MO 10: Cluster

Time: Tuesday 10:30–13:00 Location: MER 02

MO 10.1 Tue 10:30 MER 02

Electron transfer mediated decay in Ar-Kr clusters — •Marko Förstel[1], Melanie Mucke[1], Tiberiu Arion[1], Alex M. Bradshaw[1,2], and Uwe Hergenhahn[1] — [1]Max-Planck-Inst. für Plasmaphysik, Albert-Einstein-Str. 15, 12489 Berlin, Germany — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Non-local autoionization processes in weakly bonded systems are receiving an increasing amount of attention, due to their universal appearance in clusters and liquids, and due to their interdisciplinary relevance. Most investigations have addressed Interatomic Coulombic Decay (ICD), in which a primary vacancy decays to a charge-separated two-hole state by ultra-fast energy transfer to a neighbouring site. In some systems however, autoionization into charge-separated states can also be mediated by electron transfer. This so-called Electron Transfer Mediated Decay (ETMD) connects different sites in a weakly bonded system solely by electron correlation, and leads to concerted changes in the electronic structure on a fs time scale. So far it has only been described theoretically. Here we present a clear demonstration of ETMD(3), an autoionization channel in which three different sites take part simultaneously. We recorded electron-electron coincidence spectra of Ar-Kr clusters after photoionization. An electron with the kinetic energy range from 0 to approx. 1 eV is found in coincidence with the Ar 3s cluster electron. This low kinetic energy electron can be attributed to a $Ar+Kr^+ + Kr^+$ final state which forms after electron transfer mediated decay.

MO 10.2 Tue 10:45 MER 02

Matrix isolation of PTCDA molecules in rare gas samples: clusters vs. bulk matrices — •Matthieu Dvorak[1], Markus Müller[1], Alexandre Rydlo[2], Stefan Minniberger[2], Wolfgang Harbich[2], and Frank Stienkemeier[1] — [1]Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg im Breisgau — [2]Institut de Physique des Nanostructures, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne

Matrix isolation spectroscopy of chromophores in rare gas matrices is a convenient way to unravel properties of the host media. The chromophore used in the present case is the PTCDA molecule ($C_{24}H_8O_6$), a perylene derivative, the fluorescence properties of which are well characterized. The influence of large argon and neon clusters or matrices on the emission and absorption spectra of PTCDA molecules have been studied. Attaching PTCDA molecules to large neon and argon clusters results in an increase of the spectral resolution of more than one order of magnitude when compared to PTCDA probed at thin films or in organic solvents at room temperature. In cryogenic rare gas matrices, site-specific isomers are observed, resulting in a broadening of the absorption spectrum and a splitting of the lines in the fluorescence spectrum. From the comparison between cluster and cryogenic matrix measurements, it can also be concluded that neon and argon clusters are solid and the studied molecules reside on the cluster surface. The quasi absence of PTCDA dimer formation implies a lack of mobility which can be interpreted as the surface being solid.

MO 10.3 Tue 11:00 MER 02

Gas Phase Vibrational Spectroscopy of Cerium Oxide Cluster Cations — •Torsten Wende[1], Asbjörn Burow[2], Pieterjan Claes[3], Marek Sierka[2], Gerard Meijer[1], Peter Lievens[3], Joachim Sauer[2], and Knut R. Asmis[1] — [1]Fritz-Haber-Institut d. MPG, Berlin — [2]Humboldt Universität Berlin — [3]K.U. Leuven, Belgium

Cerium oxide is one of the most reactive rare earth metal oxides and play an important role in many catalytic applications. A key property of ceria (CeO_2) is the ability to release, store and transport oxygen ions which relies on the accommodation of electrons in localized f-orbitals. The theoretical description of localized Ce-4f states is a demanding task. Infrared photodissociation spectroscopy (IRPDS) of gas phase clusters can provide reliable data to test different DFT approaches.

Ce-containing clusters have not been spectroscopically studied in the gas phase yet. Here, we employ IRPDS combined with DFT calculations to characterize the structure of cationic cerium oxide clusters. Vibrational predissociation spectra of rare-gas tagged $(CeO_2)_mCeO^+$ (m=0,1,...,4) and $Ce_nO_{2n-2}{}^+$ (n=2,3) clusters are measured in the 400-1000 cm^{-1} region. Structures containing a terminal Ce=O bond show a characteristic absorption band between 800-900 cm^{-1}. Larger clusters have common geometrical building units similar to bulk ceria leading to intense signals around 500 and 650 cm^{-1}. The results emphasize the importance of global optimization schemes and show that B3LYP does not always predict the correct global minimum structure.

MO 10.4 Tue 11:15 MER 02

Infrared spectra and structures of silver-PAH cation complexes — •Marco Savoca[1], Torsten Wende[2], Ling Jiang[2], Judith Langer[1], Gerard Meijer[2], Otto Dopfer[1], and Knut Asmis[2] — [1]Optik und Atomare Physik, TU Berlin — [2]Fritz-Haber-Institut, Berlin

Hybrids of metal and polycyclic aromatic hydrocarbons (PAHs) are promising building blocks for new materials with tailored optoelectronic properties. We report the first experimental mid-infrared spectra of Ag-PAH cation complexes measured in the linear absorption regime via messenger-tagging of the size-selected, cryogenically cooled complexes. The infrared photodissociation (IRPD) spectra of Ne-tagged Ag-PAH cation complexes (PAH=naphthalene-pyrene) are assigned on the basis of a comparison to simulated vibrational spectra from density functional calculations. The analysis of the IRPD spectra, which resolve IR bands as weak as a few km/mol, allows us to identify the Ag binding site and to gain valuable insight into the effects of Ag cation complexation on the geometry and charge distribution of the PAH.

MO 10.5 Tue 11:30 MER 02

IR Spectroscopy of Microhydrated Nitrate Ions: Influence of Solvent and Temperature on Structure — •Nadja Heine[1], Torsten Wende[1], Ling Jiang[1], Risshu Bergmann[1], Kenneth D. Jordan[2], Gerard Meijer[1], and Knut R. Asmis[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]University of Pittsburgh, USA

Nitrate ions, NO_3^-, play an important role in atmospheric chemistry, nuclear waste treatment and biochemical processes. For instance, NO_3^- is one of the most abundant ions in the troposphere and can be formed by rapid acid dissolution of nitric acid in aerosol particles. For a molecular-level understanding of such processes the characterization of their hydration behavior is crucial. Here, we exploit infrared photodissociation (IRPD) spectroscopy for obtaining structural information on the nitrate-solvent complexes using a time-of-flight tandem mass spectrometer combined with an ion trap. We present IRPD spectra of $NO_3^-\cdot(H_2O)_{1-4}$ as well as selected deuterated analogs, measured in the OH-/OD-stretching region (2400 - 3800 cm^{-1}) and at ion trap temperatures between 10 to 300 K. The present measurements complement our previous IRPD study of hydrated nitrate ions in the fingerprint region. The IRPD spectra of $NO_3^-\cdot(H_2O)$ and $NO_3^-\cdot(D_2O)$ in the OH-stretch region confirm a bidentate binding motif at low temperatures. At higher temperatures an additional isomer with just a single hydrogen bond is observed. The complex sequence in the OH-stretching region suggest a strong anharmonic coupling between the OH-stretch modes and low-frequency modes, which is modeled using vibrational CI calculations on a 15-dimensional potential energy surface.

MO 10.6 Tue 11:45 MER 02

High-dimensional neural network potential-energy surface for water clusters — •Vikas Sharma, Tobias Morawietz, and Jörg Behler — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany.

Studying the structural and dynamical properties of water clusters provides valuable insights into many important processes, e.g. in biology, materials science, and atmospheric chemistry. However, a prerequisite for the accurate description of water clusters is the availability of a reliable interatomic potential. In the present work artificial Neural Networks (NNs) trained to first-principles calculations are used to represent the multi-dimensional potential-energy surface of water clusters of different sizes. The quality of the NN potential is investigated by studying various stationary points as well as the vibrational frequencies of several benchmark clusters. The obtained results are compared to electronic structure data.

MO 10.7 Tue 12:00 MER 02

Comprehensive study of supersonic beams of CO_2 close to the critical point — •Wolfgang Christen, Bo-Gaun Chen, Stefan Heinig, and Klaus Rademann — Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, 12489 Berlin

The formation and growth of clusters in the gas phase is of fundamental relevance in a number of research fields as for instance atmospheric and environmental chemistry, chemical engineering, and process technology. In spite of a great deal of theoretical and experimental work open questions remain, including, for example, phase transitions close to the critical point.
Extending our earlier work[1] on pulsed, supersonic beams of pure CO_2 we present a systematic investigation of the mean flow velocity as a function of the stagnation conditions. The thermodynamic parameters comprise a wide range from medium to high pressures and sub- to supercritical temperatures with high accuracy[2]. Velocity distributions are determined using high resolution and mass-resolved time-of-flight measurements. The experimental results are compared with recent model predictions[3,4]. In particular we discuss the influence of the spinodal and the issue of liquid vs. solid clusters.

[1]W. Christen, K. Rademann, U. Even, *J. Chem. Phys.* **125**, 174307, 2006. [2]W. Christen, T. Krause, K. Rademann, *Rev. Sci. Instrum.* **78**, 073106, 2007. [3]W. Christen, K. Rademann, *Phys. Scr.* **80**, 048127, 2009. [4]W. Christen, K. Rademann, U. Even, *J. Phys. Chem. A* **114**, 11189, 2010.

MO 10.8 Tue 12:15 MER 02

XUV fluorescence spectroscopy of clusters in intense laser fields — •Lasse Schroedter[1], Andreas Kickermann[1], Andreas Przystawik[1], Marcus Adolph[2], Tais Gorkhover[2], Maria Krikunova[2], Maria Müller[2], Daniela Rupp[2], Thomas Möller[2], and Tim Laarmann[1] — [1]Deutsches Elektronensynchrotron (DESY) Photon Science, Hamburg, Germany — [2]Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany

Clusters in intense laser fields have attracted considerable interest in the last decades [1]. The most common way to study the interaction is by spectroscopy of the resulting charged particles. However, there is evidence that the measured mass spectra do not reflect the charge states that are initially formed, because charge recombination and extraction field effects are not accessible with these methods [2]. In this contribution, we present an experiment to analyze the initially produced charge states by their fluorescence. A spectrometer which is sensitive from 10 to 110 nm in the extreme ultraviolet spectral range (XUV) was designed to overcome the experimental challenges such as low fluorescence yield and low target density.

[1] Fennel et al., Laser-driven nonlinear cluster dynamics, Rev. Mod. Phys. 82 (2010) 1793

[2] Hoener et al., Charge recombination in soft x-ray laser produced nanoplasmas, J. Phys. B: At. Mol. Opt. Phys. 41 (2008) 181001

MO 10.9 Tue 12:30 MER 02

Spin and orbit moments of super paramagnetic Cobalt clusters from XMCD investigation of isolated ions by the GAMBIT experiment — •Jennifer Meyer[1], Matthias Tombers[1], Heinrich Kampschulte[1], Gereon Niedner-Schatteburg[1], Sergey Peredkov[2], Sven Peters[2], Matthias Neeb[2], and Wolfgang Eberhardt[2] — [1]Fachbereich Chemie und Forschungszentrum OPTIMAS, TU Kaiserslautern — [2]Helmholtz-Zentrum, Campus Adlershof, BESSY II, Berlin

X-ray induced circular dichroism (XMCD) arises in magnetized samples upon resonant inner shell ionization once their spins and orbit moments are sufficiently aligned e.g. by a strong external field. We operate an ion trap (GAMBIT) at BESSY II in Berlin to record XMCD spectra of isolated clusters. By standard sum rule analysis we have deduced the partial spin and orbit contributions of Cobalt cluster cations $Co_n{}^+$ ($8 \leq n \leq 23$) void of coupling to any substrate. It shows that orbit moments (per atom) in the clusters are significantly enhanced as compared to those of bulk Cobalt whereas spin contributions show little variation. The sum of both contributions compares well with the total moments from prior Stern-Gerlach experiments. Spin contributions may diminish further once a conceivable - yet undetermined - magnetic anisotropy would be taken into account. Our current experiments do not reveal evidence for such anisotropy. These obtained results provide benchmark data for further modeling. This project is part of the new Transregional Collaborative Research Center SFB TRR 88 "3MET".

MO 10.10 Tue 12:45 MER 02

Untersuchungen an freien atmosphärisch relevanten sub-10nm Partikeln — •Markus Eritt[1], Jan Meinen[2] und Thomas Leisner[1,2] — [1]Institute for Environmental Physics (IUP), Ruprecht-Karls-University, Heidelberg — [2]Karlsruhe Institute of Technology (KIT), Institute for Meteorology and Climate Research (IMK-AAF), Karlsruhe, Germany

Nanoskopische Materie aus in den oberen Atmosphärenschichten verdampfenden Meteoriten dient u.a. als Nukleationskeim für Nachtleuchtende Wolken (NLC) in der Mesopause. Die Gefrierkeime bestehen dabei primär aus Eisen- bzw. Siliziumoxid im Größenberich von 2 bis 10nm. Die in der Atmosphäre ablaufenden mikrophysikalischen Prozesse und deren Dynamik sollen unter realistischen Druck- und Temperaturbedingungen an freien Partikeln im zur Zeit im Aufbau befindlichen "Trapped Reactive Atmospheric Particle Spectrometer" (TRAPS) nachgestellt werden. Mit dem mobilen und modularen Aufbau sind neben Untersuchungen mit einem Ultrakurzpulslaser in unserem Labor auch Untersuchungen an Synchrotron- und Freie-Elektronenlaserquellen vorgesehen. Wir präsentieren neben der grundlegenden Funktionsweise der Anlage, die derzeitigen apparativen Möglichkeiten, sowie erste richtungsweisende Ergebnisse aus Extinktionsuntersuchungen mit Cavity-Ringdown Spektroskopie und Eisnukleationsexperimenten an der Partikeloberfläche.