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Nonradiative Relaxation Processes and Electronically Excited States of Nitrobenzene Studied by Picosecond Time-Resolved Transient Grating Method

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The exothermic nonradiative relaxation processes from photoexcited nitrobenzene (NB) are studied by the picosecond time-resolved transient grating method. The decay rate constants and energy of the excited NB are determined. The lifetime of the lowest excited singlet state is found to be very short (≤10 ps) and a surprisingly short lifetime of the lowest excited triplet state (∼480 ps) is detected. From quantitative measurements of the thermal energies released from the excited states of NB, the lowest excited triplet state is determined to be located at $(22-27) \times 10^3$ cm^{-1}. The triplet formation is very efficient and its quantum yield is found to be grater than 0.80. From the temperature and solvent dependence of the triplet lifetime, it is suggested that motions of the nitro group may cause the surprisingly rapid relaxation from the lowest excited triplet state to the ground state. The photophysical properties and excited states of monosubstituted nitrobenzenes are also discussed.

1. Introduction

Nitrobenzene (NB) is one of the most fundamental molecules and it possesses a variety of unique optical properties. For example, NB is one of the well-known optical Kerr media and used as the standard substance for new nonlinear optical spectroscopies.[1−5] NB is frequently used as an energy acceptor, such as an excited state or fluorescence quencher,[6−11] and as an optical heat source in photoacoustic and photothermal spectroscopies.[12−18] Furthermore, derivatives of NB and nitro substituted aromatic hydrocarbons have attracted the interest many scientists because of their unique properties such as the prominent charge transfer phenomena.[19−25] In spite of the fundamental importance of the photophysical characters of NB, the photophysical properties, dynamics, and nature of the excited states of NB have not been well understood. In 1970, Khalil et al. reported phosphorescence at low temperature with a lifetime 0.1−1 s,[26] which suggested that the lowest excited triplet (T_1) state is of $^3\pi\pi^*$ character. Repeated experiments, however, showed that this luminescence was originated from an impurity, and it is now known that fluorescence, as well as phosphorescence, has not been detected under any conditions.[27] It is well established that the time-resolved electron paramagnetic resonance (TREPR) technique is a powerful means to detect nonphosphorescent short-lived triplet state, but the triplet state of NB and its derivatives could not be detected by TREPR.[28] In addition, steady-state absorption spectra are broad and structureless in vapor and solution phases.[19,29] Even the energy of the lowest excited triplet (T_1) state of NB was only estimated to be larger than 20.6×10^3 cm^{-1} by using an energy transfer method.[30] Transient absorption after the photoexcitation of NB is rather weak.[30]

Very fast nonradiative relaxation processes and nonemissive characters are the main cause of the mysterious photophysical properties. If we can study the photophysical properties by directly detecting the nonradiative transitions, such as the internal conversion and the intersystem-crossing processes, the photodynamics of NB will become clearer and the study should be more informative. For this reason, photothermal spectroscopic methods, such as transient lens (TL) and transient grating (TG) methods, which detect the thermal energy from exothermic nonradiative transition processes, are suitable for the study of energy relaxation processes of excited molecules. In particular, the TG method is highly sensitive and has sufficiently fast time resolution.

In this study we used the time-resolved TG method for elucidating the photophysical properties, such as lifetimes of excited states and quantum yields of the triplet formation and triplet energies, of NB and its derivatives. When the photoexcited states relax nonradiatively, the released energy ultimately heats up the matrix, causing the density variation of the matrix, and an acoustic wave is observed. By analyzing the temporal profile, the dynamics and energies of the excited states can be determined. Furthermore, if the presence of the excited states can be detected as a population grating signal, faster dynamics will be observed.

2. Experimental and Analytical Sections

2.1. Experimental Section. The setup for the TG experiment has been reported elsewhere.[31] The laser system for the picosecond time-resolved TG experiment consists of a dye laser system (Continuum PD10) pumped by SHG of a Nd:YAG laser (Continuum PY61c-10). The wavelength of the dye laser, which was used as a probe beam, was 640 nm. The third harmonic of the Nd:YAG laser beam was used as a pump beam. The width of each pulse was ∼30 ps. The pump beam was split into two with a splitter. These pump beams were slightly focused by lenses and then crossed at about 30° inside a sample cell in order to generate an optical interference pattern. The laser power was ∼2 μJ/pulse, and the spot size was ∼1 mm i.d. The probe beam, passed through an optical delay line, was focused by a lens and brought into the sample cell by an angle that satisfied the Bragg condition. The diffracted probe beam, the TG signal, was separated from other pulse beams by using a pin hole and a glass filter (Toshiba R-60) and detected by a photomultiplier tube. The detected signal was averaged with a boxcar integrator (EG&G Model 4400 Series) and with an Apple Macintosh computer (Quadra 950).

For the TG measurement in the nanoseconds time scale, the experimental setup is similar to that described previously.[31] The third harmonic of a Nd:YAG laser (Spectra-Physics Quanta-

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ray Model GCR-170−10) with a 10 ns pulse width was used as an excitation beam and a He−Ne laser beam as a probe beam. The diffracted probe beam was isolated from the excitation laser beams with a glass filter (Toshiba R-60) and a pinhole, detected by a photomultiplier tube (Hamamatsu R-928), and fed into a digital oscilloscope (Tektronix TDS-520). The TG signal was averaged by a microcomputer to improve a signal to noise (S/N) ratio.

Nitrobenzene (NB) (guaranteed reagents), *o*-, *m*-, and *p*-nitrophenols (NPs) (guaranteed reagents), *o*-, *m*-, and *p*-nitrotoluenes (NTs) (guaranteed reagents), *o*-, *m*-, and *p*-nitrobenzoicacids (NBAs) (guaranteed reagents), *n*-heptane (spectrophotometric grade), *n*-decane (guaranteed reagents), *n*-tetradecane (guaranteed reagents), benzene (spectrophotometric grade), ethanol (spectrophotometric grade), and sodium dodecyl sulfate (SDS) (extra pure reagent) were obtained from Nacalai Tesque Inc. and used without further purification. Distilled water was used.

2.2. Analytical Section. The analysis of the TG method has been reported previously,[16,18,31−34] and we only briefly present the key theoretical treatment here. If there is no absorption at the probe wavelength, the experimentally observable signal (diffracted probe beam) is proportional to the square of the peak−null difference in the refractive index of matrix. Mainly, there are three sources which change the refractive index after the photoexcitaion. The first source (in this experiment) is the refractive index change of matrix, which is caused by thermal expansion (acoustic wave) resulting from photoinduced heat-releasing relaxation processes (density grating (DensG)). The time dependent $\Delta n_{\mathrm{DensG}}$ is described as[33]

$$\Delta n_{\mathrm{DensG}} = \left(\frac{\partial n}{\partial \rho}\right)_T \sum_i 4\left\{\frac{q^2 A_i Q_i}{b^2+\omega^2}\left[\frac{b}{\omega}\sin(\omega t)\exp(-dt) - \cos(\omega t)\exp(-dt) + \exp(-bt)\right] - \frac{q^2 A_i Q_i}{\tau_i^{-2}+\omega^2}\left[\frac{1}{\tau_i\omega}\sin(\omega t) \times \exp(-dt) - \cos(\omega t)\exp(-dt) + \exp(-t/\tau_i)\right]\right\} \quad (1)$$

where q is the wave vector of the grating ($q = 2\pi/\Lambda$, Λ is the fringe spacing of the grating), $\omega = \mathrm{v}q$ (v, the sound velocity), d is the acoustic attenuation rate constant, $b = \lambda_{\mathrm{w}} q^2/\rho C_{\mathrm{p}}$ (λ_{w} is the thermal conductivity, and C_{p} is the specific heat at constant pressure), τ_i is the lifetime of the excited state i, $A_i = 3\alpha/\chi\rho C_{\mathrm{p}}(1 - b\tau_i)$ (ρ is a density of the solvent, α is the thermal expansion coefficient, and χ is the compressibility), and Q_i is the thermal energy in the relaxation process from the excited state i. On the nanosecond TG experiment, the acoustic oscillation period (Λ/v) is shorter than the pulse width of the excitation pulse, and eq (1) convoluted with the excitation pulse shape can be reduced to[32]

$$\Delta n_{\mathrm{DensG}} \approx 2qA_iQ_iC[\exp(-bt) - \exp(-t/\tau_i)] \quad (2)$$

where $C = (b^2 + (\mathrm{v}q)^2)^{-1}$.

The second source to the peak−null refractive index difference is due to the change of the ground and excited states populations (the population grating (PG)). These modulations decay and/or buildup following the dynamics of the excited states. The time dependent Δn_{PG} is described as

$$\Delta n_{\mathrm{PG}} = \sum_i R_i C_i(t) \quad (3)$$

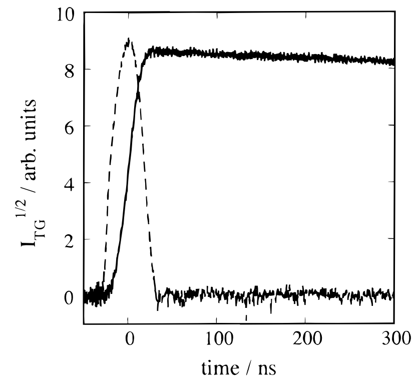

Figure 1. TG signal of NB in ethanol with the nanosecond Nd:YAG laser excitation (pump 355 nm, probe 640 nm) (solid line) and response curve (broken line).

where R_i is a constant that is determined by the refractive index change by the creation of the excited state, and $C_i(t)$ is the concentration of the excited molecule.

The third contribution is due to the temperature rise with a constant density (the temperature grating (TempG)).[16,34] This contribution becomes significant in an aqueous solution. Since C_{p} is close to C_{v} (specific heat at constant volume) in this medium, the acoustic effect is negligibly small in the TempG signal. It rises with a rate constant of the heat-releasing process and then decays by the thermal conduction between the fringes. The time dependent $\Delta n_{\mathrm{TempG}}$ is described as

$$\Delta n_{\mathrm{TempG}} = \left(\frac{\partial n}{\partial T}\right)_\rho 4\sum_i Q_i B_i[\exp(-bt) - \exp(-t/\tau_i)] \quad (4)$$

where $B_i = 1/\rho C_{\mathrm{p}}(1 - b\tau_i)$. The TempG component is much weaker than DensG in organic solvents. The sum of these modulations (DensG, PG, and TempG) contribute to the TG signal.[35] The time dependent TG signal I_{TG} is described as

$$I_{\mathrm{TG}} \propto (\Delta n_{\mathrm{DensG}} + \Delta n_{\mathrm{PG}} + \Delta n_{\mathrm{TempG}})^2 \quad (5)$$

When the pulse width of the excitation beam is not negligible compared with the acoustic period, the time dependent TG signal is described by the convolution of these contributions with the pulse shape.

3. Results

3.1. Nitrobenzene. In order to examine rather slow relaxation processes, the TG signal was measured with the nanosecond Nd:YAG laser system. The observed temporal profile of the TG signal after the photoexcitation of NB in ethanol is shown in Figure 1. It was fitted with eq (2) convoluted with the response function. It was found that this profile can be reproduced by a very fast rise (<5 ns) and a single-exponential decay by the thermal conduction process between laser-induced fringes in ethanol. In the other solvents, similar results were obtained. Thus, photoexcited NB does not show any relaxation processes in tens nanoseconds or a longer time scale.

The time profile of the picosecond time-resolved TG signal after the photoexcitation of NB in ethanol at room temperature (rt, 25 °C) is shown in Figure 2. This temporal profile was fitted by eq (5) with two different decay times, $\tau_1 \leq 50$ ps and $\tau_2 = 480 \pm 50$ ps. The best-fitted value of the parameter d is $\sim 6 \times 10^{-16}$ Np cm^{-1} s^2 and close to the literature value.[36] The ratio of the deposited thermal energies by these relaxation processes is $Q_1{:}Q_2 = 0.18 \pm 0.04{:}0.82 \pm 0.04$. The contribution

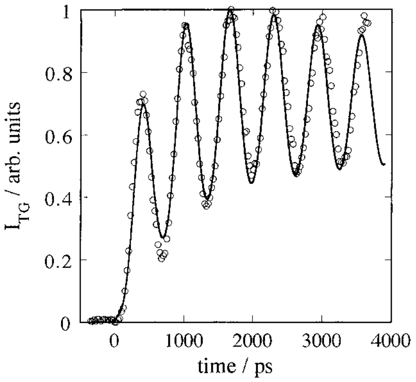

Figure 2. Picosecond time-resolved TG signal of NB in ethanol at rt with the picosecond pulsed laser system (pump 355 nm, probe 640 nm), (circles) and fitted curve (solid line).

TABLE 1: Decay Times and Thermal Energies Released in Nonradiative Decay Processes of Excited Nitrobenzene

solvent	τ_1/ps	Q_1	τ_2/ps	Q_2	Δn_{PG}
ethanol	≤50	0.18 ± 0.04	480 ± 50	0.82 ± 0.04	≤0.12
benzene	≤50	0.21 ± 0.04	750 ± 50	0.79 ± 0.04	≤0.12
heptane	≤50	0.21 ± 0.04	400 ± 50	0.79 ± 0.04	≤0.12
decane	≤50	0.21 ± 0.04	600 ± 50	0.79 ± 0.04	0.15 ± 0.12
tetradecane	≤50	0.21 ± 0.04	900 ± 50	0.79 ± 0.04	≤0.12

TABLE 2: Temperature Dependence of the Decay Time and the Released Heats of Excited Nitrobenzene in Ethanol

temp.	τ_1/ps	Q_1	τ_2/ps	Q_2	Δn_{PG}
rt	≤50	0.18 ± 0.04	480 ± 50	0.82 ± 0.04	≤0.12
0 °C	≤50	0.18 ± 0.04	550 ± 50	0.82 ± 0.04	≤0.12
−10 °C	≤50	0.21 ± 0.04	750 ± 50	0.79 ± 0.04	≤0.12
−20 °C	≤50	0.21 ± 0.04	800 ± 50	0.79 ± 0.04	≤0.12

of the PG, Δn_{PG}, was found to be ≤0.12 of the total refractive index change. The contribution of TempG is much weaker than DensG and negligible in organic solvents, too.[16,18] The time profiles in other solvents were also fitted with two different rate constants, and the results in these solvents are listed in Table 1.

Next, to study the temperature dependence of the photophysical dynamics of NB, we measured the TG signal at various temperatures from −20 °C to rt. These temporal profiles are similar to that at rt and can be reproduced with two different decay times (eqs 1, 3, and 5). For example, $\tau_1 \leq 50$ ps and $\tau_2 = 800 \pm 50$ ps are obtained for the decay times at −20 °C and the ratio of the heat energies from these relaxation processes is Q_1:Q_2 = 0.21 ± 0.04:0.79 ± 0.04. Δn_{PG} at −20 °C in ethanol was also found to be ≤0.12 of the total refractive index change. The decay times and the thermal energies determined at various temperatures are shown in Table 2. It is apparent that the decay time of the slow component becomes longer with decreasing the temperature.

In organic solvent, refractive index change after photoexcitation is primary caused by the density variation due to the heating (DensG). As a result, the acoustic oscillation, which is described by eq 1, is dominant in the TG signal. Because of the oscillating character of the DensG component, the dynamics of the excited state faster than the oscillation period becomes obscure. This is the main cause of the low time resolution (~50 ps). For observing faster dynamics, the contribution of DensG should be reduced, and for that propose, we used water as the solvent. Since $\partial\rho/\partial T$ is very small for water (even $\partial\rho/\partial T$ becomes zero at 4 °C), the DensG component can be reduced, and under such a condition, TempG and/or PG components, both of which possess much faster time response, will be observed. In order to dissolve NB in water, we used an SDS aqueous solution. The TG signal of NB in the aqueous solution measured at rt is shown in Figure 3a. This temporal profile of NB in the aqueous solution was fitted by eq 5 with two different decay times, $\tau_1 \leq 50$ ps and $\tau_2 = 400 \pm 50$ ps, for the DensG component. The ratio of the deposited heats by these relaxation processes is Q_1:Q_2 = 0.21 ± 0.04:0.79 ± 0.04. The contribution of PG with a rise time τ_1 (≤10 ps) and a decay time τ_2 was necessary for the fitting, and Δn_{PG} at rt in the aqueous solution was as large as 0.29 ± 0.10 of the total refractive index change. The TempG contribution was negligibly weak compared with the other contributions.

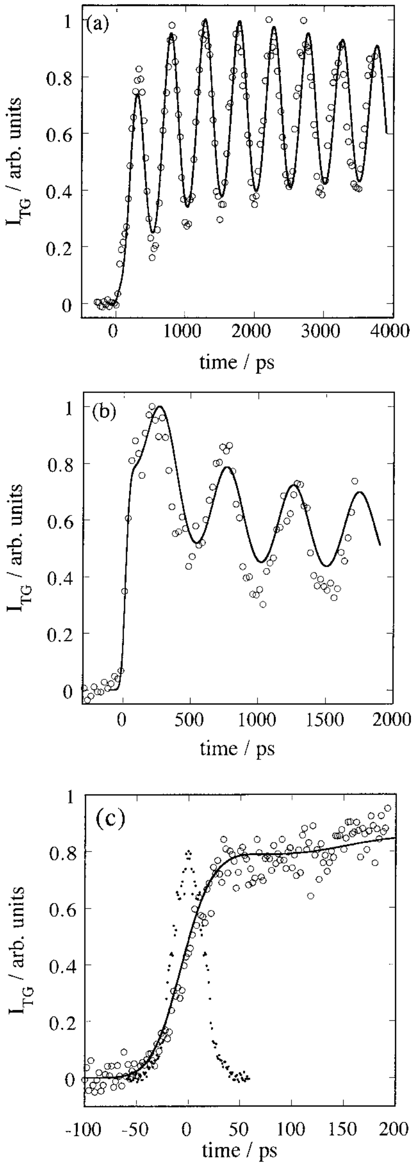

Figure 3. Picosecond time-resolved TG signal of NB in an SDS aqueous solution, (a) at rt (circles), (b) at 5.5 °C (circles), and (c) at 4.5 °C (circles) and response curve (dotted line). The fitted curves are shown by the solid lines.

The time profile at 5.5 °C (Figure 3b) was fitted by eq (5), with the same rise and decay times and Q_1:Q_2 obtained at rt. The contribution of DensG is reduced at this temperature and that of PG is relatively increased. The temporal profile of PG is the same as that at rt; it rises with a rise time of τ'_1 and decays with τ_2. Δn_{PG} was as large as 0.53 ± 0.09 of the total refractive index change. Δn_{TempG} with a rise time τ_1 (≤10 ps) and a decay time τ_2 and the ratio of Q_1:Q_2 resulting from the radiationless transitions is used for the fitting. The rise part of the TG signal at 4.5 °C is shown in Figure 3c in a fast time

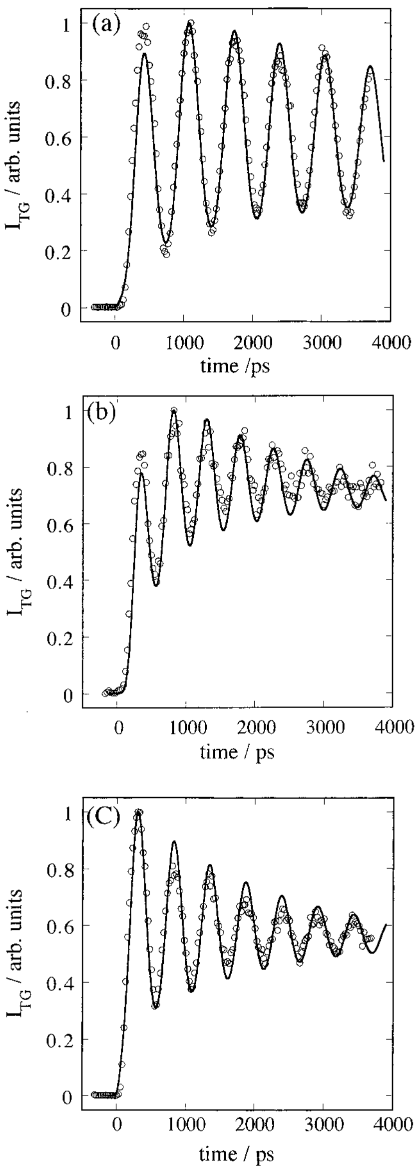

Figure 4. Picosecond time-resolved TG signal of (a) *o*-nitrotoluene/ethanol, (b) *o*-nitrobenzoicacid/benzene, and (c) *o*-nitrophenol/benzene. The fitted curves are shown by solid line.

scale. This temporal profile was fitted by eq (5), using the rise and decay times and the ratio of the deposited heats similar to those at 5.5 °C and slightly different contributions of the three TG sources. The DensG component contributed to 0.23 ± 0.09 of the total refractive index. Δn_{PG} with the rise time τ'_1 ($\leq$10 ps) and decay time τ_2 was as large as 0.57 ± 0.09 of the total refractive index. The temporal profile of Δn_{TempG} at 4.5 °C in aqueous solution is expressed by eq (4) with two rise times τ'_1 ($\leq$10 ps) and τ_2, and Q_1:Q_2 which was determined at rt.

3.2. Monosubstituted Nitrobenzenes (NBs). It is known that many monosubstituted nitrobenzenes do not emit after photoexcitation under any conditions.[27,37] In order to study the photophysical dynamics of such nonluminescent NB derivatives, the time profiles of the TG signal after photoexcitation were measured. We confirm again that radiationless transitions of those molecules are completed within tens nanoseconds after the photoexcitation by the TG measurement with the nanosecond YAG laser system. The time profiles of the TG signals of *o*-NT, *o*-NBA, and *o*-NP in the picosecond time scale are shown in Figures 4a,b,c. These temporal profiles were fitted with two different time constants similar to the case of NB. The parameters are summarized in Table 3.

TABLE 3: Decay Times and Thermal Energies Released in Nonradiative Decay Processes of Excited Nitrobenzene Derivatives

Nitrotoluene

	τ_1/ps	Q_1	τ_2/ps	Q_2	Δn_{PG}
			in Ethanol		
ortho-	$\leq$50	0.21 ± 0.04	350 ± 50	0.79 ± 0.04	0.19 ± 0.12
meta-	$\leq$50	0.21 ± 0.04	800 ± 50	0.79 ± 0.04	0.19 ± 0.12
para-	$\leq$50	0.21 ± 0.04	600 ± 50	0.79 ± 0.04	0.25 ± 0.11
			in Heptane		
ortho-	$\leq$50	0.21 ± 0.04	450 ± 50	0.79 ± 0.04	0.29 ± 0.10
meta-	$\leq$50	0.14 ± 0.04	800 ± 50	0.86 ± 0.04	0.25 ± 0.11
para-	$\leq$50	0.14 ± 0.04	600 ± 50	0.86 ± 0.04	0.18 ± 0.11

Nitrobenzoic Acid in Ethanol

	τ_1/ps	Q_1	τ_2/ps	Q_2	Δn_{PG}
ortho-	$\leq$50	0.25 ± 0.04	300 ± 50	0.75 ± 0.04	$\leq$0.12
meta-	$\leq$50	0.18 ± 0.04	450 ± 50	0.82 ± 0.04	$\leq$0.12
para-	$\leq$50	0.79 ± 0.04	800 ± 50	0.81 ± 0.04	$\leq$0.12

Nitrophenol in Benzene

	τ_1/ps	Q_1	τ_2/ps	Q_2	Δn_{PG}
ortho-	$\leq$50	0.4 ± 0.04	900 ± 50	0.6 ± 0.04	0.40 ± 0.10
meta-	$\leq$50	0.11 ± 0.04	600 ± 50	0.89 ± 0.04	0.33 ± 0.10
para-	$\leq$50	0.13 ± 0.04	600 ± 50	0.87 ± 0.04	0.25 ± 0.11

4. Discussion

First, two different lifetimes observed in the TG signal are examined. After the photoexcitation by our laser light, NB is excited to the vibrationally hot excited singlet (S_1^*) state. The vibrationally excited state relaxes to the vibrationless level of the S_1 state by the vibrational relaxation. The S_1 state should be deactivated to the T_1 state (intersystem crossing, isc) and/or the ground state (internal conversion, ic). The T_1 state relaxes to the ground state by the $T_1 \rightarrow S_0$ isc process. Photochemical reaction is negligible from any excited states of NB.[30,38] If the shorter (τ_1, $\leq$ 50 ps) and longer (τ_2, 480 ps) decay times were assigned to the relaxation times of the S_1^* state to the S_1 state and of the S_1 state, respectively, no further slow dynamics observable in the TG signal indicates that the photophysical processes complete after the decay of the S_1 state; that is, the ic process from the S_1 state to the ground state is the only relaxation path. However, under this assumption, $h\nu Q_2/(Q_1 + Q_2)$ should represent the energy of the S_1 state, which is calculated to be (22−23) × 10^3 cm^{-1}. This value seriously disagrees with the S_1 energy ((26−27) × 10^3 cm^{-1}) estimated from the absorption spectrum.[19,29] Therefore, we have to assign the longer relaxation time (τ_2) to the lifetime of the T_1 state. The shorter decay time (τ_1) should represent the relaxation time from the S_1^* to the S_1 states and also from the S_1 states. The shortest limit of the faster relaxation time (50 ps) was determined by the acoustic oscillation and can be much shorter, if the relaxation dynamics in the S_1 manifold and the S_1 relaxation are similar in organic solvents and in an aqueous solution. The rise time of PG and TempG signals in water at 4.5 °C indicates that the relaxation from the S_1^* to the S_1 states and from the S_1 state complete within 10 ps.

The energy of the S_1 state of NB is estimated to be (26−27) × 10^3 cm^{-1} from the absorption spectrum.[19,29] Because NB neither fluoresces nor phosphoresces at any temperatures in any solvents,[27] the quantum yields of fluorescence and phosphorescence, Φ_f and Φ_p, are negligible. If we separate the thermal energies involved in the relaxation processes from the excited S_1^* state into two; Q_1, the heat released by the vibrational relaxation $S_1^* \rightarrow S_1$ process and the relaxation from the S_1 state, and Q_2, the heat released by the isc process from the T_1 state, the ratio between them is expressed by $Q_1{:}Q_2 = (h\nu - E_S) + [E_S\Phi_{ic} + (E_S - E_T)\Phi_{isc}]{:}E_T\Phi_{isc}$, where E_S is the energy of the S_1 state, $h\nu$ is the excitation photon energy (28×10^3 cm^{-1}), and Φ_{ic} and Φ_{isc} are the quantum yields of the ic process and the isc process, respectively. Using the relative thermal energies from the two processes and the fact that the quantum yield cannot be larger than unity and E_T cannot be lager than E_S, Φ_{isc}, and E_T are found to be ≥ 0.80 and $(22-27) \times 10^3$ cm^{-1}. In the temperature range from -20 °C to rt, the variation of E_T was not detected.

From the energy transfer from the T_1 of NB to *trans*-piperylene, E_T was estimated to be larger than 20.6×10^3 cm^{-1}.[30] E_T determined in this work is consistent with their estimation. Hurley and Testa performed energy transfer experiments from the triplet state of NB to *cis*-1,3-pentadiene in solution.[39] They observed that the quantum yield of the *cis*–*trans* isomerization increased with increasing the concentration of *cis*-1,3-pentadiene, which suggested that the triplet lifetime of NB is very short. Even though it was very rough and crude, they have estimated a lifetime of $\sim 10^{-9}$ s from the yield of the products,[39] which is rather close to the lifetime directly determined in this study. The very short lifetime is also consistent with the relative low quantum yield for the disappearance of NB by photochemical reactions in degassed alcohol solvents reported earlier.[38] Φ_{isc} was also measured by the energy transfer experiment, but the reported value (0.67 ± 0.10)[39] is somewhat lower than that measured here. We think that the lower value of Φ_{isc} in the measurement was caused by two reasons. First, they assumed that the fraction of 1,3-pentadiene triplets which produce the *trans* isomer is 0.55.[40] However, this value could be smaller than 0.55 as suggested by Anderson et al.[41] Second, since they observed phosphorescence from the sample, the sample should be contaminated by an impurity. The impurity could make their measurement uncertain. The triplet lifetime in this study agrees well with that reported from the transient absorption study by Yip et al. ($\tau(S_1) \leq 5$ ps, $\tau(T_1) = 690$ ps in THF).[30]

All of the triplet lifetimes of NB in alkane, benzene, ethanol, and water are in a range of 400–900 ps. No drastic change in the lifetime on going from a nonpolar solvent to a polar solvent suggests that the triplet character is not sensitive to the environment. Sometimes, the characters of the excited state of NB are discussed with relation to the intramolecular charge transfer process. In particular, when electron donating group is substituted to the para position, the low-lying twisted intramolecular charge transfer (TICT) state has been suggested. However, for NB, if the T_1 state possesses considerable intramolecular charge transfer (CT) character, the fraction of the CT character may be easily changed depending on the dielectric constant of the matrix and the triplet lifetime should be sensitive to the matrix. Since we do not observe this dependence, we think that the CT character is not important in the nature of the T_1 state. This experimental result is theoretically confirmed by a molecular orbital (MO) calculation as described below.[42]

The energy level diagrams of the monosubstituted nitrobenzenes, such as NPs, NTs and so on, are similar to the energy level diagram of NB.[27] Considering the nonfluorescent and nonphosphorescent character of these NB derivatives and similar TG signals to those of NB, we can apply a similar argument to these NBs. Two different decay times of NBs in the TG signal were assigned similarly to those of NB, the shorter decay time is determined by the relaxation from the vibrationally hot S_1^* state to the S_1 state and from the S_1 state to the T_1 state. The longer decay time is the lifetime of the T_1 state. The energy of the T_1 state of NT is estimated as $(22-28) \times 10^3$ cm^{-1} and the quantum yield of the triplet formation to be ≥ 0.79. The variation of the quantum yield between *ortho*, *meta*, and *para* derivatives could not be detected. The triplet energies and quantum yields of the triplet formation of NBs are summarized in Table 4.

TABLE 4: Quantum Yields of Triplet Formation and Triplet Energies of Nitrobenzenes

	triplet energy/($\times 10^3$ cm^{-1})	Φ_{ISC}
nitrotoluene/ethanol	22–28	≥ 0.79
nitrobenzoic acid/ethanol	21–28	≥ 0.70
nitrophenol/benzene	24–28	≥ 0.86

The triplet lifetimes of *o*- NT and NBA are 1.5–2 times shorter than those of *m*- or *p*- NT and NBA. This position dependent substitution effect on the triplet lifetimes could be explained by the structural deformation in their T_1 states. As described later, our preliminary MO calculation shows that the NO_2 group is strongly bent from the phenyl plane in the excited state and the structure in the excited state is not the C_{2v} symmetry, but the C_s symmetry,[42] and this could be the cause of the short triplet lifetime. If a bulky group is attached to the *ortho* position of the nitro group, the deformation could be much easier and, then, it enhances the decay rate from the T_1 state. On the other hand, the triplet lifetime of *o*-NP is longer than those of *m*- or *p*-NP. This longer lifetime can be explained by an intramolecular hydrogen bond between $-OH$ and $-NO_2$ groups. Although there has been no report on the existence of such an intramolecular hydrogen bond in the excited states, a theoretical calculation[43] and results of the electron diffraction[43] and the microwave spectroscopy[44,45] indicate the intramolecular hydrogen bond in the ground state. Probably the hydrogen bond of *o*-NP makes the NO_2 group a little more planar than NB in the T_1 state and it slows down the nonradiative transition to the ground state.

The most striking result in this study is the ultrashort lifetime of the triplet state. Generally the triplet lifetimes of most aromatic compounds are in a range of millisecond to tens of seconds in the absence of any external quenching processes or photochemical reactions. The observed several hundred picoseconds are about 7 orders of magnitude shorter than these normal triplet lifetimes. Undoubtedly this short lifetime, very fast nonradiative transition, is the cause of the nonphosphorescent character of NB and NB derivatives. This ultrafast nonradiative transition from the T_1 state suggests a very peculiar feature in the excited states. We think this fast transition comes from very large structural changes in the excited states, and the change should be related to the NO_2 group. Since the T_1 state of nitronaphthalene phosphoresces with a lifetime of 48 ms in ether–isopentane–ethanol at 77 K[26] and the triplet character is very close to the $^3\pi\pi^*$ state of naphthalene,[46] the T_1 state of NB cannot be a $^3\pi\pi^*$ state, but the nonbonding or the σ orbital should participate in the T_1 state; that is, the structure of the T_1 state is considerably deformed from that of the ground state by the participation of these electrons from the NO_2 group. The large structural change is consistent with the very broad feature in the absorption spectrum.[19,29] Furthermore, the triplet lifetime of NB increases with decreasing the temperatures. This temperature dependence suggests that the nonradiative transition is also enhanced by the thermally activated vibrations or structural deformation.

A semiemprical calculation was carried out for NB and the results predicted very different structures in the ground and excited states.[47] Their calculated structures showed that the nitro group is orthogonal to the phenyl ring in the ground state. However, it is now known that NB has a planar structure in the ground state on the basis of some experimental results[48−50] and also theoretical ab initio calculations.[50,51] A more sophisticated MO calculation is needed for the geometries of the ground state and excited states, and we are now carrying out such a calculation. Preliminary results (CAS-SCF calculation) show that, while the geometry in the ground state is planar, the nitro group is bent from the phenyl plane in the S_1 and T_1 states by as large as ∼39°,[42] and the $\pi\pi^*$, $n\pi^*$, and $n\sigma^*$ states are completely mixed. The excitations of the S_1 and T_1 states are almost localized on the NO_2 group.

5. Conclusion

By applying the picosecond time-resolved TG method, the photophysical processes of nitrobenzene and nitrobenzene derivatives, which have been unclear for a long time, are investigated. From the thermal energies released by the radiationless relaxation processes, E_T and Φ_{ISC} of nitrobenzene are found to be $(22-27) \times 10^3$ cm^{-1} and greater than 0.80, respectively. The lifetimes of the S_1 and the T_1 states of nitrobenzene are determined to be ≤ 10 ps and ∼480 ps, respectively. The $T_1 \rightarrow S_0$ isc relaxation process with a surprisingly short lifetime suggests a large geometrical deformation in the T_1 state, and it could be attributed to the rotational and/or libration modes of the nitro group which make the Franck−Condon factor large. A preliminary MO calculation indicates that the nitro group bends from the phenyl plane. The observed position dependent triplet lifetimes of the substituted nitrobenzenes are consisted with this explanation.

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References and Notes

(1) Levenson, M. D.; Bloembergen, N. *J. Chem. Phys.* **1974**, *60*, 1323.
(2) Kurokawa, K.; Hattori, T.; Kobayashi, T. *Phys. Rev. A* **1987**, *36*, 1298.
(3) Lotshaw, W. T.; McMorrow, D.; Kalpouzos, C.; Kenney-Wallace, G. A. *Chem. Phys. Lett.* **1987**, *136*, 323.
(4) Kaczmarek, M.; Bochert, J. M.; Kielich, S. *J. Mod. Opt.* **1991**, *38*, 193.
(5) Apanasevich, P. A.; Kozich, V. P.; Vodschitz, A. I. *J. Mod. Opt.* **1988**, *35*, 1933.
(6) Albart, V.; Schmillen, A. *Z. Naturforsh. A* **1973**, *28*, 801.
(7) Gerrard, D. L.; Maddams, W. F. *Appl. Spectrosc.* **1976**, *30*, 554.
(8) Zander, M.; Breymann, U.; Dreeskamp, H.; Koch, E. *Z. Naturforsch. A* **1977**, *32*, 1561.
(9) Kawski, A.; Kojro, Z.; Kubicki, A. *Z. Naturforsch. A* **1985**, *40*, 313.
(10) Ogasawara, F. K.; Wang, Y.; McGuffin, V. L. *Appl. Spectrosc.* **1995**, *49*, 1.
(11) Ke, W.; Wu, J. *Spectrochim. Acta, Part A* **1995**, *51*, L25.
(12) Bailey, R. T.; Cruickshank, F. R.; Pugh, D.; Weir, I. J. M. *Chem. Phys. Lett.* **1984**, *87*, 125.
(13) Chen, H. M.; Scelly, Z. A. *Chem. Phys. Lett.* **1988**, *145*, 102.
(14) Chen, H. M.; Scelly, Z. A. *Chem. Phys. Lett.* **1994**, *224*, 61.
(15) Kimura, Y.; Kanda, D.; Terazima, M.; Hirota, N. *Ber. Bunsen-Ges. Phys. Chem.* **1995**, *99*, 196.
(16) Terazima, M. *Chem. Phys.* **1994**, *189*, 793.
(17) Hara, T.; Hirota, N.; Terazima, M. *J. Phys. Chem.* **1996**, *100*, 10194.
(18) Terazima, M. *J. Chem. Phys.* **1996**, *104*, 988.
(19) Nagakura, S.; Kojima, M.; Maruyama, Y. *J. Mol. Spectrosc.* **1964**, *13*, 174.
(20) Sinha, H. K.; Yates, K. *J. Chem. Phys.* **1990**, *93*, 7085.
(21) Prabhumirashi, L. S.; Kunte, S. S. *Spectrochim. Acta, Part A* **1986**, *42*, 435.
(22) Prabhumirashi, L. S.; Kunte, S. S. *Spectrochimi. Acta, Part A* **1988**, *44*, 213.
(23) Minesinger, R. R.; Kamlet, J. M. *J. Phys. Chem.* **1974**, *78*, 494.
(24) Hudson, R. A.; Sott, R. M.; Vinogrodov, S. N. *Spectrochim. Acta, Part A* **1970**, *26*, 337.
(25) Dearden, J. C.; Forbes, W. F. *Can. J. Chem.* **1959**, *37*, 1294.
(26) Khalil, O. S.; Bach, H. G.; McGlynn, S. P. *J. Mol. Spectrosc.* **1970**, *35*, 455.
(27) Seliskar, C. J.; Khalil, O. S.; McGlynn, S. P. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1974; Vol. 1.
(28) Terazima, M.; Hirota, N. Unpublished results.
(29) Vidal, B.; Murrell, J. N. *Chem. Phys. Lett.* **1975**, *31*, 46.
(30) Yip, R. W.; Sharma, D. K.; Giasson, R.; Gravel, D. *J. Phys. Chem.* **1984**, *88*, 5770.
(31) Takezaki, M.; Hirota, N.; Terazima, M. *J. Phys. Chem.* **1996**, *100*, 10015.
(32) Terazima, M.; Hirota, N. *J. Chem. Phys.* **1991**, *95*, 6490.
(33) Genberg, L.; Bao, Q.; Gracewski, S.; Miller, R. J. D. *Chem. Phys.* **1989**, *131*, 81.
(34) Okazaki, T.; Hirota, N.; Terazima, M. To be published.
(35) A contribution of the molecular volume change upon the photoexcitation of NB is neglected. Since any atomic rearrangement does not occur and also the intramolecular charge transfer is considered to be minor as described below, the effect should be minor.
(36) Miller, R. J. D.; Casalegro, R.; Nelson, K. A.; Fayer, M. D. *Chem. Phys.* **1982**, *72*, 371.
(37) Zuccarello, F.; Millefiori, S.; Buemi, G. *Spectrochim. Acta, Part A* **1979**, *35*, 223.
(38) Hurley, R.; Testa, A. C. *J. Am. Chem. Soc.* **1966**, *88*, 4330.
(39) Hurley, R.; Testa, A. C. *J. Am. Chem. Soc.* **1968**, *90*, 1949.
(40) Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* **1965**, *43*, 2129.
(41) Anderson, R. W., Jr.; Hochstrasser, R. M.; Lutz, H.; Scott, G. W. *Chem. Phys. Lett.* **1974**, *28*, 153.
(42) Takezaki, M.; Terazima, M.; Hirota, N.; Sato, F.; Nakajima, T.; Kato, S. To be published.
(43) Borisenko, K. B.; Bock, C. W.; Hargittai, I. *J. Phys. Chem.* **1994**, *98*, 1442.
(44) Hasanein, A. A.; Masoud, M. S.; Habeeb, M. M. *Spectrosc. Lett.* **1988**, *21*, 481.
(45) Leavell, S.; Curl, R. F., Jr. *J. Mol. Spectrosc.* **1973**, *45*, 428.
(46) Shiota, Y.; Yagi, M.; Higuchi, J. *Chem. Phys. Lett.* **1989**, *154*, 25.
(47) Malar, E. J. P.; Jug, K. *J. Phys. Chem.* **1984**, *88*, 3508.
(48) Boese, R.; Bläser, D.; Nussbauner, M.; Krygowski, T. M. *Struct. Chem.* **1992**, *3*, 363.
(49) Trotter, J. *Tetrahedron* **1960**, *8*, 13.
(50) Domenicano, A.; Schultz, G.; Hargittai, I.; Colapietro, M.; Portalone, G.; George, P.; Bock, C. W. *Struct. Chem.* **1990**, *1*, 107.
(51) Penner, G. H. *J. Mol. Struct.* **1986**, *137*, 121.