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Ultrafast excited-state dynamics associated with the photoisomerization of *trans*-4-diethylaminoazobenzene in solution

Yaping Wang, Song Zhang *, Simei Sun, Kai Liu, Bing Zhang **

State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, China

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ABSTRACT

The ultrafast dynamics of S_2-excited *trans*-4-diethylaminoazobenzene (*trans*-4-DEAAB) is investigated in solution by femtosecond transient absorption spectroscopy combined with quantum chemical calculations. Following excitation, the internal conversion from the S_2 state to the S_1 state occurs directly with time constant of ~0.10 ps. The *cis* isomer is observed by the partial recovery of ground-state bleach in 450–480 nm and the permanent positive absorption in 480–550 nm. The time constant of <1 ps is assigned to the lifetime of the S_1 state which decays by isomerization to the *cis*-isomer hot S_0 state and internal conversion to the *trans*-isomer hot S_0 state. The photoisomerization is deduced by inversion mechanism because of the independence between the viscosity and the S_1-state lifetime. The vibrational cooling of the hot S_0 state of *cis*-4-DEAAB occurs with ~15 ps in acetone but is shortened to ~6 ps in alcohols solvents. This shortening is due to the H-bond which forms easily in protic solvent and accelerates the flow of vibrational energy between solute and solvent.

1. Introduction

Azobenzene and its derivatives are widely applied in optical memory logical devices, molecular manipulators and photochromic molecular switches because their reversible E ⇄ Z photoisomerization can change molecular structure, dipole, absorption spectrum and dielectric constant [1–8]. In particular, azobenzene derivatives also exhibit a high potential in biological application [9–13], such as the artificial photocontrolled proteins [9] and the photoresponsive gene [10].

A diethylamino group substituted azobenzene, *trans*-4-diethylaminoazobenzene (*trans*-4-DEAAB) is of particular interest because of its para substitution of aminoethyl, which can attach to the interior position of DNA triplex. And the photoregulation is the most effective for *p*-aminoazobenzene types [14]. Comparing to azobenzene, the diethylamino group can result in a large red-shift of the $\pi\pi^*$ state which locates at ~410 nm [15]. The isomerization yield of the trans-4-DEAAB in apolar solvent is almost unity by irradiation in the visible region but reduces obviously in polar solvents [16]. These characters with the large photo-induced structural change determine the specific application of *trans*-4-DEAAB in photoelectrochemical information storage, nonlinear optics and photo-switchable gene [10,17,18]. To achieve these potential applications, it is necessary to have detailed knowledge about its ultrafast photoisomerization dynamics under different circumstances.

The photoisomerization dynamics of several amino group substituted azobenzene has also been investigated [19–22]. These studies show that the unusual roles of the first $n\pi^*$ and $\pi\pi^*$ states in the photoisomerization processes are apparently different due to substitution. Reid et al. observed that a bi-exponential decay behavior with time constants of ~0.8 ps and ~10 ps exists in the excited $\pi\pi^*$ state of *trans*-4-dimethylaminoazobenzene (*trans*-4-DMAAB) by a subpicosecond pump–probe spectroscopy [19]. The ~0.8-ps, and ~10-ps components are assigned to the lowest-lying $\pi\pi^*$ state and the isomerization, and the ground-state vibrational relaxation, respectively. However, Hirose et al. determined ultrafast photoisomerization dynamics of *trans*-4-aminoazobenzene (*trans*-4-AAB) in different solvent [20]. It is assumed that the $n\pi^*$ state is populated from the initially excited $\pi\pi^*$ state within 0.2 ps and then decays by isomerization to *cis* isomer and internal conversion to *trans*-isomer S_0 stated with time constant of ~0.6 ps and ~2 ps. It is unfortunately that the authors cannot distinguish the corresponding decay channels of these two time constants. For *trans*-4-DEAAB, the diethylamino group is proven to affect the energy of the $\pi\pi^*$ state [15]. The energetic ordering and roles of the first $n\pi^*$ and $\pi\pi^*$ in the photoisomerization and electronic deactivation processes is still unclear.

* Corresponding author. Tel.: +86 27 87198491; fax: +86 027 87198491.
** Corresponding author. Tel.: +86 27 87197441; fax: +86 027 87198491.
E-mail addresses: zhangsong@wipm.ac.cn (S. Zhang), bzhang@wipm.ac.cn (B. Zhang).

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In this paper, the ultrafast excited state dynamics and photoisomerization of *trans*-4-DEAAB, with the $\pi \rightarrow \pi^*$ excitation is investigated in ethanol, acetone and ethylene glycol by femtosecond transient absorption spectroscopy combined with quantum chemical calculations. The spectra are measured until the delay time up to 300 ps to obtain more complete information on the molecular dynamics. The quantum chemical calculations are used to present the energetic ordering, vertical excitation energies, oscillator strength and static absorption spectra of the *cis* and *trans* isomer. Following the excitation at 400 nm, ultrafast excited-state dynamics associated with the photoisomerization of *trans*-4-DEAAB are observed and analyzed in detail.

2. Experimental and computational details

Trans-4-DEAAB (98% purity) was purchased from Alfa Aesar, and used for experiments without further purification. Ethanol, acetone and ethylene glycol purchasing from Aladdin (99% purity) were used as solvents. All of them are polar solvents with viscosities of 1.2, 0.32 and 13.5 mPa s at 20 °C, respectively [23,24]. The concentration of *trans*-4-DEAAB in each solvent was 1 mM at room temperature and a fresh sample was prepared for each experiment. The static absorption spectra were conducted in a 1-mm quartz cell by the UV–vis spectrometer (INESA, L6) and normalized in all three solvents.

The apparatus used for ultrafast transient absorption measurements is based on a regeneratively amplified femtosecond laser system which has been already described in detail earlier [25]. Briefly, the 800 nm seed beam with repetition rate of 78 MHz is generated by a commercial Ti:sapphire oscillator. The seed beam is brought into the regenerative amplifier and the output used as fundamental pulse was set at repetition rate of 1 kHz, center wavelength of 800 nm, duration of 35 fs and the energy up to 1 mJ/pulse. The second harmonic generation of the fundamental pulse (400 nm) was generated by a 0.5 mm thick BBO crystal as the excitation light. The excitation intensity was set to less than 4 μJ/pulse for measurements. A portion of the fundamental pulse was focused into a 1 mm sapphire to generate a white continuum (450–690 nm). In order to correct the pulse-to-pulse intensity fluctuations and improve the measuring sensitivity, the white light was split into the probe and the reference beam by a metallic-coated beamsplitter. The polarization angle between the pump and probe beam is set at the magic angle (54.7°) for eliminating polarization and photoselection effects. The sample was contained in a flow cell with 0.2 mm quartz windows and 1 mm optical path length. The pump and probe pulses with an intersection angle of ~4° overlapped in the sample spatially, and the reference beam was focused on the sample at a different spot. The probe pulse was temporally delayed with respect to the pump pulse through a computer controlled translation stage. A CCD camera (PI-MAX, 1024 × 256 pixel array) equipped with a spectrometer (Princeton, SpectraPro 2500i) was used to collect the probe and reference beams. Each of the recorded spectra is accumulated on the CCD for typically 10000 laser shorts. The instrumental response of the system was determined to be ~0.17 ps by cross-correlation measurements between the pump and probe pulses. The cross-correlation measurements were also used to determine the precise zero time-delay at each probe wavelength. In order to eliminate any persistent offset in the optical density at long delay times, a time constant of 10,000 ps was included. The time evolutions of transient absorption data of *trans*-4-DEAAB for all three solvents were fitted by global fit analysis with singular value decomposition (SVD).

All quantum chemical calculations were carried out with the Gaussian 09 software package [26]. The molecular geometries in the electronic ground state of both *trans* and *cis*-4-DEAAB were optimized using ab initio density-functional theory with the B3LYP functional and the 6-311G++(d,p) basis set. All the minima are verified by vibrational frequency analysis at the same level of theory. The polarizable continuum model (PCM) was used to incorporate the bulk solvent effect [27]. The vertical transition energies, oscillator strengths and absorption spectroscopy were performed by the TD-DFT/B3LYP with the basis set of 6-31G in ethanol and acetone and 6-311G in ethylene glycol, respectively.

3. Results and discussion

3.1. Quantum chemical calculations

Table 1 shows the orbital transitions, configuration-interaction (CI) coefficients, vertical excitation energies, and oscillator strengths of the two lowest excited singlet states of *trans*-4-DEAAB in ethanol, acetone and ethylene glycol, respectively. For *trans*-4-DEAAB in ethanol, the first transition is from HOMO-1 to LUMO and the oscillator strength is zero, while the second transition from HOMO to LUMO is much more intense. The assignments of molecular orbitals are done by visual inspection. The HOMO-1, HOMO and LUMO are assigned to n, π and π^* orbitals, respectively, as shown in Fig. 1. Evaluation of molecular orbitals reveals that the first transition is of 99% $n \rightarrow \pi^*$ character from the CI coefficients while the second transition is of 100% $\pi \rightarrow \pi^*$ character. In acetone and ethylene glycol, the calculated results are the same as that in ethanol. It clearly demonstrates that the S_1 state is optically-forbidden with $n\pi^*$ character while the S_2 state is optically-allowed with $\pi\pi^*$ character.

3.2. Static absorption spectrum

The static absorption spectra of *trans*-4-DEAAB in ethanol, acetone and ethylene glycol were measured and shown in Fig. 2(a),

Table 1
Orbital transition, configuration-interaction (CI) coefficients, vertical excitation energy, and oscillator strength of the two lowest excited singlet states of *trans*-4-DEAAB in ethanol, acetone and ethylene glycol.

State	Orbital transition	CI coefficients	Vertical excitation/eV	Oscillator strengths
Ethanol				
S_1	HOMO-1 → LUMO	0.70531	2.51	0.0000
S_2	HOMO → LUMO	0.70709	2.97	1.1016
Acetone				
S_1	HOMO-1 → LUMO	0.70531	2.51	0.0000
S_2	HOMO → LUMO	0.70708	2.97	1.1003
Ethylene glycol				
S_1	HOMO-1 → LUMO	0.70500	2.57	0.0000
S_2	HOMO → LUMO	0.70662	2.90	1.1142