

A 25: Clusters in Molecular Physics (with MO & MS)

Time: Wednesday 14:30–16:30

Location: PH/SR106

Invited Talk

A 25.1 Wed 14:30 PH/SR106

Vibrational Spectroscopy of Cluster Complexes with Free Electron Lasers: Surface Science en Miniature — ●ANDRÉ FIELICKE — Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany

Transition metal clusters are frequently used as model systems for low coordinated sites of extended surfaces and their study can provide valuable insights into the mechanisms of surface reactions. In many cases, however, there is still a lack of information on their structures and the relationship between structure and chemical behavior. Using vibrational spectroscopy of gas-phase clusters one can obtain information about the clusters' structure or the behavior of adsorbed species. The latter provides valuable insights into the binding geometry, the activation of bonds within the ligands or reactions occurring on the clusters' surface. Cluster size specific data can be obtained using infrared multiple photon dissociation spectroscopy. To cover the required spectral range from the far to the mid-IR our experiments make use of IR free electron lasers. The talk will discuss exemplary studies about reactions on platinum clusters [1] and the activation of molecular oxygen by small gold clusters [2].

[1] D.J. Harding, A. Fielicke, Chem. Eur. J. 20 (2014) 3258

[2] A.P. Woodham, A. Fielicke, Struct. Bond. 161 (2014) 243

A 25.2 Wed 15:00 PH/SR106

Vibrational spectra and structures of C, B, and N-doped silicon clusters — ●NGUYEN XUAN TRUONG, BERTRAM JAEGER, PHILIP JÄGER, MARCO SAVOCA, ANDRÉ FIELICKE, and OTTO DOPFER — IOAP, TU-Berlin, Germany

Doping Si clusters changes their physical and chemical properties in a way that might be promising for the miniaturization trend towards nanoelectronics. Here, we investigated Si clusters doped with C, B and N with resonant infrared-ultraviolet two-color ionization (IR-UV2CI) and global optimization coupled with electronic structure methods. Doped Si clusters are irradiated with tunable IR light from a Free Electron Laser before being ionized with UV photons from an F₂ laser. Resonant absorption of IR photons leads to an enhanced ionization efficiency for the neutral clusters and provides the size-specific IR-UV2CI spectra. Structural assignment of the clusters is achieved by comparing the experimental IR-UV2CI spectrum with the calculated linear absorption spectra of the most stable isomers. Low-energy isomers are found with the help of genetic and basin-hopping algorithms. For Si_mC_n (with $m + n = 6$), we observed the systematic transition from chain like geometries for C₆ to 3D structures for Si₆. We showed for the first row doped Si₆X (with X = Be, B, C, N, O) clusters that different structures, vibrational and electronic properties can be achieved depending on the nature of the dopant atom. All dopant atoms in Si₆X have a negative net charge suggesting that Si atoms act as electron donors within the clusters. Finally, vibrational spectra and structural assignments for B and N-doped Si clusters are discussed in detail.

A 25.3 Wed 15:15 PH/SR106

(N)IR spectroscopy on two- and three-centered isolated cationic cobalt-, nickel- and cobalt/nickel - ethanol clusters — ●MARKUS BECHERER¹, DANIEL BELLAIRE¹, WEI JIN², GEORGIOS LEFKIDIS², WOLFGANG HÜBNER², and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, Fachbereich Chemie, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern — ²TU Kaiserslautern, Fachbereich Physik, Erwin-Schrödinger-Straße 47, 67663 Kaiserslautern

Clusters containing transition metals and aliphatic ligands provide model systems regarding e.g. catalytical properties, magnetism, reactivity and structure. Thus, the successive variation of size and composition of the metal clusters can give a fundamental insight on possible cooperative effects. The investigated two- and three-centered pure and combined cationic cobalt, nickel clusters are produced by applying laser ablation to a rotating metal rod and by attaching the ethanol ligand in a supersonic beam. The frequencies and frequency shifts of OH and CH stretching vibrations (between different clusters) are probed by means of IR-photofragmentation spectroscopy. A structural assignment is performed by comparing the experimental data with calculated frequencies obtained from DFT calculations. In case of the isolated cationic (cobalt)₃(ethanol)₁ and (cobalt)₃(ethanol)₁(water)₁ clusters both IR and electronic spectra (in the NIR region) are investigated

through photodissociation spectroscopy. The experimentally observed spectra serve, among other aspects, as reference for theoretical calculations especially on the electronic transitions localized on the triangular Co trimer metal centre.

A 25.4 Wed 15:30 PH/SR106

First experiments with cooled clusters at the Cryogenic Trap for Fast ion beams — ●CHRISTIAN MEYER¹, KLAUS BLAUM¹, CHRISTIAN BREITENFELD^{1,2}, SEBASTIAN GEORGE¹, JUERGEN GOECK¹, JONAS KARTHEIN¹, THOMAS KOLLING³, JENNIFER MOHRBACH³, GEREON NIEDNER-SCHATTEBURG³, LUTZ SCHWEIKHARD², and ANDREAS WOLF¹ — ¹Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany — ²Institut für Physik, Ernst-Moritz-Arndt Universität, 17487 Greifswald, Germany — ³Fachbereich Chemie, TU Kaiserslautern, Germany

The Cryogenic Trap for Fast ion beams (CTF) is an electrostatic ion beam trap for the investigation of charged particles in the gas phase located at the "Max-Planck-Institut für Kernphysik" in Heidelberg. It is suited to study thermionic and laser-induced electron emission of anions with complex multi-body structure such as clusters and molecules. They can be stored up to several minutes due to the low restgas pressure of 10⁻¹³ mbar [1] in an ambient temperature down to 15 K. The experiments were so far hampered by the ion production in a sputter source leading to excited particles with high rovibrational states. In order to be able to investigate the ground state properties of such systems a new supersonic expansion source [2] has been implemented. A laser-induced plasma is expanded into vacuum by short pulses (50 μs) of a helium carrier gas and thereby rovibrationally cooled. First tests with metal cluster will be presented and discussed.

[1] M. Lange et al., Rev. Sci. Instr., 81,055105 (2010)

[2] C. Berg et al., J. Chem. Phys. 102, 4870 (1995)

A 25.5 Wed 15:45 PH/SR106

Optical spectra and structures of C, N, and O-doped silicon clusters — ●BERTRAM K.A. JAEGER, JANINA LEBENDIG, NGUYEN X. TRUONG, ANDRÉ FIELICKE, and OTTO DOPFER — IOAP, TU Berlin, Germany

Controlled changes in physical and chemical properties of doped Si clusters provide promising candidates of nanostructures for optoelectronics, sensors or medicine. We study Si clusters doped with C, N and O via their photodissociation spectra and compare them with theoretical quantum chemical calculations. Ionic clusters are produced in a laser vaporization source, then irradiated with tunable visible light from an OPO laser in the range from 410 to 580 nm and characterized by a reflectron time-of-flight mass spectrometer. Absorption of photons leads to dissociation of the clusters, which is detected in the mass spectrum. Calculated absorption spectra are compared to experimental data for assignment of geometries and electronic parameters of the observed clusters. The most stable and low-energy isomers are found with the help of genetic and basin-hopping algorithms. All results will be compared to existing studies about IR-UV two color ionization of neutral and doped Si clusters.

Pristine and tagged Au clusters show absorption bands in the visible range and are used as a test system to verify the experimental principle.

A 25.6 Wed 16:00 PH/SR106

Angular distribution of electron and photon emission from isolated SiO₂ nanoparticles excited by femtosecond laser pulses — ●EGILL ANTONSSON, INA HALFPAP, CHRISTOPHER RASCHPICHLER, VALERIE MONDES, JÜRGEN PLENGE, BURKHARD LANGER, and ECKART RÜHL — Physical Chemistry, Freie Universität Berlin, Takustr. 3, 14195 Berlin

We excite isolated spherical SiO₂ nanoparticles (diameter: 90 nm, size distribution: 8%) with intense femtosecond laser pulses ($\lambda=800$ nm, $\tau=80$ fs, Intensity: 1-3·10¹³ W/cm²) and study the angular distribution of emitted electrons and UV photons ($h\nu>8$ eV). The nanoparticles are prepared in an aerodynamically focused beam which propagates into a high vacuum system where excitation and photoionization occurs. This ensures that fresh sample is available to each laser pulse and rules out effects due to particle-particle interactions, sample charg-

ing, and radiation damage. For electron emission, a distinct angular dependence with respect to the polarization vector of the laser pulses is observed, which varies for different photoelectron energies. High-energy photoelectrons are found to be emitted preferentially parallel to the polarization vector of the exciting laser photons, which is discussed in terms of an elastic scattering of continuum electrons at or near the surface of the nanoparticles. For low-energy photoelectrons, on the other hand, the angular dependence is quenched due to multiple inelastic scattering events of the photoelectrons in the nanoparticles which smears out angular effects.

A 25.7 Wed 16:15 PH/SR106

Vibrationally resolved UV fluorescence of diamondoids —

•TORBJÖRN RÄNDER¹, ROBERT RICHTER¹, TOBIAS ZIMMERMANN¹, ANDRE KNECHT¹, ANDREA MERLI¹, CHRISTOPH HEIDRICH¹, RAMON RAHNER¹, THOMAS MÖLLER¹, MERLE I. S. RÖHR², JENS PETERSEN², ROLAND MITRIC², JEREMY E. DAHL³, and ROBERT M. K. CARLSON³ — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin, Berlin, Deutschland — ²Institut für Physikalische und The-

oretische Chemie, Universität Würzburg, Würzburg, Deutschland — ³Stanford Institute of Materials and Energy Sciences, Stanford University

Diamondoids are a class of perfectly size- and shape selectable carbon nanoparticles, with a wide range of interesting properties. Due to the size-selectivity afforded by the diamondoids, they are ideal model systems for studying the photo-physics of hydrocarbon molecules of different sizes. We present a study of the size- and shape dependent energy resolved UV fluorescence of diamondoids, ranging from adamantane to pentamantane, using narrow band laser light as excitation source.

We conclude that previous, relatively straightforward interpretations of the fluorescence spectra recorded using synchrotron light are incomplete, and that the additional fine-structure observed in the laser excited spectra can only be properly assigned by performing computations, in our case DFT and TD-DFT was deemed sufficient to accurately describe and understand the spectral envelopes of the different sized diamondoids. The approach employed is thought to generally be applicable also for other hydrocarbon molecules.