Symposium Size Selected Metal Cluster Spectroscopies (SYMC)

jointly organized by
the Atomic Physics Division (A),
the Molecular Physics Division (MO), and
the Mass Spectrometry Division (MS)

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Isolated atomically precise metal clusters – in particular those of transition metals – and metal-molecule complexes form a fascinating microsopic world on their own. They provide for uniqe properties that relate to and interpolate between atomic and bulk metal properties. Scaling laws help to interpret, and non scalable exceptions superimpose in numerous cases which are hardly predictable. The selection of speakers of this symposium provides for a good representation of research at the very forefront in this area. The outreach is manifold and will be highlighted by the individual contributions.

Overview of Invited Talks and Sessions

(Lecture hall Paulussaal)

Invited Talks

SYMC 1.1	Thu	11:00–11:30	Paulussaal	**Infrared spectroscopic studies of molecular activation at metal clusters** — •Stuart Mackenzie
SYMC 1.2	Thu	11:30–12:00	Paulussaal	**Dynamic metal-metal cooperation in chemical reactions** — •Jana Roithová
SYMC 1.3	Thu	12:00–12:30	Paulussaal	**A closer look at the electronic structure of simple metal clusters** — •Bernd von Issendorff
SYMC 1.4	Thu	12:30–13:00	Paulussaal	**IR action spectroscopy of metal clusters, complexes and diatomics with free electron lasers** — •André Fielicke

Sessions

SYMC 1.1–1.4	Thu	11:00–13:00	Paulussaal	**Size Selected Metal Cluster Spectroscopies**

SYMC 1: Size Selected Metal Cluster Spectroscopies

Time: Thursday 11:00–13:00 Location: Paulussaal

Invited Talk SYMC 1.1 Thu 11:00 Paulussaal

Infrared spectroscopic studies of molecular activation at metal clusters — •Stuart Mackenzie — University of Oxford, UK

Infrared action spectroscopy has proven itself a powerful technique for understanding molecular activation at metal centres, be they transition metal clusters or in metal ligand complexes.

This presentation will provide and overview of these methods including several illustrative examples of our recent work involving both laboratory and IR free electron lasers. It will cover molecular activation of important species such as nitrogen and carbon oxides together with cooperative and competitive binding effects. Of particular note will be examples in which infrared absorption can drive novel bond-breaking chemistry within activated molecular adsorbates.

Invited Talk SYMC 1.2 Thu 11:30 Paulussaal

Dynamic metal-metal cooperation in chemical reactions — •Jana Roithová — Radboud University, Nijmegen, The Netherlands

Textbook descriptions of organometallic reaction mechanisms typically feature metal complexes with a single metal atom. However, these reactions frequently also give rise to polymetallic complexes, which can be crucial in the processes under study. Incorporating multiple metals renders the mechanistic explanations less straightforward and more complex, leading to the frequent exclusion of polymetallic complexes in such discussions. Many researchers tend to limit their mechanistic models to mononuclear complexes, often resorting to less favored oxidation states or high-energy steps. In my presentation, I will explore how the dynamic formation and disintegration of bimetallic complexes can facilitate these reactions, circumventing steps that are otherwise unfavorable.

Invited Talk SYMC 1.3 Thu 12:00 Paulussaal

A closer look at the electronic structure of simple metal clusters — •Bernd von Issendorff — Physikalisches Institut, Universität Freiburg

Simple metal clusters are close to ideal few to many particle quantum systems, which can be seen as a well-defined number of electrons trapped in a harmonic potential. This leads to the well know electron shell structure discovered almost 50 years ago [1], a highly discretized density of states consisting of angular momentum eigenstates. It also has direct consequences for dynamics like photoemission; the angular distribution of photoelectrons exhibits a universal behavior in accordance with a very simple model [2]. Nevertheless, the almost free electrons in simple metal clusters do interact with the structured ion background, which perturbs and mixes the electronic states. Characterizing this perturbation by measuring the electronic density of states via photoelectron spectroscopy can therefore yield information about the cluster geometric structure. On both the experimental and the theoretical part a significant progress has been made over recent years, permitting a much more detailed insight into the electronic structure of metal clusters and its interplay with the geometric structure. I will discuss examples of simple metal cluster systems of increasing complexity, from sodium over copper and silver to gold, some of them showing unexpected geometric structures as well as exotic electronic states.

[1] W. D. Knight et al., Phys. Rev. Lett. **52**, 2141 (1984)
[2] A. Piechaczek et al., Phys. Rev. Lett. **126**, 233201 (2021)

Invited Talk SYMC 1.4 Thu 12:30 Paulussaal

IR action spectroscopy of metal clusters, complexes and diatomics with free electron lasers — •André Fielicke — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Structural studies of gas-phase species that are only meta-stable can possess a number of experimental challenges: the gas-phase densities achievable are usually extremely low and often they are present in complex mixtures, e.g., broad distributions of cluster sizes and/or compositions. An approach to these difficulties offers infrared (IR) action spectroscopy that relies on mass spectrometric means to detect photo absorption processes. In my talk I will briefly discuss recent insights into the structures of neutral gold clusters obtained from far-IR spectroscopy in combination with DFT and coupled-cluster theory.[1] In this case, multiple photon dissociation of krypton complexes is used to monitor the cluster-size specific IR absorption. Furthermore, we have applied vibrational autoionization of Rydberg states for IR spectroscopy of cationic species, using weakly interacting non core-penetrating Rydberg electrons as messenger. This will be illustrated for DyO^+ for which rotationally resolved vibrational spectra have been obtained.

[1] Chem. Commun. 2022, 58, 5785; Phys. Chem. Chem. Phys. 2023, 25, 9036.