

MO 29: Cluster and Nanoparticles II (joint session MO/A)

Time: Friday 11:00–13:00

Location: HS XV

Invited Talk

MO 29.1 Fri 11:00 HS XV

N₂ activation by transition metal clusters — MAX LUCZAK, CHRISTOPHER WIEHN, DANIELA FRIES, NIELS WOLFGRAMM, CHRISTOPH VAN WÜLLEN, and ●GEREON NIEDNER-SCHATTEBURG — Fachbereich Chemie, RPTU Kaiserslautern-Landau

Size selected transition metal (TM) cluster cations and anions attach N₂ molecules under single collision cryo conditions, and they may or may not subsequently activate the adsorbates. Cryo kinetics and infrared spectra reveal details that serve to model the activation pathways by DFT calculations [1,2,3]. It shows that there is a quite general multi-step-pathway. Energetics vary by the particular TM but corresponding intermediates along the pathways seem quite similar amongst the investigated TMs. We aim to put these findings to the stage and present our current understanding for further discussions.

[1] Phys. Chem. Chem. Phys. **23**, 11345 (2021); DOI: 10.1039/D0CP06208A

[2] J. Chem. Phys. **159**, 164306 (2023); DOI: 10.1063/5.0157218

[3] J. Chem. Phys. **159**, 164303 (2023); DOI: 10.1063/5.0157217

MO 29.2 Fri 11:30 HS XV

Dynamics of CO₂ activation by transition metal ions — ●MARCEL META, MAXIMILIAN E. HUBER, MARTIN WEDELE, and MARCEL META — RPTU Kaiserslautern-Landau und Forschungszentrum OPTIMAS, Fachbereich Chemie, Kaiserslautern, Germany

Here, we present a joint experimental and theoretical study of the dynamics of ion-molecule reactions. We focus on the oxygen atom transfer (OAT) reaction between transition metal ions and carbon dioxide $M^+ + CO_2 \rightarrow MO^+ + CO$ ($M^+ = Ta^+, Nb^+, Zr^+$) [1,2]. Indirect dynamics were observed for all reactions, despite the fact that the thermal rates are close to the collision rate and the reaction is exothermic in all cases. The investigated reactions have a multi-state character and require an inter-system crossing (ISC) for their occurrence. These findings indicate the presence of a bottleneck along the reaction. The nature of the bottleneck (submerged transition state versus ISC) was investigated in a collaborative effort.

In order to achieve this, angle and energy differential cross-sections were measured using 3D velocity map imaging at different collision energies. Thermal rate constants were obtained using selected ion flow tube (SIFT). These experimental findings were supplemented by high-level theory and trajectory simulations [3]. In addition, this approach allows us to make precise assertions regarding the distribution of energy. [1] M. E. Huber et al. 8670, 26, Phys. Chem. Chem. Phys. (2024). [2] M. Meta et al., 5524, 14, J. Phys. Chem. Lett (2023). [3] Y. Liu et al. J. Am Chem. Soc., 14182, 146 (2024).

MO 29.3 Fri 11:45 HS XV

Insights into Facile Methane Activation by Transition Metal Ions via Intersystem Crossing — MARCEL META, MAXIMILIAN HUBER, ●MAURICE BIRK, MARTIN WEDELE, BORIS HEEB, and JENNIFER MEYER — RPTU Kaiserslautern-Landau, Fachbereich Chemie und Landesforschungszentrum OPTIMAS, Kaiserslautern, Germany

A model for processes like single atom catalysis can be the study of isolated transition metal ion molecule reactions in the gas phase [1,2]. Here, we present a study of kinetics and dynamics on the activation of methane (CH₄) by transition metal cations $M^+ + CH_4 \rightarrow MCH_2^+ + H_2$. The nominally spin-forbidden reaction requires intersystem crossing (ISC) to proceed. The impact of ISC on the dynamics is studied by collaborative effort combining experiment and theory.

We used crossed-beam velocity map imaging to measure differential cross sections for the carbene formation in the reaction with tantalum Ta⁺ [3]. The reaction shows dominantly indirect dynamics which is associated to the formation of a long-lived intermediate complex. Experiments for Ta⁺ are furthermore complemented by the reaction of CH₄ with zirconium Zr⁺. In addition recent preliminary theoretical studies confirmed our observations regarding the reaction with Ta⁺ and also revealed that the bottleneck of this reaction is ISC between the quintet and triplet states.

[1] D. K. Böhme, H. Schwarz, Angew. Chem. Int. Ed. 2005, 44, 2336; [2] H. Schwarz, Catal. Sci. Tech. 2017, 7, 4302; [3] M. Meta, Faraday Discuss. 2024, 251, 587

MO 29.4 Fri 12:00 HS XV

Relaxation of solvated electrons in the presence of ammonia orbital vacancies — ●AARON NGAI¹, DOMINIQUE DOMINIQUE², LUKAS BRUDER¹, WENTAO CHEN¹, ALEKSANDR DEMIANENKO¹, MICHELE DI FRAIA³, KATRIN DULITZ⁴, IOANNIS MAKOS¹, EVANGELOS MILIORDOS⁵, SITANATH MONDAL¹, OKSANA PLEKAN⁶, SOORAJ RAJENDRAN¹, FABIAN RICHTER¹, NIKLAS SCHEEL⁷, BRENDAN WOUTERLOOD¹, BRUCE YODER², CARLO CALLEGARI⁶, MARCEL MUDRICH⁷, GIUSEPPE SANSONE¹, RUTH SIGNORELL², FRANK STIENKEMEIER¹, and SEBASTIAN HARTWEG¹ — ¹Institute of Physics, University of Freiburg, Germany — ²Department of Chemistry and Applied Biosciences, ETH Zürich, Switzerland — ³CNR - Istituto Officina dei Materiali (IOM), S.S. 14, Km 163.5, 34149 Trieste, Italy — ⁴Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Austria — ⁵Department of Chemistry and Biochemistry, Auburn University, AL, US — ⁶Elettra - Sincrotrone Trieste S.C.p.A., Basovizza, Trieste, Italy — ⁷Department of Physics and Astronomy, Aarhus University, Denmark

Solvated electrons in alkali-metal ammonia solutions are fascinating species that motivate fundamental and applied studies from different fields of research. In synthetic chemistry, these solvated electrons are used as powerful reducing agents in challenging reduction reactions [1]. From a physical perspective, they exhibit peculiar concentration-dependent properties and processes, such as the spin-pairing of solvated electrons and the phase transition to a metallic state at high concentrations [2]. Recently, a photoionization study of sodium-doped ammonia clusters, revealed the production of low-energy electrons from electron-transfer mediated decay of solvated electron pairs formed by optical excitation [3]. Motivated by the observation of this optically-triggered autoionization process, we performed a time-resolved photoelectron spectroscopy study of sodium-doped ammonia clusters with extreme ultraviolet radiation at the free-electron laser FERMI. I will present preliminary results of this study, which reveals the dynamics of solvated electrons in the vicinity of ammonia valence shell vacancies and the effects of excitations induced by ultraviolet light in these fascinating cluster systems.

[1] Birch, A.J. *J. Chem. Soc.*, **0**, 430-436 (1944)

[2] Zureck, E. *et al. Angew. Chem. Int. Ed.* **48**, 44 (2009)

[3] Hartweg, S. *et al. Science* **380**, 6650 (2023)

MO 29.5 Fri 12:15 HS XV

Droplet shape and quantum vortices visualized by the spectral shape of the electronic band origin of phthalocyanine doped into superfluid helium nanodroplets — ●RUPERT JAGODE and ALKWIN SLENCZKA — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93053 Regensburg

With the help of X-ray diffraction, the global shape of superfluid helium droplets could be imaged [1]. In addition, the inner structure, which may consist of quantum vortices - a specific form of angular momentum in quantum liquids - also became visible. These findings provide a consistent interpretation for the evolution of the spectral shape at the electronic band origin of phthalocyanine with increasing droplet size. Both the droplet shape and the presence of quantum vortices should have an effect on the solvent shift of the electronic transitions of the dopant molecule. New lineshape studies were carried out with systematic variation of the effective droplet sizes and optical anisotropy studies. From these new data, some of the still open questions regarding a reversal of the solvent shift [2] as well as the imperfect reproducibility of the observed signal splitting [2] could be clarified. Obviously, electronic spectroscopy complements the observations from X-ray diffraction on droplet shapes and the presence of quantum vortices for a range of smaller droplet sizes, which are relevant as host systems in molecular spectroscopy.

[1] B. Langbehn et al., Phys.Rev.Lett. **121**, 255301 (2018), A. Ulmer et al., Phys.Rev.Lett. **131**, 076022 (2023). [2] S. Fuchs et al., J.Chem.Phys. **148**, 144301 (2018).

MO 29.6 Fri 12:30 HS XV

Broadband Femtosecond Transient Absorption Microscopy — ●MAGNUS FRANK, CHRIS REHHAGEN, and STEFAN LOCHBRUNNER — Institute for Physics and Department of Life, Light and Matter, University of Rostock, 18051 Rostock, Germany

Organic crystalline micro- and nanostructures have become of great

interest in the field of semiconductors and optoelectronics. In these applications the exciton dynamics play an important role and can determine the suitability of a certain structure. Femtosecond pump probe spectroscopy is the standard method for characterising exciton dynamics but its adoption for use on organic micro- and nanostructures is not without challenge. The main problem is increasing the spatial resolution to a level that a specific structure can be studied while maintaining a high signal to noise ratio. Additionally, tightly focussing spectrally broad light represents another challenge as chromatically compensated optics cannot be used with fs laser pulses. It is for these reasons that typically only single colour experiments are conducted.

In this work we present a transient absorption microscope that is capable of resolving singular nanostructures. We are able to reach a spatial resolution lower than $1\ \mu\text{m}$ and a sub-100 fs time resolution while managing to cover nearly the whole visible spectrum as well as parts of the NIR.

MO 29.7 Fri 12:45 HS XV

Time-resolved UV-vis Spectroelectrochemistry — ●NINA BRAUER¹, RAMISHA RABEYA¹, ROBERT FRANCKE², and STEFAN

LOCHBRUNNER¹ — ¹Institute of Physics, University of Rostock, Germany — ²Leibniz Institute for Catalysis, Rostock, Germany

Homogeneous electrocatalysis based on transition metal complexes holds great potential for carbon dioxide utilization. In order to develop an efficient catalytic system, detailed knowledge about each step of the complex reaction chain is highly desirable. Therefore, the identification of short-lived intermediates and the determination of their life-times is of crucial importance here.

Spectroelectrochemistry has proven to be a powerful experimental approach to determine the reaction dynamics during electrocatalytic processes. In this work, a time-resolved UV-vis spectroelectrochemistry setup is developed using laser pulses to achieve a time resolution of microseconds. In contrast to previous work, this enables precise detection of catalytic reaction rates down to the diffusion limit. In the experiment, a femtosecond supercontinuum is focused closely to the working electrode surface inside a custom electrochemical cell based on a quartz glass cuvette. Upon applying a potential step to the electrodes, the induced absorption change inside the diffusion layer is measured as a function of time.