

A 4: Cluster (with MO)

Time: Monday 11:00–12:45

Location: F 102

A 4.1 Mon 11:00 F 102

Vibrational Spectroscopy of the Atmospherically Relevant Clusters NO₃-(HNO₃)_m(H₂O)_n — ●NADJA HEINE¹, TARA YACOVITCH², CLAUDIA BRIEGER¹, TORSTEN WENDE¹, CHRISTIAN HOCK², KNUT ASMIS¹, and DAN NEWMARK² — ¹Fritz-Haber-Institut der MPG, Berlin — ²University of California, Berkeley, California

Ions influence various chemical and physical processes in the atmosphere, such as the electrical conductivity and the formation of polar stratospheric clouds. They also play a critical role in aerosol formation through ion nucleation. Among the most abundant anions in the troposphere and stratosphere is nitrate (NO₃⁻) and clusters of these ions with nitric acid and water. In order to understand the chemical and physical properties of these anionic clusters, as well as to test the structural predictions from previous computational studies, experimental information on the cluster structure is required. Here, we present first infrared multiple photon dissociation (IRMPD) spectra of NO₃-(HNO₃)_m(H₂O)_n measured with the infrared free electron laser FELIX in the fingerprint region (550-1800cm⁻¹), directly probing the NO-stretching and -bending modes. The assignment of the spectra is aided by electronic structure calculations. The IRMPD spectrum of m=1/n=0 is distinctly different from all other spectra exhibiting a strong absorption at 813cm⁻¹, which we attribute to a strongly bound shared proton in-between two nitrate ions, and lacking the characteristic H-O-N bending mode absorption close to 1650cm⁻¹. Addition of at least one nitric acid molecule or water breaks the symmetry of this arrangement.

A 4.2 Mon 11:15 F 102

Isomer-Selective Double Resonance Spectroscopy: Isolating the Spectral Signatures of H⁺ · (H₂O)₇ Isomers — NADJA HEINE, ●MATIAS R. FAGIANI, TORSTEN WENDE, and KNUT R. ASMIS — Fritz-Haber-Institut der Max-Planck Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Understanding how protons are hydrated remains an important and challenging research area. The anomalously high proton mobility of water can be explained by a periodic isomerization between the Eigen, H₃O⁺(aq), and Zundel, H₂O · H⁺ · OH₂(aq), binding motifs, even though the detailed mechanism is more complex. These rapidly interconverting structures from the condensed phase can be stabilized, isolated and studied in the gas phase in the form of protonated water clusters. The smallest protonated water clusters that exhibits structural isomers related to the Eigen and Zundel motifs experimentally is the protonated water hexamer H⁺(H₂O)₆. For the heptamer, H⁺(H₂O)₇, the presence of at least three isomers has been suggested but, due to spectral congestion, these could not be unambiguously assigned. Here, we present results on isomer-selective infrared/infrared (IR/IR) double resonance experiments on H⁺(H₂O)₇. Protonated water clusters are formed by electrospray ionization, mass-selected, cooled to cryogenic temperatures and messenger-tagged (H₂) in a buffer gas filled ion trap. Isomer-selective IR photodissociation spectra are measured from 2880–3850 cm⁻¹ by population-labeling IR/IR double resonance spectroscopy. Aided by electronic structure calculations four isomers, three Eigen and one Zundel-type isomers, are identified.

A 4.3 Mon 11:30 F 102

Ultraschnelle Relaxationsdynamik von SiO₂ Nanopartikeln nach Anregung im Vakuum-UV Bereich — ●CHRISTOPHER RASCHPICHLER, INA HALFPAP, HOLGER BAHRO, ALAN DORSSEERS, VALERIE MONDES, BURKHARD LANGER, JÜRGEN PLENGE and ECKART RÜHL — Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin

Es werden Experimente vorgestellt, in denen die Ionisations- und Relaxationsdynamik von isolierten, gröÙenselektierten SiO₂ Nanopartikeln ($d = 92 \pm 9$ nm) nach Anregung im Vakuum-UV Bereich mit Hilfe der zeitaufgelösten Photoelektronenspektroskopie untersucht wurden. Dabei erfolgte die primäre Anregung der freien Nanopartikel durch die 5. Harmonische eines Titan-Saphir Lasersystems bei 7,70 eV, so dass Zustände unterhalb der Leitungsbandkante von amorphem SiO₂ angeregt werden konnten. Nachfolgend führte die Mehrphotonen-Anregung durch einen zeitverzögerten Laserpuls ($\lambda = 805$ nm) zur Photoemission. Zeitaufgelöste Photoelektronenausbeutekurven spiegeln die Relaxationsdynamik der primär angeregten Nanopartikel wider, wobei

eine Lebensdauer von 120 ± 40 fs beobachtet wird. Die experimentellen Ergebnisse werden im Zusammenhang mit der nichtstrahlenden Relaxation von Defektzuständen von amorphem SiO₂ diskutiert und können zu einem verbesserten Verständnis der Ladungsträgerdynamik in dielektrischen nanoskopischen Materialien beitragen.

A 4.4 Mon 11:45 F 102

Electronic structure of diamondoid aggregates — ●TOBIAS ZIMMERMANN¹, ROBERT RICHTER¹, TORBJÖRN RANDER¹, ANDREY A. FOKIN², TETYANA V. KOSO², LESYA V. CHERNISH², PAVEL A. GUNCHENKO², PETER SCHREINER², and THOMAS MÖLLER¹ — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany — ²Institut für Organische Chemie, Justus-Liebig Universität Gießen, Germany

We investigate the electronic structure of diamondoid aggregates in the gas phase with valence photoelectron spectroscopy. The samples are aggregates of the lower diamondoids adamantane, diamantane and triamantane. The diamondoid constituents are connected with CC-single- or double-bonds. The investigations show an influence on the electronic structure of the samples by the bond type as well as the combination of the bonding partners. For singly bound aggregates only a small impact of the bond type on the electronic structure is observed. In fact a superposition of the bonding partner orbitals describes the aggregate orbitals well. The strength of quantum confinement effects is shown to depend on the bonding partner orbital energy difference. The spectra of doubly bound aggregates show significantly lower influence of the bonding partner sizes instead. Rather the HOMO can be ascribed to the CC-double-bond. Density functional theory supports our interpretations.

A 4.5 Mon 12:00 F 102

Coordination-driven magnetic-to-nonmagnetic transition in manganese doped silicon clusters — VICENTE ZAMUDIO-BAYER^{1,2}, LINN LEPPERT³, KONSTANTIN HIRSCH^{1,2}, ANDREAS LANGENBERG^{1,2}, JOCHEN RITTMANN^{1,2}, MARTIN KOSSICK^{1,2}, ROBERT RICHTER², AKIRA TERASAKI^{4,5}, THOMAS MÖLLER², BERND VON ISSENDORFF⁶, STEFAN KÜMMEL³, and ●TOBIAS LAU¹ — ¹Institut für Methoden und Instrumentierung der Forschung mit Synchrotronstrahlung, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin — ²Institut für Optik und Atomare Physik, Technische Universität Berlin, 10623 Berlin — ³Theoretische Physik IV, Universität Bayreuth, 95440 Bayreuth — ⁴Cluster Research Laboratory, Toyota Technological Institute, Chiba, Japan — ⁵Department of Chemistry, Kyushu University, Fukuoka, Japan — ⁶Fakultät für Physik, Universität Freiburg, 79104 Freiburg

X-ray Magnetic Circular Dichroism (XMCD) spectroscopy allows to obtain fundamental insight into magnetic properties of free, size-selected clusters. Using a combination of XMCD and non-empirical density functional theory, we demonstrate that the magnetic moment of MnSi_n⁺ is completely quenched as soon as a cluster size of $n = 10$ is exceeded. This is the result of a structural transition with an abrupt increase of the impurity coordination, which takes place between MnSi₁₀⁺ and MnSi₁₁⁺ and is accompanied by marked changes in the local electronic structure of the manganese impurity.

A 4.6 Mon 12:15 F 102

Infrared photo dissociation spectroscopy of perhalogenated closo-dodecaborate clusters [B₁₂X₁₂]²⁻ (X=Br, I) — MATIAS R. FAGIANI¹, ●TIM ESSER¹, JONAS WARNEKE², NADJA HEINE¹, and KNUT R. ASMIS¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ²Institute for Applied and Physical Chemistry, University of Bremen, Leobener Strasse, NW2, 28359 Bremen, Germany

Closo-dodecaborates are important materials and subject to recent research on ionic liquids, lithium ion batteries and stabilization of reactive cations. Recent collision-induced dissociation studies by Warneke et al. showed complex fragmentation patterns for the perhalogenated dianions [B₁₂X₁₂]²⁻ (X=F, Cl, Br, I). The brominated cluster [B₁₂Br₁₂]²⁻ showed a higher tendency to fragment under loss of an X⁻ anion than the iodinated cluster [B₁₂I₁₂]²⁻ which is more likely to lose a X[•] radical. In order to characterize the structure of these ions we performed infrared photodissociation (IRPD) experi-

ments. To this end, dianions are produced by ion spray, mass-selected by a quadrupole mass filter and accumulated in a cryogenically cooled ion trap which is filled with a buffer gas. The ion trap serves for accumulation, thermalization and messenger tagging of the ions. After extraction from the ion trap the ion/messenger clusters are exposed to IR radiation. IRPD spectra of $[\text{B}_{12}\text{Br}_{12}]^{2-}$ and $[\text{B}_{12}\text{I}_{12}]^{2-}$, measured in the range from 700 to 1500 cm^{-1} , are presented and assigned on the basis of electronic structure calculations.

A 4.7 Mon 12:30 F 102

Extreme ultraviolet fluorescence spectroscopy of pure and core-shell rare gas clusters at FLASH — •LASSE SCHROEDTER¹, ANDREAS KICKERMANN¹, ANDREAS PRYZSTAWIK¹, MARCUS ADOLPH², MARIA KRIKUNOVA², MARIA MÜLLER², TIM OELZE², DANIELA RUPP², CHRISTOPH BOSTEDT³, THOMAS MÖLLER², and TIM LAARMANN¹ — ¹Deutsches Elektronen-Synchrotron, DESY Photon Science, Hamburg, Germany — ²Institut für Optik und Atom-

are Physik, Technische Universität Berlin, Germany — ³SLAC National Accelerator Laboratory, Linac Coherent Light Source, USA

Rare gas clusters exposed to strong laser fields at short wavelength have attracted considerable interest in the last decade. The most common way to study the interaction is by time-of-flight spectroscopy of the resulting charged particles [1]. However, recent imaging experiments give evidence that the measured mass spectra do not reflect the charge states that are initially formed [2]. We present experiments on pure and core-shell Xe and Ar clusters to analyze the initially produced charge states by their extreme ultraviolet fluorescence. The clusters were excited by strong free-electron laser pulses from FLASH at 13 nm. Characteristic fluorescence of multiply charged species reveals detailed information on energy deposition and redistribution as a function of cluster size and FEL intensity.

[1] M. Hoener et al., J. Phys. B: At. Mol. Opt. Phys. 41 (2008), 181001 [2] C. Bostedt et al., Phys. Rev. Lett. 108 (2012), 093401