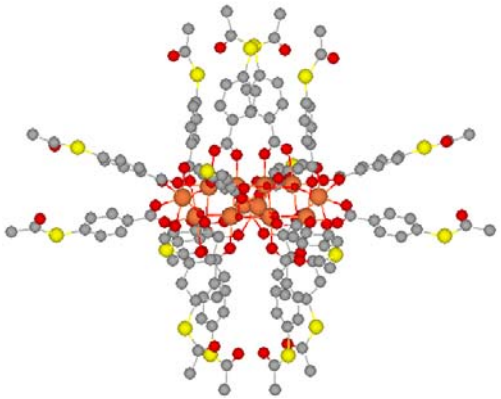
transport through the single molecule magnet Mn12

Herre van der Zant

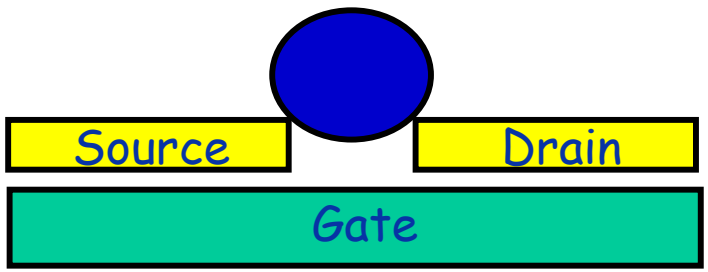


H.B. Heersche, Z. de Groot (Delft)

C. Romeike, M. Wegewijs (RWTH Aachen)

D. Barreca, E. Tondello (Padova)

L. Zobbi, A. Cornia (Modena)



interplay between molecular spin and electron transport (molecular spintronics)

Molecular Electronics and Devices group

TU Delft
Delft University of Technology
Faculty Of Applied Sciences

Kavli Institute of Nanoscience

transport through single molecules

Volume 29, number 2 CHEMICAL PHYSICS LETTERS 15 November 1974

MOLECULAR RECTIFIERS

Arieh AVIRAM
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598, USA

and

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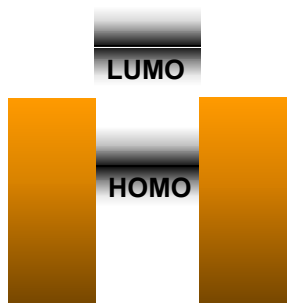
Department of Chemistry, New York University, New York, New York 10003, USA

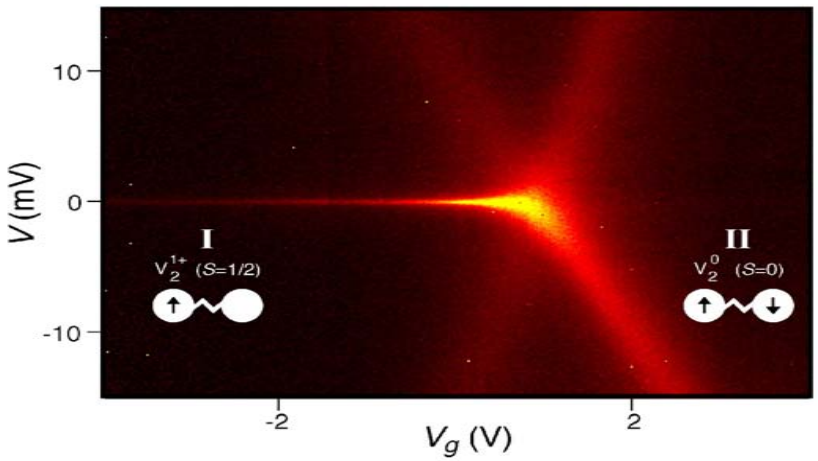
Received 10 June 1974

The construction of a very simple electronic device, a rectifier, based on the use of a single organic molecule is discussed. The molecular rectifier consists of a donor pi system and an acceptor pi system, separated by a sigma-bonded (methylene) tunnelling bridge. The response of such a molecule to an applied field is calculated, and rectifier properties indeed appear.

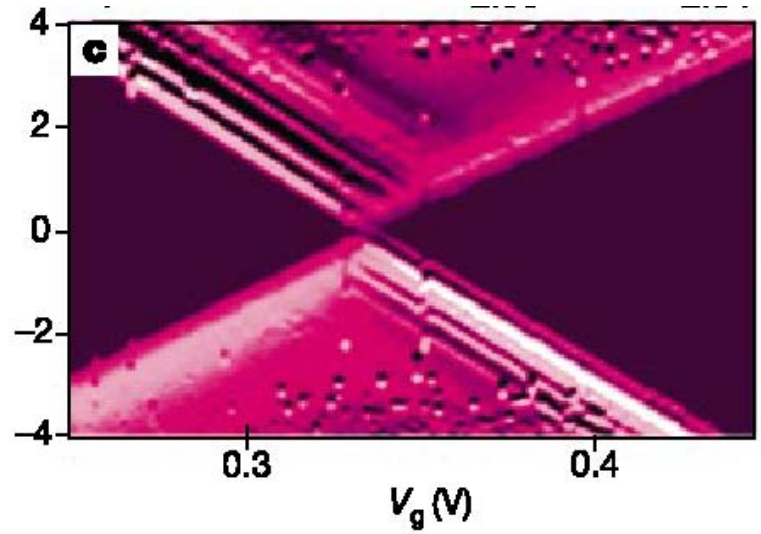
For the states $|f\rangle$, however, the unperturbed states of the pi system of the acceptor are not good enough. As studies of molecular adsorption have shown, the molecular eigenstates undergo both shift and broadening due to interaction with the electrodes. Gadzuk



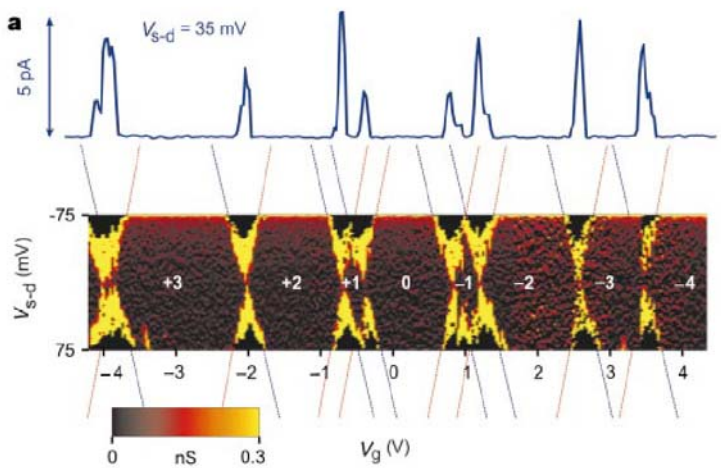
molecular transistors: quantum dots in the weak coupling limit



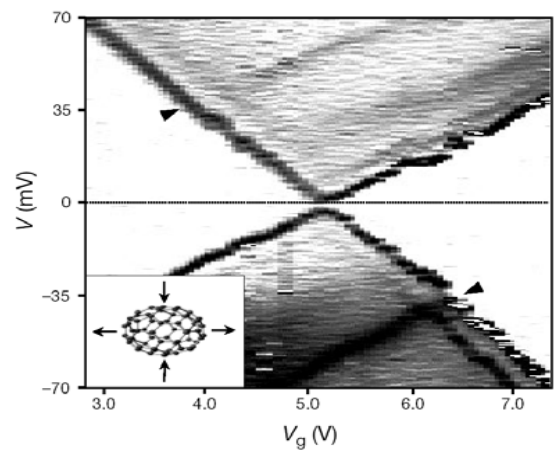
Kondo in V_2 complex: Liang *et al.*, Nature 417, 725 (2002)



Co-ion:. Park *et al.*, Nature 417, 722 (2002)



several oxidation states of OPV-5
Kubatkin *et al.*, Nature 425, 698 (2003)

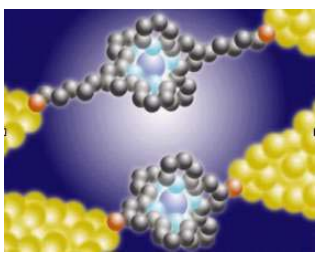


electron-phonon coupling in C_{60}
H. Park et al., Nature 407 (2000) 57

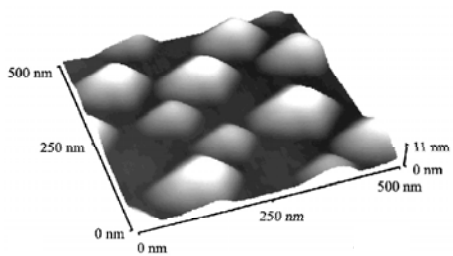
quantum dots: Coulomb blockade and discrete energy spectrum

- small box occupied by electrons (holes)
- box (island) has discrete energy spectrum
- island weakly coupled to leads: Coulomb blockade
- level broadening (Γ) << charging energy (E_c)

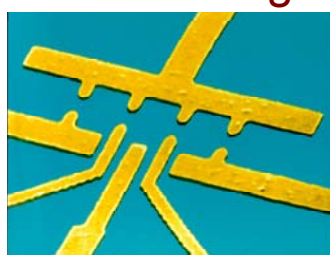
single molecule



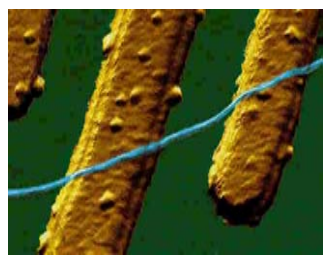
self-assembled QD



semiconducting QD

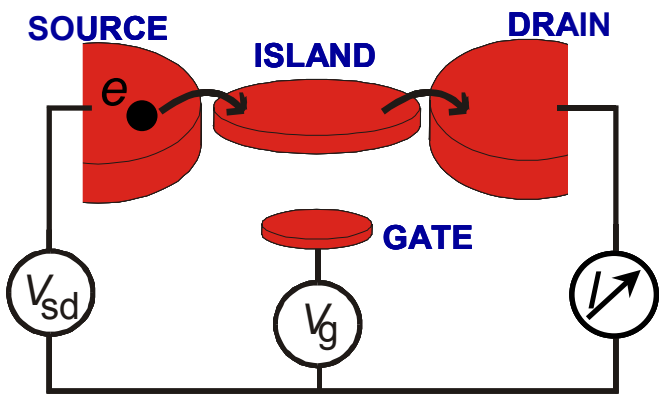


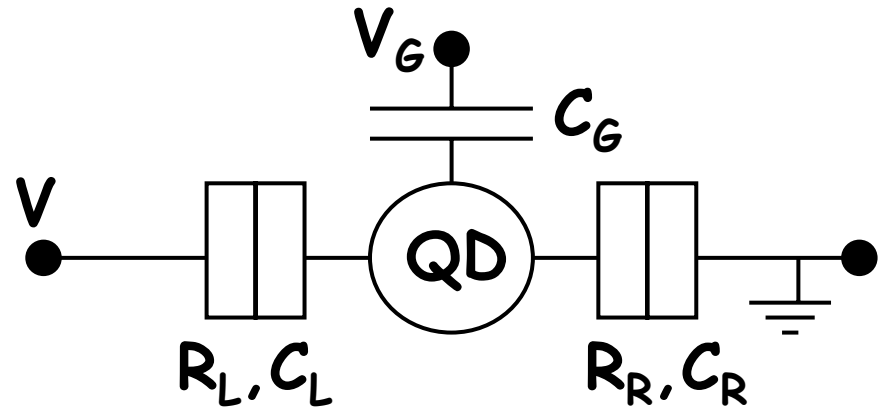
nanotube



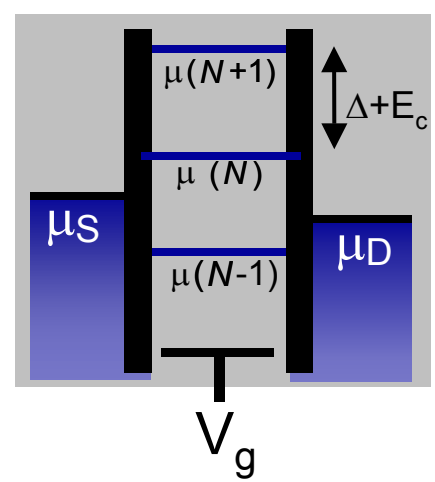
1 nm | 10 nm | 100 nm | 1μm

Coulomb blockade in quantum dots





dot coupled via tunnel barriers to source and drain reservoirs and capacitively to gate electrode

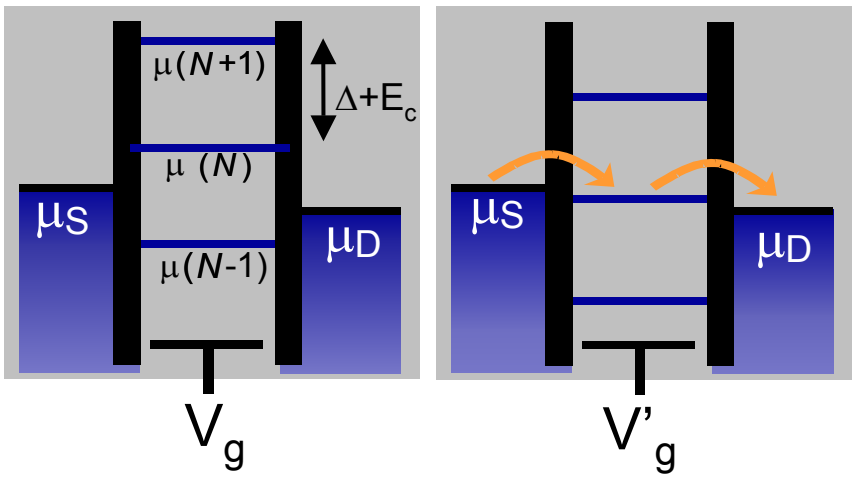


Δ: level spacing
E_c: charging energy
γ: level broadening

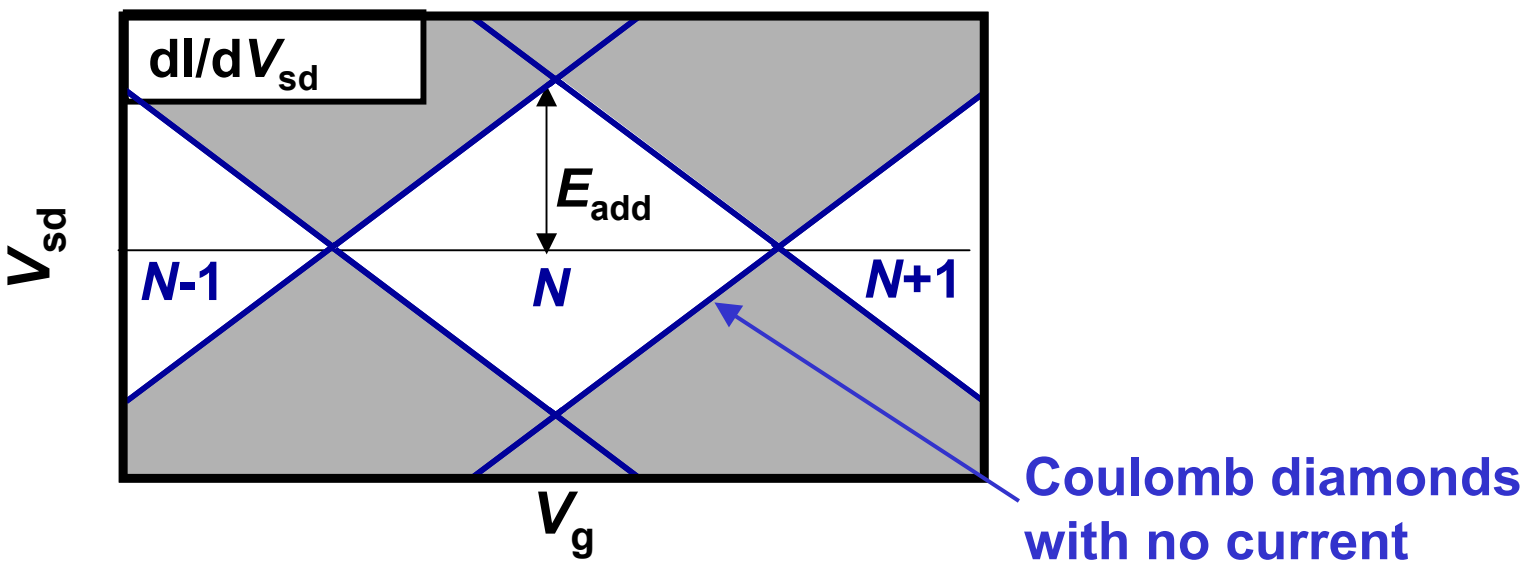
$$D_\varepsilon(E) = \frac{\gamma/2\pi}{(E-\varepsilon)^2 + (\gamma/2)^2}$$

stability diagram and Coulomb diamonds

linear regime

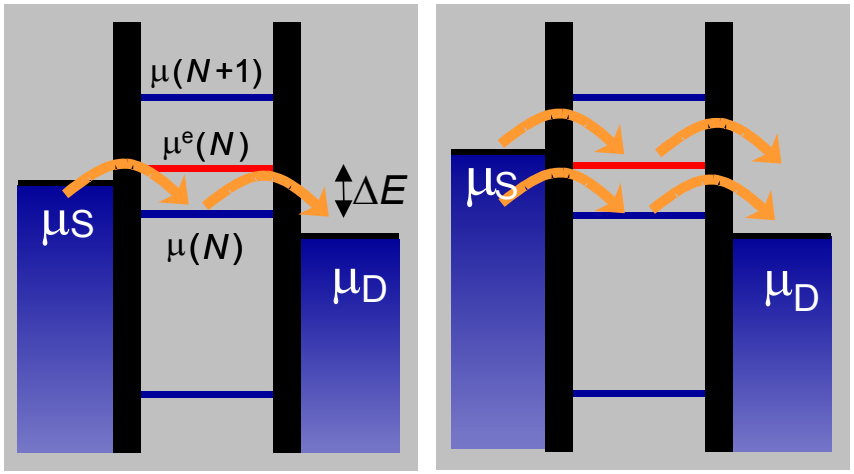


- **two 'knobs': V_{SD} and V_{gate}**
- **state contributes to transport if $\mu_s > \mu(N) > \mu_d$**

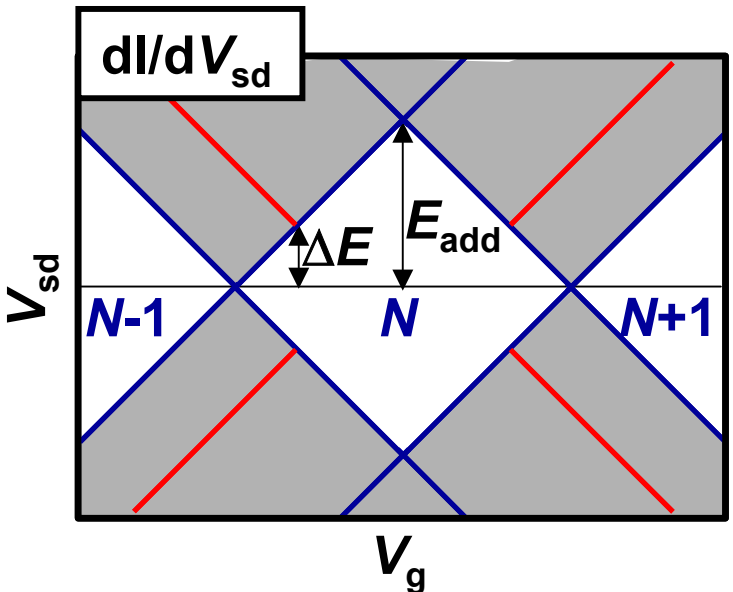


level spectroscopy

Non-linear regime



- two 'knobs': V_{SD} and V_{gate}
- state contributes to transport if $\mu_s > \mu(N) > \mu_d$



- excited states result in extra lines in stability diagram (red)
- excited states can be electronic, vibrational, or spin related

single-wall nanotubes
different regimes as a function of gate voltage

strong coupling ($R \sim R_Q$), large γ

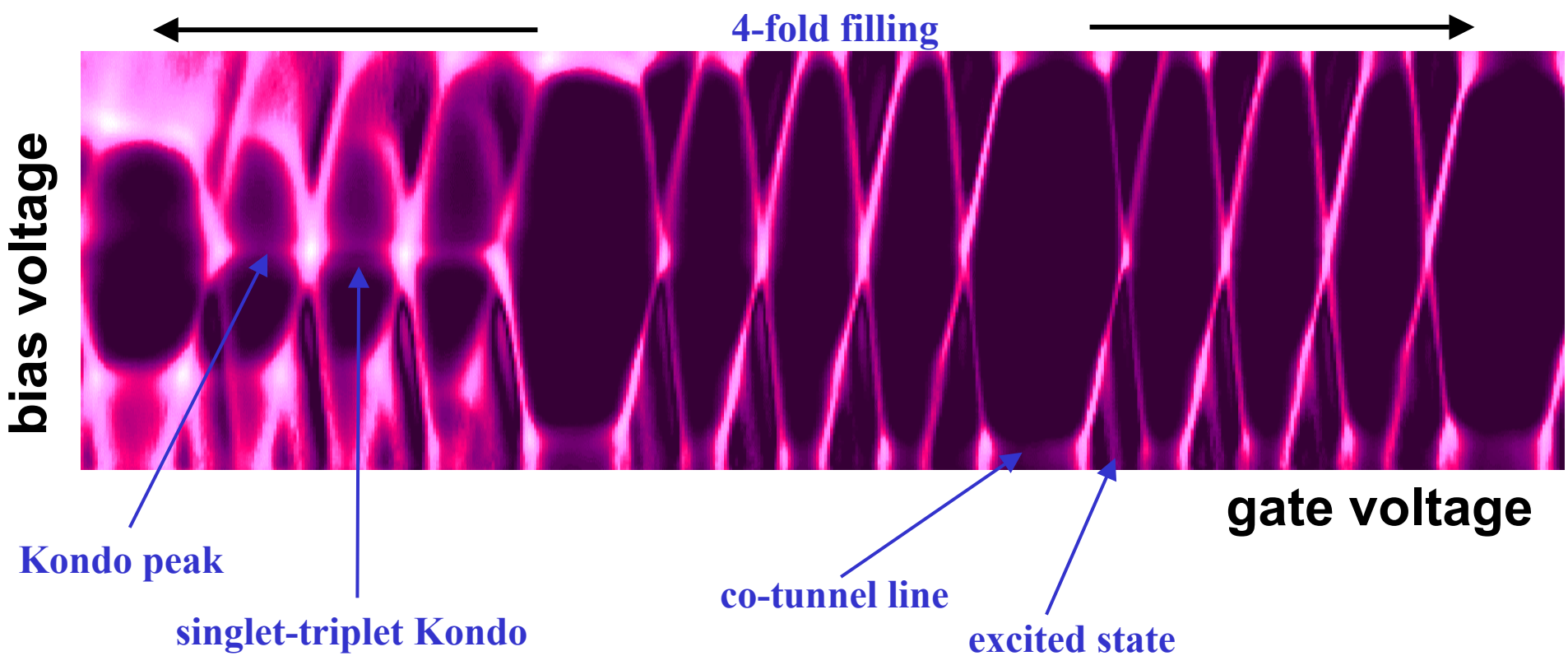
blurred CB diamonds

Fabry-Perot, Kondo physics

weak coupling ($R \gg R_Q$), small γ

sharp CB diamonds

spectroscopy



experimental approach

- **sample preparation at room temperature:**

  nanogap fabrication with electromigration of gold wires with self-assembled monolayers (‘trapping a falling molecule’)

- **measurement system:**

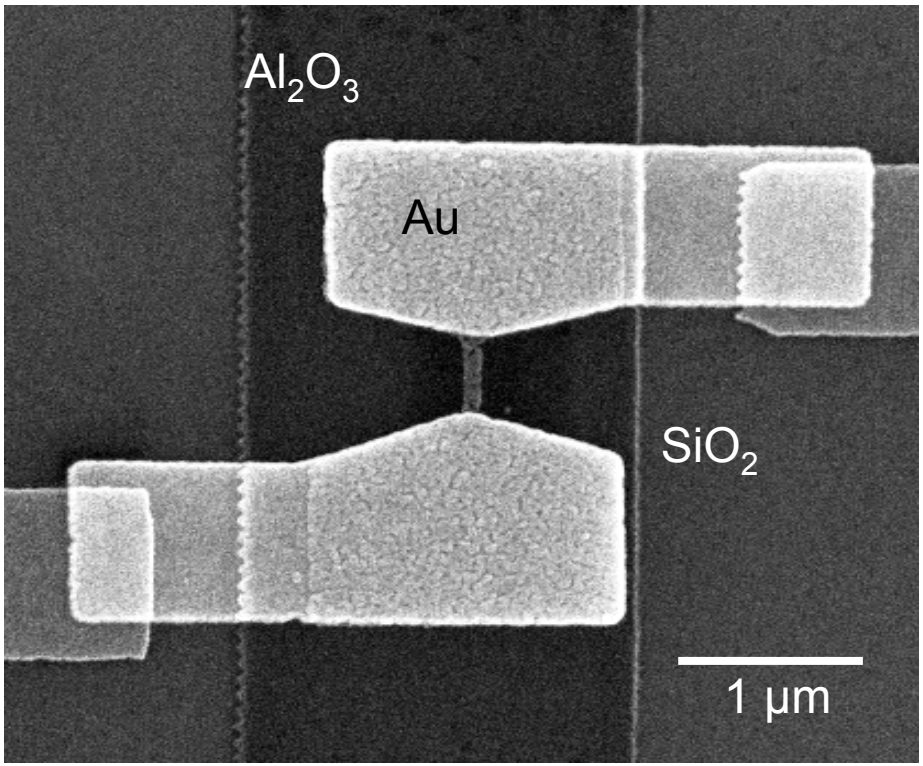
  low-temperature He-4 probe down to 1.5 K with home-made low noise electronics

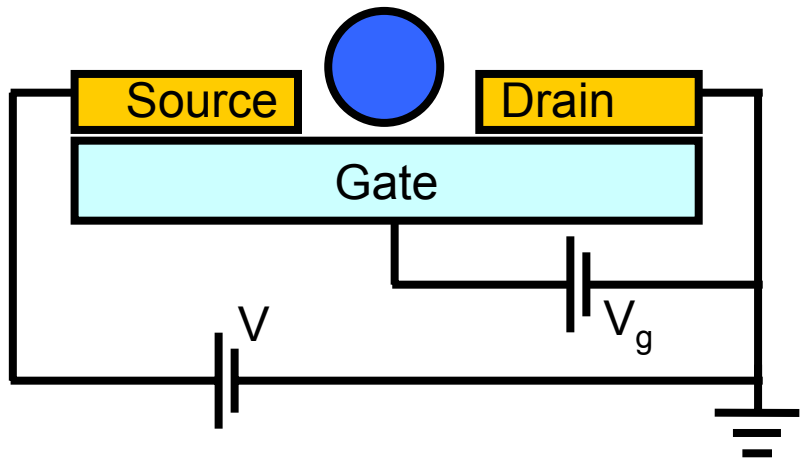
  (Desert Cryogenics Probe-Station for screening; near future dilution fridge)

- **measurements**
  - gate sweeps and identify interesting devices
  - stability diagram: current vs. bias and gate voltage (dI/dV numerically)
  - lock-in measurement (dI/dV directly)
  - temperature- and magnetic field dependent measurements

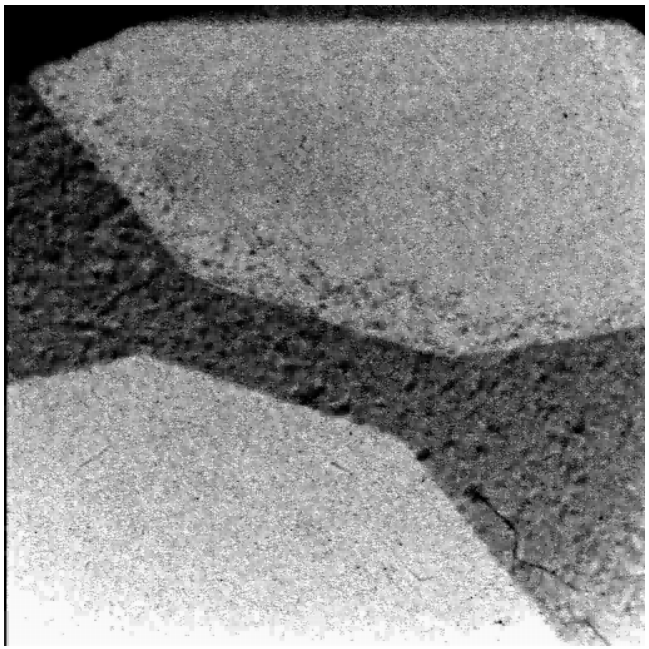
currents typically in the pA range; electron resides on the molecule for 100-1 ns

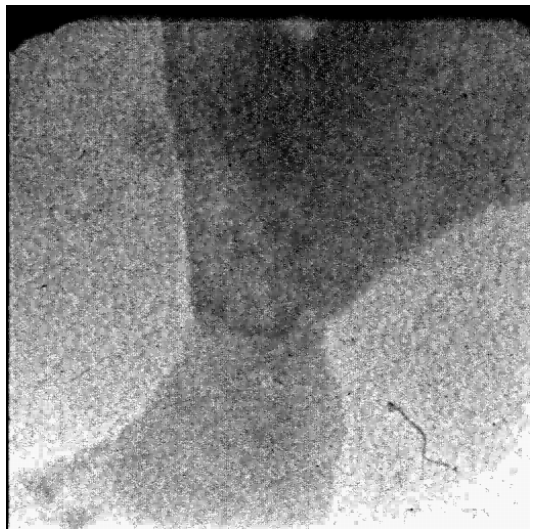
gap fabrication: electromigration on top of an aluminium gate

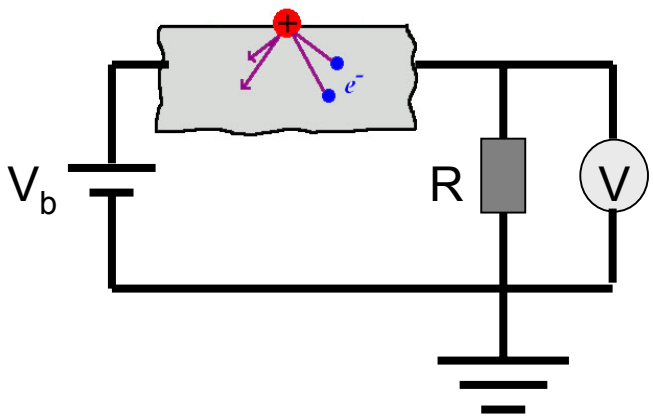




visualization of electromigration of gold wires (TEM)

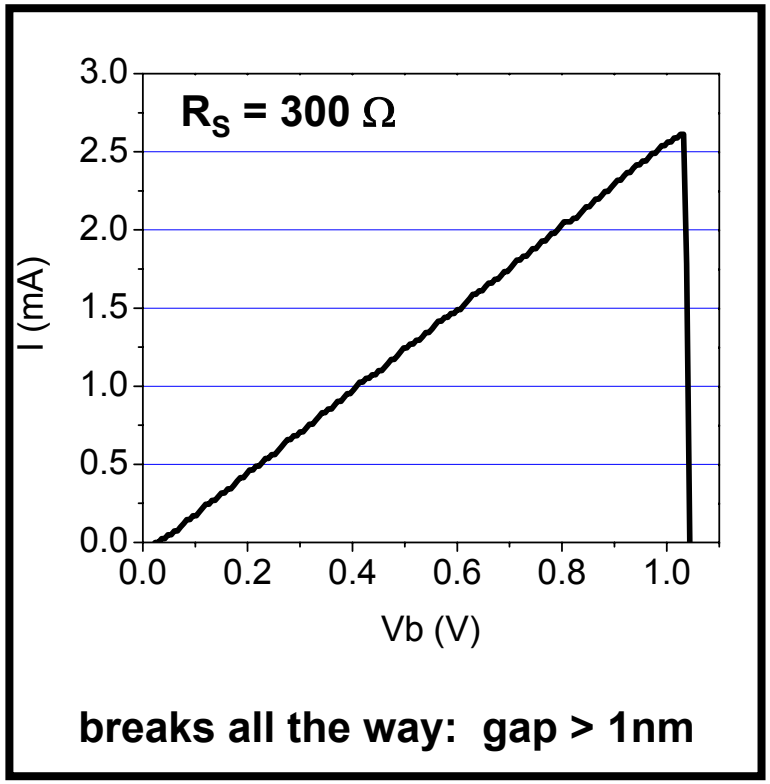


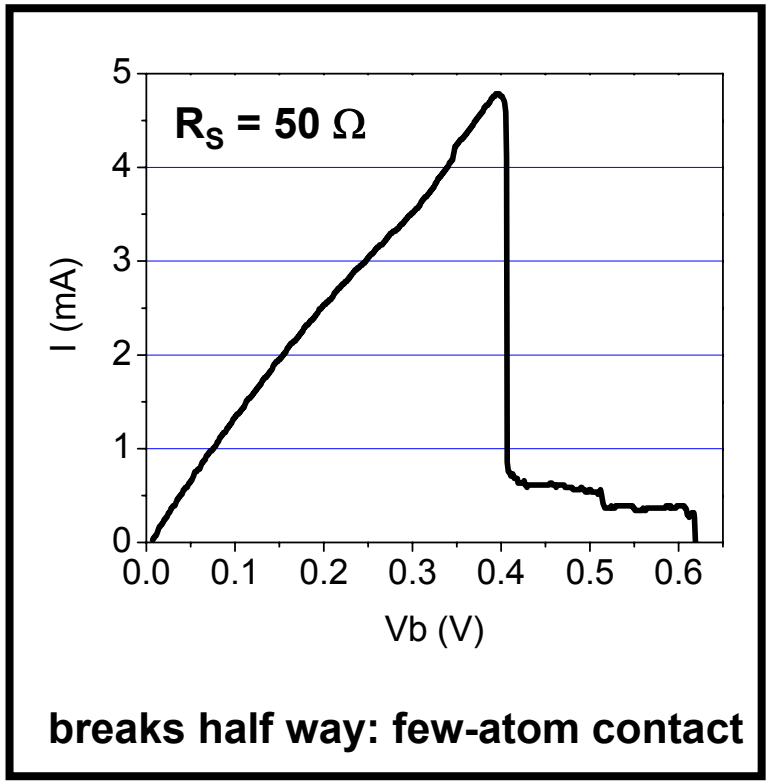


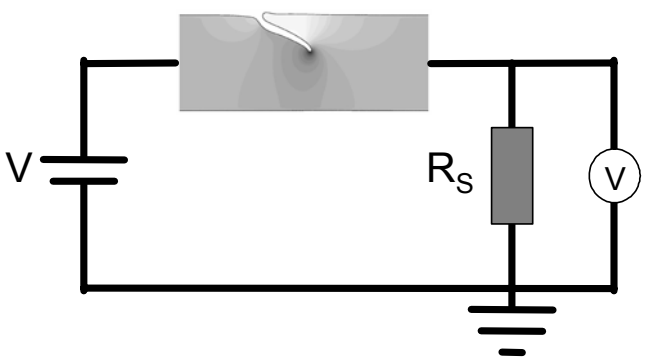


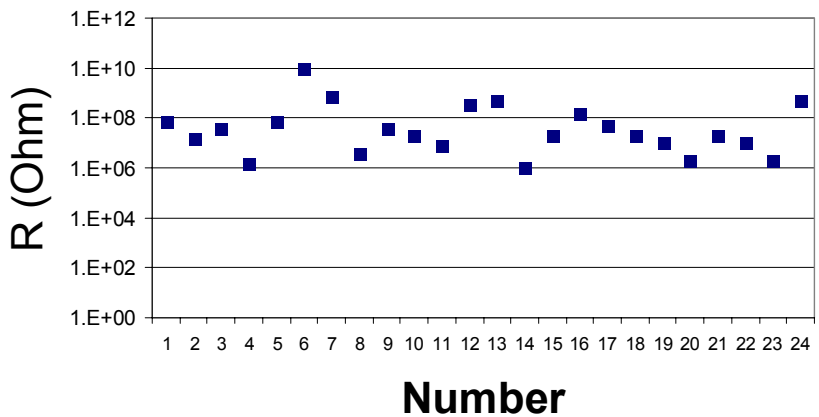
H.B. Heersche et al., to be published

electromigration: control of gap resistance

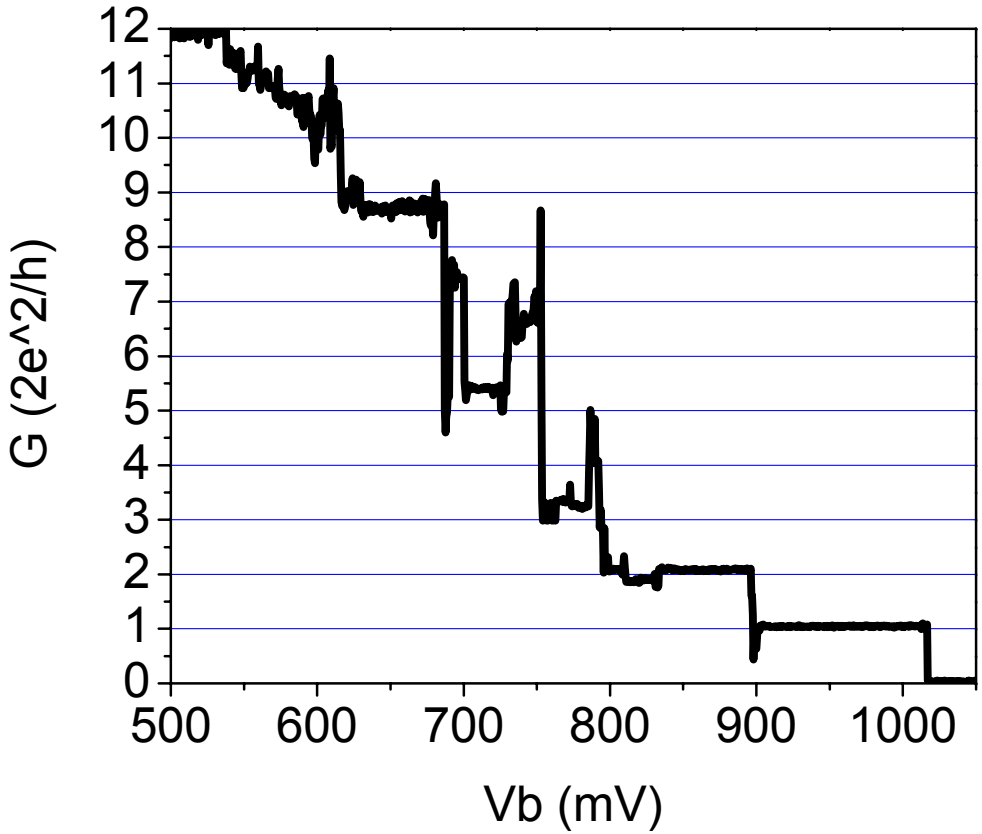


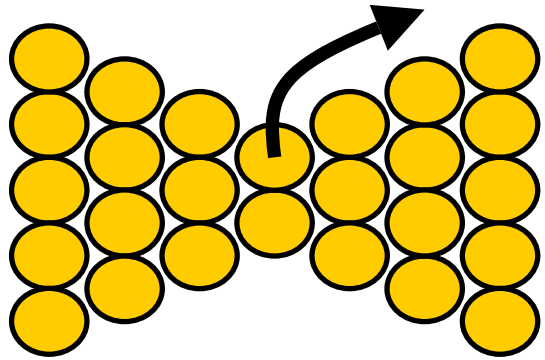


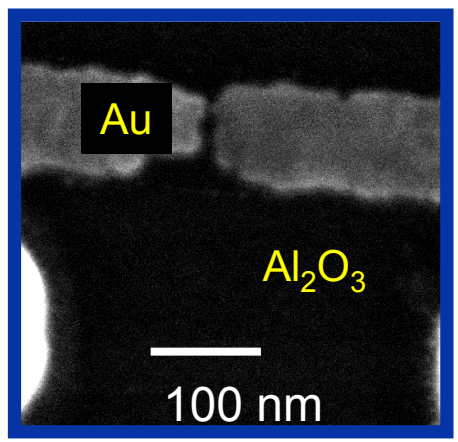




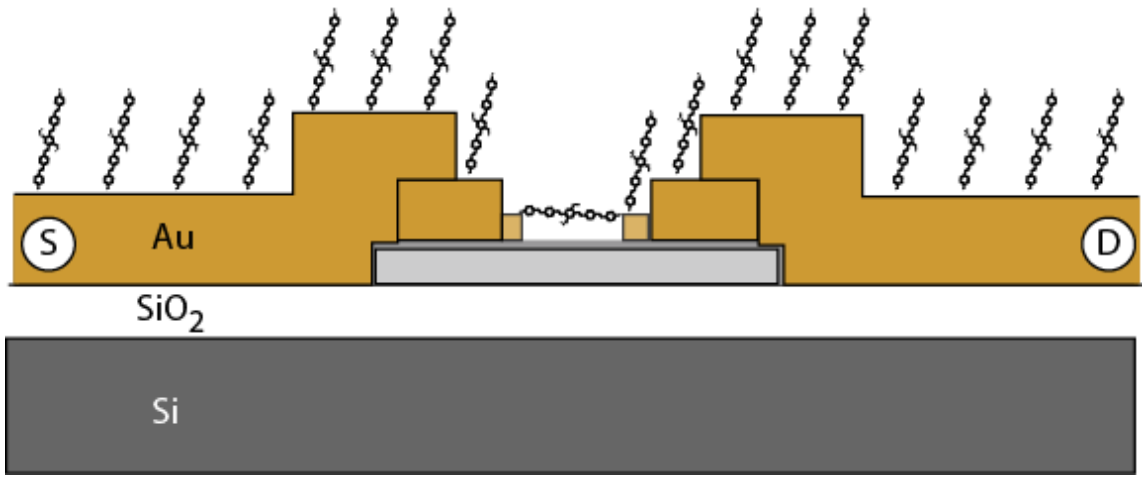
electromigration: "reproducibly" single-atom contacts







sample preparation: contacting molecules with thiol end groups



chip placed in solution

self-assembled monolayer forms

electromigration creates gap

molecule trapped in gap

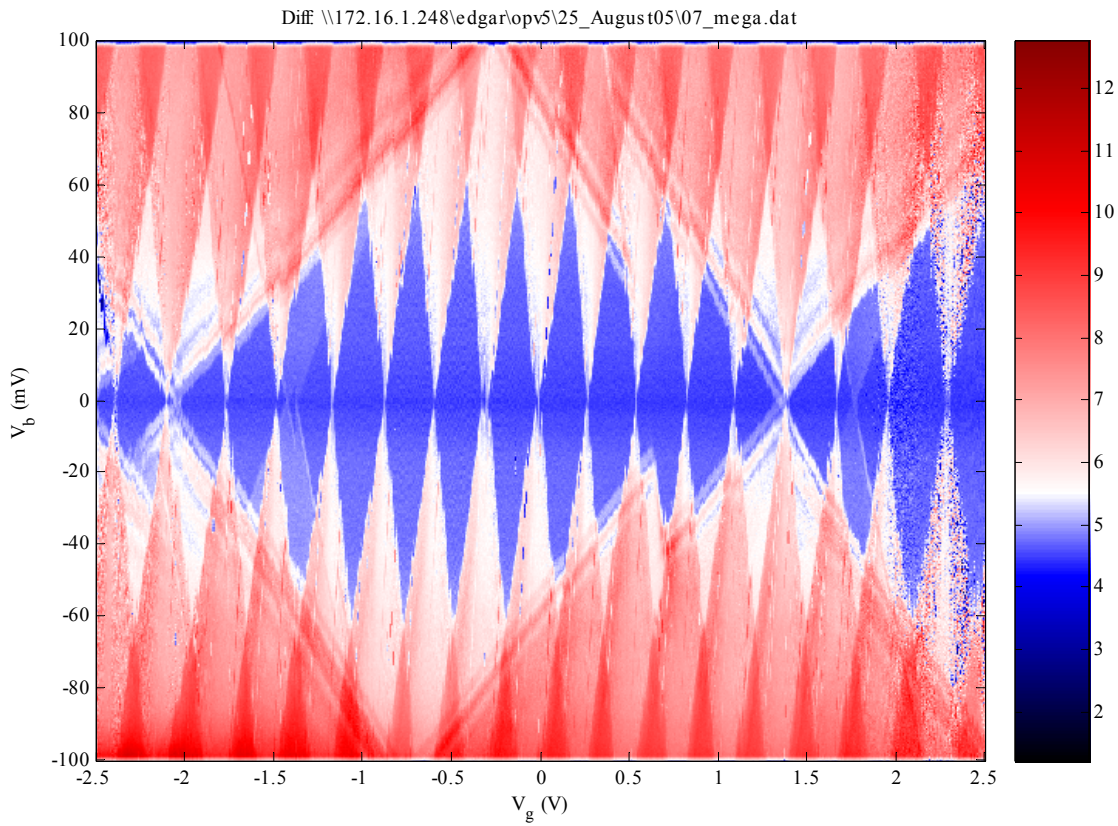
When do we have a molecule between the contacts?

- addition energy > 100 meV

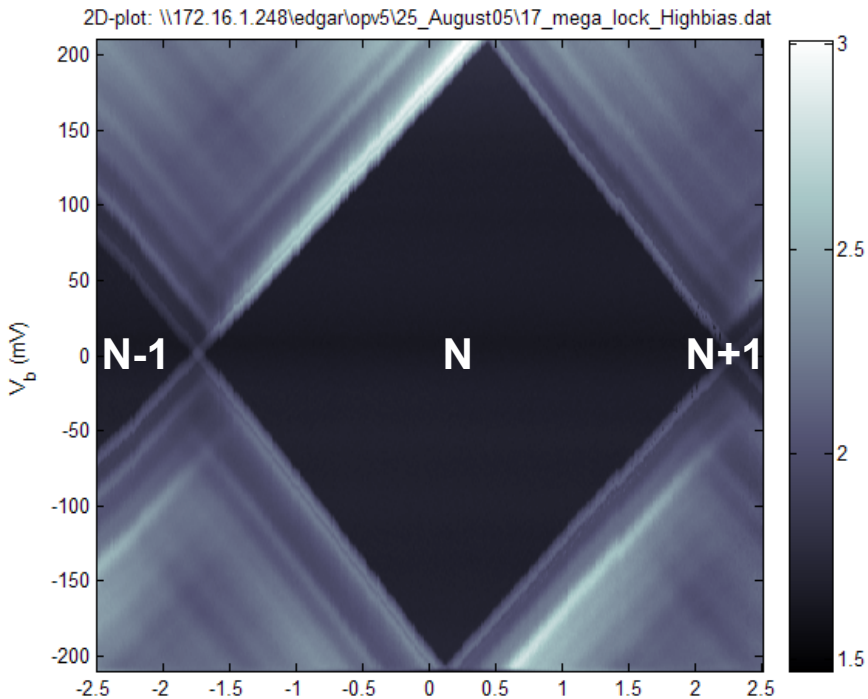
- limited number of charge states

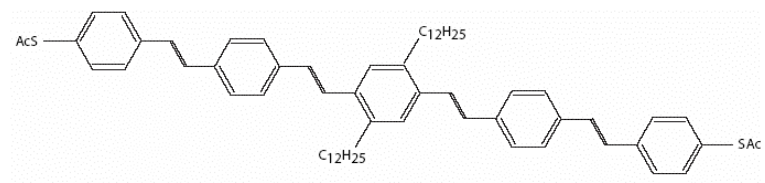
- additional molecular fingerprints:
  - vibrational modes
  - spin excitations

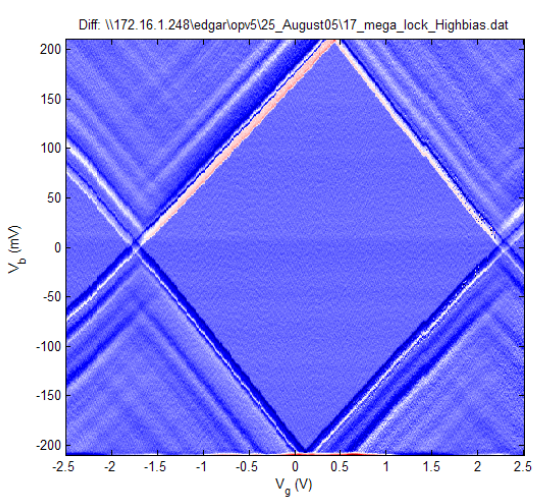
- in practice: only a few percent of the samples show molecular behavior and of those quite a few show unstable, switchy behavior



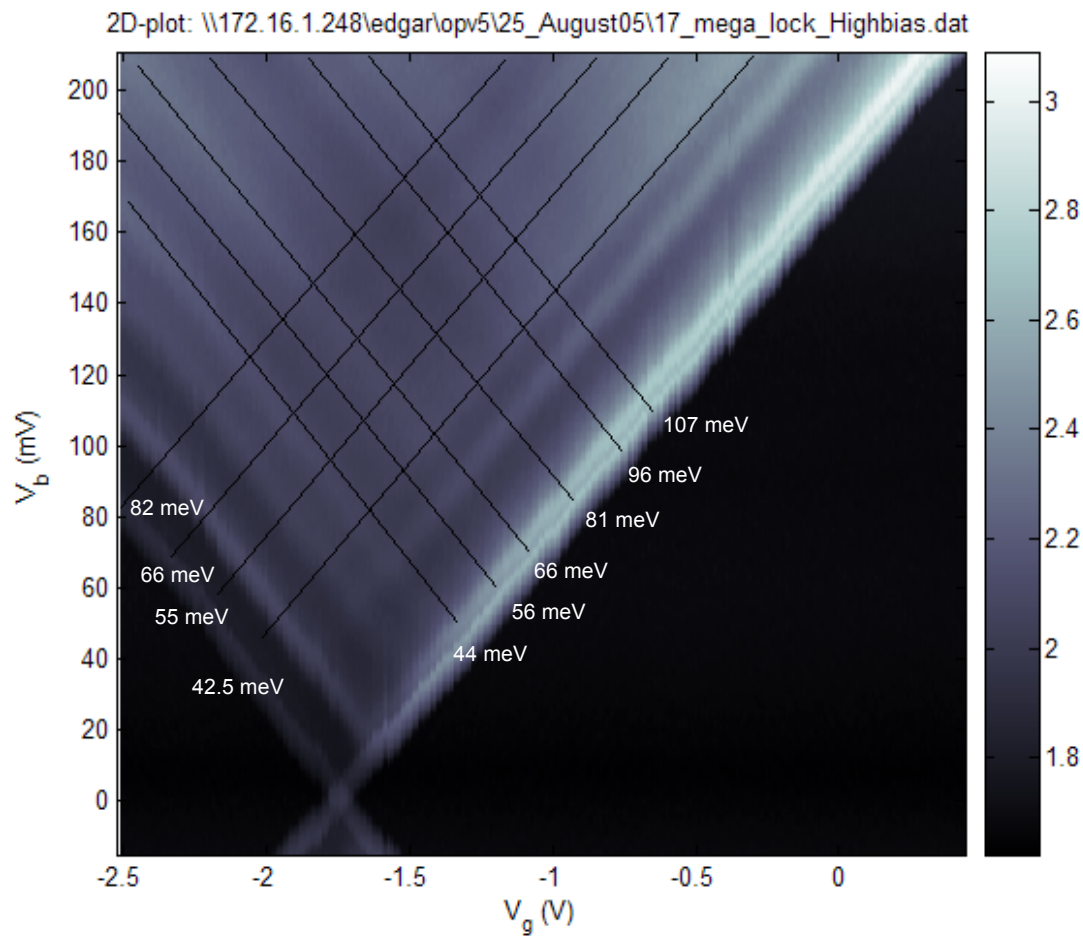
excitations in OPV-5: all lines can be mapped onto Raman spectrum



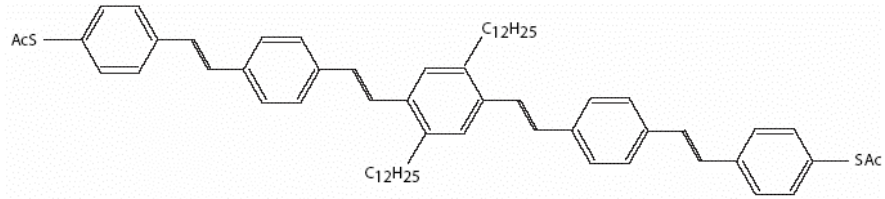


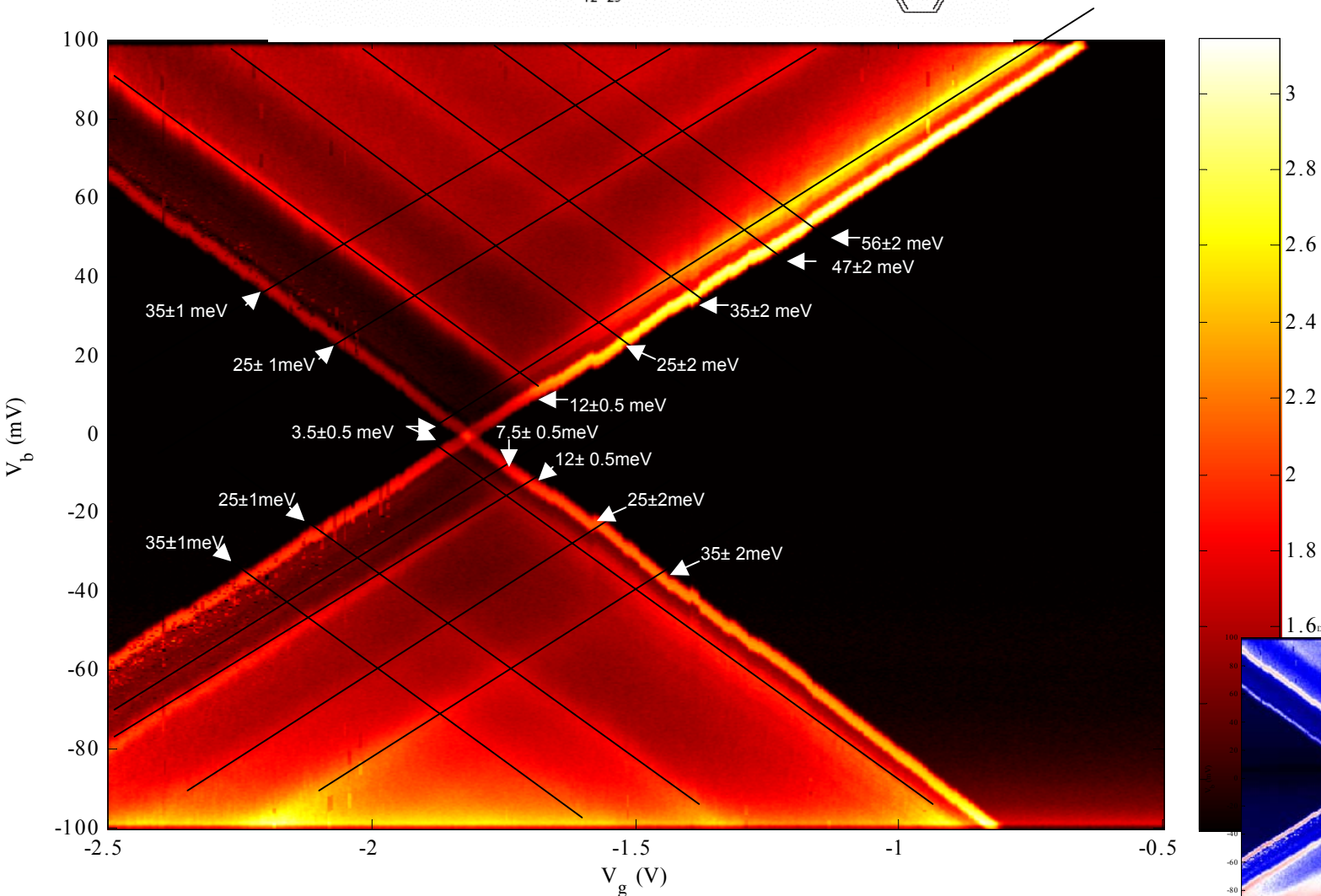


second derivative numerical



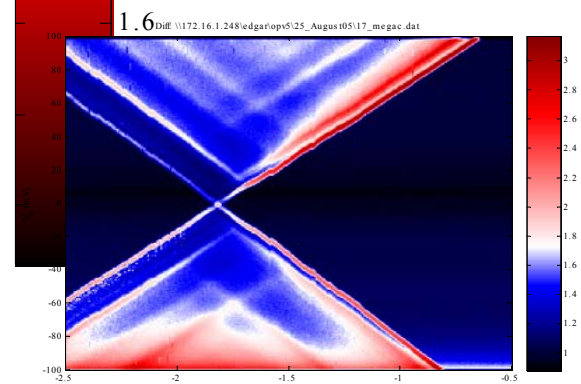
excitations due to vibrational modes (OPV-5)



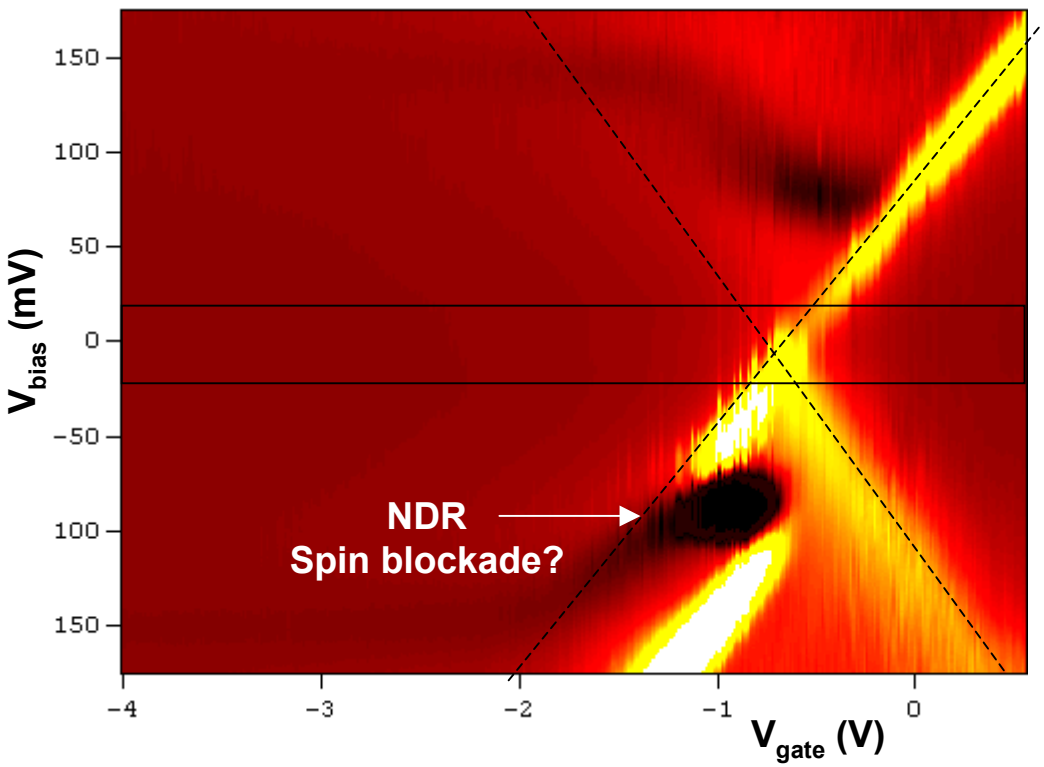


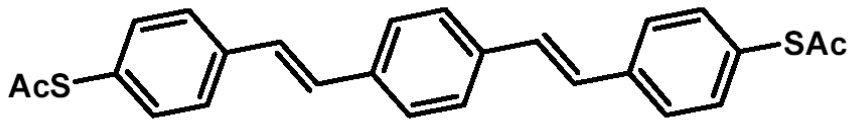
Raman Spectra

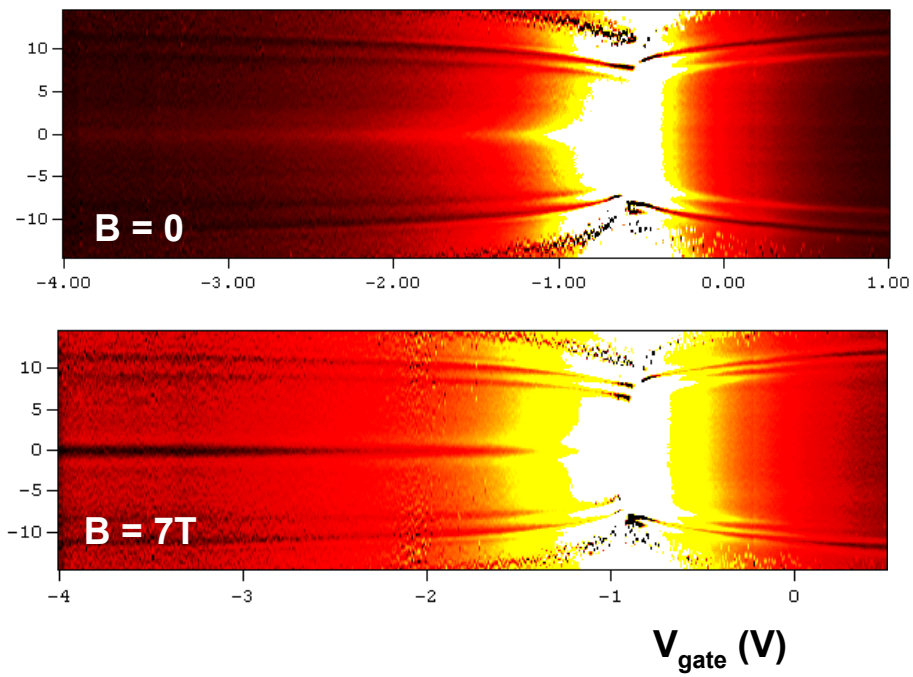
cm-1	meV
85	10.6
123.8	15.5
192.8	24.1
216.2	27.0
266	33.3
323.2	40.4
375.4	46.9
408.6	51.1
459.4	57.4
548.4	68.6
583.3	72.9
634.9	79.4



molecular junction with OPV-3: Kondo

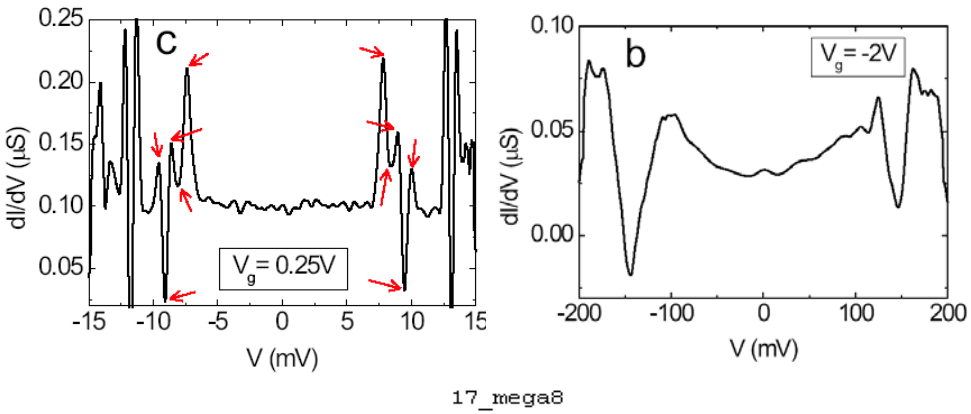


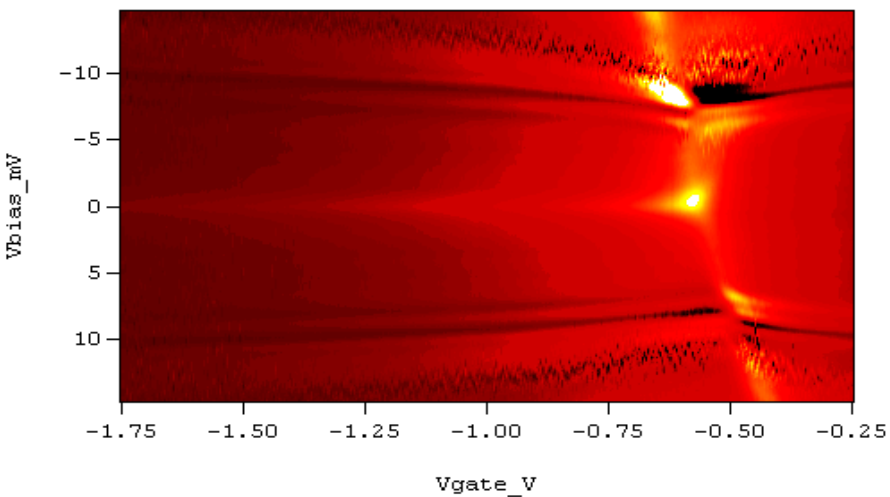




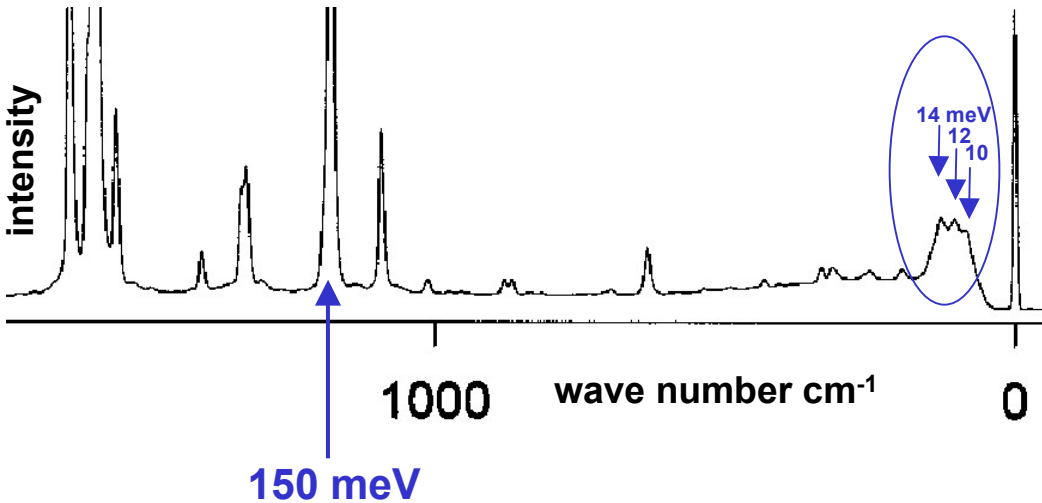
inelastic electron scattering probing vibrational modes in OPV-3

electron spectroscopy on a three-terminal device with a single OPV-3 molecule

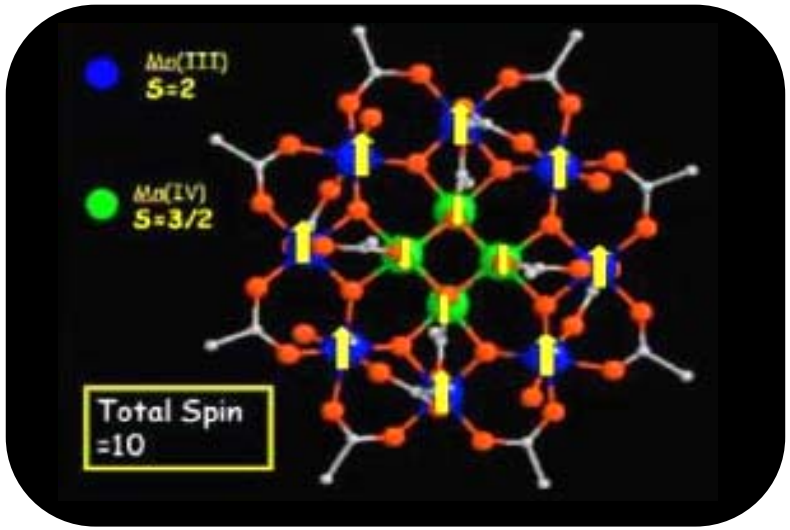




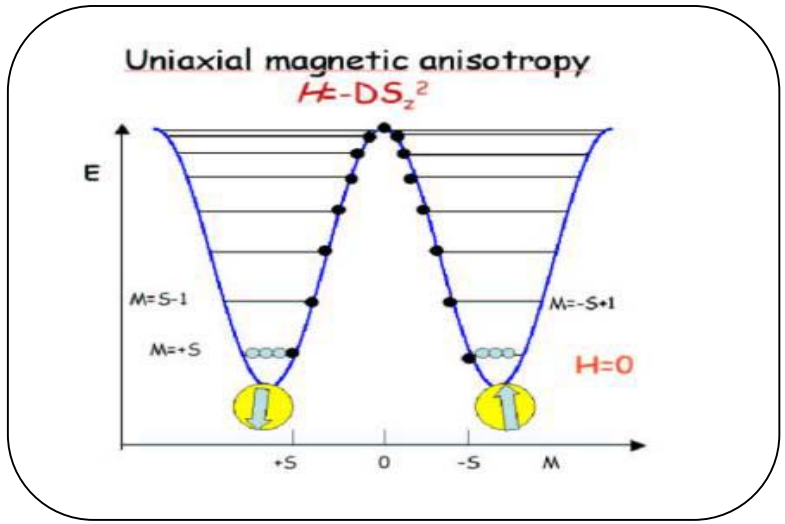
Raman data
OPV-3 molecules in solution



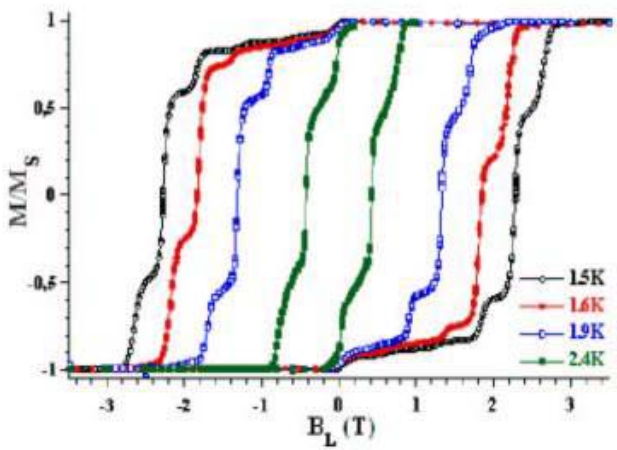
the single molecule magnet Mn-12

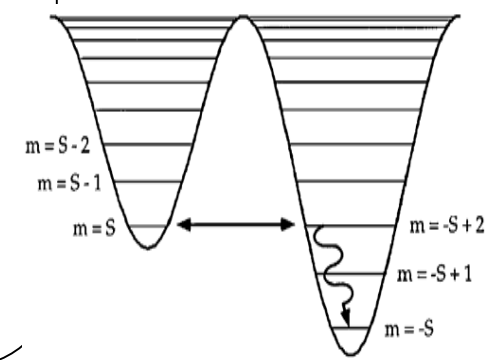


$$H = -D_{N,S} S_z^2 - \frac{1}{2} B_{4;N,S} \left(S_-^4 + S_+^4 \right)$$



B. Barbara *et al.*, Journ. Magn. Magn. Mat., 200, 167(1999)

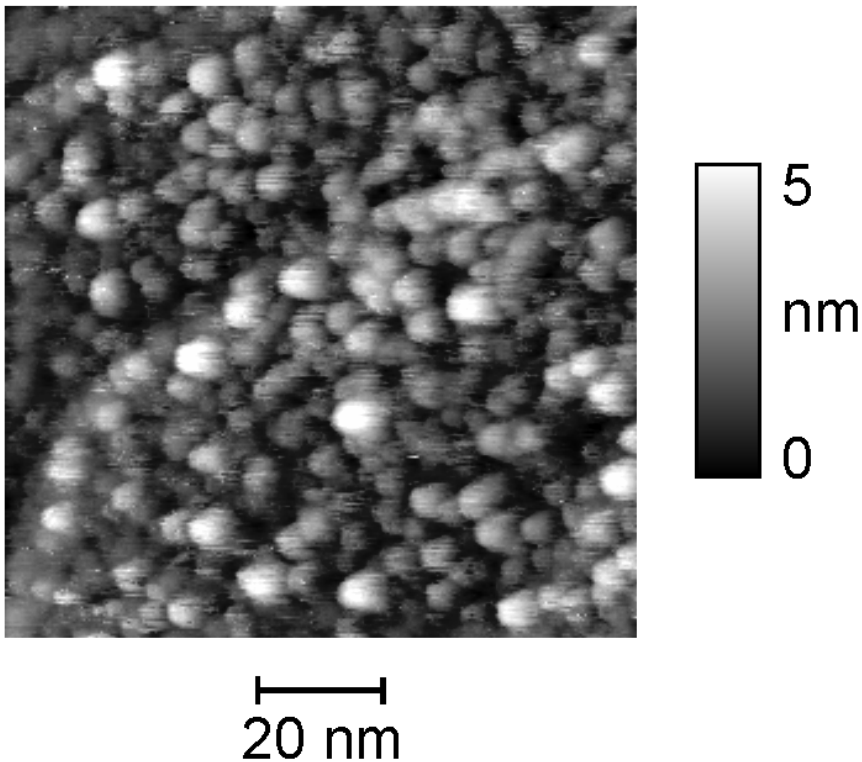


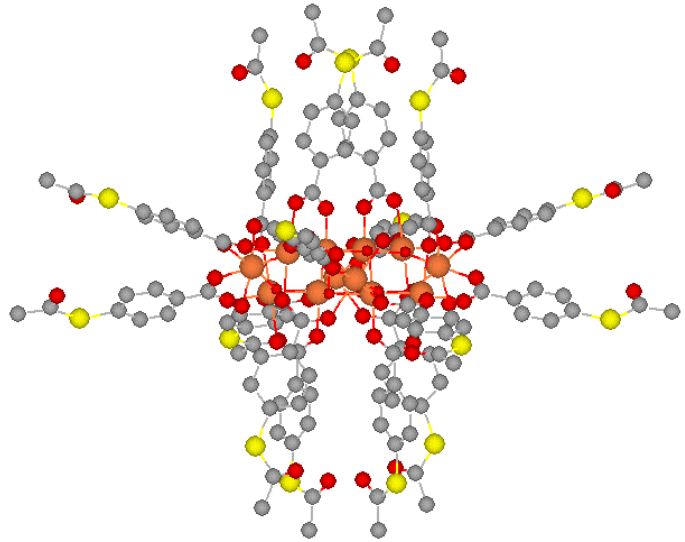


- **Mn12: high spin (S=10) + high D-anisotropy**
- **energy barrier ~ 60K (5.6 meV)**
- **hysteretic behavior**
- **quantum tunneling of magnetization when m states are aligned (Friedman *et al., 1996*)**

Mn-12 on a gold surface: ligands with thiols

STM image





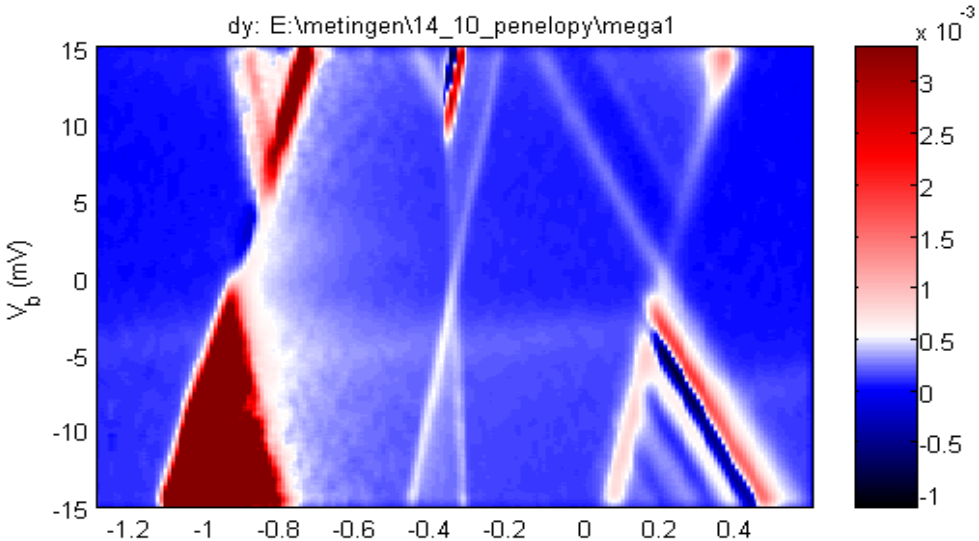
- **Mn12- derivatives that bind to gold surface have been synthesized by Cornia et al.**
- **ligands:**
  - **$HO_2(CH_2)_{15}SAc$**
  - **PhSAc**

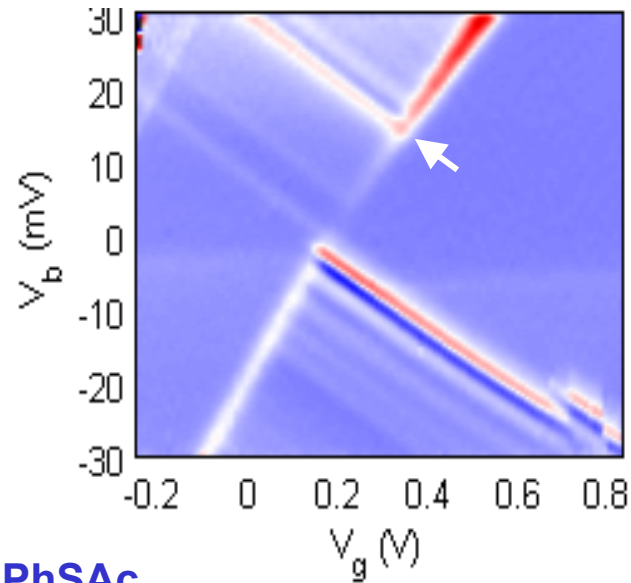
after cleaning the gold wires, we put samples in a 0.1mM solution for ~1h

A. Cornia *et al.*, *Angew. Chem. Int. Ed.*, ***42***, *1645 (2003)*

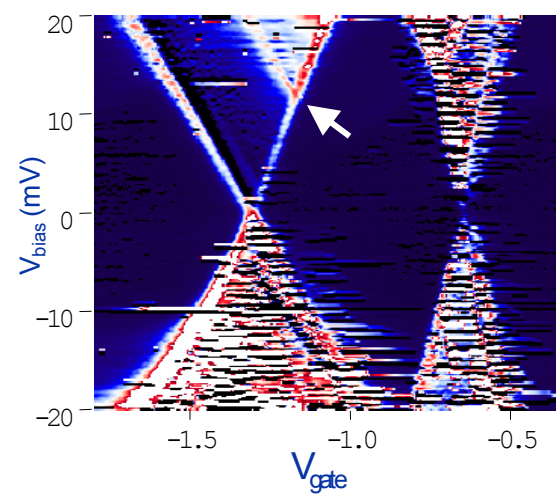
Coulomb blockade in Mn-12 junctions

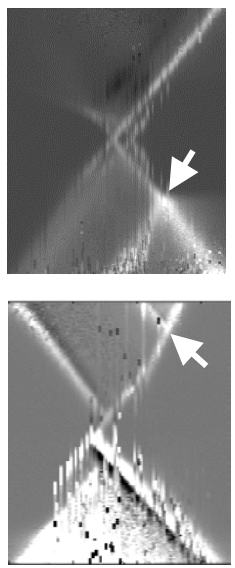
H.B. Heersche et al. cond-mat/0510732





Mn-12PhSAc



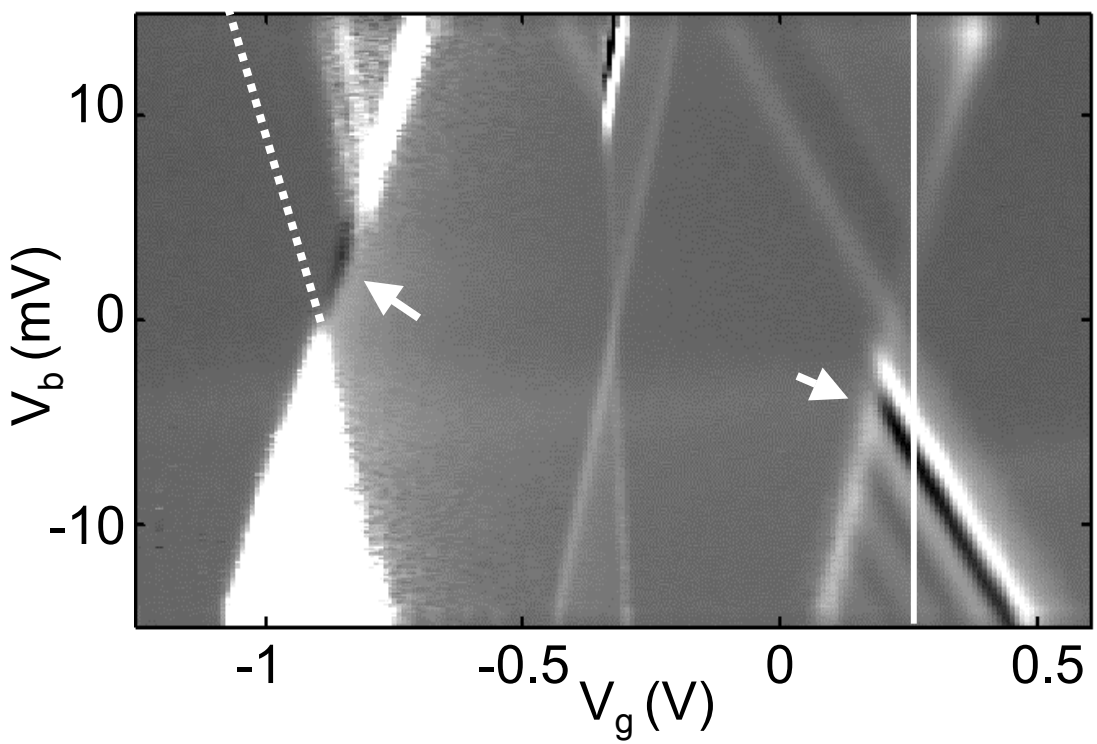


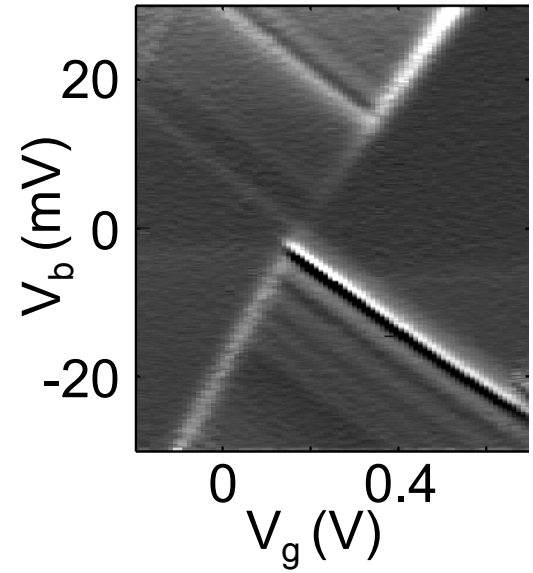
Mn-12C15SAc

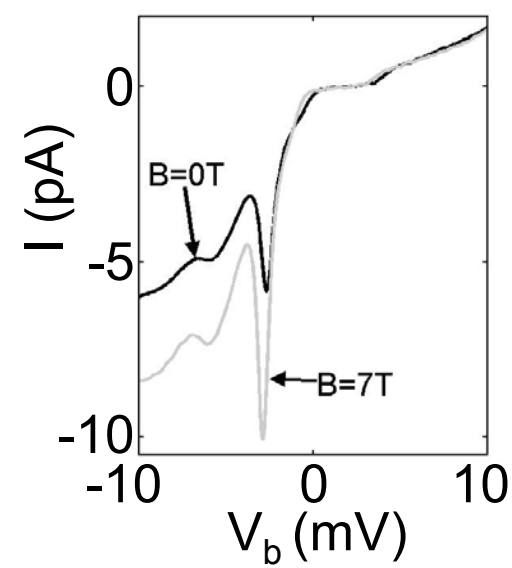
- **Mn-12 with two different ligands**
- **fingerprints (not observed in any of the other more than 1000 devices without or with other molecules) :**
  - **excitation at 14 meV (unknown origin)**
  - **low energy excitations (<10 meV) with strong negative differential conductance**

complete current suppression (CCS) and negative differential resistance (NDR)

T = 3 K

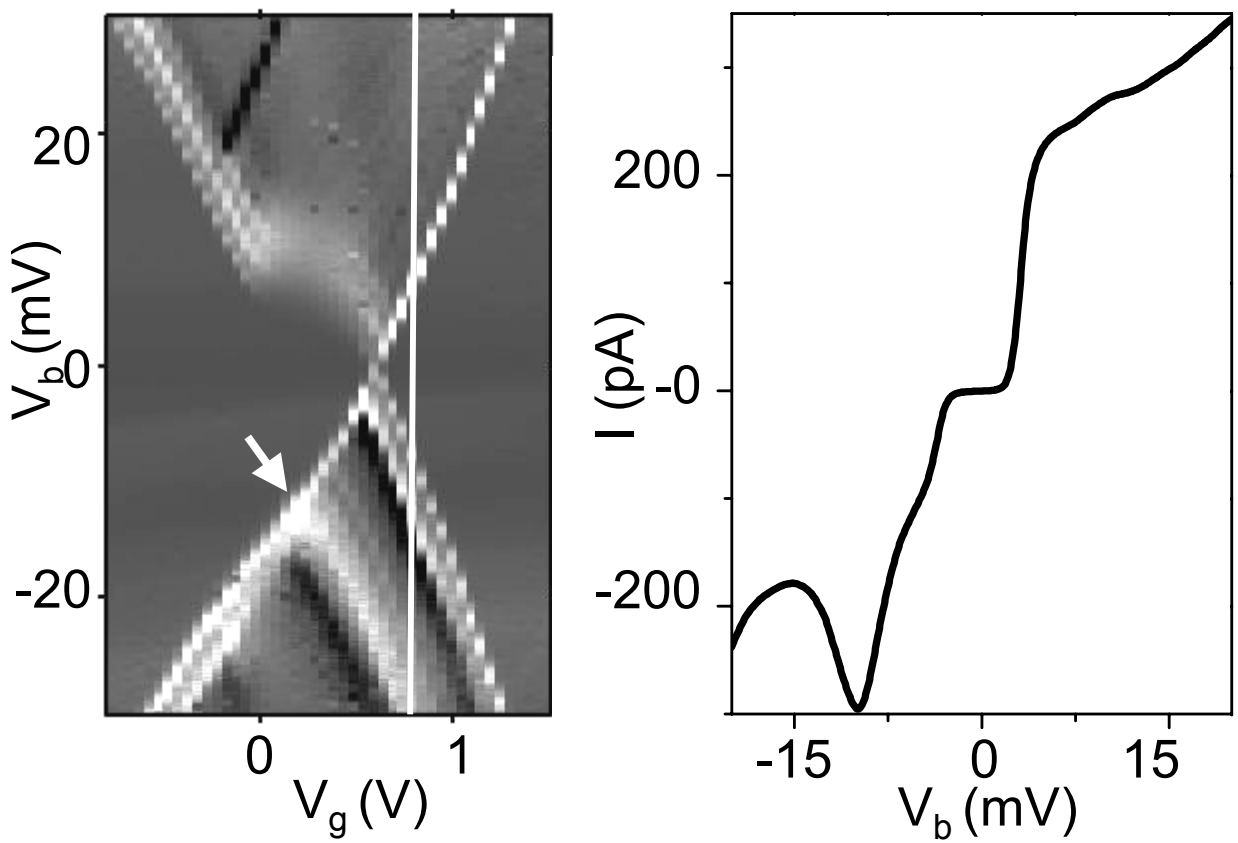






not easily explained within usual CB theory and spin blockade !

different sample showing NDR (3 meV) and excitations at the same energies

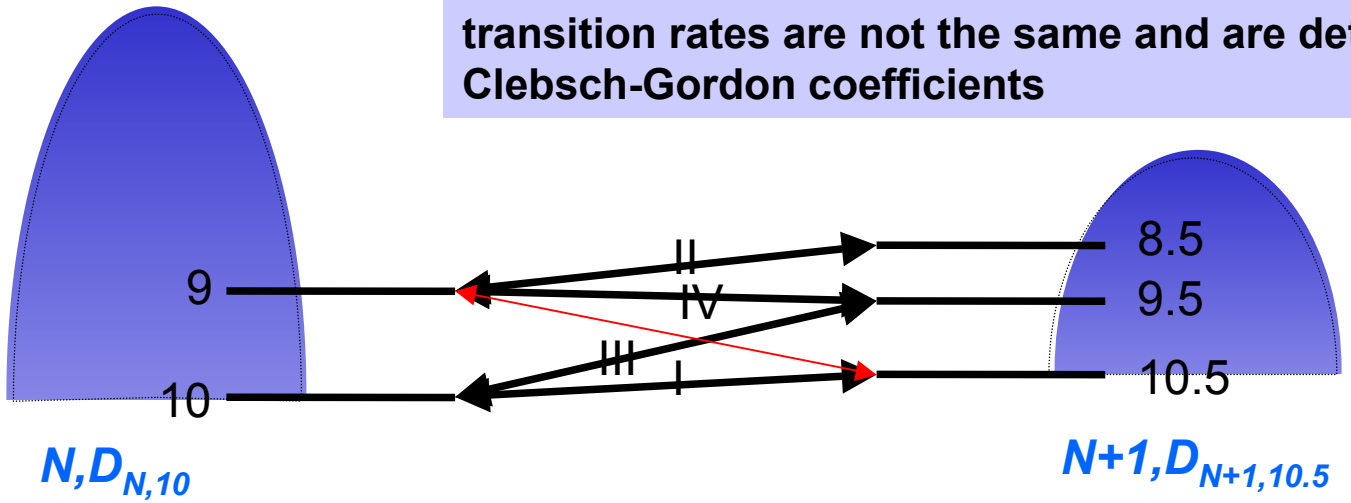


T = 1.5 K

transport: charge (±1) and spin (±1/2) change

differences in chemical potentials matter

transition rates are not the same and are determined by Clebsch-Gordon coefficients



$$H = -D_{N,S} S_z^2$$

$$\mu_{9.5}^{N+1} - \mu_{10}^{N} = (9.5)^2 D_{N+1} - 10^2 D_N$$

$$\mu_{m_z}^{N+1} - \mu_{m_z}^{N} = (m_z^{N+1})^2 D_{N+1} - (m_z^N)^2 D_N$$

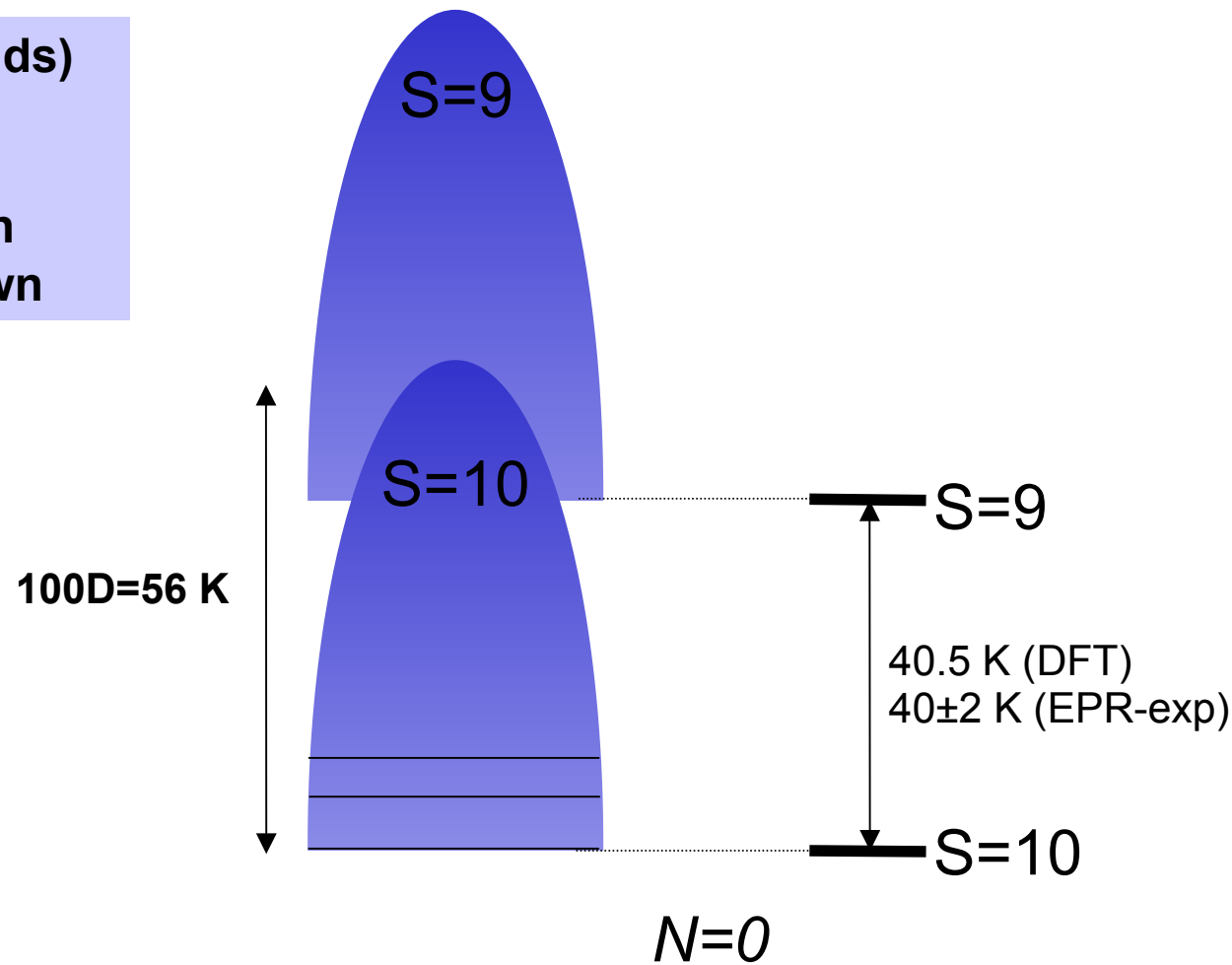
$$\left| S_z^{N+1}, m_z^{N+1} \right\rangle = \Sigma C^{S_z^N}_{m_z^N,\pm} \left| S_z^N, m_z^N \right\rangle \left| \tfrac{1}{2}, \pm\tfrac{1}{2} \right\rangle$$

Christian Romeike, Maarten R. Wegewijs
RWTH Aachen

model includes different spin manifolds

two spin excitations (manifolds) per charge state

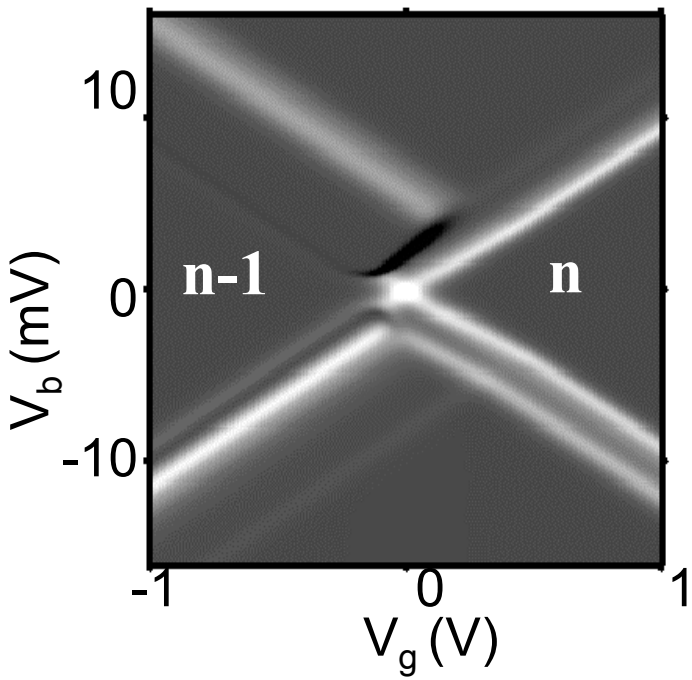
energy scales N=0 are known
energy scales N=±1 not known

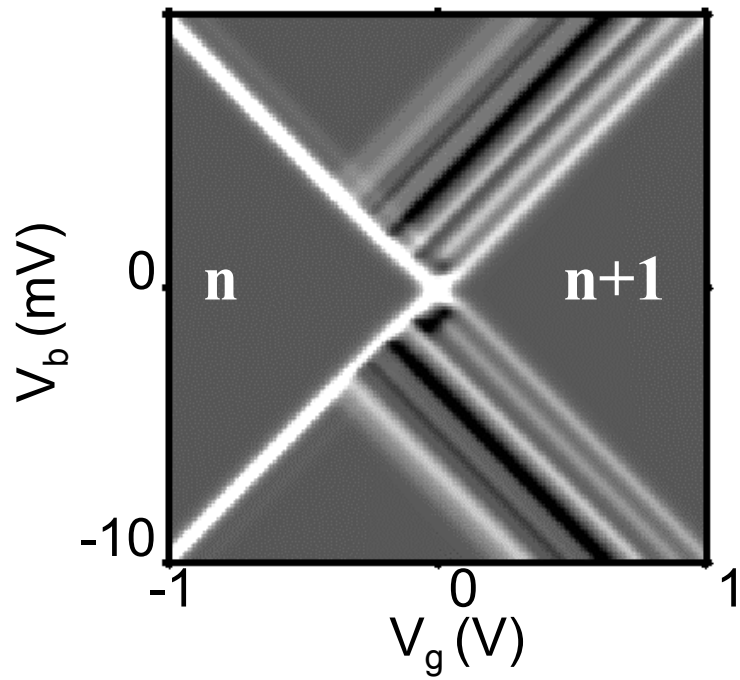


Christian Romeike, Maarten R. Wegewijs,RWTH Aachen

*Park and Pederson, PRB **70** (2004) 054414*
*K. Petukhov et al. PRB **70** (2004) 054426*

calculations: new kind of spin blockade



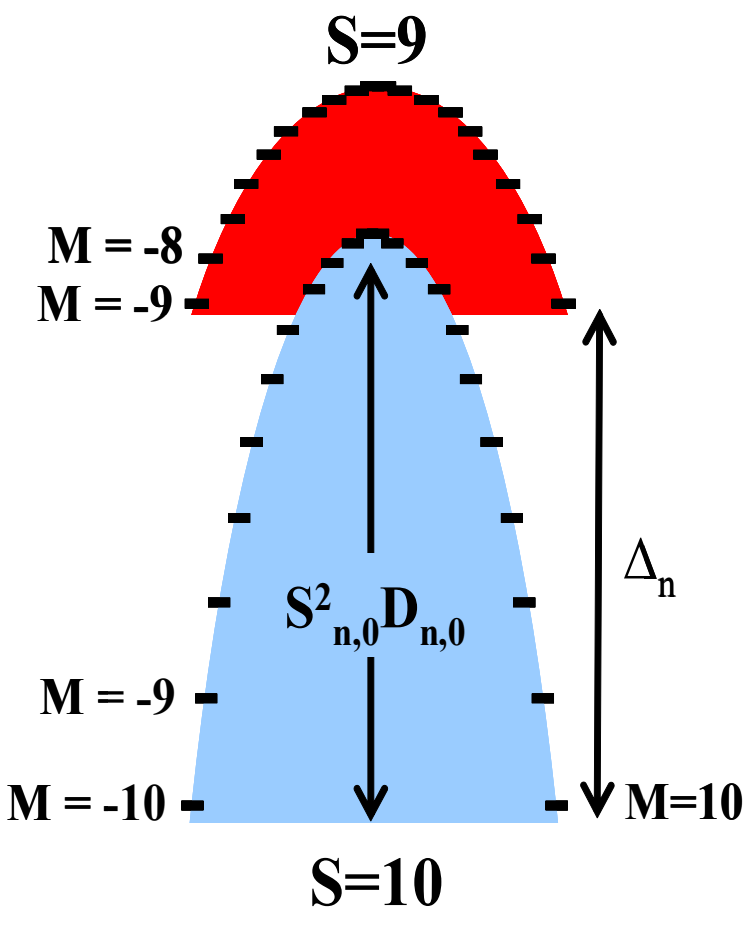


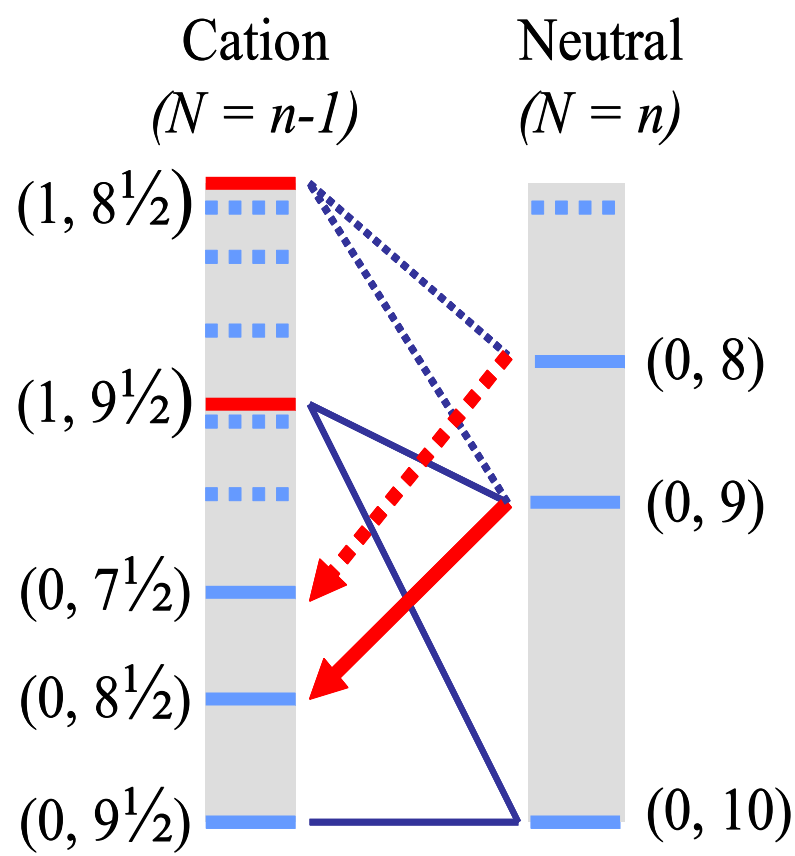
New type of spin blockade:

- **S_z, m_z selection rules instead of S selection rules only**
- **transition rates depend on Clebsch-Gordon coefficients**
- **quantum tunneling of magnetization (QTM) enhances or destroys NDC**

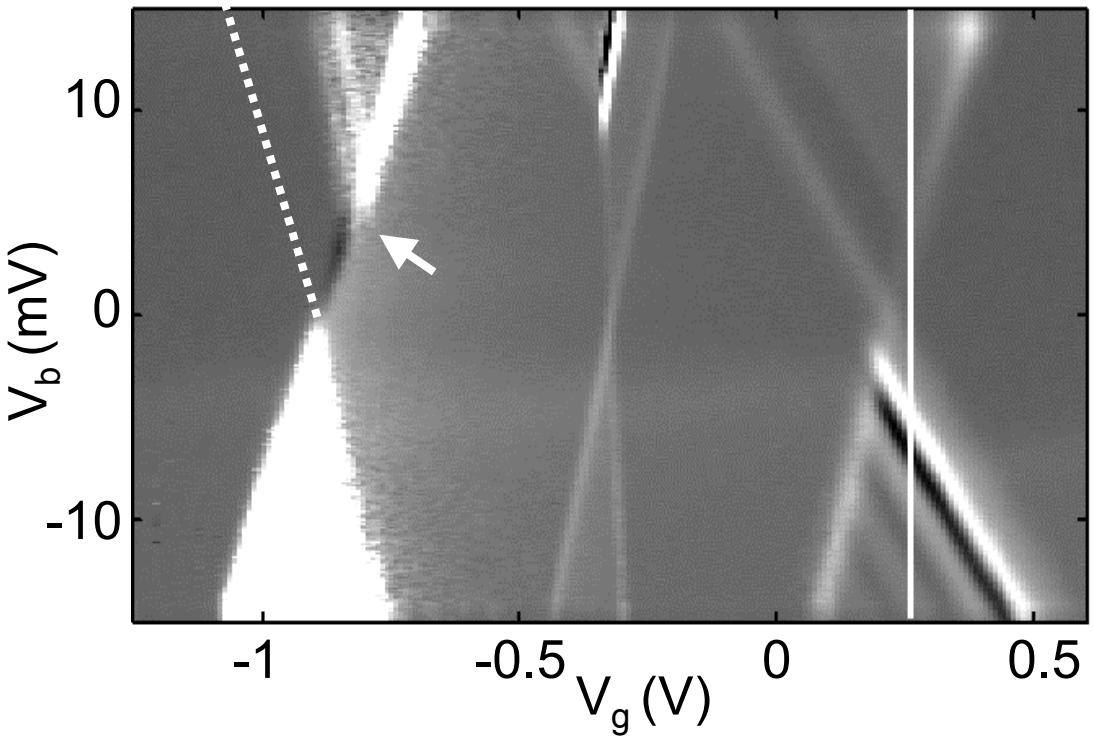
non-degenerate spin multiplets

sequential tunneling populates a blocking state that can only be depopulated slowly by a violation of spin-selection rules induced by QTM





energy scales

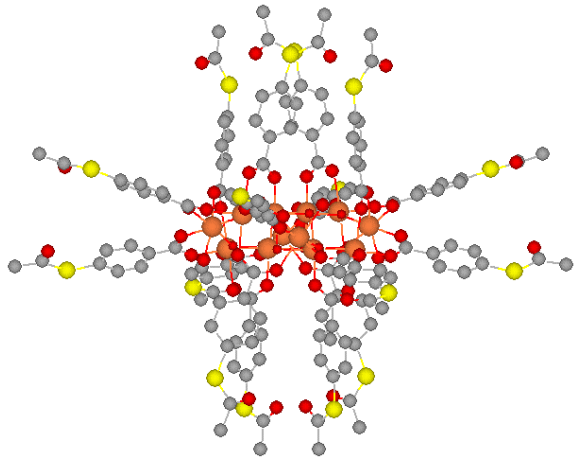


- **CSS: lifted at the energy scale of the magnetic anisotropy barrier (about 5 meV)**

- **NDR: few meV**
depends on choice of the anisotropy barrier and the distance between the two manifolds (not a unique combination but the MAB need to be different for the charge states involved)

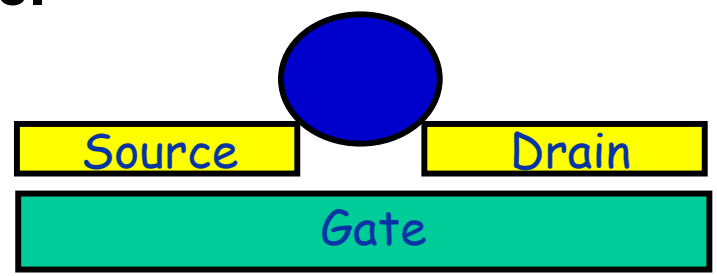
conclusions

First transport through a single Mn-12 molecule shows a new kind of spin blockade due to the presence of non-degenerate spin states.



It would be exciting to do more systematic studies at lower temperatures in a magnetic field to probe QTM (orientation of molecule with respect to field however not known).

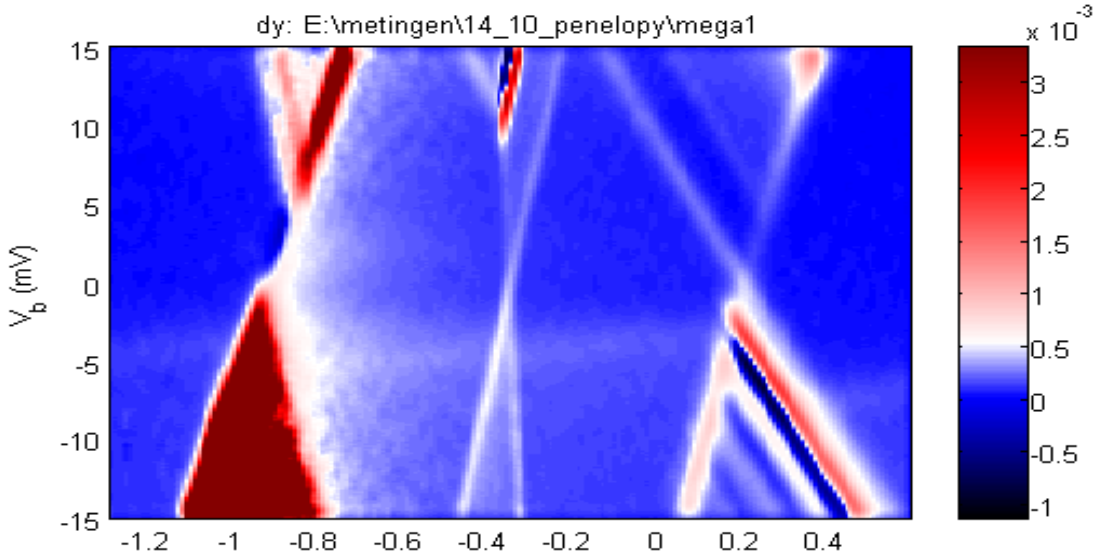
Molecular spintronics: start working in parallel on other –more simple- molecular magnetic systems.

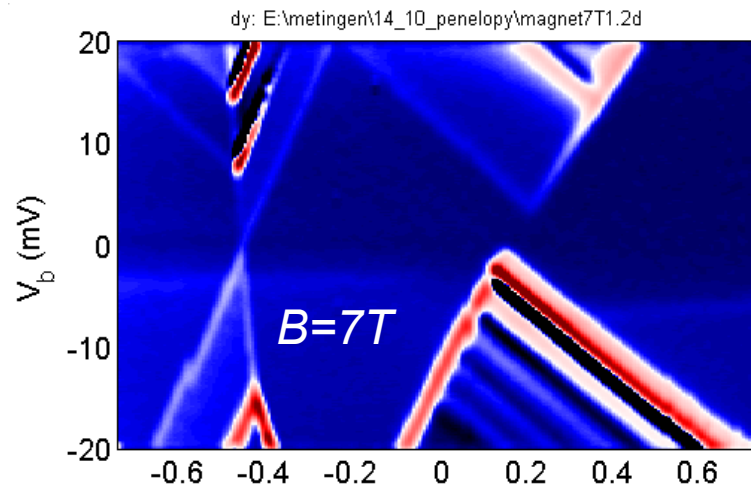


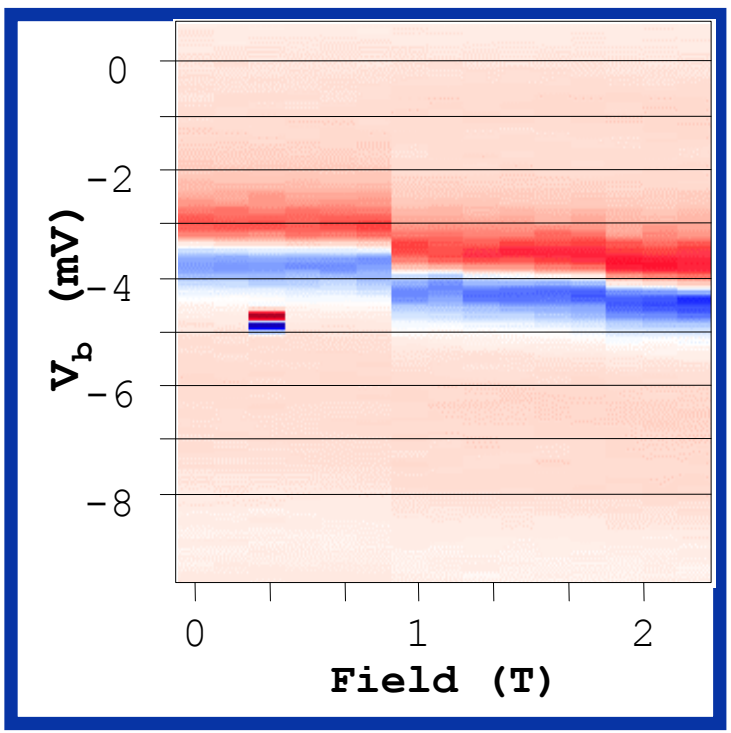
molecular quantum dots:
transition rates are dependent on the wave functions (vibrational modes, spin states, different charge states)

$$\Gamma_{L,R} \Rightarrow \Gamma_{L,R} \left| \left\langle \Psi_{after} \middle| \Psi_{before} \right\rangle \right|^2$$

magnetic field



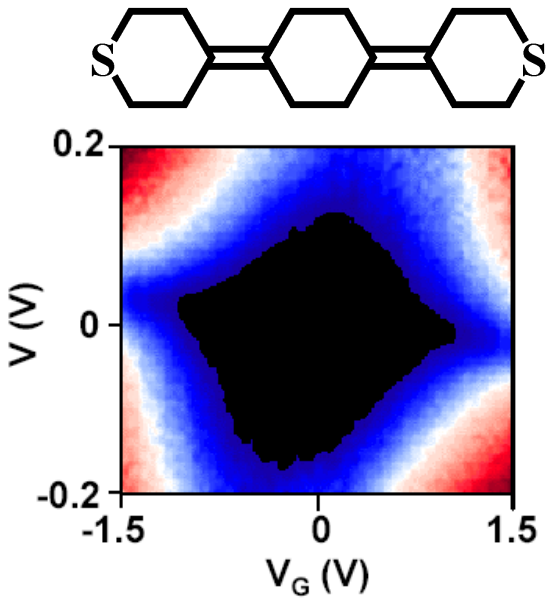


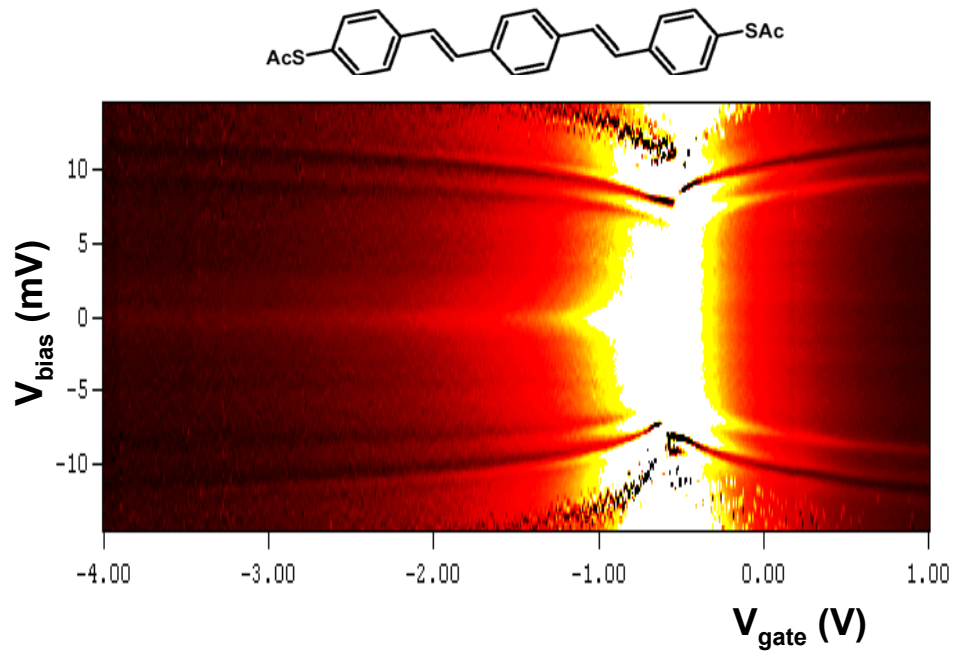


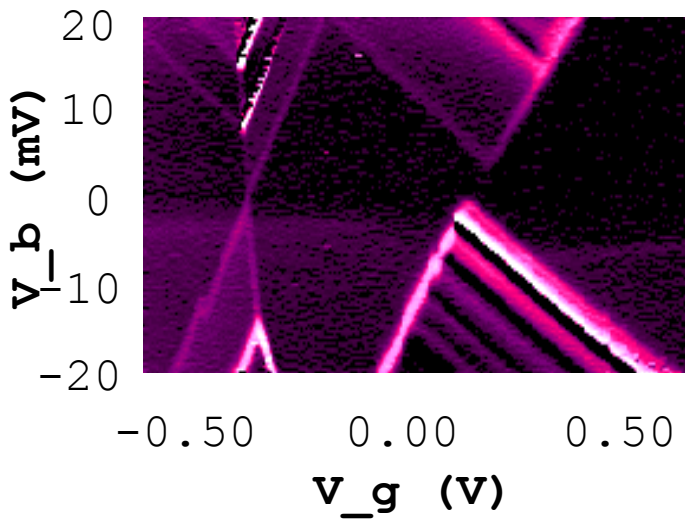
- diamond edge is suppressed
- current increases for neg. bias; decreases for pos. bias

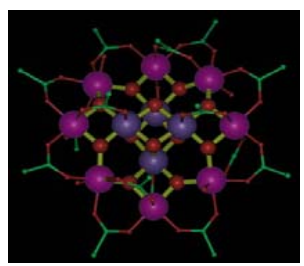
- magnetic field sweep : magnetic rearrangements?

different molecules show distinct different features





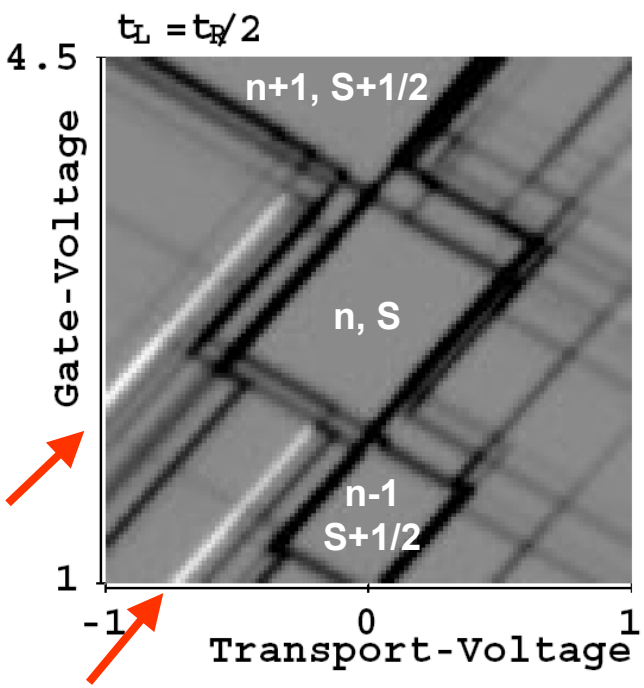




spin blockade

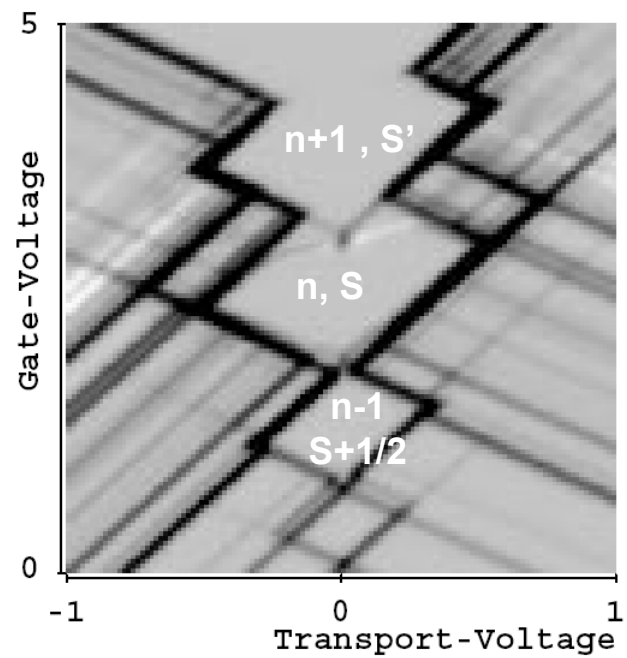
Type I: Negative Differential Resistance (NDR)

excited states with maximum spin S=n/2 are involved



Type II: complete current suppression around zero

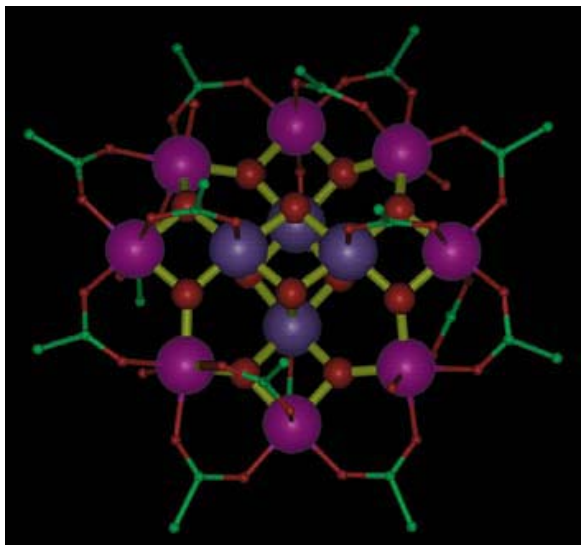
ground states with spin differing by more than ½ (e.g. S=0 ⇒ S'=3/2)



verified in semi-conducting quantum dots

DIETMAR WEINMANN*, WOLFGANG HÄUSLER, KRISTIAN JAUREGUI AND BERNHARD KRAMER (1995)

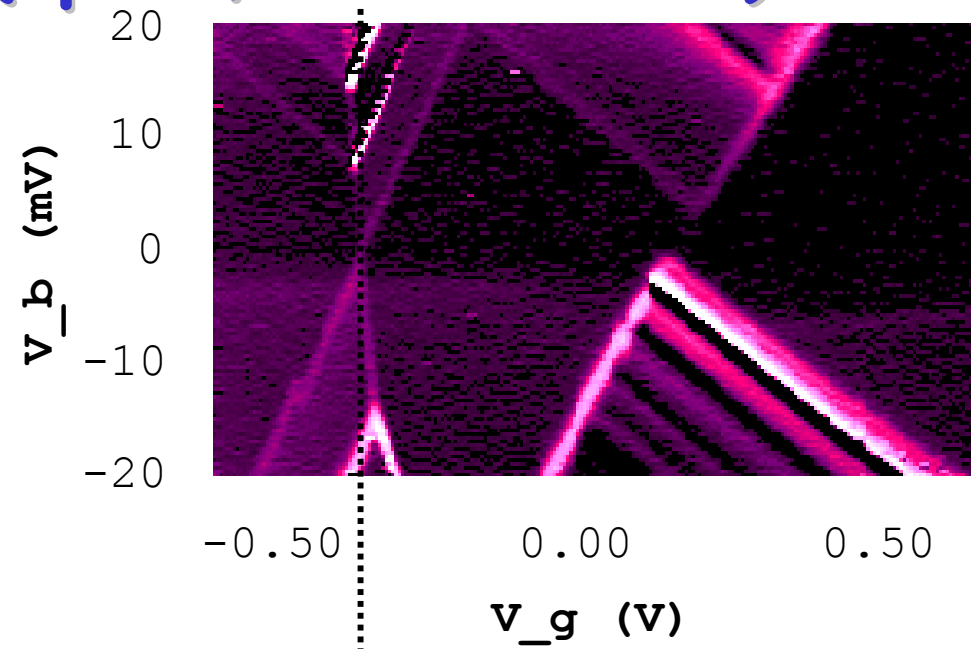
Mn-12: Coulomb-blockade physics with excitations (spin?, vibrations?)

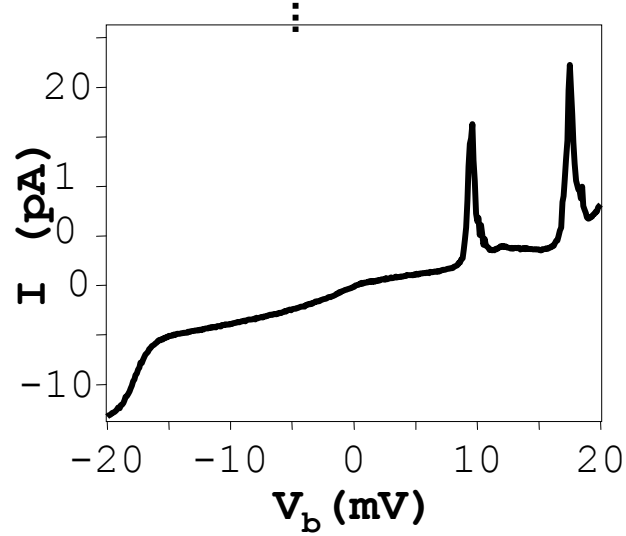


Mn(III), S=2

Mn(IV), S=3/2

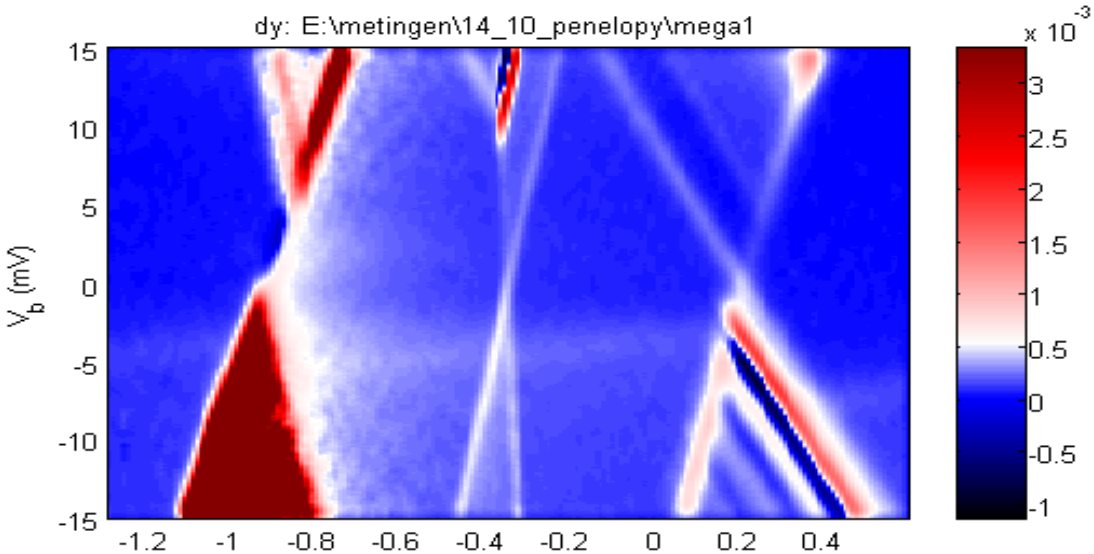
single-molecule magnet Mn-12

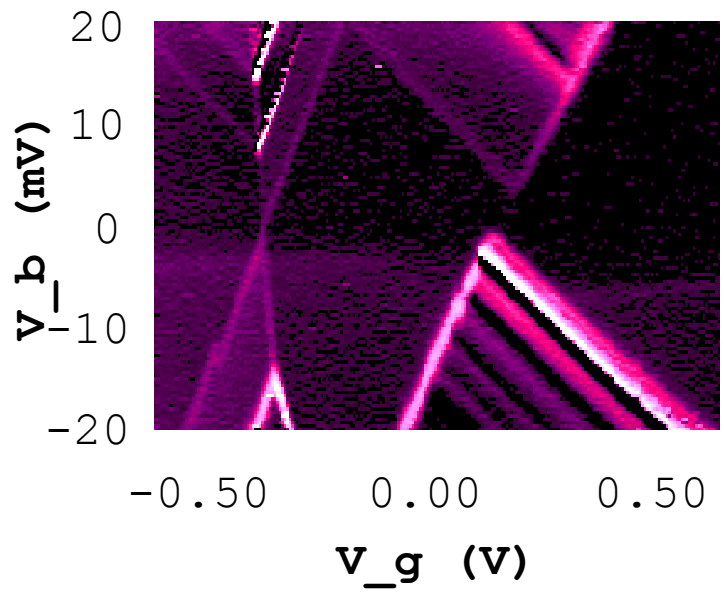
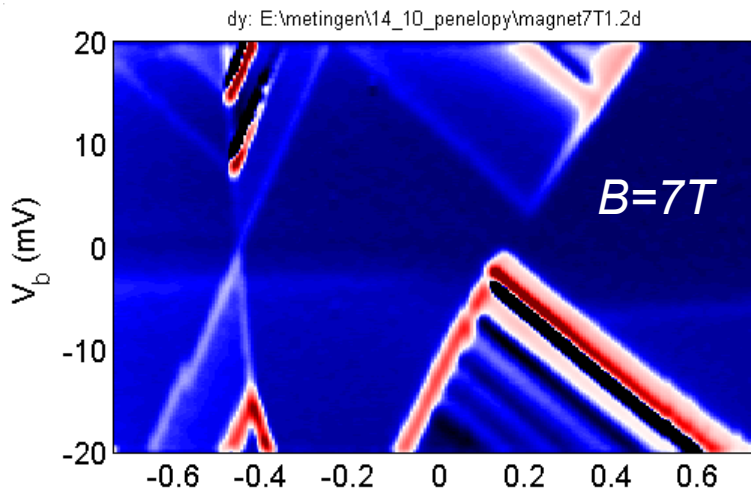




Delft unpublished results

Coulomb blockade in Mn-12 junctions





Manganese-12 molecule with PhSAc ligands, T=3K