

15 May 1998

Chemical Physics Letters 288 (1998) 77-82

CHEMICAL PHYSICS LETTERS

Femtosecond dynamics and stimulated emission from the S_2 state of a liquid crystalline trans-azobenzene

Jun Azuma ^a, Naoto Tamai ^a, Atushi Shishido ^b, Tomiki Ikeda ^b

^a Department of Chemistry, School of Science, Kwansei Gakuin University, 1-1-155 Uegahara, Nishinomiya 662, Japan ^b Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuda, Midori-ku, Yokohama 226, Japan

Received 1 December 1997; in final form 9 February 1998

Abstract

The excited-state S_2 dynamics of an azobenzene derivative, trans-BMAB, was investigated in solution by femtosecond transient absorption and picosecond single-photon timing fluorescence spectroscopies. The fluorescence was observed at 400 nm with a lifetime ~ 250 fs. The S_1 state with an absorption maximum at 410–415 nm was formed with a time constant of ~ 250 fs from the S_2 state followed by relaxation with a lifetime of ~ 2.3 ps in *n*-hexane. The stimulated emission from the S_2 state overlapped with the femtosecond transient absorption spectra just after excitation, which was confirmed by polarization absorption spectroscopy. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Photochromic reactions of some organic molecules are of considerable interest because of their wide applications, including optical information processing, data storage and nonlinear optics [1,2]. The photochromism is based on simple photochemical reactions such as bond cleavage, pericyclic, proton transfer and isomerization reactions [1]. To understand the primary processes of photochromic reactions, we have recently examined spirooxazine [3], diarylethene derivatives [4,5] and salicylideneaniline [6] by femtosecond to picosecond transient absorption and picosecond fluorescence spectroscopies. These molecules undergo C-O bond cleavage, pericyclic, and proton transfer reactions, respectively, with time constants of a few hundred fs to 1 ps depending on the type of reactions.

On the other hand, azobenzene and its derivatives are representative photochromic compounds based

on the isomerization reaction. Thin polymer films, Langmuir-Blodgett films, and liquid crystals of azobenzene derivatives have been investigated as promising systems for various applications [7-9]. In these systems, the physicochemical properties such as absorption spectrum, dipole moment, refractive index, and molecular conformation can be reversibly changed through the trans-cis isomerization of azobenzene. In contrast to stilbene, in which the dynamics of isomerization seems to be well understood [10,11], the excited-state properties and the isomerization mechanism of azobenzene are still unclear. Furthermore, it appears that the isomerization mechanism is different from that of stilbene, as it depends on the excitation wavelength. For the $\pi - \pi *$ (S_2) excitation, a rotational mechanism has been proposed for the isomerization process, whereas the isomerization proceeds through an inversion pathway under the $n-\pi * (S_1)$ excitation [12].

A recent study of trans-azobenzene has indicated



Scheme 1.

that the isomerization pathway passes through an inversion mechanism based on an analysis of resonance Raman excitation profiles and theoretical calculations [13]. A transient absorption spectroscopic study has been carried out for trans-azobenzene in various solvents [14]. It was shown that under excitation to the S_2 state at 303 nm, the lifetime of the S_2 state is ~ 1 ps, being independent of the solvent polarity and/or dielectric constant. A long-lived component existing for 13-16 ps is also observed. which can be explained by the relaxation from the intermediate to the ground state of trans-azobenzene. The isomerization dynamics of cis-azobenzene excited to the S_1 state has also been examined by femtosecond transient absorption spectroscopy [15]. However, most of these experiments are based on the rise and decay dynamics observed at selected wavelengths, and time-dependent spectral data are still unclear.

In the present study, we have investigated the excited-state dynamics of a liquid crystalline transazobenzene (4-butyl-4'-methoxyazobenzene, abbreviated here as BMAB) (Scheme 1) in solution through the excitation to the S_2 state by femtosecond transient absorption and picosecond fluorescence spectroscopies. S_2 fluorescence and the stimulated emission from the S_2 state of trans-BMAB were observed in single-photon timing and transient absorption spectra, respectively. The femtosecond polarization dynamics of transient absorption was also examined. From these results, the relaxation dynamics of S_2 and S_1 states of trans-BMAB has been discussed.

2. Experimental

BMAB was synthesized and purified according to the literature [16,17]. The sample was dissolved in n-hexane (spectroscopic grade, Kishida Chemicals) and allowed to flow through a 2 mm flow cell using a magnetic gyre pump (Micropump, 040-332) during the measurements to avoid the excitation of the photoproduct (cis-form). The concentration of trans-BMAB was $\sim 2.0 \times 10^{-4}$ M for both transient absorption and fluorescence decay measurements.

The laser system for transient absorption spectroscopy consisted of a hybridly mode-locked, dispersion-compensated femtosecond dve laser (Coherent Satori 774) which was pumped by a cw modelocked Nd:YAG laser (Coherent Antares 76S) [3]. The output of the dve laser was amplified to an energy of ~ 400 μ J at a center wavelength of 720 nm by a regenerative amplifier system (Continuum RGA60 and PTA60) with a repetition rate of 10 Hz. The second harmonics (~ 360 nm) obtained by a 1 mm BBO crystal was used as an excitation pulse. A remaining fundamental pulse was focused into a 1 cm water cell to generate a white-light continuum as probe and reference pulses. The system response function of the pump-probe method was estimated to be ~ 200 fs fwhm. The signal was analyzed by a microcomputer-controlled ICCD detector (Princeton Instruments, ICCD-576-G) at each optical delay using a translation stage (Sigma Koki, STM-500X). A temporal dispersion of the white-light continuum was corrected for the transient absorption spectra.

The fluorescence spectrum and its decay curves were measured by picosecond single-photon timing spectroscopy by using the same dye laser without amplification. The repetition rate of the excitation pulse was reduced to 3.8 MHz with an external pulse picker (Conoptics, Model 360-80, 25D, and 305). The detection system was a combination of a microchannel-plate photomultiplier (Hamamatsu, MCP R2809U), a monochromator (Japan Spectroscopic, CT-10), a constant fraction discriminator (Tennelec, TC454), and a time-to-amplitude converter (Tennelec, TC864), which gave an instrument response function of \sim 30 ps fwhm. The spectral sensitivity of the system was not corrected. The rise and decay curves of transient absorption and fluorescence were analyzed by a non-linear least-squares iterative convolution method based on a Marquardt algorithm [18].

3. Results and discussion

3.1. Absorption spectra

Fig. 1 shows the absorption spectra of trans- and cis-BMAB in *n*-hexane. Cis-BMAB was obtained by the irradiation of trans-form at 350 nm with a 150 W Xe-lamp for 16 h. The intensity of the $\pi - \pi *$ absorption ($S_2 \leftarrow S_0$) at 345 nm in the trans-form is dramatically reduced and its peak wavelength is shifted to the shorter wavelength at 305 nm by the trans-to-cis isomerization. In addition, the intensity of the $n-\pi *$ absorption ($S_1 \leftarrow S_0$) with a peak at ~ 450 nm is enhanced by the formation of cis-BMAB. This result can be interpreted in terms of selection rules based on the symmetry differences of the cis- and trans-forms [1]. The current excitation wavelength at ~ 360 nm corresponds to the excitation to the S_2 state.

3.2. Fluorescence properties

The S_1 state of trans-BMAB is generally nonemitting because of the forbidden transition and isomerization reaction in the S_1 manifold [1]. Fig. 2a illustrates a fluorescence decay curve of trans-BMAB



Fig. 1. Absorption spectra of trans- and cis-BMAB in *n*-hexane. The concentration is 6.5×10^{-5} M.



Fig. 2. (a) Fluorescence decay curve of trans-BMAB (dot) in *n*-hexane excited at 360 nm and monitored at 410 nm along with the instrument response function (—— scat) and the simulation curve (smooth line). The decay curve was analyzed by the sum of a two-exponential function. The weighted residual is shown in the upper part, and the channel width of detection is 1.11 ps/channel. (b) Fluorescence spectrum of trans-BMAB obtained from the product of the total fluorescence intensity and the amplitude factor of the fast-decay component at its respective wavelength.

excited to the S_2 state ($\lambda_{ex} \sim 360$ nm) and observed at 410 nm along with the instrument response function (30 ps fwhm). It is clear that the fwhm of the fluorescence decay curve is almost the same as the system response function, indicating the extremely short fluorescence lifetime. The decay curve was analyzed as a first approximation by a sum of two exponentials. The fast decay component has a lifetime shorter than 2 ps and its amplitude factor is larger than 0.997, originating from the S_2 state of trans-BMAB as shown later. The long decay component with a lifetime of 1.0 ns is probably due to an impurity.

The product of the total intensity and an amplitude factor of the fast component at respective wavelength is plotted as a function of wavelength. The fluorescence spectrum has a peak at ~ 400 nm, as is clearly shown in Fig. 2b. This can probably be assigned to the fluorescence from the S_2 state of trans-BMAB for the following reasons. For the S₂ fluorescence of azobenzene, Morgante and Struve have reported a lifetime of ~ 5 ps by using a picosecond Nd:glass laser and the optical Kerr gate method [19], although they have not reported the fluorescence spectrum. The fluorescence spectrum from the S_2 state of trans-azobenzene and its quantum yield were examined by Hamai and Hirayama, who reported that the fluorescence spectrum of trans-azobenzene has a maximum at 385 nm with $\Phi_{\rm f}$ ~ 1.7×10^{-5} and maximum at ~ 410 nm with $\Phi_{\rm f}$ ~ 0.9×10^{-5} for 1-methoxy azobenzene [20]. They have also estimated the S₂ lifetime of trans-azobenzene to be ~ 60 fs by using the Strickler-Berg equation. Our experimental data showing a fluorescence maximum of ~ 400 nm and a lifetime shorter than 2 ps are in good agreement with the reported values of the S2 fluorescence of trans-azobenzene and its derivative.

3.3. Transient absorption spectra

To analyze the ultrafast dynamics of trans-BMAB in the excited S_2 state, the transient absorption spectra in *n*-hexane were measured with the excitation at 360 nm as illustrated in Fig. 3. The spectrum just after the excitation has a peak at ~ 490 nm and very broad absorption in the longer wavelength region. As clearly indicated in the figure, the very rapid decay with a time constant shorter than 0.5 ps was observed at wavelength longer than ~ 600 nm and at \sim 490 nm. No rise component was detected at these bands, indicating that the spectrum just after the excitation is probably due to the $S_n \leftarrow S_2$ absorption of trans-BMAB. In addition, a broad flat part at the onset of the transient absorption ranging from 390 to 470 nm region was clearly observed just after the excitation. As discussed later, this is originated from the stimulated emission of the $S_2 \rightarrow S_0$ fluorescence.

After the disappearance of the $S_n \leftarrow S_2$ absorption bands, a new and intense absorption band appears at shorter wavelength region. The spectrum at a delay



Fig. 3. (a) A bird's-eye view of the transient absorption spectra of trans-BMAB in *n*-hexane excited at 360 nm (S_2 excitation) and probed with the white-light continuum at the magic angle condition. The spectra are illustrated up to 3 ps after excitation. (b) The transient absorption spectra of trans-BMAB in *n*-hexane at selected time windows after the excitation.

time longer than 0.3 ps has a peak at \sim 415 nm and a shoulder at \sim 550 nm. It has been reported by Lednev et al. that the transient absorption spectrum of trans-azobenzene in *n*-hexane appears in the range

from 370 to 450 nm and has a peak at 390 nm [14]. This spectrum was obtained at 0.47 ps after the excitation, and the main decay component was 0.9 +0.2 ps. They assigned this spectrum as the absorption from the S_2 state of trans-azobenzene. The spectral shape of transient absorption with a maximum at 410-415 nm observed in our study is similar to that observed by Ledney et al. The peak wavelength is shifted to the red with an energy of ~ 1500 cm⁻¹. which probably originates from the substitution of azobenzene in the 4- and 4'-positions. The main difference is the rise dynamics of this absorption band. The transient absorption spectrum at 410-415 nm is observed after the disappearance of $S_n \leftarrow S_2$ absorption at ~490 nm, although the stimulated emission from the S_2 state is overlapped in this wavelength region. In addition, the decay time of the spectrum at 410-415 nm is strongly dependent on the solvent viscosity, and has a lifetime of ~ 10 ps in ethylene glycol [21]. From these results, we assigned the absorption spectrum with a maximum at 410–415 nm to the $S_n \leftarrow S_1$ absorption of trans-BMAB. The peak wavelength of this band shifts a little to the blue (~ 410 nm) with increasing the delay time. This may be attributed to the intramolecular vibrational redistribution in the S_1 state [21].

Furthermore, this absorption band disappears completely within 10 ps, and a very weak absorption spectrum with a maximum at ~ 450 and ~ 600 nm can be observed within 20 ps, as indicated in Fig. 3b although the signal to the noise ratio is rather bad. This broad absorption spectrum remains up to 3 ns (limit of our experiments). The absorption band at ~ 450 nm corresponds to the difference spectrum of $n-\pi *$ absorption in the ground state of cis- and trans-BMAB. This result indicates that the trans-cis isomerization of azobenzene is completed within 10 ps in *n*-hexane. The absorption spectrum at ~ 600 nm probably originates from the $T_n \leftarrow T_1$ absorption of BMAB [21].

3.4. Polarization absorption dynamics

To confirm the stimulated emission in the shorter wavelength region and to analyze the excited-state dynamics of trans-BMAB, the polarization dynamics of transient absorption at 410 and 650 nm were examined, as illustrated in Fig. 4. It should be noted



Fig. 4. Polarization decay curves of transient absorption observed at 410 nm (a) and 650 nm (b). Polarization of the probe pulse was set parallel and perpendicular with respect to the pump polarization. Smooth lines in (a) and (b) are the simulation curves for perpendicular and parallel polarization decays, respectively, by a convolution of the pulse width and a two-exponential decay function. The weighted residuals for the simulation of 410 nm decay are shown in the upper part. The data were taken every 16.7 fs/channel.

that the rising parts of the parallel and perpendicular components were clearly different from each other at 410 nm, but no difference was observed at 650 nm. The parallel component at 410 nm is delayed for 200–300 fs, as compared to the perpendicular component. This provides clear evidence that negative absorption overlaps with the transient absorption of the parallel component at 410 nm. One of the most probable negative absorption is due to the stimulated emission from the S₂ state. Although the quantum yield of the S₂ fluorescence of trans-BMAB is on the order of 10^{-5} , the probability of the stimulated emission is determined by Einstein's *B* factor and therefore by the transition dipole moment of the $S_2 \leftarrow S_0$ absorption. We conclude, from the result of transient absorption spectra as shown in Fig. 3 and the polarization decay curves in Fig. 4a, that the stimulated emission from the S_2 state of trans-BMAB is observed in the transient absorption spectra just after the excitation.

The polarization decay curves of 410 and 650 nm were analyzed by a two-exponential decay function. The rise time of ~ 250 fs was observed at 410 nm with a decay time of 2.3 ps, whereas no rise component was detected at 650 nm. The decay time at 650 nm was ~ 250 fs, corresponding to the rise time at 410 nm. This time constant is not due to the rotational relaxation but the intramolecular process of trans-BMAB in *n*-hexane, since the rotational relaxation is much slower than this time constant. From these results, it can be concluded that transient absorption at the longer wavelength region (< 600 nm) is due to the $S_n \leftarrow S_2$ absorption of trans-BMAB, and the S₁ state of trans-BMAB with an absorption maximum at 410-415 nm is formed with a time constant of ~ 250 fs. The lifetime of the S_1 state is ~ 2.3 ps in *n*-hexane.

In conclusion, the femtosecond dynamics of azobenzene derivative, trans-BMAB, was investigated in *n*-hexane solution by femtosecond transient absorption and picosecond fluorescence spectroscopies under excitation to the S_2 state. It was found that the fluorescence spectrum from the S_2 state is observed at 400 nm. The lifetime of the S_2 state was estimated to be ~ 250 fs by femtosecond transient absorption spectroscopy. In addition, the S_1 state of trans-BMAB with an absorption maximum at 410–415 nm is formed with a time constant of ~ 250 fs from the S_2 state overlaps to the femtosecond transient absorption spectra just after the excitation. The isomer-

ization of trans-BMAB is completed within 10 ps. Further investigation of the solvent dependence on the isomerization dynamics of trans-BMAB is now in progress.

References

- H. Dürr, H. Bouas-Lauran (Eds.), Photochromism Molecules and Systems, Elsevier, Amsterdam, 1990.
- [2] P.J. Martin, in: M.C. Pett, M.R. Bryce, D. Bloor (Eds.), Introduction to Molecular Electronics, Edward Arnold, London, 1995, p.112.
- [3] N. Tamai, H. Masuhara, Chem. Phys. Lett. 191 (1992) 189.
- [4] N. Tamai, T. Saika, T. Shimidzu, M. Irie, J. Phys. Chem. 100 (1996) 4689.
- [5] H. Miyasaka, T. Nobuto, A. Itaya, N. Tamai, M. Irie, Chem. Phys. Lett. 269 (1997) 281.
- [6] S. Mitra, N. Tamai, Chem. Phys. Lett. 282 (1998) 391.
- [7] T. Ikeda, O. Tsutsumi, Science 268 (1995) 1837.
- [8] Z.F. Liu, A. Fujishima, K. Hashimoto, Nature 347 (1990) 658.
- [9] P.M. Blanchard, G.R. Mitchell, Appl. Phys. Lett. 63 (1993) 2038.
- [10] R.J. Sension, S.T. Repinec, A.Z. Szarka, R.M. Hochstrasser, J. Chem. Phys. 98 (1993) 6291, and references cited therein.
- [11] H. Petek, in: Y. Taniguchi, M. Irie, K. Ichimura, Y. Yokoyama, J. Hibino (Eds.), Chemistry of Organic Photochromism, Chem. Soc. Jpn., Tokyo, 1996, p.25.
- [12] H. Rau, in: H. Dürr, H. Bouas-Lauran (Eds.), Photochromism — Molecules and Systems, Elsevier, Amsterdam, 1990, p.165.
- [13] N. Biswas, S. Umapathy, Chem. Phys. Lett. 236 (1995) 24.
- [14] I.K. Lednev, T-Q. Ye, R.E. Hester, J.N. Moore, J. Phys. Chem. 100 (1996) 13338.
- [15] T. Nägele, R. Hoche, W. Zinth, J. Wachtveitl, Chem. Phys. Lett. 272 (1997) 489.
- [16] S. Tazuke, S. Kurihara, T. Ikeda, Chem. Lett. (1987) 911.
- [17] C. Weygand, R. Gabler, J. Prakt. Chem. 155 (1940) 322.
- [18] P.R. Bevington, Data Reduction and Error Analysis for the Physical Sciences, McGraw-Hill, New York, 1969.
- [19] C.G. Morgante, W.S. Struve, Chem. Phys. Lett. 68 (1979) 267.
- [20] S. Hamai, F. Hirayama, Annual Symposium on Photochemistry (Japan) (1984) 315.
- [21] N. Tamai, J. Azuma, A. Shishido, T. Ikeda, to be published.