International Conference on Quantum Fluid Clusters
QFC 2019

696. WE-Heraeus-Seminar

19 – 22 May 2019
at the Physikzentrum Bad Honnef/Germany

WILHELM UND ELSE
HERAEUS-STIFTUNG

Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see https://www.we-heraeus-stiftung.de

Aims and scope of the 696. WE-Heraeus-Seminar:

QFC 2019 is the 12th occurrence of the QFC conference series. The focus of the seminar is to stimulate the research on atomic clusters, in particular helium nanodroplets, which are strongly influenced in their properties by quantum mechanical many-body effects. It covers both fundamental aspects such as superfluidity and quantum vortices, as well as application of QFC as flying nano-cryostats for probing and synthesizing cold molecules and exotic nano-complexes. The seminar is interdisciplinary in nature, involving physics and chemistry in equal measure. Likewise, it addresses both experimentalists and theoreticians, and a panoply of different experimental and theoretical methods will be presented. In this way, the seminar provides a unique forum for the exchange of knowledge, technical knowhow, and ideas with a clear focus on QFC. Each topical session is preceded with an introductory lecture to give in-depth introductions to selected QFC-related topics of particular current interest.

Scientific Organizers:

Prof. Dr. Marcel Mudrich	Aarhus University, Aarhus, Denmark E-mail: mudrich@phys.au.dk
Prof. Dr. Henrik Stapelfeldt	Aarhus University, Aarhus, Denmark E-mail: henriks@chem.au.dk

Program

Program

Sunday, 19 May 2019

17:00 – 21:00	Registration	
from 18:30	*BUFFET SUPPER / Informal get together*	
20:00	Key note Paul Scheier	**Ionization of large Helium nanodroplets**

Monday, 20 May 2019

07:30	*BREAKFAST*	
08:45 – 09:00	Marcel Mudrich Henrik Stapelfeldt	**Opening and welcome**
09:00 – 09:45	Introductory 1 Misha Lemeshko	**Quasiparticle approach to far-from-equilibrium dynamics of molecules in Helium nanodroplets**
09:45 – 10:20	Invited 1 Adam Chatterley	**Imaging controlled complex in Helium droplets with Coulomb explosion**
10:20 – 10:50	*COFFEE BREAK*	
10:50 – 11:25	Invited 2 Frank Stienkemeier	**Two-dimensional coherent spectroscopy of doped Helium nanodroplets**
11:25 – 12:00	Invited 3 Florent Calvo	**Stepwise solvation of polycyclic aromatic hydrocarbons by Helium: curvature and dynamical effects**
12:00 – 12:45	**Poster flash**	
12:45	**Conference Photo** (in front of the Physikzentrum/Main entrance)	
12:50	*LUNCH*	

Program

Monday, 20 May 2019

14:00 – 14:45	Introductory 2 Jochen Küpper	**Controlled molecules and nanoparticles**
14:45 – 15:20	Invited 4 Daniela Rupp	**Ultrafast dynamics in Helium nanodroplets**
15:20 – 15:55	Invited 5 Vitaly Kresin	**Polar molecules entrapped in Helium nanodroplets: Electric deflection, size separation, charge migration**
15:55 – 16:30	*COFFEE BREAK*	
16:30 – 17:05	Invited 6 Aaron Laforge	**Intermolecular decay mechanisms in doped Helium droplets induced by XUV radiation**
17:05 –17:25	Hot topic 1 Sweta Erukala	**Shapes of rotating ^{3}He droplets**
17:25 - 17:45	Hot topic 2 Devendra Mani	**Accessing different binding sites of a multifunctional molecule in Helium droplets**
17:50 – 18:30	**Free discussions / Advisory board meeting**	
18:30	*HERAEUS DINNER at the Physikzentrum* *(cold & warm buffet, free beverages)*	
20:00	**Posters**	

Tuesday, 21 May 2019

08:00	*BREAKFAST*	
09:00 – 09:45	Introductory 3 Andrew Ellis	**Accessing challenging molecular species using helium droplets: clusters, complexes and ions**
09:45 – 10:20	Invited 7 Sergiy Krasnokutskiy	**Experimental characterization of the energetics of low-temperature surface reactions**
10:20 – 10:50	*COFFEE BREAK*	
10:50 – 11:25	Invited 8 Gert von Helden	**Spectroscopy of mass/charge selected cations and anions in Helium droplets**
11:25 – 12:00	Invited 9 Ruth Signorell	**Influence of electron scattering on the properties of the hydrated electron**
12:00 – 12:20	Hot topic 3 Florian Lackner	**Photoinduced formation of RbSr molecules on Helium droplets from spatially separated Rb and Sr atoms**
12:20 – 12:40	Hot topic 4 Nadine Halberstadt	**Can 0.4K He induce electronic relaxation? The case of Rb and Ba^+ @ superfluid He droplets**
12:45	*LUNCH*	
14:00 – 14:45	Introductory 4 Gary Douberly	**Infrared spectroscopy of alkyl radicals in Helium droplets and solid *para*-hydrogen**
14:45 – 15:20	Invited 10 Martina Havenith	**Acid Solvation versus dissociation at “stardust conditions”: reaction sequence matters!**
15:20 – 15:55	Invited 11 Manuel Barranco	**Superfluid Helium nanodroplets: The many impurities, many vortices cornucopia**
15:55 – 16:30	*COFFEE BREAK*	

Tuesday, 21 May 2019

16:30 – 17:05	Invited 12 Markus Koch	**Femtosecond photoexcitation dynamics of atoms and molecules inside Helium nanodroplets**
17:05 – 17:25	Hot topic 5 Alkwin Slenczka	**Stark-spectroscopic investigations of large organic molecules in superfluid Helium nanodroplets**
17:25 -17:45	Hot topic 6 Josef Tiggesbäumker	**Auger emission from the Coulomb explosion of Helium nanoplasmas**
17:50 – 18:30	**Guided discussions**	
18:30	*DINNER*	
20:00	**Posters**	

Wednesday, 22 May 2019

08:00	*BREAKFAST*	
09:00 – 09:45	Introductory 5 Andrey Vilesov	**Quantum vortices in superfluid helium droplets**
09:45 – 10:20	Invited 13 Wei Kong	**Trapping of multiple ions and suppression of multiphoton ionization by large Helium droplets**
10:20 – 10:50	*COFFEE BREAK*	
10:50 – 11:25	Invited 14 Oliver Gessner	**Ultrafast energy transfer in doped He nanodroplets studied by femtosecond XUV photoelectron imaging**
11:25 – 12:00	Invited 15 Thomas Fennel	**New routes to imaging the classical and quantum dynamics of finite systems**
12:00 – 12:45	Wrap-up Jussi Eloranta	**"Wrap up" talk of QFC2019**
12:45 – 13:00	Marcel Mudrich Henrik Stapelfeldt	**Poster awards and closing remarks**
13:00	*LUNCH*	

End of the seminar and Departure

Please note that there will be no dinner at the Physikzentrum on Wednesday evening for participants leaving the next morning.

Posters

Posters

P01	Simon Albertini	**Investigation of Au cluster deposition using Helium nanodroplets**
P02	Jakob Dall Asmussen	**Autoionization of excited He nanodroplets**
P03	Loren Ban	**Photoelectron velocity-map imaging of charged submicron-sized droplets**
P04	Ulrich Bangert	**Two-dimensional electronic spectroscopy of Rb_3 in Helium nanodroplet isolation**
P05	Ltaief Ben Ltaief	**Electron transfer mediated decay in He nanodroplets doped with heteronuclear alkali dimers**
P06	Giacomo Bighin	**Diagrammatic Monte Carlo approach to angular momentum in quantum many-body systems**
P07	Marcel Binz	**Peak shape modulations in two-dimensional electronic spectroscopy caused by intense laser pulses**
P08	Marc Briant	**Investigation of the weak hydrogen bond of some propyne complexes**
P09	Fabien Brieuc	**Fully flexible path integral simulations of fluxional molecules in bosonic clusters**
P10	Igor Cherepanov	**An angulon quasiparticle perspective on impulsive molecular alignment in ^{4}He nanodroplets**
P11	Markus Debatin	**Dopand-induced Helium nanoplasmas in strong near-infrared laser pulses**

Posters

P12	Katrin Dulitz	**Quantum-state-controlled reactive collisions between lithium atoms and metastable Helium atoms**
P13	Laura Durán Caballero	**Microsolvation of the water molecule by bosonic Helium**
P14	Alexandra Feinberg	**Experiments with large ^{3}He droplets**
P15	Johannes Fischer	**Stark-spectroscopic investigations of large organic molecules in superfluid Helium nanodroplets**
P16	Floriane Grollau	**Spectroscopy of 4(5)-Methylimidazole and its hydrates, hosted in Helium droplets**
P17	Andreas Heidenreich	**Dopant-induced ignition of Helium nanoplasmas**
P18	Masahiko Ichihashi	**Detection of low-lying electronic states of Co_m^+ in He clusters**
P19	Mallikarjun Karra	**Theoretical investigations of electronic excitation of organic species doped into superfluid Helium nanodroplets**
P20	Katharina Kolatzki	**Setup and characterization of a Helium liquid jet for diffractive imaging experiments**
P21	Smail Kouidri	**Interacting dipolar Bose gas in the presence of three-body interactions**
P22	Bennet Krebs	**Comparison of electron and ion emission from Xenon cluster induced ignition of Helium nanodroplets**

Posters

P23	Felix Laimer	**Highly charged superfluid Helium nanodroplets**
P24	Friedemann Landmesser	**Two-dimensional electronic spectroscopy of isolated, cold molecular nanosystems**
P25	Linnea Lundberg	**Hydrogenated Gold clusters produced with Helium nanodroplets**
P26	Luis Mendoza Luna	**Inefficient non-radiative relaxation of vibrationally excited Helium excimers solvated in the bulk investigated via fluorescence spectroscopy**
P27	Roman Messner	**Towards new plasmonic materials: Synthesis of K and K-Au nanoparticles with Helium nanodroplets**
P28	Moritz Michelbach	**Size distributions of supersonic beams from a pulsed valve using the titration technique**
P29	Rupert Michiels	**Time-resolved interatomic coulombic decay observed in Helium droplets**
P30	Valery Milner	**Controlled enantioselective orientation of chiral molecules with an optical centrifuge**
P31	John Niman	**Formation of polar DMSO structures in Helium nanodroplets**
P32	Sean O'Connell	**Vortex lattice in rotating prolate ^{4}He droplets**
P33	Nitish Pal	**IR spectroscopy of Glycine-water in Helium nanodroplets**

Posters

P34	Martí Pi	**Vorticity and quantum turbulence in the merging of superfluid Helium nanodroplets**
P35	Nicolas Rendler	**Experimental study of the solvation and desorption dynamic of Cs atoms attached to ^{4}He nanodroplets**
P36	Catherine Saladrigas	**Femtosecond time-resolved energy transfer dynamics in excited doped Helium nanodroplets**
P37	Arne Schiller	**Mass spectrometric investigation of corannulene-Helium cationic complexes and their absorption spectroscopy**
P38	Florian Schlaghaufer	**Rotationally resolved electronic spectroscopy of large organic molecules and their vdW-complexes in the gas phase**
P39	Gerhard Schwaab	**The THz/FIR spectrum of small water clusters**
P40	Audrey Scognamiglio	**Towards femtosecond pump-probe spectroscopy of charge-transfer complexes embedded in Helium nanodroplets**
P41	Mykola Shcherbinin	**Coulombic decay in He nanodroplets**
P42	Alkwin Slenczka	**Anthracene and Anthracene-Ar$_n$ clusters in superfluid Helium nanodroplets**
P43	Bernhard Thaler	**Photoinduced dopant-to-solvent energy transfer dynamics in helium nanodroplets studied with time-resolved photoelectron spectroscopy**
P44	Lukas Tiefenthaler	**Size distributions of Helium nano droplets**

Posters

P45	Jan Peter Toennies	**Are metal clusters in superfluid He droplets superconducting?**
P46	Leonhard Treiber	**Indium dimer fragmentation induced by femtosecond pump-probe ionization inside Helium nanodroplets**
P47	Daniel Uhl	**Photoelectron two-dimensional coherent spectroscopy**
P48	Alexandra Viel	**HENDI spectroscopy of acetylene-Ne,Ar,Kr: large amplitude motion at 0.4K**
P49	Klaus von Haeften	**Radiative and non-radiative relaxation of rotational and vibrational levels of excimers in liquid and gaseous Helium**
P50	Michael Zabel	**Auger emission from the Coulomb explosion of Helium nanoplasmas**

Abstracts of Talks

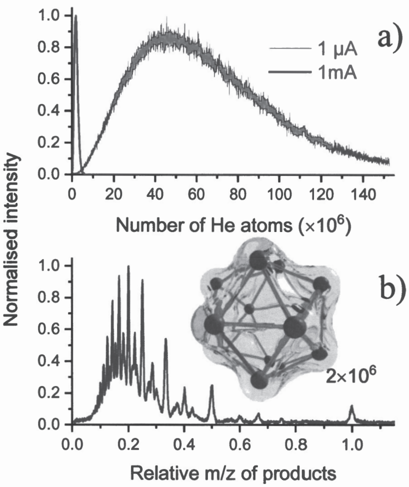
(in chronological order)

Ionization of large helium nanodroplets

F. Laimer, P. Martini, L. Kranabetter, L. Tiefenthaler, S. Albertini, F. Zappa, M. Gatchell and P. Scheier

Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Austria

Helium droplets containing between 10^5 and 10^{10} He atoms [1] were formed and subjected to electron beams of defined energy and current [2]. Mass per charge distributions were determined by electrostatic energy analyzers for positively and negatively charged droplets [3]. Utilizing two ion sources, each followed by a spherical sector field analyzer, it was possible to unambiguously determine the charge state as well as the mass of charged He droplets. Charge states higher than 65+ as well as 5- could be assigned and neutralization as well as increasing of the charge state could be achieved by the second ion source. Perfect fractional numbers of the mass per charge ratios of product ions with respect to the charged precursor droplets indicate that fragmentation exclusively happens via very asymmetric Coulomb explosion and evaporation of He atoms. These low-mass ions have been investigated by mass spectrometer systems so far [2]. Coulomb repulsion between charges of same polarity in highly-charged He droplets will lead to minimum energy configurations in the form of Coulomb crystals. Dopants will be polarized and attracted by the charged centers which thereby act as seeds for cluster growth.



The upper diagram shows size distributions measured for soft (1 μA) and hard (1 mA) ionization conditions. The panel designated with b) shows the mass per charge distribution of product ions formed upon ionization of a size-selected precursor droplets consisting of $2\times10^6\times z$ He atoms. The inset is an artists view of a Coulomb crystal in a large helium droplet.

This work was supported by the EU commission, EFRE K-Regio FAENOMENAL EFRE 2016-4

References

[1] L.F. Gomez et al., J. Chem. Phys. **135**, 154201 (2011)
[2] A. Mauracher et al., Phys. Rep. **751**, 1 (2018)
[3] U. Henne and J.P. Toennies, J. Chem. Phys. **108**, 9327 (1998)

Quasiparticle approach to far-from-equilibrium dynamics of molecules in helium nanodroplets

Mikhail Lemeshko

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Am Campus 1, 3400 Klosterneuburg Austria

Recently we have predicted a new quasiparticle — the angulon — which is formed when a quantum impurity (e.g. a molecule, atom, or electron) exchanges its angular momentum with a many-particle environment (such as lattice phonons or collective excitations in a liquid) [1,2]. Soon thereafter we obtained strong evidence that angulons are formed in experiments on molecules trapped inside superfluid helium nanodroplets [3].

In my talk, I aim to introduce the concept of angulon quasiparticles and to demonstrate how complex problems of far-from-equilibrium many-body dynamics can be simplified using this concept. In addition, I will describe novel physical phenomena that arise in molecules interacting with superfluid helium [1,5,6], as well as possible connections between matrix isolation spectroscopy and on-equilibrium magnetism.

[1] R. Schmidt, M. Lemeshko, Phys. Rev. Lett. 114, 203001 (2015)
[2] R. Schmidt, M. Lemeshko, Phys. Rev. X 6, 011012 (2016)
[3] M. Lemeshko, Phys. Rev. Lett., 118, 095301 (2017); Viewpoint: Physics 10, 20 (2017)
[4] B. Shepperson, A. A. Sondergaard, L. Christiansen, J. Kaczmarczyk, R. E. Zillich, M. Lemeshko, H. Stapelfeldt, Phys. Rev. Lett. 118, 203203 (2017)
[5] E. Yakaboylu, M. Lemeshko, Phys. Rev. Lett. 118, 085302 (2017)
[6] E. Yakaboylu, A. Deuchert, M. Lemeshko, Phys. Rev. Lett. 119, 235301 (2017)

Imaging Controlled Complex in Helium Droplets with Coulomb Explosion

A. S. Chatterley, C. Schouder and H. Stapelfeldt[1]

[1]*Department of Chemistry, Aarhus University, Aarhus, Denmark*

The structures of weakly bound complexes embedded inside helium droplets have been directly measured using Coulomb explosion imaging. Using a field-free 3D alignment technique, the complex is fixed in lab frame, and then and intense laser pulse initiates Coulomb explosion between monomers. The field-free nature of the alignment allows the Coulomb energy of intact monomers to be directly measured with velocity map imaging. By varying the relative orientation of the complex in the lab frame, the structure is directly measured.

We demonstrate this technique on systems ranging from OCS complexes, to tetracene dimers, and even to complexes of C_{60}. Using a time-resolved particle imaging camera, we can also measure heterodimers, which is demonstrated by finding the structure of a bromobenzene – I_2 complex. The outlook for the technique includes imaging femtosecond dynamics of complex motions, and even imaging bimolecular reactions in a helium droplet.

Two-Dimensional Coherent Spectroscopy of Doped Helium Nanodroplets

Lukas Bruder, Ulrich Bangert, Marcel Binz, Friedemann Landmesser, Daniel Uhl, and Frank Stienkemeier

Institute of Physics, University of Freiburg, D-79104 Freiburg, Germany

For measuring ultra-fast dynamics, we have established 2-dimensional coherent electronic spectroscopy (2DES), well-know from bulk biological systems, for very dilute targets [1]. With 2DES one can follow real-time dynamics on femtosecond time scales and unravel energetic structures and couplings. In particular, for excitation and electron transfer processes in organic molecular structures 2DES can provide rich information on the corresponding processes. In combination with helium nanodroplet isolation a high spectro-temporal can be achieved. As a first experiment, we probed alkali-doped helium droplets. The recorded 2D maps provide the real-time evolution of both vibrational dynamics and desorption processes.

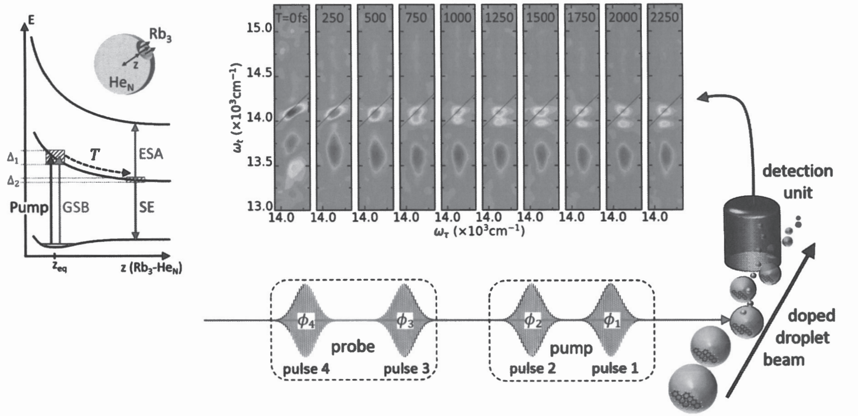

Figure 1: In 2D spectroscopy the interaction with 4 femtosecond laser pulses reveals the time evolution upon electronic excitation. The central feature in the plotted sections of the 2D maps reveals the desorption of a Rb_3 molecule from a helium nanodroplet.

References

[1] L. Bruder, U. Bangert, M. Binz, D. Uhl, R. Vexiau, N. BouloufaMaafa, O. Dulieu, F. Stienkemeier, Nature Communications 9: 4823, (2018).

Stepwise solvation of polycyclic aromatic hydrocarbons by helium: curvature and dynamical effects

F. Calvo[1] **and E. Yurtsever**[2]

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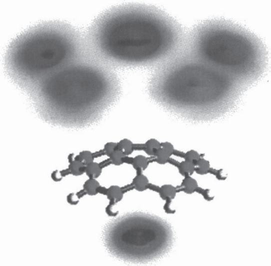
[2] Chemistry Department, Koç University, Istanbul, Turkey

The progressive solvation of cationic polycyclic aromatic hydrocarbons (PAHs) and PAH dimers was investigated computationally by means of path-integral molecular dynamics simulations employing carefully designed polarizable force fields. The completion of the first solvation shell was particularly scrutinized and different binding regimes are clearly identified with their own extent of nuclear delocalization. The preference for helium atoms to bind strongly near aromatic facets is further reflected on the different affinities on either sides of curved PAHs such as the corannulene cation (see figure) [1].



The most stable configuration found for 7 helium atoms around the corannulene cation

Ring-polymer molecular dynamics simulations were also performed to get insight into the possible time-dependent behavior of perylene dimers under the cryogenic environment of larger droplets containing hundreds of helium atoms. The enhanced localization of rare gas atoms in the vicinity of aromatic planes gives rise to metastable configurations in which a few solvent atoms are sandwiched between the PAH molecules [2].

References

[1] M. Gatchell et al., Faraday Discussions (in press).
[2] F. Calvo, E. Yurtsever, and O. Birer, J. Phys. Chem. A **120**, 1726 (2016)

Controlled molecules and nanoparticles

J. Küpper

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Department of Chemistry, Universität Hamburg, 20146 Hamburg, Germany
Center for Ultrafast Imaging, Universität Hamburg, 22761 Hamburg, Germany

High-resolution imaging of molecular structure and dynamics has evolved as a key paradigm to unravel the spatiotemporal evolution of (bio)molecular systems during chemical reactions. In the limit of the simultaneous observation of ultrafast electronic and nuclear dynamics with intrinsic temporal and atomic-level spatial resolution, we have dubbed this the "quantum molecular movie".
Generally, these novel imaging approaches strongly benefit from, or simply are enabled by, strongly controlled samples that allow to experimentally average over many molecules while still observing the single molecule's "movie".

In this introductory lecture, I will discuss our approaches to control molecular samples, ranging from small few-atomic molecules over molecular clusters mimicking reaction pairs or solvated molecules to large biological molecules and nanoparticles. The control schemes include fast cooling of particles, the deflection and focusing of molecules and particles, and the separation of individual quantum states or molecular species – in order to create samples of identical molecules. Furthermore, the molecules can be fixed in space or even converted into species with special properties using laser alignment or electric-field orientation techniques to make sure the imaged samples, in laboratory space, have an identical look.

References

[1] Y.-P. Chang, D.A. Horke, S. Trippel, and J. Küpper, *Int. Rev. Phys. Chem.* **34**, 557–590 (2015).
DOI: 10.1080/0144235X.2015.1077838
arXiv:1505.05632 [physics]

Ultrafast Dynamics in Helium Nanodroplets

Daniela Rupp

Max-Born-Institute Berlin, Germany

Extremely intense short-wavelength and ultrashort pulses of free-electron lasers (FEL) and high harmonic sources (HHG) allow novel experiments with highest spatial and temporal resolution. One key example is diffraction imaging of individual nanoparticles, i.e. the measurement of elastically scattered photons forming an interference pattern which encodes structural information. This enables the study of such fragile structures as combustion aerosols or superfluid helium nanodroplets and time-resolved investigations of e.g. laser induced ultrafast melting in metal nanoparticles. Even electronic processes due to excitation and ionization change the scattering response and can therefore in principle be traced [1]. While electron dynamics occur on a timescale shorter than the typical tens of femtosecond pulse durations, an exciting development can be expected from the current progress at both FEL and HHG sources towards high-intensity attopulses.

In my talk I will present static and time-resolved diffraction experiments on helium nanodroplets using extreme ultraviolet (XUV) pulses. The comparably long wavelengths allow for the measurement of wide-angle diffraction patterns that contain three-dimensional information [2], thus enabling the structural characterization of superfluid spinning droplets [3,4]. To trace the XUV induced dynamics in helium nanodroplets, we have developed a novel concept using two XUV pulses of different wavelengths for capturing consecutive images of the same droplet. Further, ultrafast bleaching effects were observed in helium nanodroplets irradiated with moderately intense infrared laser pulses (10^{11} W/cm²) and imaged with near-resonant HHG pulses. Both results exemplify the capability of diffraction imaging to visualize ultrafast nanoscale dynamics in highly excited matter.

References

[1] C. Bostedt et al. *Ultrafast X-ray scattering of xenon nanoparticles: imaging transient states of matter*, Phys. Rev. Lett. **108**, 093401(2012)
[2] I. Barke et al. *The 3D-architecture of individual free silver nanoparticles captured by X-ray scattering*, Nat. Commun. **6**, 6187 (2015)
[3] D. Rupp et al. *Coherent diffractive imaging of single helium nanodroplets with a high harmonic generation source*, Nat. Commun. **8**, 493 (2017)
[4] B. Langbehn et al. *Three-dimensional shapes of spinning helium nanodroplets*, Phys. Rev. Lett. **121**, 255301 (2018)

Polar molecules entrapped in helium nanodroplets: Electric deflection, size separation, charge migration

J. Niman[1], B. Kamerin[1], D. Merthe[1], L. Kranabetter[2], Vitaly Kresin[1]

[1] Department of Physics, University of Southern California, Los Angeles, USA

[2] Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Austria

A polar molecule captured within a superfluid helium nanodroplet can become fully oriented when it passes through a static electric field. Once so aligned, it can experience an intense force from the field's gradient. We show that such forces are able to deflect beams of nanodroplets, composed of tens of thousands of He atoms, by up to a few millimeters. These droplets, with their substantial deflections, appear to be the most massive neutral systems studied by molecular beam "deflectometry." The deflection data are used to extract the first and second moments of the nanodroplet size distribution. Furthermore, since each host droplet deflects according to its mass, the neutral fragile nanodroplets can be filtered by size by means of spatially filtering the deflected beam. To illustrate this technique, we measure the ionization probability of embedded molecules as a function of droplet size and determine the mean free path for the migration of charge through the helium matrix. The method is applicable to a variety of molecules and can be utilized for size-dependent spectroscopic studies.

This work is supported by the US National Science Foundation (CHE-1664601).

References

[1] D. J. Merthe and V. V. Kresin, "Electrostatic deflection of a molecular beam of massive neutral particles: Fully field-oriented polar molecules within superfluid nanodroplets," J. Phys. Chem. Lett. **7**, 4879 (2016).

[2] J. W. Niman, L. Kranabetter, B. Kamerin, D. J. Merthe, and V. V. Kresin, subm. for publication.

Intermolecular decay mechanisms in doped helium droplets induced by XUV radiation

A. C. LaForge[1]

[1] *Department of Physics, University of Connecticut, Storrs, CT, USA; aaron.laforge@uconn.edu*

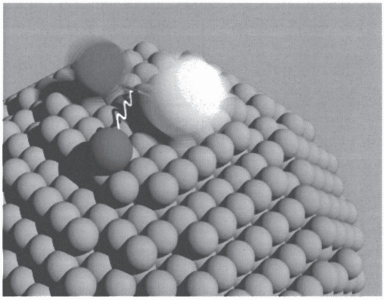

Fig. 1: Schematic for dICD

As opposed to purely molecular systems where electron dynamics proceed only through *intramolecular* processes, weakly-bound complexes such as helium droplets offer an environment where local excitations can interact with neighboring embedded molecules leading to new *intermolecular* relaxation mechanisms. Here, we report on our recently published results [1] where we observed a strongly enhanced double ionization mechanism due to energy transfer termed double intermolecular Coulombic decay (dICD). To experimentally observe this mechanism, dimers consisting of two alkali metal atoms were attached to the surface of helium droplets. The dICD process, schematically shown in Fig. 1, occurs through an electronically excited helium atom (red), produced by synchrotron radiation, interacting with the neighboring alkali dimer (blue and white) resulting in energy transfer and double ionization. Although an alkali dimer attached to a He nanodroplet is a model case, dICD is potentially relevant for any system where it is energetically allowed.

dICD belongs to a special class of decay mechanisms where energy is exchanged between neighboring atoms or molecules leading to enhanced ionization rates. Seemingly ubiquitous in weakly-bound, condensed phase systems such as van der Waals clusters or hydrogen-bonded networks like water, these processes can contribute to radiation damage of biological systems by producing particularly harmful low-energy electrons. dICD could strongly enhance such effects through the production of two electrons for each decay. We will also discuss recent results on electron transfer mediated decay [2], a process where charge and energy are exchanged between neighboring molecules, as well as give an outlook on how these processes can be observed in larger, biologically-relevant systems.

References

[1] *A. C. LaForge et al., Nature Physics 15, 247 (2019)*
[2] *A. C. LaForge et al., Phys. Rev. Lett. 116, 203001 (2016)*

Shapes of Rotating ^{3}He Droplets

Swetha Erukala[1], Deepak Verma[1], Sean M. O'Connell[1], Alexandra Feinberg[1], Catherine Saladrigas[2], Benjamin Toulson[2], Mario Borgwardt[2], Niranjan Shivaram[3], Ming-Fu Lin[3], Andre Al Haddad[5], Christoph Bostedt[5,6], Peter Walter[3], Oliver Gessner[2] and Andrey F. Vilesov[1]

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[2]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
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[4]Laboratory for Femtochemistry (LSF), Paul Scherrer Institut, 5232 Villigen-PSI, Switzerland
[5]École Polytechnique Fédérale de Lausanne, Route Cantonale, 1015 Lausanne, Switzerland

Recent advent of X-ray free electron lasers (XFEL) has enabled the study of rotation in free isolated superfluid ^{4}He droplets.[1] The work presented here extends our study of rotating quantum fluids to non-superfluid ^{3}He droplets. Sub micrometer sized ^{3}He droplets are obtained from free jet expansion of liquid ^{3}He at temperatures less than 3 K and studied via X-ray scattering at the LCLS XFEL.[2] The obtained shapes and sizes of rotating ^{4}He and ^{3}He droplets have been compared. In contrast to superfluid ^{4}He droplets, ^{3}He droplets (T » 0.15 K) are devoid of quantum vortices. Tracing of quantum vortices inside ^{4}He droplets have been previously achieved through doping with large number of Xe atoms.[3] This work presents the first experimental study of the formation dynamics of atomic clusters in a homogenous, vortex-free quantum fluid.

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Accessing Different Binding Sites of a Multifunctional Molecule in Helium Droplets

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Superfluid helium droplets provide a unique ultracold (0.4 K) environment to study intermolecular complexes. There are many known examples where helium droplets facilitated the formation of local minima structures – that might not be accessible in the gas phase – for such complexes.[1-5]

We have studied complexation of a multifunctional molecule – propargyl alcohol ($H-C\equiv C-CH_2-OH$, hereafter abbreviated as PA) – with water. Due to the presence of two potential H-bond acceptor as well as donor groups –hydroxyl and acetylenic – in PA, multiple structures are possible for a 1:1 PA···water complex. Our mass-selective infrared spectroscopic studies in helium droplets, complemented with high-level ab initio calculations, reveal the selective formation of two local minimum structures. These structures are bound via O-H···O (with water as H-bond donor) and -C≡C-H···O (with propargyl alcohol as H-bond donor) interactions; and are less stable by 4.9 kJ/mol and 12.7 kJ/mol, respectively, as compared to the global minimum structure for the complex. The details will be presented in the talk.

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Accessing challenging molecular species using helium droplets: clusters, complexes and ions

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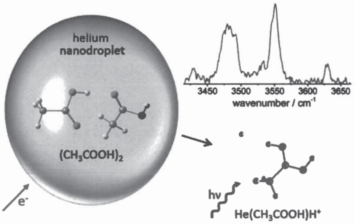
This presentation will describe recent work on the infrared spectroscopy of molecules and clusters in helium nanodroplets and will be divided into two parts: (1) the investigation of neutral hydrogen-bonded clusters and complexes, including the formic acid dimer,[1] and (2) the use of helium nanodroplets to create helium-tagged ions for IR photodissociation spectroscopy. The work on neutral formic acid dimers builds on our previous study of acetic acid dimer[2] and, like the latter, confirms the exclusive formation of metastable hydrogen-bonded isomers in liquid helium.

As well as their intrinsic interest as local minima on complex potential energy surfaces, the neutral dimers can act as precursors for the production of helium-tagged molecular ions and we will show how this technique has been applied in our laboratory. One example is protonated acetic acid, whose IR spectrum has been recorded for the first time via this technique (see below).



The mass-selective IR spectra provide structural information on the bare ions but can also be used to reveal the effect of helium tagging on the vibrational behavior of ions.

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Experimental Characterization of Low-temperature Surface Reactions

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Low-temperature reactions on the surface of cosmic solid particles ("dust") are thought to be responsible for the formation of complex organic molecules observed inside "dark" molecular clouds and planet-forming disks. These molecules could later be delivered to planets and facilitate the formation of biopolymers. However, there is a lack of quantitative experimental data on the relevant surface reactions. We describe an experimental technique, which can be used to measure the energy released in reactions of a single pair of reactants.[1] These data can be directly compared with the results of quantum chemical computations leading to unequivocal conclusions regarding the reaction pathways, the presence of energy barriers, and the final reaction products. In the experiment superfluid He nanodroplets are used as a nanocalorimeter and as a third body. Therefore, reactions investigated inside superfluid He nanodroplets are analogues to those occurring on chemically inert surfaces, for example, water ice surfaces. The new method was applied to study the reactions of C atoms with H_2, CO_2, O_2, NH_3 and C_2H_2 molecules. The formation of HCH, C_2O_2, CO + O, $HCNH_2$, and triplet cyclic-C_3H_2 products has been revealed. The method has applications beyond laboratory astrophysics in studying surface reactions.

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

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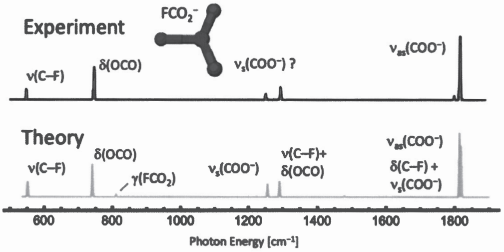
Helium droplets can pick up mass/charge selected ions from an ion trap and the doped droplets can be investigated using optical spectroscopy. We use that technique to investigate cations and anions ranging in size from ions containing only a few ions up to mass/charge selected protein ions containing several thousand atoms.

Here, we will present recent results on small mass/charge selected anions, specifically products from reactions between fluoride (F^-) ions with CO_2 and H_2O. It is observed that in the ion source region of our mass spectrometer, FCO_2^- as well as an ion that is heavier by the mass of one H_2O molecule are readily formed. Those ions can be mass/charge selected, stored in an ion trap and be picked up by helium droplets.

The doped droplets are irradiated by tunable IR light from the FHI free electron laser. Upon the resonant absorption of IR photons, the helium atoms are evaporated and/or the ion is ejected from the droplet. Monitoring the ion yield as a function of IR wavenumber gives the IR spectrum of the ion. The experimental spectra can be compared to theoretically predicted spectra. In the case of the FO_2^- ion, narrow lines with a width close to the linewidth of the FEL can be observed (see Figure). With the help of high-level theory, those lines can be assigned to stem from various modes, including some Fermi resonances. The spectrum and the structure of the ion 18 amu higher in mass are surprising and will be discussed.



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Influence of electron scattering on the properties of the hydrated electron

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The interest in the hydrated electron stems from its role in Chemistry, radiation damage and from the fact that it is one of the simplest quantum solutes. The ground state structure of the hydrated electron is surrounded by a controversy. Does it form a cavity with an s-like orbital character? What is the exact value of its binding or ionization energy? Is there a long-lived surface-bound state with distinct energetics? Experimentally, these properties have been probed with photoelectron spectroscopy – for excess electrons in anion water clusters and hydrated electrons in liquid microjets. The issue with existing data is that they neglect the influence of electron scattering in the liquid on the genuine properties of the hydrated electron. As a result, the experimental binding energy is artificially high and the photoelectron angular distribution is too isotropic compared with the corresponding genuine value. This contribution takes a closer look at the effects of electron scattering on the binding energy and the orbital character (photoelectron angular distribution). A detailed electron scattering model allows the quantification of the influence of electron scattering for hydrated electrons in liquid water and in water clusters, and thus the retrieval of genuine properties from experimental data.

Photoinduced formation of RbSr molecules on helium droplets from spatially separated Rb and Sr atoms

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Besides the use as cold matrix for spectroscopic studies, superfluid helium droplets have served as an inert environment for the synthesis of molecules and clusters. These systems are formed upon the successive capture and coagulation of dopant atoms and molecules. [1] However, there have been a few observations that seemed to indicate cases of separated dopants on one droplet not forming bonds but remaining isolated. [2]

We performed a systematic study of helium droplets doped with one rubidium and one strontium atom. We show that besides the formation of RbSr molecules upon pickup [3], there is a probability of finding separated Rb and Sr atoms on one droplet. [4] Upon excitation of the Sr-He$_N$ $5s5p\ {}^1P^o_1 \leftarrow 5s^2\ {}^1S_0$ transition the isolated atoms react and form a molecular bond. This is demonstrated by resonant two-photon ionization spectroscopy, where the initially excited Sr-He$_N$ transition can be followed on mass channels corresponding to Rb atoms and RbSr molecules. A similar scenario is found for droplets doped with two Sr atoms. Furthermore, a comparison between R2PI and laser induced fluorescence spectra suggests that ground state Sr atoms can reside at the surface as well as inside the droplet.

The results provide evidence for an alternative pathway that can be undertaken by dopants upon pickup by a helium droplet and suggests that a situation with spatially separated dopants on one helium droplet may not be an exotic phenomenon restricted to weakly bound species.

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Can 0.4K He induce electronic relaxation? The case of Rb and Ba^+ @ superfluid He droplets

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The possibility that helium can induce transitions, even at the very low temperature (0.4K) of the ^4He nanodroplets, between electronic states of an excited atom or ion is investigated.

In the case of Ba^+ excited to the 6p ^2P state a realistic model built on diatomics-in-molecules (DIM) interactions with diabatized He-Ba^+ curves and atomic spin-orbit coupling as inputs provides potential energy surfaces and couplings for an arbitrary size He_nBa^+ cluster [1]. This has allowed us to identify several possible electronic relaxation mechanisms which could potentially explain the expulsion of barium ions from helium nanodroplets observed experimentally upon Ba^+ photoexcitation.

In the case of Rb a combined experimental and He-DFT theoretical investigation of the formation of free RbHe exciplex molecules from laser-excited Rb-doped He nanodroplets has been conducted[2]. Only due to $^2P_{3/2}$ - $^2P_{1/2}$ spin-relaxation does the RbHe exciplex detach from the He droplet surface, as observed experimentally.

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Infrared Spectroscopy of Alkyl Radicals in Helium Droplets and Solid *para*-Hydrogen

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Alkyl radicals are produced by either flash-vacuum pyrolysis or photolysis of organic precursors and trapped in either helium droplets or solid *para*-H_2 matrixes. Infrared spectra are assigned via comparisons to anharmonic frequency computations at high-levels of electronic structure theory. Effective Hamiltonian computations are employed to account for the spectral complexity observed in the CH stretching region, which results from an extensive network of anharmonic resonance polyads [1,2].

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Acid Solvation versus Dissociation at "Stardust Conditions": Reaction Sequence Matters!

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Chemical reactions at ultra-low temperatures are of fundamental importance to primordial molecular evolution as it occurs on icy mantles of dust nanoparticles or on ultra-cold water clusters in dense interstellar clouds. As we show, studying reactions in a stepwise manner in ultra-cold helium nanodroplets by mass-selective IR spectroscopy provides an avenue to mimic such "stardust conditions" in the laboratory. In our joint experimental/theoretical study, in which we successively add H_2O molecules to HCl, we disclose a unique IR fingerprint at 1337 cm^{-1} that heralds hydronium (H_3O^+) formation and, thus, acid dissociation generating solvated protons. In stark contrast, no reaction is observed when reversing the sequence by letting HCl interact with preformed small embryonic ice-like clusters. Our *ab initio* simulations demonstrate that not only reaction stoichiometry but in particular the reaction sequence needs to be explicitly considered to rationalize ultra-cold chemistry.

Superfluid helium nanodroplets: The many impurities, many vortices cornucopia

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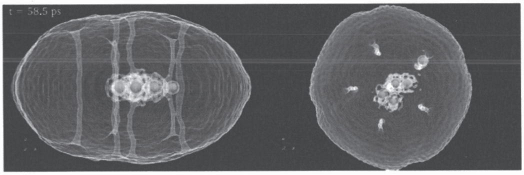
In this talk, some results recently obtained within the ^{4}He-DFT and TDDFT frameworks [1] will be presented. In the first part, the capture of several impurities by vortex-free and vortex array-hosting superfluid ^{4}He nanodroplets will be discussed, generalizing the results obtained by Coppens *et al.* on the capture of an impurity by a vortex line [2]. Figure 1 shows a lateral (left) and top (right) view of the capture of 6 Ar atoms sent at 360 m/s against a ^{4}He$_{5000}$ droplet hosting a six vortex array.

In the second part, aspects related to the structure and stability of rotating mixed ^{3}He-^{4}He droplets will be discussed, extending a previous study on spinning superfluid ^{4}He nanodroplets [3]. Figure 2 shows the appearance of a ^{3}He$_{6000}$-^{4}He$_{1500}$ droplet spinning around the z axis; it hosts a three-vortex linear array in the superfluid ^{4}He$_{1500}$ core (bottom), whereas the ^{3}He$_{6000}$ crust (top) is in the normal phase. The angular momentum deposited in the droplet is $4\times h/2\pi$ per atom.

Figure 1



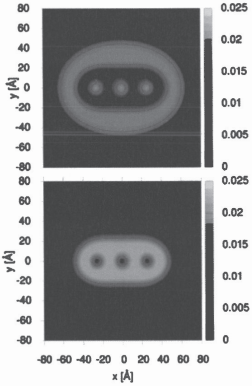


Figure 2

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Femtosecond Photoexcitation Dynamics of Atoms and Molecules inside Helium Nanodroplets

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Superfluid helium nanodroplets (He_N) represent a promising approach to study femtosecond dynamics in previously inaccessible systems. Here, we present first time-resolved investigations of single indium (In) atoms and In_2 molecules located inside He_N, obtained by combining time-resolved photoelectron/-ion spectroscopy and time-dependent helium density functional theory modelling.

In the case of In atoms, photoexcitation triggers an expansion of the He bubble within 600 fs, which is represented by a 300 meV shift of the photoelectron kinetic energy (Fig. 1a). Simulations reveal that In excited-state electronic energy is converted into He kinetic energy (pressure waves) during this process [1]. The bubble expansion is followed by an oscillation of the He bubble with a period of (28±1) ps, and ultimately leads to ejection of the dopant from the droplet after ~60 ps.

In the case of In_2, photoexcitation initiates a very similar response of the He solvent (Fig. 1b). Superimposed we find a strong periodic modulation of the photoelectron signal, indicating coherent nuclear wave packet (WP) motion of In_2 with a 0.42 ps period. The slowly decaying periodic signal reappears after 150 and 300 ps, representing the half and full revivals of the WP, respectively. Appearance of these revivals demonstrates that the He-induced influence on coherent nuclear motions can be lower by a factor of 10-100 compared to conventional solvents.

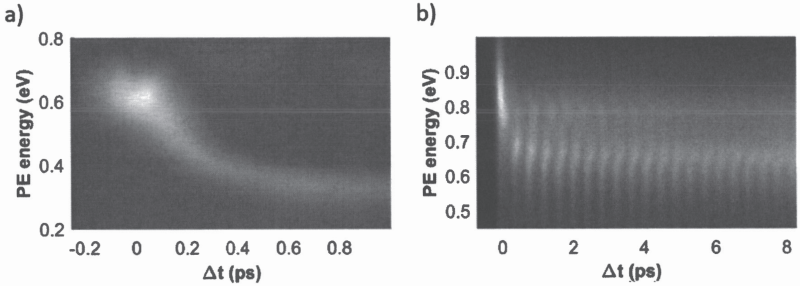

Fig. 1: Transient photoelectron kinetic energy for In (a) and In_2 (b) inside He_N.

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Stark-Spectroscopic Investigations of Large Organic Molecules in Superfluid Helium Nanodroplets

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Superfluid helium nanodroplets serve as a gentle and ultracold (T = 0.37 K) host system for molecular and atomic species as well as weakly bound (van der Waals) complexes [1]. The latter is synthesized *in situ* by successive droplet doping with multiple gaseous species. Probing the dopant by means of electronic spectroscopy reveals purely molecular features, characteristics of the helium bath and attributes resulting from the interplay between dopant and helium environment, which are subsumed under the concept of microsolvation, which becomes apparent in spectral features like line splitting, the appearance of a phonon wing or helium induced shifts of electronic transitions.

For the example of large organic molecules and molecular compounds, we focus on the dopant to helium interaction. To get an insight into the mutual interplay between host (helium droplet) and guest (organic molecule) highly resolved electronic Stark spectroscopy is used. Thereby, the Stark electric field induces optical anisotropy as a result of hindered rotation, which becomes effective on the intensity and on the line shape in the corresponding electronic spectra. We present Stark-spectra of polar chloroaluminiumphthalocyanine (AlClPc) and phthalocyanine-water-complexes

(Pc-H_2O) and in addition, the non-polar species phthalocyanine and porphine. The Stark spectra of all these dopant species reveal field induced optical anisotropy and in the case of the non-polar species higher order field effects. By comparison with simulations of helium adapted Stark spectra we observe significant deviations from the experiment. All our studies in helium droplets are accompanied by corresponding gas phase spectra, which are subject of a follow up poster.

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Auger Emission from the Coulomb Explosion of Helium Nanoplasmas

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The long-time correlated decay dynamics of strong-field exposed helium nanodroplets is studied by means of photoelectron spectroscopy. As a result of the adiabatic expansion of the laser-produced, fully inner-ionized nanoplasma, delocalized electrons in the deep confining mean field potential are shifted towards the vacuum level. Meanwhile, part of the electrons localize in bound levels of the *helium ions*. The simple hydrogen-like electronic structure of He^+ results in clear signatures in the experimentally observed photoelectron spectra, which can be traced back to bound-free and bound-bound transitions. Auger electron emission takes place as a result of the transfer of transition energy to weakly bound electrons in the quasifree electron band. Hence, the spacial and temporal development of the nanoplasma cloud is encoded in the experimental spectra, whereas the electronic properties of He^+ help resolve the different contributions.

Quantum vortices in superfluid helium droplets

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Free superfluid helium droplets constitute a versatile medium for a diverse range of experiments in physics and chemistry that extend from studies of the fundamental laws of superfluid motion to the synthesis of novel nanomaterials.[1] The emergence of quantum vortices in rotating helium droplets is one of the most dramatic hallmarks of superfluidity.[2] This talk provides an introduction to quantum vorticity in helium droplets, followed by a historical account of experiments on vortex visualization in bulk superfluid helium and a more detailed discussion of recent advances in the study of the rotational motion of isolated, nano- to micrometer-scale superfluid helium droplets. Ultrafast X-ray and extreme ultraviolet scattering techniques enabled by free-electron lasers and high-order harmonic generation have facilitated the in situ detection of droplet shapes and the imaging of vortex structures inside individual, isolated droplets.[3-8] Finally, the talk gives an outlook toward some of the scientific opportunities that arise from the discussed scattering techniques.

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Trapping of Multiple Ions and Suppression of Multiphoton Ionization by Large Helium Droplets

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Recently, there is a surge of research activities on large superfluid helium droplets, partly triggered by the possibility of synthesizing nanostructures using these droplets, and partly motivated by the need to cool macromolecules for field induced alignment and orientation. Large droplets are also shown to solvate heliophobic electrons and anions, approaching bulk-like behaviors. In this presentation, we provide evidence that multiple cations can coexist and that failure of charge transfer results in coexistence of He_2^+ and neutral aniline (A) or neutral aniline cluster (A_n) in a large superfluid helium droplets containing more than 10^6 atoms/droplet. Multiphoton ionization also fails in these large droplets because of the caging effect of the surrounding helium atoms. Energetic electrons, on the other hand, can achieve a much higher energy than typical photons from tunable lasers, and electron impact ionization offers the additional benefit of size reduction. The size reduced ionized droplets containing the aniline dopant can simultaneously eject He_2^+ and A^+ upon resonant excitation of A^+. The optical spectroscopy of He_2^+, however, also demonstrates multiphoton resonances of neutral aniline, implying failed charge transfer between the two species, although the ionization energy of aniline is lower than that of helium by 16 eV. Upon electronic excitation of neutral aniline, the solvation cavity is forced to adjust to the new electronic cloud, inducing a shock wave that can propagate throughout the droplet, ejecting He_2^+ located near the droplet surface.

Ultrafast energy transfer in doped He nanodroplets studied by femtosecond XUV photoelectron imaging

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Despite the deceptively simple electronic structure of the helium atom, electronically excited states of helium nanodroplets and, in particular, their relaxation dynamics are still relatively poorly understood.[1] Coupled electronic-nuclear dynamics in pure He droplets typically proceed on femtosecond to picosecond timescales and include intra- and inter-band relaxation as well as the ejection of Rydberg atoms and molecules. The advent of ultrafast XUV spectroscopy based on high-order harmonic generation (HHG) has facilitated the discovery and characterization of several of these mechanisms with femtosecond temporal resolution.[2] More recently, steady-state energy domain studies have demonstrated the existence of a remarkable variety of solute-solvent energy- and charge-transfer phenomena in He nanodroplets doped with impurities such as noble gas atoms[3,4] as well as alkali atoms and molecules.[4,5] In particular, the efficacy of indirect dopant ionization mechanisms as well as the correlated photoelectron kinetic energy distributions depend on a number of parameters such as the photon energy, dopant location (droplet surface vs bulk), droplet size, and the nature of the dopants. Efforts are now underway to disentangle the underlying physics by HHG based ultrafast photoelectron imaging. In these experiments, doped droplets are electronically excited by a femtosecond XUV pulse, followed by further excitation or ionization with a second near-infrared or UV pulse and photoelectron spectra are recorded as a function of pump-probe time delay. Latest developments and experimental results will be discussed.

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New routes to imaging the classical and quantum dynamics of finite systems

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When compared to atoms and solids, the collective and correlated electron dynamics in finite systems under intense light fields can be substantially modified, enhanced and controlled by local near-fields [1-3]. Near-fields result from electronic polarization and charge separation and can unfold on femtosecond or even attosecond time scales [4]. In this talk, two novel routes for characterizing the classical and quantum aspects of the underlying light-matter interactions at the nanoscale will be discussed. Though being fundamentally different conceptually, both schemes have come in reach with current short-wavelength FEL sources providing multicolor pump-probe pulses with exquisite control over the timing.

The first scenario – the *"nanoplasma oscilloscope"* – is motivated by previous theory work [5-7] on the XUV ionization of clusters and aims at tracing the complex evolution of space-charge potentials in laser-illuminated nanostructures. Such information is inaccessible with scattering methods such as coherent diffractive imaging but important for the understanding of non-linear plasma formation dynamics, radiation damage and relaxation processes in finite systems. Preliminary experimental data from a recent beam time at FERMI and the related theoretical analysis will be discussed.

The second scenario – the "*quantum coherent diffractive imaging*" (QCDI) - aims at exploring the non-linear response of extended nanosystems through near-field driven coherent quantum dynamics. So far, single-shot diffraction images recorded with soft x-ray and XUV pulses have been shown to contain information on the three-dimensional shape of nanosystems, as was demonstrated for faceted silver particles and rotating helium nanodroplets [8,9,10], and where analyzed assuming linear response scattering. Single-shot diffraction with XUV field, however, also provides a promising route to tracing spatiotemporal population dynamics. We simulated the nonlinear response of Helium droplets under resonant 1s-2p excitation as a model using a coupled quantum-electromagnetic simulation based on a few-level approximation and utilizing the finite-difference time-domain method. The nonlinear modifications of the diffracted field through coherent bound state dynamics will be presented [11]. Our results illustrate the potential for spatiotemporal characterization of collective excitation dynamics in nanosystems and motivate new metrologies in the emerging field of quantum coherent diffractive imaging, paving the way into the realm of attosecond quantum imaging.

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“Wrap up” talk of QFC2019

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I will present an overview of QFC 2019 conference and highlight possible new directions of research in the field.

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Abstracts of Posters

(in alphabetical order)

Investigation of Au cluster deposition using helium nanodroplets

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The size dependent properties of nano materials in general and atomic clusters in particular enable scientific and industrial applications inaccessible by other means. Features like size, morphology or density depend on a variety of deposition parameters, as was shown by Volk et al. [1]. Our aim is to investigate the observable cluster properties in dependence of the deposition parameters like temperature, pressure or charge state. Furthermore, the biological activity of thereby functionalized surfaces is to be assessed and the possibility of industrial applications is to be evaluated.

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Autoionization of excited He nanodroplets

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He nanodroplets that are excited by resonant XUV radiation undergo relaxation into long-lived excited states which proceeds on different time scales. Following ultrafast electronic or interband relaxation, the He* excitation localizes inside a void bubble which migrates to the droplet surface. Eventually, nearly unperturbed He atoms in different low-lying excited states emerge, depending on the photon energy and the size of the droplet. The dynamics of this relaxation process are probed on the ultrashort time scale by pump-probe measurements using XUV pulses from a tunable free-electron laser (FERMI, Trieste), and on a long time scale using synchrotron radiation.

Following laser excitation, He nanodroplets can autoionize if they are doped with impurity atoms or molecules, M. The Penning reaction or interatomic Coulombic decay (ICD) process,

$$(\mathrm{He}^* + \mathrm{M})\mathrm{He}_N \rightarrow (\mathrm{He} + \mathrm{M}^+ + e)\mathrm{He}_N, \qquad (1)$$

generates dopant ions and electrons with energy specific to the dopant species. This process was found to be extremely efficient for alkali metal atoms bound to the surface of the droplets [1]. When attaching two alkali metal atoms to one droplet, a dimer forms. The latter was recently found to efficiently double ionize by the process

$$(\mathrm{He}^* + \mathrm{M}_2)\mathrm{He}_N \rightarrow (\mathrm{He} + \mathrm{M}_2^{++} + 2e)\mathrm{He}_N,$$

(2) which we named “double interatomic Coulombic decay (dICD)” [2]. In the meanwhile, reaction (1) has been found to occur for different types of dopant species such as alkaline-earth metals [3,4], rare gas atoms, and organic molecules (acetylene, acenes [5]). Furthermore, even pure He nanodroplets autoionize upon resonant excitation if more than one He* per droplet is excited. The characteristic feature in the electron spectrum for this reaction,

$$(\mathrm{He}^* + \mathrm{He}^*)\mathrm{He}_N \rightarrow (\mathrm{He} + \mathrm{He}^+ + e)\mathrm{He}_N, \qquad (3)$$

gradually broadens and shifts to lower energies as the He droplet is multiply excited and evolves into a nanoplasma by collective autoionization [6,7].

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Photoelectron velocity-map imaging of charged submicron-sized droplets

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Photoelectron velocity-map-imaging (VMI) studies on submicron-sized droplets have been increasingly important in elucidating the properties of low-energy electrons in the condensed phase [1-5]. An important, but often neglected, aspect of droplet VMI is the droplet charge. Common droplet generation techniques lead to a known, but non-trivial charge distribution [6]. The presence of an additional electrostatic potential can modify electron transport and lead to, among other effects, a Coulomb barrier to electron escape [7,8].

To explore and characterize the effects of positive and negative charge on low-energy electron transport, we performed a combined experimental and modeling study. We recorded photoelectron VMI spectra of size-selected dioctyl phthalate (DOP) droplets while varying the charge distribution in a controlled way. A probabilistic scattering model [3,9] was extended to include both classical and quantum effects of the electrostatic potential on the electron escape process. Good agreement between the experimental results and the extended scattering model was obtained.

As a result, we have gained quantitative understanding of droplet charge effects on the electron escape process. These findings make an important contribution to the development of droplet VMI as a technique to study low-energy electron transport in the condensed phase.

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Two-dimensional electronic spectroscopy of Rb_3 in helium nanodroplet isolation

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We present the first two-dimensional electronic spectroscopy (2DES) study of cold molecules (sub Kelvin internal temperature) prepared by helium nanodroplet isolation (HENDI) [1]. 2DES is widely used to investigate coherent and incoherent dynamics in molecular systems giving detailed insight into system bath interactions, charge/energy transfer and structural changes [2]. The mostly few and narrow spectral features observed in HENDI experiments strongly simplify 2D spectra, leading to less ambiguous interpretations and an easier comparison to theory. Furthermore, 2DES can be used to study the remaining interaction of dopants with its superfluid helium environment.

As a first benchmark system, we studied Rb_3 molecules in the quartet state attached to helium nanodroplets. The acquired 2D spectra show the same spectral features as previously measured with high-resolution linear spectroscopy [3], showing that the resolution is limited by the system itself and not the 2DES method. The observed dynamics show the repulsion of the excited Rb_3 from the helium nanodroplet in real time.

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Electron transfer mediated decay in He nanodroplets doped with heteronuclear alkali dimers

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Energy and charge transfer mechanisms -- correlated decay processes (CDP) -- in weakly bound systems, e.g. hydrogen bonded clusters or noble gas clusters, currently attract considerable interest due to their important role in understanding the nature of interaction between high energetic radiation and materials relevant for biology. Among these CDP are the well-known interatomic/molecular Coulombic decay (ICD) [1-3] and electron transfer mediated decay (ETMD) [4, 5]. ICD and ETMD lead to ejection of low-kinetic energy electrons, which are generally proven to be genotoxic and can efficiently induce irreparable damage in DNA such as DNA-double strand breaks [6]. Here we report measurements on two competitive charge transfer mechanisms with different alkali-dimers, e.g. Rb—K, Rb—Na, K—Na, K—K, Na—Na and Cs—Cs, attached to He nanodroplets by employing velocity map imaging spectrometry in combination with EUV synchrotron radiation. One process is observed following EUV photoionization of He nanodroplets and another upon removal of a 4d electron from one of the atoms forming the alkali dimers (Here, Cs—Cs dimers will be considered as a showcase). These two processes are detected simultaneously, and their contribution in the measured electron spectra can be controlled by tuning the photon energy on the 4d giant resonance of Cs. Most of the electron spectra recorded upon EUV photoionization of He nanodroplet doped with different alkali atoms show a broad and prominent feature where its maximum is lying between 5-7 eV as low-kinetic energy. This feature is identified as due to ETMD; i.e. $He^+ + K\text{—}Rb + e_{ph} \rightarrow He + [KRb]^{2+} + e_{ph} + e_{ETMD} \rightarrow He + K^+ + Rb^+ + e_{ph} + e_{ETMD}$. The 4d electron photoionization of Cs atoms doped in He nanodroplet leads to a doubly Cs^{2+} and Cs^+ singly charged fragments. Those fragments are detected in coincidence, and their measured 2D map mass spectra clearly show a Coulomb explosion features. They are interpreted as originating from an Auger decay process, which in turn induces an electron transfer from neighboring Cs dopant sites; i.e. $He + Cs^{3+}\text{—}Cs + 2e_{Aug} + e_{ph} \rightarrow He + Cs^{2+} + Cs^+ + 2e_{Aug} + e_{ph}$.

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Diagrammatic Monte Carlo approach to angular momentum in quantum many-body systems

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We introduce a Diagrammatic Monte Carlo (DiagMC) approach to molecular impurities, possessing rotational degrees of freedom [1]. The technique is based on a diagrammatic expansion [2] that merges the usual Feynman diagrams with the angular momentum diagrams known from atomic and nuclear structure theory, thereby incorporating the non-Abelian algebra inherent to quantum rotations. Due to the peculiar way in which angular momenta couple, the configuration space is larger with respect to most DiagMC applications, and a new class of updates is needed in order to span it completely.

We exemplify the technique by obtaining an all-coupling solution of the angulon model - essentially a molecular impurity in a quantum many-body environment - showing that our approach correctly recovers the strong-coupling limit. However, the technique is general and can be applied to a broad variety of systems possessing angular momentum degrees of freedom, thereby establishing a far-reaching connection between DiagMC techniques and molecular simulations. Potential applications of the formalism include a precise determination of static and dynamical properties of molecules immersed in superfluid helium or solid parahydrogen, as well as of Rydberg atoms in Bose-Einstein condensates.

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Peak shape modulations in two-dimensional electronic spectroscopy caused by intense laser pulses

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Usually, two-dimensional electronic spectroscopy (2DES) experiments are performed in the regime where perturbation theory holds and the signal can be described by the third-order polarization. However, to measure nonlinear signals, higher laser intensities are generally of advantage as the signal scales with higher order of the incident light fields. Furthermore, new 2DES schemes have been implemented [1,2] where tight focusing is crucial and thus laser intensities beyond the weak-perturbation limit may be reached. Recently, a theoretical description for 2DES experiments beyond the weak perturbation limit has been reported [3] showing peak shape modulations and phase shifts, which may be exploited to gain additional information but can also lead to artifacts. In collinear 2DES experiments, we explore these high intensity effects in our lab by studying a simple, clean model system comprising of a rubidium atom vapor. This provides a direct intuition of intensity effects in 2D spectroscopy.

Furthermore related to coherent spectroscopy we want to exploit 2DES together with helium nanodroplet isolation (HENDI) to perform a time resolved study of the rubidium-helium exciplex formation dynamics.

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Investigation of the weak hydrogen bond of some propyne complexes

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The formation of some molecular complexes depends on a subtle equilibrium between several forces of low intensities (van der Waals, hydrogen, etc.). These forces allow the existence of flexible molecular systems having a large number of degrees of freedom of deformation. This flexibility is particularly, but not only, found in biological molecules and is at the origin of their adaptation according to their environment. An interesting case occurs when a low intensity interaction exists between two molecules, one of which has a certain propensity to be both donor and acceptor of a proton. For example, an alkyne molecule having a triple bond, orbital Π, and an acid hydrogen atom on its termination.

It is in this context that the complexes of propyne (with a propyne or a water molecule) have been studied on the Gouttelium device[1]. The technique called "HElium NanoDroplet Isolation" (HENDI)[2] was used to acquire infrared spectra which inform on these flexible complexes. Helium droplets proved to be very convenient micro-reactors to form complexes whose stoichiometry are controlled at the molecular level like the two complexes $(CH_3CCH)_2$ and $CH_3CCH\ldots H_20$ studied here. Furthermore, the helium droplets being superfluid ($T_{goutte} \approx 0.4$ K), they do not disturb too much, at a first approximation, the complexes. Once the helium droplet has been doped with both molecules, those migrate within the droplet to form a complex bound by low intensity bonds. Infrared absorption spectra in the region of the C-H vibration of the propyne molecule are recorded to probe the complex, and thus the low intensity bonds. The spectra are compared to simulations based on Ab-initio calculations performed at the MP2 level. These calculations document the potential energy surface of the complexes and gave the parameters used to simulate the spectra.

Several bands of infra-red spectra have been observed and attributed to the complexes and their conformers. Some of them have been attributed to the lowest energy complex. The full interpretation of the experimental and theoretical results will be detailed at the conference.

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Fully Flexible Path Integral Simulations of Fluxional Molecules in Bosonic Clusters

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In the first part, we will describe a recently developed methodology based on a hybrid PIMD/PIMC [1] technique coupled with highly accurate interaction potentials [2] and advanced thermostatting techniques [3] to study doped superfluid clusters. We will show in particular that this methodology allows Path Integral (PI) simulations of reactive molecule in superfluid helium cluster (up to ∼100 He atoms) at ultra low temperature (as low as 0.5 K) including the full flexibility of the molecule.

In a second part, we will present the first results obtained on the microsolvation of protonated methane (CH_5^+) with ^4He. CH_5^+ is chosen here as the prototypical fluxional molecule exhibiting large amplitude motion that are usually neglected in PI simulations of doped superfluid clusters, since the impurity is often treated in the rigid body approximation. These results show that structural properties of the molecule are not perturbed by the surrounding helium thus confirming that choosing He as tagging agent is a valid choice, for instance, in tagging spectroscopy experiments. [4] Moreover, these simulations demonstrate that both large amplitude motion and molecular vibration have a significant impact on the microsolvation shell. In particular, an intricate coupling between these molecular motions and the bosonic exchange of Helium is uncovered. [5] Overall this study unambiguously shows that the microsolvation of fluxional molecules can only be successfully studied if the full flexibility of the solute molecule is taken into account.

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An angulon quasiparticle perspective on impulsive molecular alignment in ^{4}He nanodroplets

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Angular momentum redistribution is a key to understanding phenomena taking place in a variety of quantum systems, from collision-induced nuclear reactions to magnetism in condensed matter systems. Here we describe the alignment of a molecule trapped inside a ^{4}He droplet [1, 2] from the point of view of angular momentum transfer between the molecule and the many-body helium bath. A short off-resonant laser pulse induces molecular axis alignment by creating a broad rotational wave packet. The angular momentum gained from the electric field by the molecule can be then transferred to the helium bath via excitation of bosonic collective modes (phonons) with non-zero angular momentum.

We developed a dynamical theory of angulons [3] – quasiparticles consisting of a rotating impurity dressed by a field of surrounding bath excitations. We demonstrate that the rotational wave packet dynamics observed in experiment cannot be understood in terms of interference of the rigid rotor states due to the strong interactions with surrounding helium. Our approach might be generalized to the case of linearly chirped laser pulses paving the way for studying an optical centrifuge for molecules in ^{4}He droplets.

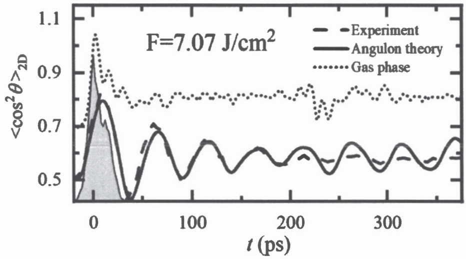

Figure 1. Alignment of an I_2 molecule trapped in a ^{4}He droplet by a 20 ps laser pulse: expeiment (dashed), theory (solid) and free rotor evolution (dotted)

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Dopand-induced helium nanoplasmas in strong near-infrared laser pulses

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A doped helium nanodroplet irradiated by intense near-infrared (NIR) laser pulses forms a highly ionized nanoplasma even at laser intensities where the helium is not directly ionized. First seed electrons which start the electron impact ionization avalanche of the whole droplet can be provided either by dopant atoms or direct ionization of helium using XUV photons. The dynamics of ignition and explosion of the nanoplasma depends not only on the number and the kind of dopants but also on the droplet size and laser intensity. We present time-of-flight mass spectra of the ions synchronously recorded with single shot velocity map imaging (VMI) measurements of electrons. Using this technology we investigate the effects of various dopants on the ignition probability of the plasma.

Quantum-state-controlled reactive collisions between lithium atoms and metastable helium atoms

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The 2^3S_1 state of helium is the longest-lived neutral atomic state and the most energetic metastable state of an atom. These characteristics make this species an important source of stored energy in ionospheric and discharge plasmas. In our experiments, we study quantum-state-controlled Penning collisions between lithium atoms and metastable helium atoms at various collision energies, e.g., to study the influence of electron-spin polarization on the reaction rate and to observe quantum resonance effects at low collision energies. For this, we use an experimental apparatus which consists of a discharge source for the production of metastable helium atomic beams and a magneto-optical trap (MOT) for ultracold lithium atoms [1].

In this contribution, I will show results illustrating that the reaction rate dramatically depends on the initial electronic state of the Li scattering target. I will also describe the experimental characterization of a new optical quenching scheme [2] which makes it possible to distinguish the relative contribution of the He(2^1S_0) and He(2^3S_1) states to the reaction rate. This scheme makes it possible to fully deplete the population of He(2^1S_0) in the supersonic beam via optical excitation to the 4^1P_1 state. Since it is based on simple and inexpensive diode laser technology, the method can be implemented in many laboratories in a straightforward manner. I will also show preliminary results on the selective reactive scattering of He(2^3S_1) with Li atoms using this approach.

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Microsolvation of the Water Molecule by Bosonic Helium

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Since the discovery of superfluidity in bosonic helium [1], the study of this macroscopic manifestation of quantum mechanics has been an important field of research. Numerous studies have focused on superfluid clusters [2], some of them including molecular impurities [3]. In the low temperature regime where superfluid behavior can be found, nuclear quantum effects (NQE) are important. The canonical approach to account for the quantum nature of nuclei in simulations are methods based on path integrals (PI), such as PI Molecular Dynamics (PIMD) or PI Monte Carlo (PIMC).

In this work, microsolvation complexes of a fully flexible water molecule with up to 30 ^{4}He atoms are studied for the first time at a temperature of T=1.25 K using a hybrid PIMD/PIMC technique [4] developed in our group, where all the interactions are described with Neural Network Potentials [5]. The behavior of energetic and structural properties, as well as the superfluid response and the permutation statistics of helium is studied as a function of the number of helium atoms in the cluster. Striking differences in these properties between the first and second solvation shells are disclosed.

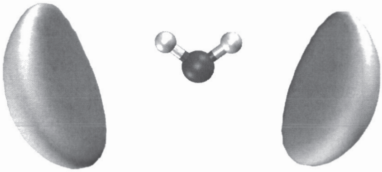

Figure 1: Probability density of finding an helium atom around the water molecule for the $H_2O(^4He)_2$ cluster at a temperature of 1.25 K.

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Experiments with Large ^{3}He Droplets

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This presentation discusses the results of our recent X-ray coherent diffraction imaging (CDI) measurements with large ^{3}He droplets at LCLS SLAC National Accelerator Laboratory. ^{3}He droplets were produced in a continuous molecular beam at low temperature (2 - 4 K). The diameter and aspect ratio distributions were characterized yielding an average droplet diameter of 300 nm. CDI experiments with doping of ^{3}He droplets by different molecules are presented and discussed.

Stark-Spectroscopic Investigations of Large Organic Molecules in Superfluid Helium Nanodroplets

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Superfluid helium nanodroplets serve as a gentle and ultracold (T = 0.37 K) host system for molecular and atomic species as well as weakly bound (van der Waals) complexes [1]. The latter is synthesized *in situ* by successive droplet doping with multiple gaseous species. Probing the dopant by means of electronic spectroscopy reveals purely molecular features, characteristics of the helium bath and attributes resulting from the interplay between dopant and helium environment, which are subsumed under the concept of microsolvation, which becomes apparent in spectral features like line splitting, the appearance of a phonon wing or helium induced shifts of electronic transitions.

For the example of large organic molecules and molecular compounds, we focus on the dopant to helium interaction. To get an insight into the mutual interplay between host (helium droplet) and guest (organic molecule) highly resolved electronic Stark spectroscopy is used. Thereby, the Stark electric field induces optical anisotropy as a result of hindered rotation, which becomes effective on the intensity and on the line shape in the corresponding electronic spectra. We present Stark-spectra of polar chloroaluminiumphthalocyanine (AlClPc) and phthalocyanine-water-complexes
($Pc-H_2O$) and in addition, the non-polar species phthalocyanine and porphine. The Stark spectra of all these dopant species reveal field induced optical anisotropy and in the case of the non-polar species higher order field effects. By comparison with simulations of helium adapted Stark spectra we observe significant deviations from the experiment. All our studies in helium droplets are accompanied by corresponding gas phase spectra, which are subject of a follow up poster.

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Spectroscopy of 4(5)-Methylimidazole and its hydrates, hosted in helium droplets

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Histidine is a biological molecule that is one of the two amino acids exhibiting a tautomeric equilibrium. Moreover, this molecule has the specificity to be acceptor and donor of proton. This confers to the histidine molecule several roles as a proton transfer mediator in various proteins. These two properties are due to by the imidazole cycle, which is a side chain of histidine. It appears important to understand how the tautomeric equilibrium and the proton transfer evolve according to its environment. Unfortunately, histidine is a complicate system and its size could be a problem for theoretical calculations and for helium droplets deposition. The 4(5)-Methylimidazole molecules were chosen as simple model of histidine. These molecules and their hydrates were characterized by infrared (IR) spectroscopy in helium droplets.

The Gouttelium device [1] allowed recording IR spectra of the two tautomers by using the "Helium NanoDroplet Isolation" technique (HENDI) [2]. The purpose was to characterize unambiguously the two tautomers via the tautomeric signature: the NH vibrational stretching. The recorded bands and DFT calculations allowed estimating the constant of tautomerization ($K_T(43°C)=4.7$), which was not accurately known. We also evaluate the rotational constants of the 4-methylimidazole in order to simulate its spectrum.

In a second step, the 4(5)-Methylimidazole-Water complexes were formed by the deposition of the two species on helium droplets. A search of the signal of the NH stretching of the methylimidazole and of the symmetric and asymmetric stretch of the OH of water was performed. The results constitute the first study of these complexes embedded on helium droplets.

The different spectra and preliminaries conclusions will be presented at the conference.

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Dopant-induced ignition of helium nanoplasmas

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Helium (He) nanodroplets irradiated by intense near-infrared laser pulses form a nanoplasma by avalanche-like electron impact ionizations even at lower laser intensities where He is not directly field ionized, provided that the droplets contain a few dopant atoms which provide seed electrons for the electron impact ionization avalanche. Using molecular dynamics simulations, we elucidate the mechanism which induces ionization avalanches, termed ignition, in He nanodroplets doped with small calcium (Ca_n), xenon (Xe_n) and mixed calcium-xenon (Ca_mXe_n) clusters. We find that the partial loss of seed electrons from the activated droplets starkly assists ignition, as the Coulomb barrier for ionization of He is lowered by the electric field of the dopant cations, and this deshielding of the cation charges enhances their electric field. In addition, the dopant ions assist the acceleration of the seed electrons ("powered flyby") by the laser field, supporting electron impact ionizations of He and also causing electron loss by catapulting electrons away.

Detection of Low-lying Electronic States of Co_m^+ in He Clusters

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Metal possesses band structures in the electronic states, and the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are located in the conduction band which consists of a large number of energy levels. In a small metal cluster, the density of states decreases, and the spacing between the energy levels becomes wider. The electronic structures of the metal clusters are closely related to their reactivity, and particularly the studies on the reactivity of transition metal clusters have exhibited their specificity. Recently we have developed a technique to form cluster complexes, $Co_m^+He_n$, by use of low-energy collision between clusters. Here, we demonstrate the spectroscopy of the cluster complexes.

We carried out the low-energy collision experiments by using a merging-beam apparatus [1,2]. In the collision between Co_m^+ (m = 1-7) and He_N (<N> ~ 30000), the cluster complexes, $Co_m^+He_n$, were observed, and it was found that the yield of $Co_m^+He_n$ is inversely proportional to the relative velocity between Co_m^+ and He_N in a low velocity region, while it levels off and steeply decreases in a higher velocity region. This profile suggests that the charge-induced dipole interaction dominates at the low velocities and the hard-sphere collisions occur with the increase of the relative velocity. At the higher velocities, Co_m^+ which collided with the periphery of He_N cannot stop at the inside of He_N and passes through it.

Photodissociation spectra of $Co_m^+He_n$ were measured in the wavenumber range of 5000-7000 cm^{-1}. We found that $Co_3^+He_n$ have low intensity of the photofragment, but $Co_6^+He_n$ have relatively large intensity of the photofragment, Co_6^+. This dissociation comes from the electronic excitation of Co_6^+, and suggests that Co_6^+ has electronic transitions in this low-energy (0.65-0.85 eV) region. These electronic excitations should be related with the reactivity of the clusters, and a typical example is shown in the reaction of Co_m^+ with NO.

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Theoretical investigations of electronic excitation of organic species doped into superfluid helium nanodroplets

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High-resolution electronic spectroscopy (Stark or field-free) of large organic molecules and molecular complexes doped into superfluid helium nanodroplets poses many intriguing questions at the interface of physics and chemistry — especially with regard to solvation and rotation. In our recent work, we have noted the apparent absence of the predicted free rotation of free base phthalocyanine and free base porphine in He droplets[1,2] upon electronic excitation. This calls into question our present understanding of the rotational dynamics of large impurities in superfluid He, and begs for alternative methods, both theoretical and experimental, in order to clarify the exact nature of the dopant-bath interaction before and after electronic excitation. To this end, we present some preliminary data on the glyoxal-helium ab initio PESs both in the ground and the lowest excited state of the glyoxal molecule. In addition, we also investigate the demands placed by the Angulon theory[3] on the nature of dopant-bath PES anisotropies in the two electronic states in order for the rotational sub-structure to be drastically squeezed. When extended across many dopant species, we expect this combined approach to reveal the exact cause for the apparent lacking of a rotational sub-structure in the electronic excitation spectra of 'larger' dopants as opposed to 'smaller' species, leading to a better understanding of the fundamental London Dispersion Forces behind complex formation and/or solvation in superfluid helium.

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Setup and characterization of a helium liquid jet for diffractive imaging experiments

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State-of-the-art XUV and X-ray facilities enable the in-depth investigation of light-matter interaction via novel methods such as single-particle coherent diffractive imaging. For such experiments, large helium droplets constitute a suitable target; they have a simple electronic structure and exhibit interesting properties like superfluidity. Additionally, they can be used as a cooling matrix for embedded atoms and molecules.

One way of creating these droplets is a helium liquid jet, which disintegrates in a Rayleigh-type breakup, forming large droplets with diameters of a few microns. Compared to the other regimes of helium droplet generation, droplets produced from jet disintegration have a narrower size distribution. Together with their comparably large size, this makes them a suitable target for time-resolved diffractive imaging experiments not just at free-electron lasers but also at high-harmonic generation sources, where the photon flux is much lower.

Recently, we have constructed and characterized a source for a helium liquid jet, which will be put into use for example at the SQS endstation at the European XFEL. Via shadowgraphy methods, we can analyze the jet's shape and the droplet size. Complementary, our setup allows to determine the average droplet size via collision with external gas particles. First results will be presented.

Interacting dipolar Bose gas in the presence of three-body interactions

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We present our numerical results to examine the effect of the three-body interactions of dipolar Bose gas at finite temperature by using the generalized Hartree-Fock-Bogoliubov approximation (GHFB). We determine the different densities via the geometry of the trap. We also study the effect of three-body interactions on collective excitations by demonstrating that it treats them as if it were a number of atoms greater than the number present in the trap.

Keywords:Generalized Hartree-Fock-Bogoliubov approximation (GHFB); Bose-Einstein-condensation (BEC); Contact interaction (CI); Dipolar interaction (DI); Three-body interactions (TBI).

PACS numbers: 21.10.Pc,21.60.-n,21.60.Jz

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Comparison of Electron and Ion Emission from Xenon Cluster Induced Ignition of Helium Nanodroplets

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The charging dynamics of helium droplets driven by embedded xenon cluster ignition in strong laser fields is studied by comparing the abundances of helium and highly charged Xe ions to the electron signal. Femtosecond pump−probe experiments show that near the optimal delay for highly charged xenon the electron yield increases, especially at low energies. The electron signature can be traced back to the ionization of the helium environment by Xe seed electrons. Accompanying molecular dynamic simulations suggest a two-step ionization scenario in the Xe−He core−shell system. In contrast to xenon, the experimental signal of the helium ions, as well as low-energy electron emission show a deviating delay dependence, indicating differences in the temporal and spacial development of the charge state distribution of Xe core and He surrounding. From the pump−probe dependence of the electron emission, effective temperatures can be extracted, indicating the nanoplasma decay.

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Highly charged superfluid helium nanodroplets

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Superfluid helium nanodroplets[1] have been widely used as a cryogenic matrix in studies of complexes such as gold clusters[2]. To provide better insight on the nature of superfluid helium nanodroplets and their interaction with embedded dopants, the influence of electron impact ionization on pristine superfluid helium nanodroplets has been investigated. Both positively and negatively charged droplets with uniform velocity, produced via supersonic jet expansion and electron impact ionization, are mass selected in an electrostatic sector according to their kinetic energy. The charged droplets are then again subjected to electron bombardment and separated for their mass to charge ratio by a second electrostatic sector.
Depending on polarity, ionization parameters and droplet size, the resulting mass to charge distribution of the product droplets varies greatly. Multiply charging of selected droplets can be observed for cationic as well as for anionic droplets.

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Two-dimensional electronic spectroscopy of isolated, cold molecular nanosystems

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Two-dimensional electronic spectroscopy (2DES) is an ideal tool to investigate dynamics in molecular systems yielding a high degree of information [1]. To perform spectroscopic studies of isolated systems at very low temperatures we combine 2DES with helium nanodroplet isolation (HENDI) and exploit the phase-modulation technique established by Marcus et al. [2]. The combination of acousto-optic phase-modulation with lock-in detection greatly improves the signal-to-noise ratio and the sensitivity in this scheme [3]. Recently, we have performed the first 2DES study of isolated, cold molecular nanosystems by studying Rb_2 molecules in their weakly-bound high-spin state on the surface of helium nanodroplets [4]. We analyze the photodynamics in Rb_2 molecules excited to the previously discussed triplet resonance ($1^3\Sigma_u^+ \rightarrow 1^3\Pi_g$) at 13500 cm^{-1} with distinct spin-orbit components ($0_g^{\pm}$, 2_g) of the excited state [5]. Correlated to this resonance, we find a cross peak (CP) and two exited state absorption (ESA) features that oscillate coherently as a function of the system's evolution time. We interpret the ESA beating as a vibrational wave packet of the excited state oscillating with a period of ≈1550 fs, which is in good agreement with Franck-Condon calculations. The CP feature can be explained by a relaxation/tunneling into the outer potential well of the 0_g^+ state that is perturbed by the helium environment.

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Hydrogenated gold clusters produced with helium nanodroplets

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Clusters of gold with added hydrogen are interesting, for example because of the possible use of metal nanoparticles in hydrogen storage devices for fuel cells. Efficient, chemical storage of molecular hydrogen would be much safer than storing the explosive gas under high pressure in conventional tanks. Bulk gold is not efficient in hydrogen storing, but small gold clusters are [1]. In our experiments we produce neutral, mixed gold-hydrogen clusters in helium nanodroplets. [2] Using electron impact we ionize the doped helium nanodroplets and charged complexes containing gold and hydrogen are detected with a time-of-flight mass spectrometer.
The resulting data (see figure 1) shows distinct "magic" combinations where, for each number of gold atoms, some numbers of added hydrogen atoms are more abundant than other numbers [3]. Theoretical calculations show that the molecular structures corresponding to these "magic" numbers are gold clusters saturated with hydrogen, and adding or removing more hydrogen will lower the H_2 binding energy [3].

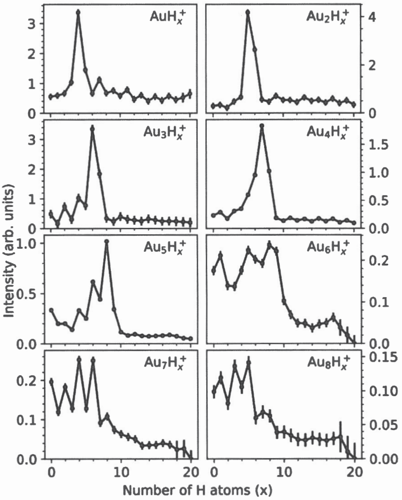

Figure 1: Experimental abundances of $Au_nH_x^+$, for n = 1–8 and x = 0–20.

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Inefficient non-radiative relaxation of vibrationally excited helium excimers solvated in the bulk investigated via fluorescence spectroscopy

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The spectroscopy of single molecules in helium sheds light on the molecular interactions in a unique quantum environment. In this work, fluorescence spectra of gaseous and liquid helium were recorded in the visible and infrared regions of the electromagnetic spectrum; the excitation was generated via a corona discharge in a bespoke spark cell under cryogenic conditions and for a wide range of pressures, covering the liquid and gaseous phases of helium (1). It is already known that in these experiments both He_2^* fully solvated in the bulk as well as He_2^* within gas pockets embedded in the liquid helium are created (2). Here, we report the observation of molecular spectra for vibrationally excited states of the c-a (triplet) and C-A (singlet) He_2^* transitions. The lineshift and linewidth dependence on pressure have been investigated for several of the identified rotational lines across different isotherms.

Our analysis revealed that above a threshold pressure, excimers are fully solvated in liquid helium and hence no fluorescence is observed from high rotational levels. Vibrational hot bands have been identified for both the triplet and the singlet transitions, thus suggesting that when the excimer is solvated, the non-radiative relaxation mechanisms of the excimers are inefficient. The existence of metastable vibrationally excited helium excimers within liquid helium can be explained because the helium excimers are diatomic molecules with a fairly large vibrational energy spacing, similar to the findings by Chandler and Ewing in rare gas matrices (3; 4; 5) and Nauta and Miller in superfluid helium droplets (6).

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Towards new plasmonic materials: Synthesis of K and K-Au nanoparticles with helium nanodroplets

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We report on experiments on K and bimetallic K-Au nanoparticles produced under UHV conditions by synthesis in helium nanodroplets. In particular, bimetallic K-Au nanoparticles are promising candidates as building blocks for future meta-materials due to their excellent plasmonic properties. Considering the growing importance of plasmonic technology with diverse applications for example in photovoltaics, medical diagnostics, catalysis and surface enhanced Raman spectroscopy, the search for better plasmonic materials constitutes an important task for both science and industry. The investigated particles were fabricated by coagulation of metal atoms after pickup by cold helium nanodroplets. The employed experimental techniques encompass *in-situ* in-flight spectroscopy, as well as *ex-situ* examinations via transmission electron microscopy. Beam depletion spectroscopy reveals a strong resonance in plain K clusters isolated in He_N at about 600 nm, in agreement with experiments on free K clusters [1]. The position of the resonance depends on the K partial pressure in the pickup region, i.e. the size of the nanoparticles. After adding a Au pickup zone subsequently to the K pickup region, a blue shift of the resonance is observed, towards the well-known localized plasmon resonance of plain Au nanoparticles. A very important aspect of our current research is to test the possibility of passivating the highly reactive K clusters with a Au shell, which may be possible with the helium droplet technique [2,3]. First TEM investigations show promising results, opening up new perspectives for the production of novel materials and material combinations for plasmonics with helium droplet based nanoparticle synthesis.

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Size distributions of supersonic beams from a pulsed valve using the titration technique

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Pulsed valves offer a variety of advantages over continuous beam sources such as reduced gas load and enhanced beam intensity. In cooperation with UBC, Vancouver, we developed a magnetically driven valve (CRUCS valve) for pulse durations down to 20µs, repetition rates up to 500 Hz, and with choice of valve materials for different applications. In addition, we implemented liquid nitrogen cryo-cooling to produce e.g. large argon cluster. For many applications the size distribution of the cluster beam is an essential parameter for running an analyzing experiments. To determine the size distribution, we use the so-called titration technique, which has been used to determine helium cluster sizes of continuous supersonic beams [1]. Here, we present a systematic study of cluster size distributions by varying the expansion parameters of the pulsed valve. We apply this technique to argon and nitrogen cluster.

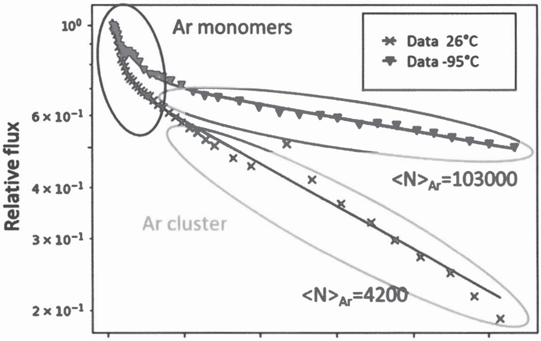

Figure 1. The Argon flux of a pulsed supersonic beam for two temperatures after passing a chamber with variable pressure. The decay of the signal is used to calculate the mean cluster size distribution.

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Time-resolved interatomic Coulombic decay observed in helium droplets

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When weakly-bound complexes are multiply excited by intense radiation, energy can be exchanged between neighbors through an interatomic decay process leading to a strong enhancement in ionization[1]. Specifically, interatomic Coulombic decay (ICD) is an energy transfer process which has been observed in a multitude of weakly-bound, condensed phase systems such as van der Waals clusters or hydrogen bonded networks like water[2,3]. Here, we perform the first time-resolved measurements on resonantly excited helium droplets using photon energies of 21.6 eV created by the FERMI free electron laser. After excitation on the helium droplet resonance the system undergoes a fast electronic relaxation to the lower lying atomic excited states of helium, which then subsequently decay via ICD. The excited states of helium can be depleted with our probe laser with 400 nm wavelength and various pump-probe delay, therefore measuring the effective timescale for ICD for various droplet sizes and excitation densities.

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Controlled enantioselective orientation of chiral molecules with an optical centrifuge

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We initiate unidirectional rotation of chiral molecules with an optical centrifuge and detect their spatial orientation by means of Coulomb explosion imaging. We show that the centrifuge-induced orientation of one of the molecular axes in the laboratory frame depends on the relationship between the chiral handedness of the enantiomer and the direction of the laser-induced molecular rotation. The effect is reproduced in the numerical simulations of the centrifuge excitation followed by Coulomb explosion of the centrifuged molecule. The demonstrated technique offers not only an alternative way of differentiating between molecular enantiomers, but also a new approach to enantioselective manipulation of chiral molecules with light.

Formation of Polar DMSO Structures in Helium Nanodroplets

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Pendular laser spectroscopy measurements [1] on polar molecules submerged in helium nanodroplets have demonstrated that they may assemble into configurations with unusual polarities. A famous example is the formation of long extended chains of HCN [2]. The key mechanism of this behavior is that the molecules approach each other under the guidance of mutual long-range electrostatic forces and find themselves "frozen" into interesting metastable structures.

In this work we examine the behavior of polar solvent dimethyl sulfoxide (DMSO) molecules with the use of our recently developed deflection technique [3,4], whereby nanodroplets doped with polar molecules are deflected by a strong external inhomogeneous electric field. By measuring the average deflection of DMSO-doped helium nanodroplets as a function of the partial pressure of the pick-up cell and carefully modeling the deflection pattern, we determine the electric dipole moments of $(DMSO)_{n=2,3}$ structures inside the droplets.

The deflections reveal, in a direct way, that the molecules line up non-linearly with respect to each other and form a metastable state with a total dipole moment that is distinctly different from that of the global minimum-energy structure. For example, in the case of $(DMSO)_2$ the total dipole moment is found to be non-zero, in contrast with the minimum-energy configuration of the dimer and in fact greater than the monomer's dipole moment. This is in agreement with theoretical simulations of metastable dimer formation. Possible geometries of the dimer and trimer structures will be discussed. The deflection patterns of higher order fragment peaks in the electron-impact mass spectrum also provide insight into DMSO dimer and trimer fragmentation channels.

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Vortex Lattice in Rotating Prolate ^{4}He Droplets

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So far, lattices of quantum vortices have been observed in axially symmetric, rotating superfluid ^{4}He or rotating Bose-Einstein condensates (BECs).[1-3] Vortex configurations in rotating superfluids lacking axial symmetry have been discussed theoretically[4,5], but experimental observation of such systems proves to be challenging.[6] Here, we present a study of vortices in microscopic free, prolate superfluid ^{4}He droplets rotating around the short axis. The vortices were doped with Xe atoms and studied via coherent x-ray scattering at the LCLS free-electron laser. It was found that the vortices form a distorted lattice within the droplet. We compare the shapes of classical droplets executing rigid body rotation to rotating prolate superfluid droplets, the angular momentum of which has contributions from quantum vortices and capillary waves.[7]

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IR Spectroscopy of Glycine-Water in Helium Nanodroplets

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We have studied water induced zwitterionization of glycine using Helium nanodroplets isolation infrared spectroscopy. In the past, this process has been studied using matrix isolation infrared spectroscopy [1]. However, no spectroscopic fingerprint for zwitterion formation could be assigned, unambiguously. This triggered various theoretical studies for predicting the energetic stabilization and vibrational fingerprint of zwitterionic glycine-$(H_2O)_n$ (n=1-10) clusters [2]. In this study, we exploited the barrier free diffusion property of helium droplets to stepwise add water molecules to one molecule of glycine. Herein we present the infrared spectra of glycine-$(H_2O)_n$ clusters recorded in the range of 1000-1850 cm^{-1}, using the free electron lasers (FELs) at FELIX laboratory in Nijmegen.

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Vorticity and quantum turbulence in the merging of superfluid Helium nanodroplets

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We have studied the merging of two ^{4}He droplets at zero temperature due to their Van der Waals mutual attraction. The merging shows the appearance of density structures evolving in time which closely match the experimental observations by Vicente et al. [J. Low Temp. Phys. **121**, 627 (2000)]. We show that quantized vortex-antivortex ring pairs are nucleated at protrusions on the surface that either shrink and evanesce, or annihilate inside the droplet producing a roton burst. The merging process also nucleate ring structures that in some cases have been identified as quantized vortex-antivortex wrapping the outer droplet surface. Analysis of the energy spectrum discloses the existence of a first regime where turbulence arises from vortex-antivortex ring annihilation characterized by a power law close to that of the Kolmogorov spectrum, followed by another time interval where roton radiation dominates leading to a weak-wave turbulence regime.

Experimental study of the solvation and desorption dynamic of Cs atoms attached to ^{4}He nanodroplets

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The versatility of helium nanodroplet isolation spectroscopy (HENDI) has led to many experiments where it is of vital importance to understand the interplay between the dopant and the helium environment. Despite the low perturbative environment provided by the superfluidity of helium nanodroplets, numerous dynamics are triggered by the electronic excitation of the dopant. The repulsive electron-He interaction can, for example, result in the ejection of electronically excited dopants [1] which can be accompanied by electronic relaxation induced by the helium environment [2]. In some cases, pairwise He-dopant interaction can even lead to the formation of He-dopant exciplexes [2]. Relaxation and exciplex formation strongly depend on the dopant species and still lack a detailed understanding. To gain a more in-depth understanding of these processes, we present investigations of the real-time desorption dynamics of photo-excited cesium atoms attached to helium nanodroplets using femtosecond imaging spectroscopy. Preliminary results on the fall-back time of cesium ions are compared to the results of time-dependent density functional theory simulations [3] and to the findings of earlier studies on cesium and rubidium atoms attached to helium nanodroplets [4-6].

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Femtosecond Time-Resolved Energy Transfer Dynamics in Excited Doped Helium Nanodroplets

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Helium nanodroplets are often utilized as a spectroscopic matrix because they are optically transparent and weakly interact with atomic and molecular dopants. In contrast, when exposed to XUV radiation, the droplet is electronically excited and subsequently undergoes a variety of relaxation mechanisms. This makes helium droplets an excellent system to study host-dopant energy and charge transfer processes in complex systems approaching macroscopic dimensions. We are interested in studying energy transfer between the excited droplet environment and embedded dopants, as well as the competition between these energy transfer processes and internal droplet relaxation mechanisms. Previously, energy transfer to a noble gas dopant in an electronically excited droplet was observed in a steady-state experiment [1]. Indirect ionization of the dopant is particularly pronounced for energies at which the droplet exhibits strong absorption. In a complementary femtosecond time-resolved experiment, we want to probe the underlying energy transfer mechanisms in the time domain [2]. Using a high harmonic generated femtosecond XUV pulse to electronically excite the droplet and a UV probe pulse to modulate the photoelectron signal produced from the energy transfer to a noble gas dopant, we monitor the energy-transfer yield as a function of pump-probe time delay. New pump-probe results and future directions will be presented.

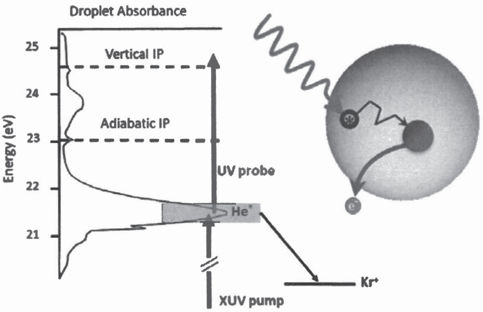

Figure 1: Time domain XUV pump- UV probe excitation scheme to study energy transfer from an electronically excited helium droplet to a noble gas dopant, such as krypton.

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Mass spectrometric investigation of corannulene-helium cationic complexes and their absorption spectroscopy

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Polycyclic aromatic compounds (PAHs) are a class of hydrocarbons considered to play a role in the molecular evolution of carbon species in interstellar space and to be a possible carrier of diffuse interstellar bands (DIBs), producing great interest in the spectroscopy of such species for comparison with astronomical data [1]. We present here the results of our investigations of the PAH corannulene ($C_{20}H_{10}$).

The experiment couples a helium nanodroplet source and two pickup chambers, followed by an electron impact ion source. Low-mass ions are extracted orthogonally, superimposed with the beam of a tunable laser and detected by a time-of-flight mass spectrometer [2], enabling us to obtain absorption spectra of $He_nC_{20}H_{10}^+$ complexes with up to 60 He atoms.

For $HeC_{20}H_{10}^+$, we were able to identify seven previously assigned bands between 5800 and 6000 Å [3] as well as six newly found bands between 5500 and 5760 Å. We also observed a near-linear redshift of the bands for every helium atom attached, up to 32 helium atoms. The results of our investigation are discussed and compared to state-of-the-art molecular dynamics simulations.

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Rotationally resolved electronic spectroscopy of large organic molecules and their vdW-clusters in the gas phase

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Rotationally resolved electronic spectra and Stark spectra of phthalocyanine derivatives and their clusters with atoms (Ar) and small molecules (H_2O) are recorded in the gas phase. The observed rotational band shapes reveal the structure and polarity of the molecular systems for both the ground and the electronically excited state. These spectra serve as benchmark for corresponding spectra recorded in helium droplets. By means of a rule of thumb for transition from gas phase to helium droplet conditions we simulate the rotational envelope and corresponding Stark spectra and compare them to the helium droplet spectra which are subject of a follow-up poster. Matches and mismatches provide insight to the microsolvation of molecules and van-der-Waals-clusters in helium droplets and in particular to the degree of freedom of rotation coupled to electronic excitation under the influence of the helium environment.

The THz/FIR spectrum of small water clusters

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Since decades the understanding of water-water interactions on the molecular level is subject to numerous experimental and theoretical studies. Experimental spectra of intermolecular modes of small water clusters $(H_2O)_n$ with $n \leq 6$ are well studied in the mid-infrared [1] and in the fingerprint region. [2,3] From experimental data it is well known that the global minimum structure of the dimer is singly H-bonded whereas water clusters with $n = 2\text{-}5$ form cyclic structures. High resolution studies in the low frequency range have focused mostly on the microwave region (Brooks Pate) and the region below 100 cm^{-1} [4,5] which is dominated by torsional bands. Due to the lack of tunable high power lasers, only a few studies were tackling the translational and librational bands. [6,7]

In combination with the free electron laser at FELIX, we have used our helium droplet spectrometer to study the far-infrared spectrum of small water clusters. Helium droplets provide a soft matrix which is well suited for spectroscopic investigations. They enable the step-wise formation of weakly bound aggregates at low temperatures of 0.37 K. Mass selective and pressure dependent measurements are used to assign spectral signals to distinct aggregates. So far, we were able to assign the majority of hindered translational and librational bands of the water dimer and trimer. For the latter, the number of spectral bands exceeds the number of normal modes expected in this frequency range. An unambiguous assignment is still pending.

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Towards femtosecond pump-probe spectroscopy of charge-transfer complexes embedded in helium nanodroplets

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Macroscopic organic systems are promising systems for the development of efficient and inexpensive solar cells[1]. However, the fundamental processes of photocurrent generation, such as the excitation energy and the charge transfer of the donor-acceptor system, are still not fully understood. Experimental studies are therefore required to obtain a detailed understanding of the involved dynamics in order to drive further technical developments. We are aiming at characterizing these processes using femtosecond pump-probe spectroscopy in helium nanodroplets combined with photoelectron/-ion imaging, which enables to access information about the mass, charge and energy distributions of ions and photoelectrons produced upon electronic excitation and subsequent ionization.

The unique properties of rare-gas clusters – transparency, ability to capture and cool down to milliKelvin temperatures, neutrality – make helium nanodroplet isolation spectroscopy (HENDI) an excellent technique for the study of the energetic and the dynamical properties of these systems [2]. The work presented here is mainly focused on the properties of the C_{60}-pentacene complex, whose time-scales for electron transfer have already been theoretically and experimentally investigated among the solid-state community [3], [4].

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Coulombic decay in He nanodroplets

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This poster contribution presents different types of correlated decay processes induced by energetic photons in He nanodroplets which are related to interatomic Coulombic decay (ICD). In connection with this, the dynamics of elastic and inelastic scattering of photoelectrons and photoions dynamics in He nanodroplets is discussed.
While the photoelectron spectra of ICD in He droplets show great resemblance to those previously measured for free He_2 dimers [1] indicating negligible electron-He scattering, the ion kinetic energy distributions show substantial difference [2].

Besides dimer-like ICD, an other type of interatomic decay was recently observed in synchrotron experiments with large (>10^6 He atoms) He droplets. It proceeds in the following way: one of the He atoms is ionized by an energetic (>45 eV) photon. The obtained photoelectron creates an excited He atom inside the droplet by impact excitation, and once it is slowed down far enough to get recaptured by the residual photoion, it forms a second excited He atom. Subsequent autoionization of the two He* excitations results in a characteristic peak, independent of photon energy but strongly dependent on the He droplet size.

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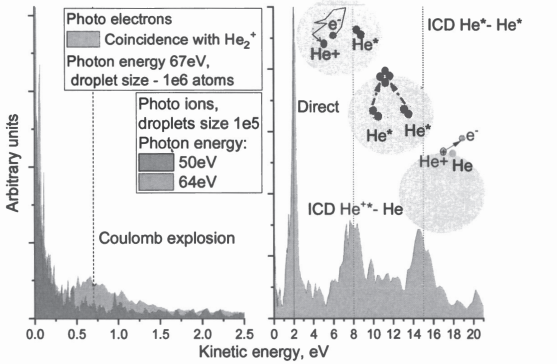

Left: Photoion spectrum, peak at 0.7 eV appears for hv>50eV, is due to Coulombic repulsion between initial photo ion and the one created via electron impact

Right: 8eV peak is usual type of ICD, 2eV – ICD satellite electron, 15 eV peak – CED.

Anthracene and Anthracene-Ar_n clusters in superfluid helium nanodroplets

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Clusters consisting of a single anthracene molecule and a variable number of argon atoms generated in superfluid helium nanodroplets are investigated by means of electronic spectroscopy. The Ar induced shift of the electronic resonance frequency together with the fine structure induced by the helium environment are the experimental observables which provide information on the configuration of the clusters. As to be expected the helium environment promotes the stabilization of numerous cluster configurations which are not observed in the gas phase. Besides the identification of those configurations reported also from corresponding gas phase investigations [1,2] the helium droplet experiment reveals significant influence of the surrounding helium on the formation of clusters. Apart from additional metastable configurations, clusters with more than 4 argon atoms do not appear to form rigid structures.

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Photoinduced dopant-to-solvent energy transfer dynamics in helium nanodroplets studied with time-resolved photoelectron spectroscopy

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For the investigation of ultrafast photoinduced dynamics in molecular systems with femtosecond time resolution, helium nanodroplet (He_N) isolation represents an attractive candidate to study otherwise inaccessible systems. Such ultrafast investigations are performed as pump-probe experiments, where a first pulse triggers and a second pulse probes the dynamics with precise time delay. It is well known, however, that photoexcitation of atoms or molecules, located within a bubble inside the droplet, can lead to a pronounced dopant-helium related response due to a strong interaction of the excited electronic state with the quantum fluid. Here, we present a systematic investigation of the photoexcitation process of a single indium (In) atom inside a He_N, in particular the dependence on the photoexcitation wavelength and the droplet size.

By applying time resolved photoelectron/photoion spectroscopy and time-resolved density functional theory simulations, we could previously show that photoexcitation triggers an expansion of the solvation shell bubble within a few hundred femtoseconds [1], during which the excess energy of the excitation process is converted into helium kinetic energy. After the expansion, the bubble starts to oscillate with a period of about 30 ps, accompanied by the ejection of the atom from the droplet within 50 ps.

Our new results for different excitation wavelengths show that an increase in excess energy is directly related to an increase in kinetic energy of the surrounding He. We find that the bubble dynamics are purely local effects, influenced solely by the first solvation shell layer around the dopant. For the case of indium, the dependence of the ejection time on the droplet size is surprisingly weak. This independence indicates that the atom in its ground state resides close to the droplet edge, but is still fully immersed. Our results are important for future studies on more complex systems, as system-intrinsic dynamics will have to be disentangled from helium-induced dynamics, which are influenced by the experimental parameters.

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Size Distributions of Helium Nano Droplets

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Super fluid helium droplets are frequently used in experiments as a super cold matrix for the analysis of molecules and atoms.

In recent experiments, size distributions of helium nano droplets formed in free jet expansion [1] have been analyzed. Since the cross section in the pickup process directly corresponds to the size of the droplet, a good knowledge of the size distributions in the beam is crucial. In experiments like those entailing the formation of super fluid helium nano droplets doped with clusters of C60 and smaller molecules [2], the super cold matrix of the helium droplets is used. Furthermore, the size of a droplet affects how much energy can be dissipated from its dopants due to evaporative cooling.

The helium droplets are formed in a free jet expansion with a nozzle diameter of 5um at temperatures of 4 K to 9 K. The droplets are then ionized via electron impact ionization with low electron energy in order not to alter the size distribution. Using an electrostatic analyzer, the droplets are filtered according to their mass to charge ratio. A channel electron multiplier is used to detect the charged particles.

In another approach, the helium droplets are ionized more strongly to create multiple charges in the droplets. Using the multiply charged helium droplets the size distribution can be evaluated.

The size distributions are found to be strongly dependent on the nozzle temperature. Thus it appears that the clustering process depends strongly on the temperature of the expanding Helium.

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Are Metal Clusters in Superfluid He Droplets Superconducting?

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In our 1996 Physical Review Letter we pointed out that small metal clusters in *He* droplets can be expected to be superconducting. [1] Since then we are not aware of any confirming experiments. The purpose of this contribution is to propose some simple experiments by which the superconductivity of metal clusters in *He* droplets could be established. If superconductivity could be established it might be possible by deposition to create a novel type of macroscopic thin film superconductor [2].

Since 1970 a number of experiments have reported superconductivity in small clusters of *In*, *Tl* and *Pb* with diameters of 2.2 nm (N = 150) inside porous glass [3, 4]. More recently, the negative magnetic susceptibility (Diamagnetism) of monodisperse colloidal lead particles with diameters between 4.4 and 20 nm, which were in an inert shell of tin oxide, was reported [5]. Indirect evidence for superconductivity comes from molecular beam photoionization measurements on free aluminum clusters by the Kresin group. For the magic Al_{66} cluster they observed an increase of the electronic density of states expected for a superconductor, which was not found for the other *Al* clusters. From this observation they expect a superconductivity transition temperature of unusually high $T_c \geq 100\ K$. [6].

We propose two methods to establish the superconductivity of metal clusters in *He* droplets: (1) Deflection of the metal cluster doped He droplet beam after passage through a magnetic field. Being strongly diamagnetic the superconducting droplets will be deflected (Messner-Ochsenfeld effect). (2) Heating and depletion of the doped He droplet beam after passage through a microwave resonator. When the microwave frequency ν, is greater than superconducting energy gap Δ, $h\nu > \Delta$ the resulting heating [7] will lead to extensive evaporation of *He* atoms from the droplet.

In the poster we will present estimates of the magnitudes to be expected. We hope that such experiments will soon be undertaken.

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Indium dimer fragmentation induced by femtosecond pump-probe ionization inside helium nanodroplets

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Measurement of ultrafast photoexcitation dynamics of isolated indium (In) atoms inside superfluid helium nanodroplets (He_N) has recently proven the feasibility of He_N as cold containers for femtosecond time resolved spectroscopy [1]. As next step towards more complex systems, photoexcitation dynamics of indium dimers (In_2) were studied with femtosecond time-resolved photoelectron (PE) and photoion (PI) spectroscopy. Photoexcitation of the In_2 $B^3\Pi_g(II) \leftarrow X^3\Pi_u$ transition at 345 nm triggers a combination of solvation shell dynamics comparable to the In atom case [1] and coherent wave packet dynamics of In_2 in the excited state. Low decoherence of the wave packet motion enables the observation of vibrational revivals in bare In_2 after ejection from the droplet.

Ionization with the probe pulse prior to the ejection solely allows for PE detection and prevents the detection of In_2^+ because ions are trapped inside the He_N. However, In^+ and $In\text{-}He_n^+$ (n = 1, 2, 3, ...) complexes are detected for ionization shortly after photoexcitation, which we ascribe to a small fraction of dimers that undergo fragmentation inside the droplet. Ejection of these ions seems to be enabled by kinetic energy release during fragmentation. As time resolved PE/PI measurements show, these ion fragments are not related to bare In_2 produced by complete droplet evaporation during pickup and the absence of narrow lines in the PE spectra indicates that fragmentation takes place in the ionic state and not in the neutral excited state. This fragmentation channel is of importance for the interpretation of time-resolved photoionization experiments and expected to play a role in future investigations of more complex systems.

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Photoelectron two-dimensional coherent spectroscopy

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Two-dimensional electronic spectroscopy (2DES) is a powerful tool to explore coherences and correlations on ultrafast time scales. Until now, 2DES studies have mostly been conducted in the condensed phase. We have thus built a setup to perform 2DES experiments on molecular and cluster beams in the gas phase. To achieve sufficiently high sensitivity for our gas-phase studies, we have adapted the phase modulation technique developed by Marcus et al. [1]. Our setup can additionally be combined with an energy-resolved photoelectron detection which adds an additional dimension to the 2D spectra. For this purpose, we built a magnetic bottle spectrometer to combine photoionization with energy-selective detection of photoelectrons. In this way, binding energies are deduced from the time-of-flight, processed in a self-made gating module and combined with a lock-in detection to increase the sensitivity.

In a further step, we are working on a software-based lock-in amplifier to improve the data acquisition. In combination with a time-to-digital converter, this can move the analog signal processing to a completely digital signal processing. With this concept, the signal gating and demodulation takes place on a regular personal computer.

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HENDI spectroscopy of acetylene-Ne,Ar,Kr : large amplitude motion at 0.4K

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The Helium NanoDroplet Isolation (HENDI) [1] technique is used to study weakly bound complexes made of one acetylene molecule and one rare gas atom. More specifically, infrared spectra in the C_2H_2 asymmetric stretching frequency range are recorded for complexes with neon [2], argon [3] and krypton [3]. The obtained spectra with clear rotational lines are enriched by the acetylene Fermi resonance and by the presence of the two ortho and para species.

The subtle balance of forces in place, both within the floppy complexes and between the complex and the helium droplet quantum environment, provides room for testing theoretical models. With the help of the in-house VRBoundScat program [4,5], simulations of the experimental spectra are proposed. They are based on exact computation of oscillator strengths of isolated complexes with effective parameters introduced to reproduce the effect of the helium environment. The full interpretation of the experimental and theoretical results will be presented.

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Radiative and non-radiative relaxation of rotational and vibrational levels of excimers in liquid and gaseous helium

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Non-radiative relaxation of molecules in fluids is a topic of great interest in chemical and physical research. In most cases, vibrational relaxation of molecules in liquids is fast, but exceptions are known. These include diatomic molecules with large vibrational energy separation such as CO [1] as well as weakly interacting solvents such as superfluid helium [2].

We have studied the rotational and vibrational relaxation of He_2^* for a wide range of pressures in helium at cryogenic conditions, covering both the liquid and the gas phases. A corona discharge was employed to generate electronically excited He_2^* and the dispersed fluorescence was measured at high resolution. The electronic radiative lifetime served as a clock. Under these conditions, the fluorescence spectrum exhibits rotationally resolved lines [3]. Line shifts and line broadening whose magnitude depends on pressure and temperature are observed. In previous studies, the analysis of line shift, width and intensity revealed that in gaseous helium excimers are rotationally hot, however, in liquid helium they begin to cool rather efficiently at a rate of at least 10^{10} to 10^{11} Ks^{-1}. At pressures above 3 bar practically all excimers are in a thermalised state [3].

Here, we have extended our study to the c→a and C→A transitions. Fluorescence from vibrationally hot ($v=1$) states were observed both in the gas and the liquid phases, indicating inefficient non-radiative vibrational relaxation. In the liquid phase, only fluorescence from the rotational ground state was observed, indicating efficient rotational relaxation similar to what we had found earlier for the $v=0$ state. The weak vibrational relaxation is attributed to the relatively low density of vibrational states for diatomic molecules in monatomic solvents. It is plausible that rotational relaxation of He_2^* in liquid helium is mediated by excitations of the solvent. Efficient coupling between the rotational modes of diatomic molecules and collective excitations has been observed before for CO in superfluid helium droplets [4].

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Auger Emission from the Coulomb Explosion of Helium Nanoplasmas

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The long-time correlated decay dynamics of strong-field exposed helium nanodroplets is studied by means of photoelectron spectroscopy. As a result of the adiabatic expansion of the laser-produced fully inner-ionized nanoplasma, delocalized electrons in the deep confining mean field potential are shifted towards the vacuum level. Meanwhile, part of the electrons localize in bound levels of the helium ions. The simple hydrogen-like electronic structure of He^+ results in clear signatures in the experimentally observed photoelectron spectra, which can be traced back to bound-free and bound-bound transitions. Auger electron emission takes place as a result of the transfer of transition energy to weakly bound electrons in the quasifree electron band. Hence, the spacial and temporal development of the nanoplasma cloud is encoded in the experimental spectra, whereas the electronic properties of He^+ helps to resolve the different contributions