# *Investigating the Switching Dynamics of an Ammonium-tagged Azobenzene in the Gas Phase and in Polar Solvents*



Project Manager
Prof. Dr. Hermann A. Wegner

Researchers
Marcel A. Strauss

Principal Investigator
Prof. Dr. Hermann A. Wegner

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Clusters
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Software
GAUSSIAN

Institute
Institute of Organic Chemistry

University
Justus Liebig University Giessen

## Introduction

Our investigation aimed at determining the photo-physical properties of an ammonium tagged azobenzene **1** in comparison to the unsubstituted compound **2** in different solvents and in the gas phase. The computational study was performed to support the obtained experimental data. Focus was laid on the activation parameters for the thermal *Z* to *E* isomerization. The absorption of the azobenzene molecule **1** was studied in the gas-phase by measuring photo-induced fragmentation of ions as a function of time. Here, assignment of the bands to the corresponding isomers was supported by time-dependent DFT calculations.

## Methods

We used the Gaussian16 Software to conduct our computations. Structures were optimized in the gas phase applying the B3LYP-D3 method with the def2-TZVP basis set. Single point energy (SPE) computations on a B2PLYP-D3/def2-TZVP level with and without the SMD solvent model were conducted using the previously optimized B3LYP structures. For the time-dependent DFT computations also the optimized B3LYP structures were used. Therefore, the BHLYP method was applied, showing the best agreement with the experimental data. Molecular structures were visualized using the CYLview software.

## Results



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The rates for the *Z* to *E* isomerization of **1** and **2** in different solvents and at different temperatures were determined in order to gain insight into the stabilizing or destabilizing influence of the ammonium tag on the *Z*-isomer. By DFT computations we were able to reproduce the observed tendencies. The computations predict for both compounds a higher activation barrier in MeOH compared to DMSO, which was observed in the experiments by the slower isomerization in MeOH. Furthermore, the free energy of activation for **1** in water was calculated to be highest of all investigated samples, which was confirmed by the experiments. Additionally, the higher activation barrier for **2** in comparison to **1** is reproduced correctly. The results provide essential background information on the influence of the charge attached on the switching properties, which will be of special interest for applications in photopharmacology or water-based host-guest chemistry. In collaboration with the group of Prof. Andersen, we investigated the positively charged ammonium tagged azobenzene compound **1**. The measurements of the absorption-cross section of **1** in the gas-phase were performed at the electrostatic ion storage ring ELISA in Aarhus. This technique provided information on prompt as well as delayed fragmentation, and a single dissociation channel after one-photon absorption was identified. The spectra in solution and in the gas-phase, showed a weak $S_0 \rightarrow S_1$, a strong $S_0 \rightarrow S_2$, and a broad absorption band in the UV regime. The ratio of the various absorption bands depends on the *E* to *Z* isomerization fraction and could be tuned by light irradiation. 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 **1** into a neutral trimethylamine and a charged azobenzene molecule after one photon absorption. The azobenzene was initially in the *E* state and exposure to 300 nm light increased the fraction of *Z* isomers. The absorption spectrum of the irradiated 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. The bands were assigned through time-dependent DFT calculations. Vertical transition energies for the *E* as well as for the *Z* isomers were calculated. Though the calculations for higher excited states show discrepancies to the experimental data, they predict an increased absorption for the *Z* isomers in the UV range, in agreement with the experiment. In conclusion, these supporting computations were of high value to us in explaining our experimental observations.

## Outlook

Our computational resources allow the reliable description of activation parameters for azobenzene isomerization as well as the possibility to predict changes of the absorption spectra upon modifying the azobenzene scaffold. These benefits from computations can save a lot of synthetic work by providing promising guidelines for targeted changes of the azobenzenes

properties. Future investigations will also be conducted with support from accompanying computational studies on the Skylla Cluster Gießen.

## Figures





## Publications

[1]Gruber, E.; Strauss, M. A.; Wegner, H. A.; Andersen, L. H. 2019: Action-spectroscopy studies of positively charge-tagged azobenzene in solution and in the gas-phase. J. Chem. Phys. 150, 8, 84303. https://doi.org/10.1063/1.5085743

[2] Strauss, M. A.; Wegner,H. A. 2019: Influence of an Ammonium Tag on the Switching Dynamics of Azobenzenes in Polar Solvents. ChemPhotoChem 1016, 293. https://doi.org/10.1002/cptc.201800264

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