

The 15th International Conference on Quantum Fluid Clusters

23 - 26 June 2024, Aarhus, Denmark



Venue:

Aarhus Institute of Advanced Studies (AIAS), Aarhus University,
Buildings 1630-1632, Høegh-Guldbergs Gade 6B, 8000 Aarhus C, Denmark

Local organizers:

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CARLSBERG FOUNDATION

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About QFC 2024

Welcome to the QFC 2024 which is the 14th occurrence of the QFC conference series founded in 1989! We are particularly happy to host this conference in Denmark for the first time. It carries on the tradition of bringing together researchers from all over the world working with helium nanodroplets and related clusters and nanosystems.

Helium nanodroplets have fascinated physicists and chemists for several decades due to their peculiar quantum many-body properties, notably superfluidity and quantum vortices, which are still subject of ongoing research. On the other hand, helium nanodroplets serve as flying nano-cryostats for synthesizing and probing cold molecules, ions and nano-complexes at ultralow temperature. The rapid development of experimental and theoretical methods now allows us to resolve the spectra, dynamics and structure of pure and doped helium nanodroplets with unprecedented resolution, paving the way to new and exciting experiments, simulations and applications.

The conference comprises a **keynote lecture** as a kick-off event on Sunday evening. Each morning session is preceded by **introductory lectures**. The **invited talks** are complemented with **rising star presentations** given by prospective young researchers. Two **poster sessions** are scheduled on Monday and Tuesday evening. The conference is concluded by a **wrap-up talk** that reviews the conference and highlights future prospects. The **conference dinner** will be held at Møntmestergaarden at Den Gamle By, which is a magnificent setting at walking distance of the conference site.

We wish you a stimulating and pleasant stay at the QFC 2024 and in Aarhus,

Marcel, Henrik and Brigitte

The Venue – Aarhus Institute of Advanced Studies (AIAS)

The Aarhus Institute of Advanced Studies hosts about 40 fellows at the same time for short or long-term research stays. Fellows are selected solely on the basis of excellence and come from all over the world.

AIAS was established in June 2013, based on the classical ideas of an Institute for Advanced Study, with IAS Princeton as a model.

Getting to Aarhus University and AIAS:

By air

Aarhus Airport

The airport is about 40 km from Aarhus city centre. The 50-minute journey can easily be made using the frequent airport bus. From Aarhus Airport, busses are coordinated in accordance with the flight schedule. You can get off both at Aarhus University (bus stop Nordre Ringgade) and the city centre by the train station.

You can find the airport bus schedule

here: [https://www.midttrafik.dk/koereplaner/lufthavnsbusser-\(airport\)/aarhus-airport-\(uk\).aspx](https://www.midttrafik.dk/koereplaner/lufthavnsbusser-(airport)/aarhus-airport-(uk).aspx)

Billund Airport

The bus from Billund Airport (Route 912X) stops at the train station in the city centre. The duration is about 1½ hours. You can find the bus schedule

here: <https://www.bll.dk/en/parking-and-transport/to-and-from-the-airport/busser/>

Copenhagen Airport

From Copenhagen Airport you can either go by domestic flight to Aarhus Airport, which is a 45 minutes flight, or take the direct 3 hour train ride to Aarhus train station.

Taxi

Please note that taxis are expensive in Denmark. A taxi trip to Aarhus from Billund Airport will cost about DKK 1700 (approx. USD 300), and from Aarhus Airport the price is about DKK 600 (approx. USD 90).

By train

The train station is situated in the city centre (see location on the map to the right). You can find time tables and buy your e-ticket online at www.dsb.dk/en/;

Bus in Aarhus

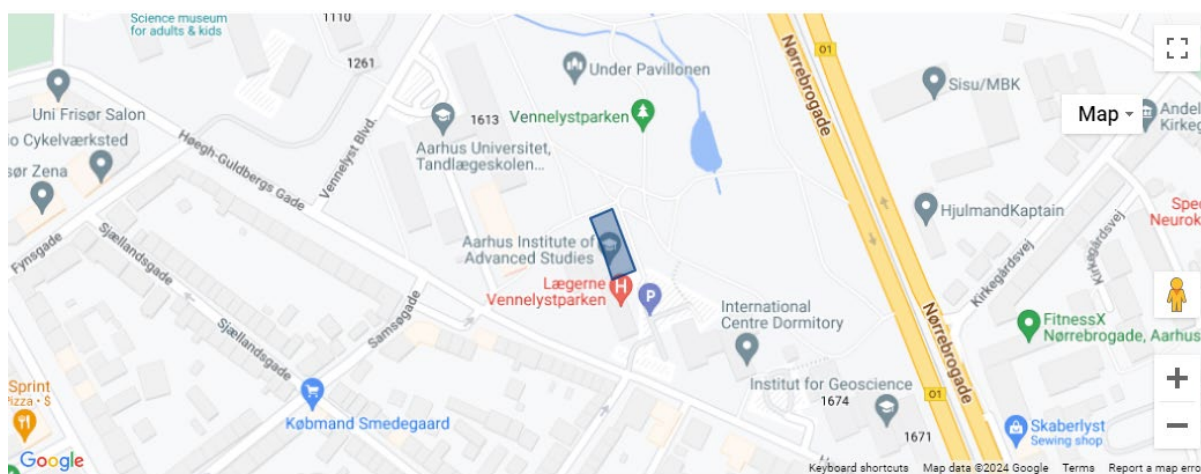
The following busses will take you from the city centre of Aarhus to AIAS:

Bus 1A: Leaves from Banegårdspladsen, a few minutes' walk from the train station, about every 10 minutes. Take the bus in the direction of Trige/Lystrup and get off at the bus stop Nørreport, a 5 minutes walk from AIAS.

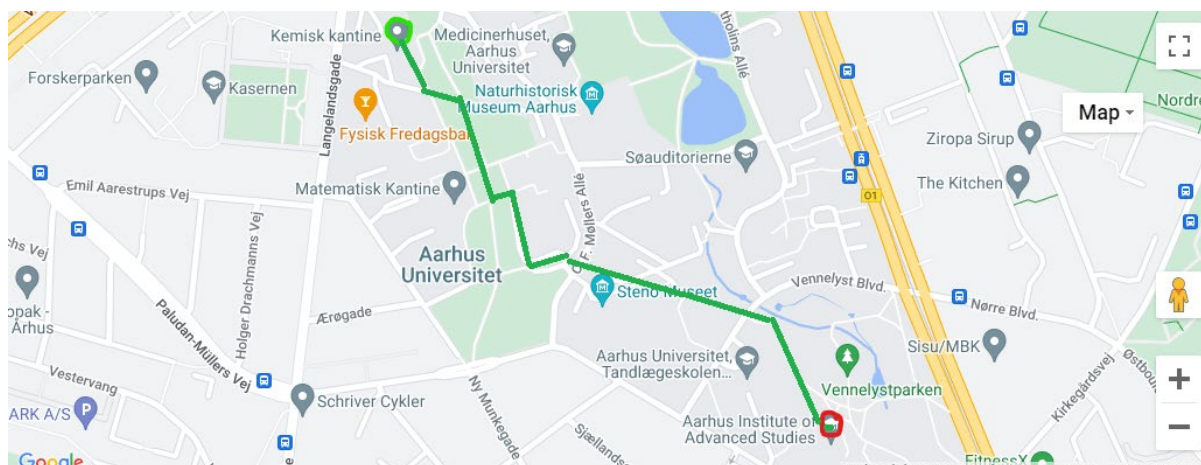
Bus 14: Leaves from Banegårdspladsen/Park Allé, a few minutes' walk from the train station, about every 20 minutes. Take the bus in the direction of Skejbjergparken and get off at the bus stop at Nørreport, a 5 minutes walk from AIAS.

Bus 17: Leaves from Banegårdspladsen/Park Allé, a few minutes' walk from train station, about every 30 minutes. Take the bus directed to Studstrup and get off at the stop called Nørreport, a 5 minutes walk from AIAS.

Bus 33: Leaves from Banegårdspladsen, a few minutes' walk from the train station, about every 30 minutes. Take the bus in the direction of Aarhus Ø and get off at the bus stop Nørreport, a 5 minutes walk from AIAS.



The Chemistry Canteen - route map from AIAS



Getting around in Aarhus



Aarhus is the second-largest city in Denmark, located on the east coast of the Jutland peninsula. Known for its vibrant cultural scene, Aarhus is home to numerous museums, theaters, and music venues, including the ARoS Aarhus Art Museum, which is famous for its rainbow panorama walkway. The city is also renowned for its rich history, with landmarks such as the Aarhus Cathedral, one of the tallest and longest churches in Denmark, and Den Gamle By, an open-air museum that recreates urban life from the 16th century to the 1970s.

Aarhus is a hub for education and research, hosting Aarhus University, one of the largest and most prestigious universities in Denmark. The city has a lively student population, contributing to its youthful and dynamic atmosphere. Additionally, Aarhus boasts a variety of parks, beaches, and green spaces, making it a pleasant place for outdoor activities.

The culinary scene in Aarhus is diverse and innovative, with numerous restaurants offering both traditional Danish cuisine and international flavors. The city's waterfront area, Aarhus Ø, features modern architecture, trendy cafes, and a bustling harbor, further enhancing its appeal as a destination.

Aarhus is also well-connected, with efficient public transportation and cycling paths, reflecting Denmark's emphasis on sustainability and green living.

On foot

In Aarhus most sights are within reach on foot. Aarhus features many picturesque locations in harmonic contrast to modern architecture.

Take the opportunity to go for at least one walk through the city.

By bike

Aarhus is made for biking, and this is reflected in the excellent bike path infrastructure, which you will find almost everywhere in Denmark. Just be aware that Aarhus stretches an elevation of about 80 meters so be ready for some inclines.

Visit Aarhus webpage offers information about easy bike rental in Aarhus.

By bus

Aarhus has a dense local bus network which is serviced by the yellow busses. Please note that, in contrast to the regional public transport (blue busses), it is not possible to buy tickets inside local public transport (yellow busses) anymore. Ticked machines (available on chosen bus stops and stations), the Midttrafik web shop or the Midttrafik app are the recommended options to buy a ticket. The Rejseplanen web application and Midttrafik live app can help to gain an overview of available bus connections. Non-digital patrons are asked to call +45 70 210 230 or visit Aarhus bus station for help and guidance.

By tram

Aarhus is the first city in Denmark to have a tram network (Letbanen). It is not possible to buy a ticket on the tram. Please use the same options as mentioned for regional transport busses (yellow busses) to purchase a ticket for the tram.

By

taxi

To book a taxi, please call this telephone number (+45) 8948 4848 (Aarhus Taxi) or ask at your hotel. There is also a taxi stand right outside the main exit of the train station and conveniently located taxi stands all over the city.

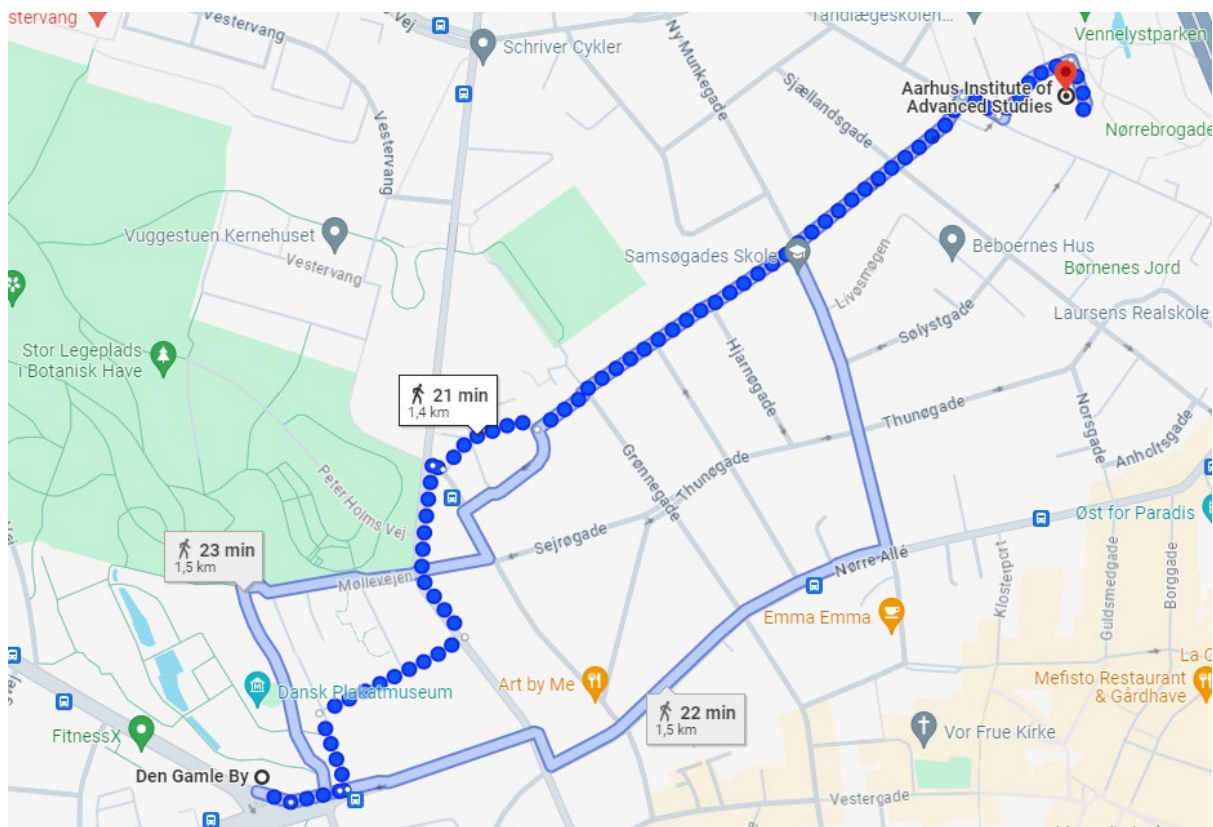
Den Gamle By

Den Gamle By (lit. "The Old Town") is an open-air town museum located in the Aarhus Botanical Gardens, in central Aarhus, Denmark.

In 1914, the museum opened as the world's first open-air museum of its kind, concentrating on town culture rather than village culture, and to this day it remains one of just a few top rated Danish museums outside Copenhagen, serving more than 400,000 visitors pr. year.

Today the museum consists of 75 historical buildings collected from 20 townships in all parts of the country. The town itself is the main attraction but most buildings are open for visitors; rooms are either decorated in the original historical style or organized into larger exhibits of which there are 5 regular with varying themes. (Source: Wikipedia)

Route from AIAS to “Den Gamle By” – entrance Aarhus Porten



The conference dinner

The largest and most impressive buildings are the Mintmaster's Mansion from Copenhagen (c. 1683), the Mayor's House from Aarhus (c. 1597), a merchant's house from Aarhus (c. 1723) and the Aalborg Estate from Aalborg (c. 1570 and 1807). Many smaller buildings of diverse persuasions are scattered around the site, ranging from ordinary residences to a small dock for boat construction, a tobacco barn, several watermills and a windmill.



The Mintmaster's Mansion

The Old Town. View from the lakeside

18.15 - Arrival at Den Gamle By, entrance Aarhus Porten

18.30 - Conference dinner

- Welcome drink and snacks served in the Kamin Hall

- First course:

Faroese Smoked Salmon

Vegetarian:

Leeks

Poached leeks, smoked cream cheese, crisp bread & herbs from gardens

- Main Course:

Chicken from Hopballe

Vegetarian:

Fried mushrooms & peas

Green asparagus, carrot puree and potatoes with lovage

- Dessert - Den Gamle By's Chocolate cake

- Coffee/tea with sweets

22.00 - Goodbye

AU-Guest – wireless network for guests

Guests at AU who need wireless network access can use the AU-Guest network.

1. Turn WIFI on (on your mobile, tablet or PC) under Settings.
2. Select the AU-Guest network.
3. Open a web browser, for example Safari, Internet Explorer or Google Chrome.

A login website will automatically appear as illustrated below.

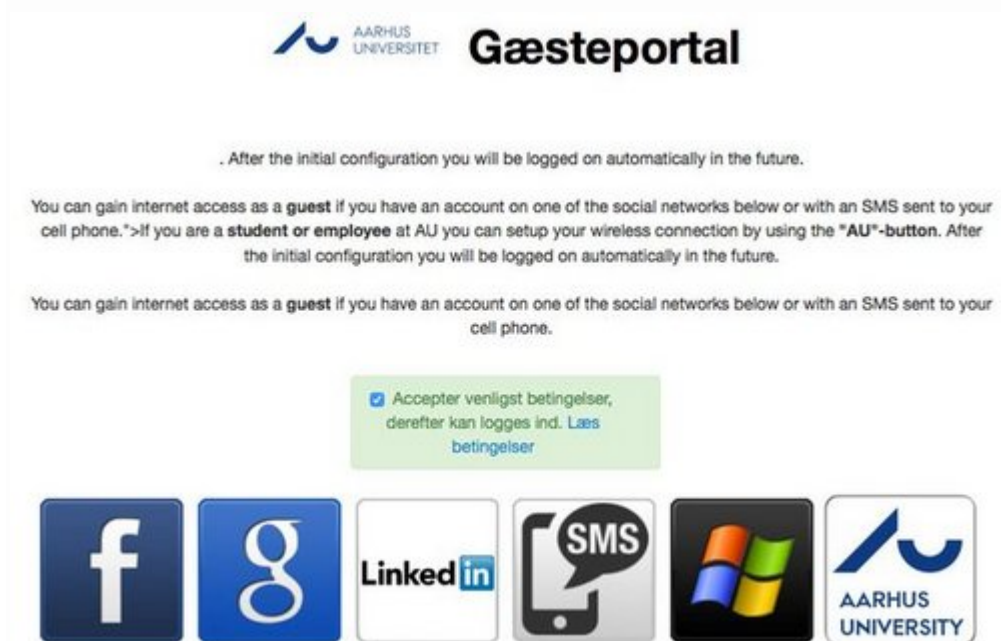
If the login website does not appear, please write www.au.dk in the browser.

4. Log on to the internet by using one of the accounts below:

- Facebook
- Google Drive
- LinkedIn
- SMS (only Danish telephone numbers)
- Microsoft account (for example outlook.dk, hotmail.com)

If you click the AU logo, a new website will appear. From this website, you can download the installation software for eduroam.

AU-Guest access is for the internet only. AU-Guest does not provide access to internal services such as file and print servers.



	Sunday 23 June	Monday 24 June	Tuesday 25 June	Wednesday 26 June
8:45 - 9:00	Registration and light dinner	Welcome	Introductory: A. Ellis	Introductory: N. Halberstadt
9:00 - 9:45		Introductory: A. Vilesov	Invited: E. Gruber	Invited: M. Lemeshko
9:45 - 10:20		Invited: D. Rupp	Coffee	Coffee
10:20 - 10:55		Coffee	Invited: T. Fennel	Invited: V. Milner
10:55 - 11:30		Invited: J. Harris	Invited: S. Krishnan	Invited: H. Høj Kristensen
11:30 - 12:05		Invited: V. Kresin	Rising star: Björn Bastian	Rising star: Arne Morlok
12:05 - 12:30		Rising star: Amandeep Singh	Lunch at Chemistry	Lunch at Chemistry
12:30 - 14:00		Lunch at Chemistry	Invited: L. Poisson	Invited: M. Koch
14:00 - 14:35		Invited: M. Havenith	Invited: M. Kunitski	Invited: S. Høgh Albrechtsen
14:35 - 15:10		Invited: S. Kuma	Coffee	Coffee
15:10 - 15:45		Invited: F. Calvo	Invited: L. Ben Ltaief	Invited: J. Wu
15:45 - 16:15		Coffee	Rising star: M. Stadlhofer	Wrap-up talk: F. Stienkemeier
16:15 - 16:50		Invited: G. von Helden	Posters	Lab visits and free discussions
16:50 - 17:25		Invited: M. Šekutor	and meeting of the QFC board	
17:25 - 17:50		Rising star: Olga Lushchikova	Conference dinner Møntmestergaarden, DGB	
18:30 - 20:00		Keynote speech: W. Ernst	Dinner at Chemistry	Individual dinner in town
20:00 - 21:00			Posters	

30 years of ultracold helium nanolabs – history and future perspectives

Wolfgang E. Ernst¹

¹*Institute of Experimental Physics, Graz University of Technology, Graz, Austria*

Abstract: More than 60 years ago, Erwin Willy Becker published a paper about beams of condensed helium¹. Becker developed methods for uranium isotope enrichment in Karlsruhe based on the separation nozzle process where a high-speed gas stream, comprising UF₆ highly diluted by hydrogen or helium, is forced to turn through a very small radius, separating ²³⁵UF₆ from ²³⁸UF₆ due to centrifugal forces. The observation of cold and slow beams of “condensed” hydrogen and helium were more or less a side effect.

Even earlier, one hundred years ago, the Institut für Strömungsforschung in Göttingen had been opened under the leadership of Professor Ludwig Prandtl and became a center for research on fluid dynamics. In 1969 under the roof of the Max Planck Society, one of the departments of the Institute for Fluid Dynamics was devoted to the study of molecular beams and headed for over 30 years by Jan Peter Toennies. Gas flow through tiny nozzles became a tool for surface studies and in another branch, subject of fundamental research on clusters.

Toennies and his group picked up on Becker’s findings and published their detailed research on helium cluster formation at various conferences from 1985 onward². During the same time, Giacinto Scoles, Professor at the University of Waterloo and later at Princeton University, used his sensitive cryogenic bolometer detection method to study IR spectra of molecules attached to inert gas clusters (first SF₆ on Ar_n) via the now widely used “pickup technique”³.

While at first the helium clustering process and fundamental questions about finite superfluidity fascinated the small community, the application of the 0.4 Kelvin cold helium droplets as “nanolab” and as low temperature and weakly interacting confinement for atoms and molecules started to gain interest about 30 years ago. Helium droplets were doped with foreign atoms and molecules that cooled down to the droplet temperature, thus allowing for a special matrix spectroscopy. Rotational and vibrational motion of dopants inside the droplets were almost unhindered. Evidence of the anticipated finite size superfluidity in helium droplets showed up as sharp rotational lines after molecular IR excitation, as collective helium roton modes, and as vortices, all detected via measurements on dopant molecules. Due to the low temperature and almost negligible helium interaction, weak van der Waals bonds could be formed among dopants and otherwise unstable molecular conformations were observed and spectroscopically investigated. Numerous nanolab applications in a widening helium community allowed new spectroscopy in the frequency and time domains, aggregation of weakly bound clusters, creation of tailored nanoparticles, cold reaction dynamics, and more. In this talk, examples will be shown and future developments anticipated.

References:

1. Erwin W. Becker, *Z. Naturforschg.* (1961), **16a**, 1259.
2. H. Buchenau, R. Gotting, R. Minuth, A. Scheidemann, and J. P. Toennies: The Characterization of Helium Clusters in a Molecular Beam, *Lect. Notes Phys.* (1985), **235**, 157-69.
3. T.E. Gough, M. Mengel, P.A. Rowntree, and G. Scoles, *J. Chem. Phys.* (1985), **83**, 4958-4961.

Infrared spectroscopy of molecular ions in helium droplets

Andrey F. Vilesov

vilesov@usc.edu, University of Southern California, Los Angeles, USA

Molecular ions are important intermediates in the chemistry of condensed phase and upper atmosphere as well as in astrochemistry. Therefore, great strides were done in developing new techniques for spectroscopy of ions. We show that the electron impact ionization of the helium droplets doped with molecules yields diverse molecular ions or ionic clusters embedded in the droplets of few thousand He atoms. Infrared spectra are obtained using release of the cations from the droplets upon laser excitation, followed by mass spectrometric detection. This experimental approach enables the study a wide range of ionic molecular species. Some topics highlighted in this talk will include:

- Rotation of small molecular ions in He droplets,
- Isomers of carbo-cations,
- Structure of radical cation clusters,
- Ion molecule reactions and protonation at low temperature.

Imaging the structure and dynamics of helium nano- and microdroplets

Daniela Rupp

Nanostructures and Ultrafast X-ray Science, LFKP, D-PHYS, ETH Zurich, Switzerland

For the past decade, we have been able to take snapshots of individual nanoparticles in a vacuum using elastic light scattering of intense X-ray pulses. As a result, the structure of helium droplets is now better understood, we have gained control over e.g. the number of quantum vortices, and their importance as perfect model systems for light-matter interaction studies has grown once again.

Helium clusters, nano- and microdroplets are particularly suitable for the investigation of ultrafast electron dynamics on the shortest time scales. They are a relatively simple two-electron atoms and their weak interatomic interaction results in a gradual and traceable transition of properties from atomic to macroscopic matter.

In our experiments, we are investigating whether it is possible to reproducibly switch electronic properties of nanoscopic matter with an optical laser pulse, an important question for the development of all-optical data processing. Attosecond transient absorption measurements (ATAS) on helium gas had revealed that through AC Stark shift and light-induced states (LIS), an optical laser pulse can completely change the absorption of the material at a certain frequency. We have now shown in CDI experiments using intense higher harmonic (HHG) pulses that the scattering response of a helium droplet can also be transiently switched faster than one laser cycle.

In the context of newly emerging attopulses at X-ray free-electron lasers, this first-of-its-kind experiment opens up a whole new range of possibilities to resolve ultrafast dynamics such as coherent excitation in nanoscale matter in space and time.

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A proposal for detecting the spin of a single electron in superfluid helium

Jack Harris

Yale University, USA

The electron bubble in superfluid helium has two degrees of freedom that may offer exceptionally low dissipation: the electron's spin and the bubble's motion. If these degrees of freedom can be read out and controlled with sufficient sensitivity, they would provide a novel platform for realizing a range of quantum technologies and for exploring open questions in the physics of superfluid helium. We will describe a promising scheme for accomplishing this by trapping an electron bubble inside a superfluid-filled opto-acoustic cavity and reading out its spin using techniques of MRFM (Magnetic Resonance Force Microscopy).

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Stern-Gerlach deflection of magnetic molecules and clusters embedded in helium nanodroplets

Vitaly V. Kresin

University of Southern California, USA

Magnetic beam deflection experiments on free molecules and clusters are complicated by the fact that their rotational and vibrational temperatures are often poorly known and sometimes ill-defined. Furthermore, internal excitation reduces their magnetic susceptibility. Helium nanodroplet embedding ensures well-defined cryogenic conditions for the dopants, as well as a high degree of field orientation of their magnetic moments. This orientation, analogous to that observed for electric deflections of polar dopants [1], makes it possible to use a Stern-Gerlach magnet [2] to obtain measurable beam deflections even for heavy nanodroplets carrying magnetic impurities.

Measurements on Fe(II) and Co(II) chloride molecules reveal strong paramagnetism of monomers (implying efficient spin thermalization and orbital angular momentum quenching), and antiferromagnetic ordering in dimers and trimers. Measurements on Na₂ dopants, in turn, exhibit in the most overt way possible the formation of high-spin alkali dimer complexes on nanodroplet surfaces.

Deflection measurements also demonstrate that even at fixed beam conditions, the average nanodroplet size carrying a specific dopant changes substantially as the pick-up density is varied. This has implications for characterization of droplet size statistics. An expression describing this effect was derived and verified by modeling of pick-up probabilities.

This work is supported by the US National Science Foundation (CHE-2153255).

[1] J. W. Niman *et al.*, Phys. Rev. Lett. 123, 043203 (2019); Phys. Chem. Chem. Phys. 21, 20764 (2019); J. Chem. Phys. 153, 081101 (2020); Phys. Chem. Chem. Phys. 24, 10378 (2022).

[2] J. Liang *et al.*, Rev. Sci. Instrum. 91, 053202 (2020).

Contact Information: Vitaly Kresin, Department of Physics and Astronomy, University of Southern California, Los Angeles, CA 90089-0484, USA. Email: kresin@usc.edu

Infrared spectroscopy of CH_5^+ and Radical Cations in Helium Nanodroplets

Amandeep Singh¹, Sofia H. Allison², Andrew A. Azhagesan¹, Deepak Verma³ and Andrey F. Vilesov¹

¹University of Southern California, Los Angeles, USA

²Mount St. Mary University, Emmitsburg, USA

³Intel Corporation, Hillsboro, USA

Superfluid helium nanodroplets are unique matrices that could be used as nano-test tubes to study the infrared spectra of small carbocations. The electron impact ionization of helium droplets doped with clusters of methane molecules generates a variety of carbocations. In this work, we successfully produced CH_5^+ methanium cations upon ionization of methane dimers in helium droplets and using an addition reaction of protons with methane molecules inside helium droplets. The ions were studied by the pulsed infrared laser spectroscopy technique in the C-H stretching range. The spectra show two strong and broad infrared bands and a weak shoulder for CH_5^+ reflecting its highly fluxional nature. The dependence of infrared band intensity on the pressures of reactant gases was studied to understand the formation reaction. Furthermore, the final confirmations of product formation were made by measuring the laser-dependent mass spectra. Finally, the CH_5^+ spectrum is compared with the spectrum of CH_4D^+ . This paper also report the spectra of the methane dimer radical cations $(\text{CH}_4)_2^+$.

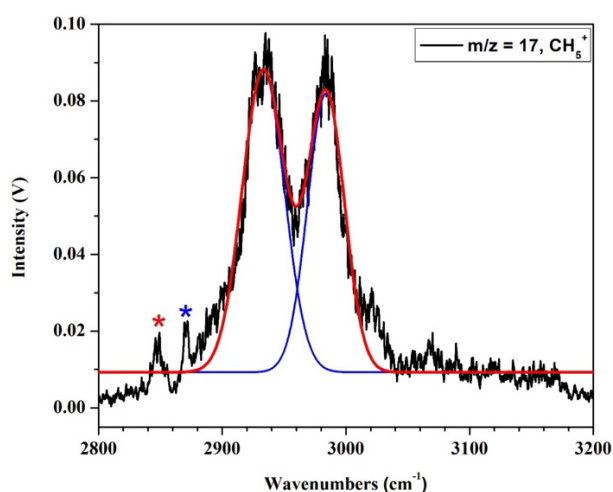


Figure 1: Infrared spectrum of CH_5^+ cations in helium nanodroplets. The Gaussian fitting is shown with a red trace and the individual Gaussian curves are shown with a blue trace. The red asterisk shows the band corresponding to fragmentation from $(\text{CH}_4)_2^+$ cations and the blue asterisk shows the band corresponding to fragmentation from $\text{CH}_5^+ - \text{CH}_4$ cations.

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Hydrogen bonding in the H₂S dimer: New insights from experiment and theory

Martina Havenith¹

¹*Department of Physical Chemistry II, Ruhr University Bochum, 44801 Bochum, Germany*

Hydrogen bonding is a central concept in chemistry and biochemistry and so it continues to attract intense study. Here, we examine hydrogen bonding in the H₂S dimer, in comparison with the well-studied water dimer, in unprecedented detail. We record a mass selective IR spectrum of H₂S dimer in superfluid He nanodroplets. We are able to resolve the rotational substructure of each of the three distinct bands and assign these to the vibration-rotation-tunneling transitions of the para-para, ortho-para, and ortho-ortho dimer of a single IR vibration. Based on a high-level potential energy and dipole moment surfaces, we compute the vibration-rotation-tunneling dynamics and far-IR spectrum with rigorous quantum methods. Calculated rotational constants of the ortho-para H₂S dimer are found to be in good agreement with previously measured microwave values. Six intramolecular mode VSCF/VCI calculations provide the fundamental frequencies and intensities of the four SH-stretch modes, with a focus on the most intensive, the donor bound SH mode which is experimentally observed. Dissociation energies, D_0 , of the para-para, ortho-para, and ortho-ortho nuclear spin isomers of H₂S dimers are predicted; for para-para also from Diffusion Monte Carlo calculations in full dimensionality. Based on our results, we propose a substantially increased delocalization and strong mixing of intermolecular modes compared to the water dimer. The less directional nature of the hydrogen bonding can be quantified in terms of weaker electrostatic and more important dispersion interaction. The present study reconciles all previous spectroscopic data, serves as a sensitive test for the potential energy and dipole moment surface.

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Email: martina.havenith@rub.de

Spectroscopy Identification of Hemi-bonded Structure of Water Cation Clusters in Helium Droplets

Arisa Iguchi^{1,2}, Amandeep Singh³, Stefan Bergmeister⁴, Andrew A. Azhagesan³, Kenta Mizuse⁵, Asuka Fujii⁶, Hajime Tanuma¹, Toshiyuki Azuma², Paul Scheier⁴, **Susumu Kuma**² and Andrey F. Vilesov³

¹Tokyo Metropolitan University, Tokyo, Japan

²RIKEN, Saitama, Japan

³University of Southern California, Los Angeles, US

⁴Universität Innsbruck, Innsbruck, Austria

⁵Kitasato University, Sagamihara, Japan

⁶Tohoku University, Sendai, Japan

The ionization in water is an essential process in various chemical environments. Understanding the fate of H_2O^+ and e^- in the presence of surrounding water molecules is of fundamental interest. Ionic water clusters have been targets of such studies to elucidate the structures of excess-charged species. Previous theoretical calculations suggested that two key motifs of the $(\text{H}_2\text{O})_n^+$ cation are the well-known proton-transferred (PT) structure ($\text{H}_3\text{O}^+\cdot\text{OH}$) and the metastable hemibonded (Hemi-) structure $(\text{H}_2\text{O}\cdot\text{OH}_2)^+$. The existence of the latter, where two H_2O moieties share the excess charge with a bond order of $1/2$, is the crucial question in understanding the mechanism of forming a hydrogen bond network in ionized water. However, due to a significant potential barrier between the PT and Hemi structures, the existence of the Hemi-type water dimer cation has not been obtained clearly.

In the present study [1], we performed infrared spectroscopy of the water dimer cation $(\text{H}_2\text{O})_2^+$ in the helium droplet produced by ionization of the neutral water dimer. We observed the OH stretching bands and identified the molecular structure of $(\text{H}_2\text{O})_2^+$ by their spectra. In addition to the proton transfer type observed by the tagging method previously, we obtained new vibrational peaks corresponding to the Hemi-type $(\text{H}_2\text{O}\cdot\text{OH}_2)^+$. This finding indicates that a metastable Hemi-structure was realized in the droplet by rapidly cooling the dimer cation. The extension to larger water cation clusters $(\text{H}_2\text{O})_n^+$ ($n \geq 3$) provides the further information on the ionized water network.

[1] A. Iguchi, A. Singh, S. Bergmeister, A. A. Azhagesan, K. Mizuse, A. Fujii, H. Tanuma, T. Azuma, P. Scheier, S. Kuma and A. F. Vilesov, *J. Phys. Chem. Lett.* **14**, 8199 (2023).

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Solvation of alkali ions in helium droplets: an atomistic perspective on the mechanisms and associated time scales

F. Calvo

Laboratoire Interdisciplinaire de Physique (LiPhy), CNRS & Université Grenoble Alpes, France

Abstract: The post-ionization solvation of heliophobic alkali atoms in contact with helium droplets was recently investigated experimentally [1] by pump-probe spectroscopy, using an auxiliary, heliophilic xenon ion as a repelling center. In the present contribution, the experimental system has been theoretically modeled through the various ionization and solvation steps, up to the ejection of the alkali possibly solvated by a number of helium atoms, using ring-polymer molecular dynamics simulations employing accurate interaction potentials for the sodium and potassium cases. With the aim to provide a statistical picture of the ejection of the microsolvated alkali ion, we notably examine the time-dependent mechanisms of how the solvent coats the ion at the earliest stages following ionization, and find that the solvation is concomitant with a significant diving of the ion inside the droplet. Compared to sodium, the greater heliophilic character of potassium leads to smaller solvation shells upon ejection.

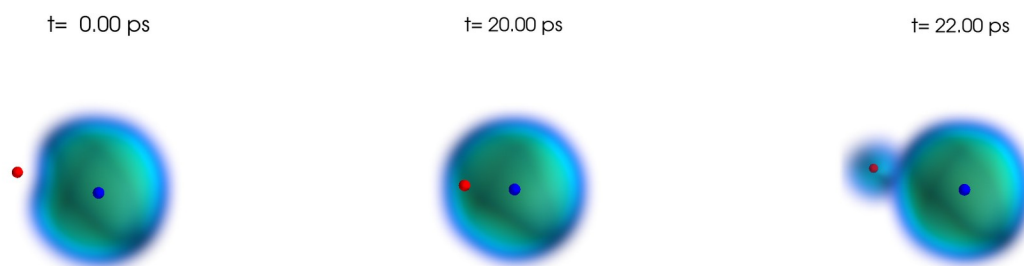


Fig 1. Ionization of a sodium atom (in red) in contact with a 1000-atom helium nanodroplet, followed after 20 ps by the ionization of the xenon atom (in blue), as simulated using ring-polymer molecular dynamics simulations

References:

1. S. H. Albrechtsen *et al.*, *Nature* (2023), **623**, 319.

Infrared Spectroscopy of Mass/Charge Selected Cations and Anions in Helium Droplets

América Y. Torres-Boy, Katja Ober, Gerard Meijer and **Gert von Helden**

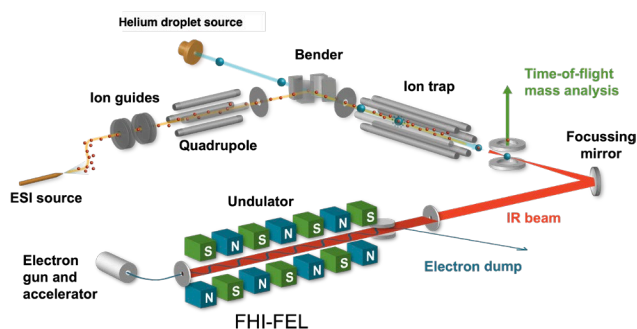
Fritz Haber Institute of the Max Planck Society, 14195 Berlin, Germany

Helium droplets can pick up mass/charge selected ions from an ion trap and the doped droplets can be investigated using optical spectroscopy. We use that technique to investigate cations and anions ranging in size from ions containing only a few atoms up to mass/charge selected protein ions containing several thousand atoms. The figure below shows a schematic of the experimental setup. Ions are generated using a nano electrospray source. After mass/charge selection using a

quadrupole, ions are injected and stored in an ion trap. Helium nanodroplets, generated by a cooled pulsed valve, are then allowed to traverse the trap. The droplets travel at a beam velocity of ≈ 500 m/s and even relatively small droplets containing only a few hundred helium atoms have a kinetic energy that is higher than the longitudinal trapping potential of the ion trap.

When a droplet picks up an ion via mechanical impact, the ion will be cooled to the equilibrium temperature of the droplet (0.4 K), and the ion doped droplet can exit the trap. Doped droplets are irradiated using tunable IR light from the FHI free electron laser. After resonant absorption of multiple photons, droplets evaporate and the bare ion is detected in a time of flight mass spectrometer. Plotting the IR yield as a function of IR frequency gives an IR spectrum. The droplet evaporation process involves the absorption of many IR photons. Results from kinetic modeling of the absorption/evaporation process will be presented.

During the presentation, several systems will be discussed. Among them is the proton-bound dimer of dihydrogen phosphate and formate for which high resolution IR spectra were recently measured. The results show that, contrary to the initial expectation that the stronger phosphoric acid would donate a proton to formate, both experiment and theory show that all exchangeable protons are located in the phosphate moiety. Some H-bending modes of the non-deuterated complex are found to be sensitive to the helium environment. In the case of the partially deuterated complexes, the experiments indicate that internal dynamics leads to isomeric interconversion upon IR excitation.



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Characterization of Diamondoid Clusters Formed In Helium Nanodroplets

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Abstract: Diamondoids are versatile building blocks in nanomaterial design, but only recently the field expanded to preparation and study of diamondoid covalent assemblies, *i.e.*, molecules composed of diamondoid cage subunits connected by a heteroatom.¹ Spontaneous self-assembly of diamondoid derivatives is known to be strongly influenced by intermolecular London dispersion interactions. We therefore investigated diamondoid agglomeration in helium nanodroplets (HNDs) as that is a medium suitable for characterizing weakly-bound supramolecular clusters.^{2,3} We confirmed that organization of diamondoid covalent assemblies in HNDs was indeed predominantly governed by dispersion when derivatives of low polarity (hydrocarbons and ethers)² were studied, whereas introduction of more polar functional groups to diamondoid scaffolds³ resulted in a formation of more complex nanostructured supramolecular networks. By combining experimental results with a computational analysis we gained deeper insights into the forces governing self-organization and agglomeration behavior of diamondoids, which has important implications for their use in nanotechnology.

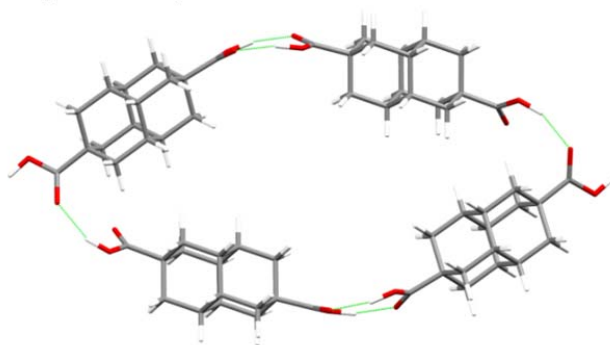


Fig 1. Computed cyclic assembly of 4,9-diamantanedicarboxylic acid molecules formed in HNDs

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Modelling catalytic processes:

Structure and reactivity of metal clusters in superfluid helium nanodroplets

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Gas-phase metal clusters present a significant opportunity for probing catalytic processes at the molecular level. They afford precise control over the structure, charge, and composition of catalytically active sites, thereby enhancing activity compared to bulk metal due to their small size, high surface-to-volume ratio, and size-dependent physical and chemical properties.^[1]

This study focuses on investigating the structure and reactivity of coinage metal clusters (Cu, Ag, Au) formed within multiply-charged superfluid helium nanodroplets to elucidate fundamental catalytic mechanisms. Given the strong influence of active site structure on catalytic activity, we examine the structures of positively and negatively charged metal clusters with sizes up to ten atoms. These clusters are meticulously solvated in helium, and the resulting complexes are analyzed using mass spectrometry. Computational analysis of the most stable complexes aids in estimating cluster structures.^[2]

Furthermore, charged clusters are reacted with molecules of interest, such as CO₂ or acetylene, to unravel their size-dependent reactivity. IR photo detachment spectroscopy of helium-tagged complexes^[3], play a crucial role in unravelling the intricate details of the cluster-molecule interactions providing direct insights into the structural arrangement and bonding nature of the molecules bound to the clusters.

Our comprehensive understanding of these properties not only advances fundamental knowledge of catalysis at the nanoscale but also provides insights into the rational design of efficient and selective catalysts for chemical transformations.

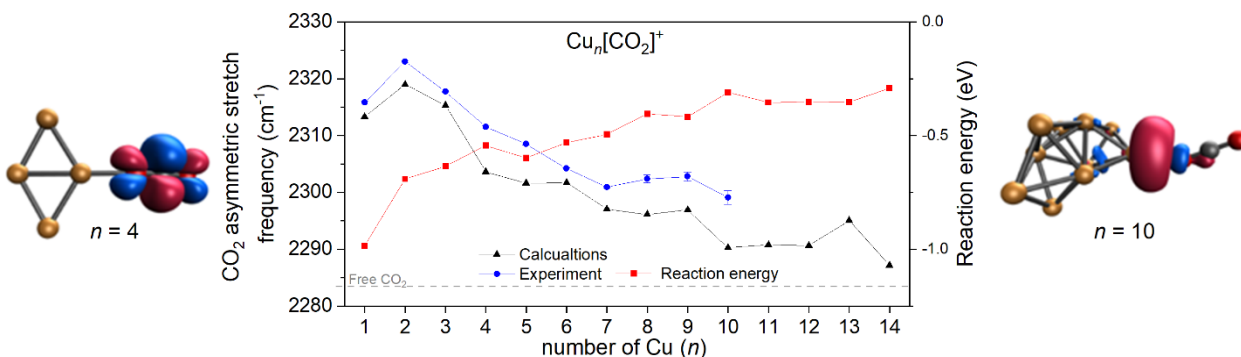


Fig.1: The frequency of the asymmetric stretch vibration of CO₂ bound to copper clusters of different sizes (n), obtained experimentally (blue circles) and computationally (black triangles). The dashed line represents the frequency for free CO₂. Additionally, the binding energy of CO₂ to each cluster is depicted with red squares. Geometric structures for selected configurations are also presented.

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Helium-Tagged Molecular Ions

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Our latest findings on helium-tagged molecular ions will be presented. As this is an 'introductory talk', it will be shown how these ions are produced by electron ionization of molecule-doped helium nanodroplets and then probed using infrared photodissociation spectroscopy, using essentially a standard helium nanodroplet/laser spectroscopy setup. The focus will then switch to small ions and how their spectroscopic properties change as the number of helium atoms added is altered. This will include the ions H_3O^+ , H_2O^+ and CH_3^+ . All three ions show significant changes in their spectra as the number of helium atoms is varied. This is most dramatic in the case of H_3O^+ , where the two rotational constants of the core molecular ion undergo a reversal in magnitude as the number of helium atoms is increased. This rotational decoupling response appears to be related to shell closures of the helium around the H_3O^+ and, as will be shown, hybrid path integral molecular dynamics/Monte Carlo calculations can reproduce this behaviour quite accurately.

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Probing singly and multiply charged atomic and molecular ion species within helium nanodroplets

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Helium nanodroplets are an exciting and versatile matrix, facilitating the efficient trapping and cooling of dopants from the gaseous phase. These nanodroplets enable the investigation of the spectroscopic properties of cold atoms, molecules, and clusters—both neutral and charged—at temperatures below 1K. Moreover, the unique properties of helium nanodroplets allow for the stabilization and examination of transient and metastable species, typically inaccessible in conventional experimental setups due to their short-lived nature.

In this contribution, we demonstrate that multiply charged helium nanodroplets can be used to efficiently form helium tagged molecular ions, which allows to perform messenger-type spectroscopy. Upon photoabsorption, the loosely bound helium tag is evaporated, and the resulting photofragment is detected using a time-of-flight mass-spectrometer. This method yields a practically background-free signal, ensuring a high signal-to-noise ratio and producing high-quality spectra even for weak absorption lines at reduced data acquisition times [1,2].

Furthermore, we will discuss the capability of multiply charged helium nanodroplets to generate multiply charged dopant ions of low stability. The presence of multiple charge centres within a single helium nanodroplet, located near the surface, makes them accessible to subsequent interaction with metastable helium atoms. This process leads to the post-ionization of singly charged ions and the formation of multiply charged atomic, molecular or cluster ions [3-5]. This novel methodology paves the way for exploring the formation, stability, and spectroscopy of highly charged metastable species.

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Electronic Quantum State Dynamics in Helium Droplets traced by Coherent Diffractive Imaging

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Single-Shot Coherent Diffractive Imaging (CDI) has become a mature tool to capture the structure and dynamics of nanoscale systems such as viruses, nanoparticles and helium droplets in free flight. The conventional application of the underlying single-shot imaging implies that the imaging pulse interacts instantly and perturbatively with the target such that the diffraction image reflects the target shape and (unperturbed) optical properties via the linear-response field propagation through (and around) the target. Especially the advancing capabilities of intense XUV light sources render the question important, at which point non-linear quantum state dynamics driven by the imaging pulse become significant. In this talk I will discuss an attempt to tackle this question theoretically by means of scattering simulations that include field propagation and local quantum state dynamics for the example of Helium droplets [1]. It will be shown for the example of resonantly driven Helium droplets that the departure from the strictly linear regime may open up a wide range of opportunities to track and drive quantum state population dynamics [2]. Options for associated new metrologies in the field of CDI will be discussed.

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Photoelectron dynamics in alkali-doped He nanodroplets and nanoplasmas - correlated and collective processes

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In the paradigmatic quantum fluid clusters, He nanodroplets, we probed the correlated dynamics of electrons when they are doped with alkali atoms following extreme ultraviolet photoexcitation [1]. Quite remarkably, in this two-component system when He is either photo-excited or -ionized directly, the system undergoes a cascade of interatomic Coulombic decay (ICD) steps as it relaxes and fragments [2]. Electron-ion-ion coincidence spectroscopy reveals intriguing ICD pathways for very efficient the multiple ionization of the doped alkali cluster involving their inner-valence ionization.

Secondly, when these alkali doped clusters are subjected to intense near-IR femtosecond pulses leading to massive ionization of a nanodroplet into a nanoplasma, collective electron-ion dynamics dominates the progression of this system. The evolution of this nanoplasma involves dynamics from the femto- to nano-second timescales. Through single-shot coherent diffraction imaging enabled by x-ray free-electron lasers, here FLASH at Hamburg, in combination with photoelectron imaging, our work reveals contrasting expansion dynamics for the surface-resident alkali atoms in contrast to rare-gas dopants which reside in the droplet interior.

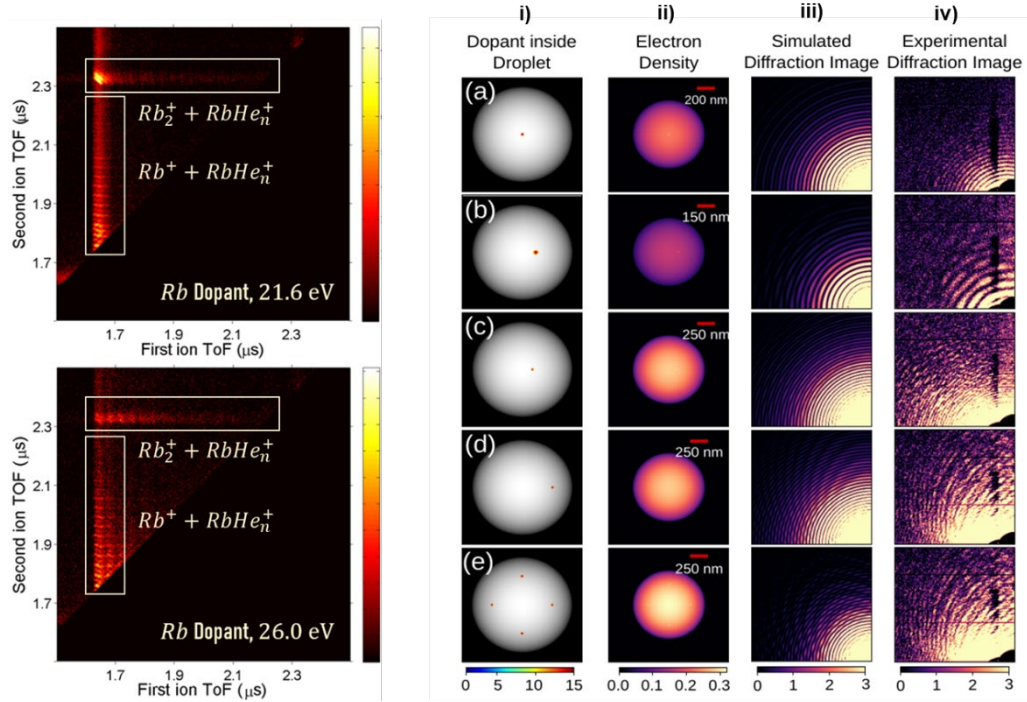


Figure 1: (*left panel*) Ion-ion time-of-flight coincidence maps displaying the correlated double ionization of dopant alkali, here Rb, photoions results from correlated interatomic Coulombic decay cascade when hosted on He nanodroplets. (*right panel*) A series of experimentally observed coherent diffractive imaging images, column iv) alongside the

corresponding simulated image, column iii), originating by considering the geometry shown in column i) of the dopant Xe cluster (red dot) positions in a He nanodroplet (grey sphere); the electron density map of each configuration in column i) is depicted in column ii).

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- [3] B. Langbehn *New Journal of Physics* 24.11 (2022): 113043.
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Intramolecular dynamics vs solvation dynamics in the case of molecules deposited on argon clusters

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Deposition of molecules on argon cluster is a method of choice to model experimentally the solvation dynamics of excited species¹. Here, we present the dynamics of two types of molecules in such environment. First, 1,4-Diazabicyclo(2.2.2)octane (DABCO), which is a model molecule. It was excited in the first excited state, a long-lived state. A complex multiscale dynamics is observed. It reveals subtle couplings between the clusters and the molecule². Second, a series of dithienylethene molecules were investigated because they have photochromic properties. The latter are due to an intramolecular electrocyclic reaction. The corresponding dynamics is largely documented in the literature in various environments: gas phase, liquid phase and crystalline phase. The present study within finite size argon clusters enlightens the dynamical role of the solvent, explaining differences observed in the dynamics between the different phases³.

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Structure and field-induced dynamics of small helium clusters

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Small helium clusters are peculiar few body quantum systems. The helium dimer has a single weakly bound state of a huge spatial extent. About 80% of its probability distribution resides in the classically forbidden tunneling region [1]. This is why such objects are termed “quantum halos”. The helium trimer has two bound states, excited one of which is of Efimov nature [2]. We utilize laser-triggered Coulomb explosion imaging for measuring spatial probability distributions of these quantum objects. Application of an additional laser pulse in a pump-probe manner allows us to observe the structural picosecond response dynamics of small helium clusters upon interaction with a strong laser field.

The results on He₂ [3], He₃ as well as HeNe dimer will be discussed.

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Interatomic Coulombic decay in excited large pure He nanodroplets

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Ionization of matter by energetic radiation generally causes complex secondary reactions which are hard to decipher. Using high-resolution electron spectroscopy, we report here on observation of an indirect ionization process—Interatomic Coulombic Decay (ICD) [1]—in large He nanodroplets irradiated by weak synchrotron radiation. It is based on the formation of two excited He atoms in the He nanodroplets following absorption of EUV photons of either low $h\nu$ energies near the He ionization potential (IP) or high $h\nu$ energies lying above the He photoelectron impact excitation threshold— $h\nu \geq 44.4$ eV. For sufficiently low $h\nu$ near the He IP, formation of the two excited He atoms is due to two $h\nu$ absorption events by the He nanodroplets [2]. For high $h\nu \geq 44.4$ eV, photoelectron impact excitation and electron-He⁺ recombination are responsible for the formation of the two excited He atoms [3]. While the first excited atom is formed just via impact excitation driven by the primary photoelectron, the second excited atom is a result of electron-atom collisions and friction-induced slowdown of the inelastically scattered electron until it gets re-captured by the original residual ion (See Fig. 1). The correlated decay—ICD—of the pair of excited atoms formed at $h\nu \geq 44.4$ eV produces a characteristic ICD electron signal. We find that this ICD becomes the dominant process of electron emission in nearly the entire EUV range in droplets with radius ≥ 40 nm. It likely plays an important role in other dense systems exposed to ionization radiation as well, including biological matter.

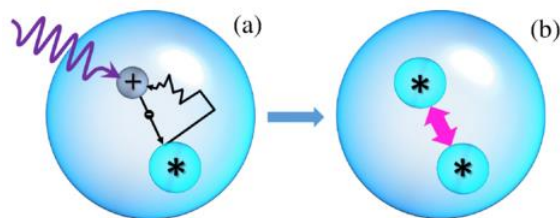


Fig 1. Illustration of ICD mechanism in He droplets induced by photoelectron impact excitation and electron-He⁺ recombination (a), leading to two He excitations which subsequently decay by ICD (b).

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Real-Time Tracking Mg Cluster Formation Inside He Droplets: Energy Pooling and Ion Ejection

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Abstract: Time-resolved covariance photoelectron and -ion spectroscopy allowed us to observe the photoinduced formation of Mg clusters from an initially dilute, foam-like aggregate of Mg atoms inside liquid helium droplets. Here, we propose a detailed description of the photo-formation process including the dynamics of the involved electrons and atoms. Photo-formation is initiated by photoexcitation at 282.5 nm, under conditions to photoexcite multiple Mg atoms within the aggregate. During cluster formation, the energy of two or more Mg* atoms can be pooled (Fig. 1a) by collisions between Mg and He atoms: One excited and one ground state Mg atom collide to form an excited state Mg* dimer. The dimer then interacts with another excited Mg* atom to form highly excited Mg* atoms or an excited Mg₃ cluster with excess nuclear kinetic energy. Ionization with the probe pulse subsequently produces electrons and ions with energies reflecting the population of the different vibronic states of the nascent Mg cluster. The excess kinetic energy due to energy pooling and probe ionization leads to fragmentation of some clusters. Very fast ionic fragments will leave the droplet solvation potential, making them available for covariance detection. The photoelectron spectra associated with different ionic fragments are shown in Fig. 1b. Here, the mean electron kinetic energy is proportional to the detected fragment size, indicating that electronic energy is converted into kinetic energy of the fragments. The average size of the detected ions also decreases over time, pointing to fragmentation of the neutral photo-formed magnesium clusters.

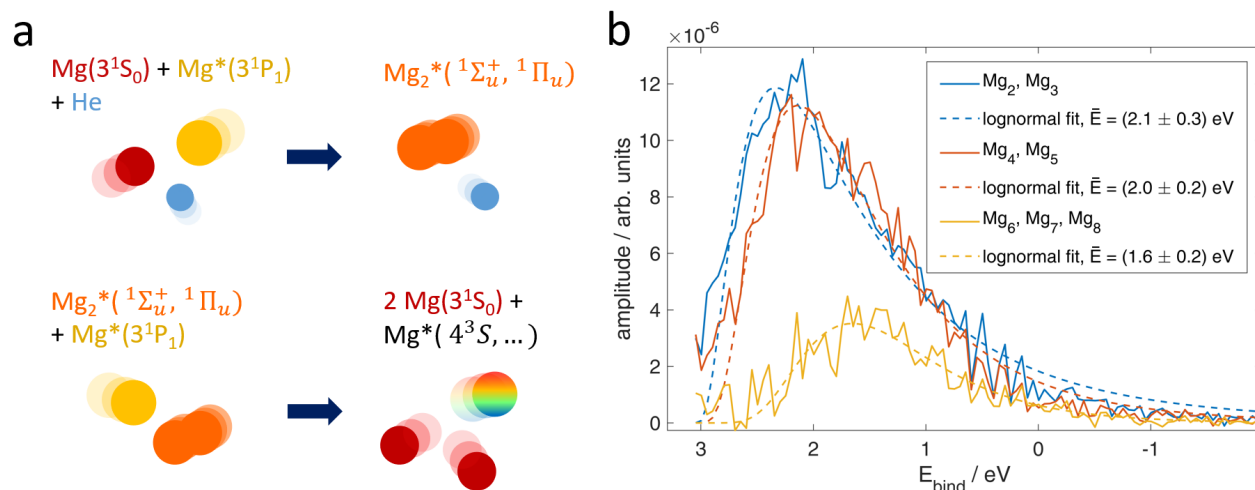


Fig 1. a) The energy pooling process involving two excited Mg* atoms: He-mediated Mg-Mg* collision leads to Mg₂* formation. Subsequently, the excited dimer collides with another excited Mg* atom, leading to highly excited Mg* population and release of kinetic energy.

b) Photoelectron spectra (time-integrated from 0.1 ps to 5 ps) correlated with different Mg cluster masses are shown, indicating a decrease of mean electron kinetic energy as the ion cluster size decreases.

Real Time Dynamics Simulation of Pure and Doped Helium Nanodroplets using ^4He -TDDFT

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The time-dependent dynamics of doped or pure helium nanodroplets poses numerous challenges due to the highly quantum nature of this unusual “solvent” and to its eminent superfluid properties. Helium Time-dependent Density Functional Theory (^4He -TDDFT), which describes the time evolution of the helium density rather than that of the many-body wave function, results from a compromise between accuracy and feasibility. It has emerged as a powerful tool to simulate and help understand many experimental results over the years.[1]

In this Introductory Lecture the method will be presented, focusing on its recent and future applications in our groups. These include

- Nanodroplet collisions as a possible alternative mechanism to nucleate vortices[2]
- A direct view on time-dependent ion solvation[3, 4]
- Coulomb explosion of dialkali molecules on the droplet surface
- Pickup and clustering inside helium droplets[5]

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Angular momentum of small molecules: quasiparticles and topology

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I will present our recent findings on small molecules kicked by laser pulses. First, I will describe a technique that allows to probe highly excited molecular states in the presence of an environment, such as superfluid ^4He , and a corresponding theory based on angulon quasiparticles that is capable of describing such states, in good agreement with experiment.

Second, I will show how that even the simplest of existing molecules - closed-shell diatomics not interacting with one another - host topological charges when driven by periodic far-off-resonant laser pulses. A periodically kicked molecular rotor can be mapped onto a "crystalline" lattice in angular momentum space. This allows to define quasimomenta and the band structure in the Floquet representation, by analogy with the Bloch waves of solid-state physics. In such a momentum space we predict the occurrence of Dirac cones with topological charges, protected by reflection and time-reversal symmetry. These Dirac cones -- and the corresponding edge states -- are broadly tunable by adjusting the laser strength and can be observed in present-day experiments by measuring molecular alignment and populations of rotational levels. This paves the way to study controllable topological physics in gas-phase experiments with small molecules as well as to classify dynamical molecular states by their topological invariants.

Rotational Control of Helium Dimers in Superfluid Helium

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I will discuss our recent results on coherent excitation and coherent control of metastable helium dimers (He_2^*) inside bulk superfluid helium by means of shaped ultrashort laser pulses. I will present an experimental study of the laser-induced rotation of helium dimers inside the superfluid ^4He bath at variable temperature. The coherent rotational dynamics of He_2^* is initiated in a controlled way by ultrashort laser pulses, and tracked by means of time-resolved laser-induced fluorescence. We detect the decay of rotational coherence on the nanosecond timescale and investigate the effects of temperature on the decoherence rate. The observed temperature dependence suggests a non-equilibrium evolution of the quantum bath, accompanied by the emission of the wave of second sound [1].

I will also report on the experimental demonstration of the rotational control of helium dimers by a periodic sequence of linearly polarized femtosecond pulses (a pulse train). We show that the degree of rotational excitation of He_2^* can be enhanced or suppressed by varying the period of the pulse train, whereas the directionality of molecular rotation can be controlled by the relative angle between the polarization vectors of pulses in the train [2].

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Femtosecond timed imaging of rotation of alkali dimers on the surface of helium nanodroplets

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Alkali dimers, Ak_2 , residing on the surface of helium nanodroplets, are doubly ionized by an intense fs laser pulse leading to Coulomb explosion into two Ak^+ fragment ions. We show that the kinetic energy of these fragment ions can be used to identify if the dimers were initially populated in the $X\ ^1\Sigma_g^+$ ground state or in the lowest-lying triplet state $a\ ^3\Sigma_u^+$ [1, 2]. We use the quantum-state-sensitive detection to investigate rotational dynamics of dimers in either the X or in the a state.

The work presented here focuses on the time-dependent alignment of Na_2 , K_2 , and Rb_2 on He nanodroplet surfaces. The dimers are set into rotation by a 1 ps alignment pulse and their instantaneous spatial orientation measured by Coulomb explosion with an intense delayed 50 fs probe pulse. The measured alignment traces show distinct periodic features that differs qualitatively from that expected for freely rotating gas phase molecules. Instead, the observed alignment dynamics of Na_2 (see Fig. 1) and of K_2 in the $a\ ^3\Sigma_u^+$ state agree with that obtained from a 2D rigid rotor model, strongly indicating that the rotation of each dimer occurs in a plane – defined by the He droplet surface [3, 4].

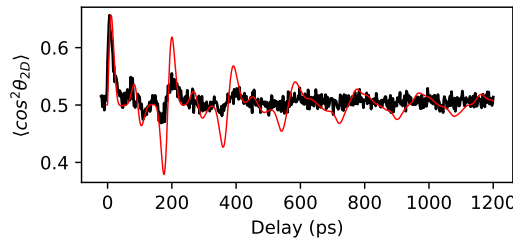


Figure 1: Time-dependent degree of alignment for Na_2 in the $a\ ^3\Sigma_u^+$ state (black) and the expected alignment trace from a 2D rigid rotor model (red) with inhomogeneous broadening.

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Rotational anisotropy decay as a tool to characterize the size distribution of doped rare-gas cluster beams

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Size-dependent effects are of particular interest in cluster physics. While precise size-dependent studies can be conducted for charged cluster species, determining the size of neutral clusters remains a challenge. Empirical models exist to predict the mean cluster size in a cluster beam based on expansion parameters [1]. However, in our experiments we are interested in the interaction between dopant molecules and cluster species. In this case, it is not clear how the size distribution of the doped clusters can be inferred from the empirical models. Effects such as evaporative cooling after doping, dopant pick-up and sticking probabilities can lead to differences in the size distribution between the initial cluster beam and the doped clusters. We present a promising method to determine the doped cluster size distribution by measuring the decay of rotational anisotropy in a femtosecond pump-probe experiment (see Fig. 1a). The dephasing rate of the initially observed anisotropy is related to the doped cluster size distribution as different distributions lead to different ensembles of rotational frequencies. Challenges, like low sample density in the gas phase and dominating linear background signals are overcome by phase-modulation and lock-in detection [2]. Preliminary results suggest a high sensitivity on the cluster size of ± 50 atoms (see Fig. 1b). The approach is applicable to continuous and pulse beam expansion conditions.

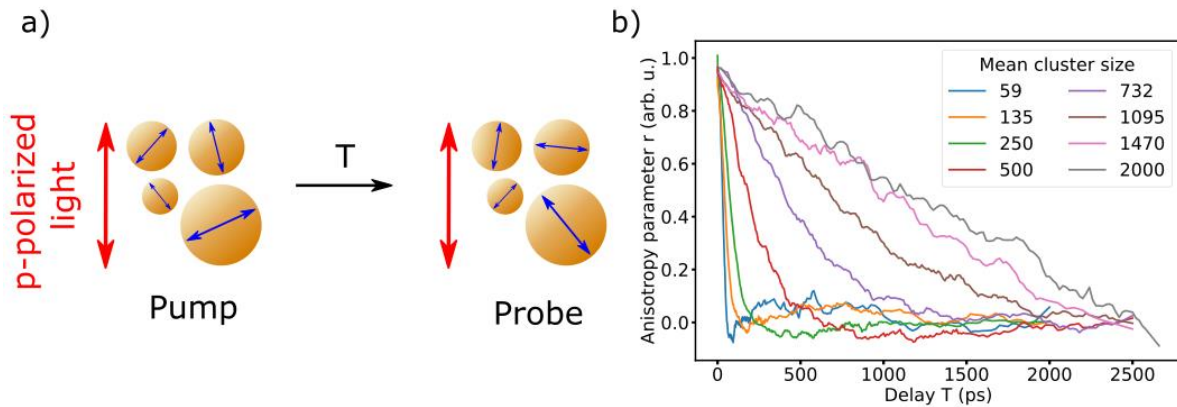


Fig 1. (a) Dephasing of the initially excited dipole moments, indicated by the blue arrows on the clusters. (b) Decay of the anisotropy parameter for argon clusters with a mean cluster size between 60 and 2000 atoms.

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Photodissociation and Photoassociation inside He Nanodroplets

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Helium nanodroplets (He_N) provide promising opportunities to explore the dynamics of photochemical reactions in the time domain, in particular for aggregates that are otherwise difficult to form. Time-resolved photoelectron spectroscopy has proven to be a valuable method for following the electronic population dynamics of dopants inside He_N . In contrast, insight into nuclear structure dynamics of dopants is usually veiled in He_N due to the large solvation energy of ions which prevents their detection. Ion solvation also impedes electron-ion coincidence techniques, which would provide unique insight into fragmentation processes and the underlying conversion of electronic into nuclear energy.

Ion ejection from droplets can, however, be facilitated by supplying additional kinetic energy, for example, through resonant excitation of nonbonding ionic states, as recently demonstrated for In_2^+ [1]. Ionization to dicationic states with strong Coulomb repulsion presents another way to supply the ions with sufficient kinetic energy to overcome the droplet solvation potential. This approach naturally leads to Coulomb explosion imaging (CEI), a technique that directly measures the interatomic distance of two cations. We apply CEI to study the photodissociation of iodine (I_2) excited above the A-state dissociation limit inside helium droplets. The time-dependent ion velocity distributions inform about the kinetics of the dissociating I atoms within the droplet, including deceleration in the neutral and cationic state and respective solvation energies.

In a third example, the photoinduced formation of van der Waals clusters from a metastable, foam-like aggregate of Mg atoms is presented, with focus on underlying energy transfer processes. Energy pooling of several photoexcited Mg^* atoms populates highly-excited Mg states and yields energy transfer to kinetic degrees of freedom. The additional kinetic energy released during the cluster formation process in combination with probe photon energy facilitates cluster fragmentation and ion fragment ejection from the droplet. The covariance detection of electrons with ejected ions allows us to separate the photoinduced cluster formation process from the concurrent photoexcitation dynamics of initially dense clusters, which are present in some of the droplets. Only due to this separation we gain insight into parameters like cluster formation time, energy flow to highly excited states and electronic-to-nuclear energy conversion.

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The primary steps of ion solvation in helium nanodroplets

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Recently, we have obtained experimental results on the solvation dynamics of a single alkali cation in liquid helium, measured with atomic resolution and with femtosecond time resolution [1].

A single Na, K or Li atom sitting in its equilibrium position on the surface of a He nanodroplet is ionized by a 50 fs laser pulse. Thereby, an alkali ion, Ak^+ , is introduced instantly to the liquid helium solvent from the gas phase. Hereafter, the Ak^+ ion will gradually pick up helium atoms to form a solvation complex, Ak^+He_n . After a time delay, a Xe atom, residing in the interior of the droplet, is ionized by a 50 fs probe pulse. The created Xe^+ ion pushes the Ak^+He_n complex away from the droplet, due to the internal Coulomb repulsion. The mass and velocity of all Ak^+He_n complexes are recorded by the combination of a Velocity Map Imaging (VMI) spectrometer and a Tpx3CAM detector.

We find that the distribution of attached helium atoms is Poissonian for the first few helium atoms. The first 3 helium atoms for Li^+ , the first 5 atoms for Na^+ and the first 11 atoms for K^+ all attach at a constant rate of 1.8 He/ps, in droplets containing 5200 helium atoms on average. This is in good agreement with TDDFT simulations of the process. The time-dependent mean dissipated energy from the complexes to the droplet have also been extracted from the same measurement. Finally, a novel analysis of the detected Ak^+He_n kinetic energies provide droplet size resolution of the above results.

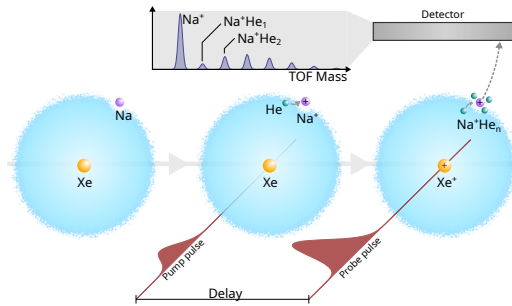


Figure 1: Schematic figure showing the principle of the experiment. Solvation of the Na cation is started by the pump pulse, and the solvation complex is ejected when the probe pulse ionizes the Xe atom in the interior. The time dynamics of the number of He atoms attached to the Na^+ ion can thereby be measured.

Light-induced ultrafast dynamics of molecules in helium nanodroplets

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The newly developed reaction microscopy of helium-nanodroplet (He_N) target recoil ion momentum spectroscopy (He_NTRIMS) allows us to explore the ultrafast dynamics of in-droplet molecules driven by femtosecond laser pulses [1,2], where the electrons and ions ejected from an in-droplet molecule are measured in coincidence.

By performing pump-probe experiments in the He_NTRIMS , we capture in real time the collision-induced ultrafast dissipation of vibrational nuclear wave packet dynamics of D_2^+ ion embedded in a He_N [3]. Our results show that, differing from the behaviors of the in-droplet neutral molecules, the charged ions in the He_N interior strongly couple to the He solvent via ion-He collisional interactions, leading to the extremely fast collisional dissipation dynamics within $\sim 140\text{fs}$. Our findings underscore the crucial role of ultrafast collisional dissipation in shaping the molecular decoherence dynamics during solution chemical reactions, particularly when the solute molecules are predominantly in ionic states.

Furthermore, we explore the spatial scale of the matter wave of a cold molecule with respect to the He_N by diagnosing the angular nodal structures in the photoelectron momentum distributions (PMDs). The preserved and nodal structures in the PMDs allows us to identify and characterize the delocalization of the lightest H_2 and localization of heavier D_2 and O_2 molecules, whose de Broglie wavelength is comparable to or smaller than droplet size.

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Proton-Bound Ionic Systems: Insights from Infrared Action Spectroscopy in Helium Droplets

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Abstract: Infrared (IR) Action Spectroscopy in Helium Droplets of isolated molecular ions and ionic clusters has been proven to be an effective technique for the experimental characterization of molecular systems.[1] Because the ions are examined at the equilibrium temperature of the helium droplet (0.37 K), this method presents a significant advantage greatly reducing the spectral congestion.

This study employs cryogenic action spectroscopy to investigate the proton-bound dimer of dihydrogen phosphate and formate ($[\text{H}_2\text{PO}_3 + \text{H} + \text{HCOO}]^-$). Experimental observations show that all three exchangeable protons are located within the phosphate unit. This finding contradicts expectations based on proton affinity and pK_a values, where the stronger phosphoric acid is expected to transfer a proton to the formate unit. Some H-bending modes of the non-deuterated complex are found to be sensitive to the helium environment. In the case of the partially deuterated complexes, the experiments indicate that internal dynamics lead an interconversion process between these two Isotopomers inside the He droplet after photon excitation.

The elucidation of each vibrational band, the hydrogen-bond interactions between the two moieties and spectroscopic details of each deuterated form of the complex is thoroughly examined and discussed.

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Investigation of the reactivity of gold clusters via He tagging spectroscopy

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Modern chemistry lays special emphasis on the understanding and advancement of catalytic performance by unveiling the basic steps of catalytic reactions. Gas-phase metal clusters offer a promising potential for gaining an in-depth view of the energetics and kinetics of bond-making and bond-breaking process in catalytic reactions at the molecular level.^[1] Additionally, the high surface-to-volume ratio and the high number of uncoordinated sites of clusters can enhance the catalytic potential of metals compared to their bulk configurations.

A vivid example of such behaviour is gold. A noble metal in bulk, prized for its inertness, can become a potent catalyst when reduced to small enough particles, as demonstrated by examples involving CO and various hydrocarbons.^[2] When particles consist of only a few atoms (clusters), each atom becomes significant, and clusters exhibit size-dependent properties.

This work focuses on investigating the structure and size-dependent reactivity of small cationic gold clusters Au_n^+ ($n = 1-5$), which are formed within multiply-charged superfluid helium nanodroplets and furthermore reacted with carbon dioxide (CO_2)_x ($x = 1-4$) or acetylene (C_2H_2)_y ($y = 1-4$). These complexes are solvated with helium, unclosing the possibility to employ IR photodetachment spectroscopy of the He-tagged cluster ions.^[3]

The experimentally obtained IR spectra are complemented by in-house computational analysis. This synergy not only enables a deeper understanding of the cluster-molecule interaction, including structural arrangement and bonding characteristics, but also serves as a benchmark for existing computational methods.

The gathered information on these cluster-molecule complexes will further broaden the understanding of catalysis at the nanoscale, laying the foundation for future designs of efficient and selective catalysts for chemical reactions.

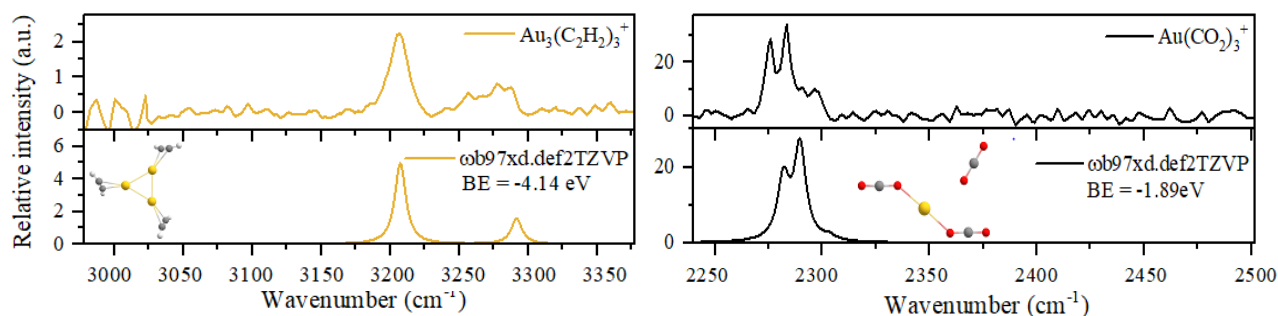


Fig. 1: IR spectrum of $\text{Au}_3(\text{C}_2\text{H}_2)_3^+$ (dark yellow) and $\text{Au}_3(\text{CO}_2)_3^+$ (black) showing the asymmetric stretch vibration of C_2H_2 and CO_2 , respectively. The experiment is supported by quantum chemical calculations at $\omega\text{b97xd.def2TZVP}$ level of theory, providing insight into the structure and the binding energy (BE) of both complexes.

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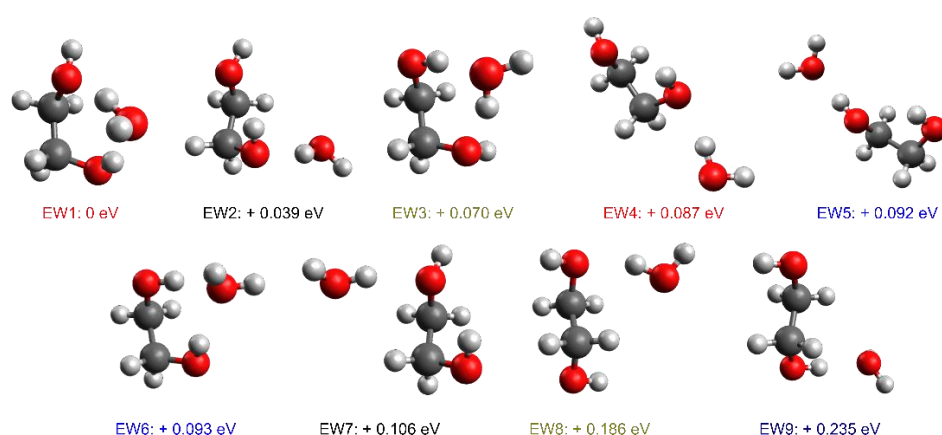
Infrared Spectroscopy of Ethylene Glycol and Ethylene Glycol Water Clusters in Helium Nanodroplets

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Ethylene glycol is the simplest sugar alcohol and is theorised to be important in the formation of life as a precursor to simple sugars like glycolaldehyde.¹⁻³ Ethylene glycol has been found in both the interstellar medium and on comets forming in interstellar ices.³ It has been shown that interactions with water affect the chemical dynamics of ethylene glycol necessitating further investigations.² Here, helium nanodroplets were utilised for their superfluid properties at low temperature which mimics the environment of interstellar space in a laboratory setting. This allowed us to obtain the spectra of the ethylene glycol water complex and ethylene glycol monomer in an environment approximate to interstellar space. These spectra were compared to quantum chemical calculations of various predicted structures of these clusters. Four conformers of ethylene glycol water complexes were required to assign the spectrum with contributions from trans ethylene glycol conformers which were not observed in the monomer data.

Figure 1:



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Infrared spectroscopy of cations in helium nanodroplets

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Abstract: Here, we describe our pulsed helium droplet apparatus for spectroscopy of molecular ions. Our approach involves the doping of the droplets of about 10 nm in diameter with precursor molecules, such as ethylene, followed by electron impact ionization. Droplets containing ions are irradiated by the pulsed infrared laser beam. Vibrational excitation of the embedded cations leads to the evaporation of the helium atoms in the droplets and the release of the free ions, which are detected by the quadrupole mass spectrometer. In this work, we upgraded the experimental setup by introducing an octupole RF collision cell downstream from the electron impact ionizer. The implementation of the RF ion guide increases the transmission efficiency of the ions. Filling the collision cell with additional He gas leads to a decrease in the droplet size, enhancing sensitivity to the laser excitation. We show that the spectroscopic signal depends linearly on the laser pulse energy, and the number of ions generated per laser pulse is about 100 times greater than in our previous experiments. These improvements facilitate faster and more reproducible measurements of the spectra, yielding a handy laboratory technique for the spectroscopic study of diverse molecular ions and ionic clusters at low temperature (0.4 K) in He droplets.

Elucidation of the Isomers of Ammonia-Water Cation Clusters by Infrared Spectroscopy

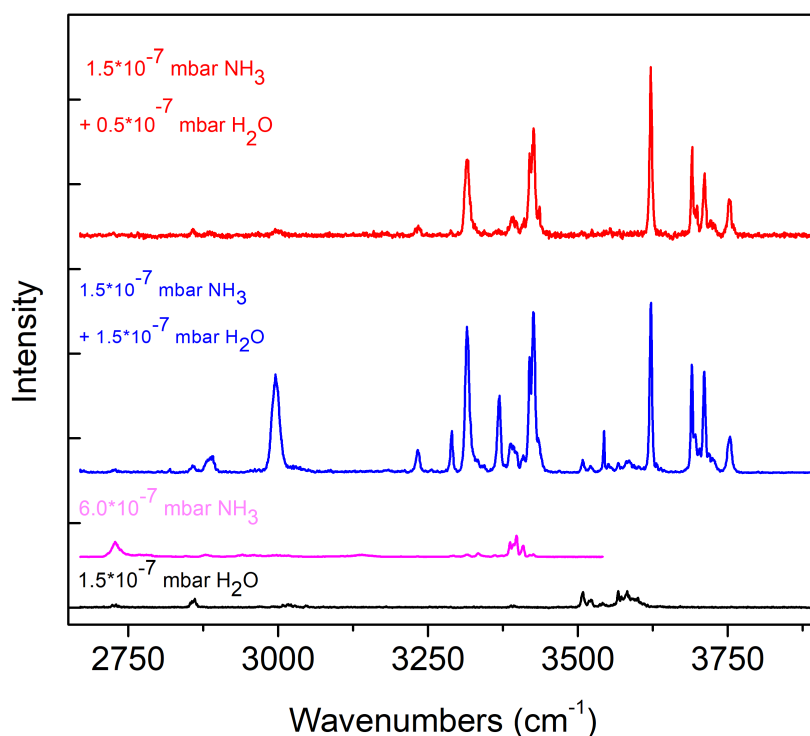
Tom Bernaards,¹ Amandeep Singh,¹ Arisa Iguchi,^{2,3} Zane Golpariani,¹ Prakashraj Nehrudass¹

Susumu Kuma,³ Andrey Vilesov¹

¹University of Southern California, USA, ²Tokyo Metropolitan University, Japan, ³RIKEN Institute, Japan

The work discusses the infrared spectra of multiple isomers of the ammonia-water cation cluster obtained using helium droplets. Multiple spectra, at mass channel $m/z=35$, are recorded at different pressures of ammonia and water present inside the instrument's pickup chamber. Recorded spectra are compared to previous quantum chemical calculations.¹ A description of the experimental apparatus used is included.² Pickup pressure dependencies of individual bands are fitted to the Poisson distribution and used to determine how many individual molecules must be captured by the helium droplets to form the different isomers of $\text{NH}_3\text{-H}_2\text{O}^+$. Mass spectra of different bands corresponding to the respective isomers are used to show fragmentation patterns of $\text{NH}_3\text{-H}_2\text{O}^+$ after laser excitation and droplet evaporation.

Fig 1. Infrared spectra at mass channel $m/z=35$ for different pickup pressures of water and ammonia



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Hydrogen bonding in the H₂S dimer: New insights from experiment and theory

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Abstract: In the condensed phase H₂S forms a network where one molecule is surrounded by 12 neighbors. This can only be achieved if the main bonding interaction is due to van der Waals interactions rather than hydrogen bonding. However, at temperatures below 4 K the situation changes if H₂S dimer is formed via a pulsed nozzle, and it was found that H₂S forms a hydrogen like bonded interaction which shows similar properties to water dimer.^[1] Here, the results of the investigation of H₂S dimer in superfluid helium droplets are presented. Three signals in the region of the bond donor (2570-2630 cm⁻¹) were recorded mass-selectively at m/z= 34 and assigned to vibration-rotation-tunneling transitions of the para-para, para-ortho and ortho-ortho species by so-called pick-up curves and high-resolution spectra which resolve the rotational substructure of those signals. In combination with theoretical calculations, the tunneling splitting of the H₂S dimer was modeled and compared to water dimer.^[2] It appears that H₂S dimer is much floppier than water dimer. However, the excited state was found to be similar to the ground state of water dimer.

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Infrared spectroscopy of CH_5^+ and Radical Cations in Helium Nanodroplets

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Superfluid helium nanodroplets are unique matrices that could be used as nano-test tubes to study the infrared spectra of small carbocations. The electron impact ionization of helium droplets doped with clusters of methane molecules generates a variety of carbocations. In this work, we successfully produced CH_5^+ methanium cations upon ionization of methane dimers in helium droplets and using an addition reaction of protons with methane molecules inside helium droplets. The ions were studied by the pulsed infrared laser spectroscopy technique in the C-H stretching range. The spectra show two strong and broad infrared bands and a weak shoulder for CH_5^+ reflecting its highly fluxional nature. The dependence of infrared band intensity on the pressures of reactant gases was studied to understand the formation reaction. Furthermore, the final confirmations of product formation were made by measuring the laser-dependent mass spectra. Finally, the CH_5^+ spectrum is compared with the spectrum of CH_4D^+ . This paper also report the spectra of the methane dimer radical cations $(\text{CH}_4)_2^+$.

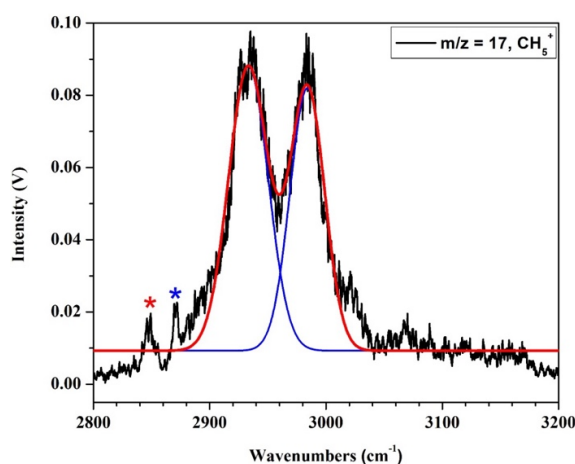


Figure 1: Infrared spectrum of CH_5^+ cations in helium nanodroplets. The Gaussian fitting is shown with a red trace and the individual Gaussian curves are shown with a blue trace. The red asterisk shows the band corresponding to fragmentation from $(\text{CH}_4)_2^+$ cations and the blue asterisk shows the band corresponding to fragmentation from $\text{CH}_5^+ - \text{CH}_4$ cations.

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Setup for time- and energy-resolved fluorescence measurements of collective effects in polyacene aggregates attached to rare gas clusters

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Abstract: Collective effects in organic semiconductors affect excited state lifetimes, important for organic optoelectronic and photovoltaic applications. A complete understanding of the energy level structure, and decay mechanisms require high spectral and temporal resolution. We present a setup combining conventional laser-induced fluorescence (LIF) spectroscopy with time-correlated single photon counting (TCSPC) and discuss advantages and implementation challenges. Using wavelength-tunable nanosecond dye laser pulses allows us to measure high-resolution LIF spectra of transitions to highly excited states of tetracene embedded in superfluid helium nanodroplets, or deposited on solid rare-gas clusters. The newly implemented TCSPC detection in combination with a femtosecond laser system is aimed at studying radiative and non-radiative decay mechanisms connected to collective effects in aggregates of polyacenes. This technique allows us to cover the sub-ns lifetime region not previously reachable in our fluorescence measurements.

He-Tagged Action Spectroscopy of PAHs

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Measuring absorption spectra of cold molecules in the gas phase holds significant importance, particularly in identifying absorption characteristics in stellar spectra originating from molecular species in interstellar space. However, only a handful of molecules have been exclusively associated with such absorption features thus far. Among the promising candidates are polycyclic aromatic hydrocarbons (PAHs). PAHs are a class of large, carbon-based molecules composed of fused aromatic rings, which exhibit enhanced stability compared to other similarly-sized molecular species and have been found abundantly in the interstellar medium [1]. Furthermore, they are considered the building blocks for even more complex compounds in the ISM.

With IR spectroscopy as a tool for finding the unique molecular signatures of molecules in the gas phase, we can gain valuable insight into the composition and specific identification of different PAH molecules as carriers of absorption features in the interstellar medium. Our work focuses on pristine PAH clusters, as well as mixed complexes. In the latter case, the PAH clusters are decorated with single atoms or small hydrocarbon compounds, allowing us to study the formation and isomeric structures of more complex molecules.

To do so, we utilise superfluid helium nanodroplets as an ultra-cold and inert reaction matrix for the formation of neutral or charged PAH clusters [2], where additional He attachment serves as a non-perturbing messenger for high-resolution IR absorption spectra [3].

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Size-dependent development of the plasmon resonance in silver cluster anions

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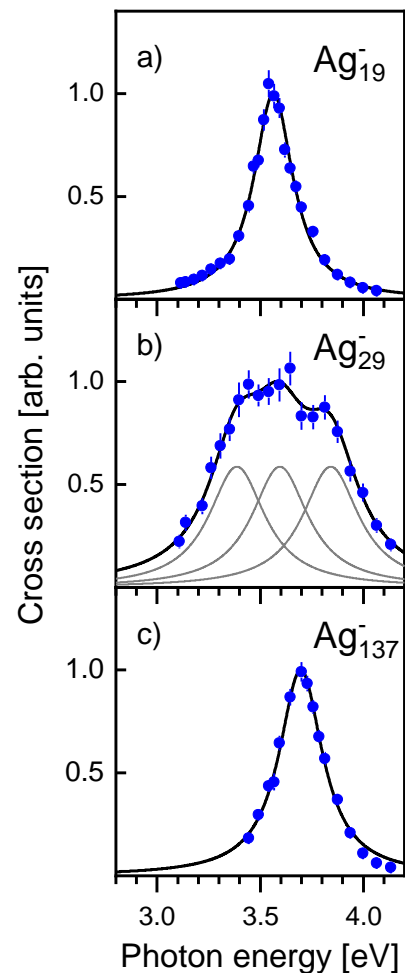
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Numerous applications ranging from efficient solar cells to cancer treatment profit from the interaction between nanoparticles and light. In the case of metal clusters, one often takes advantage of collective resonances of the valence electrons, which lead to a strong increase of the cross section at a certain wavelength. Previous studies already showed, that the resonance energy can be tuned via size and charge state of the nanoparticles [1]. However, systematic measurements to explore the development of the plasmonic resonance in metal clusters concentrate on small sizes. In the case of free silver particles only few experimental results are available for systems larger than $N = 20$ atoms [2,3].

We conduct photoelectron spectroscopy on anionic silver clusters Ag_N^- in a size range $N = 7 - 800$. By extracting photodetachment cross sections (Fig. 1), we gain insights into the collective resonances. At $N = 55$, we observe a transition from a blueshift to a general redshift of the plasmon energies with decreasing cluster size. However, the resonance energies for sizes below $N = 55$ are oscillating whereby the maxima are found at known electronic shell closures. On top, a splitting of the resonance is observed at a few smaller cluster sizes (e.g. Ag_{29}^- , Fig. 1b), hinting on a deformation of the particle.

Fig 1. Photodetachment cross sections of silver clusters Ag_N^- with $N = 19, 29$ and 137 (blue circles). The experimental data are fitted by either a single Lorentz function (black line, a and c) or by a combination of three Lorentzians with same area and width (black line, b).



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Time-resolved photoelectron spectroscopy of isolated tetracene

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Abstract:

Helium nanodroplets (HeND) provide a cold and non-perturbing environment to study single atoms, molecules and complexes thereof [1]. Combining this with femtosecond (fs) time-resolved photoelectron spectroscopy, ultrafast excitation dynamics such as energy transfer between individual dopant molecules can be investigated. Unravelling such signals from measurements containing a distribution of complex forms, can be challenging especially in addition to the difficulties presented by photoelectron spectroscopy of doped HeND. Within the superfluid helium environment, low kinetic energy electrons in particular can be scattered by the droplet atoms or become trapped within the droplet [2].

Thus it is necessary to first understand the base system, in this case isolated tetracene, where the ultrafast relaxation dynamics following UV excitation has been studied [3]. The excitation into the bright singlet state S₆, is followed by the ultrafast relaxation into various dark lower-lying states whose energetic structure till now had not been experimentally determined.

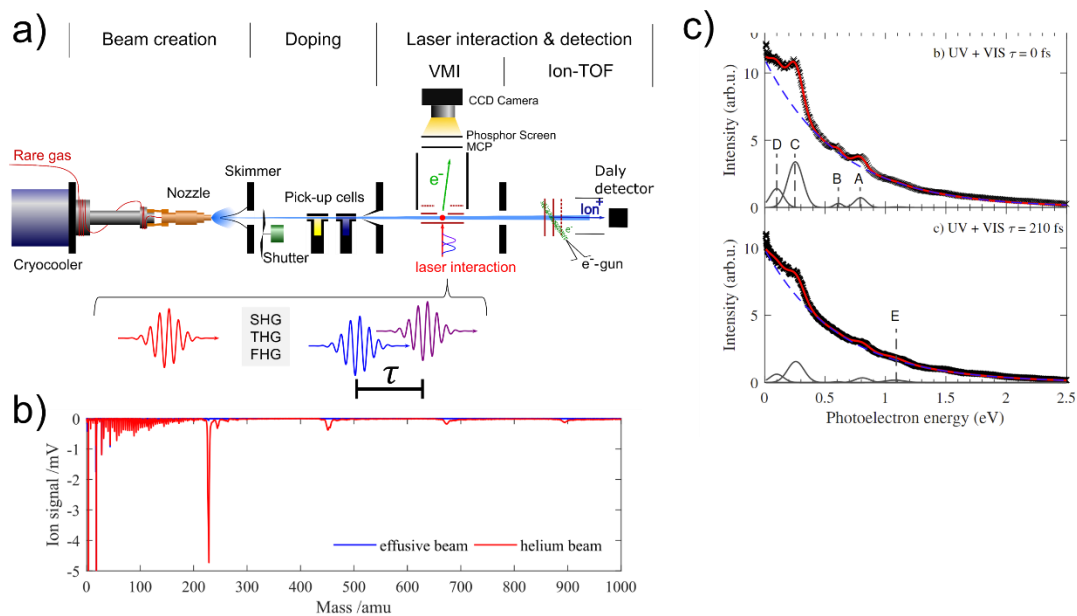


Fig 1. a) Schematic diagram of the experimental setup. b) Time of Flight (TOF) mass spectrum of tetracene in an effusive beam (blue) and doped in helium droplets (red). c) Photoelectron spectrum of effusive tetracene at two delay times between the UV pump and VIS probe pulse.

References:

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Long pulse alignment of alkali dimers on the surface of helium nanodroplets

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Abstract: It was recently shown that Na₂ dimers can be non-adiabatically aligned on the surface of superfluid He nanodroplets using a moderately intense 1 ps long laser pulse. The interaction with the droplet partially confines the rotation to the tangent plane of the droplet surface.¹

In this work, we use a ~200 ps long alignment pulse to study the laser-induced alignment dynamics of Ak₂ dimers (Ak = Li, Na, K, Rb) in the near adiabatic regime. The dynamics are probed by Coulomb explosion of the Ak₂ dimers, whose fragments are then analysed in a velocity map imaging spectrometer setup, using the TPX3Cam to capture individual ion hits.

An example alignment trace measured for Na₂ is shown in Fig. 1(a). The traces for both electronic states closely mirror the shape of the alignment pulse during its presence, with dimers in the ³Σ state reaching the highest degrees of alignment measured for Na₂ on the surface of He droplets. The post-pulse dynamics, however, differ: For the ¹Σ state no significant oscillatory dynamics are present, whereas the ³Σ state experiences revivals ~200 ps apart due to rotational coherence. Spectral analysis of the alignment traces, Fig. 1(b), reveals a peak indicating a non-vanishing coherence between the j=0 and j=2 rotational states. The post-pulse dynamics therefore offer time-resolved insight into the dynamics of the decay of population and coherence.²

From the long pulse alignment experiments with Ak₂ dimers on the surface of He droplets we will be able to (i) find the rotational temperature of the dimers by comparing with simulations³ and (ii) estimate the timescales of decoherence.

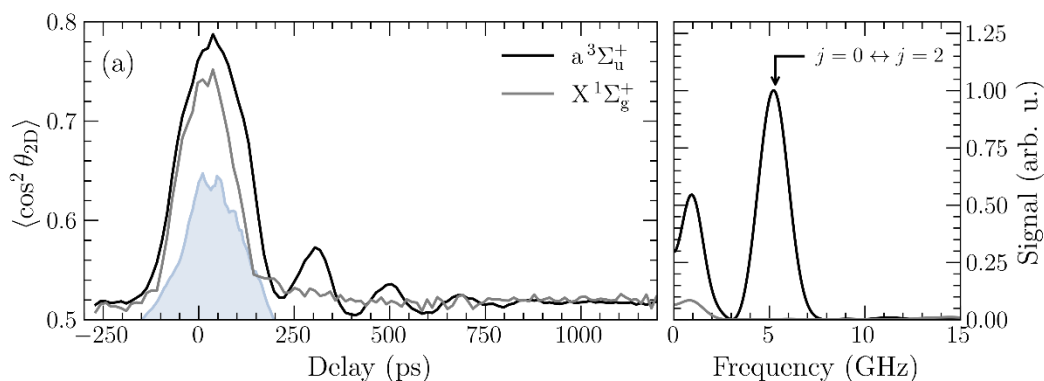


Fig 1. Rotational coherence spectroscopy of Na₂. (a) The laser-induced alignment dynamics in the time-regime of the triplet and singlet states. The blue shaded area is the pulse envelope. (b) Fourier analysis of the alignment traces.

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Real-Time Tracking Mg Cluster Formation Inside He Droplets: Energy Pooling and Ion Ejection

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Abstract: Time-resolved covariance photoelectron and -ion spectroscopy allowed us to observe the photoinduced formation of Mg clusters from an initially dilute, foam-like aggregate of Mg atoms inside liquid helium droplets. Here, we propose a detailed description of the photo-formation process including the dynamics of the involved electrons and atoms. Photo-formation is initiated by photoexcitation at 282.5 nm, under conditions to photoexcite multiple Mg atoms within the aggregate. During cluster formation, the energy of two or more Mg* atoms can be pooled (Fig. 1a) by collisions between Mg and He atoms: One excited and one ground state Mg atom collide to form an excited state Mg* dimer. The dimer then interacts with another excited Mg* atom to form highly excited Mg* atoms or an excited Mg₃ cluster with excess nuclear kinetic energy. Ionization with the probe pulse subsequently produces electrons and ions with energies reflecting the population of the different vibronic states of the nascent Mg cluster. The excess kinetic energy due to energy pooling and probe ionization leads to fragmentation of some clusters. Very fast ionic fragments will leave the droplet solvation potential, making them available for covariance detection. The photoelectron spectra associated with different ionic fragments are shown in Fig. 1b. Here, the mean electron kinetic energy is proportional to the detected fragment size, indicating that electronic energy is converted into kinetic energy of the fragments. The average size of the detected ions also decreases over time, pointing to fragmentation of the neutral photo-formed magnesium clusters.

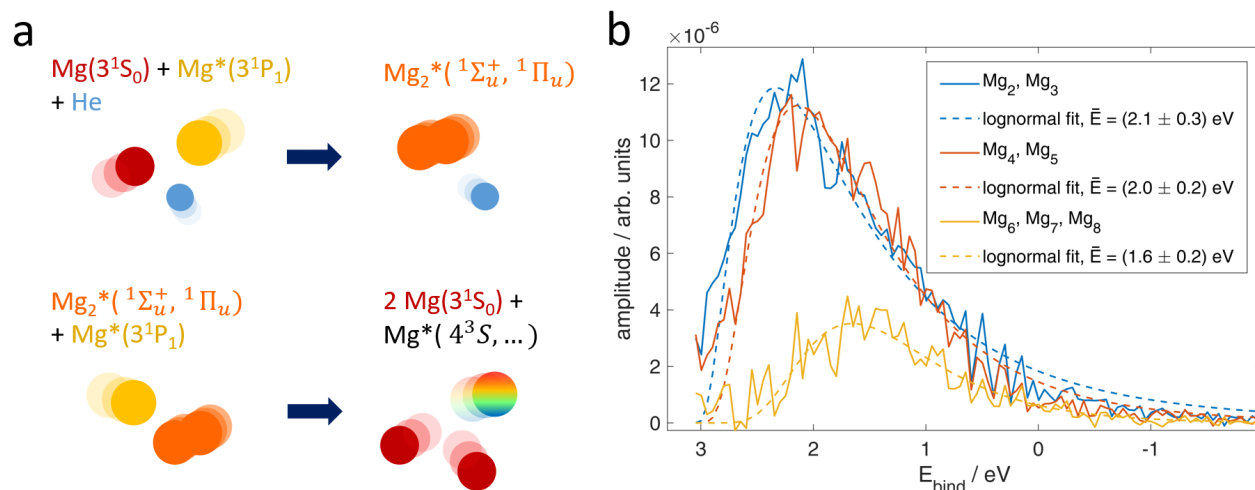


Fig 1. a) The energy pooling process involving two excited Mg* atoms: He-mediated Mg-Mg* collision leads to Mg₂* formation. Subsequently, the excited dimer collides with another excited Mg* atom, leading to highly excited Mg* population and release of kinetic energy.

b) Photoelectron spectra (time-integrated from 0.1 ps to 5 ps) correlated with different Mg cluster masses are shown, indicating a decrease of mean electron kinetic energy as the ion cluster size decreases.

Alkali Metal Trimers on Helium Nanodroplets

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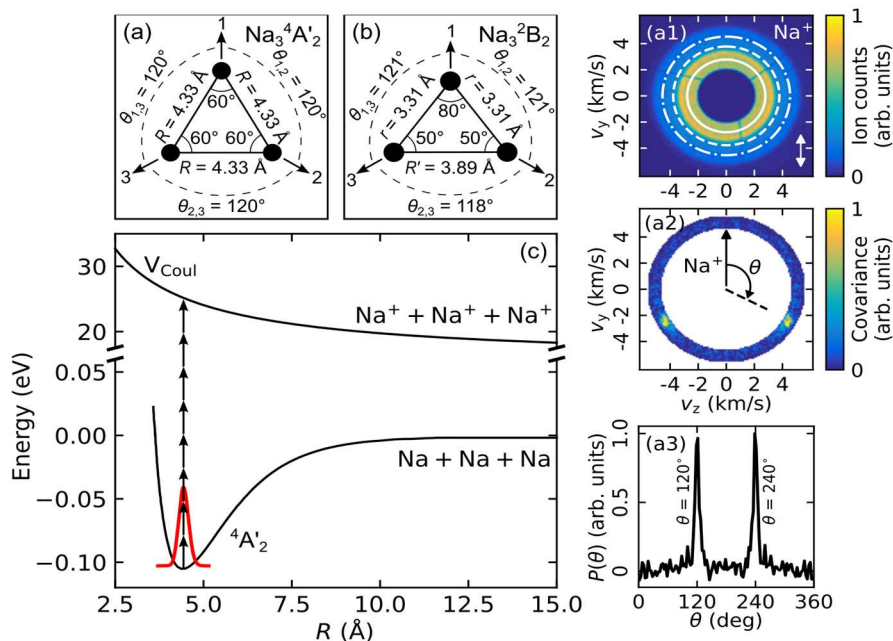
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Small alkali oligomers located on the surface of helium nanodroplets are Coulomb exploded by multiphoton absorption from a femtosecond pulse, producing Ak^+ fragments. Here we focus on the alkali trimers and the structural information that can be gained from velocity map imaging of the Ak^+ ions [1]. The kinetic energy distribution as well as the threefold covariance analysis of the ions display characteristics in line with the predicted equilateral triangular structure of the lowest quartet state $^4\text{A}'_2$ for each alkali trimer. Using Coulombs law, the distribution of internuclear separations $P(R)$ for Na_3 , K_3 , and Rb_3 are determined and compared to the theoretical $|\Psi(R)|^2$.



Panel (a) and (b) depict the predicted structure of the lowest quartet ($^4\text{A}'_2$) and lowest doublet ($^2\text{B}_2$) state [2,3]. Subfigure (c) depicts the potential energy surface of Na_3 in the $^4\text{A}'_2$ state [4] as well as the Coulomb potential. The red curve represents the vibrational ground state, and the arrows symbolize the eight 400 nm photons needed to reach the Coulomb curve (not to scale). (a1) shows the Na^+ ion image where the Na_3 channel falls outside of the dot-dashed line (The other regions are dimer channels). (a2) Threefold covariance of the Na_3 channel visualizing the correlations in the emission angles of the Na^+ fragments. (a3) Angular distribution of the covariance image.

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Photodissociation Dynamics of I₂ Molecules Inside He Nanodroplets

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Abstract: We investigate the influence of superfluid He on the kinetics of iodine (I) atoms after photodissociation of I₂, using femtosecond pump-probe ionization and Coulomb explosion imaging. The influence of the quantum solvent manifests itself in decelerated dissociation kinetics and enhanced predissociation. We excite I₂ molecules inside He droplets (~4.3 nm radius) to the dissociative electronic A-state with a resonant femtosecond laser pulse (350 nm to 700 nm wavelength) and subsequently use strong-field probe-pulses (800 nm) to ionize one or both I atoms (Fig. 1a), which are detected via velocity map imaging. While two distinct branches, representing single- and double-ionization, can be seen in gas-phase measurements (Fig. 1b), the He-droplet results only show a single, broader velocity distribution (Fig. 1c). Surprisingly, measurements with delays of roughly 10 ps between the two laser pulses reveal higher velocities of the ions in He than in gas phase, indicating the confinement of both atoms within the droplet. To establish a mechanistic understanding of the atomic kinetics dictated by the He influence, we develop a simple model to describe the movement of neutral and cationic I atoms. We assume that after acceleration due to dissociation our open-shell atoms are first decelerated until they reach Landau velocity, which traps them inside the droplet due to the solvation energy. Ionization of both I atoms simultaneously leads to acceleration due to Coulomb repulsion and deceleration at a presumably higher rate than the neutral atoms. The kinetic energy increase might enable I⁺ to overcome the increased solvation energy. Despite its simplicity, our model seems to capture the most important aspects of the atomic movement quite well. Finally, excitation of I to the bound B-state typically results in wavepacket oscillations in the gas-phase with a weak decay due to predissociation. In strong contrast, in He droplets the transient velocity distribution (Fig. 1d) shows strong similarities to the A-state measurements, suggesting that the predissociation rate is significantly enhanced by the He environment.

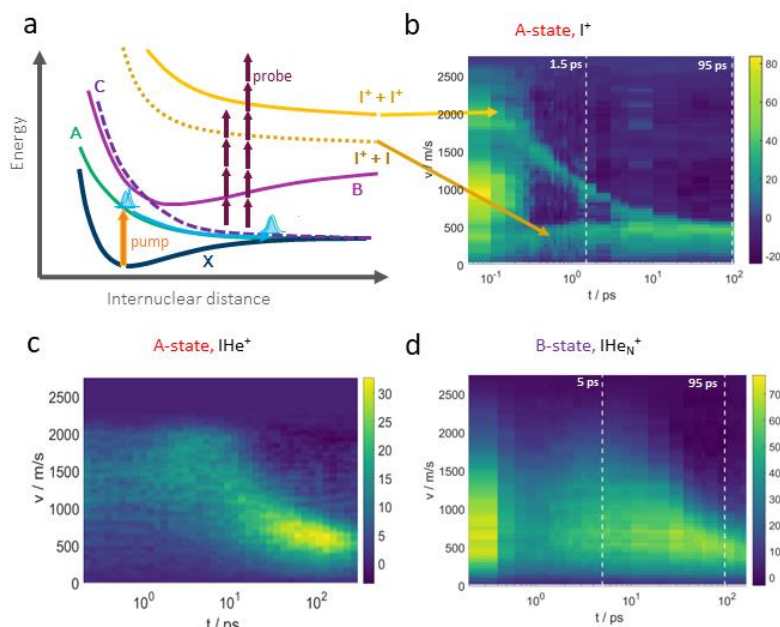


Fig 1. Photodissociation dynamics of I₂ in gas-phase and inside He. **(a)** Sketch of the potential energy curves of iodine, including the pump excitation (orange) and multiphoton ionization (purple) to the single and double ionized cationic states. **(b)** Time-dependent pump-probe velocity distribution of I⁺ atoms for excitation to the A-state with 700 nm pump. Two branches, corresponding to ionization to the single and double cationic state respectively, are visible. **(c)** Same as (b) but for IHe⁺ ions and A-state excitation at 700 nm inside He droplets. **(d)** Same as (c) but for B-state excitation at 600 nm and IHe_N⁺ ions (= 1 to 20).

Time-resolved Coulomb Explosion Imaging of Vibrational Wave Packets in Alkali Dimers on the Surface of Helium Nanodroplets

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Vibrational excitation of alkali-metal homodimers Ak_2 situated on the surface of helium nanodroplets is achieved via non-resonant stimulated Raman scattering, induced by a moderately intense femtosecond pump pulse. Following excitation, the molecules undergo Coulomb explosion due to an intense, time-delayed femtosecond probe pulse. The kinetic energy spectrum of the ion fragments $P(E_{\text{kin}})$ is subsequently captured using a velocity map imaging spectrometer.

The pump-probe scheme employed here enables the time-resolved imaging of the square of the nuclear wave function $|\Psi(R)|^2$, equivalent to $P(R)$. The kinetic energy spectrum of the ion fragments allows for selective investigation of the dynamics of dimers formed in either the $X\ ^1\Sigma_g^+$ ground state or the lowest-lying triplet state a $^3\Sigma_u^+$. The distribution of internuclear distances $P(R)$ is reconstructed from $P(E_{\text{kin}})$ via a Jacobian transformation. Alkali-metal dimers are expected to be well-suited for reconstruction of the square of their nuclear wave functions, given that upon double ionization and removal of the two valence electrons of the Ak_2 dimer due to the probe pulse, the resulting closed-shell configuration of the dication Ak_2^{2+} exhibits only a single repulsive potential curve. Consequently, conservation of energy gives a unique correspondence between R and E_{kin} .

The helium droplet's temperature of 0.4 K ensures that only the vibrational ground state in the triplet state of the dimers is populated prior to interaction with the pump pulse. For K_2 and Rb_2 , the vibrational dynamics are recorded in the triplet state for ~ 180 and ~ 40 vibrational periods, respectively. The expectation value of the internuclear separation $\langle R \rangle$ exhibits a single-frequency oscillatory pattern, indicative of a two-state vibrational wave packet in the electronic triplet state of the dimers. The vibrational dynamics reveal a slow attenuation of the vibrational amplitude, with a lifetime of 0.3 ns. This loss of contrast in the vibrational amplitude is attributed to decoherence resulting from interactions with the helium environment. These findings align with prior experiments on vibrational dynamics in the triplet state of alkali dimers.

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Combination of interferometric measurements with depletion spectroscopy

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Abstract:

Combining helium nanodroplet isolation spectroscopy [1] with interferometric techniques such as wave packet interferometry (WPI) [see figure 1 (a)] and two-dimensional electronic spectroscopy (2DES) allows us to study molecular processes in cold environments with high spectro-temporal resolution [2]. Action-detection is essential for these experiments due to the low target density. However, studying non-radiative photodynamics in organic molecules poses still a challenge in these experiments. Fluorescence detection is limited to radiative processes and photoionization probes are challenging to implement due to the high ionization potential of organic molecules. Hence, in this project we aim to address this challenge by combining interferometric measurements with helium depletion spectroscopy [see figure 1 (b)]. This approach sets the basis for 2DES experiments. As a test system we study the photo-isomerization in the well-known organic photoswitch azobenzene.

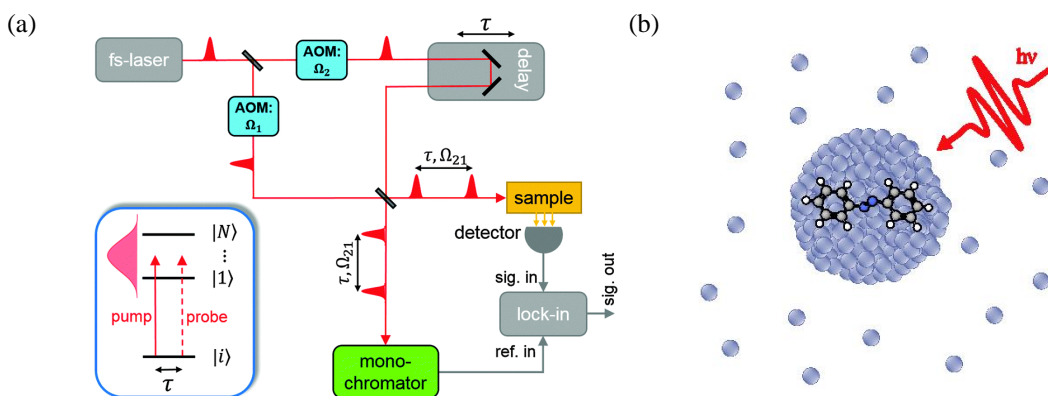


Fig 1. (a) Phase-modulated wave packet interferometry setup [3]. (b) Helium evaporation upon laser excitation.

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Atom and femtosecond resolved solvation dynamics of single alkali ions in liquid helium nanodroplets

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Recently, the first experimental results on the solvation dynamics of a single Na⁺ ion in liquid helium nanodroplets were reported [1]. Theoretical studies show that similar solvation dynamics can be observed for other alkalis [2]. Here, novel experimental results on the solvation dynamics of Li⁺ and K⁺ are presented. The solvation dynamics are also studied for different droplet sizes.

Helium droplets are formed by expanding high purity helium into vacuum. The droplets are then doped with a Xe atom in the center and an alkali metal atom, Ak, at the surface. The doubly doped droplets are irradiated by a fs pump laser pulse, selectively ionizing the alkali metal atom. The formed alkali ion dissolves into the helium droplet by binding of individual helium atoms. The solvation process is probed by ionizing the Xe atom with an intense, delayed probe pulse, pushing the Ak⁺ ion out of the droplet due to the Coulomb repulsion from the Xe⁺ ion, or, if the Ak⁺ ion has been solvated by n He atoms, an Ak⁺(He) _{n} complex instead.

Measurements on Li⁺ show that individual helium atoms bind at a constant rate of 1.9 ps⁻¹ for the first five atoms for a droplet containing $N_{\text{droplet}} \approx 5.2 \cdot 10^3$ He atoms indicating a Poissonian solvation process. The binding dynamics of subsequent He atoms deviates from linearity. This is ascribed to a sharp decrease of the Li⁺(He) _{n} evaporation energy for $n > 6$ due to the small size of the Li⁺ ion.

Measurements on the larger K⁺ ion show a constant helium atom binding rate of 1.8 ps⁻¹ for the first 12 He atoms ($N_{\text{droplet}} \approx 5.2 \cdot 10^3$ He atoms). K⁺ has a flat evaporation energy curve for the first 12 He atoms, which explains the larger range of constant rate for K⁺ compared to Li⁺.

An important question to address is whether the finite size of the helium droplets influences the solvation rate of single alkali ions. Measurements on increasing droplet sizes for solvation of Na⁺ and K⁺ reveal a general trend of increasing rate of solvation with Na⁺ increasing from 1.5 ps⁻¹ for $N_{\text{droplet}} \approx 3.6 \cdot 10^3$ He to 2.2 ps⁻¹ for $N_{\text{droplet}} \approx 9 \cdot 10^3$ He atoms and K⁺ increasing from 1.7 ps⁻¹ for $N_{\text{droplet}} \approx 3.6 \cdot 10^3$ He atoms to 2.2 ps⁻¹ for $N_{\text{droplet}} \approx 9 \cdot 10^3$ He atoms.

The droplet size measurements on Na⁺ and K⁺ indicate that the rate of solvation depends mostly on the solvent's capacity to encompass a charge, while the measurements on Li⁺ and K⁺ indicate that the ionic properties lead to different statistical interpretations of the solvation process.

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Rotational Control of Helium Dimers in Superfluid Helium

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I will discuss our recent results on coherent excitation and coherent control of metastable helium dimers (He_2^*) inside bulk superfluid helium by means of shaped ultrashort laser pulses. I will present an experimental study of the laser-induced rotation of helium dimers inside the superfluid ^4He bath at variable temperature. The coherent rotational dynamics of He_2^* is initiated in a controlled way by ultrashort laser pulses, and tracked by means of time-resolved laser-induced fluorescence. We detect the decay of rotational coherence on the nanosecond timescale and investigate the effects of temperature on the decoherence rate. The observed temperature dependence suggests a non-equilibrium evolution of the quantum bath, accompanied by the emission of the wave of second sound [1].

I will also report on the experimental demonstration of the rotational control of helium dimers by a periodic sequence of linearly polarized femtosecond pulses (a pulse train). We show that the degree of rotational excitation of He_2^* can be enhanced or suppressed by varying the period of the pulse train, whereas the directionality of molecular rotation can be controlled by the relative angle between the polarization vectors of pulses in the train [2].

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Solvation dynamics of alkali (Ak) cations into an superfluid Helium nanodroplet

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The sinking of alkali cations in superfluid ^4He nanodroplets is investigated theoretically using ^4He time-dependent density functional theory at zero temperature [1,2]. The simulations show the progressive build up of the first solvation shell around the ions. The number of helium atoms in this shell is found to linearly increase with time during the first stages of the dynamics. This points to a Poissonian capture process, as concluded in the work of Albrechtsen et al. on the primary steps of Na^+ solvation in helium droplets [3]

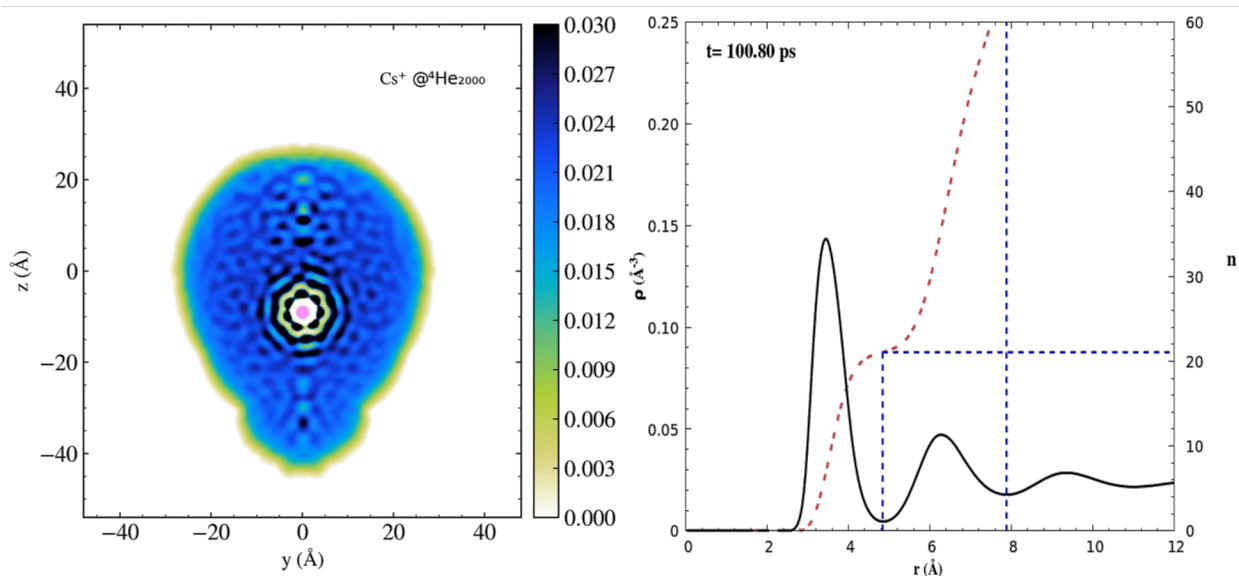


Fig 1. Illustration of the Cs^+ solvation dynamics into a $^4\text{He}_{2000}$ nanodroplet at $t=100.8\text{ps}$. **Left panel:** two-dimension cut of the helium density in a symmetry plane and ion position. **Right panel:** spherical average (solid black line) of the helium density as a function of the distance from the ion position, number of He atoms n (red dashed line). The blue vertical dashed lines mark the radius of the first and second solvation shell obtained in a preliminary static calculation; and the blue horizontal line shows the number n of helium atoms in the first solvation shell.

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Merging dynamics of superfluid ^4He droplets and quantum vortex nucleation:

^4He -TDDFT simulation

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The study of vortices in Helium droplets has been a subject of continuous interest since they were first detected in droplets made of $\sim 10^{8-11}$ atoms. These very large droplets (VLD) are believed to acquire angular momentum when interacting with the walls of the nozzle [1], which is then stored as quantum vortices and/or capillary waves upon normal to superfluid transition. We explore here another mechanism for quantum vortex nucleation, $^4\text{He}_N + ^4\text{He}_N$ collisions, using the ^4He -TDDFT approach. Different initial conditions such as impact parameter (b) and relative velocity (v_0) are explored. In a VLD beam, Kolatzki *et al.* [2] have observed equidistant drops with almost uniform size which could sometimes coalesce downstream. The relative velocities explored here are somewhat higher than the ones in that experiment, but they are within the range of the ones in smaller droplets experiments produced by gaseous helium expansion. We also studied a non-symmetric $^4\text{He}_{300} + ^4\text{He}_{700}$ collision. We evidence the nucleation of quantum vortices upon collision, which are produced at indentations appearing at the surface of the merged droplet, making this process independent of droplet size [3]

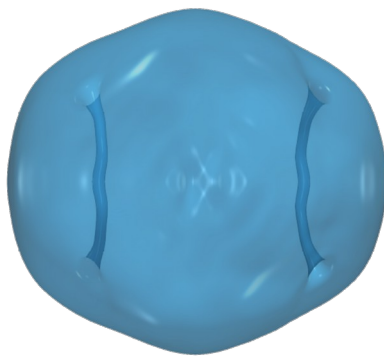


Fig 1. Droplet hosting two vortex lines following a $^4\text{He}_N - ^4\text{He}_N$ collision ($N = 500$; $b = 3R/2 \text{ \AA}$; $v_0 = 40 \text{ ms}^{-1}$; $t = 359 \text{ ps}$). Note that the nucleation of the two vortex lines was simultaneous in this symmetric collision.

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Not fluid yet fluxional subnanometric metal clusters. Cluster-support interactions and their influence on the Jahn-Teller effect.

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Subnanometric metal clusters exhibit properties that differ significantly from nanoparticles and bulk materials due to their fluxional geometries and complex electronic structures [1]. These properties are particularly interesting for applications in catalysis, photocatalysis, and other nano- and biotechnological fields [1]. Metal clusters can be synthesized and deposited on surfaces using helium nanodroplets [1]. Open-shell Cu_3 and Ag_3 clusters, characterized by their triangular shapes, undergo symmetry changes due to Jahn-Teller distortions [2], resulting in dynamic structural fluctuations [3]. Both high-resolution spectroscopy and high-level *ab initio* theory has shown that these clusters do not settle into a single, stable structure associated to a single potential minimum but fluctuate in between several minima. It has been recently found that open-shell bipyramidal Cu_5 clusters are Jahn-Teller fluxional molecules as well [3]. The structural fluxionality may contribute to enhanced activity in catalysis and photocatalysis [1,3]. The effectiveness of (photo-)catalysts depends significantly on the interactions between quantum metal clusters and their supporting materials, such as graphene. In this poster, the influence of cluster-support interaction on a Jahn-Teller effect is illustrated. In quest of studying helium nanodroplet-mediated support-deposition [1], a general scheme to get accurate open-shell subnanometric metal clusters-support interactions is also presented (work in progress).

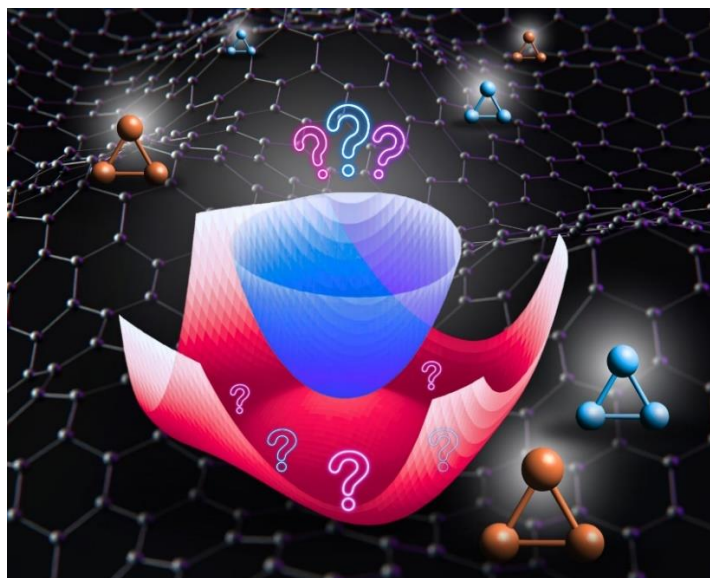


Fig 1. Graphical abstract.

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Theoretical study of benzene-nitrogen and benzene-hydrogen cation clusters

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Intermolecular interactions involving aromatic rings dictate the properties and reactivity of many organic compounds.¹ For example, clusters involving benzene, have the ability to chemically ionise volatile organic compounds (VOCs). In this study, benzene - hydrogen ($\text{C}_6\text{H}_6\text{-H}_2$) and benzene - nitrogen ($\text{C}_6\text{H}_6\text{-N}_2$) cations have been studied to better understand the structure and dynamic behaviour of simple aromatic clusters.^{2,3} Both cations were studied computationally using *ab initio* methods as well as density functional theory. Here we report the obtained cluster structures along with predicted energetic data. We briefly discuss future work in which our computational data can be compared to experimental observations of $(\text{C}_6\text{H}_6\text{-H}_2)^+$ and $(\text{C}_6\text{H}_6\text{-N}_2)^+$ contained in helium nanodroplets using mass spectrometry and IR spectroscopy.

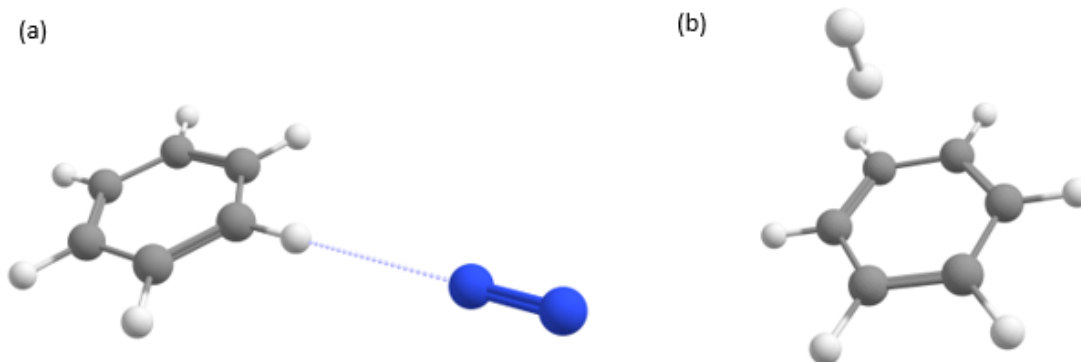


Fig 1. Calculated structures of (a) $(\text{C}_6\text{H}_6\text{-N}_2)^+$ and (b) $(\text{C}_6\text{H}_6\text{-H}_2)^+$.

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Coherent diffraction imaging of micrometer-sized liquid helium droplets

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Abstract: In recent years, coherent diffraction imaging (CDI) has been established as a reliable tool for tracking the shape and ultrafast laser-induced dynamics of individual free-flying nanoparticles.[1] In such experiments, a first light pulse often starts the dynamics. Then, the particle is imaged by XUV or X-ray light pulses by recording the scattered light with a spatially resolving detector, e.g., a microchannel plate detector (MCP). Here, helium droplets are a popular target for many reasons. For example, they can serve as ultracold deposition matrices to embed other particles, cool them down, and transport them to the interaction region. For different experimental purposes, it is necessary to produce helium droplets of various sizes and shapes. In recent years, we have pushed the so-called "Göttingen-type" [2] continuous flow nozzle toward creating slower (below 50 m/s), bigger (5 μm), and rounder droplets.[3] This way, we could image the liquid helium jet and subsequent droplets via shadowgraphy, allowing us to monitor the jet's quality directly.

In conventional CDI experiments with single free-flying targets, the light focus is usually much bigger than the particle. This implies that the target is fully and homogeneously illuminated, and one can assume that only the particle size and shape determine the diffraction signal. In our recent experiments, this was not the case anymore: The focus of our XUV light source was in the same size range as the irradiated helium droplets. Thus, the detectable signal contained information not just about the particle but also about the light focus itself.

The recorded CDI images show new and intriguing features: We observe bright and big spots, sometimes concentric around the detector middle, sometimes asymmetrical - apparently depending on whether the droplet has been hit centrally or not. Additionally, with a second MCP we could image the transmitted XUV beam profile after interacting with the helium droplets. Some of these images contain shadowlike features, which might correlate to the amount of light absorbed or scattered by the droplets. This poster will show the first results from our experiments and the outlook on possibilities for simultaneous scattering and absorption spectroscopy on free-flying single particles.

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Signatures of IR-laser dressing in coherent diffractive imaging

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Single-shot coherent diffractive imaging (CDI) enables the capture of a full diffraction image of a nanostructure using a single flash of XUV or X-ray light. The resulting scattering image encodes both the geometry and the optical properties of the target. So far, this method has mainly been employed for ultrafast structural characterization [1]. However, CDI can also be utilized to resolve ultrafast optical property changes caused by e.g. transient excitation from nonlinear scattering [2], or by illumination with a second ultra-short laser pulse.

Here, we explore the expected signatures for the latter case theoretically, where simultaneous exposure to a strong IR field can induce transient optical properties. To this end, the effective optical properties emerging from the laser dressing must be determined and used to describe the resulting scattering process, which we model using the well-known Mie-solution. We extract the effective optical properties from the dipole response of a local quantum description based on an atom-like solution of the time-dependent Schrödinger equation. The identification of the states and processes responsible for these properties and the corresponding features in the diffraction image is performed by a systematic comparison with results for a few-level system.

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Tracking photo-induced intra/inter-atomic/molecular dynamics in seeded helium nanodroplets at Maloja endstation of SwissFEL

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Abstract: The weakly-bound, ultracold, inert, and superfluid environment of helium nanodroplets acts as an ideal prototype condensed-phase system, where foreign atoms and molecules can be easily seeded, and different intra/inter-atomic/molecular processes can be investigated. Here, I report on the status of the ongoing development of a seeded helium nanodroplets injector and summarize its use with the time resolved X-ray spectroscopic methods (transient - XPS and XAS) available at the Maloja endstation of SwissFEL. These unique experimental capabilities provide a site-selective probe to unravel photochemical reactions in real-time using the ultrashort - tunable two-color soft X-ray FEL and optical laser pulses at this SwissFEL's ATHOS beamline [1,2]. In future, this injector can also be used for single-shot coherent diffractive imaging experiments [3].

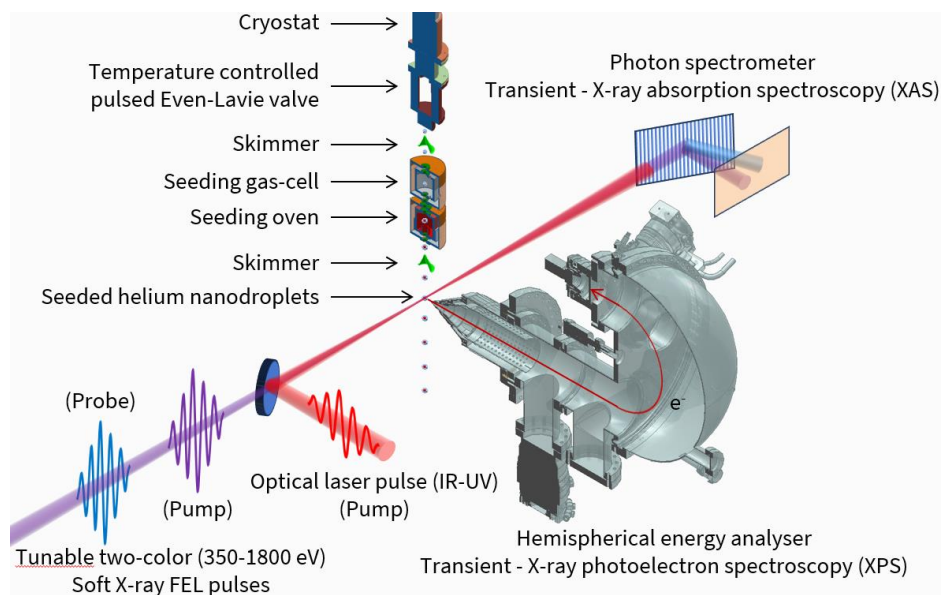


Fig 1. Experimental schematics with the seeded helium nanodroplets source under construction at Maloja. Helium nanodroplets, generated via supersonic expansion of pressurized helium gas through a cryogenically-cooled pulsed gas valve and a skimmer, will be seeded via collisional pickup of foreign atoms and molecules in a gas cell or oven. The time-resolved dynamics in these seeded helium nanodroplets, induced by optical laser or X-ray FEL pulses, can be probed by ultrafast X-ray FEL pulses, using transient- X-ray photoelectron and X-ray absorption spectroscopies.

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Double excitation of helium initiates interatomic Coulombic decay in helium nanodroplets

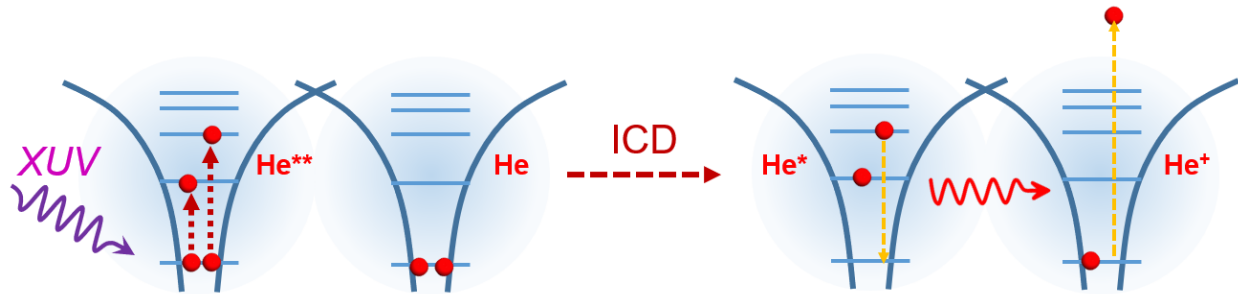
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Interatomic Coulombic decay (ICD) involving a doubly excited atom is observed for the first time. ICD is a non-local correlated electronic process which plays an important role in weakly bound complexes exposed to high-energy radiation. We use liquid helium nanodroplets (HNDs) as a well-suited model system and apply two methods for high-resolution electron spectroscopy in the extreme-ultraviolet (EUV) regime. This allows us to quantify the ICD probability and to analyze details of the process.¹

Slow electrons from inelastic scattering of photoelectrons in the nanodroplet have the same energy as the ICD electrons. This experimental challenge is overcome by fine energy scans across the $2s2p^+$ resonance. We identify the ICD contribution that is shown to proceed by relaxation into $\text{He}^* \text{He}^+$ atom-pair states. The process competes with the ultrafast autoionization of doubly excited He^{**} (17.5 fs decay time) and is expected to become more efficient in denser media. This type of ICD could consequently be relevant in other systems such as water and solvated metal atoms.

Fig 1. Schematics of the decay of a doubly excited He state by interatomic Coulombic decay (ICD)



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The size-dependence of the relaxation dynamics of ^3He and ^4He clusters and droplets studied by fluorescence excitation spectroscopy

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When ^3He and ^4He clusters and droplets are electronically excited, they relax by emission of fluorescence in the near infrared, visible and vacuum ultra violet spectral ranges due to excited helium atoms and helium excimers being ejected into vacuum. To investigate this relaxation process in detail, we have performed time-correlated near-infrared and visible (NIR/VIS) fluorescence excitation spectroscopy for a wide range of cluster and droplet sizes.

While the spectral features broadly follow the vacuum ultraviolet excitation (VUV) spectra, differences between the NIR/VIS and the VUV fluorescence excitation spectra are observed, for the example the much lower intensity in the 2p region compared to excitations at $n = 3$ and higher principal quantum numbers.

An analysis of the intensity dependence with cluster and droplet size by normalisation of the NIR/VIS spectra to the VUV fluorescence shows that for states with $n = 3$ and higher, the process of energy transfer and ejection from the surface into vacuum is restricted to the outer shell of the clusters and droplets. This feature is attributed to the size of the orbitals which, for $n = 3$ and higher, greatly exceeds internuclear separation. This has two important consequences: (1) energy transfer becomes increasingly efficient with n , enabling efficient ejection from the surface (2) stable atomic-like orbitals cannot form within the liquid, but at the surface where there is free space in the direction of the surface normal vector.

For states with $n = 2$, the situation is completely different, Owing to the relatively large internuclear separation in liquid helium, the size of the wavefunctions related to the $n = 2$ states fits well within the space between neighbouring atoms. As a consequence, atomic-like states can exist with only moderate perturbation of the 2s and 2p levels. Under these conditions, transfer of energy is possible by excitation hopping, which competes with radiative and non-radiative decay, making ejection and NIR/VIS fluorescence progressively inefficient for increasingly larger droplets.

Non-radiative decay competing with fast, direct ejection of helium atoms was also identified at the surface where a barrier was identified, separating these two processes. The barrier height was found to decrease with increasing quantum number n .

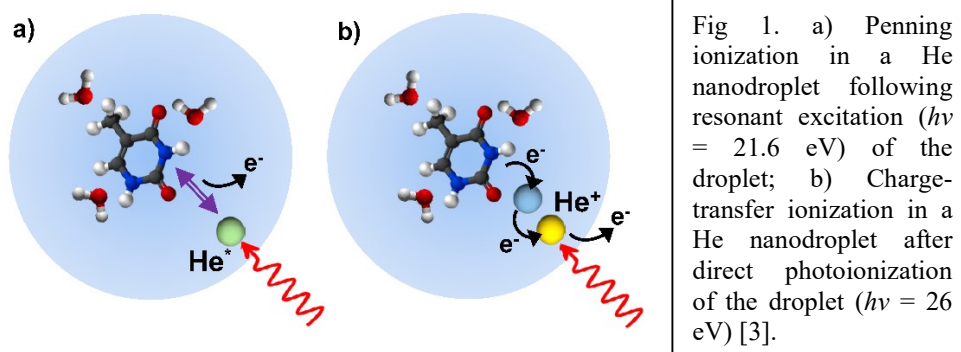
XUV photoionization of free and embedded water clusters and microhydrated biomolecules

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Water is a crucial component of all living organisms and of the Earth's surface and atmosphere. Understanding how water interacts with ionizing radiation is important in the context of radiation damage in biology and the photochemistry of the atmosphere. Water clusters allow us to study the properties of water in various states of aggregation from molecular vapor to microdroplets. We present studies of the ionization mechanisms of small water clusters, both free and embedded in He nanodroplets, irradiated by extreme ultraviolet (XUV) synchrotron radiation. Our photoelectron-photoion coincidence (PEPICO) imaging spectrometer was recently upgraded to double-sided electron-ion imaging to detect mass spectra and kinetic energy distributions of the fragment ions and mass-selective photoelectron spectra [1]. In this way we 1) assess the efficiency and impact of Penning ionization and charge-transfer ionization of water clusters through interaction with resonantly excited and ionized He nanodroplets, respectively [2]; 2) We unravel double-photoionization mechanisms in free water clusters. 3) Biomolecules (DNA bases) are found to be protected against fragmentation by complex formation with a few water molecules in He nanodroplets [3]. Site-selected photoionization of free microhydrated biomolecules (uracil) are found to feature characteristic photoelectron spectra.



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Ion and electron interactions with He nanodroplets

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Dopants in He nanodroplets are efficiently ionized through secondary ionization processes. Upon resonant excitation of the droplet, ionization of dopants happens through Penning ionization where a metastable excited He* atom decays to its ground state and transfers its energy to the dopant. Upon direct ionization of the droplet, a dopant can be ionized by charge transfer to the He⁺ created in the droplet. The efficiencies of these two ionization mechanisms depend on the dopants' location in the droplet relative to the position of the excited He* or He⁺ ion. We have experimentally determined the efficiencies and the optimal droplet sizes for Penning and charge-transfer ionization of Li atoms sitting on the droplet surface and O₂ molecules submerged in the droplet bulk [1]. We modelled the droplet size-dependent ionization efficiency taking into account both the dopant pick-up efficiency and the efficiency of the Penning/charge-transfer ionization mechanism.

The ability to study the Penning and charge-transfer ionization mechanisms of dopants in He nanodroplets greatly depends on the efficiency of detecting the produced electrons and ions. We have systematically measured the ejection probabilities of electrons and ions as a function of He droplet size; We found that both ions and electrons remain bound to the droplets to a large degree when the droplet size increases to 10⁴ and 3×10⁶ He atoms per droplet, respectively [1]. Additionally, the angular distribution of electrons emitted from large droplets is asymmetrically distorted as the droplets become opaque to both the XUV photons and the emitted electrons, see Fig. 1 [2]. However, even for large droplets the energy loss by elastic collisions remains rather low (≤10 %) for those electrons that are emitted from the droplets, whereas a large fraction of electrons never leaves the droplets. This considerably limits the possibility of using He nanodroplets as test tubes for performing photoelectron spectroscopy of embedded dopants.

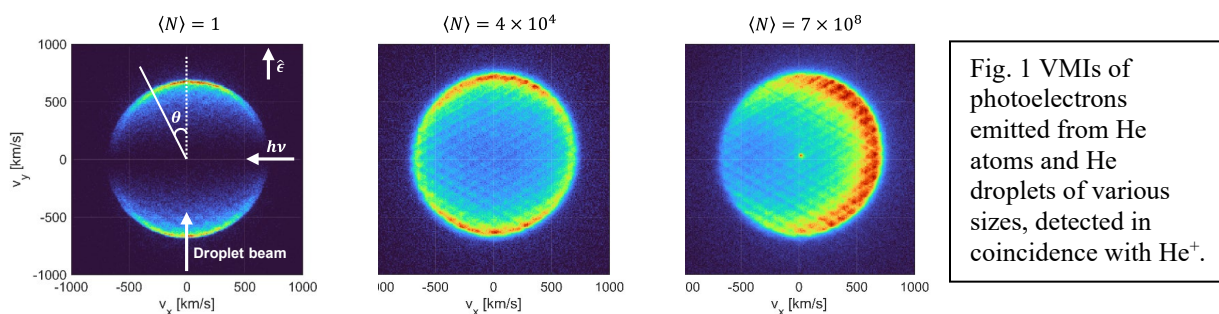


Fig. 1 VMIs of photoelectrons emitted from He atoms and He droplets of various sizes, detected in coincidence with He⁺.

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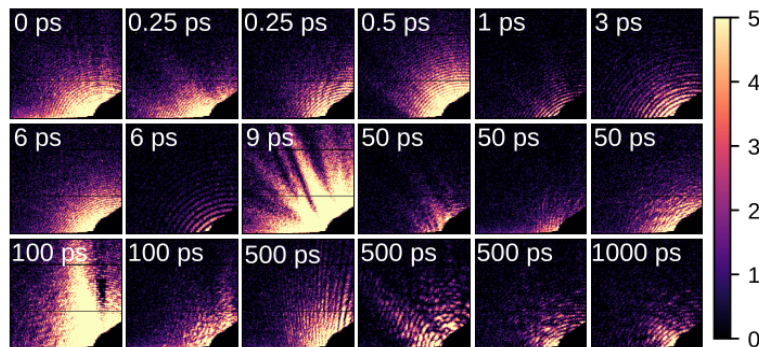
Dynamics of Nanoplasma Formation in Potassium-Doped Helium Nanodroplets Studied via Soft X-ray Diffraction Imaging

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Abstract: Our research focuses on the nanoplasma dynamics of potassium-doped helium nanodroplets (HNDs) using intense soft X-ray FEL pulses. We employ diffraction imaging to determine droplet sizes and correlate them with the kinetic energies of nanoplasma electrons. By utilizing two different dopants, xenon, and potassium, we investigate the effect of doping positions on nanoplasma dynamics. We found the indications of large potassium clusters staying inside helium droplets near the surface. Our experimental setup involves igniting the nanoplasma with a near-infrared (NIR) pulse and capturing the dynamics through soft X-ray diffraction snapshots from FELs. This study provides insights into the structural and dynamic properties of helium nanodroplets doped with alkali metals, contrasting them with rare gas elements, and reveals the influence of different dopant sites on diffraction images.

Fig 1. Evolution of nanoplasma dynamics in potassium-doped helium nanodroplets: For pump-probe delays exceeding 9 ps, a ray-like pattern emerges, while droplet disintegration occurs at larger delays of 500-1000 ps.



Exploring nanoplasma evolution in helium nanodroplets

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In this study, we present measurements performed at the European XFEL aimed to investigate nanoplasma formation and evolution inside Helium nanodroplets (HNDs). These measurements were done using a novel technique utilizing femtosecond time-resolved near infrared (NIR) pump/X-ray probe coherent diffraction imaging (CDI) to monitor the plasma in femtosecond temporal and nanometer spatial resolution. The HNDs could be seeded with single-electron control, achieving cleaner and more controlled conditions than previous studies.

Preliminary findings show a significant decrease in the He⁺ ion signal as pump-probe delays transition from negative to positive, indicating that an X-ray seeding effect is taking place at negative delays. We tentatively attribute this effect to an increased electron abundance inside the droplet caused by the preceding XFEL pulse, subsequently promoting the formation and growth of the nanoplasma in the electric field of the NIR laser [2].

Future analysis will involve the evaluation of X-ray diffraction patterns for different delays and polarizations of the NIR laser to investigate the effect of seeding on the formation and evolution of the nanoplasma. This analysis could provide further insight into the early stages of plasma formation and help test and improve theoretical predictions [1].

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A new helium droplet source setup for nanoparticle surface deposition

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In recent years, helium nanodroplets (HNDs) have proven to be a highly versatile cryogenic matrix for growing clusters and nanoparticles. By impacting the droplets onto a surface, such produced clusters and nanoparticles can be deposited relatively gently, as the helium acts like a cushion on impact. This technique therefore offers enormous potential for the development of unique materials and coatings that cannot be produced by other means.

Recently, our group was able to show that doping of multiply charged HNDs leads to a coagulation of dopants around each charge center within the droplets [1]. This effect can be utilized to produce clusters of highly uniform sizes [2].

The present contribution provides an overview of a novel setup developed by our group named HYDRA. In this apparatus, helium nanodroplets are formed through supersonic expansion and multiply charged via electron impact ionization. Subsequently, the molecular beam passes through an oven in which gas-phase dopants are picked up by the droplets. Finally, the HNDs collide with a selected surface mounted onto a retractable sample holder. Due to the significantly higher droplet flux compared to other instruments currently used in our labs, this setup allows for surface deposition of clusters grown in doped helium droplets both in neutral or multiply charged state within a reasonable time frame. Various benchmarks and comparisons with other experiments in our lab will be presented, as well as preliminary deposition results with bismuth as a dopant material.

Moreover, we present our investigation on the splashing of HNDs upon surface impact, leading to backscattering of the majority of nanoparticles [3]. Currently, we test two strategies to circumvent this problem: (i) deceleration of the charged and doped HNDs below the Landau critical velocity and (ii) utilization of a primary target for splashing and a secondary target for deposition of the backscattered nanoparticles.

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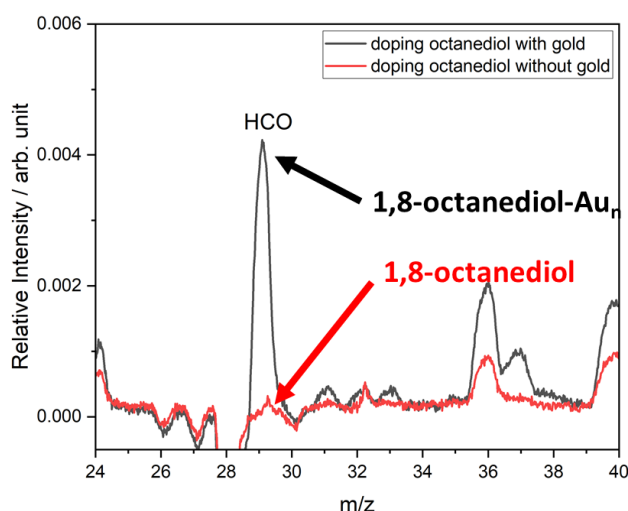
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Investigation on the dynamics of single atom catalysis in superfluid helium nanodroplets

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We introduce an experimental approach on the dynamics of single atom catalysis in superfluid helium nanodroplets. Single-atom catalysts have recently emerged as a new type of catalysts which are comprised of one metal atom and has different catalytic properties compared to bulk-particle catalysts. The common way to form single-atom catalysts is to isolate a single metal atom on a supporting surface, which makes it difficult to characterize the catalytic activity of the single atom and separate the influence of the surface. Superfluid helium nanodroplets can be an ideal tool to form the isolated molecule-metal atom complexes by doping the reactant molecule and the metal atom successively. Specifically, we were able to form 1,8-octanediol- Au_n ($n=0-2$) complexes without a supporting surface by sequentially doping octanediol and a gold atom in helium droplets. After ionizing the complexes by electron impact and comparing the fragment, it has been found that the complexes with Au atoms prominently produce more CHO^+ in this dissociative reaction than the complexes without Au. We plan to use femtosecond pump-probe spectroscopy and photoelectron-photoion coincidence methods to study the real-time dynamics of the octanediol- Au_n complex during the reaction.



The mass spectrum of 1,8-Octanediol and gold doped in Helium droplets with the oven heated to 980oC
(black line: the oven with gold, red line: the oven without gold)

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Rotational anisotropy decay as a tool to characterize the size distribution of doped rare-gas cluster beams

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Size-dependent effects are of particular interest in cluster physics. While precise size-dependent studies can be conducted for charged cluster species, determining the size of neutral clusters remains a challenge. Empirical models exist to predict the mean cluster size in a cluster beam based on expansion parameters [1]. However, in our experiments we are interested in the interaction between dopant molecules and cluster species. In this case, it is not clear how the size distribution of the doped clusters can be inferred from the empirical models. Effects such as evaporative cooling after doping, dopant pick-up and sticking probabilities can lead to differences in the size distribution between the initial cluster beam and the doped clusters. We present a promising method to determine the doped cluster size distribution by measuring the decay of rotational anisotropy in a femtosecond pump-probe experiment (see Fig. 1a). The dephasing rate of the initially observed anisotropy is related to the doped cluster size distribution as different distributions lead to different ensembles of rotational frequencies. Challenges, like low sample density in the gas phase and dominating linear background signals are overcome by phase-modulation and lock-in detection [2]. Preliminary results suggest a high sensitivity on the cluster size of ± 50 atoms (see Fig. 1b). The approach is applicable to continuous and pulse beam expansion conditions.

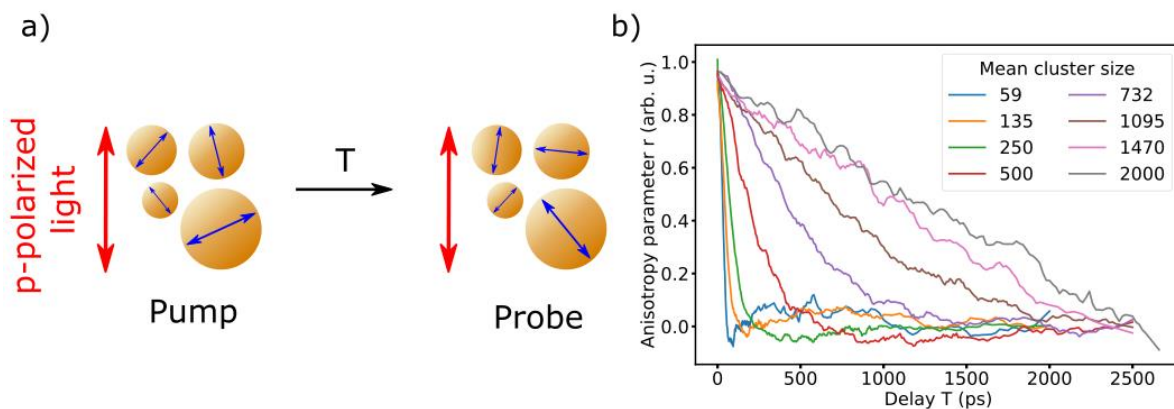


Fig 1. (a) Dephasing of the initially excited dipole moments, indicated by the blue arrows on the clusters. (b) Decay of the anisotropy parameter for argon clusters with a mean cluster size between 60 and 2000 atoms.

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Modelling catalytic processes:

Structure and reactivity of metal clusters in superfluid helium nanodroplets

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Gas-phase metal clusters present a significant opportunity for probing catalytic processes at the molecular level. They afford precise control over the structure, charge, and composition of catalytically active sites, thereby enhancing activity compared to bulk metal due to their small size, high surface-to-volume ratio, and size-dependent physical and chemical properties.^[1]

This study focuses on investigating the structure and reactivity of coinage metal clusters (Cu, Ag, Au) formed within multiply-charged superfluid helium nanodroplets to elucidate fundamental catalytic mechanisms. Given the strong influence of active site structure on catalytic activity, we examine the structures of positively and negatively charged metal clusters with sizes up to ten atoms. These clusters are meticulously solvated in helium, and the resulting complexes are analyzed using mass spectrometry. Computational analysis of the most stable complexes aids in estimating cluster structures.^[2]

Furthermore, charged clusters are reacted with molecules of interest, such as CO₂ or acetylene, to unravel their size-dependent reactivity. IR photo detachment spectroscopy of helium-tagged complexes^[3], play a crucial role in unravelling the intricate details of the cluster-molecule interactions providing direct insights into the structural arrangement and bonding nature of the molecules bound to the clusters.

Our comprehensive understanding of these properties not only advances fundamental knowledge of catalysis at the nanoscale but also provides insights into the rational design of efficient and selective catalysts for chemical transformations.

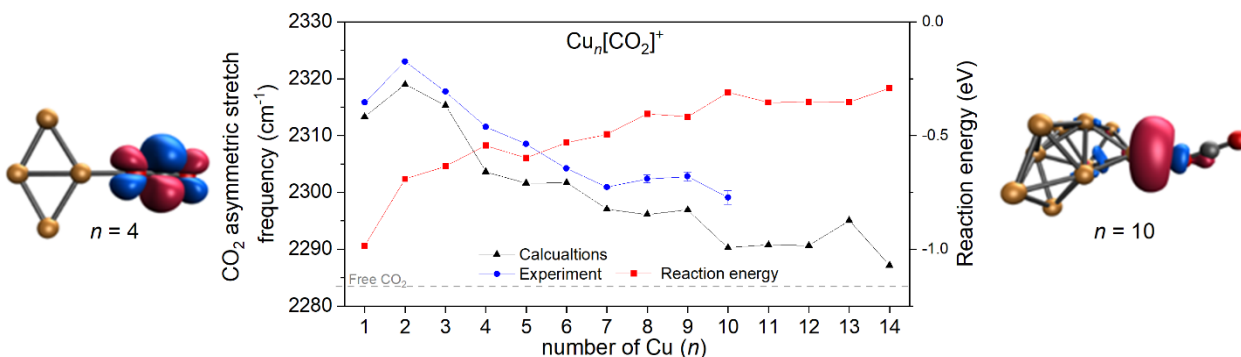


Fig.1: The frequency of the asymmetric stretch vibration of CO₂ bound to copper clusters of different sizes (n), obtained experimentally (blue circles) and computationally (black triangles). The dashed line represents the frequency for free CO₂. Additionally, the binding energy of CO₂ to each cluster is depicted with red squares. Geometric structures for selected configurations are also presented.

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Intensity dependent ion and electron emission from size-selected metal clusters

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Single-sized clusters of Ag_{309}^- are accumulated within a digital Paul trap and exposed to intense optical laser pulses, leading to the formation of nanoplasmas of known initial conditions. Using field-free diagnostics, the resulting Coulomb explosion is analyzed, giving electron distributions and charge-state resolved ion energy spectra, see Fig. 1. Experiments on the well-defined target result in comprehensive information on the particle emission and reveals details of nanoplasma dynamics not yet available. These are for example the subtle interplay between electron and ion dynamics, which becomes apparent in the intensity-dependent development of maximum and average values, as well as the at first counter-intuitive observation that the highest recoil energies show up at lower charge states.

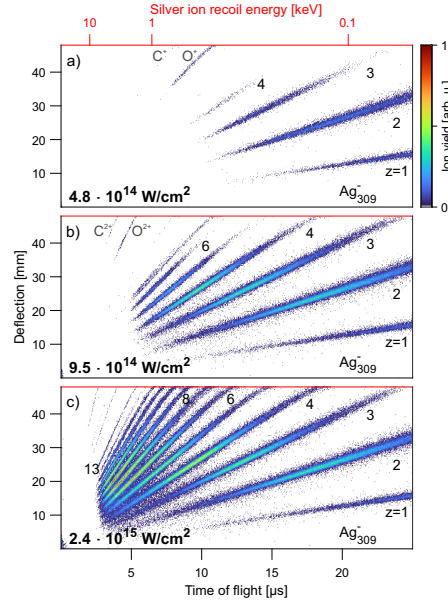


Figure 1: TOF-deflection histograms of energetic ions, resulting from strong field Coulomb explosions of Ag_{309}^- (a) $I_L = 4.8 \cdot 10^{14} \text{ W/cm}^2$, (b) $I_L = 9.5 \cdot 10^{14} \text{ W/cm}^2$ and (c) $I_L = 2.4 \cdot 10^{15} \text{ W/cm}^2$. Each stripe corresponds to the energy spectrum of a given charge state Ag^{z+} , as indicated in the figure. Also, signals from fast carbon and oxygen ions (as indicated) are identified. The feature in the lower left corner stems from high energetic photons.

Secondary electron statistics upon highly charged helium nanodroplets colliding with metal surfaces

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In recent years, the helium nanodroplet (HND) technique has gained interest as a particularly advantageous method for the growth of clusters and the gentle deposition of these particles on surfaces. The impact is cushioned by the surrounding liquid helium and prevents fragmentation [1]. Recently, it was shown at the University of Innsbruck that splashing and backscattering of particles in the deposition process are not negligible and significantly reduce deposition rates [2]. It appears that helium nanodroplets behave like ordinary liquid droplets when splashed onto a surface, but so far the interaction of multiply charged HND on different surfaces has not been investigated in detail. Understanding the deposition of kinetic and potential energy upon impact of an ionized projectile on a solid surface is crucial for the study of deposition processes [3].

In the experiment presented in this contribution, helium nanodroplets are produced in a supersonic gas expansion and multiply charged via electron impact ionization. After ionization, the droplets store a considerable amount of potential energy in form of both ionized and excited helium atoms. After mass-per-charge selection of the droplets with a quadrupole bender, the droplets collide with a metal target placed in a newly designed experimental chamber. In the soft deposition of multiply charged nanoclusters using the HND technique, it is assumed that the release of potential energy due to ion-surface interaction is the most important form of interaction. Quantifying the emission of secondary electrons as a result of this interaction may therefore provide great insight into the underlying mechanics of the multiply-charged HND-surface interaction. In this work, the emission of secondary electrons is investigated for different charge states and energies of the HNDs.

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Spectroscopy Identification of Hemi-bonded Structure of Water Cation Clusters in Helium Droplets

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The ionization in water is an essential process in various chemical environments. Understanding the fate of H_2O^+ and e^- in the presence of surrounding water molecules is of fundamental interest. Ionic water clusters have been targets of such studies to elucidate the structures of excess-charged species. Previous theoretical calculations suggested that two key motifs of the $(\text{H}_2\text{O})_n^+$ cation are the well-known proton-transferred (PT) structure ($\text{H}_3\text{O}^+\cdot\text{OH}$) and the metastable hemibonded (Hemi-) structure $(\text{H}_2\text{O}\cdot\text{OH}_2)^+$. The existence of the latter, where two H_2O moieties share the excess charge with a bond order of 1/2, is the crucial question in understanding the mechanism of forming a hydrogen bond network in ionized water. However, due to a significant potential barrier between the PT and Hemi structures, the existence of the Hemi-type water dimer cation has not been obtained clearly.

In the present study [1], we performed infrared spectroscopy of the water dimer cation $(\text{H}_2\text{O})_2^+$ in the helium droplet produced by ionization of the neutral water dimer. We observed the OH stretching bands and identified the molecular structure of $(\text{H}_2\text{O})_2^+$ by their spectra. In addition to the proton transfer type observed by the tagging method previously, we obtained new vibrational peaks corresponding to the Hemi-type $(\text{H}_2\text{O}\cdot\text{OH}_2)^+$. This finding indicates that a metastable Hemi-structure was realized in the droplet by rapidly cooling the dimer cation. The extension to larger water cation clusters $(\text{H}_2\text{O})_n^+$ ($n \geq 3$) provides the further information on the ionized water network.

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Observation of ordered shell structures in the helium solvation of multiple charged monoatomic ions

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The solvation of ions in liquid helium is a research field with a long history. It is well known that an ion in liquid helium forms a region of high density in its direct vicinity due to electrostriction (*Atkin snowball*). In the helium attachment to the ion, usually shell structures can be detected. The investigation of these structures is of interest because the size and number of shells can provide information about geometric and/or chemical properties of the embedded ion. A review article by González-Lezana et al. gives a tabular overview of the number and size of shells for a variety of different ions, that were investigated in the past [1]. This summary of research shows, that despite the large number of measured systems, there is a very limited number of studies on the He solvation of multiply charged impurities.

Recent studies in our laboratories showed that helium solvated Ca^{2+} ions, formed inside multiply charged helium nanodroplets, show the formation of up to four ordered solvation shells. Besides beneficial geometric properties, the double charge of the impurity has proven to be decisive for the large amount of helium attachment [2]. Following this investigation, our experimental setup was extended by a second ion source, enabling the formation of multiply charged ions inside the droplets by sequential Penning ionization [3].

In this contribution our most recent measurements on the solvation of doubly charged ions of elements of the rare earth metals (holmium and yttrium) are presented.

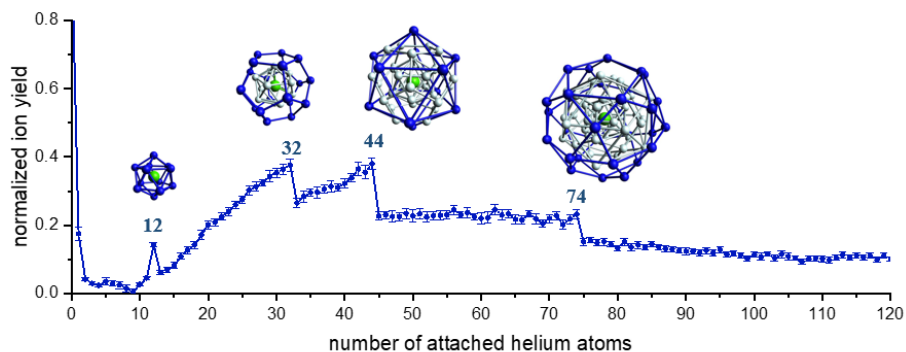


Fig 1. Closed shell structures in the helium solvation of Ho^{2+} can be detected in the ion abundance curve.

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Droplet size distributions in pulsed helium droplet beams in the condensation regime

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Beams of superfluid helium droplets produced by expansion of helium through an aperture/nozzle into vacuum consist of streams of individual droplets with size distributions which depend on the temperature T_0 , pressure P_0 , and state (gas or liquid) of the helium on the high pressure side of the aperture, and also on whether the expansion is pulsed or continuous. Various regimes have been identified, including those where liquid flash and Rayleigh break-up processes dominate (low temperatures, large droplets), and the condensation regime at higher temperatures ($T_0 \gtrsim 12$ K) which in general produces more stable distributions of smaller droplets. Operation in the condensation region is of particular importance to understand since the droplets produced are of sizes widely used for spectroscopic studies of captured molecules.

Size distributions for continuous beams in this regime have been studied in detail, with average sizes of around 10^4 atoms (at $P_0=2.0$ MPa, $T_0 \sim 20$ K) and log-normal distributions, but pulsed beams (which are particularly well suited to spectroscopy applications) are less well understood. While the expansion dynamics at a given (P_0, T_0) can be expected to be similar, previous reports have shown larger mean droplet sizes (by up to two orders of magnitude [1,2]) and bimodal exponential size distributions [3]. In this work we use a commercial RGA (residual gas analyser) to ionise a pulsed droplet beam prior to passing it into an electrostatic cylindrical deflector to determine size distributions from the droplet kinetic energy, in a technique similar to that used by Laimer *et al.* [4]. Our results show that in our pulsed nozzle setup at temperatures corresponding to the condensation regime the beam consists of two distinct velocity components, which each have a distinct log-normal distribution of droplet sizes.

We will further compare the results from two different beam sources to previous work to provide important new information for future spectroscopic studies.

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