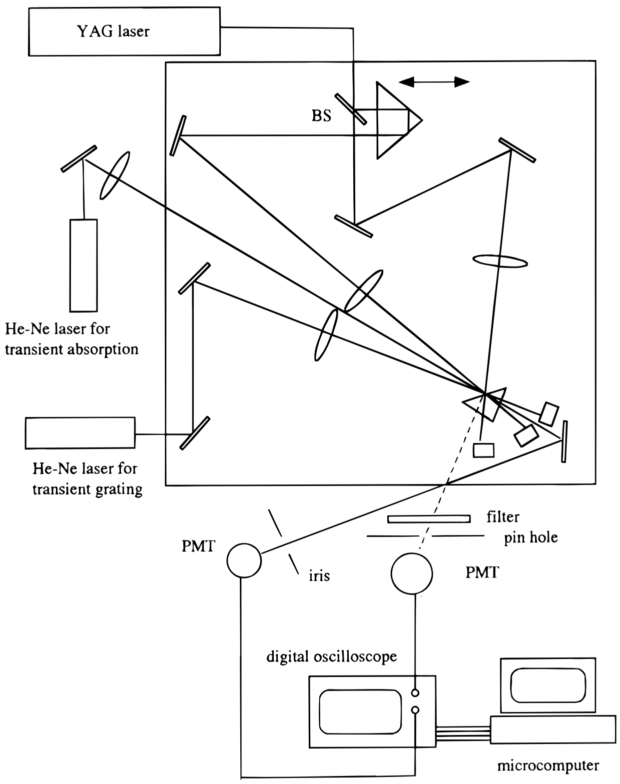


Figure 1. Experimental setup of the TG measurement with a high wavenumber: BS, beam splitter; PMT, photomultiplier,

All solutes, benzophenone, 1-nitronaphthalene, anthracene, phenazine, fluorenone, benzil (purchased from Nacalai tesque), 4,4′-dimethylbenzophenone, 2-nitrofluorenone, and Michler's ketone (4,4′-bis(*N*,*N*-dimethylamino)benzophenone) (Tokyo Kasei) were purified by recrystallization. Solvents (benzene, hexane, acetonitrile, acetone) of spectrograde were used as received.

4. Results and Discussion

4.1. *D* of Benzophenone in the T_1 State. Figure 2a shows the observed TG signal after the photoexcitation of benzophenone (BP) in benzene under the nitrogen saturated condition. The signal rises quickly with our instrumental response time, decays to a certain intensity, and shows a growth−decay curve. The excited-state dynamics of BP has been extensively studied, and it is well-known that the photoexcited S_1 state deactivates to the T_1 state within 10 ps and the quantum yield of the T_1 state formation is almost unity.[26a] The feature in the fast time range can be explained by the interference between the thermal grating (δn_{th}) due to the $S_1 \rightarrow T_1$ intersystem crossing and the species (phase) grating (δn_s) due to the creation of the T_1 state. The presence of the interference dip indicates that the magnitude of $|\delta n_{th}{}^0|$ is larger than $|\delta n_1 + \delta n_2|$ and signs of $\delta n_{th}{}^0$ and $\delta n_1 + \delta n_2$ are opposite. Since $\delta n_{th}{}^0$ is negative for most of organic solvents, $\delta n_1 + \delta n_2$ should be positive. Considering the absorption spectra of the S_0 and T_1 states and the Kramers−Kronig relationship, we can predict that the signs of both δn_{S_0} and δn_T in eqs 6a and 6b are positive.[26] Hence, the positive sign of $\delta n_1 + \delta n_2$ means that the main part of the signal comes from the presence of BP in the T_1 state ($\delta n_T > \delta n_{S_0}$ and $|\delta n_2| > |\delta n_1|$). The fact that the thermal grating signal does not reach the baseline indicates that there is a nonnegligible contribution of

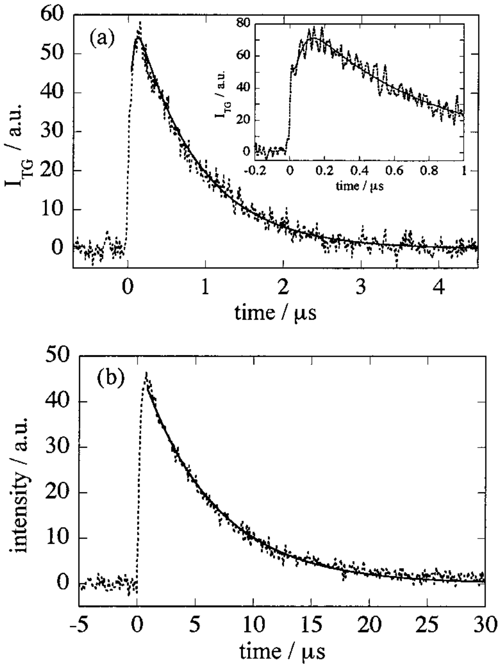


Figure 2. (a) TG signal after photoexcitation of benzophenone in benzene under the nitrogen saturated condition (long T_1 lifetime condition) and (b) TA signal under the same condition. The experimental observed signals and the best fitted signals by a biexponential function are shown by the broken and solid lines, respectively. The inset shows the feature in a faster time scale.

the amplitude grating in the signal (δk_s). This assignment is rationalized from the reported triplet−triplet absorption spectrum.[25b] The relative amplitude of the thermal grating to the species grating increases with increasing the excitation laser power. This power dependence is explained by the stepwise multiphoton excitation from the T_1 state.

A simple and straightforward analysis of the temporal profile of the species grating signal may be a fitting by a single exponential function, and indeed, we found that the fitting works reasonable well. (Actually, we fitted the TG signal including the thermal grating component. Hence this is a biexponential fitting. However, since the lifetime of the thermal grating signal under the present condition is known from the reported D_{th} of the solvent and the used q^2, the lifetime can be fixed in the fitting. In this sense, we use a term of "single exponential fitting".) Considering the signs of δn_1 and δn_2, we may think that the δn_1 term in eq 5 is much smaller than δn_2. If we assume this negligible contribution of the δn_1 term, the decay rate constant of the species grating signal should be given by $D_T q^2 + k_T$. The decay rate constant of the T_1 state (k_T) is measured by the TA signal simultaneously (Figure 2b). The time profile can be fitted well by a single exponential function with a rate constant of k_T. This single exponential decay indicates that the triplet−triplet annihilation process can be neglected under the present conditions. From these data, D_T of BP in benzene is determined as 1.9×10^{-9} m^2 s^{-1}. This value is considerably larger than D_{S_0} (1.34×10^{-9} m^2 s^{-1}).[27]

However, it is also plausible that the δn_1 term in eq 5 cannot be neglected but the observed single exponential feature of the TG signal is just due to close decay rate constants of two exponential terms of eq 5. In this case, the profile should be fitted by a biexponential function. If the signal is noise free, we can certainly differentiate between the single exponential and biexponential functions. However, if two rate constants are close to each other, the difference in the main part of the signal is very small (Figure 3). Because of the finite S/N ratio of the experimental signal, it is very difficult to fit the experimental curve by a biexponential function with four adjustable parameters (two decay rate constants and two preexponential factors) without ambiguity. To remove this ambiguity, we use a reported value of D_{S_0} for one of the decay rate constants ($D_{S_0} q^2$)[27] and it is fixed in the least-squares fitting. By reducing the number of the adjustable parameters, we can determine the other rate constant, $D_T q^2 + k_T$ rather uniquely. Using k_T from the TA signal, we obtained $D_T = 1.5 \times 10^{-9}$ m^2 s^{-1}. The obtained D_T is still larger than D_{S_0}, but the difference is now much smaller than that from the single exponential fitting case.

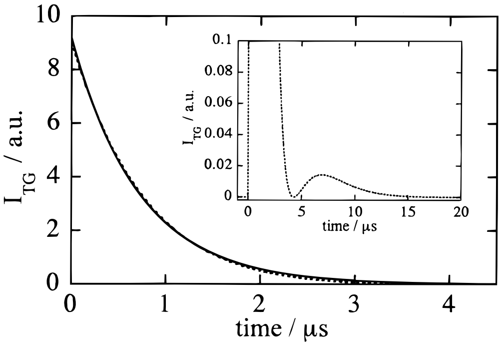


Figure 3. Calculated TG signal of $\{5 \exp(-t/2\ \mu s) - 2 \exp(-t/2.5\ \mu s)\}^2$ (dotted line). This signal can be fitted reasonably well by a single exponential function of $\{3.02 \exp(-t/1.44\ \mu s)\}^2$ (solid line). When we amplified the signal in the longer time region, the deviation from the single exponential function is notable (inset). However, within a finite S/N, the difference may not be notable in the experimentally observed signal.

We obtained two different D_T from the above two analyses. Which is the correct D_T? To answer this question, we measure the TG signal under a different condition described in section 2 (partially oxygen purged condition). A key point of this measurement is that the relative contribution of the δn_1 term decreases with increasing k_T, and the observed TG signal under $k_T \gg |D_T - D_{S_0}|q^2$ condition can be always analyzed by a single exponential function with a decay rate constant of $D_T q^2 + k_T$ (eq 8). Therefore, if the δn_1 term in eq 5 is negligible under the long T_1 lifetime condition, the TG signal should be always single exponential with a decay rate constant of $D_T q^2 + k_T$ under any condition of k_T. On the other hand, if the δn_1 term cannot be neglected under the long T_1 lifetime condition, the relative contribution of the δn_1 term becomes smaller as k_T becomes larger (eq 6a). In this case, the lifetime of the TG signal by the single exponential fitting depends on k_T. D_T determined under the condition of $k_T \gg |D_T - D_{S_0}|q^2$ should be different from that obtained under the long T_1 lifetime condition.

Figure 4 shows the TG signal under the partially deoxygenated condition, under which condition the triplet lifetime is 700 ns. From the lifetime of the TG signal by the single exponential fitting, D_T is obtained as 1.5×10^{-9} m^2 s^{-1}, which is smaller than D_T determined by the single exponential fitting but close to D_T from the biexponential fitting analysis. Therefore, we conclude that the δn_1 term in eq 5 under the nitrogen-saturated condition should not be neglected in the analysis.

We expect a large ambiguity in the parameters from the biexponential fitting of an experimentally observed signal, in particular in a case that the two lifetimes are close to each other.[28] In our analysis, we found that D_T sensitively depended on D_{S_0} that was fixed for the fitting. However, even if we used slightly different D_{S_0}, the difference, $D_T - D_{S_0}$, remained almost constant. Therefore, we think that the absolute value of D_T may change depending on the D_{S_0} we use, but the difference between

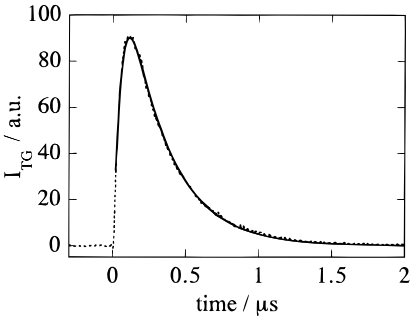


Figure 4. TG signal (broken line) after photoexcitation of benzophenone in benzene under a partially nitrogen saturated condition (short T_1 lifetime condition) and the best fitted curve by a single exponential function (solid line).

D_T and D_{S_0} may be more accurate; that is, the analysis certainly shows that D_T is larger than D_{S_0}.

This conclusion, larger D_T than D_{S_0}, is also supported by the signs of δn_1 and δn_2. According to eq 6 under the long lifetime condition, if D_T is smaller than D_{S_0}, the sign of δn_1 and δn_2 should be the same. However, the biexponential fitting of the observed signal always shows different signs ($\delta n_1 > 0$ and $\delta n_2 < 0$). This different sign is expected only when D_T is larger than D_{S_0}. Therefore, we conclude that D_T is close to D_{S_0} but definitely D_T is larger than D_{S_0}; the triplet molecules diffuse faster than the ground-state molecules.

As described above, D_T can be determined under both of the long and short T_1 lifetime conditions. Under the short T_1 lifetime condition, the TG signal can be fitted by a single exponential function and this fitting should be more accurate than the biexponential fitting. However, the relative contribution of k_T in the decay rate constant of the TG signal ($D_Tq^2 + k_T$) is significantly larger and the accuracy of k_T seriously affects the accuracy of D_T. On the other hand, although the biexponential fitting may be less accurate under the long T_1 lifetime condition, k_T is usually comparable to or negligibly smaller than D_Tq^2. Therefore, a better choice we use for the measurement of D_T depends on the signal intensities of the TG and TA signals. If the accuracy of the decay rate constant of the TA signal is good, the short T_1 lifetime condition may be preferable. However, generally, the S/N of the TG signal is much better than the TA signal and the decay rate of the TA signal under the same excitation power condition as the TG measurement is less accurate. Hence, D_T under the long T_1 lifetime condition may be more accurate.

We examined the concentration dependence of D_T and found that D_T of BP was insensitive to the concentration within a range of 10×10^{-3}–0.9×10^{-3} M.

BP in other solvents such as acetonitrile give similar TG signals, although the relative intensity of the thermal grating is weaker. The analysis and the assignment of the signal are similar to those in benzene and the determined D_T and k_T under the nitrogen-bubbled condition are listed in Table 1.

4.2. The Other Systems. Figure 5a depicts the TG signal of anthracene in benzene. The essential features of the signal are similar to the case of BP. The fast decaying signal is the thermal grating signal, and the rest of the signal can be fitted by eq 5. Again, a reported value of D_{S_0} is used. The TA signal indicates that the decay of the T_1 state is negligible in the time range of the TG measurement, and hence D_T can be calculated only from the decay rate constant of the TG signal.

Burkhurt reported D_T of anthracene in methylcyclohexane and cyclooctane.[20] It was reported that D of anthracene considerably decreased from 2.67×10^{-9} to $<1.0 \times 10^{-9}$ m^2 s^{-1} in methylcyclohexane with increasing concentration from 0.99×10^{-5} to 12.4×10^{-5} M. Nickel and co-workers

TABLE 1: Diffusion Constants ($D/10^{-9}$ m^2 s^{-1}) of Organic Molecules in the Ground (S_0) State and T_1 State and the Triplet Decay Rate Constants (k_T) under the Oxygen Purged Condition[a]

		acetone	benzene	acetonitrile	hexane
benzophenone	D_T	2.84	1.48	2.37	
	D_{S_0}	2.75	1.34[b]	2.22	
	k_T	2.2×10^5	1.6×10^5	2.3×10^5	
4,4′-dimethyl benzophenone	D_T	2.69	1.43	2.24	
	D_{S_0}	2.55	1.26	2.09	
	k_T	2.2×10^5	1.0×10^5	0.8×10^5	
anthracene	D_T	-	1.49	3.09	3.63
	D_{S_0}	2.85[c]	1.41	2.57[d]	3.35[e]
	k_T	$<10^3$	$<10^3$	$<10^3$	$<10^3$
phenazine	D_T	2.98	1.59	2.68	
	D_{S_0}	2.91	1.44	2.62	
	k_T	1.4×10^5	0.8×10^5	0.7×10^5	
1-nitronaphthalene	D_T	3.11	1.61	2.78	3.45
	D_{S_0}	3.03	1.49	2.59	3.15
	k_T	4.2×10^5	3.7×10^5	3.0×10^5	4.9×10^5
fluorenone	D_T	2.86	1.50	2.30	
	D_{S_0}	2.77	1.37	2.27	
	k_T	3.2×10^4	0.6×10^4	4.0×10^4	
2-nitrofluorenone	D_T	2.70	1.43	2.27	
	D_{S_0}	2.63	1.30	2.15	
	k_T	4.3×10^4	4.0×10^4	5.0×10^4	
benzil	D_T	2.74	1.39	2.33	
	D_{S_0}	2.63	1.30	2.15	
	k_T	2.0×10^4	1.6×10^4	2.3×10^4	
Michler's ketone	D_T	2.61	1.33	2.29	
	D_{S_0}	2.36	1.16	1.93	
	k_T	7.8×10^4	7.0×10^4	9×10^4	
C_{60}	D_T			0.91	
	D_{S_0}			0.91[f]	

[a] Some of D_{S_0} indicated by the superscripts were taken from the literature described below. The other D_{S_0} were calculated from these reported values with corrections of the molecular sizes and viscosities by the Stokes–Einstein relation (eq 9). [b] Reference 27. [c] Roussy, G.; Thiebaut, J. M. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2375. [d] Koracs, J.; Bullina, T.; Rodin, R. L.; Balasubramanian, D.; Applequiest, J. *J. Am. Chem. Soc.* **1965**, *87*,120. [e] Reference 22. [f] Haselmeier, R.; Holtz, M.; Kappes, M. M.; Michael, R. H. *Ber. Bunsen-Ges. Phys. Chem.* **1994**, *98*, 878.

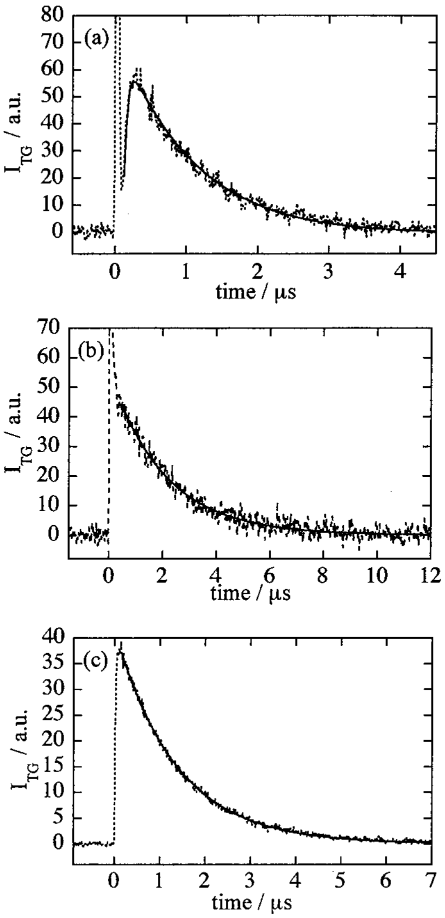


Figure 5. TG signal (broken lines) after photoexcitation of (a) anthracene, (b) C_{60}, and (c) Michler's ketone in benzene under the nitrogen-saturated condition (long T_1 lifetime condition) and the best fitted curves (solid lines).

determined D of some molecules in the relatively long-lived T_1 states (anthracene, diphenylanthracence, and pyrene) by a similar but carefully designed method.[22] They concluded that D_T of anthracene in hexane is 3.2×10^{-9} m^2 s^{-1} and observed almost no concentration dependence in a range of 1.0×10^{-5} to $\sim 5.3 \times 10^{-5}$ M. Our D_T reported here are close to their value.

Although the detailed profiles of the TG signals of the other systems depend on the solutes and the solvents, the essential features are similar to BP or anthracene, as we described. They can be analyzed in the same manner. Figure 5b represents the time profile of the TG signal of C_{60} in benzene. There appears no interference dip between the thermal grating and the species grating signals. The lack of the dip indicates that the species grating signal mainly comes from the amplitude grating component. This signal can be fitted by a single exponential function.

The determined D_T and k_T of 4,4′-dimethylbenzophenone, phenazine, fluorenone, 1-nitronaphthalene, 2-nitrofluorenone, C_{60}, and benzil are summarized in Table 1. (The decay rate constants of the T_1 state (k_T) are measured simultaneously with the TG signal under the same conditions. The values listed are typical rate constants under the oxygen-purged condition. The TA signal of anthracene cannot be fitted by a single exponential function, probably because of the T−T annihilation process. However, since the lifetime is sufficiently long compared with the decay rate of the TG signal, the exact k_T is not important for determining D_T.)

4.3. Diffusion of Molecules in the T_1 States. When we consider the diffusion process of the excited molecules, we must separate it into the molecular diffusion and the excitation energy transfer processes. In this case, we think that the observed D_T are not affected by the energy transfer process because of the following reasons. First, as stated above, Nickel et al. clearly showed that D_T of anthracene does not depend on the concentration.[22] We also confirmed that D_T of anthracene does not depend on the concentration within a range of $\sim 10^{-3}$ M. Since the extinction coefficients of some molecules, e.g., BP, at 355 nm are not large, we could not confirm the concentration independence of D_T below 10^{-3} M. However, for 2-nitronaphthalene, we confirmed that the observed time profile was essentially unchanged within a concentration range of 3×10^{-3}−3×10^{-4} M. This concentration independence indicates that the excitation diffusion is governed by the molecular diffusion not the energy transfer process. Second, even if the intermolecular energy transfer is not negligible, the triplet energy transfer process is induced by the exchange mechanism, which is a very short range interaction. Hence, the excited triplet molecule should closely contact with the ground-state molecule for the energy transfer. In this case, the diffusion process of the excited molecule is expected to be determined by the molecular diffusion itself, not by the energy transfer.

One of the main conclusions in this study is that we could successfully measure D of many organic molecules in the T_1 states mostly for the first time. This TG method is the most general method for obtaining D_T. We find that D_T of many organic molecules in organic solvents are very close to D_{S_0}. However, at the same time, it is certain that D_T are slightly ($\leq$5−10%) larger than D_{S_0}, except for C_{60}. Previously we reported that many transient radicals diffuse slower than the parent molecules or analogous closed shell molecules.[4−13] Furthermore, carbenes, which possess the triplet spin multiplicity in the ground state, also diffuse slower than the closed shell molecules. Considering these facts, we initially expected that D_T were smaller than D_{S_0}. In this respect, D_T measured here may be unexpected. In the following, we briefly discuss the origin of the faster diffusion of the T_1 molecules.

Frequently, the determined D are compared with ones calculated from the Stokes−Einstein equation

$$D_{SE} = k_B T / f \pi \eta r \tag{9}$$

where k_B is the Boltzmann constant, T is the temperature, η is the viscosity, r is the radius of a spherical particle, and f represents the boundary condition of the diffusion ($f = 6$ and 4 for the stick and slip boundary conditions, respectively). According to this equation, it is predicted that molecules with the same volume and the same shape should possess the same D. The molecular structures in the T_1 states are sometimes different from those in the ground state, and the different structure could be a possible cause of the slight difference of D_T from D_{S_0}. Although the exact geometries in the T_1 state are not known for these molecules, we think that the geometries of, in particular, anthracene, phenazine, and fluorenone are rather rigid and the structural change is not significant by the excitation. Hence, we believe that the effect of this structural change to D is not important.

In a series of our previous papers, we have shown that many transient radicals diffuse slower than the closed shell analogous molecules.[4−13] This slower diffusion is attributed to an attractive intermolecular interaction between the radicals and solvents. Morita and Kato calculated the electronic structures of hydrogen-abstracted radicals and the parent molecules and revealed very prominent difference in the intramolecular local polarizability.[29] An MD simulation showed that the origin of the slower diffusion of the radicals is the larger local polarizability of the radicals compared with the parent molecules. Bagchi and co-workers clearly showed that D is sensitive to the intermolecular interaction.[14,15] D decreases with increasing the intermolecular interaction. The faster diffusion of the T_1 molecules may indicate that the intermolecular interaction is weaker between the T_1 molecule and solvents than that between the ground-state molecule and solvents.

One of possible origins of the faster diffusion of the T_1 molecules is the change of the dipole moment by the excitation. In fact, the dipole moment of BP in the T_1 state is found to be smaller than that in the ground state (2.1 D in the T_1 state and 3.0 D in the S_0 state).[30] To examine this possibility, D_T of fluorenone and Michler's ketone (4,4′-(*N*,*N*-dimethylamino)-benzophenone) are compared. In particular, the T_1 state of Michler's ketone possesses a charge transfer (CT) character and the dipole moment increases by the photoexcitation from 5.3 D in the ground state to 8.4 D in the T_1 state.[30] Figure 5c depicts the TG signal of Michler's ketone. The feature of the signal, the dip between the thermal grating and the species grating, is very small (not clearly seen in Figure 5c), indicating that the TG signal mostly consists of the amplitude grating. In this case, hence, the signal can be analyzed by a single exponential function. The determined D_T of Michler's ketone and fluorenone (dipole moment is 3.4 and 4.8 D in the ground state and T_1 state, respectively)[30] (Table 1) are found to be larger than D_{S_0}. Furthermore, if the decrease of the dipole moment is the cause of the larger D_T, this effect is expected to be sensitive to the polarity of the solvent. On the contrary, the observed D_T is generally 5−10% larger than D_{S_0} in polar as well as nonpolar solvents. Therefore, the change of the dipole moment in the T_1 state is not the cause of the different D_T from D_{S_0}. In other words, as long as the molecular shape and size are exactly the same, we may conclude that the effect of the dipole moment to the diffusion is not large in most of the cases.

The difference in D might be explained by the different intermolecular interaction caused by the change of the molecular orbitals by the excitation. Although D_T are slightly larger than D_{S_0} in all the solvents we examined, the ratios of D_T/D_{S_0} in benzene are slightly larger than those in the other solvents. This fact may indicate that the solute−solvent interaction is sensitive to the excitation in benzene. The solvent dependence and the different D between the T_1 and the S_0 state may be rationalized by the ab initio MO calculation, as successfully shown for the transient radical case. However, since the difference in D is small in this case, precise calculations will be necessary for revealing the molecular origin of these observations and it would be more challenging. It is also interesting to note that the molecules in the T_1 states diffuse slightly faster than in the ground states regardless of the nature of the T_1 states. For example, the T_1 states of phenazine, anthracene, fluorenone, and nitrofluorenone are in the $^3\pi\pi^*$ character, while the T_1 states of benzophenone, dimethylbenzophenone, and benzil are in the $^3n\pi^*$ character, and the T_1 state of Michler's ketone is in the CT character. Spectroscopically, these states show totally different behaviors for the solvent effect, while they behave similarly with regards to the diffusion process. Furthermore, D_T/D_{S_0} do not seem to correlate with the triplet lifetimes (k_T^{-1}).

D_T of most of the molecules are slightly larger than D_{S_0}, whereas D_T of C_{60} is found to be the same as D_{S_0}. We think that the smaller difference between D_T and D_{S_0} of C_{60} is due to the large size of C_{60}. D is determined by the hydrodynamics friction as well as the additional (or reduced) friction from the intermolecular interaction. When the molecule becomes larger, the hydrodynamic friction becomes more important and the relative contribution of the intermolecular interaction becomes smaller. This tendency was observed before for the transient radical case.[4] D_T of C_{60} may be another example of this effect.

5. Conclusion

We investigated the TG signals after the creation of the T_1 states in solution by a setup with a high grating wavenumber. The decay of the species grating signal is close to single exponential. It was not apparent in the beginning whether the depletion of the ground-state molecule contributes to the signal or it is negligible. The contribution of the ground-state molecule was examined by measuring the TG signal under two different experimental conditions; longer and shorter T_1 lifetimes compared with $(D_T - D_{S_0})q^2$. These experiments support that the signals should be analyzed in terms of the molecular diffusion of the T_1 state as well as the ground state. By biexponential fittings of the signals with fixed D_{S_0}, we determine D_T of many organic molecules in solution, most of them, for the first time. D_T of all molecules in this study are close to but slightly larger than D_{S_0}.

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References and Notes

(1) Alwattar, A. H.; Lumb, M. D.; Birks, J. B. In *Organic molecular photophysics*; Birks, J. B., Ed.; Wiley: NewYork, 1973; Vol. 1, pp 403−456.

(2) Cussler, E. L. *Diffusion*; Cambridge University: Cambridge, U.K., 1984. Tyrrell, H. J. V.; Harris, K. R. *Diffusion in liquids*; Butterworth: London, 1984.

(3) *Free radicals*; Kochi, J. K., Ed.; Wiley: NewYork, 1973; Vol. 1..

(4) Terazima, M.; Hirota, N. *J. Chem. Phys.* **1993**, *98*, 6257−6262.

(5) Terazima, M.; Okamoto, K.; Hirota, N. *J. Phys. Chem.* **1993**, *97*, 13387.

(6) Terazima, M.; Okamoto, K.; Hirota, N. *J. Chem. Phys.* **1995**, *102*, 2506.

(7) Okamoto, K.; Terazima, M.; Hirota, N. *J. Chem. Phys.* **1995**, *103*, 10445.

(8) Terazima, M.; Tomioka, H.; Hirai, K.; Tanimoto, Y.; Fujiwara, Y.; Akimoto, Y. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2361.

(9) Kimura, Y.; Kanda, D.; Terazima, M.; Hirota, N. *J. Phys. Chem. B* **1997**, *101*, 4442.

(10) Okamoto, K.; Hirota, N.; Terazima, M. *J. Phys. Chem. A* **1997**, *101*, 5269.

(11) Okamoto, K.; Hirota, N.; Terazima, M. *J. Phys. Chem. A* **1997**, *101*, 5380.

(12) Okamoto, K.; Hirota, N.; Terazima, M. *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 185. Okamoto, K.; Hirota, N.; Terazima, M. *J. Phys. Chem. A* **1998**, *102*, 3447.

(13) Terazima, M. *Res. Chem. Intermed.* **1997**, *23*, 853.

(14) Srinivas, G.; Bhattacharyya, S.; Bagchi, B. *J. Chem. Phys.* **1999**, *110*, 4477.

(15) Biswas, R.; Bhattacharyya, S.; Bagchi, B. *J. Phys. Chem. B* **1998**, *102*, 3252.

(16) Noyes, R. M. *J. Am. Chem. Soc.* **1959**, *81*, 566−570.

(17) Noyes, R. M. *J. Phys. Chem.* **1965**, *69*, 3182−3183.

(18) Avakian, P.; Merrifield, R. E. *Phys. Rev. Lett.* **1964**, *13*, 541.

(19) Ern, V.; Avakian, P.; Merrifield, R. E. *Phys. Rev.* **1966**, *148*, 862. Ern, V. *Phys. Rev. Lett.* **1969**, *22*, 343.

(20) Burkhart, R. D. *J. Phys. Chem.* **1977**, *81*, 370.

(21) Meyer, E. G.; Nickel, B. *Z. Naturforsch.* **1980**, *35A*, 503. Nickel, B. *Ber. Bunsen-Ges.* **1972**, *76*, 582.

(22) Nickel, B.; Nickel, U. *Ber. Bunsen-Ges.* **1972**, *76*, 584. Nickel, B.; Meyer, E. G. In *Proceedings of the International Conference on Luminescence*; Williams, F., Ed.; Plenum Press: New York, 1973.

(23) Terazima, M. *Chem. Phys. Lett.* **1994,** *218*, 574−578.

(24) Rose, T. S.; Righini, R.; Fayer, M. D. *Chem. Phys. Lett.* **1984**, *16*, 13. Rose, T. S.; Newell, V. J.; Meth, J. S.; Fayer, M. D. *Chem. Phys. Lett.*

1988, *145*, 475. Meth, J. S.; Marshall, C. D.; Fayer, M. D. *Solid State Commun.* **1990**, *74*, 281.

(25) Eichler, H. J.; Gunter, P.; Pohl, D. W. *Laser induced dynamic gratings*; Springer-Verlag: Berlin, 1986. Kogelnik, H. *Bell. System Technol. J.* **1969**, *48*, 2909.

(26) (a) Wilkinson, F. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: New York, 1975; Vol. 2. (b) Bensasson, R.; Land, E. J. *Trans. Faraday Soc.* **1971**, 6*7*, 1904.

(27) Donkers, R. L.; Leaist, D. G. *J. Phys. Chem. B* **1997**, *101*, 304.

(28) Spiegel, D. R.; Marshall, A. H.; Jukam, N. T.; Park, H. S.; Chang, T. *J. Chem. Phys.* **1998**, *9*, 267.

(29) Morita, A.; Kato, S. *J. Am. Chem. Soc.* **1997**, *119*, 4021. Morita, A.; Kato, S. *J. Chem. Phys.* **1998**, 108.

(30) Shimamori, H.; Uegaito, H.; Houdo, K. *J. Phys. Chem.* **1991**, 9*5*, 7664.