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Femtosecond photoisomerization of *cis*-azobenzene

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Abstract

Femtosecond transient absorption measurements of the photoisomerization of azobenzene excited at 435 nm in the long-wavelength ($n\pi^*$) band are presented. For *cis*-azobenzene the experiments reveal an extremely fast photoproduct formation with a dominating 170 fs and a weak 2 ps component. During the decay of the excited state some oscillatory features are found. Vibrational cooling of the hot photoproducts in the ground state occurs on a time scale of 10 ps. A slower initial photoreaction, which can be described by two time constants, 0.32 and 2.1 ps, is found for the *trans*-isomer. The experimental results support the idea, that excitation of the S_1 ($n\pi^*$) bands of azobenzene leads to photoisomerization via inversion at one of the nitrogen atoms. © 1997 Elsevier Science B.V.

1. Introduction

Azobenzene is a molecule, where the photoinduced *cis–trans* isomerization allows various applications as a light triggered switch [1]. Azobenzene liquid crystals have been used successfully as image storage devices with fast response time [2]. Photoregulation of enzyme activity via attached photochromic azo groups has been demonstrated [3]. Peptide oligomers containing azobenzene have proven to be an ideal material for erasable holographic data storage [4]. A new and exciting field is the investigation of the dynamic properties of peptides. Here, azobenzene, inserted in a linear or cyclic chain of amino acids can act as fast optical trigger, which is able to modulate the peptide conformation [5,6].

The basis for all these applications is the photoisomerization of azobenzene between the stable *trans* and the metastable *cis* conformation. Since *cis* and *trans* isomers exhibit spectrally well-separated absorption bands in the UV–visible absorption spectrum, reversible photoswitching between the two conformations is possible. The static photophysical properties of azobenzene have been studied in detail. The absorption spectrum in the visible and near UV is determined by low lying ($n\pi^*$) bands between 380 and 520 nm and the ($\pi\pi^*$) bands at 330 nm (*trans*) and 275 nm (*cis*). For the photoisomerization itself, two different pathways are proposed, which depend on optical excitation: excitation of the ($n\pi^*$) state should lead to an in plane inversion at one of the two N atoms, whereas after a ($\pi\pi^*$) transition a rotation around the N=N double bond should be favoured [7,8]. This view is supported by the observation of a wavelength dependent quantum yield of the photoisomerization process: for the *cis*-to-*trans*

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isomerization of azobenzene, the quantum yield in ethanol increases from 28%, when exciting the ($\pi\pi^*$) transition, to 51%, when the ($n\pi^*$) transition is excited [1,9]. The experimental investigation of the isomerization pathways is possible directly by time resolved spectroscopy. However, only few experiments with sufficient time resolution have been performed until now [10–13]. In a recent study [11], transient absorption data of *trans*-azobenzene after excitation of the S_2 ($\pi\pi^*$) excited state were reported. The observed multi-exponential decay was fitted with two components (~ 1 and ~ 13 ps) and explained by the formation of an intermediate (S_2 or S_1) state — a twisted conformer of *trans*-azobenzene. Similar reaction dynamics were found for a S_2 ($\pi\pi^*$) excited *trans*-azobenzene compound, carrying an electron withdrawing and an electron accepting substituent at the two phenyl rings [13]. The ground state vibrational relaxation processes following optical excitation of *cis*-azobenzene were investigated in detail by time resolved IR spectroscopy and the different kinetic components could be assigned to intermolecular energy distribution processes [12].

In the present paper we investigate the ultrafast photoisomerization of azobenzene with femtosecond time resolution. The lowest electronic ($n\pi^*$) transition is excited, allowing to study the dynamics of the photoreaction from one, well-defined electronic state, without disturbing interference of preceding internal conversion processes.

2. Materials and methods

2.1. Material and sample preparation

For the time resolved experiments, azobenzene (purity > 98%, > 97% *trans*; Merck, Germany) dissolved in ethanol (purity > 99%; Merck) was used at two concentrations, $c_{\text{'cis'}} = 6.25$ mM for studies on the *cis*-isomer and $c_{\text{trans}} = 19$ mM for the *trans*-isomer. For the experiments on *trans*-azobenzene the molecules were exited only once. For the experiments on *cis*-azobenzene the samples were obtained according to the following procedure: the solution was pumped through two different cuvettes in a closed cycle. The first cuvette had an optical pathlength of 0.5 mm and was used for the femtosecond experiments, in the second 1 mm cuvette illumination by a cw light source (see below) established a photostationary *cis/trans* balance. From the absorption spectrum of this '*cis*' sample (see Fig. 2a, dashed line), the content of the *cis* isomer could be determined to be approximately 75%. Upon excitation of the '*cis*' sample at 435 nm, the different extinction coefficients for the ($n\pi^*$) transitions of *cis*- and *trans*-azobenzene ($\epsilon_{cis} = 1470\ \mathrm{M^{-1}\ cm^{-1}}$, $\epsilon_{trans} = 405\ \mathrm{M^{-1}\ cm^{-1}}$ [14,15]) cause increased excitation of *cis* molecules: as a consequence, approximately 90% of the excited molecules were initially in the *cis* configuration.

A 1000 W Hg–Xe lamp was used to prepare the photostationary *cis/trans* balance. Spectral selection of the light by a water and two glass filters (4 mm WG 320 and 2 mm UG11; Schott, Germany) leads to a broadband excitation of the *trans* ($\pi\pi^*$) band from 320 to 390 nm with a maximum at 366 nm (a strong Hg line). After passing a quartz glass fibre bundle, the light was imaged on the 1 mm cuvette (spot size 2 cm^2) to irradiate the solution with a power of 100 mW.

2.2. Time resolved spectroscopy

The time resolved measurements were performed with a Ti:Sapphire laser-amplifier system operating at a central wavelength of 870 nm. The ultrashort light pulses of the Ti:Sapphire oscillator were amplified in a regenerative chirped pulse amplifier pumped by a 20 Hz Nd:YAG laser. This set-up provided light pulses with a duration of 100 fs (FWHM) for the experiments described here. Light at a wavelength of 435 nm was obtained by frequency doubling of the laser fundamental in a 1 mm thick LBO crystal.For excitation of the azobenzene one part (3 μJ) of the second harmonic light was focused on a 0.2 mm spot in the cuvette. The flow rate of the dye solution in the cuvette was high enough to exchange the excited volume between successive excitations. To keep the *cis/trans* balance constant during the measurements of the '*cis*' sample, the preilluminated azobenzene was irradiated in another cuvette with a Hg–Xe lamp (see above).

Probing pulses obtained by femtosecond continuum generation in water by the second harmonic light pulses (435 nm) or by the laser fundamental (870 nm) allowed to investigate a wide spectral region. Probing pulses were spectrally selected by a double monochromator and recorded by single-channel detection in the near UV from 350 nm to 480 nm. A multi-channel detection system was used in the spectral region from 443 to 750 nm. The experiments performed with the multi-channel detection system had an improved signal to noise ratio. The detection systems have been described previously [16,17]. Time zero and instrumental response function were determined before and after each experiment by control measurements, i.e. either by absorption bleaching in dyes or by two-photon absorption in glass filters. Depending on the probing wavelength, the width (FWHM) of the cross correlation traces were between 130 and 240 fs.

All transient absorption data shown in this paper were measured under the 'magic angle' of 54.7° between the polarisations of the pump and probe beam to avoid reorientation effects.

In the figures the transient absorption data up to 1 ps are plotted on a linear time scale. A logarithmic time scale is used for longer delay times.

3. Results

The transient absorption dynamics of azobenzene in ethanol were investigated in the wavelength region between 350 and 750 nm following a 100 fs excitation pulse at 435 nm. The excitation wavelength is near the maximum of the nπ^* transition of both isomers (see Fig. 2a) and therefore allows the observation of the photoreactions induced by the excitation of *trans*- or *cis*-azobenzene, respectively.

Transient absorption data of '*cis*'-azobenzene are shown in Fig. 1 for four selected spectral positions. Around time zero, a strong induced absorption is found. The shape and position of this transient — its asymmetry and its delay relative to time zero — suggest that it cannot be caused by an instantaneous process like two-photon absorption. Apparently it is due to excited state absorption upon formation of the S_1 (nπ^*) state. Excited state absorption is present throughout the entire spectral region investigated. The largest amplitudes of this signal are found at 360 and 563 nm (Fig. 1a and d). In order to show the spectral properties of the excited state of *cis*-azobenzene, we plotted in Fig. 2b the absorption changes observed at a delay time of $t_D = 100$ fs, where the excitation process is finished and where only a small fraction of the molecules has left the excited electronic state. The spectrum shows two regions with strong induced absorption around 360 and 550 nm. The absorption increase is weak around 435 nm, where bleaching of the original (nπ^*) ground state band and possibly stimulated emission are superimposed to the excited state absorption. The strong excited state absorption around 360 nm points to electronic states ~ 3.5 eV above the populated S_1 state.

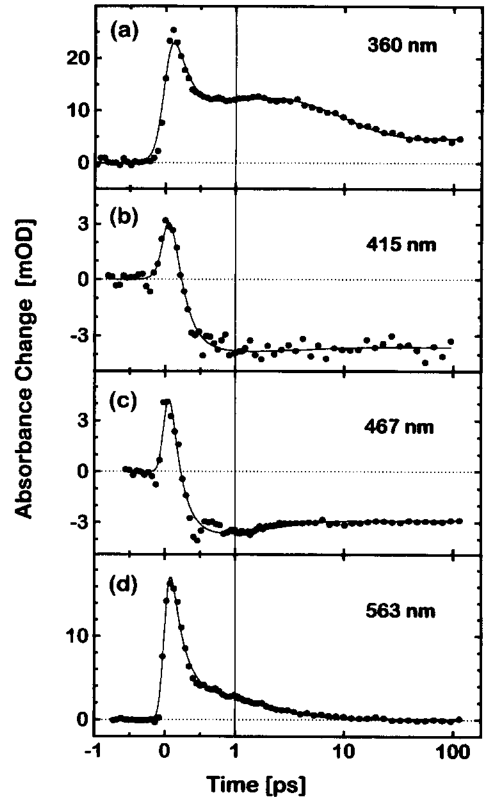

Fig. 1. Transient absorbance changes of so-called '*cis*'-azobenzene in ethanol after 435 nm excitation at four selected spectral positions. Results from probing wavelengths of: (a) 360 nm (predominant *trans*-azobenzene absorption), (b) 415 nm and (c) 467 nm (predominant *cis*-azobenzene absorption), and (d) 563 nm (no significant ground state absorption) are shown. Data points are plotted as dots, the fit functions as lines. A linear time scale is chosen for delay times between −1 and 1 ps, a logarithmic scale for longer times.

At all wavelengths, the initial absorption rise is followed by a fast absorption decrease. This decay occurs with a time constant of 180 fs and clearly exhibits deviations from an exponential behaviour. Fig. 1c, and also curves at other wavelengths show pronounced modulations superimposed to the exponential decay during the first 500 fs. At later delay times we find absorption dynamics with a time constant of 2 ps (relative amplitude $\leq 20\%$). Remaining weaker transients have time constants in the 10–20 ps range. The exact values depend on the probing wavelength, e.g. at 360 nm a value of 20 ps, at 500 nm a value of 10 ps was found.

The absorption changes persistent at late delay times have the following properties: In the long-wavelength wing of the *trans* ($\pi\pi^*$) band (λ_{pr} = 360 nm, Fig. 1a), one finds a long lasting absorption increase, while in the region of the ($n\pi^*$) ground state absorption band (Fig. 1b and c) the absorption decreases. The spectral characteristics (measured at 49 wavelengths between 360 and 750 nm) agrees well with the steady-state difference spectrum of the *cis*-to-*trans* transition and indicates that the whole isomerization reaction, including subsequent cooling processes is completed within 100 ps.

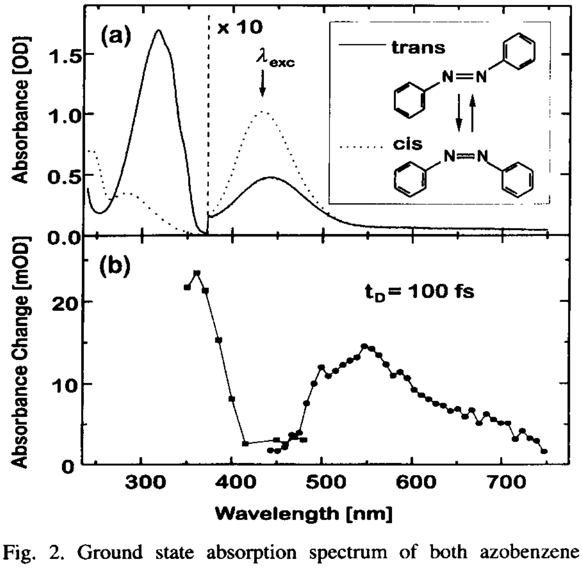

Fig. 2. Ground state absorption spectrum of both azobenzene samples (*trans* and '*cis*') in ethanol (a), and transient difference spectrum 100 fs after exciting '*cis*'-azobenzene with a 435 nm pulse (b). Experimental data were obtained with single channel detection (squares) and multi-channel detection (circles).

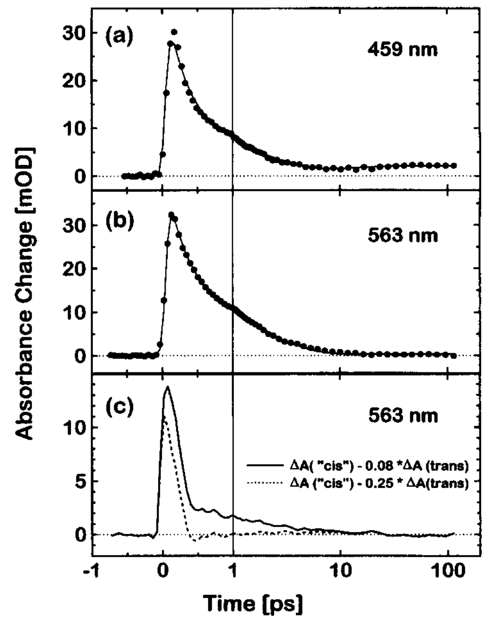

Fig. 3. Temporal evolution of the absorption changes for *trans*-azobenzene (a) and (b) and a corrected 563 nm signal of *cis*-azobenzene (c), where different contributions of the *trans*-isomer were subtracted from the data shown in Fig. 1d.

Fig. 3 shows results from the *trans*-to-*cis* isomerization. The ($n\pi^*$) state of pure ($> 97\%$) *trans*-azobenzene was excited at 435 nm and the absorption changes were analysed over the range 440–750 nm. The overall characteristics of the curves was very similar at all wavelengths, no matter if the probing wavelength was within (Fig. 3a, $\lambda_{pr} = 459$ nm) or outside (Fig. 3b, $\lambda_{pr} = 563$ nm) the range with considerable ground state absorption. In every experiment an initial strong induced absorption is found, which is attributed to the electronically excited S_1 ($n\pi^*$) state of the *trans* isomer. The signal decays wavelength independent in a clearly non-monoexponential way and can be approximated by two time constants, 0.32 and 2.1 ps, and with relative amplitudes of 2 to 1. From a comparison of Figs. 3b and 1d, it is evident that the overall decay of the electronic excited state occurs much slower for the *trans* isomer than for the *cis* isomer.

The experiment on pure *trans*-azobenzene in combination with the known concentration of *trans*-azobenzene in the so-called '*cis*' sample allows to deduce the time dependence of pure *cis*-azobenzene.

For the given cross-sections and concentrations, 8% of the *trans* signal has to be subtracted from the '*cis*' signal. The result is shown in Fig. 3c (solid line) for $\lambda_{pr} = 563$ nm. Compared to Fig. 1d, the 2 ps component is reduced in the 'corrected *cis*' transient; however, its amplitude is still ~ 15% of the total signal amplitude. The initial decay of the pure *cis* state is approximated best by a 170 fs time constant, instead of the 180 fs found in the original uncorrected '*cis*' curves (Fig. 1). Interestingly, the ps contributions visible in the original '*cis*' curve vanish completely for all long wavelengths, $\lambda_{pr} > 563$ nm, if a higher *trans* part (25%) is subtracted from the 'cis' curves, (see, e.g., Fig. 3c, dashed line).

4. Discussion

As compared to other isomerising molecules like stilbene [18–22], azobenzene has the advantage that the two isomers show clearly separated ($\pi\pi^*$) absorption bands and different absorption cross-sections for the *cis* and *trans* ($n\pi^*$) bands. These features allow, in the case of the *cis*-to-*trans* isomerization, to follow the photoreaction via the disappearance of the (*cis*) reactant (around 430 nm) and the formation of the (*trans*) product absorption band (around 360 nm). The assignment of the photoisomerization process to one of the observed transients can be achieved in the following way: (1) at 360 nm, within the *trans* product band, a strong absorption increase is found after the decay of the 170 fs kinetic component (see Fig. 1a); (2) around 430 nm (see Fig. 1b and c), in the *cis* reactant band, the absorption is decreased by the 170 fs transient to the final level of the isomerized molecules; and (3) the absorption increase observed at 563 nm and assigned to excited state absorption, decays to more than 80% with the 170 fs transient. All these data suggest that the *cis*-to-*trans* isomerization proceeds extremely fast within 170 fs. They also allow to explain the 10–20 ps component: As shown above, the formation of azobenzene in the electronic ground state is extremely fast. During this process, most of the excitation energy and — for the *cis*-to-*trans* reaction — the energy difference between the *cis* and the *trans* form remains in the molecule and leads to vibrationally hot product molecules with modified absorption spectra [23]. Thermal redistribution and energy transfer to the surrounding solvent are known to occur in picoseconds. The absorption decrease found in the long-wavelength wing of the *trans* absorption band with 20 ps and the variation of the time constant with wavelength support the interpretation, that the 10–20 ps transient is due to vibrational cooling of the azobenzene molecule. The direct study of the vibrational modes via transient spectroscopy in the IR region [12] leads to the same conclusion.

The observed femtosecond dynamics allow to draw some conclusions on the topology of the S_1 potential energy surface. The different speed of the initial reaction (170 and 320 fs for *cis*- and *trans*-azobenzene, respectively) leads to the assumption that the shape of the S_1 potential surface strongly depends on the isomer excited. The ultrafast isomerisation time of excited *cis*-azobenzene indicates that the initial reactive motion of the molecule should proceed along a steep and barrierless pathway. The absorption dynamics related to this photoisomerization process show pronounced nonexponential character due to modulations present at very early delay times (see, e.g., Fig. 1c). Such a behaviour is expected from theoretical simulations of femtosecond pump-probe experiments on ultrafast photoreactions proceeding via conical intersection of the S_1 and the S_0 potential surface. They show, that under conditions similar to those found in *cis*-azobenzene, a strong interplay between oscillatory motion and absorption data should exist [24,25].

Within the present model, the slow 2 ps component found in both samples can be explained as follows: During the fast and directed motion of the majority of the molecules, a smaller fraction leaves the reactive pathway and carries out diffusion-type motion on the S_1 potential surface. Because of the weaker gradient of the S_1 potential surface of the *trans* side, a larger amount of the exited *trans* molecules performs the slower reaction. As a consequence, the amplitude of the 2 ps component is twice as high compared to *cis*-azobenzene.

In general, two pathways are possible for the isomerization reaction (Fig. 4): (1) the nuclear motion consisting of a torsion of the N–N bond, where the torsional angle φ is changed from 0° to 180° (for $\varphi = 90°$, the planes of the two phenyl rings are perpendicular to each other); and (2) the inversion

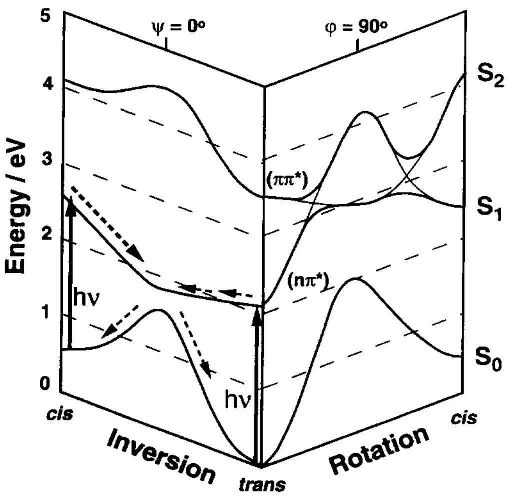

Fig. 4. Schematic representation of the potential energy surfaces for the S_1 photochemical reactions of both azobenzene isomers. The curves are adapted from the calculations of Monti et al. [8] and from results reported in [7,11].

along the ψ coordinate (leading to a transition state with a linear N–N-phenyl conformation for $\psi = 0°$). The shape of the S_1 potential energy surface calculated in [8] shows that a large barrier exists for the rotational pathway, while the inversion pathway is barrierless: the observed reaction dynamics allow to conclude that, under the experimental conditions of excitation in the $(n\pi^*)$ band, the inversion pathway is highly probable since the ultrafast formation of product molecules argues against other solutions. Thus, the present results from the time resolved experiments are in agreement with the current view of the isomerization pathway in azobenzene for the case of the $(n\pi^*)$ transition [7,8,11,26].

Within the known potential surfaces for azobenzene, the ultrafast kinetic processes after excitation with 435 nm pulses can be summarised as follows (see Fig. 4): for the *cis* form a rapid reaction — e.g., via wavepacket like motion — brings the system from the initially populated Franck–Condon state on the S_1 potential energy surface towards the region where fast internal conversion to the ground state is possible. The whole process takes about 170 fs. Considering the slopes of the simple one-dimensional potential energy surfaces (Fig. 4), one would expect a blue shift of the excited state absorption during this initial reaction. For *cis*-azobenzene the experimental time resolution does not allow to resolve such a rapid spectral change. For *trans*-azobenzene the transient absorption changes are due to three contributions: bleaching of the ground state absorption, stimulated emission and excited state absorption. For such a complex situation it is not surprising, that a blue shift is not observed experimentally.

The further reaction proceeds as follows: a small fraction of molecules misses the direct transition region and undergoes internal conversion after some diffusion-type motion on the 2 ps time scale. On the ground state surface, rapid motion occurs to the minima related to *trans*- or *cis*-azobenzene. It can be seen in IR experiments [12], that a large amount of the excess energy is dissipated to the vibrational system of the molecule. The cold ground state is finally reached via energy conduction to the surrounding solvent on the 10–20 ps time scale. For the reaction starting with *trans*-azobenzene, the photoisomerization was found to be considerably slower and biexponential with time constants of 0.32 and 2.1 ps. The slower initial reaction speed points to a weaker slope of the potential surface in the vicinity of the Franck–Condon region, as suggested by the calculations in [8]. As a consequence, the initial reaction is less directed and diffusion like processes on the S_1 surface may be more important in *trans*-azobenzene, which is reflected in the larger amplitude of the 2 ps kinetic component.

In conclusion, we have presented first femtosecond experiments on the photoisomerization of azobenzene excited in the lowest $(n\pi^*)$ electronic state. This photoisomerization proceeds fast with $\tau \approx 170$ fs and is one of the fastest photoreactions ever observed. Azobenzene is an ideal system to study an ultrafast isomerisation process. It has well-separated absorption bands for both isomers and is small enough to allow a complementation of femtosecond data by a detailed theoretical description in the near future.

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