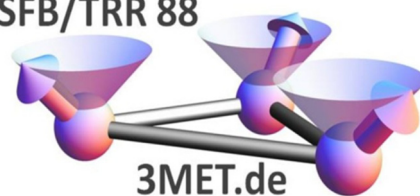


FTMS

Fachtagung für hochaufgelöste Massenspektrometrie

Book of Abstracts

SFB/TRR 88



Fachgruppe FT-MS und hochauflösende Massenspektrometrie der DGMS

21.-22. September 2017

in Kaiserslautern

Inhaltsverzeichnis

Grußworte

Liebe Mitglieder und Gäste unserer DGMS-Fachgruppe,

ich freue mich sehr, Sie zum Treffen der „Fachgruppe FTMS und hochauflösende Massenspektrometrie“ der Deutschen Gesellschaft für Massenspektrometrie an der Universität Kaiserslautern zu begrüßen. Dass unser DGMS-Fachgruppentreffen hier stattfinden kann, verdanken wir der Bereitschaft von Gereon Niedner-Schatteburg und Marc Prosenc, die freundlicherweise als lokale Veranstalter für uns alles so gut vorbereitet haben. Dank gebührt auch allen, die mit ihrer aktiven Teilnahme den wissenschaftlichen Gehalt unseres Fachgruppentreffens ausmachen und natürlich den Firmen, die mit Ihrem Sponsorenbeitrag das Treffen großzügig unterstützen.

Unsere Fachgruppe ist unter den derzeit sieben DGMS-Fachgruppen von mittlerer Größe, obwohl eine enorme Anzahl von MassenspektrometikerInnen heute routinemäßig mit Hochauflösung und exakter Masse zu tun hat – aber es ist eben in vielen Bereichen Routine geworden.

Ihren Anfang nahm die Fachgruppe FTMS mit Treffen von Anwendern und Entwicklern der FT-ICR-Geräte bei Michael Przybylski in Konstanz. Inzwischen haben die FT-ICR-Massenspektrometer durch Orbitraps und hochauflösende TOF-Geräte in Sachen Auflösung und Massengenauigkeit starke Konkurrenz bekommen. Aus diesem Grund wurde unsere Fachgruppe 2010 nach dem Treffen in Mülheim bei Wolfgang Schrader, der 2010–2015 als Fachgruppensprecher wirkte, thematisch erweitert und entsprechend umbenannt. Damit sollte die Fachgruppe „FTMS und hochauflösende Massenspektrometrie“ für alle diejenigen interessant sein, die Entwicklung – apparativ oder methodisch – auf diesem Gebiet betreiben. Ebenso dürfte die Fachgruppe ein Forum bieten, sich gezielter als auf großen Tagungen zum Themenkomplex zu informieren, neue Kontakte zu knüpfen und bestehende zu pflegen.

Wenn Ihnen dieses familiäre Treffen gefallen hat und es ein paar wissenschaftliche Anreize setzen konnte, würde es unserer Fachgruppe sicher gut tun, wenn Sie davon Ihren Kollegen erzählen, damit unsere DGMS-Fachgruppe auch 2019 wieder zu einem inspirierenden Treffen zusammen kommen kann.

Damit ein nächstes Fachgruppentreffen auch wirklich stattfinden kann, muss die Fachgruppe weiter bestehen. Zu diesem Zweck werden wir auf unserer kurzen Mitgliederversammlung wieder einen Sprecher/Sprecherin und VertreterIn wählen und uns eine Satzung im Einklang mit der Satzung der DGMS geben. Vielleicht denkt ja auch schon jemand aus unserem Kreis darüber nach, das kommende Treffen zu organisieren?

Nun wünsche ich uns allen eine gute Tagung

Jürgen Gross

Fachgruppensprecher

Vorwort

Liebe Kollegen,

im Namen des Sonderforschungsbereichs **3MET.de** und der TU Kaiserslautern begrüßen wir Sie zur Fachtagung für hochaufgelöste Massenspektrometrie in Kaiserslautern. Wir möchten uns an dieser Stelle für die Unterstützung unserer Sponsoren Bruker und Thermo Fischer Scientific bedanken, sowie bei der TU Kaiserslautern und unserem Transregio-Sonderforschungsbereich **3MET.de** und der DFG für die großzügige Förderung und Unterstützung.

Wir wünschen allen eine schöne, diskussions- und lehrreiche Tagung und freuen uns auf einen regen Austausch zwischen Nachwuchswissenschaftlern und etablierten Kollegen.

Gereon Niedner-Schatteburg

Marc Heinrich Prosenc

Programm

Donnerstag, 21.09.2017

9:00 Uhr: Begrüßung

9:15 Uhr Vortrag Martin Beyer

9:45 Uhr Vortrag Marianne Engeser

10:15 Uhr: Kaffeepause

11:00 Uhr Vortrag Julian Bergmann

11:30 Uhr Vortrag Jochen Friedrich

12:00 Uhr: Lunch

14:30 Uhr Vortrag Rainer Wolf

15:00 Uhr: Postersession

16:30 Uhr: Vortrag Jennifer Mohrbach

17:00 Uhr: Vortrag Aikaterini Kondyli

17:30 -18:00 Uhr: Mitgliederversammlung der Fachgruppe FTMS und hochauflösende Massenspektrometrie

19:30 Uhr: Konferenzdinner im „21“

Freitag, 22.09.2017

9:20 Uhr: Vortrag Basem Kanawati

9:50 Uhr: Vortrag Lutz Schweikhard

10:20 Uhr: Kaffeepause

11:00 Uhr: Vortrag Yuri Tsybin

11:30 Uhr: Vortrag Dietrich Volmer

12:00 Uhr: Verabschiedung

Wer am **Mittwoch** schon anreist, ist herzlich willkommen, mit uns ab 20:00 Uhr Wein zu trinken!

Abstracts

UV-VIS Spectroscopy and Photochemistry of Trapped Ions Using FT-MS

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While infrared spectroscopy of ions is a mature field, the potential of UV-VIS spectroscopy of ions is barely touched. Ben Freiser pioneered the field in the 1980s, using lamps and monochromators.^[1] In our preliminary work, we used the same approach to investigate the photochemistry of $V^+(H_2O)_n$, $n = 1-4$, with a high-pressure mercury lamp and band-pass filters.^[2] With optical parametric oscillators (OPOs), modern laser technology offers much more powerful tools to cover wide range of wavelengths, which can be used e.g. for the photodissociation of peptide ions.^[3] FT-MS is, compared to time of flight techniques or quadrupole mass filters, inherently slow, with a duty cycle in the range of seconds. High-resolution spectroscopy over a wide wavelength range, which requires the recording of 10^3 - 10^4 mass spectra, is not the prime application of FT-MS instruments. However, the combination of high mass resolution, long trapping times, flexible mass selection capabilities in a collision-free environment and simultaneous detection of all fragments with high fidelity of absolute intensities gives FT-MS significant advantages over other techniques for specific problems. Selected examples which illustrate these advantages include photochemical hydrogen formation in the $Mg^+(H_2O)_n$, $n = 1-5$, system, as well as the photochemistry of glyoxylate in sea-salt clusters.

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One-electron reduction of isolated metallo-supramolecular aggregates

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Are the metal centres in metallo-supramolecular aggregates electronically isolated from each other? Is there an information transfer via ligands or space? How redox-innocent are the ligands? Gaining knowledge on the redox behaviour of metallo-supramolecular aggregates in solution is highly desirable, but rather difficult due to the inherent lability of the system: It is hard to oxidise or reduce only the aggregate of interest – and not affect one of the other compounds of the (desired) manifold of species present in equilibrium. Herein, a means is presented to study the reduction of isolated supramolecular aggregates under well-defined conditions using mass-spectrometry.

During ETD and ECD, a single electron is attached to the metallo-supramolecular aggregate. The resulting reduced species is either characterised by high resolution tandem mass-spectrometry or can even be subjected to another reducing step (ECD/ECD) prior to analysis. The presented examples include the stepwise reduction of a copper(II) helicate revealing otherwise inaccessible mechanistic details of its interconversion to the respective copper(I) congener with different stoichiometry.[1] Single-electron reduction of homoleptic metallosupramolecular squares shows the non-innocence of bipyridine ligands [2] whereas a similar experiment with bimetallic squares [3] enables the differentiation between different reduction sites. The effect of linker length is illustrated by reduction of dinuclear gold macrocycles of various ring sizes.[4]

Experimental

High-resolution electrospray ionisation (ESI) mass spectra were recorded on a Bruker Apex IV FT-ICR or a Thermo Fisher Scientific LTQ Orbitrap XL mass spectrometer. A series of multiply charged cations typically is observed for metallo-supramolecular aggregates due to abstraction of several anions during the ESI process. After mass-selection of the species of interest, one-electron reduction is performed in the gas phase using the electron capture dissociation (ECD) technique in the FT-ICR or the electron transfer dissociation (ETD) method in the ion trap module of the Orbitrap XL instrument. Reduction products of interest were again isolated and fragmented by collision-induced dissociation (CID) or subjected to a second one-electron reduction step.

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(Ultra-)High Resolution Multiple-Stage Tandem Mass Spectrometry in A Time-of-Flight Mass Spectrometer

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Hans Geissel^{1,2}, Johannes Lang¹, Alexander Pikhtev³, Christoph Scheidenberger^{1,2}, Wolfgang
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A novel method has been developed for (ultra-)high resolution precursor selection in a multiple-reflection time-of-flight mass spectrometer (MR-TOF-MS). First, ions are collected in an RF-trap and dispersed in time-of-flight according to their mass-to-charge ratio. Then mass-selective re-trapping allows separating even isobaric ions in the same RF-trap [1,2]. The process can be repeated multiple times, enabling the first tandem-in-time multiple-stage tandem mass spectrometry (MS^N) in a TOF-MS with (ultra-)high resolving power in every stage [3].

The setup, a custom-built mobile MR-TOF-MS, mounted inside a single frame of 0.8 m³, consists of an atmospheric pressure inlet for various ion sources (e.g. nanoESI), an ion preparation system (RFQ-ion-guide, -mass-filter, -cooler and -trap), a time-of-flight analyzer and a detector [4,5]. In each stage of tandem MS ions are re-trapped mass selectively and CID can be applied to produce and measure their fragments. A software package was designed and developed for hardware control, data acquisition and for online and offline analysis.

The mobile MR-TOF-MS can reach mass resolving power up to 300,000. For precursor isolation, Re-trapping efficiencies up to 35 % and mass separation powers (FWHM) in excess of 70,000 of caffeine molecules were reached. Glutamine and Lysine were successfully isolated from their respective isobaric contaminants and their isolated dissociation spectra have been measured. Tandem mass spectrometry with two stages (MS/MS) and three stages (MS³) has been performed on the protonated ion of Lysine. Furthermore, the applicability of the method to crude oil analysis has been demonstrated by applying precursor isolation (mass window: ~0.05 u @ mass 337 u) and tandem mass spectrometry on a crude oil sample [3].

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Enabling Routine Isotopic Fine Structure Analysis by Harmonics Detection

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¹Bruker Daltonik GmbH, Bremen, Germany; ²Bruker Daltonics Inc., Billerica, MA; ³The Institute for Energy Problems of Chemical Physics Russian Academy of Sciences, Moscow, Russia

Several years ago, comprehensive analysis of complex mixtures using IFS information typically required FT-ICR systems equipped with high field magnets, i.e. 9.4T or preferred higher field strengths. With the advent of improved detection and processing technologies such as Absorption Mode Processing (AMP)¹ and the dynamically harmonized cell^{2,3}, the achievable mass resolution in complex mixtures increased dramatically and enabled a routine access to IFS information even with low field (7T) FT-ICR instruments. The performance will be further up to n-fold improved if multiple harmonics now can be efficiently detected. The detection of these multiple harmonics as well as new FT-ICR cell geometries require an improved understanding and control of the ion motion in the ICR cell. Particularly, the control and minimization of the magnetron motion⁴ proved to be a key requirement to enable routine IFS analyses of complex mixtures.

Here we provide an overview on instrumental advances enabling the control over the magnetron motion. A 7T solariX 2xR instrument is used to demonstrate the improved performance, especially routine access to a broadband resolving power of 1,000,000 or more for complex samples such as crude oils. Recent results of Asphaltenes will be shown. AMP and multiple harmonics detection help further increase the analysis speed at constant resolution, which if combined enables IFS analysis for routine LC separation workflows. Data of a pharmaceutical mixture analyzed by LC/MS show isotopic patterns revealing IFS with excellent correlation to relative ratios of individual atoms, as well as accurate mass detection.

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How can we get more productivity in the analysis of HMS data?

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High resolution mass spectrometers are widely spread in analytical laboratories for routine analysis. A significant increase in productivity can be achieved by high mass accuracy and high resolution mass spectra. Results can be obtained faster and are more valid.

Today excellent experimental data can be obtained with various type of instruments. However, nevertheless we wonder, whether we really get optimum results out of experimental data or whether there is still room for improvement. For data analysis a lot of tools exist in the field of bioanalytics, but in the analysis of chemicals software tools are missing or could be improved. This mainly concerns to the determination of molecular formulas from compounds with various hetero atoms.

This lecture is thought as a kickoff to come into a discussion, what is still missing and how we can develop new or improved software tools in collaboration with university and/or the vendors.

In the lecture examples will be discussed such as

- Calculation of molecular formulas from complex isotope pattern
- Optimization of isotope pattern analysis in terms of mass accuracy, signal intensity and mass defect
- Determination of elemental compositions with the help of fine structured isotope pattern
- Improvement of the (interactive) comparison of experimental and theoretical isotope pattern
- Reduction of the number of hits in elemental composition in the case of defined multiple number of elements
- Individual definition of super atoms for the analysis of oligomers (repeating units)
- mass defect as a tool for element specific detection
-

Cryo Tagging Infrared Spectroscopy and Temperature Controlled Kinetic Studies in a Tandem Trap Mass Spectrometer

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A tandem cryo trap FT-ICR mass spectrometer has been equipped with two separately operable ion sources. This setup is used for the kinetic and spectroscopic investigation of the adsorption behavior and adsorbate influences on transition metal containing complexes and naked transition metal clusters under isothermal cryo conditions. Gas phase infrared multiple photon dissociation (IR-MPD) experiments in conjunction with density functional theory (DFT) computations enable the analysis of adsorbate induced changes on the structure and spin multiplicity of transition metal cores. The investigation of cluster adsorbate complexes as isolated species in the gas phase enables insight into the metal-adsorbate bonding and unravels structure-reactivity relationships. ^[1-3]

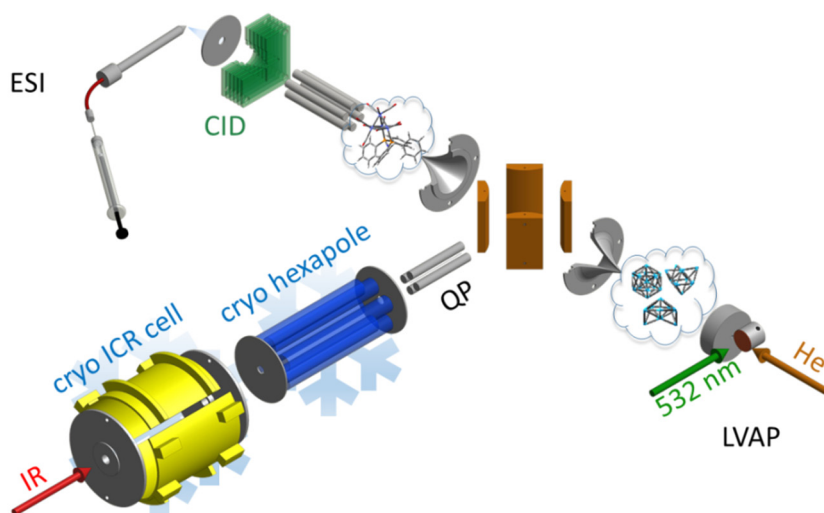


Fig. 1: Schematic drawing of the dual source tandem cryo trap FT-ICR MS setup. Ions are generated in a Laser VAPorization (LVAP) source or in an Electro Spray Ionization (ESI) source. Either type of ions is injected into the first ion trap (cryo hexapole) via a switchable 90° ion bender and a quadrupole mass filter (QP). The cryo cooled ions and their reaction products are guided into the cryo ICR-cell, where they are isolated, irradiated by IR laser pulses and detected.

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Investigation of chemical alteration on crude oil fouling by high resolution mass spectrometry

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Introduction

Crude oil fouling still remains one of the biggest unresolved problems in petroleum industry. The deposition of unwanted material in upstream operations has various environmental and operational effects (loss of thermal efficiency, catalyst poisoning, plugged pipelines, product instability etc.). This phenomenon is until now poorly understood not only because of the complex chemical nature of crude oil, but also due to the various reaction mechanisms involved. Formation of crude oil fouling can undergo through several pathways such as autoxidation, polymerization and thermal decomposition. Reducing fouling is of great importance and a deeper understanding on the reaction mechanisms is necessary. High resolution mass spectrometry is a powerful tool for complex mixtures, enabling crude oil characterization on a molecular level.

Experimental

A lab build reactor was used for testing a light Arabian crude oil. The samples were heated at a temperature range from 150°C to 450°C under oxygen and argon conditions. Samples were collected and measured after 3 days. For mass spectrometric analysis a research-type Orbitrap Elite was used. Spectra were collected in SIM mode with a mass resolution of 480000 (at m/z 400, 1.5s transient). ESI in positive ion mode was used with a potential of 4kV.

Results

The reactions to investigate the fouling of crude oil, which describes the deposition of solid material on surfaces within a large industrial reactor, were simulated in the laboratory using a laboratory built reactor. The results obtained under oxygen and argon conditions at different temperatures show formation of new compounds after thermal treatment mostly with high number of carbon and Double Bond Equivalent (DBE). A general trend for the heteroatom containing classes shows an increase by increasing the temperature. Under inert conditions this trend also exists but in lower degree as the absence of oxygen reduces the reactivity of the mixture. The nitrogen containing species detected after heating at 450 °C were three times higher compared to the unreacted sample. The increase of the aromaticity of these species indicates that the processes of dehydrogenation and polymerization might take place. We are studying the behavior of extremely complex samples on the molecular level to better understand the activity and the formation of fouling material during the reaction. At 350°C and 450°C formation of more solid material was observed than at lower temperature. We will present the results from these studies showing that ultrahigh resolution mass spectrometry is the method of choice for investigating such complex reactions.

Novel Aspects

Ultrahigh resolution mass spectrometry was used to investigate the complex reaction of fouling as it occurs in industrial reactors.

FT Artifacts in Ultra high resolution Fourier Transform Mass Spectrometry

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Abstract:

Time-domain transient truncation at the end of an FTMS acquisition causes side lobes development around each main signal in the frequency and mass spectra. Depending on the pressure in the ICR cell region, the interference from the side lobes can be severe, especially under ultra-high vacuum. These wiggles can unfortunately leak into mass lists (by many peak picking algorithms) and add noise to m/z lists, since they do not have any chemical meaning. The problem intensifies with longer time-domain acquisitions and represents an urgent issue, which needs to be solved for the future of ultra-high vacuum FTMS, especially when new high memory digitizers emerge, which enable longer discrete time signal storage. The origin of the FT-artifacts was thoroughly investigated and a new filter was developed for automatic recognition and elimination of the wiggles from FT-ICR mass spectra based on evaluation of resolution and FWHM data of FT signals.

Precision mass spectrometry of exotic nuclei at ISOLTRAP

Lutz Schweikhard for the ISOLTRAP collaboration (<https://isoltrap.web.cern.ch/isoltrap>)

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The ISOLTRAP [1] collaboration has measured the masses of short-lived nuclei at ISOLDE/CERN for almost three decades [2,3]. The research fields include nuclear structure, the origin of the elements and fundamental symmetries. ISOLTRAP has evolved to a setup consisting of four ion storage devices, a linear RFQ trap (cooler and buncher) [4], a multi-reflection time-of-flight (MR-ToF) component [5], and two Penning traps, one for the preparation of the ion ensembles and a second for the actual ion-cyclotron-resonance (ICR) mass measurements.

For most of the time only the time-of-flight resonance detection [6] has been used and further developed, e.g. by introducing the quadrupolar excitation [7] and axialization [8] or the Ramsey scheme for the excitation of the ion motion [9]. Since a few years, the MR-ToF device, originally implemented for ion separation [10], has also been employed as a mass spectrometer of its own, which allows to extend the measurements to very exotic species (with lifetimes of only a few tens of milliseconds and very low production yields). Recently, the Phase-Imaging ICR method, developed at SHIPTRAP [11], has been implemented at ISOLTRAP as well, which increased the resolving power by more than an order of magnitude compared to ToF-ICR MS for the same measurement time.

The presentation will give a short review of the history of ISOLTRAP and will then focus on the methods and corresponding advantages of the newer MR-ToF and PI-ICR components, as well as a couple of applications with these devices such as mass measurements of $^{53,54}\text{Ca}$ and $^{52,53}\text{K}$ [12] and of the nuclear isomers in ^{127}Cd and ^{129}Cd [13], respectively.

References:

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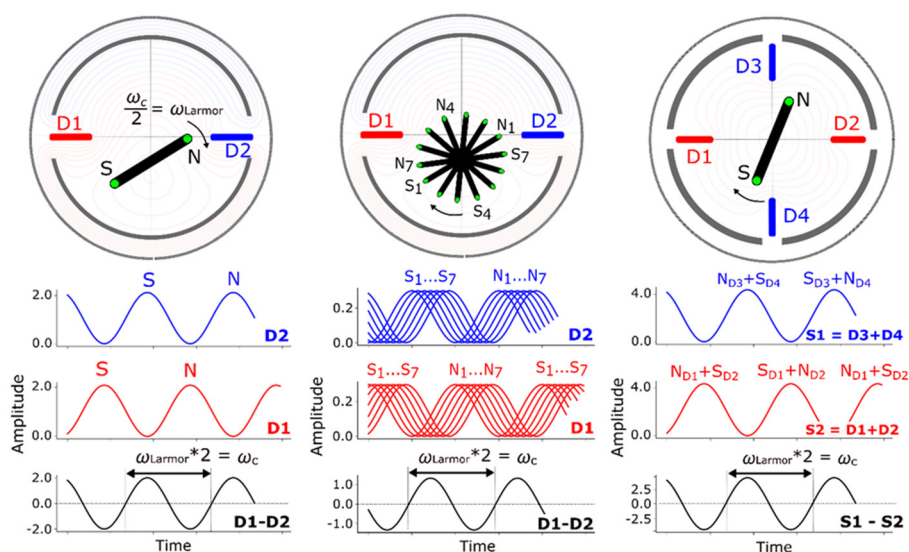
FT-ICR MS at the Cyclotron Frequency

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Advances in environmental and life sciences require improved performance of even the most powerful analytical techniques to target the extreme complexity of modern samples, including Fourier transform mass spectrometry (FTMS). Further improving of the FTMS performance is feasible via developments in (i) mass analyzer operating principles, (ii) ion detection principles and data acquisition electronics, and (iii) sophistication in data processing. We will review our recent advances in these areas and demonstrate their impact on the corresponding applications. Particularly, we will describe a fundamentally novel approach to ion cyclotron resonance FTMS, enabling its operation at the true cyclotron frequency instead of the commonly employed reduced cyclotron frequency. The key toward this capability is in the novel type of ion structures: ion slabs, elliptic cylinders or stars, as depicted by the figure below.

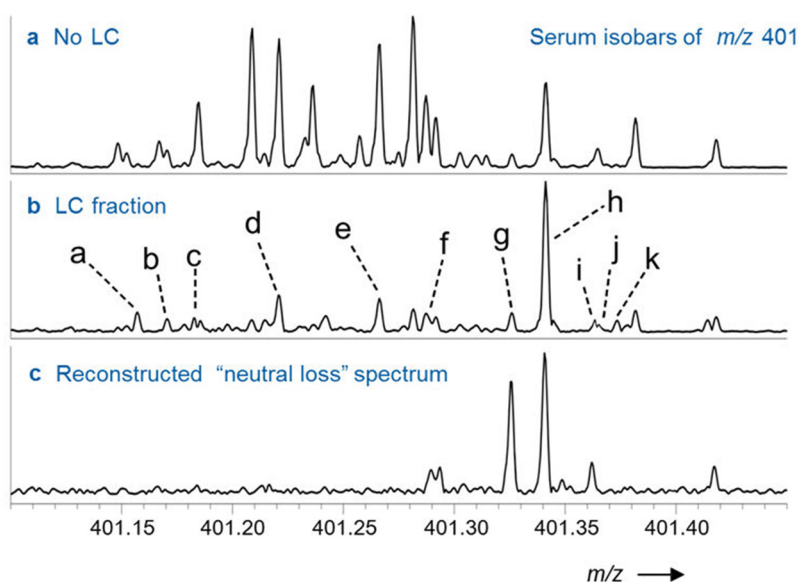


Ultra-High resolution mass spectrometry supports the accurate quantification of vitamin D metabolites in human biofluids

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LC-MS/MS assays based on low resolution triple quadrupole mass spectrometers have become the primary choice for high-end analyses of vitamin D in biological fluids such as human serum. These analyses of the concentration levels of Vitamin D in human serum are challenging for several reasons, however, including problems with ionization efficiency and mass spectral selectivity. The latter are only partially addressed through the application of stable isotope internal standards. In LC-MS/MS of vitamin D compounds, co-eluting isomeric and isobaric ions have the potential to interfere in the analysis, even in MS/MS mode. These selectivity issues arise from improper choice of MRM transitions and serious interferences therefore remain a problem in many published assays. This presentation describes systematic errors and accuracy issues of LC-MS/MS for vitamin D metabolites in human serum. The experiments for visualization and subsequent characterization of interfering isomeric and isobaric compounds utilized low resolution triple quadrupole MS, medium resolution QqTOF, ultra-high resolution FTICR-MS and ion mobility instruments. In the presentation, interferences from both endogenous and exogenous compounds are considered and it will be shown how they impact specificity of analysis and potential systematic errors. It will also be demonstrated that for low resolving power QqQ instruments, multiple isomers/isobars influence chromatographic peak areas in MRM experiments, with subsequent significant systematic errors. Many of these issues cannot be resolved by implementing medium resolution QqTOF mass spectrometers, as resolving power is insufficient. FTICR-MS on the other hand enabled detailed characterization of the “isobaric space” of vitamin D in human serum and identification of several of the culprit species. The presentation highlights a technical solution for avoiding or minimizing these interferences from isobars and isomers based on gas-phase differential ion mobility spectrometry (DMS)-MS/MS.



Poster

Stabilizing the Carbon Dioxide Radical Anion in Salt Clusters

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Marine aerosols [1] consist of a variety of compounds and are of great importance for many atmospheric processes, such as backscattering of solar radiation via clustered sea salt particles [2]. With mass spectrometry, this study investigates the photodissociation cross section and the photochemical reaction products of sea salt clusters doped with glyoxylate [3], which appears in organic aerosols. Figure 1a) shows the photodissociation cross sections for several cluster sizes from 300–400 nm. The most interesting fragment is the one where a carbon dioxide radical anion is stabilized in the NaCl cluster. This happens in the deeper UV from 225–250 nm, but also in the actinic region from 310–370 nm, which is relevant for tropospheric reactions (Figure 1b). Supporting ab initio calculations showed that the broad absorption in this wavelength range is due to the ability of the glyoxylate to rotate almost freely along its O-C-C-O angle.

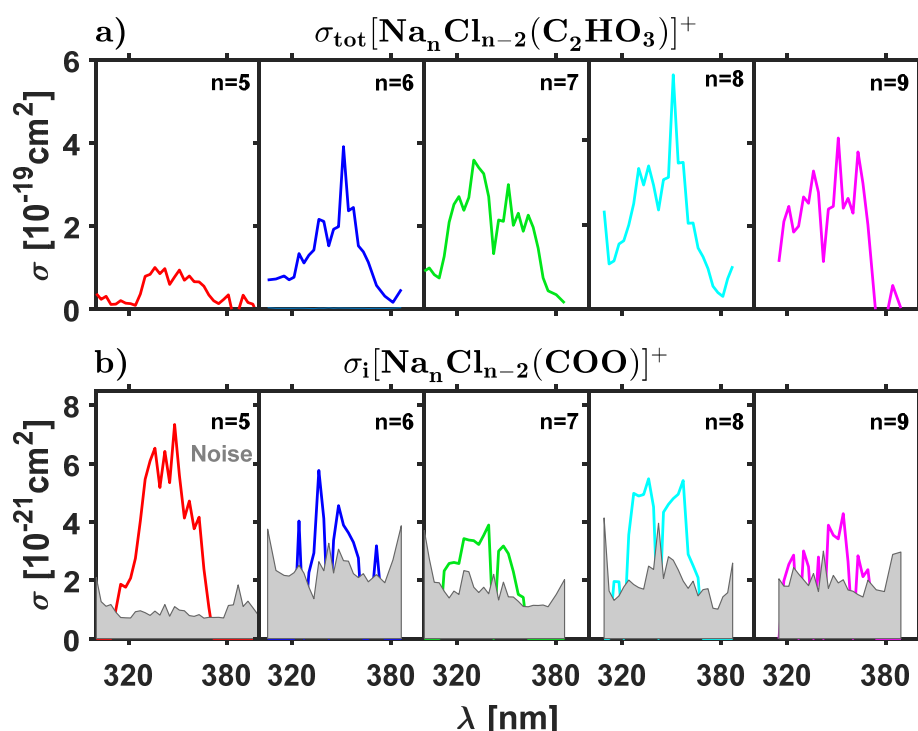


Figure 1: (a) Total photodissociation cross section of the clusters $[\text{Na}_n \text{Cl}_{n-2} (\text{C}_2\text{HO}_3)]^+$ and the (b) contribution of the fragment $[\text{Na}_n \text{Cl}_{n-2} (\text{COO})]^+$.

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IR spectroscopy and reactivity studies of hydrated $\text{CO}_2^{\bullet-}$

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Gas phase studies have provided significant contributions to the understanding of activated CO_2 .^[1] The metastable $\text{CO}_2^{\bullet-}$ is stabilized by a solvation shell and $\text{CO}_2^{\bullet-}(\text{H}_2\text{O})_n$ can be studied readily by Fourier transform ion cyclotron resonance (FT ICR) mass spectrometry. An EKSPLA NT 277 optical parametric oscillator system is coupled into the reaction cell, covering the 2235-4000 cm^{-1} region at 1000 Hz pulse repetition rate.

The products of the reaction between $\text{CO}_2^{\bullet-}(\text{H}_2\text{O})_n$ and the two small organic molecules 3-butyn-1-ol and 1-amino-3-butyne are investigated. Reaction enthalpies are calculated via nanocalorimetry.^[2] Kinetics for long reaction delays reveal reaction pathways. Special attention is given to the potential formation of ring structures and covalent bonds.

$\text{CO}_2^{\bullet-}(\text{H}_2\text{O})_n$ ($n_{\text{avg}} \approx 43$) is studied in the O-H stretch region (2700-4000 cm^{-1}) via IR photodissociation spectroscopy. It shows bulk-water like absorption behavior and a small local absorption maximum at 3710 cm^{-1} , which corresponds to the free O-H stretch vibrations at the surface of the cluster.^[3]

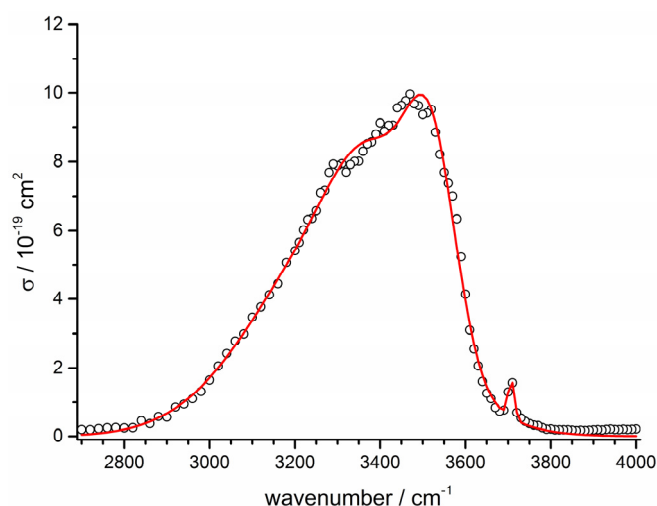


Figure 1. Infrared photodissociation spectrum of $\text{CO}_2^{\bullet-}(\text{H}_2\text{O})_n$ ($n \approx 43$) in the OH-stretch region.

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Historical charcoal additions potentially improve stability of soil organic carbon

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Improving the stability of soil organic carbon (SOC) and soil's capacity to store SOC are promising ways to mitigate climate change. Recently, several studies showed that additions of charred biomass (e.g. charcoal) elevated SOC stocks and stabilized natural organic matter; however, the mechanisms for C stabilization are hardly known.

We investigated SOC, dissolved organic matter (DOM) and particulate organic matter (POM) of two different soils and their counterparts with former inputs (several decades ago) of charcoal by means of elemental analysis. Further, hot water extracts (HWE) of soils and applied charcoal were investigated by the ESI-FTICR-MS for molecular level details of thousands of inherent organic compounds, solid state NMR is made for soils and charcoal, respectively.

Charcoal additions increased substantially concentrations of black C, total C and total N in bulk soil, however, concentration of water extractable SOC and N remained unchanged. Pattern of the POM size fractions changed with a relative increase in the free POM fraction and a decrease in the occluded POM fraction and soil particles <20 µm. However, all POM fractions in charcoal enriched soils were augmented with C and N.

Organic compounds found in HWEs of soils and charcoal contained a broad range of molecules, which highly varied in their polarity and aromaticity. Highly condensed hydrocarbons were found however exclusive in charcoal HWEs. This is in contrast to molecular composition measured of Cambisols and Luvisols, which were generally less aromatic (lignin range only). Surprisingly, differences between molecular composition of soil and their charcoal enriched forms were negligible – in contrast to solid state NMR investigations.

This study confirmed previous findings that charcoal additions increase SOC long-lastingly. Further, an assumed abrasion resistance of charcoal particles may explain elevated free POM fractions, which thereby may act as sorbent of soil organic matter. So stabilized, partially and slowly charcoal ageing under oxidation and hydratisation lead to structures similar to humic acids. A comparison to wildfire influenced soil samples complete the investigations.

Aspects: Charcoal addition with long range depot effect lead to an effective carbon-sequestration in contrast to wild fire clearing.

Praxistest von Jeffamine M-2005 zur internen Kalibrierung für exakte Massen in der positiv-Ionen MALDI-TOF-MS

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Für die matrix-unterstützte Laserdesorption/Ionisation (MALDI)^[1] in Kombination mit Flugzeit-massenspektrometrie (TOF-MS) wurde ein basisches Polypropylenglykol (PPG), nämlich Jeffamine M-2005 (Huntsman (Germany) GmbH), als interner Massenstandard etabliert^[2]. Ein ähnliches Jeffamine (M-600) wurde bereits erfolgreich bei Direct Analysis in Real Time (DART) eingesetzt^[3]. Im Unterschied zu den sonst häufig verwendeten Polyethylenglykolen (PEGs) werden für Jeffamine aufgrund der basischen Amino-Endgruppe bessere Ausbeuten an $[M+H]^+$ -Ionen erhalten. Zur Bestimmung exakter Massen in der MALDI-TOF-MS kann Jeffamine M-2005 als neue vielseitige Kalibriersubstanz im Bereich m/z 200–1200 verwendet werden.

Jeffamine M-2005 wurde von Huntsman (Germany) GmbH zur Verfügung gestellt. Jeffamine M-2005 in Methanol (10 mg ml^{-1}) wurde 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enyliden] malononitril (DCTB, 10 mg ml^{-1} in Tetrahydrofuran) auf Probenträgern aus Edelstahl präpariert. Das Verhältnis von Analyt- zu Matrix-Lösung variierte von 1:5 bis 1:40. Zur Verwendung als interner Standard wurden die Analyt-Matrix-Lösungen bei der Probenpräparation so mit der Jeffamine-Lösung versetzt, dass die Peaks des Standards zum Analyten Intensitätsverhältnisse von ca. 1:10 bis 2:1 erreichten.

Die MALDI-TOF-Spektren wurden an einem Bruker Autoflex Speed LRF im positiv-Ionen-Reflektor-Modus, gemessen. Das Gerät wurde mit Bruker FlexControl 3.4 gesteuert und die Spektren mit Bruker FlexAnalysis 3.4 ausgewertet.

Jeffamine M-2005 kann mit Matrices wie DCTB, CHCA und DHB kombiniert werden und liefert durchweg intensive Peaks für $[M+H]^+$ -Ionen, während $[M+Na]^+$ -Ionen anders als bei nichtbasischen PEGs oder PPGs kaum auftreten. Jeffamine M-2005 ergibt ein übersichtliches Spektrum, in dem nur noch eine weitere Reihe von schwachen Peaks bei $[M+H-H_2O]^+$ auftritt. Für die bei uns üblicherweise anfallenden Proben ist DCTB^[4] eine besonders wichtige Matrix, da sie mit ihnen bei geringem Laserfluss intensive Signale und hohe Massenauflösung liefert.

Als Beispiele für die Anwendung auf Analyten unterschiedlichster Polaritäten werden Polyethylenglycole (PEG300 und PEG600), [60]Fulleren und die ionische Flüssigkeit Trihexyl(tetradecyl)-phosphonium tris(pentafluoroethyl)-trifluorophosphat in DCTB präsentiert. Mit Jeffamine M-2005 als internem Standard in DCTB-Präparationen von Analyten im Bereich von 300–1000 u lassen sich am Bruker Autoflex reproduzierbar Massengenauigkeiten von 2–5 ppm erzielen.

Eine Referenzmassenliste für Jeffamine M-2005 mit Werten von m/z 234 bis m/z 1220 ist erstellt und auf Wunsch auch elektronisch im Format für Bruker FlexControl vom Autor erhältlich.

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Reactivity of $M(\text{CO}_2)(\text{H}_2\text{O})_n^+$ cations; $M=\text{Co}, \text{Mg}$

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Hydrated singly charged metal ions doped with carbon dioxide, $M(\text{CO}_2)(\text{H}_2\text{O})_n^+$ ($M=\text{Co}, \text{Mg}$; $n<50$), in the gas phase are valuable model systems for the electrochemical activation of CO_2 . These systems are studied on a modified 4.7 T Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer Bruker/Spectrospin CMS47X with an external laser vaporization source combined with laser spectroscopy.^{[1], [2]} Since mass spectrometry does not yield direct structural information, the presence of an intact CO_2 molecule was tested via the exchange against O_2 . For both metals, the exchange is efficient, as seen in figure 1. In contrast, no exchange is observed for the negatively charged species $\text{Co}(\text{CO}_2)(\text{H}_2\text{O})_n^-$, which suggests that a C-O bond was broken to yield $\text{OCOCO}(\text{H}_2\text{O})_n^-$. Reaction rate constants k_{abs} and thermochemical information are extracted from the data in a nanocalorimetric analysis, where the average cluster sizes and integrated intensities of reactants and products are modelled with differential equations.^[3] Furthermore, absorption spectra from the ultraviolet all the way to the infrared region of the electromagnetic spectrum are measured with the combination of tuneable OPO laser systems.

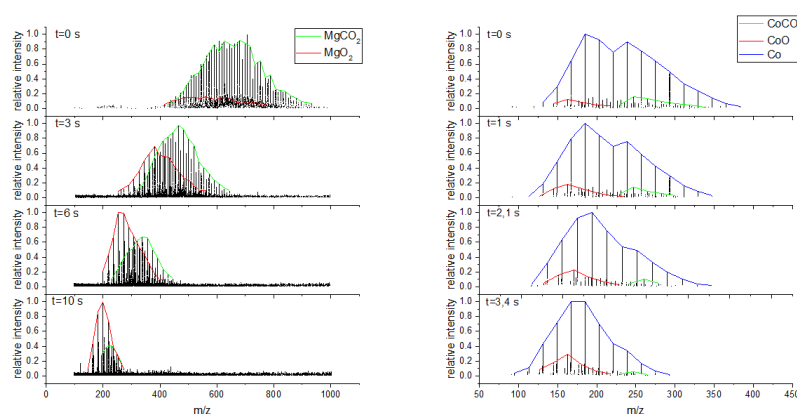


Figure 1: Mass spectra at different reaction delays. Left the reaction of $\text{Mg}(\text{CO}_2)(\text{H}_2\text{O})_n^+ \rightarrow \text{Mg}(\text{O}_2)(\text{H}_2\text{O})_n^+$, right the reaction of $\text{Co}(\text{CO}_2)(\text{H}_2\text{O})_n^+ \rightarrow \text{Co}(\text{O}_2)(\text{H}_2\text{O})_n^+$.

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Comparison of Xe/Kr atmospheric pressure photo ionisation to atmospheric pressure chemical ionisation for the analysis of complex mixtures

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Mass spectrometry has become an ubiquitous analytical technique for state-of-the-art analysis of complex samples from all research areas. The high resolving power and mass accuracy of FT-MS based techniques allow a comprehensive analysis. Nonetheless, non-targeted analysis often aims to cover a wide chemical space. Especially atmospheric pressure chemical and photo ionisation (APCI/APPI) are widely used. The ionisation in API sources is most often based on a complex reaction cascade and ionisation can be promoted via certain substances, i.e. dopants. Unfavourable ionisation artefacts are common in APCI, e.g. oxidative ionisation.

In this study APPI utilizing a Xenon lamp with photon energies of 8.4/9.6 eV was deployed and compared to classical APPI utilizing a Krypton lamp with photon energies of 10/10.6 eV and APCI utilizing a steel corona needle at low μA current. For this purpose, a modified gas phase API source (based on Bruker GC APCI II) was used, which discard solvent effects. Sample was introduced as evolved gas from coupling of the gas phase API source to a thermo balance via a heated transfer line and interface (Figure 1) ^[1]. The mass spectrometric analysis was conducted on a Bruker apex II ultra FT-MS equipped with a 7 T superconducting magnet. This allows for an elemental composition assignment and in-depth analysis of the occurring effects. Besides standard mixtures consisting of fatty acid methyl esters (FAME) and poly cyclic aromatic hydrocarbons (PAH), various petrochemical samples, such as defined distillation cuts, marine gas oil and bitumen, were investigated. The covered applicative area was broadened by sampling the thermal decomposition products (pyrolysis) of different wood types and polymers.

Based on the pyrolysis of polystyrene (a standard in thermal analysis) it turned out that also with Xe-APPI a broad oligomeric pattern up to the pentamere can be observed. Interestingly, the pattern changes drastically from APCI to APPI. Despite the fact that all decomposition products are pure hydrocarbons other species are ionized more efficiently in Kr- and Xe-APPI. This effect was also observed for distillation cuts of a crude oil. Analysis of the elemental composition assignments reveal a clear shift of the distribution between protonated (even) and radical cations (odd). APCI revealed mostly protonated ions for all investigated samples, whereas APPI give mostly radical ions. The proportion of odd-species was even higher for Xe-APPI.

In summary, the lower energy flux of Xe-APPI will result in a lower ionisation efficiency and higher limit-of-detection. Nonetheless, for investigations where sensitivity is not the most important aspect Xe-APPI can be deployed and the absence of protonated compounds leads to a further simplification of the spectra. This aspect is of high interest for ultra complex samples, such as in Petroleomics.

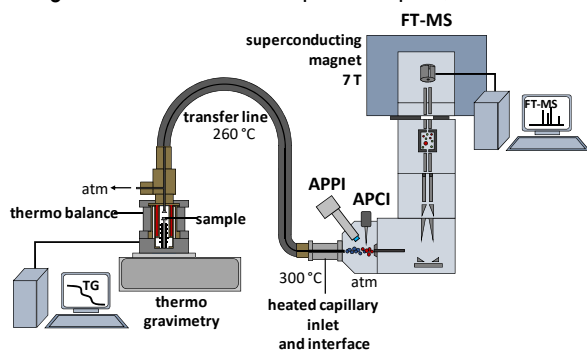


Figure 1: TG-APCI/APPI set-up utilized for studying Kr-APPI, Xe-APPI and APCI.

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FT-ICR-MS as a tool for IR Spectroscopy of Cold Ions in the Gas Phase

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For the past several years our group has been studying short-lived reactive intermediates in the gas phase. We gain insight into the mechanism of organometallic reactions by using ESI-MS to extract thermochemical data, such as bond dissociation energies (BDE) derived from CID experiments ^[1].

However, to obtain a more direct relationship between the collected data and the structure of reactive intermediates of ionic nature, ^[2] it is desirable to couple these methods, which rely solely on mass spectrometry, to spectroscopic characterizations.

We have therefore constructed an FT-ICR-MS instrument with a cryogenically cooled ICR cell. The ion trap can be cooled to less than 4 K, which allows us to use the neutral tagging technique ^[3] to record IR spectra in the spectral range of 2700-3600 cm⁻¹. Using hydrogen as neutral tag, we were able to record IR spectra of β -4-ethylphenylcobinamide and to elucidate its structure in the gas phase.

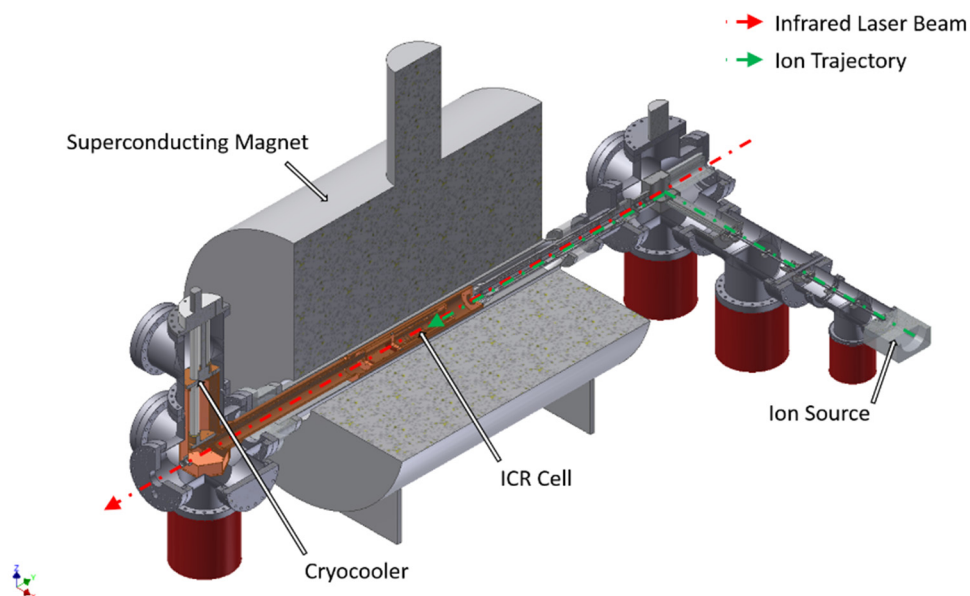


Figure 2: 3D model of our FT-ICR instrument as a tool for infrared spectroscopy of cold ion in the gas phase.

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Cold ion spectroscopy as a tool for investigation of bio-related compounds: FT-ICR-IR investigations on B₁₂ derivatives.

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Vitamin B₁₂ is an important source of radicals for biochemical radical pathways in mammals.^[1,2] The B₁₂ coenzyme is often said to be the “free radical reservoir”. In the past, our group measured the bond strengths in the B₁₂ cobinamide derivatives and compared them to computationally obtained values.^[3]

The computational prediction of favorable structures for RCbi⁺ ions is challenging, due to the presence of many flexible amide side chains, which form intramolecular noncovalent interactions.

In the current work we have probed the spectroscopic characteristics of the RCbi⁺ ions of different isomers and compared them to calculated results. This allowed for determination of the correct structure of the ion that is present in the gas phase during experiments.

The experiments were performed on a newly constructed instrument with a cryo-ICR ion trap. ESI-MS was used as a primary research technique for delivering the ions from solution to the gas phase.

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Reactions of $\text{CO}_3^-(\text{H}_2\text{O})_{0,1}$ with Formic Acid and HCl studied by FT-ICR Mass Spectrometry

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The $\text{CO}_3^{\bullet-}$ radical anion is an important intermediate in tropospheric anion chemistry. However, only a small number of reactions have been reported in the literature. The reaction of ozonide with CO_2 produces $\text{CO}_3^{\bullet-}$ via O^- transfer. Gas phase reactions of $\text{CO}_3^{\bullet-}$ with formic acid and HCl are studied via FT-ICR mass spectrometry and will be presented here.

The reaction of $\text{CO}_3^{\bullet-}$ with formic acid leads to signal loss, indicating the formation of neutral reaction products and released electrons. The electrons can efficiently be scavenged by SF_6 in the experiment. In the atmosphere they be used for production of new $\text{CO}_3^{\bullet-}$, closing a catalytic cycle (see Figure 1). Quantum chemical calculations of the potential energy surface of the reaction reveal that oxidation to CO_2 and water is the thermochemically favored reaction path.^[1]

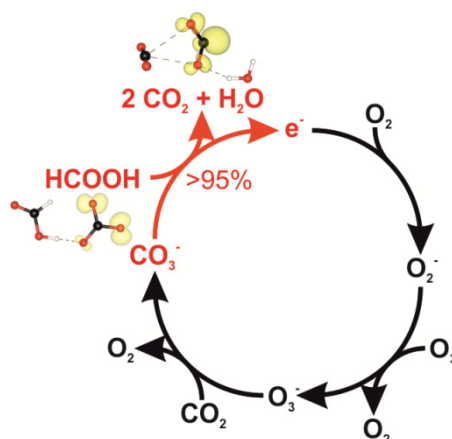


Figure 1: Cycle for $\text{CO}_3^{\bullet-}$ generation and reaction with formic acid.^[1]

No signal loss is observed in the reaction of $\text{CO}_3^{\bullet-}$ with HCl. In a first slow reaction step $[\text{OH},\text{Cl}]^-$ is formed. The $[\text{OH},\text{Cl}]^-$ quickly reacts with another HCl molecule to form HCl_2^- or Cl_2^- . Solvation of $\text{CO}_3^{\bullet-}$ with one water molecule, the most abundant form in the lower troposphere, significantly increases the reaction rate.^[2]

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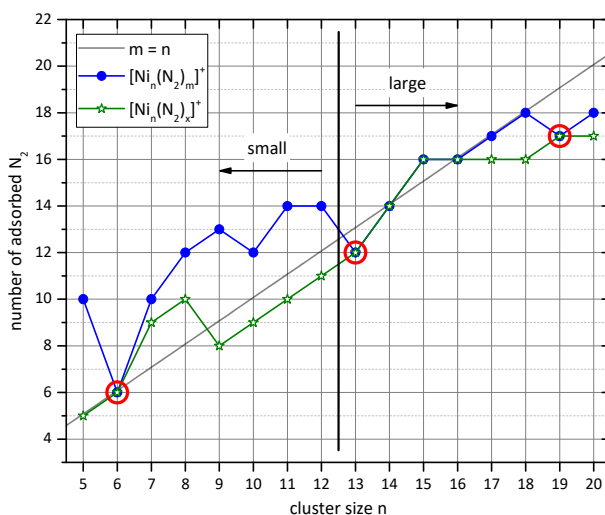
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Rough and Smooth Surfaces of Cationic Nickel Clusters probed by Cryo Kinetics and Spectroscopy

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We present the cryogenic (26 K) IR spectra of selected $[\text{Ni}_n(\text{N}_2)_m]^+$ clusters ($n = 5 - 20$, $m = 1 - m_{\text{max}}$)^{[1],[2]}, which reveal strongly n - and m -dependent features in the N_2 stretching region, in conjunction with density functional theory (DFT) modelling of some of these findings. The observed spectral features allows to define four classes of structure related surface adsorption behavior: Class (1) of Ni_6^+ , Ni_{13}^+ , and Ni_{19}^+ , are highly symmetrical clusters with all smooth surface of equally coordinated Ni atoms, that entertain stepwise N_2 adsorption up to stoichiometric $\text{N}_2 : \text{Ni}_{\text{surface}}$ saturation. Class (2) of Ni_{12}^+ , and Ni_{18}^+ are highly symmetrical clusters minus one. Their relaxed smooth surfaces reorganize by enhanced N_2 uptake towards some low coordinated Ni surface atoms with double N_2 occupation. Class (3) of Ni_5^+ , and Ni_7^+ through Ni_{11}^+ are small clusters of rough surfaces with low coordinated Ni surface atoms, some reveal semi internal Ni atoms of high next neighbor coordination. Surface reorganization upon N_2 uptake turns rough into rough surface by Ni atom migration and turns octahedral based structures into pentagonal bipyramidal structures.



Cryogenic N_2 coordination of size selected $[\text{Ni}_n(\text{N}_2)_m]^+$ clusters

Class (4) of Ni_{14}^+ through Ni_{17}^+ , and Ni_{20}^+ are large clusters with rough and smooth surface areas. They possess smooth icosahedral surfaces with some proximate capping atom(s) on one hemisphere of the icosahedron with the other one largely unaffected.

References:

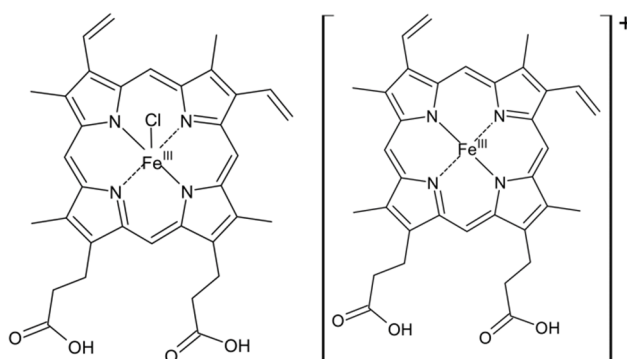
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Cryo IR Spectroscopy of [Hemin]⁺ Complexes in Isolation

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We present cryo IR spectra of isolated [Hemin]⁺ adducts with CO, N₂ and O₂ ([Hemin(CO)₁]⁺, [Hemin(CO)₂]⁺, [Hemin(¹⁴N₂)]⁺, [Hemin(¹⁵N₂)]⁺ and [Hemin(O₂)]⁺).



Scheme 1. Molecular structure of Hemin (left) and [Hemin]⁺ (right).

Well resolved bands allow for the elucidation of structure and spin multiplicity in conjunction with density functional (DFT) calculations. There is a quartet spin state for the N₂ and CO adducts, and a sextet spin state for the O₂ adduct, where the O₂ retains its triplet state. The double CO adsorption induces significant changes in the vibrational patterns of the IR spectra, which we take as strong evidence for a spin quenching into a doublet.

Cryo IR Spectroscopy of N₂ and H₂ on Ru₈⁺

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We present the cryo IR spectra of [Ru₈(H₂)_l]⁺ l = 1 – 8, [Ru₈(N₂)_m]⁺ m = 1 – 8 [Ru₈(H₂)₁(N₂)₄]⁺ and [Ru₈(N₂)₄(H₂)₁]⁺ species in isolation. The [Ru₈(H₂)_l]⁺ species with l > 1 reveal bands around 1800 cm⁻¹ which are a strong evidence for the formation of a hydride species. The [Ru₈(N₂)_m]⁺ species show spectral features between 2190 and 2300 cm⁻¹ which are attributed to the vibration of head on adsorbed N₂. There is evidence for an adsorbate induced reorganization beyond the intermittent adsorption limit of either the H₂ or the N₂ adsorbate. The [Ru₈(H₂)₁(N₂)₄]⁺ and [Ru₈(N₂)₄(H₂)₁]⁺ species reveal spectral differences in the hydride region of the IR spectra. We assign these differences to different positioning of the hydrides on the Ru cluster. This positioning is influenced by the sequence of adsorption (first H₂ and then N₂ or first N₂ and then H₂) and the possibility of migration of the hydrides.

**FT-ICR based characterization
of cold Rhodium Iron alloy cations and their N₂ adducts**

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Catalytic N₂ activation by active transition metal surfaces has always been a topic of interest. In our group we utilize customized FT-ICR instrumentation to investigate the vibrational and kinetic behavior of N₂ adsorbates on isolated transition metal complexes ^[1] as well as on transition metal clusters (Fe, Co, Ni, Rh) ^[2-5].

We couple our FT-ICR instrument to an OPO/A IR laser system to record InfraRed PhotoDissociation (IR-PD) spectra of N₂ adsorbates on cold bimetallic Rhodium Iron alloy cluster cations ([Rh_iFe_j(N₂)_m]⁺) i = j = 3 - 8 and m = 1 - 10. In comparison with DFT modelling we are able to gain information on the geometric structure and the nature of the adsorption site. As exemplified for the [Rh₃Fe₃N₂]₇⁺ cluster adsorbate complex, we find strong evidence for adsorption site specific N₂ stretch frequencies: N₂ preferentially adsorbs to Rh sites and merely after saturation of those to Fe sites as well (work in progress). This contribution documents the capabilities of our tandem cryotrap FT-ICR setup ^[6].

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Cryo Spectroscopy on “Non Classical” Dinitrogen Complexes in Isolation

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The discovery of transition metal dinitrogen complexes in 1965 launched the ever growing research field of N₂ coordination chemistry. Spectroscopically, metal-N₂ bonding manifests itself by shifted N₂ stretching vibration frequencies in relation to the (IR inactive) frequency of the free N₂ molecule. “Classical” N₂ complexes exhibit vibrational red shifts[1,2], which are well understood terms of the Dewar-Chatt-Duncanson (DCD) model[3].

Here, we present evidence of “non classical” dinitrogen complexes **[Fe₃O(OAc)₆(N₂)_n]⁺** (n = 1,2,3). We isolate and characterize the gaseous ions in a Fourier Transform - Ion Cyclotron Resonance (FT-ICR) ion trap at cryo temperatures. Infrared Photo Dissociation (IR-PD) spectroscopy as well as density functional theory (DFT) calculations reveal blue shifted N₂ stretching vibration bands. A detailed analysis of the electronic and steric interplay between N₂ and the **[Fe₃O(OAc)₆]⁺** unit indicates strengthened N-N bonds due to pronounced σ bonding and a lack of π back donation[4].

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Analysis of complex high resolution isotope pattern

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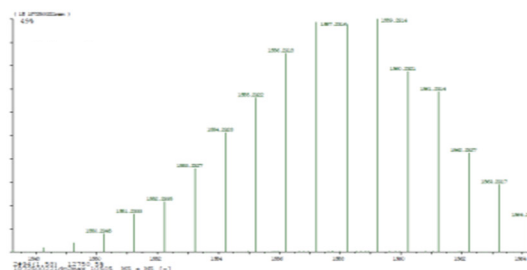
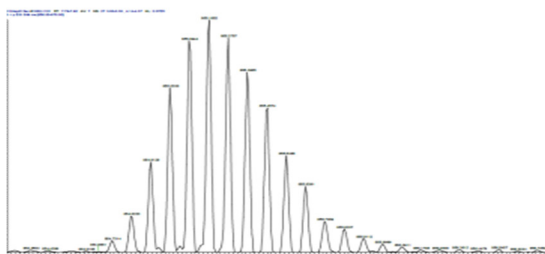
With the accessibility of modern mass spectrometers the determination of molecular formulas from high resolution mass spectral data has become a routine process in structure elucidation of small molecules.

The calculation of the elemental composition is typically based on the accurate mass of the ^{12}C -Peak. Depending of the software package used the signal heights of the corresponding isotope pattern and mass defects are used as additional criterions for the relevance of a calculated molecular formula.

However, this workflow often fails, if

- a) a high number of different hetero atoms is present, which results in a very long list of molecular formulas even in the case of very high mass accuracy
- b) or the isotope pattern is such as complex that the nominal mono isotopic mass or the single isotopes cannot be clearly assigned. This can either be the case by the presence of elements with a high number of different isotopes or with increasing molecular weights.

The poster will presents examples how to overcome these challenges.



Examples of experimentally obtained complex isotope pattern

FT Orbitrap mass spectrometric analysis of hydrocarbon contaminated soil using Soxhlet and supercritical fluid extraction

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After the first and second industrial revolutions over 0.5 million soil sites in Europe are now identified that contain some type of contamination which is the result from human industrial evolution and which needs to be remediated with an estimated annual cost of 2.4-17.3 billion euros. Especially polycyclic/heterocyclic aromatic hydrocarbons (PAXHs, X=N, O, S) originated from coal production, coking and gas plants are subjected to detailed investigation due to their carcinogenic, mutagenic and ecotoxicological effects. High-field Orbitrap FTMS with its high mass resolution and accuracy as well as different ionization methods enables a comprehensive analysis of the contaminated soil. Subsequently the efficiency of supercritical fluid extraction for contaminants in soil is investigated on a molecular level.

Experimental part

One contaminated soil and sand (spiked with crude oil) samples were extracted by Soxhlet extraction using toluene, dichloromethane, acetone : *n*-hexane (1:1) or methanol, respectively. For the supercritical fluid extraction (SFE) spiked sand, original and spiked soil samples were extracted using supercritical CO₂ (scCO₂) at 40 °C, 180 bar with a flow rate of 2 mL/min for 4 h. The residual components after SFE were extracted by a Soxhlet extractor using dichloromethane. All experiments were accomplished in triplicate and samples were analyzed by a research type Orbitrap Elite at a resolution of 960,000 (FWHM at *m/z* 400) using spectral stitching (30Da windows with 5 Da overlap) by utilizing ESI(+/-) and APPI(+).

Results and discussion

For a better understanding of the contamination of soil an extraction method was developed. To understand the behavior of PAXHs different solvents were investigated using Soxhlet extraction of a spiked sand. Using this procedure a recovery of 90% was achieved. After development of the method with a spiked sand sample the same procedure was used for investigating contaminated soil. Here, positive-ion ESI mass spectrometric analysis reveals that soil contains mainly N, NO, N₂, NS as polar classes. In the negative-ion mode besides N, NO and N₂ classes, Ox classes such as O, O₂ and O₄ were also found. As compared to crude oil the polar classes determined in soil reach a higher double bond equivalent (DBE) but involve shorter alkyl chains within a given DBE. In APPI measurements only pure hydrocarbons (HC) were detected of soil samples with a minor amount of N and O class species. Compositions in the HC class of crude oil were centralized at 0 < DBE < 20 and 10 < carbon number < 20, whereas in soil they appear at the planar limit of the DBE vs. carbon number plot indicating their high aromaticity.

The second method for studying the contamination of soil was supercritical fluid extraction. The efficiency of SFE was over 50% when studying the spiked sand sample, while the recovery of solvent extractable organic compounds from the original soil was only about 5%. The results show that using scCO₂ for the extraction is not the best method to extract hydrocarbons with high carbon number and very condensed aromatic system. Nevertheless results show that pure hydrocarbons including EPA-16 PAHs and other PAXHs with relative low DBEs (below 20) could be efficiently extracted from all samples.

New aspects

A comprehensive analysis of contaminated soil using Soxhlet and SFE extraction determines the contaminants in soil by using FTMS.

High performance analysis of complex mixtures by high-field FT-Orbitrap MS: exploring the carbon space

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Studying chemical transformations within the carbon space in complex mixtures is a growing research field. In different areas such as metabolomics, environmental studies or medical areas, the complexity of chemical problems is increasing. To be able to understand chemical or biological transformations on a molecular level high performance analytical systems are necessary. While the best possible performance regarding key factors mass resolution, mass accuracy and sensitivity is always desirable, the combination of all three parameters becomes crucial when dealing with highly complex samples. High-field Orbitrap mass spectrometer combines high resolution and accuracy with a much improved sensitivity compared to FT-ICR MS while reducing analysis time. Here, the faster transients and shorter ion transfer are key points that favor the Orbitrap.

Experimental

A heavy crude oil was used to study the capabilities of high field Orbitrap analyses using an APPI source (10.0/10.6 eV). Analyses were performed on a research-type Orbitrap Elite (Thermo Fisher, Bremen, Germany) at resolving powers of 240k, 480k and 960k @ m/z 400 by either employing full range scanning (200-1200 Da) or spectral stitching (30 Da windows, 5 Da overlap) with identical total amounts of individual scans (240-260).

Results

The thorough mass spectrometric analysis of complex mixtures suffers from the need to resolve signals from isobaric compounds. In case of crude oil one of the most crucial mass splits to cover is the 3.4 mDa difference between C₃ and SH₄. To resolve corresponding peaks of similar abundance up around 1000 Da a minimum mass resolution of approximately 300k (FWHM) is required. This resolution can be reached by a commercially available Orbitrap Elite (480k at 400 Da). For compounds at largely differing abundances however, a higher resolution is needed. The instrument used in this study allows a resolving power of 960k at 400 Da (500k at 1000 Da). An approximately 1.5-fold increase of assigned signals is observed for each doubling of the resolving power set. Mass spectral stitching leads to an increase of assignable signals by a factor of 6 to 9 while for the most abundant heteroatom classes the corresponding assignments are roughly doubled. Majority of the additionally assigned compositions is covered by low abundant heteroatom classes. The large increase in assignments can therefore be mostly attributed to the statistically increased probability to detect low abundant ions in a small mass window rather than to a minimization of ion-ion interactions

as are known to be problematic in FT-ICR MS. Considering the data achieved by FT-Orbitrap MS essentially all potential assignments are found that are theoretical possible in a certain mass range for different compound classes, thus covering a large part of the carbon space.

New aspects

Analysis of a heavy crude oil shows that more than 95% coverage within carbon space (DBE 2-21) can be achieved.

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Remarks

Remarks