

## MO 18: Cluster I

Time: Thursday 10:30–12:30

Location: F 102

MO 18.1 Th 10:30 F 102

**Bildung von Anionen in innerschalenangeregten Schwefelhexafluorid-Clustern** — ●ROMAN FLESCHE, ERTUGRUL SERDAROGLU und ECKART RÜHL — Physikalische Chemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin.

Zu den Relaxationskanälen innerschalenangeregter Moleküle, die starke lokale Dipolmomente aufweisen, gehören Ladungstrennungsprozesse unter simultaner Bildung von Anionen und Kationen. Dies wurde für einige Moleküle im Bereich der Valenzelektronenanregung wie der Innerschalenanregung gezeigt. Bisher liegen aber keine Untersuchungen zu entsprechenden Ladungstrennungsprozessen in molekularen Clustern vor. Es werden Resultate massenspektrometrischer Experimente zur gleichzeitigen Bildung von Anionen und Kationen an Schwefelhexafluoridclustern  $(\text{SF}_6)_n$  vorgestellt. Neben der Valenzelektronenanregung wird insbesondere die lokale Anregung des Schwefels bzw. des Fluors durch Innerschalenenergie (S 2p-Anregung, F 1s-Anregung) in  $\text{SF}_6$ -Clustern untersucht.

In  $\text{SF}_6$ -Clustern wird, wie im isolierten Molekül, die Bildung der Anionen  $\text{F}^-$ ,  $\text{S}^-$ ,  $\text{F}_2^-$  und  $\text{SF}^-$  gefunden. Zusätzlich werden aber aus Clustern intensive Anionen-Signale beobachtet, die dem  $\text{SF}_5^-$  zugeordnet werden. Die Abhängigkeit dieses clusterspezifischen Anionsignals von der Photonenenergie zeigt, dass Bildung von  $\text{SF}_5^-$  von der resonanten Photoionisation und Autoionisation abhängt, wobei langsame Elektronen im Cluster gebildet werden. Daher wird  $\text{SF}_5^-$  vorwiegend im Bereich von Innerschalen-Ionisationsschwellen und autoionisierenden Zuständen im Bereich der Absorptionskanten gebildet.

MO 18.2 Th 10:45 F 102

**Superhalogenic  $\text{Au}_n(\text{BO}_2)$ -based clusters: Simulation and Experiment** — ●SUSANNE S. PFEIFER<sup>1</sup>, MATTHIAS GÖTZ<sup>1</sup>, GERD F. GANTEFÖR<sup>1</sup>, and PURU JENA<sup>2</sup> — <sup>1</sup>Department of Physics, University of Konstanz, 78457 Konstanz, Germany — <sup>2</sup>Department of Physics, Virginia Commonwealth University, Richmond, USA

Superhalogens, such as  $\text{BO}_3$ , are characterised by larger electron affinities (EA) than any halogen atom. Recently they attracted considerable interest in the cluster community. Due to the ionic character of the bond among superhalogens and metallic clusters, it is possible to design a novel type of cluster-based salt, where the agglomeration of clusters is prevented by electrostatic repulsion. Hence superhalogenic clusters may lead to the synthesis of new materials with unique electronic and magnetic properties, which are tuneable by the clusters.

Herein, we study gas phase  $\text{Au}_n(\text{BO}_2)$  cluster anions using photoelectron spectroscopy and compare the experimental data to the results of DFT calculations. Surprisingly, the geometric structure and certain electronic properties of the gold clusters within  $\text{Au}_n(\text{BO}_2)$ -species are comparable to pure gold clusters, i. e. an inverse even-odd-alternation of the EA is observed also for  $\text{Au}_n(\text{BO}_2)$  clusters. This finding supports the idea of using superhalogens to stabilise metal clusters to create new bulk solids. Moreover, the EA can be increased further by modifying the  $\text{Au}_n(\text{BO}_2)$  cluster, e. g. with additional O or  $\text{BO}_2$ . Hence, the electronic properties can be adjusted.

MO 18.3 Th 11:00 F 102

**Mass-resolved velocity distributions of supersonic jets from supercritical carbon dioxide** — ●WOLFGANG CHRISTEN, TIM KRAUSE, and KLAUS RADEMANN — Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, 12489 Berlin

Supersonic molecular beams continue to constitute a versatile and popular tool in science and technology. For instance, jet expansions from dense gases are routinely used to grow clusters and nanoparticles<sup>1–3</sup>. Surprisingly, the fundamental aspects of high pressure jet expansions have not been studied in much detail, and little is known on condensation processes close to the critical point. Attempting to improve this situation and advance the comprehension of supersonic jet expansions from supercritical fluids<sup>4,5</sup> we have investigated pulsed, supersonic beams of pure  $\text{CO}_2$  at source conditions up to and beyond the critical point (7.38 MPa, 304.13 K). Employing mass-resolved time-of-flight measurements, cluster intensities and terminal flow velocities are reported as a function of stagnation pressure (0.5 – 11 MPa) and temperature (300 – 355 K). The experimental results are compared with model predictions of a real fluid treatment of the jet expansion. These calculations<sup>6</sup> provide a consistent physical picture of the supersonic jet

expansion of supercritical fluids and permit valuable insights into the nonequilibrium processes at high supersaturations.

<sup>1</sup> *J. Am. Chem. Soc.* **108**, 2100, 1986. <sup>2</sup> *Rev. Sci. Instrum.* **75**, 5048, 2004. <sup>3</sup> *J. Phys. Chem. C* **112**, 17102, 2008. <sup>4</sup> *J. Chem. Phys.* **125**, 174307, 2006. <sup>5</sup> *J. Chem. Phys.* **113**, 388, 2009. <sup>6</sup> *Phys. Scr.* **80**, 048127, 2009.

MO 18.4 Th 11:15 F 102

**Understanding the velocity bifurcation in supersonic jet expansions** — ●WOLFGANG CHRISTEN<sup>1</sup>, KLAUS RADEMANN<sup>1</sup>, and UZI EVEN<sup>2</sup> — <sup>1</sup>Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, 12489 Berlin, Germany — <sup>2</sup>Sackler School of Chemistry, Tel Aviv University, 69978 Tel Aviv, Israel

The comprehension of homogenous nucleation processes is of fundamental relevance for many research fields, including atmospheric chemistry and materials science. Supersonic beams provide the possibility to address this topic under very well defined experimental conditions, even at very high degrees of supersaturation. At higher densities of the working fluid, the velocity distribution of the generated jet is severely affected by cluster formation, eventually giving rise to several peaks<sup>1–6</sup>. So far, however, these observations were phenomenological in nature, with no quantitative explanation possible. Attempting to improve this situation and advance the comprehension of supersonic jet expansions at high source densities we have studied the transition to a second peak in the velocity distributions of free-jet expansions from supercritical fluids using mass-resolved time-of-flight measurements. These experiments are complemented by a thermodynamic description of the isentropic expansion process, considering the initial and final fluid enthalpies. For the first time this model permits a quantitative prediction of the velocity bifurcation.

<sup>1</sup> *J. Chem. Phys.* **92**, 6875, 1990. <sup>2</sup> *Phys. Rev. Lett.* **64**, 1899, 1990. <sup>3</sup> *J. Chem. Phys.* **102**, 6258, 1995. <sup>4</sup> *ibidem* **106**, 3348, 1997. <sup>5</sup> *ibidem* **125**, 174307, 2006. <sup>6</sup> *J. Phys. Chem. A* **113**, 388, 2009.

MO 18.5 Th 11:30 F 102

**Spectroscopy of PTCDA molecules attached to Ar-, Ne- and hydrogen-clusters formed inside helium nanodroplets** — ●MARKUS MÜLLER, MATTHIEU DVORAK, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Helium Nanodroplet Isolation (HENDI) spectroscopy has become a well established method for studying atoms, molecules and their complexes. The appealing physical properties of helium droplets such as their low temperature (380mK), the weak interactions with atoms and molecules, and the superfluid property make them a favorite matrix for spectroscopy.

In order to study the phase and structure of argon, hydrogen and neon clusters formed inside helium droplets, we dope them with organic molecules (PTCDA) and probe the vibronic spectrum by means of laser induced fluorescence (LIF). The width and shift as well as the line shape of the transitions observed for different sizes give us information about the interaction between the molecule and the cluster environment. By varying the cluster sizes up to some hundreds of atoms and reversing the droplet doping order, the changes in the LIF spectra can be correlated to structural modifications and phase transitions of the clusters.

MO 18.6 Th 11:45 F 102

**Cluster-induced desorption as a versatile tool for surface and interface characterization** — B.-J. LEE<sup>1</sup>, C.R. GEBHARDT<sup>2</sup>, H. SCHRÖDER<sup>3</sup>, K.L. KOMPA<sup>3</sup>, and ●M. DÜRR<sup>1</sup> — <sup>1</sup>Fakultät Angewandte Naturwissenschaften, Hochschule Esslingen, Esslingen — <sup>2</sup>Brüker Daltonik GmbH, Bremen — <sup>3</sup>Max-Planck-Institut für Quantenoptik, Garching

Cluster-induced desorption using neutral molecular  $\text{SO}_2$  clusters was employed for the investigation of alkali halides adsorbed on metals and insulators. The influence of substrate and adsorbate configuration, especially of the hydration of the respective ions on the surface, was studied. As long as the anions are efficiently screened by a hydration shell, they are effectively desorbed by means of cluster impact. To higher surface temperatures, the hydration shell is lost and a strong adsorbate-surface bond prevents efficient desorption of the

anions. Cations are seen to be desorbed from metals via a neutral desorption channel with subsequent charge separation in the cluster whereas only a positive signal is observed for desorption from insulators. The experiments demonstrate the possibility of cluster-induced desorption to monitor surface configurations which are not accessible by means of conventional heating, similar to the case of cluster-induced fragmentation-free desorption of biomolecules [1].

[1] Gebhardt *et al.*, *Angew. Chem. Int. Ed.* **48**, 4162 (2009).

MO 18.7 Th 12:00 F 102

**Ultrafast dynamics of the first electronically excited state of neutral water clusters** — •JAN P. MÜLLER, HONGTAO LIU, MARCUS BEUTLER, MASOOD GHOTBI, FRANK NOACK, WOLFGANG RADLOFF, NICKOLAI ZHAVORONKOV, C. P. SCHULZ, and INGOLF V. HERTEL — Max-Born-Institute, Max-Born-Str. 2a, 12489 Berlin

Although water is one of the most familiar substances in our life, the spectroscopic and dynamical properties of the electronically excited states of water clusters are still not well known. A great challenge for experiments is creation ultrashort VUV laser pulses, needed to study the ultrafast dynamics, at sufficient energies for coping with the low densities of typical molecular beams. Recently we succeeded to create 45 fs VUV laser pulses having energies up to 300 nJ at a wavelength of 159 nm (5<sup>th</sup> harmonic of Ti:Sapphire), formed by four wave difference frequency mixing in a gas cell filled with argon. By this means it was possible to study the time resolved dynamics of (H<sub>2</sub>O)<sub>n</sub> and (D<sub>2</sub>O)<sub>n</sub> clusters in the range n = 2–9 for the first time. The photoinduced dynamics of the  $\bar{A}$  state has been investigated by a pump probe scheme, using one VUV photon for excitation and 2–3 photons of 795 nm to ionize the clusters. Except for n = 1–2, only protonated clusters

H(H<sub>2</sub>O)<sub>n-1</sub><sup>+</sup> can be observed in the mass spectrum. For all clusters, decay lifetimes in the range of the 10-30 fs and 50-150 fs respectively have been identified. Additionally an ultrafast process is visible, agreeing well with time scale of 1.8-2.5 fs measured in the group of Fuß for the water monomer. This three decay times can be attributed to OH dissociation, internal conversion and H-ejection.

MO 18.8 Th 12:15 F 102

**Vibrationally mediated electron detachment from anionic clusters with an IR intra-cavity free electron laser** — •MARKO HAERTELT<sup>1</sup>, VIVIKE LAPOUTRE<sup>2</sup>, JOOST BAKKER<sup>2</sup>, ANDRÉ FIELICKE<sup>1</sup>, and GERARD MEIJER<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — <sup>2</sup>FOM Institute for Plasma Physics Rijnhuizen, Nieuwegein, The Netherlands

For anionic clusters photoelectron spectroscopy (PES) is up to now the most generally applied technique to probe their structure. Despite the progress in high resolution PES, e. g. via slow electron photoelectron imaging, only for a few systems vibrational resolution has been obtained. The high IR intensity provided by the new Free Electron Laser for IntraCavity Experiments, FELICE, offers the opportunity for obtaining vibrational spectra of anions via multiple photon electron detachment (MPED). For many anionic transition metal clusters the electron affinity is lower than the bond dissociation energy. Resonant excitation of an infrared active vibrational mode leads via rapid vibrational redistribution to a thermal heating of the cluster and can be followed by electron detachment rather than a fragmentation process. Recently, in a proof-of-principle experiment, we have obtained the first far IR-MPED spectra of tantalum carbide cluster anions with FELICE.