Investigation on fragmentation processes during atmospheric pressure laser ionization

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Introduction

Fragmentation of parent ions is observed for most ionization methods. Using laser ionization in vacuum [multi photon ionization (MPI)], the extent of fragmentation varies from parent ion only formation to fragmentation yielding mostly atomic ions, depending on experimental parameters. The process responsible for MPI fragmentation is thought to be the „ladder-switch-mechanism“, where the absorption of further photons above the ionization potential („ladder of energy“) is truncated at a point at which the rate of absorption can not compete with the rate of unimolecular reactions within a laser pulse of ns duration. At this maximum of absorption, the molecule „switches“ via fragmentation to an new ladder of product ions.[1]

In contrast, laser ionization at atmospheric pressure (APLI) leads always to very little fragmentation even at sufficiently high laser power densities. It has been argued that at AP excited ionic states of the parent ion are rapidly quenched to the ground ionic state by collisions with the background gas.[2] However, the timescale of such switching reactions (pico seconds) suggest that efficient fragmentation should always occur, as in observed in vacuum MPI.

Methods

- Mass spectrometer: Bruker micrOTOF equipped with a Multi Purpose Ion Source (MPIS).
- Laser systems:
  - excimer laser (KrF*, 248 nm, 0.1 – 8.5 mJ, 4-6 ns; ATL Atlex 300)
  - flash lamp pumped quadrupled Nd:YAG laser (266 nm, 1– 2.5 mJ, 5 ns; Spectron Laser Systems)
- Analytes: 3-(anthracene-9-yl) propionic acid (APA), 20 µM in Dichloromethane
- Direct infusion: 30 µl / min
- Focusing: Quartz lens with 200 mm nominal focal point
- Gaussian09, Revision C.01[3] for geometry optimizations, potential-energy surface scans and excited states calculations (with TD-DFT) using B3LYP-D/def2-TZVPP level of theory

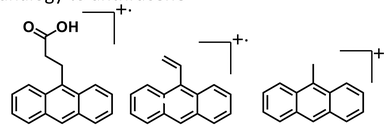
Experimental

Transfer:

- Transfer and source parameters were optimized during direct infusion using the Bruker micrOTOF
- Different anthracene derivatives and other polyaromatic molecules were chosen as analytes

Targeted molecule and fragmentation:

- 3-(anthracene-9-yl) propionic acid (APA)
- Derivatization reagent for alcohols for APLI
- Consist of: Ionophor, spacer, and anchor-group
- Fragmentation from [$M^{+\cdot}$] (m/z 250) to m/z 204 and m/z 191, respectively.
- Further fragmentation by cleavage of CH m/z 13 in analogy to anthracene



Fragmentation during APLI

- Carried out with excimer (248 nm) and Nd:YAG-laser systems (266 nm)
- Study of fragmentation with an without focussing of the laser-beam

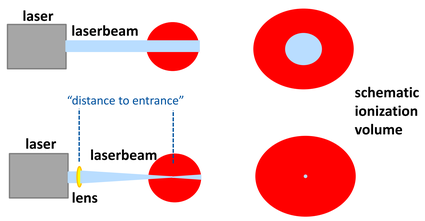


Figure 1: Schematic pathway of the laser beam and resulting ionization volume with and without focusing of the beam.

- Investigation of the extent of fragmentation in dependence of laser power density and wavelength.
- KrF* (248 nm): min. 1.0 MW/cm², max. 1.3 GW/cm²
- Nd:YAG (266 nm): min. 10 MW/cm², max. 8.3 GW/cm²

Results

Fragmentation during transfer

- Fragmentation during ion transfer is a well known process, particularly at intermediate pressures
- Ions decay through collision induced dissociation (CID). Extent of dissociation depends on the local pressure (collision number) and applied voltages (collision energy) during transfer
- Ultimately soft transfer needed to study fragmentation experiments with laser ionization at AP

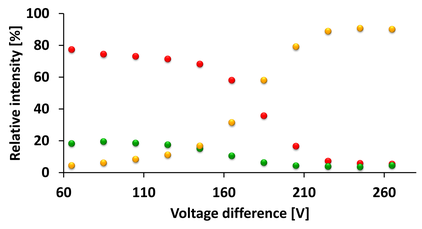


Figure 2: Fragmentation behaviour (CID) in dependence of the potential between transfer capillary exit and skimmer

Results for the focused excimer laser system

- Extent of fragmentation without focusing of the laser beam negligible
- m/z 204 and 191 are the only relevant fragments of the target analyte observed
- Increasing laser energy leads to increased signal intensity of all species
- Power densities exceeding 0.5 GW/cm² have no further effect on fragmentation behavior → saturation

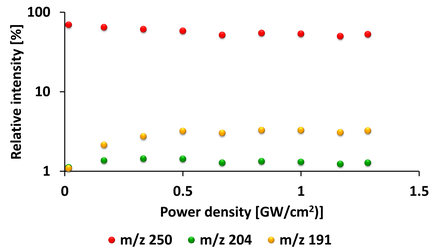


Figure 3: Fragmentation behaviour in dependence of the laser energy of the focused excimer laser system. Note log intensity scale.

Results for the focused Nd:YAG laser system

- Intensity of fragmentation dependent on lens position
- Different fragmentation behavior for target analyte: Generally the extent of fragmentation is higher
- Increase of power density has no effect on fragmentation behavior as they are already higher then with the excimer → saturation

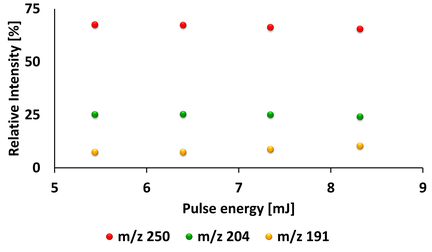


Figure 4: Fragmentation behaviour in dependence of the laser intensity of the focused Nd:YAG laser system

Influence of focal point position

- Position of the focal point inside the MPIS had only minor effects on the fragmentation extent
- Adjusting the focal point on the quartz glass window strongly increased fragmentation while damaging the glass
- Up to 70 % TIC signals attributed to fragmentation upon glass damage
- Surface ablation effects responsible for fragmentation

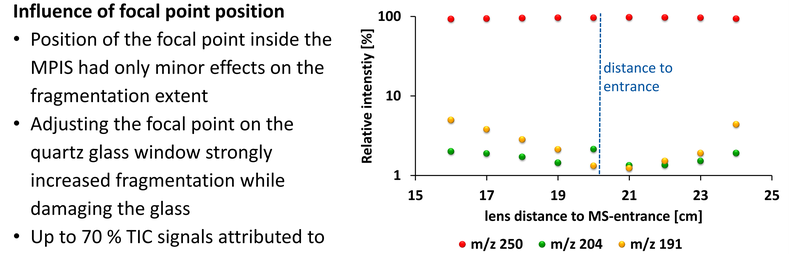


Figure 6: Fragmentation behavior in dependence of lens distance to the mass spectrometer sampling orifice

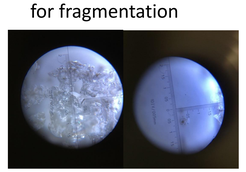


Figure 5: damaged Quartz glass window after laser irradiation (excimer/ Nd:YAG) in 10x magnification

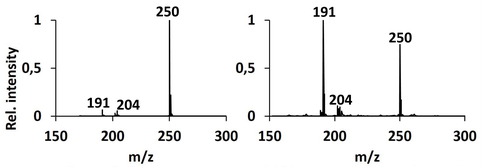


Figure 7: Fragment spectrum of APA obtained with unfocused (left) and focused (right) excimer laser radiation

Ab initio calculations

- Ionization energy (IE) for APA 6.9 eV
- Fragmentation energy (FE) 9.1 eV
- 2-photon absorption leads to 9.3 eV (Nd:YAG) / 10.0 eV (KrF*)
- two photons sufficient for both ionization and fragmentation, supporting a [1+1] REMPI process

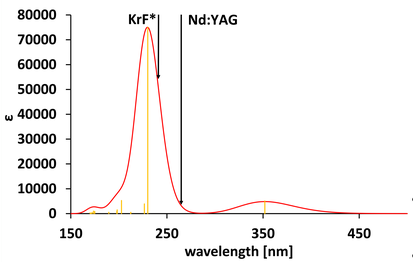


Figure 8: calculated absorption spectrum of APA using Gaussian09

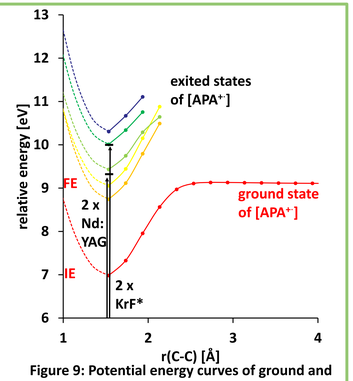


Figure 9: Potential energy curves of ground and excited states of the APA cation (calculated with TD-DFT) along the C-C dissociation coordinate

- Spectrum and IE in accord with literature for anthracene
- Both laser system in close resonance with excited states of APA^+

Summary / Outlook

- Position of focus lens impacts strongly the fragmentation during APLI
- Laser wavelength has a negligible influence on fragmentation
- Smaller fragments with m/z < 191 not detectable at atmospheric pressure
- Further study of fragment fates, e.g., charge transfer upon collisions with analyte
- Conduct experiments with other API MS-systems to search for smaller fragments
- Additional ab initio calculations to support the experimental results

Literature

[1] Dietz (1982): A model for multiphoton ionisation mass spectroscopy with application to benzene, CHEM PHYS Volume 66 p. 105-127.
[2] Kolaitis (1986): Atmospheric Pressure Ionization Mass Spectrometry with Laser-Produced Ions, ANAL CHEM 58, p. 1993-2001
[3] Frisch (2009): Gaussian09, Revision C.01, Gaussian, Inc., Wallingford CT