Paul-Drude-Institut
für Festkörperelektronik

Manipulation and spectroscopy of adsorbates by low-temperature scanning tunneling microscopy

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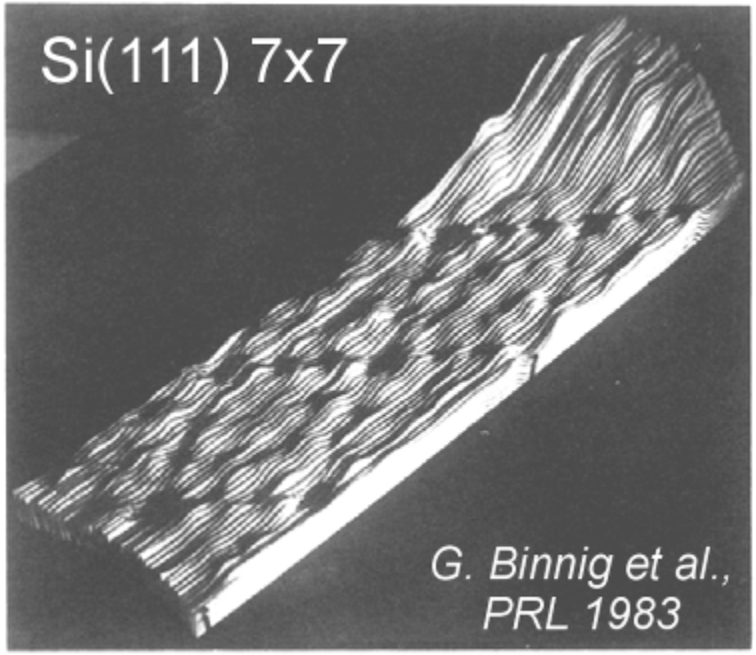
Scanning tunneling microscopy (STM)

- Announced by Gerd Binnig and Heinrich Rohrer, IBM Zürich

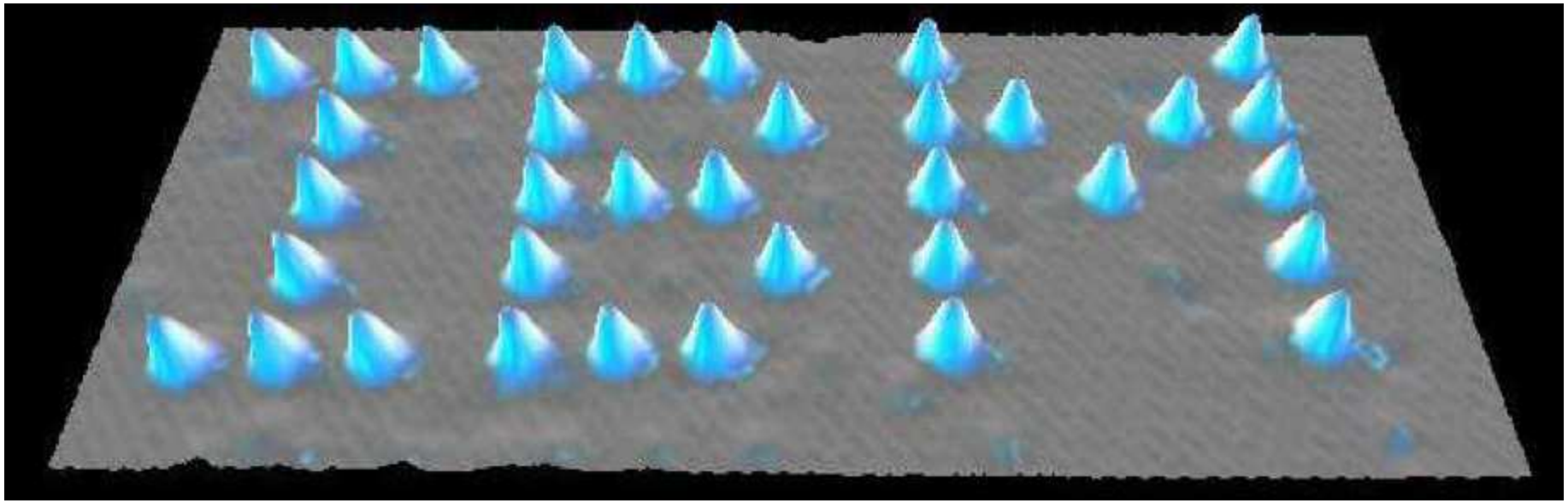


- Imaging of surfaces with atomic-scale resolution
- Nobel price in physics 1986

Atom manipulation by low-temperature STM

- Positioning of single atoms at surfaces with atomic precision

35 Xe atoms on Ni(110)

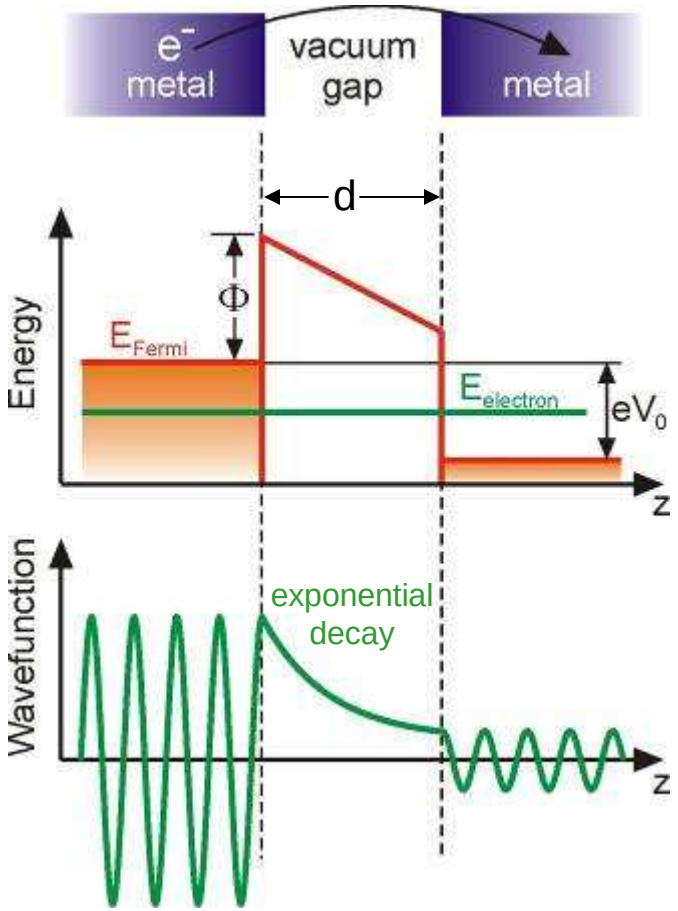


*D. M. Eigler & E. K. Schweizer, Nature **344** (1990) 524*

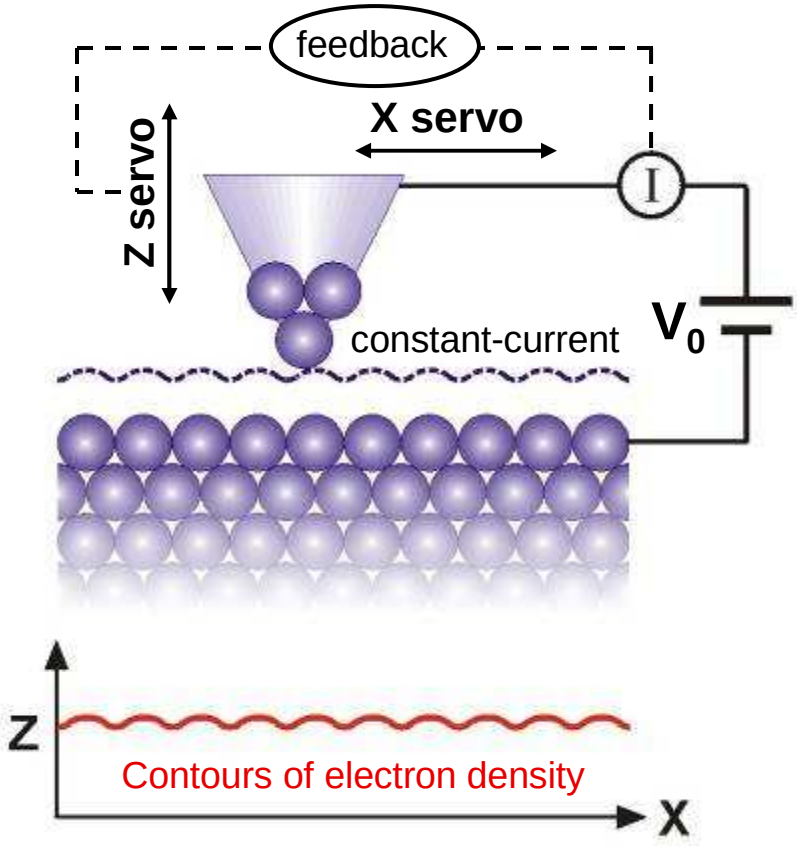
http://www.almaden.ibm.com/vis/stm/gallery.html

STM technique

1D tunnel contact



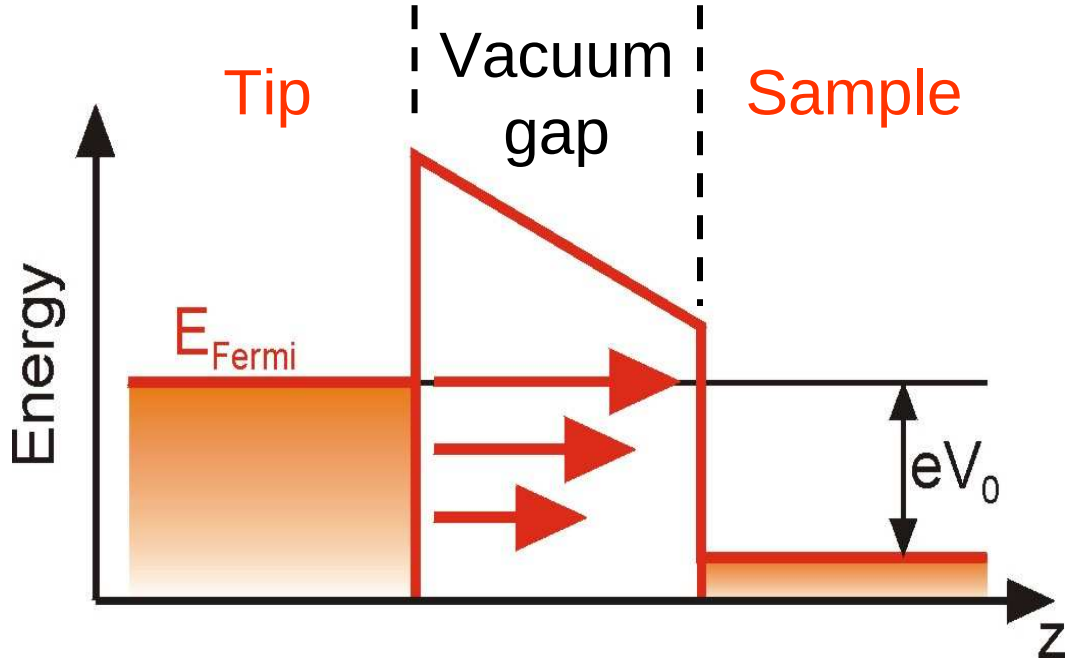
STM setup



- **Topography information**
  (constant-current mode)

$$I(z) \sim e^{-2kz}$$

Tunneling current as a function of the bias V_0



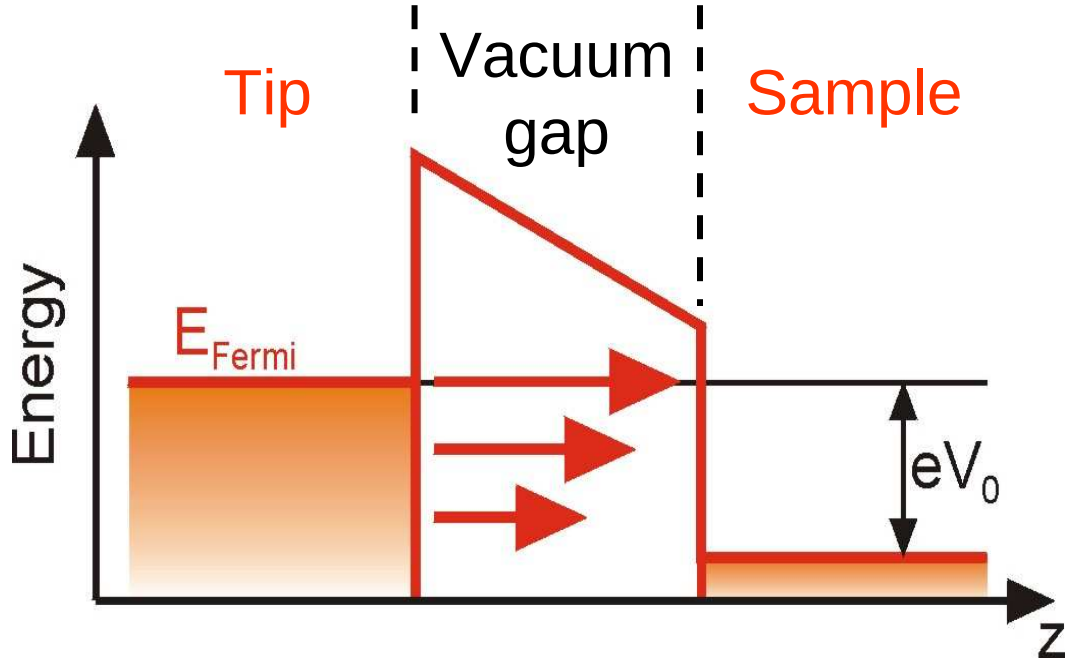
$$I(V_0) \sim \int_{E_F}^{E_F+eV_0} \boldsymbol{D_S(E)}\, D_T(E-eV_0)\, M(E,V_0)\, dE$$

$\boldsymbol{D_S(E)}$: Density of sample states

$D_T(E)$: Density of tip states

$M(E,V)$: Transmission rate

dI/dV – Spectroscopy information



$$I(V_0) \sim \int_{E_F}^{E_F+eV_0} \boldsymbol{D_S(E)}\, D_T(E-eV_0)\, M(E,V_0)\, dE$$

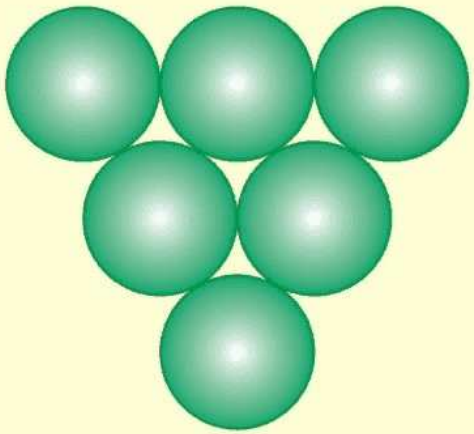
Assuming that
D_T and M are constant:

$$\Longrightarrow \frac{dI(V_0)}{dV} \sim \boldsymbol{D_S(E_F+eV_0)}$$

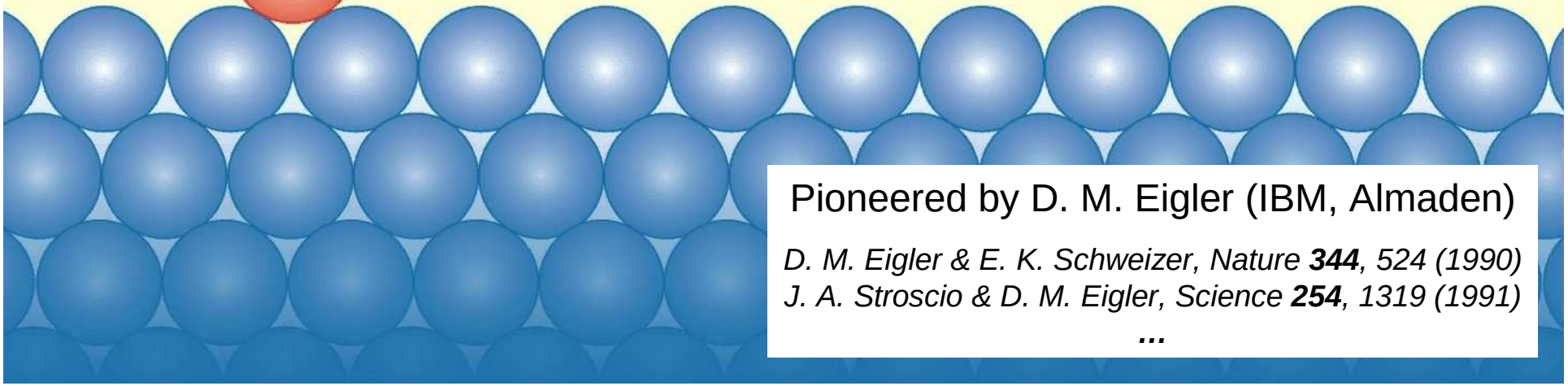
(at constant tip height)

Probing & moving adatoms on metal surfaces

Lateral manipulation



Adsorbed atom

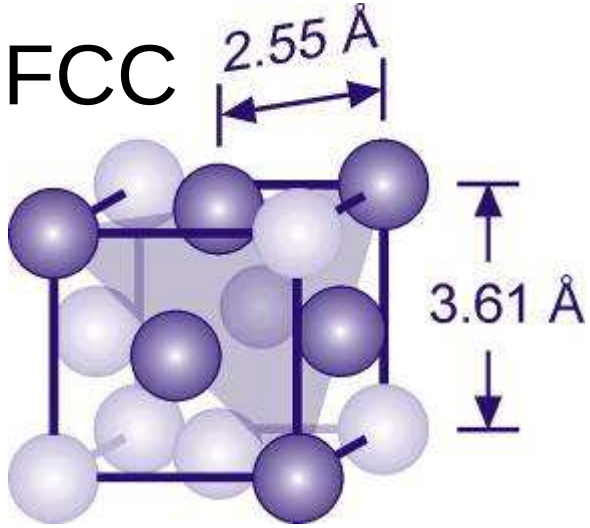


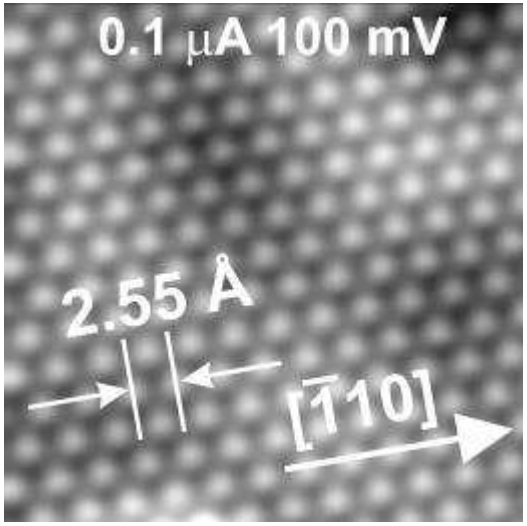
Pioneered by D. M. Eigler (IBM, Almaden)

*D. M. Eigler & E. K. Schweizer, Nature **344**, 524 (1990)*
*J. A. Stroscio & D. M. Eigler, Science **254**, 1319 (1991)*

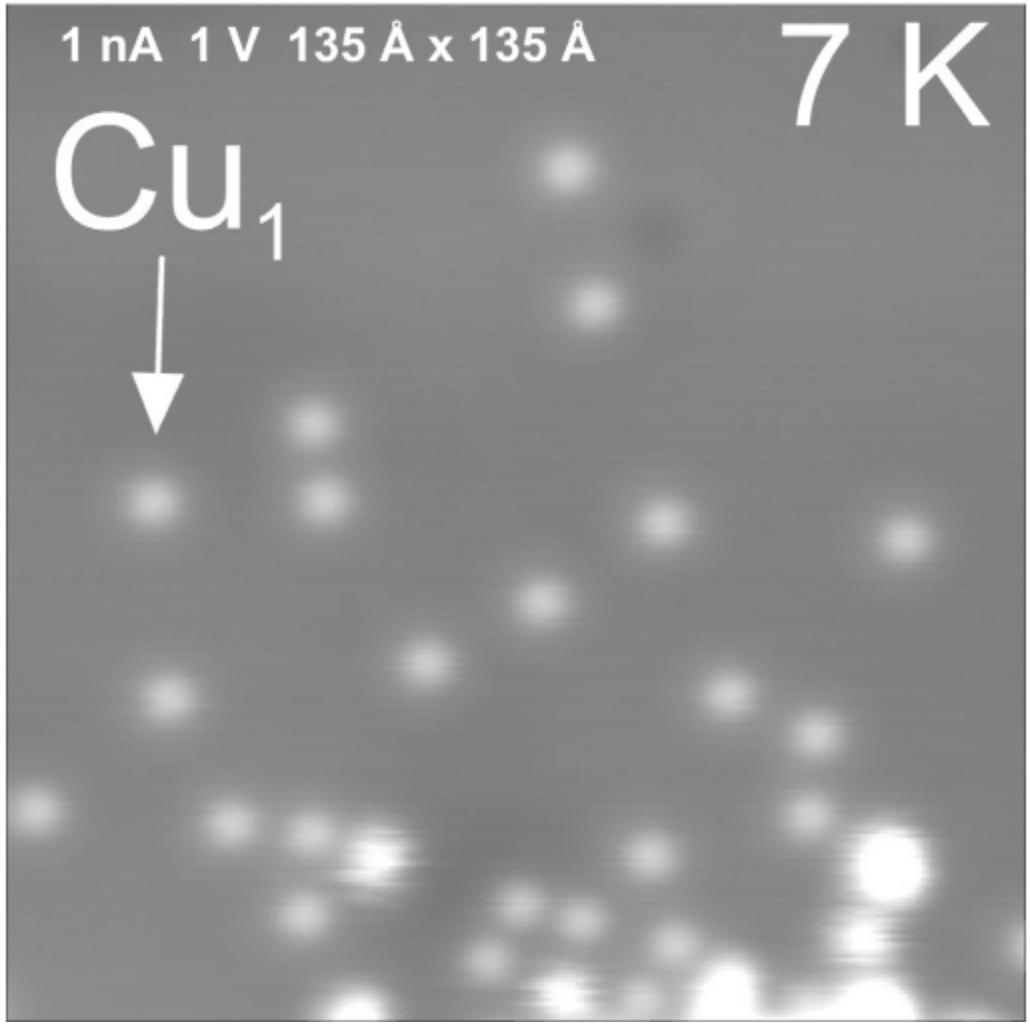
...

Assembly of monatomic adatom chains on Cu(111)





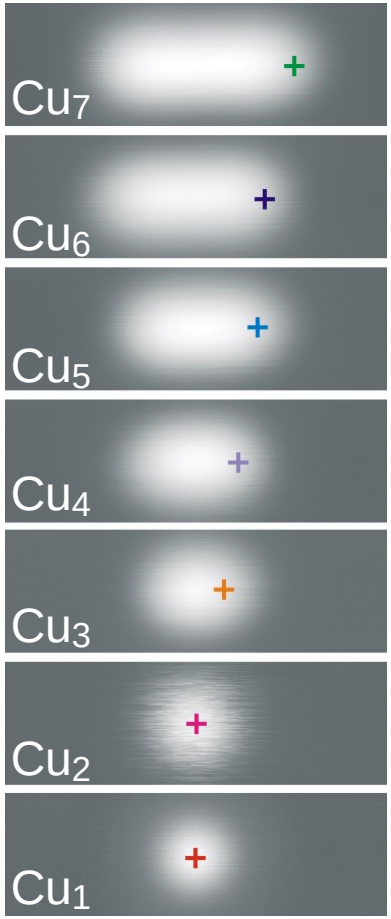
Building a Cu_{20}/Cu(111) chain



- Atom-by-atom assembly of Cu chains along the <110> direction
- chain atoms occupy nearest-neighbor lattice sites ($a_{Cu\text{-}Cu}$= 2.55 Å)

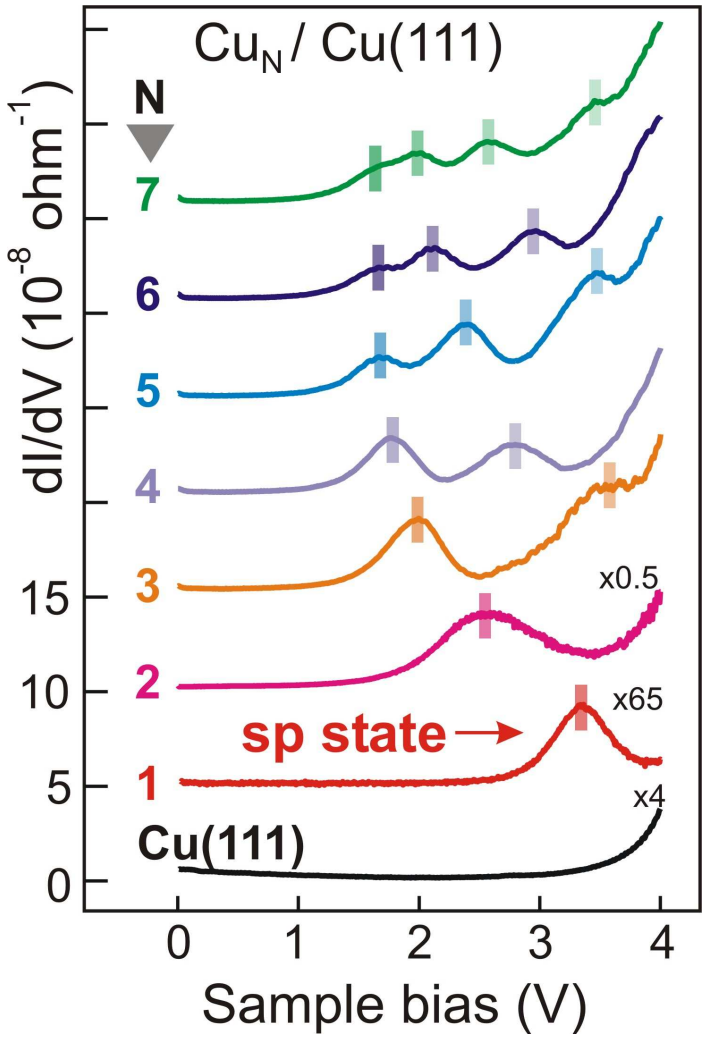
Cu/Cu(111) chains: unoccupied quantum states

Topography



35 Å x 11 Å, 7 K

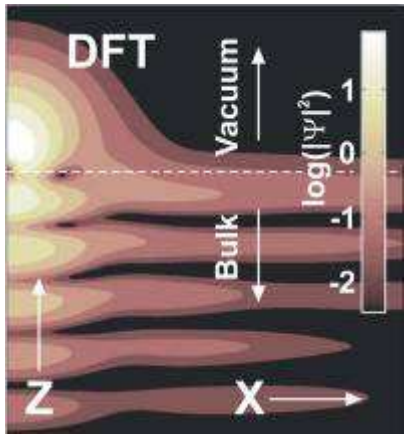
dI/dV point spectra



Cu: $3d^{10}\ 4s^{1}$

Unoccupied levels:
4s, 4p, ...

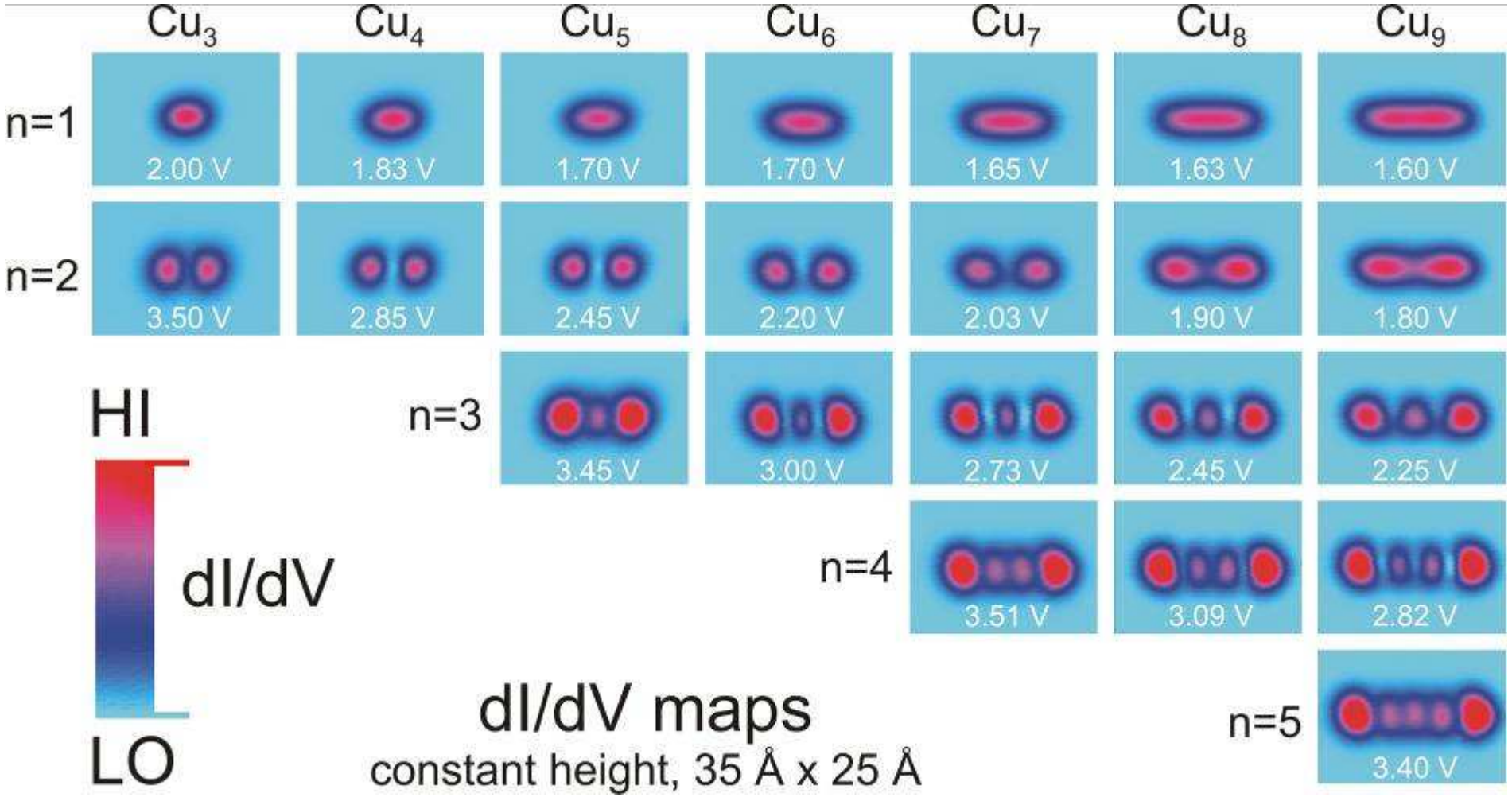
Cu adatom:
sp state



- Cu adatom chains: confined unoccupied quantum states (1D quantum box behavior)

S. Fölsch *et al*., Phys. Rev. Lett. 92, 56803 (2004); F. E. Olsson *et al*., Phys. Rev. Lett. 93, 206803 (2004)

Cu/Cu(111) chains: quantum state densities



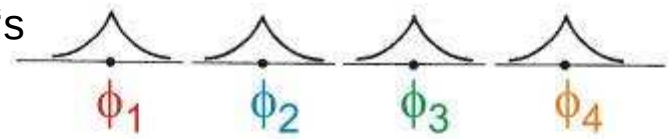
- Chain-localized electronic states: One-dimensional quantum confinement
- squared wave functions with *n* lobes and *n-1* nodes (artificial molecules)

S. Fölsch *et al*., Phys. Rev. Lett. 92, 56803 (2004)

Linear Combination of Atomic Orbitals (LCAO)

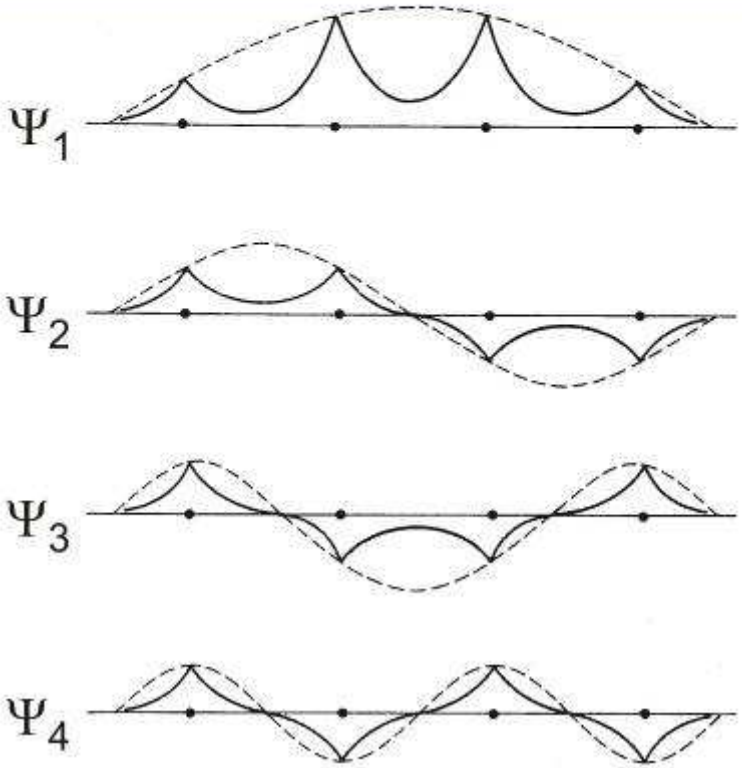
Example: Linear molecule, four identical atoms

s-like AO's



***L**inear **C**ombination of **A**tomic **O**rbitals:*

$$\Psi = c_1\,\phi_1 + c_2\,\phi_2 + c_3\,\phi_3 + c_4\,\phi_4$$



Eigenstate energies *E*(*n*,*N*) within LCAO approach

LCAO scheme:
Solving the (N×N) secular determinant for a chain of finite length

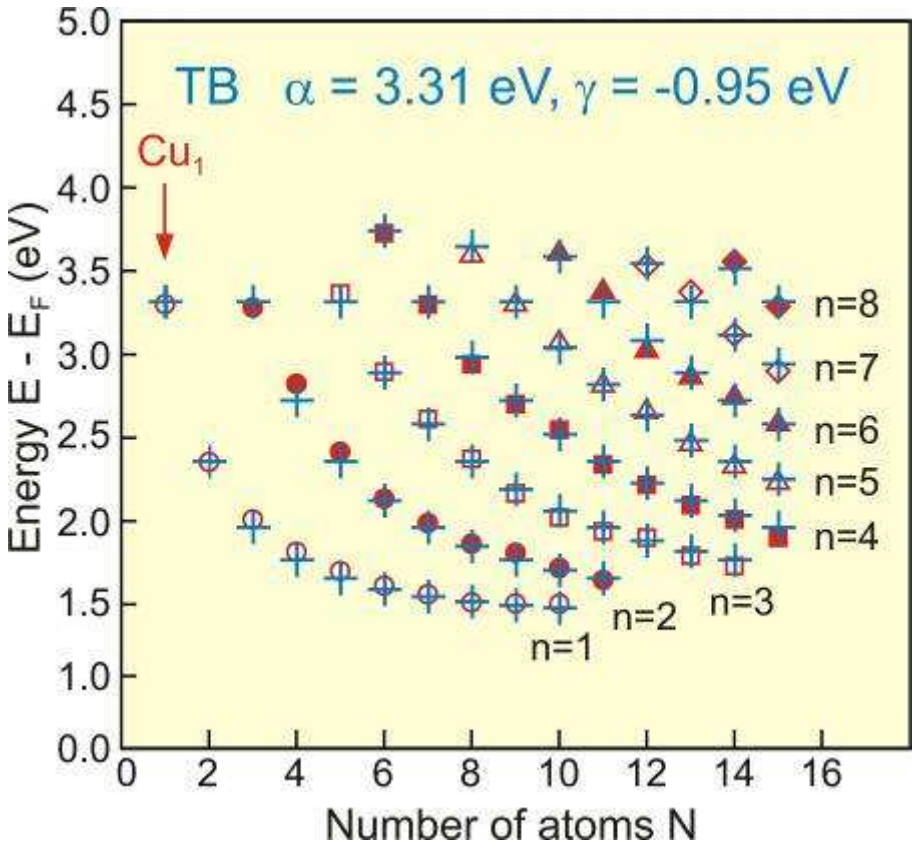
$$\begin{vmatrix} \alpha - E & \gamma & 0 & 0 & \cdots & 0 \\ \gamma & \alpha - E & \gamma & 0 & \cdots & 0 \\ 0 & \gamma & \alpha - E & \gamma & \cdots & 0 \\ 0 & 0 & \gamma & \alpha - E & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \cdots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & \alpha - E \end{vmatrix} = 0$$

Eigenvalues for an N-atomic chain:

$$E_n = \alpha + 2\,\gamma \cos\left(\frac{n\pi}{N+1}\right) \qquad n = 1,2, \ldots, N$$

α: binding energy $\langle \phi_i | H | \phi_i \rangle$
γ : hopping integral $\langle \phi_i | H | \phi_j \rangle$

Experiment and calculation



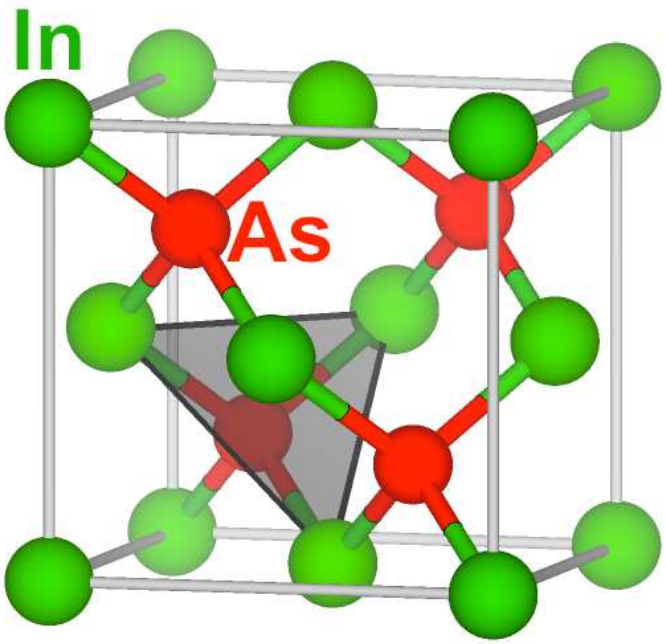
1D energy band:
$E(\Gamma)$=1.41 eV, m^*= 0.68 m_e

J. Lagoute *et al.*, Phys. Rev. B 74, 125410 (2006)

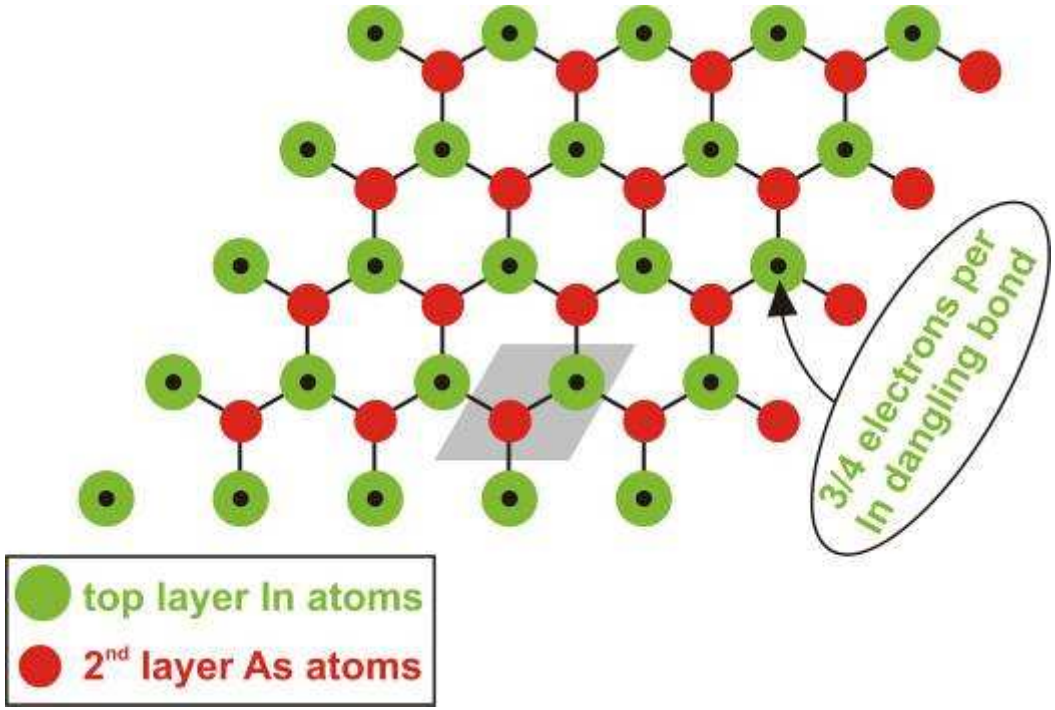
Adsorbates on semiconductor surfaces

III-V semiconductor – InAs

In: $4d^{10}\ 5s^2\ 5p^1$
As: $3d^{10}\ 4s^2\ 4p^3$



InAs(111)A
A: In-terminated



Zinc blende structure

a_0= 6.06 Å

band gap: 0.36 eV

- 3/4 electrons per In dangling bond (DB)

III-V semiconductor – InAs

In: $4d^{10}\ 5s^2\ 5p^1$
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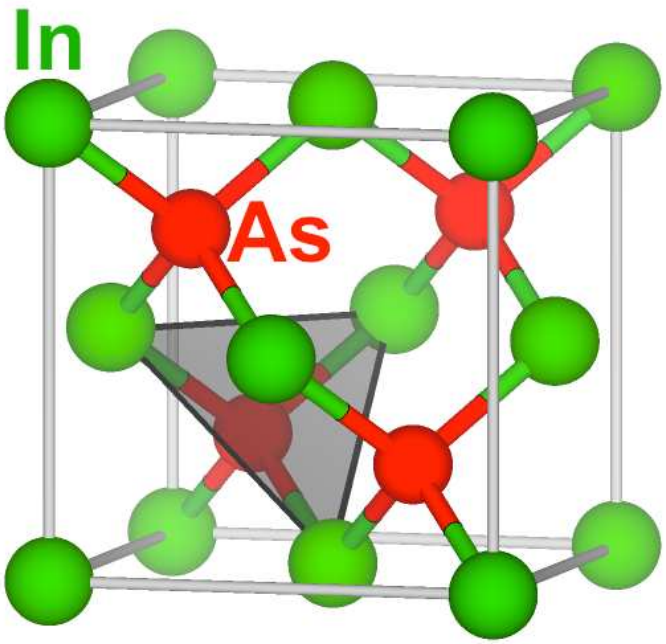

Zinc blende structure

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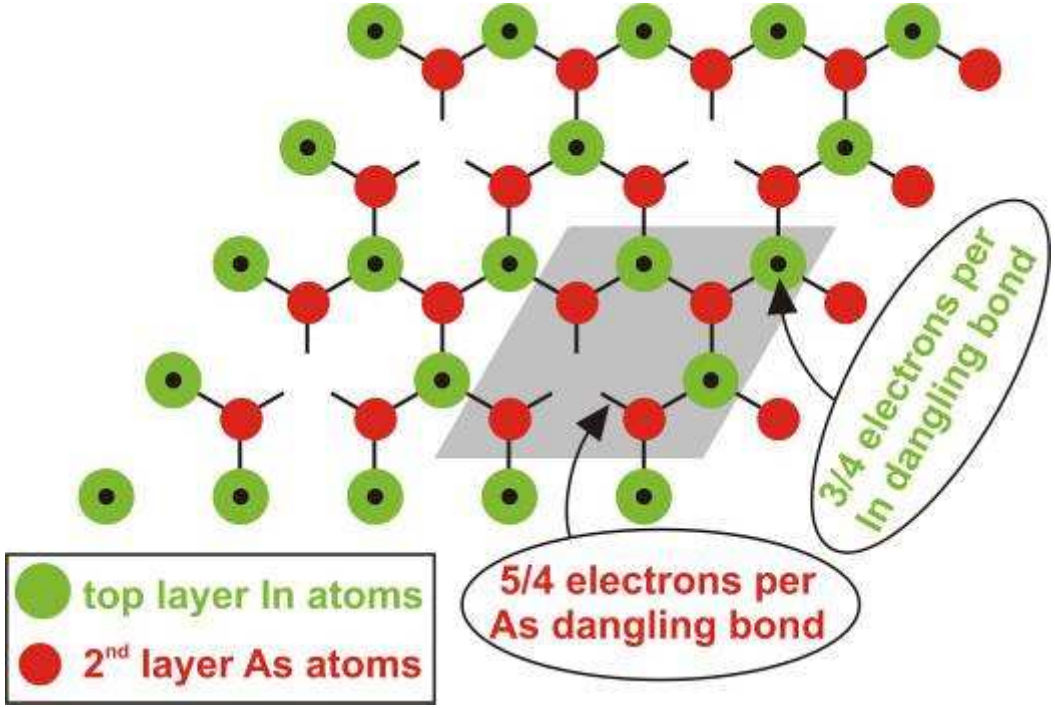
band gap: 0.36 eV

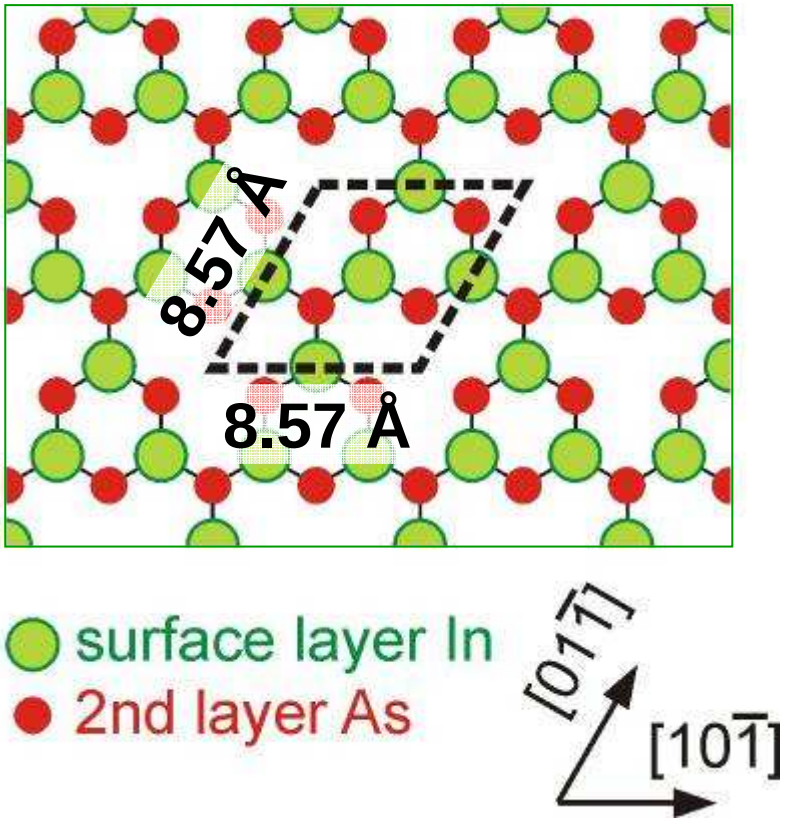
InAs(111)A-(2x2)
A: In-terminated



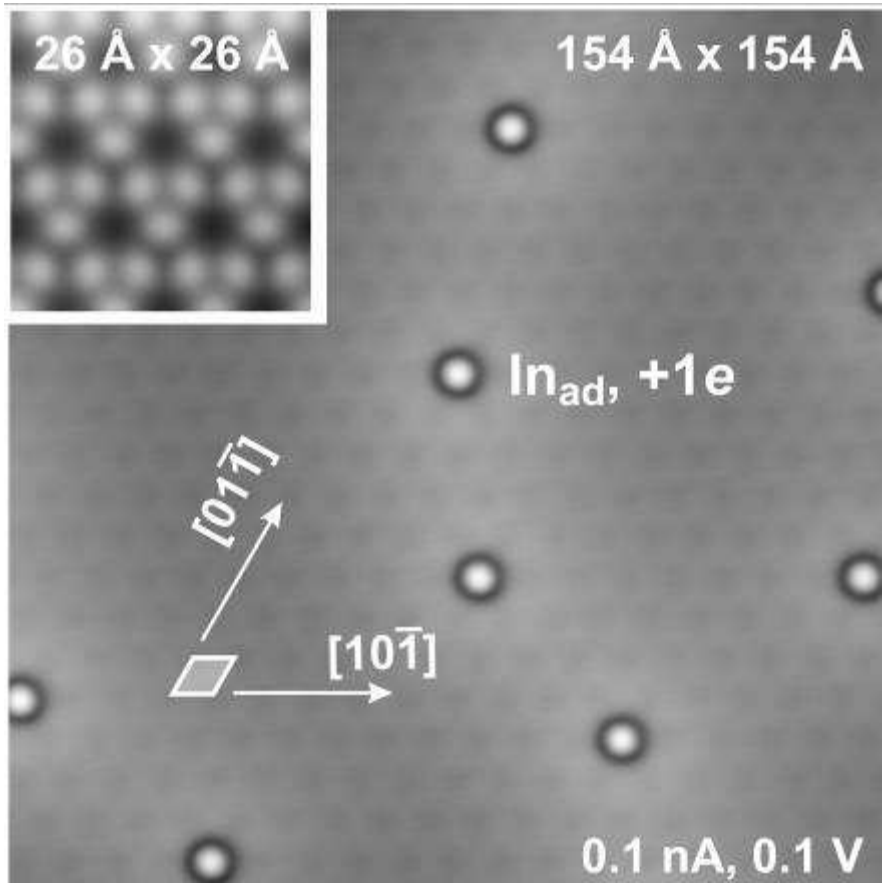
- 3/4 electrons per In dangling bond (DB)
- surface In vacancies create As DBs each with 5/4 electrons
- (2x2) In vacancy reconstruction: electron transfer from In to As creates fully empty/occupied surface DBs

InAs(111)A-(2x2) substrate surface

Surface structure



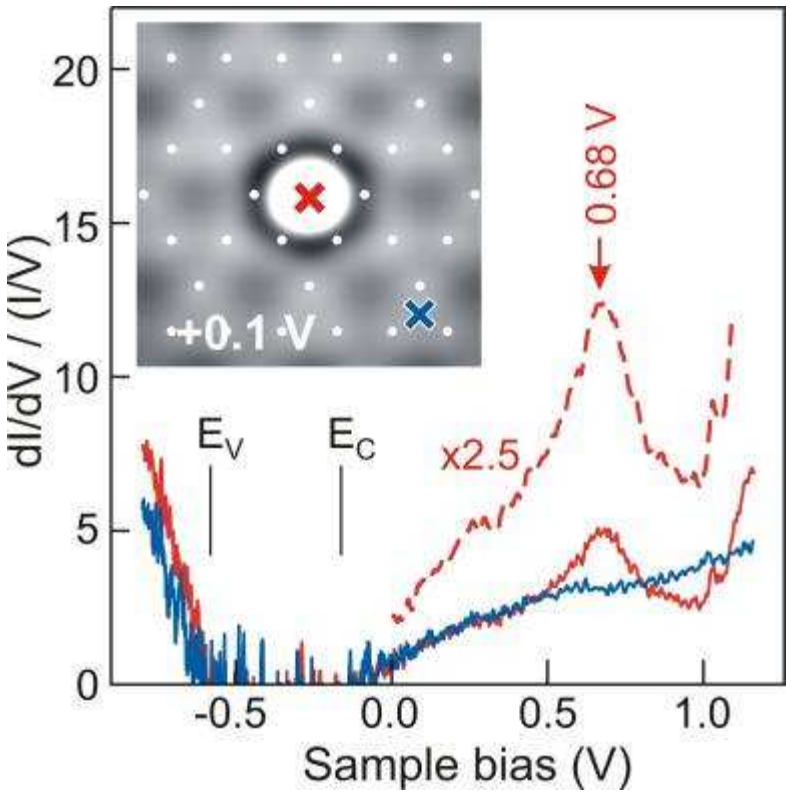
STM imaging



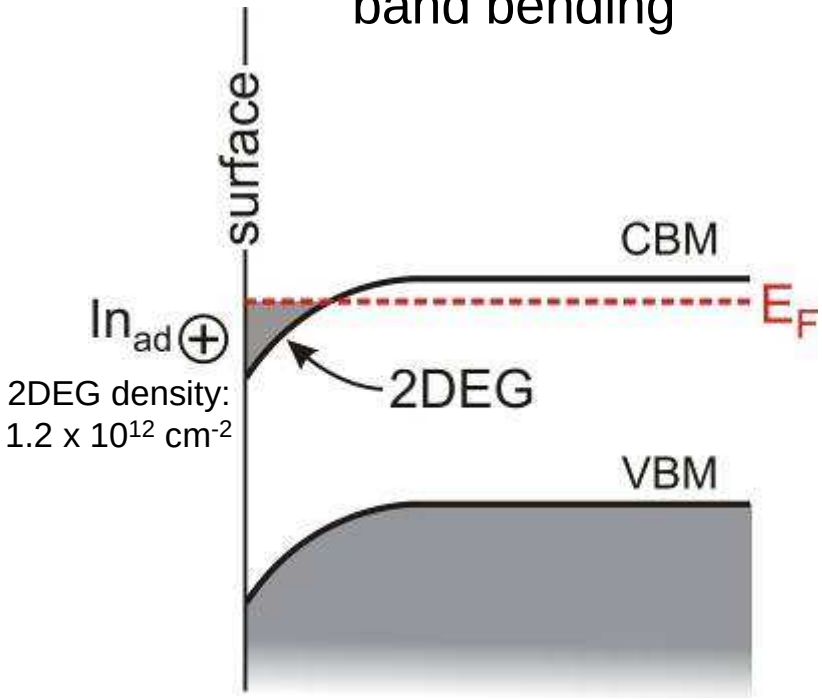
- In-terminated InAs(111)A: (2x2) reconstruction with In-vacancy structure
- (2x2) reconstruction renders the surface non-reactive: no partially filled dangling bonds
- MBE-grown surface exhibits donor-type In adatoms residing on the In-vacancy sites

Electronic properties of InAs(111)A

dI/dV spectroscopy

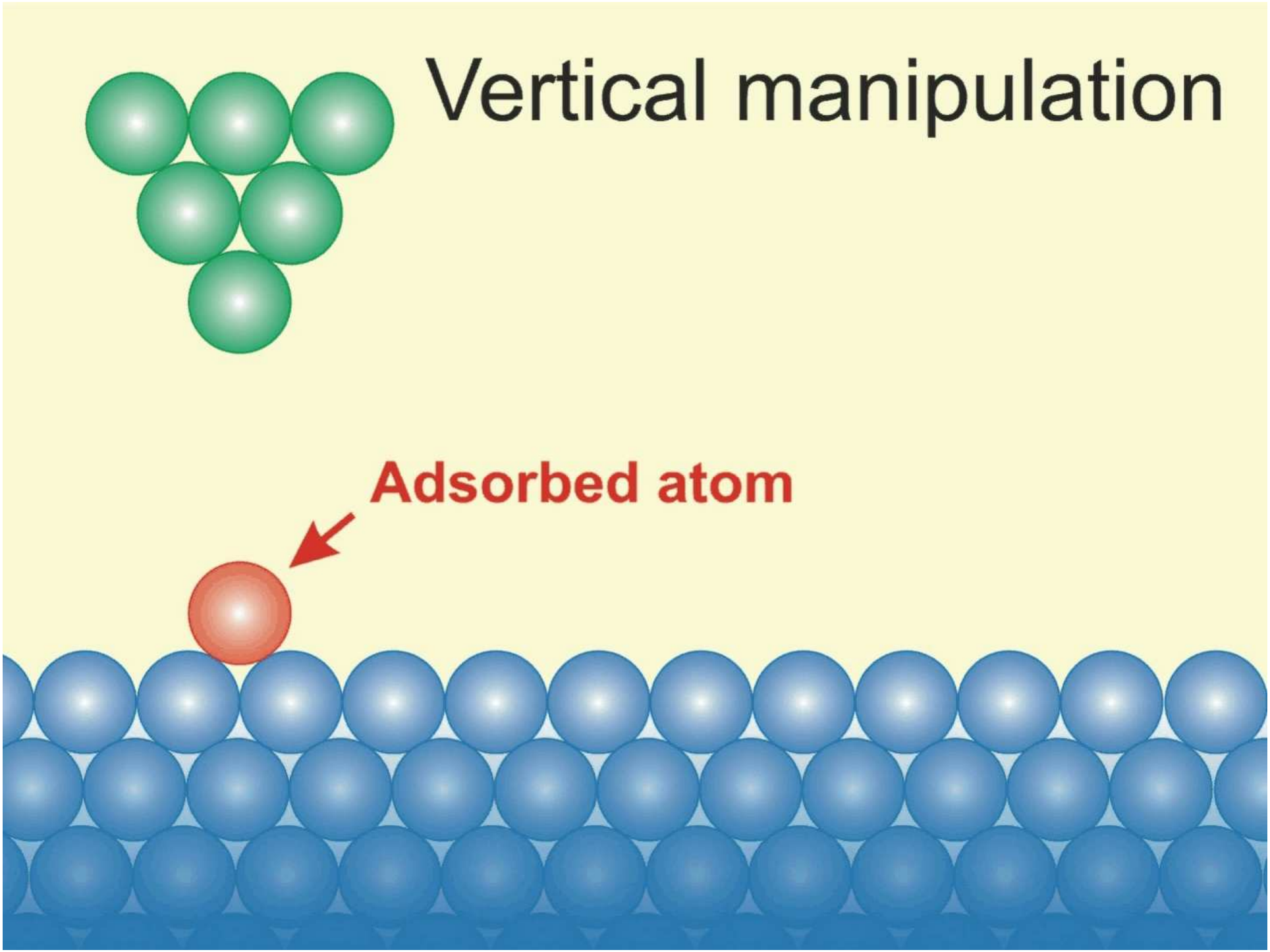


In adatom-induced band bending



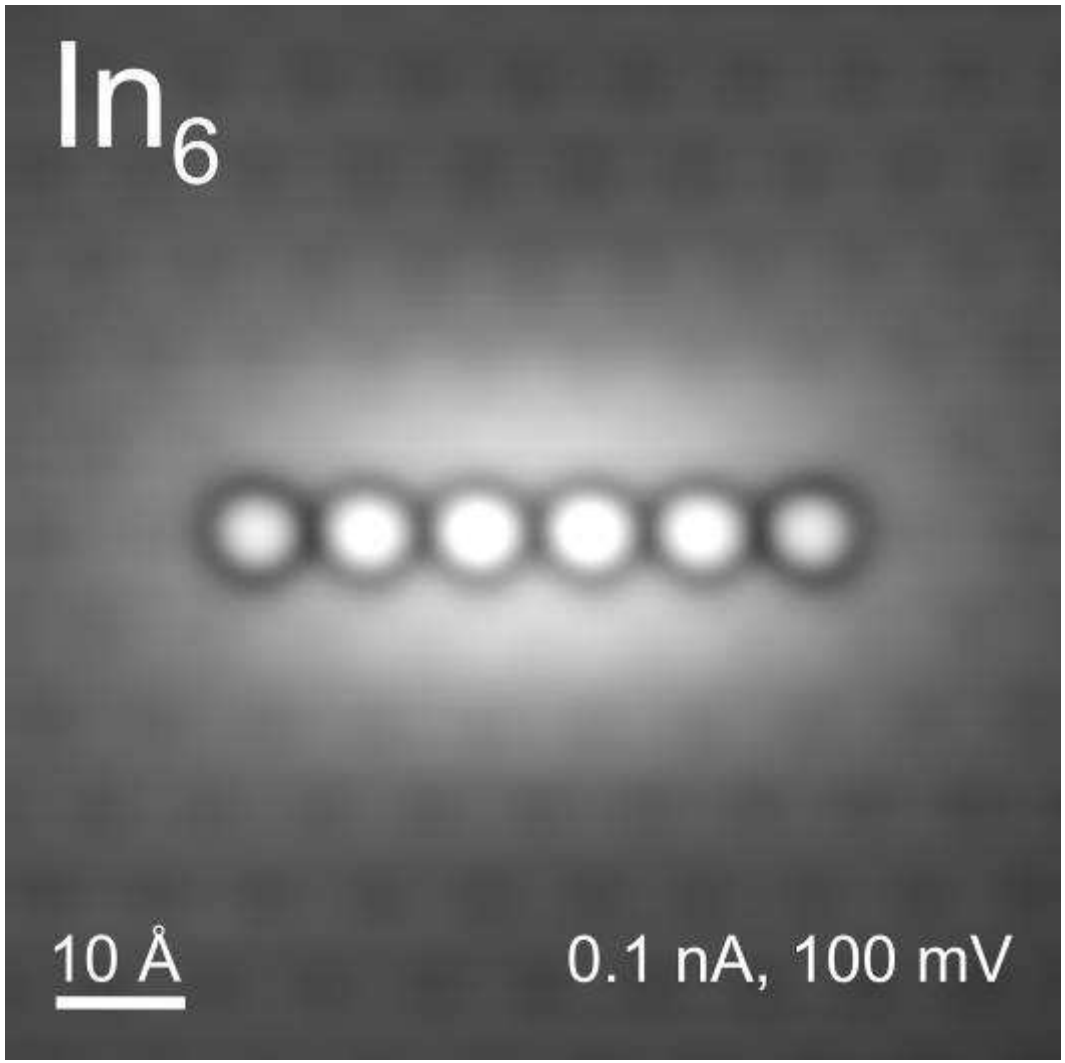
- Fermi level pinning in the conduction band due to donor-type In_{ad} atoms
- charge accumulation at the surface
- In_{ad}: unoccupied atomic orbital-derived state ~0.7 eV above E_F

Vertical manipulation



Assembling an In adatom chain on InAs(111)*A*

STM topograph

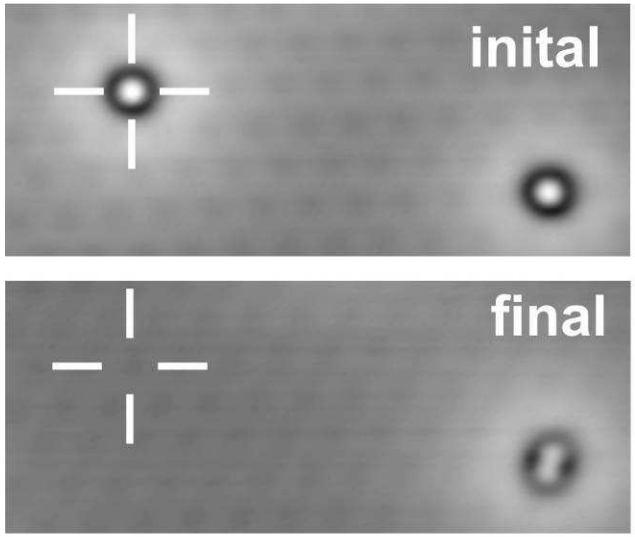


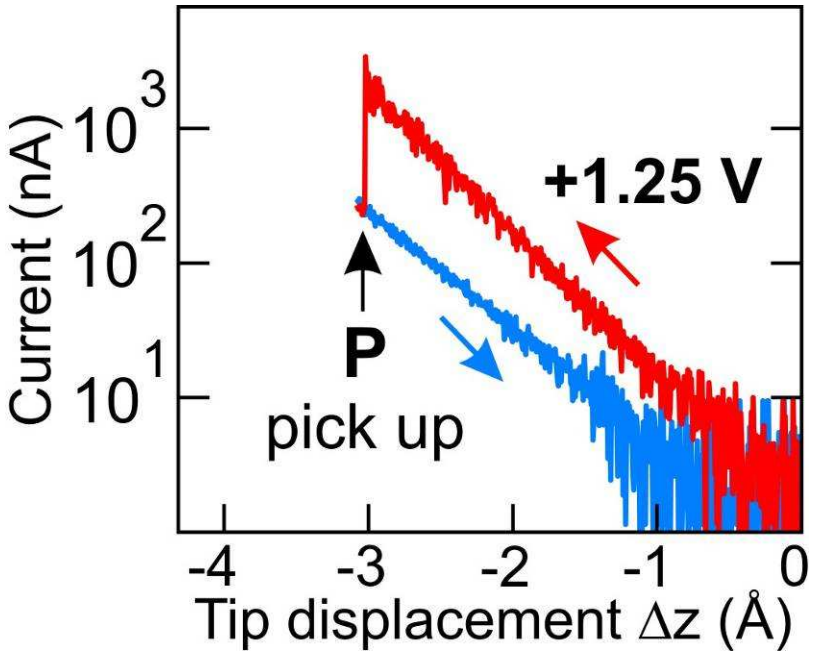
5 K

S. Fölsch *et al*., Phys. Rev. Lett. 103, 096104 (2009)
J. Yang *et al*., J. Phys. Condens. Matter, 24, 354008 (2012)

Vertical manipulation – surface-to-tip transfer

Set point values prior to manipulation: 0.1 nA, 0.5 V





- **Surface-to-tip transfer** *only* at positive sample bias > 0.7 V
- tunneling into the adatom-derived unoccupied state is important for the pick-up process
- transfer via **vibrational excitation** of the adsorbate-surface bond

S. Fölsch *et al*., Phys. Rev. Lett. 103, 096104 (2009)
J. Yang *et al*., J. Phys. Condens. Matter, 24, 354008 (2012)

Vertical manipulation – tip-to-surface transfer

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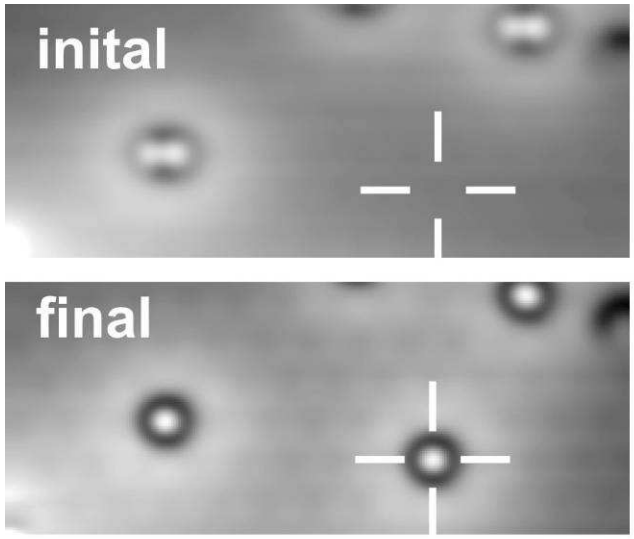
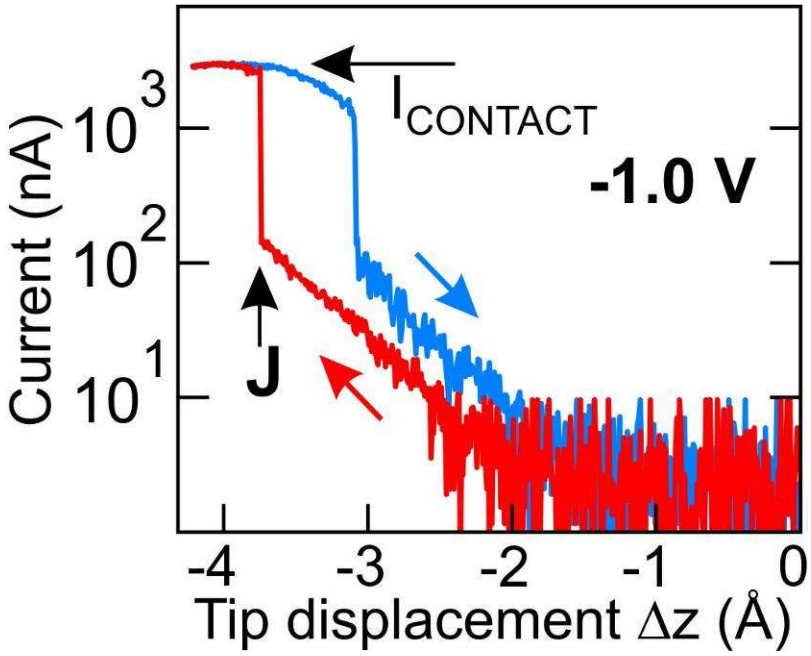




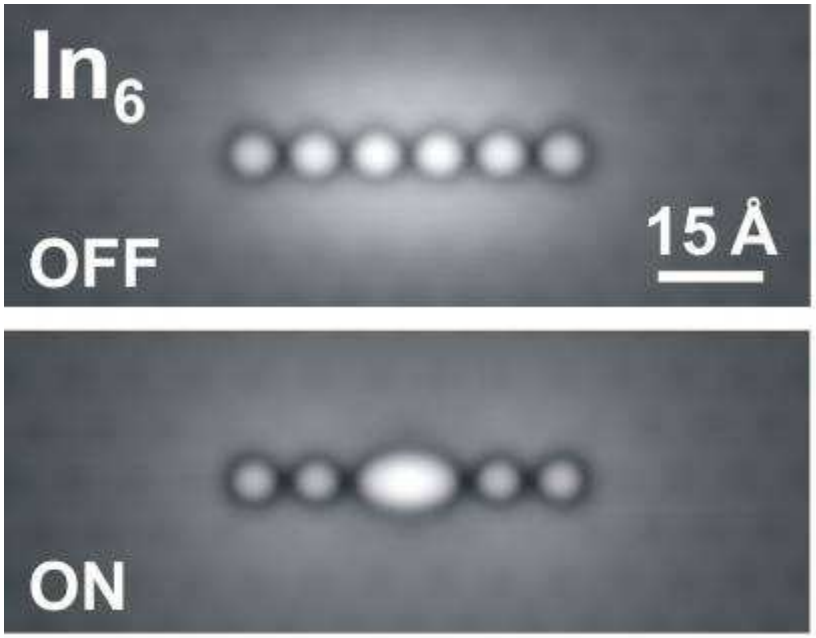
- **Jump to contact** occurs at a critical tip height (saturation of the tunneling current)
- critical tip height is bias-independent, transfer attainable also at zero bias
- tip-to-surface transfer triggered by **short-range cohesive forces** upon tip-surface contact

S. Fölsch *et al*., Phys. Rev. Lett. 103, 096104 (2009)
J. Yang *et al*., J. Phys. Condens. Matter, 24, 354008 (2012)

Atomic switches

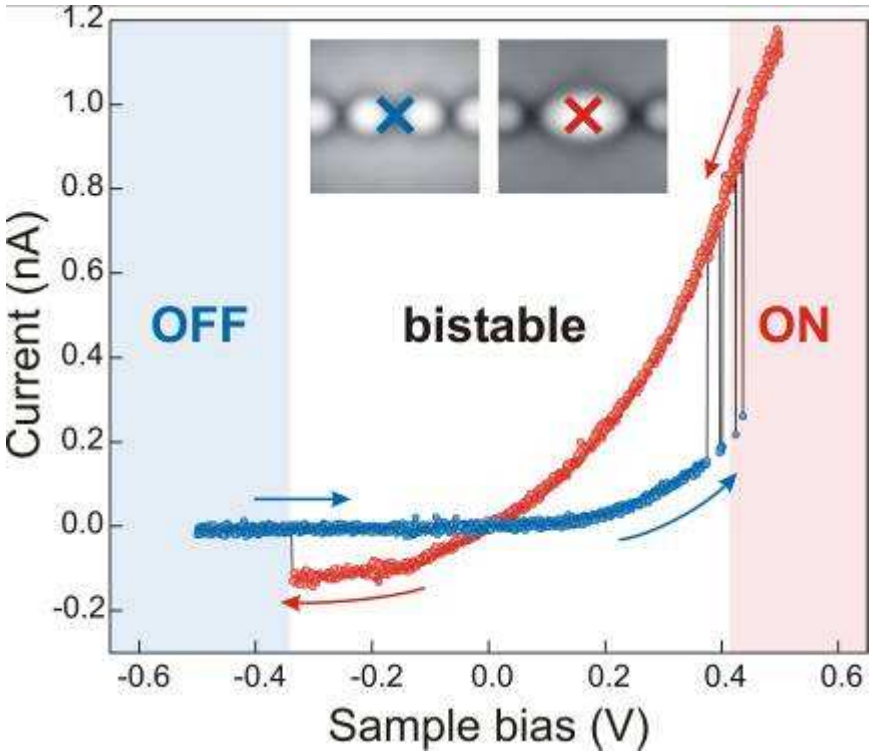
In_6 chain on InAs(111)A: a binary switch

STM topography



0.1 nA, 0.1 V

I-V curves at constant tip height



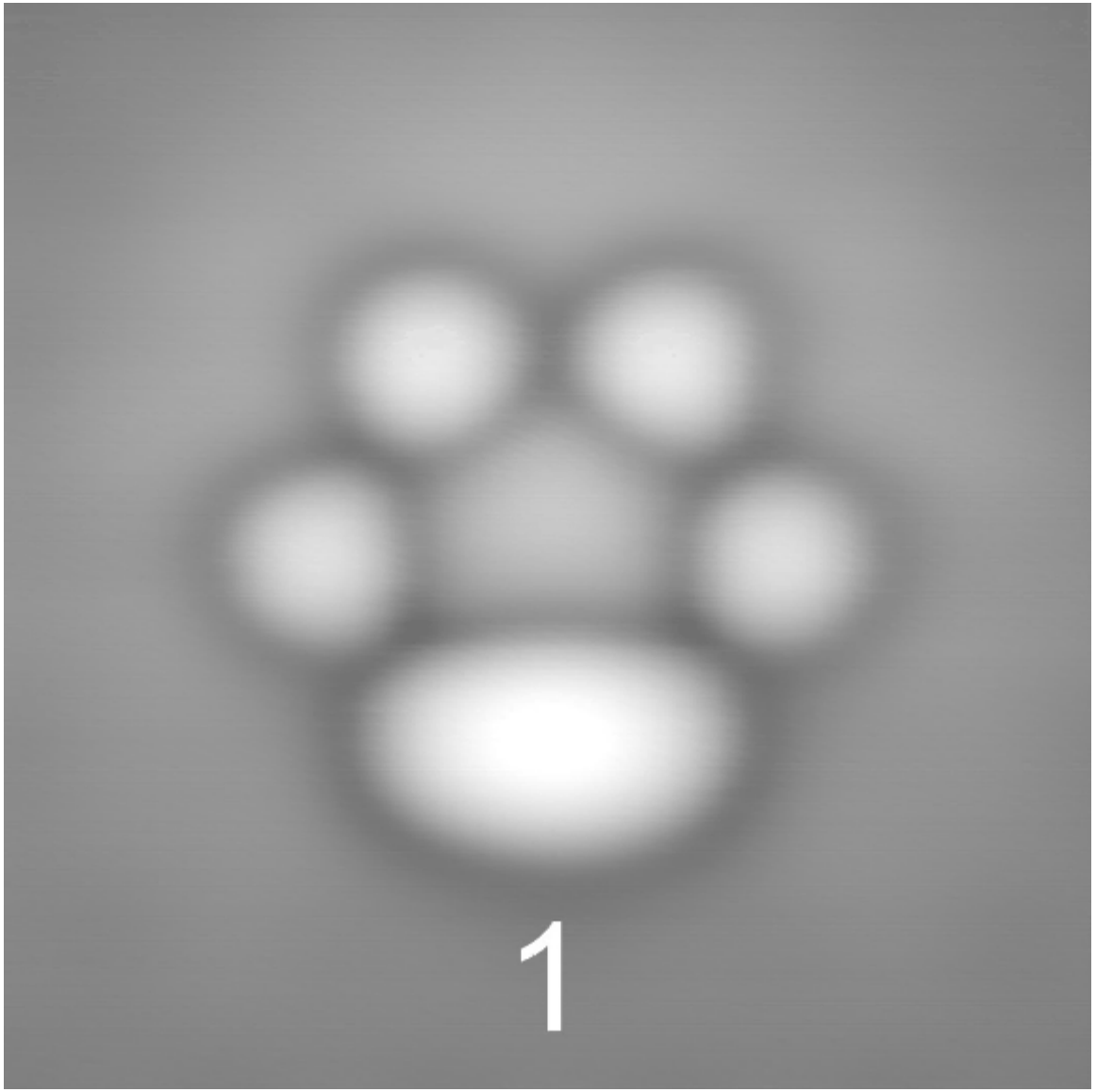
- Reversible switching of the tunnel conductance in the chain center
- bistable regime between about -0.4 V and +0.4 V
- ON and OFF states robust and stable within the switching thresholds
- switching never observed at the chain ends ➔ energetically unfavorable

J. Yang *et al*., Nano Lett. 11, 2486 (2011)

Periodic boundary conditions: In_6 ring

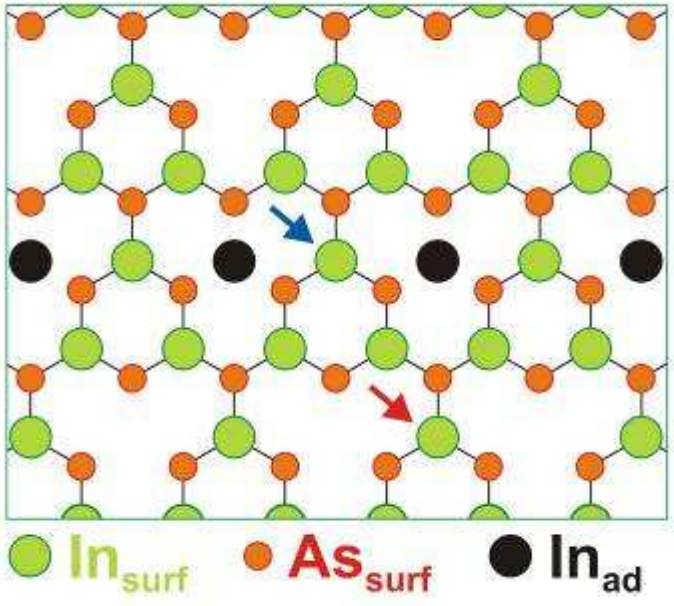
5 K

40 Å x 40 Å
0.1 nA, 0.3 V

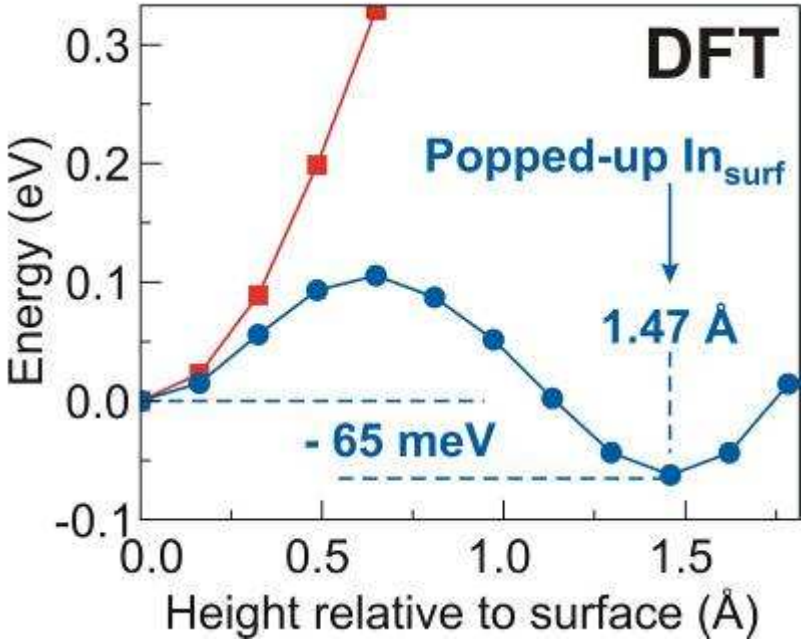


Bistability in vertical atomic height and charge state

In_{ad} chain on InAs(111)A



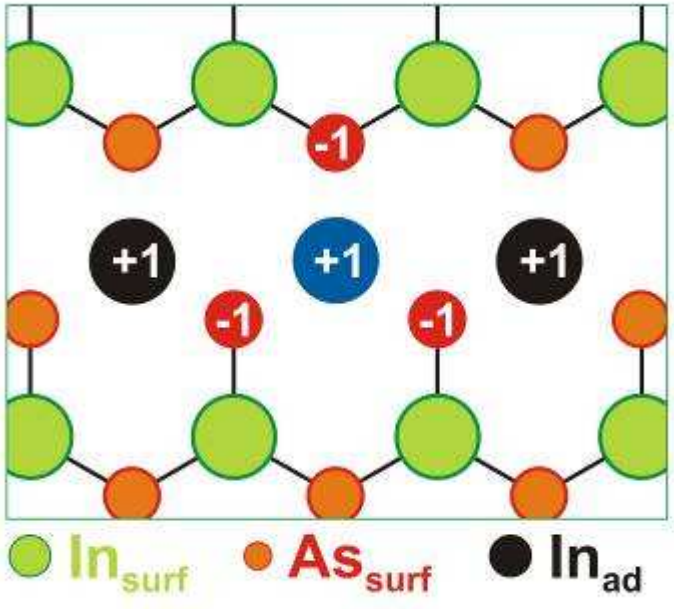
Total energy *versus* height of In_{surf}



- In_{surf} next to the chain remains stable at z=0 ("normal" In_{surf})
- In_{surf} between two In_{ad} becomes bistable and can assume a popped-up position at 1.47 Å, i.e., almost at the height of the In_{ad} atoms themselves (1.7 Å)

Bistability in vertical atomic height and charge state

In_{ad} chain on InAs(111)A



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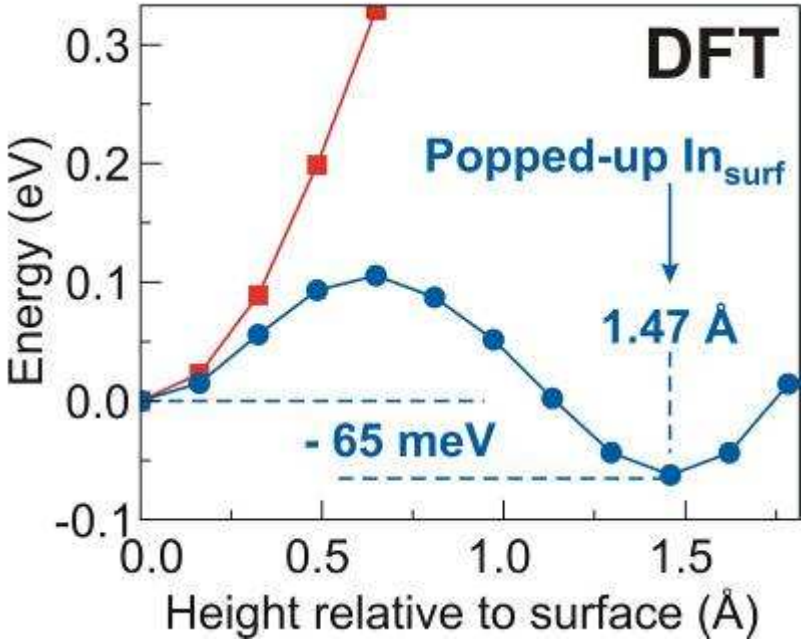


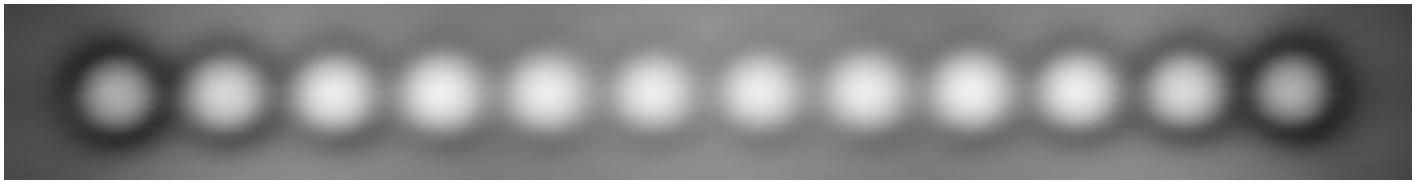
- In_{surf} next to the chain remains stable at z=0 ("normal" In_{surf})
- In_{surf} between two In_{ad} becomes bistable and can assume a popped-up position at 1.47 Å, i.e., almost at the height of the In_{ad} atoms themselves (1.7 Å)
- switching process changes the charge state of the nanostructure

Probing the steady state in extended In chains

Steady-state imaging at 0.2 V, subsequent excitation at 0.6 V (multiple switching)

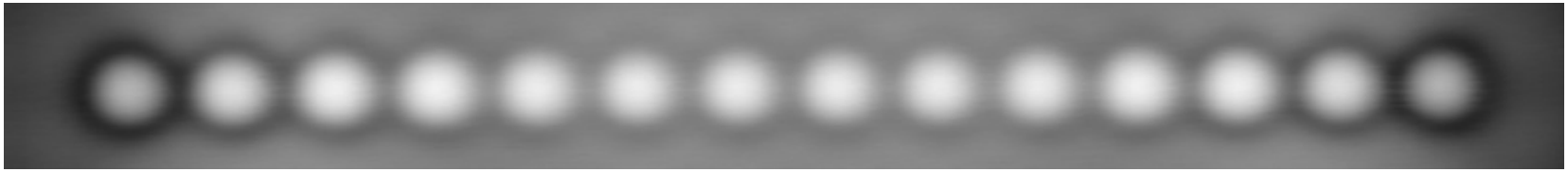
105 frames, 112 Å x 14 Å

In_{12}



102 frames, 131 Å x 14 Å

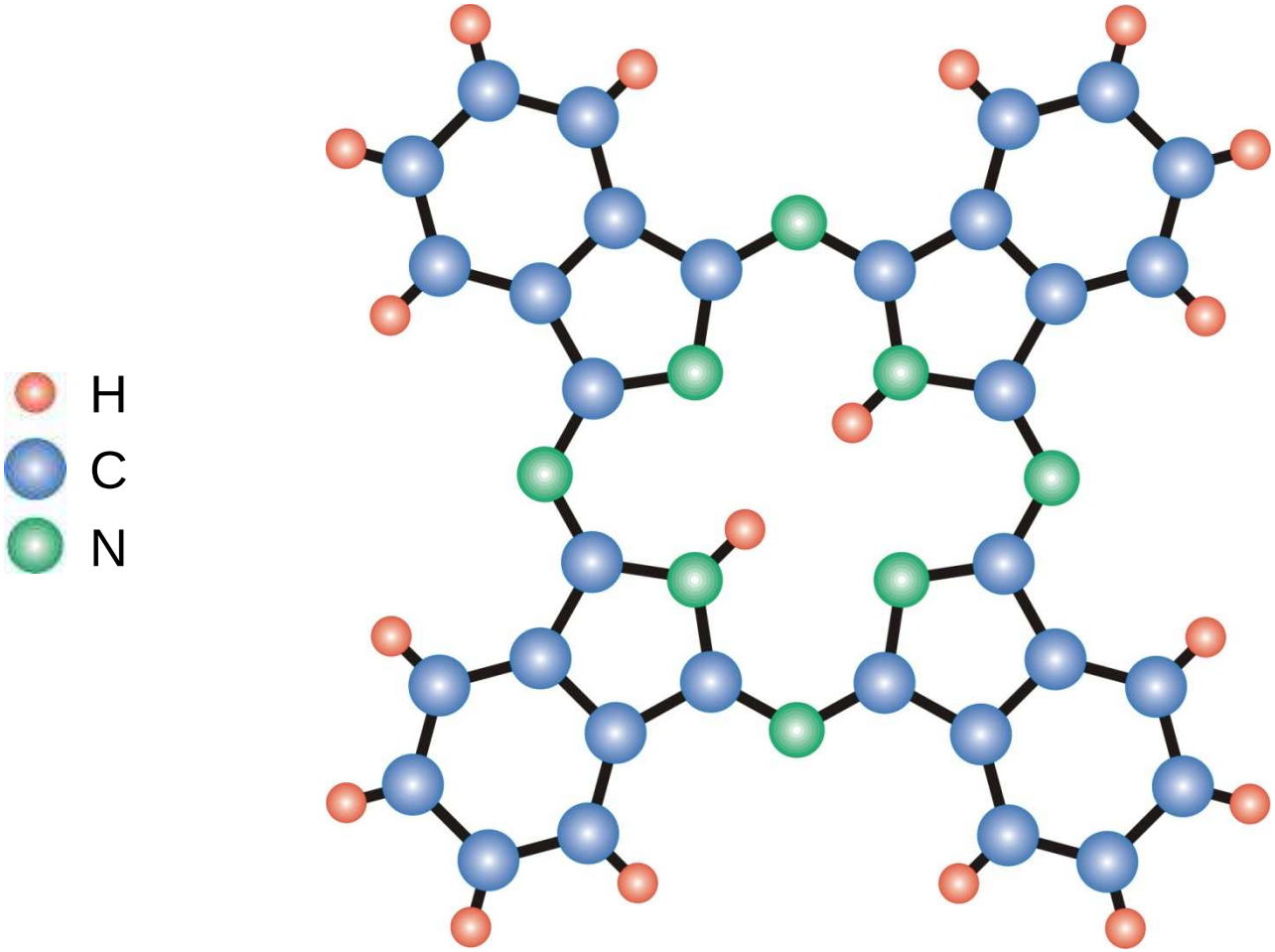
In_{14}



- Number of defects increases with chain length, suggesting a preferred defect density
- energy of the ON state determined by the balance between
  - (1) energy gain associated with a popped-up In_{surf} atom, E_0= -65 meV
  - (2) energy cost due to Coulomb repulsion between popped-up In_{surf} atoms

Pinning switchable molecules to a semiconductor surface

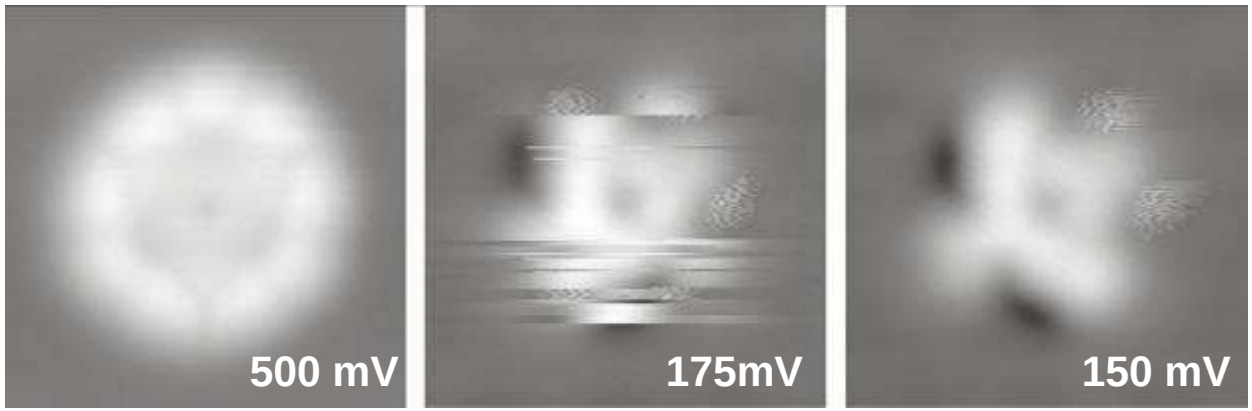
Free-base phthalocyanine (H_2Pc)

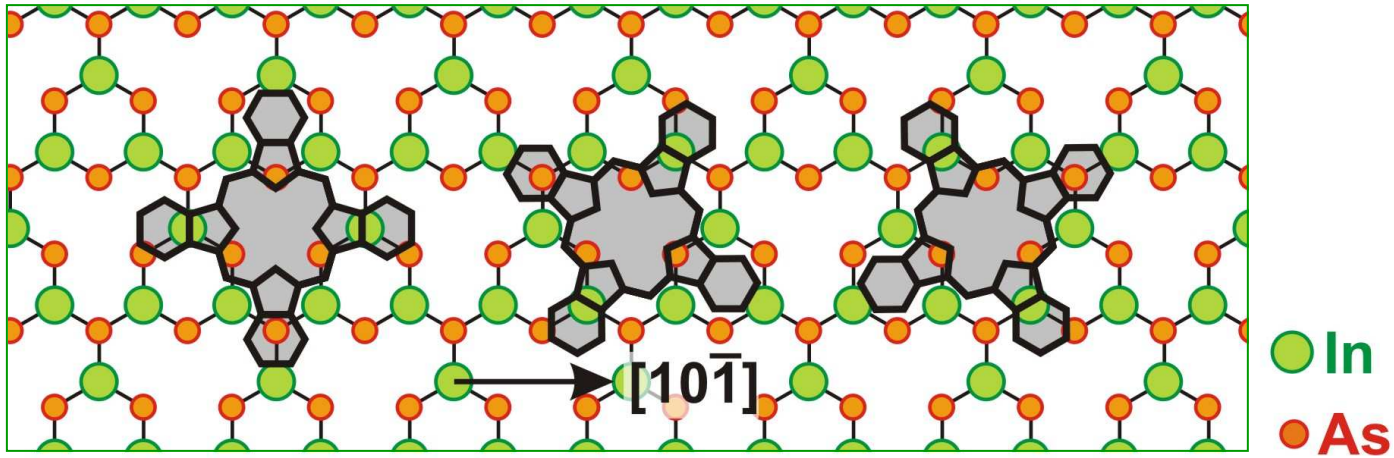


- Planar geometry with twofold D_{2h} symmetry
- two protons caged by four benzene rings via pyrrole units ➔ tautomerization reaction

$H_2Pc/InAs(111)A$ – adsorption geometry

Constant-current STM images, 50 pA, 28 Å x 28 Å, 5 K

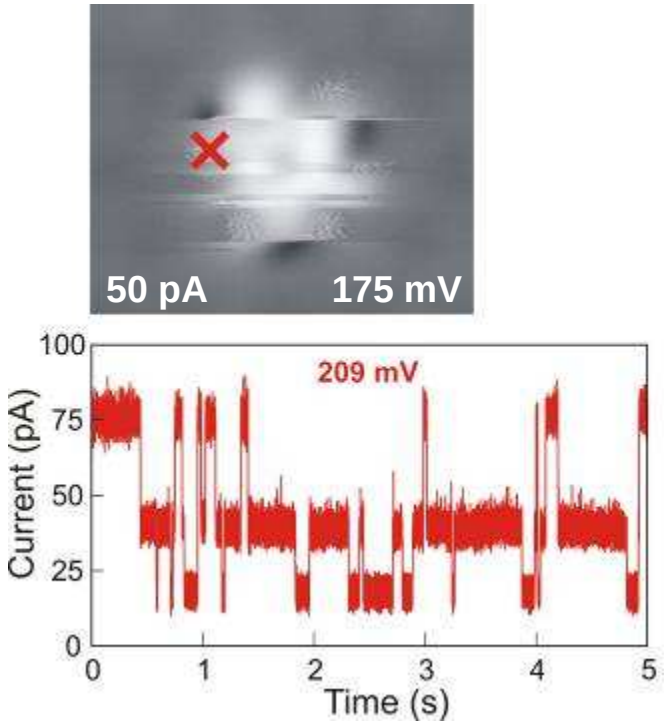




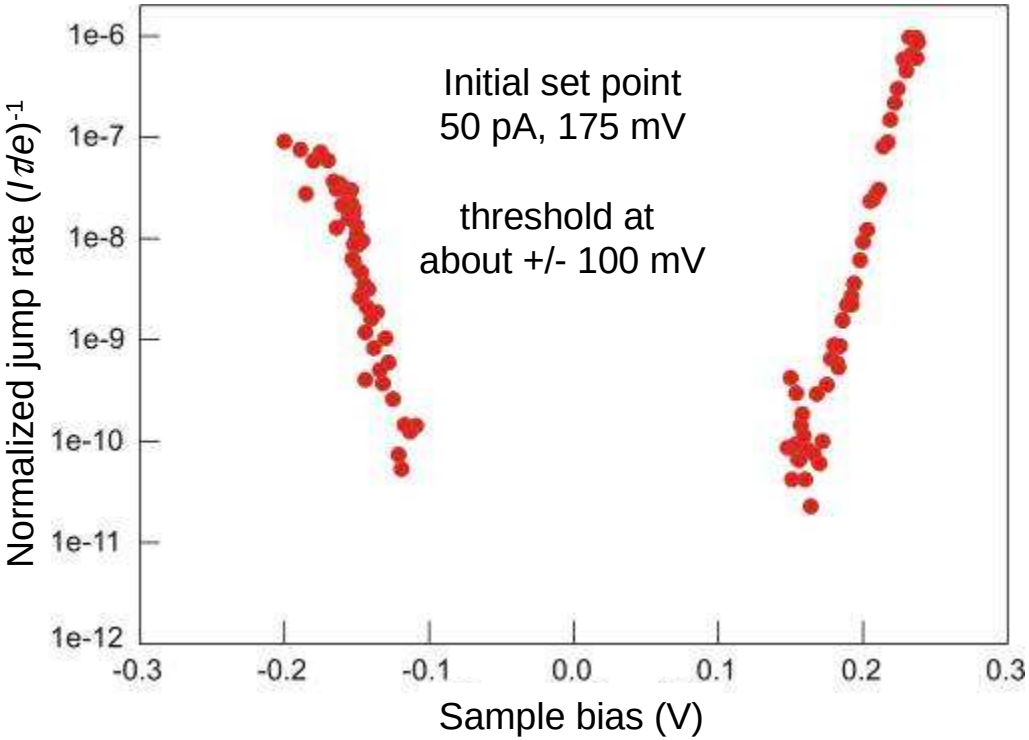
- Molecular rotation slows down with decreasing bias
- centered above In surface vacancy site ➔ *Coulomb* interactions important for bonding
- three equivalent in-plane orientations of the H_2Pc molecule

Three-level current switching due to molecule rotation

Time spectrum of the current



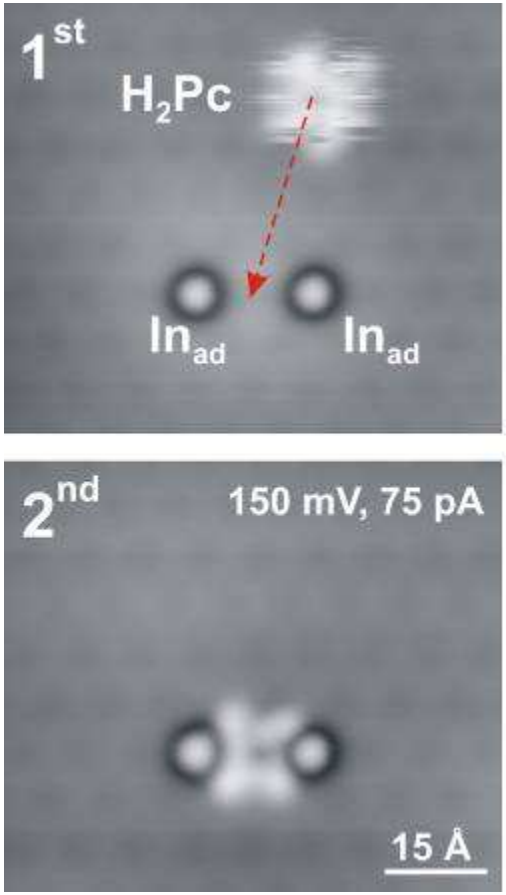
Bias-dependent jump rate



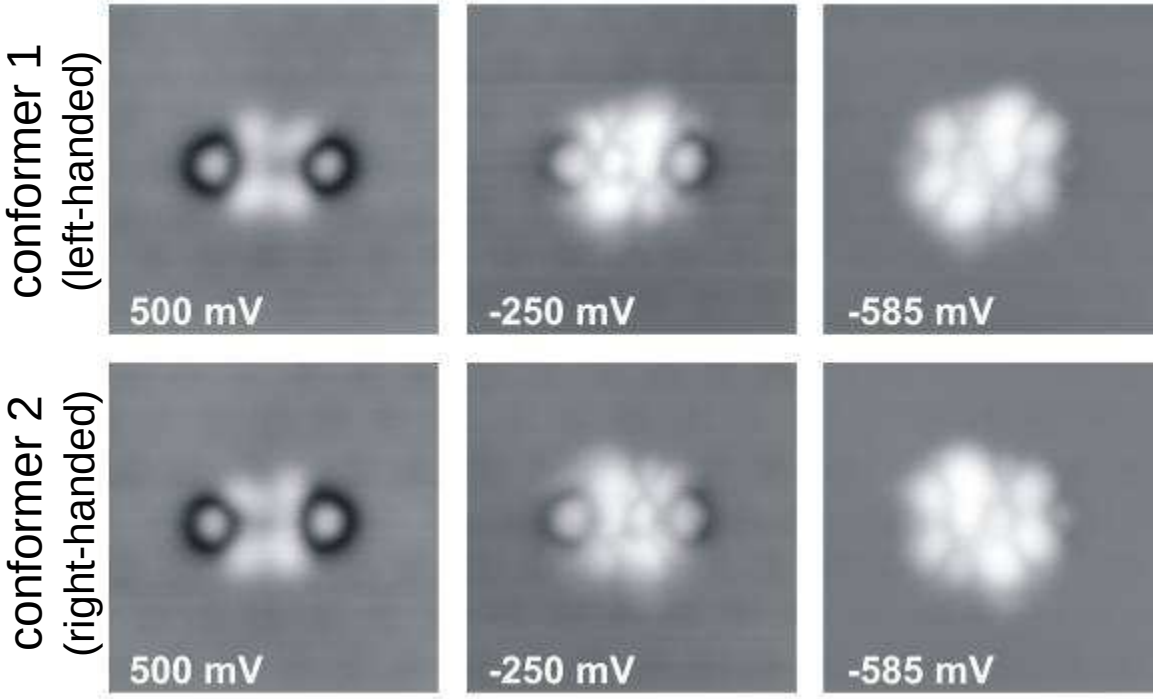
- Three-level current noise: switching between three different in-plane orientations
- normalized jump rate $(I\tau e)^{-1}$: probability per electron to induce a single rotational jump
- threshold behavior suggests that rotation is induced by inelastic excitation

Assembling an In-H_2Pc-In complex

Lateral manipulation



STM images of the In-H_2Pc-In structure, 50 pA

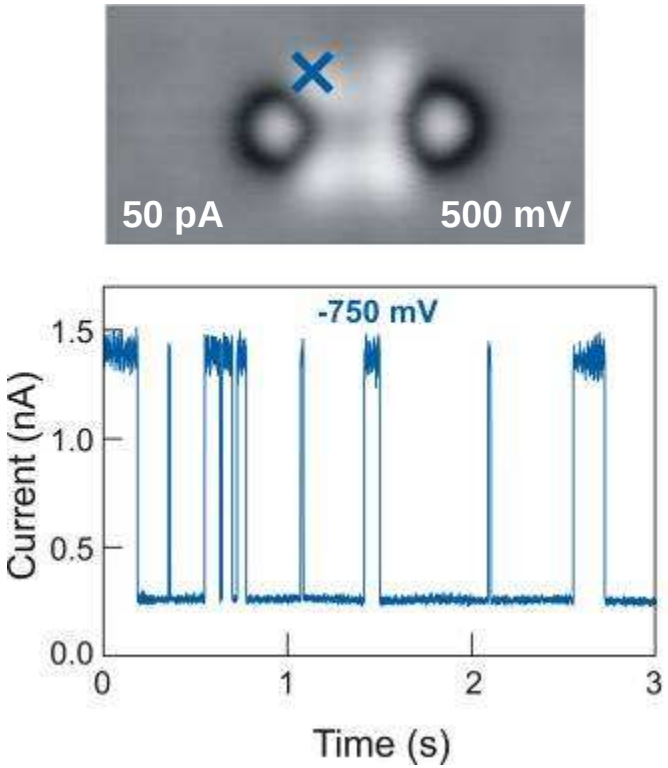


- H_2Pc repositioned by lateral manipulation (here at a constant current 4 nA, 0.36 V)
- blocking the rotation by pinning a H_2Pc between two In_{ad} atoms (spacing: 17.14 Å)
- two stable conformers showing left- and right-handed appearance ➔ tautomerization?

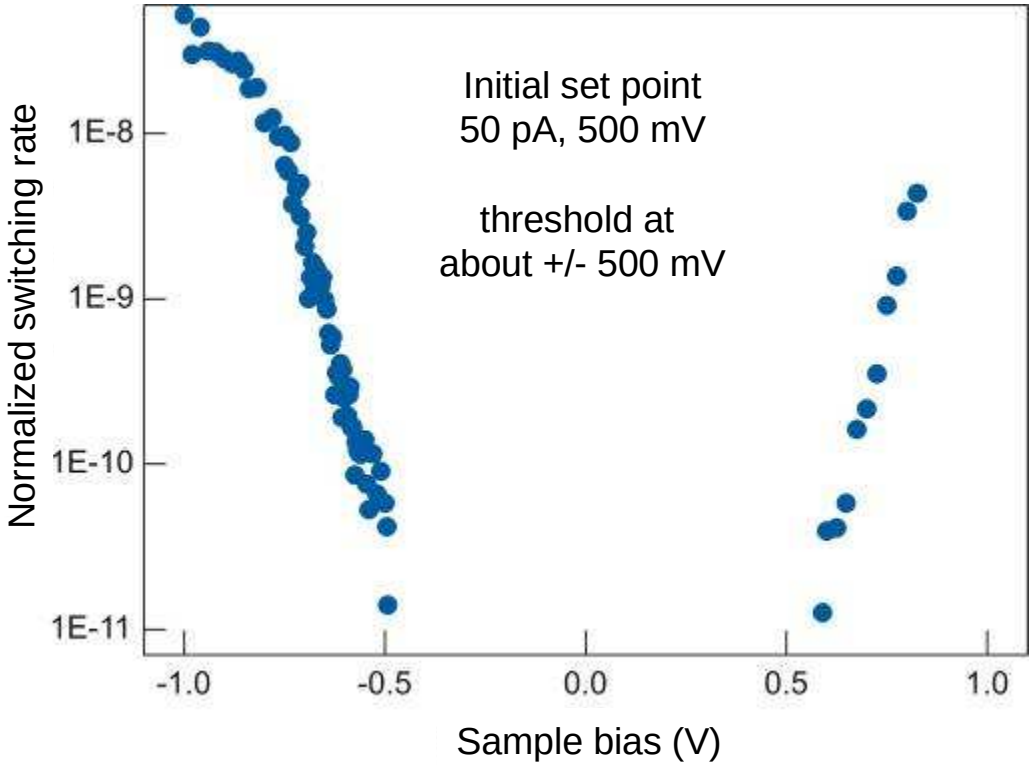
Ch. Nacci *et al*., ACS Nano 6, 4190 (2012)

In-H_2Pc-In: binary current switching

Time spectrum of the current



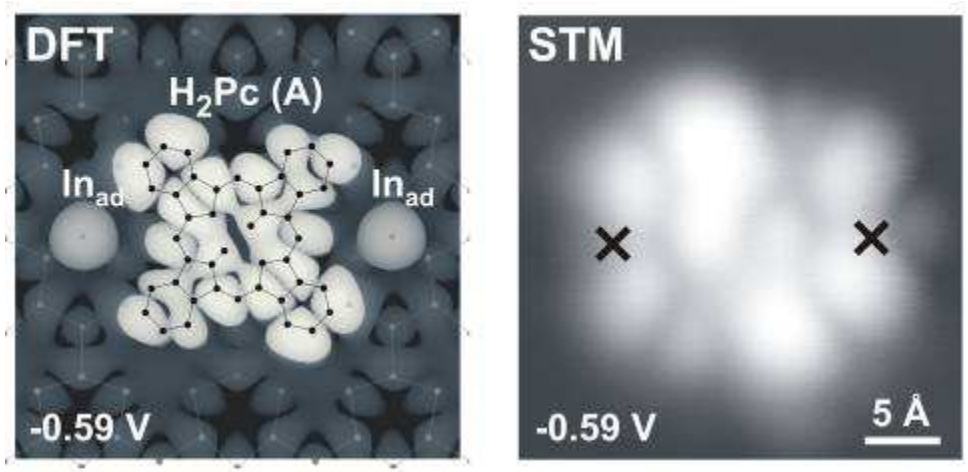
Bias-dependent switching rate



- Binary current switching with an ON-to-OFF ratio ten-to-one
- threshold behavior of the yield suggests that the switching is induced by inelastic excitation
  ➔ activation of the tautomerization reaction

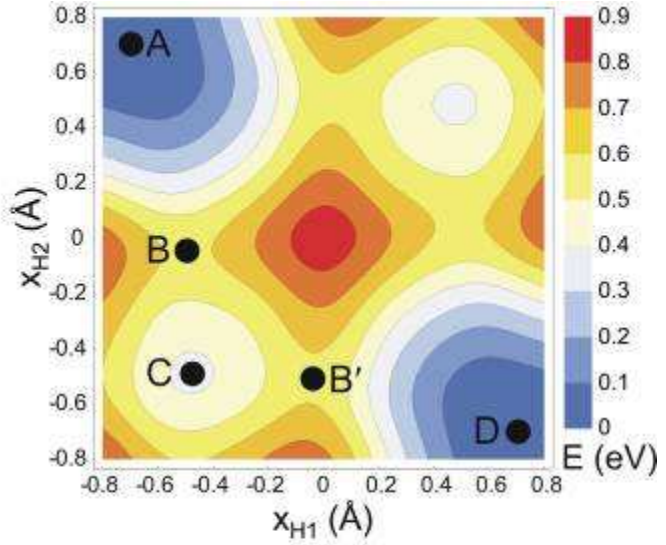
Theoretical energy landscape for H atom switching

In-H_2Pc-In complex: STM imaging

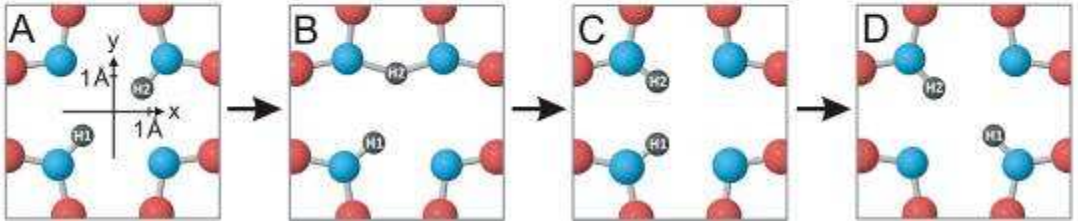


Tersoff-Hamann approach

Potential energy surface (DFT)



Reaction pathway



- Filled-state simulated STM images clearly reflect the asymmetry created by the two H atoms
- energetics of H switching virtually unaffected by the substrate and the pinning In_{ad} atoms [cf. H switching in free H_2Pc: H. Cortina *et al*., J. Phys. Chem. **107**, 8968 (2003)]

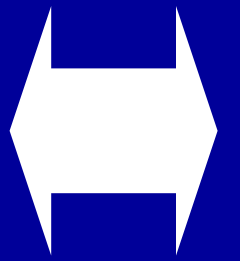
Ch. Nacci *et al*., ACS Nano 6, 4190 (2012)

‘*Take-home*’ message

- Resolution of and sensitivity to single atoms and molecules at surfaces
- Local spectroscopy probe of the electronic density of states
- Low-temperature STM: Combined approach

Manipulating matter with atomic-scale control

Assembling nanostructures from single atoms/molecules



Atomic-scale characterization

Local electronic structure and elementary excitations

Acknowledgments

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