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

**Model – Transition rates**
- System Hamiltonian
  \[ H_w = \sum \varepsilon_n c_n^\dagger c_n + \sum \varepsilon_p c_p^\dagger c_p + \varepsilon_s c_s^\dagger c_s + \sum_{k=1}^{\infty} \beta_k (t_k c_k^\dagger c_i + H.c.) \]
- Electron-vibron interaction \( H_{e-v} \) within first-order perturbation theory \( \Rightarrow \) Fermi’s golden rule for transition rates
  \[ \Gamma_{1,1} = \frac{2 \pi}{\hbar} \sum \left| \langle e_0 | H_{e-v} | 1/0 \rangle \right|^2 \times \delta (\varepsilon_0 - \varepsilon_s + \hbar \omega) \]
- Low temperatures, adsorbate level within wide-band limit
- Transition rates, e.g.
  \[ \Gamma_{1,1}^{e-v} = \frac{2 \pi}{\hbar} \sum_{\varepsilon_n} \rho_{e}^s(\varepsilon_n) \rho_{e}^{\dagger}(\varepsilon_n) \Delta \varepsilon \]
  Sketch of our model. The transfer of the PTCDA from surfaces to tip is due to several inelastic scattering events.

**Model – Transfer rate**
- Double well approximated by two truncated harmonic oscillators
- Pauli master equation, only nearest neighbor transitions
  \[ R = n \Gamma \exp \left( -\frac{(n-1)\hbar \omega}{k_B T_v} \right) \sim n \Gamma \left( \frac{T}{T_v} \right)^{1-n} \]
  Linear dependence of barrier height (\( \Rightarrow n \)) 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
  \( \Rightarrow \) 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
  \( \Rightarrow \) Density Functional Theory (DFT) helps to determine correct values for parameter

**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)

**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**