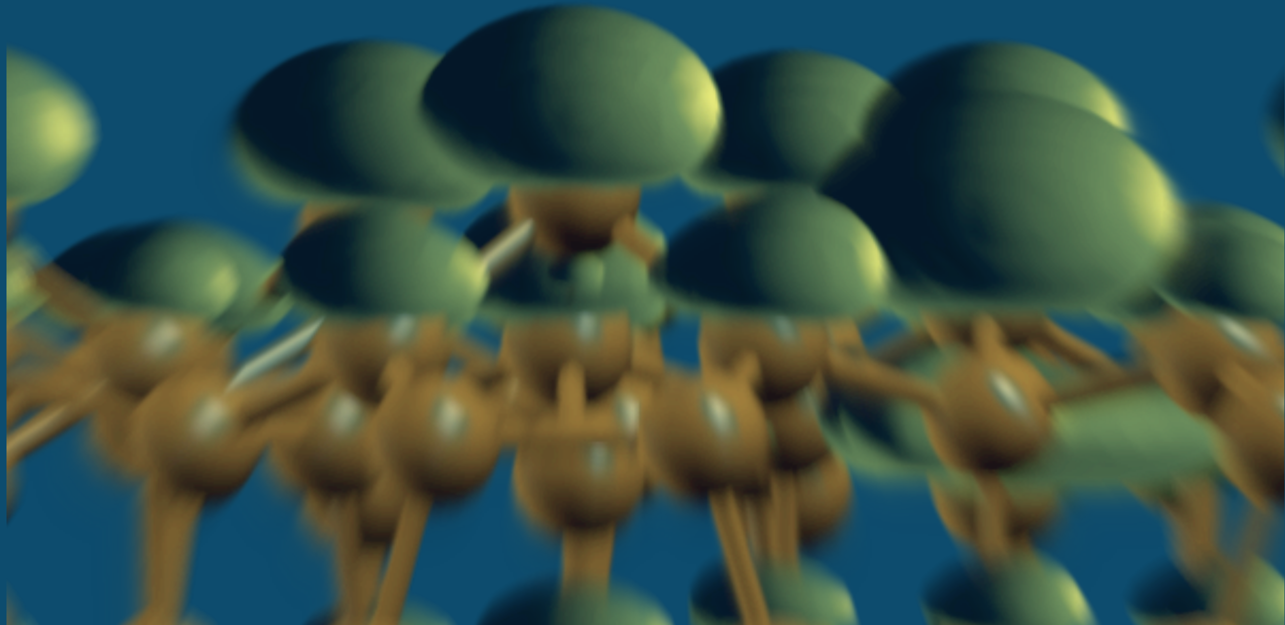
Analysis of simultaneous STM/AFM measurements at atomic scale

P.Jelínek

jelinekp@fzu.cz nanosurf.fzu.cz

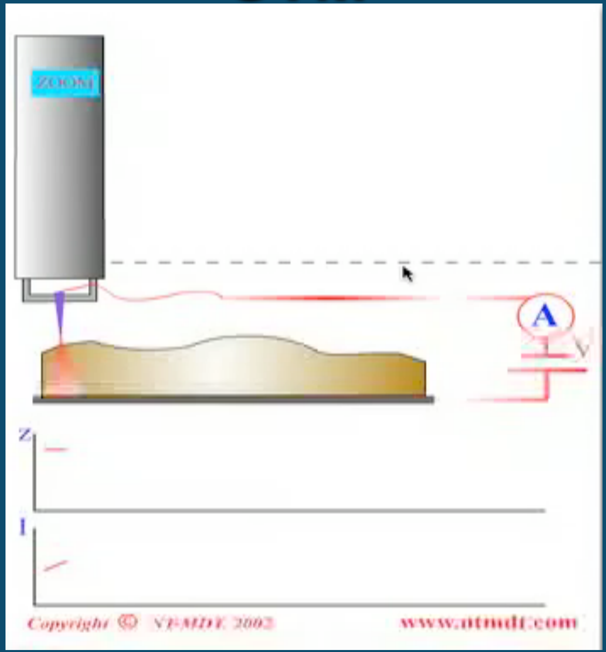


Outline

- Introduction
- Force & current:
  - Semiconductor surfaces
  - Metal surfaces
  - Graphene

SPM mechanisms

STM

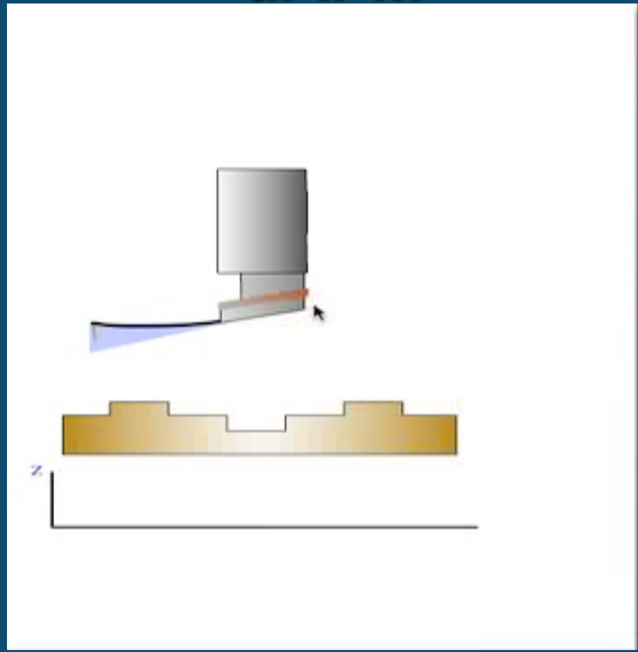


❑ **tunneling current** occurs at very short distances when the voltage is applied between the probe and the sample

❑ very **sensitive to the tip-sample distance**

❑ provides **atomic resolution** of **surfaces & their electronic structure**

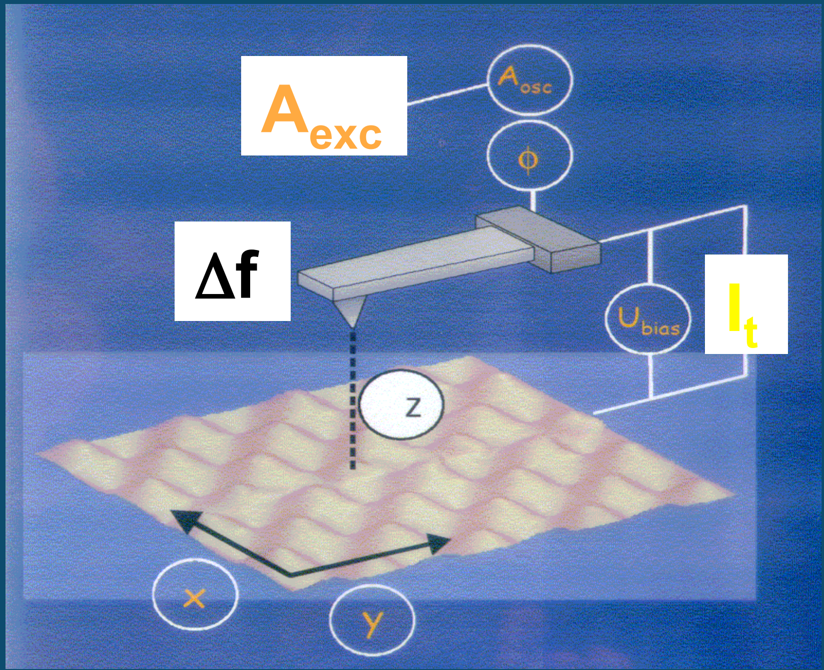
dAFM



❑ **oscillating probe** contacting ("touching") the surface changing oscillation frequency/amplitude

❑ point to point **differences** in **oscillation frequency/amplitude** make an **image contrast**.

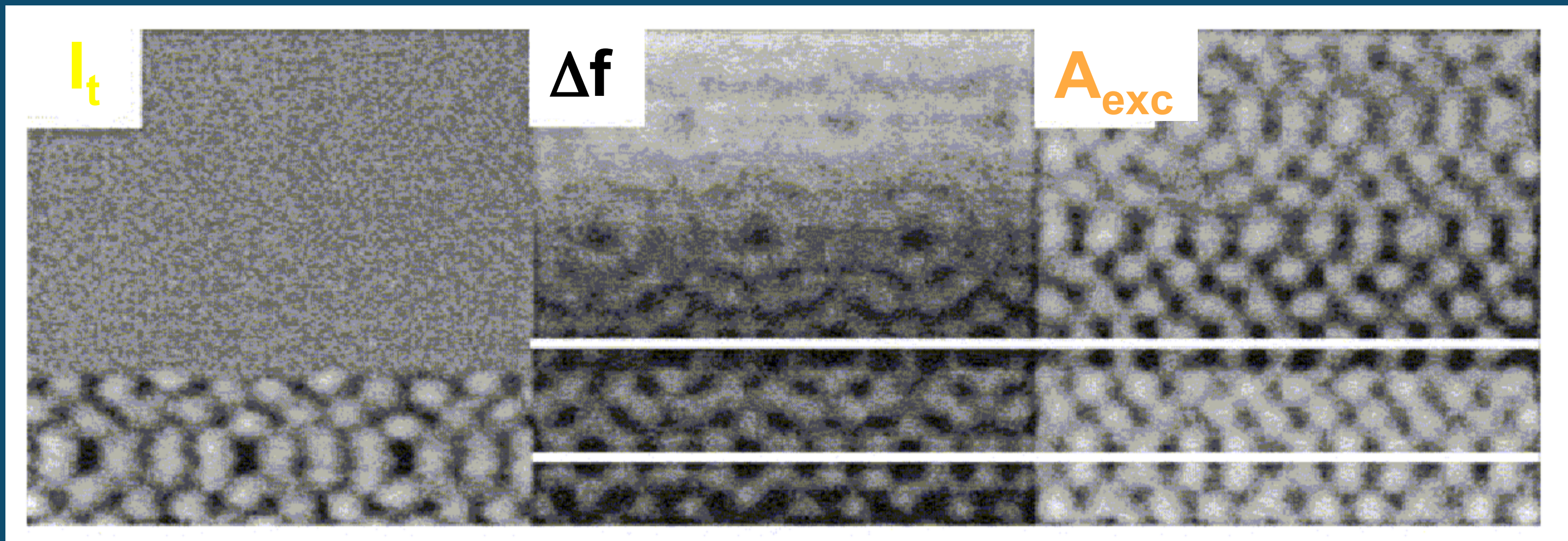
dAFM: Contrast sources



Δf: frequency shift

A_{exc}: damping (excitation)

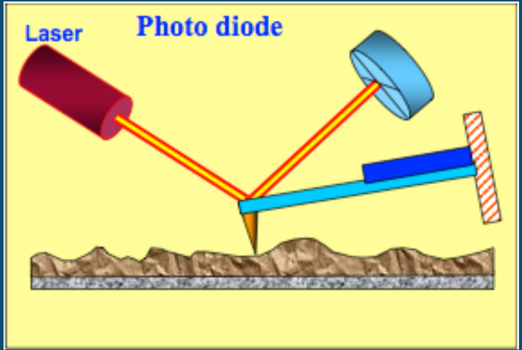
I_t: mean tunneling current

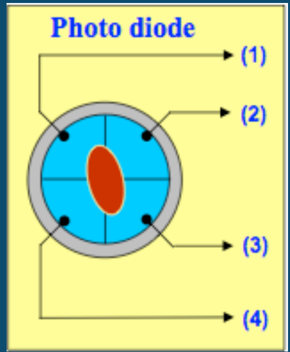


C. Loppacher et al, PRB 64, 13674 (2000)

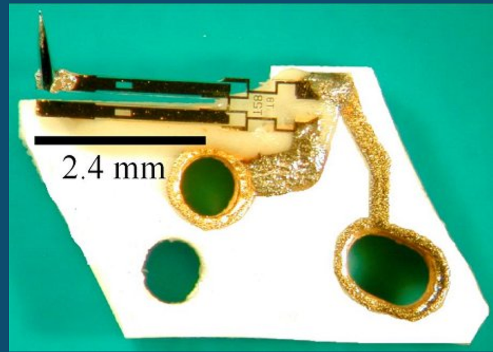
dAFM: signal detection

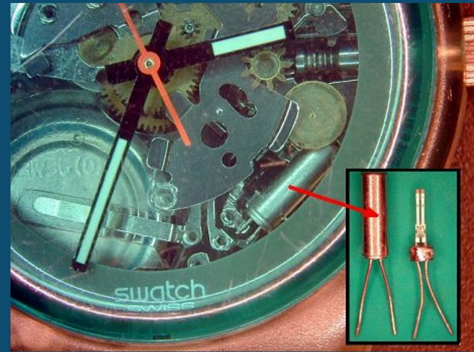
Photo diode



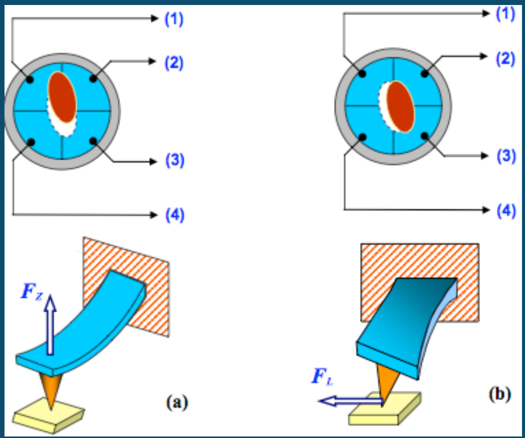


tuning fork: qPlus

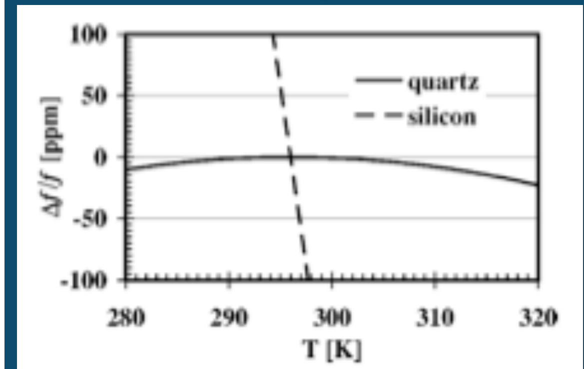




F. J. Giessibl Appl. Phys. Lett. 76, 1470 (2000)



Δf vs T



❑ 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

❑ movement of cantilever sensed by laser beam deflection

❑ silicon-based tip: chemically active

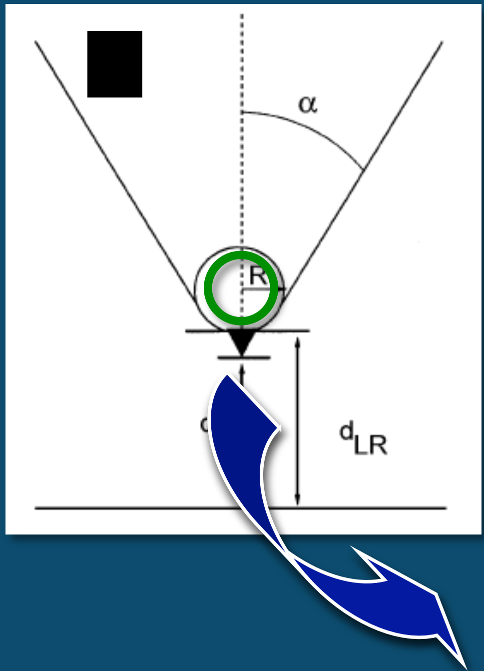
tuning fork merges STM/AFM

Forces in dAFM

$$\mathbf{F = F_V + F_{vdW} + F_{SR}}$$

Electrostatic forces

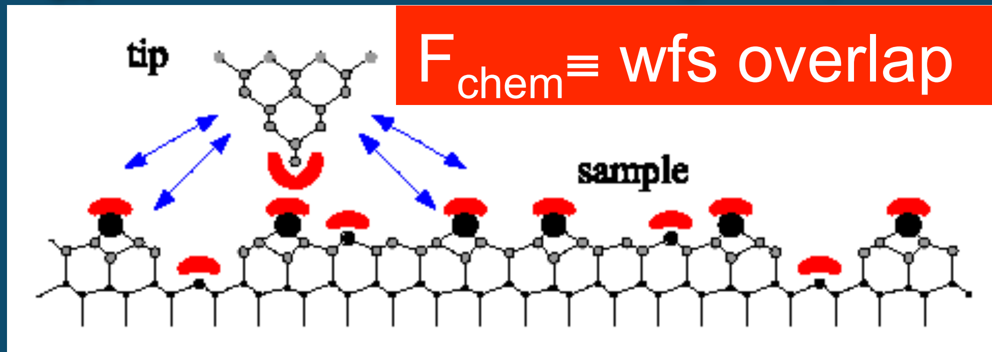
$$F_V = -\pi\epsilon_0(V_s - V_c)^2\left\{\frac{R}{d_{LR}} + s(\alpha)\left[\ln\left(\frac{L}{d_{LR}+R_\alpha}\right) - 1\right] - \frac{R[1 - s(\alpha)\cos^2\alpha/\sin\alpha]}{d_{LR}+R_\alpha}\right\}$$



Van der Waals forces

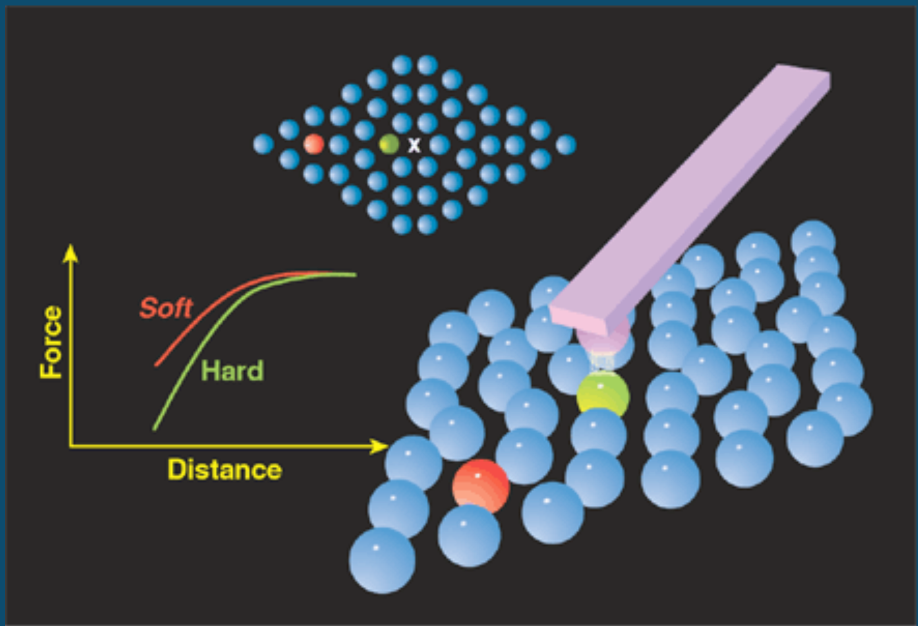
$$F_{vdW} = -\frac{H}{6}\left\{\frac{R}{d_{LR}^2} + \frac{\tan^2\alpha}{d_{LR}+R_\alpha} - \frac{R_\alpha}{d_{LR}(d_{LR}+R_\alpha)}\right\}$$

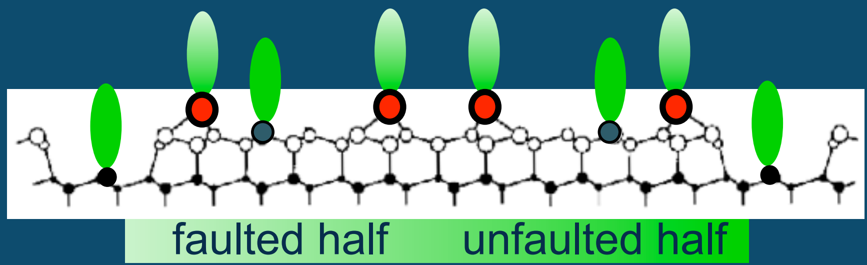
F_{SR} = Adhesion & Short Range Repulsive forces



$F_{chem} \equiv$ Short range chemical interaction: **attractive** (bonding) or **repulsive** (Pauli) depending on the distance $\Rightarrow$ **Quantum Mechanical calculation**

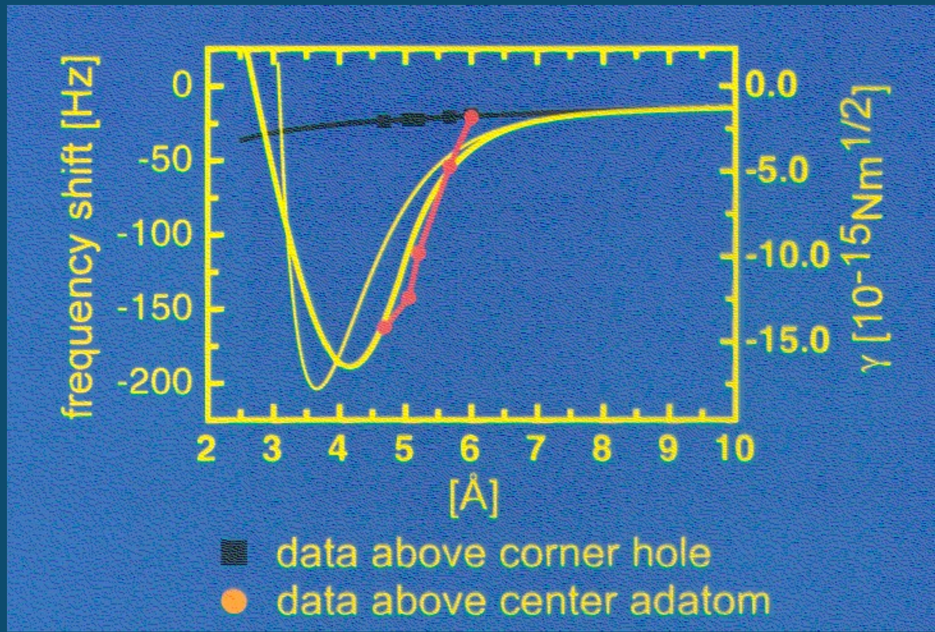
Force Site Spectroscopy: experiment & theory





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

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



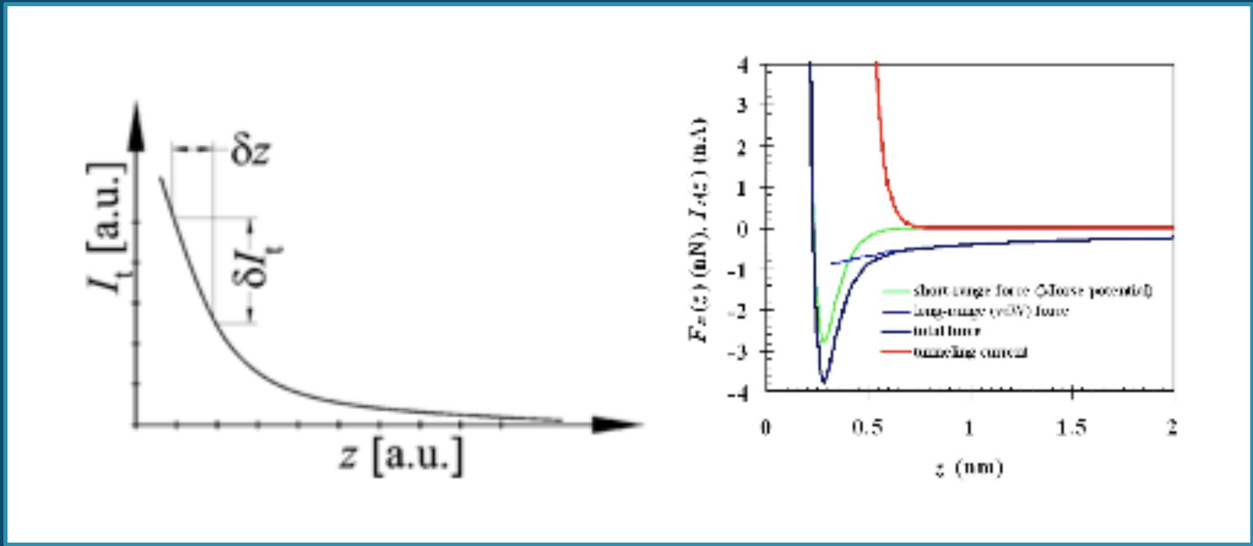
Separation of VdW and chemical interaction: substracting the corner hole contribution.

Tip-surface interactions

R. Pérez et al , PRL 78, 678 (1997)

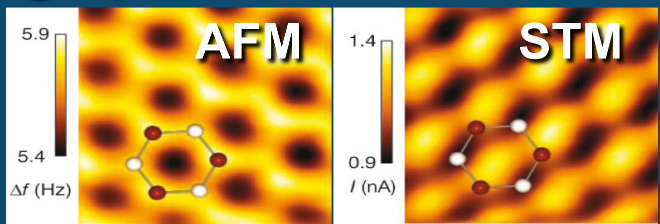
R. Pérez et al , PRB 58, 10835 (1998)

Do STM and dAFM image equally?



- ❑ relation between SR Force & Current (I ~ F^n)
- ❑ both the current and the SR Force are function of wave-function overlap

graphene



S. Hembacher et al PNAS 100, 12539 (2003).
S. Hembacher et al PRL 94, 056101 (2005)

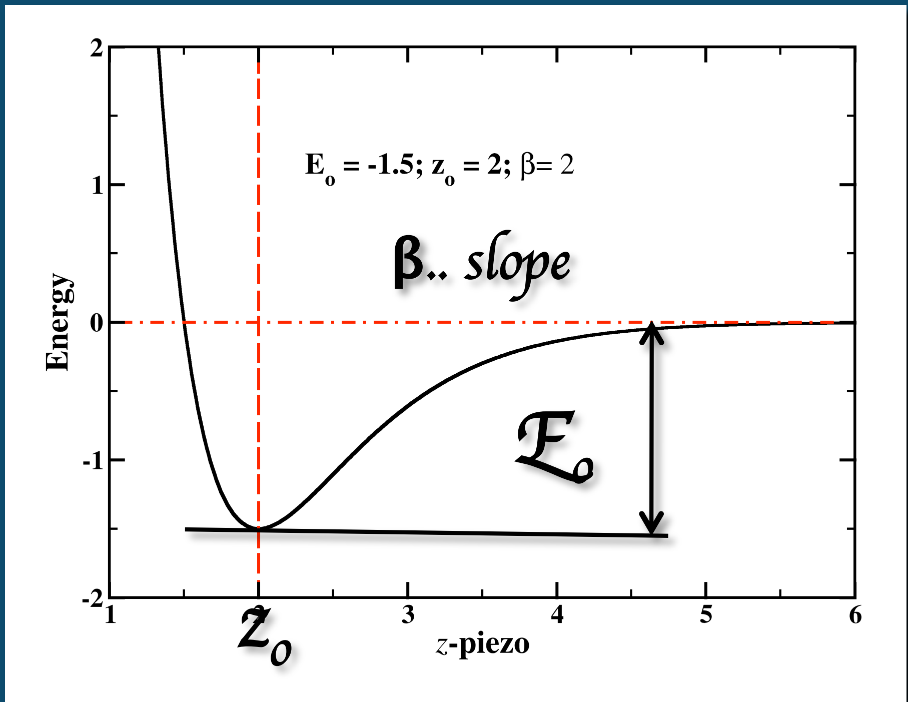
Chemical force: universality

VOLUME 47, NUMBER 9 PHYSICAL REVIEW LETTERS 31 AUGUST 1981

Universal Binding Energy Curves for Metals and Bimetallic Interfaces

J.H. Rose et al PRL 47, 675 (1981)

$$E(z) = E_o(1 + \beta(z - z_o))exp(-\beta(z - z_o))$$



Cohesive energy between two surfaces

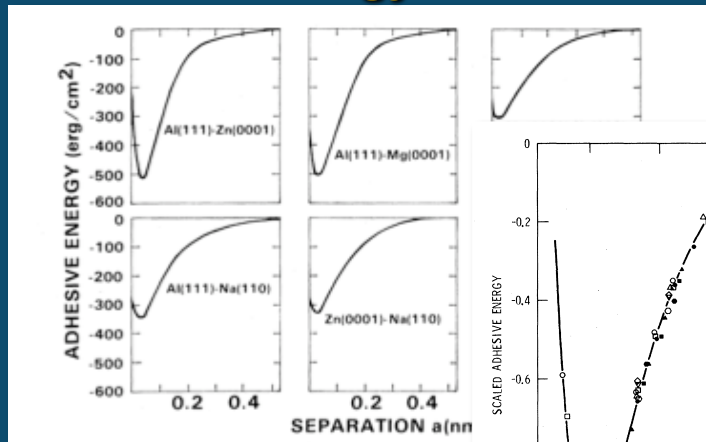


FIG. 1. Adhesive binding energy vs the separation a betw

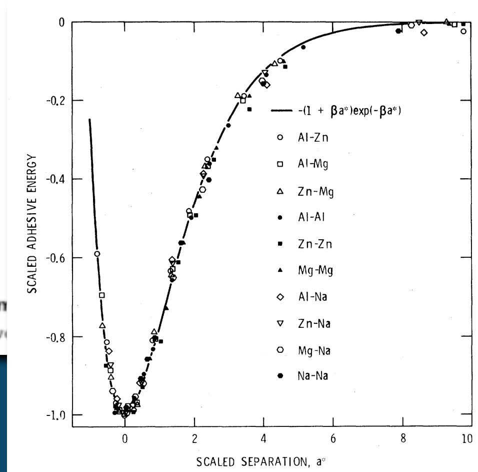
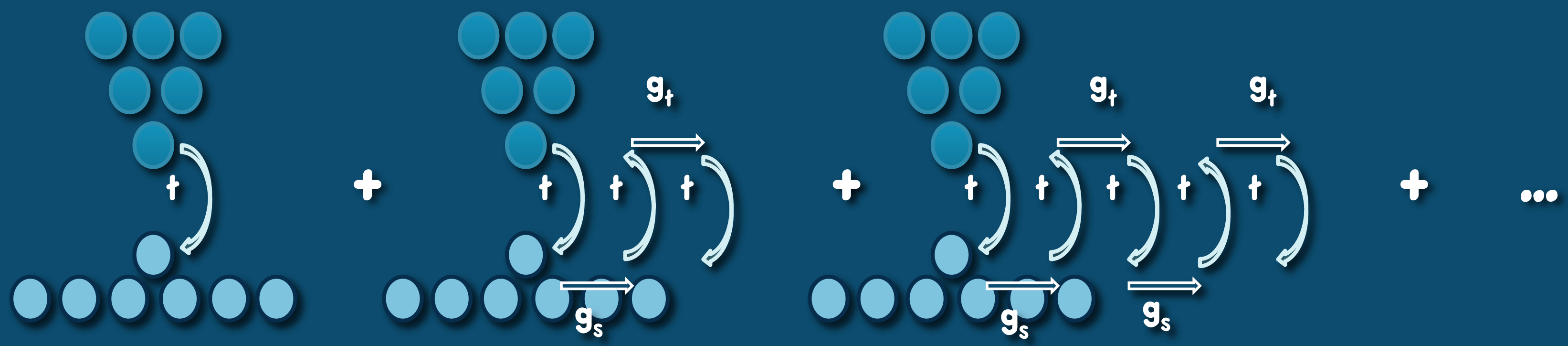


FIG. 2. Adhesive energy results from Fig. 1 (above) and Fig. 4 of Ref. 1 scaled as described in the text: $a^* = 2(a - a_m)/(\lambda_1 + \lambda_2)$.

no relaxation

- the cohesive energy between two bodies described in a simple exponential form
- contraction of z-piezo distance due to atomic relaxation??

Conductance I



conductance

$$G(\epsilon_F) = \frac{2e^2}{h} Tr\left[\tau(\epsilon_F)\tau^+(\epsilon_F)\right] = \frac{2e}{h} T(\epsilon_F)$$

GF

$$g = \frac{1}{\epsilon - \epsilon_o \pm i\eta}$$

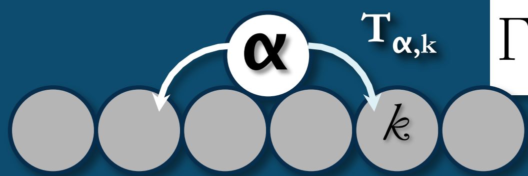
$$T(\epsilon_F) \approx g_{\alpha\alpha}(\epsilon_F)t_{\alpha,\beta}\, g_{\beta\beta}(\epsilon_F)t_{\beta,\alpha} + g_{\alpha\alpha}(\epsilon_F)t_{\alpha,\beta}\, g_{\beta\beta}(\epsilon_F)t_{\beta,\alpha} g_{\alpha\alpha}(\epsilon_F)t_{\alpha,\beta}\, g_{\beta\beta}(\epsilon_F)t_{\beta,\alpha} + \ldots.$$

$$g_{\alpha,\alpha} = i\pi\rho_\alpha$$

s-orbital only

$$T(\epsilon_F) = \frac{4\pi t^2_{\alpha,\beta}\rho_\alpha(\epsilon_F)\rho_\beta(\epsilon_F)}{(1+\pi^2 t^2_{\alpha,\beta}\rho_\alpha(\epsilon_F)\rho_\beta(\epsilon_F))^2}$$

tunneling via surface adatom



$$\Gamma = \pi T^2_{\alpha,k}\rho_k(\epsilon_F)$$

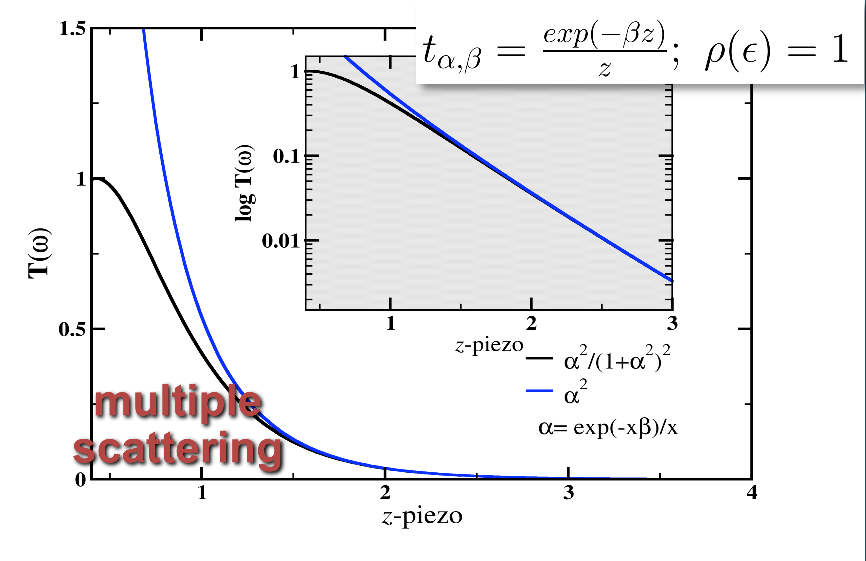
Γ … band width
$t_{\alpha\beta}$ … hopping

$$\rho(\epsilon) = \frac{1}{\pi}\left[\frac{\Gamma}{(\epsilon-\epsilon_o)^2+\Gamma^2}\right]$$

$$\rho_\alpha(\epsilon) \approx \frac{1}{\pi\Gamma}$$

Conductance II

T vs. z-piezo



Γ … band width
$t_{\alpha\beta}$ … hopping

$$T(\epsilon_F) = \frac{4\pi t^2_{\alpha,\beta}\rho_\alpha(\epsilon_F)\rho_\beta(\epsilon_F)}{(1+\pi^2 t^2_{\alpha,\beta}\rho_\alpha(\epsilon_F)\rho_\beta(\epsilon_F))^2}$$

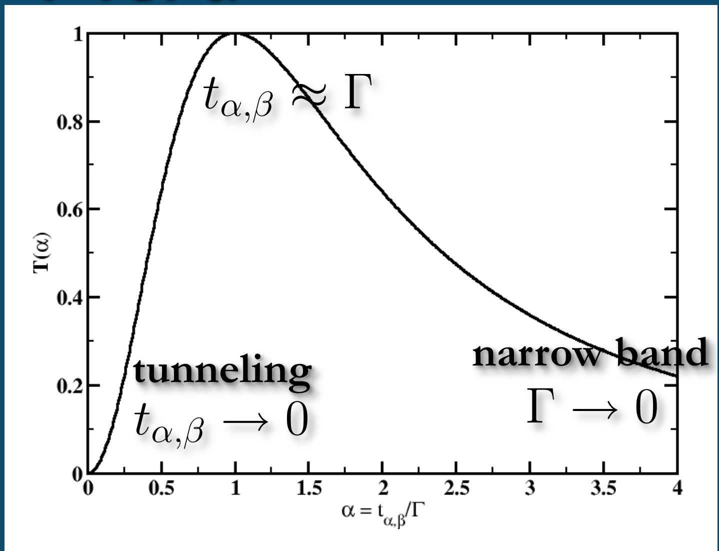
$$\rho_\alpha(\epsilon) \approx \frac{1}{\pi\Gamma}$$

$$\rho_\beta(\epsilon) \approx 1$$

$$\alpha = \frac{t_{\alpha,\beta}}{\Gamma}$$

$$T(\epsilon_F) = \frac{4\alpha^2}{(1+\alpha^2)^2}$$

T vs. α



parameters affecting the current

1) contraction of z-piezo distance
2) the multiple scattering effect
3) change of PDOS due to the chemical interaction

F&G dependence: a simple model

the tunneling current (via the Golden rule)

$$I_t = \sum |T^B_{\alpha,\beta}|^2 \delta(\epsilon_\alpha - \epsilon_\beta)$$

$$T^B_{\alpha,\beta} = \int_\Omega (\phi^*_\beta \nabla \phi_\alpha - \phi_\alpha \nabla \phi^*_\beta) d\vec{s},$$

decoupled systems α,β

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + V_1\right)\phi_\alpha = \epsilon^0_\alpha \phi_\alpha \qquad \left(-\frac{\hbar^2}{2m_e}\nabla^2 + V_2\right)\phi_\beta = \epsilon^0_\beta \phi_\beta$$

a coupled system

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + V_1 + V_2\right)\psi_i = \epsilon_i \psi_i$$

orthogonalization

$$\psi_i = \sum_{i,j} \Theta^{-\frac{1}{2}}_{ij} \phi_j$$

S² expansion

$$\Theta^{-\frac{1}{2}} = I - \frac{1}{2}S + \frac{3}{8}S^2$$

$$E^{int} = \sum_{i=\alpha,\beta} \delta h^0_{ii} + \sum_{i=\alpha,\beta} \delta E^{hop}_i = -\sum_\beta \left[S_{\alpha\beta}T^B_{\beta\alpha} + T^B_{\alpha\beta}S_{\beta\alpha}\right] + \frac{1}{2}\sum_\beta S_{\alpha\beta}S_{\beta\alpha}\left[\epsilon^0_\alpha - \epsilon^0_\beta\right] -$$

$$-\sum_\alpha \left[S_{\beta\alpha}T^B_{\alpha\beta} + T^B_{\beta\alpha}S_{\alpha\beta}\right] + \frac{1}{2}\sum_\alpha S_{\beta\alpha}S_{\alpha\beta}\left[\epsilon^0_\beta - \epsilon^0_\alpha\right] + 2\sum_\beta \frac{|T^B_{\alpha\beta}|^2}{\epsilon^0_\alpha - \epsilon^0_\beta} + 2\sum_\alpha \frac{|T^B_{\alpha\beta}|^2}{\epsilon^0_\beta - \epsilon^0_\alpha}$$

the interaction energy

$$E^{int} \approx S^2 \Delta\epsilon - S\gamma T^B + \frac{(T^B)^2}{\Delta\epsilon}$$

Atomic contact

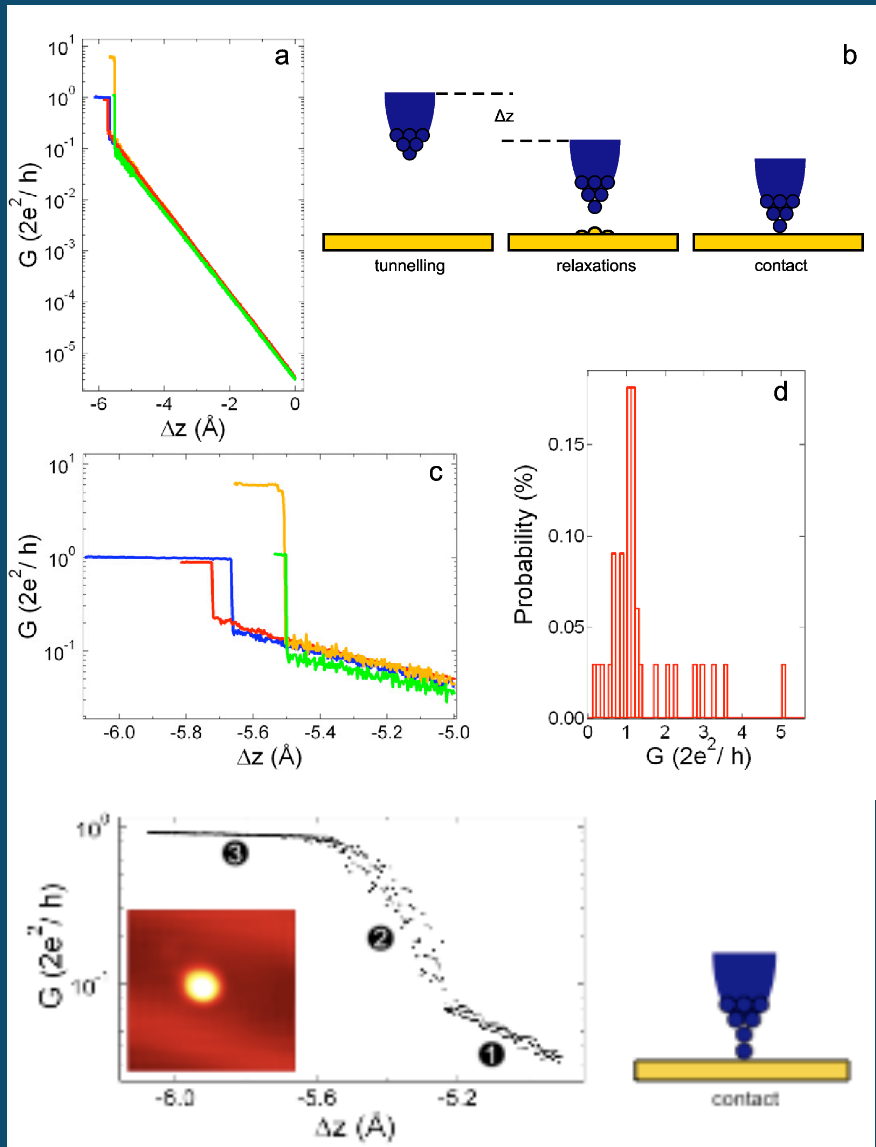
- **metal surfaces** - **monotonic increase** of the **conductance** observed while approaching the tip to the sample

- transition to the contact accompained by relaxation of the atoms

- **correlation** between the **multiple scattering** effects and the **SR forces: no** longer **exponetial behavior**

- **complete measurement of both I & F still missing**

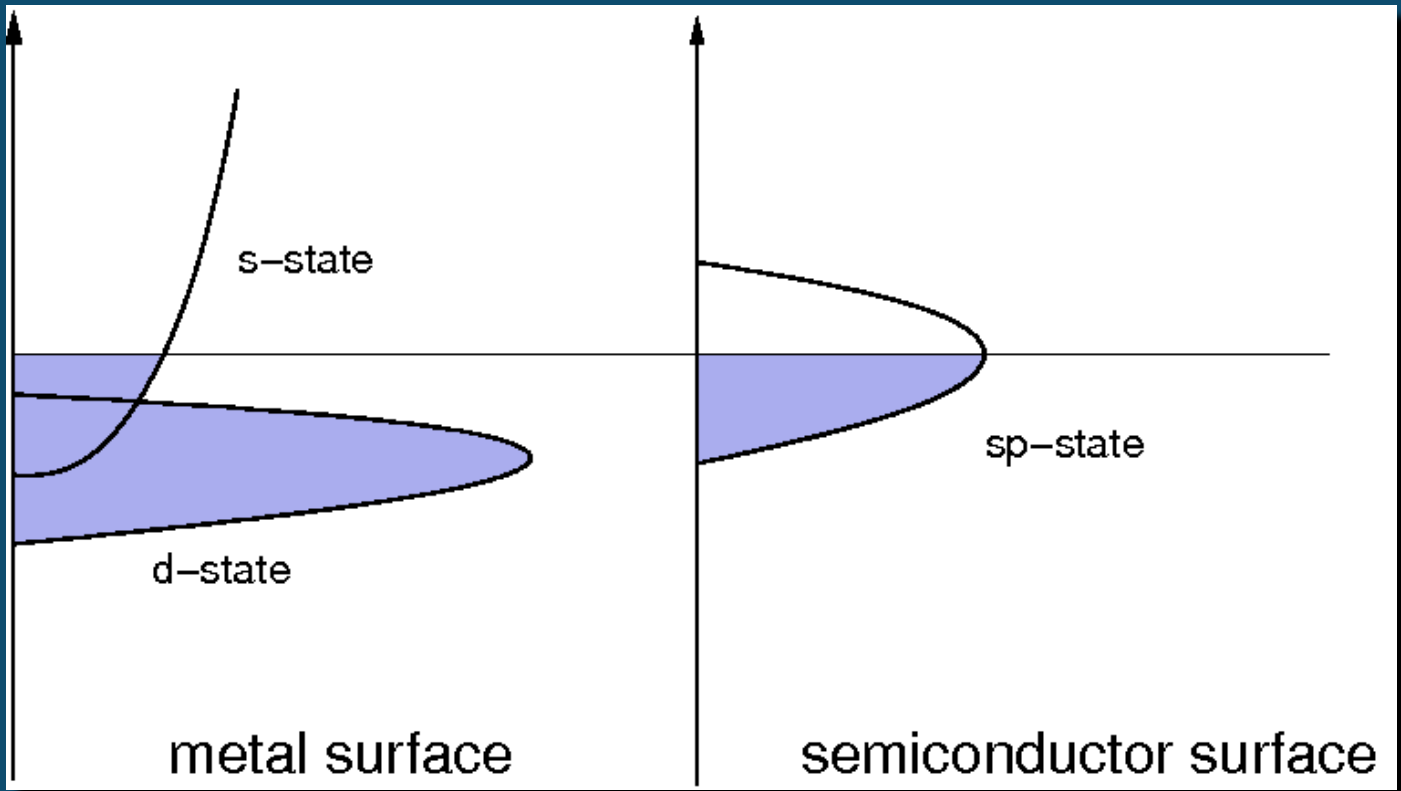
- **semiconductor surfaces??**



J.Kröger et. al. New Journal of Physics 9 153 (2007)

Electron transport at surfaces

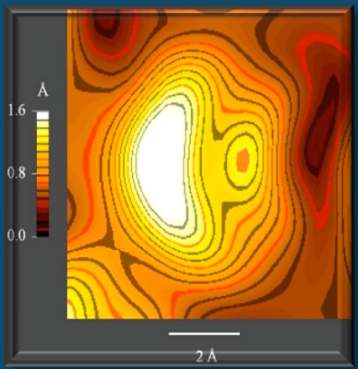
metal surface **semiconductor surface**



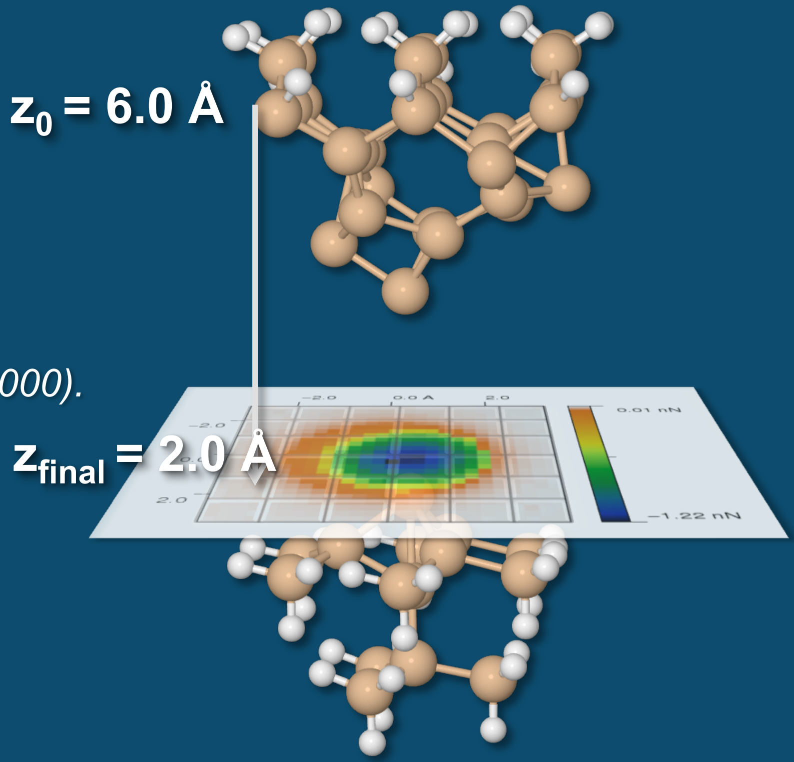
mainly delocalized s-states **localized sp *dangling bond* state**

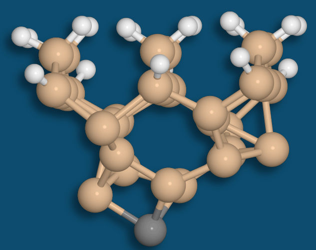
Semiconducting surfaces

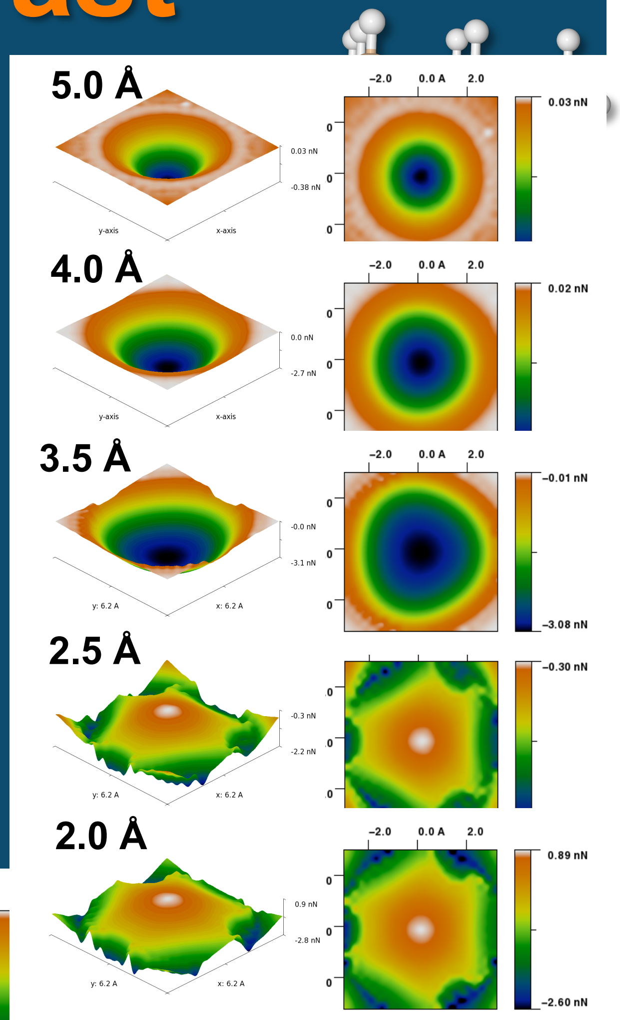
sub-Atomic contrast

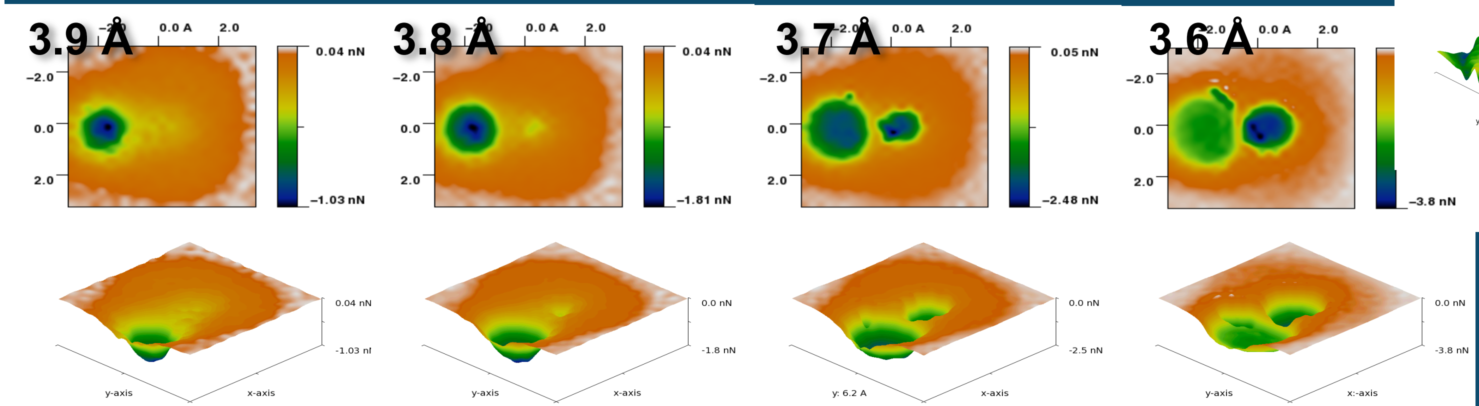


F.J. Giessibl et al, 289, 422 (2000).

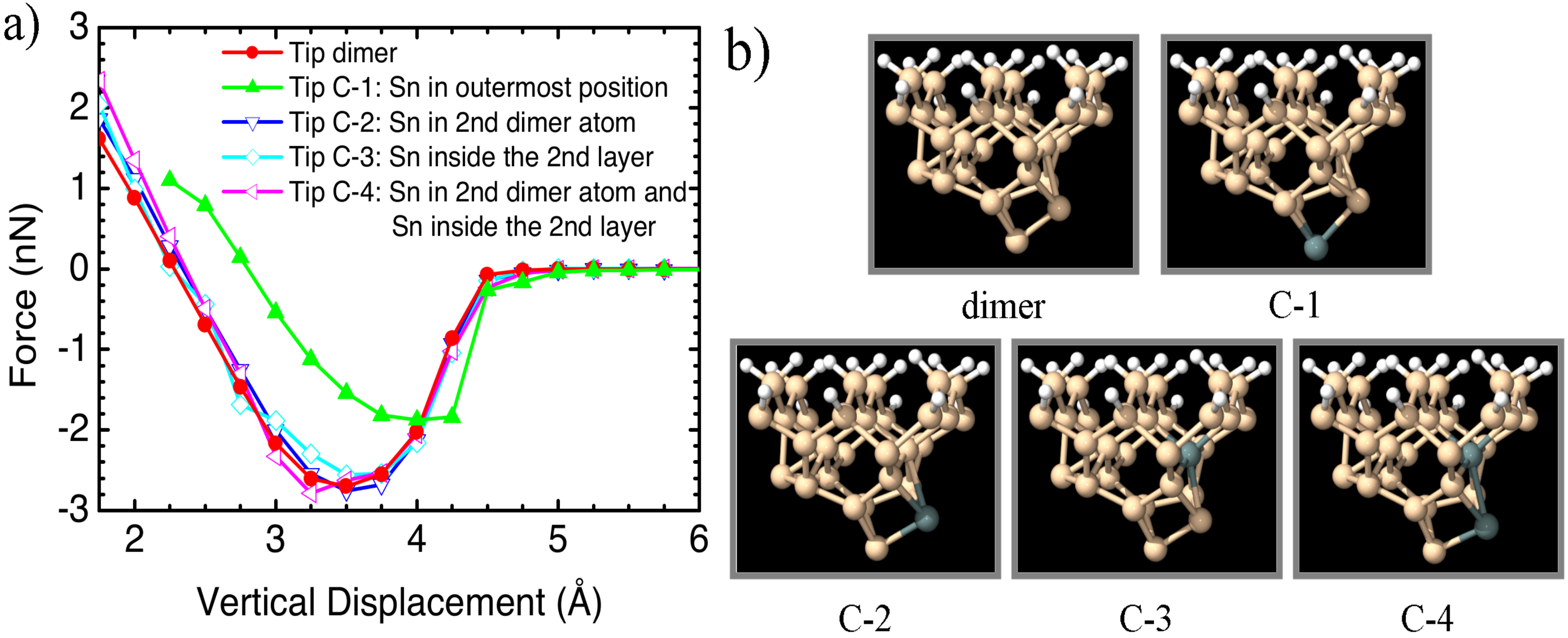








Si-based tip: interaction with Si adatom on Si(111) surface

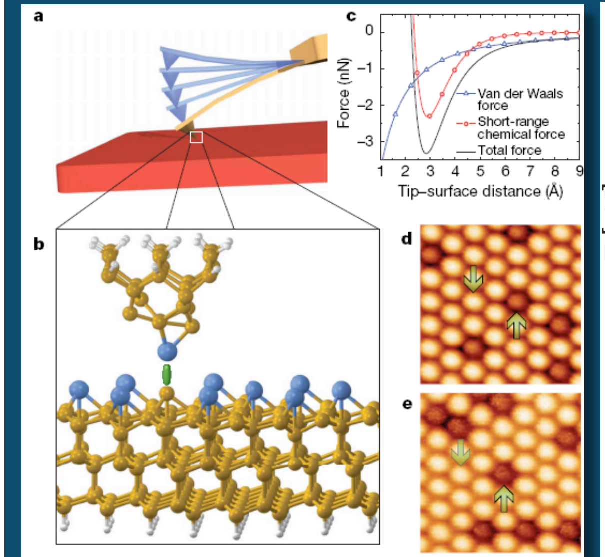


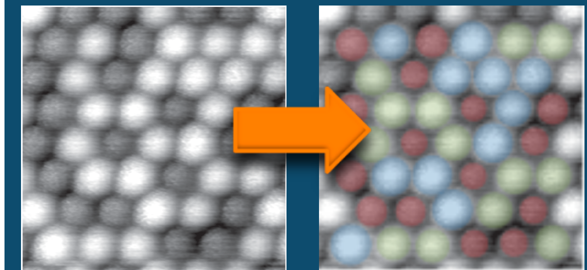
- tip-sample interaction mostly determined by apex and surface atoms
- isovalent impurities do not affect the mechanical response of AFM probe

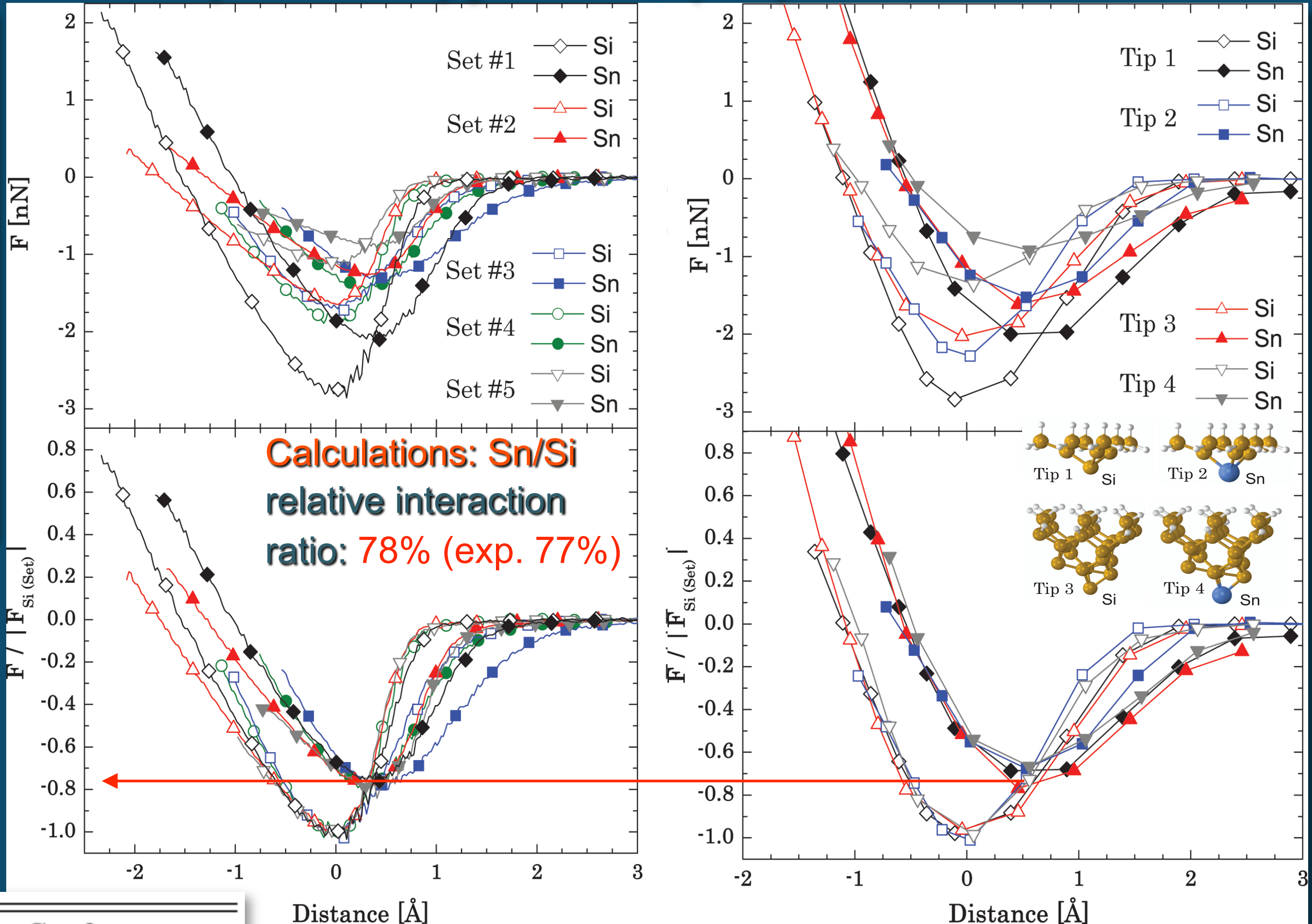
P. Pou et al Nanotechnology ***20*** *264015 (2009)*

Force & Chemical Identification

Force spectroscopy PbSn/Si(111)







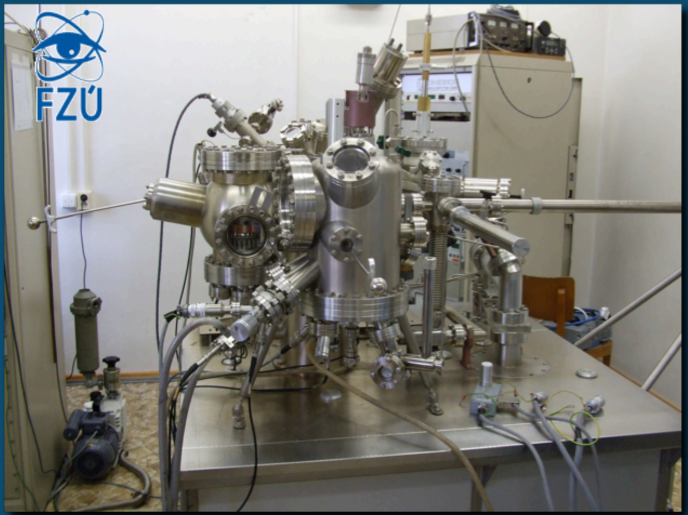
	Surface atom				Surface atom		
Tip B	Si	Sn	Pb	Tip A	Si	Sn	Pb
Si	100%	82%	67%	Si	100%	78%	62%
Sn	100%	84%	68%	Sn	100%	79%	59%
Pb	100%	82%	64%	Pb	100%	71%	54%

- the chemical sensitivity via the short-range force

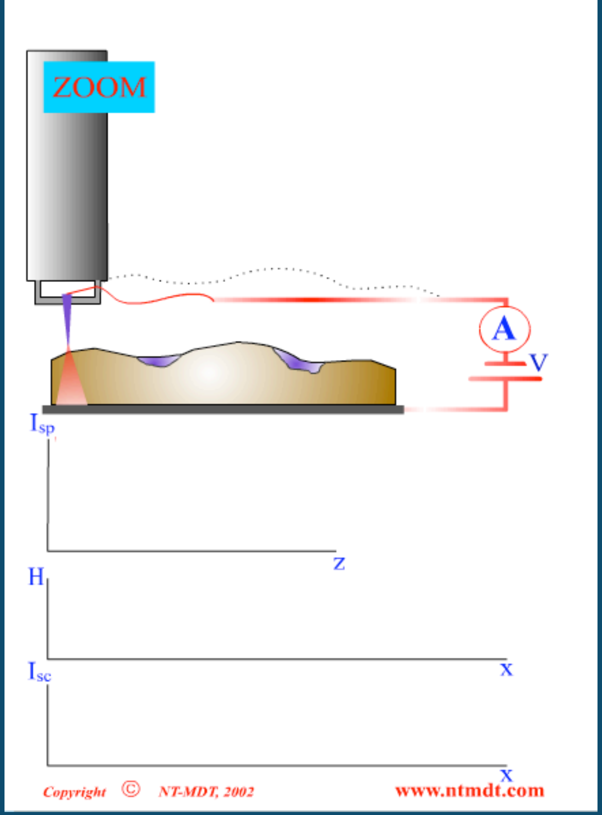
Y. Sugimoto et al **Nature 446,** 64 (2007)

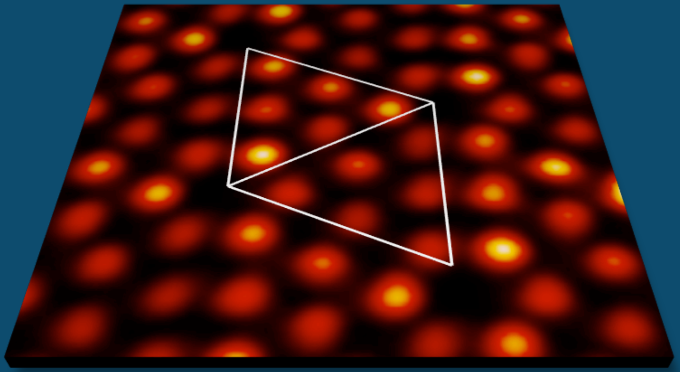
STM I-z spectroscopy: Si(111)-7x7

- standart Omicron UHV STM @ RT
- operating in the constant-height mode on a small area to minimze thermal drift
- I-z spectroscopy on an arbitrary adatom
- no adatom manipulation



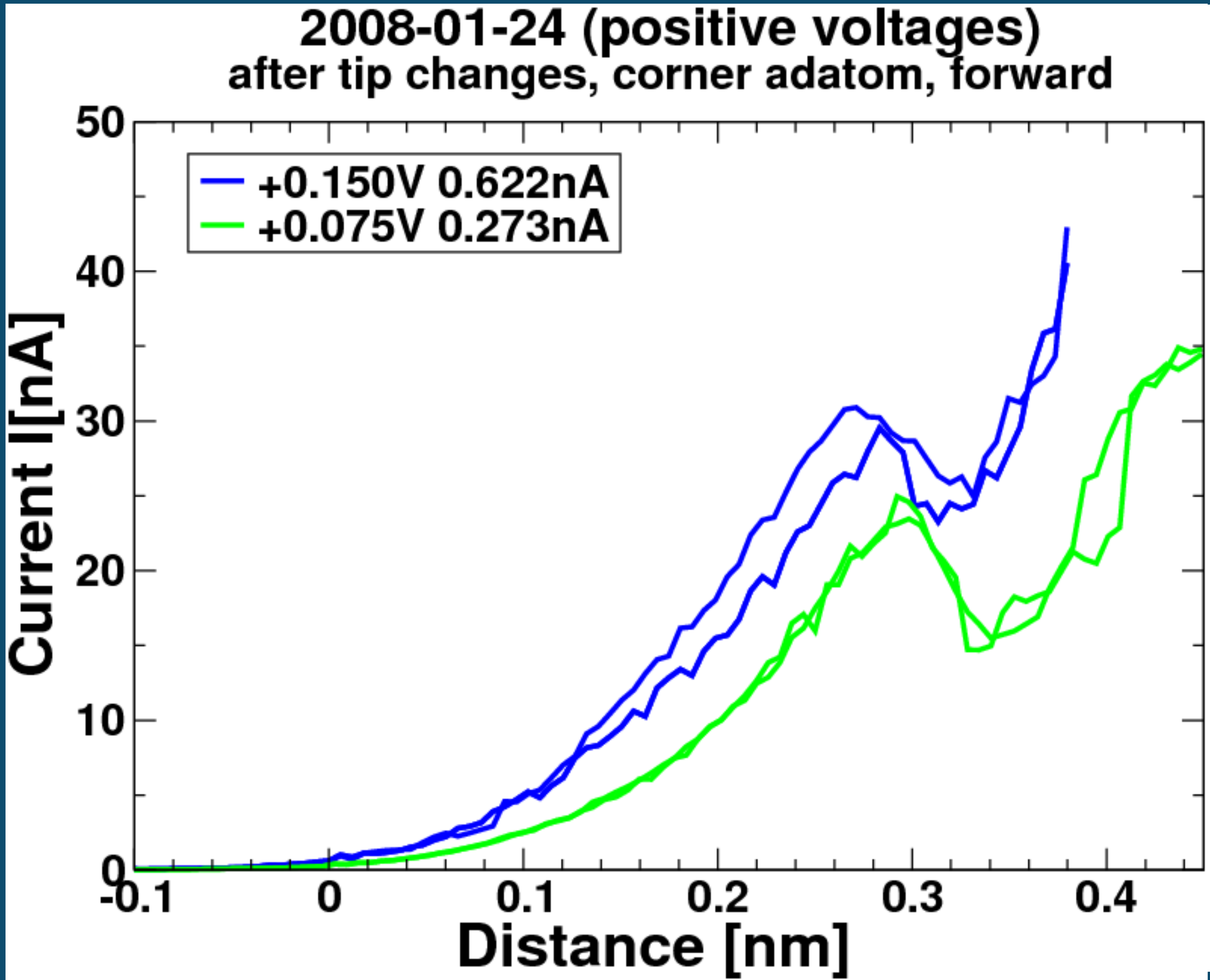
I-z spectroscopy





constant-height at -0.2V; (0.12nA)

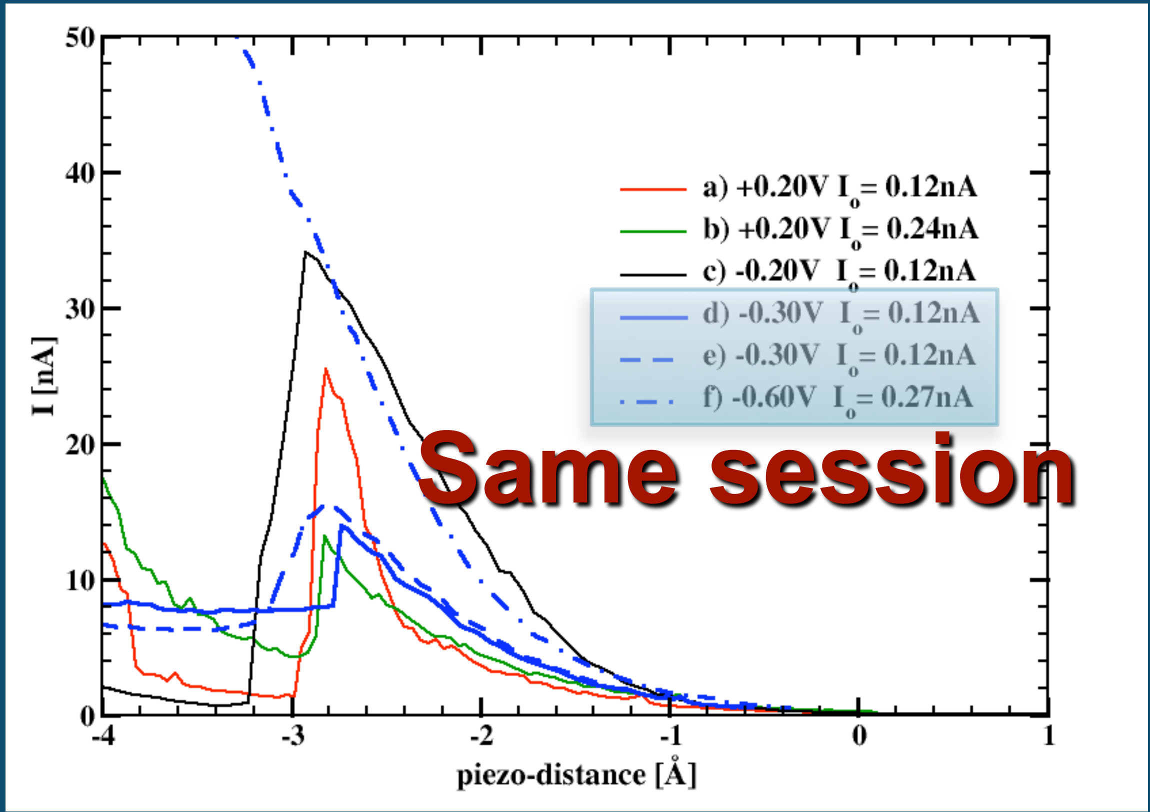
I-Z spectroscopy: results

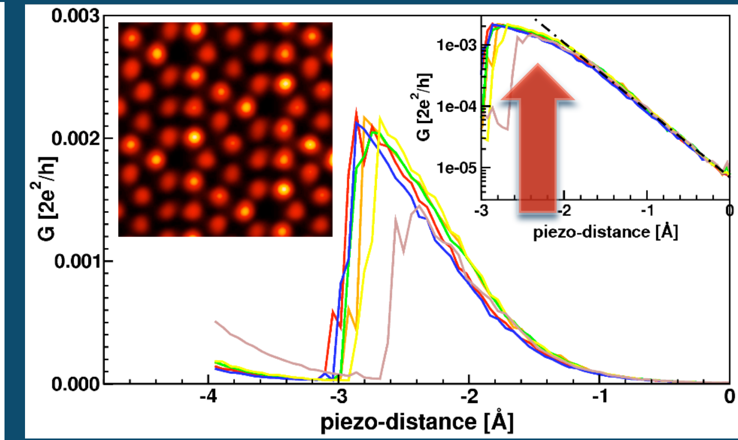


Positive bias voltage

Independent of bias voltage direction

The conductance drop: summary

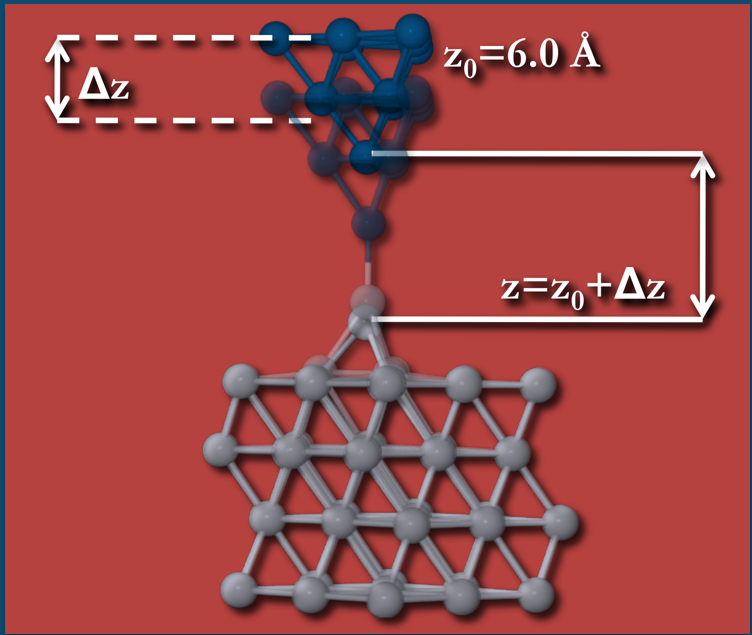




- ❑ well reproducible during different sessions
- ❑ observable only at small bias voltage
- ❑ tip structure slightly modify the shape but not the feature
- ❑ observed at both polarities and both scan z-directions of tip
- ❑ before jump almost the exponential behavior

P. Jelinek et. al. PRL 101, 176 101 (2008).

Computational details



A. Geometry optimization

- TB-DFT LDA (FIREBALL) +
- Ab-initio PW-DFT (*VASP*) ++

(XC: LDA, GGA-PW91)

+ *www.fireball-dft.org*
++ */cms.mpi .univie.ac.at/vasp/*

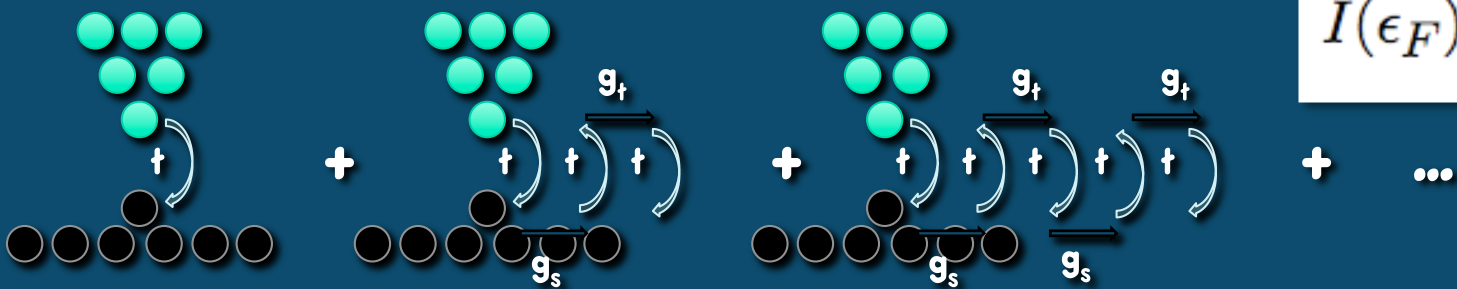
B. Transport calculations

- Greens function DFT (*FIREBALL*)+

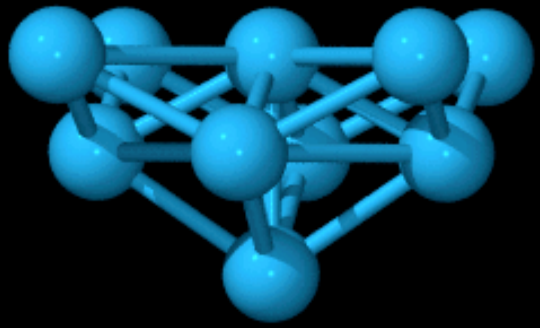
(fully relaxed structures)

+ *www.fireball-dft.org;*
J.M. Blanco et al Prog. Surf. Sci. 81, 403 (2006)

$$I(\epsilon_F) = \frac{2e}{h} T(\epsilon_F)$$

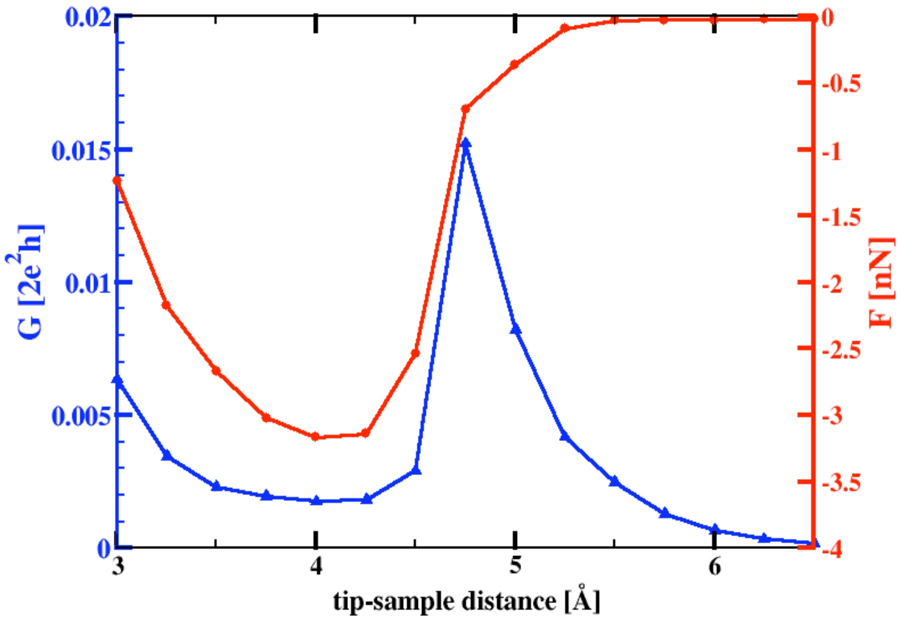


DFT simulation :CoA Si7x7 + tip W

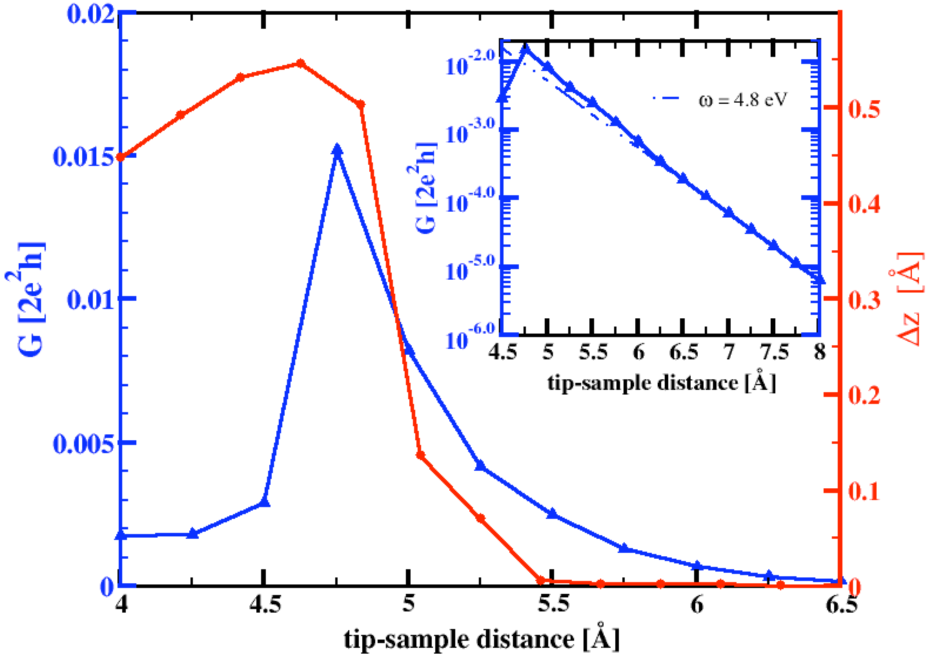


- distortion of the local structure of the tip and sample at short distances
- reversible process
- attractive short-range force onset corresponds to the drop in the conductance

Conductance and force: Si corner adatom

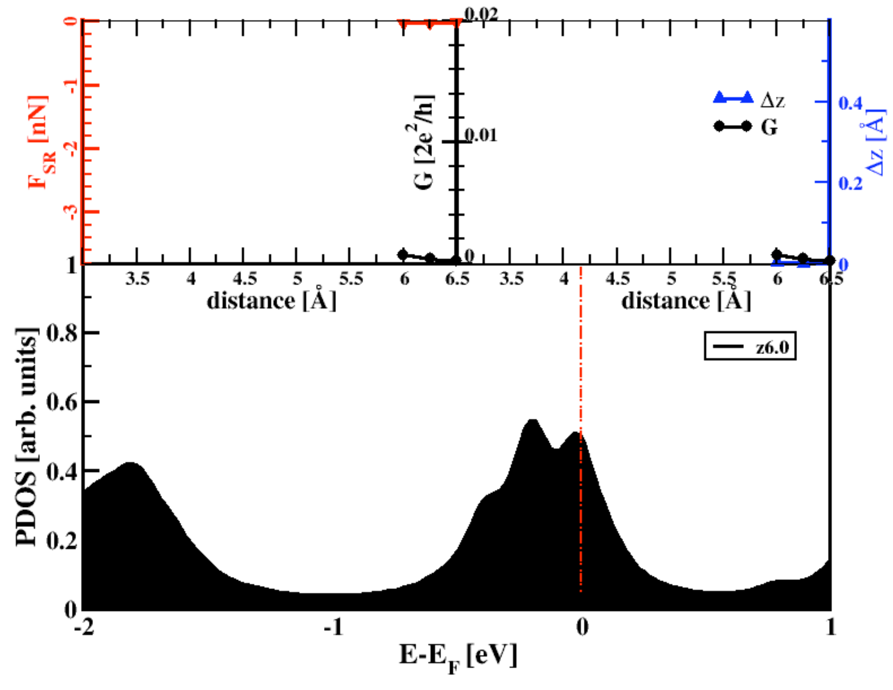


Conductance & short-range force



Conductance & adatom displacement

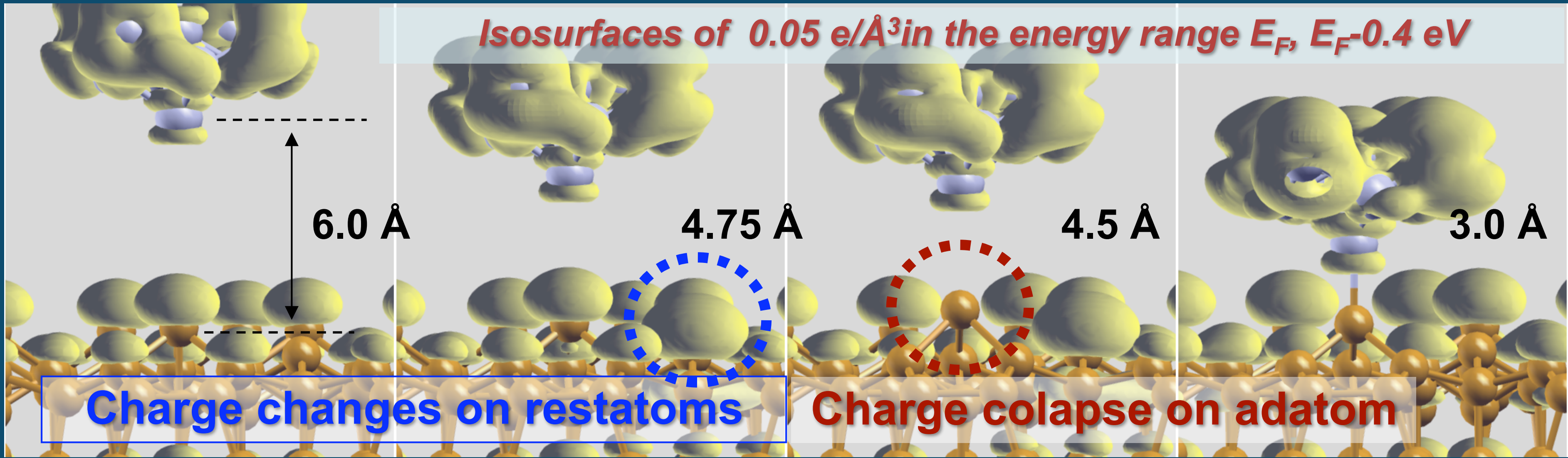
Electron density along the path



- chemical interaction between the tip and sample changes the position of Si dangling bonds near the Fermi level

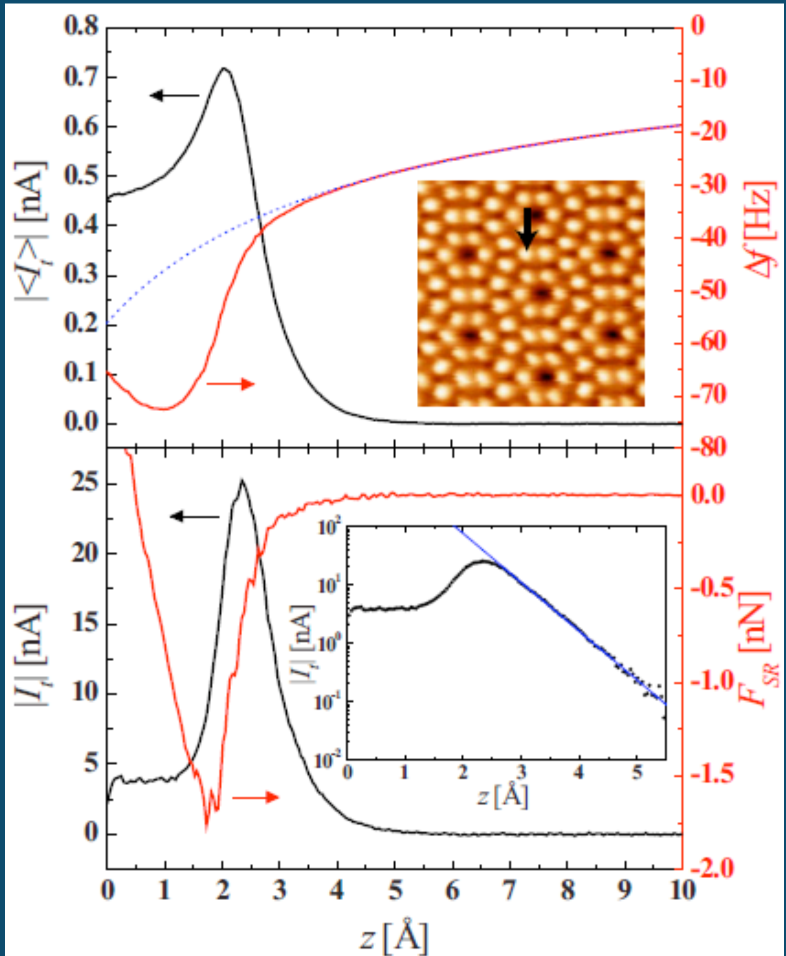
→ direct impact on the tunnelling current along the tip-sample distance

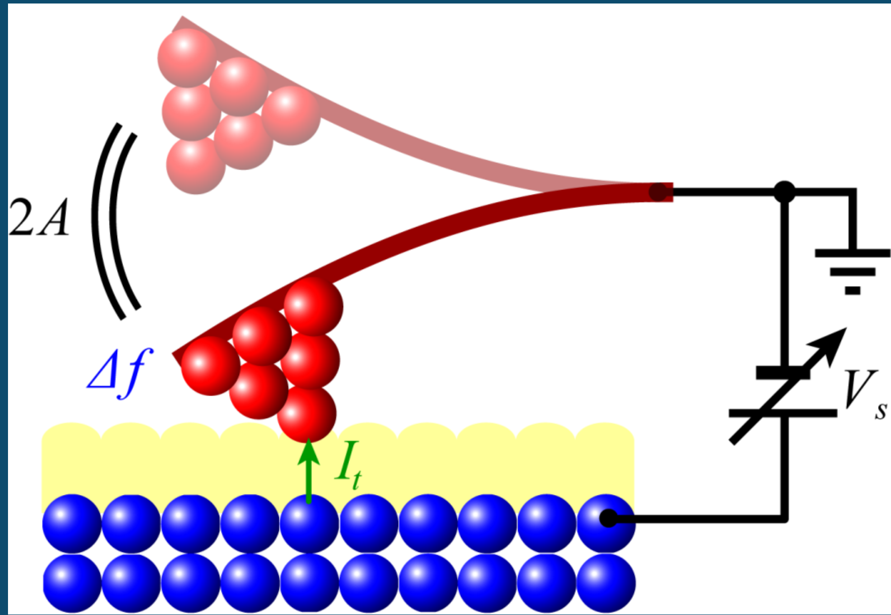
P. Jelinek et. al. PRL101 176101 (2008)



simultaneous STM/AFM: Si 7x7

D. Sawada, et al., *Appl. Phys. Lett.* 94 (2009) 173117.

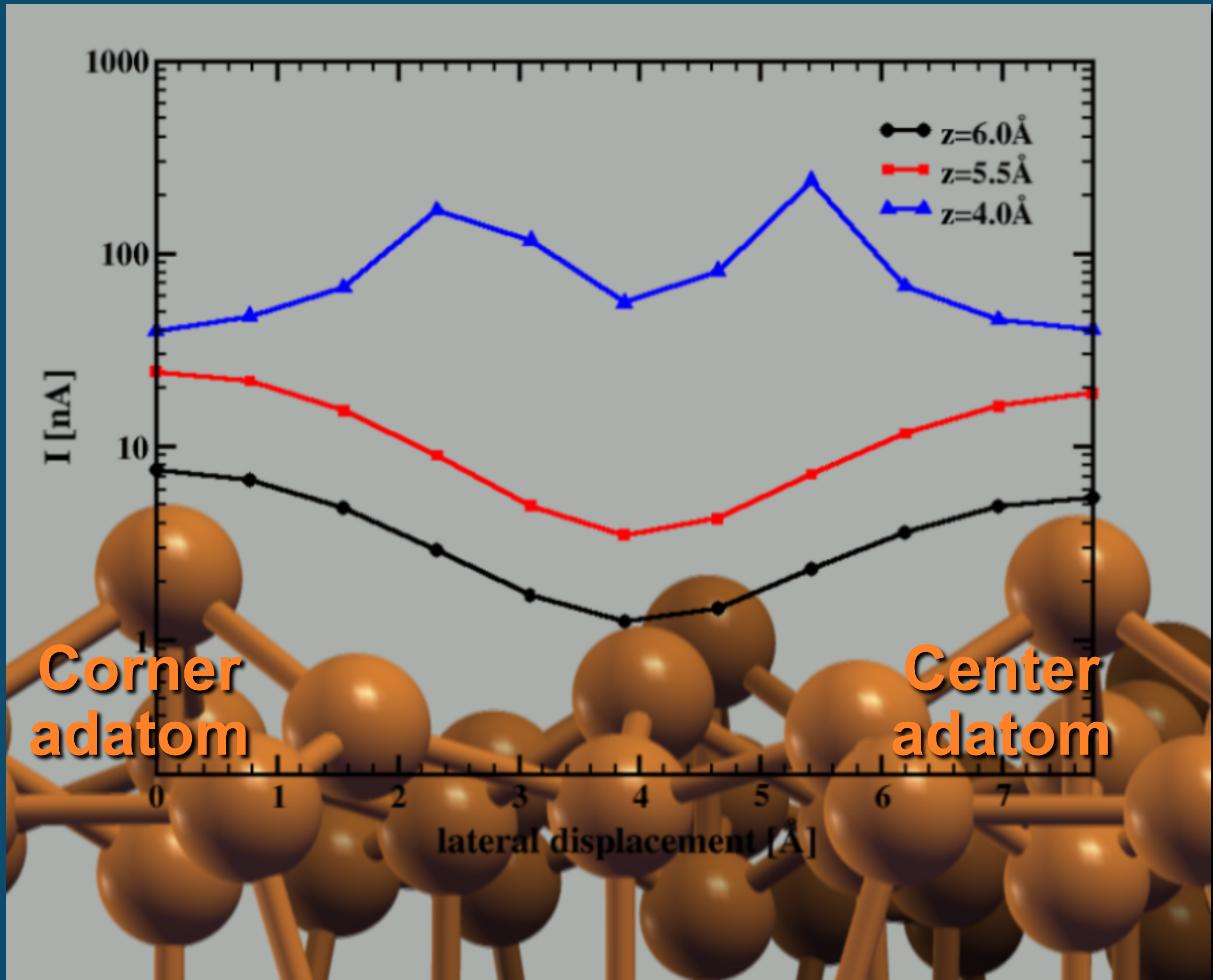




Pt-Ir coated Si cantilever
(nanoworld)
Ar ion sputtering

***f_0*=200 kHz, *k*=30 N/m, *Q*=13000, *A*=20 nm**

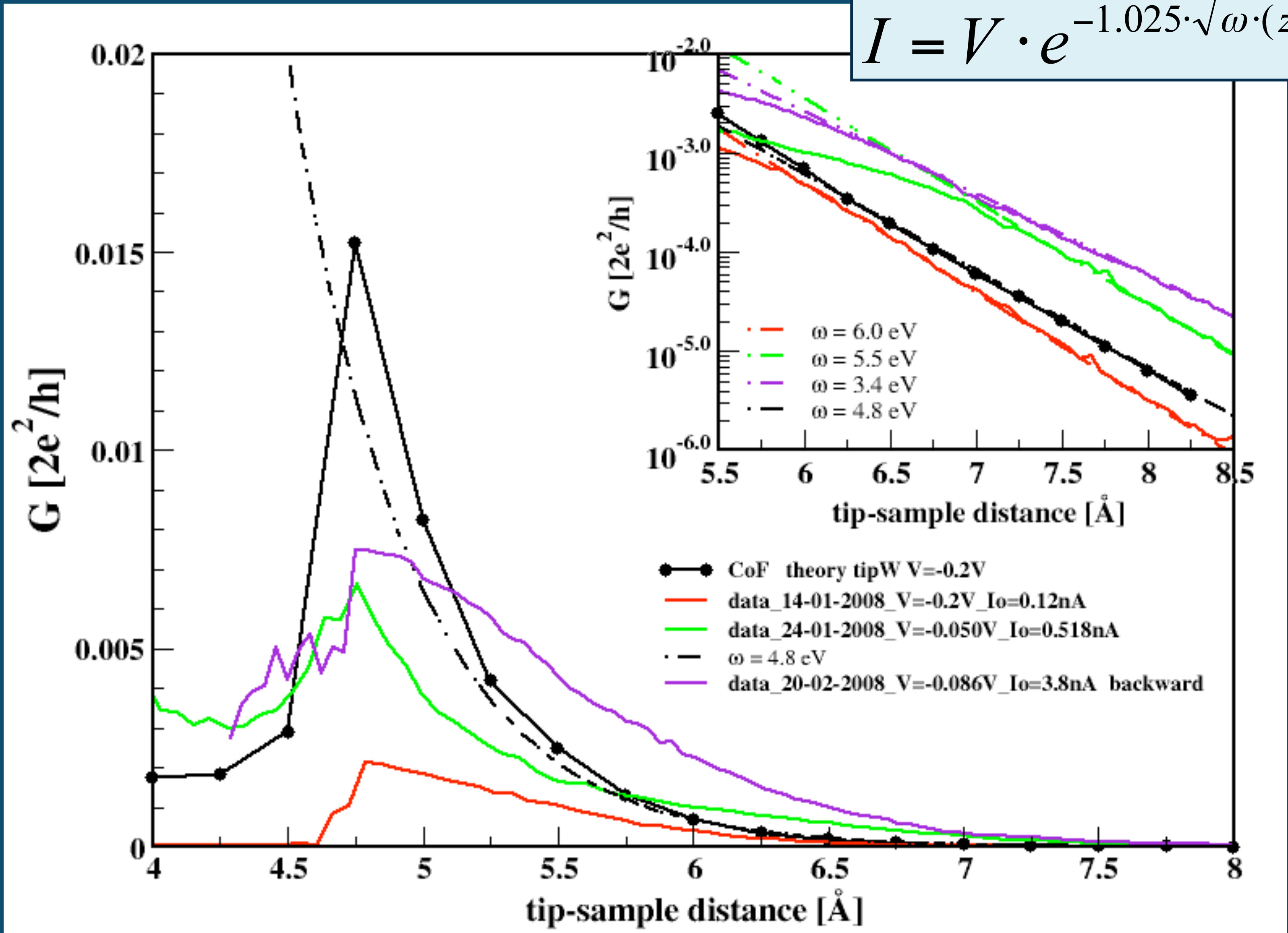
Image contrast change: lateral scan



- **Constant height profile from the corner to the central Si adatom at -0.2V**
- ***true atomic resolution*** **until the modification of the** ***dangling bond*** **state occurs**

The apparent barrier height

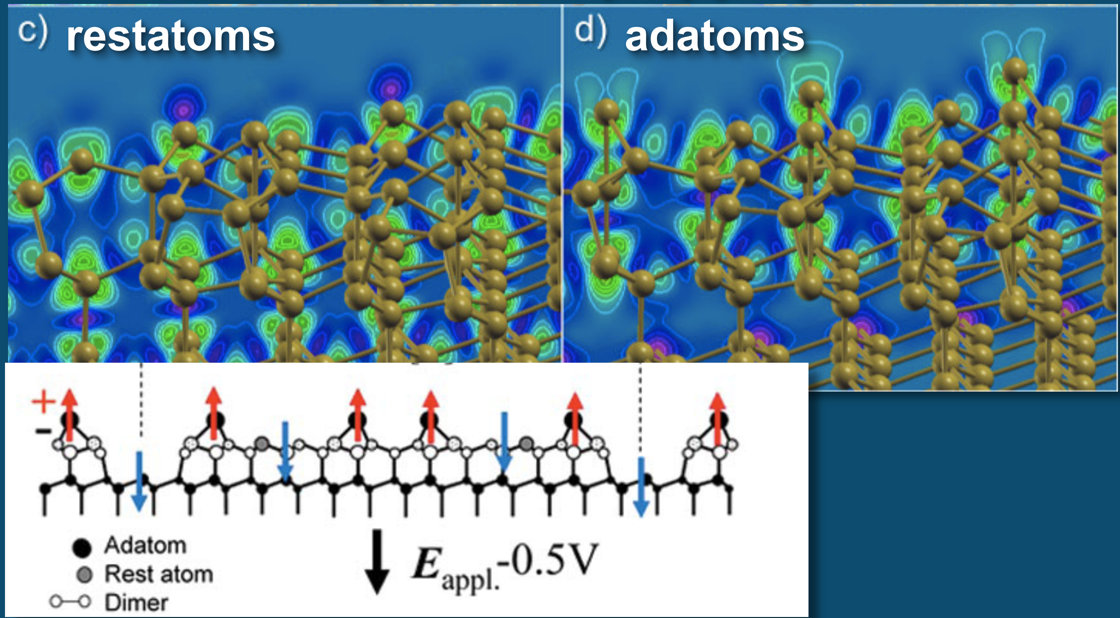
$$I = V \cdot e^{-1.025 \cdot \sqrt{\omega} \cdot (z - z_0)}$$



→ ω changes with the tip

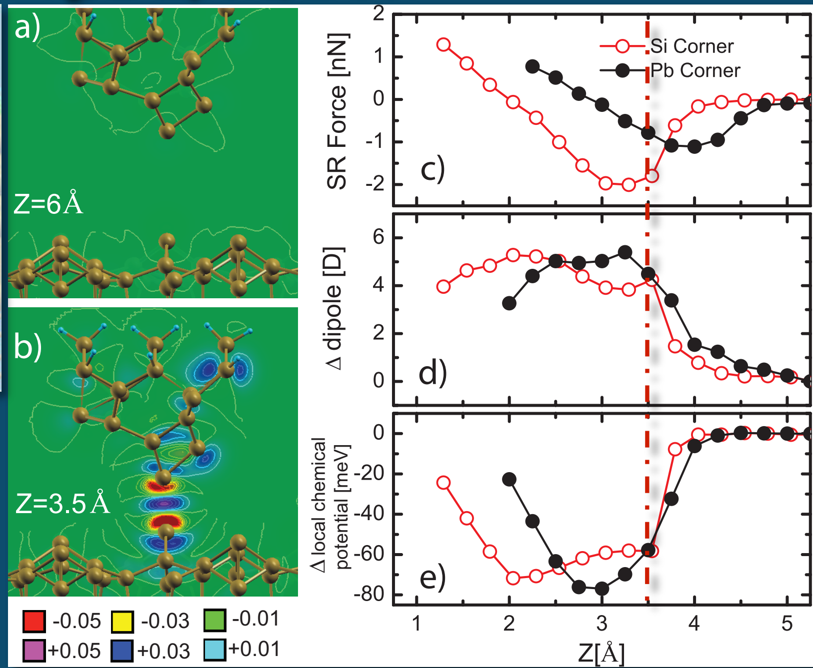
Surface charge density & forces

distribution of δρ on the Si(111)-(7x7) surface

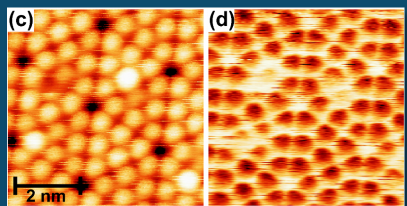


*Y. Cho and R. Hirose PRL **99** 186101 (2007)*

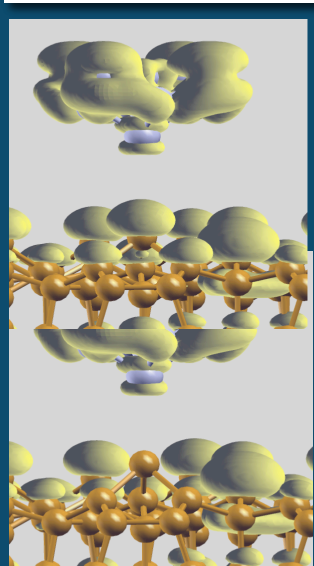
F_z, Δ dipole, Δ LCP



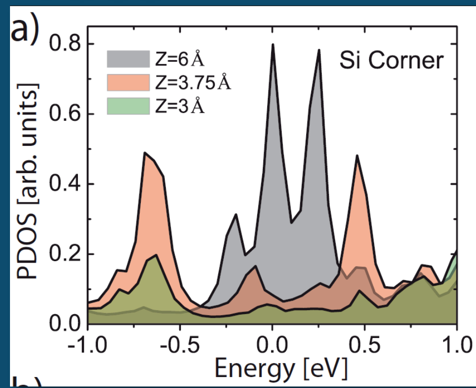
- ❑ changes on the onset of the chemical force
- ❑ the chemical force modifies PDOS & surface dipole → LCP
- ❑ origin of the atomic contrast obtained in KPFM



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

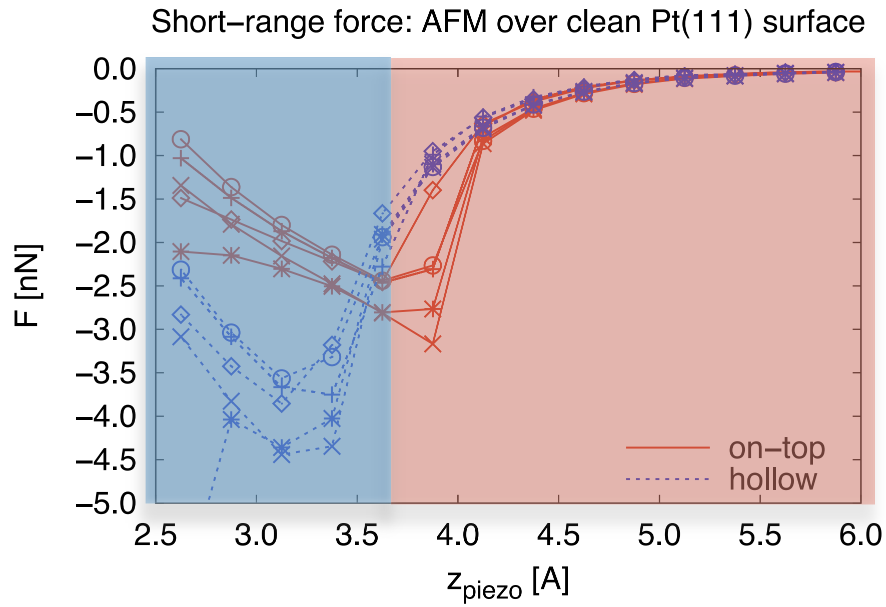


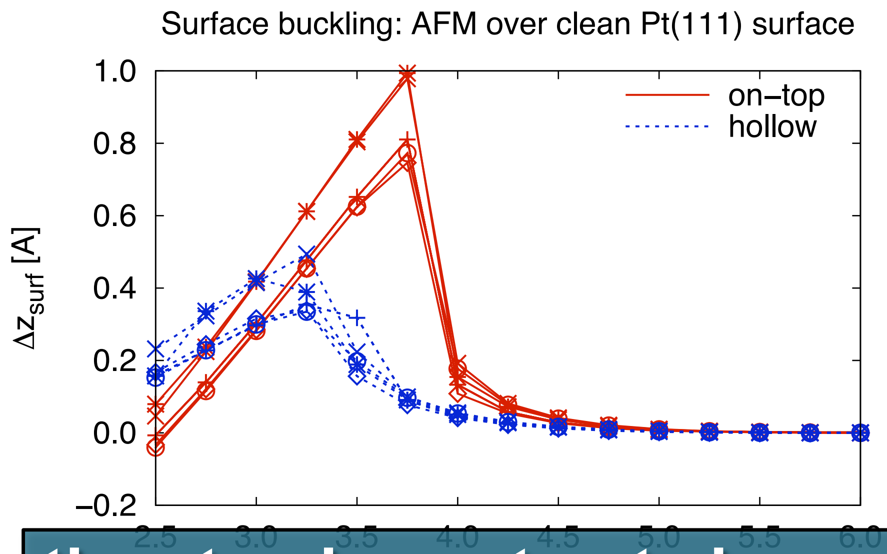
PDOS

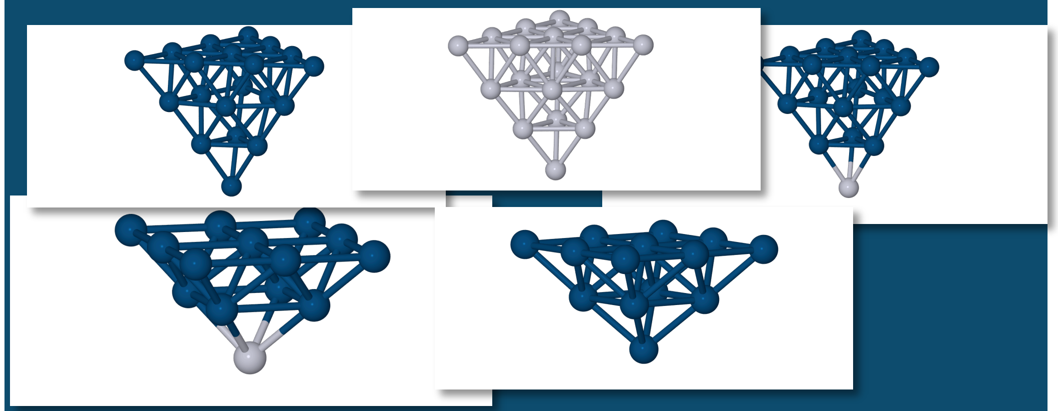


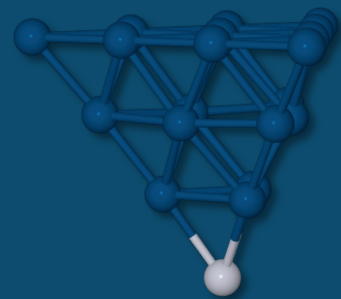
Metal surfaces

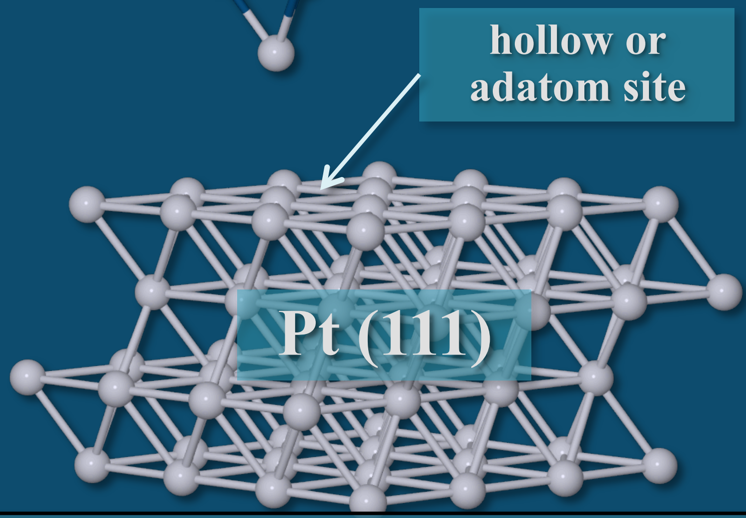
AFM: Atomic & chemical resolution I





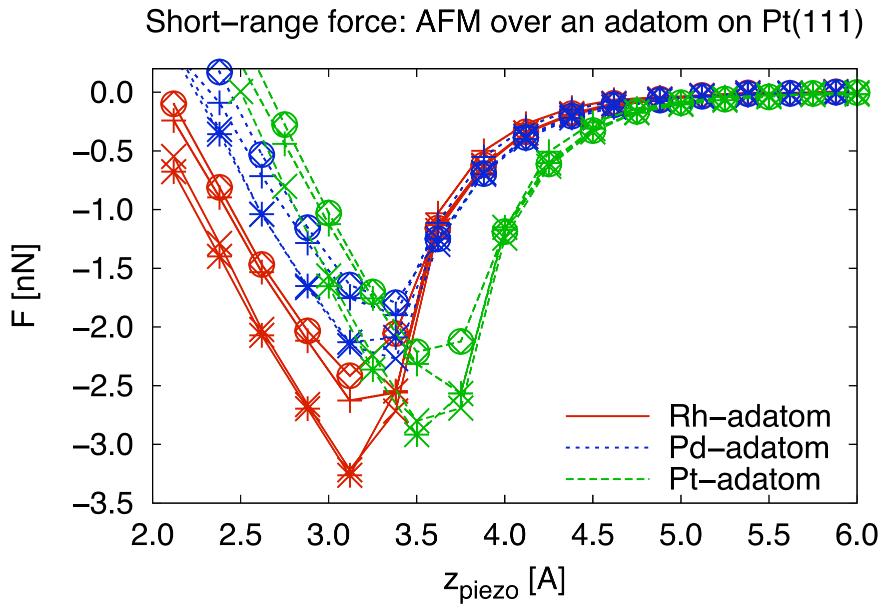


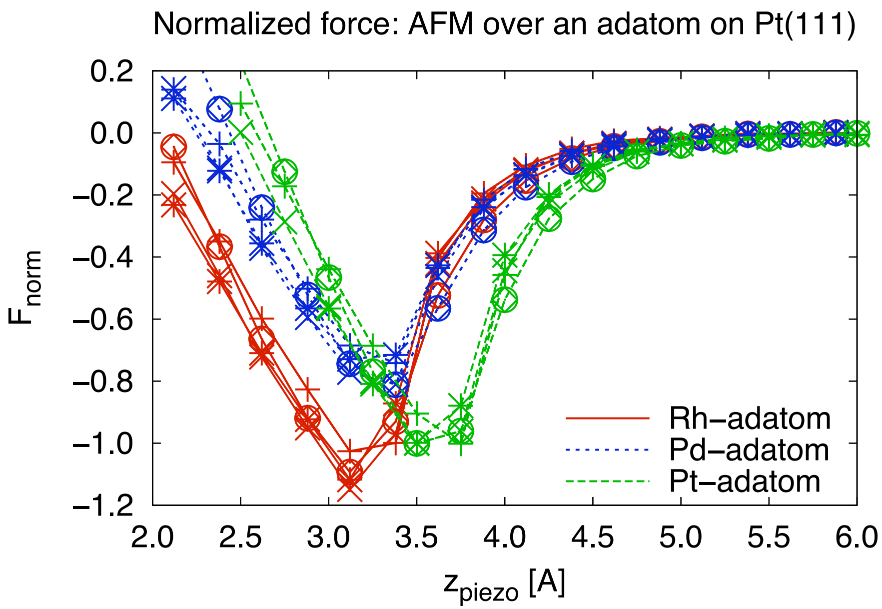


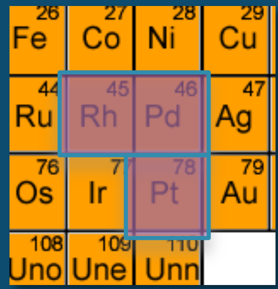


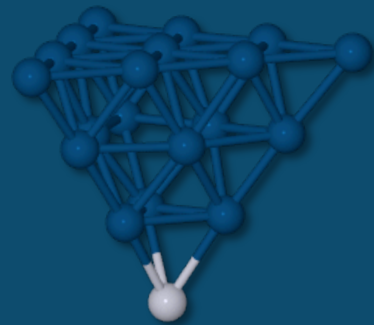
the atomic contrast changes with the tip-sample distance

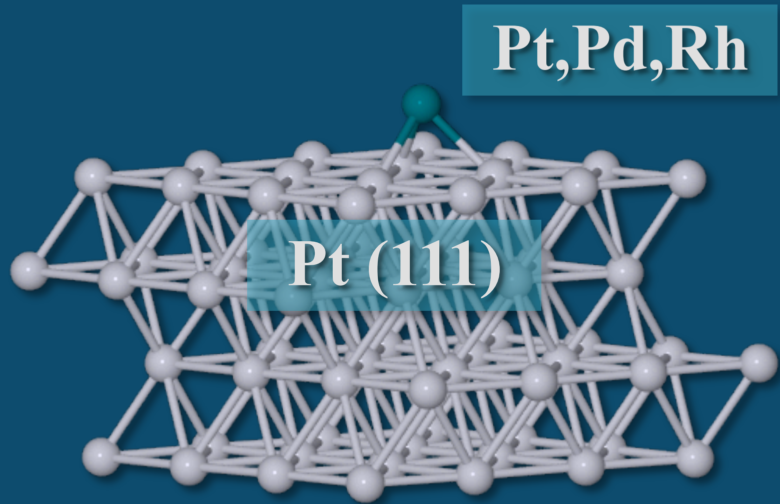
AFM: atomic & chemical resolution II











	Pt	Pd	Rh
F_{max} [nN]	-2.56÷0.4	-1.96÷0.2	-2.81÷0.5
F_{norm} [nN]	-1.00	-0.76	-1.10

Scaling I & F

general relation scaling between I and F ?

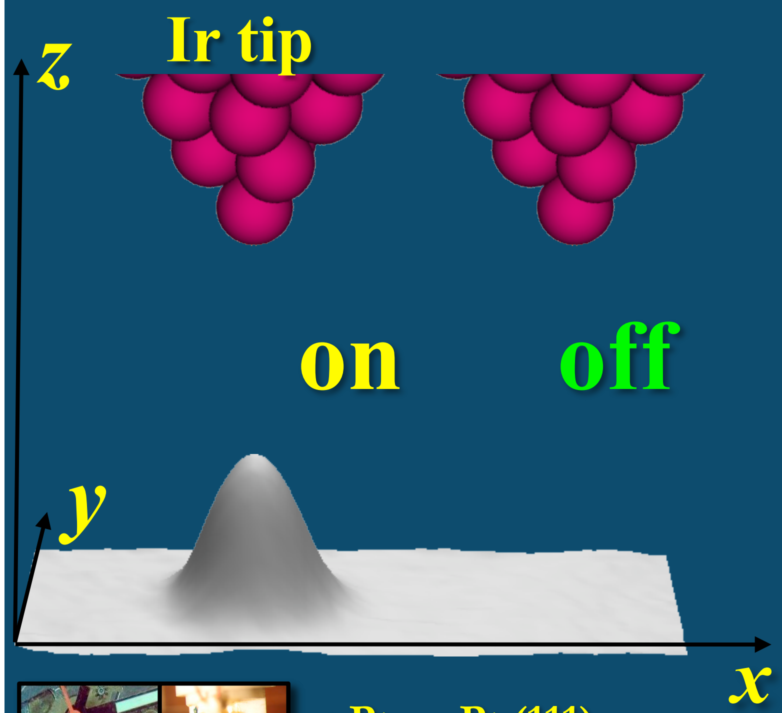
$$I \sim F^n$$

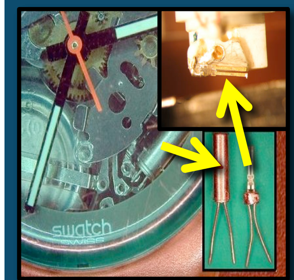
previous works:

1) **n = 2** C.J. Chen J. Phys. Cond. Mat. 3 1227 (1991)
   Ch. Loppacher et al PRB 62 16944 (2000) (Si tip @ Cu)
2) **n = 1** W. Hofer & A.J. Fisher PRL 91 036803 (2003)
   S. Hembacher et al PRL 94 056101 (2005) (W tip @ graphene)
   G. Rubio-Bollinger et al PRL 93 116803 (2004) (tip Au @ Au)
3) **n = 4** A. Schirmeisen et al. New. J. Phys. 2 29 (2000) (W tip @ Au)

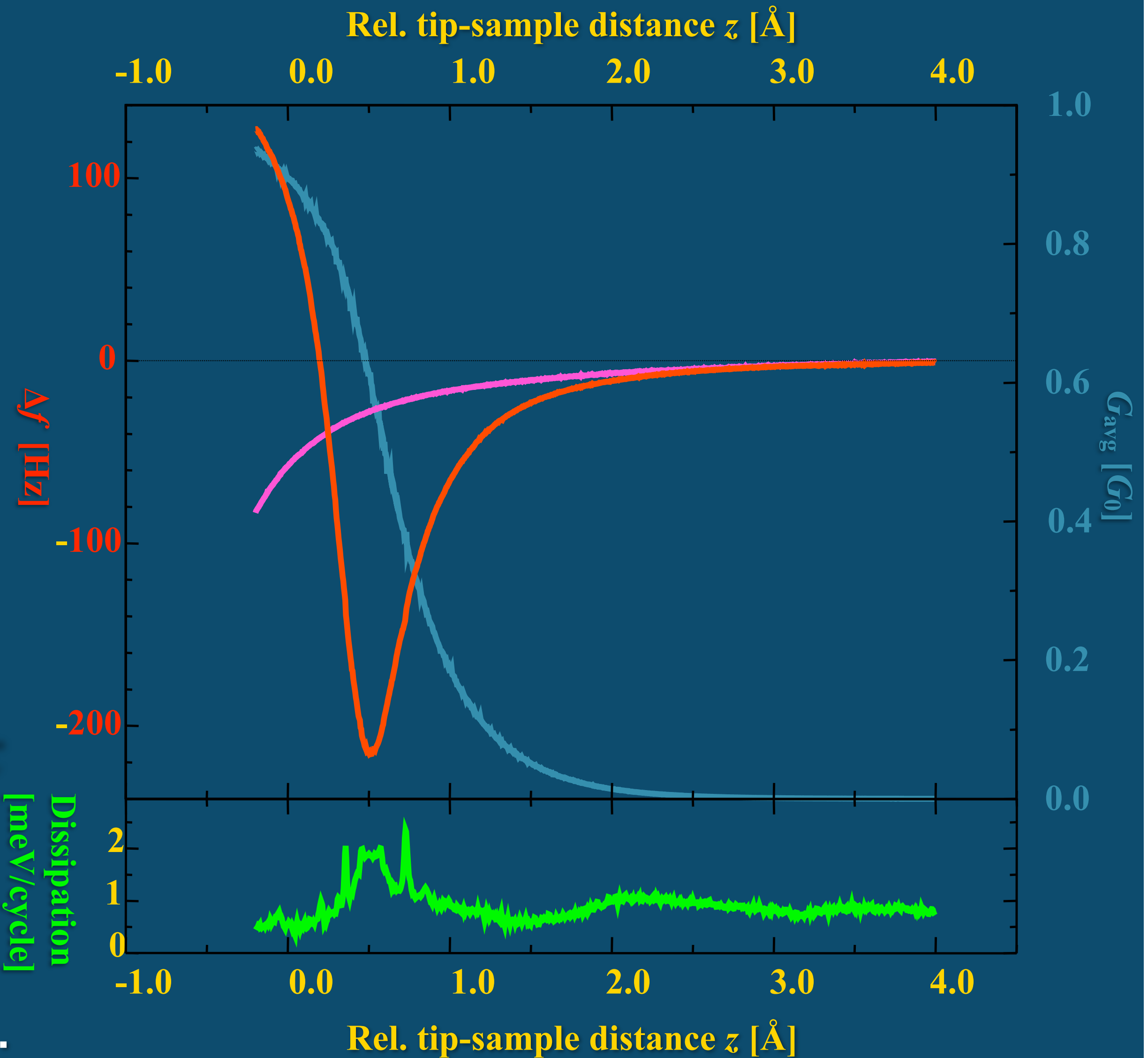
Simultaneous *G(z)* and *Δf(z)* measurement

IBM Almaden *(M. Ternes, F.J. Giessibl. A. Heindrich)*



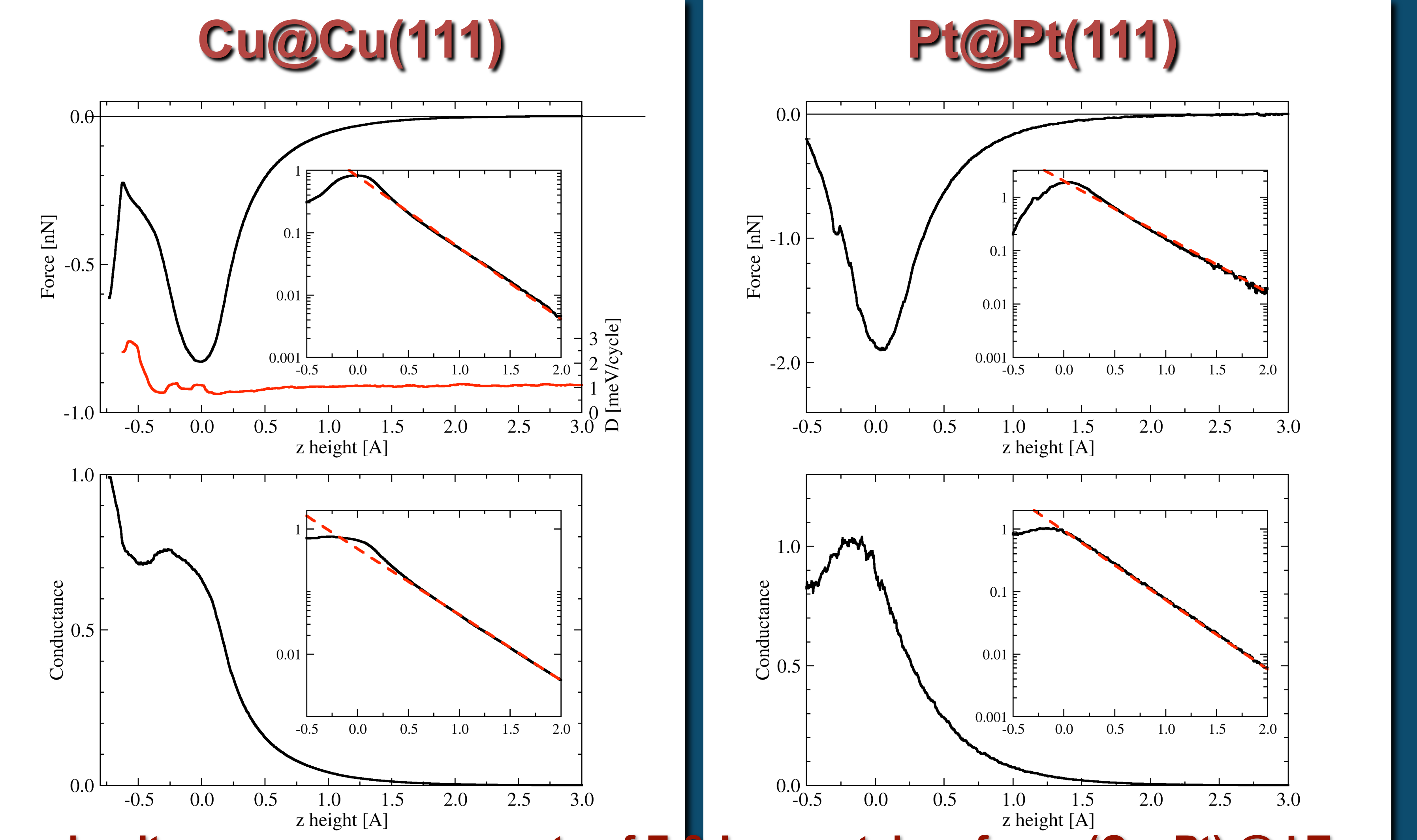


- Pt on Pt (111)
- T = 6 K
- V = 1 mV
- Modulation = 0.3 Å



Off-atom measurements:
Only long-range forces contribute

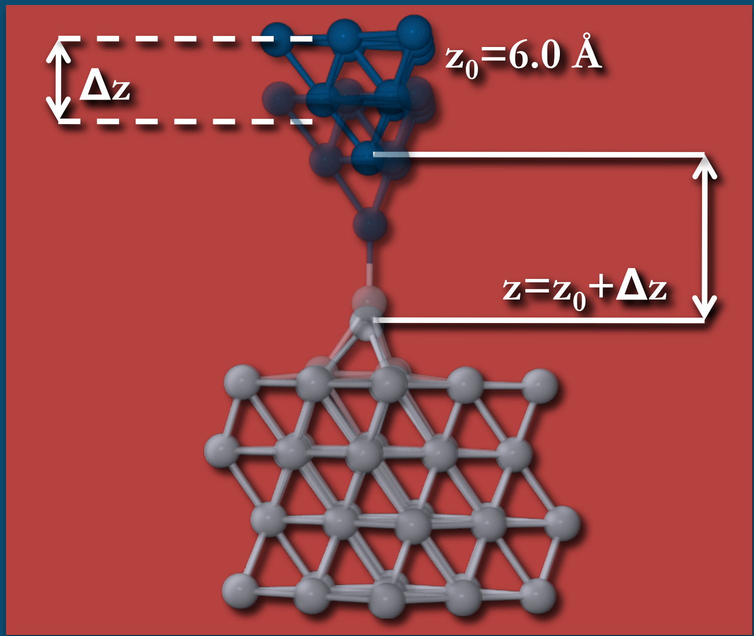
F&G measurements



simultaneous measurements of F & I on metal surfaces (Cu, Pt) @ LT

- materials with different d-band filling and mechanical properties

Computational details



A. Geometry optimization

- TB-DFT LDA (FIREBALL) +
- Ab-initio PW-DFT (*VASP*) ++

(XC: LDA, GGA-PW91)

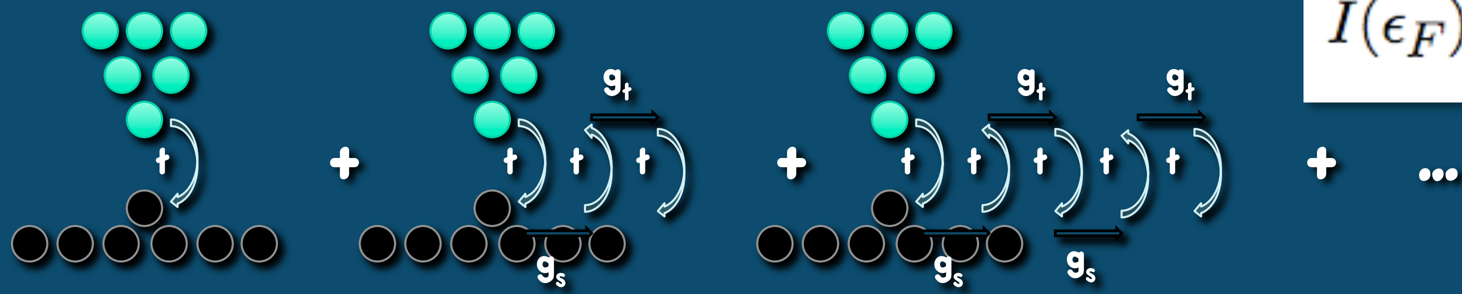
+ www.fireball-dft.org
++ */cms.mpi .univie.ac.at/vasp/*

B. Transport calculations

- Greens function DFT (*FIREBALL*)+

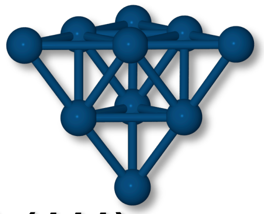
(fully relaxed structures)

+ *www.fireball-dft.org;*
J.M. Blanco et al Prog. Surf. Sci. 81, 403 (2006)

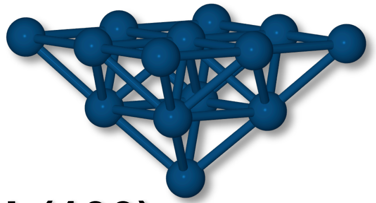


$$I(\epsilon_F) = \frac{2e}{h} T(\epsilon_F)$$

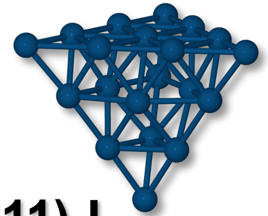
Pt@Pt: F-z theory



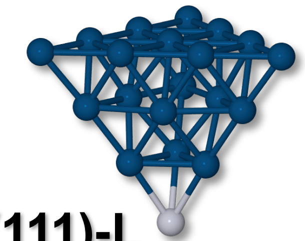
Ir(111)



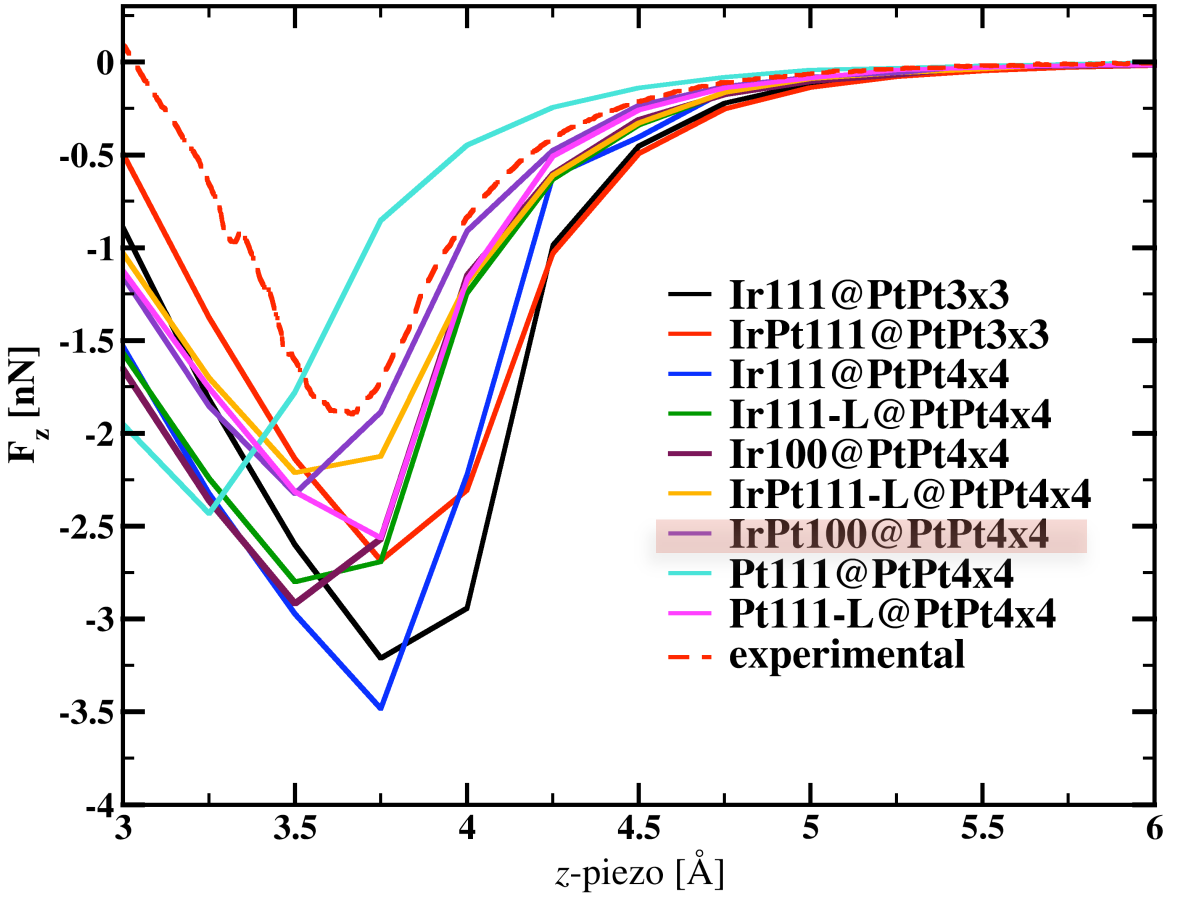
Ir(100)

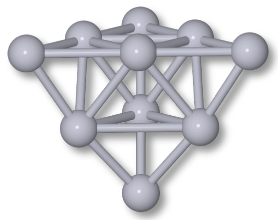


Ir(111)-L

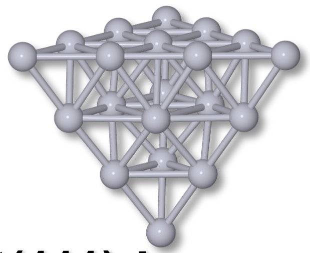


IrPt(111)-L



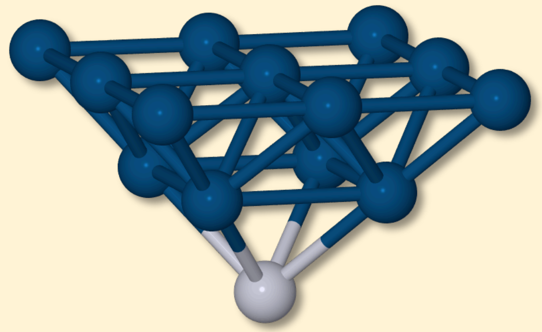


Pt(111)



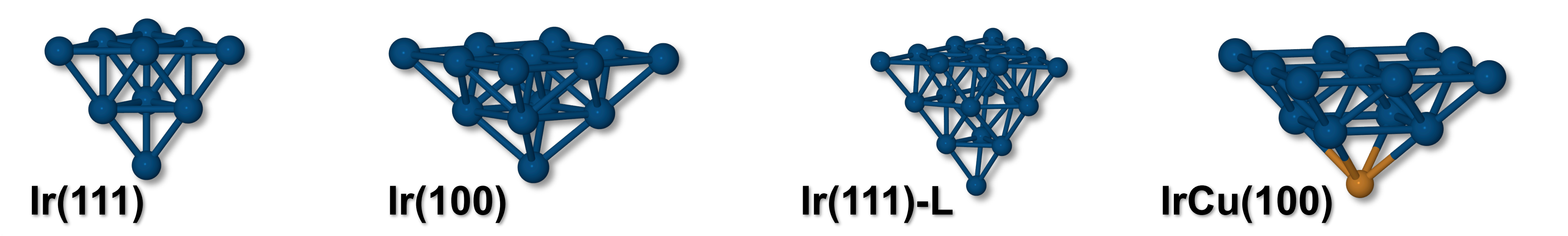
Pt(111)-L

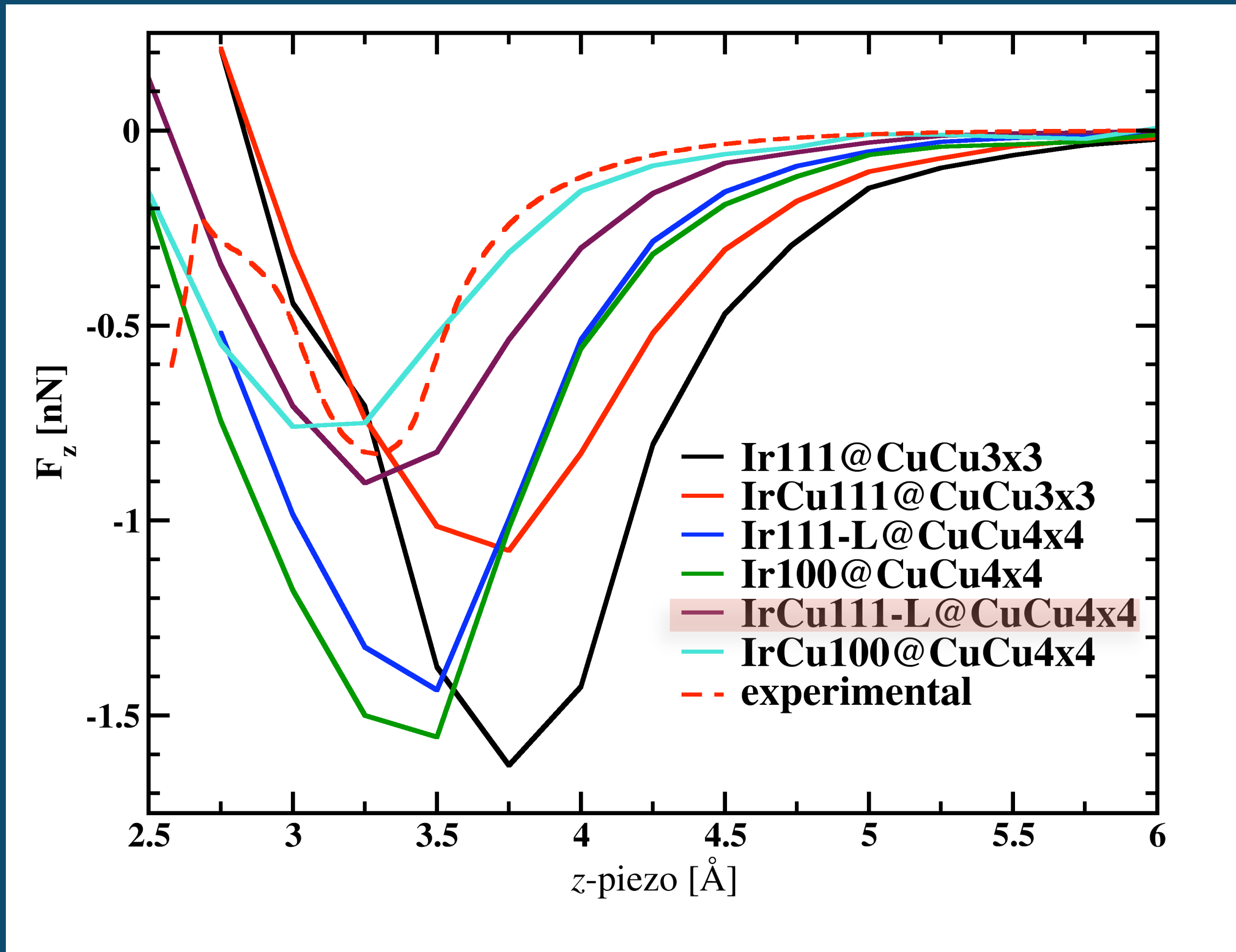
the best candidate



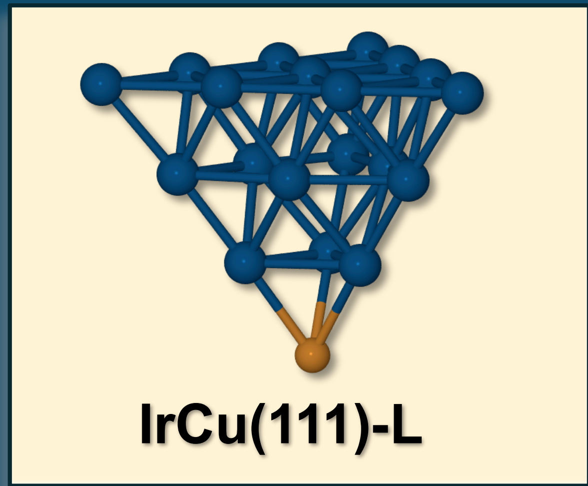
IrPt(100)

Cu@Cu: F-z theory





the best candidate



Forces & ChId: summary

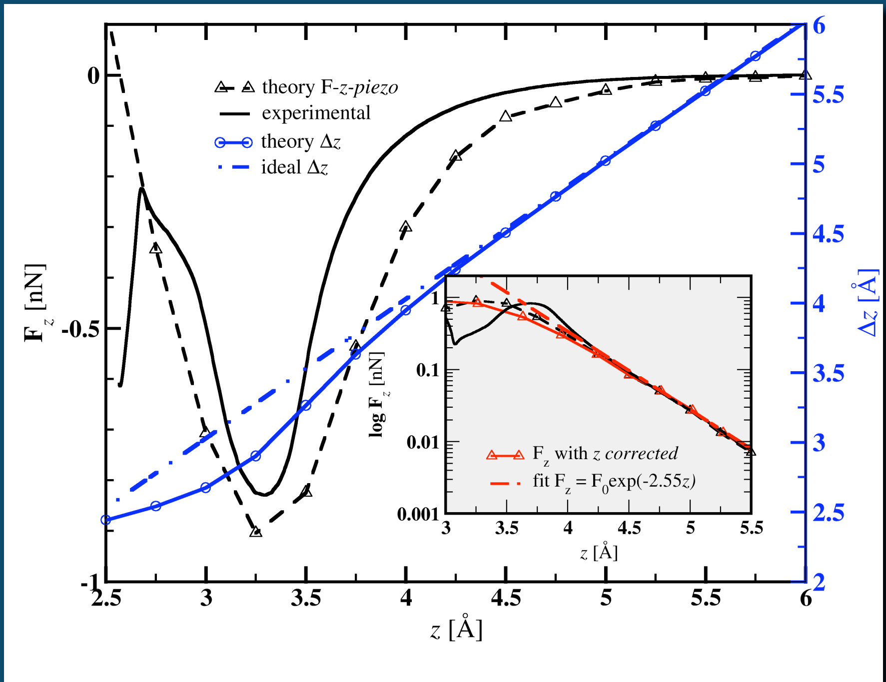
maximal force & chemical identity

	Ir-apex [nN]	Cu(Pt)-apex [nN]
Cu-adatom	1.5	0.9
Pt-adatom	3.1	2.3

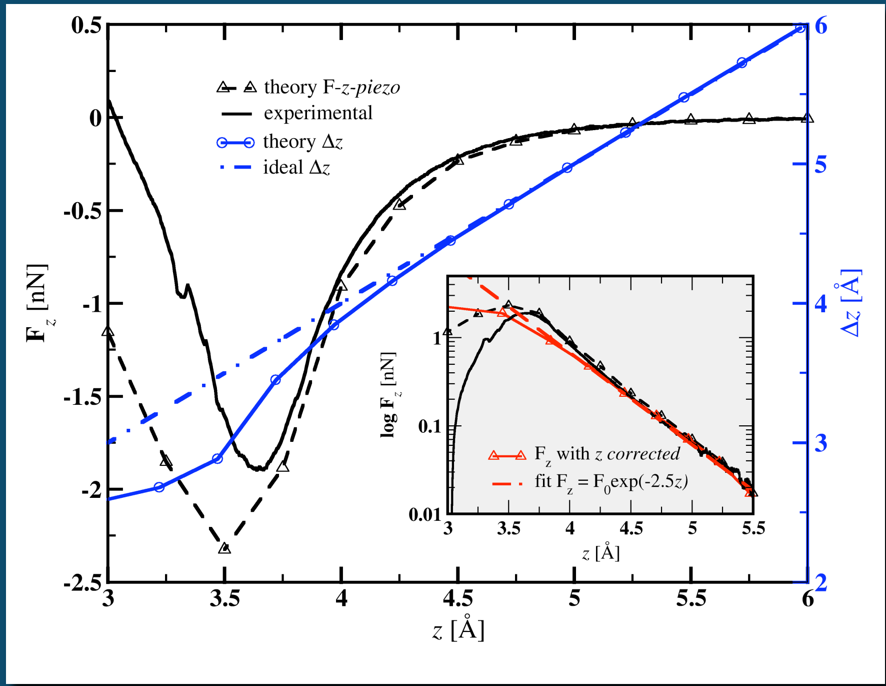
- the chemical identification possible according to the theoretical calculations
- scattered data of F_{max} for metal surface (~0.5 nN) → more delocalized interaction

Chemical force

Cu@Cu(111)



Pt@Pt(111)

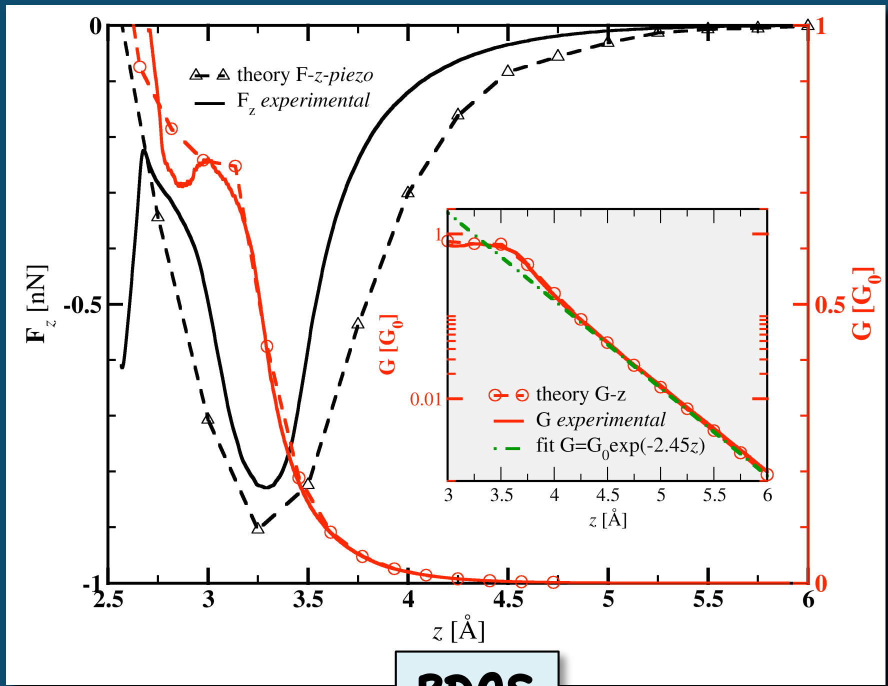


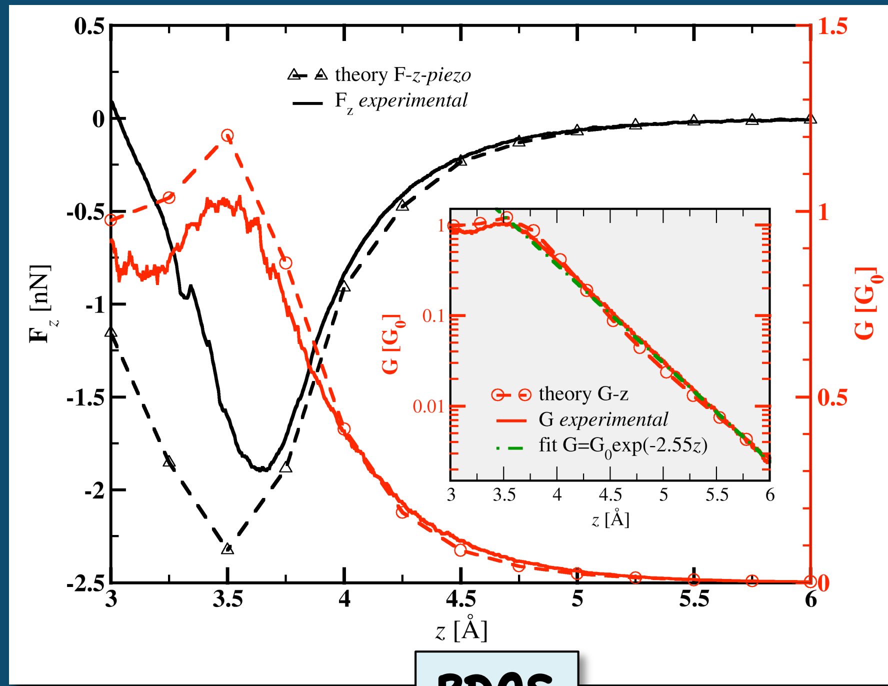
- the "*jump*" to the contact near the maximal force F_{max}
- Cu: more blunt character

Conductance

Cu@Cu(111)

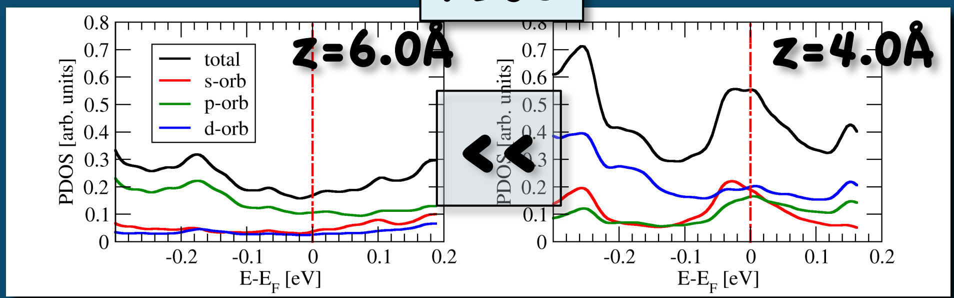
Pt@Pt(111)

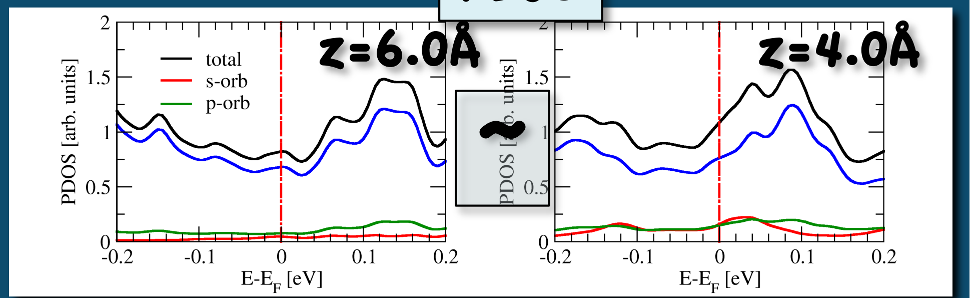




PDOS

PDOS



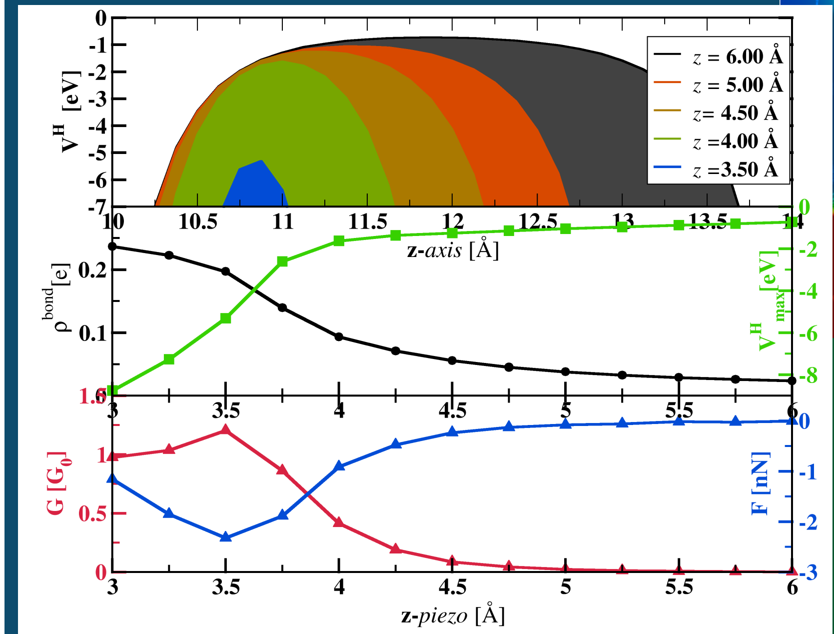


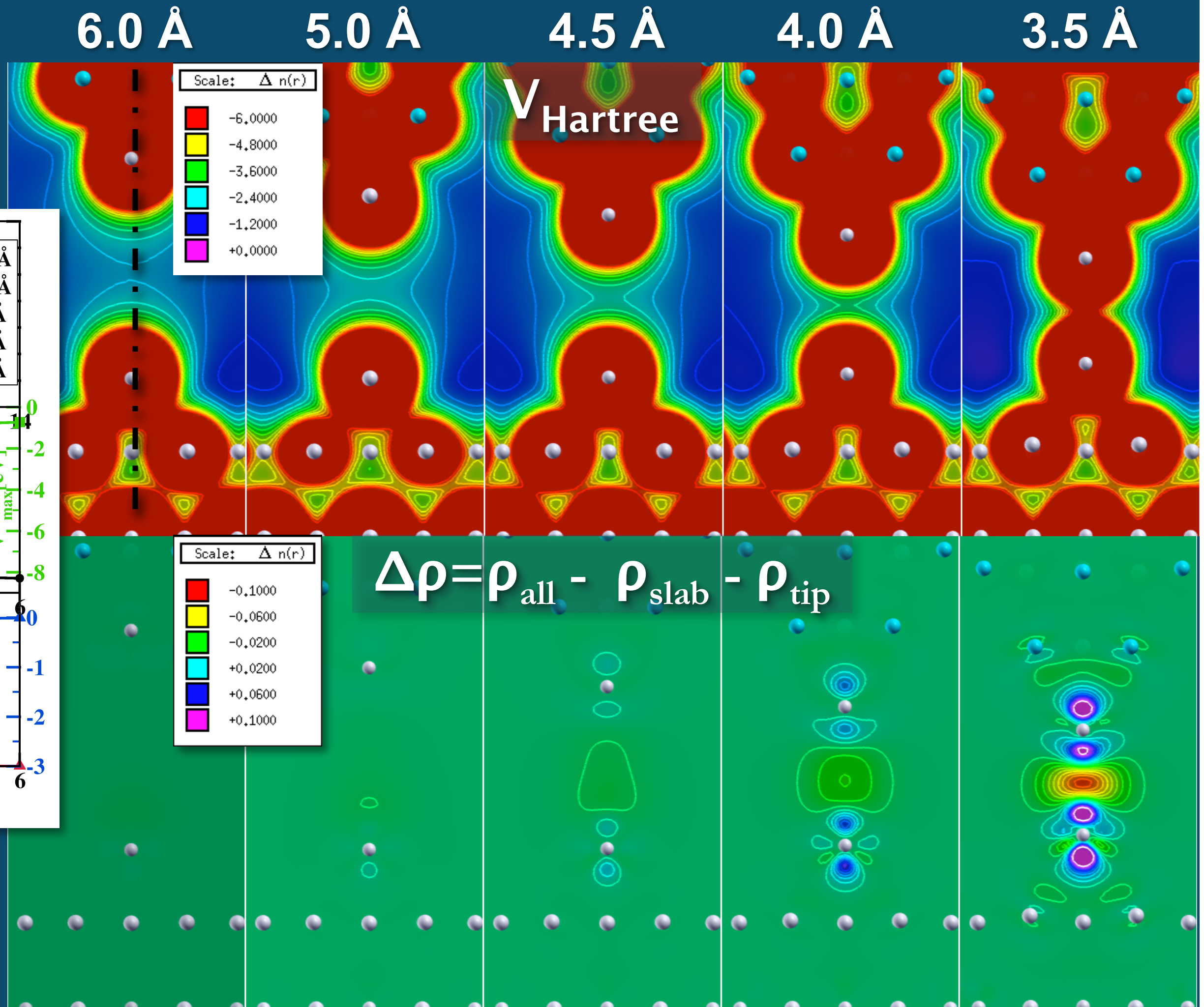
MS + PDOS + z-piezo contraction

MS + z-piezo contraction

Contact formation

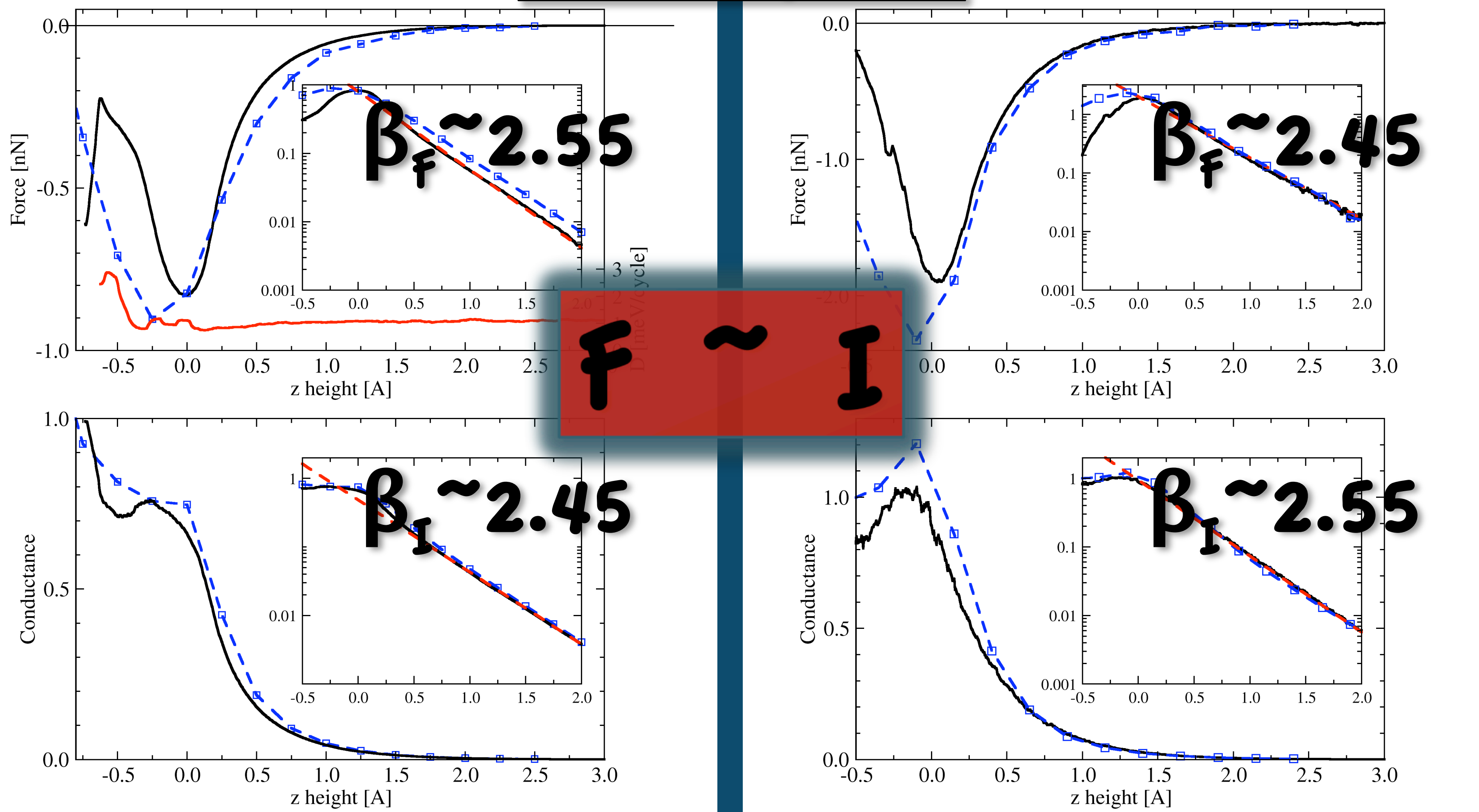
$$\rho^{bond} = \int_{\Omega} \int_{z_{appex}}^{z_{adatom}} \Delta\rho(r)\, dz\, d\Omega$$





Scaling: F&I

Cu@Cu(111) $\Gamma(z)=\Gamma_0 e^{-\beta_\Gamma z}$ Pt@Pt(111)



I & F scaling on metals

general relation scaling between I and F ?

I ~ F

previous works:

1) **n = 2** C.J. Chen J. Phys. Cond. Mat. 3 1227 (1991)
   Ch. Loppacher et al PRB 62 16944 (2000) (Si tip @ Cu)
2) **n = 1** W. Hofer & A.J. Fisher PRL 91 036803 (2003)
   S. Hembacher et al PRL 94 056101 (2005) (W tip @ graphene)
   G. Rubio-Bollinger et al PRL 93 116803 (2004) (tip Au @ Au)
3) **n = 4** A. Schirmeisen et al. New. J. Phys. 2 29 (2000) (W tip @ Au)

Cu@Cu			Pt@Pt		
F	**I**	**n**	**F**	**I**	**n**
2.55	2.45	**1.04**	2.45	2.55	**0.96**

$$I_t = \sum |T^B_{\alpha,\beta}|^2 \delta(\epsilon_\alpha - \epsilon_\beta)$$

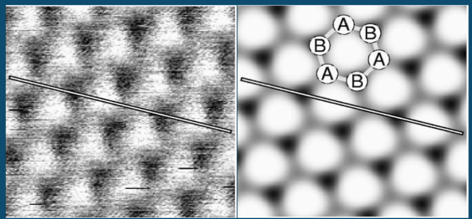
$$E^{int} \approx S^2 \Delta\epsilon - S\gamma T^B + \frac{(T^B)^2}{\Delta\epsilon}$$

Graphene

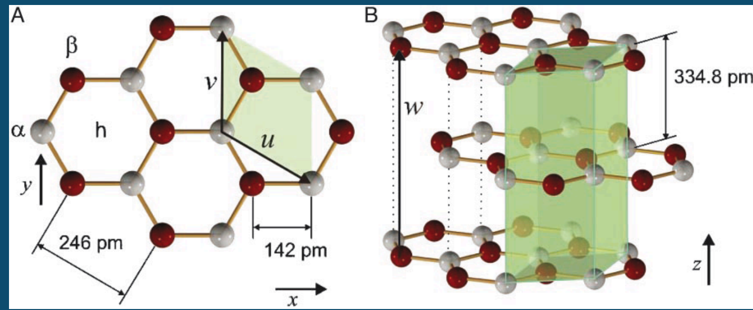
Graphene: atomic resolution

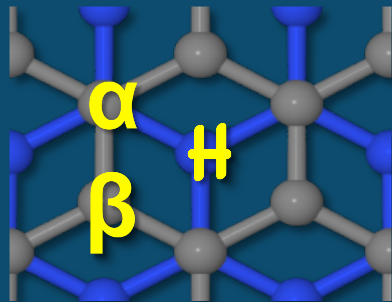
Variety of atomic contrasts observed by AFM/STM:

A. AFM: H-site

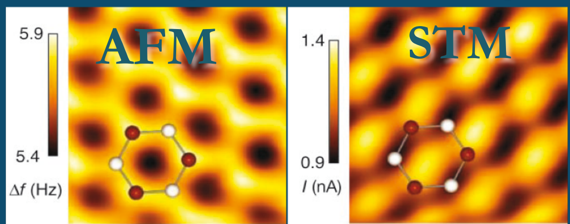


W. Allers et al, Appl. Surf. Sci. 140, 247 (1999)
H. Hölscher et al, Phys. Rev. B 62, 6967 (2000)
M. Ashino et al, Nanotechnology 16, S134 (2005)
B.J. Albers et al, Nature Nanotechnology 4, 307 (2009)

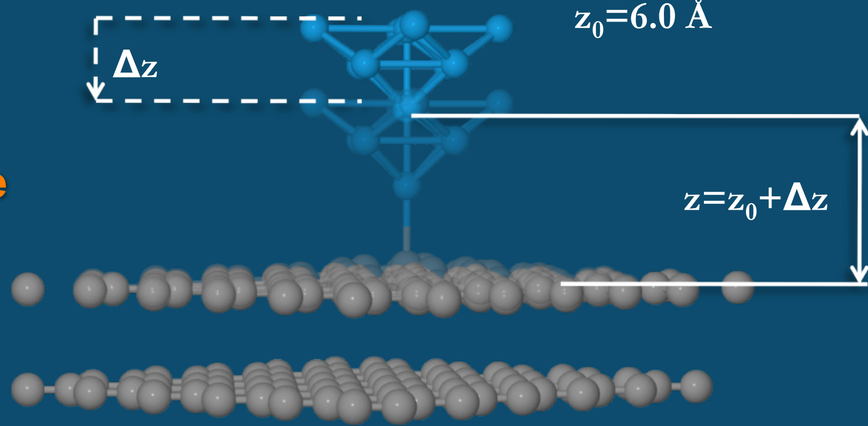




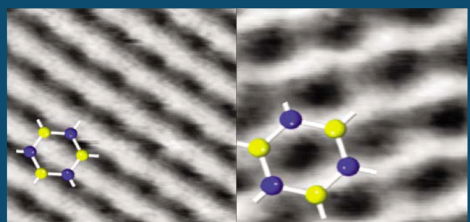
B. AFM: β>α-site STM: β-site



S. Hembacher et al PNAS 100, 12539 (2003).
S. Hembacher et al PRL 94, 056101 (2005)

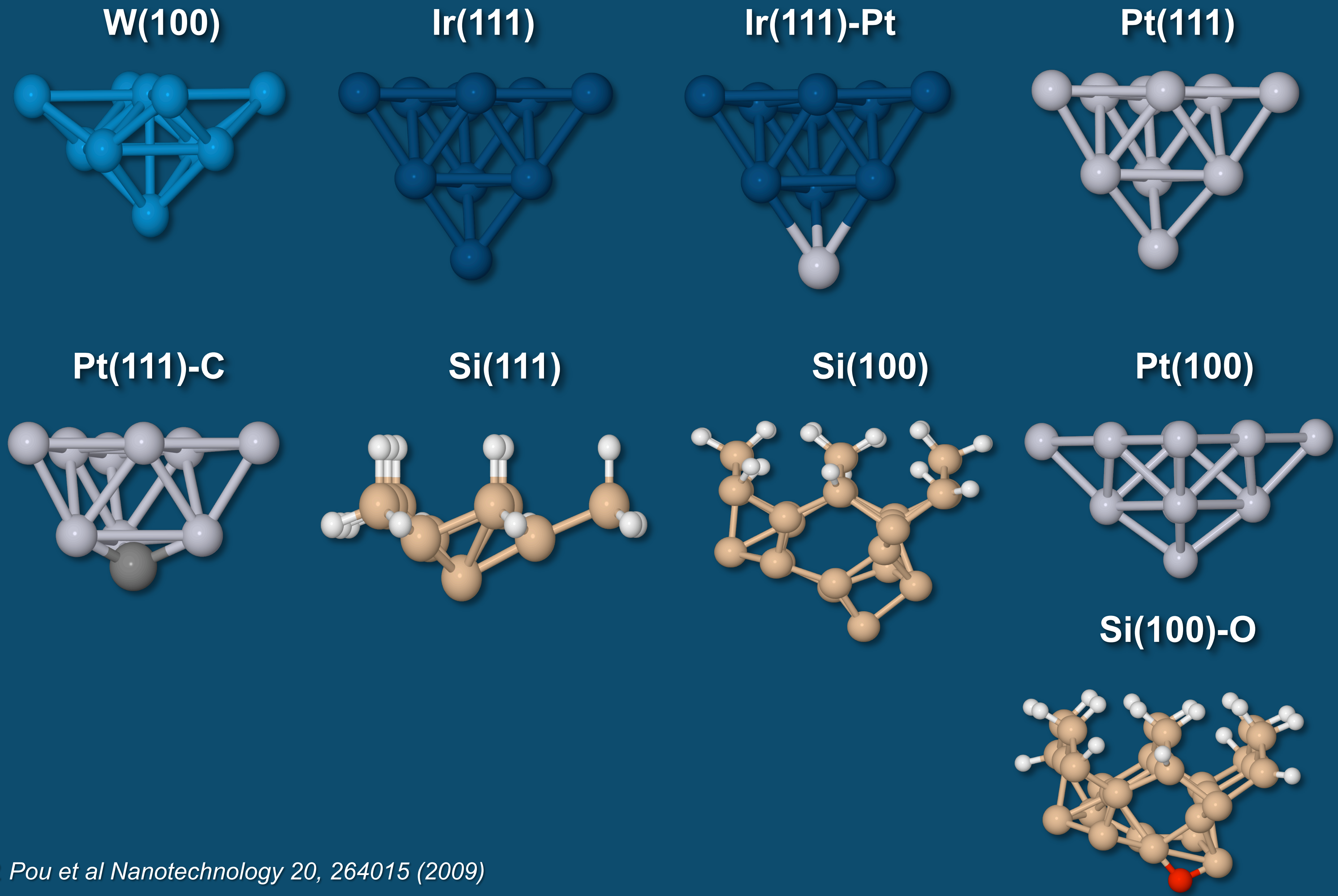


C. AFM: AR H>α-site; RP α>β-site; STM: β-site



S. Kawai and H. Kawakatsu, Phys. Rev. B 79, 115440 (2009).

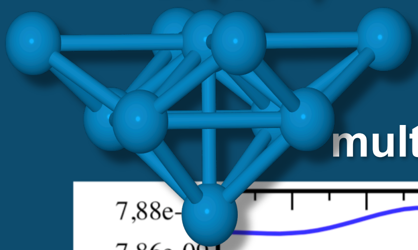
Tip models



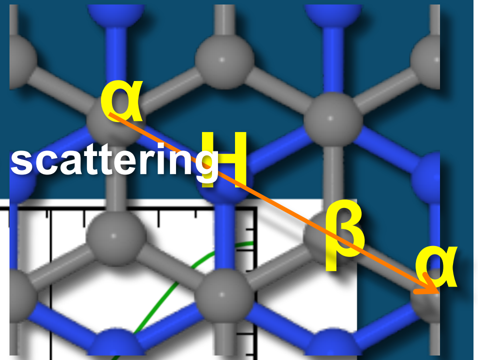
P. Pou et al Nanotechnology 20, 264015 (2009)

static STM: results

W(100)

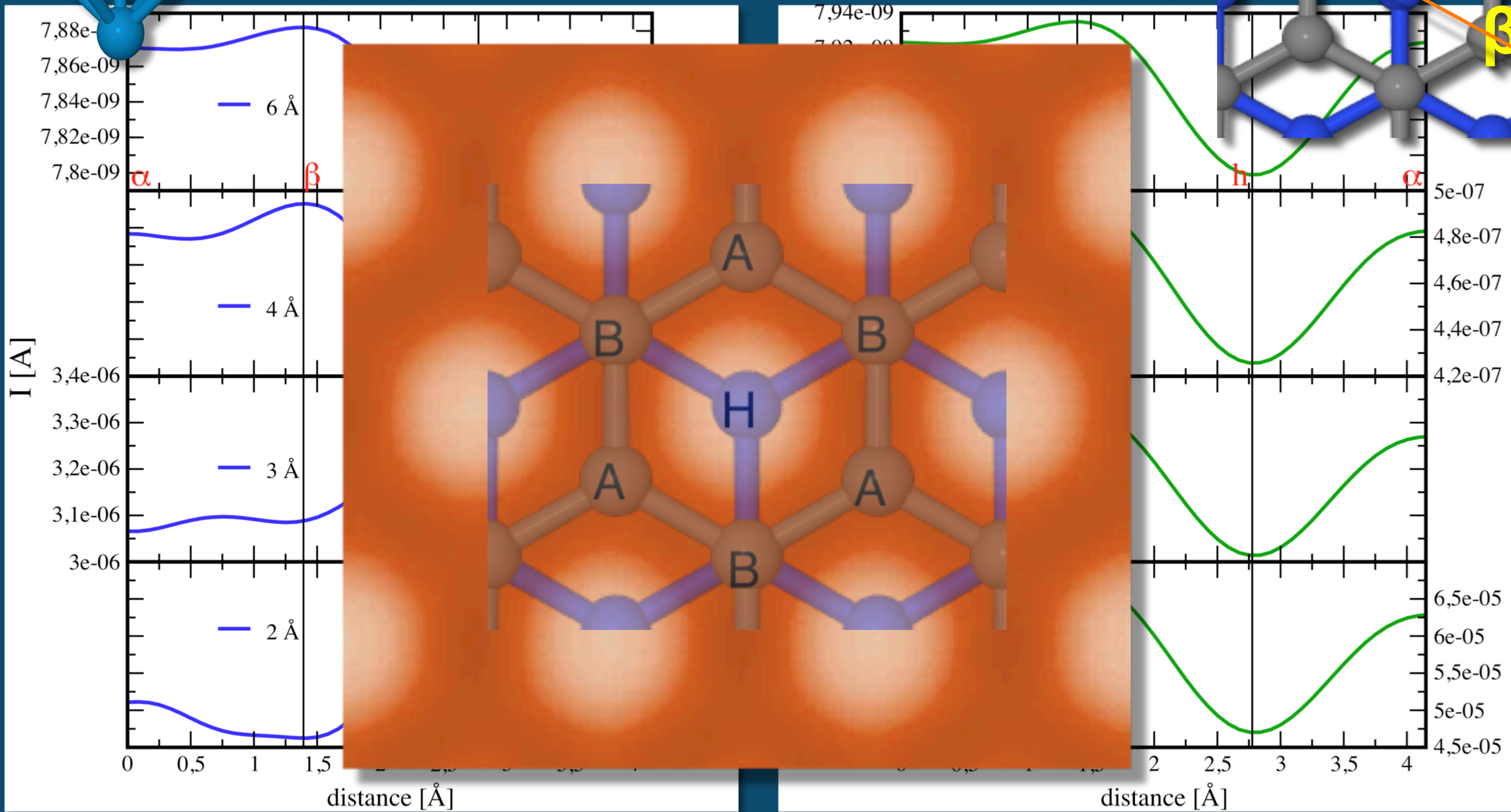


the constant height; 1024 k-points, V_{bias} = -0.5 V



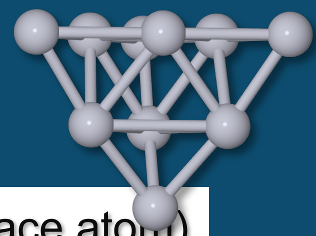
multiple scattering

NO multiple scattering

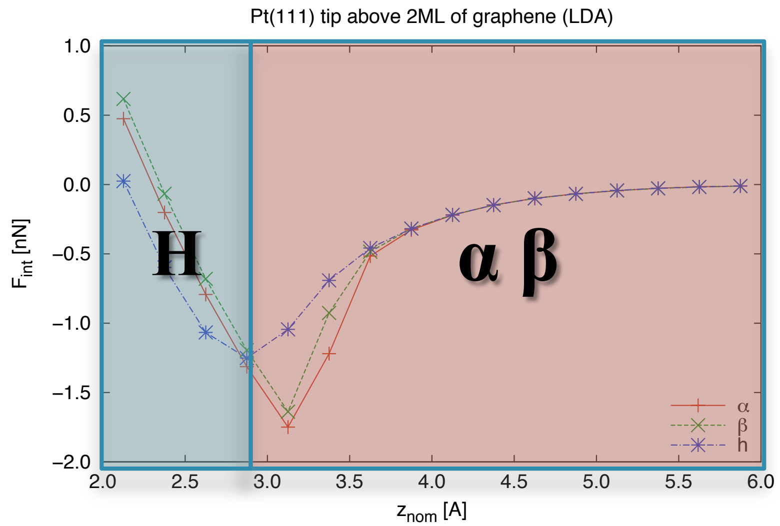


- change in the contrast with the distance
- reverse contrast in distances > 4 Å due to the multiple scattering effect

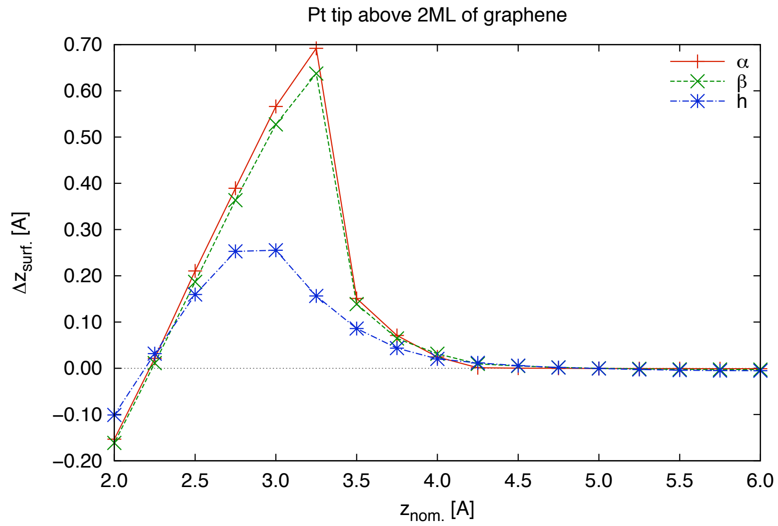
AFM: tip Pt(111)



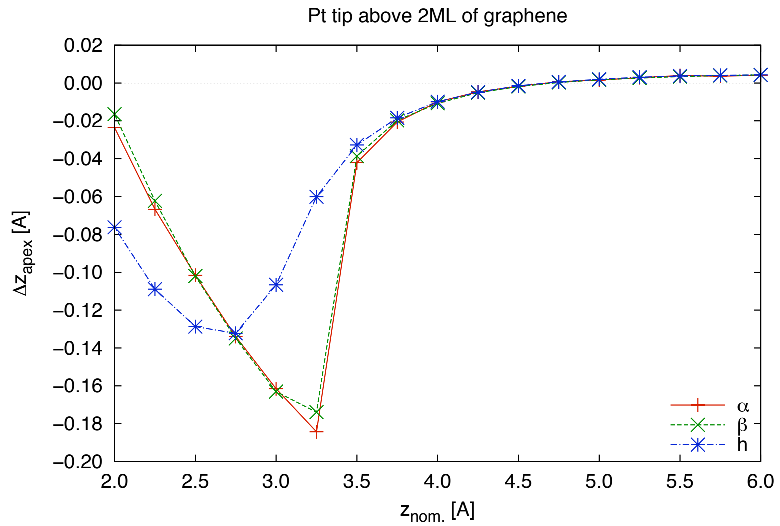
SR Force vs. piezo-distance



Δz vs. piezo-distance (surface atom)



Δz vs. piezo-distance (tip apex)



- **strong chemical bond** established
- strong vertical displacement of a sheet
- the atomic contrast
  - **the attractive regime: atomic sites**

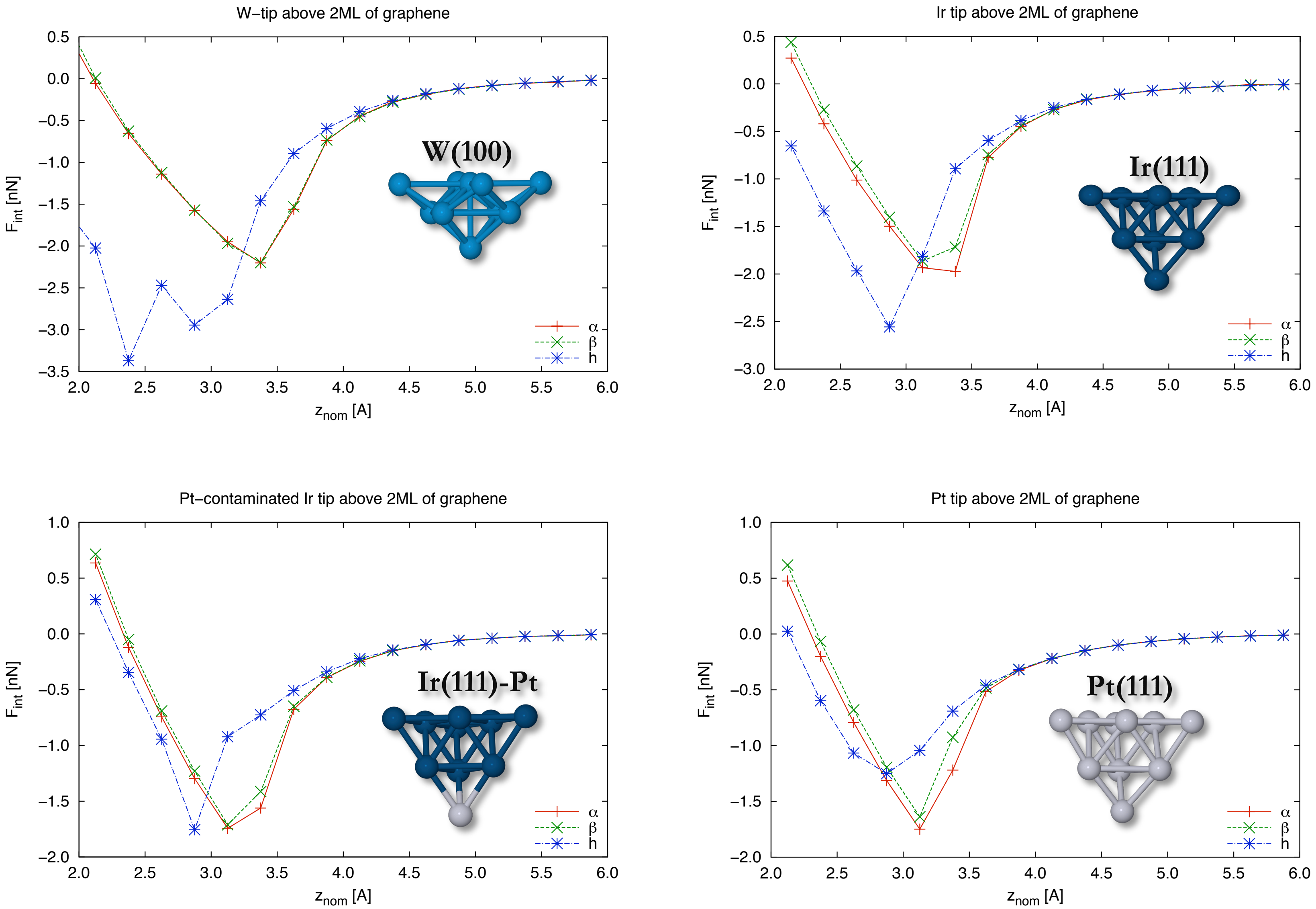
➔ strong directional covalent bond over atoms

  - **the repulsive regime: hollow site**

➔ the Pauli repulsive principle over atomic sites

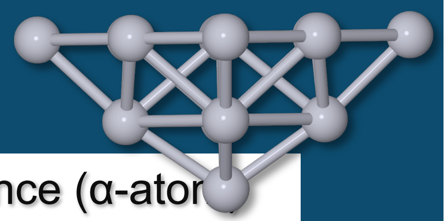
Graphite (2L): metal tips

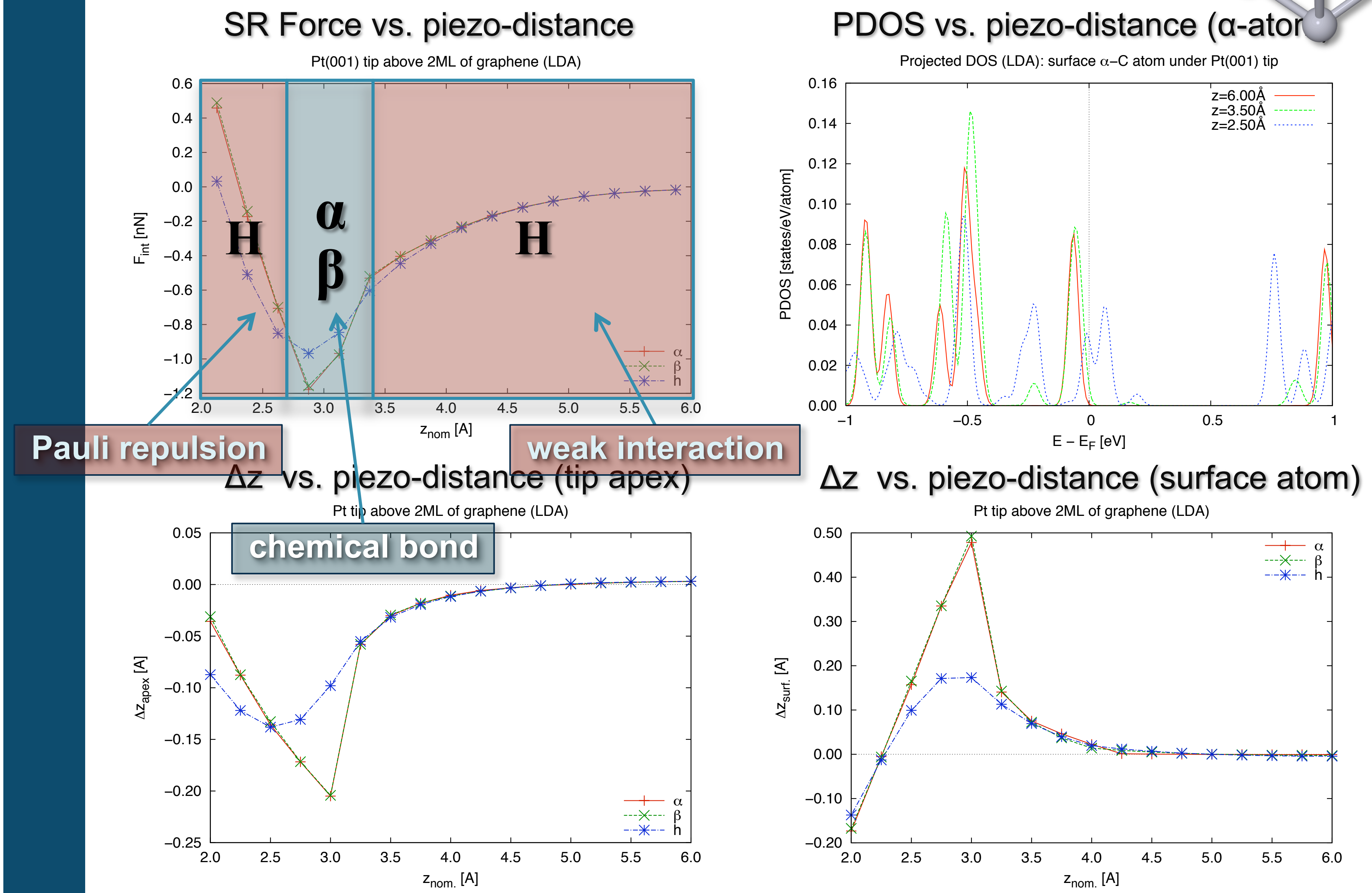
SR Force vs. piezo-distance



the repulsive regime: hollow site the attractive regime: α,β-sites

AFM: tip Pt(100)

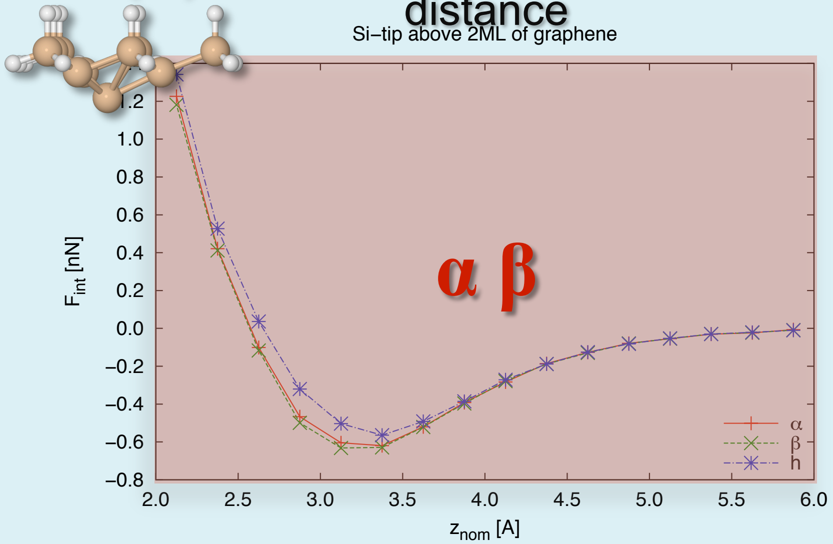




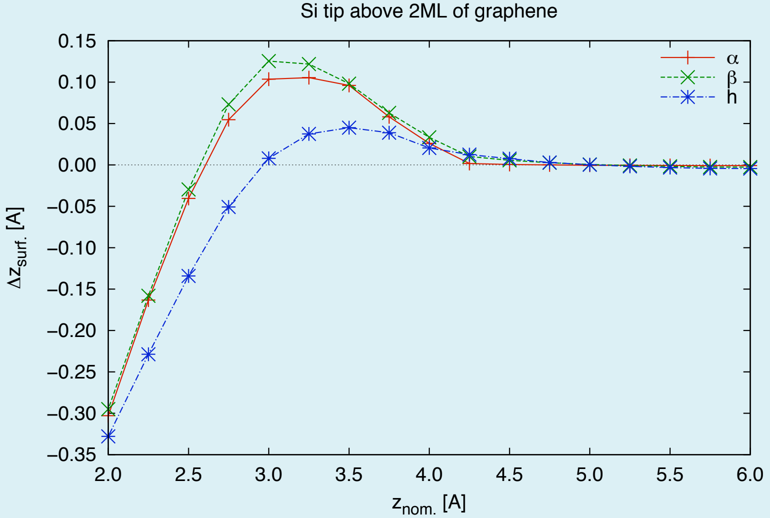
Graphite (2L): sp^3-tips

Si(111)

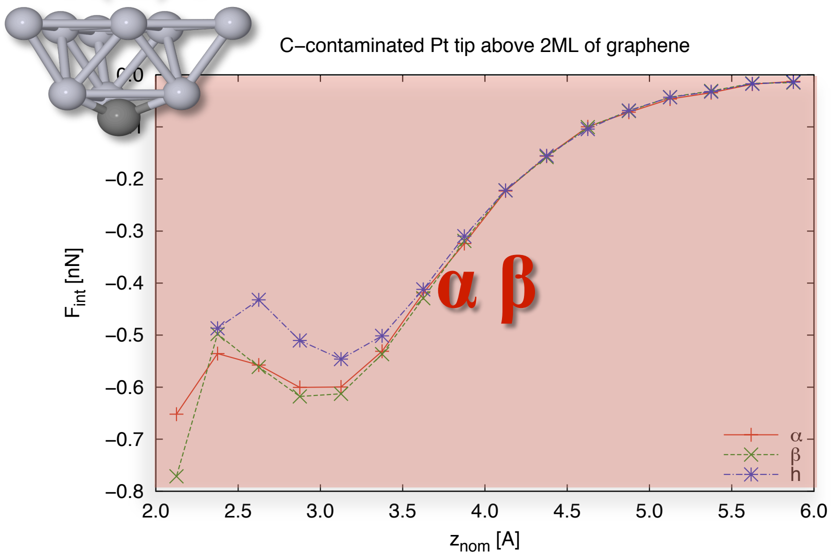
SR Force vs. piezo-distance

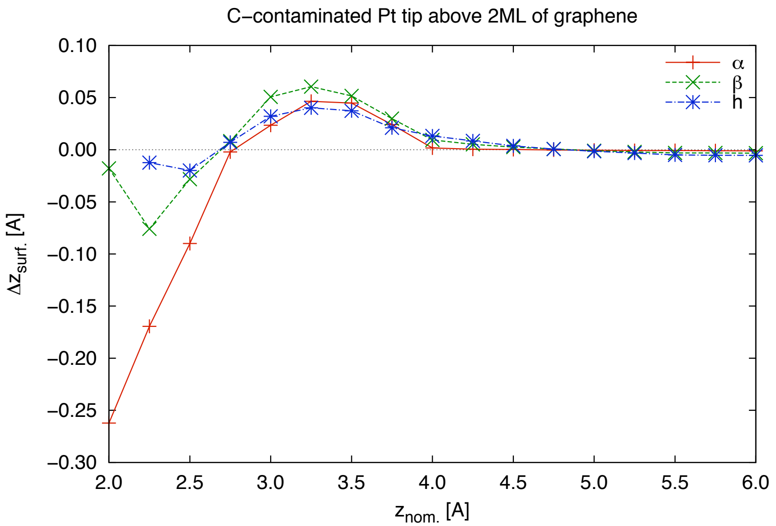


Δz vs. piezo-distance (surface atom)

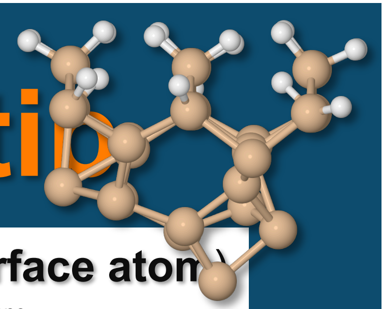


Pt(111)-C

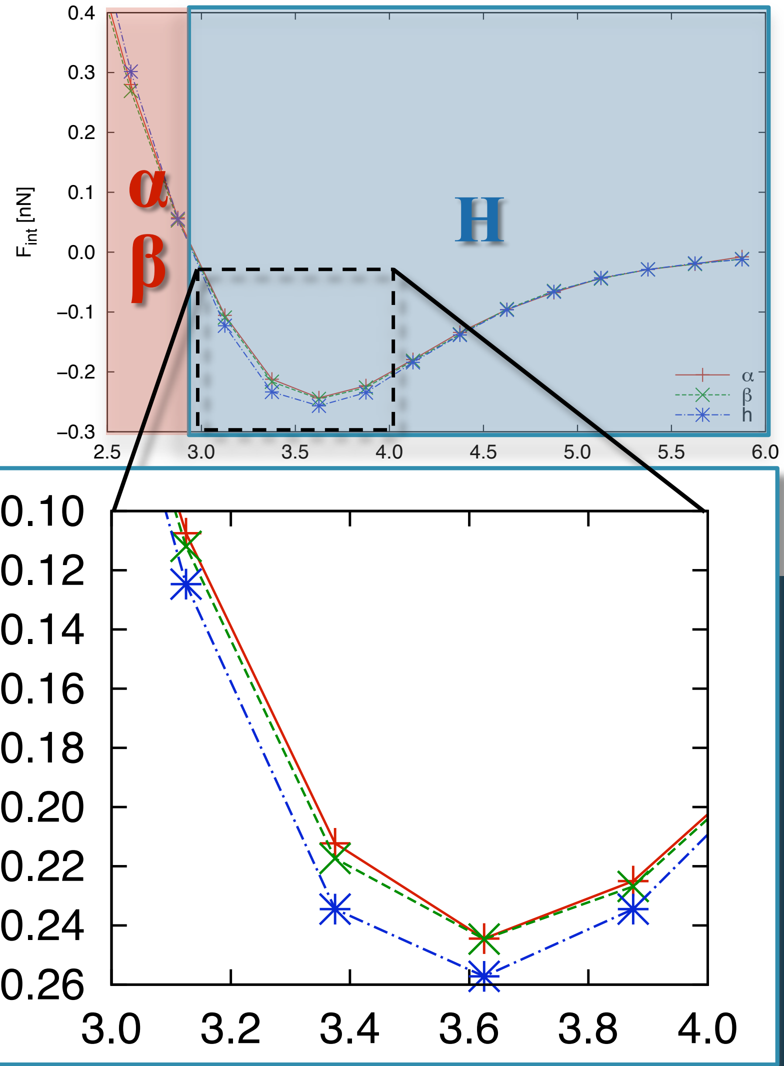




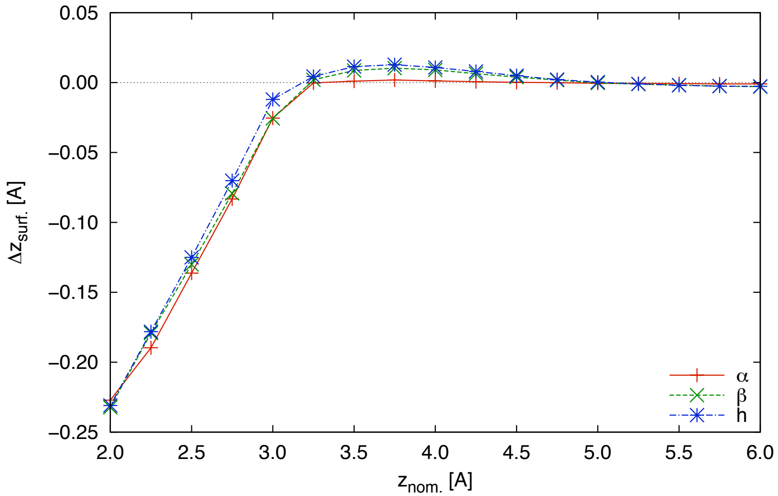
Graphite (2L): Si-dimer tip



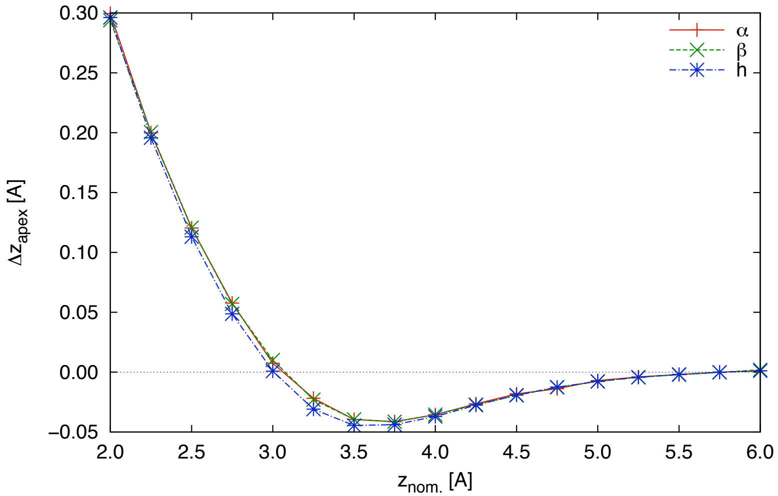
SR Force vs. piezo-distance



Δz vs. piezo-distance (**surface atom**)

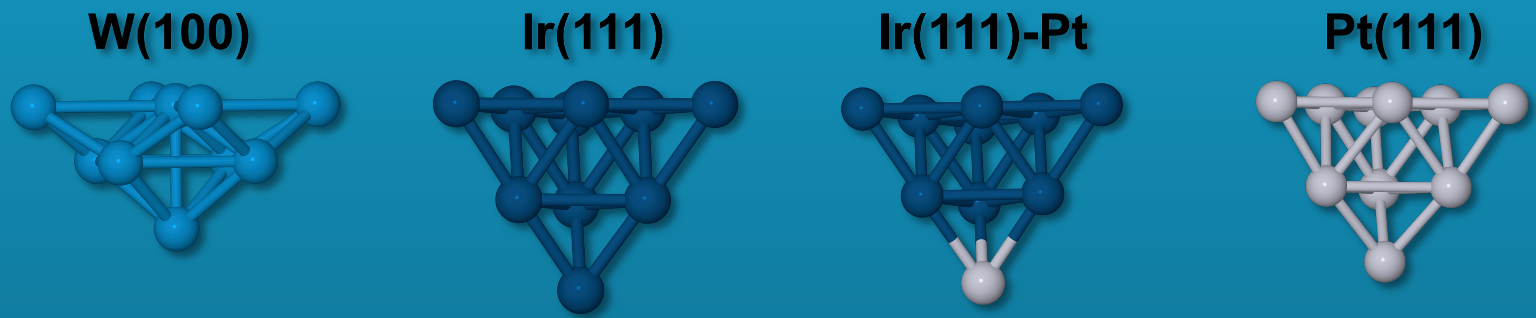


Δz vs. piezo-distance (**tip apex**)

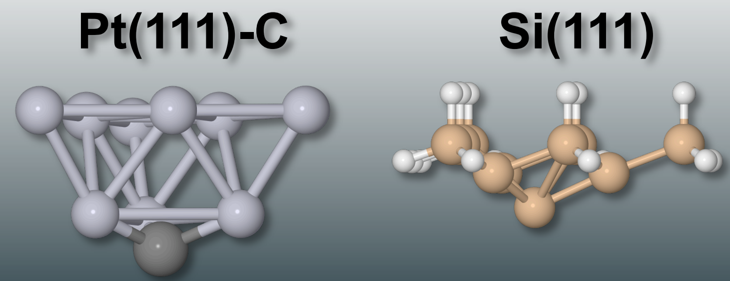


Summary II

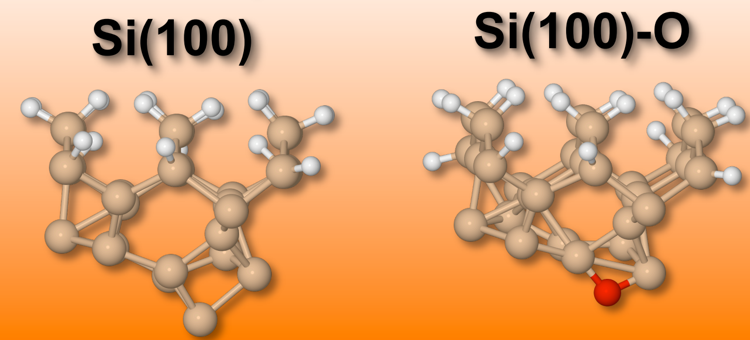
metal tips



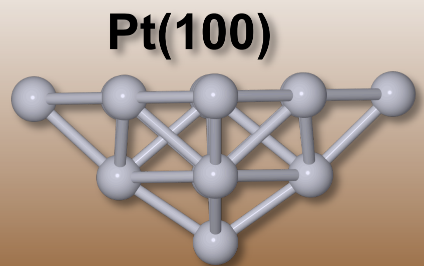
sp^3-like tips



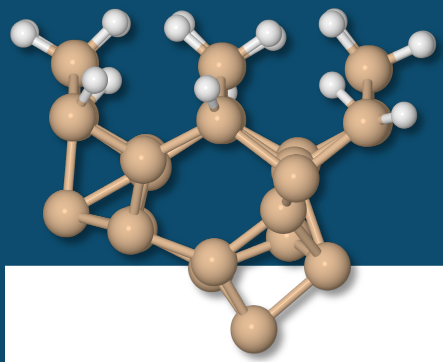
Si-dimer tip



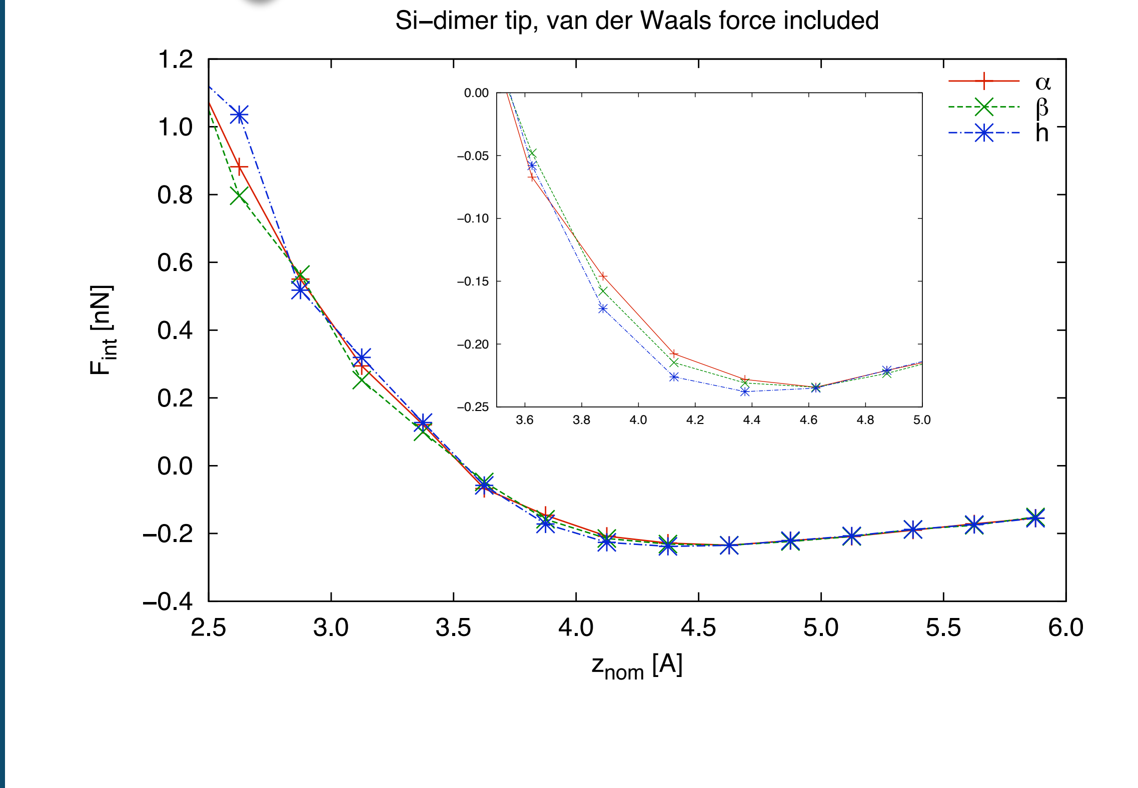
MWI tip



- defined group of tips with characteristic contrast
- metal tips: covalent bonding; AR: αβ-site RP: H-site
- sp_3-like tips: weak covalent bonding; αβ-site
- Si-dimer tip: weak bonding; H-site
- MWI tip: weak bonding; AR: αβH-sites RP: H-site



F-z: GGA + vdW



Empirical formula of vdW part

M. Elstner et al J. Chem. Phys. 114, 5149 (2002)

$$E_{vdW} = -\Sigma_{\alpha,\beta} f(R_{\alpha,\beta}) C_6^{\alpha,\beta} (R_{\alpha,\beta})^{-6}$$

$$f(R_{\alpha,\beta}) = [1 - exp(-d^*(R/R_o)^7)]^4$$

$$R_o^{\alpha,\beta} = \frac{(R_o^\alpha)^3 + (R_o^\beta)^3}{(R_o^\alpha)^2 + (R_o^\beta)^2}$$

$$C_6^\alpha = 0.75\sqrt{N_\alpha p_\alpha^3}$$

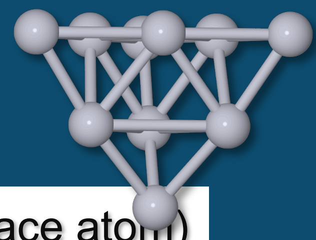
atom α	p_α [Å^3]	N_α	C_6^α [eV. Å^6]
C (sp^2)*	1.38	6.05	31.27
Si	5.4	6.05	242.14

* *M. Elstner et al J. Chem. Phys. 114, 5149 (2002)*

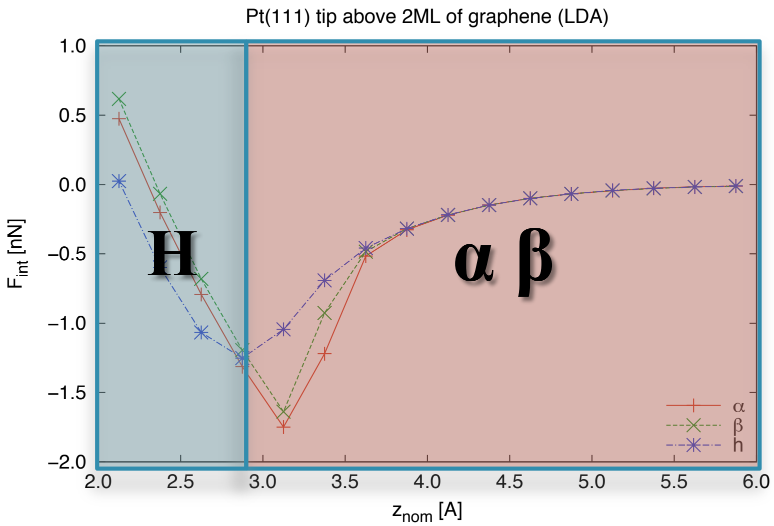
- no change in the contrast including vdW part !!

➔ the atomic contrast driven by the chemical force

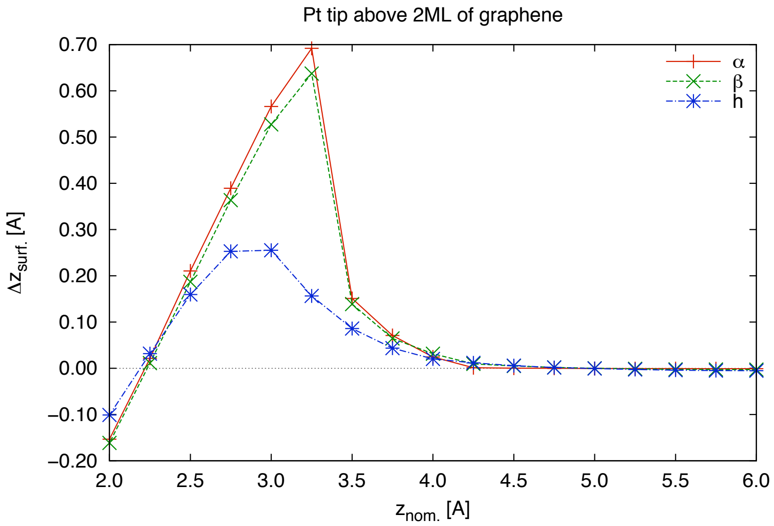
AFM: tip Pt(111)



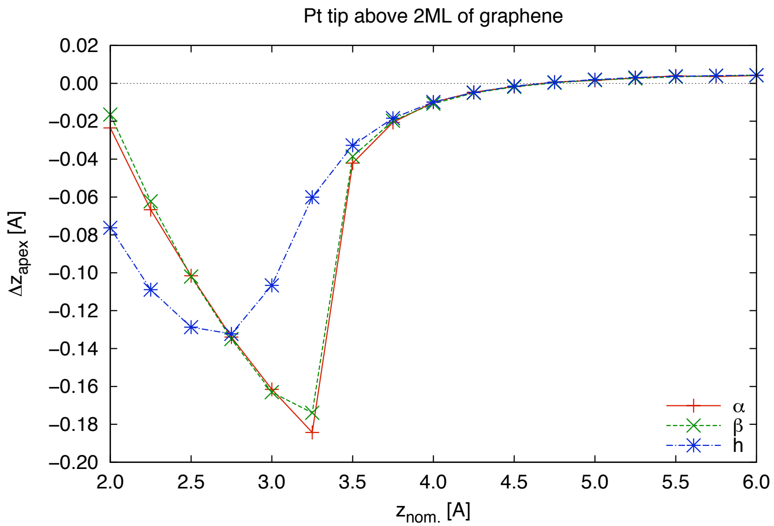
SR Force vs. piezo-distance



Δz vs. piezo-distance (surface atom)



Δz vs. piezo-distance (tip apex)



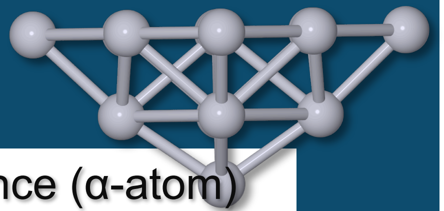
- ❑ **strong chemical bond** established
- ❑ strong vertical displacement of a sheet
- ❑ the atomic contrast
  - ❑ **the attractive regime: atomic sites**

➔ strong directional covalent bond over atoms

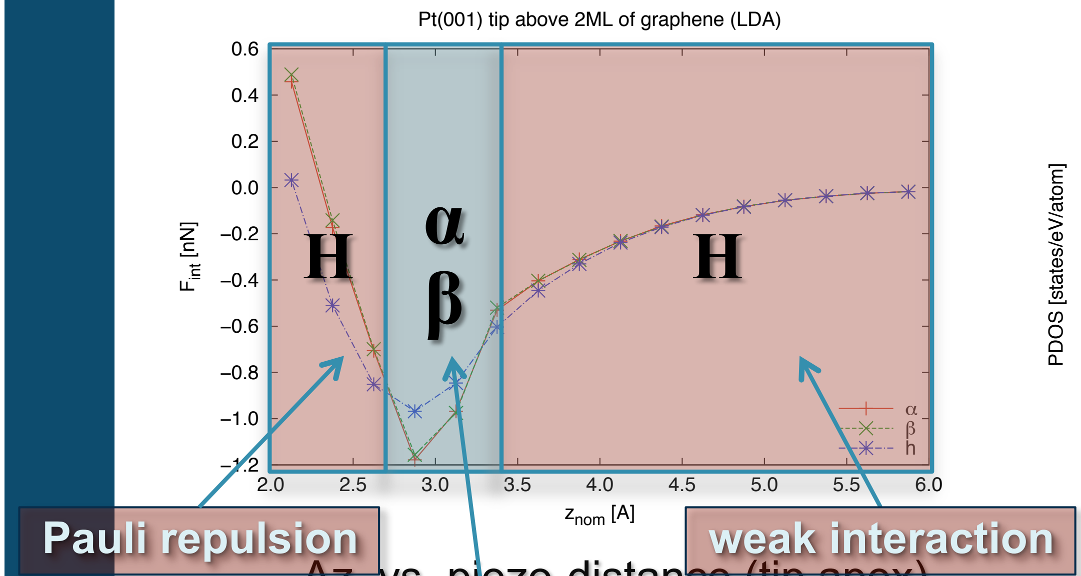
  - ❑ **the repulsive regime: hollow site**

➔ the Pauli repulsive principle over atomic sites

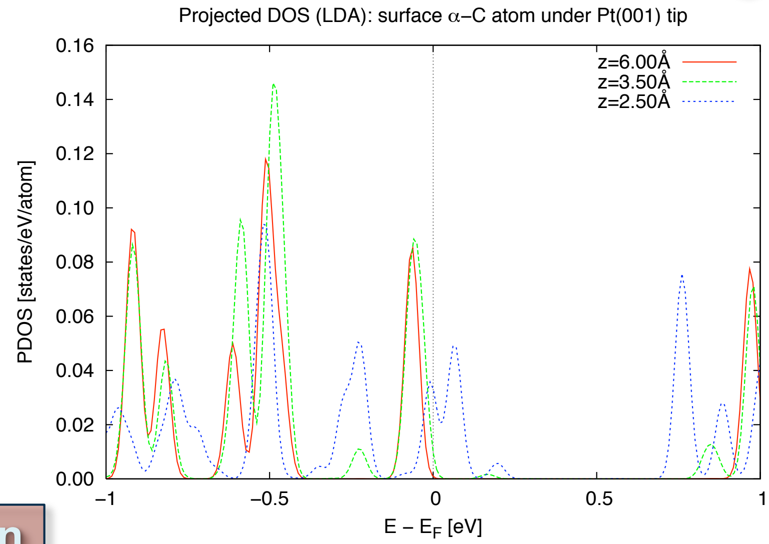
AFM: tip Pt(100)



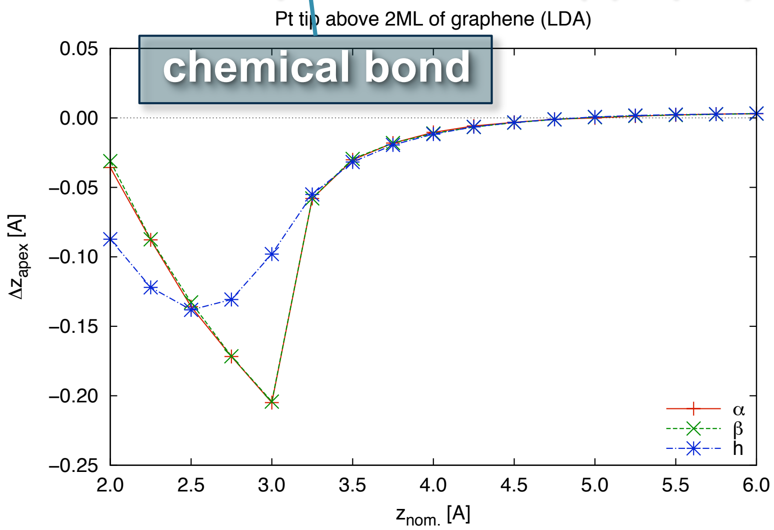
SR Force vs. piezo-distance



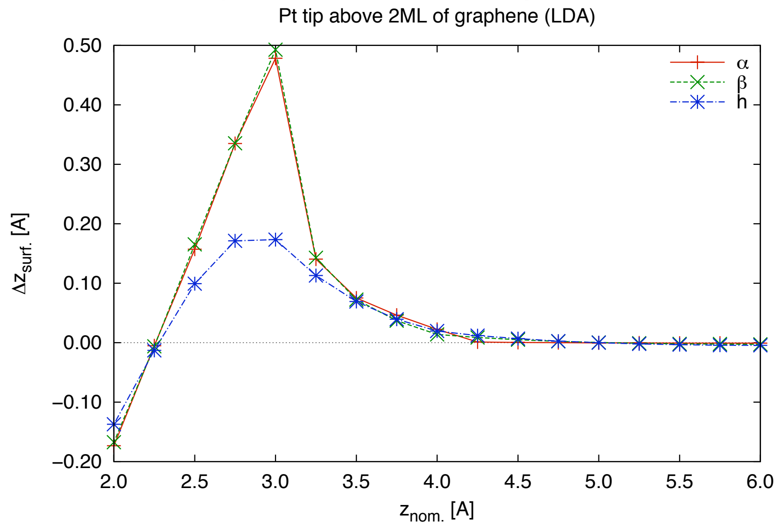
PDOS vs. piezo-distance (α-atom)



Δz vs. piezo-distance (tip apex)

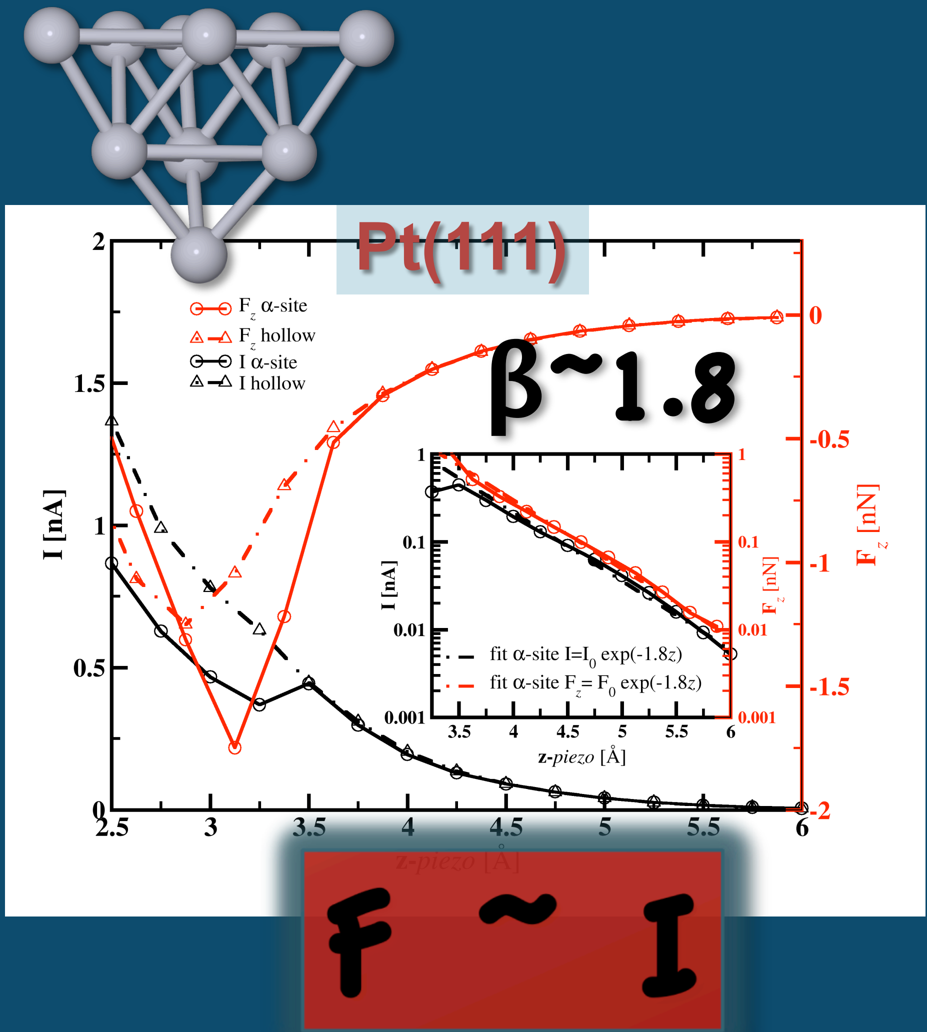


Δz vs. piezo-distance (surface atom)

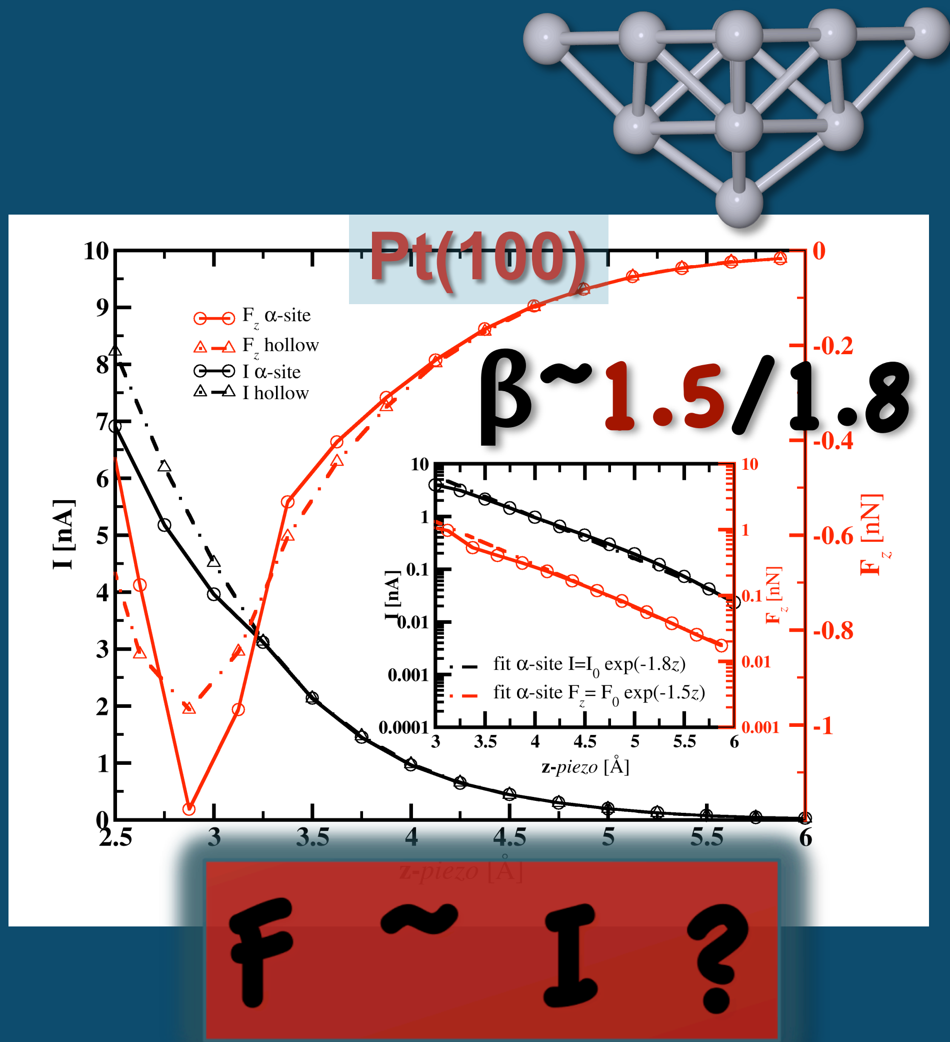


Current & Force: Pt tip

Pt(111)



Pt(100)



Summary

- universal I&F scaling at far distances

I ~ F

- the chemical identification (*theoretically*) possible on metal surfaces

- correlation between force, surface dipole moment & LCP

new generation of STM/AFM opens new horizonts in characterization/modification at atomic scale

Acknowledgement

Nanosurf **Lab (Prague, CZ)**

Cesar González

Martin Ondráček

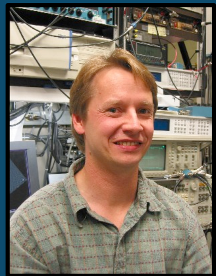
Prokop Hapala

Martin Švec

Vladimír Cháb

Markus Ternes

Franz Giessibl



Andreas Heinrich

OSAKA UNIVERSITY

Y. Sugimoto, M. Abe, O. Custance (NIMS), S. Morita

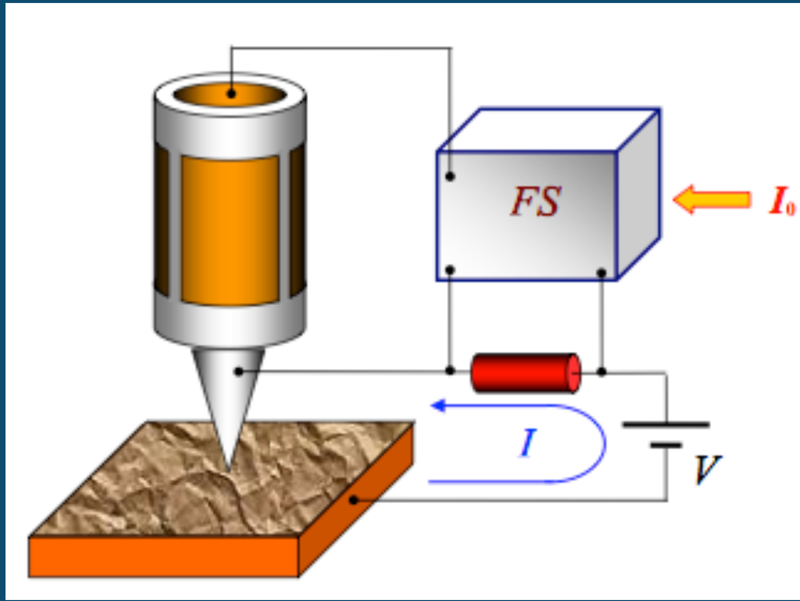
UAM UNIVERSIDAD AUTONOMA DE MADRID

P. Pou, R. Pérez

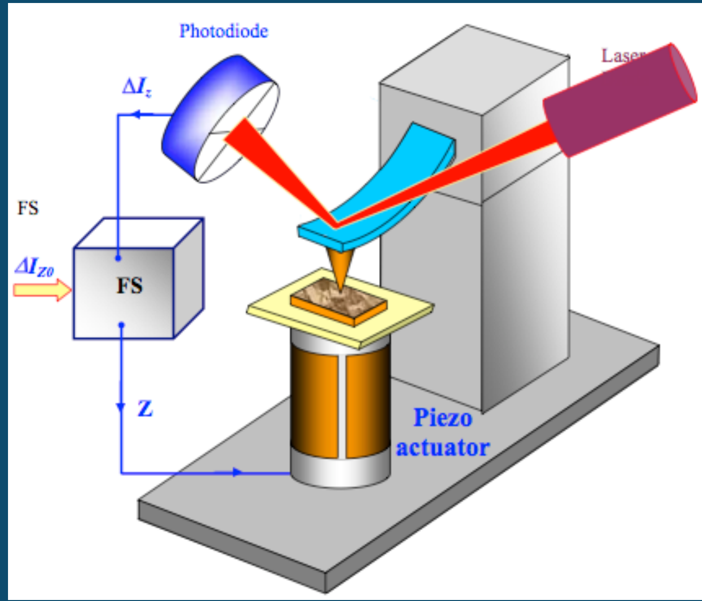
Thank you for your attention

SPM design

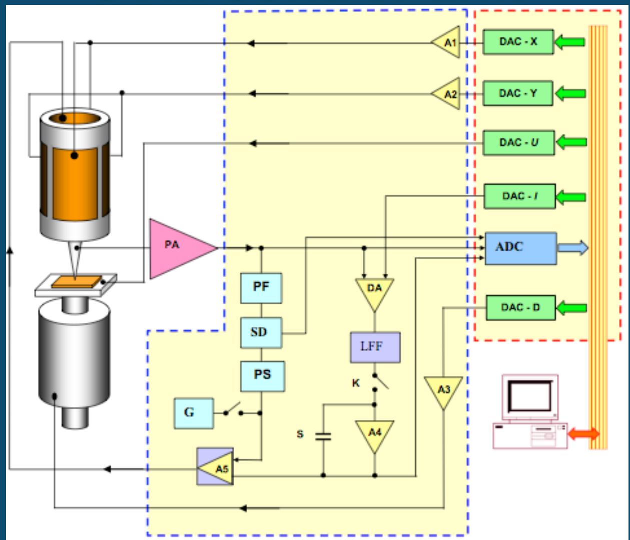
STM



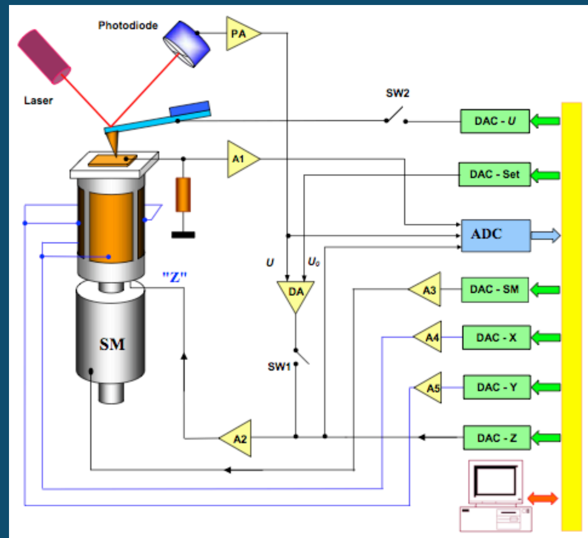
dAFM



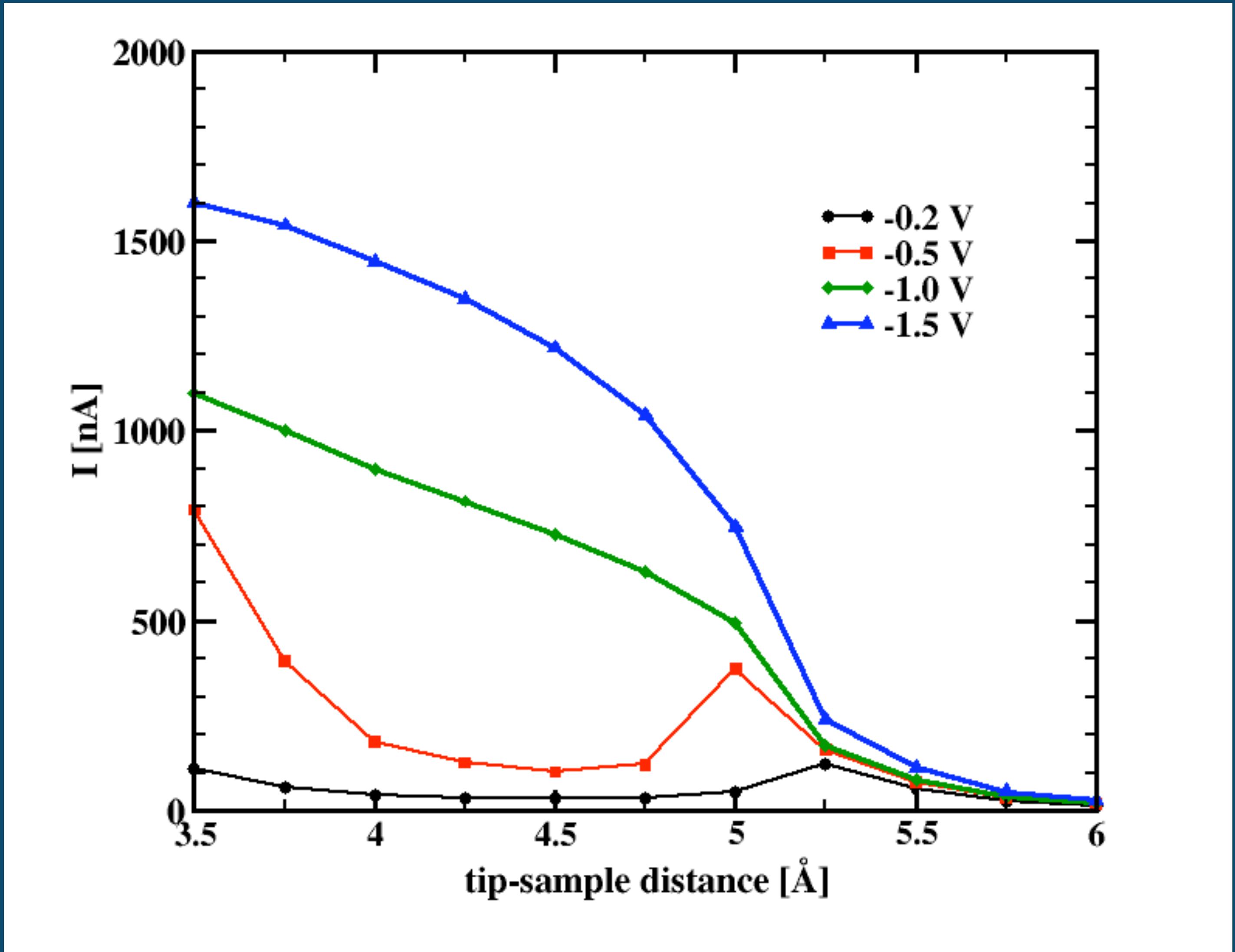
STM control unit



dAFM control unit

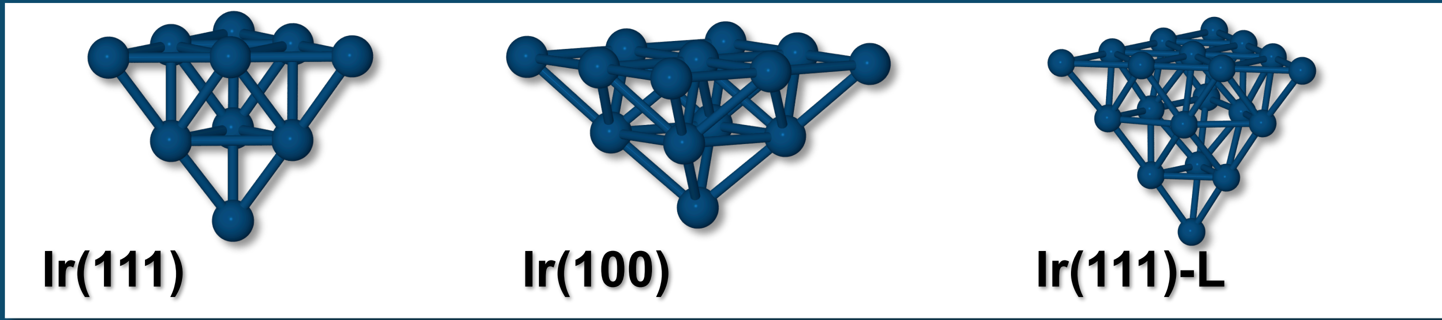


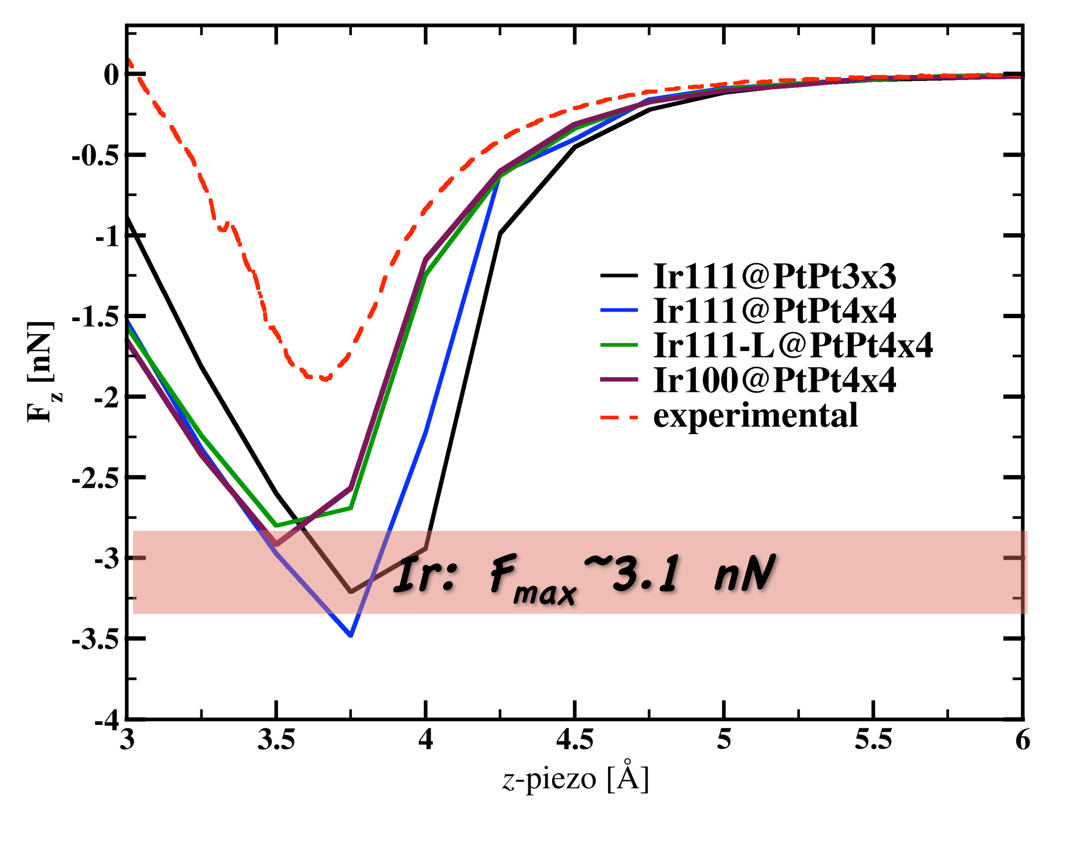
I-V dependence



- the effect of LDOS shift is smeared out at higher voltages

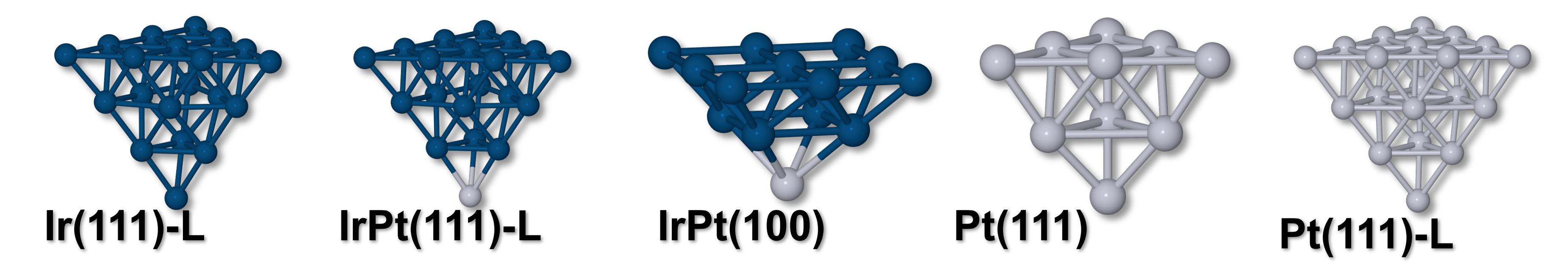
Pt@Pt: bare Ir tips

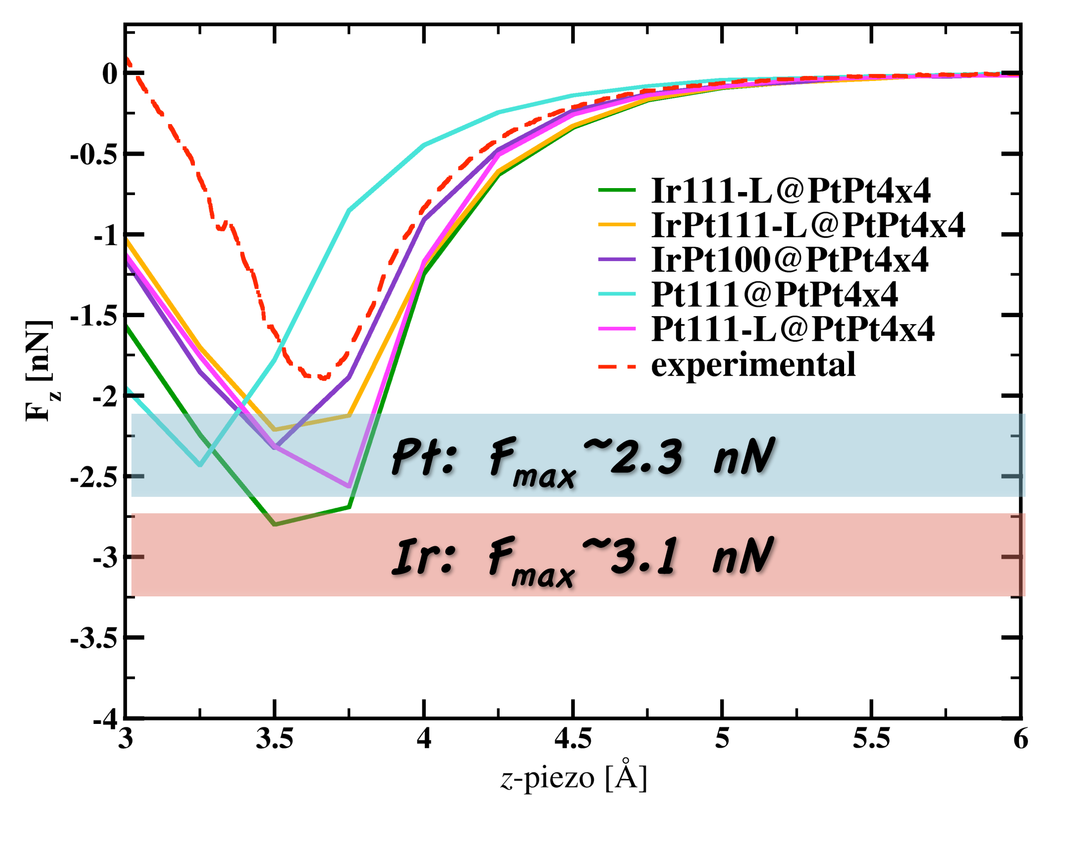




- the large tip is more soft
- apex-coordination plays role
- F_{max} ~ 3.1 ÷ 0.5 nN

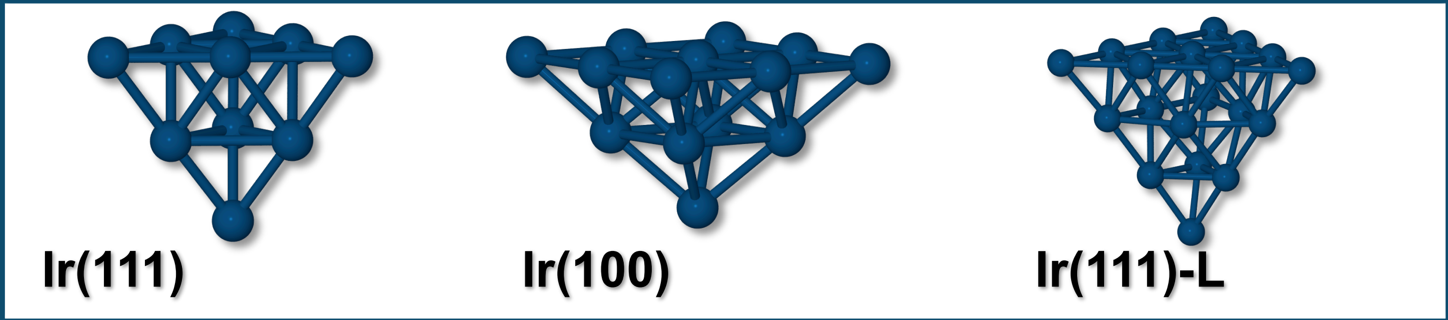
Pt@Pt: Pt apex tip

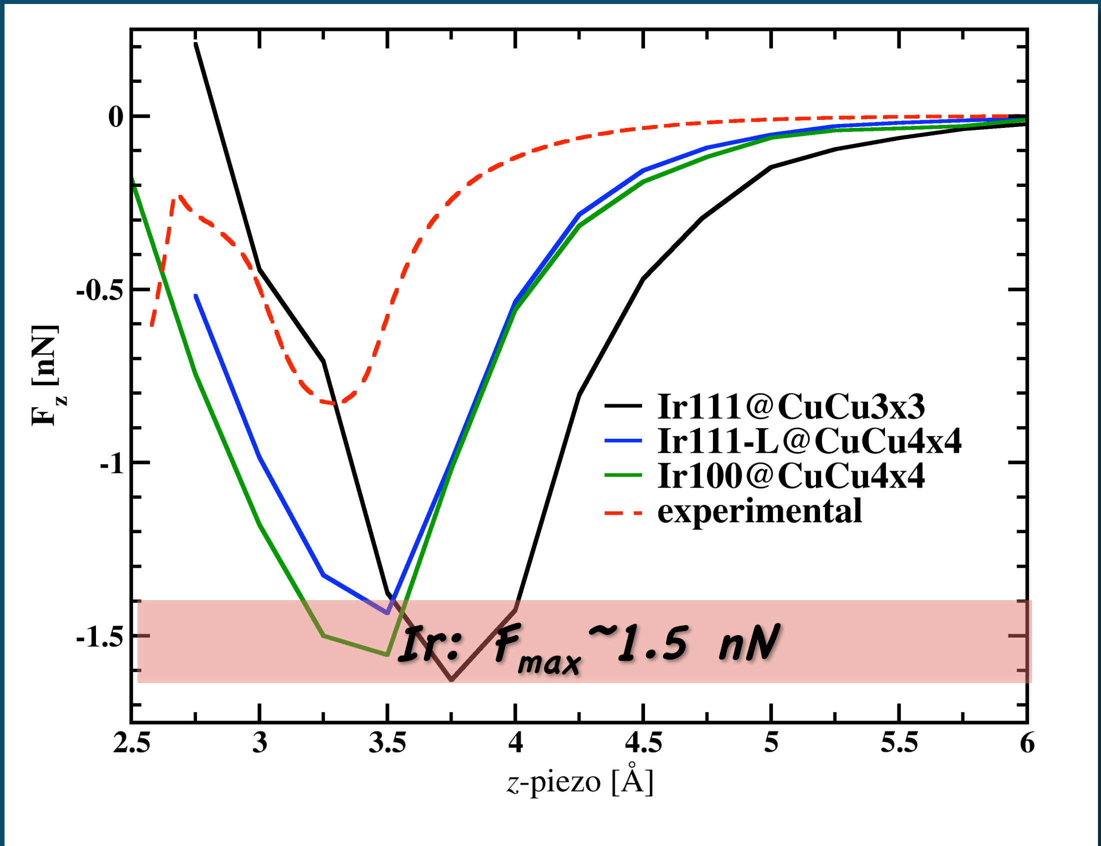




- a contaminated tip fits better the experimental data
- F_{max} sensitive to the chemical origin of apex
- F_{max} ~ 2.3 ÷ 0.5 nN (75%)

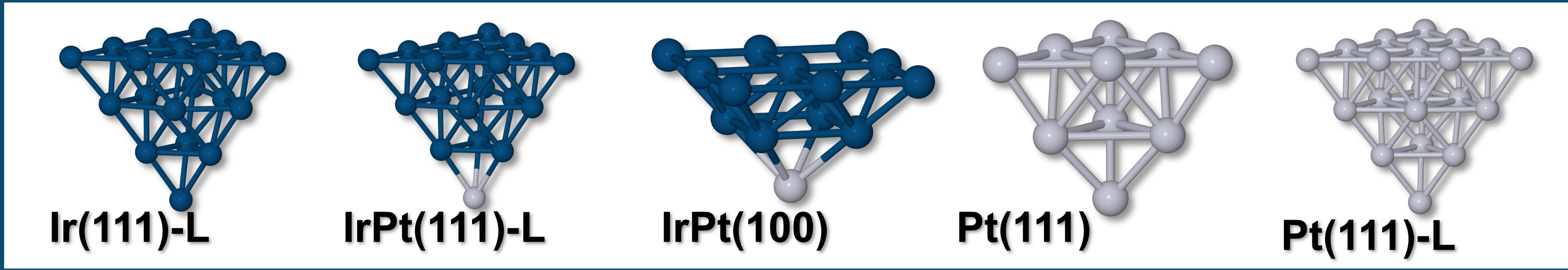
Cu@Cu: bare Ir tips

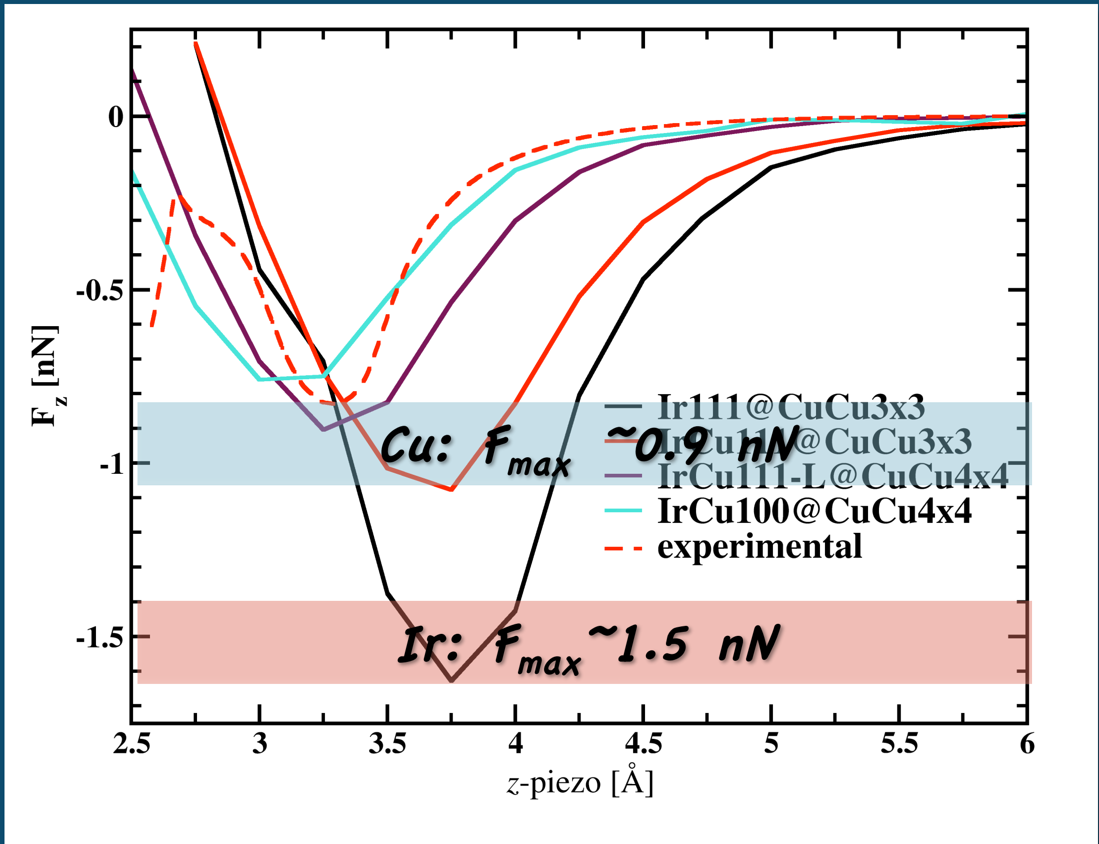




- the large tip is more soft, but differences are smaller: B_{Pt} (230 GPa) >> B_{Cu} (140 GPa)
- F_{max} ~ 1.5 ÷ 0.2 nN

Cu@Cu: Cu apex tip



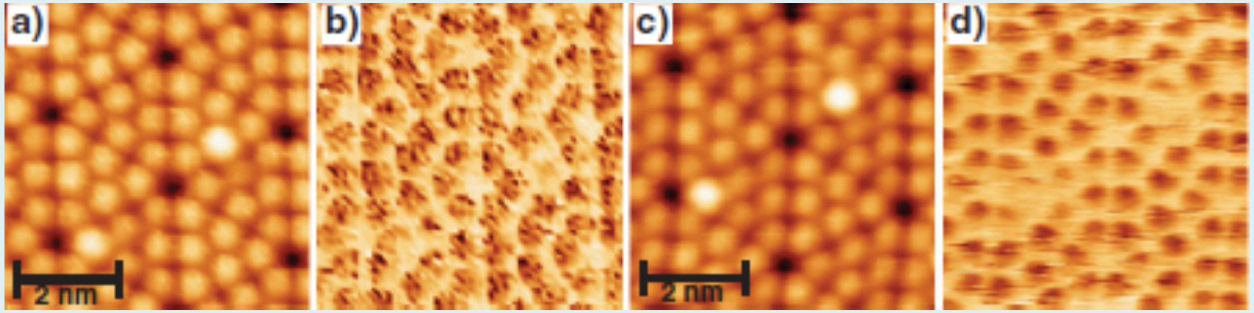


- a contaminated tip fits better the experimental data
- F_{max} sensitive to the chemical origin of apex
- F_{max} ~ 0.9 ÷ 0.2 nN (60%)

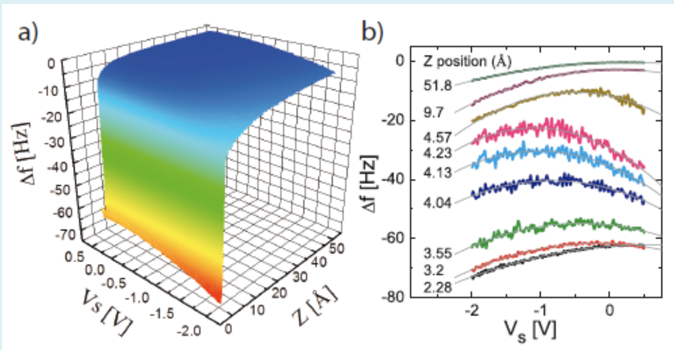
Atomic resolution in KPFM

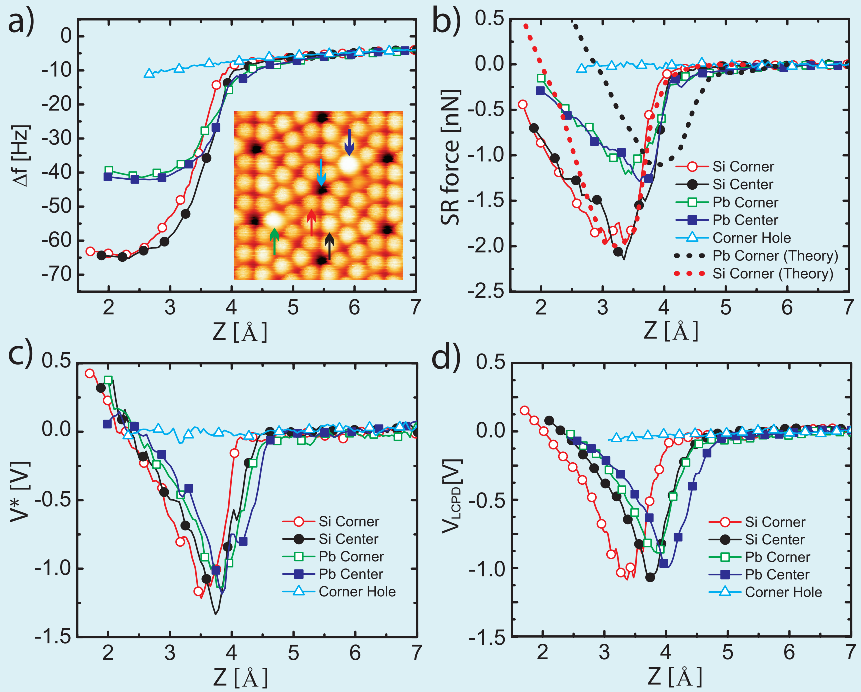
$$F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}\left[V_s - V_{LCPD} + V_{ac}\sin(2\pi f_{ac} t)\right]^2$$

topography **bias-spectroscopy** **topo+KPFM** **KPFM**



3D bias-spectroscopy





- both KPFM and B-S show drop with F_{sr}
  - df –V has parabolic behaviour

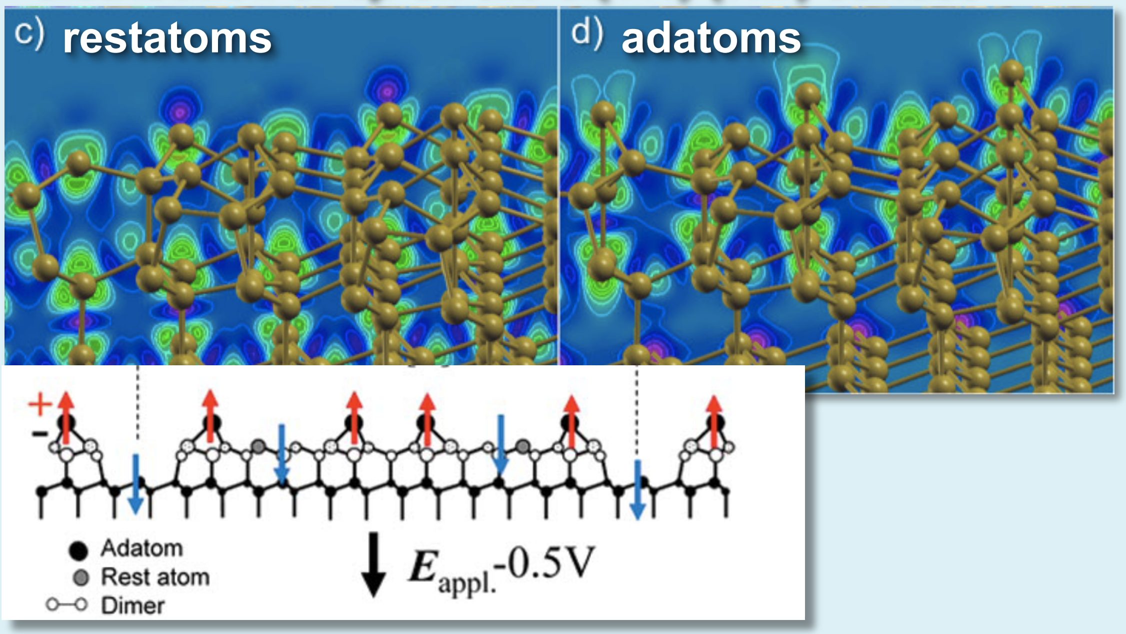
S. Sadewasser et al PRL ***113,*** *266103 (2009)*

atomic resolution in KPFM

work function on surface

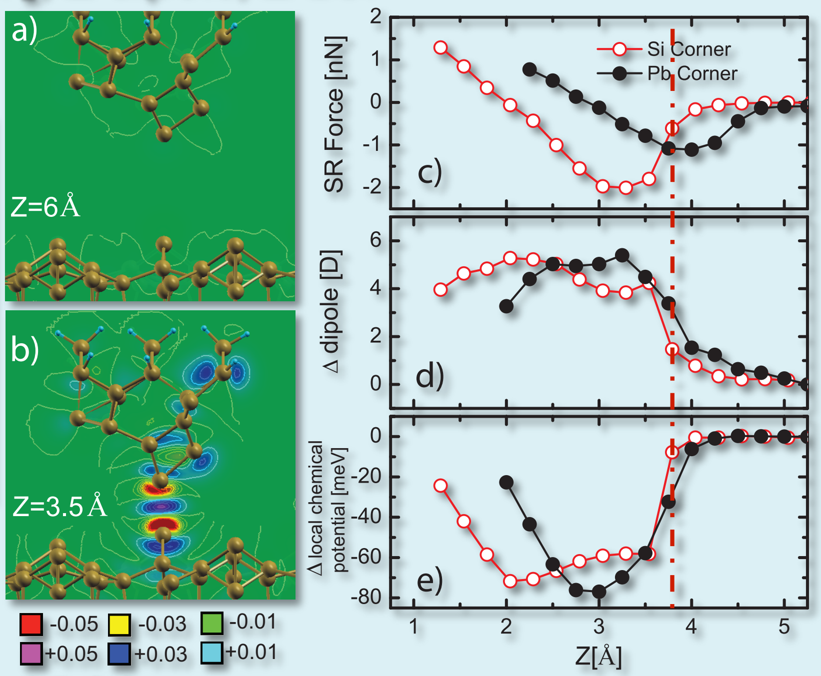
$$\phi = E_{Fermi} + \Delta_{surf}$$

distribution of δρ on the Si(111)-(7x7) surface

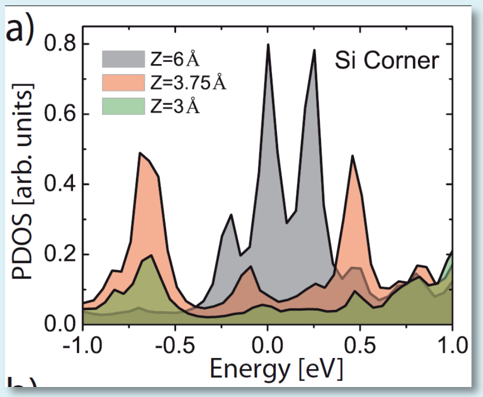


Y. Cho and R. Hirose PRL ***99,*** *186101 (2007)*

F_z, Δ dipole, Δ LCP



PDOS



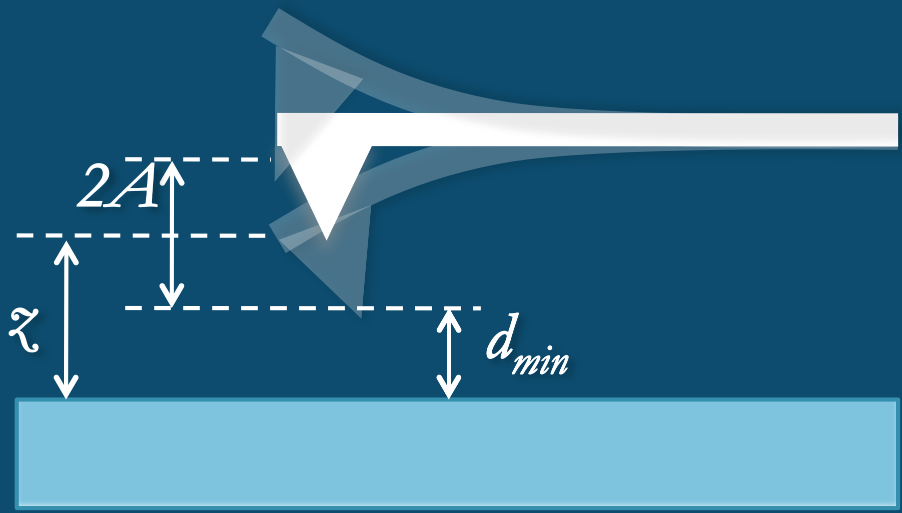
modification of surface dipole by formation of the chemical bond -> atomic scale contrast

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

STM vs. dAFM

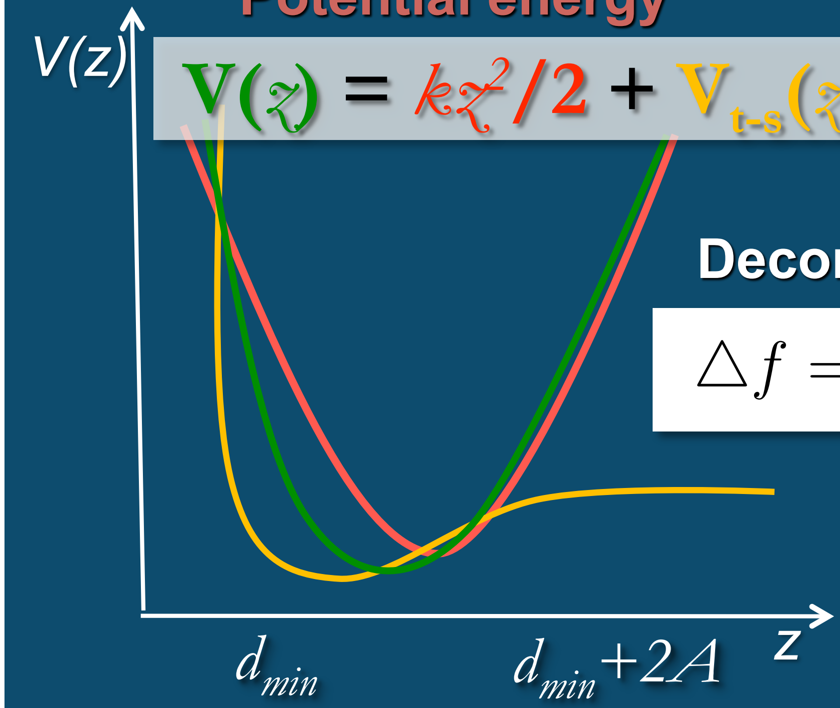
	STM	dAFM
signal	I	Δf, E_{diss}, I,..
output	topography, LDOS, e-ph coupling	topography, diss. signal, force
parameters	V_{bias}, z	E_{diss}, z, Δf, A, k,…
spectroscopy	CITS, IETS, lock-in, I-z	Force Site Spectroscopy, higher harmonics
atomic resolution	1982	1995
atomic manipulation	1989	2003
surface	conductive	arbitrary

Force vs. Δf relation



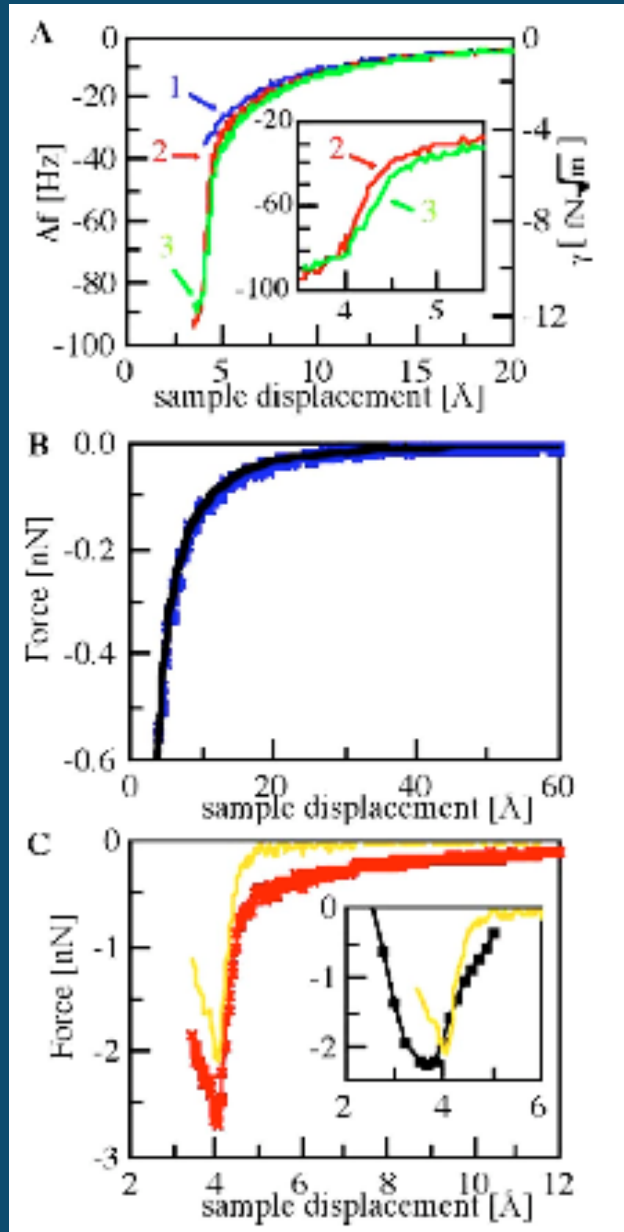
Potential energy

$$V(z) = kz^2/2 + V_{t\text{-}s}(z)$$

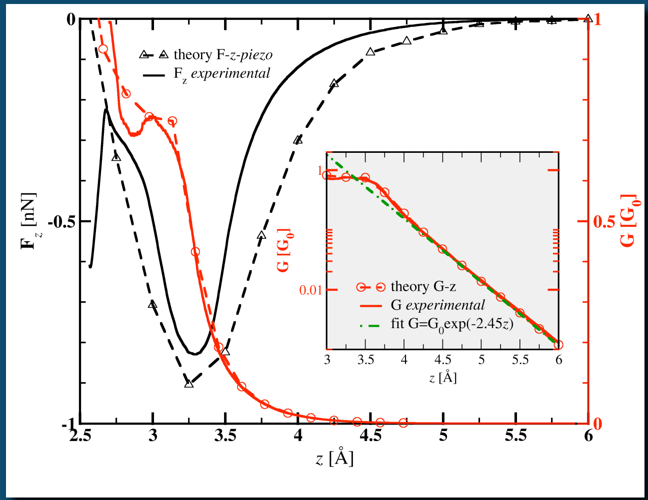


Deconvolution F vs. Δf

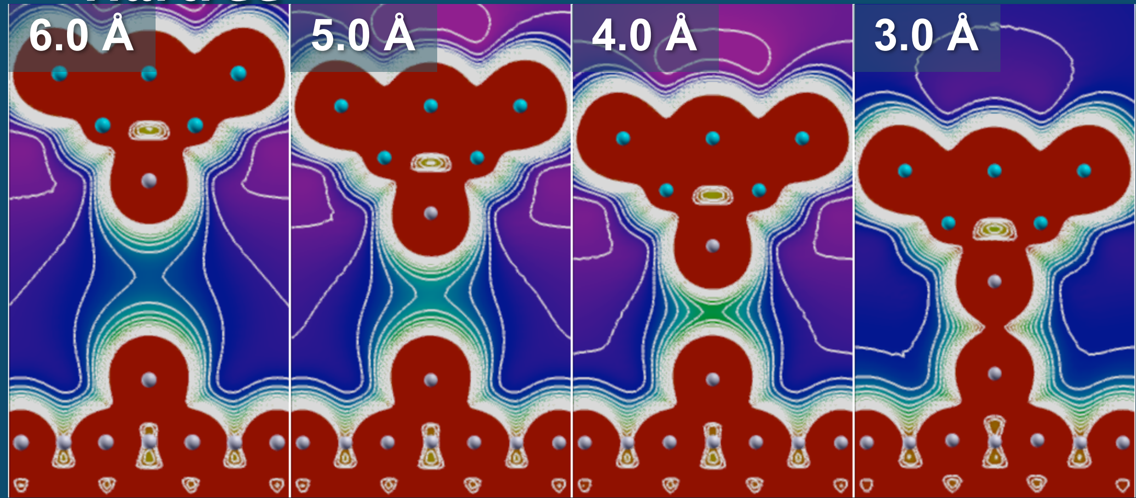
$$\triangle f = -\frac{f_o}{kA_o^2} < F_{ts} z >$$



Bond formation: Cu@Cu



$V_{Hartree}$



$\Delta\rho=\rho_{all} - \rho_{slab} - \rho_{tip}$