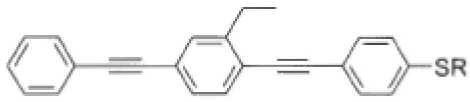
Molecular electronics

Lecture 4

Major experimental techniques in molecular electronics. Break junctions and nanopores.

Scanning probe methods

(a)



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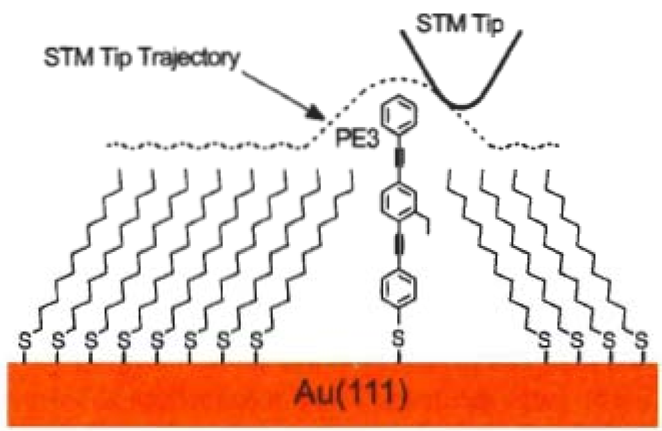
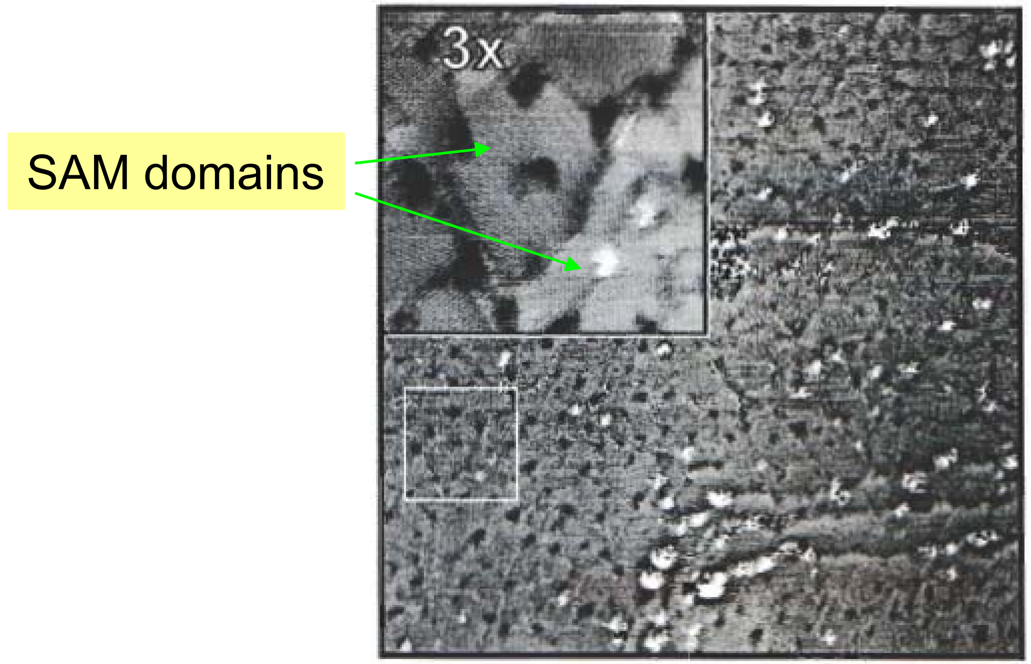


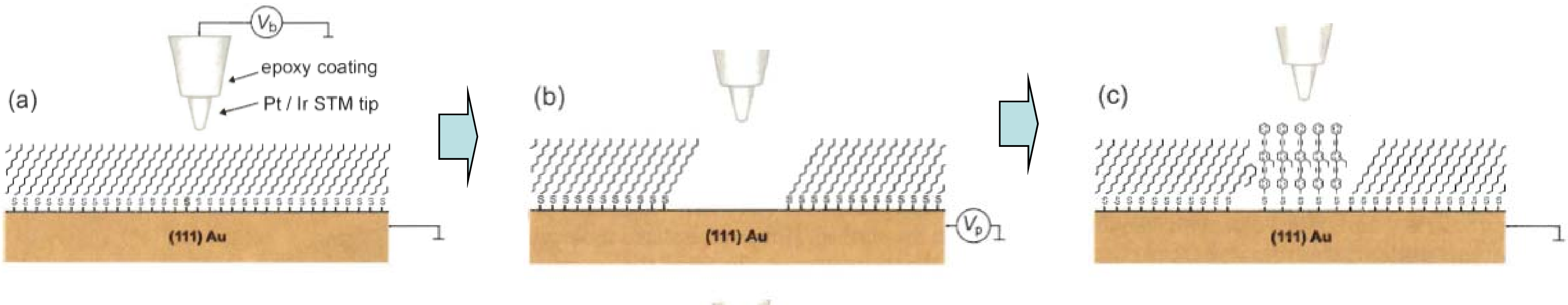


- molecular rods protruding from dodecylmercaptan layer

- advanced possibility:
  - molecules can be selectively desorbed by applying a voltage pulse or
  - by mechanical forces (AFM)

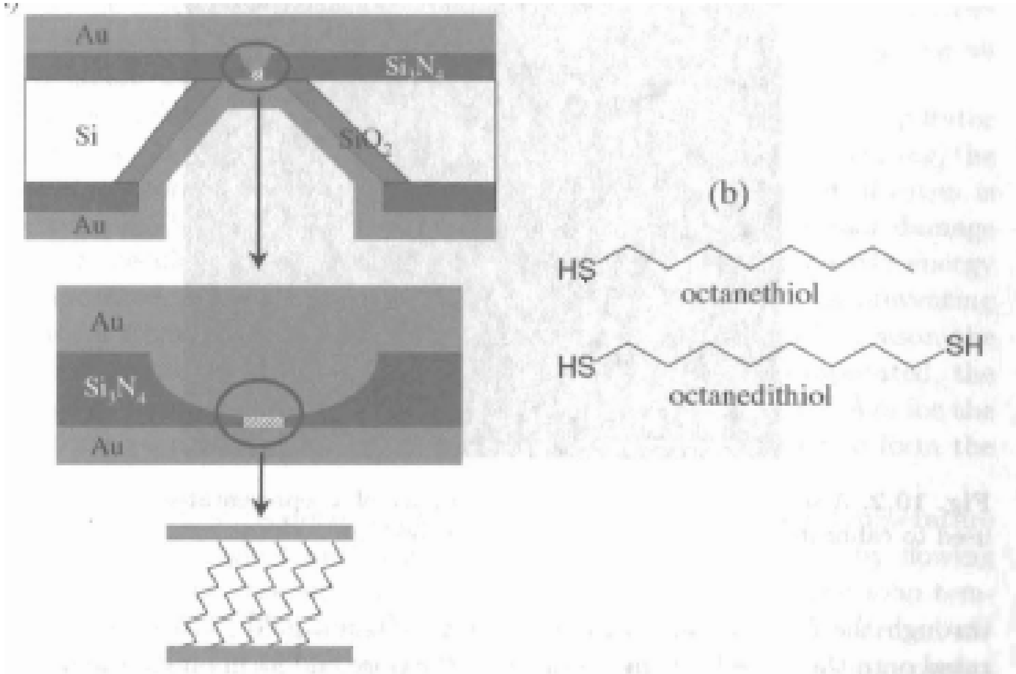
Scanning probe approach

- advanced possibilities:
  - molecules can be selectively desorbed by applying a voltage pulse or
  - by mechanical forces (AFM)



Nano-pore technique

- The experimental technique:
  - a pore is manufactured in Si-wafer coated with SiN_x.
  - a layer of gold is deposited on the front side
  - device exposed to ethanol solution of the molecules
  - gold is deposited on the back side on a liquid nitrogen cooled stage at low rate <0.1 Å/s



M.Reed et al, Intrinsic electronic conduction mechanism in self-assembled monolayers, Lect.Notes Phys. 680, 275 (2005)

Nano-pore measurement on thiols

- Thiols are well studied but what is the actual mechanism of tunneling?
- The possibilities:

Conduction Mechanism	Characteristic Behavior	Temperature Dependence	Voltage Dependence
Direct tunneling*	$J \propto V \exp\left(-\frac{2d}{\hbar}\sqrt{2m\Phi}\right)$	none	$J \propto V$
Folwer-Lordheim tunneling	$J \propto V^2 \exp\left(-\frac{4d\sqrt{2m}\,\Phi^{3/2}}{3q\hbar V}\right)$	none	$\ln(J/V^2) \propto 1/V$
Thermionic emission	$J \propto T^2 \exp\left(-\frac{\Phi - q\sqrt{qV/4\pi\epsilon d}}{kT}\right)$	$\ln(J/T^2) \propto 1/T$	$\ln(J) \propto V^{1/2}$
Hopping conduction	$J \propto V \exp\left(-\frac{\Phi}{kT}\right)$	$\ln(J/V) \propto 1/T$	$J \propto V$

Nano-pore measurement on thiols

- Generally the tunneling can involve both HOMO and LUMO but the metal level is usually close to HOMO and the influence of other levels can be neglected at low-bias

- Simmons model (takes into account finite height of the barrier, extra parameter **α** describes non-rectangular barrier).
  For low bias:

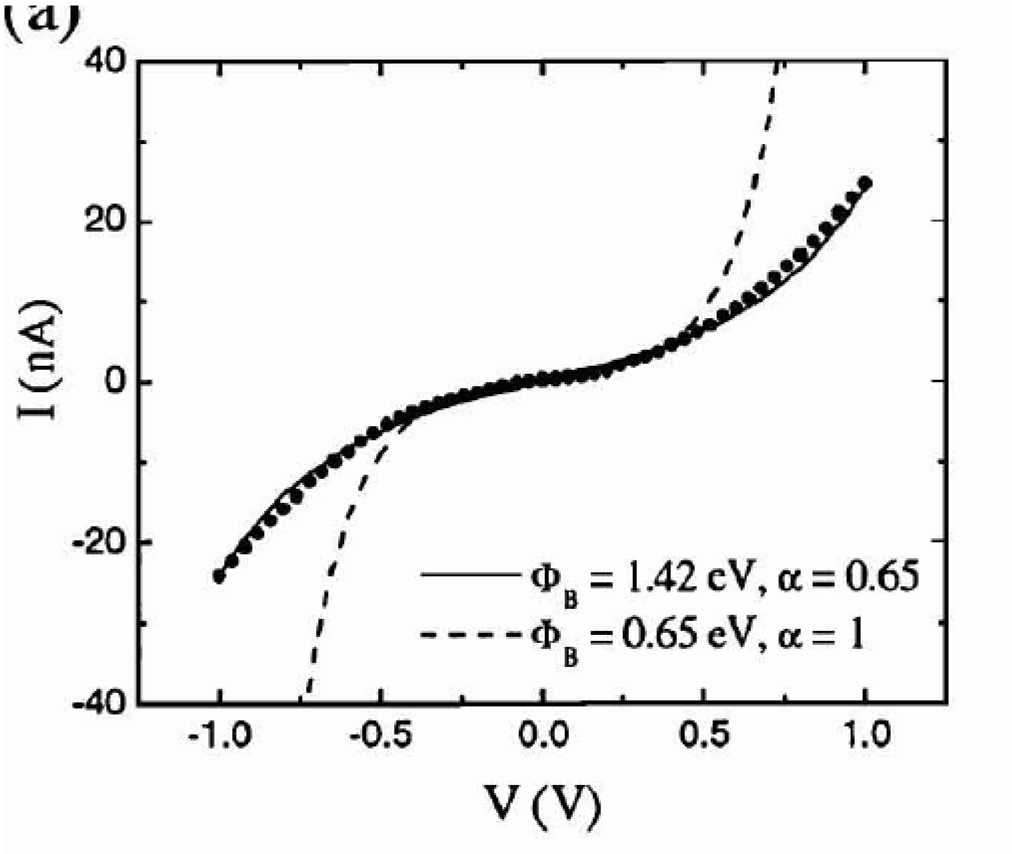
$$J \approx \left(\frac{(2m\Phi_B)^{1/2} e^2 \alpha}{\hbar^2 d} \right) V \exp\left[- \frac{2(2m)^{1/2}}{\hbar} \alpha (\Phi_B)^{1/2} d \right]$$

$$J \propto \tfrac{1}{d} \exp(-\beta_0 d), \text{ where } \quad \beta_0 = \frac{2(2m)^{1/2}}{\hbar} \alpha (\Phi_B)^{1/2}$$

- For high bias: $J \propto \frac{1}{d^2} \exp(-\beta_V d)$, where $\beta_V = \frac{2(2m)^{1/2}}{\hbar} \alpha \left(\Phi_B - \frac{eV}{2} \right)^{1/2}$

Nano-pore measurement on thiols

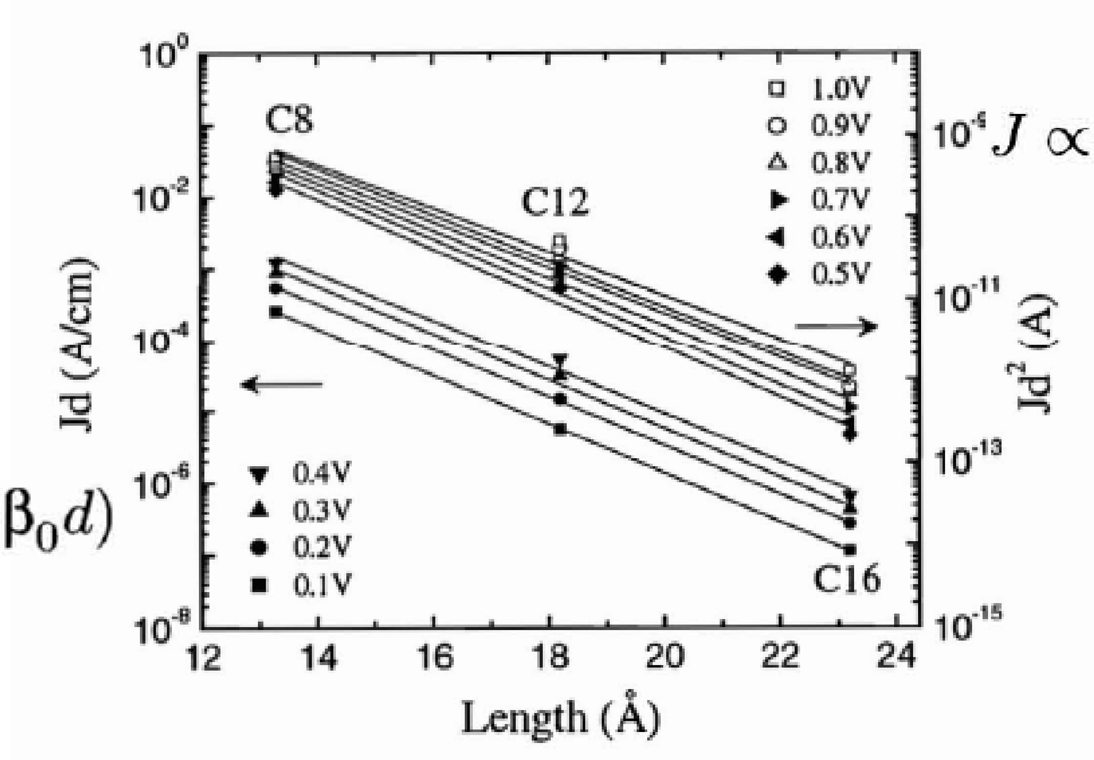
$$J \propto \frac{1}{d}\exp(-\beta_0 d)$$



- Good fitting can be observed for a Simmons model with a not rectangular barrier

Nano-pore measurement on thiols

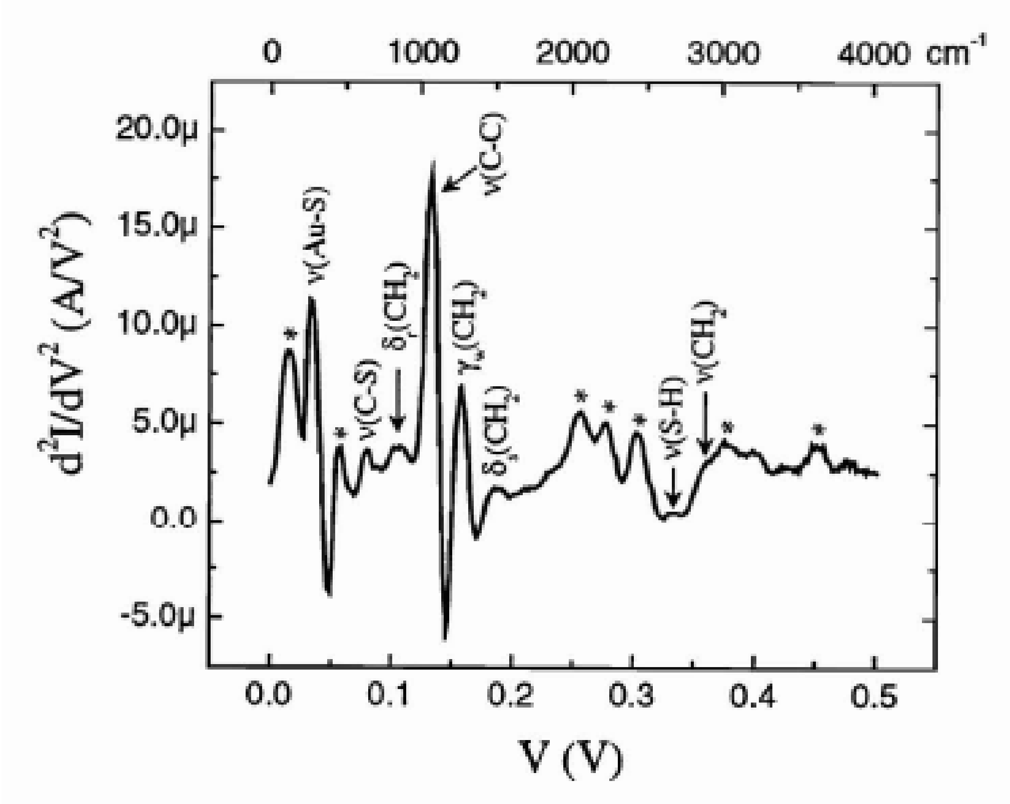
$$J \propto \frac{1}{d^2}\exp(-\beta_V d)$$



$$J \propto \frac{1}{d}\exp(-\beta_0 d)$$

- Length dependence: same parameters describe thiols of varios length.
- No prononced temperature dependence was observed

Nano-pore measurement on thiols



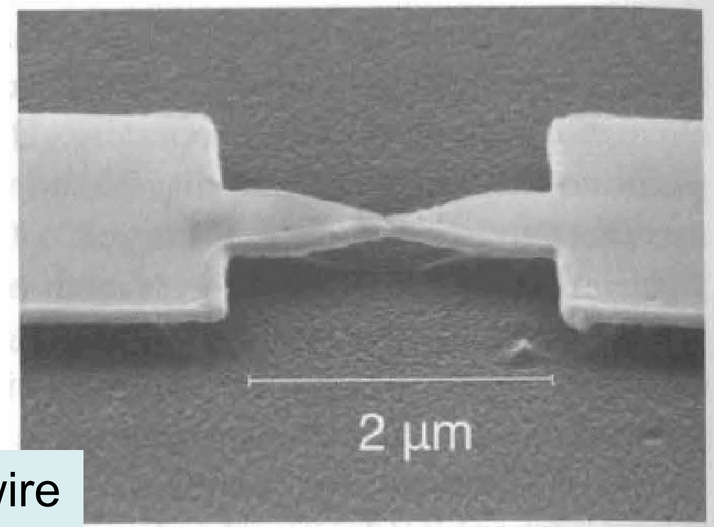
- Inelastic tunneling spectra of C8 reveals peaks that can be identified to characteristic vibrational modes of the molecule.

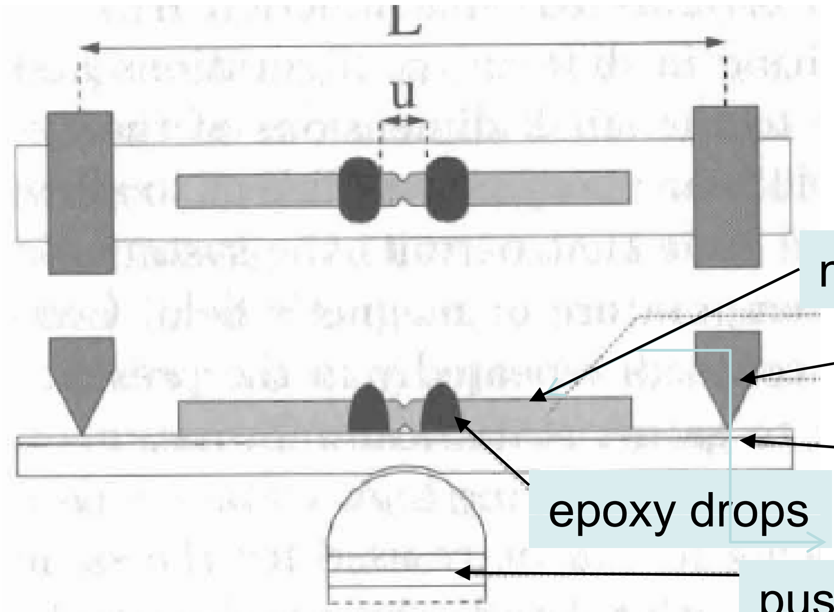
Mechanically Controlled Break Junctions (MCBJ)

(following J.van Ruitenberg et al, ”Contacting Individual Molecules using Mechanically Controllable Break Junctions”, Lect.Notes Phys. 680, 253-274 (2005)

Mechanically Controlled Break Junctions (MCBJ)

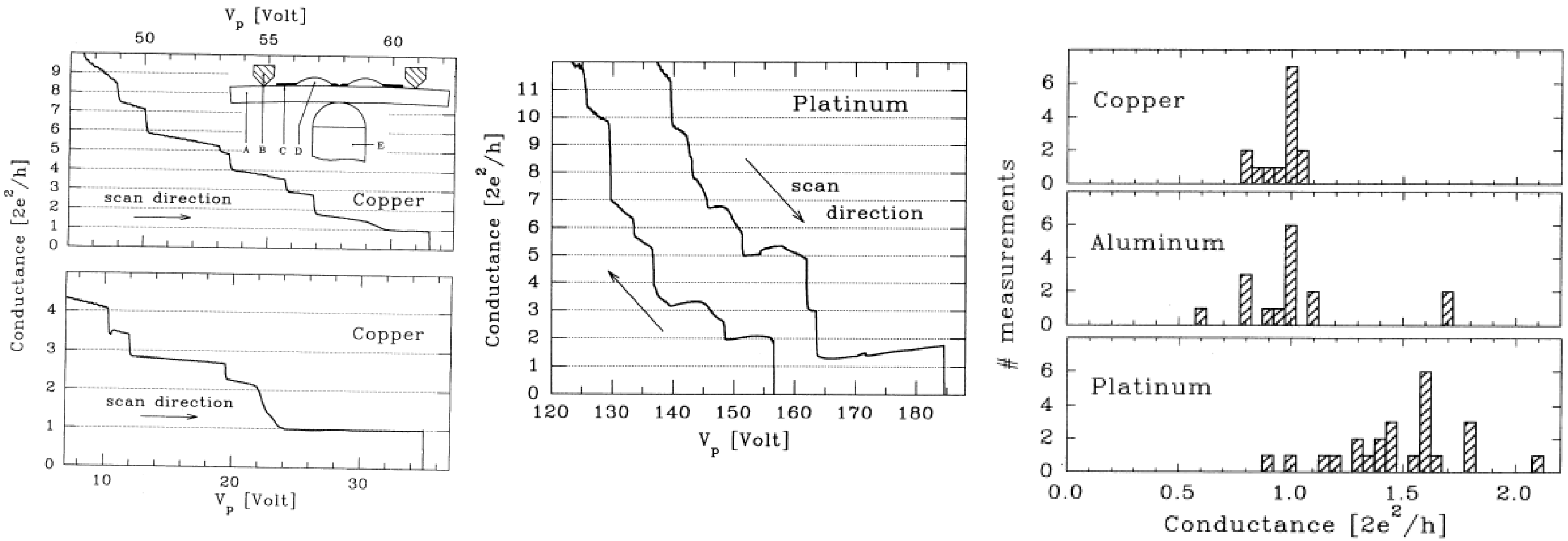
- lithographically (e-beam) fabricated notched wire





- reduction ratio of the device (electrode separation δu vs. rod displacement δx): $r = \frac{\delta u}{\delta x} = \frac{6tu}{L^2} \approx 10^{-4}$
- the junction can be calibrated using tunneling current vs. distance dependence. Junction stability typically 250pm at RT, 1pm at 4.2 K.

Mechanicall controlled break junctions



- mechanical contact breaks down to a single atom contact

J.van Ruitenbeek et al, Phys.Rev.B 48, 1993

Mechanically Controlled Break Junctions (MCBJ)

Advantages

- in comparison to scanning probe techniques molecule can be bonded to **both electrodes symmetrically**
- In comparison to lithographically defined electrodes, junctions with a small gap can be created reproducibly and controllably
- molecule configuration in the junction can be stressed or deformed during the experiment
- molecule configuration can be re-arranged on the same device gathering statistical information
- the system is compact and can be placed in magnetic field or variable temperature system

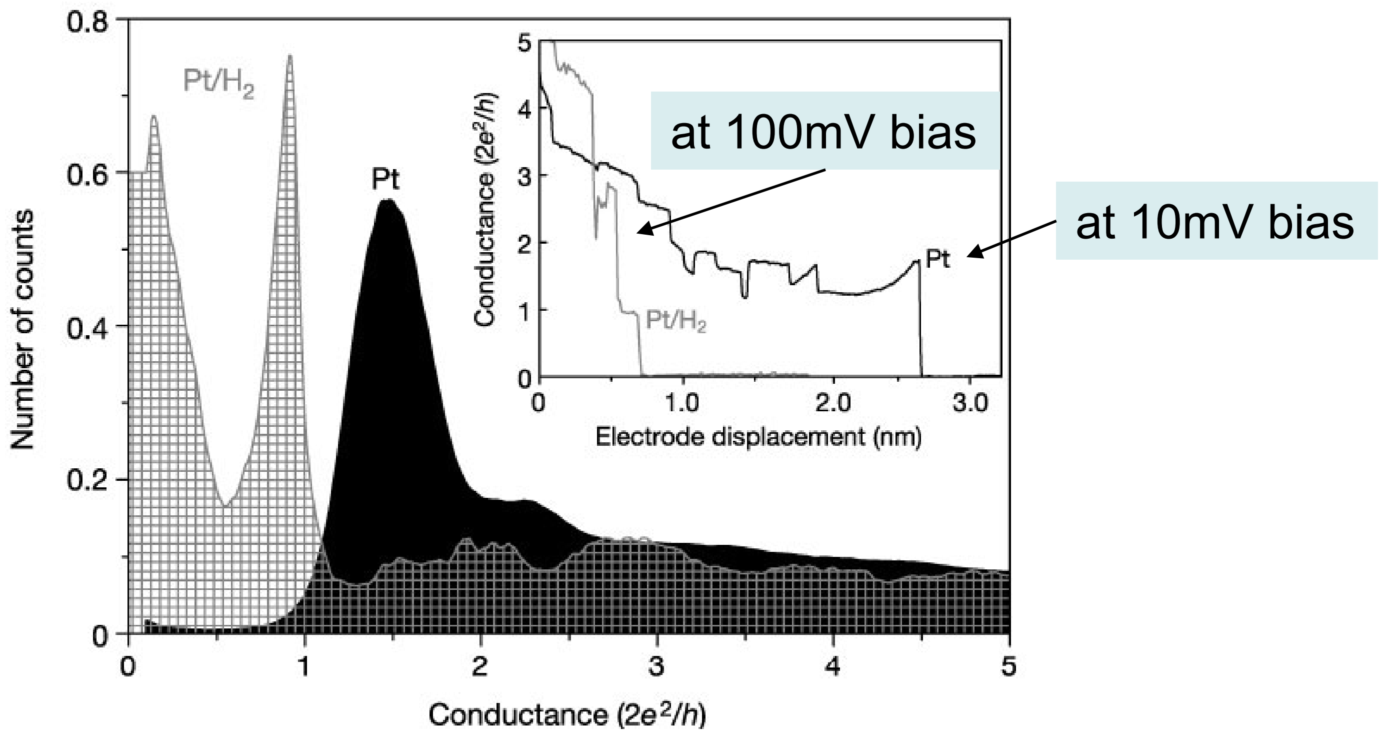
Drawback

- difficult to integrate into more complex molecular devices (future integrated circuits)

Mechanically Controlled Break Junctions (MCBJ)

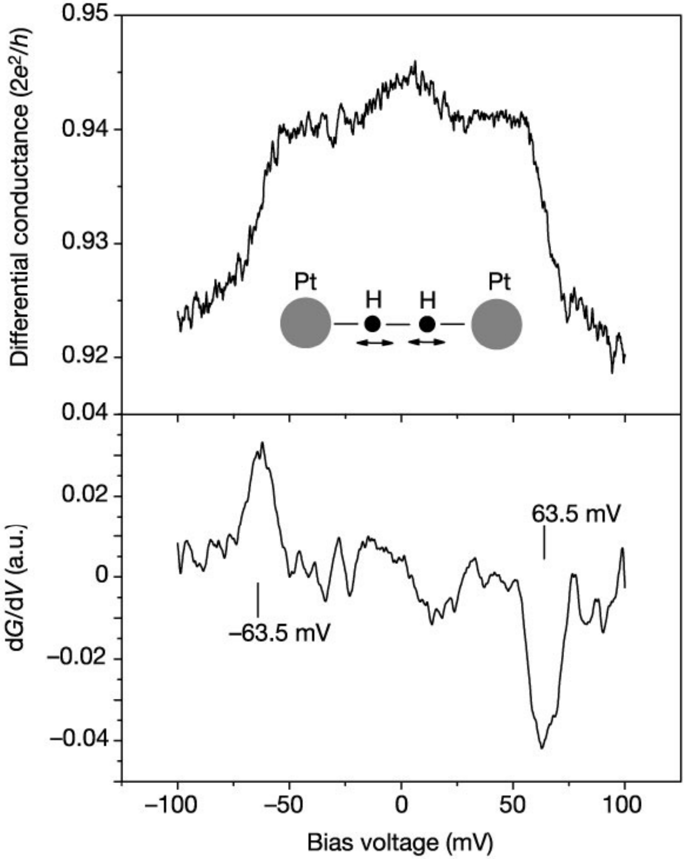
- Experimental procedures:
  - for small molecules:
    - Pt electrodes are used.
    - Junction is broken at 4.2K (cryogenic UHV)
    - Gas of molecules of interest is admitted into the chamber trough a capillary.
  - large conjugated molecules:
    - Gold electrodes are used
    - Junction is broken at room temperature
    - Droplet of solution is deposited on top
    - Junction can be further cooled down (however needs re-eatblishing at LT)

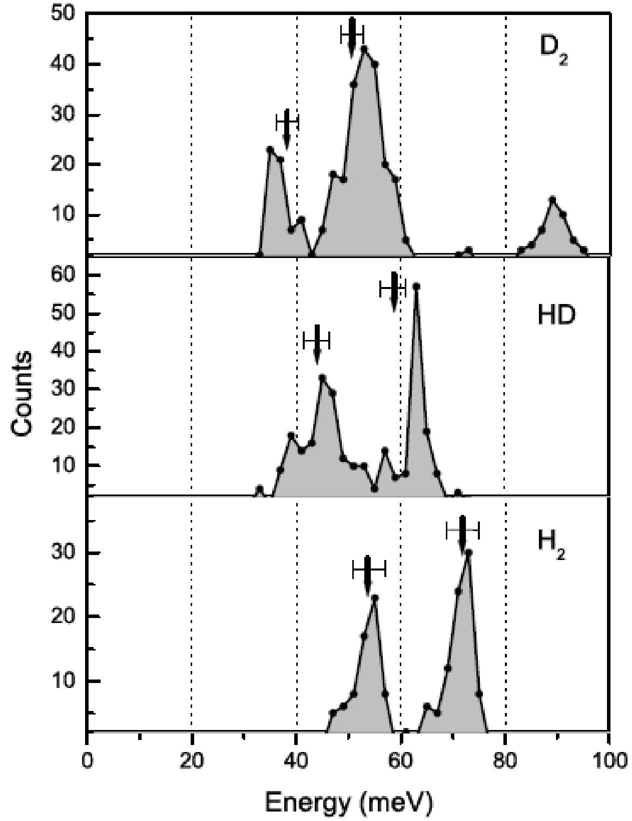
Conductance through H_2 molecule



- conductance curves (conductance vs. separation) and the last value before the jump to tunneling regime is plotted as histogram (around 10000 curves!) for clean Pt and Pt in H_2 atmosphere
- the drop in conductance is related to scattering on molecular vibration of H_2 molecule.

Conductance through H_2 molecule





- energy of molecular vibration can be established using differential conductance measurements
- it scales with the atomic mass for isotopes $\sqrt{1/2}$ for D_2, $\sqrt{3/2}$ for DH

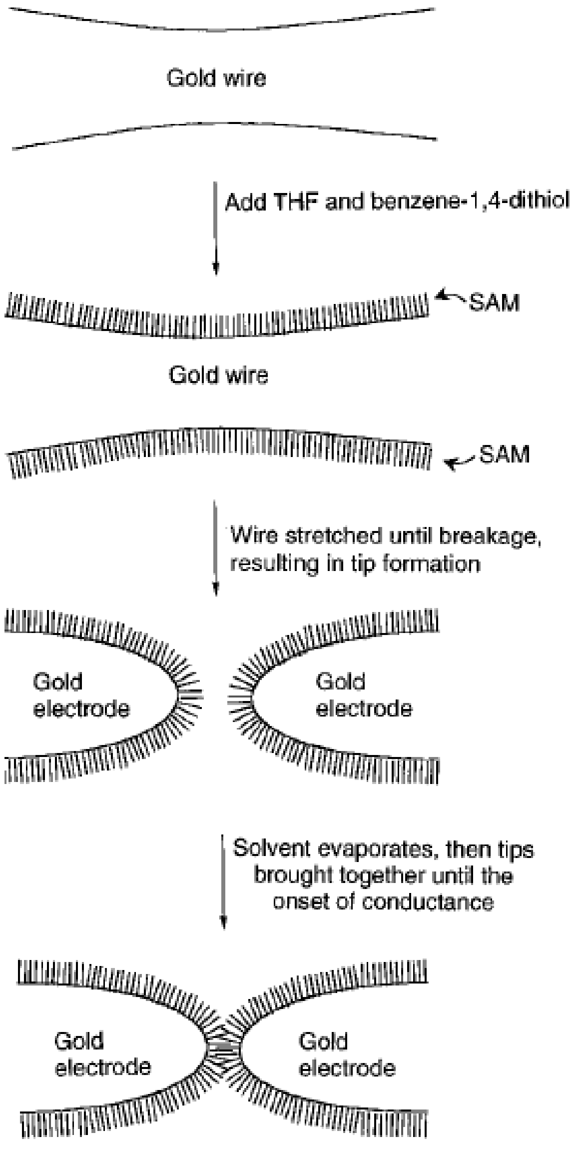
J. van Ruitenbeek et al, Nature 419, p.906 (2002)

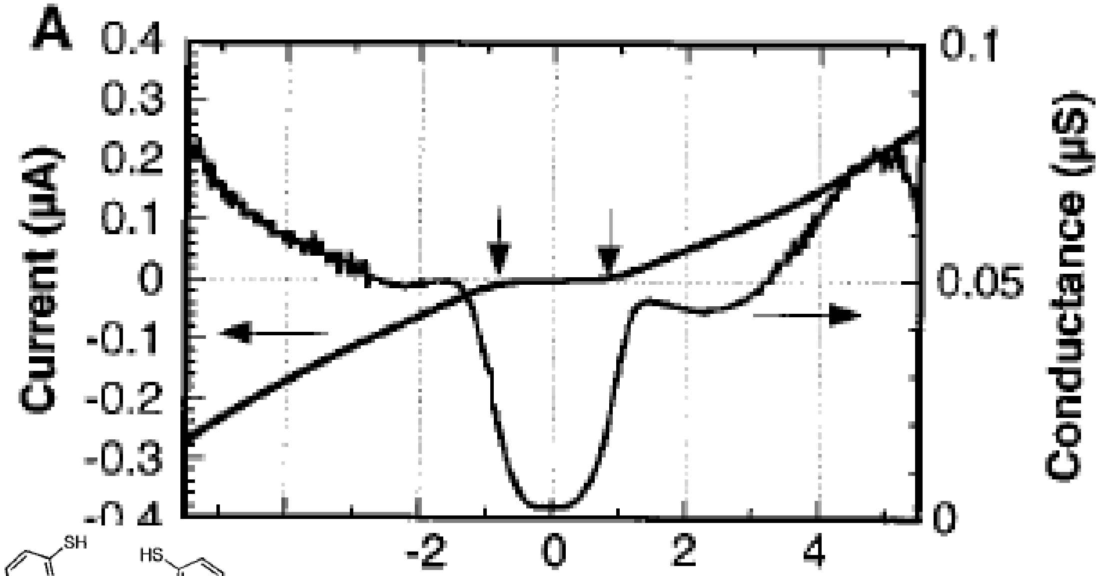
J. van Ruitenbeek et al, cond-mat/0409640

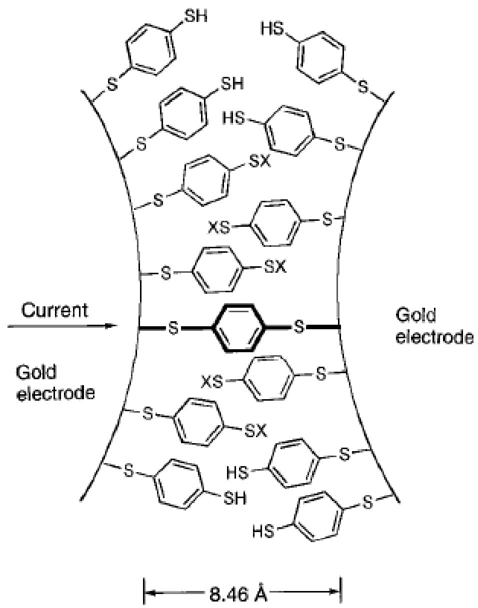
Measuring Thiol-ended molecules

- thiol-gold bond is sufficiently strong and can withstand electrodes pulling apart
- thiol-gold bond withstand relatively strong currents
- atomically sharp wires are formed on the contact upon pulling

Organic thiol-terminated molecules in MCBJ



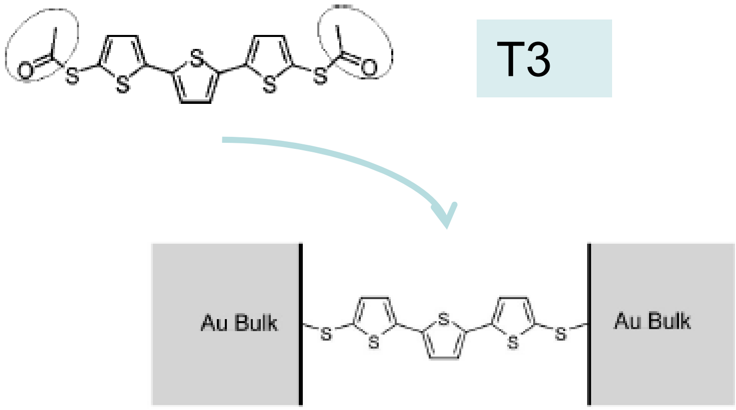


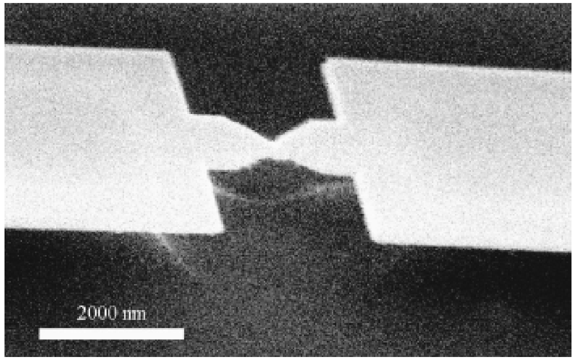


- ”The reproducibility of of the minimum conductance at a consistent value implies that the number of active molecules could be as small as **one**”

M. Reed et al, Science 278, p.252 (1997)

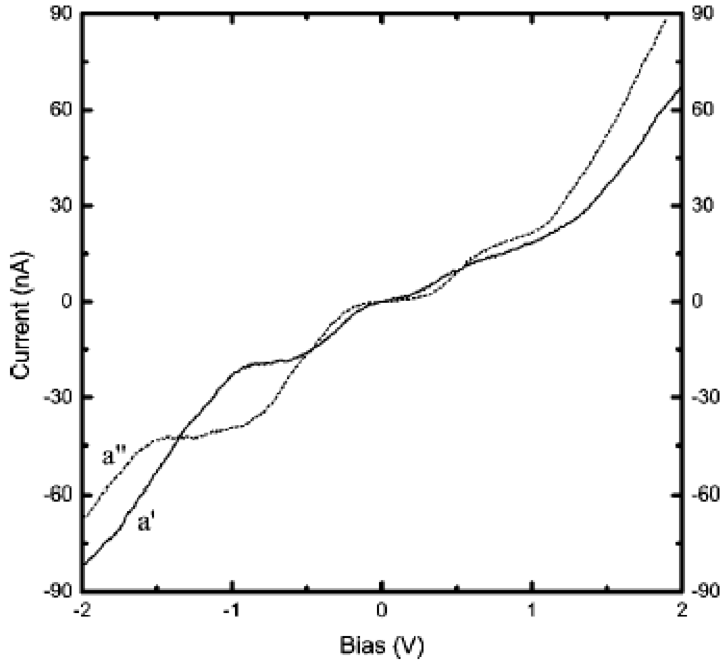
Organic thiol-terminated molecules in MCBJ





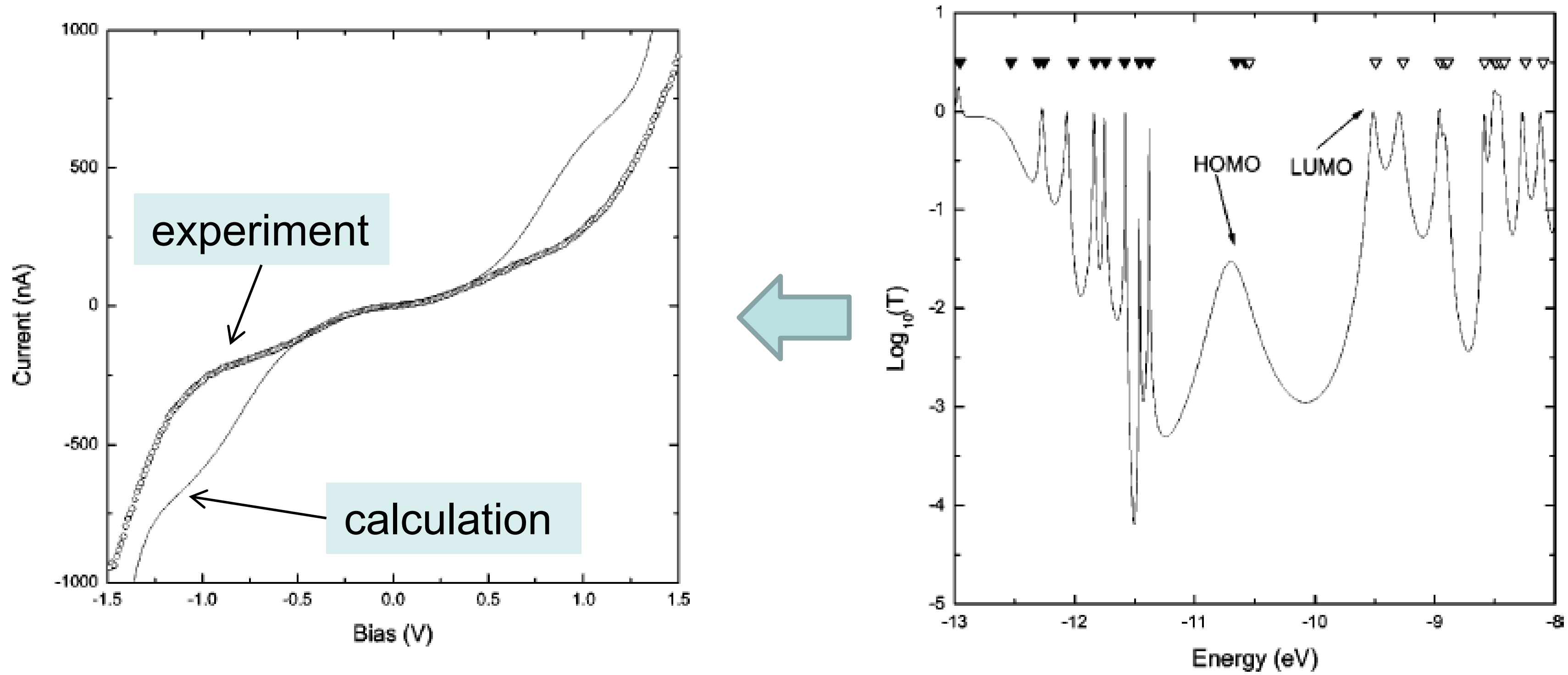
- T3 molecules deposited from a droplet (0.5mM in trichloroethane) on a freshly broken junction

- IV-curves possess step-like features that resemble Coulomb blockade.



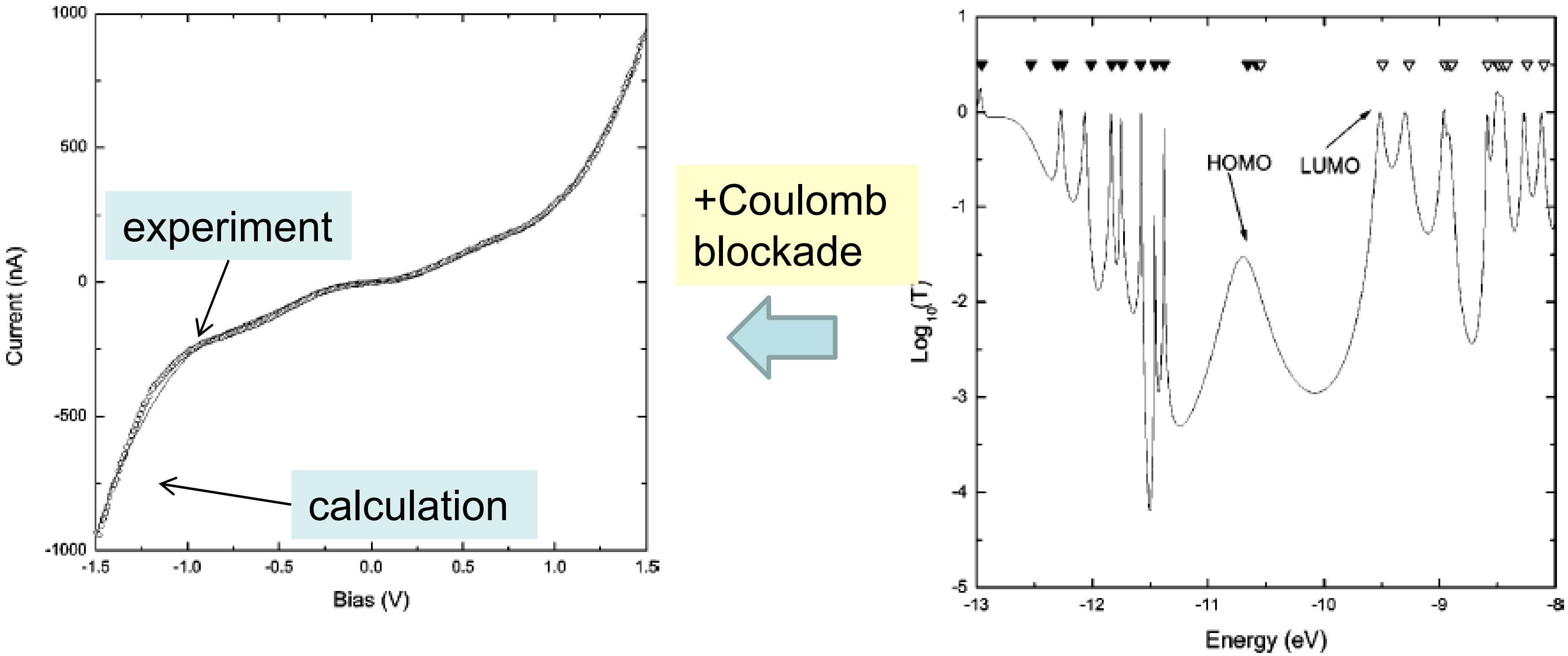
C. Joachim et al., Phys.Rev.B. 59, 1999

Organic thiol-terminated molecules in MCBJ



- **Coherent model**: coupling to electrodes is strong, electron tunneling time is much smaller than intramolecular vibronic relaxation time (electron has no time to localize on the molecule)
  - tunneling first goes through HOMO and HOMO-1
  - the only fitting parameter E_F-E_{HOMO}=0.4 eeV

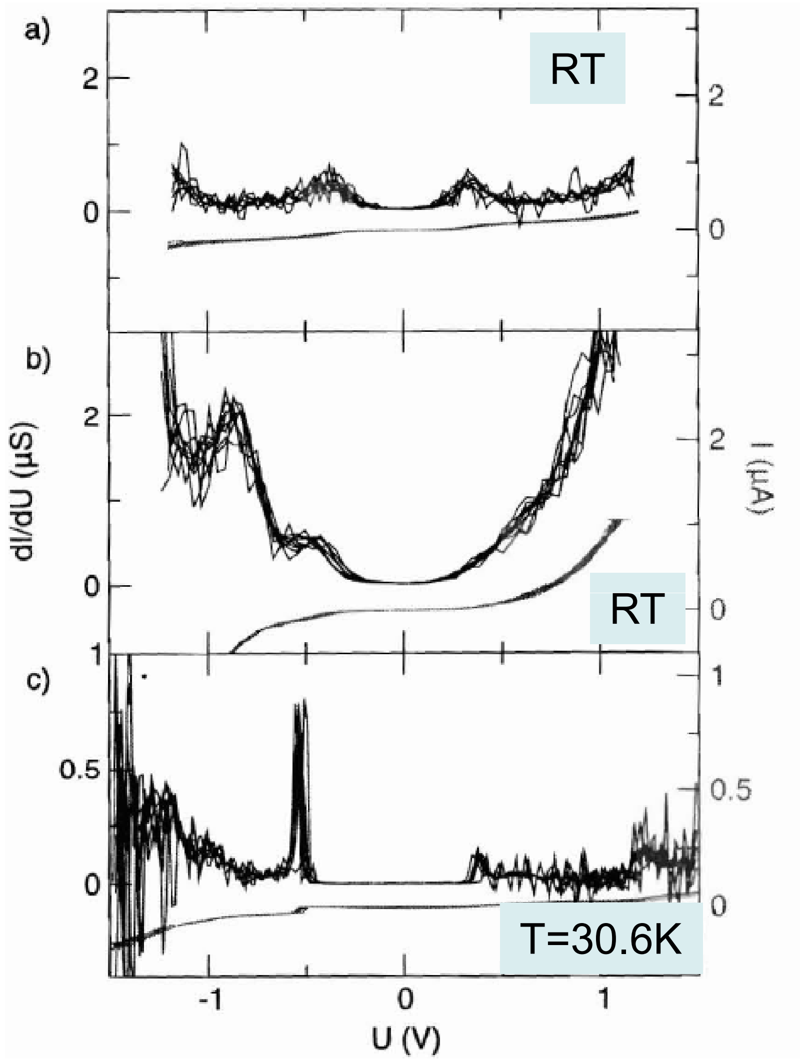
Organic thiol-terminated molecules in MCBJ

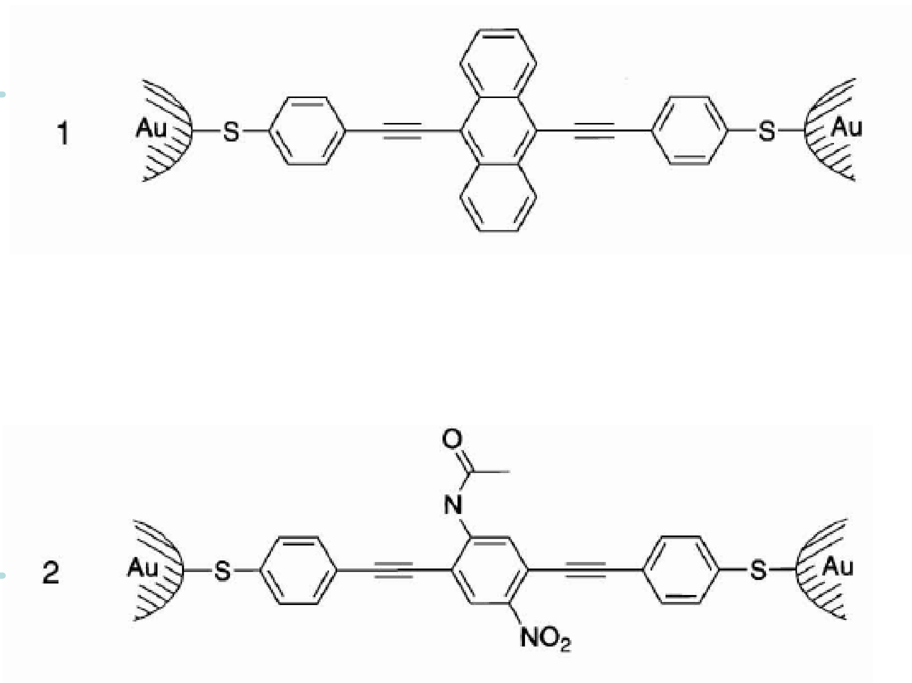


- **Sequential tunneling model**: the molecule is treated as a quantum dot with energy levels, the molecule is sequentially charged and discharged via tunneling.
  - the parameters E_F-E_{HOMO}=0.0 eV, Ec=0.19 eV

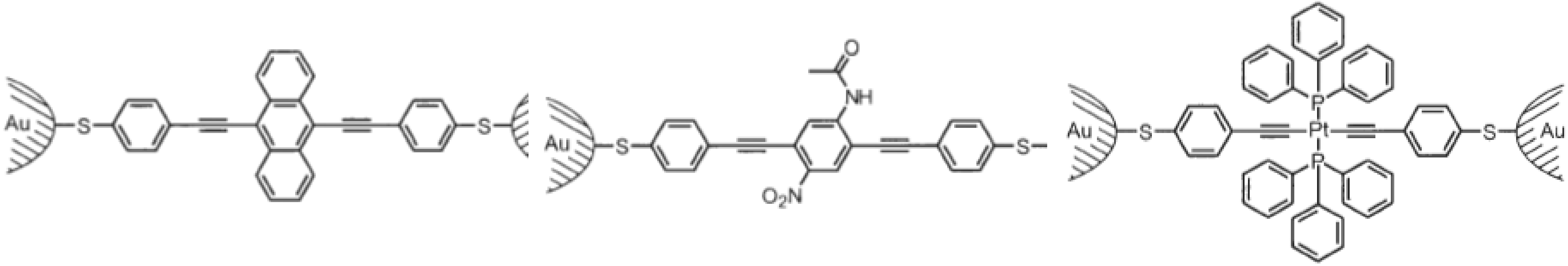
Organic thiol-terminated molecules in MCBJ

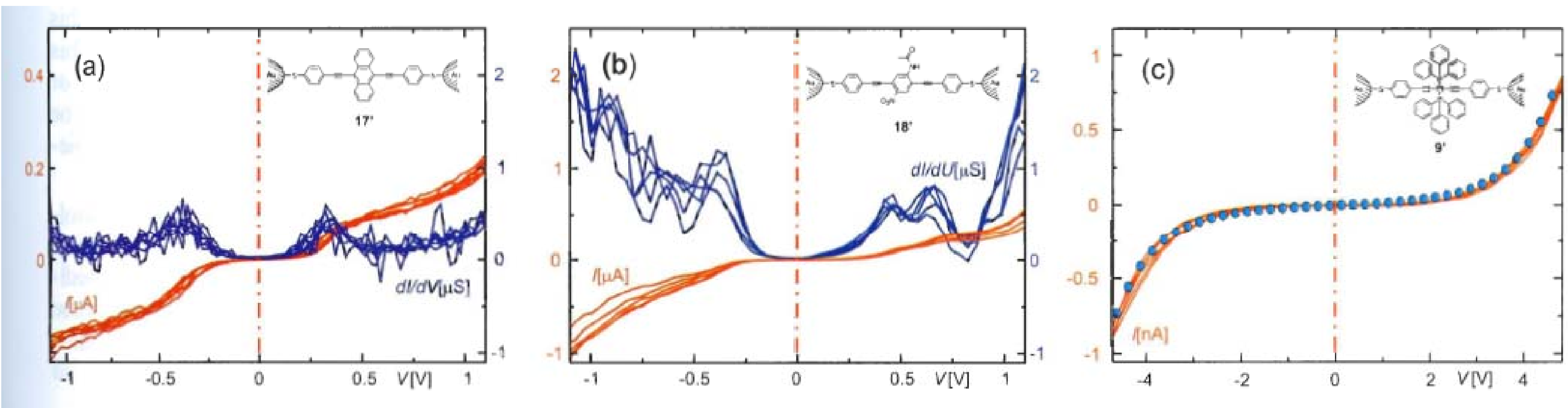
- The role of molecular symmetry





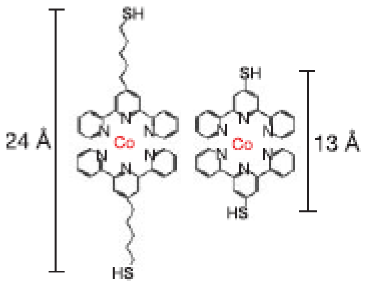
Mechanically controlled break junction

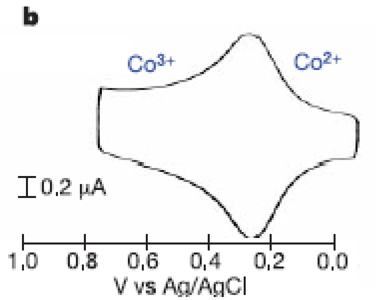




Electromigration break junctions

- electromigration technique: small current applied to a notched e-beam fabricated wire, electromigration causes thinning of the notched part.





various gate voltages