

MO 2: Cluster & Complexes

Time: Monday 14:00–15:30

Location: H2

MO 2.1 Mon 14:00 H2

Si_nO_m⁺ - Optical Absorption and Photodissociation Properties — ●TAARNA STUEDEMUND, MARKO FÖRSTEL, KAI POLLOW, ROBERT G. RADLOFF, LARS DAHLÖF, JULIAN VOSS, and OTTO DOPFER — Institut für Optik und Atomare Physik, Technische Universität Berlin, Berlin, Deutschland

The origin as well as evolutionary formation mechanisms of stars and solar systems like our own are still poorly understood. Therefore, it is essential to gain a better understanding of interstellar dust, as it is a major actor in this process. So far, it is known that such dust contains μm -sized silicate particles. On the other hand, the only molecular species that has been found in the interstellar matter (ISM) which could be a direct precursor to silicate dust is SiO [1]. To this end we present both, experimental data and quantum chemical calculations, that help to understand the dissociation and absorption behavior of possible intermediate silcon-oxide species. The ions under investigation were generated in a laser vaporization source, mass-selected and photodissociated [2]. The resulting absorption spectra are compared to TD-DFT calculations and discussed in an astrophysical context.

[1] R. Wilson et al., 1971, *Astrophys. J.* 167, L97 [2] M. Förstel et al., *Rev. Sci. Instrum.*, 2017, 88, 123110.

MO 2.2 Mon 14:15 H2

Time-resolved photon interactions of size- and charge-state selected polyanionic tin clusters — ●ALEXANDER JANKOWSKI, MORITZ GRUNWALD-DELITZ, and LUTZ SCHWEIKHARD — Institute of Physics, University of Greifswald, Germany

In contrast to many other metals, small tin clusters (Sn_n⁻ of sizes $n \lesssim 50$) are formed by so-called building blocks of Sn₇, Sn₁₀ [1-3] and, in the case of anionic clusters, Sn₁₅ [3]. These cluster sizes $n = 7, 10$ and 15 lead to corresponding fragmentation patterns [4,5] which have been confirmed and further investigated [6,7] at the ClusterTrap setup [8]. These previous findings suggested for dianionic tin clusters fission processes into two monoanionic fragments in analogy to the case of lead clusters [9]. Recently, photodissociation experiments have been performed on size- and charge-state-selected polyanionic tin clusters. By delaying the ejection/analysis of the trapped clusters with respect to the pulsed photoexcitation, time-resolved measurements allow the reconstruction of the decay pathways.

- [1] C. Majumder et al., *Phys. Rev. B* **64**, 233405 (2001)
- [2] H. Li et al., *J. Phys. Chem. C* **116**, 231-236 (2011)
- [3] A. Lechtken et al., *J. Chem. Phys.* **132**, 211102 (2010)
- [4] E. Oger et al., *J. Chem. Phys.* **130**, 124305 (2009)
- [5] A. Wiesel et al., *Phys. Chem. Chem. Phys.* **14**, 234-245 (2012)
- [6] S. König et al., *Eur. Phys. J. D* **72**, 153 (2018)
- [7] M. Wolfram et al., *Eur. Phys. J. D* **74**, 135 (2020)
- [8] F. Martinez et al., *Int. J. Mass Spectrom.* **266**, 365-366 (2014)
- [9] S. König et al., *Phys. Rev. Lett.* **120**, 163001 (2018)

MO 2.3 Mon 14:30 H2

N₂ Cleavage by Tantalum Cluster under Cryo Conditions — ●DANIELA V. FRIES, MATTHIAS P. KLEIN, ANNIKA STRASSNER, MAXIMILIAN HUBER, MARC H. PROSENC, and GEREON NIEDNER-SCHATTEBURG — TU Kaiserslautern, Kaiserslautern, Deutschland

As motivated by prior room temperature studies on Ta₂⁺[1] we investigate larger Ta_n⁺ clusters ($4 < n < 7$) and their N₂ adsorption and activation abilities by adsorption kinetics and infrared spectroscopy under cryo conditions compared with DFT calculations.

The model system Ta₄⁺ appears to be of particular interest with regard to cryo N₂ activation. Experimental results reveal peculiar details for the first and second adsorption kinetics, and the infrared signatures show no NN stretching bands in [Ta₄(N₂)₁]⁺ and [Ta₄(N₂)₂]⁺. This is consistent with cleavage of the first two adsorbed dinitrogen molecules and we unravel a multistep above edge across surface (AEAS) mechanism for the cleavage of first and second N₂ adsorbates. Cleavage of the third N₂ ligand is kinetically hindered. We recognize that substoichiometric N₂ exposure allows for spontaneous activation by Ta₄⁺, while higher N₂ exposure causes self poisoning.[2]

[1] Proc. Natl. Acad. of Sci. USA, 2018, 115, 11680-11687.

[2] *Phys. Chem. Chem. Phys.*, 2021, 23, 11345-11354.

MO 2.4 Mon 14:45 H2

Combined IR/UV spectroscopic and quantum chemical studies on chromone/methanol aggregates — ●PATRICK HORST STREBERT, POL BODEN, MARCEL META, CHRISTOPH RIEHN, and MARKUS GERHARDS — Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern, Research Center Optimas and Technical University Kaiserslautern

Dispersion forces have often been underestimated in the description of intra- and intermolecular interactions. Within aggregates, the balance between dispersion interactions and electrostatic forces can be the deciding factor for the preference of a certain binding motif and can be difficult to model with current theoretical methods. Systematic probing of dispersion interactions in aggregates with two or more possible binding motifs enables better understanding and description of these phenomena.

In this work, complexes of chromone with methanol were investigated by IR/UV laser spectroscopy in a molecular beam experiment. The experimental results are compared to theoretical predictions obtained from (TD)DFT-, DLPNO-CCSD(T)- and SAPT-calculations, including transition state calculations with respect to different isomers. The chromone molecule provides two binding sites at the carbonyl oxygen enabling us to study the balance of electrostatic and dispersion forces in the electronic ground state (S₀) as well as the electronically excited triplet state (T₁). To the best of our knowledge, we present the first IR investigations of isolated aggregates (gas phase) between an alcohol and another organic molecule in a triplet state.

MO 2.5 Mon 15:00 H2

Multi-spectroscopic investigations of NIR emissive Cr(0), Mo(0) and W(0) complexes — ●PIT BODEN¹, PATRICK DI MARTINO-FUMO¹, SOPHIE STEIGER¹, TOBIAS BENS², BIPRAJIT SARKAR², GEREON NIEDNER-SCHATTEBURG¹, and MARKUS GERHARDS¹ — ¹TU Kaiserslautern, Fachbereich Chemie and Research Center Optimas, Kaiserslautern — ²University of Stuttgart, Institute of Inorganic Coordination Chemistry, Stuttgart

In this contribution^[1] a multi-spectroscopic approach is applied for the photophysical and structural characterization of NIR emissive Cr(0), Mo(0) and W(0) carbonyl complexes containing a pyridyl-mesoionic carbene ligand. The idea is to replace luminophores based on rare-earth metals like e.g. iridium and lanthanides by more abundant elements.

Luminescence spectroscopy at variable temperature on solid samples revealed a dual emission ($\lambda_{\text{VIS}} = 666 - 700 \text{ nm}$, $\lambda_{\text{NIR}} = 918 - 950 \text{ nm}$, depending on the metal center) at room temperature and an increase of the quantum yields upon cooling to 5 K. The luminescence bands are assigned to phosphorescence according to the lifetimes obtained by time-resolved luminescence and step-scan FTIR spectroscopy. Furthermore, the step-scan FTIR analysis revealed small but significant variations of CO bond lengths in the excited state, in combination with density functional theory calculations. An excited triplet state of metal-to-ligand charge transfer character was attributed to the visible emission.

[1] P. Boden et al., *Chem. Eur. J.* **2021**, accepted.

MO 2.6 Mon 15:15 H2

Influence of metal and halide substitution on the photophysics of dinuclear copper(I) and silver(I) complexes — ●SOPHIE STEIGER¹, PIT BODEN¹, FLORIAN REHAK², JASMIN BUSCH³, STEFAN BRÄSE³, WIM KLOPPER², GEREON NIEDNER-SCHATTEBURG¹, and MARKUS GERHARDS¹ — ¹TUK, FB Chemie and Research Center Optimas, Kaiserslautern — ²KIT, Institut für Physikalische Chemie, Karlsruhe — ³KIT, Institut für Organische Chemie, Karlsruhe

This contribution presents the investigation of dinuclear copper and silver complexes with a butterfly shaped M₂X₂ core (M = Cu, Ag; X = Cl, Br). By systematically exchanging the metal and halide centers, the influence of the metals and halides on the photophysical properties is analyzed by using UV/VIS absorbance and (time-resolved) luminescence spectroscopy. Structural information about the excited states were obtained by time-resolved step-scan FTIR spectroscopy combined with quantum chemical TDDFT calculations. The presented spec-

troscopic experiments are performed at different temperatures (from 290 K to 5 K) to analyze thermally activated or suppressed photophysical processes (e.g. thermally activated delayed fluorescence, TADF). For the presented complexes, the metal exchange has a huge impact on the radiative deactivation channel and the structure of the excited

states, whereas the halide exchange has a much smaller influence. Both copper complexes show a red-shift of the emission band from TADF to phosphorescence while cooling down while a strong increase of the emission intensity without relevant spectral shift is observed for the silver complexes.