TECHNISCHE UNIVERSITÄT DRESDEN

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Modeling switching in STM molecular junctions

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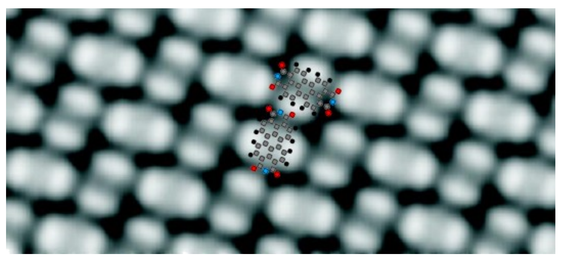
We describe here the investigation of the current switching observed in a molecular junction formed by a PTCDA molecule between an STM tip and an Ag(111) surface, which is believed to be due to the carboxylic oxygen atom switching between the surface and the tip. We use a generalized version of a model developed in 1997 by Gao *et al.* [1] to investigate the results observed in these experiments. The distribution of the switching events measured in the experiments shows a power law dependence for small bias voltages, whereas for higher voltages it first saturates and then drops again.

Experiment

- Experiments done in the Tautz group at the Forschungszentrum Jülich
- STM measurements on PTCDA on Ag(111)
- Switching between two conductance states for particular tip-surface distances



STM image of PTCDA on Ag(111) [2]

- Switches occur only if the STM-tip is located over the carboxylic oxygen atom (red dots in Fig. 1)

Model – Transition rates

- System Hamiltonian

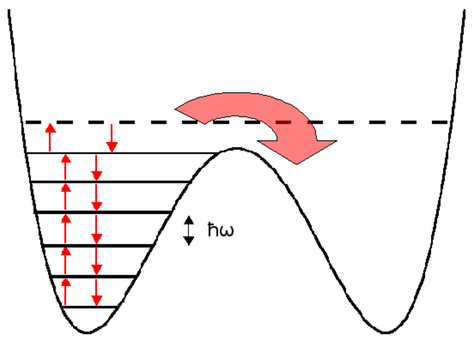
$$H_e = \underbrace{\sum_k \varepsilon_k c_k^\dagger c_k}_{\text{surface states}} + \underbrace{\sum_p \varepsilon_p c_p^\dagger c_p}_{\text{tip states}} + \underbrace{\varepsilon_a c_a^\dagger c_a}_{\substack{\text{adsorbate level} \\ \varepsilon_a=\varepsilon_a(q)=\varepsilon_0+\lambda q}} + \underbrace{\sum_{\alpha=k,p}\left(t_\alpha c_\alpha^\dagger c_a + \text{H.c.}\right)}_{\text{hopping between surface/tip and adsorbate}}$$

- Electron-vibron interaction $H_{\text{e-v}}$ within first-order perturbation theory => Fermi's golden rule for transition rates

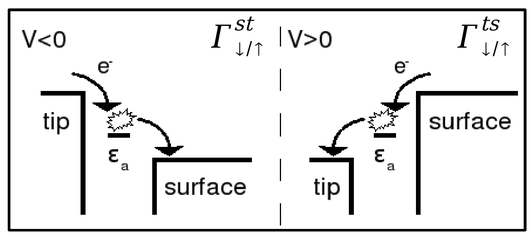
$$\Gamma_{\downarrow/\uparrow} = 2\frac{2\pi}{\hbar}\sum_{\nu,\mu}\left|\langle \mu,0/1\left|H_{\text{e-v}}\right|\nu,1/0\rangle\right|^2 \times f_\nu(1-f_\mu)\,\delta(\varepsilon_\mu-\varepsilon_\nu\mp\hbar\omega)$$

- Low temperatures, adsorbate level within wide-band limit
- Transition rates, e.g.

$$\Gamma^{st,ts}_{\downarrow/\uparrow} = 2\frac{\pi\,(\varepsilon_a')^2}{M\,\omega} \times \int_{\varepsilon_{Ft,s}\mp\hbar\omega}^{\varepsilon_{Fs,t}} \underbrace{\rho_a^{s,t}(\varepsilon\mp\hbar\omega)\,\rho_a^{t,s}(\varepsilon)}_{\substack{\text{local density of the substrate or} \\ \text{tip states for the adsorbate level}}}\mathrm{d}\varepsilon$$



Sketch of our model. The transfer of the PTCDA from surfaces to tip is due to several inelastic scattering events.



Scattering of electrons tunneling from the STM-tip to the surface via the adsorbate level.

Model – Transfer rate

- Double well approximated by two truncated harmonic oscillators
- Pauli master equation, only nearest neighbor transitions

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

Generalized temperature

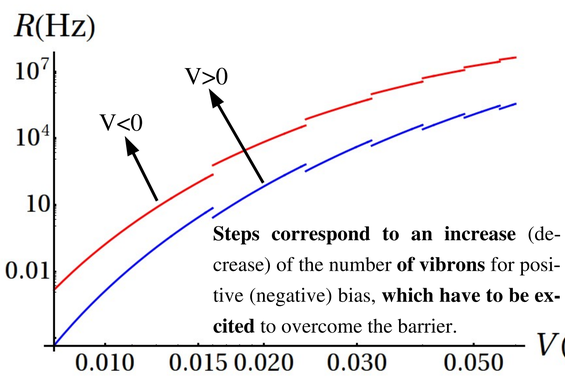
$$T_v = \frac{\hbar\omega}{k_b \ln\left(\frac{\Gamma_\downarrow}{\Gamma_\uparrow}\right)}$$

- Linear dependence of barrier height (=> *n*) on the applied bias voltage

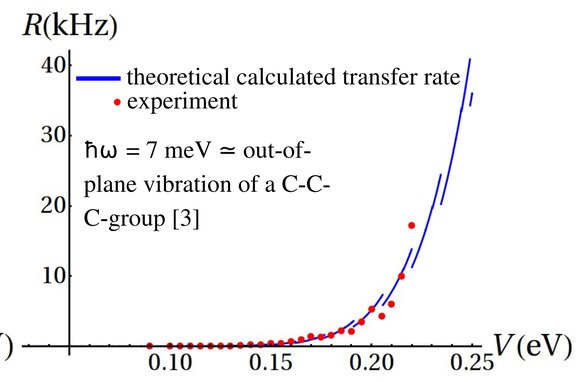
Results

- Power law behavior for small bias
- Saturation for higher bias
- For even higher bias the potential changes from a double well to a single well
  => Transfer rate becomes zero, because molecule stays at the tip or at the surface
- Fitting to measurements is quite demanding, because of many unknown constants
  => Density Functional Theory (DFT) helps to determine correct values for parameter

Log-Log-Plot of the transfer rate

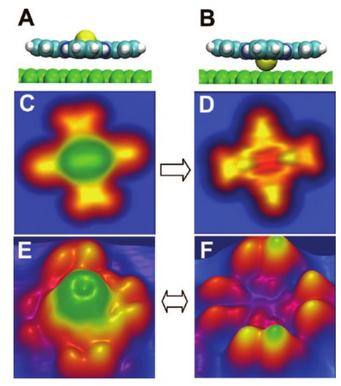


Fitting to the experiment



Other switching mechanism which can be excluded

- Quantum tunneling (probability very small; size of PTCDA)
- Thermal activation (cryogenic STM)
- Vibrational-assisted, involving 1 vibron (barrier height)
- Switching involving a metastable ionic state (small voltages induce switching)



right: Switching involving a metastable ionic state. SnPc on Ag(111) [4].

Conclusion and Outlook

- Current switching of PTCDA on Ag(111) can be described by a truncated harmonic oscillator model
- Quantitative agreement combining DFT calculations and fitting procedure to determine model parameters
- Deeper investigation of the determined parameters
- Introducing temperature and phonon-phonon interaction between surface and adsorbate

References

[1] S. Gao *et al.*, PRB **55**, 4825 (1997).
[2] L. Kilian *et al.*, PRL **100**, 136103 (2008).
[3] A.Yu. Kobitski *et al.*, J. Mol. Struc. **625**, 39 (2003).
[4] Y. Wang *et al.*, JACS **131**, 3639 (2009).