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Rheinische  
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# **Fachgruppentreffen**

## **FTMS und hochauflösende**

## **Massenspektrometrie 2015**

**17.-18. September 2015**



**[www.ftms.uni-bonn.de](http://www.ftms.uni-bonn.de)**

## Information

### Conference Site

Institut für Physikalische und Theoretische Chemie der Universität Bonn

Haus der Physikalischen Chemie

Wegeler Str. 12, 53115 Bonn

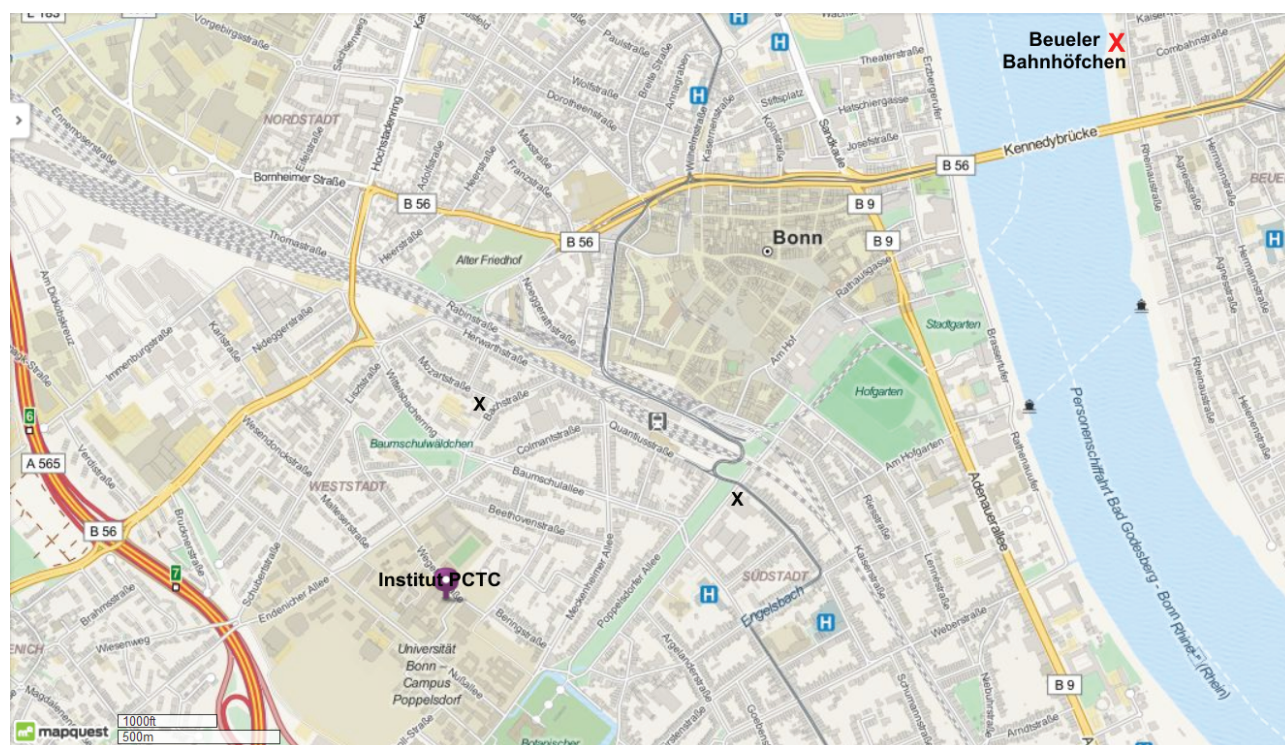
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### Conference Dinner

Beueler Bahnhöfchen

Rheinaustr. 116, 53225 Bonn



## Program

### Thursday, 17.09.2015

- 9:00 Welcome
- 9:15 Philippe Maître:  
Isomerization of peptide fragments probed by IR spectroscopy under FT-ICR conditions
- 10:15 Gereon Niedner-Schatteburg:  
Infrared spectroscopy of N<sub>2</sub> adsorption on size selected iron, nickel and cobalt cluster cations in isolation
- 10:35 *Coffee*
- 11:00 Martin Clemen:  
Fragmentation Reactions of Azo Dyes
- 11:20 Jürgen H. Gross:  
Relative Metal-Carbene Bond Strengths in Non-Heteroatom Stabilized Dimesitylcarbene Complexes of Copper, Silver, and Gold
- 11:40 Konrad Koszinowski:  
Which Cations Form in Solutions of Grignard Reagents?
- 12:00 *Lunch*
- 14:30 Yessica Brachthäuser:  
Development and characterization of an FT-QIT
- 14:50 Wayne Lippert:  
(Ultra-)High Resolution Tandem Mass Spectrometry in a Mobile MR-TOF Mass Spectrometer
- 15:10 *Poster and Coffee*
- 16:30 Stefan Grimme:  
First Principles Calculation of Electron Ionization Mass Spectra
- 17:30 Mitgliederversammlung  
der Fachgruppe FT-MS und hochauflösende Massenspektrometrie
- 19:30 *Dinner: Beueler Bahnhöfchen*

## Friday, 18.09.2015

- 9:00 Christopher P. Rüger:  
Improved processing of gas chromatography atmospheric pressure chemical ionisation ultra-high resolution mass spectrometric data for complex mixtures
- 9:20 Michael Mormann:  
Coupling Thin-Layer Chromatography and Desorption Electrospray Ionization (DESI) – Fourier-Transform Ion Cyclotron Resonance (FT-ICR) Mass Spectrometry for Glycosphingolipid Analysis
- 9:40 Jens Fuchser:  
Ultrahigh-resolution Insights in Time and Mass for Climate History by Determining Lipid Biomarkers in Marine Sediments with LDI FTMS Imaging
- 10:00 Diana Hofmann:  
Heat impact caused molecular level changes in solid and dissolved soil organic matter
- 10:20 *Coffee*
- 11:00 Xuxiao Wang:  
Studying the derivatization reaction for selective analysis of heavy crude oil by ultra-high resolution mass spectrometry
- 11:20 Ruoji Luo:  
Investigation on the photo-oxidative degradation of oil spills by FTMS
- 11:40 Christopher J. Kampf:  
Secondary brown carbon – Identification of light-absorbing compounds in aerosol mimicry by ultra-high resolution mass spectrometry
- 12:00 *Closing remarks*

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## Isomerization of peptide fragments probed by IR spectroscopy under FT-ICR conditions

Philippe Maître

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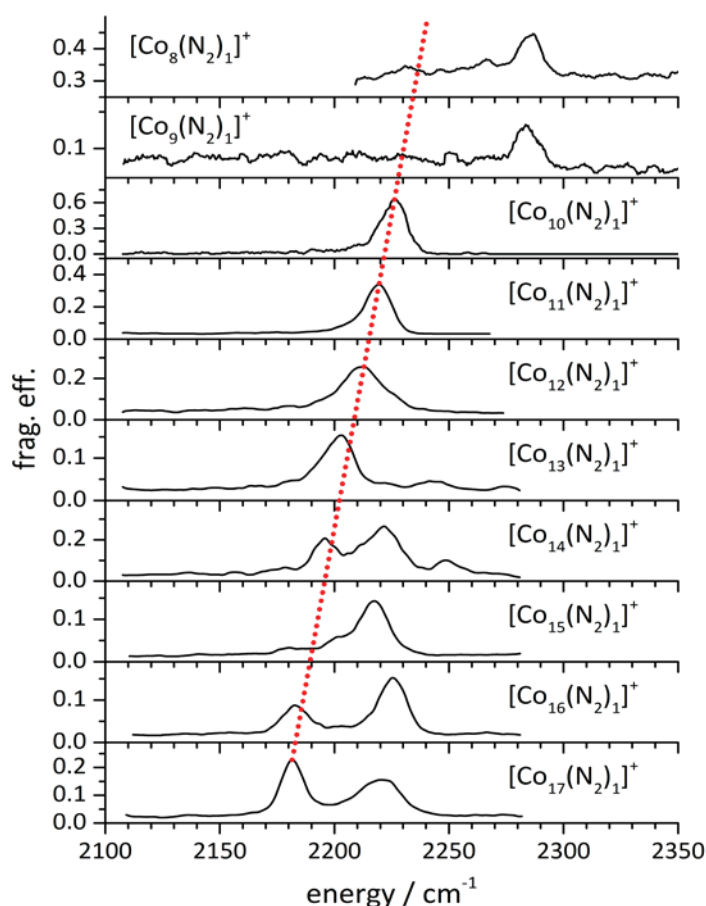
Tandem Mass spectrometry is heavily used in proteomics for determining peptide primary sequence. In these experiments, protonated peptides are collisionally activated, and their sequence is derived from their fragmentation mass spectra. For example, series of N-terminal  $a_n$  and  $b_n$  ions (n being the number of residues) corresponding to the  $C_\alpha$ -C(O) and C(O)-N bond cleavage, respectively, can be observed. Complex chemistry may also occur following or concomitant with these bond cleavages. It has been early suggested, for example, that nucleophilic attack on the electrophilic site formed upon bond cleavage could lead to a variety of structural motif for  $b_2$  ions. More recently, based on the similarity of fragmentation mass spectra of peptides with permuted sequences, it has been suggested that permutation of sequence may also occur under collisional activation of protonated peptides.

Understanding the structure, energetics, and decomposition pathways of the gas phase peptide fragments is thus central in this context. And infrared spectroscopy integrated to MS/MS has been critical for characterizing the structure of peptide fragments. An overview of recent results will be presented, with a special focus on the characterization of permuted structures resulting from macrocyclic structures formed upon head-to-tail cyclisation of peptide fragments.

## Infrared spectroscopy of N<sub>2</sub> adsorption on size selected iron, nickel and cobalt cluster cations in isolation

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Recently, we had managed to unravel the magnetic structure of 3d metals by combination of X-ray synchrotron radiation with state-of-the-art cryo FTMS ( $T_{\text{trap}} < 20$  K) [1]. Here we will present a further enhanced FTMS setup that incorporates tandem cryo trapping of size selected clusters. We have used this upgraded approach to record IR active N<sub>2</sub> stretching frequencies in isolated and size selected cobalt cluster nitrogen adsorbate complexes,  $[\text{Co}_n(\text{N}_2)_1]^+$  by virtue of InfraRed Photon Dissociation (IRPD) spectroscopy [2]. The observed frequencies of the  $[\text{Co}_n(\text{N}_2)_1]^+$  complexes ( $n = 8 - 17$ ) are significantly redshifted (2180 to 2290  $\text{cm}^{-1}$ ) with respect to the IR inactive vibrations of free N<sub>2</sub> (2359  $\text{cm}^{-1}$ ). These bands are assigned to a  $\mu_1$  head-on type of coordination of the N<sub>2</sub> to the cobalt cluster surface, revealing remarkable cluster size dependent features that still remain to interpret.



Most recently we have extended this approach to record IRPD spectra of  $[\text{Fe}_n(\text{N}_2)_1]^+$  and of  $[\text{Ni}_n(\text{N}_2)_1]^+$  complexes. The in part surprising results shall be presented and discussed.

**Fig. 1** IRPD spectra of  $[\text{Co}_n(\text{N}_2)_1]^+$  for  $n = 8 - 17$ . The dotted red line serves to guide the eye. Its slight tilt with cluster size indicates a conceivable cooperative polarization effect. Note the variation in the observed peak positions and splittings. Multiple major peaks likely indicate cluster core isomers, spin isomers or N<sub>2</sub> bonding isomers while weak sidebands to the blue may arise from combination bands (N<sub>2</sub> stretching and wagging modes). Note the “jump” of the major peak from  $n = 9$  to  $n = 10$ .

[1] *The spin and orbital contributions to the total magnetic moments of free Fe, Co and Ni clusters*, J. Meyer, M. Tombers, C. van Wüllen, S. Peredkov, W. Eberhardt, M. Neeb, S. Palutke, M. Martins, W. Wurth, and G. Niedner-Schatteburg, J. Chem. Phys (2015), accepted

[2] *Infrared spectroscopy of N<sub>2</sub> adsorption on size selected cobalt cluster cations in isolation*, S. Dillinger, J. Mohrbach, J. Hewer, M. Gaffga and G. Niedner-Schatteburg, Phys. Chem. Chem. Phys. (2015), 17, 10358

# Fragmentation Reactions of Azo Dyes

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## Introduction (88/120)

The here investigated molecules, several homologous azodyes, are small compared to those high-resolution mass spectrometry (HRMS) mostly focus on. We used HRMS to unravel fundamental reaction mechanism, where interpretation is still not easy feasible. In some compounds, an interesting fragmentation pattern is found showing the loss of a water molecule from the protonated substances. This loss strongly influences further fragmentations of the molecules and is directly dependent on the position of the carboxylic acid group in these molecules. To get a better insight, a systematic investigation is conducted.

## Experimental Methods (118/120)

The used azo compounds, methyl red, ethyl red, propyl red, ethyl yellow and 2-(4-hydroxy-phenylazo)benzoic acid are commercially available (*Sigma Aldrich*, Germany) while p-ethyl red was synthesized by ourselves [1].

All mass spectra have been recorded using an APEX III FT-ICR mass spectrometer equipped with a 7.05 T magnet (*Bruker Daltonik*, Bremen, Germany). The samples were dissolved in EtOH, diluted with MeOH/H<sub>2</sub>O/FA (50:50:0.2%) to a final concentration of 10-50 pmol/μL and ionized using electrospray ionization.

Fragmentation of the protonated molecular ions were achieved by either SORI-CID (collision gas: argon) or by VisMPD using an argon-ion-laser (*Innova 70*, *Coherent*, Santa Clara, CA, USA) in multiline mode. Irradiation duration of the laser could be varied by a homebuilt shutter system.

## Results and Discussion (289/300)

MS<sup>2</sup> investigation of Ethyl Red, which contains an azobenzene backbone with a diethylamino group in 4'-position and a carboxylic acid group in 2-position, shows an unusual fragmentation pattern. The losses of C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> from the protonated molecule are not observed [2]. The most intensive fragment is the loss of water from the carboxylic acid. The other fragments are various combinations of this water loss with neutral or radical losses from



the molecule. For example, there is the loss of 48 Da,  $\text{H}_2\text{O} + \text{C}_2\text{H}_6$ . This behavior shows the major role of the water loss in directing the whole fragmentation process.

The first modification was to change the alkyl chain lengths of the dialkylamino group. Methyl red and propyl red in this case show the same fragmentation pattern as ethyl red before. Together with the loss of water, we found the signals for the homologous alkyl losses ( $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$  or  $\text{C}_5\text{H}_{12}$ ). These losses lead to fragment signal  $m/z$  236 for all three substances and the rest of the spectra are mostly comparable.

The variation concerning the position of the carboxylic acid group changes the mass spectrum completely. These molecules do not lose water but behave as normally expected with a loss of alkyl residues. This behavior is similar to Ethyl Yellow. This demonstrates that the position of the carboxylic group has important influence on the fragmentation pathways.

All investigations are performed with respect to irradiance through the argon ion laser as well as the storage time in the ICR cell. As shown, several fragmentations are highly dependent on the irradiation time of the precursor ion, which is seen through the  $\text{MS}^2$  spectra and some  $\text{MS}^3$  spectra. This allows a direct access to the reaction mechanisms, which are quite unusual.

### References (max. 5)

- [1] H. G. O. Becker, *Organikum*, 21. Auflage, Wiley-VCH, Weinheim, **2001**.
- [2] J. Peters, J. Grotemeyer, *Rapid Commun. Mass Spectrom.* **2011**, 25, 1169-1172.

### Novel Aspects (16/20)

To explain the  $\text{MS}^2$  and  $\text{MS}^3$  mass spectra of different azo dyes, fragmentation mechanisms are suggested.

### Keywords (max. 5)

FT-ICR MS, SORI-CID, Photodissociation, Fragmentation Reactions, Fundamentals

# Relative Metal–Carbene Bond Strengths in Non-Heteroatom Stabilized Dimesitylcarbene Complexes of Copper, Silver, and Gold

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## Introduction

Many catalytic reactions rely on carbene complexes of copper, silver and gold. Heteroatom substituents at the carbene moiety lead to ylide-type ligands and more stable carbene complexes.<sup>1</sup> Quantum-chemical calculations on methoxymethylidene complexes revealed the trend  $\text{Ag} < \text{Cu} < \text{Au}$  for the strengths of the metal carbene interaction.<sup>2</sup> This is consistent with the productive collision-induced dissociation (CID) of 1,2-dimethoxycyclopropane with copper and gold cations, while the analogous CID with silver cations did not yield a Fischer carbene complex.<sup>2</sup> In the condensed phase, only a few coinage metal complexes whose free carbene ligand features an electronic triplet ground state has been reported.<sup>3;4</sup> Here, we present the first experimental determination of the relative strengths of non-heteroatom-stabilized copper, silver, and gold carbene bonds.

## Experimental

Experiments were performed on a Bruker Apex-Qe FT-ICR instrument (Bruker Daltonik, Bremen). Transition metal complex cations were analyzed by electrospray ionization from dilute solutions (ca.  $10^{-5}$  M) in dry dichloromethane. Solutions were supplied by a syringe pump at  $12 \mu\text{L min}^{-1}$ , sprayed using  $1.2 \text{ L min}^{-1}$  nitrogen nebulizer gas and  $2.0 \text{ L min}^{-1}$  desolvation gas at  $160^\circ\text{C}$ . Tandem mass spectra covering  $m/z$  180–2500 were acquired. The transition metal complex cations were mass-selected in the quadrupole as to include the entire isotopic distribution (isolation window 7–10 u). Collision-induced dissociation was effected using argon collision gas ( $0.5 \text{ L s}^{-1}$ ) in the RF-only hexapole and by varying the collision offset stepwise from 0–80 V.

## Results and Discussion

Relative bond strengths of group 11 metal fragments to dimesitylcarbene ligands were determined experimentally by measuring the center-of-mass collision energies ( $E_{\text{CM}}$ ) at the crossover of precursor and fragment ion abundance; which could be determined with good accuracy and were used as a simple tool for energy estimations.<sup>5</sup> The percentage of dimesitylcarbene,  $\text{Mes}_2\text{C}$ , dissociation was measured in relation to  $E_{\text{CM}}$ . Direct competition with the loss of the sterically demanding ancillary second ligand, imidazolyl-2-idene,  $\text{IPr}^{**}$ , was circumvented as  $\text{IPr}^{**}$  only eliminates at substantially higher collision energies. The most abundant ion of the species of interest, i.e., of intact complex cation and the fragment due to carbene loss, were selected and the intensities of all isotopic peaks of the corresponding signals, each normalized to the sum of the intensities of all signals under study, was plotted versus collision offset voltage or center-of-mass collision energy, respectively.

For the isostructural copper, silver, and gold carbene complexes,  $E_{\text{CM}}$  crossover values were observed at 0.60 eV, 0.50 eV, and 1.01 eV, respectively. The observed trend  $\text{Ag} < \text{Cu} \ll \text{Au}$  for coinage metal to carbene bond strengths is consistent with our observations of the complexes' thermostabilities in the condensed phase. The relative strength of the gold carbene bond compared to the copper and silver analogues is much higher than previously predicted for methoxy-stabilized carbene complexes.

Thus, we have directly determined the relative metal–carbene bond strengths of isostructural  $\text{IPr}^{**}$  copper, silver, and gold dimesitylcarbene cations. Collision-induced dissociation in a tandem mass spectrometer reveals a strong gold carbene bond, a weak copper carbene

interaction, and an even weaker silver carbene bond. The stability trend  $\text{Ag} < \text{Cu} \ll \text{Au}$  correlates with the ratio of energies that are required for the half-conversion to  $\text{IPr}^{**}$  metal cations and free dimesitylcarbene.

### New Aspects

First experimental determination of the relative metal–carbene bond strengths of non-heteroatom stabilized  $\text{IPr}^{**}$  copper, silver, and gold dimesitylcarbene cations.

### Keywords

coinage metal carbene complexes, bond strengths, collision-induced dissociation, breakdown graph, Fourier transform ion cyclotron resonance

### References

1. D. J. Gorin and F. D. Toste, *Nature*, **2007**, 446, 395-403.
2. L. Batiste and P. Chen, *J. Am. Chem. Soc.*, **2014**, 136, 9296-9307.
3. M. W. Hussong, F. Rominger, P. Krämer, and B. F. Straub, *Angew. Chem. Int. Ed.*, **2014**, 53, 9372-9375.
4. M. W. Hussong, W. T. Hoffmeister, F. Rominger, and B. F. Straub, *Angew. Chem. Int. Ed.*, **2015**, doi: 10.1002/anie.201506279.
5. C. A. Schalley and A. Springer, *Mass Spectrometry and Gas-Phase Chemistry of Non-Covalent Complexes*, John Wiley & Sons, Inc., Hoboken **2009**, p. 331.

## Which Cations Form in Solutions of Grignard Reagents?

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The outstanding synthetic utility of Grignard reagents  $\text{RMgX}$  has triggered a keen interest in the speciation of these compounds in solution. Yamaguchi and coworkers used cold-spray ionization (CSI) mass spectrometry to analyze solutions of  $\text{MeMgCl}$  in tetrahydrofuran (THF).<sup>[1]</sup> The authors observed a series of prominent cations, which they assigned as  $[\text{MeMg}_2\text{Cl}_3(\text{THF})_n\text{-H}]^+$ ,  $n = 3 - 5$ .<sup>[1]</sup>

We repeated these experiments with a microTOF-Q II instrument and an HCT quadrupole ion trap, both equipped with a CSI as well as a conventional ESI source (all from Bruker Daltonik). For the identification of the detected ions, their  $m/z$  ratios, isotope pattern, and gas-phase fragmentation behavior were considered. For unambiguous assignments, the higher resolving power of the microTOF-Q II instrument proved essential. With this mass spectrometer, typical accuracies of 20 ppm were achieved with an external calibration scheme.

Our experiments showed the presence of ions, whose nominal masses, isotope patterns, and gas-phase fragmentation behavior matched those reported by Yamaguchi and coworkers.<sup>[1]</sup> It therefore appears plausible that in both cases identical ions were observed. Exchanging the CSI for an ESI source had no significant effect. Remarkably, the same ions were also detected for solutions of various Grignard reagents  $\text{RMgCl}$  in THF,  $\text{R} = i\text{Pr}, \text{Bu}, \text{Oct}, \text{Dec}, \text{Ph}$ . This finding rules out the presence of the organyl group  $\text{R}$  in the observed ions and, thus, refutes the assignment of Yamaguchi and coworkers. With the help of deuterium labeling experiments, we arrive at an alternative suggestion for the identity of the ions in question.

[1] S. Sakamoto, T. Imamoto, K. Yamaguchi, *Org. Lett.* **2001**, 3, 1793.

*New aspects:*

- mass-spectrometric analysis of Grignard reagents
- use of cold-spray ionization

*Key words:*

- deuterium labeling
- memory effects
- TOF mass spectrometry

## Development and characterization of an FT-QIT

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### Introduction:

Quadrupole Ion Traps (QIT) were introduced by Paul in the 1950's, consisting of a ring and two endcap-electrodes. A RF field applied to the ring-electrode allows the storage of ions within a defined mass range inside the trap. QIT enable ion accumulation and storage for an extended period of time and thus in-situ MS/MS experiments become feasible, driven essentially by CID (Collision Induced Dissociation) processes. In addition, QIT designs are generally compact and robust. Although conventional FT (Fourier Transform) -instruments, i.e., ICR or Orbitraps exceed the performance of conventional QIT-analyzers in several categories (mass range and accuracy, dynamic range, and especially in resolving power) the combination of QIT and FT technology leads to a compact and powerful mass spectrometric setup.

### Experimental:

A three-dimensional ion trap based on the Paul design with hyperbolic electrodes in combination with a 70 eV electron ionization (EI) source or with a DC micro-plasma based ion source represents the core of the present mass spectrometric setup. Advanced electronic amplifiers allow the entirely non-destructive recording of the ion-motion within the ion trap. The ion oscillations of the electrically excited ion population is measured by a broadband detection approach of the image-currents induced on the endcap electrodes. Characterization measurements on sensitivity, dynamic range, and resolving power are carried out either using gas mixtures of highly diluted analytes in different matrix gases (i.e., toluene in N<sub>2</sub> or H<sub>2</sub>) or using the QIT as residual gas analyzer ( $p < 10^{-7}$  mbar).

### Results and Discussion:

The results presented in this contribution demonstrate that the combination of QIT and FT technology has successfully led to a powerful mass spectrometric system. Gas mixtures are introduced into the trap by means of a pulsed inlet system controlled by a magnetic needle valve. Benchmark measurements carried out with toluene in nitrogen and hydrogen demonstrate limits of detection at intermediate pptV-levels while simultaneously showing a linear response over several orders of magnitude. Advanced ion excitation schemes [e.g., broadband-, resonant-, and Stored Waveform Inverse Fourier Transform (SWIFT) excitation] are used to enhance the performance of the mass spectrometer. For instance resonant ejection with suitable excitation waveforms efficiently eliminates abundant matrix and/or background species. Thus the detection of e.g. BTX (benzene, toluene, xylene) at low ppbV-levels within an N<sub>2</sub>-matrix is achievable despite using 70eV-EI. In addition, a high dynamic range over more than eight orders of magnitude between different ion species can be realized in such experiments. As ions can be accumulated and trapped for long periods of time and as the resolving power is scalable with the length of the observed FT window, a mass resolution >10000 is achievable.

Novel Aspect:

FT-QIT with EI source and/or DC-plasma based ion source as compact and powerful mass spectrometer

Keywords:

Fourier Transform Quadrupole Ion Trap

# **(Ultra-)High Resolution Tandem Mass Spectrometry in a Mobile MR-TOF Mass Spectrometer**

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## **Introduction**

A mobile multiple-reflection time-of-flight mass spectrometer (MR-TOF-MS) has been developed. Unlike conventional time-of-flight mass spectrometers, the mobile MR-TOF-MS provides high mass resolving power and sub-ppm accuracy in a compact and transportable format [1].

In addition to highly resolved and accurate in-situ mass measurements, the device offers MS<sup>N</sup> capability via selective ion re-trapping with ultra-high mass separation power and collisional-induced dissociation (CID) as method of fragmentation.

## **Experimental Part**

The device consists of an atmospheric pressure interface (API) for various atmospheric ion sources, a dedicated RFQ beam preparation system (ion guide, mass filter, ion cooler and ion trap) and a compact time-of-flight analyzer (~ 0.5 m) with an MCP detector. All electronics, pumps and the control system are mounted with the spectrometer in one single frame of only 0.8 m<sup>3</sup> volume.

Inside the time-of-flight analyzer the ions are reflected by electrostatic mirrors and traverse the analyzer up to a thousand times. Thereby high resolution in a compact system can be achieved [1].

Selective ion re-trapping and CID are performed in the same ion trap from which the ions are injected into the time-of-flight analyzer, thus allowing for multiple consecutive (Tandem-)MS cycles [2].

## Results and Discussion

Measurements with a caesium ion source have been carried out and with a time-of-flight of over 17 ms a mass resolving power exceeding 400,000 (FWHM) has been achieved [3].

Mass selective ion re-trapping with a separation power of over 50,000 has been performed, hence offering more than an order of magnitude higher separation power than commercially available mass separators [3].

Additionally, MS/MS spectra of the two isobaric amino acids glutamine and lysine ( $R > 4000$ ) have been obtained using a nano-electrospray ion source, demonstrating isobar separation after 200  $\mu$ s time-of-flight only [2].

The instrument is ideally suited for the identification of species in biological or environmental samples and can be applied for in-situ operation at various measurement sites.

## References

- [1] T. Dickel, W. R. Plaß, J. Lang, J. Ebert, H. Geissel, E. Haettner, W. Lippert, M. Petrick, C. Scheidenberger, M. Yavor, *NIM B*, **317**, 779-784 (2013)
- [2] W. Lippert, *PhD thesis in preparation*
- [3] J. Lang, *PhD thesis in preparation*

## New Aspects

Mobile (Ultra-)High Resolution MR-TOF-MS with  $MS^N$  with high resolution in every stage.

## Keywords

Mobile, Atmospheric Pressure Interface, Multiple-Reflection Time-of-Flight Mass Spectrometry, High Resolution, Tandem Mass Spectrometry



# First Principles Calculation of Electron Ionization Mass Spectra

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## Introduction:

We present the Quantum Chemistry Electron Ionization Mass Spectra (QCEIMS) method, which is based on a mixed quantum-classical molecular dynamics (QC-MD) protocol.[1] We simulate an ensemble of molecular ions after an (e,2e) process with a certain ionization excess energy (IEE) distribution by propagating the nuclei classically on a quantum chemical potential energy surface (PES). By our fully parallelized stochastic/dynamic algorithm, one obtains a computed mass spectrum in a reasonable amount of computation time.

## Computational Details:

The QCEIMS program works with various semi-empirical and density functional theory (DFT) PES. The number of individual QC-MD production runs varies depending on the number of atoms, such that the calculated base peaks comprise around 100 counts. Furthermore, we have implemented a composite mass spectral matching score[2] for the evaluation of our calculated mass spectra.

## Results and Discussion:

We present the work-flow of QCEIMS, and discuss the details of the individual steps. The QCEIMS output trajectories can be easily visualized as reaction videos. Some representative molecular movies will be shown. We have been able to publish QCEIMS results for a number of exemplary molecules ranging from rather small molecules like the nucleobases[3,4] to organic drug molecules like taxol (>100 atoms)[5], demonstrating the versatility of our approach. We are confident that QCEIMS will become a useful computational tool for mass spectrometrists who want to predict mass spectra of certain compound classes, or who seek to investigate complex fragmentation mechanisms.

## References:

- [1] S. Grimme, *Angew. Chem. Int. Ed.* **2013**, 52, 6306
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- [3] C. A. Bauer, S. Grimme, *J. Phys. Chem. A* **2014**, 118, 11479
- [4] C. A. Bauer, S. Grimme, *Eur. J. Mass Spectrom.* **2015**, 21, 125
- [5] C. A. Bauer, S. Grimme, *Org. Biomol. Chem.* **2014**, 12, 8737

## New Aspects:

Quantum chemical prediction of EI mass spectra by a combined dynamic/stochastic method

## Keywords:

Quantum Chemistry, Molecular Dynamics, Molecular Modeling, Fragmentation Pathways

# Improved processing of gas chromatography atmospheric pressure chemical ionisation ultra-high resolution mass spectrometric data for complex mixtures

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## Introduction:

One crucial aspect in the field of ultra-high resolution mass spectrometry is data handling and treatment. Size reduction without losing significant information is a major task. Additionally challenges such as an efficient processing by means of computing costs and reliable and reproducible results occur, especially when coupling chromatographic techniques.

Recently Barrow et al. showed the capabilities of GC-APCI hyphenated to ultra-high resolution mass spectrometry.<sup>[1]</sup> Unfortunately time segments of several minutes were used, discarding the retention time information. The presented work shows the utilization of all acquired mass spectra processed individually by means of applying self-written MATLAB routines, resulting in elemental composition assignments based on specific chromatographic features and validated using the retention index and the NIST database.<sup>[2,3]</sup>

## Experimental Part:

Particulate matter was sampled during a measurement campaign on quartz fibre filter for 4 h utilizing a research ship diesel engine, which was run with light and heavy fuel oil (LFO/HFO). Filters were subsequently extracted with methanol/dichloromethane. The feed fuels were diluted in methanol/dichloromethane and directly analyzed.

Measurements were carried out using a Bruker apex II FT-ICR-MS equipped with a 7 T superconducting magnet. The MS was hyphenated to a GC. For ionisation an APCI source specialised for gas phase inlet was used. Mass spectra were acquired in positive ion mode with an acquisition speed of 0.6 Hz resulting in a resolution of circa 200,000 at  $m/z$  300. Data processing was done partly by self-written Visual-Basic- as well as MATLAB-scripts.

## Results and Discussion (max. 300):

The data processing is divided into two parts: A Visual-Basic part utilizing the Bruker Data Analysis software to calibrate ( $m/z$ -calibration external and internal), baseline correct, apply peak picking (signal/noise  $\geq 9$ ) as well as export the data (each spectra into a single ASCII-file) and a MATLAB part in which the exported data are imported and automatically processed.

The MATLAB processing involves several steps starting with a feature detection based on an approach from Tautenhahn et al.<sup>[5]</sup> Subsequently ionisation artefacts, e.g. oxygen adducts or

water loss, are discarded. Therefore time traces of feature pairs distinguishing in the exact adduct/fragment mass are compared by means of curve shape correlation and retention time overlap. Furthermore elemental composition possibilities are generated based on the exact mass and limited using a correlation (calculated based on circa. 75,000 NIST entries) between retention index, mass-to-charge ratio and double bond equivalents ( $\pi$ -  $\pi$ -interaction). Finally the elemental composition assignments are further limited using typical petroleomics restrictions. As a final step the retention index of each assignment is compared to the NIST entries generating a list of structural possibilities.

Applied to primary combustion aerosol and corresponding feed fuel chemical transformation processes such as partly oxidation of polycyclic aromatic hydrocarbons was observed. Moreover sulphuric species in the DF-PM could be revealed; most likely originating from the lubrication oil; as well as a tremendous complexity of the HFO-PM could be exposed.

The presented work point out the advantages of an improved GC-APCI-ICR-MS data processing. The whole mass spectrometric information is used. Typical ionisation artefacts are discarded automatically. Furthermore a correlation based on the data base is utilized for limiting the elemental composition possibilities. Finally the features are compared with data base entries for structural elucidation.. As a result elemental composition assignments validated by retention index and possible structure hints are generated.

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## New Aspects:

- advanced processing of GC-APCI-FT-ICR-MS data by MATLAB algorithms utilizing chromatographic information, exemplarily shown for fossil fuel and combustion aerosol

## Keywords:

Atmospheric pressure chemical ionisation (APCI), gas chromatography (GC), combustion aerosol, petroleomics, high resolution mass spectrometry (HR-MS)

# Coupling Thin-Layer Chromatography and Desorption Electrospray Ionisation (DESI) - Fourier-Transform Ion Cyclotron Resonance (FT-ICR) Mass Spectrometry for Glycosphingolipid Analysis

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**Introduction:** Owing to their complexity and heterogeneity the analysis of biological samples often poses a serious challenge which can be addressed by use of mass analysers providing a very high resolving power such as FT-ICR mass spectrometers. Alternatively, sample complexity can be reduced by chromatographic separation, e.g. by thin-layer chromatography (TLC) preceding MS analysis. Coupling a DESI ion source to a mass spectrometer provides a convenient technique to probe a TLC plate under ambient conditions [1]. Here, we show that the hyphenation of DESI with an FT-ICR mass spectrometer enables accurate and precise analysis of immunodetected glycosphingolipids (GSLs) which act as receptors of Shiga toxins (Stxs) released by enterohemorrhagic *Escherichia coli* (EHEC) [2].

**Materials and Methods:** Neutral GSLs from human erythrocytes were applied bandwise onto high-performance normal phase silica TLC plates, separated, and detected by antibody-overlay assays [2]. Subsequently, plates were submitted to DESI FT-ICR-MS analysis. Ions were generated by use of an in-house built DESI source matched to the Apollo ESI source of a Bruker Apex II FT-ICR instrument (7 T). The setup includes an automated support for sample positioning and scanning of surfaces as well as an electrically heated extension of the vacuum interface capillary. Gas-assisted electrospray is generated by a modified ESI emitter that can be positioned unrestricted to vary the distance to the sample surface and the impact angle of the spray. Tandem MS experiments were performed by use of IRMPD.

**Results and Discussion:** TLC-separated Stx GSL receptors globotriaosylceramide (Gb3Cer) and globotetraosylceramide (Gb4Cer) were detected by overlay assays with GSL-specific antibodies as well as Stx1a, Stx2a and Stx2e subtypes, combined with secondary antibodies and subsequent staining with a chromogenic substrate. Stained bands were probed by DESI FT-ICR MS and immunopositive GSLs could be desorbed and ionised directly from the TLC plate without interferences from the antibodies, Stxs or the staining reagent. Scanning the plate in the direction of chromatographic development furnished 2D spectra which showed the distribution of the different Gb3Cer and Gb4Cer lipofoms on the plate. Mass spectra mainly revealed the presence of intact sodiated analytes. Depending on the  $m/z$  range resolutions of 50.000 to 100.000 were achieved routinely with mass accuracies in the low ppm-range (external calibration). For structural elucidation precursor ions were isolated inside the ICR cell and activated by irradiation with IR photons. The observed fragmentation patterns are similar to those obtained by low energy collisional activation. Evaluation of the MS/MS spectra allowed for structural elucidation of Stx receptors both with respect to glycan sequence as well as ceramide moiety. The results presented in this study demonstrate the potential of the hyphenation of planar chromatographic separation and formation of gaseous ions directly from the surface of the TLC plate by DESI for the analysis of immunostained GSLs.

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**Novel aspects:** The combination of TLC separation, antibody overlay detection and DESI-FT-ICR-MS is a new, alternative method for the analysis of glycosphingolipids.

**Keywords:** DESI, FT-ICR-MS, IRMPD, TLC, glycosphingolipids

## Ultrahigh-resolution Insights in Time and Mass for Climate History by Determining Lipid Biomarkers in Marine Sediments with LDI FTMS Imaging

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Marine microorganisms adapt depending on habitat and ambient temperature on the structure of their membranes by modifying the lipid composition. This structural information remains after the sedimentation process, because the compounds are conserved over geological timelines. Therefore sedimented lipid biomarkers are an important source of information to reconstruct the climate history.

Conventional biomarker analysis (extraction followed by LC/MS) is labor intensive and requires sediment pieces in cm sizes; therefore the accessible temporal resolution is often low. Here we present a new method based on laser desorption Fourier Transform Mass Spectrometry (FTMS). This method was used for the detection of glycerol dialkyl glycerol tetraethers (GDGTs) in sapropels from marine sediments of the eastern Mediterranean Sea. These cell components derived from unicellular marine organisms, Archaea, which both now and then populate the global ocean. In the sediments preserved, these lipids may be used as so-called proxies. They provide, representative of direct measurements, information on prehistoric sea conditions and are used in most cases as a proxy for seawater temperature [1].

By scanning a sediment core using LDI FTMS the relative intensities of GDGTs are directly recovered from sediment cores and can be correlated with the time of sedimentation prevailing sea surface temperatures [2]. The high spatial resolution of the laser (250  $\mu\text{m}$ ) in combination with the extreme resolution of the FTMS is a prerequisite for obtaining relevant data. Because the resulting mass spectra are very complex, a quadrupole is used to pre-filter for limiting the mass range. This novel method allows the study of prehistoric climate and environmental changes in previously unimaginable temporal resolution.

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### Novel Aspect

High resolution LDI imaging of geological cores to increase the temporal resolution of the data for climate history

# Heat impact caused molecular level changes in solid and dissolved soil organic matter

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## Introduction

The ubiquitous abundance of pyrolysed, highly aromatic organic matter, called “Black Carbon” (BC), became increasingly important also beyond atmospheric aerosol: its predominant high resistance to abiotic and biotic degradation resulted in turnover times from less than a century to several millennia. This recalcitrance led to the enrichment in soils. Hence, soil BC acts an important sink in the global carbon cycle.

Soil related dissolved organic matter (DOM) is a major controlling factor in soil formation, an important pathway of organic matter transport and one of the largest active carbon reservoirs on earth.

The aim of this study was to evaluate the effects of artificially simulated wildfire by thermal treatment on the molecular composition of water extractable soil organic matter (DOM).

## Experimental

Soils from two outdoor lysimeters with different management history were investigated. Soil samples, non-heated and heated up to 350°C were analyzed for elemental composition (carbon, nitrogen and sulfur) and for bulk molecular composition by Pyrolysis-Field Ionization Mass Spectrometry (Py-FIMS) and synchrotron-based X-ray Absorption Near-Edge Spectroscopy (XANES) at the C- and N K-edges.

DOM-samples obtained by hot water extraction, desalting and concentration by solid phase extraction were subsequently analyzed by flow injection analysis in a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FTICR-MS), equipped with an ESI source and a 7 T supra-conducting magnet (LTQ-FT Ultra, ThermoFisher Scientific).

## Results and Discussion

The characteristics and differences of the FTICR-MS spectra with as many as ten or more peaks at each nominal mass are discussed: heated samples showed considerable higher intensities of even numbered peaks. An in-house developed post processing was used for further exploitation of the data with the aim of an unambiguous assignment of as many peaks as possible. Obtained mass lists were transformed for sorting and preparation/ interpretation of graphics like Kendrick and van Krevelen plots.

The heat-treated solid samples show decreasing C/N ratios and the formation cyclic and N-heterocyclic compounds in good agreement among the various methods (Py-FIMS and C- and N-XANES). Detailed insight into the hot-water extracts by FTICR-MS showed clear qualitative as well as quantitative changes in the number *and* the intensity of nitrogen and

nitrogen + sulfur containing compounds, respectively, which generally became enriched under soil heating. This demonstrates, that not only the bulk SOM is affected in structure by heat impact but also the more mobile DOM.

We assume, that heat impact volatilizes and oxidizes parts of the organic substances is as expected but another part of the substances incorporates (further) nitrogen atom(s) similar to the generation of new compounds under the conditions of plasma etching in nitrogen atmosphere. This would explain to some extent, why soils are e.g. after fire clearing of vegetation are highly fertile for a short period (better plant acceptable compounds) but become more infertile in the long run, especially under tropical conditions with frequently heavy rain that would lead to an increased leaching of compounds with higher polarity.

### **New aspects**

Thermal treated soil samples show generation of new compounds by incorporation of nitrogen atom(s).

### **Key words**

Dissolved organic carbon, nitrogen containing organics, soil, Van Krevelen plot, wildfire

# Studying the derivatization reaction for selective analysis of heavy crude oil by ultra-high resolution mass spectrometry

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## Introduction

As the worldwide supply of light crude oil decreases, more attention is paid to the use of heavy oils, but they contain significant amounts of heteroatoms, such as sulfur-containing compounds which are sources of air pollution during combustion, and therefore need more chemical upgrading. Efforts have been made toward analysing and characterizing the polyaromatic heterocycles in crude oil to facilitate chemical upgrading processes.<sup>[1]</sup>

The super complexity of heavy crude oil challenges any analytical tool. Ultrahigh-resolution mass spectrometry, such as 7 T FT-ICR MS and high-field Orbitrap Elite<sup>[2]</sup> are considered as the most powerful techniques for analysis of crudes. Derivatization reactions are developed to combine the analytical techniques for the selective analysis of heavy crude oil.

## Experiments

Heavy crude oil was dissolved in dichloroethane (DCE) and was treated with alkylating reagents (CD<sub>3</sub>I and C<sub>2</sub>H<sub>5</sub>I) in the presence of AgBF<sub>4</sub>. AgI precipitated immediately and was removed by centrifugation after 4 h and washed with dichloromethane.

Mass spectra were recorded using high-field Orbitrap MS and a 7 T FT-ICR MS (Thermo Fisher Scientific, Bremen) equipped with ESI. External mass calibration was performed using a tune mix solution.

## Results and discussion

Electrospray ionization (ESI) coupled with ultrahigh resolution mass spectrometry is an excellent method to selectively analysing polar compounds. We studied the derivatization reaction of crude oil, and that allows ionizing the non-polar components such as sulfur-containing species that are otherwise not ionisable by electrospray. Chemical methods plus ultrahigh resolution mass spectrometry enable a selective analysis of non-polar species such as S-, O-containing compounds and hydrocarbons under positive ESI mode.

DBT was chosen as a standard compound to optimize the reaction condition which is monitored by <sup>1</sup>H NMR analysis. The ethylation of DBT can reach a yield of >99%. The ethylation directly with crude oil shows a high selectivity for sulfur-containing compounds, such as S<sub>1</sub>- and S<sub>2</sub>- species with a certain mole ratio of AgBF<sub>4</sub> and alkylating reagents. Different classes, such as O-containing compounds and hydrocarbons are also selectively observable by modifying the reaction conditions. The results show that it is possible to selectively characterize the classes of compounds in crude oil by adding a chemical dimension to the analysis scheme without any fractionation and chromatographic separation. The high-field Orbitrap MS and 7 T FT-ICR MS allow following the details of these reactions.

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### **New aspects**

The combination of derivatization reaction with ultra-high mass spectrometry is suitable for selectively analysis of crude oil.

### **Keywords**

Ultra-high resolution, derivatization, mass spectrometry, crude oil, electrospray

# Investigation on the photo-oxidative degradation of oil spills by FTMS

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## Introduction

Crude oil is and will continue to be one of the most important energy sources of the near future. Accompanying its high demand oil spilled into the environment cannot be totally avoided. A better understanding of weathering processes such as photo-oxidation of spilled oil is important to help minimize environmental impacts.

High-field Orbitrap FTMS provides a mass resolution comparable to FT-ICR MS, which is sufficient for the crude oil analysis.<sup>[1]</sup> Additionally separation methods such as SARA fractionation and different atmospheric ionization (API) methods are applied before the mass spectrometric analysis.<sup>[2, 3]</sup> These can reduce the complexity of crude oil, and on the other hand trace changes of crude oil after photo-oxidation on a molecular level.

## Experimental part

After precipitation of asphaltenes from *n*-heptane, remaining maltenes were fractionated into saturates, aromatics and resins by open column chromatography on alumina (solvents: cyclohexane; dichloromethane/cyclohexane (1:1, *v:v*); methanol).

Photo-oxidation of the whole crude oil and the individual SARA fractions, each mixed with pure water, was performed under simulated solar irradiation conditions. After 24 h of irradiation oil phase samples and corresponding water soluble fractions (WSFs) were analyzed and compared to the unaltered samples.

Mass spectrometric analyses were performed on a research type FT-Orbitrap Elite at a resolution of 480,000 (FWHM of  $m/z$  400) using different ionization methods.

## Results and discussion

Major changes in the class distribution were found in the aromatic fraction which showed a significant increase of oxidized species such as  $\text{NO}_x\text{S}_y$ ,  $\text{O}_x\text{S}$  and  $\text{O}_x$  and on the other hand a remarkable decrease of non-oxidized hydrocarbon and heteroatom-containing classes.

Additionally, among the WSFs of the whole crude oil and its SARA fractions the aromatic fraction showed the most pronounced changes after both positive and negative mode ESI. In positive mode ESI OS was the dominant class in the mass spectrum, followed by  $O_x$ ,  $NO_xS$  and  $NO_x$ . In contrast to that both oxygenated hydrocarbons ( $O_x$ ) and oxidized sulfur-containing compounds ( $O_xS$ ), transferred from the aromatic fraction after irradiation to the aqueous phase, dominated the mass spectrum observed after negative mode ESI.

Results show that photo-initiated oxidation increases the polarity of crude oil species and therefore their water-solubility. The oxidation occurs across a wide range of unsaturation revealing that containing aromatic species are also affected during photo-oxidation. The photo-oxidation likely proceeds in a consecutive manner i.e. a species gets further oxidized after an initial oxidation occurred. Results also show that within one heteroatom class and DBE value species with a higher degree of alkylation tend to be oxidized more easily.

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## New aspects

The aromatic fraction of crude oil is vulnerable to photo-oxidative degradation, leading to polar, water soluble compounds.

## Keywords

Photo-oxidation, oil spill, oil weathering, water soluble fraction

## Secondary brown carbon – Identification of light-absorbing compounds in aerosol mimicry by ultra-high resolution mass spectrometry

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One of the main open questions regarding organic compounds in atmospheric chemistry today is related to the formation of optically-active compounds and the occurrence of so called brown carbon (BrC) (Andreae and Gelencsér, 2006). While organic compounds in ambient fine particles for decades have been assumed to not absorb solar radiation, thus resulting in a net cooling effect on climate (IPCC, 2007), it is now generally accepted that a continuum of light-absorbing carbonaceous species is present in fine aerosols (Pöschl, 2003).

In this study, we use a combination of analytical techniques to identify light-absorbing compounds from reactions between dicarbonyl compounds, i.e., glyoxal, methylglyoxal, acetylacetone, 2,3-butanedione, 2,5-hexanedione, and glutaraldehyde, and amine species, i.e., ammonia and glycine, at atmospherically relevant concentrations in bulk solution experiments mimicking atmospheric particulates. Product analyses were performed using UV/Vis spectrophotometry and (ultra) high performance liquid chromatography coupled to diode array detection and ion trap mass spectrometry (HPLC-DAD-ESI-MS/MS), as well as ultra-high resolution (Orbitrap) mass spectrometry (UHPLC-ESI-HRMS/MS).

We demonstrate that light-absorbing compounds are formed from a variety of atmospherically relevant dicarbonyls via particle phase reactions with amine nucleophiles. Mixed dicarbonyl experiments, where the individual dicarbonyls stayed colorless, yield light-absorbing products, e.g., dihydropyridines. Further light-absorbing reaction products were tentatively identified to be nitrogen heterocycles such as imidazoles or pyrroles, as well as open chain compounds from aldol condensation reactions. The reactive turnover was found to be higher at increasing pH values indicating the expected pH dependence of amine component protonation. The studied processes

may be of high relevance to aerosol optical properties in regions with high aerosol pH, e.g., resulting from high ammonia emissions as for example in northern India (Clarisse et al., 2009).

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## New aspects

Identification of nitrogen heterocycles as common structure motifs in secondary BrC using combined optical and (ultra-high resolution) mass spectrometric methods; Fundamental organic chemistry affects aerosol optical properties through aqueous phase processes

## Keywords

Secondary organic aerosol, brown carbon, nitrogen heterocycles, UHPLC-Orbitrap-MS

# Binding of O<sub>2</sub> and CO to Metal Porphyrin Anions in the Gas Phase

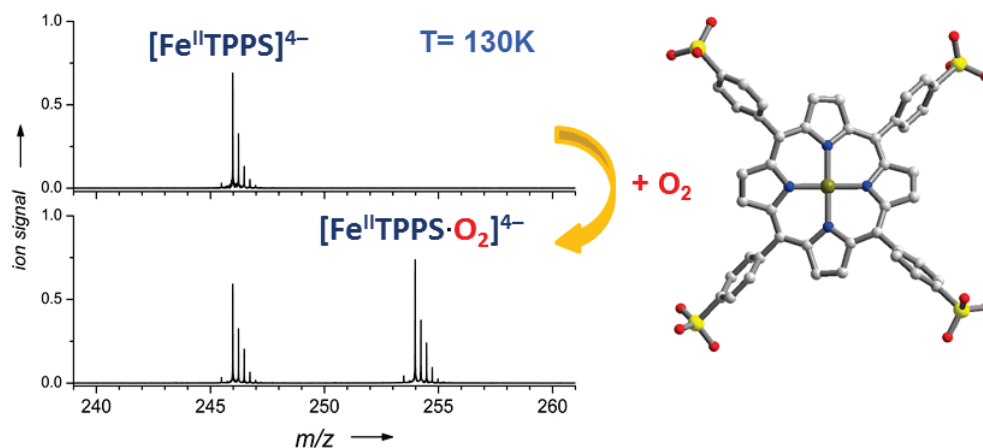
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A central goal of this project is the investigation of the structures and reactivities of mononuclear [1] and polynuclear metal-aromatics-complexes in gas phase [2]. Here we report on the redox reactivity of mononuclear multiply negatively charged heme-analogue metal porphyrin complexes with O<sub>2</sub> and CO in a FT-ICR mass spectrometer.

To study the ion chemistry of metal porphyrin complexes a modified cryogenically cooled ICR-trap [3] as well as a home-built nano electrospray source were interfaced to the FTMS-setup. The generated mass selected anions were allowed to react with O<sub>2</sub> and CO in a temperature range of 88-420K whereby at low temperatures we observe the formation of a [MTPPS+O<sub>2</sub>]<sup>4-</sup> association complex. From temperature dependent kinetics measurements we could extract rate constants assuming an equilibrium reaction. Finally reaction enthalpies or binding energies were determined for several systems. It is interesting that reactions of the trivalent [Mn<sup>III</sup>/Fe<sup>III</sup>TPPS+O<sub>2</sub>]<sup>3-</sup> as well as [(Cu<sup>II</sup>/H<sub>2</sub>)TPPS+O<sub>2</sub>]<sup>4-</sup> with O<sub>2</sub> were found to be significantly slower than of the [(Mn<sup>II</sup>/Fe<sup>II</sup>)TPPS+O<sub>2</sub>]<sup>4-</sup>, which suggests a strong dependence on the oxidation state of the metal center. Our results are compared with literature values from quantum-chemical computations for heme model systems as well as to relevant studies on proteins in condensed phase.



**Fig 1:** Left: Mass spectra of the temperature dependent association reaction of [Fe<sup>II</sup>TPPS]<sup>4-</sup> with O<sub>2</sub>. Right: Structure of tpps = tetrakis(4-sulfonatophenyl)porphyrin with a central metal atom.

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# Can Combined Quantum Chemical/Experimental Mass Spectrometry Separate the Fragmentation Cascades of Tautomers?

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We simulate electron ionization induced-fragmentation cascades of organic tautomers by employing mixed quantum-classical molecular dynamics. Each tautomer exhibits its own characteristic dissociation pathways. Therefore, Boltzmann averaging of tautomer population ratios generally improves the quality of the computed mass spectra. The origin of certain peaks can be traced back to specific tautomers and their fragmentation cascades. Information about different decomposition patterns belonging to populated isomers has been available experimentally through derivatization or hyphenated technologies. We present a fully automated, unbiased, and efficient *in silico* protocol, yielding an affirmative answer to the question posed in the title.

# Fragmentation of Amines, Investigation using energy dependent PD experiments in the FT-ICR cell in combination with DFT calculations

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## Introduction

In our MS experiments we observed that some fluorescence dye labels such as rhodamines, oxazines or parts of these structures produce unexpected losses [1][2]. Beside neutral losses we found radical fragments, which is a violation of the even electron rule [3]. In case of the investigated aniline model system either a twofold elimination of a radical or a rearrangement process and elimination of a neutral molecule forms the fragmentation product dominating the mass spectrum. In order to receive more information about the undergoing processes we performed energy dependent measurements at different wavelength and compared the results with DFT-calculations. It was possible to identify charge and geometry effects on the general mechanism as well as some energetic properties.

## Methods

All mass spectra have been recorded on a Bruker Apex FT-ICR equipped with an Apollo III source with a superconducting 7.0 T magnet (Bruker Daltonics, Bremen, Germany). The different samples have been ionized by electrospray ionization. As a light source for the PD fragmentation a Nd:YAG Laser (Continuum) has been used with different pulse length at 532 nm as well as 355 nm. The samples were dissolved in ethanol and added to a standard solvent mixture (H<sub>2</sub>O: MeOH: formic acid; 50:50:0.2) yielding a final concentration in the range of 1-5 nmol/uL. DFT calculations were done using B3LYP with different basis sets, transition states were calculated with QST3 and verified by a single negative frequency and IRC.

## Results

PD measurements of the different molecules with a diethylamino-sidegroup lead to intense fragmentation pattern in the spectra. The dominating loss of C<sub>3</sub>H<sub>8</sub> is combined with smaller fragments which are dependent on the charge position within the molecule. From the rhodamine dyes, which have an amino side group as well, we know two possible reaction pathways, a radical mechanism or a concerted neutral mechanism. Both versions are possible, the appearance of several radical fragments under different fragmentation methods indicate at least a radical part in the mechanism. The comparison of the energy dependent measurements at two different wavelength with the results of the DFT calculations point out that a two photon process is necessary for the fragmentation process of the C<sub>3</sub>H<sub>8</sub>-Fragment. The smaller fragments in the PD spectra show a different energy dependence in the experiment, which indicates a varied fragmentation pathway. The experimental data were verified by the results of DFT calculations, which point out a strong impact of the charge position on the geometry of the sidegroup. This geometry change has an influence on the formed fragments which is in good agreement with our experimental results.

It was possible to identify parts of the fragmentation mechanism with the combination of a modified model system, PD experiments and DFT calculations with a modified experimental setup.



## Novel Aspects

Fragmentation of dye molecules with short pulse PD within the ICR cell and DFT calculations to identify fragmentation pathways.

## Keywords

Photodissociation, Fragmentation, Mechanism

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# Generating open-shell supramolecular squares with electron transfer dissociation

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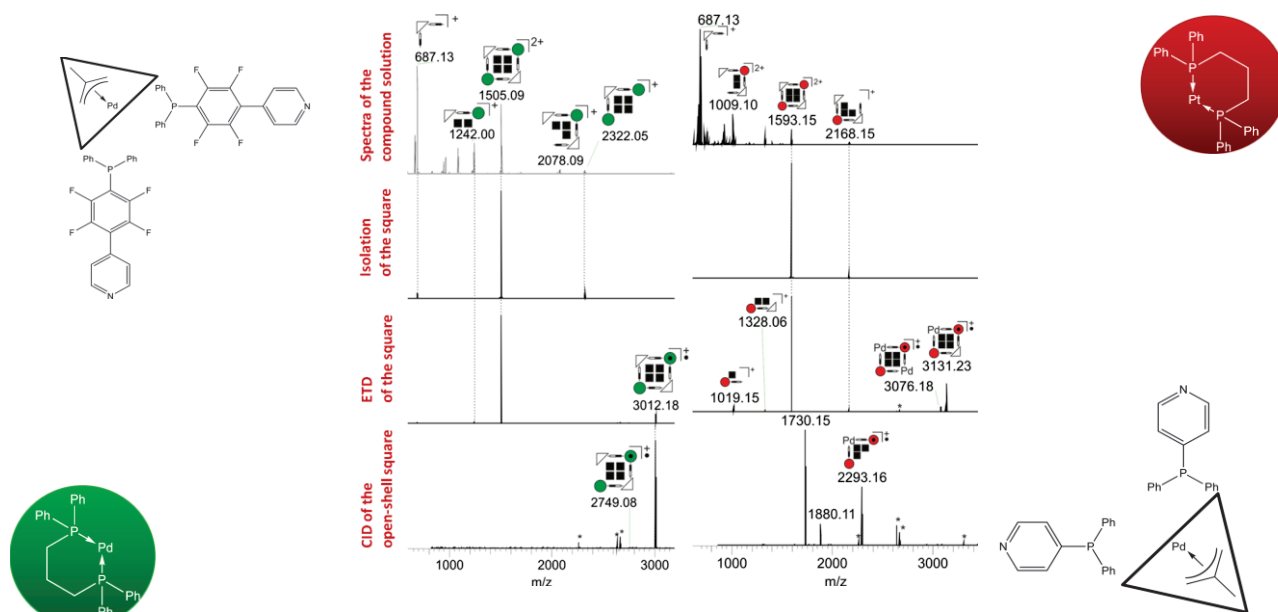
Selective self-assembly of square-like homo- and heterometallamacrocycles of the form  $[\{\text{Pd}(\eta^3\text{-2-Me-C}_3\text{H}_4)(\text{L}^n)_2\}_2\{\text{M}(\text{dppp})\}_2](\text{CF}_3\text{SO}_3)_6$  (dppp = 1,3-bis(diphenylphosphino)propane) [py = pyridine, M = Pd, Pt,  $\text{L}^n = 4\text{-PPh}_2\text{py}$  ( $\text{L}^1$ ),  $4\text{-C}_6\text{F}_4\text{PPh}_2\text{py}$  ( $\text{L}^2$ )] containing allyl corners has been achieved. Analysis with ESI MS shows a series of polycationic closed-shell squares. Further analysis with  $\text{MS}^n$ -experiments came to the following conclusions:<sup>[1]</sup>

*Bond strength: Pt-N > Pd-P > Pd-N*

*Less Coulomb repulsion for longer linker = more stable squares*

To analyse open-shell polycationic species, electron-transfer dissociation (ETD) can be used. This method has been specially developed for peptides, but can also be used for polycationic supramolecular metal assemblies to generate open-shell species via electron transfer.<sup>[2]</sup>

A  $10^{-5}$  molar solution of the respective square in acetone was introduced into a LTQ-Orbitrap XL-ETD hybrid mass spectrometer. The doubly charged square was isolated and reacted with fluoranthene as electron transfer reagent. After electron-transfer the produced single charged open-shell square was further analyzed by collision induced dissociation (CID).



*Fragmentation for the open-shell squares is determined by the metal, not the ligand.*

*The electron is probably located at the metal-dppp corner.*

*Fragmentation for Pt-containing squares is much more complex.*

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Keywords: Supramolecular self-assembly, ETD, open-shell, CID, metal complex

# Photodissociation of Oxazine 170 in the ICR-cell using different laser sources

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## Introduction

Fragmentation patterns of compounds containing alkylated amino functions and conjugated  $\pi$ -electron systems tend to be more complex than stated in literature.

Loss of  $C_3H_8$  out of diethylated amino substitutions were investigated in extend in our group.<sup>[1-3]</sup> To get an deeper insight into fragmentation mechanisms different molecule sizes, alkylation patterns and conjugated systems at all were subject of our research. In this work we focus on oxazine 170, a commercially available fluorescence dye.

Fragmentation of this compound could be introduced by collisions and different laser wavelength ranging from visible to UV.

## Experimental methods

Oxazine 170 was purchased from radiant dyes (Wermelskirchen, Germany). Labeling with deuterium was done following<sup>[4]</sup>.

For all experiments an APEX III ion cyclotron resonance mass spectrometer (Bruker Daltonik, Bremen, Germany: 7.05T magnet, Apollo I ESI source) was used.

After isolating in ICR-cell different fragmentation methods could be employed. Collisional activation were engaged using argon gas and accelerating ions using off-resonance SORI function. Photodissociation was achieved by guiding fixed frequencies of a Nd:YAG laser system or tunable wavelength of a dye laser into ICR-cell.

For fixed frequencies repetition rate of laser pulses was 20Hz in the latter case it was 10Hz. A home build circuit was used to control number of shots. Usually 10 to 20 laser shots were used for each acquisition.

## Results, discussion

Oxazine 170 ( $m/z$  332.173) shows numerous fragmentations, including loss of  $C_3H_8$ . The most intense fragment is found at  $m/z$  303.134. To build this the molecule has to liberate  $C_2H_5$  as radical which is in contradiction to the even electron rule. We found that violation of the ee-rule are quite common for compounds including alkylated amino functions and conjugated  $\pi$ -electron systems.

From mechanistical point of view at least two ways concerning the loss of  $C_3H_8$  become obvious: one across a rearrangement process forming propane and one reaction path including the loss of an ethyl and a methyl radical.

To investigate these reactions in more detail various activation methods were used. Collision induced dissociation photodissociation using different wavelength. First experiments were carried out using harmonic generation of the fundamental wavelength delivered by a Nd:YAG laser system (532 nm, 355 nm, 266 nm).

For further ongoing spectroscopic research on this type of reactions we now introduced a tunable dye laser system emitting wavelength in the range from 520 to 560 nm.

First results of this study will be presented in this work. Using these wavelength it was possible to access Oxazine 170 isotopomers with different amount of deuteriums than using the fixed frequencies of Nd:YAG based systems.

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## Novel aspects

Photodissociation of oxazine 170 with and without isotope labeling using collisions and fixed (visible and UV) or tunable wavelength (visible).

## Keywords

Oxazine 170, photodissociation, ICR, deuterium-labeling

# New separation approach for asphaltene investigation: argentation chromatography coupled with ultrahigh resolution mass spectrometry

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## Introduction

Heavy crude oil analysis attracts a lot of interest nowadays due to our increased energy needs which demands new alternative energy sources. It is known as one of the most complex mixture therefore high resolution MS is often used together with additional separation steps. In this study we focus on the *n*-heptane-insoluble fraction which is called asphaltenes. Asphaltenes possess highly condensed aromatic structure with relatively high heteroatom (N, O, S) content which is responsible for the difficulties during oil transportation and refining processes (e.g. pipe clogging).<sup>[1]</sup> Their poor solubility and tendency of aggregation formation causes an elaborate task to find proper conditions for their analysis. Argentation chromatography is introduced here as a new separation approach for asphaltene investigation.

## Experimental section

Argentation chromatography was performed on UltiMate 3000 HPLC system. Silver(I)-mercaptopropano silica gel (10  $\mu\text{m}$ ) was synthesized in our laboratory and packed into a stainless steel column (250 mm x 4.6 mm). As optimized separation conditions, a mixture of toluene and chloroform were used as mobile phase with increasing amount of dimethyl sulfoxide as an additional solvent to compete with the asphaltene compounds.

MS analysis was performed on a research-type LTQ-Orbitrap Elite MS with a resolving power of 480000 at  $m/z$  400. A combination of APPI and APCI source was used for ionization. Additionally, UV detector was applied at 300 nm.

## Results and discussion

In this study a chromatographic method has been developed to simplify and separate complex aromatic mixtures such as crude oil asphaltenes.

The conditions of argentation chromatography before MS detection applied in previous studies<sup>[2]</sup> were not feasible for asphaltene investigation. Owing to their poor solubility the solvent system has to be changed to a mixture of toluene and chloroform. The separation is based on the interaction between the silver ions ( $\text{Ag}^+$ ) bonded to a silica gel surface and the  $\pi$ -systems of the polycondensed aromatic compounds. The elution was taking place depending on the amount of dimethyl sulfoxide (0-5%) as an additional solvent to supersede the asphaltene molecules possessing increasing degree of unsaturation. Asphaltene molecules were separated and detected up to double bond equivalents (DBE) of 40 in the mass range of 200-800.

With online coupling the effectiveness of the separation can be monitored on a molecular level. It provides detailed information since each individual scan can be analysed which are recorded in every 1.5 second through the whole separation. Reconstructed ion chromatograms (RIC) of selected mass traces demonstrate that isomeric compounds can be separated using

this approach. Compounds having the same chemical composition can have various structural features (e.g. fused or non-fused core, basic or non-basic N-atom) resulting in different strengths of interaction with the silver(I) ions through different steric effects. The composition of the mobile phase has a significant role in separation efficiency which is discussed in this presentation.

### **Novel aspect**

Argentation chromatography is coupled to high resolution MS to introduce a new approach for asphaltene investigation.

### **Keywords**

Heavy crude oil, asphaltenes, hyphenated techniques, argentation chromatography, online coupling

### **References**

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# Enamine Radical Cations in Solution and in the Gasphase

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## Introduction

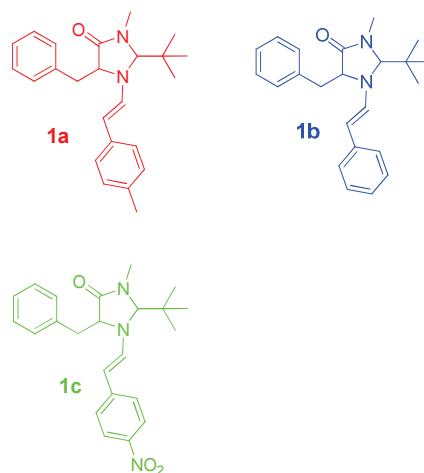
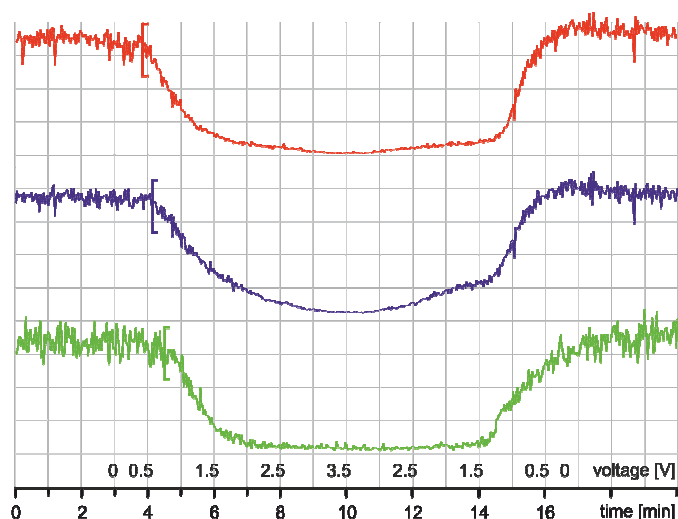
SOMO catalysis has obtained large interest as a new and powerful version of enantioselective organocatalysis which includes radical steps initiated by a one-electron oxidation.<sup>[1]</sup> ESI mass spectrometry has been established as an excellent tool for the successful investigation of reaction mechanisms in solution because it can transfer reactive intermediate species from solution into the gas-phase and enables their mass spectrometric characterization.<sup>[2]</sup> The combination with an online microreactor technique allows the detection of short-lived, reactive molecules such as radical species. The key intermediate of SOMO catalysis, the enamine radical cation, has been postulated, but had not been observed directly until we could detect it using ESI-MS coupled with a microreactor system.<sup>[3]</sup>

## Experimental

The enamine radical cation species for four common imidazolidine-4-one organocatalysts were obtained by oxidizing acetonitrile solutions of the respective enamine in a flow reactor electrochemical cell coupled directly to the ESI needle. We were able to identify the enamines and the respective radical cations by exact mass measurements and MS/MS techniques.

## Results and Discussion

The break down curves (signal abundance vs. EC-voltage) of the enamines are shifted to specific voltage areas. These results are consistent with cyclovoltammetric measurements. Electron-rich enamines are oxidized at a lower potential than electron-poor systems.



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# Examination of Gas-phase Cationic Ions of Ergothionine and Related Derivatives via Infrared Multiple Photon Dissociation (IRMPD) Spectroscopy

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## Introduction

The structure of cationic molecular ions of Ergothionine, Hercynine and other histidine-derivatives are investigated to study the influence of tautomeric equilibria on binding motifs to  $H^+$  and  $Na^+$ . Special attention is paid to the features of 5-membered N-heterocycle side-chains and to the influence of the permanently charged tri-methylated N-terminus of the amino acid natural compounds.

The fundamental understanding of the tautomeric equilibrium and the structure of ET in cationic complexes are to be investigated by tandem-MS<sup>1</sup>, theory and IRMPD-spectroscopy.<sup>2</sup> The work of Armentrout *et al.* on molecular ions of histidine and 4-phenyl-imidazole with IRMPD-spectroscopy, theory and guided ion beam tandem MS serve as reliable benchmark-results.<sup>3,4</sup>

## Experimental Section

IRMPD-MS: Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer with an electrospray ionization (ESI) source, coupled to a free electron laser for infrared experiments (FELIX) were used to perform the infrared multiple photon dissociation (IRMPD) experiments.

Target molecular ions are trapped, mass selected and irradiated with wavelength-tunable laser light<sup>5</sup> in the ICR cell. The action spectra are generated by acquiring the depletion of the precursor ion and the abundance of the product ions vs. the energy of the photons used for activation. Computed IR-spectra are compared to the experimental action spectra for structure identification. ESI-MS/MS experiments of the molecular ions complements the IRMPD-studies.

Computations: The B3LYP functional of Density Functional Theory (DFT) as well as the 6-311G\*\* basis set was used for all calculations.

## Results and Discussion

The protonated  $[ET + H]^+$  and the sodiated  $[ET + Na]^+$  molecular ions of Ergothioneine were probed. The IRMPD-spectrum of the former precursor ion  $[ET + H]^+$  at  $m/z$  230 provides experimental evidence for the concomitant presence of several isoenergetic en-thioles as well as thione tautomers, reflecting their virtually identical stability according to theory. In case of the sodiated molecular ion  $[ET + Na]^+$  at  $m/z$  252 the experimental IRMPD-spectrum clearly

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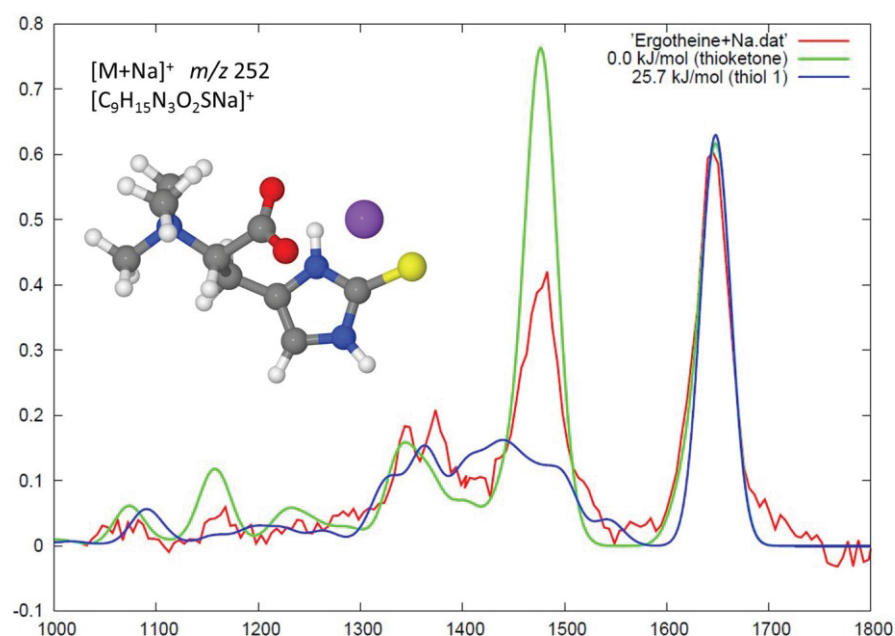
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<sup>5</sup> N.C. Polfer, J. Oomens, *Mass Spectrom. Rev.* **2009**, 28, 468.



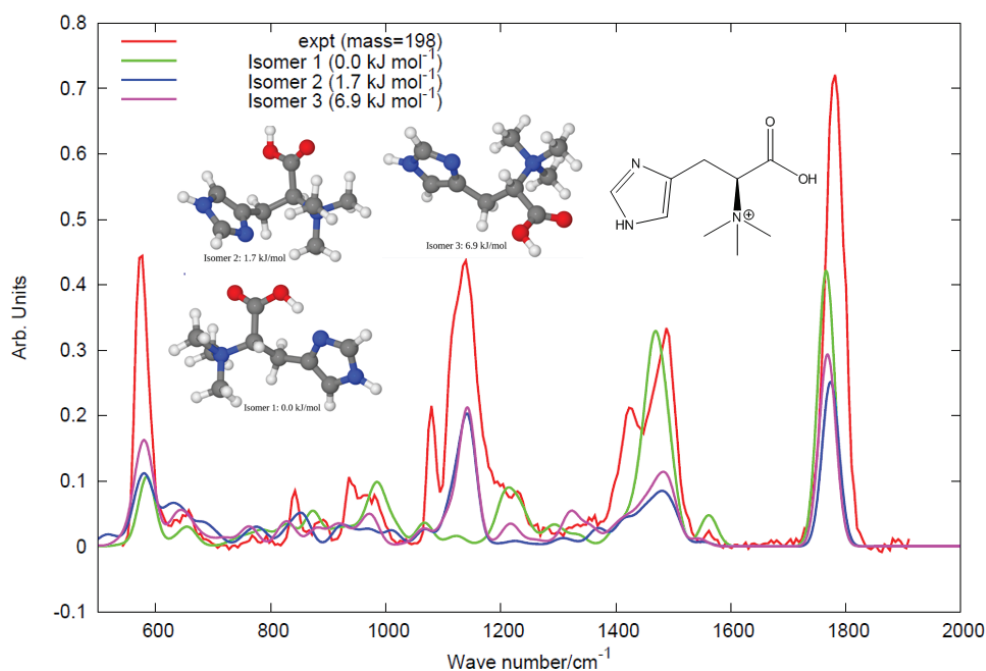
exhibits features pointing towards the exclusive presence of the substantially more stable thione isomer the gas phase (Figure 1).

In an additional set of IRMPD-measurements of the molecular ions of *N,N,N*-trimethyl-histidine (hercynine) and *N,N,N*-trimethyl-*N*-methyl-imidazole-histidine as well as their sodiated analoga were probed. The resulting IRMPD-spectra exhibit obvious similarities between the IRMPD-spectrum of ET and the ones of the other betaines evidencing the important role of the tri-methylated N-terminus in the relevant conformations of ET.



**Figure 1:**  $[\text{ET} + \text{Na}]^+$  IRMPD spectrum and computed spectra of en-thiole and thione tautomers clearly evidencing the exclusive presence of the thione isomer the gas phase.

For the cationic molecular ion of hercynine (*N,N,N*-trimethyl-histidine) at  $m/z$  198 theory finds three stable isomers with energies of 0 kJ/mol, 1,7 kJ/mol and 6,9 kJ/mol (Figure 2). The experimental spectrum is not matching either of the computed spectra as Figure 3 illustrates, but the Boltzmann-weighted composite spectrum at 298K does, suggesting the presence of these isomers in the gas-phase.



**Figure 2:** Experimental IRMPD spectrum of Hercynine at  $m/z$  198 and computed spectra of three relevant conformers.

#### New Aspects

Fundamental study of the binding motifs of important natural products to protons and sodium cations. The intrinsic influence of the nature of the counterion on tautomeric equilibria in respective molecular ions is probed in the gas phase allowing undisturbed comparison with computational analysis.

#### Keywords

IRMPD-spectroscopy, DFT-Calculation, gas-phase analysis of ergothionein and hercynine molecular ions

## Mass Spectrometric Challenges: Investigations of a $\text{HAuCl}_4$ catalysed reaction

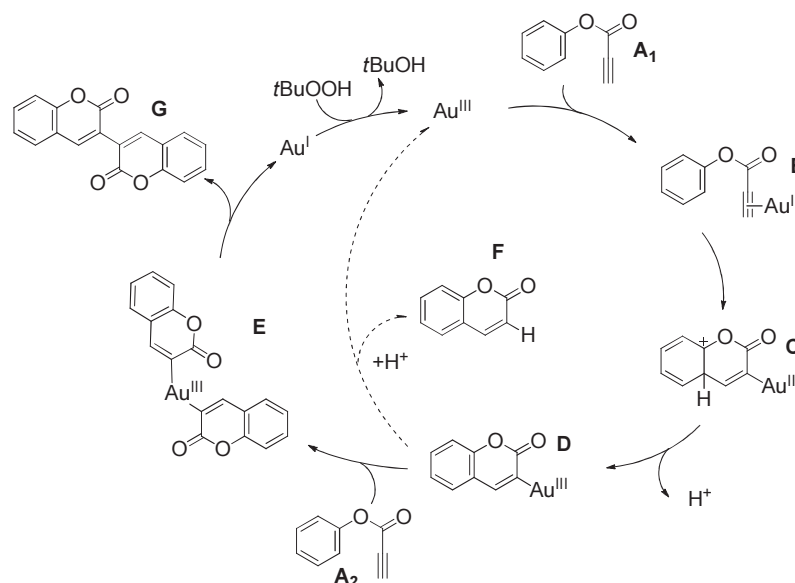
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The discovery of the reactivity of gold compounds started a so-called gold rush in chemical research. Since then the application of gold in organic catalysis increased rapidly.

*Wegner et al.* reported a gold-catalyzed domino cyclization and oxidative coupling reaction for the synthesis of dicoumarin in 2008.<sup>[1]</sup> During their investigations of a metal-catalyzed cyclization of arylpropionic esters into coumarin precursors, they discovered a second product, which originated from a oxidative coupling of two coumarin subunits. Dicoumarin derivatives are interesting because they take part in medical applications.<sup>[2]</sup>

The first step of the domino cyclization/oxidative coupling reaction has already been studied by *Wegner et al.*<sup>[1]</sup> Our research goal is the characterization of the real constitution of the catalyzing species **B**, **C**, **D** and **E**. The combination of  $\text{Au(I)}/\text{Au(III)}$  as catalyst is a hot, controversial issue.<sup>[3]</sup>



Unfortunately the concentration of the reaction mixture is too high and the solvent isn't able to form a stable electrospray. Another problem is the corrosion of the stainless steel ESI-needle caused by the aggressive chlorauric acid.

We developed a method to investigate the  $\text{HAuCl}_4$  containing reaction solution by electrospray ionisation-mass spectrometry. Two negatively charged gold(III) containing reactive intermediates as well as the substrate and the products and their temporal evolution up to 6 h could be detected.

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## The gas phase structure & reactivity of iridium and rhodium Cp\* dimers

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In order to study the gas phase structure and reactivity of chloropentamethylcyclopentadiene iridium and rhodium dimers, a combination of ESI-MS and UV photodissociation carried out in an FT-ICR mass spectrometer and travelling wave ion mobility mass spectrometry (TWIMS) was applied. Nanoelectrospray ionization of the neutral dimer complexes  $[(\text{Cp}^*\text{MCl}_2)_2]$ ,  $\text{M} = \text{Ir}$  or  $\text{Rh}$ , in dichloromethane produces a monocationic complex for each via bond heterolysis (eq 1) and loss of an anionic chloride ligand. The mass selected ions may then be subjected to UV light to produce another monocationic complex possessing via bond homolysis (eq 2) and loss of a chloro radical. Reactivity toward  $\text{O}_2$  and  $\text{H}_2\text{O}$  neutral species of both the coordinatively unsaturated dimer systems are thus open to be explored.

