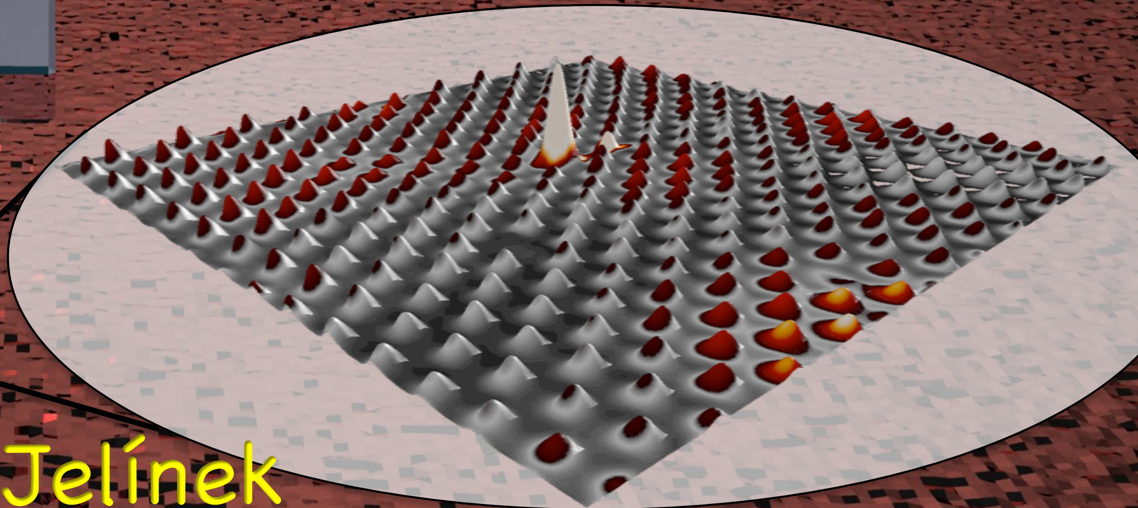
Rastrovací mikroskopie: naše oko do světa atomů.

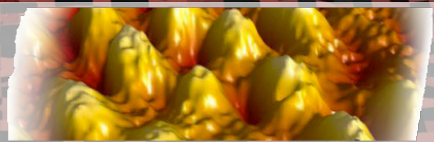


Pavel Jelínek

Fyzikální Ústav AV ČR, v.v.i.

jelinekp@fzu.cz nanosurf.fzu.cz

NANOSURF LAB



FZÚ

Outline

- Introduction
- STM
- AFM
- What next?

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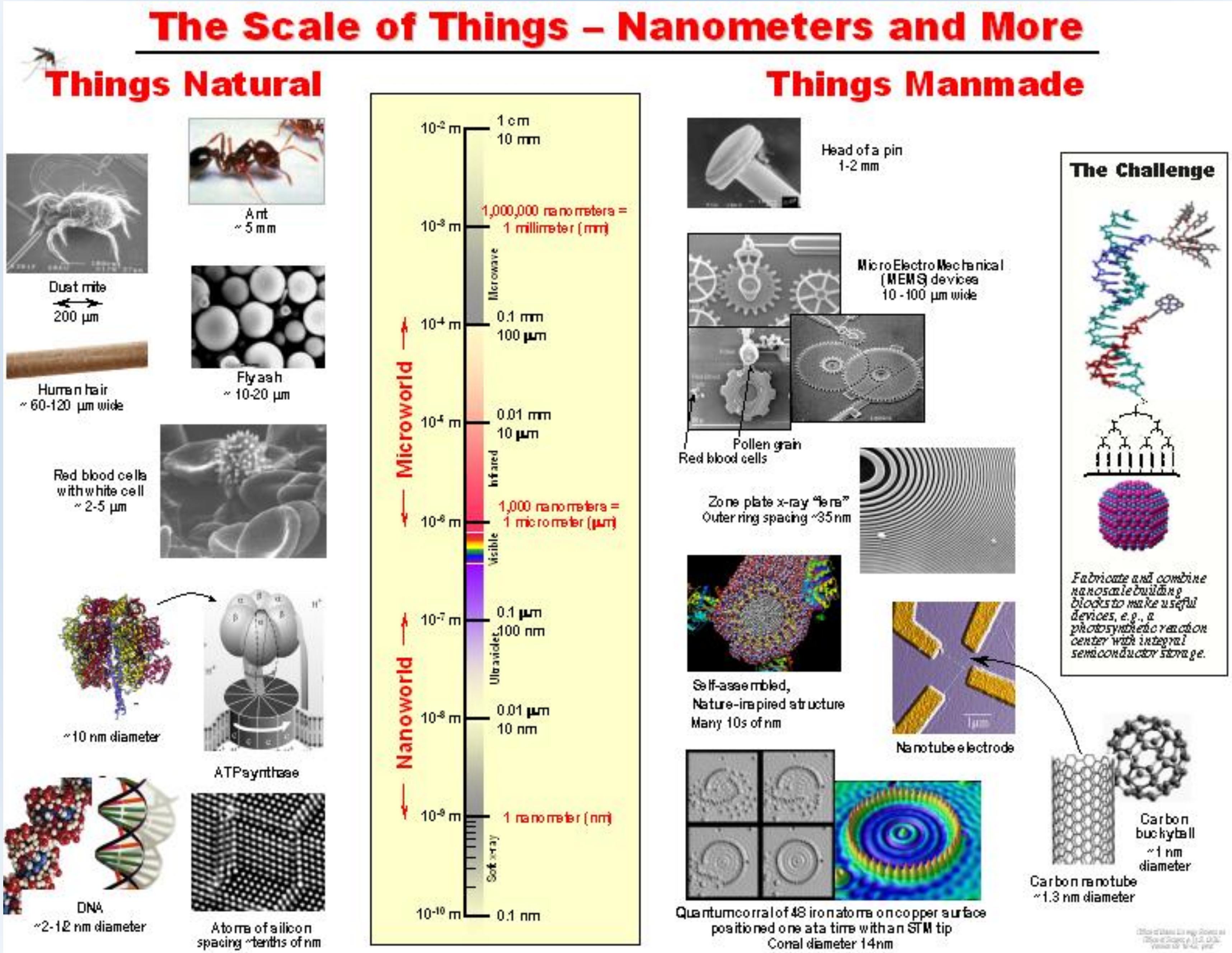
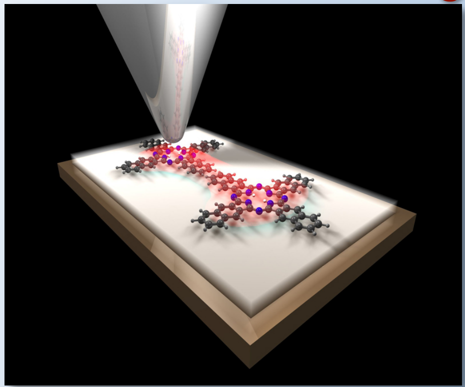
- AFM
- What next?

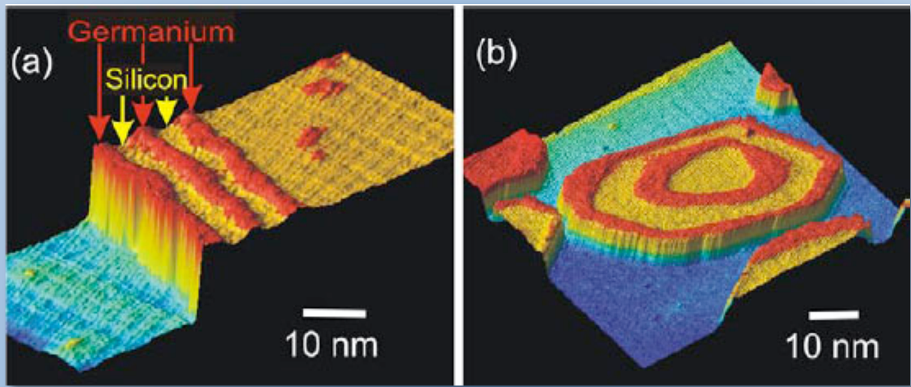


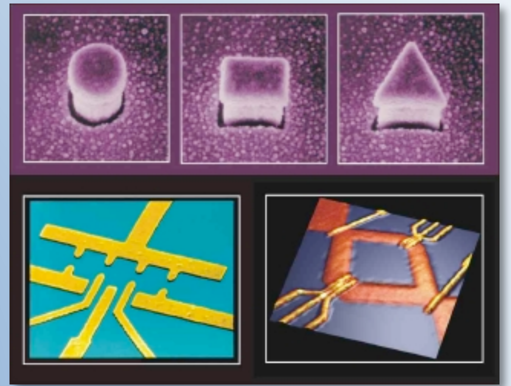
The Scale of Things – Nanometers and More
Things Natural
Things Manmade
Ant
~ 5 mm
Dust mite
200 μm
Human hair
~ 60-120 μm wide
Fly ash
~ 10-20 μm
Red blood cells
with white cell
~ 2-5 μm
~10 nm diameter
ATP synthase
DNA
~2-1/2 nm diameter
Atoms of silicon
spacing ~tenths of nm
10⁻² m
1 cm
10 mm
1,000,000 nanometers =
1 millimeter (mm)
10⁻³ m
Microwave
10⁻⁴ m
0.1 mm
100 μm
10⁻⁵ m
0.01 mm
10 μm
Infrared
1,000 nanometers =
1 micrometer (μm)
10⁻⁶ m
Visible
10⁻⁷ m
0.1 μm
100 nm
Ultraviolet
10⁻⁸ m
0.01 μm
10 nm
10⁻⁹ m
1 nanometer (nm)
Soft x-ray
10⁻¹⁰ m
0.1 nm
Microworld
Nanoworld
Head of a pin
1-2 mm
MicroElectroMechanical
(MEMS) devices
10 -100 μm wide
Pollen grain
Red blood cells
Zone plate x-ray "lens"
Outer ring spacing ~35 nm
Self-assembled,
Nature-inspired structure
Many 10s of nm
Nanotube electrode
Carbon nanotube
~1.3 nm diameter
Carbon
buckyball
~1 nm
diameter
Quantum corral of 48 iron atoms on copper surface
positioned one at a time with an STM tip
Corral diameter 14 nm
The Challenge
Fabricate and combine nanoscale building blocks to make useful devices, e.g., a photosynthetic reaction center with integral semiconductor storage.

Nanoscale electronics

Building blocks: atomic clusters, molecules & atoms

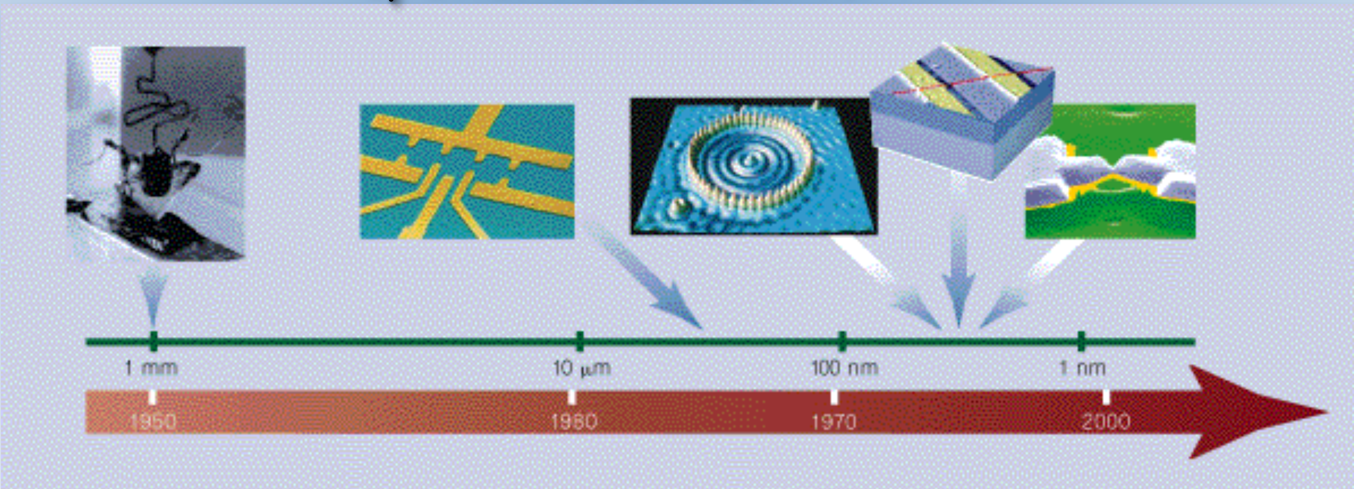




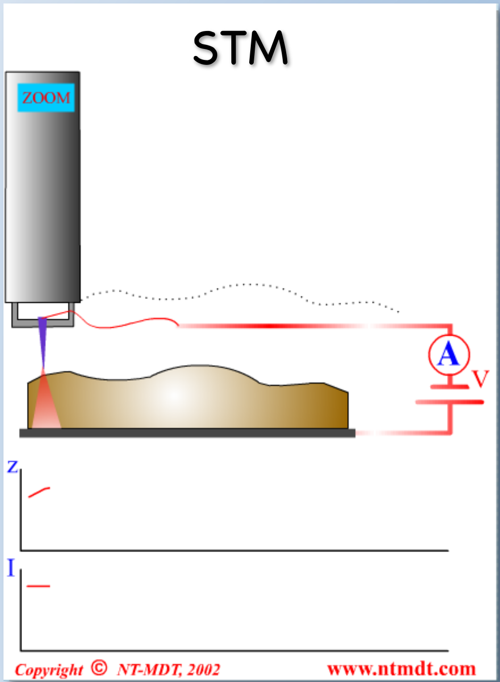


...we need to see, recognize & assemble them

Spatial resolution vs. time

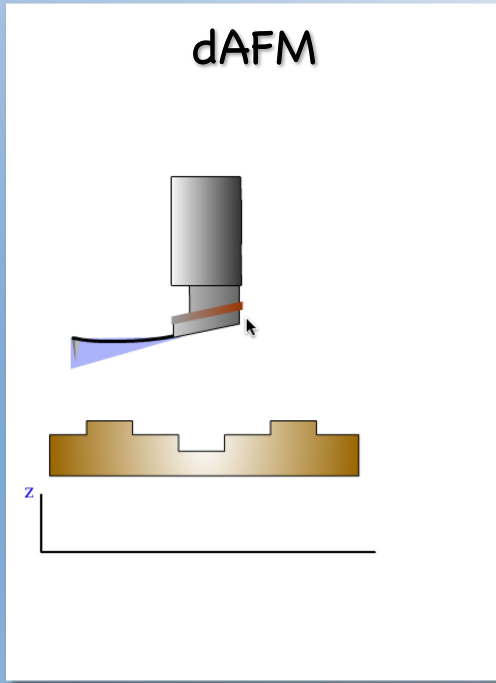


Scanning Probe Microscopy



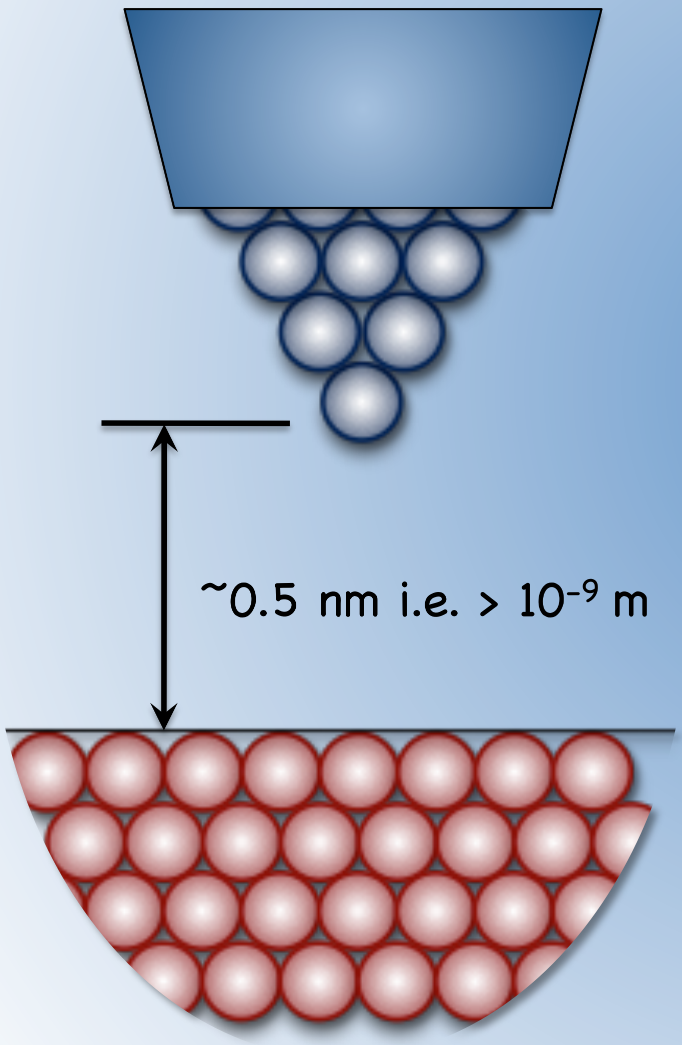
- ❑ tunneling current occurs at very short distances when the voltage is applied between the probe and the sample
- ❑ provides atomic resolution of surfaces & their electronic structure

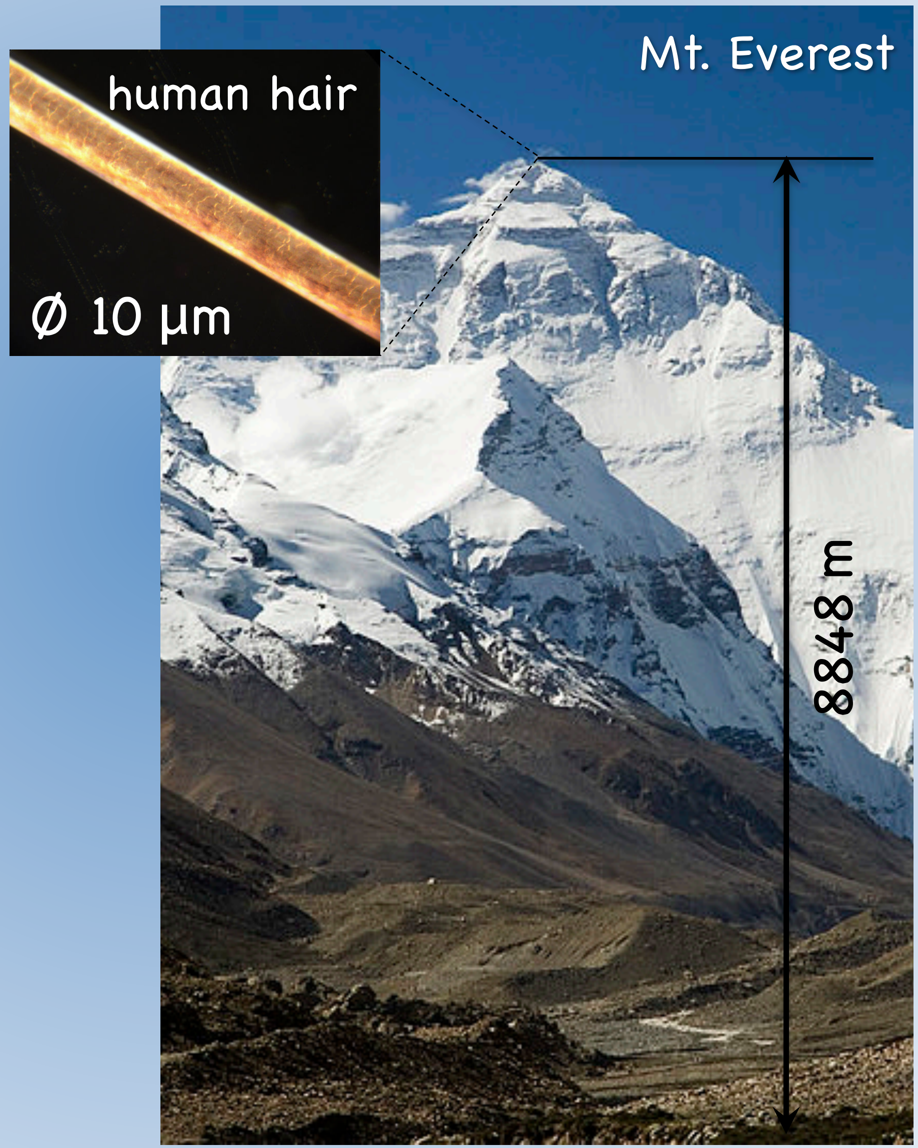
Analogy of gramophone



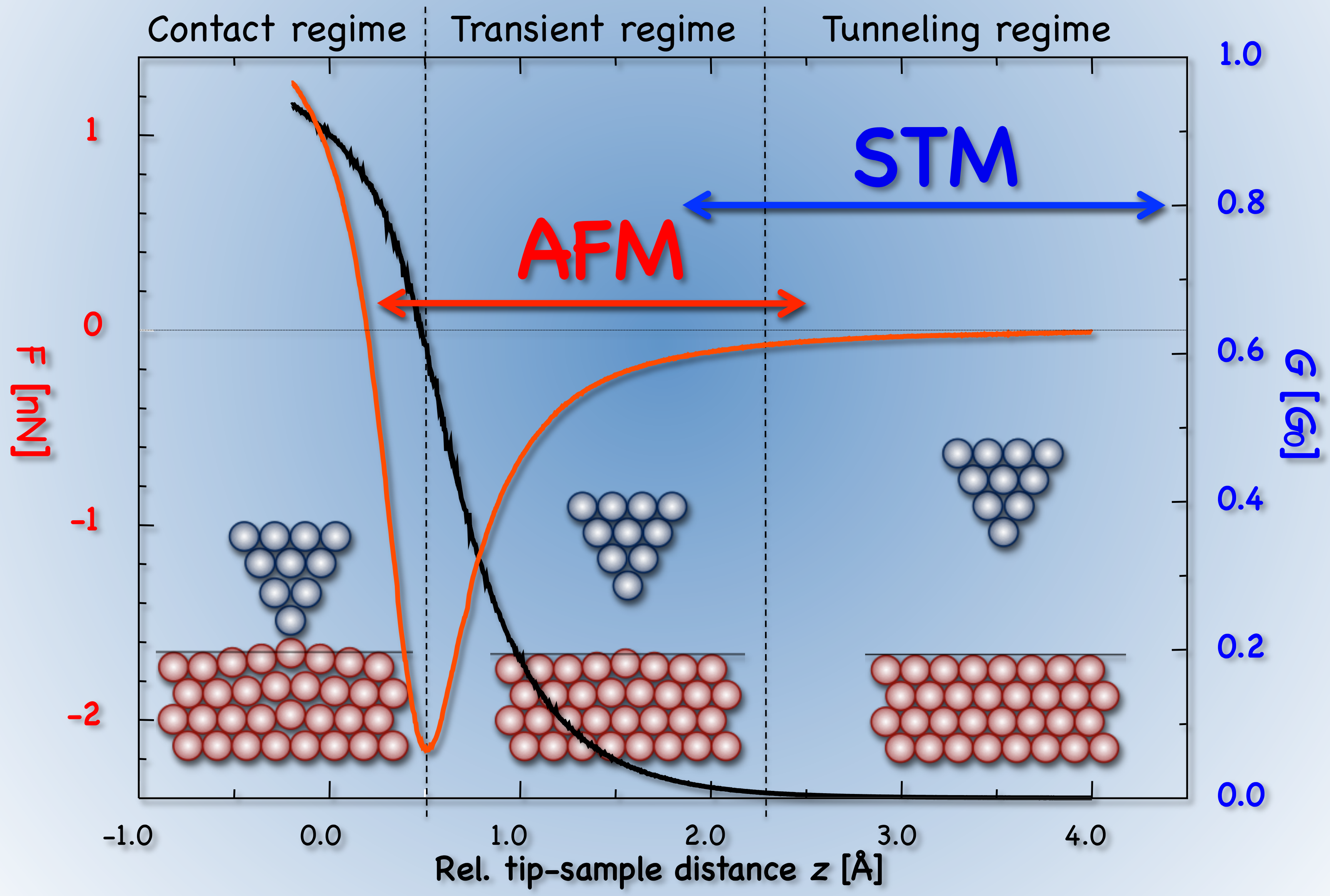
- ❑ oscillating probe contacting ("touching") the surface changing oscillation frequency/amplitude
- ❑ point to point differences in oscillation frequency/amplitude make an image contrast.

Distance between tip and sample

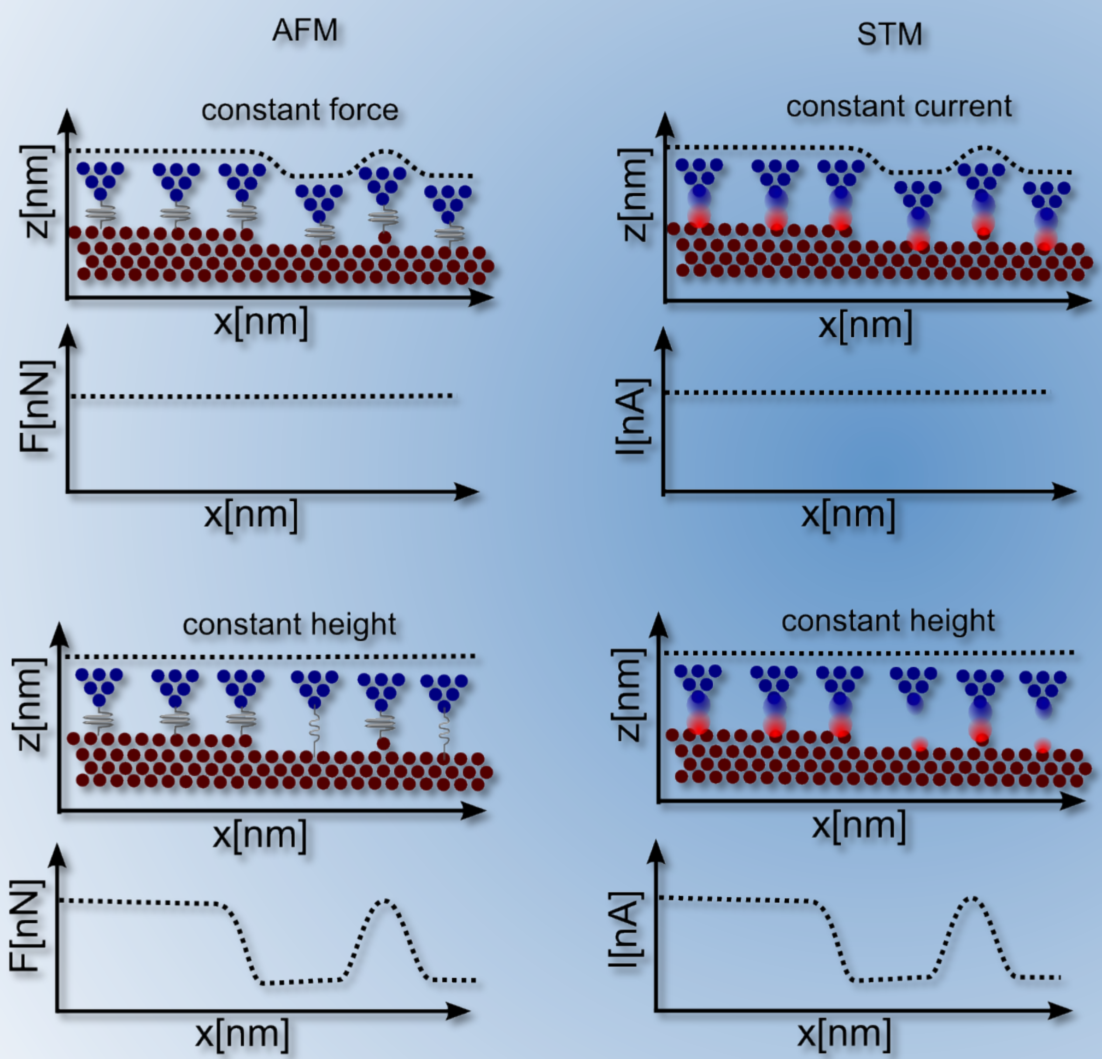




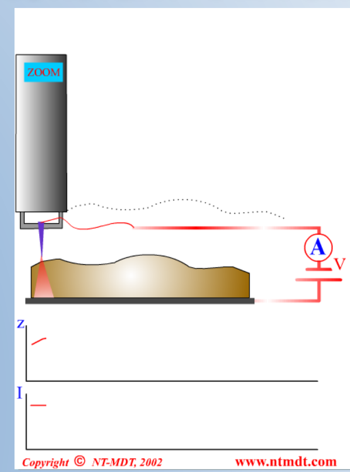
Tip-sample interaction



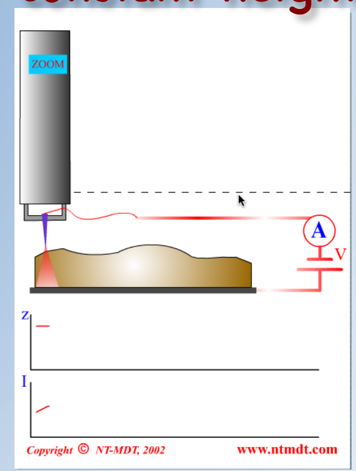
Basic operation modes



constant current



constant height



Outline

- Introduction
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Birth of STM

G. Binning et al, Phys. Rev. Lett. 49, 57–61 (1982)

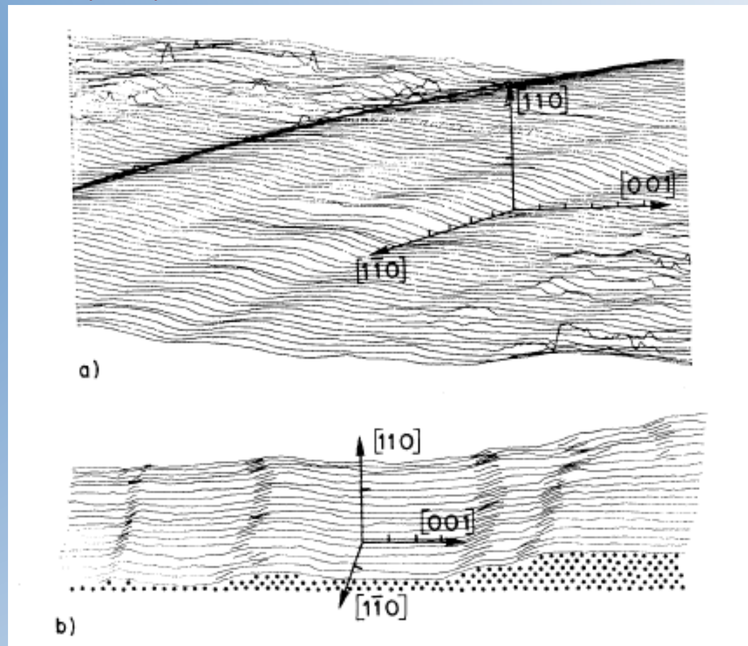
Surface Studies by Scanning Tunneling Microscopy

G. Binning, H. Rohrer, Ch. Gerber, and E. Weibel

IBM Zurich Research Laboratory, 8803 Rüschlikon-ZH, Switzerland

(Received 30 April 1982)

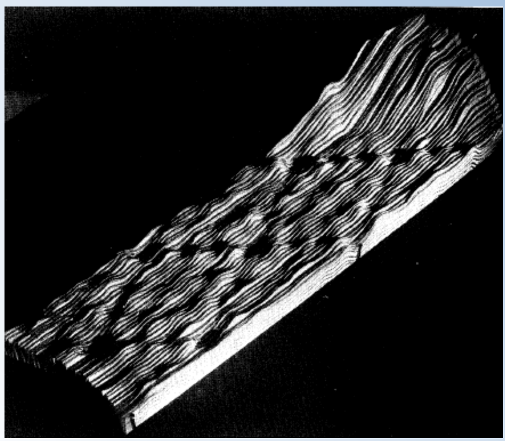
Au(110) surface

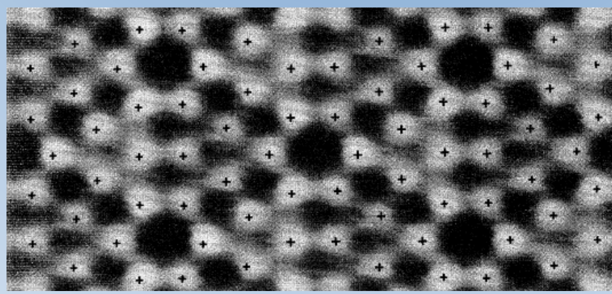


Nobel Prize for Physics 1986:
G. Binnig and H. Rohrer

7 × 7 Reconstruction on Si(111) Resolved in Real Space

G. Binning et al, Phys. Rev. Lett. 50, 120–123 (1983)

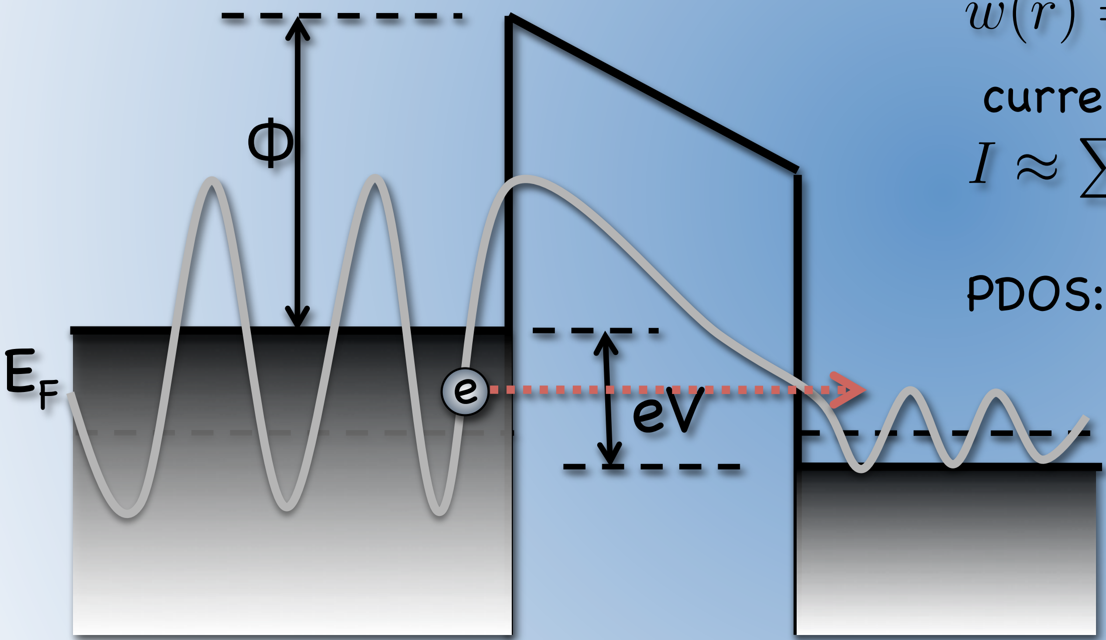




Mechanism of STM: tunneling

exponential decay in the barrier

$$\psi(r) = \psi(0)\exp(-\kappa r) \quad \kappa = \frac{\sqrt{2m_e(\phi - E)}}{\hbar}$$



probability to find e- behind the barrier

$$w(r) = |\psi(r)|^2 = |\psi(0)|^2 \exp(-2\kappa r)$$

current proportional to the probability

$$I \approx \sum_{E_n} |\psi_n(0)|^2 \exp(-2\kappa r)$$

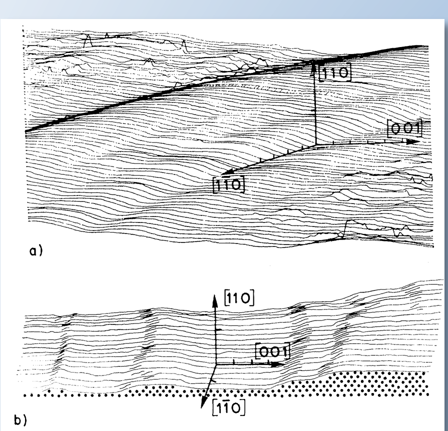
PDOS: $\rho(z,\omega) = \frac{1}{\epsilon}\sum_{E_n} |\psi_n(z)|^2$

the current depends exponentially on distance -> key for the atomic resolution

$$I \approx V\rho_s(0,E_F)\exp(-2\kappa d) \approx V\rho_s(0,E_F)\exp(-1.025\sqrt{\phi}d)$$

Atomic scale images

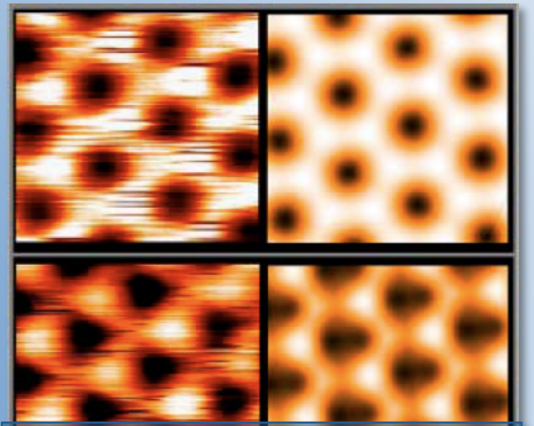
Au(110) surface



Si(111)-(7x7) surface

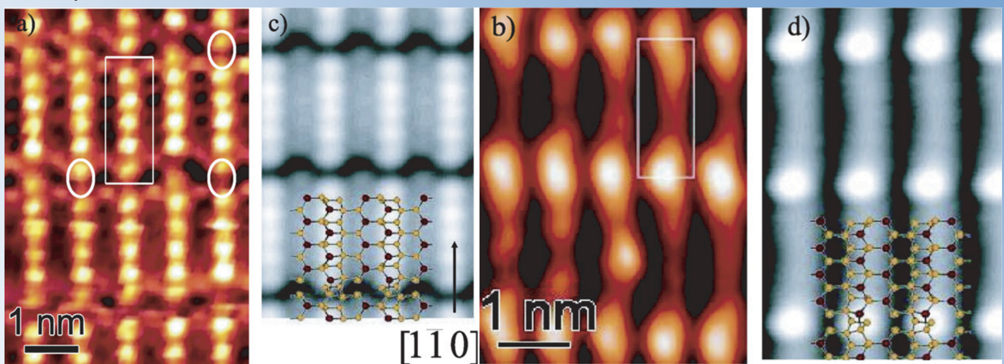
C. Binning et al, Phys. Rev. Lett. 47, 57 (1982)

O/Ru(0001) & O/Pd(111)

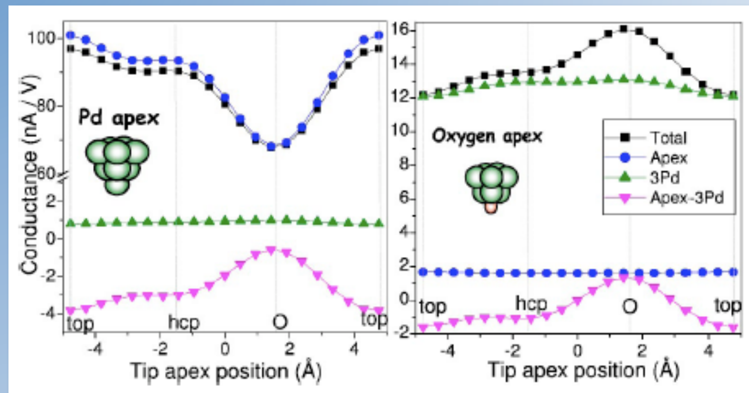


strong tip-dependence

exp. & theory: Si(112)-(6x1)/Ga surface



P.C. Snijder et al, Phys. Rev. B 72, 125343 (2005)

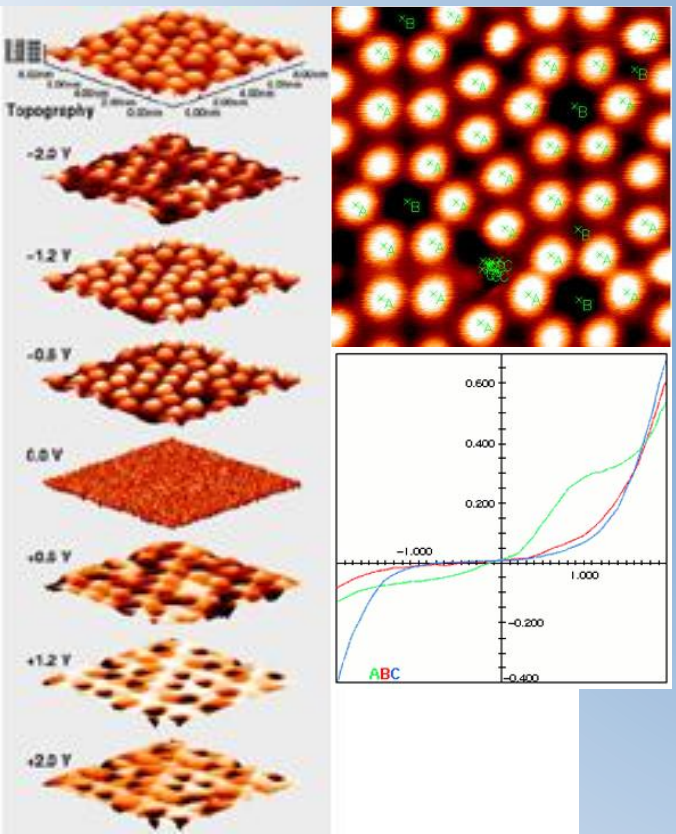


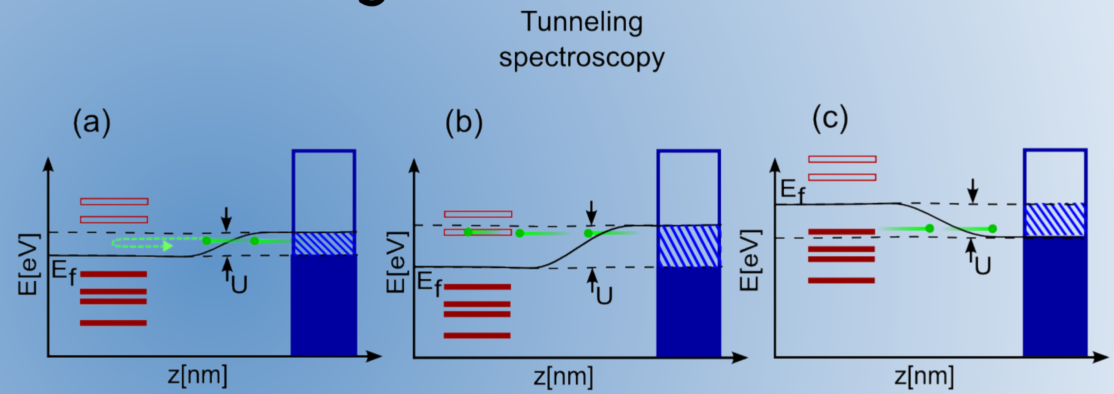
F. Calleja et al, Phys. Rev. Lett. 92, 206101 (2004)
J.M. Blanco et al Phys. Rev. B 71, 113402 (2005)

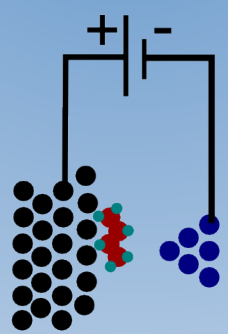
Elastic spectroscopy: PDOS

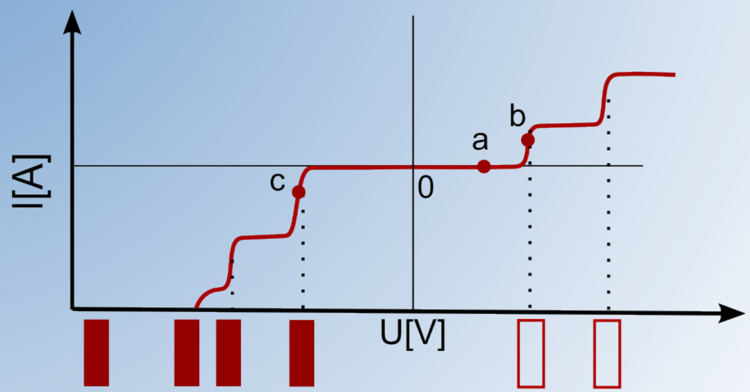
N.D. Lang Phys. Rev. B 34 5947 (1986)
R.M. Feenstra et al Surf. Sci 181, 295 (1987)

- Current-imaging-tunneling spectroscopy (CITS)
- lock-in techniques (constant height mode) $\frac{dI}{dV} \approx \rho_s(E_F + eV)$



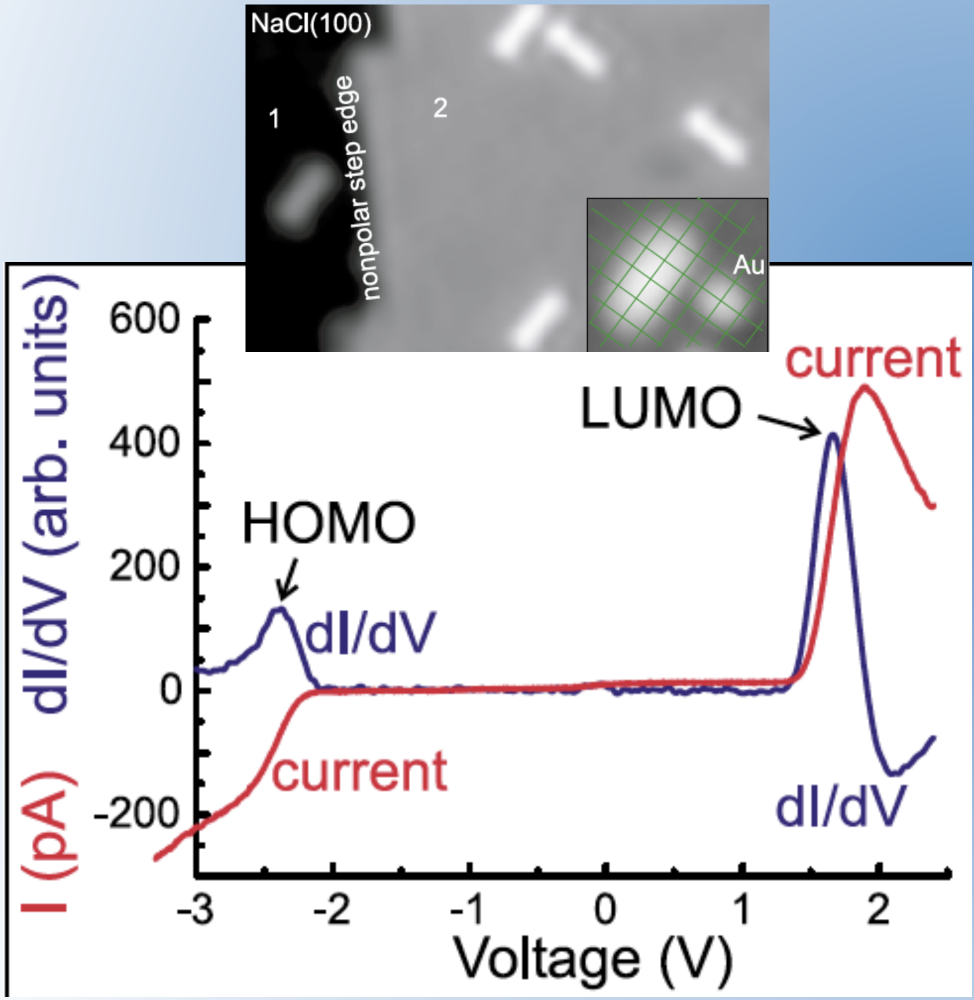


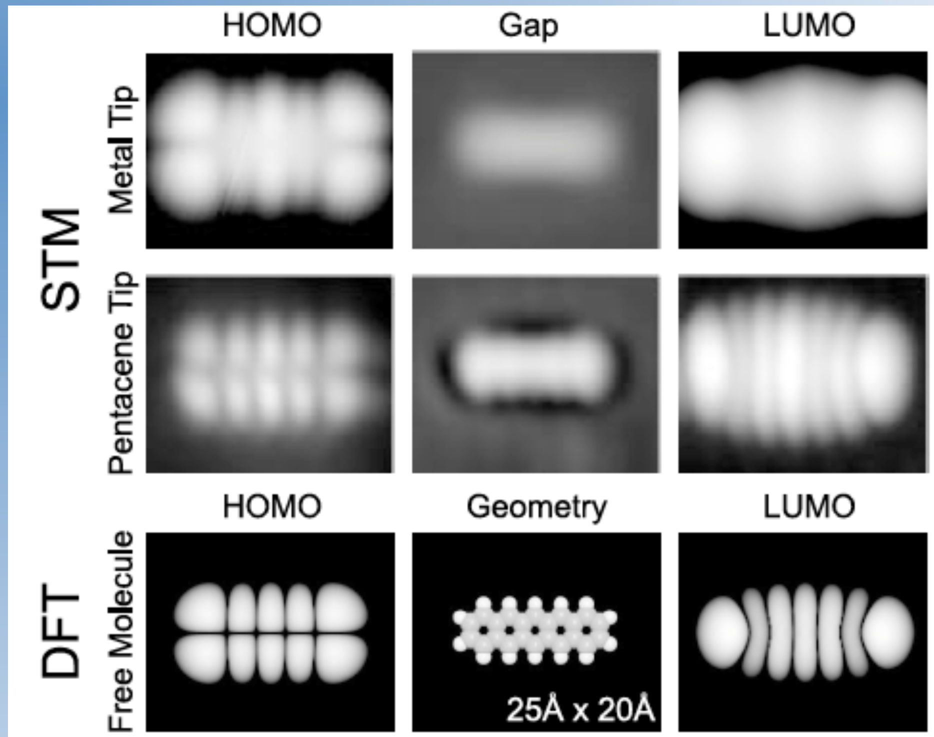




Imaging molecular orbitals

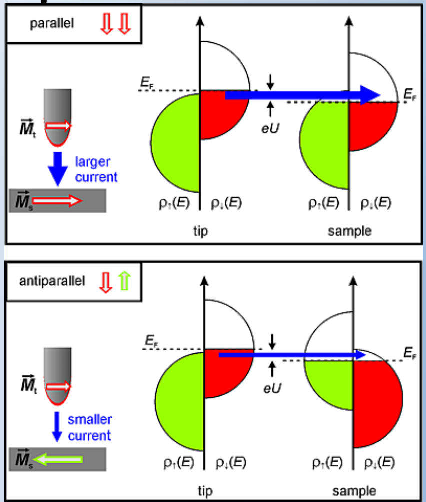
*L. Gross et al, Science **325**, 1110 (2009)*

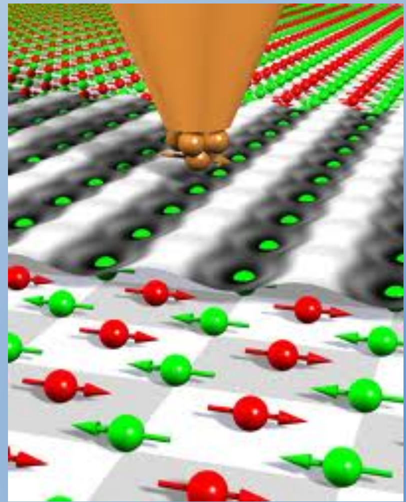




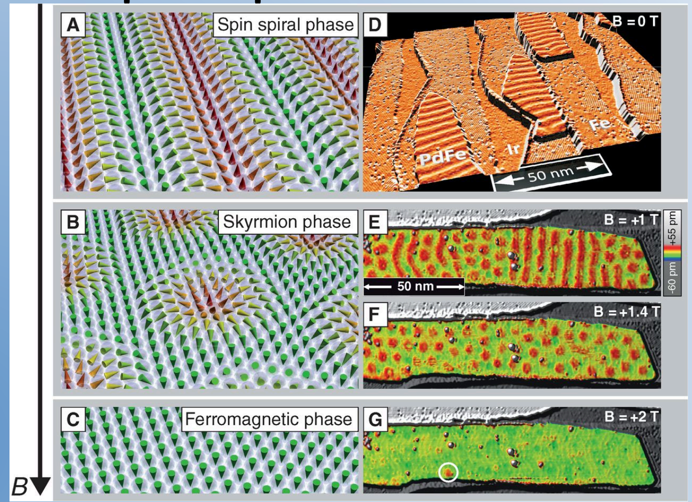
Spin polarized STM

Spin resolution on atomic scale

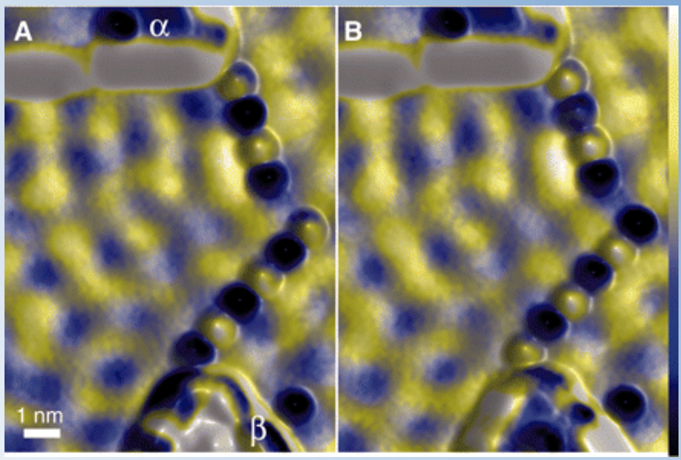


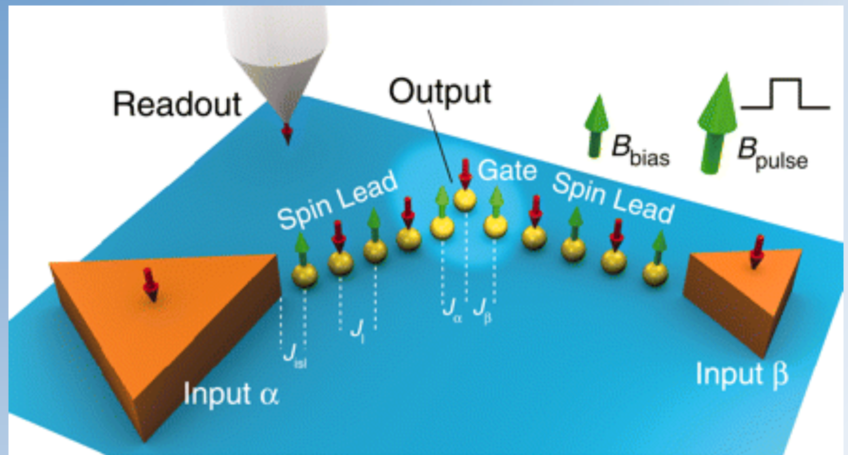


Complex spin structures



Realizing All-Spin-Based Logic Operations Atom by Atom

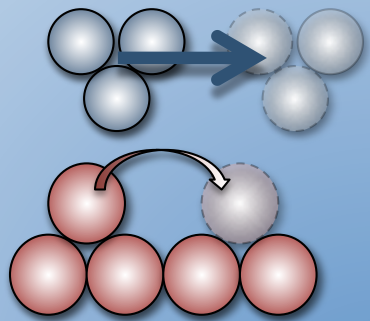




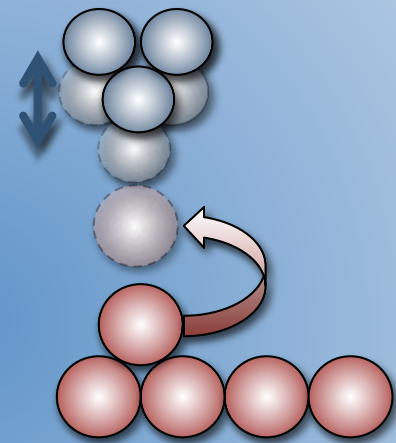
A. A. Khajetoorians et al, Science 332, 1062 (2011)

Atomic Manipulation

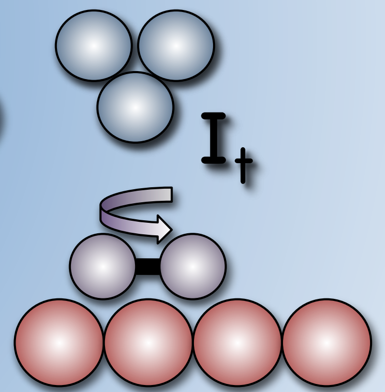
- lateral



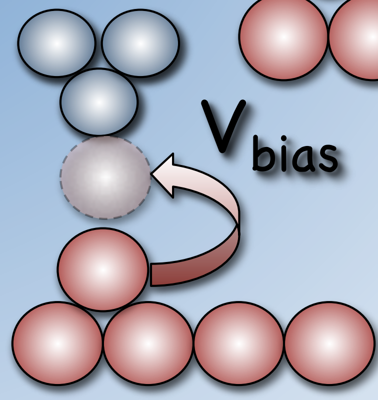
- vertical



- induced by inelastic tunneling



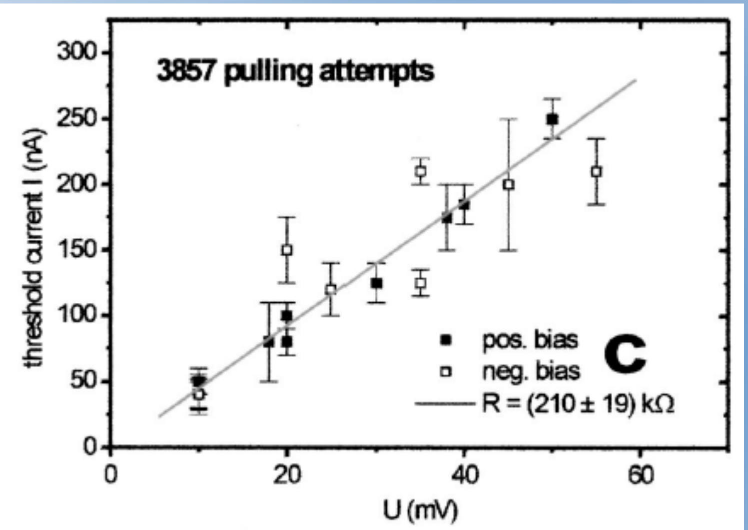
- induced by electric field

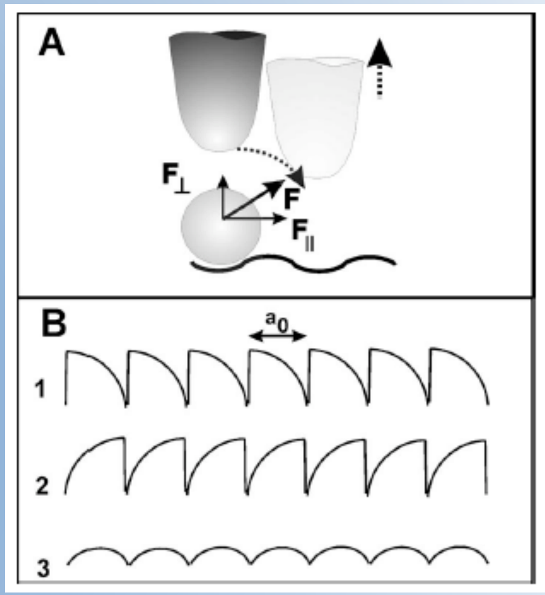


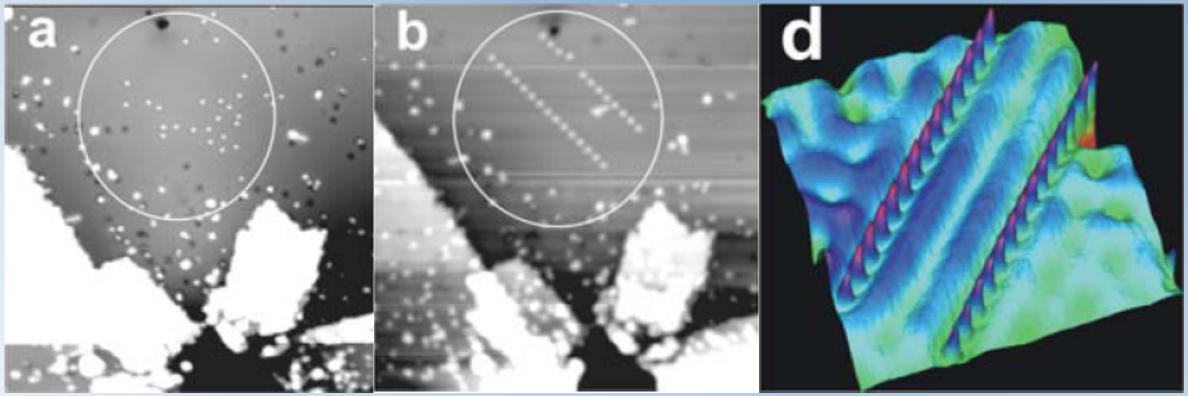
Lateral Manipulation

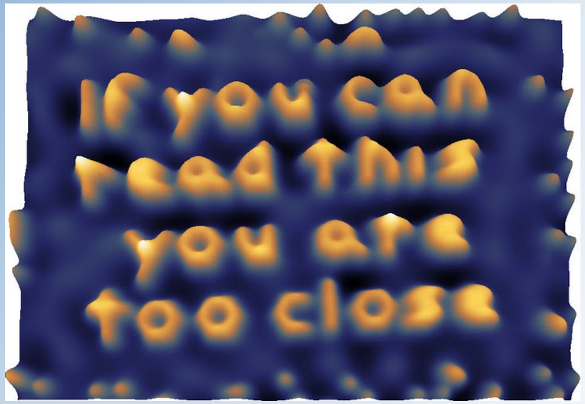
L. Bartles et al, PRL 79, 697 (1997)

- pushing (1), pulling (2) & sliding (3)modes



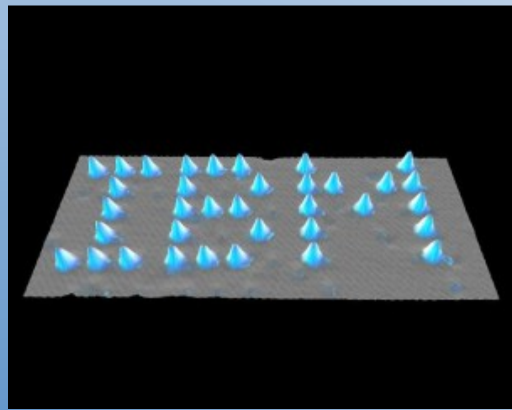




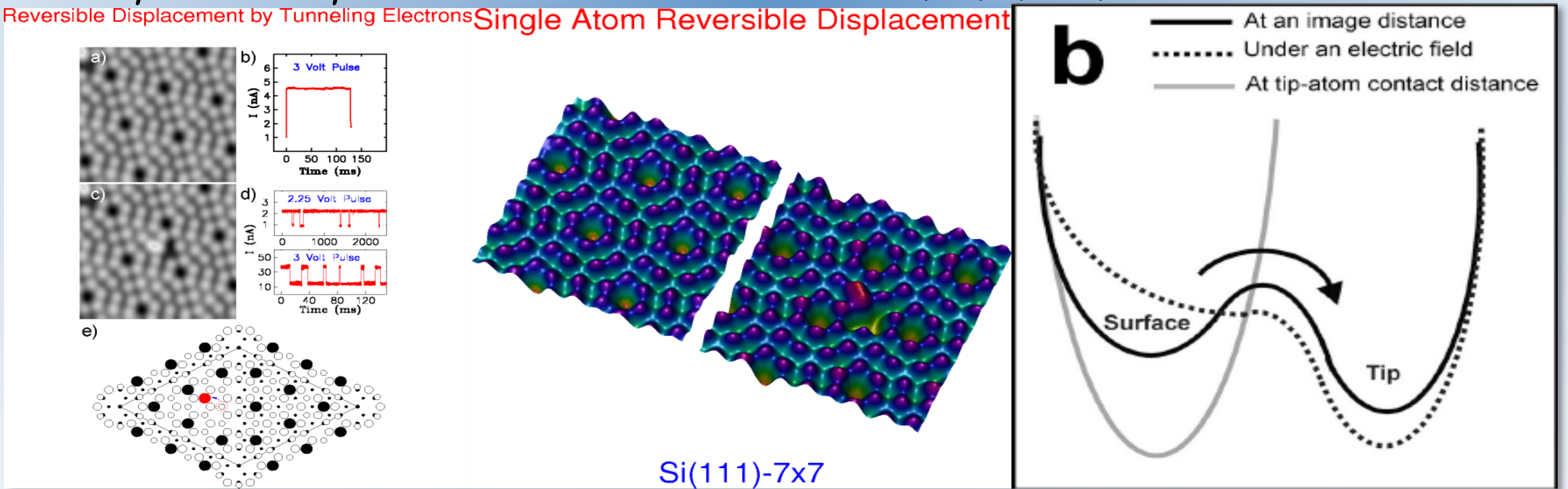


Vertical Manipulation

- induced by
  - electric field
  - inelastic tunneling processes
  - mechanical contact



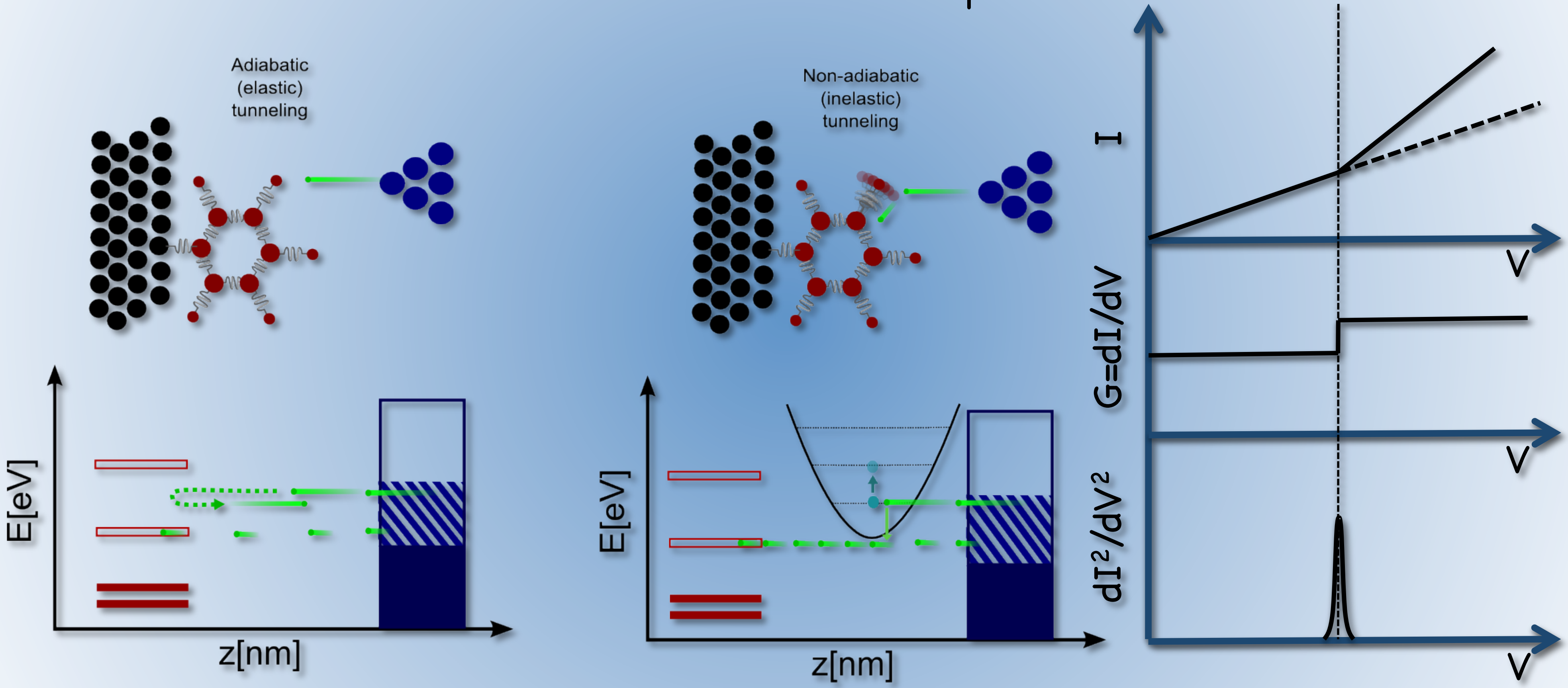
Site Specific Displacement of Si Adatoms on Si(111)-(7x7)



B.C. Stipe et al, Phys. Rev. Lett. 79, 4397 (1997).

Inelastic electron spectroscopy

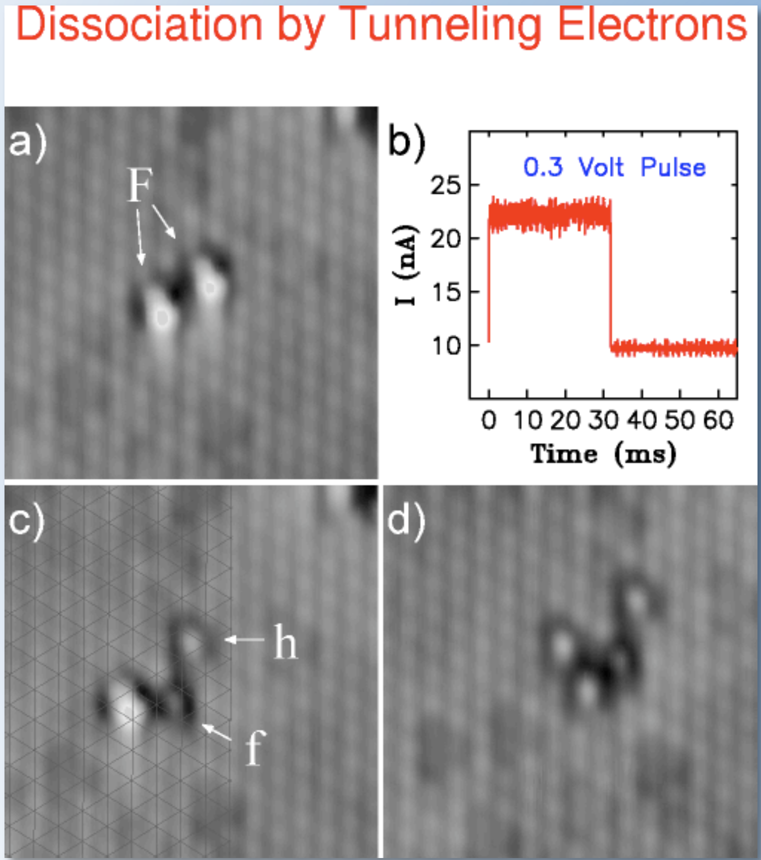
Interaction between electron and vibration modes opens new transmission channels

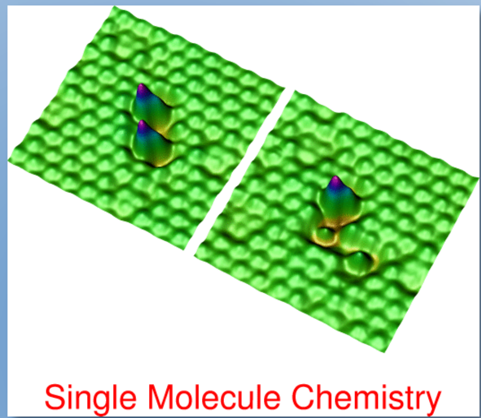


Reference missing!!!

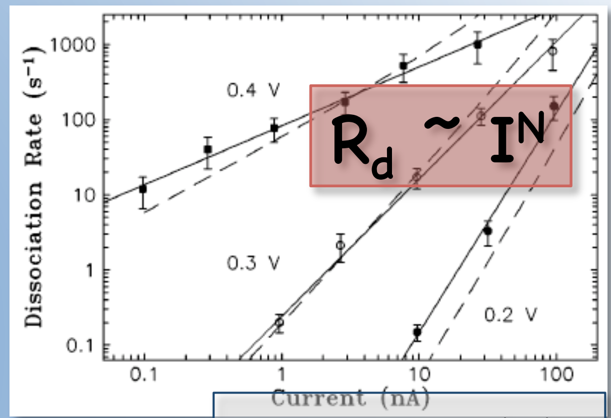
Dissociation by inelastic current

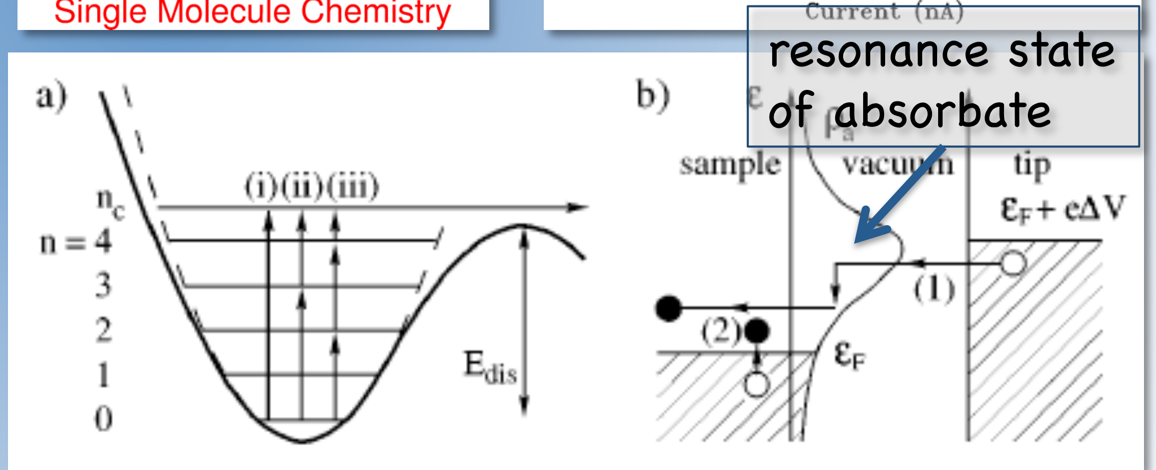
B.C. Stipe *et al Phys.* Rev. Lett. 78, 4410 (1997).





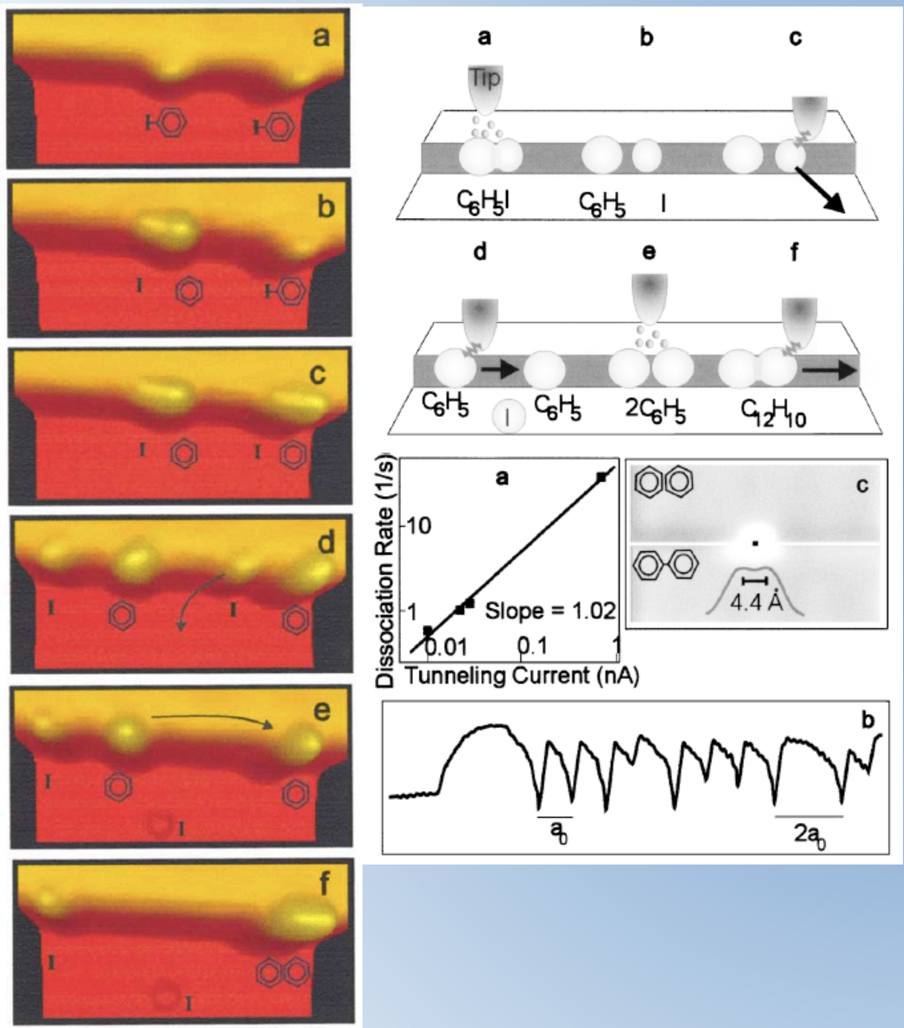
diss. rate vs. current





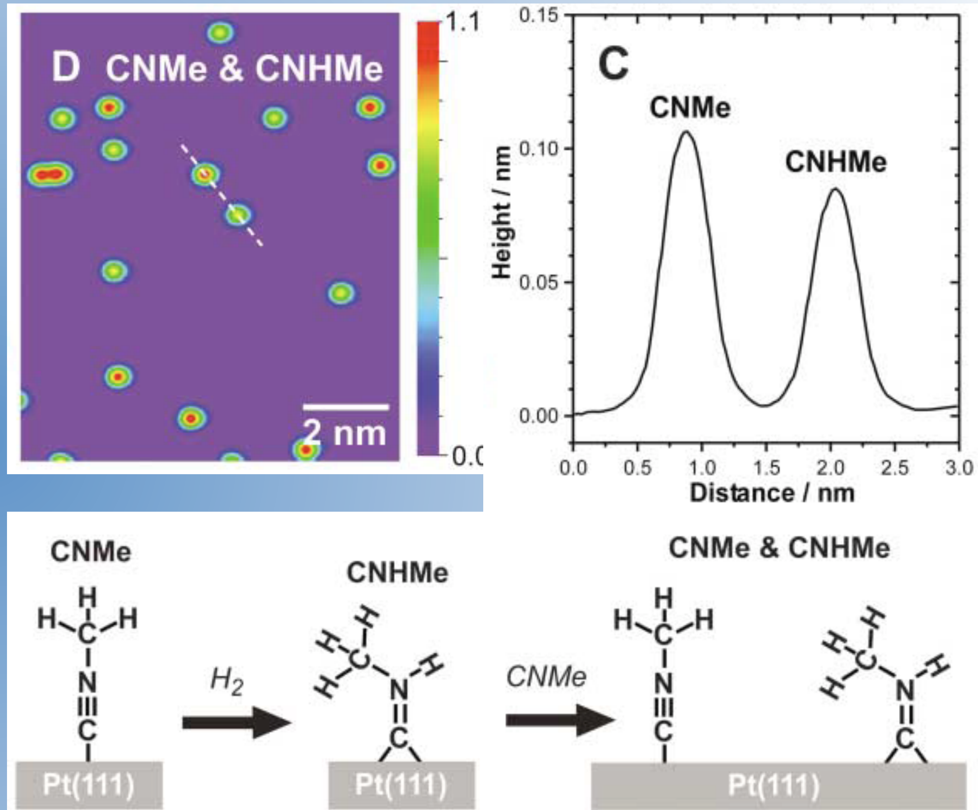
Chemistry by STM

Complex chemical (Ullman) reaction



S. W. Hla, *et al. Phys.Rev.Lett 85, 2777 (2000)*

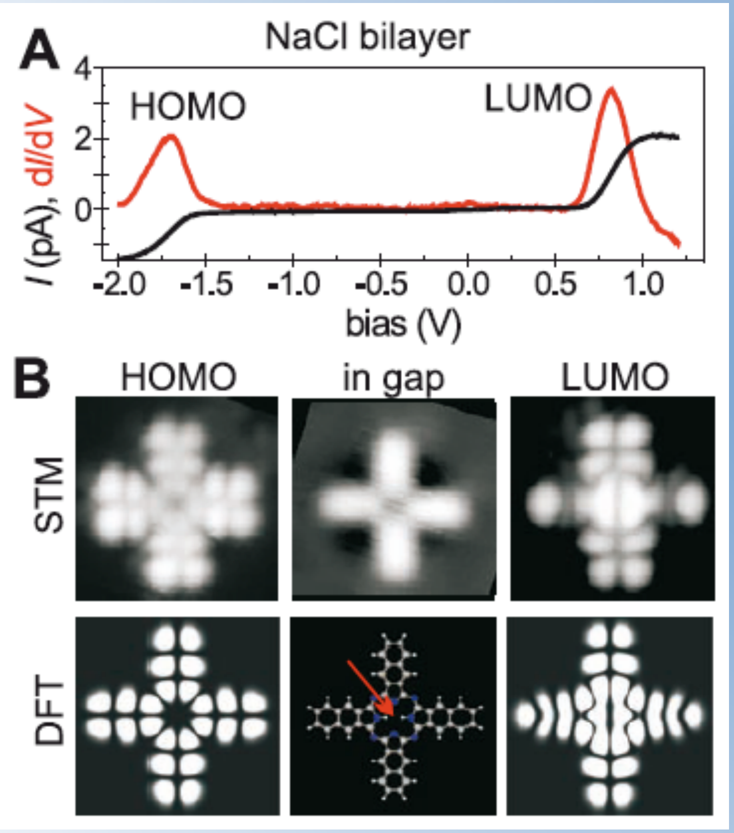
Hydrogenation of a Single Molecule



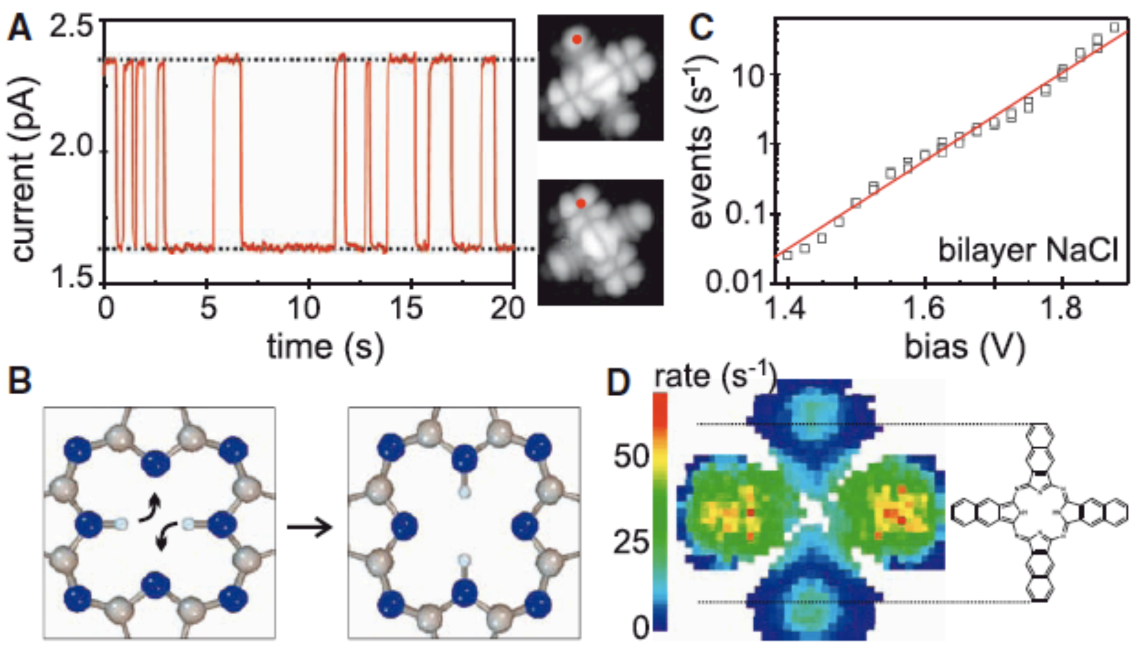
S. Katano, *et al. Science 316, 1883 (2007)*

Molecular imaging/switching by means of STM

imaging molecular states



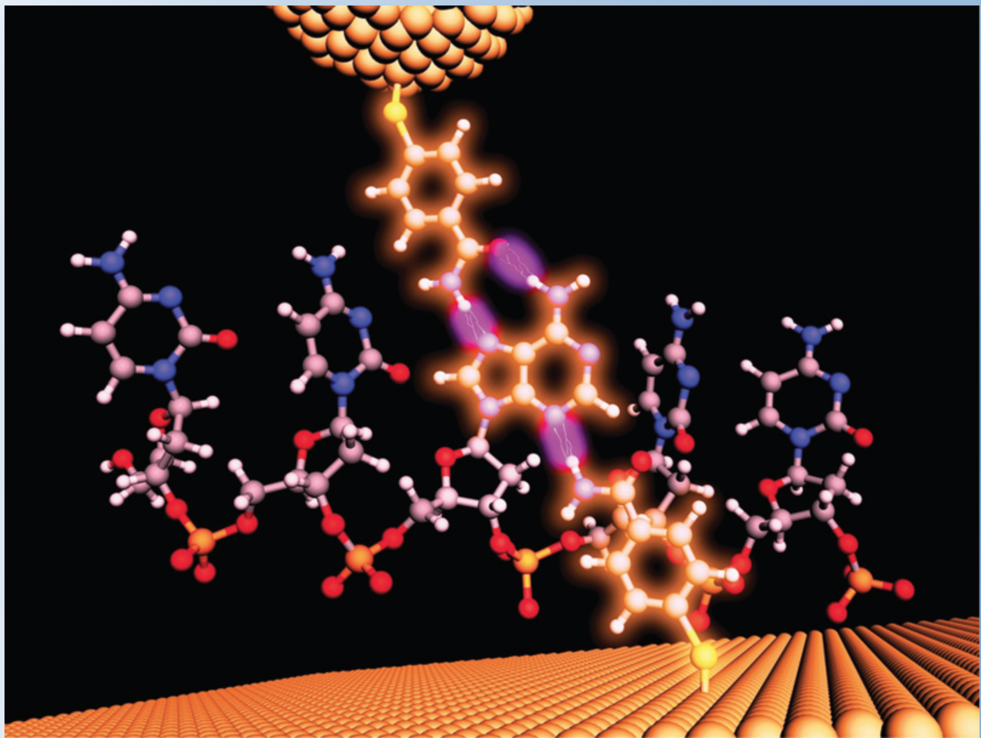
hydrogen switching by tunelling current

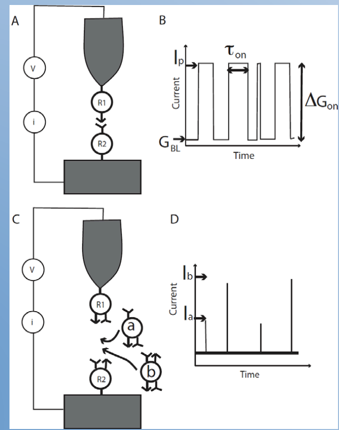


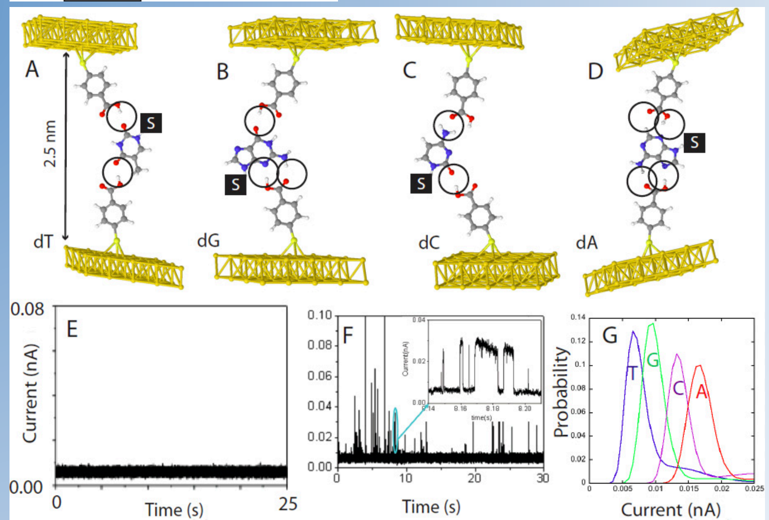
P. Liljeroth et al, Science ***317***, *1203 (2007)*

DNA sequencing using current

The tunneling current senses different DNA base pairs when functionalized tip used



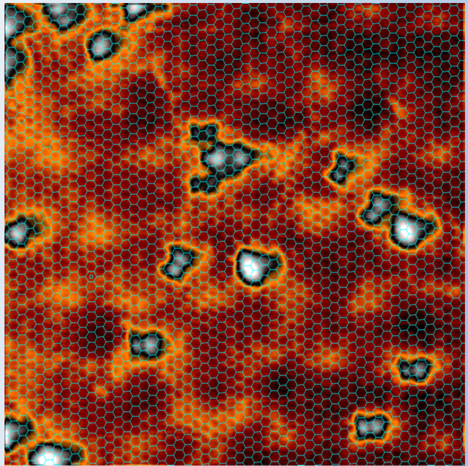


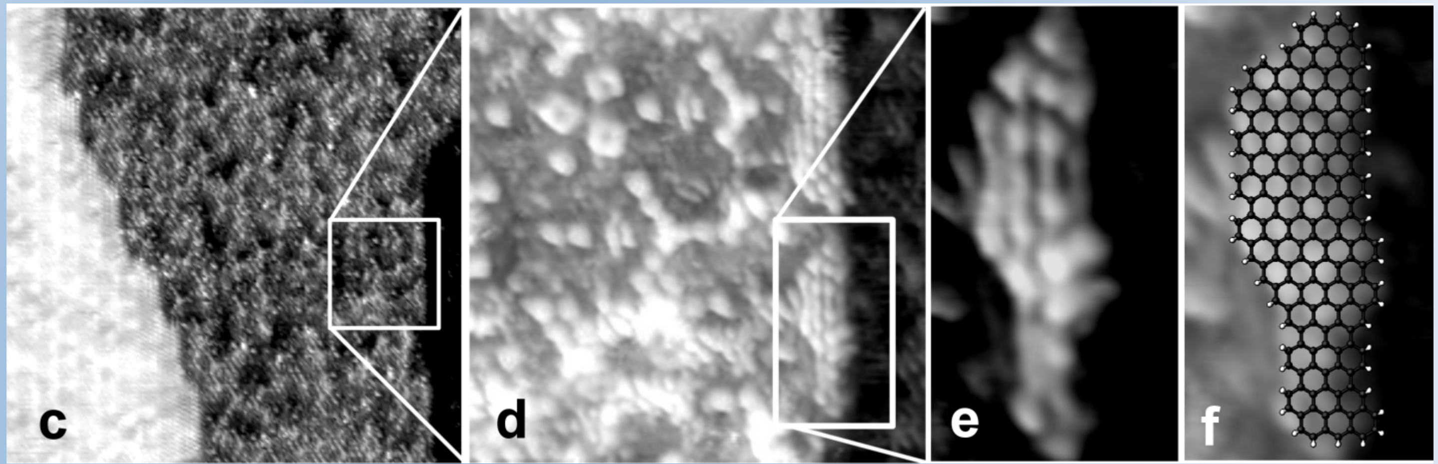


S. Lindsay, et al. Recognition tunneling. Nanotechnology 21, 262001 (2010).
S.Huang, et al, Nature Nanotechnology 2010, 5, 868-873 (2010).

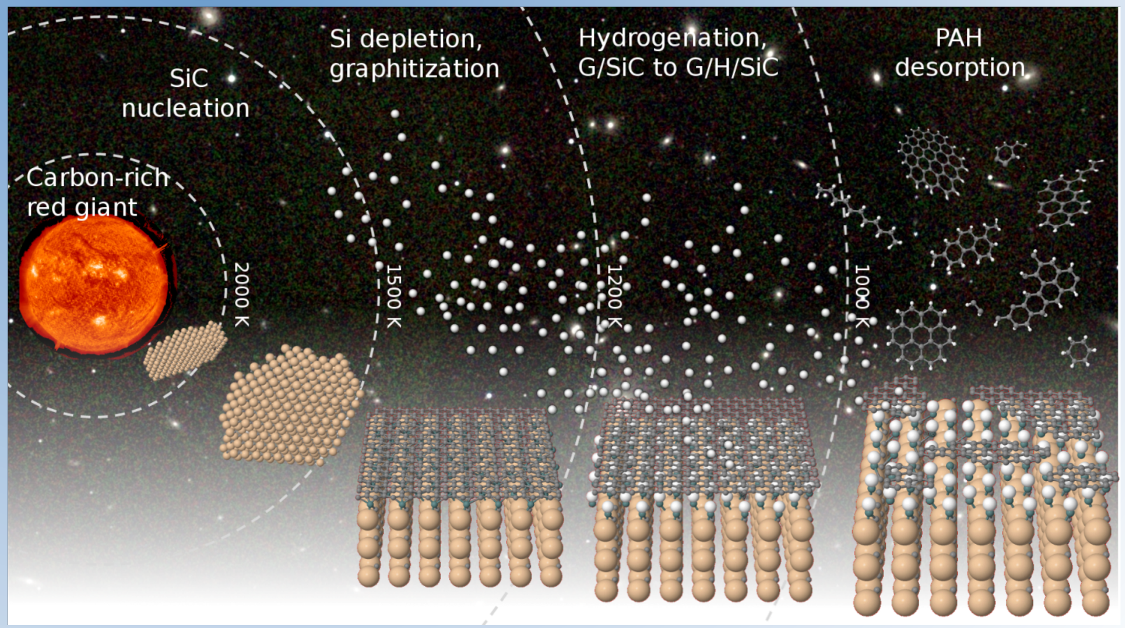
STM & Astronomy

PAHs and related species can be efficiently produced on the surface of SiC grains upon high-temperature exposure to atomic hydrogen in the interstellar medium.





- in circumstellar environments, SiC grains are covered by a graphene layer
- H-etching under UHV conditions disrupts graphene

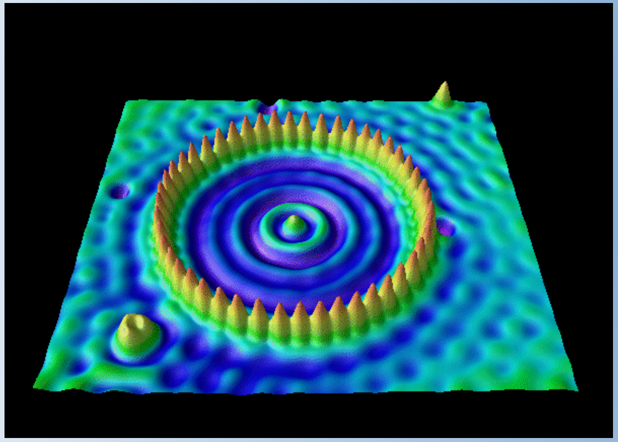


P. Merino et al (submitted)

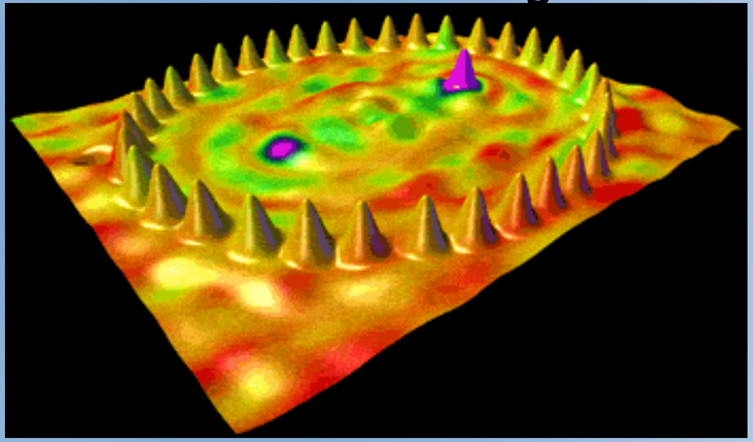
STM & Quantum phenomena

SPM is not only based on quantum phenomena but it also provides the direct access to nanoscale where quantum phenomena emerge.

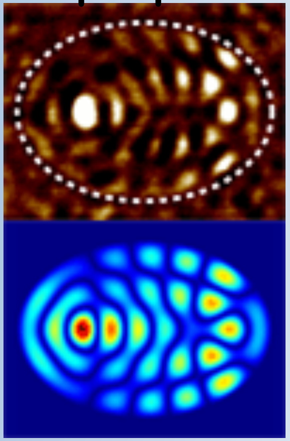
Quantum corrals



Quantum mirage



Quantum superposition



M. F. Crommie et al Nature 363, 524 (1993).
H. C. Manoharan et al Nature 403, 512 (2000).
Ch. Moon et al Nature Physics 4, 454 - 458 (2008)

Outline

- Introduction
- STM
- **AFM**
- What next?

AFM

- design & roadmap
- atomic scale images
- atomic manipulation

AFM

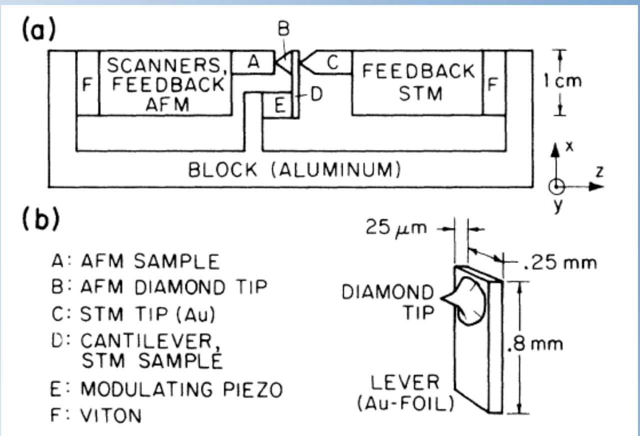
- design & roadmap
- atomic scale images
- atomic manipulation

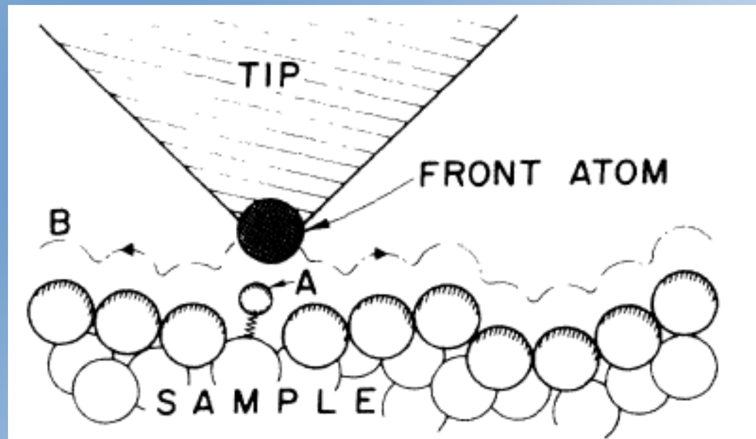
1986: birth of AFM

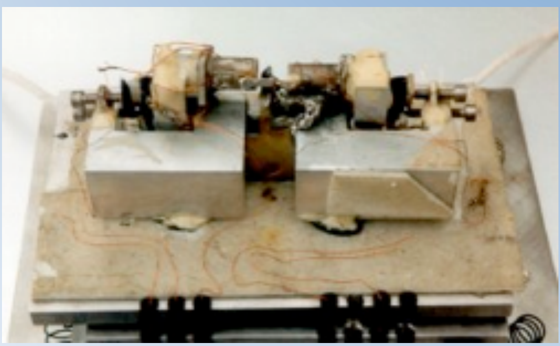
VOLUME 56, NUMBER 9 PHYSICAL REVIEW LETTERS 3 MARCH 1986

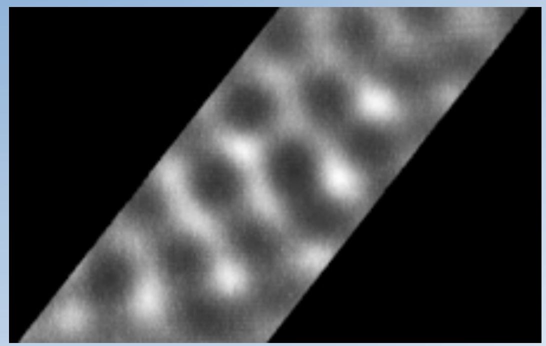
Atomic Force Microscope

G. Binnig[(a)] and C. F. Quate[(b)]
Edward L. Ginzton Laboratory, Stanford University, Stanford, California 94305
and
Ch. Gerber[(c)]
IBM San Jose Research Laboratory, San Jose, California 95193
(Received 5 December 1985)

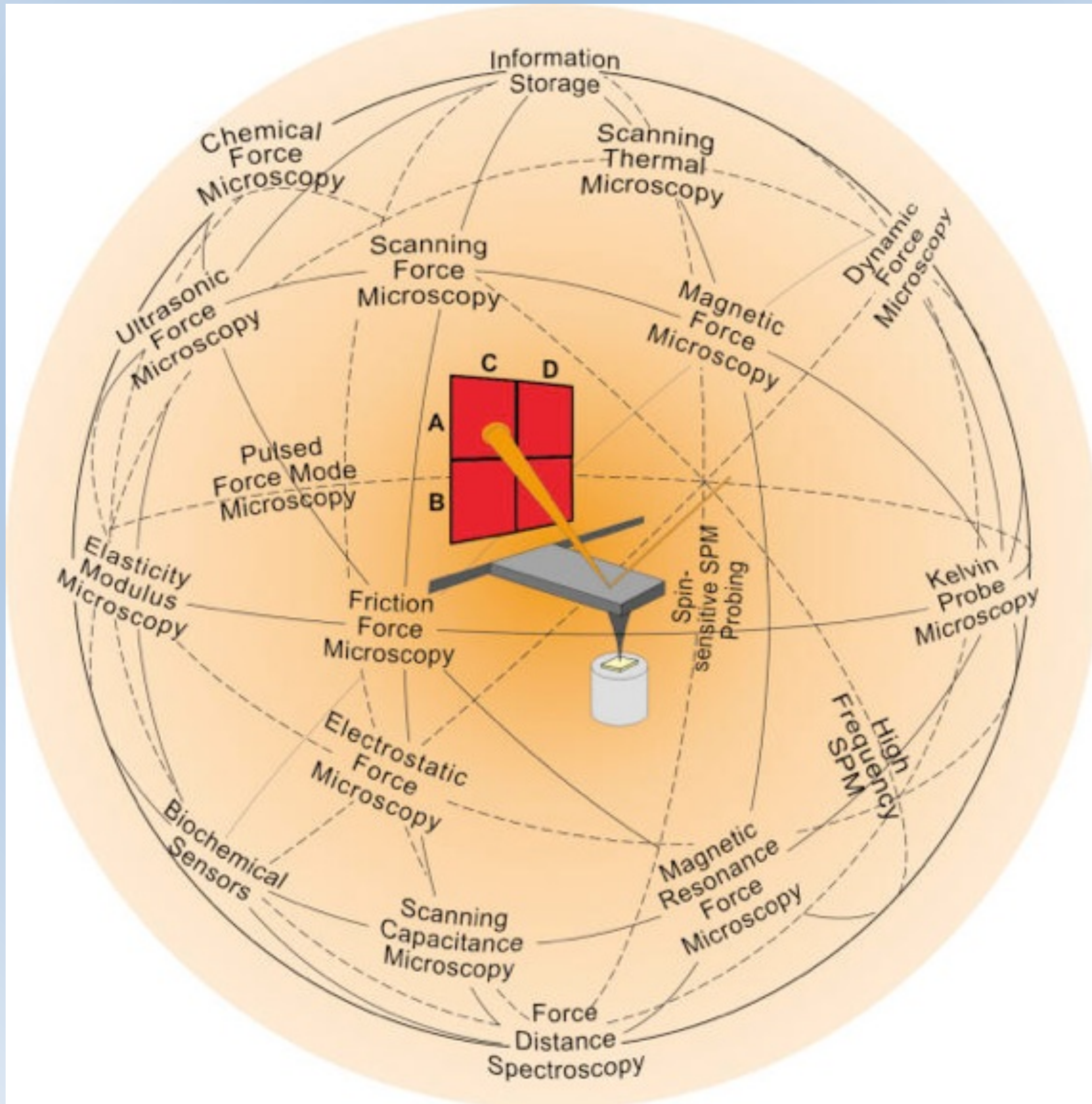








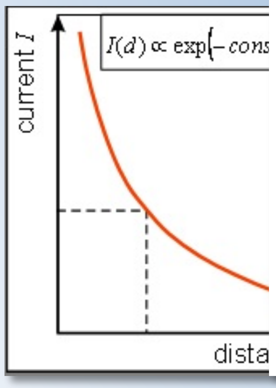
AFM World



Information Storage
Chemical Force Microscopy
Scanning Thermal Microscopy
Scanning Force Microscopy
Dynamic Force Microscopy
Ultrasonic Force Microscopy
Magnetic Force Microscopy
C
D
A
B
Pulsed Force Mode Microscopy
Elasticity Modulus Microscopy
Spin-sensitive SPM Probing
Friction Force Microscopy
Kelvin Probe Microscopy
Electrostatic Force Microscopy
High Frequency SPM
Biochemical Sensors
Magnetic Resonance Force Microscopy
Scanning Capacitance Microscopy
Force Distance Spectroscopy

Main obstacles of dAFM

- jump-to-contact instabili
  - interplay between A,
- large b
  - attr
- large si
  - wea
    wea
- non-mo
  - more

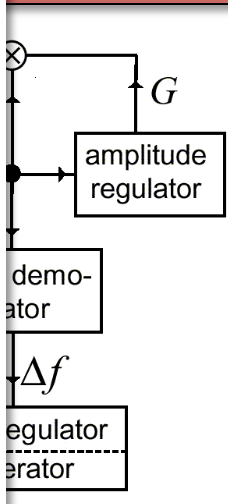


Experimental parameters

- The spring constant of the cantilever k
- r f_o
- Q
- r ϕ
- mple V_t

TABLE I. Operating parameters of various FM-AFM experiments: *, early experiments with nearly atomic resolution, experiments with standard parameters (classic NC-AFM) on semiconductors, metals, and insulators; **, small-amplitude experiments; ***, internal cantilever damping calculated from $\Delta E = 2\pi E/Q$. When Q is not quoted in the original publication, a Q value of 50 000 is used as an estimate.

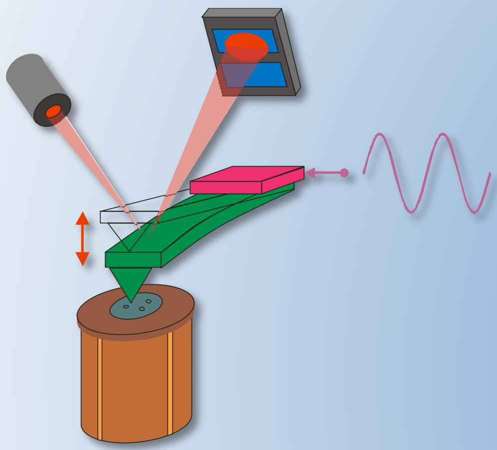
Year	k N/m	f_0 kHz	Δf Hz	A nm	γ fN$\sqrt{m}$	kA nN	E keV	ΔE_{CL} eV***	Sample	Ref.
1994*	2.5	60.0	−16	15.0	−1.26	37.5	1.8	0.06	KCl(001)	Giessibl and Trafas (1994)
1994*	2.5	60.0	−32	3.3	−0.29	8.25	0.1	0.4	Si(111)	Giessibl (1994)
1995	17.0	114.0	−70	34.0	−66.3	544	61	14	Si(111)	Giessibl (1995)
1995	43.0	276.0	−60	40.0	−75.6	1720	215	27	Si(111)	Kitamura and Iwatsuki (1995)
1995	34.0	151.0	−6	20.0	−3.91	680	42	5	InP(110)	Sugawara *et al.* (1995)
1996	23.5	153.0	−70	19.0	−28.8	447	27	3.3	Si(111)	Lüthi *et al.* (1996)
1996	33.0	264.0	−670	4.0	−23.6	132	12	1.45	Si(001)	Kitamura and Iwatsuki (1996)
1996	10.0	290.0	−95	10.0	−3.42	100	3.1	0.4	Si(111)	Güthner (1996)
1997	30.0	168.0	−80	13.0	−21.9	390	16	2	NaCl(001)	Bammerlin *et al.* (1997)
1997	28.0	270.0	−80	15.0	−15.7	420	20	2.5	TiO_2(110)	Fukui *et al.* (1997)
1997	41.0	172.0	−10	16.0	−4.96	654	33	4	Si(111)	Sugawara *et al.* (1997)
1999	35.0	160.0	−63	8.8	−10.1	338	10	1.4	HOPG(0001)	Allers *et al.* (1999a)
1999	36.0	160.0	−60.5	12.7	−18.1	457	18	2.3	InAs(110)	Schwarz *et al.* (1999)
1999	36.0	160.0	−92	9.4	−19.8	338	10	1.2	Xe(111)	Allers *et al.* (1999b)
1999	27.4	152.3	−10	11.4	−2.2	312	11	1.4	Ag(111)	Minobe *et al.* (1999)
2000	28.6	155.7	−31	5.0	−4.1	143	2.2	0.04	Si(111)	Lantz *et al.* (2000)
2000	30.0	168.0	−70	6.5	−6.6	195	4.0	0.5	Cu(111)	Loppacher *et al.* (2000)
2001	3.0	75.0	−56	76	−46.9	228	54.1	7	Al_2O_3(0001)	Barth and Reichling (2001)
2002	24.0	164.7	−8	12.0	−1.5	288	2.2	1.4	$KCl_{0.6}Br_{0.4}$	Bennewitz, Pfeiffer, *et al.* (2002)
2002	46.0	298.0	−20	2.8	−0.46	129	1.1	0.13	Si(111)	Eguchi and Hasegawa (2002)
2000**	1800	16.86	−160	0.8	−387	1440	3.6	11	Si(111)	Giessibl *et al.* (2000)
2001**	1800	20.53	85	0.25	+29.5	450	0.4	1	Si(111)	Giessibl, Bielefeldt, *et al.* (2001)

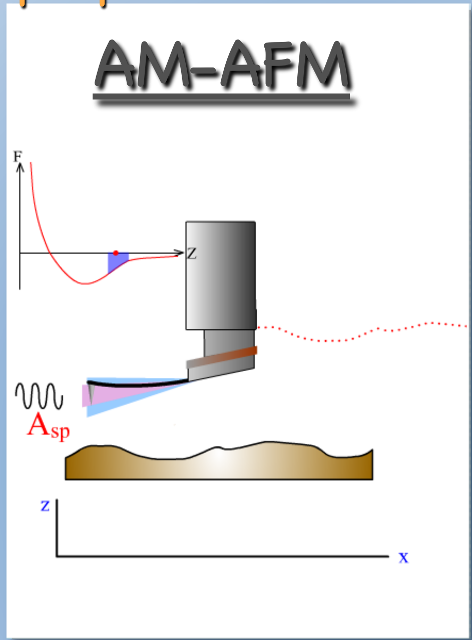


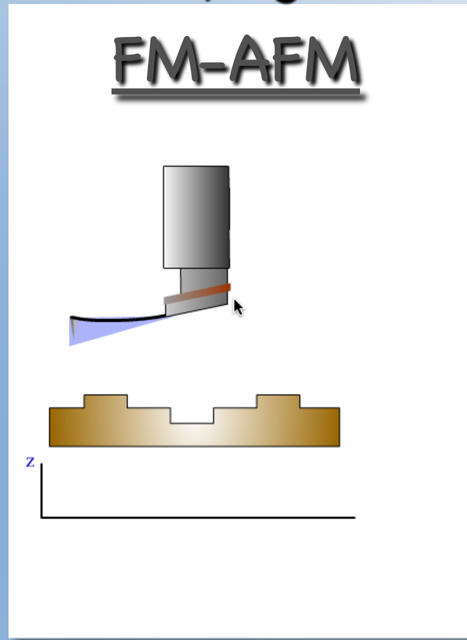
dAFM includes more complicated control unit than STM

dynamic Atomic Force Microscope

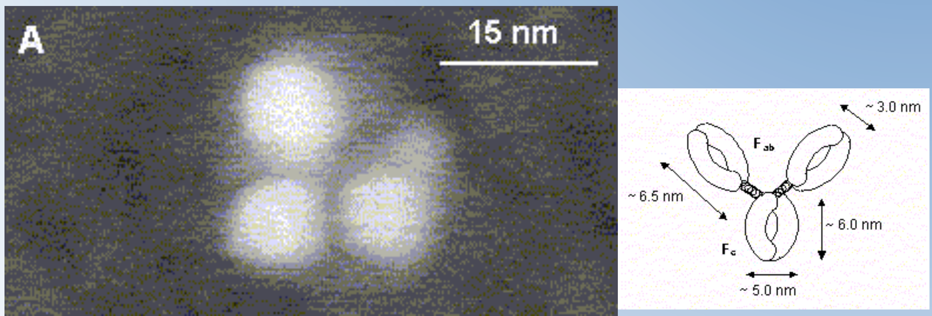
dAFM measures the interaction between the tip and the sample by means of the dynamic properties of the cantilever carrying the tip



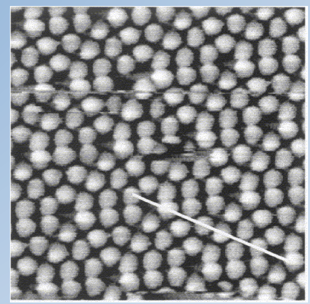




- obtain molecular resolution images of biological samples in ambient conditions.



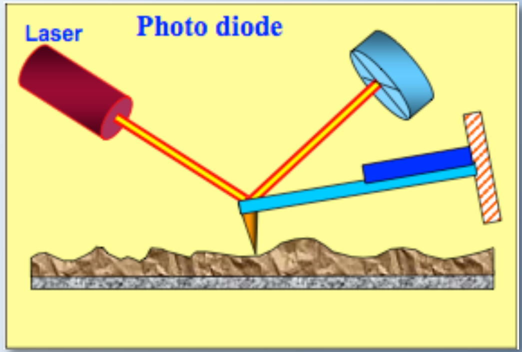
- atomic scale resolution in UHV

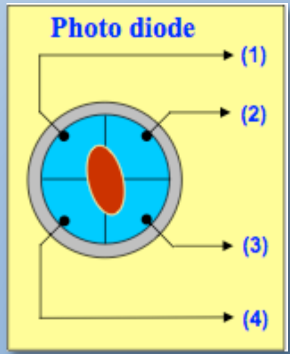


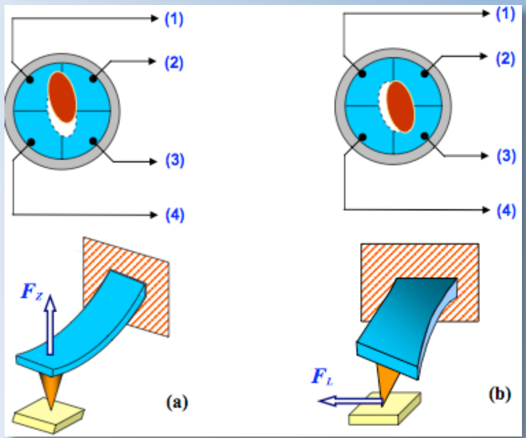
R. García and R. Perez Surf. Sci. Rep. 47, 197 (2002); F.J. Giessibl Rev. Mod. Phys. 75, 958 (2003).

dAFM: signal detection

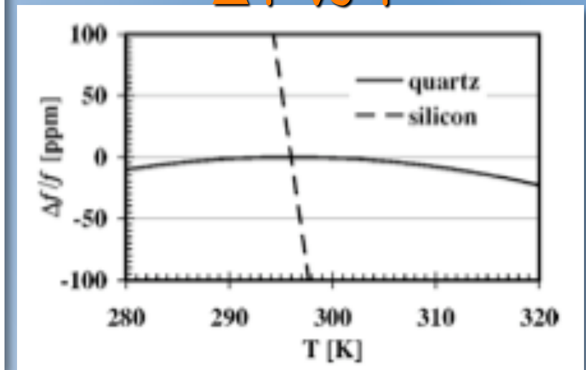
Photo diode





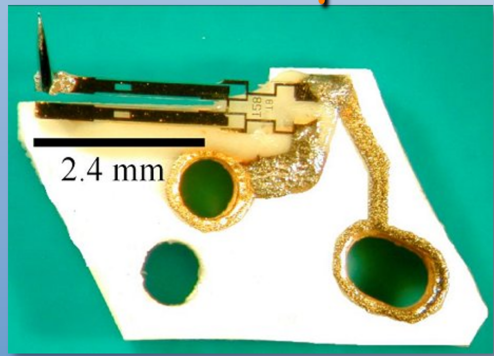


Δf vs T



- ❑ movement of cantilever sensed by laser beam deflection
- ❑ silicon-based tip: chemically active
- ❑ many variants for parameter (k,f_o,A etc.)

qPlus sensor

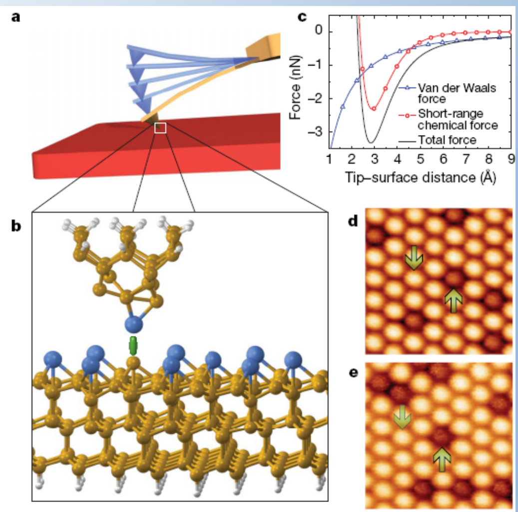


F. J. Giessibl Appl. Phys. Lett. 76, 1470 (2000)

- ❑ oscillation source: quartz tuning fork from watches
- ❑ conductive tip: both current and frequency shift
- ❑ small amplitude 0.1-10Å; sensible enough to detect the tunneling current
- ❑ high spring constant; reduced configuration space of parameters

Forces in AFM

Total force is composed by several both long-range and short-range components



Total force $F_{ts} = F_{el} + F_{vdW} + F_{chem}$

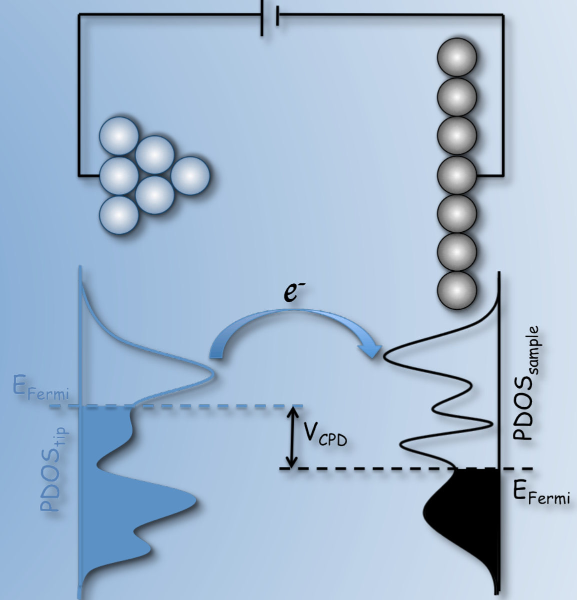
a) van der Waals forces

$$F_{vdW} = -\frac{A_H R}{6z^2}$$

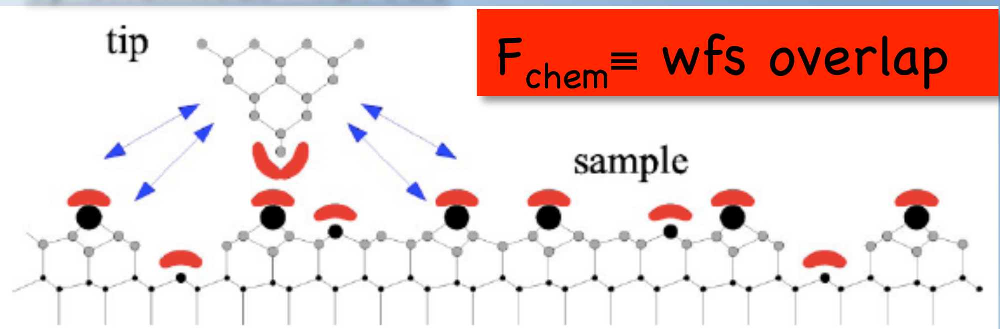
(sphere-plane geometry)

b) electrostatic forces

$$F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}(V - V_{CPD})^2$$



c) chemical forces



F_{chem} ≡ wfs overlap

Origin of atomic contrast in AFM

	Force (nN)	Gradient (N/m)
Microscopic VdW	−0.02	0.15
Spherical (R = 40 Å) VdW	−0.50	2
Tip without DB	−0.07	2
Tip with DB	−0.39	10–12

F_{chem} ≡ Short range chemical interaction: attractive (bonding) or repulsive (Pauli) depending on the distance ⇒ Quantum Mechanical calculation

AFM Roadmap

Invention of STM

G. Binnig et al PRL 49, 57 (1982)

Concept of FM-AFM introduced

T.R. Albrecht J.Appl. Phys. 69, 668 (1991)

1982 1986 1991 1995

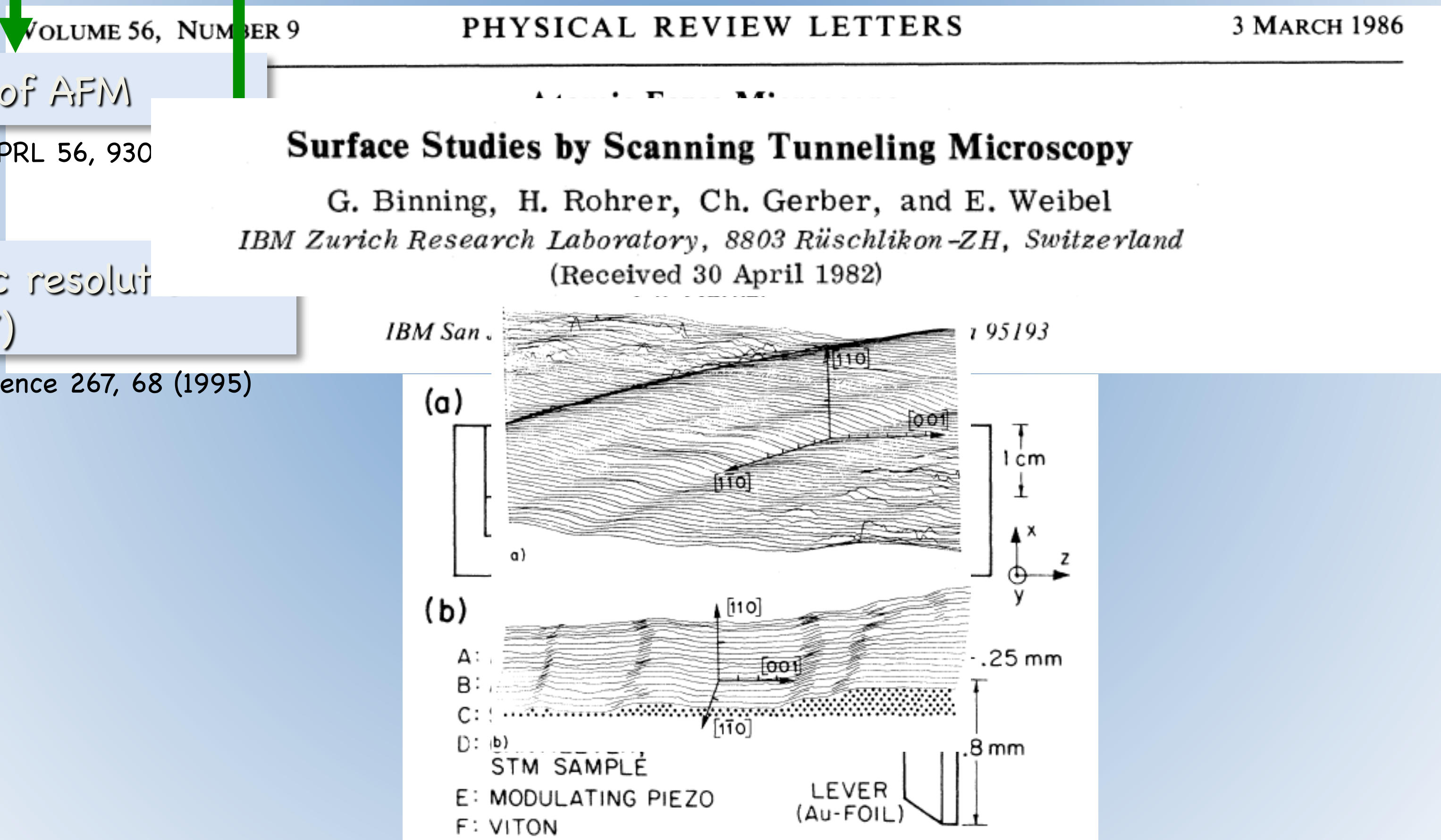
Years

Invention of AFM

G. Binnig et al PRL 56, 930

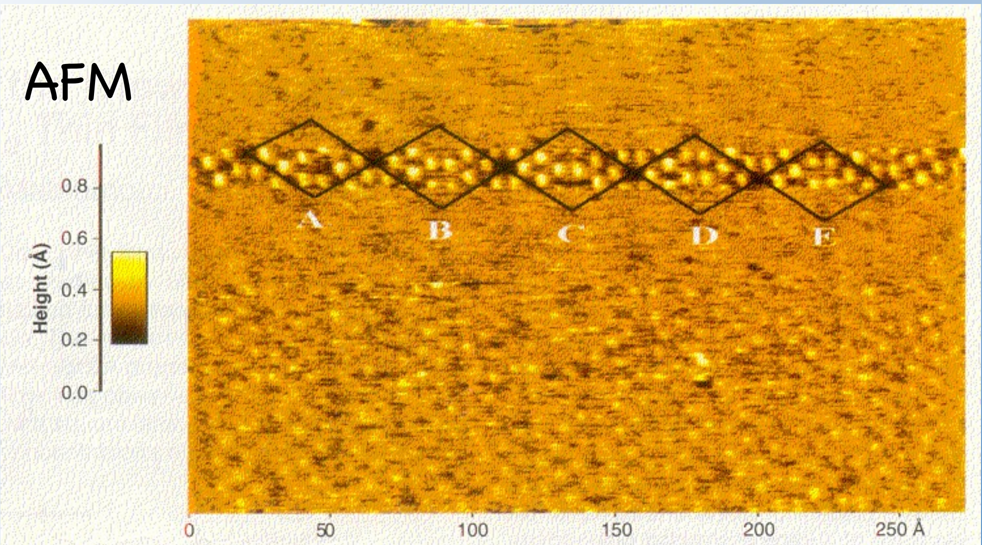
True atomic resolut Si(111)-(7x7)

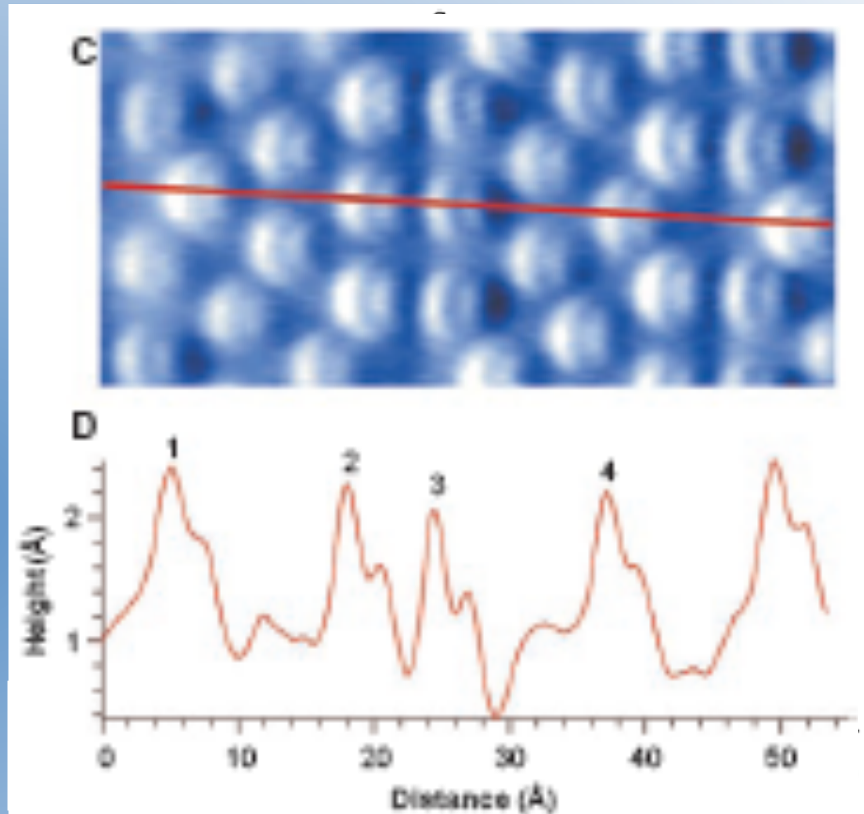
F.J. Giessibl Science 267, 68 (1995)



Atomic resolution in FM-AFM:Si(111)-7x7

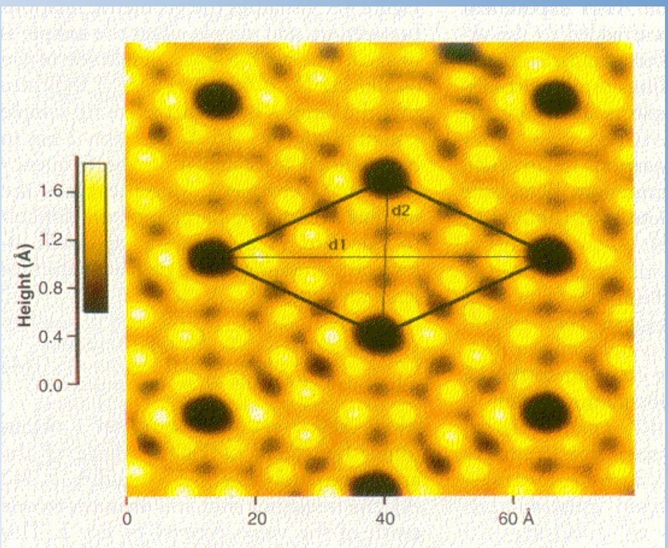
F.J. Giessibl, Science 267, 68 (1995)





faulted half untaulted half

STM



12 adatoms

6 rest atoms

corner hole

dimers

AFM Roadmap

1982 1986 1991 1995 1999 2001 Years

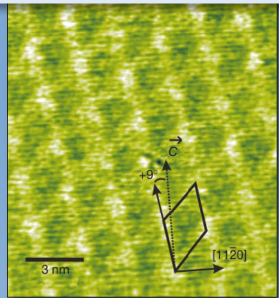
Invention of STM
G. Binnig et al PRL 49, 57 (1982)

Concept of FM-AFM introduced
T.R. Albrecht J.Appl. Phys. 69, 668 (1991)

Invention of AFM
G. Binnig et al PRL 56, 930 (1986

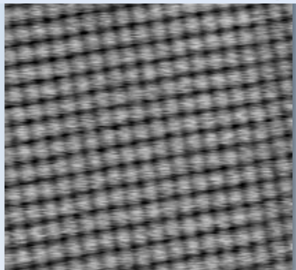
True atomic resolution Si(111)-(7x7)
F.J. Giessibl Science 267, 68 (1995)

Atomic resolution of insulator (Al_2O_3)



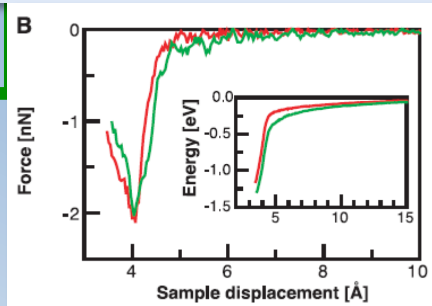
C. Barth et al, Nature 414, 54 (2001)

Atomic resolution on metal surface Cu(111)



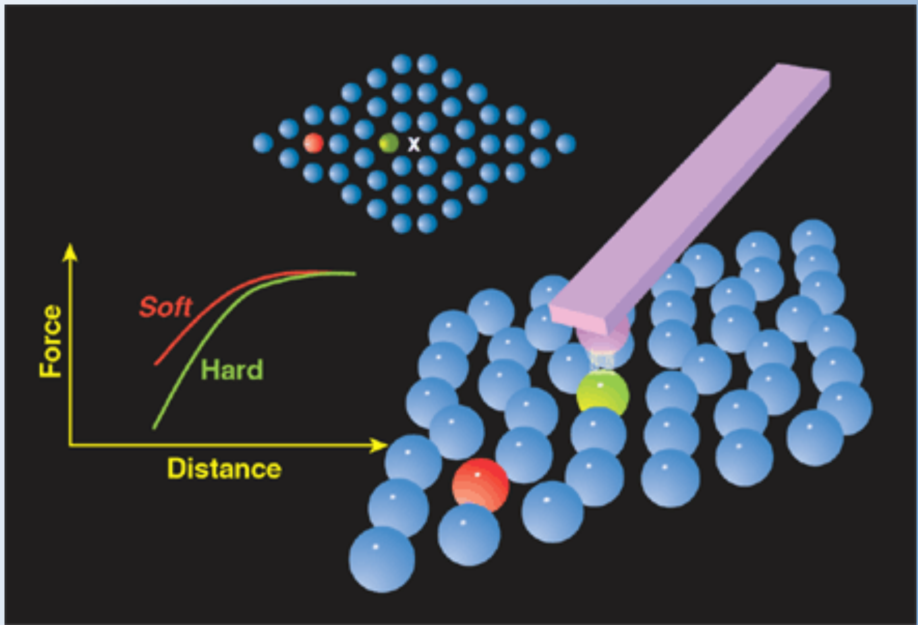
C. Loppacher et al, ASS 140, 287 (1999).

Force Site Spectroscopy



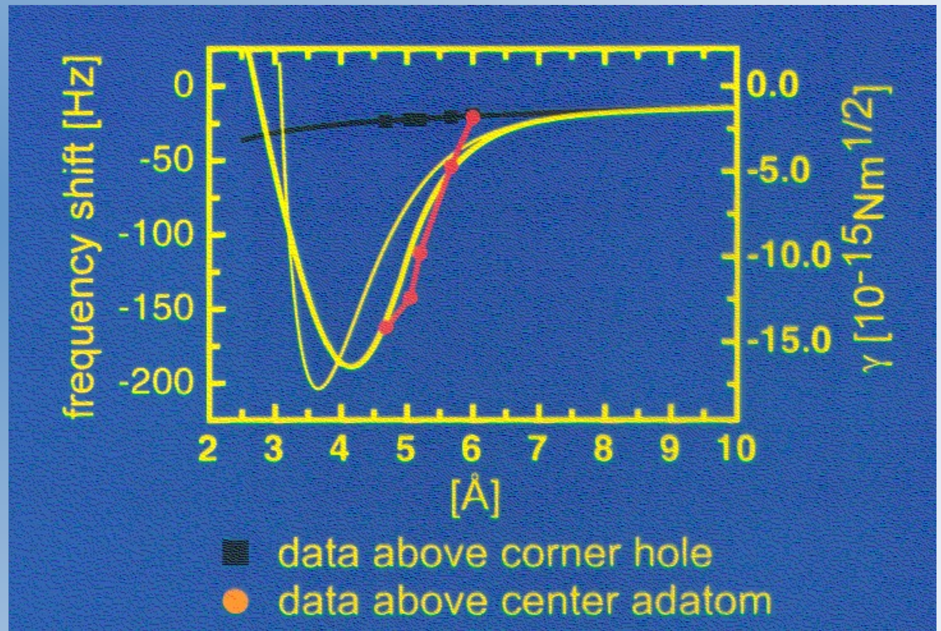
M.A. Lantz et al, Science 291, 2580 (2001)

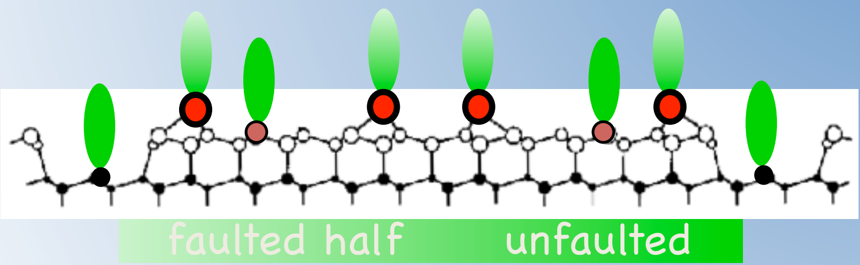
Force Site Spectroscopy: experiment & theory



M. Lantz et al, PRL 84, 2642 (2000)

M. Lantz et al, Science 291, 2580 (2001)

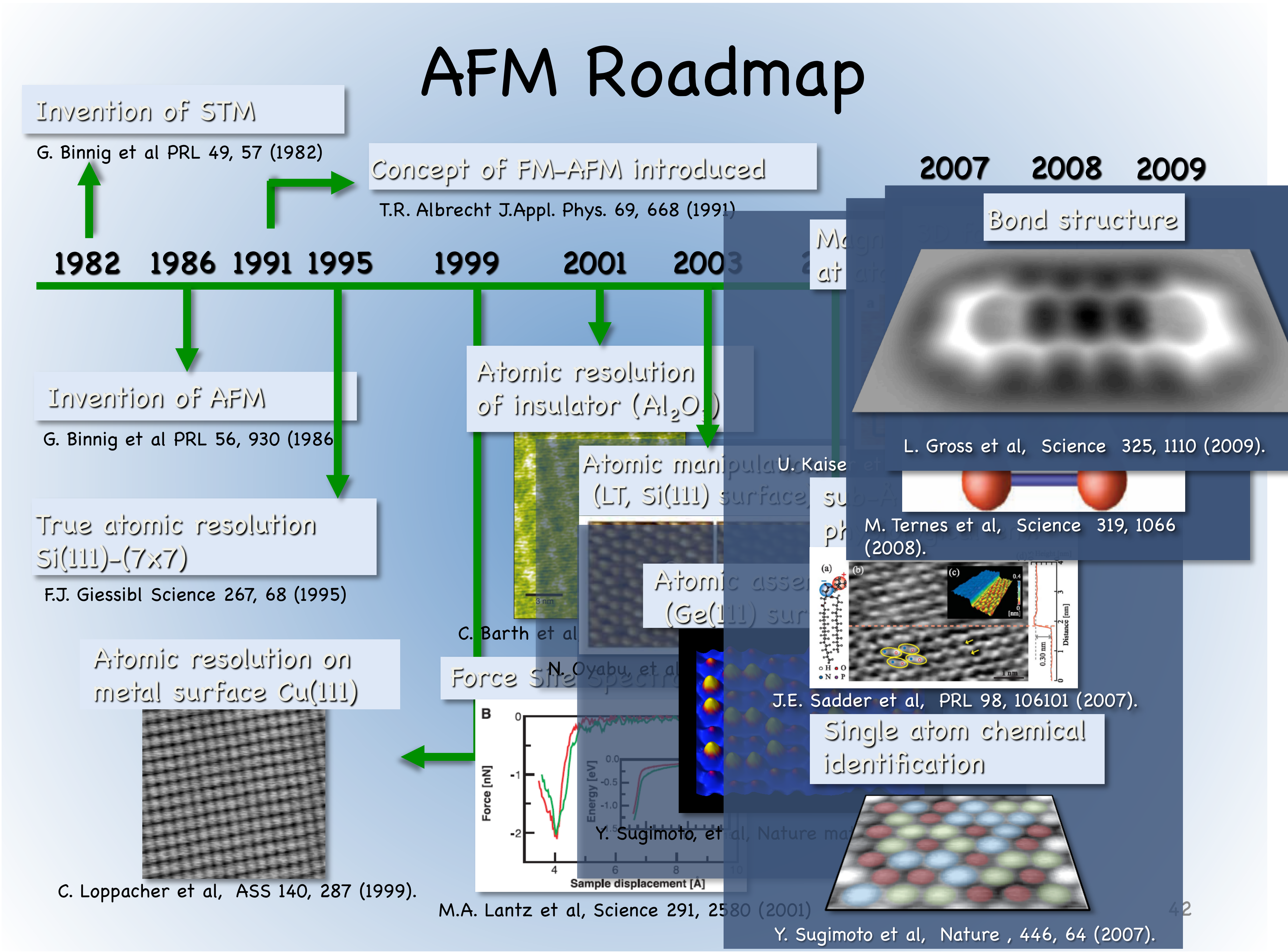




Separation of VdW and chemical interaction: substracting the corner hole contribution.

Tip-surface interactions

R. Pérez et al , PRL 78, 678 (1997)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1986
1991
1995
1999
2001
2003
2007
2008
2009
Bond structure
L. Gross et al, Science 325, 1110 (2009).
Invention of AFM
G. Binnig et al PRL 56, 930 (1986
Atomic resolution
of insulator (Al2O3)
True atomic resolution
Si(111)-(7x7)
F.J. Giessibl Science 267, 68 (1995)
Atomic manipulation
(LT, Si(111) surface)
M. Ternes et al, Science 319, 1066 (2008).
C. Barth et al
Atomic resolution on
metal surface Cu(111)
C. Loppacher et al, ASS 140, 287 (1999).
Force
Force [nN]
Energy [eV]
Sample displacement [Å]
M.A. Lantz et al, Science 291, 2580 (2001)
J.E. Sadder et al, PRL 98, 106101 (2007).
Single atom chemical
identification
Y. Sugimoto et al, Nature , 446, 64 (2007).
42

Status of dAFM

- true atomic resolution of arbitrary surface & in liquids
- 3D measurements of atomic forces
- force and energy dissipation control at atomic scale
- measurements of mechanical response (tribology)
- mechanical manipulation of individual atoms
- mechanical assembly atom by atom
- chemical & spin atomic scale resolution

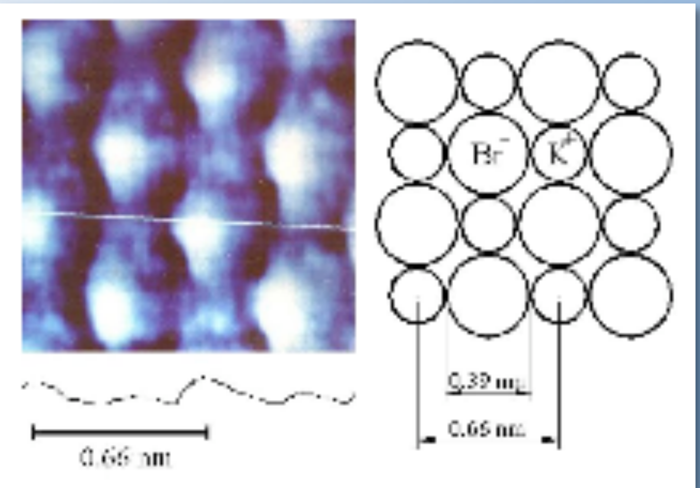
AFM

- design & roadmap
- atomic scale images
- atomic manipulation

Imaging contrast at surfaces

Ionic surface

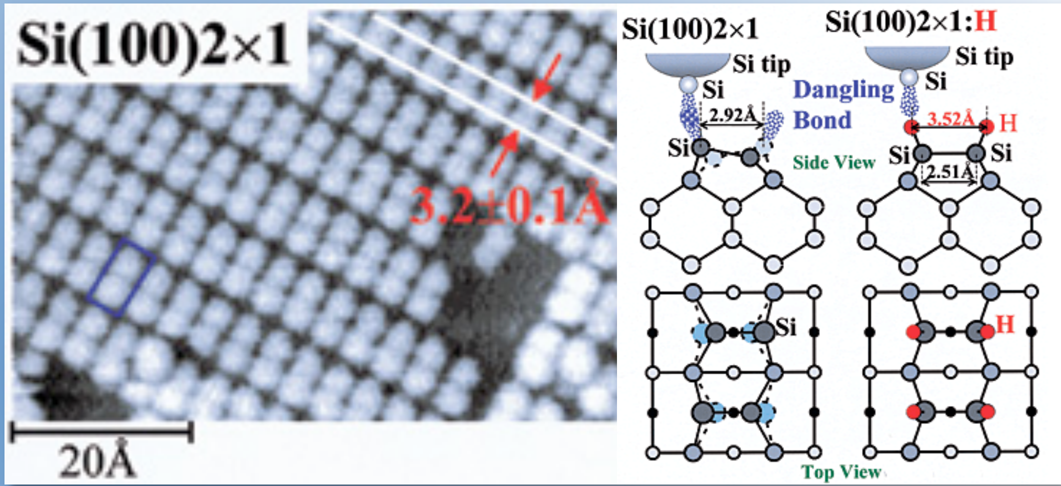
KBr(001)



- tip dependent contrast frequently changed
- image contrast: long-range coulombic interaction between charged atoms & the chemical interaction
- point charge approx. questionable: we need charge distribution from quantum mechanical treatment

Semiconductor surface

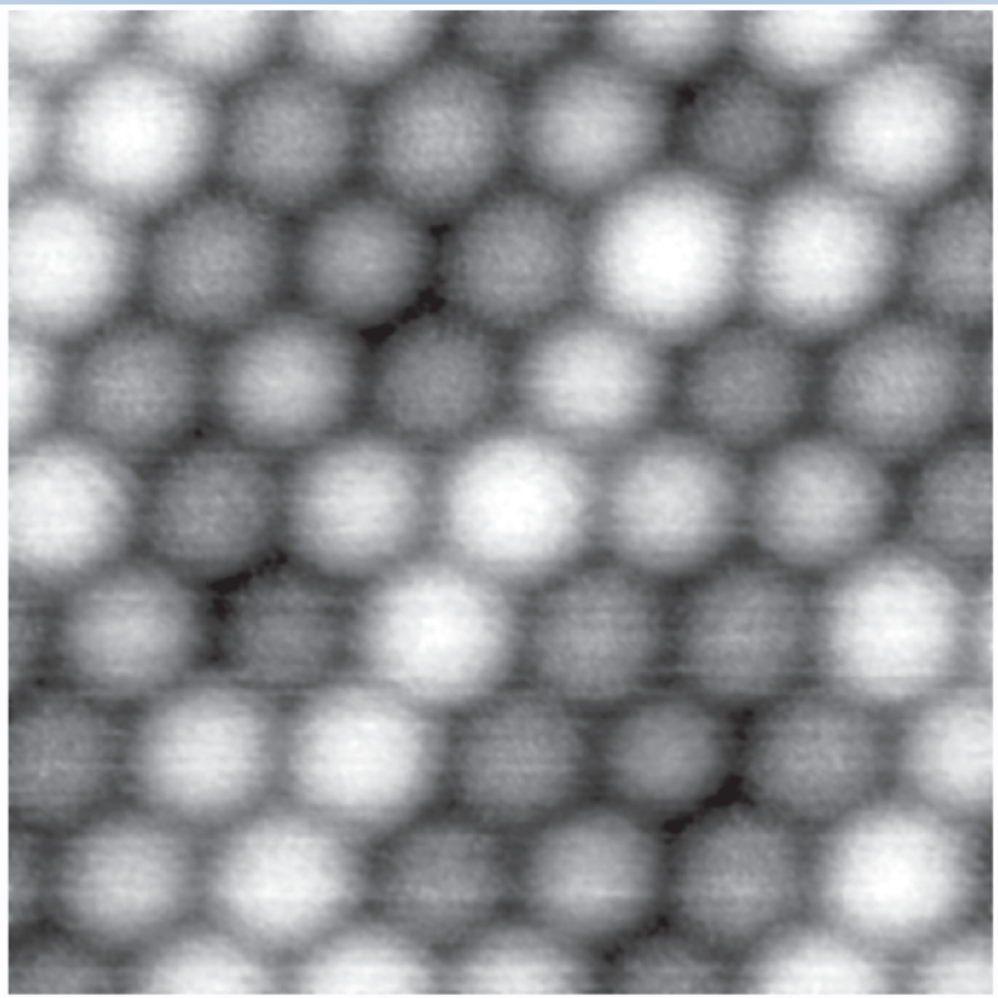
Si(100)-2x1



- less tip dependent contrast
- image contrast: short range chemical interaction between apex and surface atom
- quantum mechanics has to be used to image modeling

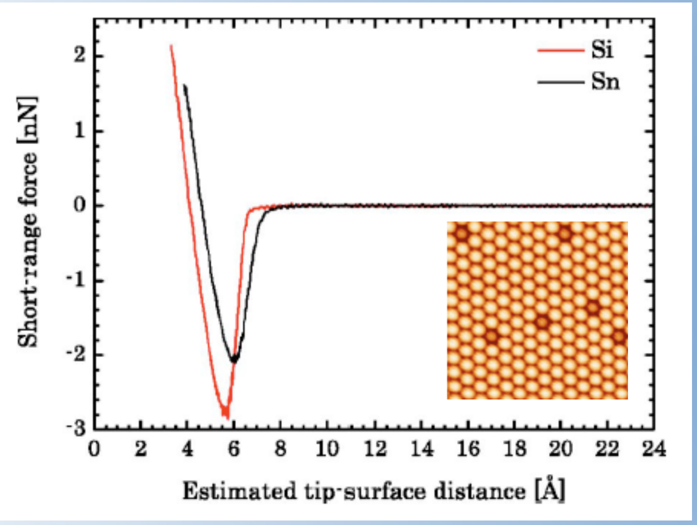
*R. Bechstein et al Nanotechnology **20**, 505703 (2009).*

Who is there?



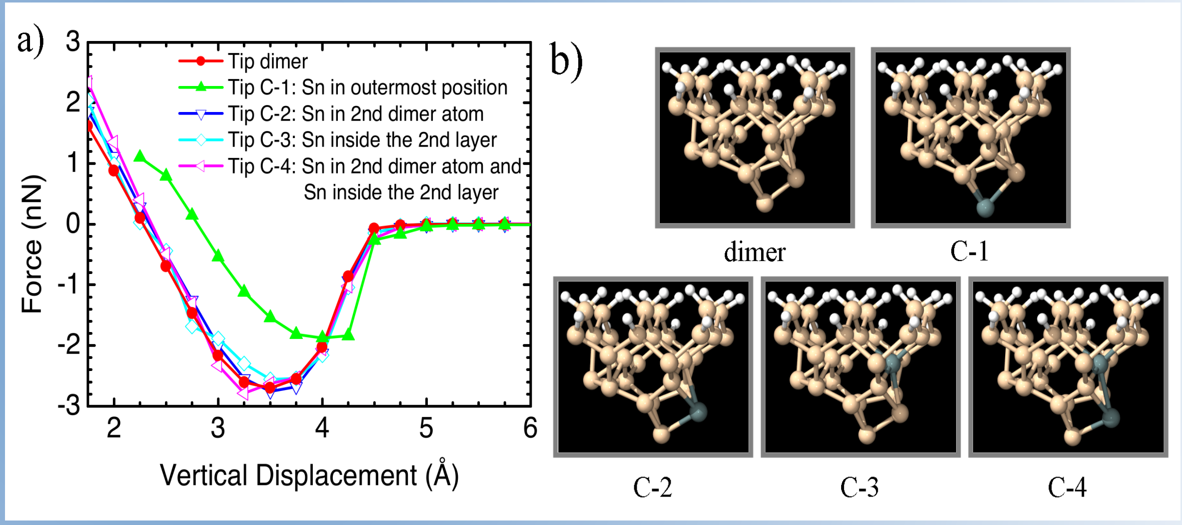
F-z spectroscopy: the chemical force

Force site spectroscopy Sn/Si(111)



Y. Sugimoto et al Phys. Rev. B 73 205329 (2006)

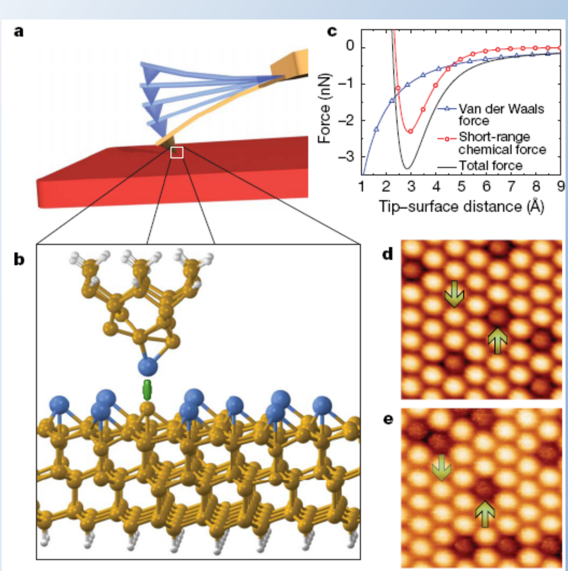
DFT calculations on Si adatom

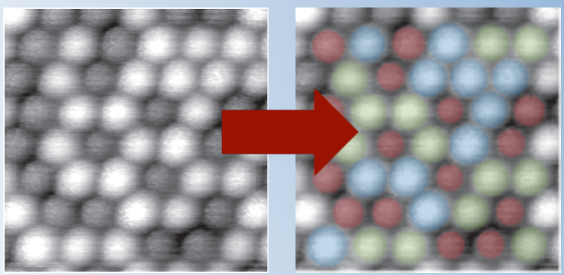


P. Pou et al Nanotechnology 20 264015 (2009)

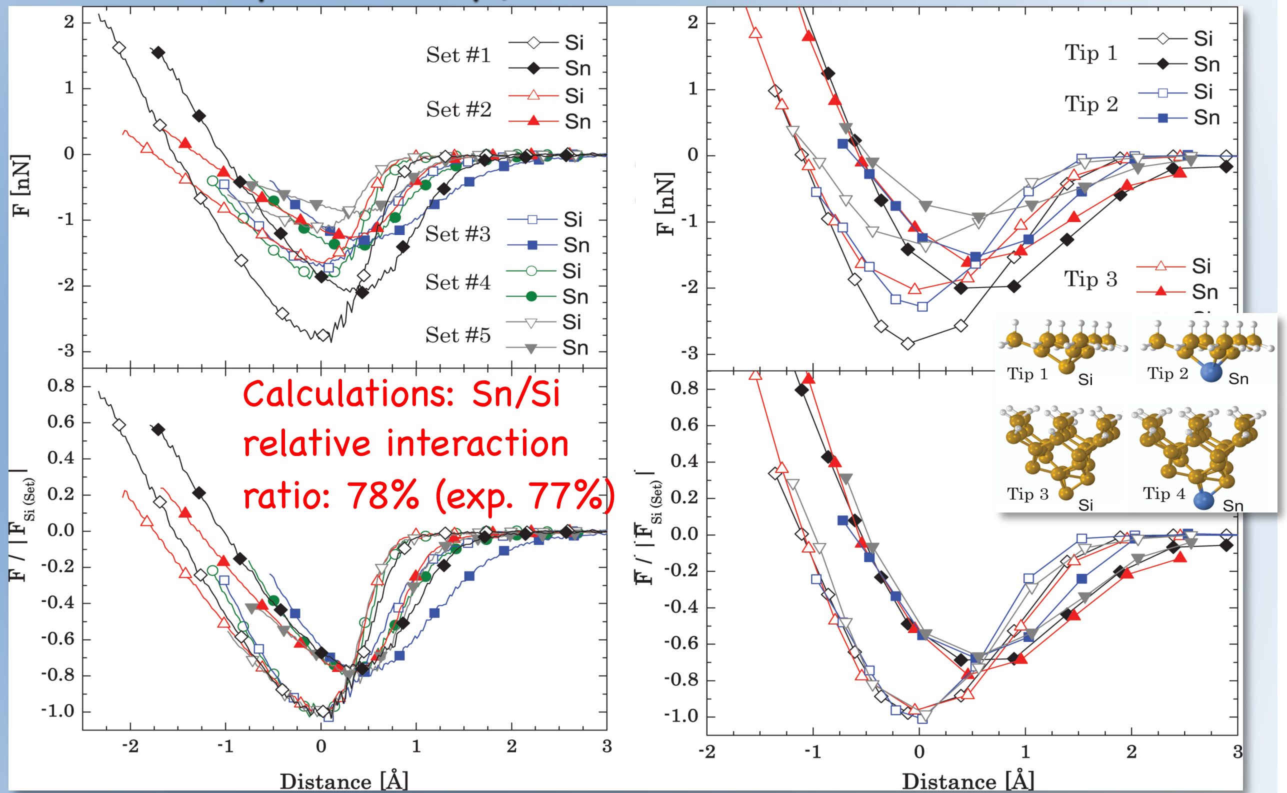
- tip-sample interaction mainly determined by apex and surface atoms
- isovalent impurities do not affect the mechanical response of AFM probe

Force and the chemical identification





Force spectroscopy PbSn/Si(111)



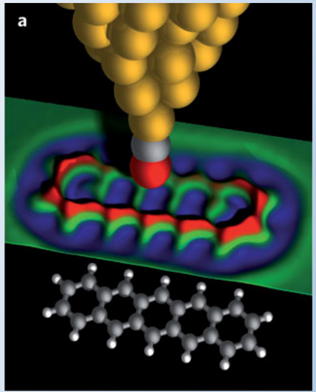
	Surface atom				Surface atom		
Tip B	Si	Sn	Pb	Tip A	Si	Sn	Pb
Si	100%	82%	67%	Si	100%	78%	62%
Sn	100%	84%	68%	Sn	100%	79%	59%
Pb	100%	82%	64%	Pb	100%	71%	54%

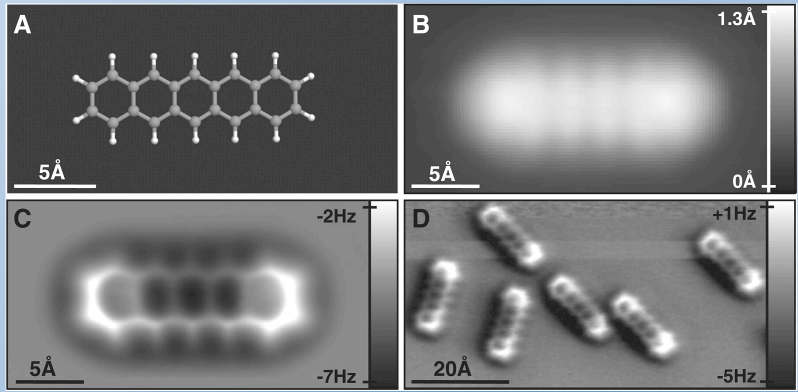
- the chemical sensitivity via the short-range force

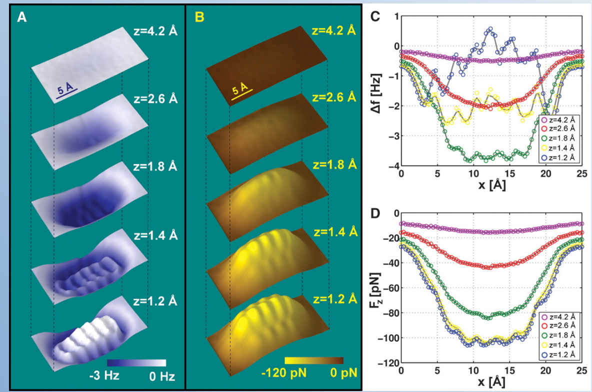
Y. Sugimoto et al, Nature 446, 64 (2007)
M. Setvin et al ACS Nano 6, 6969 (2012)

Molecular identification

High resolution images of molecules by means of nc-AFM

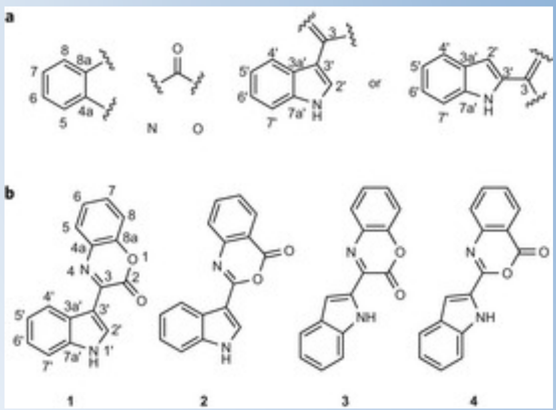


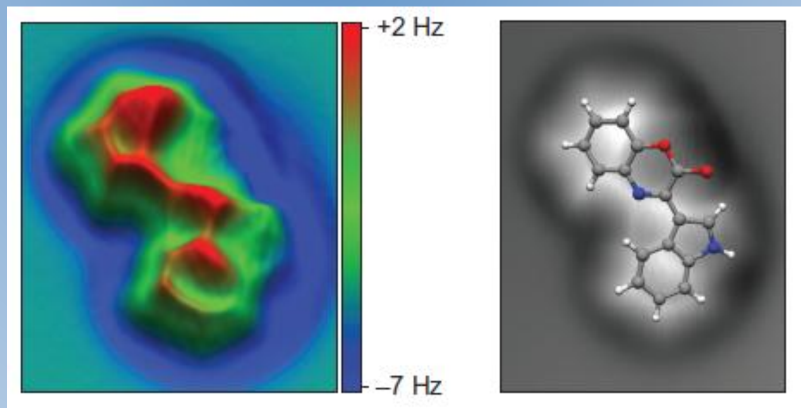




L. Gross, et al , Science 325, 1110-1114 (2009).

Organic structure determination using atomic-resolution scanning probe microscopy.



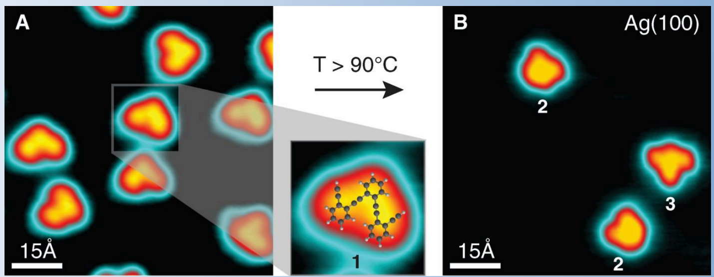


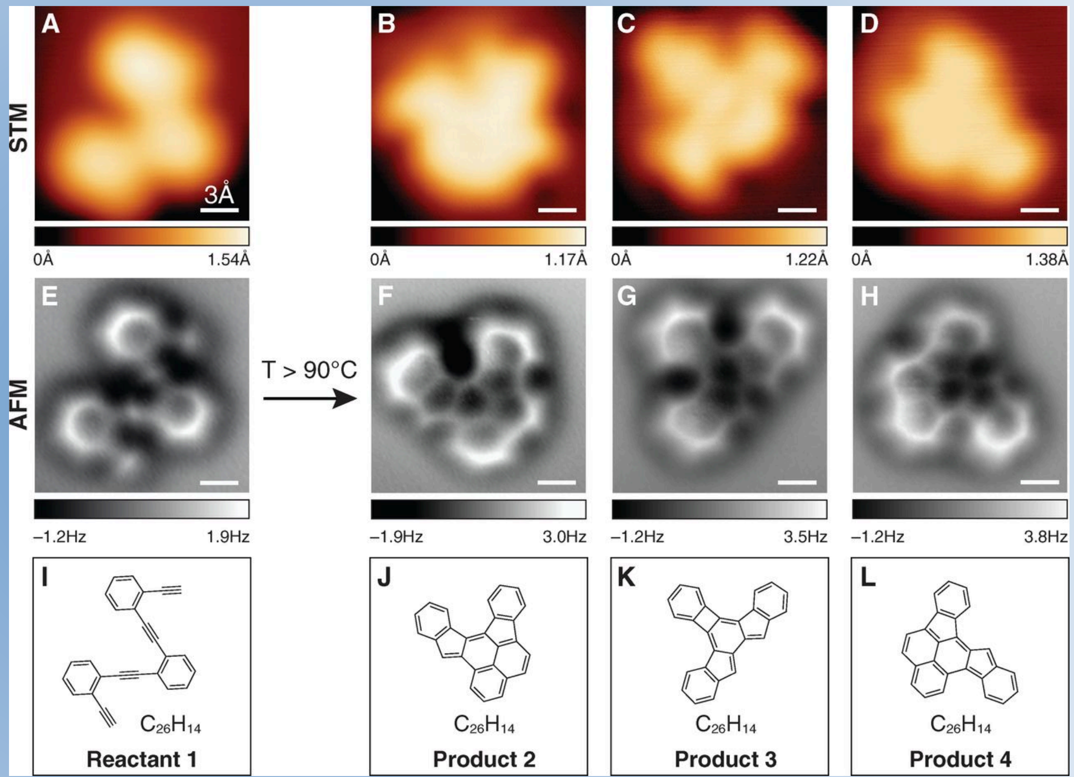
NMR and mass spectrometry do not succeed in the unambiguous determination of the chemical structure of unknown compounds.

L. Gross, et al , Nature chemistry 2 (10), 821-5 (2010).

Tracking chemical reactions

Direct Imaging of Covalent Bond Structure in Single-Molecule Chemical Reactions

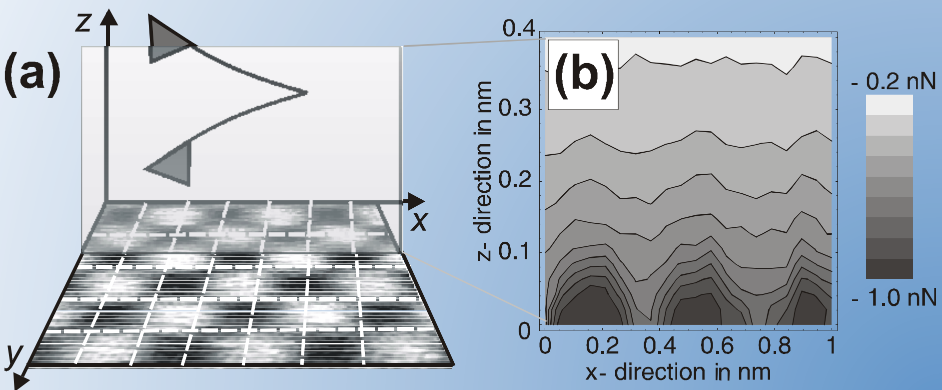




D.G. de Oteyza et al, Science 340, 1434-1437 (2013).

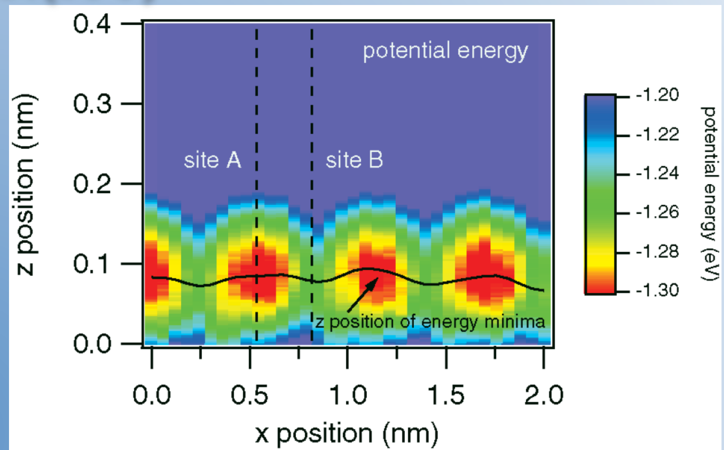
Beyond standard imaging: 3D maps

NiO(100)



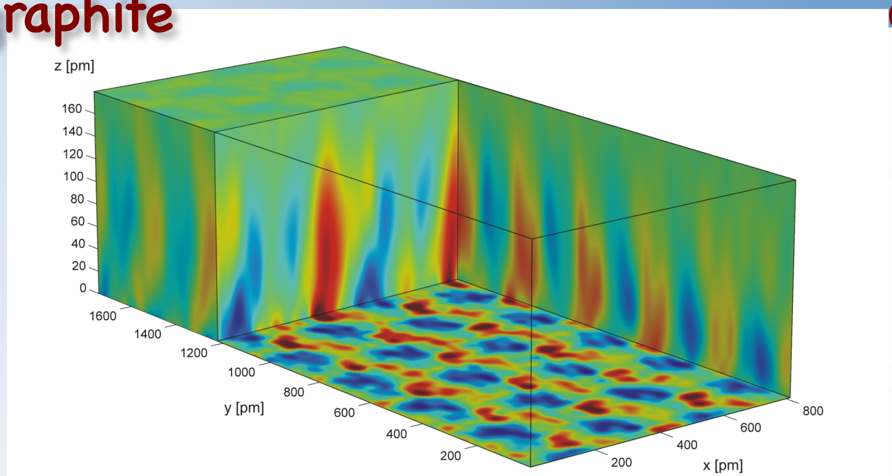
H. Hölscher et al, Appl. Phys. Lett. 81, 4428 (2002)

NaCl(100)



A. Schirmeisen et al, Phys. Rev. Lett. 97, 136101 (2006)

graphite

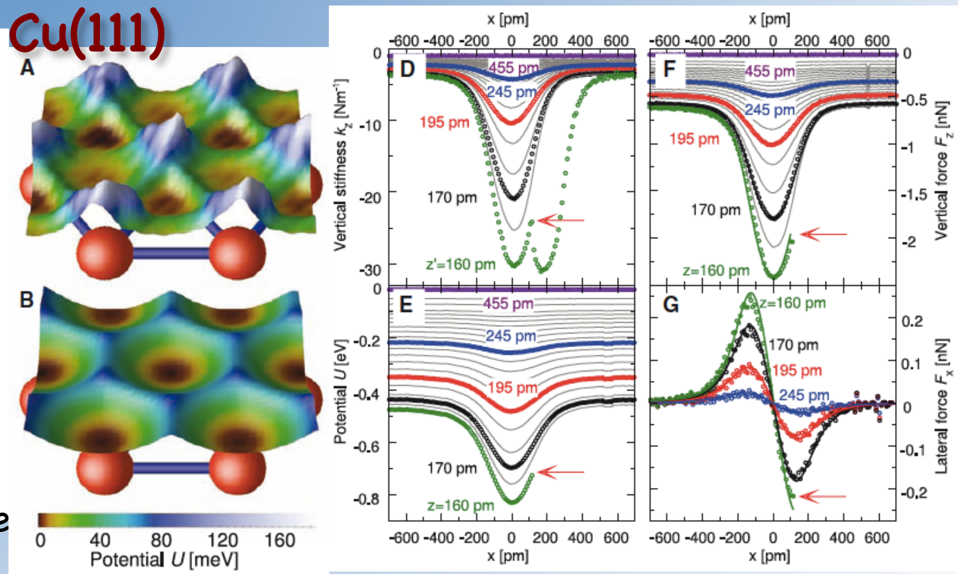


Grid of 119 × 256 force curves = 30464 force curve

T = 6 K acquisition time 40 hours

B.J. Albers et al, Nat. Nanotech. 4, 307 (2009)

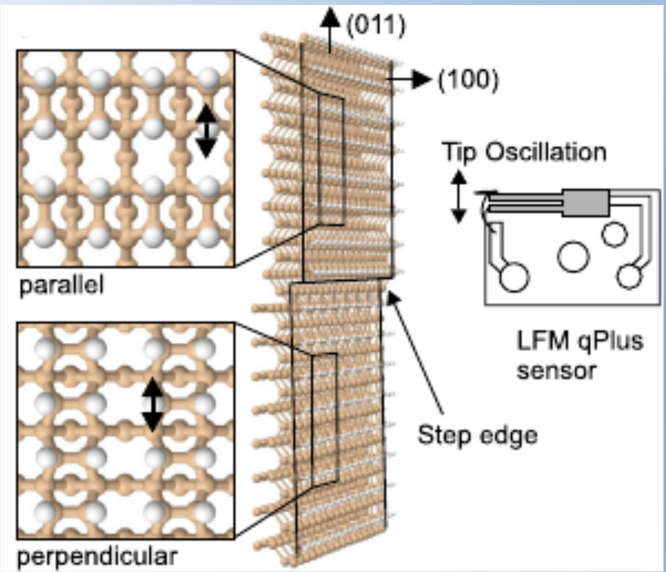
Cu(111)

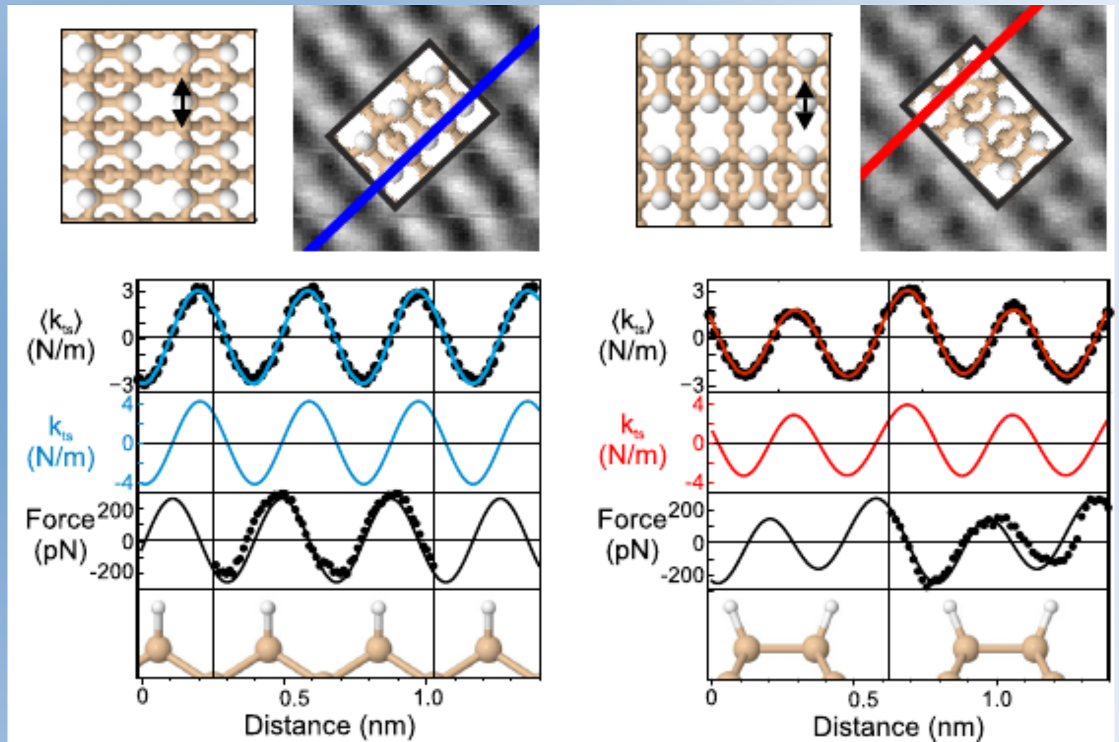


M. Ternes et al, Science 319, 1066 (2008)

Sensing lateral forces

Lateral force with atomic resolution measured on semiconductor surface



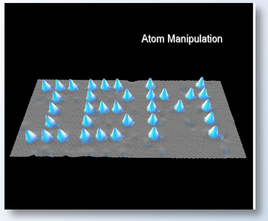


Understanding fundamental processes of friction on atomic scale

A. J. Weymouth et al, Phys. Rev. Lett. (2013)

AFM

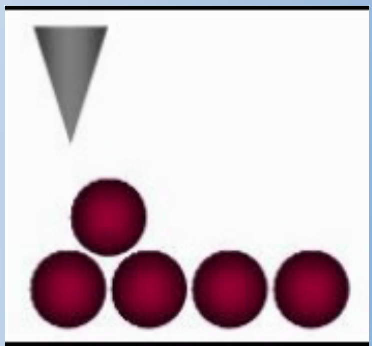
- design & roadmap
- atomic scale images
- atomic manipulation

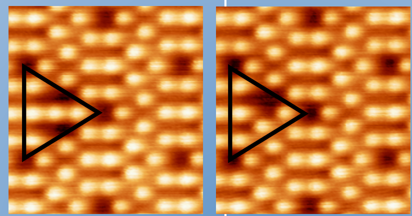


Atom manipulation using force

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

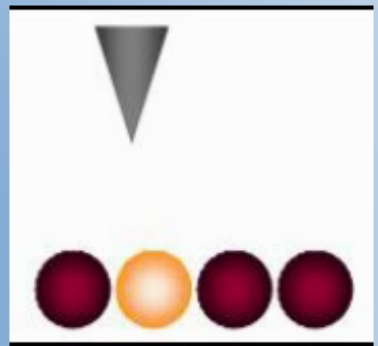
Standard lateral manipulation

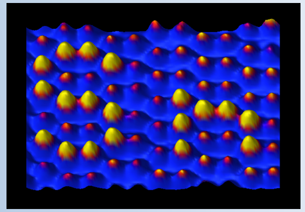




Y. Sugimoto, et al, PRL 98 106104 (2007).

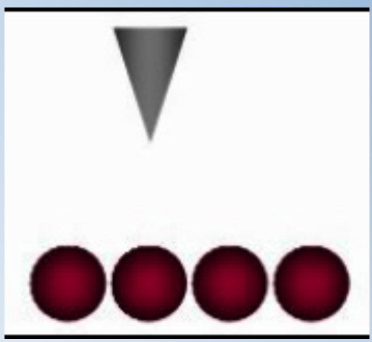
Interchange lateral manipulation

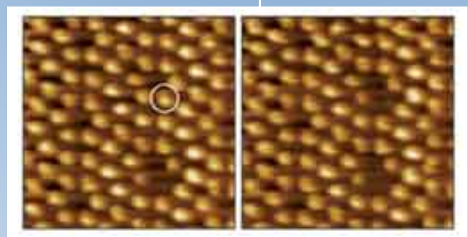




Y. Sugimoto, et al, Nature materials 4 156 (2005).

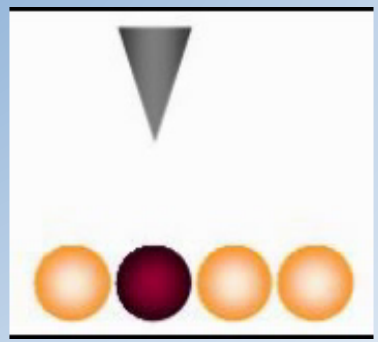
Standard vertical manipulation

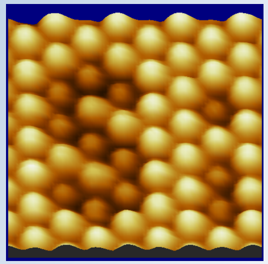




N. Oyabu, et al, PRL 90 176102 (2003).

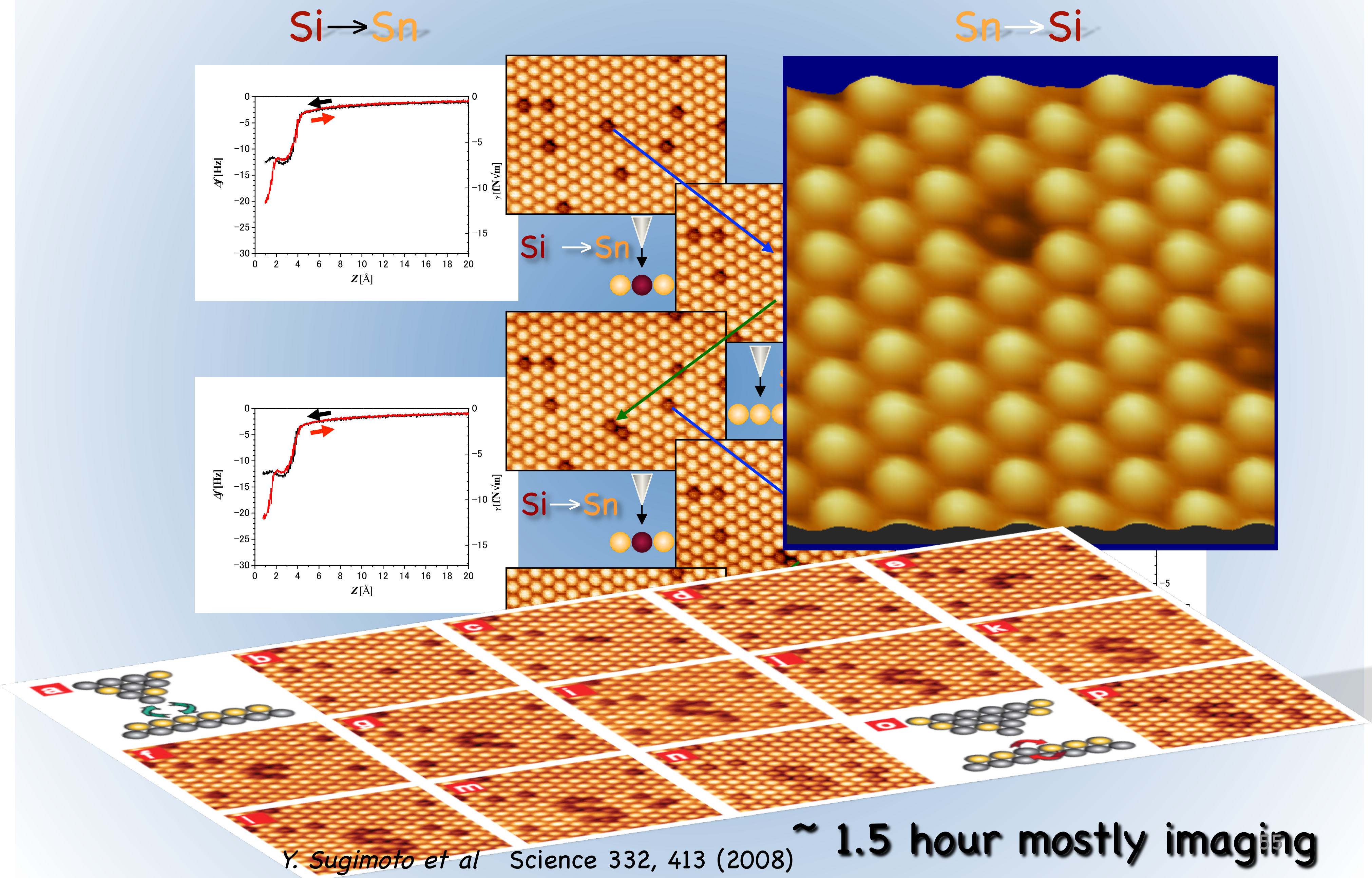
Interchange vertical manipulation





Y. Sugimoto et al Science 332, 413 (2008)

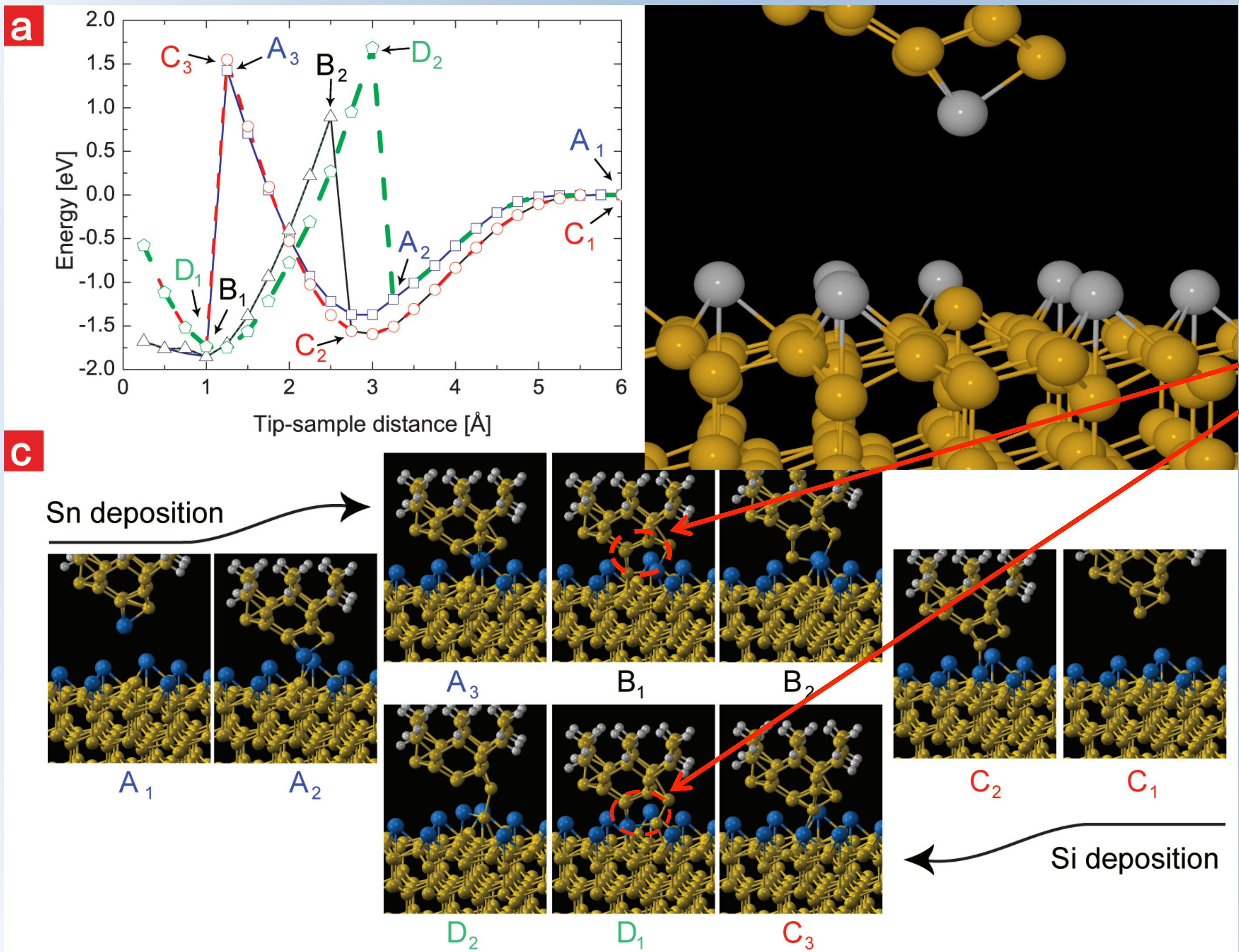
Atomic pencil: 'Si' @ RT by Si atoms



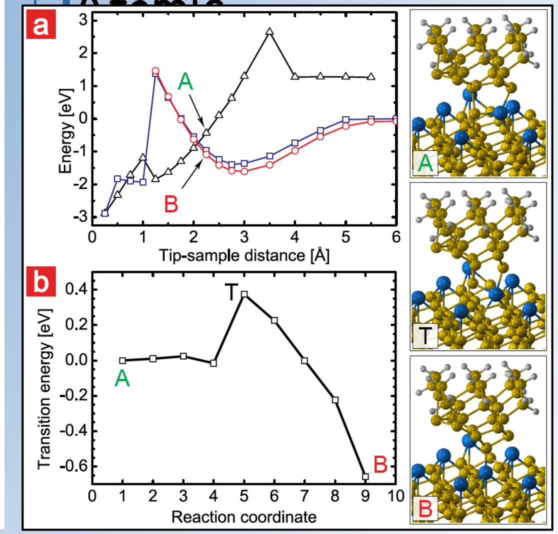
~ 1.5 hour mostly imaging

Y. Sugimoto et al Science 332, 413 (2008)

Insight from theory



- Vertical manipulation as combination of mechanical and thermal process.
- Formation of characteristic *dimer structure* along deformation path (energetically stable).
- Atomic



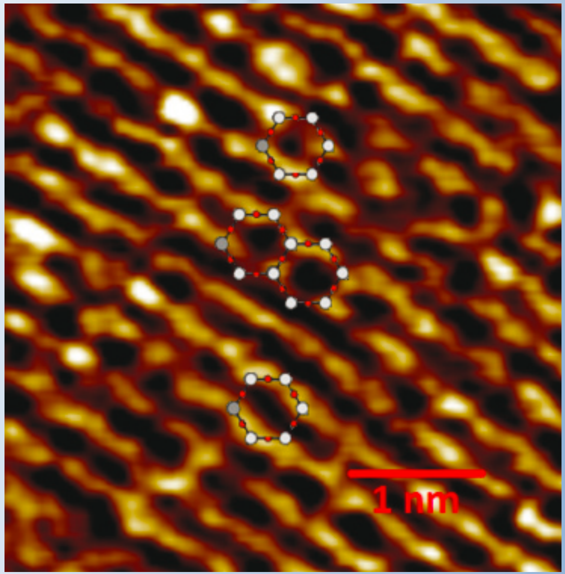
Y. Sugimoto et al Science 332, 413 (2008)

Outline

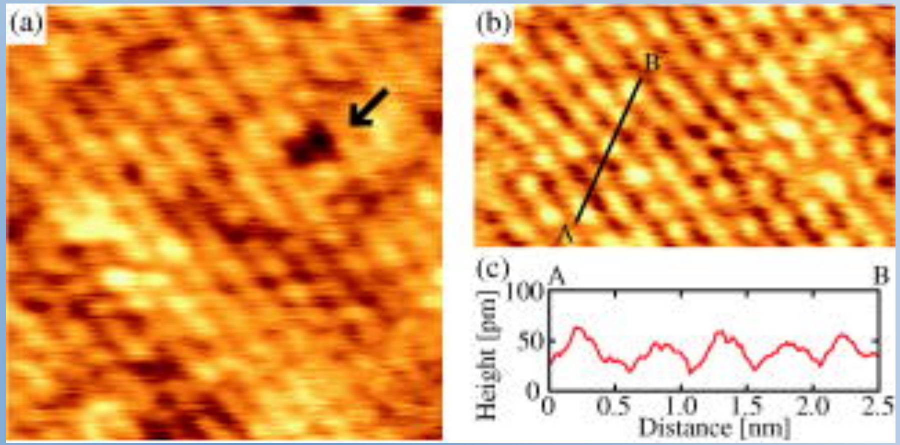
- Introduction
- STM
- AFM
- What next?

Atomic resolution in liquids by means of nc-AFM

Mica in liquids

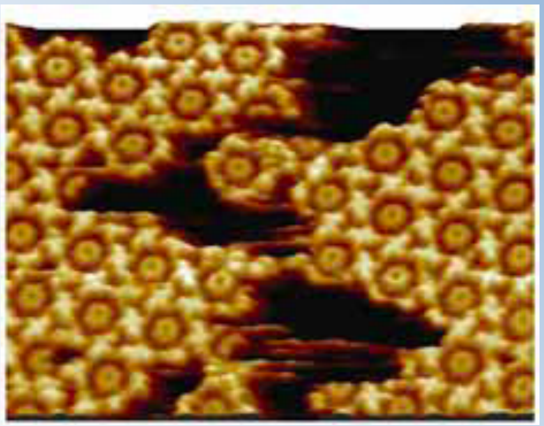


SAM on Au surface



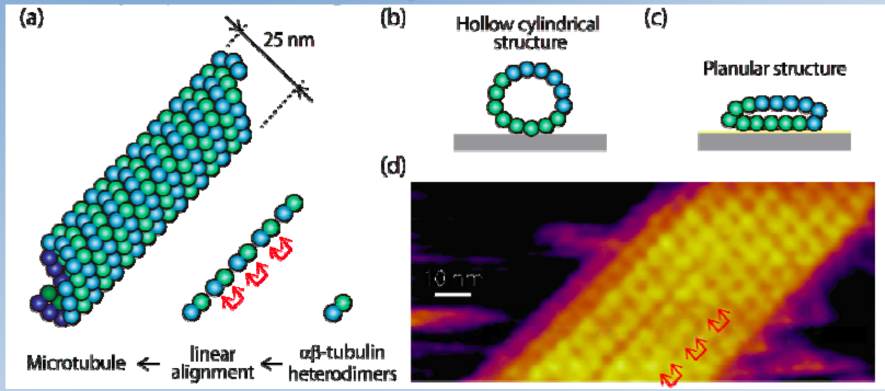
T. Fukuma et al Appl. Phys. Lett. 86, 034103 (2005);

Antibody molecule on mica



H. Yamada group, Kyoto University, Japan

Microtubule in liquid



T. Fukuma group, Kanazw University, Japan

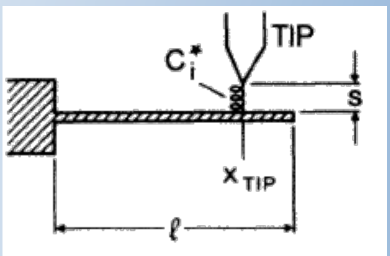
Feeling force and current together

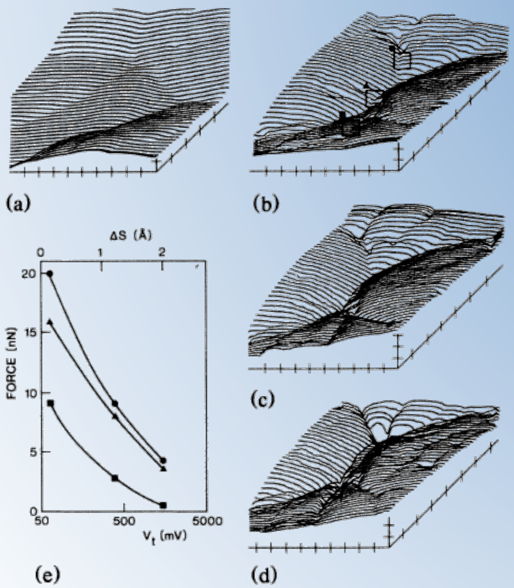
VOLUME 57, NUMBER 19 PHYSICAL REVIEW LETTERS 10 NOVEMBER 1986

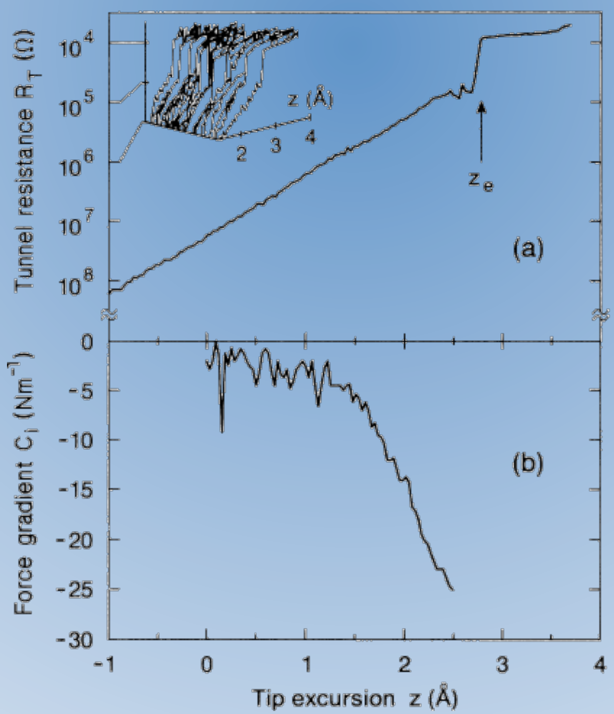
Experimental Observation of Forces Acting during Scanning Tunneling Microscopy

U. Dürig, J. K. Gimzewski, and D. W. Pohl
IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland
(Received 15 May 1986)

U. Dürig, J. K. Gimzewski, and D. W. Pohl, Phys. Rev. Lett. 57, 2403 (1986).







Current vs. distance
- exponential law
  log $R_t = \Phi$

Forces vs. distance
- far distance: vdW forces
  $F_{vdW} \sim const/d^3$
- close distance:
  $F_{chem} \sim const * e^{-\lambda z}$

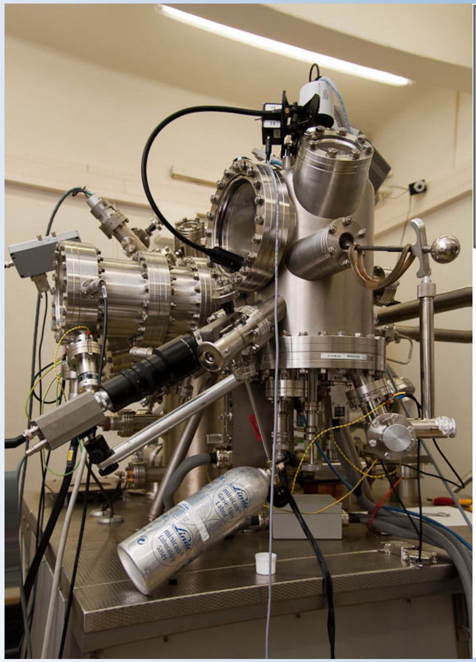
U. Dürig et al Phys. Rev. Lett. 65, 349 (1990).

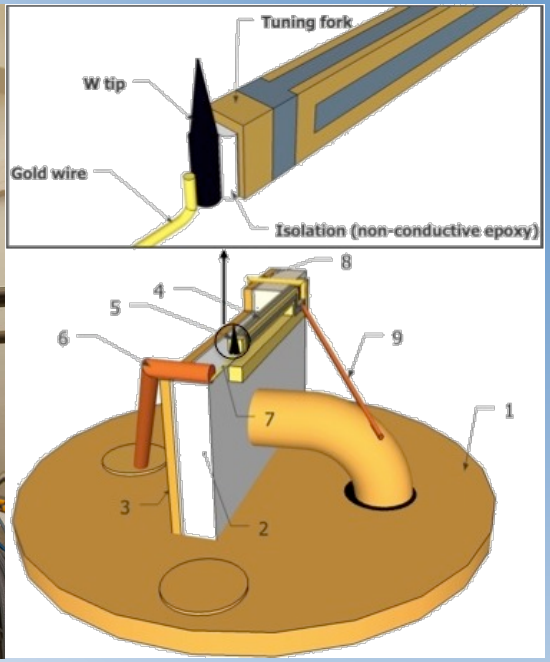
Experimental setup @ FZU

Simultaneous acquisition of Δf, I, ΔE as function of z distance @ RT

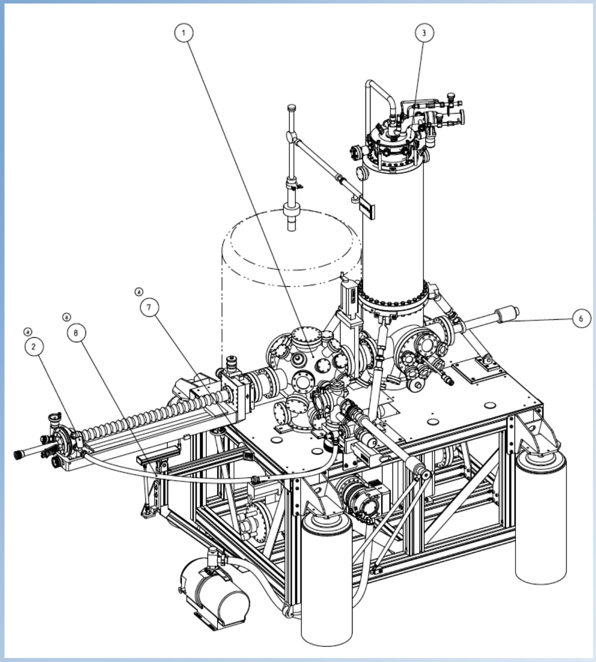
- Modified Omicron VT UHV AFM/STM[1]
- Simultaneous AFM/STM @ RT without cross-talk[1]
- Home built qPlus sensor [2] with improved performance[3]
- Specs UHV LT-AFM/STM (August 2013)

VT AFM/STM (1000-40K)





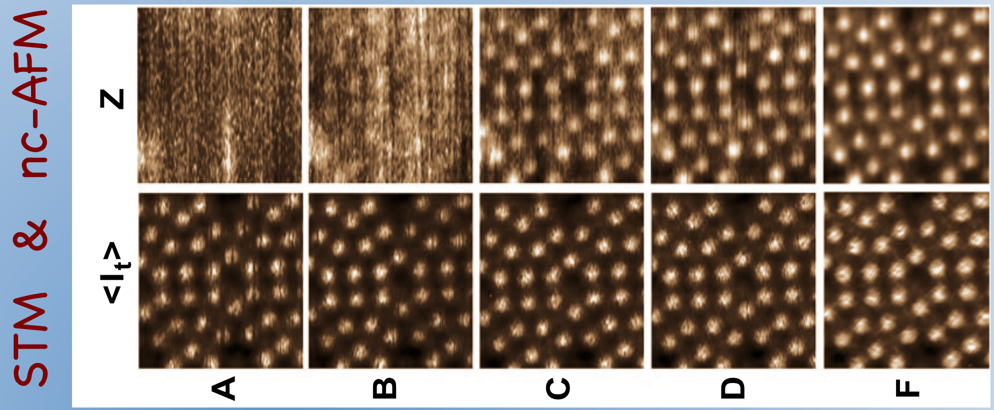
LT AFM/STM (4K)



[1] Z. Majzik et al, Beilstein J. Of Nanotech. 3, 249 (2012).
[2] F.J. Giessibl , App. Phys. Lett. 70, 2529 (1997).
[3] J. Berger et al, Beilstein J. Of Nanotech. 4, 1 (2013).

Different channels

Novel way to merge STM & nc-AFM into one instrument



tip approach

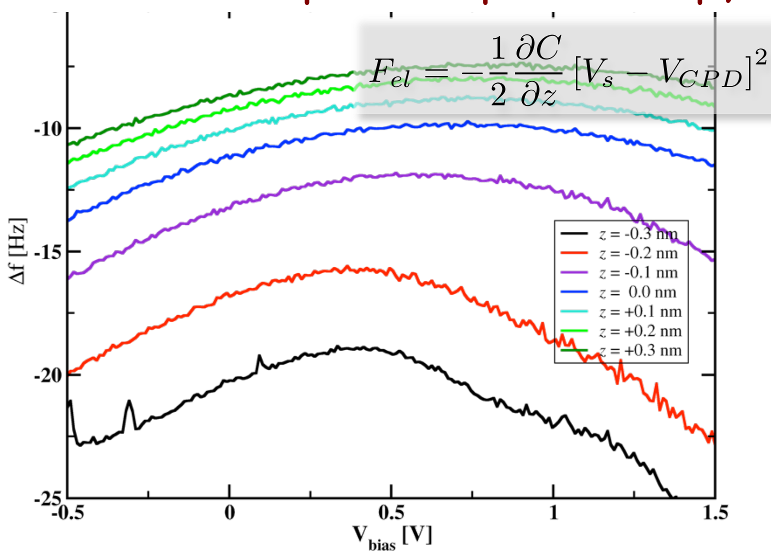
$U_{BIAS} = 0.4$ V, $f_0 = 71096$ Hz, $k = 4354$ N/m, $a_{osc} = 0.13$ nm

Available techniques:

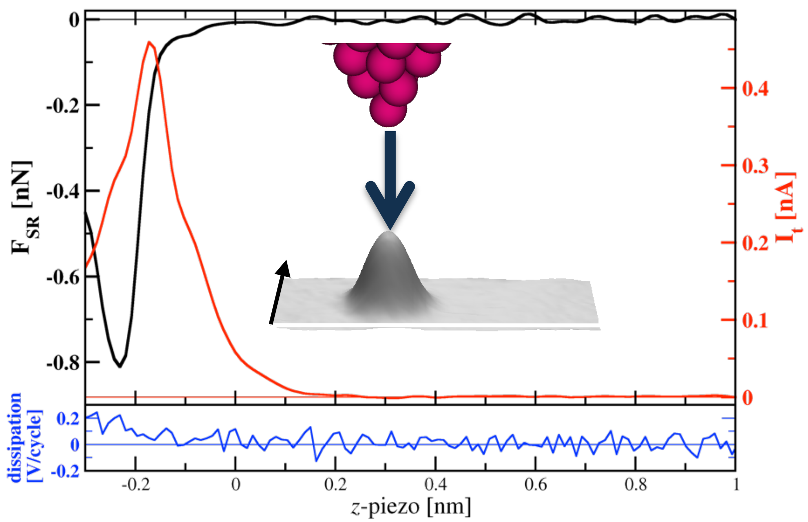
- tuning fork sensor
- length extension resonators
- coated Si-cantilevers

Δ f-V (Kelvin probe) spectroscopy

$$F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}[V_s - V_{CPD}]^2$$



Force/current spectroscopy

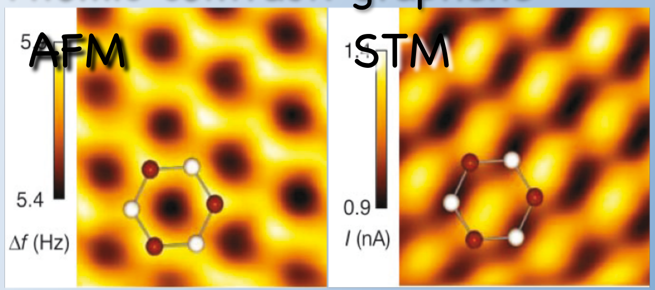


Prospective applications

Probing nanostructures by Force and Current

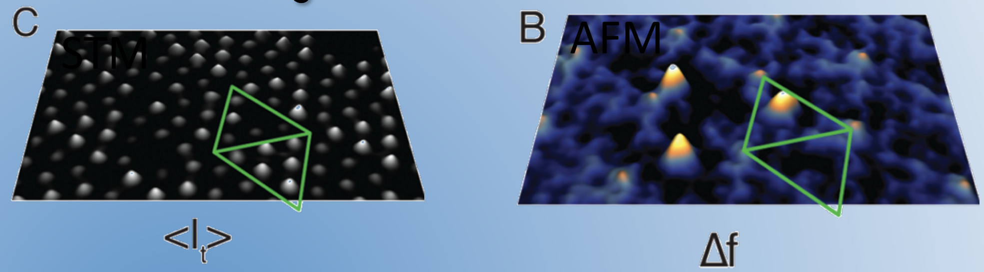
Ultimate atomic resolution in SPM

Atomic contrast: graphene



S. Hembacher et al PNAS 100, 12539 (2003)

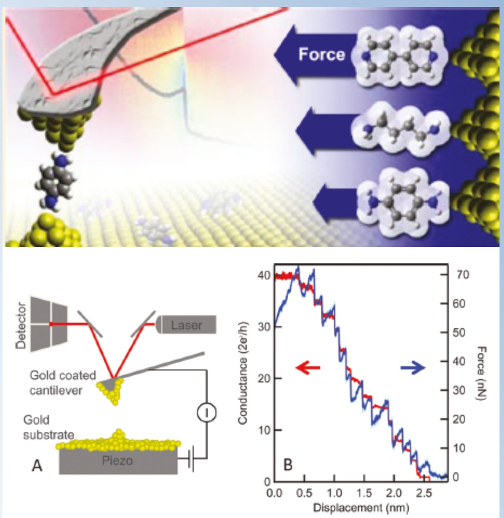
Molecular recognition on semiconductor surfaces

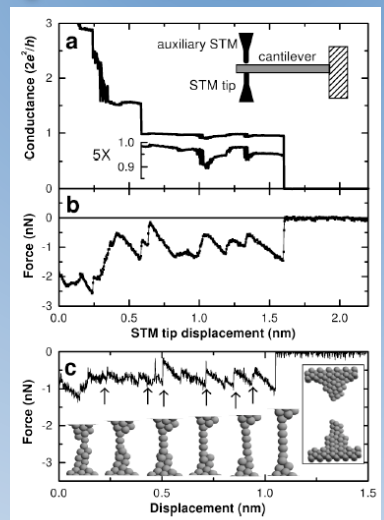


Z. Majzik et al ACS Nano 7, 2686 (2013)

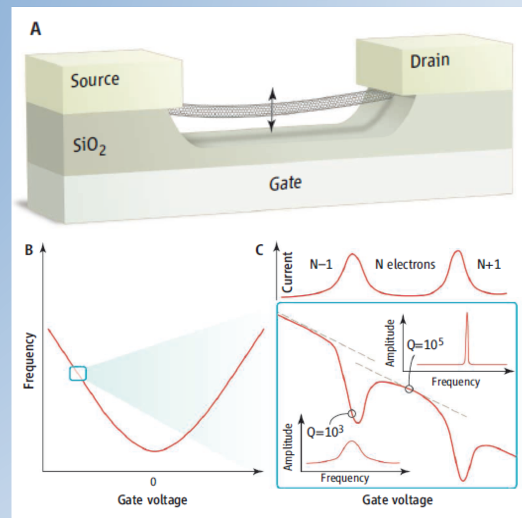
Do STM and AFM provide a similar atomic contrast ?

Nanowires & molecular junctions





NEMS

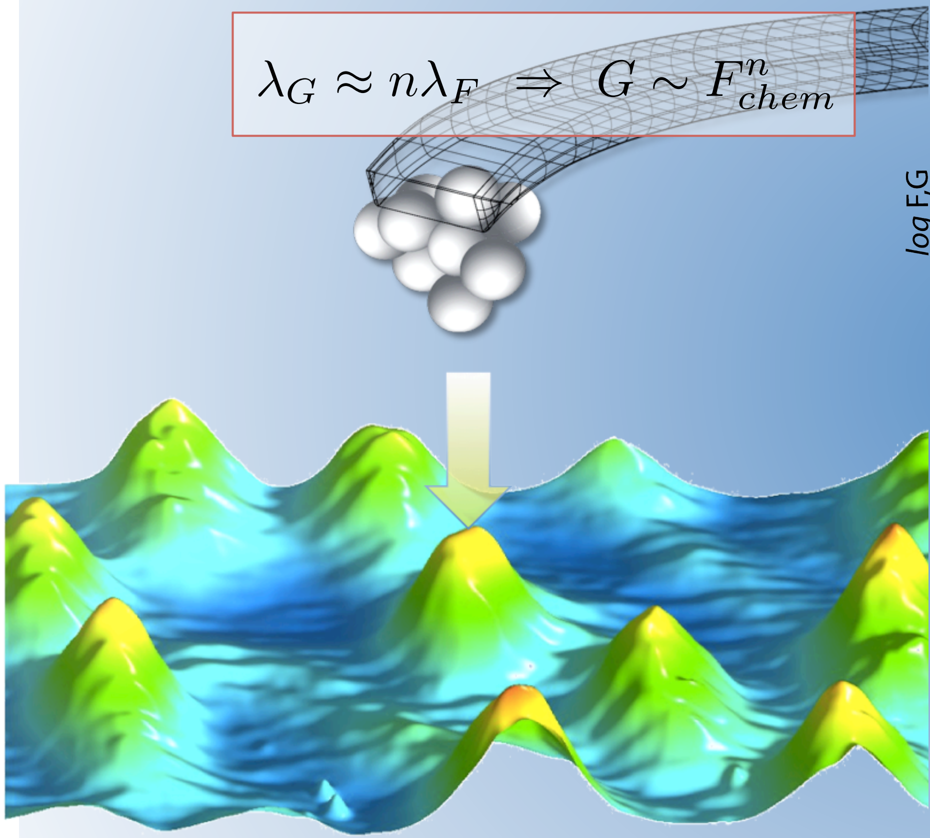


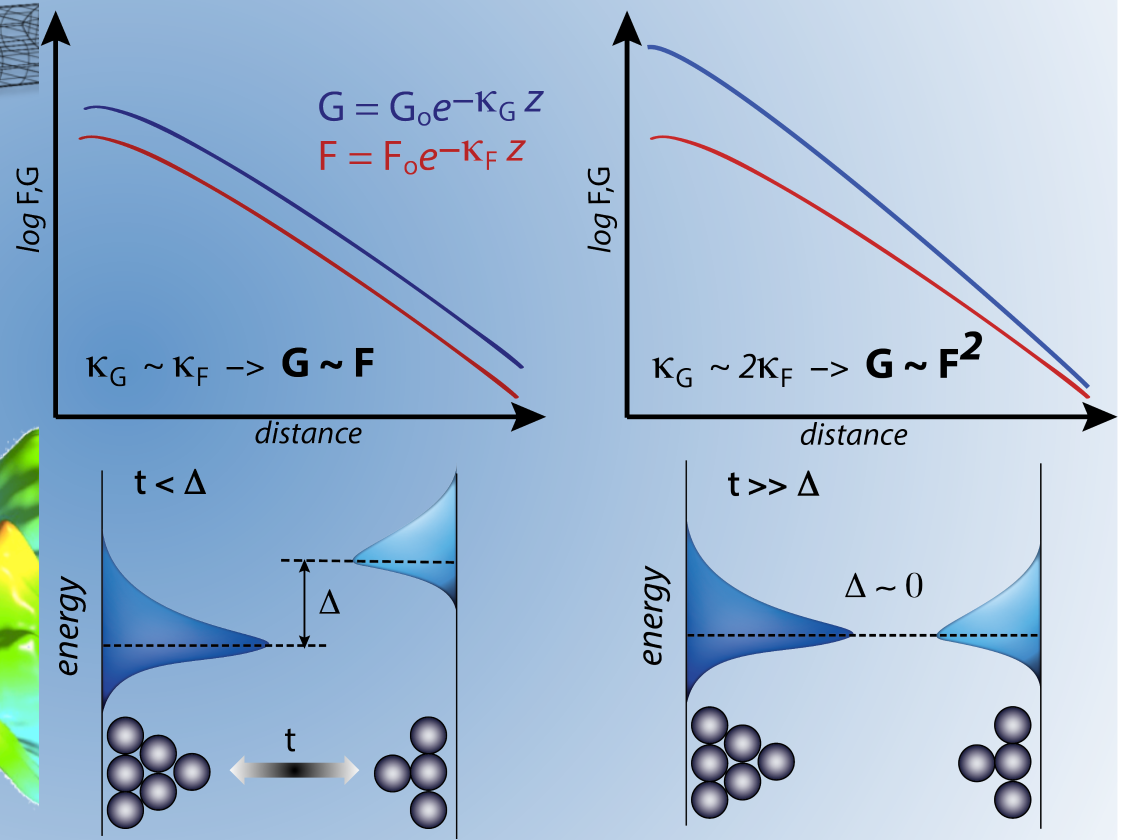
M. Frei et al NanoLett. 11, 1518 (2011). G. Rubio-Bollinger et al PRL. 87, 026101 (2001). J. Hone et al Science 325, 1084 (2009)

Fundamental relation between force and current at atomic scale

The relation driven by quantum degeneracy by frontiers orbitals

$$\lambda_G \approx n\lambda_F \;\Rightarrow\; G \sim F^n_{chem}$$

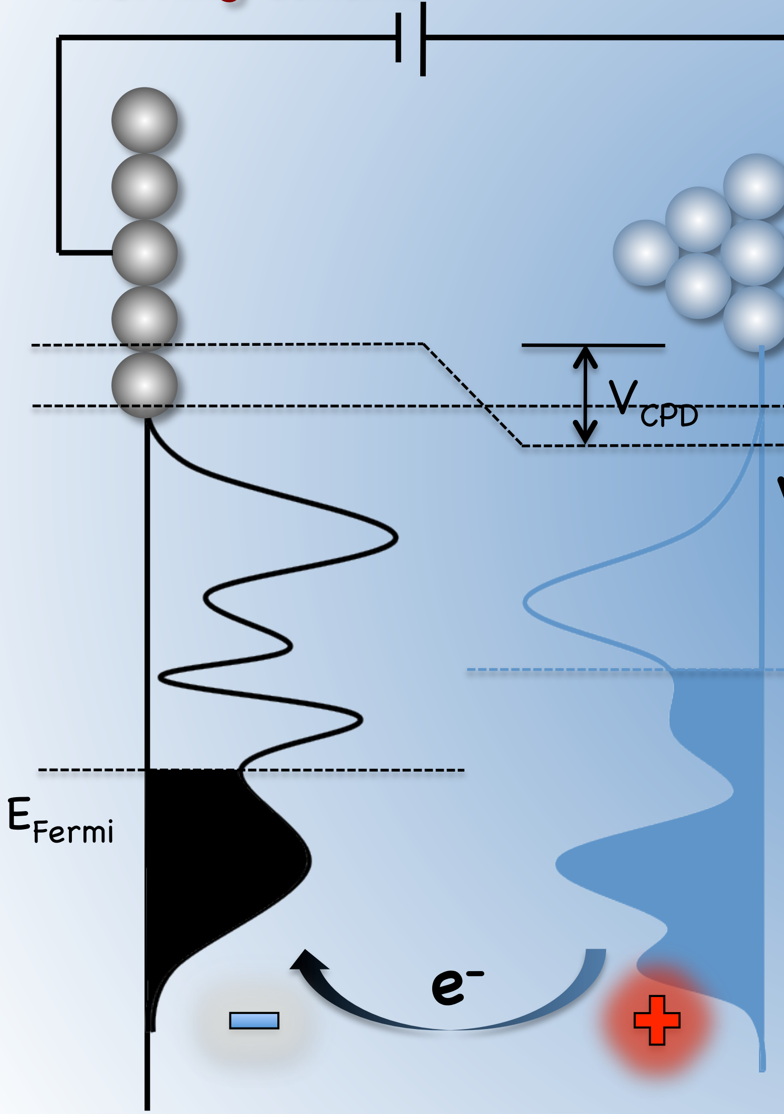




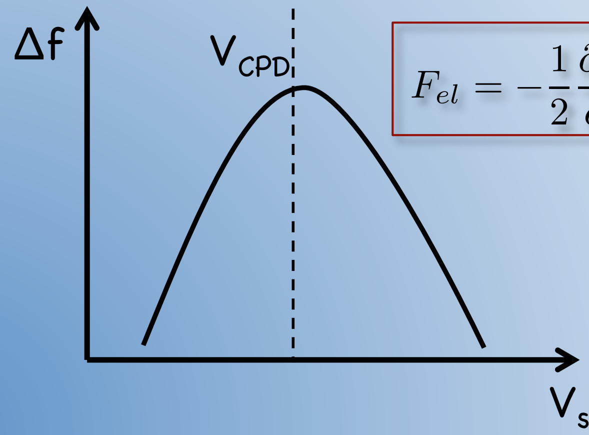
M. Ternes et al Phys. Rev. Lett. 106, 176101 (2011).
P. Jelínek et al, JPCM 24, 084001 (2012).
Y. Sugimoto et al Phys. Rev. Lett. 111, 106803 (2013).

Basic principles of KPFM

Working scheme



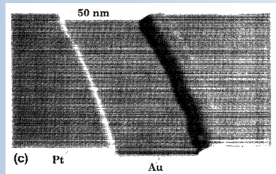
Bias vs. frequency shift



$$F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}\left[V_s - V_{CPD}\right]^2$$

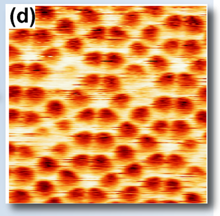
Work function difference

M. Nonnenmacher *et al*, *APL* 58, 2921 *(1991).*



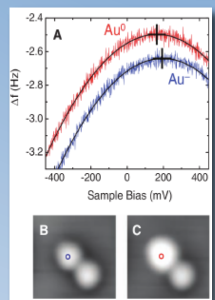
True atomic resolution

S. Sadewasser *et al*, *PRL 113*, *266103 (2009).*



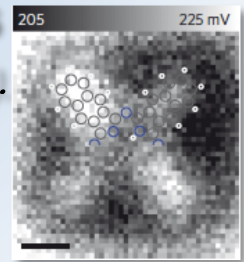
Charge states at atomic scale

L. Gross et al, Science, 324, 1428 (2009).



Charge distribution in molecules

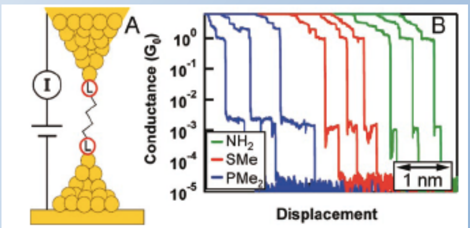
F. Mohn et al, Nature Nano. 7, 227 (2012).



Motivation

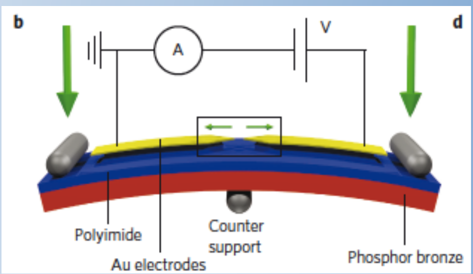
Force or current

STM



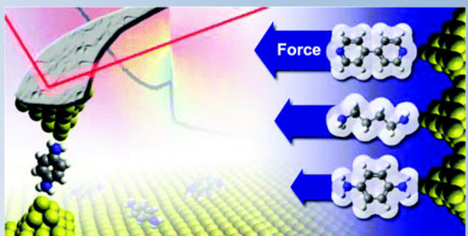
Y. S. Park et al, JACS 129, 15768 (2007).

MCBJ



M.L. Perin et al, Nature Nano 8, 282 (2013).

AFM

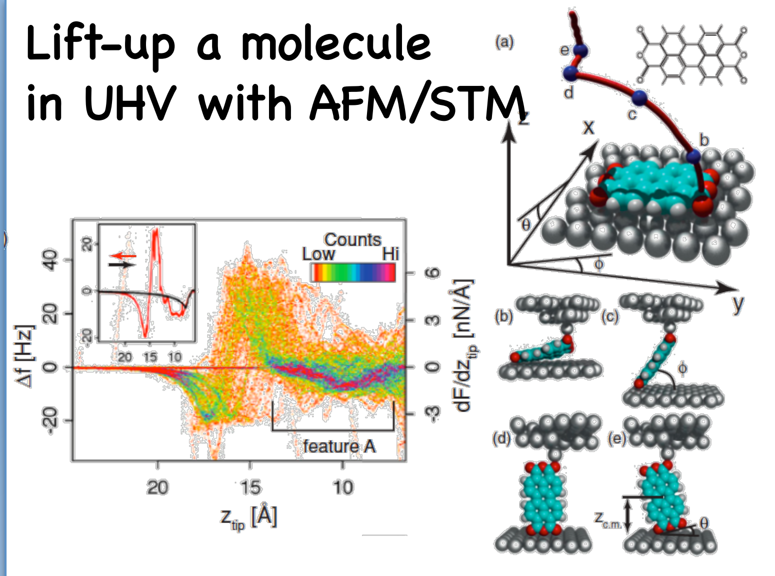


S.Y. Quek et al, Nature Nano 4, 230 (2009).

Force and current

nc-AFM/STM (qPlus)

Lift-up a molecule in UHV with AFM/STM

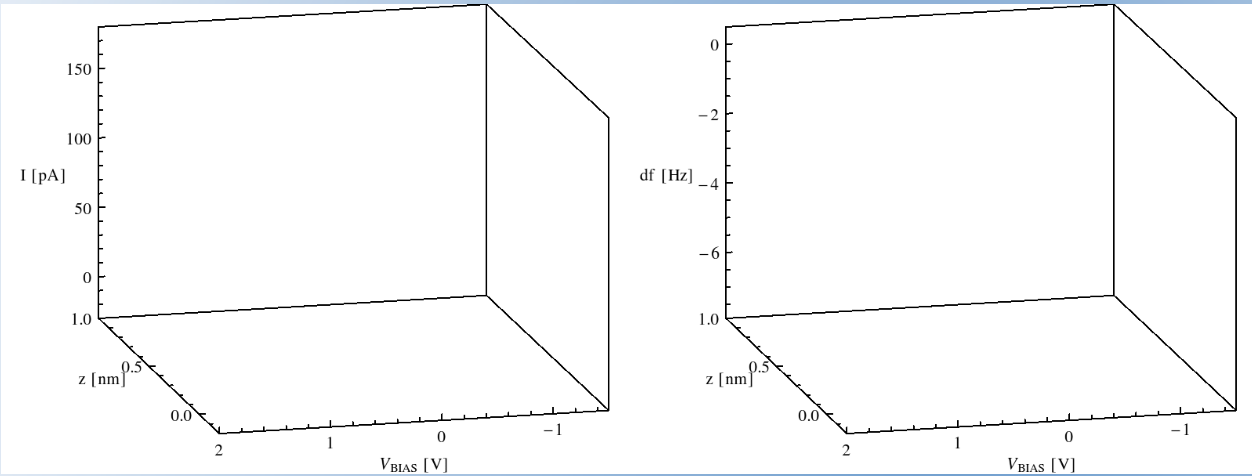


N. Fournier et al Phys. Rev. B84, 035435 (2011).

Understanding of forces acting during formation of molecular junction on semiconductor surface

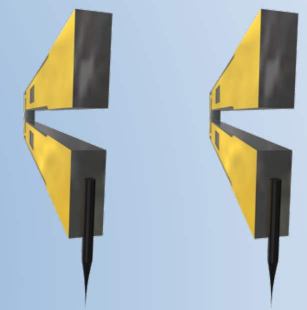
2D mapping in V,z space

Δf, I & E_{diss} (z;V) spectroscopy off/on molecule

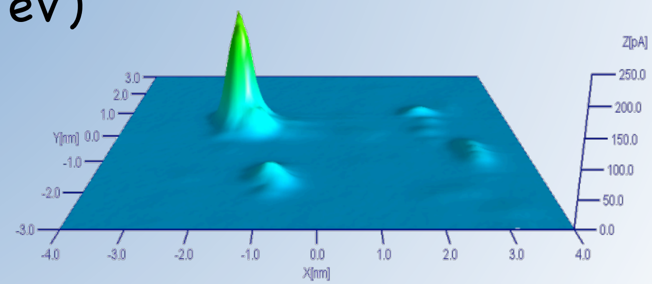


ON $z(V_1)$, $z(V_2)$,..

OFF $z(V_1)$, $z(V_2)$,..

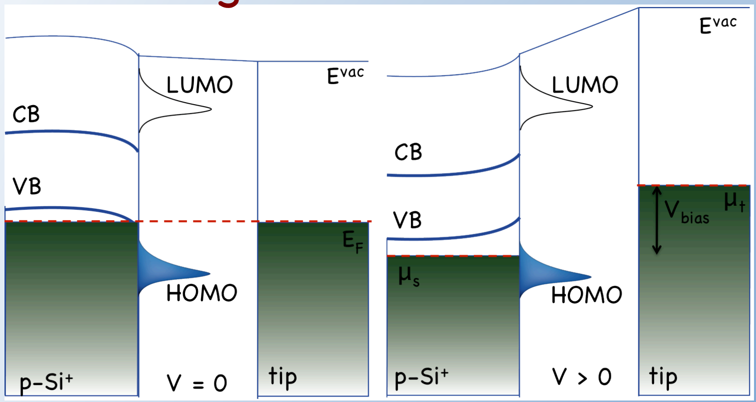


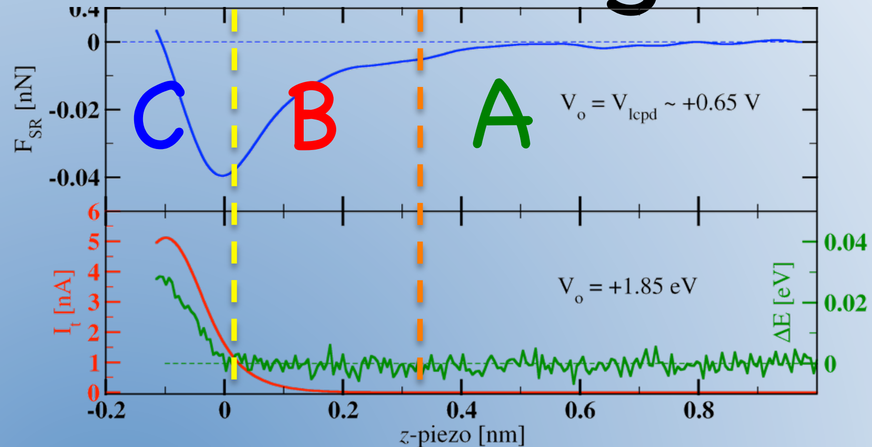
- constant height STM @ high bias V_o to resolve molecules
- approx 40 Δf-z curves @ different biases V_i (ΔV=0.1 eV)
- acquisition loop:
    - Δf-z curve @ given bias V_i
    - constant height scan @ V_o
    - x,y set point adjustment tracking molecule
- total time > 2 hours
- no tip changes during acquisition



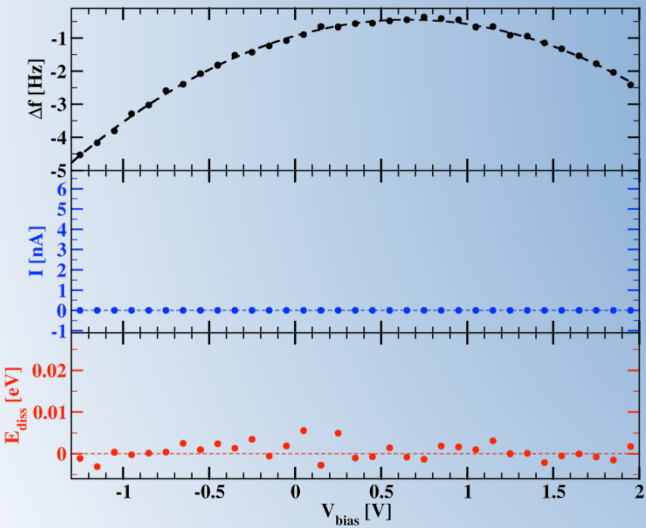
Different interaction regimes

Band diagram





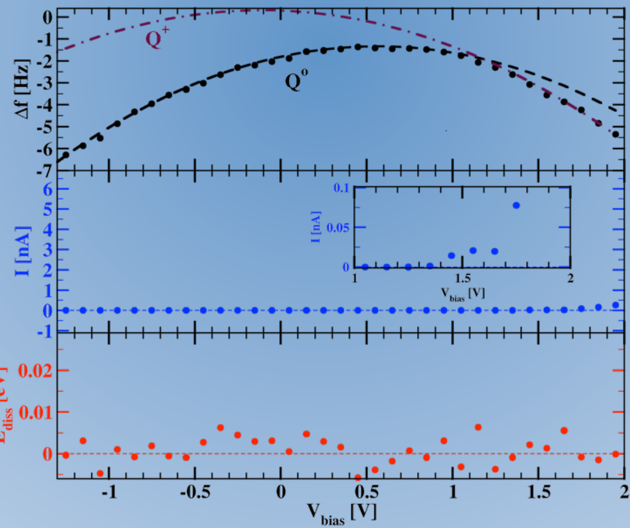
A. Classical regime



$$F_{el}^{LR}(z,V) = -\frac{1}{2}\frac{\partial C(z)}{\partial z}\left(V - V_{LCPD}\right)^2$$

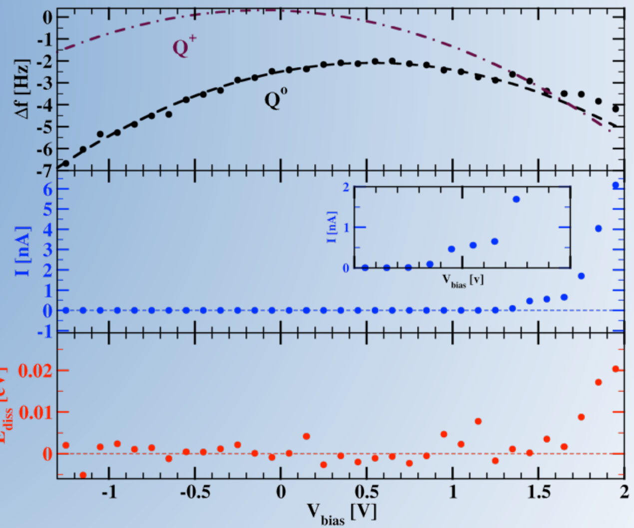
No difference between molecule and surface

B. Charge regime



HOMO depopulated at elevated bias

C. Phantom regime



$$F_{el}(z,V,I) = -\frac{1}{2}\frac{\partial C(z)}{\partial z}\left(V - V_{LCPD} - IR_s\right)^2$$

J. Weymouth et al., PRL 106, 226801 (2011).

R ~ 1-10 GΩ depending on bias

Thank you for your attention