MO 35: Spectroscopy in He Droplets

Time: Friday 10:30–12:30 Location: MER 02

MO 35.1 Fri 10:30 MER 02

Femtosecond time-resolved EUV photoion imaging studies of pure helium nanodroplets — •Oliver Bünermann[1,3], Oleg Kornilov[2,3], Oliver Gessner[3], Daniel M. Neumark[3,4], and Stephen R. Leone[3,4] — [1]Institute for Physical Chemistry, Georg-August-University Göttingen — [2]Max-Born-Institute, Berlin — [3]Ultrafast X-ray Science Laboratory, Chemical Sciences Division, Lawrence Berkeley National Laboratory — [4]Department of Chemistry, University of California, Berkeley

The relaxation dynamics of electronically excited helium nanodroplets are investigated by femtosecond time resolved photoion imaging studies. The droplets are excited into a broad absorption band centered at 23.8 eV. The electronic and nuclear dynamics following this excitation are monitored by photoionization with a 785nm probe pulse. A Wiley-McLaren time of flight spectrometer equipped with a time- and position sensitive delay line detector facilitates the measurement of mass selective ion kinetic energy distributions. Different relaxation processes are identified and characterized, for example the ejection of highly excited helium atoms and dimers happening on a 220 fs timescale. The combination of these results with photoelectron imaging measurements allows for a new level of insight into the electronic and nuclear dynamics of electronically excited helium nanodroplets.

MO 35.2 Fri 10:45 MER 02

Ultrafast relaxation and emission of Rydberg He atoms from excited He droplets — •Oleg Kornilov[1,3], Oliver Bünermann[2,3], Oliver Gessner[3], Daniel Haxton[3], Daniel Neumark[3,4], and Stephen Leone[3,4] — [1]Max-Born-Institute, Berlin — [2]Institute for Physical Chemistry, Georg-August-University Göttingen — [3]Ultrafast X-ray Science Laboratory, Chemical Sciences Division, Lawrence Berkeley National Laboratory — [4]Department of Chemistry, University of California, Berkeley

Real time dynamics of electronically excited pure He droplets is studied by time-resolved photoelectron spectroscopy. The droplets are excited by a femtosecond EUV pulse into an excitation band centered at 23.8 eV and are probed by 785 nm pulses. Transient angular distributions of photoelectrons reveal emission of atoms in excited Rydberg states. Perturbed Rydberg states model of the droplet excited band is formulated. Photoelectron spectra calculated on this assumption are in good agreement with observations. Comparison to the results of a complimentary photoion study helps to follow fragmentation of excited and ionized droplets.

MO 35.3 Fri 11:00 MER 02

Doped Helium droplets: Velocity-map-imaging of ions in a pump-probe setup — •Andreas Kickermann[1], Andreas Przystawik[1], Lasse Schroedter[1], Sven Toleikis[1], Stefan Düsterer[1], Harald Redlin[1], Marion Harmand[1], Andrew M. Ellis[2], Marius Lewerenz[3], Robert E. Zillich[4], Klaus von Haeften[2], and Tim Laarmann[1] — [1]Deutsches Elektronen-Synchrotron (DESY) Photon Science, Hamburg, Germany — [2]University of Leicester, UK — [3]Université Paris Est, Marne-la-Vallée, France — [4]Johannes-Kepler-Universität, Linz, Austria

Helium nanodroplets have been proven to be excellent systems to study the properties of molecules and small compounds, which are embedded inside the droplets. Due to the ultra low temperature of the droplets the embedded particles are cooled down and can be studied isolated from the environment. We present a design of a velocity-map-imaging (VMI) spectrometer, that is integrated in a setup enabling pump-probe experiments with XUV-free electron lasers. Due to the high intensity and photon energy of such light sources the spectrometer has to be able to catch the ions created in a coulomb explosion without losing the angular information and the kinetic energy resolution. By temporal gating we are able to distinguish between different fragment ions, which will allow experiments on size-dependent ultrafast molecular dynamics in embedded Helium droplets.

MO 35.4 Fri 11:15 MER 02

Time resolved spectroscopy of rubidium exciplexes in helium nanodroplets with shaped femtosecond pulses — •Christian Giese[1], Terence G. Mullins[1], Marcel Mudrich[1], Frank Stienkemeier[1], and Matthias Weidemüller[2] — [1]Physikalisches Institut, Universität Freiburg, Hermann-Herderstr. 3, 79108 Freiburg, Germany — [2]Physikalisches Institut, Universität Heidelberg, Philosophenweg 12, 69120 Heidelberg

Alkali-doped helium nanodroplets are peculiar complexes due to the extremely weak binding of the atoms to the droplet surface. Electronic excitation may induce desorption of the atom off the droplets or the formation of alkali-helium exciplex molecules [1,2]. In order to gain detailed insight into the formation dynamics of RbHe* exciplex molecules, Rb-doped helium droplets are studied by femtosecond pump-probe spectroscopy using shaped pulses.

[1] Phys. Rev. Lett. 93, 023402 (2004)
[2] Phys. Rev. Lett. 100, 023401 (2008)

MO 35.5 Fri 11:30 MER 02

Rotational constants of molecules in small Helium droplets — •Andreas Przystawik[1], Andreas Kickermann[1], Lasse Schroedter[1], Marion Harmand[1], Stefan Düsterer[1], Harald Redlin[1], Sven Toleikis[1], Andrew Ellis[2], Robert Zillich[3], Marius Lewerenz[4], Klaus von Haeften[2], and Tim Laarmann[1] — [1]Deutsches Elektronensynchrotron (DESY) Photon Science, Hamburg, Germany — [2]University of Leicester, UK — [3]Johannes-Kepler-Universität, Linz, Austria — [4]Université Paris Est, Marne-la-Vallée, France

Molecular spectroscopy in Helium droplets has developed into a tool for studying the vibrational and rotational motion at sub-Kelvin temperatures and thereby greatly simplifying the analysis and understanding of the investigated molecules. The superfluid nature of the droplets enable to observe the nearly undisturbed rotation of a molecule. On the other side superfluidity is a macroscopic property. That means finite size effects and details of the interaction between the molecule and the inner Helium solvation layers affect the rotational constants. Considerable efforts were taken to measure this perturbation [1,2].

Here, we will present a new experimental approach to this topic that may enable a simpler assessment of the droplet size dependent rotational constants for small droplets. First data on CO in small Helium clusters chosen as a model system will be discussed.

[1] L.A. Surin *et al.*, Phys. Rev. Lett. **101**, 233401 (2008)
[2] R.E. Zillich, K.B. Whaley, K. v.Haeften, JCP **128**, 094303 (2008)

MO 35.6 Fri 11:45 MER 02

Line broadening in electronic spectra of molecules doped into superfluid helium nanodroplets — •Ricarda Riechers[1], Dominik Pentlhner[2], and Alkwin Slenczka[1] — [1]Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93053 Regensburg, Germany — [2]Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

Line broadening was found in the electronic spectra of several organic compounds doped into superfluid helium droplets. The investigation of photochemical processes such as proton transfer by means of electronic spectroscopy showed also line broadening. This observation is counterintuitive to what is expected from helium droplets, a host system at a temperature of 0.37 K. It is in contrast to sharp transitions in the corresponding gas phase spectra. Evidently, the line broadening is due to the interaction between dopant and helium environment. Electronic spectra of phthalocyanine derivatives, anthracene derivatives [1], some pyomethene dye molecules and 3-hydroxyflavone [2] (as a photochemical system), allow to deduce a mechanism explaining all the observed variations of line broadening including earlier reports on aniline [3] and adenine derivatives [4]. According to this mechanism electronic spectroscopy in superfluid helium droplets appears to be highly sensitive to changes in the electronic density distribution.

[1] D. Pentlehner et al., J. Chem. Phys. 133, 114505 (2010). [2] R. Lehnig et al., J. Chem. Phys. 131, 194307 (2009). [3] E. Loginov et al., Phys. Rev. Lett. 95, 163401 (2005). [4] S. Smolarek et al., Phys. Chem. Chem. Phys. 12, 15600 (2010).

MO 35.7 Fri 12:00 MER 02

High Resolution IR Spectroscopy of Deuterated Water Dimers in Helium Nanodroplets — Gerhard Schwaab[1], Anna Gutberlet[2], and •Martina Havenith[1] — [1]Physical Chemistry II, Ruhr University Bochum, D-44780 Bochum — [2]Purdue University,

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Water dimer is a highly flexible molecule showing three different tunneling pathways. As basic building block of larger water clusters it has attracted a lot of experimental and theoretical interest.

Here, we report on the IR-spectra of dimers of HDO as donor with H_2O and HDO as acceptor embedded in superfluid helium nanodroplets in the region of the O-D stretch vibration. Due to acceptor donor interchange, only the energetically lower d-bonded species survive the rapid cooling process to the droplet temperature of 0.37 K. For HDO$\cdots$DOH the donor stretch as well as the acceptor stretch vibration could be observed. Possible assignments will be discussed. The observed molecular constants will be compared with gas phase and matrix data.

MO 35.8 Fri 12:15 MER 02

Spectroscopy of PTCDA Monomers and Oligomers Attached to Helium Nanodroplets and Rare Gas Clusters — •Markus Müller, Matthieu Dvorak, Sebastian Müller, and Frank Stienkemeier — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

PTCDA (3,4,9,10 perylen-tetracarboxylic dianhydride) with its semiconducting properties is an auspicious material for organic device applications in photovoltaics and light-emitting diodes. To learn about the internal energy structure and possible deexcitation paths we employ helium nanodroplet isolation (HENDI)-spectroscopy as a well established technique to analyze the vibrational structure of molecules as well as excitonic transitions of complexes and nanostructures at low temperatures (380mK).

Laser induced fluorescence (LIF) excitation and emission spectra provide insight into the vibrational structure of the electronic ground state and the first electronically excited state. Emission intensities allow to determine the fraction of internal relaxation before emitting a photon. We will present LIF absorption and emission spectra of PTCDA monomers, dimers and oligomers attached to helium nanodroplets. Furthermore, measurements on neon and argon clusters have been performed in order to study the effect of the different cryogenic environments.