# MO 14 Clusters of Atoms and Small Molecules

Zeit: Freitag 16:30–18:30 Raum: HU 2091

## Hauptvortrag

MO 14.1 Fr 16:30 HU 2091

**The geometric and electronic structure of simple metal clusters** — •Bernd v.Issendorff — Department of Physics, University of Freiburg, 79104 Freiburg, Germany

Photoelectron spectroscopy on free, cold, size-selected clusters is an ideal tool to study the electronic structure of these particles. Clusters of simple metals like alkali or noble metals exhibit a strongly discretized electron density of states, the so-called electron shell structure, which can be seen as the eigenstates of free electrons in a spherical well. Closer examination reveals that the shells are subject to relatively strong crystal field splitting effects; this allows one to extract information about the particle geometrical structure from the spectra. Icosahedral symmetry prevails in the size range of 50-500 atoms, but decahedral structures are observed as well.

MO 14.2 Fr 17:00 HU 2091

**THE STRUCTURE OF ISOLATED TeSe FROM ROTATIONAL INVESTIGATIONS: SPECTROSCOPIC ANALYSIS, POTENTIAL PARAMETERS, AND HYPERFINE INTERACTION** — •Jens-Uwe Grabow[1], Deike Banser[1], Melanie Schnell[1], Emilio J. Cocinero[2], Alberto Lesarri[2], and Jose L. Alonso[2] — [1]Institut für Physikalische Chemie und Elektrochemie, Universität Hannover, D-30167 Hannover — [2]Departamento de Quimica Fisica, Facultad de Ciencias, Universidad de Valladolid, Prado de la Magdalena, s/n, E-47071 Valladolid

Laser ablated tellurium selenide clusters were isolated in pulsed rare gas supersonic expansions. With the production conditions monitored and optimized by the aid of time-of-flight (TOF) mass spectrometry, surprisingly strong pure rotational transitions originating from energy levels up to J = 6 were found in the frequency range from 3.6 to 26.4 GHz.

As the first intermetallic group VI compound investigated microwave spectroscopically we were able to identify the electronic ground state and the first six vibrationally excited state rotational spectra of 43 isotopomers of the tellurium selenide diatomic in natural abundance by Fourier transform microwave (FT-MW) spectroscopy.

The dataset was analysed using a multi-isotopomer fit to a Dunham-type expression which includes terms that allow for Born-Oppenheimer breakdown corrections. The transitions of 16 isotopomers, either containing $^{125}Te$ or $^{123}Te$ and/or $^{77}Se$ showed splittings due to spin-rotation coupling.

MO 14.3 Fr 17:15 HU 2091

**Size-dependent study of hot electron relaxation dynamics in tungsten cluster anions** — •Jörg Stanzel, Florian Burmeister, Matthias Neeb, and Wolfgang Eberhardt — BESSY GmbH, Albert-Einstein-Str. 15, 12489 Berlin

Electron dynamics in metal clusters are influenced by individual properties like geometry and electronic structure. Therefore clusters comprised of a small number of atoms underlie a strong size dependence. To address this issue a number of pump & probe measurements have been reported so far, some concentrated on sizes of a few atoms [1], others on nanoparticles with sizes ranging from 2.2-30 nm [2].

Here we present a study of hot electron relaxation dynamics in small mass-selected tungsten cluster anions ($W_n^-$) in the gas phase. Relaxation time constants were obtained using femtosecond time-resolved pump & probe photodetachment spectroscopy.

[1] N. Pontius et al. Phys. Rev. Lett. **84**, 1132 (2000); N. Pontius et al., Phys. Rev. B **67**, 035425 (2003); YD. Kim et al., Phys. Rev. B **70**, 035421 (2004).
[2] A. Arbouet et al., Phys. Rev. Lett. **90**, 177401 (2003).

MO 14.4 Fr 17:30 HU 2091

**Zeitaufgelöste Photoelektronenspektroskopie an massenselektierten Clustern** — •Marco Niemietz, Markus Engelke, Peter Gerhardt, Felix von Gynz-Rekowski, Young Dok Kim und Gerd Ganteför — Fachbereich Physik, Universität Konstanz, D-78457 Konstanz

Die Strukturen und Eigenschaften kleinster Nanopartikel können sich dramatisch mit der Anzahl der Atome ändern. Kleine Metallcluster besitzen eine niedrigere Zustandsdichte als das zugehörige Festkörpermaterial. Entsprechend unterschiedlich sollte die Dynamik angeregter Elektronen sein. Für kleinste Goldcluster beispielsweise ergeben sich sehr lange Relaxationszeiten im Nanosekundenbereich [1].

Mittels Pump-Probe Photoelektronenspektroskopie an Clusteranionen können diese Relaxationszeiten größenabhängig untersucht werden [2,3]. Eine Serie von Spektren, aufgenommen für verschiedene Verzögerungen zwischen Pump- und Probe-Puls, zeigt die zeitliche Entwicklung des elektronischen Systems. Es werden Daten für Silbercluster diskutiert.

[1] M. Niemietz, P. Gerhardt, G. Ganteför and Y. D. Kim, Chem. Phys. Lett. **380**, 99 (2003)
[2] P. Gerhardt, M. Niemietz, Y. D. Kim, and G. Ganteför, Chem. Phys. Lett. **382**, 454 (2003)
[3] Y. D. Kim, M. Niemietz, P. Gerhardt, F. v. Gynz-Rekowski, and G. Ganteför, Phys. Rev. B **70**, 035421 (2004)

MO 14.5 Fr 17:45 HU 2091

**Auf der Suche nach inorganischen Fullerenen: magische MoS- und WS-Cluster** — •Nils Bertram[1], Young Dok Kim[1], Gerd Ganteför[1], Jelena Tamuliene [2], Gotthard Seifert[2], Qiang Sun[3] und Puru Jena[3] — [1]Fachbereich Physik, Universität Konstanz, D-78457 Konstanz. — [2]Institut für Physikalische Chemie und Elektrochemie, TU Dresden, D-01062 Dresden. — [3]Department of Physics, Virginia Commonwealth University, Richmond, USA.

Molybdänsulfid und Wolframsulfid sind als Festkörper dem Graphit sehr ähnlich. Wie beim Graphit, das unter bestimmten Bedingungen den bekannten Bucky Ball formt, können auch MoS und WS geeignete Materialien zur Erzeugung besonders stabiler Fullerene sein. Darüber hinaus wird theoretisch eine stabile zweidimensionale Plättchenstruktur postuliert.

Wir präsentieren neue massen- und photoelektronenspektroskopische Ergebnisse magischer MoS- und WS-Cluster. Z. B. weist $Mo_4S_6^-$ ein großes HOMO-LUMO-Gap von über 2 eV auf und ist somit ein sehr stabiler magischer Cluster [1]. Im Fall von MoS konnten Chevrelcluster auf der Basis des Grundbausteins $Mo_6S_8$ in der Gasphase erzeugt und mittels PES untersucht werden. Für größere Cluster, für die Fulleren- oder Plättchenstrukturen von der Theorie vorausgesagt sind, konnten Massen- und Photoelektronenspektren aufgenommen werden, die genaue Zuordnung der Strukturen ist noch in Arbeit.

[1] N. Bertram, Y. D. Kim, G. Ganteför, Q. Sun, P. Jena, J. Tamuliene and G. Seifert: Experimental and theoretical studies on inorganic magic clusters: $M_4X_6$ (M=Mo,W; X=O,S), Chem. Phys. Lett. 396, 69 (2004).

MO 14.6 Fr 18:00 HU 2091

**Interatomic Coulombic Decay (ICD) in Heteroclusters of Ne and Ar** — •S. Barth, S. Marburger, S. Joshi, V. Ulrich, O. Kugeler, and U. Hergenhahn — Max-Planck-Institut für Plasmaphysik, Boltzmannstr. 2, 85748 Garching

A non-radiative, non-local decay process in weakly bound systems, the Interatomic/molecular Coulombic Decay (ICD) [1], has recently been discovered in Ne clusters [2]. In this decay process, emission of an outer valence electron into the continuum is mediated by an ultrafast energy transfer from a neighbouring atom or molecule, which makes the process very sensitive to the chemical environment of the excited site. This is exemplified by a recent measurement of the lifetime of Ne $2s^{-1}$ states in Ne clusters, which yielded 6(1) fs for bulk sites, and more than 30 fs for surface sites [3].

As a step towards an analytical application of ICD, we have investigated the ICD signal of a Ne/Ar mixture coexpanding in a supersonic beam. By changing the nozzle temperature, regimes of pure Ar clusters coexisting with Ne monomers, and of mixed clusters consisting of an Ar core surrounded by Ne layers can be selected. In our experiment we show the appearance of an ICD signal pertaining to a decay of Ne $2s^{-1}$ into Ar $3p^{-1}$Ne $2p^{-1}$ states which is unambiguously related to the formation of a bound system containing Ne *and* Ar.

[1] L. S. Cederbaum *et. al.*, Phys. Rev. Lett. **79**, 4778 (1997).
[2] S. Marburger *et. al.*, Phys. Rev. Lett. **90**, 203401 (2003).
[3] G. Öhrwall *et. al.*, Phys. Rev. Lett. **93**, 173401 (2004).

MO 14.7 Fr 18:15 HU 2091

**Infrared Spectroscopy of Cluster Anions** — •J. Mathias Weber, Holger Schneider, and A. Daniel Boese — Institut für Physikalische Chemie, Universität Karlsruhe, Kaiserstr. 12, 76128 Karlsruhe

Molecular clusters are relevant model systems for the study of intermolecular interaction potentials governing the structures of molecular complexes. Structural information on clusters can be gained from infrared photodissociation spectroscopy in molecular beams, and we have applied this technique to several species, probing the interaction of various anions with $CO_2$. The experimental results are interpreted in the framework of density functional theory calculations with anharmonic calculations of vibrational spectra.

Halide-$CO_2$ complexes afford the study of the interaction $CO_2$ with closed shell anions of low reactivity. The results are compared with those for $Au^- \cdot CO_2$, which is relevant for the study of catalytic oxidation of CO. This complex shows strong interaction between $CO_2$ and the $Au^-$ anion, with a strongly deformed $CO_2$ unit. Complexes of $O_2^-$ with $CO_2$ show very intersting motifs of ion solvation. The $\pi^*$ orbital offers a template with four *a priori* equivalent binding sites for the structure of the microsolvation environment. However, only one $CO_2$ ligand is strong bound, with additional molecules weakly attached to the resulting $CO_4^-$ anion.