Atom-by-atom nano structuring and single-atom chemical identification at room temperature

Oscar Custance

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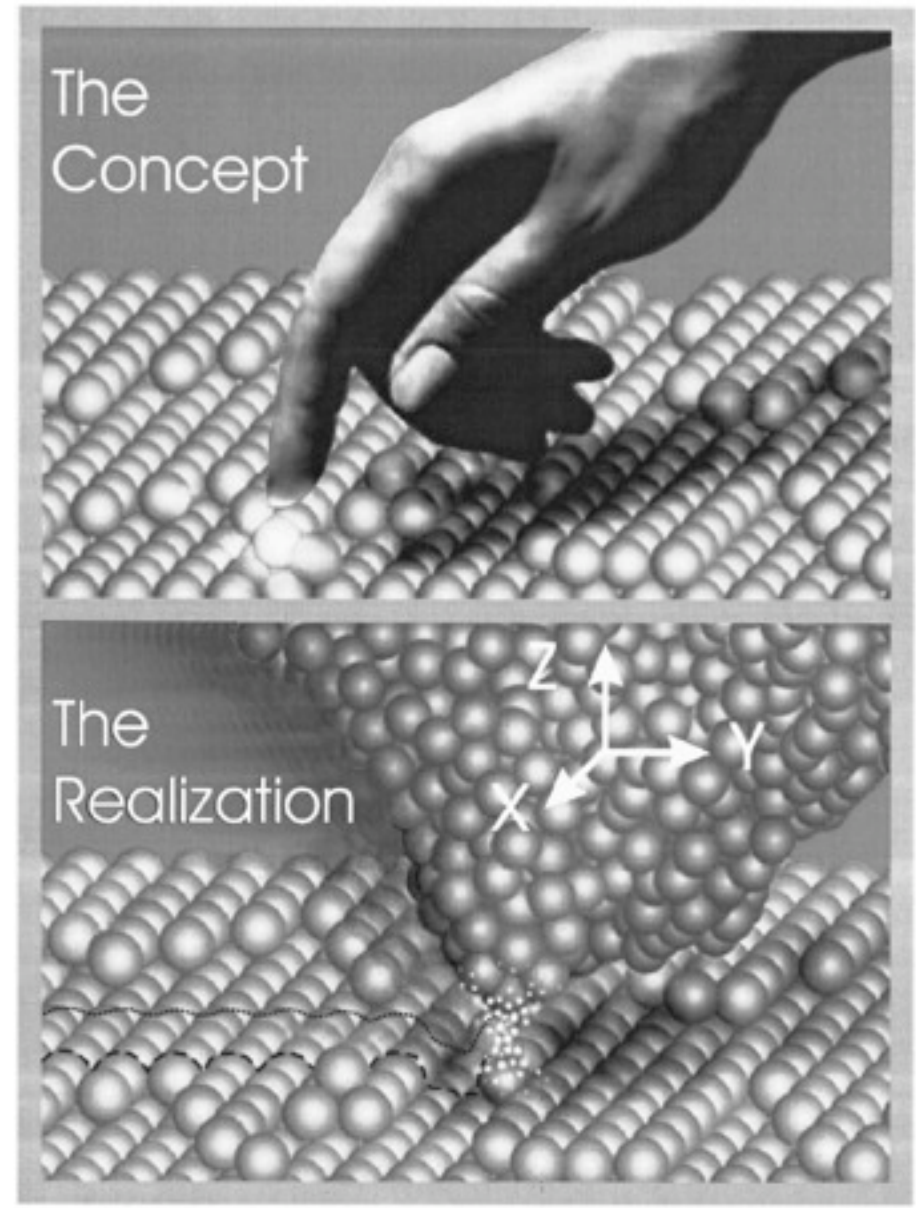
Yoshiaki Sugimoto

Masayuki Abe



"In Touch With Atoms"

G. Bining & H. Rohrer

Rev. Mod. Phys. **71** S324, (1999)

Collaborators

OSAKA UNIVERSITY

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Akademie věd ČR

Pavel Jelinek

Outline

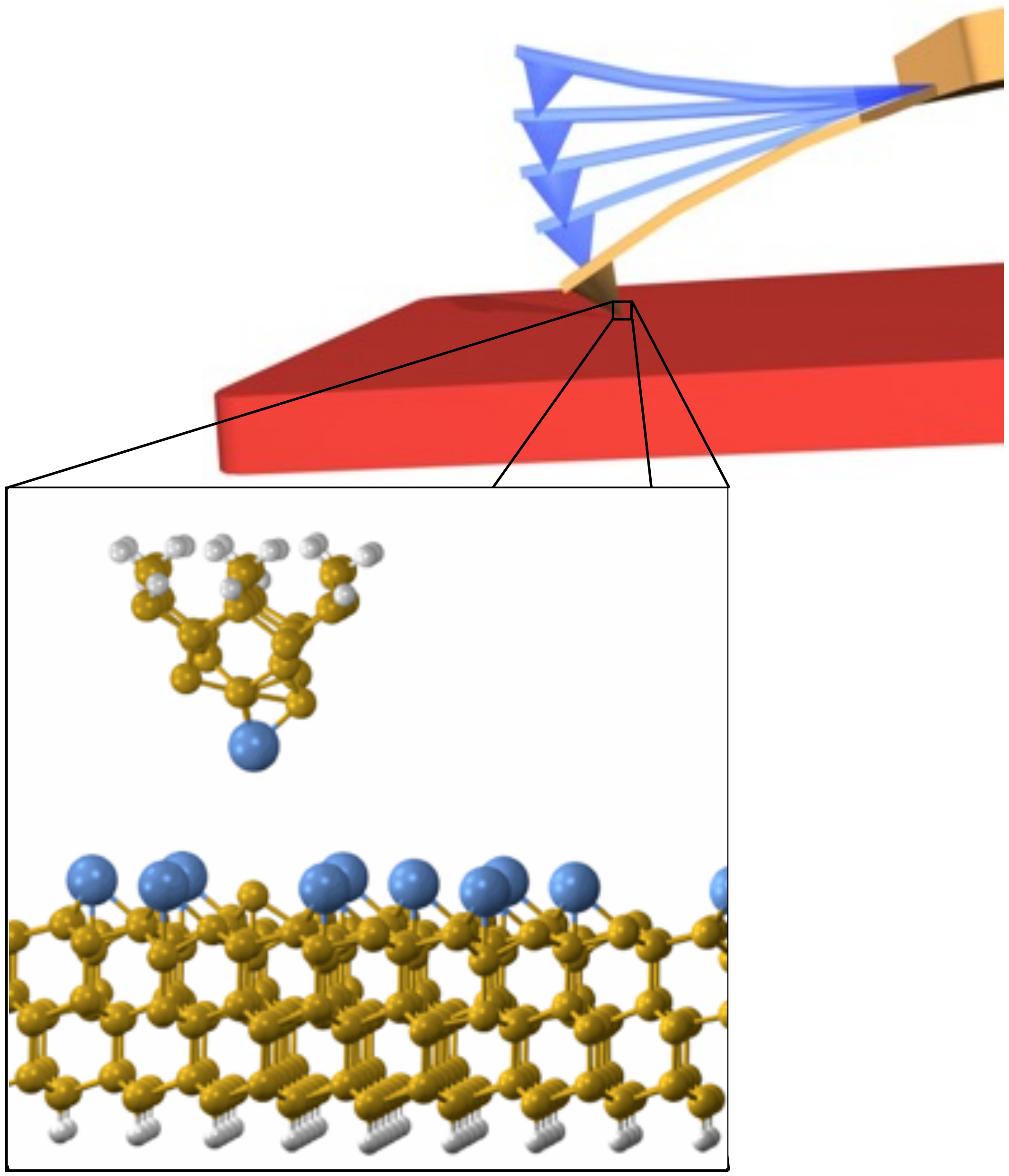
- Brief introduction to experimental technique: FM-AFM
- Nano-structuring atom by atom using AFM
    - Lateral interchange atom manipulation
    - Vertical interchange atom manipulation
- Chemical identification of individual atoms with AFM
- Summary

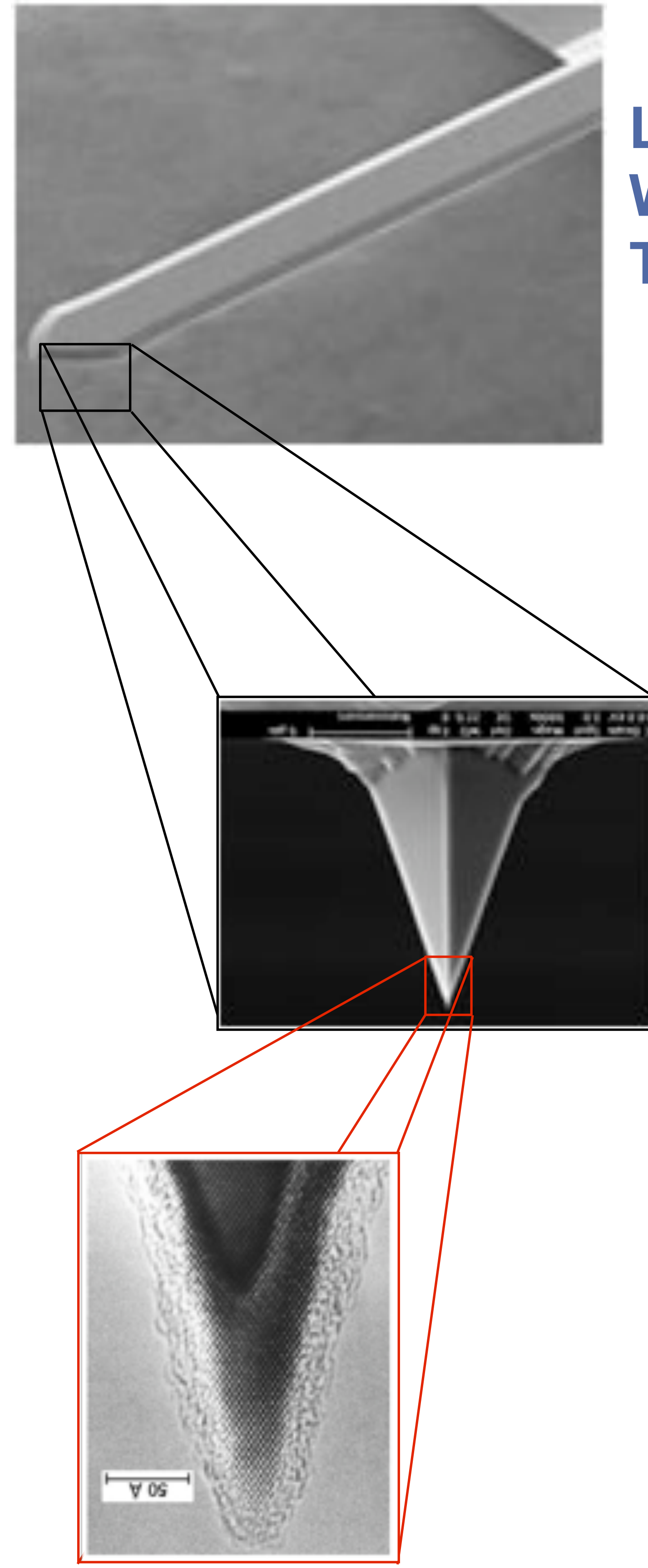
Instrumentation

Atomic resolution dynamic force microscopy

Frequency-Modulation AFM

(Non-contact AFM)



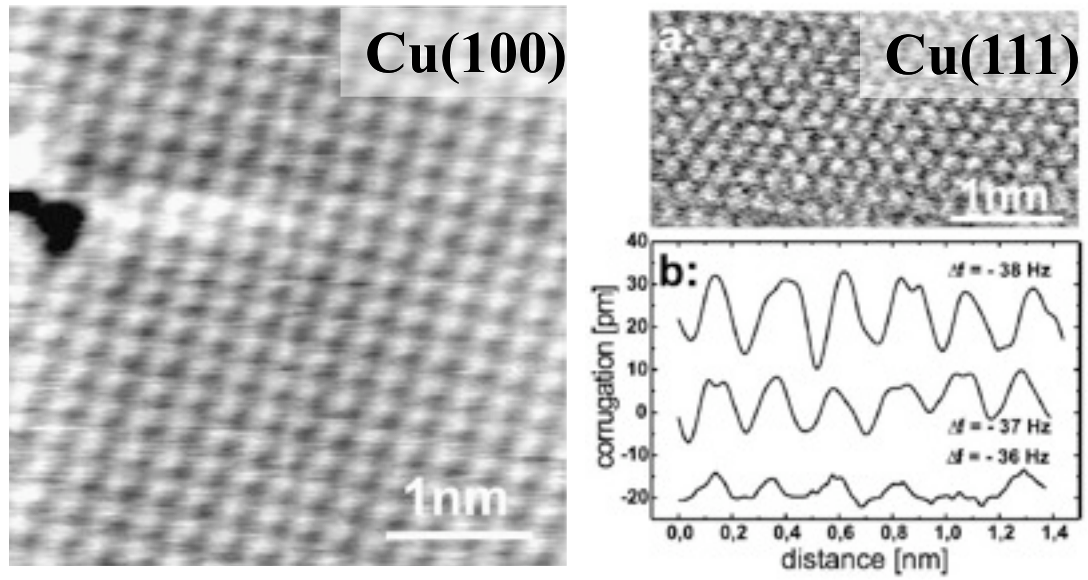


Length ~225 μm
Width ~38 μm
Thickness ~7 μm

Height ~12 μm

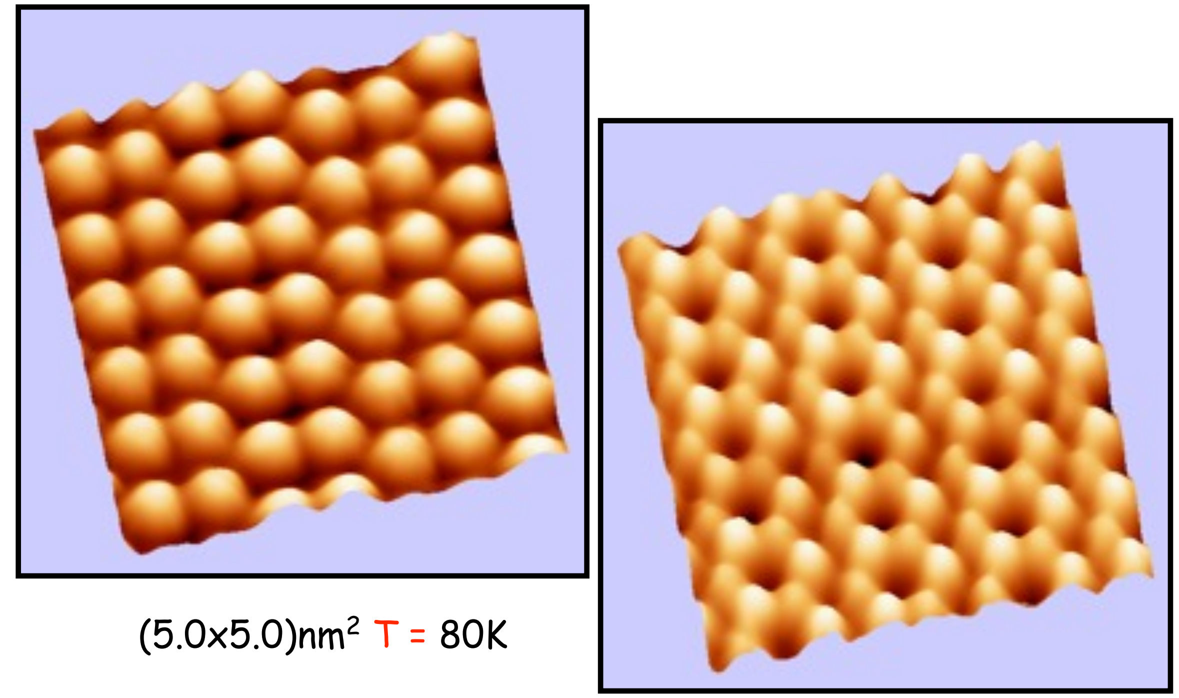
Atomic resolution dynamic force microscopy

Cu(100) and Cu(111)



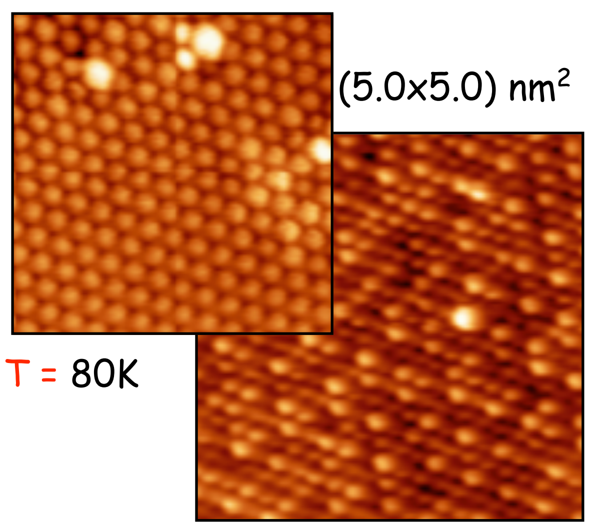
Ch. Loppacher et al., Phys. Rev. B, **62**, 16944 (2000)

Ge(111)-c(2x8)



(5.0x5.0)nm^2 T = 80K

CeO_2(111)

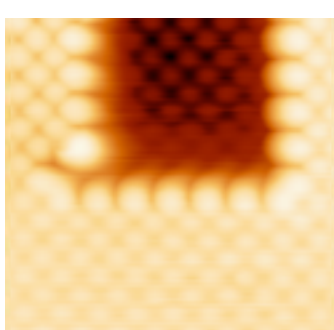


(5.0x5.0) nm^2

T = 80K

(7.7x7.7)nm^2

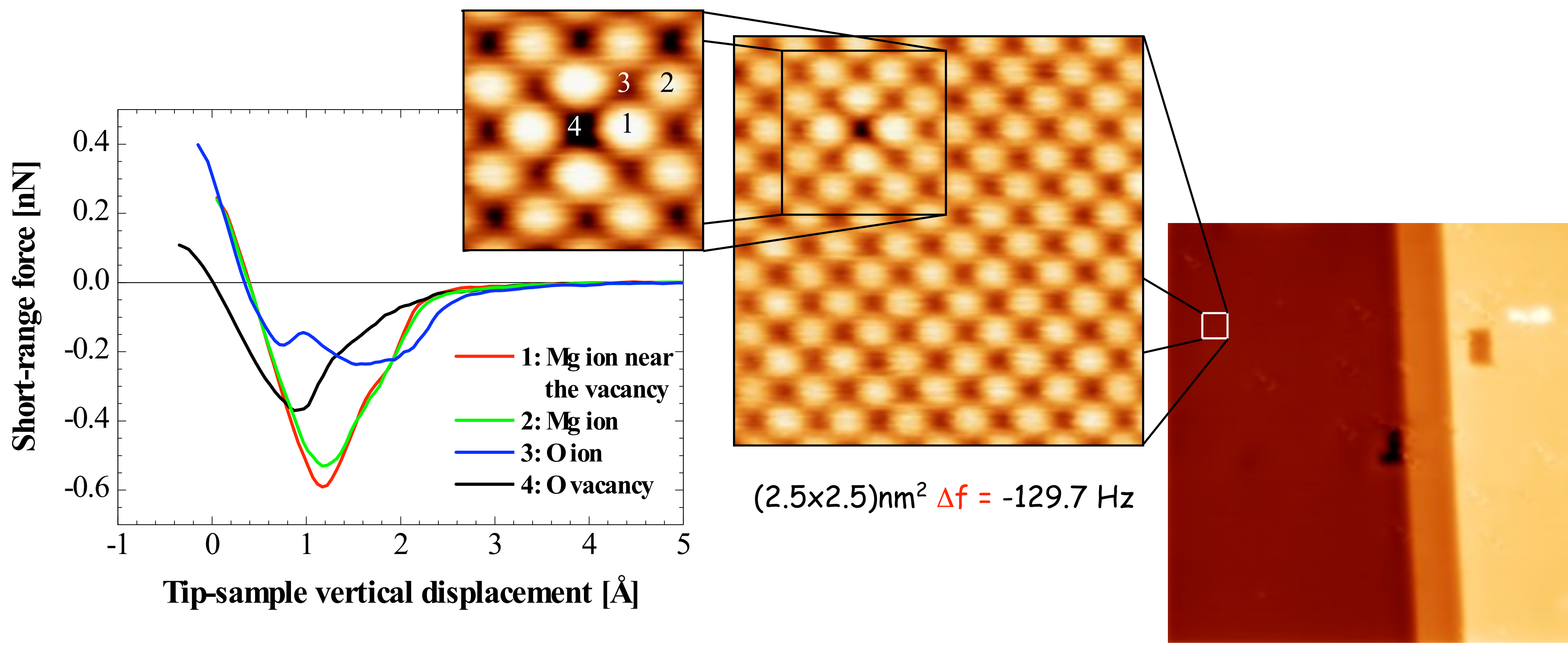
KBr(100)



(5.1x5.1) nm^2

T = 80K

MgO(100)

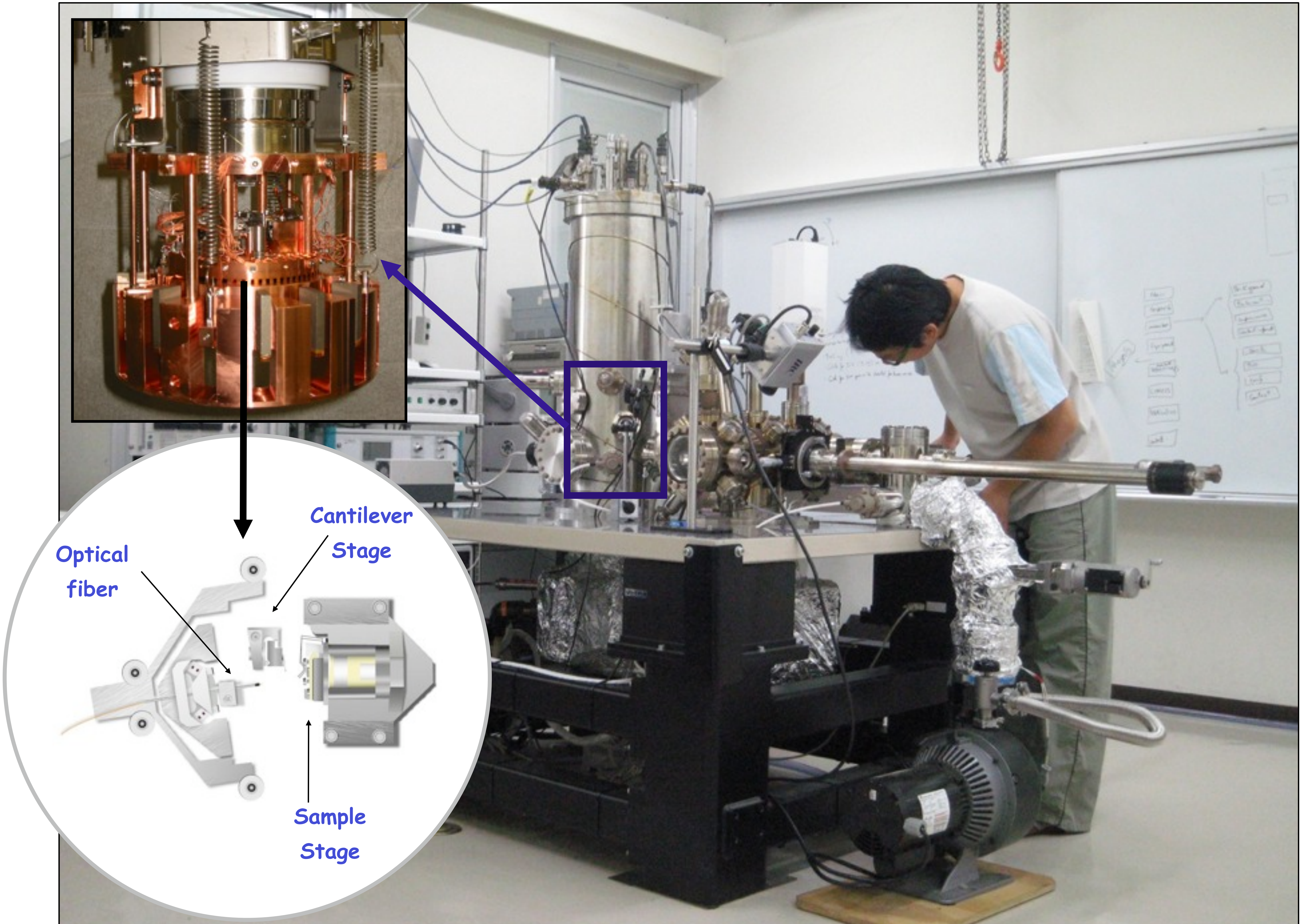


(2.5x2.5)nm^2 Δf = -129.7 Hz

f_0 = 175048.0Hz A = 2.4 nm K = 38.3 N/m Q = 186857 T= 80K

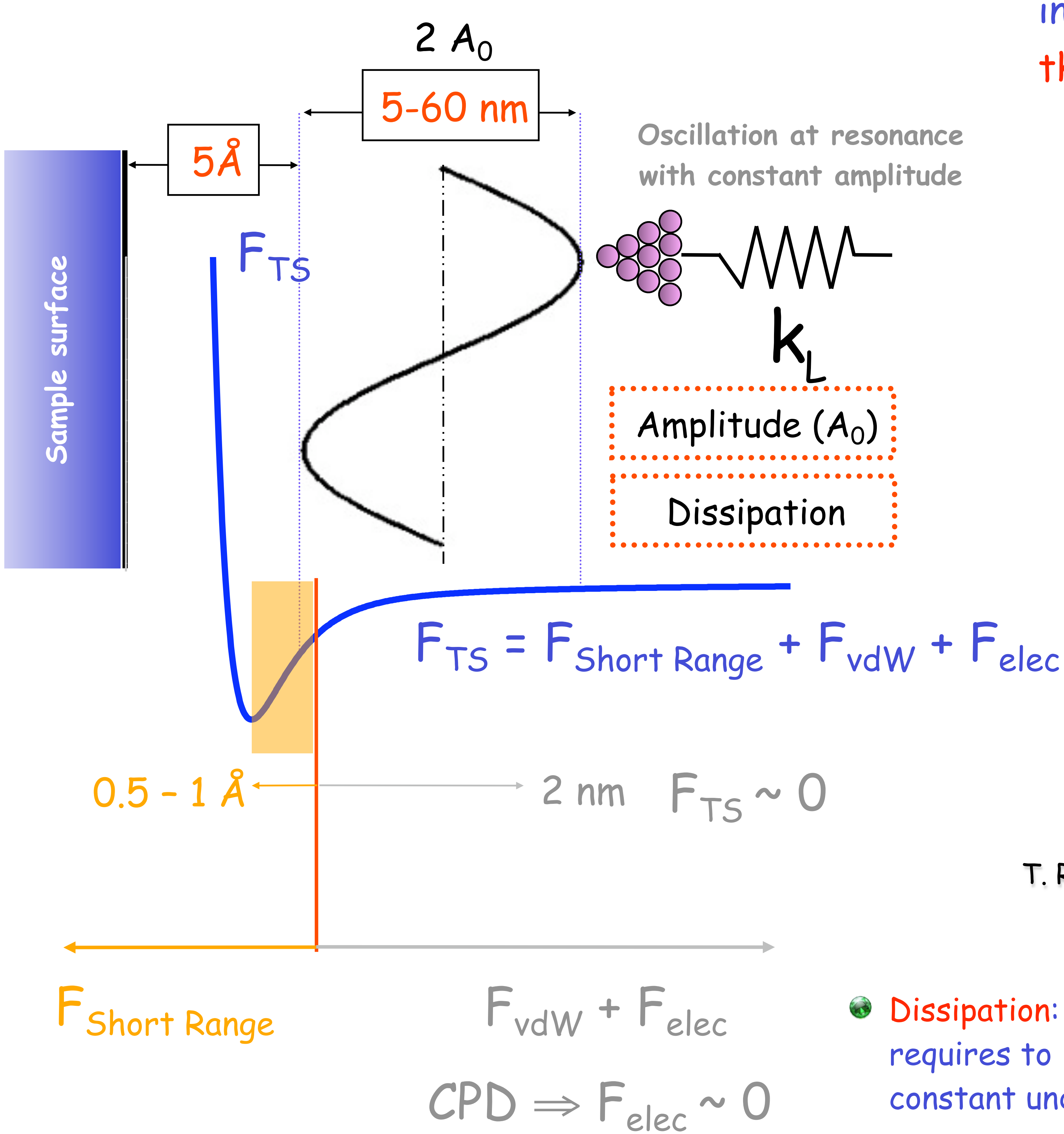
(50 x 50)nm^2 Δf = -40.8 Hz

UHV-AFM & Interferometric Detection

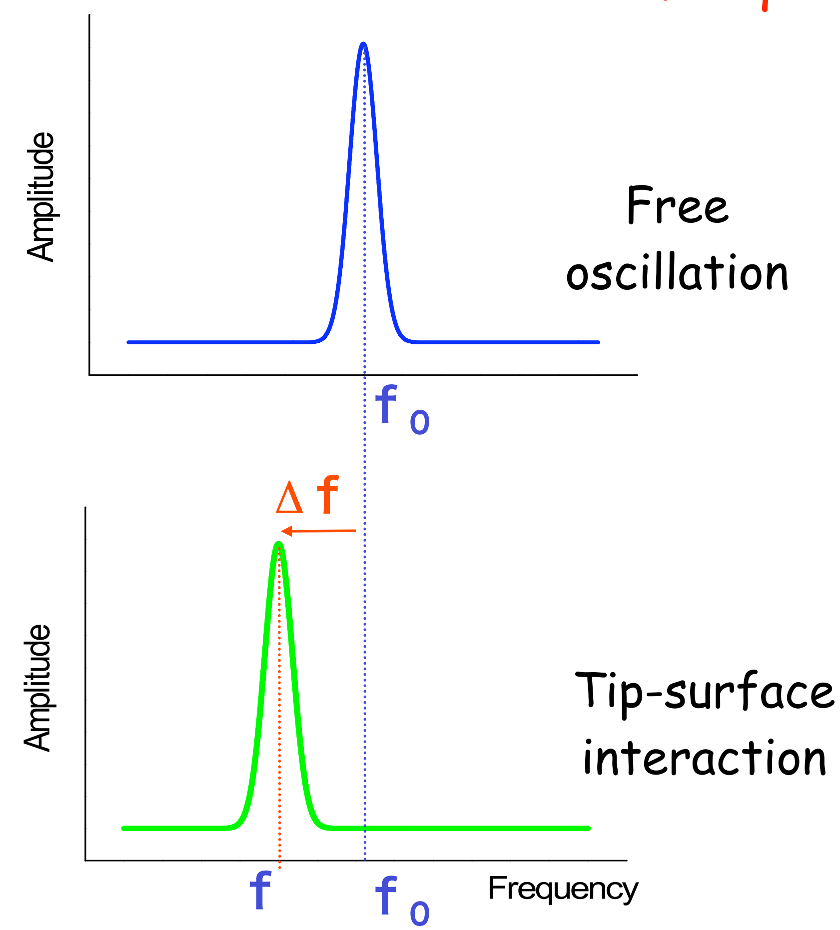


Frequency Modulation Detection Method

- Dynamic force microscopy in UHV:



- The presence of an tip-surface interaction force produces a **shift on the 1st mechanical resonant frequency**



$$\Delta f = f - f_0$$

T. R. Albrecht, P. Grütter, D. Horne, and D. Rugar, J. Appl. Phys. 69, 688 (1991)

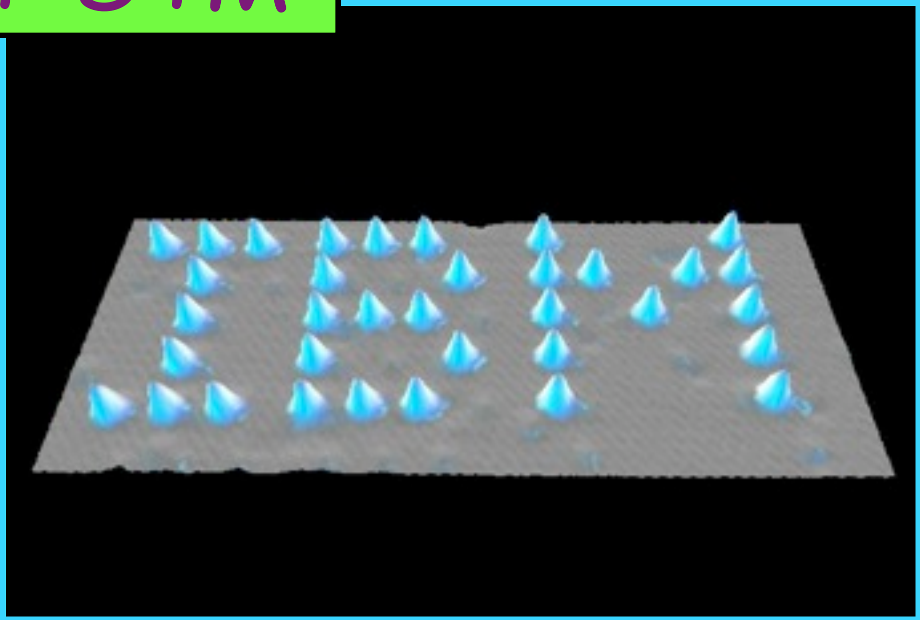
- Dissipation: Additional amount of energy the cantilever requires to keep the oscillation amplitude at resonance constant under a non-conservative tip-surface interaction

Nano structuring atom by atom

at room temperature

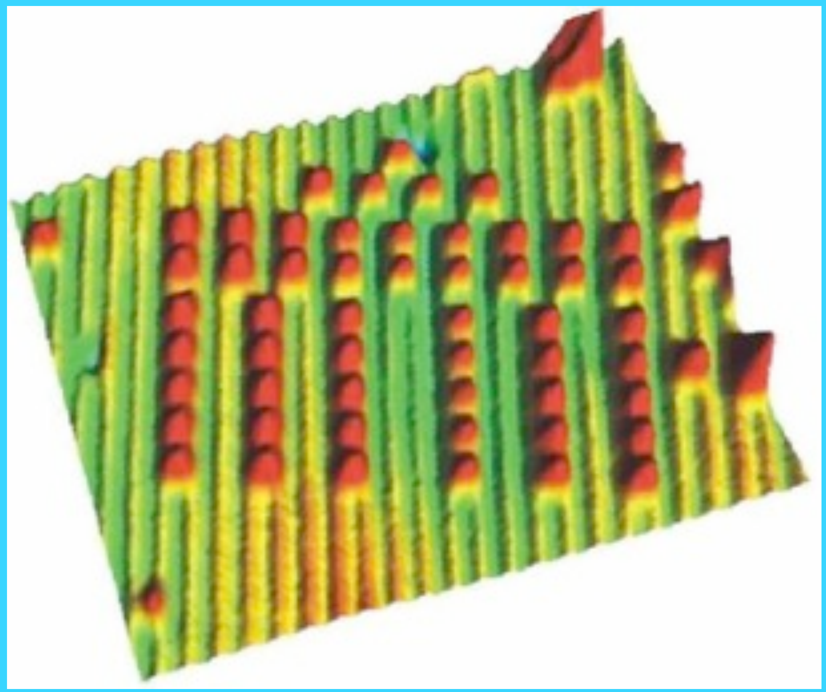
Nano structures by atom manipulation

LT-STM



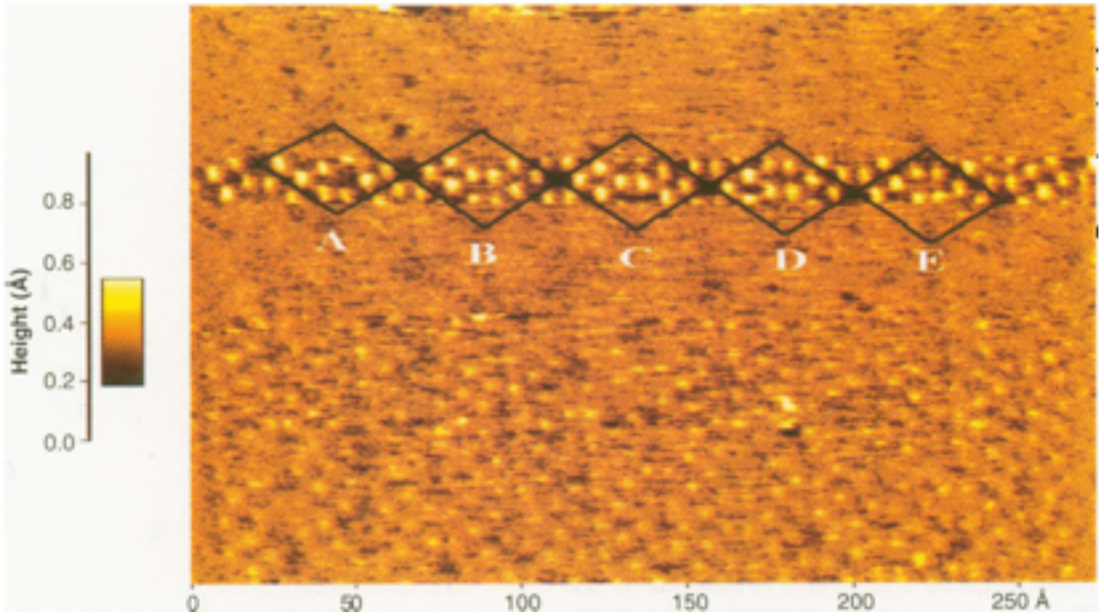
D. M. Eigler, C.P. Lutz et al.

IBM Almaden Research Center (USA)



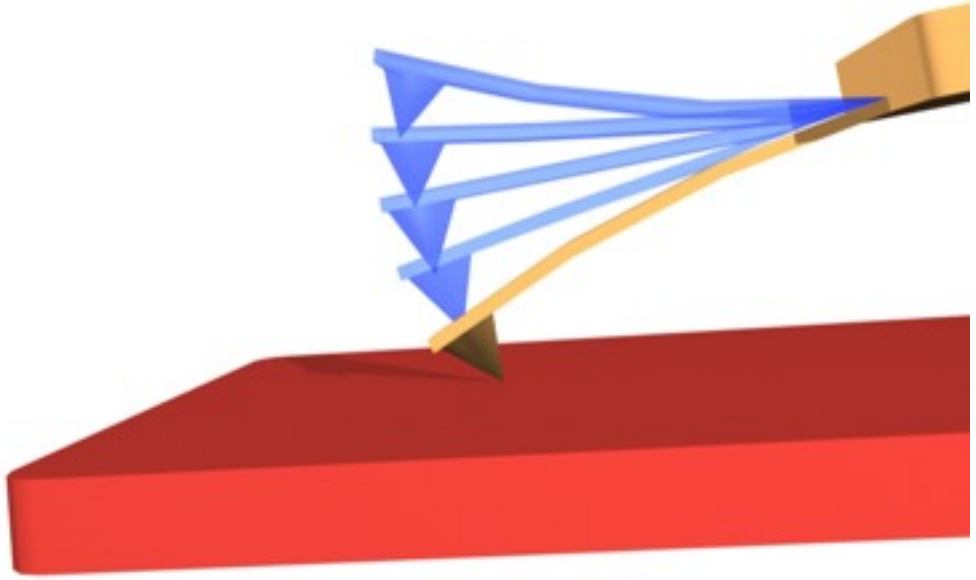
G. Meyer, K.-H. Rieder et al.

Freie Universität Berlin (Germany)



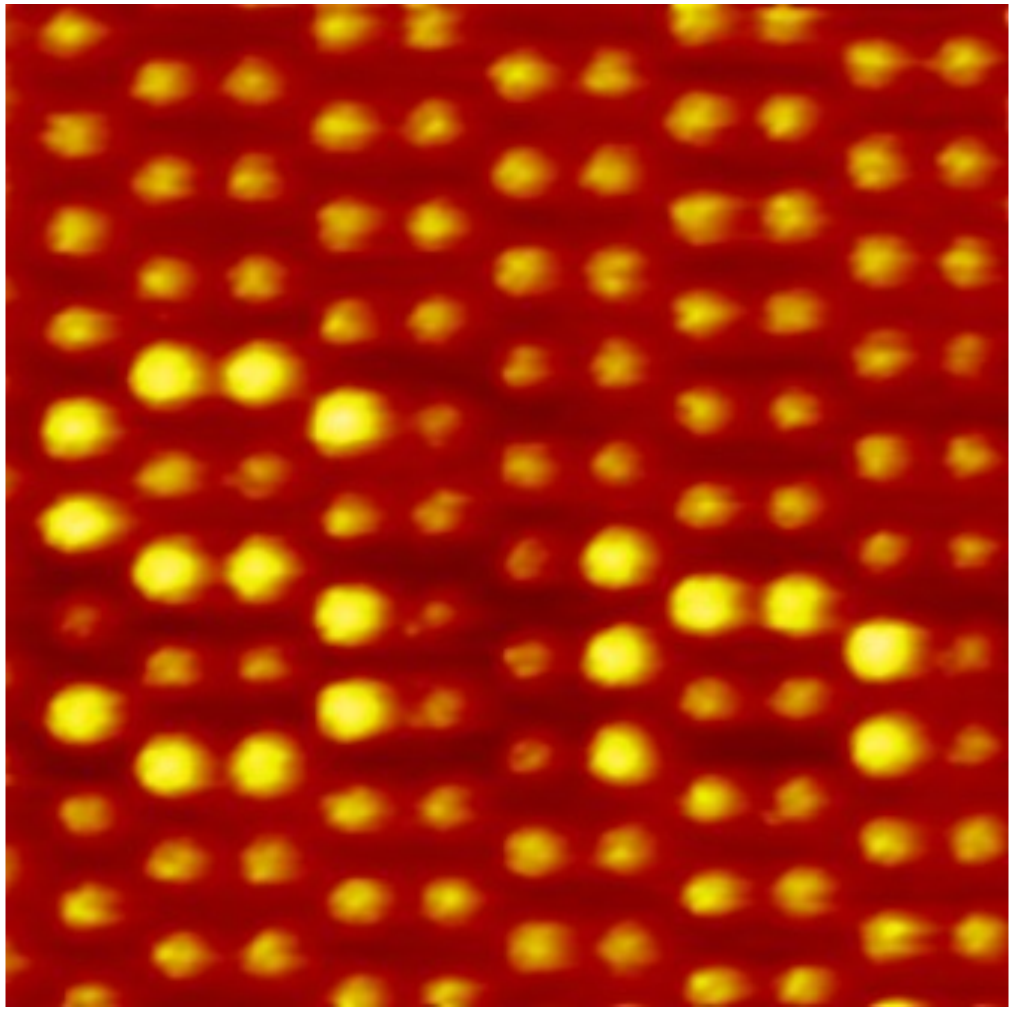
F. J. Giessibl Science **267** 68 (1995).

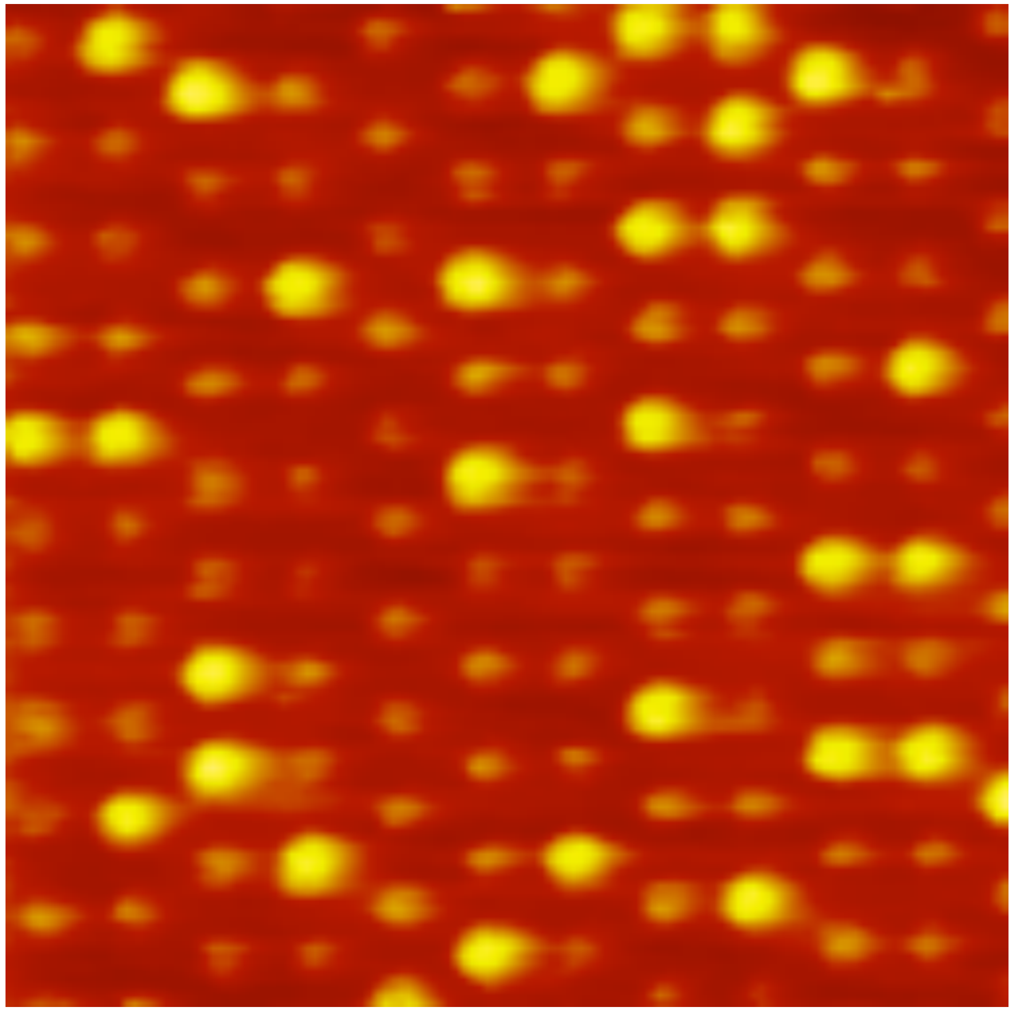
Can we manipulate atoms with the AFM?



First Demonstration of Atom Manipulation with AFM

- First demonstration of the AFM capability for the manipulation of individual atoms

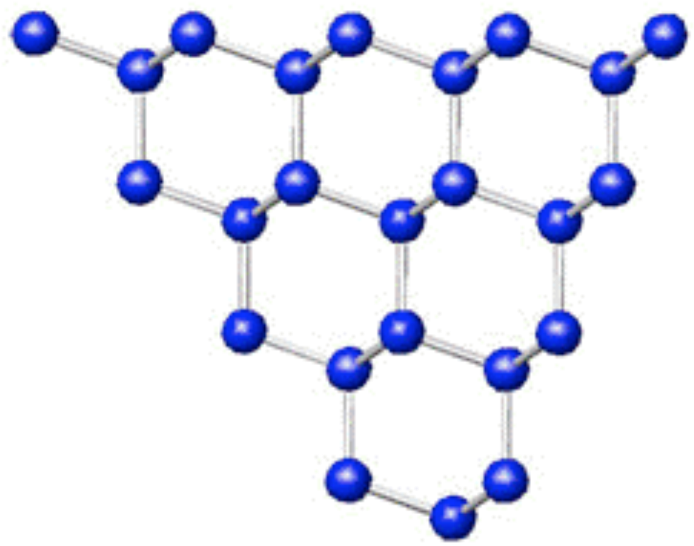


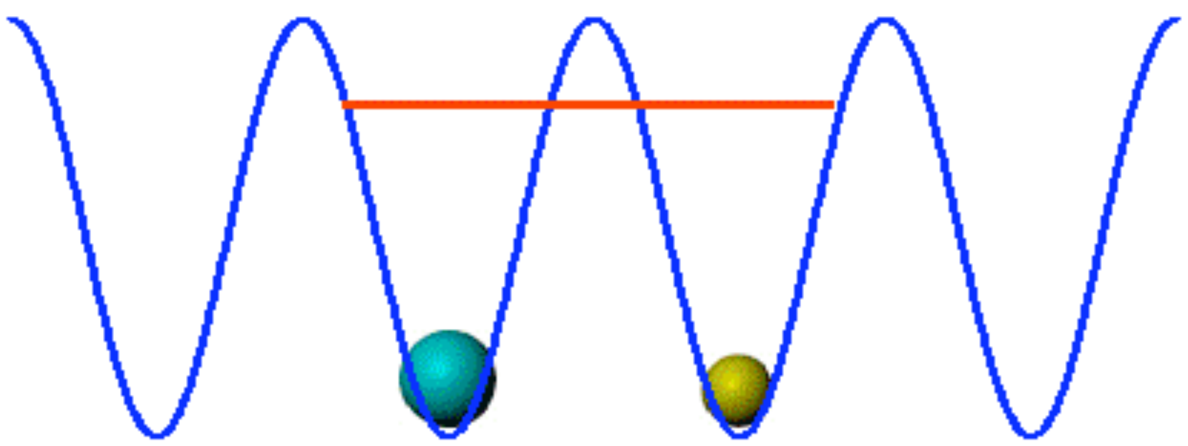


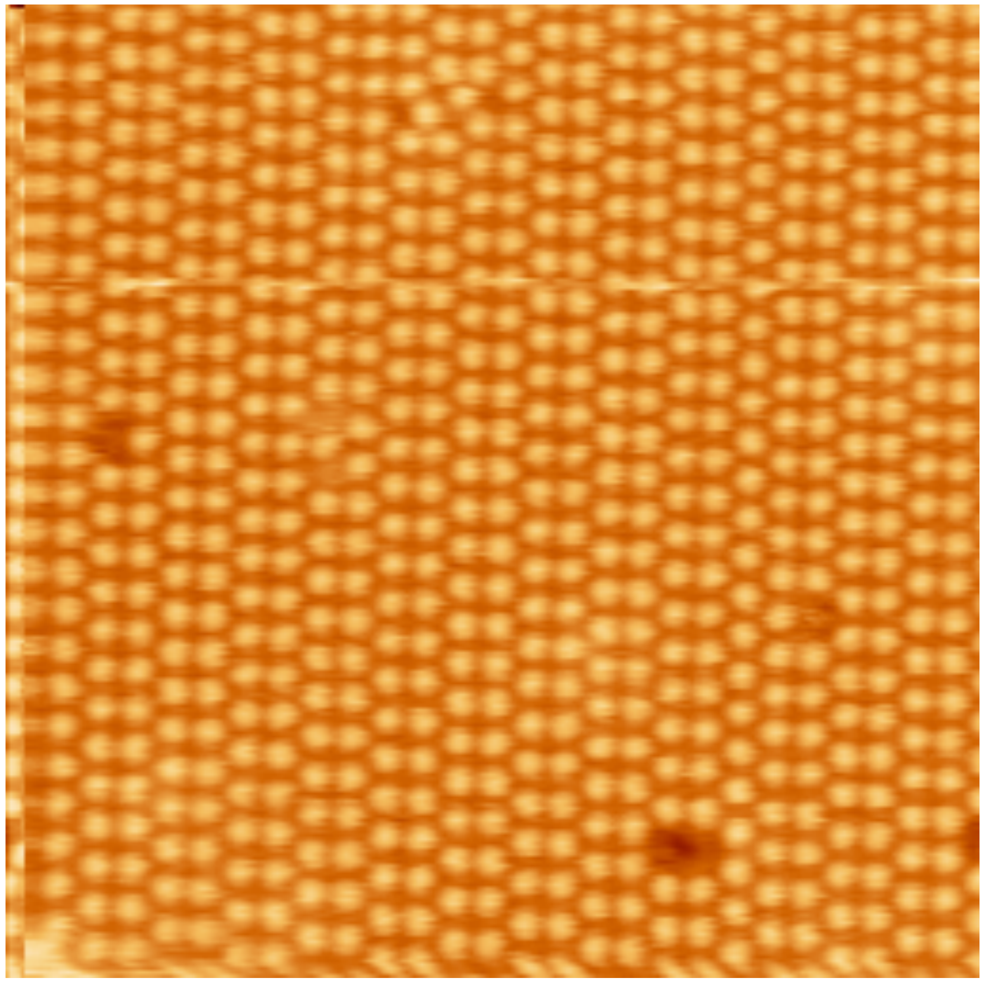
- Substitutional Sn atoms on the Ge(111)-c(2x8) surface
- More than 120 manipulation events in a 9 hours experiment performed **at room temperature**
- These patterns remain stable at the surface for long periods of time: a **minimum mean lifetime of 25 hours** is estimated for these structures

Nature Materials 4 156 (2005)
Nature Nanotecnology 4 803 (2009)

Controlling the natural diffusion energy barriers



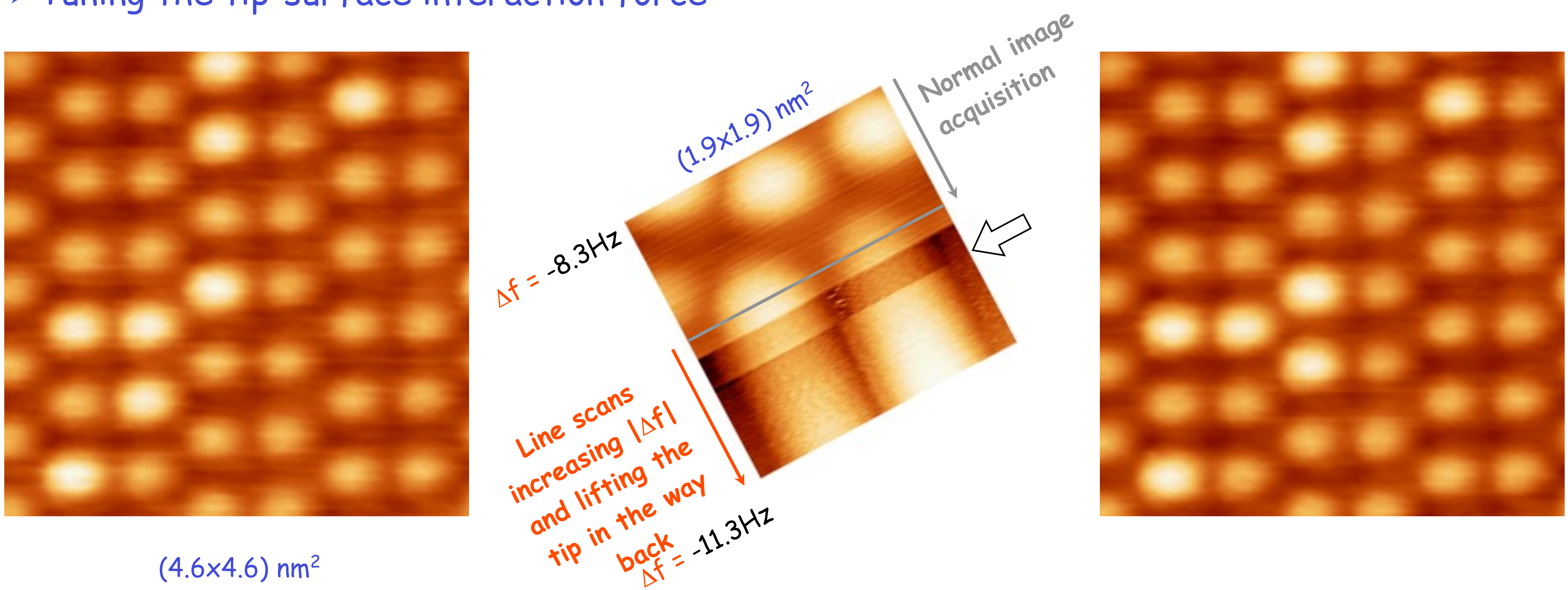




Nature Materials **4** 156 (2005)
Nature Nanotecnology **4** 803 (2009)

Manipulation protocol and mechanism

- Manipulation procedure:
  - ➢ Appropriate selection of the tip scan direction
  - ➢ Tuning the tip-surface interaction force



(4.6x4.6) nm^2

Δf = -8.3Hz

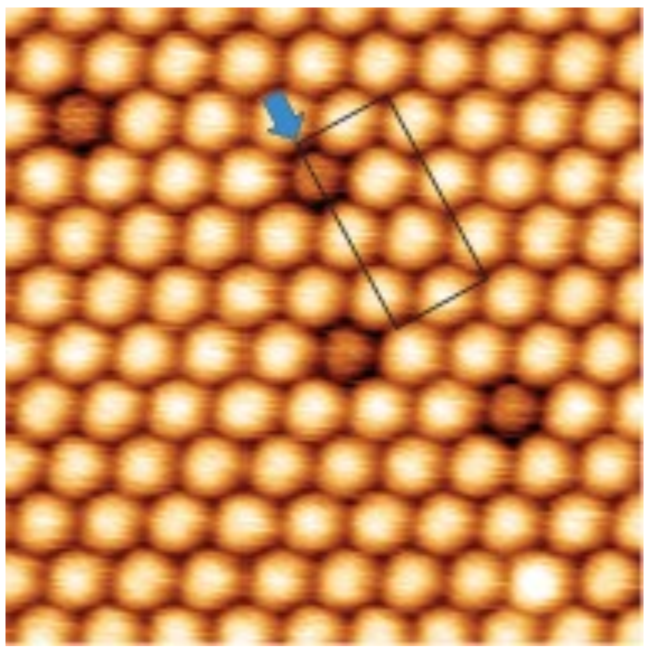
NC-AFM topographic images:

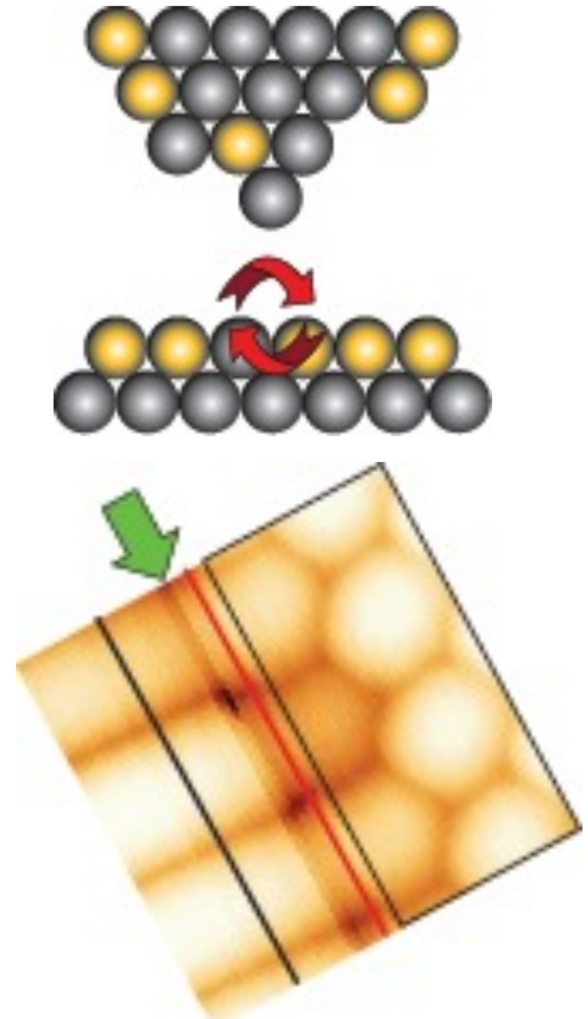
f_0 = 169430.0 Hz A = 17.6 nm K_L = 34.8 N/m RT

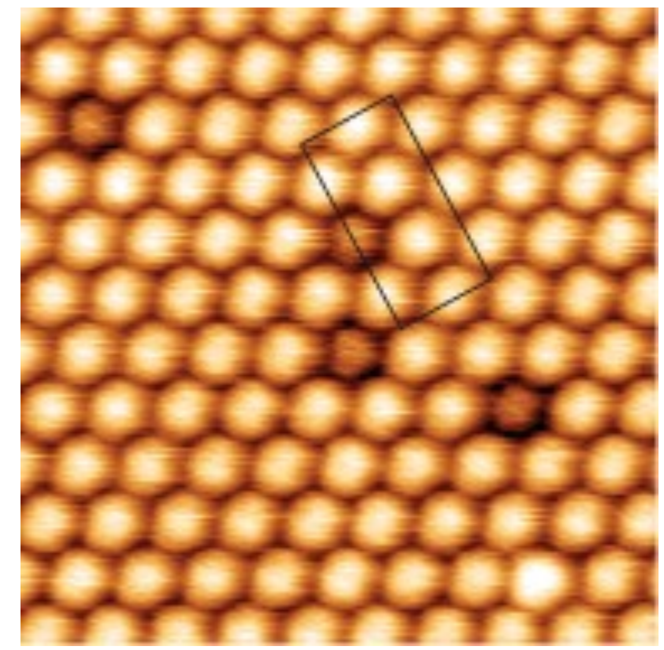
Nature Materials 4 156 (2005)
Nature Nanotecnology 4 803 (2009)

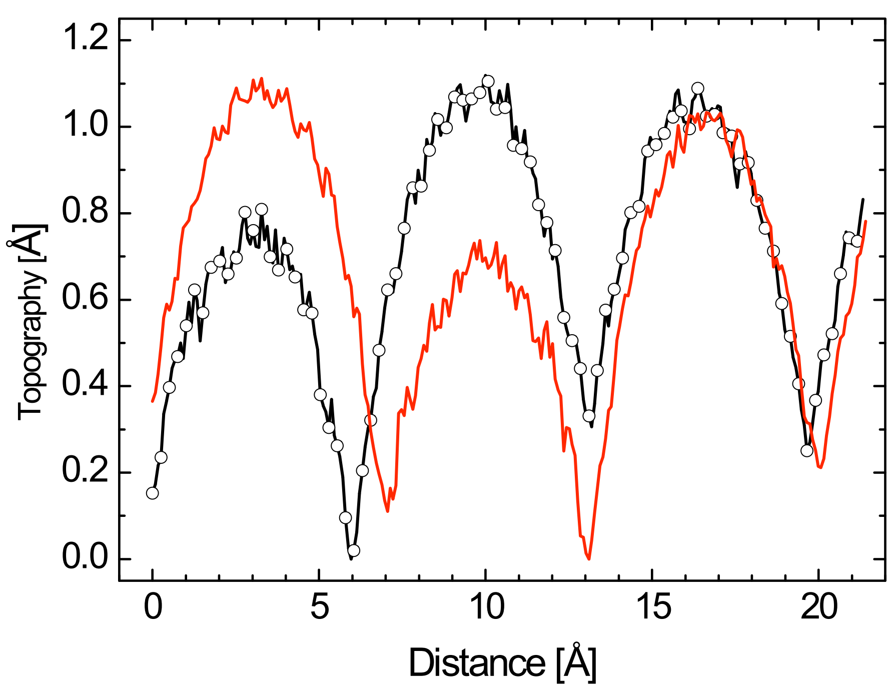
Reproducibility in other surfaces

- Sn/Si(111)-(√3x√3)R30° at room temperature









NC-AFM topographic images:

f_0 = 173993.1 Hz

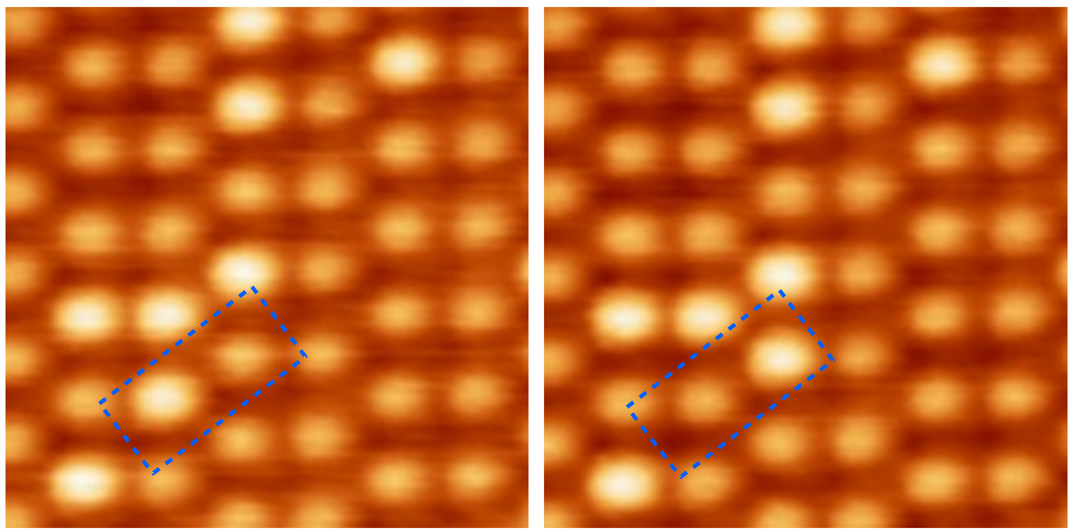
A = 33.1 nm

K_L = 35.4 N/m

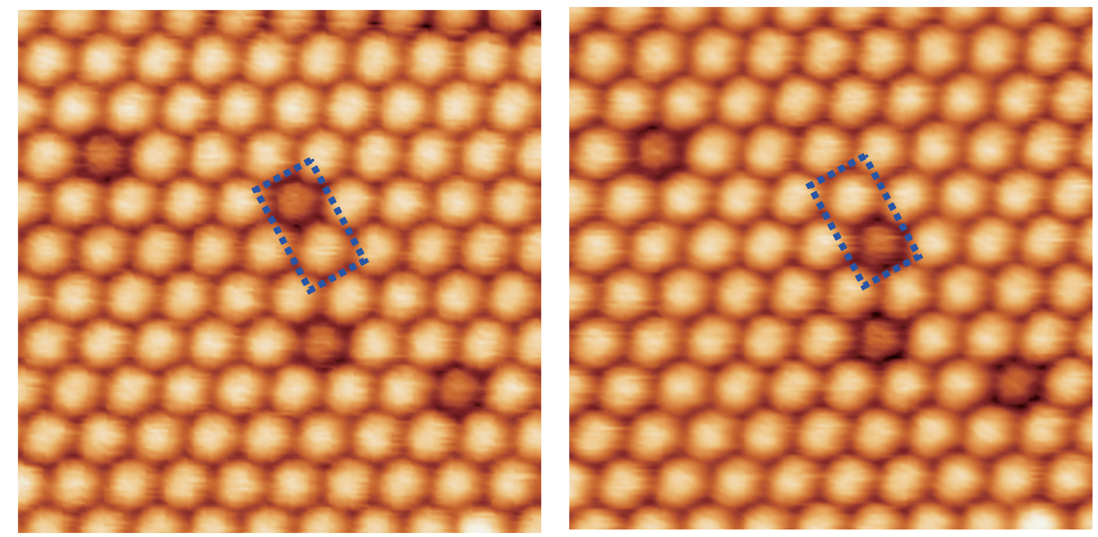
Nature Materials **4** 156 (2005)

Nature Nanotecnology **4** 803 (2009)

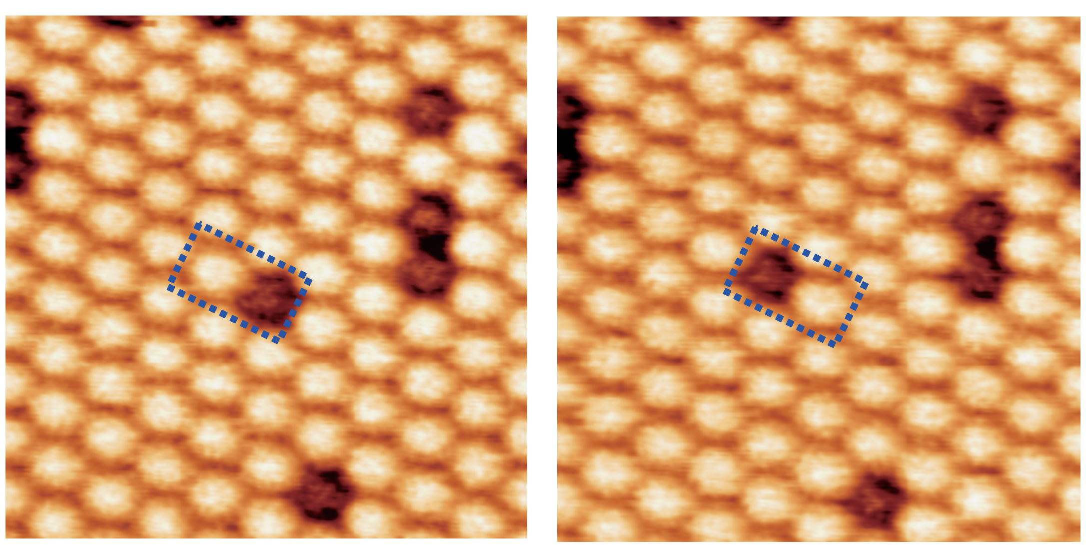
Lateral interchange atom manipulation on different surfaces



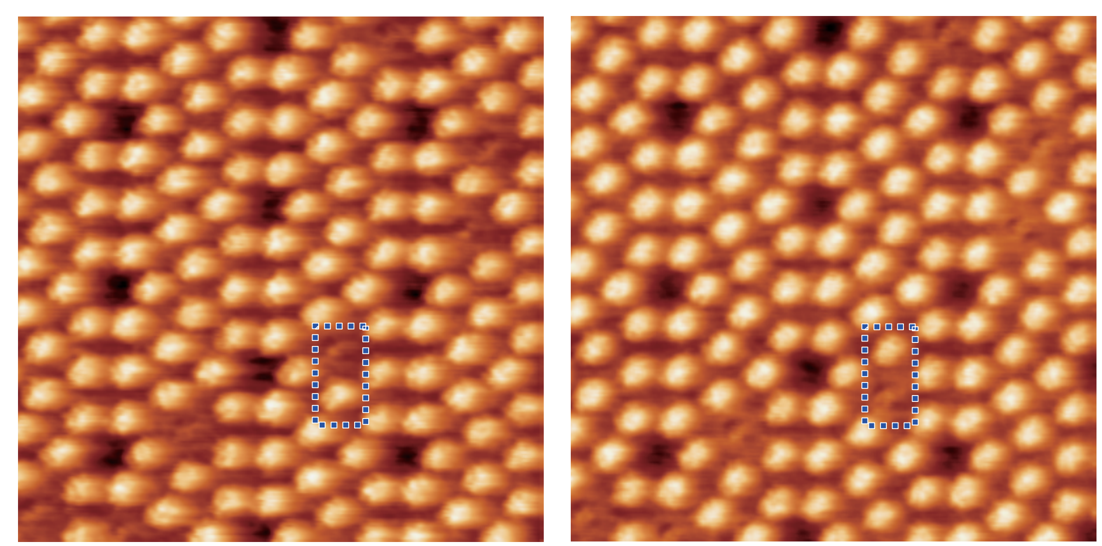
Sn/Ge(111)-c(2x8)



Sn/Si(111)-$(\sqrt{3}\times\sqrt{3})$R30



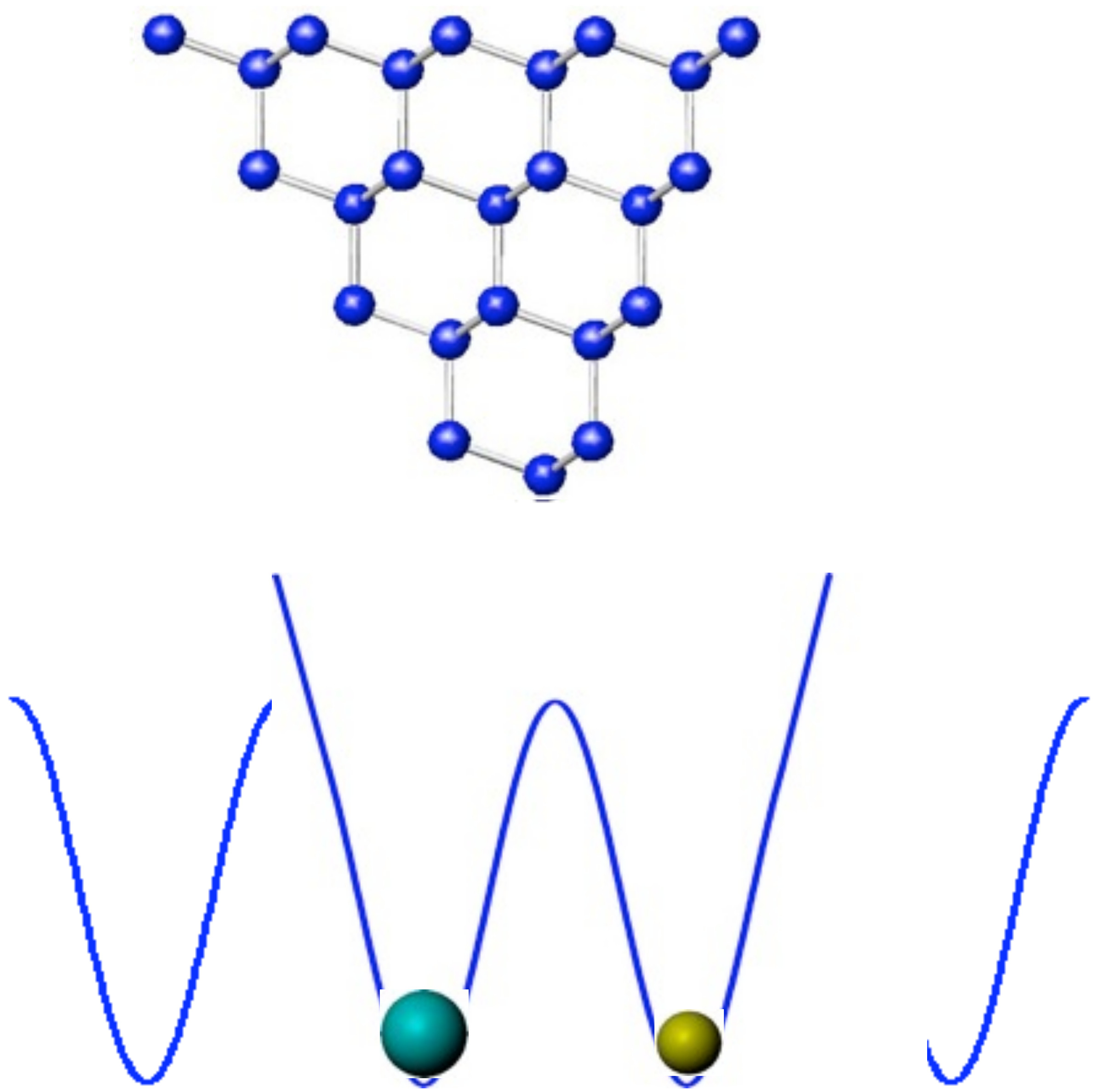
In/Si(111)-$(\sqrt{3}\times\sqrt{3})$R30

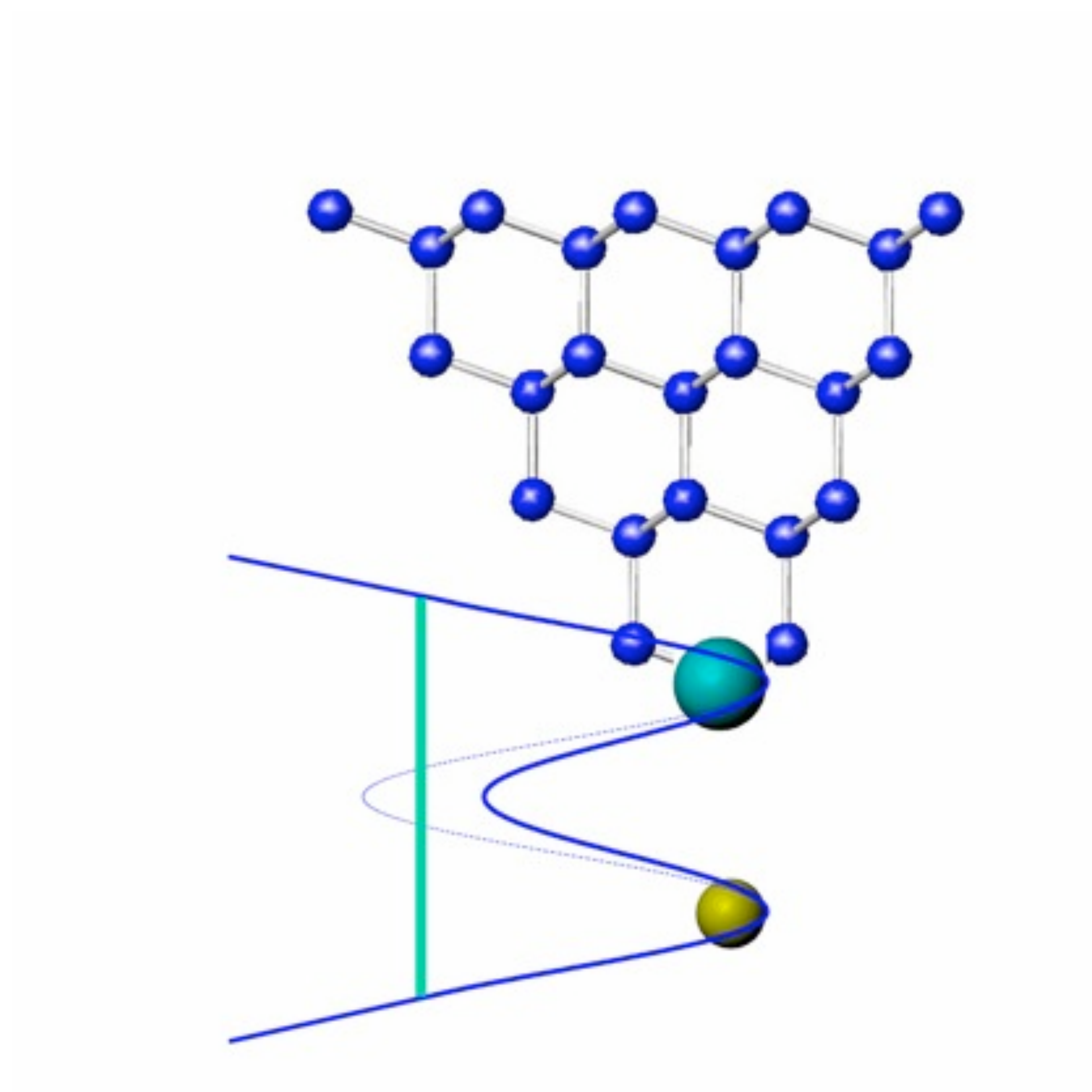


Sb/Si(111)-(7x7)

Nature Materials **4** 156 (2005)
Nature Nanotecnology **4** 803 (2009)

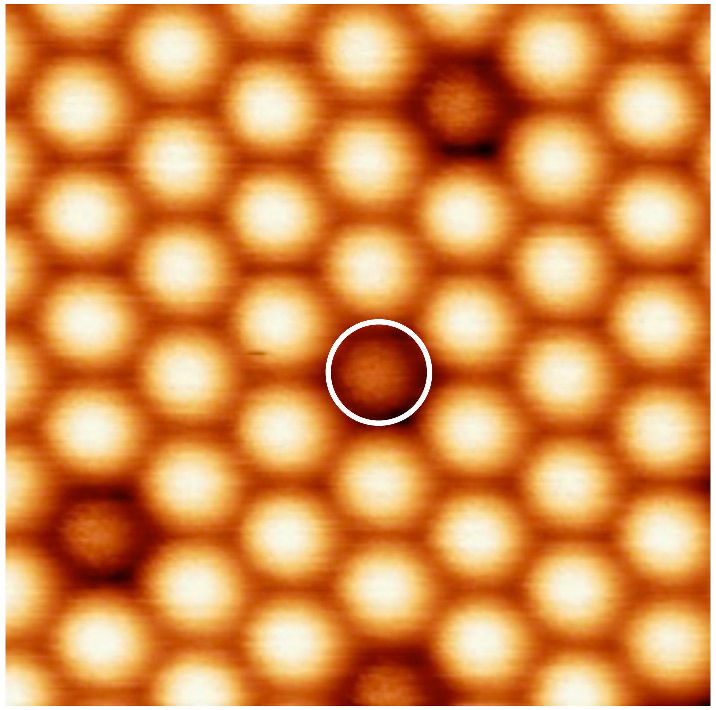
Interchange atom manipulation

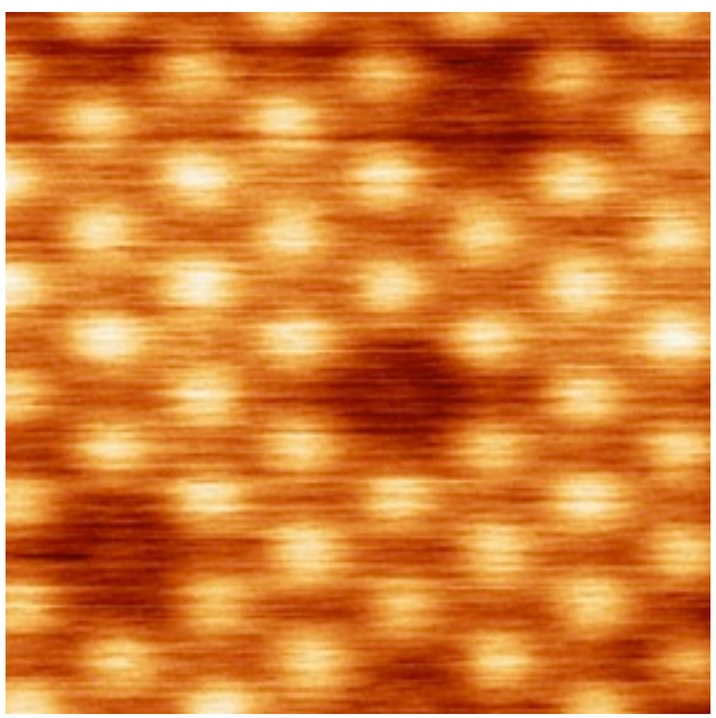


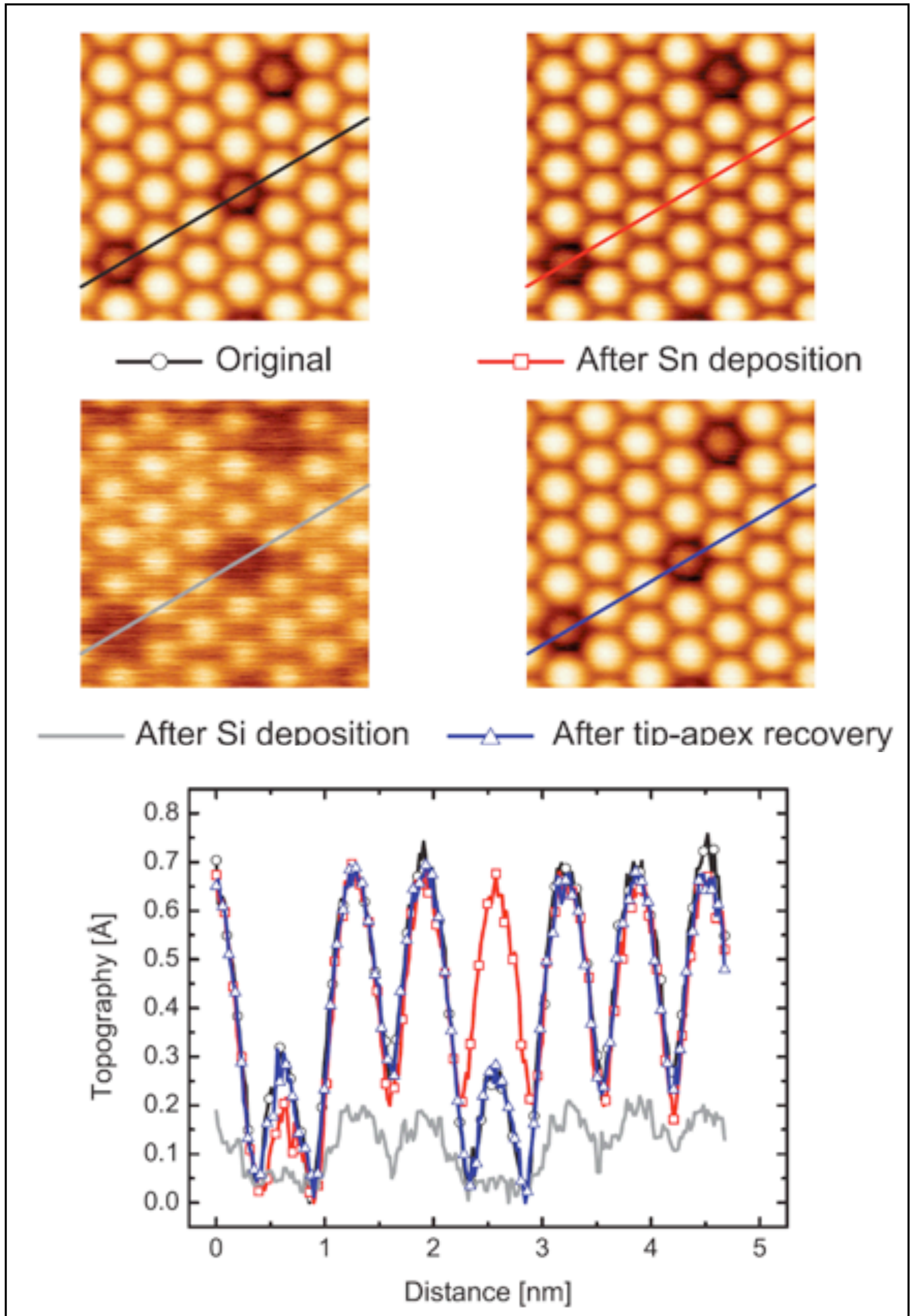


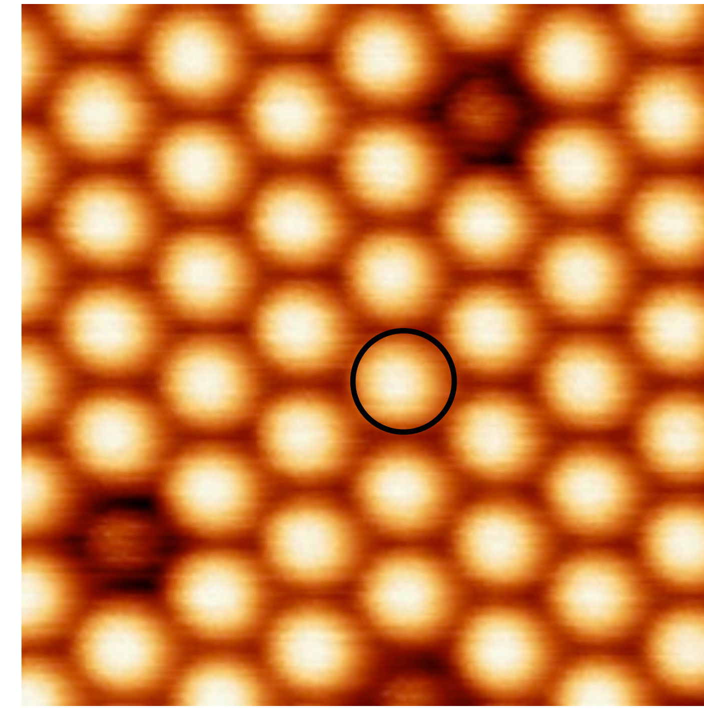
Vertical interchange manipulation

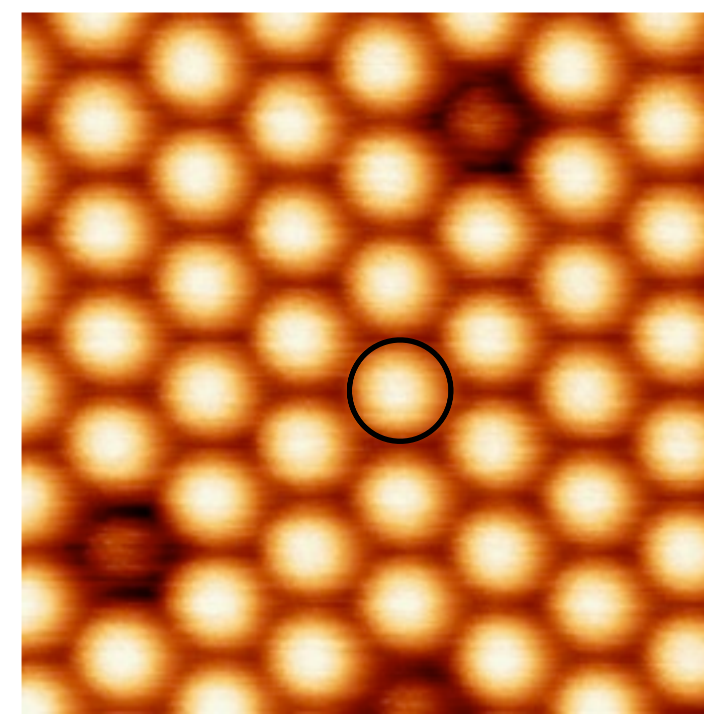
Vertical interchange manipulations in the Sn/Si











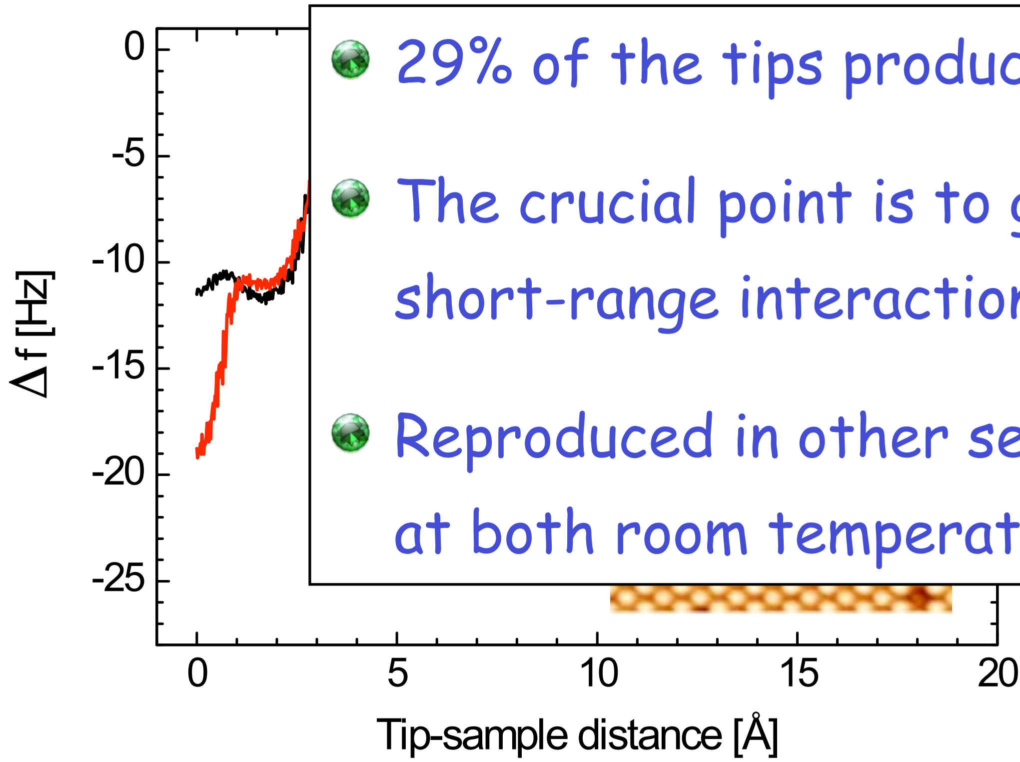
Science **322** 413 (2008)

Nature Nanotecnology **4** 803 (2009)

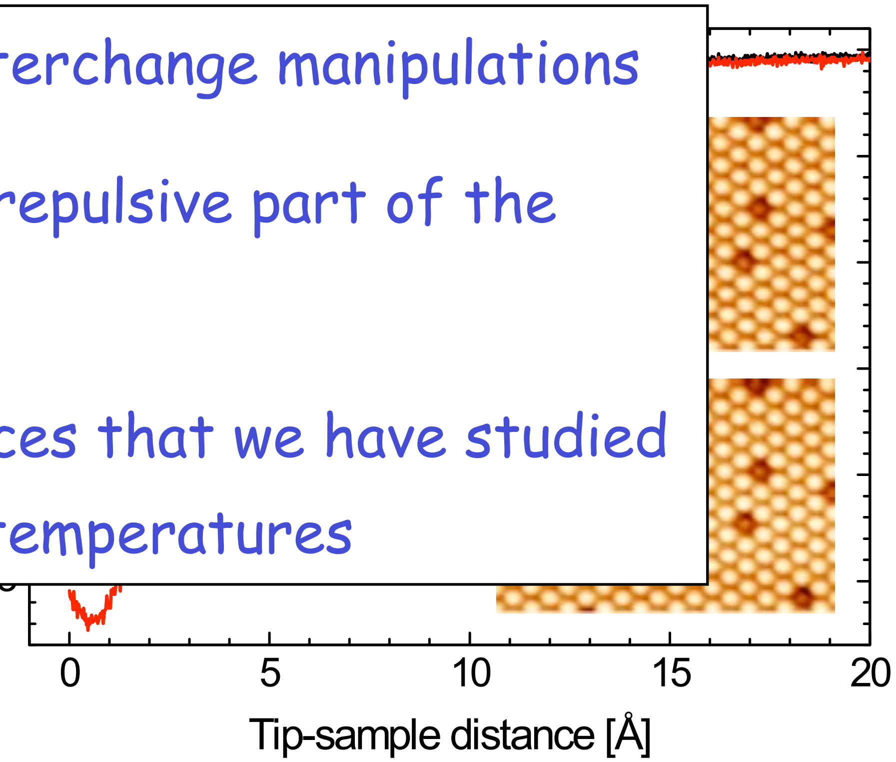
f_0 = 193738.0 Hz; A = 21.9 nm; K_L = 48.8 N/m; Δf = -7.3Hz

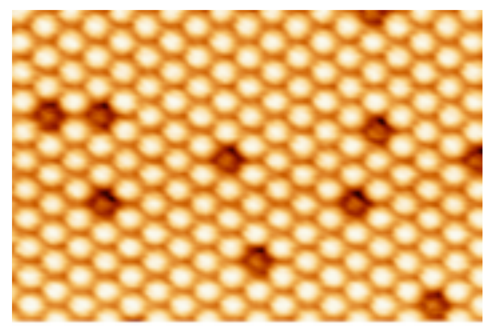
Reproducibility of these manipulations

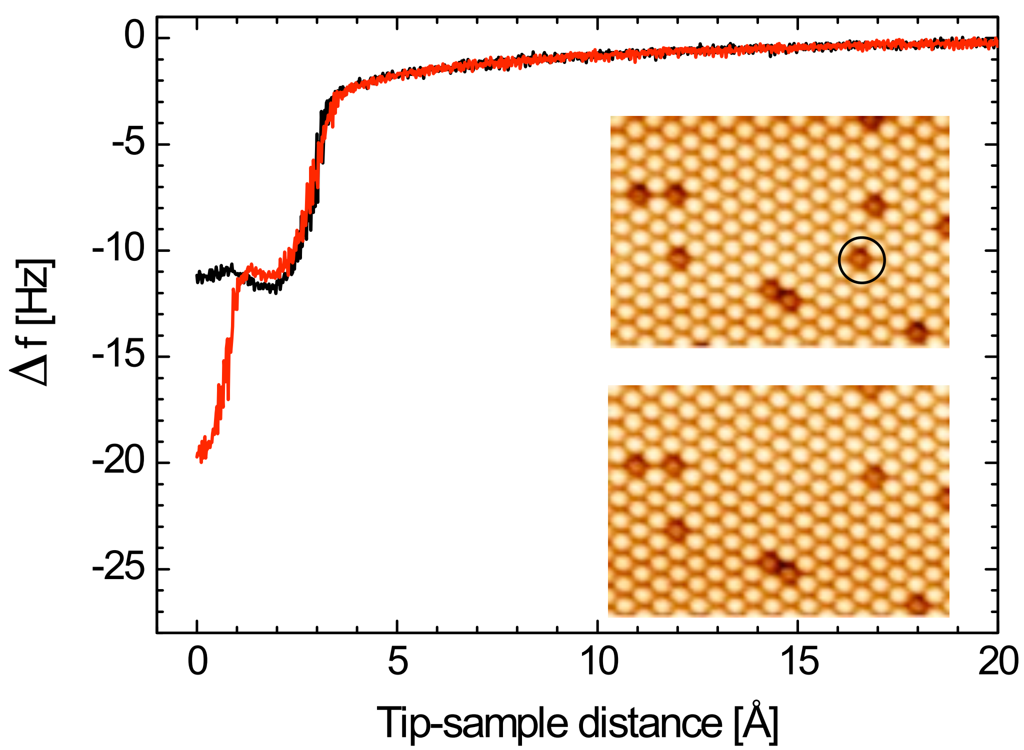
- Consecutive alternate vertical interchange manipulations

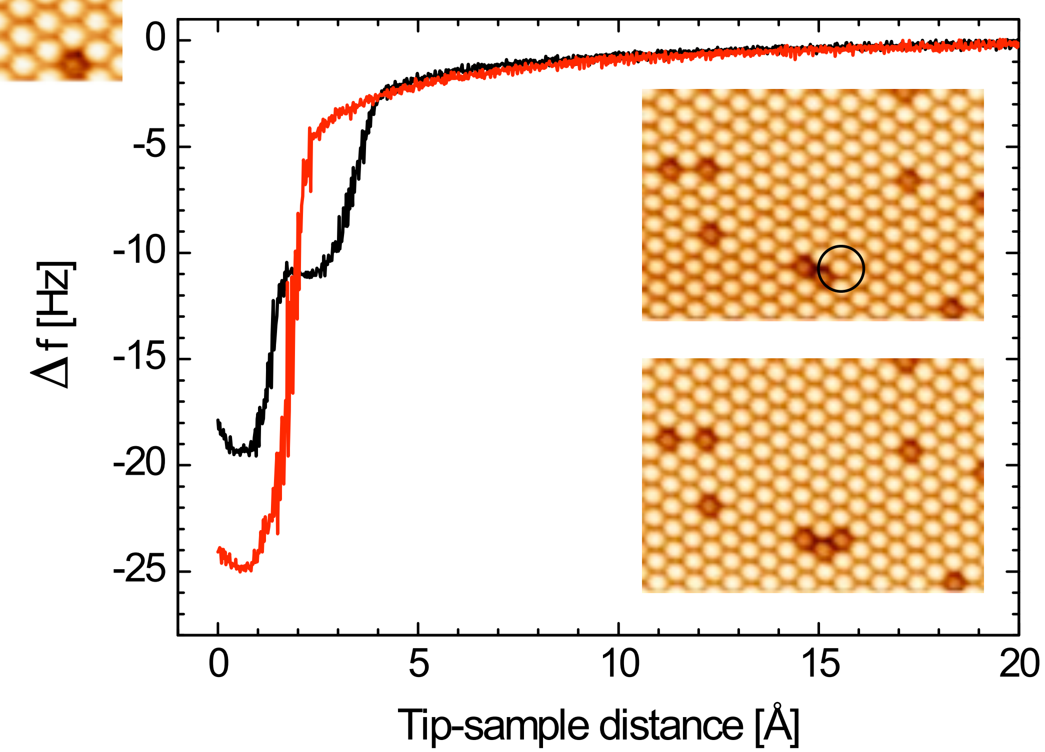


- 29% of the tips produce these vertical interchange manipulations
- The crucial point is to gently explore the repulsive part of the short-range interaction
- Reproduced in other semiconductor surfaces that we have studied at both room temperature and cryogenic temperatures





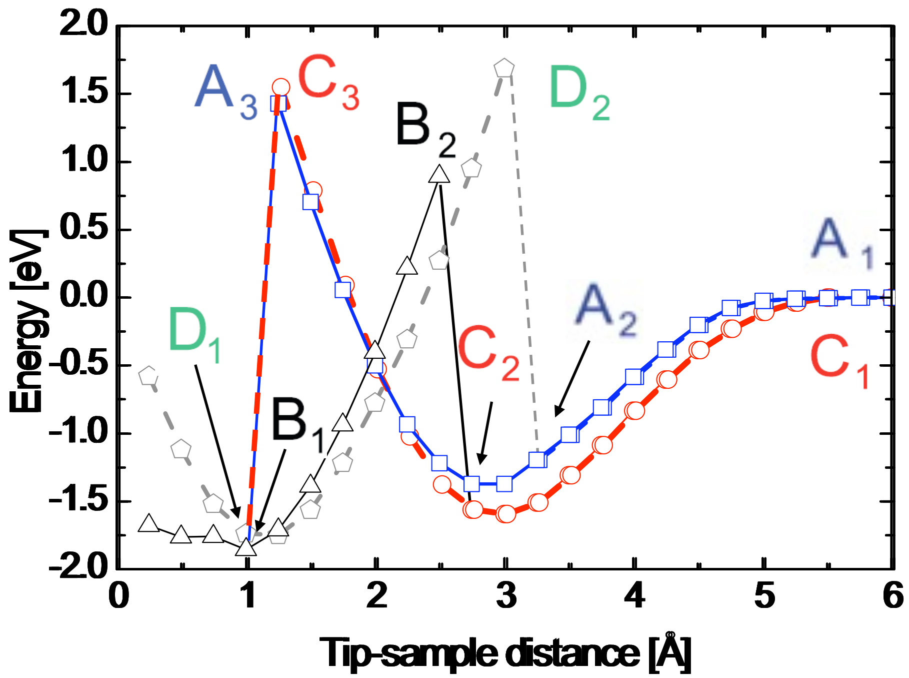


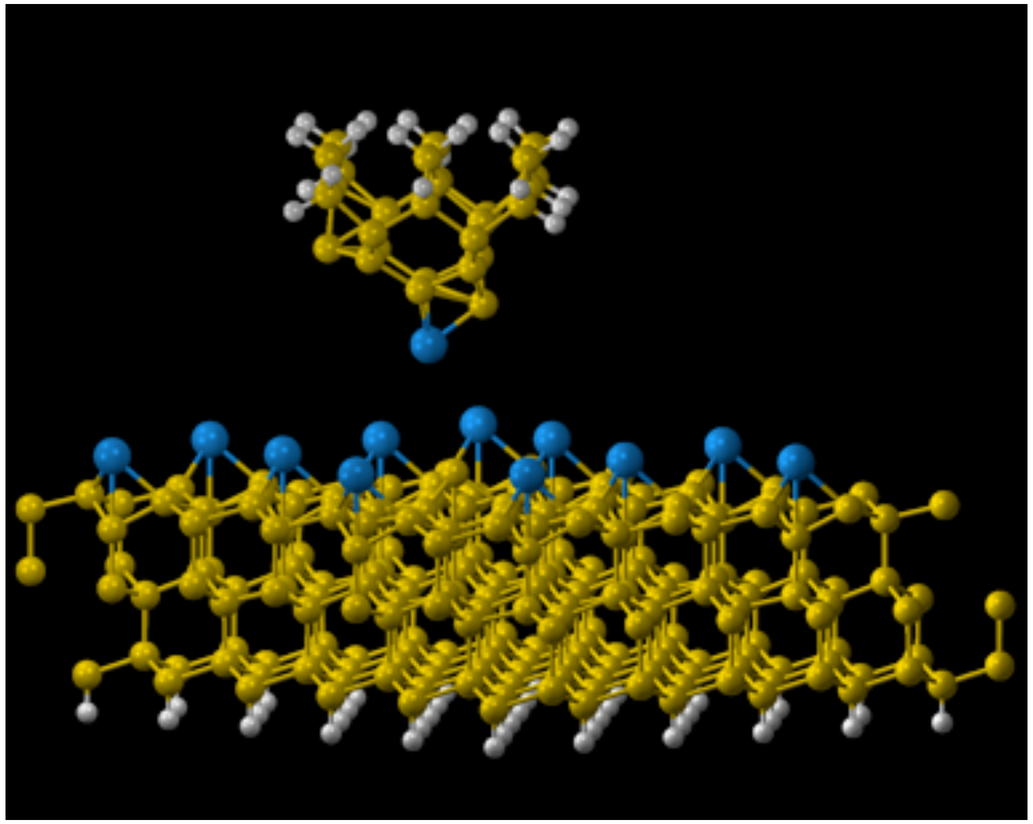


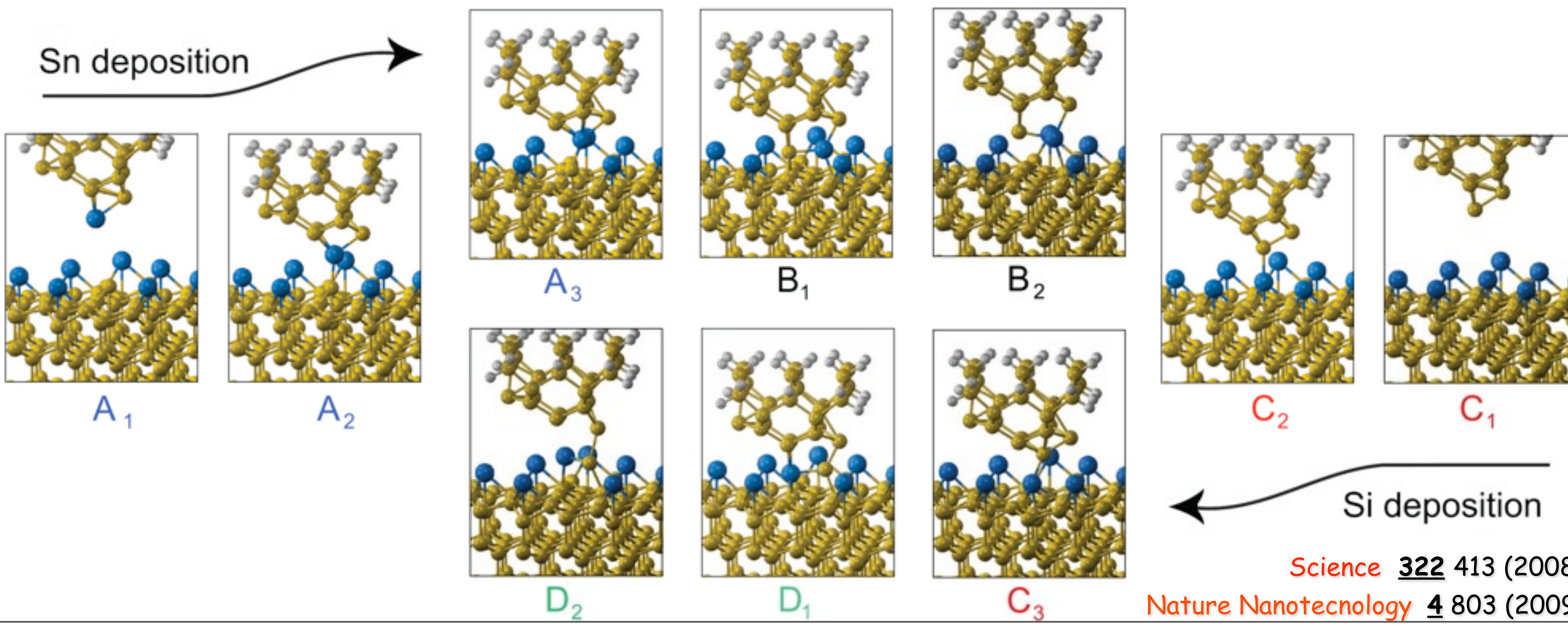
Science **322** 413 (2008)
Nature Nanotecnology **4** 803 (2009)

f_0 = 162299.7 Hz; A = 21.9 nm; K_L = 28.7 N/m; Δf = -3.1 Hz

Manipulation mechanism: DFT simulations



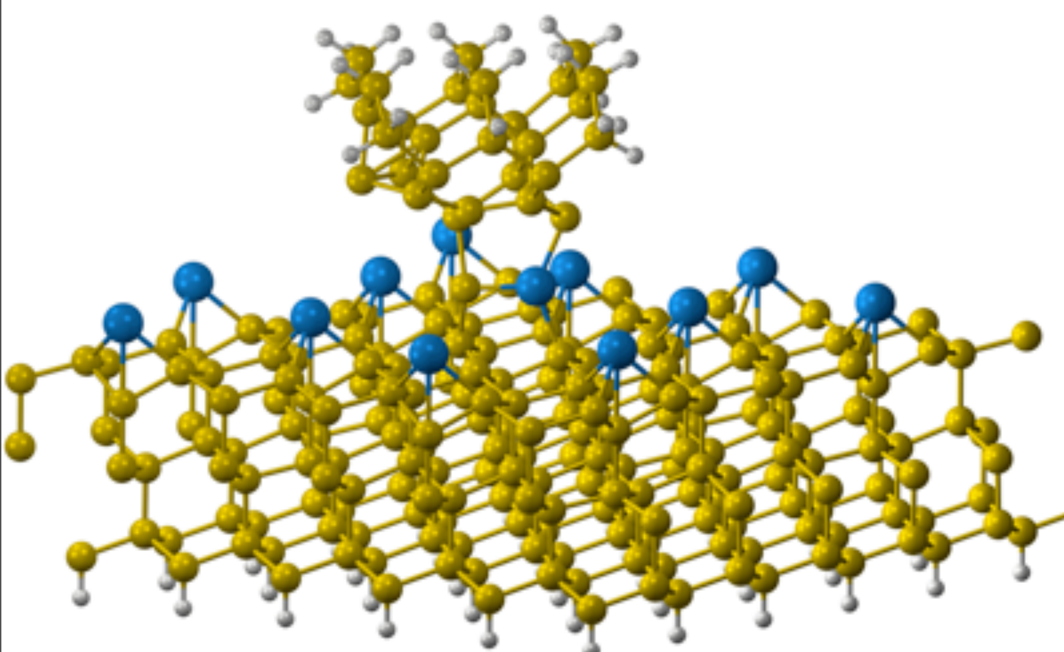


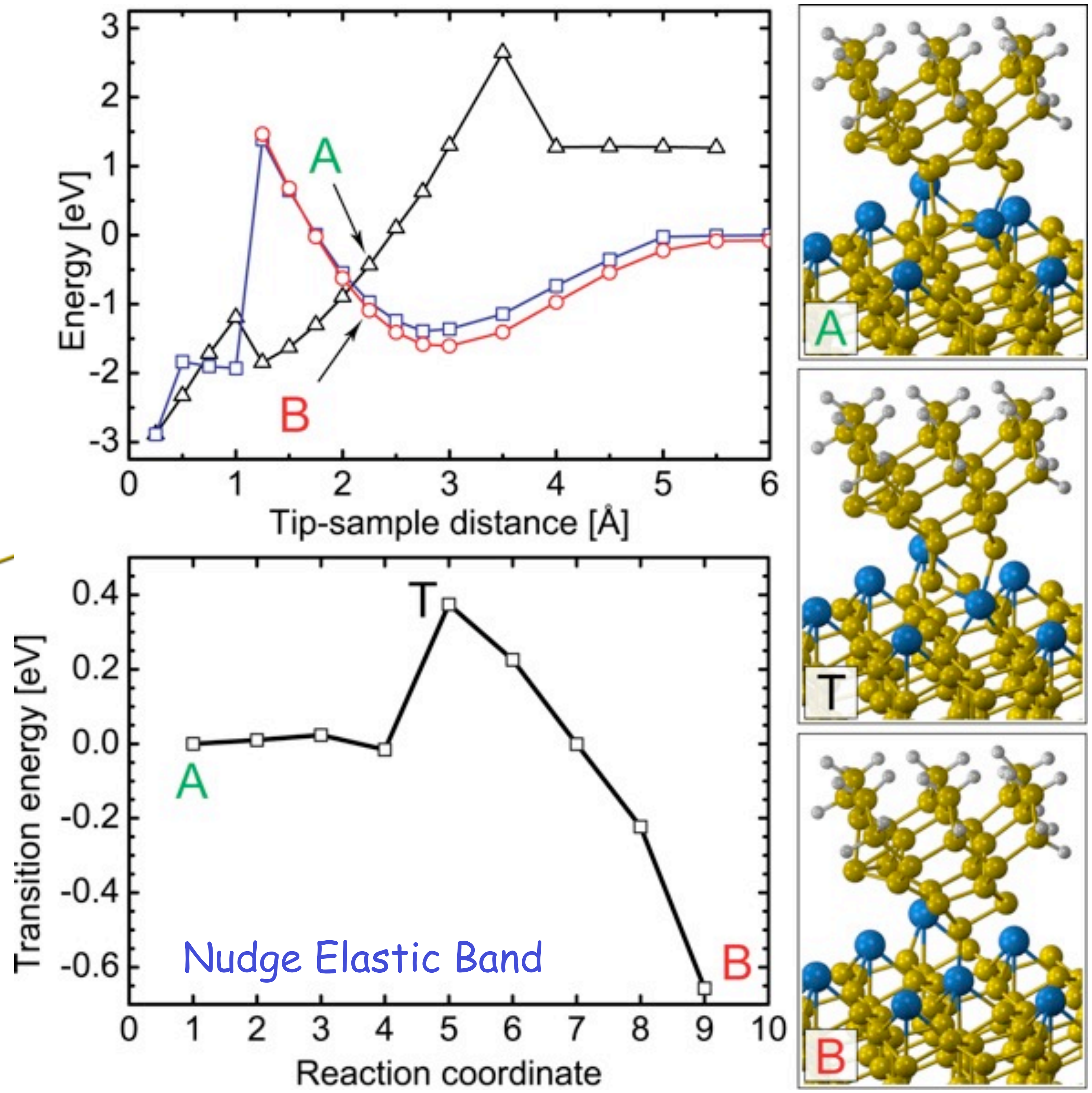


Science **322** 413 (2008)

Nature Nanotecnology **4** 803 (2009)

Typical barriers involved in these vertical manipulations



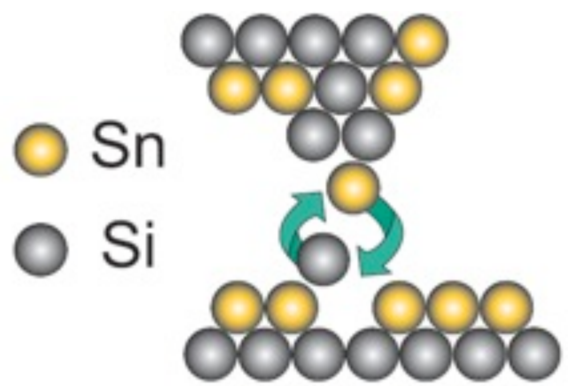


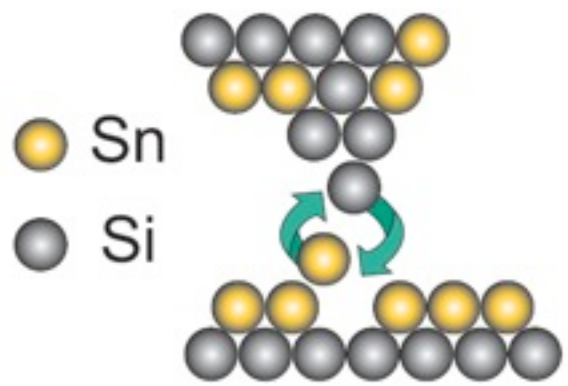
Science **322** 413 (2008)

Nature Nanotecnology **4** 803 (2009)

Atomic pencil

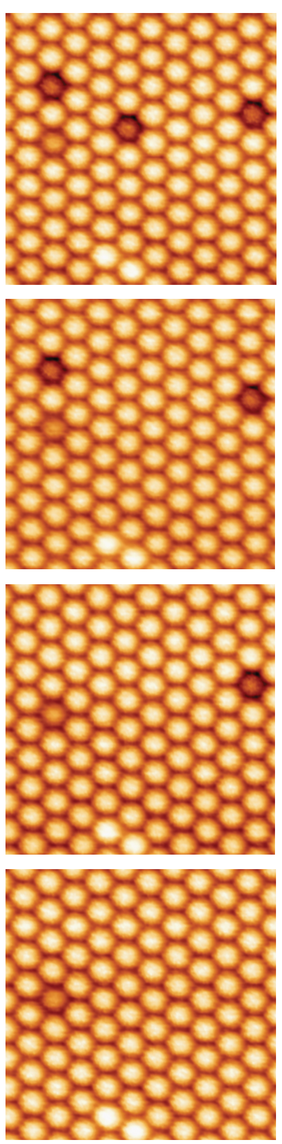
- We could, in principle, "write" with atoms

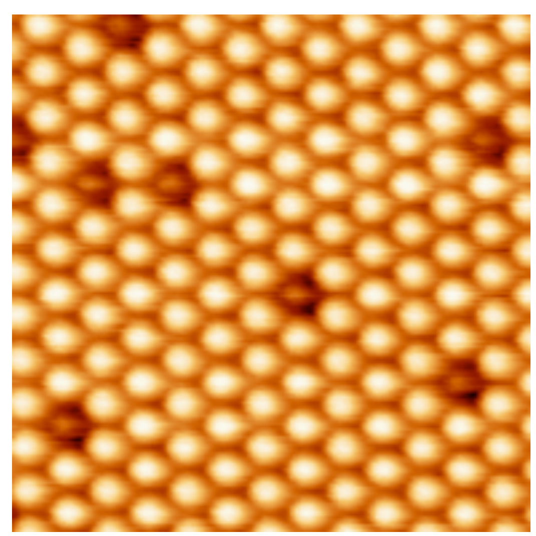




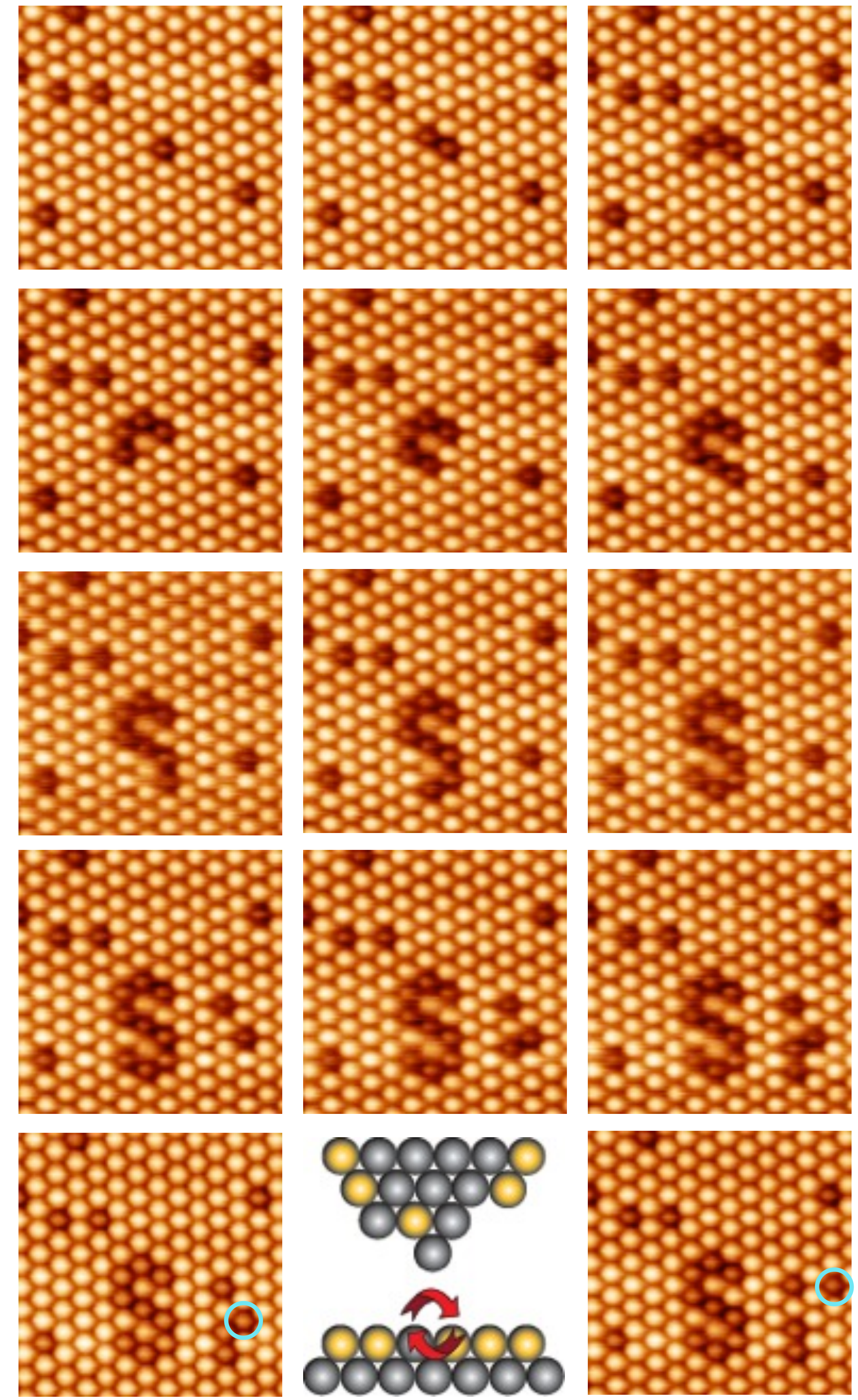
Erase (Sn deposition)

Plot (Si deposition)





Construction time: 1.5 hours

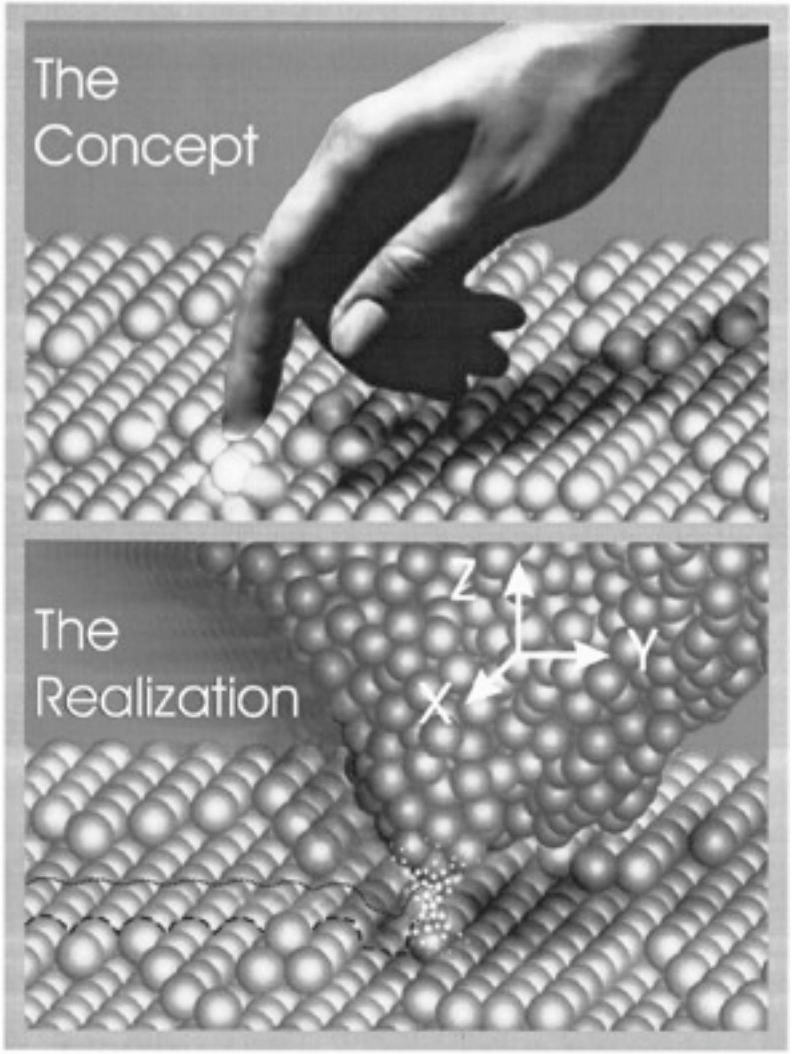


Science **322** 413 (2008)

Nature Nanotecnology **4** 803 (2009)

Chemical identification of individual atoms with AFM

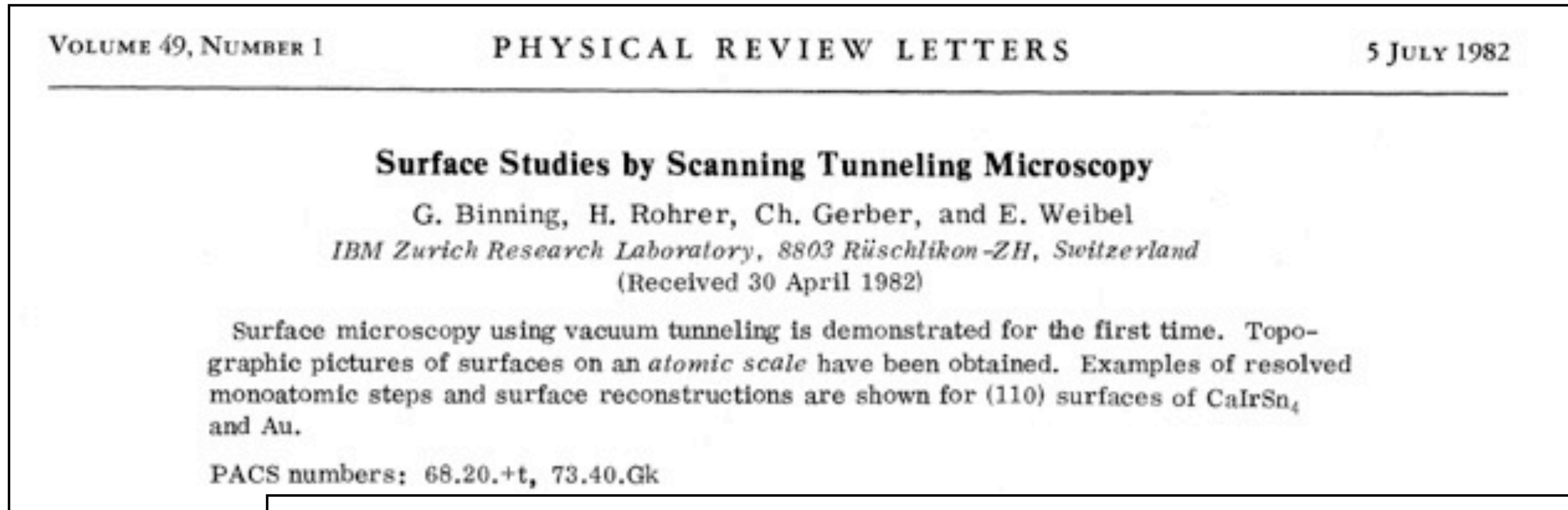
Searching for atomic chemical specificity with SPM



"In Touch With Atoms"

G. Bining & H. Rohrer

Rev. Mod. Phys. **71** S324, (1999)



VOLUME 49, NUMBER 1 PHYSICAL REVIEW LETTERS 5 JULY 1982

Surface Studies by Scanning Tunneling Microscopy

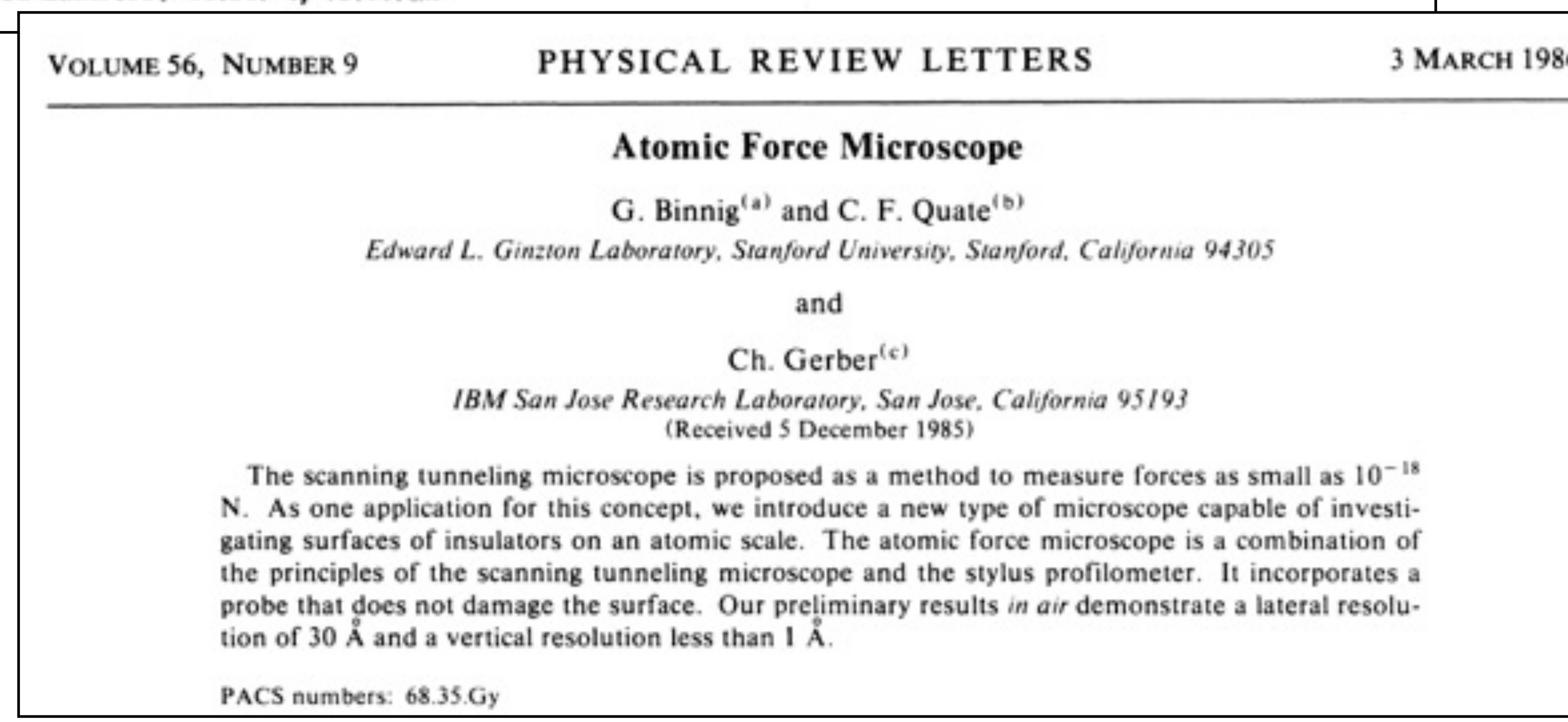
G. Binning, H. Rohrer, Ch. Gerber, and E. Weibel

IBM Zurich Research Laboratory, 8803 Rüschlikon-ZH, Switzerland

(Received 30 April 1982)

Surface microscopy using vacuum tunneling is demonstrated for the first time. Topographic pictures of surfaces on an *atomic scale* have been obtained. Examples of resolved monoatomic steps and surface reconstructions are shown for (110) surfaces of $CaIrSn_4$ and Au.

PACS numbers: 68.20.+t, 73.40.Gk



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)

The scanning tunneling microscope is proposed as a method to measure forces as small as 10^{-18} N. As one application for this concept, we introduce a new type of microscope capable of investigating surfaces of insulators on an atomic scale. The atomic force microscope is a combination of the principles of the scanning tunneling microscope and the stylus profilometer. It incorporates a probe that does not damage the surface. Our preliminary results *in air* demonstrate a lateral resolution of 30 Å and a vertical resolution less than 1 Å.

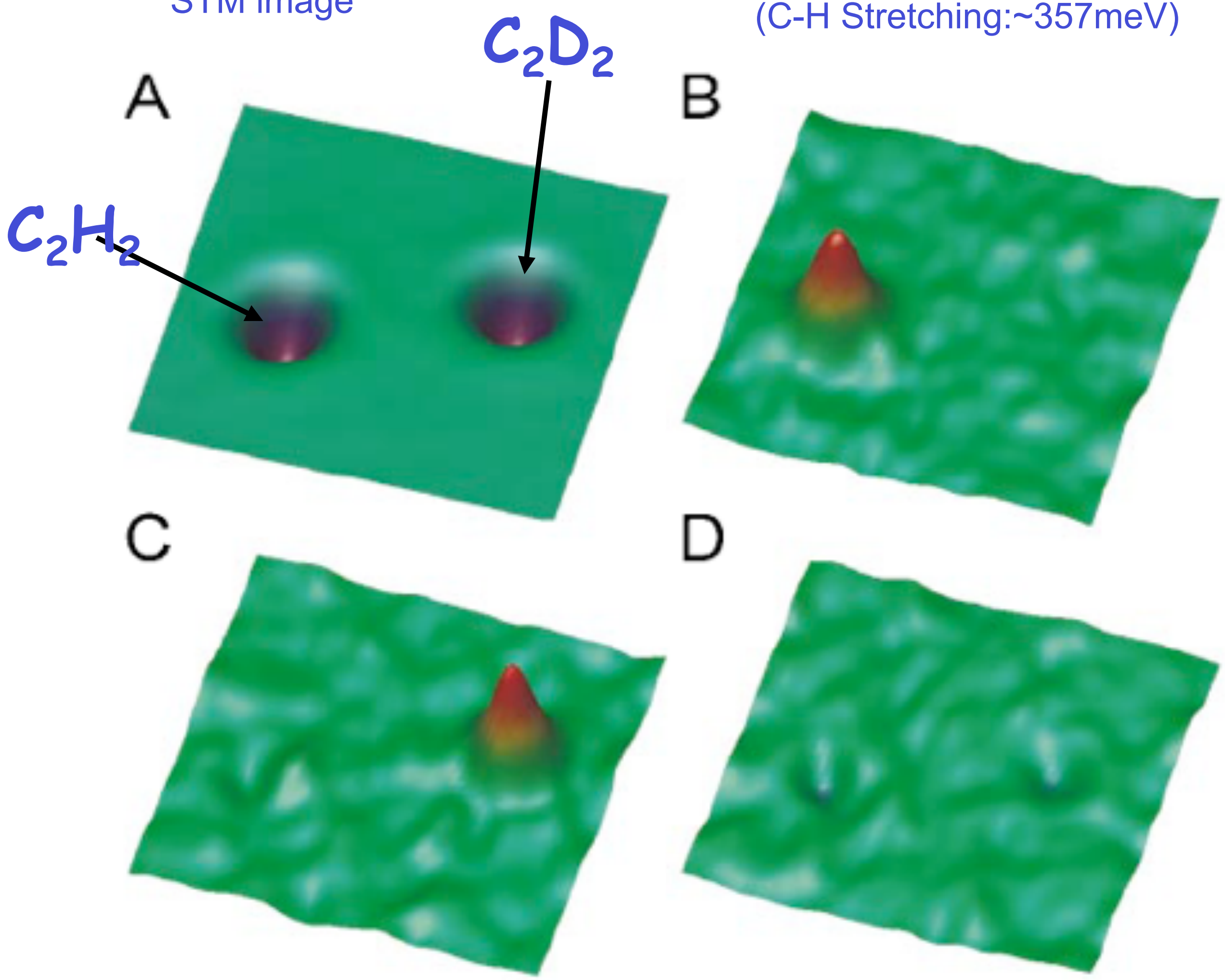
PACS numbers: 68.35.Gy

Chemical identification with STM: IETS

Kondo resonance, quantum Spin excitation & Single Molecule Vibrational Spectroscopy

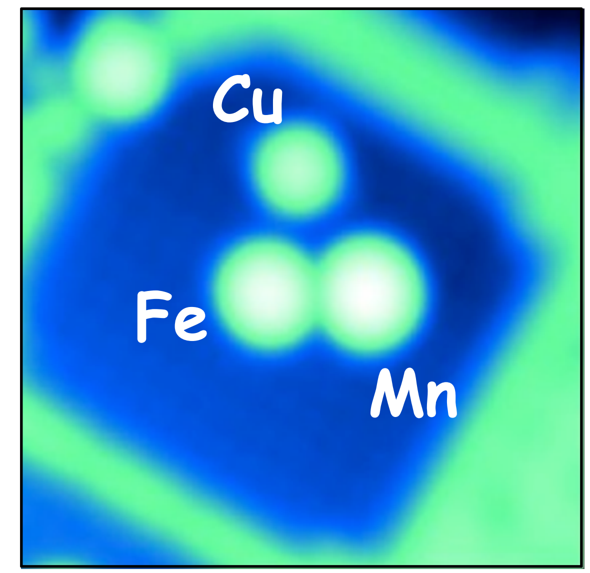
Constant current STM image

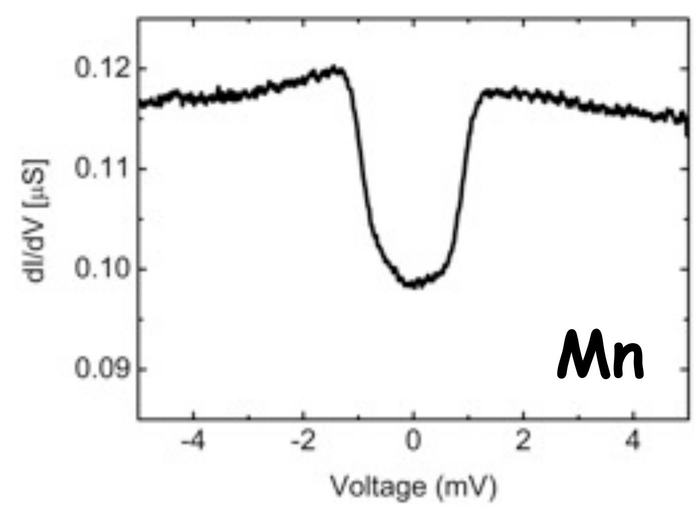
dI²/d²V Image @ 358 mV (C-H Stretching:~357meV)

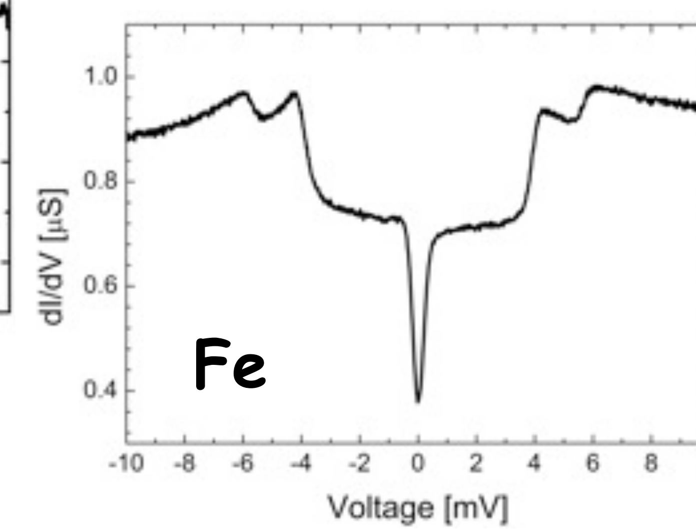


dI²/d²V image @ 266 mV (C-D Stretching: ~270meV)

B. C. Stipe, M. A. Rezaei, W. Ho
Science **280** 1732 (1998).







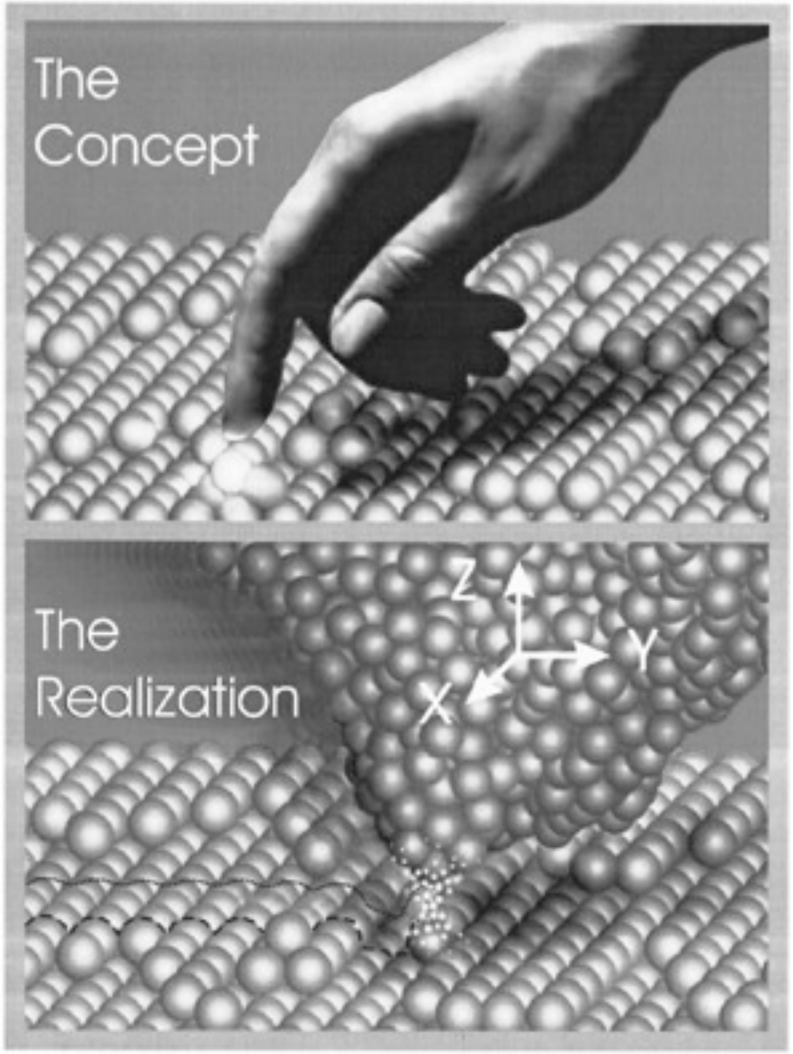
Courtesy of Sebastian Loth

IBM Almaden Research Center

A. J. Heinrich, et al. Science **306** 466 (2004).

C. F. Hirjibehedin, et al. Science **312** 1021 (2006).

Searching for atomic chemical specificity with SPM



"In Touch With Atoms"

G. Bining & H. Rohrer

Rev. Mod. Phys. **71** S324, (1999)

VOLUME 49, NUMBER 1 PHYSICAL REVIEW LETTERS 5 JULY 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)

Surface microscopy using vacuum tunneling is demonstrated for the first time. Topographic pictures of surfaces on an *atomic scale* have been obtained. Examples of resolved monoatomic steps and surface reconstructions are shown for (110) surfaces of $CaIrSn_4$ and Au.

PACS numbers: 68.20.+t, 73.40.Gk

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)

VOLUME 56, NUMBER 9 PHYSICAL REVIEW LETTERS 3 MARCH 1986

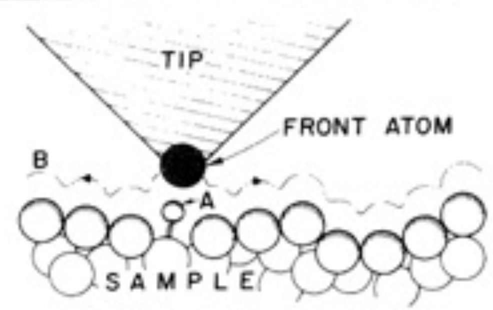


FIG. 1. Description of the principle operation of an STM as well as that of an AFM. The tip follows contour *B*, in one case to keep the tunneling current constant (STM) and in the other to maintain constant force between tip and sample (AFM, sample, and tip either insulating or conducting). The STM itself may probe forces when a periodic force on the adatom *A* varies its position in the gap and modulates the tunneling current in the STM. The force can come from an ac voltage on the tip, or from an externally applied magnetic field for adatoms with a magnetic moment.

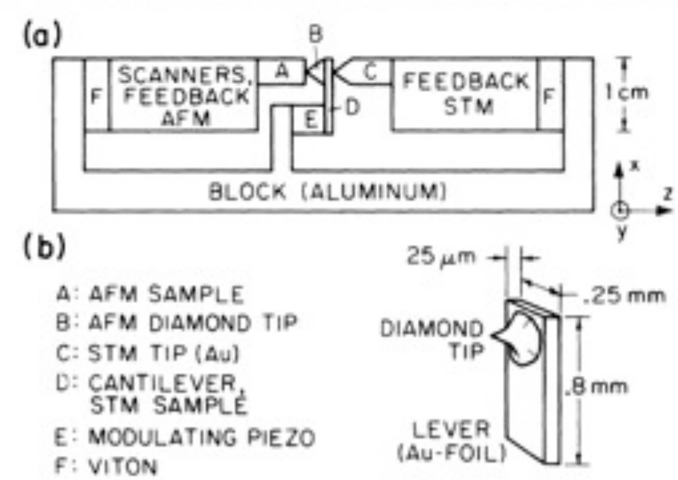
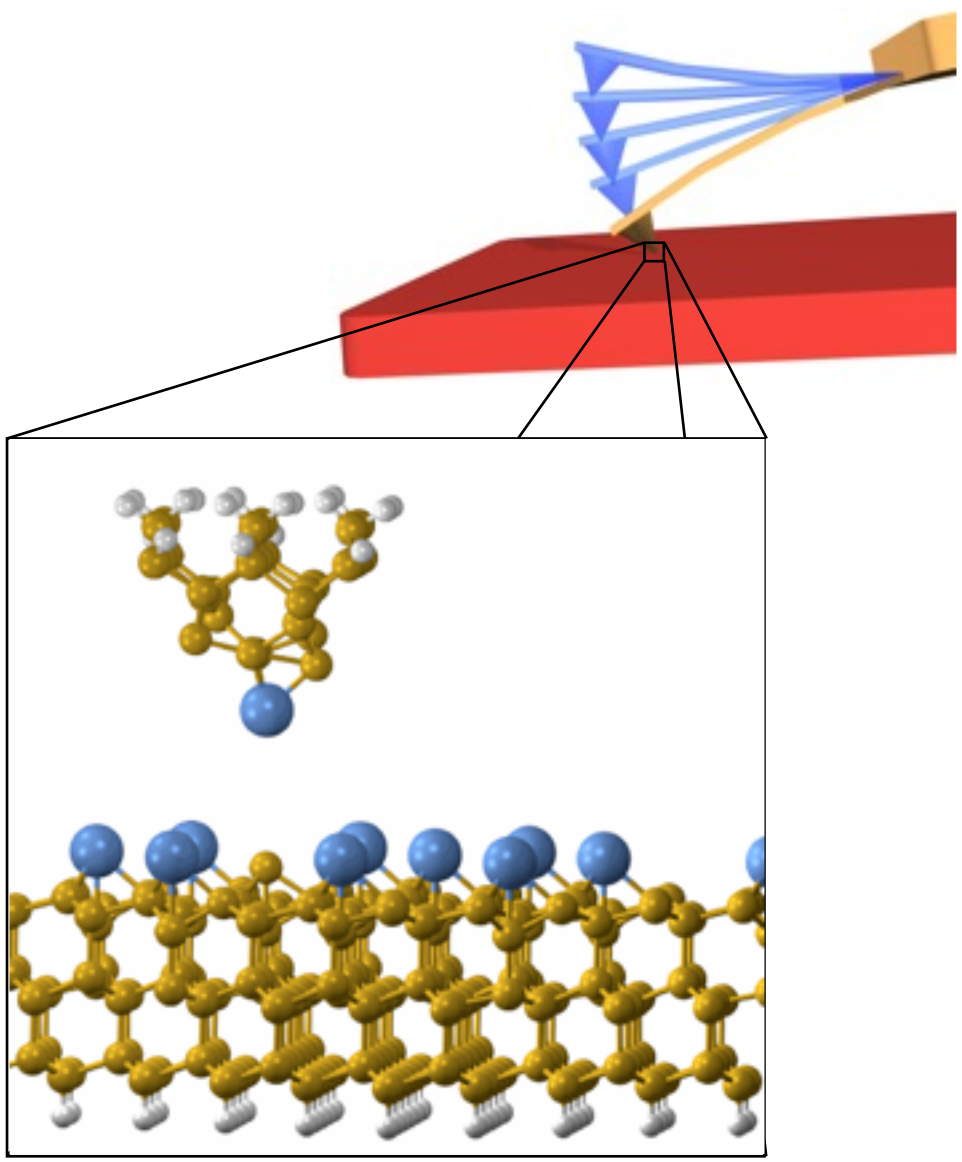


FIG. 2. Experimental setup. The lever is not to scale in (a). Its dimensions are given in (b). The STM and AFM piezoelectric drives are facing each other, sandwiching the diamond tip that is glued to the lever.

Short-range chemical interaction forces: imaging mechanism

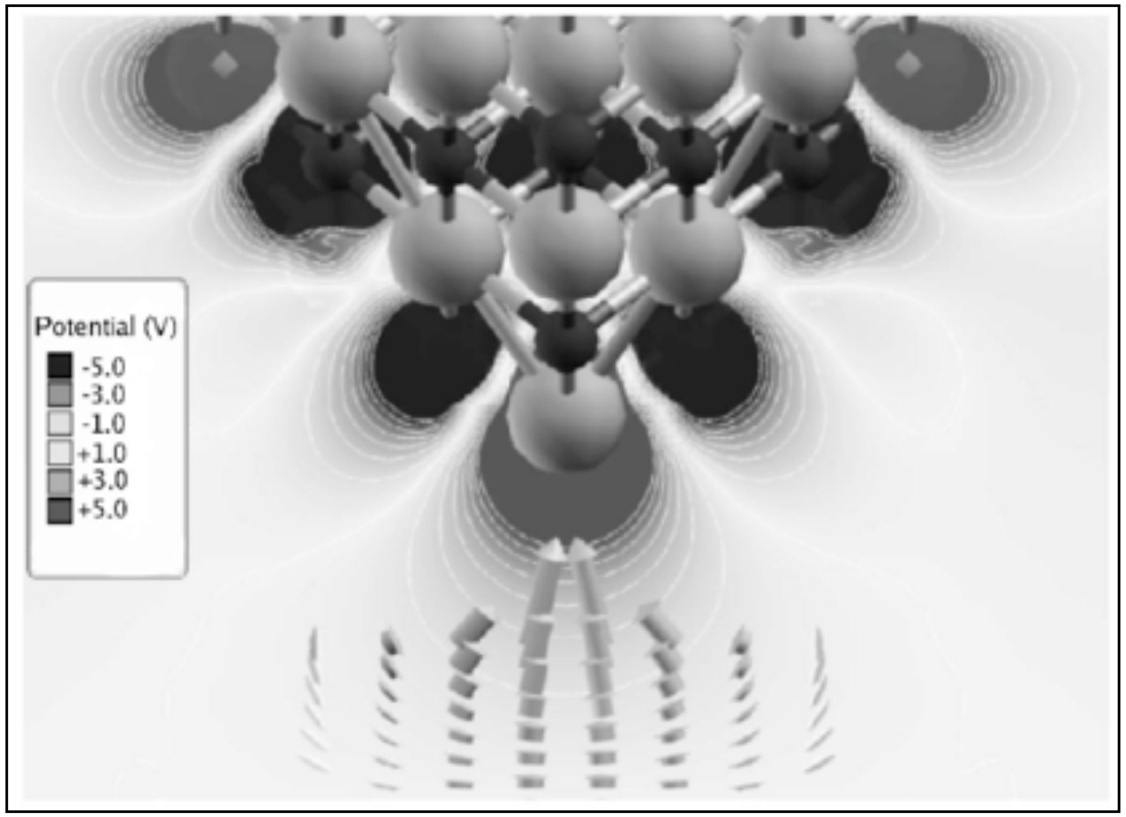
- **The onset of a covalent bond formation** between the outermost tip atom and the surface atoms in **semiconductor surfaces**.

R. Perez, M. C. Payne, I. Štich, and K. Terakura
Phys. Rev. Lett., **78**, 678 (1997)



- **The confined electrostatic interaction** between the outermost tip atom (that should have a polar nature) and the opposite polarity atomic species at the surface in **insulating (polar) surfaces**.

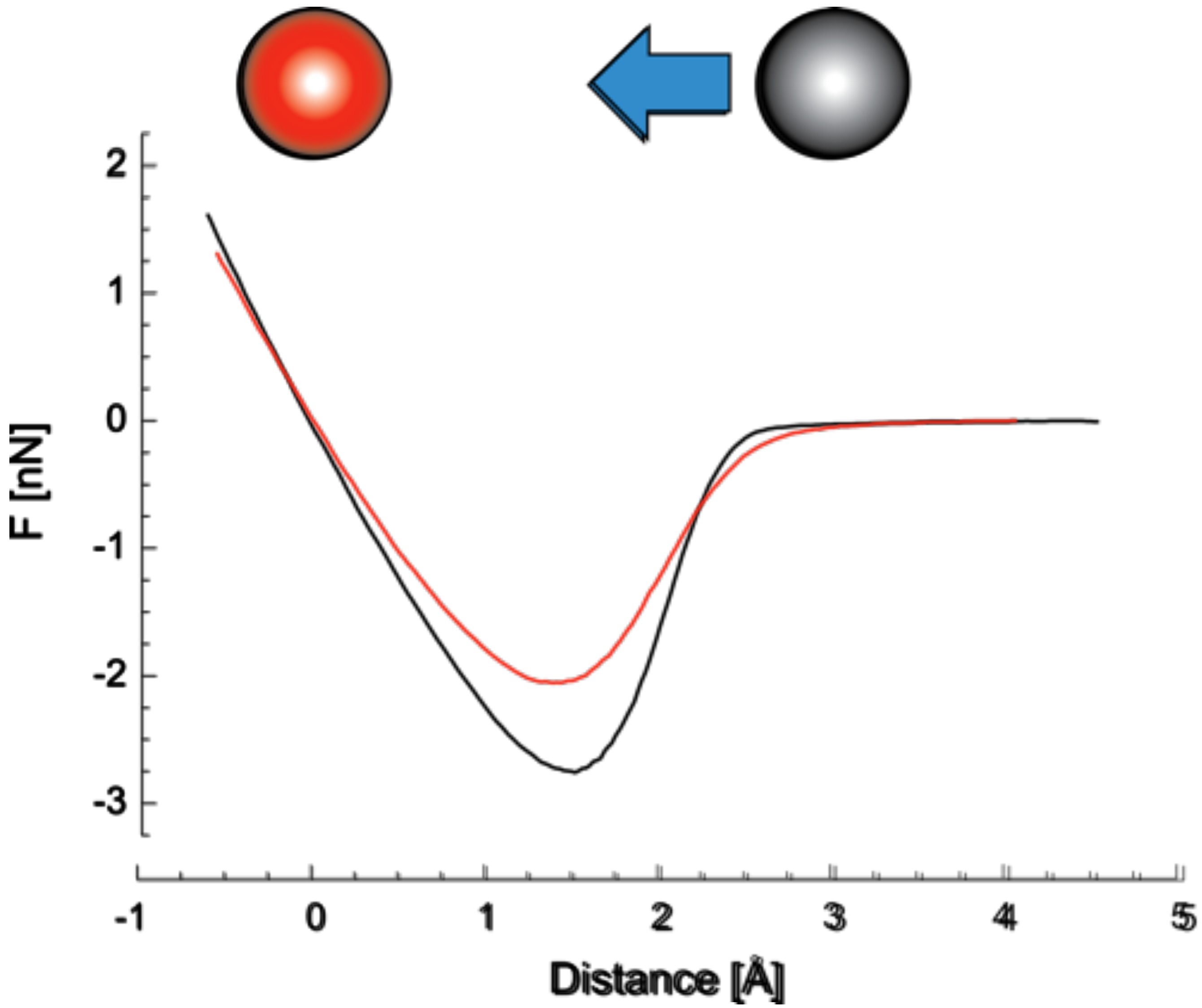
A.I. Livshits, A.L. Shluger, A.L. Rohl & A.S. Foster
Phys. Rev. B **59**, 2436 (1999)



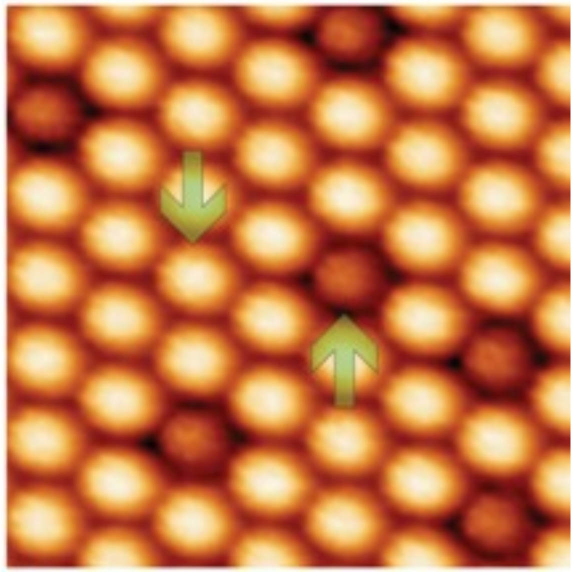
M. B. Watkins and A. L. Shluger
Phys. Rev. B **73**, 245435 (2006)

Arrows represent the gradient of the electrostatic potential

Bonding forces should bear chemical information

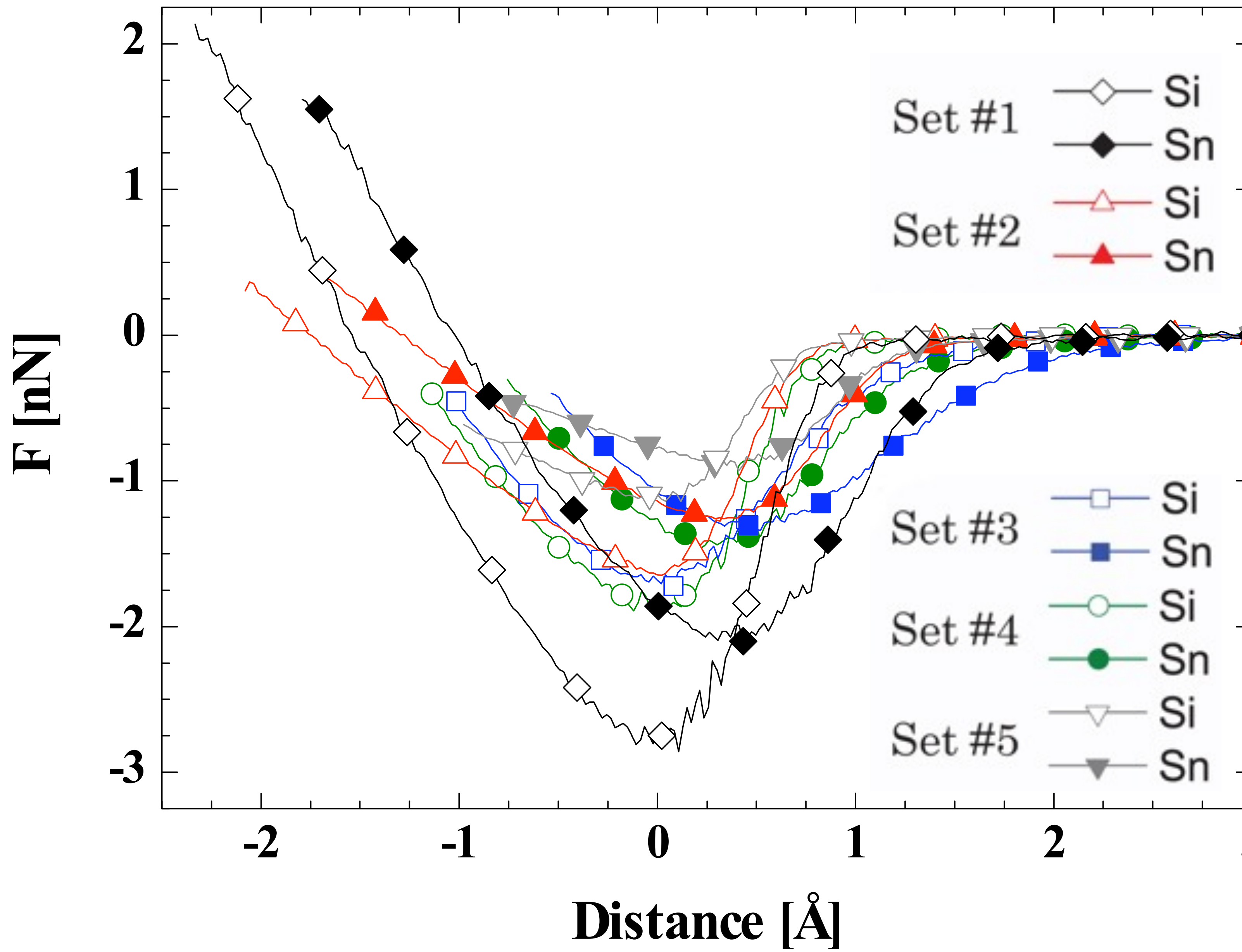


Precise measurement of short-range forces: Sn/Si(111)



(4.3x4.3) nm^2

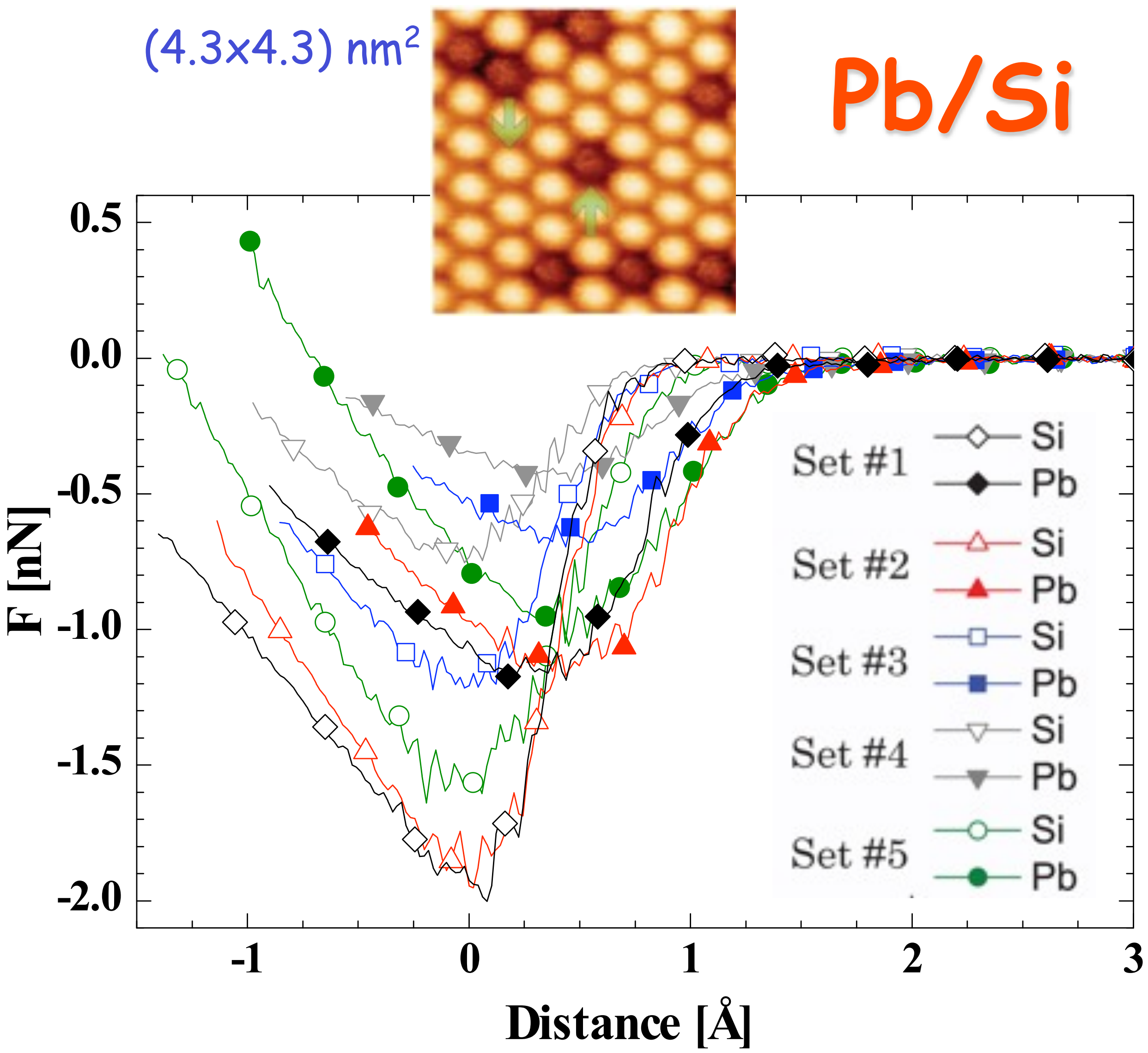
- **100 $\Delta f(z)$** characteristics per force curve.
- Acquisition over the top-most part of the atom with a **lateral precision better than ±0.1 Å.**
- Atoms in **equivalent local surface configuration**
- **Electrostatic force minimized**
- Force conversion from the **averaged $\Delta f(z)$ curve**
- **Identical analysis protocol**

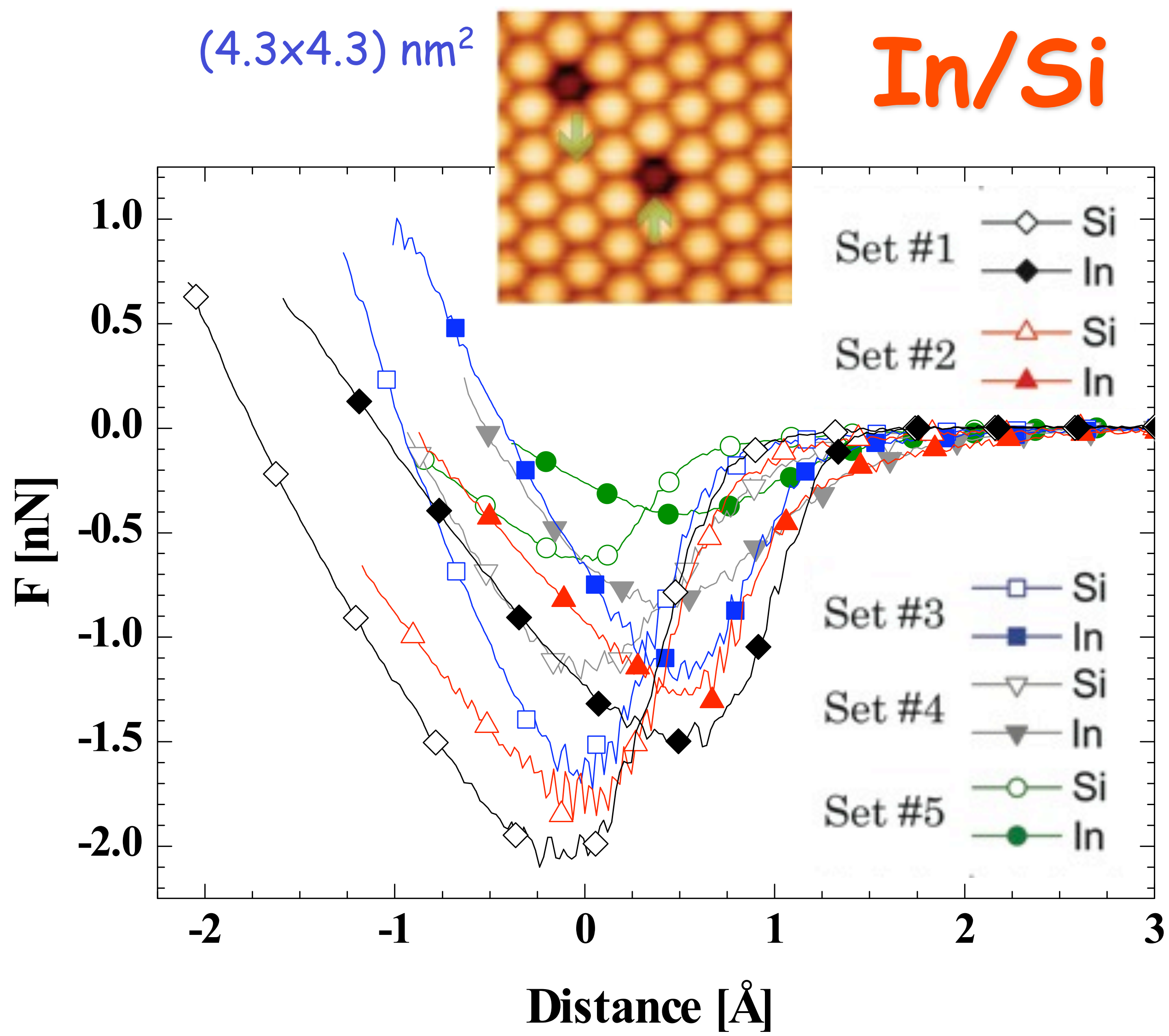


Sets of short-range chemical forces measured over Sn and Si atoms in several sessions using tips-apex terminations with different structure and composition

Nature **446** 64 (2007)

Precise measurement of short-range forces



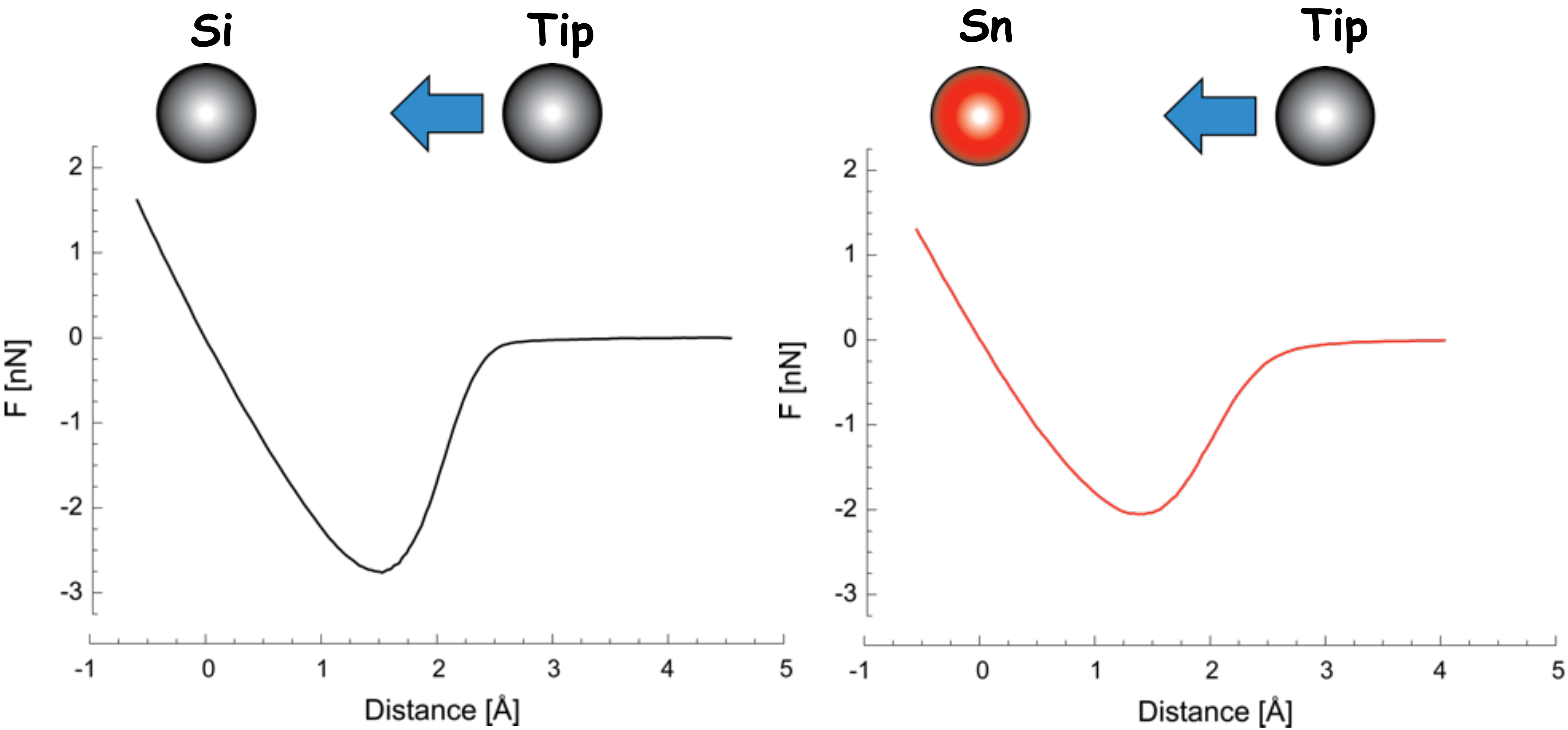


Only one common feature: the Si curve provides the stronger SR force values

The relative interaction ratio of the maximum attractive short-range force within a set (for the same tip) remains nearly constant independently on the tip

Nature **446** 64 (2007)

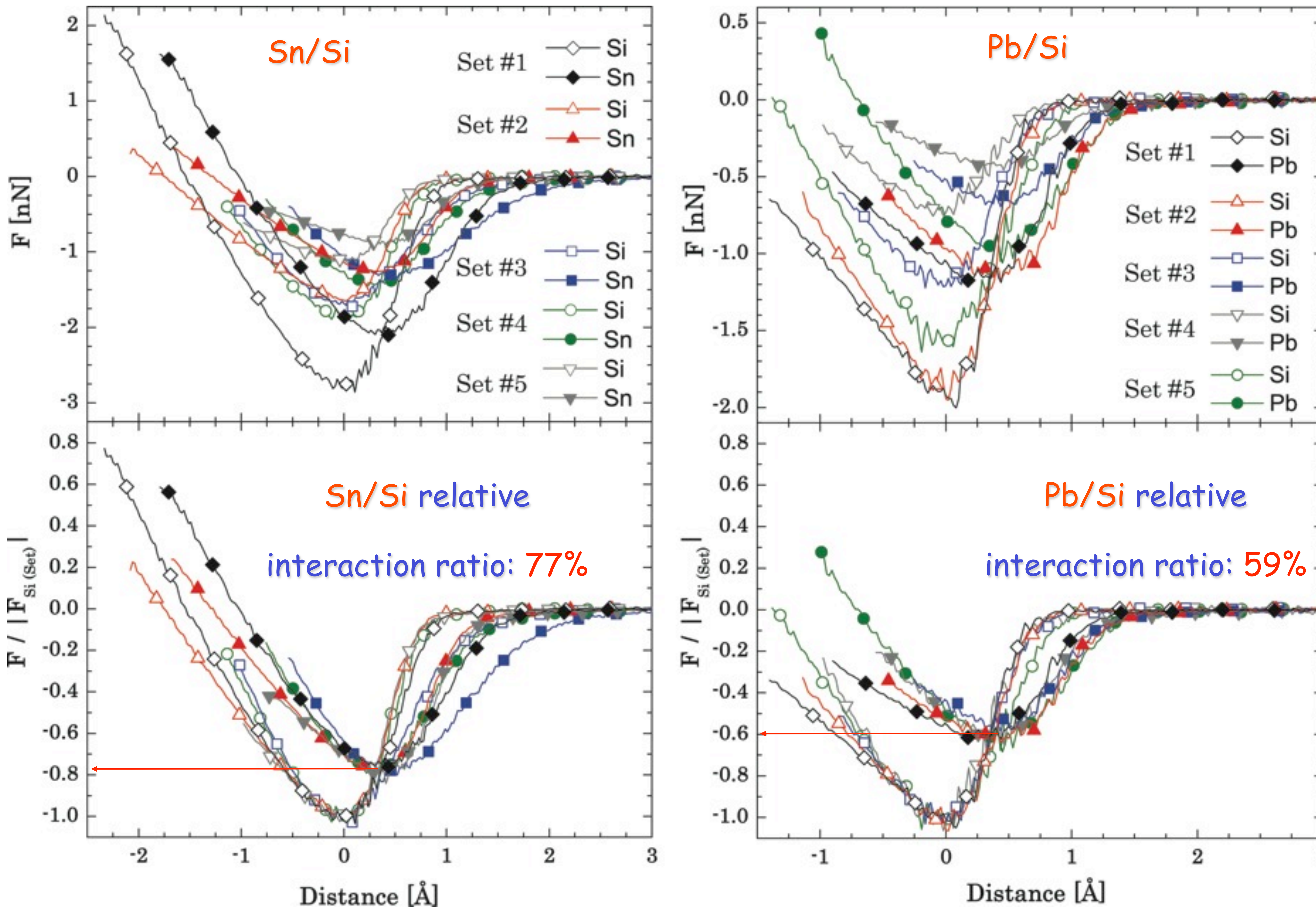
Relative interaction ratio of the maximum attractive forces



The relative interaction ratio of the maximum attractive short-range force within a set (for the same tip) remains nearly constant independently on the tip

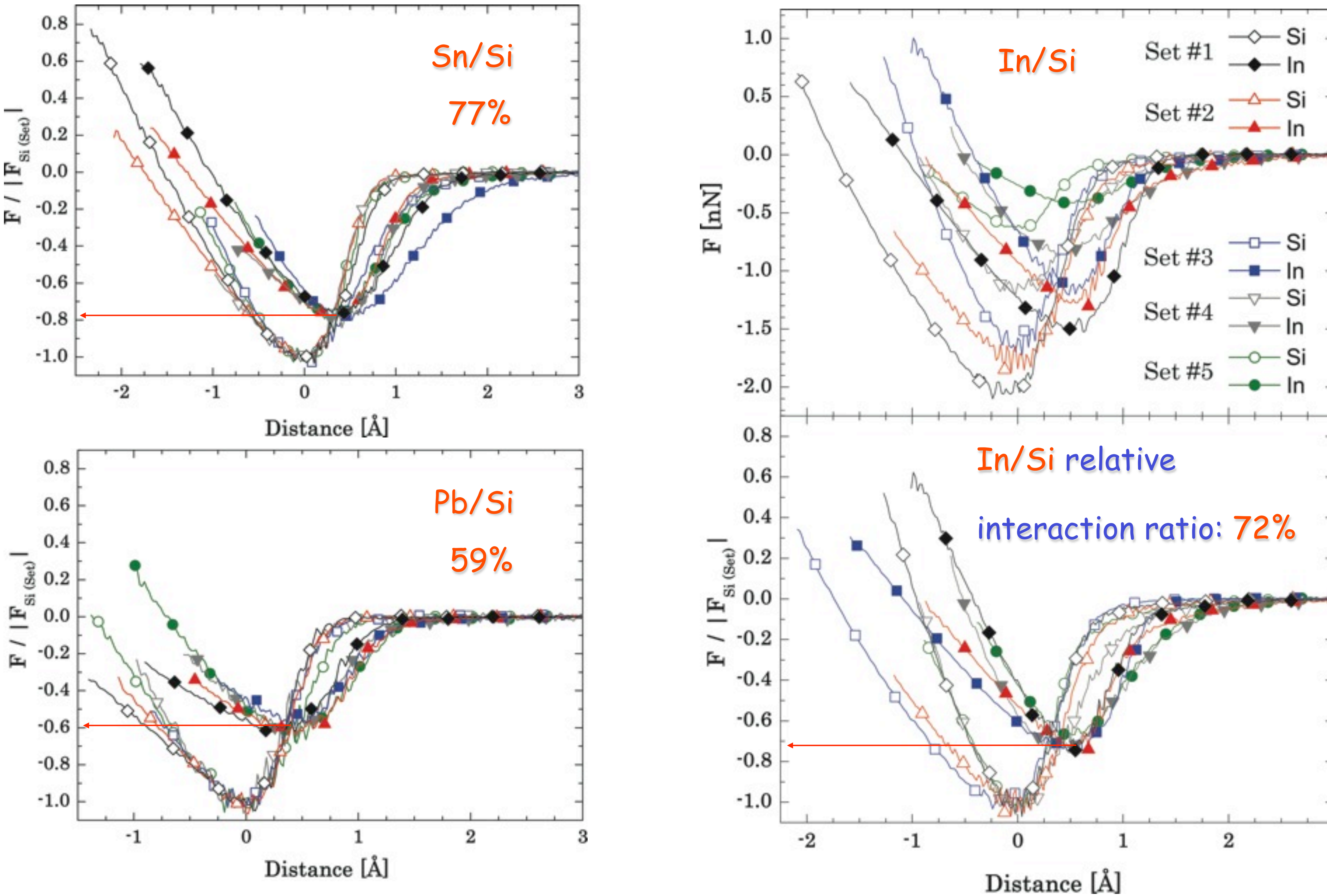
Nature **446** 64 (2007)

Normalization and relative interaction ratio



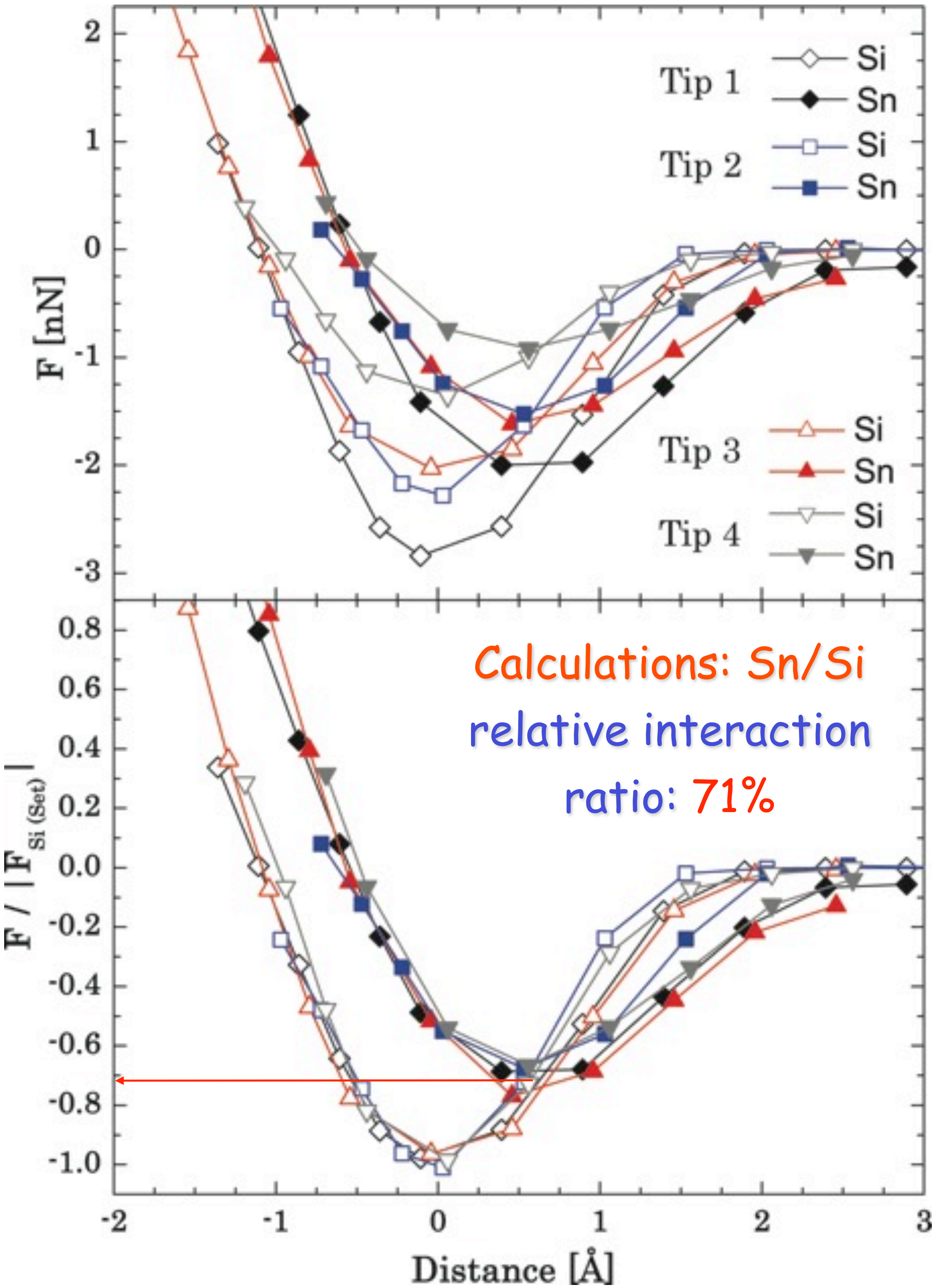
Nature **446** 64 (2007)

Not only a property of the Group IV: In & Si



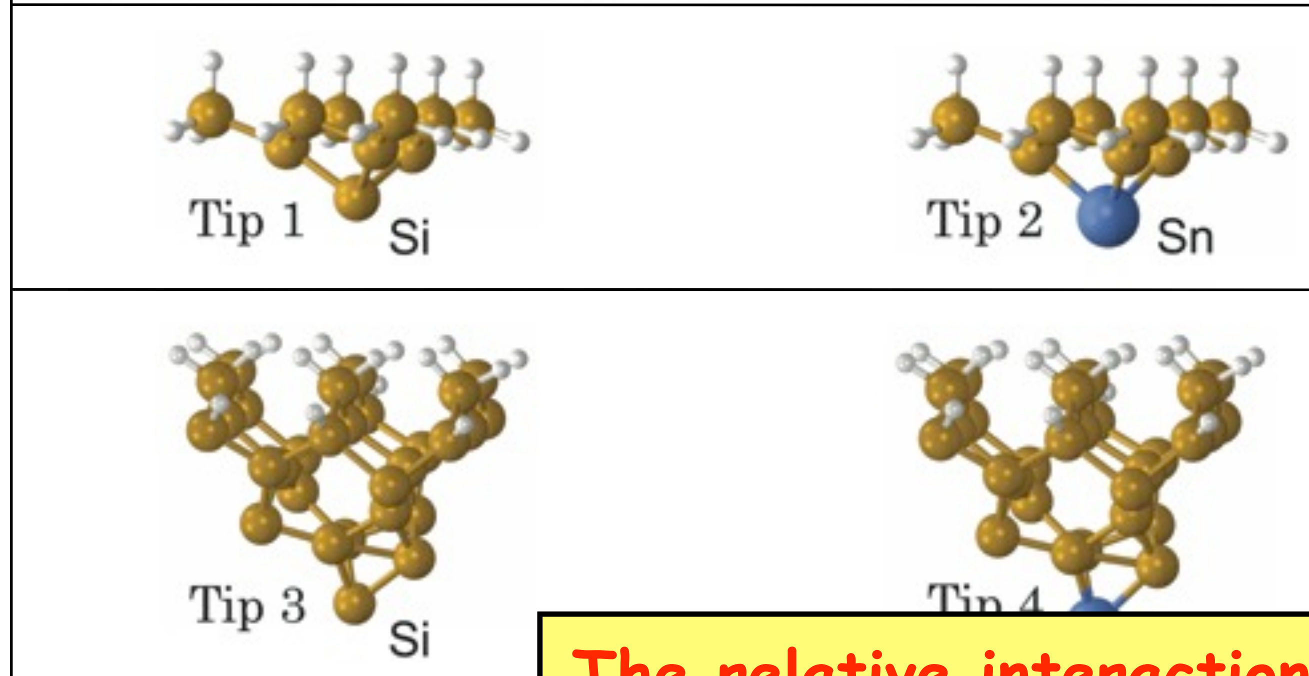
Nature **446** 64 (2007)

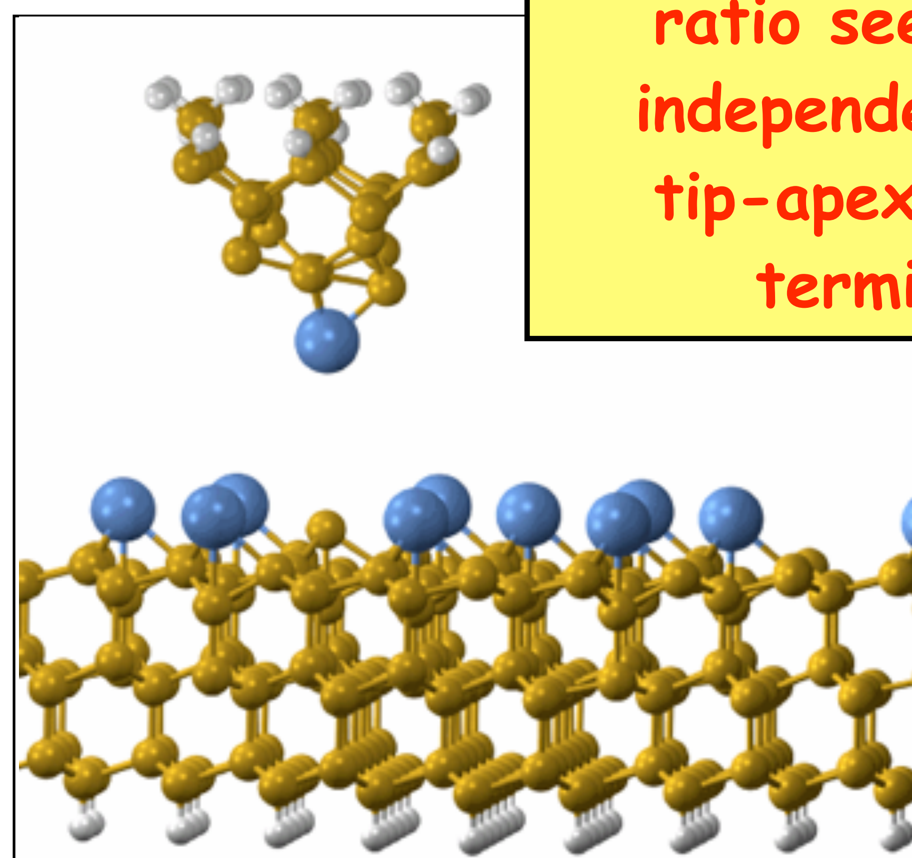
First-principles calculations: Sn & Si



Nature **446** 64 (2007)

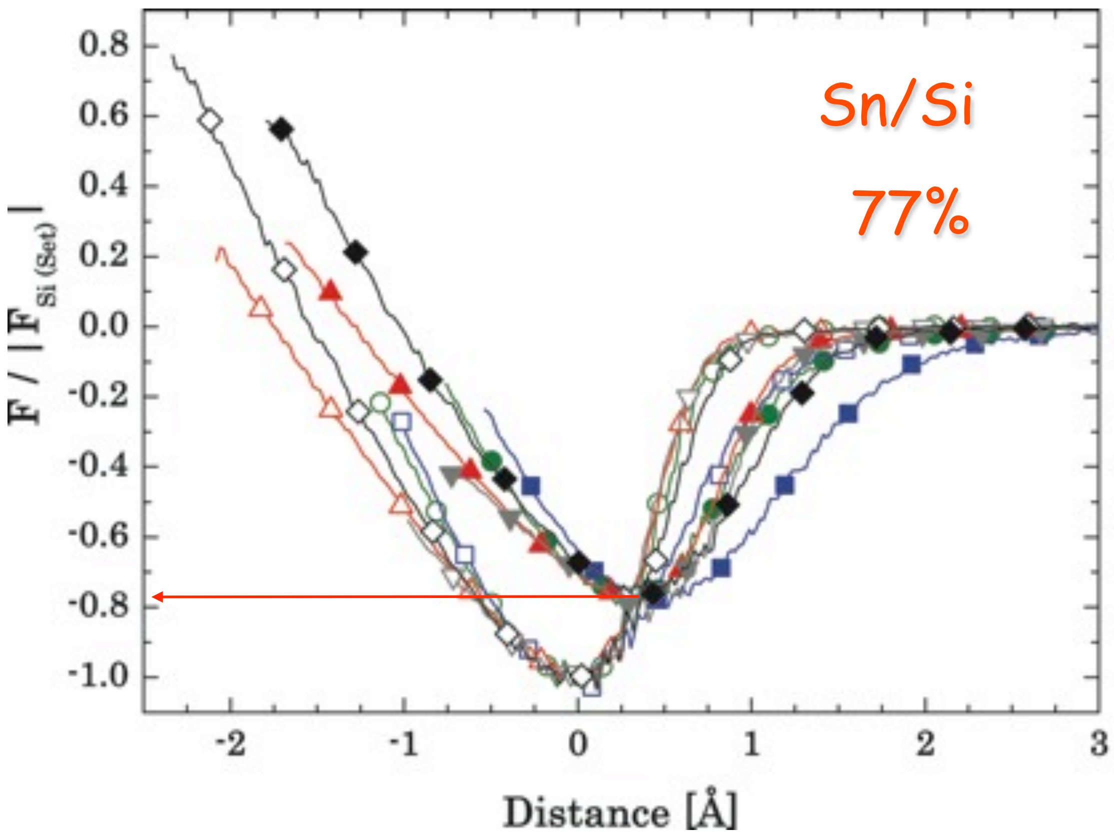
Same structure but different tip-apex chemical termination

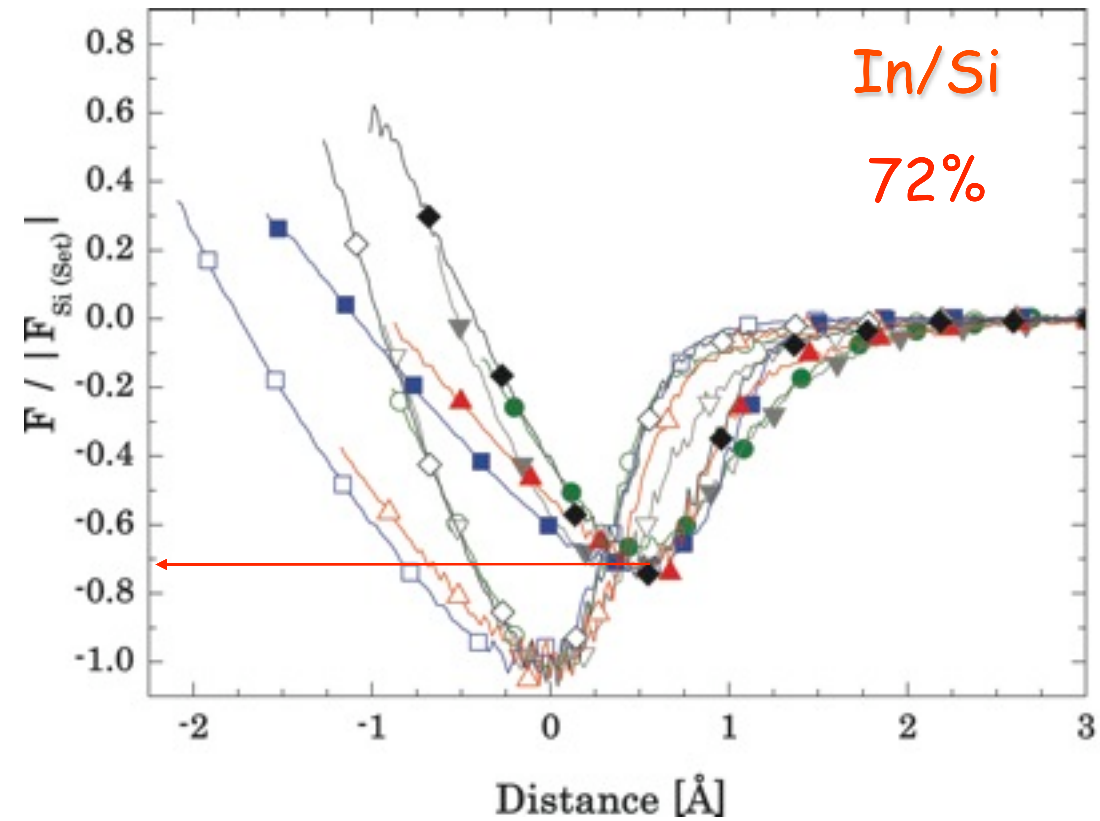


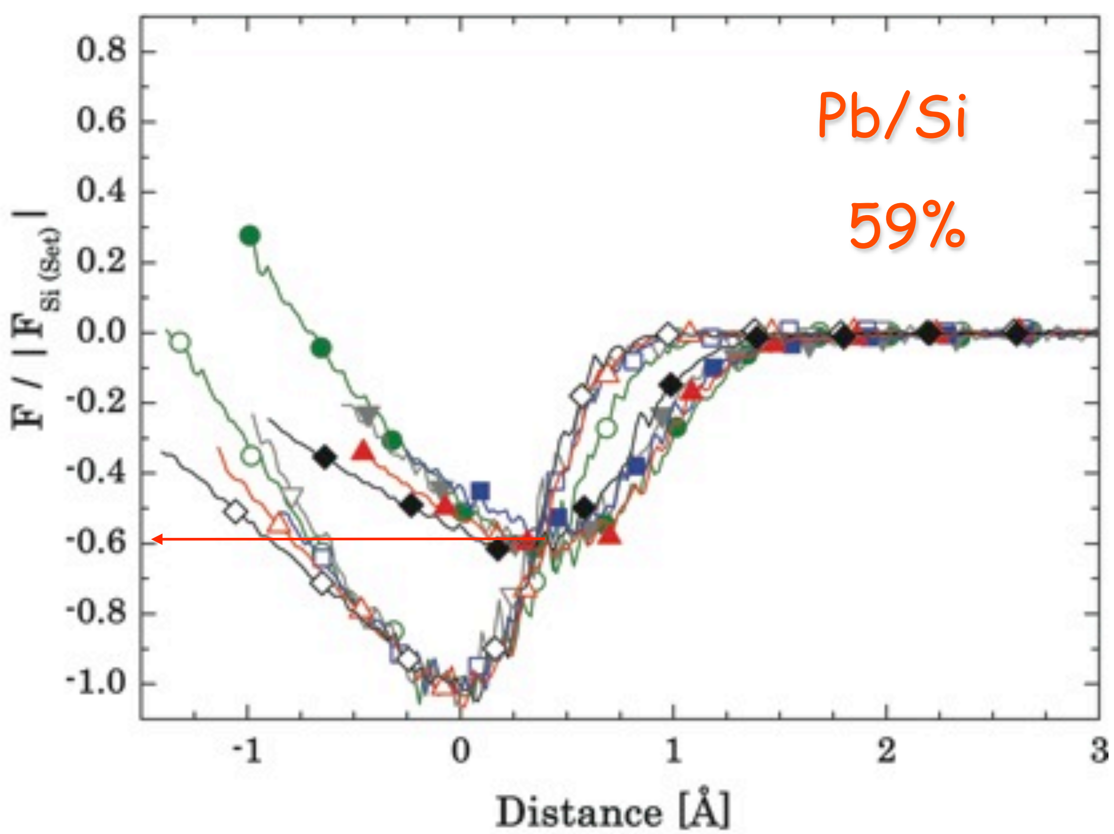


The relative interaction ratio seems to be independent of the tip-apex chemical termination

The essence of the relative interaction ratio







The relative interaction ratio for two atomic species probed with the same tip, is a quantification of the relative strength these surface atoms have to interact with the outermost atom of the tip apex.

… and this property, almost independent on the tip, can be used as a fingerprints for the chemical identification of individual atoms.

A challenging system

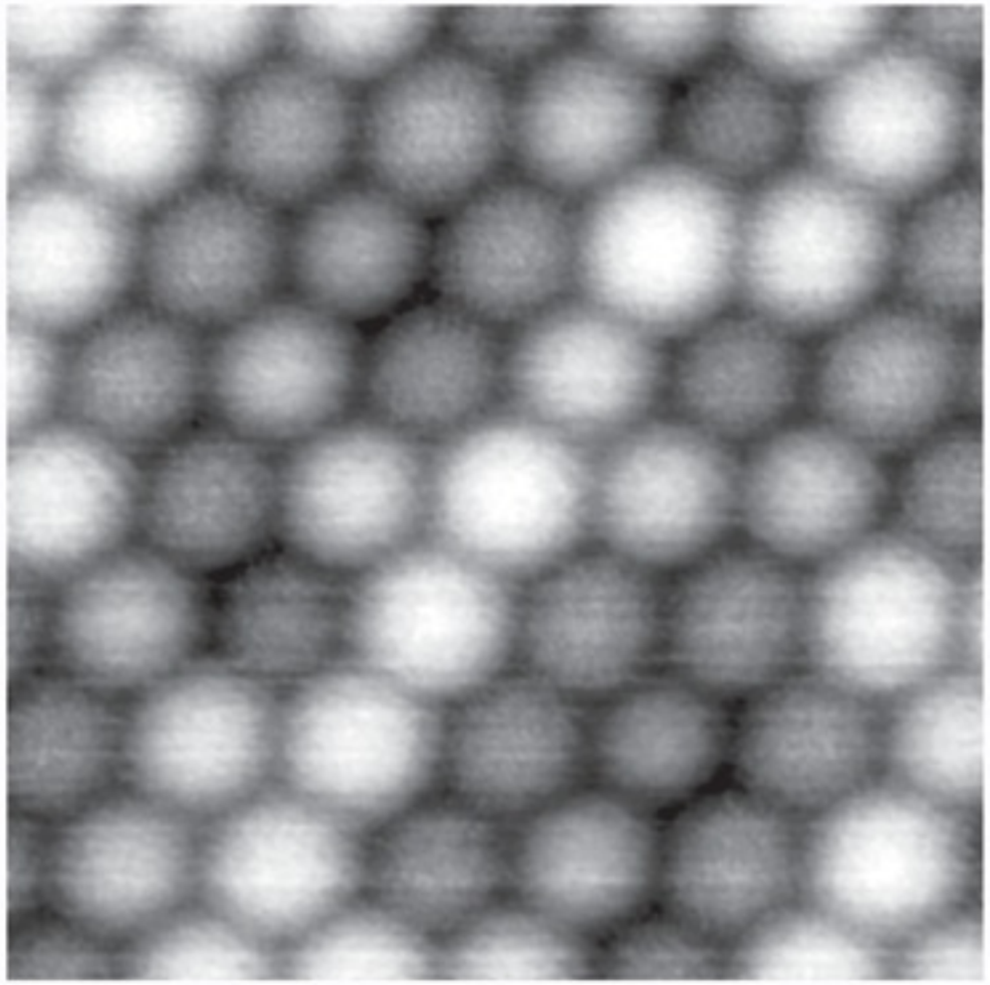
- A single-atomic overlayer alloy of Group-IV elements on a Si(111) substrate.

Sn: ~ 33%

Pb: ~ 33%

Si: ~ 33%

- At this surface these atoms have:
  - Very similar surface electronic structure
  - Adsorb on equivalent surface positions (T_4)
  - Intermix randomly
  - Topography dependence on the number of first-neighboring Si atoms

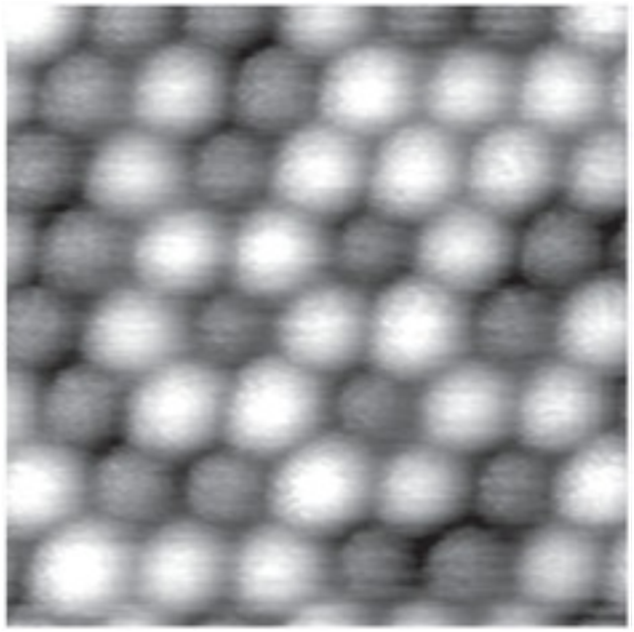


(4.3x4.3) nm^2

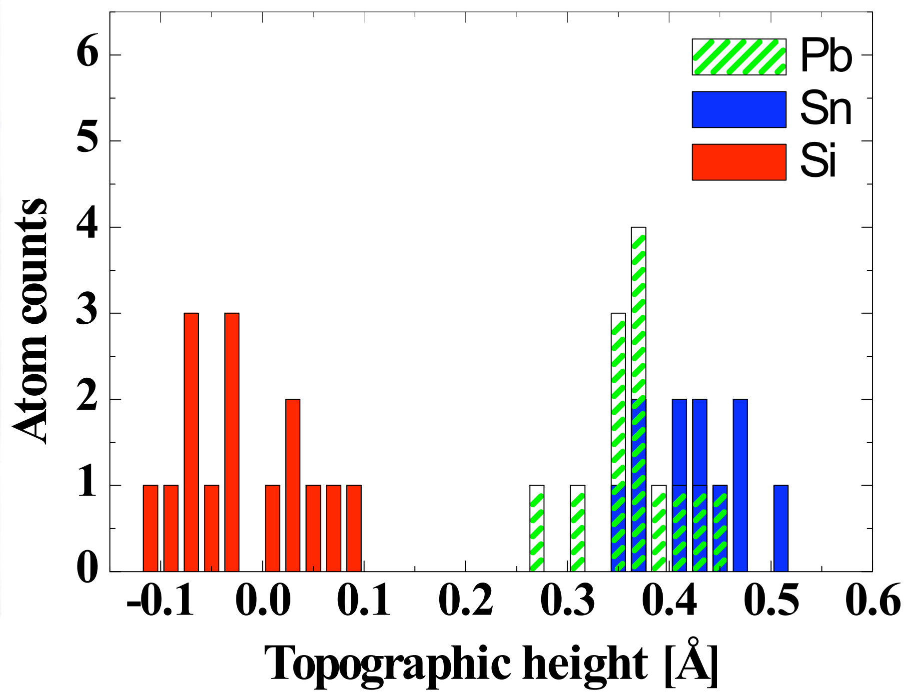
Facing the problem of identifying single atoms with very similar chemical properties and identical adsorption sites at room temperature!!!

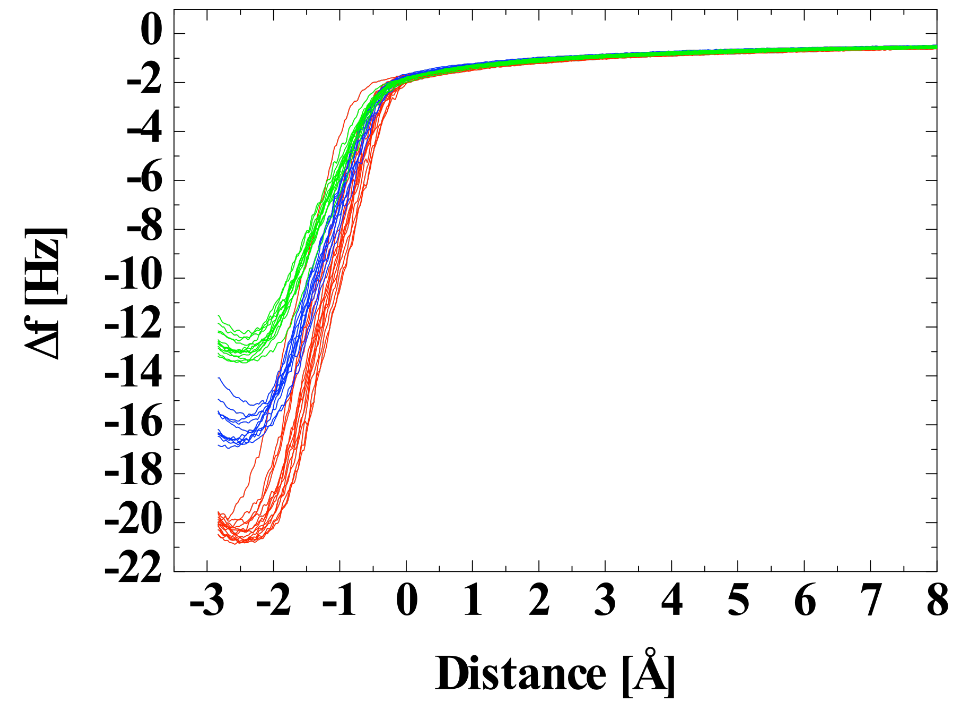
Nature **446** 64 (2007)

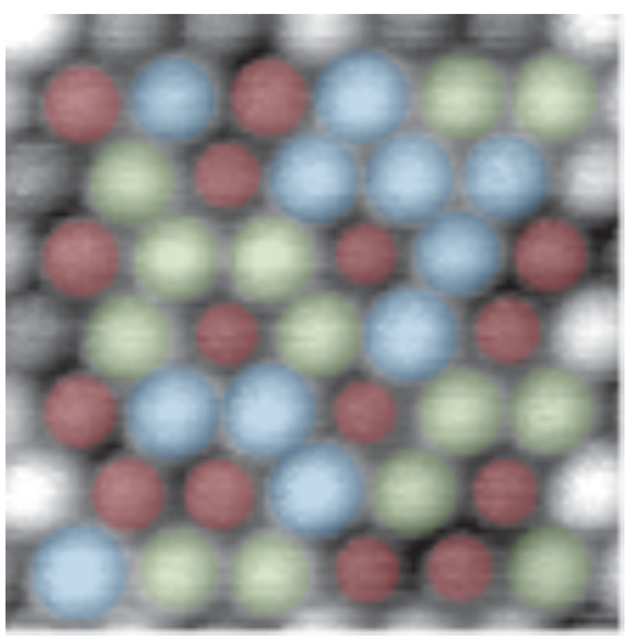
Identification: local homogeneous distribution of Si atoms

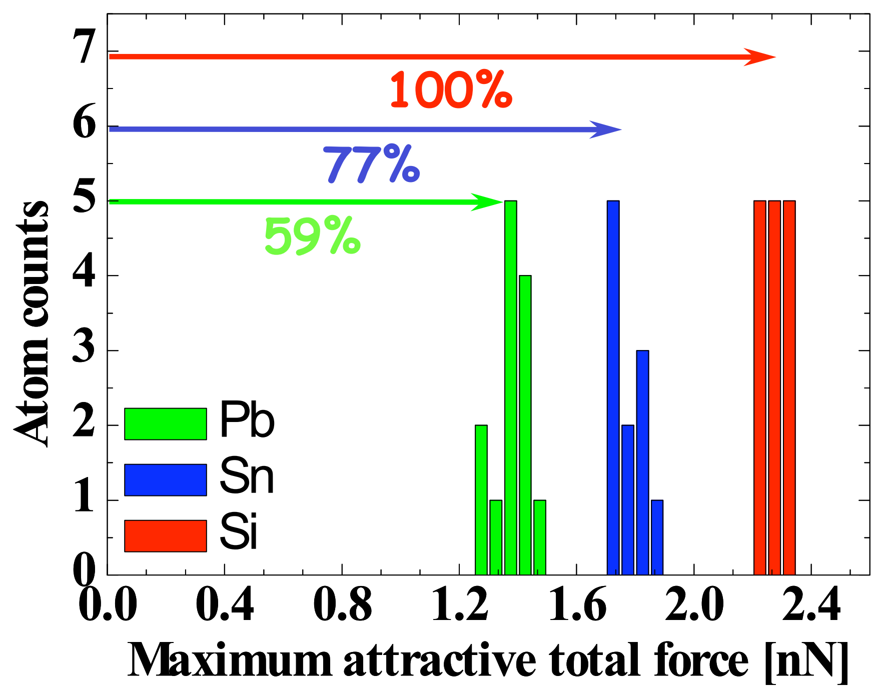


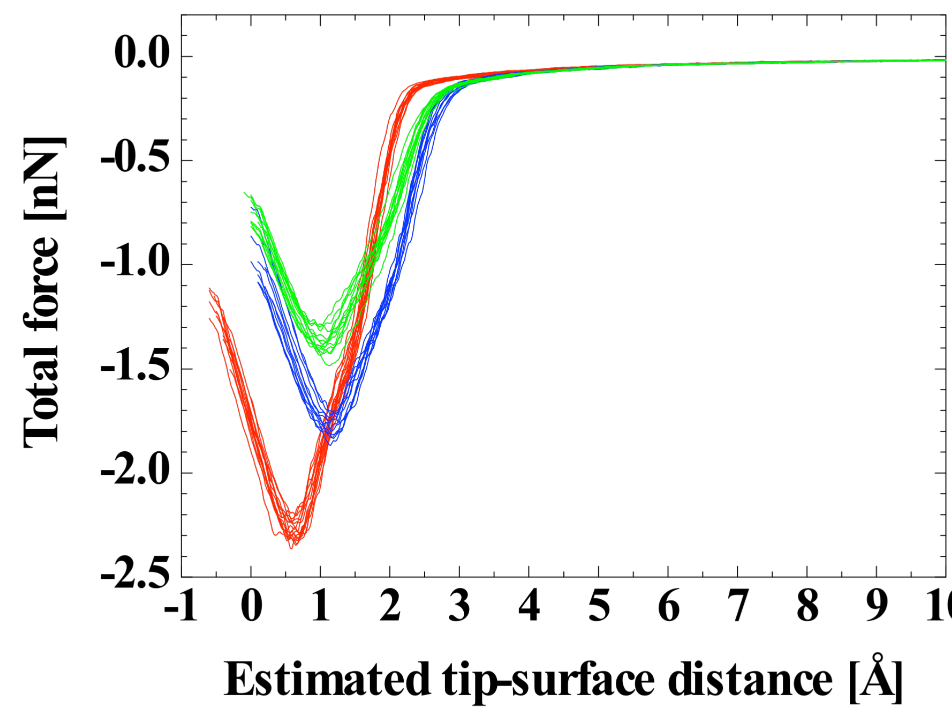
(4.3x4.3) nm^2







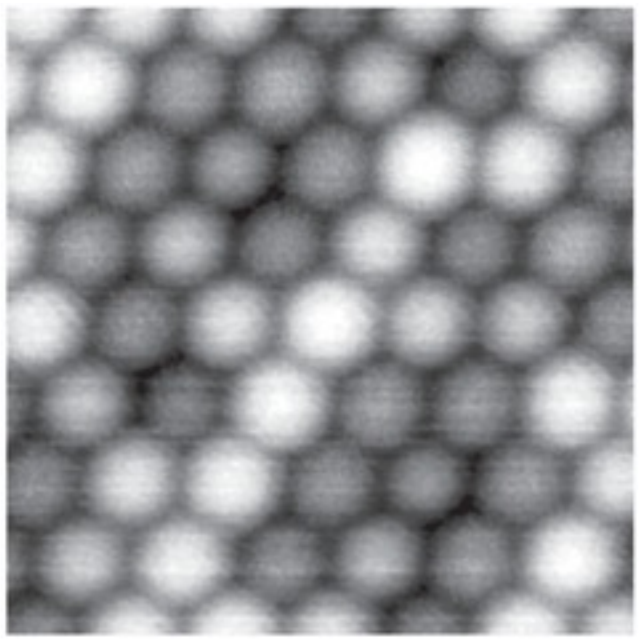




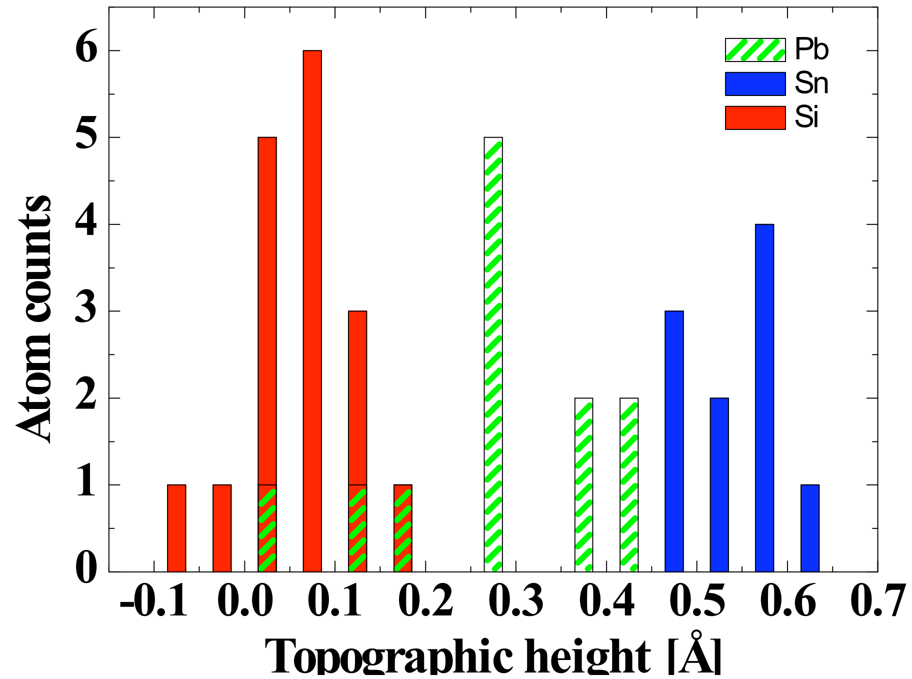
Only 10 Δf(Z) averaged per force curve

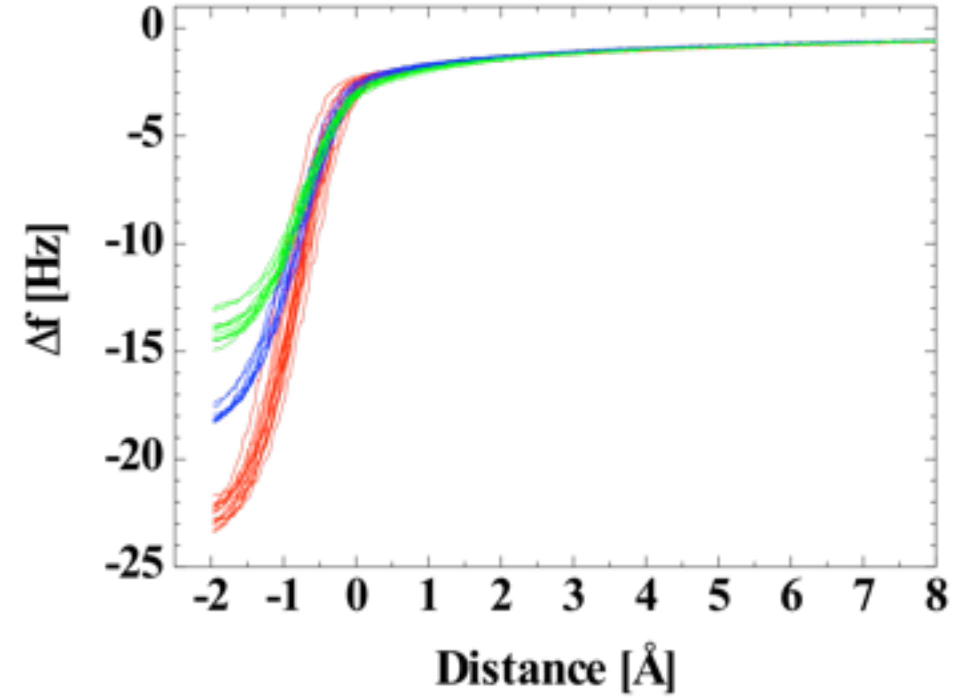
Nature **446** 64 (2007)

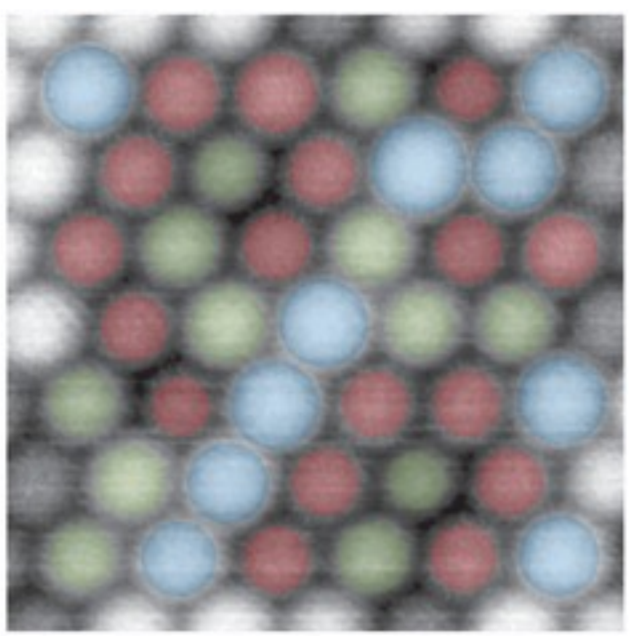
Identification: local clustering of Si atoms

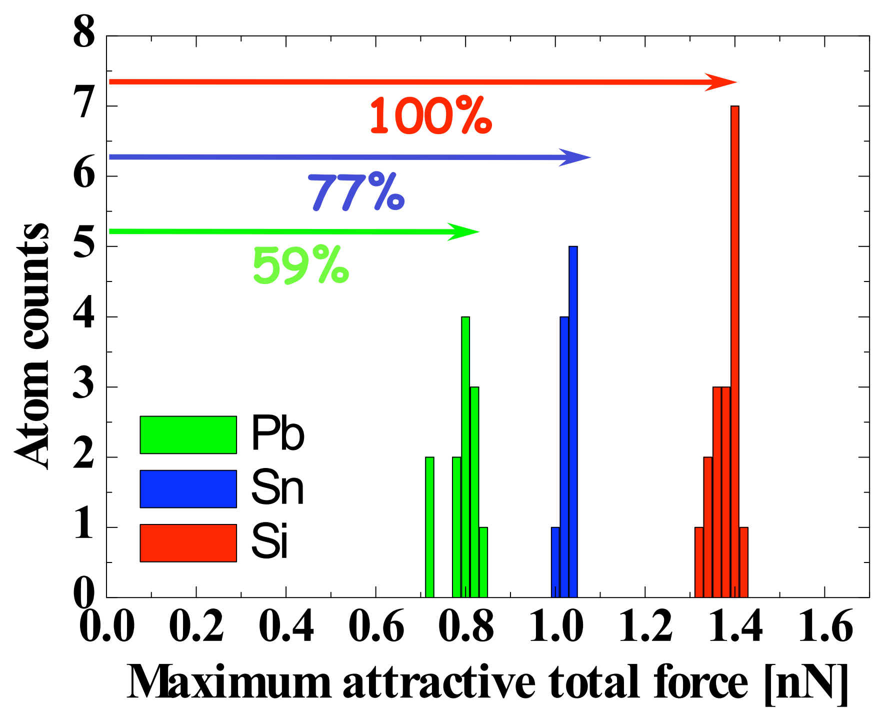


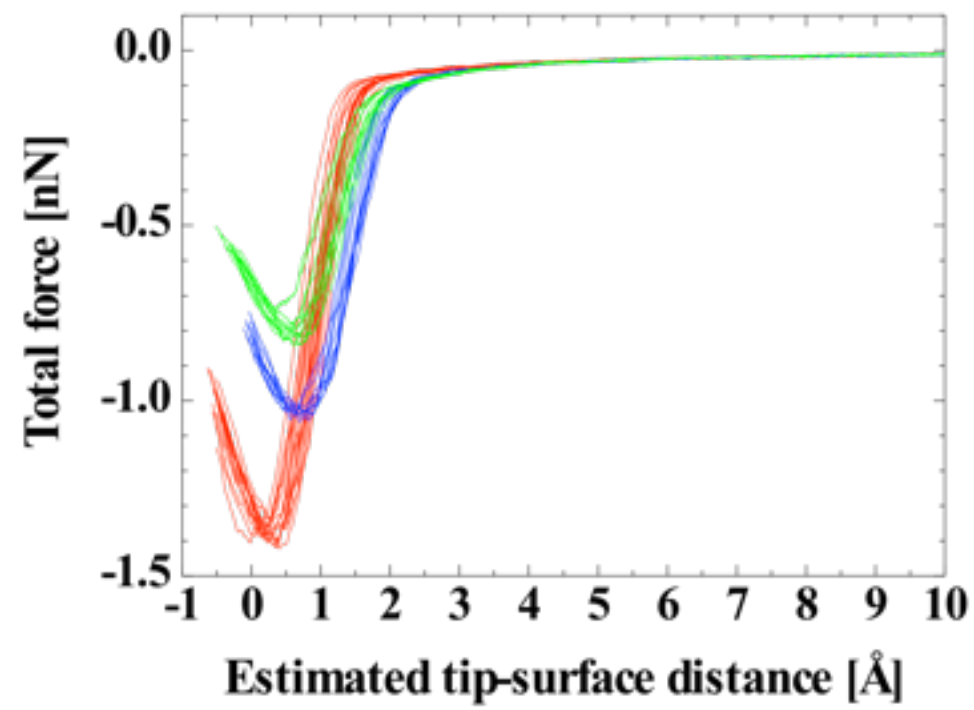
(4.3x4.3) nm^2







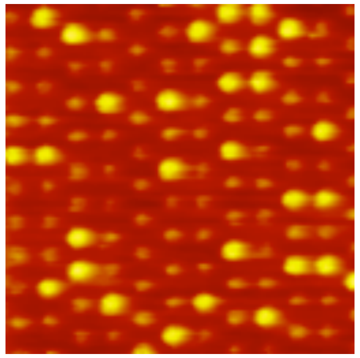




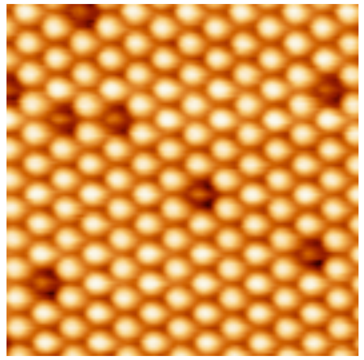
Only 10 Δf(Z) averaged per force curve

Nature **446** 64 (2007)

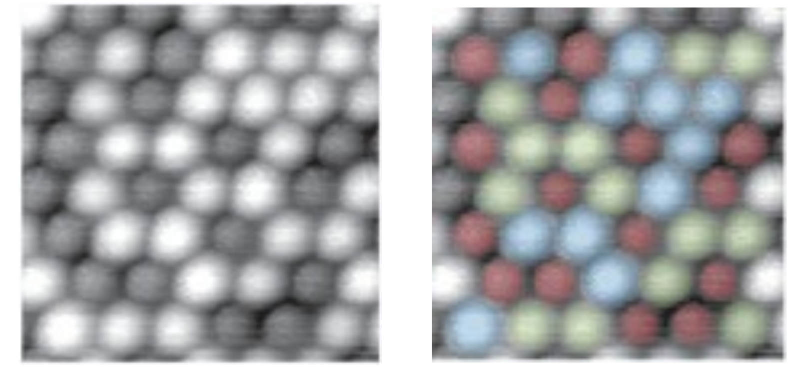
Applying AFM to solve scientific or technological problems



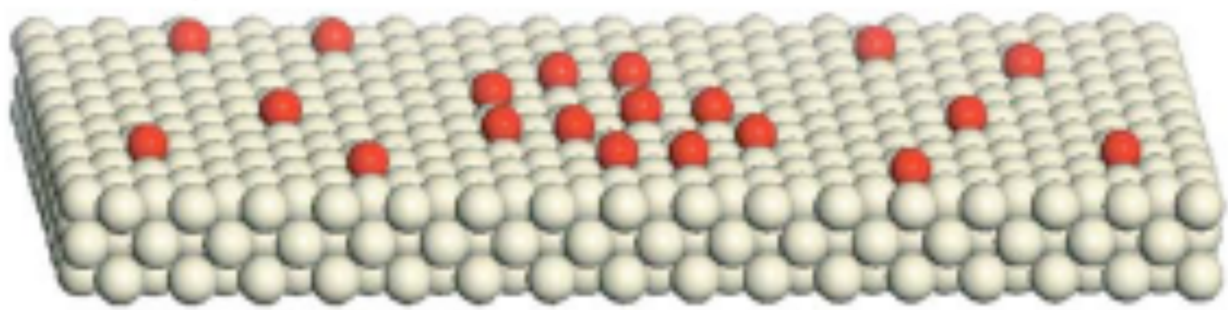
Nature Materials **4** 156 (2005)

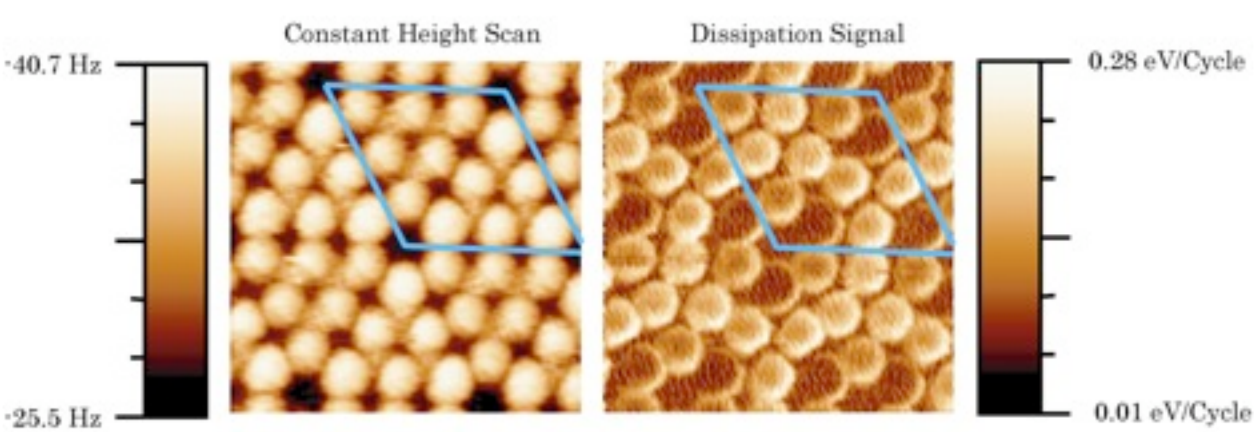


Science **322** 413 (2008)



Nature **446** 64 (2007)

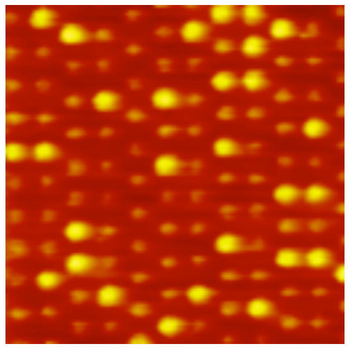


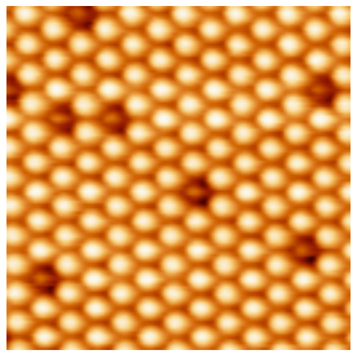


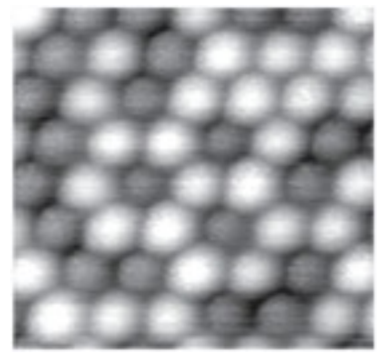
Phys. Rev. Lett. **96** 106101 (2006)

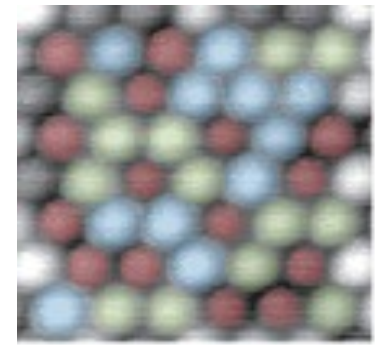
Summary

- Atomic resolution AFM has become a fundamental tool in nanoscience with enough potential to clarify problems of scientific and technological relevance.

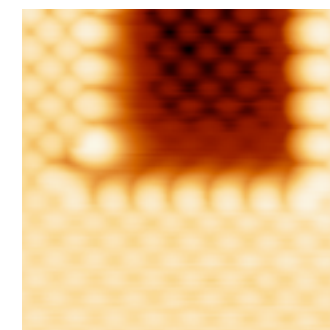




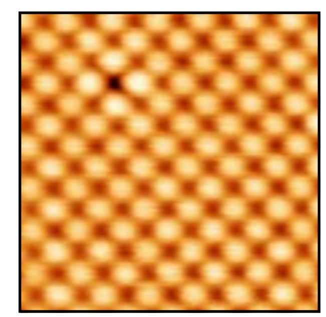




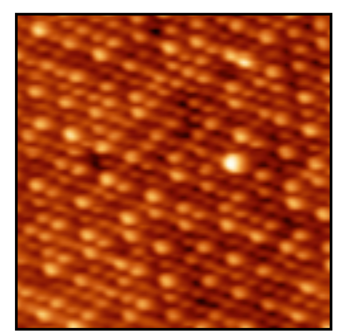
KBr(100)



MgO(100)



CeO_2(111)



- AFM provides access to the atomic structure of insulating surfaces

- Similar atomic-scale results are now starting to be reproduced in liquid environment