UNI BASEL

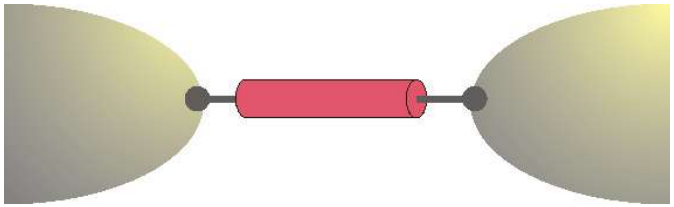
SNI SWISS NANOSCIENCE INSTITUTE
EINE INITIATIVE DER UNIVERSITÄT BASEL UND DES KANTONS AARGAU

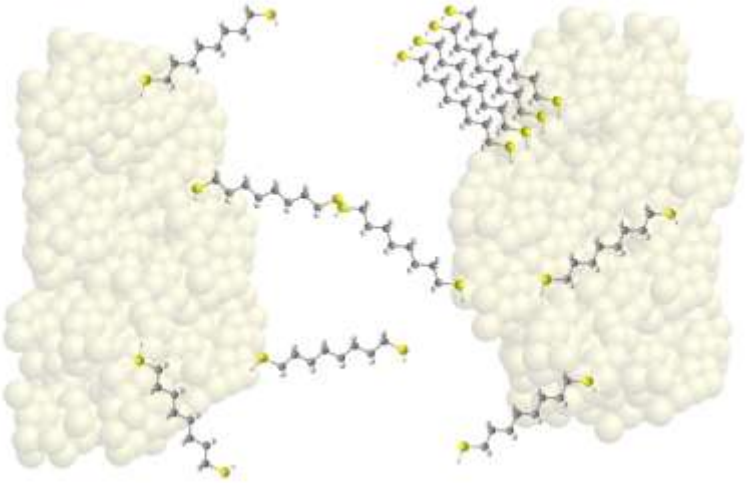
Molecular and carbon-based electronic systems

Lecture 6
Molecular junctions basics II
& spectroscopy

Vorlesung Uni Basel, HS2017

molecular junction





nanometer and molecular-scale junctions

- structural disorder — *electrodes and junction geometry*
- interactions — *anchoring*, *self-assembly, polymerization*
- fluctuations — *mobility of (surface) atoms, molecular distortions, multiple local energy minima*

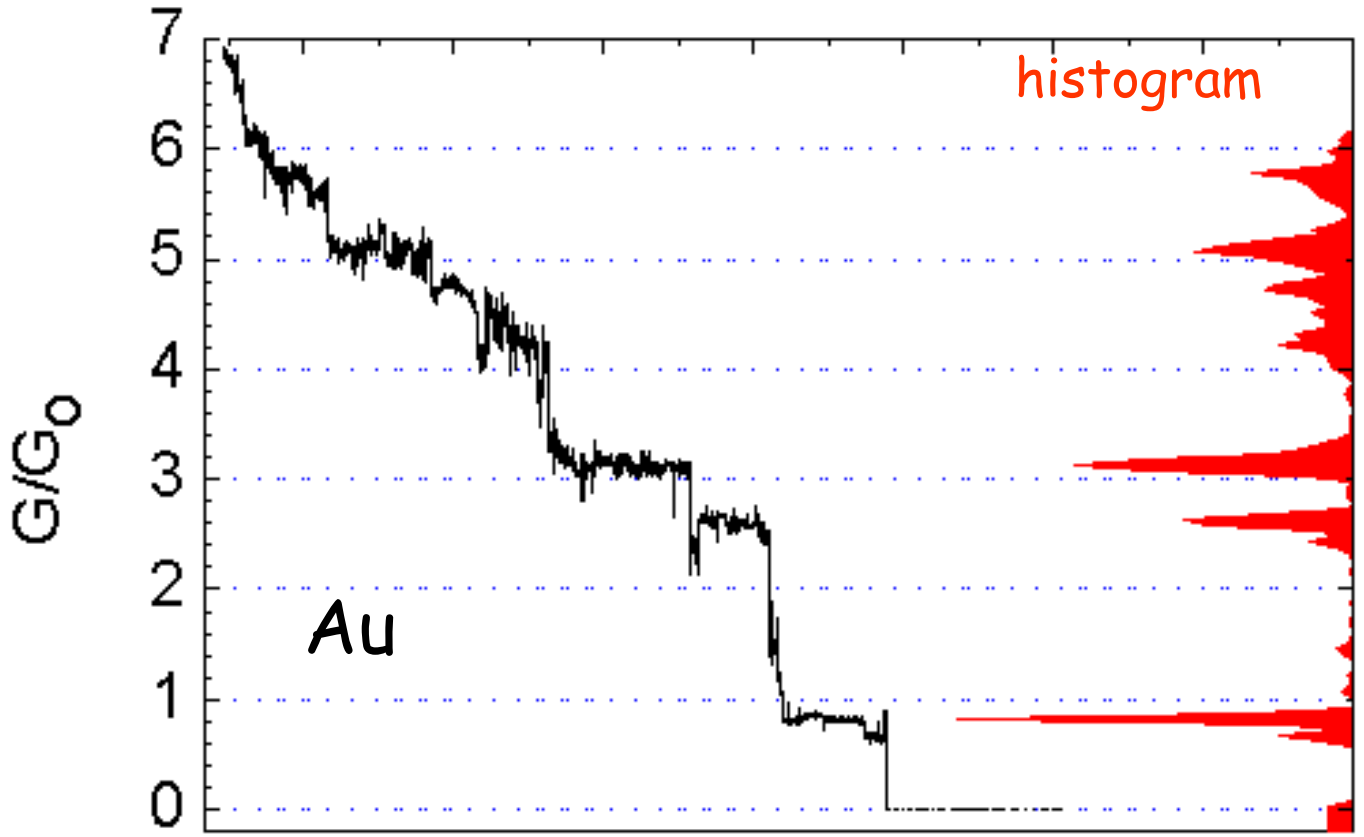
typ. energies

- Au-Au, Au-S bond — 0.7-1.5eV *Kawai et al., APL 2008, Tao et al., JACS 2009, JL arrays*
- surface Au-Au — ~ 0.3eV
- benzene-benzene — ~ 0.1eV *Jorgensen et al., JACS, 1990*

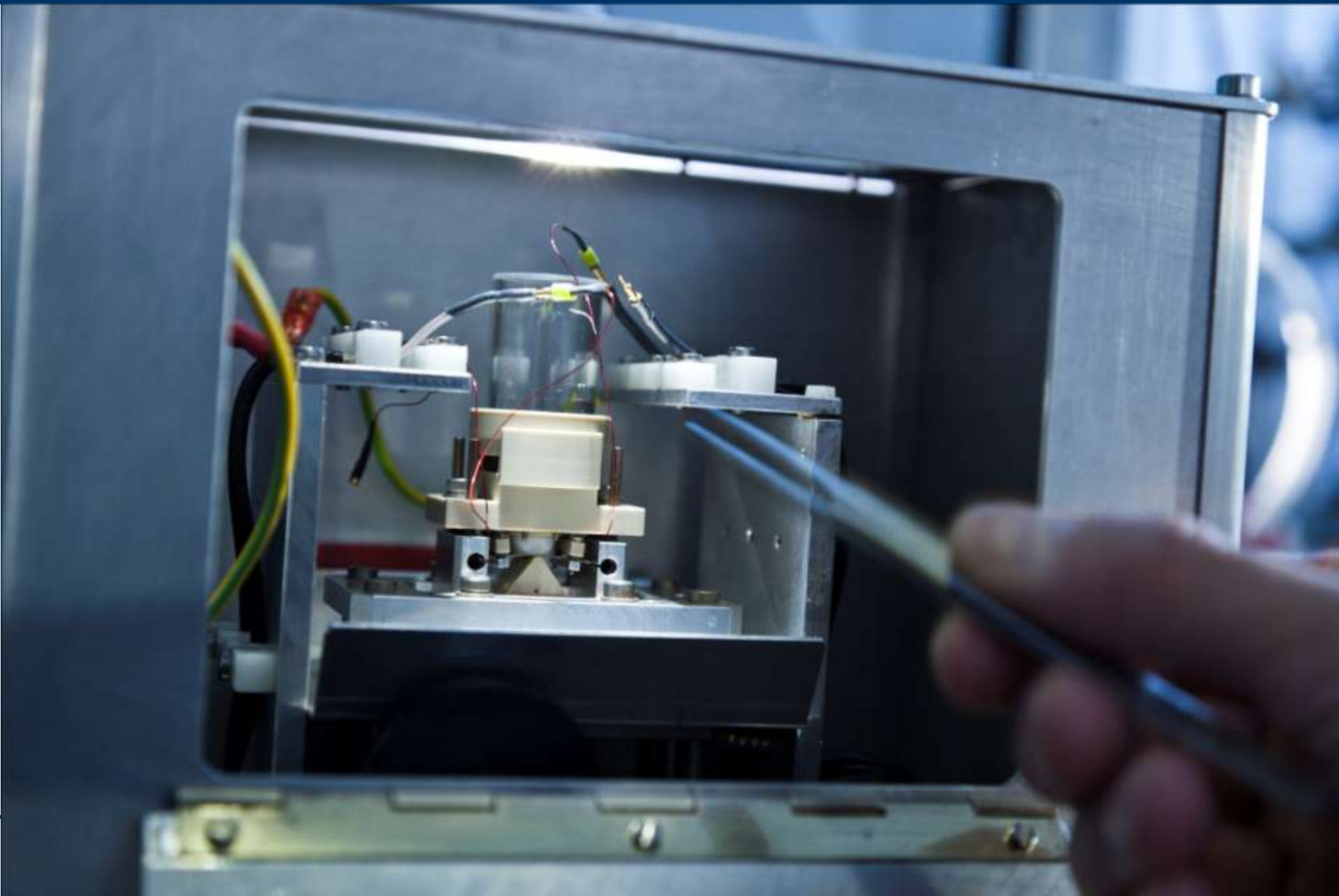
break junctions

Conductance quantization for Au contact

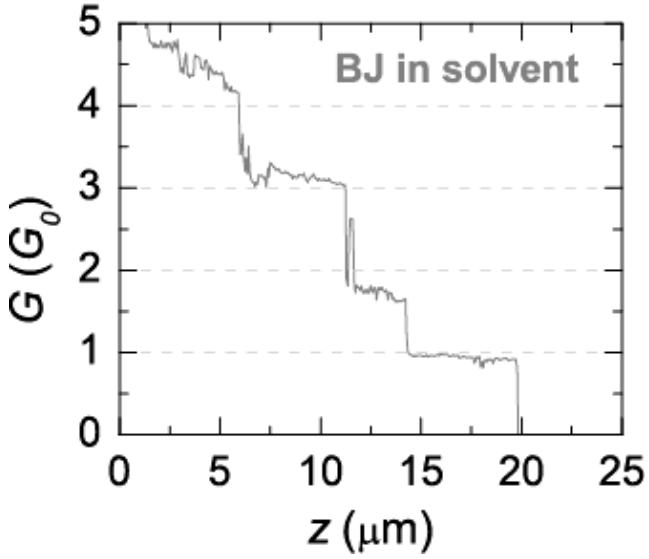
n = 1 with T = 1 ⇨ $G = \frac{2e^2}{h}\sum_n T_n = G_0 = \frac{2e^2}{h}$ = **77.5 μS**

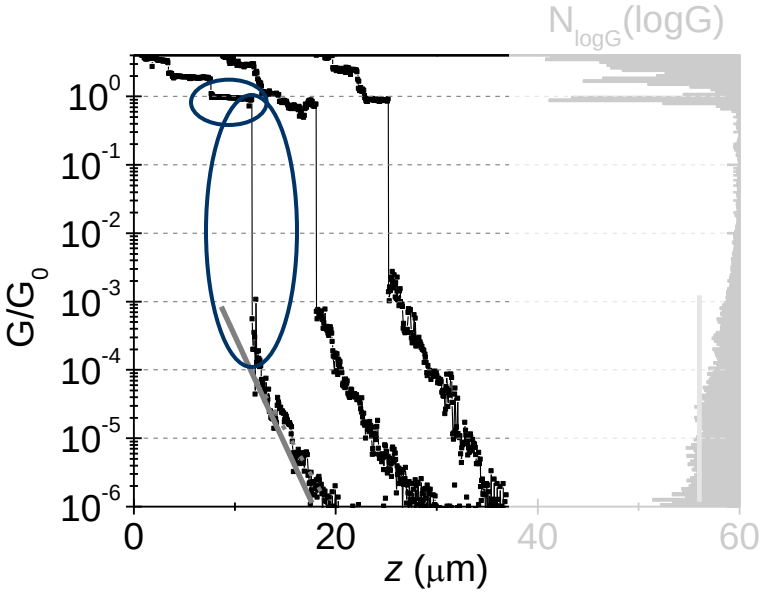


break junctions in liquid environment



opening: conductance vs elongation



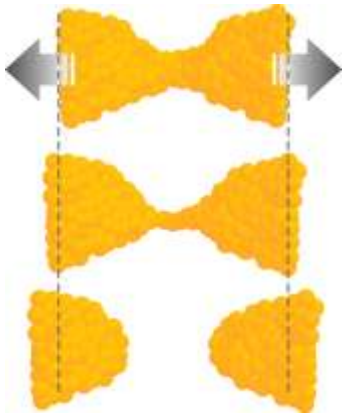


break junction opening
(solvent:THF/mesitylene 1:4 v/v)

conductance quantization, plateaus

$$G_0 = \frac{2e^2}{h} = 77.5\mu S$$

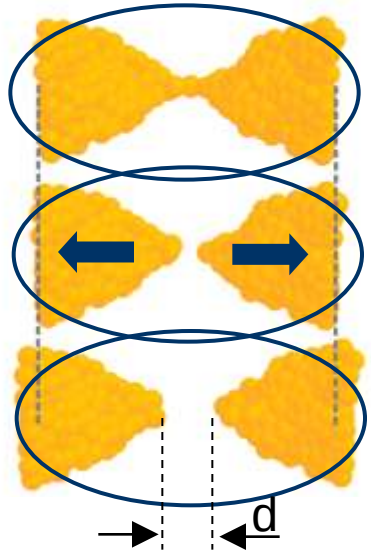
cf e.g. Agrait et al., Phys. Rep. 2003



- last Au G-plateau (~1G_0)
- breaking of Au bridge
- tunneling regime

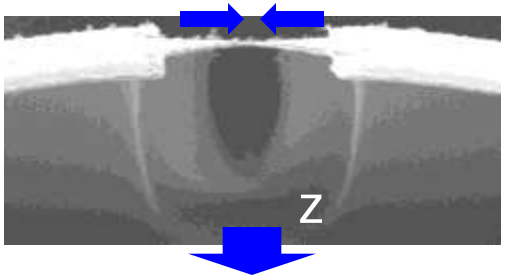
$$G \propto e^{-\beta d}$$

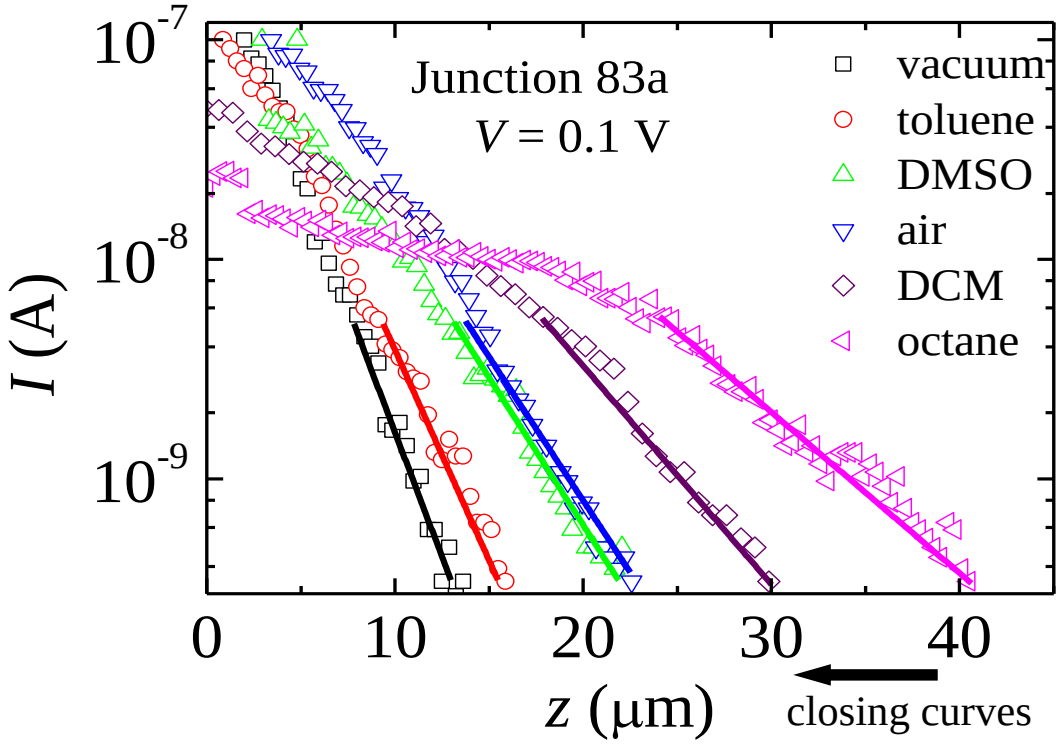
- statistics: histogram
  tunneling background
  ⇔ const.



tunneling regime

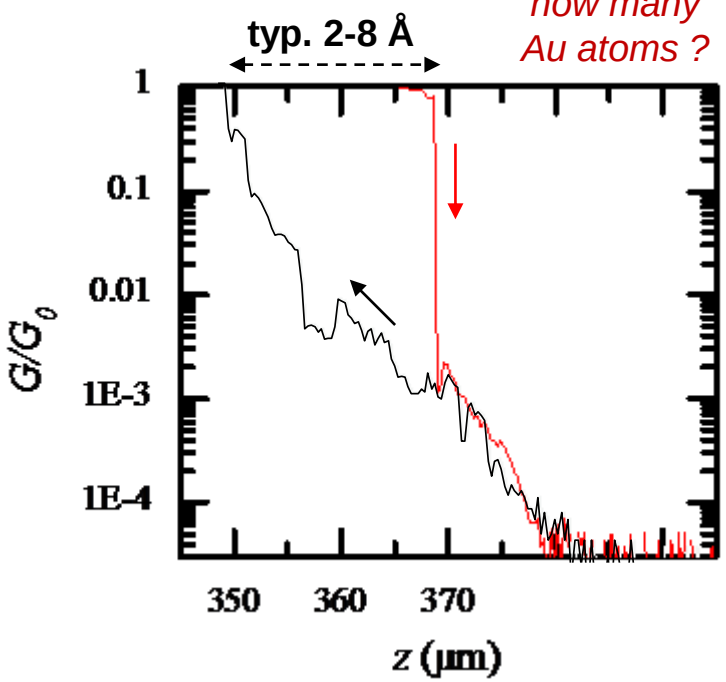
gap open,
close the
junction





opening-closing trace

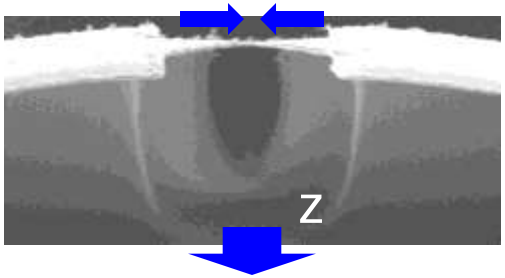
how many Au atoms ?



liquid ~ effective medium in first approx.

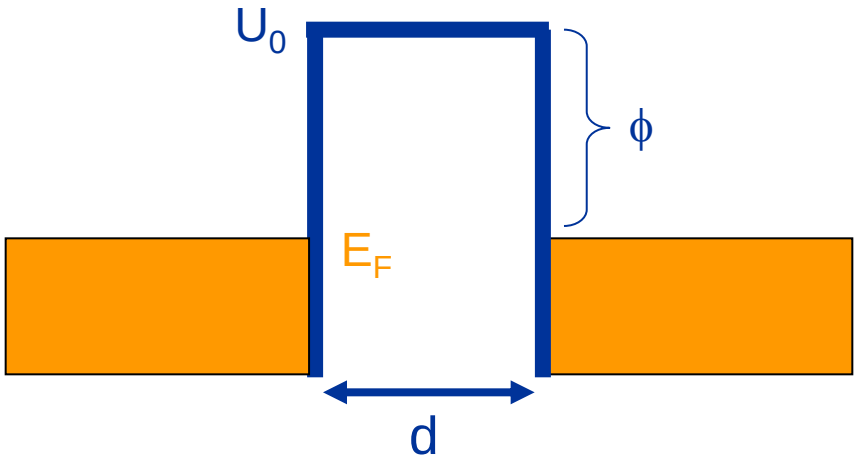
tunneling regime

gap open, close the junction



$$I \propto \exp\left(-\frac{2d}{\hbar}\sqrt{2m\phi}\right)$$

d=r·z r = reduction factor



$$B = 2r\sqrt{2m\phi}/\hbar$$

$$\rightarrow \quad I \propto e^{-Bz}$$

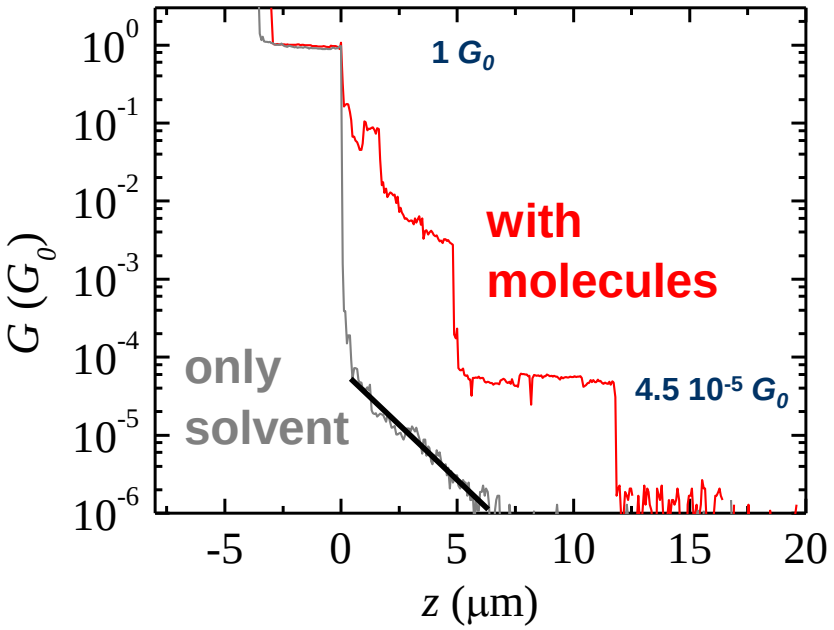
$\phi = U_0 - E_F$

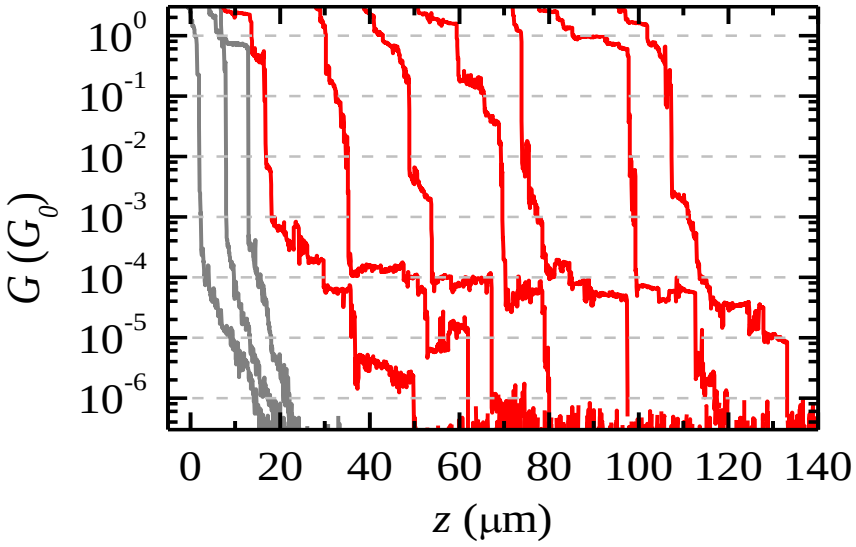
in vacuum: metal workfunction

in solvent: apparent barrier height

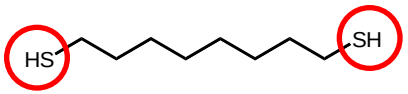
contacting simple molecules

signature of a molecular junction





example: alkanedithiols

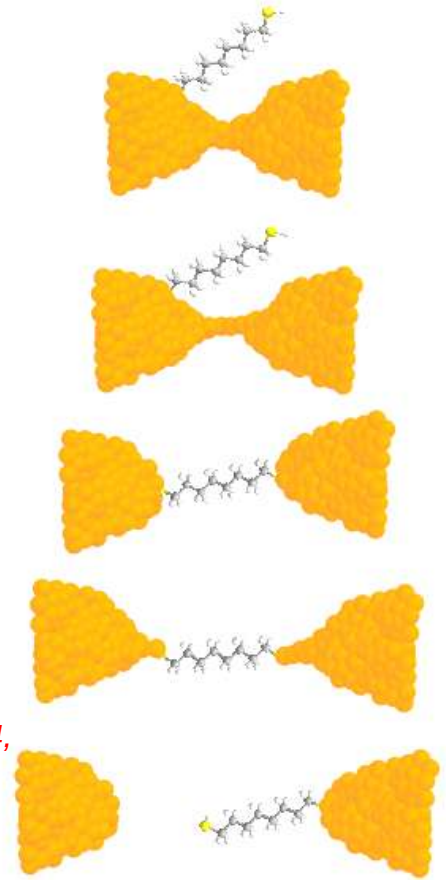


large HOMO-LUMO gap (few eV), ~ no solvent effect

molecular signature:

plateau *(at $G \ll G_0$)*

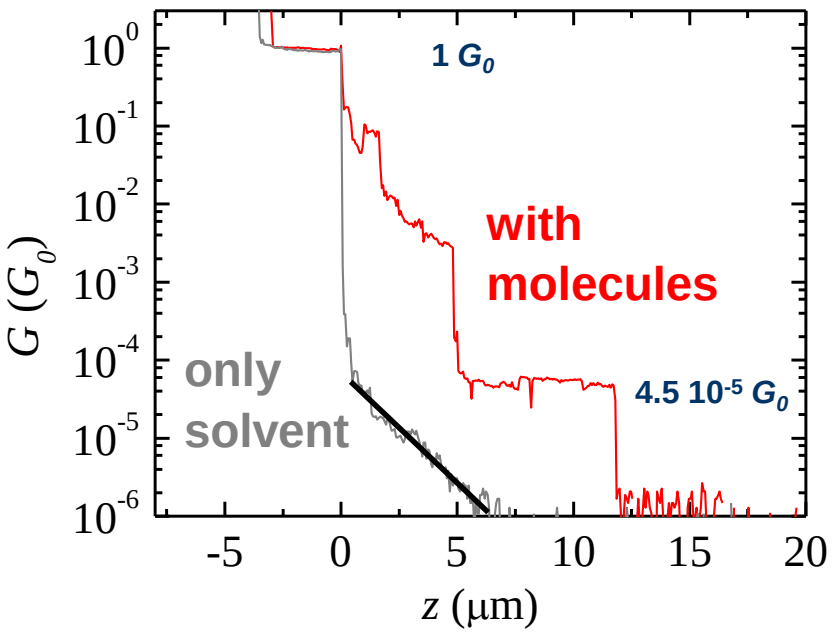
(Reichert et al., PRL 2002, Tao et al., Science, 2003, Nano Lett. 2004, JACS 2007)

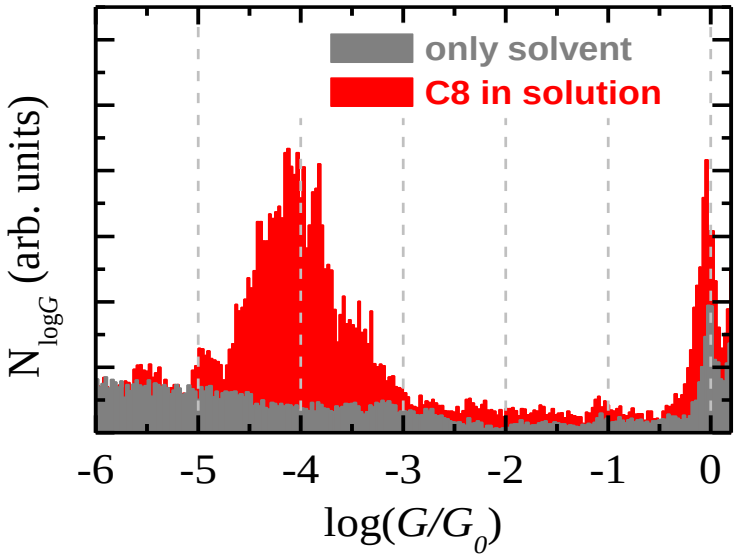


only solvent: Mesitylene

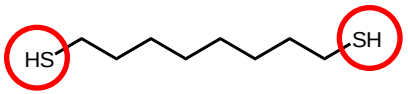
with molecules:0.1 M octanedithiol in Mesitylene

signature of a molecular junction

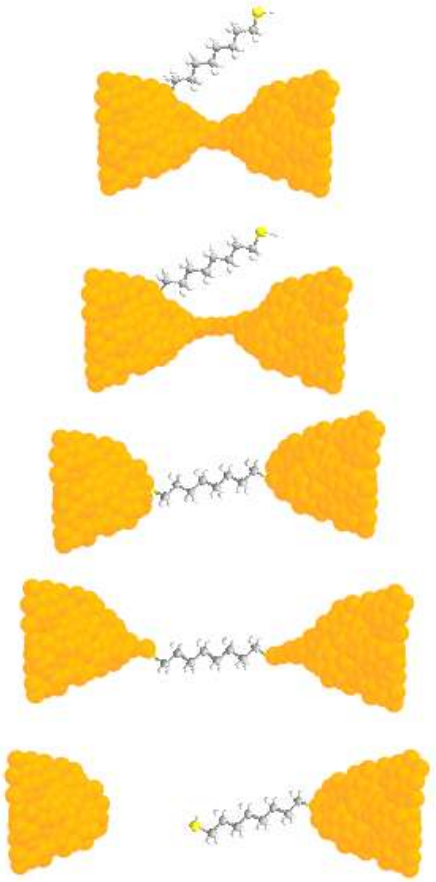




model system: alkanedithiols



large HOMO-LUMO gap (few eV), ~no solvent effect



molecular signature:
plateau *(at $G \ll G_0$)*
⇔ ***peak in (log-G) histogram***

- ***plateau in 20-60% curves***
- ***conductance window > 6 orders of mag.***

M.T. Gonzàlez et al., Nano Lett. (2006) & New J. Phys. (2008)

understanding transport through molecules

Landauer approach to electron transport

Electronic transport as scattering problem

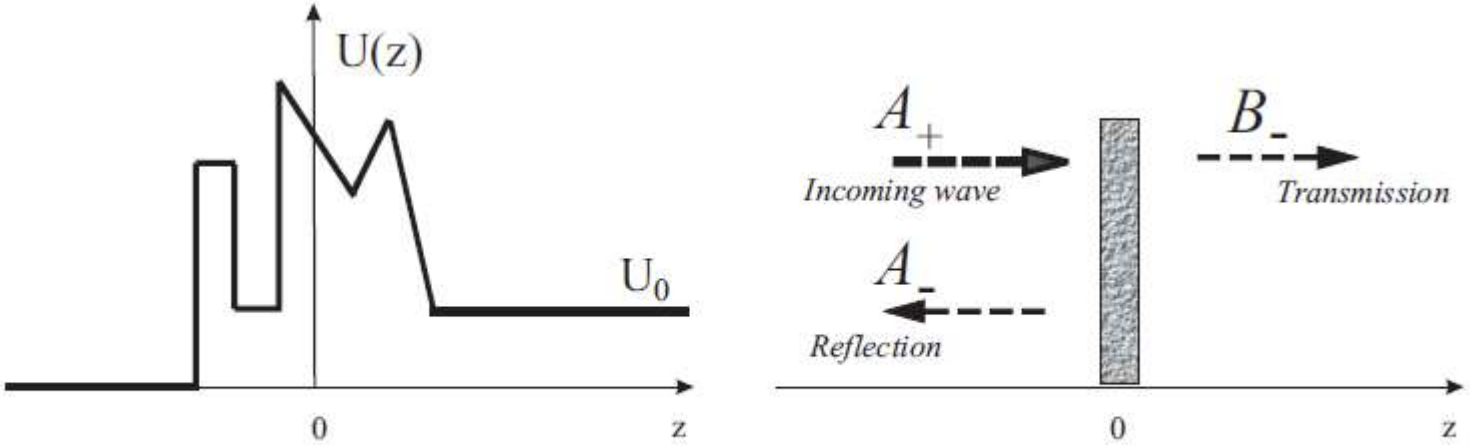
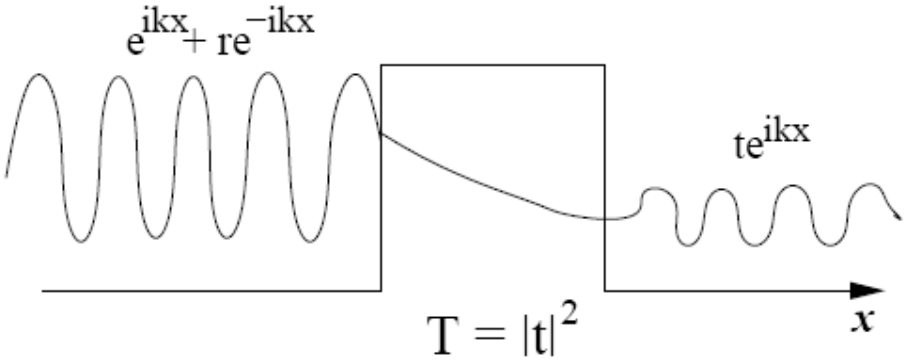


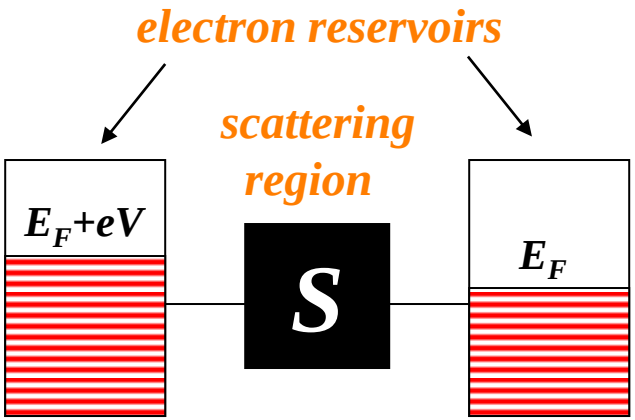
Fig. 1.2. One-dimensional potential. Reflection and transmission.

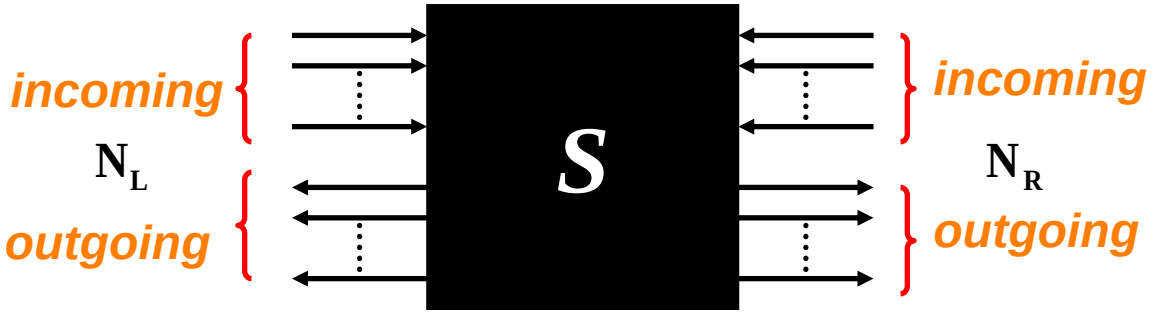
R. Landauer, IBM J. Res. Dev. 1, 223 (1957)

Landauer approach to electron transport

Electronic transport as scattering problem







$$G = \frac{2e^2}{h} T(E_F)$$

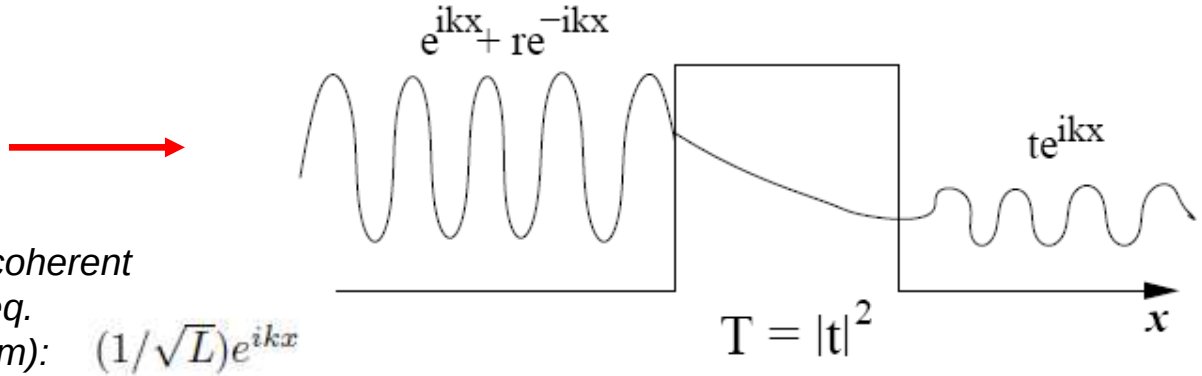
G = conductance
$T(E_F)$ = transmission at the Fermi energy

see Cuevas, Molecular Electronics, World Scientific

R. Landauer, IBM J. Res. Dev. 1, 223 (1957)

Landauer approach to electron transport

Electronic transport as scattering problem



one electron approach, phase coherent electrons in reservoir, thermal eq. plane waves (L: lenght of system): $(1/\sqrt{L})e^{ikx}$

electrical current density (calc. on right hand side of scattering potential) carried by one electron

$$J_k = \frac{\hbar}{2mi}\left[\psi^*(x)\frac{d\psi}{dx} - \psi(x)\frac{d\psi^*}{dx}\right] = \frac{e}{L}v(k)T(k) \qquad v(k) = \hbar k/m$$

group velocity

solid state device: sum over k (many electrons) and add Fermi distrib. for Left and Right reservoirs

$$J_{L\to R} = \frac{e}{L}\sum_k v(k)T(k)f_L(k)[1 - f_R(k)]$$

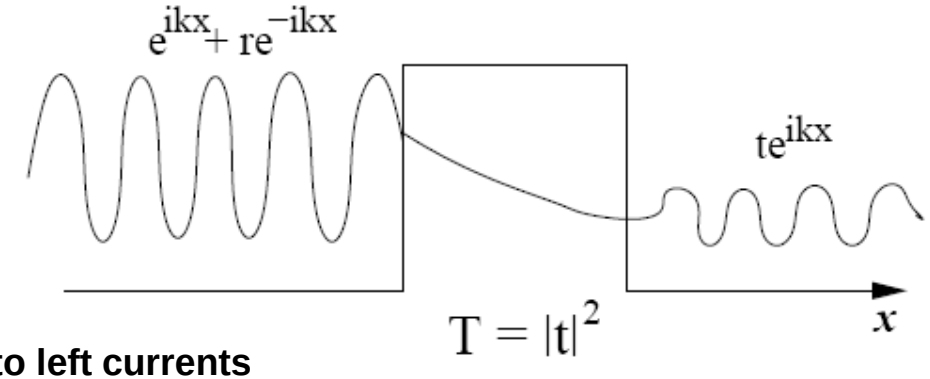
integrate $(1/L)\sum_k g(k) \to 1/(2\pi)\int g(k)dk$

variable change $dk/dE = (dE/dk)^{-1} = m/(\hbar^2 k)$ using $E = \hbar^2 k^2/(2m)$

conducting electrons: Fermi gas (non-interacting electrons)

Landauer approach to electron transport

Electronic transport as scattering problem



hence, we can write the **left to right** and **right to left currents**

NB: *the transmission probability is the same, no matter in which direction the barrier is crossed*

$$J_{L\to R} = \frac{e}{h}\int dE\, T(E) f_L(E)[1 - f_R(E)] \qquad J_{R\to L} = \frac{e}{h}\int dE\, T(E) f_R(E)[1 - f_L(E)]$$

total current through junction

NB: 1D situation: no difference between total current and current density

$$I(V) = J_{L\to R} - J_{R\to L}$$

spin →

$$I(V) = \frac{2e}{h}\int_{-\infty}^{\infty} dE\, T(E)[f_L(E) - f_R(E)]$$

Landauer

at T=0, low bias voltages (linear regime)

$$I = GV \quad \text{with} \quad G = (2e^2/h)T \qquad G_0 = \frac{2e^2}{h}$$

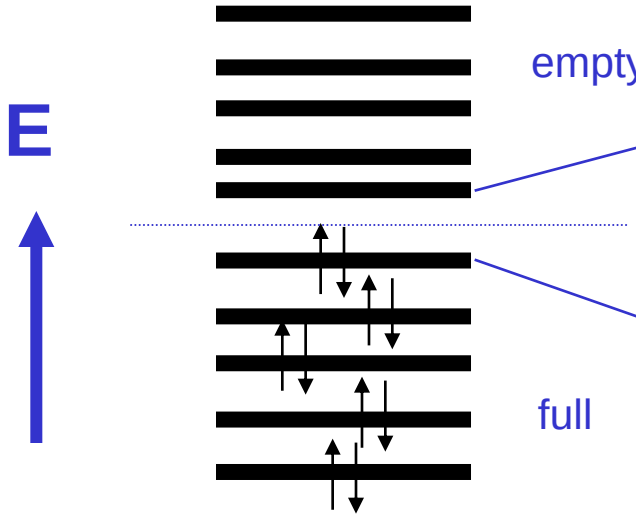
conductance quantum

and $T=T(E_F)$

$$G_0 \simeq (12.9k\Omega)^{-1}$$

molecular energy levels

(isolated) molecule
quantum system with spectrum of discrete energy states (molecular orbitals)



LUMO = lowest unoccupied molecular orbital

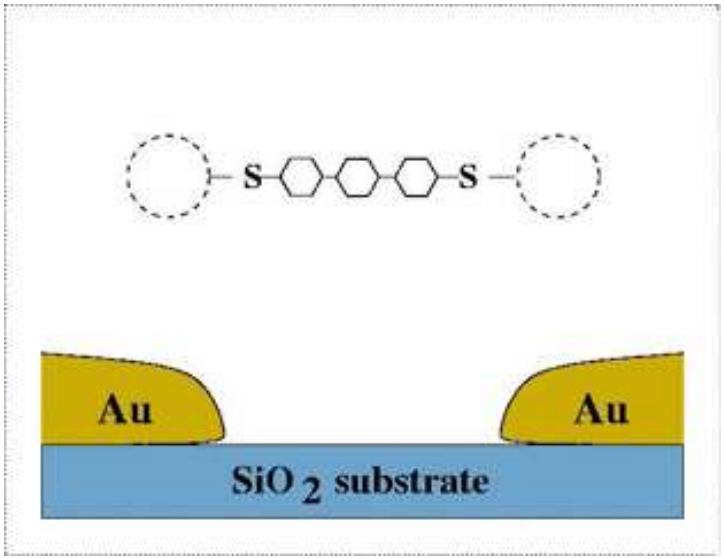
(HOMO-LUMO gap from light absorption)

HOMO = highest occupied molecular orbital

⇨ ‘Particle in a box’: molecule is small box

box smaller ⇔ levels more spaced ($\delta E > k_B T$)

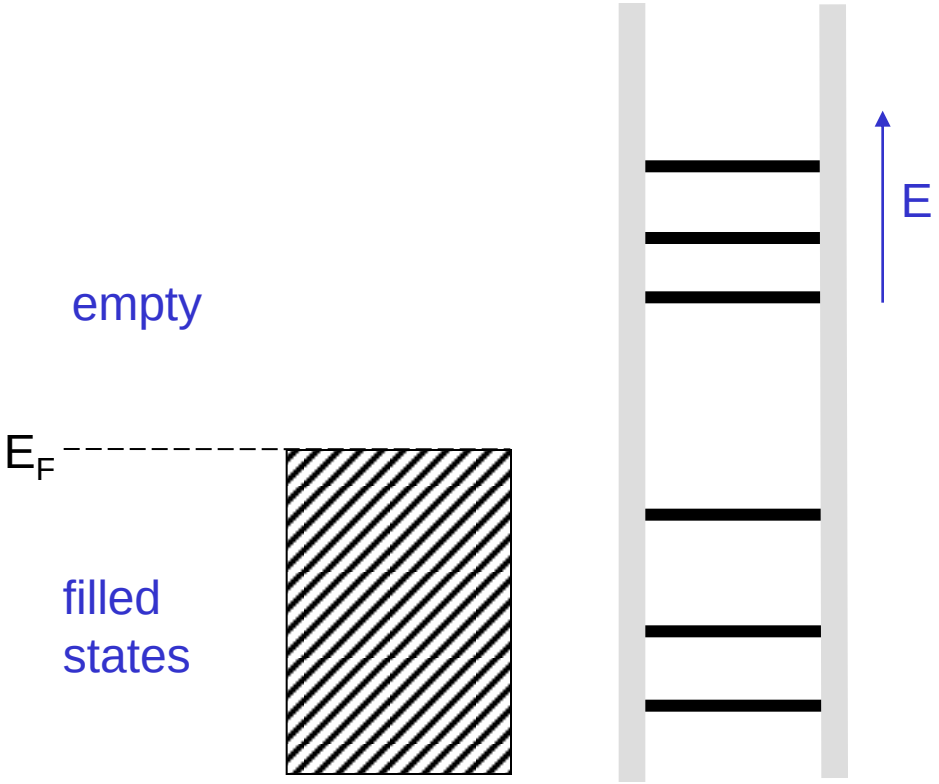
making contact…



Univ. Karlsruhe

Au: many levels: ~ continuous

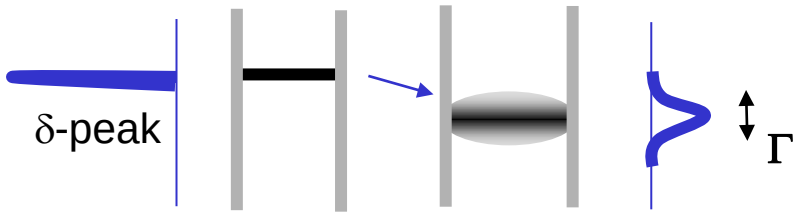
molecule: few discrete, levels



⇨ typ. 2 regimes: weak or strong coupling

"good" contact

energy levels



- **broadening**: Γ

  delta function

  ⇨ Lorentzian DOS

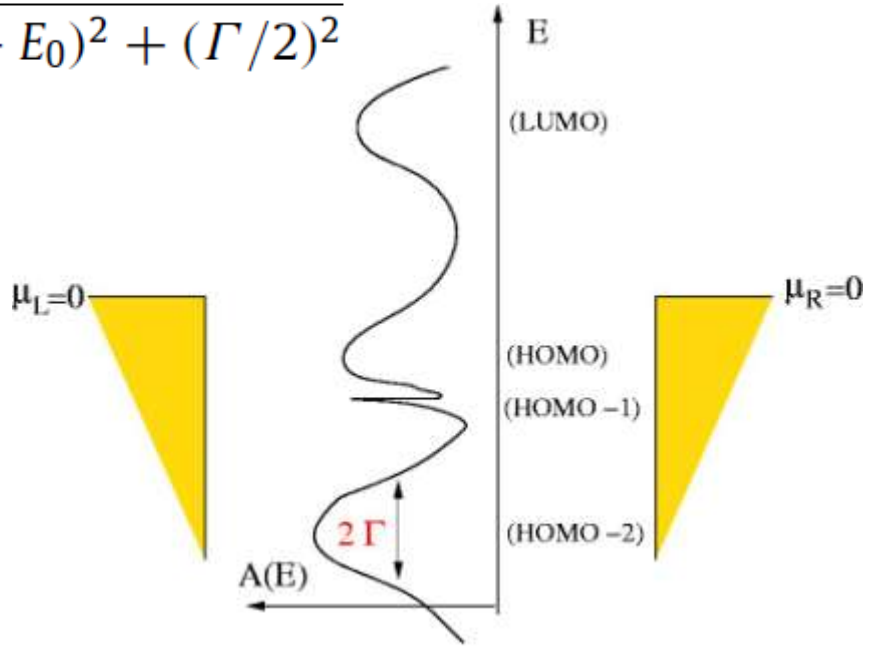
$$D(E) = \frac{1}{2\pi} \frac{\Gamma}{(E - E_0)^2 + (\Gamma/2)^2}$$

$$\Gamma = \Gamma_L + \Gamma_R$$

  relate Γ to typical resilience time τ:

  Heisenberg $\Delta E \, \Delta t > h$

  hence $\Gamma = h/\tau$



- **shift:** equil. ⇔ charge transfer

  typ. from electrode to molecule

"good" contact

current

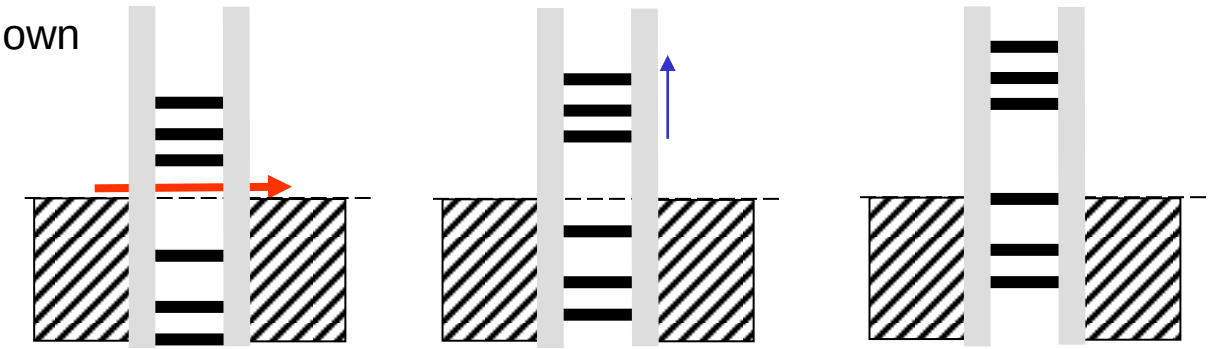
- **molecule seen as scatterer (Landauer)**
  ⇨ def. transmission function T(E)
  molecular orbitals ⇔ peaks in T(E)

$$I(E,V) = \frac{2e}{h} \int_{-\infty}^{\infty} \overline{T}(E,V)[f(E-\mu_2)-f(E-\mu_1)]dE$$

current ~ transmission probability x nb of states

- **at low bias:**
  E_F in HOMO-LUMO gap, I and G=U/I small

- **gating:** moving levels up/down

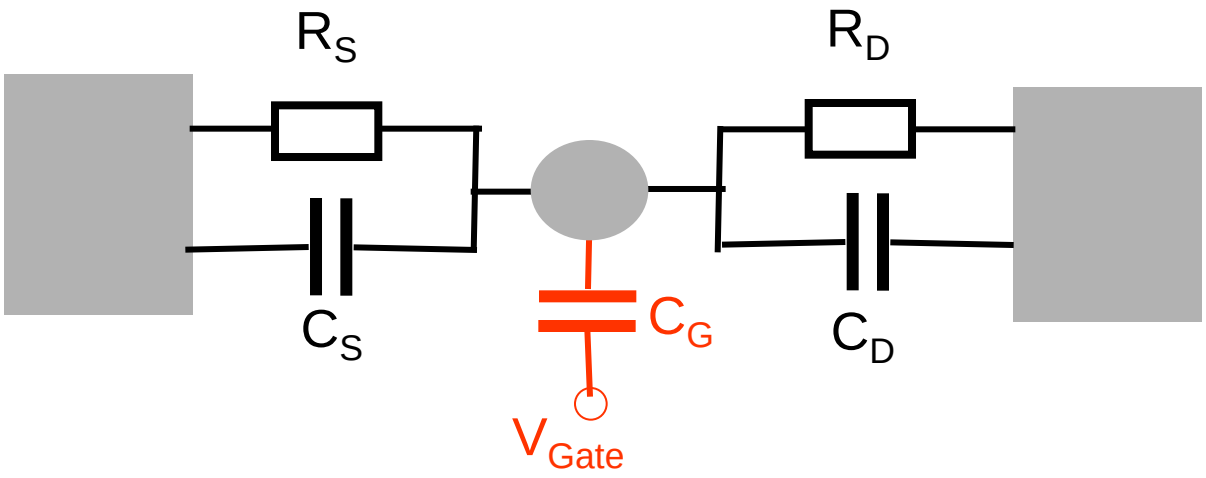


'Tunneling', small G

Level lines up, G ⇗

"bad" contact ⇨ capacitance

Equivalent circuit, **R large, C small**

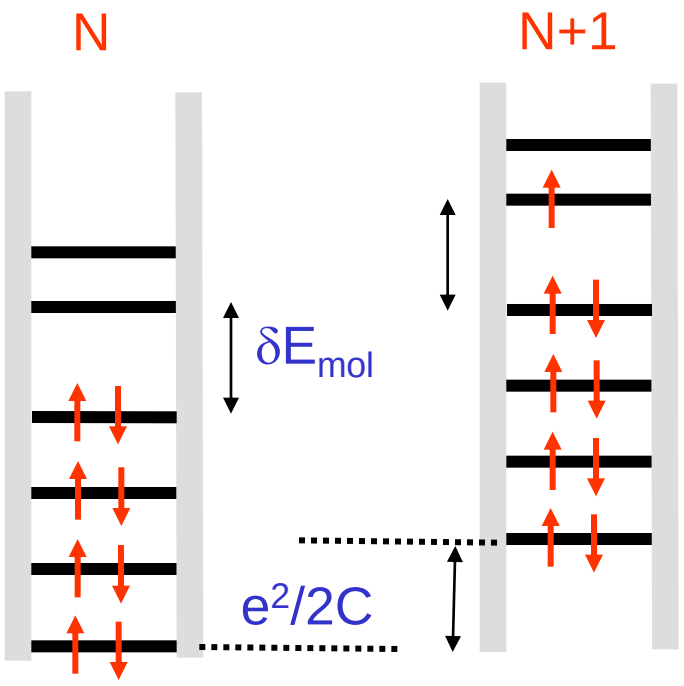


1. Residence time e^- : $\Delta t = R_t C$
2. Charging energy e^-: $E_C = e^2/2C$

Coulomb Blockade

If $E_C = e^2/2C \gg k_B T$

Then: Charging by one electron changes **all** energy levels!



Transport only if

$eV > \delta E_{mol} + \mathbf{e^2/2C}$

'Coulomb blockade'

contacts

too weak coupling: like semiconductors qdots

boring for molecular electronics…

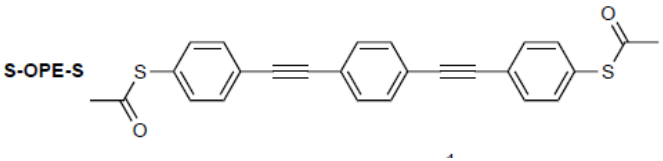
rather work with a GaAs structure, more stable and reproducible

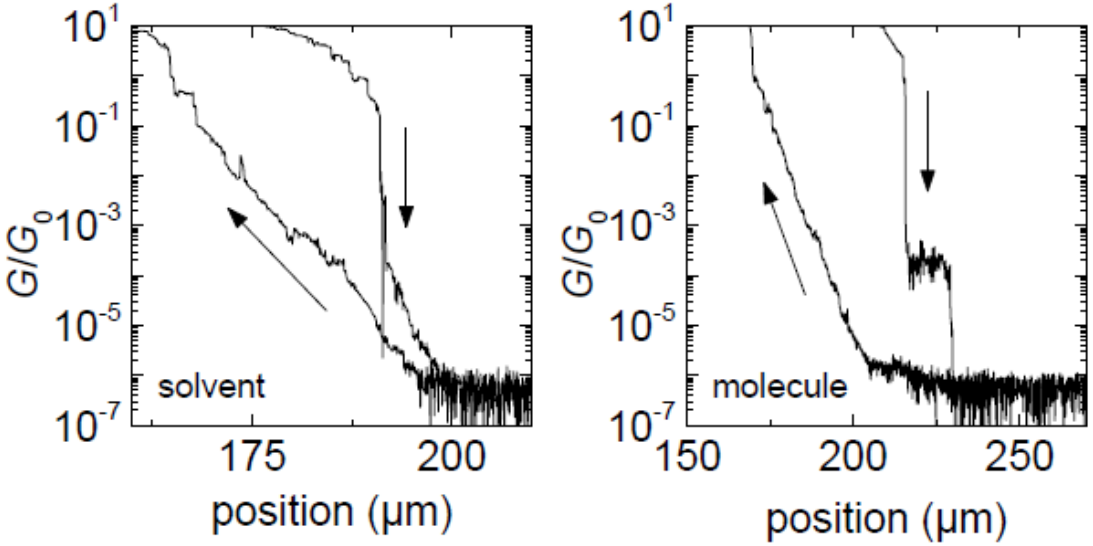
too strong coupling: loose molecular signature… boring again

⇨ **control coupling to preserve integrity of molecular orbitals**
in particular for **active** devices (otherwise, loss of functionality)

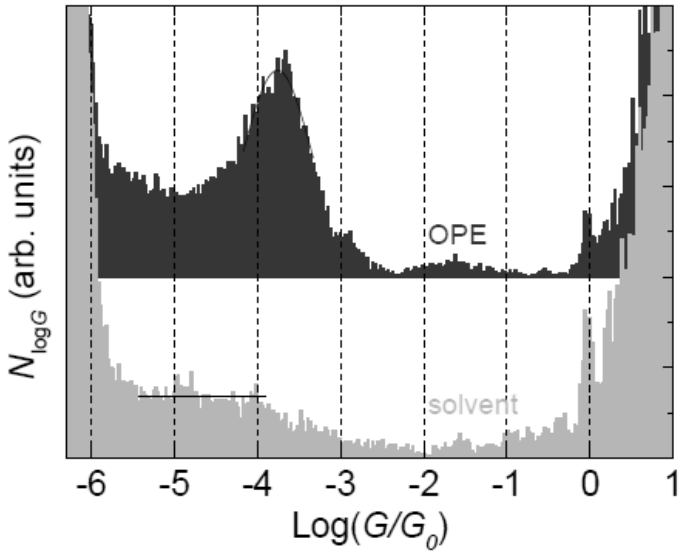
conjugated molecules

molecular junction in a break junction



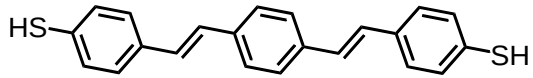


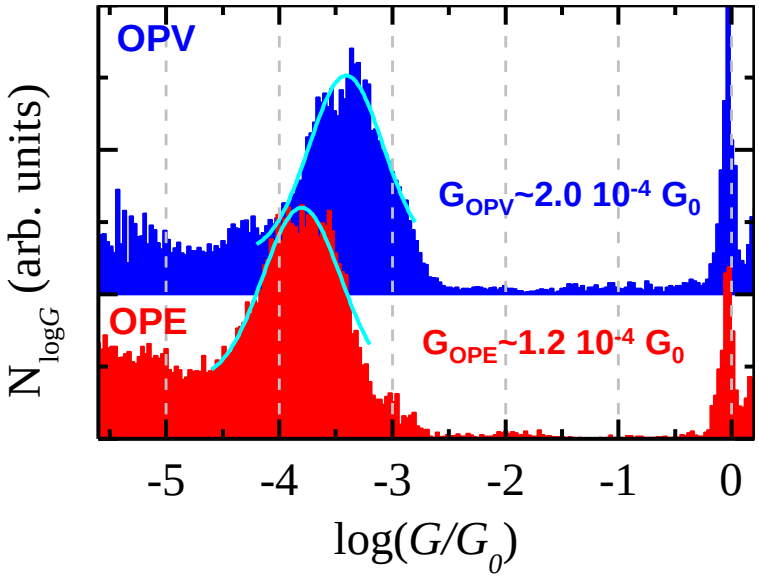
statistical approach



conjugated systems

OPV





OPE

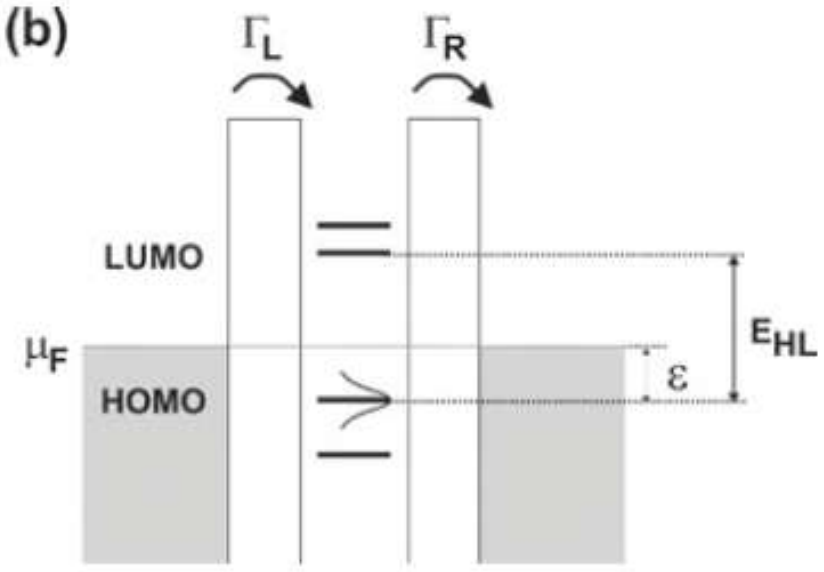
NB: acetyl-protected molecule: deprotection necessary

- experimental data **G_{OPV} / G_{OPE} ~ 1.7**
- theory* **G_{OPV} / G_{OPE} ~ 2**

NB: *calc.* G_{OPE} ~ 10-200nS

meas. G_{OPE} ~ 10nS

simplified description
elastic, coherent tunneling,
no e$^-$-e$^-$, no e$^-$-ph

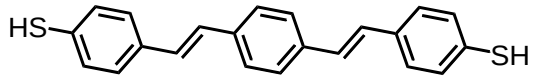


molecules: M. Mayor, *Basel;* ***M. Bryce****, Durham*

**Brandbyge et al.; Nano Lett. (2006); Sankey et al., J. phys. Chem. (2004)*

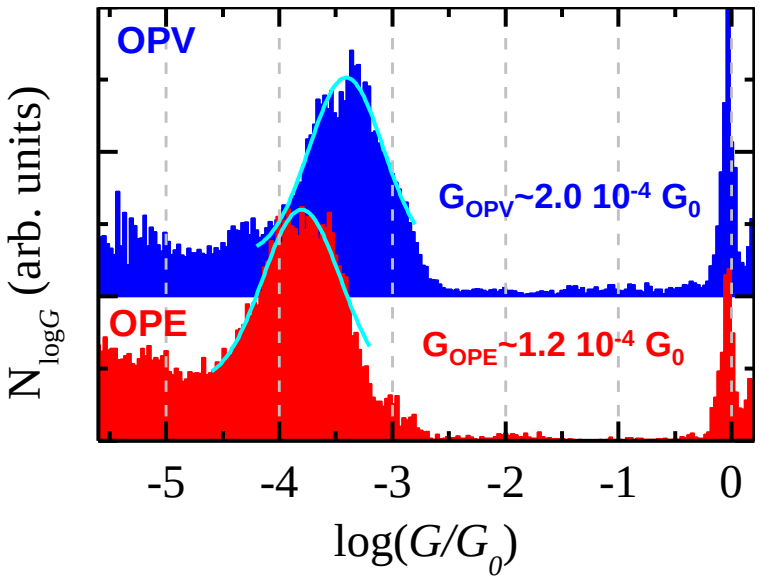
R. Huber et al. JACS 130, 1080 (2008)

conjugated systems

OPV 

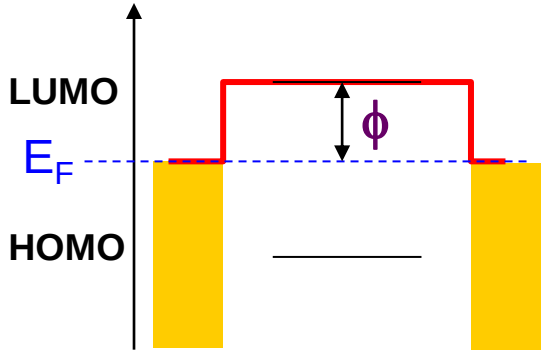
OPE 

NB: acetyl-protected molecule: deprotection necessary



- experimental data **G_{OPV} / G_{OPE} ~ 1.7**
- theory* **G_{OPV} / G_{OPE} ~ 2**
  NB: *calc.* G_{OPE} ~ *10-200nS*
  meas. G_{OPE} ~ *10nS*
- simple estimate **G_{OPV} / G_{OPE} ~ 3.6**

- **single-step through-molecule tunneling**



$$G = Ae^{-\beta d}$$

$$\beta \propto \sqrt{\phi} \propto \sqrt{\frac{|E_{LUMO} - E_{HOMO}|}{2}}$$

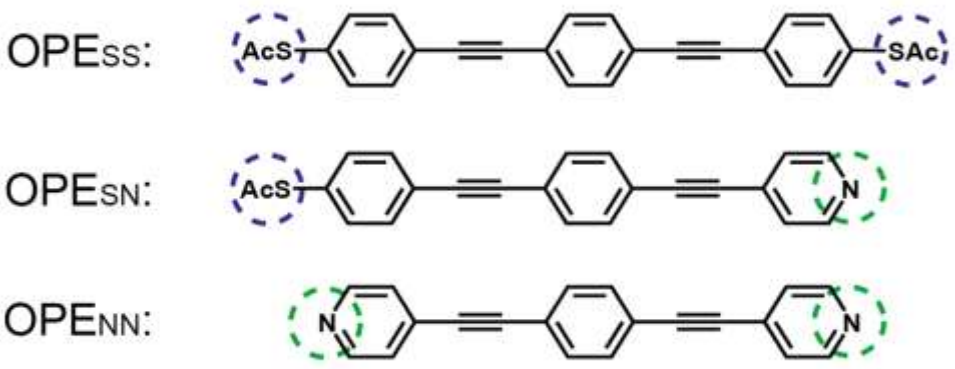
d molecule length
A ~ G_0 (1st approx.)
(A: linked to Au-S bond)

molecules: M. Mayor, *Basel;* ***M. Bryce****, Durham*

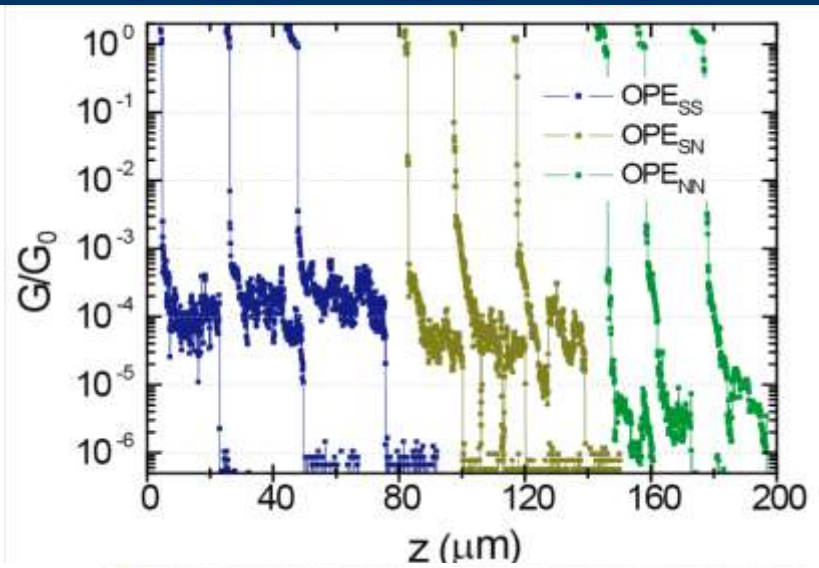
**Brandbyge et al.; Nano Lett. (2006); Sankey et al., J. phys. Chem. (2004)*

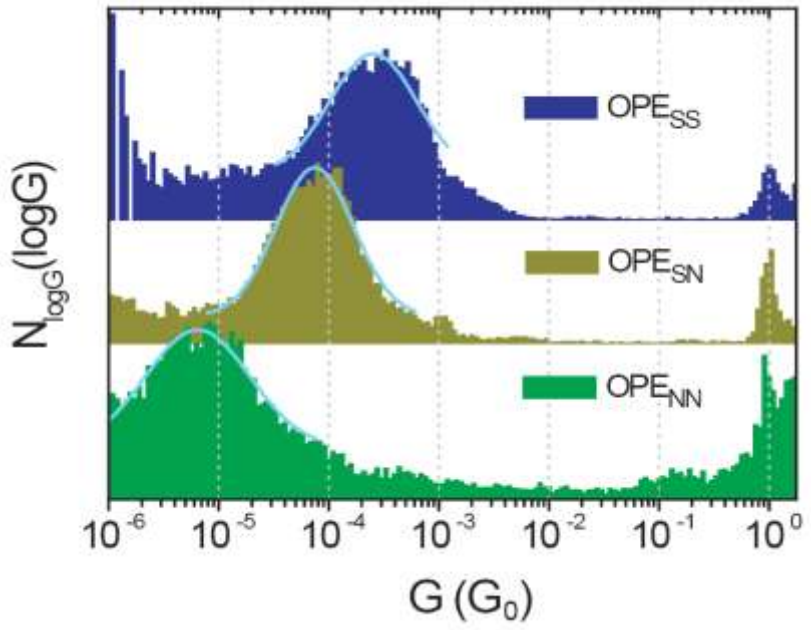
R. Huber et al. JACS 130, 1080 (2008)

contacts: thiols and pyridines



Molecule	No. of samples	G (G_0)	Length (Å)
OPE_{SS}	4 (1)		20.7 (S,S)
OPE_{SN}	3 (1/2)		18.7 (S,N)
OPE_{NN}	4 (1/35)		16.6 (N,N)





molecules: S. Grunder, M. Mayor et al.

S. Wu et al.

contacts: thiols and pyridines

simple tunneling model:

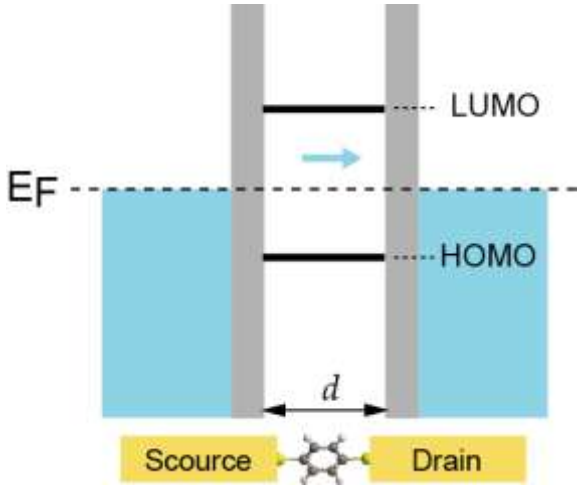
$$G = A_{left} \cdot A_{right} \cdot e^{-\beta d}$$

β: decay constant (β_{OPE} = 0.3 Å^{-1})

d: length of molecule

A: contact conductance

Frisbie et al., JACS (2002), Tao et al., JACS (2006)



symmetric

OPE-SS: $G_{SS} = A_S^2 \cdot e^{-\beta dSS}$ contact ~ 54 kΩ[1]

OPE-NN: $G_{NN} = A_N^2 \cdot e^{-\beta dNN}$ contact ~ 460 kΩ[1]

asymmetric

OPE-SN: $G_{SN} = A_S \cdot A_N \cdot e^{-\beta dSN}$

discrepancy (~ x3) between measured and value anticipated from meas. above

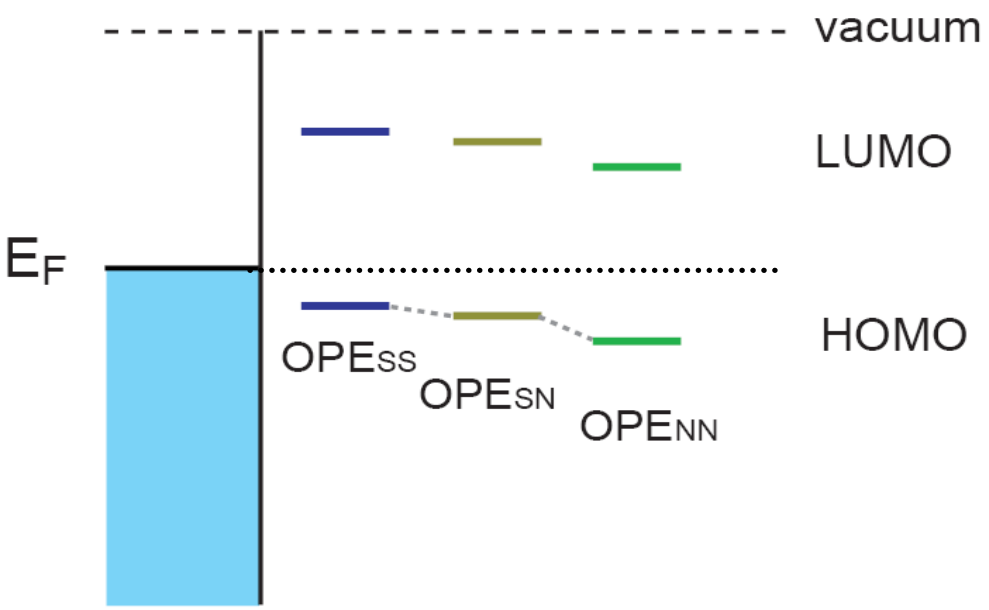
⇨ *simple tunneling model does not hold*

⇨ *for asymmetric OPE-SN, thiol anchors dominate*

[1] in agreement with F. Chen *et al*., JACS 128, 15874 (2006); Y. S. Park et al., JACS 129, 15768 (2007).

S. Wu et al.

contacts: level alignment



calculations
(alkanedithiols, alkanediamines)

dominant orbital: HOMO
dithiol E_H-E_F ~ 2eV
diamine E_H-E_F ~ 3eV
(E_{HL} ~ 8eV)
McDermott et al., J. Phys. Chem. C (2009)

⇨ **spectroscopic measurement ?**

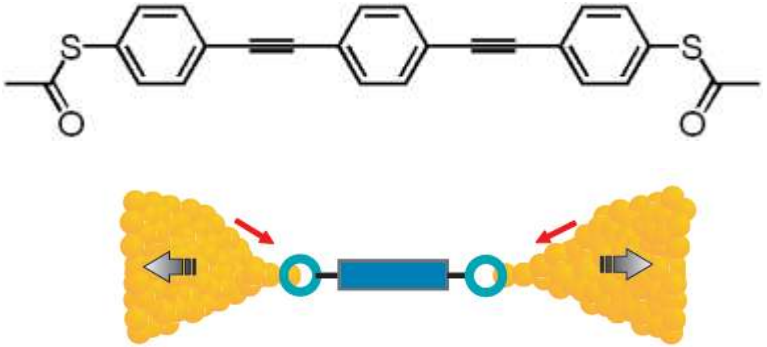
upon binding charge transfer, level alignment

S-Au strong covalent bonding (-δ on S) ⇨ $|E_F-E_H|$ ↘, G ↗

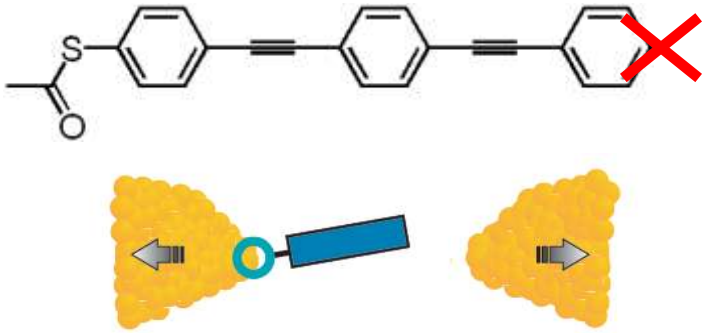
Pyridine N-Au weak donor-acceptor bonding (+δ on N) ⇨ $|E_F-E_H|$ ↗, G ↘

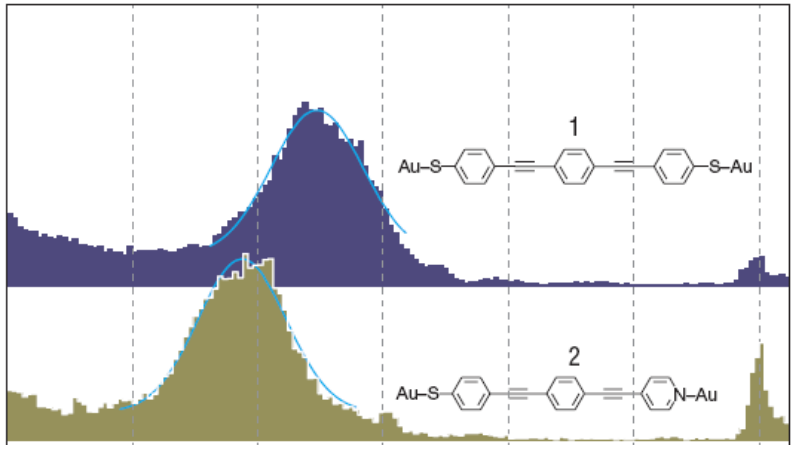
importance of **intermolecular interactions**

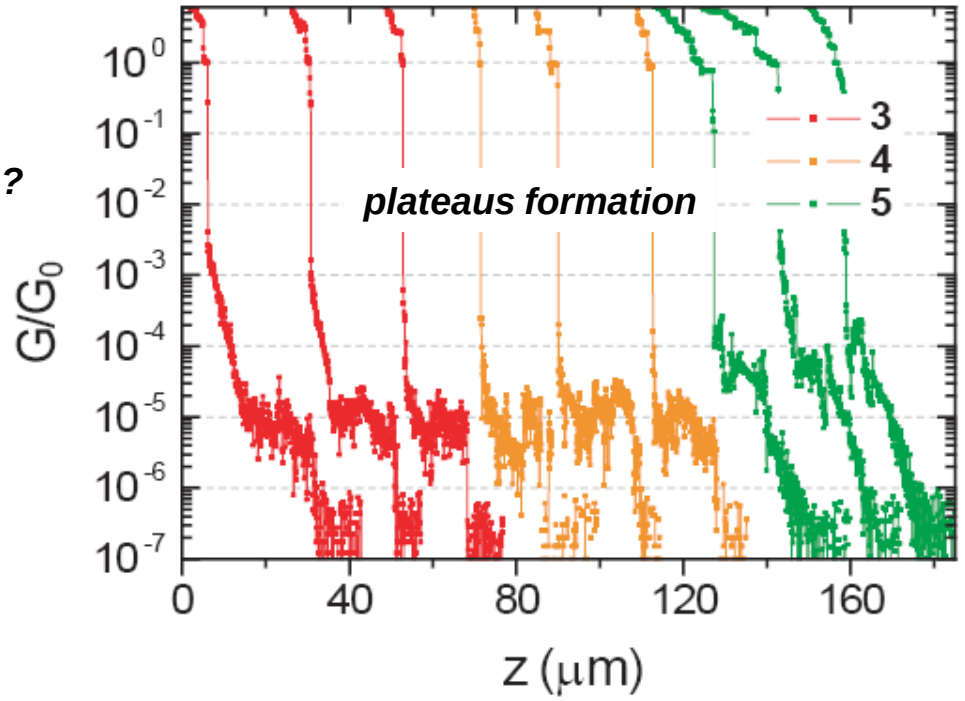
OPE: oligo (phenylene ethynilene)



what happens with a single anchor group ?







molecules: *M. Mayor, Basel*

importance of **intermolecular interactions**

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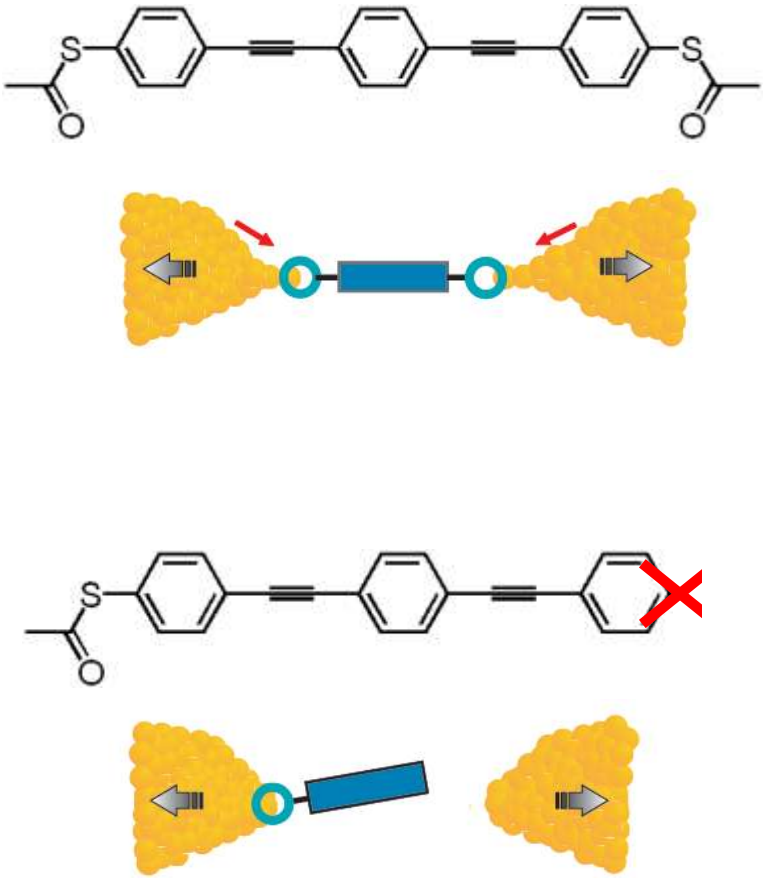

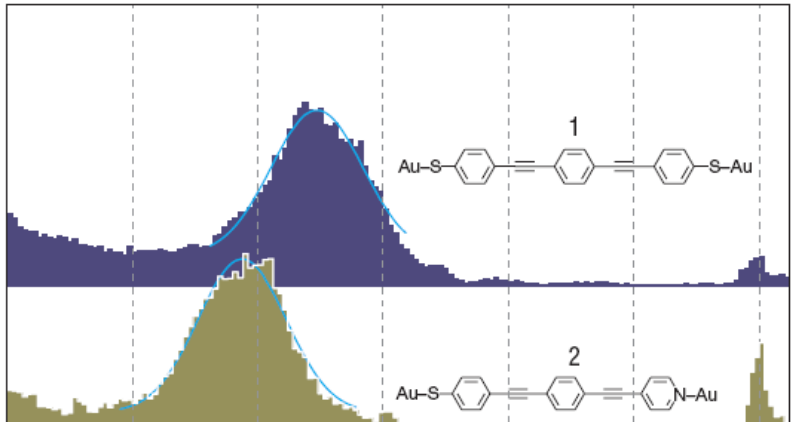

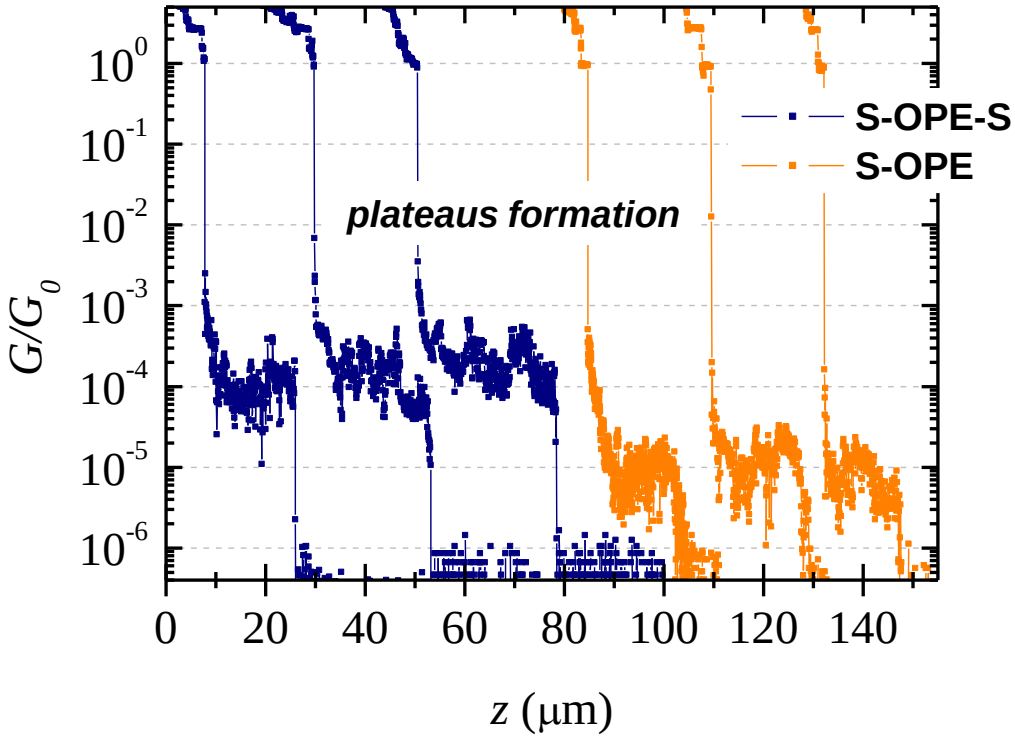

molecules: *M. Mayor, Basel*

importance of **intermolecular interactions**

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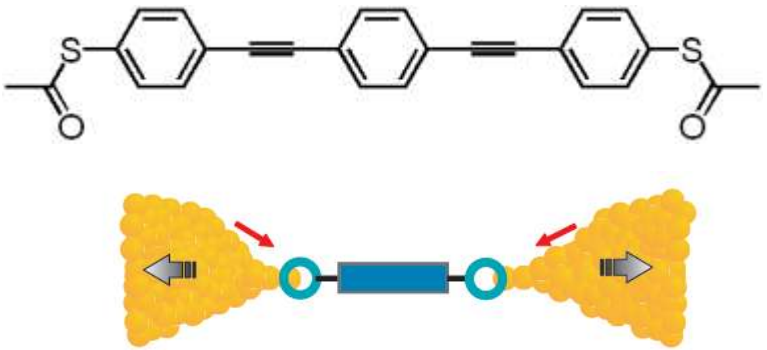
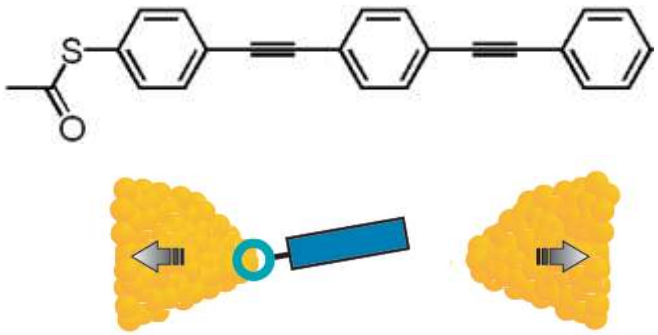
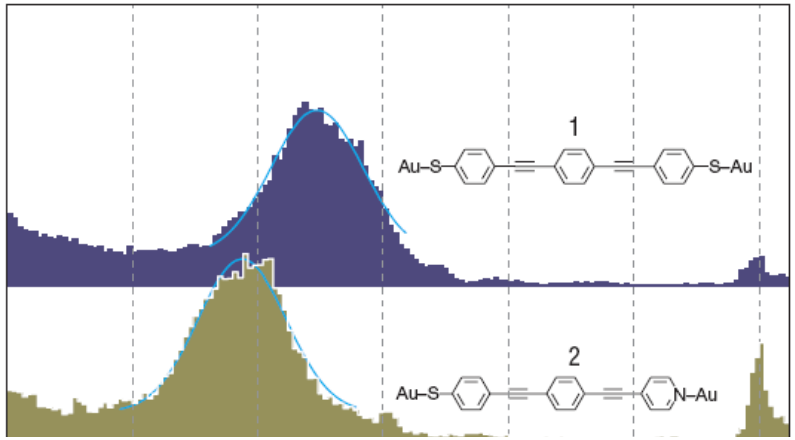
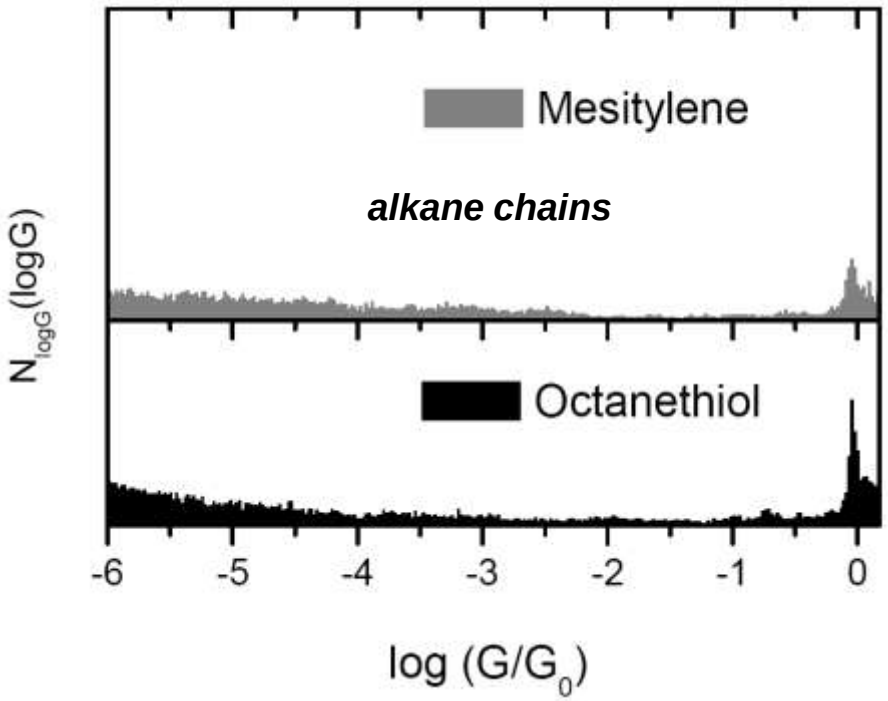








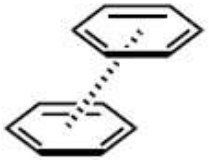
molecules: *M. Mayor, Basel*

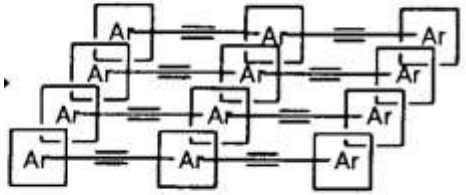
importance of intermolecular interactions

⇨ π-stacking

aggregation of conjugated compounds

Burley et al., Science (1985); Hunter et al., JACS (1990), M. Levitus et al. JACS (2001)





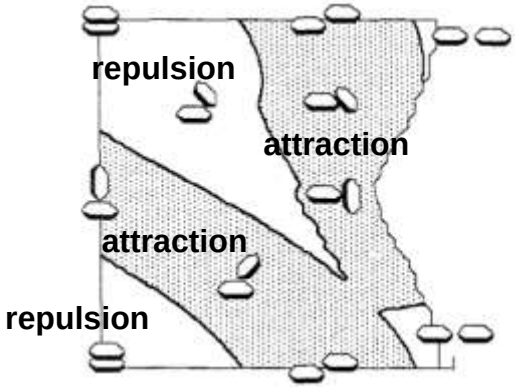
benzene-benzene interaction

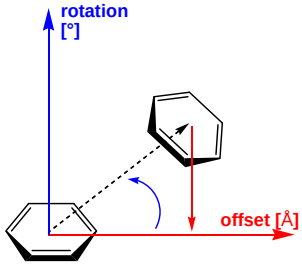
E ~ 70meV to 100meV

~ 2.7 k_BT to 4 k_BT

~ 1.6 to 2.4 kcal/mol

Jorgensen et al., JACS, 1990





benzene-CNT interaction

E ~ 0.1 – 0.2 eV

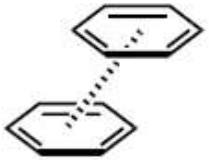
Tournus et al., PRB 2005; Zhao et al., APL 2003

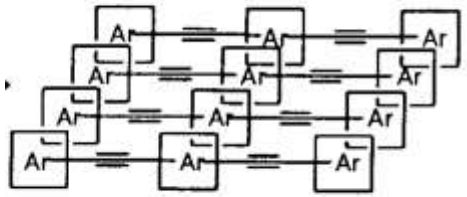
importance of intermolecular interactions

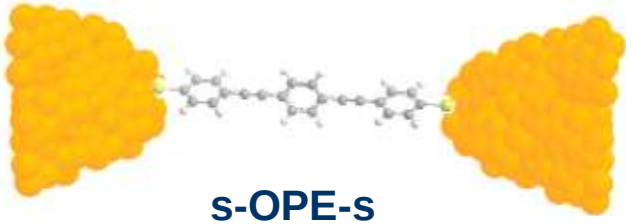
⇨ ***π-stacking***

aggregation of conjugated compounds

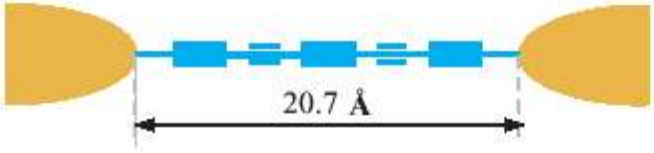
Burley et al., Science (1985); Hunter et al., JACS (1990), M. Levitus et al. JACS (2001)



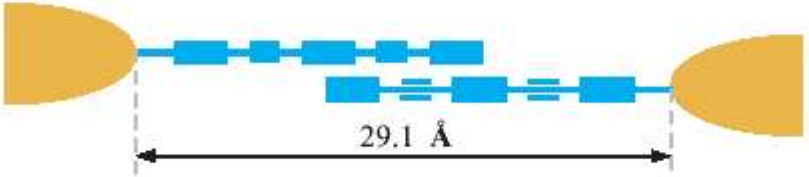




s-OPE-s

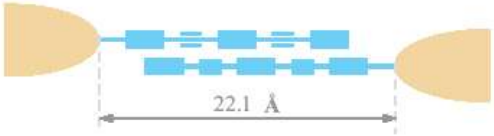


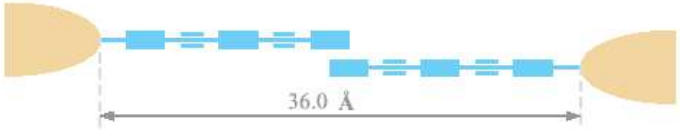
s-OPE



- **experimental data** $G_{sOPE} / G_{sOPEs} = 20$
- $G = Ae^{-\beta d}$ $G_{sOPEs}/G_{sOPE} = 12$

d = molecule length
A = contact conductance
β = decay constant, for OPE: β_{OPE}=0.3 Å^{-1}





S. Wu et al. (2008), Nature Nanotech.

importance of intermolecular interactions

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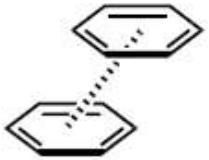
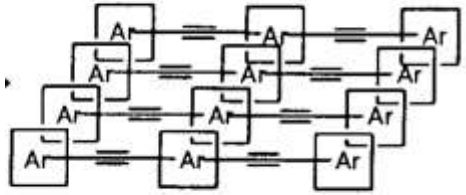
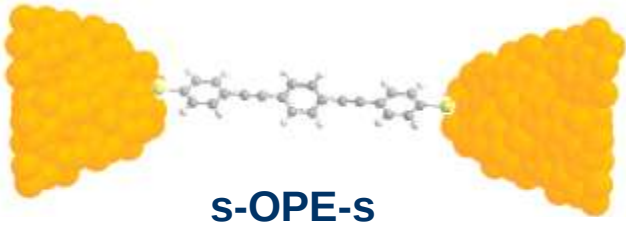
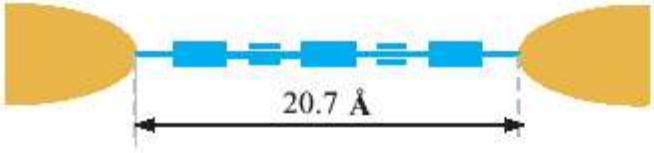


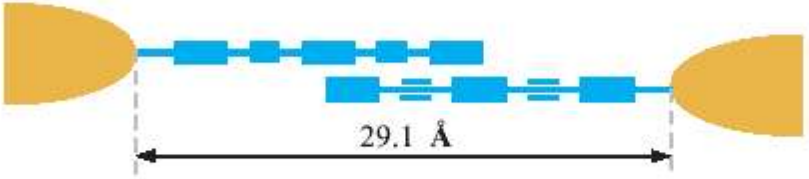


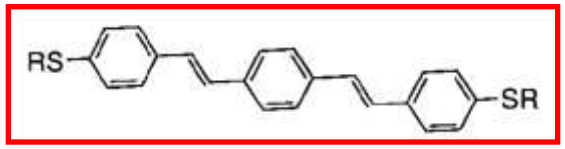


s-OPE-s

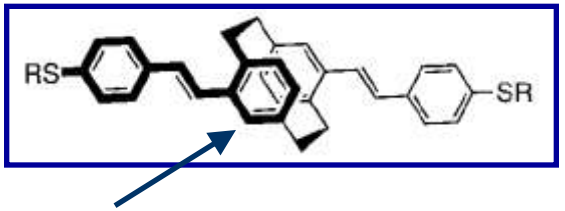


s-OPE





≈equivalent to



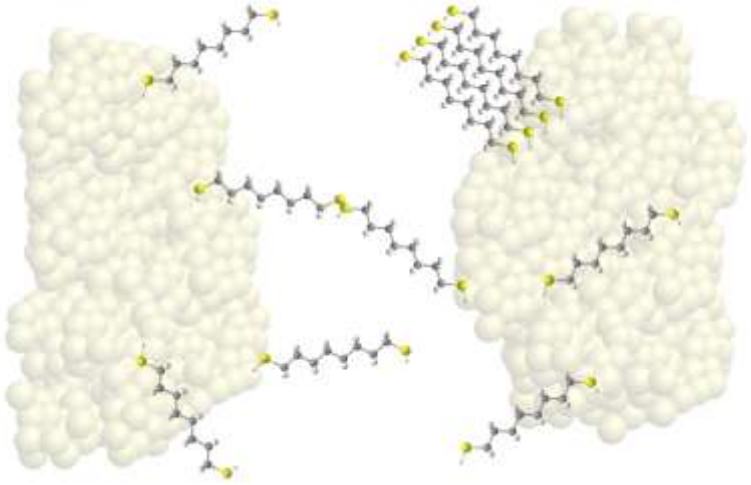
strong through-space π-conjugation

D. S. Seferos, J. G. Kushmerick et al. PNAS (2005)

S. Wu et al. (2008), Nature Nanotech.

spectroscopy

molecular junction formation



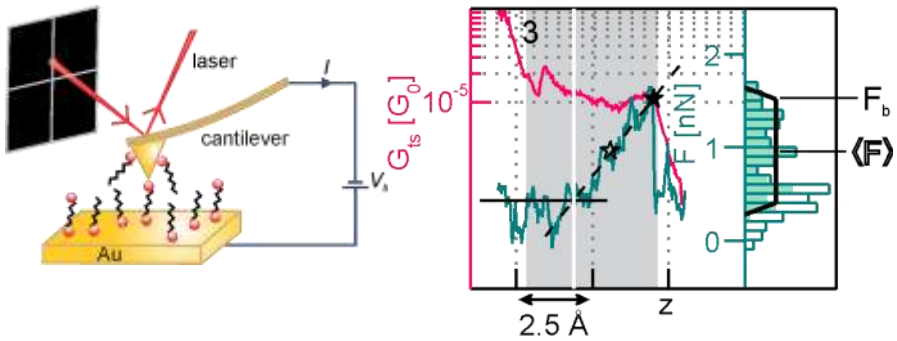
drifting molecules, stochastic anchoring, random clustering ⇨ ***undefined junction geometry & conductance***

drifting surface atoms, metal protrusions ⇨ **undefined electrostatic landscape**

⇨ **variability, low-yield and lack of control in key electrical parameters**

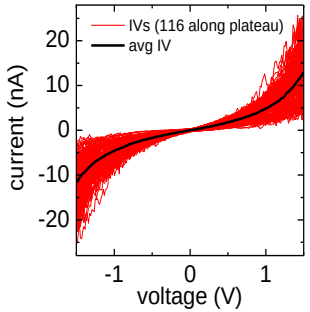
force spectroscopy

force-conductance correlation

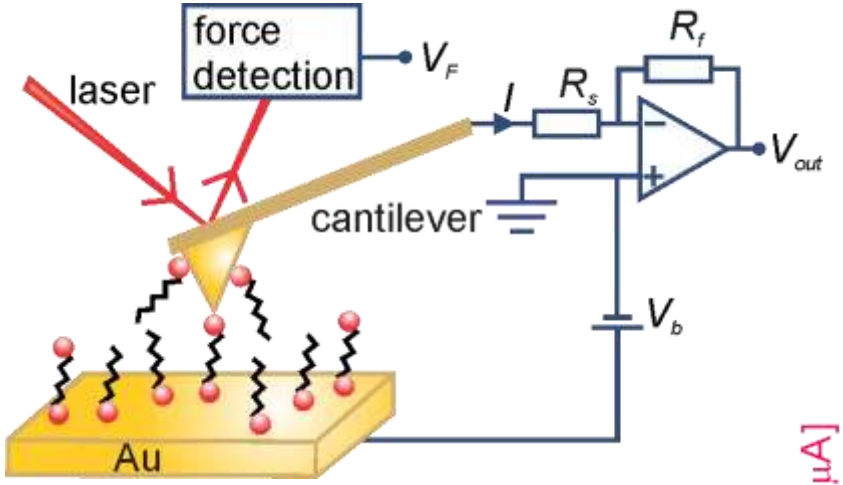


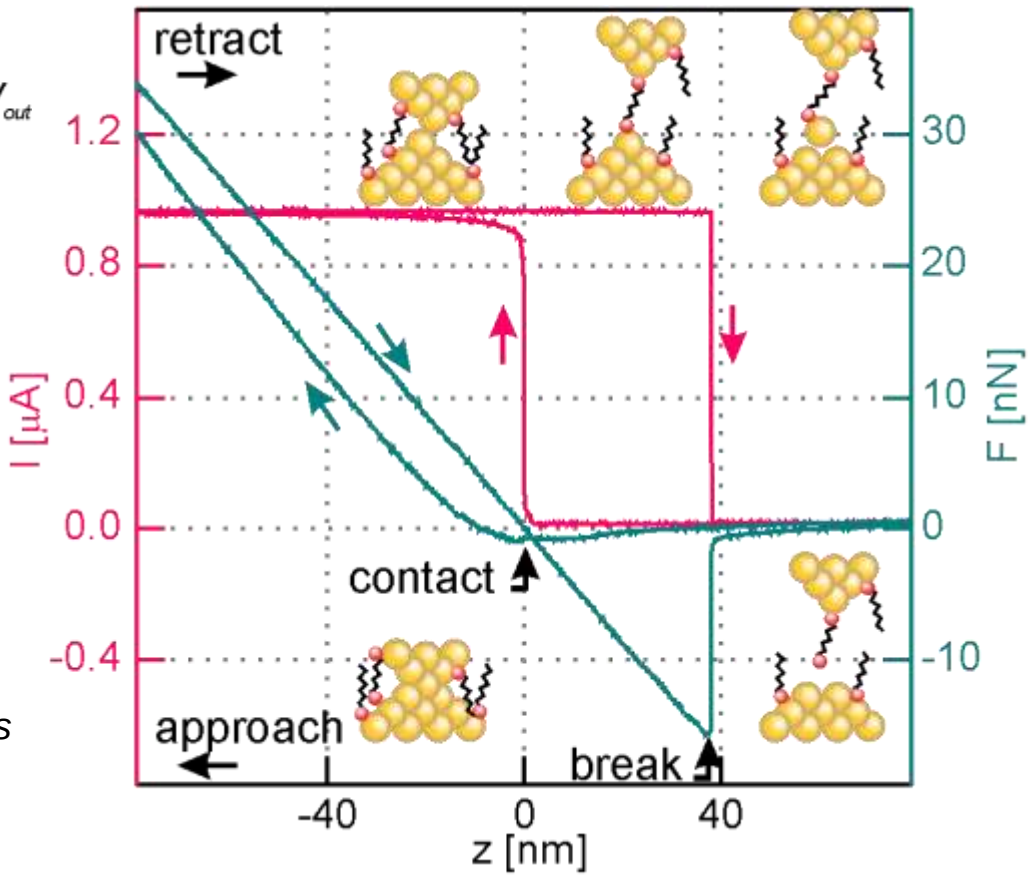
current-voltage spectroscopy

fast IV characteristics in the non-linear regime



octanedithiol junctions investigated by C-AFM





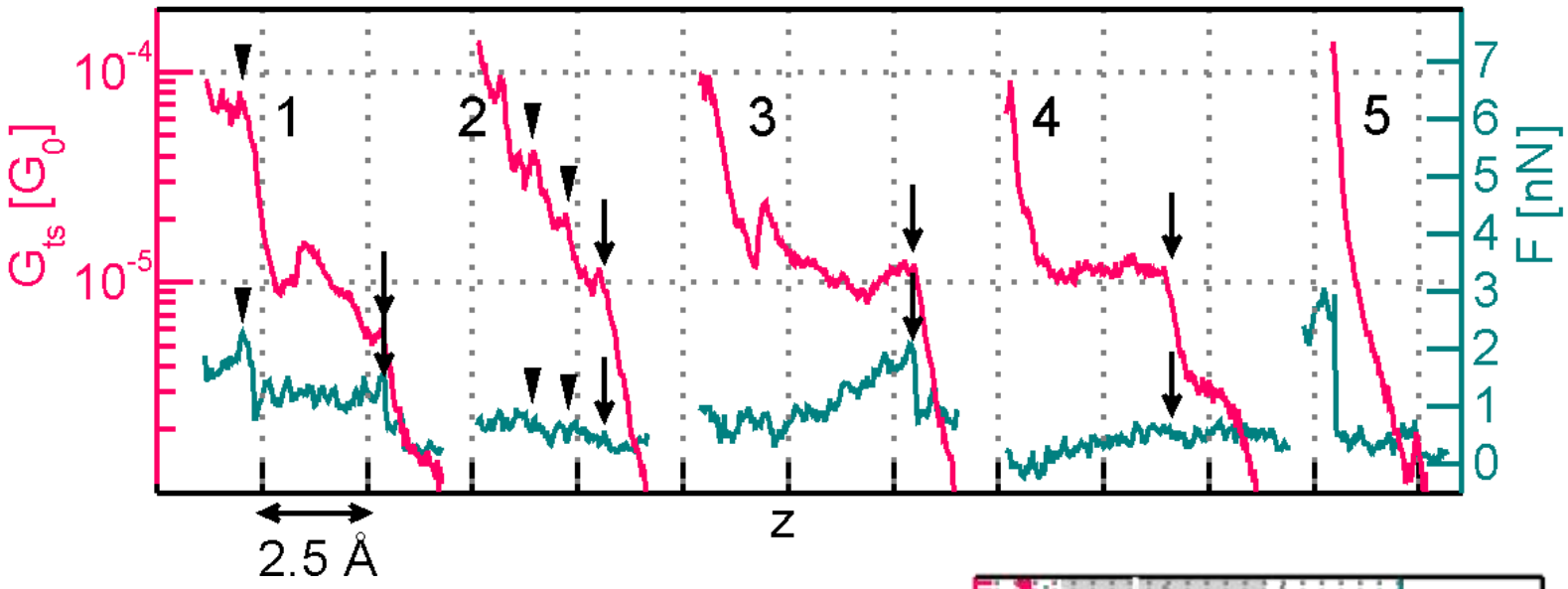
substrate: Au on SiO2/Si
cantilever: Si, Au-coated
typ. 4 N/m

NB: both surfaces coated with alkanes monothiols

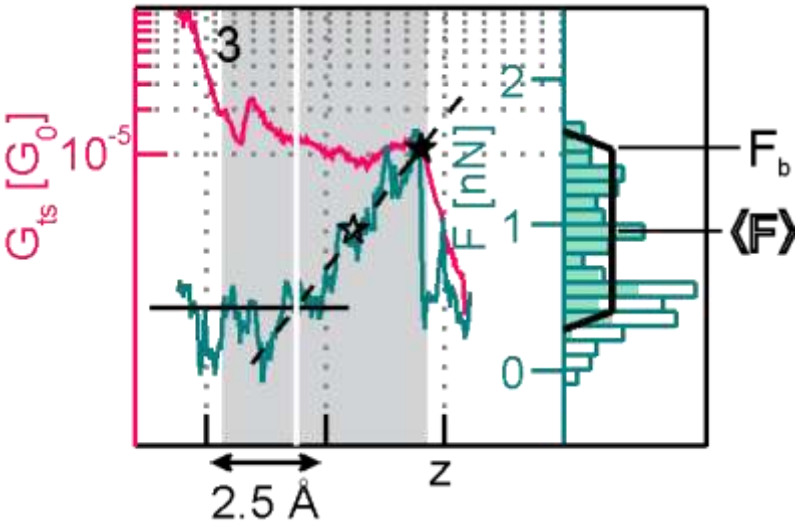
approach: ~ 200nm/s, Fmax: 15nN for Au-molecule-Au junctions
retraction: ~15nm/s
environment: mesitylene

C. Nef et al., Nanotech. 2012

retraction curves: octanedithiols junctions



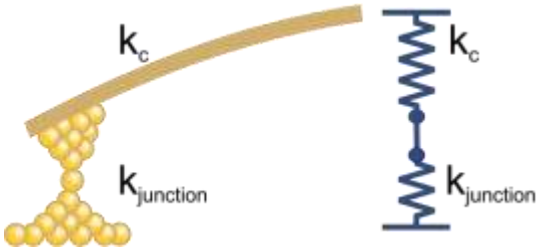
- **last G plateau close to 10^{-5} G_0**
- **curve 3** (20%)**:** dashed line:4.1 N/m
  (k_c of cantilever: 4.2 N/m)
- **force histogram**
  ★: breaking force $\mathbf{F_b}$
  (1.5nN here)
  ☆: mean force **<F>**

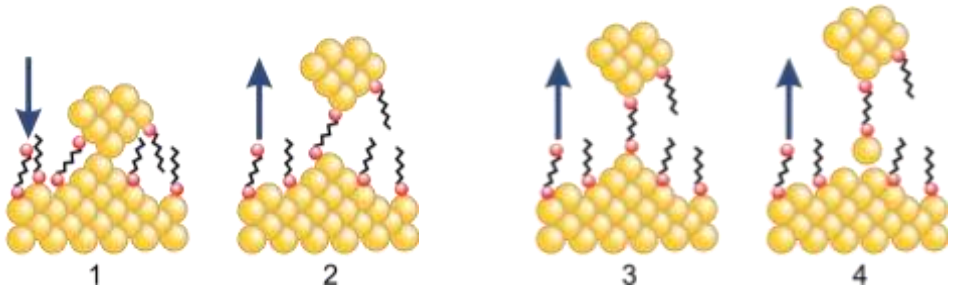


NB: noiseless F curve ⇔ rectangular force histo

C. Nef et al.

retraction curves: octanedithiols junctions





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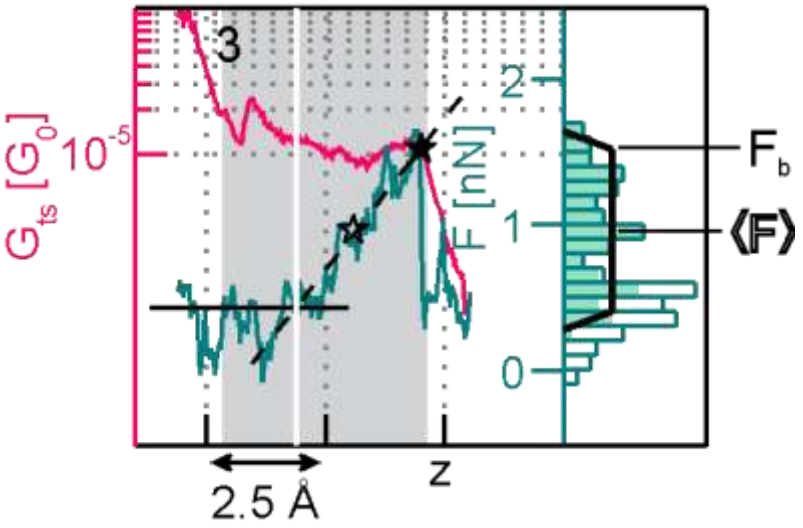
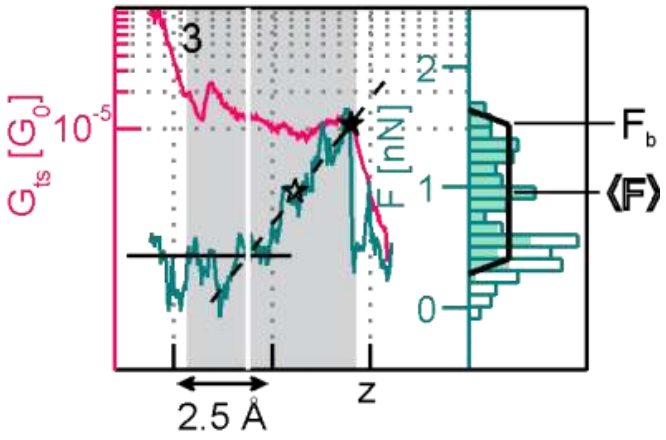


NB: noiseless F curve ⇔ rectangular force histo

C. Nef et al.

octanedithiols junctions: scatter plot (2D histo)

2D histogram for 1 pair of (G,F) curves



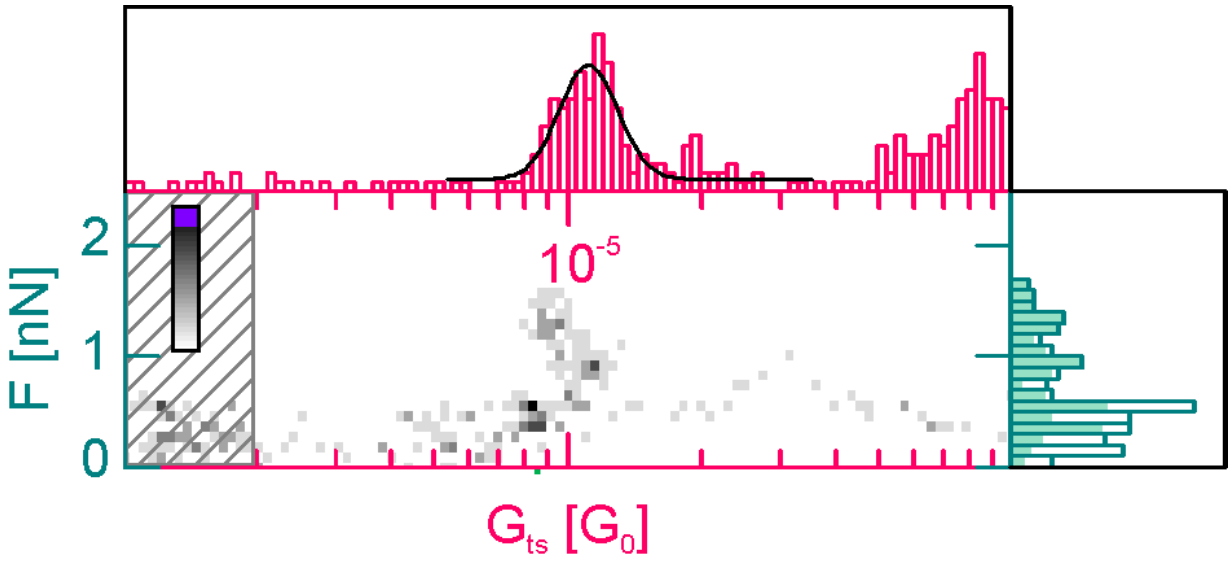
- data from pulling (F>0)
- binning of G and F

$$\Delta \log(G_{ts}/G_0) = 0.02$$

$$\Delta F = 100 \text{ pN}$$

- building the 2D histo:

(*1 point in G curve and its corresponding point in F curve contribute 1 count in the 2D histo at the correponding bin)*



C. Nef et al.

octanedithiols junctions: scatter plot (2D histo)

115 (G,F) curves

G histo: peak

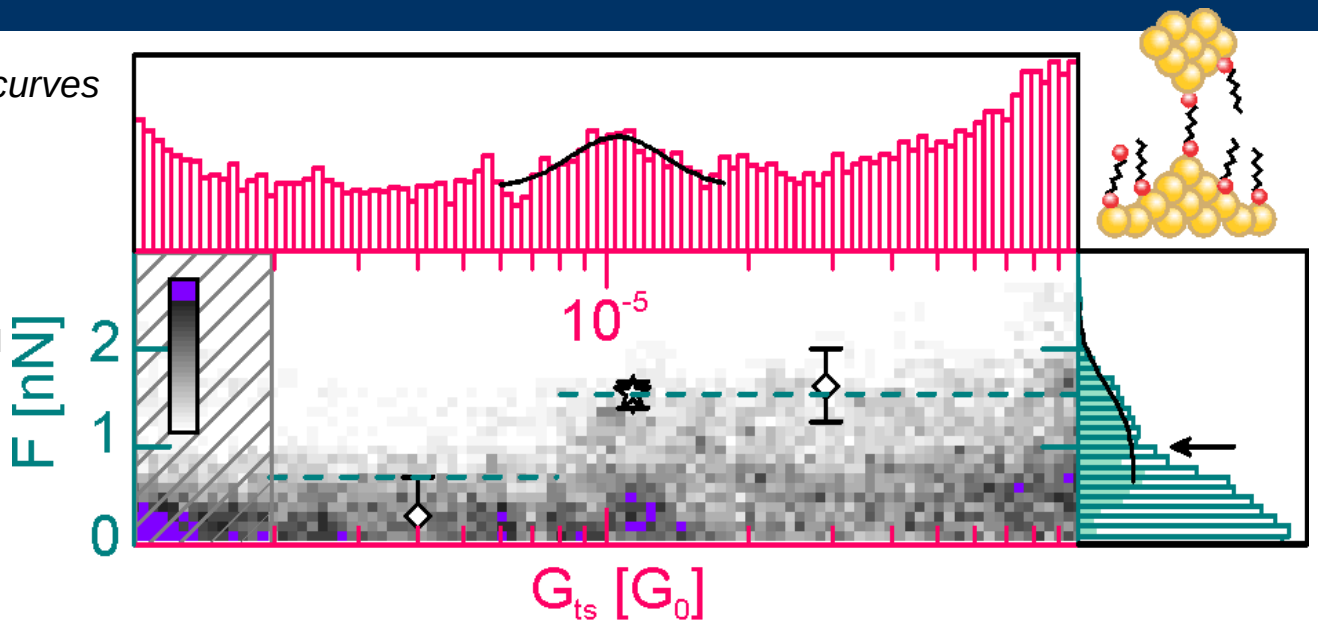
$G_{mol} \approx 1.1\ 10^{-5}\ G_0$

F range: jump at 0.8 G_{mol}

dashed lines: 0.7 nN & 1.6 nN

♢: **<F> ~ 0.3nN**

for G < *8 10^{-6} G_0*



C. Nef et al.

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dashed lines: 0.7 nN & 1.6 nN

♢: **<F> ~ 0.3nN**

for G < *8 10^{-6} G_0*

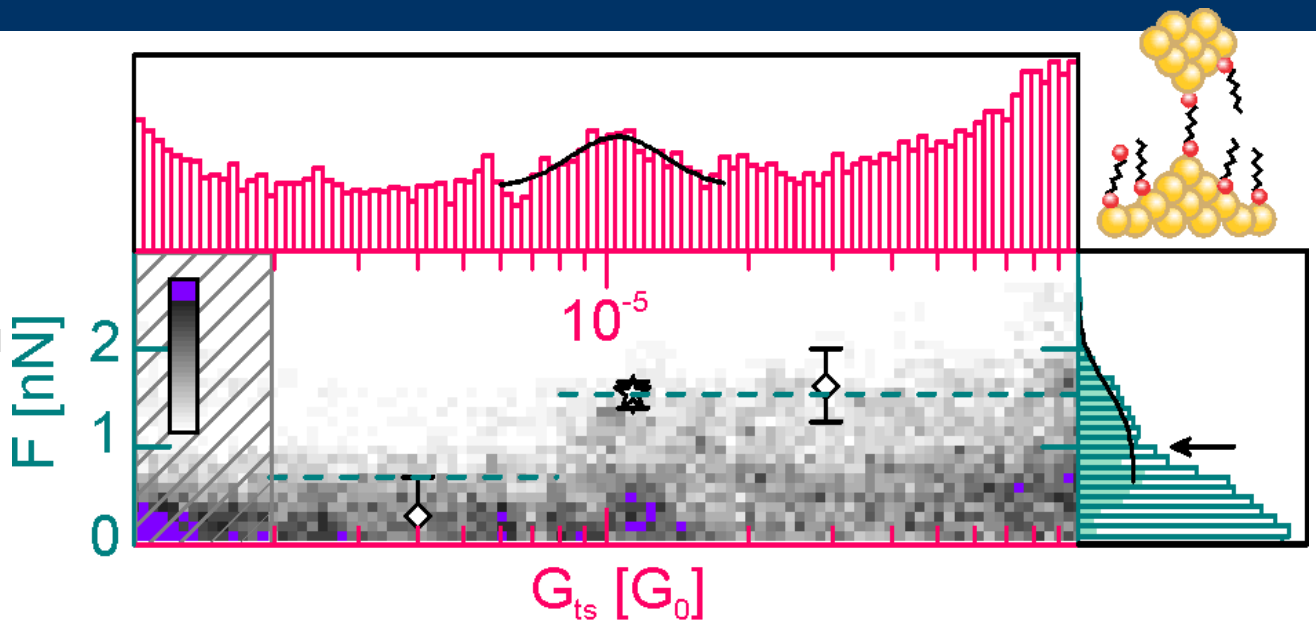
♢: **<F_b> ~ 1.6nN**

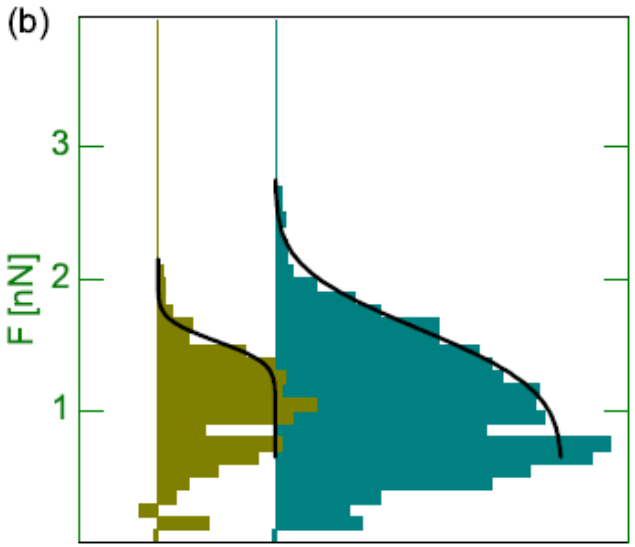
for G > *8 10^{-6} G_0*

☆: **<F_b> ≈ 1.5 ± 0.1 nN**

mean breaking force **around G_{mol}**

(0.8 -1.6 10^{-5} G_0)





F_b normally distributed ⇨

$$F(x) = \frac{A}{\sqrt{2\pi}\sigma}\int_{-\infty}^{x} e^{-1/2\left(\frac{t-\mu}{\sigma}\right)^2} dt$$

$$F(x) = \frac{A}{2}\left[1 + erf\left(\frac{x-\mu}{\sqrt{2}\sigma}\right)\right]$$

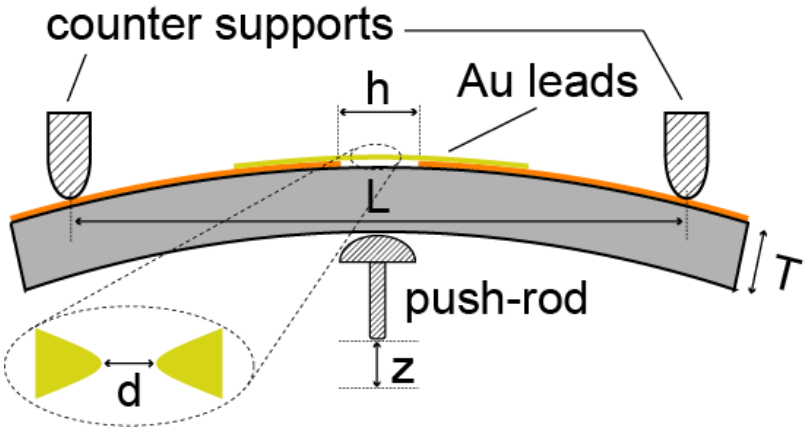
$\mu \Leftrightarrow$ <F_b>

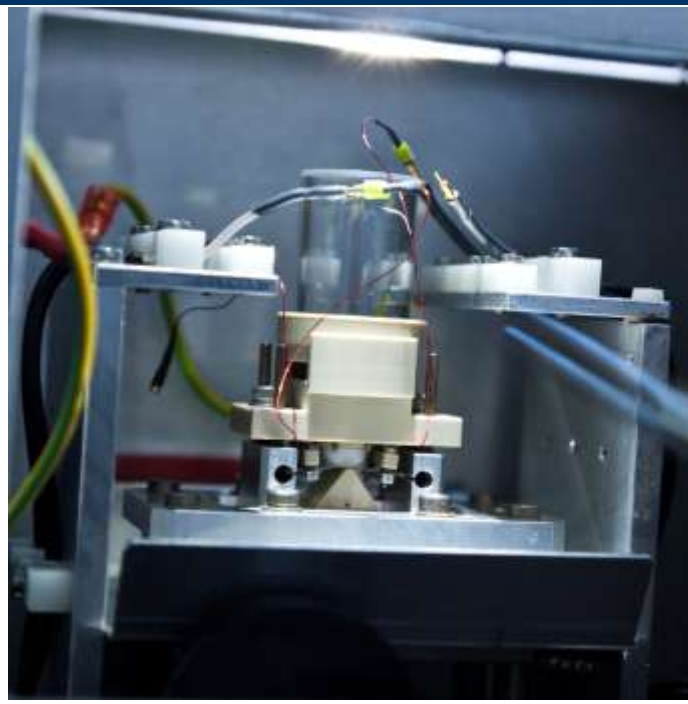
C. Nef et al.

current-voltage spectroscopy

current-voltage spectroscopy

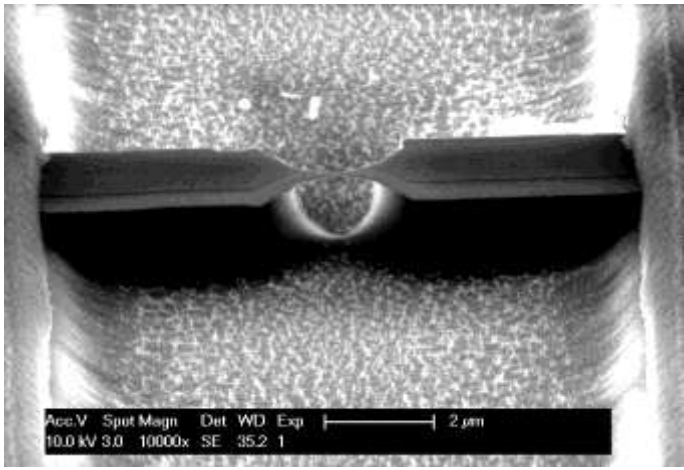
Mechanically controllable break junctions





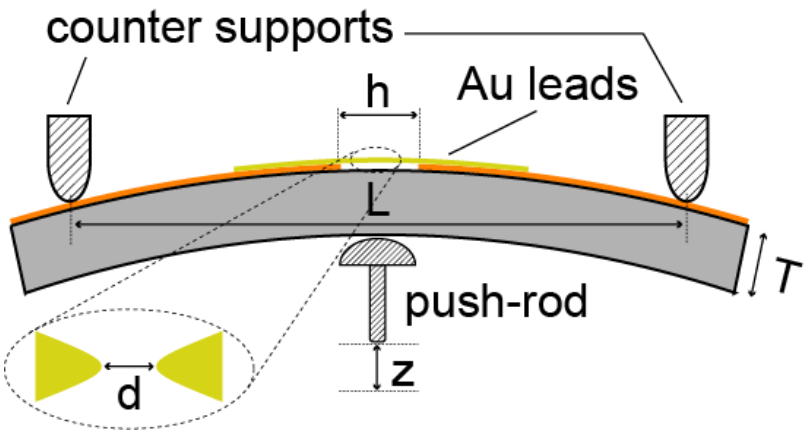
Measurements ramp V during opening cycles while recording I
1 IV in 10ms (200pnts per IV)

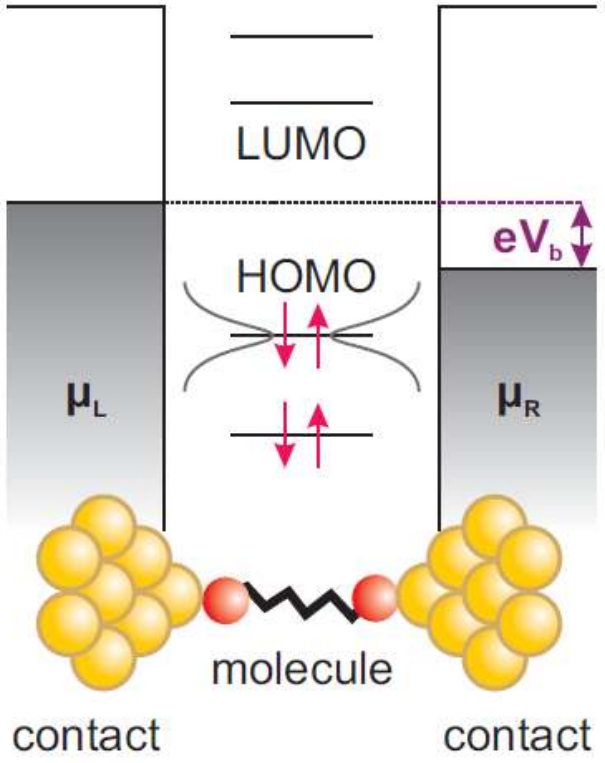
rate of opening typ. 1Å/s
i.e. ~0.01 Å motion during 1 IV



current-voltage spectroscopy

Mechanically controllable break junctions





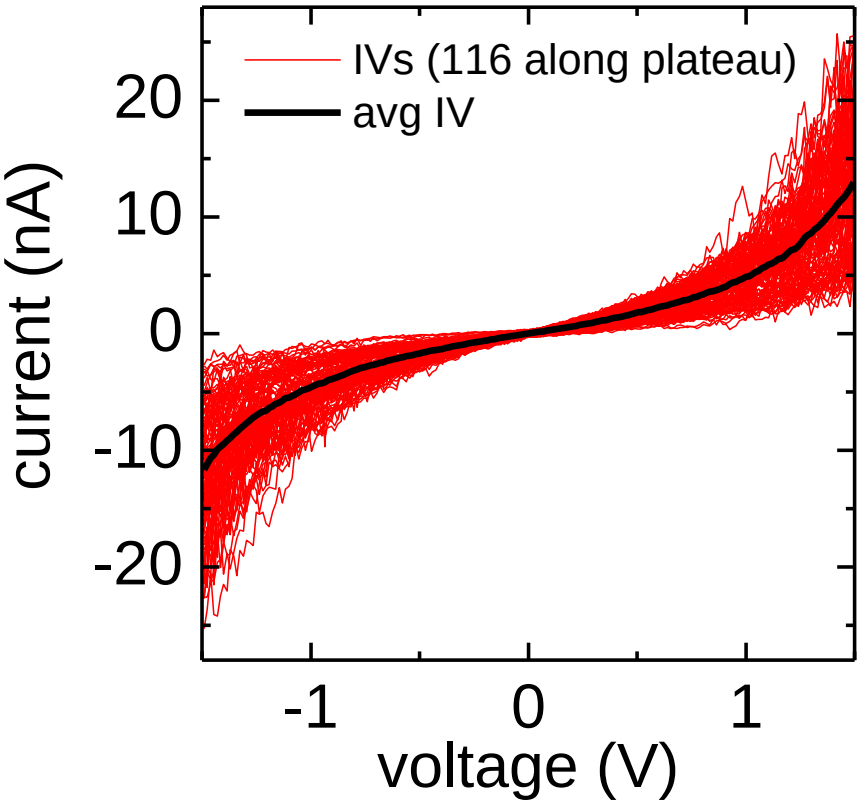
Measurements ramp V during opening cycles while recording I
1 IV in 10ms (200pnts per IV)

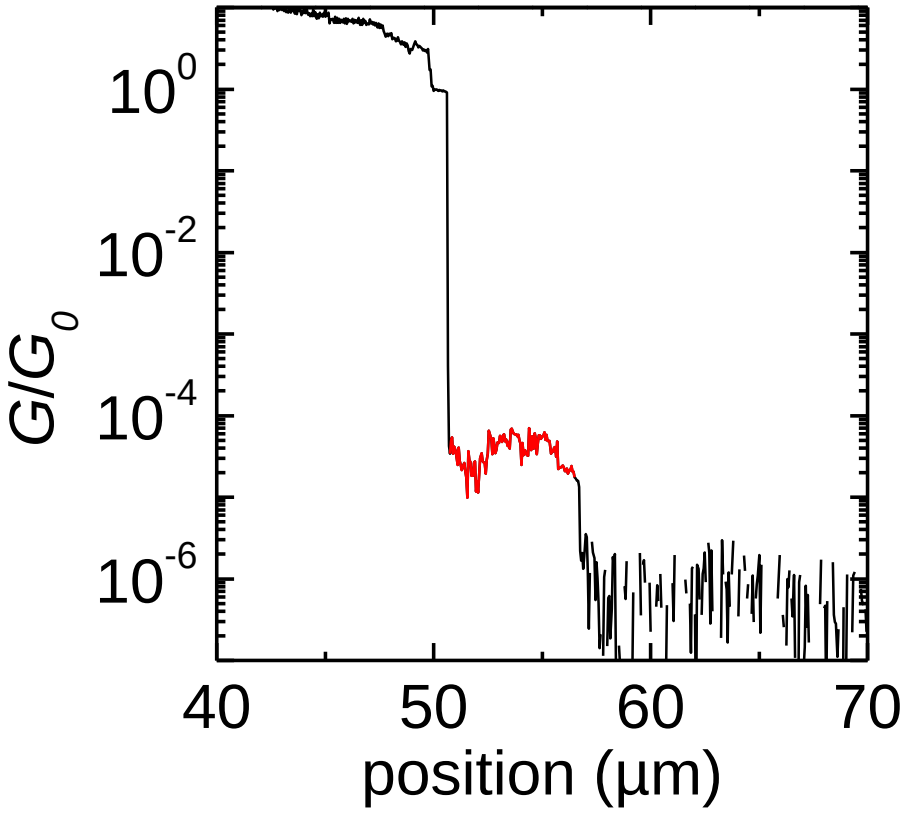
rate of opening typ. 1Å/s
i.e. ~0.01 Å motion during 1 IV

IV characteristics in MCBJ

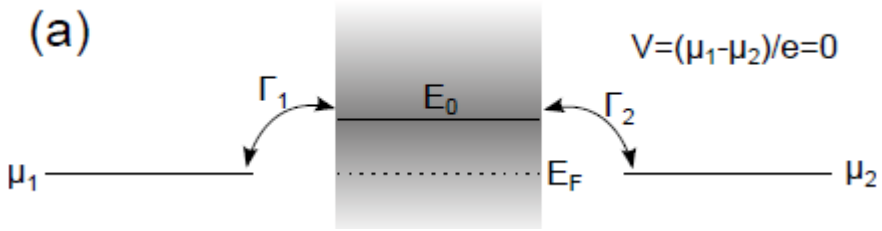
G trace built from from IV curves

linear fit of IV curves in low-bias regime (±0.1V)





simple one-level model



$$I(E,V) = \frac{2e}{h} \int_{-\infty}^{\infty} T(E,V)[f(E-\mu_2) - f(E-\mu_1)]dE$$

molecular level broadening: Lorentzian *(Breit-Wigner)*

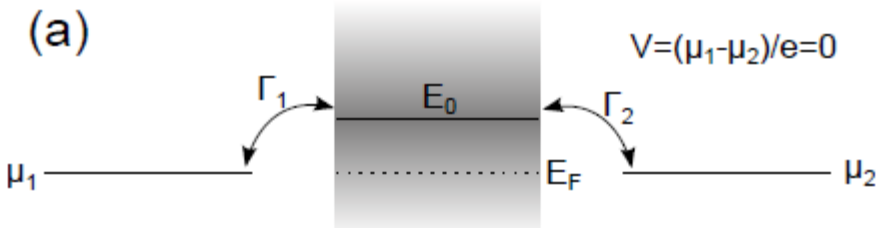
$$D_e(E) = \frac{(\Gamma_1 + \Gamma_2)/\pi}{(E - E_0(V))^2 + (\Gamma_1 + \Gamma_2)^2}$$

transmission function from DOS and coupling constants

$$T(E,V) = 4\pi D_e(E) \frac{\Gamma_1 \Gamma_2}{\Gamma_1 + \Gamma_2}$$

and $$T(E,V) = \frac{4\Gamma_1 \Gamma_2}{(E - E_0(V))^2 + (\Gamma_1 + \Gamma_2)^2}$$

simple one-level model



voltage drop at contacts *(asymmetric coupling): forced to be* $\propto 1/\Gamma$

$$\frac{\frac{eV}{2} - E_F(V)}{\frac{eV}{2} + E_F(V)} \stackrel{!}{=} \frac{{\Gamma_1}^{-1}}{{\Gamma_2}^{-1}}$$

thus $$E_F(V) = \frac{eV}{2} \cdot \frac{\Gamma_1 - \Gamma_2}{\Gamma_1 + \Gamma_2}$$

and we have, for the voltage-dependent molecular level position

$$E_0(V) = E_0 + E_F(V) = E_0 + \frac{eV}{2} \cdot \frac{\Gamma_1 - \Gamma_2}{\Gamma_1 + \Gamma_2}$$

The amount of shift for Ef is weighted by the coupling constants: the level shifts towards the better coupled electrode.

Boundary conditions

$$E_F = 0 \text{ for } \Gamma_1 = \Gamma_2$$

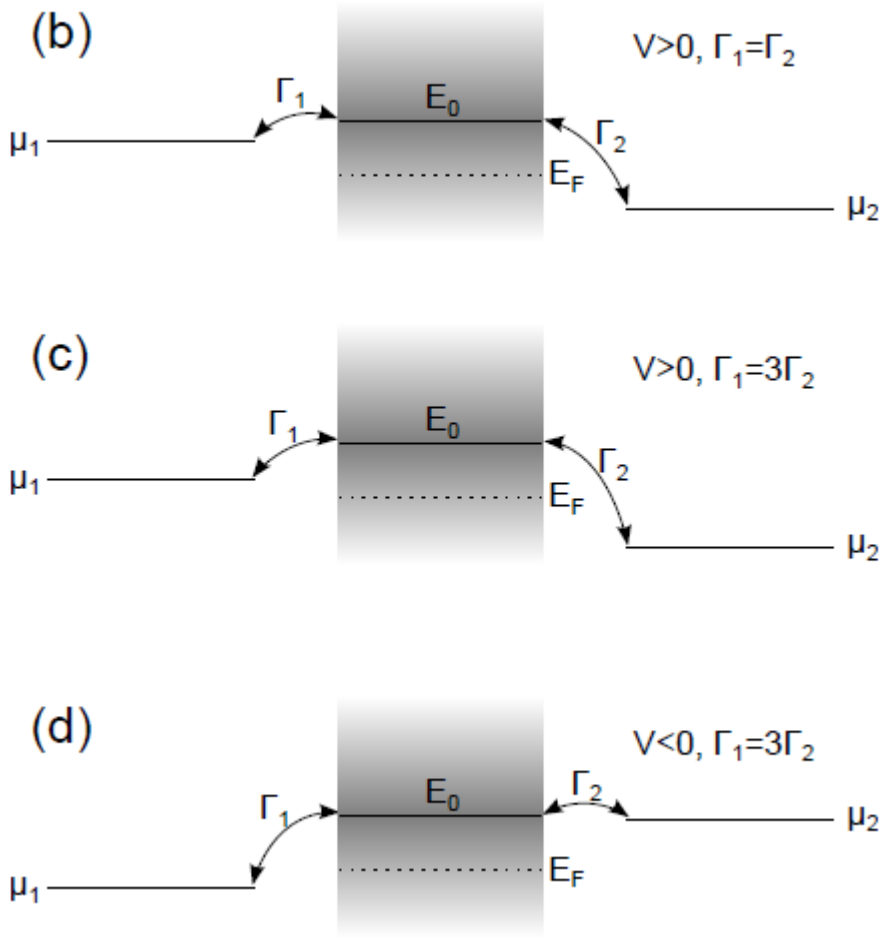
$$E_F = eV/2 = \mu_1 \text{ for } \Gamma_1 \gg \Gamma_2$$

$$E_F = \mu_2 \text{ for } \Gamma_2 \gg \Gamma_1$$

simple one-level model

$$E_0(V) = E_0 + E_F(V) = E_0 + \frac{eV}{2} \cdot \frac{\Gamma_1 - \Gamma_2}{\Gamma_1 + \Gamma_2}$$

examples of E_F shit



simple one-level model

Analytical expression for the current

$$I(E,V) = \frac{2e}{h} \int_{}^{\infty} T(E,V)[f(E-\mu_2) - f(E-\mu_1)]dE$$

At low T , Fermi functions ≈ Heaviside step functions, and

$$I(V) = \frac{2e}{h} \int_{\frac{-eV}{2}}^{\frac{eV}{2}} T(E,V)dE$$

Using the expressions

$$T(E,V) = \frac{4\Gamma_1\Gamma_2}{\left(E - E_0(V)\right)^2 + \left(\Gamma_1 + \Gamma_2\right)^2}$$

$$E_F(V) = \frac{eV}{2} \cdot \frac{\Gamma_1 - \Gamma_2}{\Gamma_1 + \Gamma_2}$$

we can write

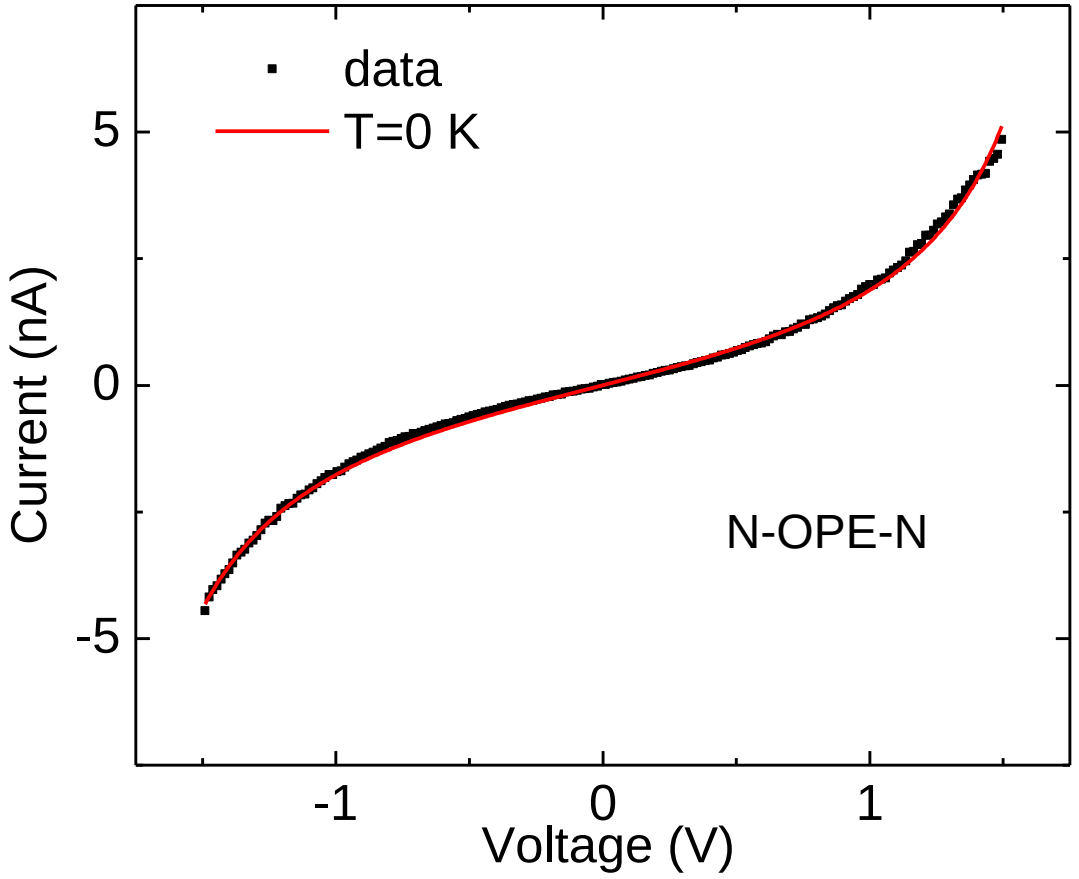
$$I(V) = \frac{8e}{h} \cdot \frac{\Gamma_L\Gamma_R}{\Gamma_L + \Gamma_R} \left[\arctan\left(\frac{2E_0 + eV\left(\frac{\Gamma_L - \Gamma_R}{\Gamma_L + \Gamma_R} + 1\right)}{2\left(\Gamma_L + \Gamma_R\right)} \right) - \arctan\left(\frac{2E_0 + eV\left(\frac{\Gamma_L - \Gamma_R}{\Gamma_L + \Gamma_R} - 1\right)}{2\left(\Gamma_L + \Gamma_R\right)} \right) \right]$$

3 fit parameters Γ_1, Γ_2, $E_0 = E_0(V)$

one level model: fitting

fitting parameters

$\Gamma_{low}, \Gamma_{high}, E_0$



one level model: fitting

fitting parameters

$\Gamma_{low}, \Gamma_{high}, E_0$

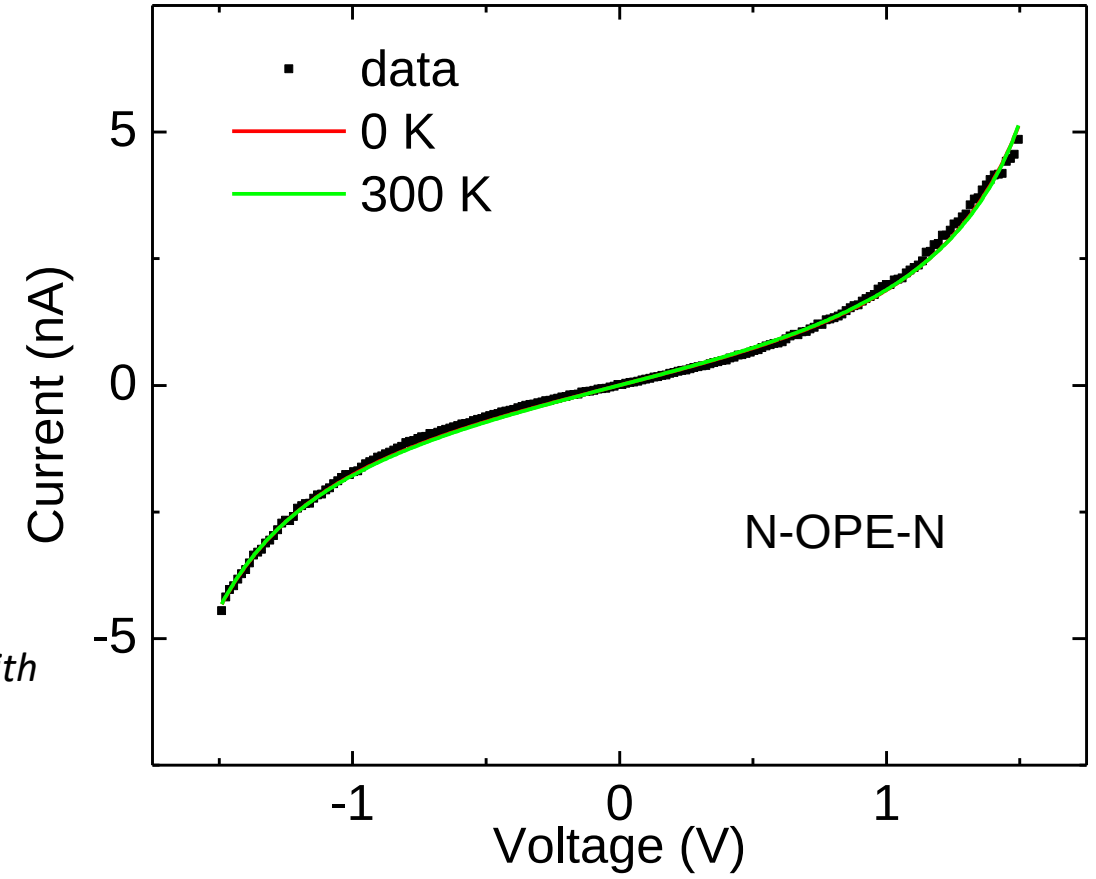
from fit

$\Gamma_{low} \approx 2.1$ meV

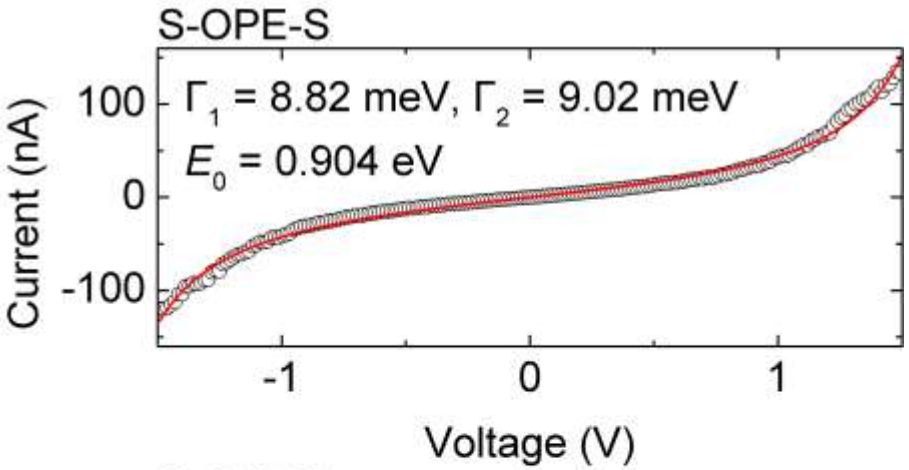
$\Gamma_{high} \approx 2.2$ meV

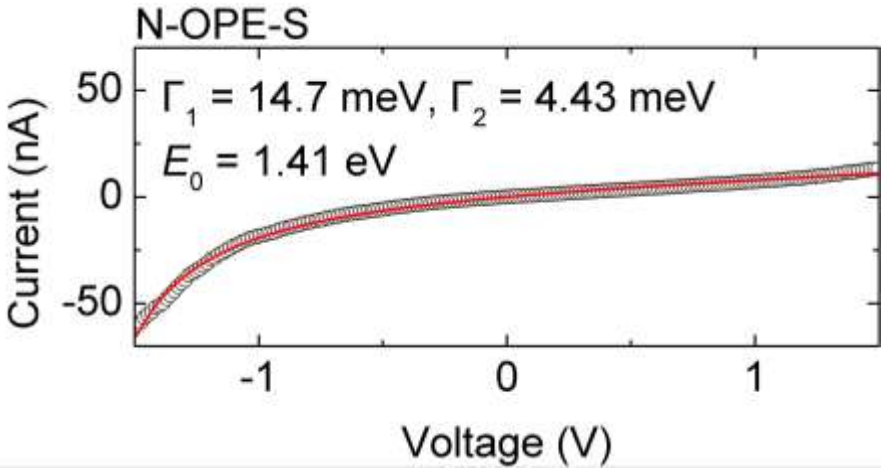
$E_0 \approx 1.0$ eV

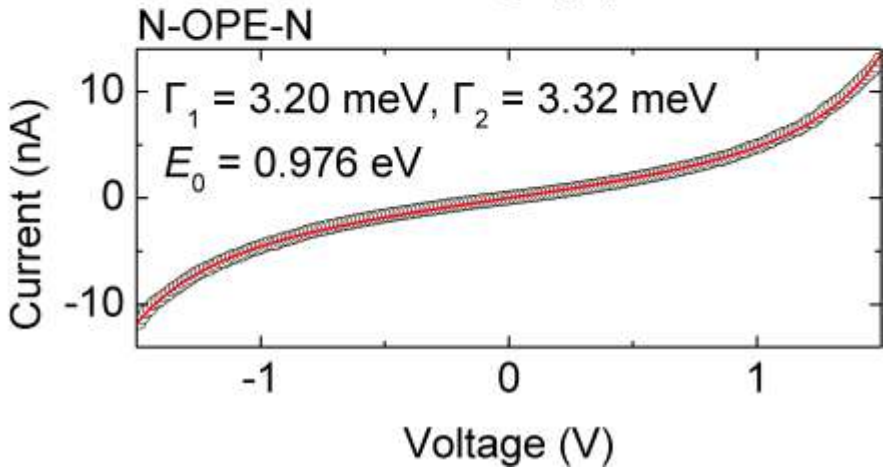
NB no substantial difference with T=0 fit (not at resonance)



one level model: fitting avg IV curves







fitting parameters

Γ_1, Γ_2, E_0

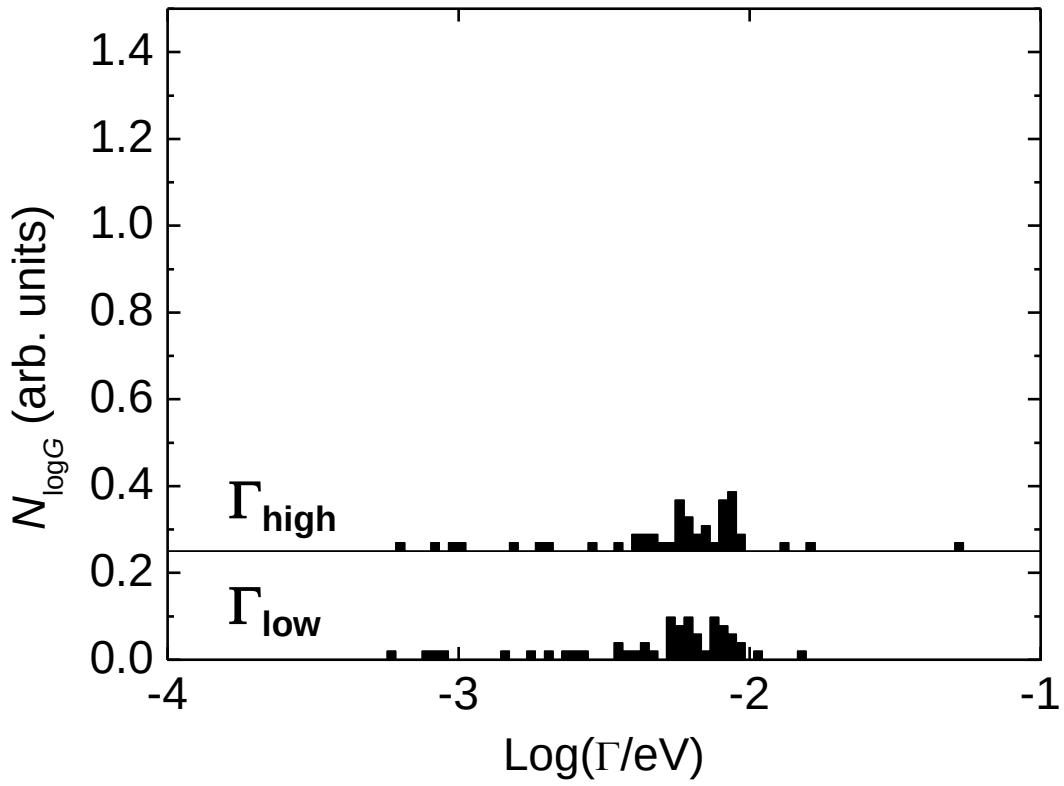
⇨ ***symmetry of molecule reflected in symmetry of average IV***

⇨ ***coupling is different for N and S***

NB: no substantial effect of T on fitting (not at resonance)

statistics for coupling constants

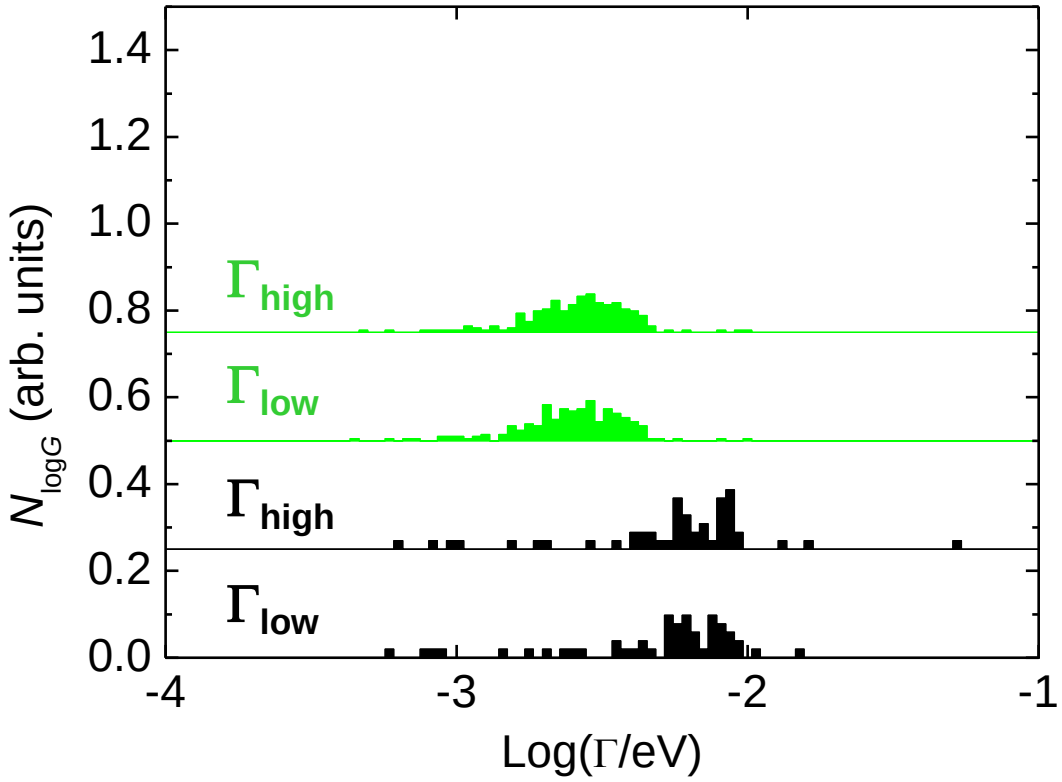
S-OPE-S



statistics for coupling constants

N-OPE-N

S-OPE-S

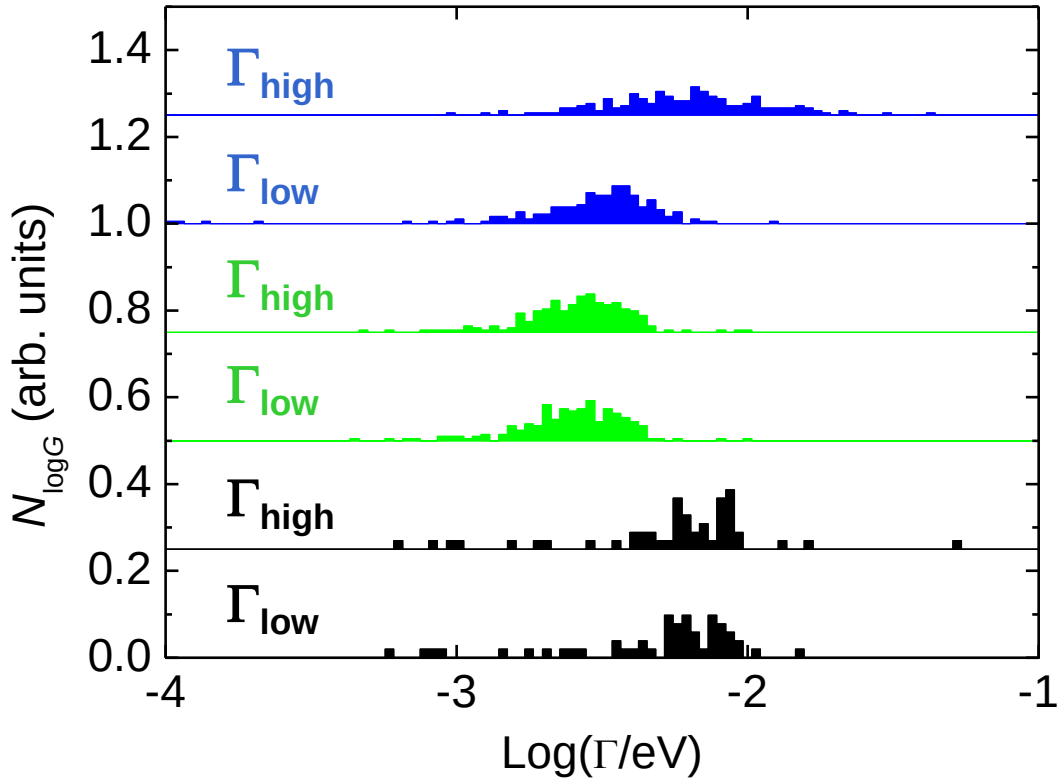


statistics for coupling constants

N-OPE-S

N-OPE-N

S-OPE-S



statistics for coupling constants

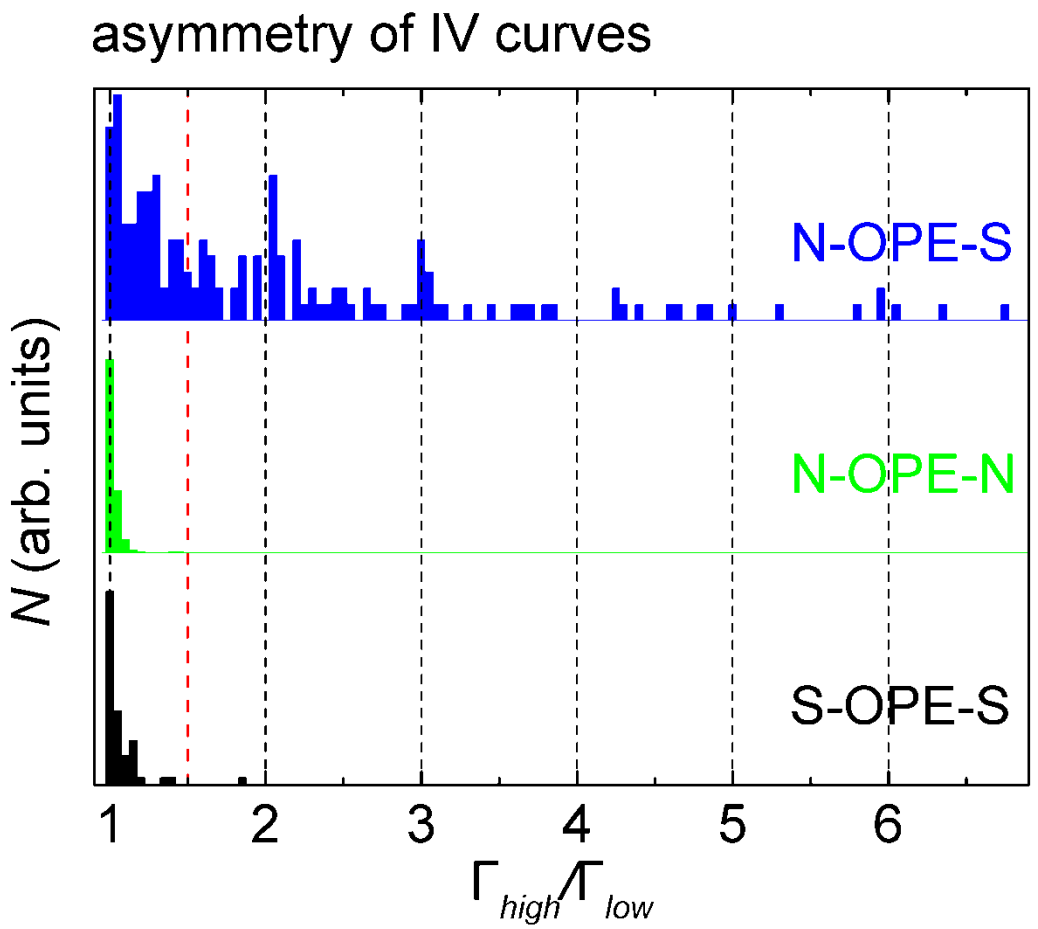
plateaus statistics

N-OPE-S: 183
108 asymmetric (60%)
threshold: 1.5

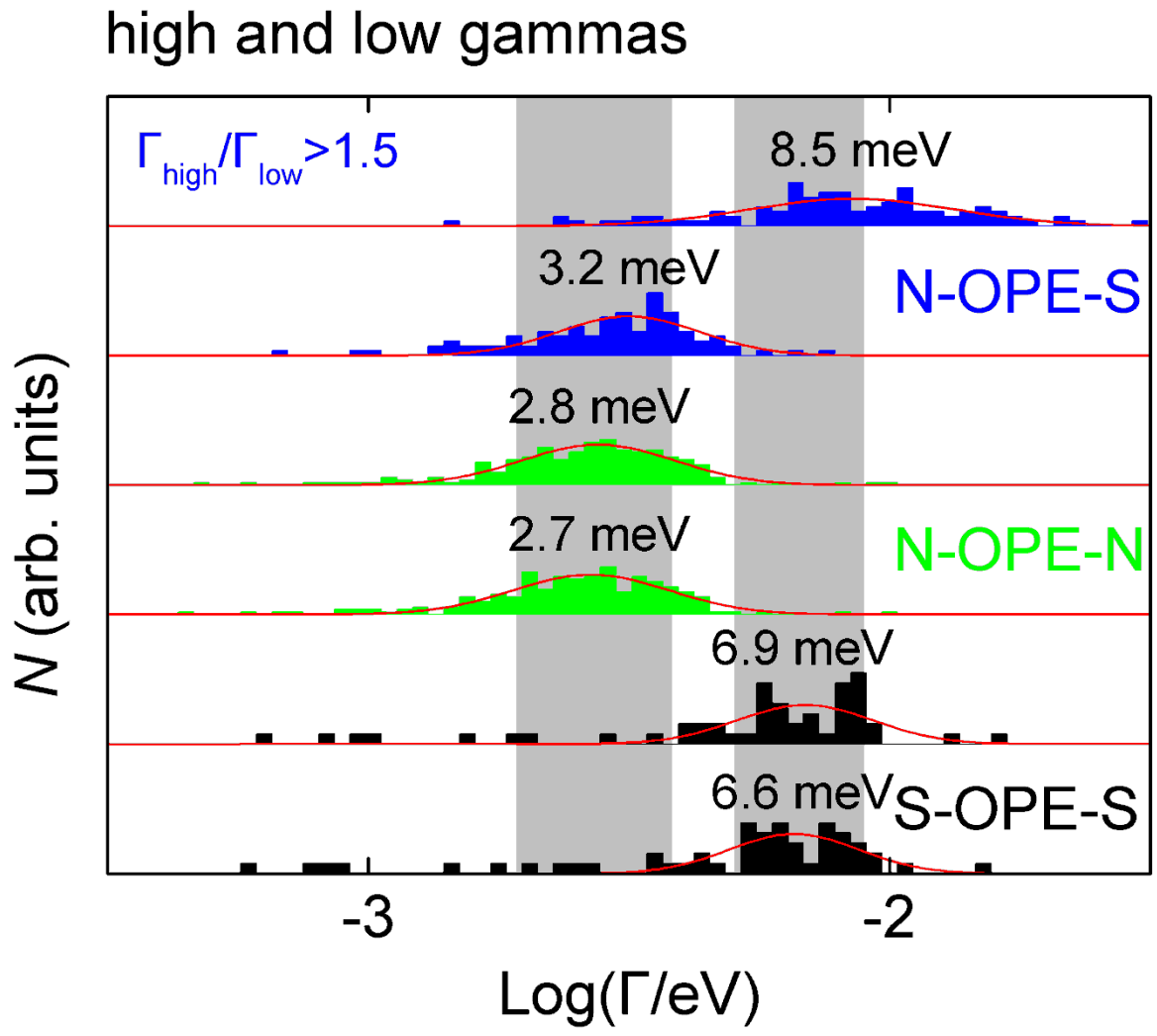
N-OPE-N: 205

S-OPE-S: 51

ratio $\Gamma_{high} / \Gamma_{low}$



statistics for coupling constants



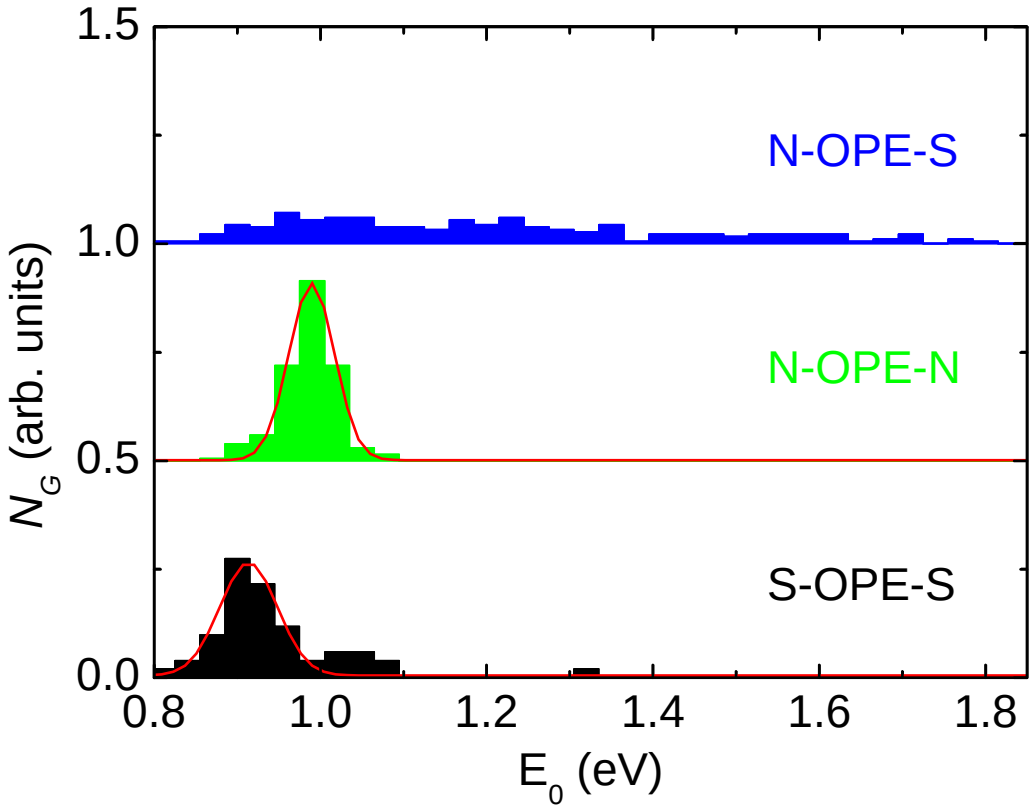
for recent parameter values for sym and asym molecules, see e.g.:
Zotti et al., Small (2010), Kirchner et al., A. Phys. Pol. A (2012), Y.Kim et al., Nano Lett. (2012), Wandlowski et al., JACS (2012)

statistics for level position

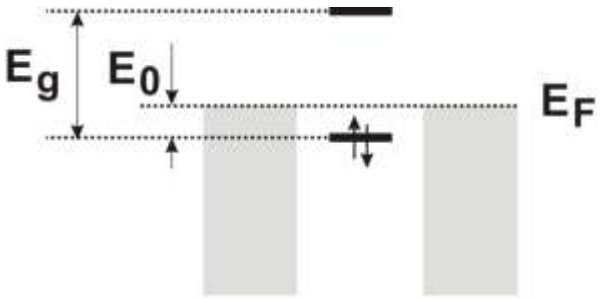
peak values for level position

N-OPE-N: $E_0 \approx 0.99$ eV
(w ≈ 50meV)

S-OPE-S: $E_0 \approx 0.91$ eV
(w ≈ 70meV)



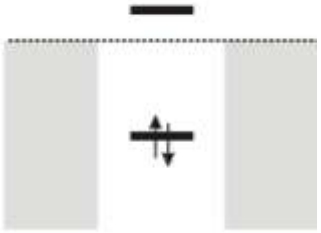
statistics for level position



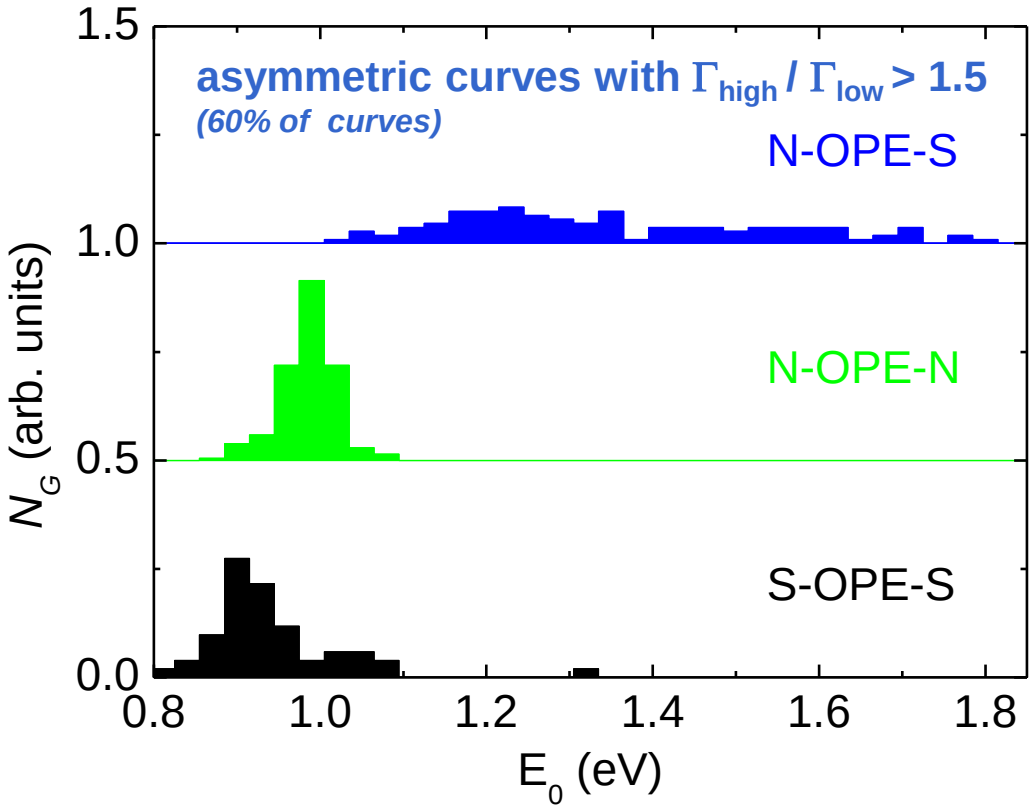
- for N-OPE-S, expect:

$$E_0 \in [E_0^S, E_0^N]$$

- HOMO, LUMO…



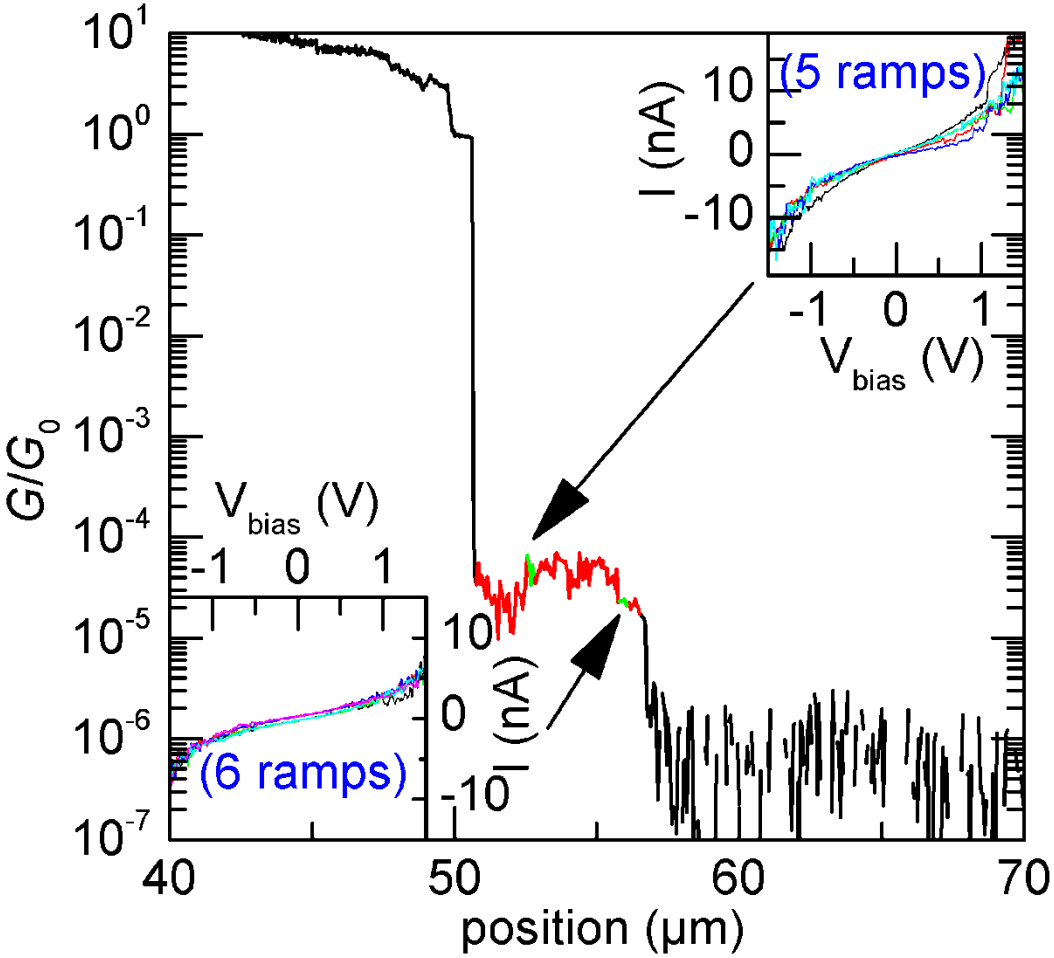
$$max(E_0) = E_g/2$$



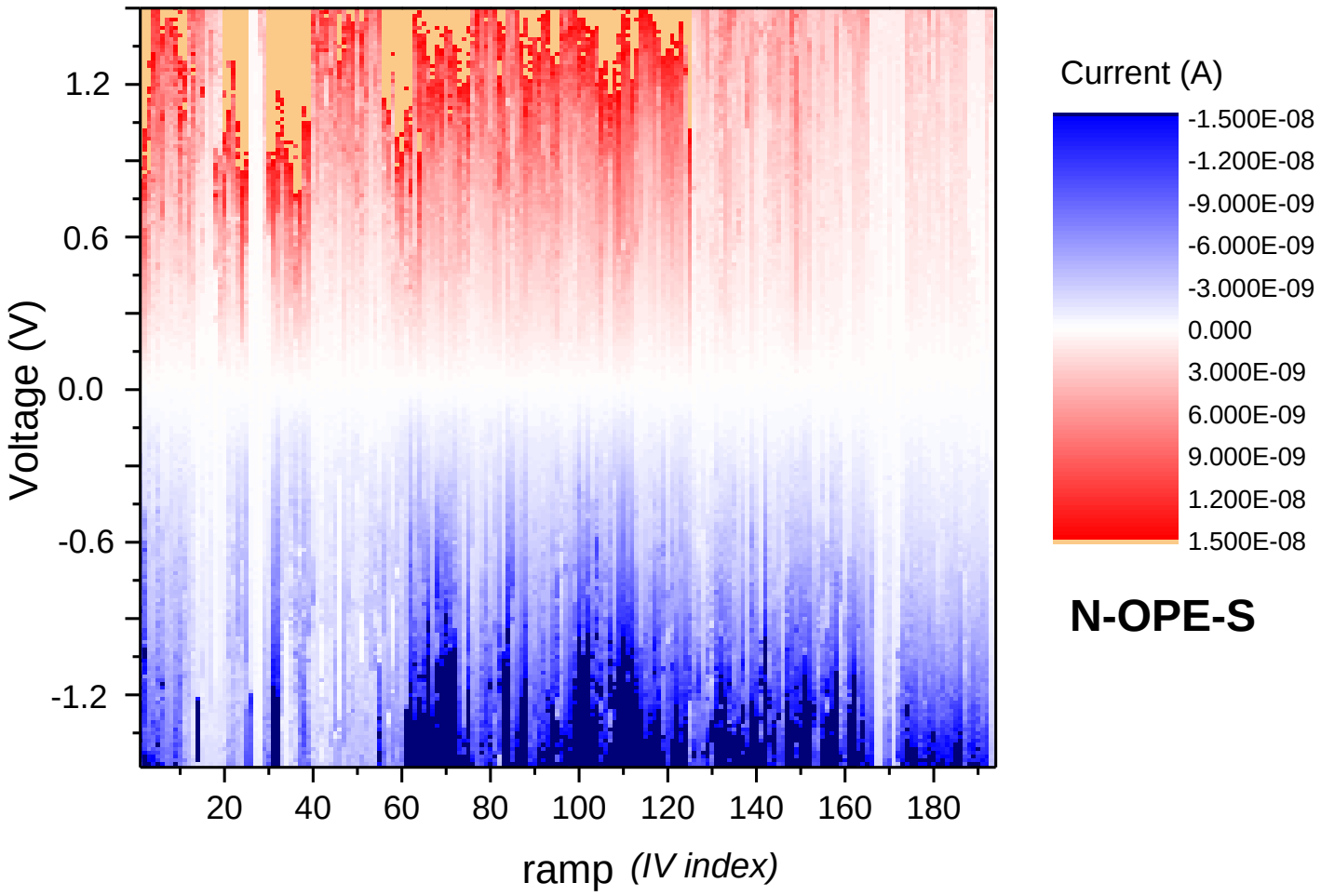
⇨ ***HOMO-mediated transport for S-OPE-S***
LUMO-mediated transport for N-OPE-N

for thermopower meas, see e.g.: Reddy, Majumdar et al., JACS (2011), APL (2010), Science (2007)

evolution of individual IVs



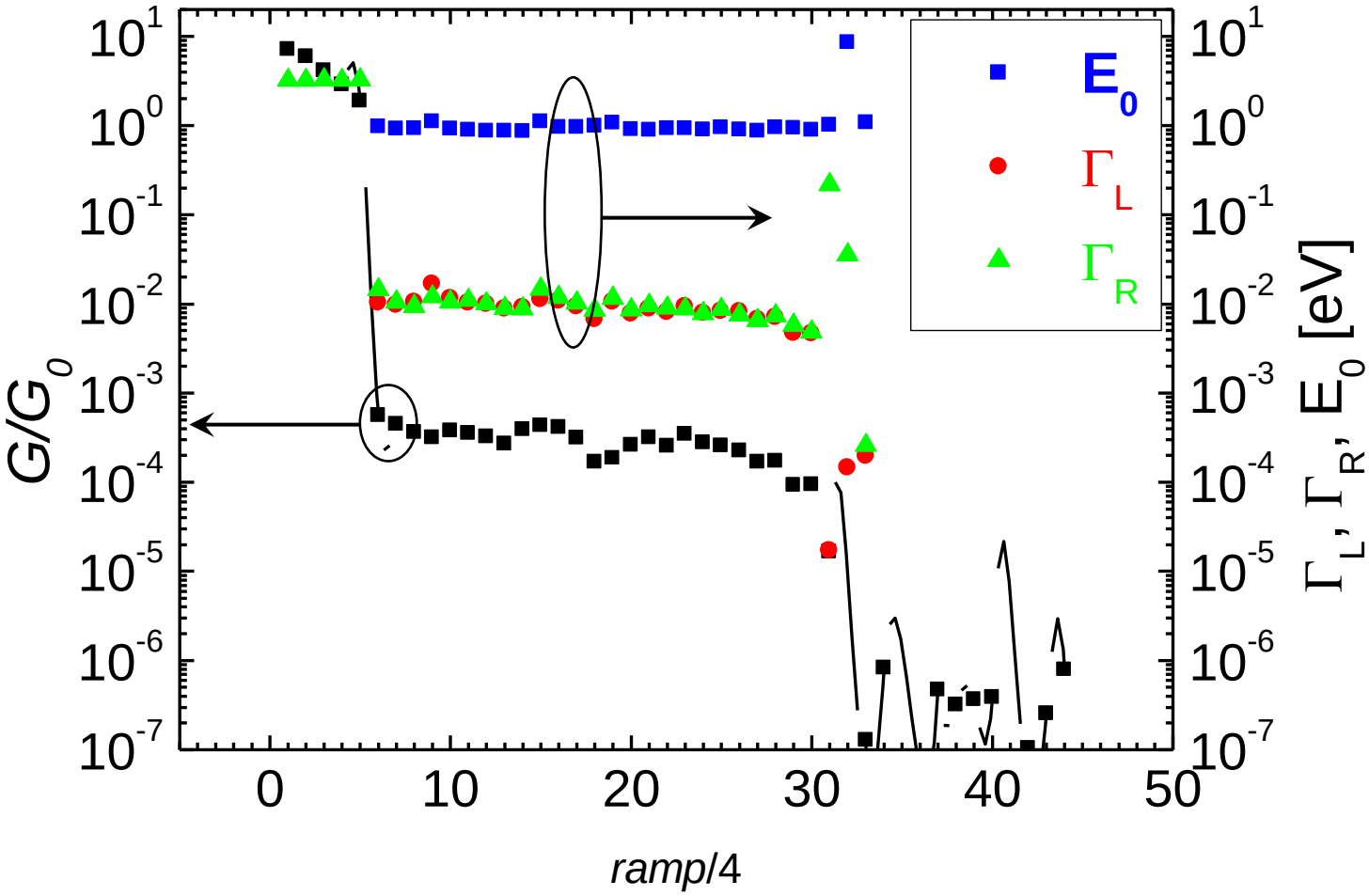
IVs along a conductance plateau



evolution of IVs parameters along conductance plateaus

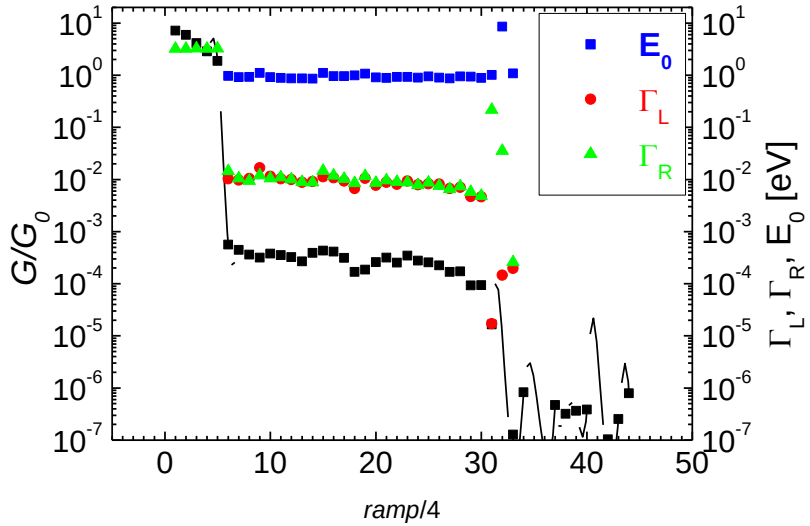
S-OPE-S

local averaging over 4 IVs
to limit effect of "broken" IVs (jumps, steps)

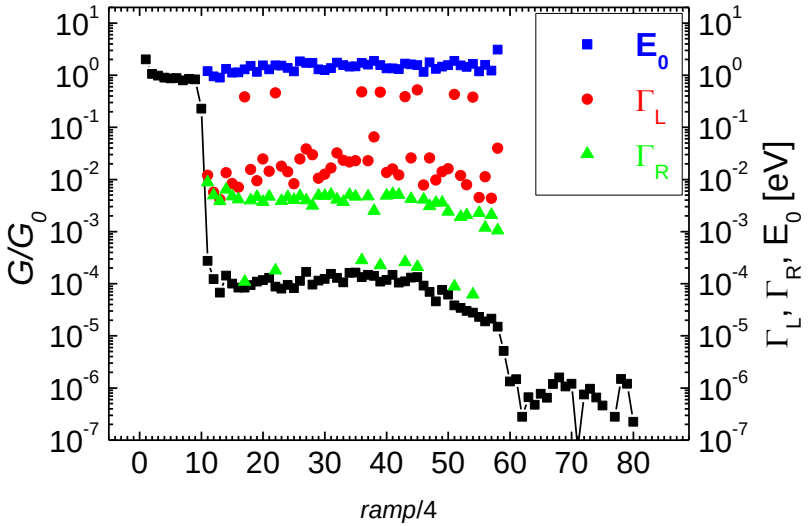


evolution of IVs parameters along conductance plateaus

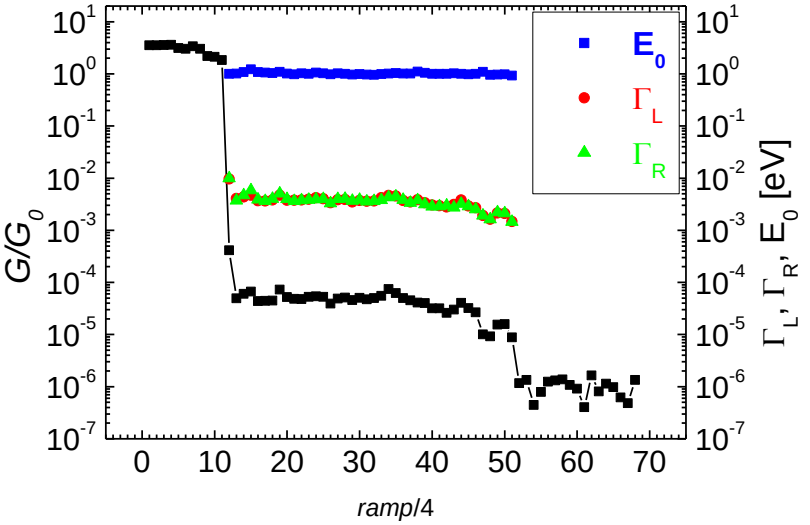
S-OPE-S



N-OPE-S



N-OPE-N



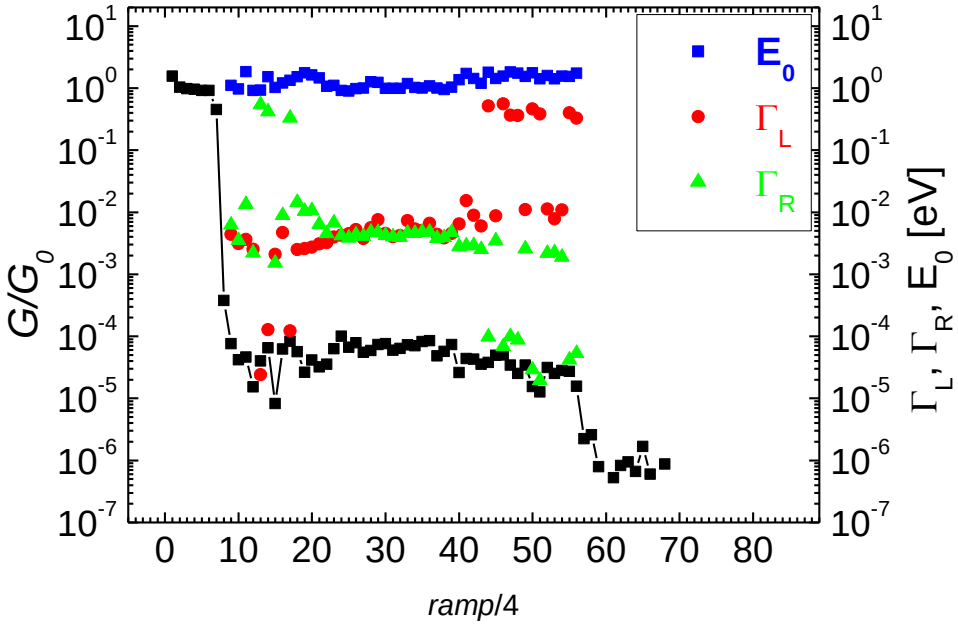
⇨ asymmetric IVs during most of plateau length for N-OPE-S

NB: fits to locally averaged IVs (4) to limit effect of "broken" IVs (jumps, steps)

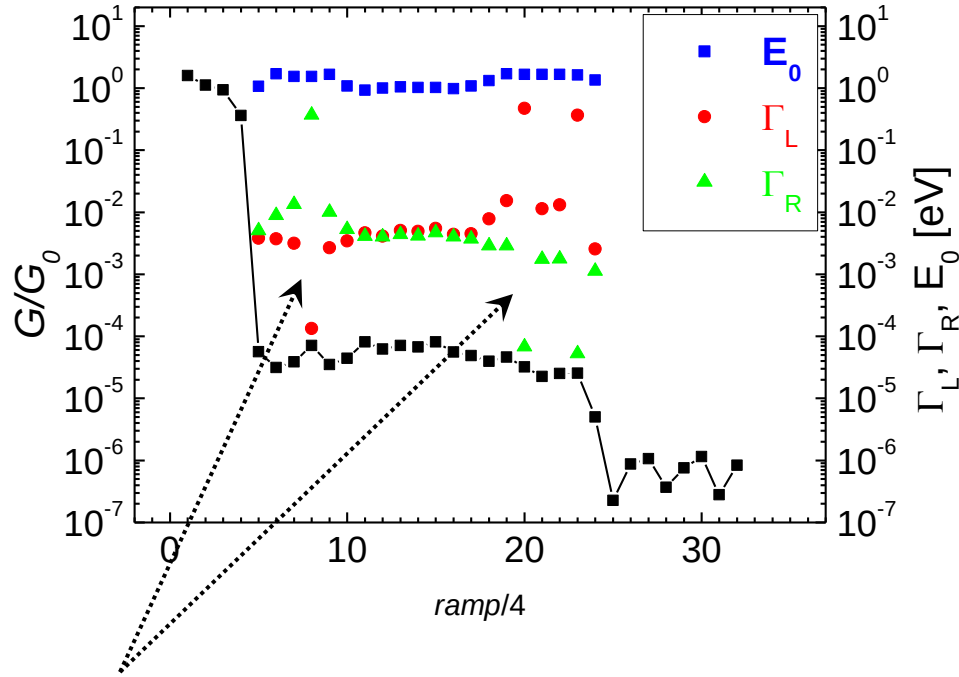
asymmetric molecule: a particular case

avg. IV ~ symmetric but individual IVs are not all symmetric

N-OPE-S



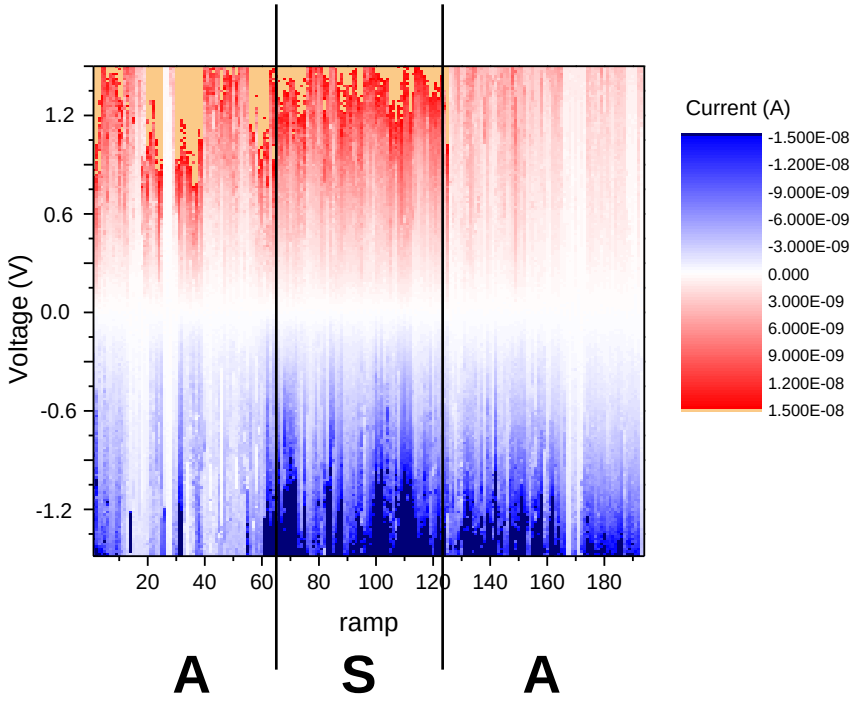
averaging over 10 IVs



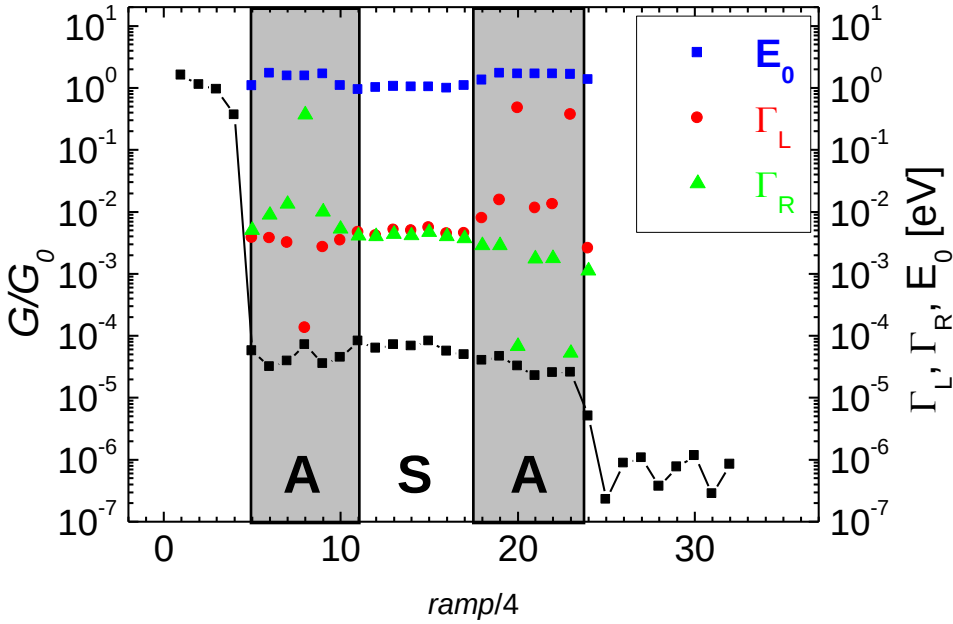
inversion of IV curve asymmetry

asymmetric molecule

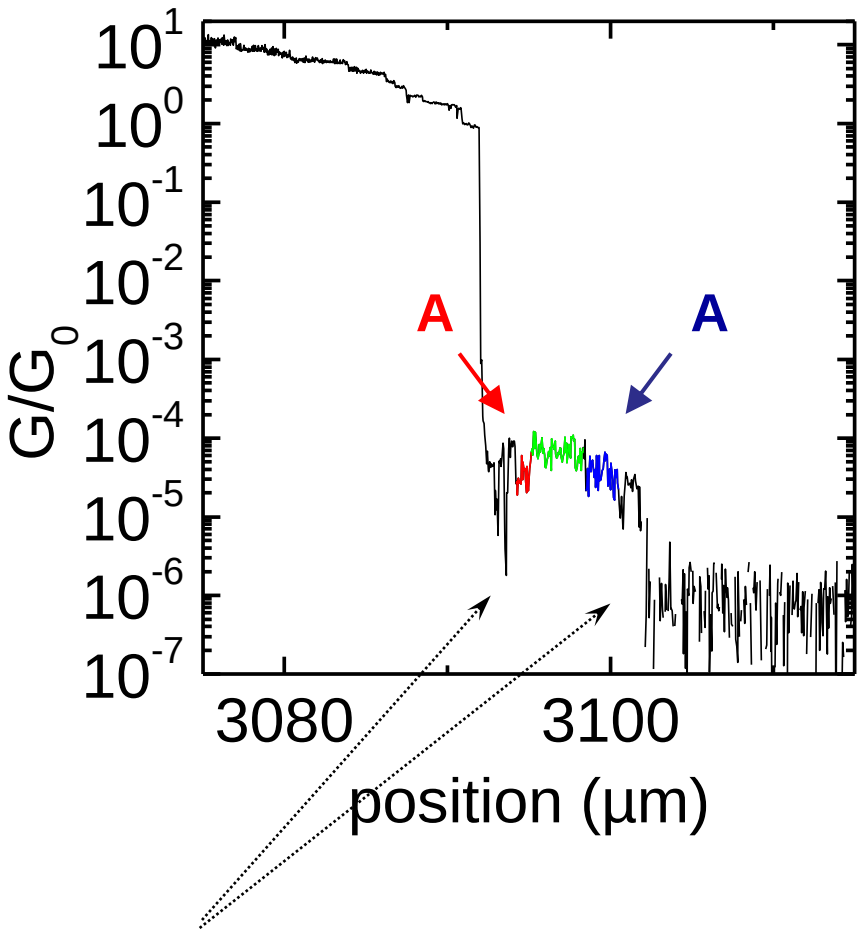
N-OPE-S

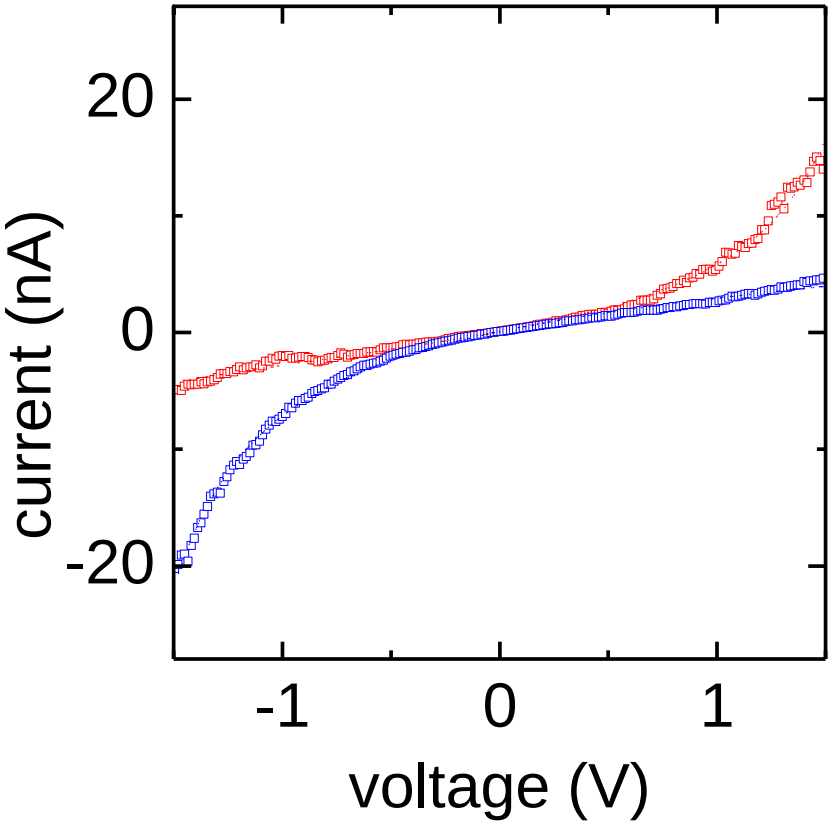


averaging over 10 IVs



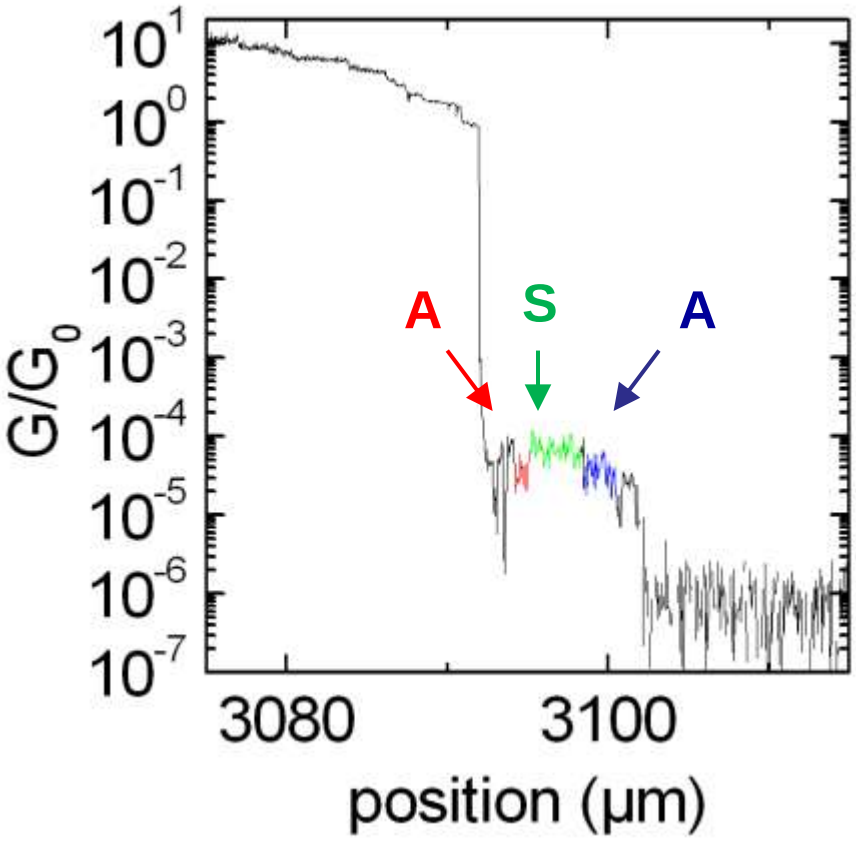
asymmetric molecule

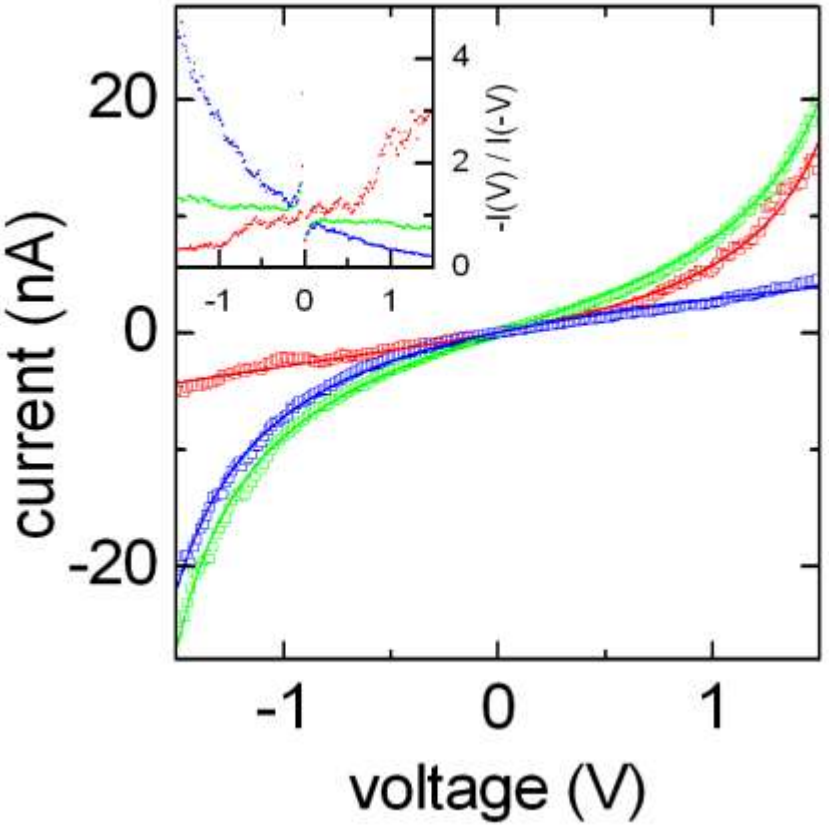




exclude very noisy ("dynamic") region

asymmetric molecule



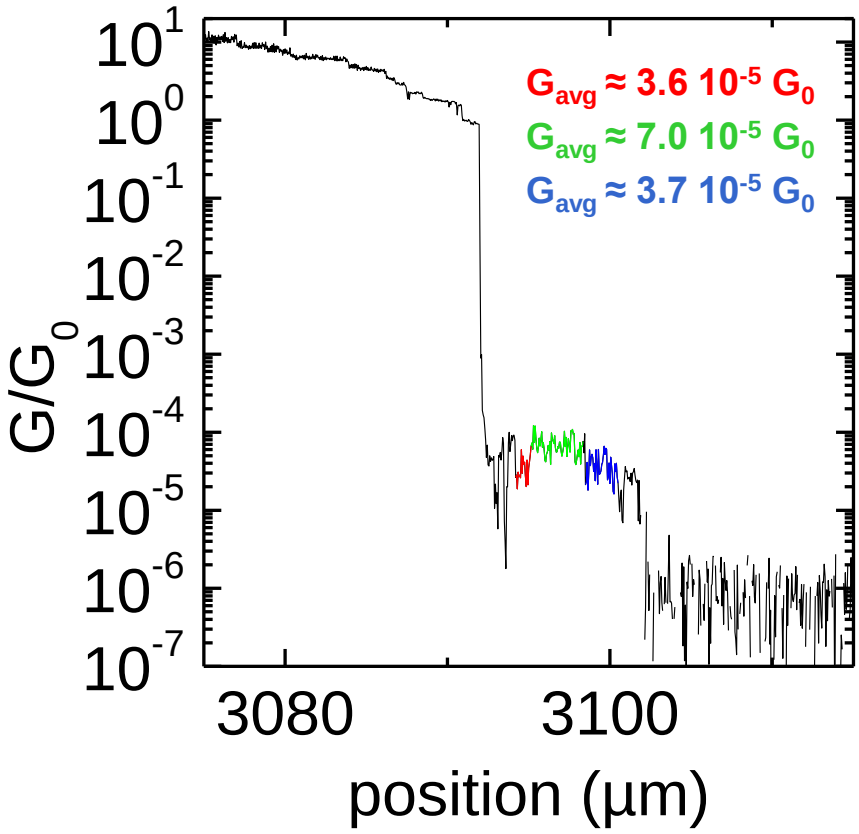


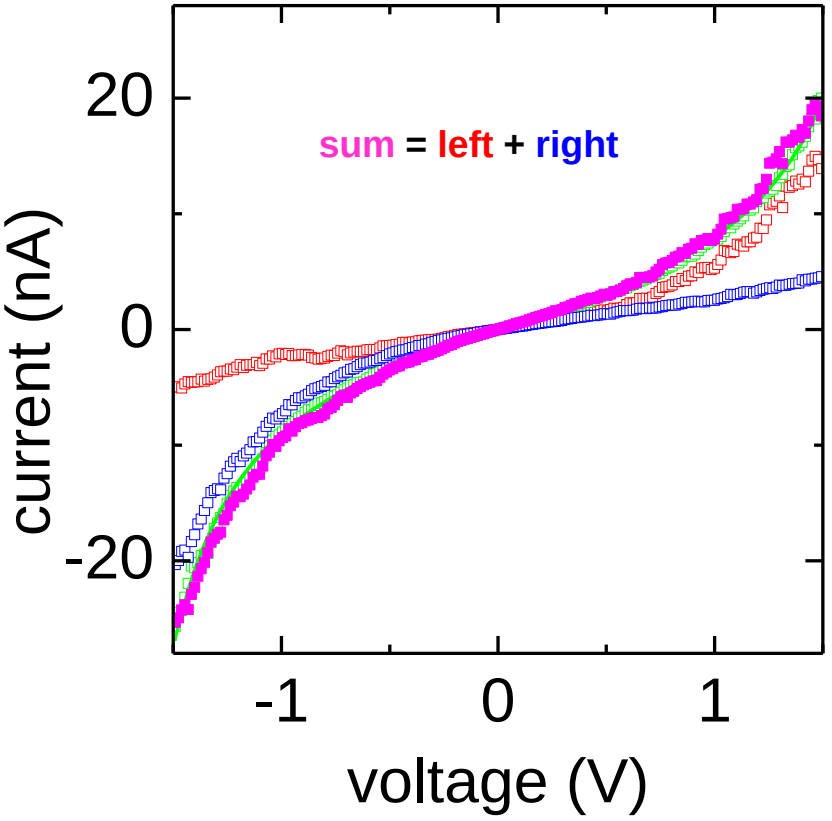
$E_0 \approx$ 1.4 eV
$\Gamma_L \approx$ 3.0 meV
$\Gamma_R \approx$ 7.0 meV

$E_0 \approx$ 0.97 eV
$\Gamma_L \approx$ 4.6 meV
$\Gamma_R \approx$ 4.2 meV

$E_0 \approx$ 1.6 eV
$\Gamma_L \approx$ 12.9 meV
$\Gamma_R \approx$ 2.6 meV

asymmetric molecule



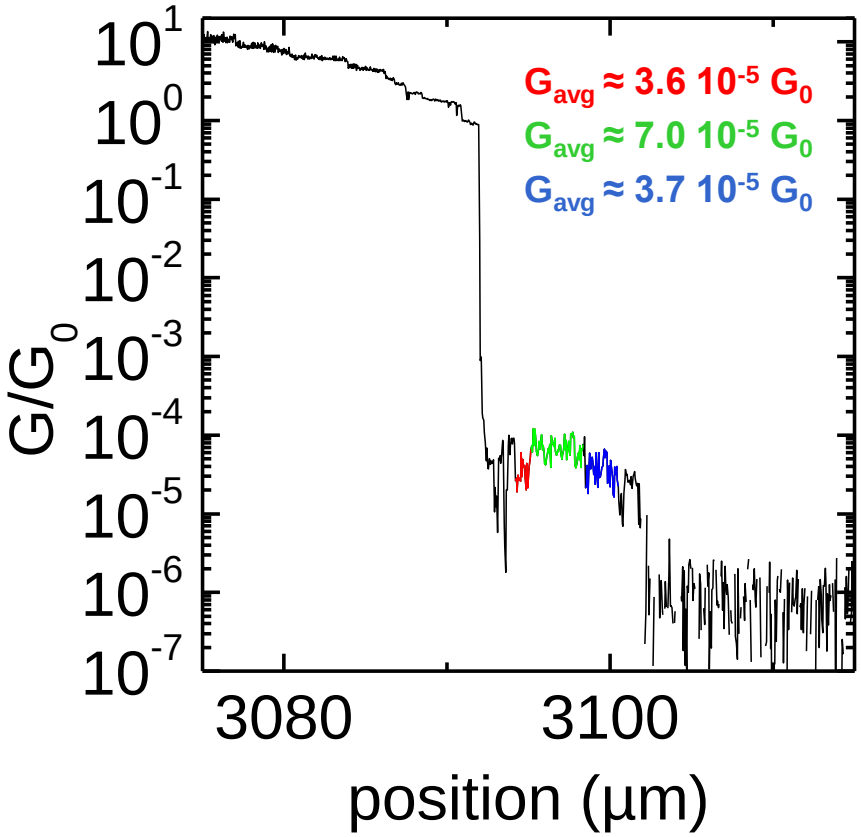


$E_0 \approx$ 1.4 eV
$\Gamma_L \approx$ 3.0 meV
$\Gamma_R \approx$ 7.0 meV

$E_0 \approx$ 0.97 eV
$\Gamma_L \approx$ 4.6 meV
$\Gamma_R \approx$ 4.2 meV

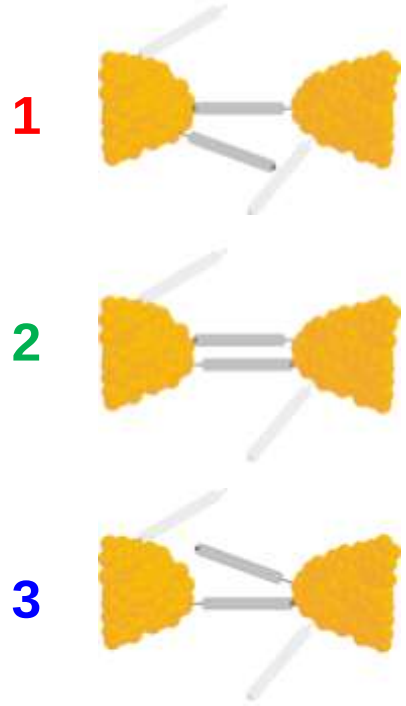
$E_0 \approx$ 1.6 eV
$\Gamma_L \approx$ 12.9 meV
$\Gamma_R \approx$ 2.6 meV

asymmetric molecule



multiple bridging (?)

(*cf G values*)



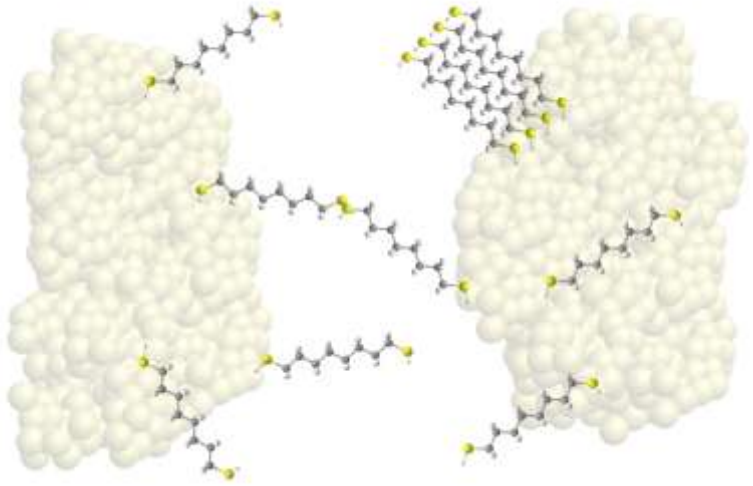
NB: **interference effects** due to multiple pathways: no such observation here

NB: **2-level model** (e.g. 2 orbitals or 2 mol. with 1 dominant level): no consistent fitting

NB: other posible explanations: $\Gamma, E_0 \neq$ const. during stretching, interplay between coupling and level position *(cf e.g.: "bowl"-shaped plateaus, BDT: Tao et al., Nat. Nano 2012);* effect of image charges/screening, partial charge transfer electrode – molecule

outlook

outlook: molecular junction formation



drifting molecules, stochastic anchoring, random clustering ⇨ ***undefined junction geometry & conductance***

drifting surface atoms, metal protrusions ⇨ **undefined electrostatic landscape**

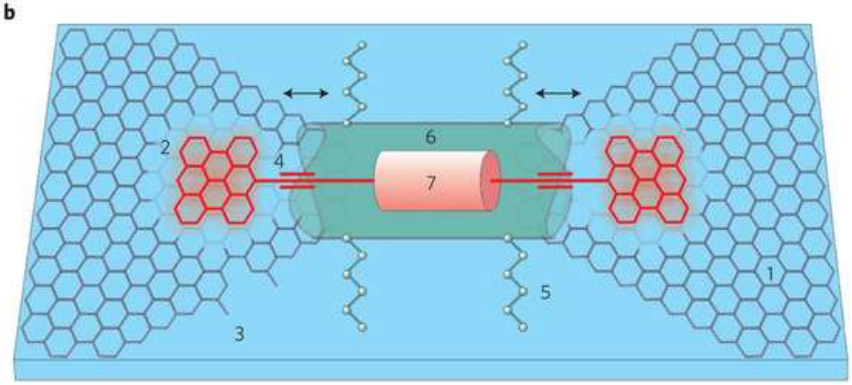
⇨ **variability, low-yield and lack of control in key electrical parameters**

Carbon-based contact materials as electrodes

FLG	vd Zandt et al., Nano Lett. 2011
SWNT	Krupke et al., Nat. Nanotech. 2010
C-fiber tips	Agrait et al., Nanoscale Res. Lett. 2012

⇨ **monolayer graphene ... ?**

⇨ ***paradigm shift for molecular electronics***



Lörtscher, Nat. Nano 2013