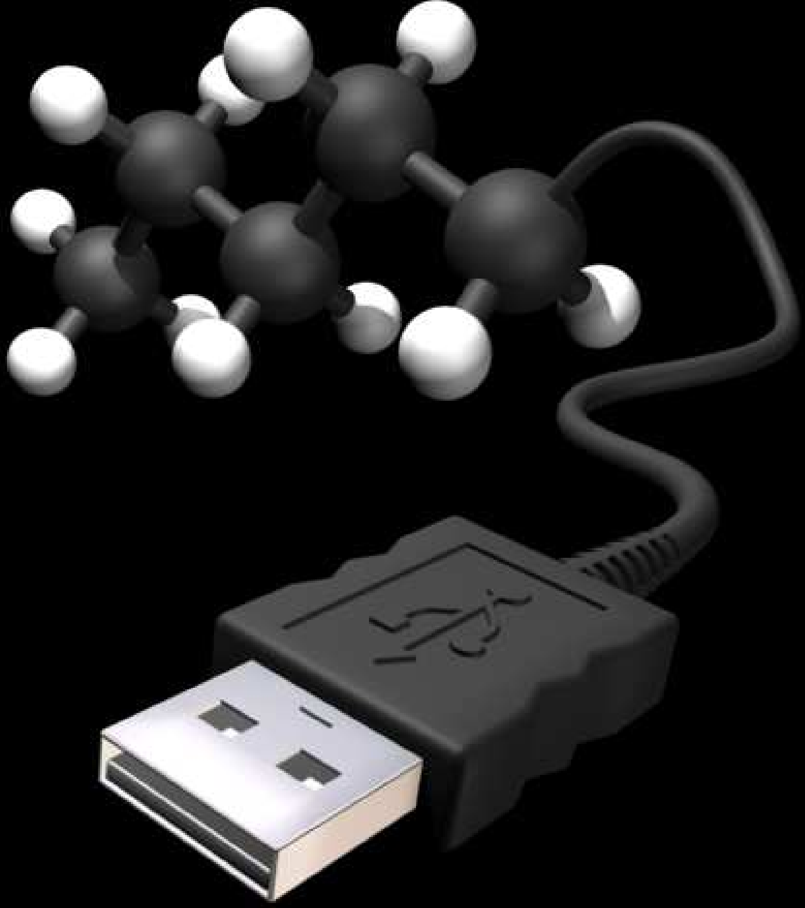
Quantum transport in single-molecule systems



Jan van Ruitenbeek, Leiden University

College de France, 17 May 2011

Outline

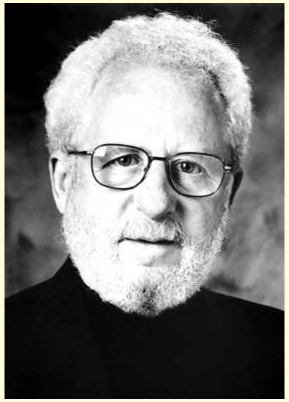
- Introduction
- Basic concepts
- Key experimental techniques
  single-molecules
- Beyond conductance measurements
  - thermopower
  - Raman scattering
  - Inelastic signals in conductance
  - shot noise
- Special topics
  Cross-over from PCS to IETS
- Future directions, open problems

Ref: Molecular electronics: an introduction to theory and experiment,
Juan-Carlos Cuevas and Elke Scheer,
World Scientific, 2010

Plastic electronics

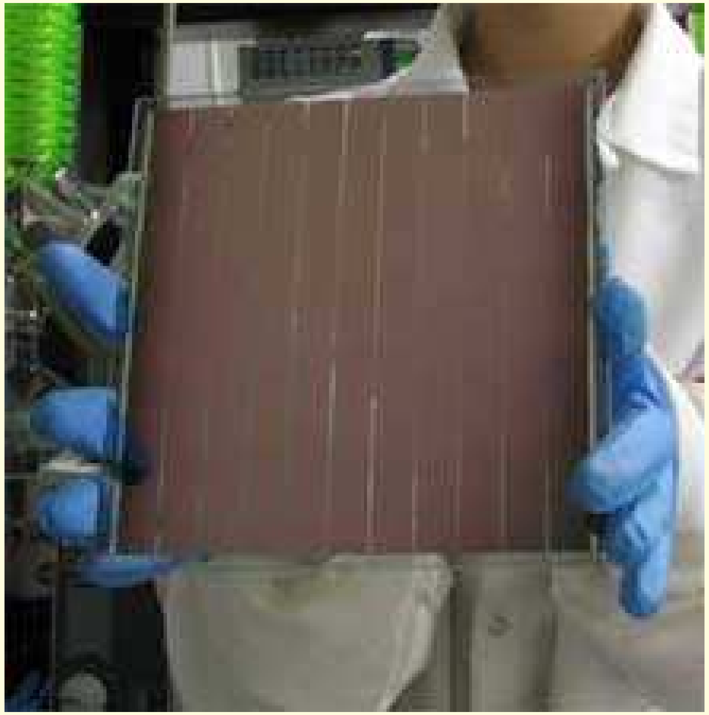
- Plastic: usually insulators
- 1977, Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa: conductive polymers iodine-doped polyacetylene. Nobel Prize in Chemistry in 2000.

- Technology for plastic electronics on thin and flexible plastic substrates was developed at Cambridge University's Cavendish Laboratory in the 1990s.



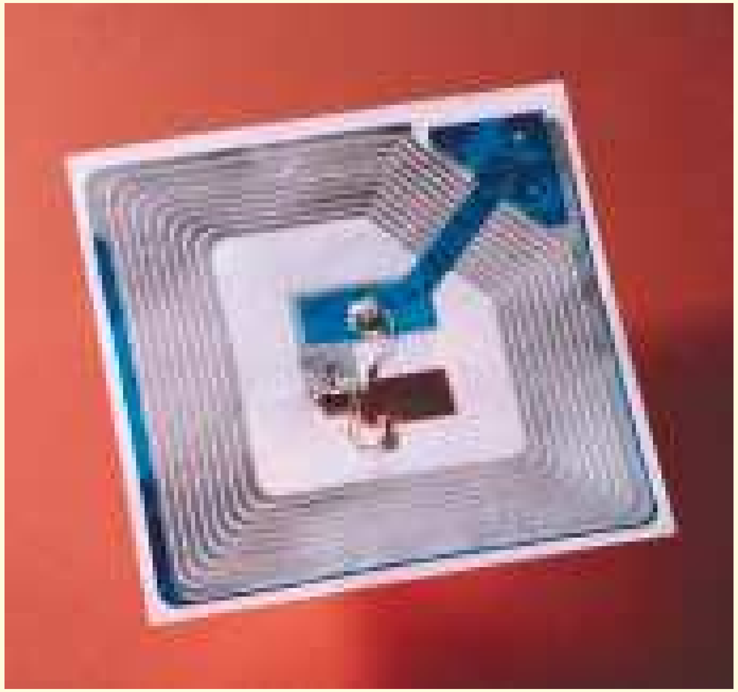

Organic solar cells

Mass production at Konarka company, Lowell, MA, USA

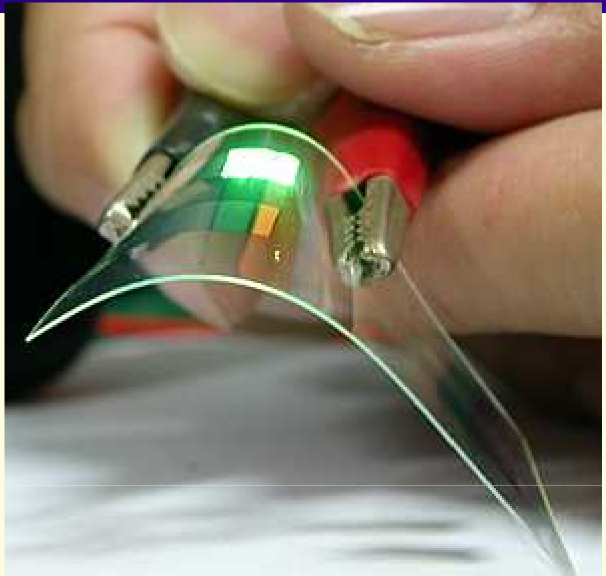


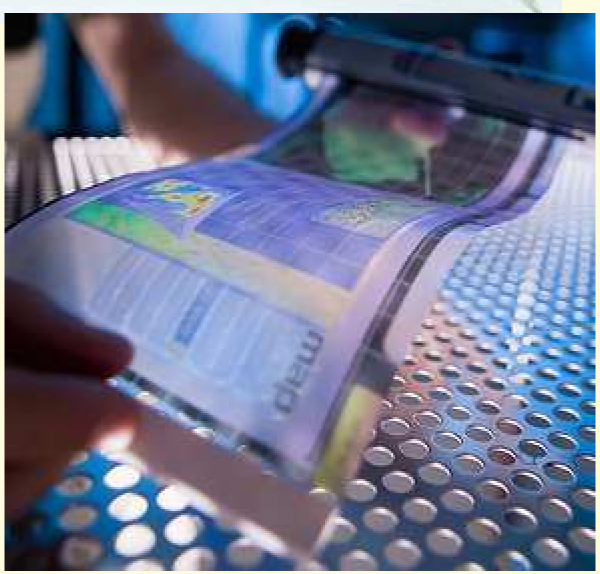
Solarmer Energy, El Monte, Ca, USA

Polymer electronics



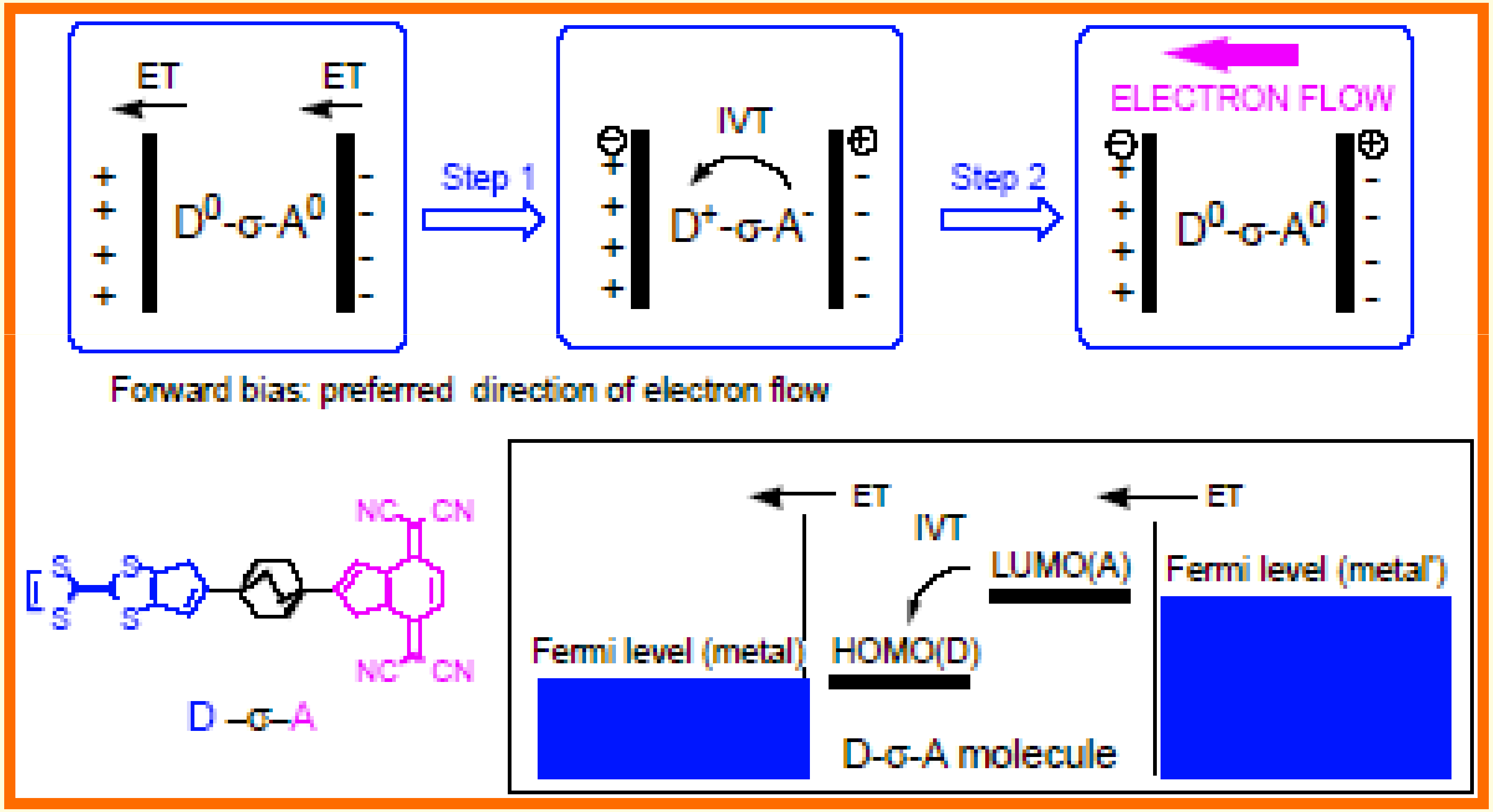
OLED





Engineering molecular properties

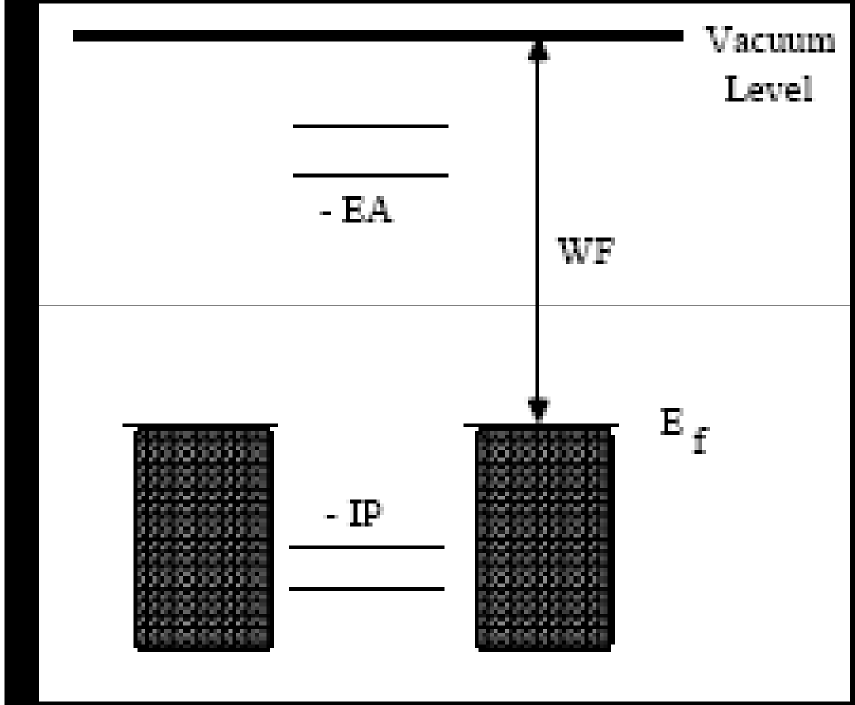
a unimolecular zwitterionic rectifier



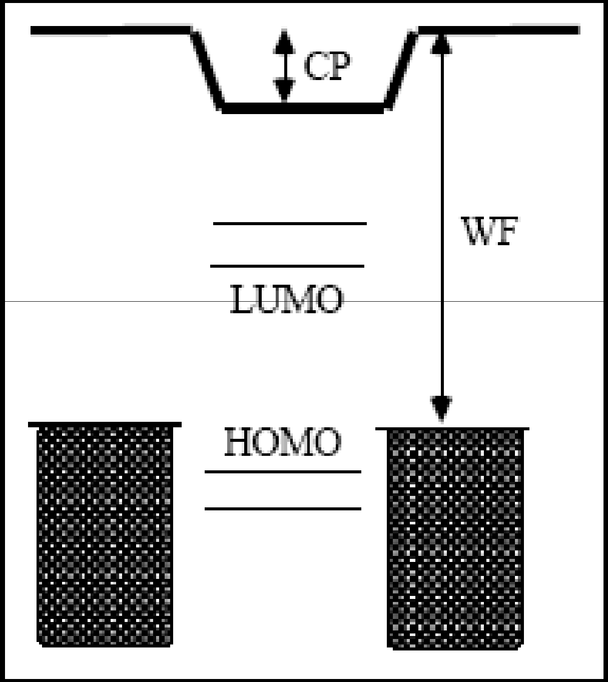
A. Aviram & M. A. Ratner, *Chem. Phys. Lett Lett*. **29,** 277 (1974)

Basic concepts

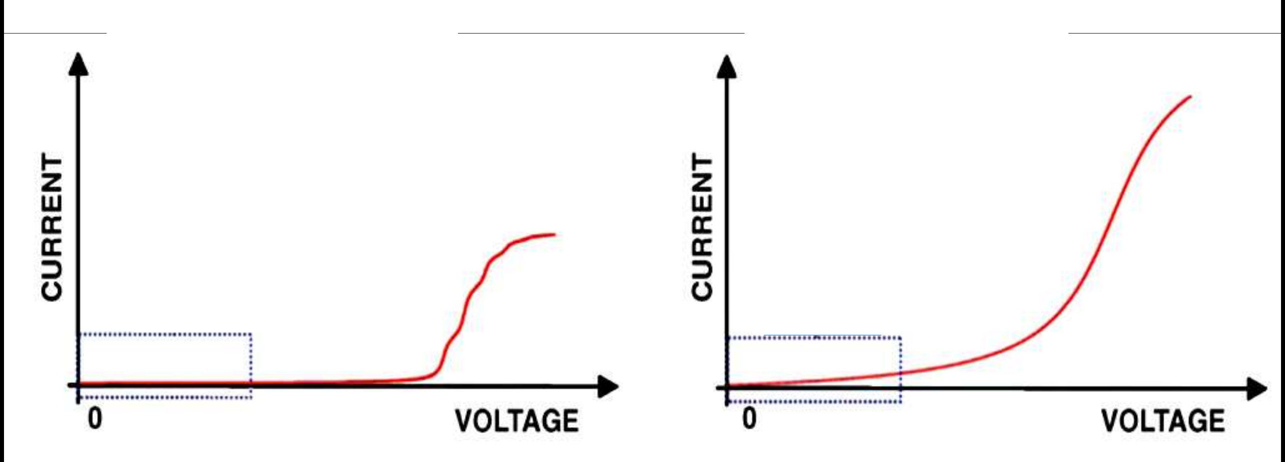
Standard picture of molecular transport

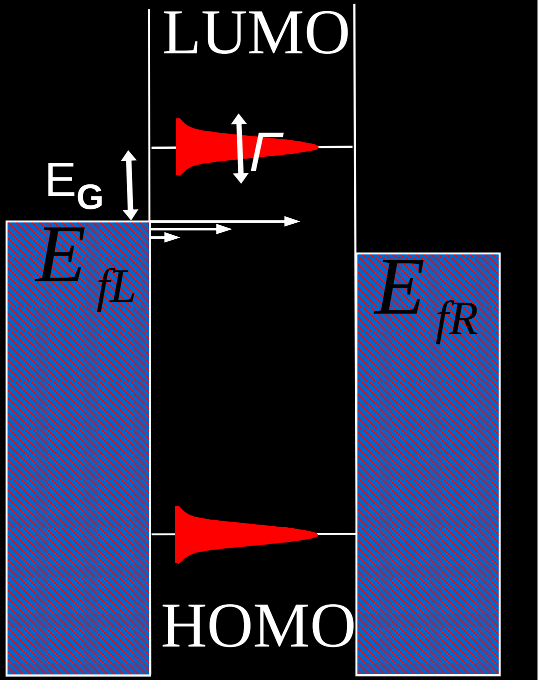


Coupling →



Different transport regimes



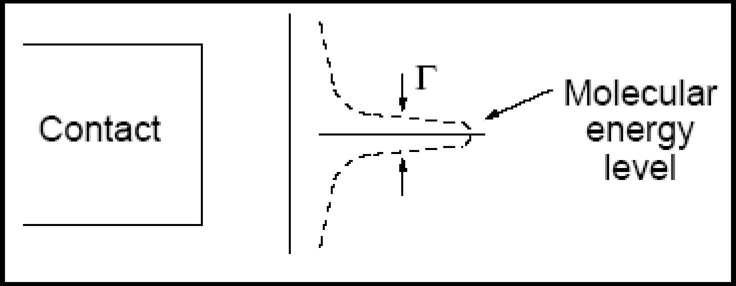


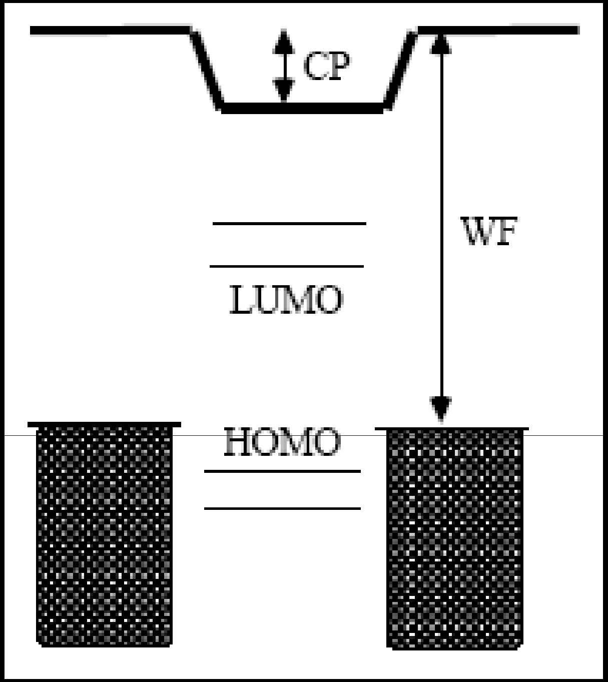
Low-coupling $\Gamma\longrightarrow$ High-coupling

Off-resonance ($E_G \geq \Gamma$)

A. Troisi and M. A. Ratner, Small, **2**, 172 (2006)

Resonant transport





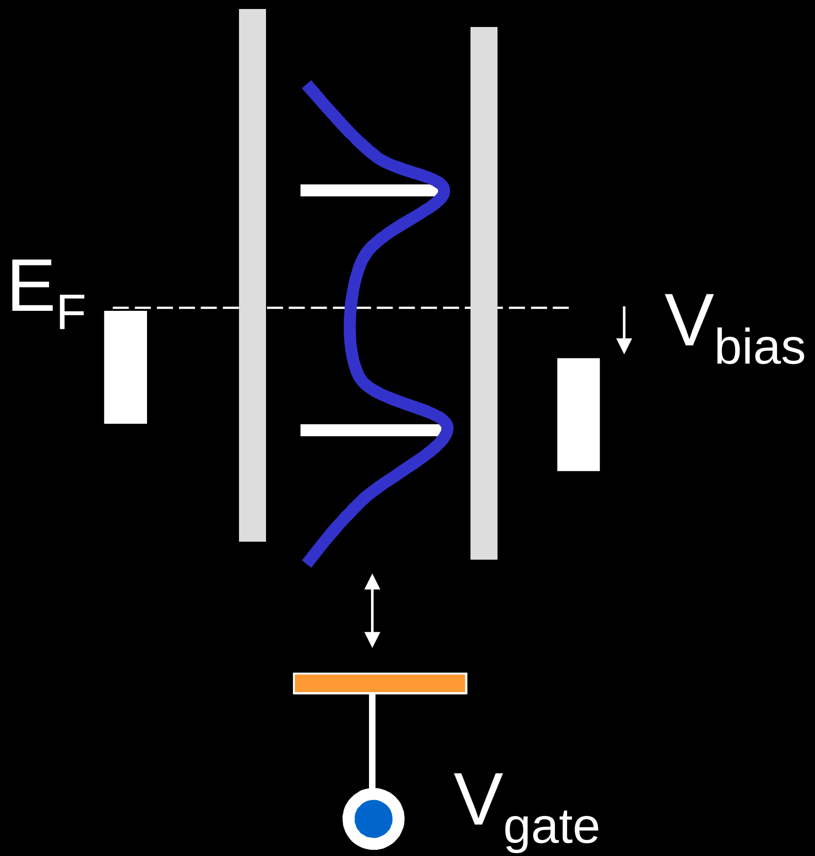
$$T = \frac{\Gamma_L \Gamma_R}{\left(E_F - E_0\right)^2 + \left(\Gamma_L + \Gamma_R\right)^2 / 4}$$

$$\Gamma_L \approx \Gamma_R \text{ and } \left(E_F - E_0\right) << \Gamma: \quad T \to 1$$

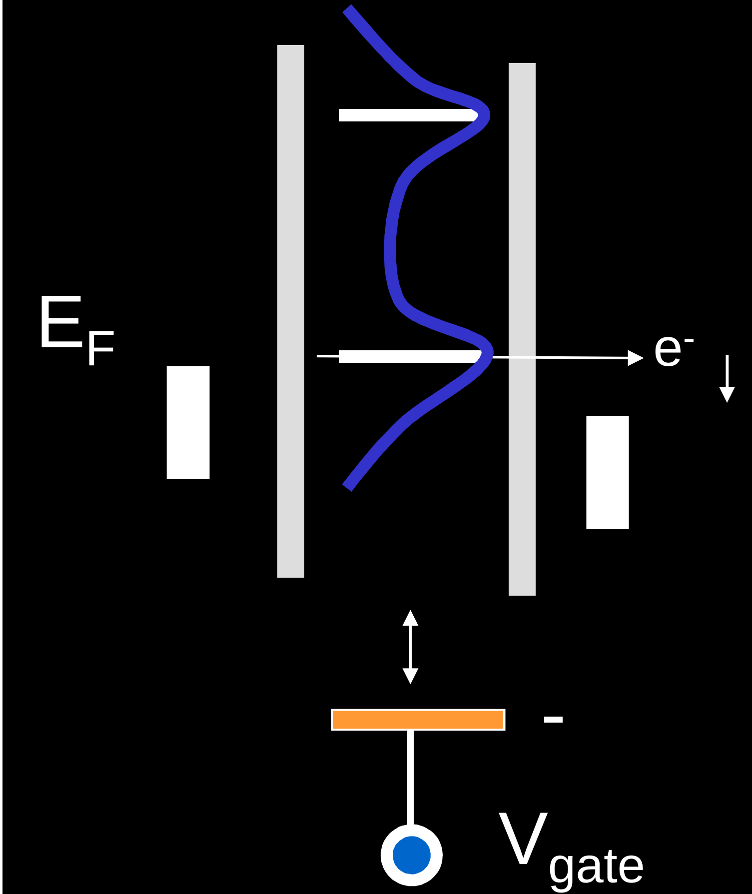
More typically $\left(E_F - E_0\right) >> \Gamma: \quad T << 1$

Gate control

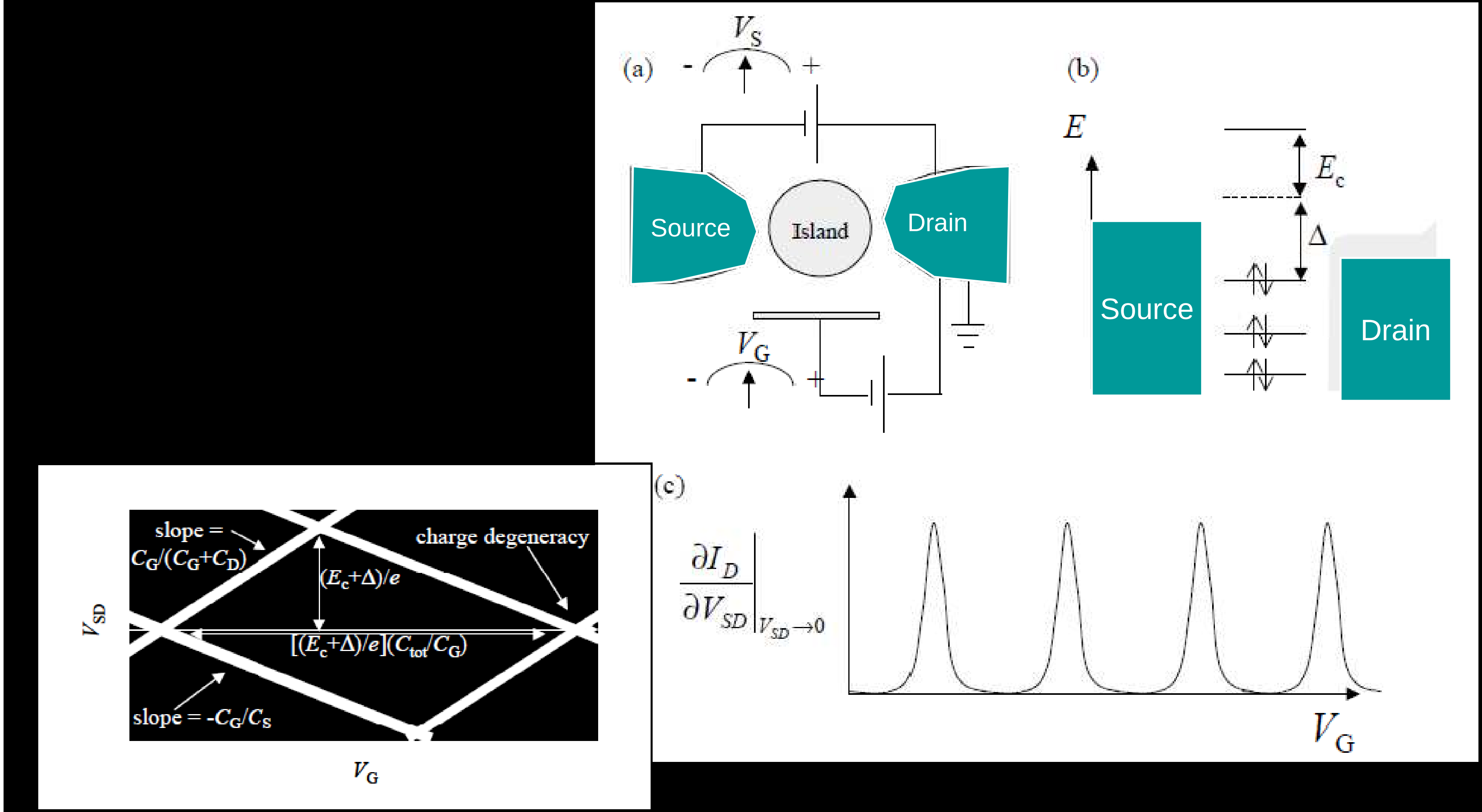
Low current



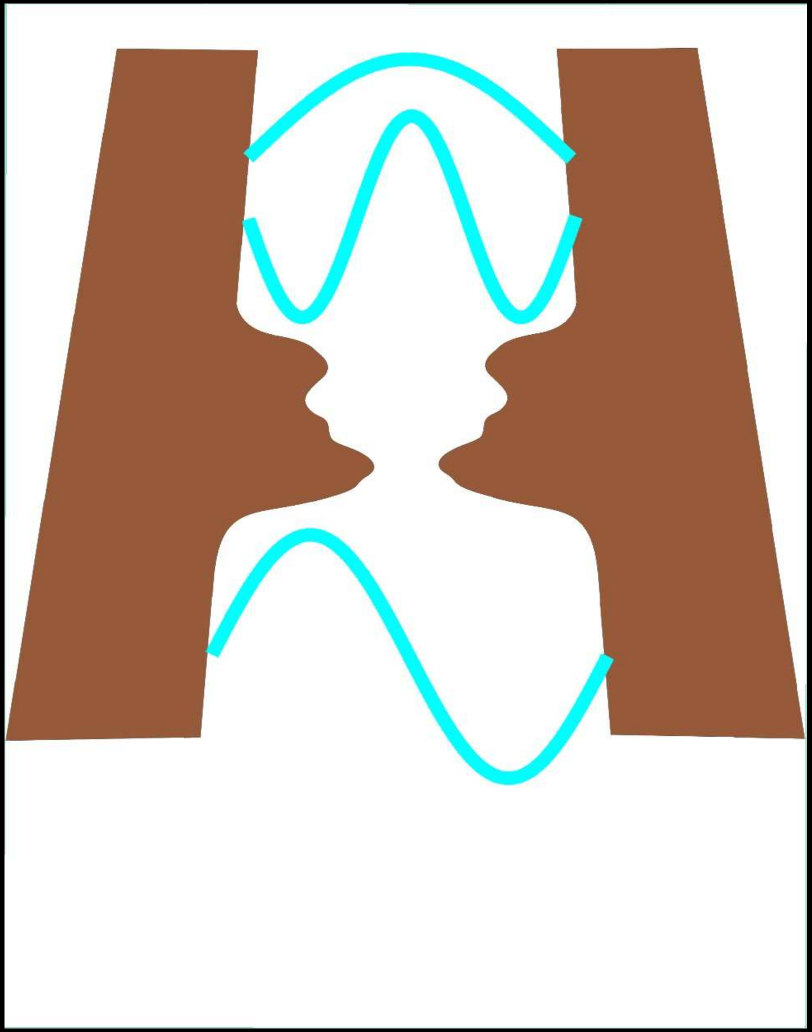
Higher current



Limit of weak coupling:Coulomb blockade



Limit of strong coupling: conductance eigenchannels



Incoming waves $\boxed{\vec{i}_l}$

Outgoing waves $\boxed{\vec{o}_r}$

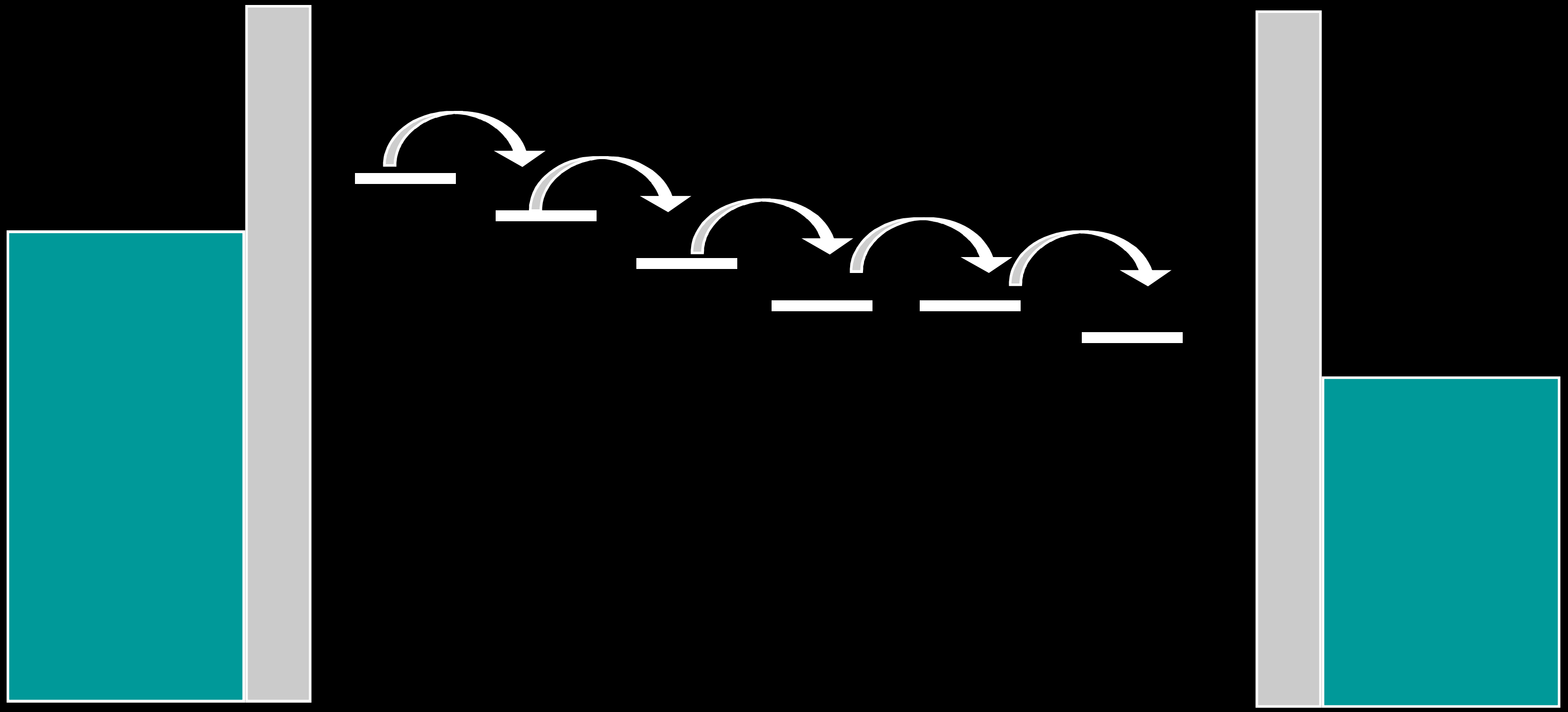
Matrix of transmission ampl.

$$\boxed{\vec{o}_r = \hat{t}\,\vec{i}_l}$$

Landauer:

$$\boxed{G = \frac{2e^2}{h}\mathrm{Tr}(\hat{t}^\dagger \hat{t}) = \frac{2e^2}{h}\sum_n T_n}$$

Limit of very long molecules: hopping



Break-up of coherence due to

Electron-vibration interactions (polarons)

or

Disorder (intra-molecular tunnelbarriers)

plus electron-electron interactions

Distinguishing feature of molecular junctions

In what are molecules different from quantum dots?

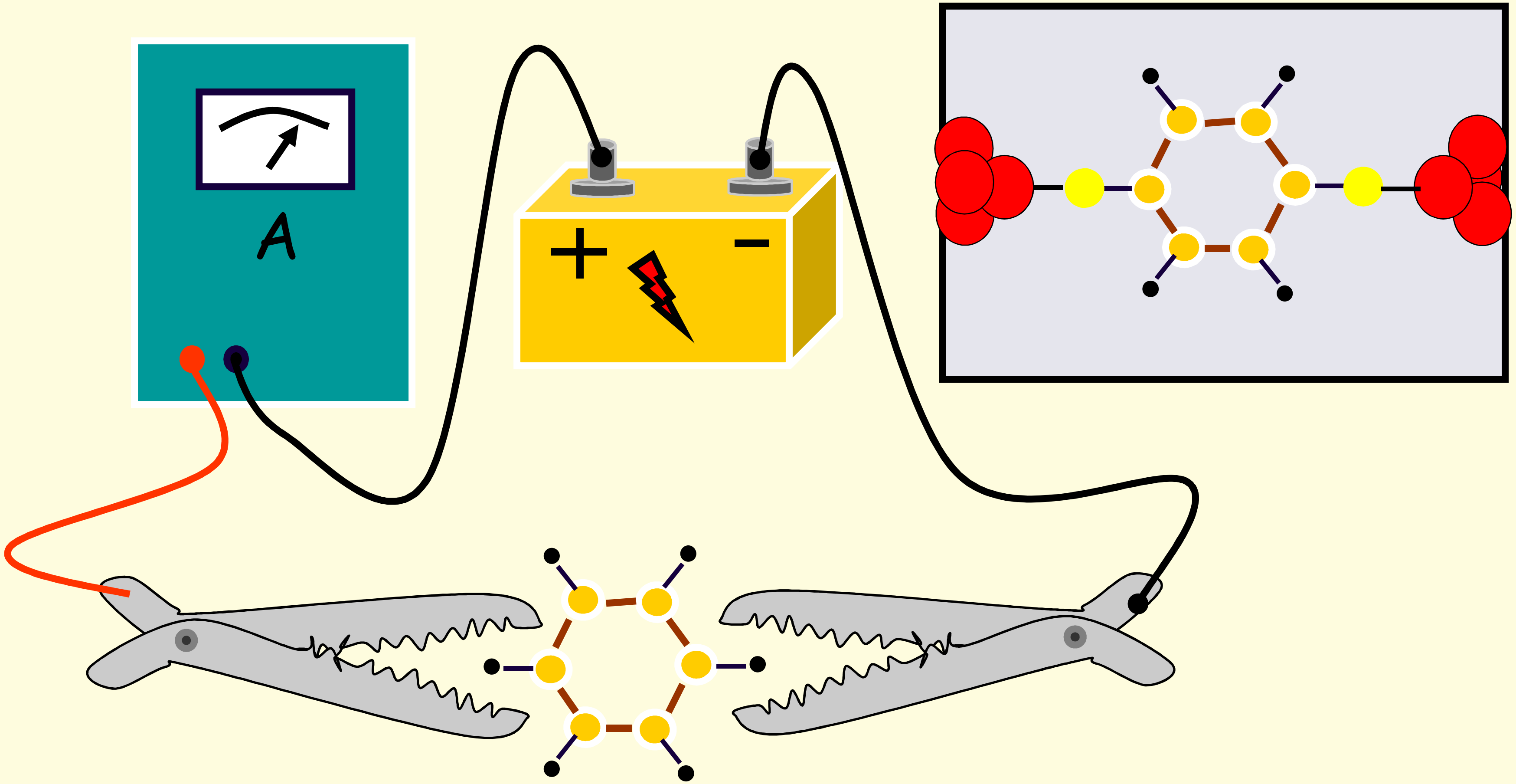
Ionic degrees of freedom

- Electron-ion interaction
  - signatures in differential conductance
  - heating
  - polaron formation
- Bias-induced conformational changes

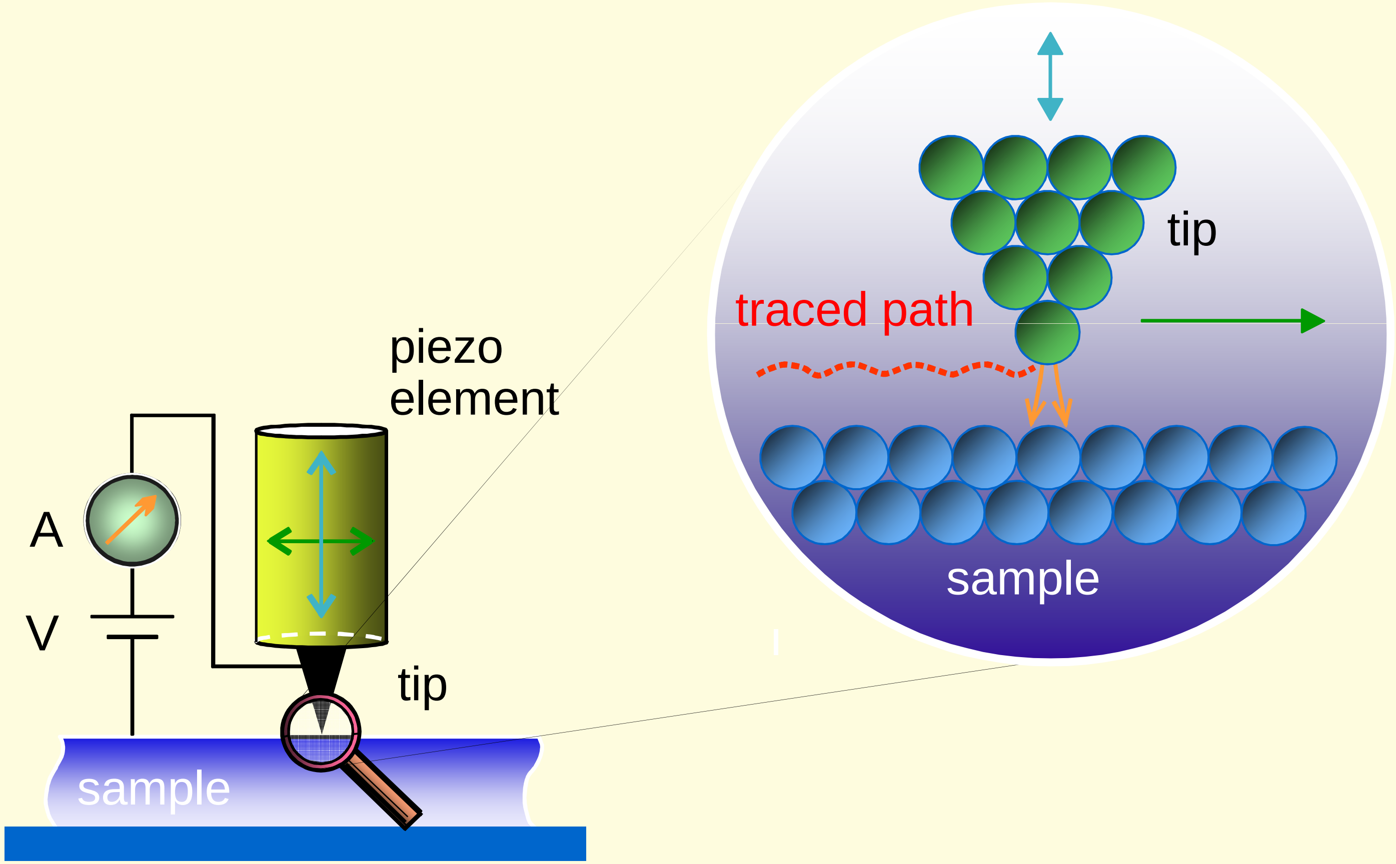
Key experimental techniques

Single-molecules

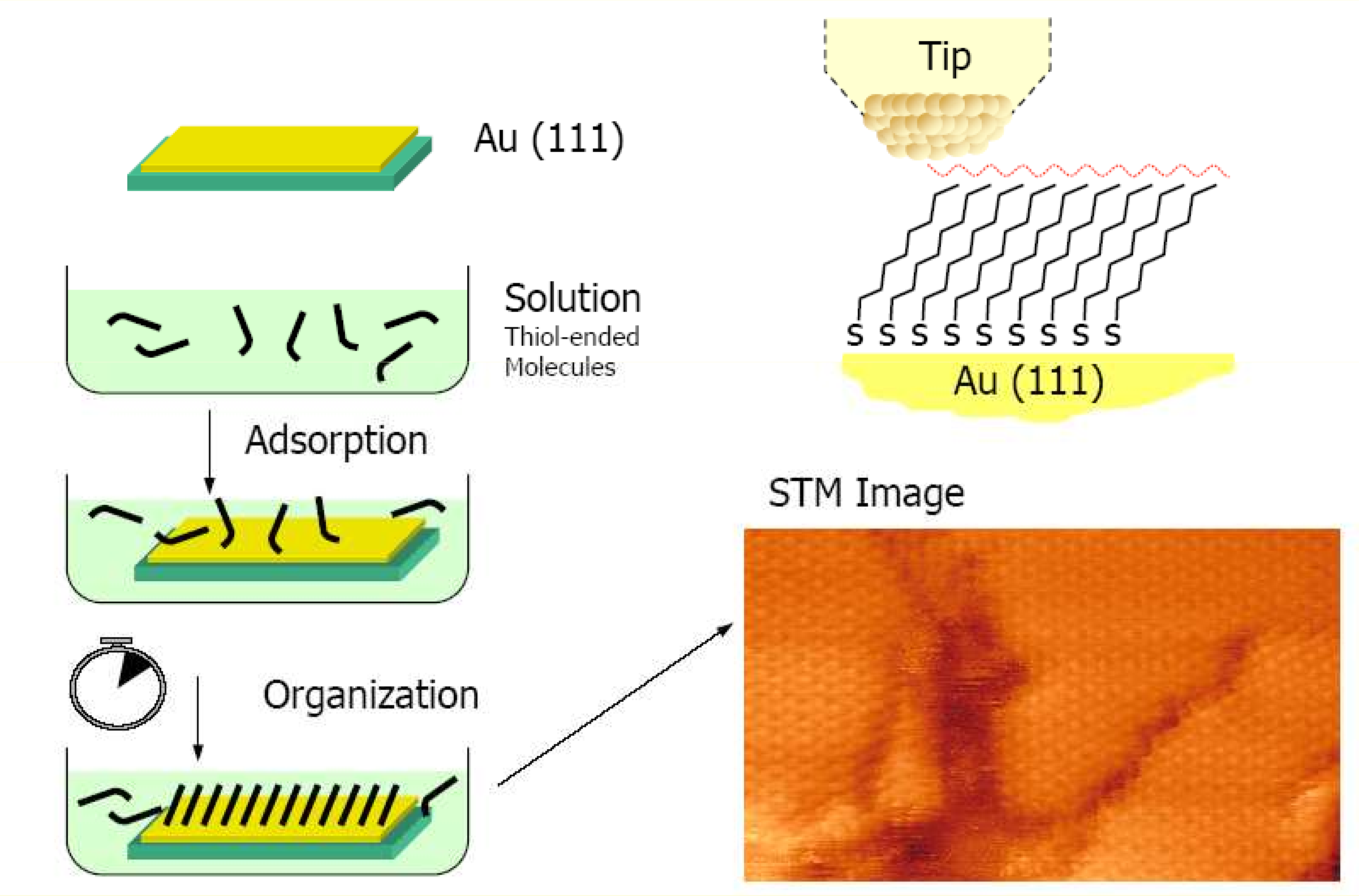
The principle of the measurements



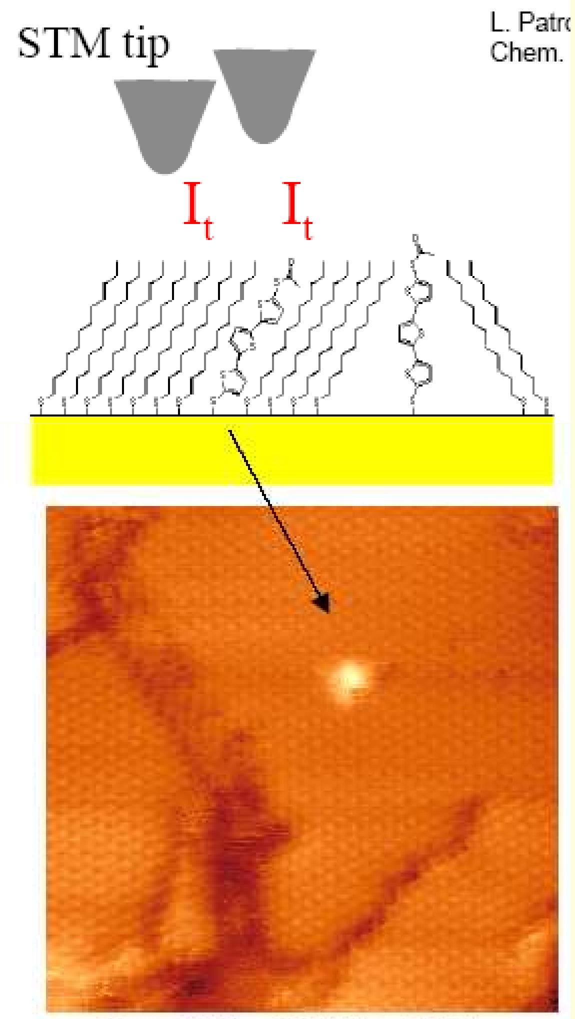
Techniques for adjusting the gap: STM



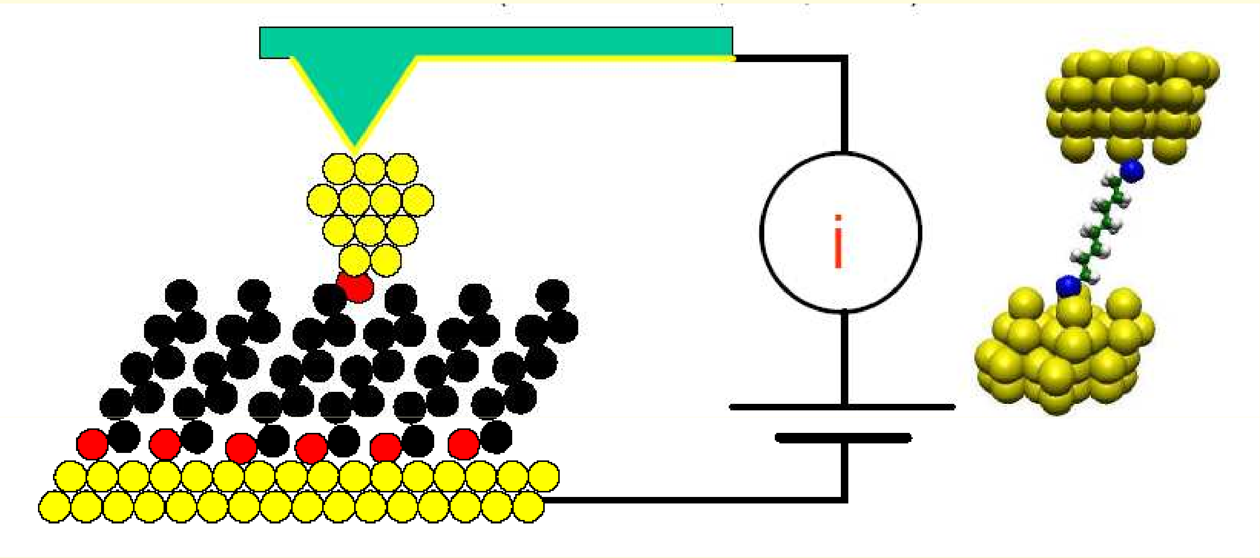
Deposition of molecules: self-assembly



Techniques for adjusting the gap: STM



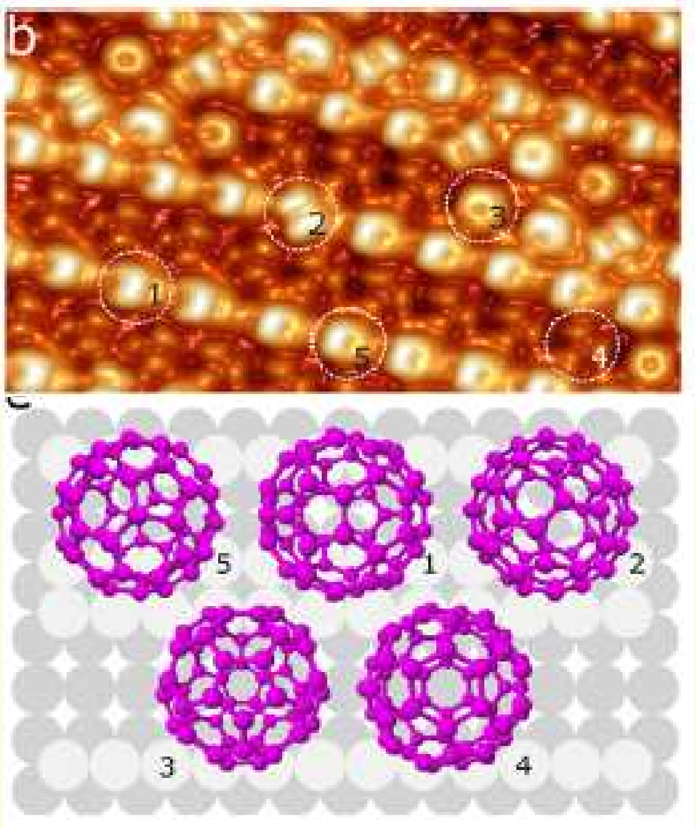
28 nm T3,Vt = +0.78V, It = 10.7pA

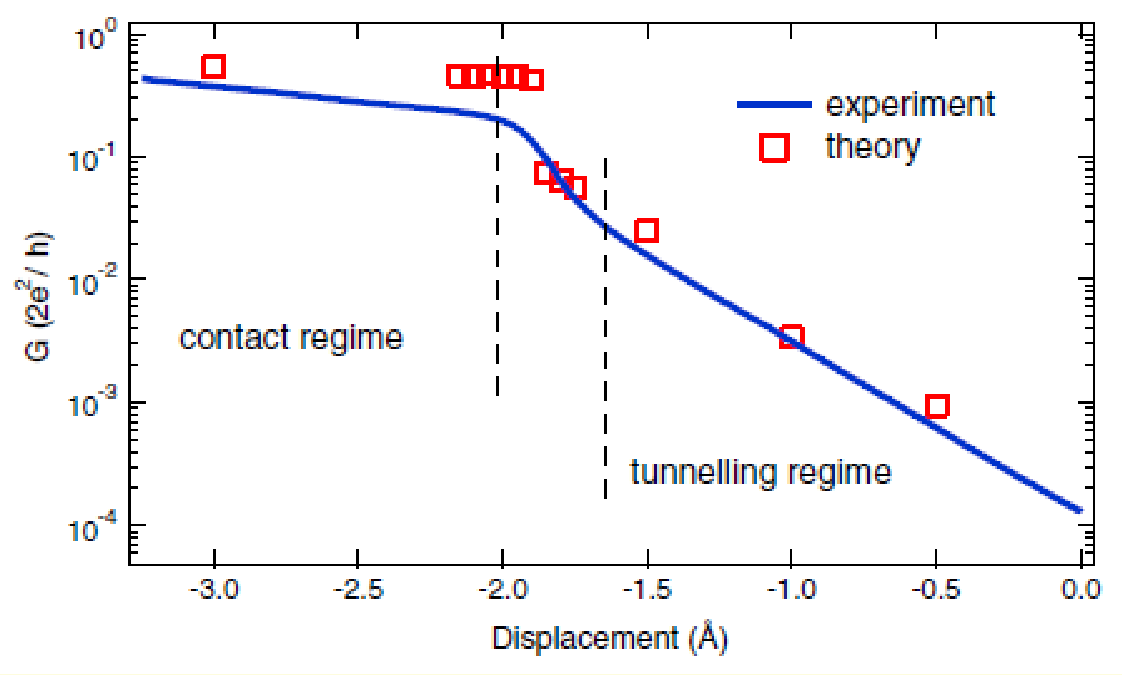


STM on self-assembled monolayers

Stuart Lindsay and his group, Arizona State University, USA
Paul Weiss and his group, Penn State, USA

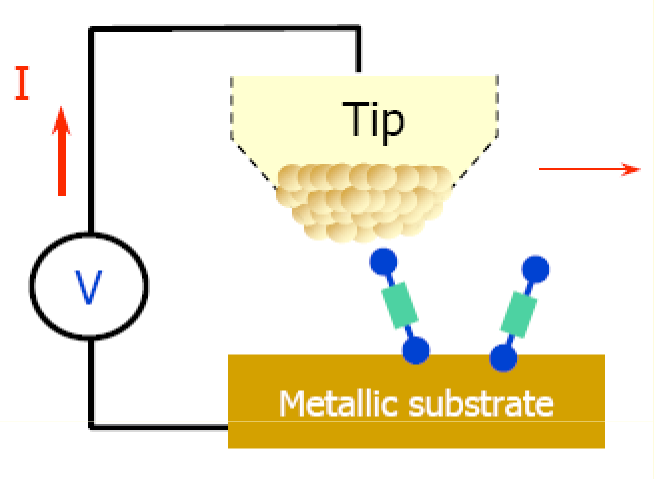
UHV-LT-STM: C_{60}





Néel, Kröger, Limot, Frederiksen, Brandbyge, Berndt, PRL **98** (2007) 065502

Techniques for adjusting the gap: STM



Advantages

Imaging + electrical measurements
Tip manipulation
Versatile and fast (at room temp.)

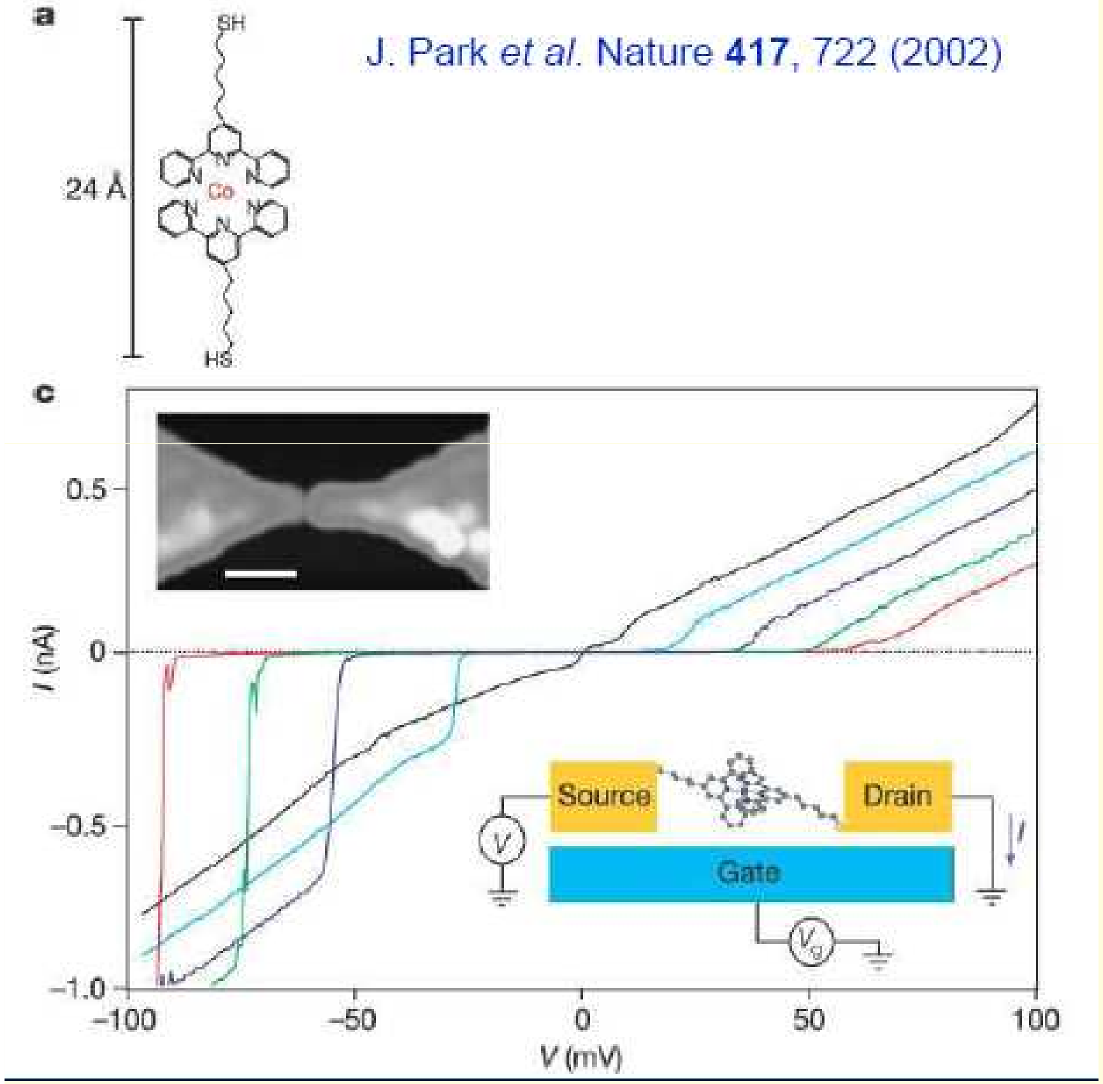
Drawbacks

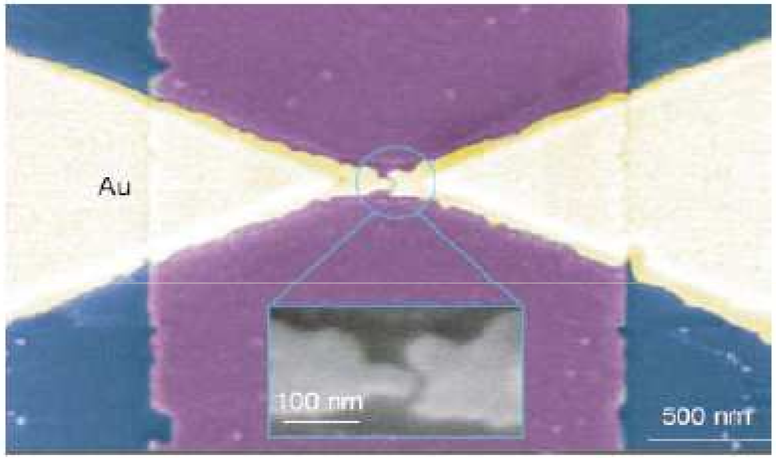
Surface preparation requirements
Combination LT + UHV complicated
Top-contact poorly defined

C. Joachim et al Phys. Rev. Lett. **74** (1995)2102
S. Datta et al Phys. Rev. Lett. **79**(1997) 2530
L. A. Bumm et al Science **271** (1996) 1705
A. Dhirani et al J. Chem. Phys. **106** (1997) 5249
V. Langlais et al, Phys. Rev. Lett. 83 (1999) 2809
L. Patrone et al Chem Phys. **281** (2002) 325

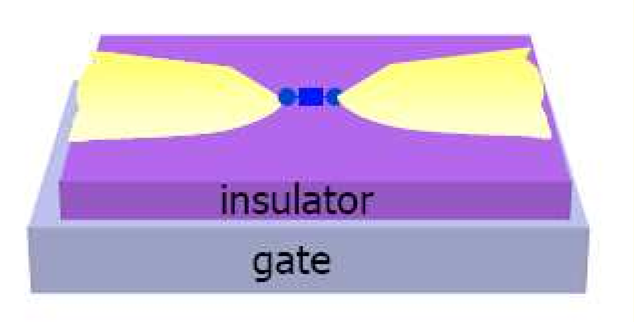
Break junction by electromigration

J. Park *et al.* Nature **417**, 722 (2002)





Techniques for adjusting the gap: electromigration break junction



Advantages

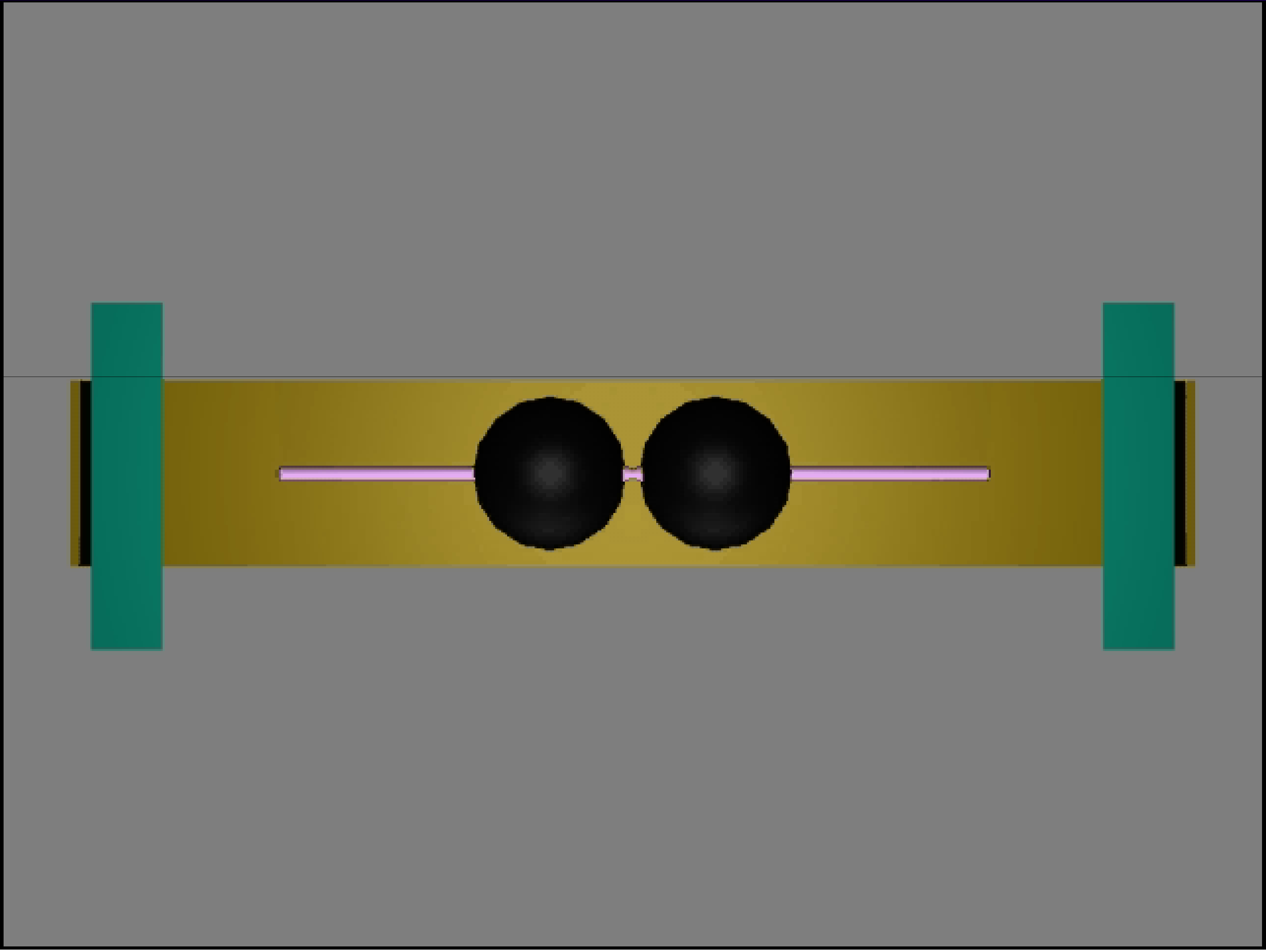
- stable for extended periods
- Can be cycled in temperature and field
- Gate electrode coupling

Drawbacks

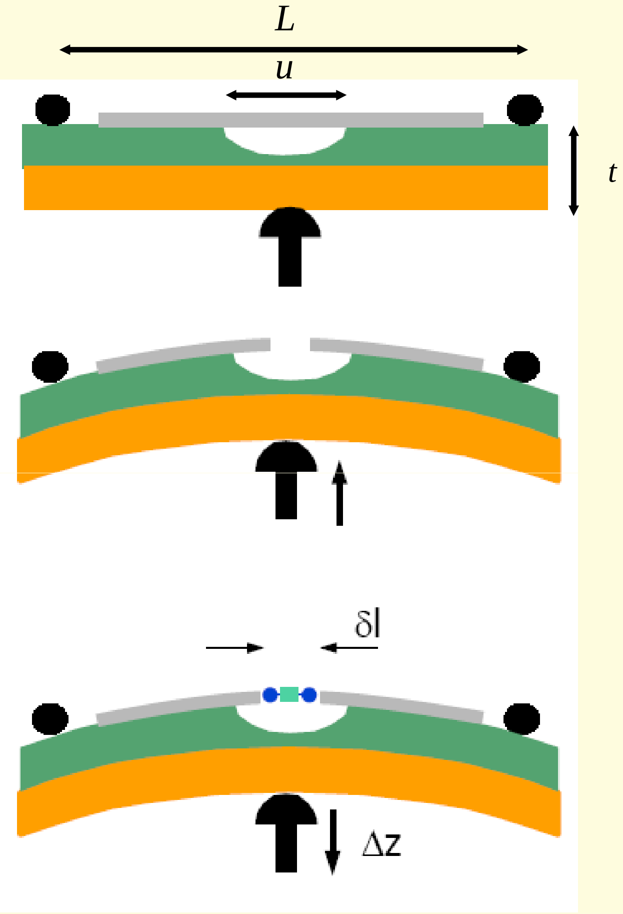
- Every junction is different
- Limited statistics
- no geometric information
- danger of formation of nanoparticles

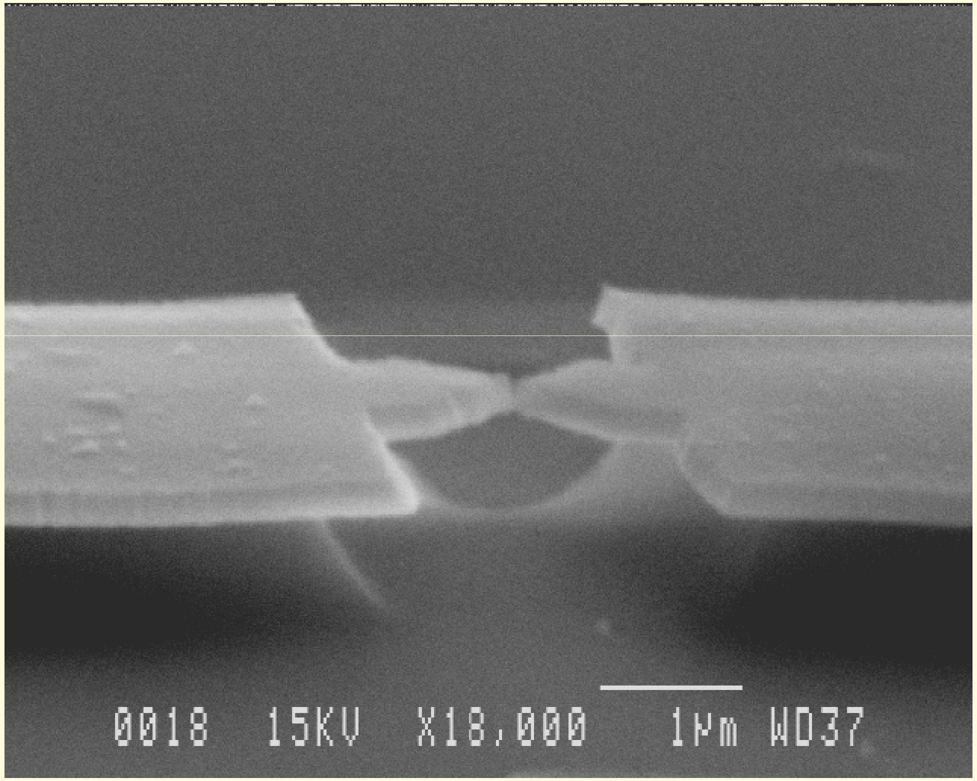
H. Park et al, APL 1999
M. Lambert et al., Nanotechnology 2003
Park et al , Nature 407 (2000) 57-60
Liang et al Nature 2002
Park et al Nature 2002
Osorio et al Adv. Mater. 2007

Mechanically Controllable Break Junction



Lithographically fabricated MCBJ

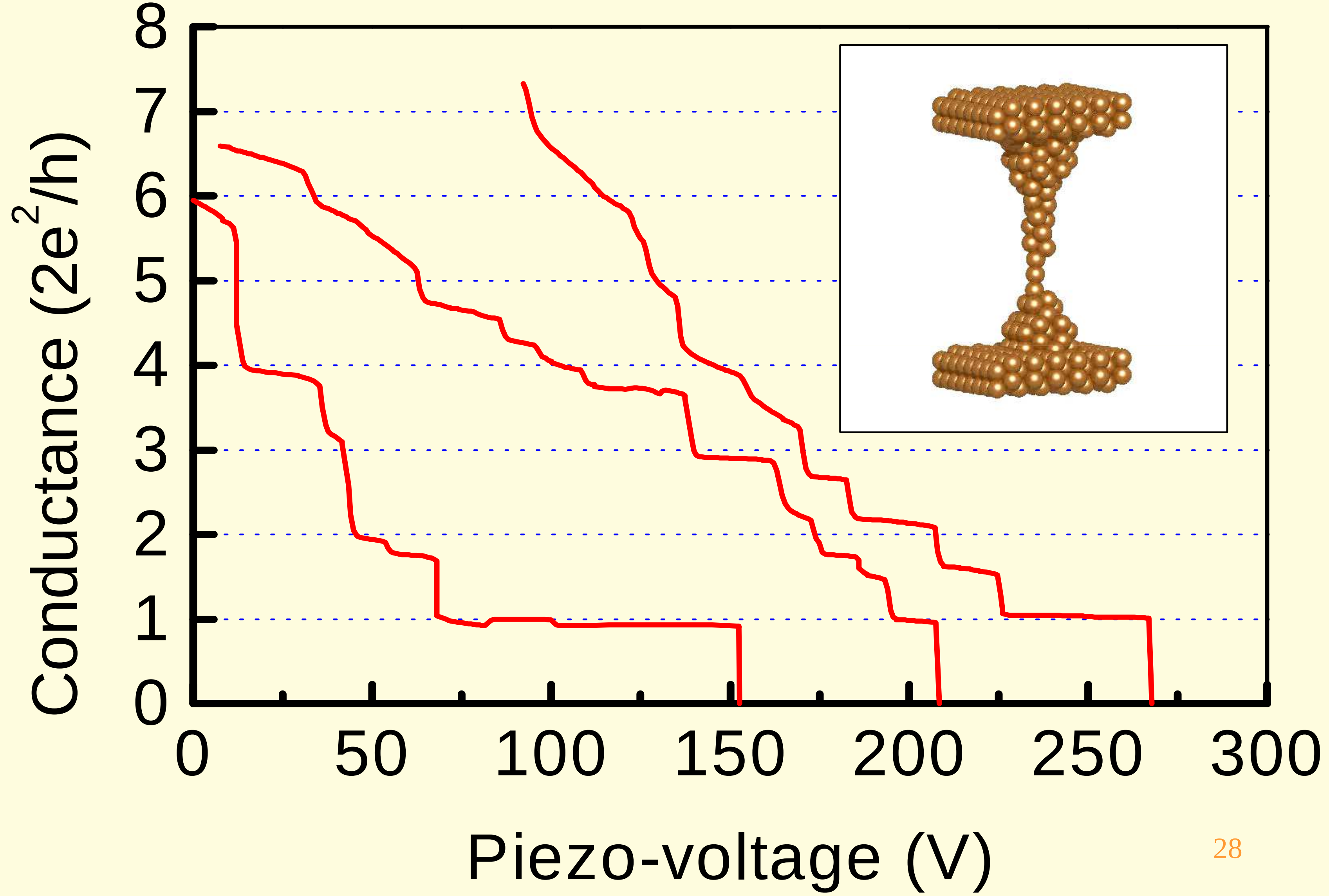




$$\frac{\delta I}{\Delta z} = \frac{6ut}{L^2}$$

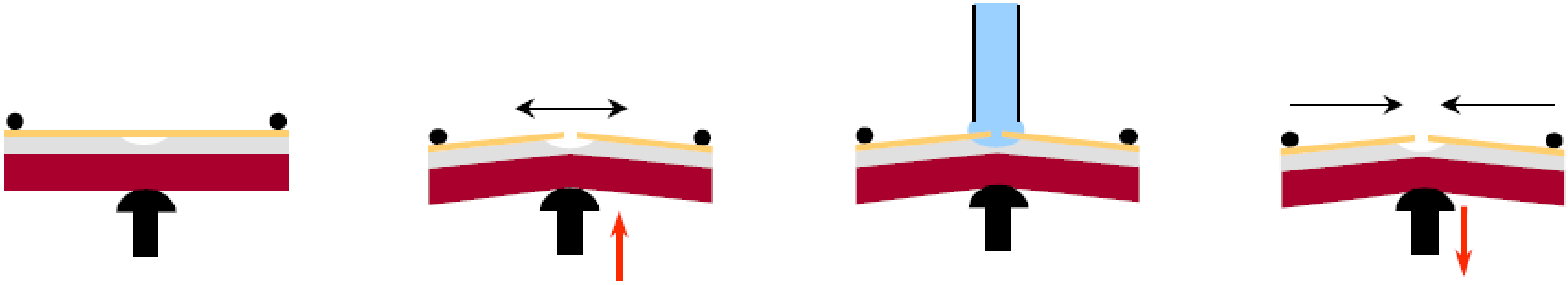
van Ruitenbeek, Alvarez, Piñeyro, Grahmann, Joyez, Devoret, Esteve and Urbina. Rev. Sci. Instrum. **67** (1995) 108

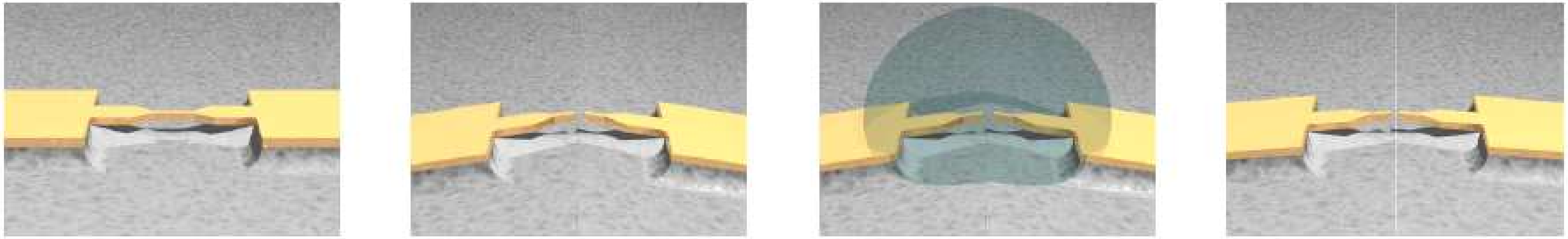
Conductance for Au contacts at 4.2 K

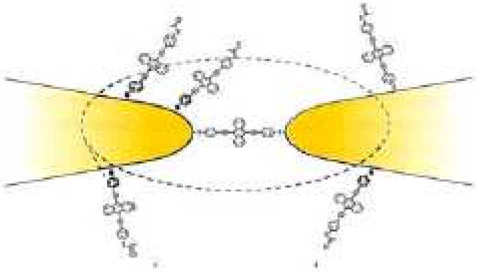


Deposition of molecules

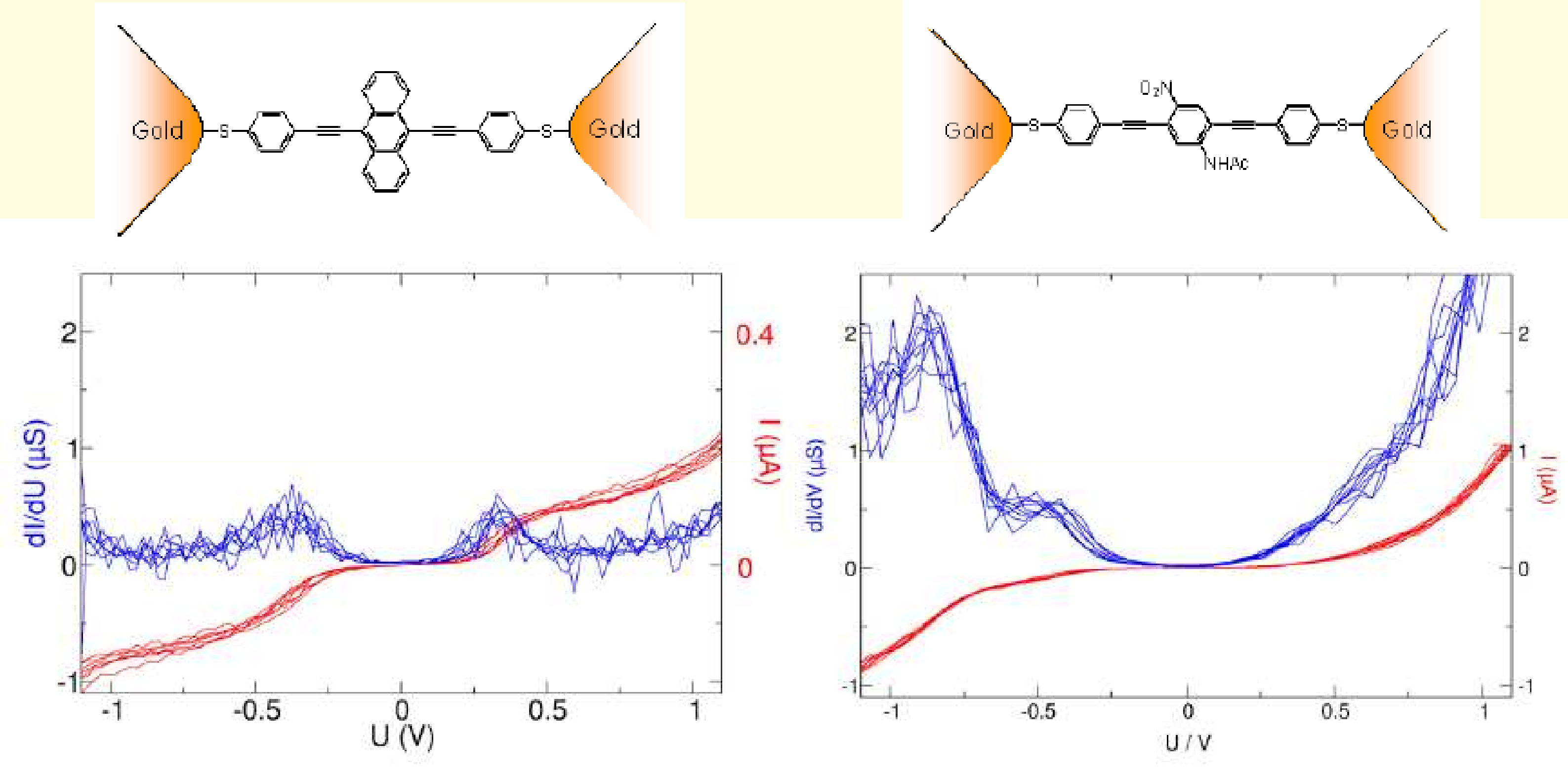
Experimental procedure

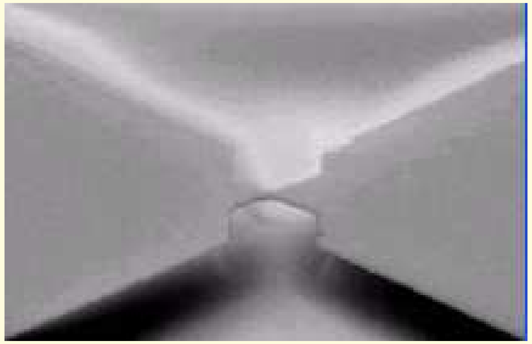






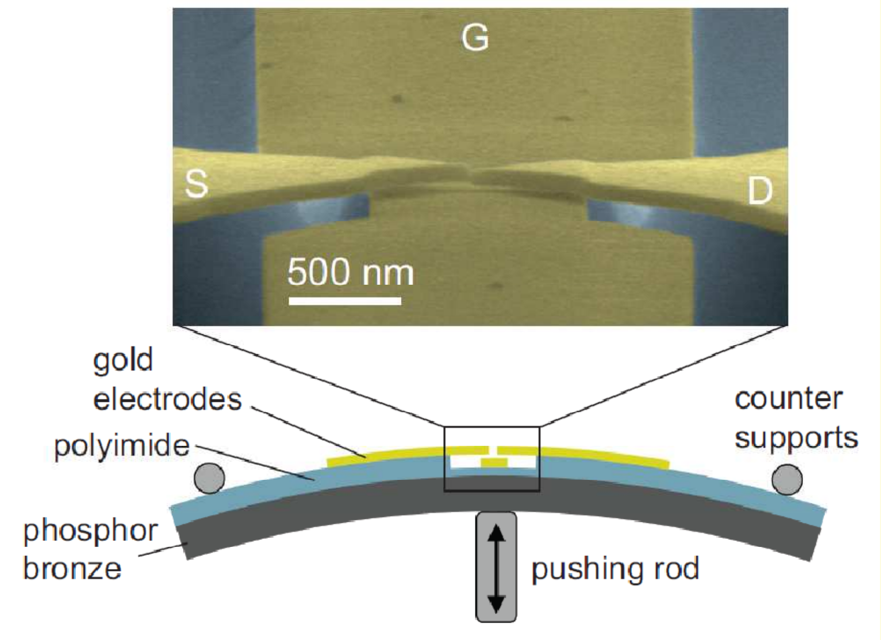
Thiol-coupled individual molecules

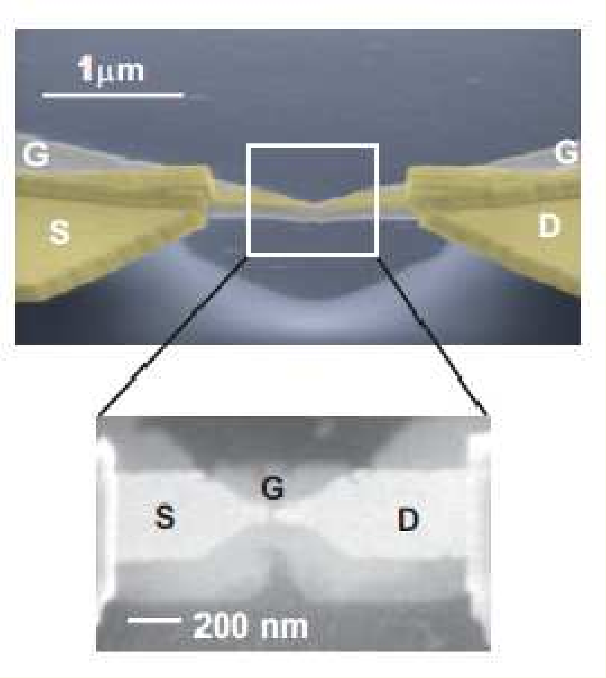




J. Reichert *et al.*, Phys. Rev. Lett. **88**, 176804 (2002)
M.A. Reed *et* al., Science **278**, 252 (1997)

Three terminal molecular junctions



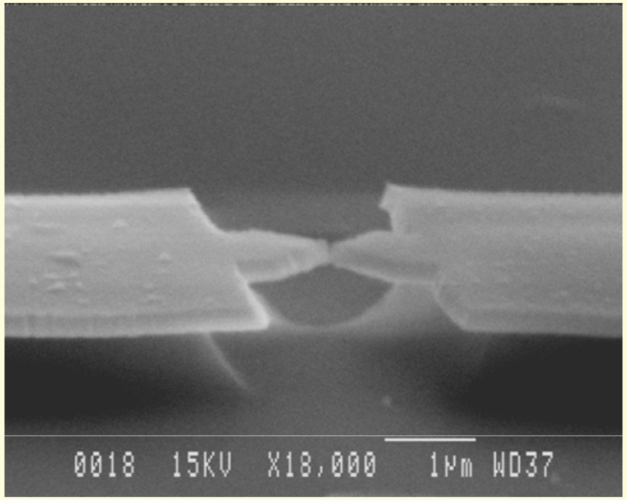


Martin, Smit, van der Zant, and van Ruitenbeek, Nano Lett. **9** (2009), 2940
C.A. Martin, PhD thesis

Techniques for adjusting the gap: mechanically controllable break junction

Advantages

- fast and easy, also at low T
- statistical averaging
- any metal for electrodes
- high stability



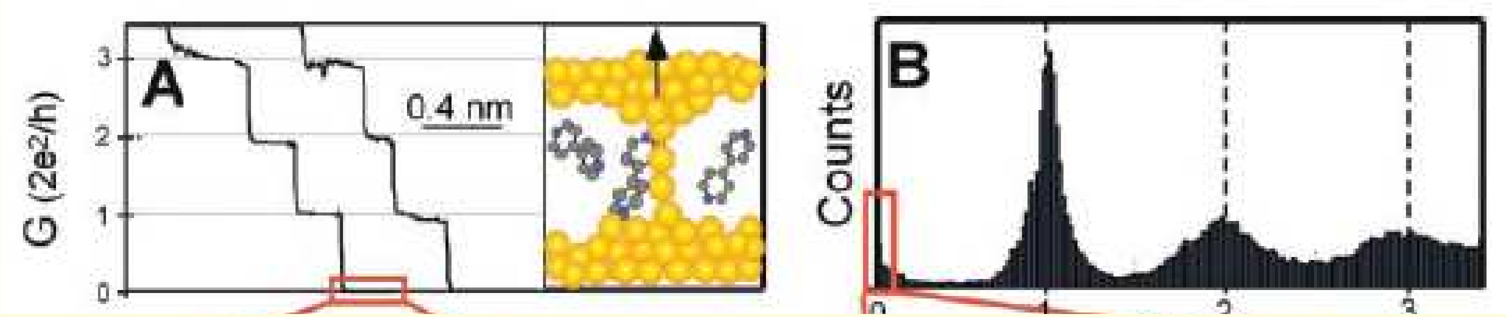
Drawbacks

- no cycling in field or temperature
- weak gate coupling
- no geometric information

Muller et al Physica C, 1992
Muller et al PRL 1992
Ruitenbeek et al Rev Sci. Instrum. 1996
Reed et al. Science 1997

Molecules in solution: conductance histograms

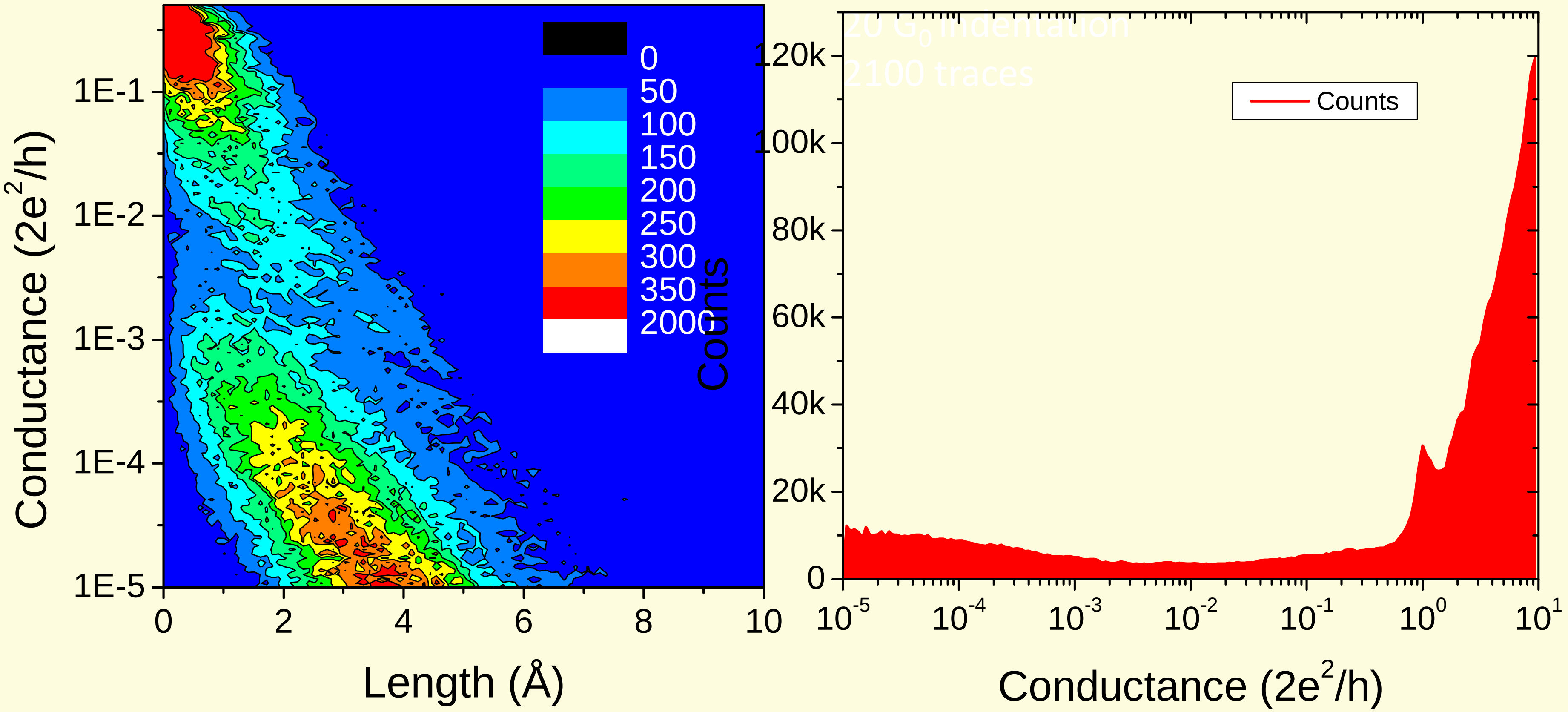
(room temperature)



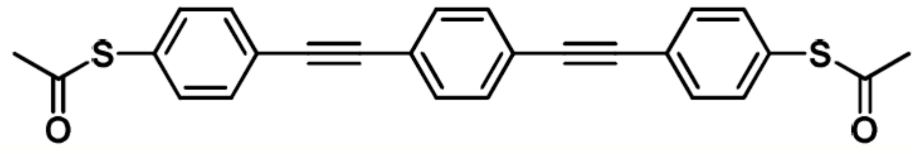
B. Xu, & N.J. Tao, Science **301** 1221 (2003)

2D histograms: test clean Au in vacuum

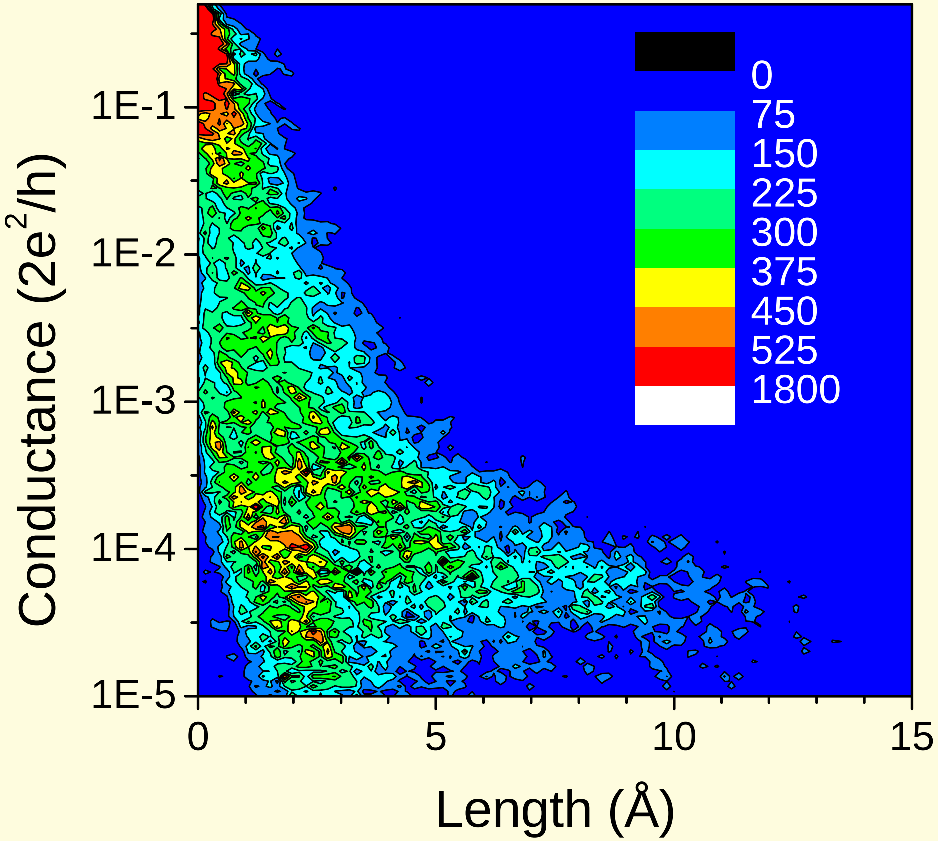
Sample 090515_0:
1 nm/s
100 mV bias
20 G_0 indentation
2100 traces

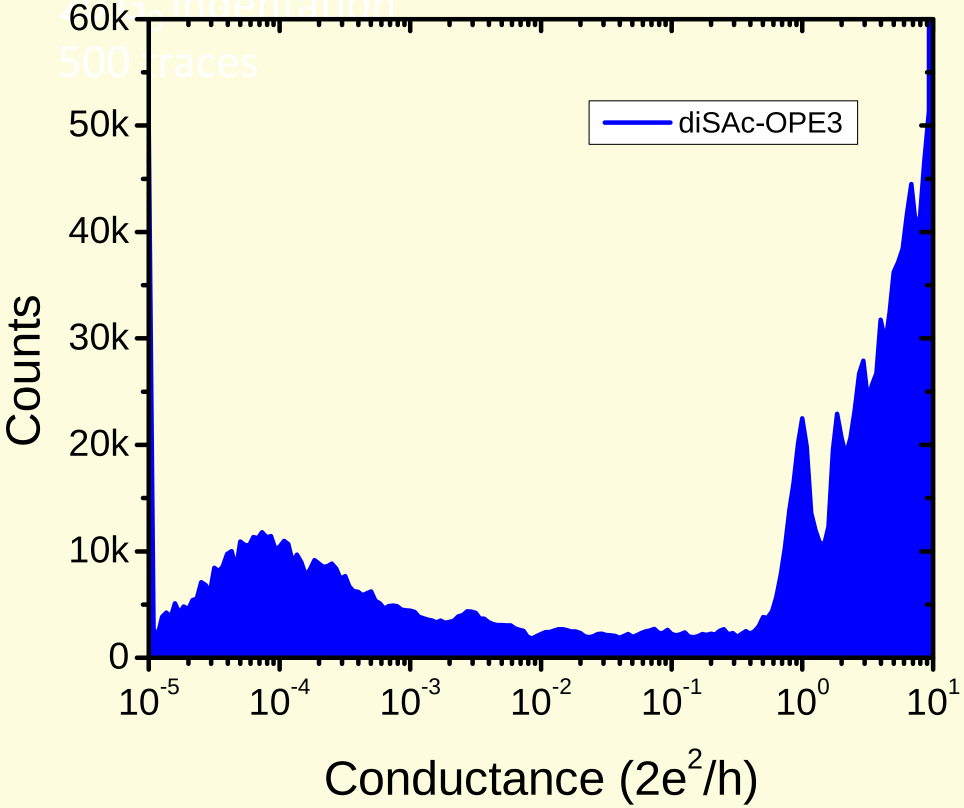


Au/OPE3-dithiol

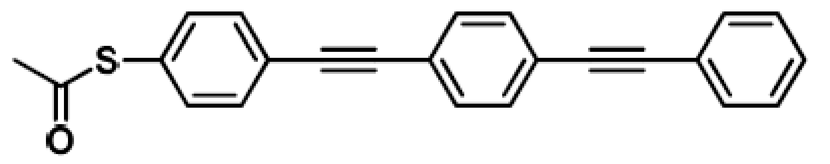


Sample 091116_5:
1 nm/s
50 mV bias
20 G_0 indentation
500 traces



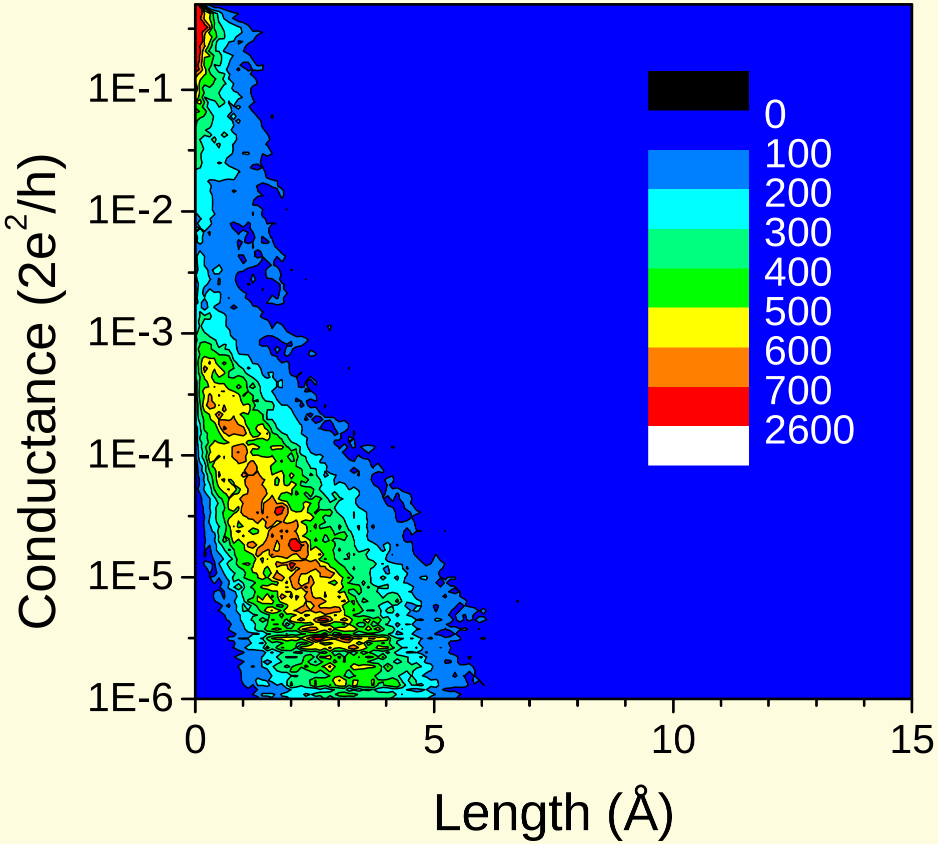


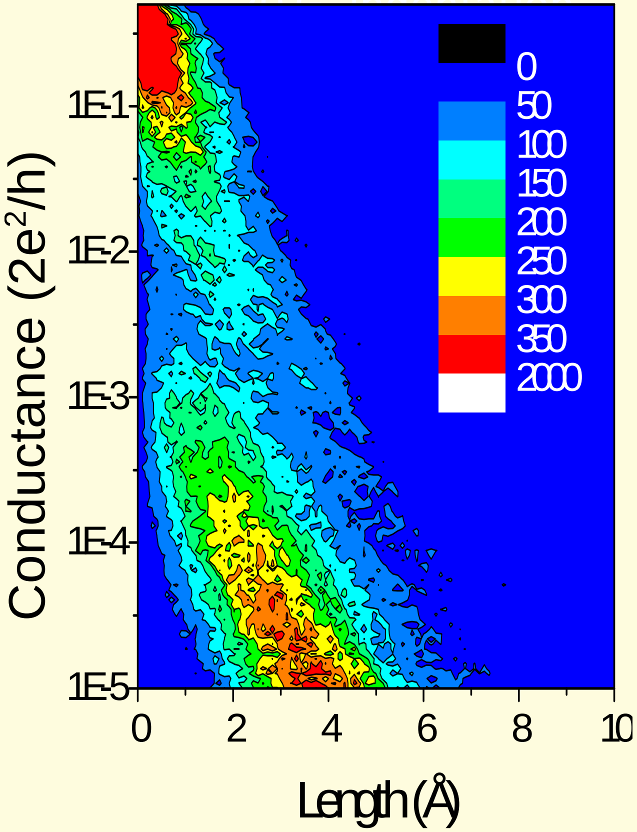
Au/OPE3 monothiol



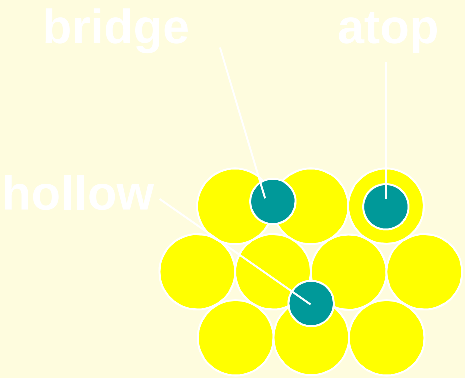
Nominally clean
Au junction

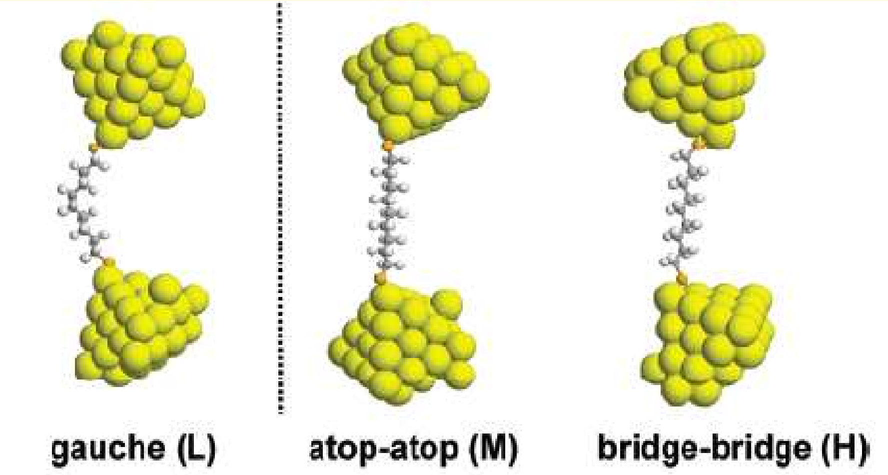
Sample 091207_8:
1 nm/s
50 mV bias
20 C, indentation

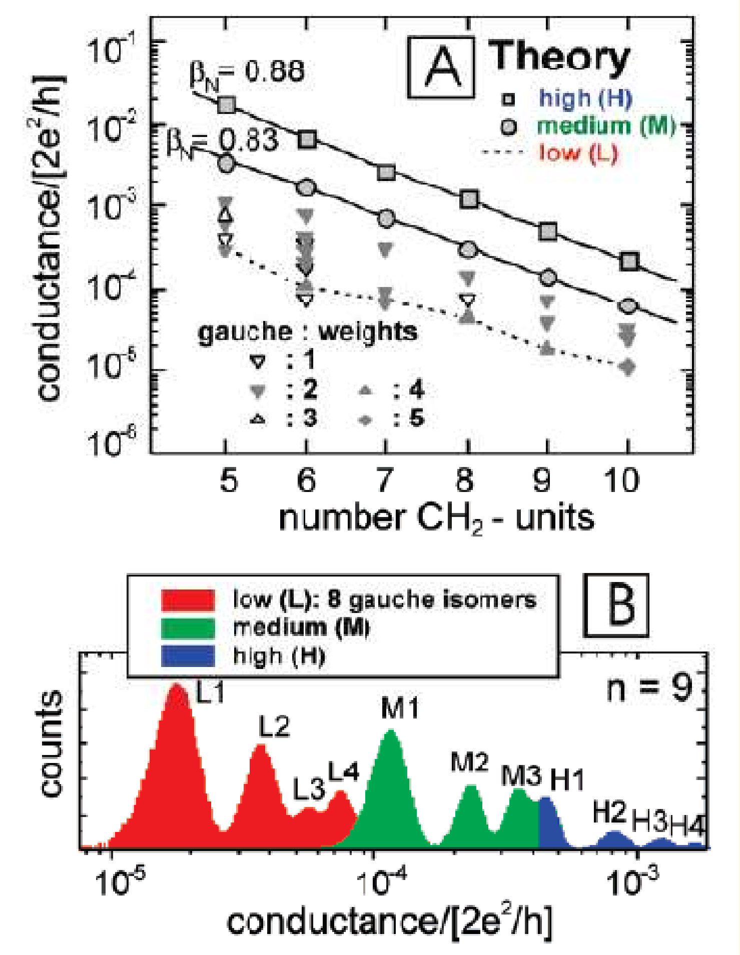




Alkanedithiols: a model system

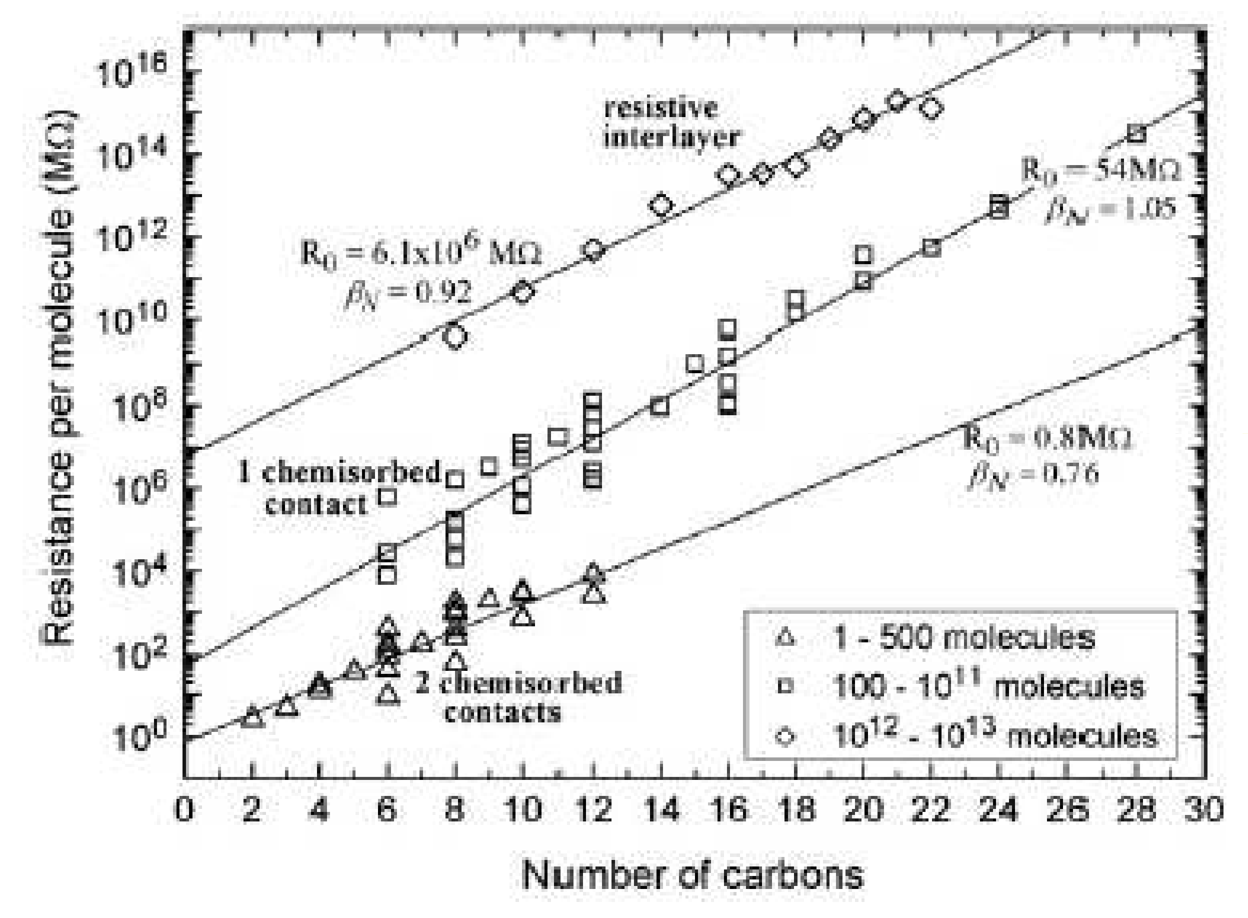






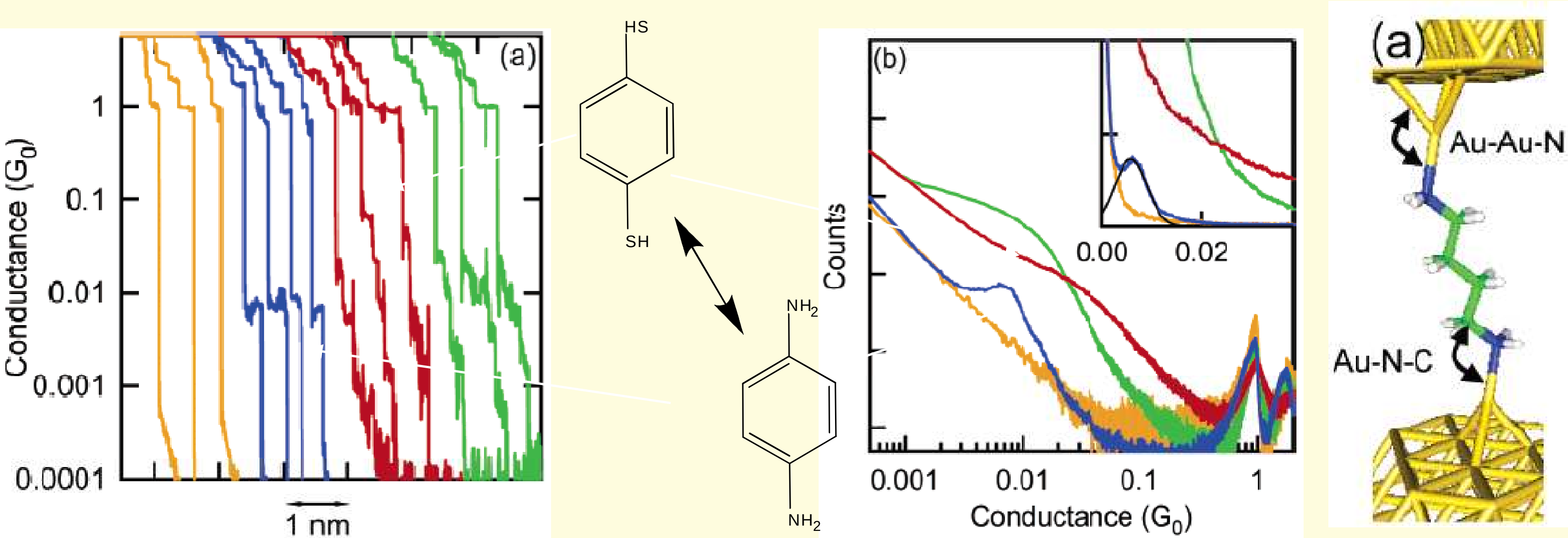
Li et al., JACS ASAP, 2008

Systematics of alkane conductance



Akkerman & de Boer, J. Phys.: Condens. Matter **20** (2008) 013001

Can the reproducibility be improved?



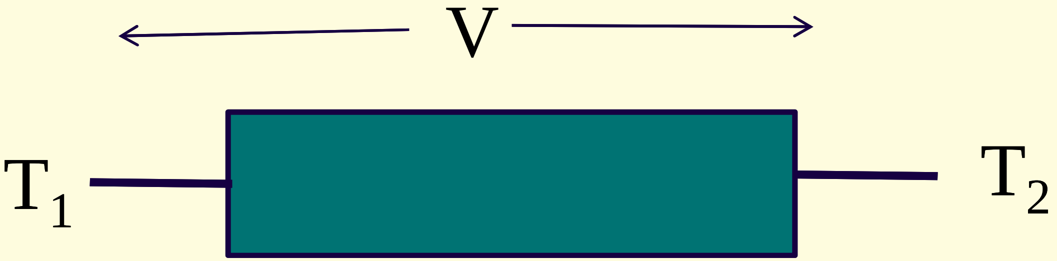
Venkataraman et al., Nano Lett. (6) 3, 2006

- compared to thiols the amine-gold bond is weaker
- the low-bias conductance of amines is more clearly defined

Beyond conductance measurements:

Thermopower

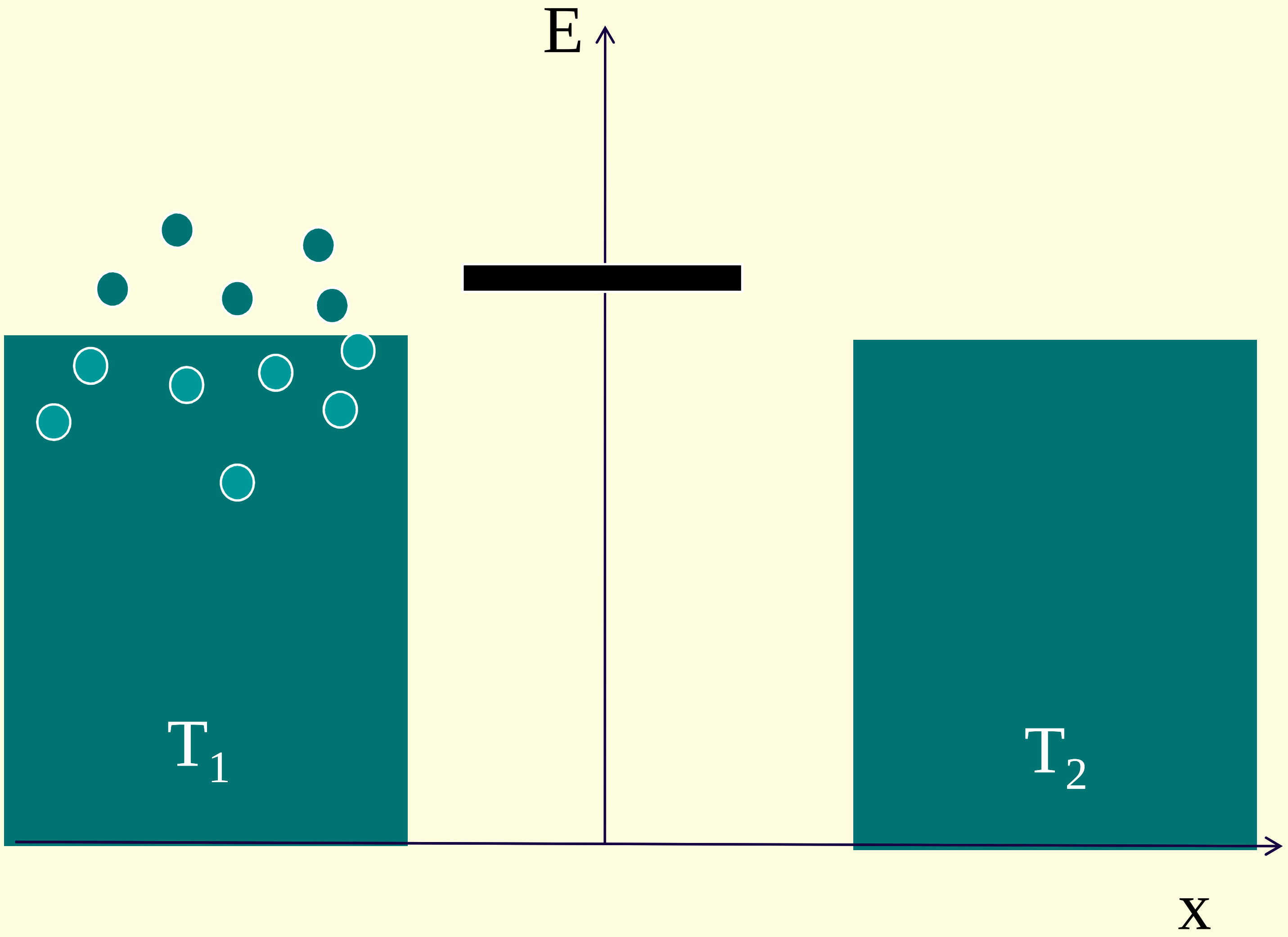
Principle of thermopower



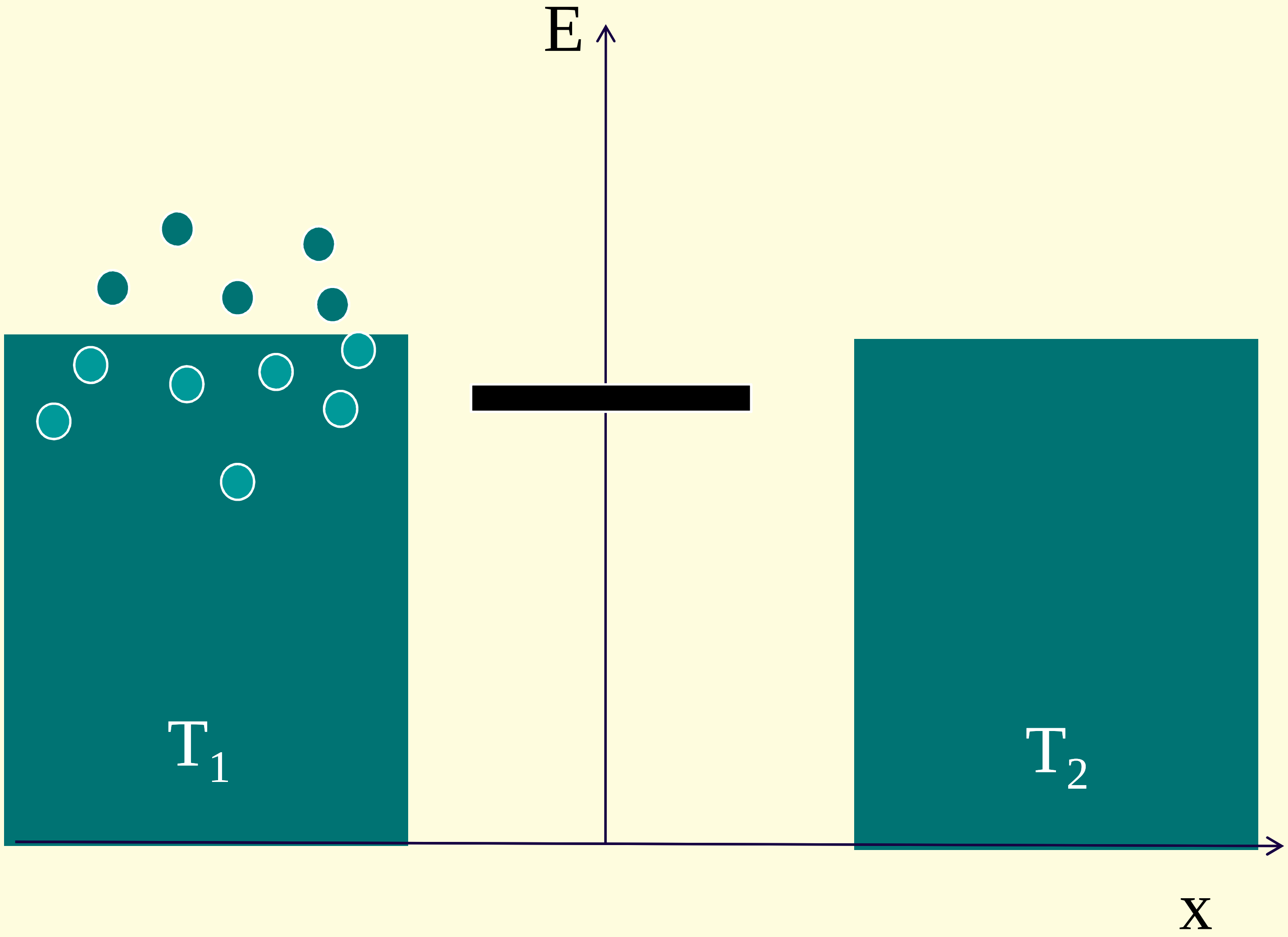
$$S = \frac{V}{T_2 - T_1}$$

$$S \propto \frac{T}{G}\frac{\partial G}{\partial \mu}$$

Principle of thermopower

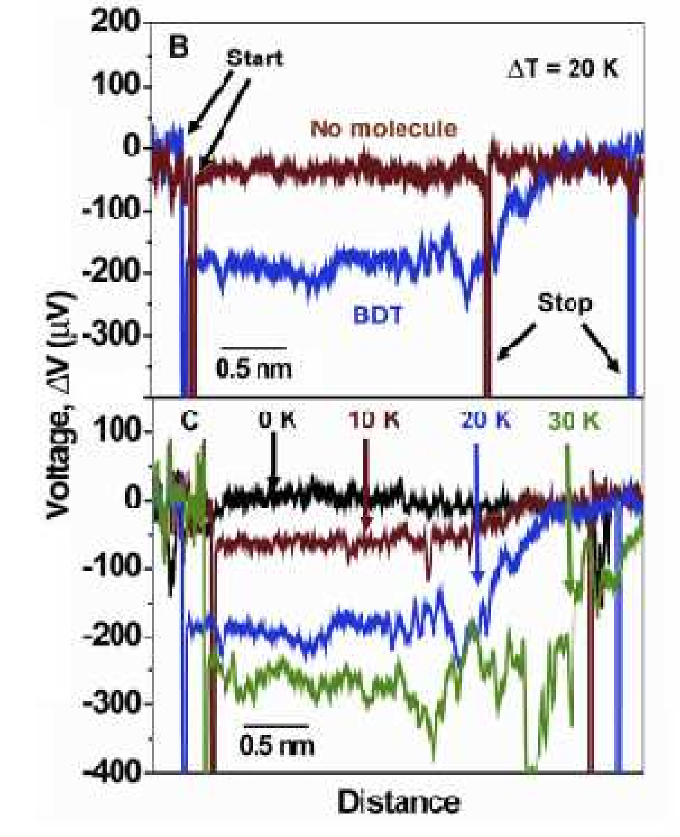


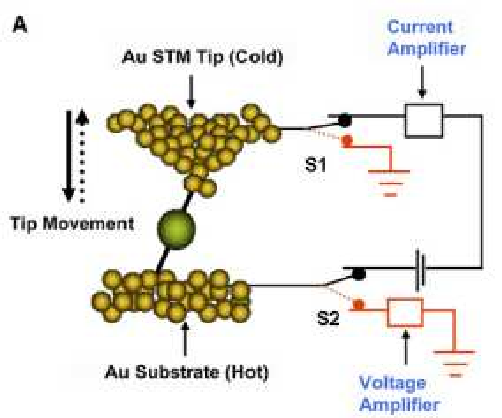
Principle of thermopower

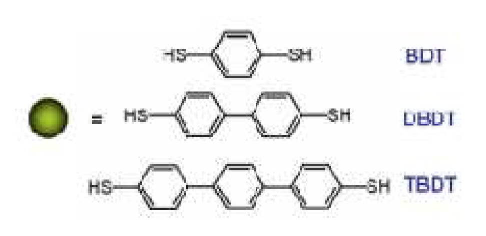


Thermopower

Reddy, Jang, Segalman & Majumdar, Science **315** (2009) 1568

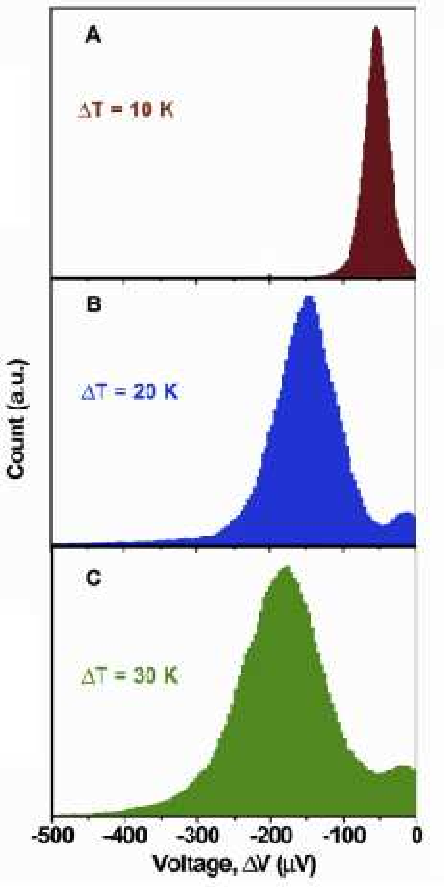


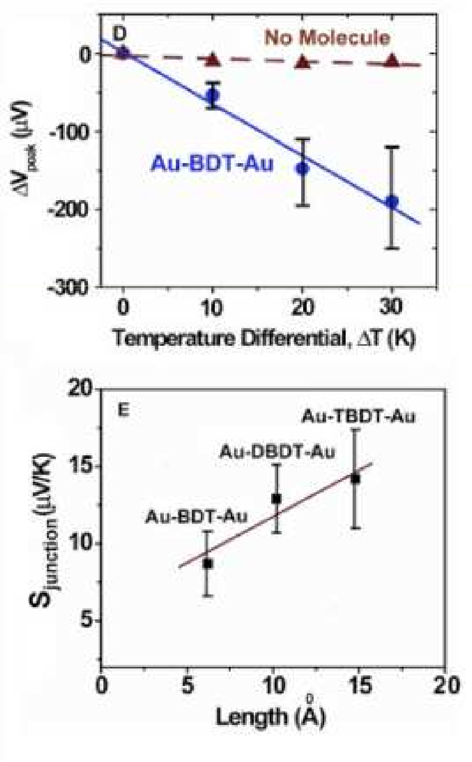




Thermopower

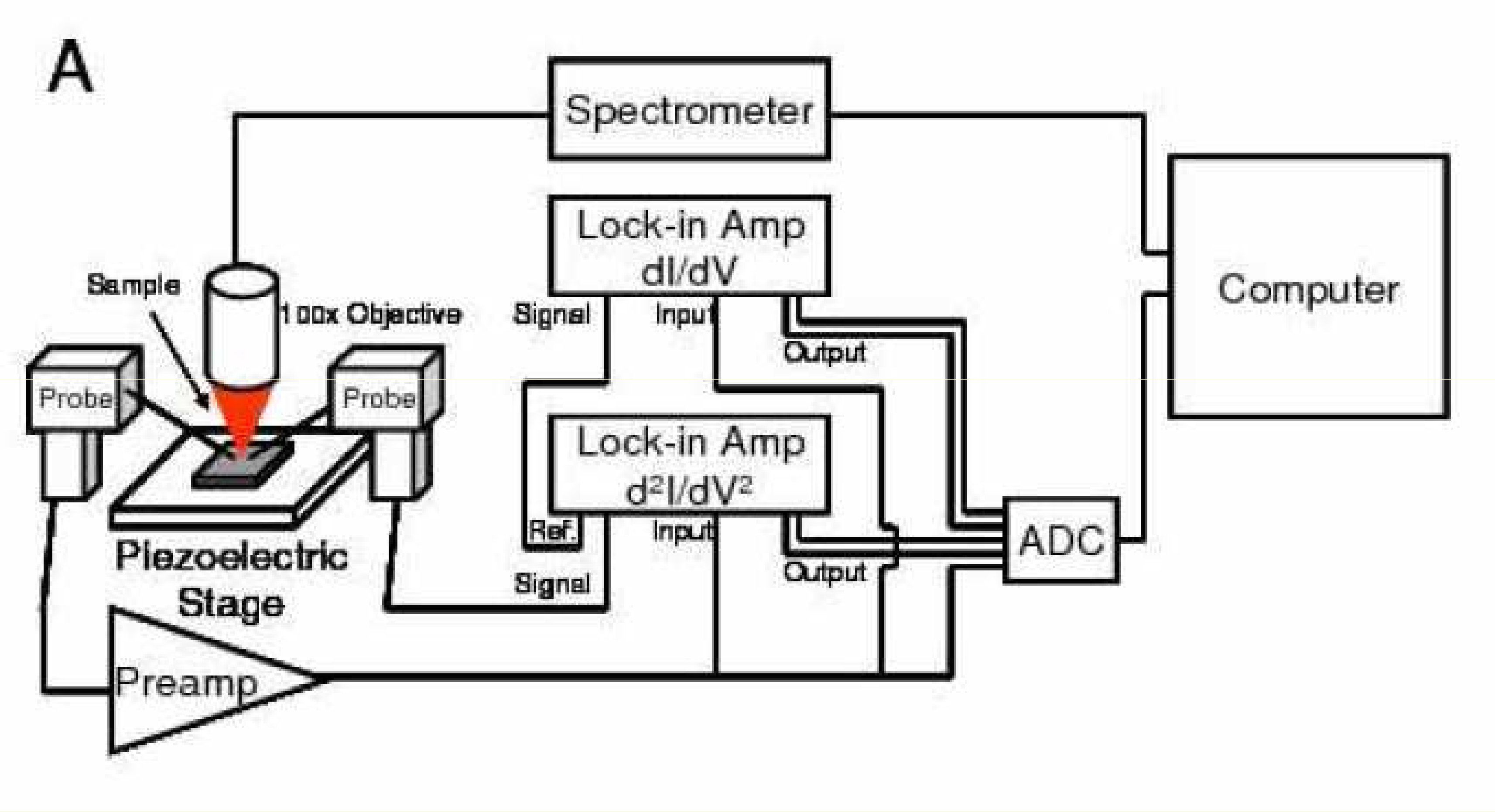
Reddy, Jang, Segalman & Majumdar, Science **315** (2009) 1568





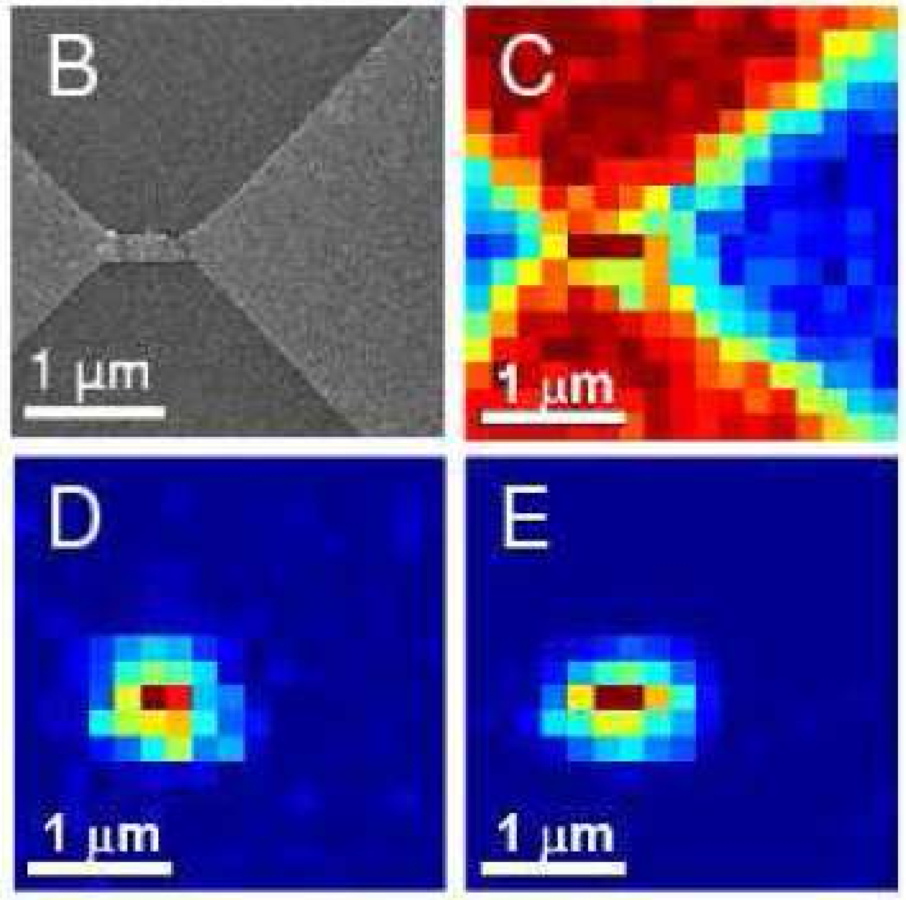
Raman scattering

Single molecule Raman spectroscopy



Ward, Scott, Keane, Halas, & Natelson,
J. Phys.: Condens. Matter **20**, 374118 (2008).

Single molecule Raman spectroscopy

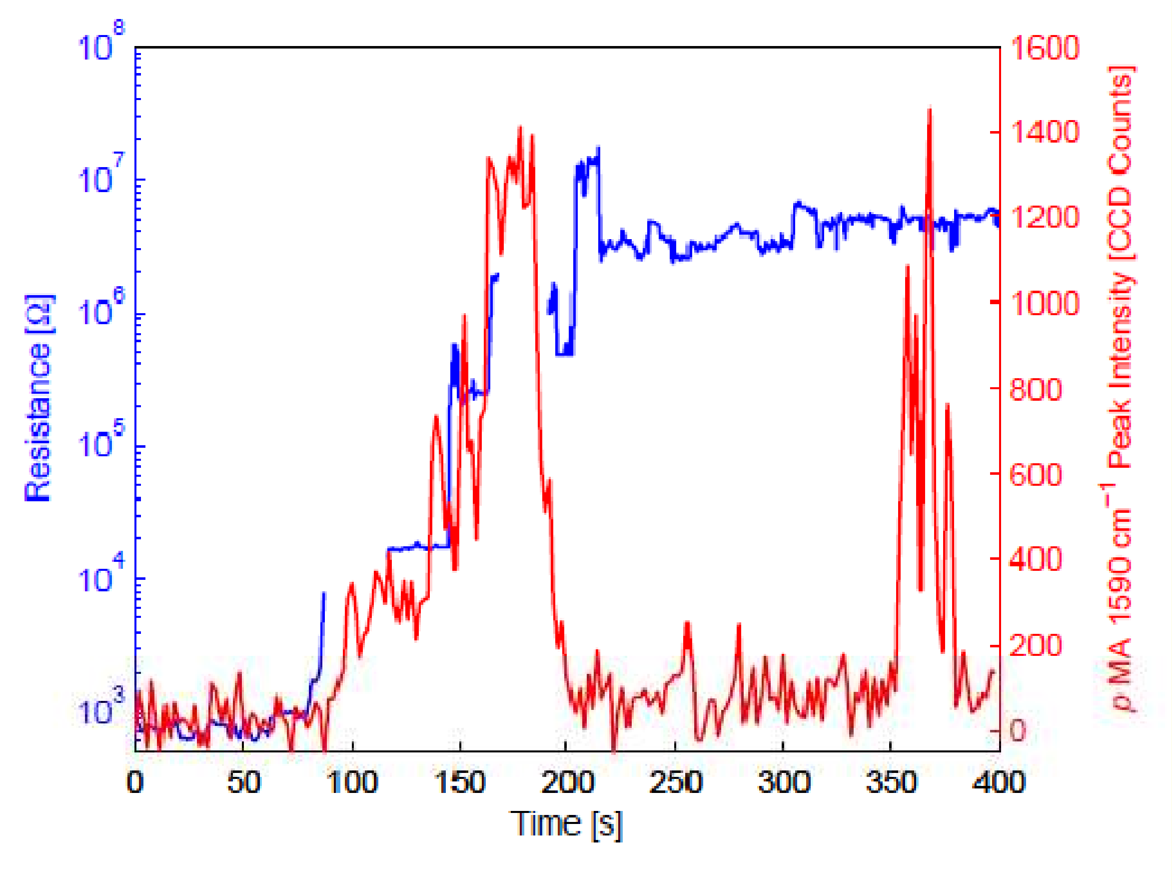


Substrate
Si 520 cm^{-1} peak

1590 cm^{-1} mode

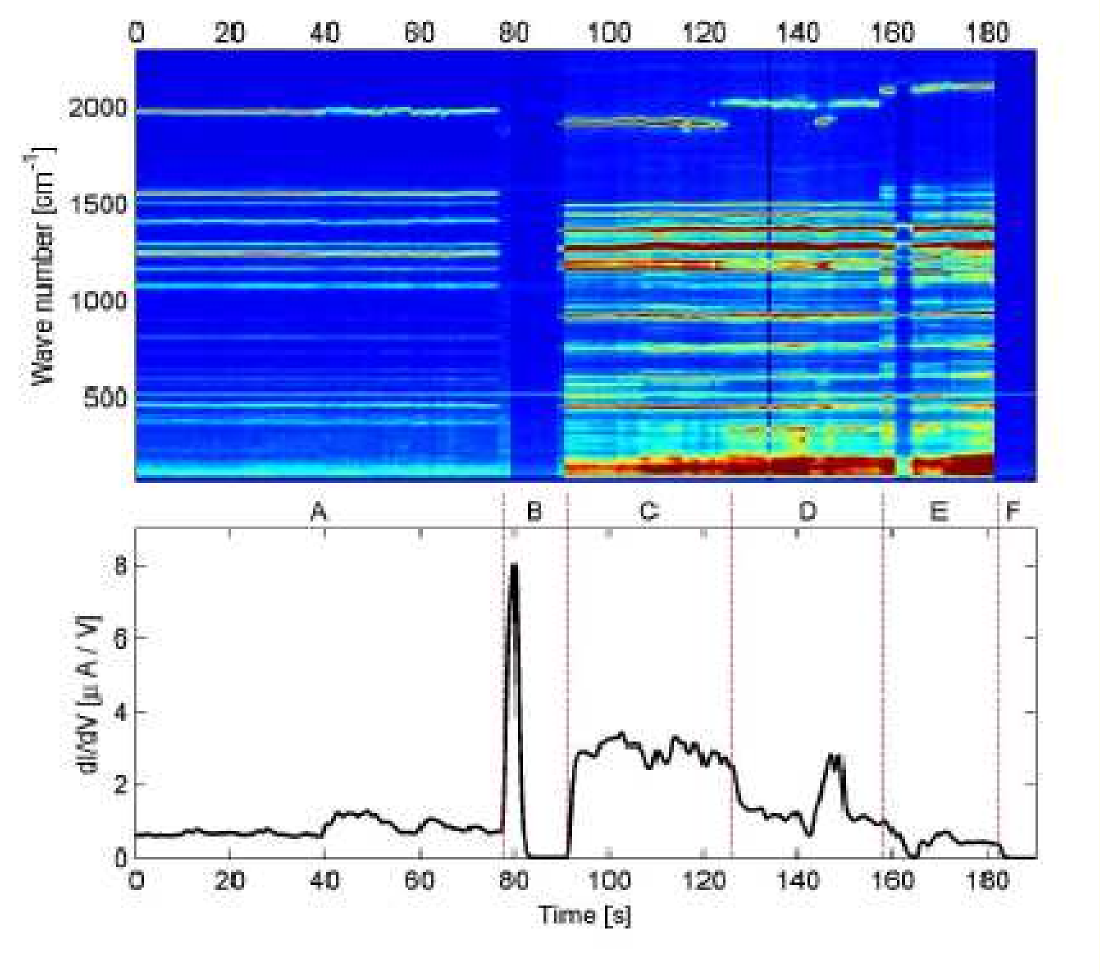
Ward, Scott, Keane, Halas, & Natelson,
J. Phys.: Condens. Matter **20**, 374118 (2008).

Single molecule Raman spectroscopy



Ward, Scott, Keane, Halas, & Natelson,
J. Phys.: Condens. Matter **20**, 374118 (2008).

Single molecule Raman spectroscopy



Ward, Scott, Keane, Halas, & Natelson,
J. Phys.: Condens. Matter **20**, 374118 (2008).

Advantages of low temperatures

- Junctions can be held stable for days

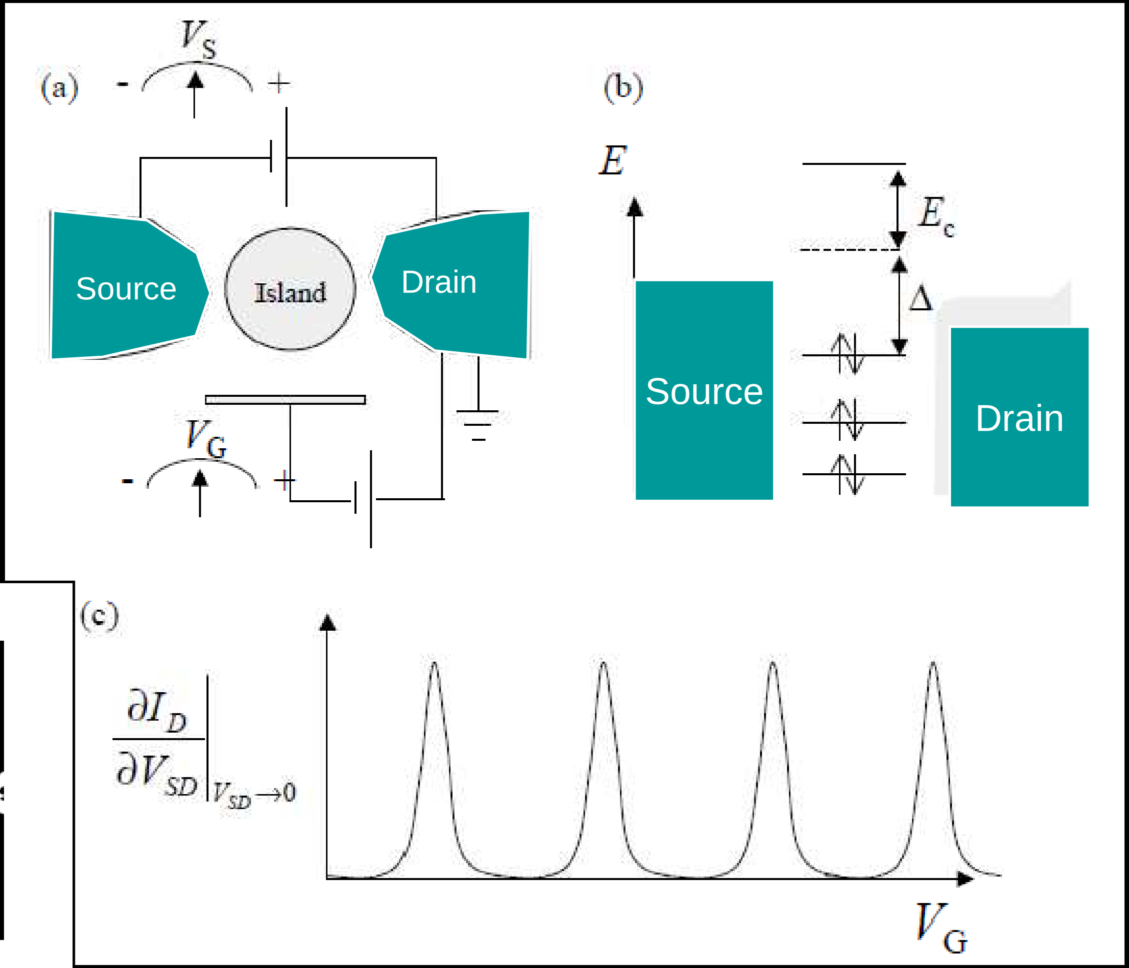
- Analysis tools available that are only effective at low T
  - * Vibration mode spectroscopy
  - * Shot noise
  - * Superconducting subgap structure
  - * Thermopower

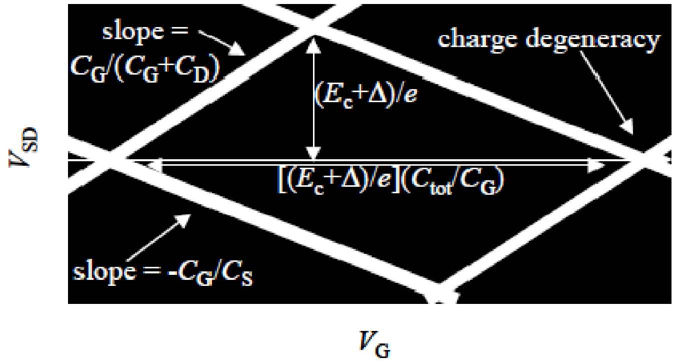
- Interesting effects appear most clearly

Inelastic scattering signals in conductance

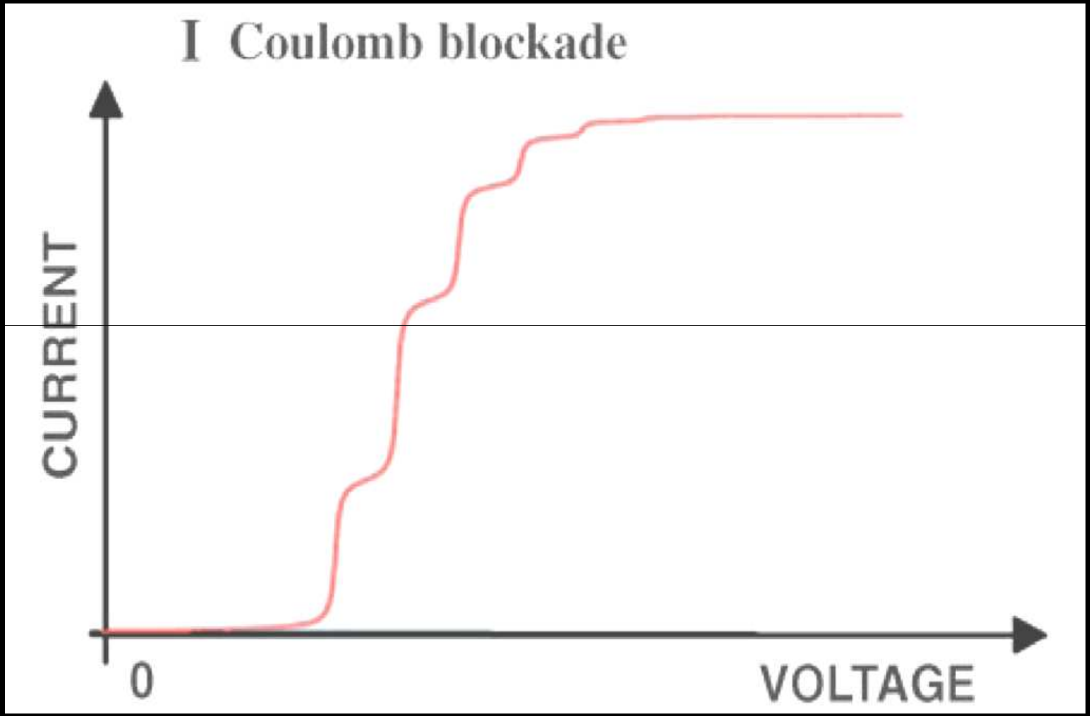
1. Weakly coupled molecules
2. Strongly coupled molecules

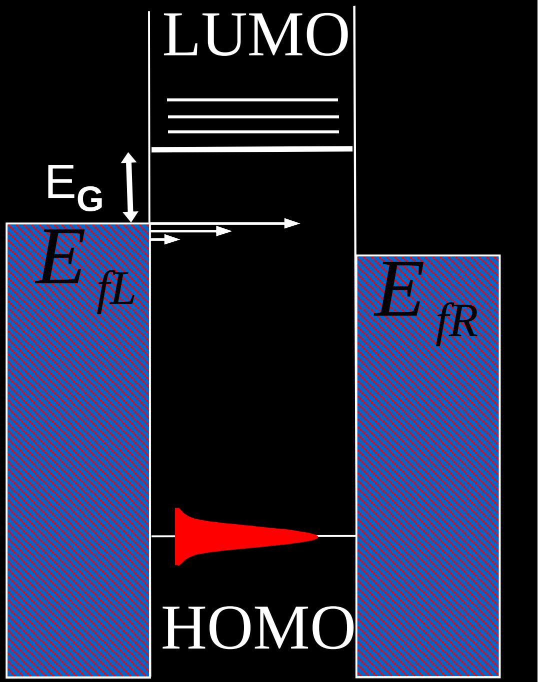
Coulomb blockade



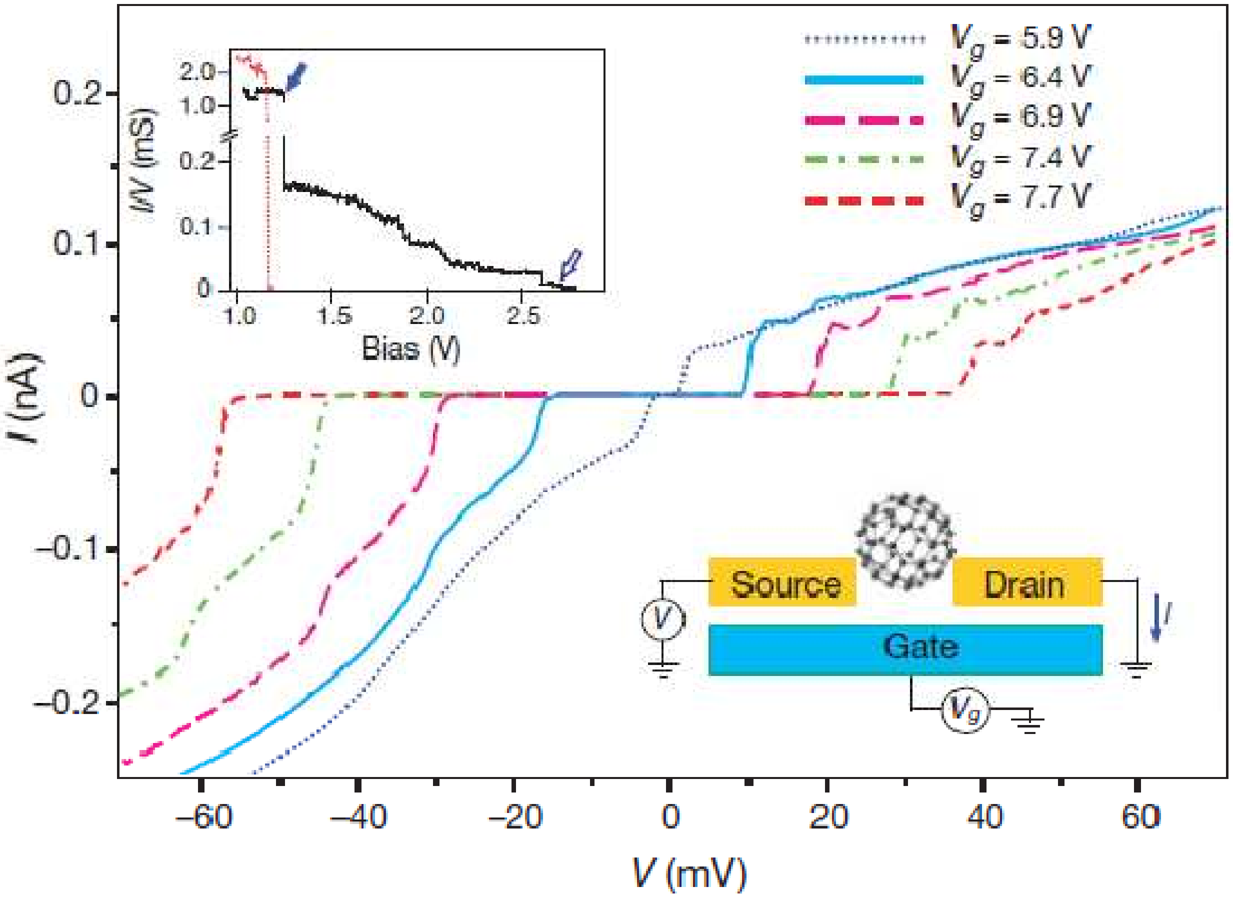


Vibration modes in Coulomb blockade





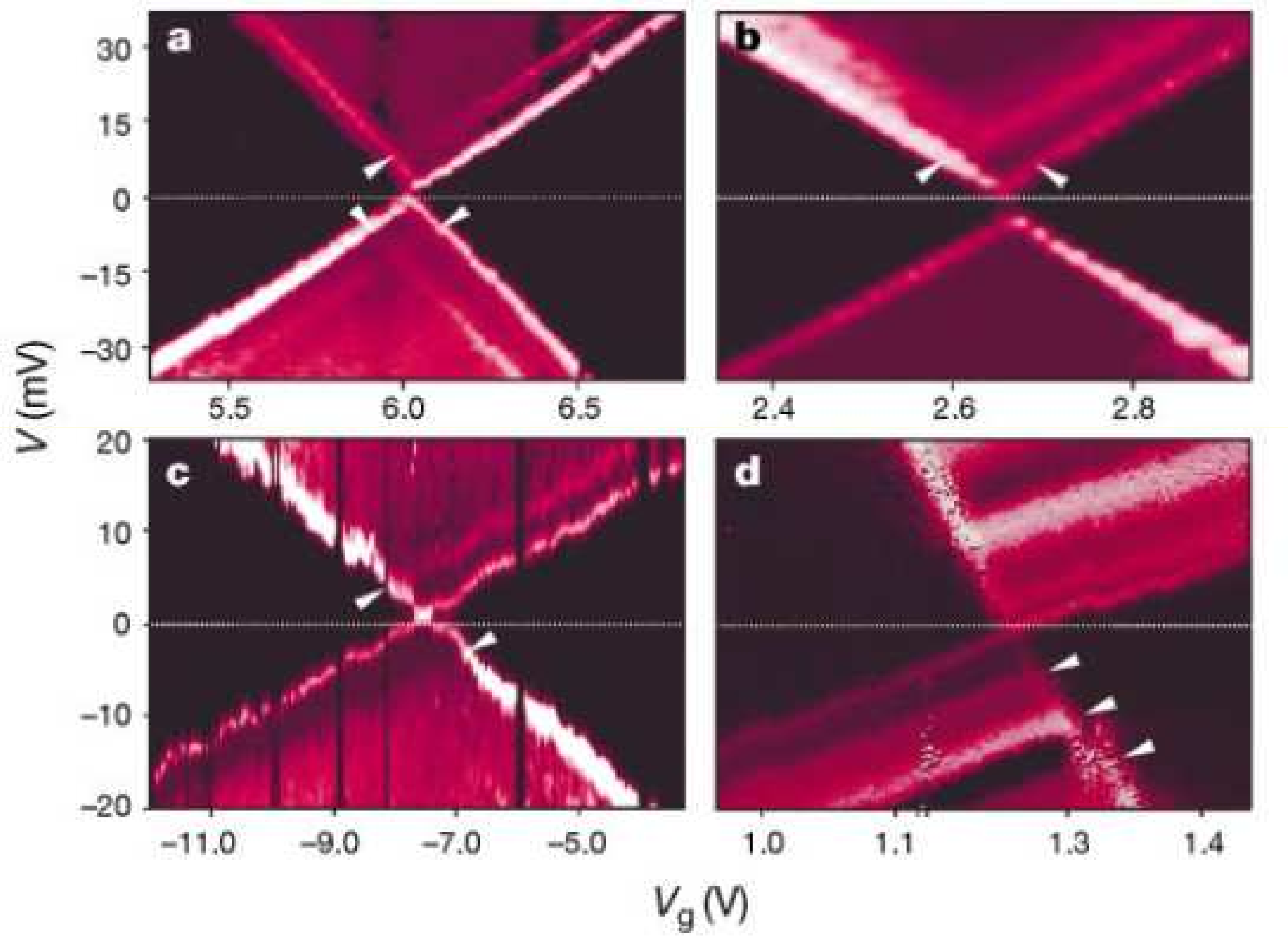
Break junction by electromigration



C_{60}

Park, Park, Lim, Anderson, Alivisatos and McEuan, Nature **407** (2000) 57

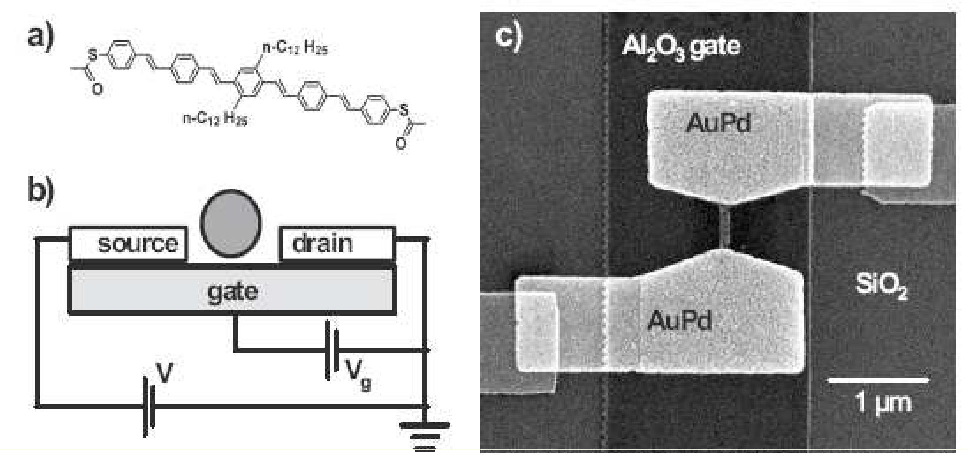
Break junction by electromigration

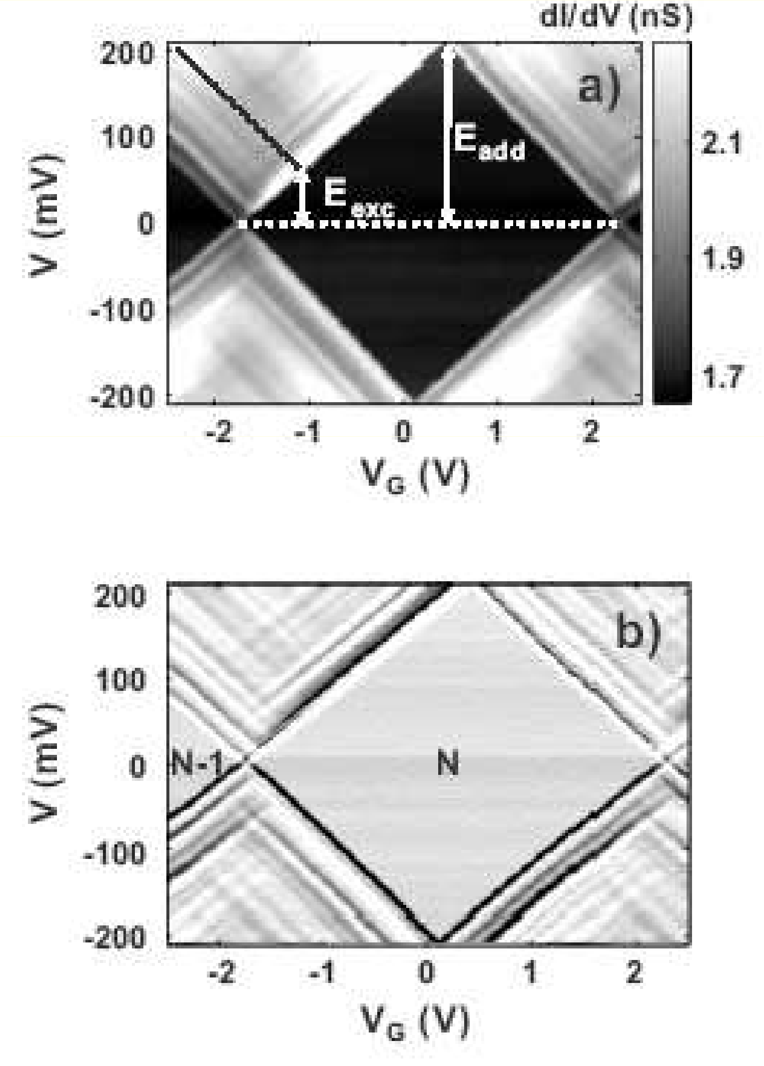


C_{60}

Park, Park, Lim, Anderson, Alivisatos and McEuan, Nature **407** (2000) 57

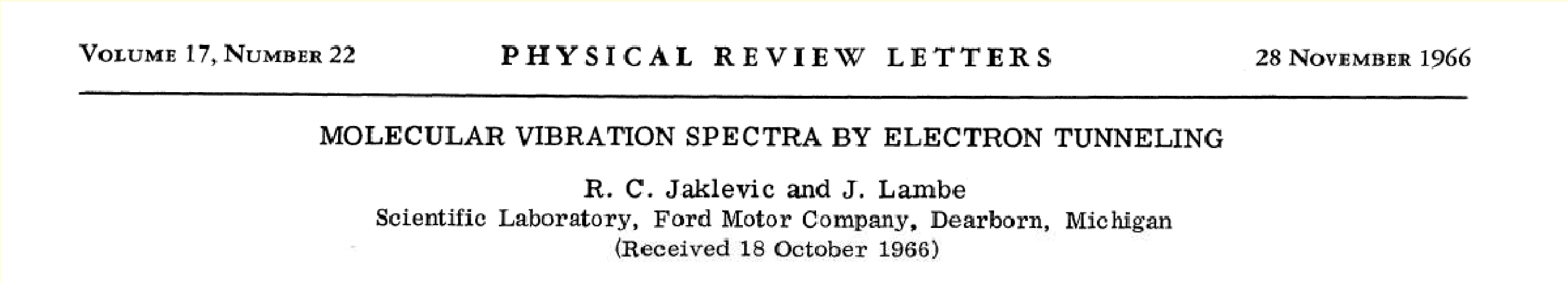
Break junction by electromigration





Edgar A. Osorio, Kevin O’Neill, Nicolai Stuhr-Hansen, Ole F. Nielsen, Thomas Bjørnholm,and Herre S. J. van der Zant*
Adv. Mater. 19 (2007) 281

Inelastic Electron Tunneling Spectroscopy IETS

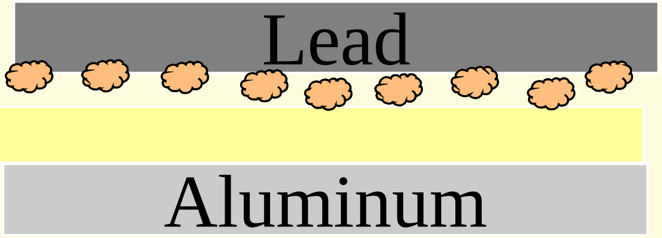


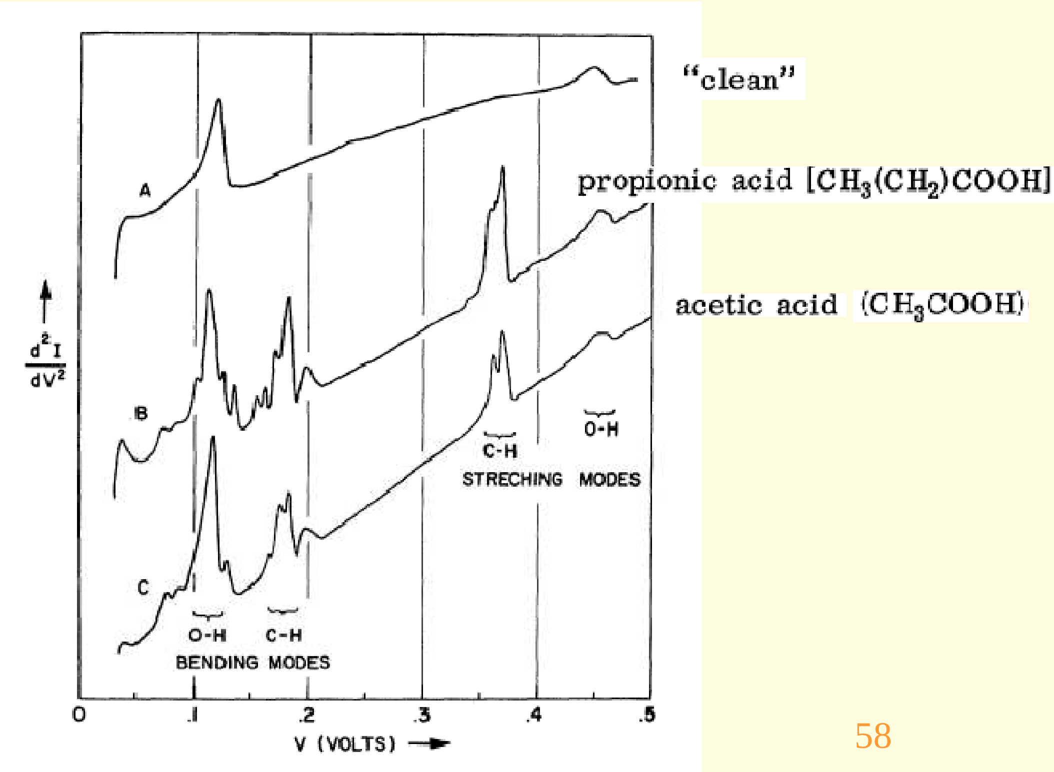
VOLUME 17, NUMBER 22 PHYSICAL REVIEW LETTERS 28 NOVEMBER 1966

MOLECULAR VIBRATION SPECTRA BY ELECTRON TUNNELING

R. C. Jaklevic and J. Lambe
Scientific Laboratory, Ford Motor Company, Dearborn, Michigan

(Received 18 October 1966)



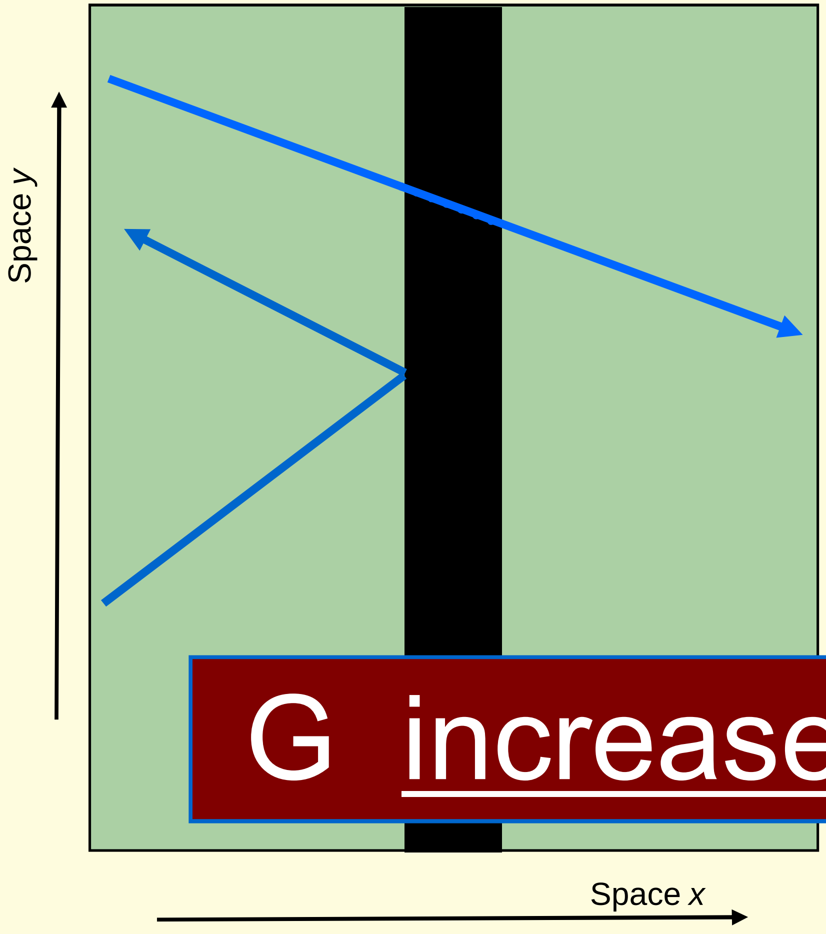


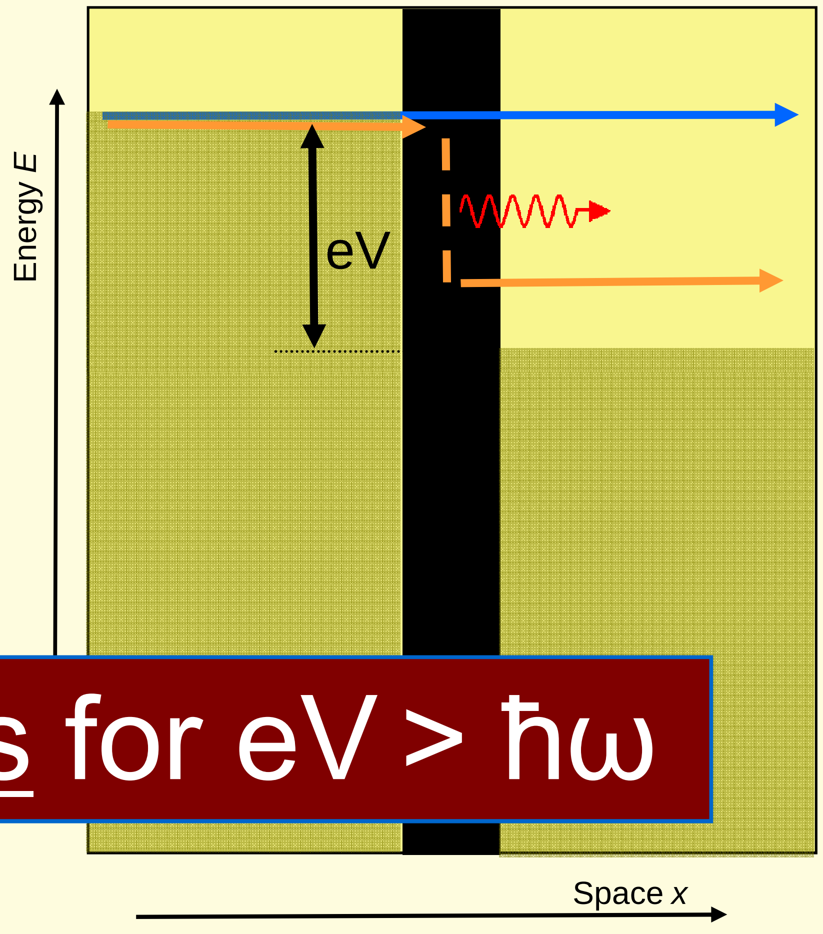
"clean"

propionic acid [$CH_3(CH_2)COOH$]

acetic acid (CH_3COOH)

Principle of inelastic electron tunneling spectroscopy

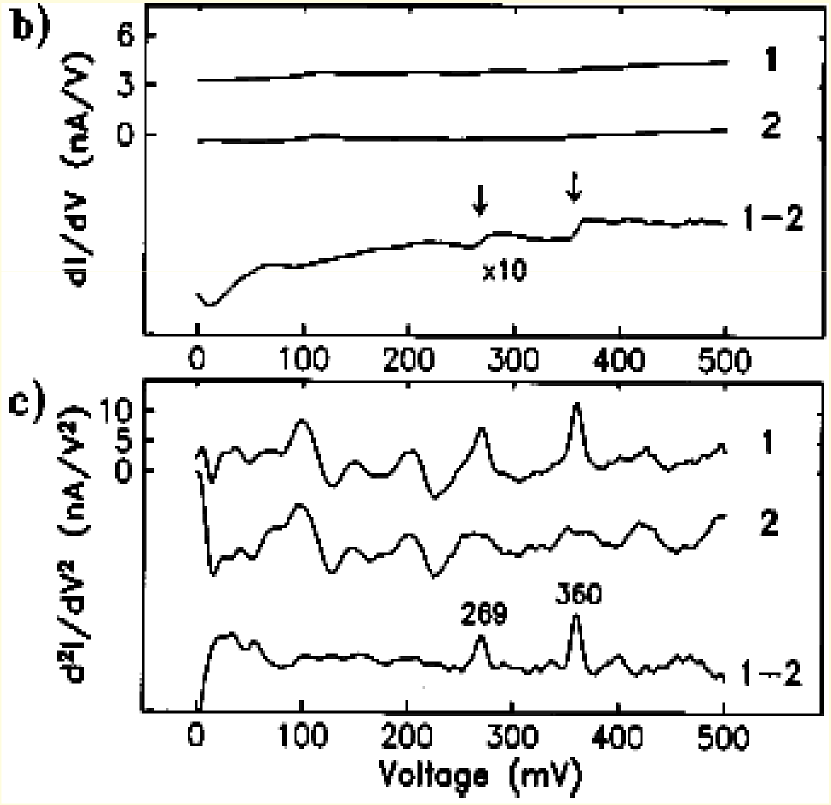


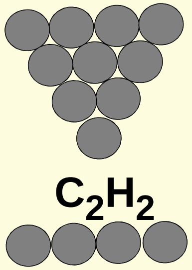


G increases for $eV > \hbar\omega$

Inelastic Electron Tunneling Spectroscopy

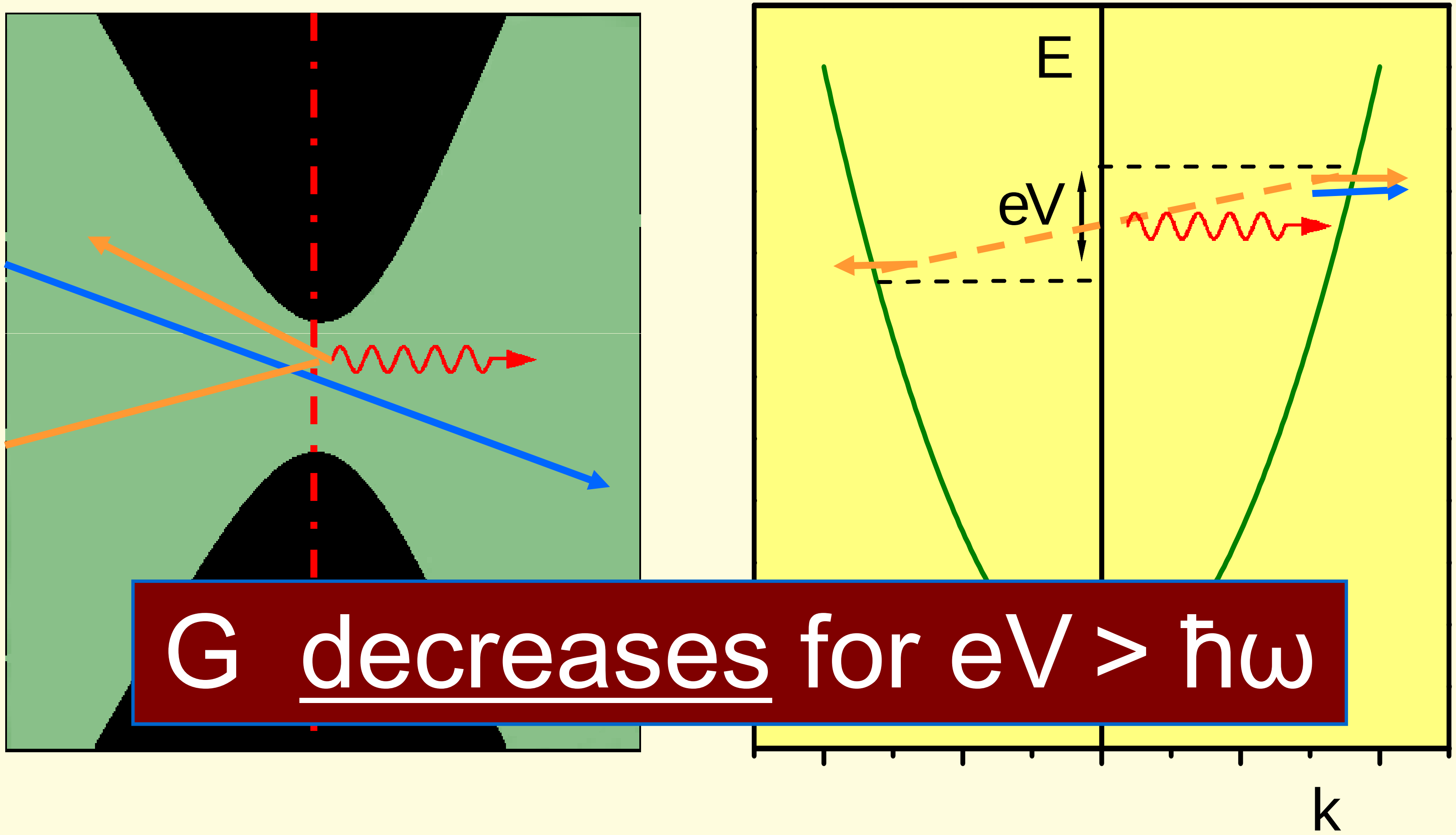
Typically low transmission probability



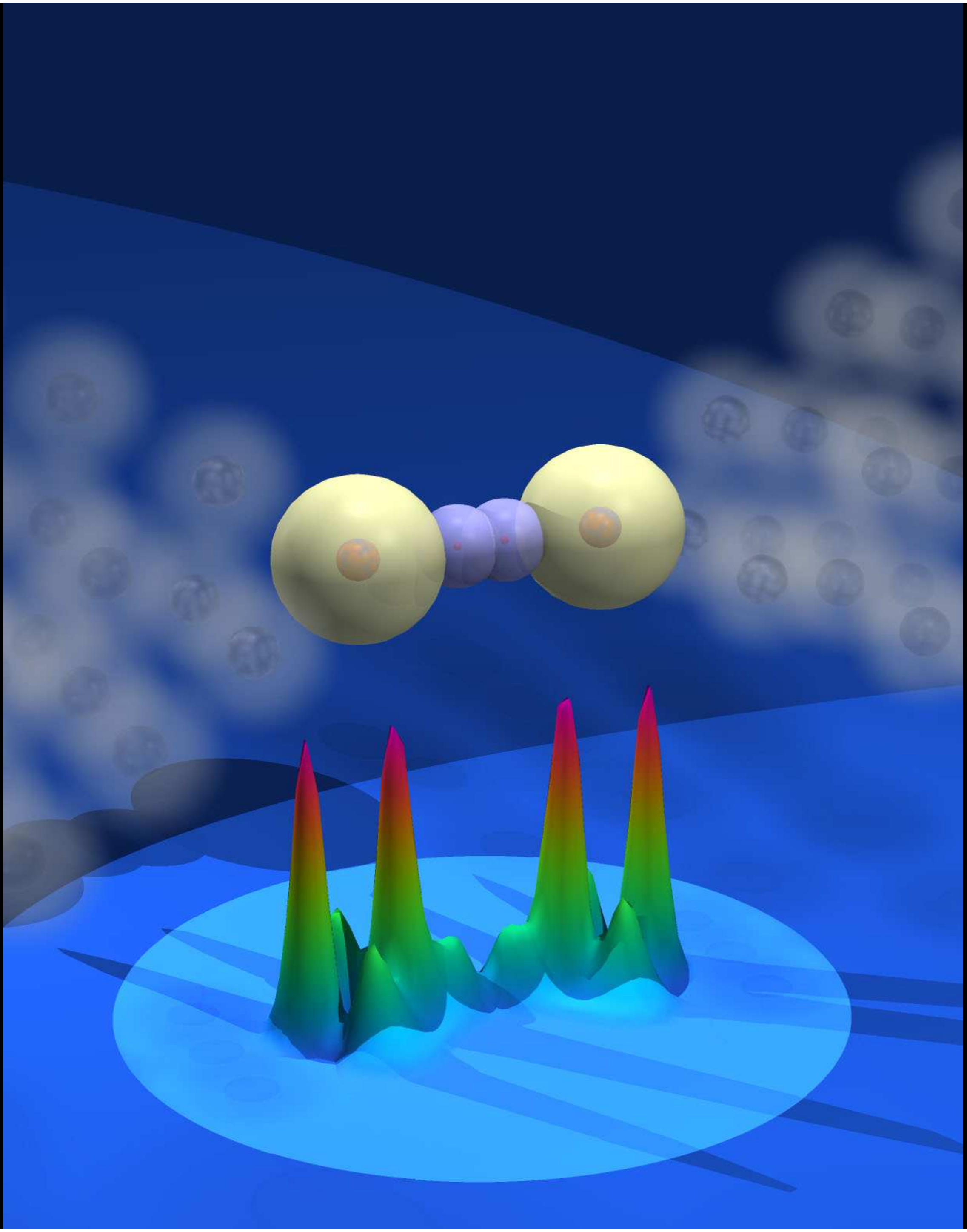


Stipe *et al*. Rev. Sci. Inst.**70** (1999), 137

Principle of point contact spectroscopy

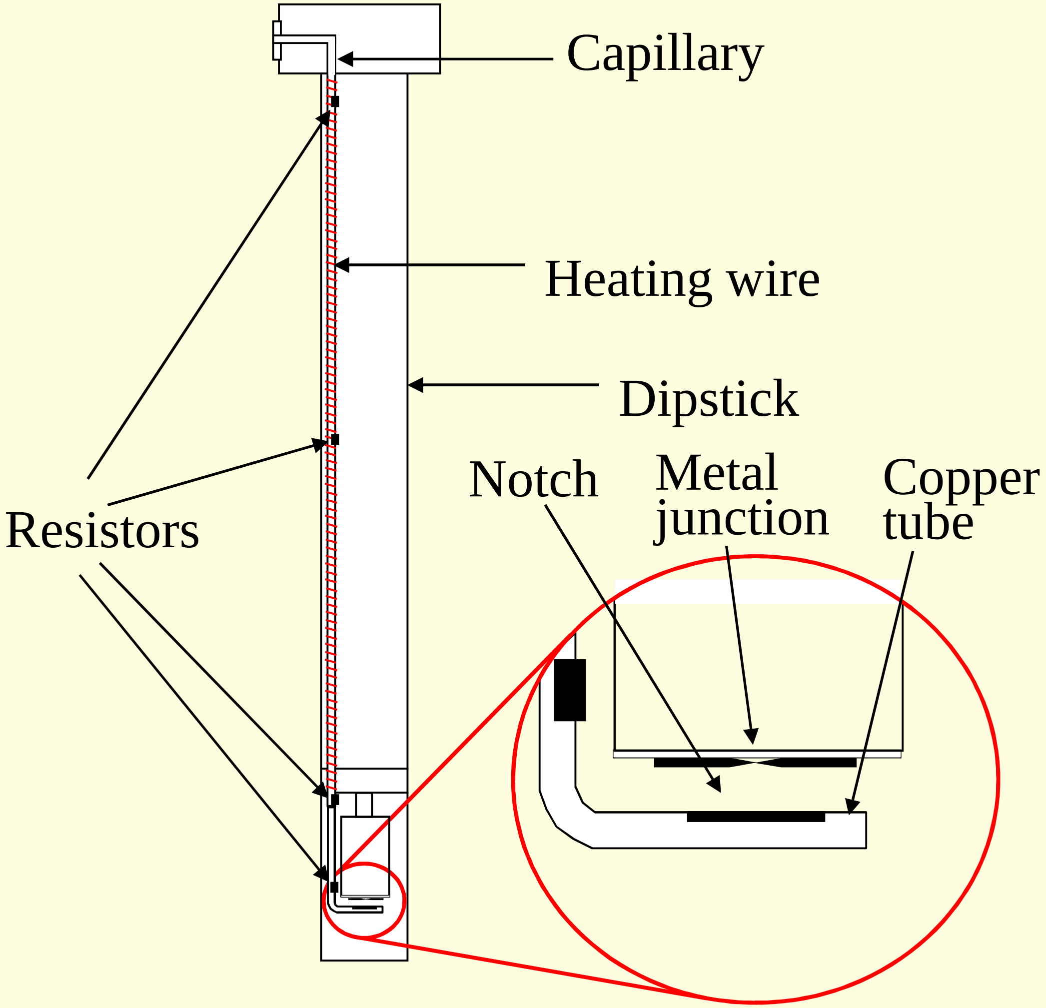


G decreases for eV > $\hbar\omega$



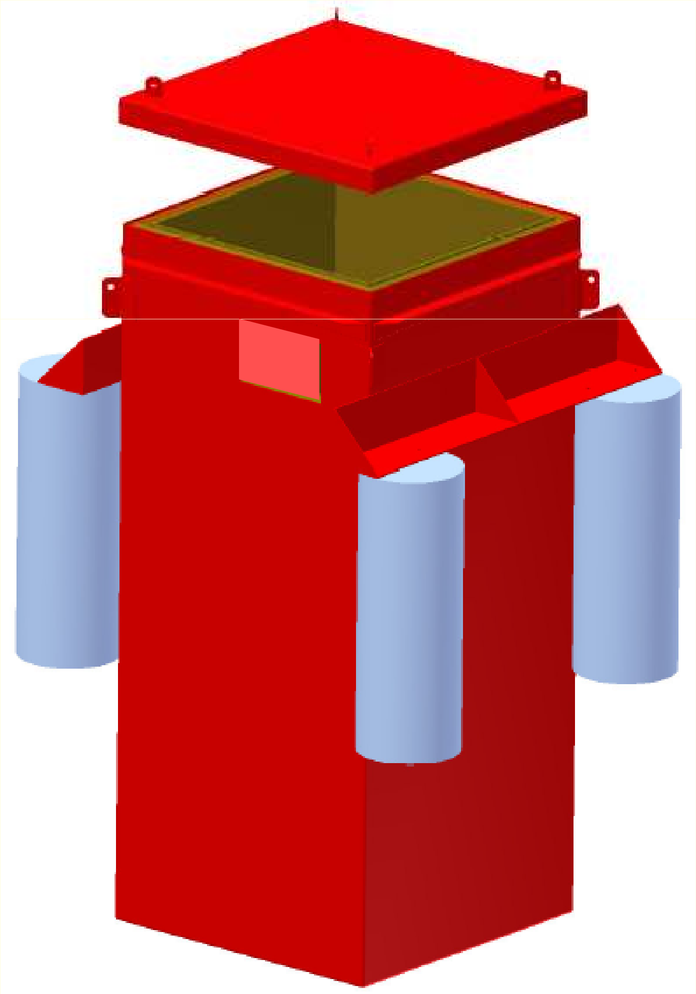
Deposition of molecules

Molecule dozer

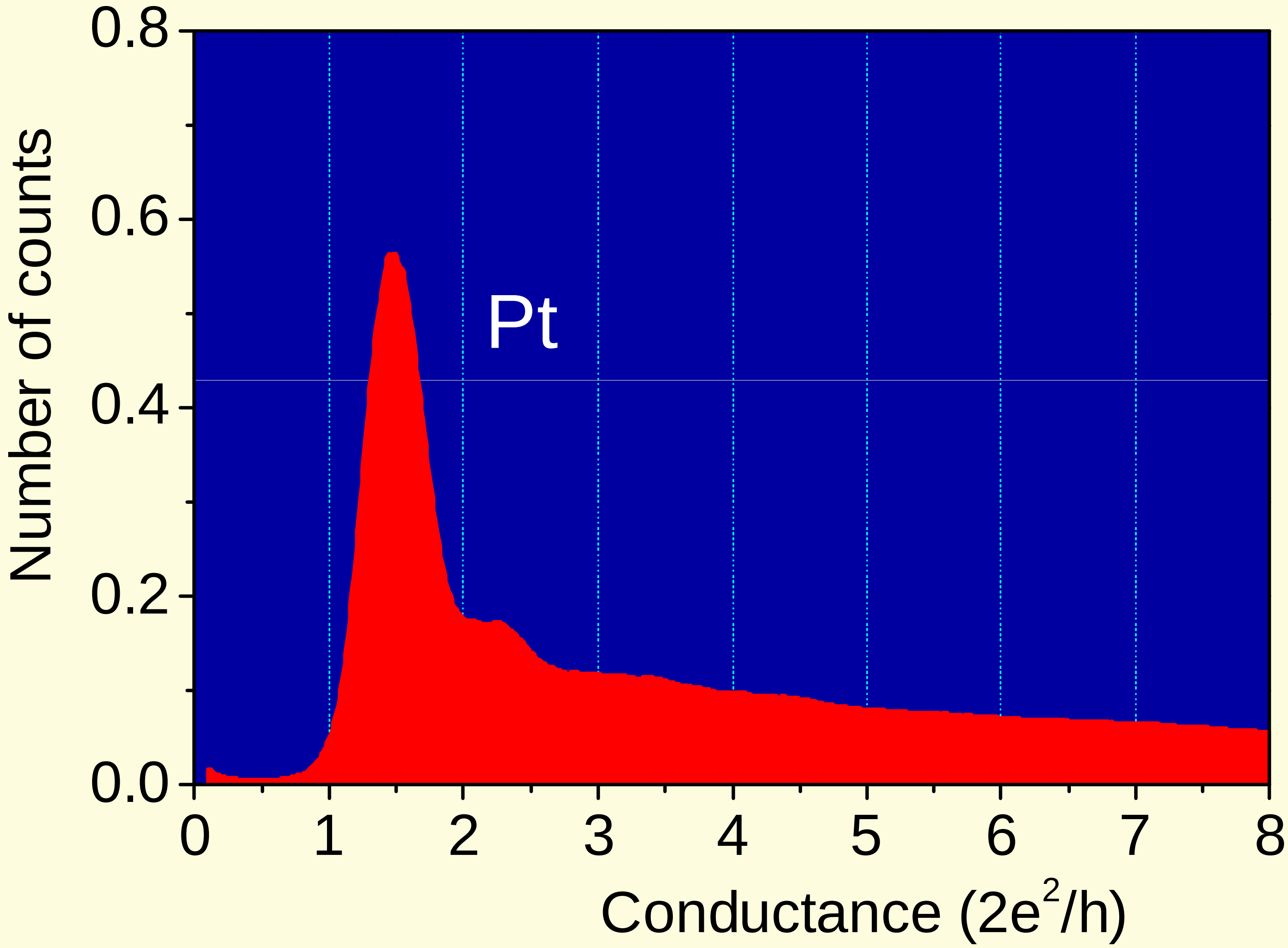


Dipstick

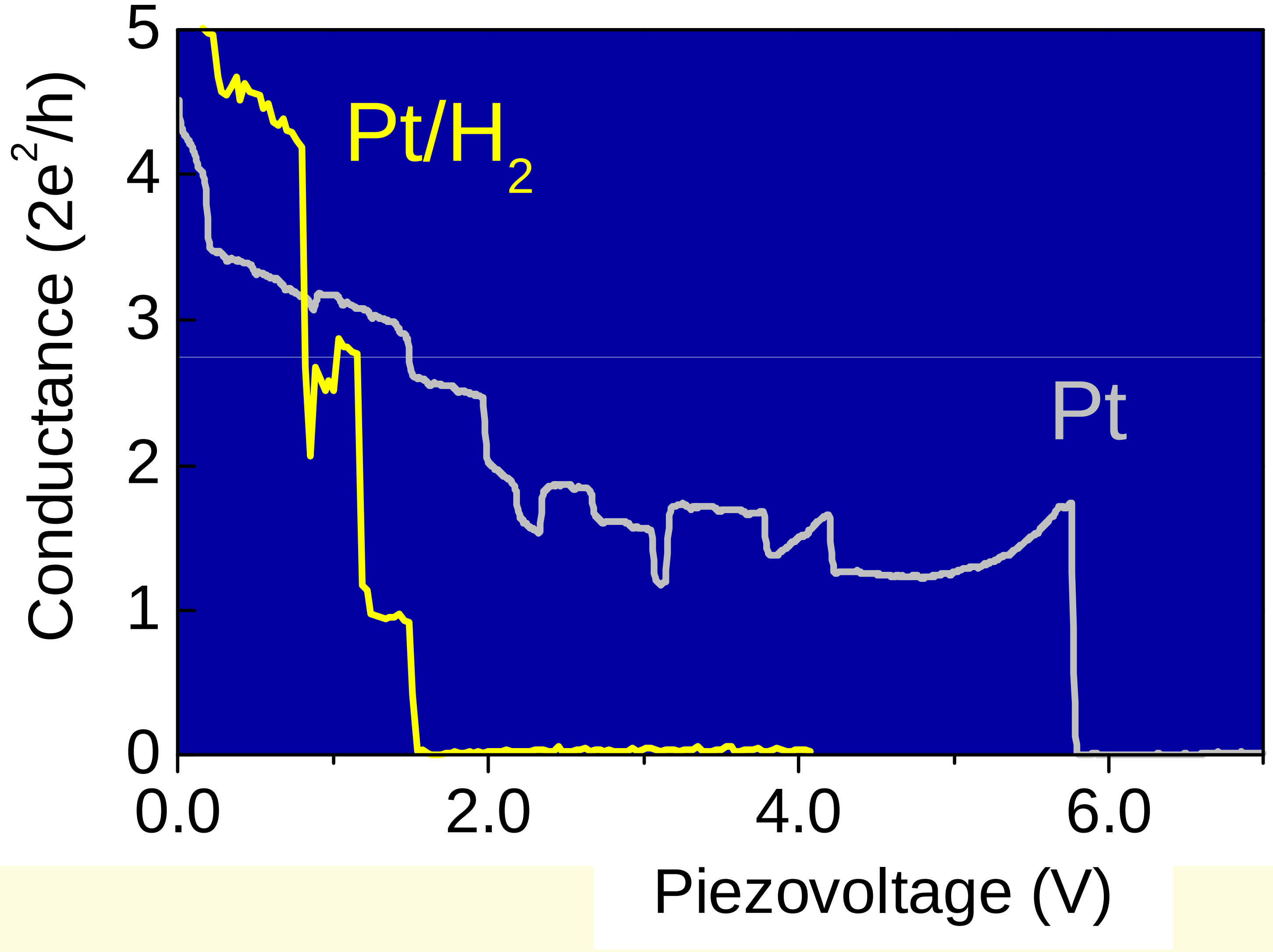
Faraday cage



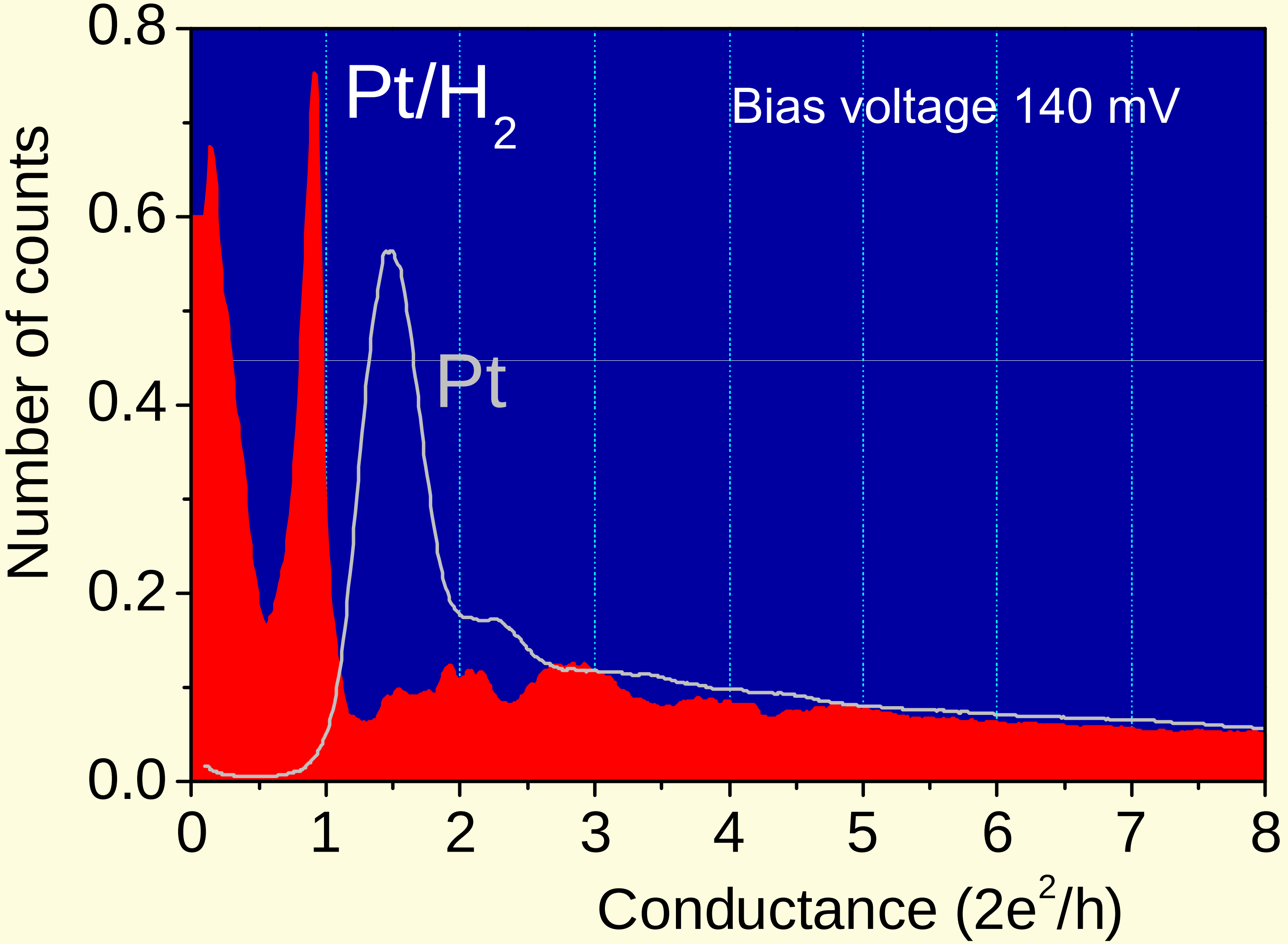
Conductance histogram for Pt



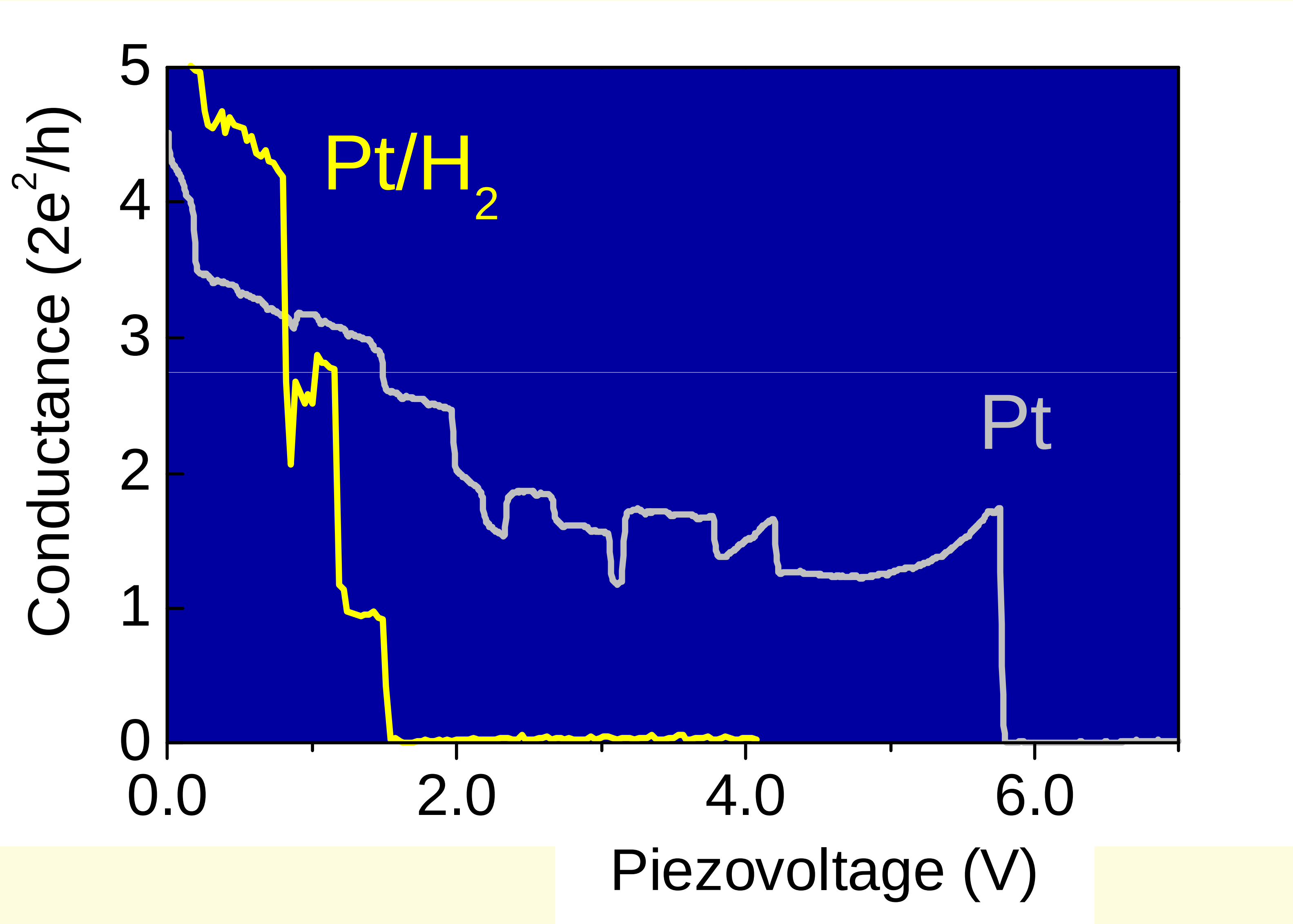
Conductance curve for Pt/H_2



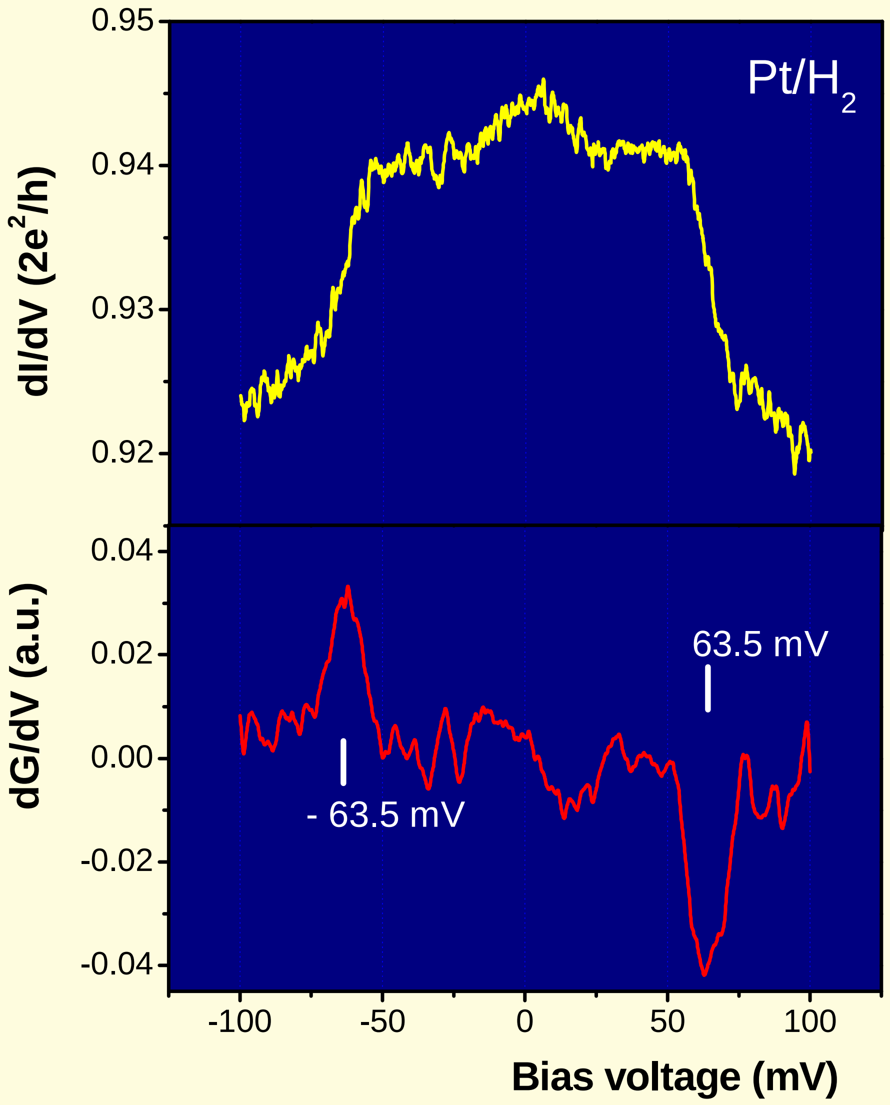
Conductance histogram for Pt/H_2



Conductance curve for Pt/H_2



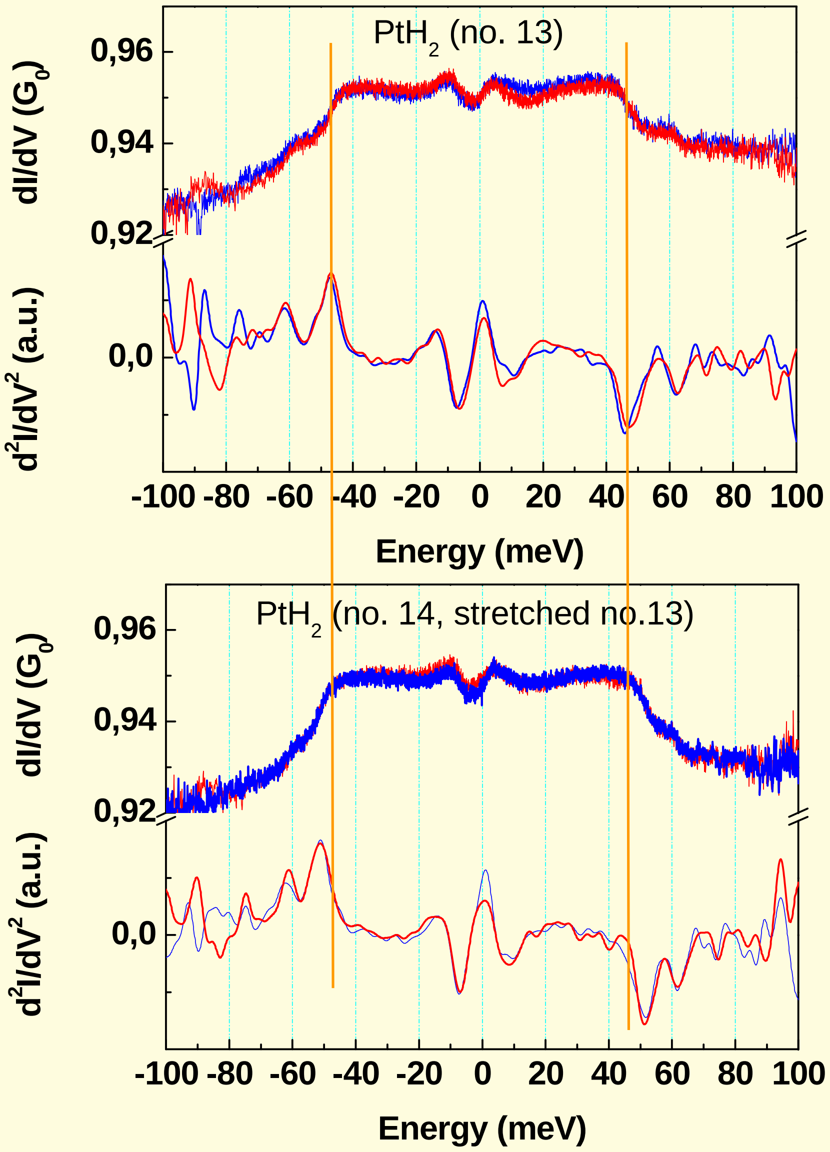
Point contact spectrum for Pt/H_2



Modulation: 1 mV, 7 kHz
Recording time: 10 s
Temperature: 4.2 K

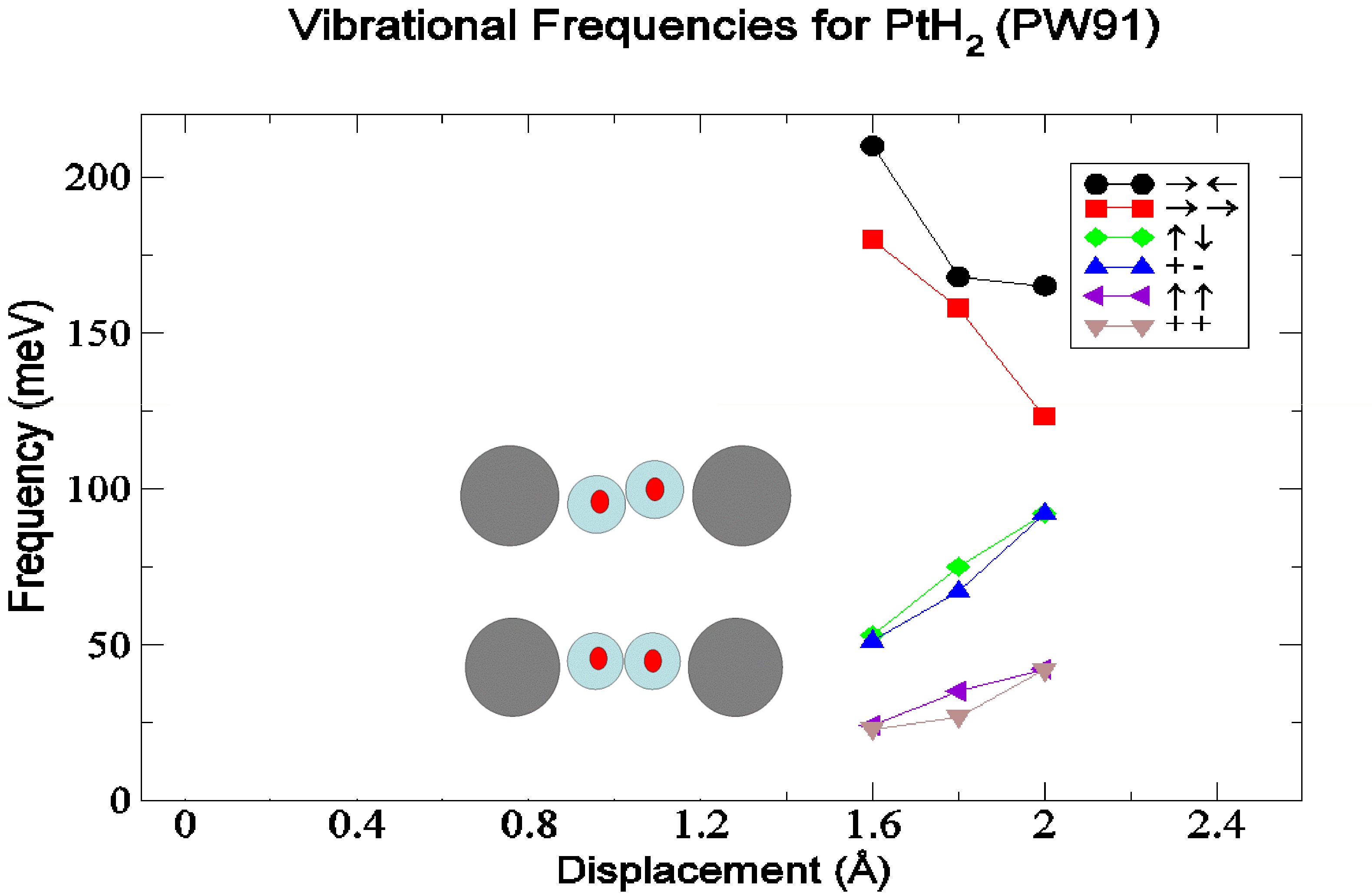
R.H.M. Smit, Y. Noat, C. Untiedt, N.D. Lang, M. van Hemert & JMvR, Nature **419** (2002) 906

Pt-H_2: Frequencies and stretching dependence



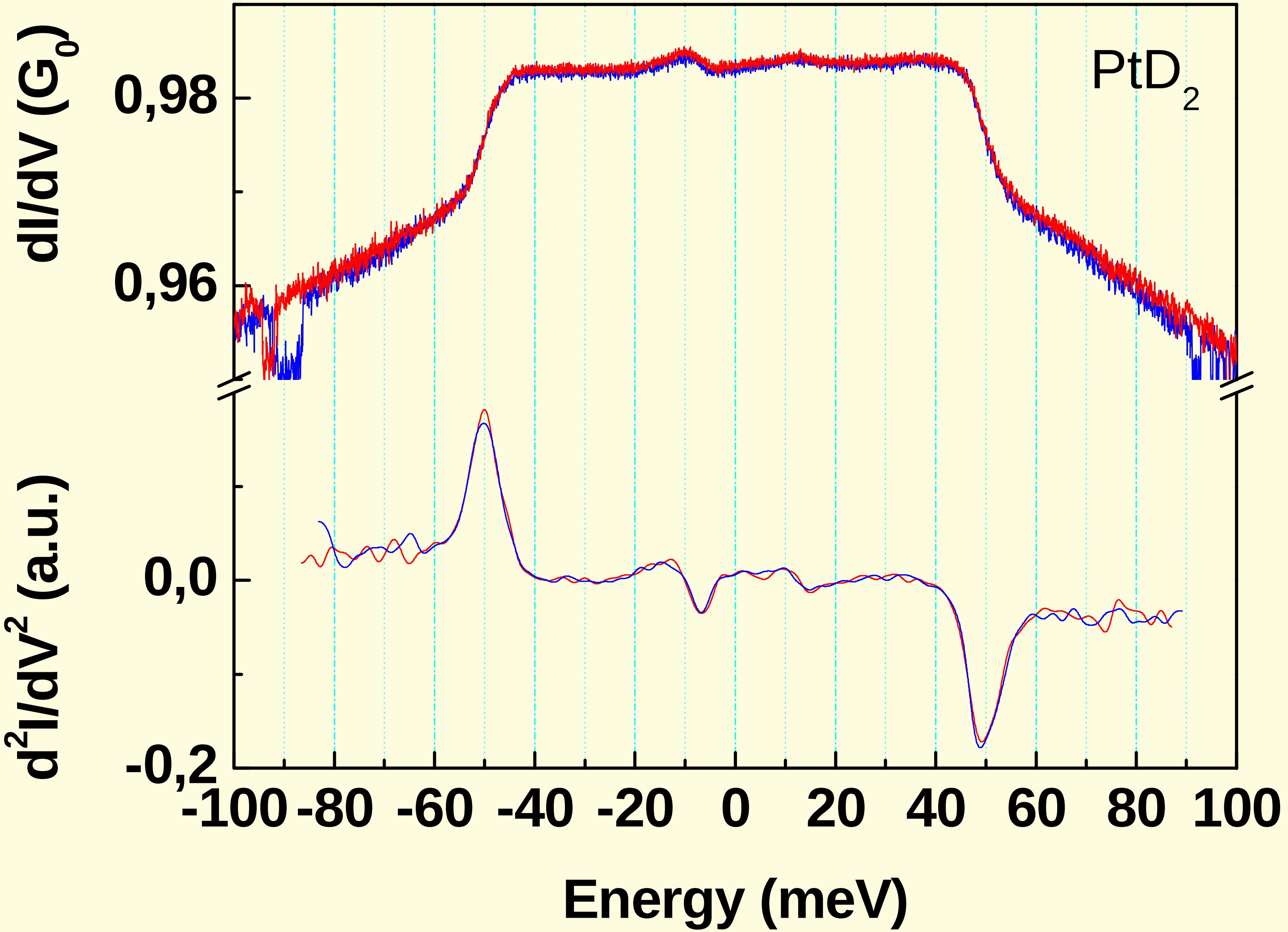
D. Djukic, K.S. Thygesen,
C. Untiedt, R.H.M. Smit,
K.W. Jacobsen and JMvR,
Phys. Rev. B, **71** (2005) 161402

DFT calculations

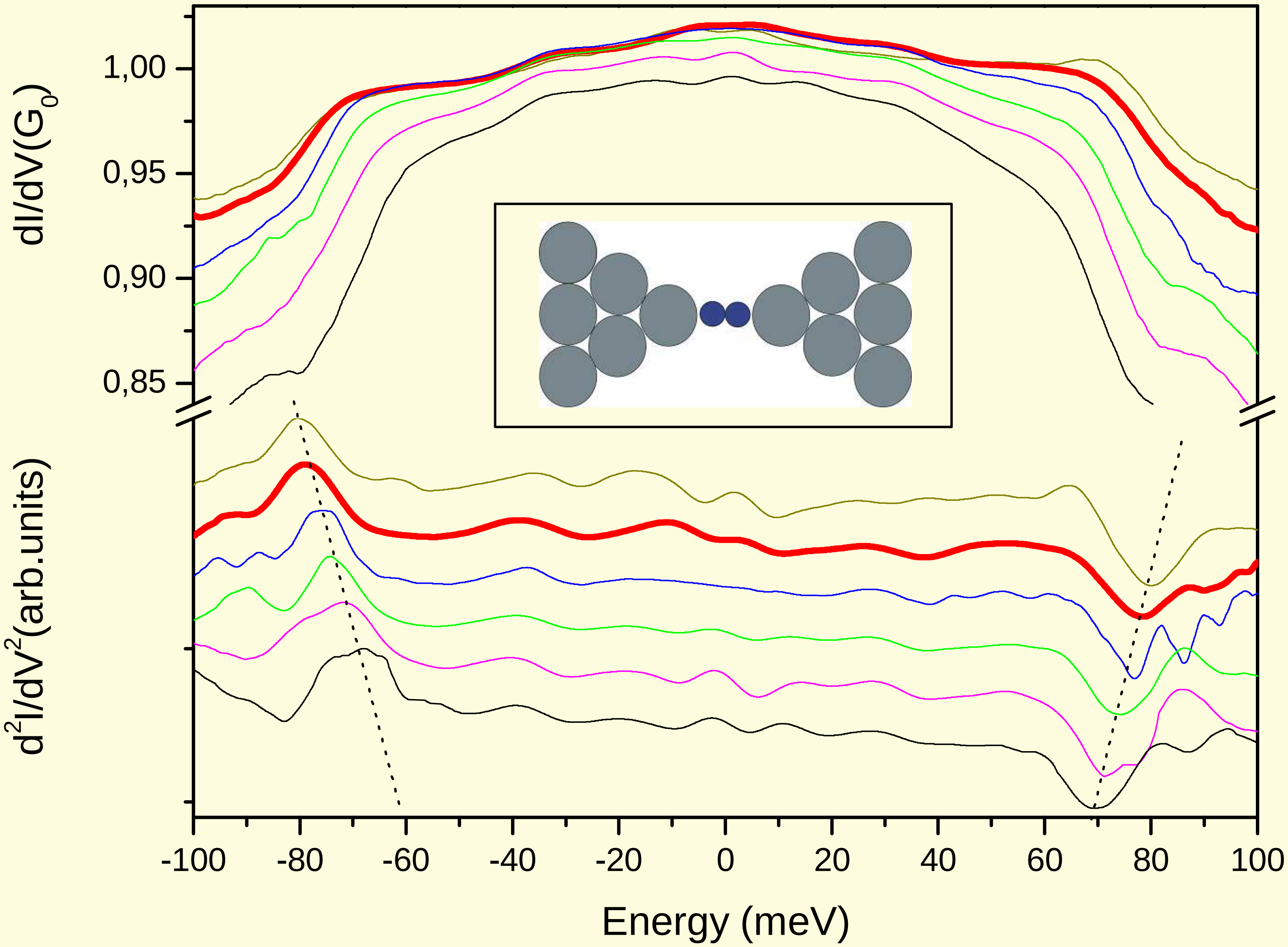


D. Djukic, K.S.Thygesen, K.W. Jacobsen, *et al.*, Phys. Rev. B, **71** (2005) 161402(R)

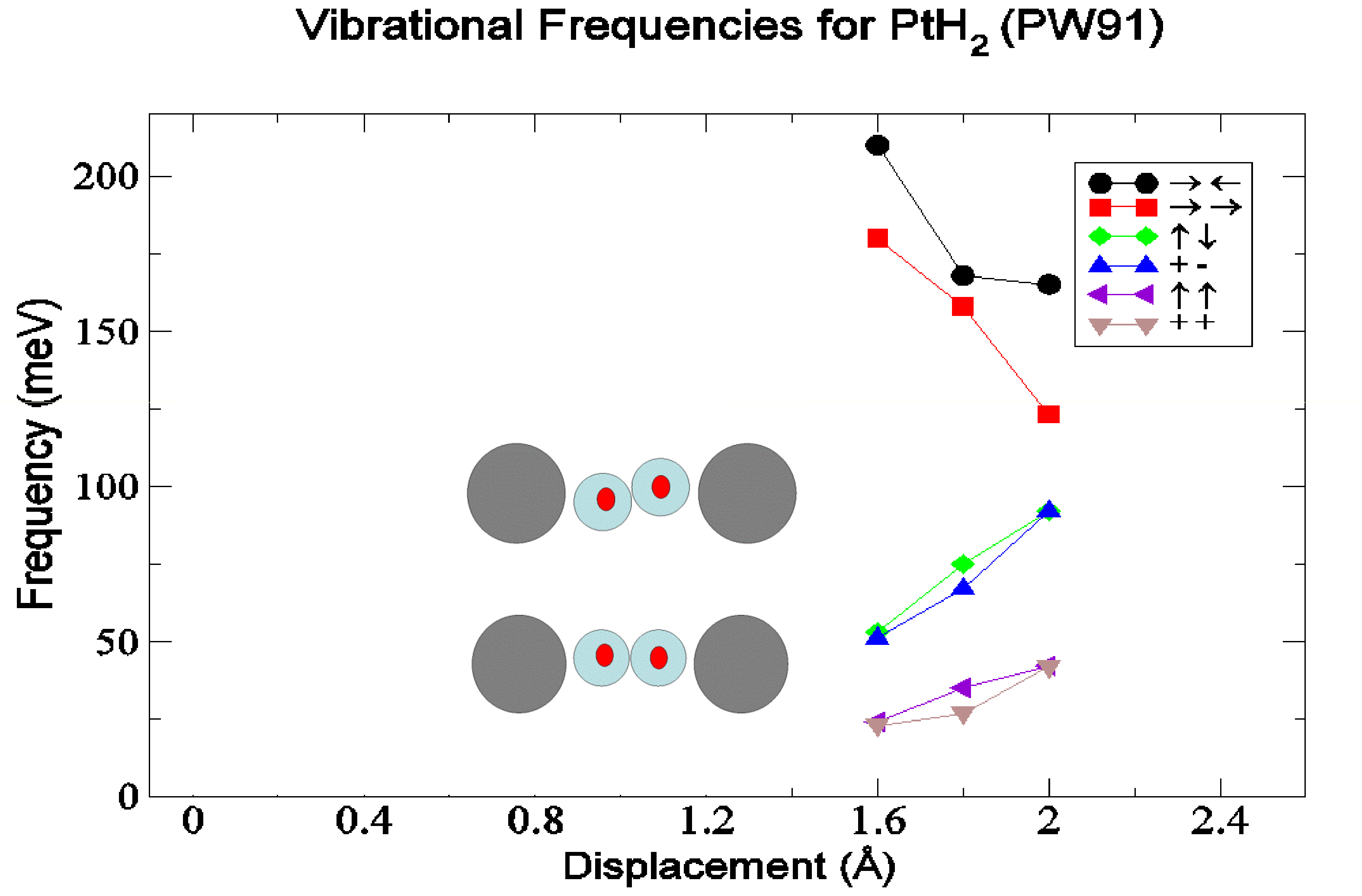
Vibration modes for Deuterium, Pt–D_2–Pt



The longitudinal mode for Pt-D_2-Pt

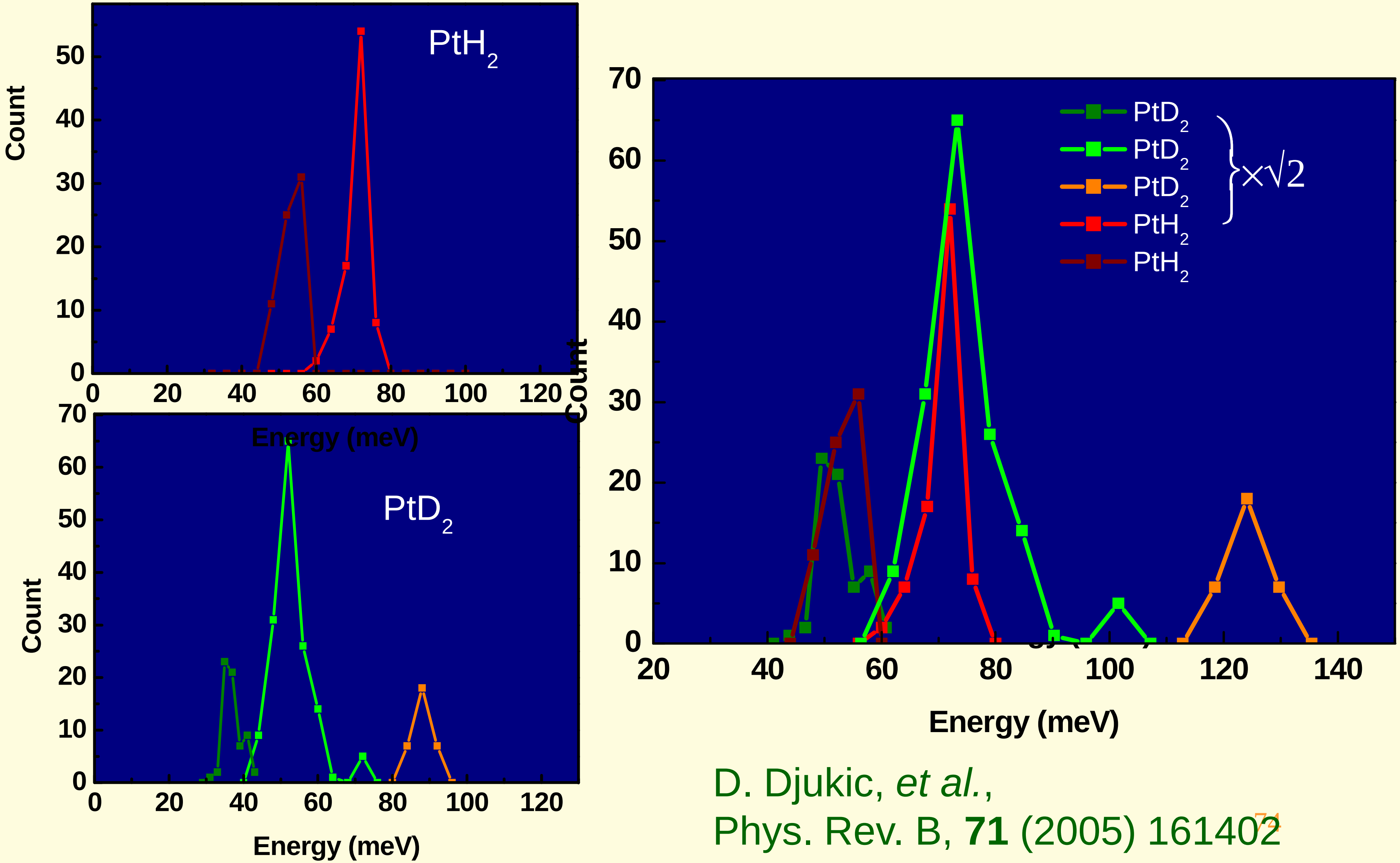


DFT calculations


Vibrational Frequencies for PtH_2 (PW91)

D. Djukic, K.S.Thygesen, K.W. Jacobsen, *et al.*, Phys. Rev. B, **71** (2005) 161402(R)

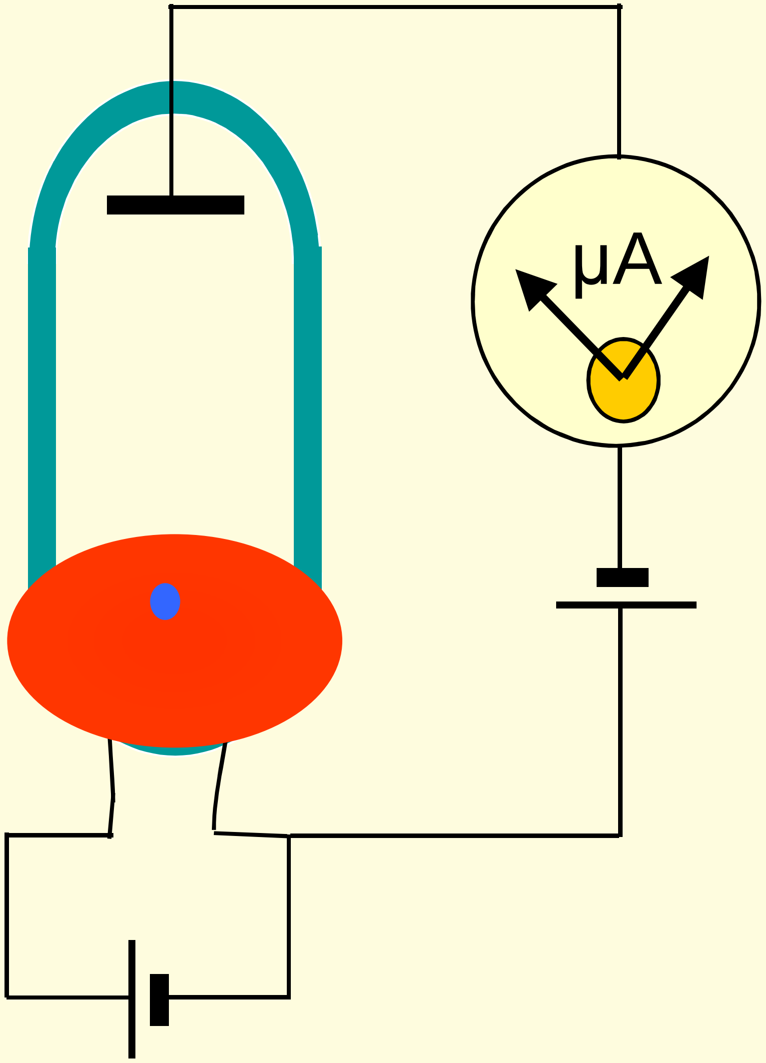
Comparison H_2 and D_2



D. Djukic, *et al.*,
Phys. Rev. B, **71** (2005) 161402

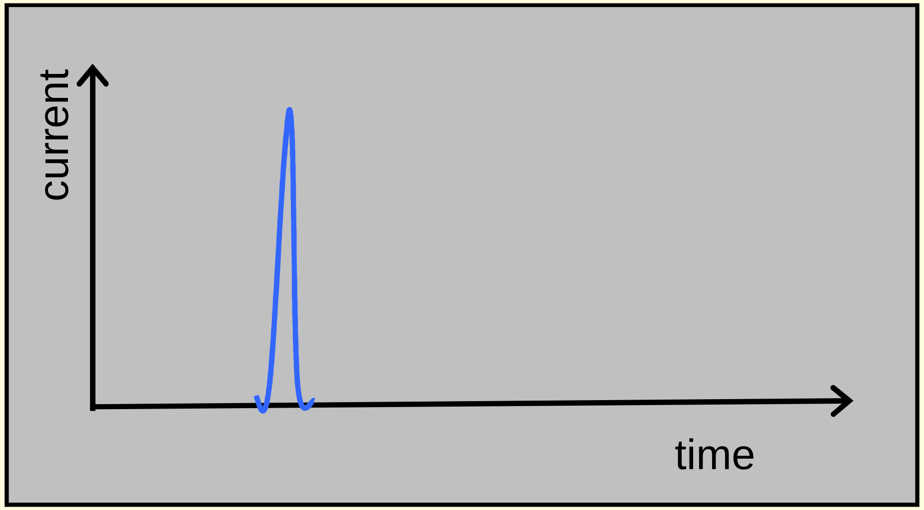
Shot noise

Shot noise

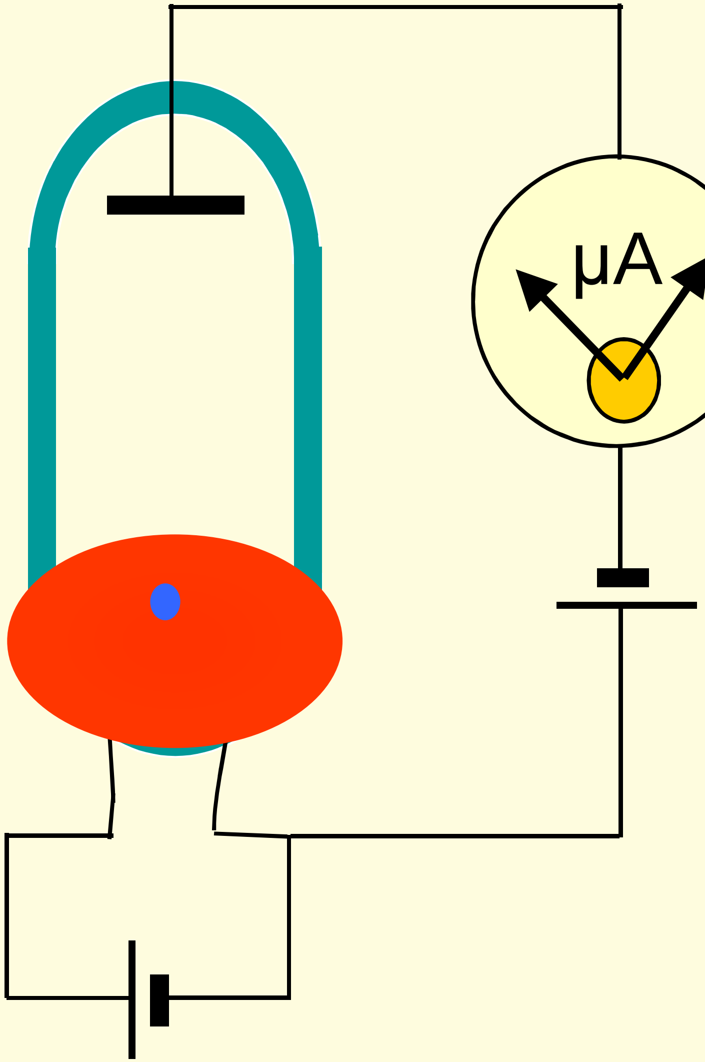


Vacuum diode

W. Schottky (1918)



Shot noise



Vacuum diode

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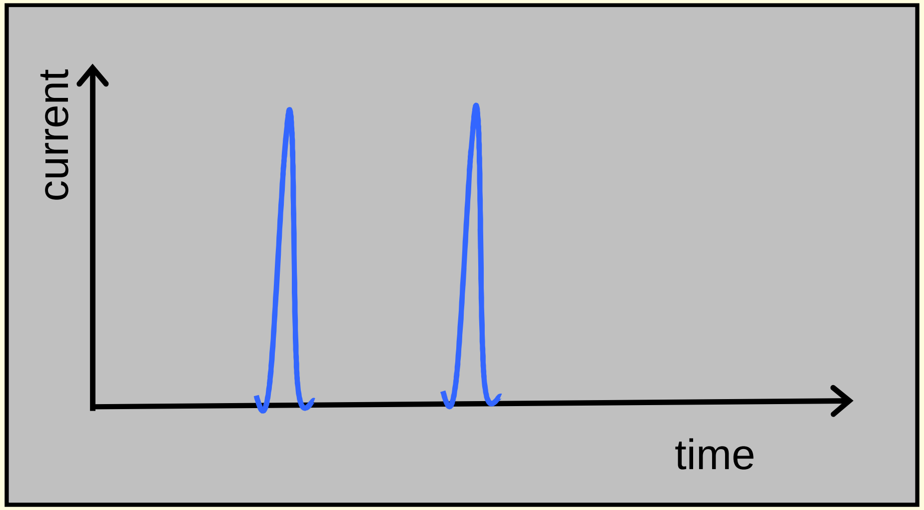
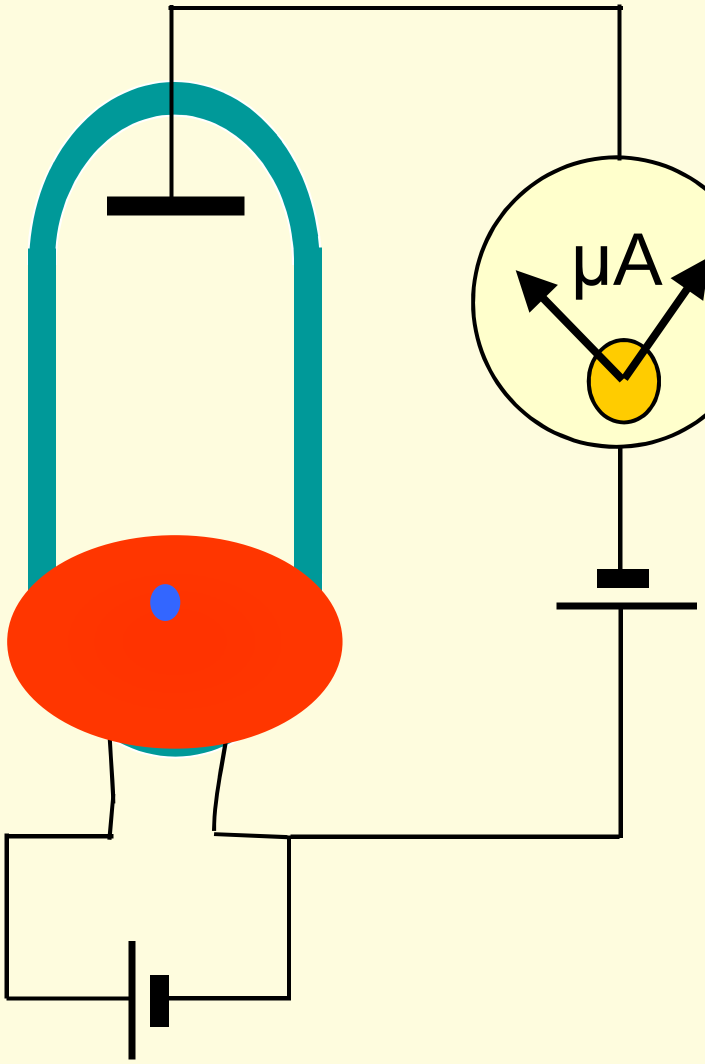


Shot noise



Vacuum diode

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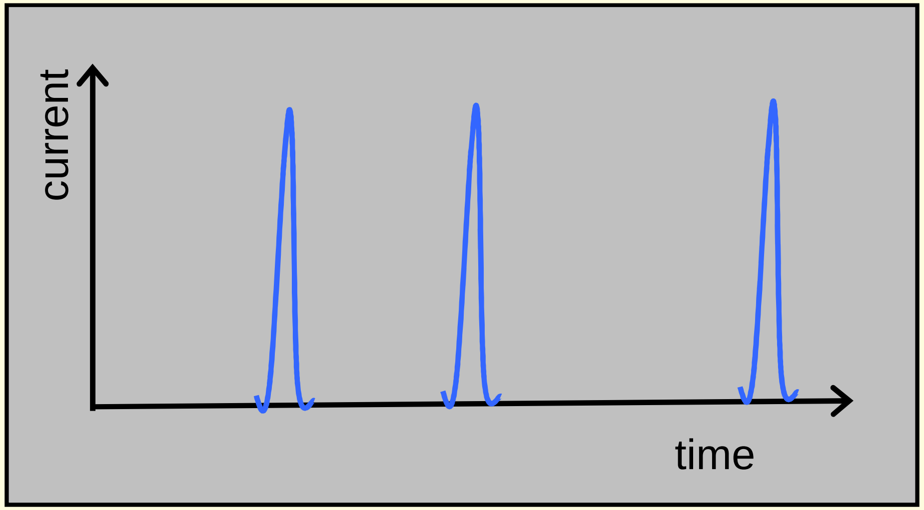
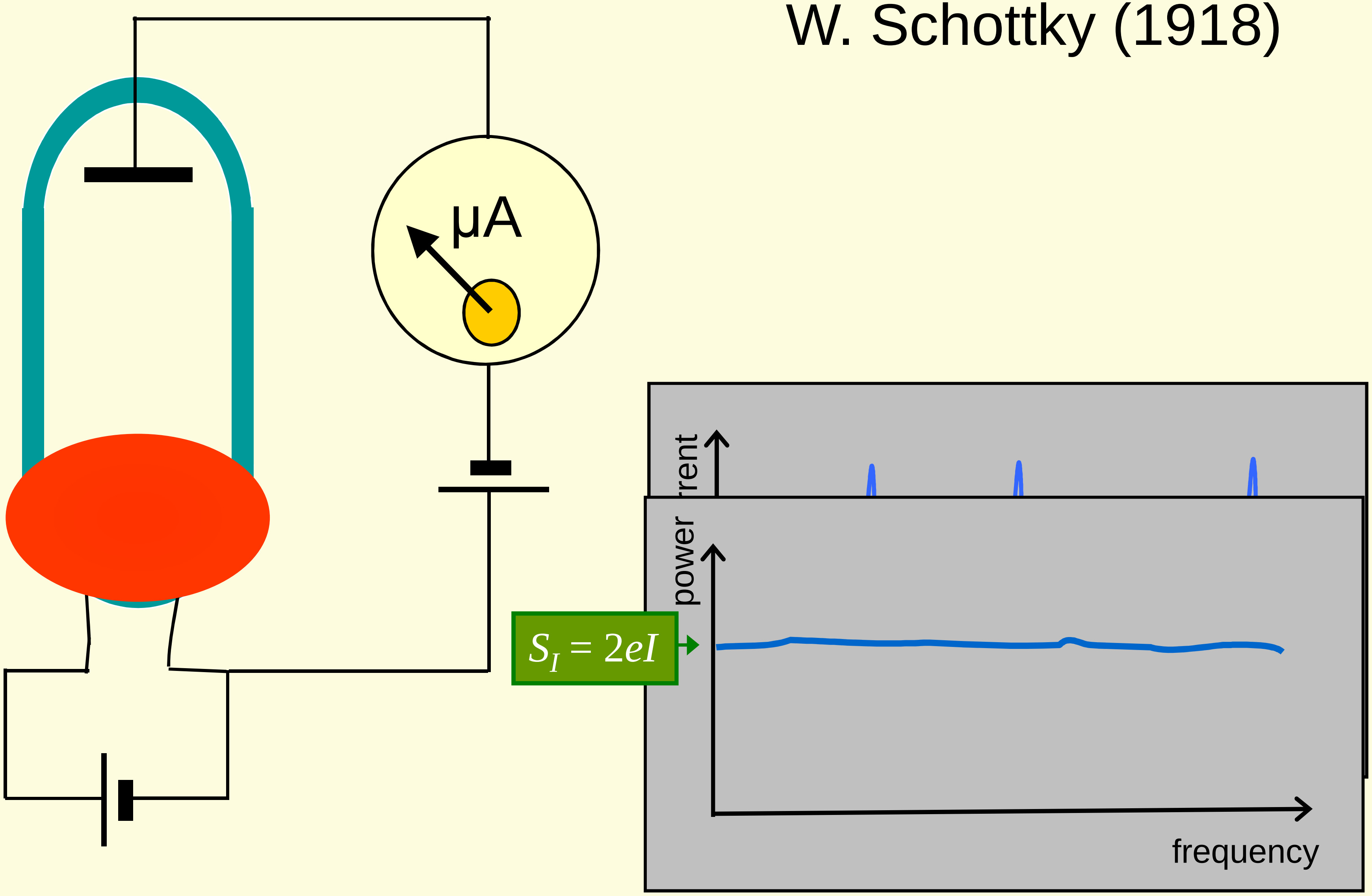


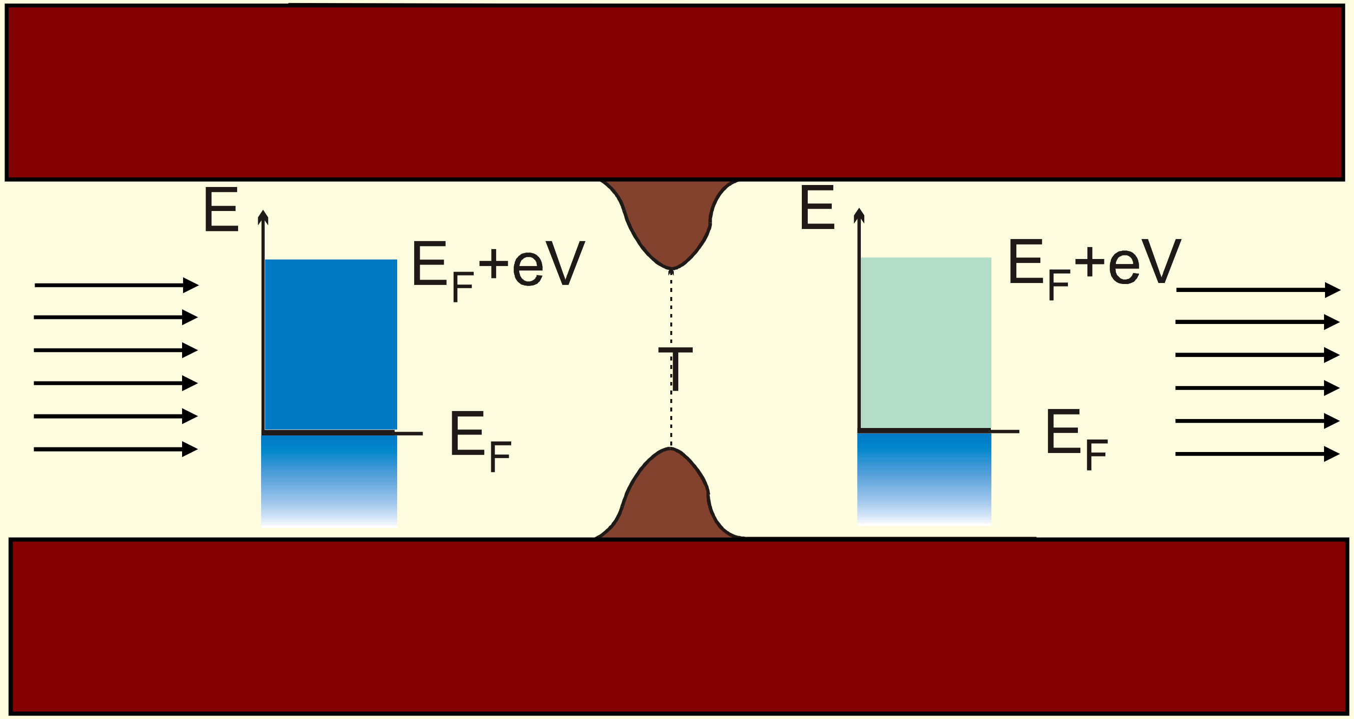
Shot noise

W. Schottky (1918)



$S_I = 2eI$

Transmission probablilites from shot noise



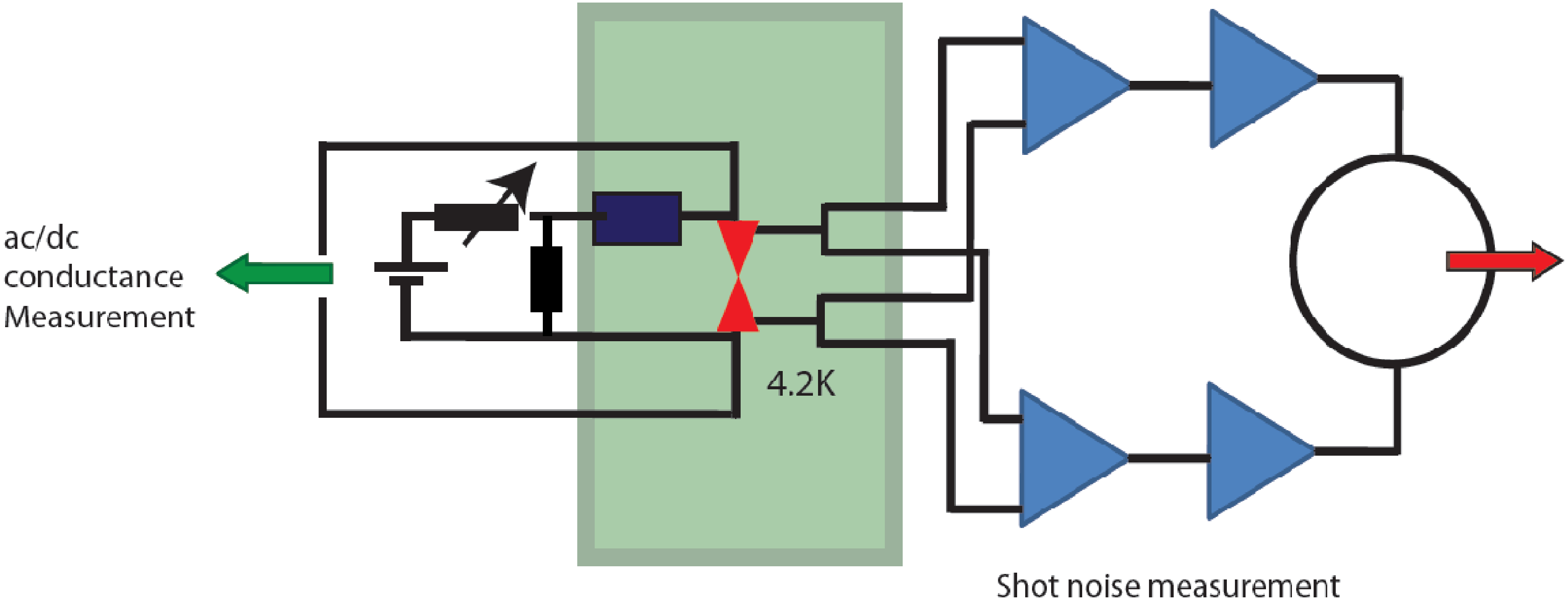
Multiple channels and finite temperature

General expression:

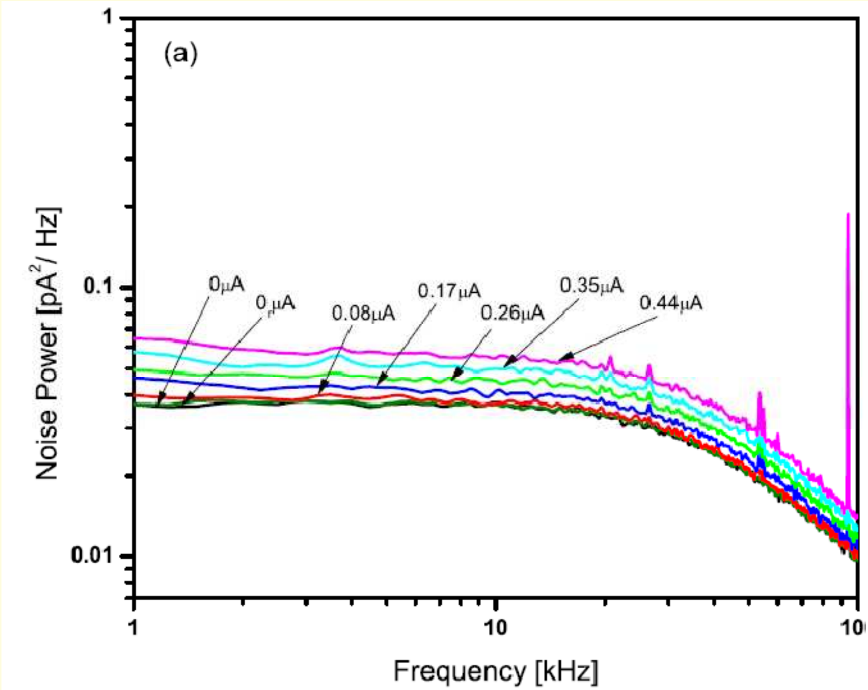
$$S_I = 2eV\frac{2e^2}{h}\coth\left(\frac{eV}{2k_BT}\right)\sum_n T_n(1-T_n)+4k_BT\frac{2e^2}{h}\sum_n T_n^2$$

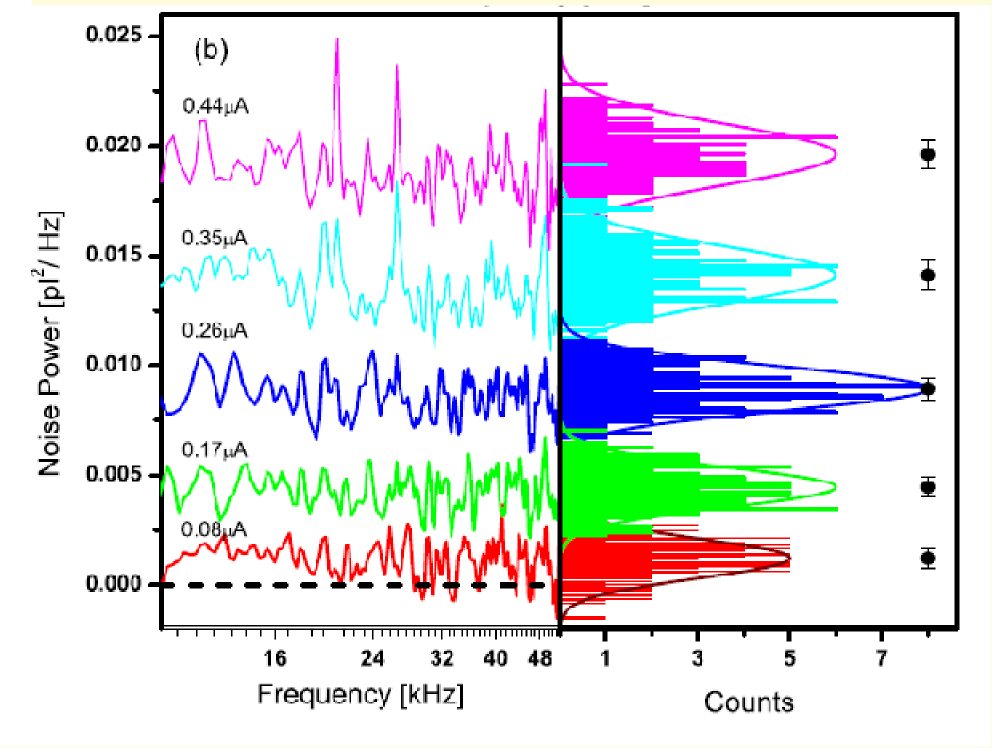
V.A. Khlus, Sov. Phys. JETP **66** (1987) 592
G.B. Lesovik, JETP Lett. **49** (1989) 592
M. Büttiker, Phys. Rev. Lett. **65** (1990) 2901

Experimental technique

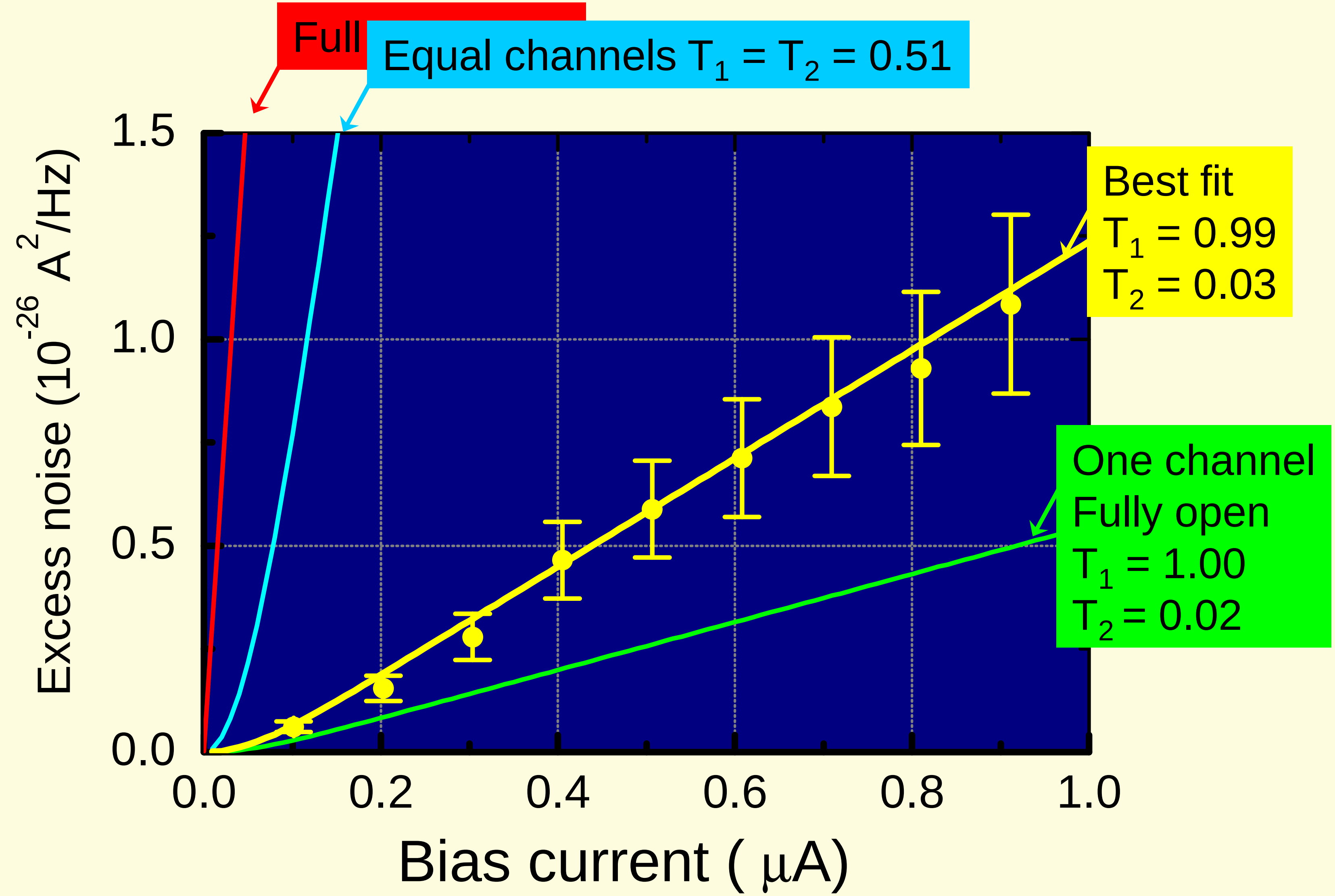


Noise signal analysis





Shot noise as a function of current, Au atomic contact at $G=1.02\ G_0$



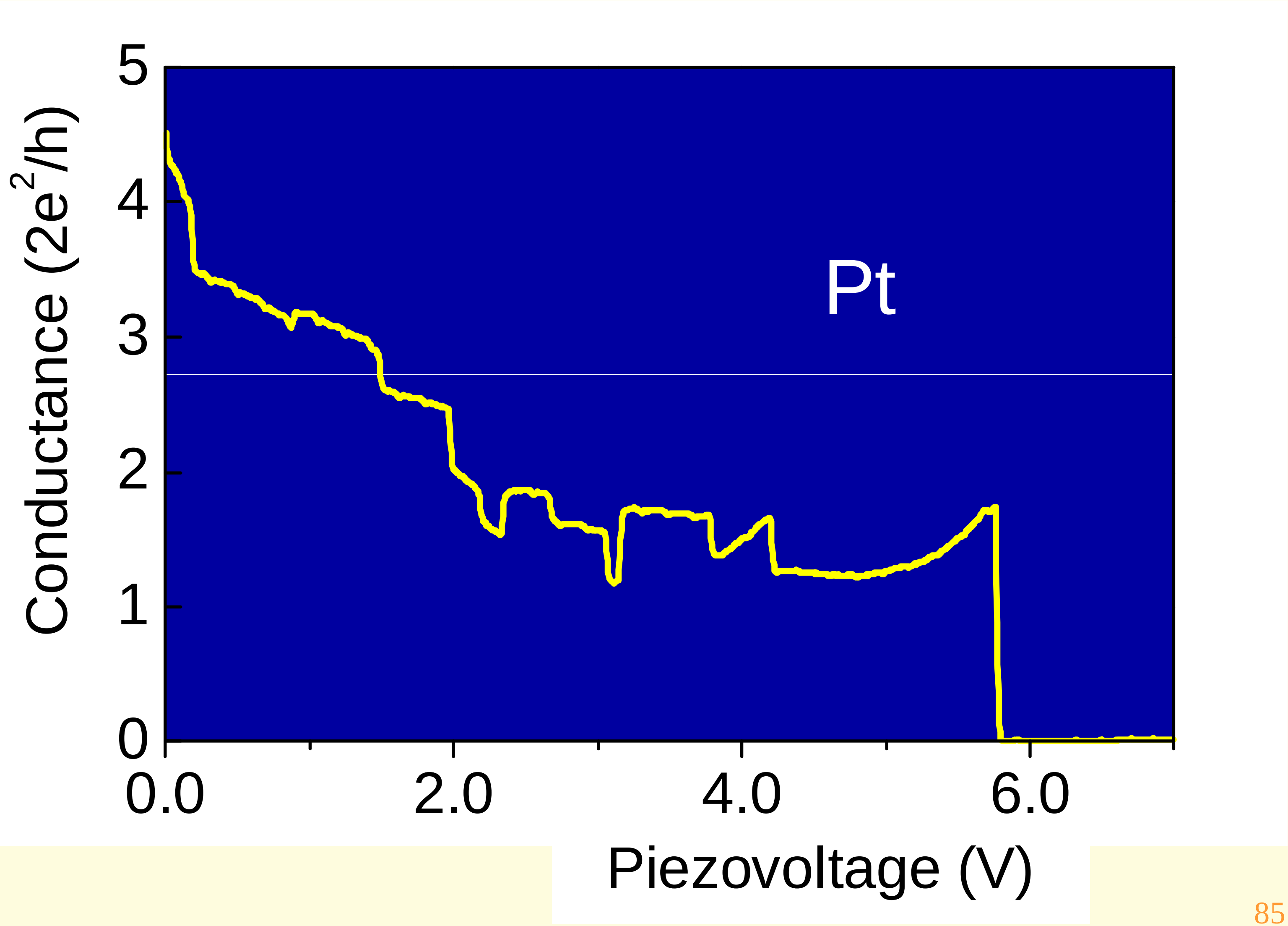
Full

Equal channels $T_1 = T_2 = 0.51$

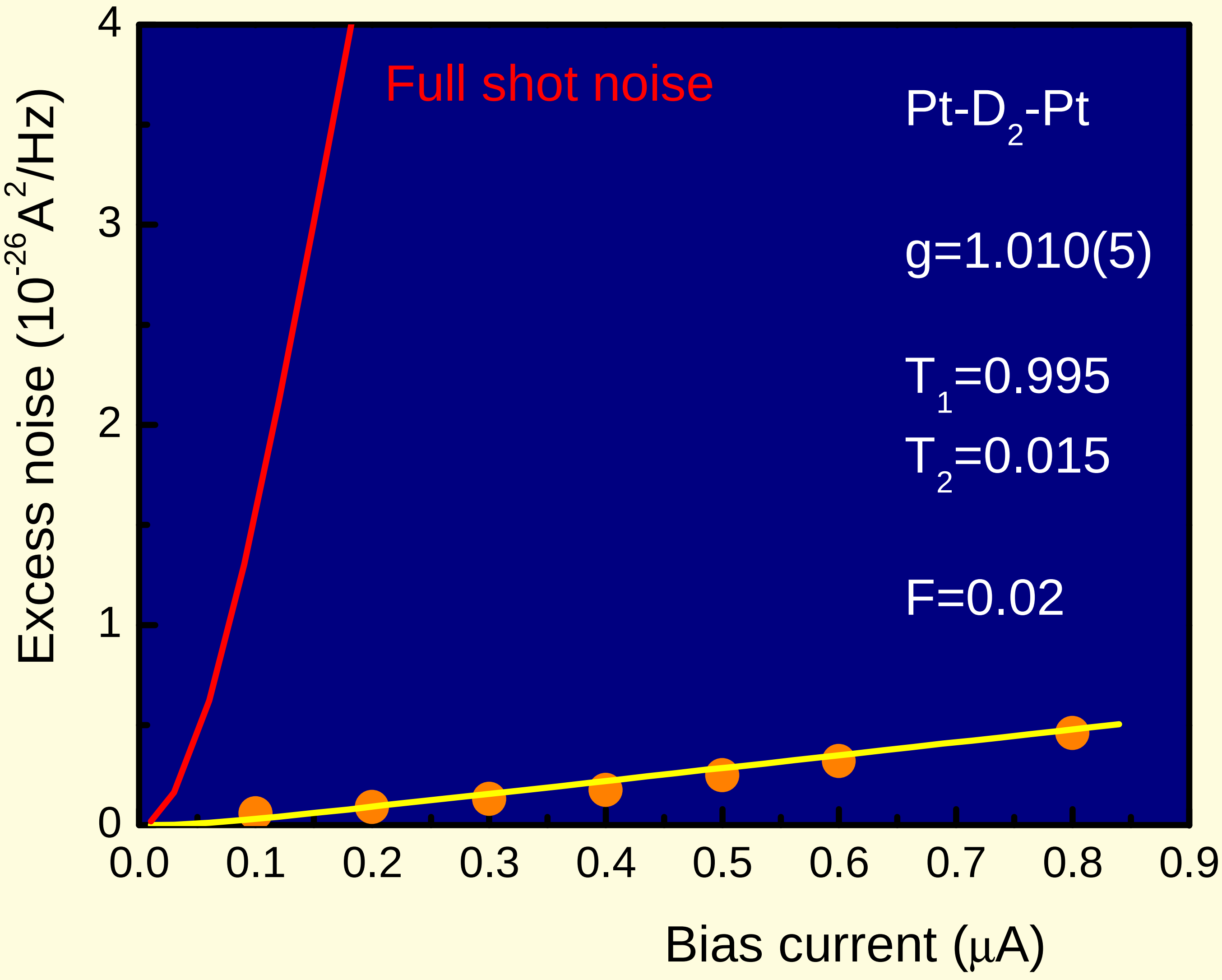
Best fit
$T_1 = 0.99$
$T_2 = 0.03$

One channel
Fully open
$T_1 = 1.00$
$T_2 = 0.02$

Conductance curve for Pt



Shot noise on Pt-D_2 junctions

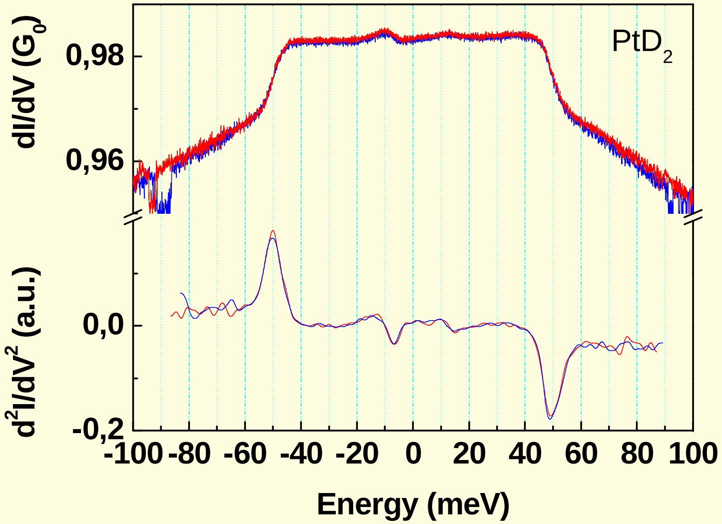


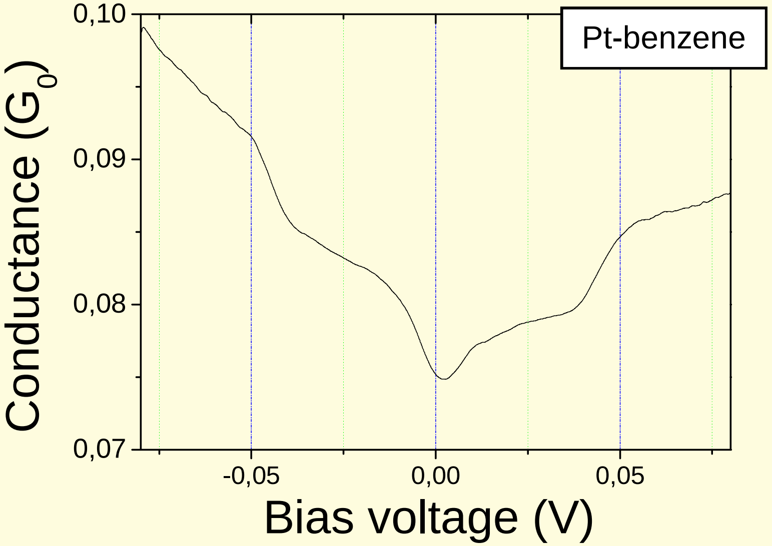
D. Djukic & JMvR, Nano Lett. **6** (2006)

Special topic:

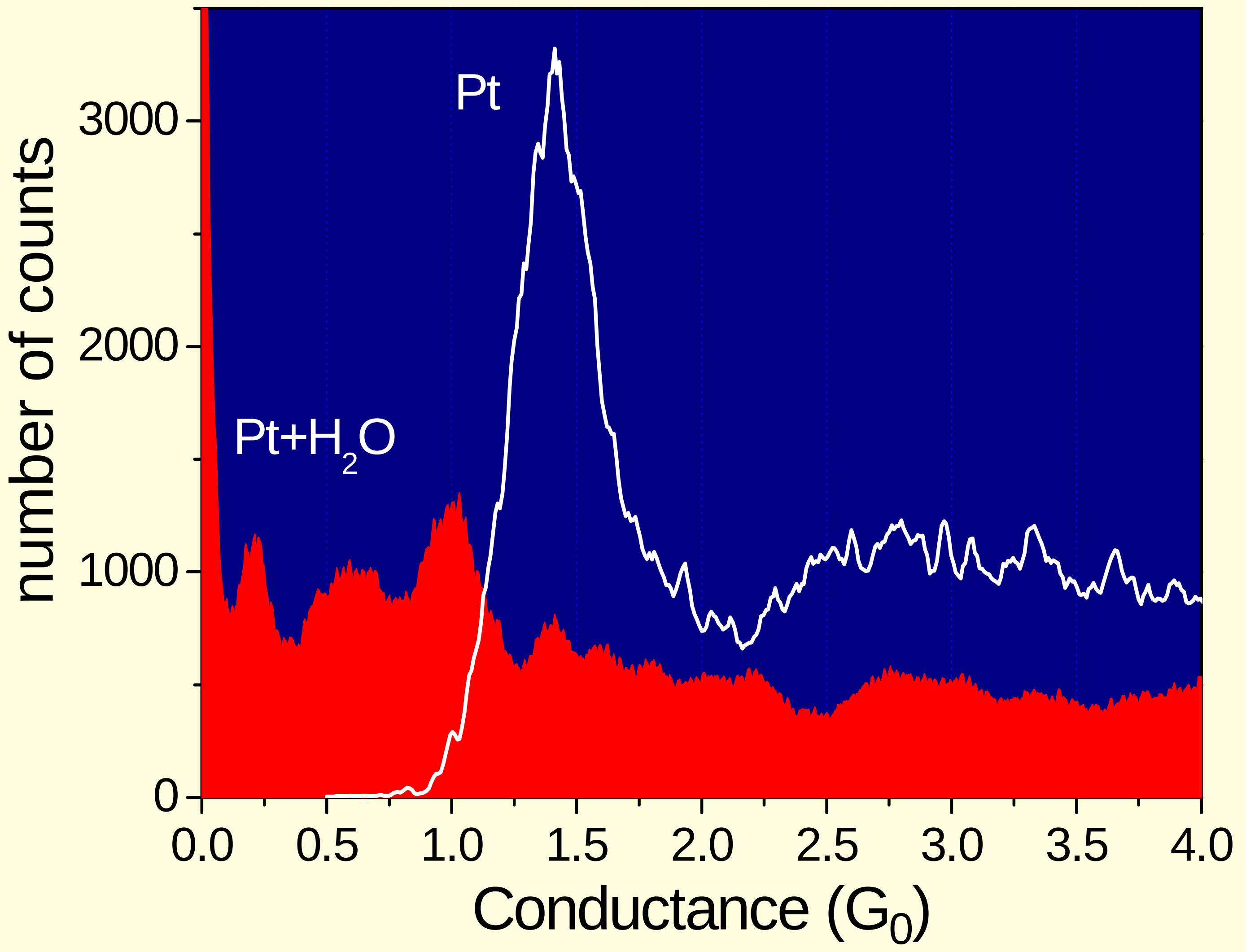
cross over between IETS and PCS

Appearance of vibration mode features in experiment

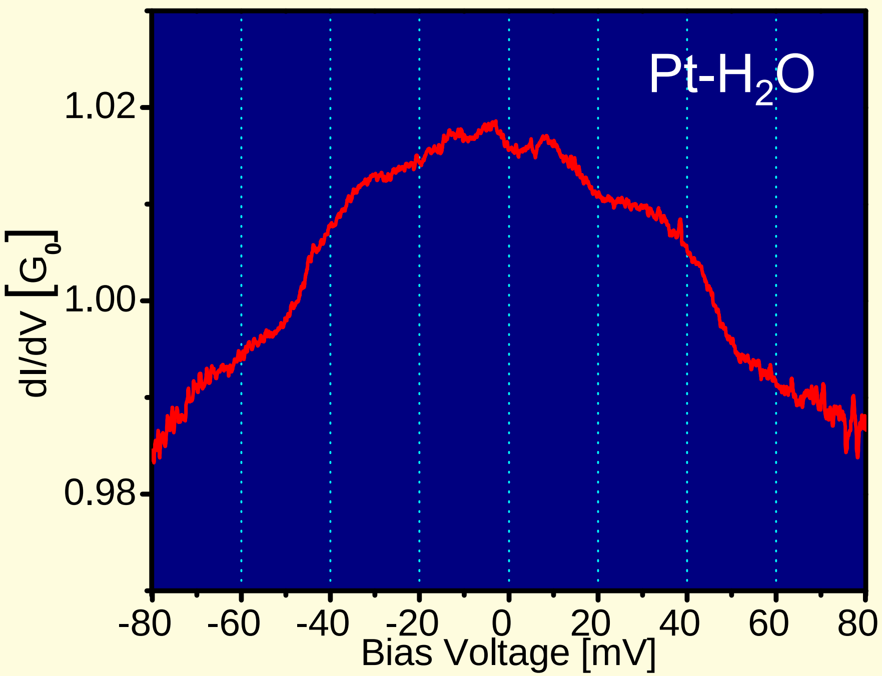


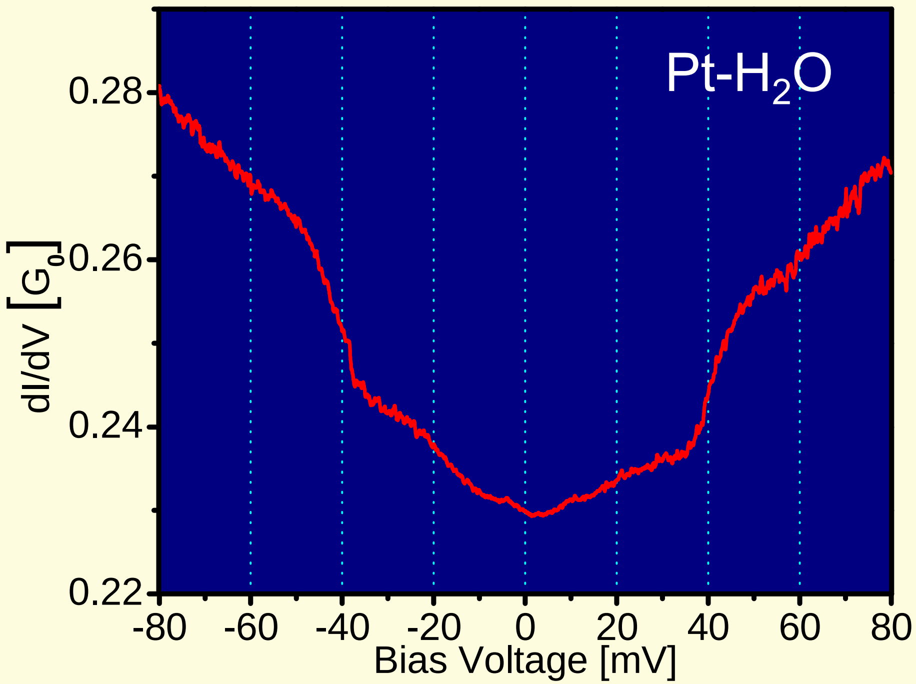


H_2O between Pt leads



Spectra at high and low conductance for Pt/H_2O

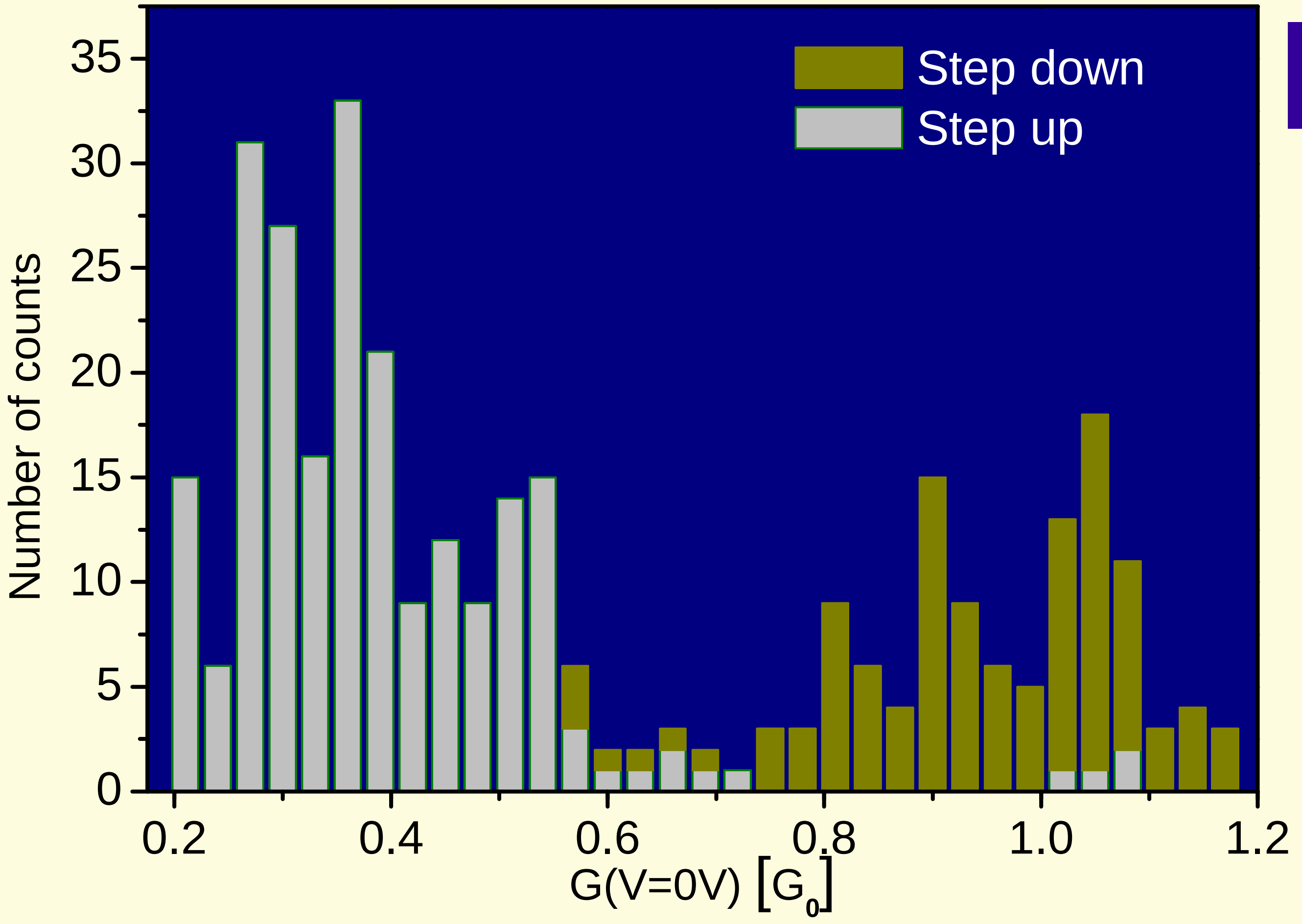




G=1.02 G_0

G=0.23 G_0

Crossover between PCS and IETS

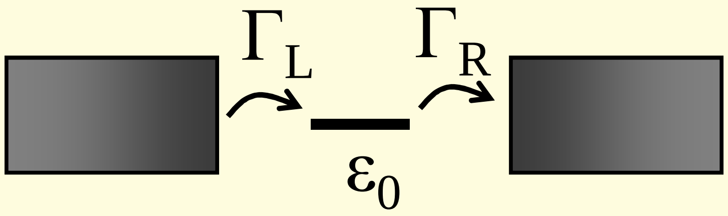


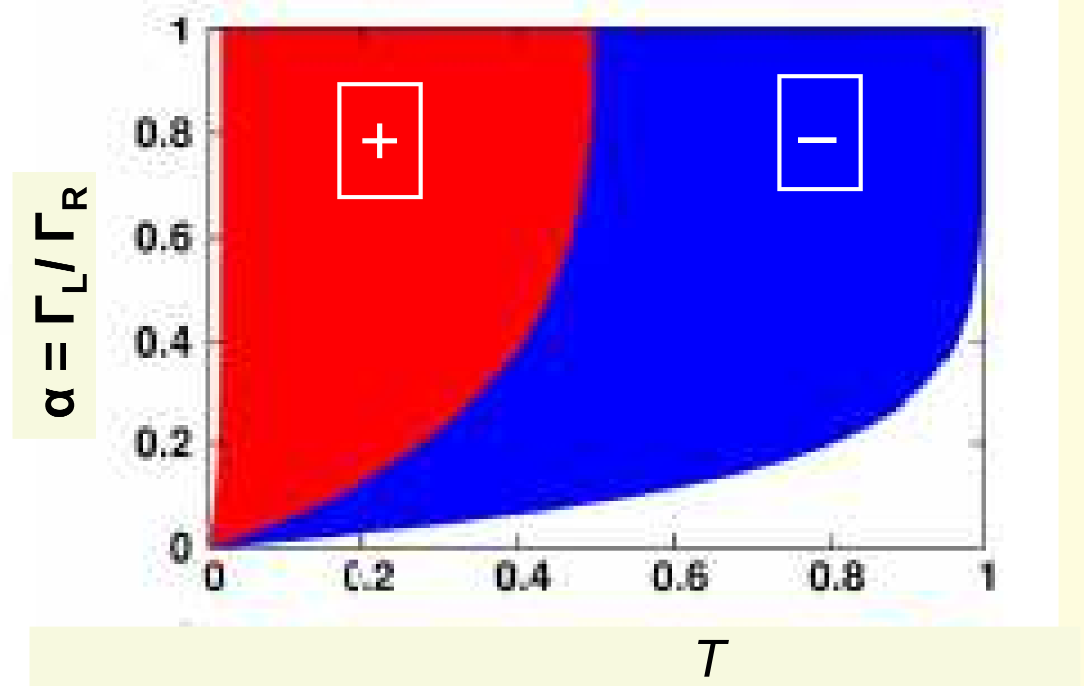
Pt-H_2O

Crossover at ~0.55–0.65 (> 0.5). Do we have a single channel?

O. Tal, M. Krieger, B. Leerink, & JMvR, Phys Rev Lett **100**, 196804 (2008)

Inelastic signals in the conductance





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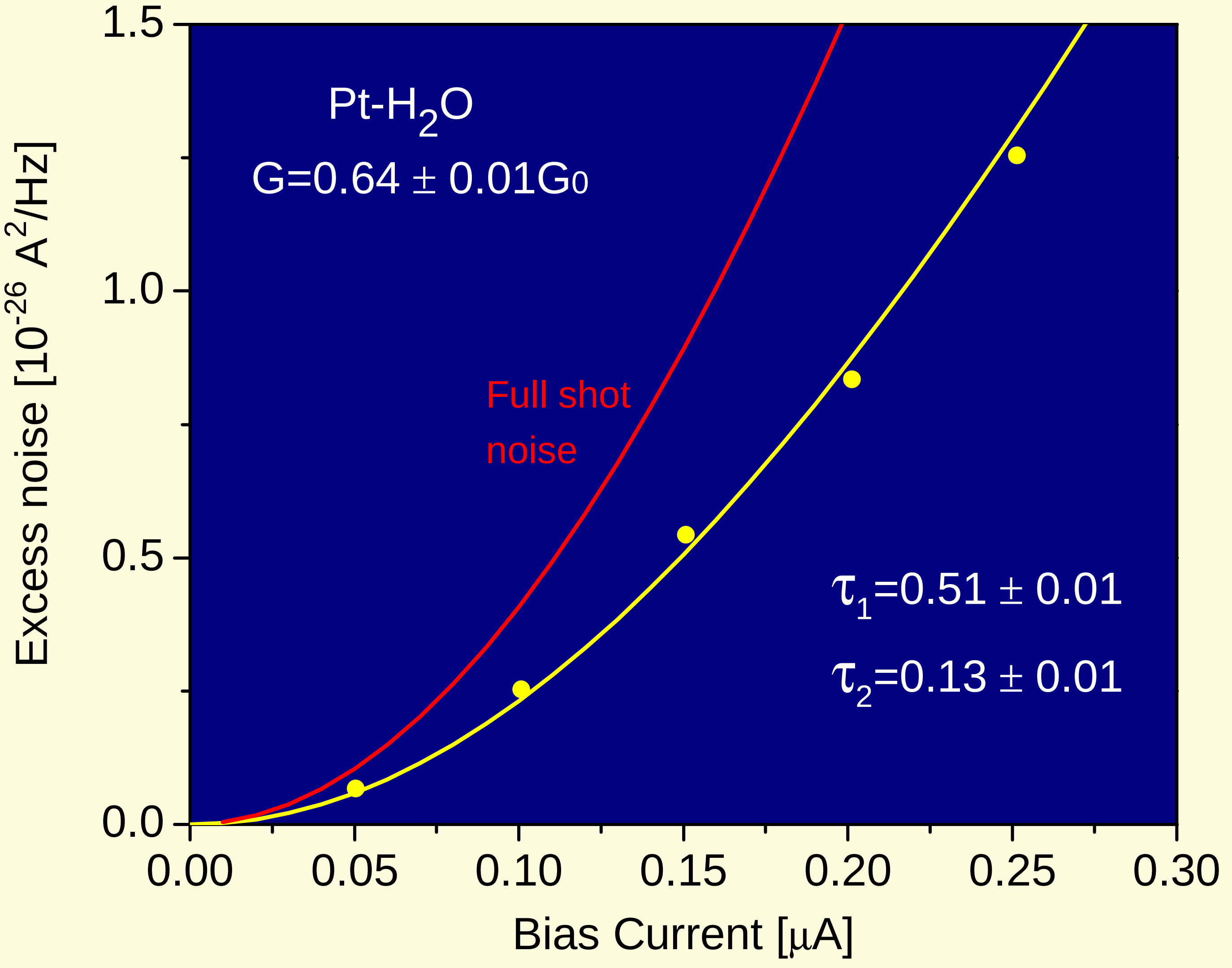
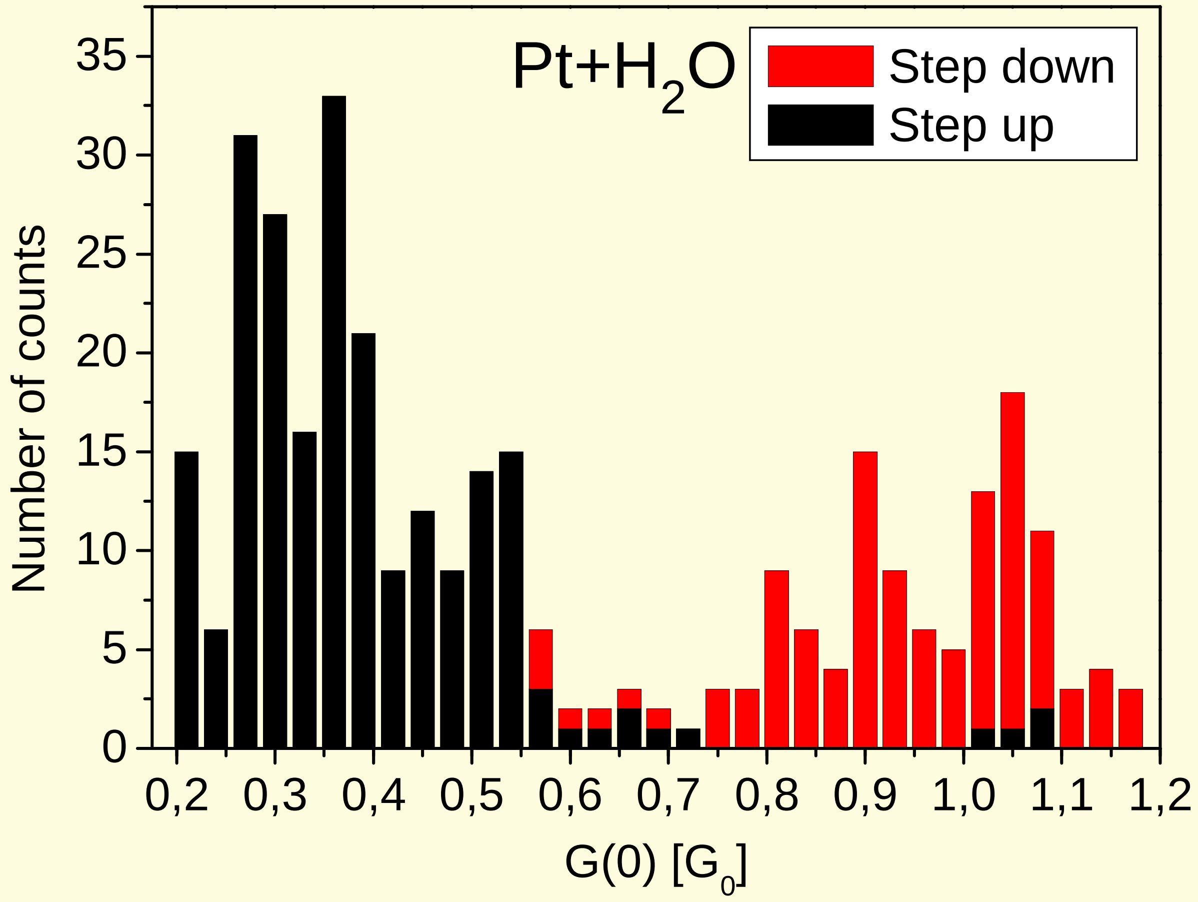
The transmission of the conductance channels from shot noise



Cross over between PCS and IETS



Crossover at G~0.55–0.65. The main channel crosses 0.5

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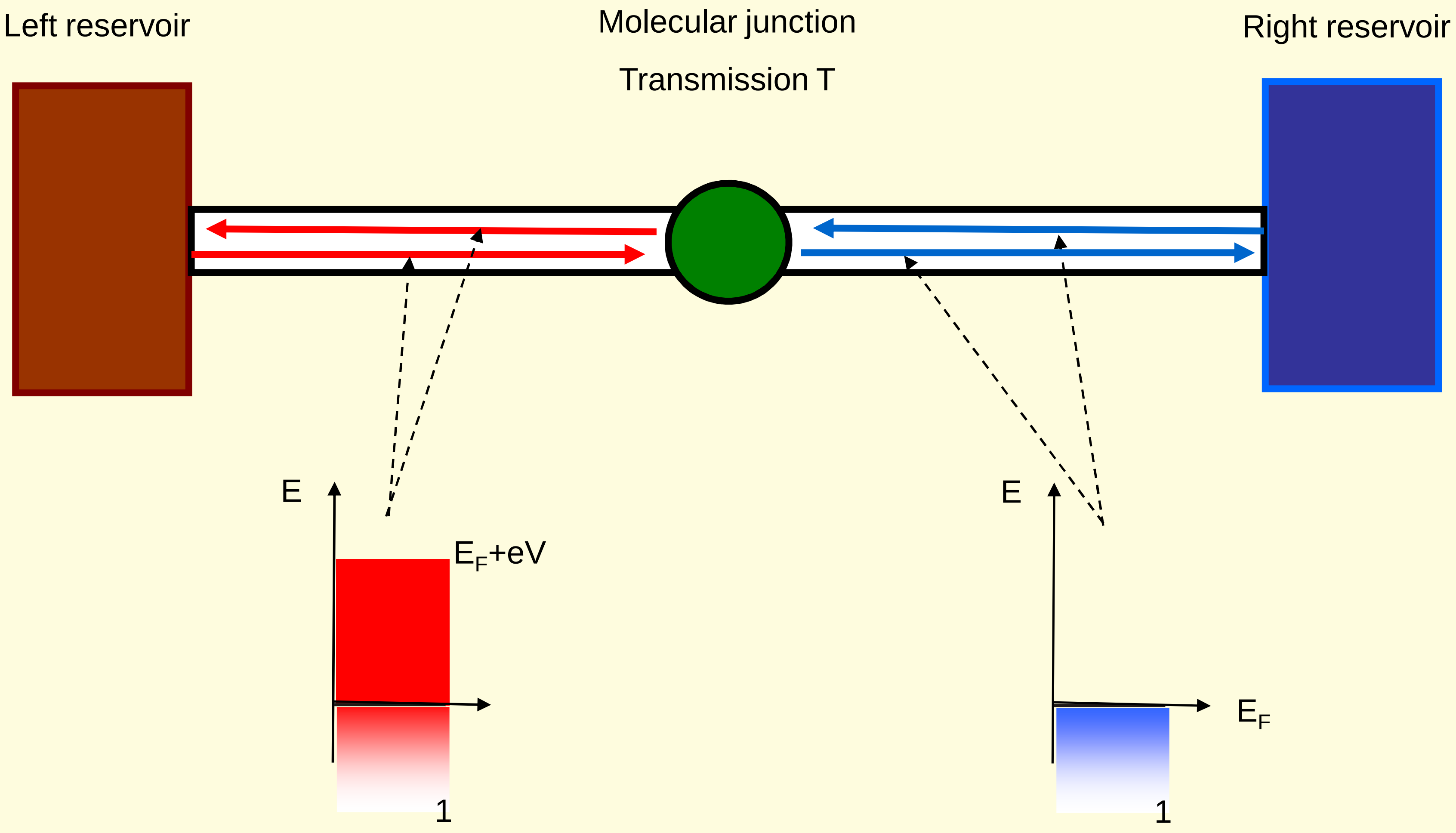
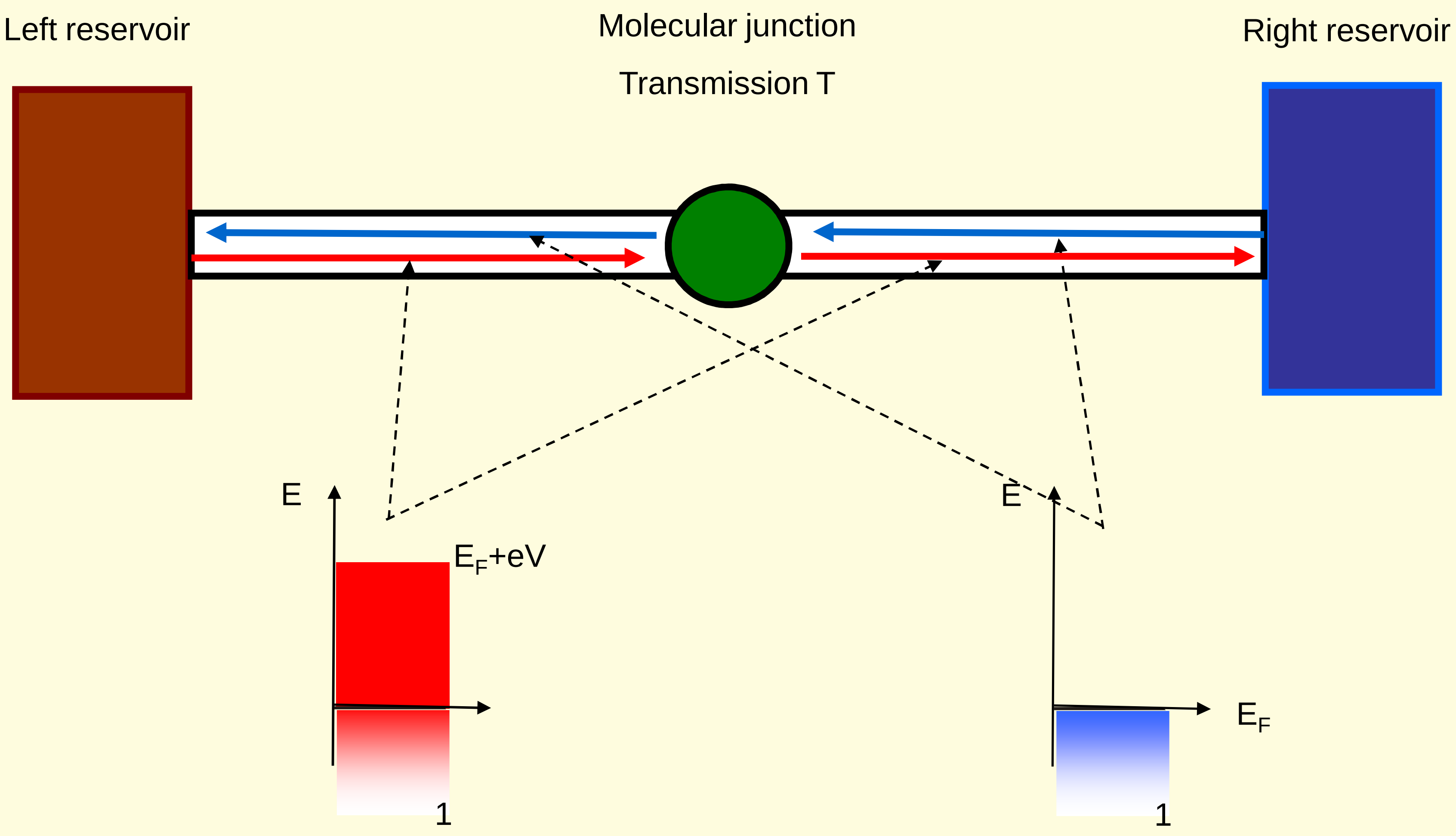
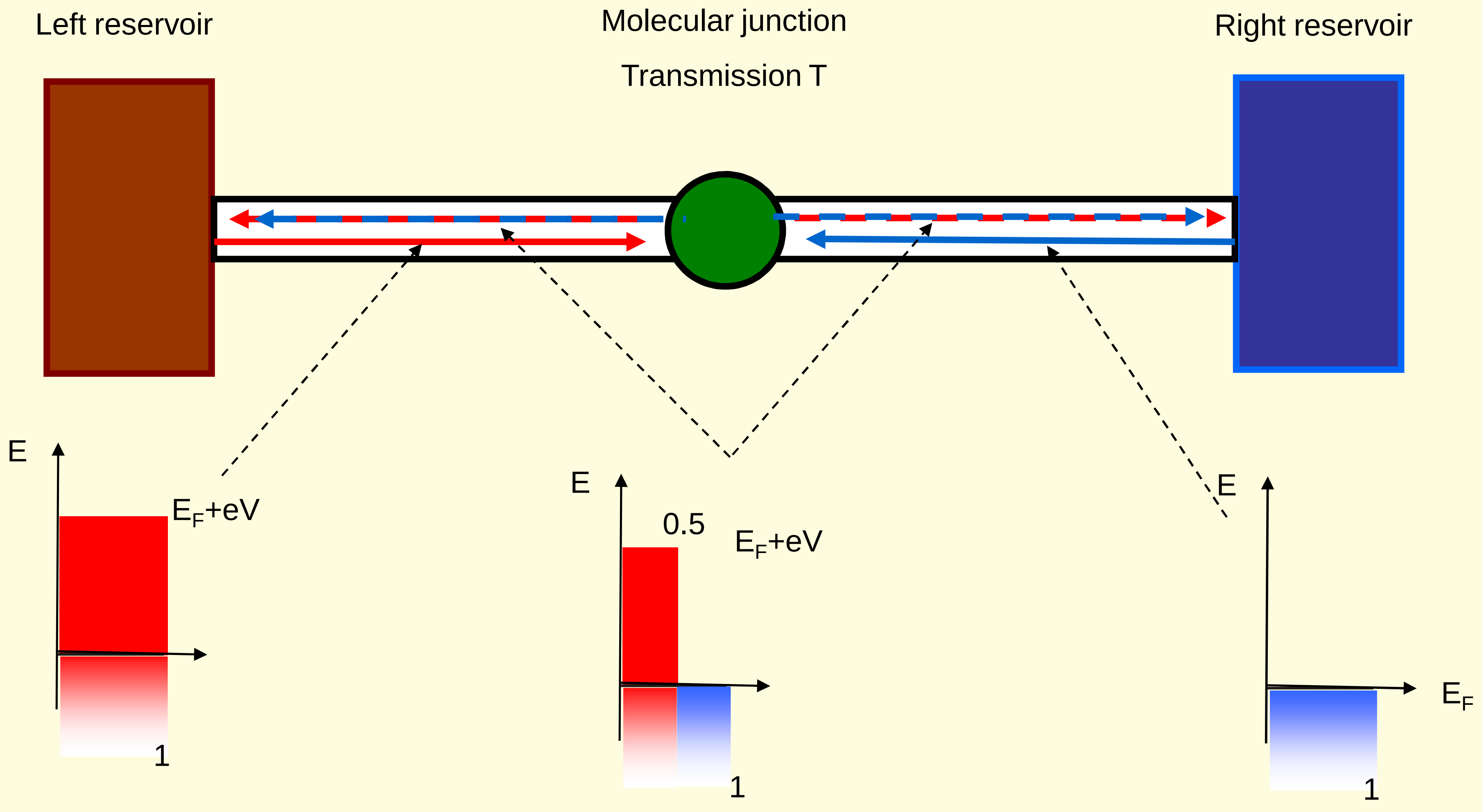
Increased G by inelastic scattering at T<<1



Reduction of G by inelastic scattering at T=1



Simple argument for cross over at T = 0.5



Left reservoir

Molecular junction

Transmission T

Right reservoir

E

E_F+eV

1

E

0.5

E_F+eV

1

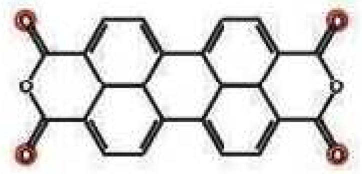
E

E_F

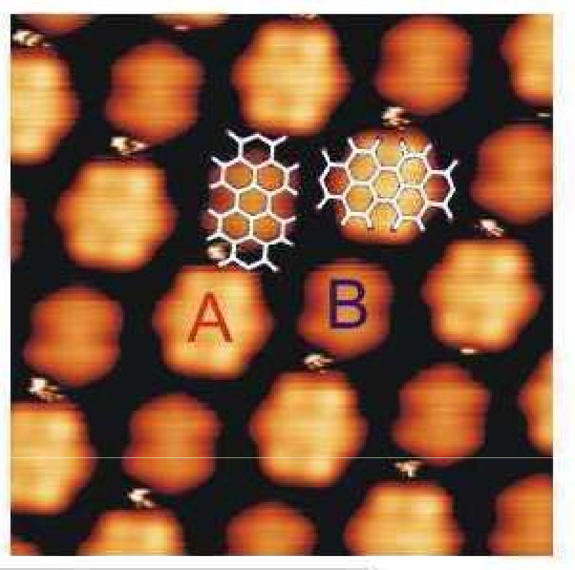
1

Outlook

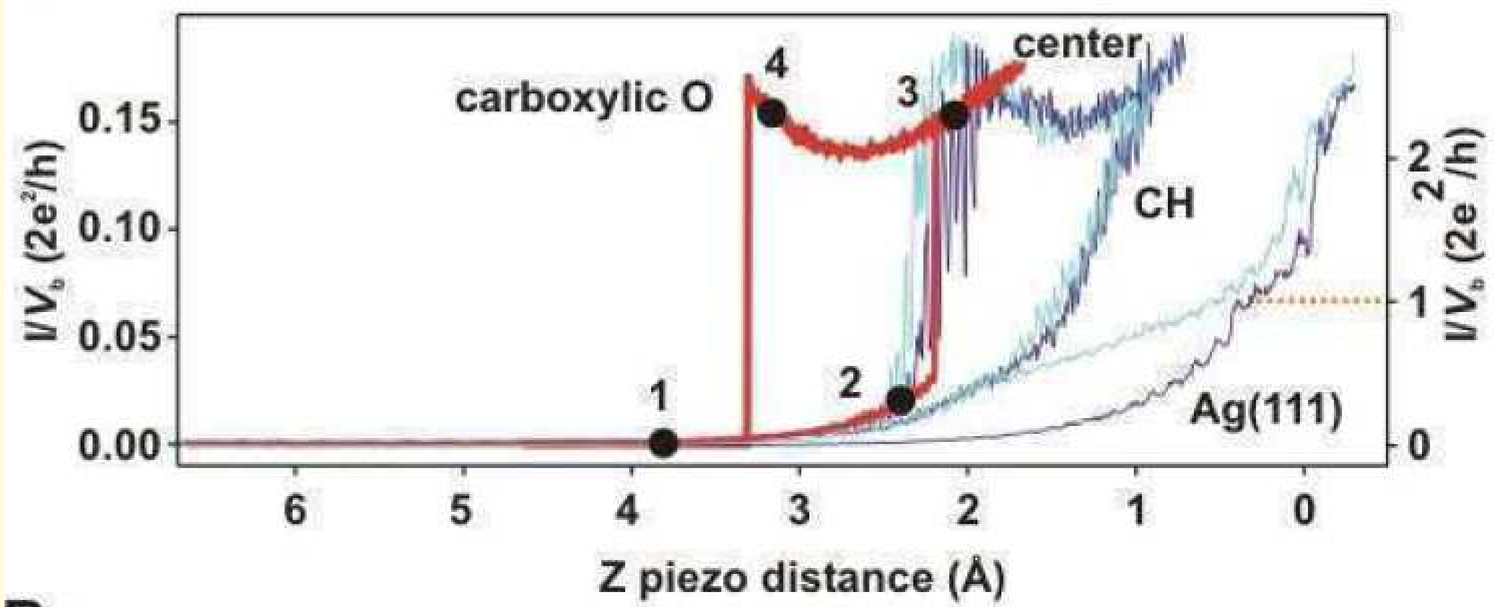
Low-temperature STM



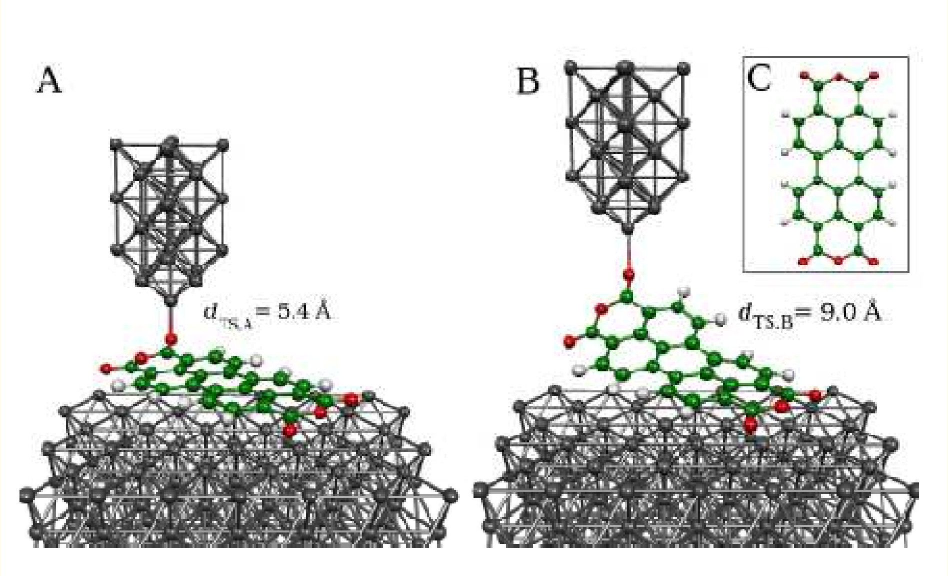
PTCDA



R. Temirov, A. Lassise, F.B. Anders, F.S. Tautz, (Bremen) preprint



STM: Pealing off a molecule



Pump, Temirov, Neucheva, Soubatch, Tautz, Rohlfing, Cuniberti,
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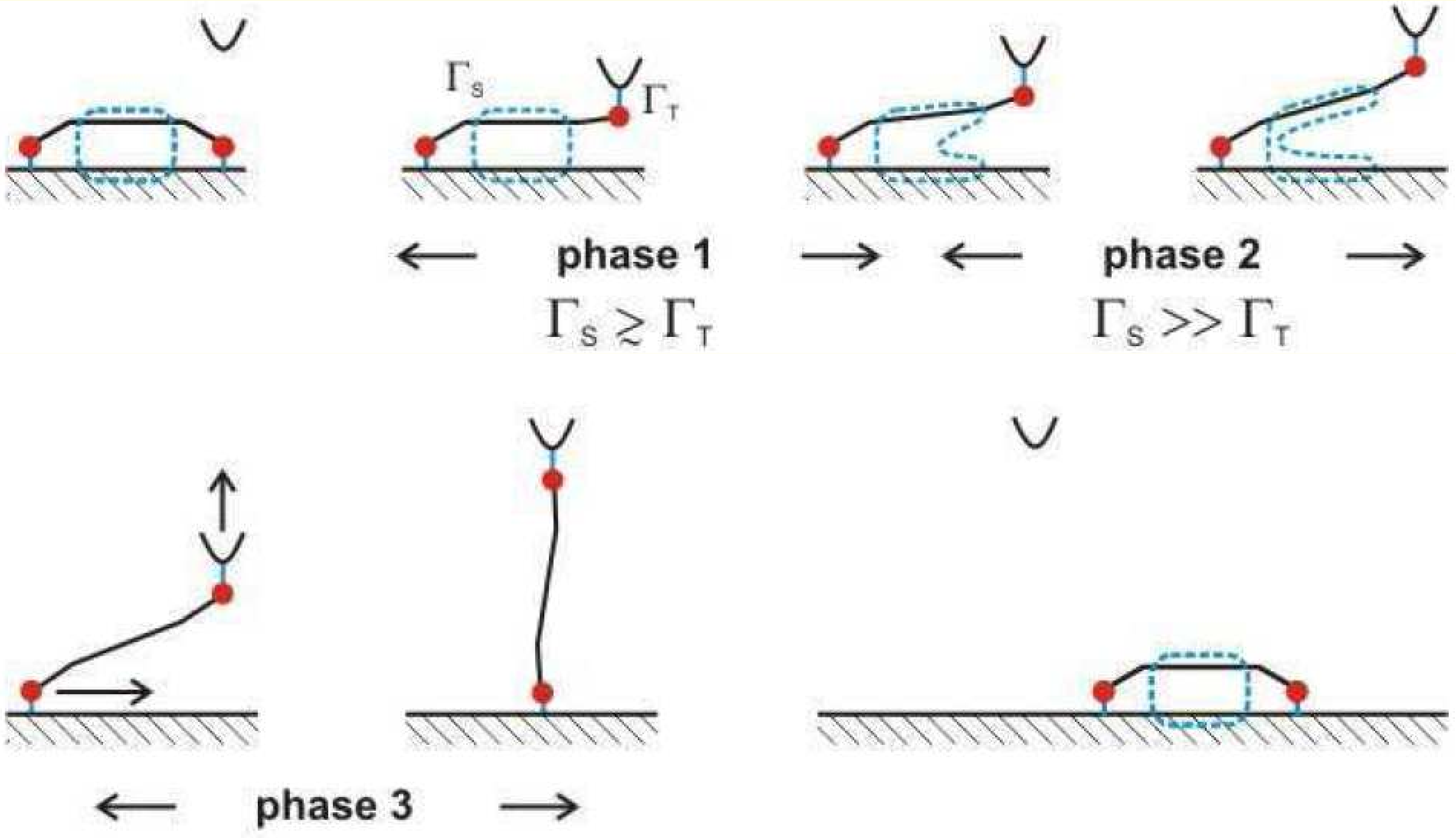
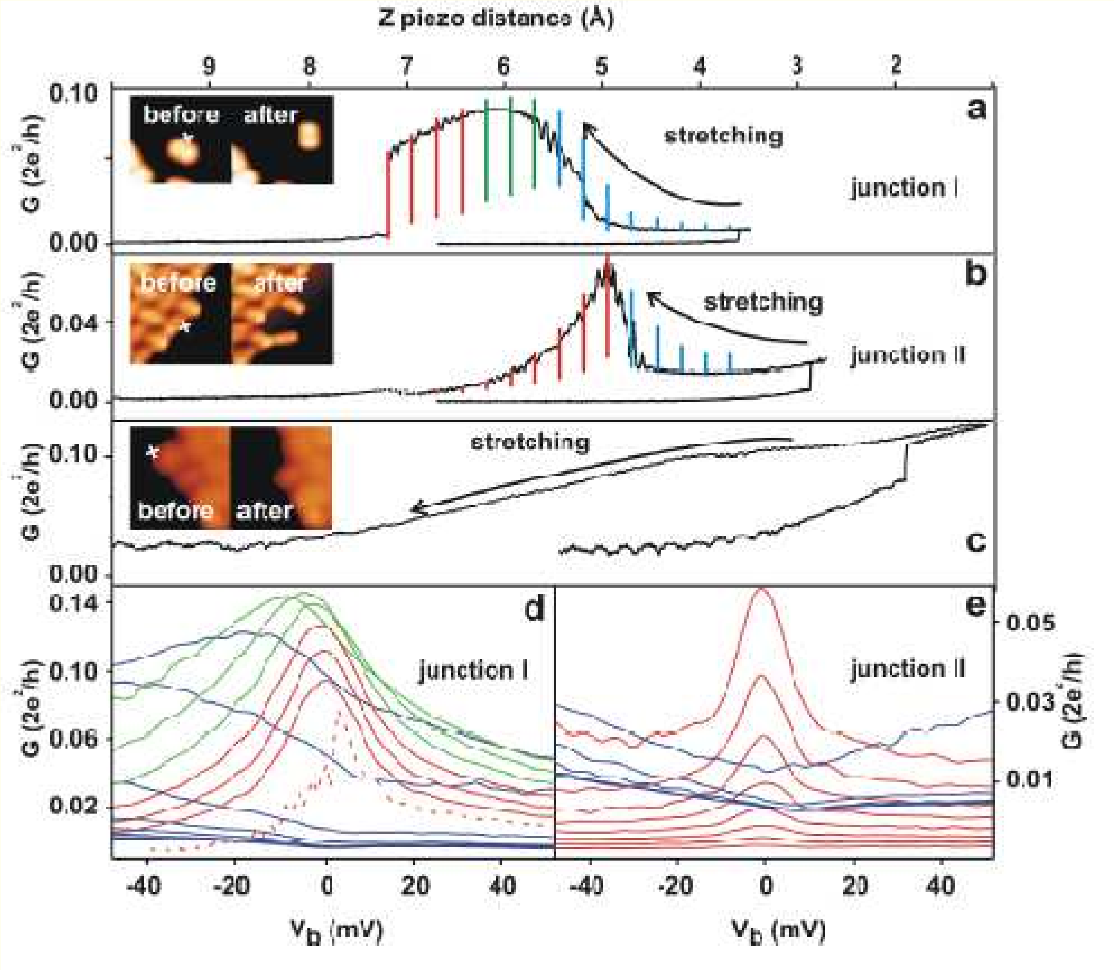
Low-temperature STM



R. Temirov, A. Lassise, F.B. Anders, F.S. Tautz, (Bremen) preprint

Pealing off a molecule



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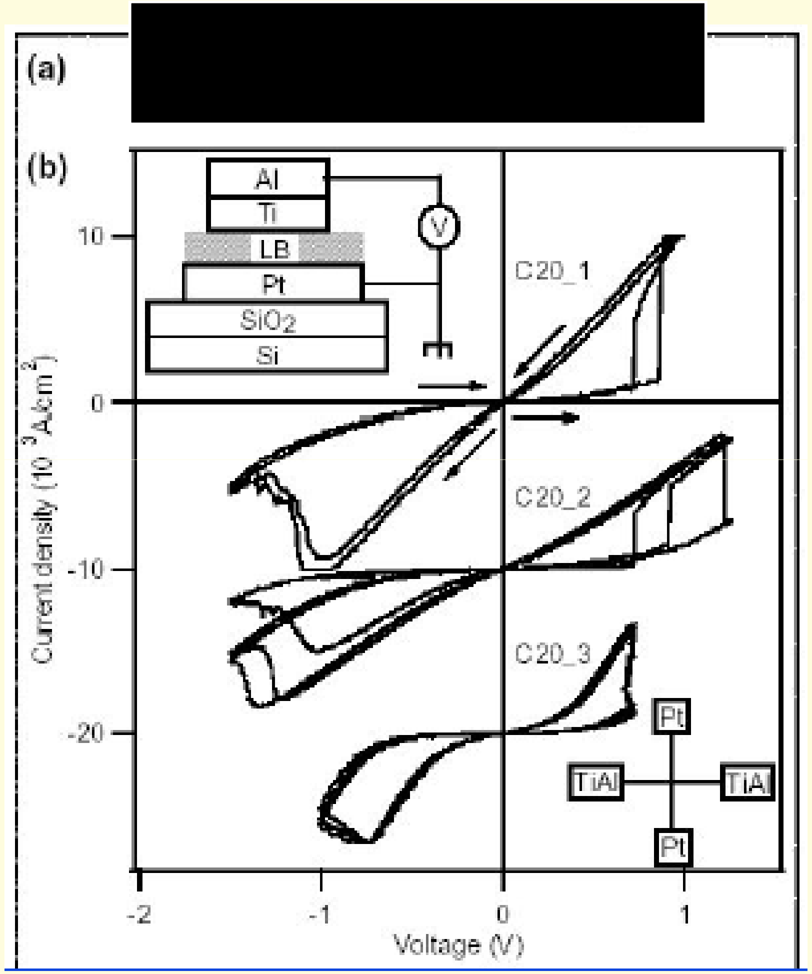
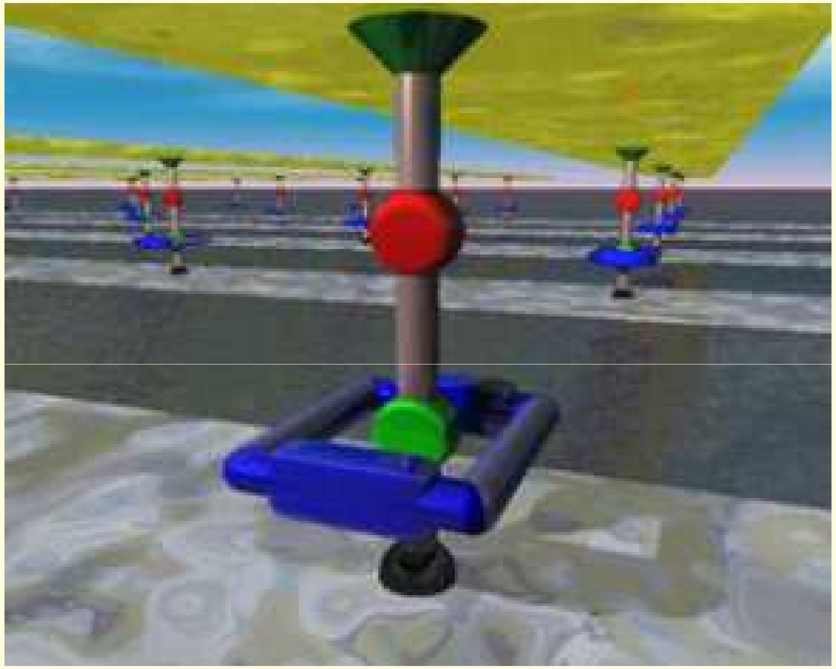
Two-state molecules: memory

[redacted]





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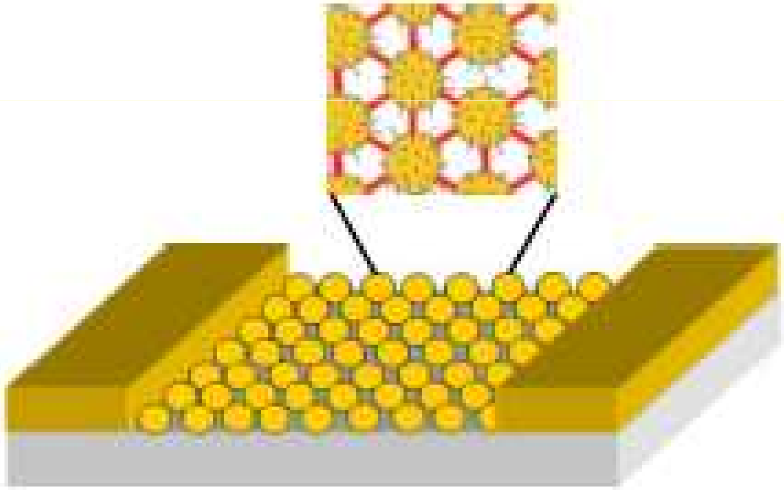
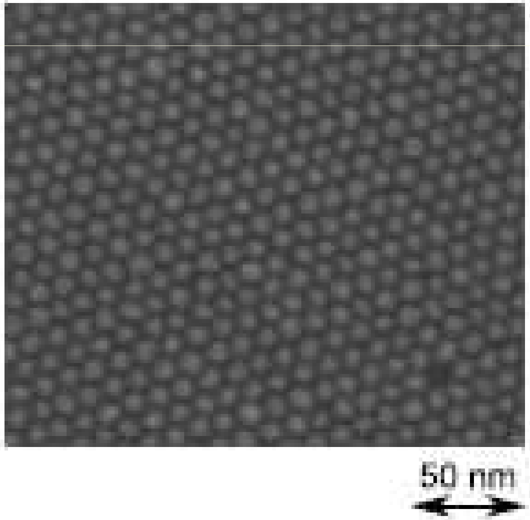
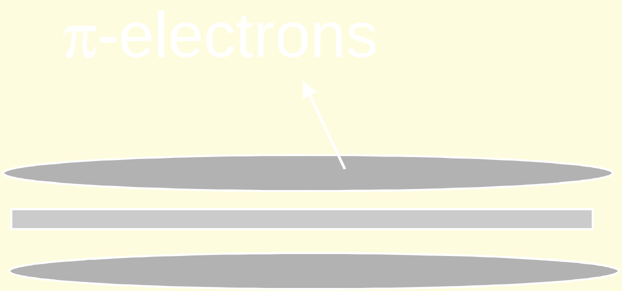
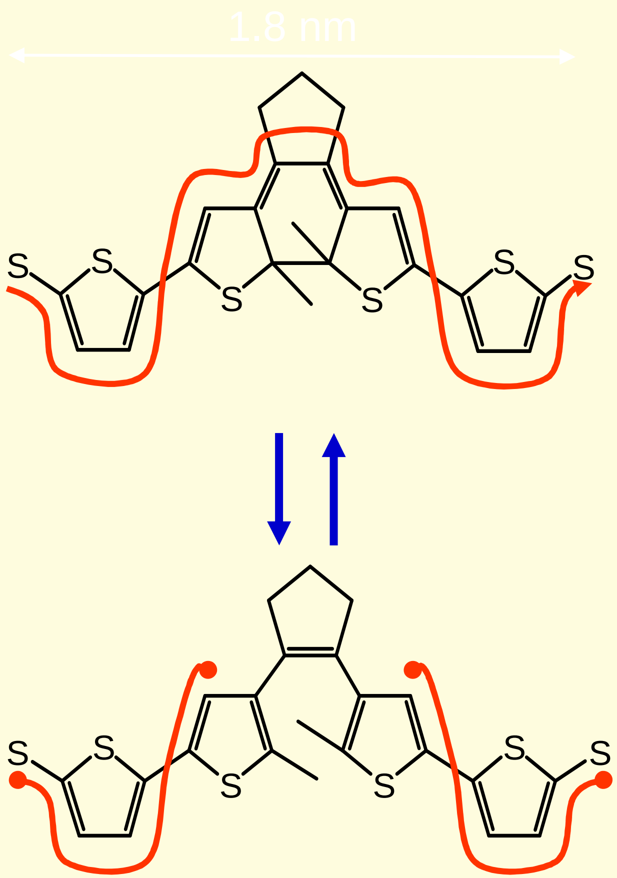




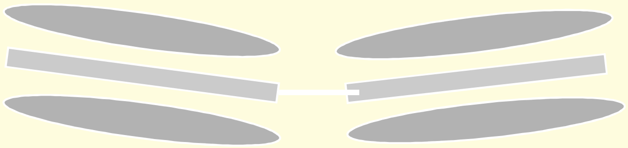
Recent result: Molecular Switch



ON



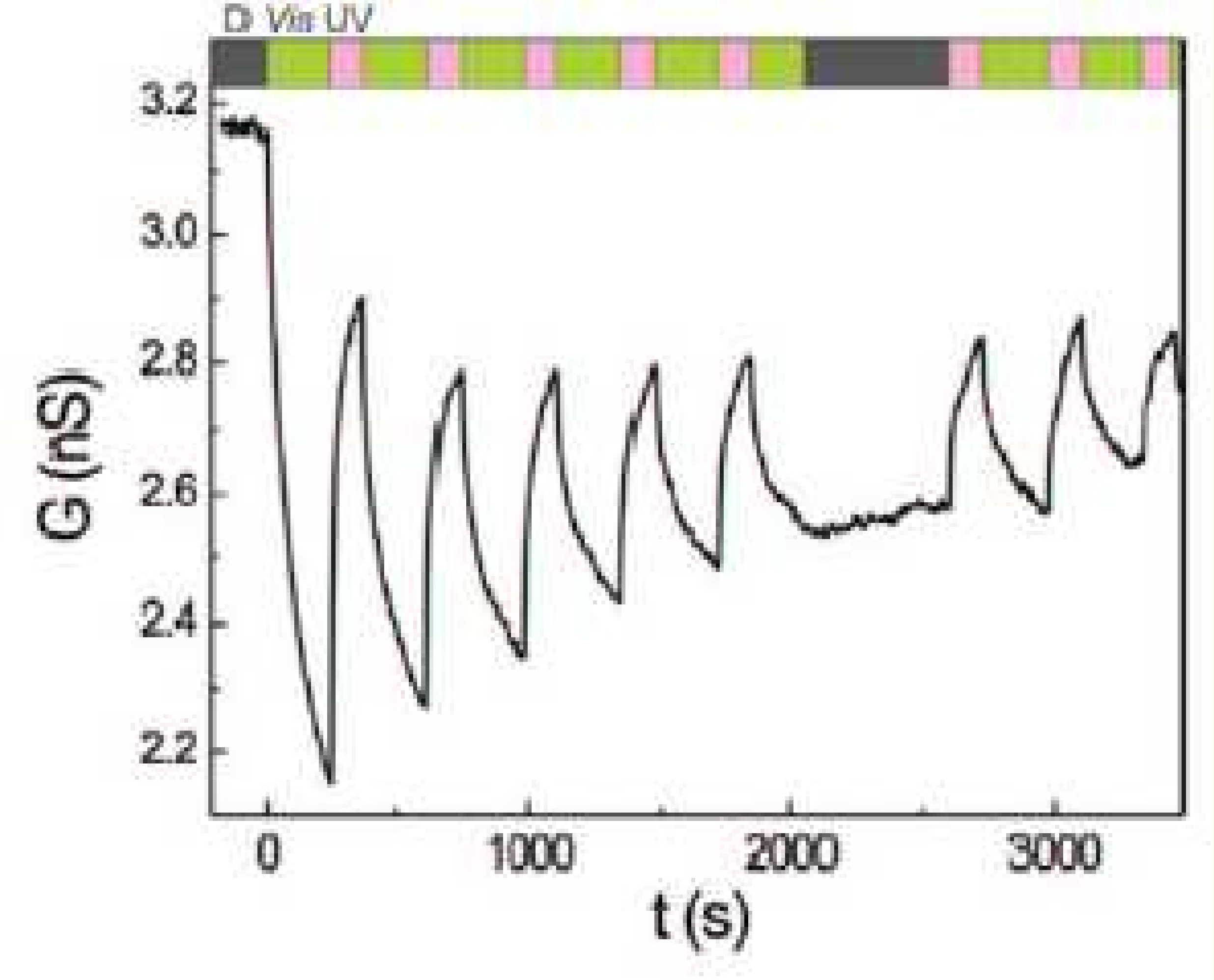
External ↓↑ stimulus



OFF

'conjugation' broken

Light controlled conductance switching



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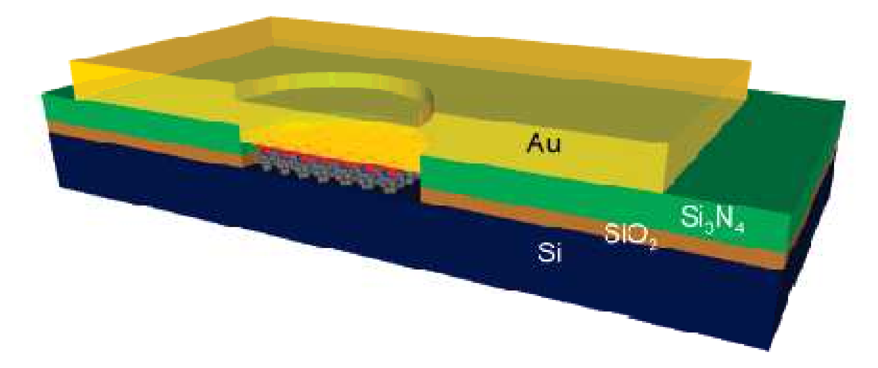
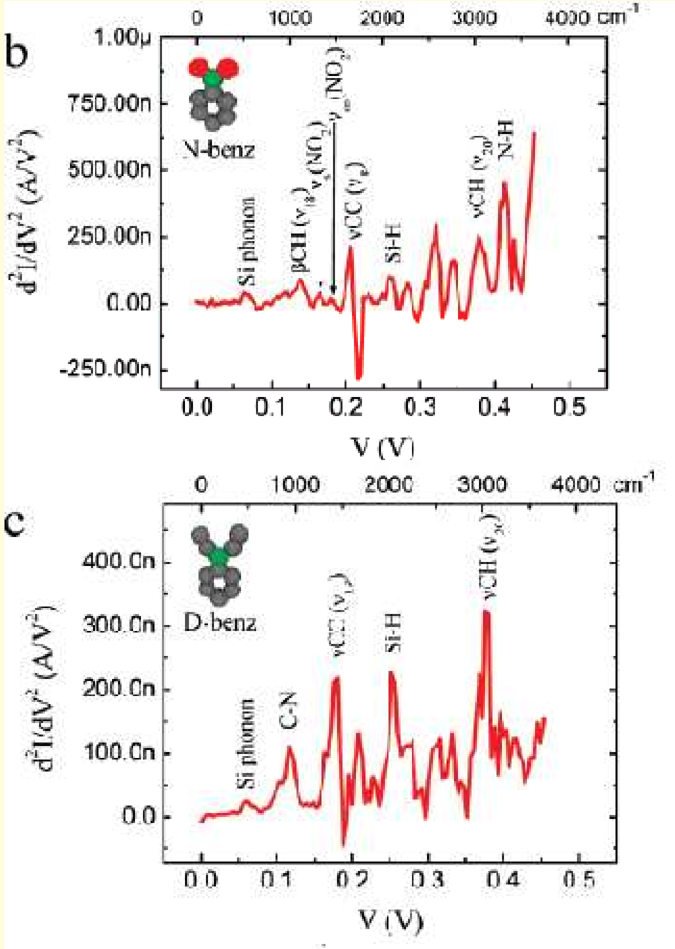
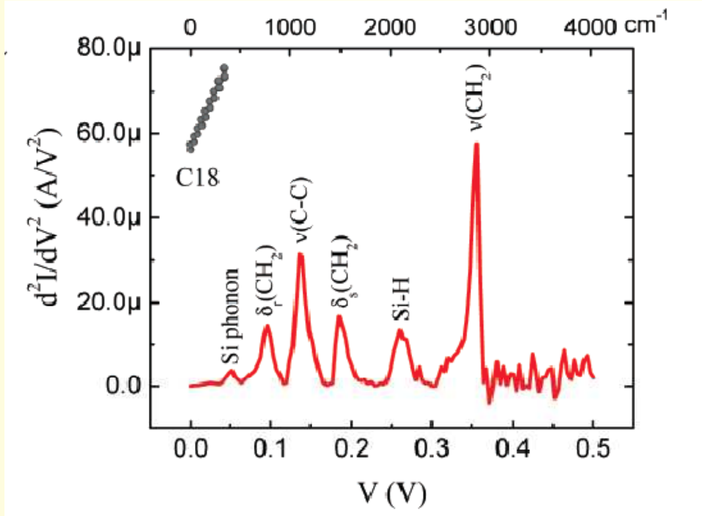
Integration to Si







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Most important challenges

- Can we understand the IV curves?
- Can we make single molecule devices reproducibly? Or can we work our way around it?
- Can we identify polaron effects in conductance?
- Can we understand and control the heat dissipation in molecular devices?
- Can we make a single-molecule diode with sufficient asymmetry for applications?
- Can we make a reliable voltage controlled switch?
- Can we develop a route towards higher level composite molecular structures?

- How to proceed?
- → systematic variations in series of molecules
- → Model systems
- → UHV-STM
- → molecule-semiconductor devices