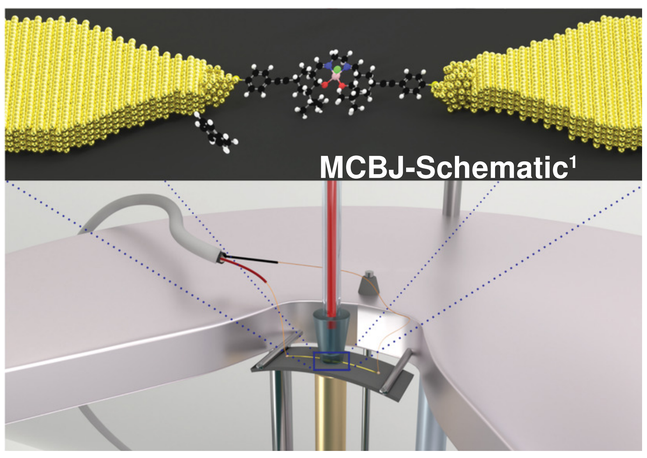
Simulations of the Evolution of Molecular Binding in Mechanically controlled Break-Junctions

Lokamani[1,6], Filip Kilibarda[6], Florian Günther[2], Jeffrey Kelling[1], Alexander Strobel[6], Peter Zahn[6], Guido Juckeland[1], Kurt V. Gothelf[3], Elke Sheer[4], Sibylle Gemming[5] & Artur Erbe[6]

[1] Department of Information Services and Computing, Helmholtz-Zentrum Dresden Rossendorf, 01328 Dresden, Germany
[2] Instituto de Física de São Carlos, Universidade de São Paulo (USP), São Carlos, Brazil
[3] Department of Chemistry and Interdisciplinary Nanoscience Center, Centre for DNA Nanotechnology, iNANO, Gustav Wieds Vej 14, Aarhus C, 8000 Denmark
[4] Department of Physics, University of Konstanz, 78457 Konstanz, Germany
[5] Institute of Physics, Technische Universität Chemnitz, 09107 Chemnitz, Germany
[6] Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden Rossendorf, 01328 Dresden, Germany

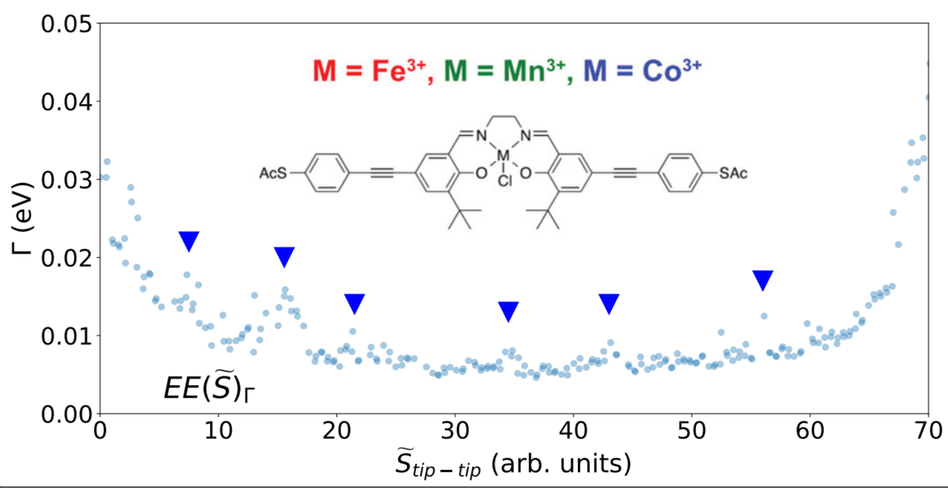
HZDR

HELMHOLTZ ZENTRUM DRESDEN ROSSENDORF



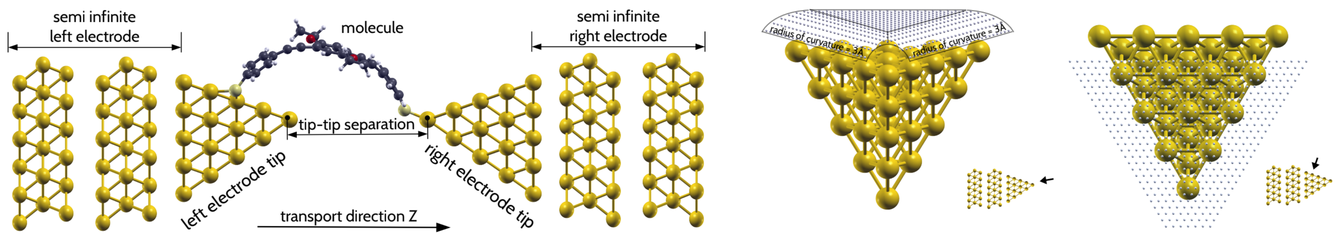
MCBJ → extremely precise measurements of IV characteristics of single molecules using atomistically structured metallic electrodes

Single opening curve measurements on Co-Salen



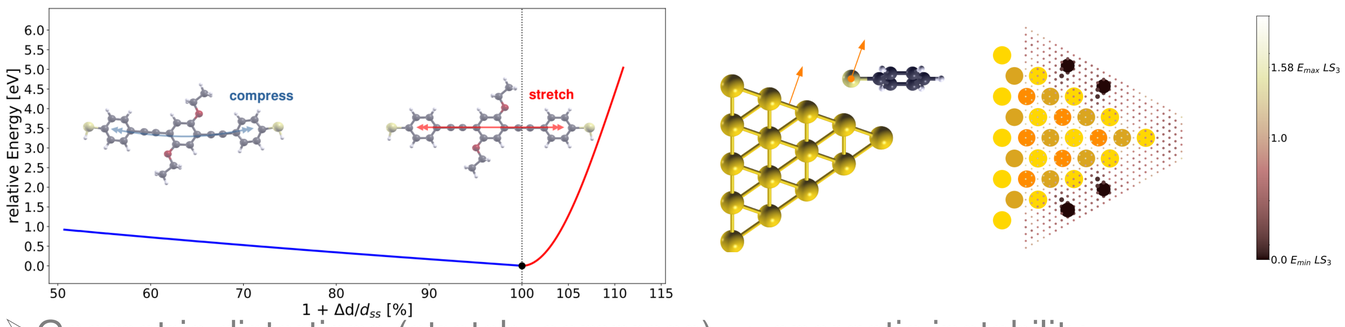
- Consecutive acquisition of 2 IV-curves at single bridge position
- **„stretch"-evolution Gamma Γ** shows falling trend for shorter tip-tip separation and rising trend before breakoff.
- recurrent peaks/protrusion blue triangles

Transport simulation setup



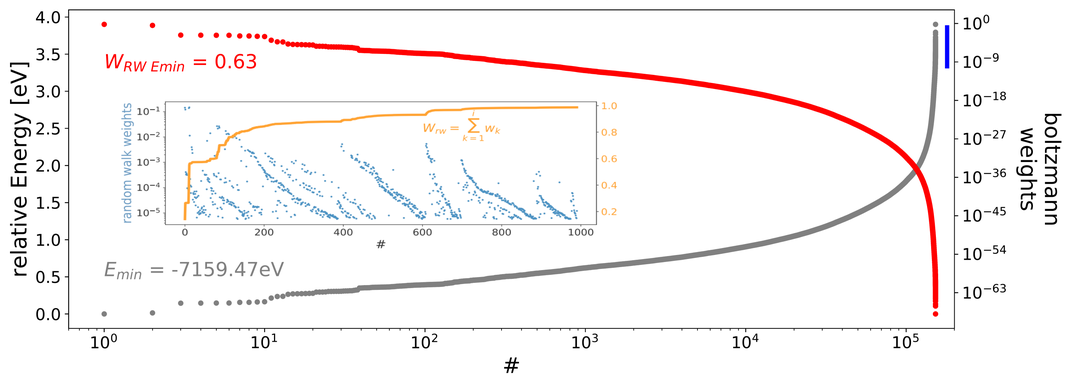
- Transport setup – scattering region with molecule and semi infinite electrodes
- Electrodes – equilateral tip with edge length 4 x 2.885 Å
- 540 grid points on facets | Local fcc-coordination symmetry

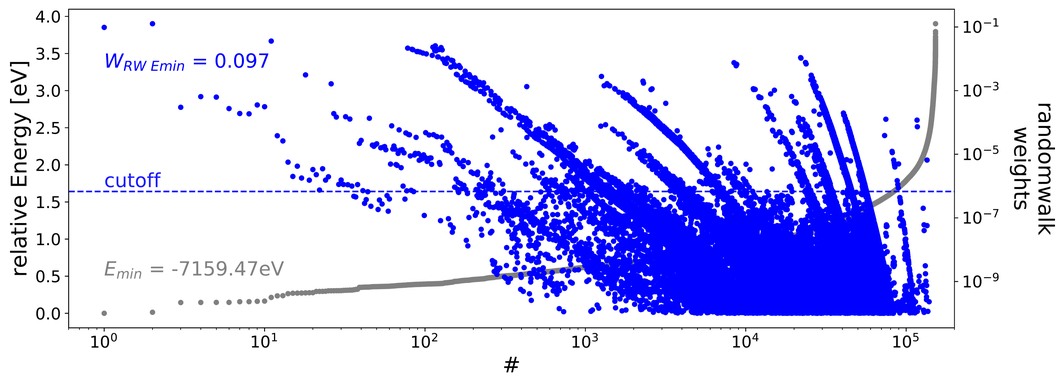
Concurrent processes – Geometric distortion vs Anchoring on facets



- Geometric distortions (stretch, compress) → energetic instability
- Competing with anchoring binding energy on Au-facets
- Energy landscape not flat (see color code) → **(non-)equilibrium state?**

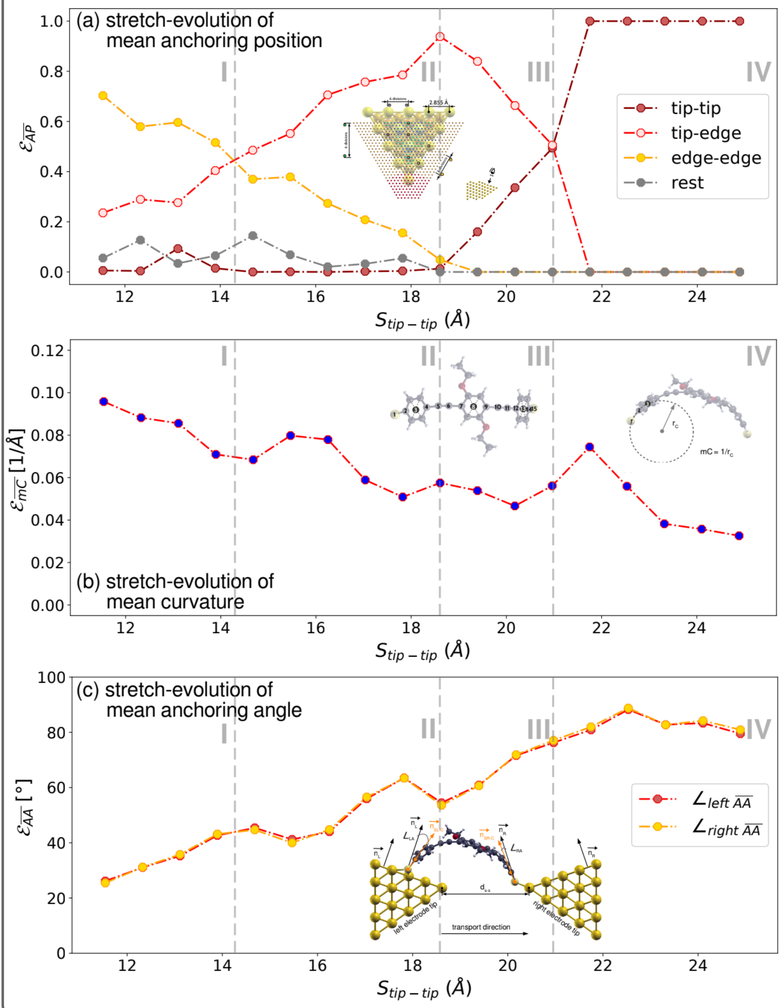
Statistical averaging of ε and Γ



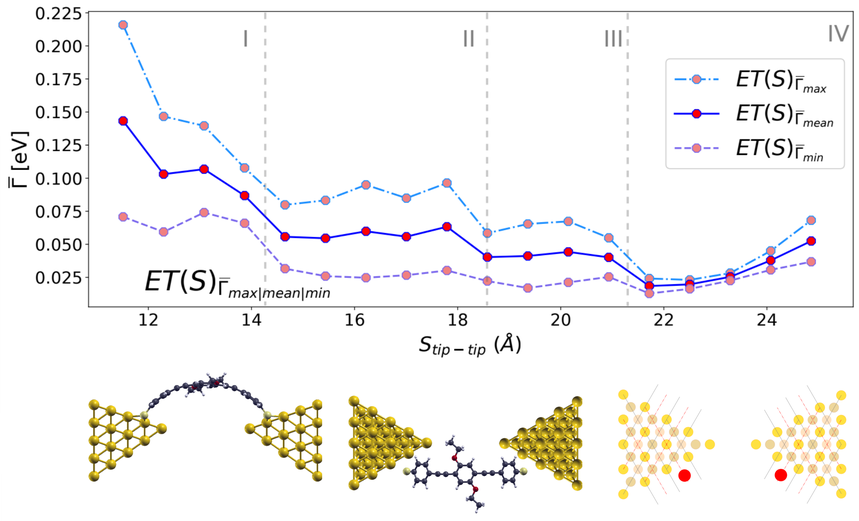


- (Non-)equilibrium weights evaluted using master equation[2]
- Random walk stepping between neighboring anchor positions on grid with Metropolis transition rate.
- Local minima supressed in equilibrium [by Boltzmann weight] accumulate significant random walk weights

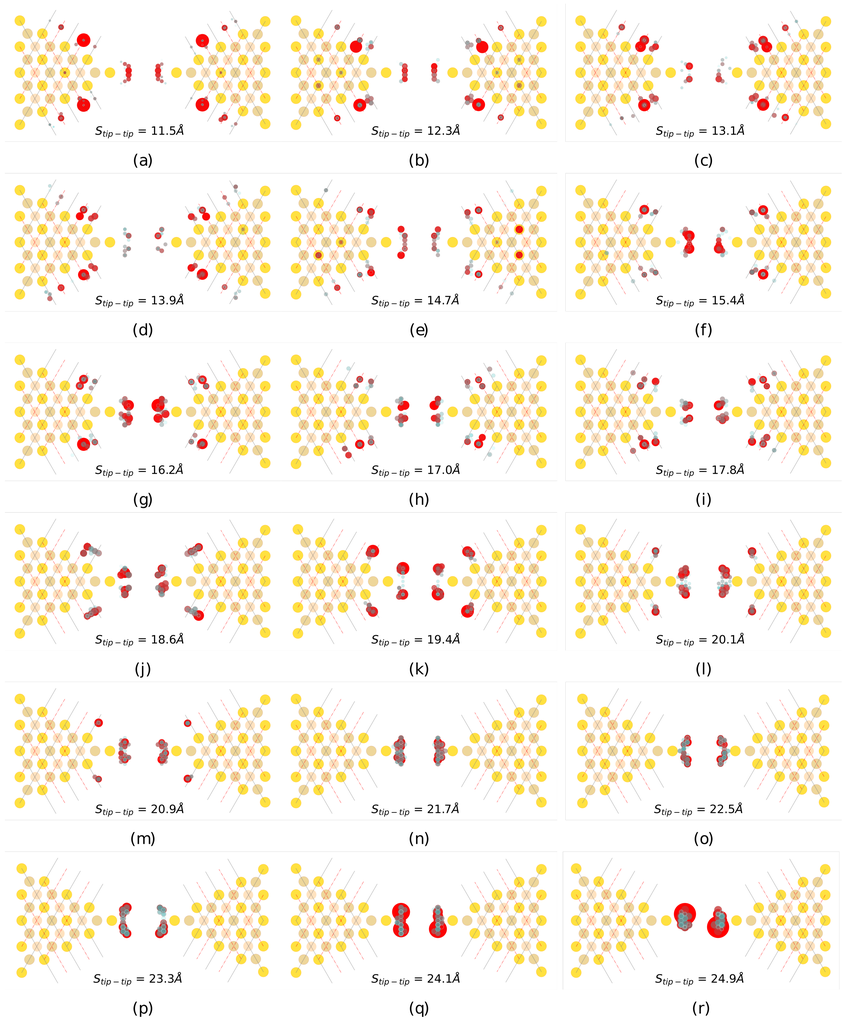
Geometric structural descriptors | „stretch"-evolution of Gamma Γ | Realspace projection of Gamma Γ evolution



Mean anchoring position characterizes docking of sulphur atoms on the **Au(111)** facet, mean curvature of the molecular backbone accounts for bending/streching after docking, mean anchoring angle define the canting angle ∠ **Au-S-C**.



- **Rising/falling** trends and local **maxima** for tip-tip seperation < **22Å** associated with shift of dominant anchoring positions btw. **top** and **bridge** sites along facet edges and **planarity** of the molecule
- **Rising** trend before break-off associated with additional **rotational** degrees of freedom



Notes on High-throughput Calculations using DFTB+[3,4]

Tip-separations in the range from 11.5 Å to 26.46 Å in steps of 0.825 Å

possible anchoring configurations per tip-tip separation = 291600

Transport calculation for up to 1000 configurations sorted w.r.t random walk weights acquired after 10000 Metropolis steps

References and Acknowledgements

[1] Filip Kilibarda et. al., https://doi.org/10.1002/aelm.202100252
[2] https://doi.org/10.1016/B978-044452965-7/50008-8
[3] B. Aradi, B. Hourahine, and Th. Frauenheim, DFTB+, a sparse matrix-based implementation of the DFTB method, J. Phys. Chem. A, 111 5678 (2007)
[4] Elstner, M. and Porezag, D. and Jungnickel, G. and Elsner, J. and Haugk, M. and Frauenheim, Th. and Suhai, S. and Seifert, G.. Self-consistent-charge density-functional tight-binding method for simulations of complex materials properties, PRB 58, 7260 (1998)

Computational resources at HZDR and ZIH TU Dresden, and financial support from HGF Nanonet, SG: HGF W2/W3 and HGF DCM-MatDNA

Dipl.-Ing. Lokamani | HZDR | FWCC and FWIO | m.lokamani@hzdr.de | www.hzdr.de