

A 6: Clusters (with MO)

Time: Monday 10:30–12:30

Location: BEBEL SR144

A 6.1 Mon 10:30 BEBEL SR144

Infrared spectroscopy of doped silicon clusters — ●NGUYEN XUAN TRUONG, MARCO SAVOCA, ANDRÉ FIELICKE, and OTTO DOPFER — Institut für Optik und Atomare Physik, TU Berlin, Germany

Doped Si clusters are investigated with resonant infrared-ultraviolet two-color ionization (IR-UV2CI) combined with global optimization and DFT calculations. Neutral Si_mX_n clusters are irradiated with tunable IR light from a free electron laser before being ionized with UV photons from an F_2 laser. Resonant absorption of IR photons leads to an enhanced ionization efficiency for the neutral clusters and provides the size-specific IR spectra. Structural assignment of the clusters is achieved by comparing the calculated linear absorption spectra of the most stable isomers with experimental data. For Si_mC_n (with $m+n=6$), we found the systematic transition from chain like geometries for C_6 to 3D structures for Si_6 [1]. For further first row doped Si_6X (with $\text{X} = \text{Be}, \text{B}, \text{C}, \text{N}, \text{O}$) clusters, additional properties have been calculated, such as binding and ionization energies, and natural bond orbitals. All X dopant atoms in Si_6X have a negative net charge suggesting that Si atoms act as electron donors within the clusters. Moreover, the overall structures of Si_6X strongly depend on the nature of the dopant atom (size and valency). While for some of the most stable Si_6X clusters one Si atom in the original Si_7 structure is simply substituted ($\text{X} = \text{Be}, \text{B}, \text{C}$), other cases exhibit a completely different geometry ($\text{X} = \text{N}, \text{O}$).

[1] M. Savoca, A. Lagutschenkov, J. Langer, Dan J. Harding, A. Fielicke, O. Dopfer, *J. Chem. Phys. A* **117**, 1158 (2013).

A 6.2 Mon 10:45 BEBEL SR144

Vibrational Spectra and Structures of Silicon Hydride Cluster Cation — ●MARTIN ANDREAS ROBERT GEORGE, MARCO SAVOCA, JUDITH LANGER und OTTO DOPFER — IOAP TU Berlin, Germany

Silanes and their derivatives and ions are fundamental species in a variety of chemical disciplines. IR spectra of silicon hydride cluster cations Si_xH_y^+ produced in a supersonic plasma molecular beam expansion of SiH_4 , He, and Ar are inferred from photodissociation of cold Si_xH_y^+ -Ar/Ne complexes obtained in a tandem quadrupole mass spectrometer coupled to an electron impact ionization source and an octopole ion trap. In addition, the clusters are characterized in their ground electronic states by quantum chemical calculations to investigate the effects of ionization and Ar/Ne complexation on their geometric, vibrational, and electronic structure. We present initial results for Si_2H_6^+ [1], Si_2H_7^+ [2] and Si_3H_8^+ [3], which have complex potential energy surfaces, with low-energy isomers featuring unusual three-center two-electron (3c-2e) bonding. The IR spectrum of disilanium, Si_2H_7^+ , a fully H-passivated Si_2 core with a Si-H-Si bridge is described by a 3c-2e bond. The excess proton in the Si-H-Si bridge generates three additional fundamentals, which provide the fingerprint of the 3c-2e bond.

[1] M. Savoca, M.A.R. George, J. Langer and O. Dopfer, *Phys. Chem. Chem. Phys.* **15**, 2774-2781 (2013) [2] M. Savoca, J. Langer and O. Dopfer, *Angewandte Chemie* **125**, 1376 (2013) [3] M.A.R. George, M. Savoca, O. Dopfer, *Chem. Eur. J.* **19** 45 (2013)

A 6.3 Mon 11:00 BEBEL SR144

Measuring the efficiency of ICD in neon- and in water clusters — ●MARKO FÖRSTEL¹, TIBERIU ARION², LASSE HARBO³, CHAO FAN ZHANG⁴, and UWE HERGENHAHN¹ — ¹Max-Planck-Institute for Plasmaphysics, Greifswald, 17491, Germany — ²University of Hamburg, CFEL, Luruper Chaussee 149, 22761 Hamburg, Germany — ³Dept. of Physics and Astronomy, Aarhus University, Aarhus, 8000, Denmark — ⁴Dept. of Physics and Astronomy, Uppsala University, Uppsala, 75121, Sweden

In our contribution we focus on the measurement of the efficiency of intermolecular coulombic decay (ICD) in neon clusters and in water clusters.

Quite uniquely, our setup allows the quantitative determination of the efficiency of ICD relative to other competing channels. We introduce this technique and discuss the ICD efficiency after inner valence ionization in neon clusters, in water clusters and in clusters of heavy water.

By comparing the ICD efficiency in water and heavy water we can estimate the influence of the dynamics of the two systems on the ICD efficiency. Using these results we can obtain limits on the decay rate

of ICD in large systems, i.e. water clusters with a mean size of $N = <60>$.

A 6.4 Mon 11:15 BEBEL SR144

Microsolvation of the Formanilide Cation (FA^+) in a Non-polar Solvent: Infrared Spectra of $\text{FA}^+\text{-L}_n$ clusters ($\text{L}=\text{Ar}, \text{N}_2$) — ●JOHANNA KLYNE¹, AUDE BOUCHET¹, MATTHIAS SCHMIES¹, MITSUHIKO MIYAZAKI², MASAOKI FUJII², and OTTO DOPFER¹ — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin — ²Chemical Resources Laboratory, Tokyo Institute of Technology, Japan

The peptide linkage is an essential component in biochemical recognition processes since its geometry, depending on its local environment, defines the conformation of proteins. Elucidating the sequential microsolvation of peptides is therefore crucial for a full description of their behaviour in biological media. The stepwise microsolvation of cationic formanilide ($\text{FA}^+\text{-L}_n$) is characterized by IR spectroscopy of size-selected clusters generated in a molecular beam, combined with density functional calculations. Formanilide is the simplest aromatic molecule containing a peptide linkage ($-\text{NH}-\text{CO}-$). The observation of size- and isomer-specific NH stretch frequencies reveals the microsolvation of FA^+ in a nonpolar ($\text{L}=\text{Ar}$) and a quadrupolar ($\text{L}=\text{N}_2$) solvent. Such aromatic amides exhibit at least two competing binding sites for nucleophilic ligands, namely H-bonding to the acidic N-H group of the amide and π -stacking to the phenyl ring. The H-bound $\text{FA}^+\text{-L}$ dimer with L binding to the NH proton of the amide is the most stable isomer. Subsequent ligands are weaker bound to the aromatic ring (π -stacking). These results demonstrate an ionization-induced change of the preferred binding motif from π -stacking to H-bonding.

A 6.5 Mon 11:30 BEBEL SR144

CO binding to small transition metal alloy clusters — DAVID YUBERO VALDIVIELSO¹, WIELAND SCHÖLLKOPF², and ●ANDRÉ FIELICKE¹ — ¹Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

We report on first experiments performed with the new infrared Free Electron Laser at the Fritz-Haber Institute in Berlin. The intense and widely tunable (so far 400–2300 cm^{-1}) IR radiation from the FEL is used to obtain cluster size and composition selective IR spectra of CO complexes of metal alloy clusters via IR multiple photon dissociation. Investigating the binding of carbon monoxide to metal sites via vibrational spectroscopy is frequently used to characterize their electronic and structural properties. The activation of the C-O bond that is probed via the C-O stretching frequency highly depends on the nature of the metal, leading to a transition from molecular to dissociative chemisorption for the earlier transition metals. This is usually related to the rise of the d band center towards the earlier transition metals that allows for a stronger interaction with the CO's $2\pi^*$ orbitals. For pure clusters of many transition metals the binding of CO and the influence of cluster size and charge is well studied. We here aim to obtain an understanding of the effects of alloying on the CO activation, using it as a gauge for the change in the electronic structure in terms of the d band level. Results are presented for small alloy clusters composed from Co and Mn atoms.

A 6.6 Mon 11:45 BEBEL SR144

Gas Phase Vibrational spectroscopy of Messenger-tagged Aluminum Oxide Clusters Anions — ●MATIAS R. FAGIANI¹, XIAOWEI SONG¹, WIELAND SCHÖLLKOPF¹, SANDY GEWINNER¹, FLORIAN A. BISCHOFF², JOACHIM SAUER², and KNUT R. ASMIS^{1,3} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ²Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, D-12489 Berlin, Germany — ³Lehrstuhlvertretung am Wilhelm-Ostwald-Institut, Universität Leipzig, Linnéstr. 2, D-04103 Leipzig, Germany

Alumina structures of reduced dimensionality are of interest in astrophysics and atmospheric chemistry, as well as in nanostructured ceramic materials and solid catalysts. Little is known, experimentally, concerning the geometric structure of such clusters. Vibrational spectroscopy combined with electronic structure calculations provides more detailed insight into the geometric and electronic structure of

these clusters.

Here, we present infrared photodissociation (IRPD) spectra of aluminum oxide cluster anions, focusing mainly on the fully-oxidized, electronic closed-shell clusters. The cluster anions are formed in a sputtering source. Mass-selected anions are trapped, cooled to cryogenic temperatures and messenger-tagged (D_2) in a buffer gas filled ion trap. Photodissociation spectra are measured from 400 to 1200 cm^{-1} with the widely tunable IR radiation of the free electron laser FHI FEL. The spectra are assigned and cluster structures are determined by comparison with the results of density functional calculations.

A 6.7 Mon 12:00 BEBEL SR144

Optical Properties of Supported Size Selected Ag Clusters in the Small Size Limit studied by SHG spectroscopy — PHILIPP HEISTER, •TOBIAS LÜNSKENS, ARAS KARTOUZIAN, MARTIN TSCHURL, and UELI HEIZ — Chair of Physical Chemistry, Department of Chemistry and Catalysis Research Center, Technische Universität München, Lichtenbergstraße 4, 85748 Garching, Germany

The optical properties of noble metal nanoparticles have received considerable interest in the past decades due to their Localized Surface Plasmon Resonance (LSPR). These collective oscillations of conduction band electrons can be described classically by extensions of Mie theory for particle diameters down to 2 nm. For particles consisting of only a few atoms, this classical description does not hold true anymore. Only a few experimental investigations of this small size limit are reported so far. In those studies the optical properties of metal clusters in the gas phase and metal clusters embedded in rare gas matrices were investigated.

We present Second Harmonic Generation spectra of mono-dispersed silver clusters (Ag_n, n<55). These clusters were generated by a laser vaporization source, size selected by a Q-MS and soft-landed onto a

SiO₂ target. Spectra of individual sizes were recorded under UHV conditions. The spectra reveal a clear size dependency, which is discussed by comparison with literature.

A 6.8 Mon 12:15 BEBEL SR144

Surface Scattering of (CO₂)_n off Si(111)/SiO₂ — BO-GAUN CHEN and •WOLFGANG CHRISTEN — Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, <http://clusterlab.de>

Employing a pulsed high-pressure supersonic jet expansion and a dedicated setup for the experimental investigation of chemical processes occurring between neutral, van der Waals bound clusters and a solid surface¹, we report on the angular distribution of large CO₂ clusters scattered off a Si(111)/SiO₂ surface under ultrahigh vacuum conditions. Scattered particles are detected using time resolved mass spectrometry. A translator stage provides the possibility to sample both the incoming beam (target surface retracted) and to determine the angular and velocity distribution of scattered particles. Angular information is obtained by rotating the target surface, the velocity of scattered particles is determined by changing the distance between surface and mass spectrometer.

The presented studies cover a very broad range of cluster sizes, n , $5 \cdot 10^3 < n < 2 \cdot 10^5$ molecules per particle, and focus on the influence of source entropy, realized by accurately setting stagnation pressure and temperature. We observe an interesting dependence of the angular distribution of scattered CO₂ monomers on source conditions, i.e. the scattering angle seems to reflect the expansion path, allowing to distinguish between cluster condensation via expansion on the gaseous or on the liquid side of the critical point, and an intermediate regime where the expansion passes the metastable gas-liquid region.

¹ W. Christen, K. Rademann, *Rev. Sci. Instrum.* **77**, 015109 (2006).