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

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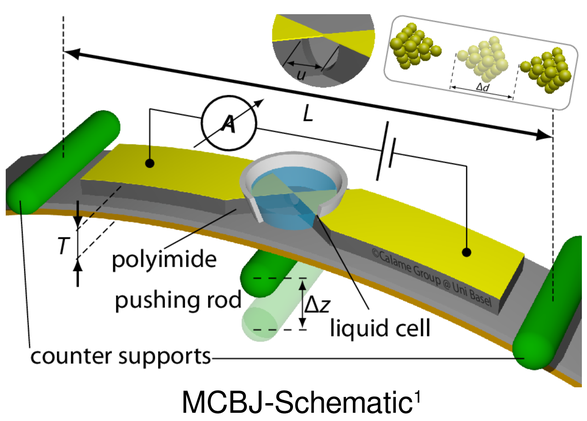
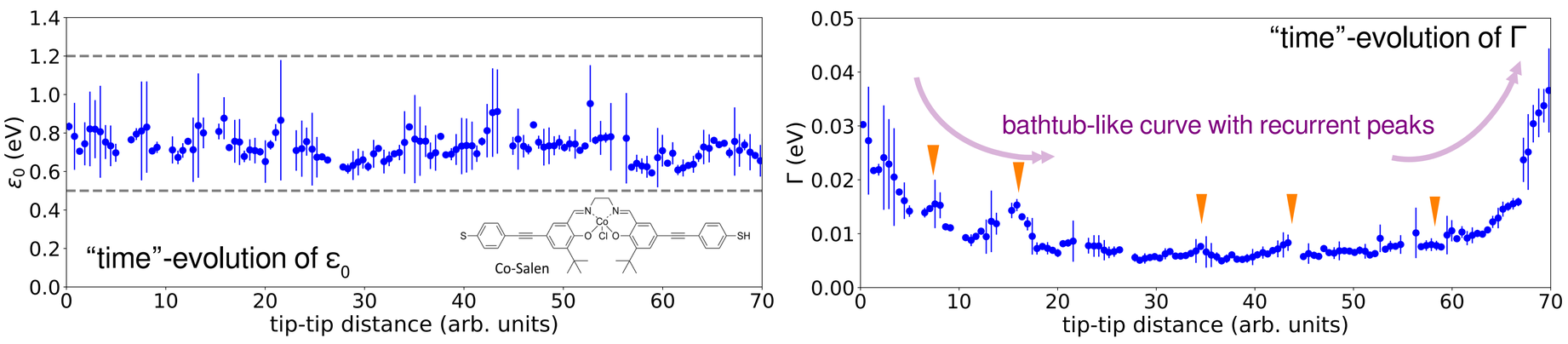


MCBJ-Schematic[1]

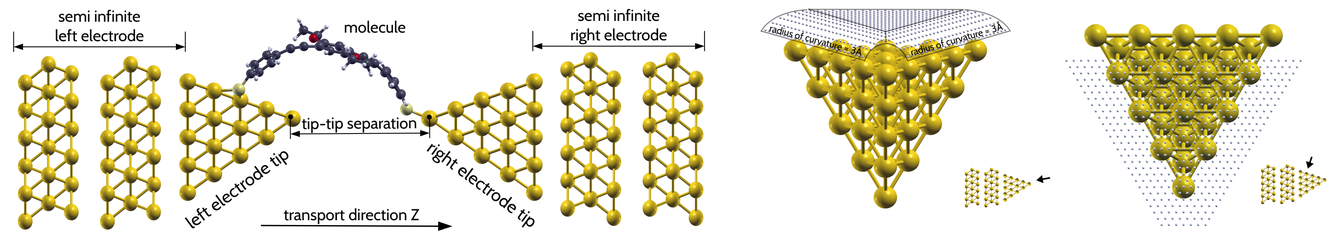
- MCBJ → extremely precise measurements of IV characteristics of single molecules using atomistically structured metallic electrodes

Single opening curve measurements on Co-Salen



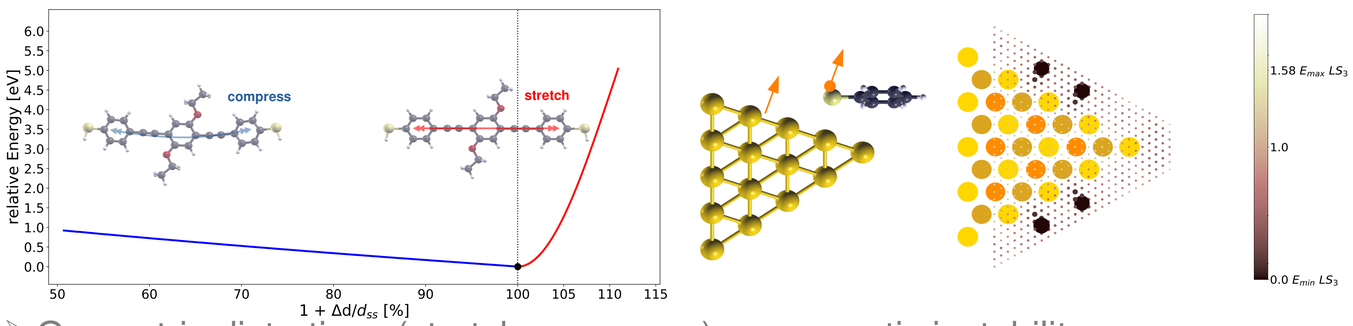
- Consecutive acquisition of 2 IV-curves at single bridge position → variation of parameters shown using red bars (blue dots show mean value)
- „**time“-evolution ε$_0$** fluctuates in the range 0.5 to 1.2 eV | „**time“-evolution Γ** bathtub-like curve w. recurrent peaks (orange triangles)

Transport simulation setup



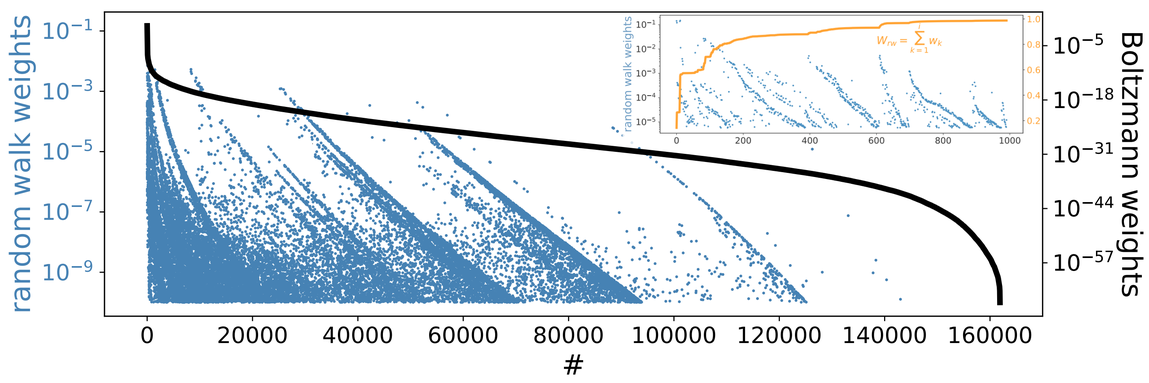
- Transport setup – scattering region with molecule and semi infinite electrodes
- Electrodes – equilateral tip with edge length 4 x 2.885 Å
- 540 grid points on facets | Local fcc-coordination symmetry

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

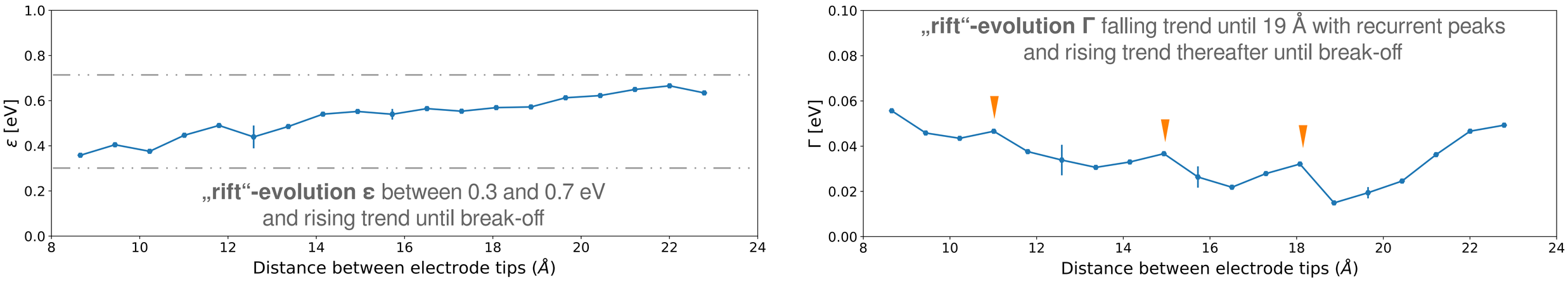


- (Non-)equilibrium weights evaluted using master equation[2]
- Random walk stepping between neighboring anchor positions on grid with Metropolis transition rate
- local minimal suppressed in equilibrium [by Boltzmann weight] accumulate significant random walk weights

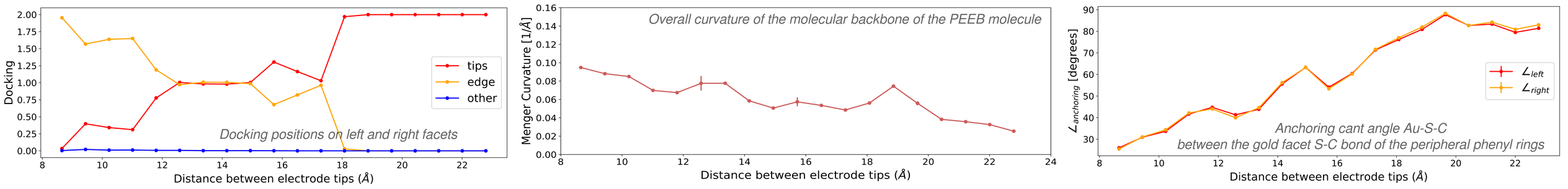
Notes on High-throughput Calculations using DFTB+[3,4]

Tip-separations in the range from 11.5 Å to 26.46 Å in steps of 0.825 Å
possible anchoring configurations per separation = 291600
Transport calculation for up to 1000 configurations
sorted w.r.t random walk weights acquired after 10000 Metropolis steps

„rift”-evolution of Epsilon ε and Gamma Γ | Geometric structural characteristics



- „**rift“-evolution** → Evolution of epsilon ε and Gamma Γ as tip-seperation increases → matches experimental findings
- „**rift“-evolution ε** → rising trend until break-off | „**rift“-evolution Γ** → falling trend with recurrent peaks followed by a rising trend until break-off



- Rising trend in „**rift“-evolution ε** due to decreasing induction of image charge[5] and renormalization of energy levels as the electrode shrinks towards the tip
- „**rift“-evolution ε** should reveal an overall falling trend due to the reduction in available charge states
- Peak-like features due to flattening of the molecule | Rising trend due to improving cant angle Au-S-C

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References

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