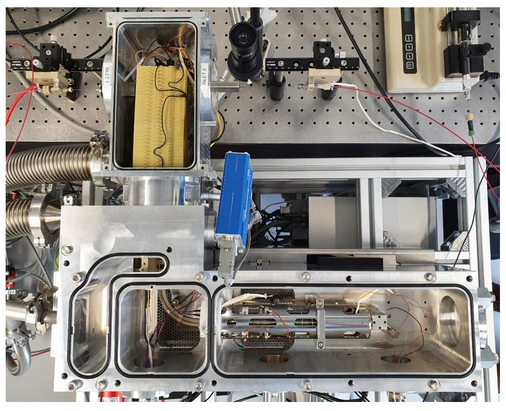
UNIVERSITÄT LEIPZIG

Chemistry of Reactive Intermediates
Junior Research Group Warneke

Ion Soft-landing

- Electrospray ionization mass spectrometry (ESI-MS) is widely used in chemical analysis.
- Inside the mass spectrometer ions can be excited to generate highly reactive fragment ions which are not amenable in the condensed phase.
- Ion soft-landing allows the deposition of mass selected gaseous ions on surfaces and therefore enables their utilization for preparative applications.

Experimental Setup



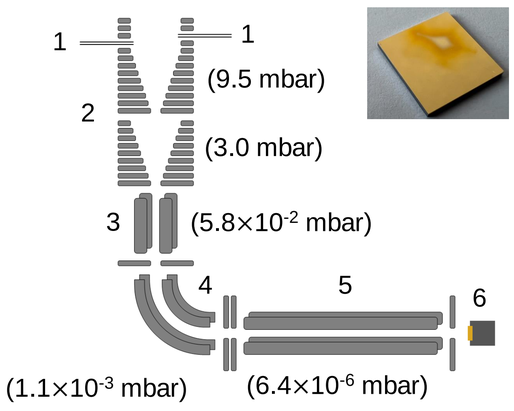
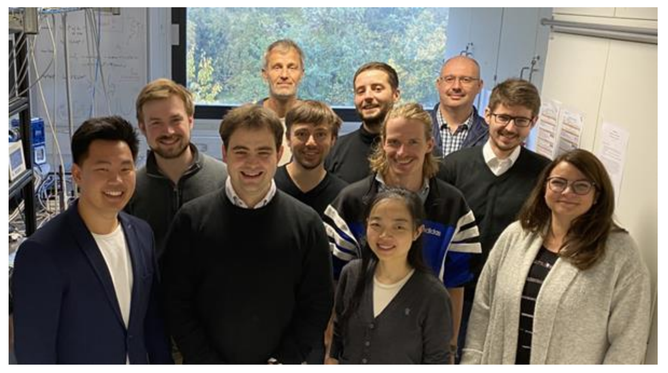


Figure 1. Photography of the ion soft-landing instrument (left). Scheme of the instrument (right) with 1) inlet capillaries, 2) double ion funnel system, 3) collision cell, 4) bending ion guide, 5) resolving quadrupole and 6) sample holder with a gold target. Typical pressure regions during deposition are given in brackets.[1] Deposition target with visible spot.

Surface Analysis

- Liquid extraction surface analysis (LESA) of deposited surfaces and mass spectrometric investigation
- *Ex situ* measured IR spectra of the reaction products on the surface in reflection mode
- XPS measurements with cooperation partners

Team / Contact



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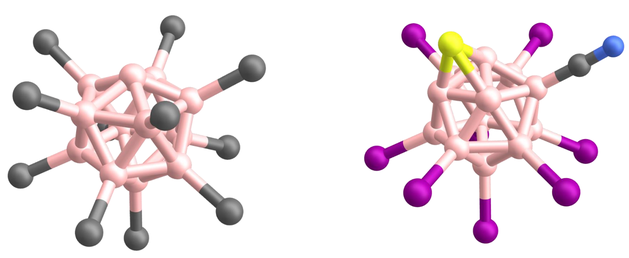
Chemistry with Reactive Anionic *closo*-Borate Fragments

- Collision induced dissociation (CID) of anionic *closo*-borates leads to highly reactive fragment ions. Examples are shown below.



$[B_{12}X_{11}]^-$ $[B_{12}I_8SCN]^-$

- $[B_{12}X_{11}]^-$ (X = halogens, CN) are known as electrophilic anions and show extraordinary reaction behavior in the gas phase.[2]
- $[B_{12}Br_{11}]^-$ reacts with atmospheric N_2 in the collision cell to form stable $[B_{12}Br_{11}N_2]^-$ ions, which were detected with IR spectroscopy and LESA after deposition.
- $[B_{12}I_{11}]^-$ showed „anion-anion-reaction-products“ when deposited on $[B_{12}I_{12}]^{2-}$.[3]

Stabilizing Undercoordinated Metal Cations

- Undercoordinated metal centers play an important role in catalysis and hydrogen isotope separation.
- We generate undercoordinated metal complexes *via* fragmentation in the gas phase. Ion soft-landing enables their deposition from the gas phase on surfaces.
- We probe the reactivity of undercoordinated metal complexes on surfaces under various conditions and investigate their stabilization using weakly coordinating counterions.
- Example: $[Ru(bpy)_2]^{2+}$ shown in Figure 2.

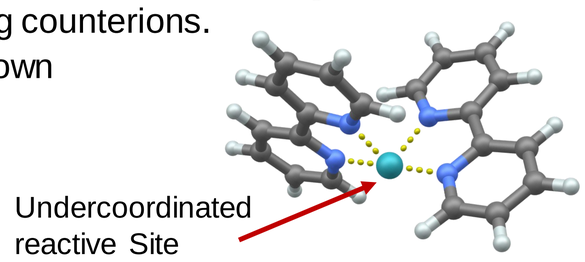


Figure 2. Structure of $[Ru(bpy)_2]^{2+}$ (bpy = bipyridine).

Selective Binding of Fragments by Ion Soft-landing

- Proof of concept study: The fragment ions $[B_{12}I_{11}]^-$ and $[B_{12}I_8SCN]^-$ were bound to Leucylproline and the binding motive is investigated and compared.
- $[B_{12}I_{11}]^-$ binds *via* the alkyl chain (see Figure 3), but $[B_{12}I_8SCN]^-$ attacks a functional group.

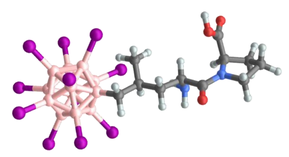
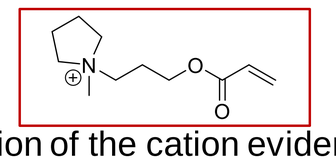
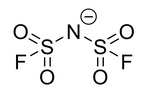


Figure 3. Assumed structure of the reaction product $[B_{12}I_{11}(C_{11}H_{19}N_2O_3)]^{2-}$.

Investigating the Chemistry in Charge-imbalanced Layers

- How do permanently charged ions react, if they are deposited on surfaces without their counterions?
- Investigations performed with the cations of ionic liquids.





- Polymerization of the cation evidenced in the layer if charge-balancing counterions are absent.

Joint Lab: Surface Engineering with Mass-selected Molecular Ions

- Joint lab with the Leibniz Institute of Surface Engineering (IOM).
- Cooperation with the IOM group “Switchable molecularly functionalized surfaces” (Monakhov)[4] for applications in molecular electronics.
- Deposition of molecular memory units (polyoxometalates (POMs)) stabilized as host-guest-complexes with cyclodextrin.
- Imaging and resistive switching of deposited units by scanning tunneling microscopy and spectroscopy.

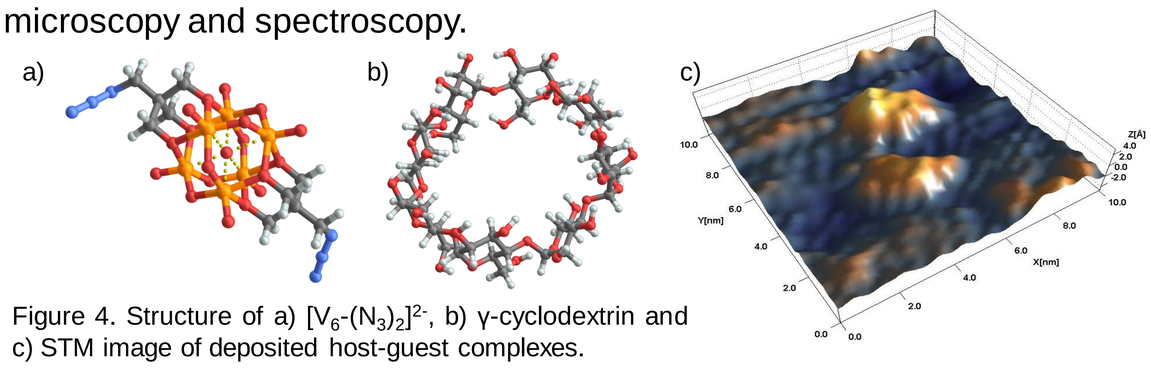


Figure 4. Structure of a) $[V_6\text{-}(N_3)_2]^{2-}$, b) γ-cyclodextrin and c) STM image of deposited host-guest complexes.

References

[1] H. Y. Samayoa-Oviedo, K.-A. Behrend, S. Kawa, H. Knorke, P. Su, M. E. Belov, G. Anderson, J. Warneke, J. Laskin, *Anal. Chem.* **2021**, *93*, 14489.
[2] M. Mayer, M. Rohdenburg, S. Kawa, F. Horn, H. Knorke, C. Jenne, R. Tonner, K. R. Asmis, J. Warneke, *Chem. Eur. J.* **2021**, 27, 10274.
[3] F. Yang, K. A. Behrend, H. Knorke, M. Rohdenburg, A. Charvat, C. Jenne, B. Abel, J. Warneke, *Angew. Chem. Int. Ed.* **2021**, 60, 24910.
[4] F. Yang, M. Moors, D. A. Hoang, S. Schmitz, M. Rohdenburg, H. Knorke, A. Charvat, X.-B. Wang, K. Y. Monakhov, J. Warneke, *ACS Appl. Nano Mater.* **2022**, 5, 14216.