TECHNISCHE UNIVERSITÄT DRESDEN

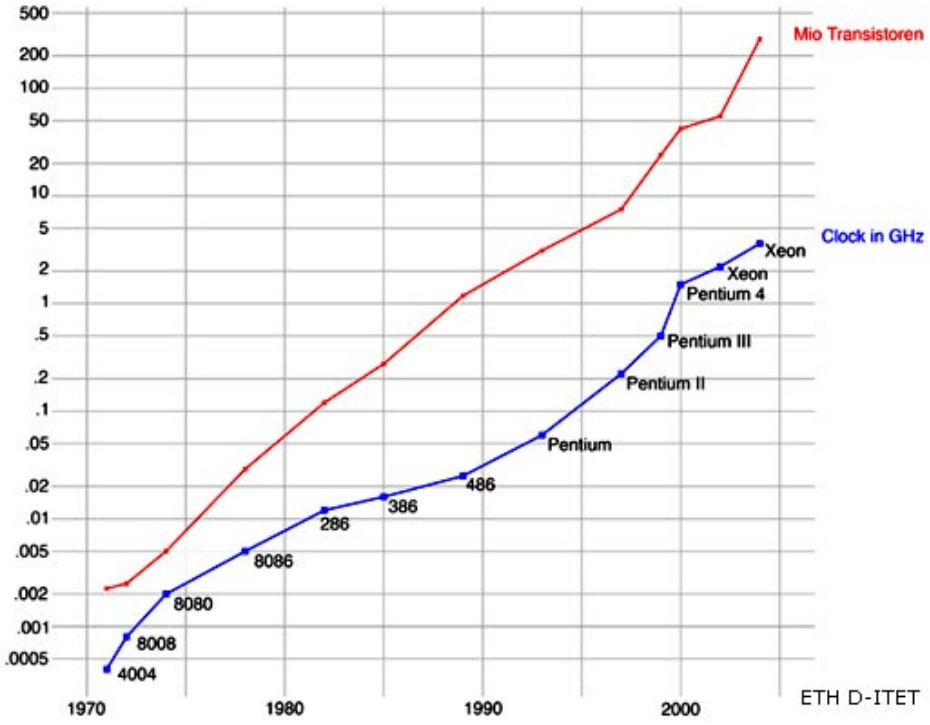
Institute for Material Science, Chair "Materials Science and Nanotechnology"

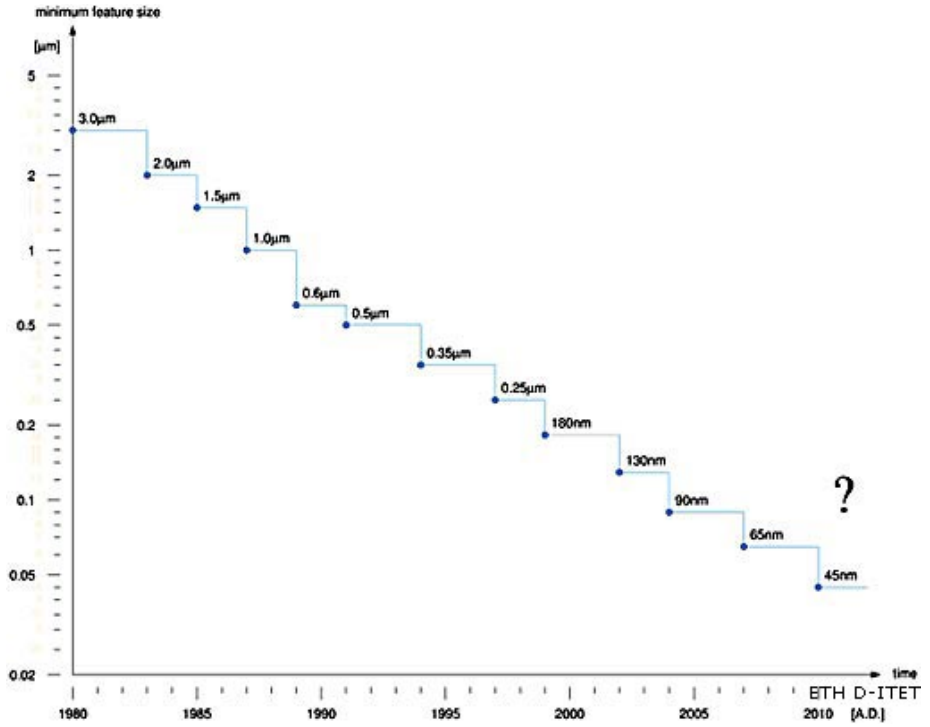
Towards molecular electronics:

Ab initio modeling of molecule–surface interactions

T. Brumme, IMPRS seminar, Dresden, 09.03.2011

Moore's law – Consequences and limitations



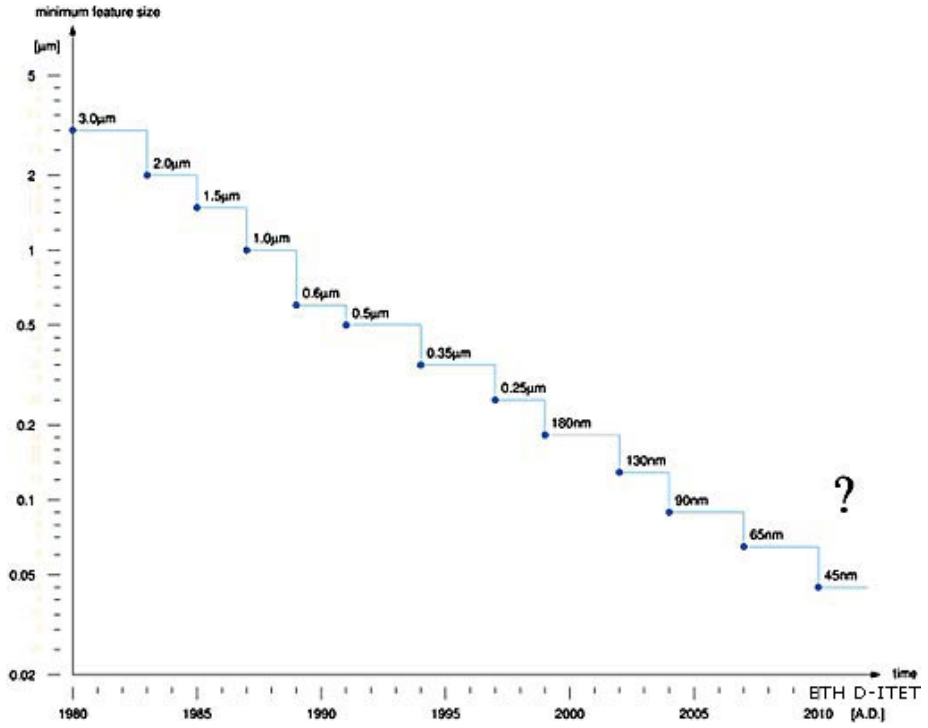


ETH Zürich, Roadmap der Mikroelektronik – eine Schlüsseltechnologie, 09.02.2011.
http://www.ethistory.ethz.ch/rueckblicke/departemente/ditet/weitere_seiten/hgs1_roadmap

Moore's law – Consequences and limitations

- 2003 clock speed saturated
- Multi-core CPUs as remedy
- DUV and EUV

- Lithography with UV?
- Power dissipation?
- Leakage current?
- Quantum effects?
- ...

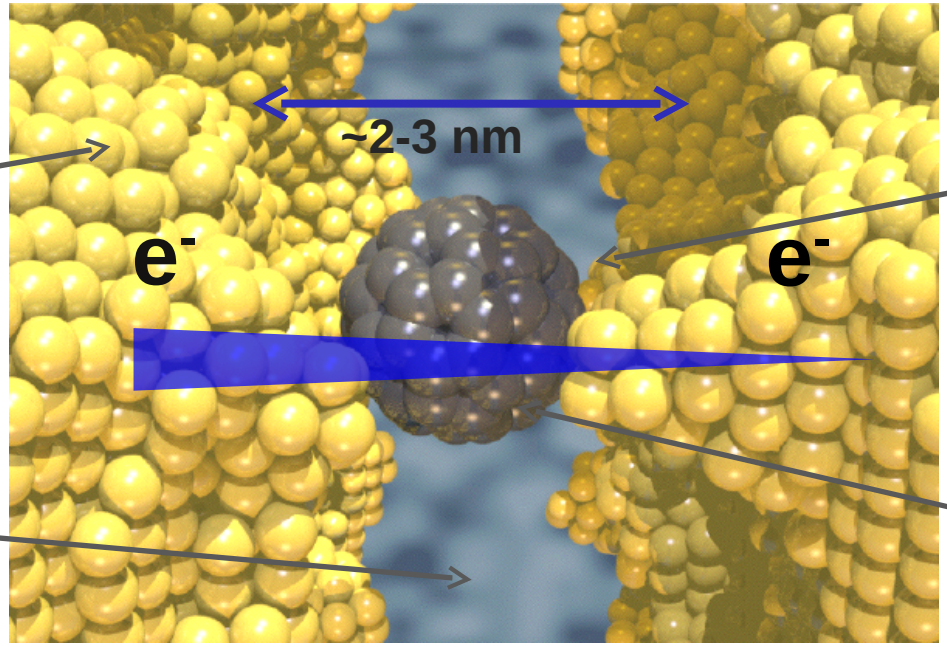


→ Molecular electronics / spintronics

Molecular electronics – Open questions / challenges

electrode electronic structure

environment

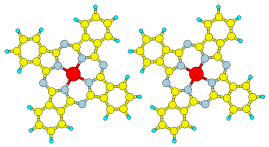


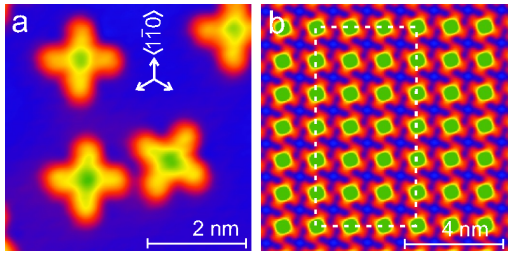
electrode-molecule interface

Molecular structure and dynamical properties

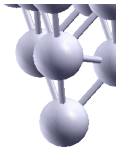
[E. Scheer, Uni Konstanz]

1 Electronic properties of molecules on surfaces

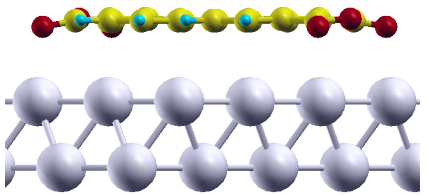




2 Dynamical bi-stability of a molecular junction



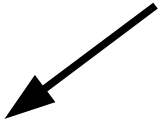
3 Outlook

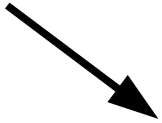


Open questions

Adsorption position / structure

Physisorption – Chemisorption ?





- Gas phase structure
- Van der Waals interaction
  - 2 separate weakly interacting systems
  - HOMO-LUMO gap relative to surface electronic structure

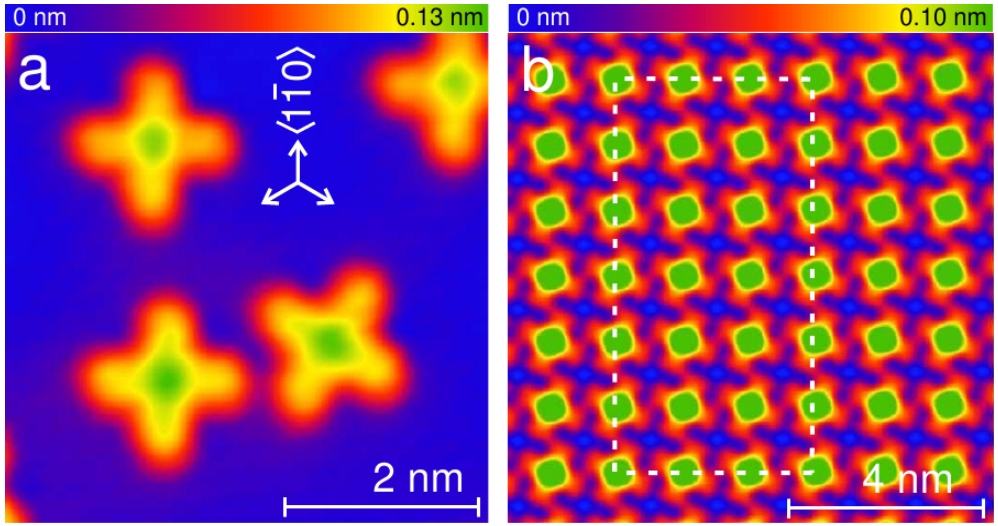
- Possibly distorted structure
- Chemical bond
  - Charge transfer
  - Hybridization
  - Reorganization of the energy levels

Methods

- Density functional theory – QuantumEspresso / SIESTA
  (http://www.quantum-espresso.org/, http://www.icmab.es/siesta/)
- Plane-wave basis set / Localized atomic orbitals
- Different approximations for E_{xc}
- Surfaces modeled with up to 6 layers
  => ~ 300 atoms for the largest system

Iron-phthalocyanine on Ag(111)

- Coverage-driven electronic decoupling of FePc from a Ag(111) substrate

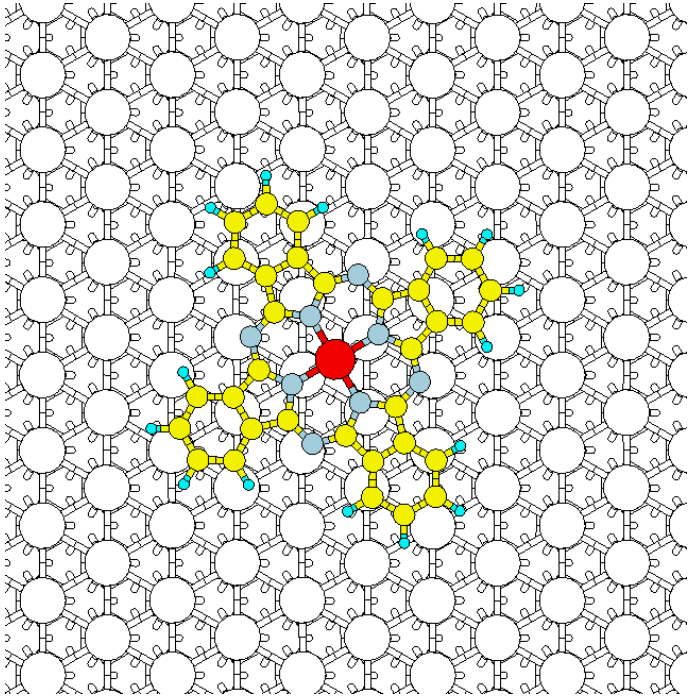


Constant-current STM images of (a) single FePc molecules and (b) a molecular superstructure on Ag(111).

T.G. Gopakumar, T. Brumme, J. Kröger, C. Toher, G. Cuniberti, R. Berndt, submitted (2011).

Iron-phthalocyanine on Ag(111)

- Single molecule adsorbs in bridge position



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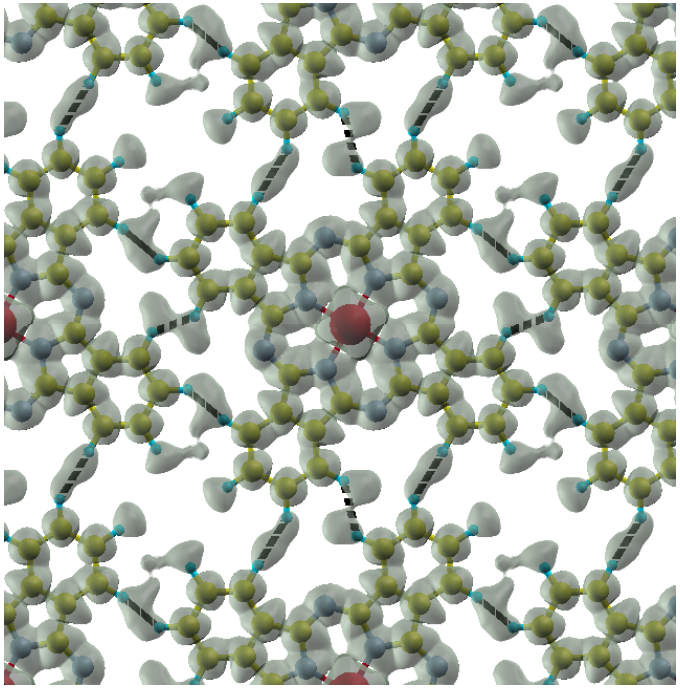
Iron-phthalocyanine on Ag(111)

- Single molecule adsorbs in bridge position
- Interaction between single FePc



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Iron-phthalocyanine on Ag(111)

- Single molecule adsorbs in bridge position
- Interaction between single FePc
  - => Increased adsorption height
  - => Reverse chemisorption
  - => Partial decoupling

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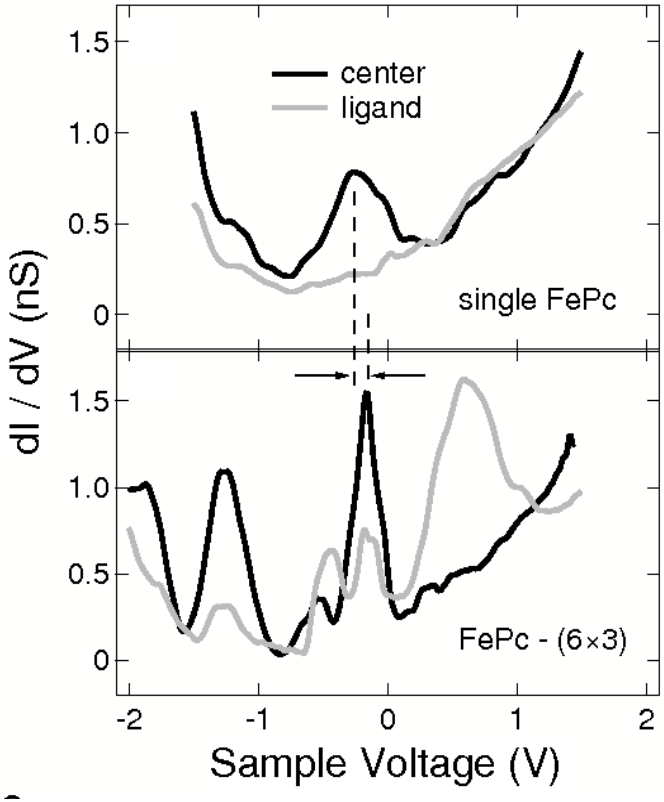

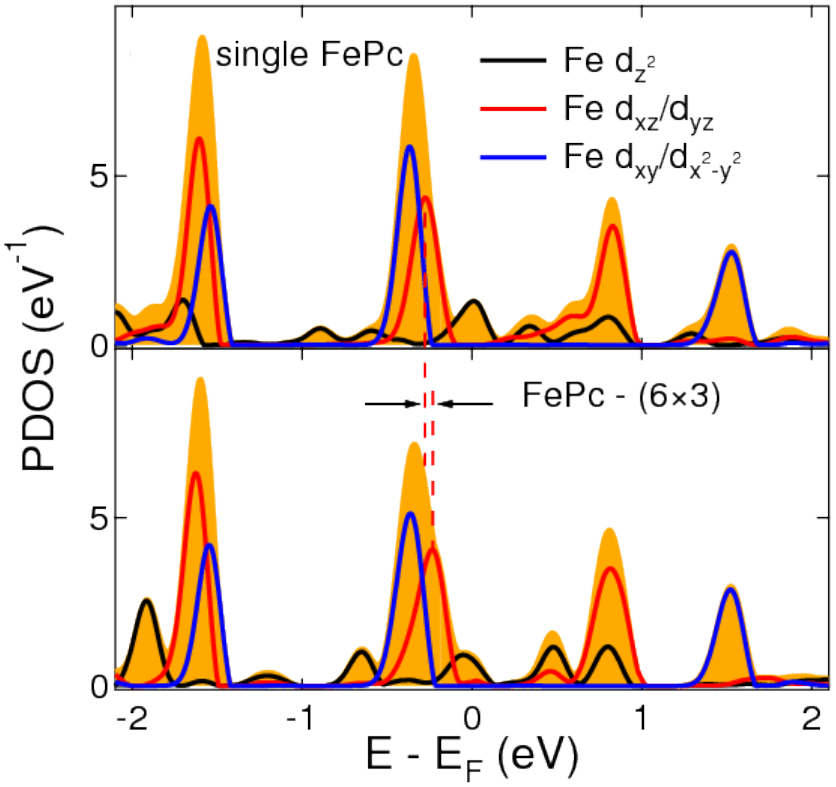

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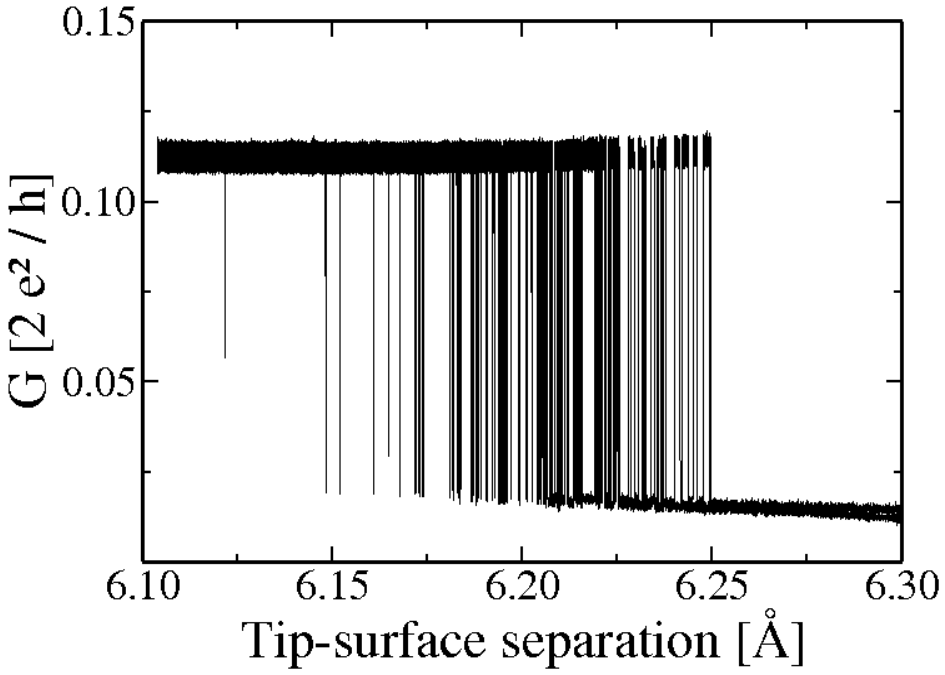
Electronic properties of molecules on surfaces

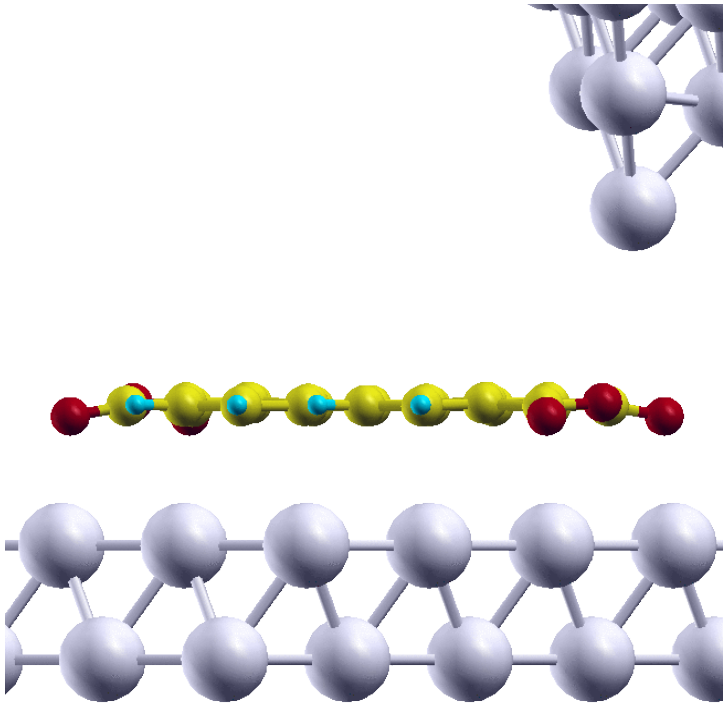
Iron-phthalocyanine on Ag(111)

- Single molecule adsorbs in bridge position
- Interaction between single FePc
  - => Increased adsorption height
  - => Reverse chemisorption
  - => Partial decoupling
- Monolayer of FePc molecules represents regular grid of scattering centers
  - => Changed surface electronic structure

T.G. Gopakumar, T. Brumme, J. Kröger, C. Toher, G. Cuniberti, R. Berndt, submitted (2011).

Dynamical bi-stability of a molecular junction





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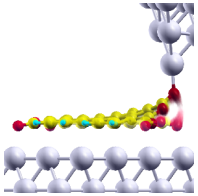
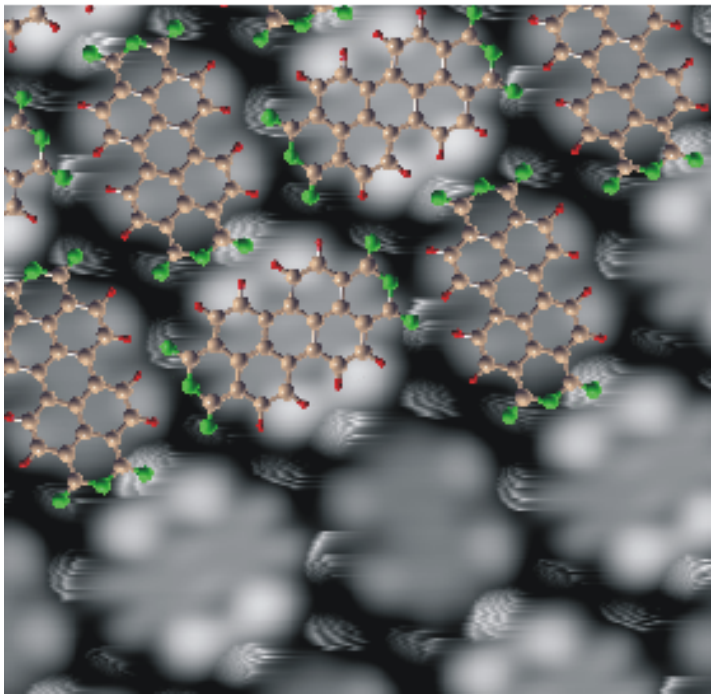


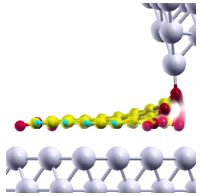
Dynamical bi-stability of a molecular junction

PTCDA on Ag(111)



- Highly ordered metal-organic interface
- Switching of oxygen (green) between surface and STM tip

T. Brumme *et al.*, submitted (2011).



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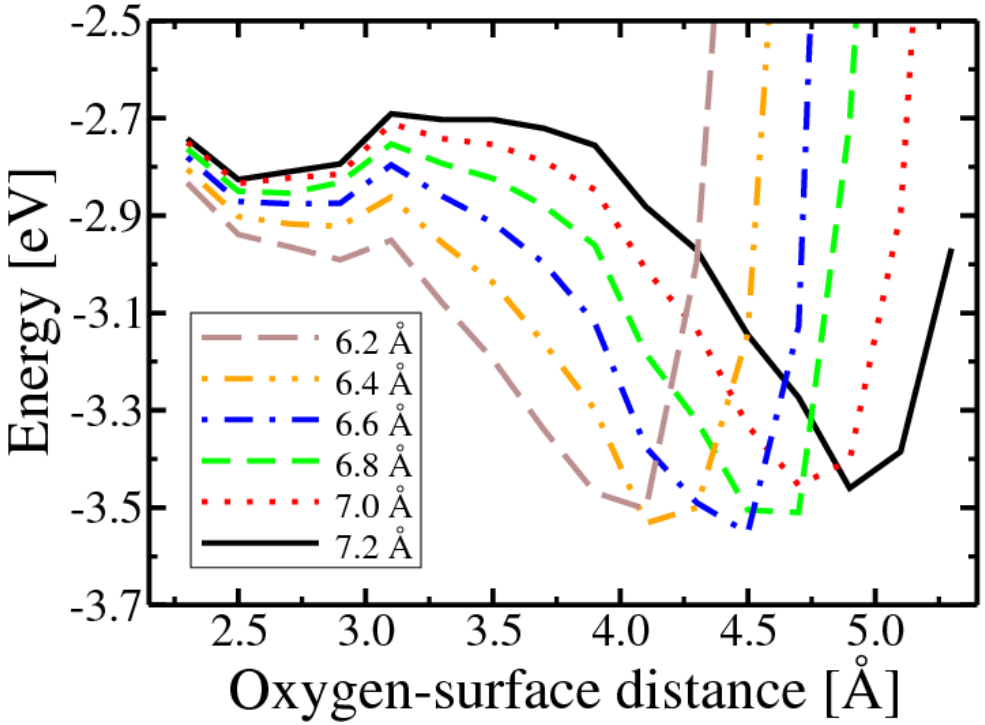
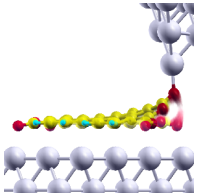


- Highly ordered metal-organic interface
- Switching of oxygen (green) between surface and STM tip
- DFT calculations reveal highly asymmetric double well

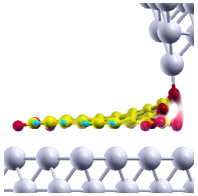
T. Brumme *et al.*, submitted (2011).



Dynamical bi-stability of a molecular junction

Can we explain the physical mechanism behind the switching?

T. Brumme *et al.*, submitted (2011).



Dynamical bi-stability of a molecular junction

Vibrational heating in single-molecule junctions

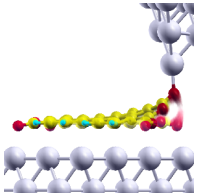
- Vibrational excitation of the C=0 bond by scattering of tunneling electrons
- Standard Transfer Hamiltonian for combined tip-molecule-substrate-system

$$H = \sum_{\alpha=s,t} \varepsilon_\alpha c_\alpha^\dagger c_\alpha + \varepsilon_m c_m^\dagger c_m + \sum_{\alpha=s,t} \left(T_{\alpha m} c_\alpha^\dagger c_m + H.c. \right) + \hbar\omega b^\dagger b$$

$$H_{e-v} = \lambda_0 \left(b^\dagger + b \right) \left(c_m^\dagger c_m \right)$$

- Excitation/relaxation rates given by Fermi's Golden Rule

T. Brumme *et al.*, submitted (2011).



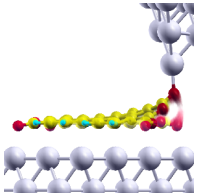
Dynamical bi-stability of a molecular junction

- Transition rates

$$\Gamma_{\downarrow} = 2\,\frac{2\pi}{\hbar}\sum_{i,f}\left|\langle f,0|H_{e-v}|i,1\rangle\right|^2\,\mathrm{F}_i\left(1-\mathrm{F}_f\right)\,\delta\left(\varepsilon_f-\varepsilon_i-\hbar\,\omega\right)$$

$$\Gamma_{\uparrow} = 2\,\frac{2\pi}{\hbar}\sum_{i,f}\left|\langle f,1|H_{e-v}|i,0\rangle\right|^2\left(1-\mathrm{F}_f\right)\mathrm{F}_i\,\delta\left(\varepsilon_f-\varepsilon_i-\hbar\,\omega\right)$$

T. Brumme *et al.*, submitted (2011).



Dynamical bi-stability of a molecular junction

- Transition rates

$$\Gamma_{\downarrow} = 2\,\frac{2\pi}{\hbar}\,\lambda_0^2 \int \left(\rho_m^f(\varepsilon+\hbar\omega)\,\rho_m^i(\varepsilon)\left[1-\mathrm{F}^f(\varepsilon+\hbar\omega)\right]\mathrm{F}^i(\varepsilon)\right) d\varepsilon$$

$$\Gamma_{\uparrow} = 2\,\frac{2\pi}{\hbar}\,\lambda_0^2 \int \left(\rho_m^f(\varepsilon)\,\rho_m^i(\varepsilon+\hbar\omega)\left[1-\mathrm{F}^f(\varepsilon)\right]\mathrm{F}^i(\varepsilon+\hbar\omega)\right) d\varepsilon$$

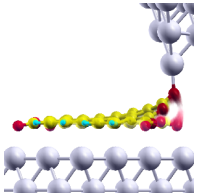
- Molecular level broadened due to interaction with surface (Δ^s) and tip (Δ^t)

$$\rho_m^{s,t}(\varepsilon) = \frac{\Delta^{s,t}}{\left(\varepsilon-\varepsilon_m\right)^2 + \left(\Delta^s+\Delta^t\right)^2}$$

- Low temperature limit

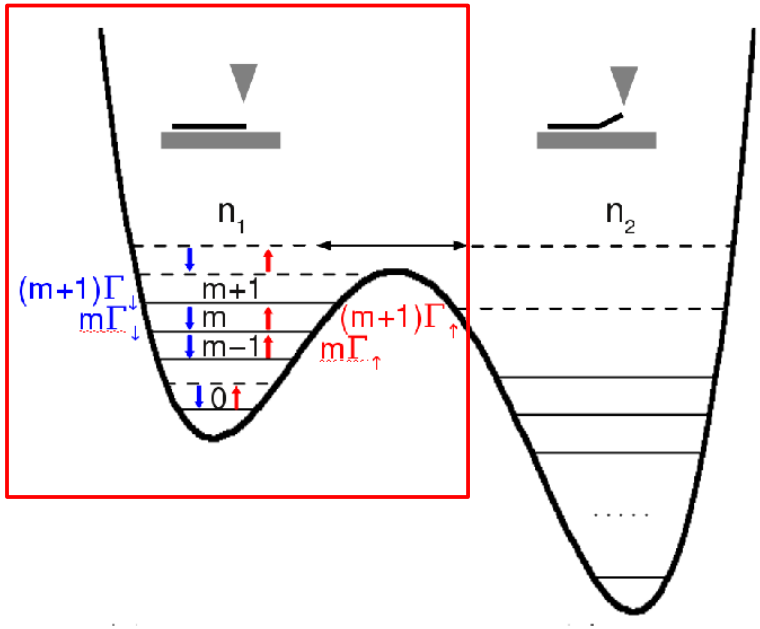
$$\mathrm{F}(\varepsilon) = \left[\exp\left(\frac{\varepsilon-\varepsilon_F}{k_B T}\right) + 1\right]^{-1} \simeq \Theta\left(\varepsilon_F-\varepsilon\right)$$

T. Brumme *et al.*, submitted (2011).



Dynamical bi-stability of a molecular junction

- Transfer rate between two wells of a double well?
- Highly asymmetric double well
  => Pauli master equation for truncated harmonic oscillator
- Transfer rate[*]



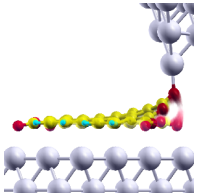
$$R \simeq n\,\Gamma_{\uparrow} \exp\left(\frac{(n-1)\hbar\omega}{k_B T_v}\right) = n\,\Gamma_{\uparrow}\left(\frac{\Gamma_{\uparrow}}{\Gamma_{\downarrow}}\right)^{n-1}$$

Transition rate from sub-critical level to crossing level

Population of the level (n-1), characteristic temperature $T_v = \dfrac{\hbar\omega}{k_B \ln\left(\frac{\Gamma_{\downarrow}}{\Gamma_{\uparrow}}\right)}$

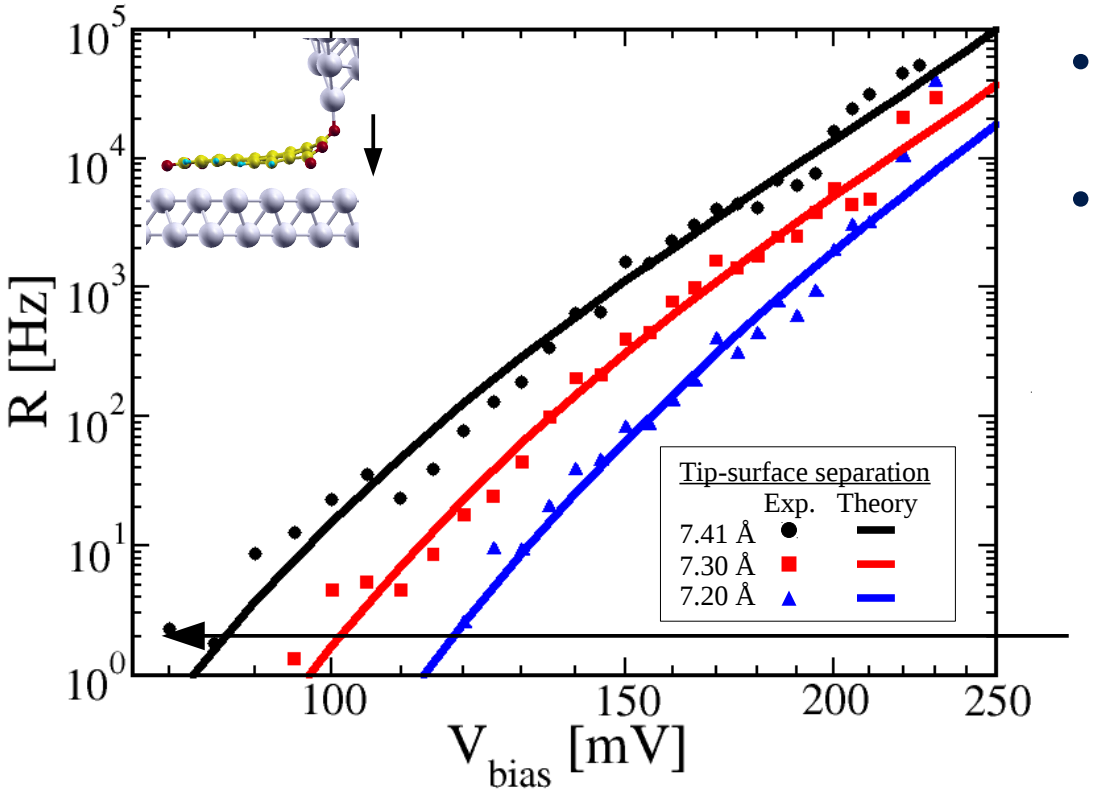
T. Brumme *et al.*, submitted (2011).

[*] S. Gao et al., PRB **55**, 4825 (1997).

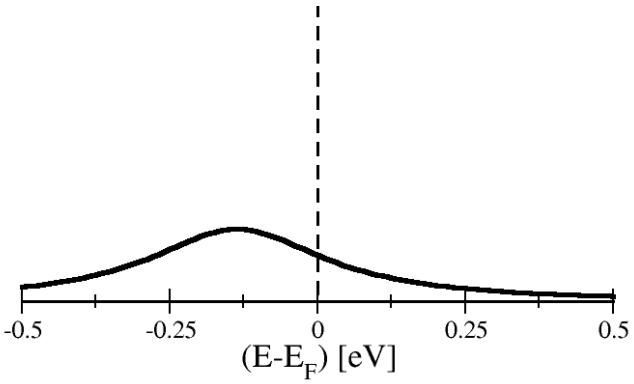


Dynamical bi-stability of a molecular junction

Switching from tip to surface



- Exponential dependence on applied bias voltage
- Electrons tunnel through broad level below the Fermi energy



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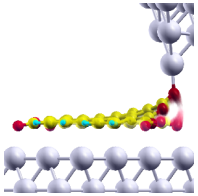

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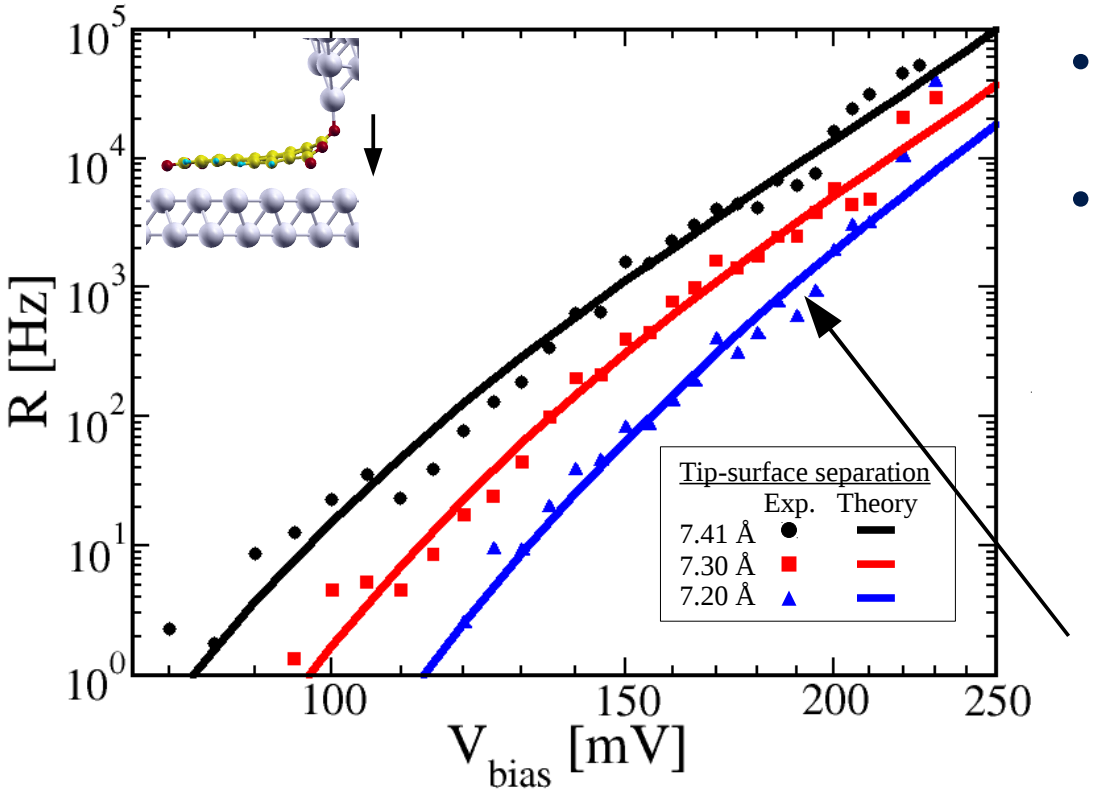

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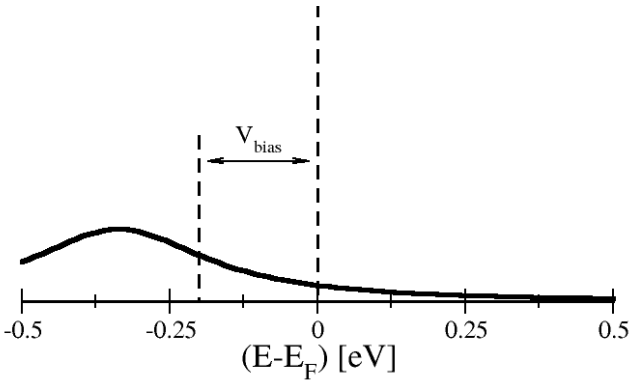

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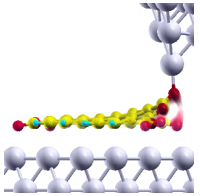
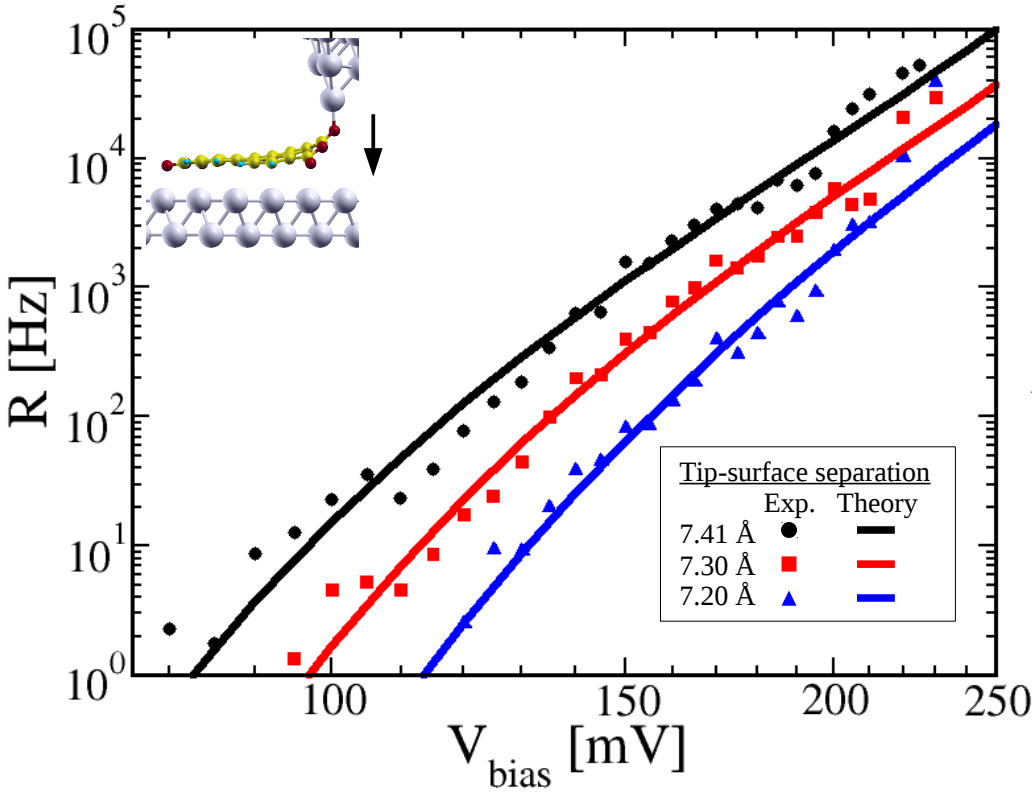


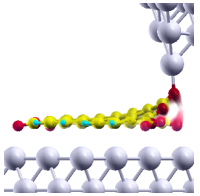
Dynamical bi-stability of a molecular junction

Switching from tip to surface



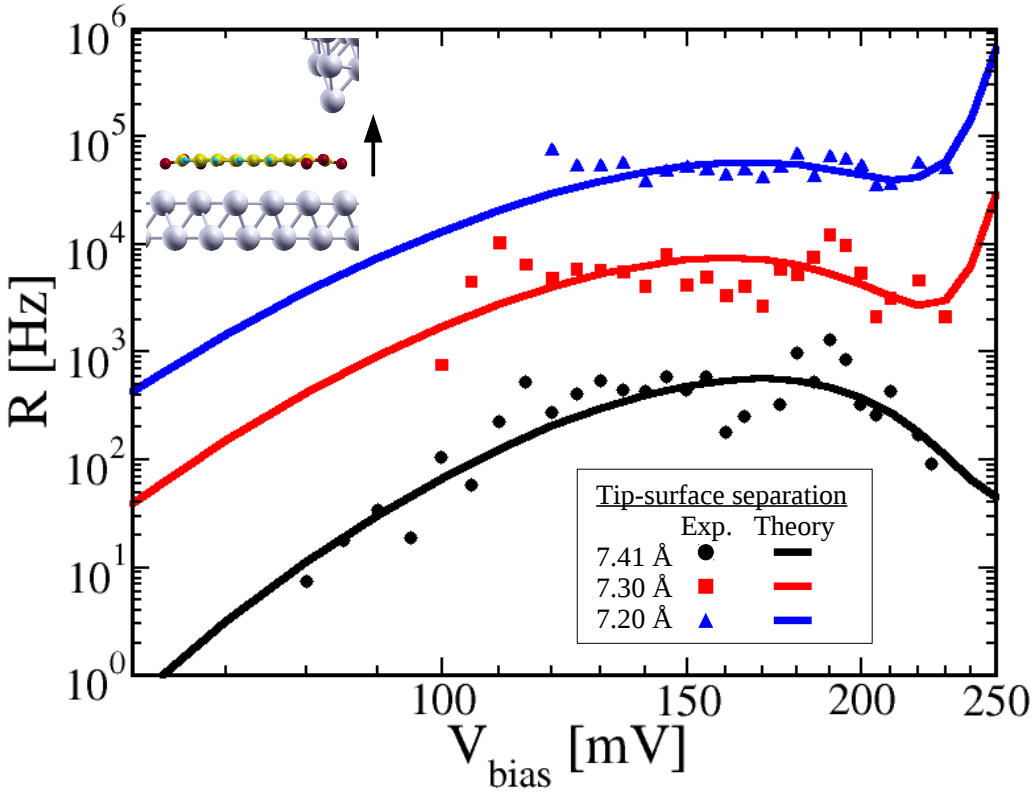
- Exponential dependence on applied bias voltage
- Electrons tunnel through broad level below the Fermi energy
- Higher rates for large tip-surface separations

T. Brumme *et al.*, submitted (2011).



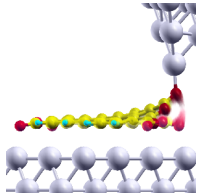
Dynamical bi-stability of a molecular junction

Switching from surface to tip



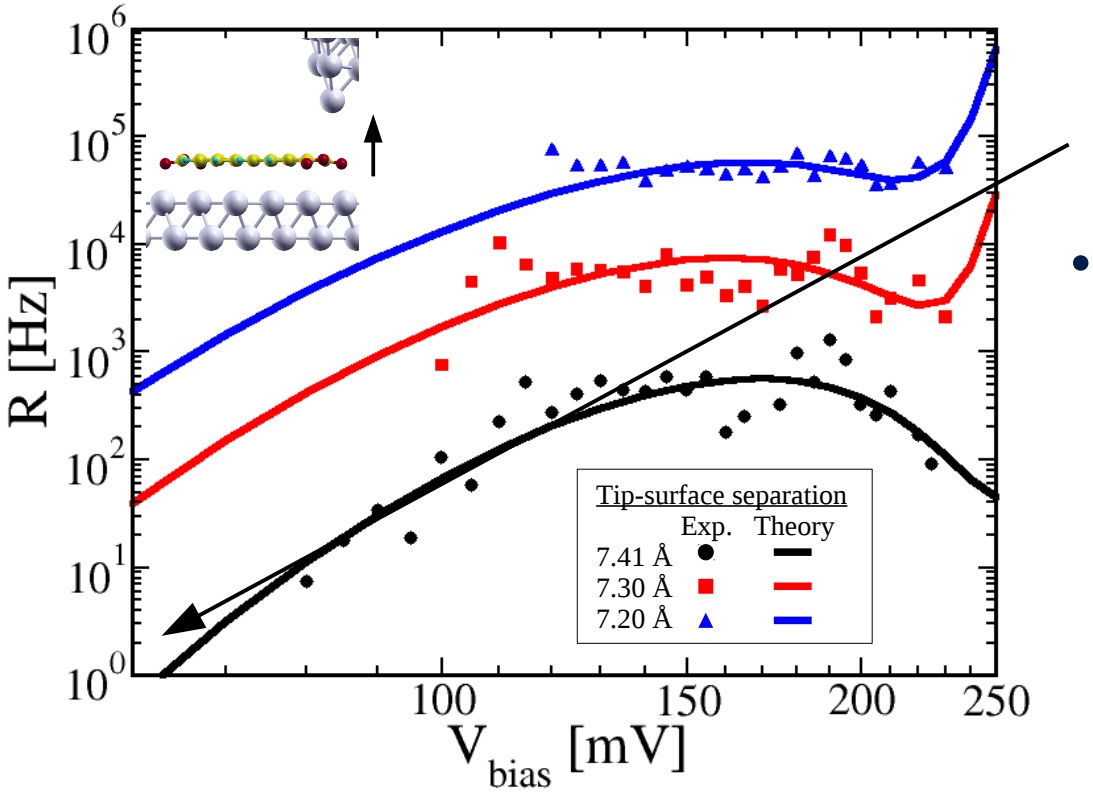
- Electrons tunnel through narrow level above the Fermi energy

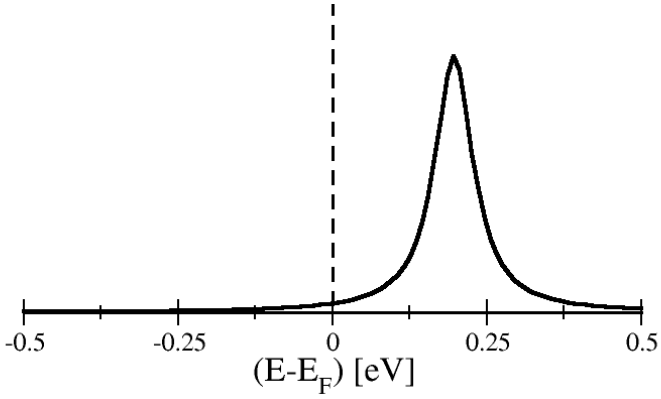
T. Brumme *et al.*, submitted (2011).



Dynamical bi-stability of a molecular junction

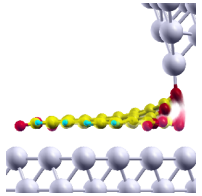
Switching from surface to tip





- Decreasing rate when molecular level gets into resonance with Fermi energy (dissipation of vibrational energy, $\Gamma_{\downarrow}$, increases)

T. Brumme *et al.*, submitted (2011).



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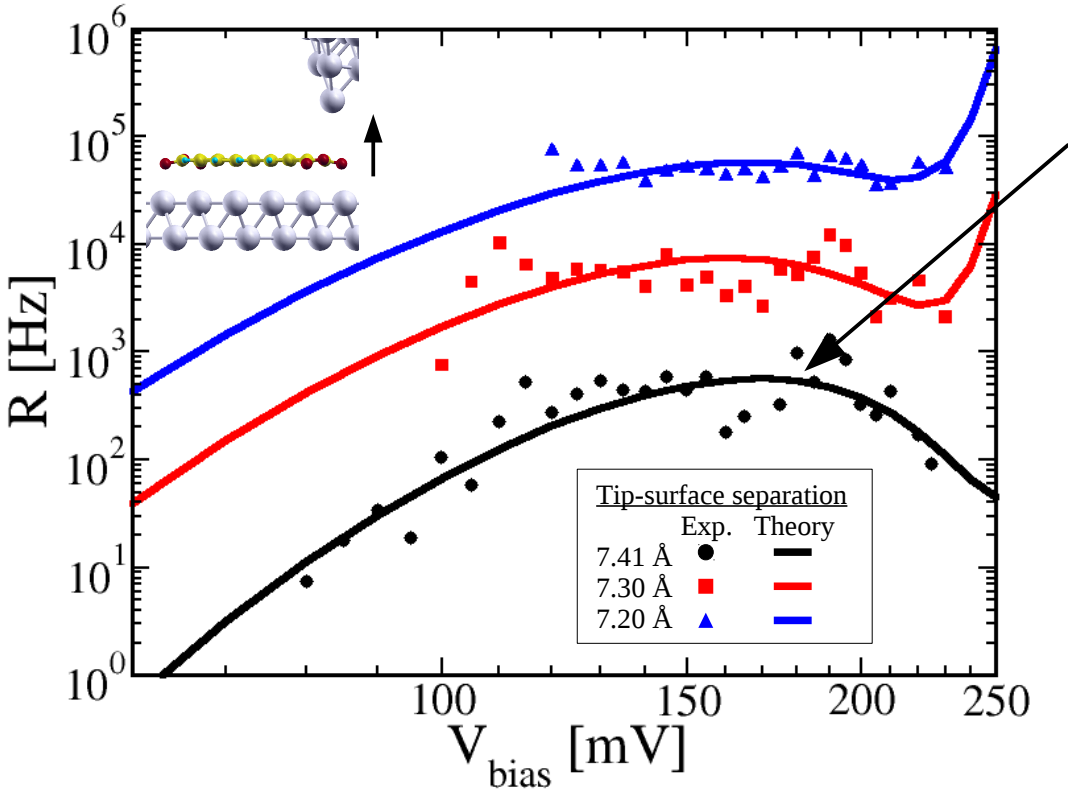
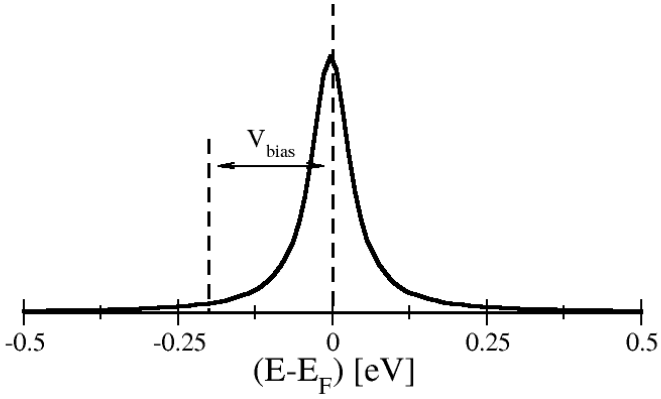
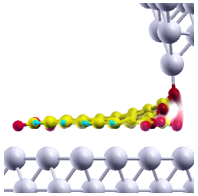




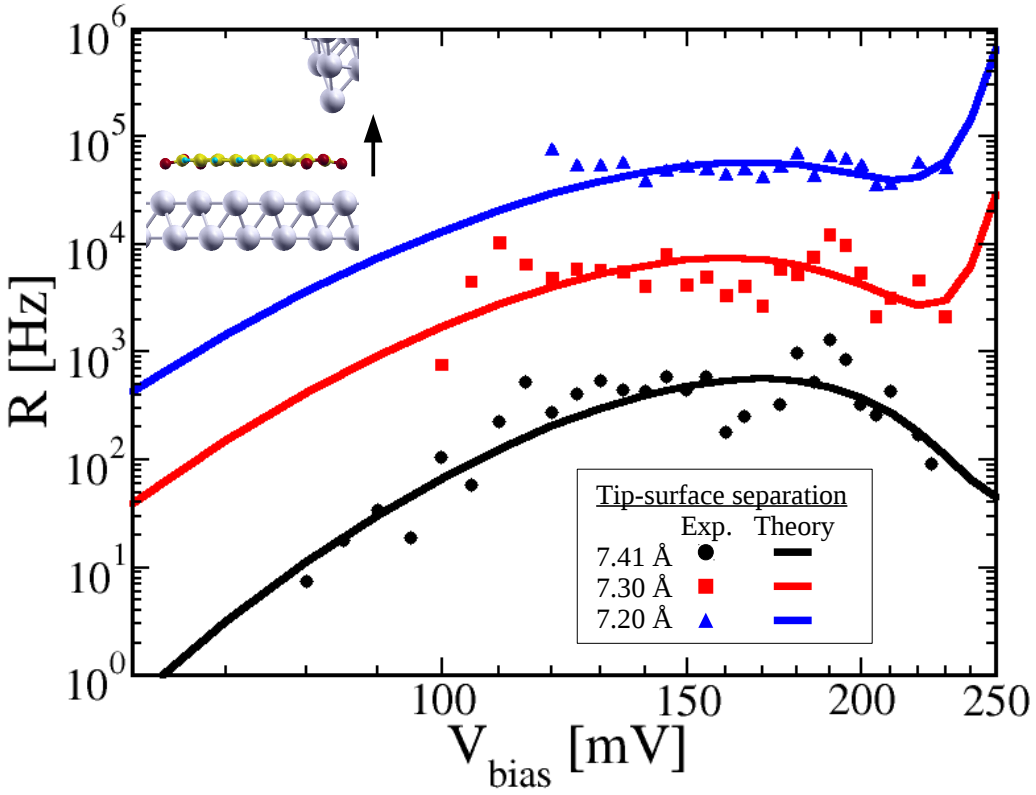
- Decreasing rate when molecular level gets into resonance with Fermi energy (dissipation of vibrational energy, $\Gamma_{\downarrow}$, increases)

T. Brumme *et al.*, submitted (2011).



Dynamical bi-stability of a molecular junction

Switching from surface to tip



- Electrons tunnel through narrow level above the Fermi energy
- Decreasing rate when molecular level gets into resonance with Fermi energy (dissipation of vibrational energy, $\Gamma_{\downarrow}$, increases)
- Lower rates for large tip-surface separations

T. Brumme *et al.*, submitted (2011).

Outlook

- Bias influence on double-well
- Transfer rate for “non-equilibrium” situation
- Magnetic molecules
- Interaction between tunneling electrons, vibrations and localized spins
- Single molecules as logic gates

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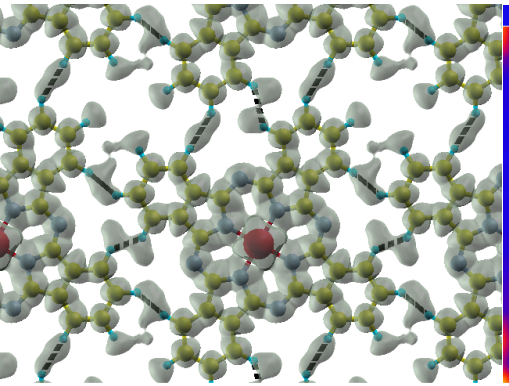
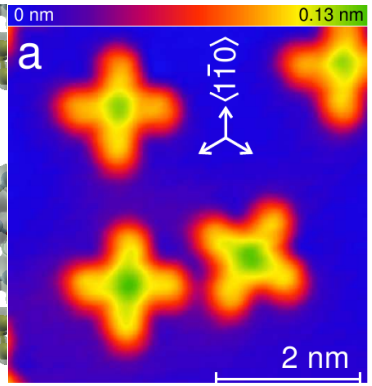
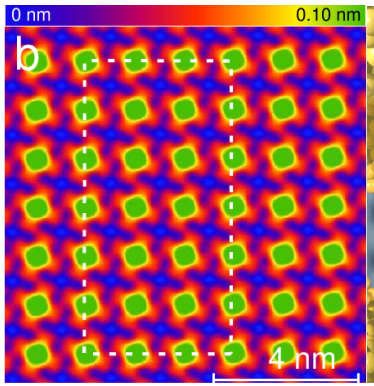
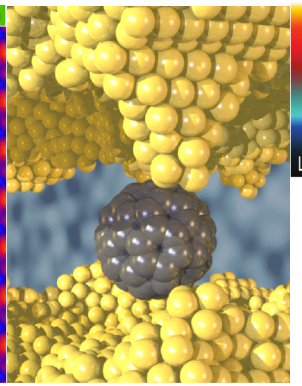
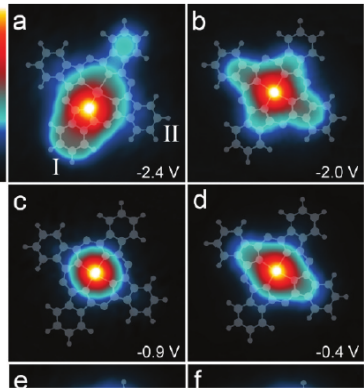


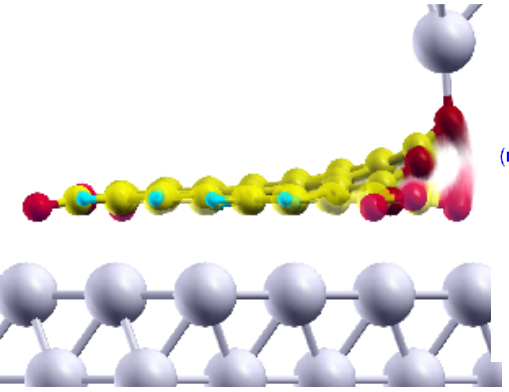








Thank you for your attention!



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