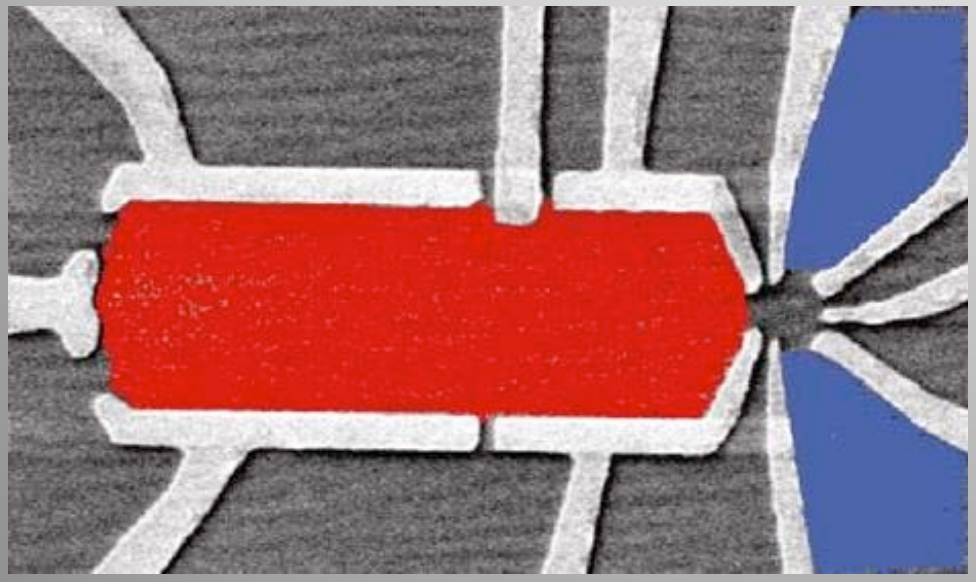
Nanostructures and molecular devices

Douglas Natelson
Dept. of Physics and Astronomy
Rice University

Goldhaber-Gordon group, Stanford



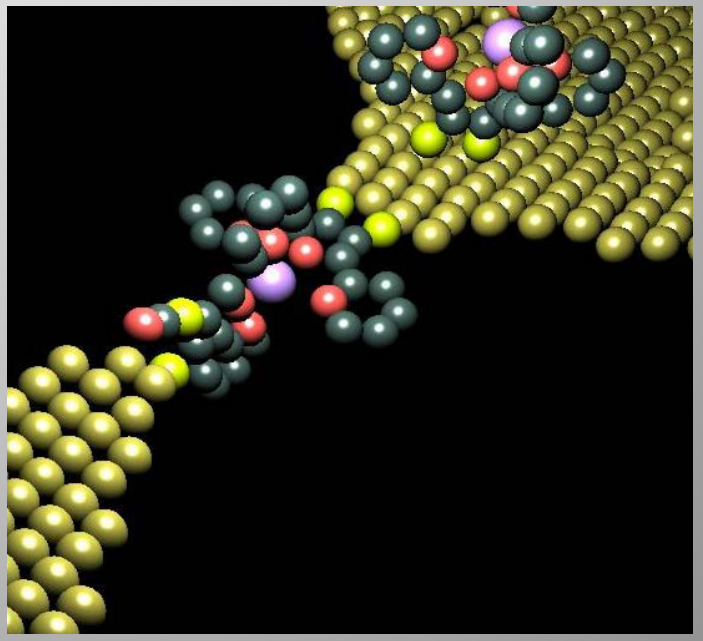


Image: J.W. Ciszek

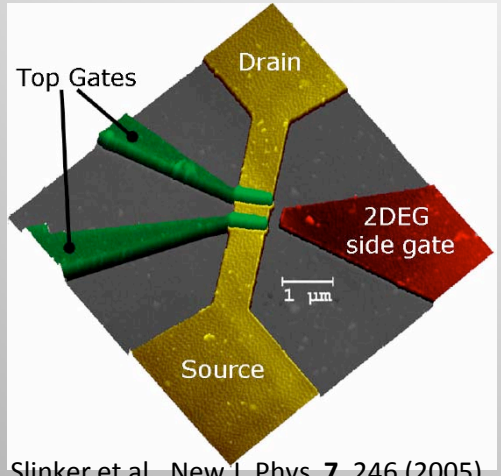
Outline

- Preliminaries and background
- 2-terminal single-molecule measurements
- Single-electron devices - Single-molecule transistors vs. semiconductor dots
- Inelastic processes
- Kondo physics – nanostructures for quantum impurity problems
- Noise
- Optics in the mix

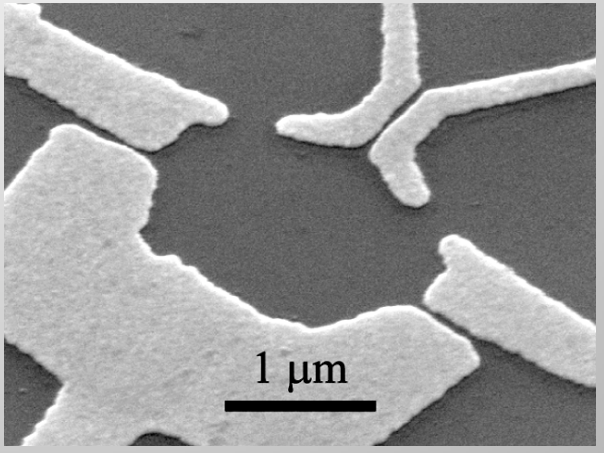
Themes: Model systems for quantum impurities + nonequilibrium response

Taxonomy of nanostructures

Semiconductor quantum dots (gate-defined)

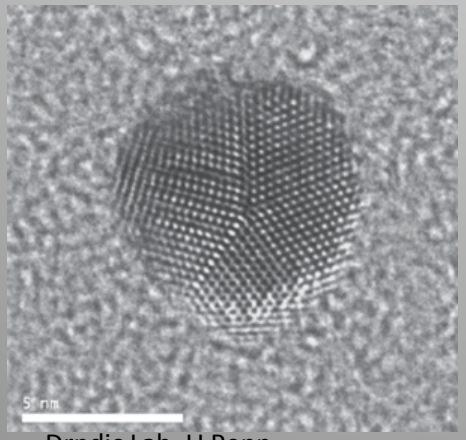


Slinker et al., New J. Phys. **7**, 246 (2005)

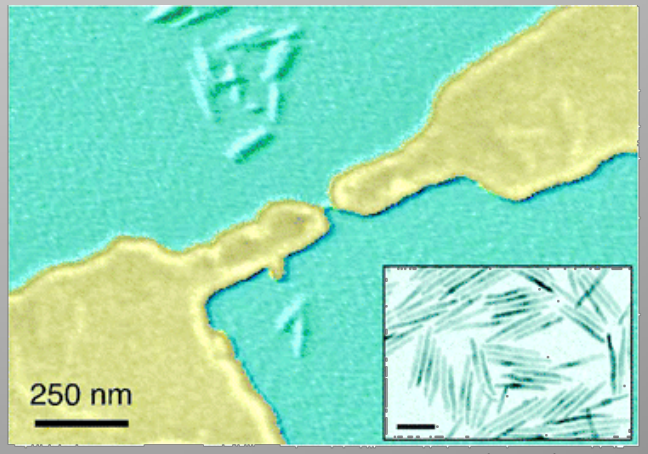


Schoenenberger, Basel

Semiconductor QD (nanocrystals)



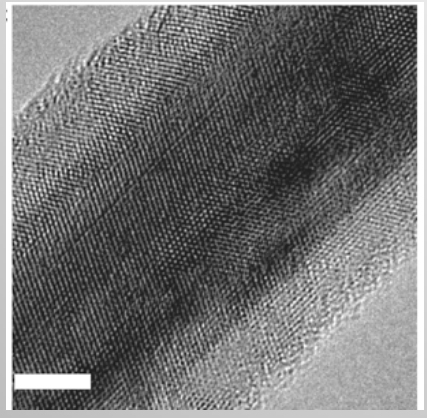
Drndic Lab, U Penn



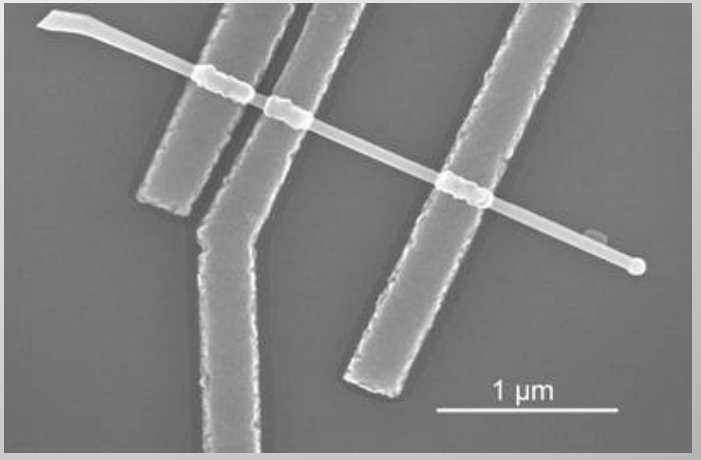
Gudiksen *et al.*, *Nano Lett.*, **5**, 2257 (2005)

Taxonomy of nanostructures

Semiconductor QD (nanowires)

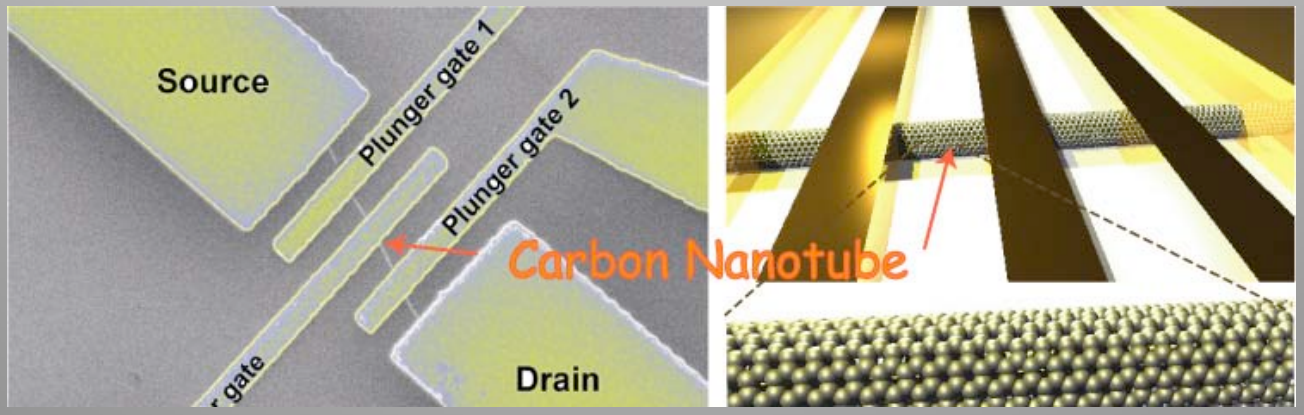


Lu et al., PNAS **102**, 10046 (2005)



Doh et al., Science **309**, 272 (2005)

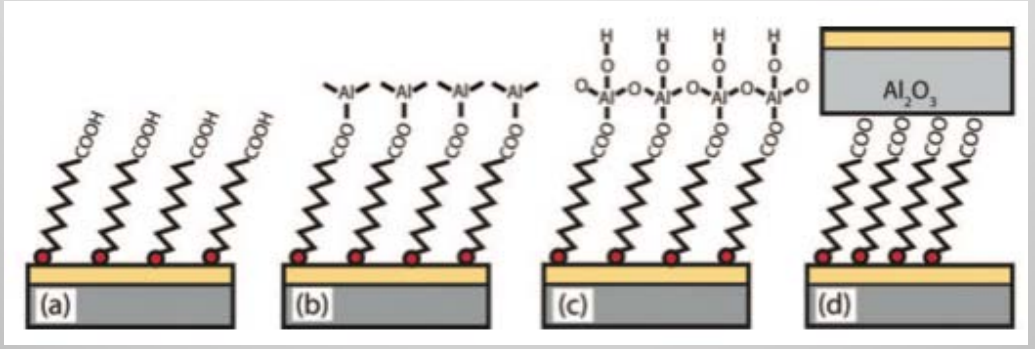
Carbon nanotubes



Schoenenberger group, Basel

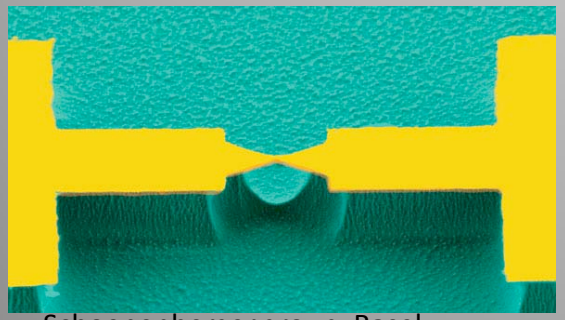
Taxonomy of nanostructures

Molecular junctions (large area)

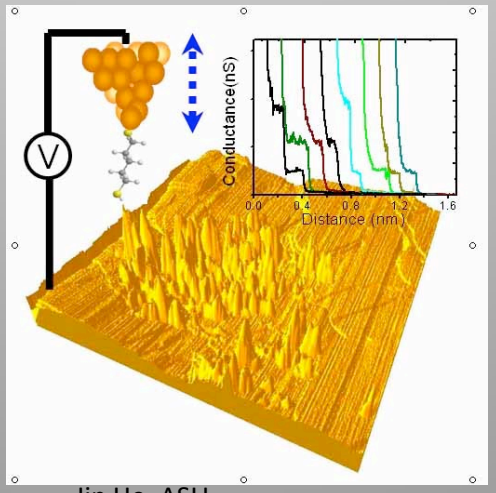


Preiner and Mellosh, APL **92**, 213301 (2008)

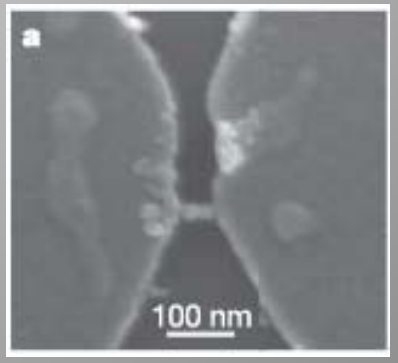
Single-molecule junctions (2 terminal)



Schoenenberger group, Basel



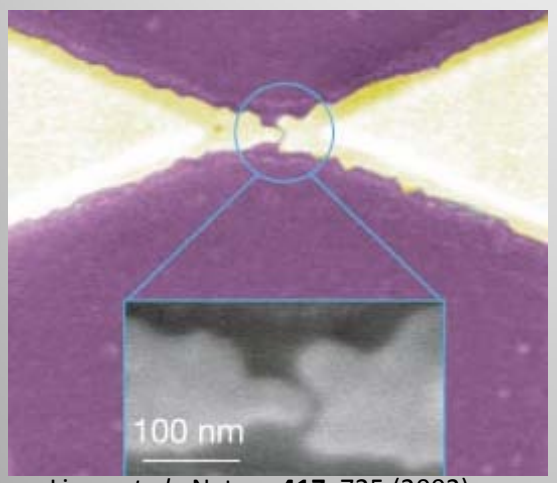
Jin He, ASU



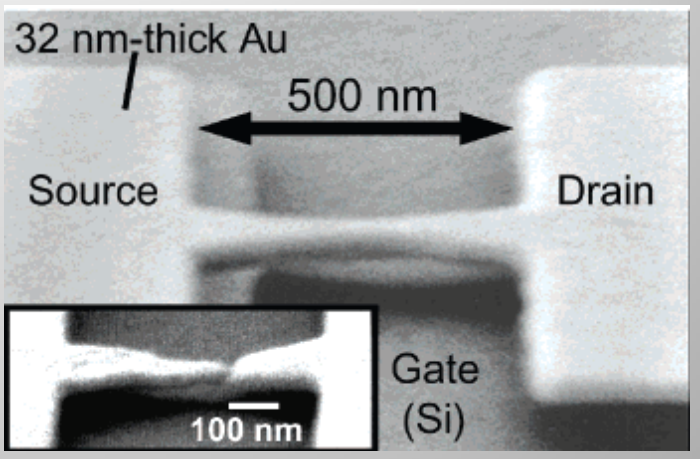
Dadosh *et al*., Nature **436**, 677 (2005).

Taxonomy of nanostructures

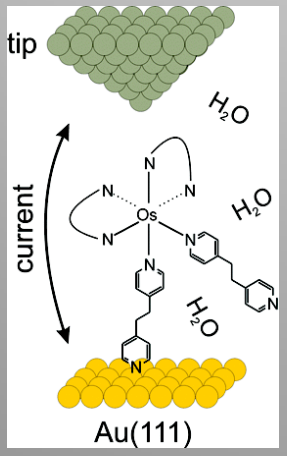
Single-molecule transistor (3 terminal)



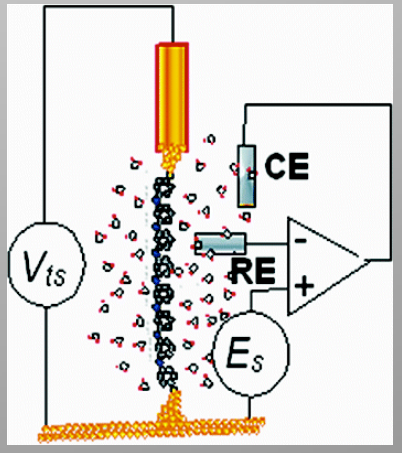
Liang *et al*., Nature **417**, 725 (2002).



Champagne *et al*., NL **5**, 305 (2005).



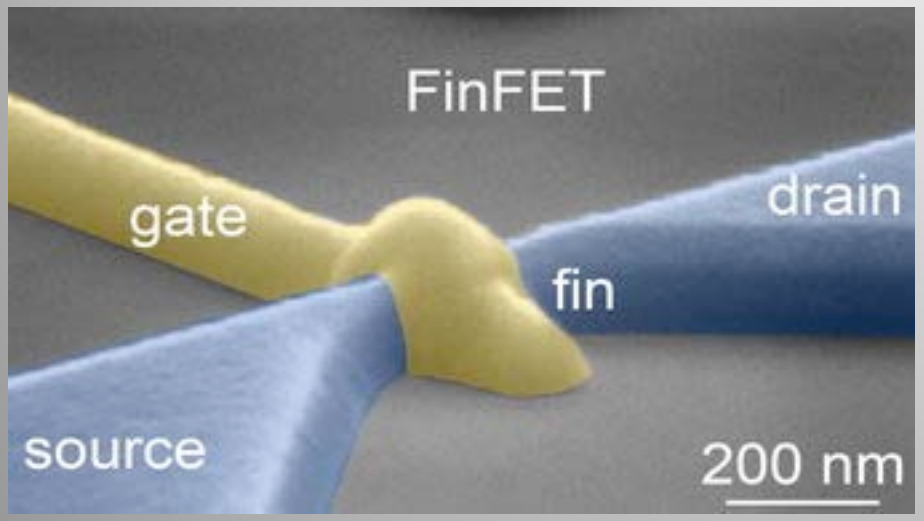
Albrecht *et al*., Nano Lett. **5**, 1451 (2005)

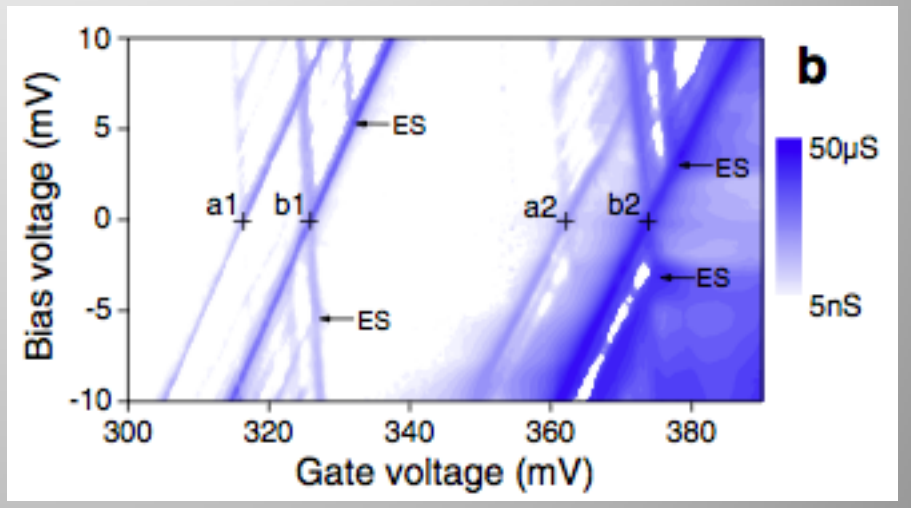


Chen *et al*., Nano Lett. **5**, 503 (2005)

Taxonomy of nanostructures

Single-atom transistor (3 terminal)



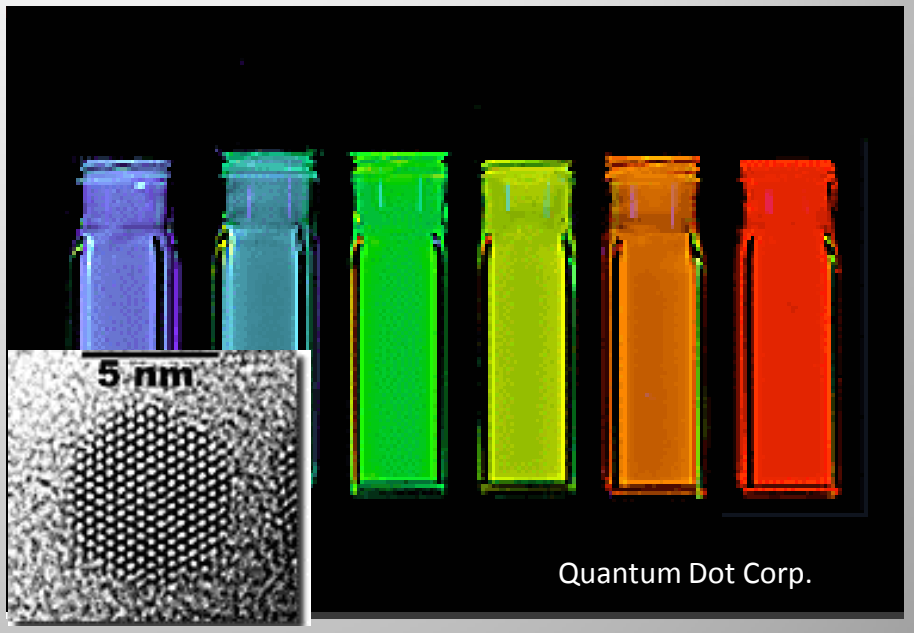


Sellier *et al*., PRL **97**, 206805 (2006)

Transport measurements have been made through individual dopant atoms.

Energy scales – quantum confinement

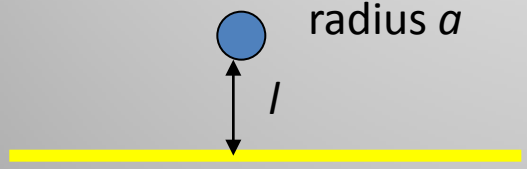
- Confined electrons can only have certain energies.
- Smaller system = larger energy spacing of allowed states.



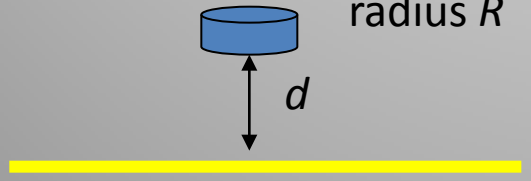
- This matters when energy intervals are big compared to available energies (*e.g. eV* or $k_B T$).
- For (3 nm)^3 of sodium, level spacing $\Delta E \sim 3\,\mathrm{meV} \sim 35\,\mathrm{K}$
- For 1-2 nm molecule, $\Delta E \sim 100\,\mathrm{meV} \sim 1160\,\mathrm{K}$
- Important at room temperature for electrons in small molecules!

Energy scales – Coulomb repulsion

- A great "miracle" of condensed matter physics: often we can get away with ignoring electron-electron interactions.
- Classically, capacitive charging. (A simplifying approximation!)
- $E_c = \frac{Q^2}{2C}$



$$C = 4\pi\kappa\varepsilon_0 a\left(1+\alpha+\frac{\alpha^2}{1-\alpha^2}+....\right), \qquad \alpha = \frac{a}{2l}$$



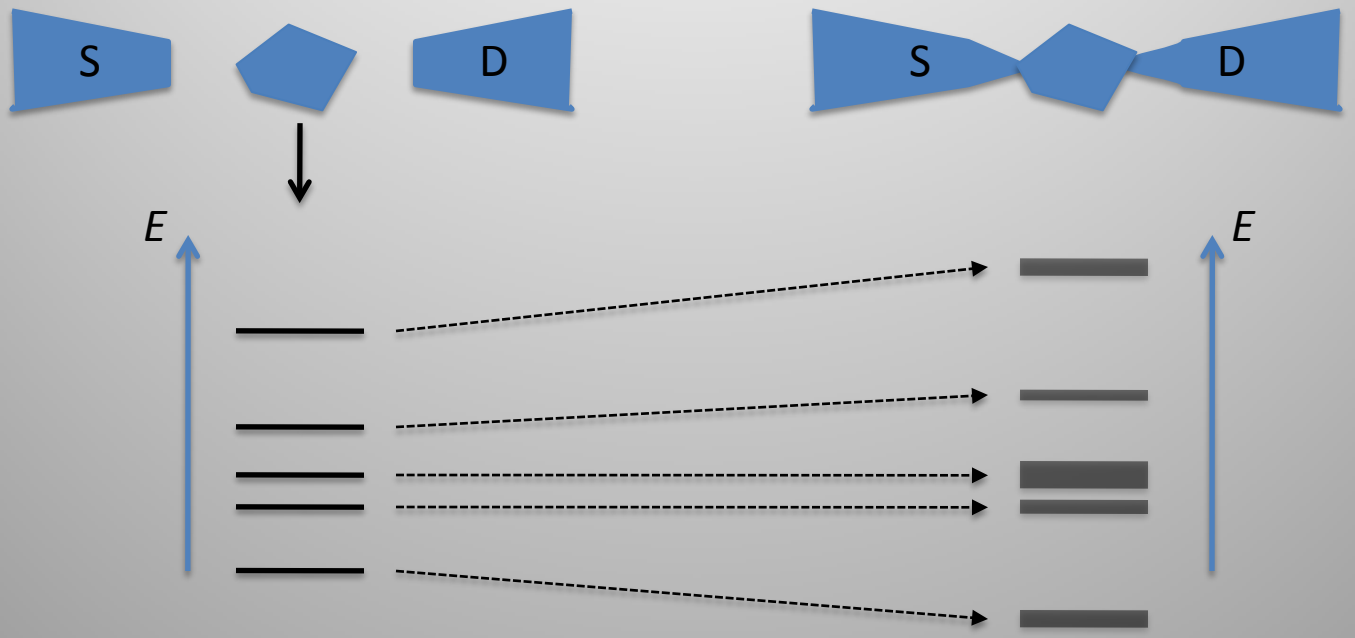
$$C = \begin{cases} \dfrac{\kappa\varepsilon_0\pi R^2}{d} & d << R \\ 8\kappa\varepsilon_0 R & d >> R \end{cases}$$

Can make systems where charging energy is larger than $k_B T$.

Room temperature → C ~ 3 x 10^{-18} F. For vacuum, → a ~ 28 nm

Energy scales – Lifetime broadening

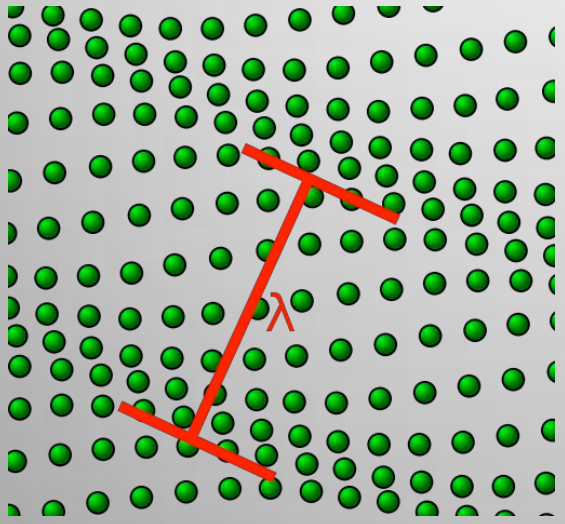
- Coupling a quantum system w/ the “outside world” perturbs states.
- Shift of energy levels + lifetime broadening



- Characteristic energy scale = $\Gamma = \hbar/\tau$

Energy scales – vibrational processes

- Acoustic phonons – gapless!



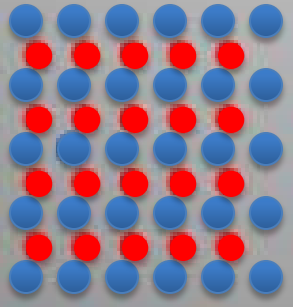
wikipedia

Typical sound speed ~ 8 km/s (Si), 5 km/s (GaAs)
Energy = $h\, c_s / \lambda$

For λ = 100 nm, energy in Si = 0.3 meV

Timescale ~ 10^{-12} s

- Optical phonons – tens of meV. Ex.: Gold optical phonon ~ 11 meV.



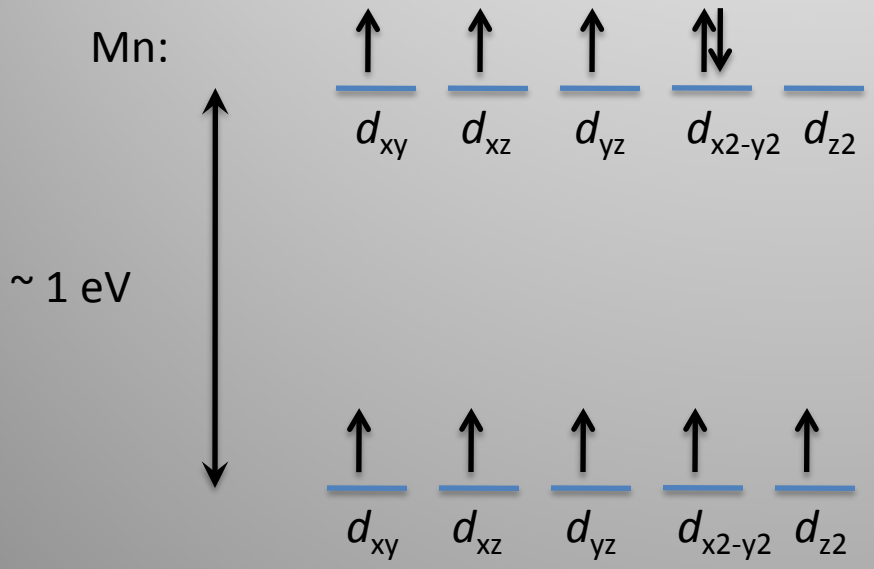
Local (within a unit cell) motion for k = 0.

Similar energy scale for local molecular vibrations

35 meV

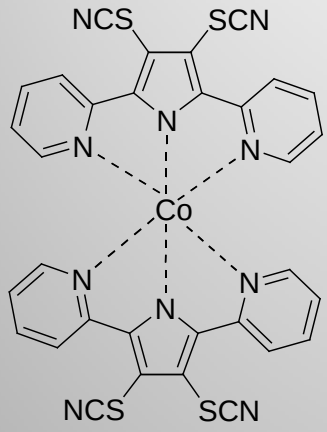
Energy scales – exchange

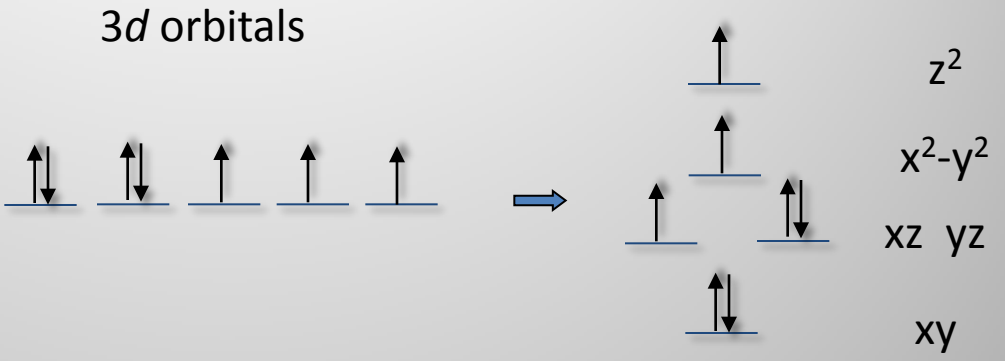
- Consequence of Coulomb interaction.
- Aligning spin lowers overall energy by forcing electrons to stay far apart.
- “Hund’s rule”
- Can be very important in transition metal atoms.



In GaAs dots, e.g., exchange effects are typically smaller (fractions of a meV).

Energy scales – crystal/ligand fields





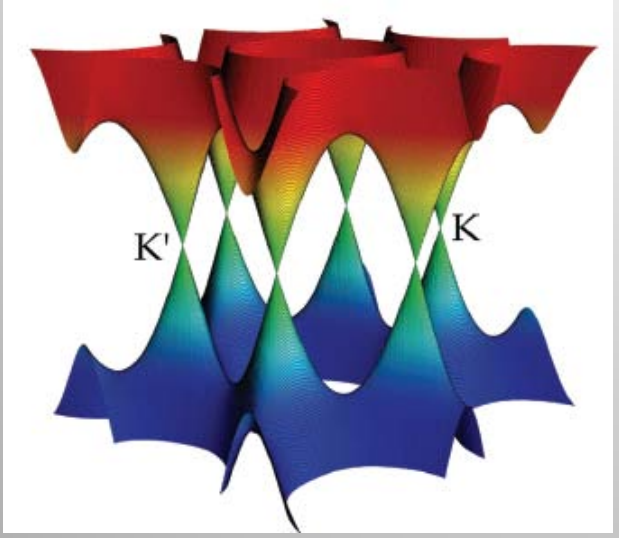
Interactions w/ neighboring atoms break degeneracy of single-electron orbitals.

Splittings ~ 0.1 eV.

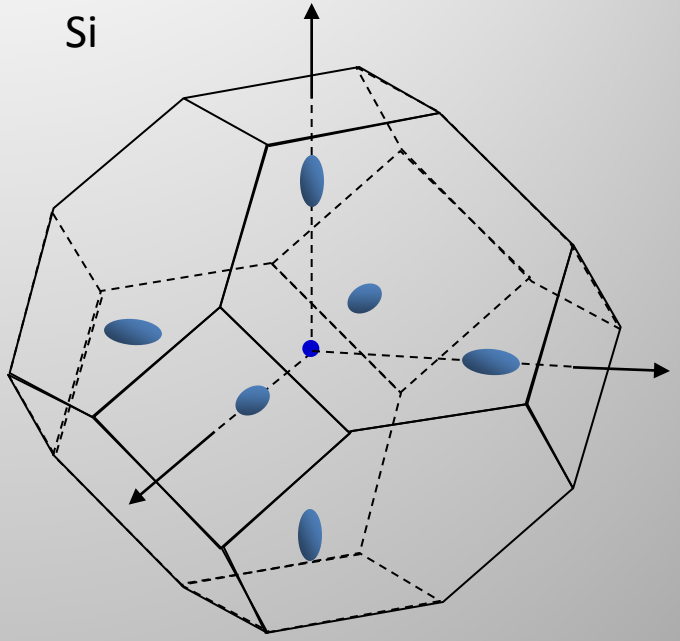
Not relevant in semiconductor/nanotube dots.

Energy scales – valley splittings

Graphene



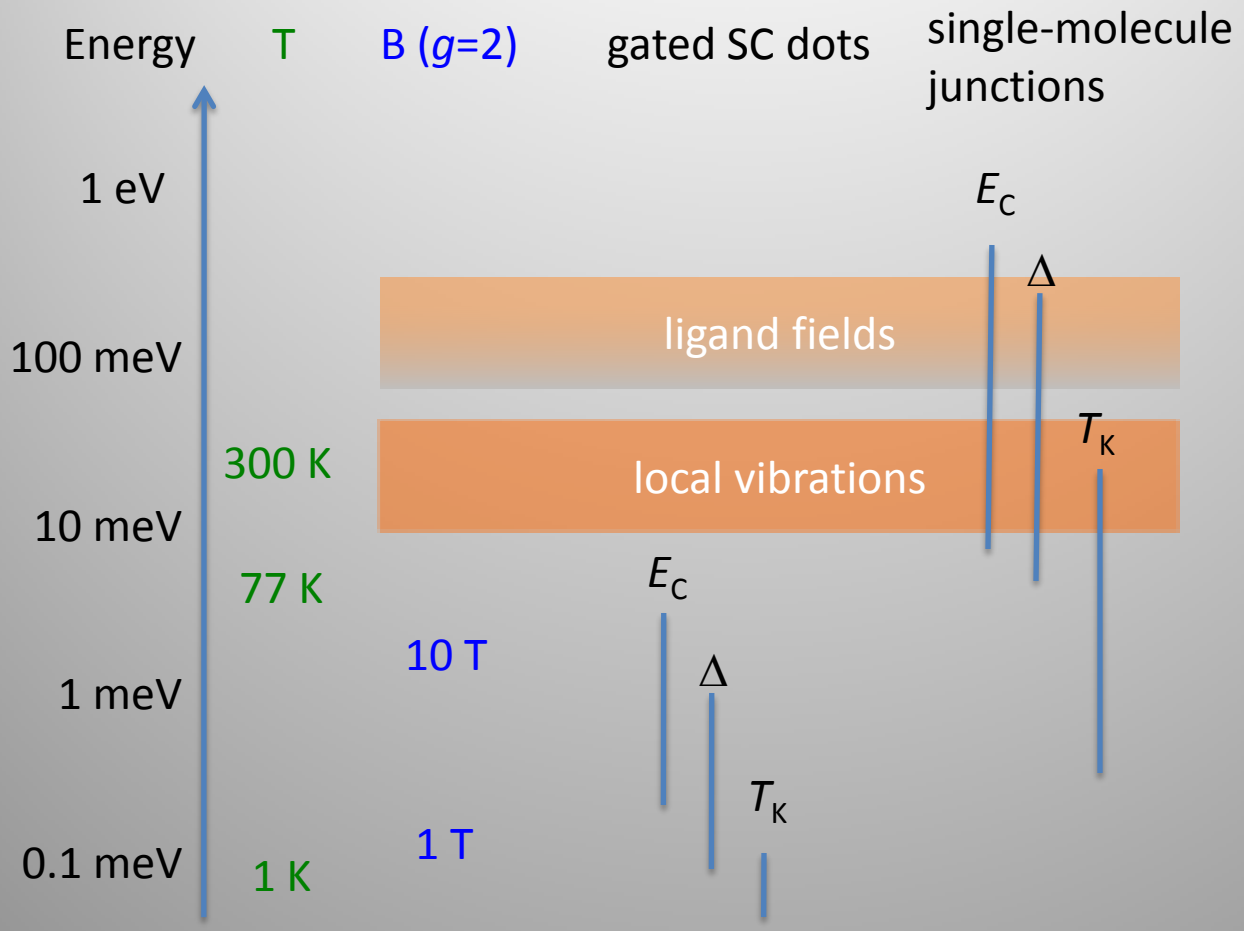
Si



In semiconductors, conduction band often has valley degeneracy.

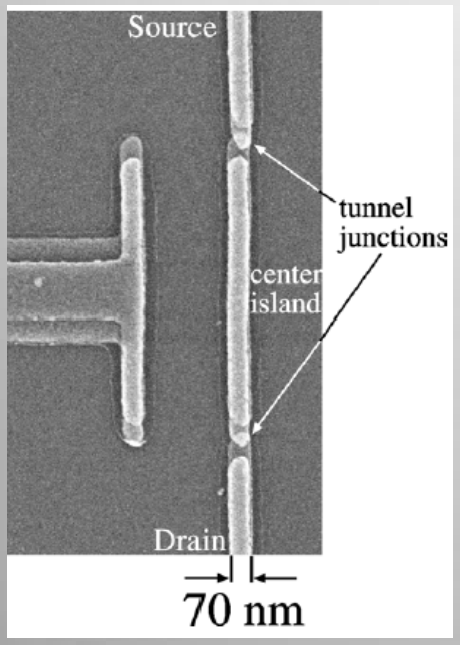
Degeneracy may be split by strain, interface effects ~ meV scale.

Energy scales



Energy scales

D. Berman, PhD thesis, MIT (1998)

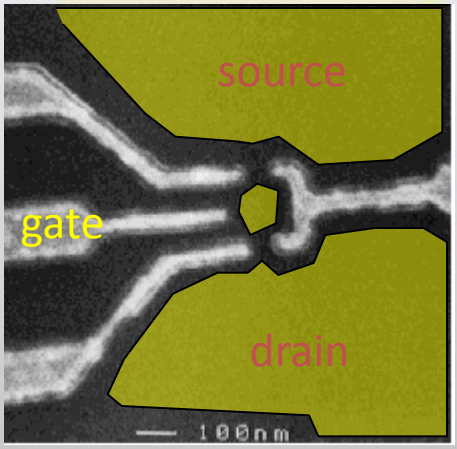


Aluminum SET

$\Delta \sim 5.9\times10^{-8}$ eV

$E_c \sim 4\times10^{-4}$ eV

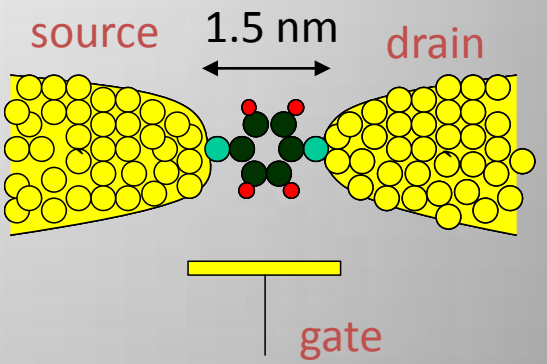
Goldhaber-Gordon *et al.*, Nature **391**, 156 (1998)



GaAs/AlGaAs SET

$\Delta \sim 4\times10^{-4}$ eV

$E_c \sim 2\times10^{-3}$ eV



Single-molecule transistor

$\Delta > 0.1\,\mathrm{eV}$

$E_c > 0.1\,\mathrm{eV}$

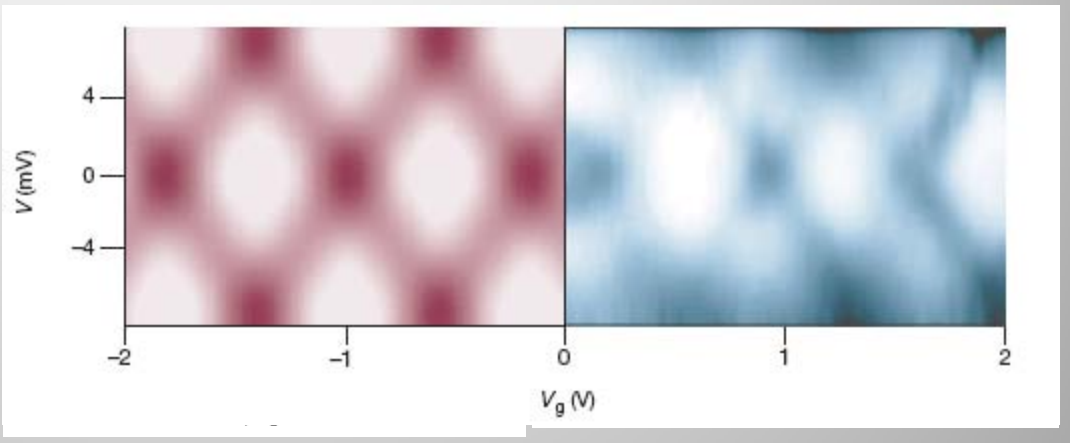
Transport regimes

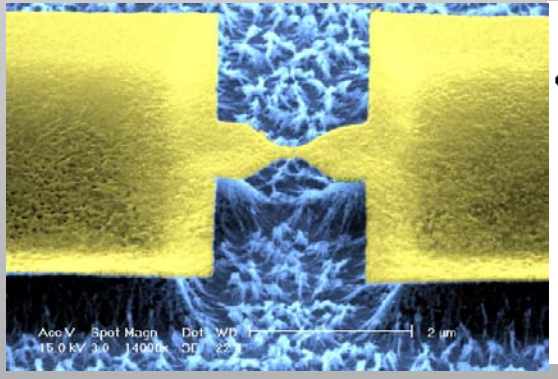
Strong coupling (coherent)

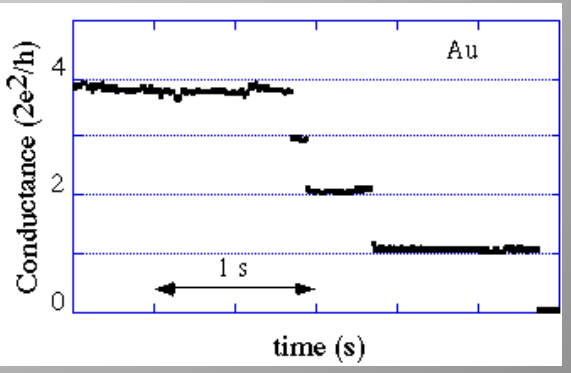
Γ > Δ

Landauer-Buttiker

Best to think about electronic states that span from one lead to the other, through the device.





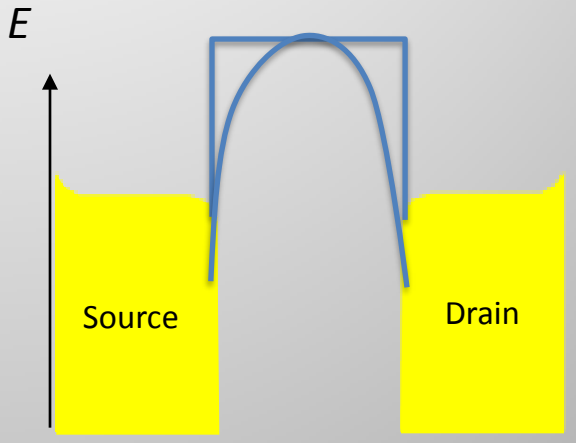


From van Wees, Groningen

Transport regimes

"Weak" coupling (coherent)

- Single barrier
- Off-resonant transport
- Conductance (per channel)
$< 2e^2/h$

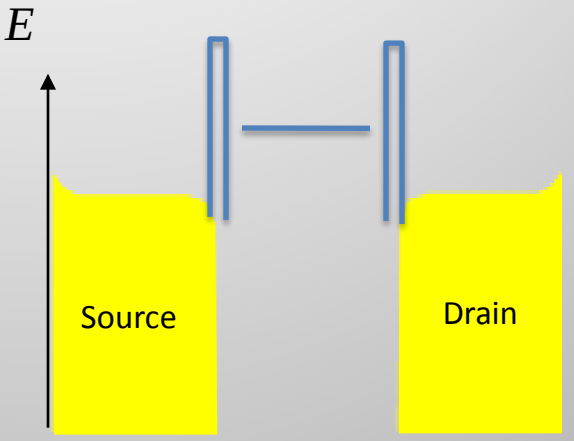


- Transmission exponentially suppressed with length and barrier height
- Most relevant these days in molecular devices
(back to this in a couple of slides!).
- Some subtle issues at work – screening, timescales.
- (Charging effects = dynamical Coulomb blockade)

Transport regimes

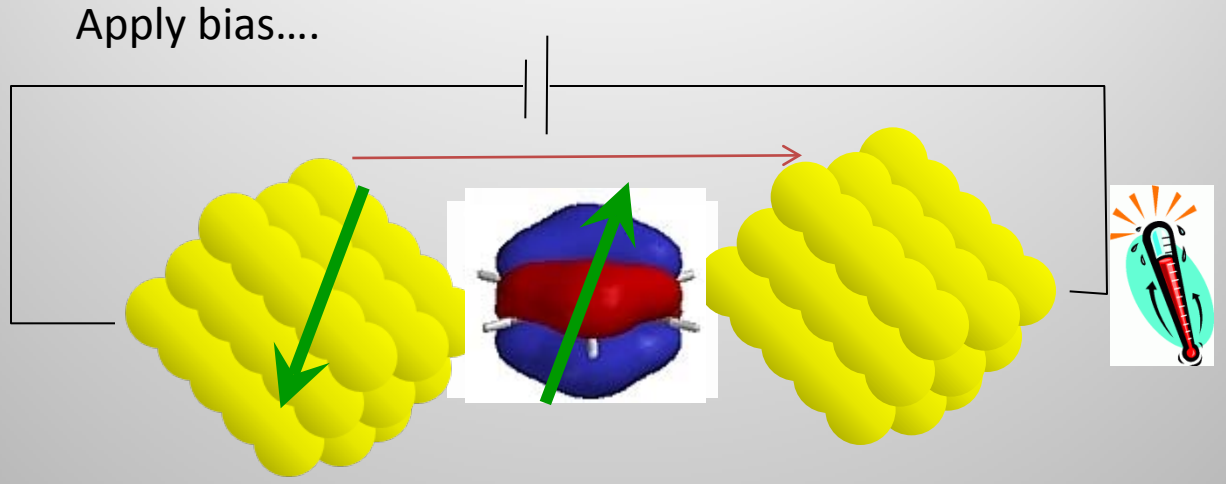
“Weak” coupling

- Two barriers
- Sequential vs. resonant tunneling
- Coulomb charging very important!



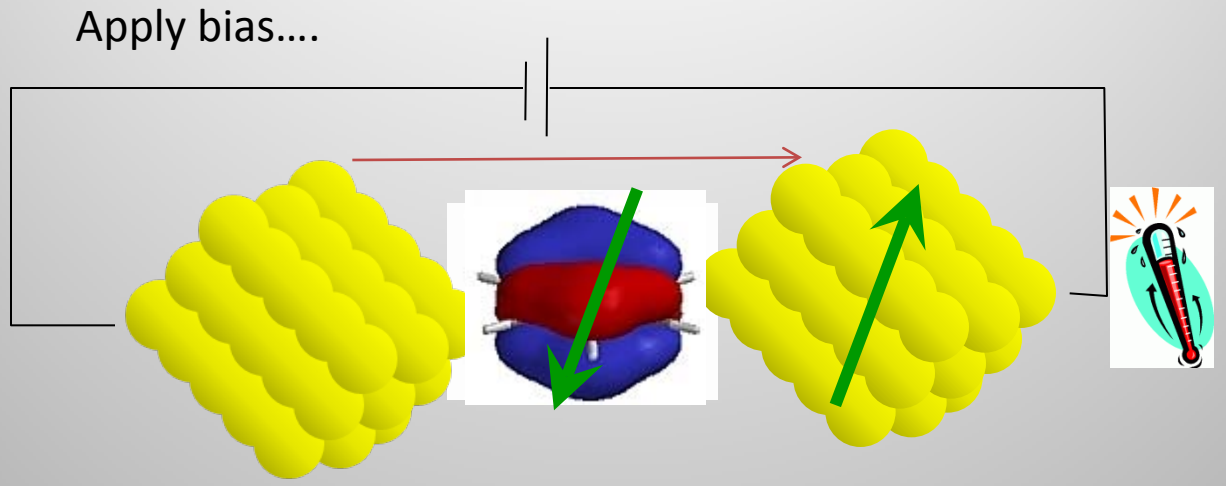
- Gate electrode can discrete shift level spectrum relative to source and drain
- Relevant in semiconductor structures + some molecular junctions.

Transport – what can happen?



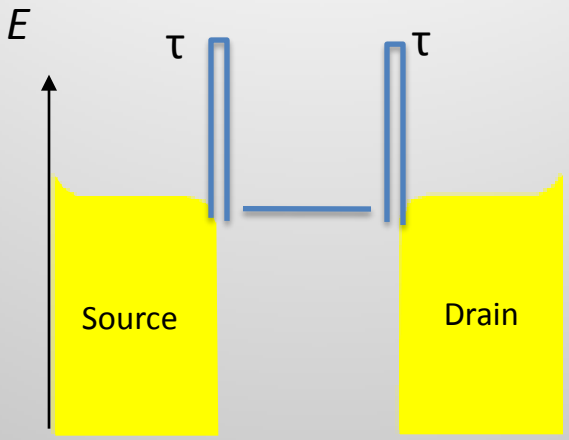
- “Hot” electrons in the metal leads.
- Molecular vibrations.
- Vibrations in the electrodes.
- Electronic transitions in the molecule
- Chemical reactions
- Quantum entanglement.

Transport – what can happen?



- “Hot” electrons in the metal leads.
- Molecular vibrations.
- Vibrations in the electrodes.
- Electronic transitions in the molecule
- Chemical reactions
- Quantum entanglement.

Transport – importance of coherence



τ = transmission probability for each barrier, individually

Sequential tunneling: Conductance ~ $\tau \times \tau$

Resonant tunneling: Conductance ~ 1 (consequence of constructive interference)

Experimental parameter space

Temperature:

down to 4.2-1.6 K easily (LHe)
300 mK (3He refrigerators)
~ 50 mK (dilution refrigerator)

Challenges:
Cooling the electrons.
Measuring the temperature.

Frequency:

DC to tens of kHz – standard for *V* and *I* measurements
100 kHz-hundreds of MHz – "RF"
GHz and higher – microwave

Challenges:
Noise vs. bandwidth.
Impedance matching.

Voltage:

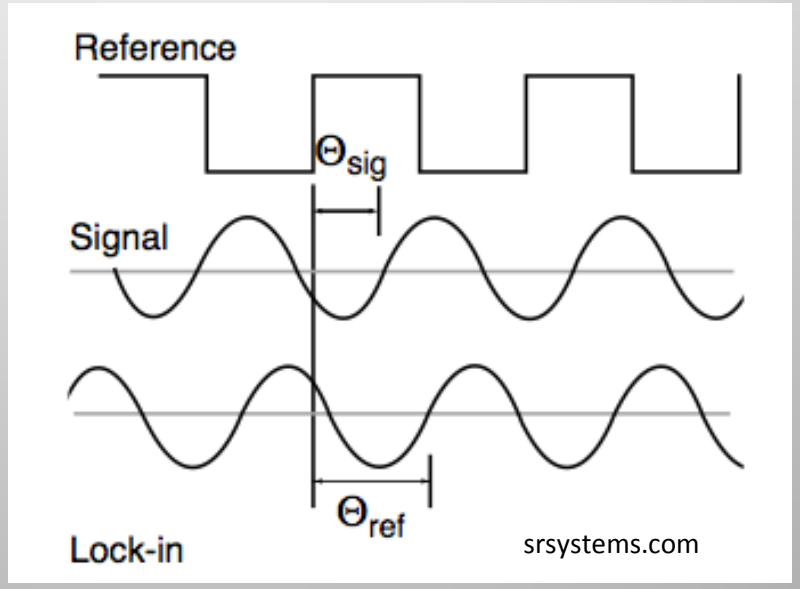
pV to V; supplies via programmable source, fn gen, batteries + op-amps
Detection via amplifiers (differential; single-ended)
Tradeoff: noise, input impedance

Current:

fA to A; supplies via programmable source (can be *V* + series *R*)
Detection usually via transimpedance amplifiers (not differential)
Tradeoff: noise, input impedance, output impedance

Lock-in amplifier

Lock-in amplifiers allow us to recover small (known ω) ac signals from noise at other ω.



$V_{\mathrm{sig}} \sin(\omega_0 t + \phi_{\mathrm{sig}})$

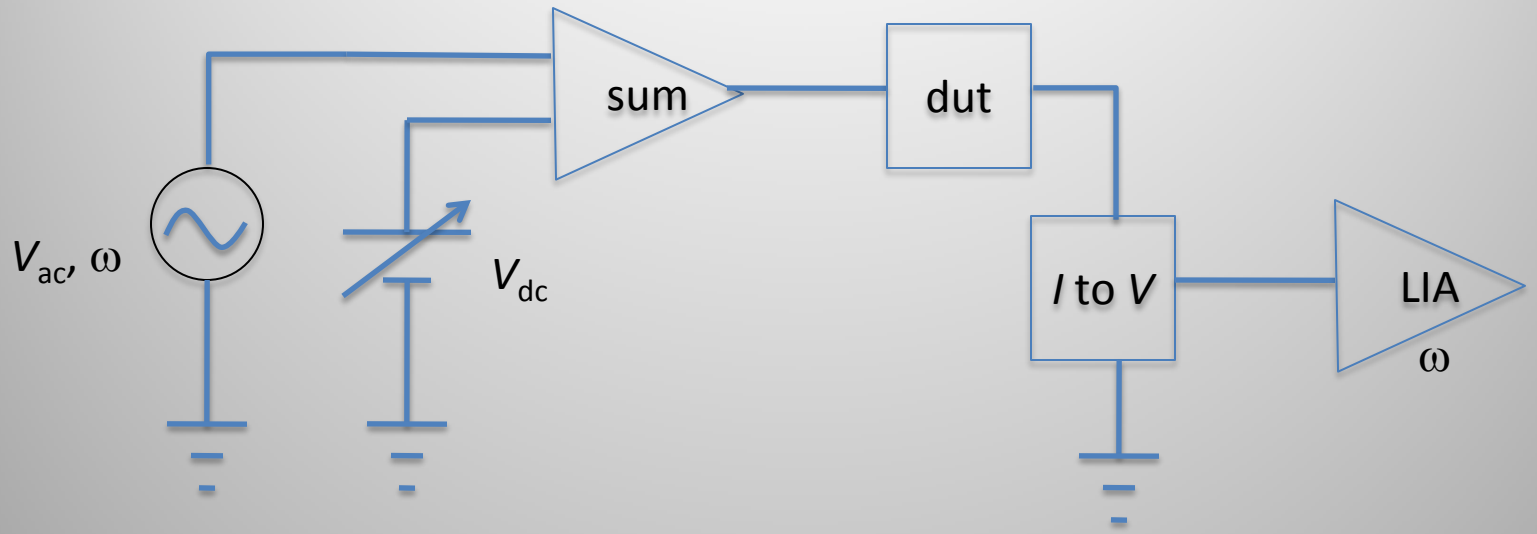
$V_{\mathrm{L}} \sin(\omega_{\mathrm{L}} t + \phi_{\mathrm{ref}})$

A lock-in amplifier multiplies the two sinusoids, and then low-pass filters to get rid of ac components.

$$\begin{aligned} V_{\mathrm{psd}} &= V_{\mathrm{sig}} V_{\mathrm{L}} \sin(\omega_0 t + \phi_{\mathrm{sig}}) \sin(\omega_{\mathrm{L}} t + \phi_{\mathrm{ref}}) \\ &= (1/2) V_{\mathrm{sig}} V_{\mathrm{L}} \cos([\omega_0 - \omega_{\mathrm{L}}]t + \phi_{\mathrm{sig}} - \phi_{\mathrm{ref}}) \\ &\quad - (1/2) V_{\mathrm{sig}} V_{\mathrm{L}} \cos([\omega_0 + \omega_{\mathrm{L}}]t + \phi_{\mathrm{sig}} + \phi_{\mathrm{ref}}) \end{aligned}$$

DC only: $V_{\mathrm{psd}} = (1/2) V_{\mathrm{sig}} V_{\mathrm{L}} \cos(\phi_{\mathrm{sig}} - \phi_{\mathrm{ref}})$

Measuring conductance



$$I = I_0(V_{\mathrm{dc}}) + \frac{\partial I}{\partial V}(V = V_{\mathrm{dc}})V_{\mathrm{ac}}\cos(\omega t) + \frac{1}{2}\frac{\partial^2 I}{\partial V^2}V_{\mathrm{ac}}^2\cos^2(\omega t) + \mathrm{h.o.t.}$$

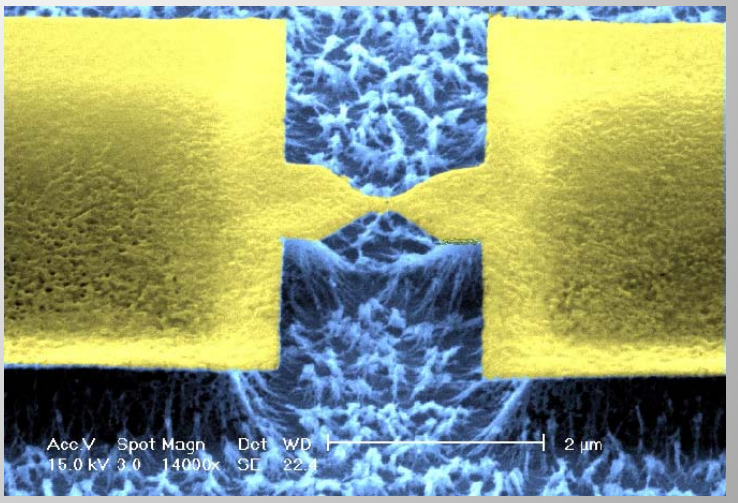
Differential conductance

Atomic-scale contacts

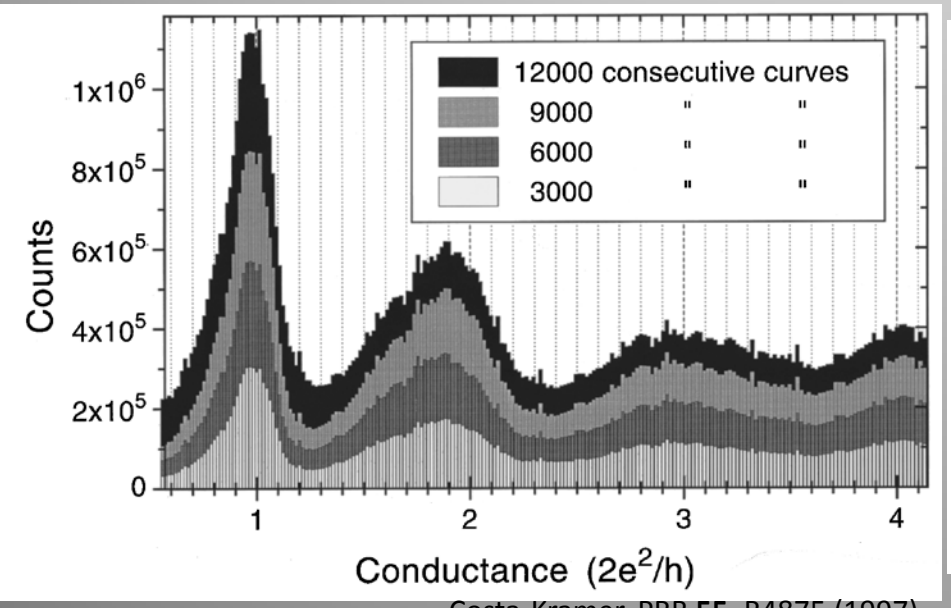
Simplest nano“device”: atomic-scale metal contact.

Make by breaking a wire.

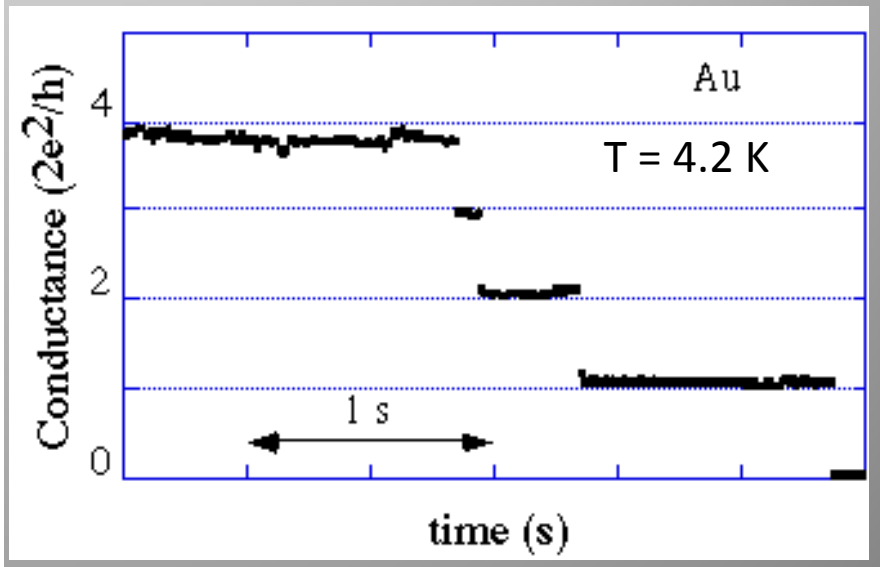
I-V essentially linear, but preferred values of conductance show up.



From van Wees, Groningen

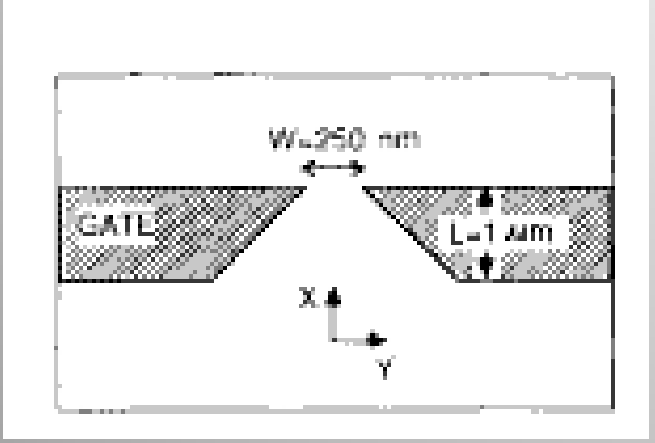


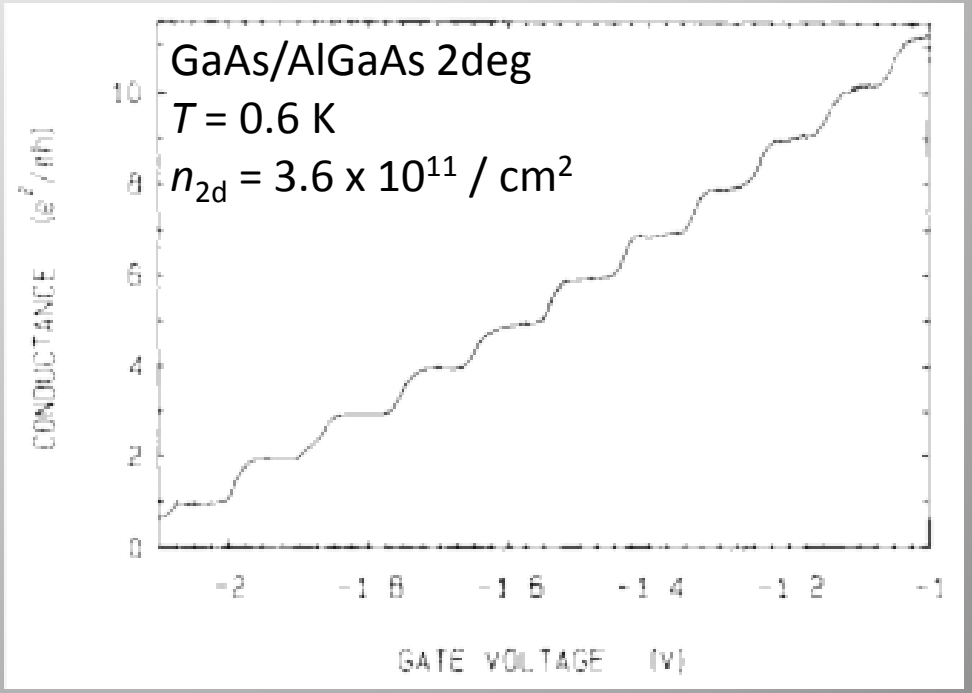
Costa-Kramer, PRB **55**, R4875 (1997)



Conductance quantization

People had seen something similar in semiconductor structures:





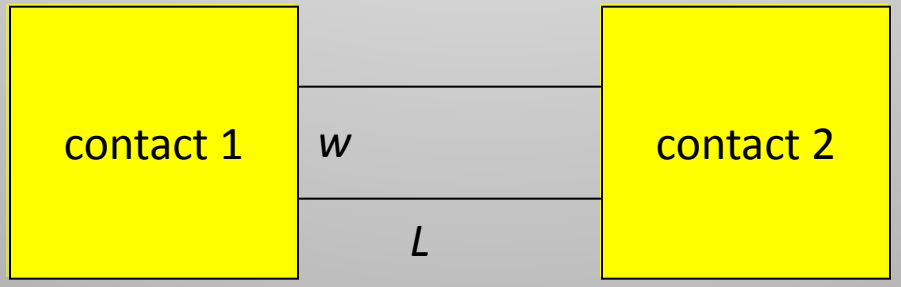
- How much can a single electronic mode conduct?
- Conductance is ***quantized***.
- A single, perfect electronic channel has conductance $2e^2/h$.

Van Wees *et al.*, PRL **60**, 848 (1988)

Landauer-Büttiker approach

Consider two macroscopic leads, connected by small number of quantum "channels".

(EM analogy: big cavities connected by piece of waveguide)
Assumes noninteracting, independent particles, no inelastic scattering.



Landauer (1959) did general case:

$$G = \frac{e^2}{h} \sum_{i,\sigma} \tau_{i,\sigma}$$

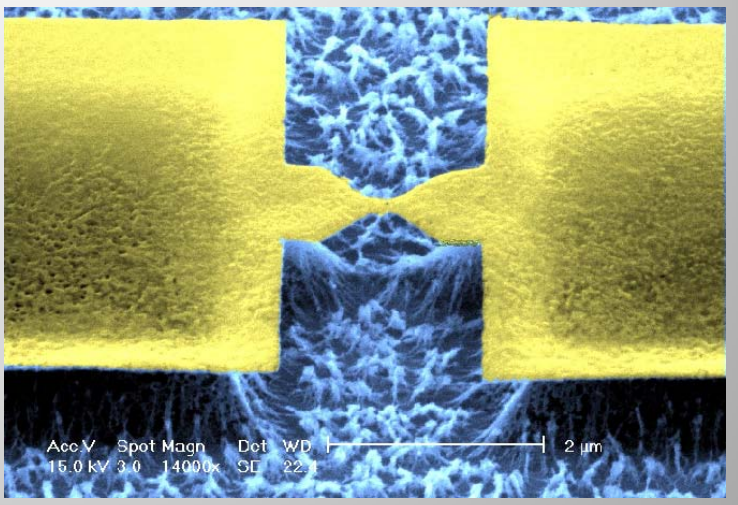
Here $\tau_{i,\sigma}$ is the transmission probability for the *i*th channel, spin σ.

Atomic-scale contacts

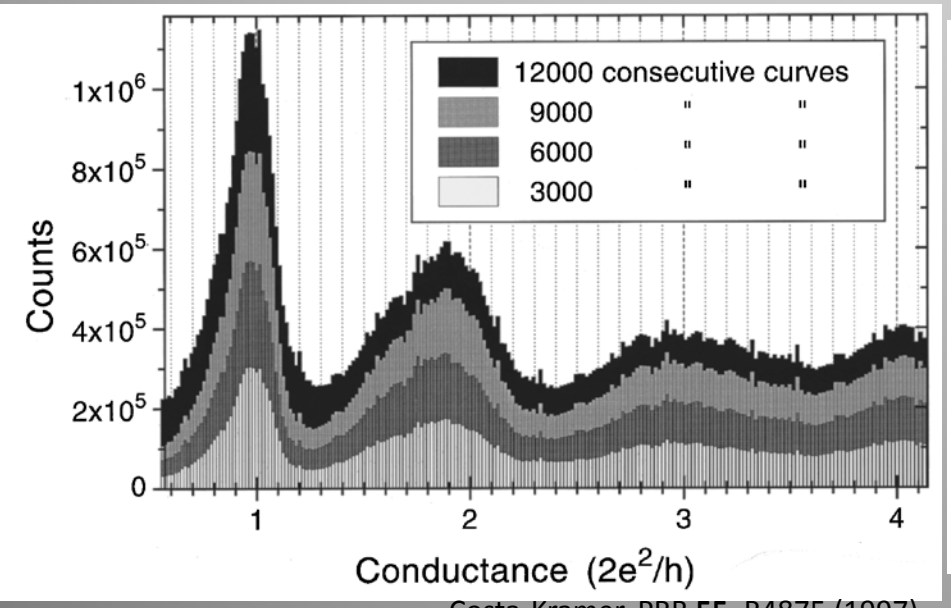
Landauer formula is *suggestive*, but is it really applicable here?

What about chemistry? Are peaks in histogram just signs of particular atomic configurations?

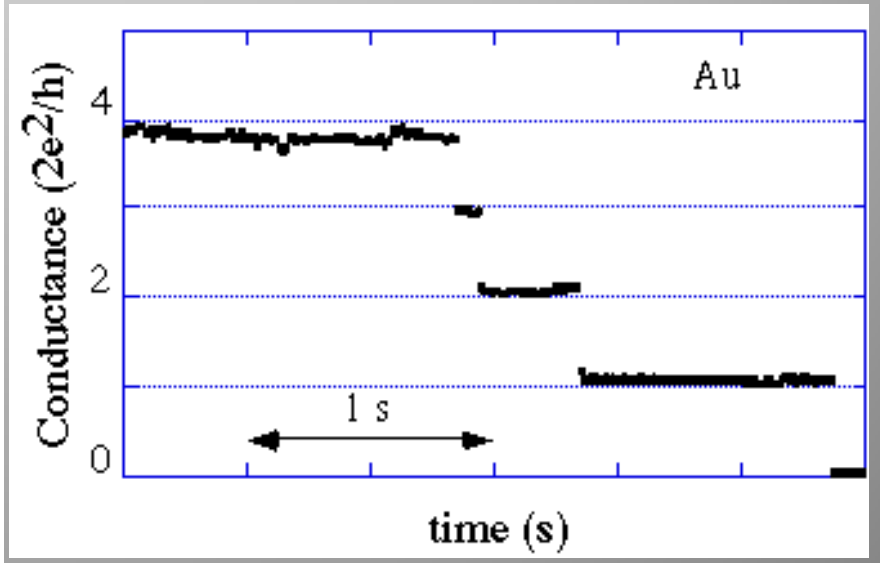
How can we tell? ***Noise!***



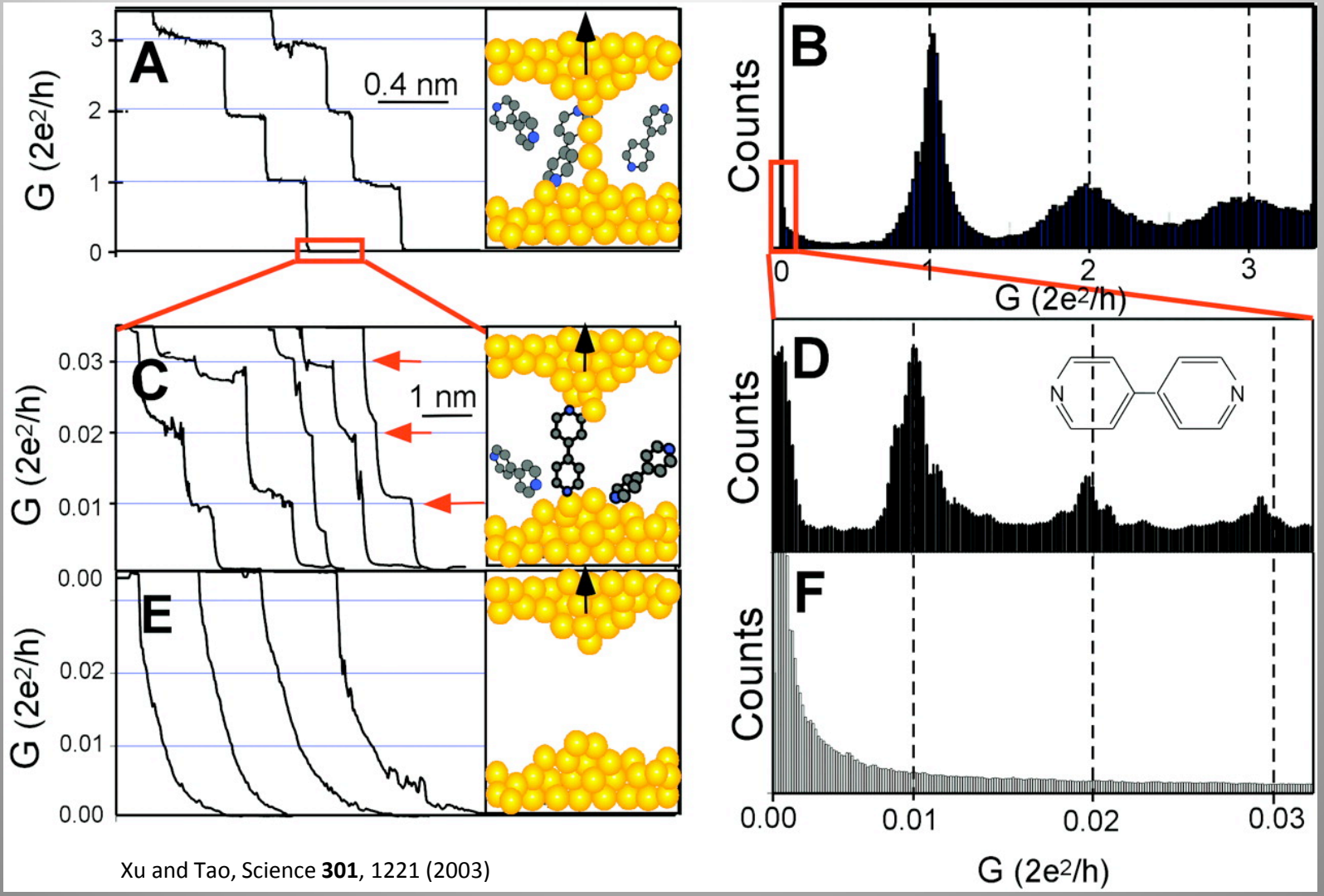
From van Wees, Groningen



Costa-Kramer, PRB **55**, R4875 (1997)



Single-molecule junctions

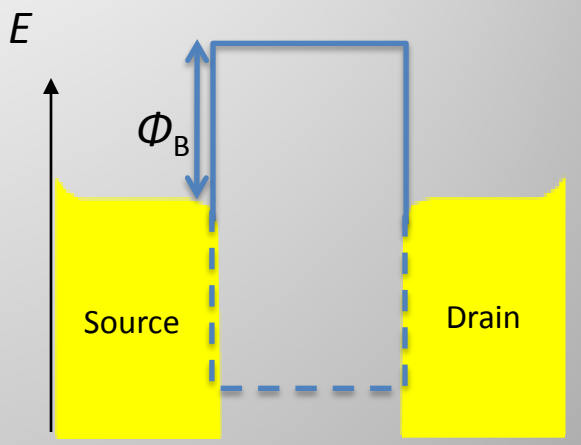


Xu and Tao, Science **301**, 1221 (2003)

Single-molecule junctions

What do we want to know here?

- Is this simple effective barrier picture valid?
- Can we infer the barrier height from measurements?
- Are the carriers “electron”-like or “hole”-like?



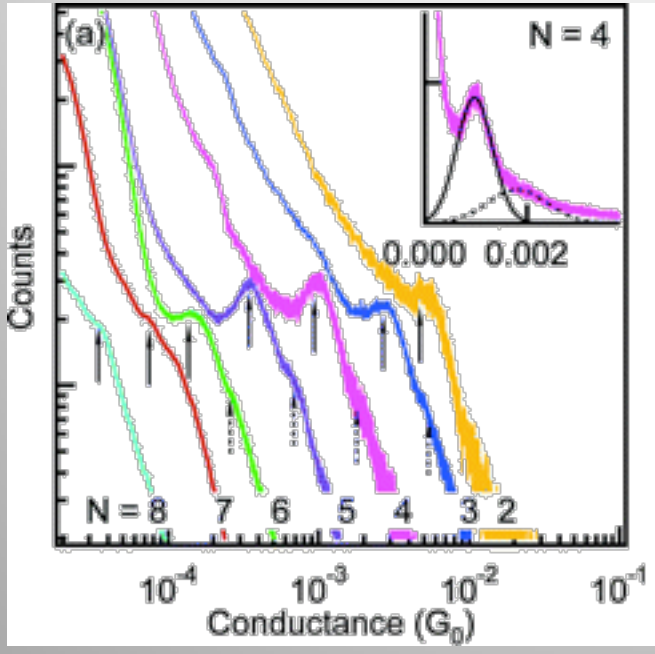
General thinking: $G = G_* \exp(-\beta L)$, where G_* is related to the molecule-metal contact, and β is the decay constant,

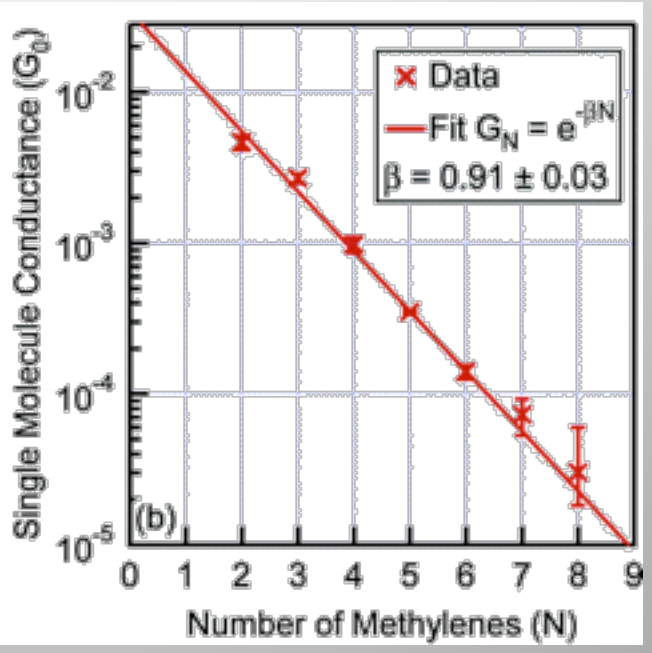
$$\beta = \sqrt{\frac{2m\varphi_B}{\hbar^2}}$$ for *e*-like carriers at the Fermi level.

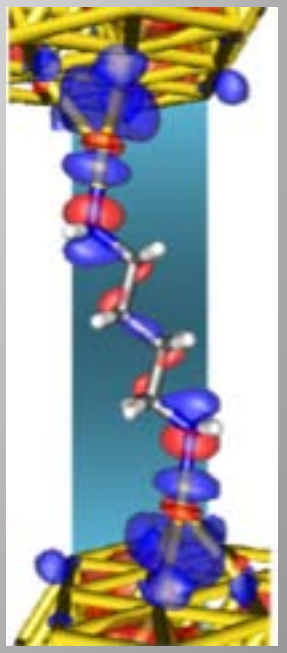
Things we can measure:

Conductance (low-bias) for transmission coefficient; higher bias to infer barrier heights, etc.; length-dep?

Single-molecule junctions



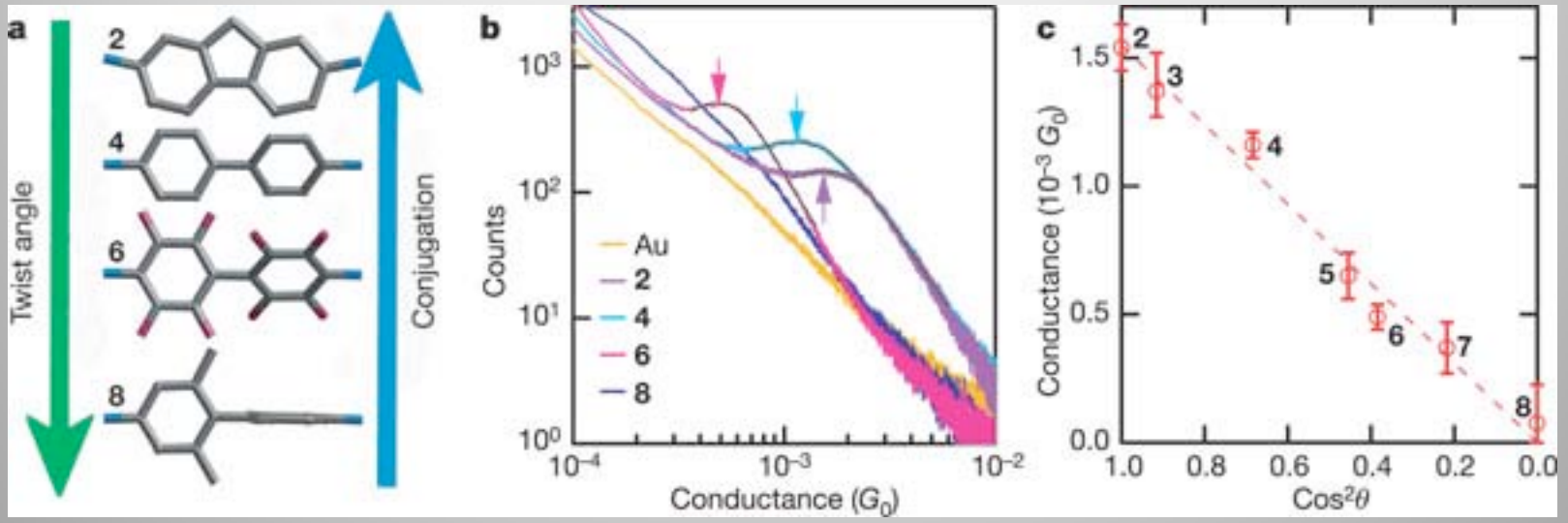




Venkataraman *et al.*, Nano Lett. **6**, 458 (2006)

- Conductance decreases exponentially with length of molecule (effective barrier picture), decay constant = β.
- With appropriate end groups (-NH_2 here), well-defined peak in conductance histograms are obtained.
- Extrapolation to zero length should tell us something about the contacts and the matrix element there.

Single-molecule junctions



Venkataraman *et al*., Nature **442**, 904 (2006)

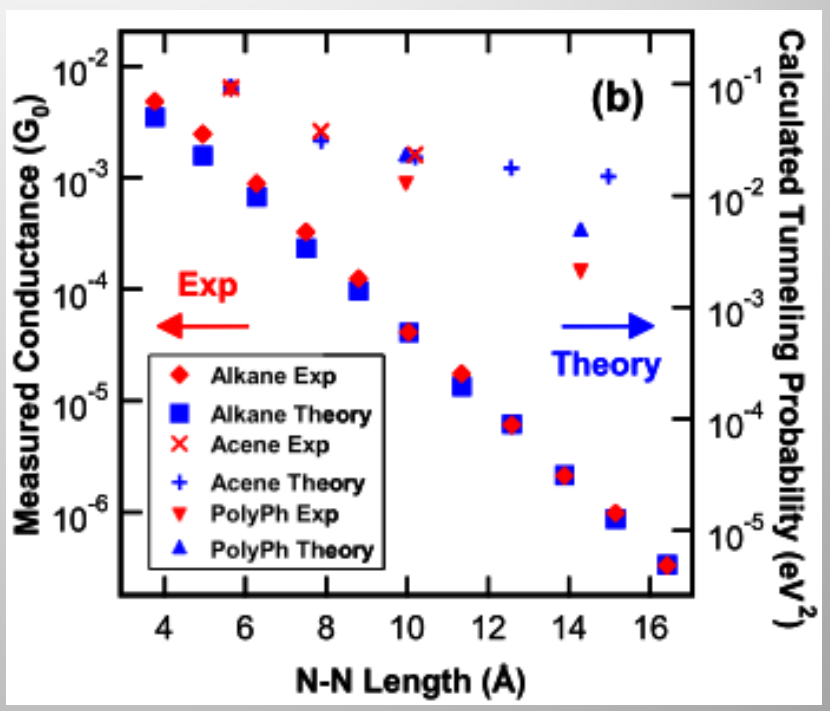
- Can fix the end groups and vary the molecule.
- Here, looking at effect of breaking the molecular "conjugation" by varying degrees.

Single-molecule junctions

- Conjugated molecules (polyphenylenes) have a smaller decay constant that saturated molecules (alkanes).

- Consistent with conjugated molecules having smaller HOMO-LUMO gaps, and therefore smaller barrier heights.

- With appropriate quantum chemistry calculations, theory captures trends well.

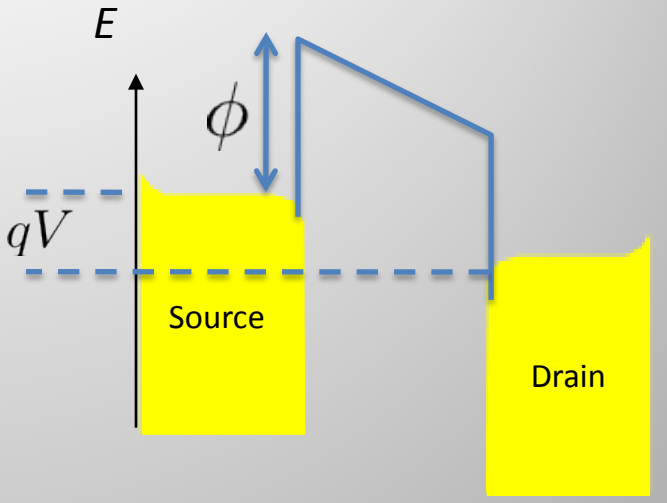


Hybertsen *et al.*, J. Phys.: Condens. Matter **20,** 374115 (2008)

Very crude effective barrier model seems to do surprisingly well (near zero bias). Can we learn more?

Transition voltage spectroscopy

Beebe *et al*. suggested a way to infer more information from *I*-*V* characteristics.



Simmons model of (low bias) tunneling
J. G. Simmons, J. Appl. Phys. **34**, 1793 (1963).

$$I = \frac{qA}{4\pi^2\hbar d^2}\left(\left(\phi - \frac{qV}{2}\right)\exp\left(-\frac{2d\sqrt{2m_e}}{\hbar}\sqrt{\phi - \frac{qV}{2}}\right) - \left(\phi + \frac{qV}{2}\right)\exp\left(-\frac{2d\sqrt{2m_e}}{\hbar}\sqrt{\phi + \frac{qV}{2}}\right)\right)$$

Low bias limit: $$I \propto V\exp\left(-\frac{2d\sqrt{2m_e\phi}}{\hbar}\right)$$

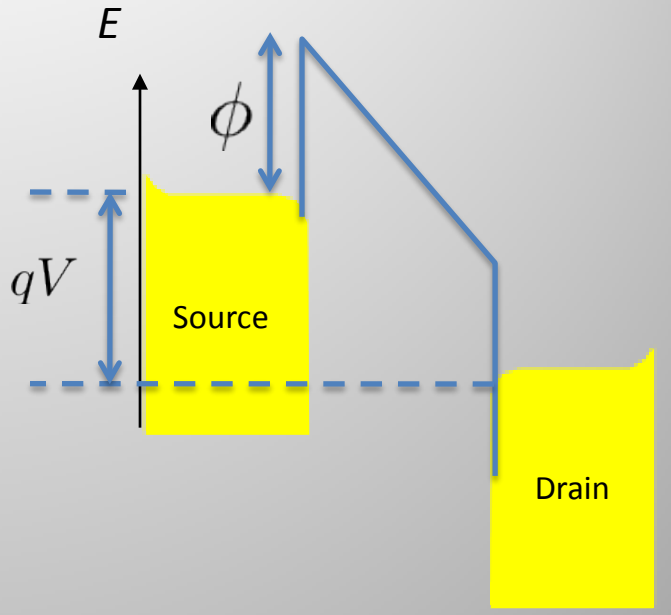
$$\ln\left(\frac{I}{V^2}\right) \propto \ln\left(\frac{I}{V}\right) - \frac{2d\sqrt{2m_e\phi}}{\hbar}$$

Beebe *et al*., PRL **97**, 026801 (2006)

Transition voltage spectroscopy

At high bias, crossover to Fowler-Nordheim tunneling.

Effective triangular barrier, tuned by bias.



$$I \propto V^2 \exp\left(-\frac{4d\sqrt{2m_e\phi^3}}{3\hbar qV}\right)$$

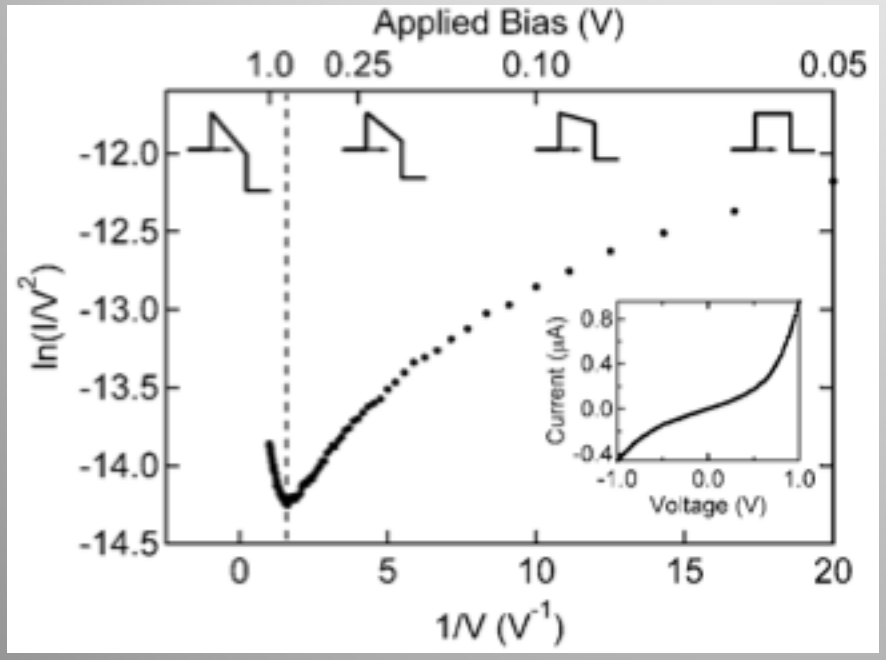
$$\ln\left(\frac{I}{V^2}\right) \propto -\frac{4d\sqrt{2m_e\phi^3}}{3\hbar q}\left(\frac{1}{V}\right)$$

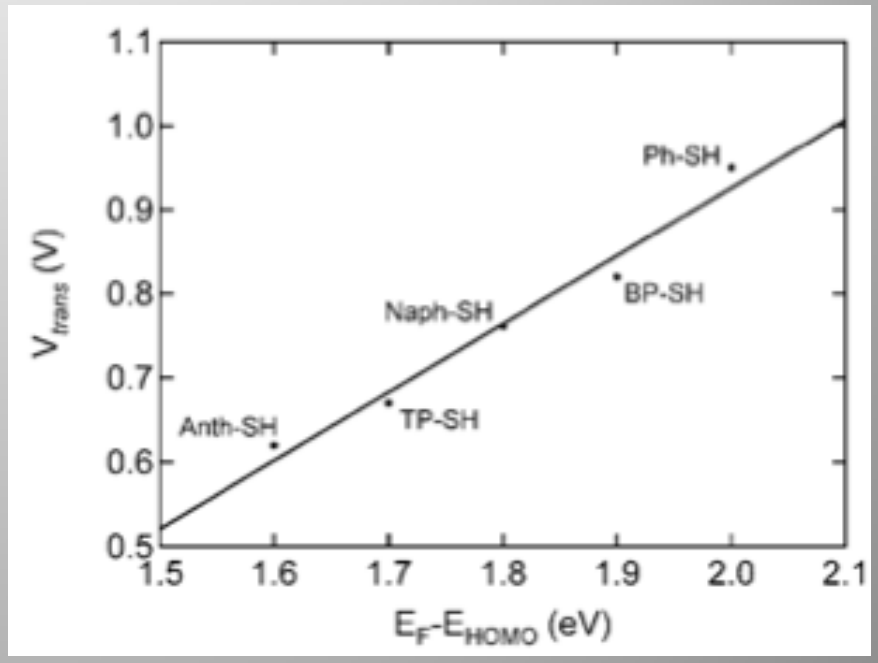
Idea: Plotting data as ln (I/V^2) vs. ($1/V$) should show the crossover, at a voltage V_{trans} that should be related to ϕ.

Beebe *et al.*, PRL **97**, 026801 (2006)

Transition voltage spectroscopy

Idea: Plotting data as ln (I/V^2) vs. ($1/V$) should show the crossover, at a voltage V_{trans} that should be related to ϕ.

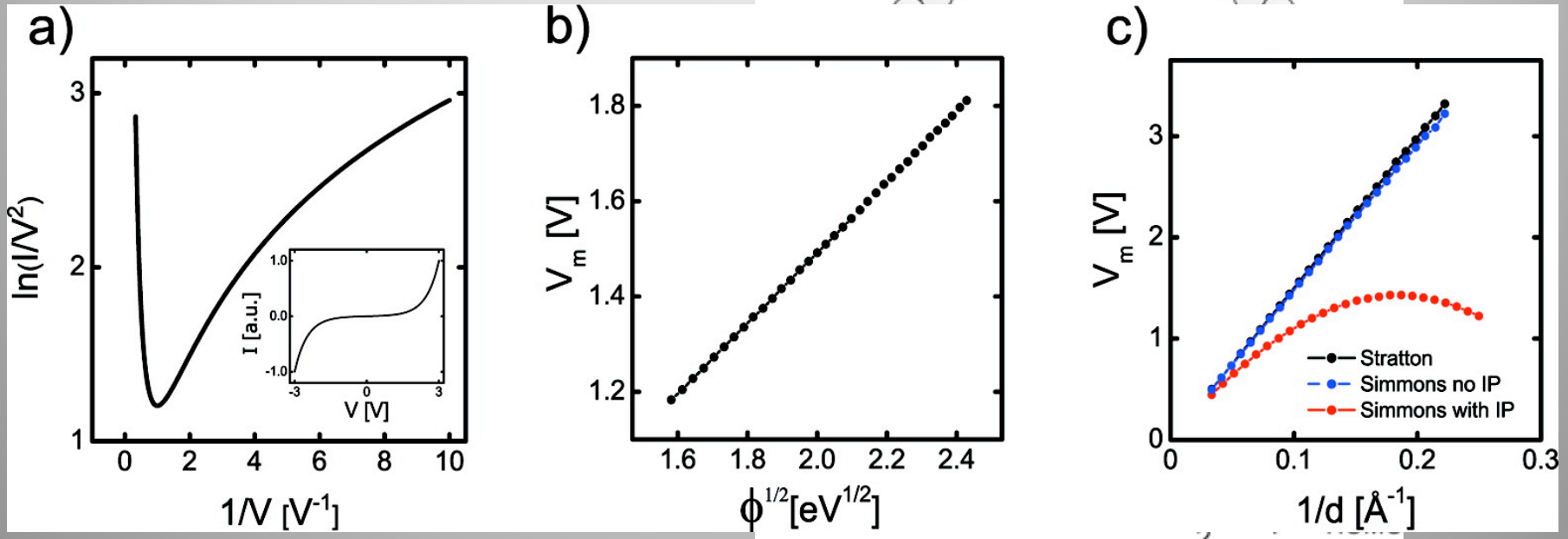




Beebe *et al*., PRL **97**, 026801 (2006)

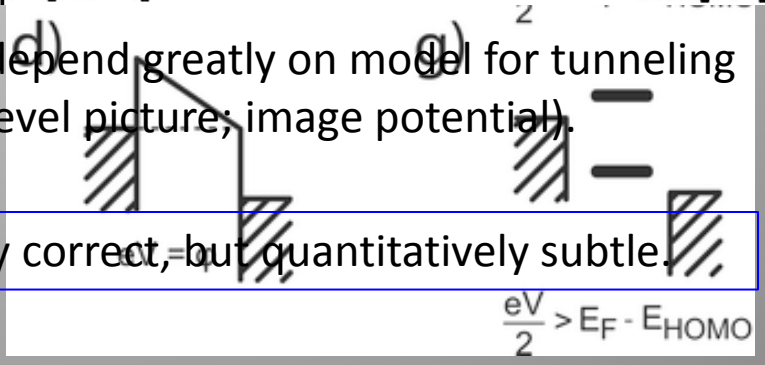
Transition voltage spectroscopy

The story is not that simple.



Detailed interpretation of V_{trans} depend greatly on model for tunneling (linear voltage drop; molecular level picture; image potential).

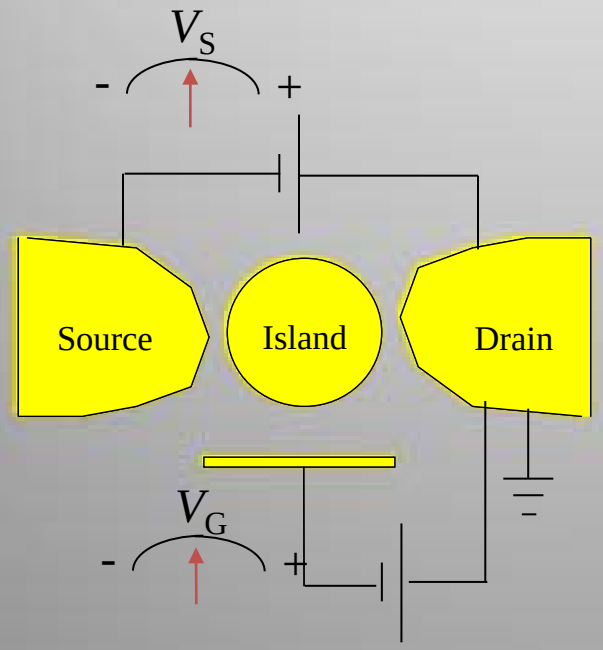
Bottom line: TVS is qualitatively correct, but quantitatively subtle.

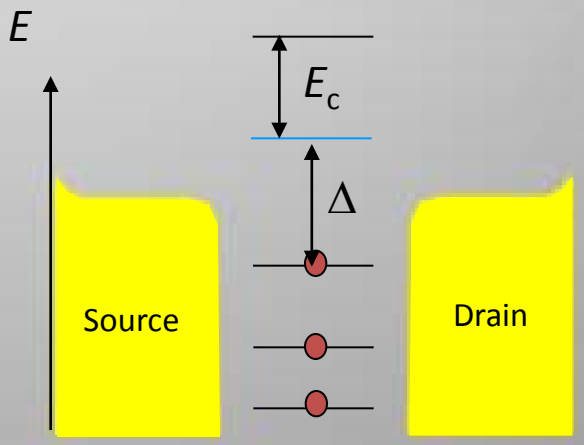


Huisman *et al.*, Nano Lett. **9**, 3909 (2009)

Single-electron devices – model

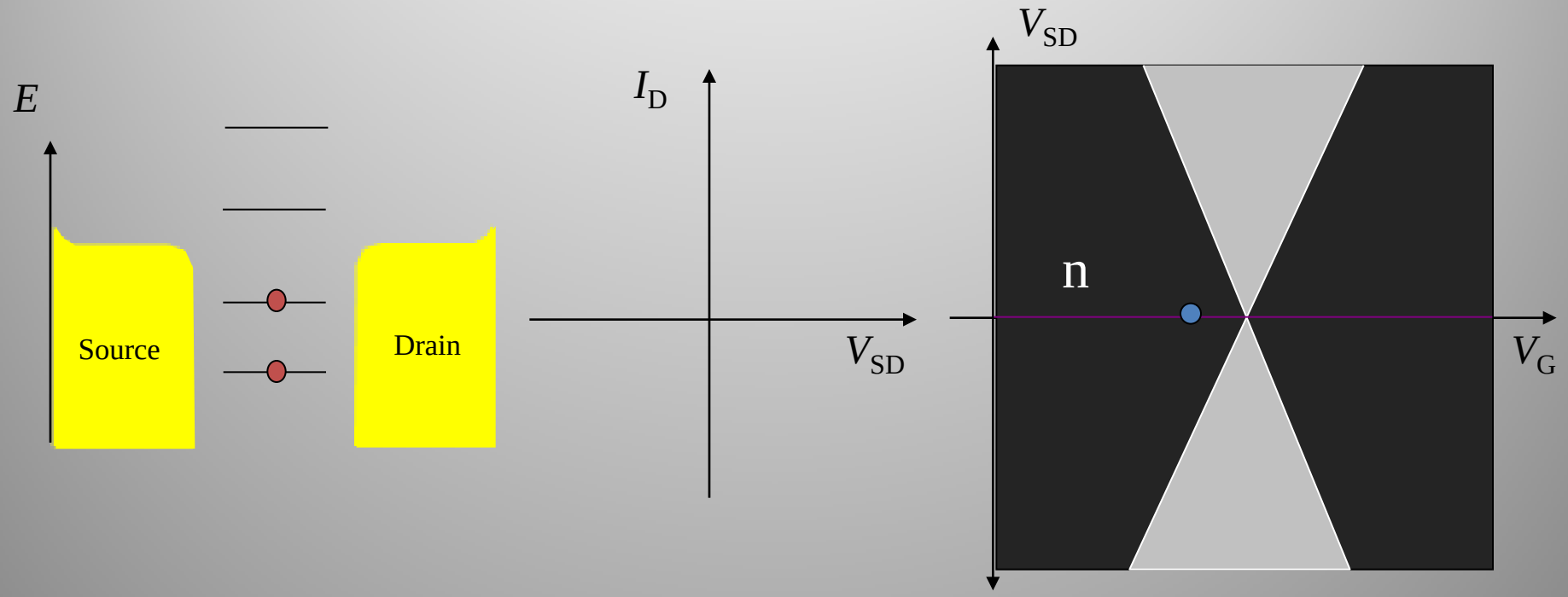
- Electron-electron interactions can dominate transport properties.
- Δ = single-particle level spacing, lowest energy of e-h excitation
- E_c = Coulomb charging energy (constant interaction model)





Single-electron devices

- Data usually presented as *differential conductance*.
- Can overcome blockade with source-drain bias.



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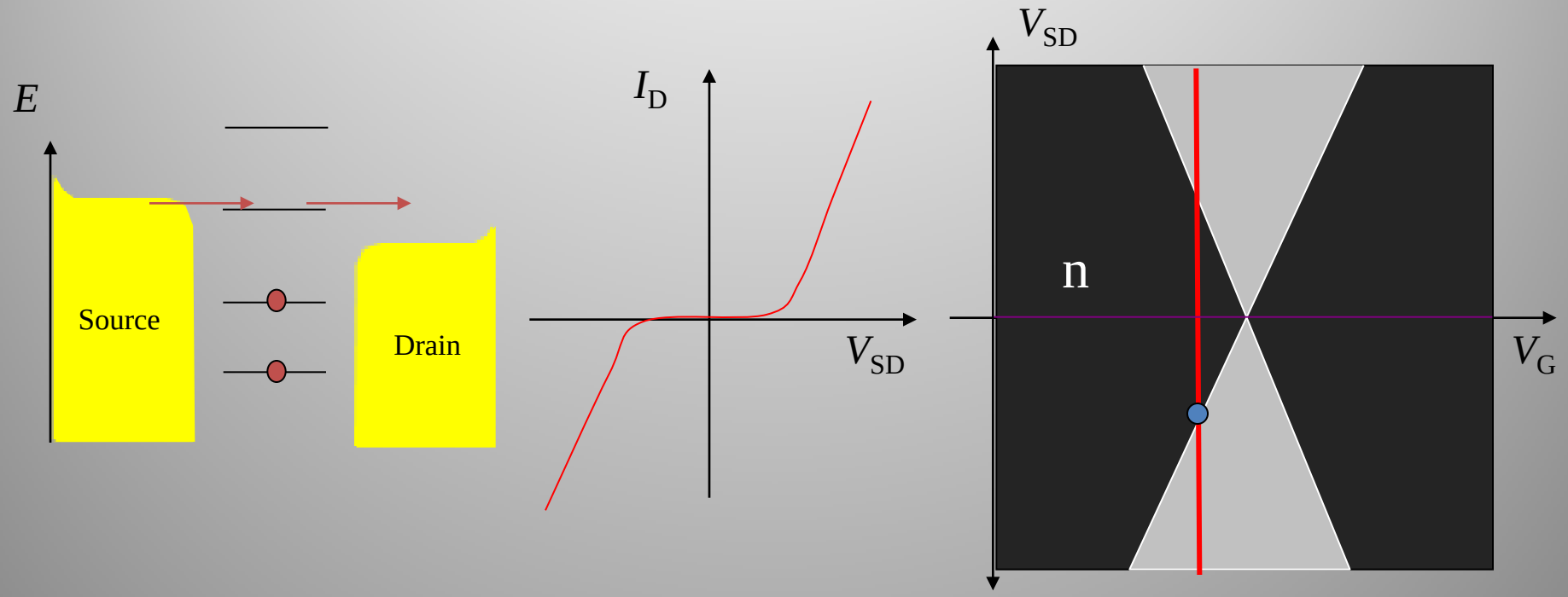
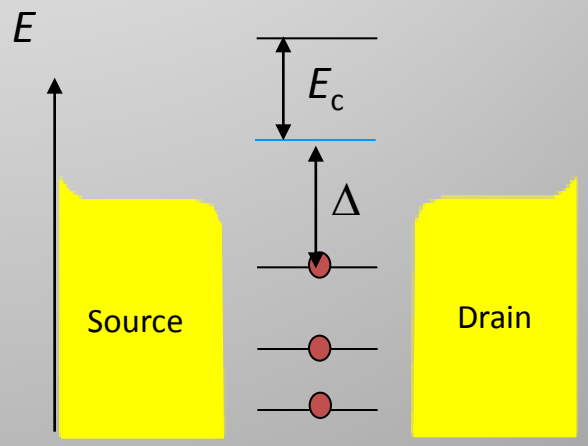


Single-electron devices – Coulomb blockade regime

- Δ = single-particle level spacing, lowest energy of e-h excitation
- E_c = Coulomb charging energy

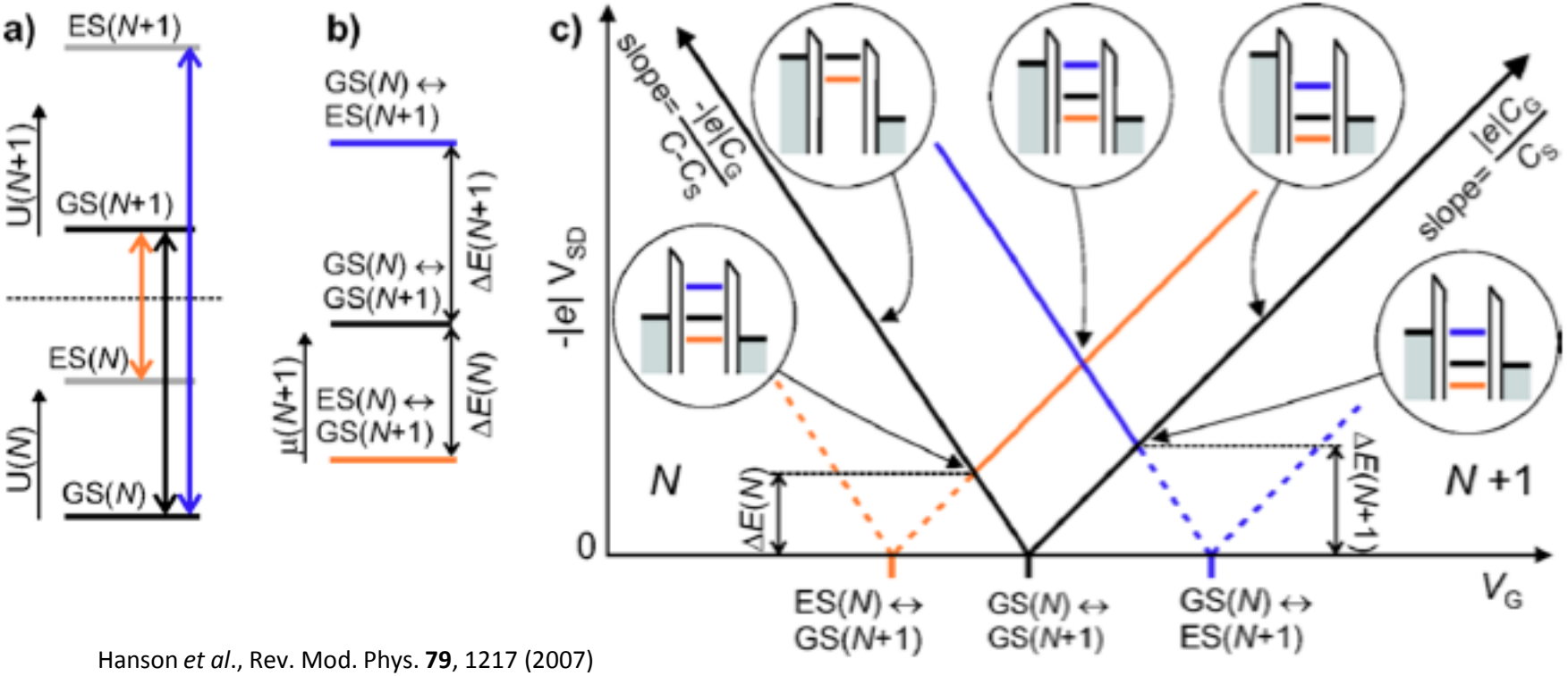
Weak coupling limit: No current flows unless bias is sufficient to bring level into alignment.

"Coulomb blockade"



In metal islands + early semiconductor dots, E_c dominates – hence the name.

Single-electron devices – Stability diagrams

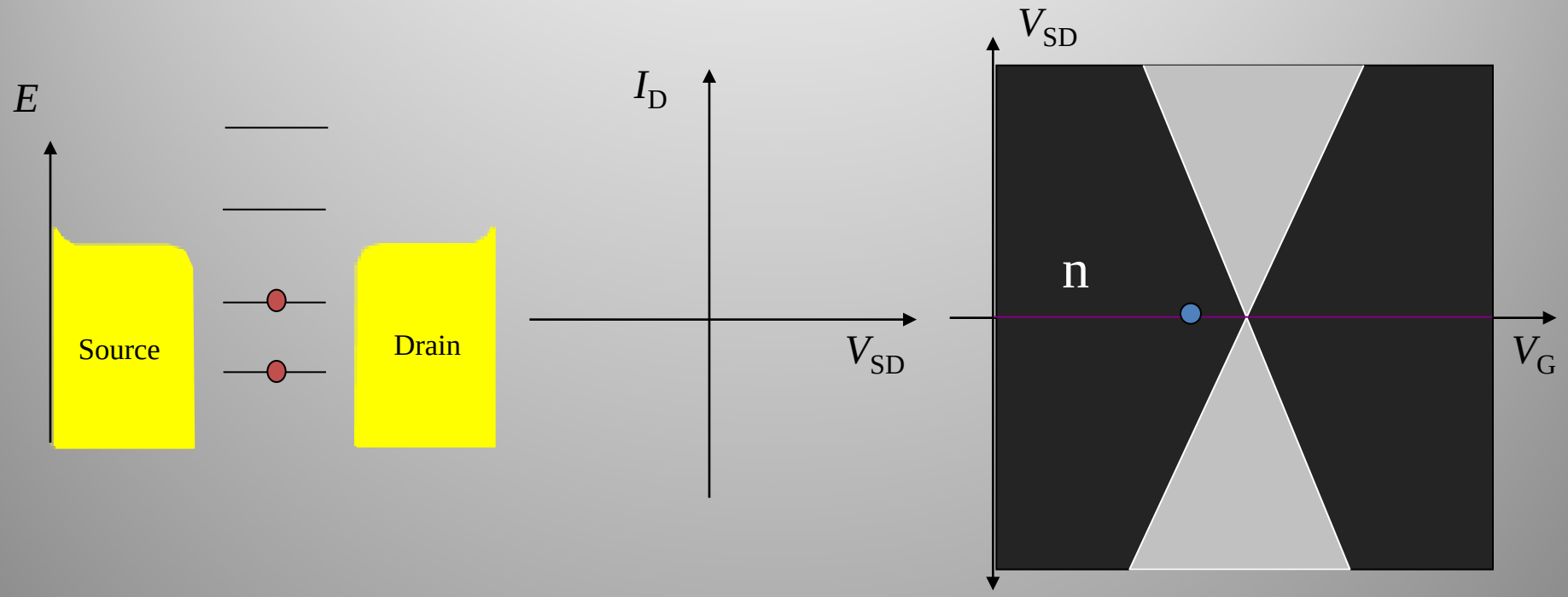


Hanson *et al*., Rev. Mod. Phys. **79**, 1217 (2007)

Depending on gate + source-drain bias, can stabilize different numbers of electrons on the island.

Single-electron devices

- Data usually presented as *differential conductance*.
- Gate shifts levels, discretely changes avg island charge.



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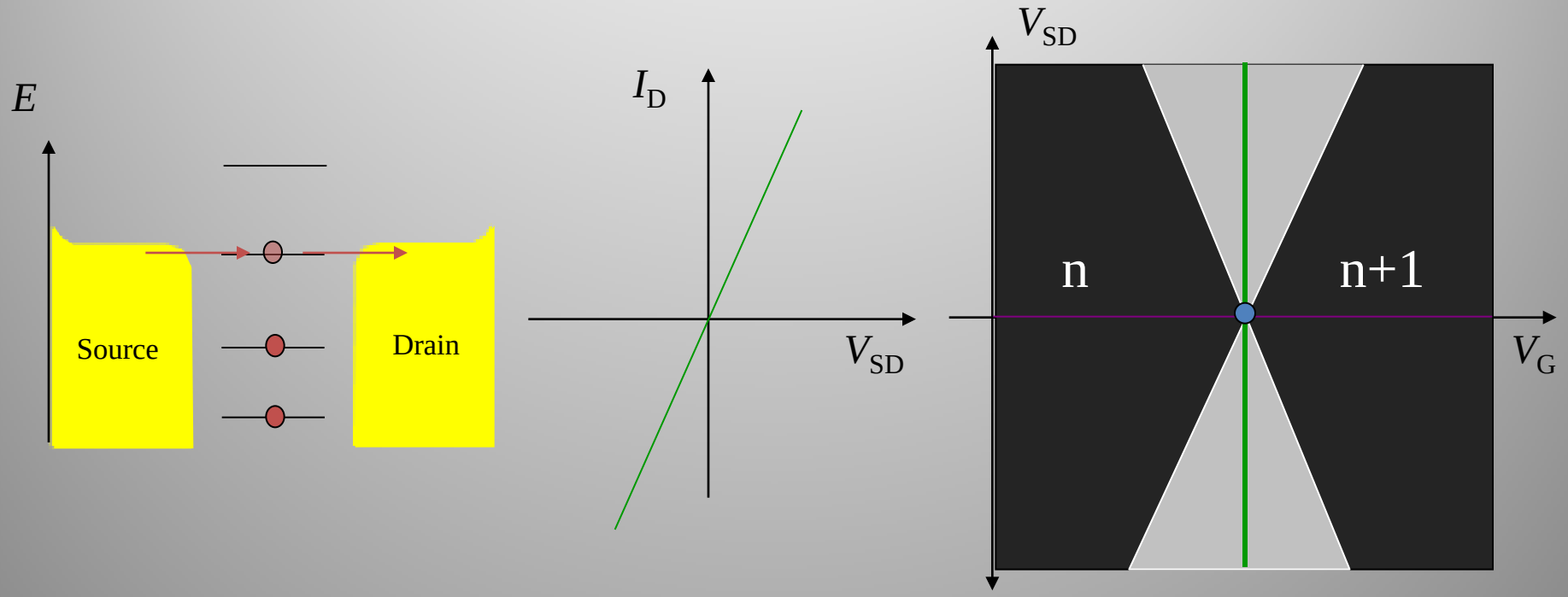
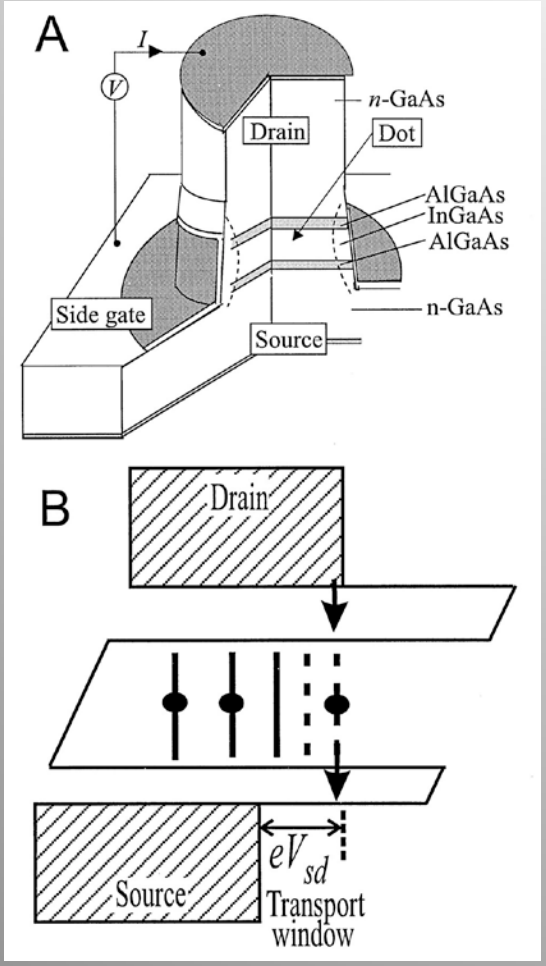
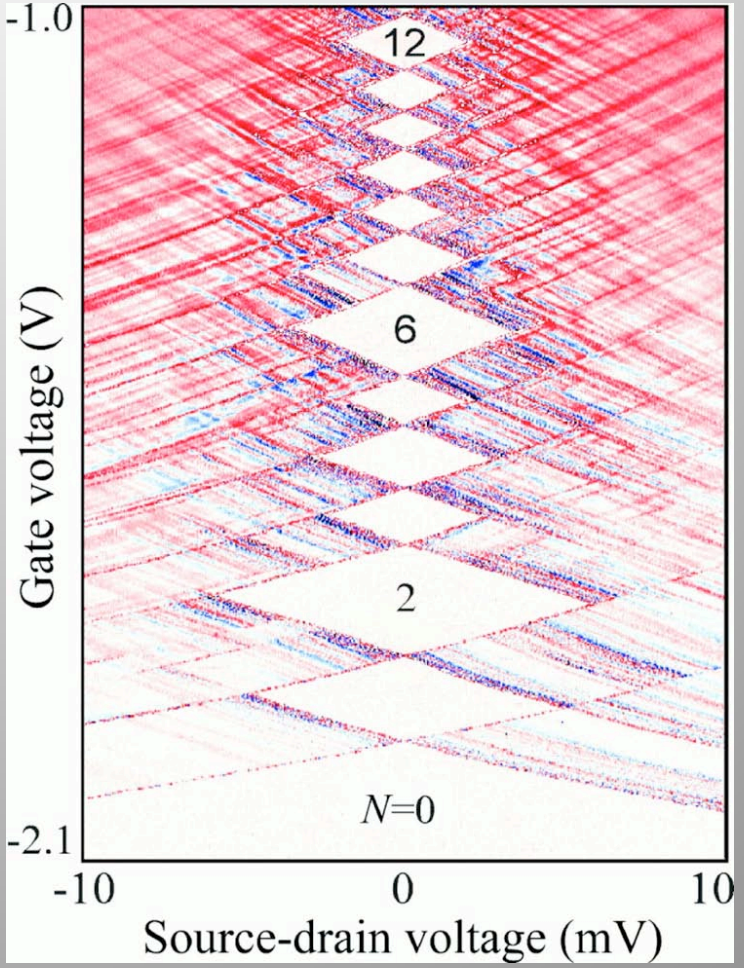


Semiconductor (vertical) dot example



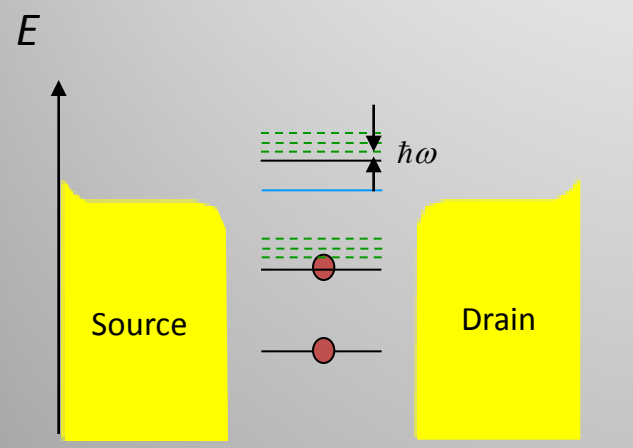


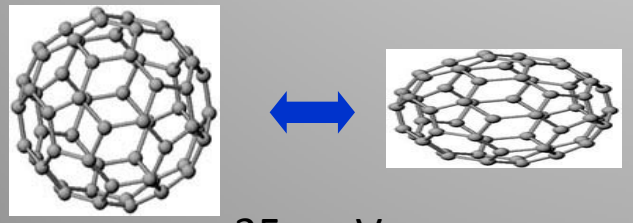
Kouwenhoven *et al.*, Science **278**, 1788 (1997).

Excited state transport

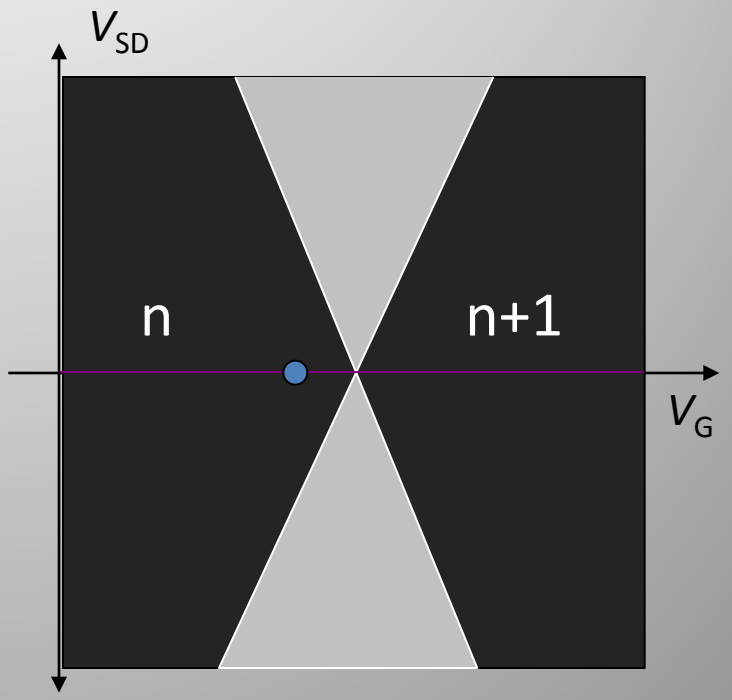
One molecule-specific feature:

Vibrational resonances



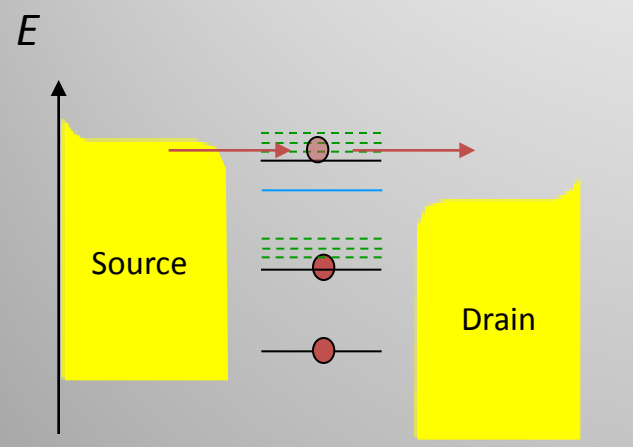


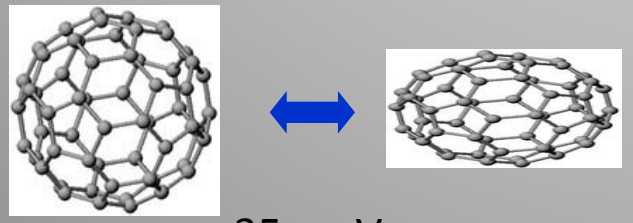
35 meV



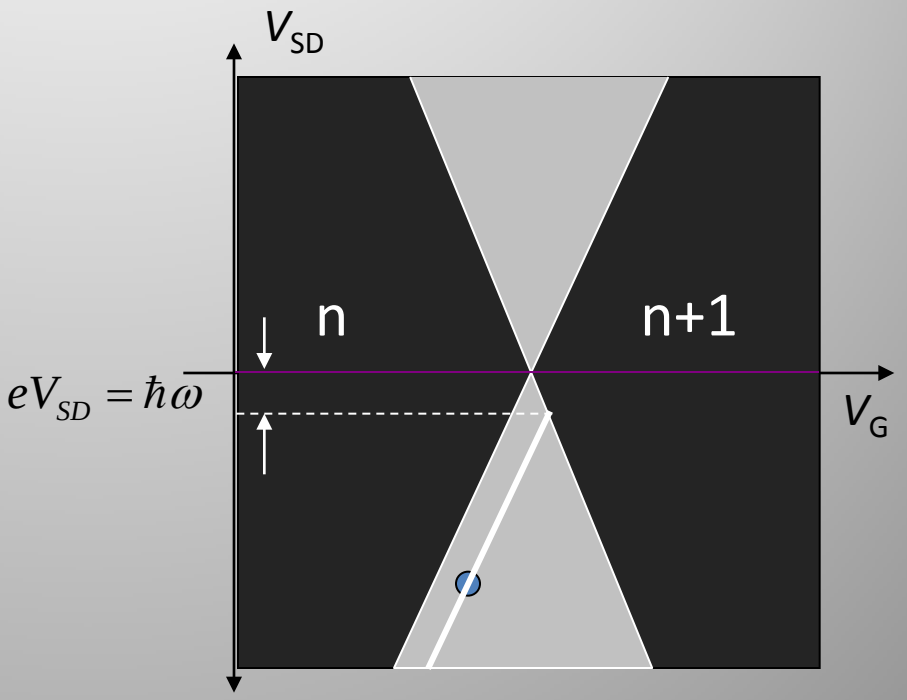
Excited state transport

One molecule-specific feature: Vibrational resonances



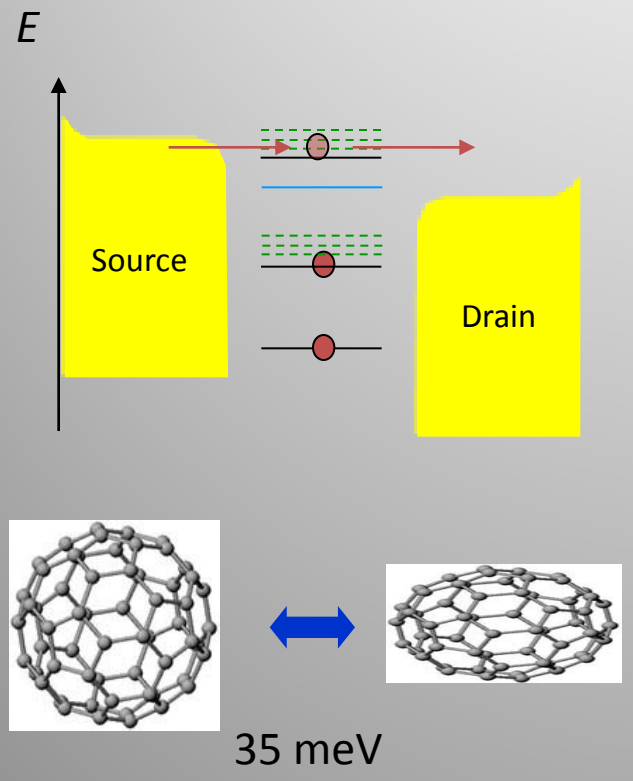


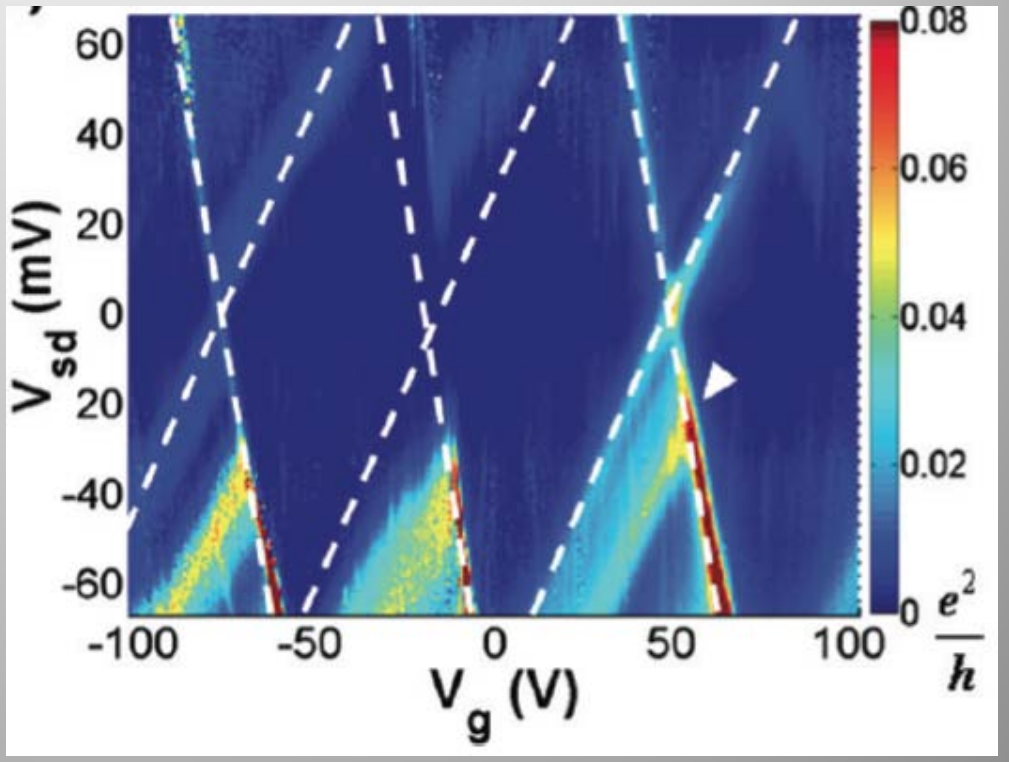
35 meV



Excited state transport

One molecule-specific feature: Vibrational resonances

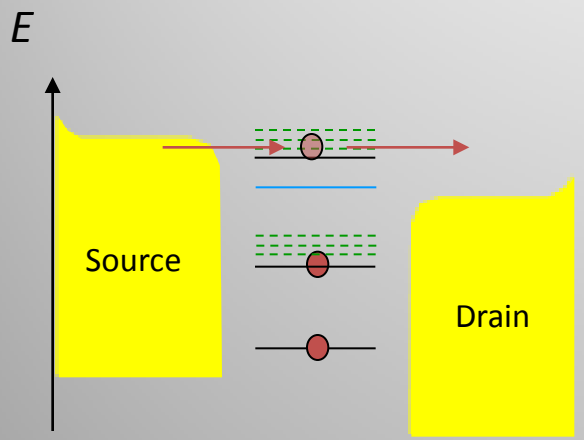


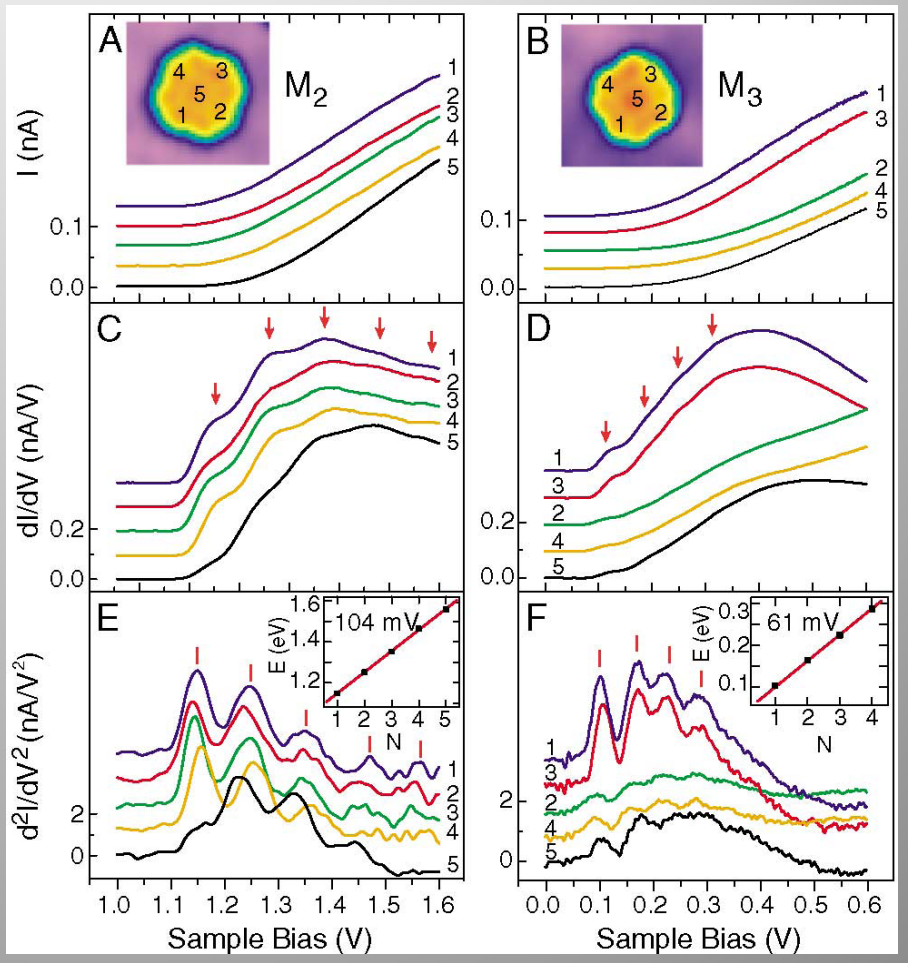


Scott and Natelson, ACS Nano **4**, 3560 (2010)

Excited state transport

One molecule-specific feature: Vibrational resonances

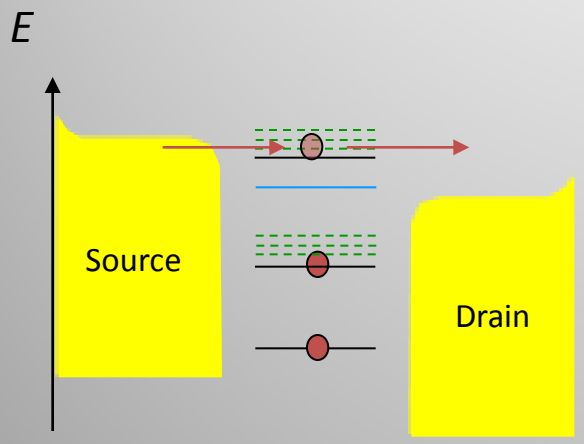


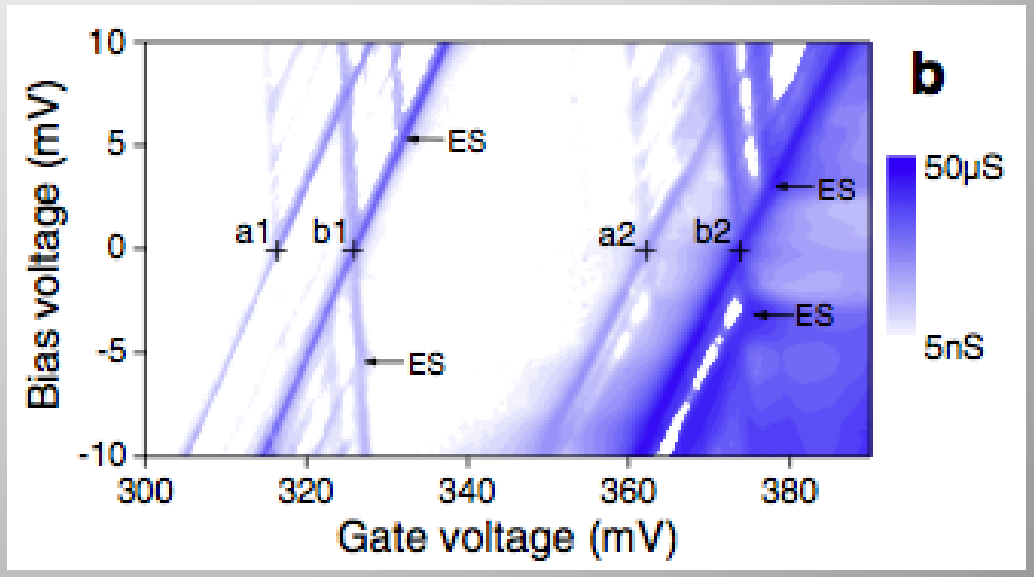


Qiu *et al.*, PRL **92**, 206102 (2004)

Excited state transport

Similar signatures in semiconductor dots:

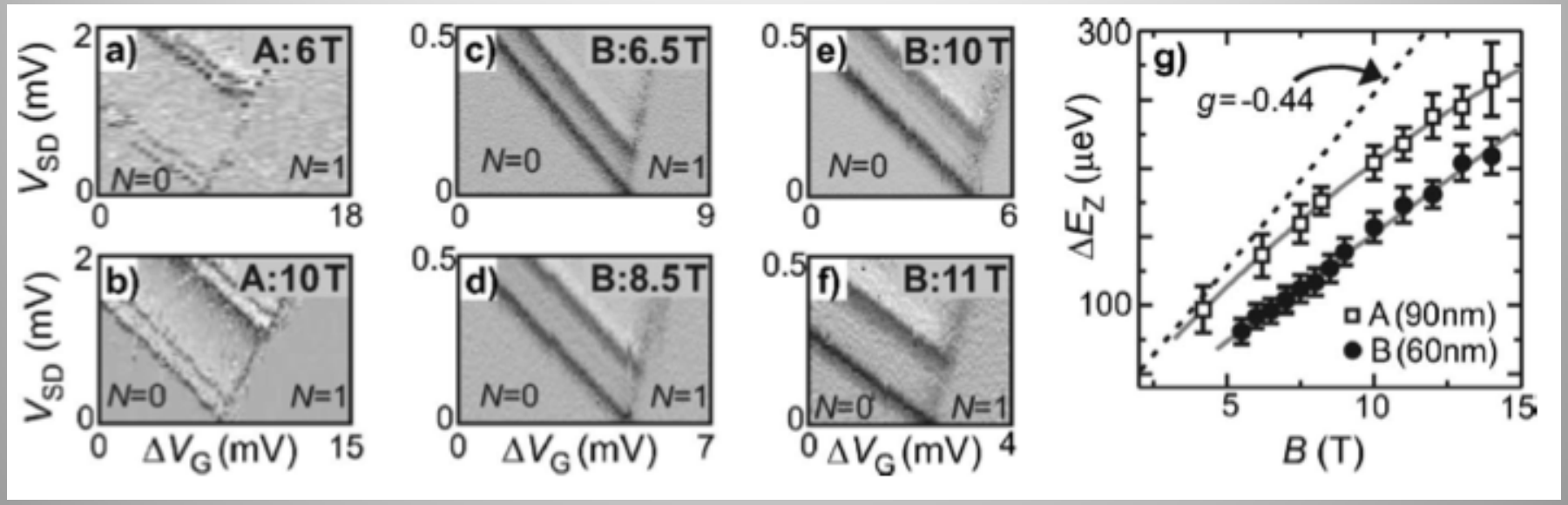




Sellier *et al.*, PRL **97**, 206805 (2006)

Identifying excited states

The Zeeman effect provides a convenient way to track single-particle levels.



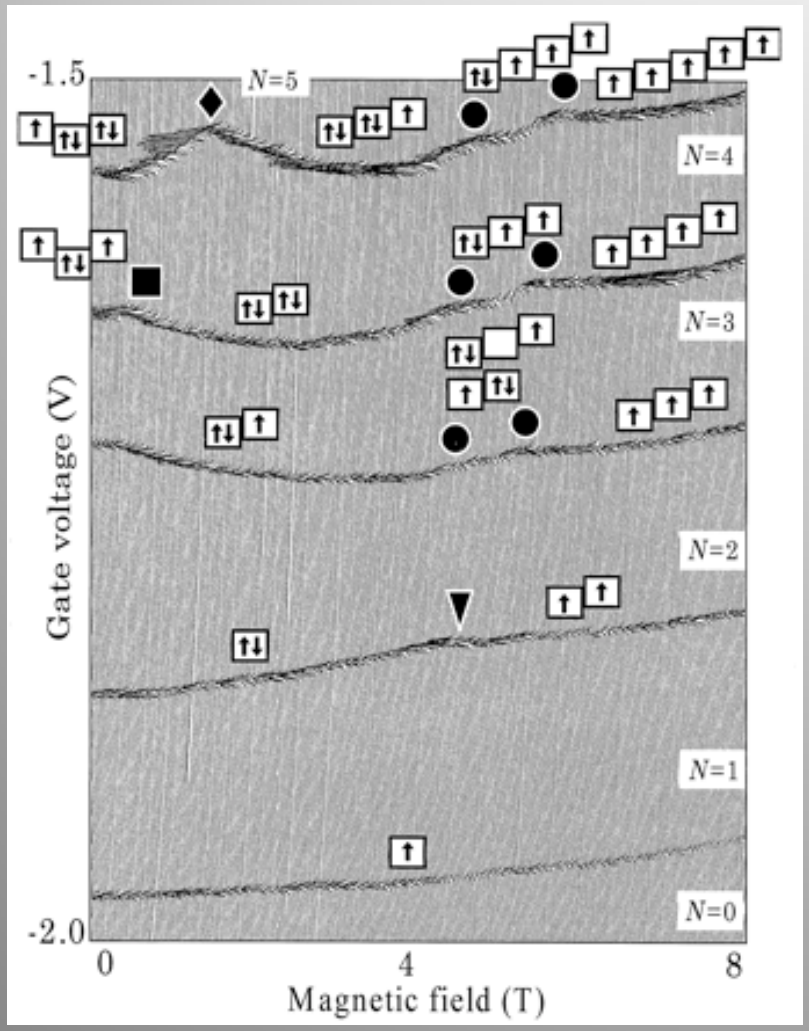
Hanson *et al*., Rev. Mod. Phys. **79**, 1217 (2007)

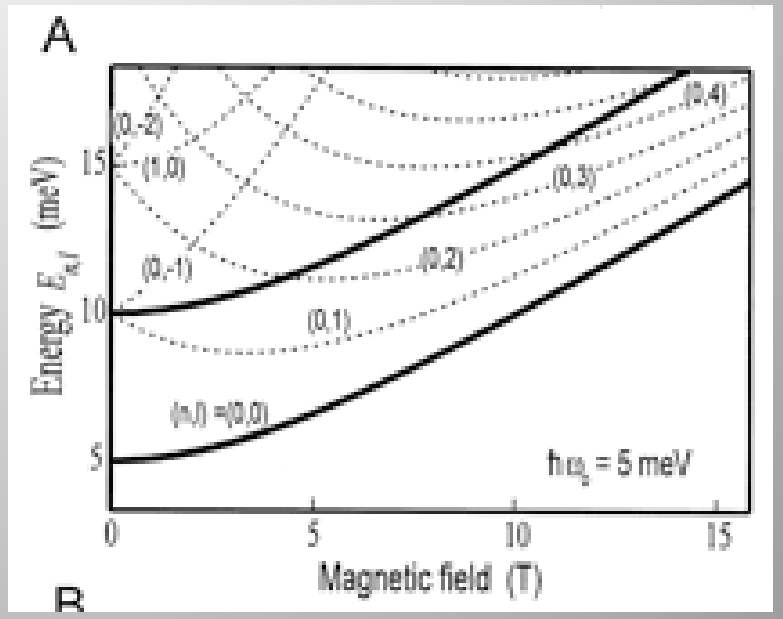
B in plane of 2deg = (nominally) pure Zeeman.

B normal to plane of 2deg = Zeeman + orbital effects (via Aharonov-Bohm phase)

Identifying excited states

Zeeman + orbital response are a convenient way to track single-particle levels.

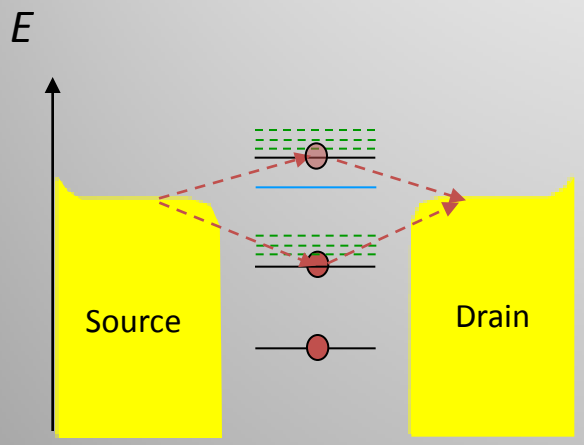


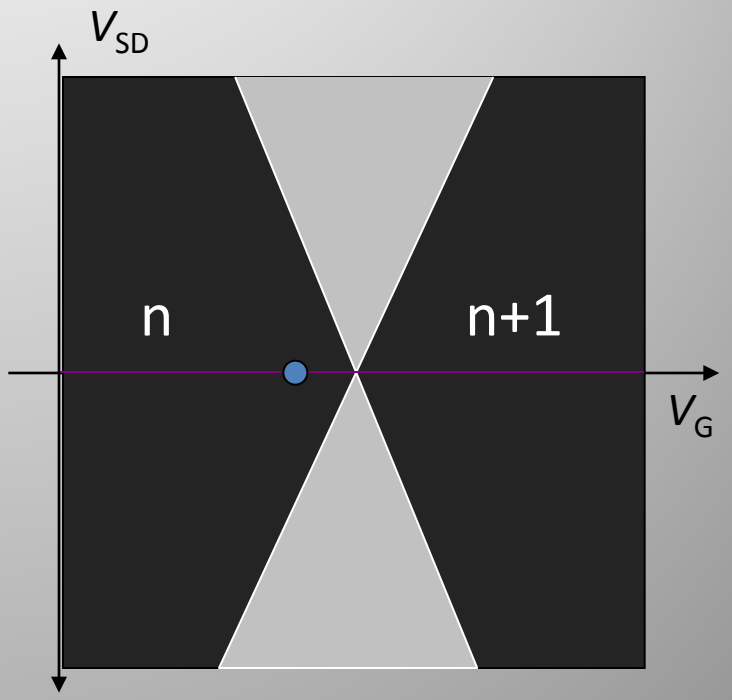


Kouwenhoven *et al.*, Science **278**, 1788 (1997).

Higher order processes

- In 2nd order, can have *virtual transitions.*
- Virtual state violates energy conservation….





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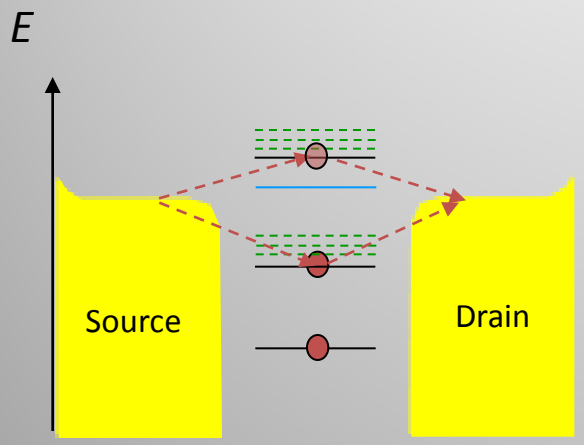
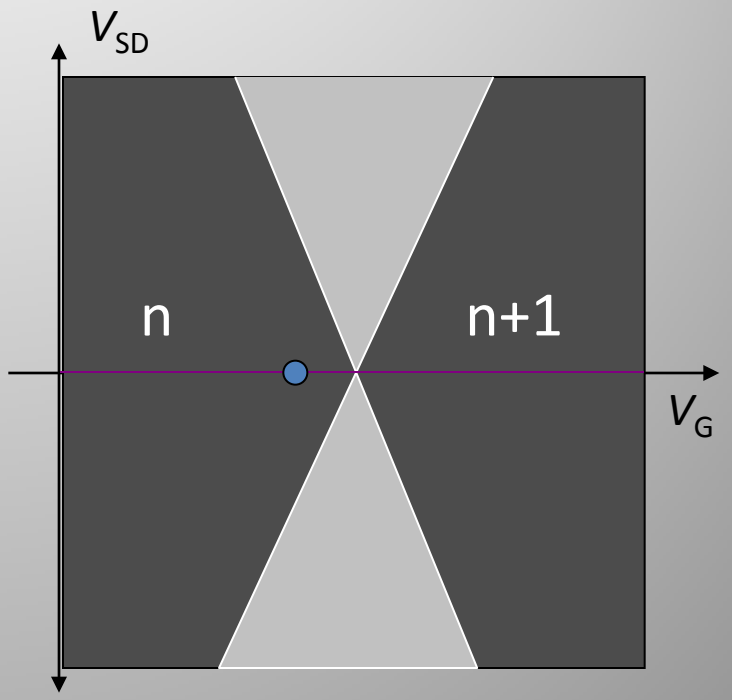


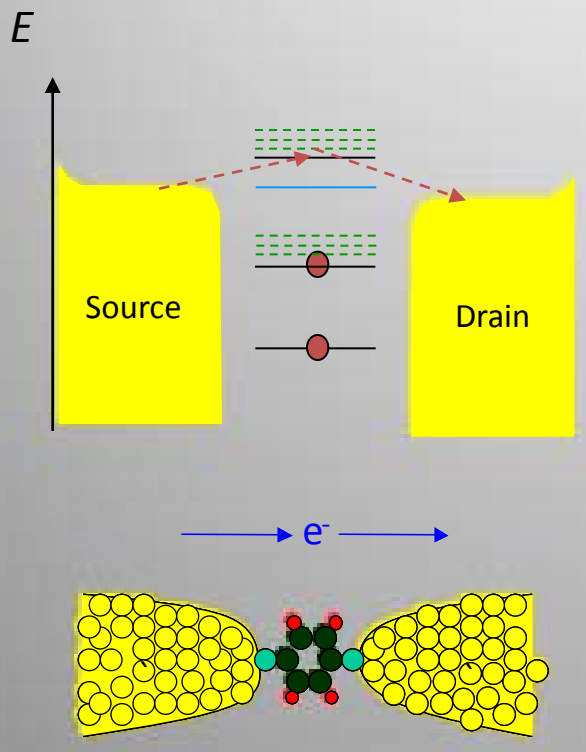


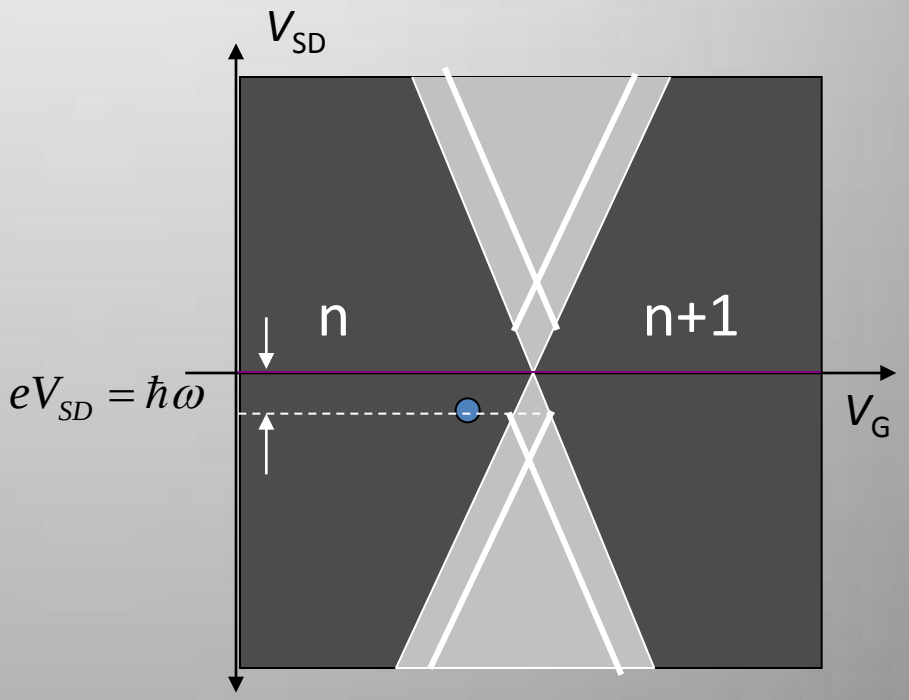
- Nonzero conduction in “blockade”.
- Physicist: “Elastic cotunneling”
- Chemist: “superexchange”
- This is the **off-resonant** tunneling routinely seen in, *e.g.*, alkyl SAMs.

M. A. Ratner, J. Phys. Chem. **94**, 4877-4883 (1990)

Inelastic cotunneling

- Can also have *virtual transitions* that leave system excited….





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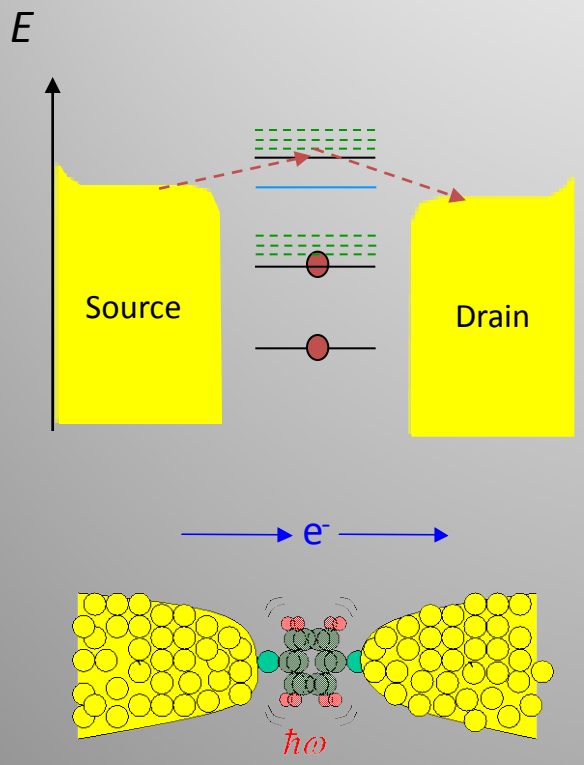
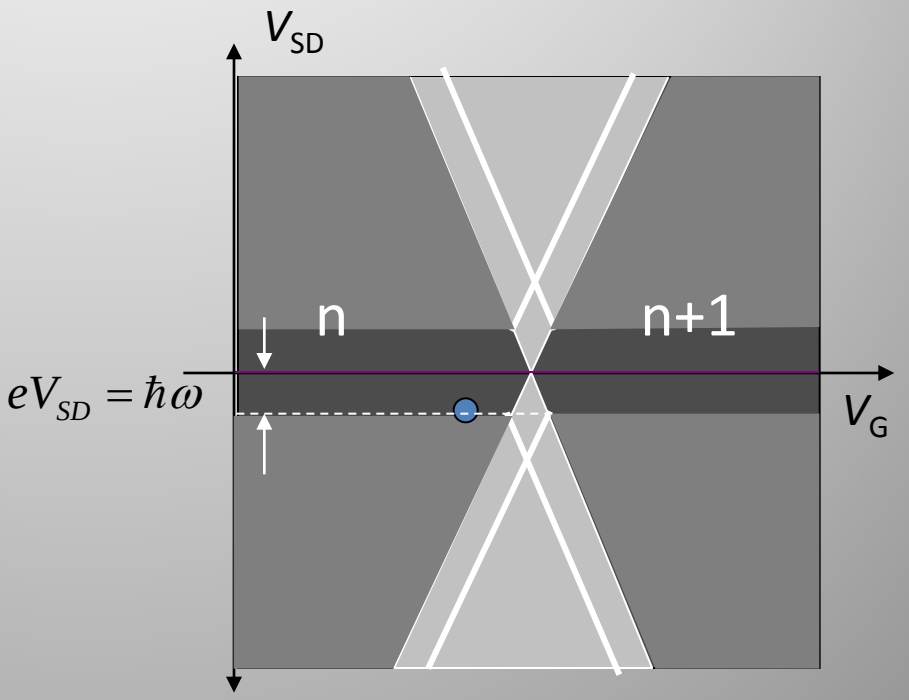
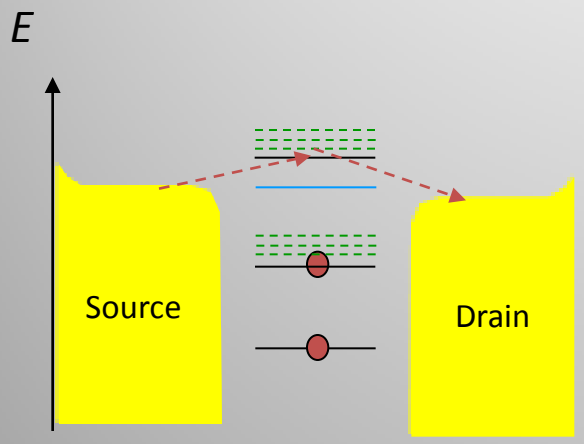
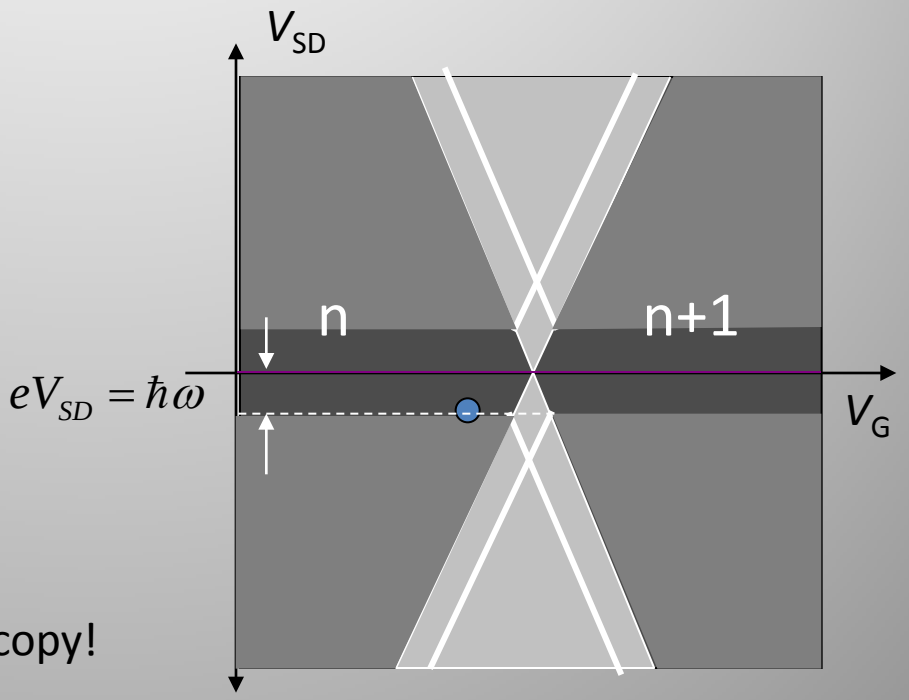




Inelastic cotunneling

- Can also have *virtual transitions* that leave molecule excited….





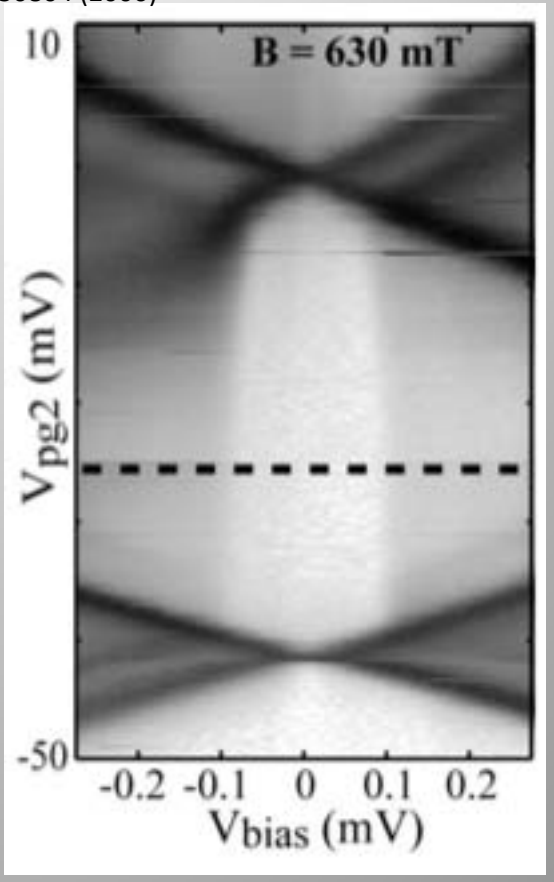
- SET person: “inelastic cotunneling”
- Inelastic Electron Tunneling Spectroscopy!
- As shown, peak in 2nd derivative.

Inelastic cotunneling – semiconductor dot

Sigrist *et al.*, PRL **96**, 036804 (2006)

GaAs dot embedded in an interferometer (!).

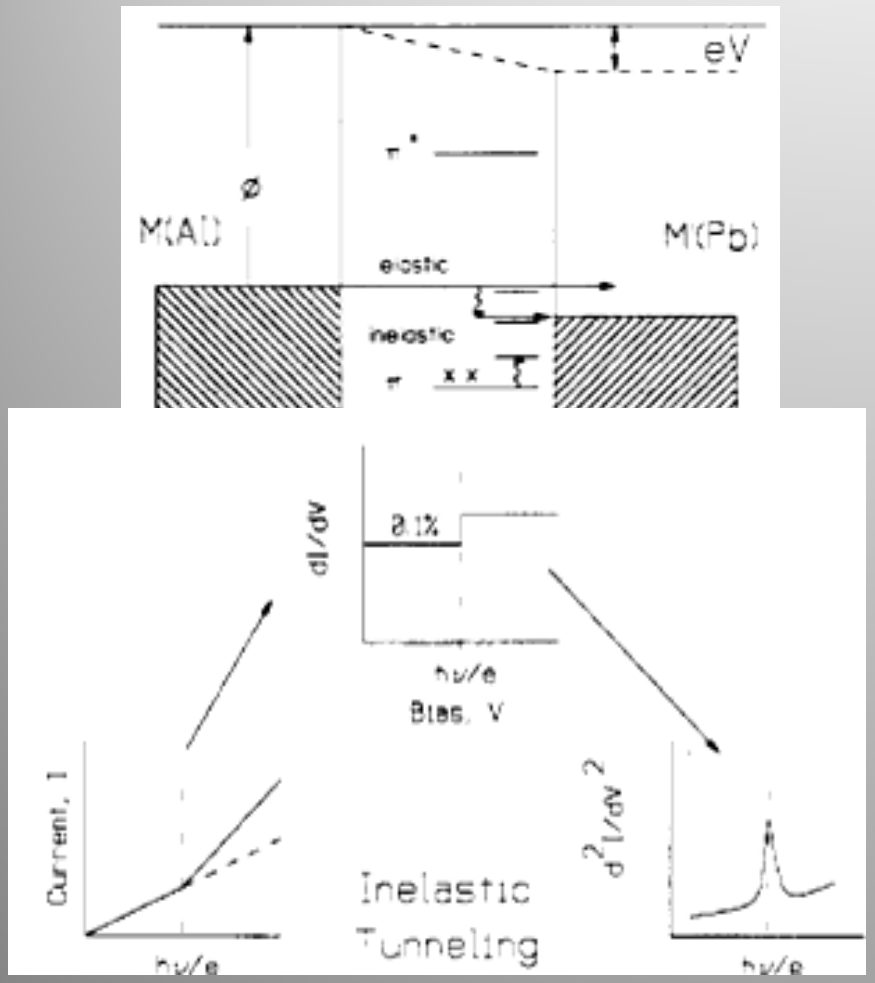
Clear step-like discontinuity in conductance in middle of blockaded regime.



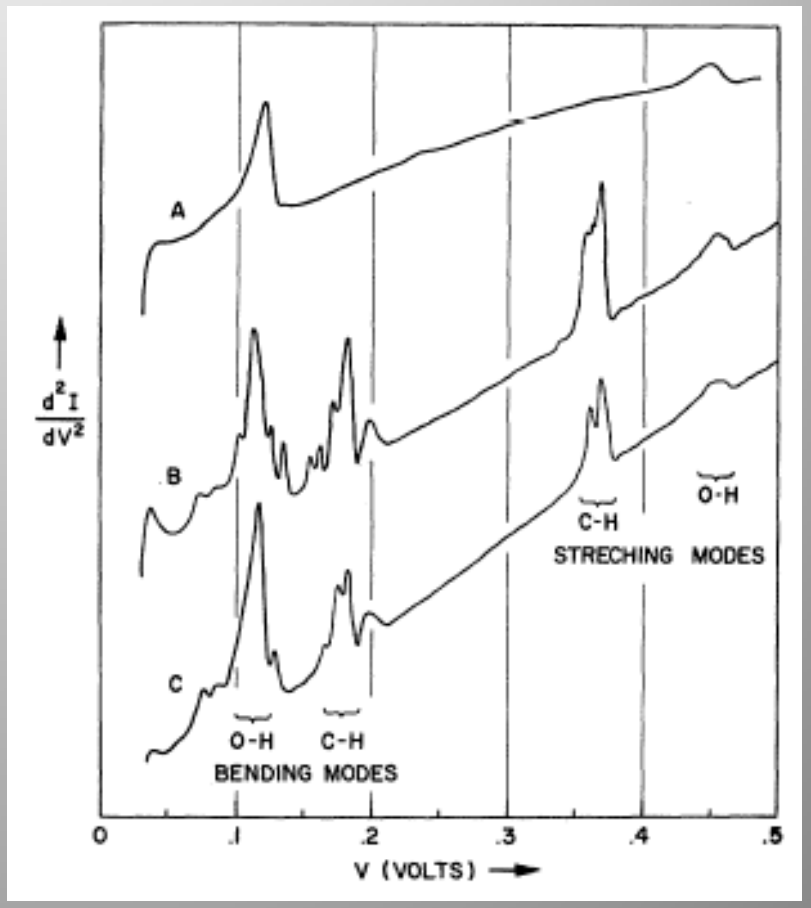
Coherence of the inelastic cotunneling process demonstrated by looking at interference fringes (source-drain conductance vs. external magnetic field while in inelastic cotunneling-dominated regime).

Inelastic electron tunneling spectroscopy (IETS)

- Discovered in 1966: tunneling electrons can vibrationally excite molecules embedded in a tunnel barrier.



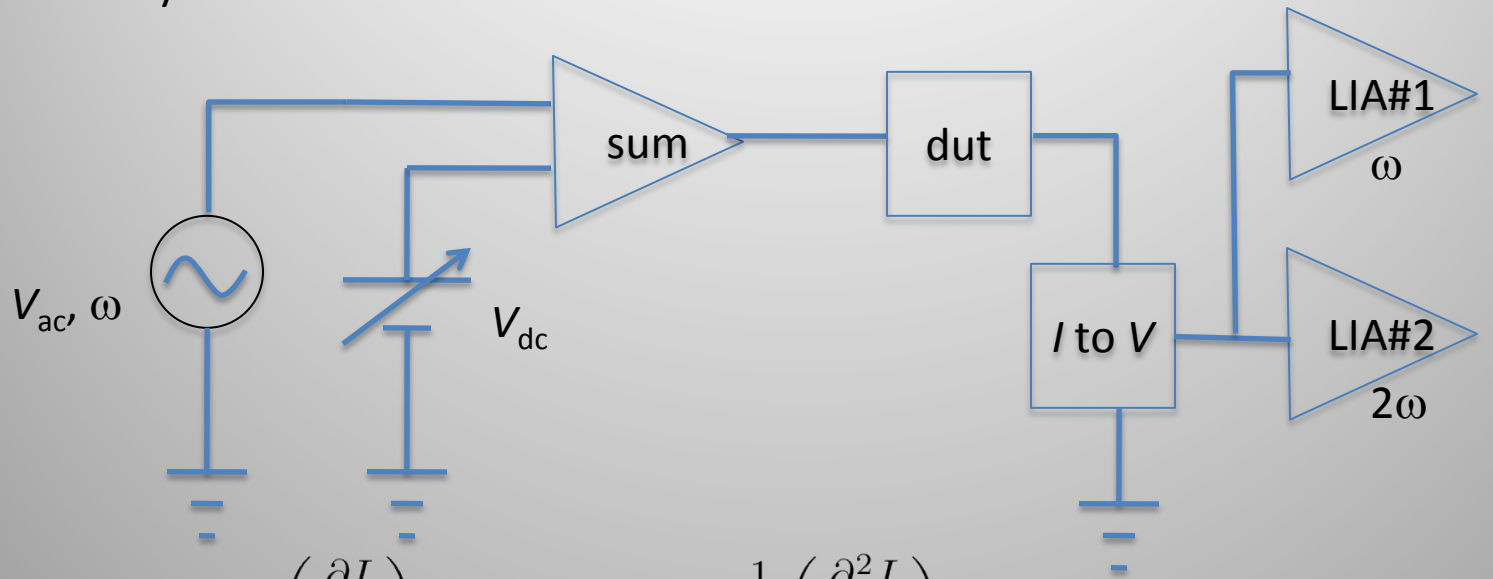
Hipps, J. Chem. Phys. **97**, 7803 (1997).



Jaklevic and Lambe, PRL **17**, 1139 (1966).

Inelastic electron tunneling spectroscopy (IETS)

How do you measure IETS?



$$I(V) = I_0(V_{\mathrm{dc}}) + \left(\frac{\partial I}{\partial V}\right)_{V_{\mathrm{dc}}} V_{\mathrm{ac}}\cos(\omega t) + \frac{1}{2}\left(\frac{\partial^2 I}{\partial V^2}\right)_{V_{\mathrm{dc}}} (V_{\mathrm{ac}}\cos(\omega t))^2 + \ldots$$

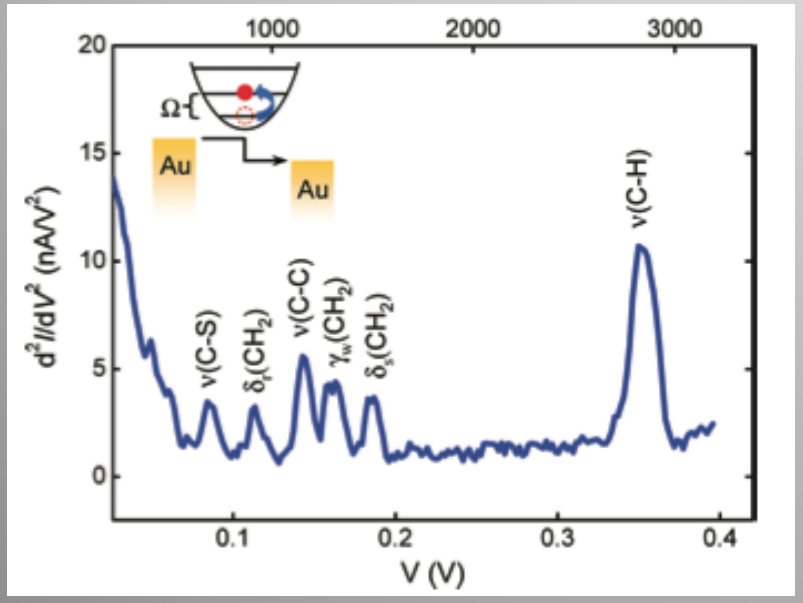
$$= \left[I_0(V_{\mathrm{dc}}) + \frac{1}{4}\left(\frac{\partial^2 I}{\partial V^2}\right)_{V_{\mathrm{dc}}} V_{\mathrm{ac}}^2\right] + \left(\frac{\partial I}{\partial V}\right)_{V_{\mathrm{dc}}} V_{\mathrm{ac}}\cos(\omega t) - \frac{1}{4}\left(\frac{\partial^2 I}{\partial V^2}\right)_{V_{\mathrm{dc}}} V_{\mathrm{ac}}^2\cos(2\omega t) + \ldots$$

Lock-in amplifier set at 2w can be used to measure IETS signal.

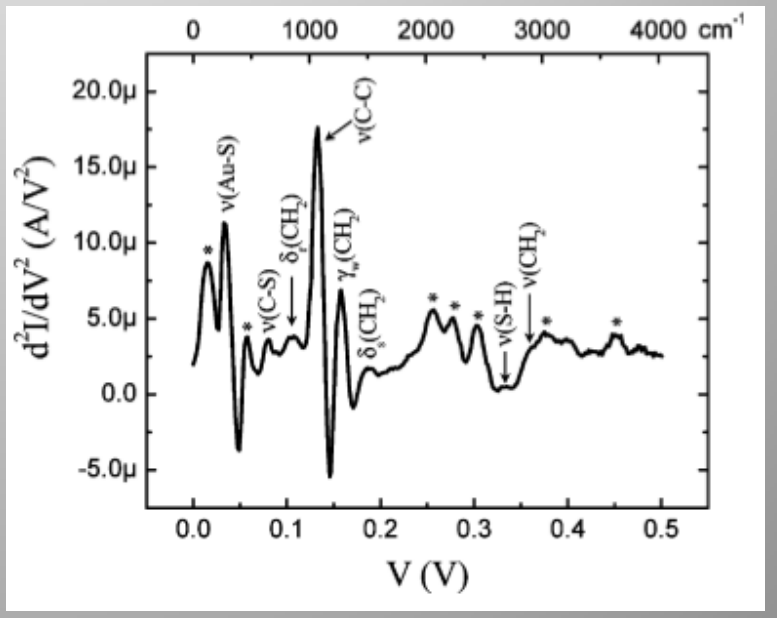
IETS challenges

Challenges:

- Data acquisition can be slow.
- Signals generally weak….
- Most big vibrational features at quite high energies.
- Broadening of lines is significant (~ 5.4 $k_B T$, + 1.22 V_{ac}).
- Line shapes can be distorted.



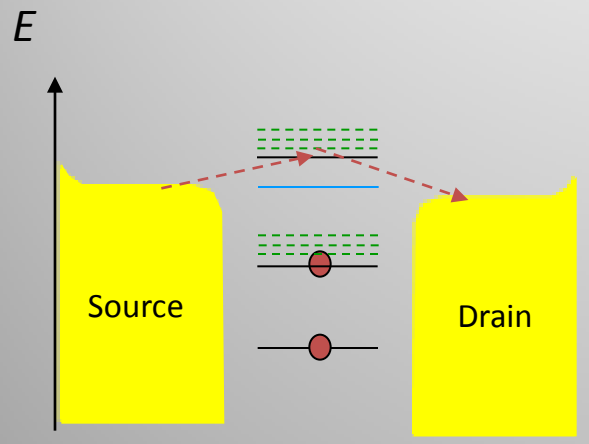
Song *et al*., J. Phys. Chem. *C,* **114**, 20431 (2010)

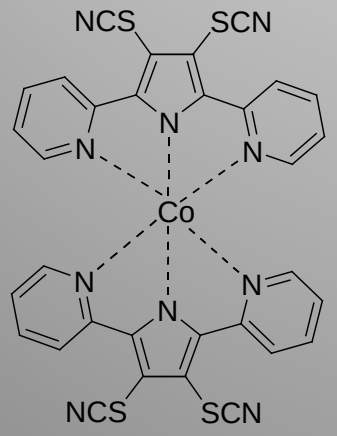


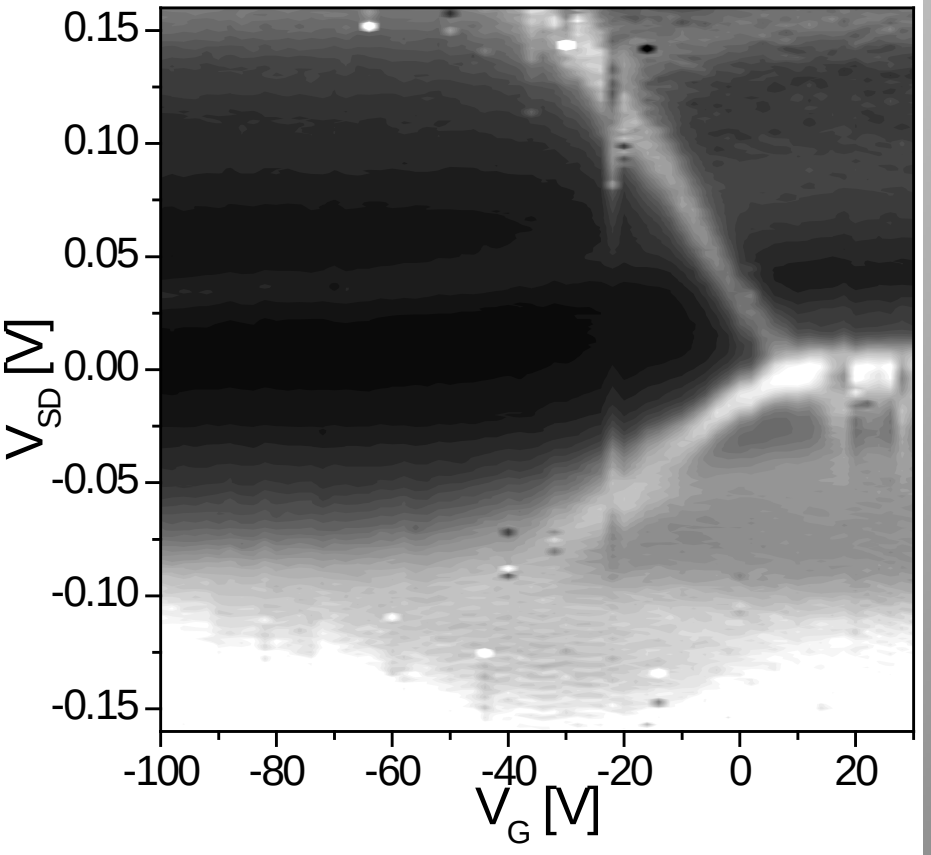
Wang *et al*., Nano Lett. **4**, 643 (2004)

IETS in SMTs?

- Definitely see features in the blockaded regime that look like inelastic cotunneling.







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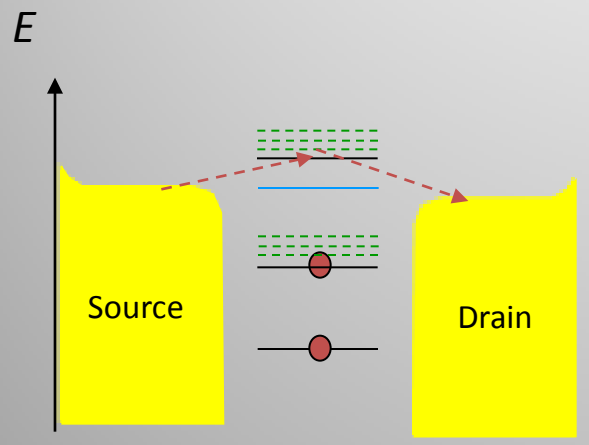
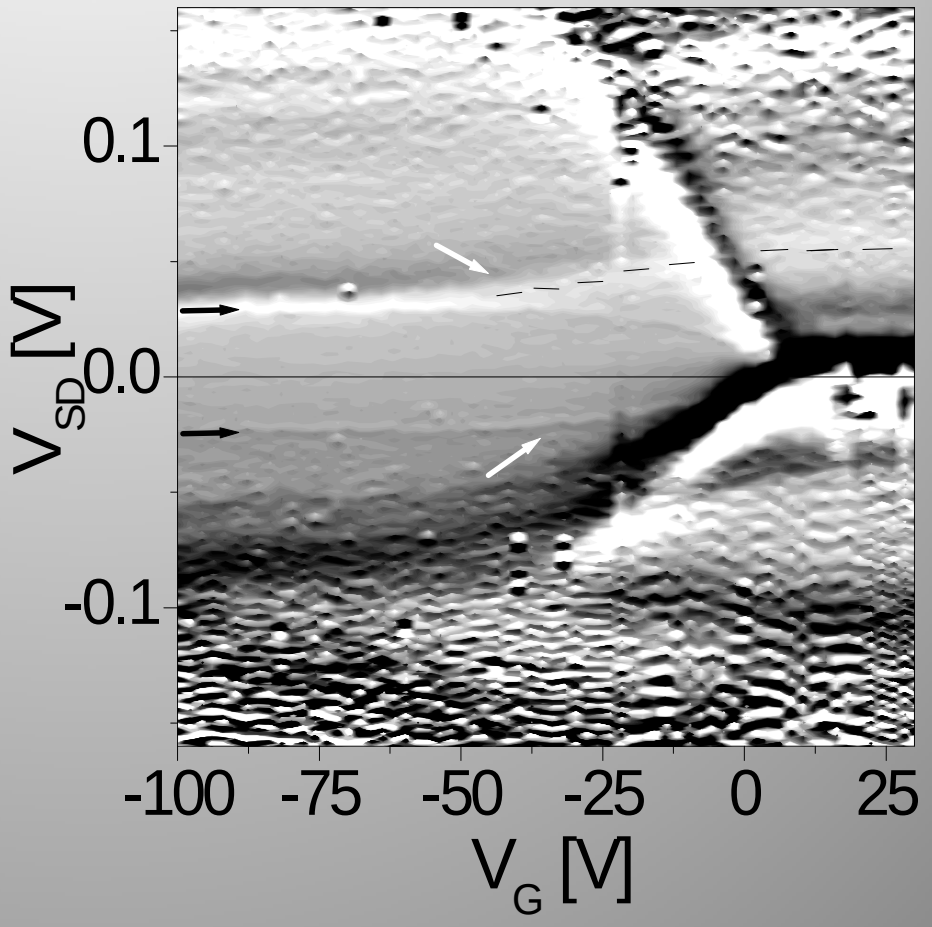


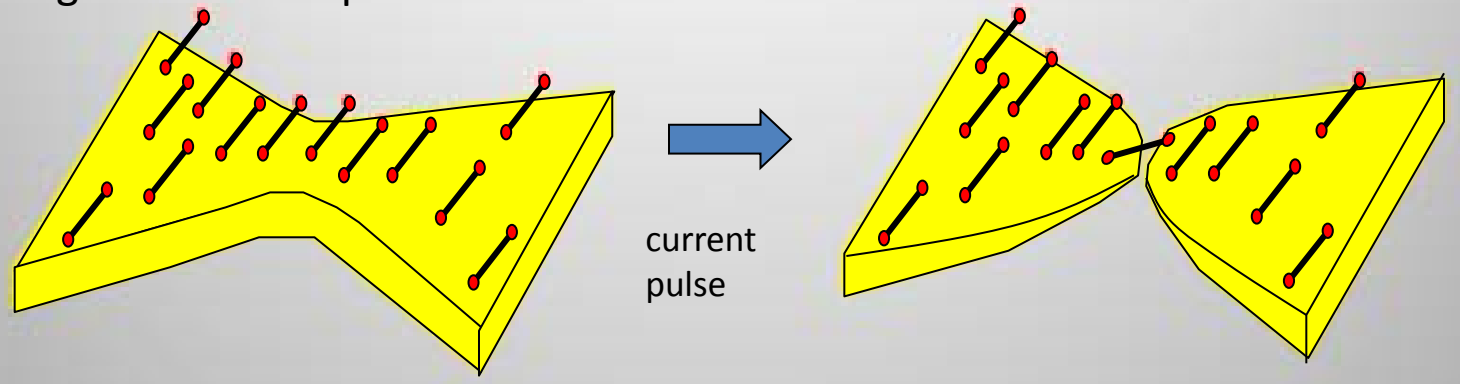


- Energies are far too low to be electronic excitations.
- Lineshapes aren't simple, and lines shift near electronic levels!

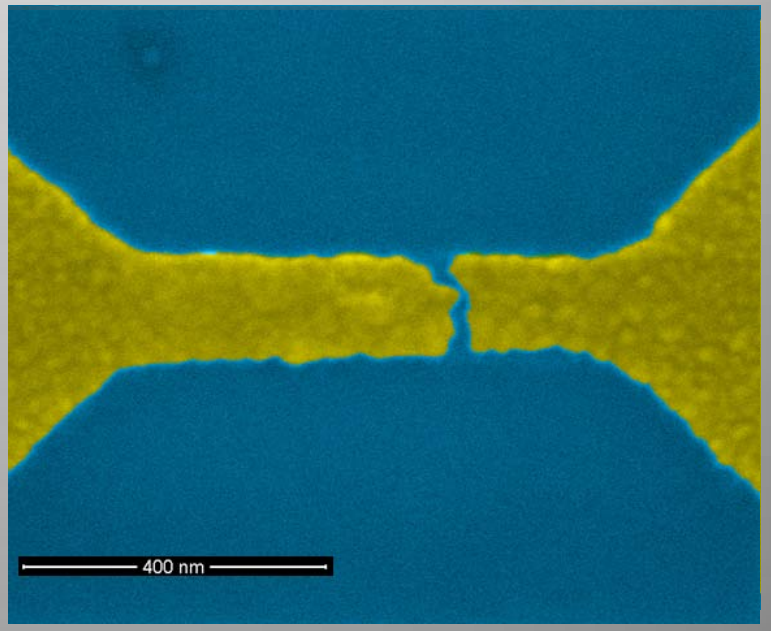
How we make single-molecule devices

Electromigration technique

Park *et al.*, *APL* **75**, 301 (1999)



- Analogous to STM:
- Conduction dominated by tunneling volume ~ 1 molecule.
- Every device is different!
- Can't "see" what's going on!
- Vibrational fingerprint?



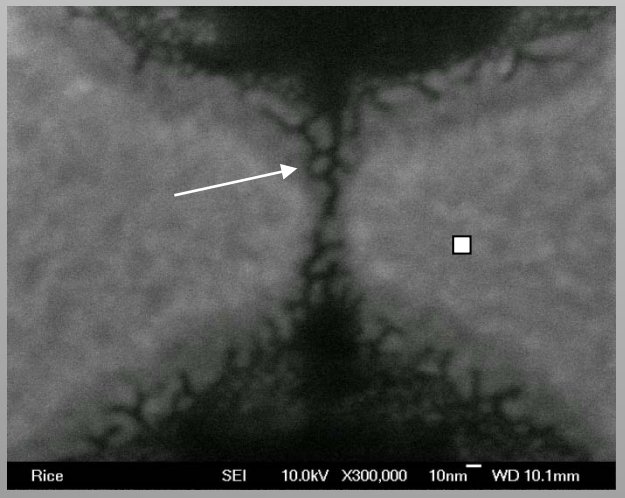
How do you know what you have?

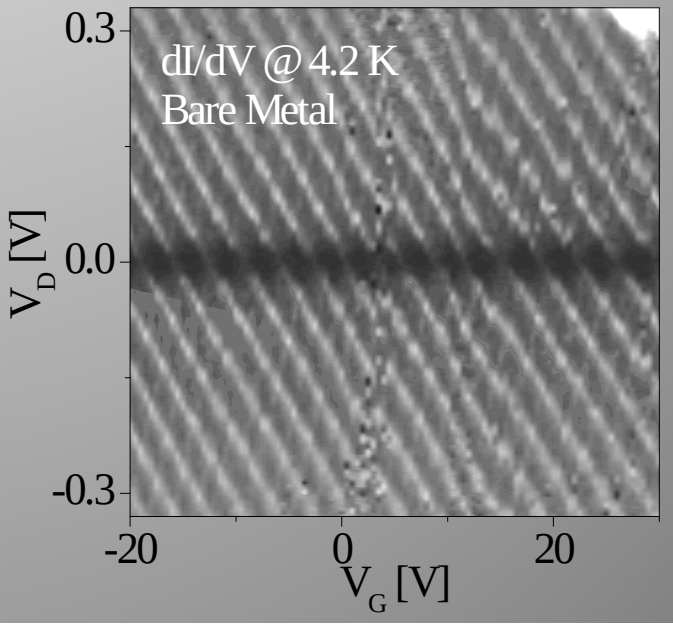
Tunneling conductances depend exponentially on geometry….

Statistical approach and systematic characterization are essential!

- Effects only present in samples *with* molecules?
- Charging energy and charge states sensible?
- Molecule-specific features?
- Optical measurements! (***new!***)

Example of a potential pitfall: metal blob from breaking process.

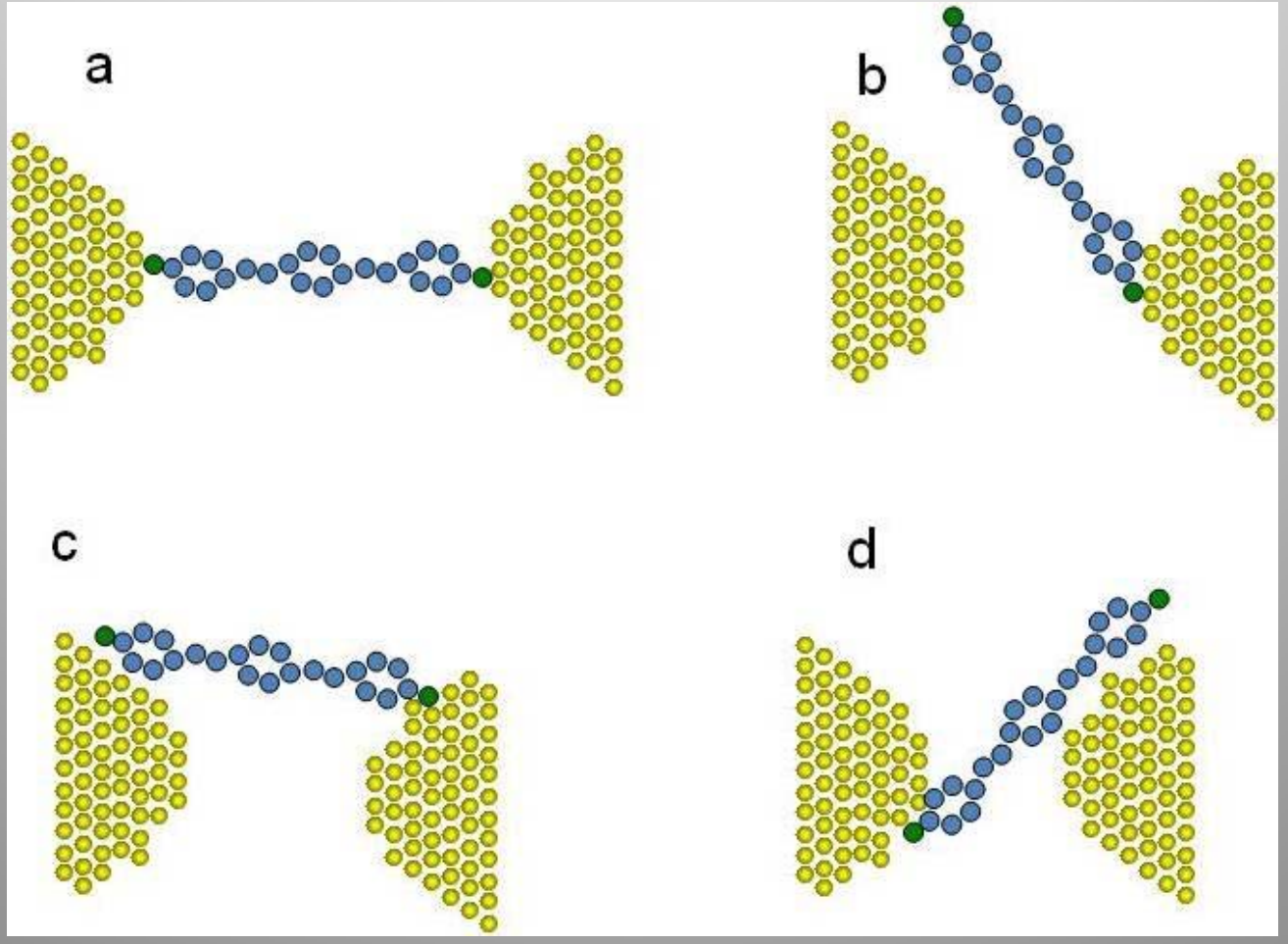




How do you know what you have?

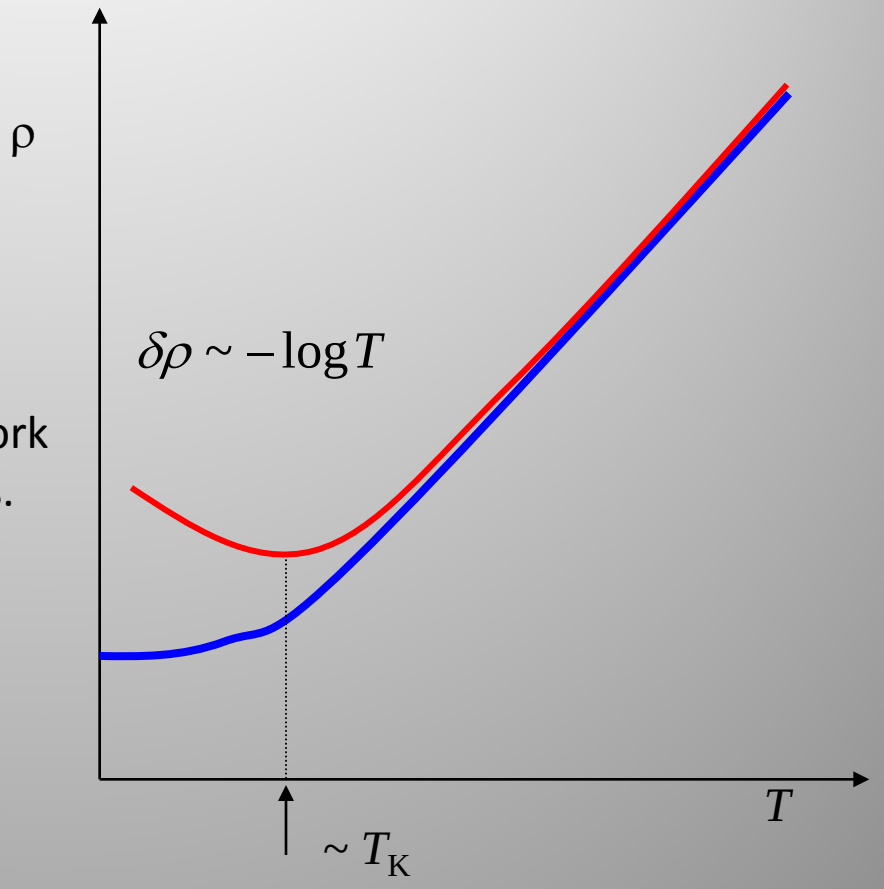
Many junction configurations are possible!

In general, in electromigrated junctions, we ***don't*** have the idealized situation.



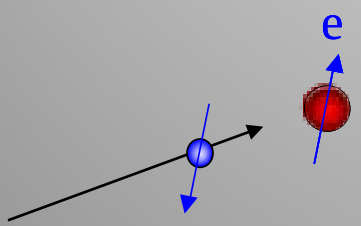
The Kondo effect

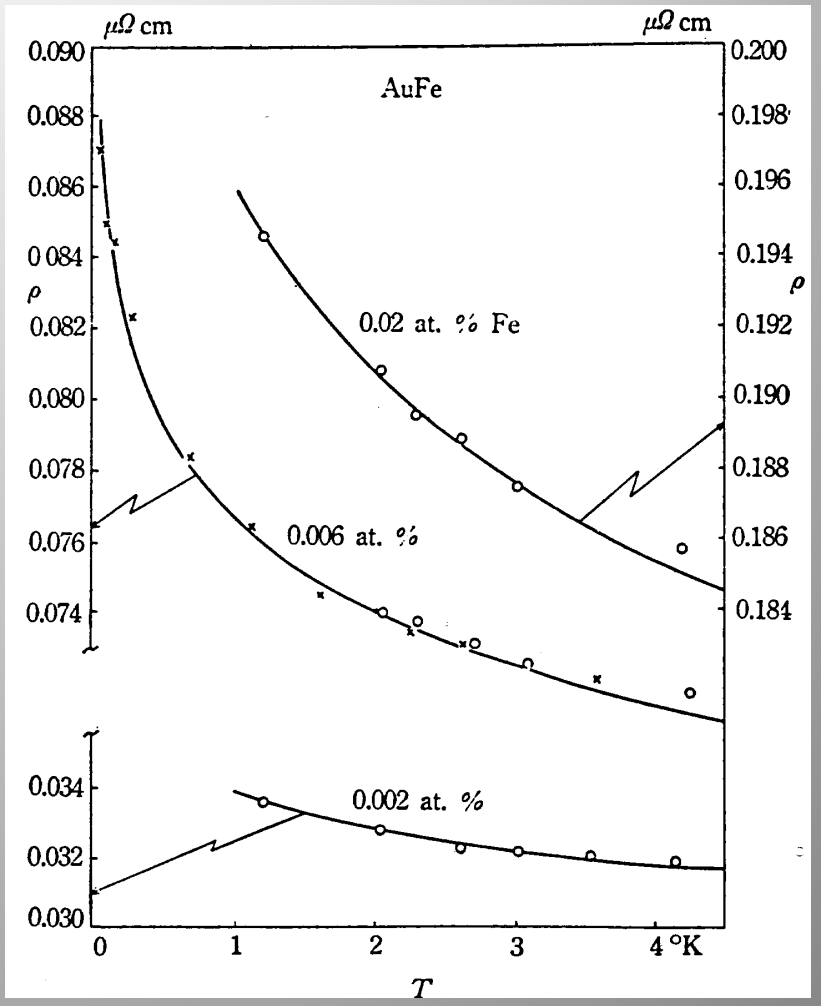
- "Standard model" of normal metals: resistivity to *decrease* as *T* decreases.
- Resistivity saturates at low *T* as phonons freeze out.
- Discovered in 1930s that this doesn't work for metals with dilute magnetic impurities.
- Minimum in resistivity at material-dependent temperature scale.



The Kondo effect

- Perturbative treatment by Kondo (1964).
- Spin-flip scattering leads to *antiferromagnetic exchange* between local spin and conduction electrons.
- Enhanced scattering = increased ρ
- Characteristic temperature scale T_K





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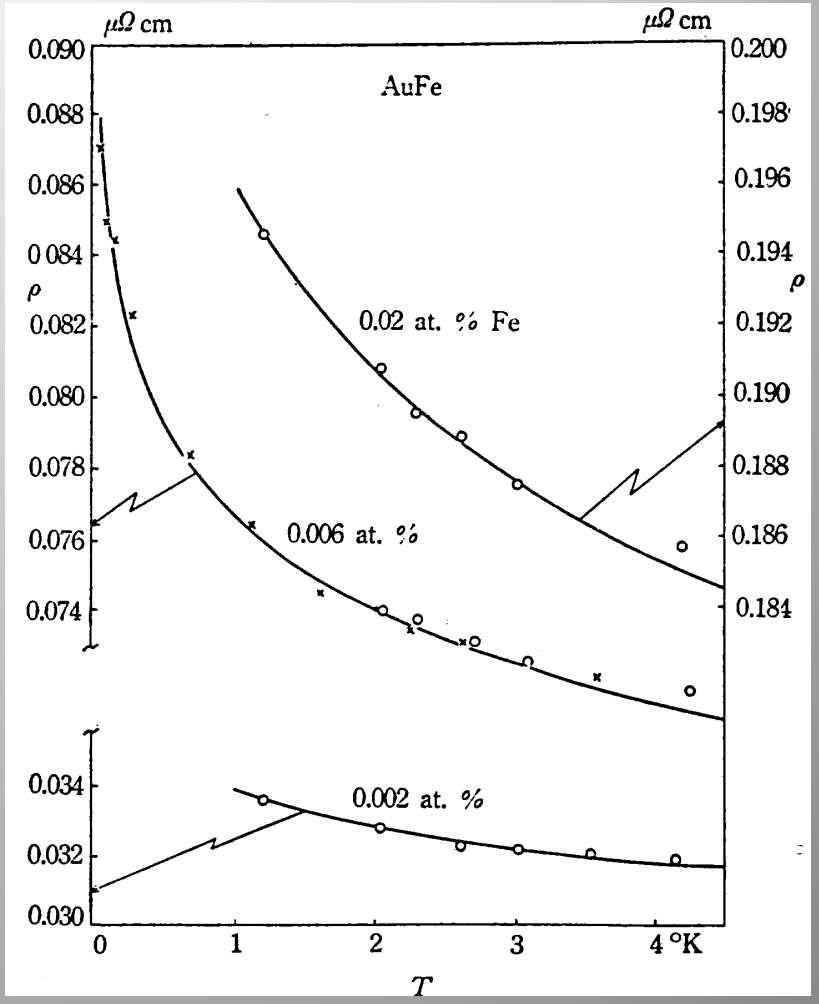
virtual state



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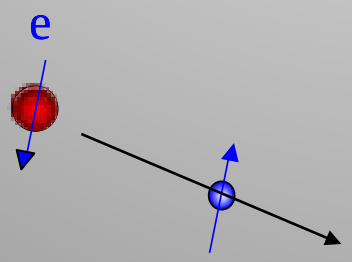

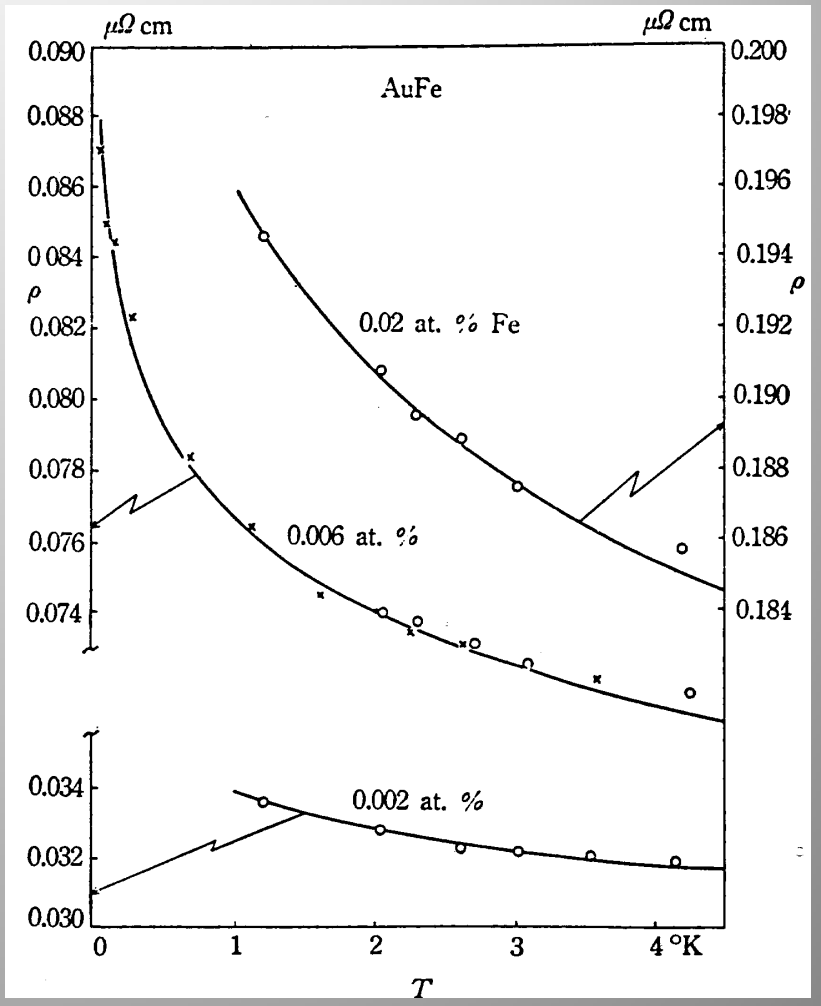

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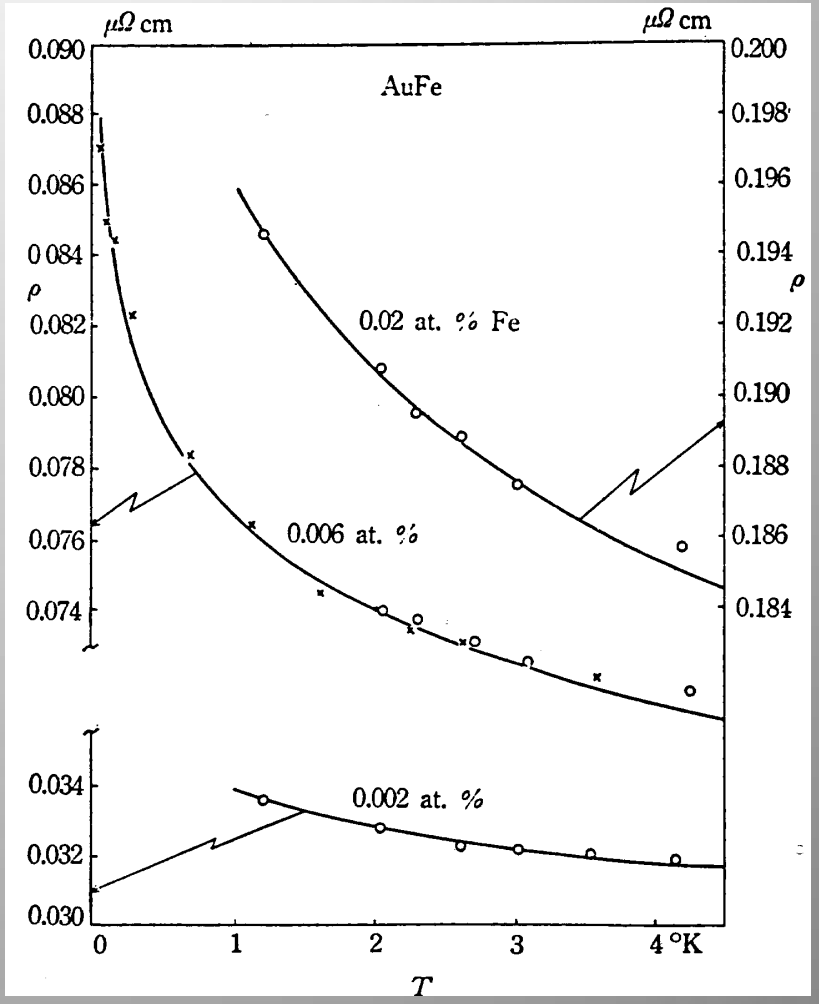
- Ground state: many-body singlet

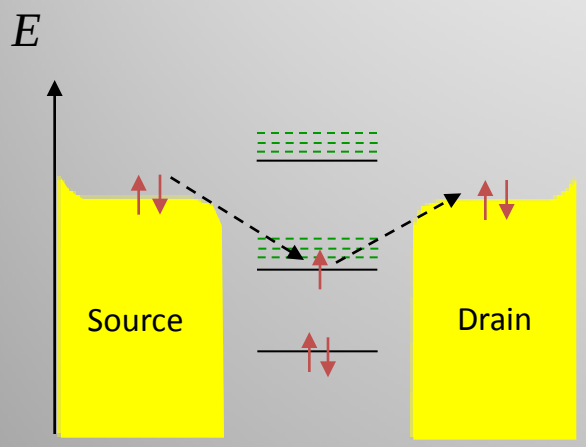
$$\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right)$$

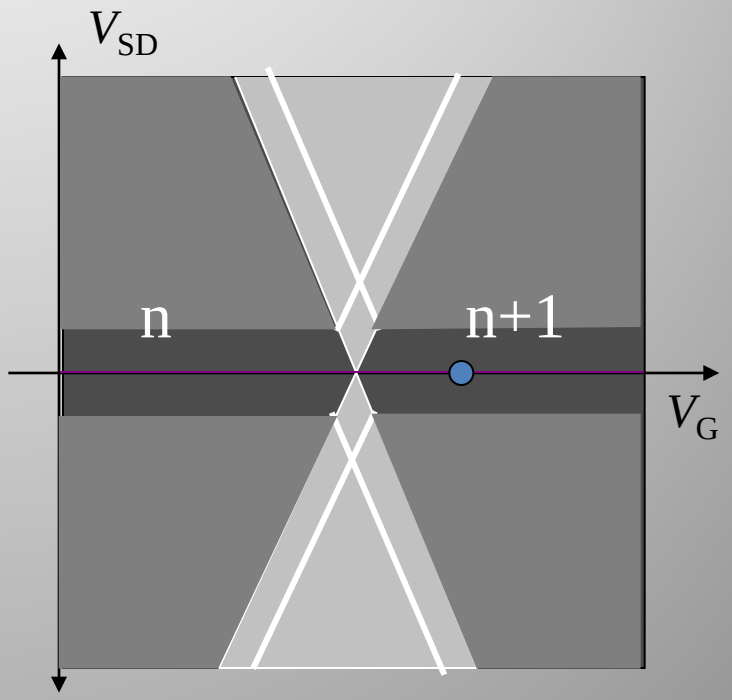
- $T << T_K$, ρ becomes constant.



Kondo in single-electron devices

Kondo leads to prominent features in differential conductance.





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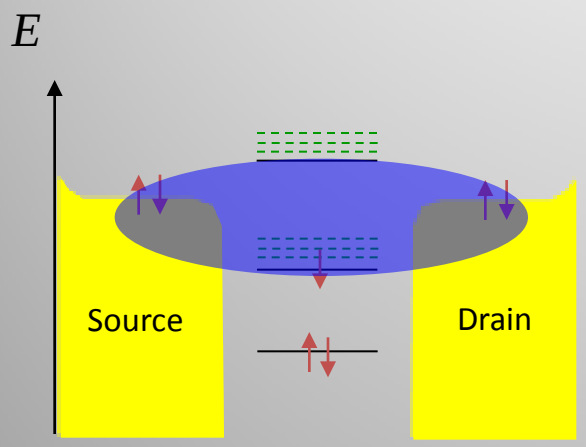
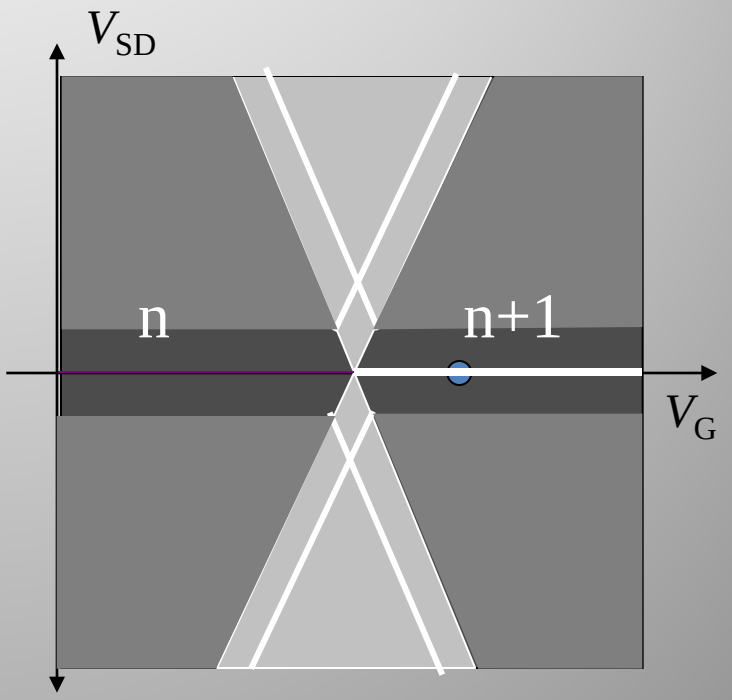




- Result is many-body Kondo state.
- In this case, ***forward*** scattering.

- At $T = 0$, unpaired spin is screened; ***resonant conduction*** maximized.

Kondo physics – terminology

Γ = width of localized level, due to coupling with leads.

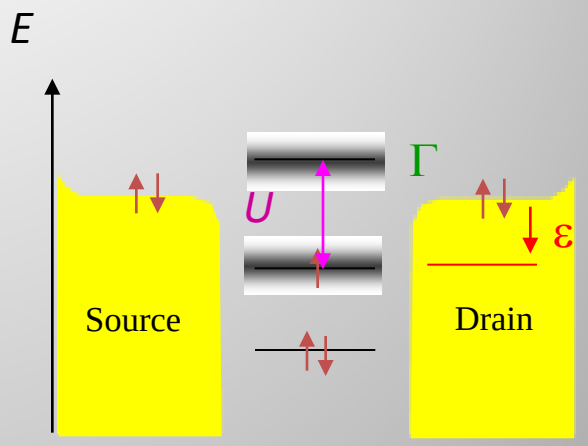
- In SMT, fixed by geometry.
- In semiconductor dot, tunable.
- Width of Coulomb deg. point at $T = 0$ sets Γ in units of gate voltage.

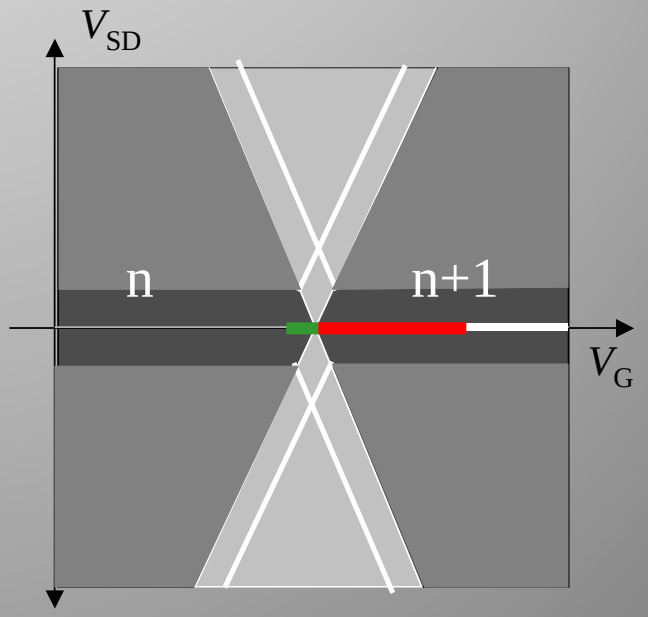
ε = difference between localized level and Fermi energy of leads.

- In SMT and semiconductor dots, **tuned** by gate voltage.

U = on-site repulsion, E_c

$$T_K \sim \frac{\sqrt{\Gamma E_c}}{2} \exp\left(\frac{-\varepsilon(E_c - \varepsilon)}{\Gamma E_c}\right)$$





Kondo regime

- Enhanced density of states at Fermi level of leads.
- Peak in conductance near zero bias

Two ways of extracting T_K:

$$G(T) - G_b = \frac{2e^2}{h}\frac{(4\Gamma_S\Gamma_D)}{(\Gamma_S+\Gamma_D)^2} f(T/T_K)$$

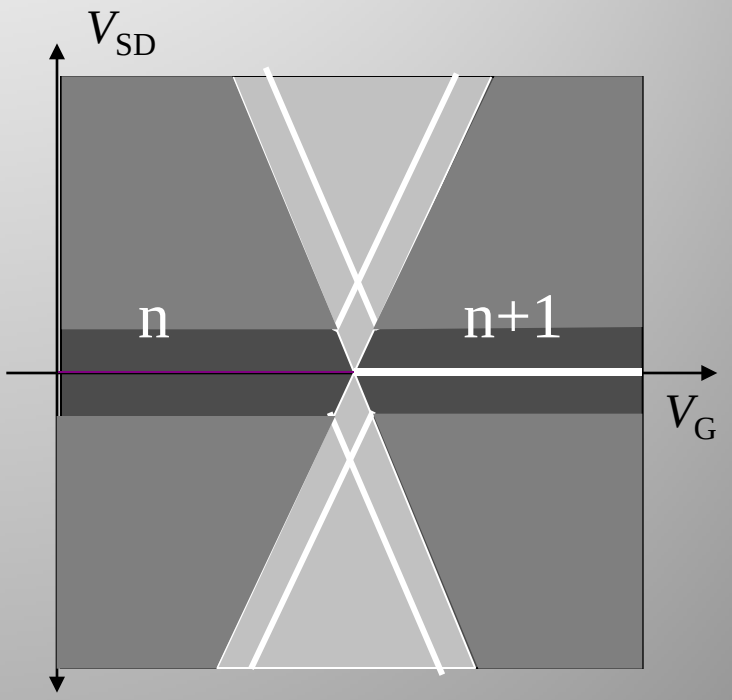
$$f(T/T_K) = (1 + (2^{1/s} - 1)(T/T_K)^2)^{-s}$$

$$s \approx 0.22$$

$$@\ T = T_K, f = 1/2.$$

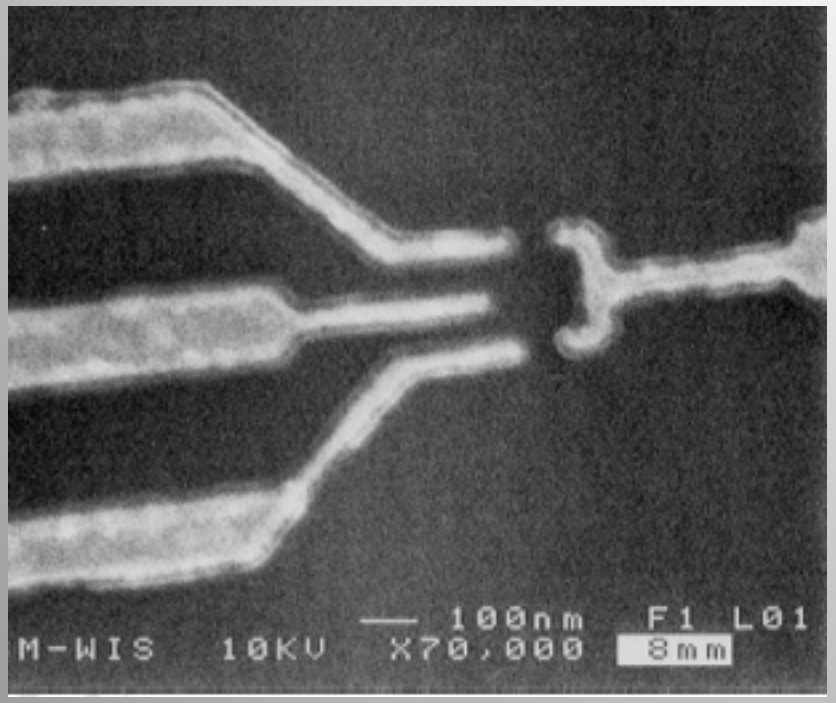
Zero bias resonance FWHM proportional to $k_B T_K / e$ for $T << T_K$.

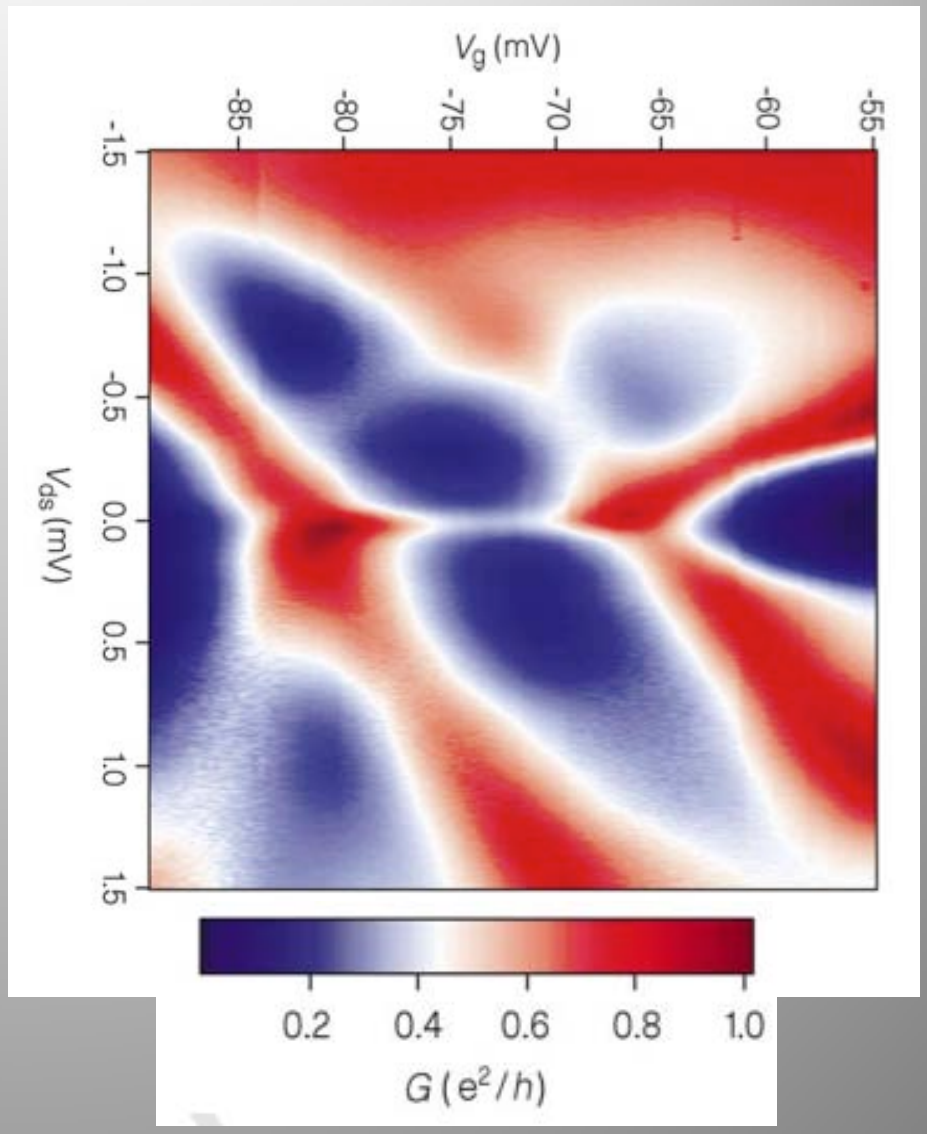
$$\text{fwhm} = \frac{2}{e}\sqrt{(\pi k_B T)^2 + 2(k_B T_K)^2}$$



Maximum G-$G_b = 2e^2/h$ for perfectly symmetric coupling to leads.

Kondo example: GaAs dot





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

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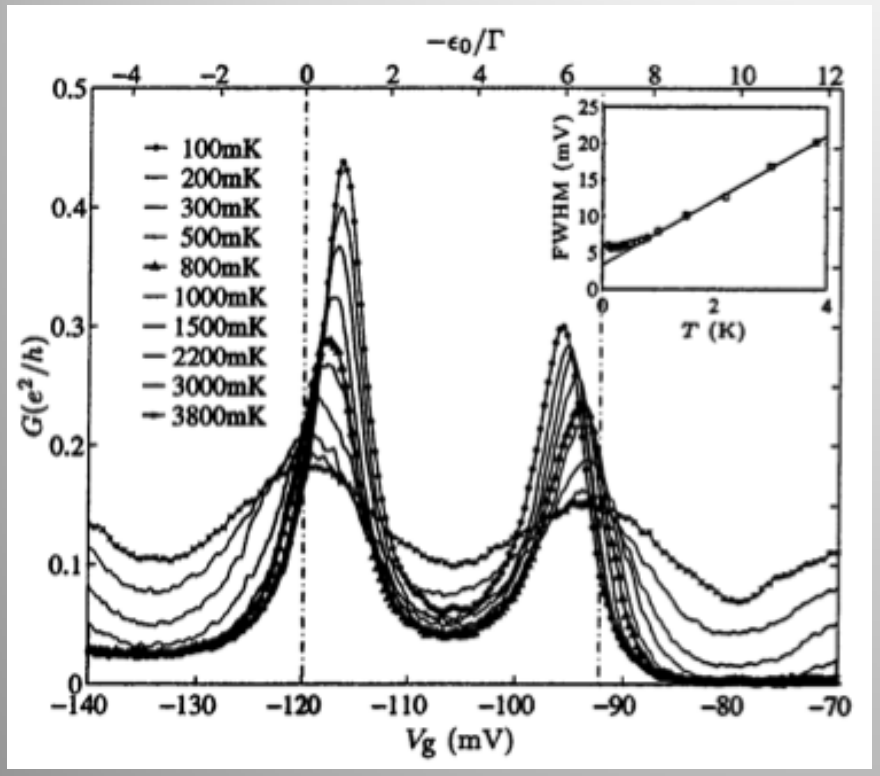
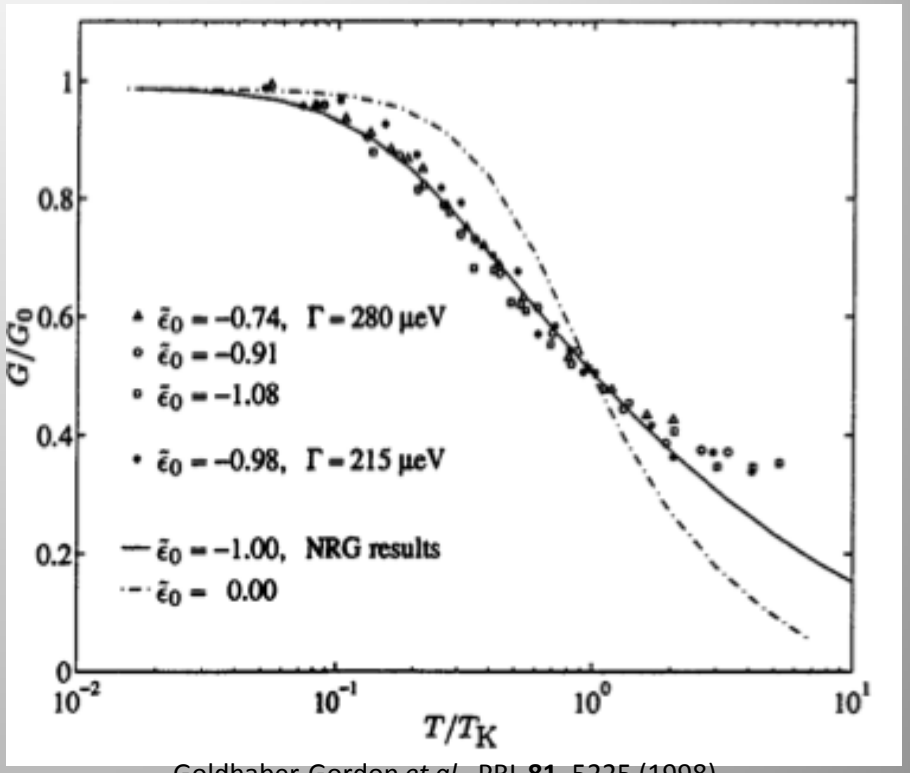




Goldhaber-Gordon *et al.*, PRL **81**, 5225 (1998)

Can infer T_K from T dependence of zero-bias conductance.

Must be careful, because there can be background conductance unrelated to Kondo physics.

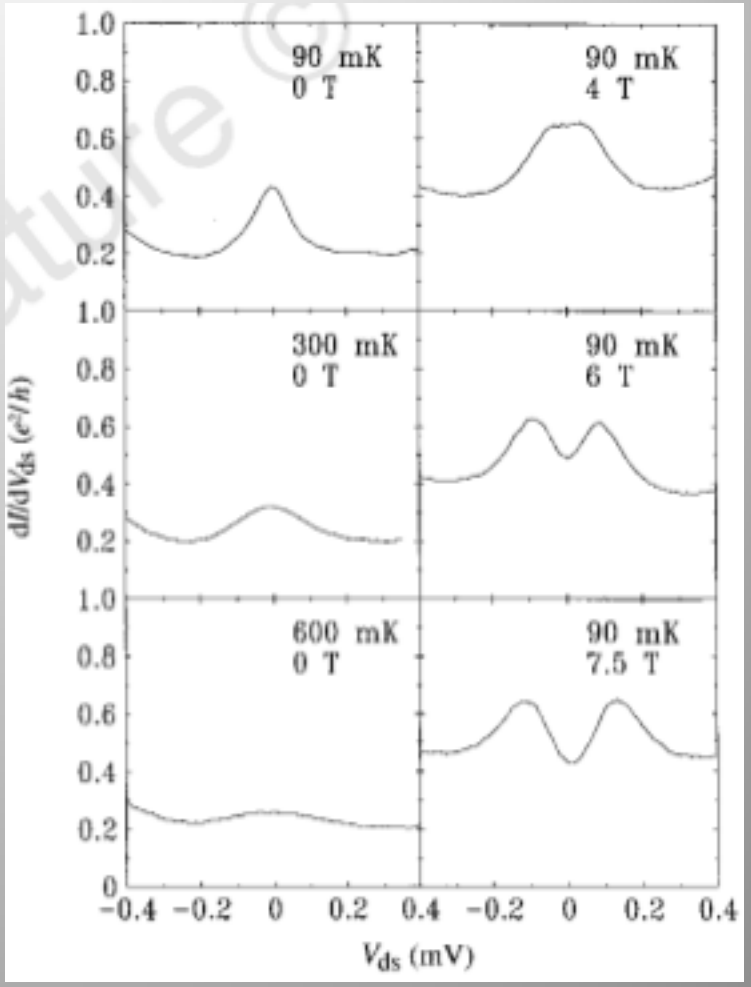
Kondo example: GaAs dot

Finite-bias data contain more information than just the zero-bias conductance.

Challenge: In general, finite bias situation is complicated, nonequilibrium problem.

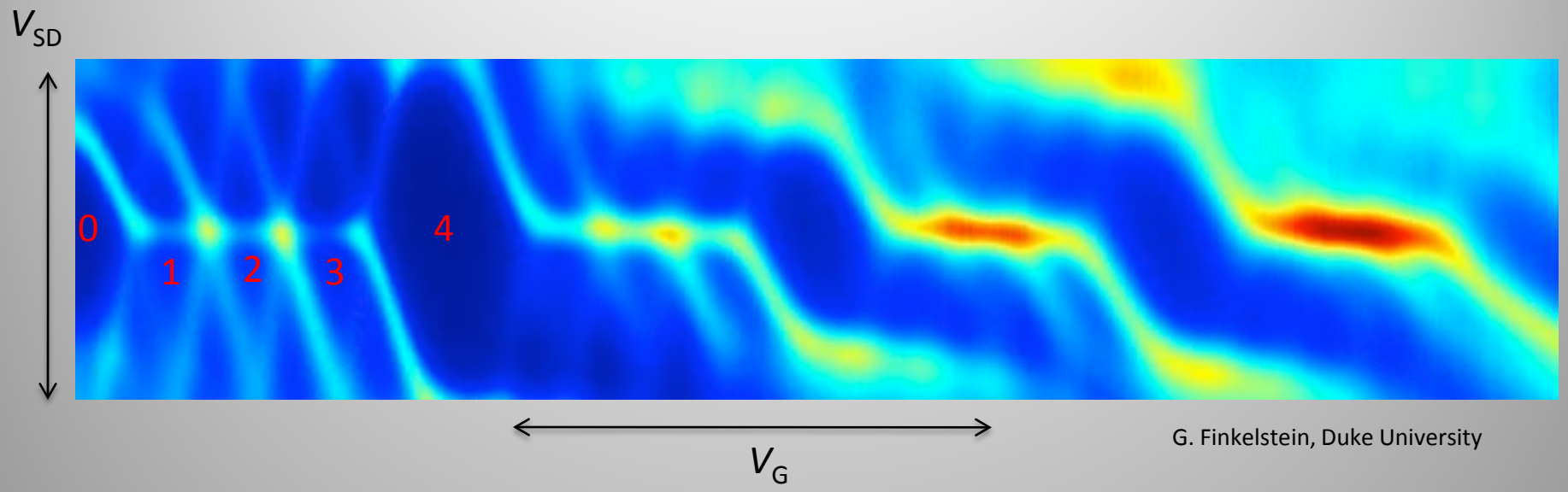
Interpretation is sometimes simple. e.g., Zeeman effect.

Applied (in-plane) magnetic field suppresses Kondo at zero-bias, splits peak by an amount $2g\mu_B B$.



Goldhaber-Gordon *et al.*, PRL **81**, 5225 (1998)

Kondo example: Carbon nanotube

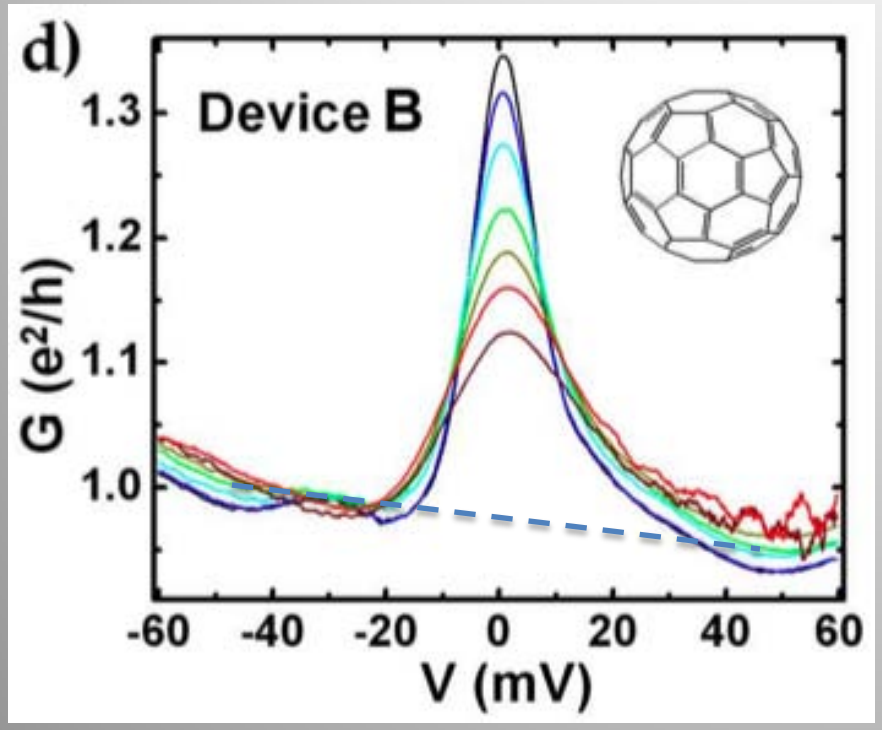


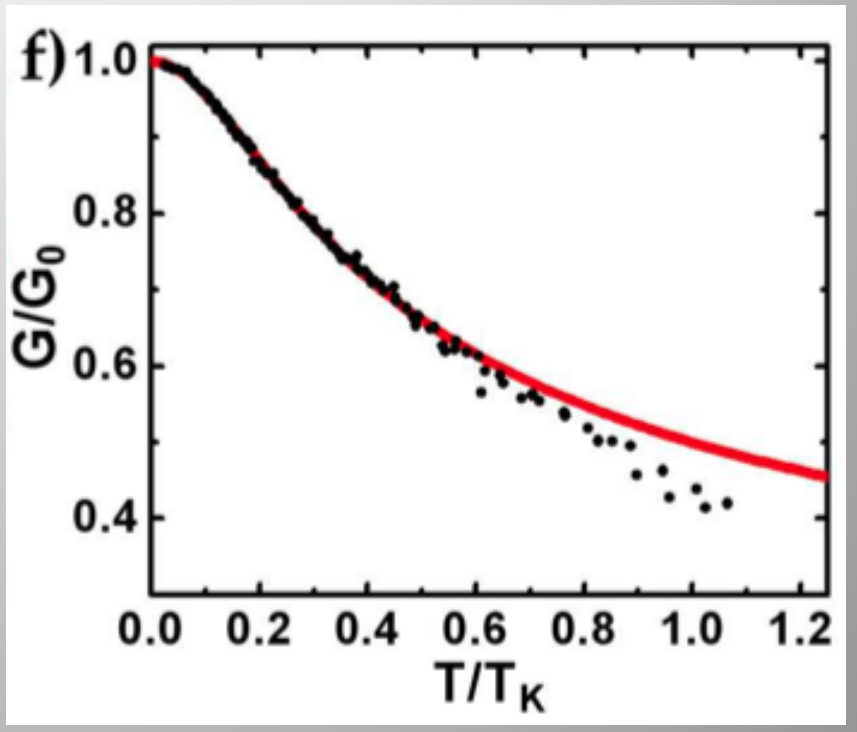
G. Finkelstein, Duke University

Carbon nanotube case is different.

- "Shells" w/ each hold four electrons (two degenerate K points in nanotube band structure, each can accommodate spin-up + spin-down)
- Still have Kondo for two electrons added! SU(4) Kondo

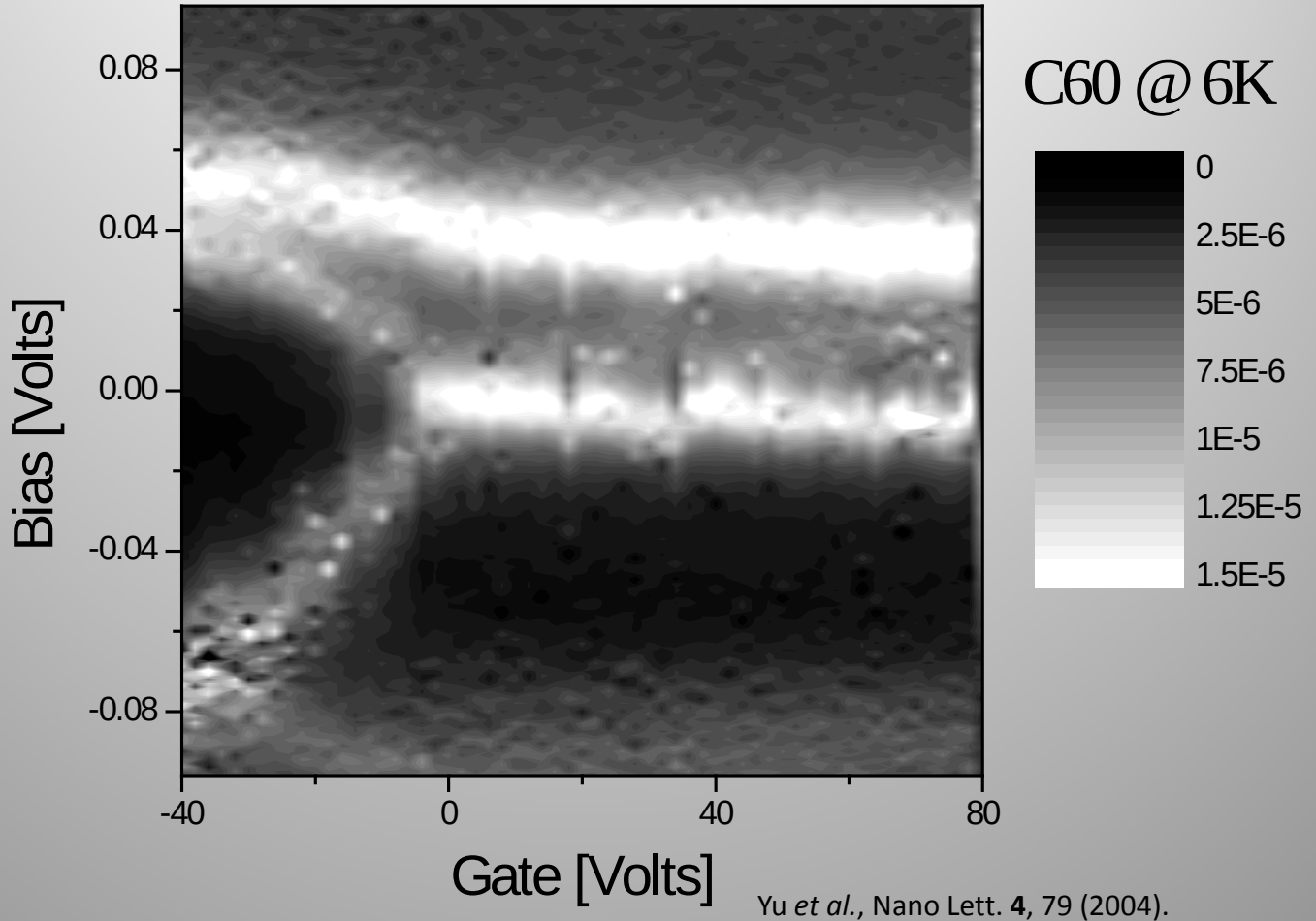
Kondo in SMTs: C_{60}





Scott *et al.*, PRB **79**, 165413 (2009).

Kondo in SMTs: C_{60}

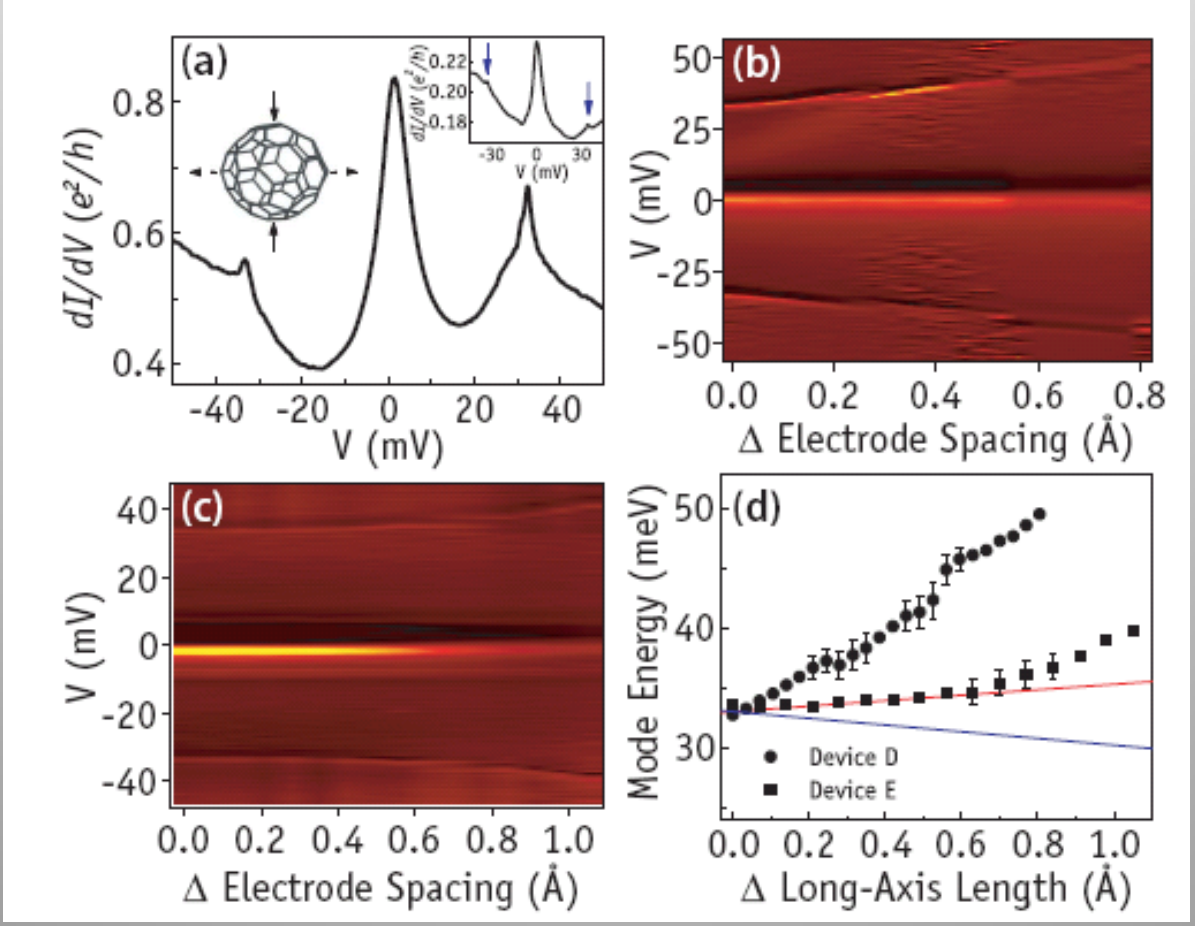


Yu *et al.*, Nano Lett. **4**, 79 (2004).

Kondo resonance combined with ~ 35 meV parallel resonance.

Inelastic tunneling process + Kondo physics.

Kondo in SMTs: C_{60}

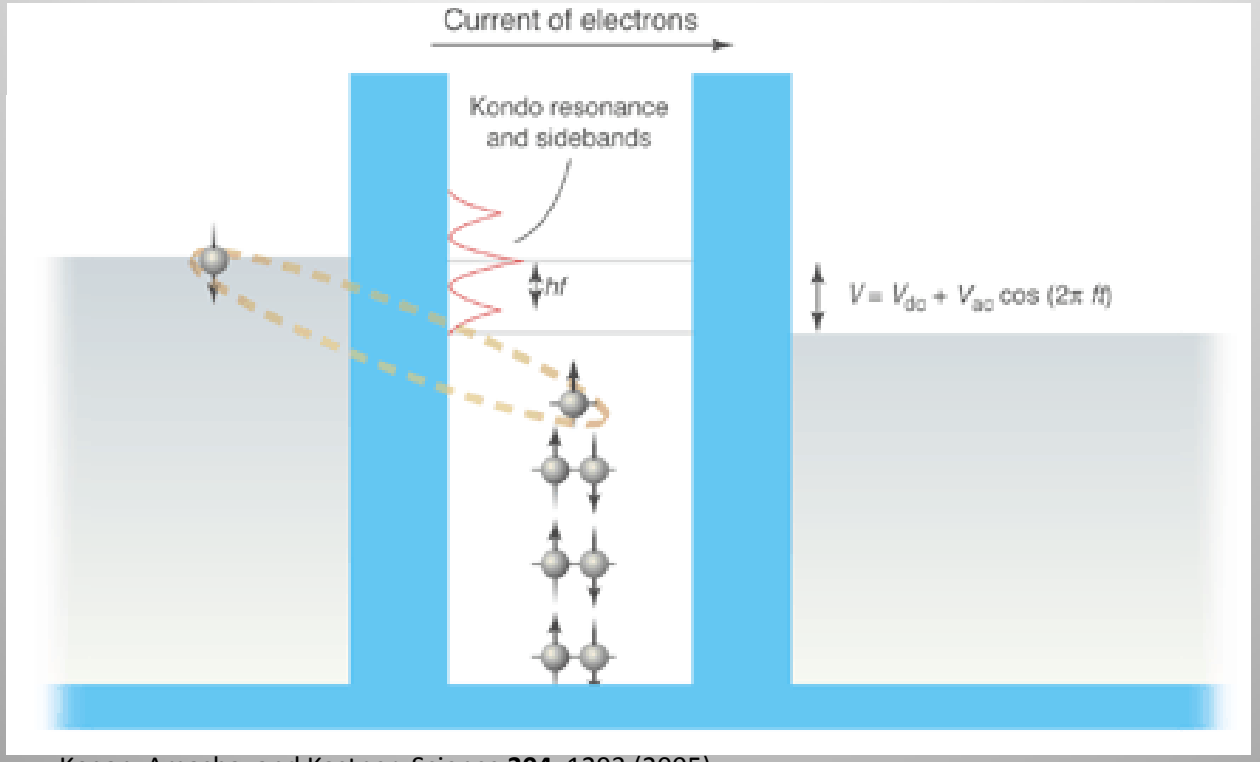


Parks *et al.*, PRL **99**, 026601 (2007).

Kondo resonance combined with ~ 35 meV parallel resonance.

Inelastic tunneling process + Kondo physics.

Inelastic satellites and Kondo



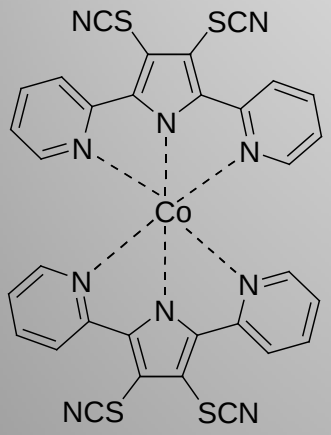
Kogan, Amasha, and Kastner, Science **304**, 1293 (2005)

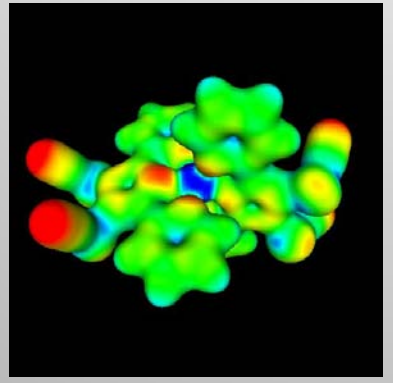
Photon (rather than phonon) Kondo sidebands are visible in GaAs dots in Kondo regime.

Active topic: how does dissipation affect Kondo state?

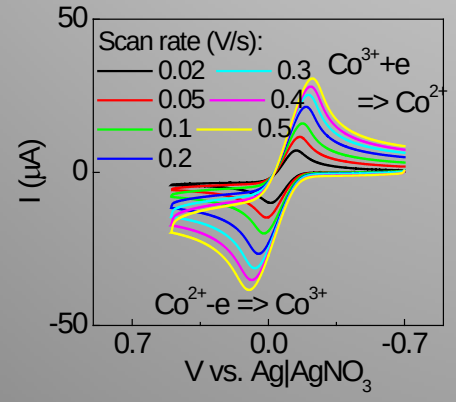
Kondo in transition metal complexes

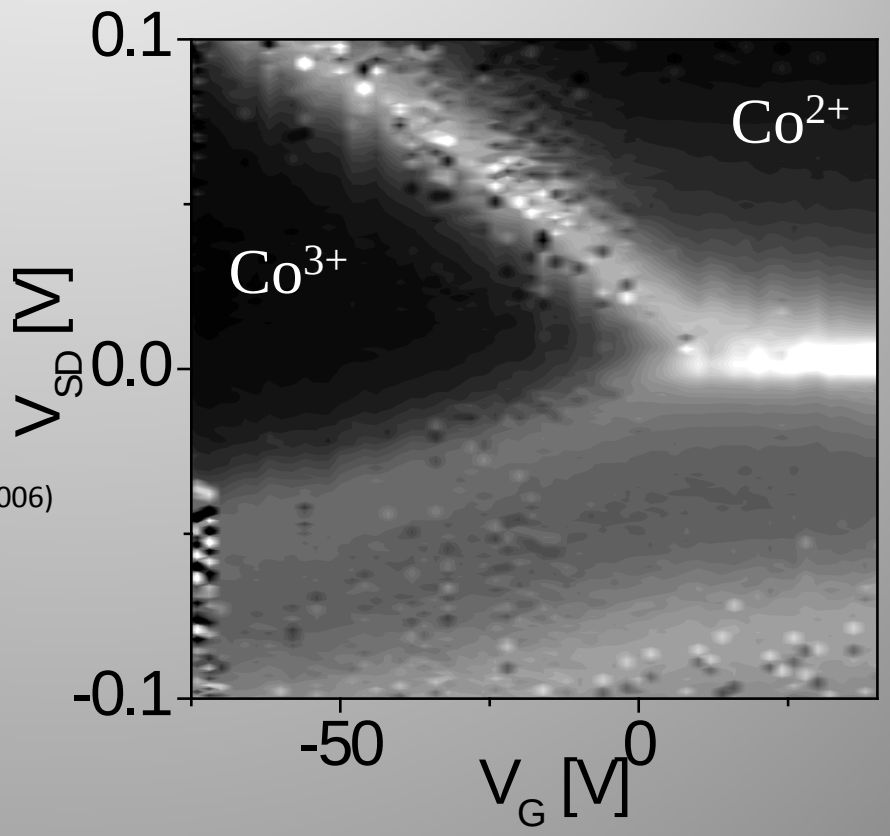
Can deliberately get Kondo physics by working with molecules that contain unpaired electrons.





Ciszek *et al.*, JACS **128**, 3179 (2006)





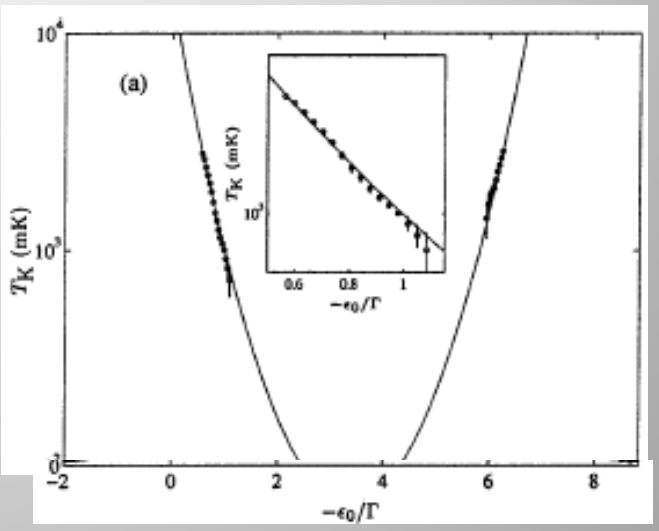
Kondo physics – expected V_G dependence

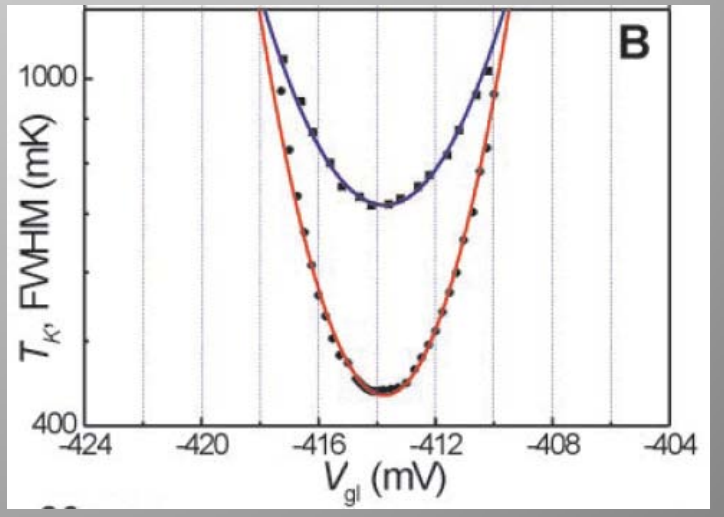
$$T_K \sim \frac{\sqrt{\Gamma E_c}}{2} \exp\left(\frac{-\varepsilon(E_c-\varepsilon)}{\Gamma E_c}\right)$$

(Quadratically) exponentially sensitive to V_G when gating away from charge degeneracy!

Confirmed experimentally in GaAs quantum dots.

Goldhaber-Gordon *et al.*, PRL **81**, 5225 (1998)

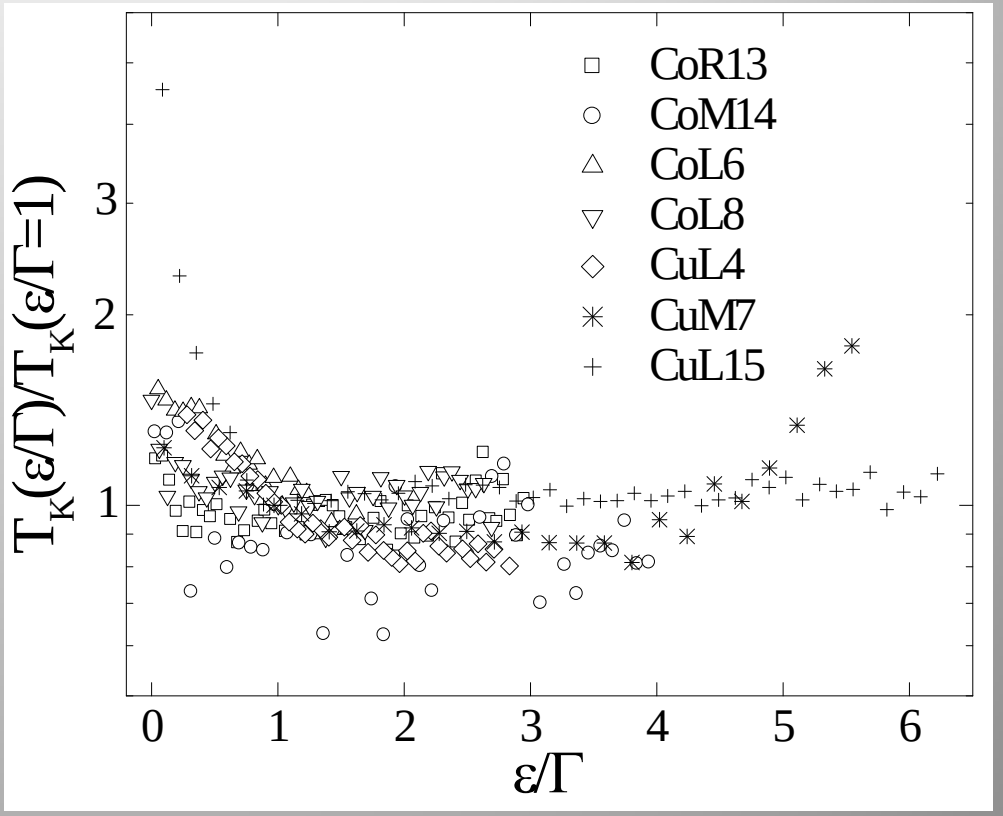




Van der Wiel *et al.*, Science **289**, 2105 (2000)

Anomalous gate dependence

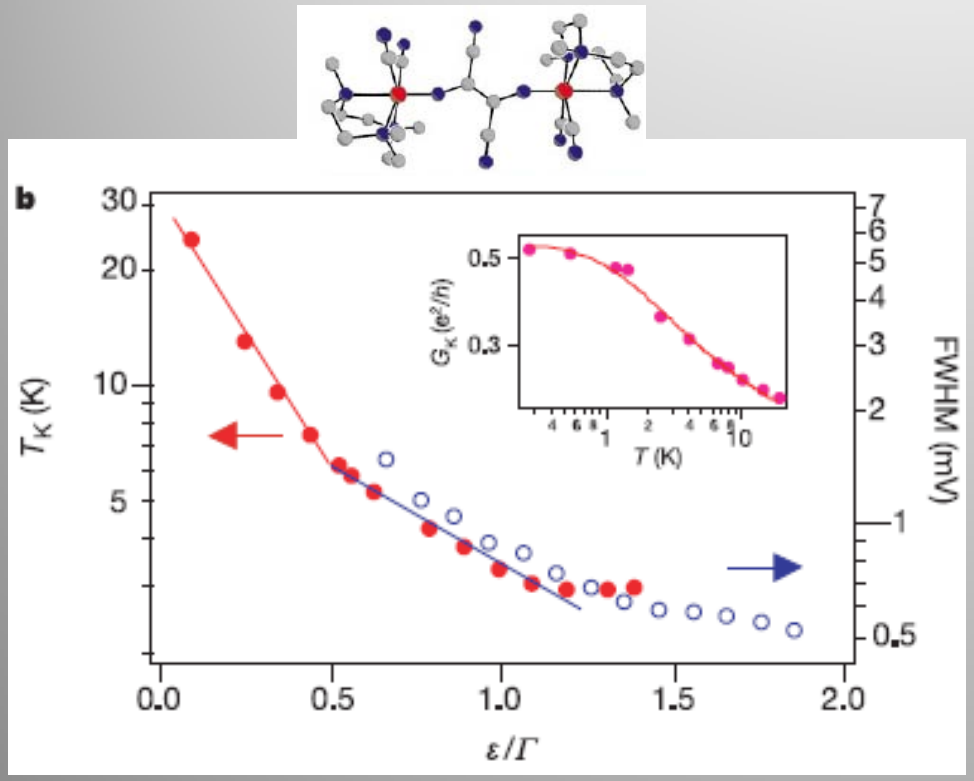
- T_K **not** exponentially dependent on V_G in these devices.
- Demonstrates that SMTs have **nontrivial** many-body physics.



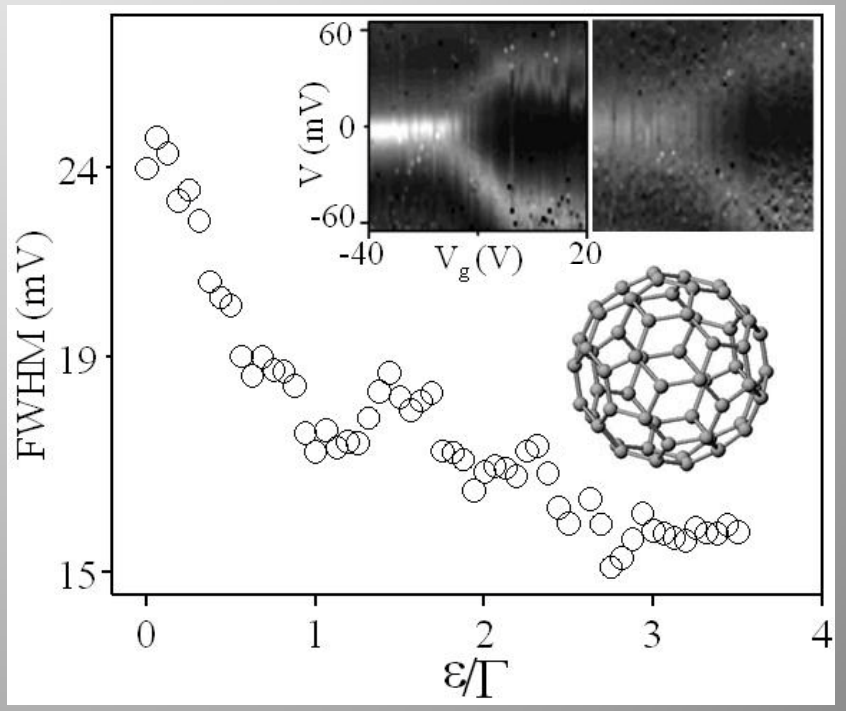
Yu *et al.*, PRL **95**, 256803 (2005).

Anomalous gate dependence

Weak V_G dependence seen in past experiments:



Liang *et al*., Nature **417**, 725 (2002).



Yu and Natelson, Nano Lett **4**, 79 (2004).

Not universal – varies from molecule to molecule.

Model Hamiltonian for molecular case

Leads (KE) dot (KE) Constant interaction Gate coupling

$$H = \sum_{k,\sigma,\alpha\in \mathrm{S,D}} \epsilon_{\alpha\sigma}(k) c^{\dagger}_{\alpha k\sigma} c_{\alpha k\sigma} + \sum_{\nu\sigma} \epsilon_{\nu\sigma} d^{\dagger}_{\nu\sigma} d_{\nu\sigma} + E_{\mathrm{c}} N^2 - eV_{\mathrm{G}} N$$

$$N \equiv \sum_{\nu\sigma} d^{\dagger}_{\nu\sigma} d_{\nu\sigma}$$

$$+ \sum_{k,\sigma,\nu,\alpha\in \mathrm{S,D}} t_{\nu k\alpha}(\{x_l\}) c^{\dagger}_{\alpha k\sigma} d_{\nu\sigma} + \mathrm{H.c.}$$

Dot-lead coupling

$$H_{\mathrm{v}} = \sum_{l} \hbar\omega_l a^{\dagger}_l a_l, \quad x_l \propto a^{\dagger}_l + a_l$$

local vibrational modes

$$H_{\mathrm{ev}} = \sum_{l\nu\sigma} \lambda_{\nu l} x_l \hbar\omega_l d^{\dagger}_{\nu\sigma} d_{\nu\sigma}$$

local vibrational coupling

$$H_{\mathrm{ph}} = \sum_{q} \hbar\Omega_q b^{\dagger}_q b_q$$

bulk phonons

$$H_{\mathrm{v-ph}} = \sum_{lq} \beta_{lq} x_l X_q, \quad X_q \propto (b^{\dagger}_q + b_q)$$

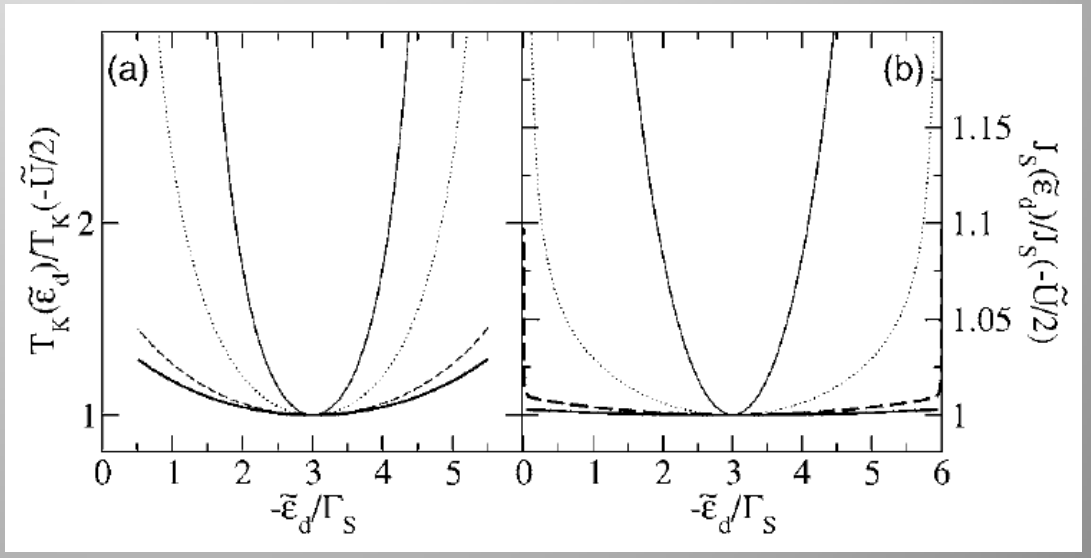
local vibration to bulk phonons

Possible explanation?

Coupling to local vibrational modes = renormalization of energy scales

Anderson-Holstein model

Moderate coupling to local phonon mode leads to renormalized Kondo *J*: enhanced T_K, weak gate dependence.



Balsiero *et al.*, PRB **74**, 235409 (2006).

Kondo physics – universality

Are all Kondo systems (spin ½, SU(2)) created equal?

In truly ideal Kondo dot model, at zero T and zero V, only natural energy scale is $k_B T_K$.

Makes sense that one should then be able to describe full response *near* that limit in a universal form.

$$\frac{\Delta G(V,T)}{G_0} = f\left(\frac{eV}{k_B T_K}, \frac{T}{T_K}\right)$$

$$\frac{eV}{k_B T_K} < 1, \qquad \frac{T}{T_K} < 1$$

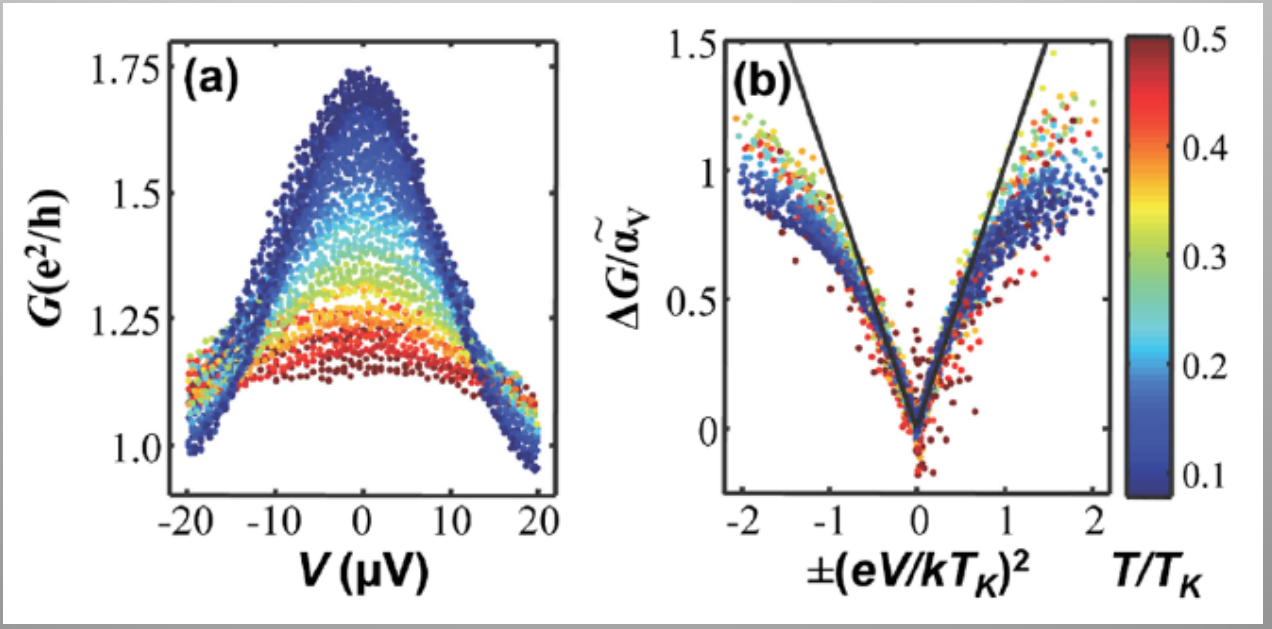
Finite bias Kondo scaling

Universal scaling at finite bias in the Kondo regime is predicted (up to $T \sim 0.1\text{-}0.2\ T_K$, $eV_{SD} \sim 0.1\text{-}0.2\ k_B T_K$).

$$\frac{G(T,0)-G(T,V)}{c_T G_0} = F\left(\frac{T}{T_K}, \frac{eV}{kT_K}\right)$$

$$\approx \alpha\left(\frac{eV}{kT_K}\right)^2 - c_T\gamma\left(\frac{T}{T_K}\right)^2\left(\frac{eV}{kT_K}\right)^2$$

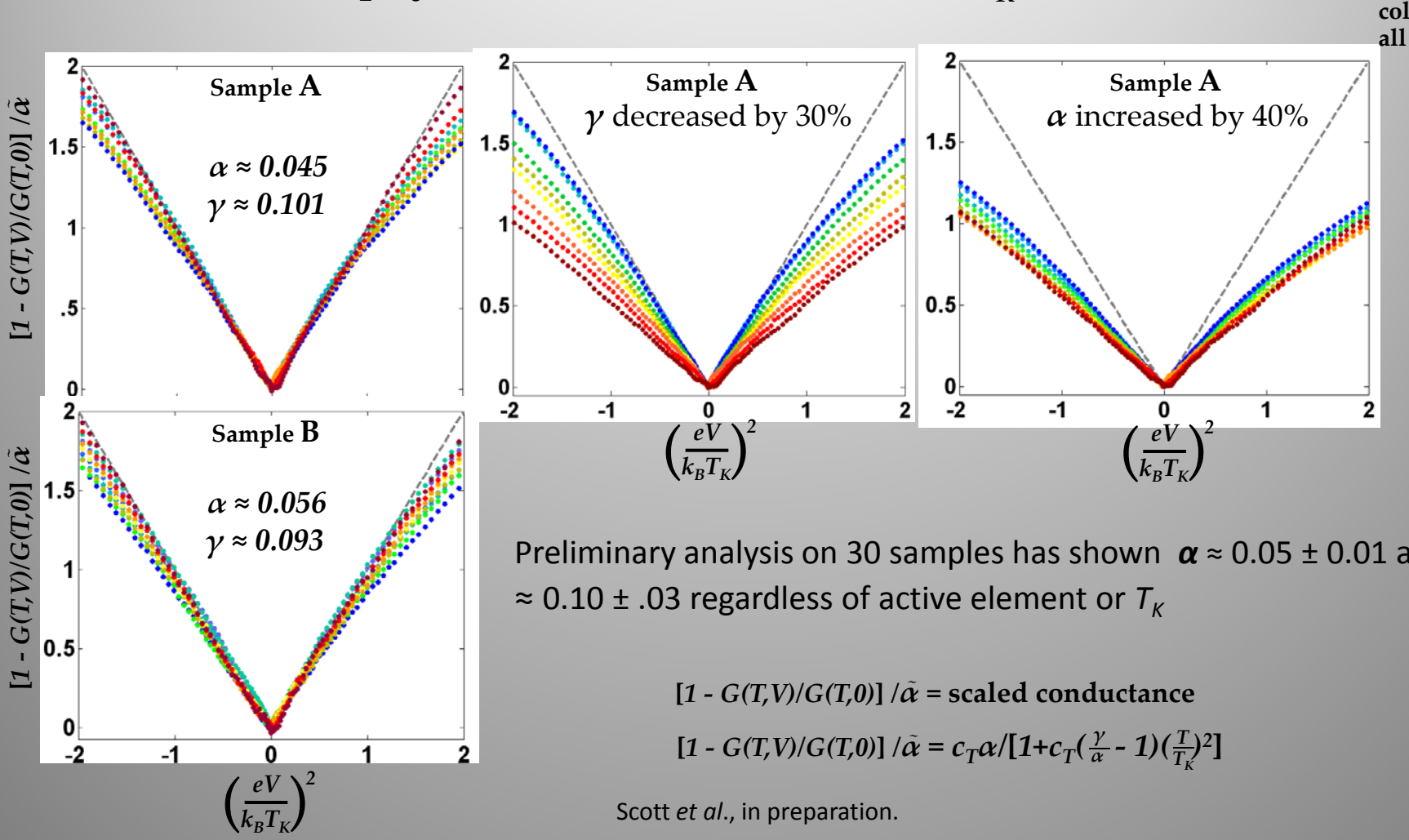
Tested in GaAs dot, $T_K \sim 240$ mK:



Grobis *et al*., PRL **100**, 246601 (2008)

Finite bias Kondo scaling

$$\frac{G(T,0) - G(T,V)}{c_T G_0} \approx \alpha \left(\frac{eV}{k_B T_K}\right)^2 - c_T \gamma \left(\frac{T}{T_K}\right)^2 \left(\frac{eV}{k_B T_K}\right)^2$$



Preliminary analysis on 30 samples has shown $\alpha \approx 0.05 \pm 0.01$ and $\gamma \approx 0.10 \pm .03$ regardless of active element or T_K

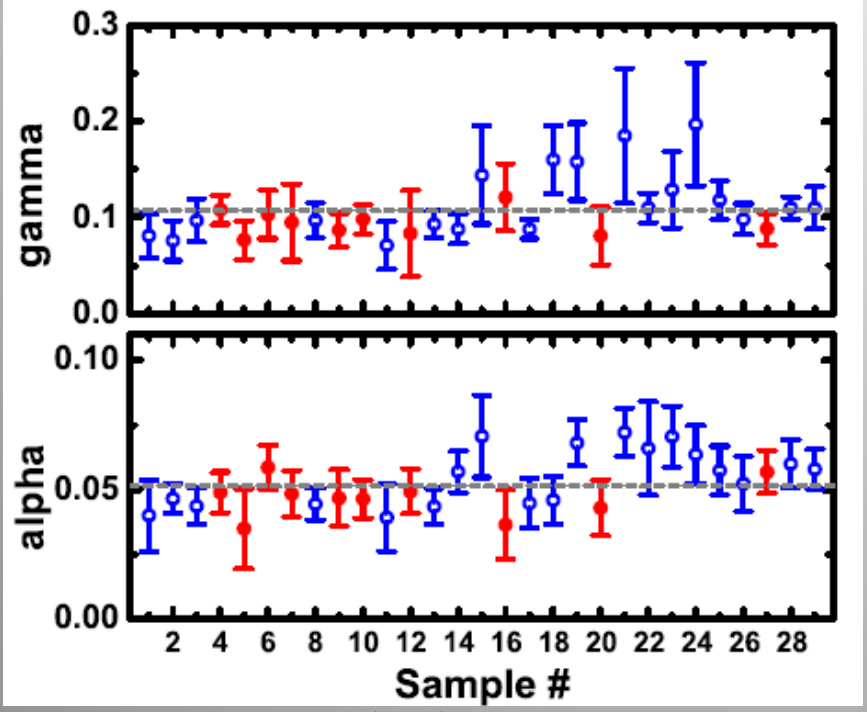
$[1 - G(T,V)/G(T,0)] / \tilde{\alpha}$ = **scaled conductance**

$$[1 - G(T,V)/G(T,0)] / \tilde{\alpha} = c_T \alpha / [1 + c_T (\tfrac{\gamma}{\alpha} - 1)(\tfrac{T}{T_K})^2]$$

Scott *et al.*, in preparation.

Finite bias Kondo scaling

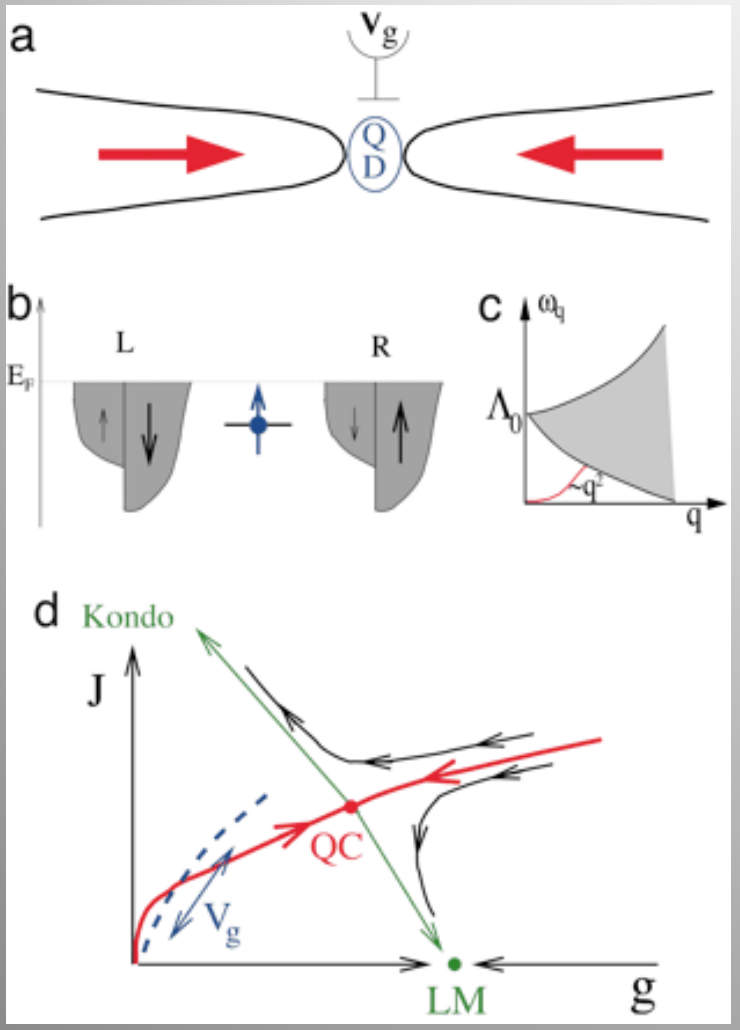
$$\frac{G(T,0) - G(T,V)}{c_T G_0} \approx \alpha \left(\frac{eV}{k_B T_K} \right)^2 - c_T \gamma \left(\frac{T}{T_K} \right)^2 \left(\frac{eV}{k_B T_K} \right)^2$$



- The candidate functional form for scaling does work.
- Very good consistency across devices with wide-ranging T_K and asymmetry.
- Systematic difference in our alpha and that seen in GaAs dot.
- Systematic difference in our alpha and theory predictions (~ 0.15 - 0.3).

Scott *et al.*, PRB **79**, 165413 (2009).

Quantum phase transitions w/ dots?



Kirchner *et al.*, PNAS **102**, 18824 (2005)

Consider a quantum dot coupled to *ferromagnetic leads*.

FM leads can have spin waves.

Usual Kondo: local spin interacts w/ conduction electrons.

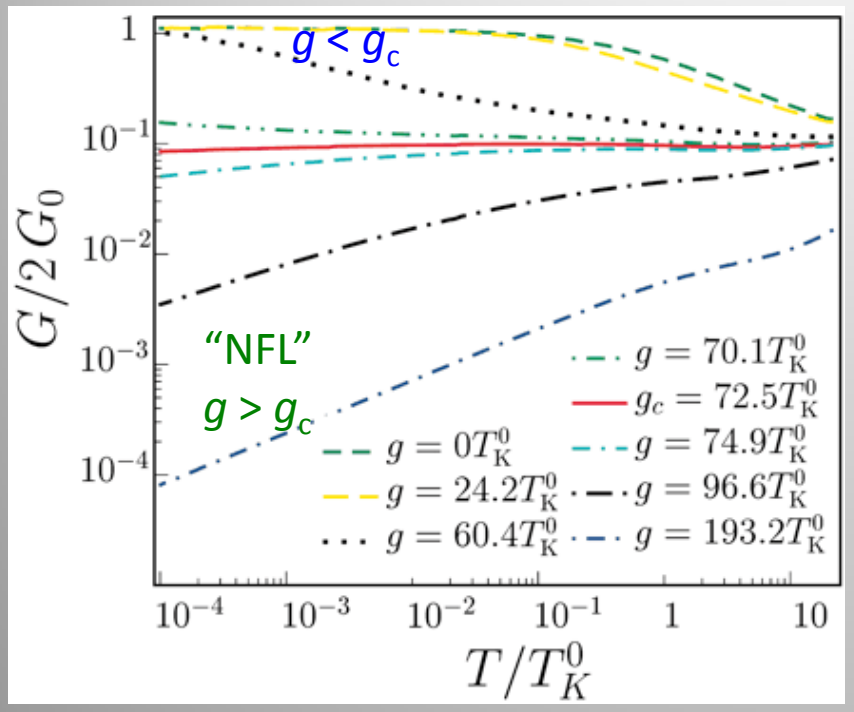
Ground state: Kondo singlet (Fermi liquid)

Gate voltage tunes T_K.

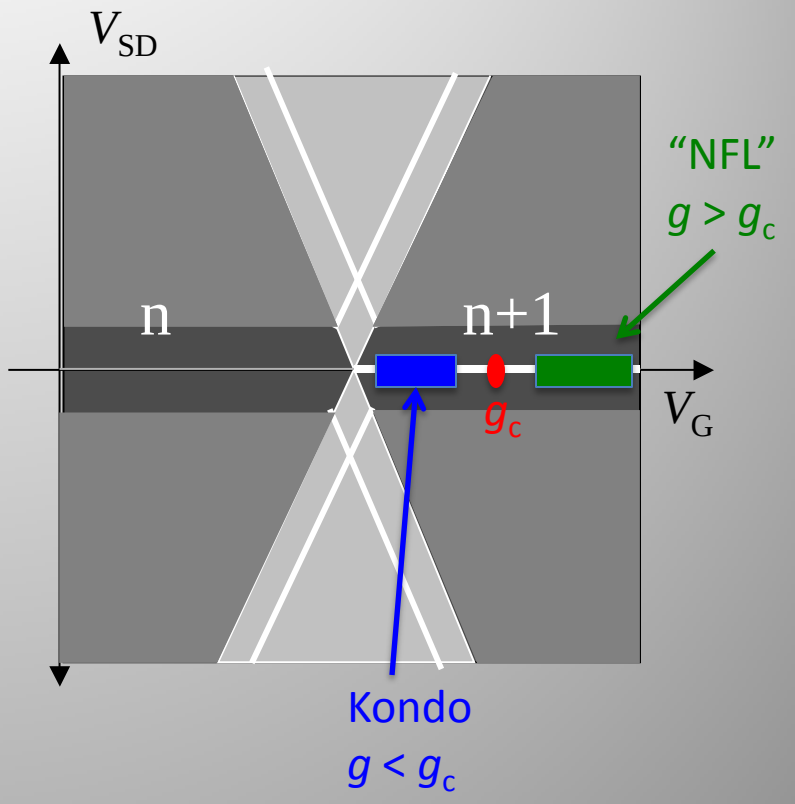
Gate voltage *also tunes* coupling of local moments to spin waves, *g*.

Large enough *g*: Kondo singlet disrupted.

Quantum phase transitions w/ dots?



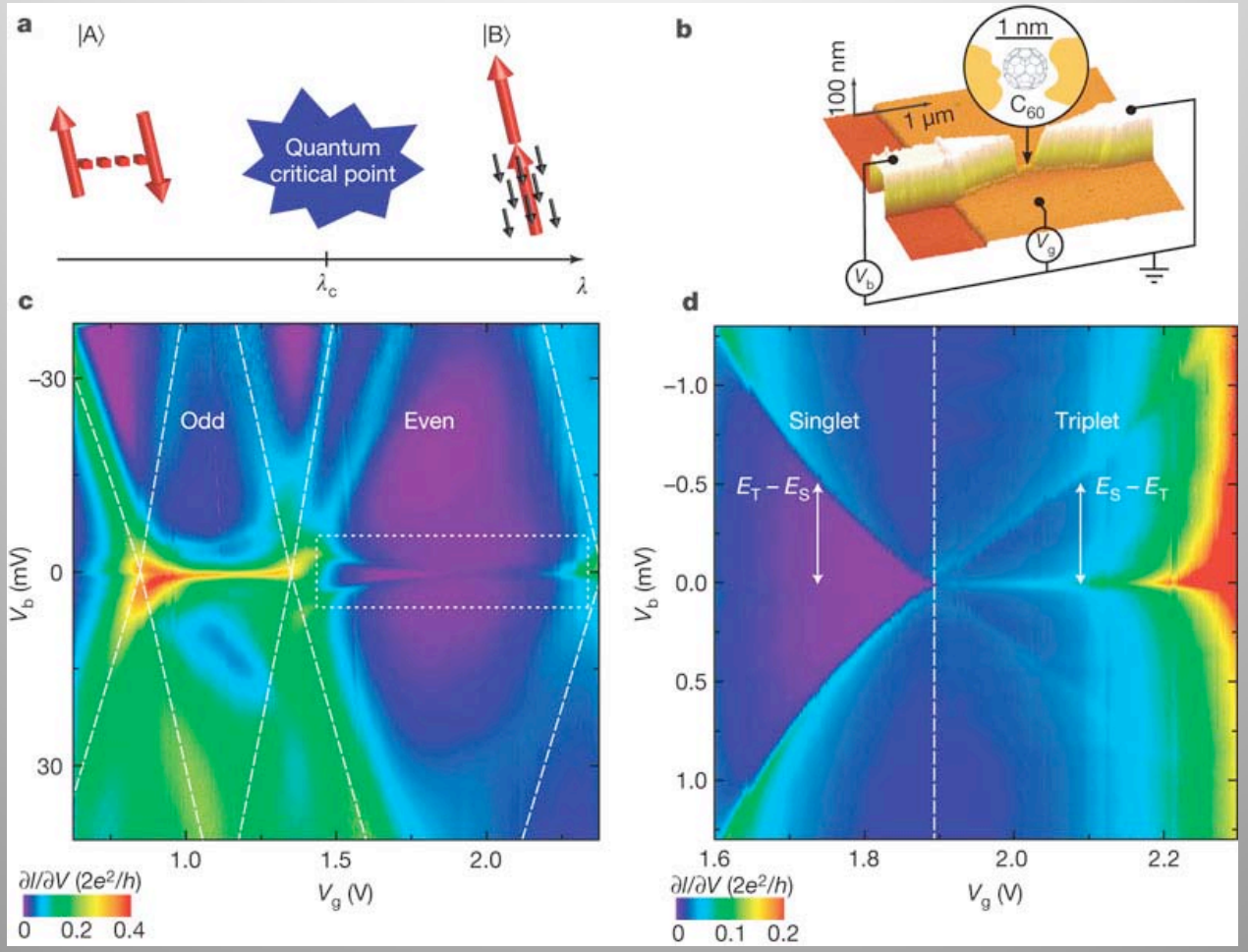
Kirchner *et al.*, PNAS **102**, 18824 (2005)



Idea: As function of V_G, should be able to tune from Kondo to NFL regime.
Identify these regimes by T dependence of zero-bias conductance.

Quantum phase transitions w/ dots?

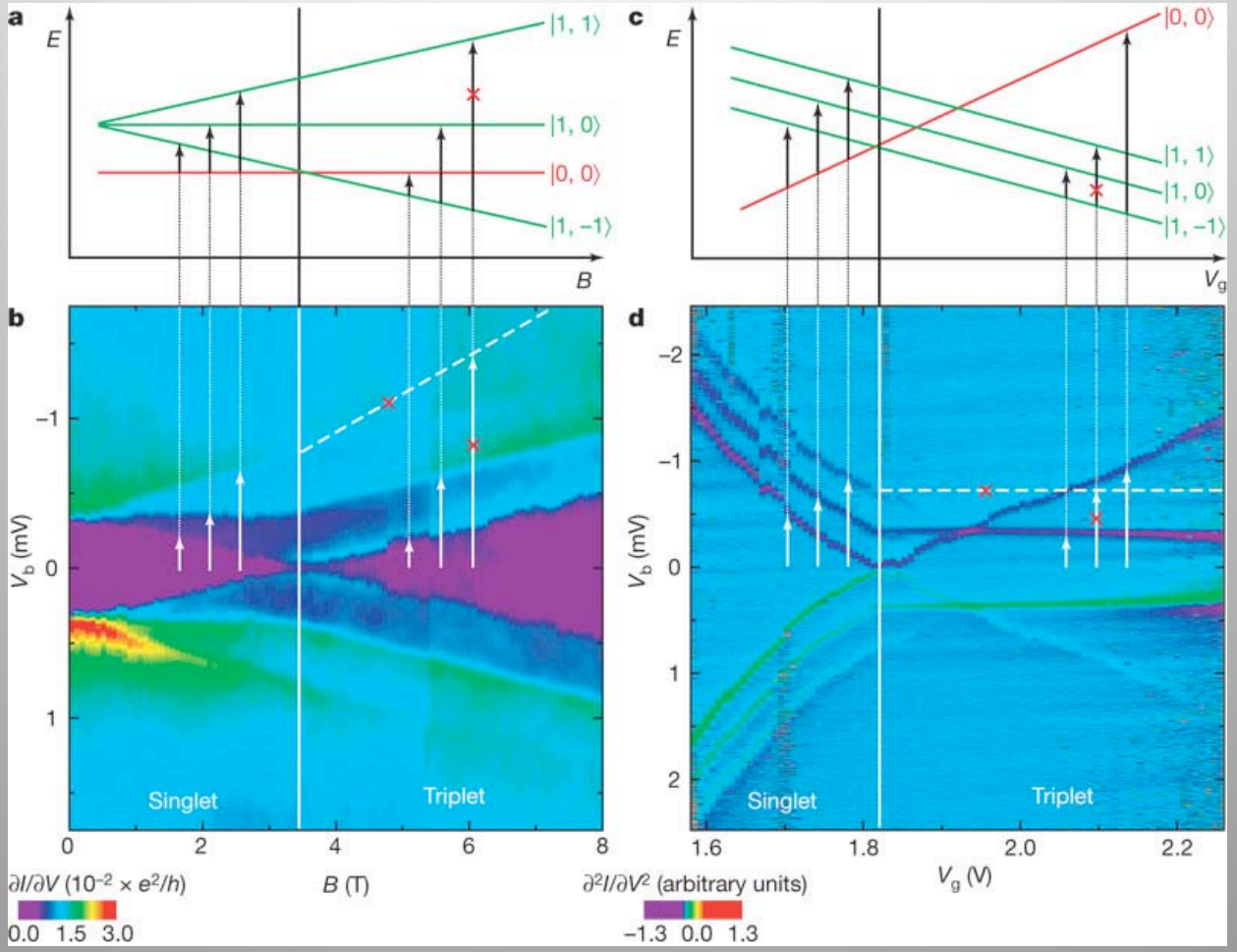
Roch *et al.*, Nature **453**, 633 (2008)



Singlet (Fermi liquid) to underscreened spin-1 Kondo in C_{60} SMT.

Quantum phase transitions w/ dots?

Roch *et al.*, Nature **453**, 633 (2008)



Unclear: why does gate tune energy of singlet and triplet states this way.

Part I Take-home Messages

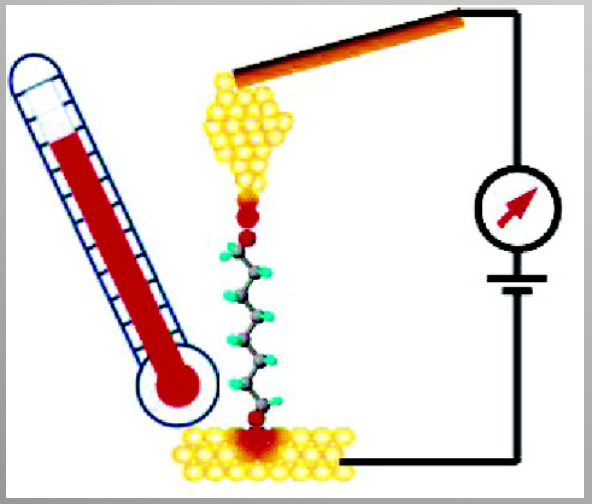
- Semiconductor and molecular junctions can be described by similar language.
- Energy scales are different – lots of physics in molecular systems not relevant in quantum dots.
- In general, finite bias = fundamentally nonequilibrium problem.
- Nonequilibrium = nonthermal distributions of electrons + vibrations.
- Good structures for quantum impurity physics; again, molecular physics a bit different.

Beyond dc transport

There is great interest in moving beyond dc transport, in both dots + molecular junctions.

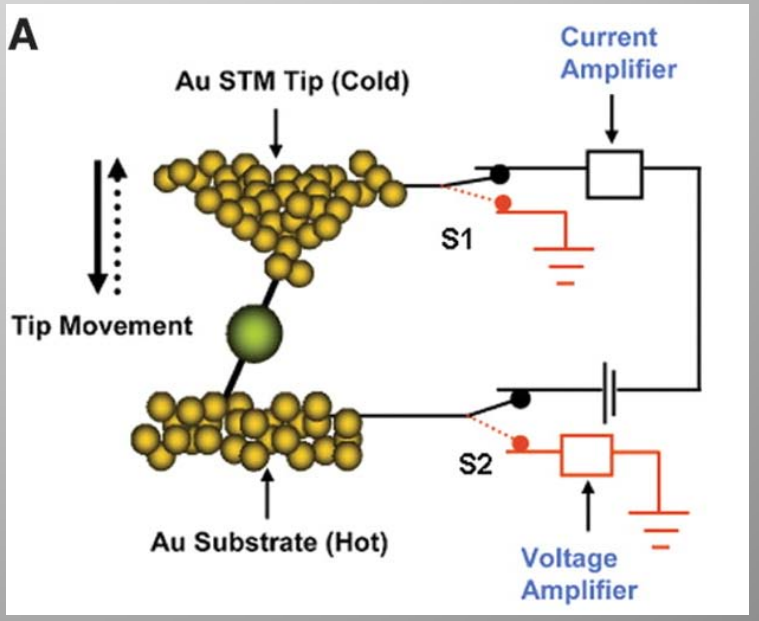
In molecular junctions in particular, great need for further information.

Force measurements @ breaking (inferring **effective temperature**)



Xu *et al.*, *Nano Lett.* **6**, 1240-1244 (2006)

Thermopower



Reddy *et al.*, *Science* **315**, 1568-1571 (2007)

Beyond dc transport

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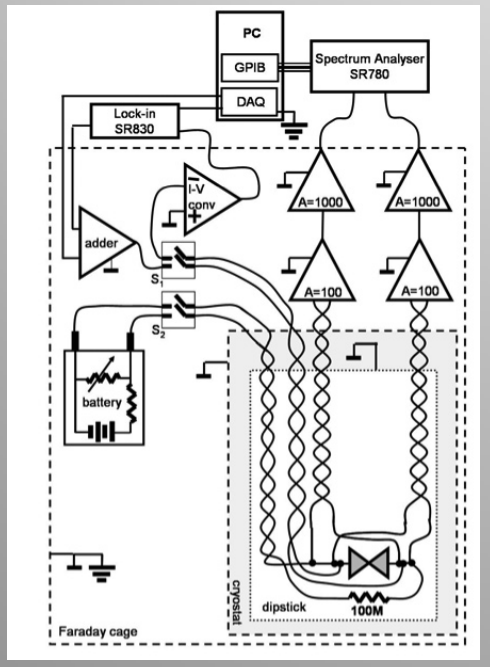
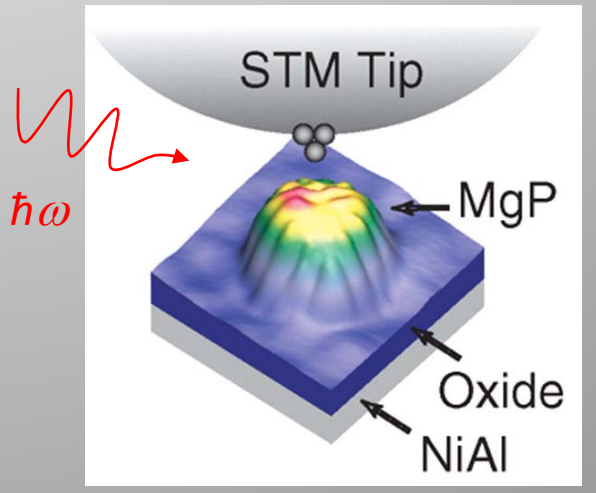
In molecular junctions in particular, great need for further information.

Shot noise



Djukic and van Ruitenbeek, *Nano Lett.* **6**, 789-793 (2006)

Optical response



Wu *et al.*, *Science* **312**, 1362-1365 (2006)

Johnson-Nyquist noise

Fluctuation-dissipation theorem → noise in *equilibrium* conductors

Johnson + Nyquist (1928)

"White" noise

$$S_I = 4k_B T \cdot G$$ A²/Hz (for *f* < ~ optical freq)

$$S_V = 4k_B T \cdot R$$ V²/Hz (for *f* < ~ optical freq)

Nonequilibrium, beyond conductance: "shot" noise

Conductance: tells us ***average current*** under certain voltage bias.

If charge was *continuous*, that would be the end of the story.

However, charge comes in discrete lumps….

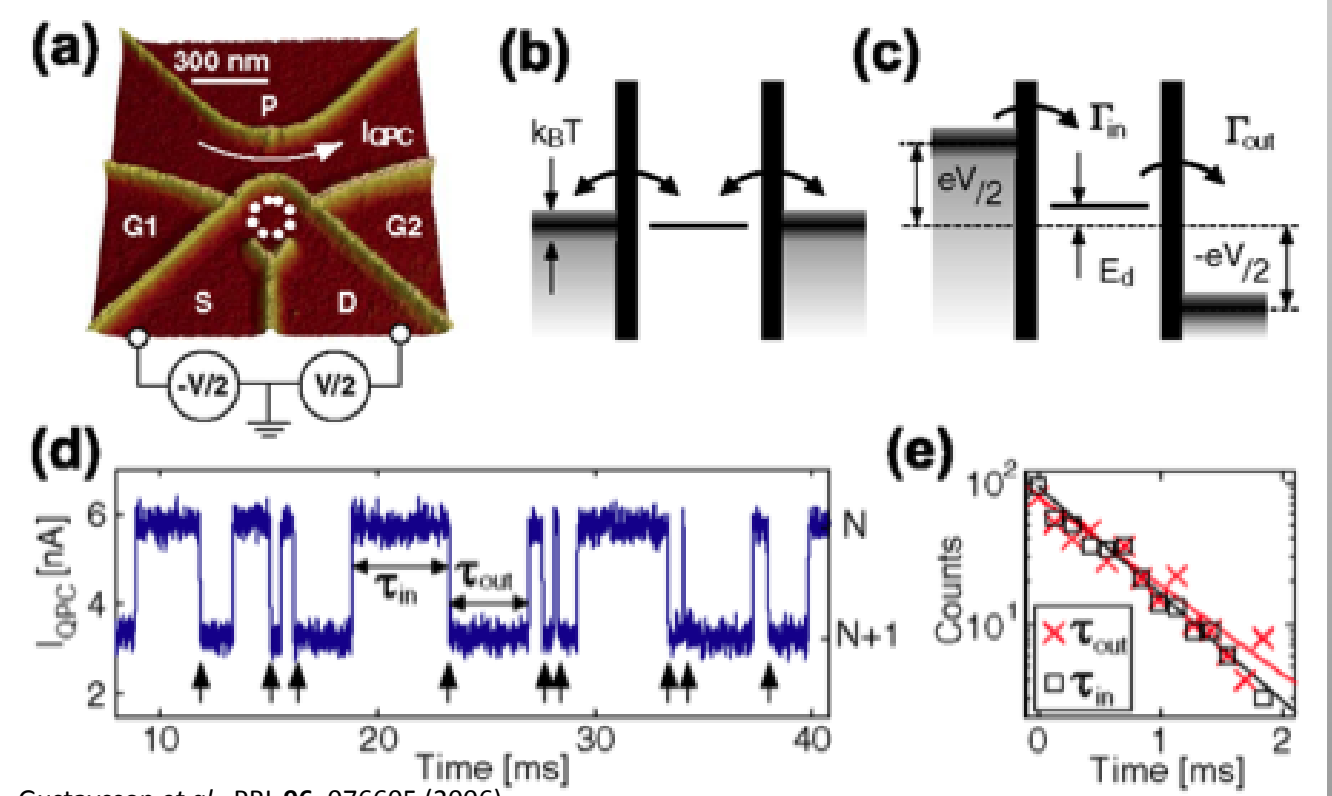
Theorist fantasy: ordered list of arrival times for each electron.

16:07:23.0000315
16:07:23.0000319
16:07:23.0000371
16:07:23.0000389
16:07:23.0000400
16:07:23.0000422
16:07:23.0000430
16:07:23.0000463
.
.
.

Now we can compute $\langle I \rangle$, as before, as well as $\langle (I - \langle I \rangle)^2 \rangle$ (within some bandwidth)

Direct observation of individual tunneling events

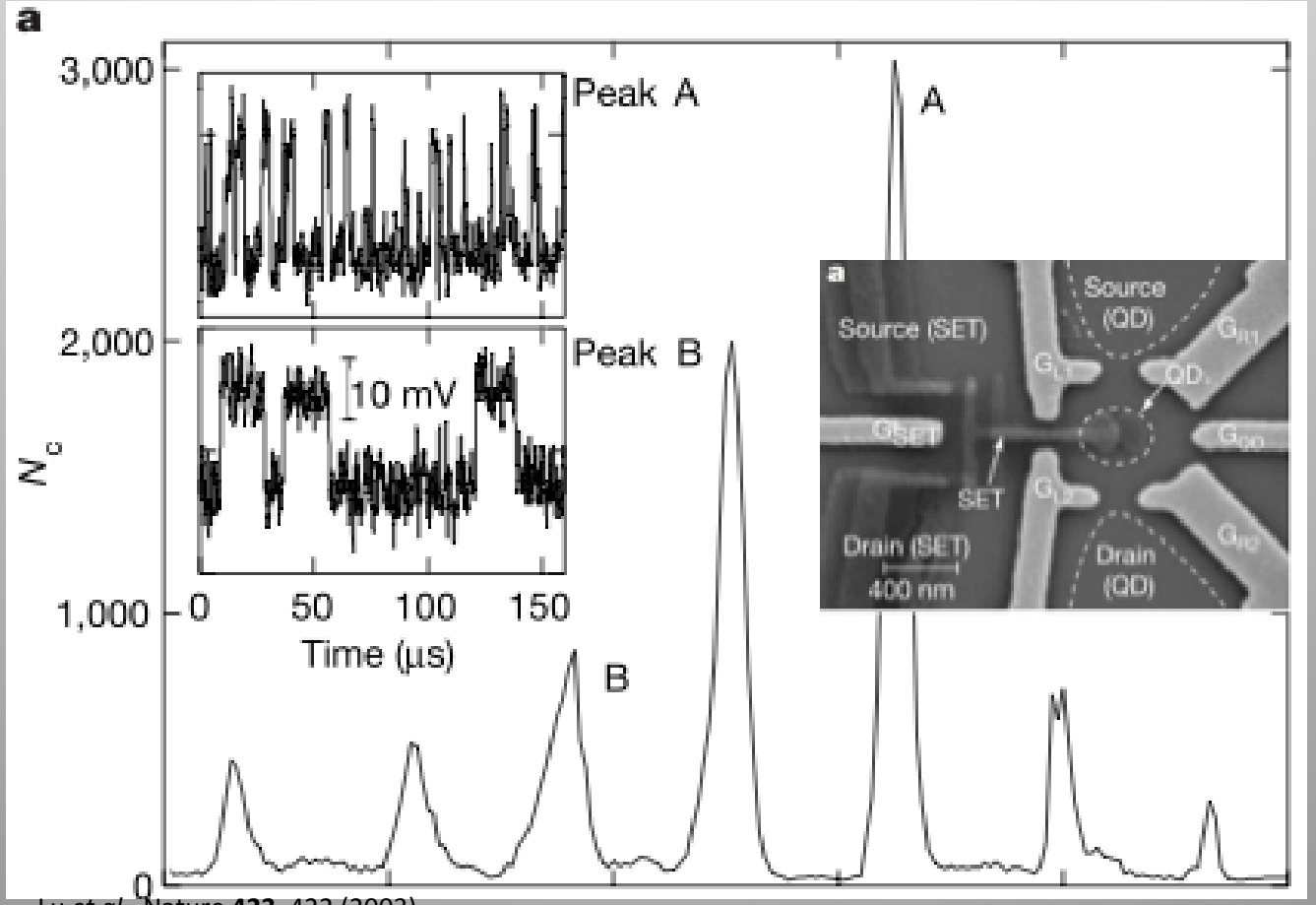
Capacitively coupled quantum point contact



Gustavsson *et al.*, PRL **96**, 076605 (2006)

Direct observation of individual tunneling events

Capacitively coupled rf single-electron transistor



Lu *et al.*, Nature **423**, 422 (2003)

Shot noise

http://www.geocities.com/bioelectrochemistry/schottky.htm

Classical: Schottky (1918)

Noninteracting electrons

Arrivals as Poisson process.

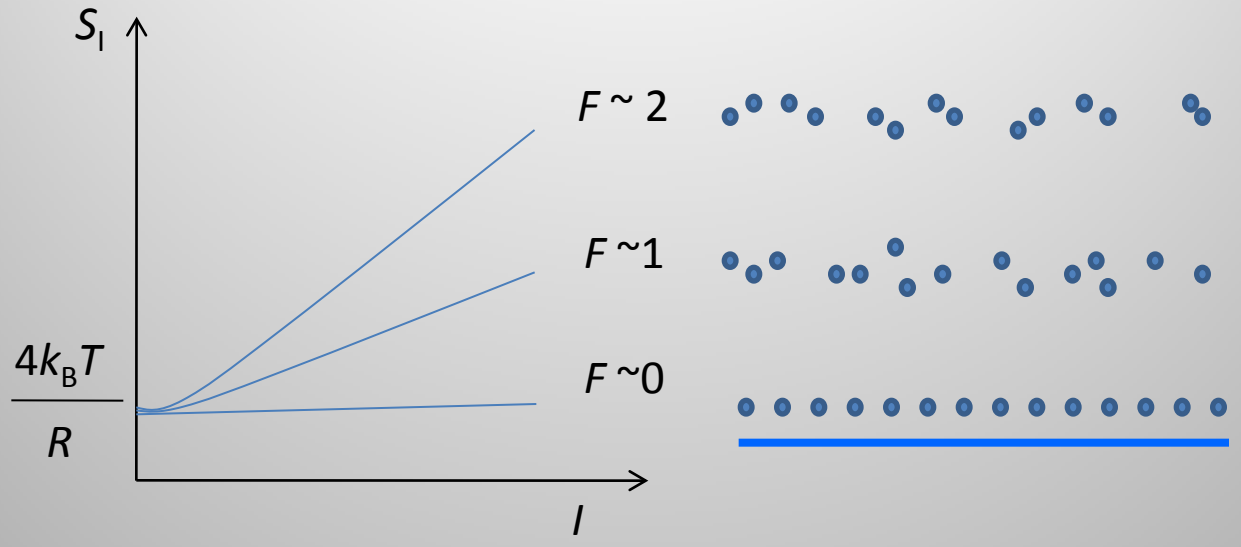
$$S_{I,cl} = \left\langle \left(I - \langle I \rangle \right)^2 \right\rangle = 2e\langle I \rangle$$

What if e^- arrivals are not independent? More generally:

$$S_I = 2e\langle I \rangle \cdot F$$

$F \equiv$ Fano factor

Shot noise



- Fano factor tells you about correlations between electron arrivals.
- e.g., $F = 2$ for Poissonian arrival of *pairs*, as in SC tunnel junction.
- In this sense, *F* tells you about *effective charge* of excitations.
- ***F* → 0 in macroscopic systems at moderate temperatures** – inelastic scattering effectively smears out the conductance channels.

Shot noise – quantum case

$T = 0$

$$S_I = 2eV\frac{2e^2}{h}\sum_i \tau_i(1-\tau_i)$$

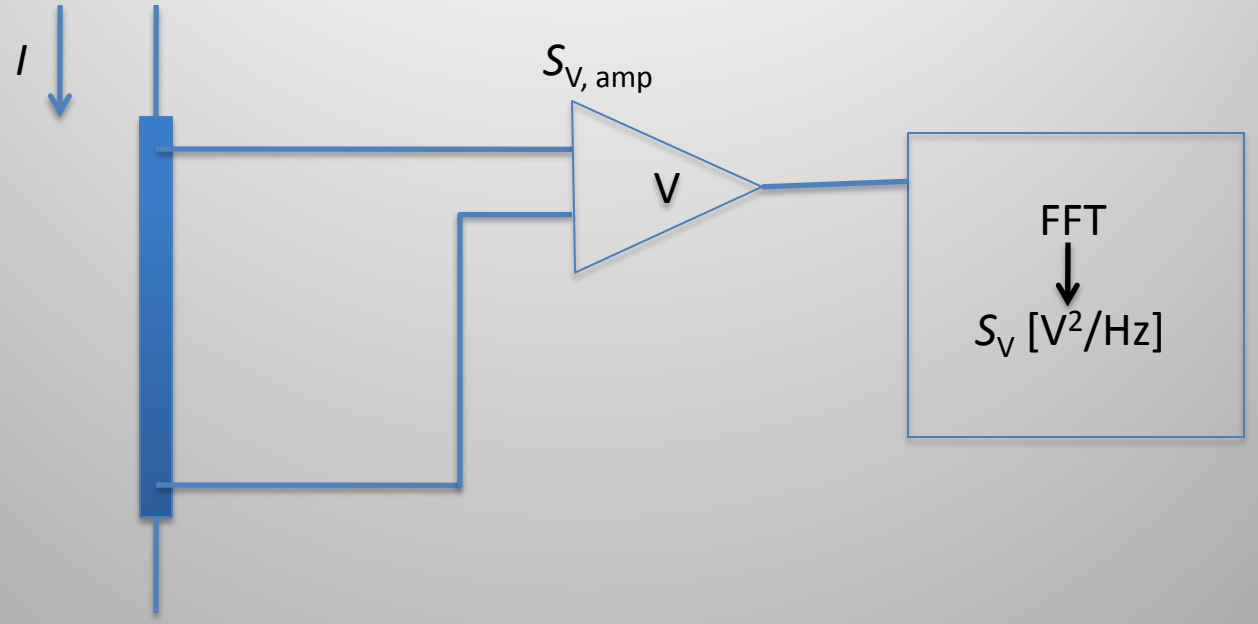
$T \neq 0$

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

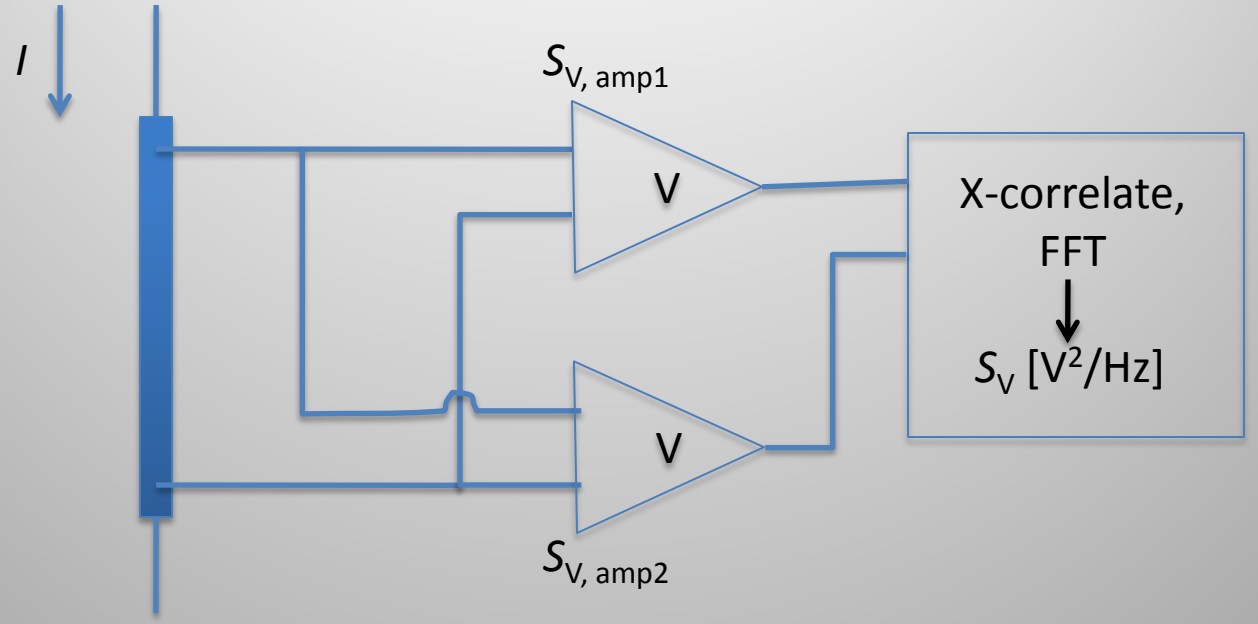
If conductance quantization *really* comes from Landauer physics, expect **suppression** of noise whenever $\tau_i \sim 1$.

Blanter and Büttiker, Phys. Reports **336**, 1-166 (2000)

How do you measure noise?

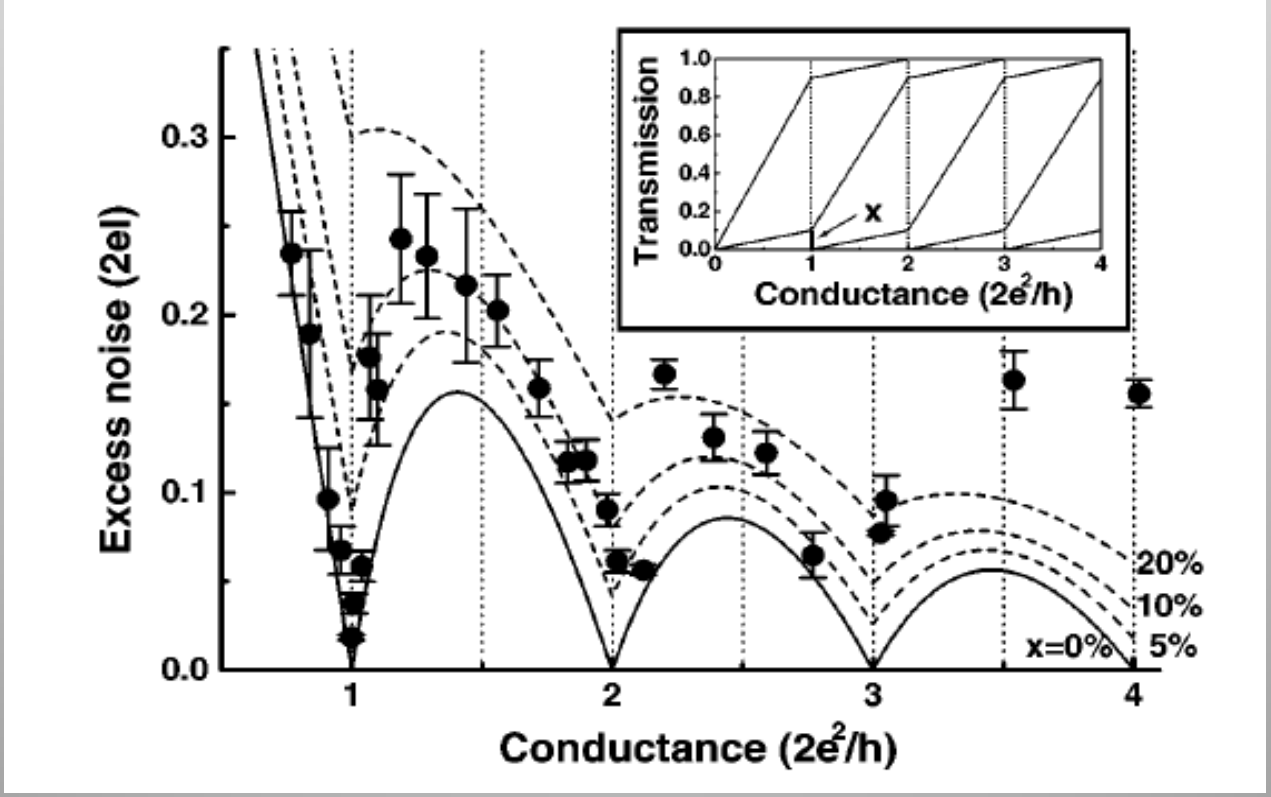


How do you measure noise?



Advantage: Gets rid of (nominally uncorrelated) amplifier noise, with sufficient averaging.

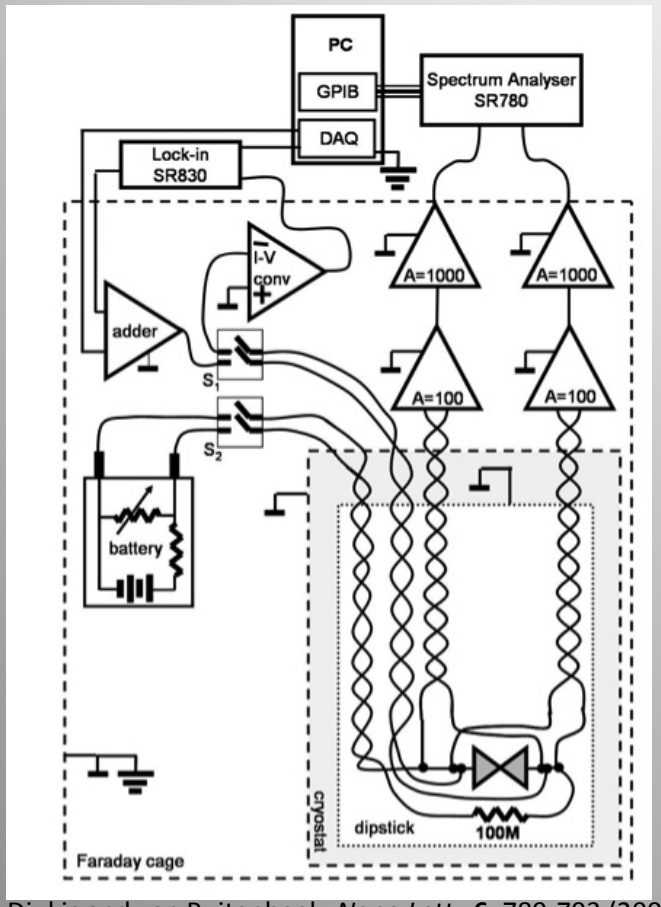
How do you measure noise?



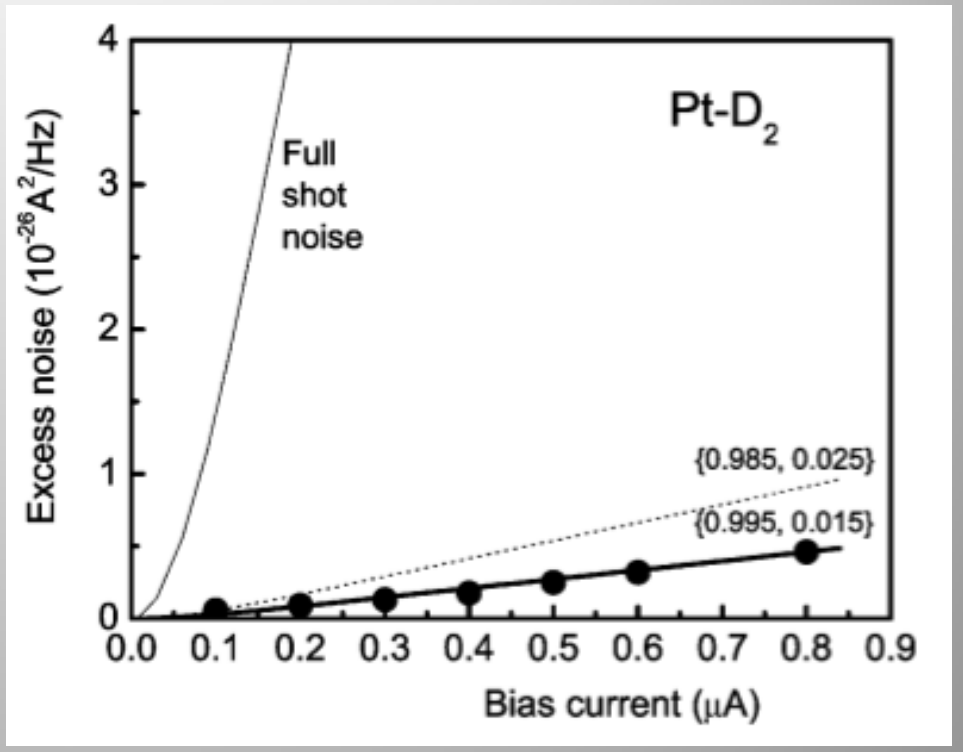
van den Brom and van Ruitenbeek, PRL **82**, 1526 (1999)

Shows expected shot noise suppression when conductance is quantizes – confirms quantum nature of transport!

How do you measure noise?



Djukic and van Ruitenbeek, *Nano Lett.* **6**, 789-793 (2006)



In (highly conducting) molecular junction case, allows identification of transmission coefficients.

Low frequency method: challenges

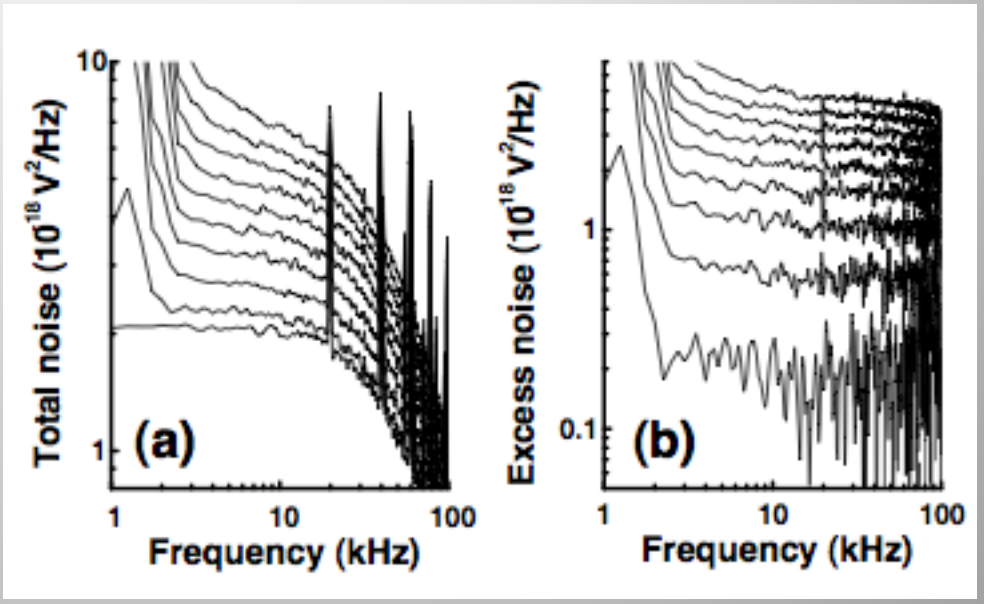
Capacitive attenuation of signal

$$\nu_{\mathrm{roll-off}} \approx \frac{1}{2\pi RC}$$

Minimal stray capacitance on order of hundreds of pF

$$\frac{1}{G_0} = \frac{h}{2e^2} \approx 12.9\ \mathrm{k\Omega}$$

$$\rightarrow \nu_{\mathrm{roll-off}} \approx 10\mathrm{s\ of\ kHz}$$



van den Brom and van Ruitenbeek, PRL **82**, 1526 (1999)

May be mitigated partially by characterization of *C*, but still limiting.

Note that relevant voltages to be measured are small! At I = 100 nA, $G \sim G_0$ (ignoring suppression),

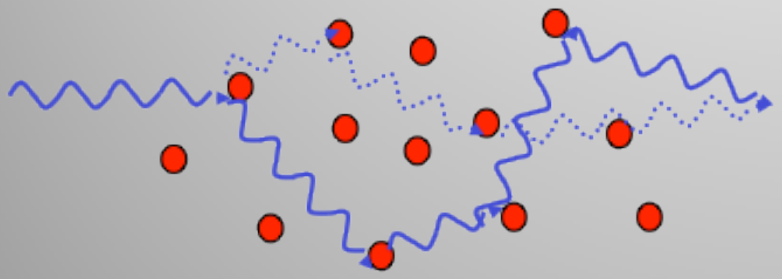
$$S_V = 2eI/(G^2) \approx 5.3 \times 10^{-18}\ \mathrm{V^2/Hz}$$

$$\rightarrow (\delta V)_{\mathrm{rms}} \approx 2.4\ \mathrm{nV}/\sqrt{\mathrm{Hz}}$$

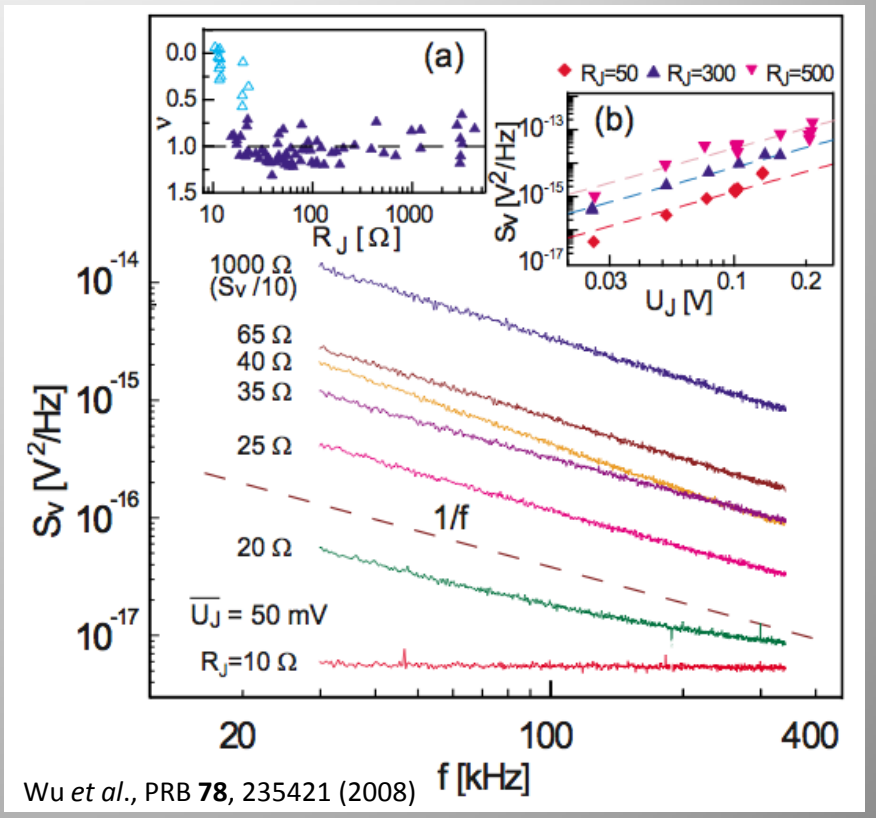
Another challenge: 1/*f* noise

Resistance fluctuations w/ distribution of relaxation times leads to voltage fluctuations w/ 1/*f* power spectrum.

Origin (in quantum case): quantum interference.



Interestingly, still visible in nanocontacts.



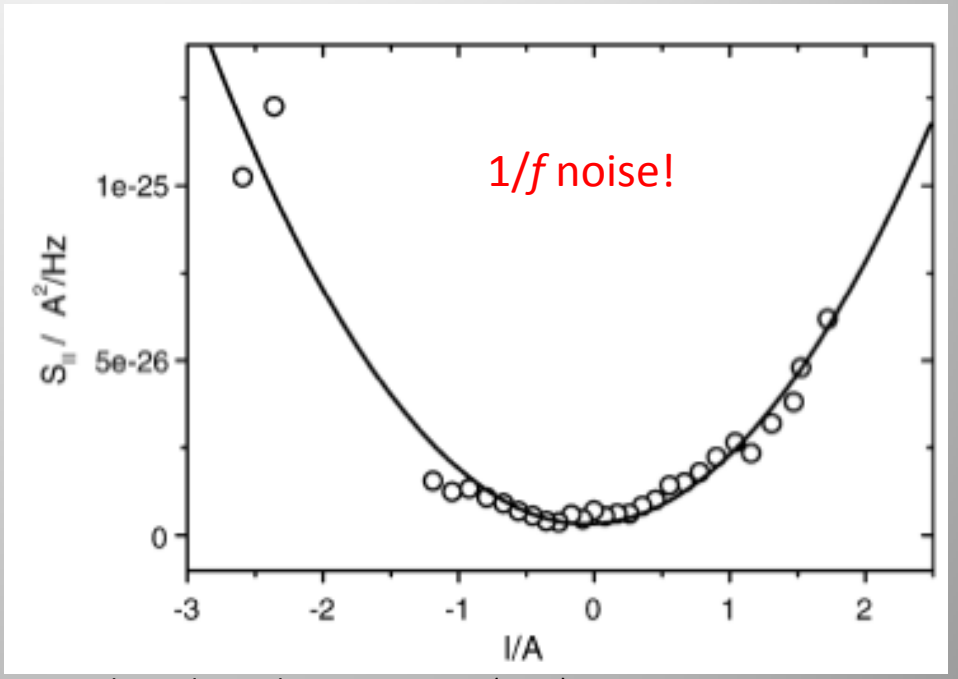
Wu *et al*., PRB **78**, 235421 (2008)

Another challenge: 1/*f* noise

Fortunately, can distinguish this experimentally from shot noise.

$$I\delta R \rightarrow \delta V \qquad S_{V,\ 1/f} \propto I^2$$

Need to look at scaling of noise signal w/ bias current.

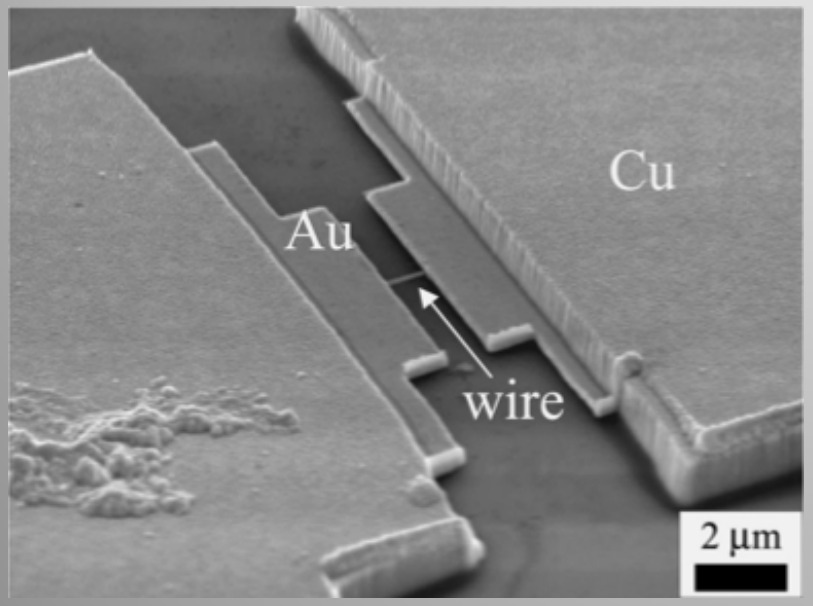


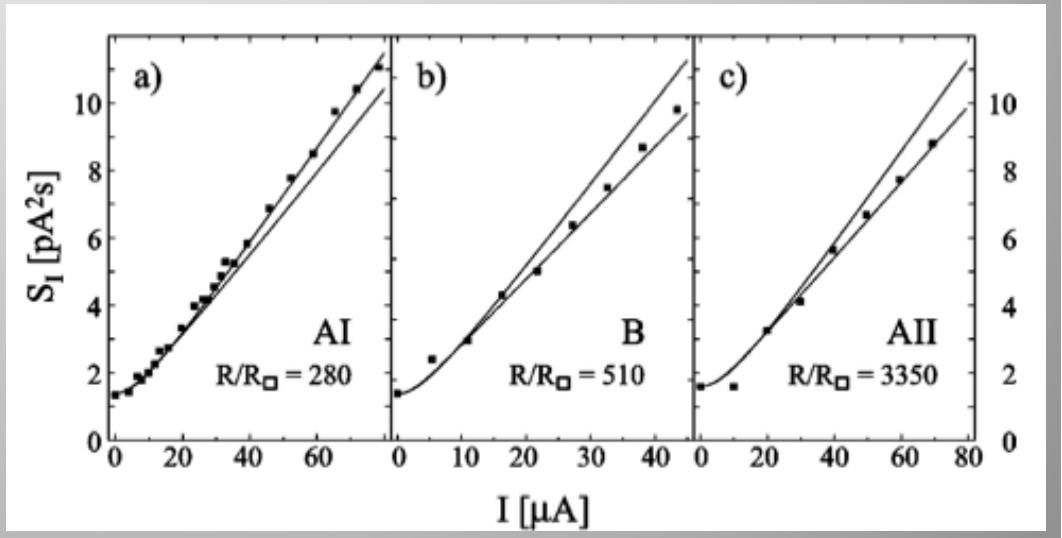
Ochs *et al.*, Faraday Disc. **131**, 281 (2006)

Prediction of modified Fano factors

There are predictions of modified Fano factors.

Example: diffusive mesoscopic wire $F \to 1/3$

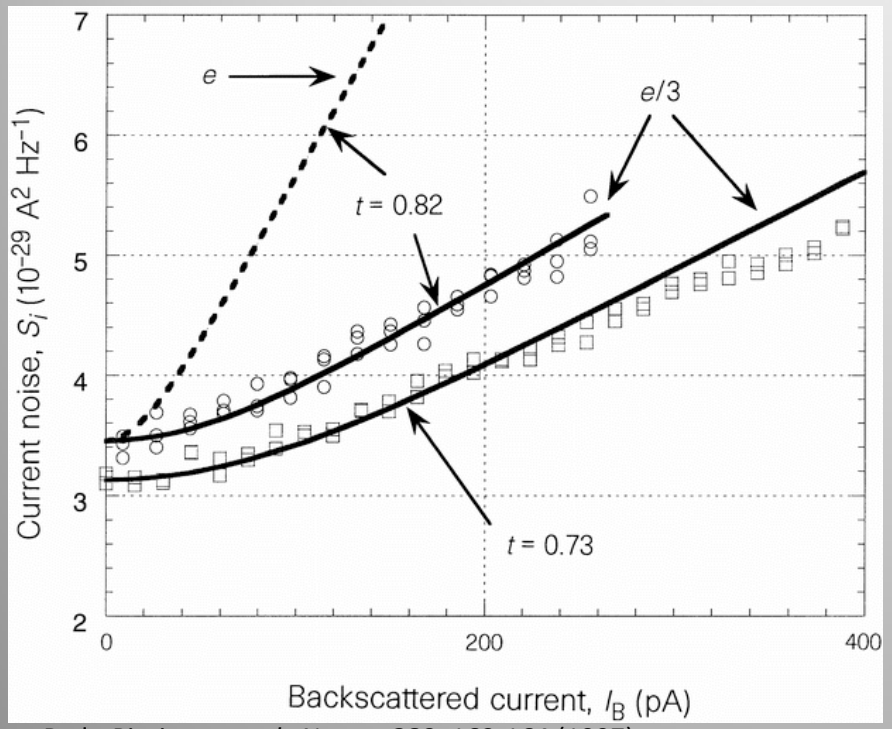




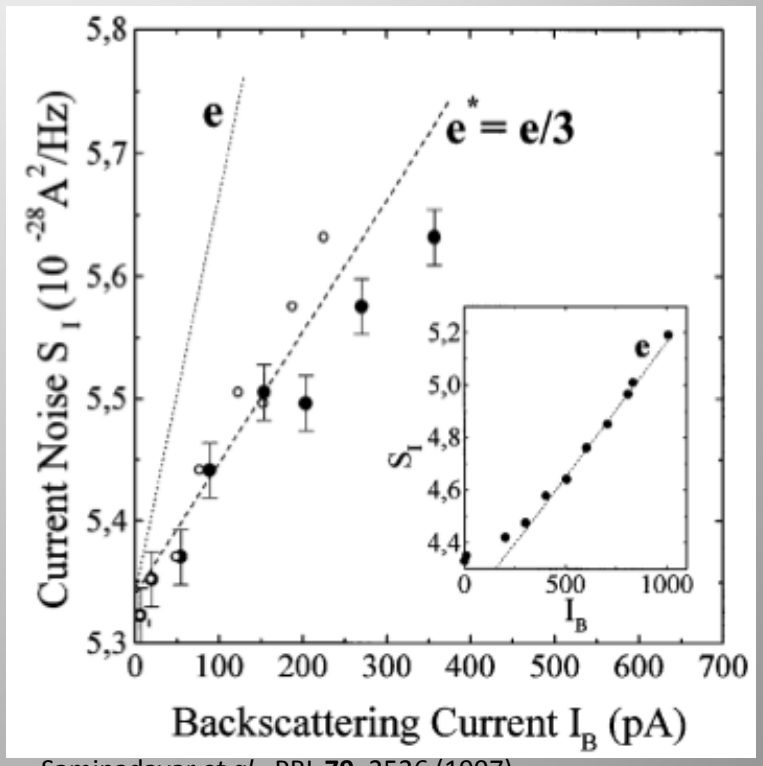
Henny *et al.*, PRB **59**, 2871 (1999)

Prediction of modified Fano factors

Example: fractional charge in fractional quantum Hall systems $F \to 1/3$ for $\nu = 1/3$



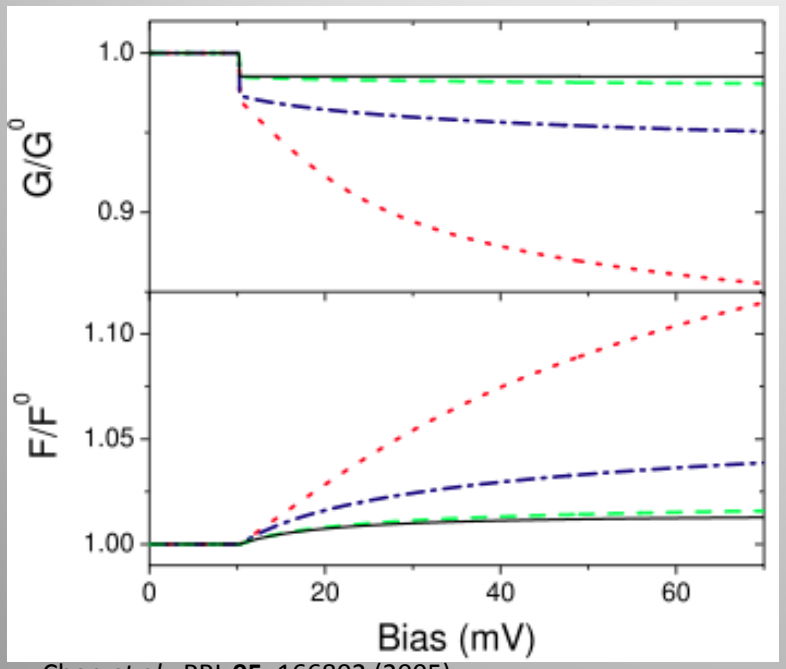
R. de-Picciotto, *et al.*, Nature **389**, 162-164 (1997)



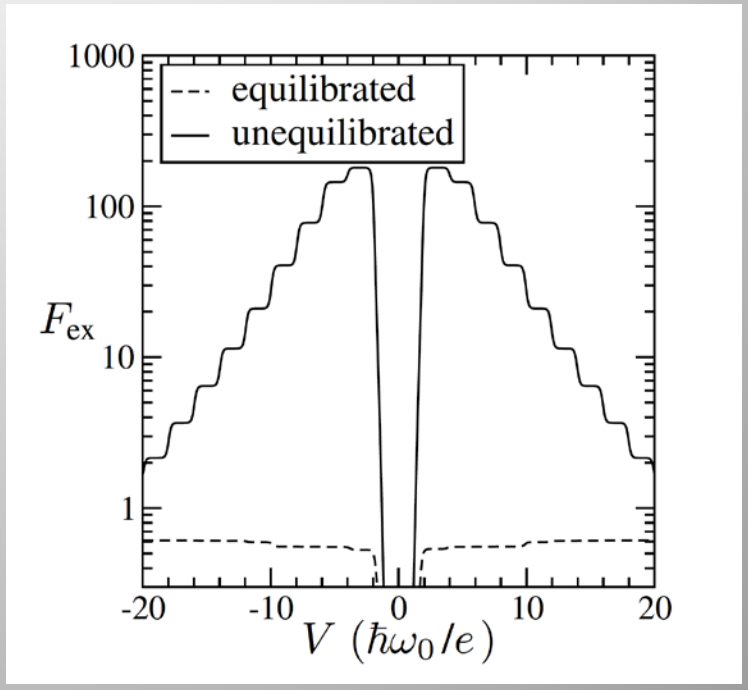
Saminadayar *et al.*, PRL **79**, 2526 (1997)

Prediction of modified Fano factors

Enhanced Fano factor due to *e*-vib coupling



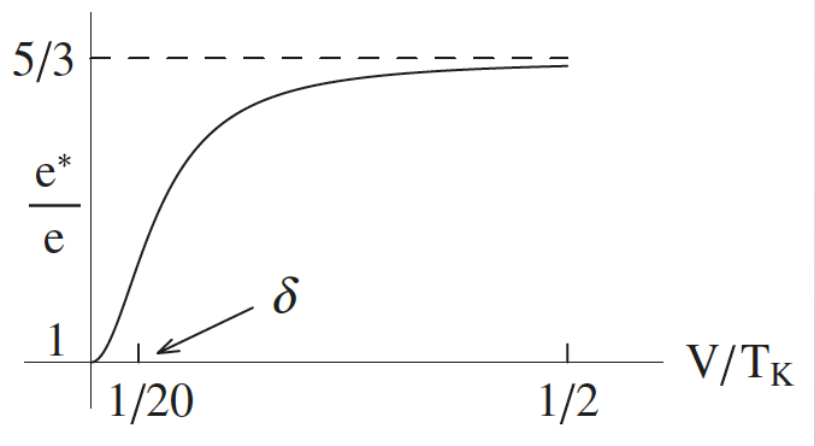
Chen *et al*., PRL **95**, 166802 (2005)



Koch and von Oppen, PRL **94**, 206804 (2005)

Heuristically, electron-vibrational coupling renormalizes

Modified Fano factors in the Kondo regime

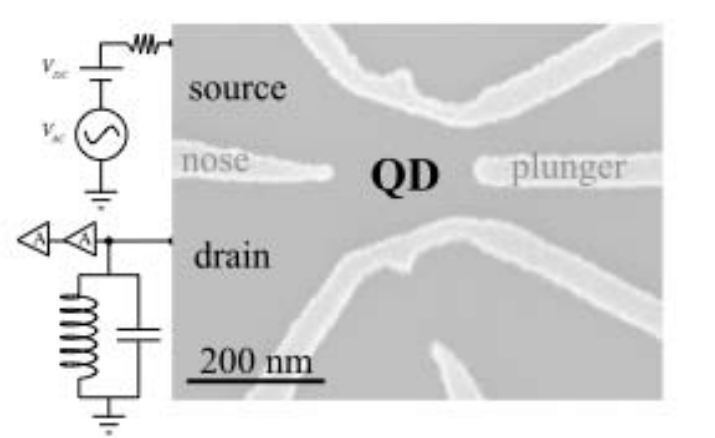


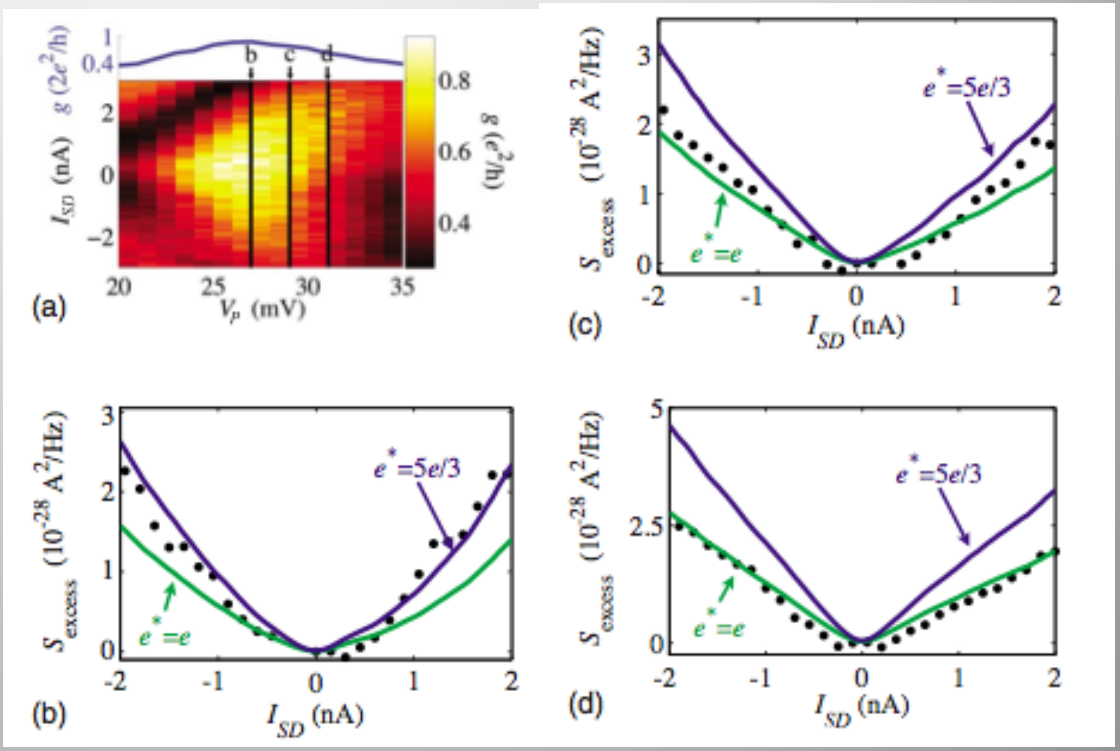
Prediction that finite *V* leads to modification of Fano factor.

Idea: back-scattering + creation of e-h pair = some two-particle contribution.

Sela *et al*., PRL **97**, 086601 (2006)

Experimental evidence





Zarchin *et al.*, PRB **77**, 241303(R) (2008)

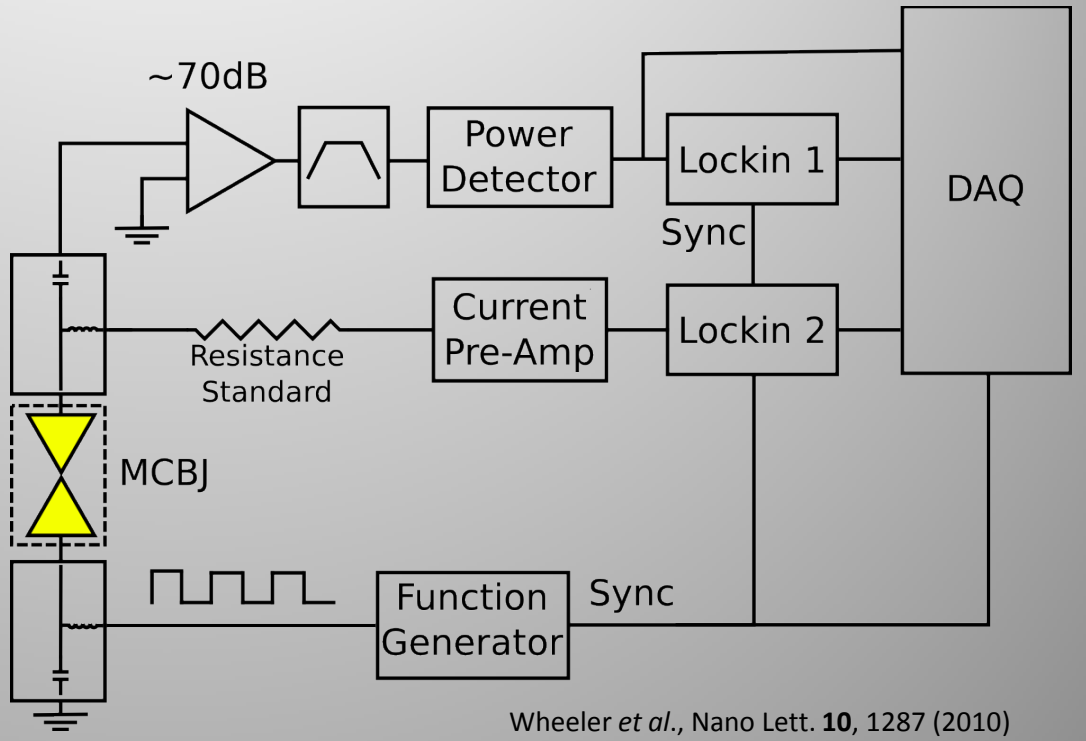
Higher frequency approach to noise measurement

There are several higher frequency methods for measuring the noise.

The example at right is one approach – directly measure rf power.

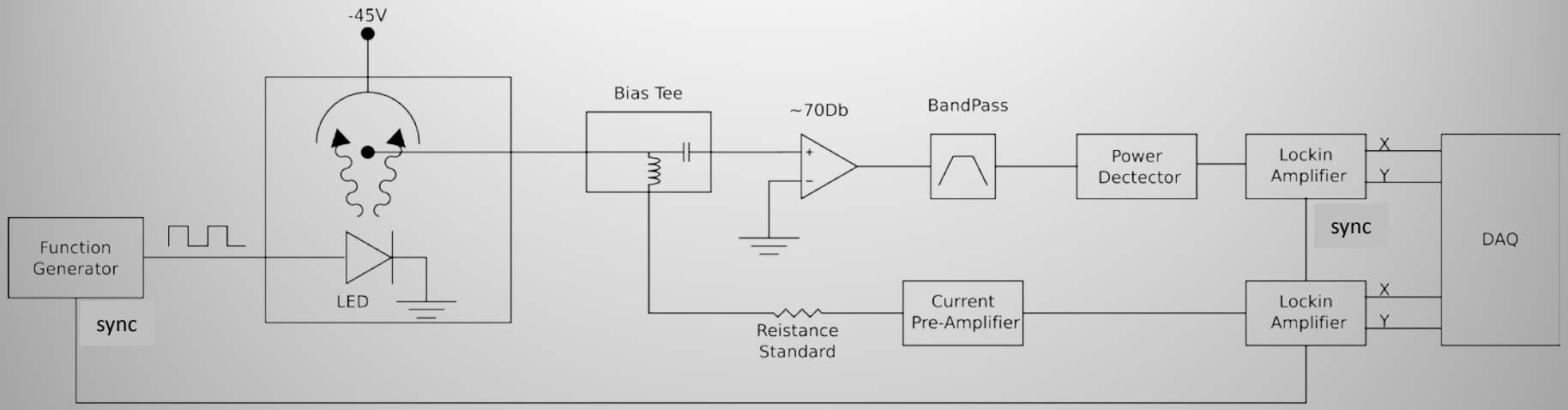
Using lock-in synced to bias eliminates Nyquist-Johnson contribution.

Improvements (not shown): on-chip impedance matching; low-*T* amplifiers.



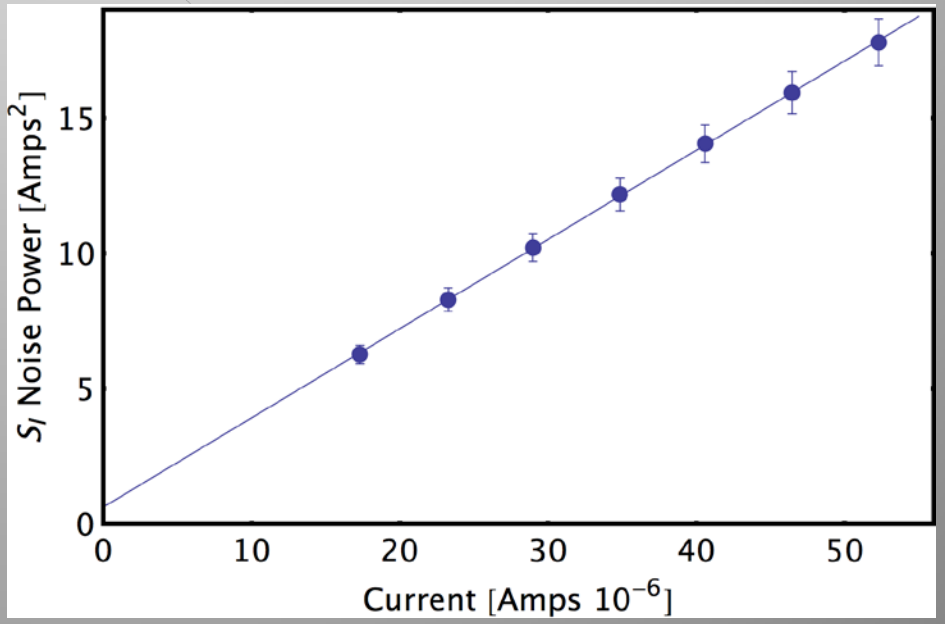
Wheeler *et al.*, Nano Lett. **10**, 1287 (2010)

Higher frequency approach to noise measurement



Test this approach using a vacuum photodiode as shot noise source.

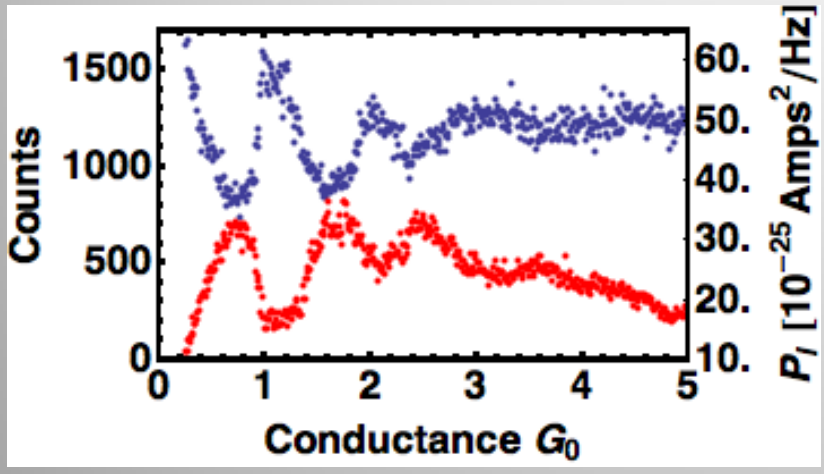
When corrected for impedance mismatch, find $S_I = 2\ e\ I$ to within 2%.

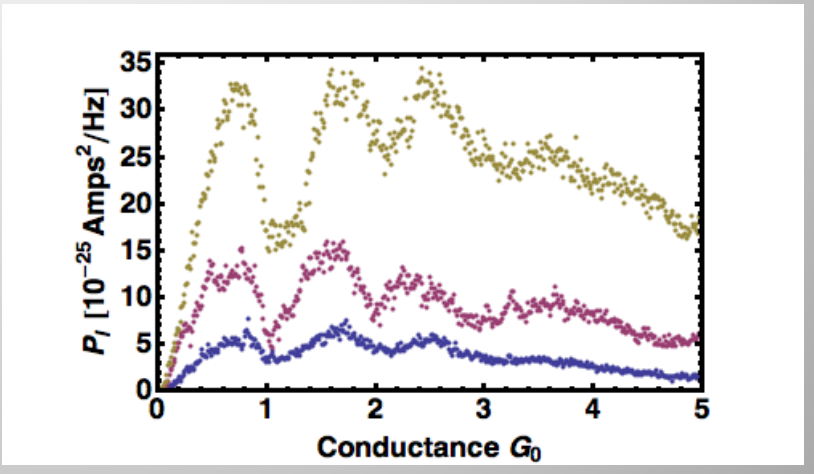


Wheeler *et al.*, Nano Lett. **10**, 1287 (2010)

Higher frequency approach to noise measurement

Wheeler *et al.*, Nano Lett. **10**, 1287 (2010)





Shot noise suppression at quantized conductance survives at 300 K.

Neat demonstration that quantum coherence is relevant at the few nm scale even at room temperature.

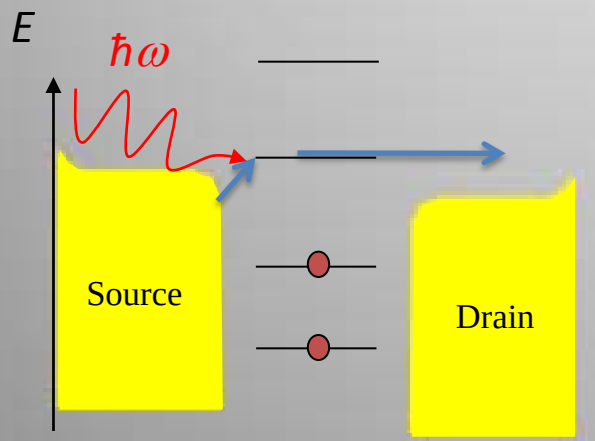
Optics and transport in nanojunctions

What happens in the presence of light?

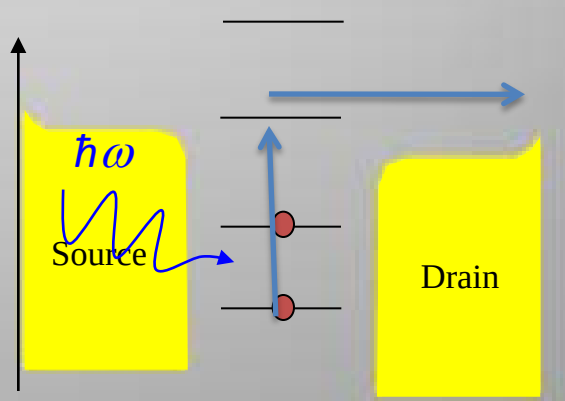
Things can become very complicated very quickly.

IR/visible light = molecular energy scales; microwaves = semiconductor dot scales

Photon-assisted tunneling

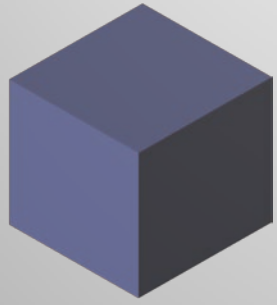


Internal state spectroscopy

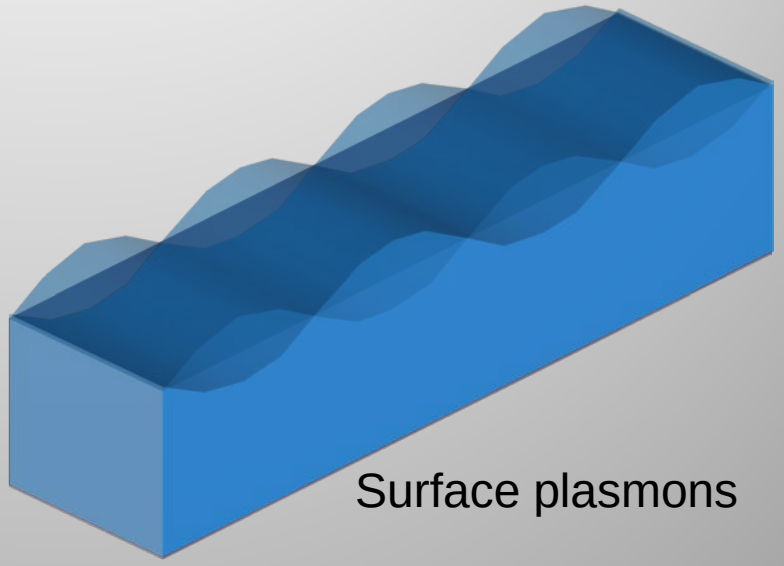


Plasmons

Plasmons = collective modes of (incompressible) electronic fluid



Bulk plasmons

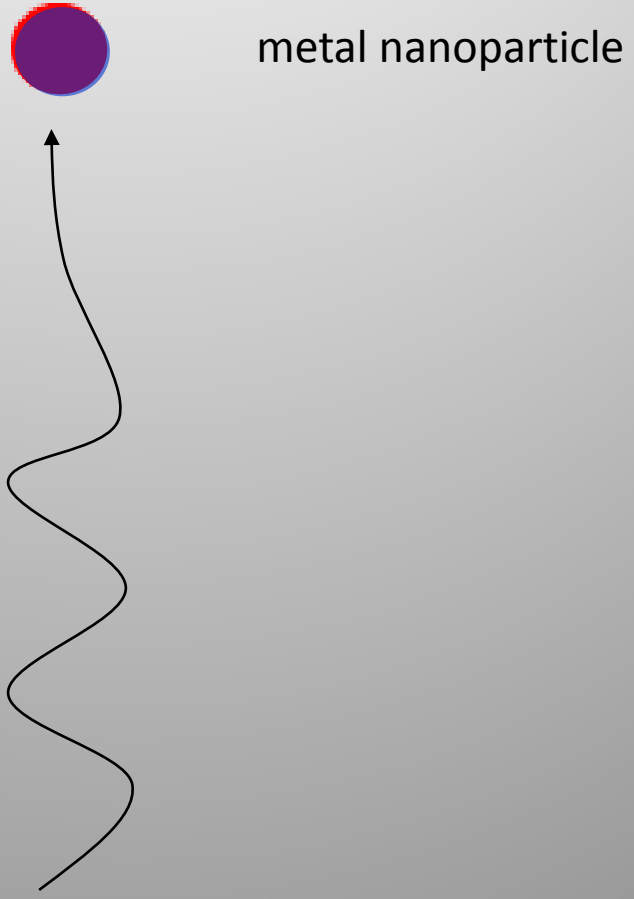


Surface plasmons

- Light can excite plasmons in metal nanostructures – big local electric fields.
- **Optical antennas**, producing voltages at optical frequencies.
- Those voltages are hard to measure, but they do have consequences….

Plasmons and surface-enhancement

Plasmons = sound waves in the electron fluid.



Plasmons and surface-enhancement

Plasmons = sound waves in the electron fluid.

metal nanoparticle

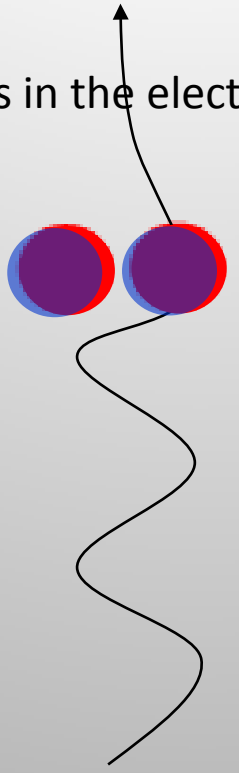
Plasmons and surface-enhancement

Plasmons = sound waves in the electron fluid.

metal nanoparticle

Plasmons and surface-enhancement

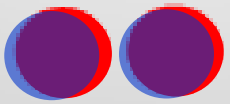
Plasmons = sound waves in the electron fluid.



metal nanoparticle dimer

Plasmons and surface-enhancement

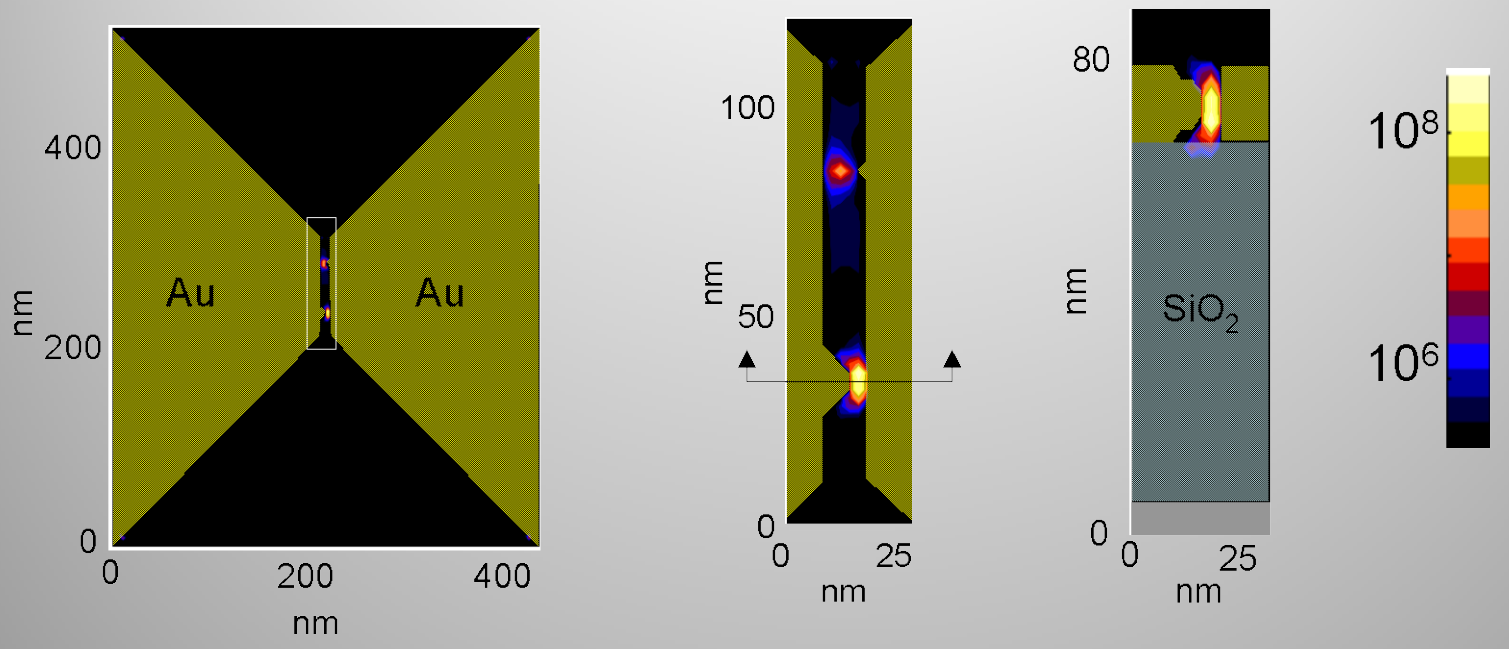
Plasmons = sound waves in the electron fluid.



metal nanoparticle dimer

- Local electric field can be much larger ($g(\omega)$) than incident field!
- Raman scattering rate ~ $g(\omega)^2\ g(\omega')^2$
- If $g(\omega)$, $g(\omega')$ ~ 1000 each, then Raman enhanced by 10^{12}.
- Single-molecule sensitivity possible in surface-enhanced Raman spectroscopy (SERS).

What are the plasmon modes here?



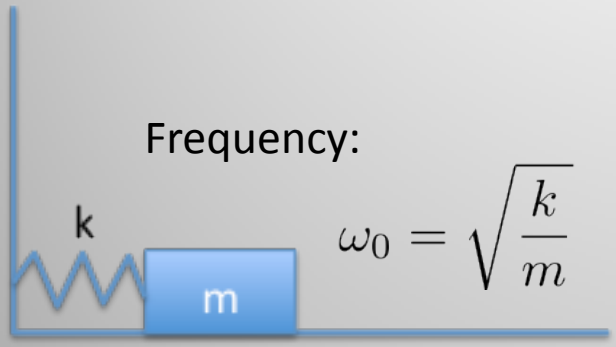
- EM calculations (FDTD) show that nanometer-scale protrusions can lead readily to intensity enhancements approaching 10^6 (!).
- Where do these highly local plasmon modes come from?

Hybridization

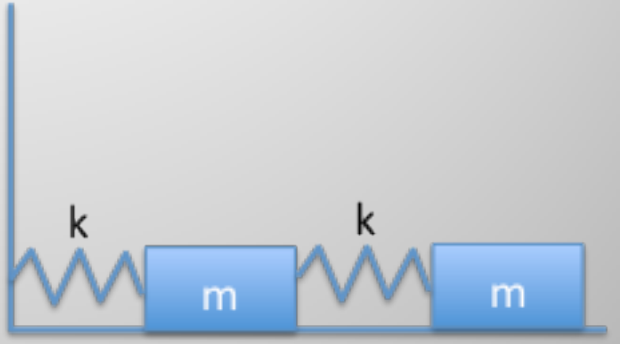
One oscillator

Frequency:

$$\omega_0 = \sqrt{\frac{k}{m}}$$

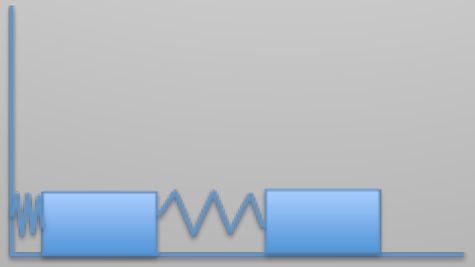


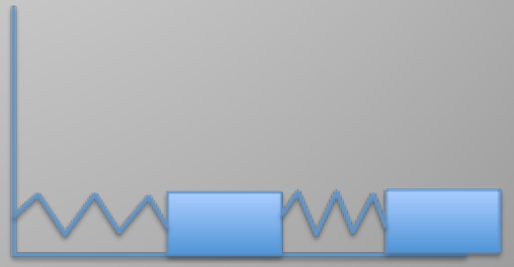
Coupled oscillators



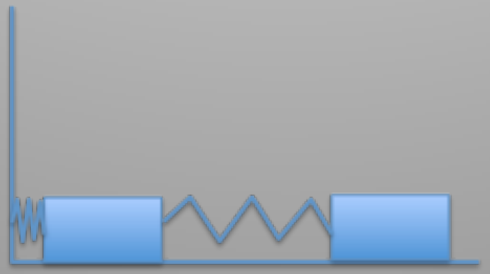
New eigenmodes!

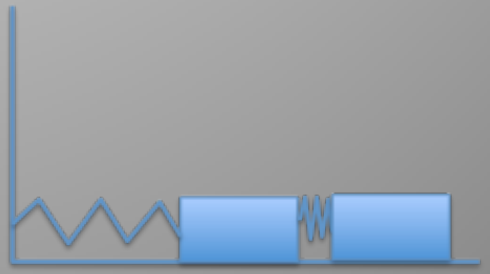
Symmetric
(lower frequency)



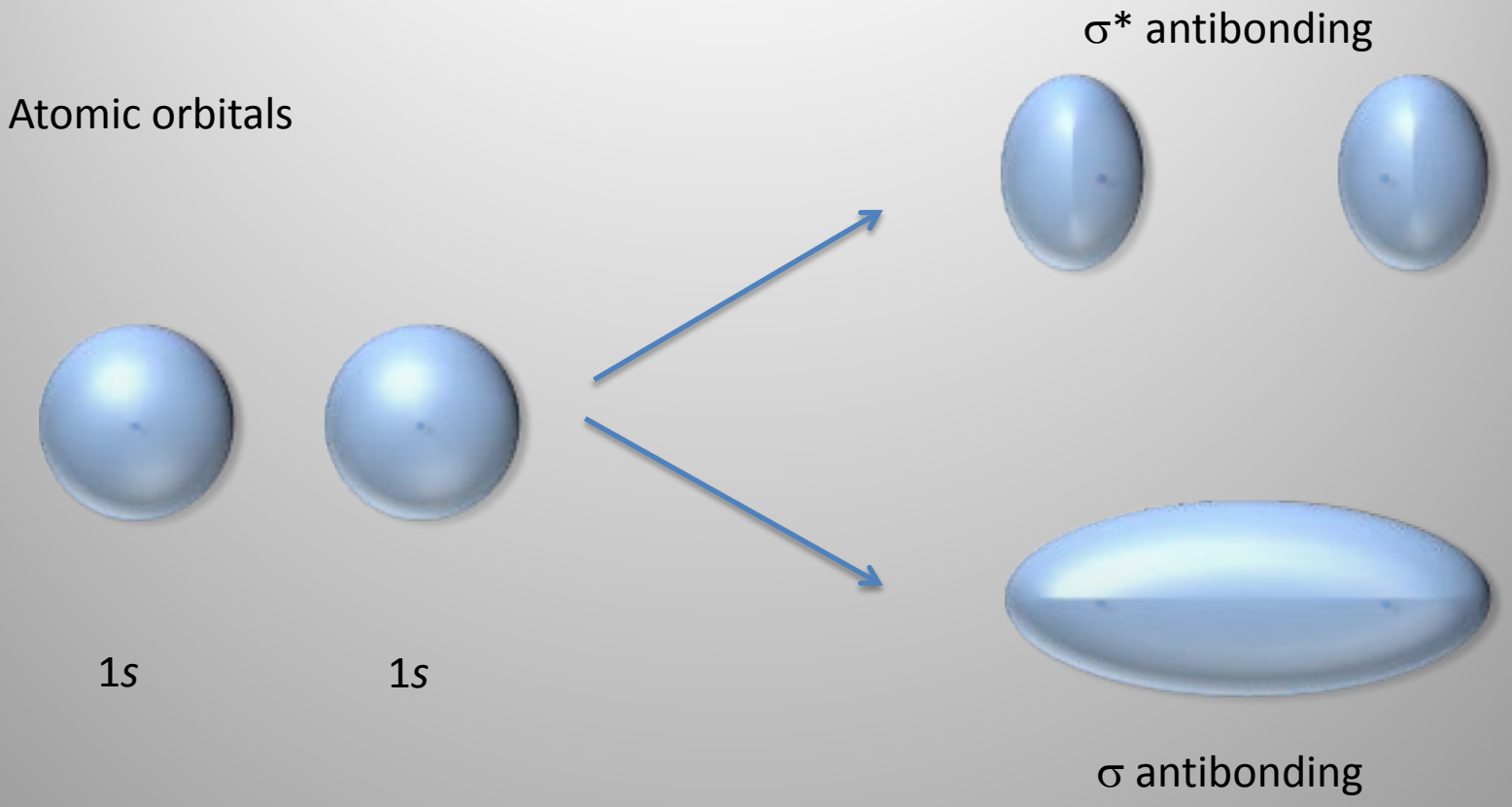


Anti-symmetric
(higher frequency)



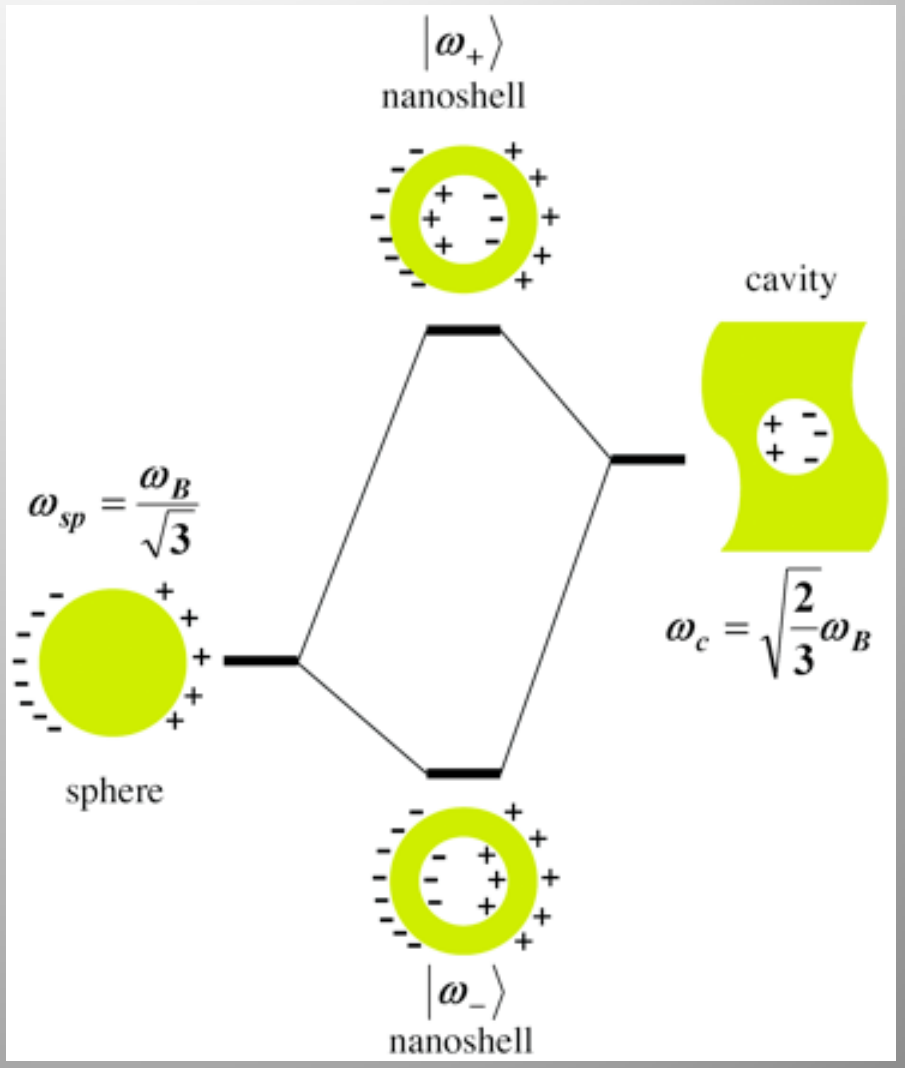


Hybridization



Plasmon hybridization

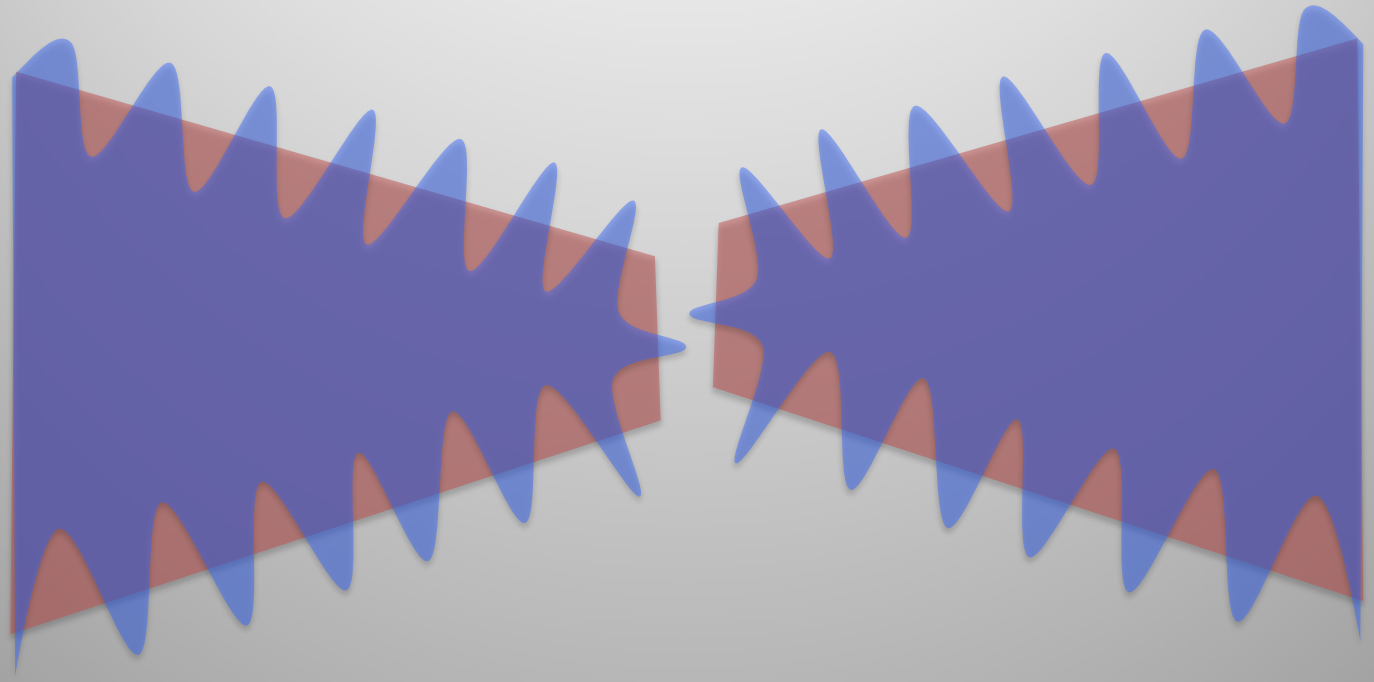
Same ideas can apply to plasmon modes in complex structures.



E. Prodan *et al*., Science **302** 419-422 (2003).

Plasmon hybridization

In our case, each electrode supports a *continuum* of edge plasmons.



Very local interaction = series of localized plasmon resonances “built out of” hybridized edge/surface plasmons from the electrodes.

Optical rectification

Tunneling nonlinearity can lead to DC current from AC bias.

$$I(V) = I_0(V_{\mathrm{dc}}) + \left(\frac{\partial I}{\partial V}\right)_{V_{\mathrm{dc}}} V_{\mathrm{ac}}\cos(\omega t) + \frac{1}{2}\left(\frac{\partial^2 I}{\partial V^2}\right)_{V_{\mathrm{dc}}} (V_{\mathrm{ac}}\cos(\omega t))^2 + \ldots$$

$$= \left[I_0(V_{\mathrm{dc}}) + \frac{1}{4}\left(\frac{\partial^2 I}{\partial V^2}\right)_{V_{\mathrm{dc}}} V_{\mathrm{ac}}^2\right] + \left(\frac{\partial I}{\partial V}\right)_{V_{\mathrm{dc}}} V_{\mathrm{ac}}\cos(\omega t) - \frac{1}{4}\left(\frac{\partial^2 I}{\partial V^2}\right)_{V_{\mathrm{dc}}} V_{\mathrm{ac}}^2\cos(2\omega t) + \ldots$$

Light induces some V_{opt} across our gap, oscillating at ~ 10^{15} Hz.

Rectification (photocurrent) can lead to a means of quantitatively estimating the field enhancement factor! (*provided that tunneling is fast!*)

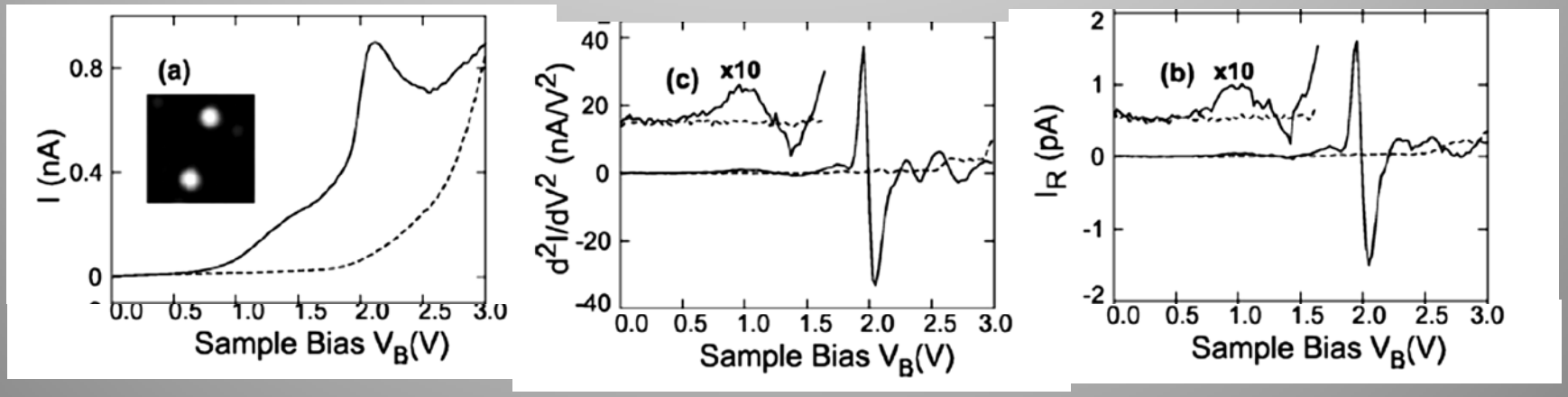
Optical rectification

This has been shown to work quantitatively at microwave frequencies.

THE JOURNAL OF CHEMICAL PHYSICS **124**, 021105 (2006)

Atomic-scale rectification at microwave frequency

X. W. Tu, J. H. Lee,[a] and W. Ho[b]
Department of Physics and Astronomy and Department of Chemistry, University of California, Irvine, California 92697-4575



Validity of classical rectification

In general, correct quantum treatment = **photon-assisted tunneling**.

Tien-Gordon (perturbative) approach:

$$\alpha \equiv \frac{eV_{\rm ac}}{\hbar\omega}$$

$$I(V_{\rm dc};\alpha,\omega) = \sum_{n=-\infty}^{\infty} J_n^2(\frac{\alpha}{2}) I_0(V_{\rm dc} + n\hbar\omega/e)$$

First order in alpha:

$$\begin{aligned} I(V_{\rm DC}, V_{\rm opt}, \omega) - I(V_{\rm DC}) &= I(V_{\rm dc};\alpha,\omega) - I_0(V_{\rm dc}) \\ &= \frac{1}{4} V_{\rm ac}^2 \left[\frac{I(V_{\rm dc}+\hbar\omega/e) - 2I(V_{\rm dc}) + I(V_{\rm dc}-\hbar\omega/e)}{(\hbar\omega/e)^2} \right]. \end{aligned}$$

If α << 1 and nonlinearity varies little (i.e., DOS is "boring") over

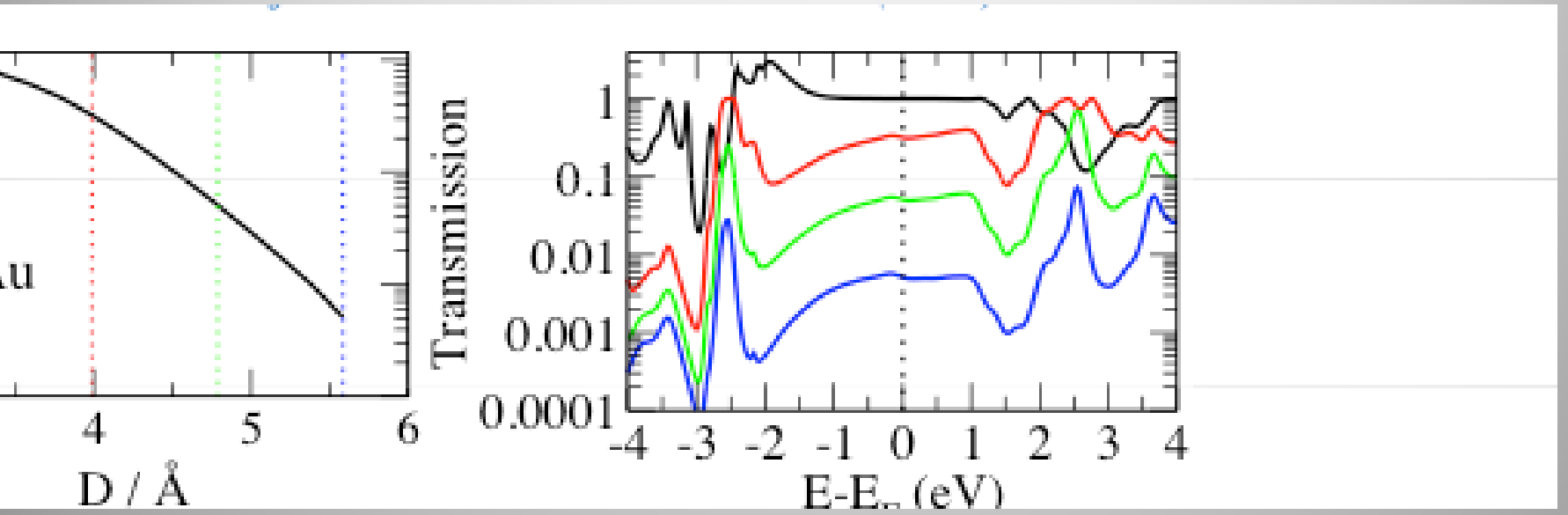
$$[(E_{\rm F} + eV_{\rm dc}) - \hbar\omega/e, (E_{\rm F} + eV_{\rm dc}) + \hbar\omega/e]$$

then classical rectification picture is reasonable.

J. C. Cuevas

Validity of classical rectification

Viljas and Cuevas, PRB **75**, 075406 (2007)



DFT calculations originally done for Au contacts show that we are likely in luck as far as DOS goes, as long as junctions are *clean*.

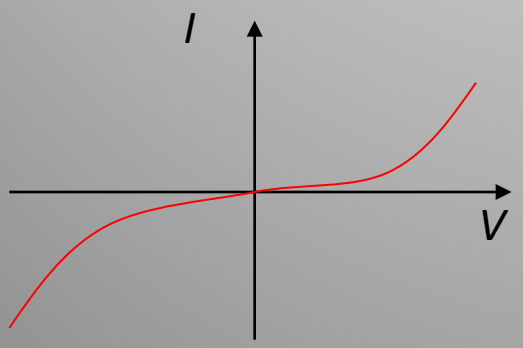
Optical rectification

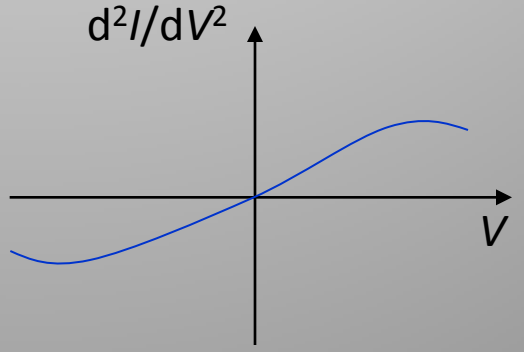
How would this work?

- Use low freq measurement ($\omega_{low} = 2\pi \times 2$ kHz) with known V_{ac} , and use lock-in at $2\omega_{low}$ to measure (d^2I/dV^2) as a function of V_{dc}.

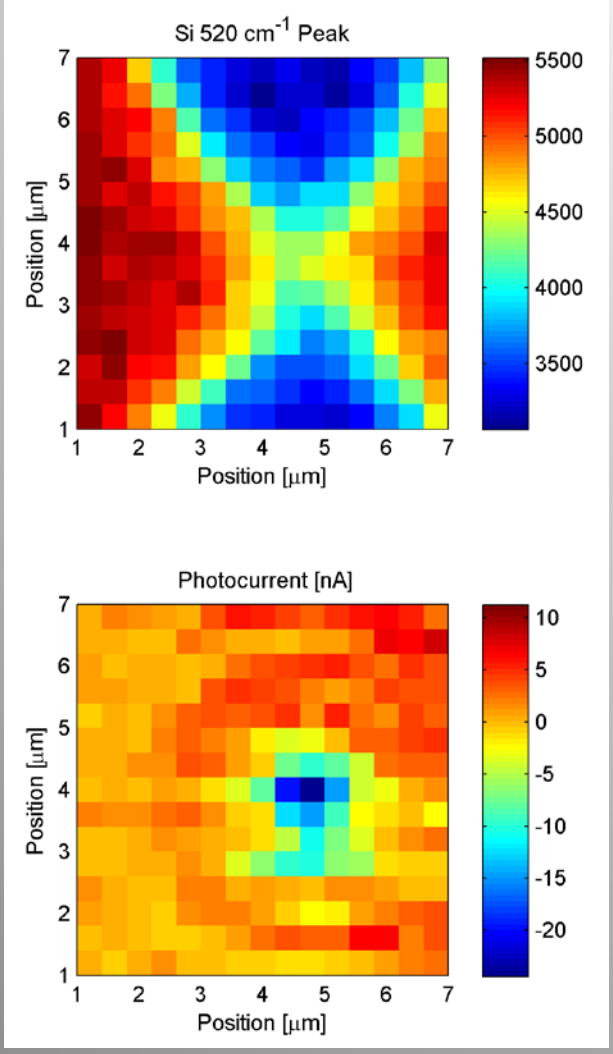
- Simultaneously, measure the photocurrent as a function of V_{dc} (use a second lock-in and chop the light).

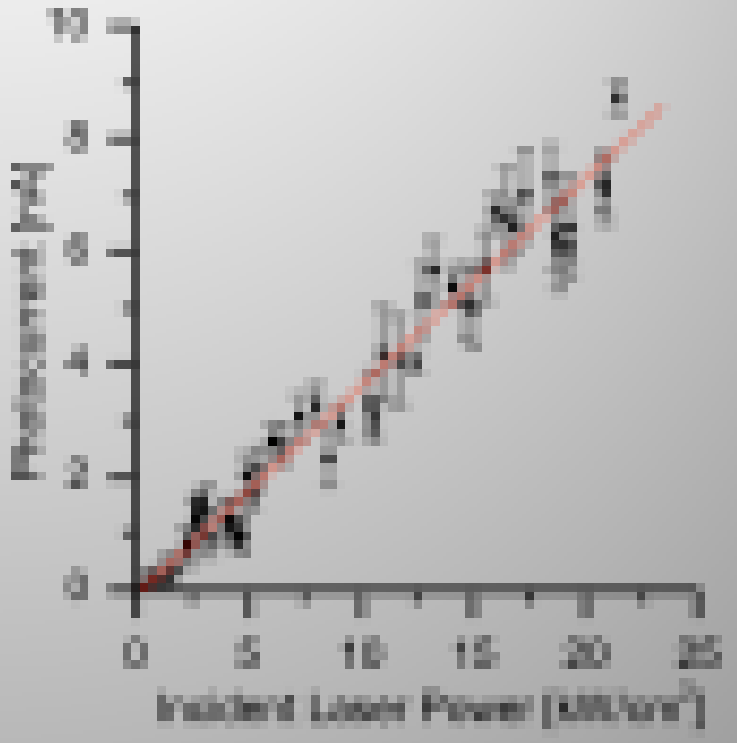
- Adjust V_{ac} until the two signals (2nd harmonic + photocurrent) are identical. Voila – V_{ac} should now = V_{opt}.



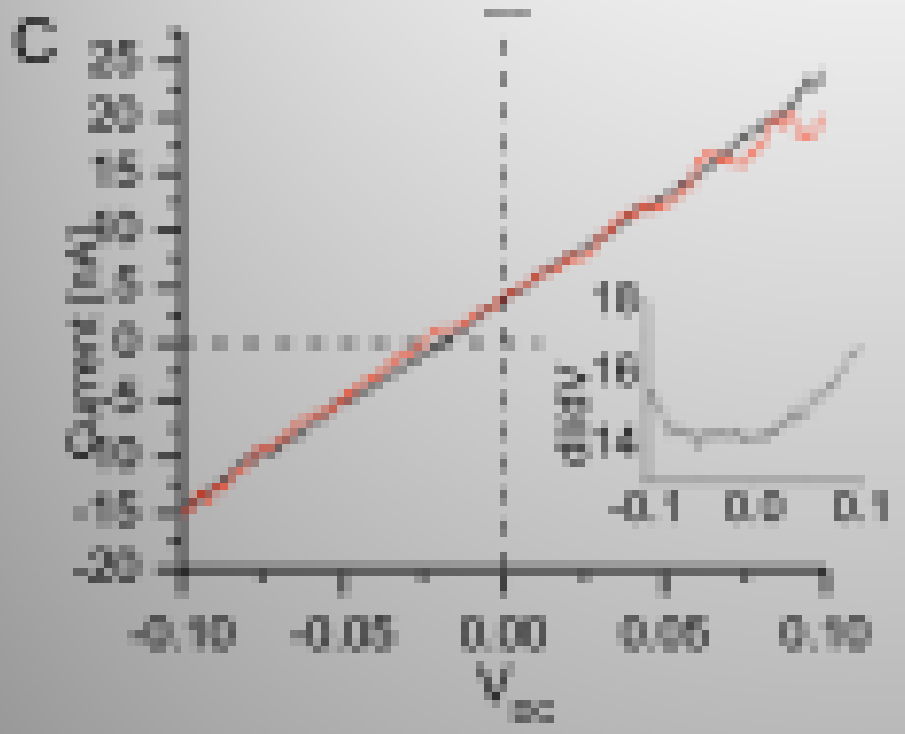


Cross-checks





Examples:



d*I*/d*V* in units of nA/V.

Quantitative agreement between I_{photo} and $(1/4)d^2I/dV^2\ V_0^2$ happens when V_0 = 32.4 mV.

Measured d*I*/d*V* at V_{dc} = 0 implies an interelectrode gap of ~ 0.092 nm, implying local field = 3.6 x 10^8 V/m.

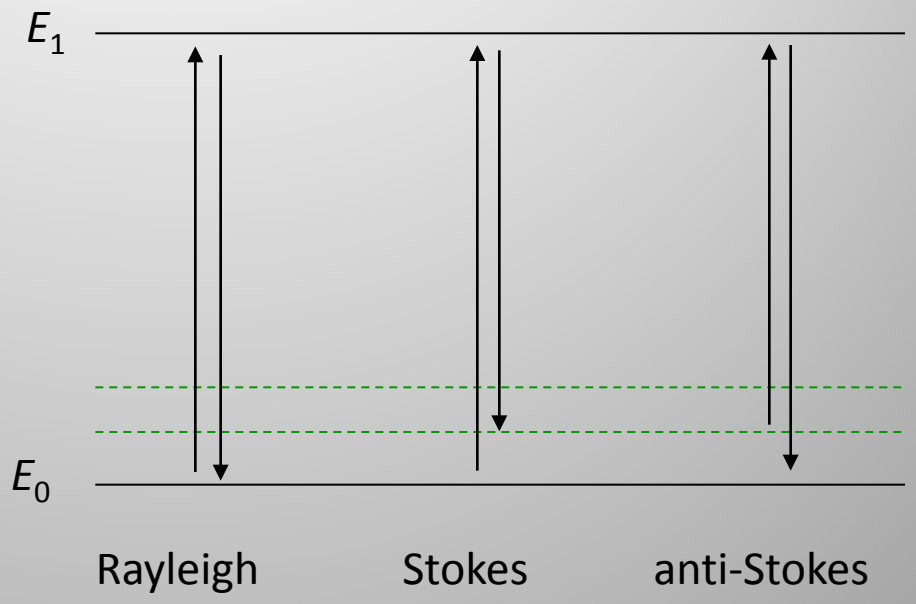
Implied field enhancement ~ 1230x

Raman spectroscopy

Optics provides additional access to microscopic distributions.

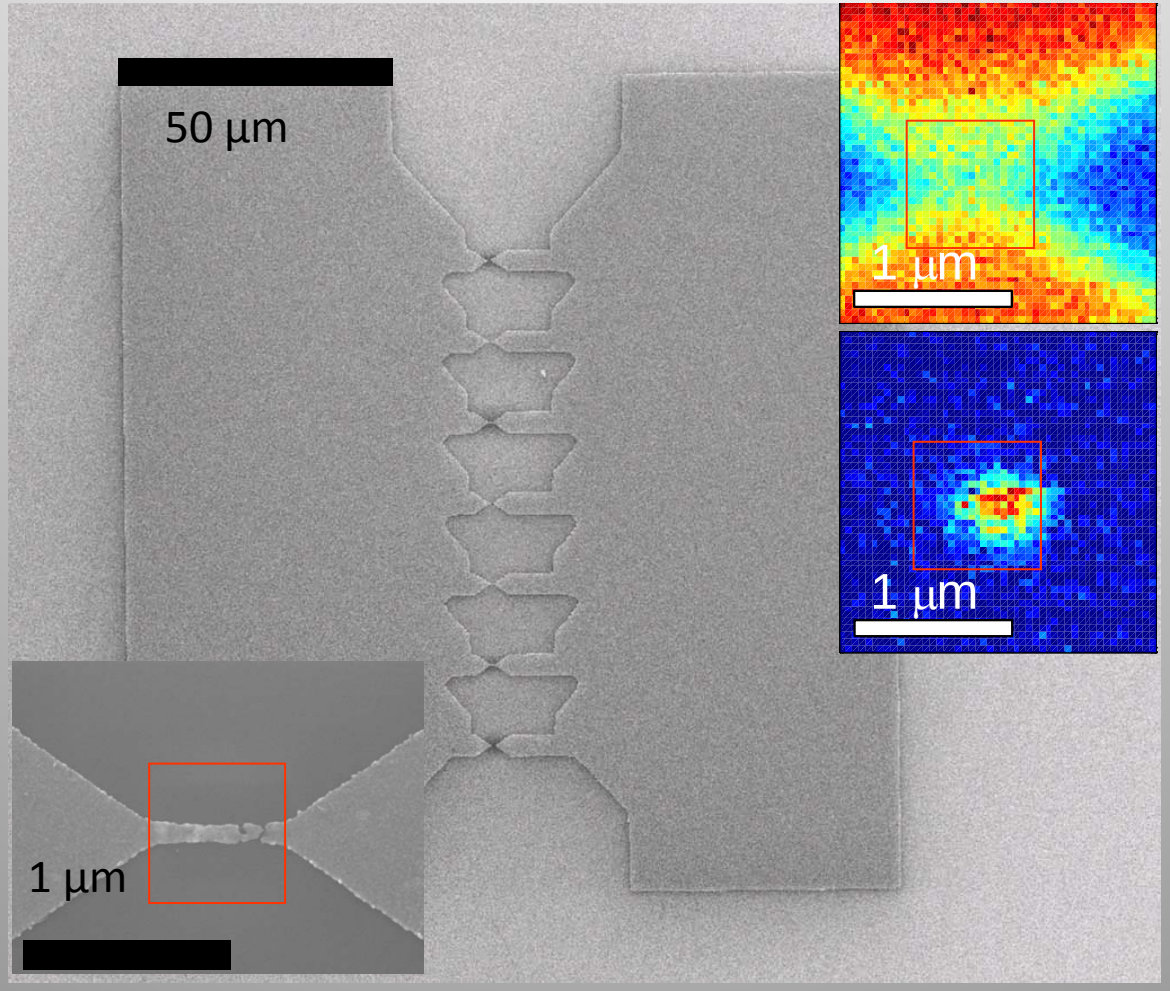
In particular, for molecular junctions, use ***Raman***.

- Inelastic light scattering.
- Requires $\alpha = \alpha(r)$.
- Time-varying r from vibrations (ω_0) leads to sum + difference frequency generation with incident light (ω).



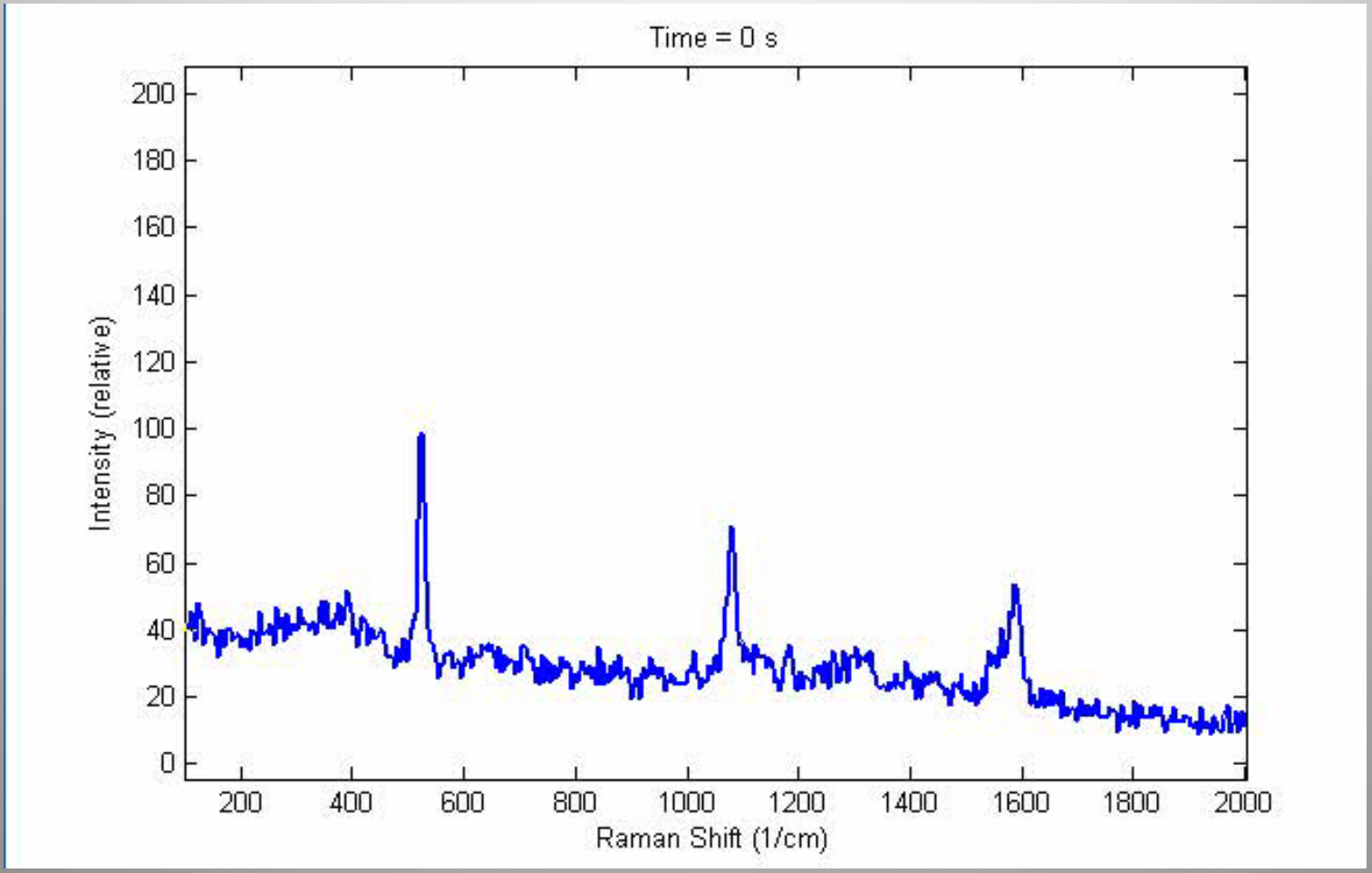
- Cross sections typically 10^{-29} cm^2 - very small!
- Stokes/anti-Stokes ratio can tell you temperature due to Boltzmann occupancy factor.

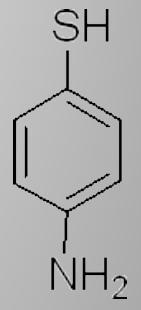
Raman spectroscopy of nanoscale gaps



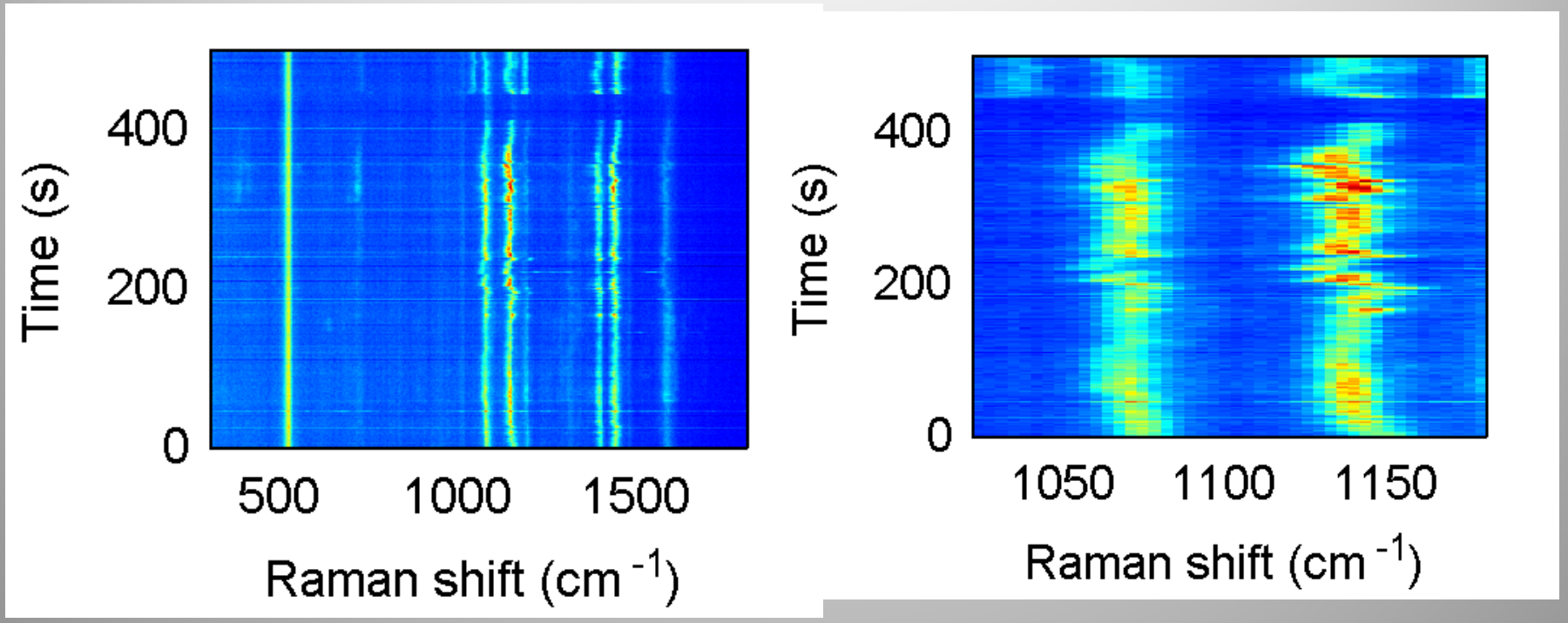
Nanoscale gaps are ***ideal*** for surface-enhanced Raman spectroscopy.

Raman spectroscopy of nanoscale gap



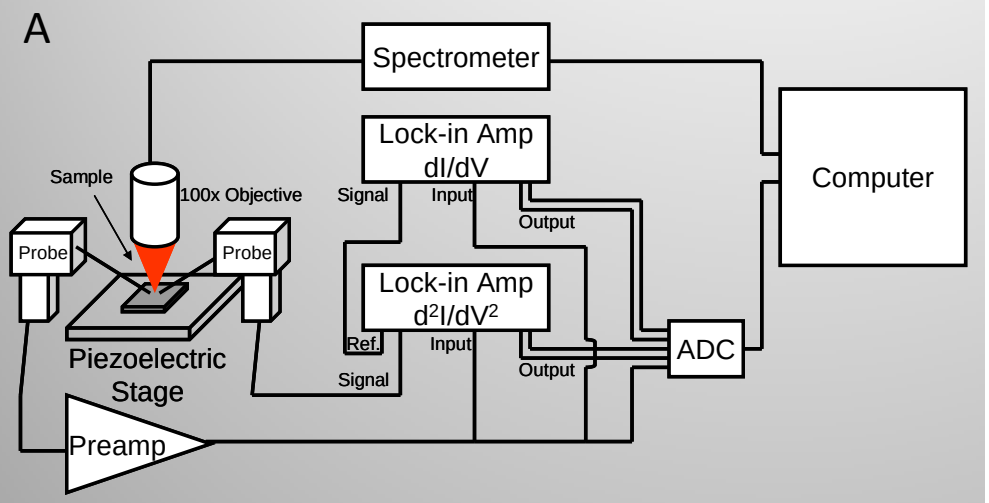


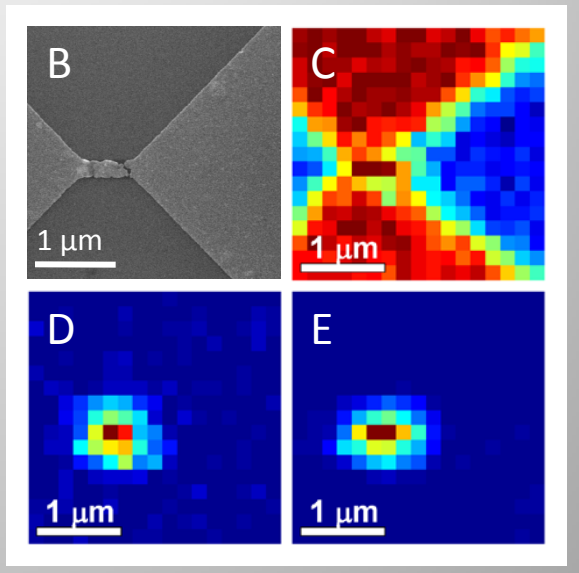
Vibrational Spectroscopy



- At nanogap, large SERS signal, “blinking”, and spectral diffusion.
- Simultaneous transport + Raman would open *many* possibilities.

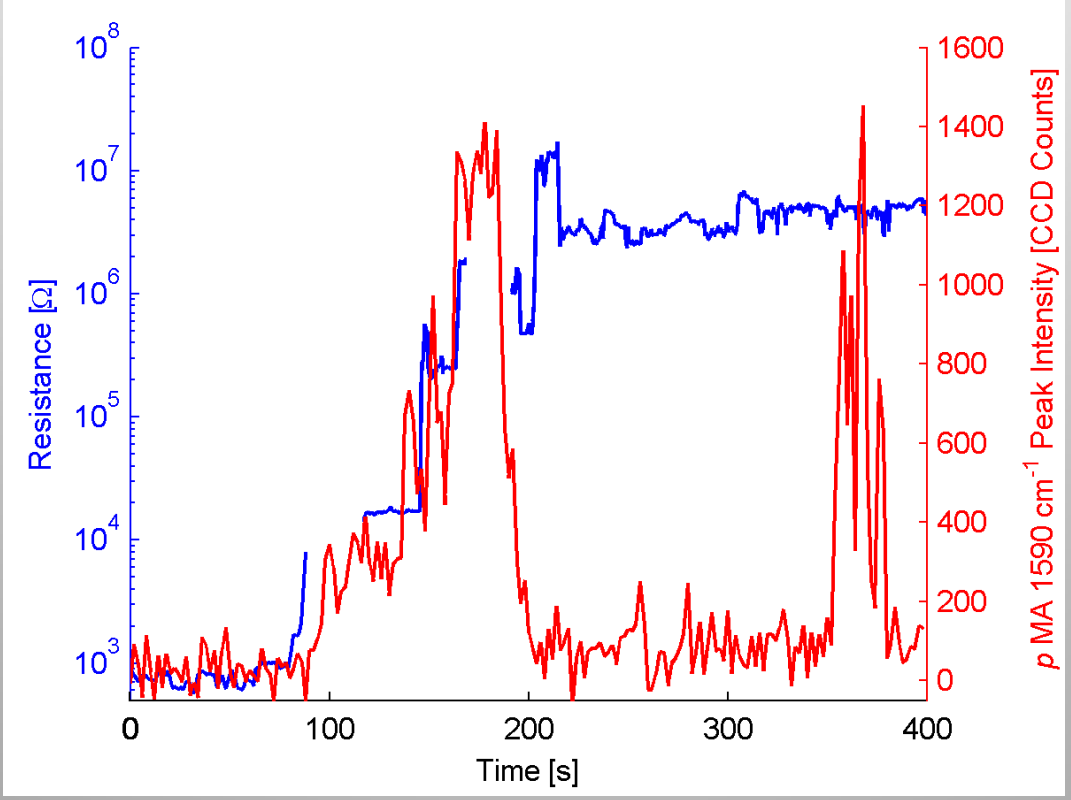
Vibrational Spectroscopy





Remember, data so far taken in air, at room temperature.

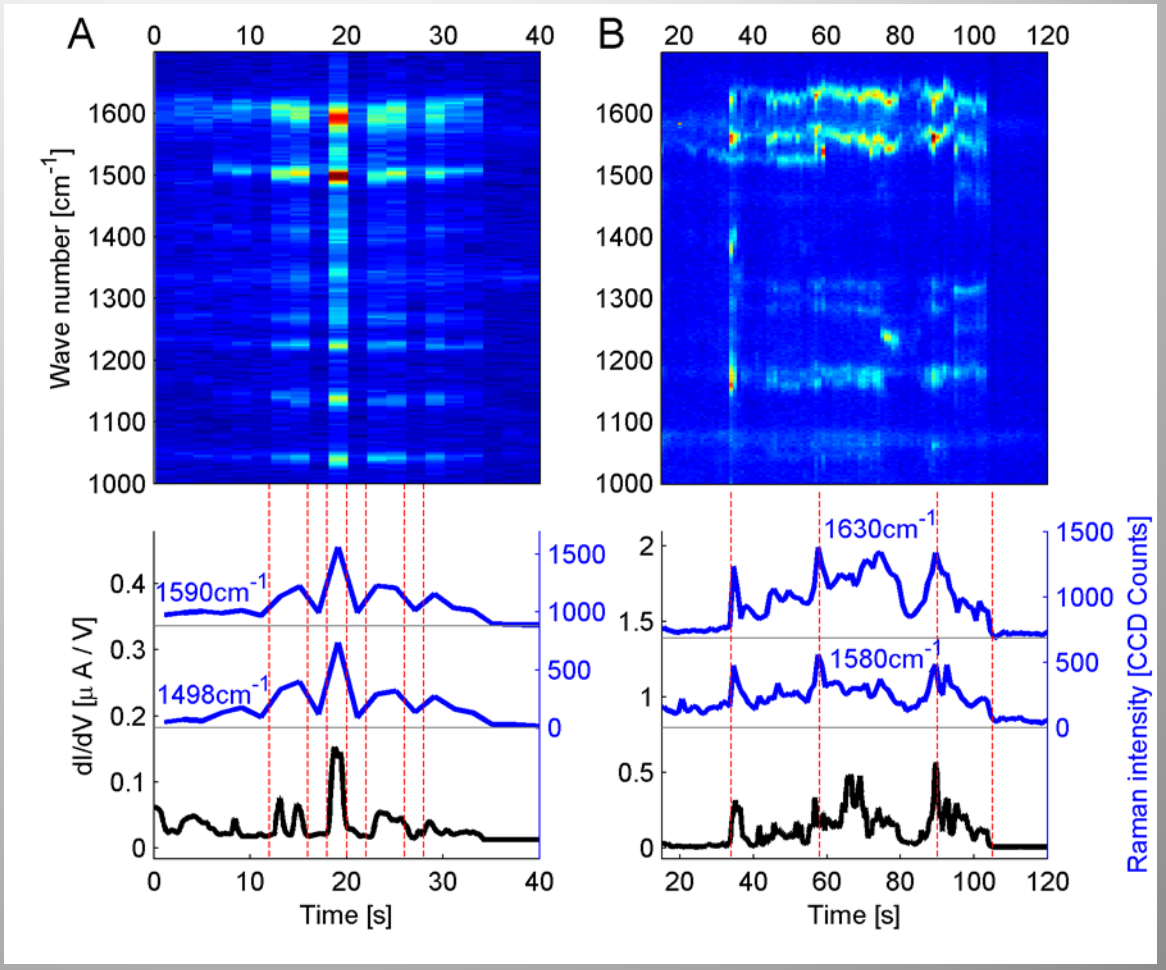
Transport + SERS

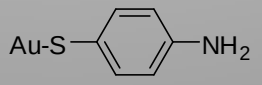


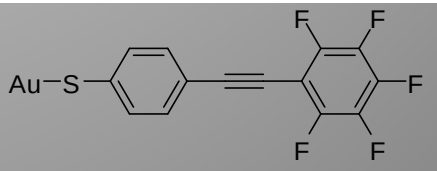
- Enhancement “turns on” as junction is migrated.
- Inter-electrode plasmon modes form once conductance ~ 10^{-4} S.

Transport + SERS

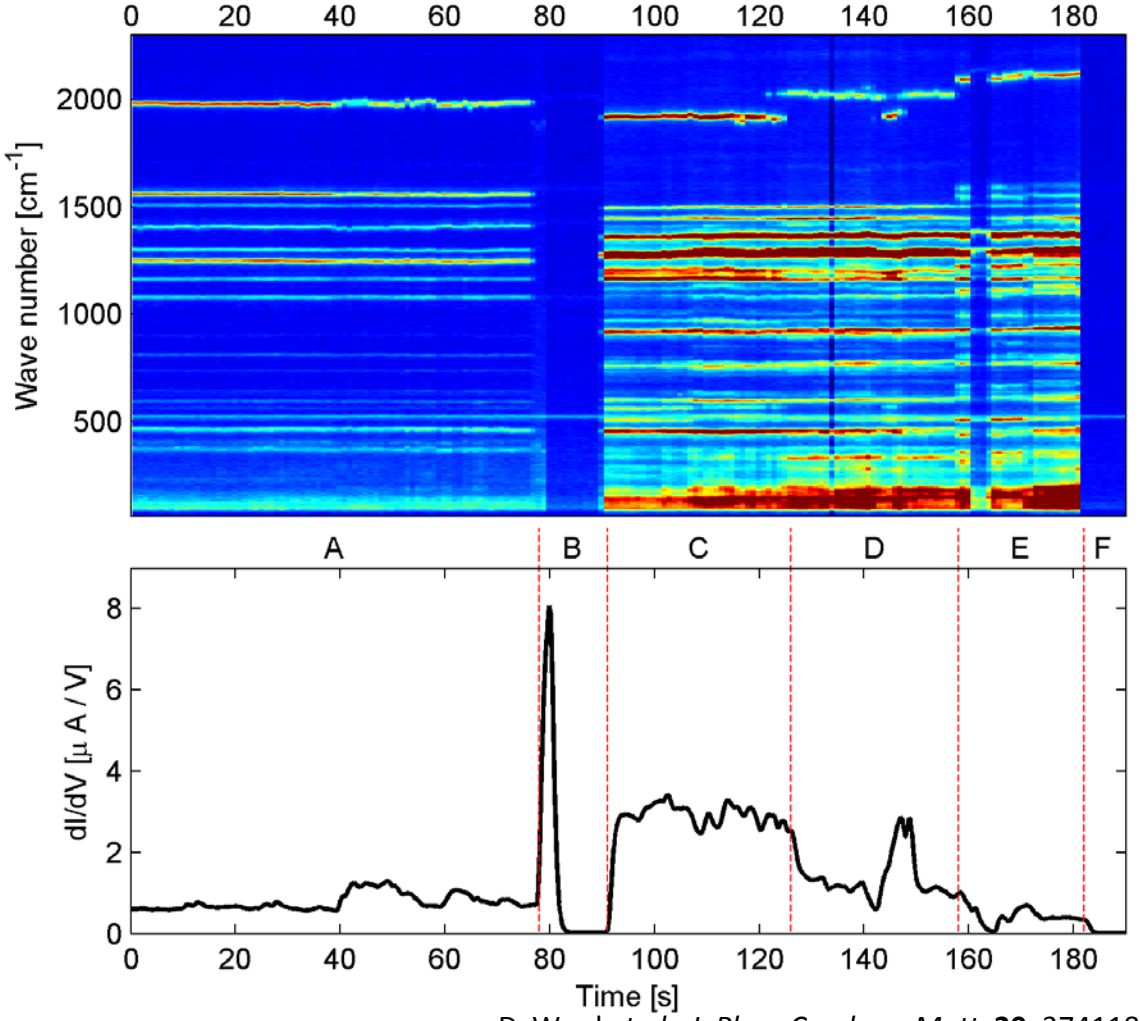
- Raman and transport correlate very strongly in time.
- **Demonstrates single-molecule Raman sensitivity.**

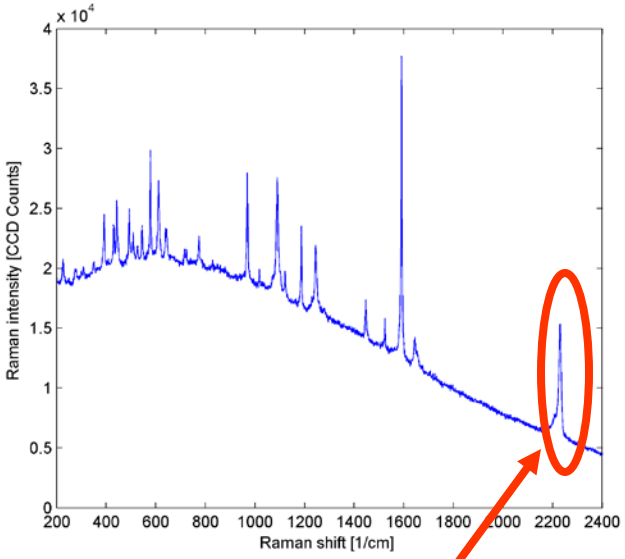


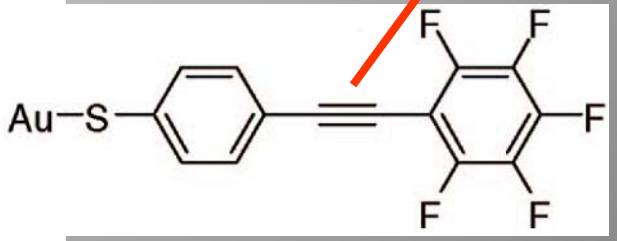




Simultaneous conduction + SERS







D. Ward *et al.*, *J. Phys. Condens. Matt.* **20**, 374118 (2008).

Stokes-AntiStokes and local temperature

$$\frac{AS(\omega')}{S(\omega)} = \left(\frac{\sigma_{AS}}{\sigma_S}\right)\left(\frac{g(\omega')}{g(\omega)}\right)^2\left(\frac{\omega'}{\omega}\right)^4 \exp\left(-\frac{\hbar\delta\omega}{k_B T_{eff}}\right)$$

- Ratio of antiStokes to Stokes intensities provides a measure of excited state population, and therefore ***effective*** temperature.

- The exponential makes things challenging.

Ignoring cross-section and enhancement issues,
450 cm^{-1} mode at 80 K → AS/S = 3.8×10^{-4}.
So, 10000 Stokes counts → 3.8 antiStokes counts

- SERS itself can lead to optical pumping of excited state.

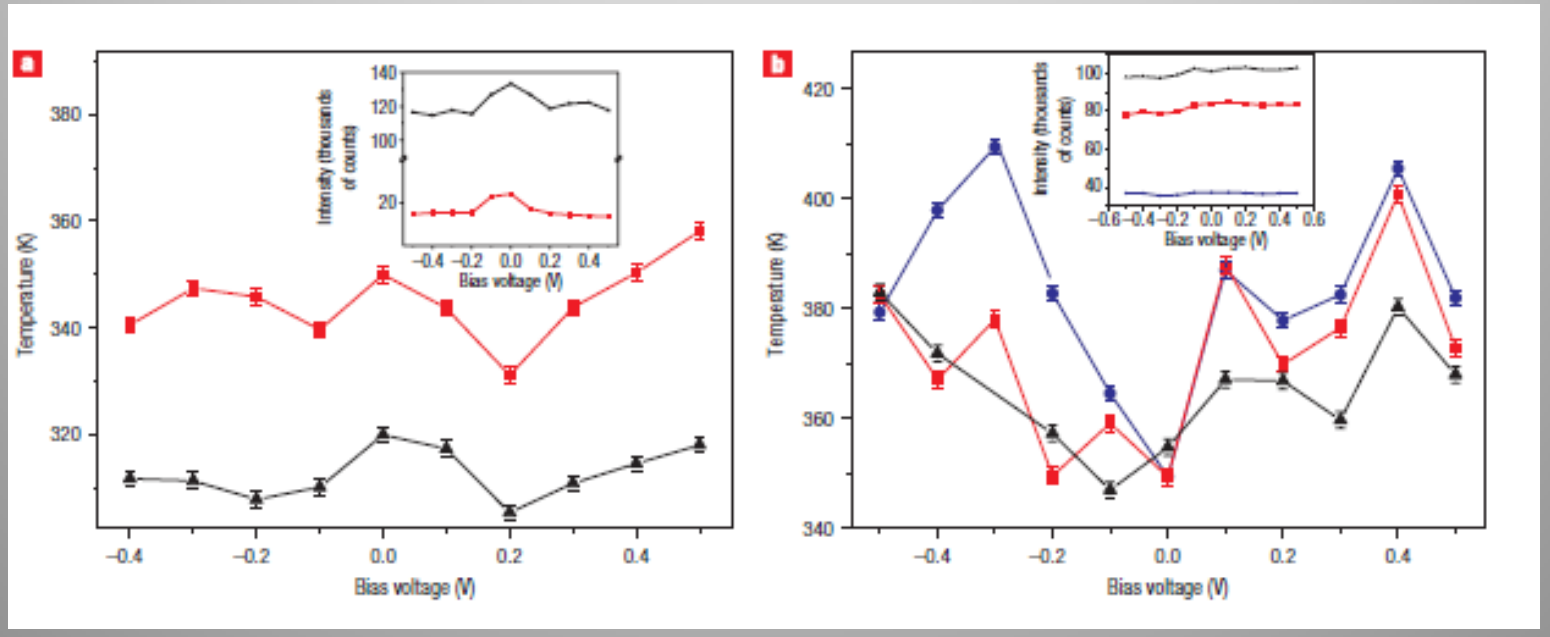
Can we see bias-driven effects?

Stokes-AntiStokes and local “temperature”

Detection of heating in current-carrying molecular junctions by Raman scattering

ZVI IOFFE†, TAMAR SHAMAI†, AYELET OPHIR, GILAD NOY, ILAN YUTSIS, KOBI KFIR, ORI CHESHNOVSKY* AND YORAM SELZER*

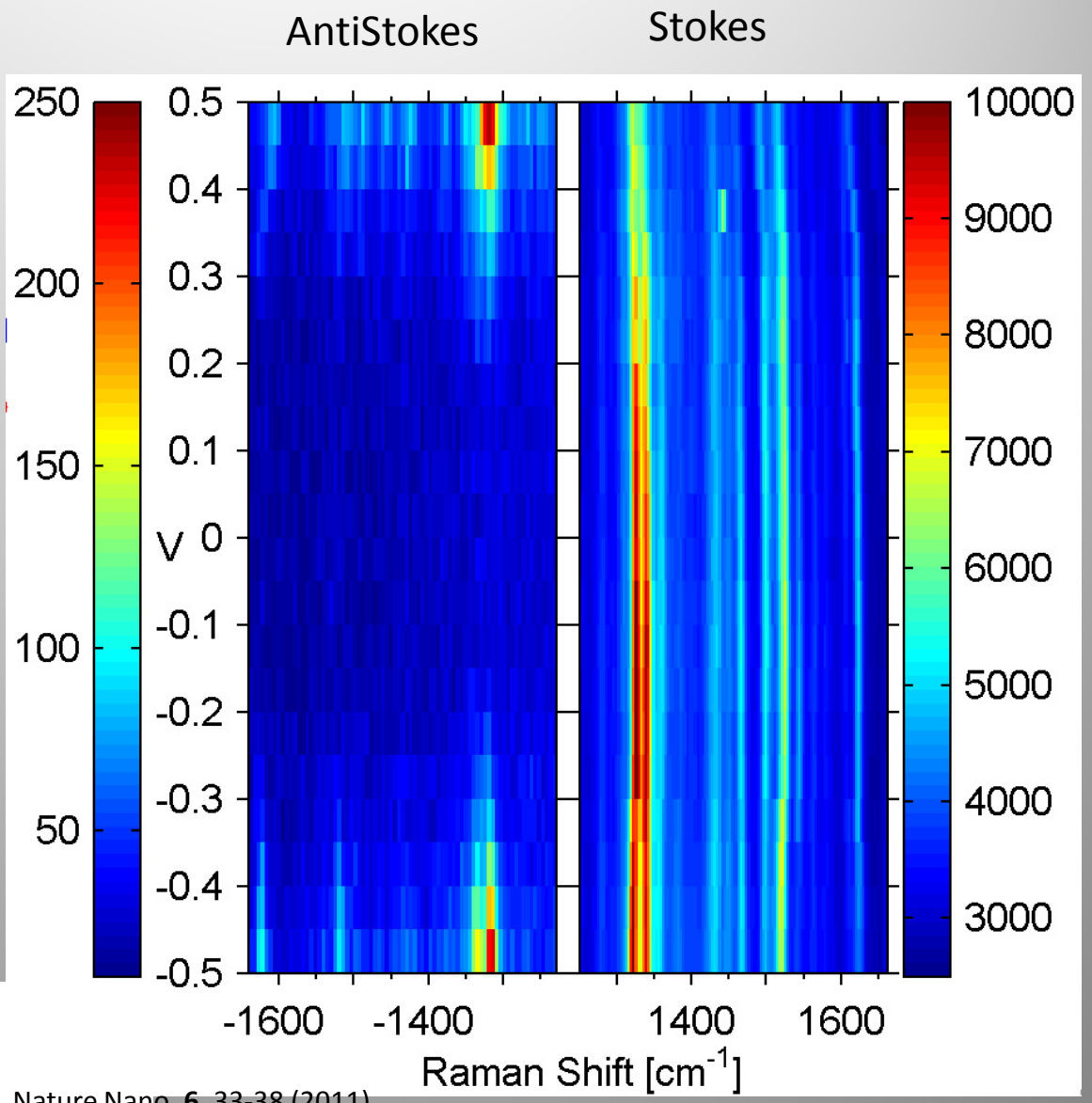
Nature Nanotechnology **3**, 727 - 732 (2008)



Suggestive, though puzzling.

Electrical vibrational pumping

As bias is increased and current starts to flow, antiStokes Raman lines turn on!

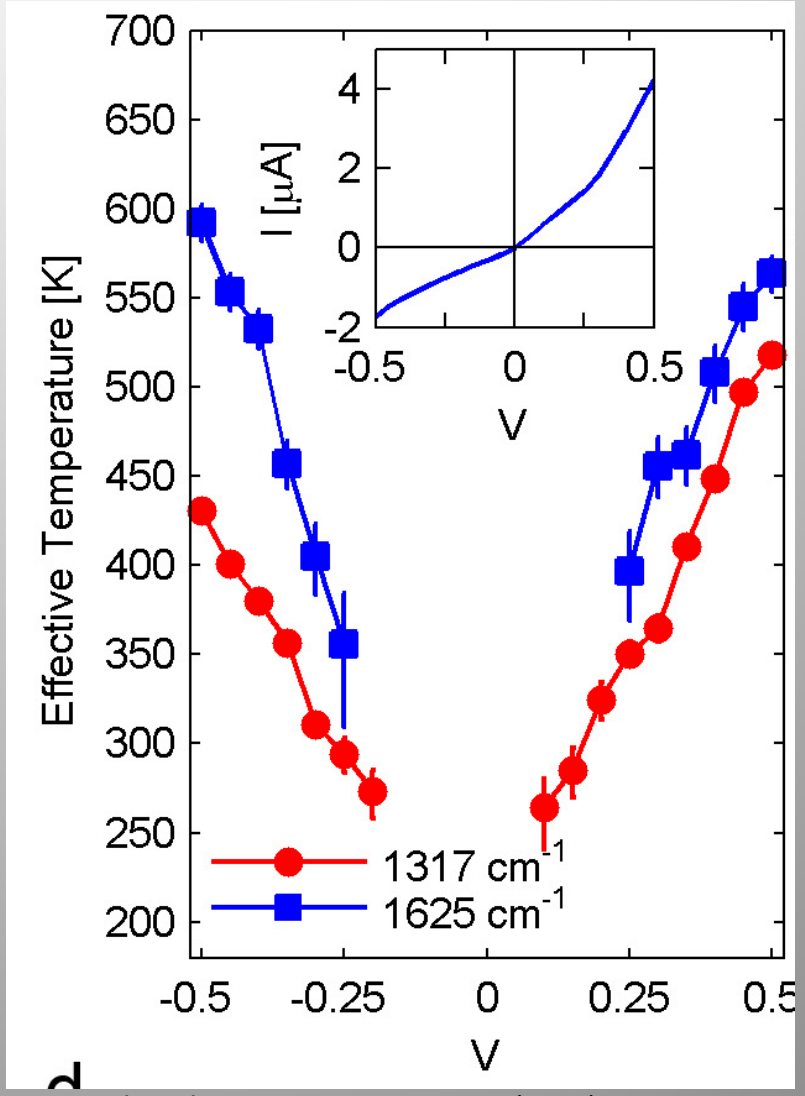


D. Ward *et al.*, Nature Nano. **6**, 33-38 (2011).

Electrical vibrational pumping

As bias is increased and current starts to flow, antiStokes Raman lines turn on!

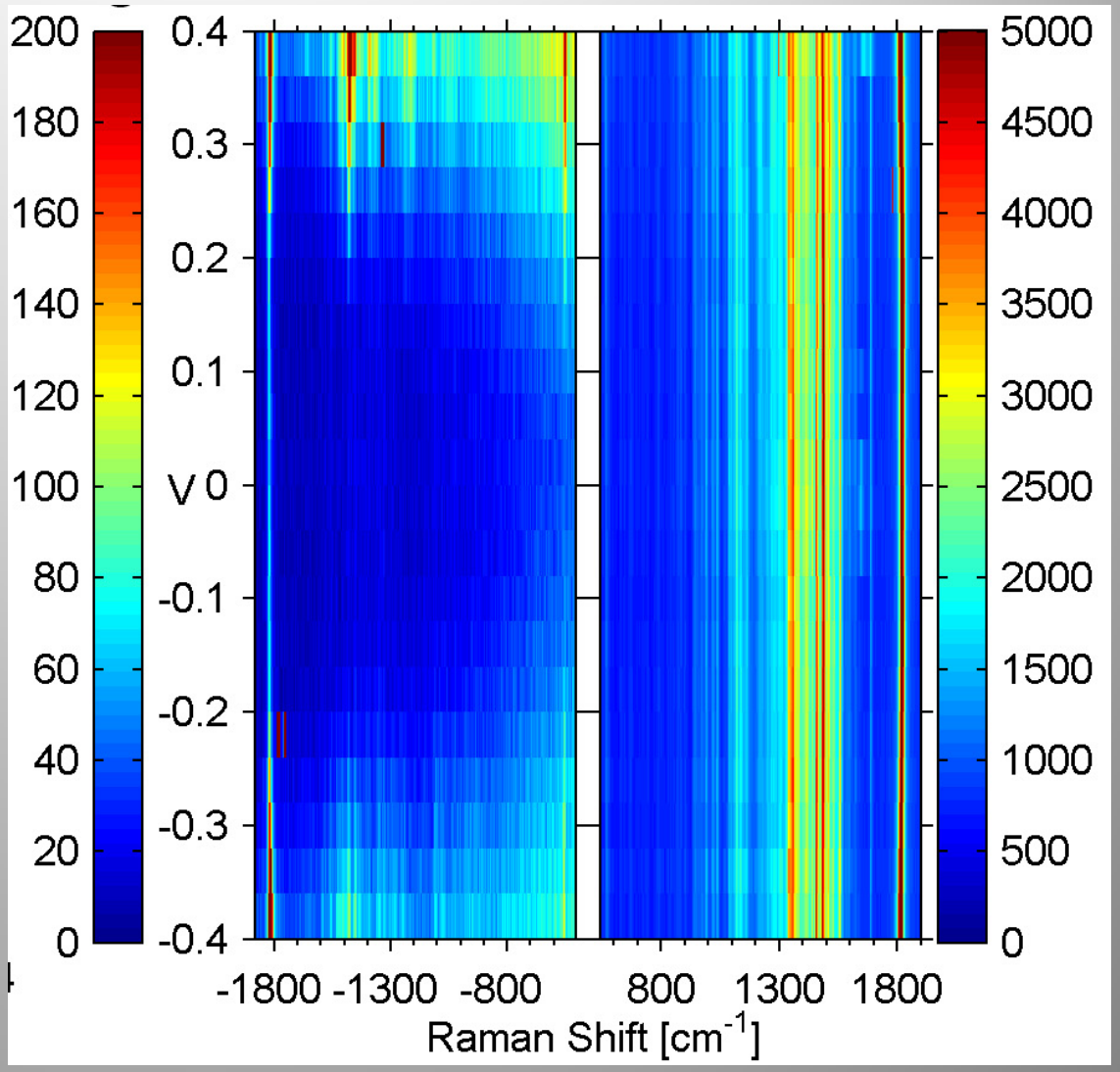
From AS/S ratio, can infer ***effective*** vibrational temperatures – really a measure of vibrational occupancy.



D. Ward *et al.*, Nature Nano. **6**, 33-38 (2011).

Electrical and optical vibrational pumping

A second example….

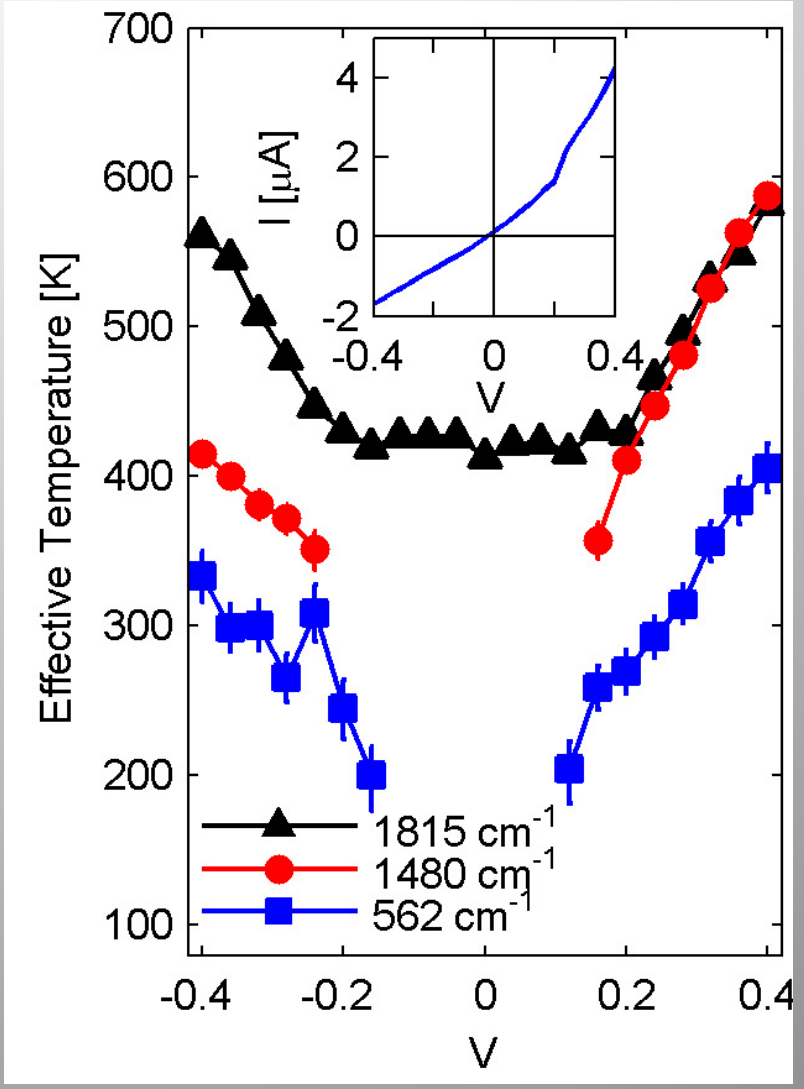


D. Ward *et al*., Nature Nano. **6**, 33-38 (2011).

Electrical and optical vibrational pumping

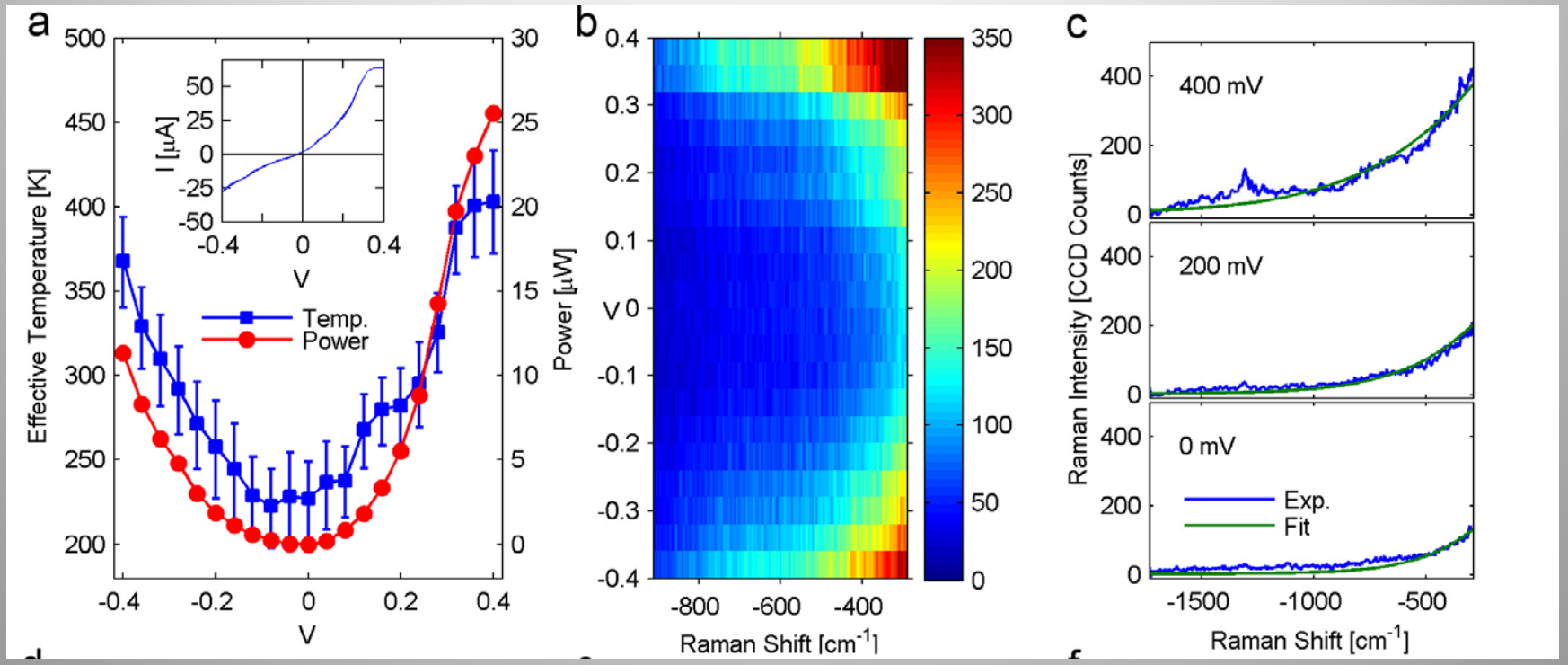
Optically pumped line always well above ambient *T*.

Asymmetry in conduction = asymmetry in heating.



D. Ward *et al*., Nature Nano. **6**, 33-38 (2011).

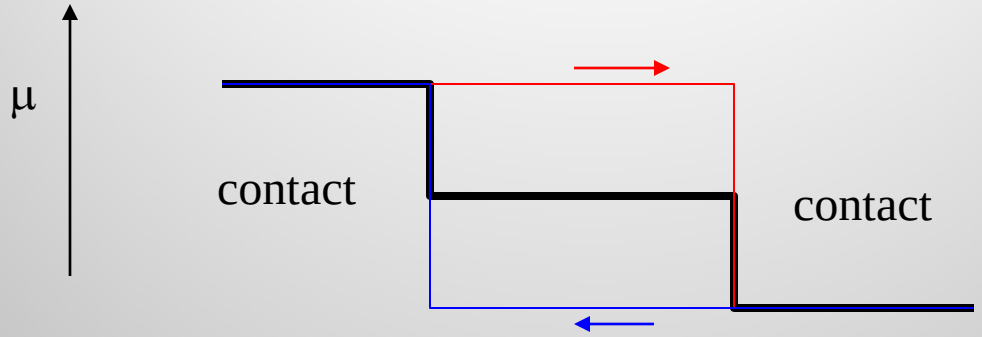
Electronic heating, too.



- SERS Stokes continuum thought to be *electronic Raman*.
- AntiStokes only possible due to electrons above the Fermi energy.
- AntiStokes continuum increases with bias!
- Can fit using Fermi distribution to find **effective** *electron* temperature.

D. Ward *et al*., Nature Nano. **6**, 33-38 (2011).

Significant electronic heating is a surprise



- Landauer-Buttiker picture of transport assumes that all dissipation happens “far away” from the junction….
- Right-moving carriers are at chemical potential of left side until they reach right contact.
- Left-moving carriers are at chemical potential of right side until they reach left contact.
- Bold curve represents average of chemical potential.

Part II Take-home Messages

- Noise provides valuable information beyond basic dc transport.

- Specific predictions exist for noise and how it is modified by, e.g., Kondo, though not in the case of molecules.

- Optical methods provide other ways of accessing local physics in molecular junctions, including vibrational and electronic distributions.

- However, the cost is an increase in complexity, including thorny issues about equilibration and thermalization.