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Action-spectroscopy studies of positively charge-tagged azobenzene in solution and in the gas-phase ^{EP}

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ABSTRACT

The absorption of a positively charge-tagged azobenzene molecule is studied in the gas-phase by measuring photoinduced fragmentation of ions as a function of time. This technique provides information on prompt as well as delayed fragmentation, and a single dissociation channel after one-photon absorption is identified. The spectra in solution, as well as in the gas-phase, show a weak $S_0 \rightarrow S_1$, a strong $S_0 \rightarrow S_2$, and a broad absorption band in the UV regime. The bands are assigned through time dependent density functional theory calculations. The ratio of the various absorption bands depends on the *trans* to *cis* isomerization fraction and may be tuned by light irradiation. Gas-phase absorption spectra are presented and discussed in terms of *trans* and *cis* isomers.

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INTRODUCTION

The azobenzene (AB) scaffold and its derivatives have attracted large attention in fundamental and applied research areas.^{1,2} The large interest in these versatile molecules relies on the clean, efficient, and reversible *trans* to *cis* photoisomerization ability, which enables the creation of photo-triggerable systems. One intriguing field of application is based on the photomechanical properties of azobenzene, the substantial geometric change in the molecule during isomerization, applicable in molecular motors,³ micropumps, and valves or articulations in robotics.² The attachment of ring substituents enables the tuning of the photochromic properties and isomerization mechanism of AB.¹ Besides shifting the absorption spectrum to longer wavelengths, which is of considerable interest for applications in medicine and photopharmacology,⁴ with the appropriate ring substituents, it is possible to control the back isomerization (*cis* to *trans*) rate. A slow back reaction can be used in information storage materials⁵ and a

fast one in information-transmitting systems.⁶ The AB molecular unit may also be built into more complex networks, thus producing photoresponsive polymers⁷ or be embedded into biological systems to drive functional changes in peptides, proteins, nucleic acids, lipids, and carbohydrates.⁸ Moreover, investigations are ongoing to study how structural constraints of AB complexes can prevent the isomerization of the photoswitch units. The complete dissipation of the UV excitation as heat may make the AB be applicable as UV-absorbers, for example, in sunscreens.⁹

Azobenzene and its derivatives show *trans* to *cis* isomerization upon photoexcitation in the UV-visible part of the spectrum on a time scale of femtoseconds.¹⁰ The thermally stable state of the AB molecule is the elongated *trans* configuration (t-AB), whereas the bent *cis* configuration (c-AB) is less stable by approximately 0.5 eV.¹¹ In the gas-phase, the t-AB is almost planar with twisted phenyl rings at about 30°,¹² whereas c-AB is non-planar.¹³ The *cis* converts back to the *trans* configuration when exposed to UV light, or left

in the dark.¹¹ The thermal *cis* to *trans* back reaction depends strongly on the chemical architecture and the local environment, with a time scale ranging from milliseconds to hours, or even days. Spectroscopically, AB in the two stages of isomerization, *trans* and *cis*, has some unique features. The *trans* form shows a weak $n-\pi^*$ ($S_0 \rightarrow S_1$) absorption band at about 440 nm and a stronger $\pi-\pi^*$ ($S_0 \rightarrow S_2$) band at about 320 nm. The *cis* form, on the other hand, has a stronger $n-\pi^*$ ($S_0 \rightarrow S_1$) absorption band at about 440 nm, whereas $\pi-\pi^*$ transitions are found below 300 nm.¹ The strong electronic absorption of the conjugated π system can be tailored by ring substitution to lie anywhere from the ultraviolet to the visible region. Adding ortho- or para-substituents with an electron-donating group leads to a red-shifted absorption spectrum and a shorter lifetime of the *cis* isomer. Adding an electron-donor on one side and an electron-acceptor substituent on the other side leads to a strongly asymmetric electron distribution with a significantly red-shifted absorption spectrum and an even shorter *cis* isomer lifetime.

Since the discovery of the isomerization process of azobenzene by Hartley in 1937,¹⁴ experimental as well as theoretical efforts have been made to elucidate the isomerization pathways of this system. The observation of the higher quantum yield when excited to the S_1 state compared to the S_2 state was originally explained by two different isomerization mechanisms.¹⁵ Excitation to the S_2 state would weaken the π bond allowing rotational isomerization, while $S_0 \rightarrow S_1$ excitation would result in isomerization by inversion. This hypothesis was doubted after performing measurements of rotation-restricted systems, which have shown almost wavelength-independent quantum yields. Later studies suggested that other mechanisms, different from pure rotation or inversion, such as concerted inversion and inversion-assisted rotation, are possible.¹⁶ A recent computational study on the competing reaction mechanisms presents a global scheme of the isomerization path of azobenzene along the S_1 and S_2 for free-rotation as well as restricted-rotation in different AB systems.¹⁷ The authors show the rotational mechanism as the isomerization path along S_1 , in agreement with most of recent computational studies.^{18,19} The S_2 state decays very efficiently to the S_1 state at a pedal-like non-rotated geometry, at which S_2 and S_1 are degenerated. Moreover, they show for the S_2 potential energy surface (PES) another downhill coordinate,

which is less favoured but still possible and leads to a crossing with the S_3 state. The possible bifurcation of the relaxation on S_2 may explain the lower quantum yield after excitation in S_2 .

The quantum yield of the photoisomerization of azobenzene does not only depend on the excitation wavelength, but the isomeric form (*trans* or *cis*) and the solvent properties (polarity and viscosity) also influence the isomerization mechanism. Quite recently, ion mobility spectrometry was applied to investigate photoisomerization of selected *trans* and *cis* isomers of negatively charge-tagged azobenzene in the gas-phase.²⁰

In the present study, the absorption spectra of positively charge-tagged azobenzene in solution as well as isolated in *vacuo* are presented. Our action-spectroscopy technique in the gas-phase is based on time-resolved photo-fragment detection and reveals the total absorption cross section (neglecting a very low fluorescence quantum yield).²¹ Our investigations are crucial for designing new pump-probe schemes to obtain internal isomerization times in the gas-phase by fast fs laser pulses.²²

EXPERIMENTAL AND COMPUTATIONAL METHODS

Synthesis

To study the azobenzene chromophore in the gas-phase, the storage ring ELISA (ELeCtrostatIc Storage ring for ions, Aarhus) at Aarhus University was used. Since the storage-ring technique is only applicable to ions, a charged model of the azobenzene chromophore was designed. The ammonium tagged azobenzene compound was prepared in three steps (see Fig. 1), wherein *p*-methylazobenzene (2) was prepared under conditions previously applied for the generation of *ortho*-substituted azobenzenes²³ and the synthesis of 4-(bromomethyl)azobenzene (3) and *N,N,N*-trimethyl[*p*-phenylazophenyl]methyl) ammonium bromide (4) was conducted following the modified procedures published by Hu and co-workers.²⁴ A detailed description of the synthesis can be found in the [supplementary material](#).

Experimental solution phase studies

The kinetic measurements were conducted with a SPECORD® 200 PLUS UV/Vis spectrophotometer equipped

FIG. 1. Synthesis of the ammonium tagged azobenzene chromophore.

with two automatic eightfold cell changers and a Peltier thermostat system for temperature control. The samples were measured in QS High Precision Cells made of Quartz Suprasil® by Hellma Analytics with a light path of 10 mm. The sample volume was 3 mL and the sample concentration 6×10^{-5} M. Irradiation at 302 nm was conducted with a 3UV-38 handheld lamp (8 W) by UVP in steps of 2 min. For each sample, the spectra were recorded starting from 700 nm to 210 nm with a scan speed of 20 nm/s at 25 °C. The chromophores were dissolved in methanol. More information are found in the [supplementary material](#).

Experimental gas-phase studies

The absorption studies in the gas-phase were performed at the ELISA ion-storage ring,^{25–27} shown schematically in Fig. 2. The methanol-dissolved chromophores were brought into the gas-phase by using an ion source, based on the electrospray ionization technique.²⁸ After electrospraying with a flow rate of 150 μ L/hour through a steel needle, the solvent molecules were evaporated off in a heated capillary, kept at 80 °C. Ions were accumulated in a 22-pole radio frequency ion trap and cooled translationally as well as internally to the trap temperature (cooled to 100 K with liquid nitrogen) by collisions with He buffer gas. The produced gas-phase ions were extracted from the trap by switching the trapping voltages for 40 μ s, subsequently accelerated as a bunch to a kinetic energy of 22 keV and mass selected using a bending magnet. Following injection into the ring, the cations were stored for several ms ($\sim 65 \mu$ s revolution time) at a pressure of about 10^{-10} mbar. A nanosecond pulsed EKSPLA (NT232-50-SH-SFG) laser system provided laser light in the region of 210–700 nm. The laser was operated at 25 Hz repetition rate with a pulse duration of about 4 ns. The laser was fired some ms after the injection, and each ion bunch was exposed to a single laser pulse only. The laser-pulse energy was controlled by neutral density Schott glass filters and a variable

attenuator, based on transmission coefficients through an angled quartz crystal. The laser was operated either in a merged or crossed beam configuration (see Fig. 2). For the presented data, a microchannel-plate detector (MCP) and a secondary electron detector (SED) were used to detect delayed and prompt action/fragmentation, respectively. The SED detector consists of a thin indium oxide coated glass plate, which allows laser light to pass, and a channeltron to detect secondary electrons from the particle impact. To avoid damage to the coating, the SED was used in the crossed beam laser setup for wavelengths below 350 nm. Above this threshold, the merged beam laser setup was favoured due to the increased signals.

Data analysis

At ELISA, the absorption of a photon by the molecule is registered by detecting a neutral fragment leaving the storage ring and hitting a detector (action-spectroscopy). The absorption-cross section at a certain wavelength is proportional to the number of neutrals formed after photoabsorption at this wavelength and is obtained by integrating the yield of neutral fragments over time for dissociation (see Fig. 3). To distinguish neutrals, induced by laser absorption and those originating from collisions with the residual gas, an action-signal time window A (time window after the laser was fired) and a background window B (time window before the laser was fired) are set and the corresponding integrated counts for the “laser on” and “laser off” status (see Fig. 3) are extracted. The single photon absorption cross section is obtained as

$$\sigma(\lambda) = \frac{N_A(\lambda) - N_{A0} \frac{N_B(\lambda)}{N_{B0}(\lambda)}}{N_B(\lambda) \frac{E_{\text{puls}}(\lambda)}{1/\lambda}},$$

with λ being the wavelength, N_A being the signal when the laser is on, N_{A0} being the signal when the laser is off, N_B being

FIG. 2. The ELISA ion-storage ring equipped with an electrospray-ion source (shown separately), a nanosecond pulsed laser system, and two detectors for neutral product detection. For the presented measurements, the laser was operated in either merged or crossed beam configuration.

FIG. 3. Number of neutrals hitting the detector as a function of time after injection into the ELISA storage ring. The gray signal shows the detected particles when the laser is off, the blue shows the detected action when the laser is on. The signal time window A and the background window B for the analysis are marked. Note that the laser induced signal is about one order of magnitude above the background count rate ($\lambda = 430$ nm).

the background when the laser is on, N_{B_0} being the background when the laser is off, and $E_{puls}(\lambda)$ being the measured laser pulse energy. The normalization to the number of stored ions and the number of photons is ensured by the division of $N_B(\lambda) \frac{E_{puls}(\lambda)}{1/\lambda}$.

Calculations

The stability of the *cis* isomer of the positively charge-tagged azobenzene in the gas-phase was also studied by computational methods to estimate the activation barrier for the thermal *cis* to *trans* isomerization. All computations were carried out with the Gaussian 16 software package.²⁹ Geometry optimizations were performed on a B3LYP-D3 level using the def2-TZVP basis set.^{30–33} Additionally, single point energy (SPE) computations on a B2PLYP-D3/def2-TZVP level were conducted using the previously optimized B3LYP structures (see [supplementary material](#)).³⁴ The vertical excitation energies of excited states of the *trans* and the *cis* isomer for the gas-phase were computed to support the examination of the experimental spectra. Therefore, time-dependent density functional theory (DFT) computations were also performed with the previously optimized B3LYP structures.³⁵ The BHLYP method was applied, since previous studies already showed that with this method, azobenzene spectra can be simulated with high accuracy.^{36,37}

RESULTS AND DISCUSSION

The absorption spectra of positively charged azobenzene in the solution phase as well as in the gas-phase are shown in [Fig. 4](#). Both spectra exhibit a weak S_1 band in the 400–480 nm range and an intense S_2 band in the 260–360 nm range as known from the neutral AB form. The calculated excitation

FIG. 4. Normalized absorption cross section for the ammonium tagged azobenzene compound in solution and in the gas-phase. Both spectra show a weak S_1 band (400–480 nm) and a stronger S_2 band (260–360 nm). For better visibility, a zoomed-in image of the weak S_1 band is shown. The solid line fits the data points in the gas-phase with sum of Gaussians to guide the eye. The calculated vertical transitions ($S_0 \rightarrow S_n$) for the *trans* isomer are plotted by vertical lines with the height of the bars indicating the oscillator strength of the specific transition.

energies for the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions are in good agreement with the measured data, even though slightly red-shifted. The absorption spectra show a third intense band in the 220–250 nm range.

Our action-spectroscopy technique in the gas-phase is based on time-resolved photo-fragment detection. By absorbing a photon, the chromophore is excited from the ground state S_0 into the excited state S_n . After excitation, fast internal conversion brings the chromophore back into the ground state with an excess energy corresponding to the absorbed photon energy (here between 2 and 5.6 eV). Upon coupling to the nuclear degrees of freedom, this results in a hot molecule in the electronic ground state. Since the chromophore is isolated *in vacuo* and the excess energy can only leave the molecule through slow infrared emission, this leads to a statistical dissociation of the complex. The time scale of the dissociation process depends on the absorbed energy and is therefore wavelength dependent. Storing the molecules in the electrostatic ion ring on a time scale of several ms gives access to the observation of this statistical decay and prompt, as well as delayed action can be observed. With the given experimental setup, we measure prompt signals with no time delay by the SED arrangement (in the crossed-beam as well as the merged-beam configuration), and at the MCP detector, we detect action at times down to about a quarter of a revolution time and up to tens of ms after laser excitation. In [Figs. 5\(a\)](#) and [5\(b\)](#), the delayed and prompt action detected

FIG. 5. (a) Delayed fragmentation of AB after photoexcitation at 430 nm and 340 nm measured with the MCP detector. Bunches of fragments are periodically hitting the detector, corresponding to the time structure of the stored ion beam. The action becomes faster at shorter wavelengths. (b) Prompt action after photoexcitation at 300 nm, measured with the SED detector. This measurement was performed in crossed-beam configuration. The photo-induced signal is seen in the middle of the first bunch after excitation by the laser light. The first sharp peak is induced by scattered laser light. (c) Yield of the delayed ($\lambda = 440$ nm) signal and (d) prompt ($\lambda = 320$ nm) signal as a function of laser-pulse energy. The solid line shows a linear fit through the data and ensures that we are having single-photon absorption conditions to a good approximation. [(e) and (f)] Fragment mass spectra registered on the MCP after photoexcitation at 440 nm (e) and 300 nm (f). In both cases, one single peak is registered, which corresponds to the dissociation into a neutral trimethylamine and a charged azobenzene molecule.

at the MCP (a) and SED (b) detector after laser excitation at 430 nm (a), 340 nm (a), and 300 nm (b) are shown. In the S_1 band, a delayed action is observed. The action becomes faster at shorter wavelengths, eventually resulting in a prompt signal only [Fig. 5(b)].

To establish the nature of the prompt signal (single versus multiple-photon absorption), we measured the yield of the prompt and the delayed contributions as a function of the laser-pulse energy. The delayed yield as well as the prompt yield are at low pulse energy a linear function of the laser-pulse energy [see Figs. 5(c) and 5(d)], ensuring that we are having single-photon absorption conditions to a good approximation. To determine the dissociation channel, we performed fragment mass spectroscopy at ELISA,³⁸ which is based on a rapid switching of the ring voltages from the storage of parent ions to the storage of fragment ions. In Figs. 5(e) and 5(f), the fragment-ion signal is plotted as a function of the ring voltages. Only fragmentation into a neutral trimethylamine (59 amu) and a charged azobenzene molecule (195 amu) was identified in the S_1 and S_2 bands.

Two isomeric forms of AB exist, with the *trans* configuration being the stable one. Our calculations yield an activation energy of 1.5 eV for the *trans* to *cis* isomerization in the gas-phase and an activation energy of 0.8 eV for the *cis* to *trans* isomerization (see Fig. 6). Exposing the sample to 300 nm light (≈ 4 eV) drives the *trans* $\rightarrow$ *cis* photoisomerization and leads to an increase in the *cis* isomer contribution. By $^1\text{H-NMR}$ measurements, the *trans* to *cis* ratio of Fig. 4 in deuterated methanol was determined at the photostationary state. The data revealed that with irradiation at 302 nm, up to 43% of the azobenzene can be switched to the *cis* state. At 25 °C, thermal back-isomerization occurs at a rate of $1.09 \cdot 10^{-6} \text{ s}^{-1}$. This is equal to a half-life of 176.2 h, which allows easy sample handling when further exposure to light is avoided.

In Fig. 7, the absorption spectrum in solution is shown after UV irradiation for several minutes. An increase in the S_1 peak together with a decrease in the S_2 peak is clearly visible. Moreover, a new absorption band appears at around 250 nm. It increases with the irradiation time and

FIG. 6. Activation barrier for the isomerization in the gas-phase calculated at the B2PLYP-D3/def2-TZVP//B3LYP-D3/def2-TZVP level of theory. Energies are given in eV. The molecular structures were visualized using the CYLview software.³⁹

FIG. 7. The irradiation of AB solution at 300 nm drives the *trans* $\rightarrow$ *cis* photoisomerization which leads to an increase in the *cis* isomer contribution in the absorption spectrum. An increase in S_1 together with a decrease in the S_2 peak is observed. The solid lines represent measurements in solution after UV irradiation for several minutes. The same observation was also obtained for the measurements in the gas-phase as indicated by single measurement points.

is assigned to *cis* isomers. An increase in absorption to S_1 with increased irradiation time is also observed in the gas-phase which is indicated by single-measurement points in Fig. 7.

To investigate the absorption of the *cis* isomers in the gas-phase in more detail, we irradiated the sample at 300 nm for 15 min and performed afterwards action-spectroscopy at ELISA. Figure 8 shows the absorption spectrum of an untreated and a pretreated sample. For both measurements, the ion trap was cooled by liquid nitrogen to 100 K and the methanol-dissolved chromophores were kept dark and cooled to 275 K while being electrosprayed. The untreated sample can be considered to be in the *trans* state, while for the pretreated sample, *trans* as well as *cis* isomers will coexist after the pretreatment over a period of several days. Even though our experimental setup does not allow a selection of the isomers and thus shows overlapping spectra of the two coexisting isomers, differences between the untreated and the pretreated samples are clearly visible. The increase in the absorption of the S_1 state as well as an increase in the absorption in the UV regime are evident and can be assigned to the *cis* isomers. The calculated vertical transition energies for the *trans* as well as for *cis* isomers are drawn as vertical lines with the height corresponding to the calculated oscillator strength. Even though the calculations for higher excited states show discrepancies to the experimental data, they predict an increased absorption for *cis* isomers in the UV range, in agreement with the experiment.

FIG. 8. Absorption spectra of the unirradiated (red) and irradiated (300 nm) samples (blue) in the gas-phase. The unirradiated sample corresponds to the *trans* state, while the irradiated sample has *trans* and *cis* isomers. The measurements were performed with a cooled ion trap, and the methanol-dissolved chromophores were kept in dark and cooled to 275 K while being electrosprayed. Besides the decrease of the S_2 state, an increase of the S_1 state and an increase of the absorption in the UV regime were observed for the irradiated sample, which is assigned to an increase in the *cis* isomers. The calculated transition states (red for *trans* and blue for *cis* isomers) are shown as bars with the height corresponding to the calculated oscillator strength.

CONCLUSION

We measured the absorption-cross section of the positively charged ammonium tagged azobenzene compound in solution and in the gas-phase. The measurements in the gas-phase were performed at the electrostatic ion storage ring ELISA in Aarhus. In both cases, a weak $S_0 \rightarrow S_1$ band and a stronger $S_0 \rightarrow S_2$ absorption band were measured. In addition, a broad absorption band was detected in the UV regime. Time-resolved action-spectra showed delayed action for the S_1 band, which changed into a prompt signal for wavelengths smaller than 340 nm. Fragmentation mass spectroscopy investigations showed a single dissociation channel, and the fragmentation of the ammonium tagged azobenzene into a neutral trimethylamine and a charged azobenzene molecule after one photon absorption. The sample was initially in the *trans* state and exposure to 300 nm light increased the fraction of *cis* isomers. The coexistence of *trans* and *cis* isomers remained over days, if the pretreated sample was kept cold and in the dark. The absorption spectrum of the pretreated sample showed an increase in the S_1 band, a decrease in the S_2 band, and increased absorption in the UV regime in the gas-phase as well as in the solution phase. These changes are assigned to an increased contribution of *cis* isomers. Our studies provide the intrinsic absorption properties of the ammonium-tagged azobenzene complex. The spectroscopy is essential for the design of new fs pump-probe schemes for obtaining

internal isomerization time scales of gas-phase azobenzene chromophores.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for a detailed description of the sample synthesis and of the UV-VIS measurements in solution with the determination of the photostationary state. Computed coordinates and energy parameters of the *trans*- and *cis*-isomers are attached.

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