

MO 3: Electronic I

Time: Monday 16:30–18:15

Location: MO-H5

Invited Talk

MO 3.1 Mon 16:30 MO-H5

Electronic Properties of Small Gold Cluster Cations — ●MARKO FÖRSTEL¹, KAI POLLOW¹, TAARNA STUEMUND¹, NIMANOAH NAHVI¹, NIKITA KAVKA², ROLAND MITRIC², and OTTO DOPFER¹ — ¹TU Berlin, Berlin, Germany — ²Uni Würzburg, Würzburg, Germany

Recent instrumental improvements allow us to take a close look at the properties of excited states of metal cluster ions.^[1] The electronic properties of these clusters are of particular interest, as they vary greatly depending on geometry and composition. Thus they hold great potential towards tailored optical or catalytic properties. Unfortunately, theoretical predictions of their properties can be tricky due to relativistic effects and a strong multi-reference character. Detailed experimental information are thus of particular importance.

In this talk we discuss optical spectra of small gold cluster cations and compare them with those obtained by various quantum chemical calculations. We show that TD-DFT calculations make robust predictions only in special cases and even mislead in others.^[2] Furthermore, we discuss the interaction of the clusters with atomic and molecular ligands in the ground and excited states using the example of Au₂⁺-X with X = Ar, N₂ and N₂O. It can be seen that the Au₂⁺ - ligand interaction is weak in the ground state and decreases even further in the excited state.^[3,4]

[1] Förstel *et al.* Rev. Sci. Instr. 88, 2017 [2] Förstel *et al.* Angew. Chem. Int. Ed. 58, 2019 [3] Förstel *et al.* Angew. Chem. Int. Ed. 123, 2020 [4] Förstel *et al.* Chem. Eur. J. 27, 2021

MO 3.2 Mon 17:00 MO-H5

Simulation of Two-Dimensional Electronic Spectra of molecular aggregates: a Hierarchy of Stochastic Pure State approach — ●LIPENG CHEN¹, DORAN I.G. BENNETT², and ALEXANDER EISFELD¹ — ¹Max Planck Institute for the Physics of Complex Systems, Nöthnitzer Str 38, Dresden, Germany — ²Department of Chemistry, Southern Methodist University, PO Box 750314, Dallas, TX, USA

Modern techniques of time-resolved nonlinear optical spectroscopy have expanded our understanding of the photophysics of molecular aggregates, which is of particular importance for unravelling excitonic relaxation and dephasing processes in both artificial materials and photosynthetic complexes. In particular, two dimensional electronic spectroscopy has become a powerful technique to probe molecular excitons in the visible region and reveal couplings and relaxation pathways. We develop a new methodology for simulating two dimensional electronic spectra of molecular aggregates with strong coupling of electronic excitation to a structured environment by combining the stochastic hierarchy of pure states (HOPS) method with the nonlinear response function formalism. In our approach, the third-order response functions are evaluated by employing a novel propagation scheme where the combined ket and bra states are propagated in an augmented electronic Hilbert space. The new approach shows fast convergence properties with respect to the number of stochastic trajectories, providing a promising technique for numerical calculation of two dimensional spectra of large molecular aggregates.

MO 3.3 Mon 17:15 MO-H5

Chlorophyll Excitation in Photosystem 1 Tuned by the Protein Environment: Insights from Fully Atomistic QM/MM — ●SEBASTIAN REITER, FERDINAND KISS, and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwig-Maximilians-Universität München, München

Photosystem 1 (PS1) is one of the most efficient natural light-harvesting systems. Energy is absorbed by an antenna complex of chlorophylls and transferred to a reaction core, where it drives one of the fundamental redox processes of photosynthesis. Understanding the high efficiency of PS1 requires an accurate evaluation of the chlorophyll absorption energies, affected by their natural environment (site energies). However, this is challenging because not only the full electrostatic environment but also dynamic effects must be taken into account. In this work, we present accurate site energies of all 96 chlorophylls in the asymmetric unit of PS1 in *S. elongatus*. Therefore, we

constructed a fully atomistic model of the trimeric PS1 complex in a solvated lipid membrane to describe the environment as thoroughly as possible. With this extensive structural model, we sampled geometries from classical trajectories and calculated site energies for each chlorophyll with the high-level DFT/MRCI method in a QM/MM scheme. Our results identify dynamic energy sinks in the antenna complex and reveal a fundamental asymmetry in the reaction center. Moreover, we are able to separate the environmental influence into the electrostatic interaction of the chlorophyll with its surroundings and the structural constraints imposed by neighboring residues.

MO 3.4 Mon 17:30 MO-H5

Threshold Photoelectronspectra of pyrolyzed Trimethylantimony and Trimethylarsenic compounds. — EMIL KARAEV¹, ●MARIUS GERLACH¹, PATRICK HEMBERGER², and INGO FISCHER¹ — ¹Institut für physikalische und theoretische Chemie, Würzburg, Germany — ²Swiss Light Source, Villigen, Switzerland

Our group already investigated the pyrolysis of methylated group V compounds X = N[1], P[2], Bi[3]. While the stable isomers of nitrogen were H-N-CH₂, N-CH₂ and H-N-CH, bismuth showed only Bi-CH₃. For phosphorus the isomers H-P-CH₂, P-CH₃ and P-CH₂ were observed. In order to fill the gap in the periodic table trimethylarsenic and trimethylantimony were pyrolyzed. The emerging reactive species were characterized with the PEPICO setup of the VUV beamline at the Swiss Light Source in Villigen, CH. The observed mass-selected threshold photoelectron spectra were interpreted using quantum chemical calculations and Franck-Condon simulations.

Our results show that Antimony behaves similarly to bismuth, only forming Sb-CH₃. Arsenic on the other hand showed H-As-CH₂, As-CH₃ and As-CH₂, which is analogous to phosphorus.

[1] F. Holzmeier, M. Lang, K. Hader, P. Hemberger, I. Fischer, J. Chem. Phys. 2013, 138, 214310.

[2] D. P. Mukhopadhyay, Unpublished work.

[3] D. P. Mukhopadhyay, D. Schleier, S. Wirsing, J. Ramler, D. Kaiser, E. Reusch, P. Hemberger, T. Preitschopf, I. Krummenacher, B. Engels, I. Fischer, C. Lichtenberg, Chem. Sci. 2020, 11, 7562*7568.

MO 3.5 Mon 17:45 MO-H5

Spectroscopy of Potassium Clusters Isolated in Helium Nanodroplets — ROMAN MESSNER, ROBERT DI VORA, WOLFGANG E. ERNST, and ●FLORIAN LACKNER — Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria

We explore the evolution of the electronic spectrum of potassium clusters isolated in helium droplets from single atoms and molecules up to nanometer sized clusters. A supercontinuum laser equipped with a tunable filter is used to excite the potassium clusters. In combination with a time-of-flight mass spectrometer atomically precise spectra up to K₁₁₀ are recorded. Spectra for larger clusters within a selected size range are also recorded, revealing insight into the properties and growth of potassium nanoparticles in helium droplets. While small molecules exhibit multiple distinct spectral features, a collective resonance emerges at about 600 nm in the spectra of larger clusters. With increasing cluster size, this resonance continuously shifts towards the blue.

MO 3.6 Mon 18:00 MO-H5

Laser Spectroscopy of Shell-Isolated Au Nanoparticles Functionalized with Rhodamine B Molecules in Helium Nanodroplets — ●ROMAN MESSNER, WOLFGANG E. ERNST, and FLORIAN LACKNER — Institute of Experimental Physics, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria

Nanoparticles comprising three different materials in a core@shell@shell configuration are synthesized in cold helium droplets by sequential doping. Rhodamine B molecules form complexes in helium droplets that give rise to a strong fluorescence upon laser excitation, which enables an in-situ investigation of the synthesized structures. In the presence of a Au core, the rhodamine B fluorescence is quenched due to excitation transfer from excited shell molecules to the Au particle. The addition of an intermediate hexane layer inhibits the contact between Au core and RB shell, which results in the recovery of the fluorescence.