

## MO 19: Cluster III (joint session MO/A)

Time: Thursday 10:30–12:30

Location: S HS 001 Biologie

**Invited Talk** MO 19.1 Thu 10:30 S HS 001 Biologie  
**Optical spectroscopy of small metal clusters: a deeper look at Au<sub>4</sub><sup>+</sup>** — ●MARKO FÖRSTEL, WOLFGANG SCHEWE, and OTTO DOPFER — TU Berlin, IOAP, Hardenbergstr. 36, 10623 Berlin

The catalytic properties of small metal clusters strongly depend on local structure. This is especially the case for very small clusters, where every new atom changes the physical and thus catalytic properties tremendously. For example, gold clusters show catalytic properties at sizes down to three atoms!

With a new setup we were able to measure the optical absorption spectrum of such small gold clusters in hitherto unavailable quality.<sup>[1]</sup> These spectra allow for the first time to directly access the structure of the ground and excited state via comparison of the measured vibrational frequencies and Franck-Condon progressions to those from calculated structures. Surprisingly, we find that the optical spectrum cannot be explained by assuming that it stems solely from the rhombic ground state structure of Au<sub>4</sub><sup>+</sup>.<sup>[2]</sup>

[1] M. Förstel, B. K. A. Jaeger, W. Schewe, P. H. A. Sporkhorst, O. Dopfer, Improved tandem mass spectrometer coupled to a laser vaporization cluster ion source *Rev. Sci. Instr.* 2017, 88, 123110.

[2] M. Förstel, W. Schewe, O. Dopfer, Optical spectroscopy of the Au<sub>4</sub><sup>+</sup> cluster: Resolved vibronic structure indicates an unexpected isomer, *submitted*.

MO 19.2 Thu 11:00 S HS 001 Biologie  
**Activation of Methane by Free Gold Clusters: Ion-Trap Kinetics, IR-Spectroscopy, and Ab Initio Theory** — ●THORSTEN BERNHARDT<sup>1</sup>, SANDRA LANG<sup>1</sup>, JOOST BAKKER<sup>2</sup>, ROBERT BARNETT<sup>3</sup>, and UZI LANDMAN<sup>3</sup> — <sup>1</sup>Institute of Surface Chemistry and Catalysis, University of Ulm, 89069 Ulm, Germany — <sup>2</sup>Institute for Molecules and Materials, FELIX Laboratory, 6525 ED Nijmegen, The Netherlands — <sup>3</sup>School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430, USA

Amongst all the metals gold exhibits the least inclination to undergo chemical reactions with other elements. It is therefore even more surprising that few nanometer sized gold particles and gold clusters consisting of very few atoms display excellent catalytic properties. In order to demonstrate the ability of small gold clusters to activate methane, we previously performed gas phase reaction kinetics experiments in an octopole ion trap. These experimental studies revealed the particular catalytic properties of the gold dimer to activate methane and to convert two methane molecules to ethylene at thermal reaction conditions. These experiments have now been complemented by infrared multi photon dissociation experiments employing the free electron laser FELICE at the University of Nijmegen. These spectroscopy investigations demonstrated that the interaction of methane with small gold cluster cations leads to selective C-H-bond dissociation and the formation of hydrido-methyl complexes.

MO 19.3 Thu 11:15 S HS 001 Biologie  
**Interspecies energy transfer in heterogeneous Ar<sub>2</sub>-N<sub>2</sub> clusters quenching predissociation** — ●HUDA OTTO, DANA BLOSS, ANDREAS HANS, XAVER HOLZAPFEL, CATMARN KÜSTNER-WETEKAM, CHRISTIAN OZGA, PHILIPP SCHMIDT, ARNO EHRESMANN, and ANDRÉ KNIE — Institut für Physik und Center for Interdisciplinary Nanostructure Science and Technology (CINSaT), Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany

Loosely bound systems, like Ar<sub>2</sub>, are of technical and biological interest. For example, the Ar dimer (Ar<sub>2</sub>) is used as a medium in excimer lamps, and decay processes in such noble gas dimers are showcase examples to explain radiation damage in organic tissues. Ar<sub>2</sub> consists of two *van-der-Waals bound* Ar atoms. This binding type affects the energy transfer between van-der-Waals bound atoms, called clusters. Doping an Ar cluster with a molecule, like N<sub>2</sub>, allows to investigate the effect of molecular vibrations on energy transfers in a loosely bound environment. Here, different vibronic states of N<sub>2</sub> in an Ar<sub>2</sub>-N<sub>2</sub> cluster were addressed. In gaseous N<sub>2</sub> the resonant excitation of these vibronic states lead to non-radiative predissociation, whereas if the N<sub>2</sub> is van-der-Waals bound on an Ar cluster, the absorbed energy is redistributed within the cluster, resulting in photon emission from

perturbed Ar dimers. Thus, an interspecies energy transfer from a N<sub>2</sub> molecule to an Ar dimer must occur. During the talk evidences for the interspecies energy transfer in heterogeneous Ar<sub>2</sub>-N<sub>2</sub> clusters will be discussed further.

MO 19.4 Thu 11:30 S HS 001 Biologie  
**Electron and photon interactions with size-selected lead clusters** — STEFFI BANDELOW, ●ALEXANDER JANKOWSKI, STEPHAN KÖNIG, GERRIT MARX, LUTZ SCHWEIKHARD, and MARKUS WOLFRAM — Institute for Physics, University of Greifswald, Germany

At the ClusterTrap-setup [1], the dissociation pattern of photoexcited lead cluster ions has been of interest in recent studies [2,3]. It was shown that lead transitions from a metallic [4] to a non-metallic fragmentation behavior [2] when approaching smaller cluster sizes. In further investigations, size-selected trapped negatively charged lead clusters are exposed to an electron beam. This leads to electron attachment [5,6] as well as collision-induced dissociation [6]. The resulting product ions reveal first hints of fission processes, where doubly negatively charged clusters break up into two singly charged fragments. The most prominent fragments observed are Pb<sub>10</sub><sup>1-</sup>, and Pb<sub>n-10</sub><sup>1-</sup>, where *n* is the precursor cluster size. This interpretation is confirmed by photodissociation studies of size- and charge-state selected dianionic lead clusters [7].

- [1] F. Martinez *et al.*, *Int. J. Mass Spectrom.* 365-366 (2014) 266.
- [2] S. König *et al.*, *J. Phys. Chem. C* 121 (2017) 10858.
- [3] M. Wolfram *et al.*, *J. Phys. B: At. Mol. Opt. Phys.* 51 (2018) 044005.
- [4] P.J. Brucat *et al.*, *J. Chem. Phys.* 84 (1986) 3078.
- [5] A. Herlert *et al.*, *Phys. Scripta* T80 (1999) 200.
- [6] S. König *et al.*, *Int. J. Mass Spectrom.* 421 (2017) 129.
- [7] S. König *et al.*, *Phys. Rev. Lett.* 120 (2018) 163001.

MO 19.5 Thu 11:45 S HS 001 Biologie  
**Photophysics investigation of pyrrole and pyrrole-water<sub>1</sub> clusters** — ●MELBY JOHNY<sup>1</sup>, SEBASTIAN TRIPPEL<sup>1,2</sup>, and JOCHEN KÜPPER<sup>1,2,3</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY, Hamburg — <sup>2</sup>The Hamburg Center for Ultrafast Imaging, Universität Hamburg, Hamburg — <sup>3</sup>Department of Physics, Universität Hamburg, Hamburg

The properties of atoms and molecules are strongly dependent on their local environment and hydrogen bonds are of universal importance in chemistry and biochemistry. Therefore, it is highly desirable to bridge the gap between single, isolated molecules and molecules in solvation.

Here, we show the investigation of the photophysics of pyrrole and the single hydrogen bonded pyrrole-water<sub>1</sub> clusters via site-specific x-ray ionisation and strong field ionisation by intense near-infrared laser pulses. The photo-fragmentation owing to core-shell ionisation at nitrogen(N 1s) were analyzed by means of photoelectron photoion-photoion coincidence(PEPIPICO) imaging. A 3D-imaging detector, Timepix3 was used for coincidence detection of strong field ionisation of pyrrole and pyrrole-water<sub>1</sub>. For pyrrole-water<sub>1</sub> clusters, we observed proton or hydrogen atom transfer from pyrrole moiety to the hydrogen bonded water molecule and the fragmentation dynamics is significantly different from bare pyrrole.

MO 19.6 Thu 12:00 S HS 001 Biologie  
**Superelectrophilic Behaviour of closo-Dodecaborate Monoanions** — KNUT R. ASMIS<sup>1</sup>, MARTIN MAYER<sup>1</sup>, JONAS WARNEKE<sup>2</sup>, and ●MAX GRELLMANN<sup>1</sup> — <sup>1</sup>Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnestr. 2, 04103 Leipzig (Germany) — <sup>2</sup>Department of Chemistry, Purdue University, West Lafayette, IN 47907 (USA)

Bond formation with an electron-rich system, known as electrophilicity, is commonly observed in electron-deficient molecules. Binding noble gases at room temperature was a marking property predominantly of strong, dicationic systems, therefore termed as \*superelectrophiles\*. Gas-phase skimmer collision induced dissociation (sCID) lead to the formation of closo-dodecaborate monoanions [B<sub>12</sub>X<sub>11</sub>]<sup>-</sup>, showing a high reactivity towards electron-rich systems for instance dinitrogen, dioxygen and noble gases (Ngs). In particular, the clusters [B<sub>12</sub>X<sub>11</sub>]<sup>-</sup> (X = Cl, CN) have been observed to form spontaneously B-Ng bonds with a substantial degree of covalent interaction, thus show-

ing a superelectrophilic behaviour despite being negatively charged. A significant blue shift of the CO stretching mode when bound with its carbon tail to a closo-dodecaborate monoanion, observed by using infrared photodissociation (IRPD) spectroscopy, verified the suspected electron-deficiency at the binding site of the cluster. Quantum chemical calculations revealed that the anions unite several molecular properties, which lead to a dipole discriminating chemistry, facilitating the addition of Ngs. On this account, small dipole moments of alkanes could be a promising property to introduce the anions into C-H-bond activation.

MO 19.7 Thu 12:15 S HS 001 Biologie

**Photofragmentation of small bismuth clusters** — •PAUL FISCHER, GERRIT MARX, and LUTZ SCHWEIKHARD — Institut für Physik, Universität Greifswald, 17489 Greifswald, Germany

Bismuth clusters  $\text{Bi}_n^{+/-}$  in the size range  $n = 2$  to 19 have been pro-

duced by laser ablation and stored in an electrostatic ion beam trap (EIBT) [1,2]. The trap allows the retention of size-selected ions and their separation from contaminant ions with high resolving powers [3].

Photofragmentation has been performed by use of nanosecond laser pulses ( $\lambda = 532\text{nm}$ ). Product patterns include multiple cluster sizes, depending on the selected precursor. To further investigate the fragmentation pathways of the clusters, parameters such as the laser-pulse energy and timing have been varied. In many cases, the preliminary data evaluation suggests pathway competition and only a few sequential decays. The size of the primary neutral fragment being evaporated shifts with increasing precursor cluster size.

[1] H. Wollnik et al., J. Mass Spectrom. Ion Processes 96(3):267-274(1990)

[2] D. Zajfman et al., Phys. Rev. A 55:R1577-R1580(1997)

[3] P. Fischer et al., Rev. Sci. Instrum. 89:015114(2018)