The 10th International workshop on

ELECTROSTATIC STORAGE DEVICES
ESD 10

Aarhus University, Denmark
June 16-19 2025

Book of abstracts

Program
Invited talks
Contributed talks
Posters

DEPARTMENT OF PHYSICS AND ASTRONOMY
AARHUS UNIVERSITY

The 10th International workshop on ELECTROSTATIC STORAGE DEVICES ESD 10

Auditorium: building 1523, 3rd floor
Lunch/poster session: building 1520, 7th floor

Monday 16th June

09.00 - 10.30	**Session 1: Opening** – Chair: Henrik B. Pedersen
09.00 - 09.15	Welcome
09.15 - 10.00	**Opening lecture:** *Three decades of electrostatic ion trapping: Already?* **Daniel Zajfman**, Weizmann Institute of Science, Rehovot, IL
10.00 - 10.30	*Probing molecular mutual neutralization reactions of atmospheric importance using the ion storage facility DESIREE* **Richard Thomas**, Stockholm University, SE
10.30 - 11.00	Coffee break
11.00 - 12.40	**Session 2: Internal dynamics in molecules** – Chair: Andreas Wolf
11.00 - 11.30	*State manipulations of negative ions during storage* **Dag Hanstorp**, University of Gothenburg, SE
11.30 - 12.00	*Peptide Bond Formation in Amino Acid Clusters* **Yoni Toker**, Bar Ilan University, IL
12.00 - 12.20	*The not even just odd even-odd effect in the cooling of gold clusters* **Klavs Hansen**, Tianjin University, CN
12.20 - 12.40	*Internal decay processes in homonuclear dimer anions using trapped ions in an EIBT and electron spectrometer* **Oded Heber**, Weizmann Institute of Science, Rehovot, IL
12.40 - 13.30	Lunch break

13.30 - 15.10	**Session 3: Related fields & perspectives** – Chair: Holger Kreckel
13.30 - 14.00	*Charge-Detection Mass Spectrometry and Hypervelocity Ice Grain Impacts* **Robert Continetti**, University of California San Diego, USA
14.00 - 14.30	*Quantum or Classical? Rethinking Laser-Matter Interactions in Intense Fields* **Lars Bojer Madsen**, Aarhus University, DK
14.30 - 14.50	*Minute-scale Storage of Multiply Charged Helium Nanodroplets inside an Electrostatic Ion Beam Trap* **Matthias Veternik**, University of Innsbruck, AT
14.50 - 15.10	*Development of an X-ray photoelectron spectrometer to investigate chirality in biomolecular ions* **Bart Oostenrijk**, Deutsches Elektronen-Synchrotron DESY, DE
15.10 – 17.00	**Poster session I**

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Tuesday 17th June

09.00 - 10.25	**Session 4: Photo-induced processes & spectroscopy** – Chair: Steen Brøndsted Nielsen
09.00 - 09.45	**Topical lecture:** *Spectroscopy and dynamics of cold molecular ions* **Lars H. Andersen**, Aarhus University, DK
09.45 - 10.05	*IR and UV spectroscopy of gas-phase monohydrated protonated guanine* **Satchin Soorkia**, Université Paris-Saclay, FR
10.05 - 10.25	*Freezing Out Structural Effects: Gas-Phase Fluorescence from Rhodamine Homodimers and Trimers at Cryogenic Temperatures* **Iden Djavani-Tabrizi**, Aarhus University, DK
10.25 - 11.00	Coffee break
11.00 - 12.30	**Session 5: New techniques & developments** – Chair: Christine Joblin
11.00 - 11.30	*Measurement of dissociation and radiative cooling rate of PAH cations using room temperature and cryogenic electrostatic storage rings* **Jerome Bernard**, Claude Bernard University Lyon, FR
11.30 - 11.50	*A new setup to study the reactivity and spectroscopy of isomer selected molecular clusters* **Anne P. Rasmussen**, CNRS, FR & Aarhus University, DK
11.50 – 12.10	*Phase Space Manipulation and Evaporative Cooling of Ions in an Electrostatic Ion Beam Trap* **Deepak Sharma**, Max Planck Institute for Nuclear Physics, Heidelberg, DE
12.10 – 12.30	*Low Energy Electron Cooling at the Cryogenic Storage Ring* **Jonas Bechtel**, Max Planck Institute for Nuclear Physics, Heidelberg, DE
12.30 - 13.30	Lunch break
13.30 - 15.05	**Session 6: Intermolecular processes** – Chair: Richard Thomas
13.30 - 14.15	**Topical lecture:** *A glimpse into the world of ICD and ETMD* **Lorenz S. Cederbaum**, Heidelberg University, Heidelberg, DE
14.15 - 14.45	*Interatomic/molecular Coulombic decay (ICD): Toward exploring vibrational ICD in hydrated anion beams* **Ltaief Ben Ltaief**, Aarhus University, DK
14.45 - 15.05	*Radiative cooling of the deprotonated cyan fluorescent protein chromophore anion* **Mark H. Stockett**, Stockholm University, SE
15.05 - 17.00	**Poster session II**

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Wednesday 18th June

09.00 – 10.20	**Session 7: Collisions** – Chair: Henning T. Schmidt
09.00 - 09.30	*Ion-neutral Merged-Beams Experiments at the CSR* **Holger Kreckel**, Max Planck-Institute for Nuclear Physics, Heidelberg, DE
09.30 - 10.00	*Fast and slow fullerene collisions at DESIREE* **Michael Gatchell**, Stockholm University, SE
10.00 – 10.20	*Electron Transfer to Ar^+ studied with a Reaction Microscope in a Cryogenic Storage Ring* **Felix Herrmann**, Max Planck Institute for Nuclear Physics, Heidelberg, DE
10.20 - 11.00	Coffee break
11.00 - 12.40	**Session 8: Mass spectrometry & nuclear physics** – Chair: Robert Continetti
11.00 - 11.30	*Facets of Electrostatic Ion Beam Traps (My life with MR-ToF devices)* **Lutz Schweikhard**, University of Greifswald, DE
11.30 – 12.00	*Mass spectrometry and separation at ISOLDE/CERN* **Lukas Nies**, European Organization for Nuclear Research, Geneva, CH
12.00–12.20	*Planar electrostatic ion traps for mass spectrometry* **Dmitry Grinfeld**, Thermo Fisher Scientific, DE
12.20 - 12.40	*High-sensitivity spectroscopy of radioactive ions within a ConeTrap* **Daniel Bettaney**, University of Manchester, UK
12.40 - 13.30	Lunch break
14.00 – 15.30	**Lab tours – coffee by auditorium from 15.00**
15.30 – 18.00	**Excursion: Walk to and own time at ARoS art museum**
18.00-21.00	**Conference dinner (ARoS)**

Auditorium: building 1523, 3rd floor
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Thursday 19th June

09.00 - 10.30	**Session 9: Photo-induced processes & spectroscopy** – Chair: Lars H. Andersen
09.00 - 09.30	*Cold ion spectroscopy with LUNA2* **Thomas Toft Lindkvist**, Aarhus University, DK
09.30 – 09.50	*Towards multi-color laser action spectroscopy of highly excited* H^+_3 *in the CSR* **Lukas Berger**, Max Planck Institute for Nuclear Physics, Heidelberg, DE
09.50 – 10.10	*Accurate lifetime measurement of the* $5d\,^2D_{3/2}$ *metastable state of singly charged barium* **Paul Martini**, Stockholm University, SE
10.10 - 10.30	*Velocity Map Imaging with No Spherical Aberrations* **Yehuda Ben Shabo**, Bar Ilan University, IL
10.30 - 11.00	Coffee break
11.00 - 12.30	**Session 10: Collisions** – Chair: Lutz Schweikhard
11.00 - 11.30	*Electron-ion Recombination at the Cryogenic Storage Ring* **Leonard Isberner**, Max Planck-Institute for Nuclear Physics, Heidelberg, DE
11.30 – 11.50	*State-Selective Mutual Neutralization between* Ba^+ *and* Au^- *Ions* **Rachel Poulose**, Stockholm University, SE
11.50 – 12.10	*Momentum Imaging of Electrons and Recoil Ions from Anion–Neutral Interactions with a Reaction Microscope in a Cryogenic Ion Storage Ring* **Michael Schulz**, Max Planck Institute for Nuclear Physics, Heidelberg, DE
12.10 – 12.30	*A new generation of compact transportable cryogenic electrostatic storage device: Polar Mini-Ring* **Suvasthika Indrajith**, Université Lyon, FR
12.30 - 13.30	Lunch break
13.30 - 15.15	**Session 11: Related fields & perspectives** – Chair: Klavs Hansen
13.30 - 14.15	**Topical lecture:** *The PAH Model: Current Status and Perspectives* **Christine Joblin**, Institut de Recherche en Astrophysique et Planétologie, Toulouse, FR
14.15 – 14.35	*Probing the balance between dissociation and radiative cooling in interstellar Polycyclic Aromatic Hydrocarbon cations* **Arun Subramani**, Stockholm University, SE
14.35 – 14.55	*Action spectroscopy and photophysics of* $C_{11}H_9^+$ *species* **Ana Lozano**, Université de Toulouse, FR
15.00 - 15.30	Coffee and departure

The 10th International workshop on
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Invited talks

Electrostatic Ion Traps at CERN-ISOLDE

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Electrostatic ion traps, in the form of Multi-Reflection Time-of-Flight (MR-ToF) devices, are used at radioactive ion beam facilities such as CERN-ISOLDE to manipulate ion beams for different purposes. Without the need for radio-frequency or magnetic fields, these devices perform mass spectrometry, laser spectroscopy, beam purification, and beam composition identification. The technique is fast and can perform high-resolution measurements with a mass resolving power of $\mathrm{m}/\Delta\mathrm{m} > 10^5$ in a very short amount of time ($<$ 100ms), which is especially important when studying short-lived radioactive isotopes. In this contribution, we will explore the use of ISOLDE's different MR-ToF devices.

With the ISOLTRAP MR-ToF mass spectrometer, atomic mass measurements have now been routinely performed for over ten years [1], contributing to our understanding of nuclear structure and the strong interaction within the atomic nucleus. Recently, expanding on the device's capabilities, excitation energies of nuclear isomeric states were measured to investigate nuclear structure through theory calculations [2, 3]. Furthermore, the device was extensively used to investigate ISOLDE's ion beam composition, for example, to identify actinides and actinide-containing molecules to examine and improve production pathways for beyond-the-standard-model research and medical applications [4,5,6].

In another MR-ToF device, developed in collaboration between ISOLDE and the MIRACLS experiment, collinear laser fluorescence spectroscopy was performed for the first time on radioactive ions trapped with a stored kinetic energy exceeding 10 keV. While conventional devices used at similar facilities are operated at standard ion beam energies of one to two keV, the newly developed ISOLDE MR-ToF device is capable of storing ion beam energies of up to ten to 20 keV, promising faster and more precise measurements and mass separation [7].

References:
[1] F. Wienholtz et al., Nature **498**, 346–349 (2013)
[2] L. Nies et al., Phys. Rev. Lett. **131**, 222503 (2023).
[3] L. Nies et al., Phys. Rev. Lett. **131**, 022502 (2023).
[4] M. Au, et al., Phys. Rev. C **107**, 064604 (2023).
[5] M. Au, et al., Nucl. Instrum. Methods.: B **541**, Pages 375-379 (2023).
[6] M. Au et al., J. Radioanal. Nucl. Chem. **334**(1):367-379 (2024).
[7] F. M. Maier, et al., Nucl. Instrum. Methods.: A **1056**, 168545 (2023).

Facets of Electrostatic Ion Beam Traps (My life with MR-ToF devices)

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There are several aspects of Electrostatic Ion Beam Traps (EIBTs) and their applications. This contribution gives an overview of my contacts with them.

After my first closer but still more peripheral acquaintance in 2005 at ESD-1 in Eilat, it so happened that my doctoral student Markus Eritt went to Daniel Zajfman's group at Rehovot to study small metal clusters in an EIBT [1]. When he returned for writing up, Robert Wolf looked for a master-thesis topic and we decided that ISOLTRAP at ISOLDE/CERN would profit from another mass separation step: A Multi-Reflection Time-of-Flight (MR-ToF) instrument would be just the right tool for that job. Thus, Robert built this new ISOLTRAP component at Greifswald moved it to CERN and continued his work for his dissertation [2]. Almost immediately, it became clear that this instrument expanded ISOLTRAP's capability also with respect to mass spectrometry proper: Its measurements were faster and needed less ions than the Penning traps, i.e., it reached nuclides with shorter lifetimes and lower production yields [3,4].

Nowadays, the ISOLTRAP MR-ToF mass spectrometer is routinely involved in mass separation and mass spectrometry, the latter not only for precision measurements (recent examples in [5]), but also as an analytical tool for the identification of the particles delivered from ISOLDE. Prominent examples are the confirmation of RaF^+ [6] and several other radioactive compounds [7]. It also serves as a highly-sensitive and highly-selective ion detector for resonance-ionization laser spectroscopy [8].

Meanwhile, and independent of this development, Christian Breitenfeldt went to the MPIK at Heidelberg to perform metal-cluster experiments at the Cryogenic Trap for Fast ion beams (CTF) [9]. Furthermore, a second MR-ToF device was built at Greifswald for additional technical developments and related studies, such as space-charge effects [10].

This setup again went to CERN where it became the heart of MIRACLS' proof-of-principle project (Multi-Ion-Reflection Apparatus for Collinear Laser Spectroscopy) [11]. To this end, it was equipped with phototubes for fluorescence-light detection. Later on, the experiments also included electron detachment from anionic atoms [12].

With both earlier instruments gone, a new setup was built, and named Cluster MR-ToF MS as it was (mostly) dedicated to the study of atomic clusters. Several investigations have been performed on clusters produced by laser ablation in high vacuum [13]. More recently, the setup was expanded to include a magnetron sputtering cluster condensation source [14]. Nevertheless, the latest studies were on laser-ablated thorium and uranium compounds, with a highlight on thorium clusters [15].

As for current and future developments: Some considerations have moved to higher trapping energies [16]. And on the low-energy side, "mass production" organized at the TU Darmstadt resulted in "DA's MR-ToF" instruments [17] at Boston, Groningen, Innsbruck, Mainz, Manchester, (in alphabetical order) and for PUMA/CERN (which had triggered this project). Thus, stay tuned for upcoming results.

[1] M. Eritt, thesis 2008
[2] R.N. Wolf, thesis 2013
[3] M. Rosenbusch, thesis 2015
[4] F. Wienholtz, thesis 2019
[5] L. Nies, thesis 2023
[6] R.F. Garcia Ruiz *et al.*, 2020
[7] M. Au *et al.*, 2023
[8] B.A. Marsh *et al.*, 2018
[9] C. Breitenfeldt, thesis 2016
[10] M. Rosenbusch *et al.*, 2013
[11] S. Sels *et al.*, 2020
[12] in preparation
[13] P. Fischer, thesis 2020
[14] Giesel *et al.*, 2024
[15] P. Fischer *et al.*, 2025
[16] F.M. Maier *et al.*, 2023
[17] M. Schlaich *et al.*, 2024

Probing molecular mutual neutralization reactions of atmospheric importance using the ion storage facility DESIREE

M. Poline[1], A. Dochain[2], S. Rosén[1], M-C. Ji[1], P. Martini[1], M. Larsson[1], H. Cederquist[1], H. Zettergren[1], H. T. Schmidt[1], S. Ndengué[3], E. Quintas-Sánchez[4], R. Dawes[4], S. G. Ard[5], N. S. Shuman[5], A. A. Viggiano[5], and Richard D Thomas[1]

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ABSTRACT

The evolution of plasma environments is defined and governed by balances between ionizing processes, chemical rearrangements, and neutralisation reactions such as mutual neutralisation (MN). Measuring and explaining these processes in detail is fundamental to understanding and modelling non-local thermal equilibrium environments, such as atmospheric plasmas.

Until recently, experimental studies of MN involving molecular ions in flow tubes and merged-beams were limited to measurements of overall reactivities without information of the mechanism or the products. The cryogenic Double ElectroStatic Ion Ring ExpEriment facility makes such studies possible [1-4]. Here, it is possible to control and manipulate the internal energies of the ions, fine-tune their collision energy, and identify the reaction products and the states they are in. This opens possibilities to reach new insights on balances between different MN reaction pathways and their dynamics, and here I focus on MN relevant to atmospheric phenomenon such as sprites. Investigating reactions involving molecular oxygen and nitrogen ions, I probe competition between product channels and unravel effects of internal energy.

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1. R. D. Thomas et al., Rev. Sci. Instrum. 82, 065112 (2011)
2. H. T. Schmidt et al., Rev. Sci. Instrum. 84, 055115 (2013)
3. M. Poline et al., Phys. Rev. Lett. 132, 023001 (2024).
4. A. Bogot et al., Science 383, 285 (2024).

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Isolated Green Fluorescent Protein Chromophore Anions: Indeed They Shine

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Lars H. Andersen[1], and Steen Brøndsted Nielsen[1]

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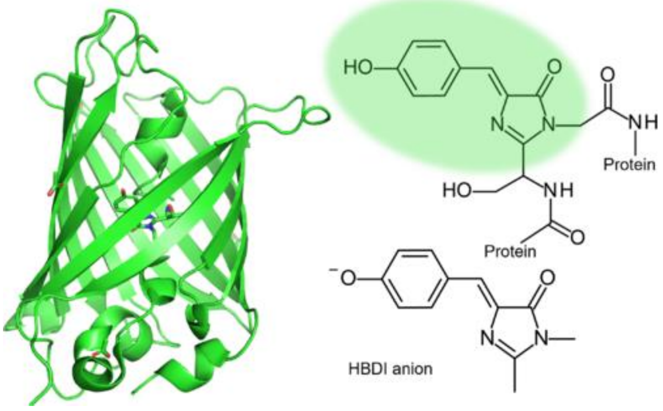

Figure 1: GFP and its chromophore.

The green fluorescent protein (GFP) derived from the jellyfish *Aequorea victoria* consists of a barrel-like β-sheet structure wherein its photoactive chromophore molecule is buried (Fig. 1). Upon exposure to blue-light irradiation the chromophore undergoes excited-state proton transfer, resulting in an anionic form that fluoresces with a yield of 80%. Our group performed the first gas-phase action absorption measurements of the HBDI- model chromophore (Fig. 1) in 2001, which revealed an absorption band maximum in line with that of the protein [1]. The protein microenvironment is, however, essential for fluorescence as photo-excited bare HBDI anions quickly undergo internal conversion through a conical intersection in a twisted geometry. Thus, earlier attempts to measure gas-phase fluorescence at room temperature all failed. Here, we unequivocally show that the chromophore exhibits fluorescence in the gas phase when cooled to low temperatures ($< 150\,\mathrm{K}$) [2] in accordance with previous predictions [3]. LUNA2 experiments at 100 K reveal an absorption-band maximum at 481.6 ± 0.2 nm (in agreement with photoinduced action spectroscopy [3]) and maximum emission at 483.6 ± 0.5 nm [2]. Remarkably, both values closely resemble those for proteins cooled to 77 K. After excitation at the 0-0 transition, we estimate radiation is the dominant pathway back to the ground state. Franck-Condon simulations at the ωB97XD/aug-cc-pVDZ level of theory nicely reproduce the experimental spectra and identify the fluorescent form to be planar, and that an in-plane scissoring mode ($80\,\mathrm{cm}^{-1}$) is active for both absorption and emission.

References:

[1] S. Brøndsted Nielsen, A. Lapierre, J. U. Andersen, U. V. Pedersen, S. Tomita, & L. H. Andersen. *Phys. Rev. Lett.*, **2001** *87*, 228102.

[2] T.T. Lindkvist, I Djavani-Tabrizi, L. H. Andersen, & S. Brøndsted Nielsen. *Phys. Rev. Lett.,* **2025**, *134*, 093001.

[3] L. H. Andersen, A. P. Rasmussen, H. B. Pedersen, O. B. Beletsan, & A. V. Bochenkova. *J. Phys. Chem. Lett.*, **2023**, *14*, 6395.

Measurement of dissociation and radiative cooling rate of PAH cations using room temperature and cryogenic electrostatic storage rings

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In the interstellar medium's harsh and variable radiation fields, the fate of polycyclic aromatic hydrocarbon (PAH) cations depends on their ability to radiate and resist fragmentation. Modeling their evolution demands precise knowledge of dissociation and radiative cooling rates over a broad range of excitation energies. It is now well established that PAHs can non-destructively relax internal energy via recurrent fluorescence (RF), which is a delayed fluorescence process from thermally excited electronic states. This process, which competes with and quenches dissociation at internal energies up to several eV above dissociation energy, has been experimentally investigated in electrostatic storage devices for over a decade. Electrostatic storage rings (ESRs) provide excellent ways to confine small, isolated clouds of PAH cations under astrophysically relevant conditions to study the relaxation dynamics over a broad timescale, depending on the internal energy.

In previous studies[1,2,3], measuring the RF rates, k_{RF}, required knowledge of the dissociation rates, $k_{diss}(E)$, as a function of internal energy. The method involved producing energized PAH cations with a broad internal energy distribution (IED) in a plasma ion source, allowing them to relax in the ESR until spontaneous dissociation became negligible, and then re-exciting them at different storage times via laser absorption to induce dissociation decays reflecting the internal energy distribution. However, the $k_{diss}(E)$ curve is often poorly known, or available only at a few energy values, and typically inferred from statistical models such as RRKM theory or Arrhenius laws. Moreover, possible contributions from different isomers present in the PAH cation beam were averaged in these earlier studies.

In the present work, we report new direct measurements of $k_{diss}(E)$ for PAH cations, using sharp, low-energy IEDs combined with two-photon absorption in the near-UV range. These measurements also allow us to probe the role of isomerization through the analysis of the dissociation decay curves. These results prefigure the expected outcomes from the new Polar Mini-Ring setup, currently under construction, which will be operated at the DESIRS VUV beamline of Synchrotron SOLEIL under single-photon absorption conditions.

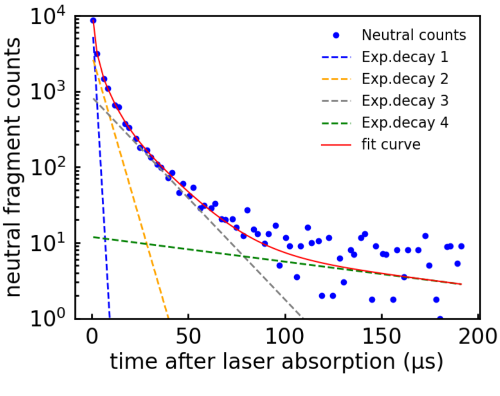

Figure 1: Naphthalene cation laser-induced decay (330 nm) recorded for sharp IED peaked at 8.1 eV.

[1] J Bernard, *et al.*, *Physical Chemistry Chemical Physics* **25 (15)** 10726–10740 (2024)
[2] S Martin, *et al.*, *Physical Review A* **92 (5)**, 053425 (2015)
[3] S. Martin *et al.*, *Phys. Rev. Lett.* **110**, 063003 (2013)

Quantum or Classical? Rethinking Laser-Matter Interactions in Intense Fields

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When intense laser light interacts with matter, a series of nonlinear processes such as ionization and frequency up-conversion occur. Traditionally, these processes have been described from a semiclassical perspective, where the electronic and nuclear degrees of freedom are treated quantum mechanically, while the photonic degrees of freedom are treated classically. For example, in the key process of attosecond physics, high-harmonic generation (HHG), electrons in the generating medium are described using quantum mechanics, while both the driving and emitted light are treated classically. Similarly, questions of photon statistics are typically ignored in studies of excitation and ionization induced by intense laser light.

Recently, however, researchers have begun using quantized treatments of the electromagnetic field for HHG and ionization, and experiments have reported the generation of quantum light from HHG. These new approaches allow us to better understand the generating medium, gain insights into the quantum nature of the generated light, and even explore the possibility of driving the medium with nonclassical light.

In my talk, I will present the current status of this emerging research area from a theoretical perspective. I will address the question posed in the title and encourage reflection and discussion about the relevance of a fully quantum optical approach for ESD-related studies.

A glimpse into the world of ICD and ETMD

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How does a microscopic system like an atom or a small molecule get rid of the excess electronic (or vibrational) energy it has acquired, for instance, by absorbing a photon or by impact with an ion or electron? If this microscopic system is isolated, the issue has been much investigated and the answer to this question is more or less well known. But what happens if our system has neighbors as is usually the case in nature or in the laboratory? In a human society, if our stress is large, we would like to pass it over to our neighbors. Indeed, this is in brief what happens also to the sufficiently excited microscopic system. A mechanism of energy transfer named ICD (Interatomic/Intermolecular Coulombic Decay) has been theoretically predicted and verified in by now many exciting experiments. This mechanism seems to prevail "everywhere" from the extreme quantum system of the He dimer to water, to systems in cavity, and even to quantum dots. The transfer is ultrafast and typically dominates other relaxation pathways.

ICD is often accompanied by ETMD (Electron Transfer Mediated Decay). As charge transfer is usually much slower than energy transfer, ICD dominates. However, ETMD can be widely operative when our microscopic system itself does not possess excess energy, i.e., when ICD is inactive. The energy needed is created by the ETMD itself. ICD and ETMD are introduced and discussed. Examples and arguments are presented which make clear that the processes in question play a substantial role in nature and laboratory.

Experimental and theoretical work on ICD, ETMD and related processes can be found in the Bibliography:
http://www.pci.uni-heidelberg.de/tc/usr/icd/ICD.refbase.html

A recent review: T. Jahnke *et al*, *Interatomic and Intermolecular Coulombic Decay*
Chem. Rev., 120, 11295–11369 (2020)

Three decades of electrostatic ion trapping: Already?

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While storing ions using electrostatic fields alone in a static configuration is prohibited by Earnshaw's theorem, it has long been known that dynamic electrostatic trapping—such as that used in storage rings—is indeed feasible. Historically, however, the field of storage rings, especially for heavy and molecular ions, has been tightly linked to high-energy physics, and as a result, the first generations of such devices were dominated by magnetic configurations.

Roughly 30 years ago (already?), the landscape shifted when the idea emerged that storage rings could be designed for much lower kinetic energies, relying entirely on electrostatic fields. Although some rudimentary systems had appeared earlier, the construction of ELISA, right here in Aarhus, marked the first fully operational low-energy electrostatic storage ring. This pioneering effort catalyzed the development of an entire family of electrostatic devices—beyond rings—that have since enabled the long-term storage and study of molecular ions.

Scientific progress often arises from either new ideas or new tools. The field of electrostatic ion storage belongs firmly to the latter category. The devices developed over the past three decades have opened new windows into molecular physics, astrochemistry, and ion-ion interactions, by allowing us to observe processes on timescales that were previously out of reach.

In my lecture, I will try (foolishly, perhaps) to trace the development of this field from its early ambitions to its current capabilities, reflecting on how a concept born from theoretical limitations turned into a powerful experimental platform.

Charge-Detection Mass Spectrometry and Hypervelocity Ice Grain Impacts

Robert E. Continetti

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One proposed spaceflight instrument for the detection of biosignatures in small icy particles – like those ejected from ocean worlds like Saturn's moon Enceladus or Jupiter's moon Europa – is an impact ionization mass spectrometer. Laboratory validation of proposed flyby sampling missions is needed to show that biosignature molecules can survive an impact at hypervelocity speeds. We developed an Aerosol Impact Spectrometer that makes use of charge-detection mass spectrometry to enable studies of the impact dynamics for single mass- and charge-selected submicron particles.[1,2] This provides an tool in the laboratory for validating the approach of sampling ocean world ice grain plumes in a flyby missions for the detection of specific biosignatures. Previously, we have applied this approach to study the impact dynamics of ice grains from 40 m/s to 2.4 km/sec, examining the coefficient of restitution and post-impact behavior including rebound, adhesion and fragmentation.[3,4] Now, using a 41-element linear accelerator (615 keV/q), this technique has been extended to allow particle velocities up to 4.2 km/sec, well above the ~2 km/sec threshold for impact ionization. Time-of-flight mass spectra obtained from the impact of ~0.8 µm diameter single charged ice grains using the Hypervelocity Ice Grain Impact Mass Spectrometer following impact have now been obtained. This technique replicates the hypervelocity impact of organic-laden submicron ice grains for in-situ mass spectrometric characterization. It is found that amino acids entrained in ice grains can be detected intact after impact at speeds up to 4.2 km/s and that the presence of salt reduces their detectability, providing an important benchmark for future missions to ocean worlds in our solar system.[5]

Acknowledgments: This work was supported by the Air Force Office of Scientific Research award MURI-22 FA9550-22-1-0199.

References

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Spectroscopy and dynamics of cold molecular ions

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In the interstellar medium (ISM), typical temperatures range from 10 to 100 K, and low-temperature laboratory measurements are essential for identifying spectroscopic fingerprints observed in astronomical data [1]. At such temperatures, most molecular vibrations relax into their ground states, effectively eliminating hot bands. Nevertheless, spectra can remain complex due to resonant structures in the photoexcited states.

Another area of growing interest is the study of biochromophores - molecular systems responsible for light harvesting in photoactive proteins. Here, low temperatures are essential for determining conformational preferences, enabling the discovery of exotic states such as dipole-bound states, and supporting fluorescence studies in the gas phase. Importantly, cold conditions provide a well-defined starting point for laser-based spectroscopy and offer a robust platform for theoretical benchmarking [2].

Over the past decades, significant progress has been made in studying cold molecular ions using ion traps and storage rings [3–7]. This presentation will highlight recent spectroscopic and dynamical studies of cold ions relevant to both the ISM and biochromophore systems, with a particular focus on the SAPHIRA storage ring, where an efficient cooling scheme enables measurements at high repetition rates.

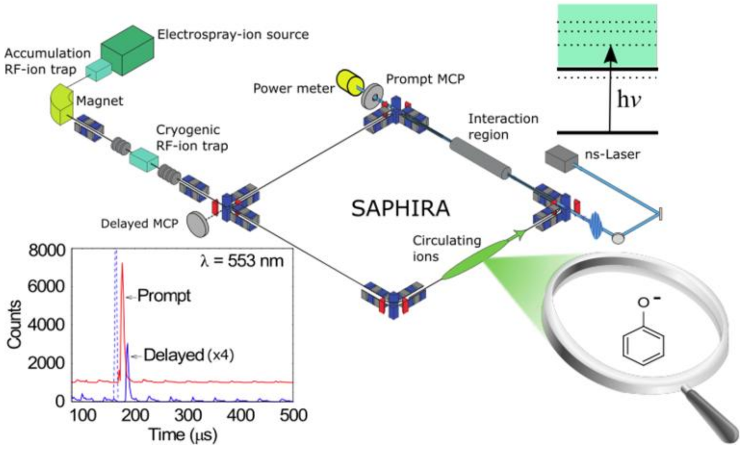

Figure 1: SAPHIRA ion-storage ring with two RF-ion traps prior to injection into the ring [7]. One is for accumulation of ions from DC-ion sources and the other for collisional cooling (He-buffer gas, 6 K). Two particle detectors are used to monitor prompt and delayed laser-induced action.

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Fast and slow fullerene collisions at DESIREE

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The advent of cryogenic ion storage rings and traps has led to a rapid development of new experimental capabilities, particularly related to the studies of complex molecular ions. Due to their large number of internal degrees of freedom and high heat capacities, complex molecular ions can remain in highly excited states long after their formation, e.g., in ion sources, necessitating long storage lifetimes of seconds or longer in order to study their cooling dynamics and reaction mechanisms at low excitation energies.

DESIREE, the Double ElectroStatic Ion Ring ExpEriment, at Stockholm University in unique amongst the cryogenic ion storage ring facilities in operating with twin rings for performing merged beam studies between beams of oppositely charged ions [1]. These have been used to successfully study mutual neutralization (MN) reactions between atomic cations and anions at collision energies down to about 100 meV for the last few years, and more recently for reactions involving small molecular ions.

In my talk I will present the first results of MN measurements at DESIREE involving complex molecular ions, specifically the reaction $C_{60}^{+} + C_{60}^{-} \rightarrow C_{60}^{*} + C_{60}$ at low collision energies [2]. We have used these measurements to develop a modeling framework for describing MN reactions between ions in interstellar environments such as molecular clouds, where large carbonaceous molecules, including fullerenes, are expected to be important charge carriers, and to derive absolute reaction cross sections and rate coefficients for astrophysical modeling [2].

I will also present work done on studying the stability of fullerene fragments formed in fast collision with atomic targets [3]. In these experiments, C_{60}^{-} ions collided with He at an energy in the center-of-mass frame of 166 eV, leading to the formation of C_{59}^{-} in prompt knockout processes. These fragments were stored in one of the DESIREE ion storage rings where we studied the cooling dynamics and survivability of these highly reactive radicals as a function of time under conditions similar to those found in dense molecular clouds. Our findings clearly show that these types of energetic collisions can lead to the formation of stable, reactive products in regions of the interstellar medium that are bombarded by stellar winds or shockwaves, e.g., from supernovae [3].

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Electron-Ion Recombination at the Cryogenic Storage Ring

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Recombination of atomic and molecular ions with free electrons are fundamental collision processes that are relevant in astrophysical environments. In atomic plasmas, the charge state distribution is governed by competing ionization and recombination processes, and thus the plasma modeling requires reliable recombination data. Small molecular ions dissociate upon electron recombination, which is an important process for the neutralization and destruction of such molecules in the cold interstellar medium.

The electrostatic Cryogenic Storage Ring (CSR) [1], located at the Max Planck Institute for Nuclear Physics in Heidelberg, Germany, offers unique possibilities to study electron recombination of low-charged heavy atomic ions as well as cold molecular ions [2-4]. The CSR provides a cryogenic environment with vacuum chamber temperatures < 10 K, resulting in an extremely low residual gas density. This enables storage of ion beams for up to several hundred seconds, which in turn allows many molecular ion species to radiatively relax to their lowest vibrational and rotational ground states in the < 10 K blackbody radiation field of the CSR [5,6]. In one section of the storage ring, a nearly mono-energetic electron beam is collinearly overlapped with the stored ion beam. This setup enables the investigation of electron-ion collisions at center-of-mass collision energies ranging from several tens of eV down to the meV range.

Here, recent electron-ion recombination experiments conducted at the CSR will be reviewed, including dielectronic recombination of low-charged heavy atomic ions and dissociative recombination of astrophysically relevant molecular ions. Special emphasis will be placed on electron collisions with fullerene ions, which exhibit strongly different reaction dynamics compared to small molecular ions.

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Interatomic/molecular Coulombic decay (ICD): Toward exploring vibrational ICD in hydrated anion beams

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Energy and charge transfer are the primary quantum-mechanical processes that govern a wide range of physical, chemical, and biological phenomena in nature. In contrast to isolated atoms/molecules, where electron dynamics occur solely through intra-atomic/molecular processes, weakly bound systems—such as hydrogen-bonded clusters—offer a unique environment in which local excitations can interact with neighboring molecules, leading to efficient interatomic/molecular decay processes mediated by energy and charge transfer, such as *Intermolecular Coulombic Decay* (ICD) [1]. ICD often leads to the emission of electrons with low kinetic energy, typically in the range of 0 to 20 eV, depending on the excitation energy and the nature of the neighboring site involved in the decay—neutral, excited, cationic, or anionic. These slow electrons can be implicated in nearly all fundamental physico-chemical phenomena underlying radiation and atmospheric chemistry. For instance, they have been proven to induce irreparable damage in living tissues such as DNA double-strand breaks [2]. Since its discovery, ICD and related processes have been observed in various weakly bound systems, ranging from rare gas clusters to bio-relevant systems [1, 3]. Over the past few years, I have been studying ICD in electronically excited pure and doped helium nanodroplets using ion-electron coincidence imaging [3]. More recently, my focus has shifted toward exploring a novel ICD process called—*vibrational* ICD (see figure 1 and [4])— in vibrationally excited hydrated anions using electron-neutral coincidence spectroscopy. In this contribution, I will report on newly ICD processes observed in helium nanodroplets, emphasizing the unique insights they offer for an efficient energy and charge transfer in a superfluid quantum nanosystem. I will also outline the necessary steps already taken toward the first experimental proof of vibrational ICD in hydrated $(H_2O\text{-}O_2)^-$ anions beam irradiated with mid-IR laser radiation.

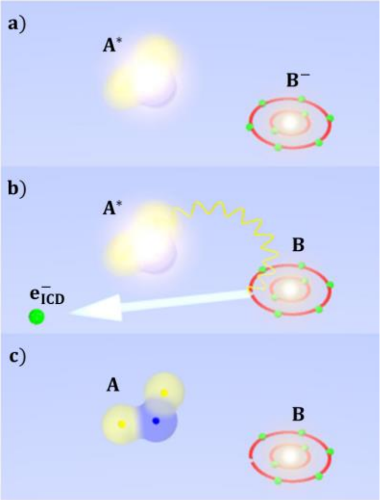

Figure 1: A possible vibrationnal ICD process occurs on a low-electron-affinity anion (B^-) attached to a vibrationnaly excited molecule A* (e.g. H_2O^*), leading to the detachement of the elctron bound to B. The detached electron from the anion is refferred to as a vibrationnal ICD electron (Adapted from [4]).

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Peptide Bond Formation in Amino Acid Clusters

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Intra-cluster bond formation (ICBF) is a process in which, following excitation of a loosely bound molecular cluster, a covalent bond is formed between neighbouring molecules within the cluster. This mechanism has been suggested as an important route towards the abiotic formation of large complex organic molecules with relevance both to astro-chemistry and towards the origin of life. Our group in recent years has thoroughly studied peptide bond formation (PBF) in amino acid clusters following different modes of excitation: low energy collision induced dissociation in a commercial mass spectrometer, high energy collision induced dissociation in the ARIBE facility in GANIL and following VUV absorption in the SOLEIL synchrotron, In our talk we will review our results including conclusive proof of PBF, the observation of strong chiral effects in some cases, specificity in PBF, and the use of MS^N to follow reaction pathways step by step. We will also show progress towards inhouse measurements towards ICBF following VUV absorption.

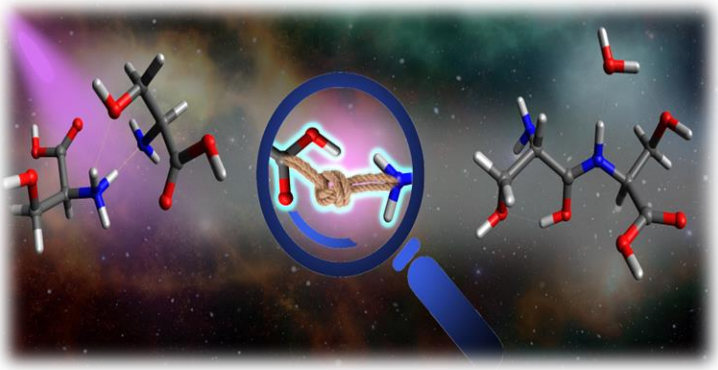

Figure 1: Illustration of PBF following VUV excitation of a protonated serine dipeptide

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The PAH Model: Current Status and Perspectives

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Proposed in the mid-1980s, the PAH model has since driven extensive experimental, theoretical, and modeling efforts aimed at understanding aromatic infrared band (AIB) spectra [1,2] and assessing the role of polycyclic aromatic hydrocarbons (PAHs) in shaping the physical and chemical conditions of star- and planet-forming regions [3]. Upon interaction with far-ultraviolet (FUV) photons, PAHs emit AIBs, contribute to gas heating, and may trigger or enhance chemical reactions. Quantifying these effects requires a detailed understanding of processes such as ionization, photodissociation, isomerization, and radiative cooling [4].

Despite substantial progress, the identification of individual PAH species in space remains highly limited. A significant gap persists between the small-to-medium PAHs (up to $C_{24}H_{11}CN$ [5]) detected by radio astronomy and the larger fullerenes (C_{60}, C_{60}^+) observed in the mid- and near-infrared [6,7]. Today, unique observational opportunities are available to address these challenges — notably through the high-resolution capabilities of the James Webb Space Telescope (JWST) [8,9], as well as sample-return missions such as Hayabusa2, which enable direct analysis of early solar system materials [10,11].

In this talk, I will provide an overview of the current status of the PAH model, highlighting both its key achievements and unresolved questions. I will discuss the challenges of integrating laboratory studies, astronomical observations, and theoretical approaches, and outline promising directions for future research. In particular, I will emphasize how cross-disciplinary efforts and new-generation laboratory facilities can help bridge the gap between model predictions and observational constraints, especially regarding PAH formation and survival in astrophysical environments.

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State manipulations of negative ions during storage

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Negative ions are unique quantum systems since the outermost electron experiences a $1/r^4$ potential due to an induced dipole, rather than the 1/r Coulomb potential characteristic of neutral atoms and positive ions. This leads to very small binding energies, significantly limiting the number of bound states. As a matter of fact, there are only five elements known to possess excited states with opposite parity to the ground state. As a consequence, the standard spectroscopic techniques used to study bound-bound transitions have generally not been applicable to negative ions.

In this presentation, it will be shown how the unique properties of a cryogenic ion storage ring can be used to circumvent this limitation in negative ion spectroscopy. We have previously successfully depleted the population in all excited states in a negative ion by applying a laser beam over 30 seconds [1]. We have now taken this one step further by repopulating a selected excited state using a narrow bandwidth cw laser, despite the fact that the transition was E1 forbidden. With this method, we managed to conduct high resolution studies of isotope shifts and hyperfine structures in Sn^-. This technique will open-up completely new possibilities for spectroscopy of negative ions.

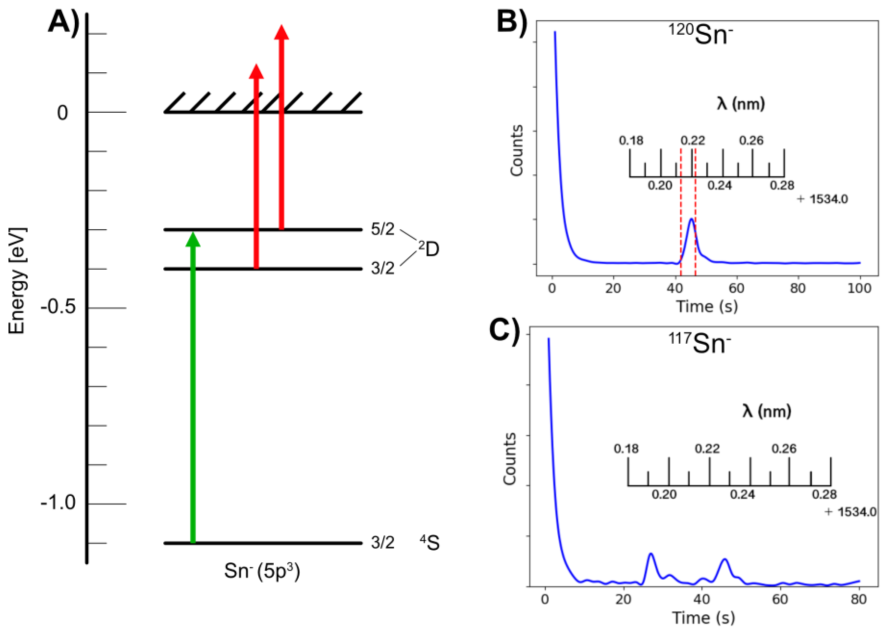

Figure 1: A) The energy level diagram of Sn^-. The red arrows represent a broadband IR laser and the green arrow represents a narrow bandwidth tunable laser around 1534 nm. **B)** and **C)** Photodetachment singal of $^{120}Sn^-$ and $^{117}Sn^-$ as a function of time after injection into the ring. The scale in the inset shows the time interval and tuning range of the tunable laser over the $5p^3\ ^4S_{3/2} \rightarrow 5p^3\ ^2D_{5/2}$ transition.

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Ion-neutral Merged-Beams Experiments at the CSR

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Reactions between neutral atoms and molecular ions play an important role for the formation of molecules in interstellar space, where they act as gateway processes for the build-up of more complex species. To perform meaningful ion-atom collision experiments, both reactants have to be prepared in defined quantum states. To this end we have constructed an ion-neutral merged-beams experiment at the Cryogenic Storage Ring (CSR) [1]. Fast beams of neutral atoms are produced by photodetachment of negative ions, before they are superimposed on a beam of cold molecular ions stored inside the CSR. The charged reaction products are recorded by various single particle detectors inside the CSR, or in a dedicated extraction beamline. Here, we will present absolute rate coefficient measurements for reactions of hydrogen molecular ions (HD^+, H_3^+) and C atoms [2,3], which are important for the onset of organic chemistry in interstellar clouds. Furthermore, we will report on recent studies of reactions between HeH^+ ions and D atoms that shed light on the efficiency of one of the first molecular reactions in the early universe [4].

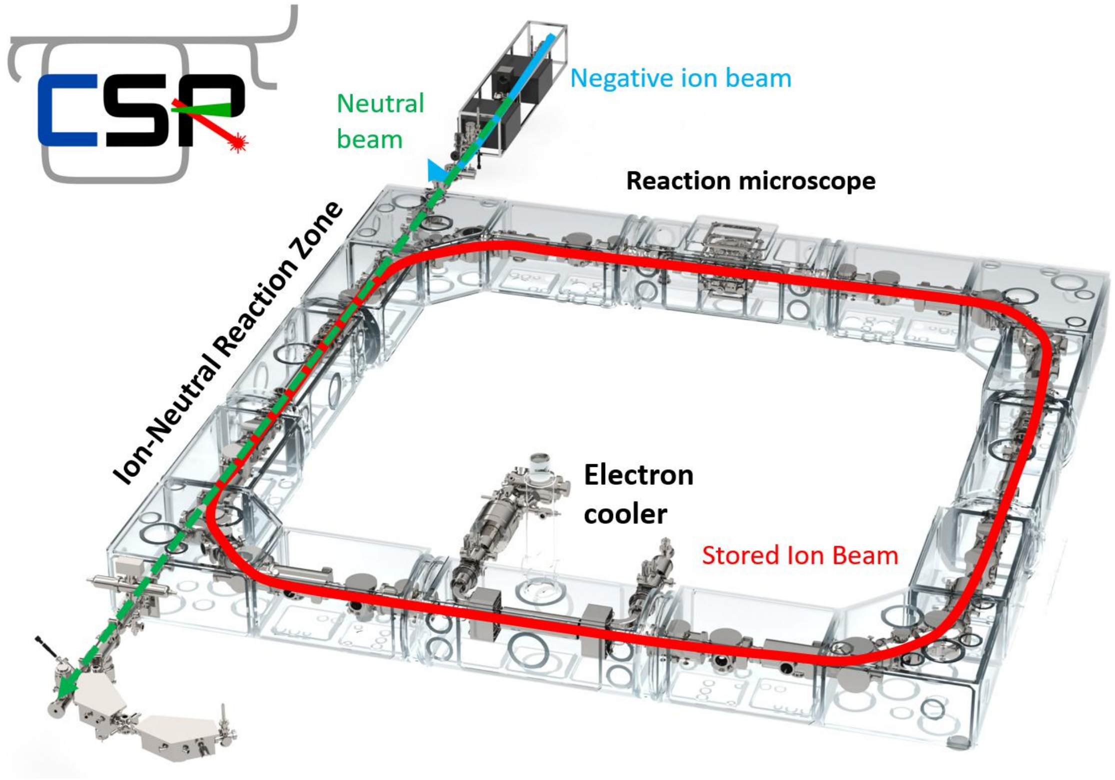

Figure 1: Schematic overview of the Cryogenic Storage Ring (CSR) with major experimental sections.

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The 10th International workshop on
ELECTROSTATIC STORAGE DEVICES
ESD 10

Contributed talks

The not even just odd even-odd effect in the cooling of gold clusters

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Spontaneous and photo-induced decays of anionic gold clusters, Au_N^-, with sizes N = 2 – 13 and 15 have been measured in the cryogenic ring DESIREE [1]. The size-selected clusters, produced in a cesium sputter source, were stored between 0.1 and 100 s. Radiative cooling is observed for all cluster sizes apart for the dimer. For N = 6 – 13 the cooling times have a strong odd-even oscillation with an amplitude that decrease with cluster size. Strikingly, the even N clusters have the faster cooling, in a complete reversal of the pattern seen for the cationic gold cluster cooling previously [2]. Another striking difference is the absolute cooling rate which is orders of magnitude slower for anions than for cations. The non-radiating dimer was observed to decay by electron emission in parallel to neutral atom emission at long times, implying a breakdown of the Born-Oppenheimer approximation. The behavior for the gold dimer anion is almost identical to the behavior seen for the copper and silver dimers [3], and contrasts strongly with decays of dimers of silicon and carbon [4,5,6].

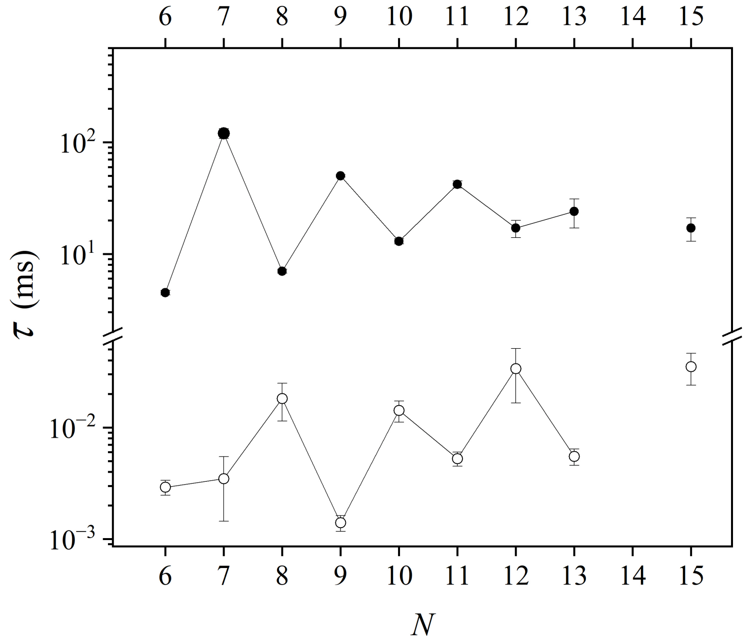

Figure 1: Cooling time constants for gold anionic and cationic clusters (filled and open circles, respectively).

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Minute-scale Storage of Multiply Charged Helium Nanodroplets inside an Electrostatic Ion Beam Trap

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Abstract

A Multi-Reflectron Time-of-Flight device (MR-ToF), initially developed in a collaboration between the TU Darmstadt and the University of Greifswald [1], is utilized to trap multiply charged helium nanodroplets (HNDs) for up to the minute range, using only electrostatic fields. Proof-of-principle measurements have shown an efficient storage with multiple thousands of revolutions of the droplets inside the device. The storage time depends strongly on the pressure in the MR-ToF vacuum chamber and has been systematically studied.

In combination with a laser, this setup provides a powerful tool to probe not only weak transitions of dopants inside the droplets, but also provides access to time-resolved processes. Future plans include Blackbody Infrared Radiative Decay (BIRD) measurements, utilizing the vacuum chamber of the device as a blackbody emitter. Excited intermolecular vibrations of water clusters embedded inside the HNDs would boil off the surrounding helium, until the droplet can no longer be detected due to insufficient kinetic energy.

Furthermore, the implementation of a so-called pick-up electrode is planned in order to study the change in charge, mass, and energy of the droplets over time. This method provides a new approach for nano-calorimetry, opening up frontiers for thermodynamic studies at the nanoscale. The development of image charge detection for multiply charged HNDs is motivated by the pioneering measurements of Hanozin et al. [2], in which significant charge loss and Rayleigh decay of aqueous droplets were observed.

This research was funded in whole or in part by the Austrian Science Fund (FWF) [10.55776/I6221, 10.55776/V1035].

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Freezing Out Structural Effects: Gas-Phase Fluorescence from Rhodamine Homodimers and Trimers at Cryogenic Temperatures

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Studying electronic communication between light-absorbers is vital to understand energy transport processes, among them photosynthesis, UV-induced DNA damage and FRET. In FRET, for instance, the rate of energy transfer between a donor and acceptor dye varies with the inter-dye separation, leading to the application of FRET to study biomolecular structure. The microenvironment such as nearby charges, however, affects the dye photophysics, which calls for fundamental studies on isolated systems and at low temperatures where spectral signatures stand out most clearly. [1-3] Here, we study the intrinsic photophysics of homodimers and homotrimers of rhodamine dyes linked together by rigid alkyne spacers at cryogenic temperatures (100 K). Fluorescence from gaseous ions is collected at the LUNA2 setup in Aarhus where mass-selected ions are stored in a cylindrical ion trap. We measure multiple absorption bands from homodimers and trimers of chemically identical cold rhodamine-575 dyes, clearly indicating that multiple conformers are being interrogated. Surprisingly, we measure large redshifts in the emission upon cooling, in contrast with an expected blueshift upon lowering the temperature. This measured Stark shift indicates geometries where two dyes are close together, which is supported by DFT calculations. These findings push our understanding of interactions between dyes at cold temperatures further and help complete our understanding of the fundamental photophysics that underlie such systems, of relevance to the use of cryo-FRET for biomolecules.

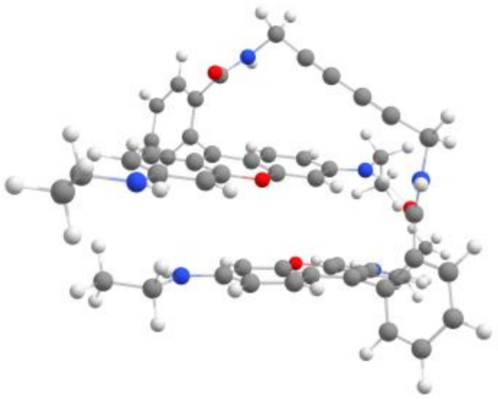

Figure 1: Computed structure of rhodamine-575 dimer, showing stacked configuration

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Development of an X-ray photoelectron spectrometer to investigate chirality in biomolecular ions.

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One of the main contemporary questions in biophysical research is the influence of chirality on the interactions between early-life molecules [1]. Despite the small chemical differences between mirror-imaged molecules (enantiomers), their biological functions can differ greatly [2]. Different enantiomers can be recognized by their circular dichroic response as an asymmetry in forward-backward photoelectron emission [3-5]. Moreover, enantio-sensitive electronic dynamics have recently been observed in a small biomolecule employing its dichroic footprint through electronic beating between Rydberg final states [6]. These results raise the desire to extend similar dichroism-based studies to systems of greater biological significance.

Developing the experiment towards larger and more fragile gas-phase biomolecules requires a gentle isolation and transfer into vacuum, e.g. in an ionic state using electrospray ionization (ESI) in combination with ion mass filtering techniques. A key challenge in developing VUV and X-ray spectroscopic techniques, as well as electron momentum imaging for biomolecular ions, lies in achieving sufficiently high sample densities. The maximum ionic sample beam density is typically five orders of magnitude lower than that of neutral beams, resulting in an ion sample density that is around the same order of magnitude as the residual gas density in ultra-high vacuum environments [7]. Efforts towards developing X-ray photoelectron spectrometers in crossed- or merged-beam geometries exist [6-11]. However, their inherent need for high ion current poses challenges to their combination with the typically lower current from ESI sources. Simultaneously, experiments using radiofrequency (RF) ion traps have been successfully developed to measure ion product mass spectra upon X-ray and VUV ionization and excitation [12,13]. Collecting the photoelectron products using such RF traps is hindered by the large difference in particle mass over charge and therefore the required RF waveforms of conventional trap designs. Due to the complex excitation and dissociation processes occurring between photon interaction and ion fragment formation, the observables available to date often cannot be clearly attributed to specific electronic processes—further highlighting the importance of photoelectron energy and/or momentum measurements.

In this work, we investigate alternative spectrometer designs aiming at an increased ion-photon overlap region from which (photo-) electrons can be extracted and their kinetic energy subsequently measured. We will present a conceptual design that combines a linear ion trap oriented colinearly with an adapted magnetic bottle design to guide the electrons to energy-analyzing detectors. The measurement of the photoelectron kinetic energy from gas-phase biomolecules would provide access to a plethora of investigations on their electronic structure dynamics. The photoelectron detection in the presented design will specifically be optimized for the measurement of the forward-backward emission asymmetry, to enable circular dichroism studies in biologically relevant chiral systems.

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Velocity Map Imaging with No Spherical Aberrations

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The goal of Photoelectron Spectroscopy (PES) is to determine the kinetic energy of electrons emitted from molecules following ionization, which can in turn be used to infer their binding energies. A widely used technique for this purpose is Velocity Map Imaging (VMI), which employs electrostatic lensing to project the initial velocities of emitted electrons onto a position-sensitive detector. This approach effectively handles a broad initial spatial distribution, though conventional implementations are limited by spherical aberrations.

In this work, we present an analytical theory of spherical-aberration-free VMI [1] and demonstrate its implementation on the Reaction Microscope (ReMi) recently installed in the Cryogenic Storage Ring (CSR) at the Max Planck Institute for Nuclear Physics in Heidelberg, Germany. We will present new experimental results from operating the CSR-ReMi in VMI mode and discuss the unique capabilities this enables, including the potential to measure kinetic energy distributions of thermionically emitted electrons. In addition, we will describe an alternative implementation of the theory using a single curved electrode.

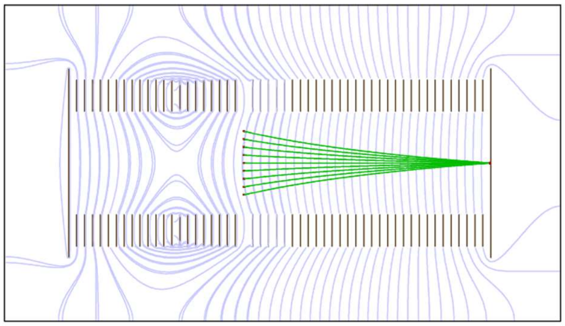

Figure: SIMION simulation of the CSR-ReMi in VMI mode. The green trajectories correspond to a beam of electrons with width of 80 mm on the direction perpendicular to the main axis of the spectrometer. All electrons have the same initial kinetic energy, and therefore focused to a point on the detector.

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A new generation of compact transportable cryogenic electrostatic storage device: Polar Mini-Ring

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In the quest for innovative tools to probe the fundamental processes governing the evolution of complex molecular systems in the interstellar medium (ISM), we are in the final stage of assembling Polar Mini-Ring, a compact, transportable and cryogenic electrostatic ion storage ring (ESR) designed to be interfaced with the tunable vacuum ultraviolet (VUV) light source at SOLEIL synchrotron radiation on DESIRS beamline [1]—an unprecedented challenge (Figure 1).

This setup will provide unique measurements of relaxation rates (dissociation, radiative cooling, and potentially isomerization) for systems such as Polycylique Aromatic Hydrocarbons (PAH) cations and their derivatives exposed to VUV photons of variable energy. Our current knowledge of PAH dissociation rates relies on heterogeneous data from different experimental setups (time-of-flight or ion traps), each probing different ranges of internal energy over distinct timescales. Extrapolating between these datasets reveals significant discrepancies. An electrostatic storage ring such as Polar Mini-Ring will resolve this issue thanks to its broad temporal range, spanning from microseconds to minutes.

At low internal energies, dissociation competes with radiative cooling, which for PAH cations can occur via recurrent fluorescence (RF) on the millisecond timescale and infrared (IR) emission over several seconds [2,3]. To accurately quantify the rates of these processes as a function of internal energy slightly above the dissociation limit, it is crucial to work in a single-photon absorption regime, tunable between 7 and 14 eV, starting from cooled ions.

The DESIRS beamline is therefore particularly well suited for irradiating PAH cations, which will be stored and cooled in Polar Mini-Ring [1]. The construction of a double-chopping device will allow the temporal structuring of the DESIRS VUV beam to match the ion storage timing in Polar Mini-Ring and generate irradiation sequences with variable duty cycles to achieve our scientific objectives.

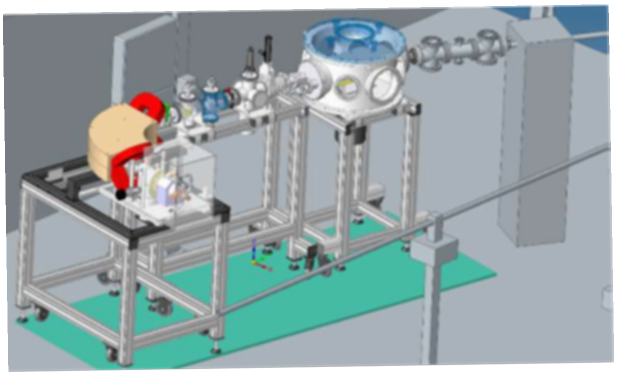

Figure 1: Implementation scheme of the Polar Mini-Ring and its dedicated ion beamline: DESIRS at SOLEIL Synchrotron.

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Electron Transfer to Ar$^+$ studied with a Reaction Microscope in a Cryogenic Storage Ring

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The CSR-ReMi, the in-ring reaction microscope at the Cryogenic Storage Ring CSR [1], was used to study interactions between a 30 keV Ar$^+$ projectile and various neutral gas targets (Ar, Ne, He) provided by a supersonic expansion source. The recoil ions were momentum-analyzed and measured in coincidence with the neutralized projectiles in the collision. The projectile scattering angle was determined from the recoil ion transverse momentum.

Fig. 1 a) shows the Q value (difference of initial- and final-state energy) for 30 keV Ar$^+$ + Ar interactions, obtained from the beam energy and the longitudinal recoil-ion momentum component. At Q = 0 eV a target electron is transferred from the target ground state to the projectile ground state. At the peak at Q = -13 eV the electron is transferred into various excited projectile states. The vertical lines indicate the expected transition energies according to the NIST database. Transfer and target excitation into various states is identified by the peak at Q = -33 eV .

Fig. 1 b) shows the scattering angle versus the Q value for the 30 keV Ar$^+$+He system. The transitions are shifted by -9 eV because of the different ionization thresholds of argon and helium. Therefore, electron transfer into projectile ground state (1) is at Q = -9 eV and into excited projectile states (2) at Q = -21 eV. The higher-lying excited states (with larger $|Q|$) only contribute for higher scattering angles. This is expected, since transitions with a larger $|Q|$ usually happen at smaller impact parameters b, which leads to higher transverse momenta and, consequently, to larger scattering angles. No target transfer excitation was observed for helium or neon targets. At Q = -3 eV an additional small peak (3) is visible. This peak corresponds to electron transfer from the target ground state into initially metastable Ar$^+$ projectile states. The narrow angular width of the metastable line compared to capture to the ground state is remarkable. The presence of metastable Ar$^+$ ions circulating in the CSR was confirmed by a lifetime measurement.

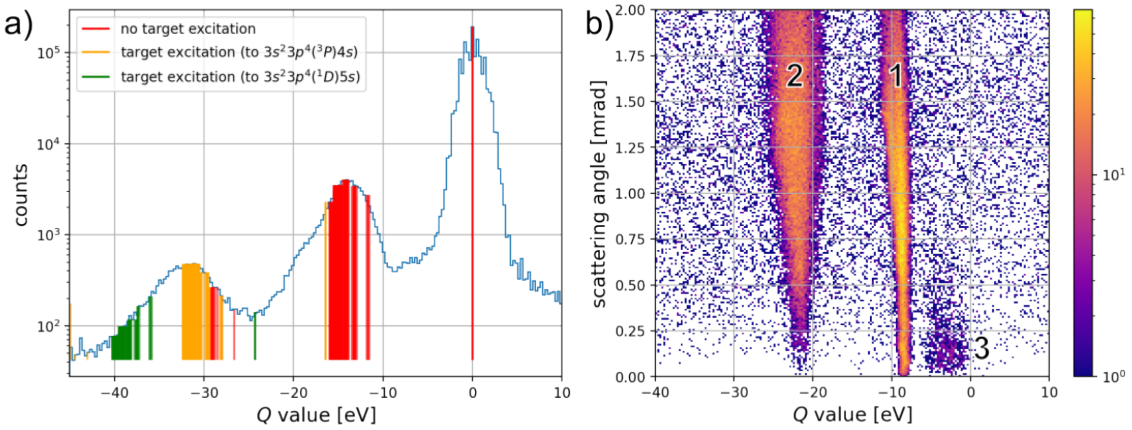

Figure 1: a) Q value for electron transfer from Ar target to Ar$^+$ projectile with 30 keV beam energy and b) Q value vs. scattering angle with He target.

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Radiative cooling of the deprotonated cyan fluorescent protein chromophore anion

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An electrospray ion source [1] has been coupled to a cryogenic electrostatic ion-beam storage ring [2] to enable experimental studies of the fundamental properties of biomolecular ions and their reactions in the gas phase on longer timescales than with previous instruments. Using this equipment, we have measured the vibrational radiative cooling rate of the deprotonated anion of the chromophore of the cyan fluorescent protein (Fig. 1), a color-shifted mutant of the iconic green fluorescent protein [3]. Time-resolved dissociation rates of collisionally activated ions are first measured to benchmark a model of the dissociation rate coefficient. Storage time-dependent laser-induced dissociation rates are then measured to probe the evolution of the internal energy distribution of the stored ion ensemble. We find that significant heating of the electrosprayed ions occurs upon their extraction from the ion source, and that the radiative cooling rate is consistent with the prediction of a simple harmonic cascade (SHC) model of vibrational relaxation, as shown in Fig. 1.

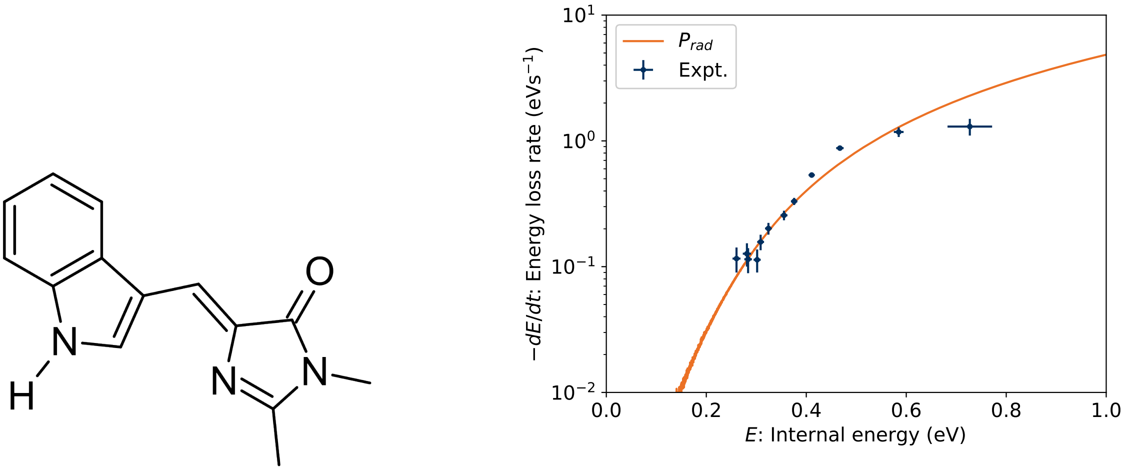

Figure 1: Left: Structure of the cyan fluorescent protein chromophore. Right: Measured energy loss rate of CFP chromophore anions compared to the total radiative power P_{rad} from SHC model.

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High-sensitivity spectroscopy of radioactive ions within a ConeTrap

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Substantial effort in the field of nuclear laser spectroscopy is presently directed towards the (future) measurement of nuclear charge radii in proton-emitting nuclear systems. The behaviour of this bulk property in such exotic nuclei is an open theoretical challenge but severe experimental challenges are encountered in attempting the spectroscopy (and measurements of such radii remain elusive). At JYFL, in Jyväskylä, Finland the laser-IGISOL collaboration, has developed spectroscopy with which we intend to make three key measurements (critical for an accurate interpretation of the radial trend in such systems). Measurement of three systems, ^{53m}Fe, ^{53m}Co and ^{52m}Fe, provides a unique opportunity to resolve the effect of being proton-unbound. Technical upgrades to the laser spectroscopy station at the IGISOL have enabled our collaboration to perform spectroscopy in the deep UV and make new measurements on radioactive species in Fe and Co ions. Successful spectroscopy of the three cases cited above (53mFe, 53mCo and 52mFe) however demands a further increase in experimental sensitivity, by at least one order of magnitude. At the IGISOL, collinear laser spectroscopy coupled with optical pumping has proved a highly successful technique, facilitating spectroscopy on manganese, niobium, yttrium and even the doubly charged yttrium ion [1-3]. We intend to couple this technique with a new electrostatic ion trap (the ConeTrap) and exploit the enhanced sensitivity to make the desired measurements. The Manchester developed ConeTrap, pioneered by Schmidt et al. [4], is an electrostatic device that is especially suitable for deployment at the IGISOL [5]. The devices have been shown to successfully contain close to 10^5 ions for time periods exceeding 100 ms (many times the atomic excitation and de-excitation lifetimes) and their injection is well matched to the ion plumes released from the IGISOL cooler-buncher. While successfully demonstrating the device was operational, tests showed that only a physically larger trap with matched injection and extraction ion optics would provide the desired spectroscopic performance. Such a trap, developed on a bespoke Manchester testbed, has now been installed at IGISOL. The upgrades, forthcoming commissioning of the device, as well as future spectroscopic opportunities will be presented.

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Probing the balance between dissociation and radiative cooling in interstellar Polycyclic Aromatic Hydrocarbon cations

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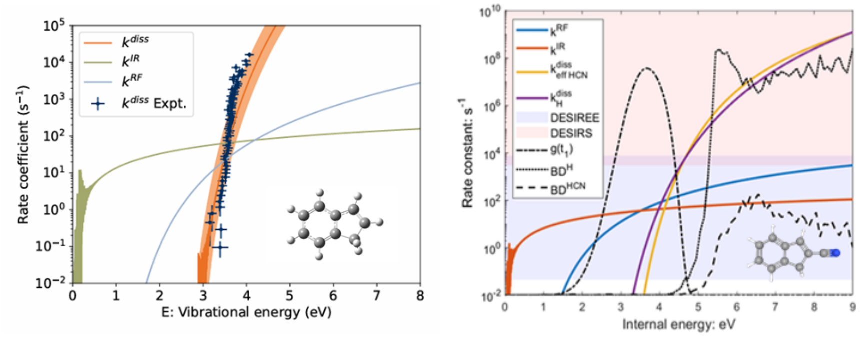
Since the first detection of a polycyclic aromatic hydrocarbon (PAH) in the cold molecular cloud TMC-1, the number of identified PAHs in space has steadily grown. Yet, current astrochemical models—while successful in predicting linear hydrocarbon abundances—underestimate PAH concentrations by several orders of magnitude. One proposed reason for this discrepancy is the omission of radiative cooling processes, which may stabilize PAHs and prevent their destruction through pathways included in the models. We present a series of studies studying the dissociation and radiative cooling (RC) dynamics of indene (Ind^+), indenyl ($[In\text{-}H]^+$) and 2-cyanoindene ($2CNI^+$) monocations, using one of the cryogenic electrostatic ion-beam storage rings at DESIREE.



(a) **(b)**

Figure 1: Dissociation and radiative cooling rate coefficients of (a) Indene and (b) 2-Cyano-indene

Indene and cyanoindene form a unique target pair, as they are the only PAHs to date where both the pristine and cyano-substituted forms have been. With the first study into indene [1], we employ the recently upgraded imaging detector system in DESIREE to obtain time resolved kinetic energy release distributions (KERD) of hydrogen loss from Ind^+. The short deadtime of the detector allows for a turn by turn analysis of the KERD, allowing for an accurate measurement of the dissociation rate coefficient and establishing that infrared cooling is the dominant RC process that competes with dissociation. The second study with dehydrogenated indene, i.e. indenyl [2], highlights the use of molecular dynamic simulations to help analyse the lifetime measurements, revealing the importance of recurrent fluorescence (RF) in closed shell PAHs for the first time. We find that RF stabilizes cations formed with energies of up to 2 eV above their dissociation threshold. The final study with cyano-indene[3], reports on the results from DESIREE and accompanying experiments performed using the synchrotron radiation source at SOLEIL. The storage ring experiments quantify the balance between fragmentation and radiative cooling, while the synchrotron experiments characterize dissociation channels by studying its vacuum ultraviolet-induced photo-dissociation. By developing a statistical model that explains both experiments, a self-consistent set of rate coefficients is obtained, that describe the main features of the dynamics of $2CNI^+$, valid across the μs-s time range, making them suitable for incorporation into astrochemical models.

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Planar electrostatic ion traps for mass spectrometry

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Electrostatic ion traps are convenient instruments in mass spectrometry because of the inherent independence of ion trajectories of the mass-to-charge ratio (m/z) under the same acceleration voltage. Therefore, the traps may be optimized for minimal ion-optical aberrations in a wide m/z range and be used to analyze, in one go, a complex mixture of ions. Ions of different species are distinguished by the mass dependence of their time of flight (ToF) as $T \propto \sqrt{m/z}$, therefore providing the grounds for time-of-flight (ToF MS), Fourier-transform (FT MS), and multi-reflection (MR MS) mass spectrometry.

A special type of ion trap uses planar ion mirrors which consist of several elongated electrodes congregated in two parallel planes on both sides of a plane of symmetry, see Fig 1. The electrodes are biased in both polarities to form focusing and reflecting electrostatic fields. Two similar mirrors facing each other make ions repetitively oscillate with multiple reflections in the first and the second mirrors alternatingly while slowly drifting in the direction of mirror elongation.

Discussed are mathematical and computational methods to construct planar electrostatic ion traps with the property of oscillatory isochronism, which means that the oscillation periods of same-mass ions are substantially equal regardless of the energy, spatial, and angular spreads. Methods of drift control and instrument fine-tuning are considered.

The multi-reflection ASTRAL mass analyzer is an example of an open electrostatic ion trap in which analyte ions are trapped for circa 50 reflections, during which they make around 35 m flight path and finally impinge on a time-resolving detector [1]. The principal ion-optical aberrations, spatial and temporal, are compensated, which allows the mass resolving power above 100,000 at the repetition rate as high as 250 broad-range mass spectra per second. The ASTRAL mass analyzer is currently used for analysis of complex biological samples [2].

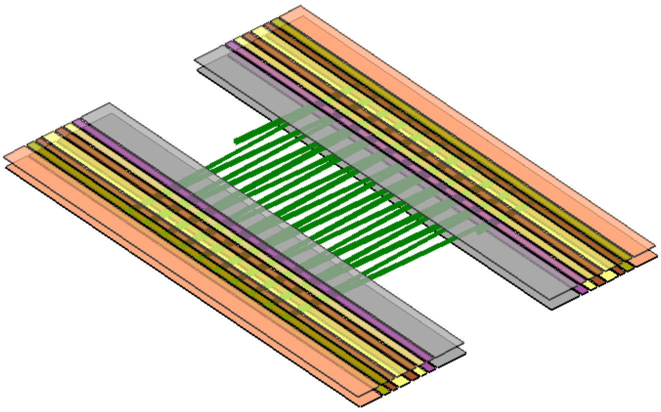

Figure 1: Example of a multireflection planar electrostatic ion trap

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Internal decay processes in homonuclear dimer anions using trapped ions in an EIBT and electron spectrometer

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Understanding internal dynamics and decay processes is crucial in gas-phase molecular anion studies. Here we investigated the long-timescale energy dynamics of Ag_2^- and Cu_2^- dimer anions. The anions are generated in a Cesium sputter source and accelerated to 4.2 keV. They are stored in an Electrostatic Ion Beam Trap (EIBT) for few seconds. A laser-assisted velocity map imaging (VMI) spectrometer records ejected electrons, while a separate detector captures neutral counterparts. The photo electron spectrum (PES) was accumulated along the trapping time, reflecting the internal energy dynamics of the ions in the trap [1]. Experiments were conducted using 635 nm and 380 nm lasers. The PES show distributions previously unreported. We simulated the PES by computing Franck-Condon factors for all allowed transitions from the Ag_2^- ground electronic state to the Ag_2 ground electronic state. Fig.1(left) shows PES for Ag_2^- at different storage times with a 635 nm laser, while Fig.1(right) presents the simulated spectra. The simulations explain the spectral shape and indicate that faster decaying transitions originate from higher rovibrational states.

Our results are compared with recent observations by Anderson et al. [2,3] who reported spontaneous decay of hot Ag_2^- and Cu_2^- dimer anions in the cryogenic DESIREE setup via fragmentation and electron emission. They attribute electron emission to vertical autodetachment (VAD) and fragmentation to tunnelling with the former showing a deviation from the Boron-Oppenheimer approximation. Here we measure the dynamics of the internal energy distributions that are below the VAD energy limit and see a decay (cooling) within the negative dimers. This may be explained by induced dipole transitions for such highly excited state of many electrons system or by a relatively large electric quadruple transition.

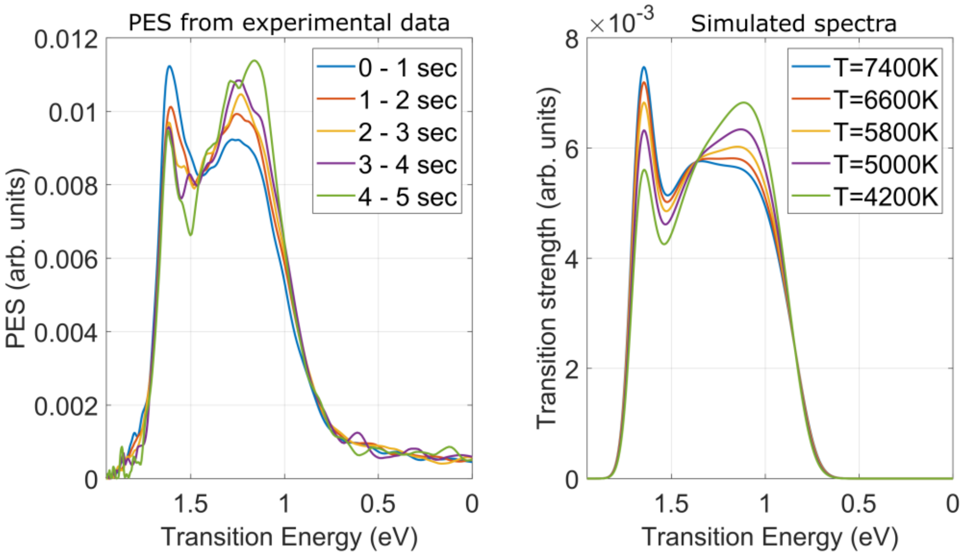

Figure 1: Experimental (left) and simulated spectra(right) for Ag_2^- . Spectra normalized for the area

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State-Selective Mutual Neutralization between Ba^+ and Au^- Ions

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Mutual neutralization (MN) is a fundamental process in which a positive and a negative ion interact, leading to electron transfer and the formation of two neutral products. In this work, we present MN studies between barium (Ba^+) and gold ions (Au^-) at the DESIREE (Double ElectroStatic Ion Ring Experiment) facility at Stockholm University. DESIREE's cryogenic infrastructure, combined with long storage times and a merged-beams setup, offers a highly controlled environment for precision measurements of low-energy collisions [1].

A central aspect of this experiment is the ability to active control and manipulate the internal quantum states of Ba^+ ions using laser-based optical pumping techniques. The ions produced in the source emerge in an unknown mixture of the ground state ($S_{1/2}$) and the metastable states ($D_{3/2}$ and $D_{5/2}$). Using two out of the three different laser wavelengths available, we selectively prepare the ion beam either in a pure ground state or in defined metastable states by optical pumping (see the attached figure). This includes both depopulation of the metastable levels to achieve a ground-state population and active laser excitation to populate the $D_{3/2}$ and $D_{5/2}$ states. This capability allows us to investigate how different initial-state configurations influence the MN process.

By comparing the MN signals under different quantum-state preparations, we are able to disentangle and extract the individual contributions from each initial state. By transferring the population among the three Ba^+ MN initial states several times during a single injection, we are able to put the three resulting kinetic-energy release distributions on the same cross-section scale.

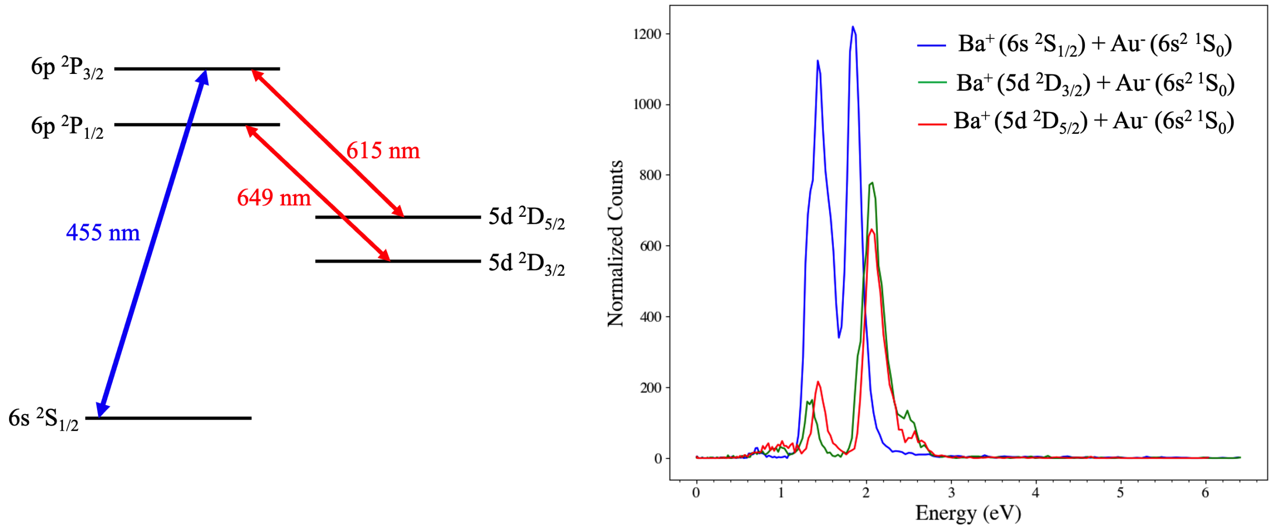

Figure 1: Left: Energy level diagram of Ba^+ with the optical pumping transitions shown. Right: Yield of neutral pairs as a function of total final channel center-of-mass kinetic energy

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Accurate lifetime measurement of the 5d $^2D_{3/2}$ metastable state of singly charged barium

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Metastable levels are excellent probes for the physical conditions in low-density astronomical plasmas [1]. Accurate measurements of the lifetimes of these levels are essential to understand such environments. However, the weak transition rate and the long time stability requirements make these measurements experimentally challenging. The metastable levels mainly decay via magnetic dipole (M1) or electric quadrupole transitions (E2), and the resulting lifetimes are in the range of milliseconds to seconds. With the development of ion trap experiments it became possible to confine atoms for extended periods of time to implement quantum algorithms and perform experiments to better understand the fundamental aspects of quantum mechanics. In this work analogues laser induced fluorescence (LIF) measurements are used to measure the lifetime of the 5d $^2D_{3/2}$ metastable state of singly positively charged barium.

For the first time, we combine a LIF probing technique with the unique capabilities of the cryogenic ions storage ring DESIREE [2,3], and use a novel pump-probe scheme based on the LIF technique previously applied at the CRYRING ion storage ring [4].This scheme involves two laser systems to manipulate the population of the ion states and probe them at different times after state preparation. These non-destructive measurements allow us to normalize the recorded signal, taking into account the quenching due to residual gas collisions and detection efficiency. The experimental results are shown in Figure 1 where Γ_{meas} is the fit to the data ignoring the contributions of the 5d $^2D_{5/2}$ level and $\Gamma_{3/2}$ is the radiative decay rate for the longer lived metastable level corresponding to a lifetime of 82.9(14) s for the 5d $^2D_{3/2}$ state.

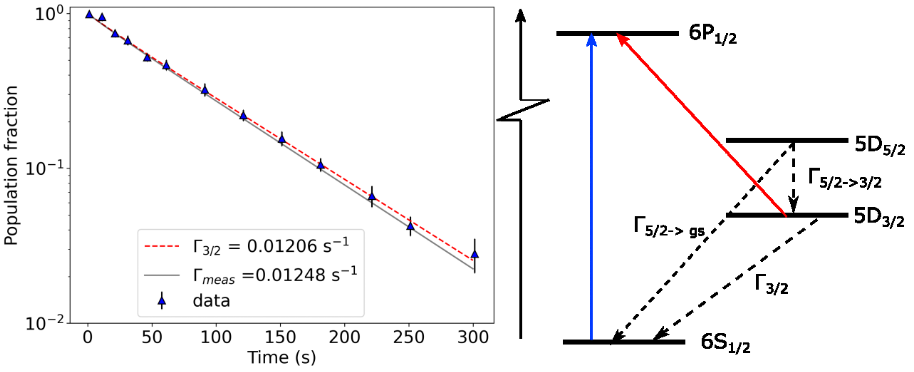

Figure 1: On the left, the experimental results are plotted as a function of delay time between pump and probe laser pulse. On the right side, the energy level diagram of Ba II shows the states involved during this experiment. The blue line indicates the pump laser while the red one shows the probe laser.

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A new setup to study the reactivity and spectroscopy of isomer selected molecular clusters

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The chemical reactivity and spectroscopy of isomers is a fundamental challenge in chemistry, particularly in cluster chemistry, where the number of possible structures increases dramatically with cluster size. We have developed a new setup that combines drift-tube ion mobility with mass spectrometry, which makes it possible to do isomer-specific gas-phase ion-molecule reactions. Taking it a step further, a newly installed cryogenic ion-trap with a time-of-flight mass spectrometer will enable us to measure the absorption spectra of the isomer-selected clusters. These spectra will serve to search for the identity of the molecular species responsible for the Diffuse Interstellar Bands (DIBs). This talk will present the newly build setup and preliminary results.

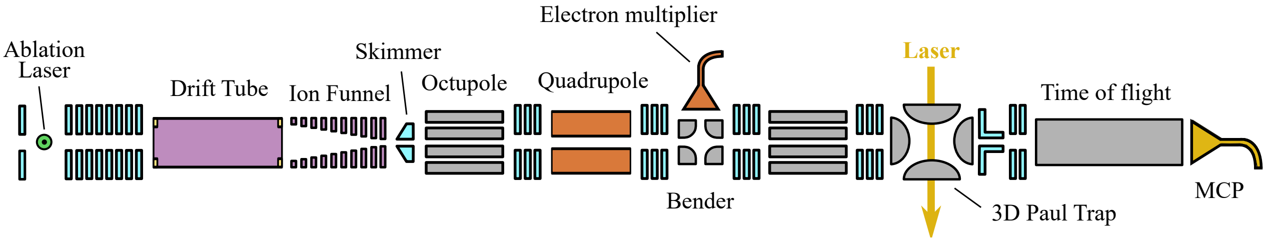

Figure 1: Illustration of the setup

Phase Space Manipulation and Evaporative Cooling of Ions in an Electrostatic Ion Beam Trap

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The electrostatic ion beam trap (EIBT) is a unique and versatile device where ions are stored between two electrostatic mirrors. The dynamics of ions and the evolution of phase space in the trap can be reproduced with a simulation based on particle-in-cell (PIC) technique [1]. The collective motions of interacting ions in the trap lead to very intriguing phenomena such as self bunching or enhanced diffusion [2], suppression of emittance growth in RF bucket [3]. A controlled manipulation of the phase space of ions opens up many opportunities for kinematical cooling of ions, such as autoresonance cooling [4].

In our preliminary results, we demonstrate the evaporative cooling of ions using RF bunching. A reduction in velocity spread and an increase in phase space density are observed. The RF frequency is kept constant, but the amplitude is reduced as a function of time. The velocity spread is determined by final RF amplitude. Fig. 1 shows the phase space of ions 100 ms after RF was stopped, allowing the ions to thermalize in the trap, for two different final RF amplitude: 0 V (left) and 0.04 V (right). The experimentally measured frequency spectrum shows good agreement with the simulation. The results are still in initial stage, and further experiments are being conducted to understand the evaporative cooling of ions using RF bunching.

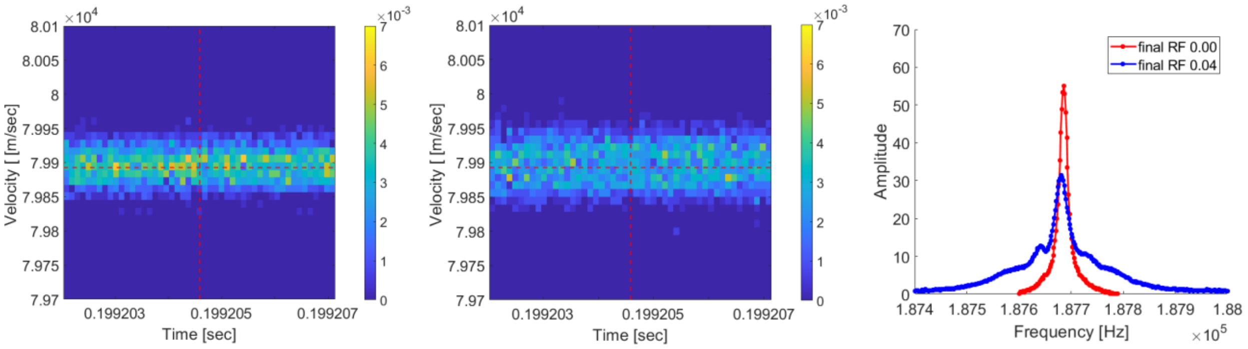

Figure 1: Phase space of ions (simulation) for two final RF amplitude 0 V (left) and 0.04 V (middle), and experimentally measured frequency spectrum (right)

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Towards multi-color laser action spectroscopy of highly excited H_3^+ in the CSR

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Although H_3^+ is the simplest polyatomic molecule, the higher excitation spectrum above 16500 cm^{-1} remains largely unexplored. These highly excited states are not only experimentally but also theoretically challenging as the H_3^+ ion begins to sample linear configurations above energies of 10000 cm^{-1}. To bridge the gap to the measured rich pre-dissociation spectrum above 35000 cm^{-1} [1] a multi-color action spectroscopy scheme has been proposed [2]. In the first step, the ions are pumped from the ground state to a transition state and then accumulated in a long-lived state at approx. 10000 cm^{-1} while stored in a storage ring. In a second step, these ions are excited to the regime of interest above 20000 cm^{-1} before they are dissociated with a UV laser and the dissociative products are recorded by a sensitive single particle detector. In this work we demonstrate the first step at the Cryogenic Storage Ring (CSR) in Heidelberg.

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IR and UV spectroscopy of gas-phase monohydrated protonated guanine

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We use UV and Infra-Red photodissociation spectroscopy to study monohydrated protonated guanine in a dual cryogenic ion trap spectrometer. The monohydrated complexes are formed through helium-mediated collisions between bare electrosprayed protonated guanine and low-pressure water vapor in a clustering trap maintained at 180 K before being transferred to a quadrupole ion trap at 10 K. The spectrum of the monohydrated complex exhibits sharp vibronic transitions at the band origin and becomes broader and higher in intensity further in the blue, which is very similar to protonated guanine but with a notable blue shift of ~1850 cm^{-1} (~0.23 eV). The UV hole-burning experiments showed that the vibronic bands recorded in the region of the band origin belong to a single conformer under our experimental conditions. The IR photodissociation spectrum in the 3000 - 3600 cm^{-1} range with the aid of theoretical calculations (SCS-CC2/aug-cc-pVDZ) allowed us to assign the structure to the lowest energy N_7-O conformer (see Figure 1 below).[1]

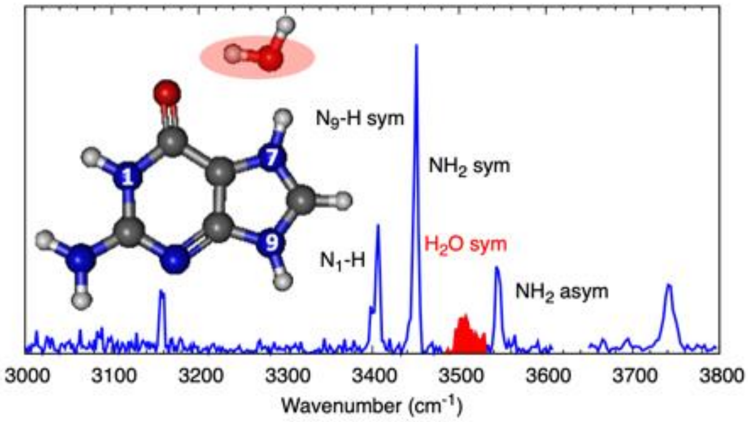

Figure 1: IRPD spectrum of G(H$^+$)...H_2O complex recorded by tracking the intensity of the fragment m/z 152, which corresponds to H_2O loss

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Momentum Imaging of Electrons and Recoil Ions from Anion–Neutral Interactions with a Reaction Microscope in a Cryogenic Ion Storage Ring

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First experiments with the CSR-ReMi, the in-ring reaction microscope of the Cryogenic Storage Ring CSR [1], studied collisions between anions and neutral atoms. The ejected electrons and recoil ions were momentum analyzed and measured in triple coincidence with the projectiles neutralized in the collision. Double coincidences between the electrons and the neutralized projectiles, with an anti-condition on recoil ion, are mainly caused by loss of a projectile electron (detachment), without a transition in the target [2].

Fig. 1 a) shows the two-dimensional, double–coincident electron momentum distribution as a function of the momentum components p_x (neutral gas jet direction) and p_y (ion beam direction), with the condition $p_z = 0 \pm 0.05$ a.u., for 300 keV Si^- + Ar collisions. A pronounced ring-like shape with a radius equal to the projectile speed (0.66 a.u.) is observed. In the quasi-free electron model, where the weak binding of the projectile electron is neglected, detachment is viewed as elastic scattering of the projectile electron from the target. The ring structure then reflects kinetic energy conservation.

Triple coincidences between all three detected particles select detachment with simultaneous target ionization (DI). In Fig. 1 b), we present the same type of momentum distribution as in Fig. 1 a), but for electrons ejected in DI. The most prominent features of this spectrum are a) a complete absence of a ring-like structure and b) a very sharp peak at zero momentum. This is a clear signature of DI being dominated by a correlated first-order process, where the two electrons are ejected by a mutual electron-electron interaction. An uncorrelated process, where the electrons are ejected by two independent interactions with the core of the respective other collision partner, should exhibit a similar ring structure as in detachment. Furthermore, the observed DI rate is about 5 times larger than expected.

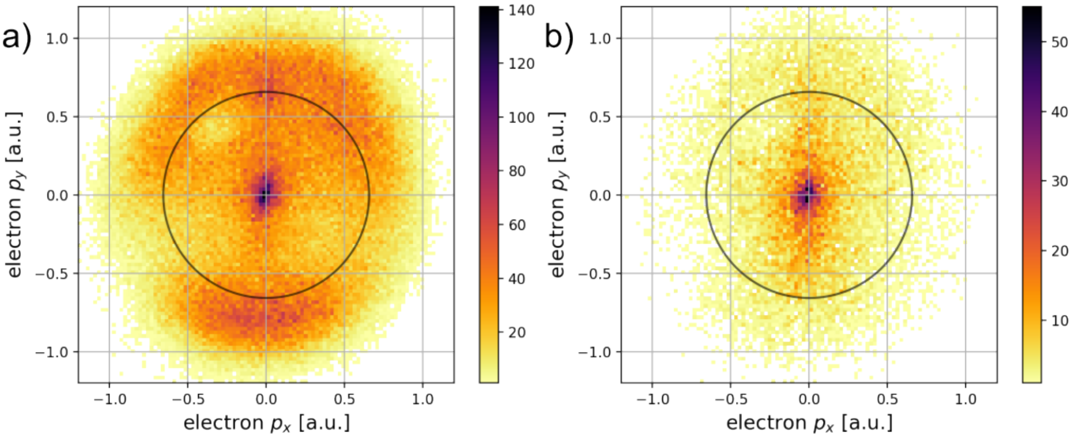

Figure 1: Electron momentum distributions for 300 keV Si^- + Ar collision; a) electron detachment, b) electron detachment with simultaneous target ionization. The black circle marks the projectile speed of 0.66 a.u.

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Action spectroscopy and photophysics of $C_{11}H_9^+$ species

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Motivated by the well-known tropylium and benzylium ions – the long-lived isomers of the dehydrogenated methylated benzene cation [1] – we investigated the analogous case for the smallest methylated polycyclic aromatic hydrocarbon (PAH), methylnaphthalene (MeNp). Previous studies identified $BzTr^+$ and $2\text{-}NpCH_2^+$ (see Figure 1) as specific isomers of $C_{11}H_9^+$ both when 1-MeNp [2] or 2-MeNp [3] are used as precursors.

In this contribution, we present a series of experiments conducted in PIRENEA, a setup dedicated to laboratory astrophysics. PIRENEA enables ion trapping on long timescales (up to ~1000 s) and allows the combination of photoprocessing with ion-molecule reactions experiments. Through our experimental results and with the help of quantum chemical calculations [4], we confirm the formation of the two previous reported isomers of $C_{11}H_9^+$ species and provide the first clear spectroscopic evidence for the presence of the $1\text{-}NpCH_2^+$ isomer (see Figure 1). In addition, we provide quantitative analysis of the relative isomer populations obtaining comparable abundances for the three isomers identified. We also report experimental evidence for conversion of $2\text{-}NpCH_2^+$ into $BzTr^+$. Finally, we briefly discuss the astrophysical implications of these results.

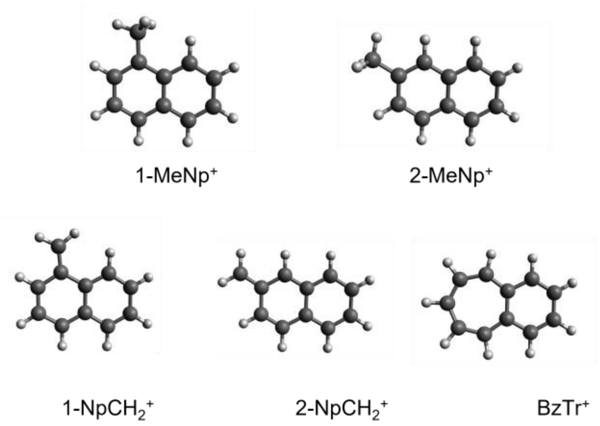

Figure 1: Molecular structure of the two isomers of the methyl-naphthalene cation, $1\text{-}MeNp^+$ and $2\text{-}MeNp^+$ (top row), and of the three expected lowest-energy isomers resulting from H loss of $MeNp^+$ (bottom row).

Acknowledgment: This work is part of the SynPAHcool project (ANR grant No ANR-21- CE30-0010).

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Low Energy Electron Cooling at the Cryogenic Storage Ring

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Electron cooling [1] is an established technique used in ion storage rings to improve the quality of the stored beam. By interaction with a nearly monoenergetic, parallel electron beam at matched velocity, the ion distribution in phase space can be compressed. This results in a smaller transverse cross section, a smaller momentum spread, an increased storage lifetime, and an overall better definition of the ion beam for collision experiments. In the usual application in high-energy magnetic storage rings, typical electron beam energies range from several hundred eV to MeV for electron cooling, i.e., at matched electron and ion beam velocities.

Compared to magnetic storage rings, electrostatic storage devices are operated at much lower ion beam energies in the keV domain. This makes electron cooling challenging due to the correspondingly lower electron beam energies needed to obtain matched velocities with the ion beam. To date, the Cryogenic Storage Ring (CSR) [2] in Heidelberg is the only electrostatic storage ring incorporating an electron cooler. With ion energies up to 300 keV per unit charge, the required electron cooling laboratory frame energies reach only a few eV.

In this contribution, we review the challenges of low-energy, low-temperature electron beam operation at CSR, including advanced electron beam production techniques, detailed space charge treatment, and laboratory frame energy calibrations. Special emphasis will be given to the recent successes in the first electron cooling of molecular anions, an order-of-magnitude increase of electron-cooled anion beam lifetimes, the apparent enhancement of the electron cooling force for anions over cations, and demonstrating electron cooling at an electron energy down to 1 eV. These achievements are crucial for future high-precision experiments at CSR.

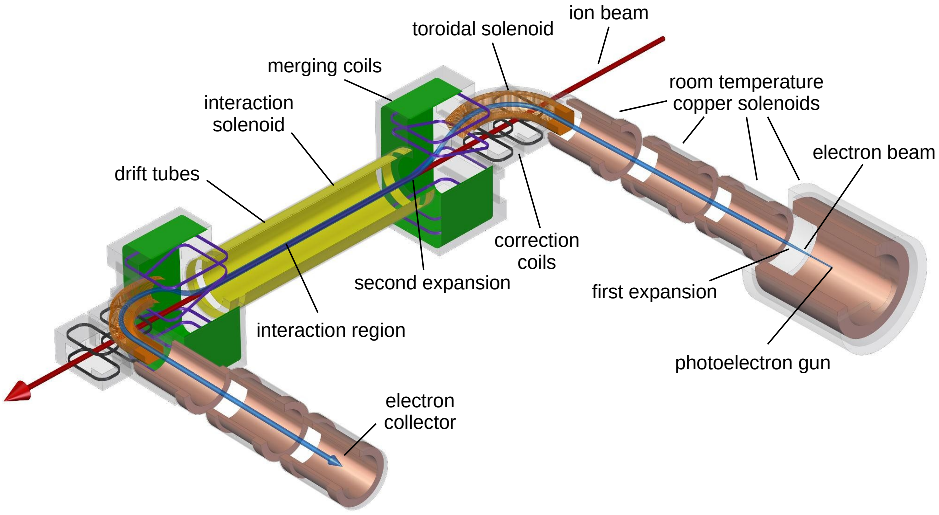

Figure 1: The CSR electron cooler

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Posters

Dissociative charge transfer collisions at CSR-ReMi

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One of the dominant processes occurring in slow ion-atom collisions is the capture of electrons from the target by the projectile. In dissociative electron transfer collisions, a molecular ion captures an electron from the target, leading to the dissociation of the molecule through various excited electronic states. For kinematically complete experiments, the target recoil ions and neutral fragments of the molecules are measured in coincidence by combining the Reaction Microscope (ReMi) with a neutral fragment detector [1]. The high-resolution Q-value obtained from the recoil ions indicates the populations of the different electronic states at the instant of electron transfer. On the other hand, scattering angle differential cross sections provide insight into the state-selective collision dynamics. Molecular ion beams exhibit additional degrees of freedom due to their vibrational motion and spatial orientations. Therefore, it is important to understand the role of vibrational motions in the charge transfer process from a bound system and the orientation effects on collision dynamics.

In the cryogenic storage ring CSR [2] at MPIK, Heidelberg, the molecular ion beams are not only cooled to the lowest vibrational states but also to a few rotational states. Therefore, the addition of the cryogenic reaction microscope at CSR (so-called CSR-ReMi) [3,4] provides an excellent platform for studying vibrational state-selective electron transfer collisions for molecular ion beams with excellent vacuum conditions. The measurements were carried out for 0.73 keV/u ArH^+-He and ArH^+-Ar slow collisions. The Q-value spectra and scattering angle-differential cross sections have been obtained from the recoil ions using inverse kinematics. The Q-value spectra (cf. Fig. 1) indicate that a few excited (including highly excited) electronic states of neutral ArH are populated at the instant of collisions. A simple classical electron transfer model is employed to qualitatively understand the state-selective populations and scattering angular distributions for different collision systems.

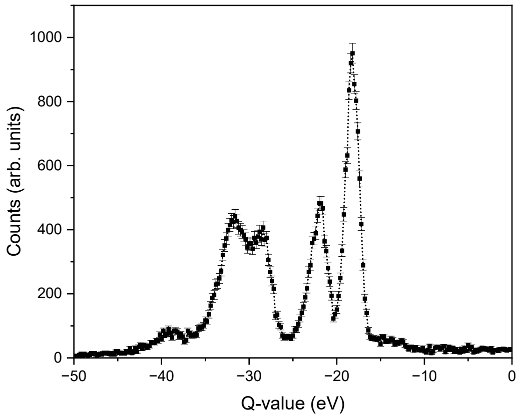

Figure 1: State-selective Q-value spectra for 0.73 keV/u ArH^+-He single-electron capture process.

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C_4^- in SAPHIRA: spectroscopy and recurrent fluorescence

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We have studied the spectroscopy and dynamics (recurrent fluorescence) of initially cold C_4^- anions under conditions mimicking the environment in interstellar space, using a combination of buffer gas cooling in a radio-frequency trap [1] and laser irradiation inside the SAPHIRA electrostatic ion storage ring [2].

The spectroscopy of the $C^2\Pi_u \leftarrow X^2\Pi_g$ transition in C_4^- was examined with 2-photon photodetachment spectroscopy [3]. Modeling of the observed photoabsorption spectrum allowed us to re-assign several vibrational transitions and to determine spin-orbit coupling constants for both the ground ($X^2\Pi_g$) and the excited ($C^2\Pi_u$) state of C_4^-. Moreover, the spectra revealed the variation of the spin-orbit coupling constants with vibrational excitation energy for specific vibrational modes of the excited state ($C^2\Pi_u$).

Using a new photon collection system inside SAPHIRA, we directly observed the emission of recurrent fluorescence from initially cold C_4^- after specific laser excitations allowing e. g. the rate of recurrent fluorescence to be determined. Moreover, the recurrent fluorescence spectra from cold C_4^- provide a direct link to the anticipated mechanism of recurrent fluorescence that involves internal conversion and inverse internal conversion upon photoabsorption.

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Vibrational Cooling of a Hot Acetylide Anion

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C_6H^- was the first anion detected in space, and since its discovery a multitude of C_nH^- (n even) anions have been detected. Current understanding suggests that they are created by radiative attachment from their neutral radical part. One such radical, the ethynyl radical (C_2H), is a fundamental component in astrochemical processes and has been found in a multitude of interstellar environments, and it is a critical part of reaction pathways to form polycyclic aromatic hydrocarbons. The appertaining acetylide anion (C_2H^-) has yet to be measured from interstellar bands, but it has been discovered in the ionosphere of Titan.

In this study, we have examined the cooling of an initially hot C_2H^-, trapped in an electrostatic ion-beam trap at 300 K. We measured, photoelectron spectroscopy using velocity map imaging in coincidence with neutral detection from the process $\tilde{\mathrm{X}}^{-}\,{}^1\Sigma^+ + h\nu \rightarrow \tilde{\mathrm{X}}^2\Sigma^+ + e^-$ below the first excited $\tilde{\mathrm{X}}^2\Sigma^+ \leftrightarrow \tilde{\mathrm{A}}^2\Pi$ mixed state.

The hot ions show a broad distribution of electron kinetic energies (eKE) (see Fig. 1), whose width and peak continuously decrease as a function of storage time until setting at a value of 262 meV (3017 meV binding energy) after 2 seconds. This is significantly different from the electron affinity for C_2H of 2969 meV and is caused by a hot rovibrational population in the anion. This is consistent with the fact that a hot rotational ensemble will decrease the eKE since the rotational constant of the anion is smaller than that of the neutral, indicating that the ensemble is not rotationally cold after 2 seconds of storage. However, the opposite effect of rotational cooling (increasing the eKE) is observed during the 2 seconds of storage. The decrease is instead attributed to cooling of the bending mode in the anion (498 cm^{-1}) since the neutral exhibits a lower energy bending mode (361 cm^{-1}), which forces vertical transitions between higher vibrational quanta to higher eKE.

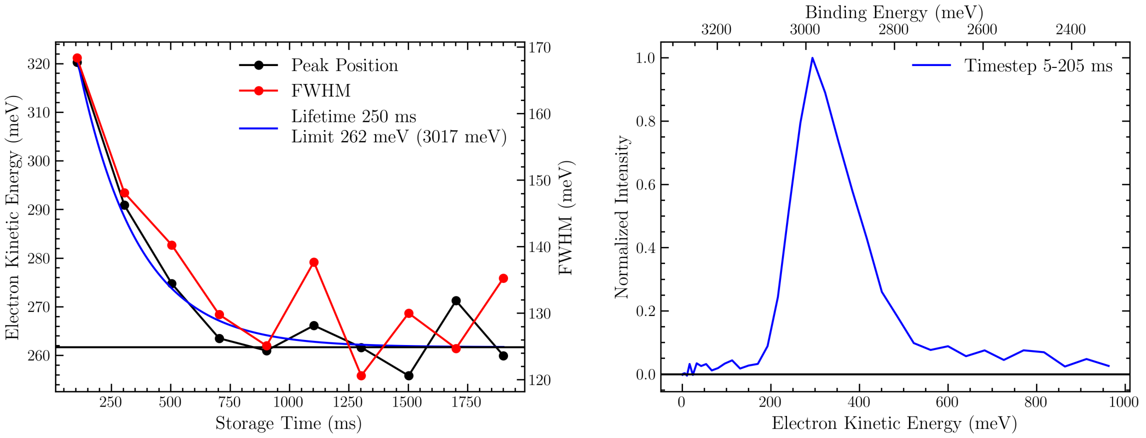

Figure 1: Right: Measured photoelectron kinetic energy spectrum integrated from 5-205 ms after trapping. Left: Electron kinetic energy peak position and FWHM as a function of storage time at room temperature. In blue an exponential fit to the decay is shown.

Recent developments at the DESIREE facility

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The Double ElectroStatic Ion Ring ExpEriment (DESIREE) facility consists of two electrostatic storage rings sharing a common straight section, the two rings are housed in an inner chamber under a cryogenic temperature of 13 K and extremely high vacuum 10^{-14} mbar [1,2]. Atomic and molecular ions with opposite charges collide in the common section at well-controlled collision energies [3,4,5].

To improve the vacuum, an aluminium plate with a surface area of 0.5 m^2 was installed inside the inner chamber and cooled down to 2.7 K to trap the residual H_2 molecules, it reduced the residual gas density to about one particle per cubic millimetre and allowing storage lifetime up to 2 hours. For storage rings operating under cryogenic temperature, the amount of room temperature black body radiation is critical for the thermal equilibrium of the stored ions; it's also essential for the planned metallic magnetic calorimeter MOCCA [6] at DESIREE. The ion beam ports of the two rings are the main access for such radiation, and by reducing the diameters of the two ports from 62 to 30 mm, the effective lifetime of C^- ions in the loosely bound metastable ^2D state was increased from 10.9 to 21.8 s compared with 2.7 ms in a room-temperature storage ring experiment [7]. Thus we conclude that the density of photons with more than 33 meV photon energy is about four orders of magnitude less than in a room-temperature environment.

In the common section, two pickups (of mirror charge of the pulsed beams) were installed 0.7 m apart to monitor the beams' positions. To secure the overlap of the two beams, two sets of movable apertures with diameters from 30 down to 1 mm were installed beside the two pickups. Recently, a new pickup was installed in the injection section of each ring, where overlap with laser beams in co-linear configuration is often required. The four 160-degree deflectors were moved 6 mm away from the centre of each ring, their new positions allow more flexible ion orbit in each ring and therefore it's easier to achieve simultaneously long storage lifetimes and good overlap of the two stored ion beams. The drift tubes in the common section were replaced by solid tubes to reduce fringe-field effects in and around the collision region, one of them was replaced by a series of movable tubes with different lengths and diameters.

A new fragment detector with a central hole of 12.5 mm was installed just after the common section in one ring, it consists of a stack of three 75 mm micro-channel plates backed by a resistive anode, it can be used to detect charged particles with an energy ratio from 0.6 to 3 comparing to the stored ions. In the other ring, a Velocity Map Imaging (VMI) device was added in the middle of the injection section, aiming to measure individual lifetime of possibly multiple metastable states of an anion at once, the VMI is under commissioning.

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