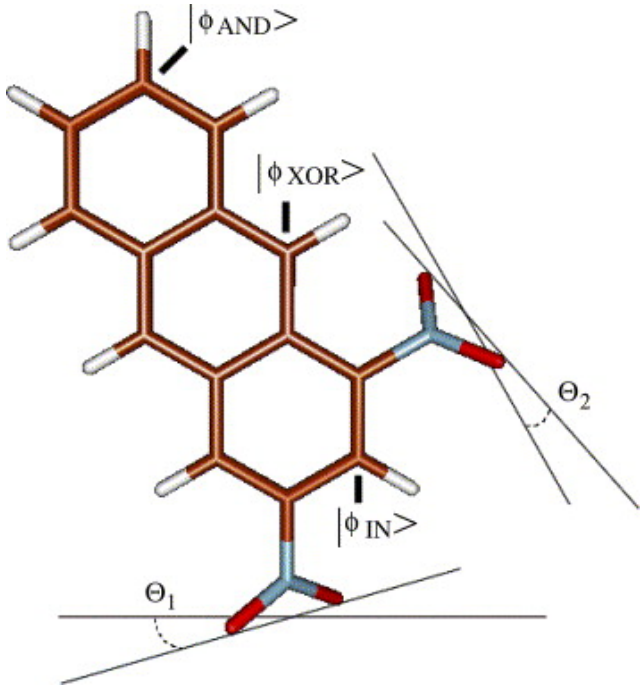
TECHNISCHE UNIVERSITÄT DRESDEN

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

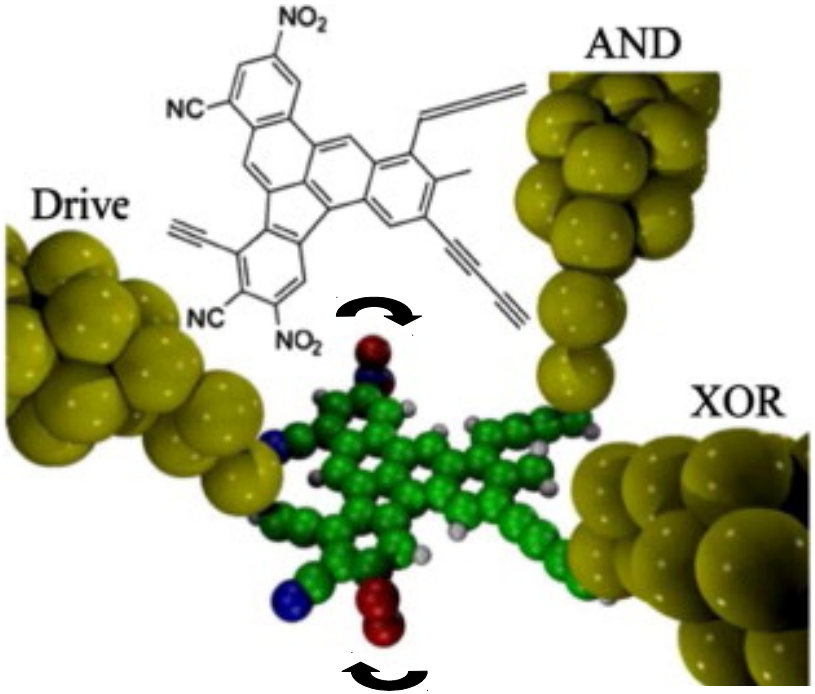
Dynamical bistability of a single PTCDA-STM junction: A combined experimental/theoretical study

T. Brumme, Olga Neucheva, Cormac Toher, Rafael Gutiérrez, C. Weiss, R. Temirov, Andreas Greuling, Marcin Kaczmarski, Michael Rohlfing, Stefan Tautz and Gianaurelio Cuniberti

Molecular logic – Design concepts



I. Duchemin and C. Joachim,
Chem. Phys. Lett. **406**, 167 (2005)

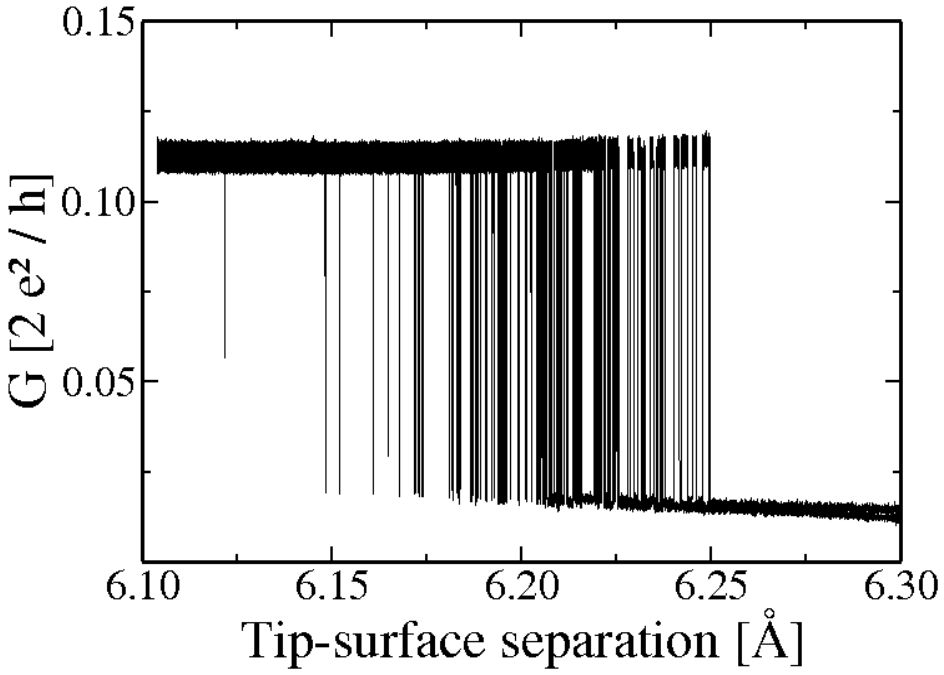


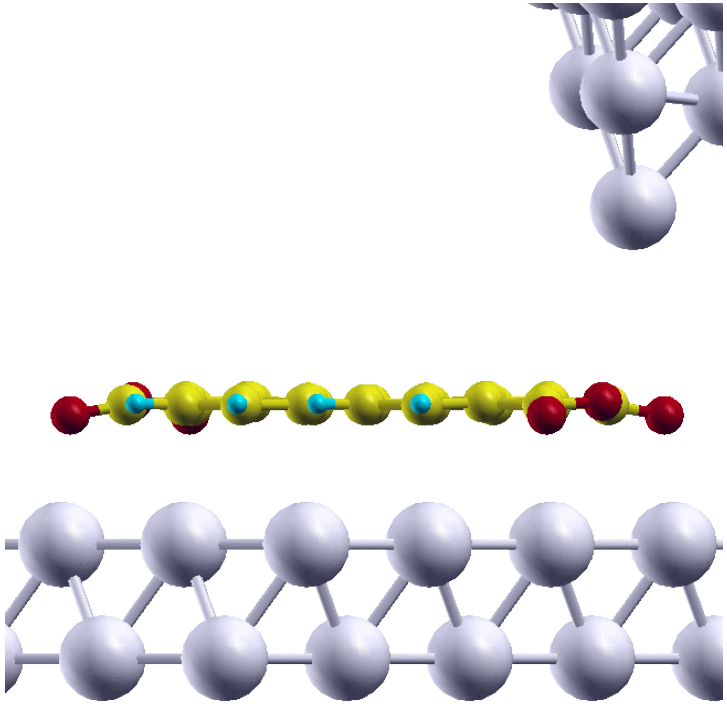
I. Duchemin, N. Renaud, and C. Joachim,
Chem. Phys. Lett. **452**, 269 (2008)

Molecular logic – Design concepts

- Many design concepts rely on conformational changes as input
- Important to understand the physical mechanisms which can induce switching
    - Field-induced switching (electric or ~~magnetic field~~)
    - ~~Light-induced switching (*e.g.* azobenzene molecules~~)
    - ~~Mechanical-induced switching~~
    - ~~Temperature-induced switching~~
    - ~~Redox-potential induced switching~~
    - Current-induced switching

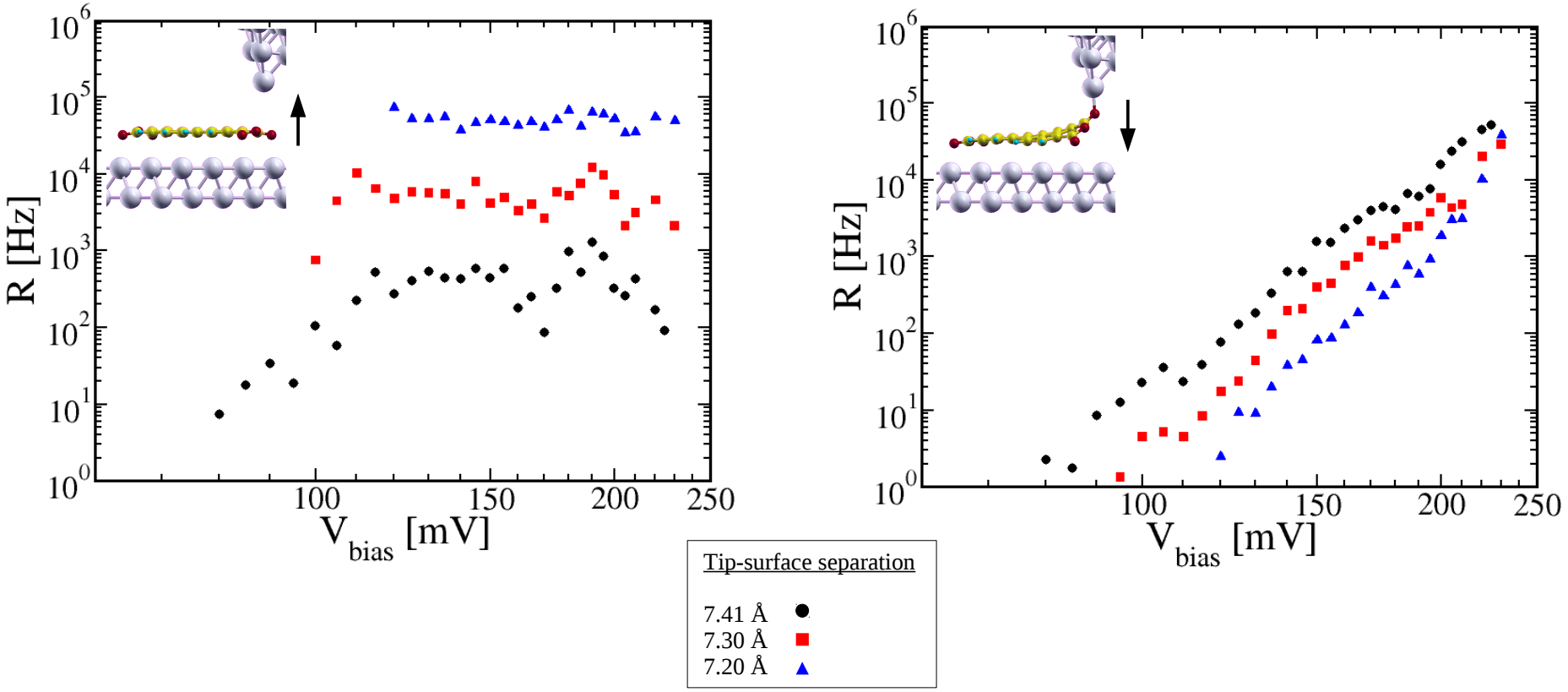
Dynamical bi-stability of a PTCDA-STM junction



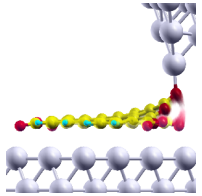


T. Brumme *et al.*, Phys. Rev. B **84**, 115449 (2011)

Dynamical bi-stability of a PTCDA-STM junction

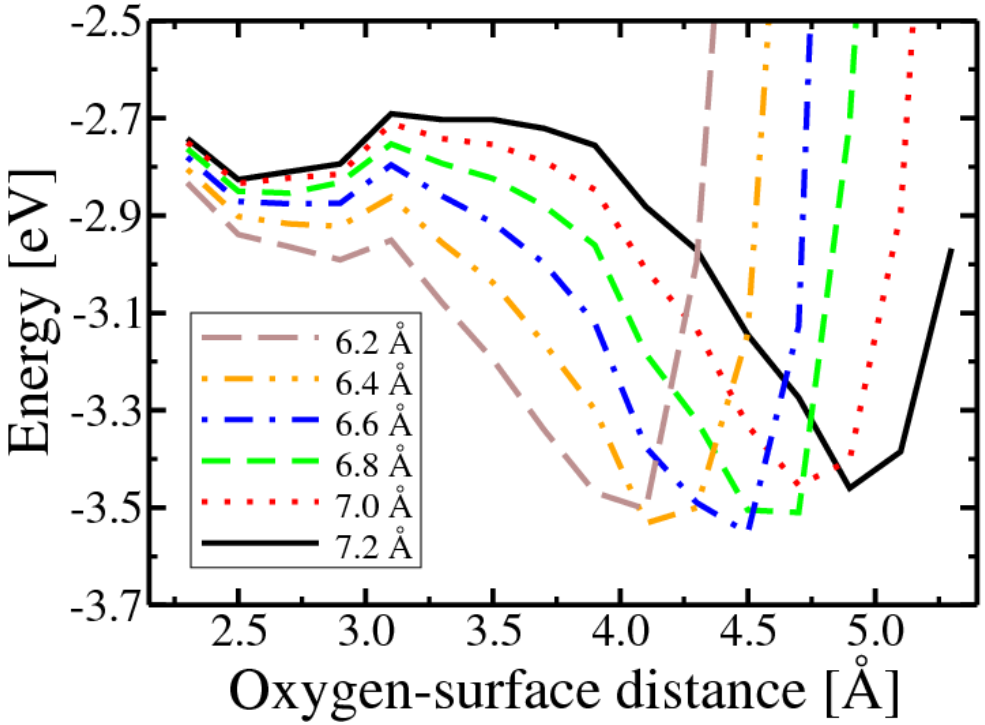


T. Brumme *et al.*, Phys. Rev. B **84**, 115449 (2011)



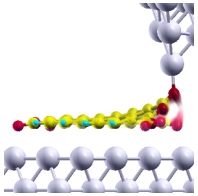
Dynamical bi-stability of a PTCDA-STM junction

PTCDA on Ag(111)



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

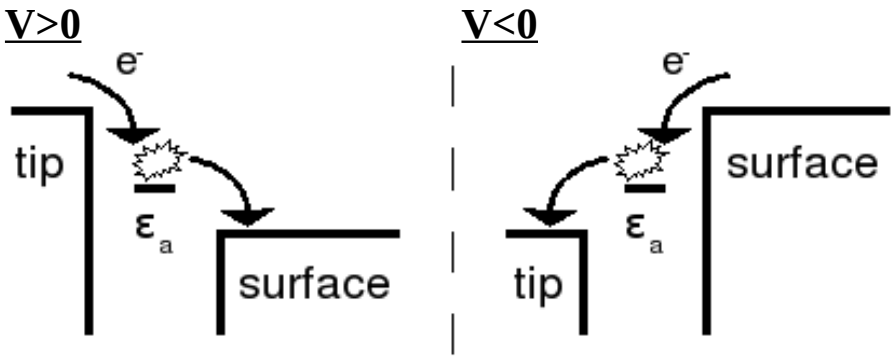
T. Brumme *et al.*, Phys. Rev. B **84**, 115449 (2011)

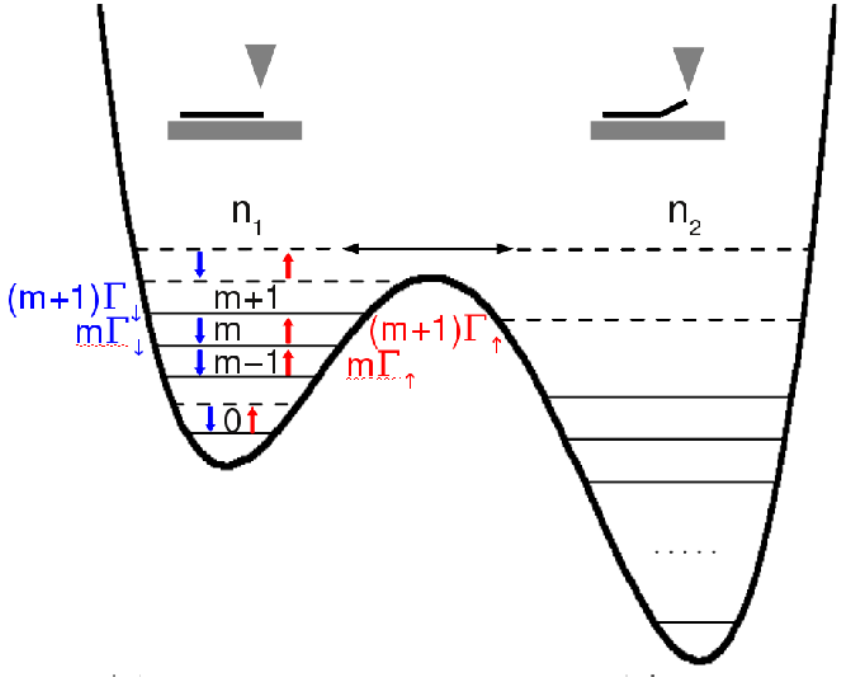


Dynamical bi-stability of a PTCDA-STM junction

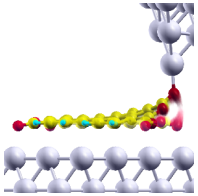
Vibrational heating in single-molecule junctions

- Vibrational excitation of the C=0 bond by scattering of tunneling electrons





T. Brumme *et al.*, Phys. Rev. B **84**, 115449 (2011)



Dynamical bi-stability of a PTCDA-STM junction

Vibrational heating in single-molecule junctions

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

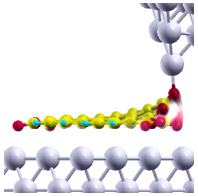
$$H = \sum_s \varepsilon_s\, c_s^\dagger\, c_s \;+\; \sum_t \varepsilon_t\, c_t^\dagger\, c_t \;+\; \varepsilon_m\, c_m^\dagger\, c_m$$
$$+ \sum_s \left(T_{sm}\, c_s^\dagger\, c_m \;+\; H.c.\right) \;+\; \sum_t \left(T_{tm}\, c_t^\dagger\, c_m \;+\; H.c.\right)$$
$$+ \;\hbar\omega\, b^\dagger\, b \;+\; \lambda_0 \left(b^\dagger \;+\; b\right) \left(c_m^\dagger\, c_m\right) \quad .$$

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

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

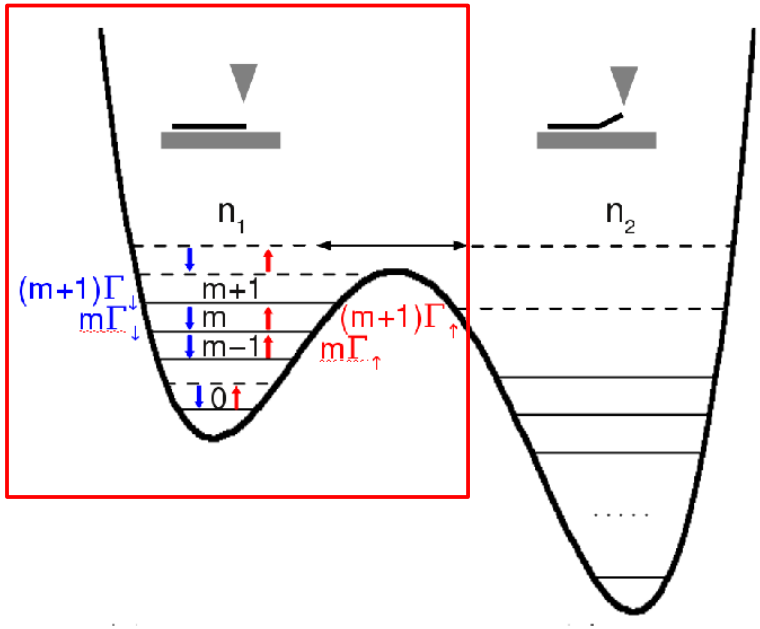
$$\Gamma_\uparrow = 2\,\frac{2\pi}{\hbar}\,\lambda_0^2 \int \left(\rho_m^f(\varepsilon)\,\rho_m^i(\varepsilon+\hbar\omega)\left[1-\mathrm{F}^f(\varepsilon)\right]\mathrm{F}^i(\varepsilon+\hbar\omega)\right) d\varepsilon$$

T. Brumme *et al.*, Phys. Rev. B **84**, 115449 (2011)



Dynamical bi-stability of a PTCDA-STM junction

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



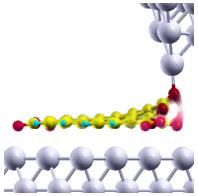
$$R \simeq n\,\Gamma_{\uparrow} \exp\left(\frac{(n-1)\hbar\omega}{k_B T_v}\right) = n\,\Gamma_{\uparrow}\left(\frac{\Gamma_{\uparrow}}{\Gamma_{\downarrow}}\right)^{n-1}$$

Transition rate from sub-critical level to crossing level

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

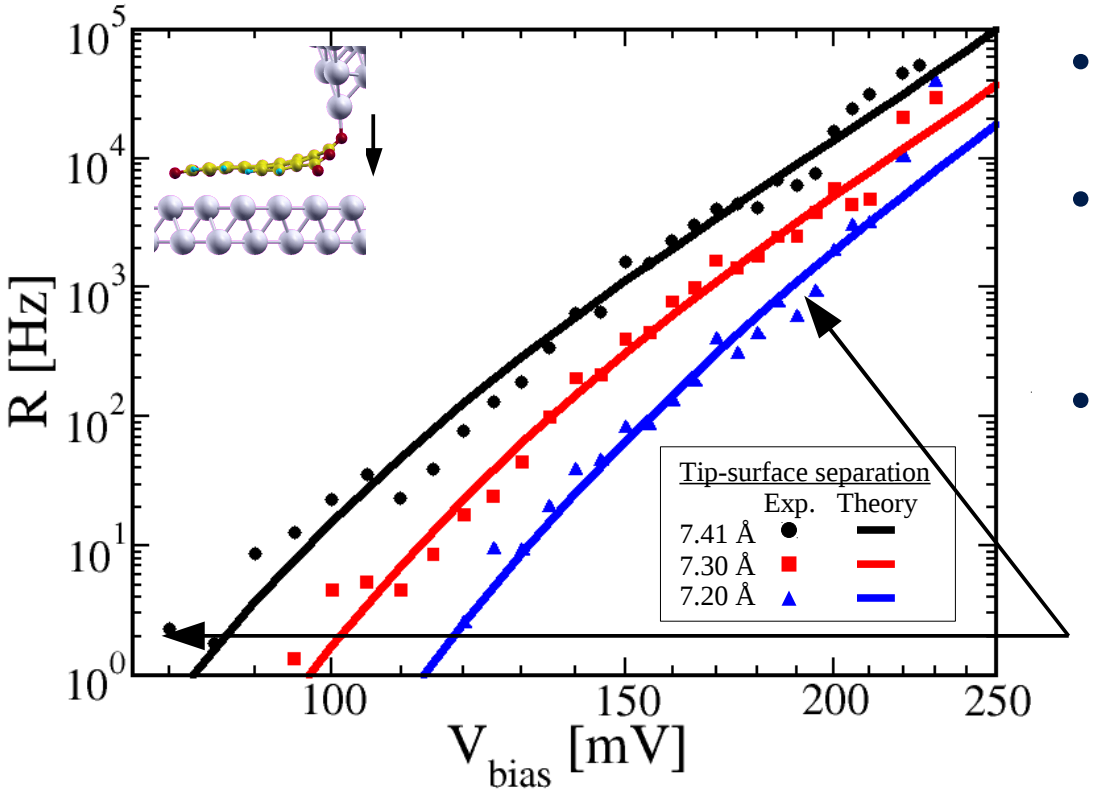
T. Brumme *et al.*, Phys. Rev. B **84**, 115449 (2011)

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



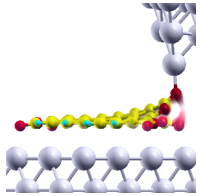
Dynamical bi-stability of a PTCDA-STM junction

Switching from tip to surface



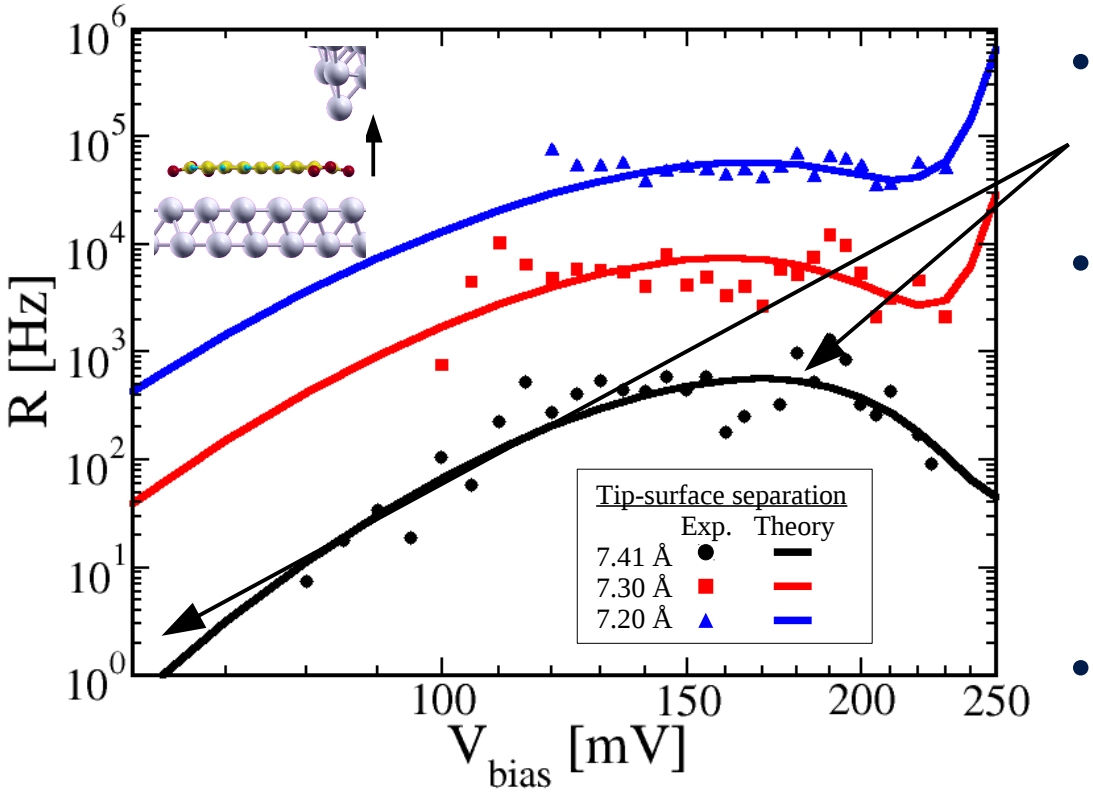
- Exponential dependence on applied bias voltage
- Electrons tunnel through broad level below the Fermi energy
- Higher rates for large tip-surface separations

T. Brumme *et al.*, Phys. Rev. B **84**, 115449 (2011)



Dynamical bi-stability of a PTCDA-STM junction

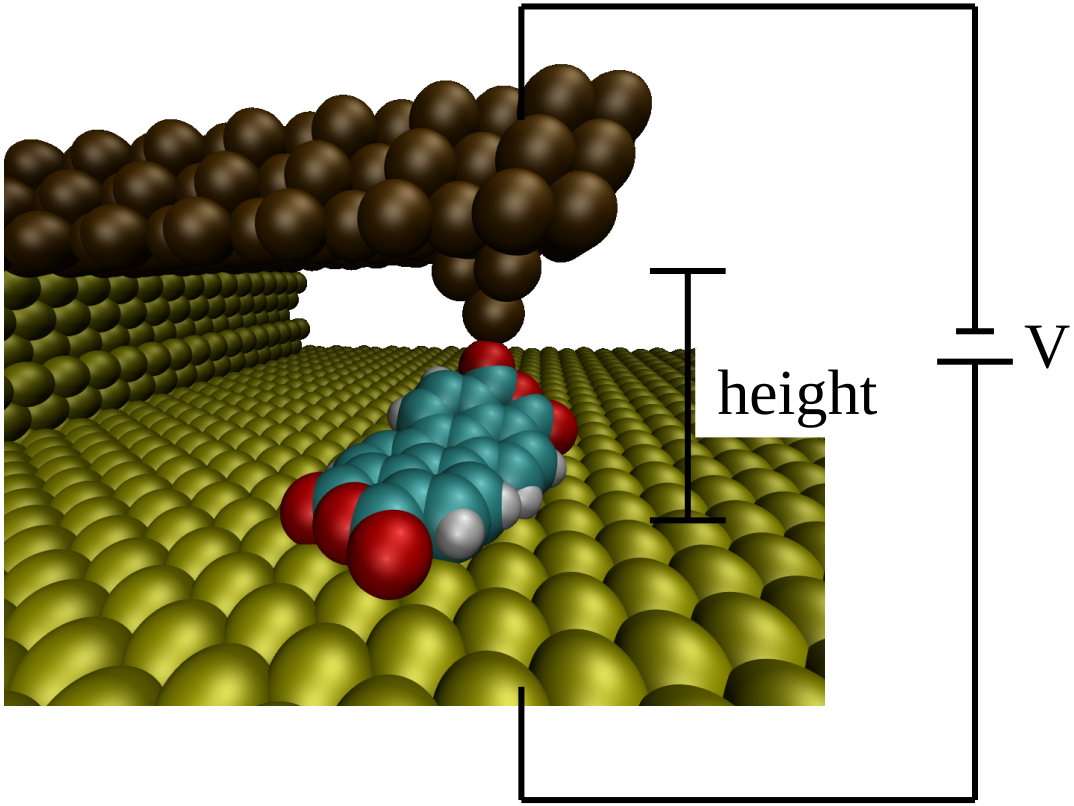
Switching from surface to tip



- 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.*, Phys. Rev. B **84**, 115449 (2011)

Molecular logic – Design concept



- Tip-surface separation as input “A”
- Applied bias voltage as input “B”
- Conductance state as output (*e.g.* high conductance as “1”)

A \ B	Large “1”	Small “0”
Large “0”	0	0
Small “1”	1	0

Conclusion

- Vibrational heating important mechanism to switch molecules
- Can be crucial to take non-constant molecular DOS into account
- Switching probability depends strongly on applied bias

- PTCDA could be used as memory element or simple AND gate

BUT

- Single PTCDA unstable at room temperature due to diffusion on surface
  => Monolayer of PTCDA !?

Acknowledgements

TuneSTM collaborators:

- Forschungzentrum Juelich:
  R. Temirov, O. Neucheva, F. S. Tautz

- University of Osnabrueck:
  A. Greuling, M. Kaczmarski, M. Rohlfing

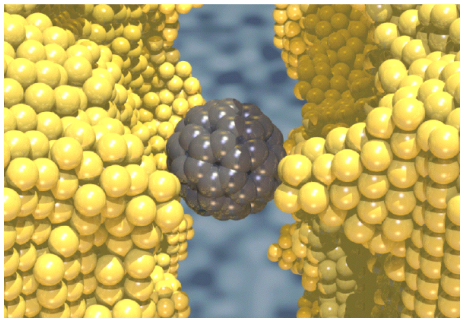
Computing methods and resources:

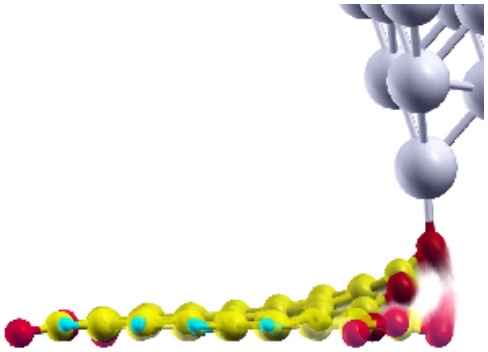
- SIESTA: J. Phys. Cond. Matter **14**, 2745 (2002)

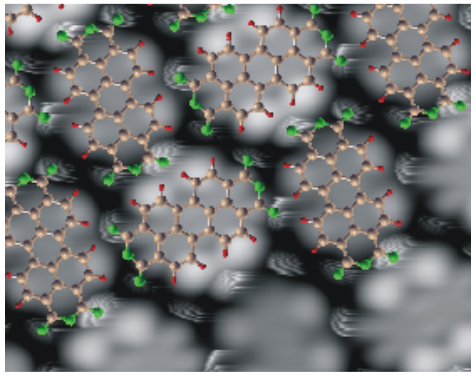
- Zentrum für Informationdienste und Hochleiststungsrechnen, TU Dresden

Funding:

- DFG: SPP 1243, Quantum transport at the molecular scale







Thank you for your attention!