Single-colour isomer-resolved spectroscopy

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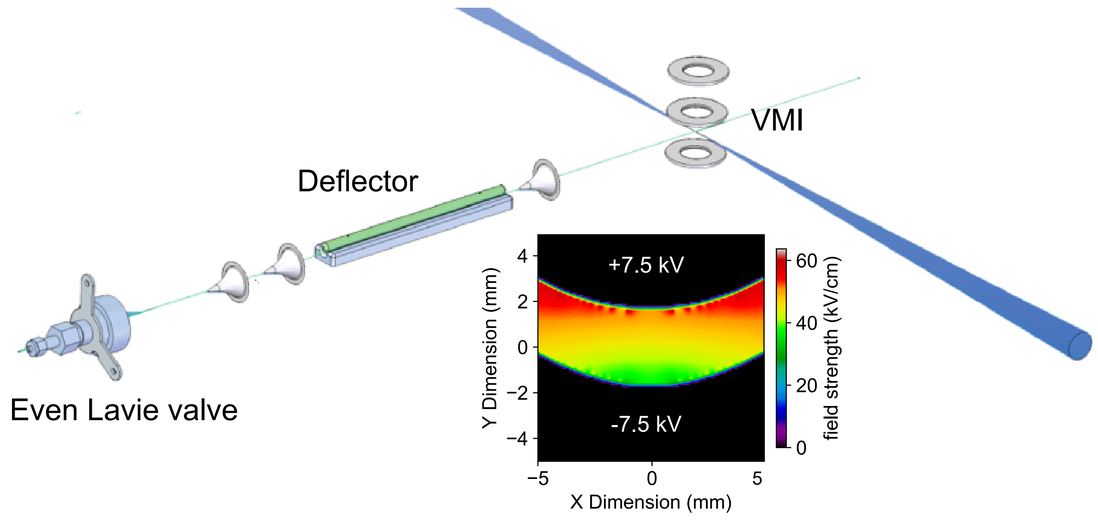
Introduction

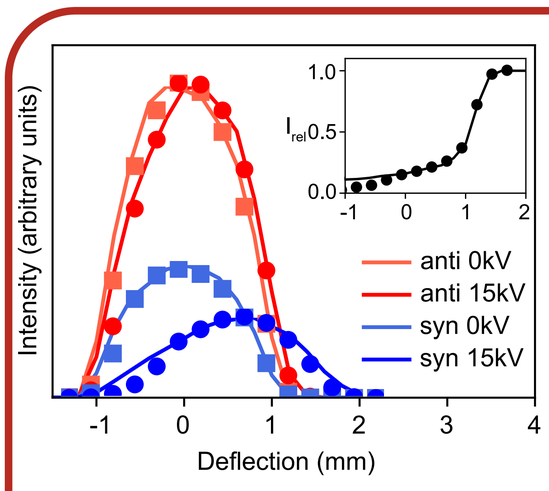
Structural isomers, such as conformers or tautomers, are of significant importance across chemistry and biology, as they can have different functionalities. In gas-phase experiments using molecular beams, formation of many isomers cannot be prevented and their presence significantly complicates assignment of spectral lines. Current isomer-resolved spectroscopy techniques heavily rely on theoretical calculations or make use of elaborate double-resonance schemes.

We show here that isomer-resolved spectroscopy can also be performed using a single laser wavelength. In particular, we demonstrate single-color isomer-resolved spectroscopy by utilizing electrostatic deflection to spatially separate the isomers.

Experimental setup

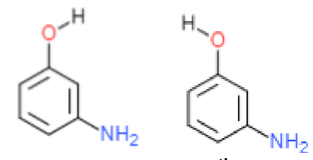


Experimental results

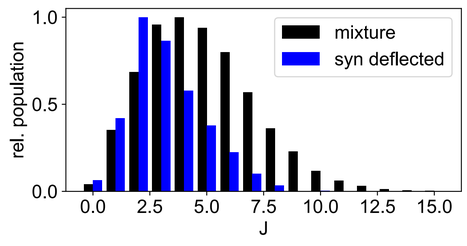


Deflection

We measured the deflection of 3-aminophenol at a potential difference of 15kV on our deflector. For the anti conformer there is hardly any deflection, which allows us to probe an almost pure sample of syn conformers above 1.2 mm, while a relatively pure sample of anti conformers can be probed around -1mm. The insert shows the relative purity of the syn conformer with respect to position.



Deflection is rotational state dependent, the lower rotational states typically deflect more than the higher states. This means the rotational energy distribution changes with probing different parts of the beam. On the right a normalised state distribution for the non-deflected beam can be seen, along which a distribution for the deflected beam around 1.4 mm, in which the relative population of the lower rotational levels has increased.



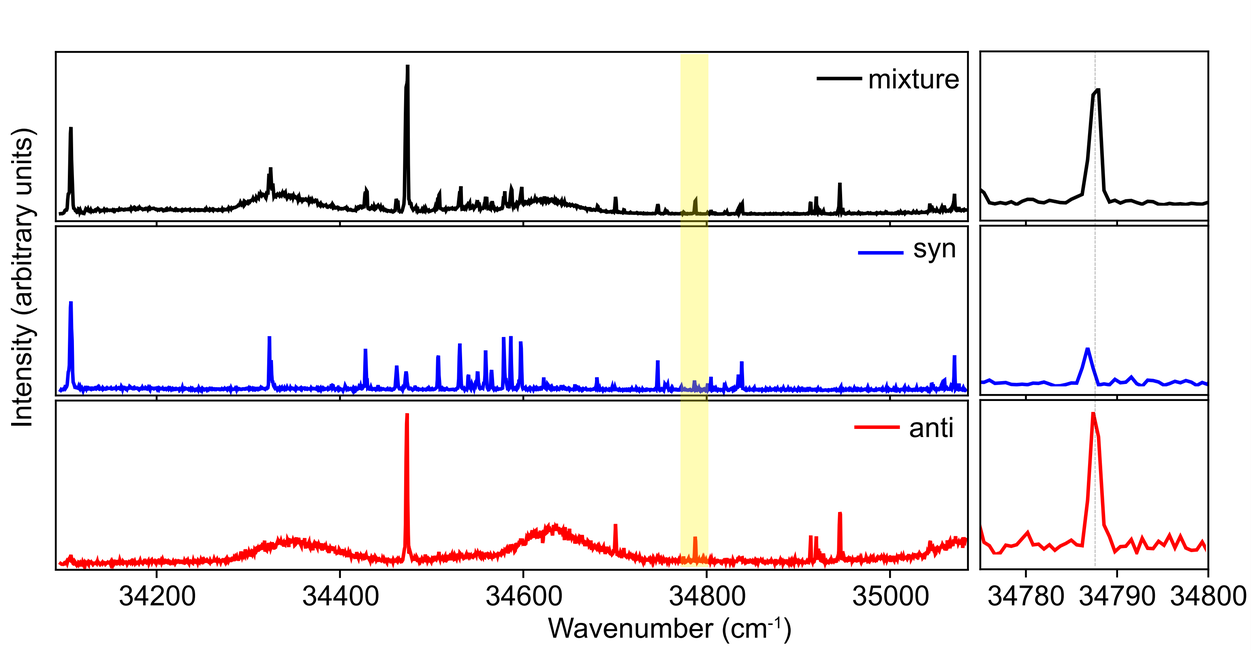
Single-colour isomer-resolved spectroscopy

The top plot shows a spectrum measured in the center of the molecular beam (around 0 mm in the image above) without any potential difference applied to the deflector.

The middle plot shows a spectrum measured on the most deflected edge of the molecular beam (around 1.4 mm in the image above) with 15 kV applied to the deflector.

The bottom plot was measured at the least deflected side of the beam, where the beam is depleted of syn conformers (around -1 mm in the image above).

A zoom-in of the highlighted area is shown on the right, where we noticed two peaks that are very close together, of which one can be assigned to the anti- and one to the syn conformer. Without the electrostatic separation this would not have been possible.



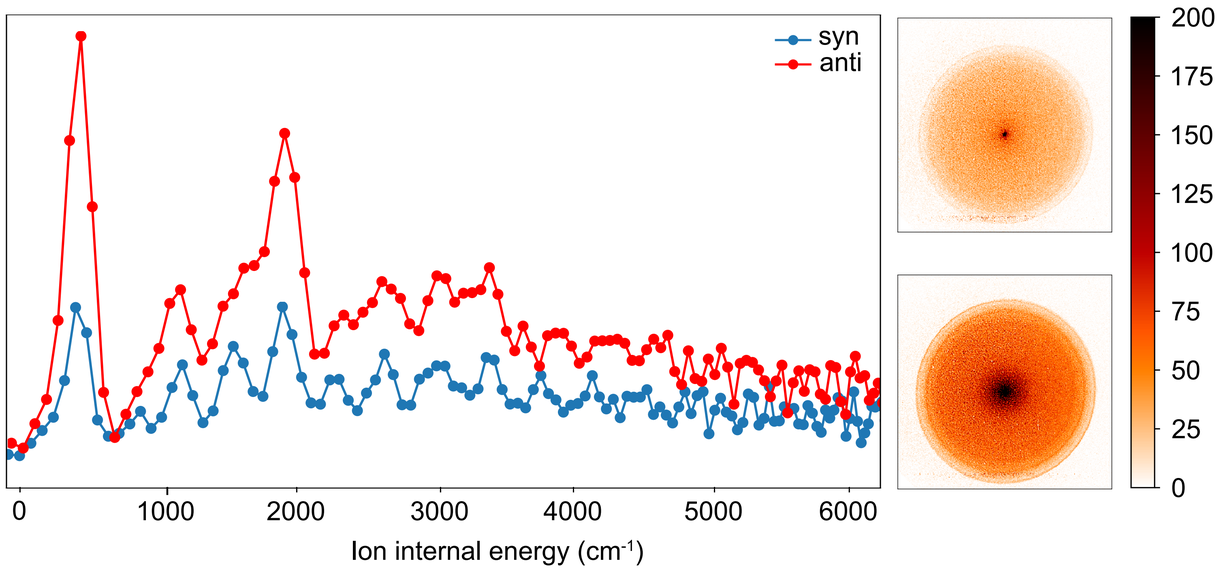


Photo electron spectroscopy

We measured photo electron images with resonance enhanced multi-photon ionization. On the right the measured photo electron images can be seen, the syn conformer on top and the anti conformer below. At first glance these images do not show a lot of structure and the main difference between the images is the intensity difference. However, if we apply an inverse Abel transform and plot the radial intensity distribution we see a structure. In the plot on the left we show the intensity against the internal energy of the ion with zero corresponding to the largest radius and towards 6000 cm^{-1} internal energy increases and the kinetic energy decreases. This shows small differences in the respective intensities of the rings exist between the conformers.

Conclusion and Outlook

We have demonstrated to be able to spatially separate the conformers of 3-aminophenol using the electrostatic deflector. This enables us to measure spectra of a single conformer and assign previously unassigned peaks to an conformer.

We further demonstrated that we can gain conformer-resolved spectroscopic insight about the corresponding cation through photo electron imaging by detecting the photo electrons from the resonance-enhanced multi-photon ionization process. The combination of these approaches enables conformer-resolved ultrafast electronic relaxation measurements through conformer- and time-resolved photo electron imaging

Acknowledgments

We gratefully acknowledge financial support by the NWO through grant STU.019.009.