# Modelling vibrations in STM single molecule junctions: a step beyond the Anderson-Holstein paradigm

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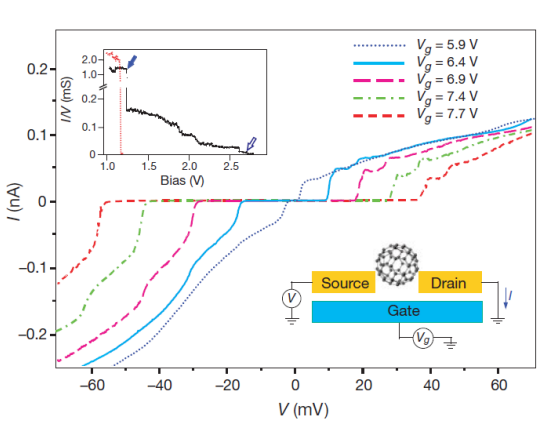
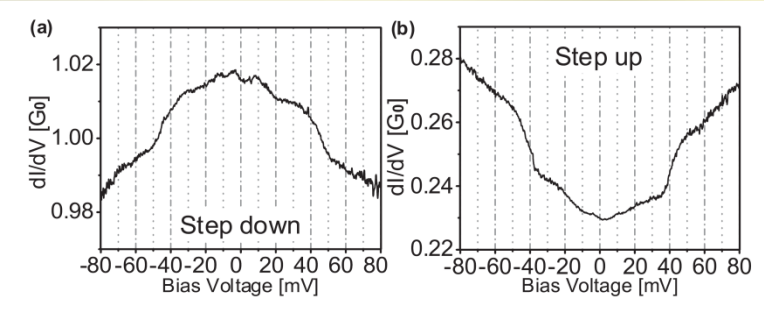
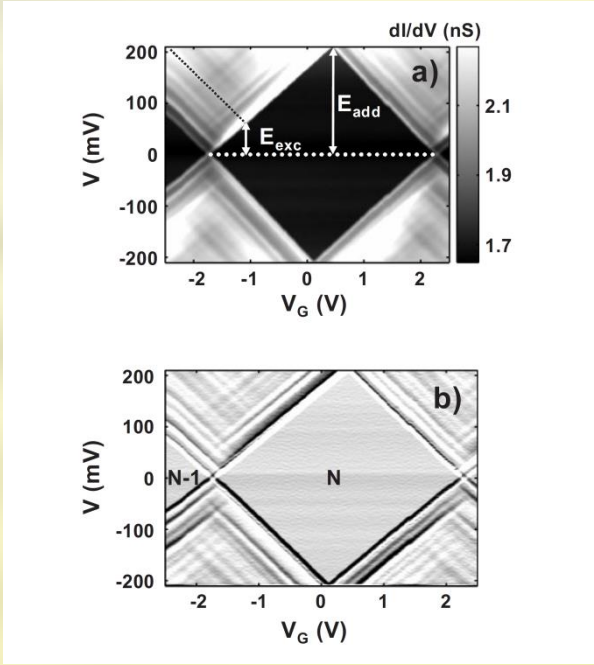
# Vibrations in single molecule junctions




H. Park et al. Nature **407**, 57 (2000)

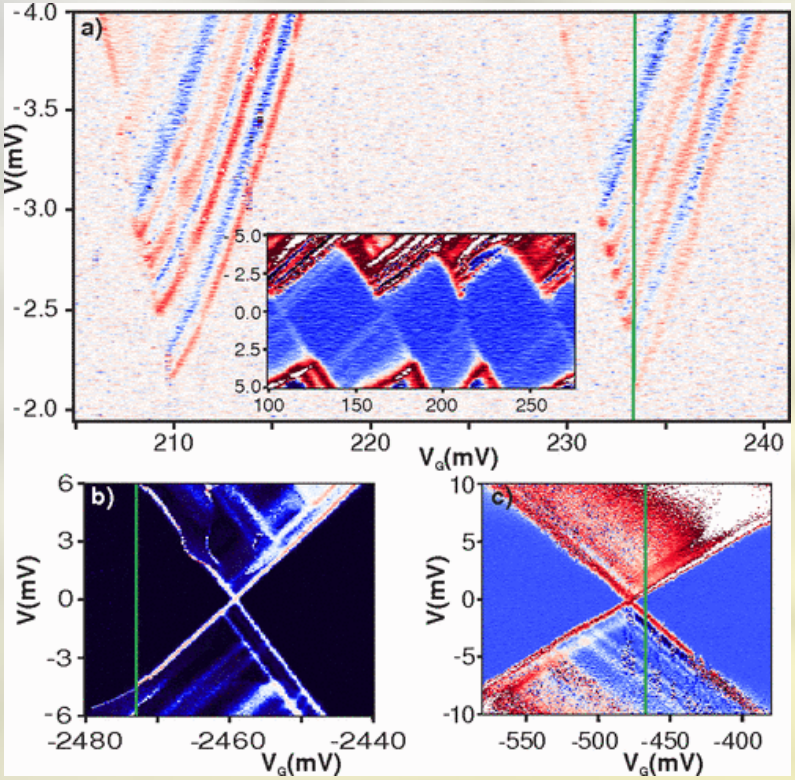



O. Tal et al. PRL **100**, 196804 (2008)

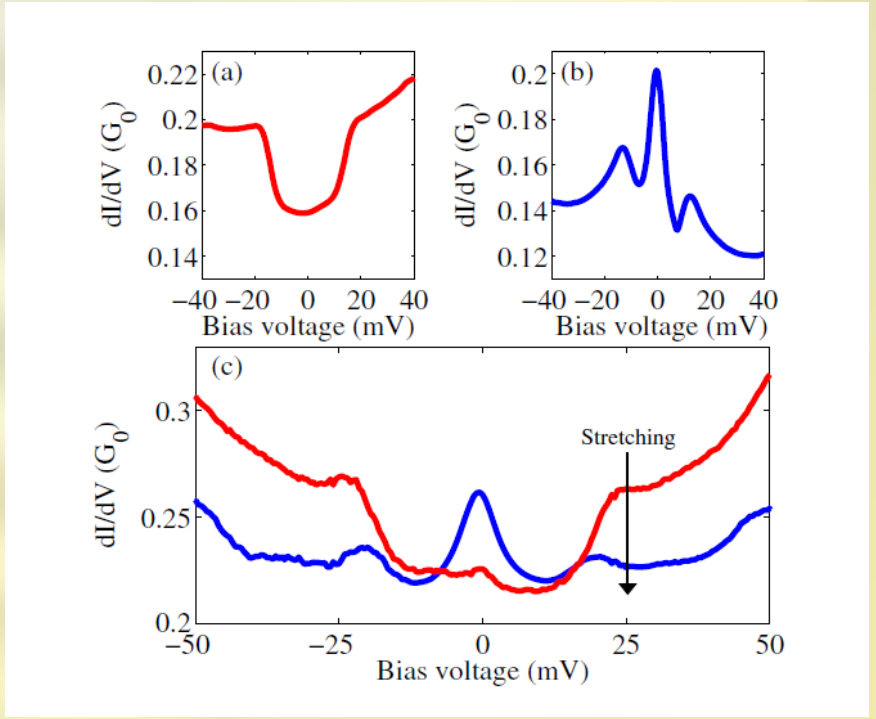



E.A.Osorio et al. Advanced Mater. **19**, 281 (2007)

# Vibrations in single molecule junctions



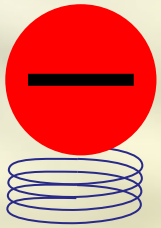

S. Sapmaz et al. PRL **96,** 026801 (2006)




D. Rakhmilevitch et al. PRL **113,** 236603 (2014)

# Anderson-Holstein model

$$H = H_{\mathrm{mol}} + H_{\mathrm{leads}} + H_{\mathrm{tun}}$$



$$H_{\mathrm{mol}} = \epsilon\, N + \frac{U}{2} N(N-1) + \hbar\omega \left( \frac{1}{2} + a^{\dagger} a \right) + \lambda N (a^{\dagger} + a)$$

# Anderson-Holstein model

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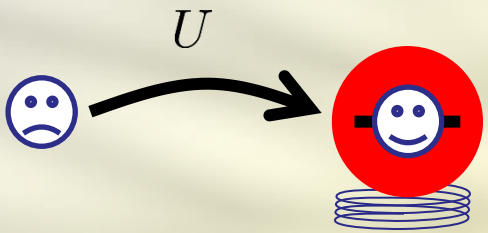
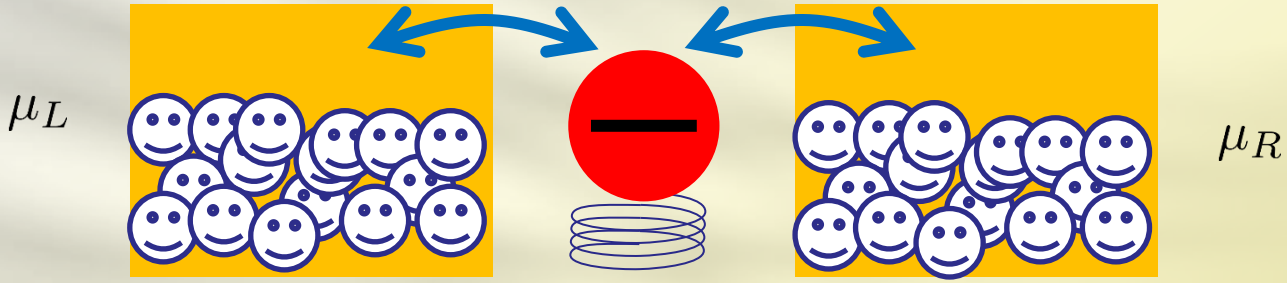



$$H_{\mathrm{mol}} = \epsilon\, N + \frac{U}{2} N(N-1) + \underbrace{\hbar\omega \left( \frac{1}{2} + a^\dagger a \right)}_{\frac{P^2}{2M} + \frac{1}{2} M\omega^2 X^2} + \lambda N (a^\dagger + a) + CX$$

# Anderson-Holstein model

$$H = H_{\mathrm{mol}} + H_{\mathrm{leads}} + H_{\mathrm{tun}}$$



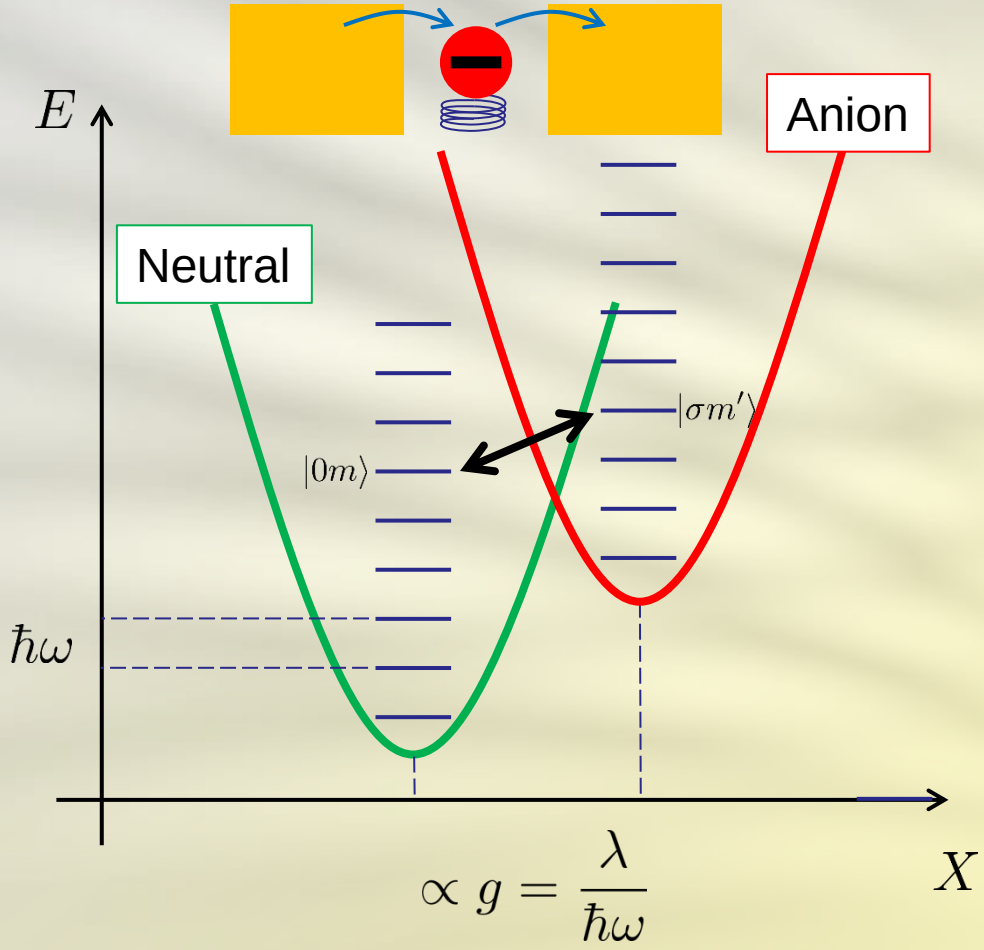

$$H_{\mathrm{mol}} = \epsilon\, N + \frac{U}{2} N(N-1) + \hbar\omega \left( \frac{1}{2} + a^\dagger a \right) + \lambda N (a^\dagger + a)$$

$$H_{\mathrm{leads}} = \sum_{\alpha\, k\, \sigma} \epsilon_{\alpha\, k\, \sigma}\, c^\dagger_{\alpha\, k\, \sigma} c_{\alpha\, k\, \sigma}$$

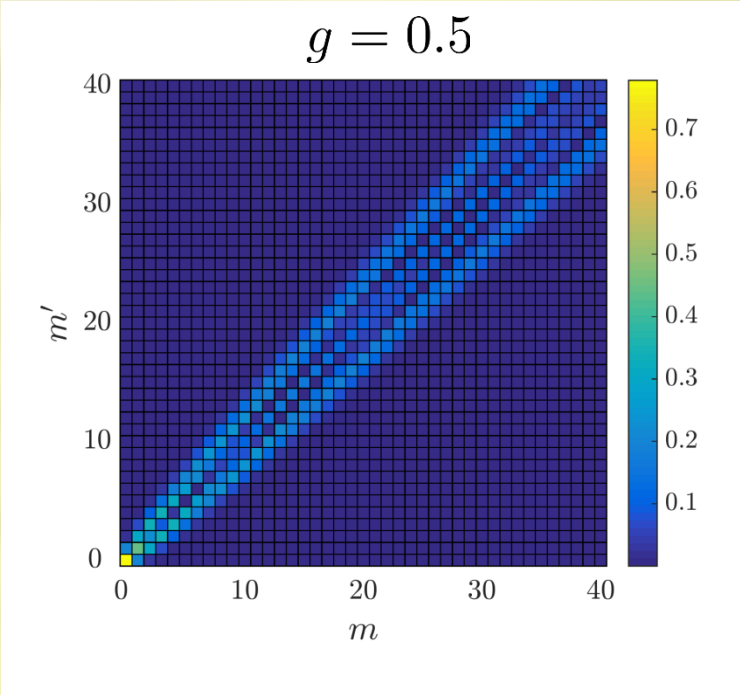
$$H_{\mathrm{tun}} = \sum_{\alpha\, k\, \sigma} t_\alpha\, c^\dagger_{\alpha\, k\, \sigma} d_\sigma + H.c.$$

$H_{\mathrm{mol}}$ is diagonalized by a polaron transformation

# Franck-Condon Picture




$$F(m, m'; g) = |\langle 0m|d_\sigma|\sigma m'\rangle|^2$$



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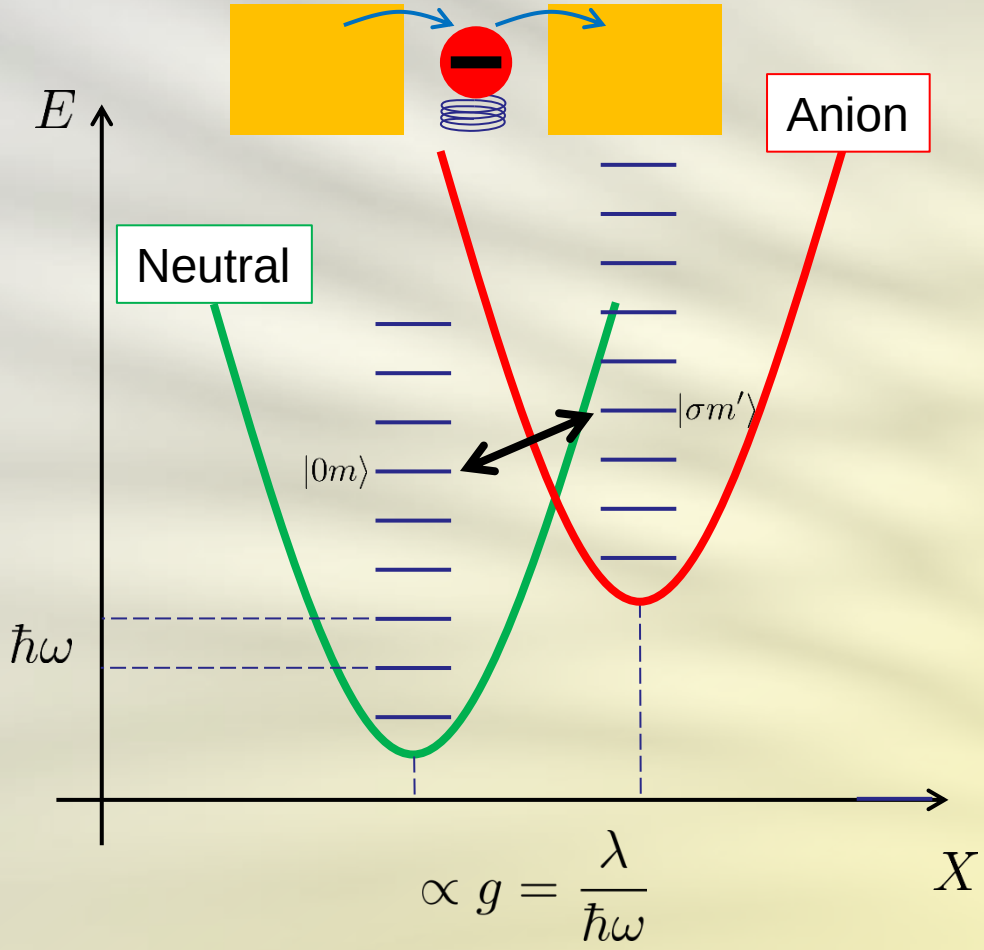


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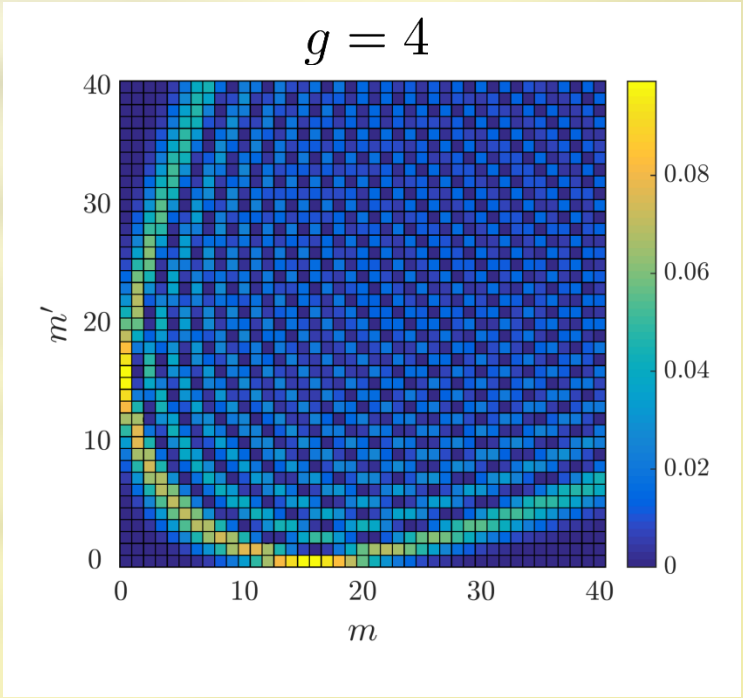


# Dynamics: rate equations

$$\dot{P}_n^N = -\sum_{\alpha m}(\Gamma_{\alpha,nm}^{N,+} + \Gamma_{\alpha,nm}^{N,-})P_n^N + \sum_{\alpha m}\Gamma_{\alpha,mn}^{N-1,+}P_m^{N-1} + \sum_{\alpha m}\Gamma_{\alpha,mn}^{N+1,-}P_m^{N+1}$$

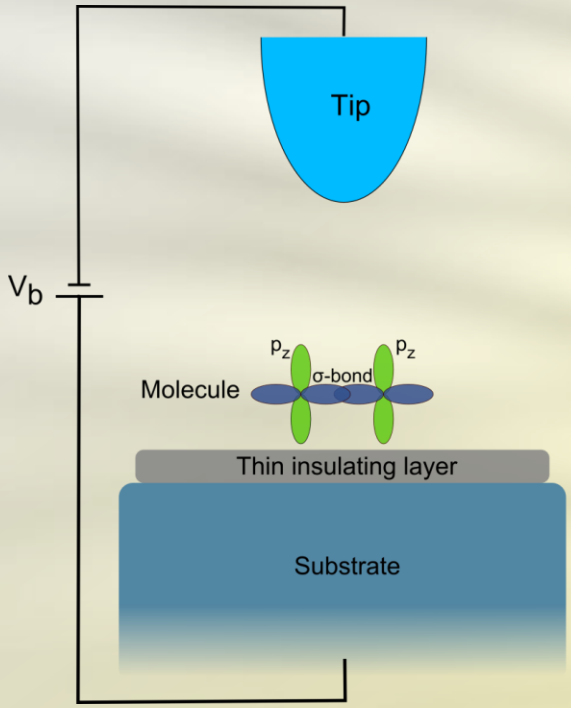
$$-\Gamma_{\mathrm{rel}}(P_n^N - \delta_{n0}\sum_m P_m^N)$$

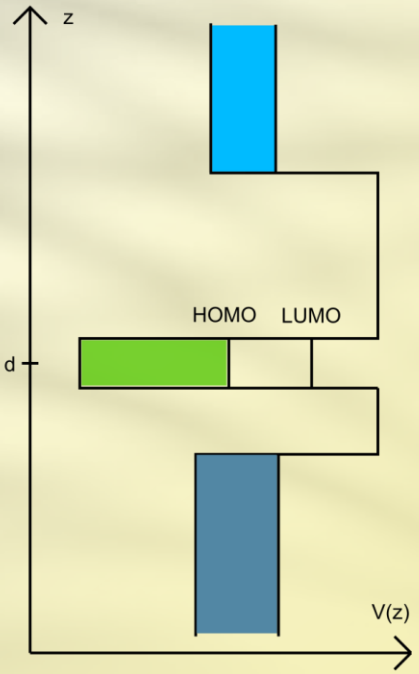
Vibrational relaxation which does NOT change the particle number

$$\Gamma_{\alpha,nm}^{M,+} = \frac{2\pi}{\hbar}|t_\alpha|^2 D_\alpha\, F(n,m;g) f^+(E_{M+1,m} - E_{M,n} - \mu_\alpha)$$

$$\Gamma_{\alpha,nm}^{M,-} = \frac{2\pi}{\hbar}|t_\alpha|^2 D_\alpha\, F(n,m;g) f^-(E_{M,n} - E_{M-1,m} - \mu_\alpha)$$

# Scanning tunnelling microscopy on thin insulating films




Strong asymmetry in the barrier strengths

$$\bar{\Gamma}_{\mathrm{tip}} \ll \bar{\Gamma}_{\mathrm{sub}}$$

Several channels for vibrational relaxation

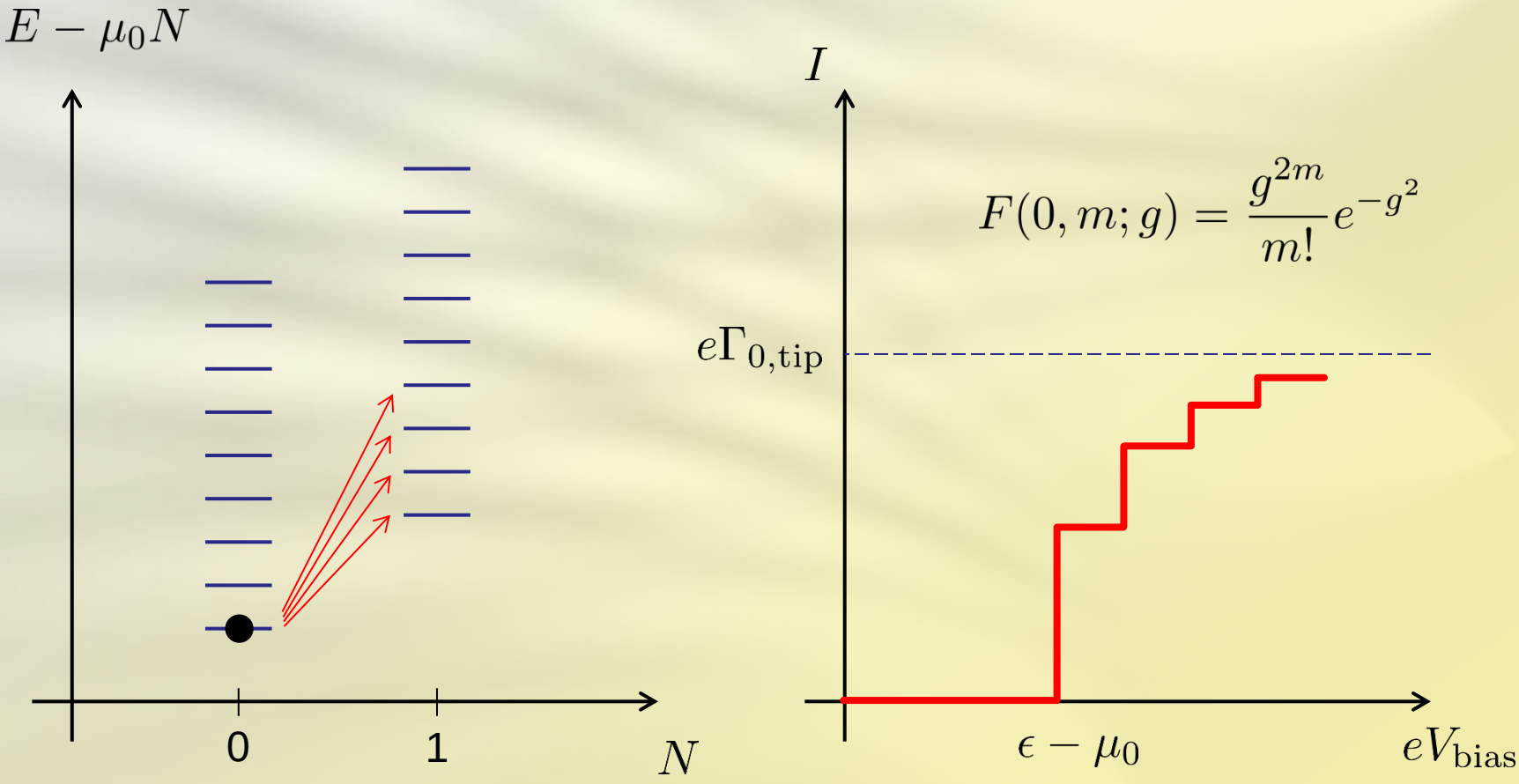
$$\Gamma_{\mathrm{rel}} \gg \bar{\Gamma}_{\mathrm{tip}}$$

Bias drop mainly on the tip side

$$\mu_{\mathrm{tip}} = \mu_0 + eV_{\mathrm{bias}}$$

# Current

$$I_{\mathrm{tip}} = e\cancel{P_0^0} \sum_m \Gamma_{0,\mathrm{tip}}\, F(0,m;g) f^+[\epsilon + m\hbar\omega - \mu_0 - eV_{\mathrm{bias}}]$$



# Role of the tip position ?

The tunnelling amplitude between the tip and the molecule depends on the tip position. E.g. for a tip with *spherical* symmetry:

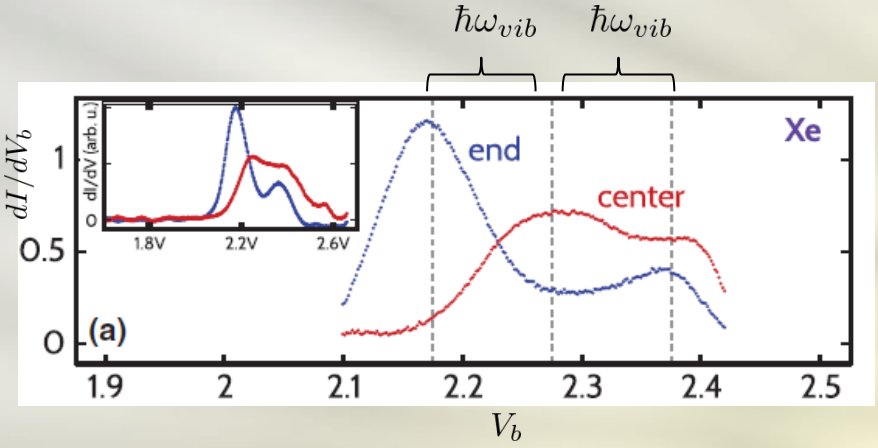
$$t_{\mathrm{tip}}(\mathbf{R}_{\mathrm{tip}}) = C\psi_{\mathrm{mol}}(\mathbf{R}_{\mathrm{tip}})$$

$$\Gamma_{0,\mathrm{tip}} = \frac{2\pi}{\hbar} D_{\mathrm{tip}}\, C^2 |\psi_{\mathrm{mol}}(\mathbf{R}_{\mathrm{tip}})|^2$$

By changing the tip position the current is **rescaled** by the profile of the molecular orbital which participates in the transport.

According to the Anderson-Holstein model, though, the current should NOT change its SHAPE.

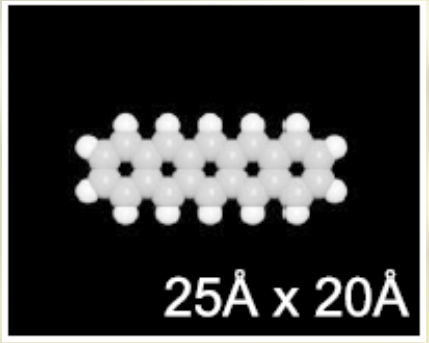
# Spatially resolved vibronic spectroscopy



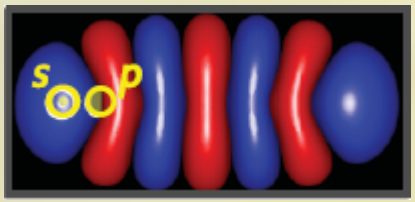

- position dependent dI/dV peaks
- the energy scale excludes higher electronic excitations
- if the tip and the (local) molecule symmetries match, the vibronic ground state transition is allowed
- if the symmetries do not match only transitions involving vibrational excited states are observed

  ⇨ “vibron-assisted tunnelling”

**Pentacene**




**LUMO**



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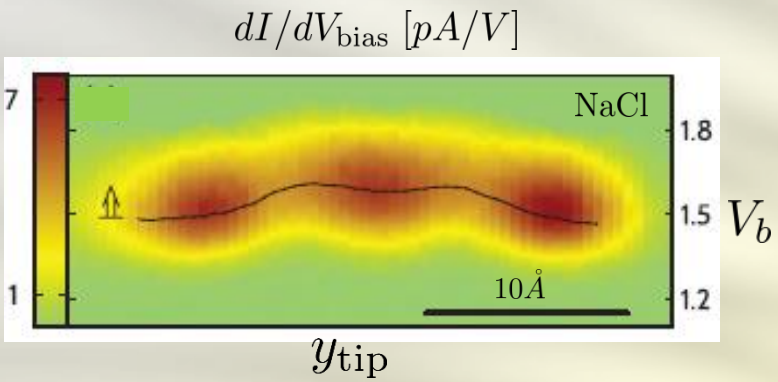


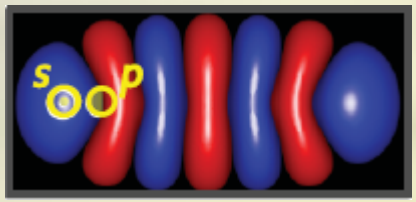


LUMO

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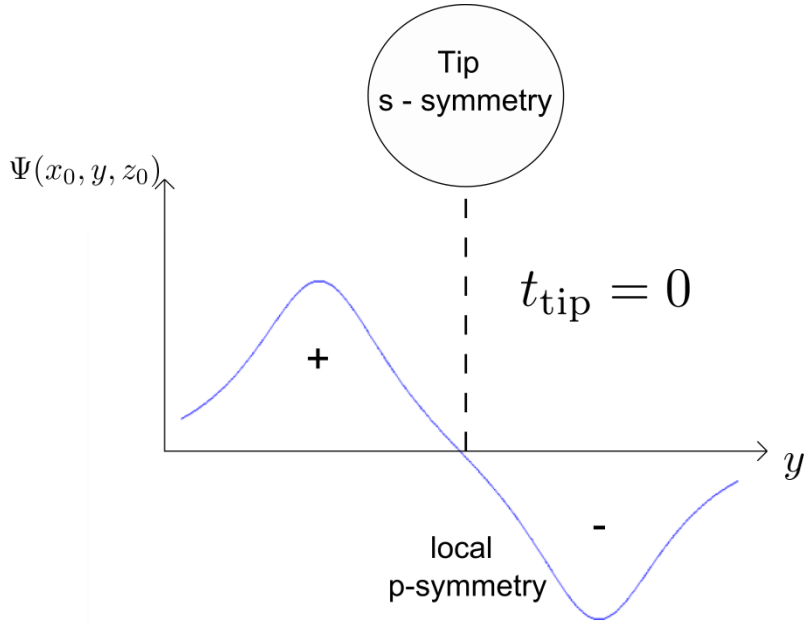
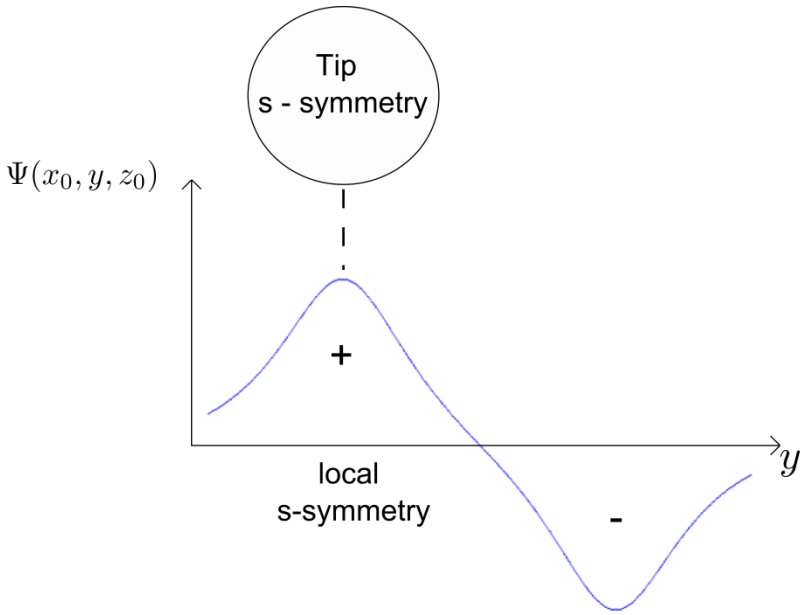
# Chen's derivative rule

$$t_{\mathrm{tip}}(R_{\mathrm{tip}}) = C\psi_{\mathrm{mol}}(R_{\mathrm{tip}})$$

Tunnelling into an odd molecular orbital formed by two $p_z$ orbitals:

$$\psi_{\mathrm{odd}}(\mathbf{r}) = \frac{1}{\sqrt{2}}\left[p_z(\mathbf{r}-\mathbf{r}_1) - p_z(\mathbf{r}-\mathbf{r}_2)\right]$$




C.J. Chen, Phys. Rev B **42**, 8841 (1990)

# Mechanical feedback

The molecular orbitals change their shape due to the molecular vibrations. Thus, the tunnelling amplitude is a function of the vibration coordinate

$$t_{\mathrm{tip}}(\mathbf{R}_{\mathrm{tip}}, X) = C\psi_{\mathrm{mol}}(\mathbf{R}_{\mathrm{tip}}, X)$$

$$\Gamma_{\mathrm{tip}} = \frac{2\pi}{\hbar} D_{\mathrm{tip}}\, C^2 |\psi_{\mathrm{mol}}(\mathbf{R}_{\mathrm{tip}}, X)|^2$$

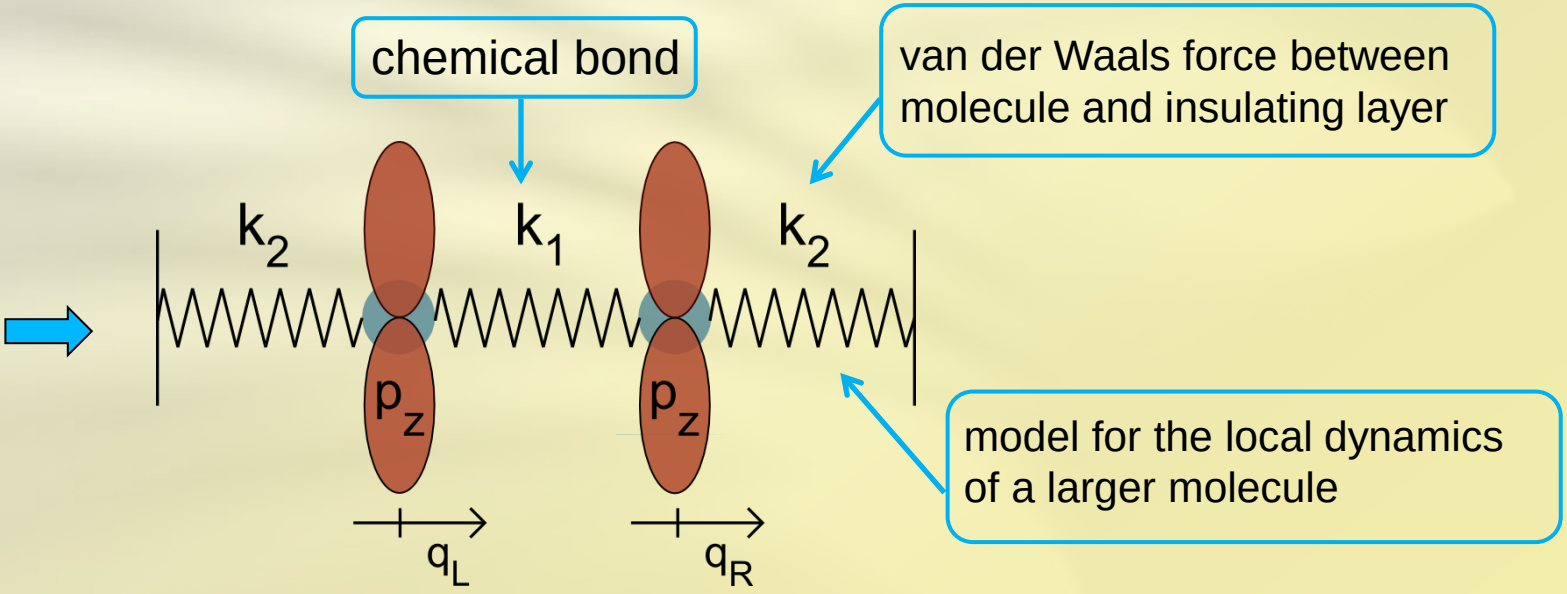
The tunnelling rates connecting the eigenstates are proportional to a set of modified Franck-Condon coefficients, e.g.

$$\Gamma^{M,+}_{\alpha,nm} = \frac{2\pi}{\hbar} D_\alpha\, \tilde{F}(n, m; g, \mathbf{R}_{\mathrm{tip}}) f^+(E_{M+1,m} - E_{M,n} - \mu_\alpha)$$

$$\tilde{F}(n, m; g, \mathbf{R}_{\mathrm{tip}}) = |\langle m| t_{\mathrm{tip}}(\mathbf{R}_{\mathrm{tip}}, X) e^{-ig\Delta X_0 P/\hbar} |n\rangle|^2$$

# Minimal model for the molecule

- molecular orbital with one nodal plane
- two vibrational modes
  - one mode moves the nodal plane
  - one mode does not move the nodal plane



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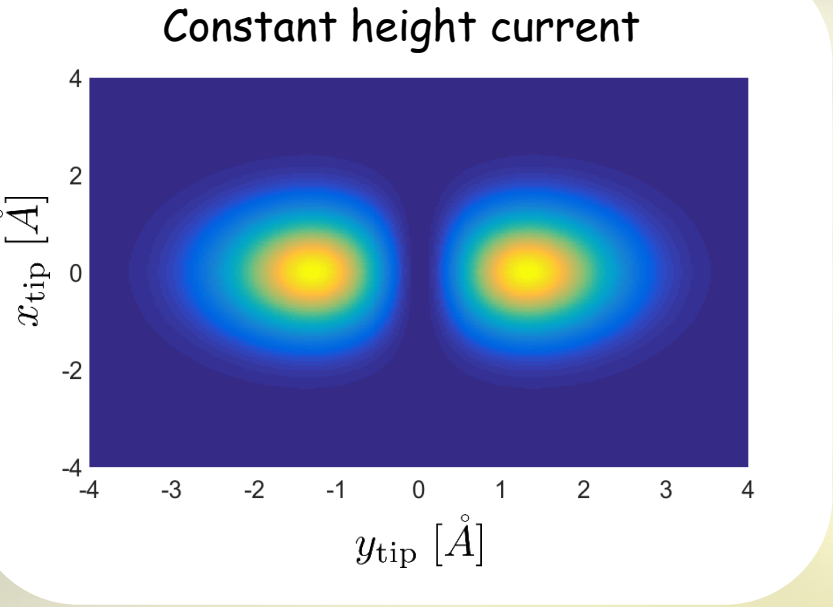
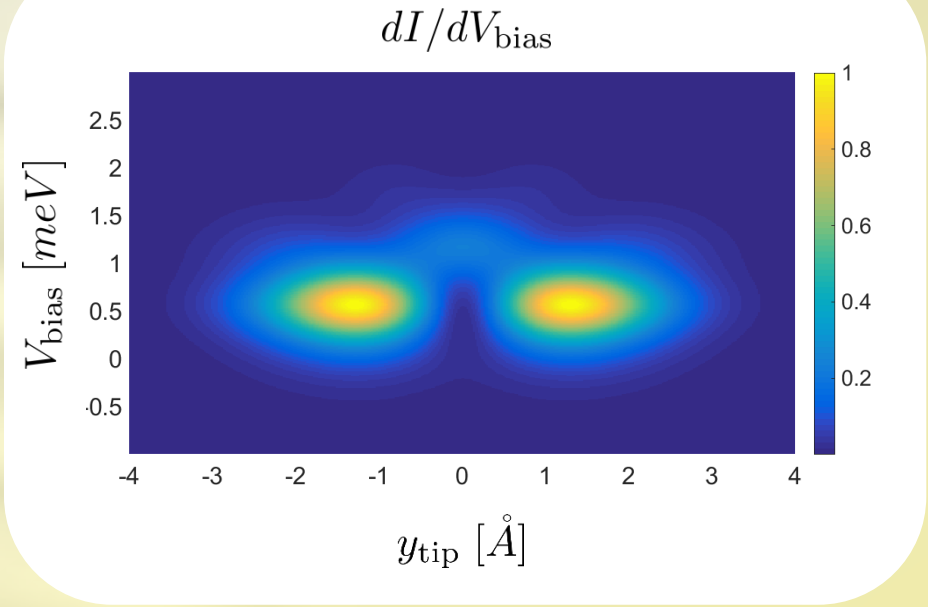
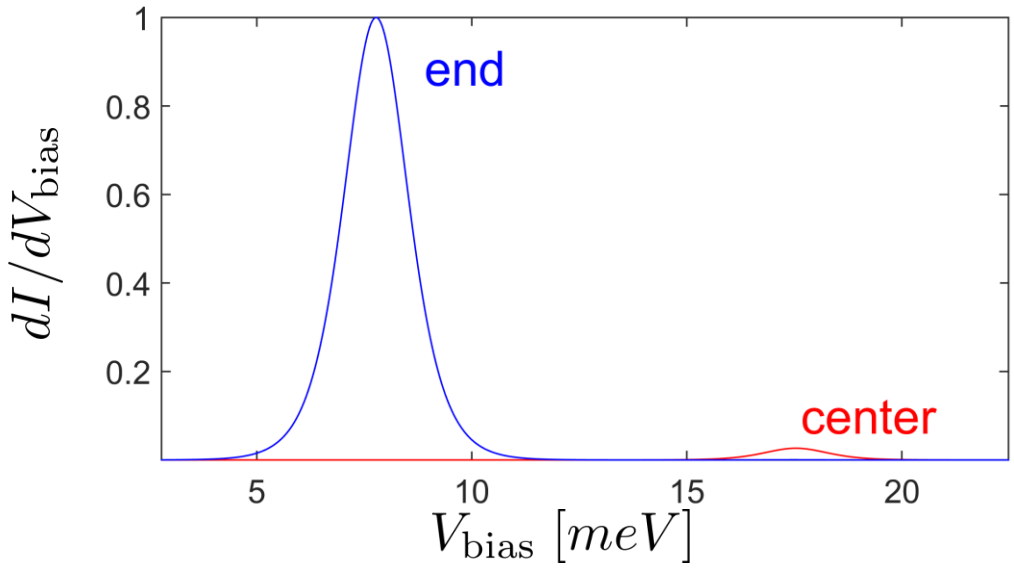


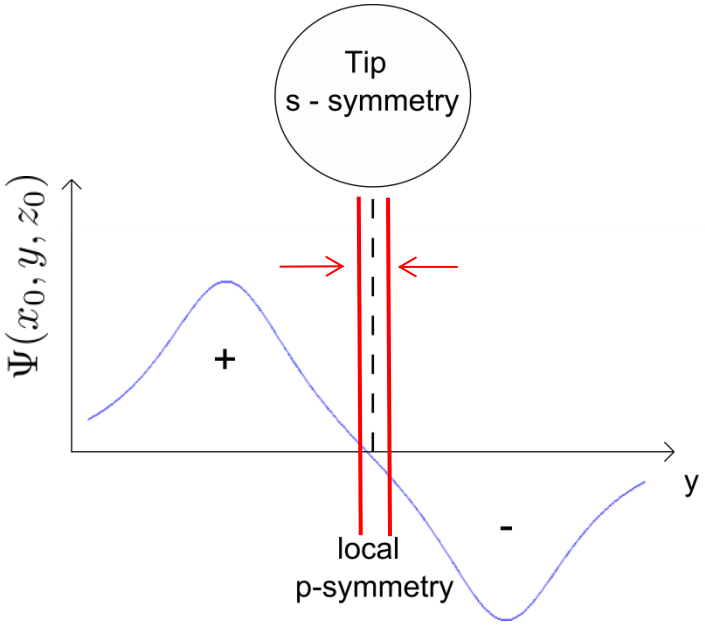




R. Kozlowsky, Master Thesis 2015

# Size of the effect

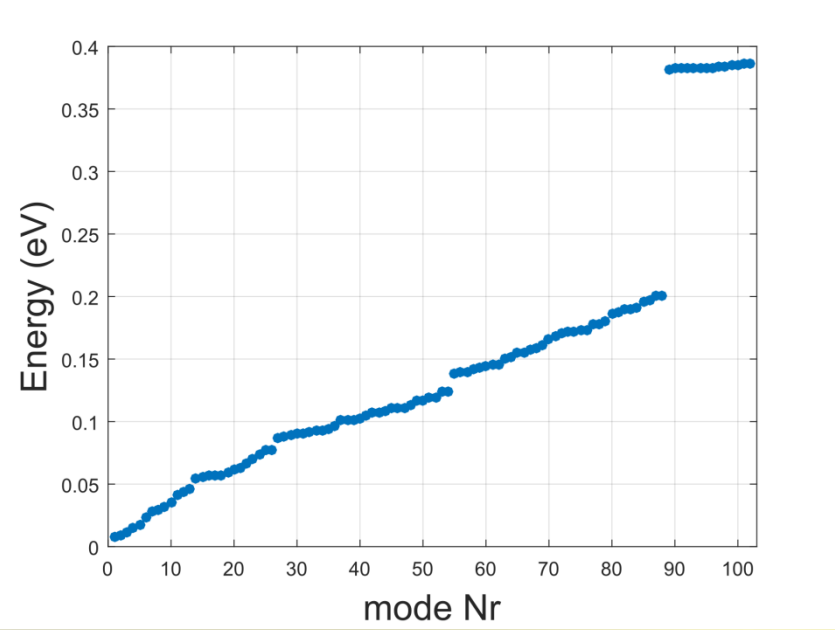
For realistic zero-point fluctuations the peak height in the center of the molecule is much smaller than the peak height at the end.

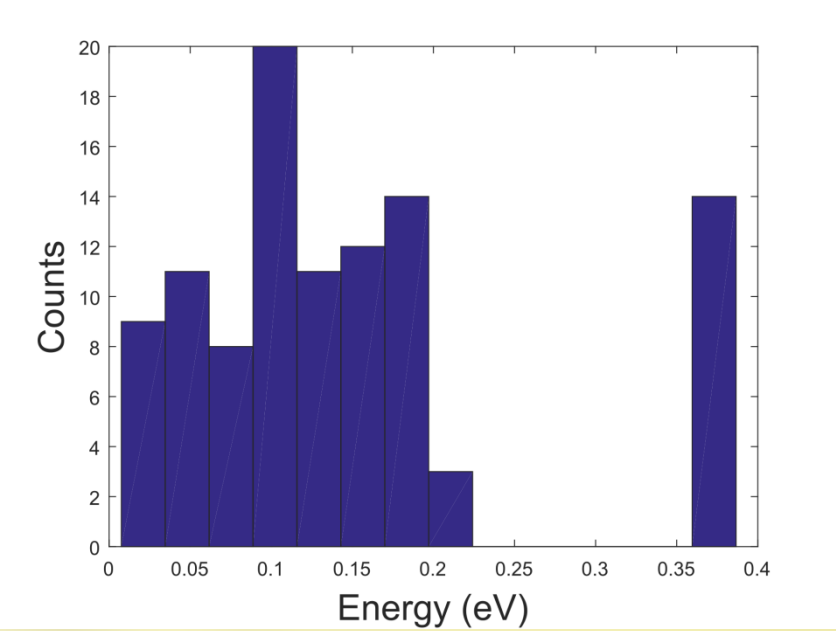


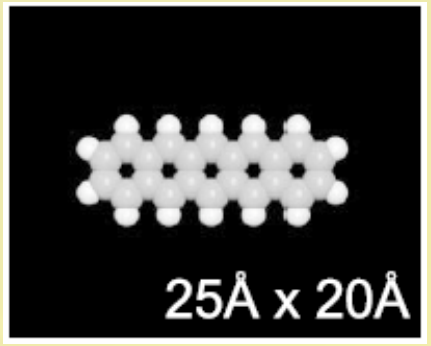

R. Kozlowsky, Master Thesis 2015

# The vibrational modes of pentacene




Frequencies and eigenmodes calculated with FHI-AIMS



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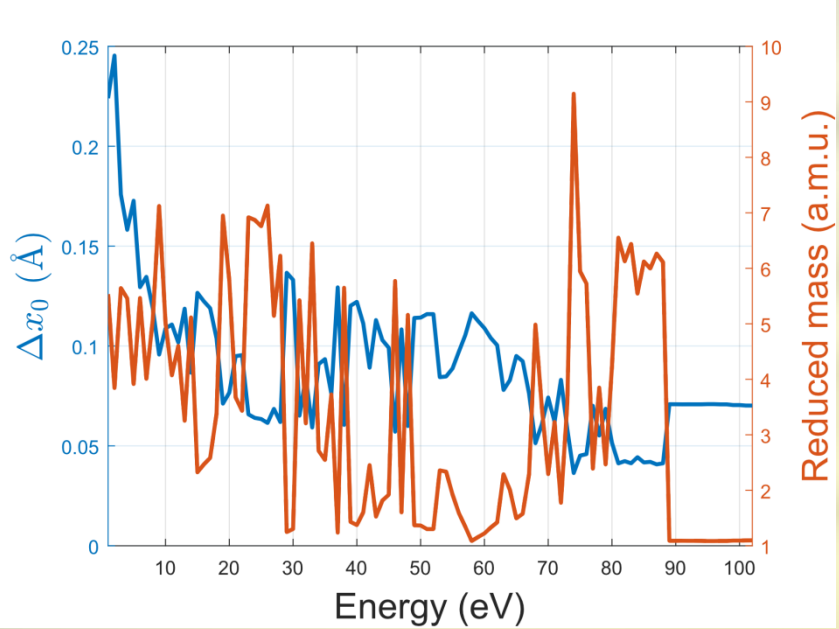
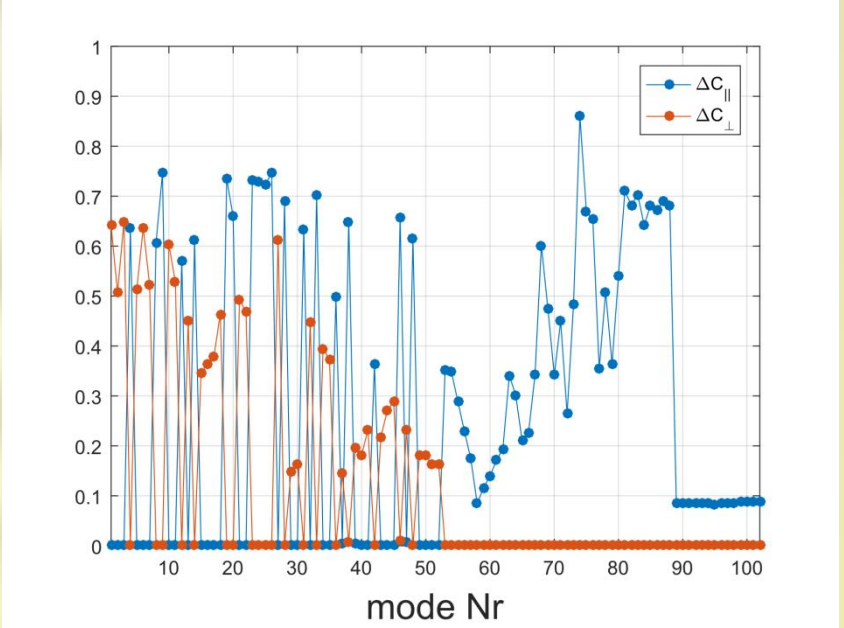
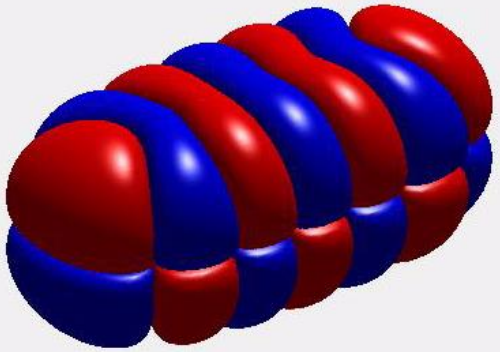


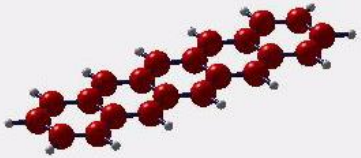



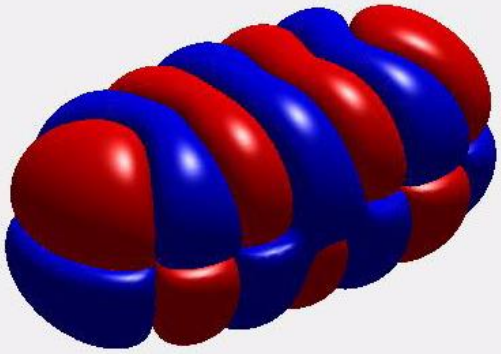

Frequencies and eigenmodes calculated with FHI-AIMS

Mode 1

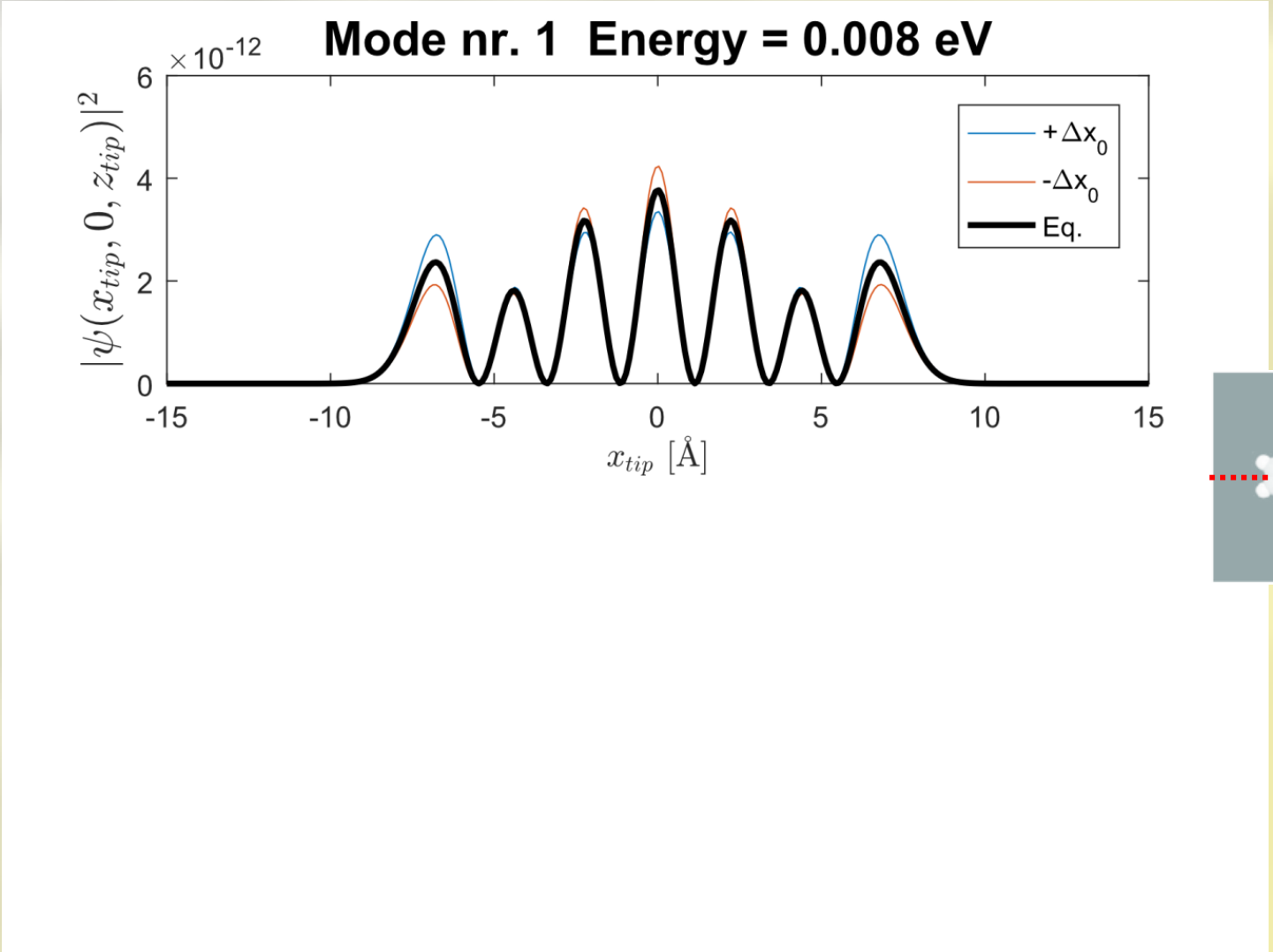


Mode 39





# The vibrational modes of pentacene



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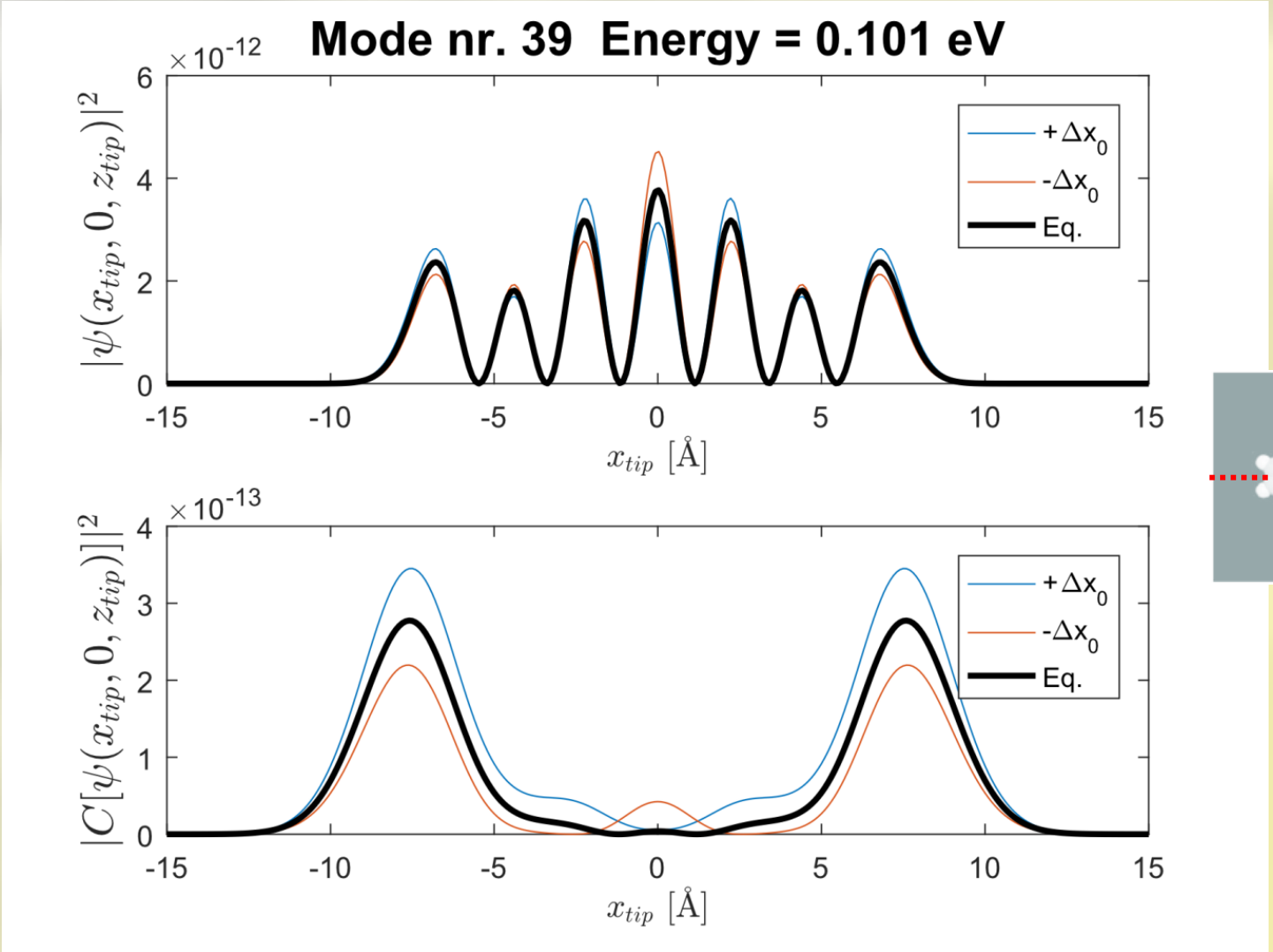
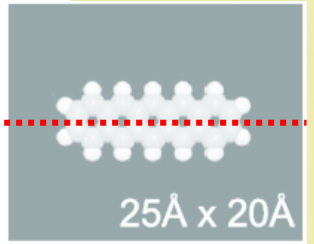
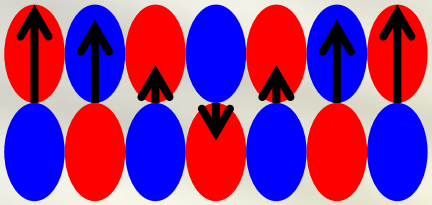


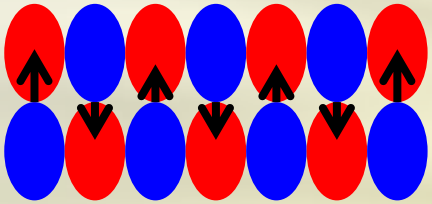
# Destructive interference

Mode 1



Electronic destructive interference
hardly affected by the vibration

Mode 39

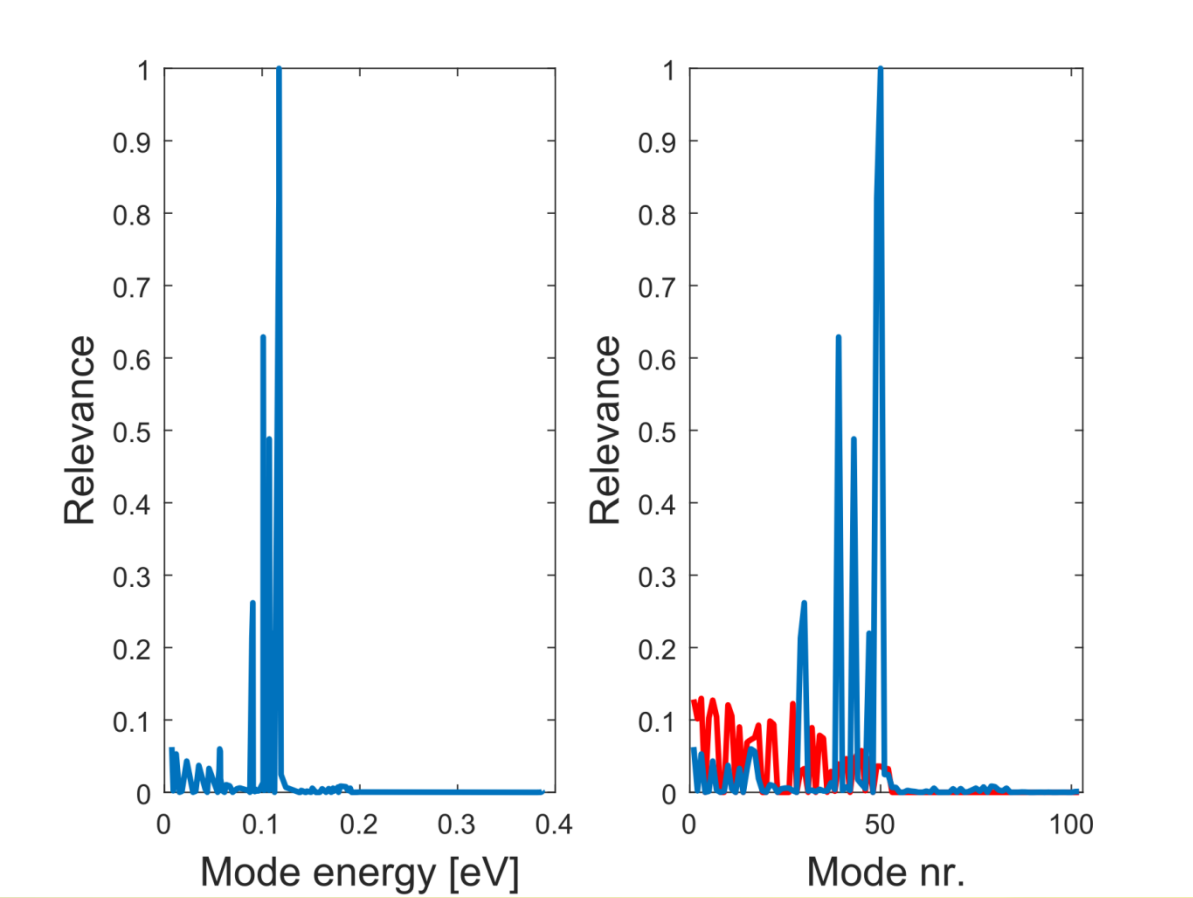


Electronic destructive interference
strongly affected by the vibration

Moreover, the out of plane oscillations of the H atoms causes in the higher energy modes a $\sigma\pi$ of the molecular orbitals.

# The vibrational modes of pentacene

Relevance = norm of the variation of the (convoluted) tunnelling rate with respect to the mode coordinate



# Summary

1. The Anderson-Holstein model fails in describing molecular vibrations in the STM setup
2. Position resolved spectroscopy reflecting tip-molecule symmetry matching has been obtained by including a mechanical feedback to the tunnelling rate
3. The effect predicted by the minimal model is much weaker than the one experimentally observed
4. A detailed analysis of the vibrational eigenmodes of pentacene reveals promising vibrational modes for a realistic improvement of the theory

Thank you
for your attention!