

HFML-FELIX Laboratory User Meeting

8 - 10 July 2019



Radboud University





Conference site

Address:

Huygens Building, Faculty of Science,
Campus of the Radboud University
Heyendaalseweg 135, 6525 AJ Nijmegen

The Huygens Building is indicated by the green circle.
HFML-FELIX Laboratory is indicated by the blue circle.

The visiting address of the HFML -FELIX Laboratory is Toernooiveld 7, 6525 ED Nijmegen, The Netherlands.

HFML - FELIX User Meeting

	8 July		9 July		10 July
12:00	Official Opening Ceremony HFML – FELIX Laboratory		Chair: Nigel Hussey		Chair: Uli Zeitler
13:00 14:00	Lunch Tour of the HFML – FELIX Laboratory	09:00 09:40 10:20	Jochen Wosnitza Vicky Wysocki Pascal Reiss		
		10:40	Coffee Break	09:00 09:40 10:20	Rembert Duine Vladimir Mironov Rianne van Outersterp
			Chair: Sandra Brünken		
		11:10 11:50 12:10 12:30	Peter Armentrout Ruben Kranenburg Sandra Lang Michele Siggel-King	10:20	Coffee Break
					Chair: Alix McCollam
		13:00	Lunch & Posters	10:50 11:30 11:50 12:10	Andrei Kirilyuk Christian van der Linde Ashish Arora Jennifer Noble
15:00	Registration	15:30	Specialized workshop HFML – FELIX Combination	12:30	Summery and Closing
	Chair: Jos Oomens		Chair: Andrei Kirilyuk		
16:00 16:10 16:30 16:50	Welcome & Opening Uli Zeitler – Jos Oomens Britta Redlich Peter Christianen Gerard Meijer	15:30 16:10 16:30	Ben Murdin Bence Bernáth Andrea Marchese	12:35	Lunch
		17:00	Introduction of the National Roadmap Developments HFML-FELIX team		
		17:30	Discussion & Breakout in smaller groups in the HFML – FELIX Laboratory		
17:40	Drinks				
		18:45	Departure for Dinner		
18:00	BBQ	19:00	Conference Dinner		

Monday 8 July

15:00 - 16:00 **Registration**
16:00 - 16:10 **Opening Workshop – Uli Zeitler & Jos Oomens**

Chair: Jos Oomens

16:10 - 16:30 **Britta Redlich – Overview FELIX**

16:30 - 16:50 **Peter Christianen – Overview HFML**

16:50 - 17:40 I1 **Gerard Meijer** (Fritz-Haber-Institut der Max-Planck-Gesellschaft)
“Science with Infrared Free Electron Lasers – sophisticated experiments at mature facilities”

18:00 **Informal BBQ**

Tuesday 9 July

Chair: Nigel Hussey

09:00 - 9:40 I2 **Jochen Wosnitza** (Helmholtz Zentrum Dresden-Rossendorf)
“Materials Research in High Magnetic Fields”

9:40 - 10:20 I3 **Vicki Wysocki** (The Ohio State University)
“Structure Analysis of Peptide Fragment Ions by IRMPD Action Spectroscopy”

10:20 - 10:40 O1 **Pascal Reiss** (University of Oxford)
“Finite electronic correlations and two-dome superconductivity across a nematic quantum phase transition”

10:40 - 11:10 **Coffee break**

Chair: Sandra Brünken

11:10 - 11:50 I4 **Peter Armentrout** (University of Utah)
“Sequential CH Bond Activation of Methane by Ir⁺: An IRMPD and Theoretical Investigation”

- 11:50 - 12:10 O2 **Ruben Kranenburg** (Dutch National Police & University of Amsterdam)
“New psychoactive substances in forensic drug cases: Strategies to tackle the drug isomer challenge”
- 12:10 - 12:30 O3 **Sandra Lang** (Ulm University)
“Water deprotonation on free calcium-manganese-oxide clusters: Gas Phase Model Systems for the Catalytically Active Center of Photosystem II”
- 12:30 - 12:40 Michele Siggel – King (University of Liverpool, Science & Technology Facilities Council)
“Introduction to FLUENCE”
- 13:00 - 15:30 Lunch & Posters**
- Chair: Andrei Kirilyuk*
- 15:30 - 16:10 I5 **Ben Murdin** (University of Surrey)
“”
- 16:10 - 16:30 O4 **Bence Bernáth** (HFML-FELIX)
“THz-pump-probe experiment on p-doped Germanium in high magnetic fields”
- 16:30 - 16:50 O5 **Andrea Marchese** (HFML-FELIX)
“Generation of a Helium plasma using intense THz radiation and high magnetic fields”
- 17:00 - 17:30 Introduction of the National Roadmap Developments
HFML-FELIX team
- 17:30 - 18:45 Discussions / Breakout session in smaller groups at different end stations in the HFML-FELIX Laboratory
- 18:45 **Departure for dinner**
19:00 Restaurant “Beau”, Driehuizerweg 285, Nijmegen

Wednesday 10 July

Chair: Uli Zeitler

- 09:00 - 9:40 I6 **Rembert Duine** (Utrecht University)
“Non-local magnon spin transport in ferro and antiferromagnets”
- 9:40 - 10:00 O6 **Vladimir Mironov** (Moscow State University)
“Fabrication of the tubular construct from polystyrene beads by acoustic radiation force in high magnetic field”
- 10:00 - 10:20 O7 **Rianne van Outersterp** (HFML-FELIX)
“Differentiation of positional isomers of drug metabolites using infrared ion spectroscopy”

10:20 - 10:50 Coffee break

Chair: Alix McCollam

- 10:50 - 11:30 I7 **Andrei Kirilyuk** (HFML-FELIX)
“All-optical switching of magnetization with IR photons and in high fields”
- 11:30 - 11:50 O8 **Christian van der Linde** (University of Innsbruck)
“IRMPD of hydrates species generated in a laser vaporization source”
- 11:50 - 12:10 O9 **Ashish Arora** (University of Münster)
“Interlayer excitons in transition metal dichalcogenide semiconductors”
- 12:10 - 12:30 O10 **Jennifer Noble** (CNRS-Marseilles University)
“Infrared resonant vibrational restructuring of amorphous solid water”
- 12:30 **Lunch**

Conference diner

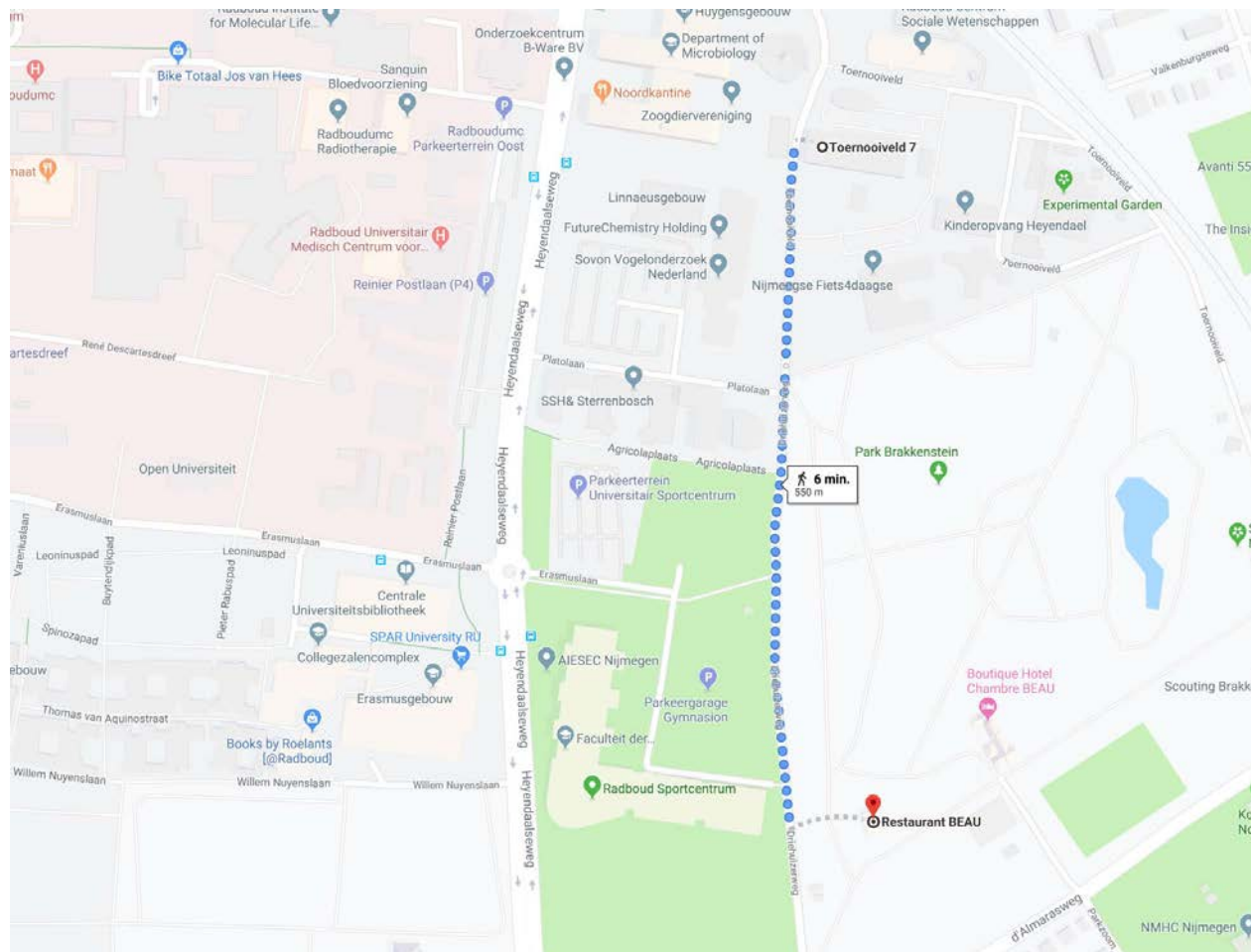
The conference diner on Tuesday July 9 will be held in **Restaurant “BEAU”**

Address

Driehuizerweg 2085

6525 PL Nijmegen

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Oral presentations

I1

Science with Infrared Free Electron Lasers – sophisticated experiments at mature facilities

Gerard Meijer

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e-mail: meijer@fhi-berlin.mpg.de

Ever since the first demonstration of a free electron laser by Madey and coworkers in Stanford in the seventies, FEL facilities have been set up at various locations to provide high power, tunable infrared radiation to users. In the beginning, some of these IR FEL facilities seemed to be "solutions, looking for a problem" whereas at others mainly quantum electrodynamics studies were performed, i.e. studies aimed at a full characterization and a better understanding of the FEL operation itself. It took some time before the operation of these IR FELs was sufficiently reliable and before the anticipated advantages in terms of wavelength tunability, pulse energy and temporal structure of the radiation could be fully exploited. Only since then, that is during the last two decades, an active IR FEL user community started to be established. This user community comprises solid state physicists and materials scientists who perform time-resolved, infrared spectroscopic studies and visible-IR sum-frequency generation experiments, for instance, and physical chemists and biochemists who perform IR spectroscopic investigations on molecules, clusters and cluster-adsorbate complexes, the latter mainly in the gas phase. During the last decade, the focus has shifted from improving the operation characteristics of the IR FELs to applying the IR FEL radiation in ever more sophisticated setups, indicative of the level of maturity that IR FELs facilities have reached. The current IR FEL facilities are sufficiently compact to be set up on the campus of a University or research institute as a dedicated tool, with optimized performance characteristics, for the "in-house" research interests. In those settings, the IR FEL radiation can be optimally used - as easily as that of any table-top laser - in the available state-of-the-art experimental setups. Only in those settings, time-consuming and more routine experiments that require the use of intense and widely tunable IR radiation can be performed as well; at external IR FEL facilities beam-time would most likely never be granted for this. The future of IR FEL facilities is in their use as a "standard" tool to obtain IR spectroscopic data in combination with other (e.g. mass spectrometric, ion mobility, reactivity, etc.) data, i.e. in their application in multidimensional characterization of ever more complex systems. This multi-dimensional characterization can also involve 2D-IR experiments, using synchronized two-color FEL operation.

12

Materials Research in High Magnetic Fields

Jochen Wosnitza

*Hochfeld-Magnetlabor Dresden (HLD), Helmholtz-Zentrum Dresden-Rossendorf, D-01328
Dresden, Germany*

High magnetic fields are one of the most powerful tools available to scientists for the study, modification, and control of the state of matter. As part of the European Magnetic Field Laboratory (EMFL, the High Magnetic Field Laboratory Dresden (*Hochfeld-Magnetlabor Dresden*, HLD) at the Helmholtz-Zentrum Dresden-Rossendorf (HZDR) allow to access pulsed magnetic fields up to 95 T on a 10 ms timescale. In these pulsed magnets, a variety of experimental methods are available for in-house and external users enabling to measure, for example, electrical transport, magnetization, dilatometry, ultrasound, ESR, and even NMR with very high resolution. As a unique feature, a free-electron-laser facility next door allows high-brilliance radiation to be fed into the pulsed-field cells of the HLD, thus making possible high-field magneto-optical experiments in the range from 5 to 250 μm . In-house research of the HLD focuses on electronic properties of strongly correlated materials at high magnetic fields. In my presentation, I will present some recent results obtained in our studies of frustrated and low-dimensional magnetic materials. Electron spin resonance studies, for example, provided exact and conclusive information on the exchange couplings for the frustrated triangular-lattice antiferromagnets Cs_2CuBr_4 and Cs_2CuCl_4 . Magnetization, nuclear magnetic resonance, and ultrasound measurements reveal the existence of a spin-nematic phase in LiCuVO_4 .

13

Structure Analysis of Peptide Fragment Ions by IRMPD Action Spectroscopy

Vicki Wysocki, Erin Panczyk, J.C. Poutsma, and Arpad Somogyi

The Ohio State University, Columbus, OH 43210

We use IRMPD action spectroscopy to determine the structure of fragment ions produced by collision-induced dissociation (CID) of small, synthetic peptides. We have performed studies on multiple bn^+ type ions and those results will be summarized. A recent and ongoing study examines the role of 5,5-dimethylproline (dmP) on $b2^+$ and $b3^+$ fragment ion formation. As characterized by solution-phase studies, including NMR analysis at The Ohio State University, dmP promotes a cis conformation of the peptide backbone. While we experimentally observed mainly oxazolone formation for the $b2^+$ ions, the $b3^+$ ions for APA, AAP, AdmPA, and AAdmP, showed different IR spectra, indicating that the steric hindrance of the dimethylproline substitution promotes macrocycle formation over the oxazolone formation observed for the proline-containing peptides. Trapped ion mobility spectrometry (TIMS) has recently been implemented on the 15 T FT-ICR mass spectrometer at Ohio State. In addition to the IR spectra collected at FELIX, TIMS-MS experiments are being performed at high mobility resolution to determine if different conformers are formed as a result of dmP substitution, and whether these conformers yield distinct CID spectra comparable to the dissociation patterns observed during IRMPD.

01

Finite electronic correlations and two-dome superconductivity across a nematic quantum phase transition

Pascal Reiss¹, David Graf², Amir A Haghighirad^{1,3}, William Knafo⁴, Loïc Drigo^{4,5}, Matthew Bristow¹, Andrew J Schofield⁶, and Amalia I Coldea¹

¹*Clarendon Laboratory, University of Oxford*

²*National High Magnetic Field Laboratory, Tallahassee*

³*Institut für Festkörperphysik, Karlsruhe Institute of Technology*

⁴*Laboratoire National des Champs Magnétiques Intenses (LNCMI-EMFL), Toulouse*

⁵*Géosciences Environnement Toulouse (CNRS), Toulouse*

⁶*School of Physics and Astronomy, University of Birmingham*

In the proximity of a nematic quantum critical point, electronic nematic fluctuations have been identified as a candidate for enhancing superconductivity in various unconventional superconductors. However, the coexistence of long-range magnetic order has hindered detailed studies of nematic criticality. To address this challenge, we combine chemical pressure in FeSe_{1-x}S_x to suppress long-range magnetic order, and physical pressure to study the uncovered nematic quantum phase transition. Using magneto-transport and quantum oscillations measurements, we trace the strength of electronic correlations and their role played in promoting superconductivity. We demonstrate that electronic correlations remain finite, the Fermi surface suffers a Lifshitz transition, and superconductivity is weakened across the nematic quantum phase transition. We interpret these results in light of recent theoretical advances.

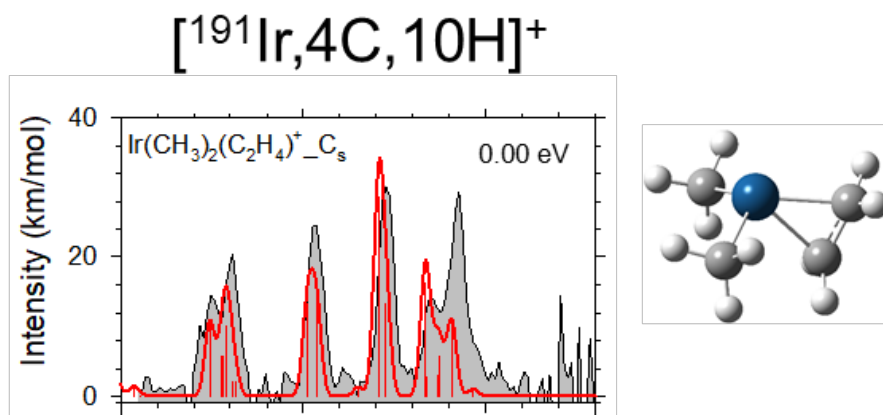
<https://arxiv.org/abs/1902.11276>

I4

Sequential CH Bond Activation of Methane by Ir⁺: An IRMPD and Theoretical Investigation

Oscar W. Wheeler, Michelle Salem, Amanda Gao, Joost M. Bakker, and **P. B. Armentrout**
University of Utah and Radboud University

The sequential activation of up to 4 CH₄ molecules by Ir⁺ is investigated through a gas-phase infrared multiple photon dissociation (IRMPD) experiment and theoretical calculations. A molecular beam apparatus was used to generate Ir⁺ by laser ablation and expose it to controlled amounts of CH₄. Product ions were irradiated with IR light from a free electron laser over the 500 – 1800 cm⁻¹ spectral range and photodissociation was monitored using a time-of-flight mass spectrometer. Experimental spectra were obtained for five distinct species: [Ir,3C,8H]⁺, [Ir,3C,10H]⁺, [Ir,4C,10H]⁺, [Ir,4C,12H]⁺, and [Ir,O,3C,12H]⁺. To identify these species, B3LYP/def2-TZVPPD geometry optimizations were performed on a variety of possible structures, with computed IR spectra compared to the experimental IRMPD spectra. This has led to the following assignments: [Ir,3C,8H]⁺ = IrCH₂(CH₃)₂⁺, [Ir,3C,10H]⁺ = HIr(CH₃)₃⁺, [Ir,4C,10H]⁺ = Ir(CH₃)₂(C₂H₄)⁺, [Ir,4C,12H]⁺ = a mixture of HIr(CH₃)(C₂H₄)⁺(CH₄), HIr(CH₃)₂(C₂H₅)⁺, Ir(CH₃)₄⁺, and (H₂)Ir(CH₃)₂(C₂H₄)⁺, and [Ir,O,3C,12H]⁺ = (H₂O)HIr(CH₃)₃⁺. Notably, evidence for C-C coupling is observed upon reaction with a fourth methane. Mechanisms for the formation of the observed products were also explored computationally by examining the reaction coordinate pathways for the reactions of methane with HIrCH⁺, IrCH₂⁺, Ir(CH₃)₂⁺, HIrCH₂(CH₃)⁺, HIr(CH₃)₃⁺, and IrCH₂(CH₃)₂⁺.



O2

New psychoactive substances in forensic drug cases: Strategies to tackle the drug isomer challenge

Ruben F. Kranenburg^{1,2}, Arian C. van Asten²

¹ *Dutch National Police*

² *University of Amsterdam*

The global drugs-of-abuse market is facing major changes over the last decade. New psychoactive substances (NPS) form an emerging group of over 700 synthetic drugs comprise of many closely related and isomeric classes of compounds. Most of these compounds are not legally controlled and sold as 'legal highs', while others are banned substances in various countries. When a 'legal high' is put under judicial control, other closely related yet uncontrolled compounds often increase in popularity and occurrence. This fuels a perpetual cycle in which increasingly diverse NPSs are continually being developed.

The transformation of the drugs-of-abuse market changes the needs of forensic drug analysis laboratories. Established methods, such as gas chromatography-mass spectrometry (GC-MS) fall short in terms of selectivity, as isomeric NPSs have identical masses, very similar fragmentation spectra and can co-elute in fast screening methods. Traditional spectroscopic measurements using FTIR or Raman find limitations in multi-component mixtures, as is often the case in adulterated samples or tablet formulations.

Thus, in forensic laboratories, a need has arisen for analytical methods capable of distinguishing known, as well as identifying yet unknown NPS isomers.

Three new strategies have been investigated in our group to tackle the isomeric NPS dilemma:

- 1) Vacuum ultraviolet (VUV) spectroscopy provides distinctive and very reproducible spectra for various ring-isomers. Selectivity-wise, GC-VUV is complementary to GC-MS for certain NPS classes consisting of both ring- and aliphatic chain isomers.
- 2) Low-energy electron ionization (EI) on a GC-Q/TOF system produces less fragmented, more information-rich, mass spectra for NPS isomers. Multivariate statistics were applied to discriminate among ring-isomers.
- 3) Infrared ion spectroscopy (IRIS) at the FELIX laboratory successfully differentiated among ring-isomeric forms of NPSs, and correctly identified an NPS directly from a complex case sample. Finally, IRIS presents a promising approach for the identification of unknown NPSs for which reference standard compounds are not available when combined with quantum chemical prediction of IR spectra for candidate molecular structures.

03

Water deprotonation on free calcium-manganese-oxide clusters: Gas Phase Model Systems for the Catalytically Active Center of Photosystem II

Sandra M. Lang, Irene Fleischer, Silvia Mauthe, Nina Zimmermann, and
Thorsten M. Bernhardt

Institute of Surface Chemistry and Catalysis, Ulm University

The catalytic oxidation of water in plants takes place at an inorganic Mn_4CaO_5 cluster located in photosystem II. To aid the design of new artificial water oxidation catalysts we embark on a novel hierarchical modeling strategy, starting with small clusters and increasing the model system's complexity in a staged, controlled manner.

In the first steps we studied the reactivity of isolated manganese oxide cluster ions, Mn_xO_y^+ , of different size and composition with D_2^{16}O and H_2^{18}O . Gas-phase ion trap experiments and infrared multiple-photon dissociation (IR-MPD) spectroscopy in conjunction with first-principles calculations, revealed the facile water deprotonation and the exchange of the oxygen atoms of the cluster with water oxygen atoms.

In a further step we investigated binary calcium manganese oxide clusters and found that the number of Ca atom is crucial to the water oxidation capabilities of the small $\text{Ca}_{4-x}\text{Mn}_x\text{O}_4^+$ and $\text{Ca}_{5-x}\text{Mn}_x\text{O}_5^+$ clusters.

Finally, we started modeling the ligand environment of the manganese-clusters cluster by small acids. First experiments identified propionic acid as the most promising candidate since the smaller acids, formic and acetic acid, easily decompose in the presence of Mn_xO_y^+ .

Michele Siggel King, University of Liverpool
“ Introduction to FLUENCE”

I5

Ben Murdin, University of Surrey

“Opportunities for THz pulsed control and measurement of silicon donors in high magnetic fields”

The electron spin of shallow donors in silicon is a promising platform for quantum computer qubits. Electric dipole transitions between the orbital states allows control over the orbit, and therefore over the interactions with neighbours. High magnetic fields offer control over the wave function in space, and THz pulses offer control over the wave functions in time. The combination of THz pulses with high field offers a unique opportunity for complete control over the interactions. I shall describe the current status of our high field spectroscopy and dynamics work, and describe some immediate possible experiments that will be available with the combination of both.

O4

THz-pump—THz-probe experiment on p-doped Germanium in high magnetic fields

B. Bernáth¹, D. Kamenskyi^{1, 2}, B. Redlich², A. F. G. van der Meer², P. C. M. Christianen¹, H. Engelkamp¹, V. Éless², K. Saeedi², A. Marchese¹, J. C. Maan^{1, 2}

¹*High Field Magnet Laboratory (HFML-EMFL), Radboud University, 6525 ED Nijmegen, The Netherlands.*

²*FELIX Laboratory, Institute for Molecules and Materials (IMM), Radboud University, 6525 ED Nijmegen, The Netherlands*

The combination of high power, pulsed THz radiation and high magnetic fields is very promising from a scientific perspective. We present the design of a THz single-color pump-probe setup inside a high-field Bitter magnet, using components that are not within the scope of regular quasi-optical THz setups. We use special waveguides and prisms to spatially separate the pump and the probe beams, which allow us to work in a cryogenic environment in a small bore magnet. Our first results show that this pump-probe insert enables studying the fast carrier dynamics in semiconductors using cyclotron resonance.

O5

Generation of a Helium plasma using intense THz radiation and high magnetic fields

A. Marchese¹, B. Bernáth¹, D.L. Kamenskyi¹, H. Engelkamp¹, P.C.M. Christianen¹, P. Gogoi¹, A. Granados del Aguila¹, J.C. Maan², A.F.G. van der Meer², B. Redlich², M. Ozerov², F. Moro³, A. Patane³

¹*High Field Magnet Laboratory, Radboud University*

²*FELIX Laboratory, Radboud University*

³*School of Physics and Astronomy, The University of Nottingham*

We have observed the unexpected creation of a Helium (He) plasma after irradiation of He gas in a strong magnetic field by intense THz pulses generated by a free-electron-laser (FEL). The plasma is formed under resonant conditions when the frequency of the THz light and the magnetic field strength match the cyclotron energy of free electrons. We found that the plasma emits bright light, composed of the typical sharp He spectral lines split in magnetic fields due to the Zeeman effect. By measuring the plasma emission and its THz transmission, we are able to perform detailed investigations of the dynamics of the plasma formation, as a function of temperature (4-300 K), He gas pressure, laser power and field strength (up to 30 T). We find that the plasma formation is a strongly nonlinear effect and we can distinguish several different phases within the plasma dynamics.

16

Non-local magnon spin transport in ferro and antiferromagnets

Rembert Duine

University of Utrecht

O6

Fabrication of the tubular construct from polystyrene beads by acoustic radiation force in high magnetic field

Alisa A. Krokhmal^{1,2}, **Vladimir A. Mironov**¹, Stanislav V. Petrov¹, Frederico D.A.S. Pereira¹, Yusef D. Khesuani¹, Vladislav A. Parfenov¹.

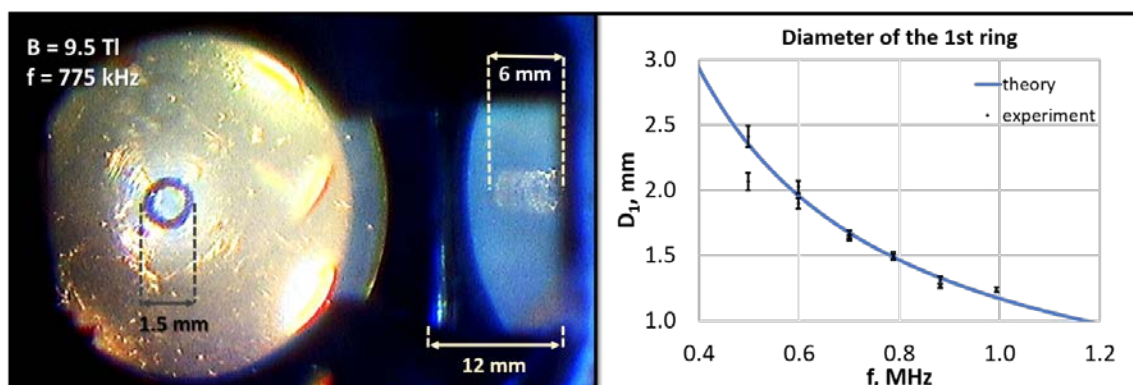
¹3D Bioprinting Solutions, Moscow, Russia

²Physics Faculty, Moscow State University, Moscow, Russia

The lack of donor organs is a major problem in modern medicine. A promising solution is the fabrication of human tissues and organs using three-dimensional bioprinting. A recently proposed magnetic levitation method for the first time used an approach without scaffolds and labels. Acoustic biofabrication of 3D tissue constructs represents a novel rapidly developing approach, which allows assembling complex structures from tissue spheroids and other spherical particles. Combining these technologies, we can construct long tubular structures of different sizes, which imitate blood vessels, an essential part of any organ.

Due to the dependence of acoustic fields on the shape and size of the ultrasound source, its operating frequency and boundary conditions, it is possible to create sufficiently complex 3D acoustic traps. When spherical particles were placed in a volume irradiated by an ultrasonic wave, an acoustic radiation force arises, which is the result of the pulse transfer from an acoustic wave to absorbing or scattering objects. In this study, the polystyrene beads were used as acoustic targets. The amplitude and direction of the radiation force depends on the specific field structure. In the experiments, the medium with beads was placed into a special cuvette from agarose, which was transparent to the ultrasound wave and did not distort the resulting field. The medium contained gadolinium to strengthen magnetic levitation effect.

After turning on the magnetic field, due to magnetophoretic effect all the beads started to levitate. The piezoelectric transducer created standing cylindrical ultrasonic waves. The acoustic radiation force formed a tube of beads. With the working frequency of 775 kHz and magnetic field in the center of setup 9.5 Tl the tube formed with the diameters of 1.5 mm and a length of 6 mm. Changes in the frequency and amplitude of the wave allowed us to manipulate the size and the width of the resulting construction.



07

Differentiation of positional isomers of drug metabolites using infrared ion spectroscopy

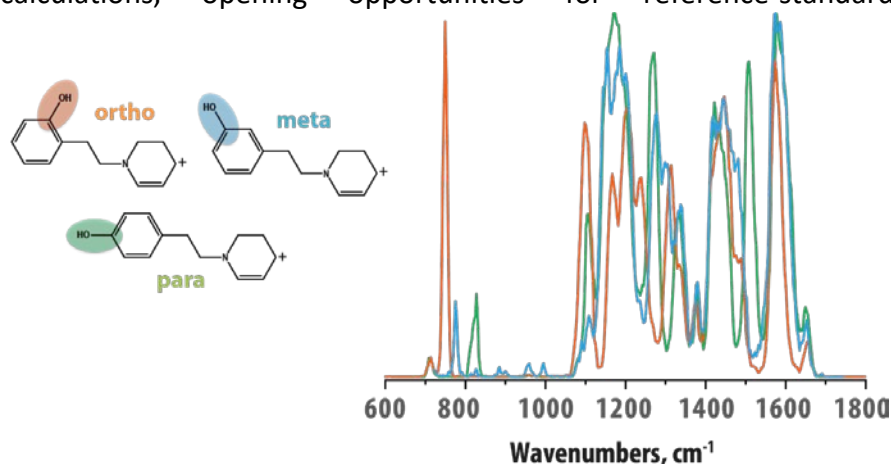
Rianne van Outersterp^a, Giel Berden^a, Valerie Koppen^b, Filip Cuyckens^b, Jos Oomens^{a,c} and Jonathan Martens^a

^aRadboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7, 6525ED Nijmegen, The Netherlands ^b Drug Metabolism & Pharmacokinetics, Janssen R&D, B-2340, Beerse, Belgium ^cvan't Hoff Institute for Molecular Sciences, University of Amsterdam, 1098XH Amsterdam, Science Park 908, The Netherlands

An understanding of the metabolism of drug candidates, including the identification of downstream drug metabolites, is a crucial step in drug development. Due to its high sensitivity and selectivity, mass spectrometry (MS) is often the analytical method of choice for metabolic profiling. However, closely related compounds may be hard to distinguish using (tandem) MS alone, as these are often isobaric and give identical fragmentation mass spectra. Therefore, alternative methods involving expensive and time-consuming purification steps are usually needed to confidently resolve full molecular structures.

Infrared ion spectroscopy (IRIS) records an IR spectrum of a mass-selected gas-phase ion directly inside a mass spectrometer. The IR fingerprint is highly sensitive to molecular structure, and can be recorded for each m/z -feature detected in a standard MS experiment. We exploit this technique, which has full MS sensitivity and compatibility, to identify small molecules resulting from untargeted MS-based experiments, including drug metabolites.

Here, we explore the use of IRIS for the differentiation of positional isomers resulting from the phase I metabolism reactions (usually oxidation, reduction or hydrolysis) that introduce a reactive or polar group on a phenyl ring in a drug molecule. The chemical modification that occurs can usually be determined from the mass spectrum, but the exact site of biotransformation often remains unknown. We demonstrate how metabolites bearing a ortho-, meta- or para-hydroxylation can be distinguished based on their IR spectra. Also, we show that identification is possible on the basis of spectra predicted by quantum-chemical calculations, opening opportunities for reference-standard free identification.



17

All-optical switching of magnetization with IR photons and in high fields

Andrei Kirilyuk

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The incessant increase in the amount of digital data boosts the demand for faster, smaller, and energy-effective data-recording technologies. One viable possibility is the all-optical approach, which allows to control the magnetization of a medium using fs laser pulses only [1].

It thus has been demonstrated, already a while ago, that the magnetization of ferrimagnetic RE-TM alloys and multilayers can be reversed by single fs laser pulses, without any applied magnetic field [2]. This switching is found to follow a very peculiar pathway, that crucially depends on the dynamic balance of net angular momentum, set by the two sublattices. This peculiarity until now causes heated debates about the exact mechanism and trajectory of the switching.

In this talk I will show how the application of low-photon-energy pulses from FELIX [3], on the one hand, and time-resolved measurements in strong magnetic fields at HFML [4], on the other, help to clarify this long-standing issue.

[1] A. Kirilyuk, A.V. Kimel, and Th. Rasing, *Rep. Prog. Phys.* **76**, 026501 (2013).

[2] C.D. Stanciu *et al*, *Phys. Rev. Lett.* **99**, 047601 (2007).

[3] C. S. Davies, T. Janssen, J. H. Mentink, A. Tsukamoto, A. V. Kimel, A. F. G. van der Meer, A. Stupakiewicz, and A. Kirilyuk, arXiv:1904.11977 (2019).

[4] J. Becker, A. Tsukamoto, A. Kirilyuk, J.C. Maan, Th. Rasing, P.C.M. Christianen, and A.V. Kimel, *Phys. Rev. B* **92**, 180407(R) (2015); A. Pogrebna *et al.*, arXiv:1903.04293 (2019).

08

IRMPD of Hydrated Species Generated in a Laser Vaporization Source

Christian van der Linde^a, Jakob Heller^a, Olga Lushchikova^b, Maximilian G. Münst^a, Milan Ončák^a, Joost M. Bakker^b, and Martin K. Beyer^a

^a *Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck*

^b *FELIX Laboratory, Radboud Universiteit Nijmegen*

A well-established laser vaporization ion source [1], as it used in our setup in Innsbruck for production of various hydrated species, is currently implemented into the FELICE beamline FT-ICR mass spectrometer. This ion source will allow us to take advantage of the very high intensities in the far infrared to study systems that are not accessible via tabletop OPO systems.

In our laboratory we studied the properties of the hydrated carbonate radical anion radical $\text{CO}_3^{\bullet}(\text{H}_2\text{O})_{1,2}$ in the infrared and UV/Visible range of the spectrum. While we obtained decent spectra in UV/Vis and in the OH stretching region, we were not able to record a well resolved spectrum in the CO stretching region. The results from our lab illustrate the benefit of the additional ion source on the FELICE FT-ICR setup.

As the laser vaporization ion source does not produce hydrated species at the moment, first experiments on the molecular beam setup at the FELICE beam line were performed with Vanadium water clusters, $\text{V}^+(\text{H}_2\text{O})_{1-4}$. Depletion infrared spectra in the range from 200-1800 cm^{-1} were recorded. A depletion at around 1650 cm^{-1} , which is observed for all cluster sizes, can be assigned to water bending mode and shows a slight redshift of the depletion minimum with increasing cluster size. Water wagging, rocking and asymmetric $\text{V}^+\text{-OH}_2$ (300 and 500 cm^{-1}) agree with the theoretical calculations. The $\text{V}^+(\text{H}_2\text{O})_1$ spectrum shows a broad absorption feature between 600 and 1000 cm^{-1} , which do not correspond to fundamental harmonic vibrations. This feature also shows a redshift for larger clusters and finally merges with the wagging and rocking modes for $\text{V}^+(\text{H}_2\text{O})_4$. A plausible explanation for this absorption is the overtone of the 300-500 cm^{-1} feature.

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09

Interlayer excitons in transition metal dichalcogenide semiconductors

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Coulomb-bound electrons and holes with spatially displaced wave functions called ‘interlayer excitons’ are important for Bose-Einstein condensation, superfluidity, dissipationless current flow, and the light-induced exciton spin Hall effect. Here, we unravel the existence of interlayer excitons in bilayer and bulk Mo-based transition metal dichalcogenides (TMDCs) i.e. MoTe₂, MoSe₂ and MoS₂ by using high-field magneto-reflectance spectroscopy (up to 29 T) combined with *GW*-BSE *ab initio* calculations [1,2]. We find that due to weak van Waals interactions, TMDC homostructures provide a cleaner and simpler system to study interlayer phenomena compared to artificially stacked TMDC heterostructures, which are difficult to fabricate with high quality. The constituent electrons and holes are individually localized in the neighboring layers of the van der Waals crystal (see figure). Interlayer excitons are formed due to the specific spin-valley coupling of the charge carriers within the individual layers of the crystal. Their optical strength originates from their mixing with intralayer B excitons [2]. In WS₂ and WSe₂, interlayer excitons are optically dark because of a reduced mixing [2]. We also find that interlayer interactions lead to a reduction of A exciton’s g-factor when the thickness of the material increases from a monolayer to the bulk [3].

Our discovery also solves the long-standing puzzle of positive g-factors in van der Waals semiconductors, and paves the way for studying collective phenomena in these materials at elevated temperatures due to their large interlayer excitonic binding energies of tens of meV.

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010

Infrared resonant vibrational restructuring of amorphous solid water

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Water ices form in dense, cold molecular clouds in the form of amorphous solid water, before undergoing various types of processing (thermal, shocks, irradiation, bombardment) which may alter their original structure. Crystalline ices have been observed in protoplanetary disks, on satellites and planets, as well as here on Earth. All of these environments represent later stages in the star and planet formation process, and are subject to irradiation processes. How is the energy injected into the vibrational modes of ices dissipated, and what structural modification results?

Here, we present the first results from a joint experimental and theoretical study of the selective mid-IR and THz irradiation of amorphous and crystalline ices. Experiments were carried out in a UHV surface science experiment at the FELIX laser facility and interpreted by comparison with molecular dynamics simulations. We will describe the new UHV setup at FELIX available to the astrochemistry community.

ABSTRACTS POSTER PRESENTATION

P1

Infrared action spectroscopy of doubly charged PAHs in a 22-pole cryogenic ion trap**S. Banhatti^{1*}**, J. Palotas², P. Jusko³, J. Oomens², S. Schlemmer¹, S. Brünken²¹Universität zu Köln, I. Physikalisches Institut²FELIX Laboratory, Institute for Molecules and Materials, Radboud University³IRAP, University of Toulouse, CNRS, CNES

PAHs (Polycyclic Aromatic Hydrocarbons) are suspected to be the carriers of aromatic infrared bands observed in the spectra of galactic and extra galactic sources, and changes in the astronomically observed band strengths are attributed to different PAH charge states existing under different conditions in the interstellar medium ^[1]. To identify these PAHs, laboratory infrared gas phase spectra are necessary to be compared to the observed astronomical data. Many previous studies employed IRMPD action spectroscopy by utilizing the intense FEL IR radiation at the FELIX laboratory, examples include a number of cationic, protonated, and anionic PAHs of varying sizes ^[2,3], and recently the dication HBC⁺⁺ ^[4].

Here we present the experimental gas-phase infrared spectra of three different PAH dications (Naphthalene²⁺, C₁₀H₈²⁺, Anthracene²⁺ and Phenanthrene²⁺, C₁₄H₁₀²⁺) in the IR fingerprint region 500–1600 cm⁻¹. The dications were produced by electron impact ionization of the corresponding vapors with 70 eV electrons. The spectra were obtained by Infrared Predissociation (IRPD) action spectroscopy of the mass-selected ions complexed in-situ with Ne in a 22-pole cryogenic ion trap setup (FELion) ^[5] operated at T = 15K using the intense and widely tunable free electron infrared lasers at the FELIX Laboratory. We also performed DFT calculations at the B3LYP 6-311+G(d,p) level for both singlet and triplet states of all ions in order to compare the vibrational frequencies to the corresponding experimental data.

Acknowledgments: This work has the support of Marie Skłodowska-Curie Actions (MSCA) Innovative Training Networks (ITN) Horizon 2020 under the grant agreement 722346. We also thank the FELIX team for their support.

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P2

Rayleigh scattering from isolated composite fermions skyrmions

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Recent light scattering experiments show that the 2D spin texture of quasiparticles with fractional charge can evidence skyrmions.¹ Fractional skyrmions are fragile states holding exotic topological properties, not fully understood. The evidence of Landau Levels (LL) and interactions in low-lying excitations of composite fermions at $1/3 \leq \nu \leq 2/5$ was studied by light scattering². Here we report resonant Rayleigh scattering (RRS) in a high-mobility GaAs/AlGaAs quantum well, where we observe σ^- -co-polarized RRS from quantum Hall isolated composite fermions (ICF) Skyrmions; at $\nu \approx 2/5$ it is two times more efficient than the $\nu = 1$ σ^+ skyrmions' scattering (Fig. 1). The enhanced scattering involves spin waves with ICF spin flipping around $\nu = 1$ σ^+ $2/5$, while at $1/3 \lesssim \nu \lesssim 2/5$ a reduced scattering reveals charge modes without spin flip. Recent theoretical works propose electrical transport to observe Skyrmions in graphene³. Here we propose electro-optical measurements under infrared irradiation that could be appropriate for observing Skyrmions in 2D van der Waals monolayers.

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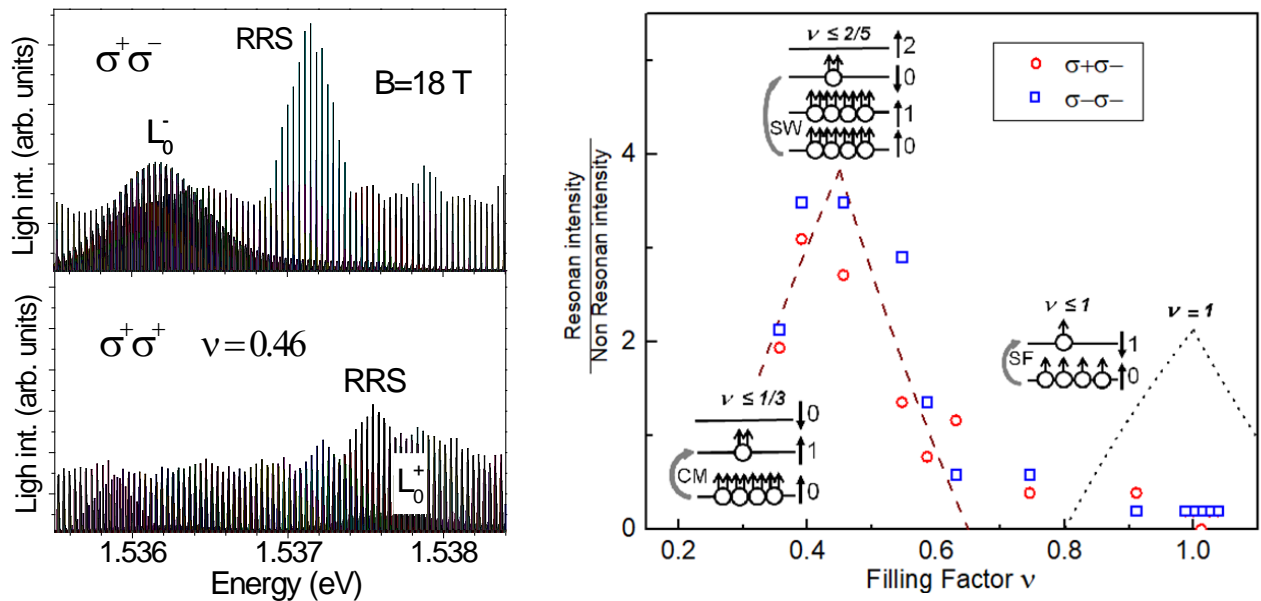


Fig. 1. Left panel: Cross and co-polarized light scattering plus emission at $1/3 < \nu = 0.46 < 2/5$ with σ^+ incident photons. Right panel: RRS intensity vs filling factor; the spin texture at $1/3 < \nu < 2/5$, is shown in the σ^+ outgoing photons (red/blue circles/squares). Numbers are LLs index, arrows spin alignment. At $1/3 < \nu < 2/5$ circles paired with two arrows indicate composite particles; number are the LLs index, arrows spin direction.

P3

Intrinsic Effects on Structure and Glycosidic Bond Stability of Fluorine Substitutions at the 2'- and 5-Positions of Protonated Cytidine Derivatives

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Nucleosides are fundamental building blocks of the genetic materials of life, deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). Nucleoside analogues often display anticancer and antiviral characteristics, and therefore are widely used as pharmaceuticals. The unique properties of fluorine make it of particular interest and medical-value as a synthetic nucleoside modification. In this work, the intrinsic properties of three groups of modified cytidine nucleosides are compared: (1) the canonical nucleosides, cytidine (Cyd) and 2'-deoxycytidine (dCyd); (2) the 2'-modified cytidines, cytosine arabinoside (araCyd; also known as cytarabine), 2'-fluoro-2'-deoxycytidine (Cydfl), cytosine 2'-fluoro-2'-deoxyarabinoside (araCydfl), and 2',2'-difluoro-2'-deoxycytidine (Cydfl₂; also known as gemcitabine); and (3) the 5-fluoro substituted systems, 5-fluorocytidine (fl⁵Cyd) and 5-fluoro-2'-deoxycytidine (fl⁵dCyd). These eight cytidine derivatives were studied in their protonated gas-phase ion forms using two types of tandem mass spectrometry complemented with computational chemistry. Comparisons of experimental infrared multiple photon dissociation (IRMPD) action spectroscopy with predicted spectra indicate fairly parallel conformational features across the eight systems. The two most prominent conformational differences are observed in the protonation site preferences of the 5-fluoro nucleosides relative to the canonical and 2'-modified systems, and the sugar puckering preference of [araCydfl+H]⁺ relative to all the others. Additionally, the highly-resolved hydrogen-stretches of the gas-phase IRMPD measurements display spectroscopic 2'-fluoro signatures that are dependent on specific local environments and allow for more definitive sugar puckering determinations. Energy-resolved collision-induced dissociation (ER-CID) experiments coupled with survival yield analysis demonstrate that the intrinsic glycosidic bond stability of the cytidine derivatives increase in the 2'-modified series following the order dCyd < Cyd < araCyd < Cydfl < araCydfl < Cydfl₂ and decrease in the 5-fluoro substituted series following the order fl⁵dCyd < dCyd < fl⁵Cyd < Cyd. Overall, the effects of fluorine modifications reinforce the primary reasoning for their incorporation into natural products for potential pharmaceutical use: minimal perturbation of molecular structures and substantial electronic chemical effects.

P4

Experimental determination of the ground state of isotopically pure silicon

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We have performed high field magnetoabsorption spectroscopy of Si:P using FTIR in magnetic fields up to 30T. The quadratic Zeeman effect (QZE) produces an energy shift proportional to the square of the product of radius and field, and therefore allows extraction of the state radius. Studying these transitions we evaluate effective mass theory of the excited states of Si:P, and extract their radii. Using isotopically pure ^{28}Si substrate we further investigate the ground state radius which is not well characterized due to the electron penetration into ion core, aka the Central Cell Correction (CCC), which is unknown.

P5

Reference-free metabolite identification by IR ion spectroscopy

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A major challenge in metabolomics is identifying the full molecular structure of low-abundance small molecules. Nanomolar concentrations can be detected by combining liquid chromatography and (tandem) mass spectrometry (LC-MS/MS), but structural information is limited to retention times and (fragment) masses, which are often inconclusive. Recently, infrared ion spectroscopy (IRIS) has emerged as a powerful analytical technique to elucidate molecular structure. IRIS combines the sensitivity of LC-MS/MS with the structural information of gas-phase IR spectroscopy and has been successfully applied for the identification of low-abundance biomarkers. However, identification using IRIS is time consuming and relies heavily on reference compounds that are often not readily available. Here we present an automated workflow to assist in the identification of detected features in an LC-MS experiment using IRIS and computational chemistry. We are able to theoretically predict IR spectra for candidate molecules that can subsequently be scored against the experimental IR spectrum of an observed m/z feature. By linking the workflow to the human metabolome database (HMDB), the user is allowed to specify search criteria which are used to find and generate candidate structures. We benchmark the workflow by identifying metabolites using only their chemical formula and experimental IR spectra as input information. Results show that the workflow is successful in scoring the correct metabolite as the best match. Additionally, it assigns high scores to metabolites closely related in structure. The latter shows the specificity of IR and the potential the workflow has in aiding the identification of unknown unknowns.

Keywords: Infrared ion spectroscopy, reference-free identification, mass spectrometry, human metabolome database, quantum chemical calculations

P6

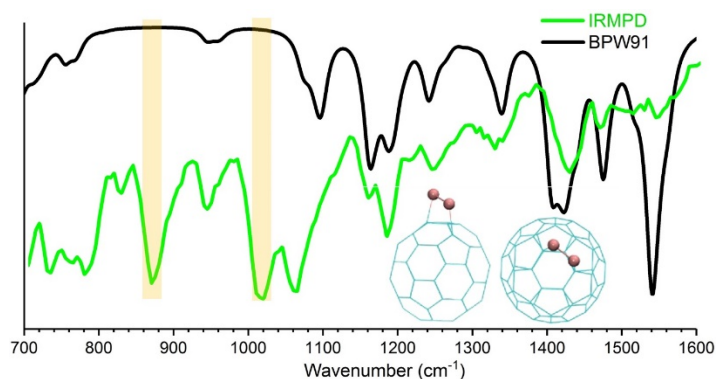
Structures of Vanadium Clusters Supported by C60 and Their Reactivity Towards Methanol

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Global issues, such as the greenhouse effect and energy shortage, urge efforts to develop alternative efficient energy storage and conversion materials. Hydrogen is a clean energy source, and its storage in metal decorated porous carbon materials has attracted extensive research interest. To understand the hydrogen storage behavior of metal functionalized carbon-based materials, the prerequisite is to understand their structures. Here, we employ C60 supported vanadium clusters as model systems. The structures of $C_{60}V_n(D_2)_m^+$ ($n = 1-10$; $m = 1-4$) have been identified via infrared multiphoton photodissociation (IRMPD) spectroscopy at FELIX Laboratory (Nijmegen, the Netherlands) and quantum chemical calculations. Furthermore, their reactivity towards methanol is also studied in a low-pressure collision cell, regarding the importance of methanol as a fuel source. It may also provide insights into the reversed process of synthesizing methanol from CO and hydrogen molecules.



P7

Selective mid-IR and THz Free-Electron Laser irradiation of water ice probed by FTIR spectroscopy

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Interstellar ice grains play a central role in the catalysis of prebiotic molecules that were essential for the development of life on Earth [1]. Tracing the physical-chemical evolution of ice grains is one of the main targets of the next NASA's space mission JWST. Hence it is important to explore in the laboratories the morphology and dynamics of such ices and how they influence the pathways to chemical synthesis. Water is the most abundant solid species found ubiquitous on interstellar grains and icy bodies in the Solar System. We have measured the irreversible structural changes induced in pure water ices of different initial structures (i.e., porous amorphous, compact amorphous, cubic crystalline, and hexagonal crystalline) by means of selective THz and mid-IR coherent, tunable pulsed radiation from the free-electron laser FELIX-1 and -2 at FELIX Laboratory in the Netherlands. The ultimate aim of this work is the study of energy relaxation dynamics at the surface and in the bulk of solid water layers. The advantage of using a free electron laser for this study is the possibility of resonantly pumping specific modes, which is a much better, selective probe for the local structure of the ice than thermal heating. Table-top laser systems (e.g., OPOs) are not adequate for this project because of their limited spectral and energy ranges [2-3]. Molecular dynamic simulations are also used to provide insight in the experimental results. Finally, we would like to invite potential external users to submit joint beamtime proposals at FELIX to perform their own experiments by means of the Dr. Ioppolo's group new ultra-high vacuum end-station designed for astro-science, surface science and catalysis applications.

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P8

Competition Between Fast Cascade Relaxation & Slow Recombination Processes in Silicon Donors & Acceptors

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Shallow donors and acceptors in silicon have been studied extensively due to their numerous advantages in the silicon based quantum computing proposals. The optically driven silicon-based quantum gates, acceptor-based spin-orbit qubit proposal, and realization of stimulated emission in the terahertz frequency range from boron acceptor centers in silicon, has renewed interest in the Rydberg, or hydrogenic transitions of these substitutional impurities (e.g. Bi [1], B [2], ...) in silicon. These applications require detailed knowledge of the orbital- state energies, wave functions, and the transition rate between them.

Here, we have investigated the population lifetimes using a combination of time-resolved pump probe spectroscopy with a THz free-electron laser, FELIX, and high resolution FTIR on isotopically purified samples.

P9

Infrared spectroscopy of grandPAHs

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We investigate the infrared spectral properties of large polycyclic aromatic hydrocarbons (grandPAHs). The photophysical properties of these aromatics are of key interest to the astronomical community, since it is hypothesized that they are abundant in interstellar space^{1,2}. Until now, most infrared spectral data has been obtained from solid phase measurements, where it is known that intramolecular interactions can cause spectral shifts and change intensities.

Using molecular beam laser spectroscopy, we obtain IR absorption spectra of isolated neutral grandPAHs at near-zero Kelvin temperatures. A wide range of systems has been studied including the full range of acenes (linear PAHs), the grand-PAHs coronene, hexabenzocoronene and dicoronylene, as well as nitrogen containing PAHs. The grandPAHs have been brought into the gas phase using laser desorption after which low rovibrational temperatures are achieved in the molecular beam. The low internal temperatures also pave the way for high-resolution electronic spectroscopy on large aromatic hydrocarbons which so far is largely absent.

For all of these systems we show that anharmonicity can extensively influence mid- and near-IR spectra. On the other hand, contrary to popular belief, we also show that low-energy global motions in the far-IR are very little influenced by anharmonicity. Besides allowing us to gain insight in the physics of aromatic hydrocarbons, these findings are key for astronomers who heavily rely on laboratory data.

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P10

Spectroscopic characterization of copper clusters for catalytic CO₂ fixation

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The catalytic recycling of CO₂ to liquid fuels, such as methanol, may help to control the atmospheric CO₂ content. Currently, methanol is produced industrially from syngas (CO₂-CO-H₂) under high temperature and pressure conditions over a Cu catalyst. A broad range of studies suggests that the most active parts of the industrial catalyst are Cu nanoparticles. To increase understanding of this reaction, we study the interaction of CO₂ and H₂ with copper clusters. For this, we elucidate the structure of Cu_n⁺ (n=1-10) clusters, both the bare clusters and their complexes with CO₂, through IR photodissociation spectroscopy in combination with Density Functional Theory. We observe that cationic copper clusters do not significantly activate of CO₂, and we expand our studies to the anionic species.

P11

IR Spectroscopy of Glycine-Water Clusters in Helium Nanodroplets

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We have studied the microsolvation of glycine with water molecules using helium droplet isolation infrared spectroscopy. Glycine exists in neutral form in gaseous state and in zwitterionic form in aqueous solutions. We address the question: “what is the minimum number of water molecules required to convert a neutral glycine molecule to its zwitterionic form?” The stepwise addition of water molecules to one glycine molecule was achieved using helium droplets isolation technique. The superfluid helium droplets allow a barrier free diffusion of the dopant molecules and enable the formation of large molecular clusters. The infrared spectra were recorded in the range of 560-1850 cm⁻¹, using the free electron lasers (FELs) at FELIX laboratory in Nijmegen.

P12

Vibrational excitement: from CO₂ to CO

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CO₂ plasmas are a promising approach to towards mitigating intermittency issues of sustainable energy sources by efficient conversion/storage of electrical energy into chemicals. In the past, 90% energy efficiency in CO₂ decomposition to CO is obtained, which is a fundamental step in fuel production from CO₂. The prevailing but yet unverified model explaining this high efficiency is based on vibrational ladder climbing: vibrational energy is transferred via collisions until the dissociation potential is reached.

We found the first experimental signatures of the mechanism in an OPO laser excitation experiment. CO₂ is excited to the first vibrational level and the consequent collisional energy transfer lead to CO₂ decomposition, which is monitored by quantitative FTIR measurements. The resulting CO production is observed to scale with the 4th power of the pressure.

In order to find unambiguous proof of the mechanism, the parameter range (power and bandwidth) is extended in our experiments with FELIX. Firstly, multi-quantum excitation is pursued ($v_3 \geq 3$) to benchmark simulations in dependence of excitation density and collision frequency. Secondly, loss of v_3 selectivity is investigated in dependence of v_1 and v_2 excitation to characterize limitations of ladder climbing dissociation.

P13

The IR spectrum of protonated buckminsterfullerene, $C_{60}H^+$

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We present what is to our knowledge the first experimental IR spectrum of gaseous protonated C_{60} . The spectrum covers the 500 – 1800 cm^{-1} range and was recorded using IR multiple-photon dissociation (IRMPD) spectroscopy employing the FELIX free electron laser and a quadrupole ion trap mass spectrometer with an atmospheric pressure chemical ionization (APCI) source. Our experimental approach allows us to record the spectrum of $C_{60}H^+$ free from any contamination of the isobaric $^{13}C^{12}C_{59}^+$ ion, which is abundant in the mass spectrum.

The significant symmetry lowering of $C_{60}H^+$ as compared to C_{60} yields a rich vibrational spectrum. We analyze this spectrum on the basis of density functional theory (DFT) computed spectra using different methods and basis sets. We believe that this spectrum is of substantial astrophysical interest, especially in light of the recent detections of C_{60} and C_{60}^+ in circumstellar environments, and Harold Kroto's hypothesis that fullerenes are most abundant in their protonated form.

P14

Laser Desorption Molecular Cluster Nozzle: *Design and experiment*

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The elucidation of the structure of model gas-phase peptides and their aggregates using infrared spectroscopy can provide crucial insights into biological mechanisms.¹ For instance, peptide fibrils consisting of stacked beta-sheets, which are present in the brains of people with Parkinson's disease, can be modelled by the stacking of smaller neutral gas-phase peptides. In our setup these neutral molecules are brought into the gas-phase by laser desorption and populated into their electronic and vibrational ground states through a supersonic expansion with argon. Thereafter they are investigated by the infrared light of FELIX, resonantly excited and ionized by a tunable UV-laser and subsequently detected by a time-of-flight mass spectrometer. This allows us to perform conformer- and mass-selective infrared spectroscopy on neutral species.²

Recently, for the first time, we demonstrated the formation of stable higher order clusters (up to $n=14$) of neutral peptides in the gas phase using laser desorption.³ It is believed that these peptide aggregates are formed just before and/or after being picked up by the argon gas pulse. The formation- and detection-intensity of higher order clusters depends on a broad range of parameters within the experiment which are not easily determined.

Here, a cluster-enhancement nozzle based on designs used in metal-cluster research⁴, but adapted to our laser desorption setup, was designed and tested in an attempt to acquire better control over cluster density and size. The nozzle is meant to delay the supersonic expansion of argon with the seeded molecules of interest by forcing the gas-pulse through a series of channels, of variable size and length. However, instead of enhancing aggregate formation, the nozzle appears to influence the effect of the supersonic expansion: obtained REMPI spectra of peptide monomers showed a significantly lower background intensity (and thus colder molecules) than is seen with the usual supersonic expansion nozzle.

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P15

Towards unraveling the reaction mechanism of CO₂ hydrogenation over metal clusters

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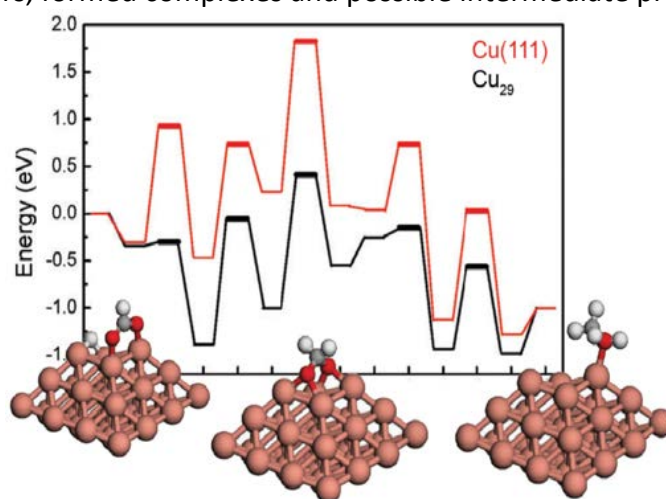
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One route to reduce atmospheric CO₂ levels is by regenerating it into a fuel. Hydrogenation of CO₂ to one of the simplest fuels, methanol, is exothermic, but due to the strength of the CO₂ bonds, the reaction requires high temperatures and a catalyst to proceed. The current industrial process is catalyzed using a Cu/ZnO/Al₂O₃ catalyst, with strong indications that the active site is formed by Cu nanoparticles with ZnO as promotor. The reaction mechanism is, however, poorly understood. To enable the development of novel, more efficient CO₂ hydrogenation catalysts, we aim to model the active site using clusters of Cu and other metals.

We are currently developing experiments, where ionic metal clusters are generated in a laser ablation source, mass-selected in a quadrupole mass filter, and stored in a RF ion trap. Here, the clusters are reacted with CO₂ and H₂ under controlled conditions (partial pressure, temperature). Products formed here are mass-analyzed using a Fourier Transform Ion Cyclotron Resonance (FTICR) mass spectrometer coupled to the Free Electron Laser for IntraCavity Experiments FELICE. Using the latter, we can then structurally characterize clusters, formed complexes and possible intermediate products.



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P16

On the role of photolytic PAH processing regarding the cosmic deuterium abundance

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All deuterium in our Universe was formed during the Big Bang nucleosynthesis era, and was uniformly distributed. However, stellar consumption of deuterium alone cannot account for all the deuterium that is missing from this otherwise uniform background. One hypothesis is that this deuterium is stored in large Polycyclic Aromatic Hydrocarbons (PAHs). Density Functional Theory (DFT) calculations allow us to estimate the concentrations of deuterium-containing PAHs, but experimental research is needed to validate these models. By studying the photo-induced elimination of H and D from D-containing PAH molecules, we aim to investigate photochemical processes underlying deuteration in the interstellar medium (ISM). Based on the analysis of the infrared multiple dissociation (IRMPD) spectra and UV dissociation mass spectra of four different PAH structural isomers - varying in shape, size, and deuterium content - we propose a scrambling mechanism for hydrogen and deuterium atoms on the rim of these PAH molecules. In protonated molecules - containing both aliphatic and aromatic sites - this will lead to a relative increase in strongly-bound, aromatic deuterium atoms. Considering that this scrambling mechanism is triggered by photonic excitation, we think that it could lead to increased deuterium enrichment as PAHs move into more exposed regions of the ISM. We believe that two different IR emission band ratios in astronomical observations could be studied to test our hypothesis.

P17

Evolution of the Fermi surfaces and electronic correlations in the high pressure phase of FeSe_{1-x}S_x

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Applied pressure can have drastic effect on superconductivity in different unconventional superconductors. Among them, bulk FeSe suffers a remarkable four-fold enhancement in its critical temperature under hydrostatic pressure compared with the ambient nematic and superconducting state [1]. The combined chemical and applied pressure in FeSe_{1-x}S_x provides important tuning parameters of the phase boundaries between the competing nematic and magnetic phases from which superconductivity emerges in these systems. The nematic order is suppressed in the vicinity of $x \sim 0.17$ [2,3] and the applied pressure gives clean access to the high-pressure phase of FeSe_{1-x}S_x [2]. Here, we present the evolution of the Fermi surface and electronic correlations in $x \sim 0.17$ in the high pressure phase up to 22 kbar determined by quantum oscillations in magnetic fields up to 45T. We find that Fermi surface increases with pressure, but the effective quasiparticle masses of the main pockets remain relatively insensitive. Additionally, we build up a detailed the phase diagram of $x \sim 0.17$ under pressure based on magnetotransport data up to 16T and discuss the normal electronic state in the low-temperature regime. We compare our results in relation to other quantum oscillations studies in FeSe_{1-x}S_x [3,4].

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