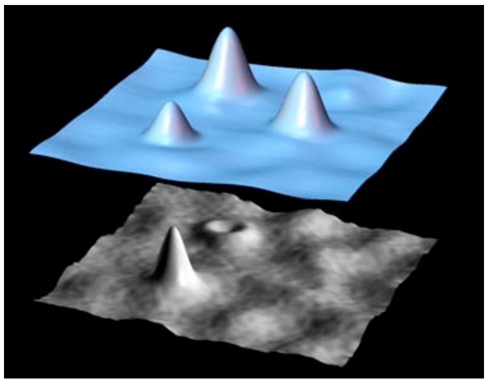
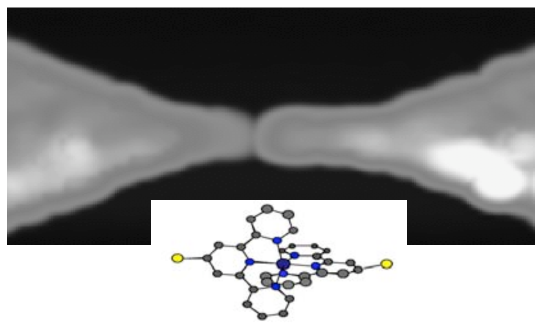
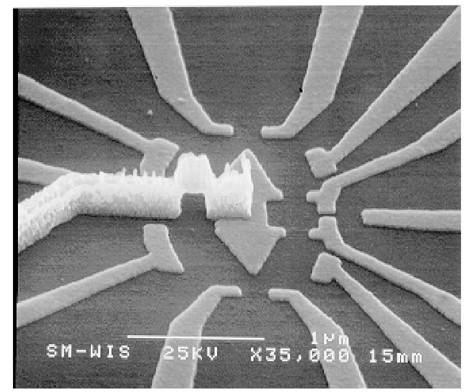
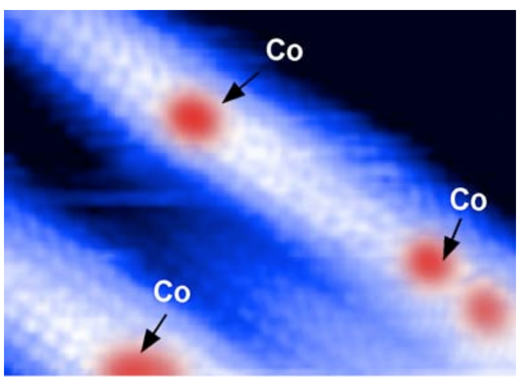
Review of Kondo Experiments

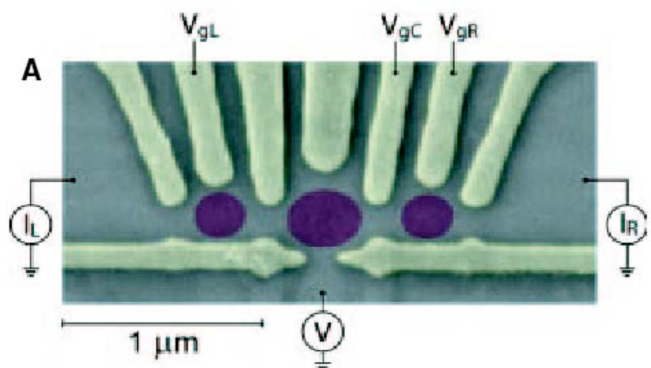
with thanks to David Goldhaber-Gordon

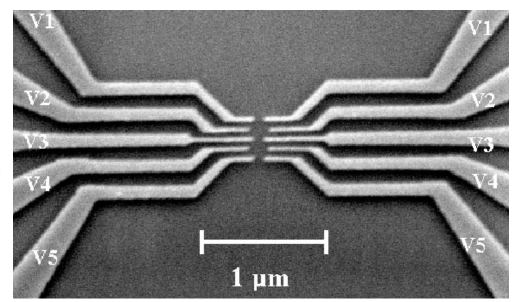




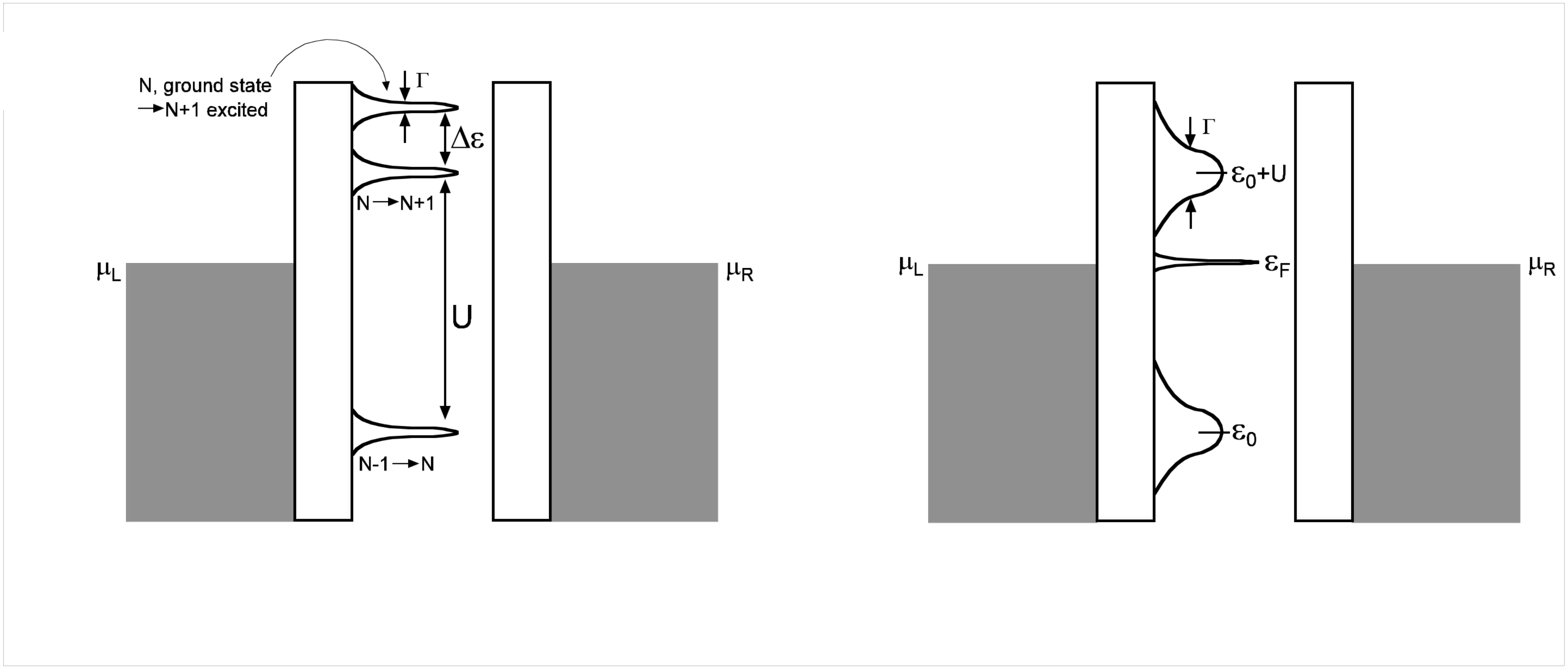




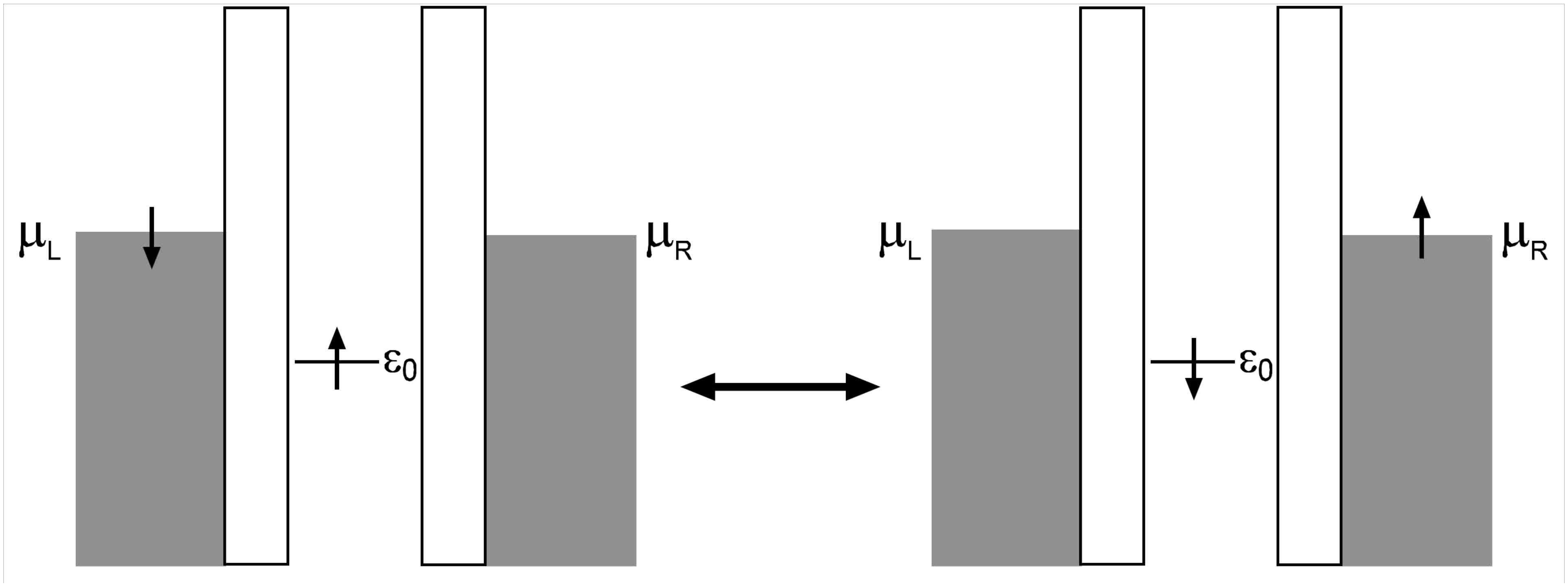




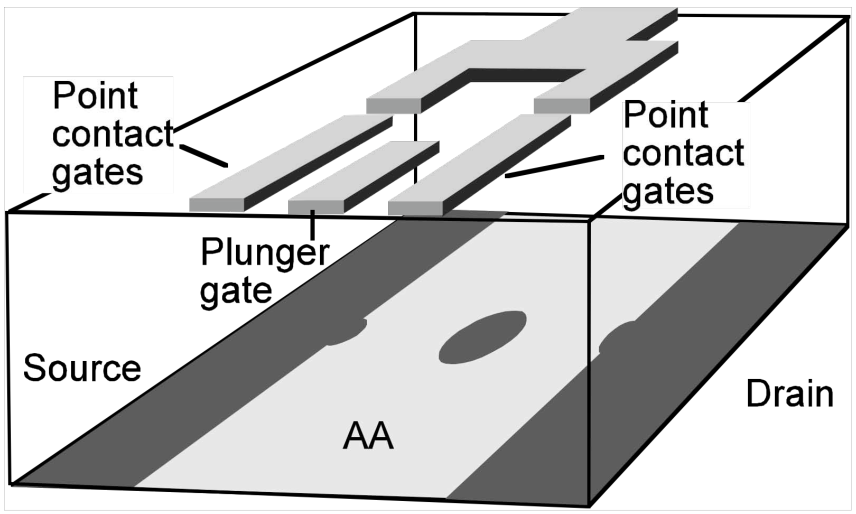
Kondo modifies density of states, transport



Kondo ground state can “slosh”



Single-electron Transistor (SET)

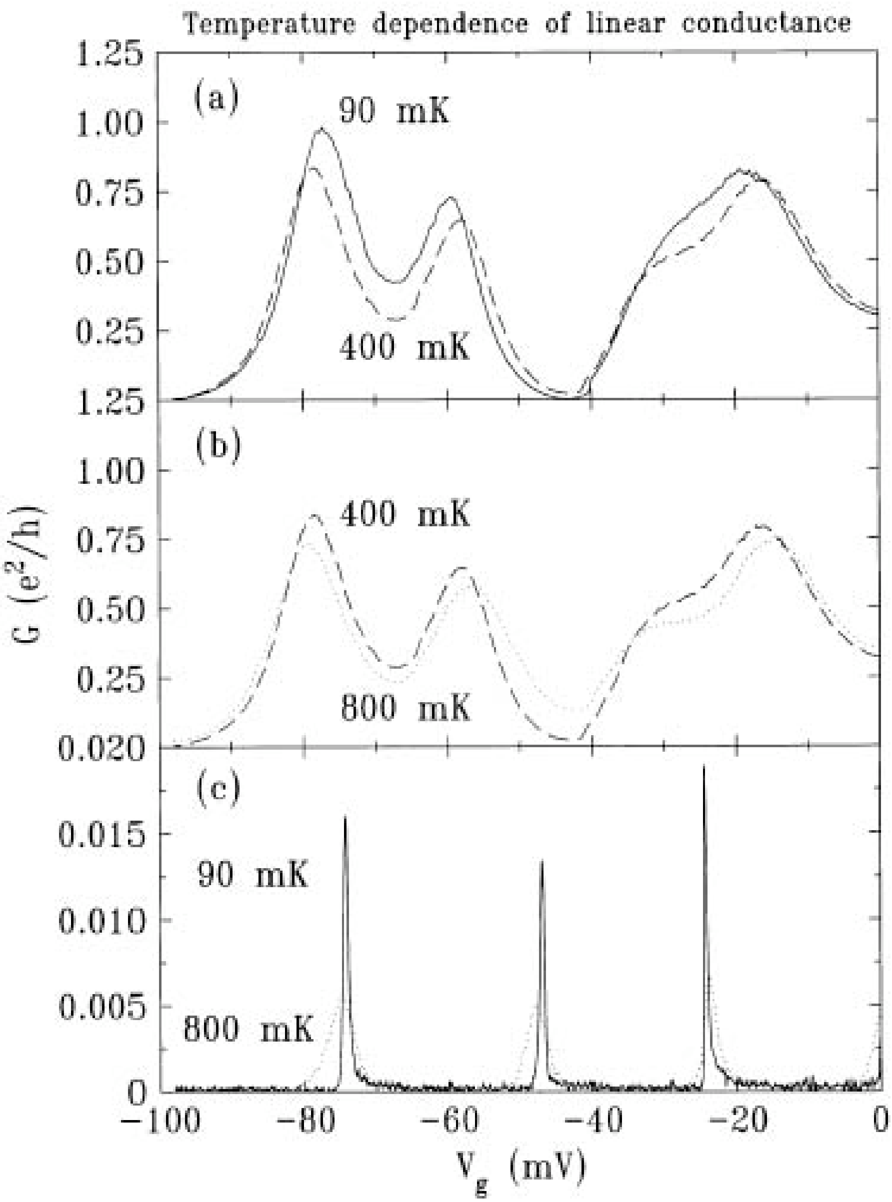


- Quantum dot coupled to two electron reservoirs
- Fully tunable
- Current turns on and off each time one electron is added

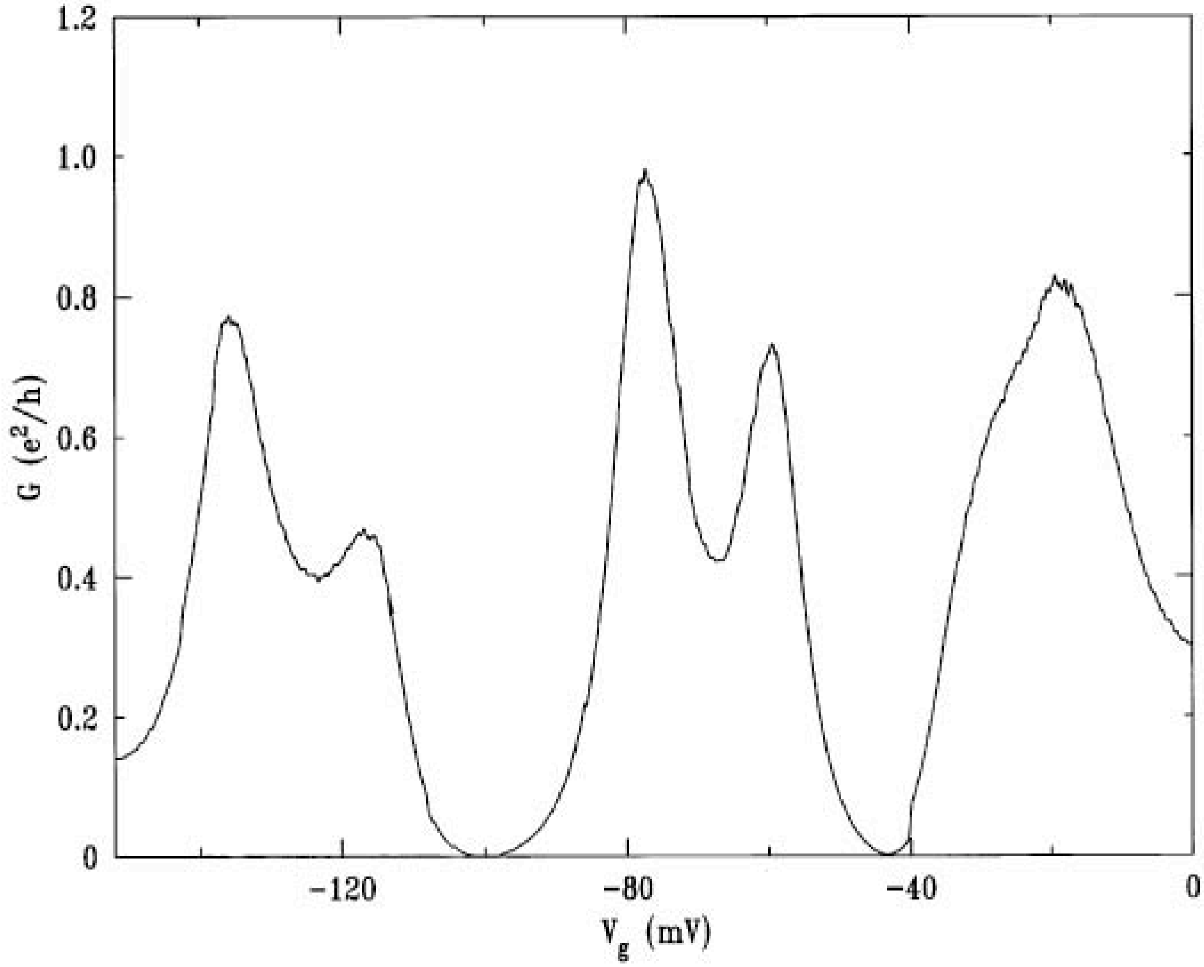
Current flows at fixed occupancy!

Goldhaber-Gordon, Kastner et al.,
Nature **391**, 156 (1998).

also
Cronenwett, Kouwenhoven et al.,
Science **281**, 540 (1998).

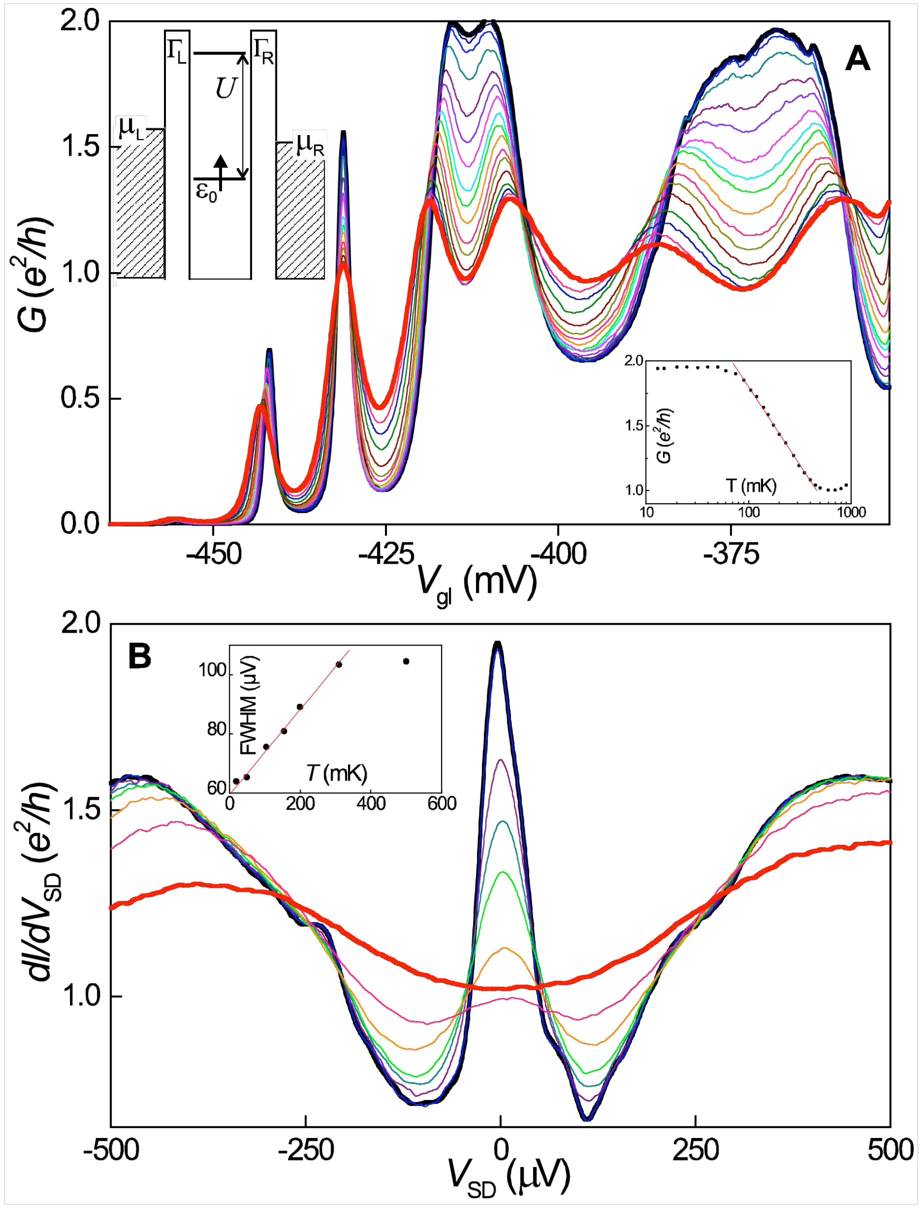


Even-odd enhanced conductance



G-G

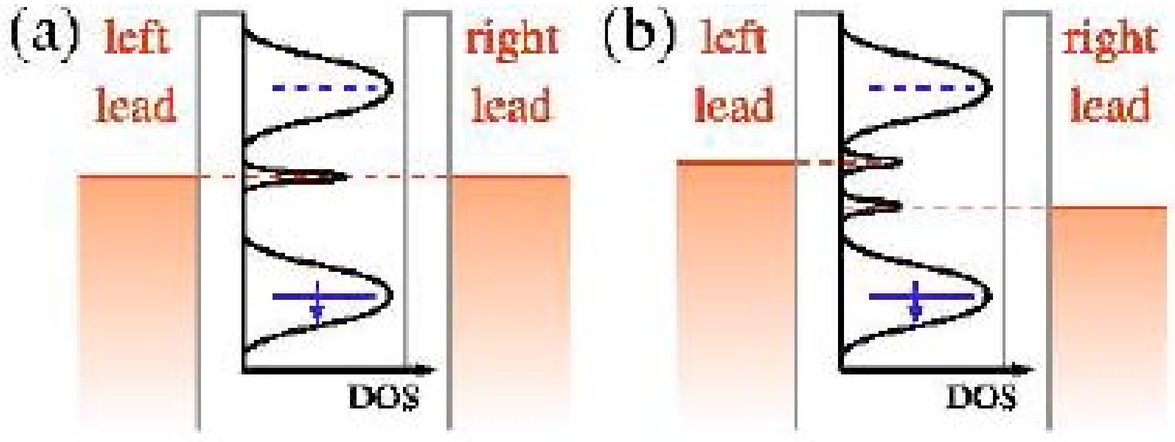
Unitary conductance in SET

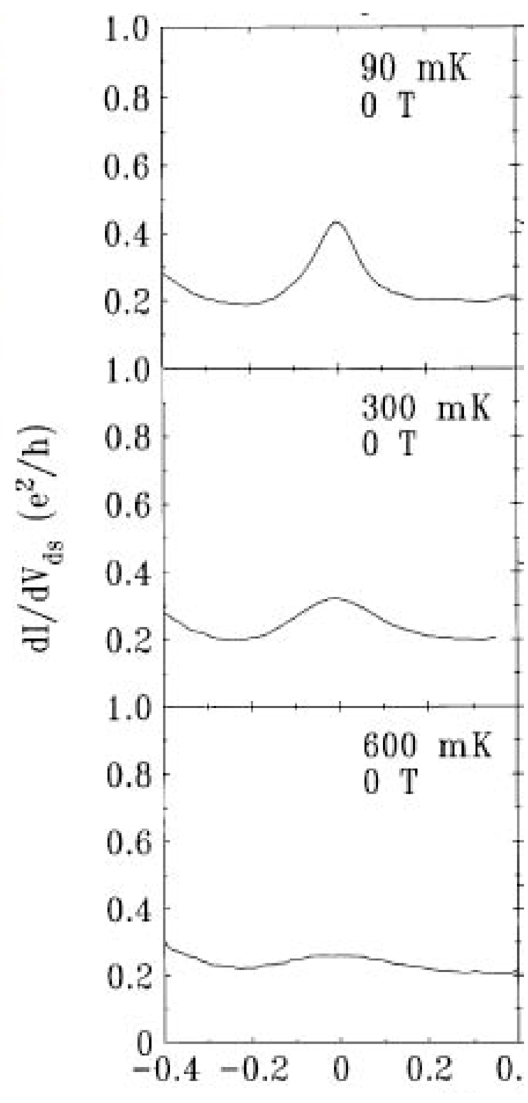


- Symmetric unitary limit of $2e^2/h$ conductance has been achieved in a SET
- Conductance saturates at low T

van der Wiel, Kouwenhoven et al. Science **289**, 2105 (2000).

Kondo resonance: Zero-bias peak in dI/dV_{ds}

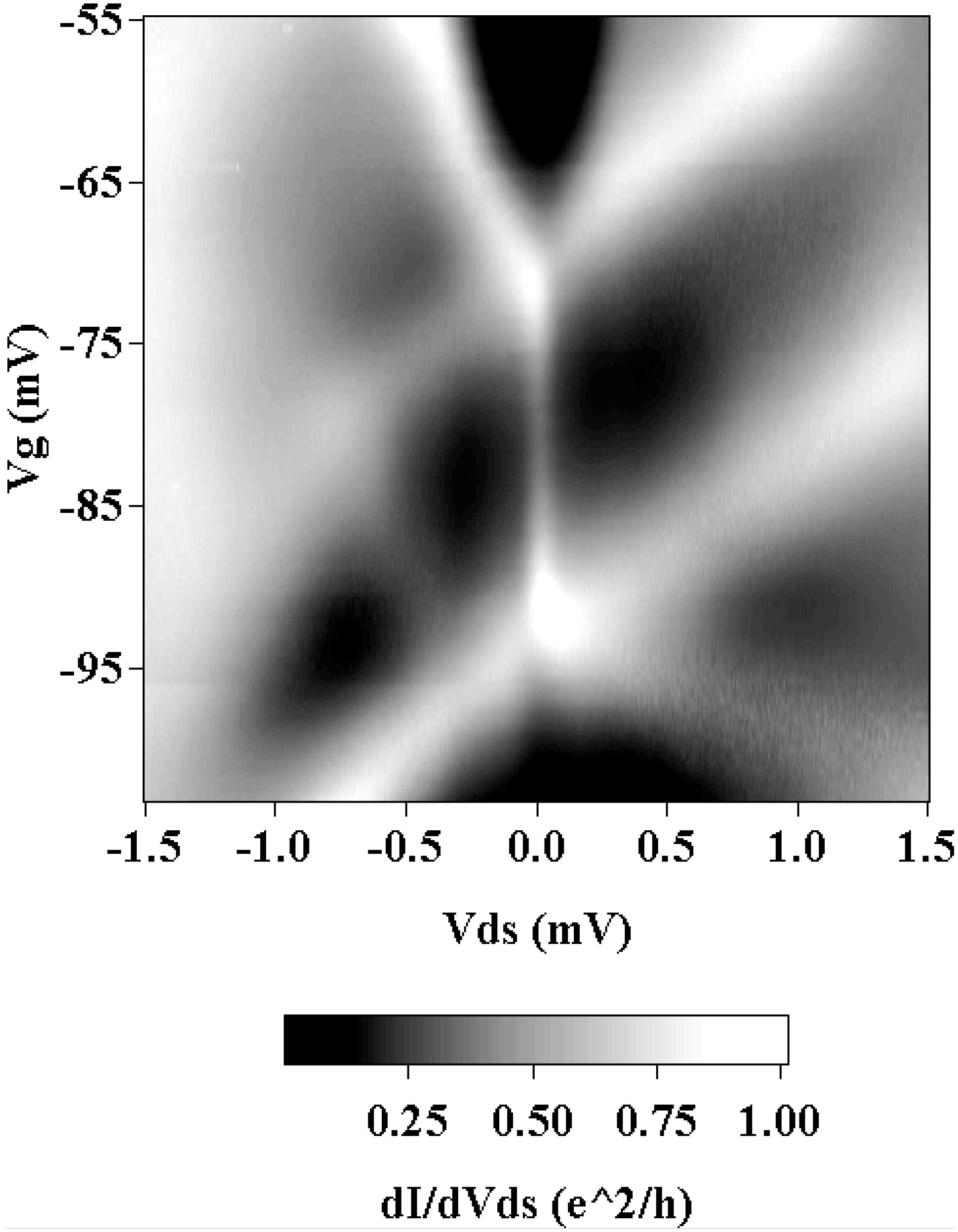




- Kondo resonances pinned to E_F on either electrode.
- Theory: peaks broaden for larger V due to inelastic effects
- The bias suppresses conductance.
- Width of peak ~ 2 $k_B T_K/e$

G-G, 1998

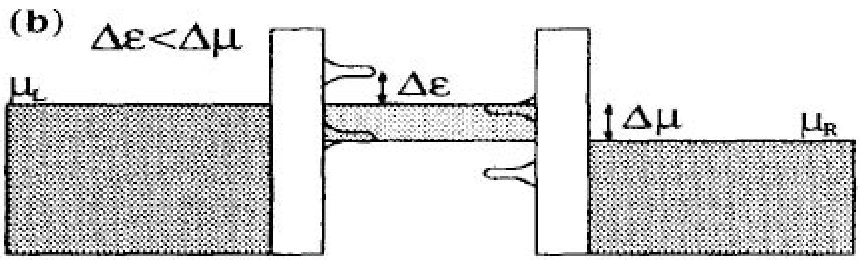
Conductance enhanced for odd occupancy



Sharp resonance indicates many-body state: lifetime longer than single electron on the quantum dot.

G-G, 1998

Applied Magnetic Fields

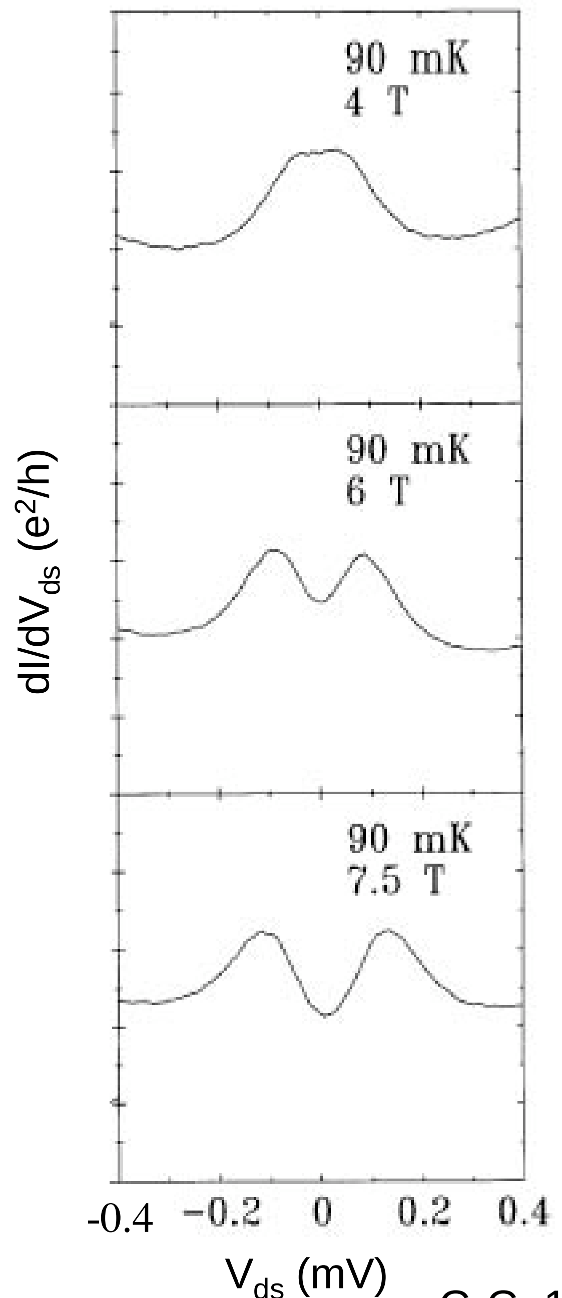


Resonances in the density of states undergo Zeeman splitting.

Peak in dI/dV restored when $\pm eV = g_{eff}\mu_B H$. (g_{eff} can be less than bare g due to Knight shift from interaction with electrons in the leads)

Can think of the peaks as due to Kondo renormalization of spin-flip scattering.

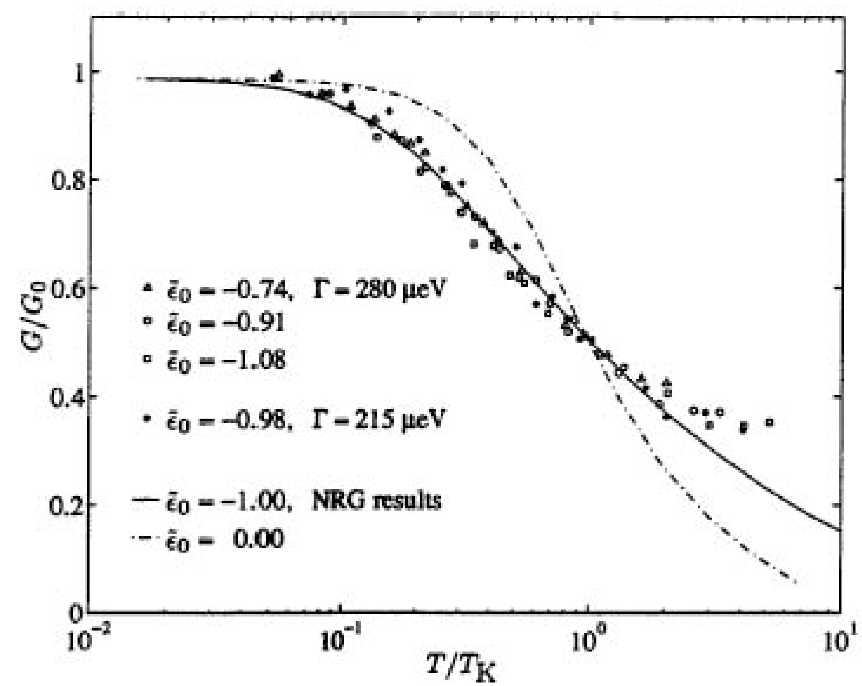
Theory: Meir Wingreen, Lee, PRL **70**, 2601 (1993).

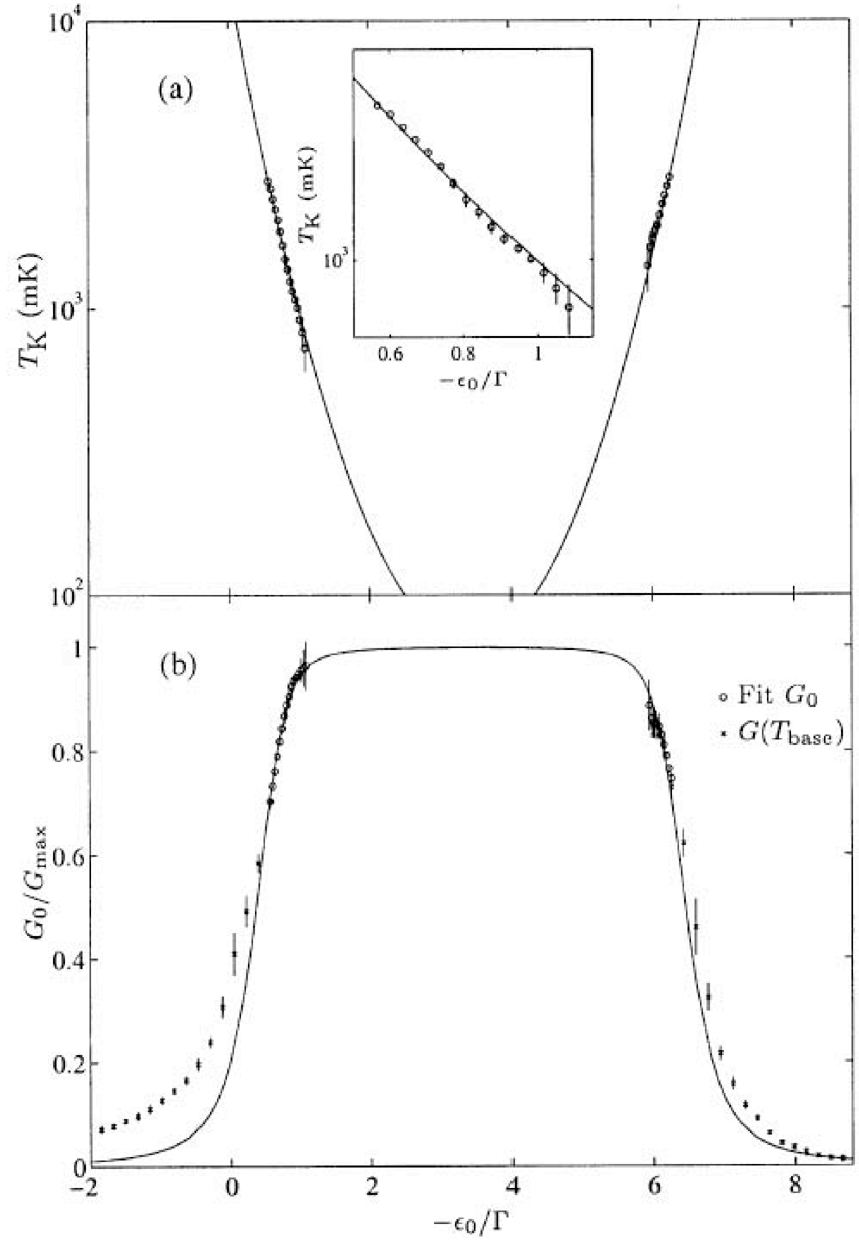


G-G, 1998

Quantitative Tests of Kondo Theory

$$T_K = \frac{\sqrt{\Gamma U}}{2}\exp\left[\frac{\pi\epsilon_0(\epsilon_0+U)}{\Gamma U}\right]$$





G-G, Kastner et al., PRL **81**, 5225 (1998)

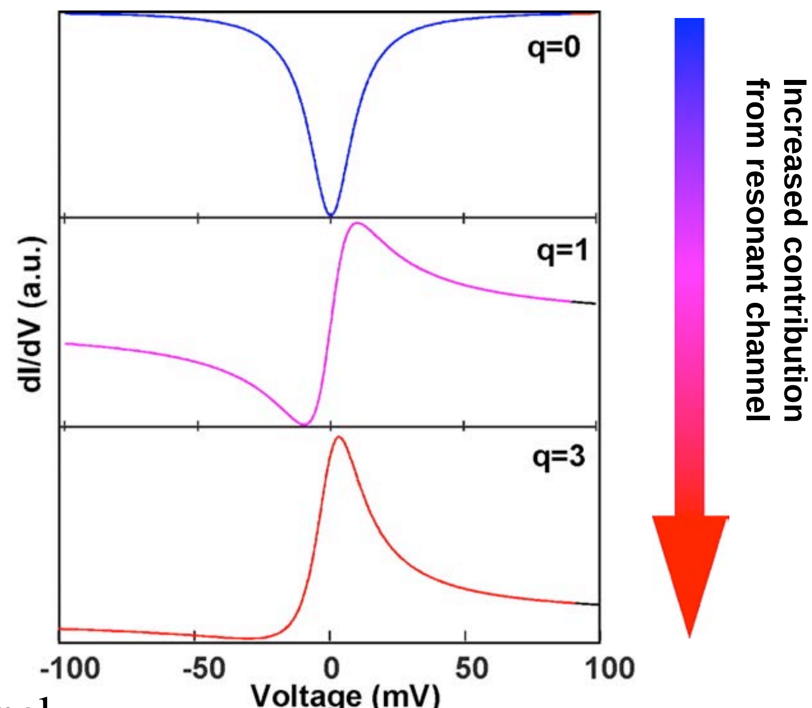
More Complicated Line Shapes

In many systems, the Kondo effect has been observed as as a "Fano resonance"

Interference from localized and continuum (resonant and non-resonant) channels

$$G = G_{\mathrm{inc}} + G_0 \frac{(\epsilon + q)^2}{\epsilon^2 + 1}$$

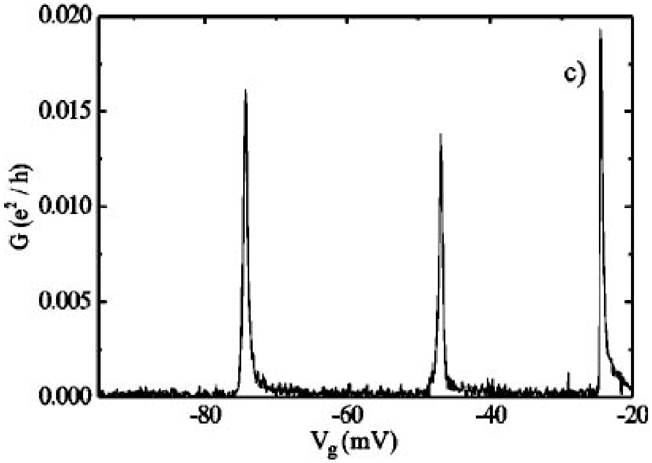
$$\epsilon = \frac{\epsilon - \epsilon_0}{W/2}$$



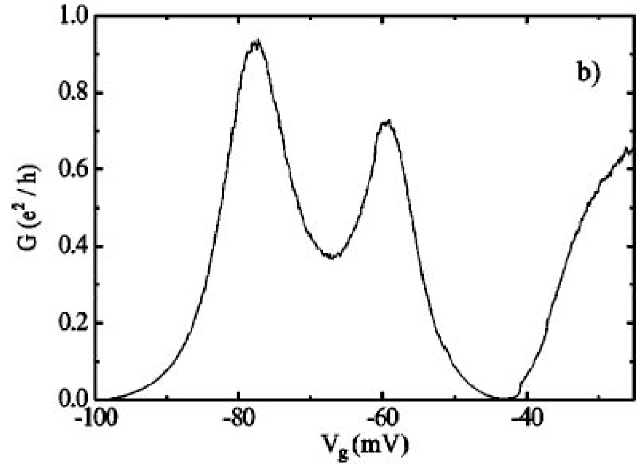
$$q \propto \frac{\text{transmission through resonant channel}}{\text{transmission through nonresonant channel}}$$

Odom, Lieber

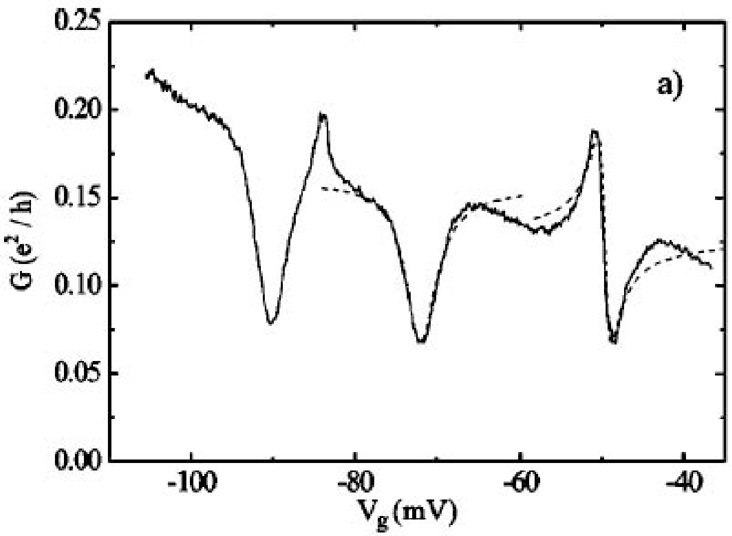
Fano Lineshapes for Single Electron Transistors



weak coupling to leads
no Kondo (T_K << T)



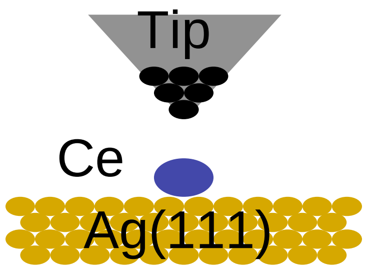
intermediate coupling to leads
Kondo enhancement in valleys



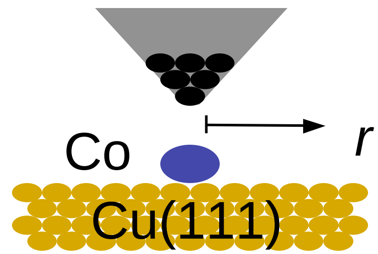
strong coupling to leads
Fano lineshapes

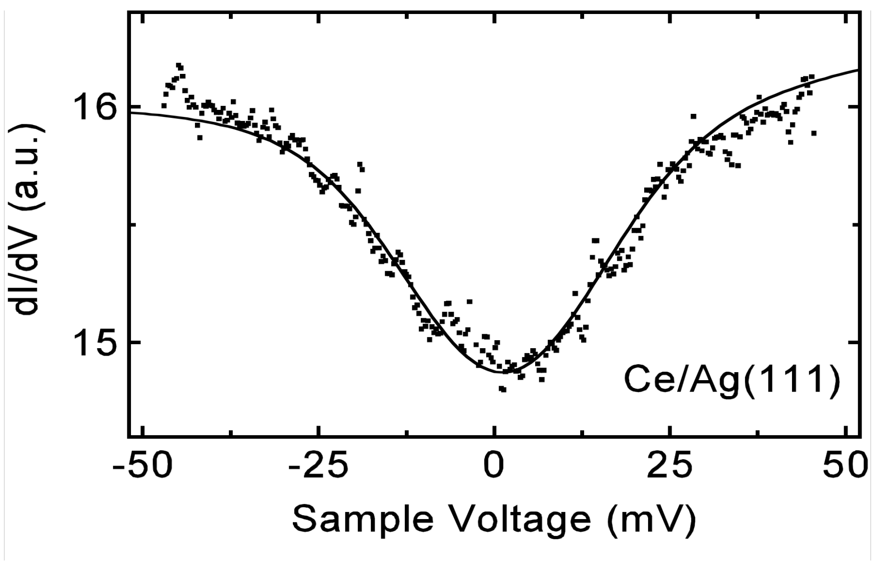
Gores, G-G, Kastner et al., PRB **62**, 2188 (2000)

Scanning tunneling spectroscopy of the Kondo resonance

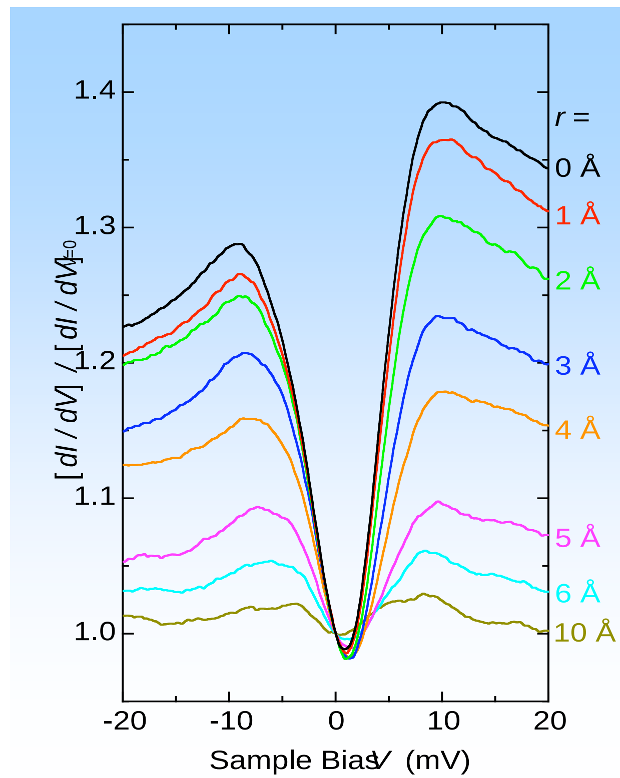


(*q* close to zero)





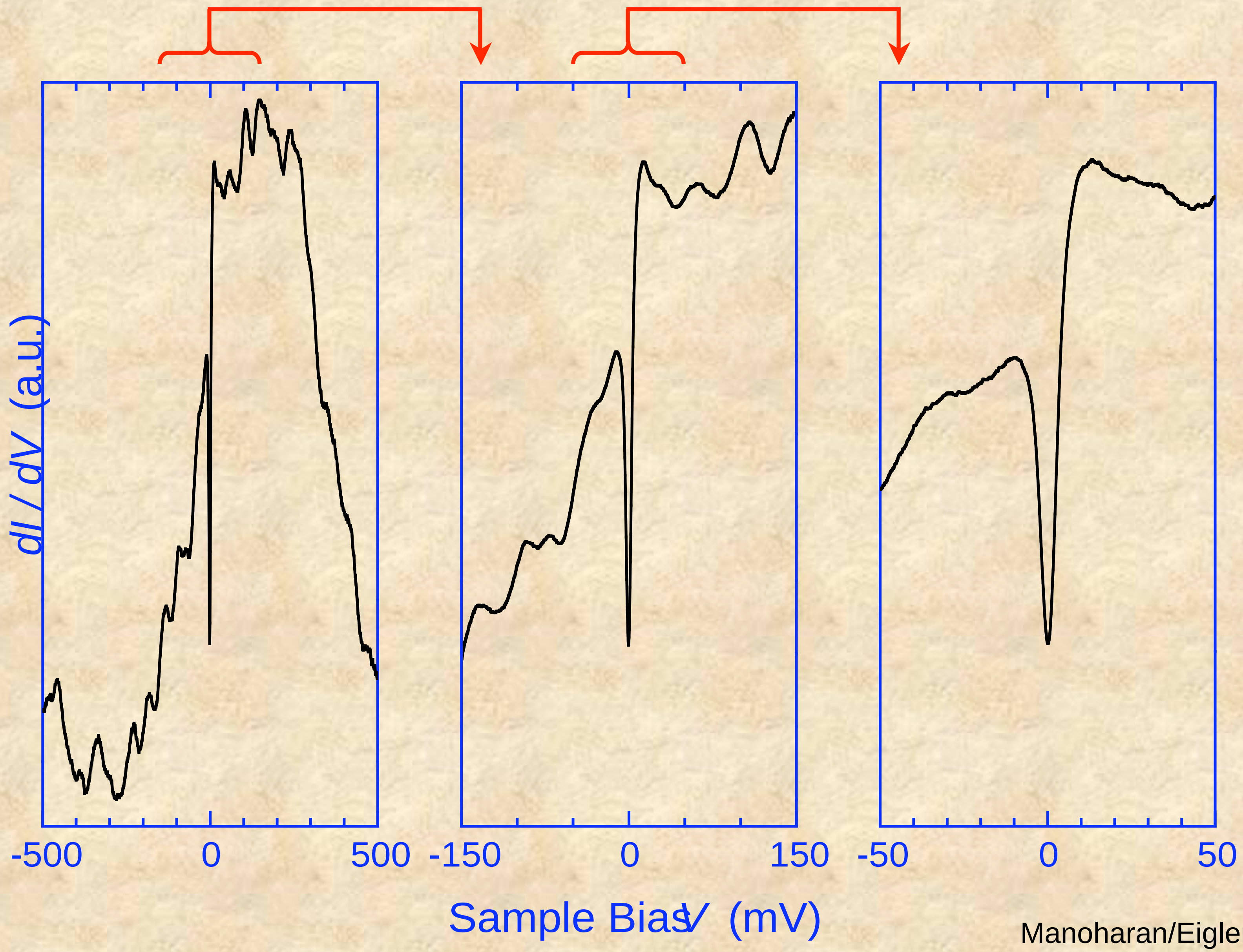
Berndt *et al.*, PRL **80**, 2893 (1998).



Manoharan/ Eigler *et al.*

after Madhavan/ Crommie) Science **280**, 567 (1998).

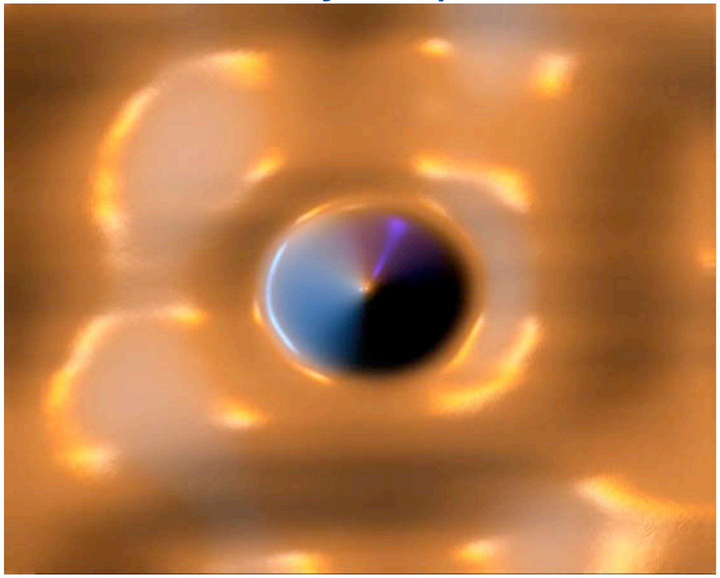
Zoom-in on the Kondo Resonance



Manoharan/Eigler

Imaging the Kondo Resonance

- Single Cobalt atom
- Simultaneously acquired 35 Å square images



Topograph

(V = 5 mV)

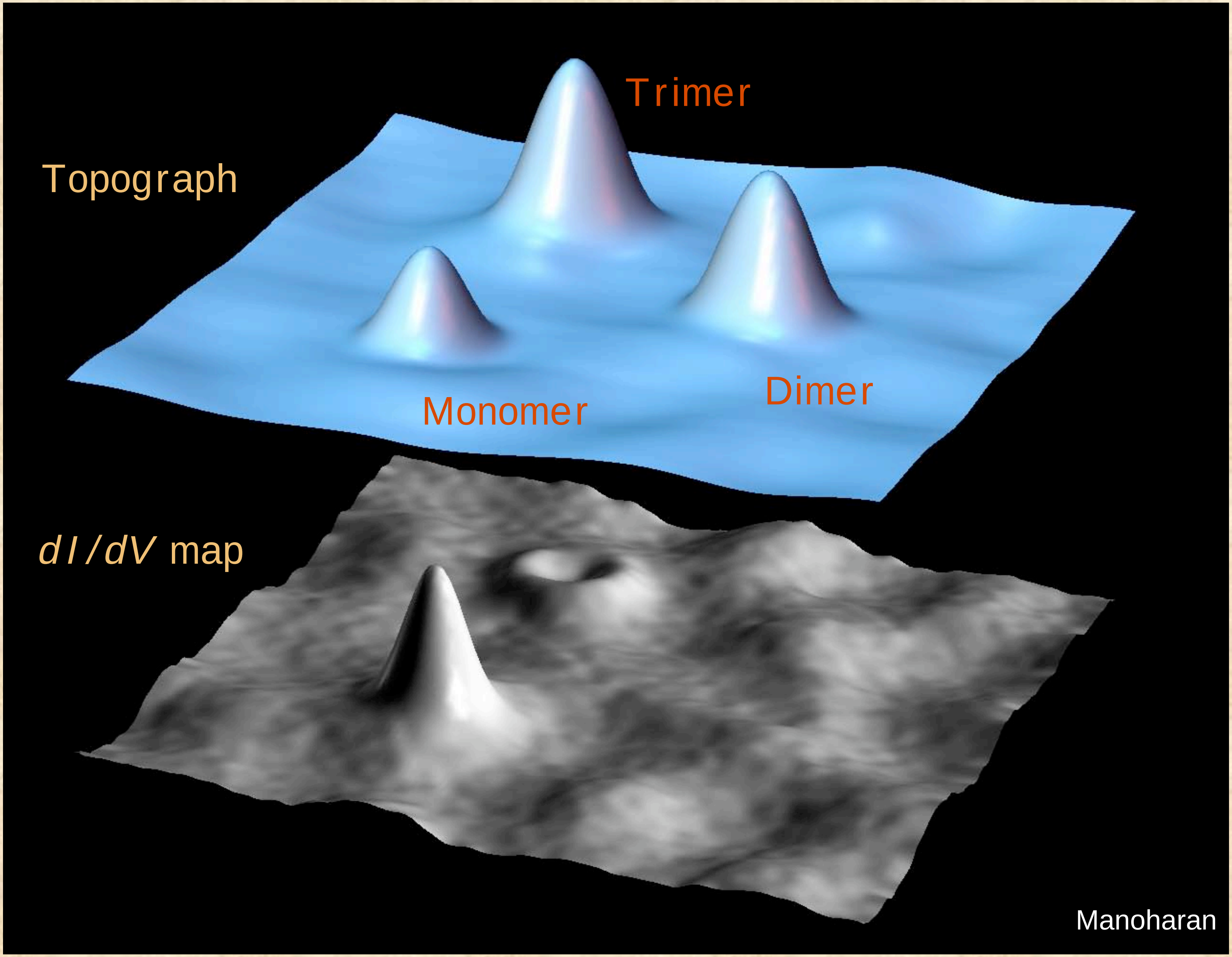
dI/dV map

(V = ±5 mV)

Spatial extend of screening cloud is small, as measured by density of states near Fermi level

Manoharan

Kondo Effect: Multiple Co Atoms



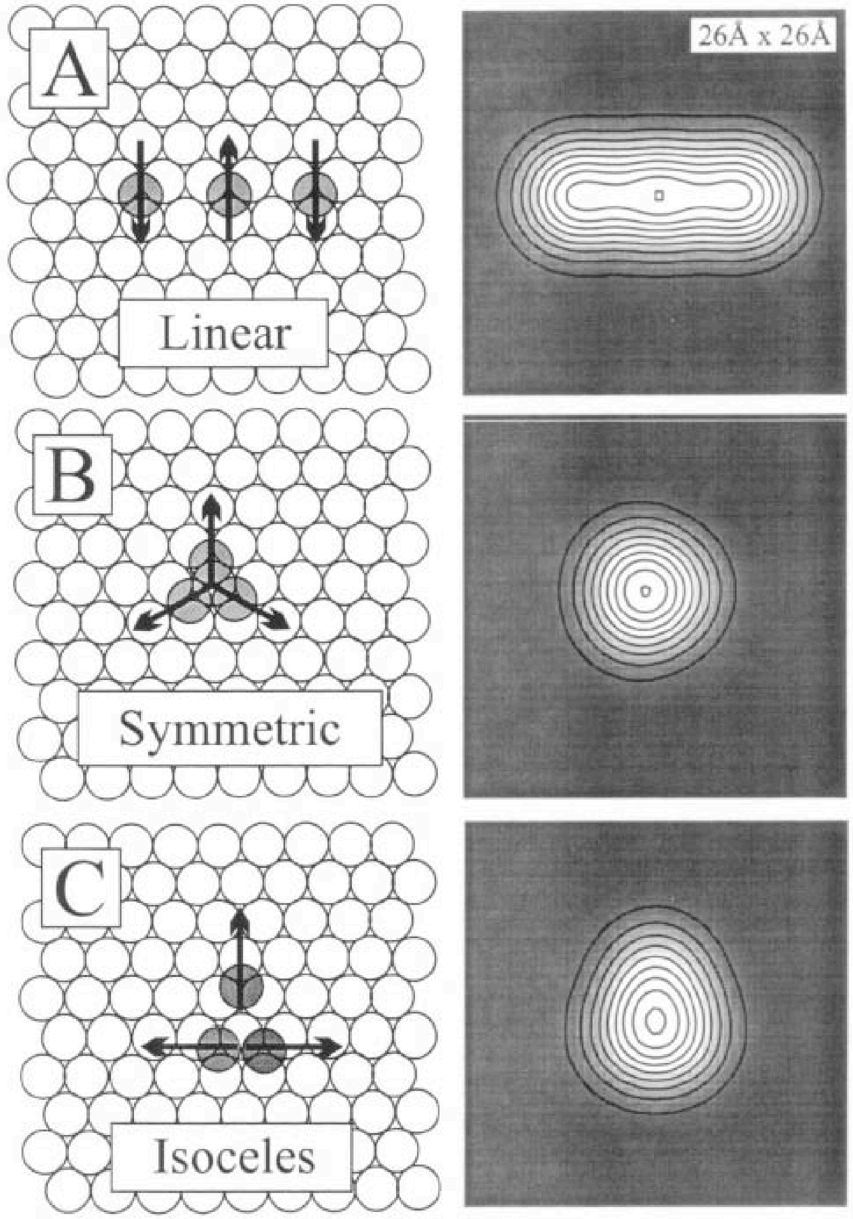
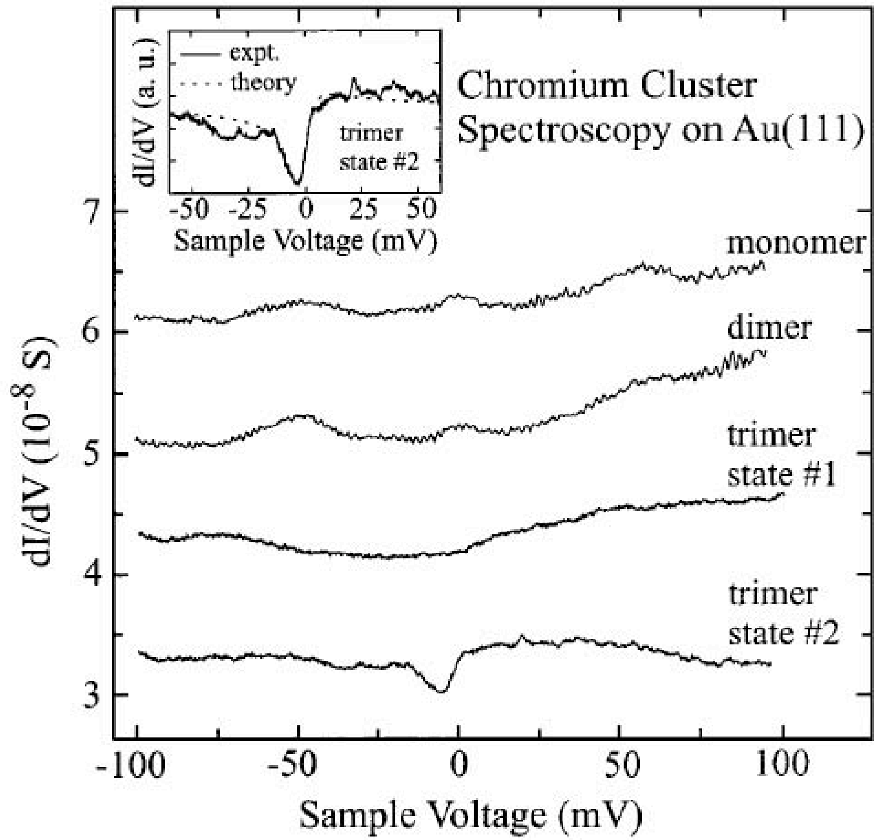


FIG. 3. Theoretical density plots on the right for three model trimer structures at left: (A) linear trimer, (B) compact symmetric trimer, and (C) compact isoceles trimer. Arrows show spin configurations predicted for these structures by Uzdin *et al.* [7].

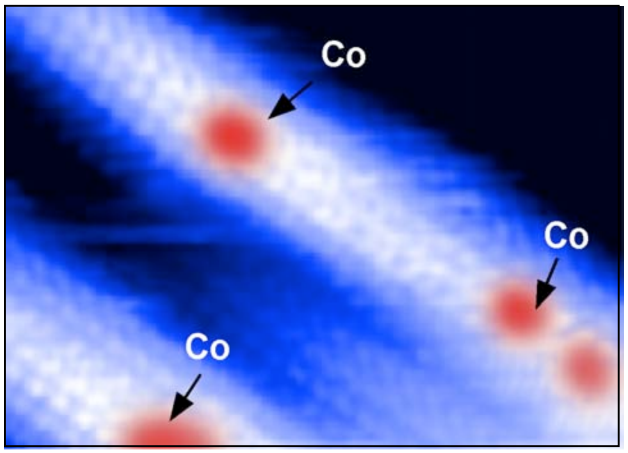


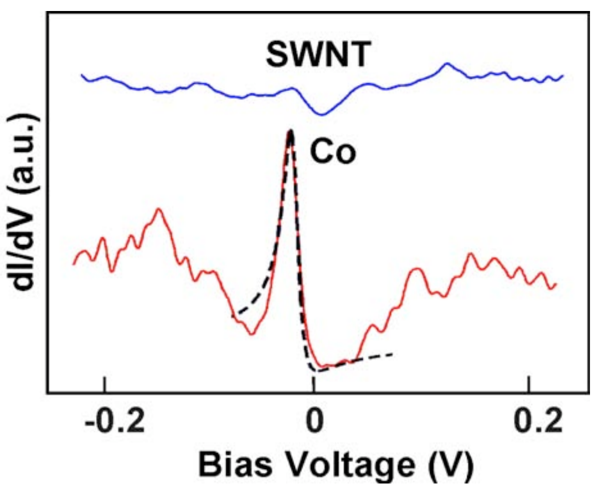
Cr trimers on Au

Jamneala, Madhavan, and Crommie
PRL 87, 256804 (2001).

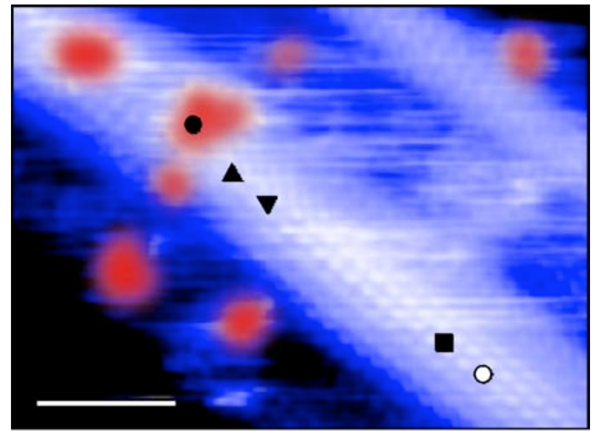
Kondo Effect in Co clusters on SWNTs

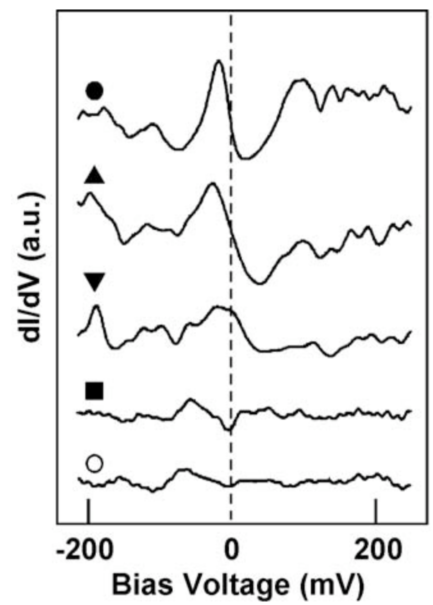
• Spectroscopic Features Near E_F





• Spatial dependence of dI/dV peak

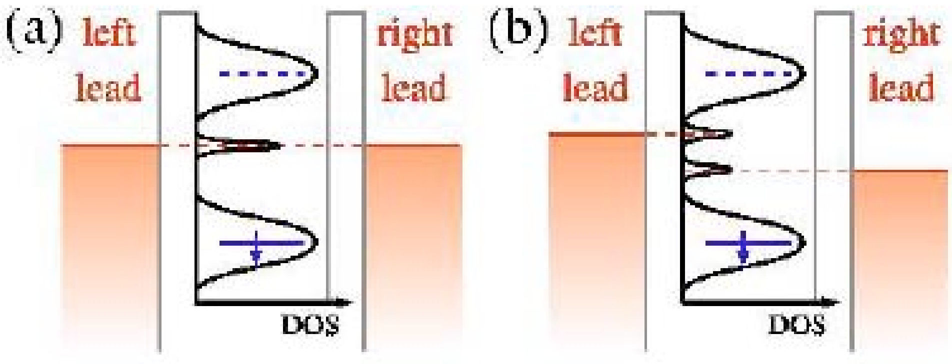


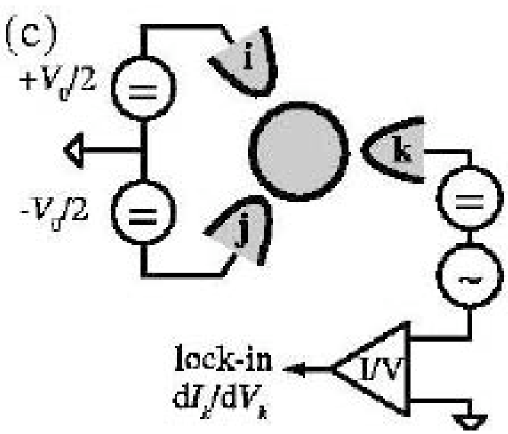


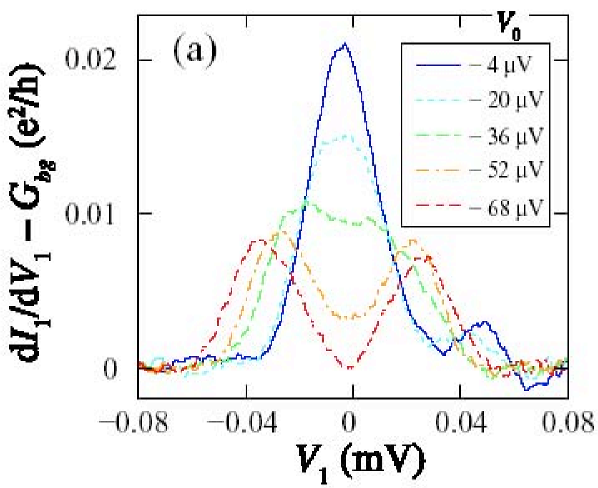
Odom, Lieber
Science **290**, 1549 (2000)

From the theoretical fit, the Co/SWNT Kondo temperature ~ 90 K

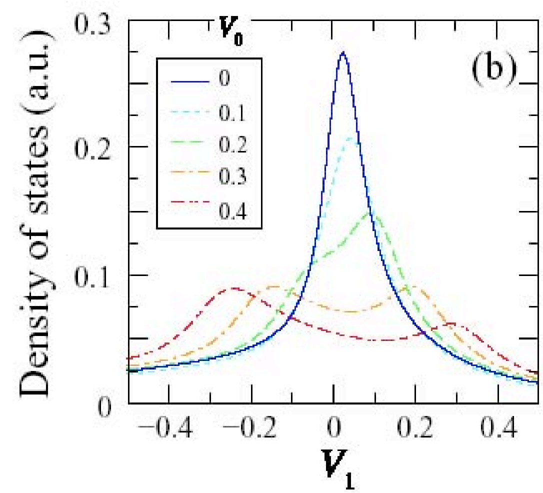
Three-terminal SET for non-equilibrium studies







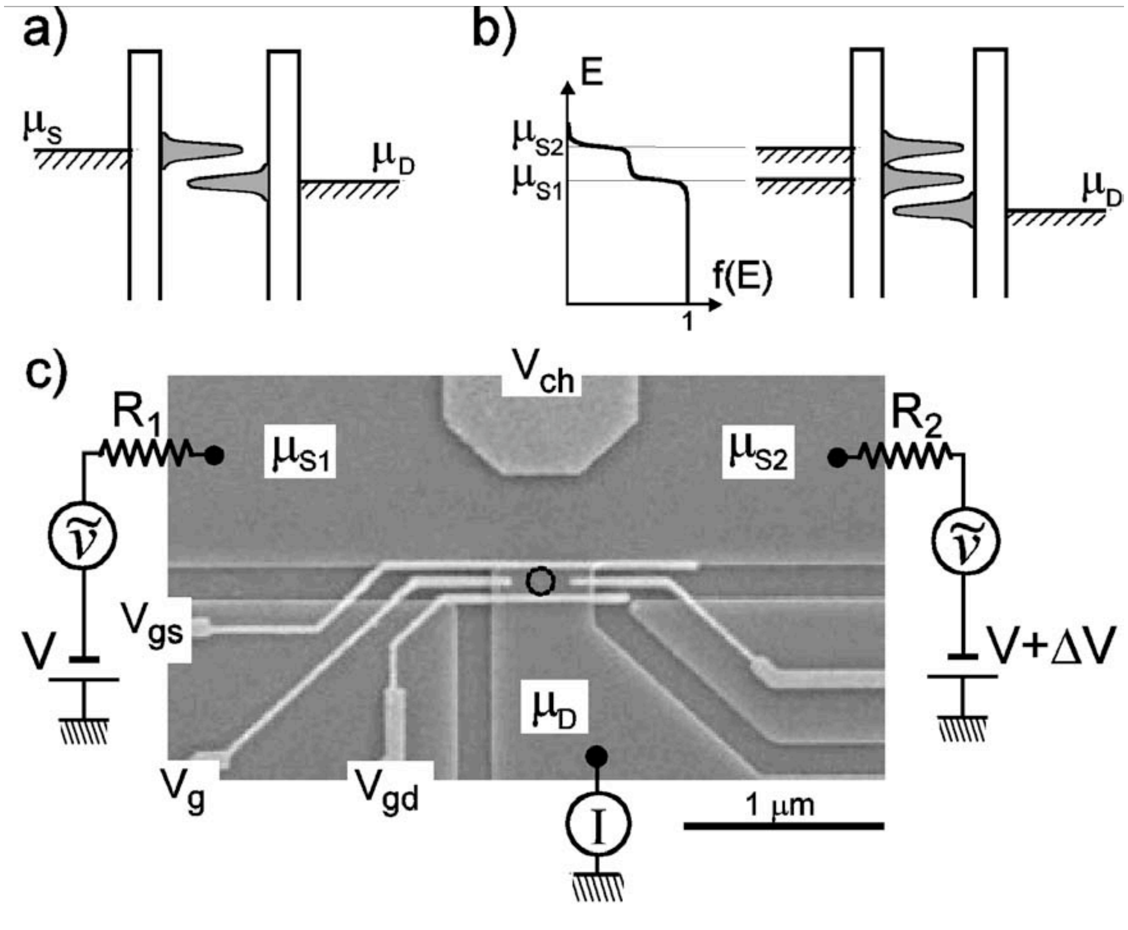
experiment



theory

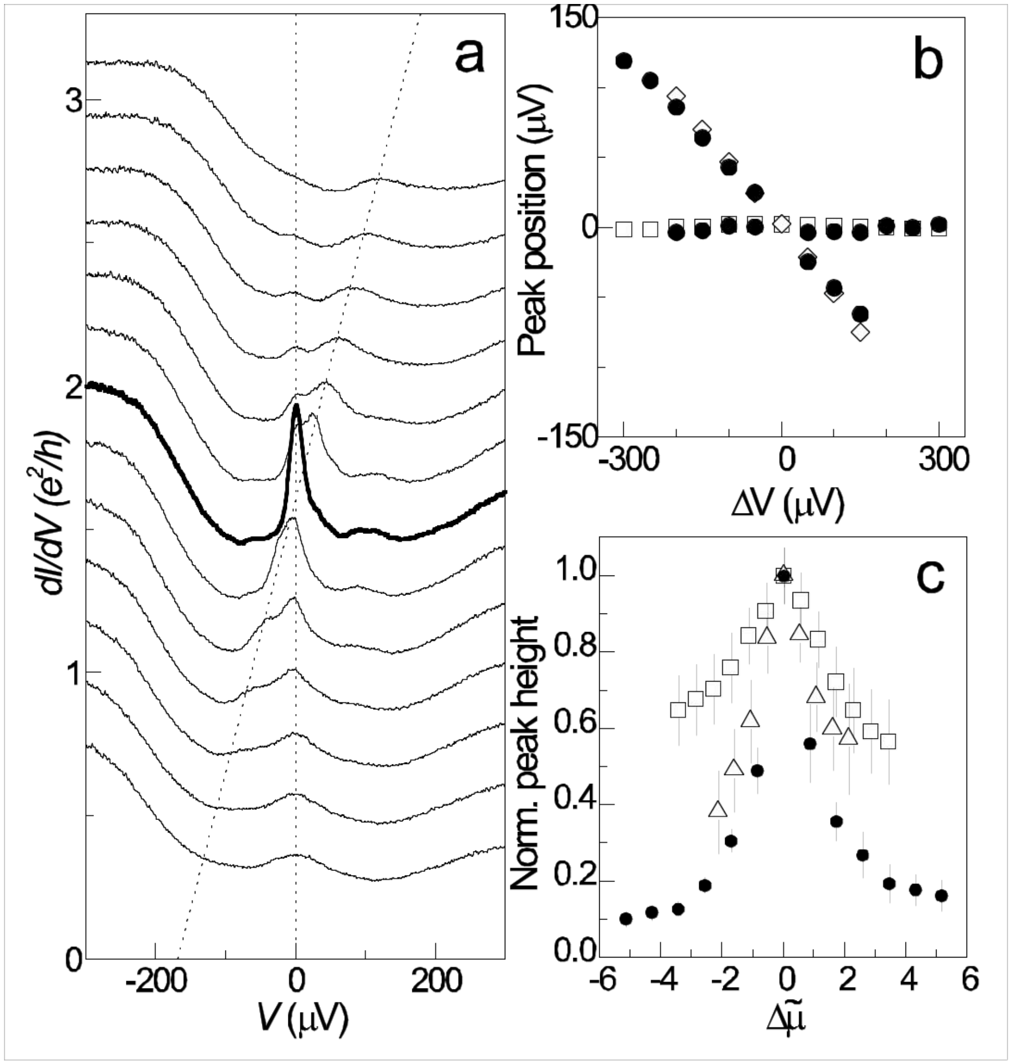
Leturcq, Ensslin et al., cond-mat/050511 (2005)

Three-terminal SET for non-equilibrium studies



De Franceschi, Kouwenhoven et al., PRL **89**, 156801 (2002).

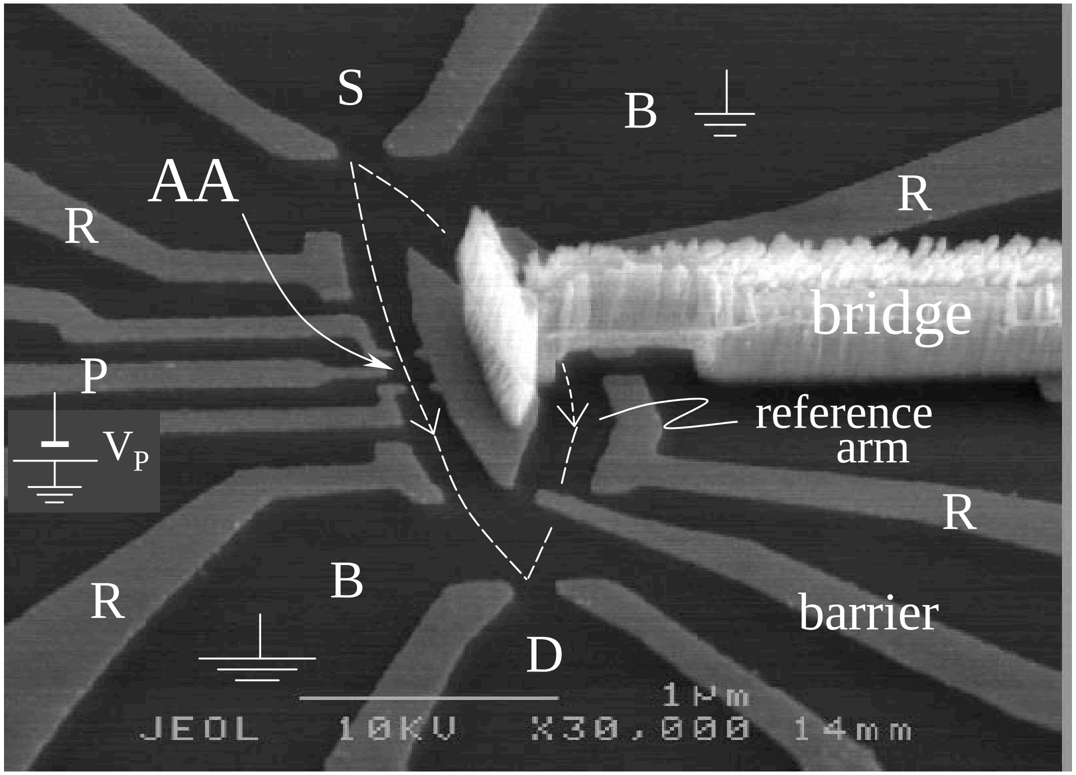
Three-terminal SET for non-equilibrium studies



- Peaks in conductance when probe is aligned with either reservoir
- Peaks get weak out of equilibrium (Kondo suppressed)

De Franceschi, Kouwenhoven

Four Terminal Interferometer with Kondo Quantum Dot



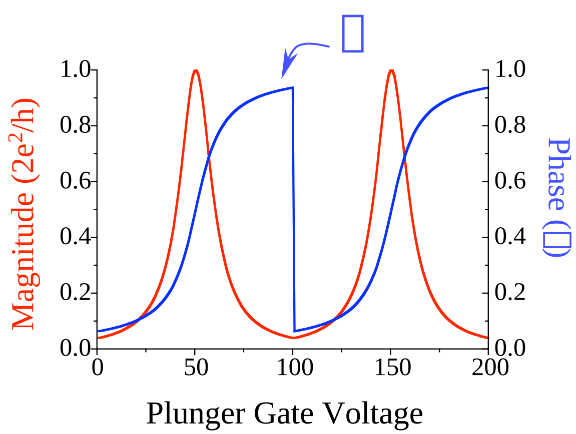
- S ….. source
- D ….. drain
- B ….. base
- R ….. reflector
- P ….. plunger gate

Ji, Heiblum et al. PRL **88**, 076601 (2002)
Science **290**, 770 (2000).
(following Schuster et al. Nature **385**, 417 (1997))

Expected Phase Evolution

Coulomb Blockade Regime

measured by R.Schuster *et al*. ('97)



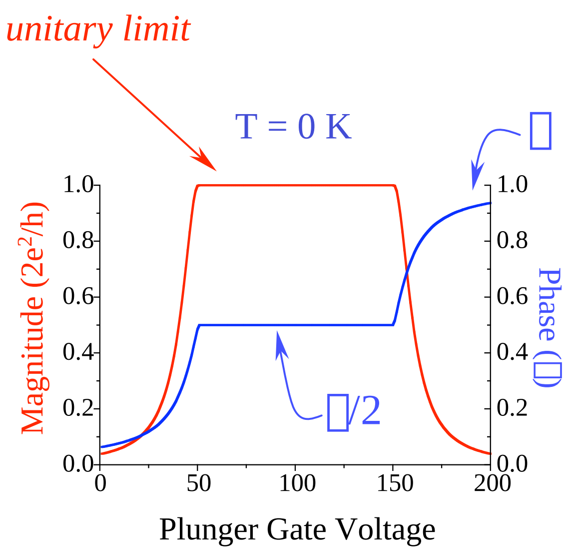
• Phase evolves across resonance
as expected

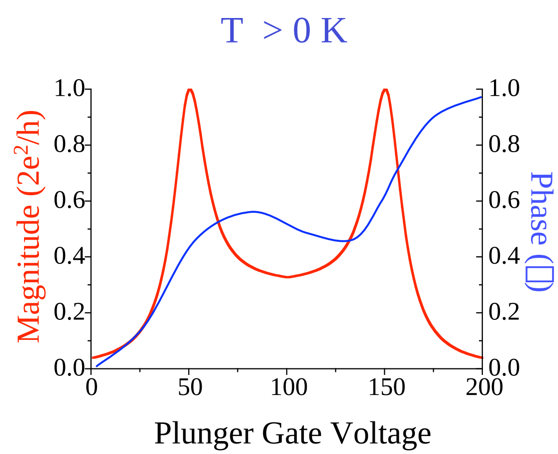
• Phase lapse in the valley
not understood

• Similarity of phase in all peaks
not understood

Kondo Correlated Regime

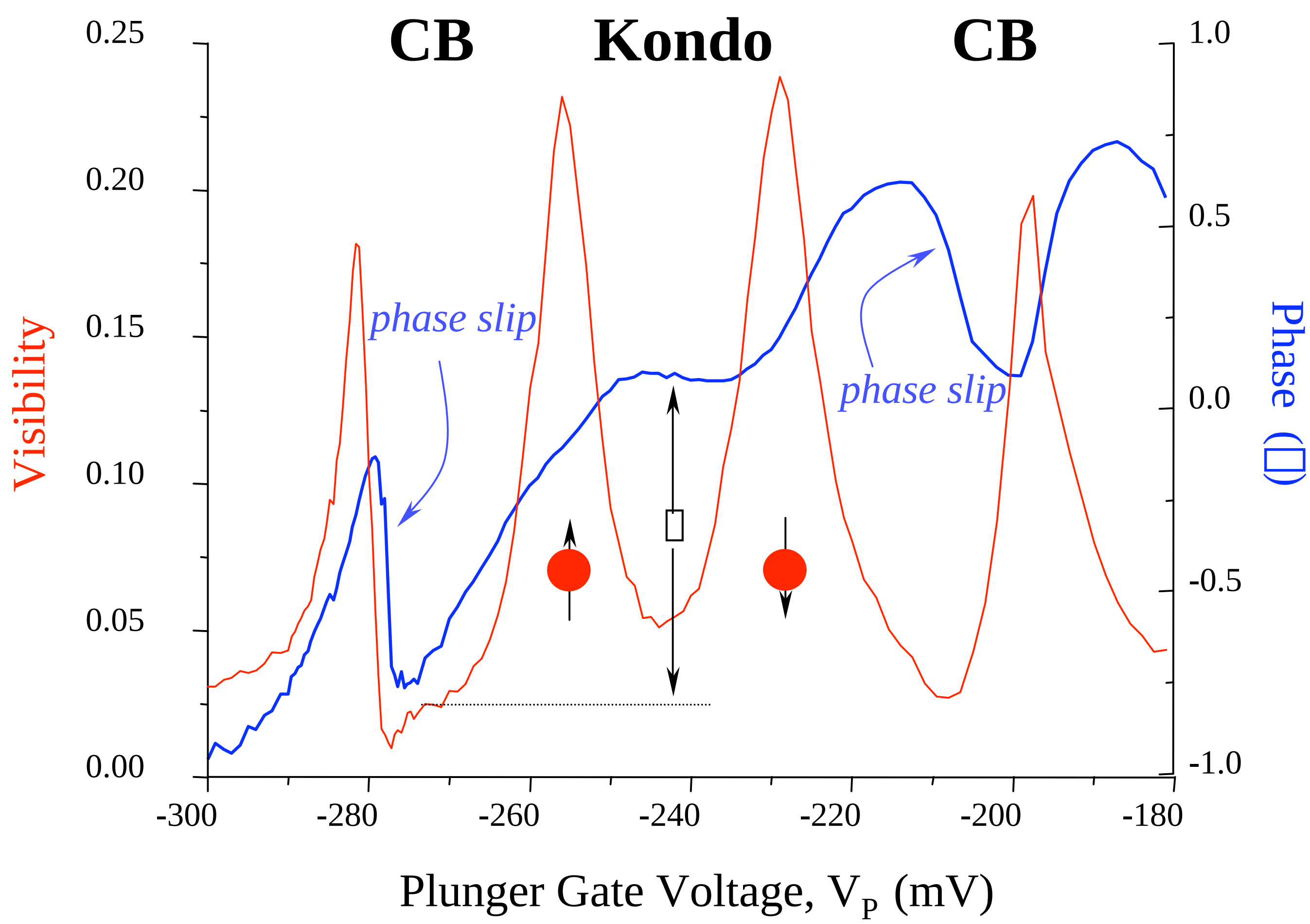
predicted by U. Gerland *et al*. (PRL 84, 3710 (2000))





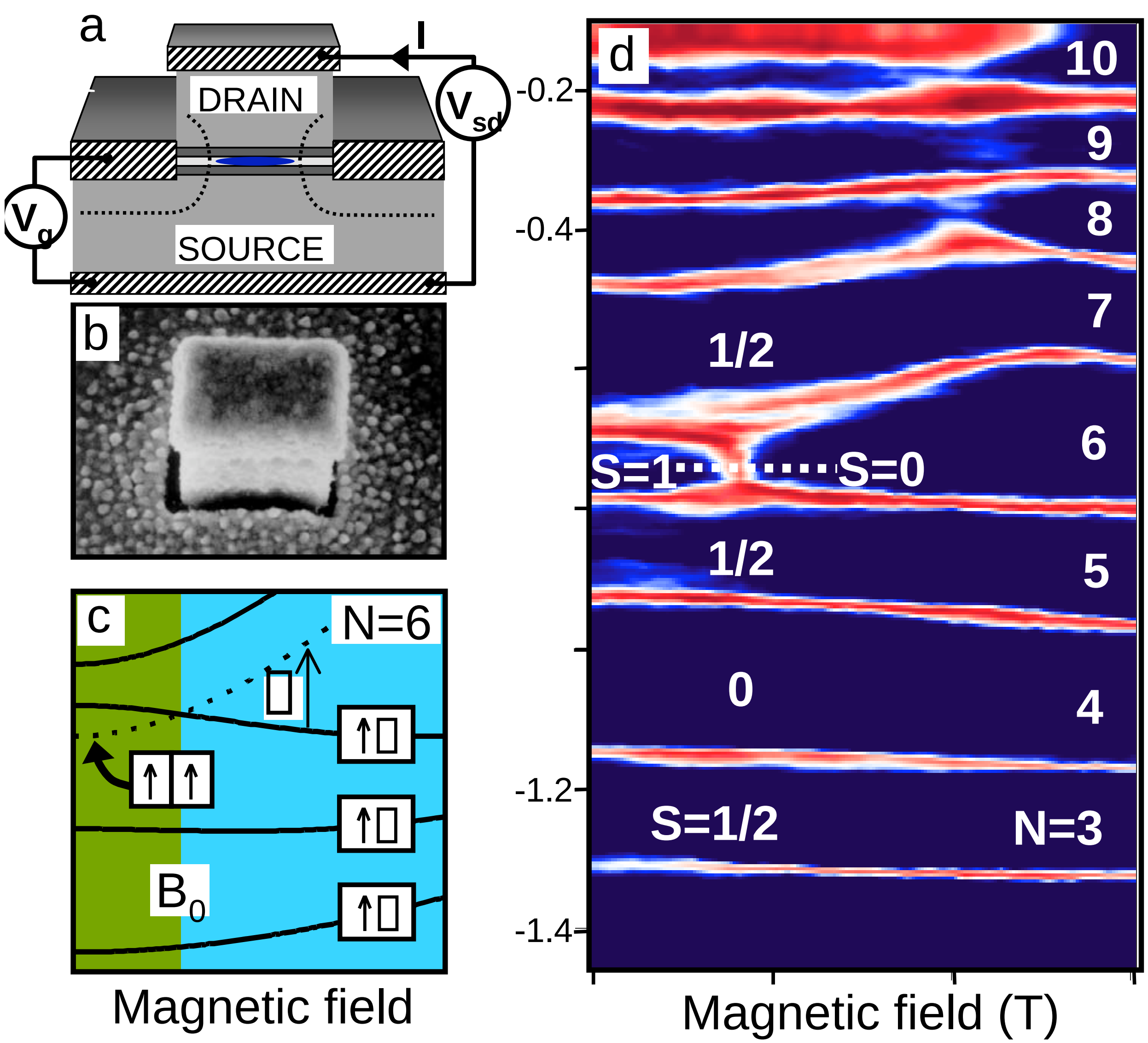
- Phase shift is a constant π/2 in the Kondo valley
- Total phase shift through two peaks is π

Measured Phase Evolution in Kondo Pair



Ji, Sprinzak, Heiblum

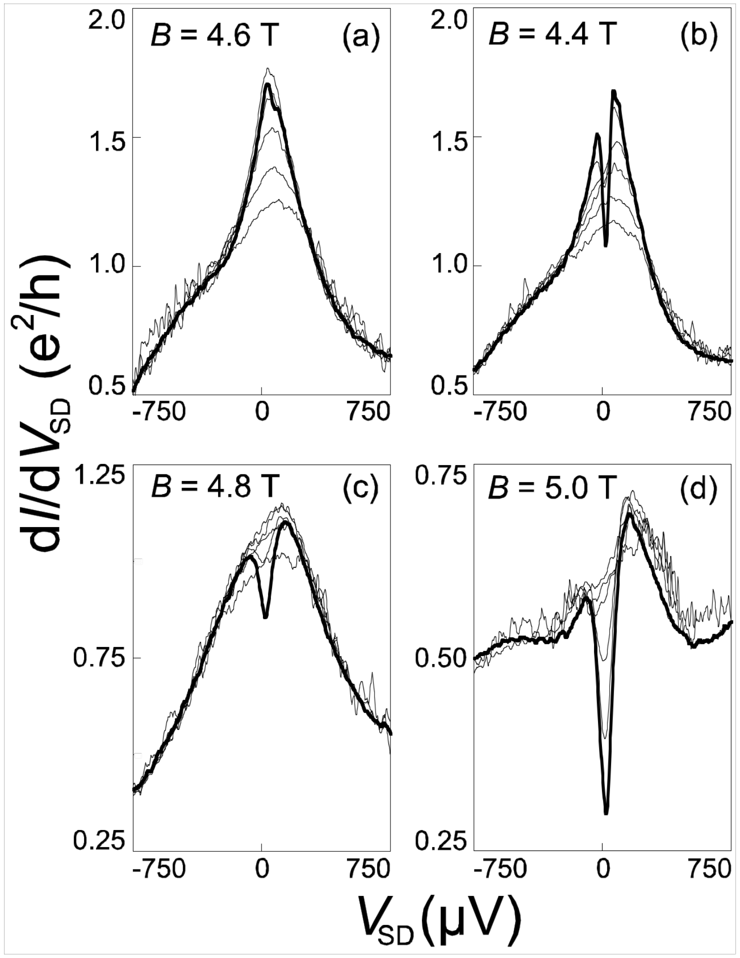
Integer-Spin Kondo (0 <-> 1)

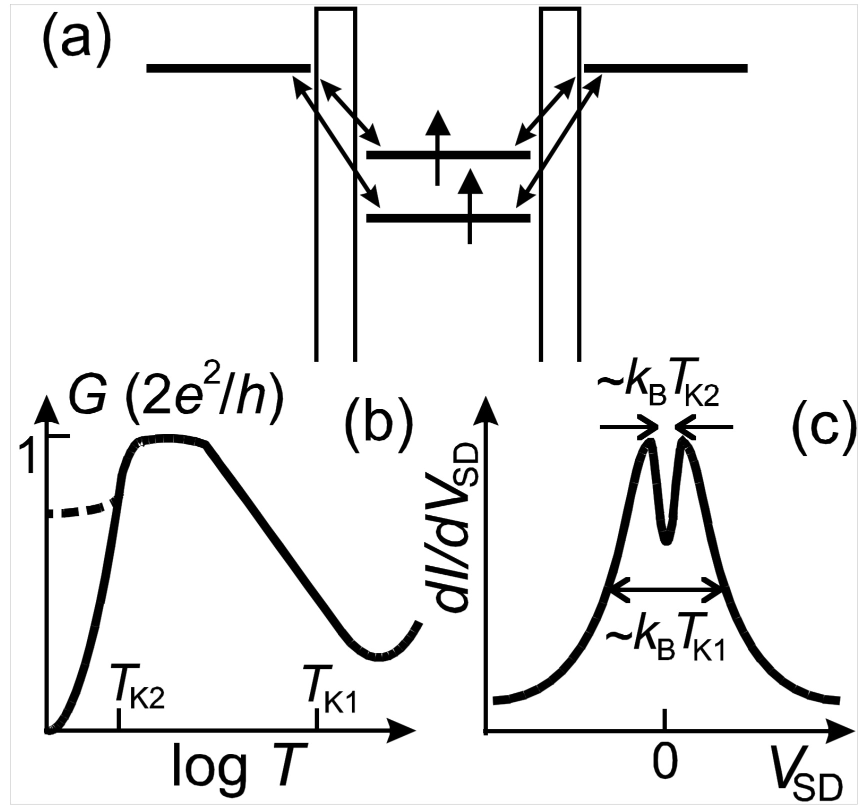


At singlet-triplet degeneracy
Sasaki, Tarucha, Kouwenhoven et al., Nature **405**, 764 (2000)

Two-Stage Kondo for S=1

Singlet-triplet degeneracy with single-channel leads





van der Wiel, Kouwenhoven et al., PRL 88, 126803 (2002)
theory by Pustilnik et al., cond-mat/0010336

Other Kondo Variants

Spin 1/2, simultaneous orbital and spin degeneracy
Sasaki, Tarucha et al., PRL **93**, 017205 (2004)

Spin 1/2, orbital degeneracy, with and without spin degeneracy
Jarillo-Herrero, Kouwenhoven et al. Nature **434**, 484 (2005)

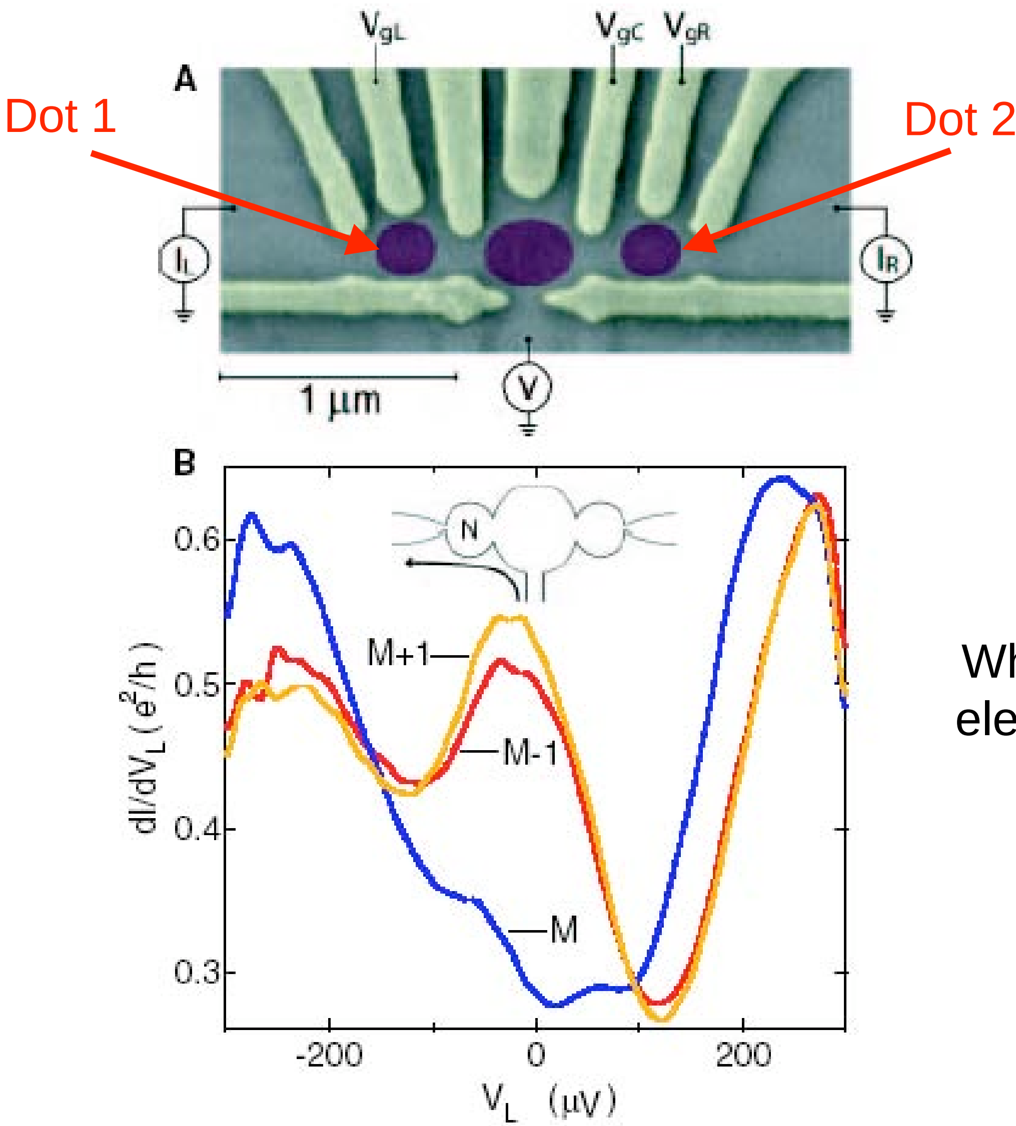
Coupling of Kondo state with microwave photons
Kogan, Amasha, and Kastner, Science **304**, 1293 (2004)

Coupling of Kondo state with vibrational modes in molecular devices
theory: Paaske and Flensberg, PRL **94**, 176801 (2005)

2-Channel Kondo effect in quantum dots
theory: Oreg and Goldhaber-Gordon, PRL **90**, 136602 (2003)

Kondo effect in single-molecule transistors
Kondo effect with magnetic electrodes
(more on these later)

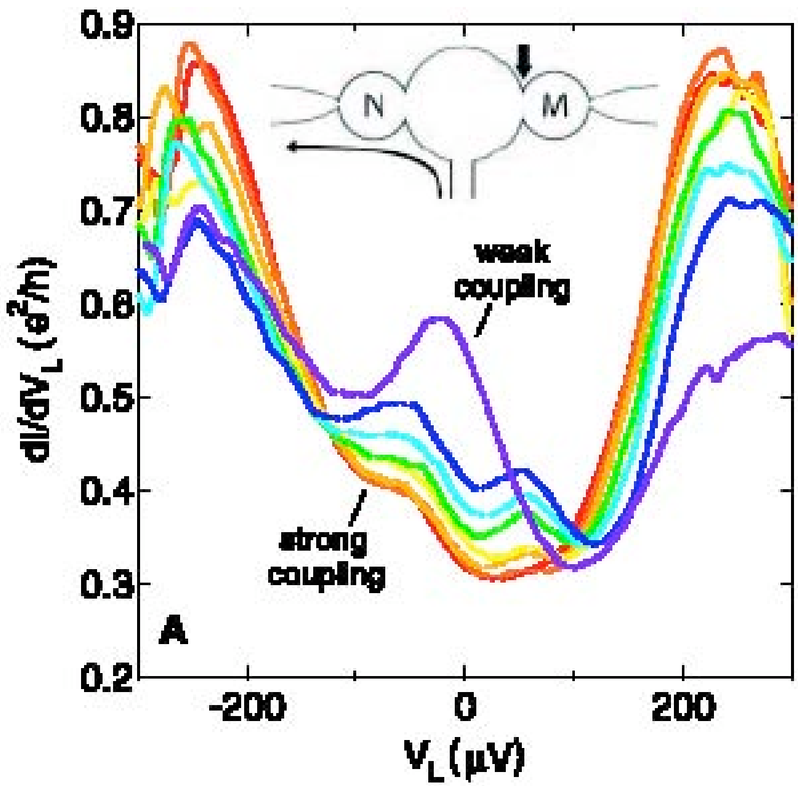
Two-impurity Kondo



Craig, Marcus et al.
Science **304**, 565 (2004)

M is odd.
When Dot 2 contains an unpaired electron, the Kondo effect in Dot 1 is suppressed.

Two-impurity Kondo



Craig, Marcus et al.
Science **304**, 565 (2004)

The coupling between the two dots is tunable.

Odd number of electrons in both dots

Making Molecular-Scale Junctions

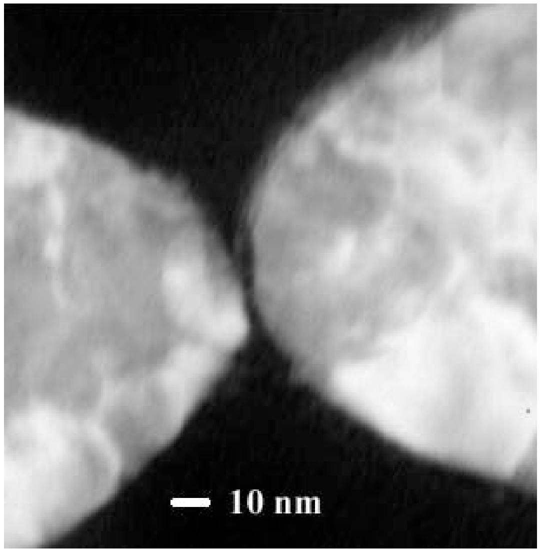
Techniques for Contacting Molecular-Scale Structures

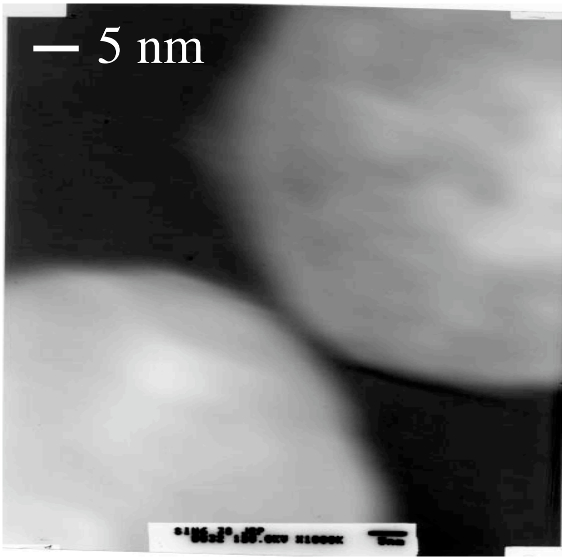
- Scanning-Probe Techniques
- Adjusting Gap Sizes Controllably
- Nanoholes, and Devices made from Self-Assembled Molecular Layers (SAMs)
- Mechanical Break Junctions
- Electromigration Break Junctions

Some Physics Results with Electromigration Junctions

- C_{60} and C_{140} devices:
  - Single-electron transistors and molecular vibrations
- Transition-metal complexes:
  - Using chemistry to control coupling to electrodes
  - Coulomb blockade and the Kondo Effect
  - Kondo Effect with Magnetic Electrodes

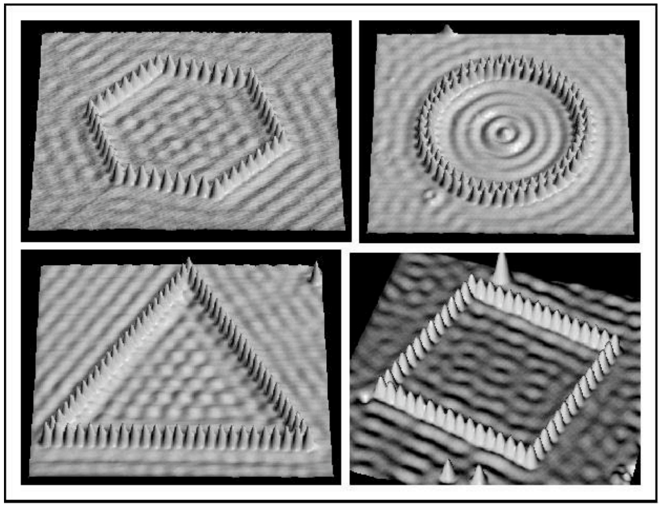
Limits of Electron-Beam Lithography





Disadvantages:
Reproducibility from device to device is about 5 nm
-- not quite to the molecular scale
Hard to maintain clean surfaces.

1. **Scanning-Probe Techniques**



Advantages

Great flexibility

Can manipulate the sample and do spectroscopy.

Spatial Information

Force Information

Disadvantages

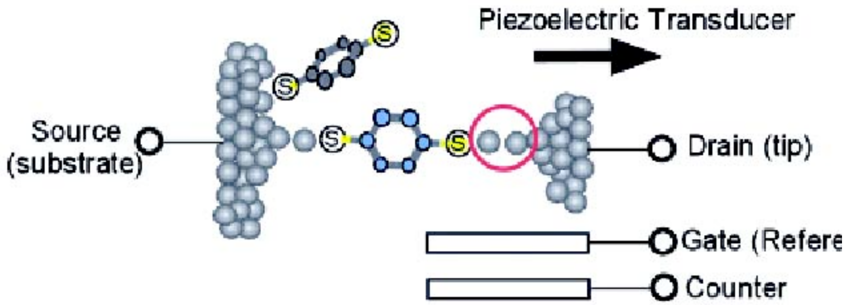
Hard to make gates to tune energy levels

Hard to imagine making circuits

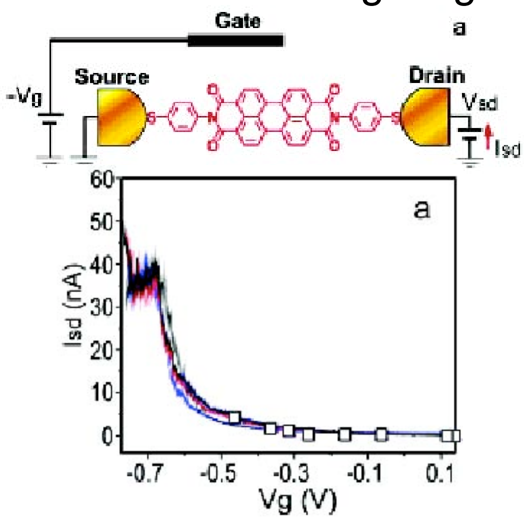
Vibration and drift

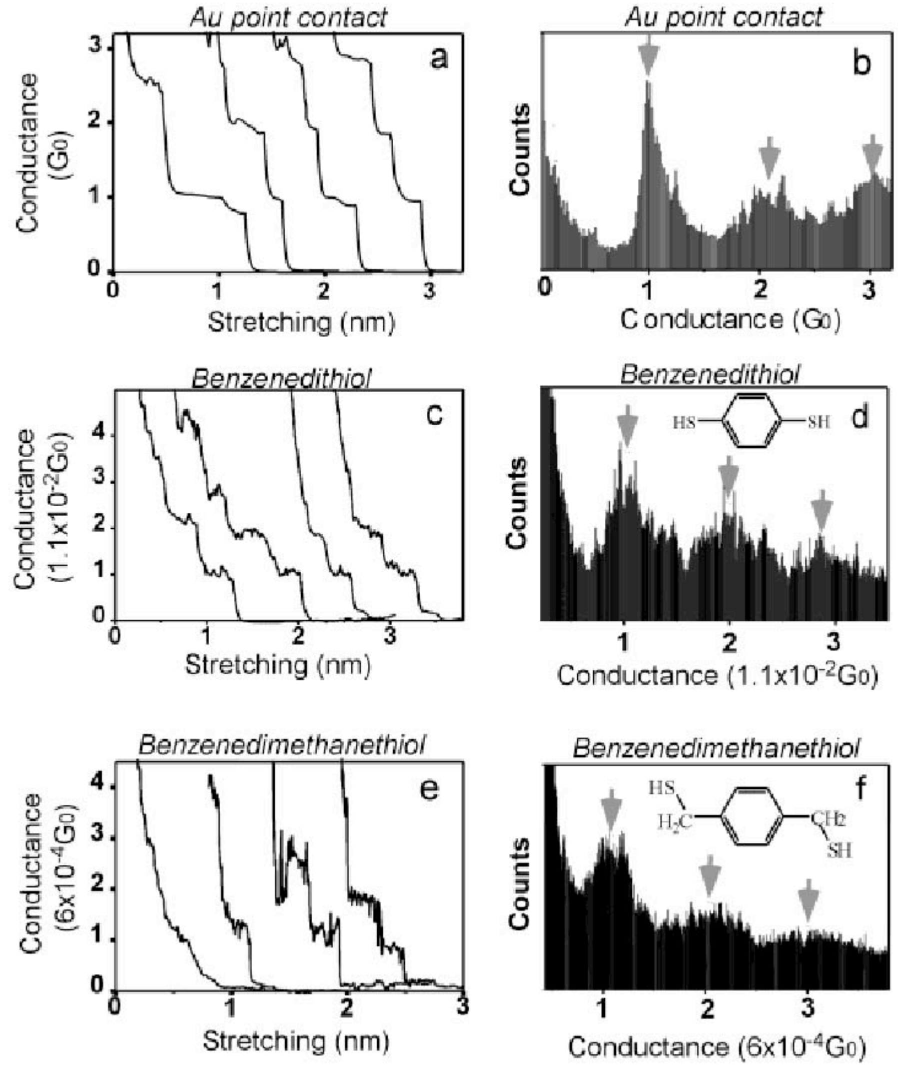
Hard to cool to low T for best spectroscopy

Electrical lines must be filtered for best spectroscopy



recent demonstration of
electrochemical gating



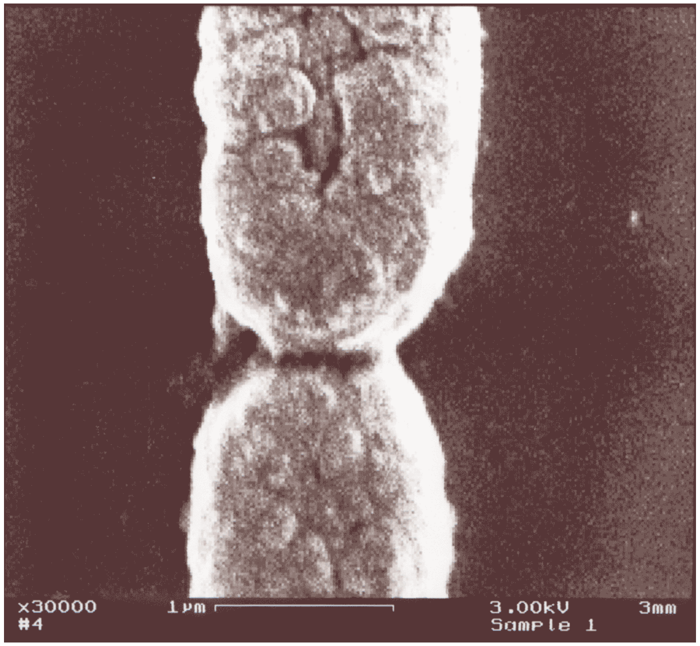


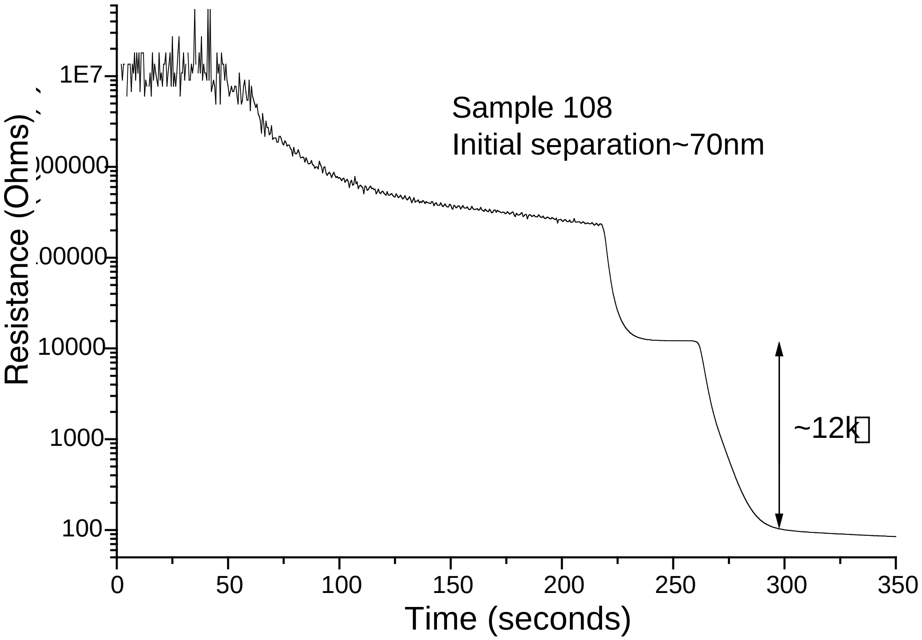
B. Xu and N. J. Tao, Science **301**, 1221 (2003)
X. Xiao, B. Xu, and N. J. Tao, Nano Lett. **4**, 267 (2004)
B. Q. Xu, X. Y. Xiao, X. M. Yang, and N. J. Tao, J. Am. Chem. Soc. **127**, 2386 (2005)

2. **<u>Adjusting the Size of The Gap</u>**

Electrodeposition (Morpurgo *et al.*, Appl. Phys. Lett. **74**, 2084 (1999))

Electrochemical Etching (Y. V. Kervennic *et al.*, Appl. Phys. Lett. **83**, 3782 (2003))

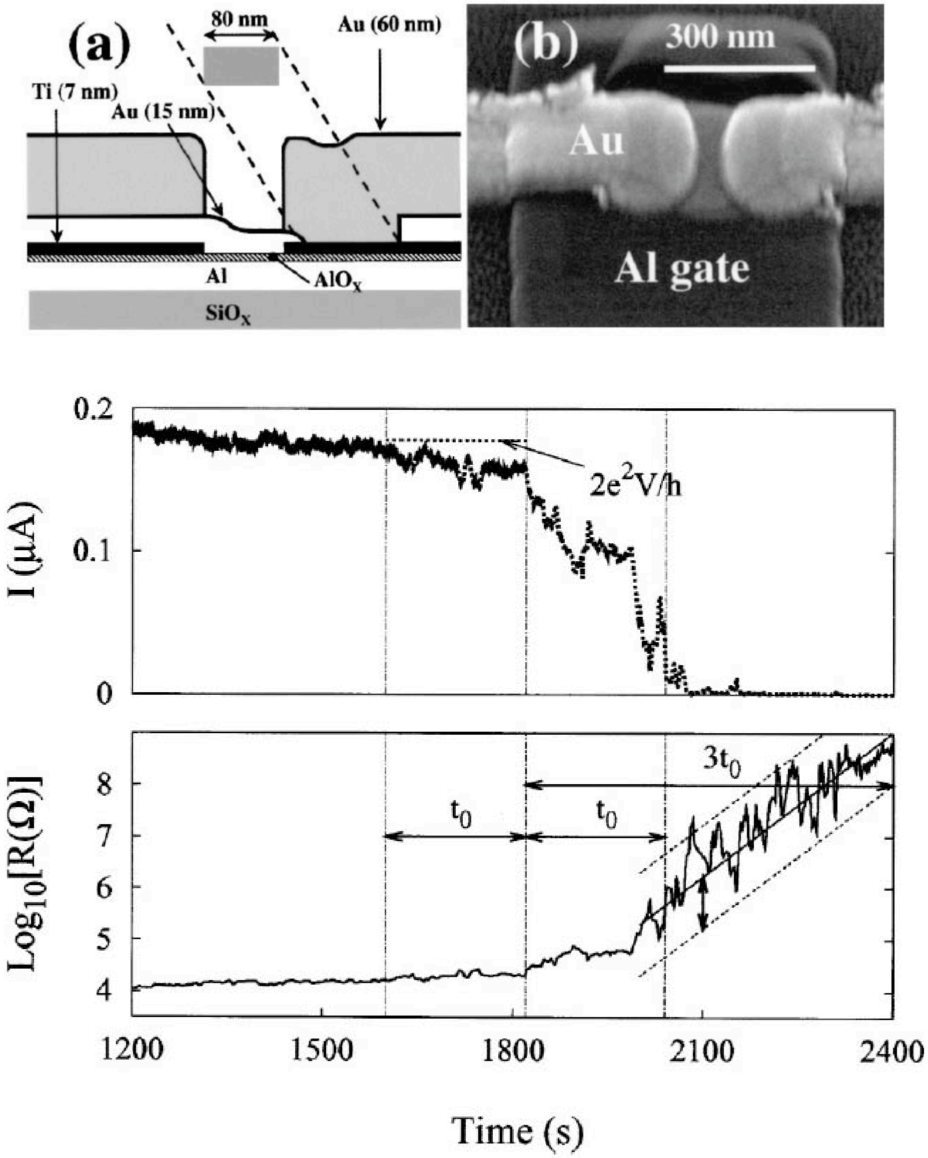




Advantages: Easy to do.

With electrodeposition, can make electrodes from different materials.

Disadvantages: Difficult to maintain surface cleanliness



Electrochemical etching of a thin gold layer.

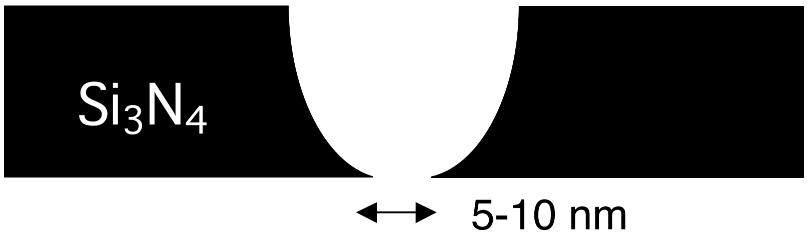
Exponential dependence of resistance as a function of time suggests a constant etch rate, even on near-atomic scales.

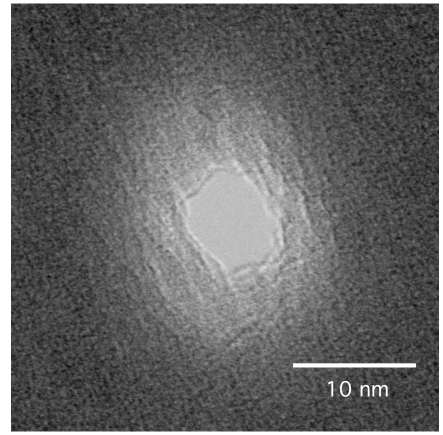
Controlled gap spacing?

Y. V. Kervennic et al., Appl. Phys. Lett. **83**, 3782 (2003).

3. Nanoholes

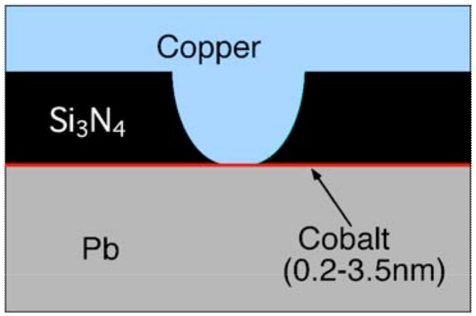
Ralls, Buhrman (1989)



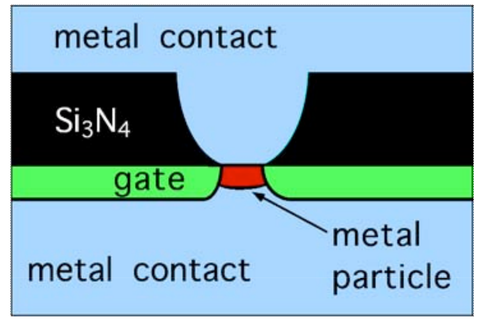


Wide variety of uses:

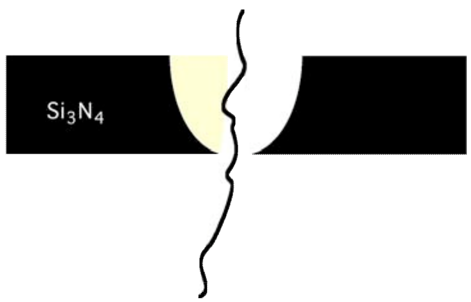
metal interfaces, spin filtering, Andreev reflection



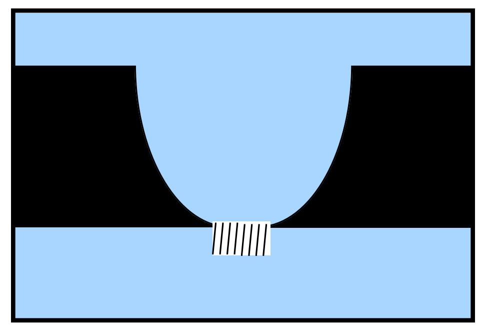
quantized states in nanoparticles



DNA transport (Brandon, Golovchenko)



self-assembled monolayers (Reed)



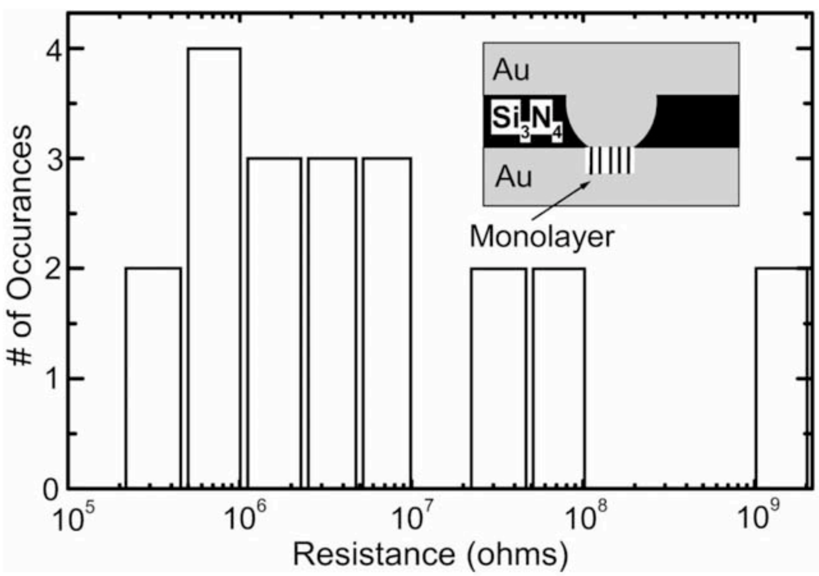
Disadvantages of Studying Molecular Layers with Nanoholes

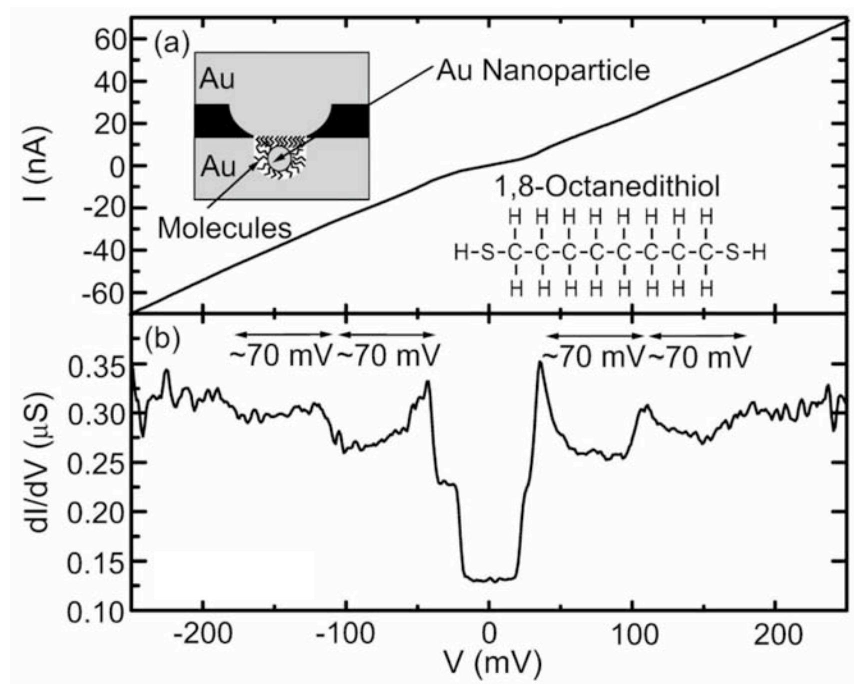
Hard to measure single molecules

No gate to tune molecular energy levels

What happens to the monolayer when metal is deposited on top?

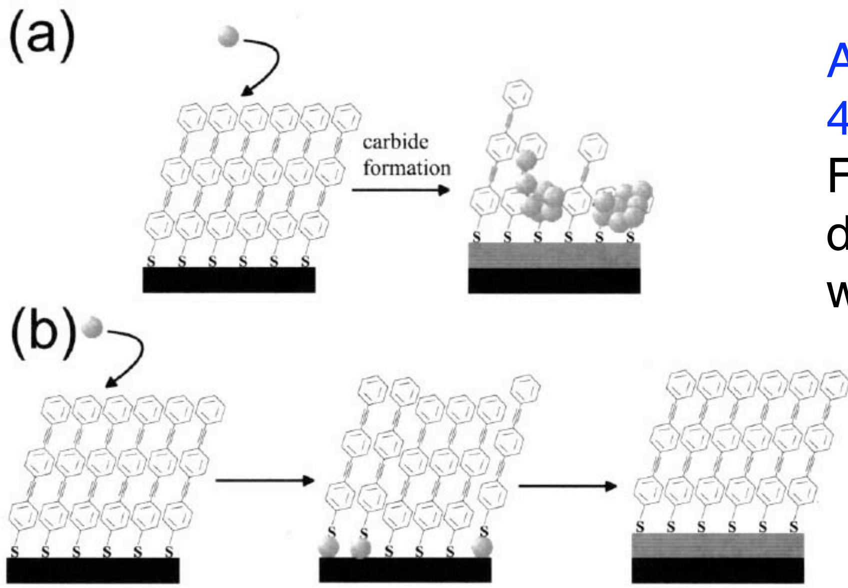
Must be very careful to avoid leakage currents through nitride above 77 K.





More on evaporating metals onto molecular monolayers:

These are problems for nanoholes, but even more so for larger contacts on top of molecular layers.



A. V. Walker et al., Appl. Phys. Lett. **84**, 4008 (2004)

From IR spectroscopy and SIMS, determine that evaporated Ti reacts with self-assembled monolayer

Au evaporated at room temp can penetrate barrier. Molecules float on top.

J. W. P. Hsu et al., J. Vac. Sci. Technol. B **21**, 1928 (2003):

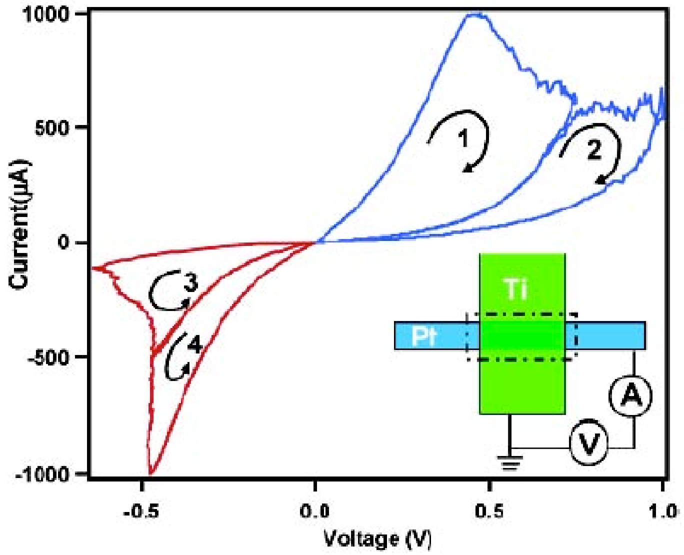
From analysis of transport through GaAs/octanedithiol SAM/metal devices,

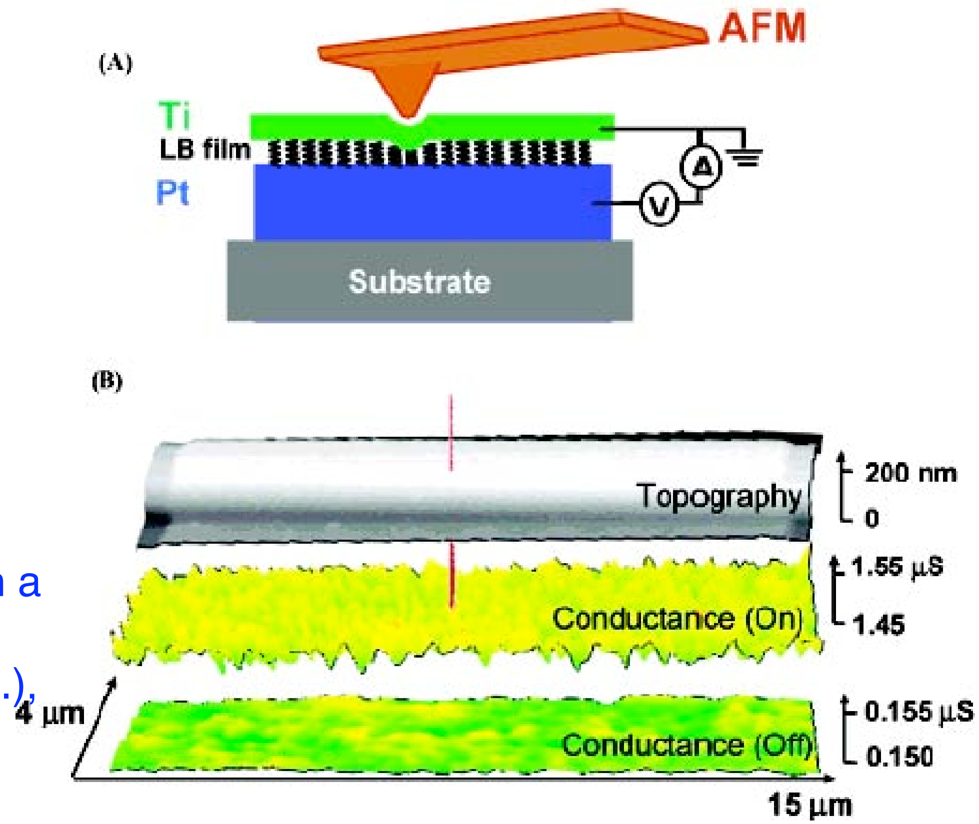
~ 35% of layer has penetrating gold for evaporation with room-temp substrate

~ 1% of layer has penetrating gold for evaporation with -15 C substrate

Even when the initial evaporation does not produce metallic shorts through a molecular layer, subsequent application of voltages can produce metal filaments.

C. N. Lau, D. R. Stewart, R. S. Williams, Marc Bockrath, Nano Lett. **4**, 569 (2004).

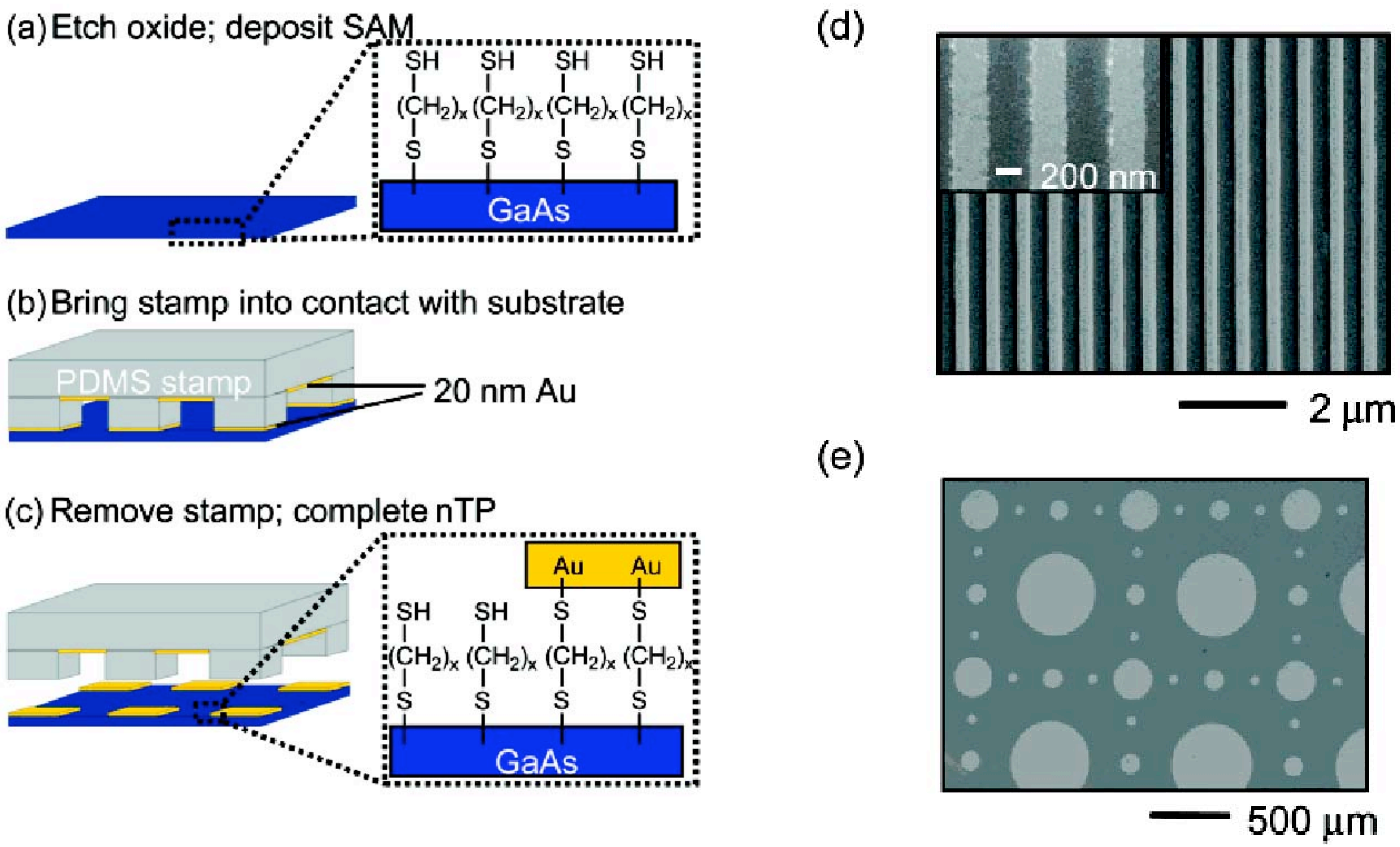




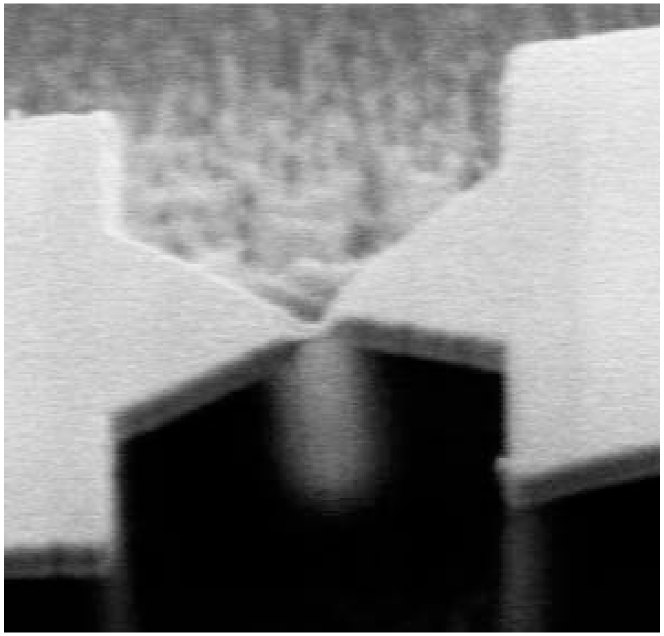
An applied voltage can be used to switch a $Pt/C_{18}/Ti$ device between high and low conductance states (compare Heath, etc.), but the change is due to a local metal filament, not the molecules.

A Gentler Way for Putting Metal Contacts on Top of Molecular Layers: nanoTransfer Printing

Y.-L. Loo, D. V. Lang, J. A. Rogers, J. W. P. Hsu
Nano Lett. **3**, 913, (2003)



4. Mechanical Break Junctions



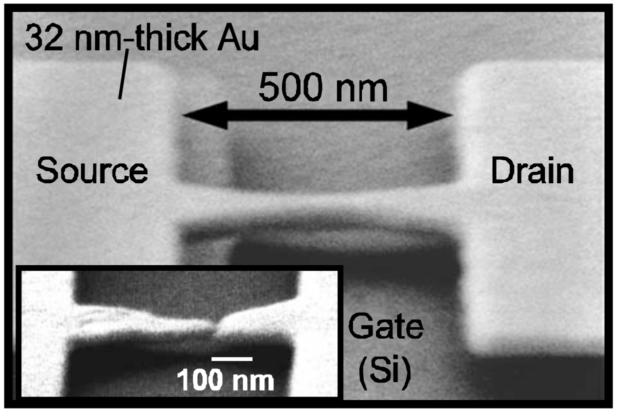
Used for studying molecules
(Reed, Saclay, Leiden, Karlsruhe)

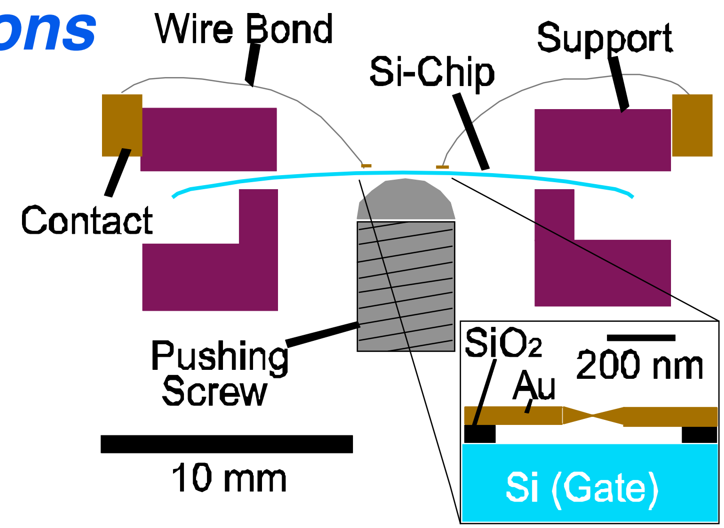
Advantage: Very mechanically stable
Can pull on molecule, look for change in resistance

Disadvantages:

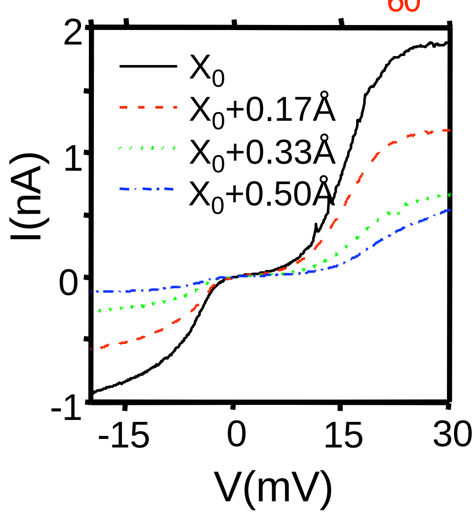
- Some molecule studies have used large electric fields -- diffusion of gold is a worry.

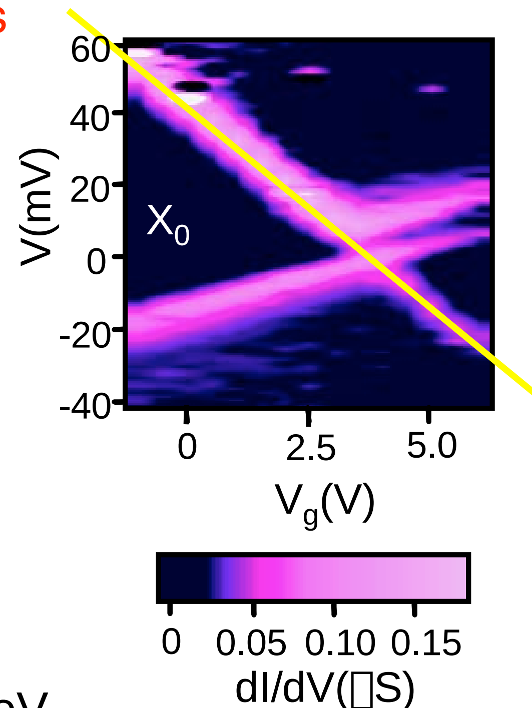
Gated Mechanical Break Junctions

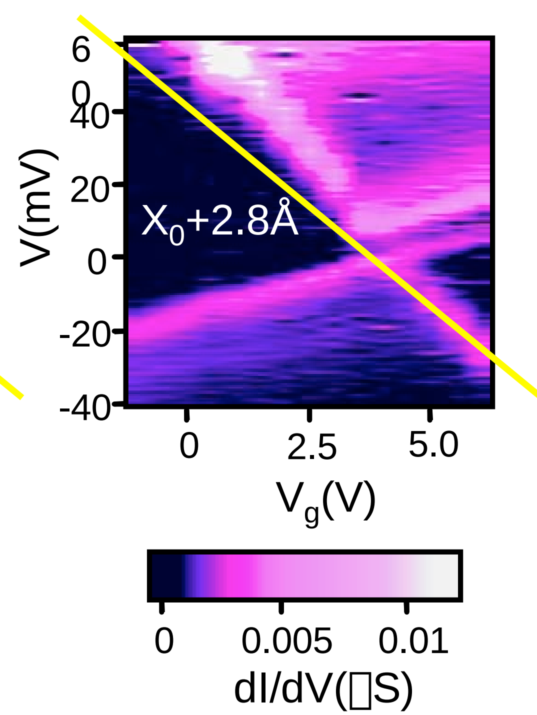




C_{60} devices





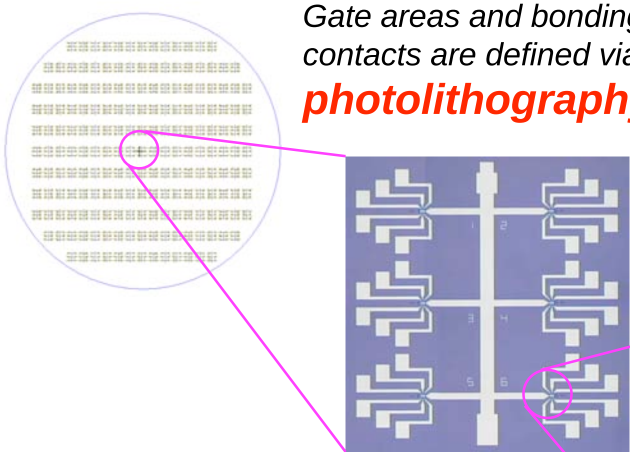


Total displacement = 5 Å
with stability better than 1 pm.
Energy shift by the gate = 160 meV

Alex Champagne et al., Nano Letters **5**, 305 (2005)

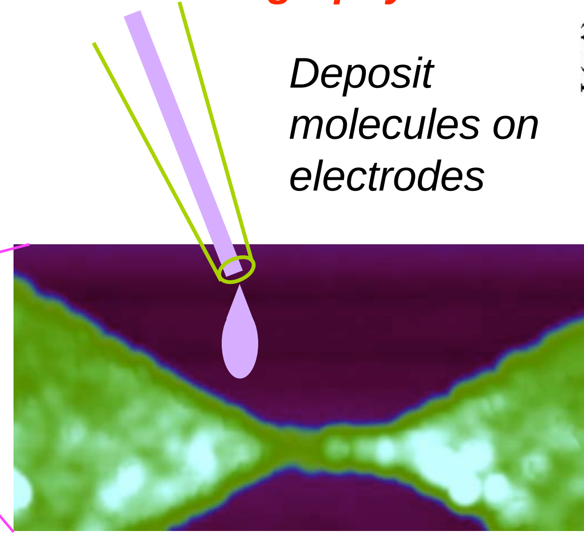
5. Electromigration Break Junctions (Park, McEuen, et al., Appl. Phys. Lett. 75, 301 (1999))

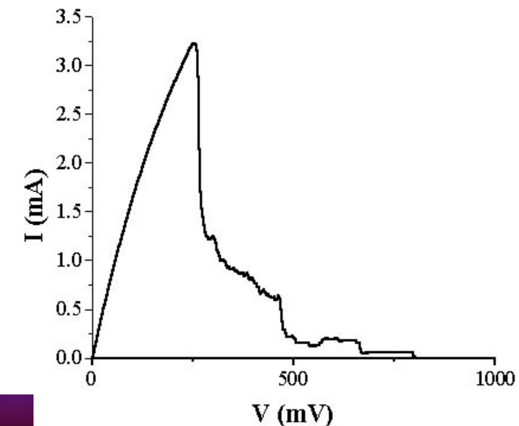
Gate areas and bonding contacts are defined via ***photolithography***.



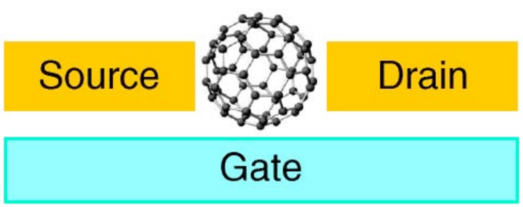
Nanowires are generated by ***e-beam lithography***.

Deposit molecules on electrodes

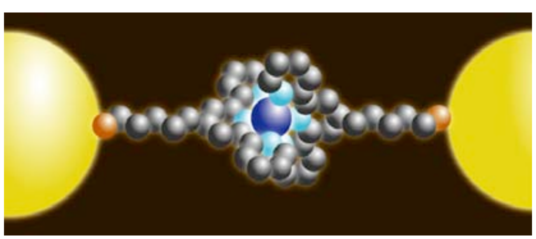




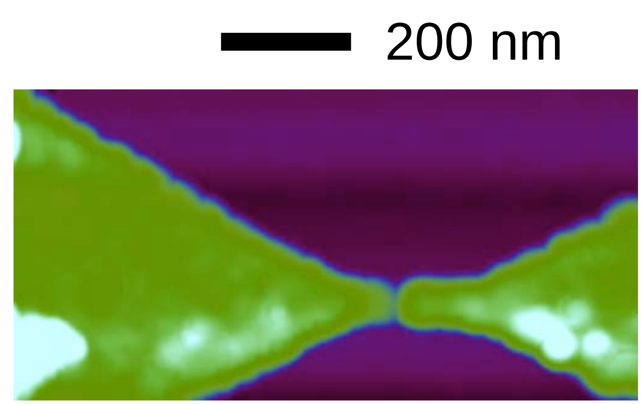
Pass large currents: electromigration – Induced Gap formation.
(Park, *et al. APL* 75, 301)



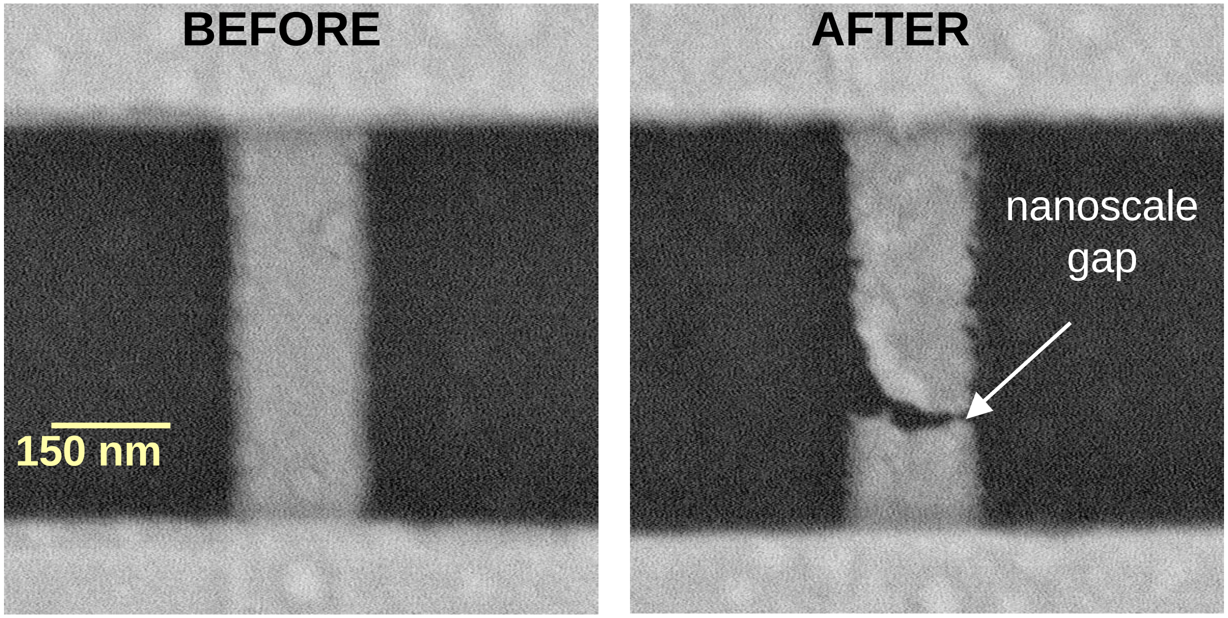
C_{60}



Cobalt

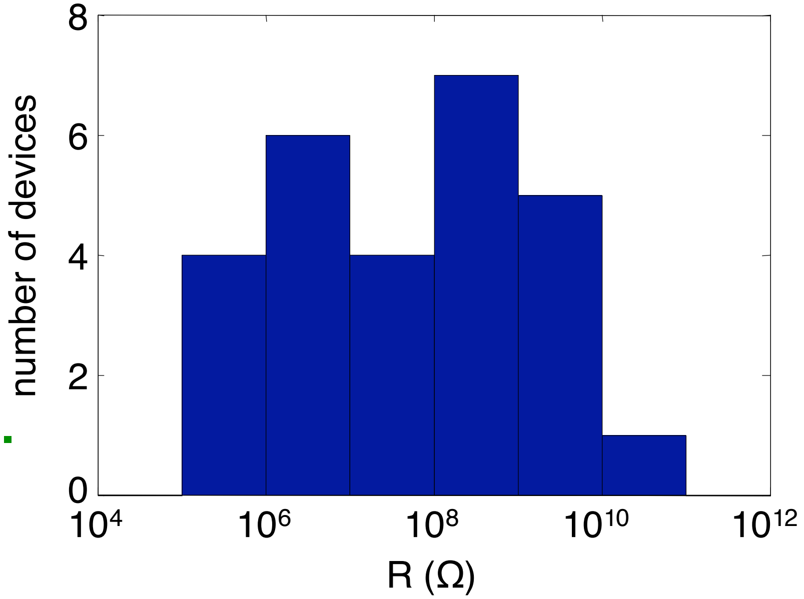


Electromigration Junctions



Pt

- After breaking, the gap width can be estimated from the tunneling resistance.
- Typically 1-3 nm wide. Relaxation occurs when the devices are warmed to room temperature.

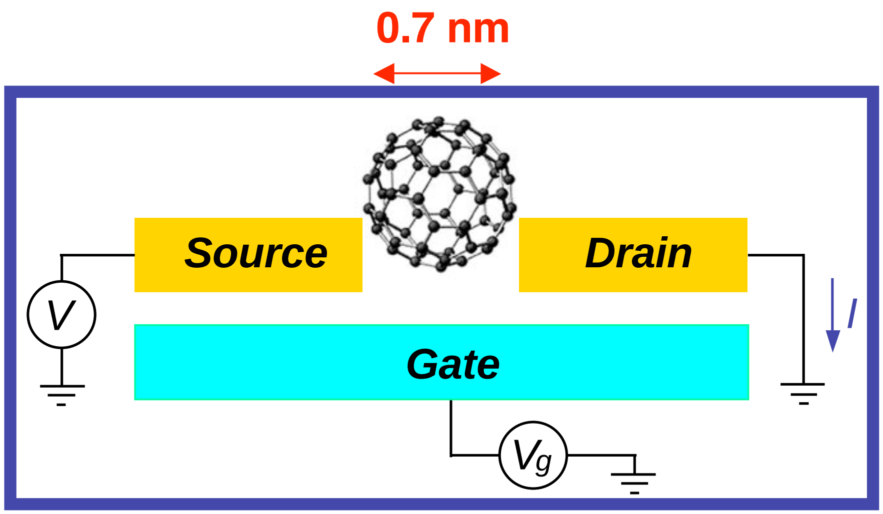


Flexible way to make gated nanojunctions.

Single electron transistors based on individual C_{60} molecules

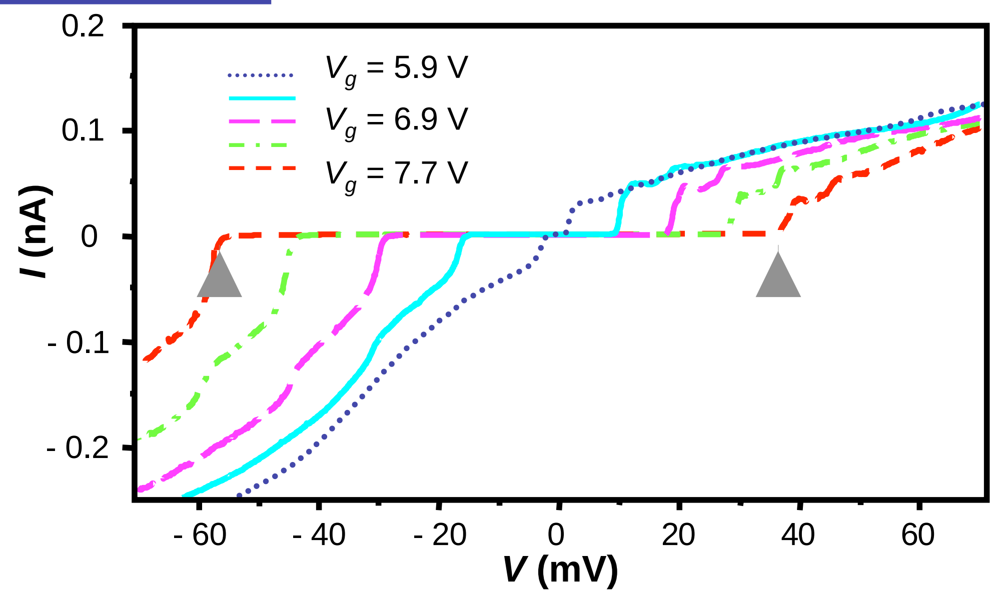
"a quantum ball and spring"

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

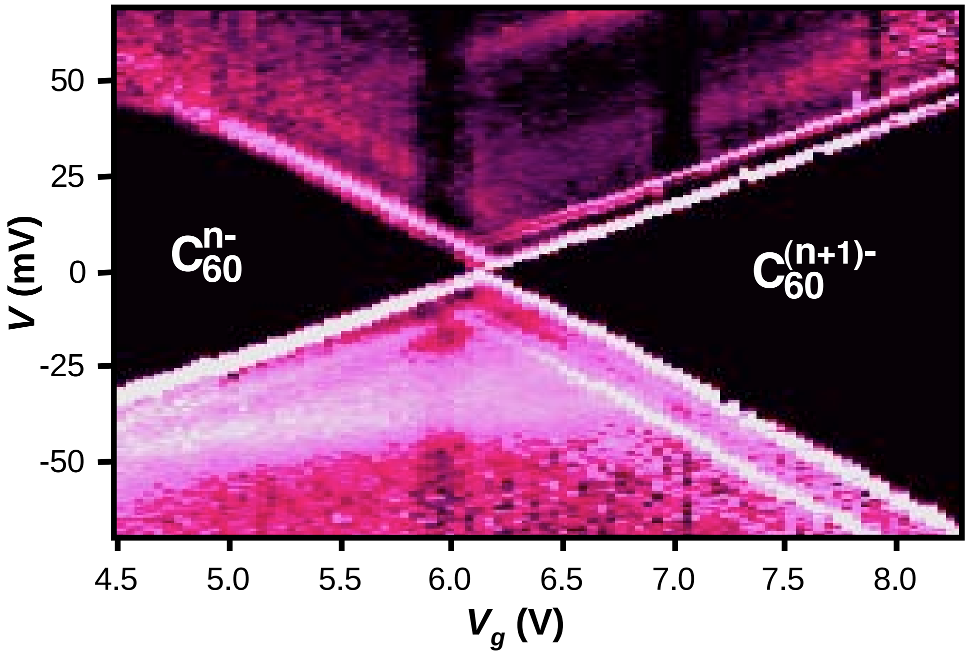


After forming the nm-scale gap, deposit C_{60} in toluene solution.

- *I-V curves at different gate voltages*

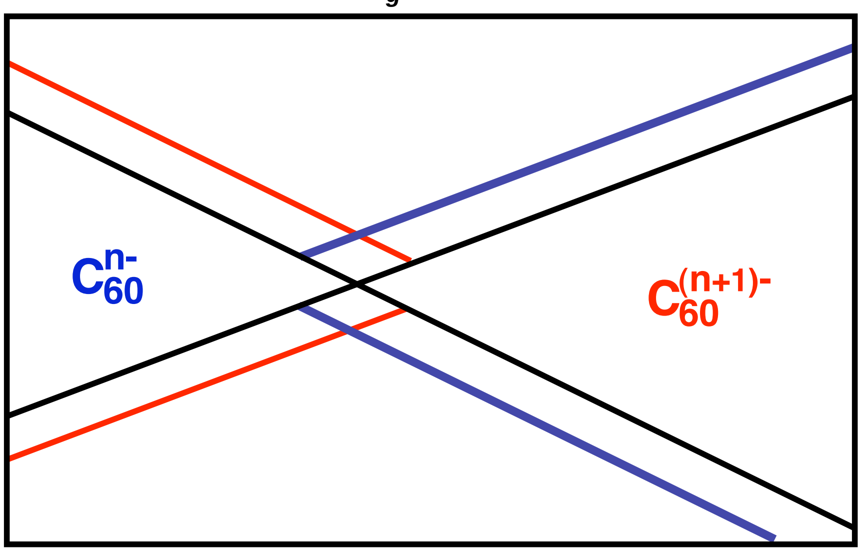


Reading excitation energies



Bias voltage at the intersections

→ **excitation energy**



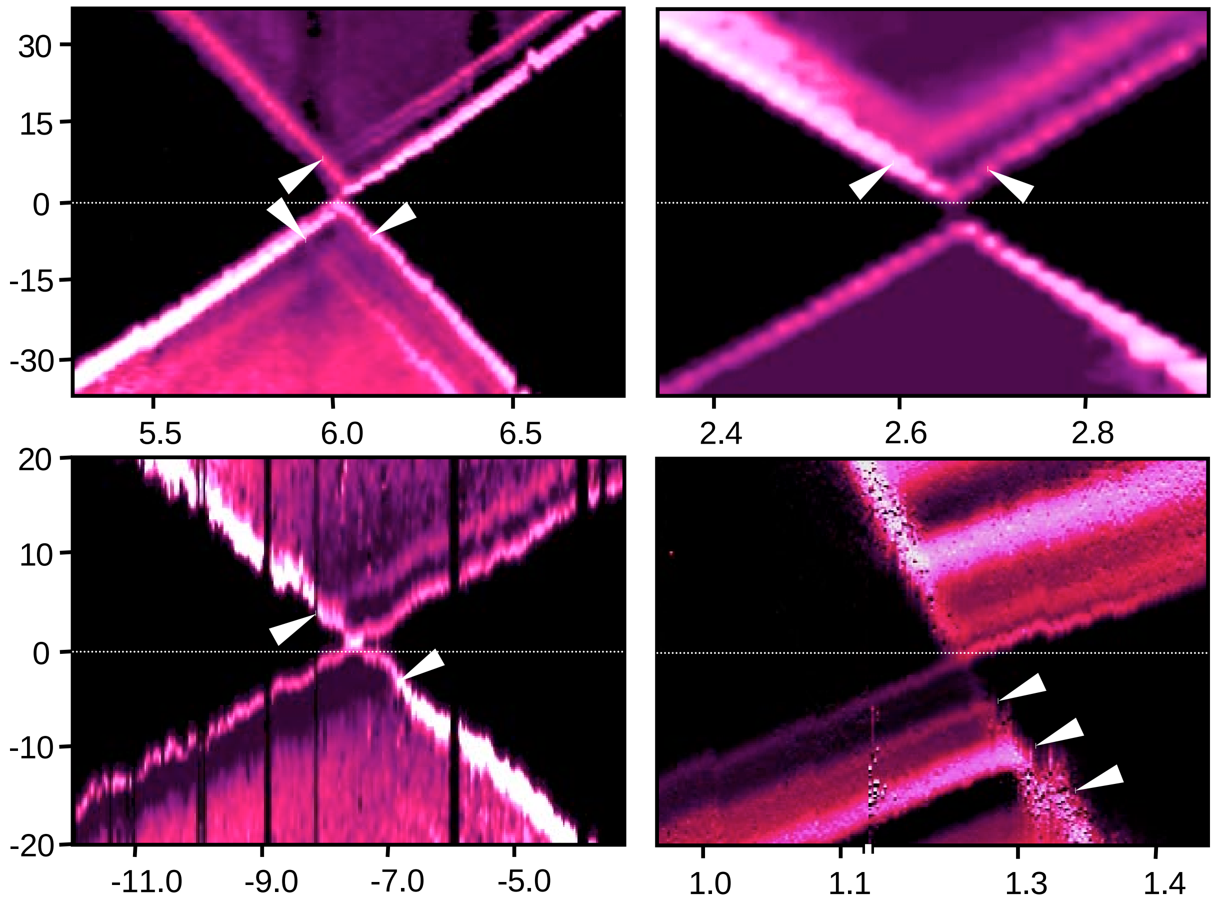
Red lines - excited states of $C_{60}^{(n+1)-}$

Blue lines - excited states of C_{60}^{n-}

Black lines - ground states

Multiple devices - 5 meV excitation

- 5 meV excited levels *in both charge states*.
- *Multiple lines* with an equal spacing.



Excitations of a C_{60} molecule

Electronic excitation?

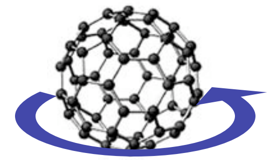
- measured energy is too low
- charge state dependent
- multiple lines not explained

  (Green, *et al. J. phys. Chem.* **100**, 14892)

Rotational excitation?

$\hbar^2 / 2I \sim 0.6\ \mu\text{eV}\ (\ll 5\ \text{meV})$

- measured energy is too large



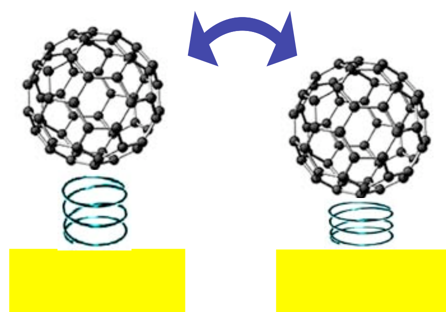
Vibrational excitation

…charge state independent

…explains multiple lines

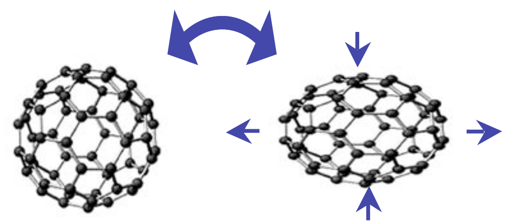
- Vibration against the surface

  (~ 5 meV)



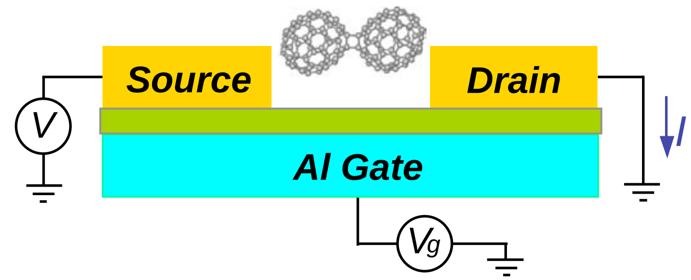
- Internal vibration

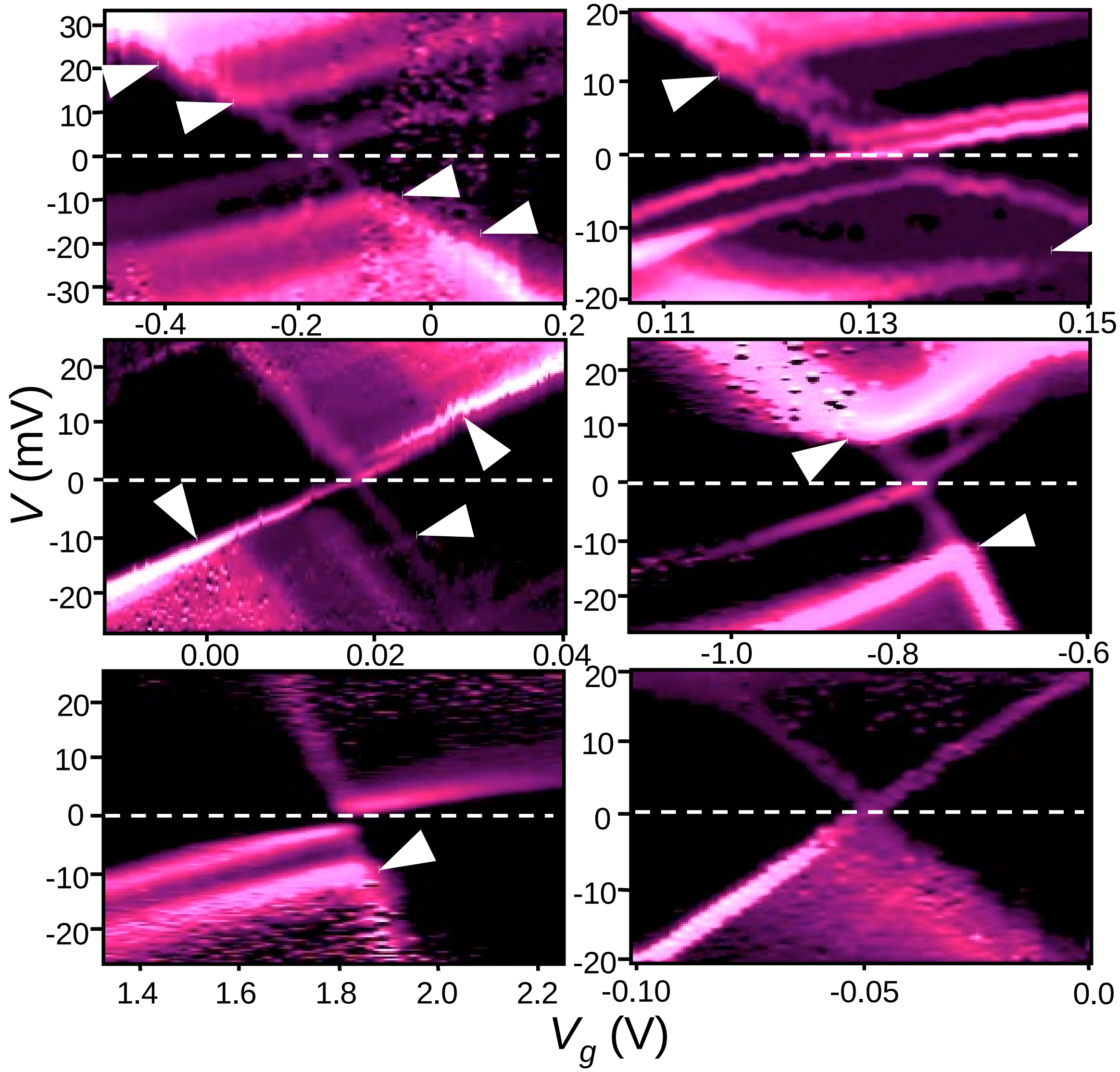
  (> 33 meV)



C_{140} Transistors

11 meV internal stretching mode





Excitations commonly observed near 11 meV and sometimes 22 meV.

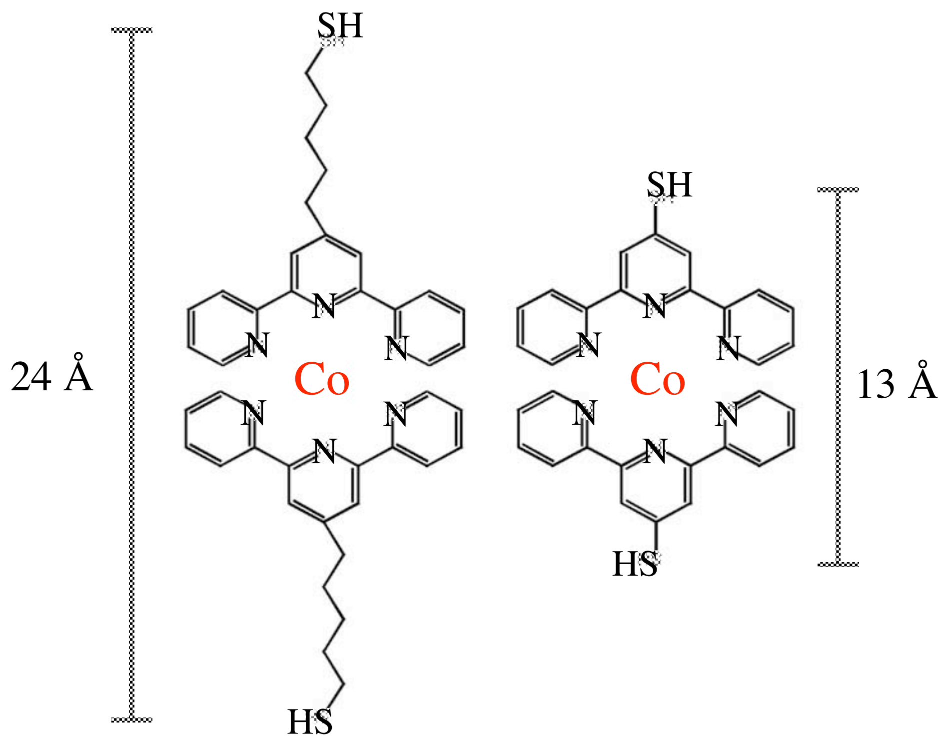
Other lower-energy states are observed, too.

Sometimes the 11 meV line is absent.

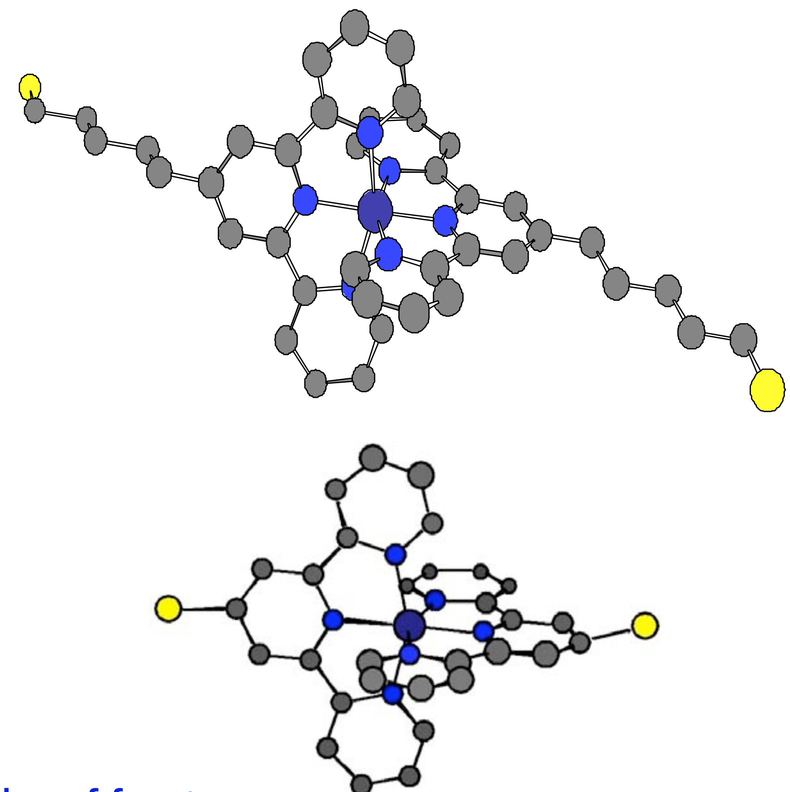
A. N. Pasupathy et al.
Nano Lett. **5**, 203 (2005).

Designer molecules for making transistors

J. Park, A. N. Pasupathy et al., Nature 438, 457 (2003)



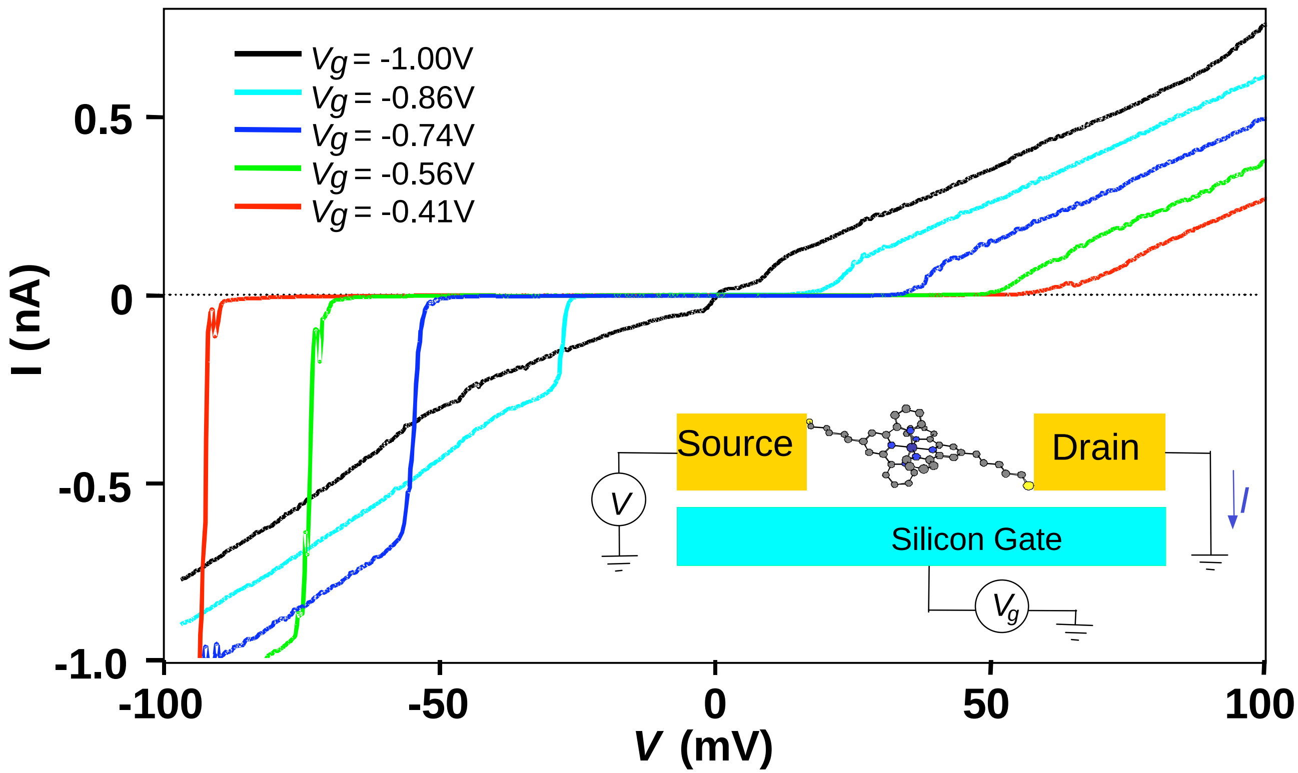
$Co^{2+}(tpy(CH_2)_5SH)_2$ $Co^{2+}(tpySH)_2$

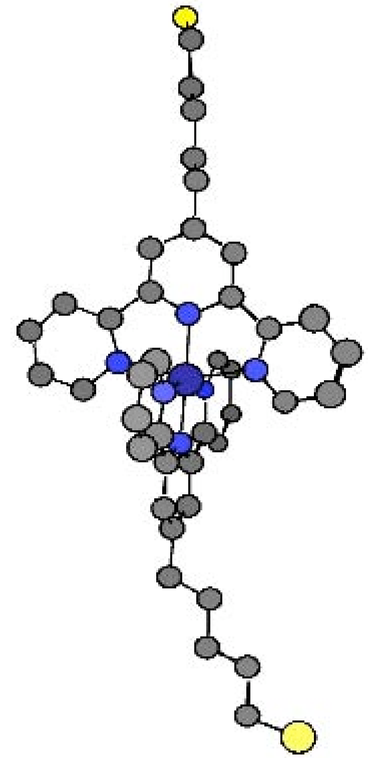


- Longer molecule: Coulomb-blockade effects.
- Shorter molecule: Kondo effect.

Related measurements, different molecules : H. Park (Harvard)

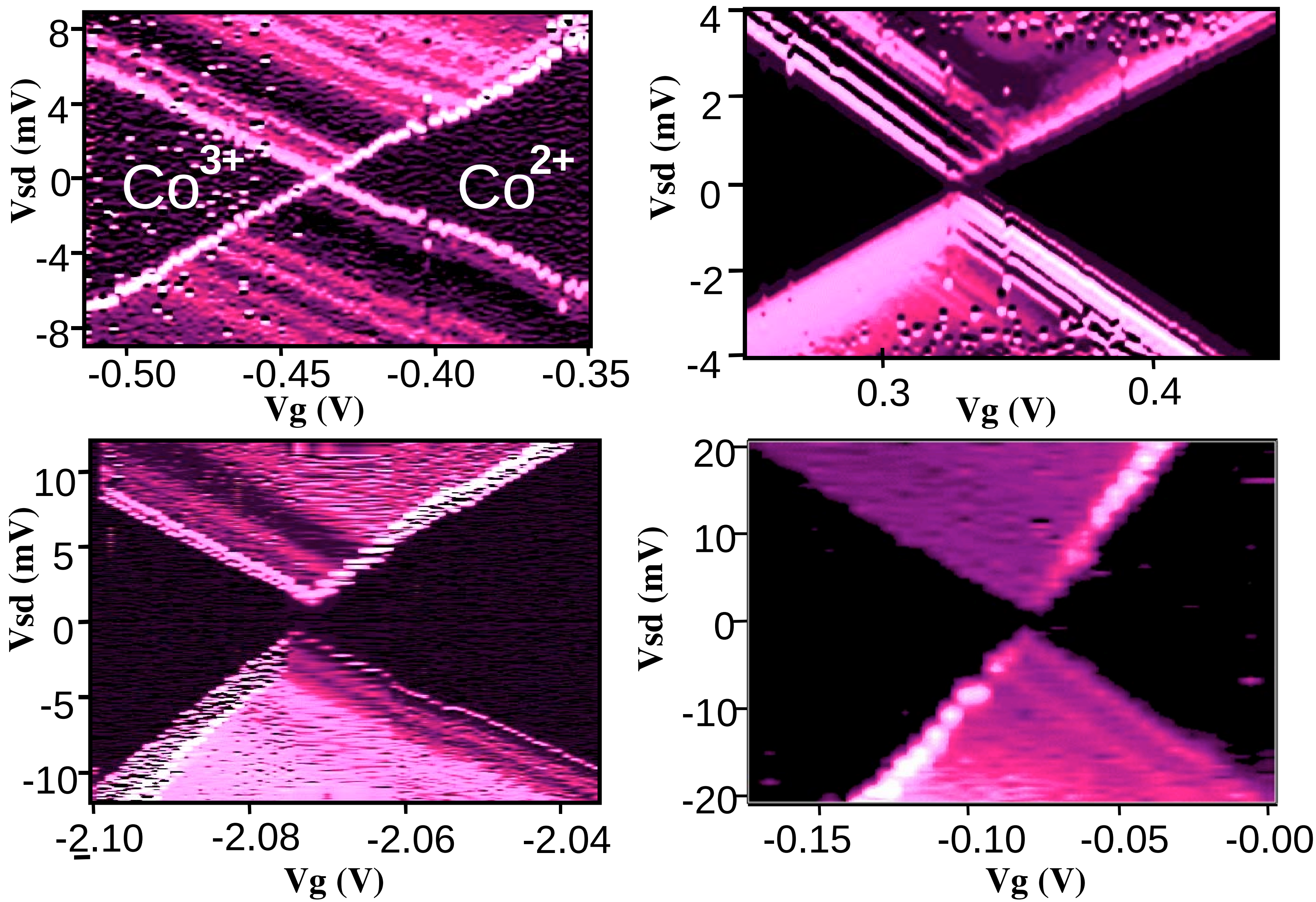
Coulomb-Blockade Effects in the Longer Molecule



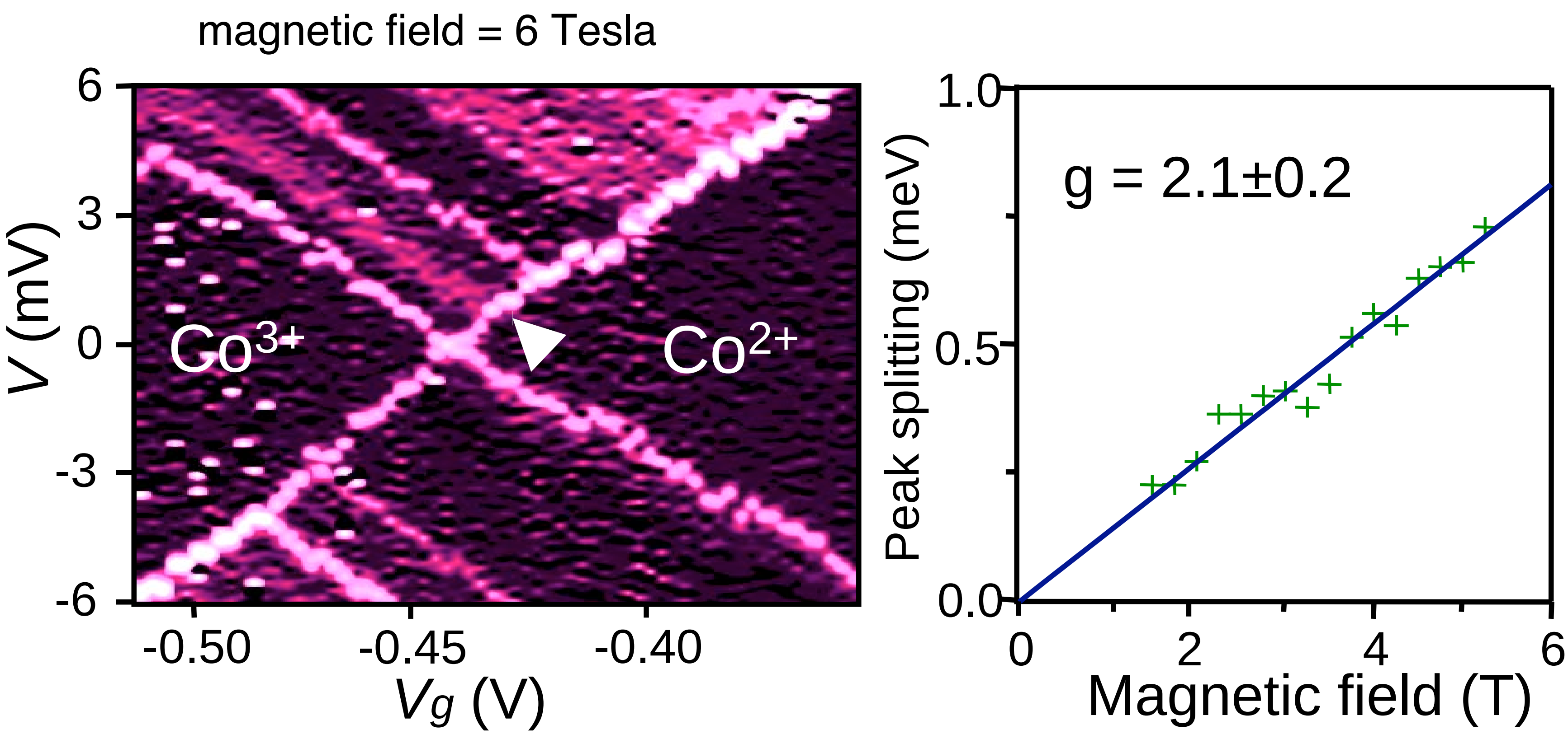


- High resistance (> megaOhms) - single electron charging.
- Coulomb blockade > 150 meV (unstable beyond this).

Excited quantum levels in the longer molecule

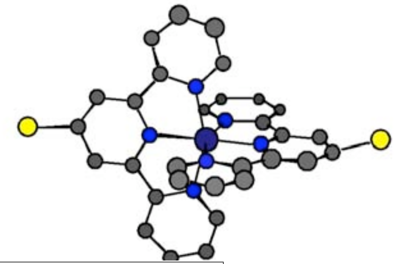


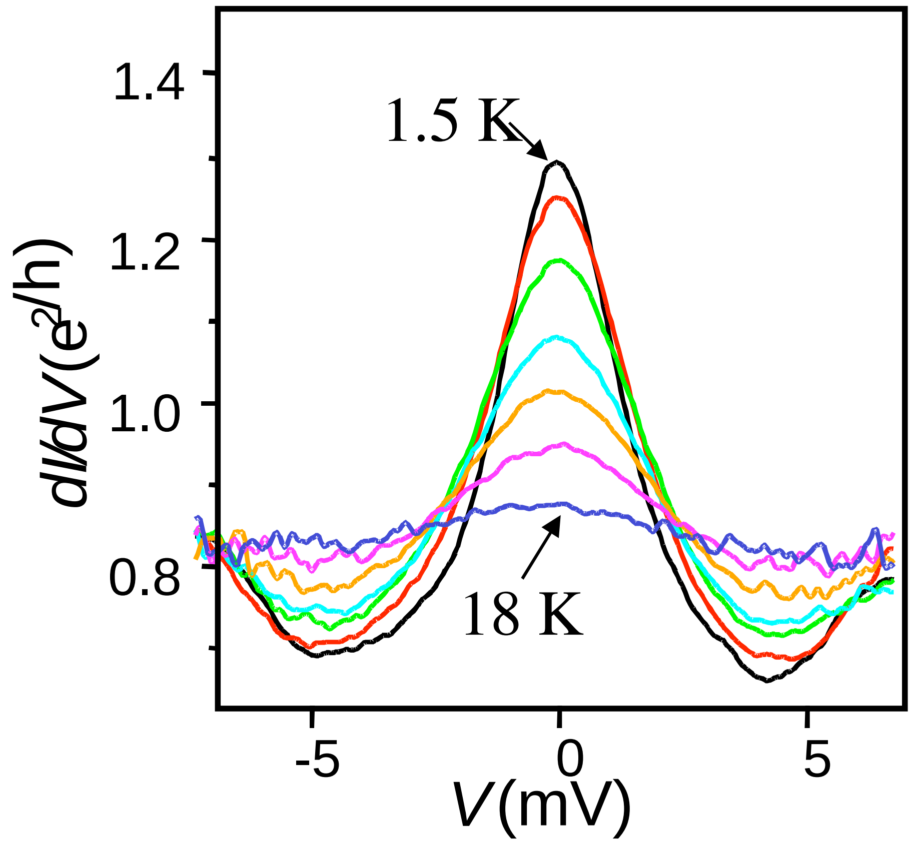
Zeeman Splitting in a Magnetic Field

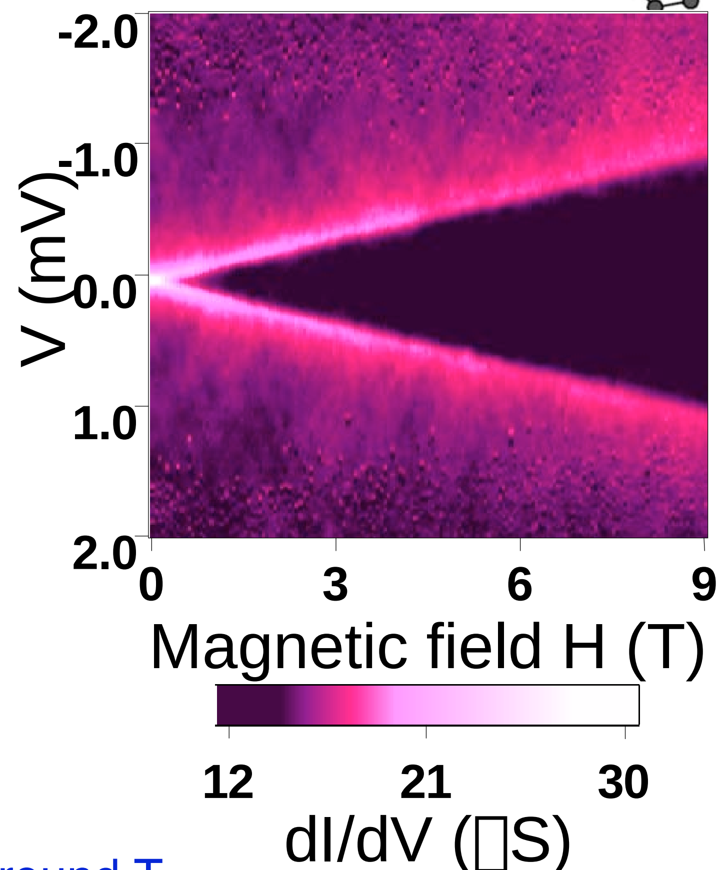


S=1/2 for Co^{2+}, S=0 for Co^{3+}.

The Kondo Effect in the Shorter Co(tpySH)$_2$



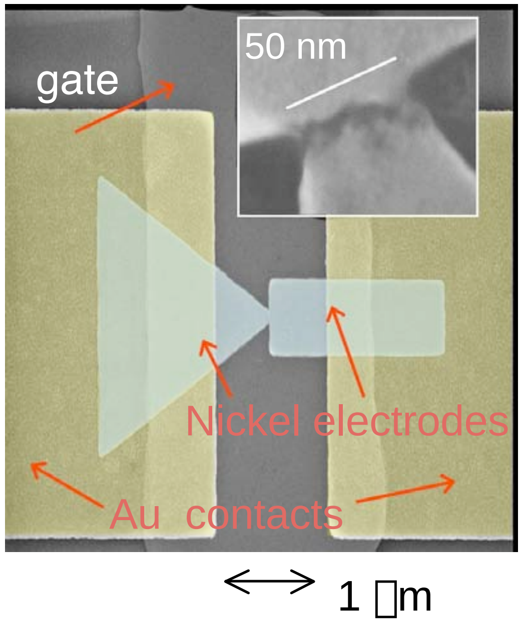


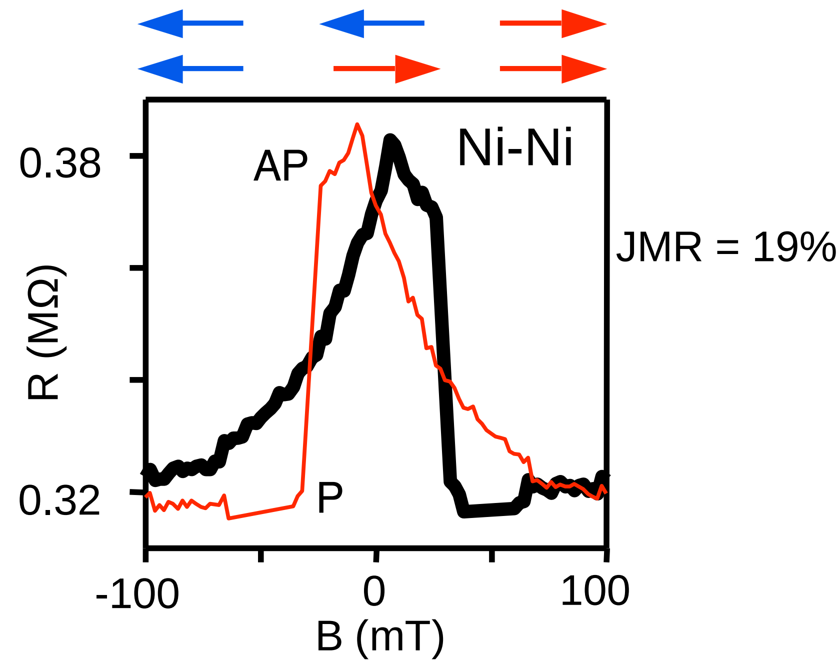


- Often high conductance ~ 2 e^2/h
- Peak height decreases logarithmically around T_K
- Peak splits as a function of magnetic field.
- Kondo temperatures vary from < 1 K to > 50 K.

Abhay Pasupathy, Jiwoong Park, Jonas Goldsmith et al., Nature **417**, 722 (2002).

Ferromagnetic electrode fabrication





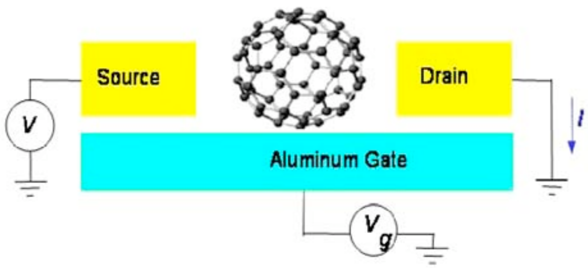
- Shape anisotropy affects the switching fields – electrodes switch independently

- Tunneling MagnetoResistance (TMR) of a bare nickel point contact

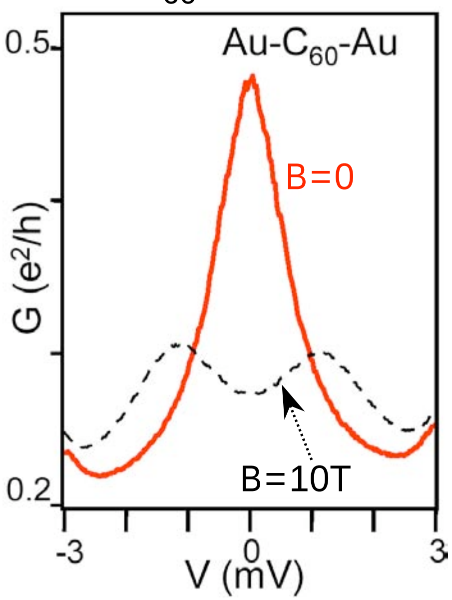
For P = 0.31 for Ni, Julliere estimate is

$$JMR = 2P^2/(1-P^2) = 21\%$$

Kondo effect in C_{60} molecules with and without magnetic electrodes



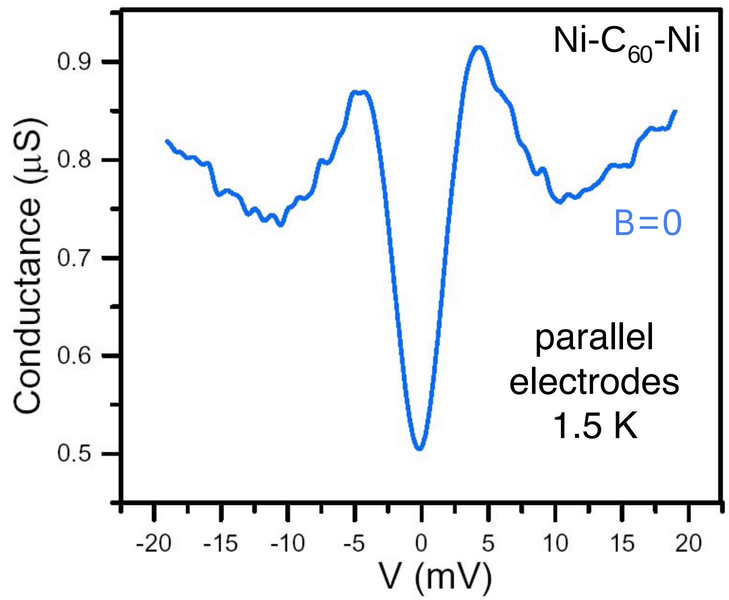
- Au – C_{60} – Au



No splitting for B=0

(see also Natelson group, Nano Lett. 4, 79 (2004))

- Ni – C_{60} – Ni ferromagnetic sample



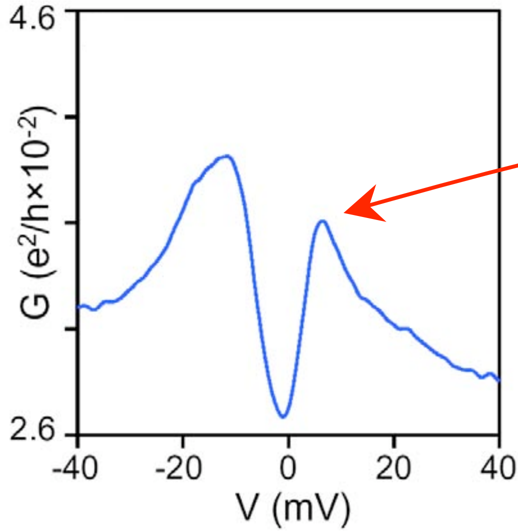
Splitting of zero-bias anomaly due to exchange interaction

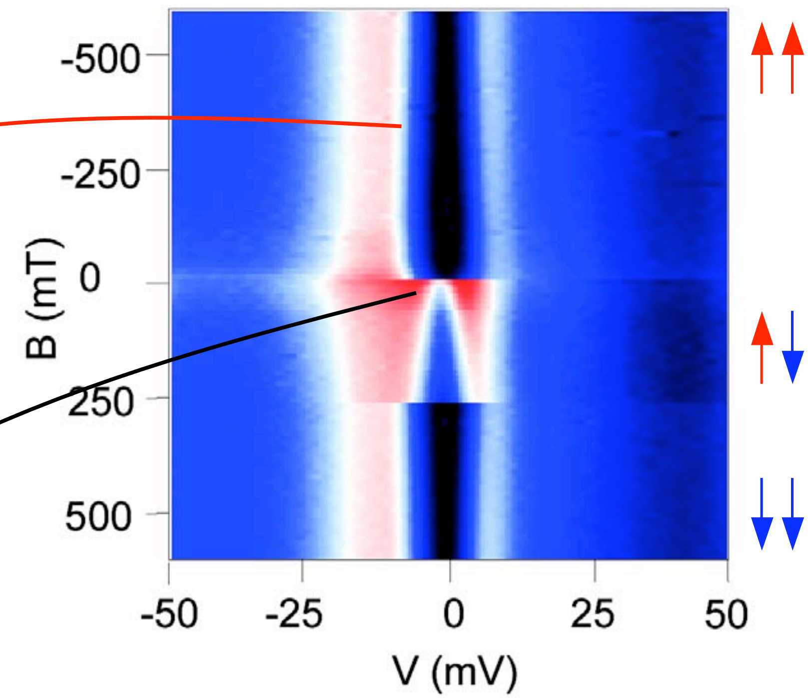
Cannot be due to magnetic field.
5 meV splitting would require >50 T.

Abhay Pasupathy, Jan Martinek et al.
Science **306**, 86 (2004)

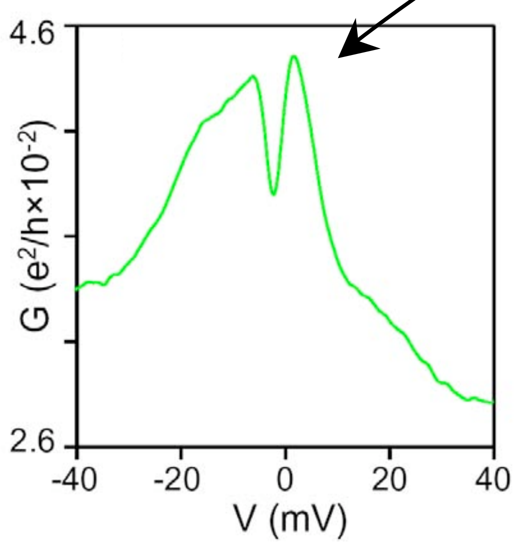
Kondo splitting depends on electrode orientation

- **Parallel**





- **Antiparallel**

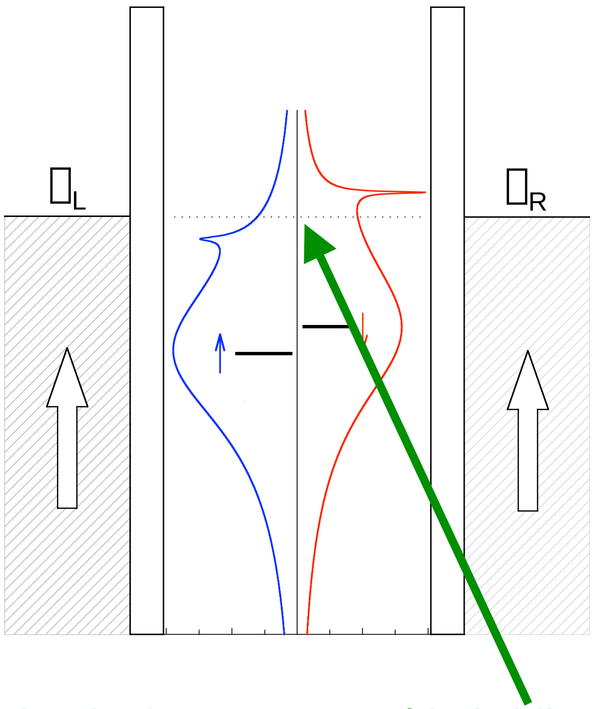


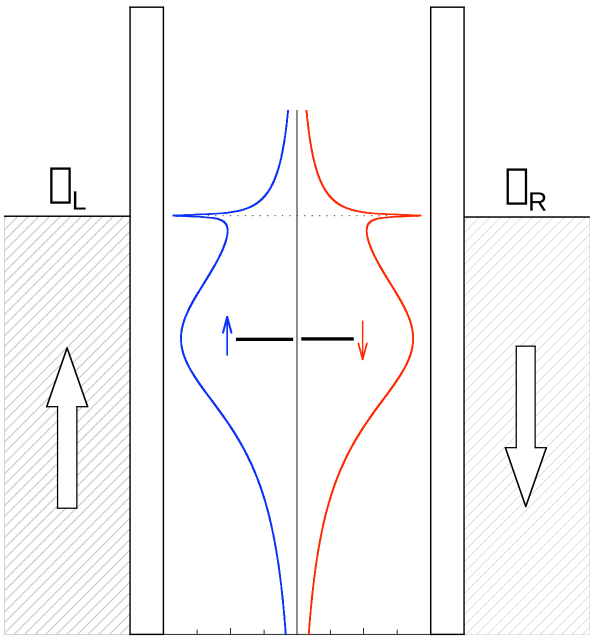
- Large splitting for parallel moments
- Reduction of splitting when moments are antiparallel
- Gradual change corresponds to noncollinear geometry

Good agreement with theory of Kondo effect with magnetic electrodes (J. Martinek et al., PRL 2003)

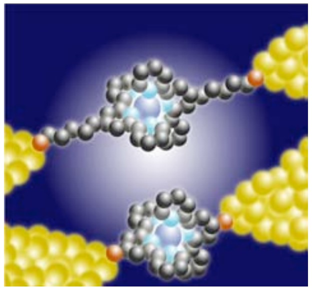
Density of States of Quantum Dot with Magnetic Electrodes

- Parallel Moments in Electrodes
- Antiparallel Moments in Electrodes (equal coupling)





Splitting is due to unequal hybridization between the quantum well state and the spin-polarized states in the electrodes -- resulting in a very large effective field.



Tools for Studying Electron and Spin Transport in Single Molecules

There are several complementary techniques for molecular-scale device fabrication.

- Need more experimental “knobs” -- ways to make systematic studies of molecular transport properties (e.g., combine gating, mechanical motion, light, in situ chemical modification, etc.)
- Understanding/control of the metal-molecule connection is a challenge.
- More experiments need to be reproduced.
- Best to understand full distribution of devices, not just “best” ones.

It is possible to make electrical contact to individual molecules and to manipulate the energy of their electronic states with a gate to give transistor action.

The strength of electronic coupling between molecular states and the leads can be changed by adjusting the molecular structure:

- Weak coupling: Coulomb blockade, vibration-assisted tunneling
- Strong coupling: Kondo effect, vibration signals blurred or absent (f ~ □)

Measurements so far provide new insights into Kondo physics, the coupling between electronic and mechanical degrees of freedom in molecules, and spin transport through a molecule between magnetic electrodes.

Will molecular electronics ever be useful? -- Hard to say.

Challenges:

- No gain
- Devices not stable at room temperature yet
- Relatively slow speeds (long RC times)
- How to wire up many devices correctly?

At this stage, our main goal is scientific exploration.

Additional References

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