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Evidence of concerted inversion for the photon-induced molecular switching of azobenzene using rotation-free azobenzene derivatives

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The excited state relaxation of two types of azobenzene derivative excited at 350 nm in the short-wavelength ($S_2(\pi, \pi^*)$) band was studied by transient absorption spectroscopy. We compared the relaxation dynamics and the time-resolved anisotropic relaxation properties of these two molecules in liquid solution and in bulk film. The average relaxation life-time for Azo-2 in bulk film (13.2 ps) is much slower than that of Azo-2 (4.06 ps) and Azo-1(1.31 ps) in liquid solution. The time-resolved polarization anisotropy spectroscopy measurements of these samples also showed significant differences. The value of anisotropy for Azo-2 remained almost constant at about 0.2 in bulk film but decayed slowly from 0.3 in liquid solution. The value for Azo-1 in liquid solution decayed very fast from 0.4 to 0.2 within 6 ps. Our results gave new evidence for the existence of a converted inversion channel. We also concluded that the concerted inversion process and the conventional rotation process govern the relaxation for the photon-induced switches of azobenzene and its derivatives under short-wavelength band excitation.

Introduction

As the prototype molecule of photoisomerization, azobenzene and its derivatives have been the subject of many studies, not only for their photon-induced switch properties, one of the most fundamental photochemical reactions, but also for their potential applications in optical image storage systems[1,2] and laser-triggered switching.[3–5] The properties of azobenzene and its derivatives have been extensively investigated by UV-visible steady-state absorption spectroscopy,[6–8] Raman spectroscopy,[9,10] NMR[11] and theoretical calculations.[12–16] However, the mechanism of azobenzene photoisomerization is still not fully understood.

A hypothesis has been proposed,[17] that azobenzene undergoes two different isomerization processes depending on the excitation wavelength: the isomerization occurs *via* inversion around one nitrogen atom in the same molecular plane (the inversion mechanism), with visible $S_1(n, \pi^*) \leftarrow S_0$ excitation, whereas UV excitation of the $S_2(\pi, \pi^*)$ state leads to isomerization *via* rotation around the N=N double bond (the rotation mechanism). Rau and Lueddecke studied the direct *cis–trans*-photoisomerization reaction of two azobenzenophanes.[6] In these two molecules, planar inversion is free and rotation is blocked. They measured the steady state absorption spectrum of the solutions in photoreactions and dark reactions. Their results gave an experimental proof of the inversion. Femtosecond time-resolved UV-visible absorption spectroscopy technology has also been used to study *trans*- or *cis*-azobenzene[18–20] and an azobenzene-capped derivative.[21] The experimental data gave evidences to support the rotation–inversion double-channel mechanism.

However, the idea of the rotation–inversion double-channel mechanism was challenged by Fujino *et al.* who performed the experiments by picosecond time-resolved Raman and femtosecond time-resolved fluorescence setups using *trans*-azobenzene after $S_2(\pi, \pi^*)$ excitation.[22,23] Their Raman experiments found that in the $S_1(n, \pi^*)$ state, the N–N bond has a double bond nature, which is highly similar to that of the S_0 state. This indicated that the observed $S_1(n, \pi^*)$ state has a planar structure around the N=N double bond. In the case of the fluorescence studies, the results showed that the quantum yield of the $S_2(\pi, \pi^*) \leftarrow S_1(n, \pi^*)$ relaxation is almost unity, which implies that almost all molecules which are excited to $S_2(\pi, \pi^*)$ state relax to the $S_1(n, \pi^*)$ state. Thus they concluded that the isomerization of azobenzene occurs in the $S_1(n, \pi^*)$ state *via* an inversion channel in the cases of $S_2(\pi, \pi^*)$ and $S_1(n, \pi^*)$ excitation. Although there are some indirect experimental evidences to support this mechanism, the only-inversion channel could not explain the fact that the quantum yield under S_2 excitation is lower than that under S_1 excitation.[24]

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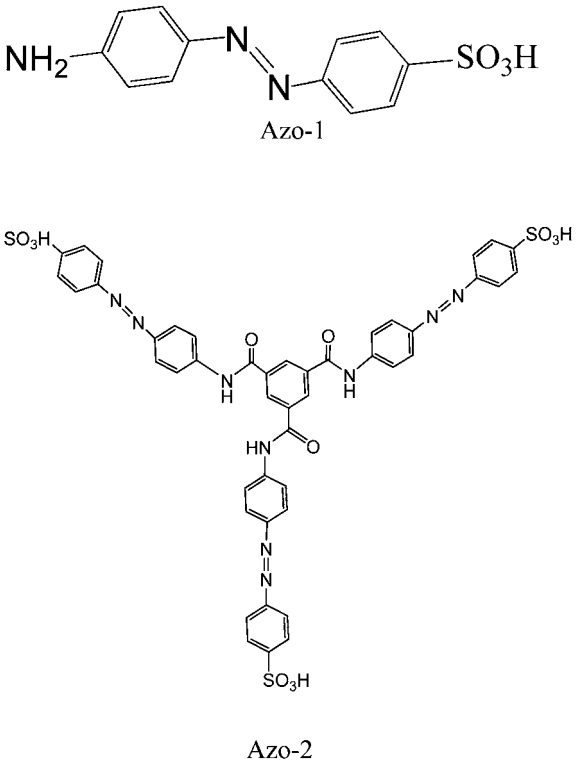
Later, a new *trans*-to-*cis*-isomerization mechanism was proposed on the basis of Diau's calculations.[25] According to the calculation results, the rotational reaction channel is a favorable electronic relaxation channel from the $S_1(n, \pi^*)$ state, forming both the *trans*-S_0 and the *cis*-S_0 states. On the other hand, the widely accepted inversion channel was excluded because the energy gap was too large, and would not allow efficient electronic relaxation to occur. Additionally, because a hot $S_1(n, \pi^*)$ species is produced by $S_2(\pi, \pi^*)$ excitation, a new relaxation channel (concerted inversion) could open *via* the converted CNN bending reaction, giving either a trans isomer or some bond-breaking products. A converted inversion means that the single-bound C–NN and NN–C invert simultaneously. These conclusions may explain why the quantum yields of $S_2(\pi, \pi^*)$ excitation are much lower than those of $S_1(n, \pi^*)$ excitation,[24] but there are few experimental evidences to explain the reason.[26–29]

In the present paper, we study the photoisomerization of two rotation-free azobenzene derivatives in liquid solution and in bulk film by femtosecond transient absorption spectroscopy. We performed the experiments using magic-angle, perpendicular and parallel geometries of pump and probe beams. Thus, we could investigate the relaxation dynamics of the derivatives' transient absorption intensities and the decay processes of the polarization anisotropy properties. Our work gives new support for the existence of a concerted inversion channel under short-wavelength ($S_2(\pi, \pi^*)$) band excitation conditions, which represents a step towards the full understanding of the photoisomerization mechanics of azobenzene and optical devices based on azobenzene.

Experiments

Scheme 1 shows the molecular structures of the two azobenzene derivatives used in our experiments. Azo-1 in Scheme 1 is 4′-aminoazobenzene-4-sulphonic acid (CAS: 104-23-4) and Azo-2 is synthesized by the procedure described in our previous work.[30,31] The solvent for the liquid solutions of Azo-1 and Azo-2 was ultrapure water and the concentrations of Azo-1 and Azo-2 were 0.05 mg mL^{-1} and 0.5 mg mL^{-1}, respectively. The quartz substrate was hydrophilized by being immersed in a mixture solution of ultrapure water, ammonia (37%) and hydrogen peroxide (volume ratio 5 : 1 : 1) for 10 h, and then cleaned with ultrapure water. The Azo-2 bulk film was prepared by spin-coating the liquid solution onto the as-prepared quartz substrate. For the Azo-1 liquid solution, both the rotation and inversion channels are free. In the case of the Azo-2 liquid solution, the rotation channel is free, but one side of the inversion channel is significantly restricted because of the molecular structure. For the Azo-2 bulk film, the rotation and inversion channels are both restricted.

The steady state absorption spectra were measured by a Shimadzu UV-2550 spectrophotometer. The transient absorption measurements were performed using the pump-probe setup described in our previous publications.[32,33] Briefly, the output of a Ti:Sapphire laser (Tsunami, Spectra Physics) pumped by an Nd:YVO laser (Millennia, Spectra Physics) was amplified by a regenerative amplifier (RGA, Spitfire, Spectra Physics), by which, 150 fs-width laser pulses centered at 800 nm with a repetition rate of 250 Hz were generated. The 350 nm pump pulses were generated though an optical parametric amplifier (OPA-800C, Spectra Physics), whereas the probe pulses were white-light continuum pulses generated by focusing the 800 nm beam into a 5 mm-thick sapphire plate. The transient absorption data were collected by a highly sensitive fiber-coupled spectrometer (Avantes AvaSpec-2048x14) connected to a computer. The group velocity dispersion of the experimental data was compensated by a chirp program. The polarization of the pump pulses was controlled by a half-wave plate corresponding to the pump wavelength. All of the measurements were performed at room temperature.



Scheme 1 Molecular structures of Azo-1 and Azo-2.

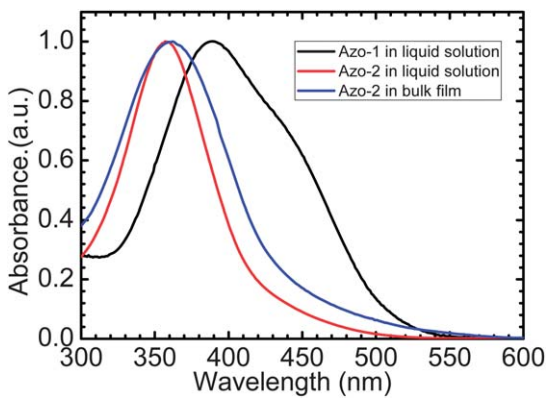


Fig. 1 Steady-state absorption spectra of Azo-1 in liquid solution (black line), Azo-2 in liquid solution (red line) and Azo-2 in bulk film (blue line).

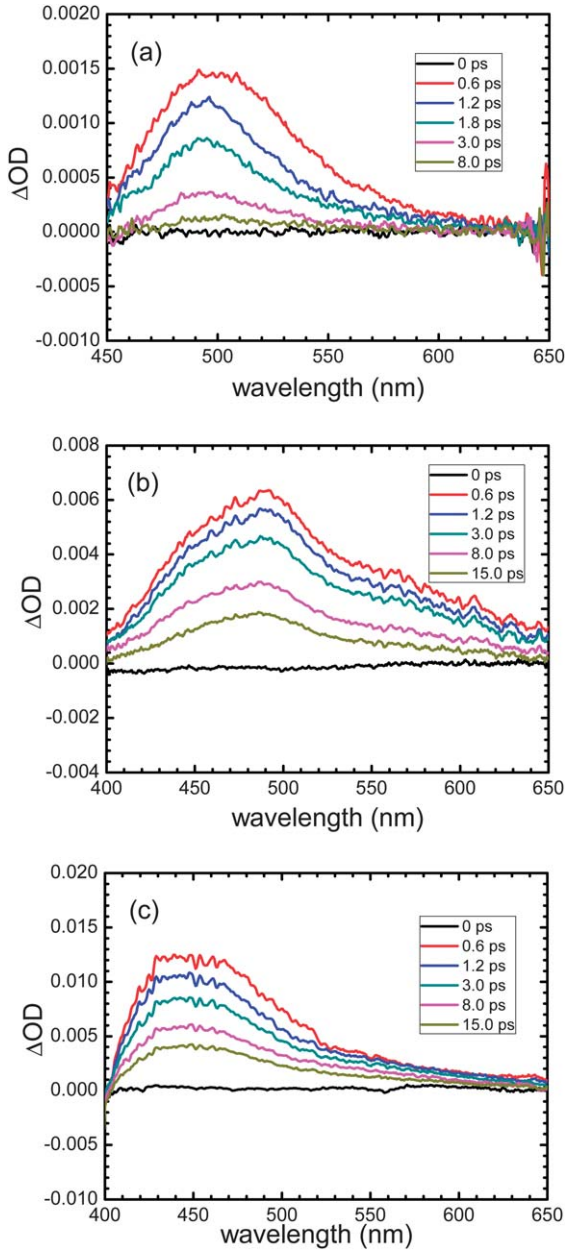


Fig. 2 Time-resolved transient absorption spectra for (a) Azo-1 in liquid solution, (b) Azo-2 in liquid solution and (c) Azo-2 in bulk film.

Results and discussion

Steady-state absorption

The normalized steady-state UV-visible absorption spectra of Azo-1 and Azo-2 in liquid solution and Azo-2 in bulk film on a quartz substrate are shown in Fig. 1. Azo-1 in liquid solution has a strong absorption band peaking at 389 nm which is attributed to $S_2(\pi, \pi^*)$ excitation, and a weaker $S_1(n, \pi^*) \leftarrow S_0$ transition band peaking at around 440 nm which is overlapped by the strong $S_2(\pi, \pi^*)$ band. Compared to the azobenzene, the $S_2(\pi, \pi^*)$ band of Azo-1 shifts to the red region because of the disubstitution with electron-donating and electron-accepting groups in the 4 and 4′ positions, respectively (push/pull substitution pattern). The spectrum of the Azo-2 liquid solution shows a strong $S_2(\pi, \pi^*)$ transition band peaking at 358 nm, whereas the $S_1(n, \pi^*) \leftarrow S_0$ transition band becomes much weaker than Azo-1. In the case of Azo-2 in bulk film, the transition band broadens a little, and the peak shifts to around 361 nm because of the aggregation. No emission is observed for any of the azobenzene derivatives using a conventional steady-state spectrofluorometer, because their fluorescence quantum yields are extremely low.

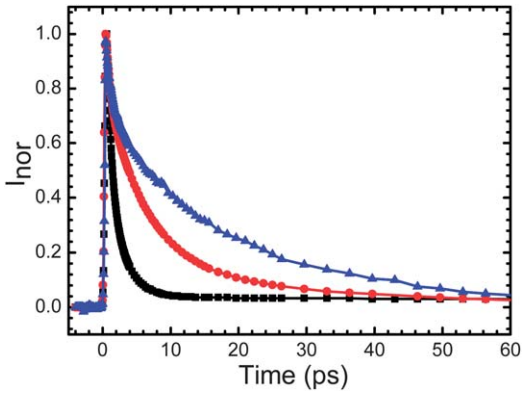


Fig. 3 Normalized transient absorption dynamics for Azo-1 in liquid solution at 500 nm (black squares), Azo-2 in liquid solution at 490 nm (red circles) and Azo-2 in bulk film at 450 nm (blue triangles). The solid lines are fitted profiles.

Table 1 Transient absorption decay times and relative amplitudes

Sample	τ_1 (ps)	A_1%	τ_2 (ps)	A_2%
Azo-1 in solution	0.65	59%	2.26	41%
Azo-2 in solution	0.54	34%	5.87	66%
Azo-2 in bulk film	0.97	32%	18.9	68%

Transient absorption spectroscopy under magic-angle conditions

Fig. 2 shows the transient absorption spectra measured with the pump and probe beams polarized at the magic angle. The 350 nm excitation pulses were chosen, which excited the molecules in the $S_2(\pi, \pi^*) \leftarrow S_0$ absorption bands. The spectra show the excited state absorption signatures peaking at 500 nm, 490 nm and 450 nm for Azo-1 in liquid solution, Azo-2 in liquid solution and Azo-2 in bulk film on a quartz substrate, respectively. The difference in the excited state absorption peaks of Azo-1 and Azo-2 in liquid solution might be due to the difference in their molecular structures. Additionally, the difference between Azo-2 in liquid solution and in bulk film results from the molecular aggregation.

Fig. 3 shows the kinetics for the three samples at the corresponding peak wavelengths. Comparing the kinetics at different wavelengths for the same sample, we could not find any detectable differences. Table 1 reports the decay times and relative amplitudes in detail. As can be clearly seen, the observed biexponential decay kinetics for all of these samples are governed by two genuine dynamical processes. However, the relaxation of

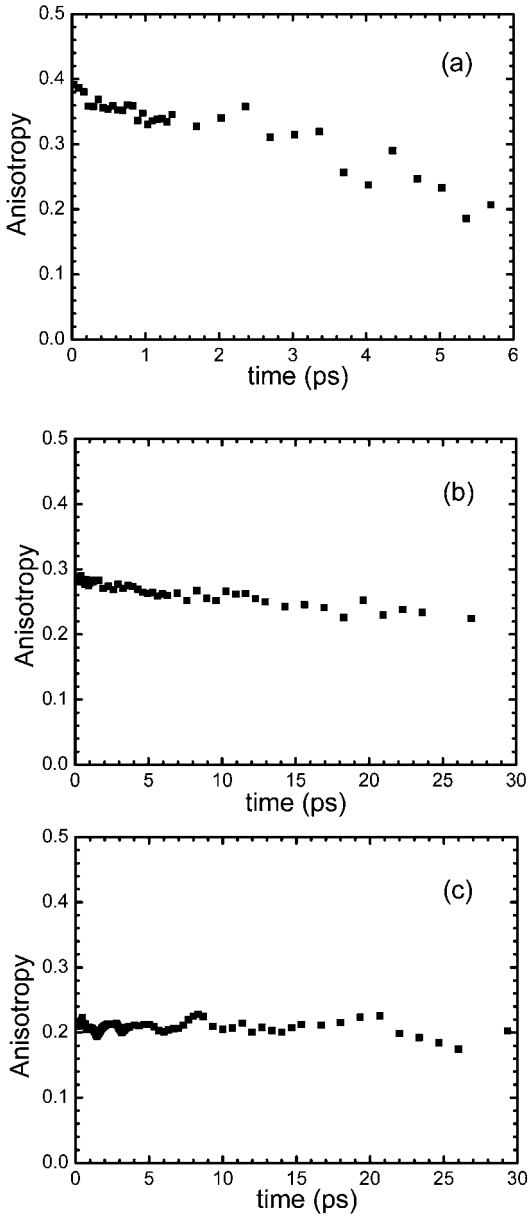


Fig. 4 Time-dependent polarization anisotropy for (a) Azo-1 in liquid solution, (b) Azo-2 in liquid solution and (c) Azo-2 in bulk film.

Azo-1 in liquid solution ($\tau_1 = 0.65$ ps, $\tau_2 = 2.26$ ps) is much faster than that of Azo-2 both in liquid solution ($\tau_1 = 0.54$ ps, $\tau_2 = 5.87$ ps) and in bulk film ($\tau_1 = 0.97$ ps, $\tau_2 = 18.9$ ps). According to the time-resolved fluorescence study,[23] the quantum yield of the $S_2(\pi, \pi^*) \rightarrow S_1(n, \pi^*)$ transition is almost unity. In our experiment, we did not measure the $S_2(\pi, \pi^*) \rightarrow S_1(n, \pi^*)$ relaxation process, because the ~110 fs time scale process is beyond the resolution of our setup. The excited absorption signatures shown in Fig. 2 are assigned to $S_1 \rightarrow S_n$ absorption. Our results are also coincident with the previous reports regarding the $S_2(\pi, \pi^*)$ excitation band.[26,34,35] The fast initial relaxation processes τ_1 (within ~1 ps) are attributed to the fast motion of the wavepackets on the S_1 potential energy surface towards the conical intersections with the S_0 potential energy surface, whereas the slow relaxation times τ_2 are attributed to the transition to the ground state S_0 *via* the conical intersections. Because of the low quantum yield of the *trans–cis*-isomerization under $S_2(\pi, \pi^*)$ excitation,[25] the relaxation process back to the *trans*-S_0 state affects the transient absorption spectra significantly. Meanwhile, the kinetic traces do not decrease to zero (Fig. 3). This gives evidence for the existence of *cis*-Azo, and the *cis*-to-*trans* process takes a very long time without photo-excitation at room temperature.[36] These results coincide with the fluorescence dynamic study of a rotation-restricted azobenzene after $S_1(n, \pi^*)$ excitation.[28] Considering the fast initial decay τ_1 of these samples, there is no significant difference between Azo-1 and Azo-2 in liquid solution. That indicates that the motion processes of the excited wavepackets on the S_1 potential energy surface to the conical intersections are almost the same in the Azo-1 and Azo-2 liquid solutions. In the case of Azo-2 in bulk film, this process might be a little slower because of the change of the environment. Compared with the fast initial decay, the slow components of the relaxation processes for the three samples show significantly different decay lifetimes. To understand the significantly different relaxation dynamics of these samples, we must look back to the molecular structures of these azobenzene derivatives. As can be seen from the C_3 symmetric structure of the Azo-2 molecule, in each of the three branches, one nitrogen atom is connected to the huge molecular structure, which could restrict the inversion around that atom, but the inversion around the other nitrogen atom is free. This means that in liquid solution for both Azo-1 and 2, the widely accepted one-side inversion channel is free. In both the Azo-1 and Azo-2 liquid solutions, rotation around the N=N double bound is also free. Since the rotation channel and the one-side inversion channel are free, there must be another pathway which affects the photoisomerization of the two azobenzene derivatives, otherwise the significant difference in τ_2 between Azo-1 and Azo-2 in liquid solutions would be unreasonable. Meanwhile, the rotation and inversion are both restricted in the Azo-2 bulk film, but the relaxation process does not change very much compared to that of its liquid solution (Fig. 3). That means that the restriction of the one-side inversion channel affects the relaxation process significantly. Only the "concerted inversion" pathway, where both angles for the single bound C–NN and NN–C change simultaneously, could explain the observed phenomenon.

Time-dependent polarization anisotropy

In order to verify the above experimental results and the idea of the "concerted inversion" mechanism, we performed the transient absorption experiments with relative parallel and perpendicular polarizations of the pump and probe beams. The value of the polarization anisotropy $r(t)$ for the transient absorption was calculated according to the relation:

$$r(t) = \frac{r_{\text{parallel}}(t) - r_{\text{perpendicular}}(t)}{r_{\text{parallel}}(t) + 2r_{\text{perpendicular}}(t)}. \quad (1)$$

As shown in Fig. 4, in the case of the Azo-1 liquid solution (Fig. 4a), the decay of the anisotropy is very fast, from 0.4 to 0.2

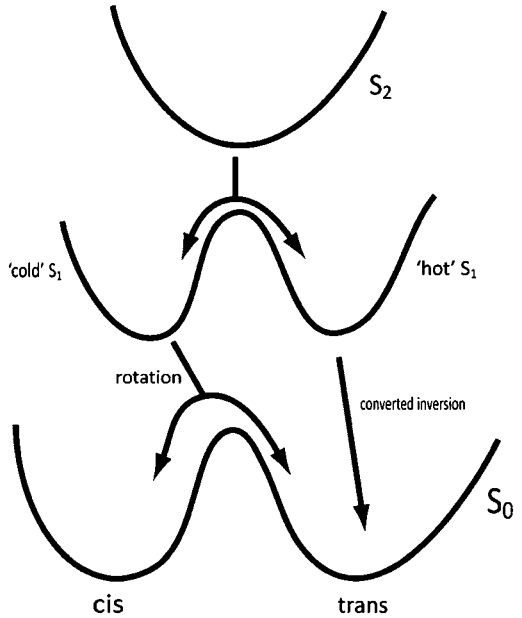


Fig. 5 Schematic representation of the excited state dynamic pathways for isomerization under S_2 excitation.

within 6 ps. The value of the anisotropy at zero delay time, $r(0)$, is nearly 0.4, indicating that the orientation of the dipole moments between excitation and relaxation are nearly parallel at $t = 0$. Compared with the Azo-1 liquid solution, the anisotropy value of the Azo-2 liquid solution (Fig. 4b) decays much slower, starting from 0.29, and in the case of the Azo-2 bulk film on a quartz substrate, the anisotropy value remains almost constant at around 0.2 (Fig. 4c). These results give strong support to the idea of a concerted inversion pathway. The 350 nm pump wavelength corresponding to the higher $S_2(\pi, \pi^*)$ excitation in our experiment acts as the important key to producing a "hot" $S_1(n, \pi^*)$ species, which would open the concerted inversion channel where the C–NN and NN–C angles change simultaneously.[25] A hot S_1 species can open a new relaxation channel through the concerted CNN bending motion. In the case of Azo-2 in liquid solution, because the concerted inversion channel is restricted, the decay of relaxation and anisotropy slows down significantly, compared with the Azo-1 liquid solution where the concerted inversion is free. For the Azo-2 bulk film, the rotation and the converted inversion are almost totally restricted because of the aggregation, so the anisotropy hardly changes during the photon-induced switching process.

Our results are well-justified according to the proposed mechanism[25] and the reported results.[29] Fig. 5 shows the excited state dynamic pathways under the higher $S_2(\pi, \pi^*)$ excitation. In these conditions, the extremely fast $S_2(\pi, \pi^*) \rightarrow S_1(n, \pi^*)$ relaxation process takes the excited wavepacket to the $S_1(n, \pi^*)$ state. Meanwhile, the hot S_1 species is produced. The converted inversion channel opens to produce some *trans*-azo and other side products. The molecular structure of Azo-2 obstructs the converted inversion, so the relaxation lifetime of Azo-2 in liquid solution becomes much slower than that of Azo-1 in liquid solution. On the other hand, the conventional rotation is also located on the midpoint of the rotational pathway because of the existence of the cold $S_1(n, \pi^*)$ species.[25] This could explain why the relaxation process of Azo-2 in the condensed phase, where the rotation channel is blocked, is slower than that in the liquid phase.

Conclusion

In summary, we studied two rotation-free azobenzene derivatives by transient relaxation and time-dependent polarization anisotropy measurements using the pump-probe setup under S_2 excitation. The observed biexponential decay kinetics is governed by two dynamical processes. The very fast decay lifetime is assigned to the initial direct relaxation on the S_1 potential energy surface and the slow decay component is attributed to the relaxation from the S_1 state to the S_0 state. The significant differences in the anisotropy relaxation properties for these samples strongly supports the existence of converted inversion. Our results also indicate that photoisomerization under S_2 excitation is governed by two channels: one is the conventional rotation channel *via* the cold S_1 species, and the other is converted inversion *via* the hot S_1 species.

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Notes and references

1 Z. F. Liu, K. Hashimoto and A. Fujishima, *Nature*, 1990, **347**, 658.
2 T. Ikeda and O. Tsutsumi, *Science*, 1995, **268**, 1873.
3 L. Ulysse, J. Cubillos and J. Chmielewski, *J. Am. Chem. Soc.*, 1995, **117**, 8466.
4 I. Willner and S. Rubin, *Angew. Chem., Int. Ed.*, 1996, **35**, 367.
5 T. Hugel, N. B. Holland, A. Cattani, L. Moroder, M. Seitz and H. E. Gaub, *Science*, 2002, **296**, 1103.
6 H. Rau and E. Lueddecke, *J. Am. Chem. Soc.*, 1982, **104**, 1616.
7 H. Rau, *J. Photochem.*, 1984, **26**, 221.
8 N. Siampiringue, G. Guyot, S. Monti and P. Bortolus, *J. Photochem.*, 1987, **37**, 185.
9 H. Okamoto, H.-o. Hamaguchi and M. Tasumi, *Chem. Phys. Lett.*, 1986, **130**, 185.
10 N. Biswas and S. Umapathy, *Chem. Phys. Lett.*, 1995, **236**, 24.
11 R. D. Curtis, J. W. Hilborn, G. Wu, M. D. Lumsden, R. E. Wasylishen and J. A. Pincock, *J. Phys. Chem.*, 1993, **97**, 1856.
12 P. Cattaneo and M. Persico, *Phys. Chem. Chem. Phys.*, 1999, **1**, 4739.
13 T. Ishikawa, T. Noro and T. Shoda, *J. Chem. Phys.*, 2001, **115**, 7503.
14 T. Ikegami, N. Kurita, H. Sekino and Y. Ishikawa, *J. Phys. Chem. A*, 2003, **107**, 4555.

15 A. Cembran, F. Bernardi, M. Garavelli, L. Gagliardi and G. Orlandi, *J. Am. Chem. Soc.*, 2004, **126**, 3234.
16 H. Fliegl, A. Kohn, C. Hattig and R. Ahlrichs, *J. Am. Chem. Soc.*, 2003, **125**, 9821.
17 H. Dürr and H. Bouas-Laurent, *Photochromism: Molecules and Systems*, ELSEVIER, Amsterdam, 2003.
18 I. K. Lednev, T.-Q. Ye, R. E. Hester and J. N. Moore, *J. Phys. Chem.*, 1996, **100**, 13338.
19 I. Lednev, T. Ye, P. Matousek, M. Towrie, P. Foggi, F. Neuwahl, S. Umapathy, R. Hester and J. Moore, *Chem. Phys. Lett.*, 1998, **290**, 68.
20 T. Nägele, R. Hoche, W. Zinth and J. Wachtveitl, *Chem. Phys. Lett.*, 1997, **272**, 489.
21 I. K. Lednev, T.-Q. Ye, L. C. Abbott, R. E. Hester and J. N. Moore, *J. Phys. Chem. A*, 1998, **102**, 9161.
22 T. Fujino and T. Tahara, *J. Phys. Chem. A*, 2000, **104**, 4203.
23 T. Fujino, S. Arzhantsev and T. Tahara, *J. Phys. Chem. A*, 2001, **105**, 8123.
24 P. Bortolus and S. Monti, *J. Phys. Chem.*, 1979, **83**, 648.
25 E. W. G. Diau, *J. Phys. Chem. A*, 2004, **108**, 950.
26 C. W. Chang, Y. C. Lu, T. T. Wang and E. W. G. Diau, *J. Am. Chem. Soc.*, 2004, **126**, 10109.
27 Y. C. Lu, E. W. G. Diau and H. Rau, *J. Phys. Chem. A*, 2005, **109**, 2090.
28 T. Pancur, F. Renth, F. Temps, B. Harbaum, A. Kruger, R. Herges and C. Nather, *Phys. Chem. Chem. Phys.*, 2005, **7**, 1985.
29 H. M. D. Bandara, T. R. Friss, M. M. Enriquez, W. Isley, C. Incarvito, H. A. Frank, J. Gascon and S. C. Burdette, *J. Org. Chem.*, 2010, **75**, 4817.
30 Y. Huang and D.-H. Kim, *Nanoscale*, 2012, **4**, 6312.
31 D. Wang, Y. Huang, J. Li, L. Xu, M. Chen, J. Tao and L. Li, *Chem.–Eur. J.*, 2012, **19**, 685.
32 Y. Jiang, H.-Y. Wang, L.-P. Xie, B.-R. Gao, L. Wang, X.-L. Zhang, Q.-D. Chen, H. Yang, H.-W. Song and H.-B. Sun, *J. Phys. Chem. C*, 2010, **114**, 2913.
33 Y. Jiang, H.-Y. Wang, H. Wang, B.-R. Gao, Y.-w. Hao, Y. Jin, Q.-D. Chen and H.-B. Sun, *J. Phys. Chem. C*, 2011, **115**, 12636.
34 H. Satzger, S. Spörlein, C. Root, J. Wachtveitl, W. Zinth and P. Gilch, *Chem. Phys. Lett.*, 2003, **372**, 216.
35 H. Satzger, C. Root and M. Braun, *J. Phys. Chem. A*, 2004, **108**, 6265.
36 M. Poprawa-Smoluch, J. Baggerman, H. Zhang, H. P. A. Maas, L. De Cola and A. M. Brouwer, *J. Phys. Chem. A*, 2006, **110**, 11926.