

## MO 16: Molecular Clusters

Time: Thursday 11:00–13:15

Location: f142

**Invited Talk**

MO 16.1 Thu 11:00 f142

**Vibrational spectra, structures, and chemical bonding of silicene hydride cluster cations** — ●OTTO DOPFER — Institut für Optik und Atomare Physik, TU Berlin

Silanes and their derivatives and ions are fundamental species in a variety of chemical disciplines. In contrast to hydrocarbon ions ( $C_xH_y^+$ ), almost no information is available for the corresponding  $Si_xH_y^+$  cations. Here, IR spectra of  $Si_xH_y^+$  cations produced in a supersonic plasma molecular beam expansion of  $SiH_4$  are inferred from photodissociation of cold Ne and Ar 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 [1-3]. We present initial results for  $Si_2H_6^+$ ,  $Si_2H_7^+$  and  $Si_3H_8^+$ , 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. New results on protonated silanols will be presented.

[1] Savoca, George, Langer, Dopfer, PCCP 15, 2774 (2013). [2] Savoca, Langer, Dopfer, Angewandte Chemie 125, 1376 (2013). [3] George, Savoca, Dopfer, Chem. Eur. J. 19 45 (2013).

**Invited Talk**

MO 16.2 Thu 11:30 f142

**Far-infrared spectroscopy of metal cluster rare-gas complexes** — DAVID YUBERO VALDIVIELSO<sup>1</sup>, VALERY CHERNY<sup>2</sup>, DENNIS PALAGIN<sup>3</sup>, JOOST M. BAKKER<sup>2</sup>, and ●ANDRÉ FIELICKE<sup>1</sup> — <sup>1</sup>Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany — <sup>2</sup>FELIX Laboratory, Faculty of Science, Radboud University Nijmegen, The Netherlands — <sup>3</sup>Physical & Theoretical Chemistry Laboratory, University of Oxford, UK

Multiple photon dissociation spectroscopy in the far-infrared [1] is used to obtain vibrational spectra of transition metal clusters in the gas phase. More precisely, weakly bound complexes of the clusters with rare-gas atoms are irradiated with monochromatic light from an IR Free Electron Laser and their wavelength-dependent depletion is used as probe for the absorption process. Experimental far-IR spectra are typically recorded in the  $85 - 500\text{cm}^{-1}$  region to cover the range of the structure-specific vibrational fundamentals, i.e., the finger-print range, for the metal clusters. Comparison with calculated vibrational spectra obtained, for instance, by using DFT methods, allows for structural assignments. I will present recent results for Ar solvation complexes of the cobalt cation, where by comparison with results from density functional theory calculations we identify distorted square, square pyramidal, and octahedral structures for  $CoAr_4^+$ ,  $CoAr_5^+$ , and  $CoAr_6^+$ , respectively.  $CoAr_5^+$  is a particularly interesting case as it appears to undergo rapid dynamics which finds its expression in a broad vibrational lineshape. A second example are the structures of binary cobalt-manganese clusters.

[1] A. Fielicke et al., Phys.Rev.Lett. 93 (2004) 023401.

MO 16.3 Thu 12:00 f142

**Fluorescence lifetime reduction of organic semiconductors attached to the surface of solid neon cluster** — ●SHARAREH IZADNIA, MARKUS MÜLLER, AARON LAFORGE, and FRANK STIENKEMEIER — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany

The collective emission of coherent light is a fundamental process in quantum mechanics. The resulting radiation leads to effects such as superradiance. One particularly fascinating manifestation of superradiance is the process of spontaneous coherent emission of light by an ensemble of identical excited atoms, which was initially predicted by Dicke [1]. Superradiance has been observed almost universally in weakly interacting systems such as hot dense gases [2]. Here, we report the experimental observation of fluorescence lifetime reduction of tetracene by directly tuning the number of molecules attached to the surface of neon clusters and excitation laser power. For average intermolecular distances greater than  $33 \text{ \AA}$ , we attribute the reduction

in fluorescence lifetime to Dicke superradiance [3], while for smaller intermolecular distances, additional lifetime reduction occurs due to the onset of non-radiative de-excitation (e.g. singlet fission).

[1] R. H. Dicke, Phys. Rev. 93, 99 (1954).

[2] N. Skribanowitz, I. P. Herman, J. Macgilli, and M. S. Feld, Phys.Rev. Lett. 30, 309 (1973).

[3] M. Müller, S. Izadnia, S. M. Vlaming, A. Eisfeld, A. LaForge and F. Stienkemeier. Phys. Rev. B 92, 121408(R) (2015)

MO 16.4 Thu 12:15 f142

**Spectroscopy and Kinetics on Metal Cluster Surfaces: The Fe/N<sub>2</sub>, Co/N<sub>2</sub> and Ni/N<sub>2</sub> systems** — ●SEBASTIAN DILLINGER, JENNIFER MOHRBACH, ANNIKA STEINER, and GERON NIEDNER-SCHATTEBURG — Fachbereich Chemie und Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany

We present kinetic data of  $N_2$  adsorption on isolated cationic Fe/Co/Ni clusters in combination with Infrared (Multi) Photon Dissociation (IR(M)PD) spectra of the cluster adsorbate complexes at cryo temperatures. We will display and discuss the cluster size range of  $n=7-20$ . We find metal, cluster size and adsorbate number dependent effects in the IR(M)PD spectra as well as in the kinetic data: Trends and exceptions superpose. For our experiments we utilized a unique tandem cryo trap setup at 12 K to 26 K.

MO 16.5 Thu 12:30 f142

**X-ray Magnetic Circular Dichroism of Heteronuclear Complexes in Isolation** — ●JOACHIM HEWER<sup>1</sup>, MATTHIAS TOMBERS<sup>1</sup>, JOHANNES LANG<sup>1</sup>, GERON NIEDNER-SCHATTEBURG<sup>1</sup>, and TOBIAS LAU<sup>2</sup> — <sup>1</sup>Fachbereich Chemie und Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, Germany — <sup>2</sup>Helmholtz-Zentrum Berlin Materialien und Energie, BESSY II, Berlin, Germany

We applied synchrotron based X-ray magnetic Circular dichroism (XMCD) spectroscopy to ligand stabilized  $[Mn_2LnL_x]^+$  complexes ( $Ln = Nd, Eu, Gd, Dy, Lu$ ;  $L =$  organic ligands) when isolated as individual ions under cryo conditions. Such investigations allow for a magnetic characterization of these complexes void of any surface or packing effects. The element selectivity of the XMCD technique allows to determine the contribution of the individual metals to the total magnetic moment of the molecules. Furthermore, sum rule analysis of the recorded XMCD spectra allows to decompose the total magnetic moment into its spin and orbital contributions. The variation of the incorporated lanthanoid ions is at the center of interest and interpretation.

MO 16.6 Thu 12:45 f142

**Tuning the optical properties of diamondoids through plasmonics** — ●ANDRÉ KNECHT<sup>1</sup>, TOBIAS ZIMMERMANN<sup>1</sup>, ANDREA MERLI<sup>1</sup>, MERLE RÖHR<sup>2</sup>, JENS PETERSEN<sup>2</sup>, ROLAND MITRIC<sup>2</sup>, THOMAS MÖLLER<sup>1</sup>, and TORBJÖRN RANDER<sup>1</sup> — <sup>1</sup>Institut für Optik und Atomare Physik, Technische Universität Berlin — <sup>2</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg

Diamondoids, subnanometer-sized carbon-cages, show interesting properties like negative electron affinity and intrinsic photoluminescence in the UV regime [1,2]. The feasibility of functionalization, as well as the size and shape selectivity of the diamondoids, gives rise to numerous possibilities to tune their optical properties. Hence, these molecular diamonds are ideal to investigate a size regime where a transition from molecular to bulk-like optical properties takes place.

Moreover, diamondoid properties can be modified through adsorption on metal surfaces [2]. Adjusting the local environment of diamondoids through the proximity of metal clusters, we can tune the metal plasmon resonance to the radiative transitions of the diamondoid [3]. To investigate these plasmon resonance coupling effects, we use ion yield spectroscopy. First ion yield spectra of Au-adamantanethiol-hybrids show significant changes in the UV absorption cross section and represent an important step towards the systematic development of novel nanoscopic plasmonic hybrid systems.

[1] R. Richter, et al., Phys. Chem. Chem. Phys. 17.6 (2015): 4739-4749. [2] W. Clay, et al., Nano letters 9.1 (2008): 57-61. [3] P. Anger, et al., Phys. Rev. Lett. 96, 113002 (2006).

MO 16.7 Thu 13:00 f142

**Theoretical investigations to photophysical properties of mono-, di- and trimetallic gold complexes** —•FABIAN DIETRICH<sup>1</sup>, ANNEKEN GRÜN<sup>1</sup>, SIMON P. WALG<sup>2</sup>, MERVE CAYIR KÜCÜKDISLI<sup>2</sup>, WERNER R. THIEL<sup>2</sup>, and MARKUS GERHARDS<sup>1</sup> —  
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<sup>2</sup>Anorganische Chemie, TU Kaiserslautern

A set of Au complexes with pyrimidinylpyridine( $\text{NH}(\text{CH}_2)_2\text{PPh}_2$ ) as well as bispyrimidinylpyridine- $(\text{NH}(\text{CH}_2)_2\text{PPh}_2)_2$  ligands are investigated since they are of great interest in synthesis due to their catalytic

activity. Quantum chemical calculations are performed for the explanation of experimental spectra. We use time dependent density functional theory (TD-DFT) to compute UV/Vis-spectra. The influence of different solvents is taken into account by the application of the polarized continuum model (PCM). The comparison with UV/Vis-measurements show the strengths of TD-DFT calculation in such cases where excitations are localized on  $\pi$ -systems and no charge transfers have to be taken into account. The metal induced shifts are represented well. Both experimental and theoretical spectra are investigated under the issue of cooperativity which will be quantified.