Effect of Potential Energy Gap between the n-π* and the π-π* State on Ultrafast Photoisomerization Dynamics of an Azobenzene Derivative

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We considered the trans → cis photoisomerization dynamics of the S_2-excited azobenzene derivatives in terms of the potential energy gap between the n-π* (S_1) and the π-π* (S_2) state. The photoisomerization dynamics of *trans*-4-aminoazobenzene (*trans*-4-AAB) which has an energy gap (3000−4000 cm^{-1}) rather smaller than that of *trans*-azobenzene (∼10000 cm^{-1}) due to an amino-substitution was investigated using UV−vis transient absorption spectroscopy. The recorded transient absorption spectra of the π-π* (S_2) excited *trans*-4-AAB in ethanol and heptanol indicated that the π-π* state of the *trans*-4-AAB decays to the n-π* state with a time constant of 0.2 ps. Following this process, the n-π* state decays to the ground state via two reaction pathways with time constants of 0.6 and 1.9 ps, and finally vibrational cooling of the ground state occurs with ∼15 ps. The π-π* state decay dynamics of the π-π* excited *trans*-4-AAB showed good agreement with that of the π-π* excited *trans*-azobenzene. On the other hand, the n-π* state decay dynamics of the π-π* excited *trans*-4-AAB was apparently different from that of the π-π* excited *trans*-azobenzene, and it corresponds well to that of the *trans*-azobenzene *directly excited to the n-π* state*. In addition, in the photoisomerization of the π-π* excited *trans*-4-AAB, we could not observe the solvent dependence of the n-π* state lifetime which has been reported in the photoisomerization of the π-π* excited *trans*-azobenzene. On the basis of the potential energy diagram of azobenzene, we considered that the similarity of the n-π* state decay dynamics observed for the π-π* excited *trans*-4-AAB and the n-π* excited *trans*-azobenzene originated from the small potential energy gap between the π-π* and the n-π* states of 4-AAB. These results indicated that not only the photoexcitation condition (π-π* excitation or n-π* excitation), but also the potential energy gap between the π-π* and the n-π* states is an important factor which determines the trans → cis photoisomerization dynamics of azobenzene derivatives.

1. Introduction

Photoisomerization of azobenzene derivatives is one of the most fundamental photochemical reactions. In addition, azobenzene derivatives are expected to provide useful applications for optical switching[1] or image storage[1,2] devices, because their photoisomerization induces changes of various chemical and physical properties such as the absorption spectrum, dielectric constant, and refractive index. Therefore, the photoisomerization dynamics of azobenzene and its derivatives has been extensively studied.[3−18]

It is well-known that the mechanism of the trans → cis photoisomerization of azobenzene depends on the excitation wavelength.[3] The excitation of *trans*-azobenzene to the n-π* (S_1) state results in photoisomerization by in-plane inversion at one N atom.[4−6] On the other hand, it is considered that photoisomerization of the *trans*-azobenzene excited to the π-π* (S_2) state may proceed by rotation around the N=N double bond.[5,7,8] However, recently it has been reported that the photoisomerization of *trans*-azobenzene proceeds via the inversion process even in the case of the π-π* excitation,[9] leaving the photoisomerization mechanism of the π-π* excited *trans*-azobenzene under discussion.

The photoisomerization dynamics of several azobenzene derivatives has also been investigated.[10−13] These studies have shown that when the π-π* transition becomes the lowest in energy due to substitution, the photoisomerization dynamics of the substituted azobenzene excited to the π-π* state is apparently different from that of the π-π* excited *trans*-azobenzene.[10,12] In this study, we focused on the potential energy of the π-π* state and investigated the photoisomerization dynamics of the π-π* excited *trans*-4-aminoazobenzene (*trans*-4-AAB) in ethanol and heptanol by using UV−vis transient absorption spectroscopy. In the case of *trans*-4-AAB, the potential energy of the π-π* state is slightly higher than that of the n-π* state (3000−4000 cm^{-1}), while the former is somewhat higher than the latter in the case of *trans*-azobenzene (10000 cm^{-1}). The transient absorption spectra indicated that the decay process of the n-π* state of the π-π* excited *trans*-4-AAB corresponds well to that of *the trans-azobenzene directly excited to the n-π* state, not to that of the π-π* excited trans-azobenzene*. This agreement of the dynamics between the π-π* excited *trans*-4-AAB and the n-π* excited *trans*-azobenzene indicated that the energy gap between the π-π* and the n-π* state has a great effect on determining the trans → cis photoisomerization dynamics of the π-π* excited azobenzene derivatives.

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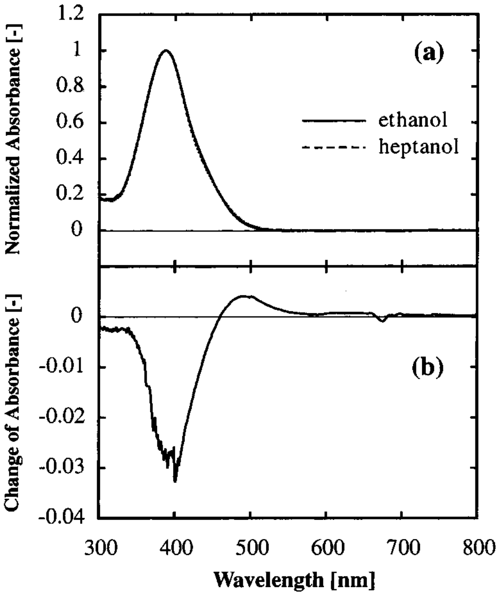

Figure 1. (a) UV−vis absorption spectra of *trans*-4-AAB in ethanol and in heptanol. (b) Change of the absorption spectrum of *trans*-4-AAB in ethanol induced by trans → cis photoisomerization.

2. Experiment

4-AAB (Aldrich), ethanol, and heptanol (Kanto Chem. special grade) were used as-received. All measurements were performed at 296 K and fresh sample solutions (1 mM) were used for each measurement. Static absorption spectra were measured by an UV−vis spectrometer (JASCO, V-570). In transient absorption measurements, a Ti:Sapphire oscillator with a regenerative-amplifier (Clark, ORC-1000 seeded by Coherent, Mira Basic; centered at 800 nm, 1 kHz repetition) was used as a light source. A part of the laser output was frequency doubled by a BBO crystal and used as a pump beam (400 nm). The rest of the beam was passed through an optical delay line and focused into a 1-cm D_2O cell to generate a white light continuum (350−750 nm), which was used as a probe beam. A small part of the probe beam was divided for use as a reference bean. The pump and probe beams were crossed at a small angle and focused on a quartz flow cell (0.5-mm path length). The power of the pump beam was less than 200 μJ/pulse and it was confirmed that no nonlinear process such as multiphoton absorption was taking place. The experiments were performed with both parallel and perpendicular polarization conditions. The intensities of the probe and reference beams were measured by a multichannel CCD spectrometer (Hamamatsu, PMA-11) and the absorption spectra were calculated by a personal computer. The response function of the whole system was about 200 fs fwhm.

3. Results

3.1. Absorption Spectra of 4-AAB. In the static absorption spectrum of *trans*-azobenzene, there are two characteristic absorption bands: a strong π-π^* absorption at 320 nm and a weak n-π^* absorption at 440 nm[3]. The wavelengths of these two absorption bands are well separated in *trans*-azobenzene (~10000 cm^{-1}). On the other hand, substitution of *trans*-azobenzene by an *o*- or *p*-amino group induces a large shift of the π-π^* absorption band to longer wavelength.[3] In the case of *trans*-4-AAB dissolved in ethanol, the π-π^* band was shifted to ~390 nm, and its long wavelength wing overlapped with the n-π^* band which shifted little by substitution (Figure 1a). Figure 1a also shows the static absorption spectrum of *trans*-4-AAB dissolved in heptanol and it was observed that the absorption spectrum of the *trans*-4-AAB in heptanol is the same as that in ethanol.

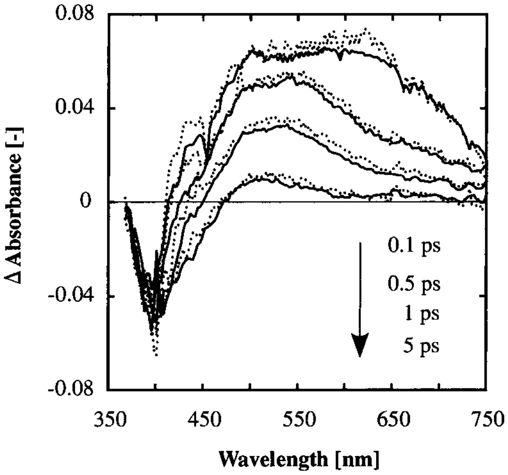

Figure 2. Transient absorption spectra of *trans*-4-AAB in ethanol (solid line) and in heptanol (dotted line) at several delay times after the excitation.

To estimate the energy gap between the π-π^* and the n-π^* absorption bands of *trans*-4-AAB, we measured the change of the absorption spectrum induced by trans → cis photoisomerization. Figure 1b shows the absorption spectrum of *trans*-4-AAB in ethanol solution after irradiation by 390 nm light for 20 min with a Xe lamp. The absorbance of 4-AAB decreased in the 350−460 nm region and increased in the 460−550 nm region. These changes of the spectrum were attributed to the decrease of the π-π^* absorption and the increase of the n-π^* absorption, respectively, on the basis of an analysis using selection rules for the symmetry differences between trans and cis isomers[3]. From the change of the absorption spectrum, we estimate the energy gap between the π-π^* and the n-π^* states of *trans*-4-AAB as 3000−4000 cm^{-1}.

3.2. Transient Absorption Spectra of 4-AAB. The excitation wavelength in the transient absorption measurements (400 nm) corresponds to the π-π^* ($S_2 \leftarrow S_0$) excitation of *trans*-4-AAB (see Section 3.1). Figure 2 shows the transient absorption spectra of the *trans*-4-AAB in ethanol at several delay times after the excitation to the π-π^* state. Just after the excitation, a broad absorption band of the excited state of the *trans*-4-AAB was observed at 410−750 nm. This band decayed within several picoseconds and the decay was faster at the long wavelength range (600−750 nm). We also observed a long-lived bleaching band of the ground state at 370−410 nm. At the wavelength range where these bands are overlapped (410−470 nm), the optical density increased for several picoseconds and then decreased, becoming negative. The absorption spectrum finally corresponded to the spectrum which reflects the difference in the absorbance between trans and cis isomers of 4-AAB.

Next, we analyzed the time evolution of the transient absorption spectra. First, the absorption band at 410−750 nm was considered. At 600−725 nm, the time evolution of the absorbance was well fitted by a triple-exponential function convoluted with the response function of the apparatus (Figure 3a). The time constants of each decay component were 0.2, 0.6, and 1.9 ps, and they were independent of the wavelength (Table 1). On the other hand, at 500−600 nm, the 0.2 ps-decay component was not observed and the time evolution of the absorbance was fitted using only the slower two (0.6 ps and 1.9 ps) decay components (Figure 3b and Table 1). At 425−475 nm, these two decay components were overlapped with the bleaching band (as for the recovery process of the bleaching

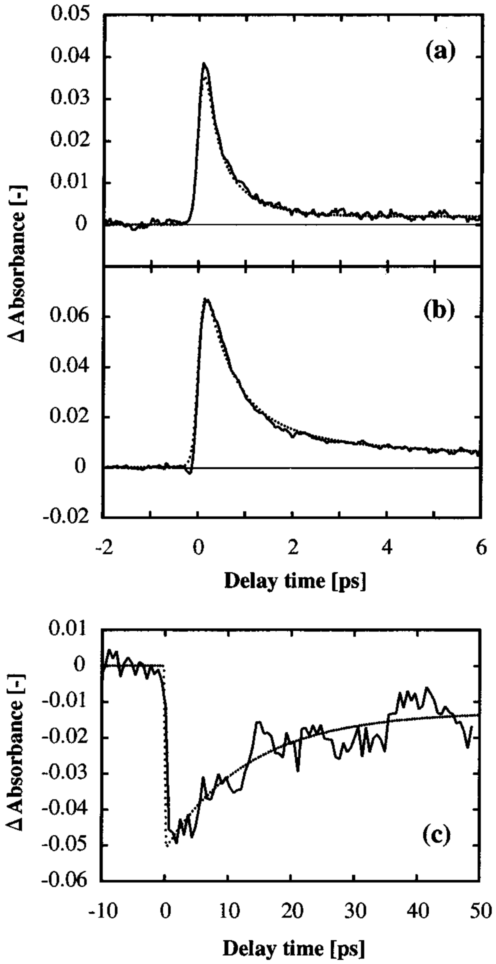

Figure 3. Time evolution of the transient absorption spectra of *trans*-4-AAB in ethanol at several wavelengths: (a) 706 nm, (b) 551 nm, (c) 391 nm. The dotted lines are results of the least-squares fittings.

band, see below). The peak positions of these three decay components were estimated by the preexponential factors: ~650 nm for the 0.2 ps-decay component and ~550 nm for the 0.6 ps- and 1.9 ps-decay components (Figure 4). The time evolutions of the transient absorption spectra in both parallel and perpendicular polarization conditions were almost the same in this time scale (~10 ps), which indicated that the contribution of reorientational dynamics was negligible. Next, the recovery of the bleaching band was investigated. The time evolution of the bleaching band was fitted well by a single-exponential function convoluted with the response function and the time constant was ~15 ps (Figure 3c and Table 1).

We also measured and analyzed the transient absorption spectrum of the *trans*-4-AAB in heptanol. Both the shape and the time evolution of the transient absorption spectrum in heptanol were almost the same as those in ethanol (Figure 2).

TABLE 1: Kinetic Parameters Determined by a Least-Square Fitting of the Transient Absorption Spectra of 4-AAB in Ethanol and Heptanol[a]

	A_1 [−][b]	t_1 [ps][c]	A_2 [−][d]	t_2 [ps][c]	A_3 [−][d]	t_3 [ps][e]	A_0 [−][f]
			in ethanol				
725 nm	0.1	1.7	0.4	0.6	1.1	0.2	0.02
699 nm	0.1	1.8	0.5	0.5	0.9	0.2	0.04
676 nm	0.1	1.9	0.5	0.5	0.9	0.2	0.04
650 nm	0.1	1.8	0.5	0.5	0.9	0.2	0.04
626 nm	0.1	1.8	0.5	0.6	1.0	0.2	0.03
599 nm	0.2	2.0	0.7	0.6	0.5	0.2	0.03
576 nm	0.2	1.8	1.0	0.6			0.06
550 nm	0.4	1.8	0.9	0.5			0.08
526 nm	0.4	1.8	0.9	0.5			0.10
500 nm	0.4	1.8	1.0	0.4			0.10
391 nm	−0.2 ± 0.1	11 ± 5					−0.6 ± 0.2
			in heptanol				
725 nm	0.2	1.8	0.4	0.5	1.0	0.2	0.05
699 nm	0.2	2.0	0.4	0.6	1.0	0.2	0.04
676 nm	0.2	2.0	0.4	0.6	1.0	0.2	0.04
650 nm	0.2	2.0	0.4	0.6	1.1	0.2	0.03
626 nm	0.2	1.9	0.4	0.6	1.0	0.2	0.03
599 nm	0.2	1.9	0.7	0.6	0.6	0.2	0.05
576 nm	0.3	1.8	0.9	0.6			0.07
550 nm	0.4	1.9	0.9	0.5			0.10
526 nm	0.4	2.0	0.8	0.5			0.11
500 nm	0.5	1.8	0.8	0.4			0.12
391 nm	−0.3 ± 0.1	13 ± 5					−0.9 ± 0.2

[a] The model function is $\int_{-\infty}^{t} f(t-s) \times R(s) \cdot ds$, $f(t) = A_1 \exp(-t/t_1) + A_2 \exp(-t/t_2) + A_3 \exp(-t/t_3) + A_0$, and $R(t)$ is the response function of the apparatus. [b] ±0.05. [c] ±0.1 ps. [d] ±0.1. [e] ±0.05 ps. [f] ±0.01 (except for 391 nm).

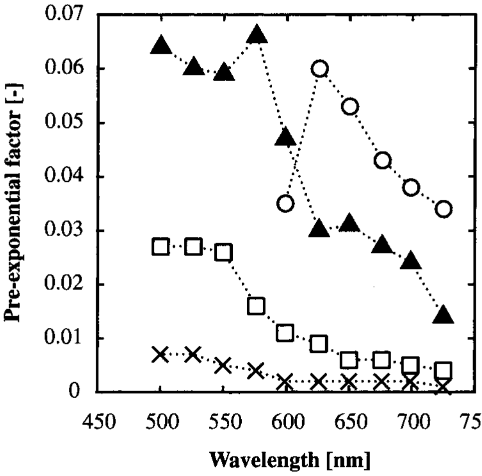

Figure 4. Preexponential factors of the three decay components of the transient absorption spectra of the π-π* excited *trans*-4-AAB in ethanol: (○) 0.2 ps-decay component; (▲) 0.6 ps-decay component; (□) 1.9 ps-decay component; (×) constant. The dotted lines are guides for eyes.

4. Discussion

We first assigned the 0.2 ps-decay component observed at 600−750 nm in the transient absorption spectrum to an absorption band of the π-π* (S_2) state of *trans*-4-AAB. Similar decay processes of the π-π* state have also been observed in photoisomerization of other azobenzene derivatives:[5,7,11,13] in the case of the π-π* excited *trans*-azobenzene, an absorption band of the π-π* state emerges at 450−500 nm and it decays within 0.2 ps.[5,7] An azobenzene derivative, *trans*-4-butyl-4′-methoxyazobenzene (*trans*-BMAB), has an absorption band of the π-π* state at 500−750 nm with a lifetime of ~0.25 ps.[11,13] We considered that the wavelength difference of the absorption band originates from the substitution of an amino group.[11]

Following the decay of the absorption band of the π-π* state, we observed a transient absorption band at 410−750 nm which decays double-exponentially with time constants of 0.6 and 1.9 ps. As stated in Section 3.2, the spectral shapes of these two decay components were almost the same (Figure 4), so we considered that these two decay components originate from the decay processes of the n-π* (S_1) state via two different pathways. Interestingly, this time evolution of the absorption band of the n-π* state corresponded well to *that of the trans-azobenzene directly excited to the n-π* state, not to that of the*

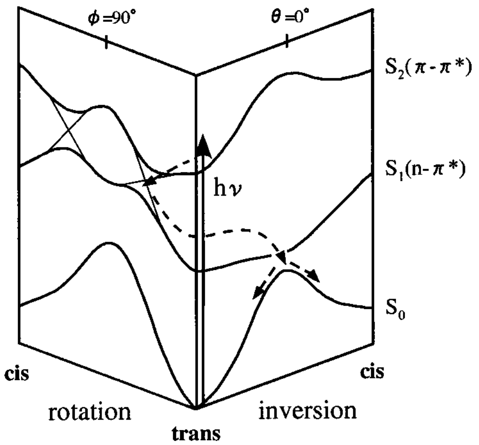

Figure 5. Schematic representation of the potential energy diagram of azobenzene.

π-π^* excited trans-azobenzene.[7] When *trans*-azobenzene is directly excited to the n-π^* state with a relatively large excess energy (~4000 cm^{-1}), the transient absorption of the n-π^* state at 370−620 nm decays double-exponentially with lifetimes of 0.6 and 2.5 ps.[7] On the other hand, in the case of π-π^* excitation, the n-π^* state of *trans*-azobenzene shows a transient absorption at 400−450 nm following the decay of the π-π^* state, which decays double-exponentially with lifetimes of 0.9 and 15 ps.[7,8]

On the basis of the potential energy diagram of azobenzene[14,15] (Figure 5), we interpreted the similarity of the time evolution of the absorption band of the n-π^* state between the π-π^* excited *trans*-4-AAB and the n-π^* excited *trans*-azobenzene as follows. When an azobenzene derivative in the trans form is excited to the π-π^* state, it decays to the n-π^* state via rotational motion on the π-π^* energy surface. In the case of *trans*-4-AAB, the energy gap between the π-π^* state and the n-π^* state (3000−4000 cm^{-1}; see Section 3.1) is rather smaller than that of *trans*-azobenzene (~10000 cm^{-1}) because of the substitution of an amino group[3]. Therefore the molecular structure of the 4-AAB at the crossing region of the π-π^* and the n-π^* energy surfaces is close to the trans form. As a result, the reaction pathway of the π-π^* excited *trans*-4-AAB after the internal conversion to the n-π^* state corresponds well to that of the *trans*-azobenzene directly excited to the n-π^* state.

The above interpretation means that in the π-π^* excitation condition, the energy gap between the π-π^* and n-π^* states has a great effect on the photoisomerization dynamics of azobenzene derivatives, especially on the reaction pathway after the internal conversion from the π-π^* state to the n-π^* state. This proposal is supported by the photoisomerization dynamics of another azobenzene derivative, *trans*-BMAB.[11,13] *trans*-BMAB has ~6700 cm^{-1} energy gap between the π-π^* and n-π^* states,[11] which is smaller than that of *trans*-azobenzene (~10000 cm^{-1}), but larger than that of *trans*-4-AAB (3000−4000 cm^{-1}). The decay process of the n-π^* state of the π-π^* excited *trans*-BMAB is similar to neither that of the π-π^* excited *trans*-azobenzene[7] nor that of the π-π^* excited *trans*-4-AAB; the n-π^* state of the *trans*-BMAB decays single-exponentially with a lifetime of 2.3 ps following the 0.3 ps-decay of the π-π^* state.[11,13]

The difference of the reaction pathway between the π-π^* excited *trans*-4-AAB and the other two azobenzene derivatives (*trans*-azobenzene and *trans*-BMAB) was also reflected in the solvent dependence of the photoisomerization dynamics. In photoisomerization of the π-π^* excited *trans*-azobenzene, the lifetime of the n-π^* state strongly depends on the solvent viscosity; ~1 ps in hexane (0.26 cP) and ~12.5 ps in ethylene glycol (18.5 cP).[9] Similar solvent dependence of the lifetime of the n-π^* state has been observed in the photoisomerization of *trans*-BMAB.[11,13] On the other hand, in the photoisomerization of *trans*-4-AAB, such solvent dependence was not observed despite the relatively large difference of solvent viscosity between ethanol (1.17 cP) and heptanol (6.65 cP) (t_1 and t_2 in Table 1). In trans → cis photoisomerization of the π-π^* excited azobenzene derivatives, the reaction pathway after the decay of the π-π^* state may include both the rotation and the inversion process (Figure 5), although any contribution of the rotation process is smaller than that of the inversion process.[7−9] Then, we considered that the solvent dependence of the lifetime of the n-π^* state reflects the contribution of the rotation process to the photoisomerization. It is reasonable that the effect of the solvent viscosity is weaker on the inversion process than the rotation process because the change of the volume is smaller in the inversion process than that in the rotation process. For example, solvent viscosity has a strong effect on the rate of the photoisomerization of *trans*-stilbene, which proceeds with rotation.[19] Therefore the solvent independence of the transient absorption spectra of the π-π^* excited *trans*-4-AAB also supports the fact that the reaction pathway of the π-π^* excited *trans*-4-AAB is similar to that of the n-π^* excited *trans*-azobenzene, that is, the in-plane inversion process.

Finally, we should mention the recovery of the bleaching band at 370−410 nm. The ~15 ps recovery process of the bleaching band was attributed to the vibrational cooling process in the ground-state rather than the decay of a bottleneck state,[7,8] because the decay component with a lifetime of >10 ps was not observed in the transient absorption at >450 nm. In addition, the rate of the vibrational cooling in the ground electronic state was ~20 ps according to time-resolved infrared spectroscopy,[16] which was reasonably consistent with our result.

5. Summary

The photoisomerization dynamics of the π-π^* excited *trans*-4-AAB in ethanol and heptanol was investigated by using UV−vis transient absorption spectroscopy. The transient absorption spectra of the π-π^* excited *trans*-4-AAB showed that the internal conversion process from the n-π^* state to the ground state corresponded well to that of the *trans*-azobenzene *directly excited to the n-π^* state*, not to that of the π-π^* excited *trans*-azobenzene. This result suggested that the photoisomerization of π-π^* excited *trans*-4-AAB proceeded with different pathways from the π-π^* excited *trans*-azobenzene, at least for the decay process of the n-π^* state. The solvent independence of the lifetime of the n-π^* state of the π-π^* excited *trans*-4-AAB supported this proposal, because the lifetime of the n-π^* state strongly depends on solvent viscosity in photoisomerization of the π−π^* excited *trans*-azobenzene. Although past studies on the photoisomerization dynamics of azobenzene derivatives mainly focused on the excitation condition (π-π^* excitation or n-π^* excitation), our experimental results indicated that the potential energy gap between the π-π^* and the n-π^* state should be considered as an important factor determining the photoisomerization dynamics of the π-π^* excited azobenzene derivatives.

References and Notes

(1) Ikeda, T.; Tsutsumi, O. *Science* **1995**, *268*, 1873.

(2) Liu, Z. F.; Hashimoto, K.; Fujishima, A. *Nature* **1990**, *347*, 658.

(3) Rau, H. *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, 1990; Chapter 4.

(4) Rau, H. *J. Photochem.* **1984**, *26*, 221.

(5) Lednev, I. K.; Ye, T.-Q.; Abbott, L. C.; Hester, R. E.; Moore, J. N. *J. Phys. Chem. A* **1998**, *102*, 9161.

(6) Nägele, T.; Hoche, R.; Zinth, W.; Wachtveitl, J. *Chem. Phys. Lett.* **1997**, *272*, 489.

(7) Lednev, I. K.; Ye, T.-Q.; Matousek, P.; Towrie, M.; Foggi, P.; Neuwahl, F. V. R.; Umapathy, S.; Hester, R. E.; Moore, J. N. *Chem. Phys. Lett.* **1998**, *290*, 68.

(8) Lednev, I. K.; Ye, T.-Q.; Hester, R. E.; Moore, J. N. *J. Phys. Chem.* **1996**, *100*, 13338.

(9) Fujino, T.; Tahara, T. *J. Phys. Chem. A* **2000**, *104*, 4203.

(10) Wachtveitl, J.; Nägele, T.; Puell, B.; Zinth, W.; Krüger, M.; Rudolph-Böhner, S.; Oesterhelt, D.; Moroder, L. *J. Photochem. Photobiol., A* **1997**, *105*, 283.

(11) Azuma, J.; Tamai, N.; Shishido, A.; Ikeda, T. *Chem. Phys. Lett.* **1998**, *288*, 77.

(12) Mayer, S. G.; Thomsen, C. L.; Philpott, M. P.; Reid, P. J. *Chem. Phys. Lett.* **1999**, *314*, 246.

(13) Tamai, N.; Miyasaka, H. *Chem. Rev.* **2000**, *100*, 1875.

(14) Monti, S.; Orlandi, G.; Palmieri, P. *Chem. Phys.* **1982**, *71*, 87.

(15) Cattaneo, P.; Persico, M. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4739.

(16) Hamm, P.; Ohline, S. M.; Zinth, W. *J. Chem. Phys.* **1997**, *106*, 519.

(17) Terazima, M.; Takezaki, M.; Yamaguchi, S.; Hirota, N. *J. Chem. Phys.* **1998**, *109*, 603.

(18) Biswas, N.; Umapathy, S. *J. Chem. Phys.* **1997**, *107*, 7849.

(19) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415.