



Deflection of Indol and Indol-water molecules in an inhomogeneous electric field

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1. Introduction

This report is a summary of my work on a project in the *Controlled Molecule Imaging* research group during DESY summer program 2013.

When atoms or molecules expand from a reservoir at high pressure into vacuum an atomic or molecular beam is created. Physical chemistry and gas-phase molecular physics experiments often use supersonic expansion through pulsed valves to create cold molecular beams (rotational temperatures of less than 1 K can be achieved). However, these beams often consist of multiple conformers (structural isomers) and clusters of different molecules. For instance, if anyone would like to do diffraction experiments with these molecular beams, the pattern would be a superposition of the conformers/clusters. Nevertheless, different conformers can be spatially separated by exploiting their specific interaction with an electric field. The production of conformer-selected samples of biomolecules will enable us to perform a new class of experiments on these systems. For example, for ultrafast electron and X-ray diffraction experiments a so called “molecular movie” (which measure chemical processes with spatial and temporal atomic resolution), the preparation of conformer-selected samples might be crucial [1].

2. Theory

2.1. Stark effect

Most molecules possess an electric dipole moment. The electric dipole moment is a measure of the separation of positive and negative electrical charges in a system of electric charges. Such molecules are called polar molecules. Molecules with a center of inversion or which cannot possess an electric dipole moment for symmetry reasons are called nonpolar.

But in an external electric field \vec{E} , dipole moments are induced in both polar and nonpolar molecules:

$$\vec{\mu}_{ind}^{el} = -\alpha \vec{E},$$

where α is polarizability (the ability for a molecule to be polarized).

In an inhomogeneous electric field the spatial variation in potential energy causes a molecule to experience a force which is dependent on the effective dipole moment, μ_{eff} , of the molecule and can be evaluated as

$$\vec{F} = \vec{\mu}_{eff}(E) \cdot \vec{\nabla} E.$$

All conformers of a molecule have the same primary structure (the same mass and the same bonds between the atoms). However, their dipole moments, which are mostly determined by the secondary structure (the orientations of the functional groups in the molecular frame) are distinct. Therefore these different species will experience a different acceleration (conformer dependent acceleration) in the presence of a strong inhomogeneous electric field. This leads to the separation of conformers as well as their quantum states.

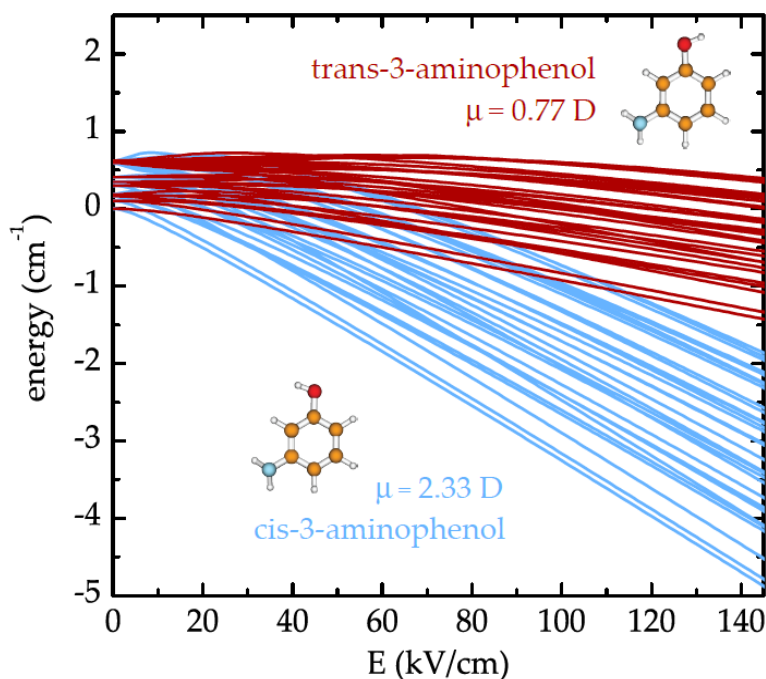


Figure 1. Molecular structures, dipole moments, and energies of the lowest rotational states of cis- and trans-3-aminophenol as a function of the electric field strength

Figure 1 shows an example of Stark curves for *cis*- (blue) and *trans*- (red) 3-aminophenol. These are the energies of the lower rotational states. As one can see from the inset the dipole moments of the two conformers are different ($\mu=0.77$ D for *trans*-3-aminophenol and $\mu=2.33$ D for *cis*-3-aminophenol) and the broader the divergence of energy is, the larger the effective dipole is.

2.2. Indole

Centuries before the structure of Indole was known, many of its derivatives were important commercial products for textile dyes and in perfume production. Even today Indoles continue to impact on both of these markets. Nowadays Indole-containing compounds are best known for their medicinal properties in the pharmaceutical industry. Moreover, recently the use of Indoles expanded into facets of agriculture, animal health, flavor enhancers and the relatively new areas of dietary supplements and nutraceuticals (food containing additives which provide extra nutritional value) [3]. Thus, experiments investigating Indole properties are essential for the pharmaceutical industry.

However, as the study of biomolecules outside of their natural environment can be met with skepticism, one needs to at least partly mimic the molecule's native environment by adding solvent molecules. In our experiments water molecules play the role of this solvent.

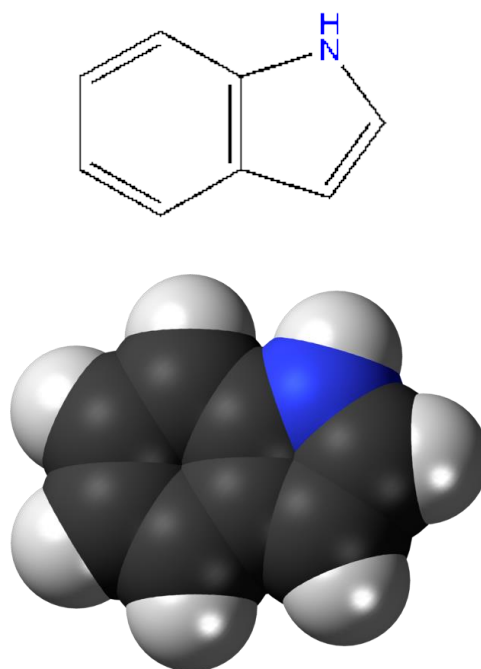


Figure 2. Skeletal formula and space-filling model of the indole molecule. Black: carbon, white: hydrogen, blue: nitrogen [4]

3. Experimental setup

A schematic of the gas-phase molecular beam setup and deflector is shown in Figure 3. It consists of three differentially pumped vacuum chambers. The source chamber housing a CW valve containing a molecular sample (backing pressure ~ 1 -7 bar, vacuum chamber evacuated to $\sim 10^{-6}$ mbar), the deflector chamber with the electrostatic deflection device (which consists of a rod and a trough (electrodes) and between them a potential difference applied to produce a strong inhomogeneous electric field), and the detector chamber housing a standard Wiley-McLaren time-of-flight (TOF) setup and a multichannel plate (MCP) detector (molecules are ionized by focused laser pulses and the ions produced are accelerated towards the MCP). Two skimmers are placed downstream from the nozzle in order to narrow the velocity distribution, to reduce the transverse velocity component of the beam and hence to collimate the molecular beam before entering the deflector.

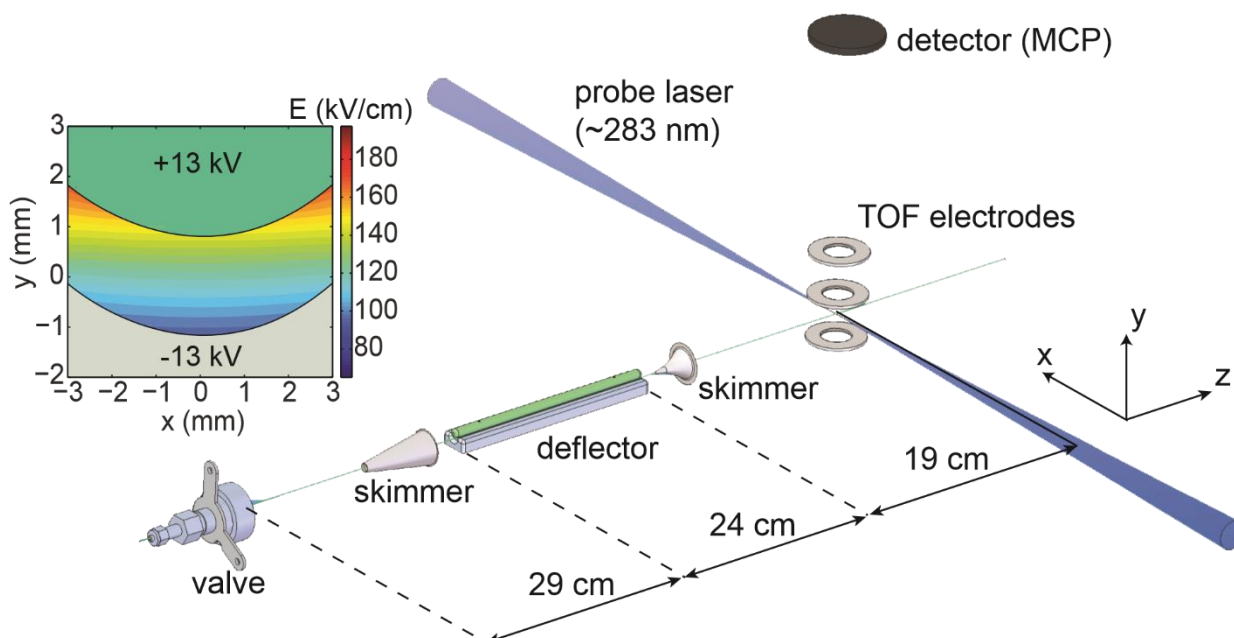


Figure 3. The experimental setup, consisting of a CW valve creating a supersonic expansion of target molecules, an electrostatic deflector and a detection region with time-of-flight mass spectrometer. The inset shows the inhomogeneous electric field created inside the deflector for voltages of ± 13 kV applied to the rod and trough, respectively. [2]

The idea behind all of this is straightforward. As molecules in a homogeneous electric field follow a straight path and in an inhomogeneous field follow a curved path, one needs a strong inhomogeneous field to enable deflection of Indole molecules. Deflection is described by the Stark force and the Stark force depends on the effective dipole moment. Therefore, the bigger the effective dipole moment a molecule has, the bigger the observed deflection. Moreover, the dipole moment of different rotational states of a molecule is not the same, as shown in Figure 1.

The ground state has the largest Stark shift and molecules residing in this state are deflected the most. Ideally one needs to isolate and use rotational ground state molecules. Therefore, the rotational temperature of the molecular beam should be made as low as possible, ~ 1 K, by using a high-pressure supersonic expansion. An inert backing gas (such as Helium or Neon) is employed because it is non-polar, which means it has no dipole moment, and thus it will not be deflected.

4. Measurements and results

By using this setup we are able to measure spatial profiles. In order to observe how the signal intensity of the Indole ions varies spatially one needs to take spatial pictures of the molecular beam while scanning y-direction with the laser (see Figure 3). And to obtain deflection profiles one needs to vary the voltage applied on the deflector's rod and trough as well.

Figures 4 and 5 show the TOF spectrum observed without and with the molecular beam respectively.

Figure 6 shows a zoomed region of the spectrum in which we are mostly interested with Indole peak.

Figure 8 shows how the deflection of Indole molecules depends on the applied voltage. Position means the position of the molecular beam relative to the laser.

On the Figure 9 spatial profiles of Indole, Indole-water, Indole-water2 and Indole-water3 are plotted together. As one can see at the position around 2.5 mm there is still a good signal from Indole, but it mostly caused by the signal from blown up Indole-water clusters.

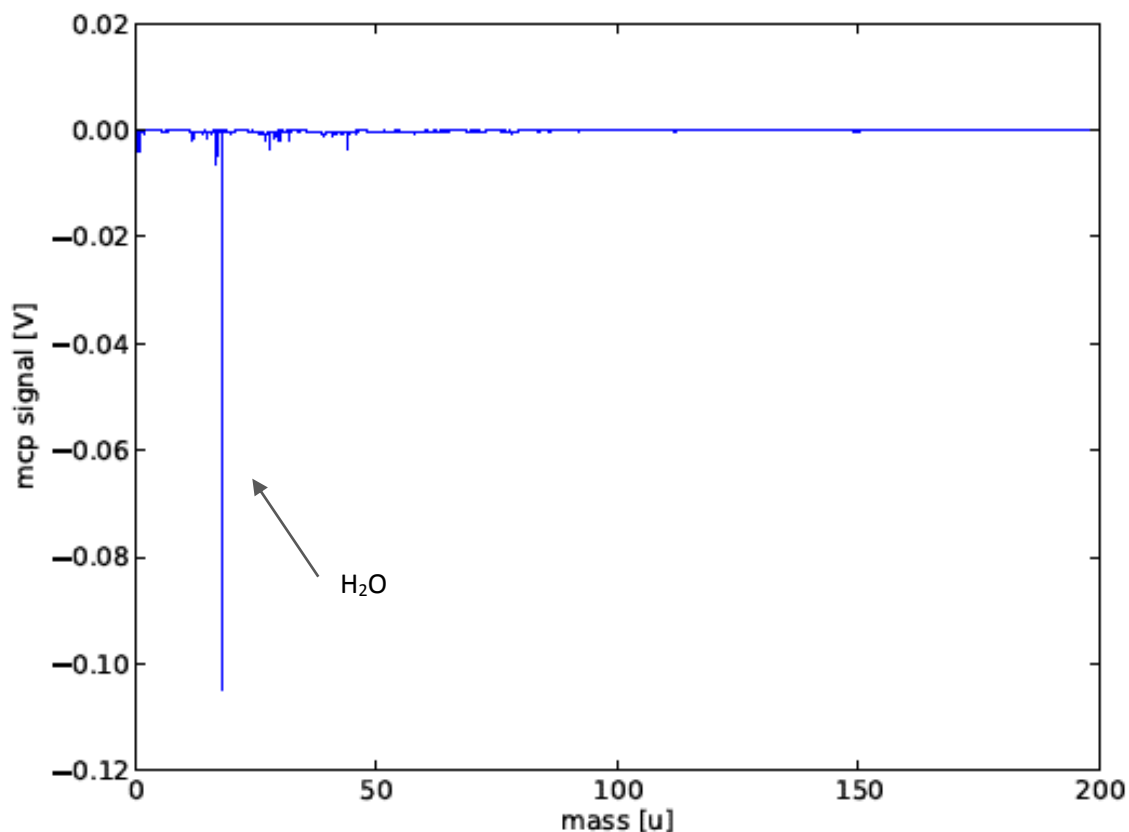


Figure 4. TOF spectrum of background.

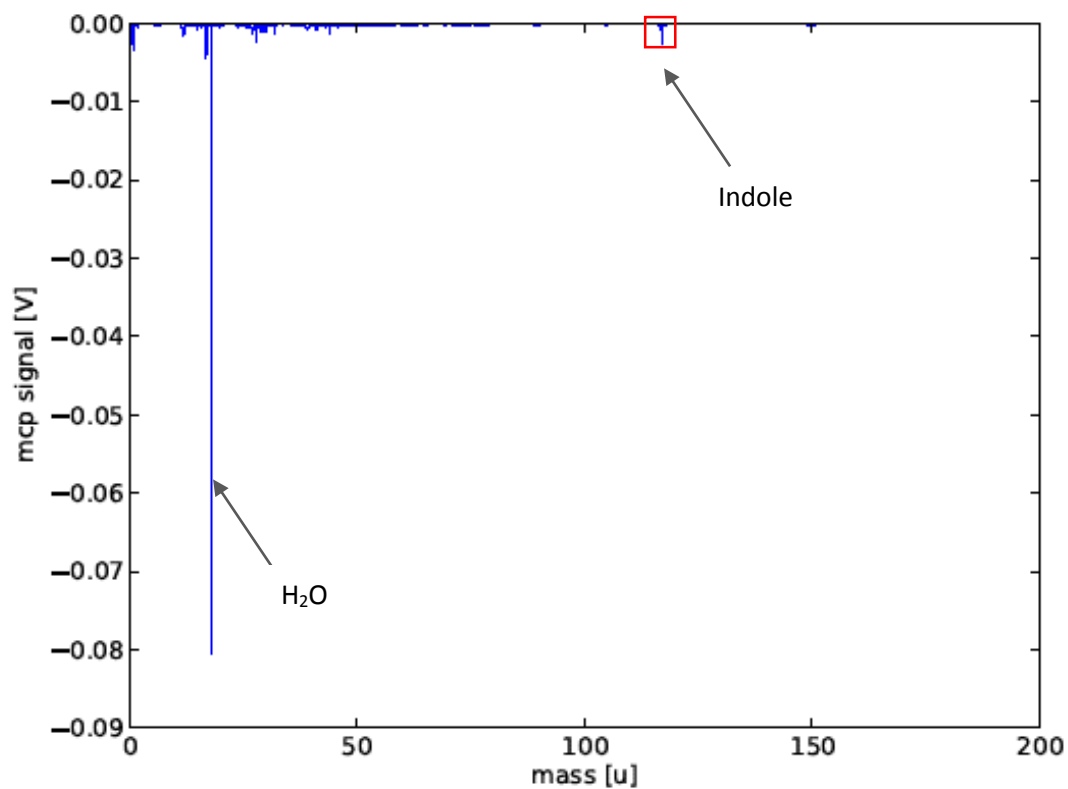


Figure 5. TOF spectrum with the molecular beam.

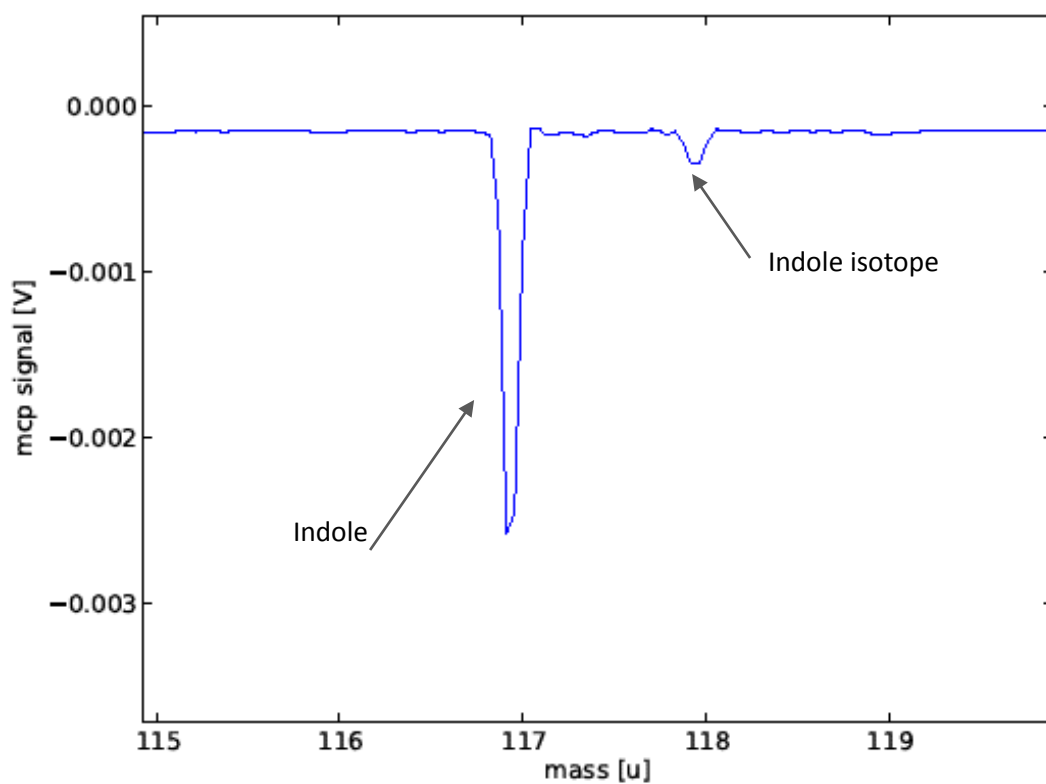


Figure 6. Zoomed TOF spectrum of Indole.

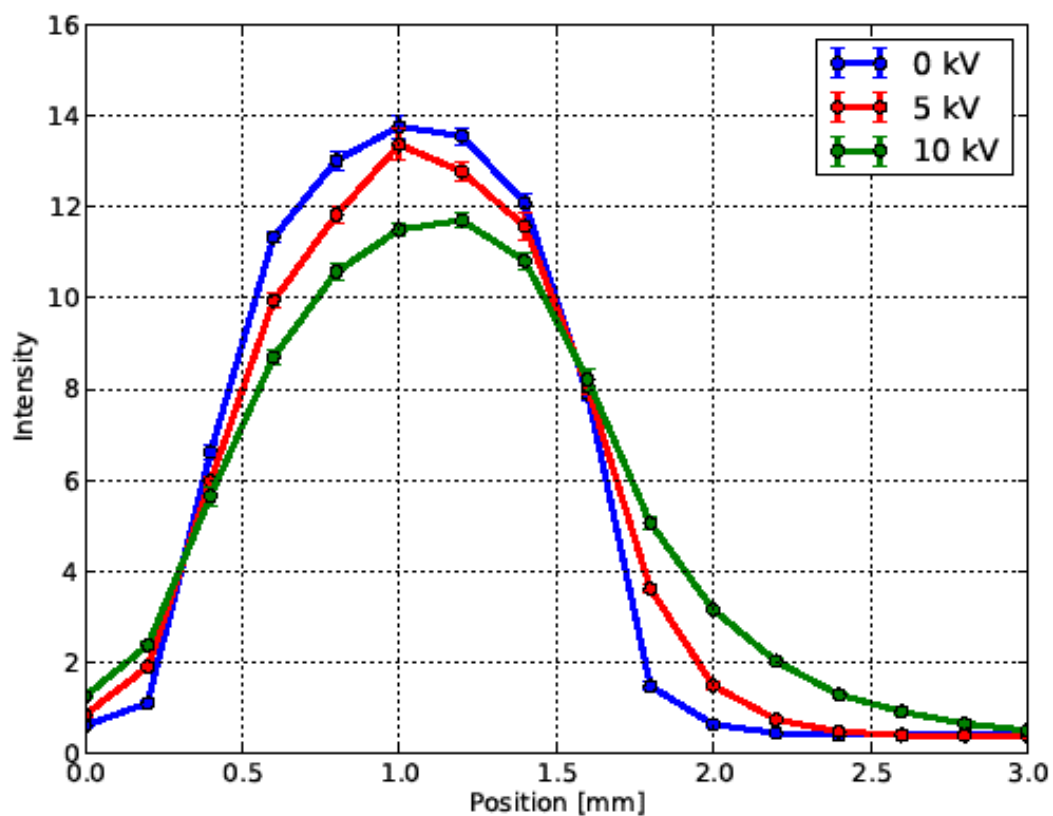


Figure 8. Deflection profile of Indole.

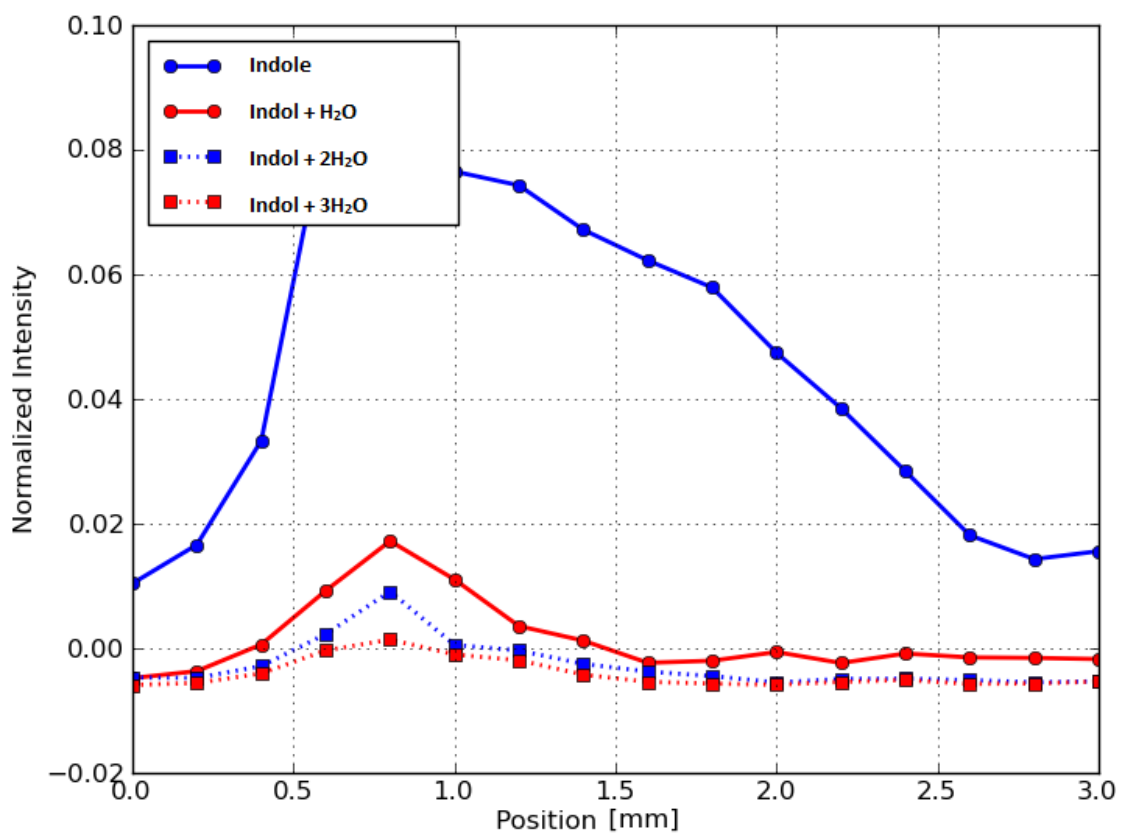


Figure 9. Deflection profile of Indole, Indole-H₂O, Indole-2H₂O, Indole-3H₂O

Conclusion

The main goal of my project here was the preparation and calibration of the setup for a more significant experiment at PETRA III: investigation of the molecular response to photoionization. A water solvent molecule attached to Indole changes the environment of the latter and allows study of the modification of Indole's intrinsic properties. After the separation of Indole and Indole-water clusters in a molecular beam using the electric deflector the deflected part of the beam serves as an ideal sample to study charge redistribution processes. The investigation of photo-induced processes in clusters of complex molecules with well-defined stoichiometries is just the first step towards the novel investigations of considerably larger systems.

Acknowledgments

I would like to thank Thomas Kierspel, my supervisor and thoughtful guide to the molecular physics, who explained to me clearly and patiently anything I wanted to know. I'd like to thank Jochen Küpper for allowing me to work in an area of physics that I might otherwise have never come across and for giving me a fantastic opportunity to participate in the experiment at PETRA III which makes my stay here complete. And of course I'd like to thank everyone in the CMI research group for their care, hospitality and jokes about Russians.

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