Vorlesung 23
Spins on Surfaces

Übersicht über die Kapitel der Vorlesung

0. Motivation

1. Die Oberfläche

2. Dünne Gase

3. Methoden der Oberflächenphysik

4. Schichtwachstum

5. Oberflächenchemie

6. Elektronische Struktur von Oberflächen

7. Oberflächenmagnetismus

8. Quantennanowissenschaften auf Oberflächen

Wiederholung: Rastertunnelspektroskopie nach Tersoff-Hamann

- Rastertunnelspektroskopie: lokale elektronische Struktur der Oberfläche

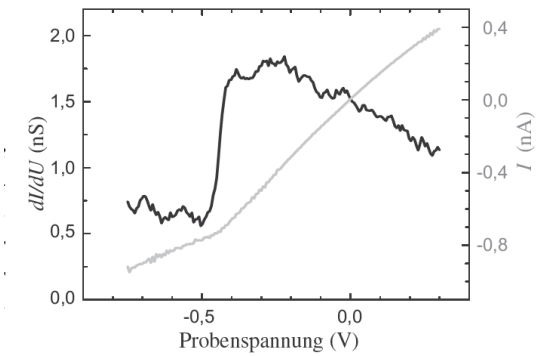
$$\frac{\partial}{\partial U} I(x,y,z_0,U) \propto e\mathcal{T}(eU,U,z_0) D_S(0) \rho^*(x,y,eU)$$
$$+ \int_0^{eU} \rho^*(x,y,E)\mathcal{T}(E,U,z_0)\frac{\partial}{\partial U} D_S(E-eU)dE$$
$$+ \int_0^{eU} \rho^*(x,y,E) D_S(E-eU)\frac{\partial}{\partial U}\mathcal{T}(E,U,z_0)dE. \quad (6.4)$$

Zustandsdichte der Probe

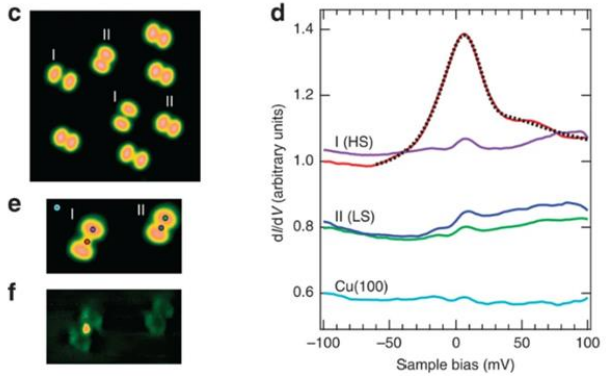
Gute Spitze?

Hintergrund

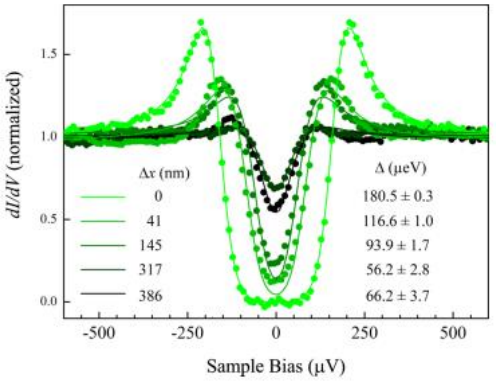
Oberflächenzustände



Kondo-Effekt



SC-Gap



Lernziele

- Inelastische Tunnelspektroskopie
- Mechanismen der Atom-Manipulation

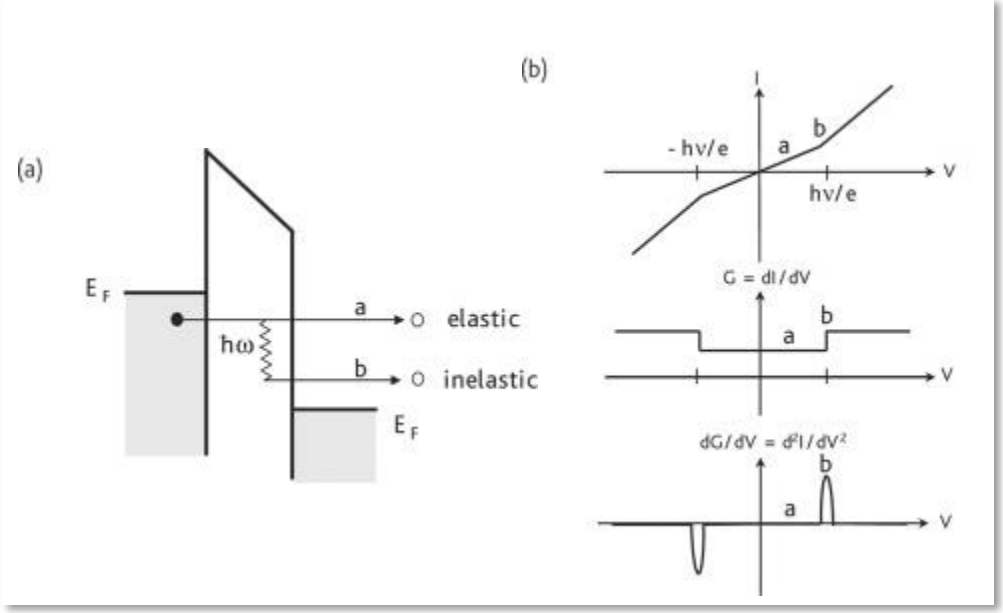
8. Quantennanowissenschaften auf Oberflächen

8.1 Inelastic Electron Tunneling Spectroscopy (IETS)
8.2 Atom Manipulation

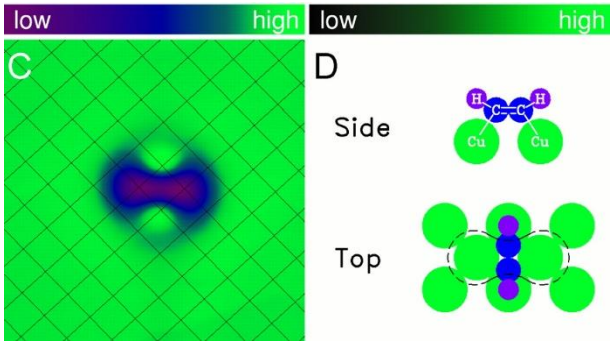
8.1 Inelastic Electron Tunneling Spectroscopy

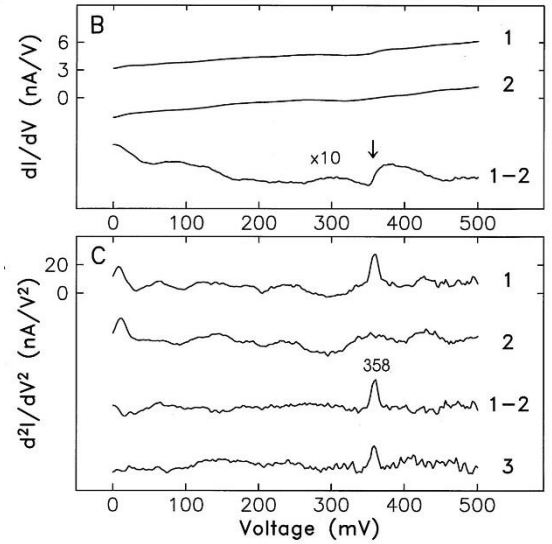
- Excite vibrations of molecular adsorbates
- Some of the tunneling electrons can lose energy by exciting vibrations.
- These inelastic processes lead to a second tunneling path, which gives an additional current contribution to the tunneling current.
- Since the incident electron should have enough energy to excite this vibration, there is a minimum energy required

$$e \cdot V_{Tunnel} = E_{Vib}$$



Acetylene molecule on Cu(100)





1: On C2H2

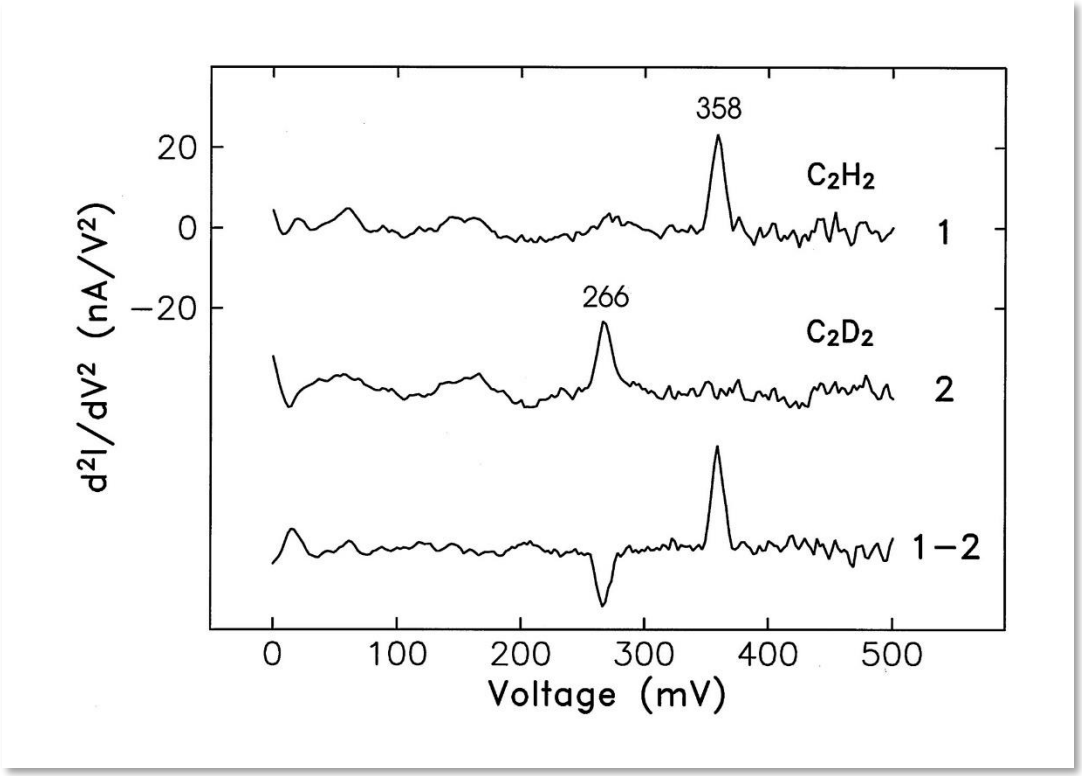
2: On copper

https://en.wikipedia.org/wiki/Inelastic_electron_tunneling_spectroscopy#

https://www.science.org/doi/10.1126/science.280.5370.1732

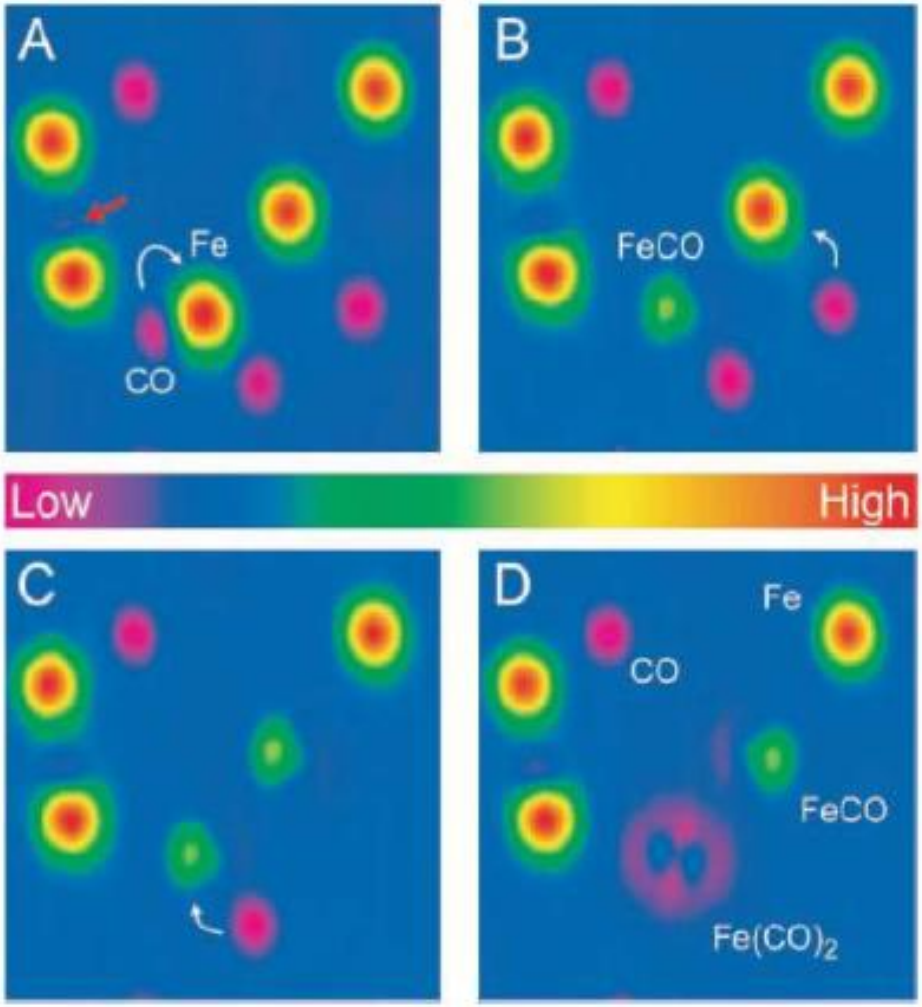
8.1 Inelastic Electron Tunneling Spectroscopy

- Konsistenz-Check: Unterschiedliche Isotope haben unterschiedliche Vibrations-Energien



https://www.science.org/doi/10.1126/science.280.5370.1732

8.1 Inelastic Electron Tunneling Spectroscopy

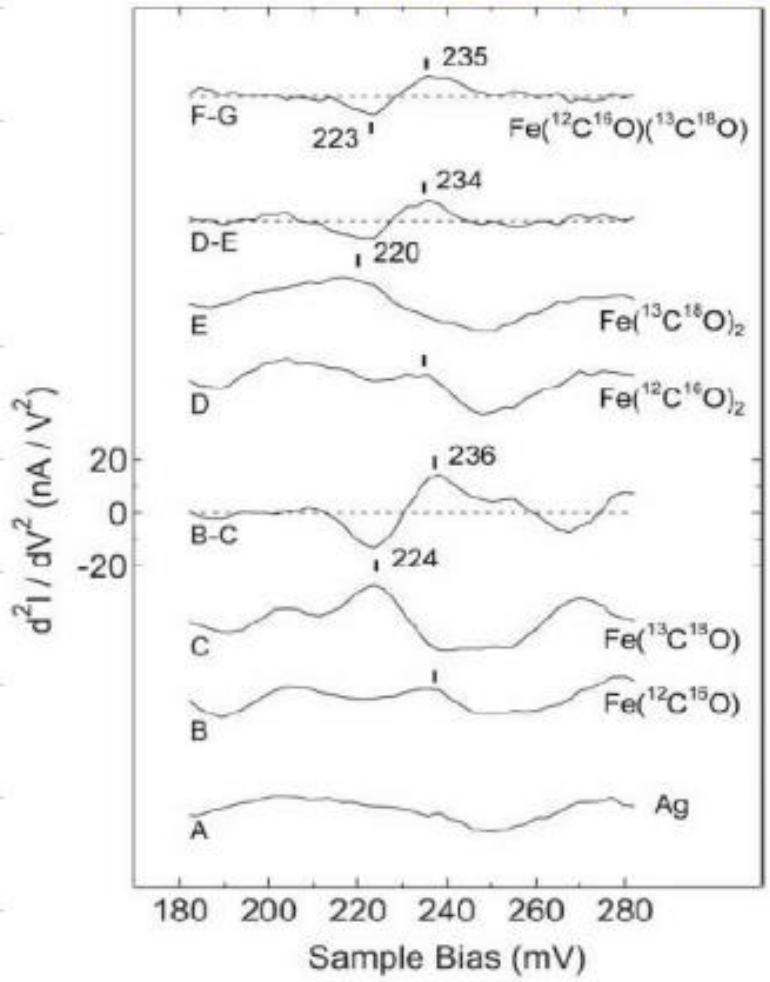


- Das physiosorbierte CO wird von der Ag(100) Oberfläche gehoben und auf ein einzelnes Fe Atom gesetzt wo es chemisorbiert.
- Es kann ein einzelner $Fe(CO)_2$ Komplex hergestellt werden.

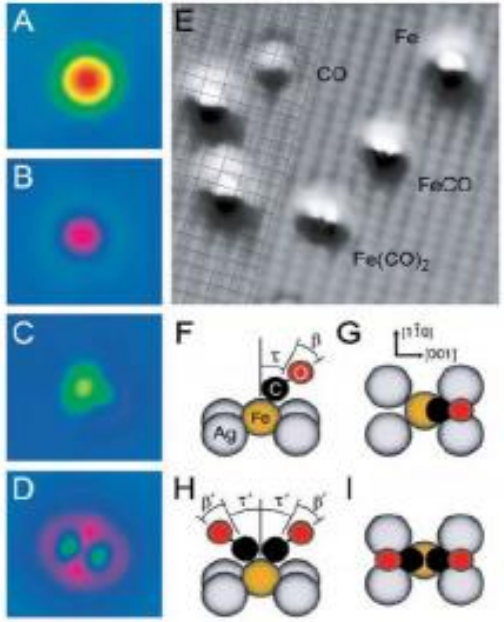
https://www.science.org/doi/epdf/10.1126/science.286.5445.1719

8.1 Inelastic Electron Tunneling Spectroscopy

Vibrationsspektroskopie einzelner Moleküle

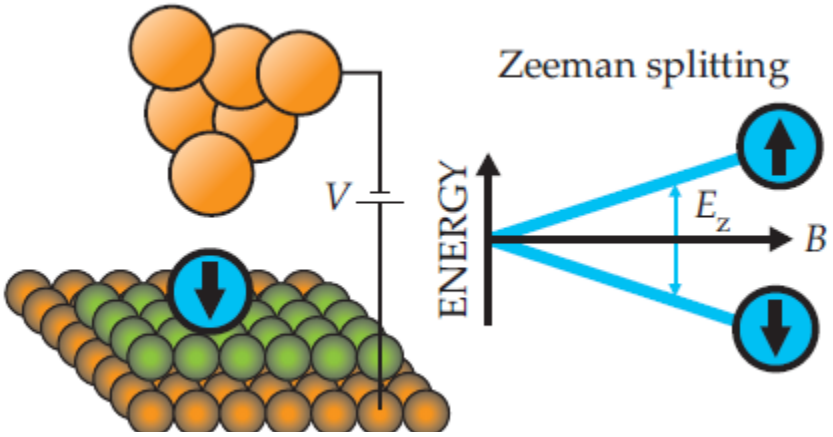


- Alle Zwischen- und Endprodukte können einzeln spektroskopiert werden und somit eindeutig identifiziert werden.
- Isotopenverschiebungen der Linien geben Auskunft über nukleare Spezies.

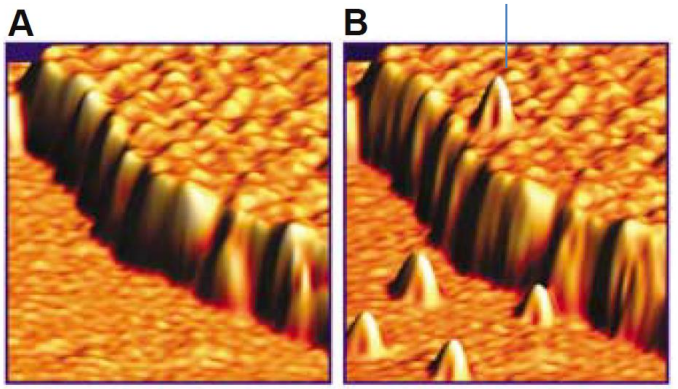


Inelastic spin flip spectroscopy

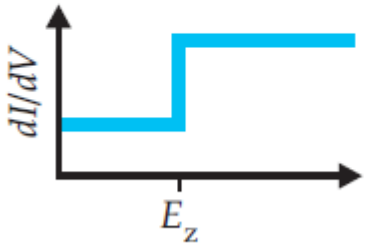
- Spin excitation of a surface spin via the tunneling current if the energy is high enough



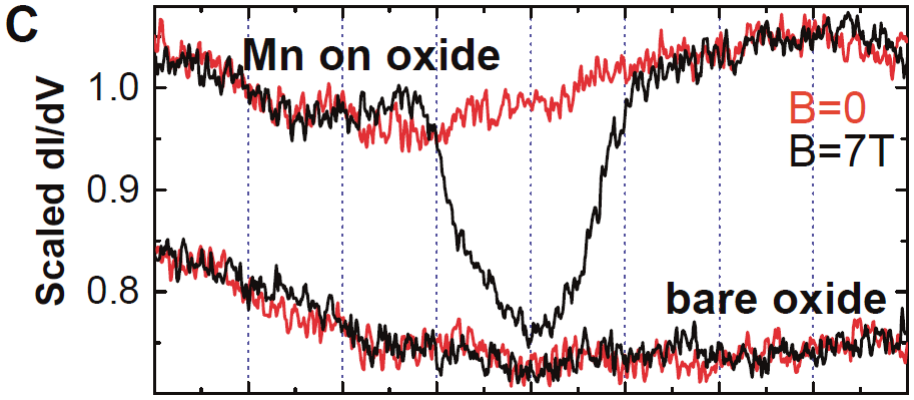
Mn on Al2O3



Spin excitation spectra



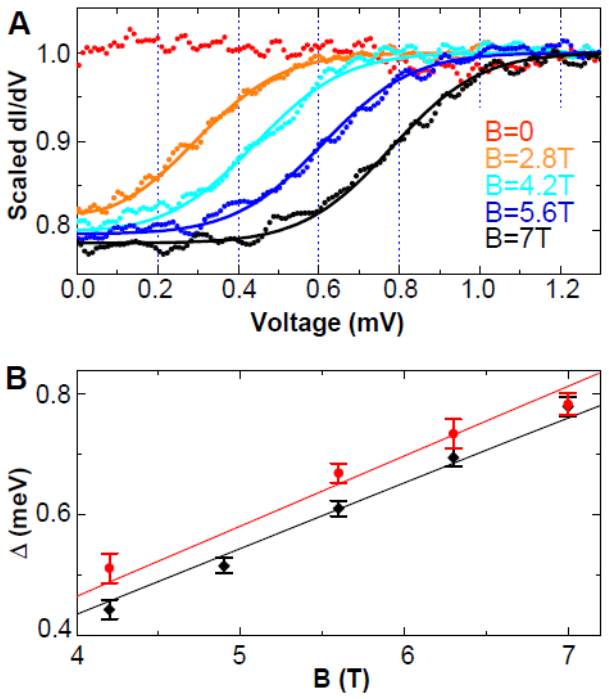
$$e \cdot V_{Tunnel} = E_{Zeeman}$$

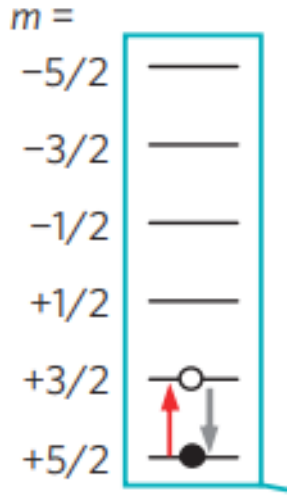


https://pubs.aip.org/physicstoday/article/68/3/42/415025/Atomic-spins-on-surfacesWhen-adapted-to-cryogenic

Measuring the Zeeman interaction

- Above a threshold voltage, electrons are able to transfer energy to these excitations during the tunnelling process.
- This additional tunneling channel results in an upward step in conductance at the threshold voltage.
- Tunneling electrons lose energy to spin-flip excitations of single Mn atoms.
- The signature of Zeeman splitting in spin-flip IETS is a step up in conductance at an energy proportional to the applied magnetic field.





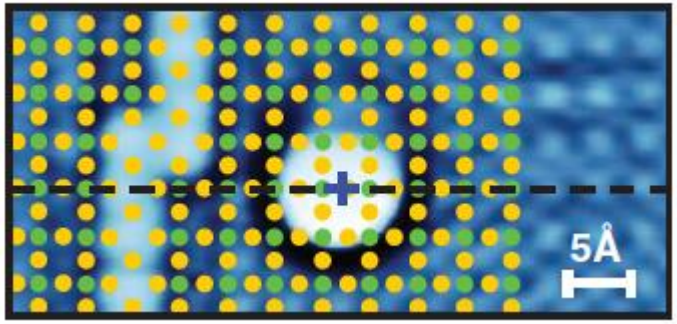
$$E_{Zeeman} = g\mu_B B$$

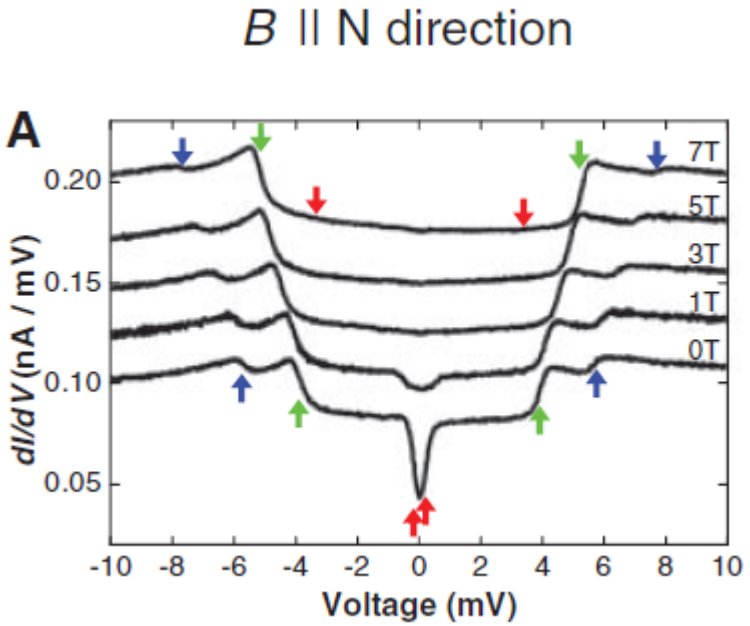
$$\hat{H} = g\mu_B \vec{B} \cdot \hat{\vec{S}}$$

$$\mu_B = 57.9 \ \mu eV/T$$

https://www.science.org/doi/pdf/10.1126/science.1101077

Magnetic Anisotropy: Fe atoms on CuN





- Magnetic atom becomes incorporated into a polar covalent surface molecular network in the copper nitride.

→ Provides magnetic anisotropy

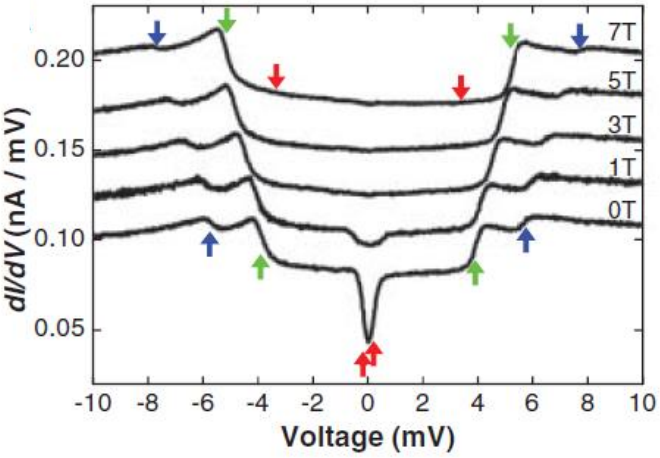
$$\hat{H} = g\mu_B \vec{B} \cdot \hat{\vec{S}} + D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2)$$

- The axial term D **splits** the degeneracy of the spin-states on the basis of the magnitude of the spin's z projection m
- the transverse term **mixes** E states of different m.

https://www.science.org/doi/pdf/10.1126/science.1146110

Magnetic Anisotropy: Fe atoms on CuN

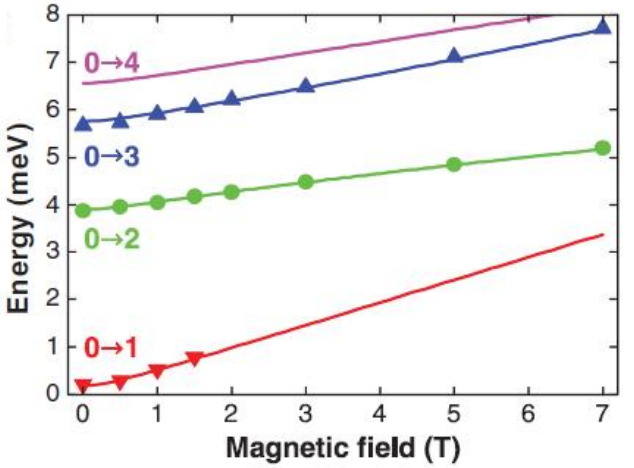
- Experimental parameters can be determined by fits to the step position and height
- For that the Hamiltonian needs to be diagolanalized and Eigenenergies need to be calculated



Fit parameters:

$$\hat{H} = g\mu_B \vec{B} \cdot \hat{\vec{S}} + D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2)$$

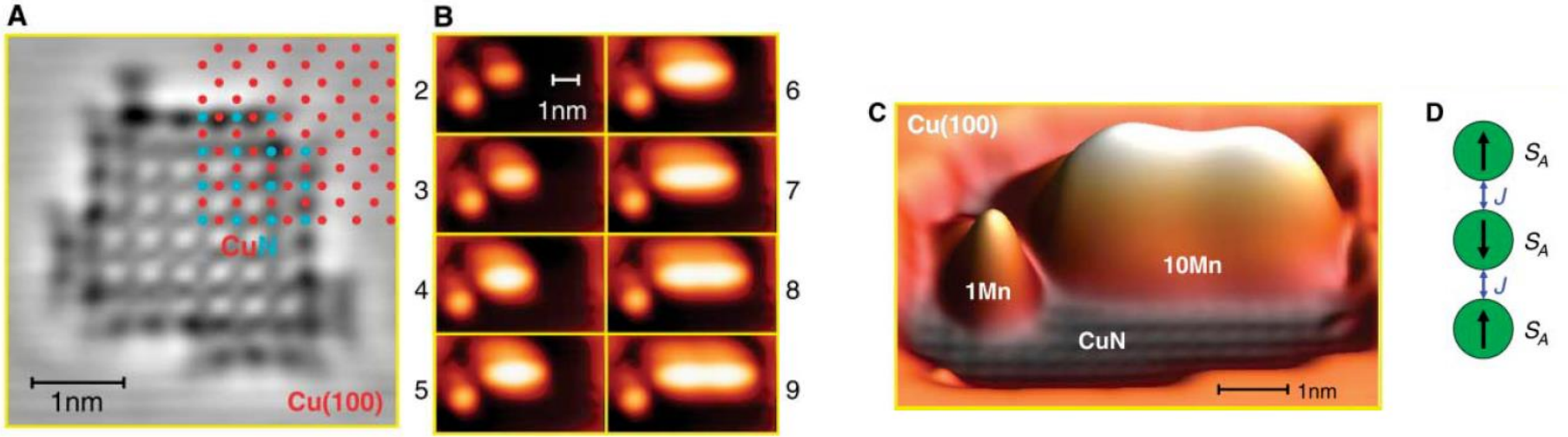
g = 2.11 ± 0.05, D = –1.55 ± 0.01 meV, and E = 0.31 ± 0.01 meV



A quantum antiferromagnetic spin chain

- Positioning atoms in close distance via atom manipulation
- Leads to additional Heisenberg exchange interaction

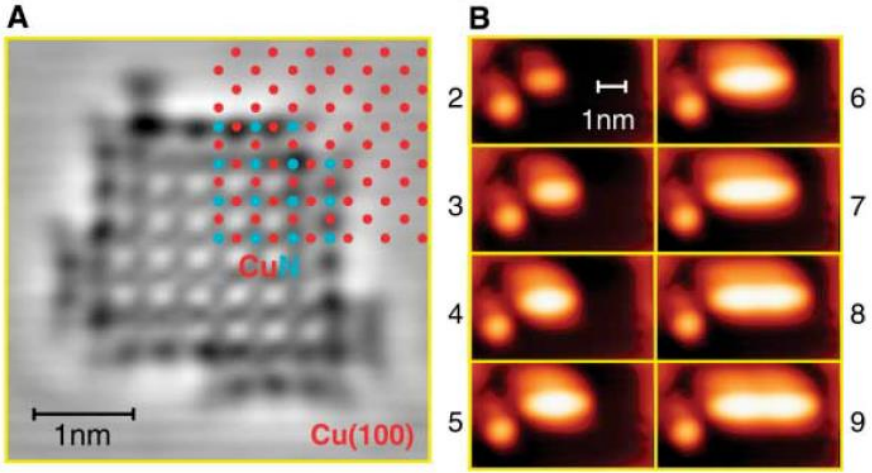
$$H_N = J \sum_{i=1}^{N-1} \mathbf{S}_i \cdot \mathbf{S}_i + 1$$

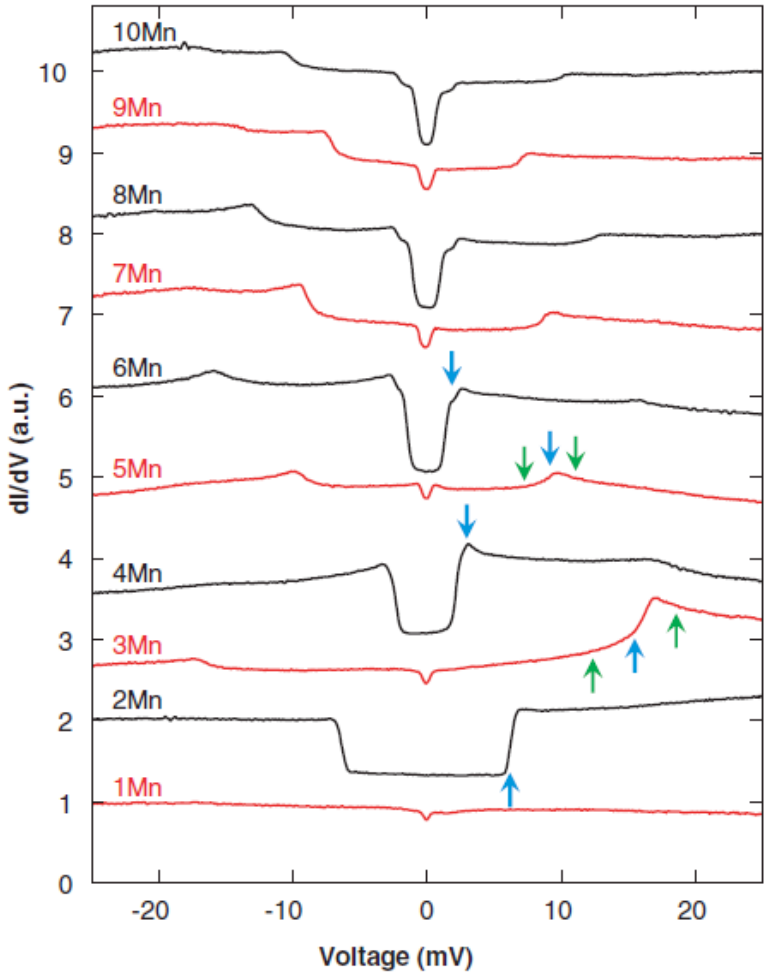


https://www.science.org/doi/pdf/10.1126/science.1125398

Length dependence

- Odd length chain: spin-flip excitation at V~0
- Even length chain: no spin-flip excitation at V~0, large step at higher voltage

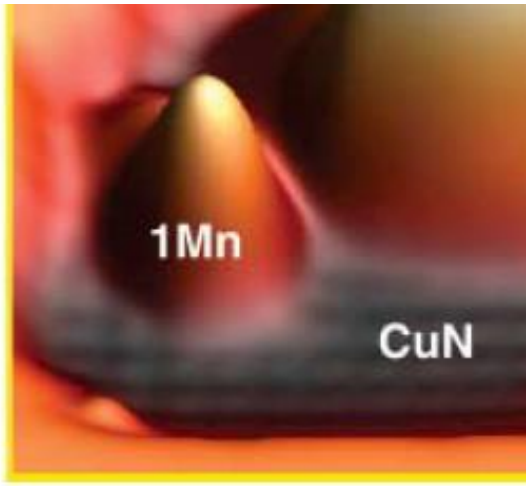


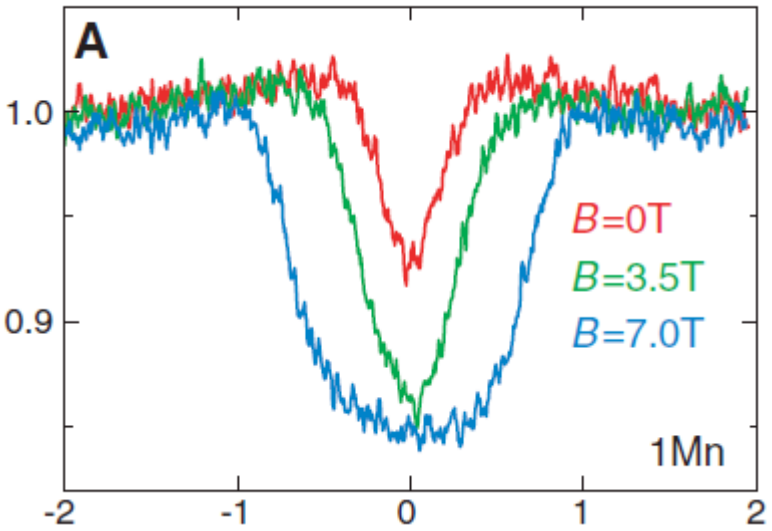


https://www.science.org/doi/pdf/10.1126/science.1125398

8.1 Inelastic Electron Tunneling Spectroscopy

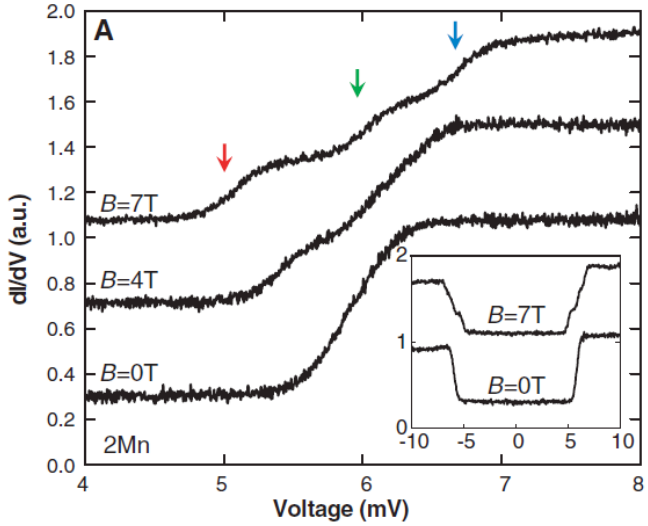
- Spectra taken on a single Mn atom on CuN
- The existence of spin-flip excitations requires S > 0 for the ground state of these chains.
- Small zero field splitting

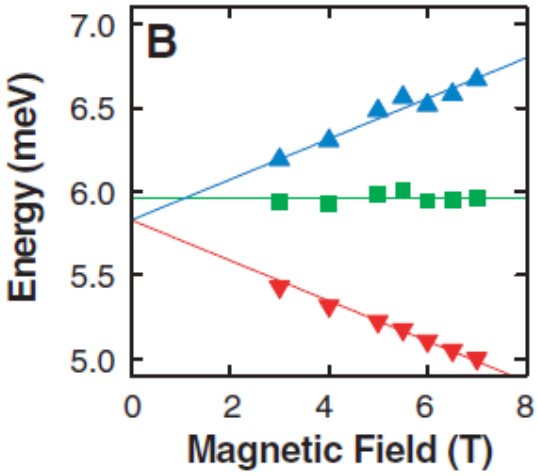


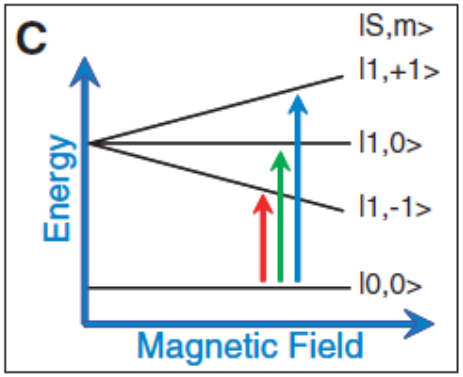


Conductance spectra of Mn dimer on CuN.

- The IETS steps thus correspond to spin-changing transitions from the ground state (with S = 0 and m = 0) to an excited state (with S = 1 and m = –1, 0, 1)





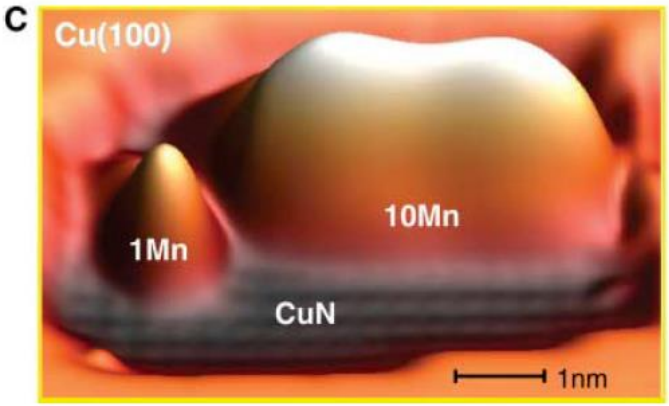


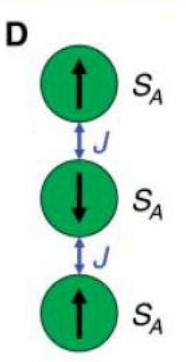
$$H_N = J\sum_{i=1}^{N-1} \mathbf{S}_i \cdot \mathbf{S}_i + 1$$

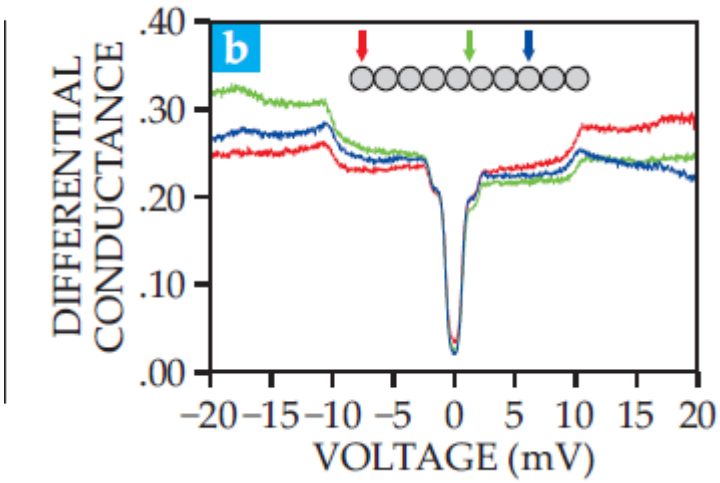
8.1 Inelastic Electron Tunneling Spectroscopy

- Excitations vary little over the chain

→ Global excitation of the chain from S = 0 and S = 1



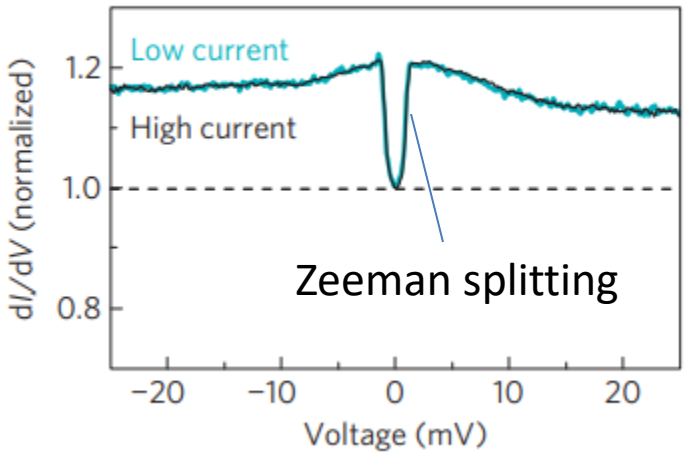


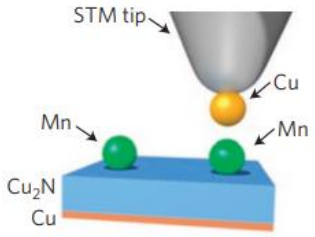


Manipulation of the Electron-Spin dynamics

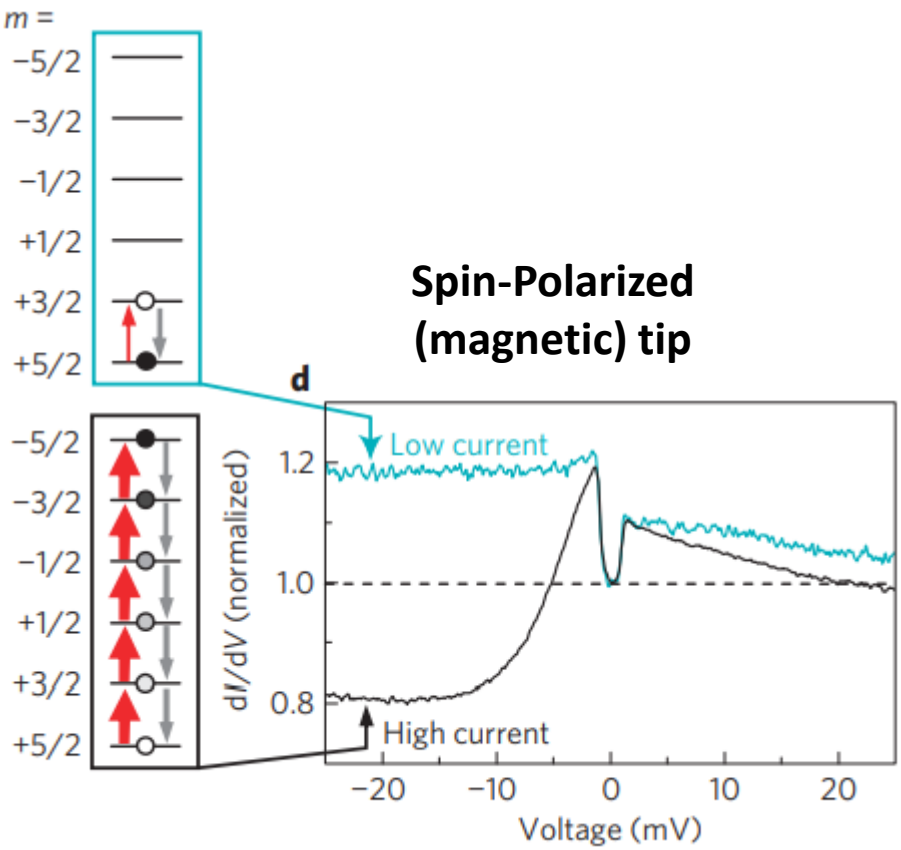
- Spin pumping with tunnel electrons

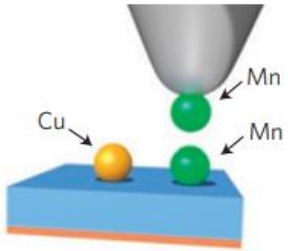
No Spin-Polarized (magnetic) tip





Spin-Polarized (magnetic) tip





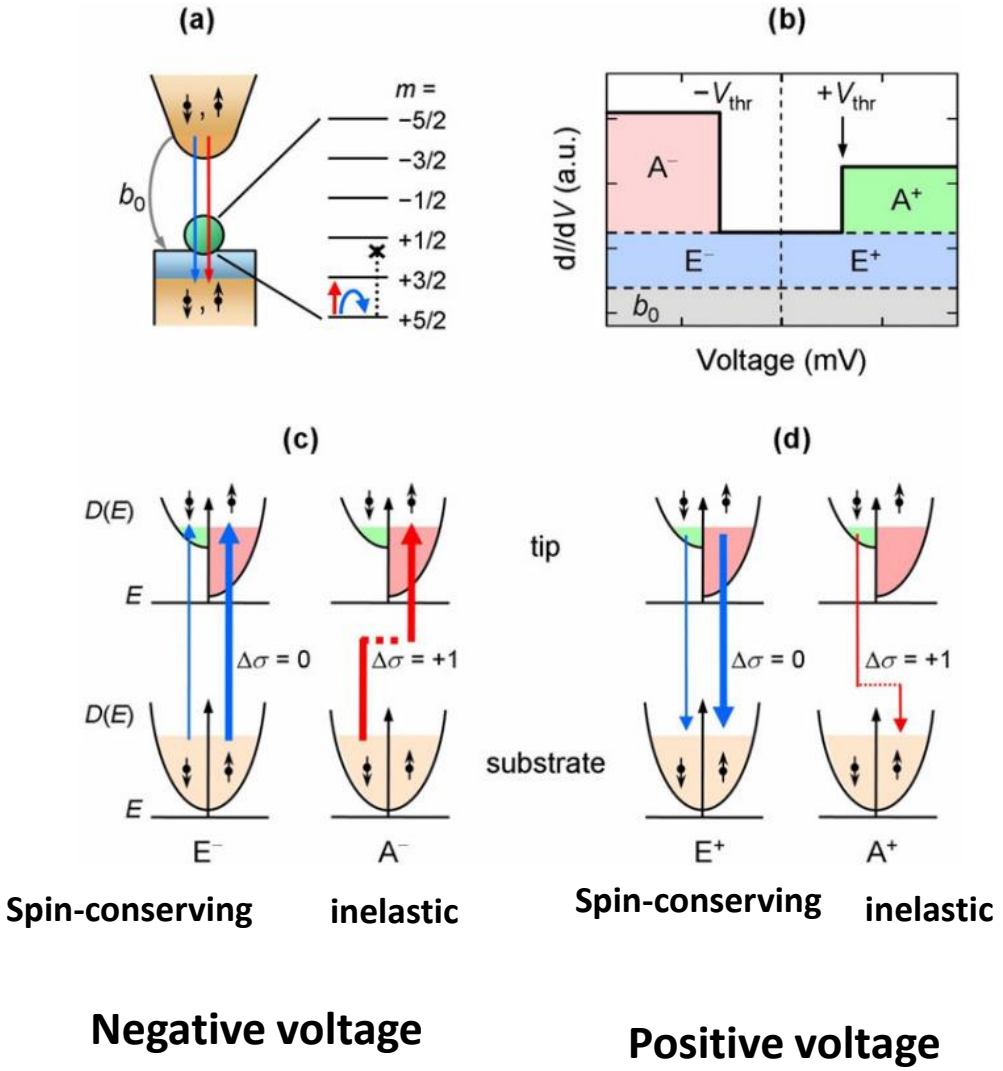
https://iopscience.iop.org/article/10.1088/1367-2630/12/12/125021/meta

8.1 Inelastic Electron Tunneling Spectroscopy

- a spin-polarized tip gives a larger step for negative V than for positive V
- This asymmetry is the consequence of a selection rule for spin excitations with tunnelling electrons

→ total spin angular momentum is conserved during the tunnelling process

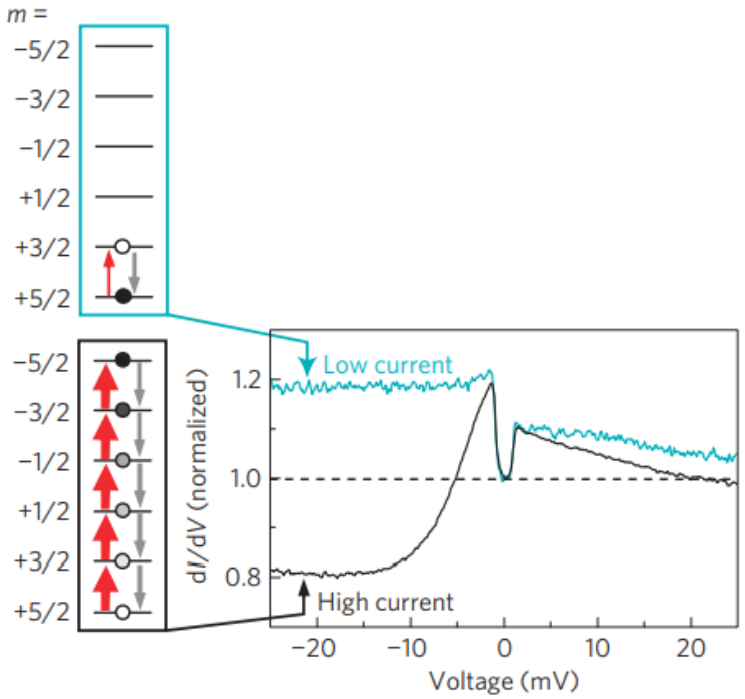
→ spin excitation changes m for the atom by −1, it requires down-electron states in the tip when current flows out of the tip (V >0), and up-electron states in the tip when current flows into the tip (V < 0)

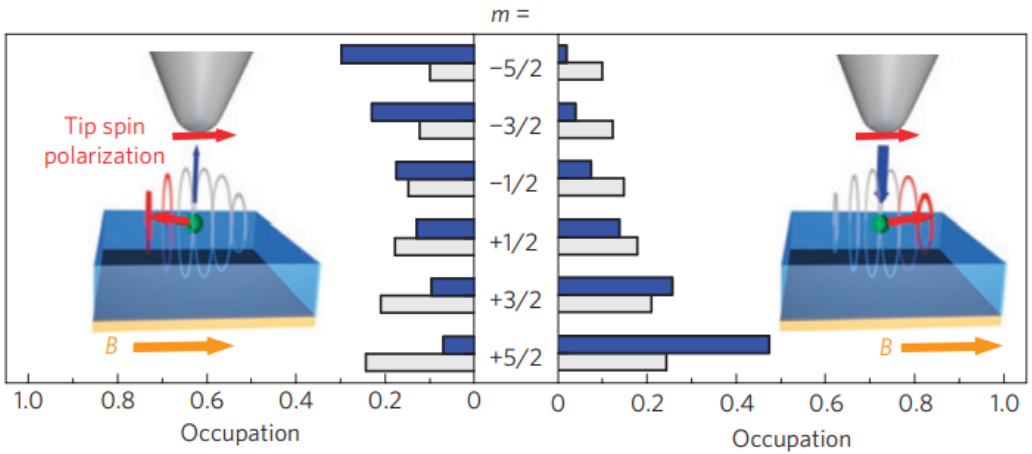


https://iopscience.iop.org/article/10.1088/1367-2630/12/12/125021/meta

8.1 Inelastic Electron Tunneling Spectroscopy

- **Spin-Pumping**: at high currents the excited electrons gets again excited before it can relax
- Depends crucially on the lifetime T1 of the surface spin
- Changes the ground state population

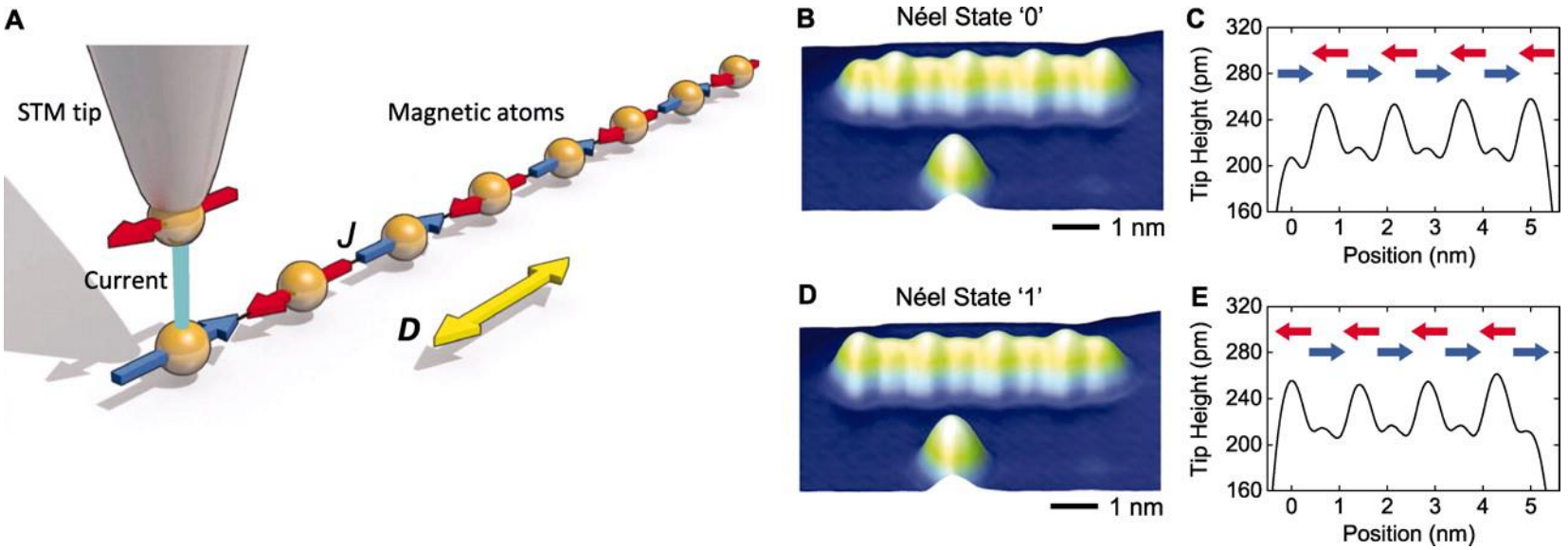




https://iopscience.iop.org/article/10.1088/1367-2630/12/12/125021/meta

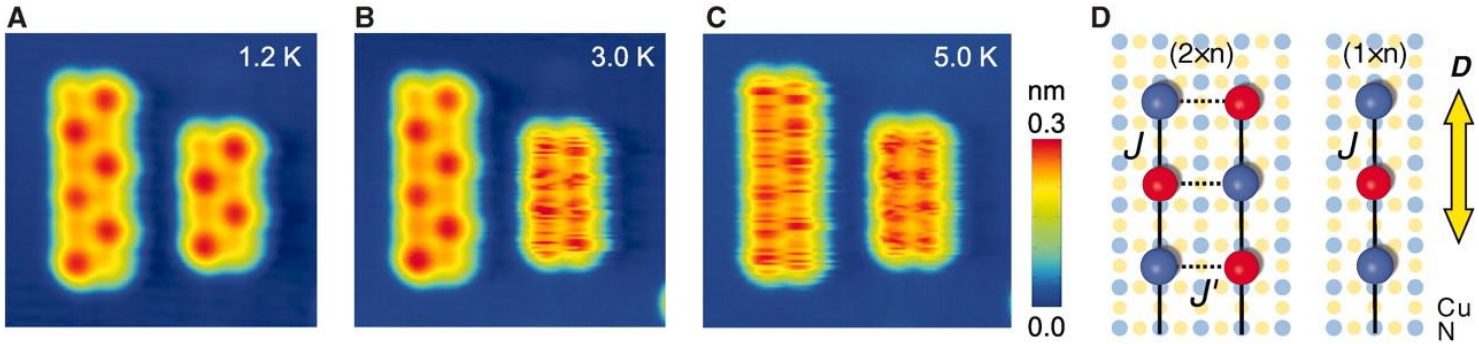
Bistable AFM array of Fe atoms.

- atoms on a surface coupled antiferromagnetically with exchange energy J.
- Surface-induced magnetic anisotropy fields cause the spins of the atoms to align parallel to the easy magnetic axis, D.
- A spin-polarized STM tip reads the magnetic state of the structure by magnetoresistive tunneling.



https://www.science.org/doi/full/10.1126/science.1214131

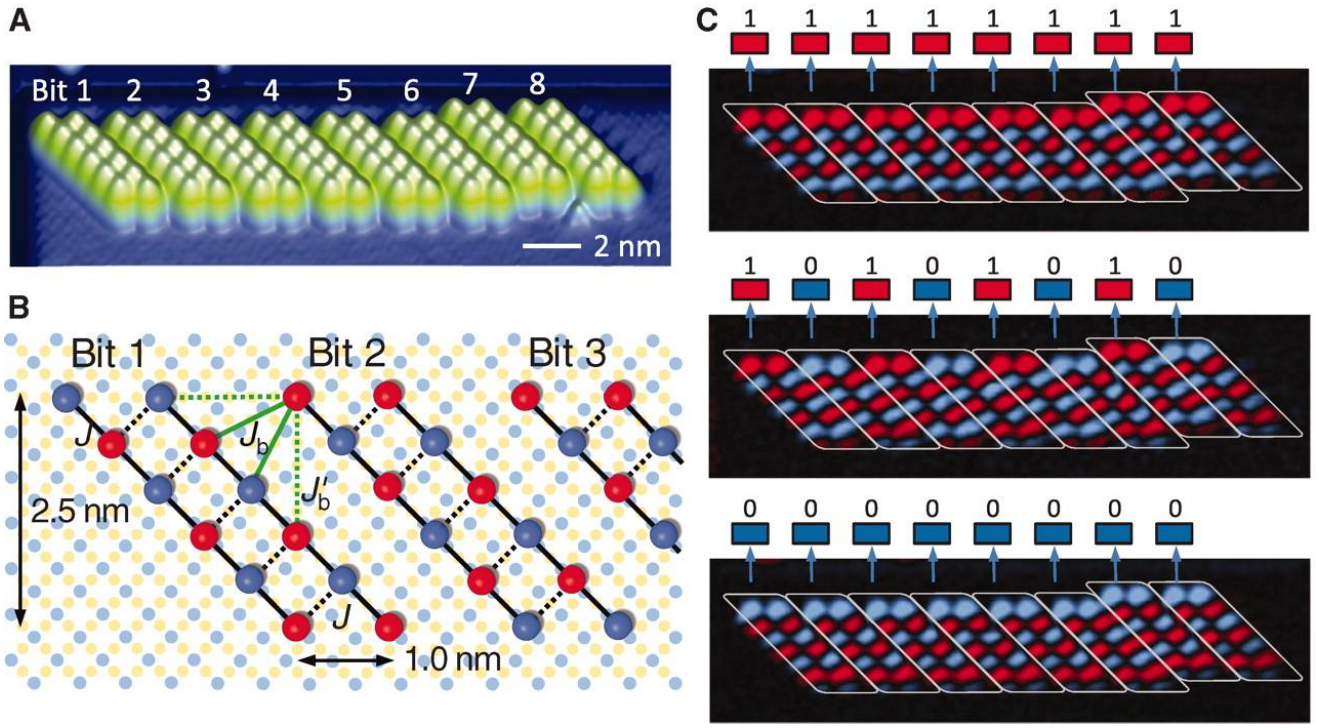
- Thermal stability of AFM arrays: (2×6) and (2×4) arrays of Fe atoms.
- Both arrays have stable Néel states at 1.2 K



https://www.science.org/doi/full/10.1126/science.1214131

8.1 Inelastic Electron Tunneling Spectroscopy

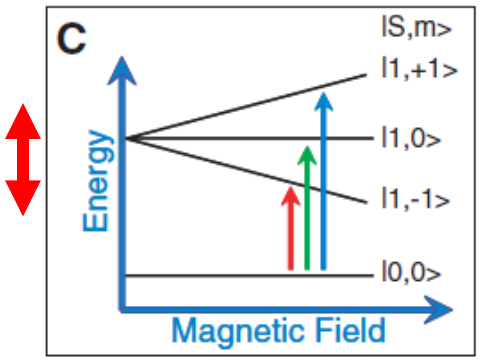
- Ultradense AFM data storage. (A) Non–spin-polarized STM image, 24 × 8 nm, of eight (2×6) arrays assembled from Fe atoms.
- Information storage in a magnetic byte. A color-coded difference between spin-polarized and spin-averaged images is shown, with red corresponding to higher tip height and blue to lower tip height in the spin-polarized image.

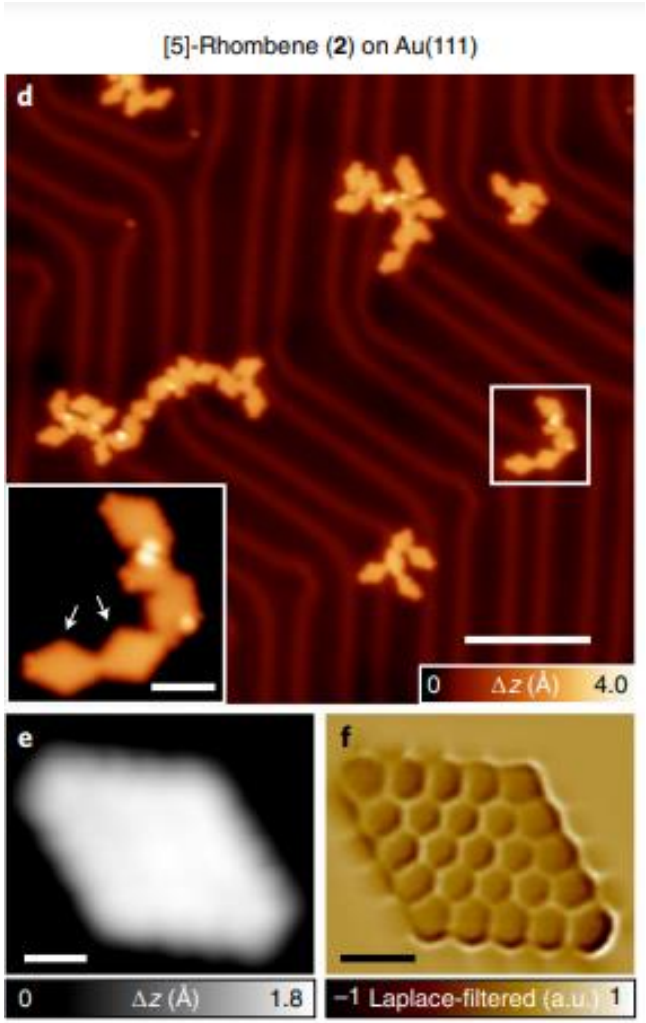


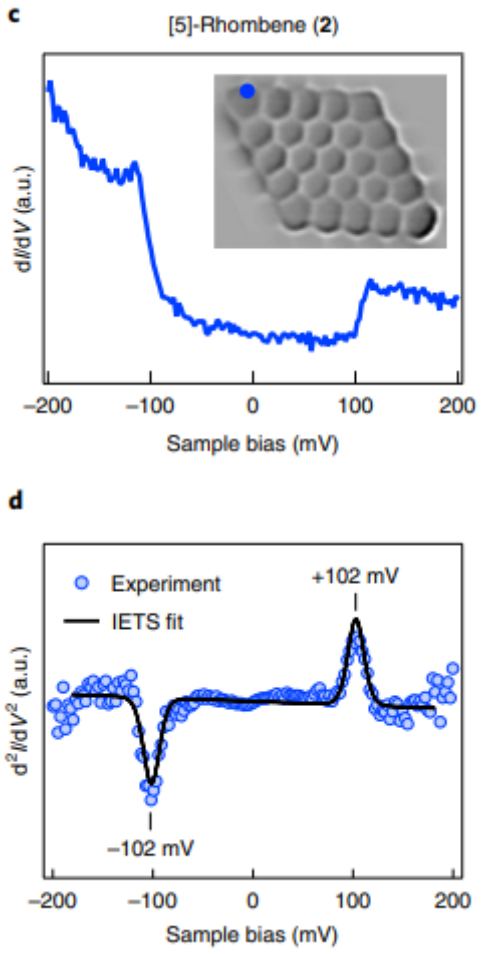
https://www.science.org/doi/full/10.1126/science.1214131

8.1 Inelastic Electron Tunneling Spectroscopy

- Magnetic exchange coupling can also appear in carbon structures and radical spins
- Here: Nanographene with magnetic spin singlet ground state
- Very large spin-spin coupling







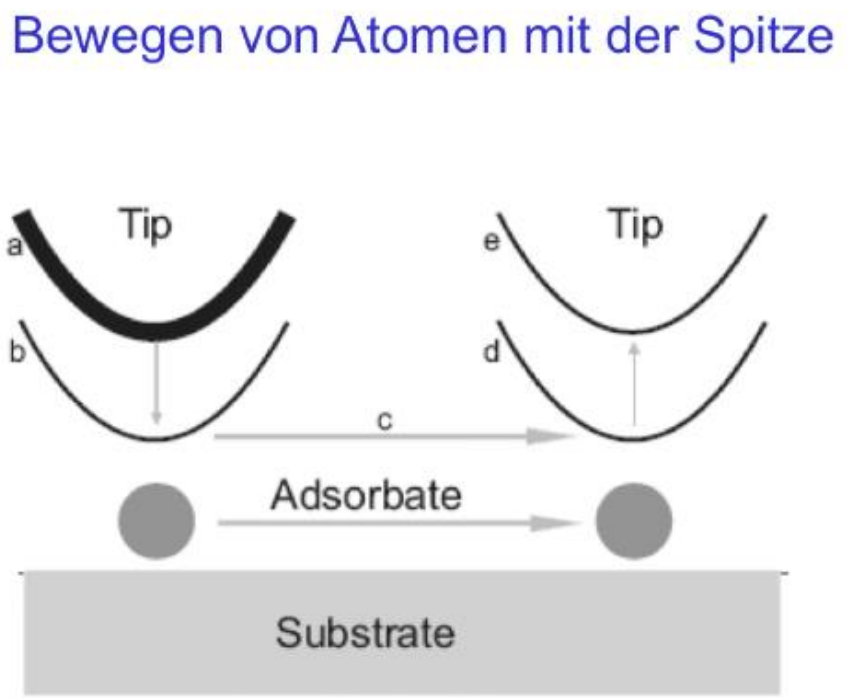
https://www.nature.com/articles/s41557-021-00678-2.pdf

8. Quantennanowissenschaften auf Oberflächen

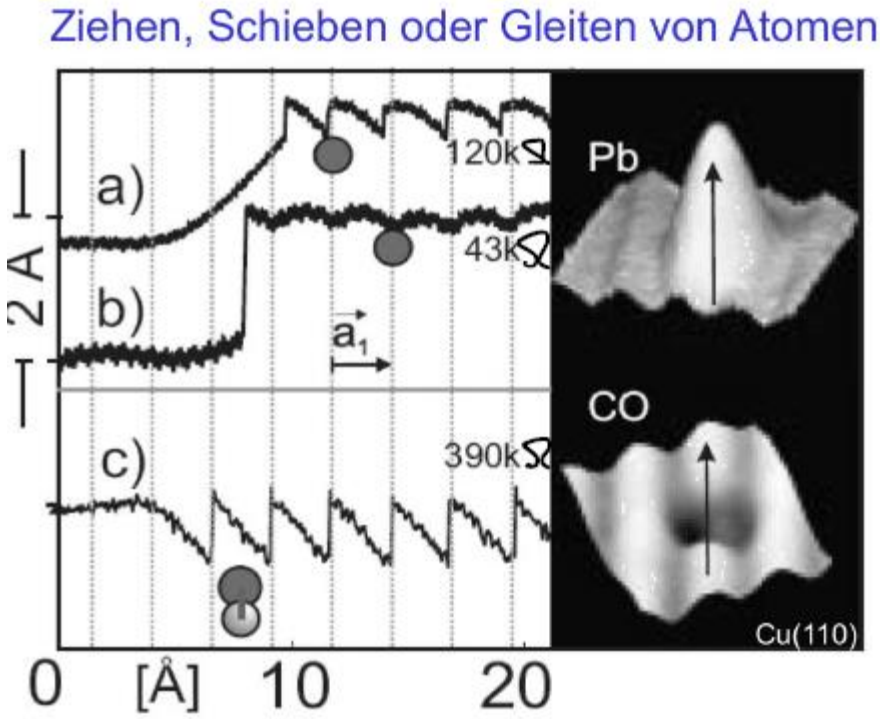
8.1 Inelastic Electron Tunneling Spectroscopy (IETS)
8.2 Atom Manipulation

Atomare Manipulation

Bei kleinem Abstand zwischen Spitze und Probe überlappen die Wellenfunktionen sehr stark
→Wir formen eine chemische Bindung
→Kräfte



a,e: Kleine Tunnelströme, so dass das STM im Wesentlichen nur abbildet (Überlapp klein)
a→b: Strom erhöhen, es entstehen Kräfte
b→c: Spitze seitlich bewegen, Adsorbat bewegt sich mit
c→d: Strom erniedrigen



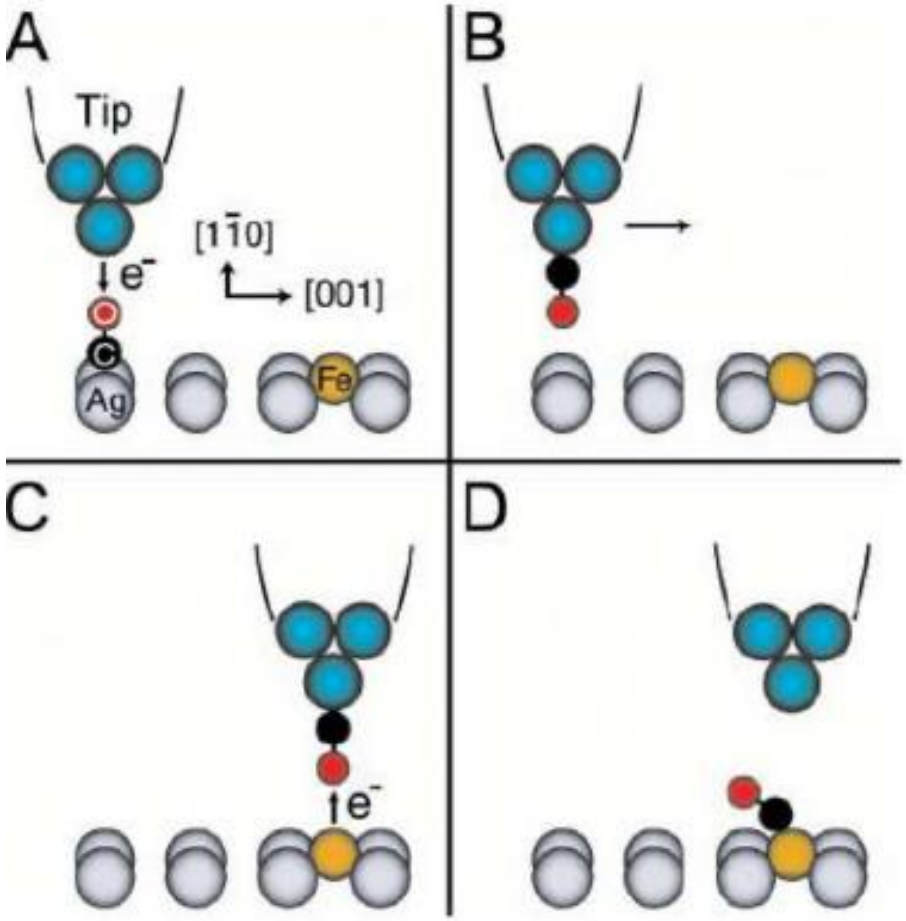
a) Attraktive Wechselwirkung, Pb springt von Gitterplatz zu Gitterplatz
b) Sehr starke attraktive Wechselwirkung: Pb Atom gleitet mit der Spitze
c) Repulsive Wechselwirkung: „schieben“ des Adsorbates

Meyer at al. Appl. Phys. A 68, 125 (1999)

A Boy and his Atom

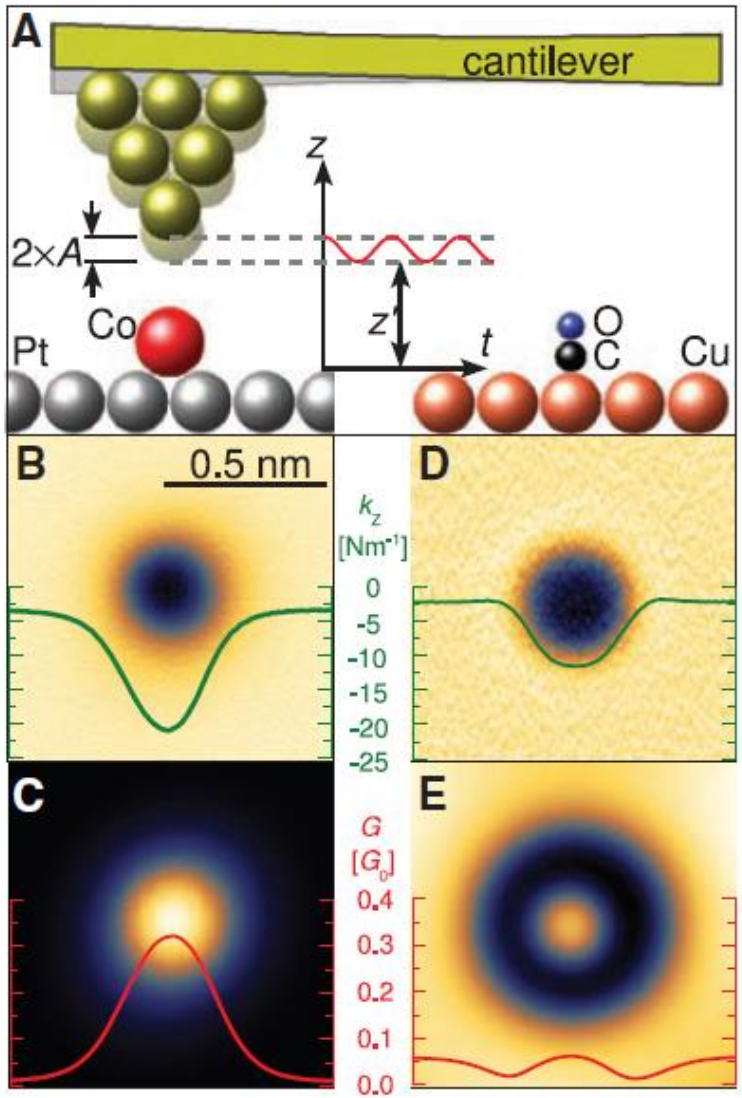
https://www.youtube.com/watch?v=oSCX78-8-q0

Vertikale Manipulation und Herstellung einer chemischen Bindung



- Locker gebundene (physiosorbierte) Moleküle können durch geeigneten Stromfluss von der Oberfläche auf die Spitze übertragen werden.
- An gewünschter Stelle können sie durch den umgekehrten Prozess wieder auf die Oberfläche gesetzt werden.
- Es lassen sich gezielt chemische Bindungen herstellen.

8.2 Atom Manipulation



- moving cobalt (Co) on Pt(111) requires a lateral force of 210 pN
- this force is independent of the vertical force.

- The lateral force can vary substantially with the chemical nature of the underlying surface as it is only 17 pN for Co on Cu(111).

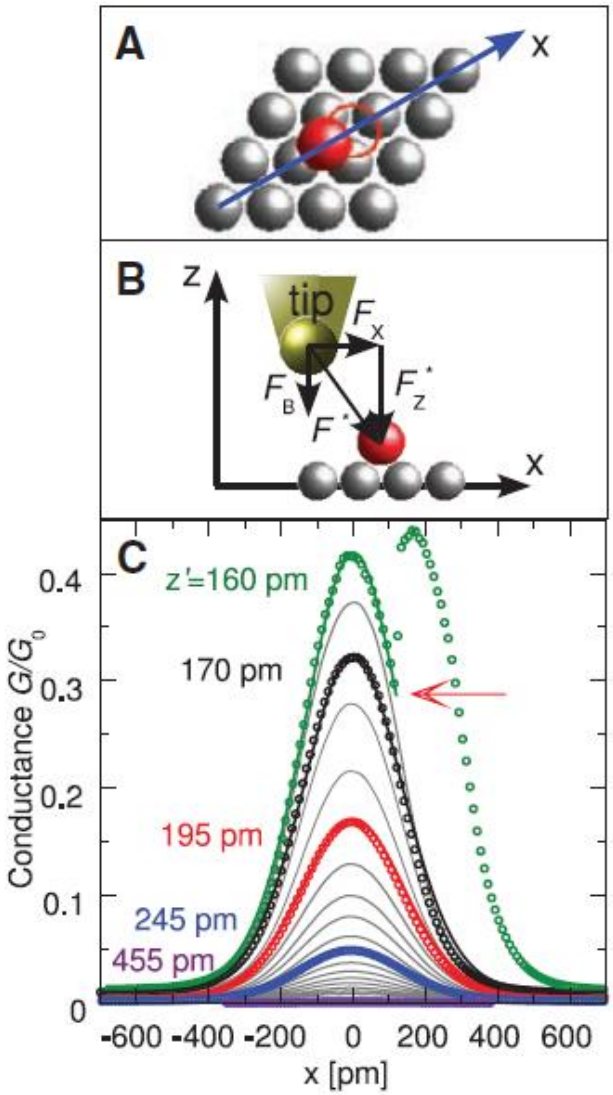
→ nature of the chemical bonding plays a strong role.

- shift of the oscillation frequency Δf, which for small A is roughly proportional to the vertical stiffness

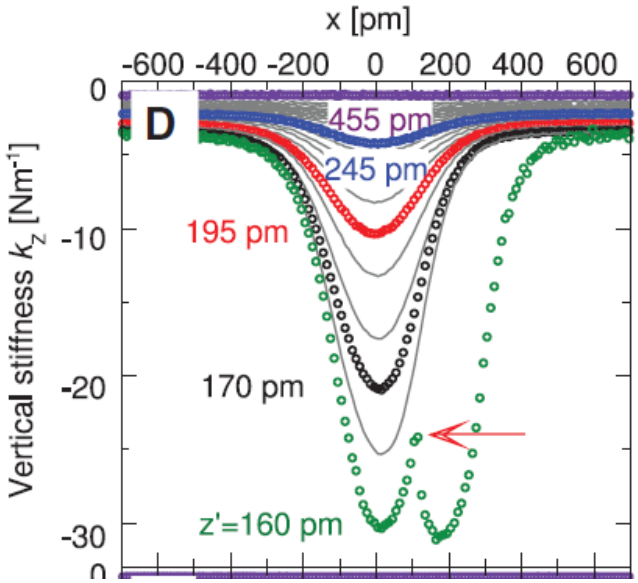
$$k_z \approx 2k_0/f_0 \times \Delta f$$

https://www.science.org/doi/epdf/10.1126/science.1150288

8.2 Atom Manipulation

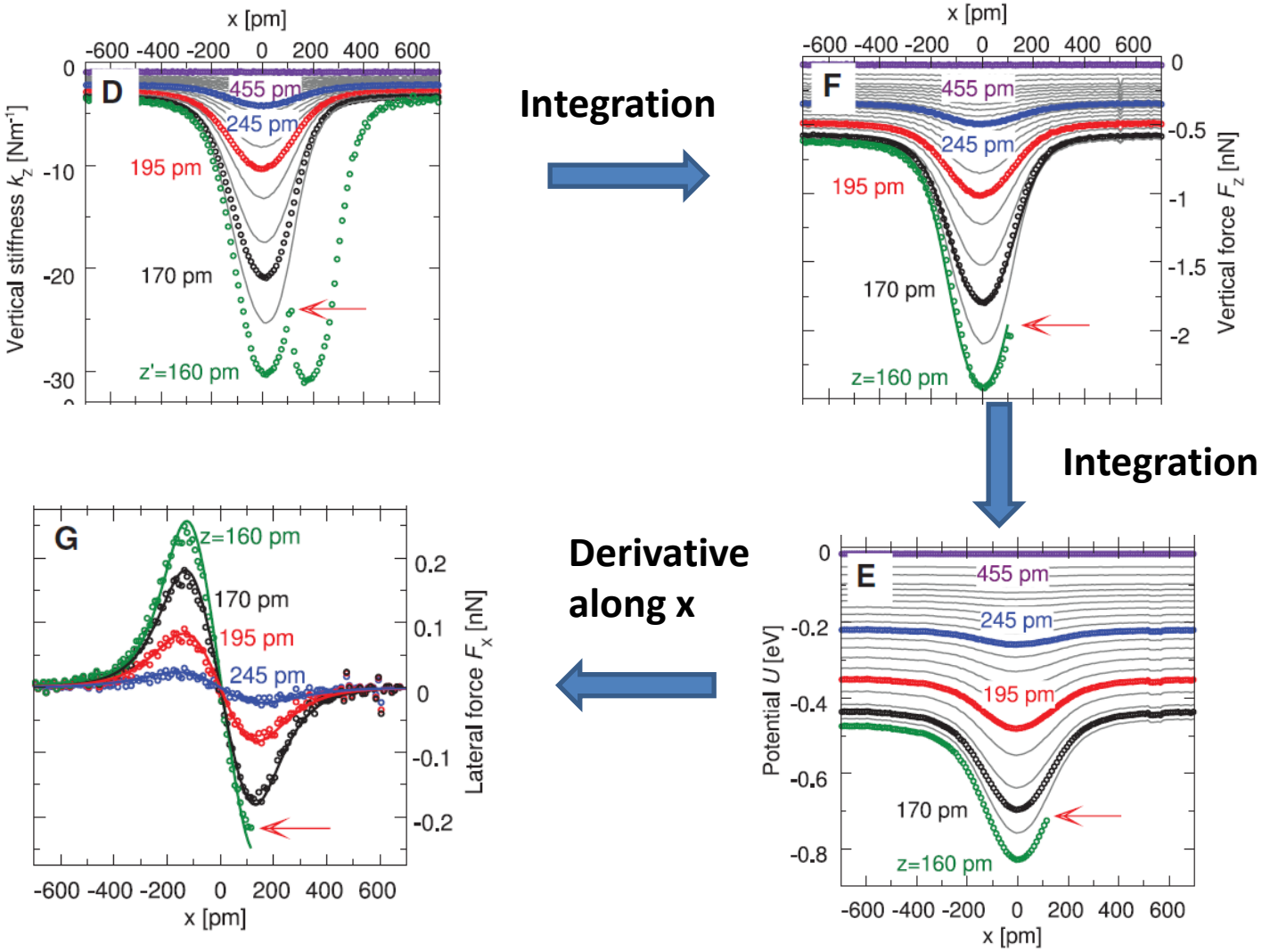


- Experiment: Scan over the atom at a certain height and detect conductance and frequency shift



https://www.science.org/doi/epdf/10.1126/science.1150288

- From these curves one can calculate the force in x- and z-direction



8.2 Atom Manipulation

- Difference between Cu and Pt substrate: both are fcc crystals and the Co atom binds at a threefold hollow site on both surfaces.

→ This indicates that the nature of the chemical bonding plays a strong role.

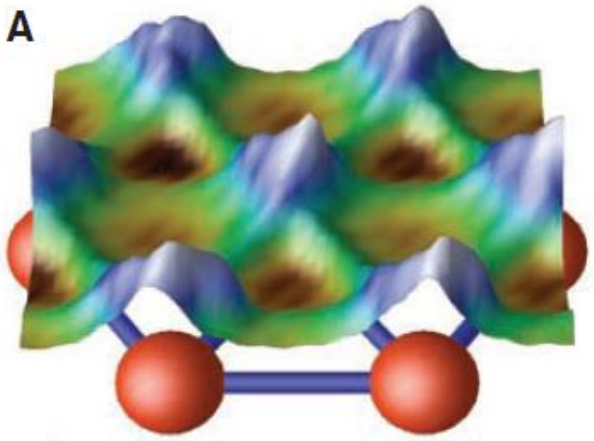
- For Cu, the bonding is dominated by hybridization of the electronic states of the Co adsorbate with the 4s metal band, which shows no discernible direction dependence.

- In contrast, extra bonding occurs on Pt resulting from its partially filled and strongly directional 5d bonds, which apparently increase the forces necessary for manipulation.

  - Co: hollow site (17 pN), CO: top site (160pN)

  → Same substrate, different interaction

Co on Cu(111)



CO on Cu(111)