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2063-4

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19 - 24 October 2009

Understanding dissipation processes in dynamic atomic force microscopy

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Understanding dissipation processes in dynamic Atomic Force Microscopy

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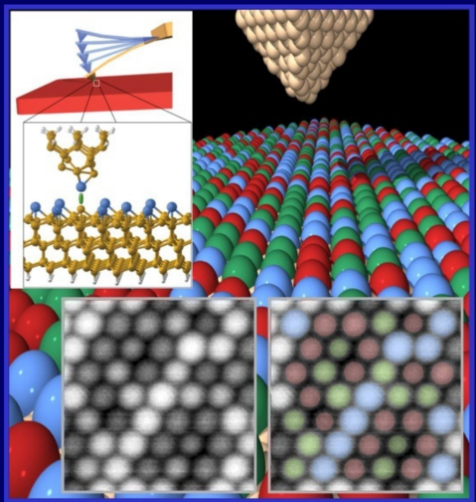
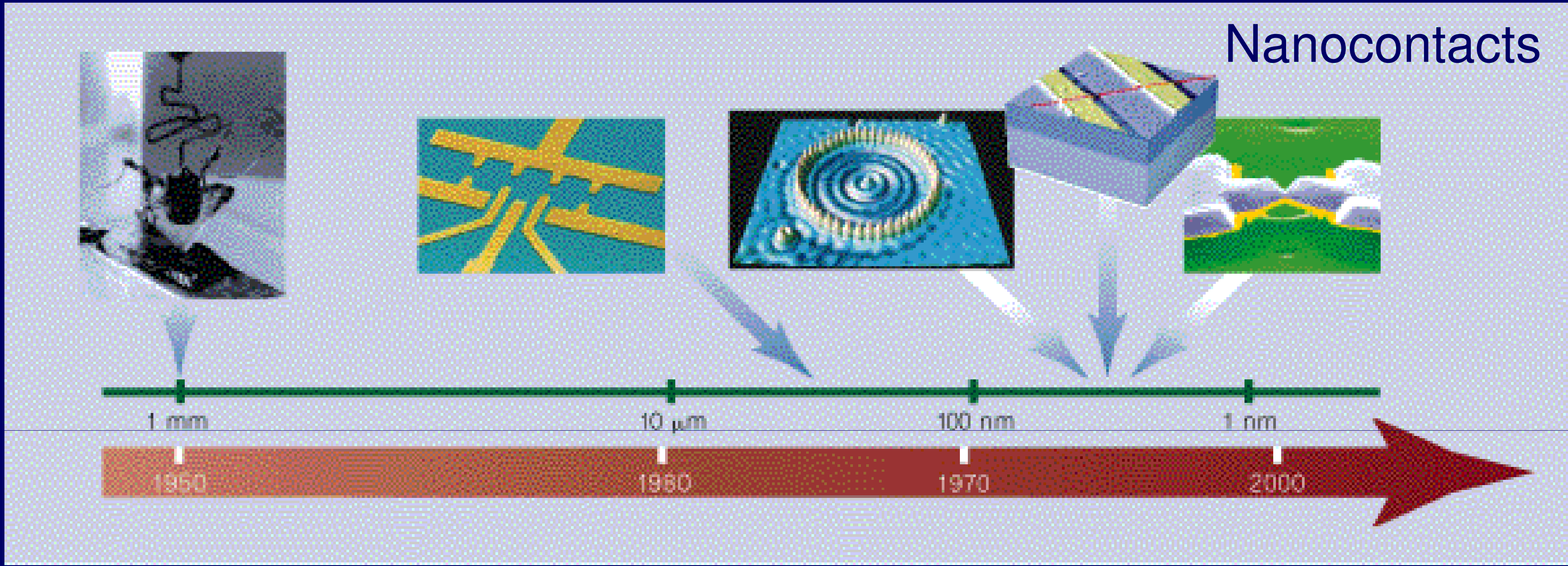
http://www.uam.es/spmth



UNIVERSIDAD AUTONOMA DE MADRID

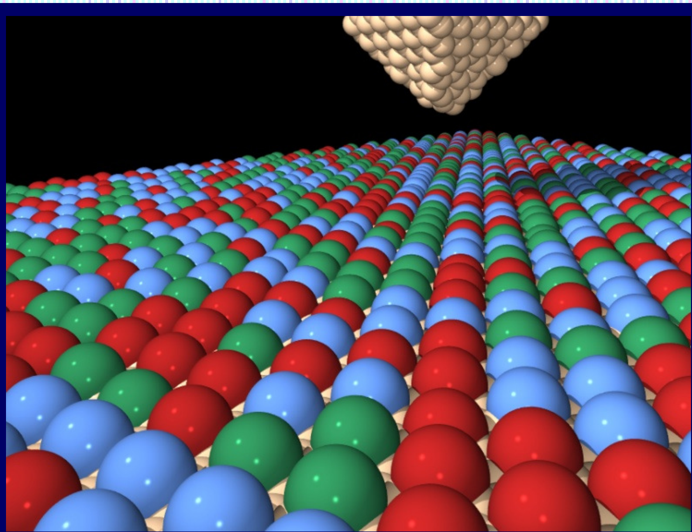
ICTP/FANAS Trends in Nanotribology,Trieste, Oct 20th 2009

Nanotechnology: Materials & Tools (SPMs)
(Atomic scale is different…)

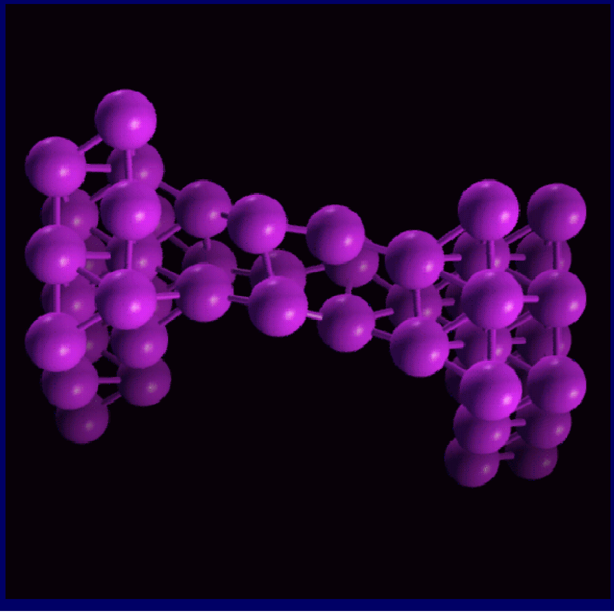


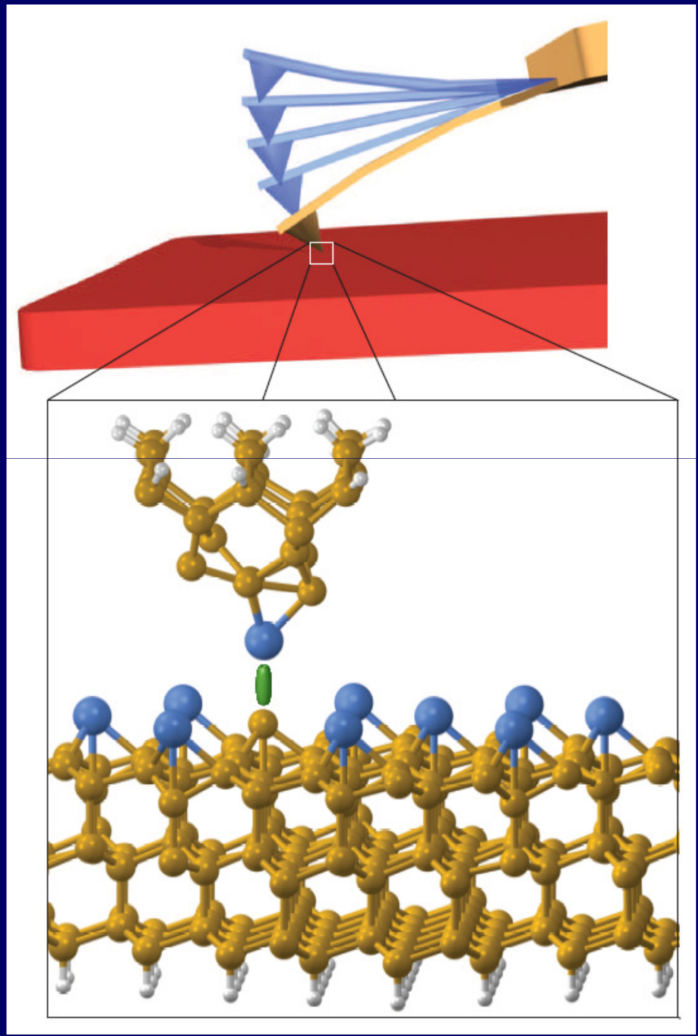
Scanning Probe Microscopes (SPMs):

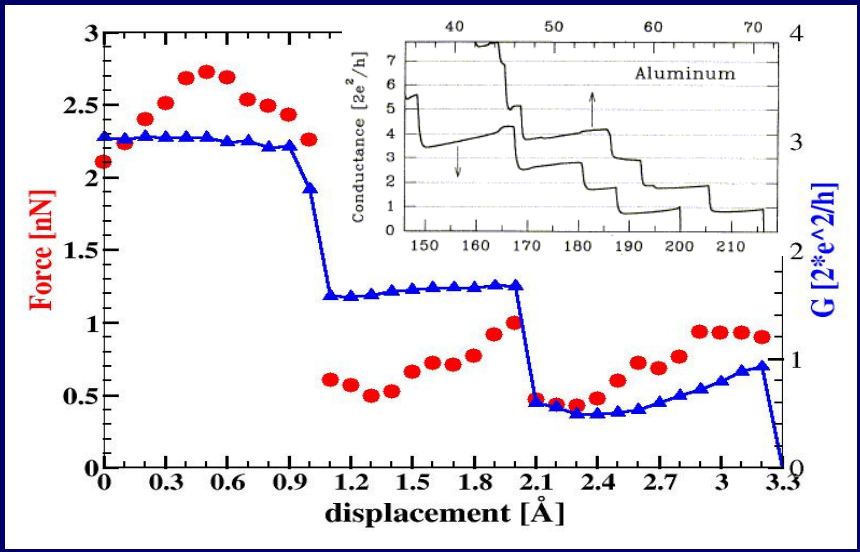
- Scanning Tunneling Microscope (STM)
- Atomic Force Microscope (AFM)
- …



Forces & Transport in Nanostructures: First-principles calculations







Methodology

"The computer is a tool for clear thinking" Freeman J. Dyson

Ab-initio total energy methods + Non-equilibrium Green's Functions

(based in Density Functional Theory)

both plane wave & local orbital basis: accuracy/efficiency balance

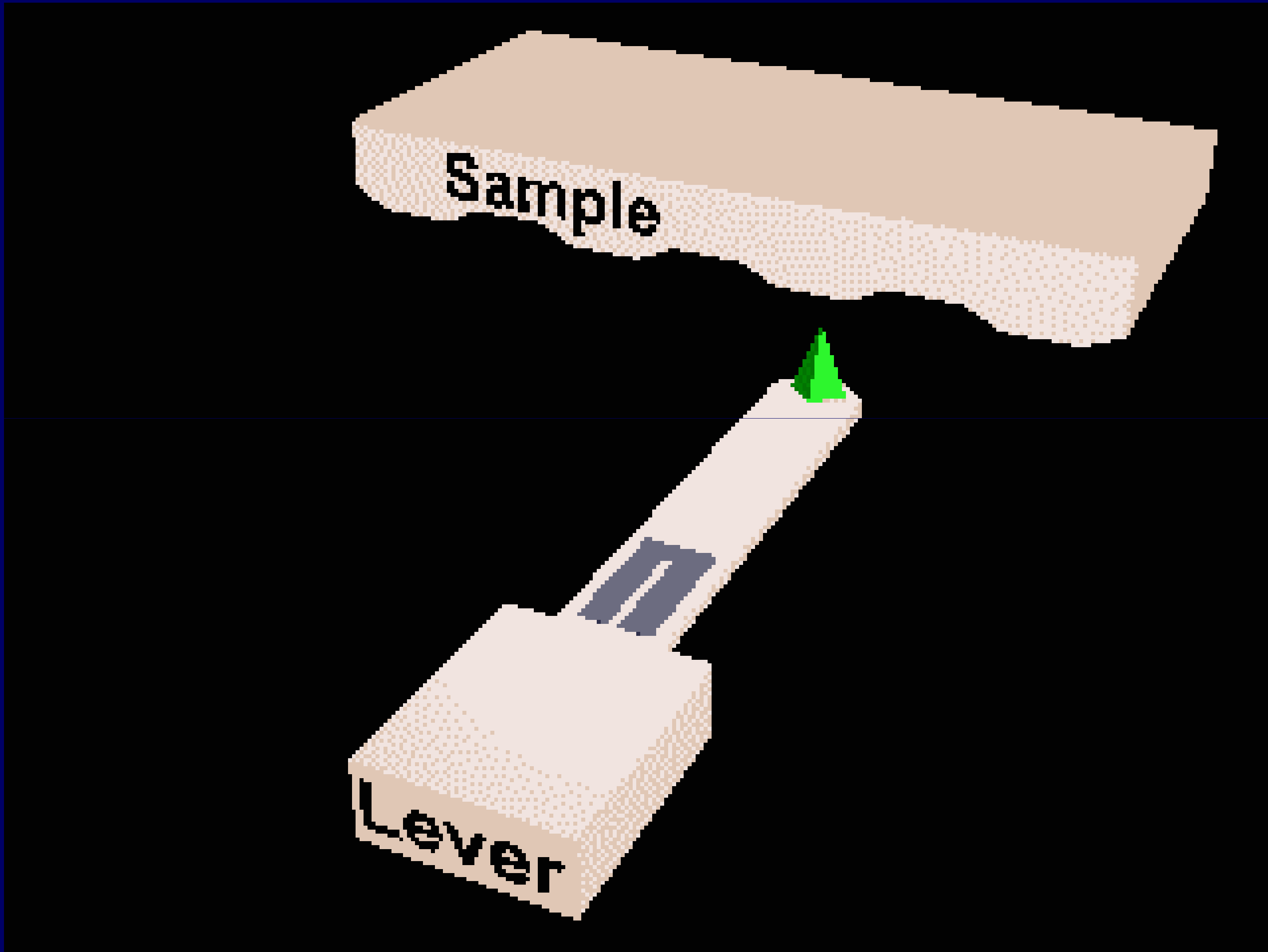
Linked with the local orbital description

Structure + electronic properties

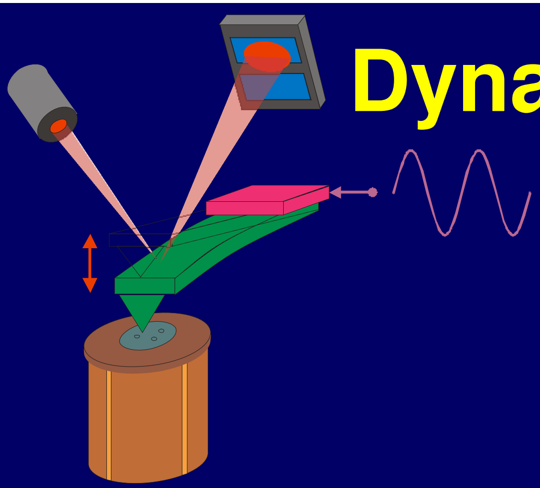
Electronic transport

FIREBALL, OPENMX
CASTEP, VASP

Dynamic AFM

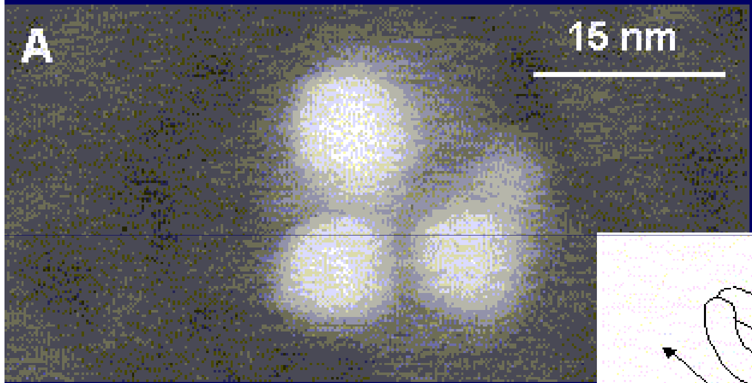


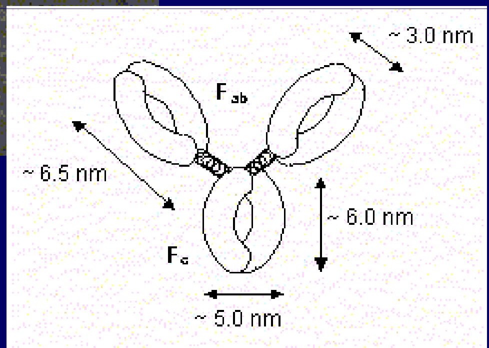
http://monet.physik.unibas.ch/famars/afm_prin.htm

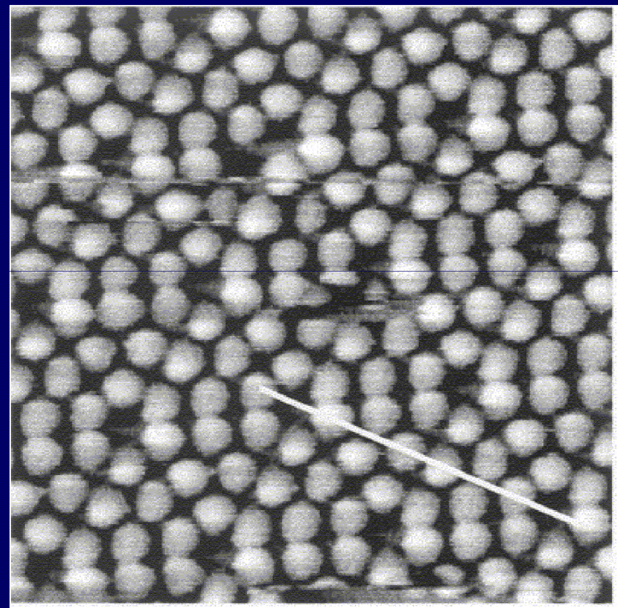


Dynamic AFM: Our Goal

Why changes observed in the dynamic properties of a vibrating cantilever with a tip that interacts with a surface make possible to:







AM-dAFM

• Obtain molecular resolution images of biological samples in ambient conditions.

•Resolve atomic-scale defects in UHV.

FM-dAFM

R. García and R. Pérez, Surf. Sci. Rep. 47, 197 (2002)

Outline

Goal: Combine theory & experiment to identify the microscopic mechanisms involved in energy dissipation

1. FM-AFM: Identification of a dissipation channel due to single atomic contact adhesion on semiconductor surfaces.

   N. Oyabu et al. Phys. Rev. Lett. 96, 106101 (2006).

2. FM-AFM: submolecular resolution in the dissipation images for PTCDA on Ag(111)

3. AM-AFM: Combining continuum models and large scale *ab initio* MD simulations to understand the dissipation mechanisms in a sexithiophene ML deposited on SiO_x

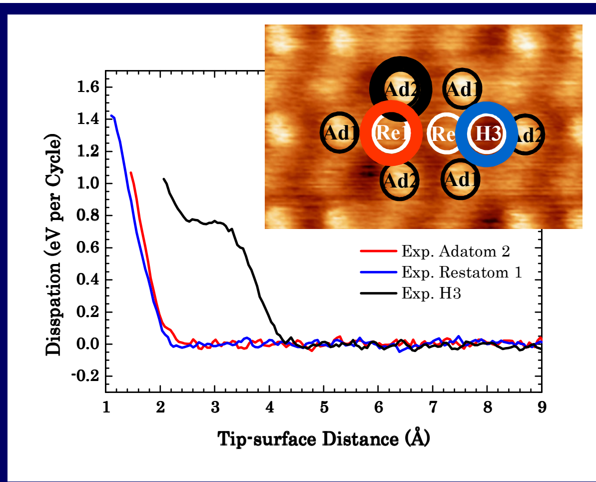
   R. García, R. Magerle and R.P., Nature Materials **6**, 405 (2007)

   N.F. Martinez et al, Nanotechnology 20, 434021 (2009) (special issue to mark the 20th Volume, 2009)

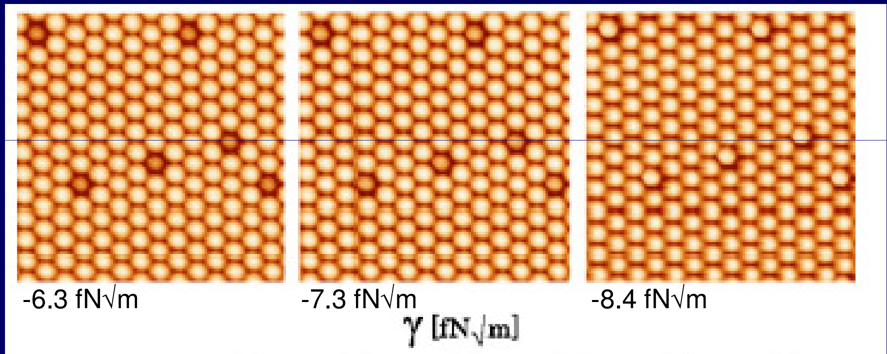
Recent developments in FM-AFM

1. DISSIPATION: Characterizing the tip structure and identifying a dissipation channel due to single atomic contact adhesion.

N. Oyabu et al. Phys. Rev. Lett. 96, 106101 (2006).



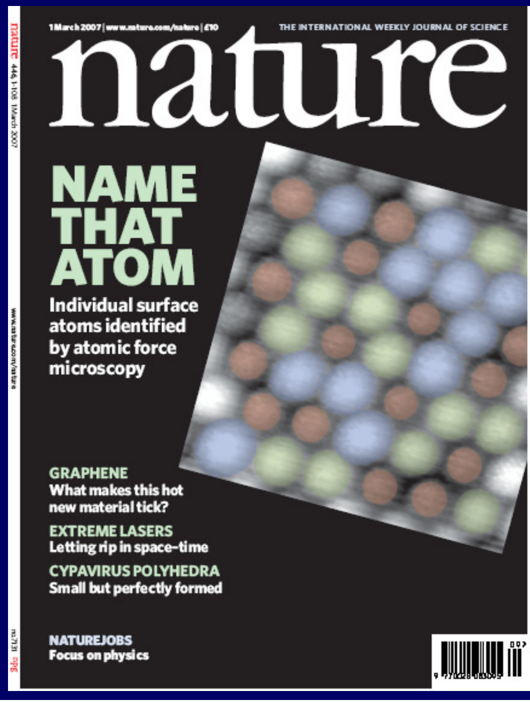
2. IMAGING: changes in topography: access to the real surface structure?



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

3. CHEMICAL IDENTIFICATION:

based on the relative interaction ratio of the maximum attractive force measured by dynamic force spectroscopy

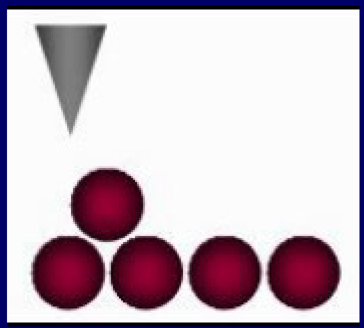


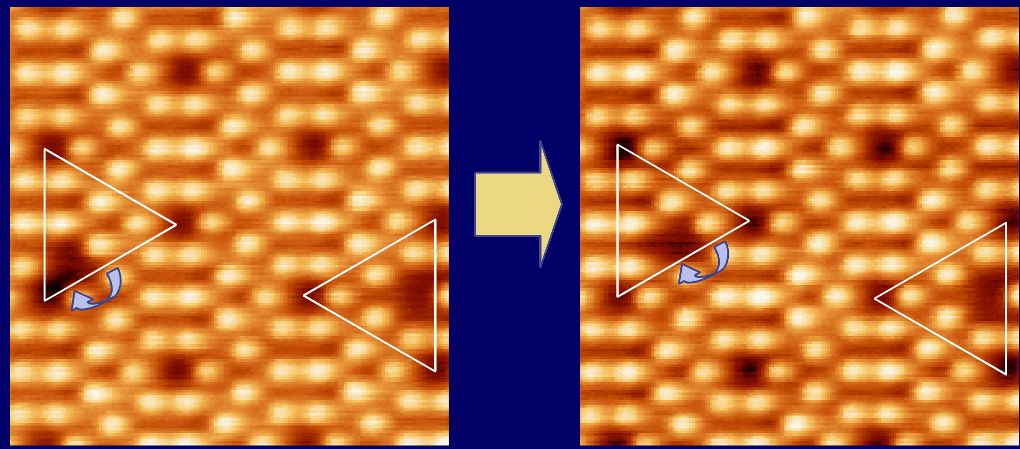
Y. Sugimoto et al Nature 446, 64 (2007).

Recent developments in FM-AFM

Understanding RT DFM-based single-atom manipulation

4. LATERAL MANIPULATION: Si vacancy on Si(111)-7x7 (tip assisted thermal hopping)

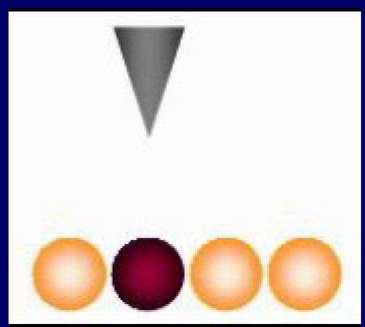


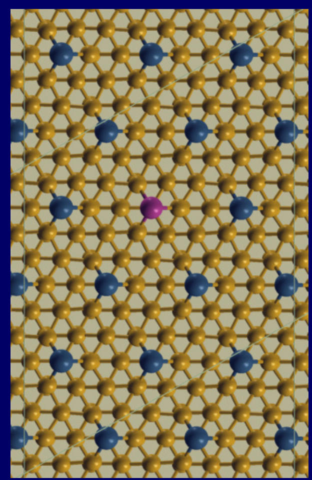


Y. Sugimoto et al. Phys. Rev. Lett. 98, 106104 (2007).

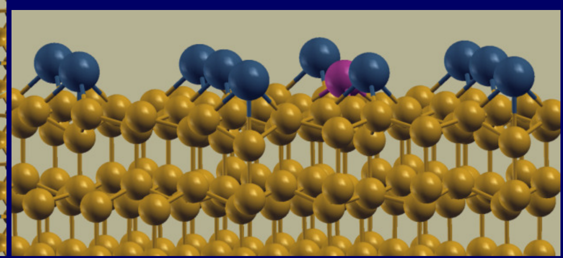
5. VERTICAL MANIPULATION:

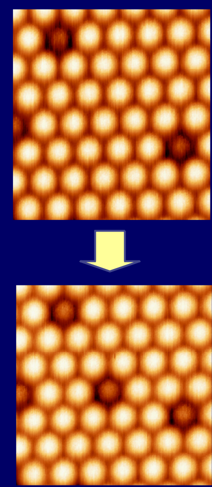
Tip/sample exchange of atoms on Sn/Si(111)





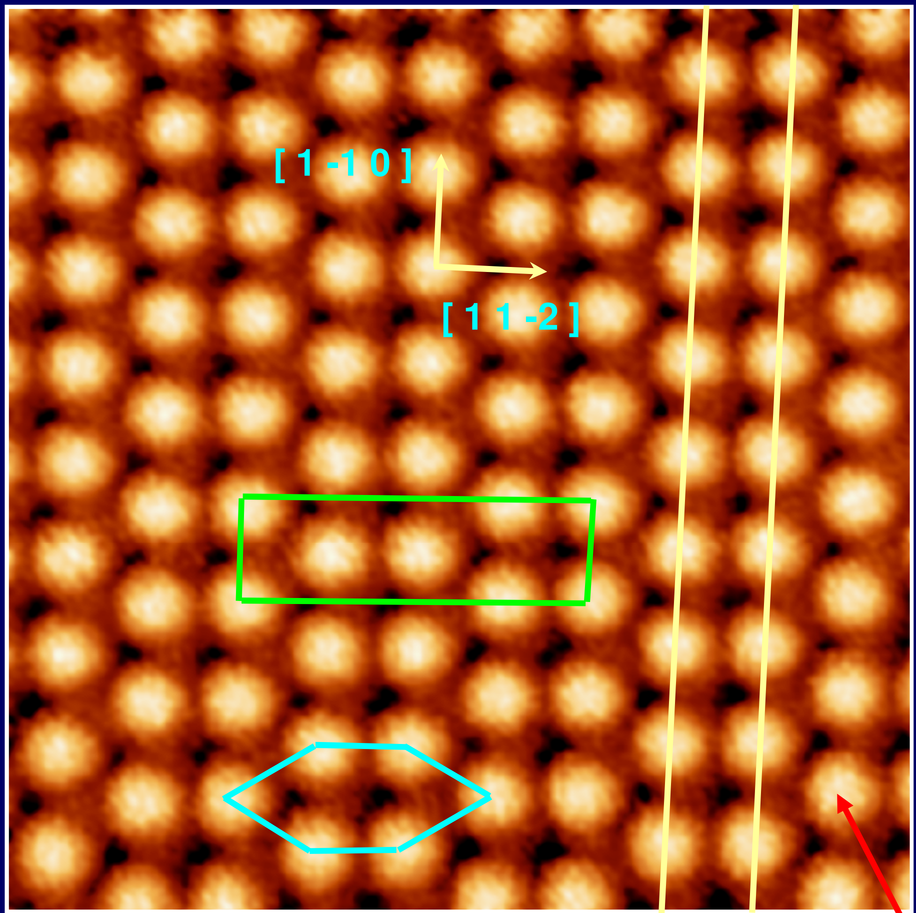
α-Sn/Si(111)-(√3x√3)



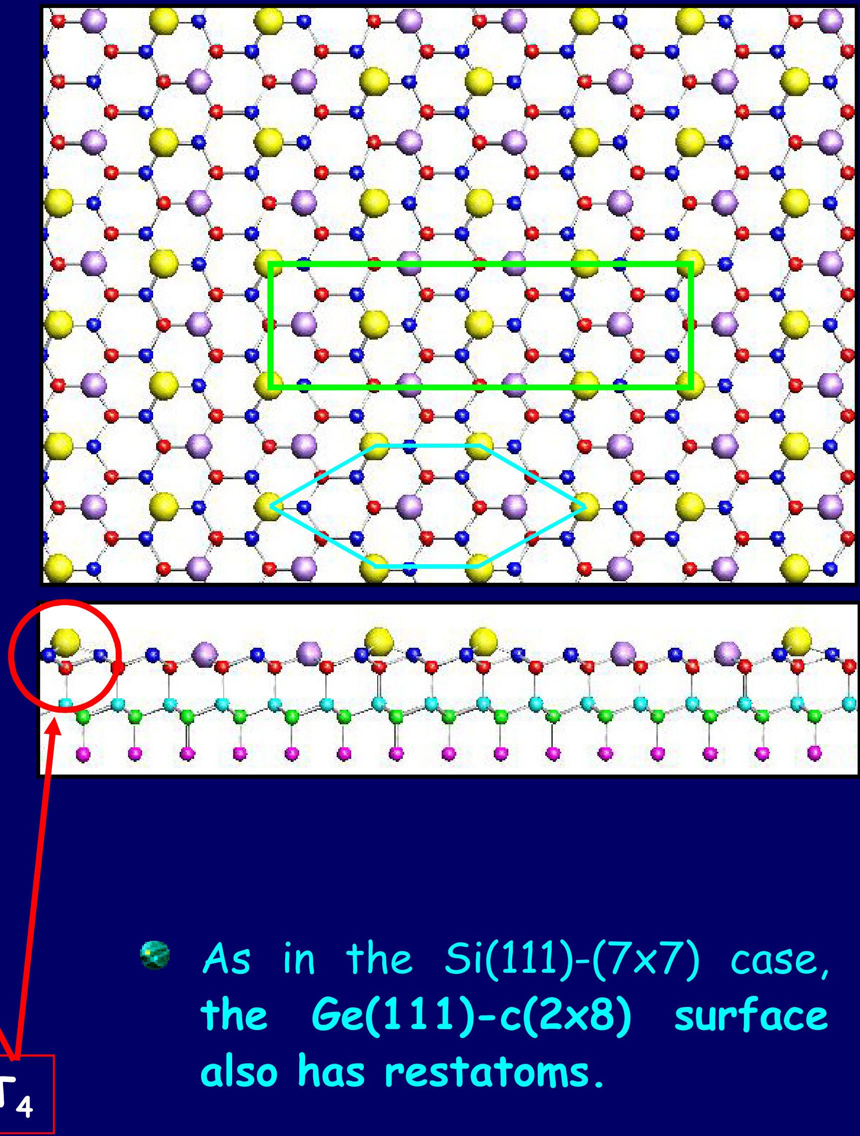


Y. Sugimoto et al., Science 322, 413 (2008).

NC-AFM images of the Ge(111)-c(2x8) surface



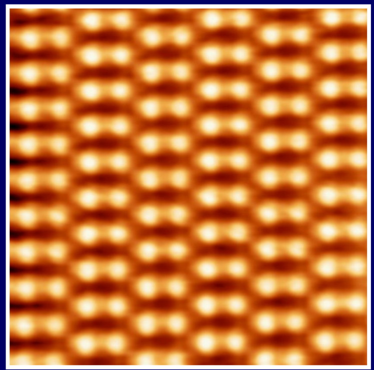
NC-AFM Topographic image (8.2x8.2)nm^2
Δf = - 10.9 Hz f_0 = 163.780,2 Hz A = 10 nm
K_L = 31.4 N/m Q = 294162 T = 80 K



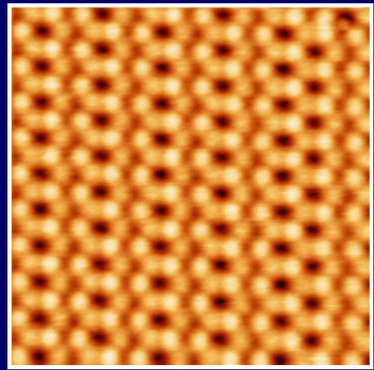
- *As in the Si(111)-(7x7) case, the Ge(111)-c(2x8) surface also has restatoms.*

Ge(111)-c(2x8): two typical topographic patterns

- The Ge(111)-c(2x8): ROOM TEMPERATURE



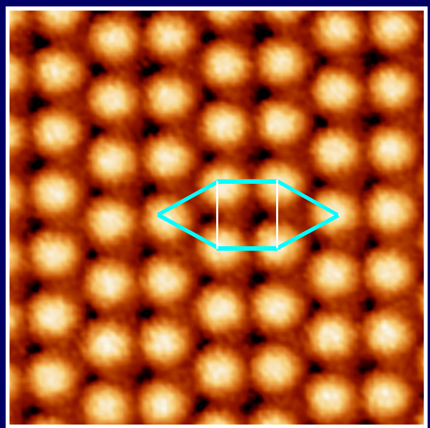
Δf = -5.3 Hz
f_0 = 161320.4 Hz
A = 19 nm
K_L = 30.0 N/m
γ = -4.1fN m$^{1/5}$



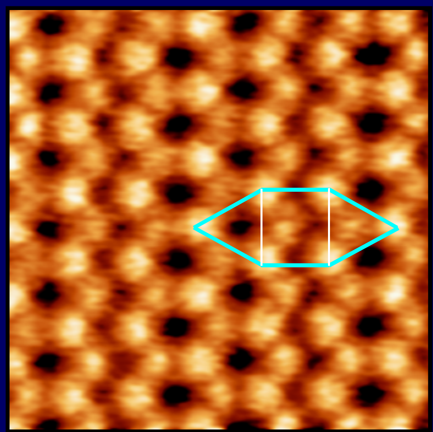
Δf = -3.0 Hz
f_0 = 161320.4 Hz
A = 19 nm
K_L = 30.0 N/m
γ = -2.3fN m$^{1/5}$

M. Abe, Y. Sugimoto, and S. Morita, *Nanotechnology*, **16**, **S68 (2005)**

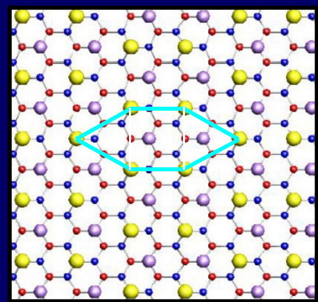
- The Ge(111)-c(2x8): LOW TEMPERATURE (80K)



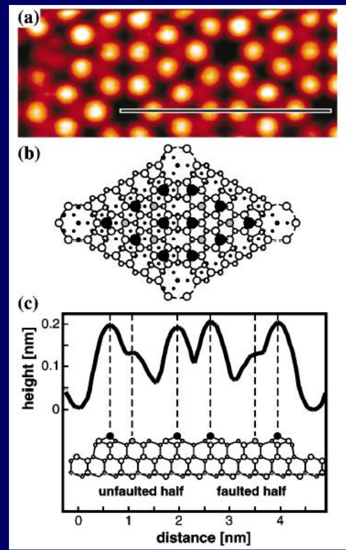
Δf = - 10.9 Hz f_0 = 163780,2 Hz
A = 10 nm K_L = 31.4 N/m

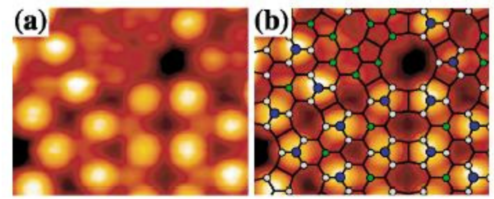


Δf = -21.5 Hz f_0 = 163875.6 Hz
A = 12.9 nm K_L = 33.4 N/m



Different from an enhancement of resolution by heating up the Si cantilevers (900°C)

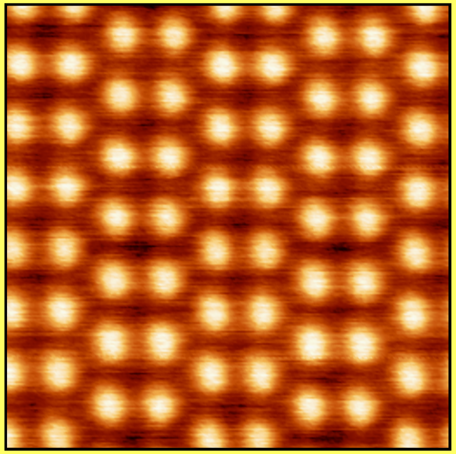




T. Eguchi and Y. Hasegawa, Phys. Rev. Lett. **89**, 266105 (2002)

Experiments in the same session

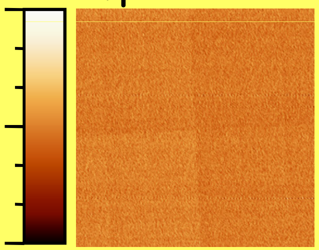
Tip A



Topography
(6x6) nm^2

Amplitude Error

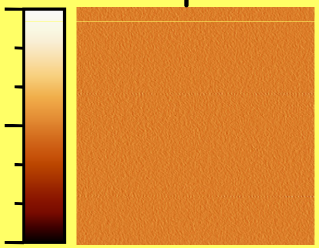
0.20 Å



-0.26 Å

Dissipation

0.61 eV/cycle



-0.59 eV/cycle

Δf =-13.4 Hz ⇒ γ = -7.94 fN √m

Imaging at a Total Force value of ≈ - 1.2 nN

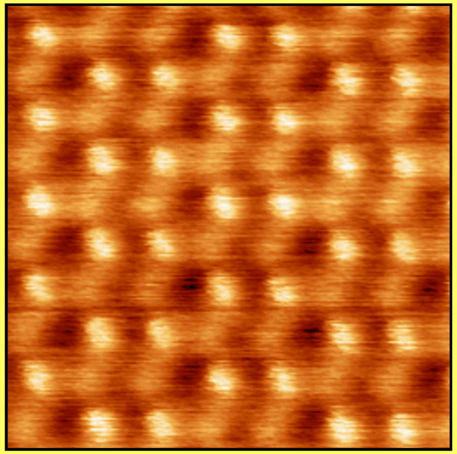
A=182 Å

Q= 259500

f_0= 183663 Hz

K = 44.3 N/m

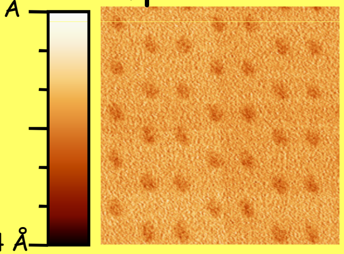
Tip B



Topography
(5x5) nm^2

Amplitude Error

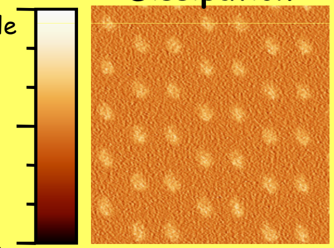
0.18 Å



-0.24 Å

Dissipation

0.54 eV/cycle



-0.47 eV/cycle

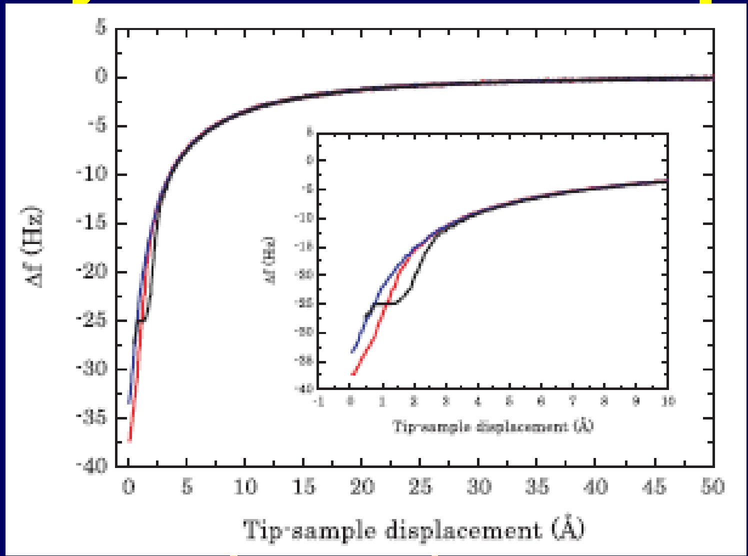
Δf =-15.5 Hz ⇒ γ = -9.18 fN √m

Imaging at a Total Force value of ≈ - 1.4 nN

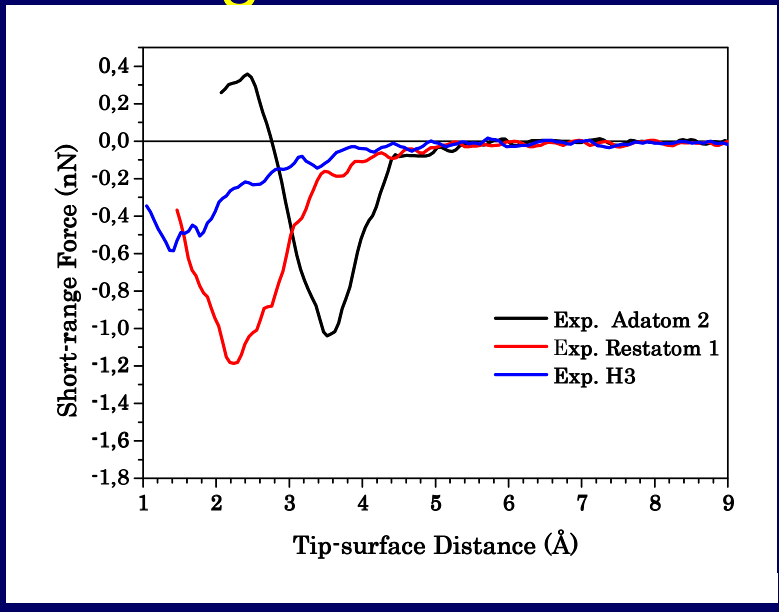
Slight Tip-Change

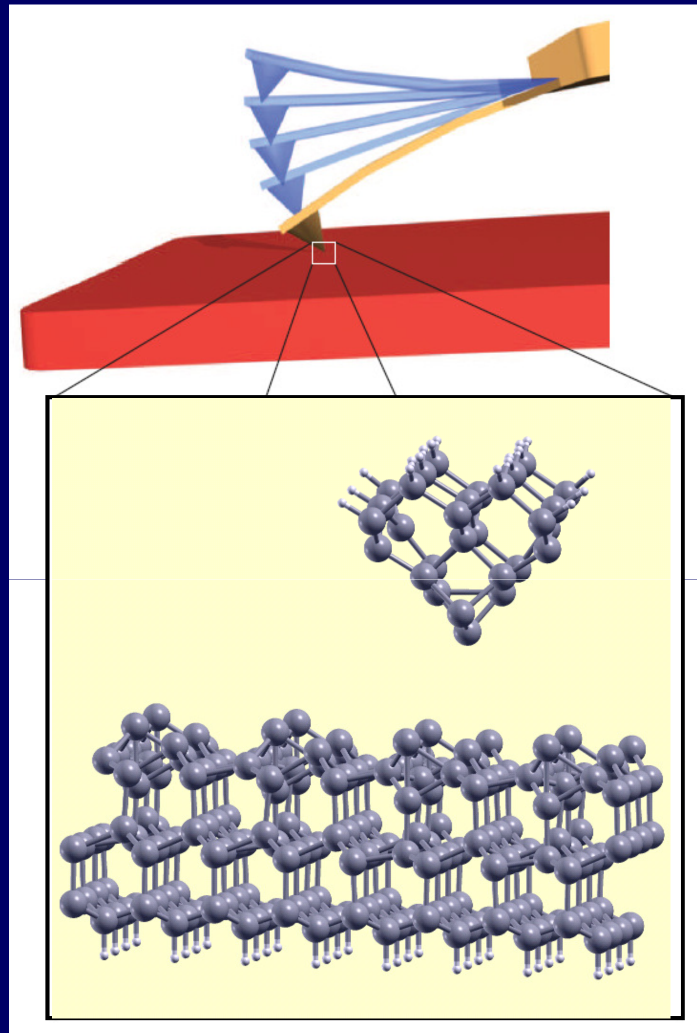
Same measurement session with the same experimental parameters !!!

Dynamic Force Spectroscopy: Access to F_{ts}



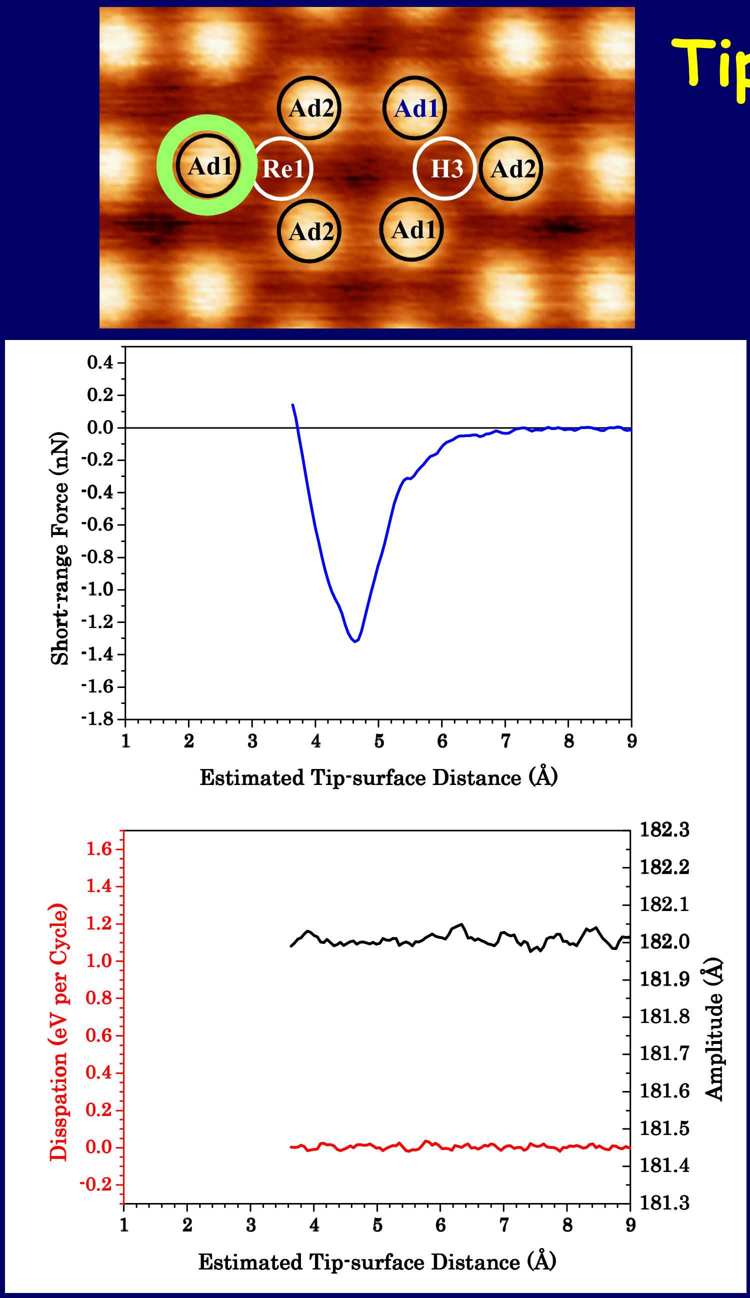
Inversion algorithms

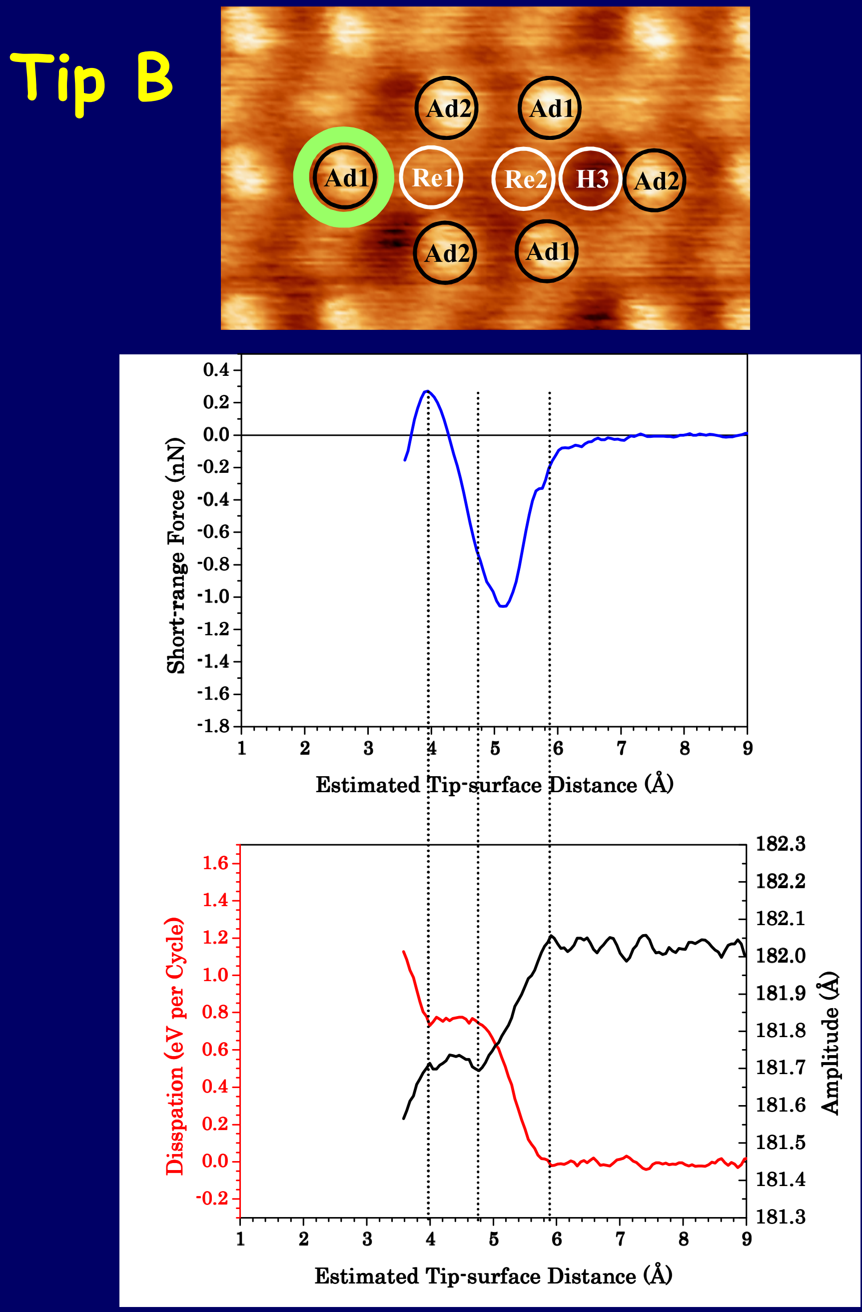




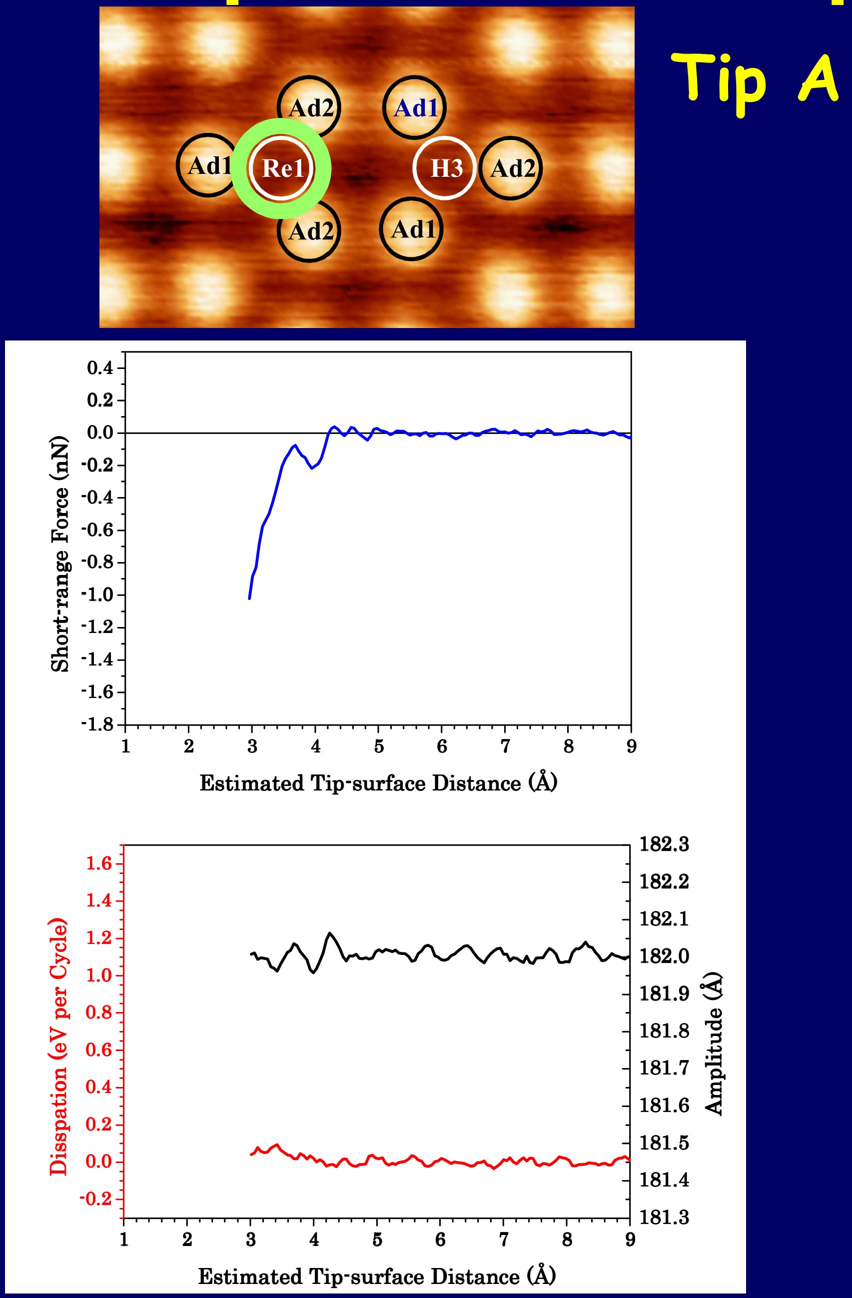
SR forces amenable to ab initio calculations

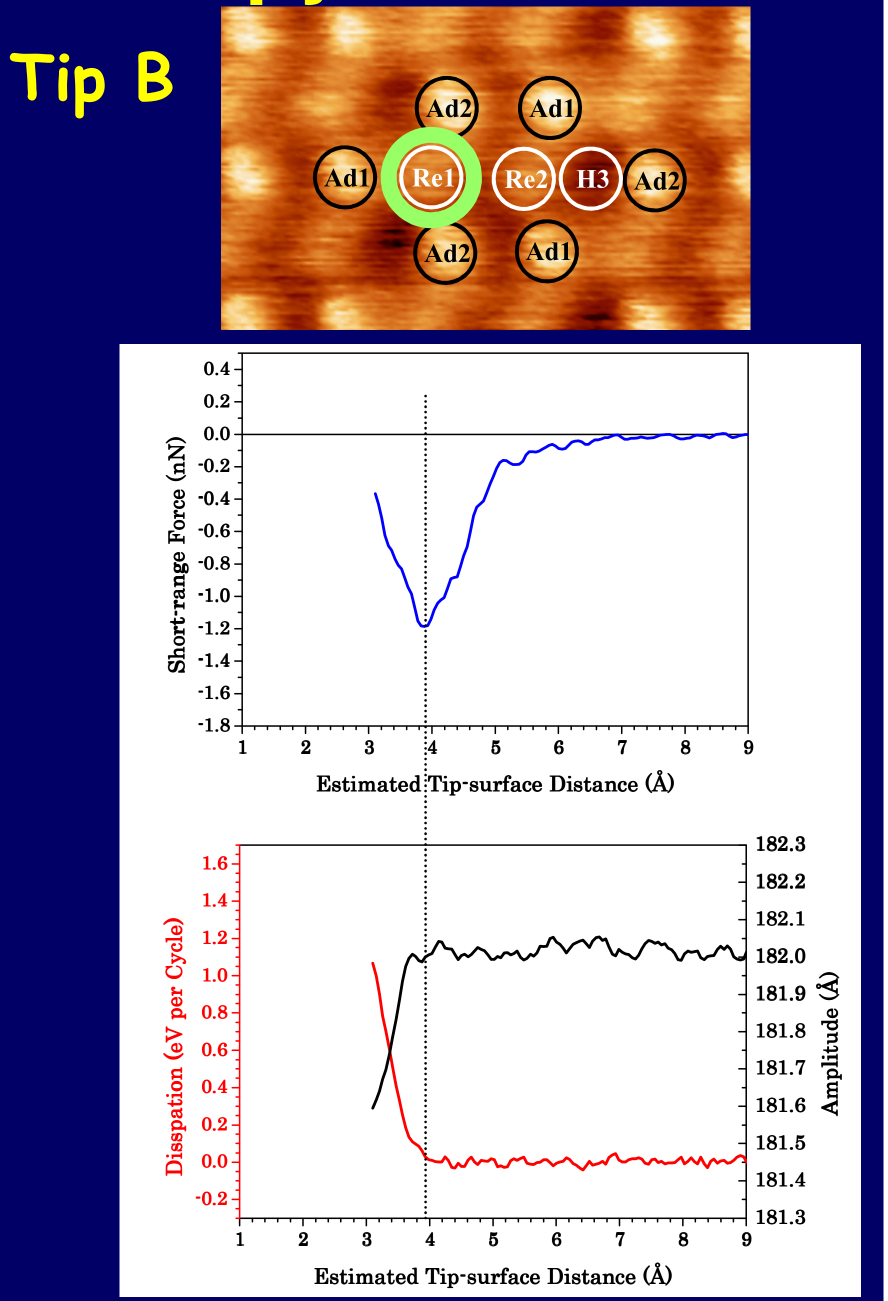
Site-Specific Force Spectroscopy: Adatom 1



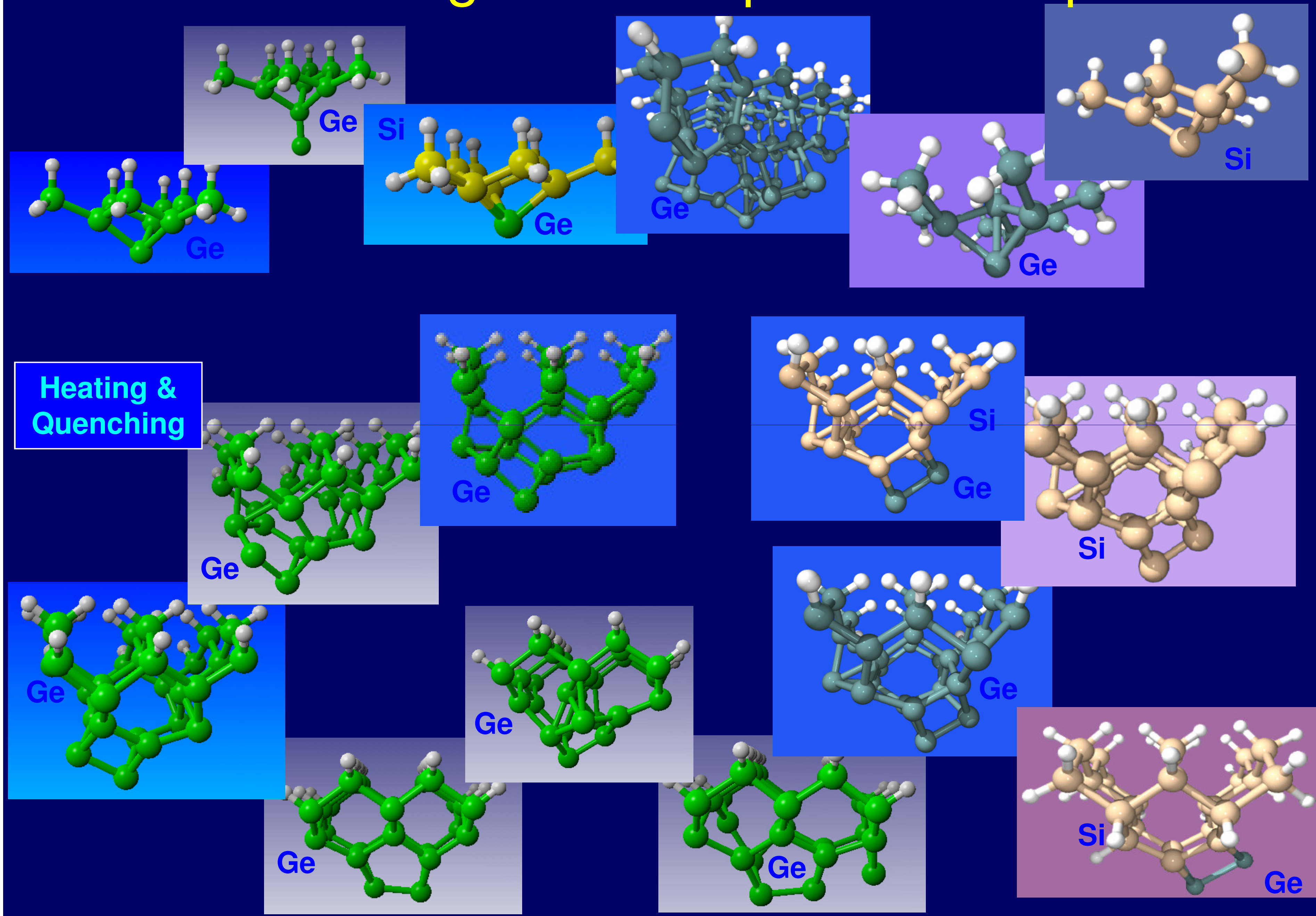


Site-Specific Force Spectroscopy: Restatom 1

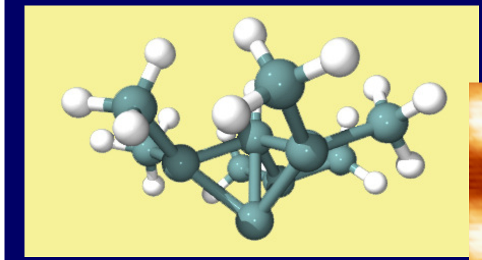




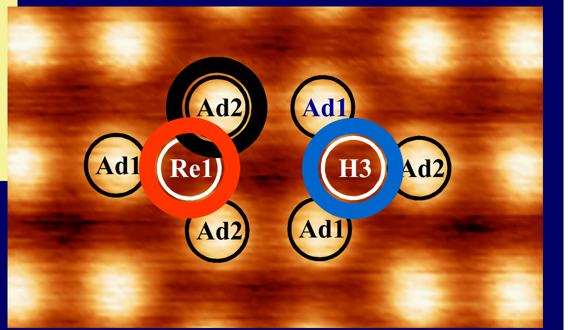
Searching for the experimental tips

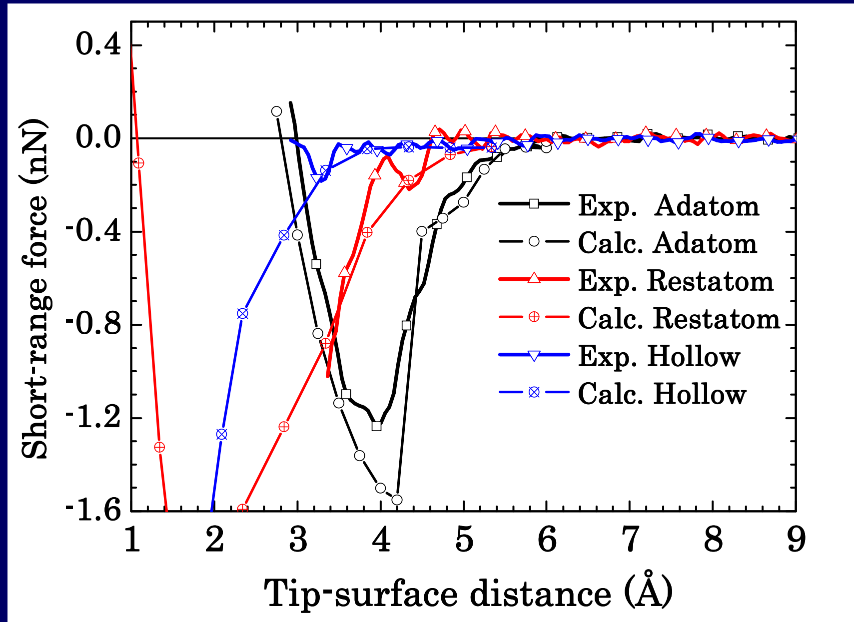


Tips selected for explaining the experiments

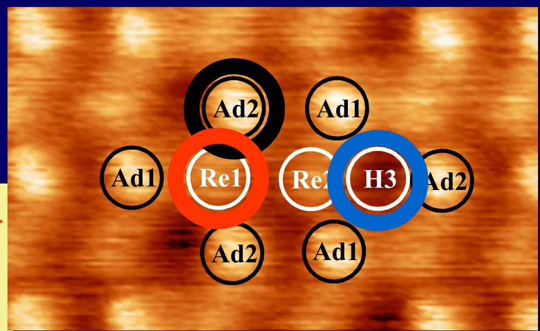


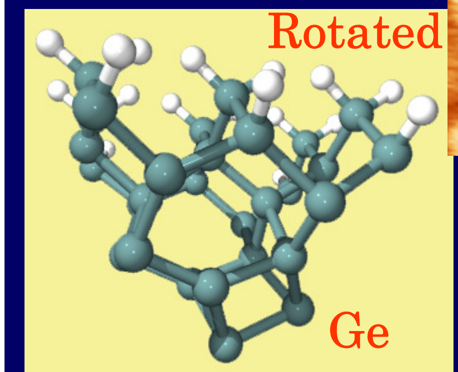
Tip A

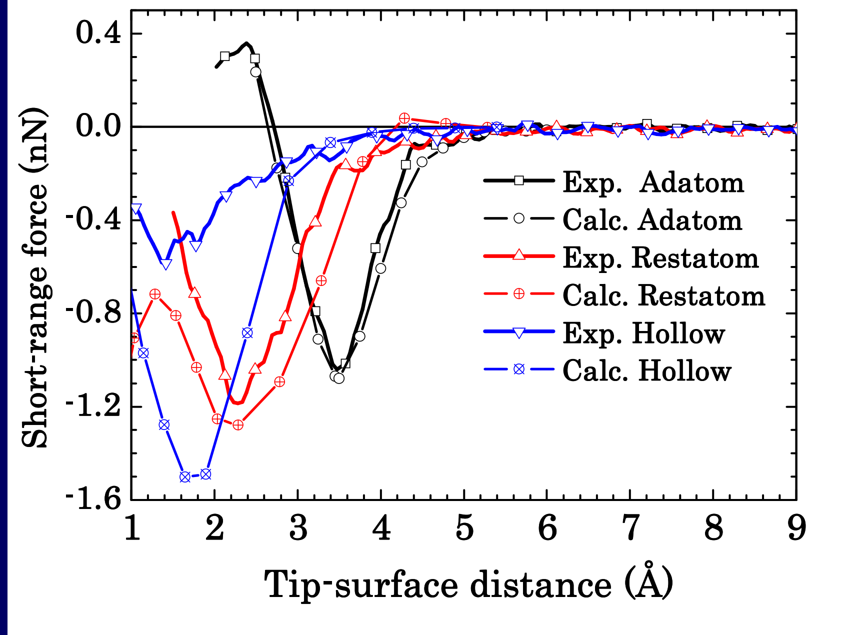




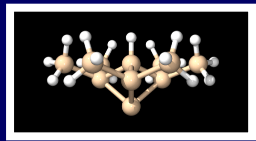
Tip B

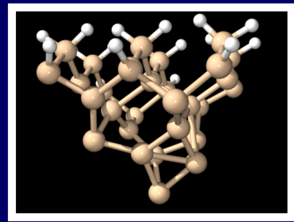




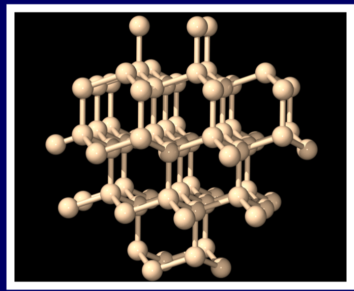


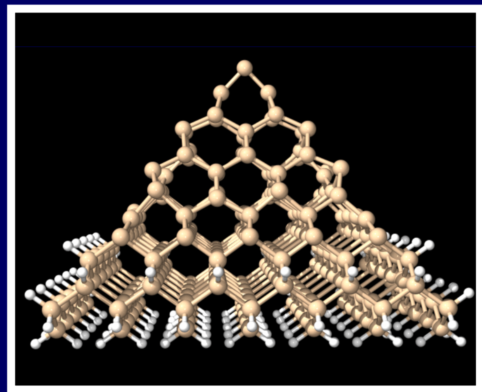
Tip apex structure: Methods & Calculations.

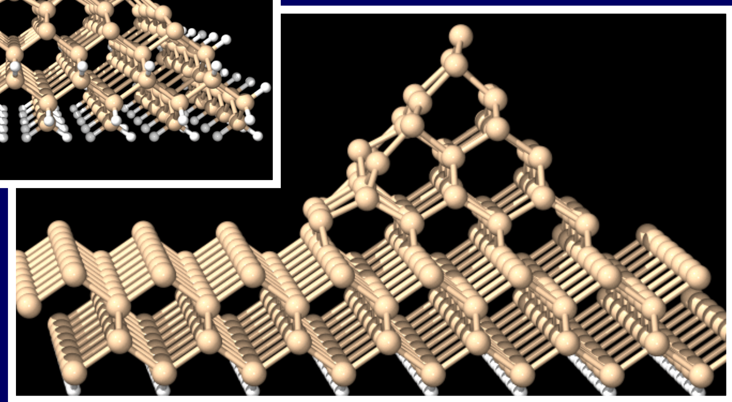




- Small tip apexes (ab-initio, < 50 atoms).
- Si cluster (ab-initio, simulated annealing, 70 atoms).
- Si Nanowire stretching (ab-initio).
- Larger tip apexes: Minima hopping method (tight binding, up to ~450 atoms):
  - Pyramid (100).
  - Surface (100) + cluster

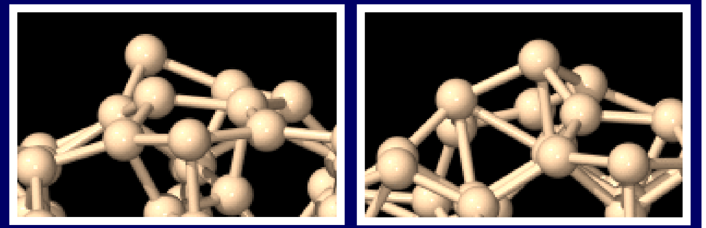


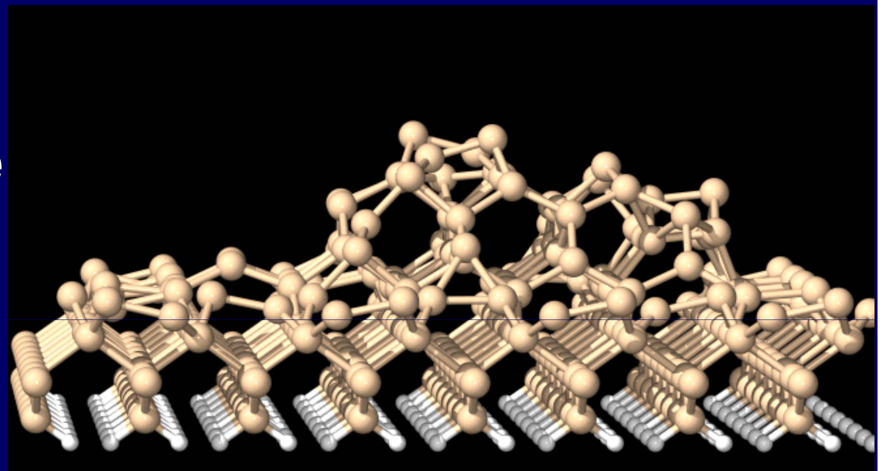




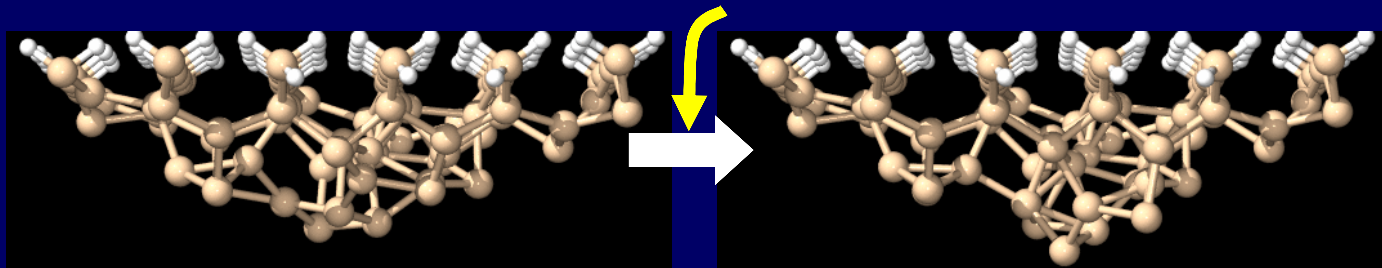
P. Pou, S.A. Ghasemi, P. Jelinek, T. Lenosky, S. Goedecker & R. P.
Nanotechnology 20, 264015 (2009)

Structure & Stability of Semicond. Tip apexes





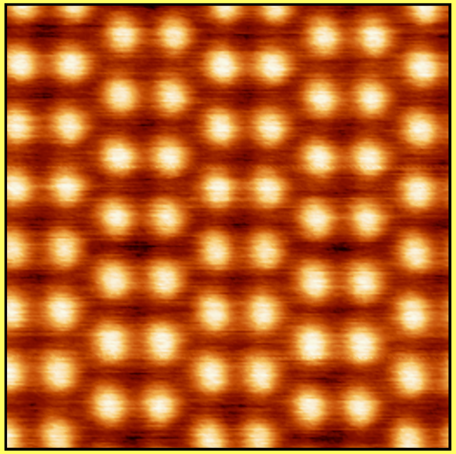
1. Structure of the outermost atoms: Tip terminations (T4, dimer) proposed in previous works are stable.
2. Last atomic layers: Both crystalline & amorphous solutions are possible
3. Sharpening. Atomically sharp tips are stable. Tip-Sample interaction helps to produce atomically sharp tips. (More work is needed.)



P. Pou, S.A. Ghasemi, P. Jelinek, T. Lenosky, S. Goedecker & R. P.
Nanotechnology 20, 264015 (2009)

Experiments in the same session

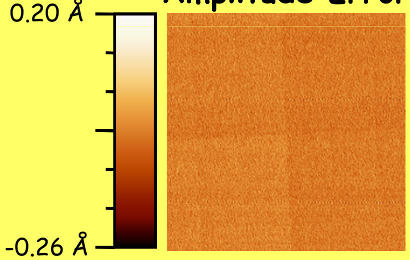
Tip A



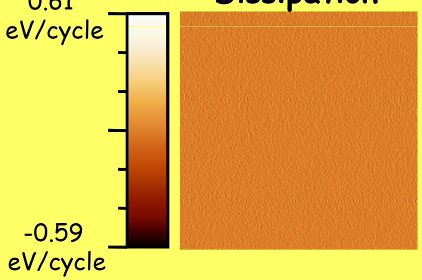
Topography

(6x6) nm^2

Amplitude Error



Dissipation



Δf =-13.4 Hz $\Rightarrow \gamma$ = -7.94 fN $\sqrt{m}$

Imaging at a Total Force value of ≈ - 1.2 nN

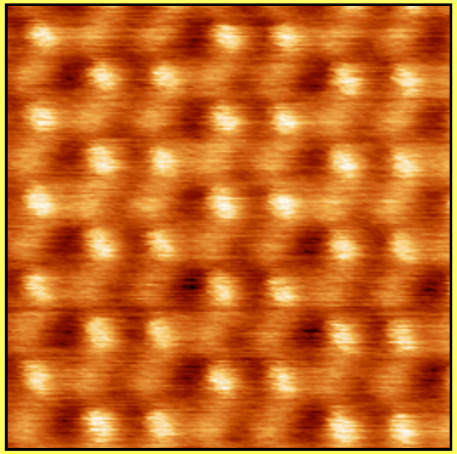
A=182 Å

Q= 259500

f_0= 183663 Hz

K = 44.3 N/m

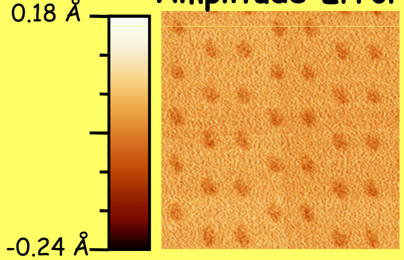
Tip B



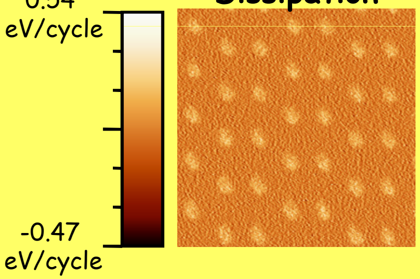
Topography

(5x5) nm^2

Amplitude Error



Dissipation



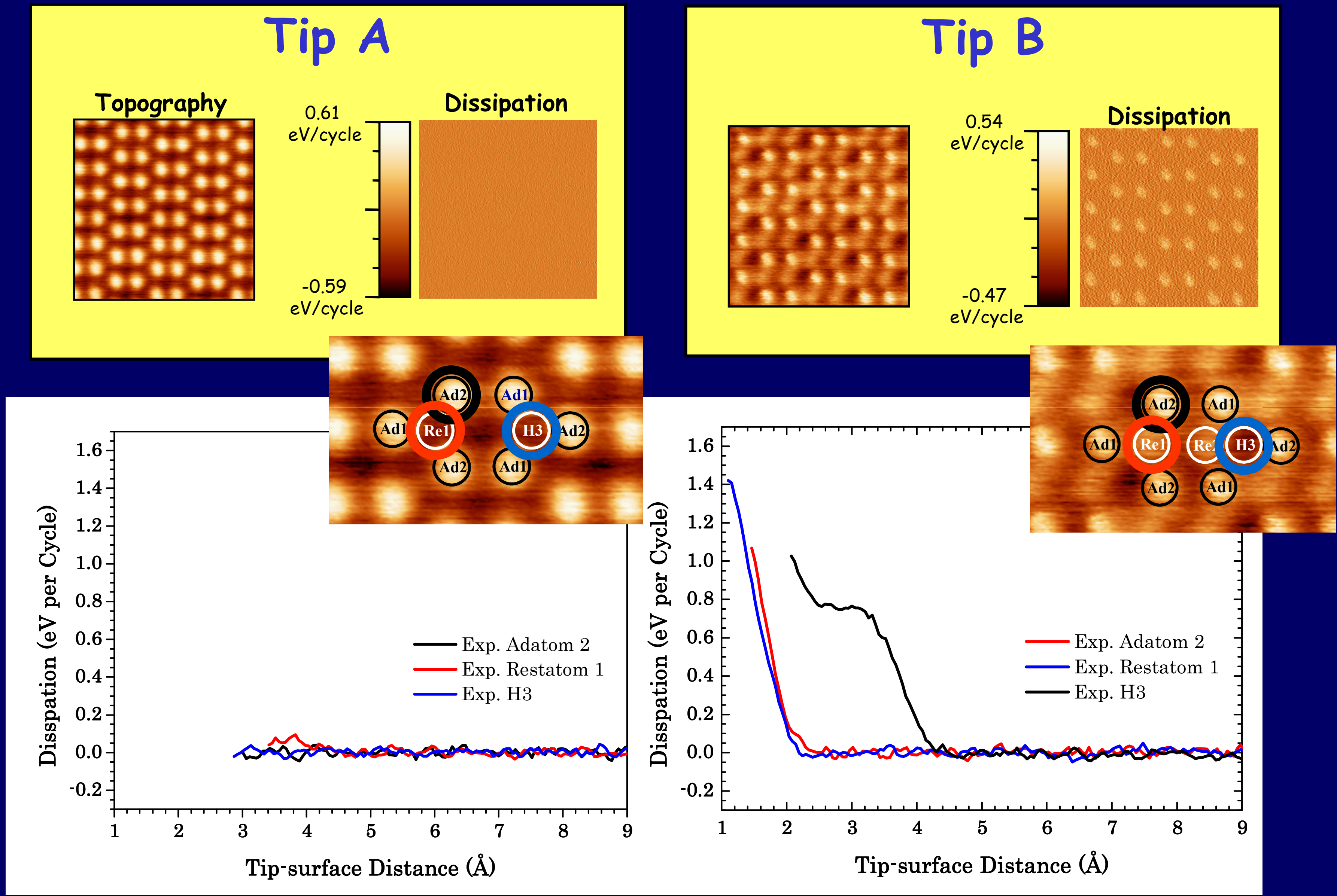
Δf =-15.5 Hz $\Rightarrow \gamma$ = -9.18 fN $\sqrt{m}$

Imaging at a Total Force value of ≈ - 1.4 nN

Slight Tip-Change

Same measurement session with the same experimental parameters !!!

Trying to explain the features in dissipation



Dissipation Mechanisms

• velocity-dependent mechanisms (fluctuation-dissipation)

$$m\ddot{z}(t)+\gamma\dot{z}(t)+kz(t)=F(\mathrm{t})$$

F(t): stochastic force

$$\gamma=\frac{1}{k_BT}\int_0^\infty\langle F(t)F(0)\rangle$$

Calculations: orders of magnitude smaller than experiment

Fluctuations of the (long-ra… …acting on charge carriers or spins

- Elect… …culated Joule dissipation.
- …um" friction (fluctuating EM fields).

…ations of the atomic positions coupled by short-range forces.

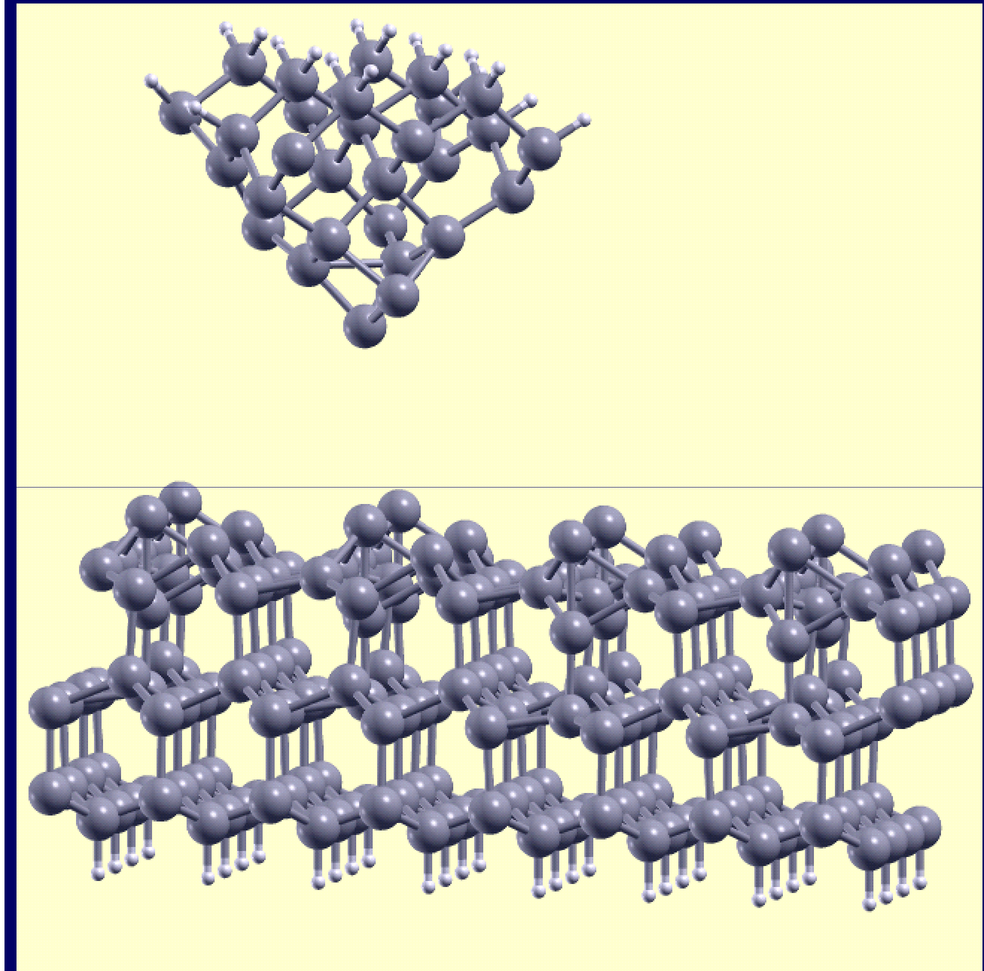
• hysteresis-related mechanisms

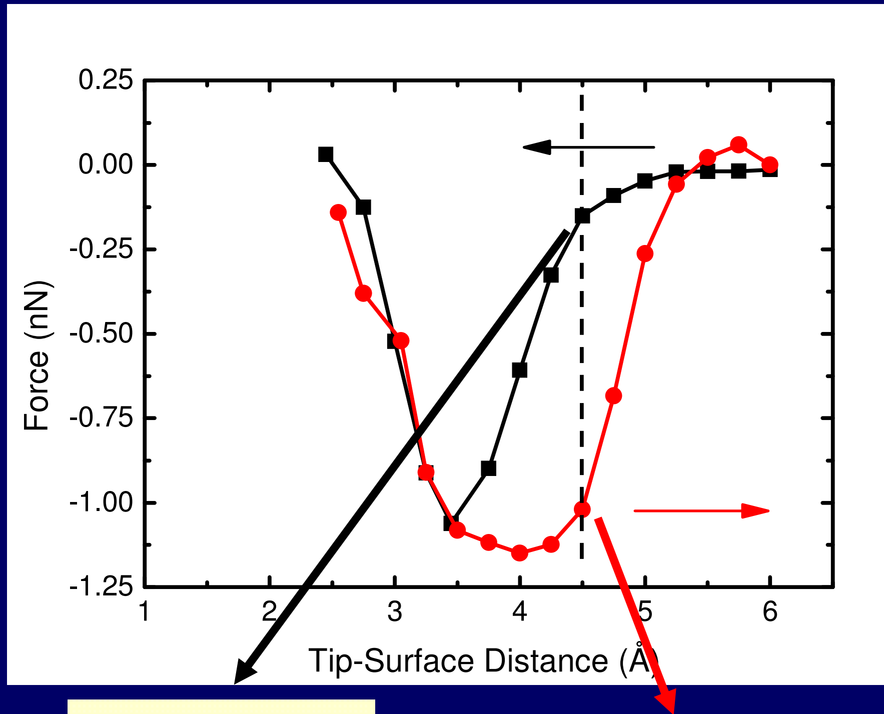
Tip-sample interaction is double-valued in a finite range of relative displacement.

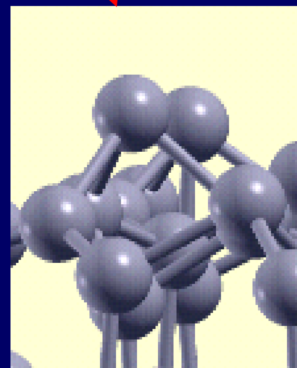
- Magnetic-field-induced hysteresis.
- Hysteresis due to adhesion.
- Hysteresis due to atomic instabilities.

L. N. Kantorovich and T. Trevethan, Phys. Rev. Lett. **93**, 236102 (2004).

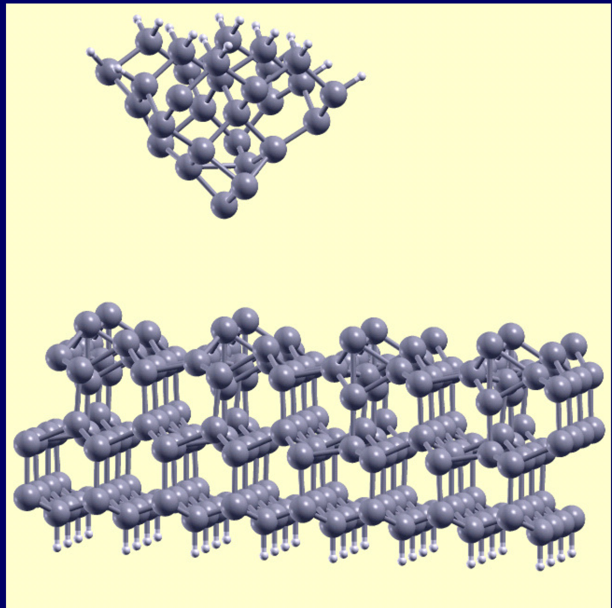
Tip B: soft mode induced by the tip-sample interaction

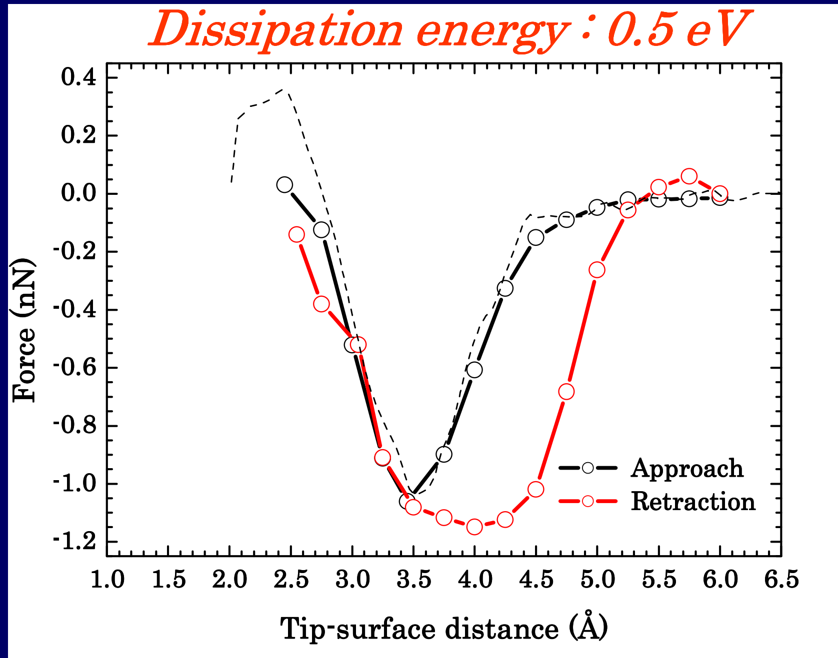


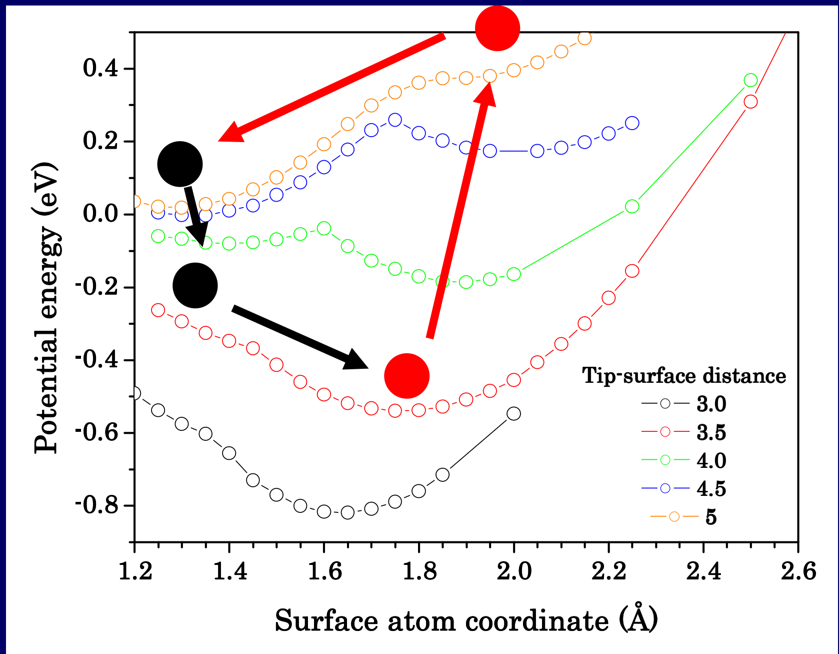


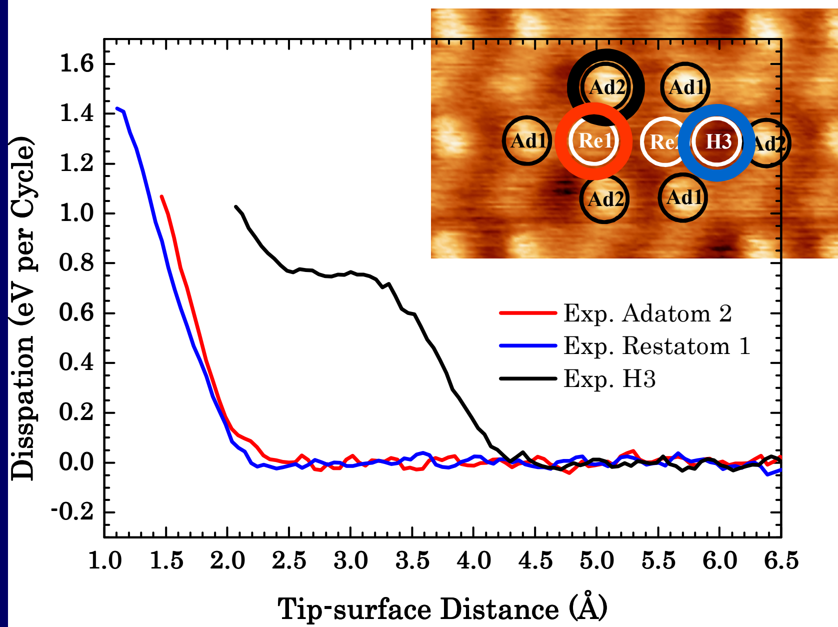


Tip B: Identification of a dissipation channel

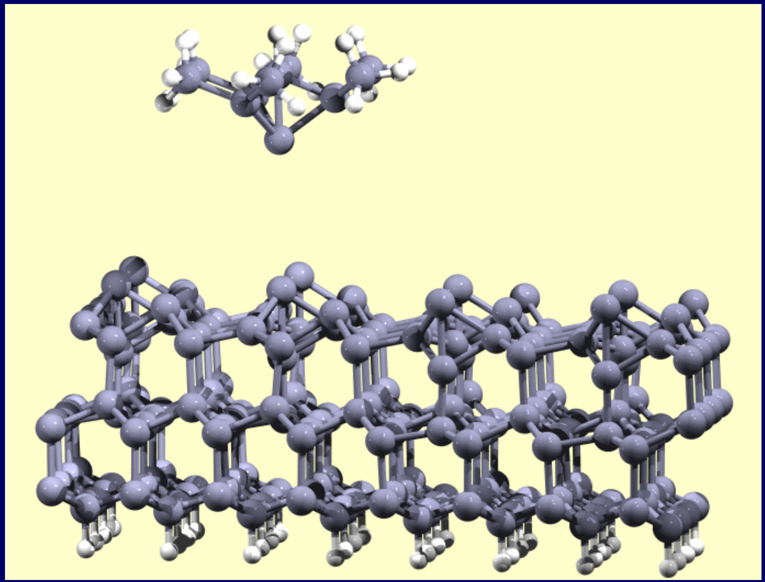


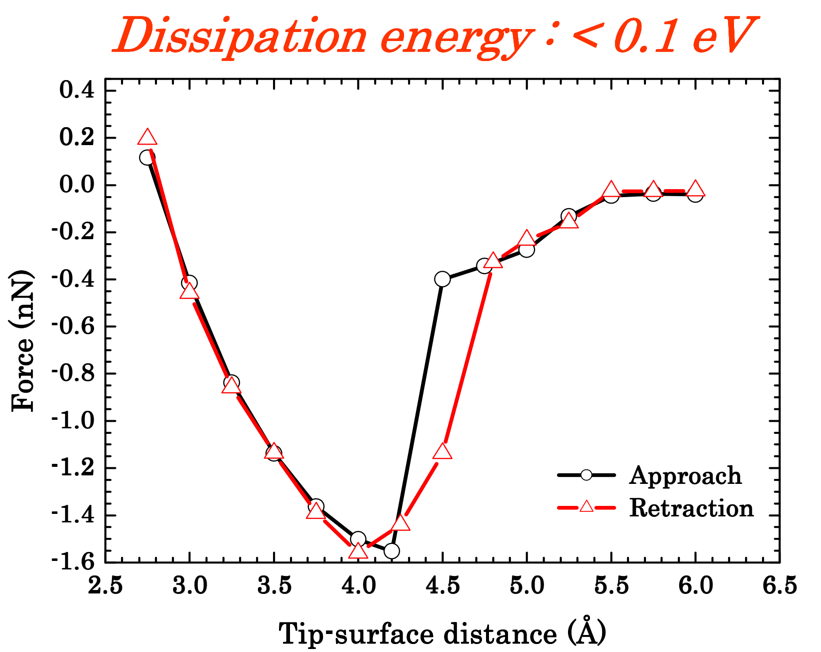


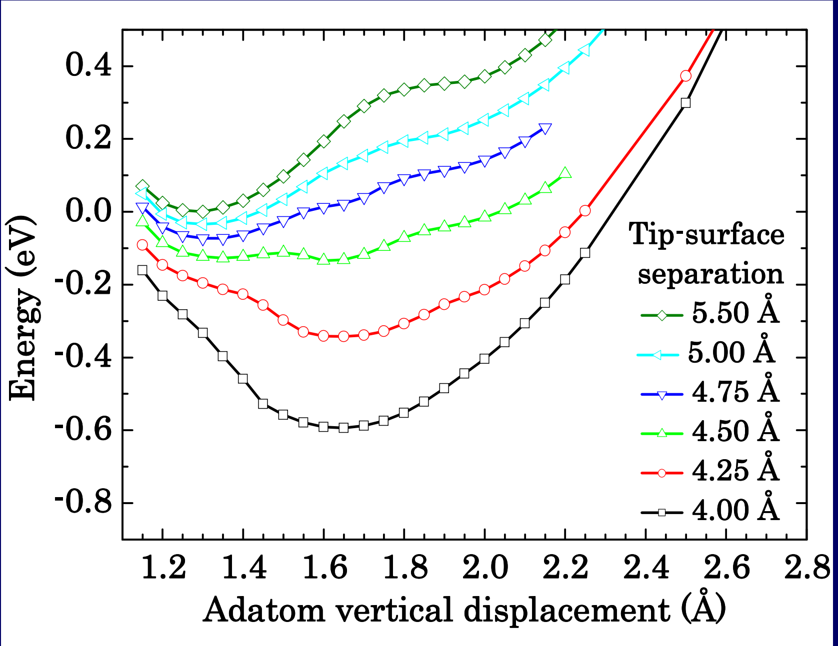


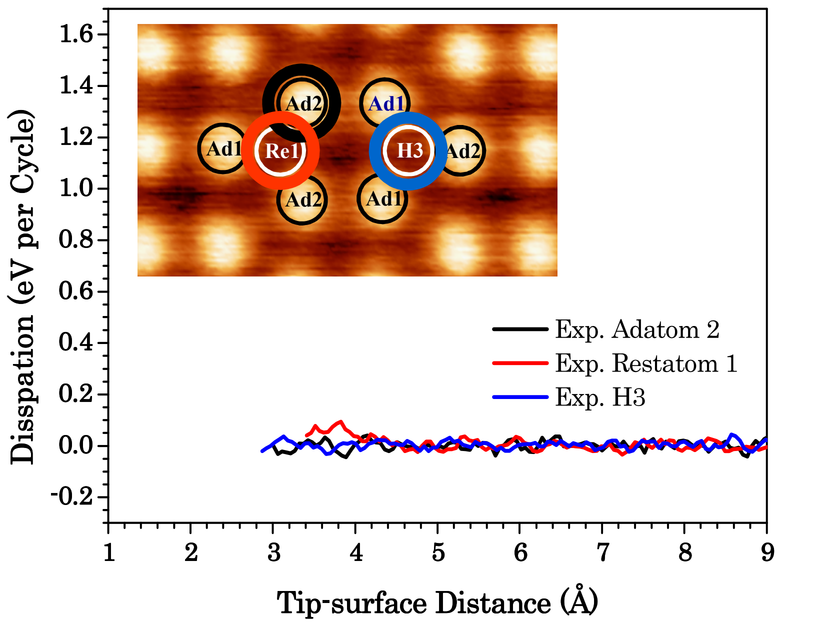


Absence of dissipation with Tip A

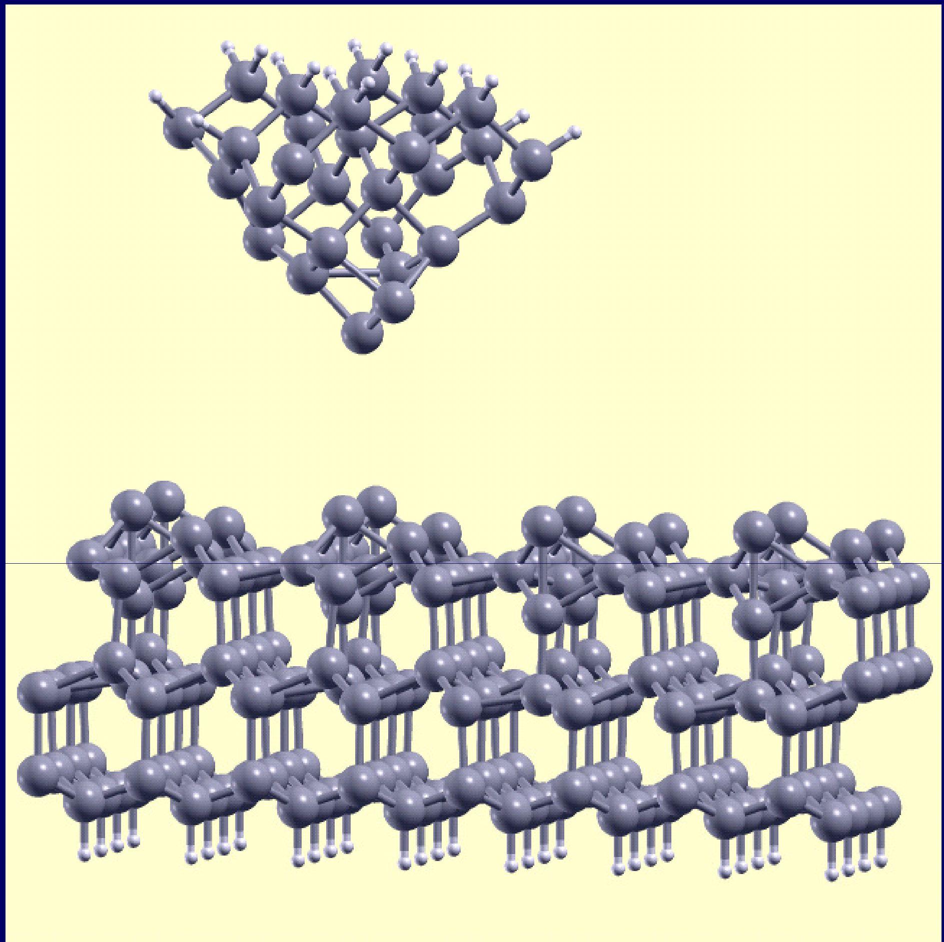


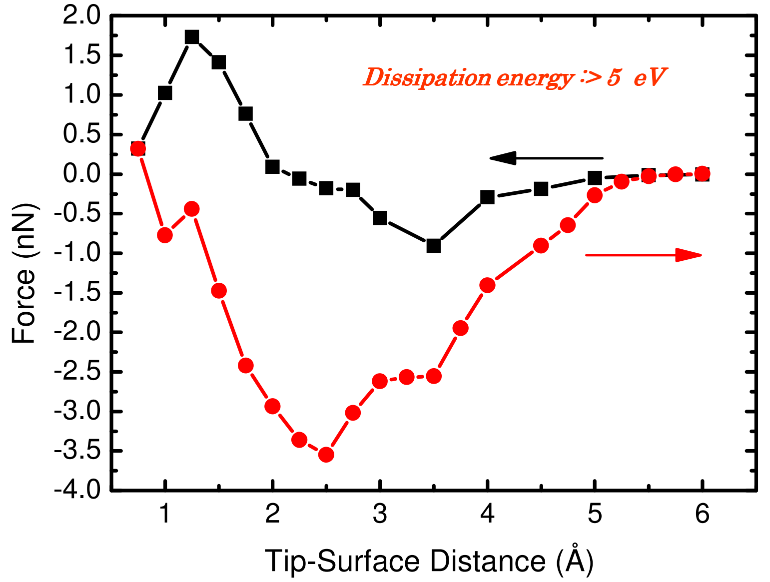


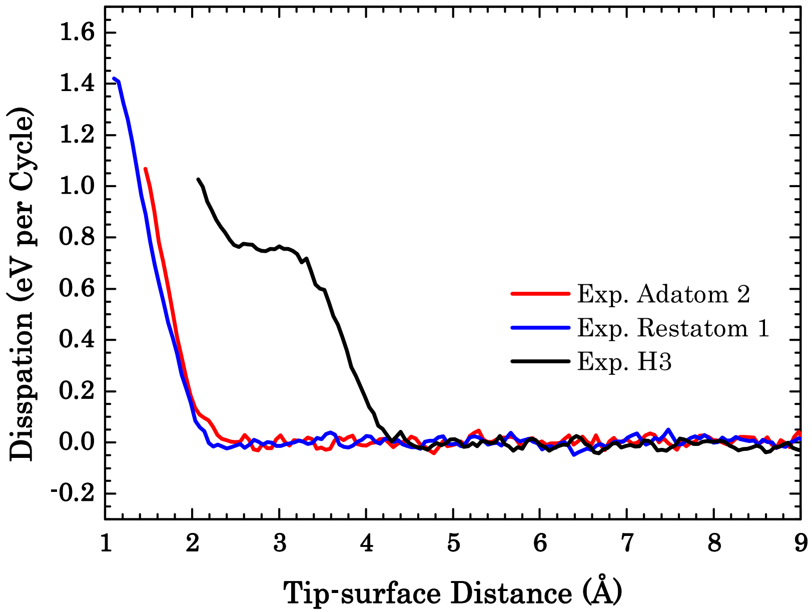


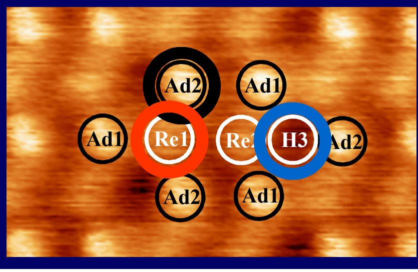


Tip B: Possible second dissipation channel



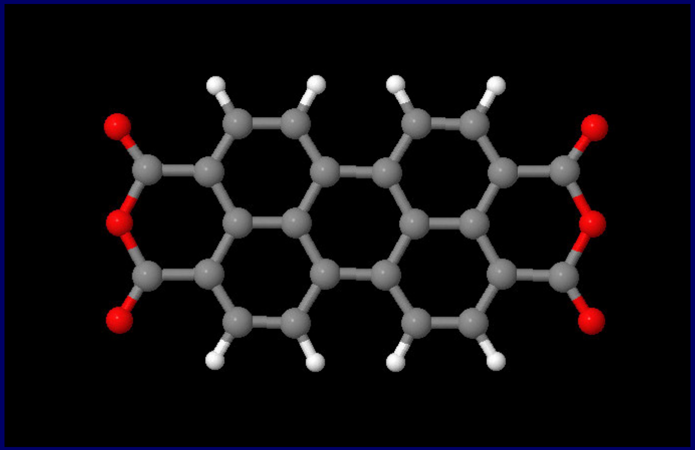






2. Submolecular resolution in FM-AFM dissipation imaging of PTCDA on Ag(111)

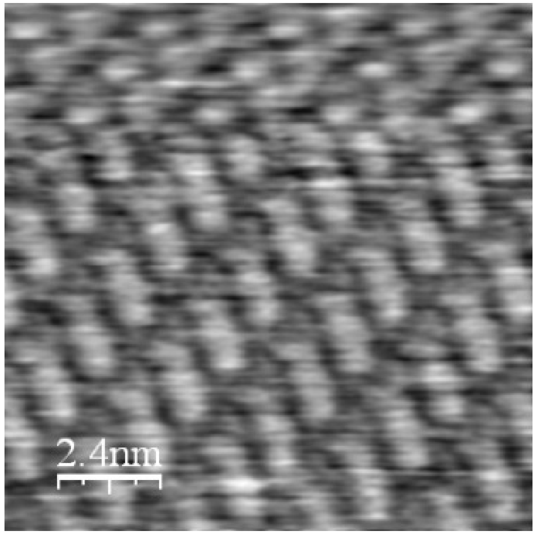
- Paradigmatic organic/inorganic interface
- Understanding the contact formation: band alingment
- Dissipation due to adhesion hysteresis: *ab initio* AFM simulations for Si tip and 1 ML PTCDA adsorbed on Ag(111).

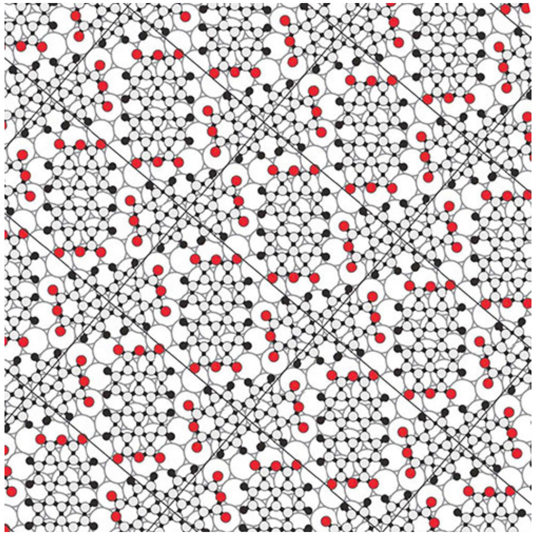


Experiments: M. Fredrich, T. Kunstmann, and R. Möller, Uni Duisburg-Essen, Germany

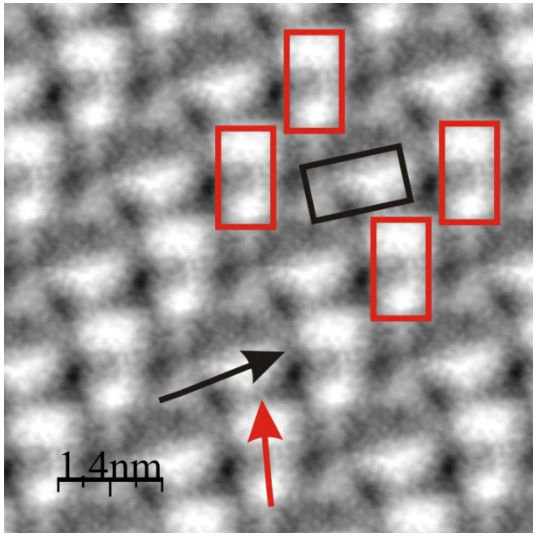
PTCDA on Ag(111): FM-AFM

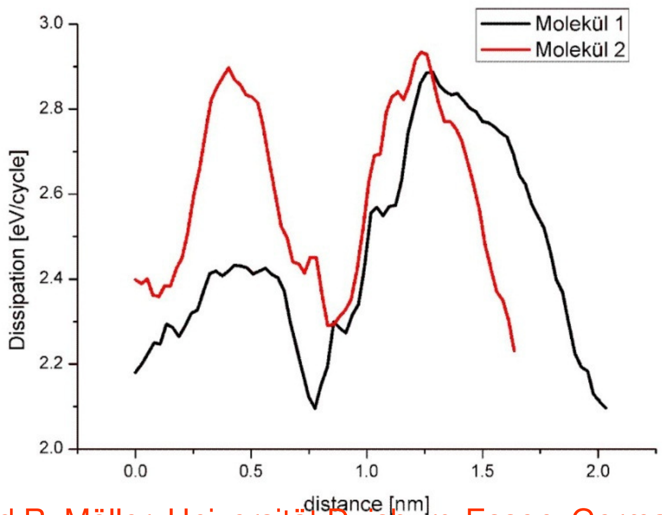
- Topography image





- Dissipation image

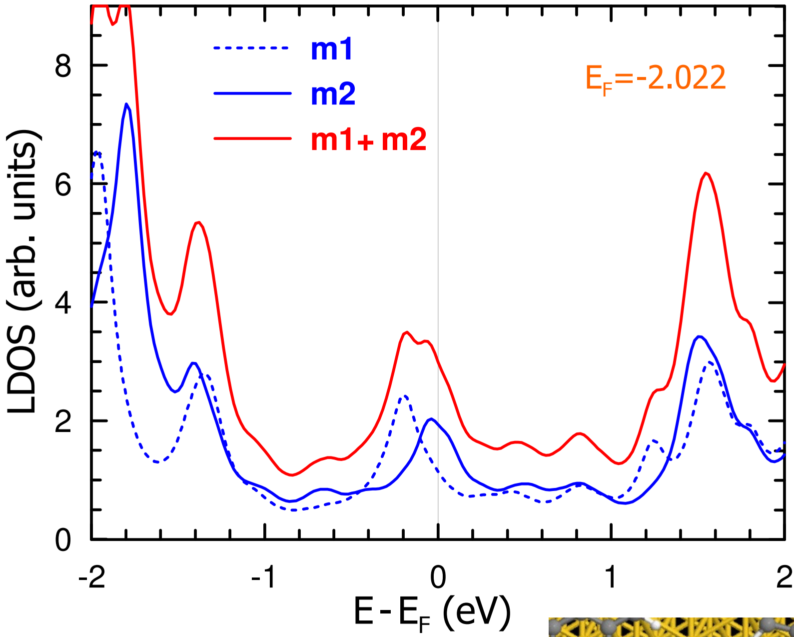


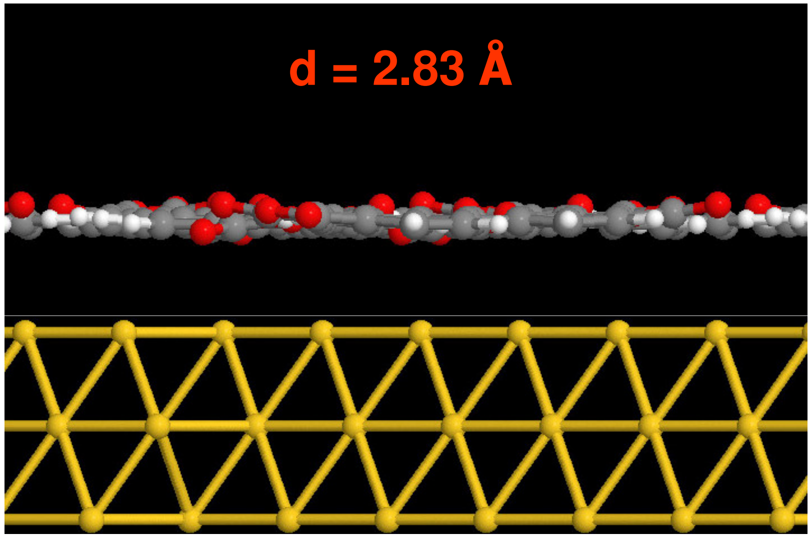


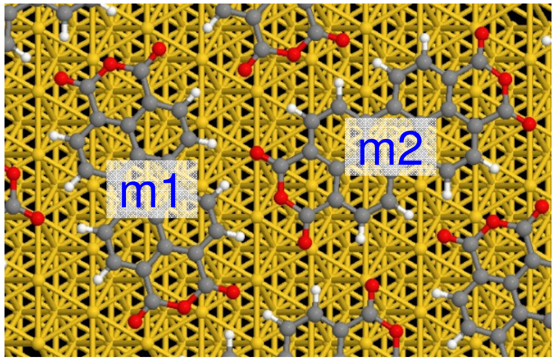
courtesy of M. Fredrich, T. Kunstmann, and R. Möller, Universität Duisburg-Essen, Germany

PTCDA on Ag(111) – fully relaxed

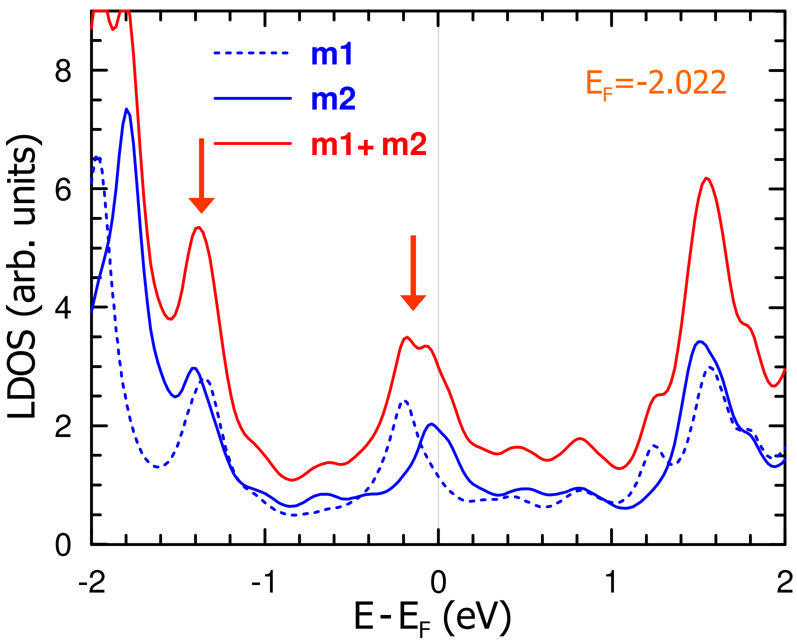
ΔE = 3.95 eV

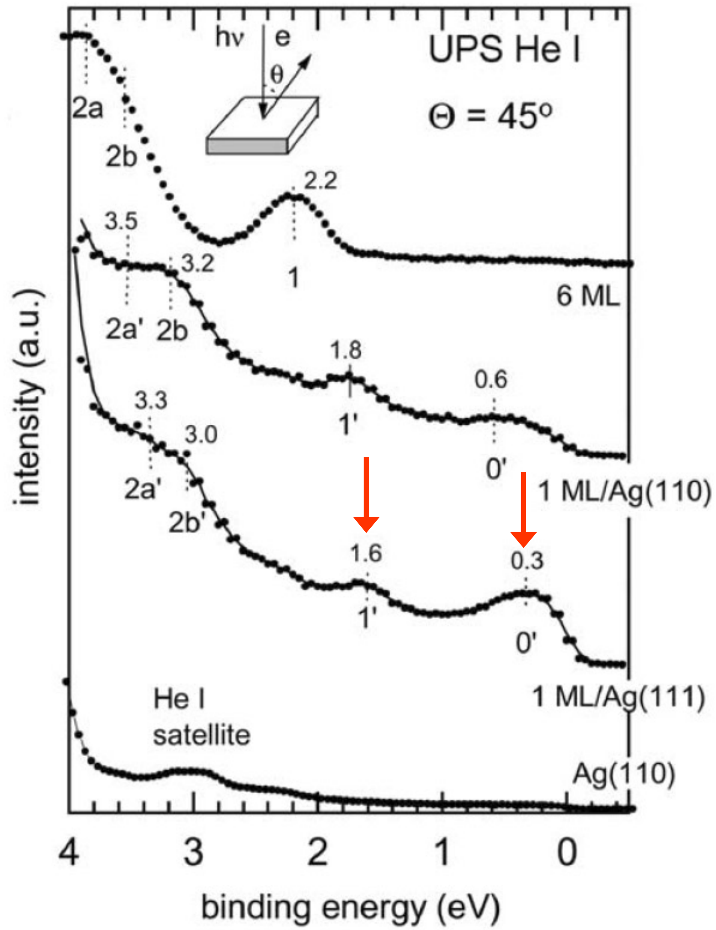






Comparison with experiment: UPS

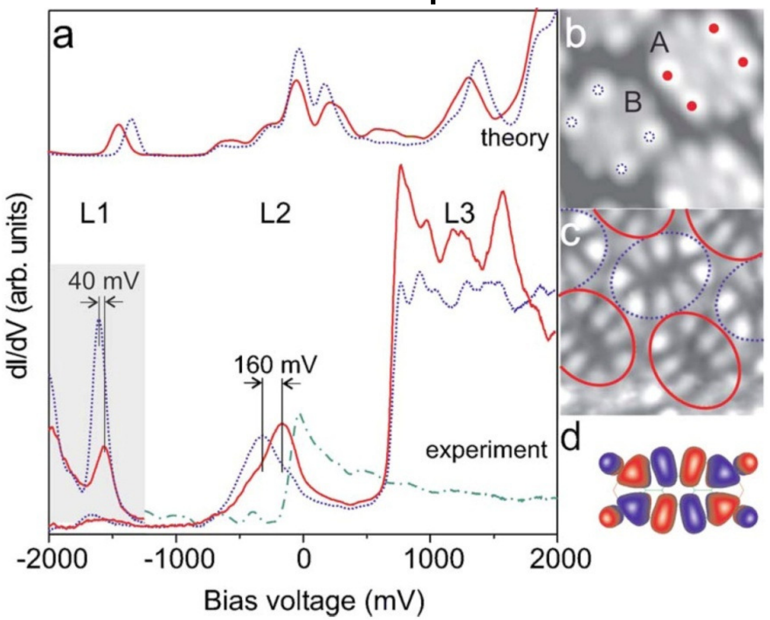




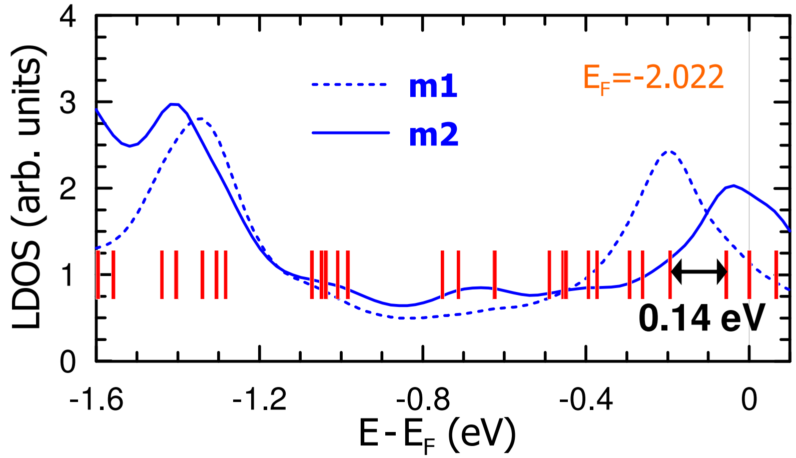
Y. Zou et al., *Surf. Sci.* **600**, 1240 (2006)

Comparison with experiment: STS

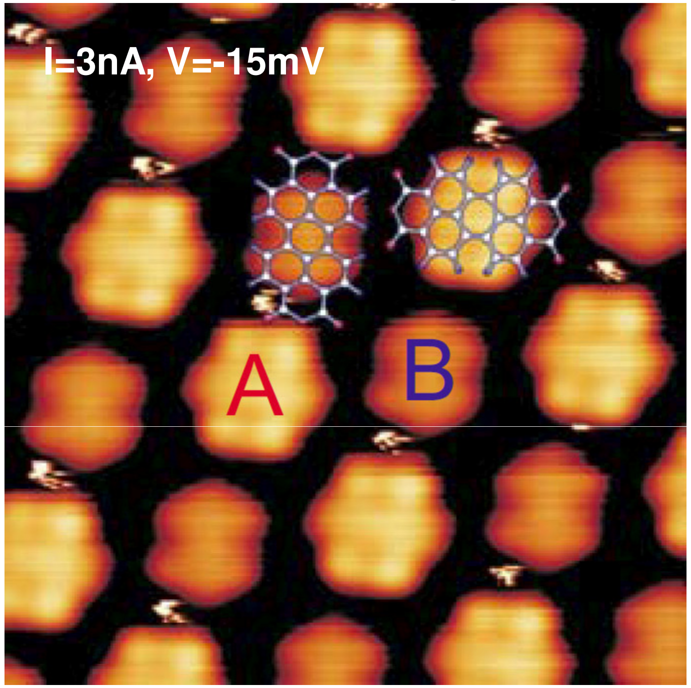
- STS spectra



A. Kraft et al., *Phys. Rev.* B **74**, 041402(R) (2006)



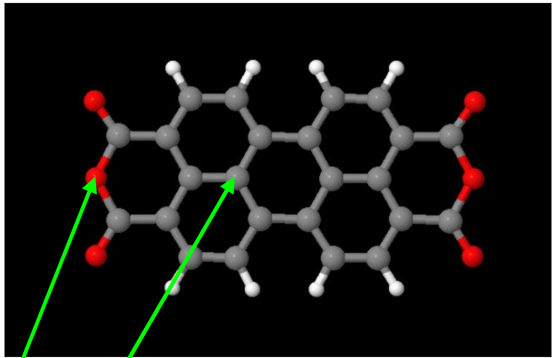
- STM image

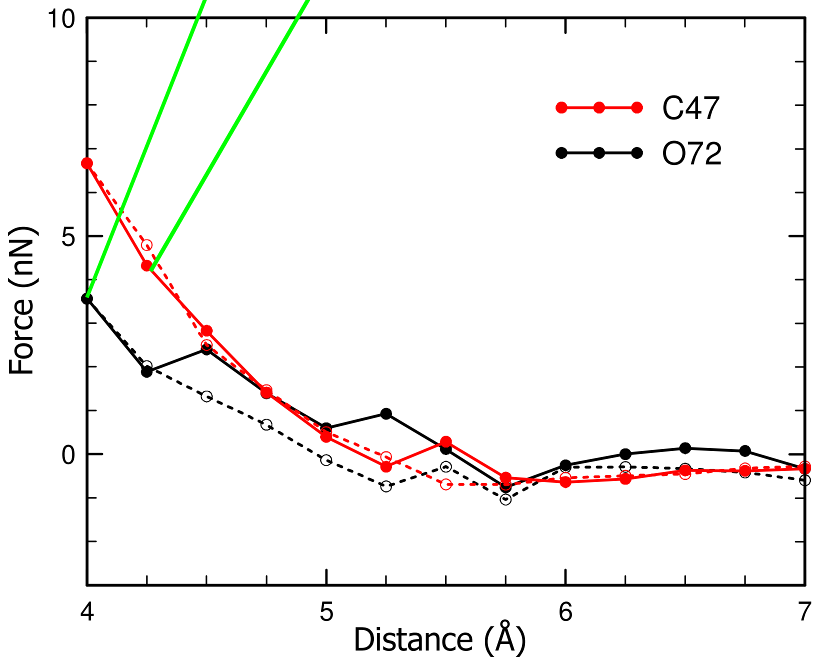


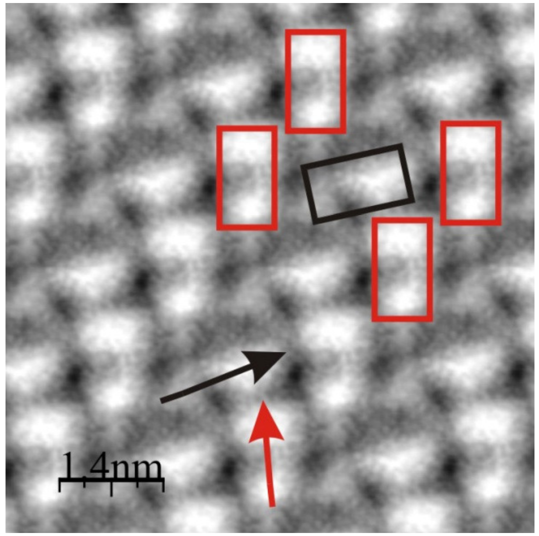
R. Temirov and F.S. Tautz (2006)

Force distance curve for two different positions

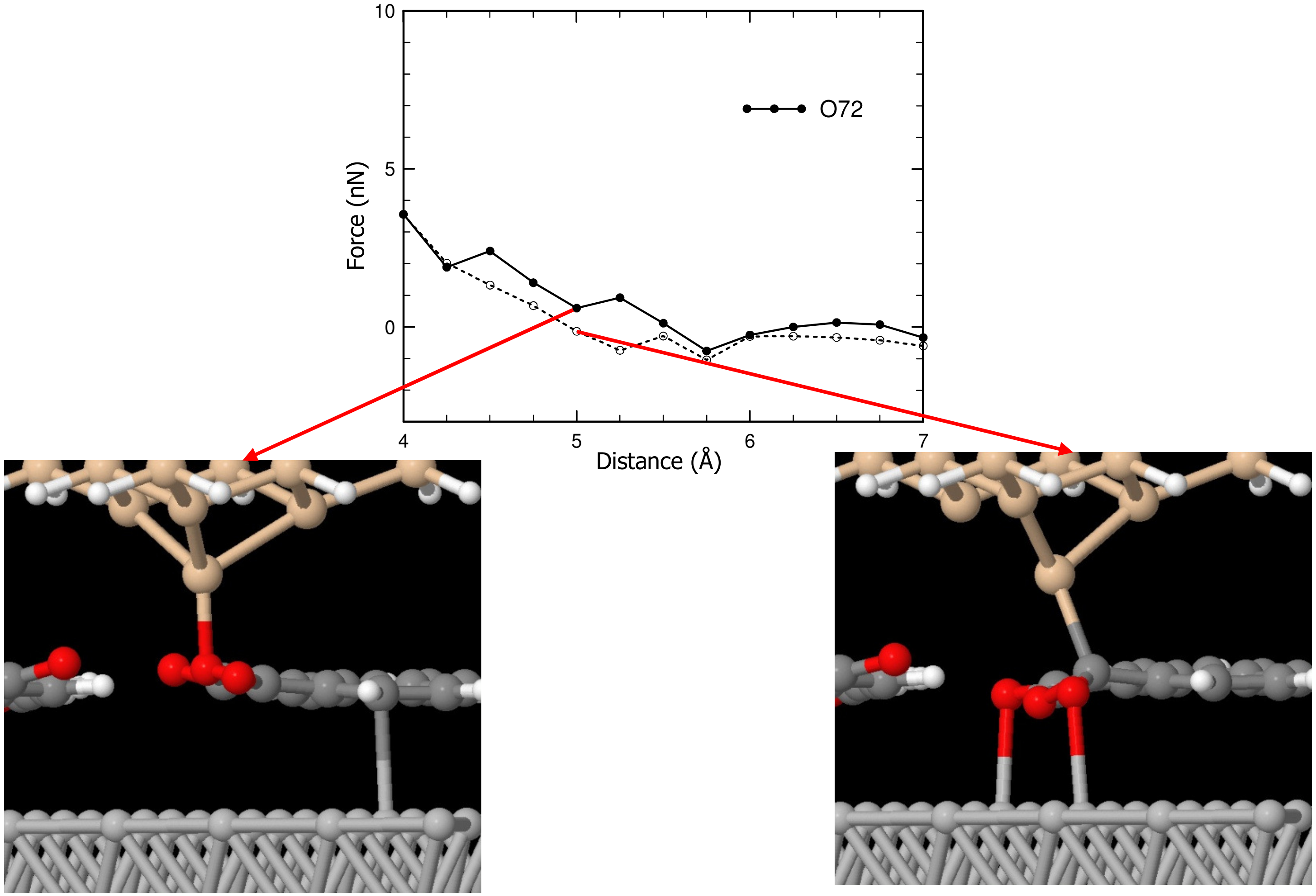
- PTCDA…







Dissipation due to adhesion hysteresis



3. Molecular scale energy dissipation in oligothiophene monolayers measured by dynamic force microscopy

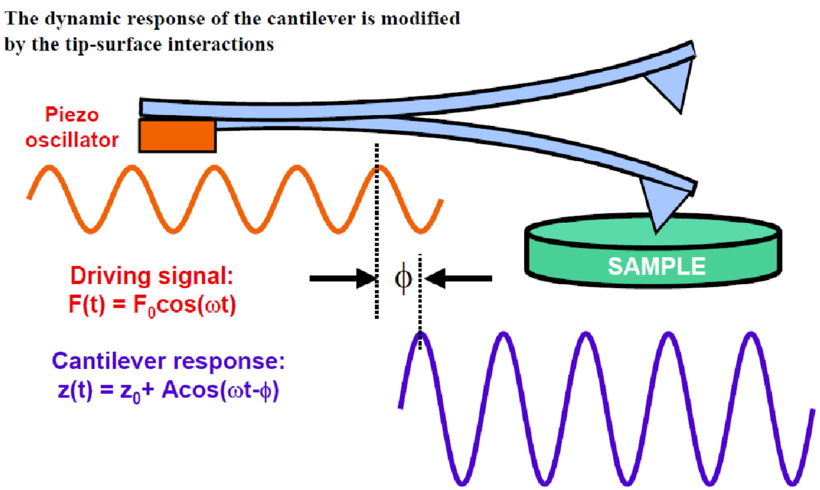
Experiments:

- Instituto de Microelectrónica de Madrid, CNM - CSIC, Spain:
  Nicolás F. Martínez, Carlos J. Gómez, Ricardo García,
- Istituto per lo Studio dei Materiali Nanostrutturatti, CNR, Bologna, Italy:
  Cristiano Albonetti, Fabio Biscarini

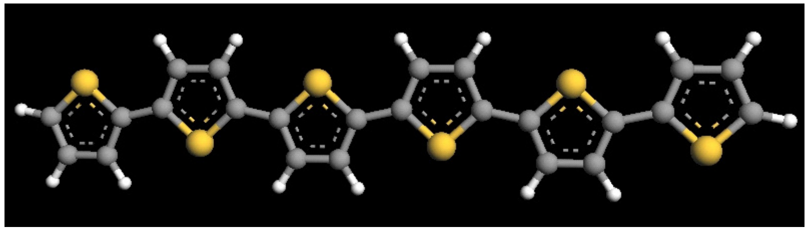
N.F. Martinez et al, Nanotechnology 20, 434021 (2009)
(special issue to mark the 20th Volume)

Motivation

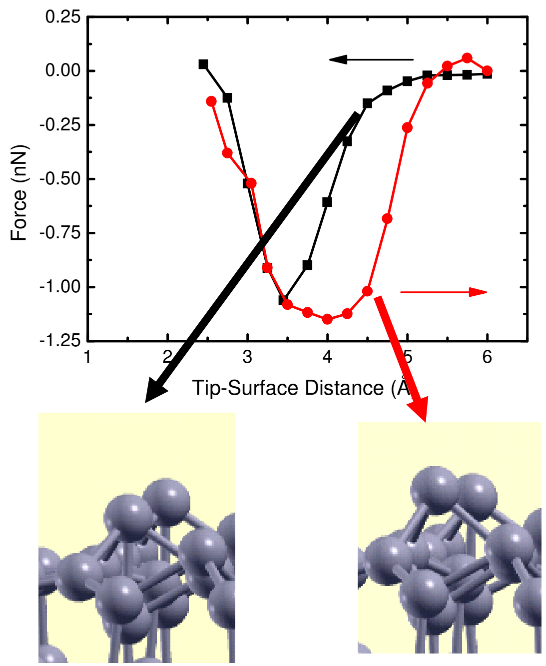
- Phase shift – energy dissipation



- Sexithiophene (T6) molecules – one of the most promising building blocks in plastic electronics.

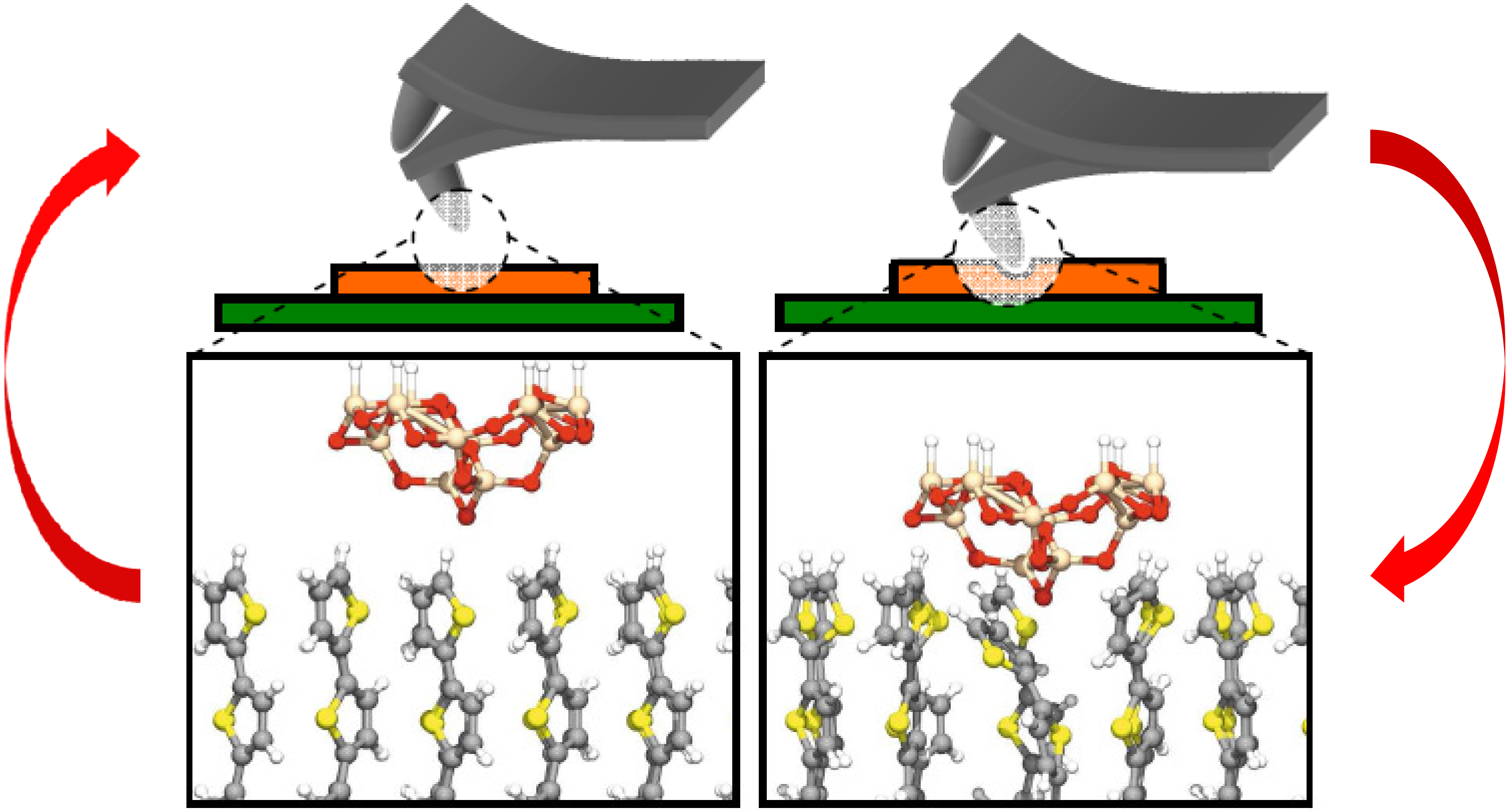


- Soft mode induced by the tip-sample interaction in FM-AFM on Ge(111)-c(2×8) – dissipation channel is related with the adhesion properties of a single atomic contact.



N. Oyabu et al., *Phys. Rev. Lett.* **96**, 106101 (2006)

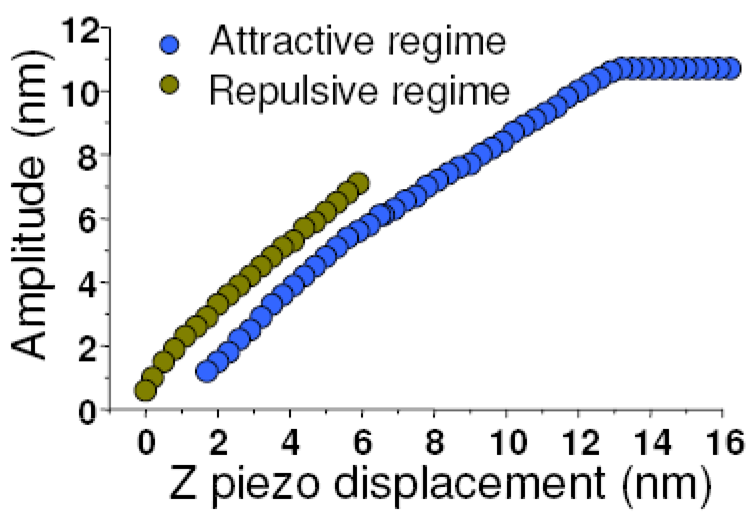
Multi-scale approach: Contact between experiments and first-priciples simulations

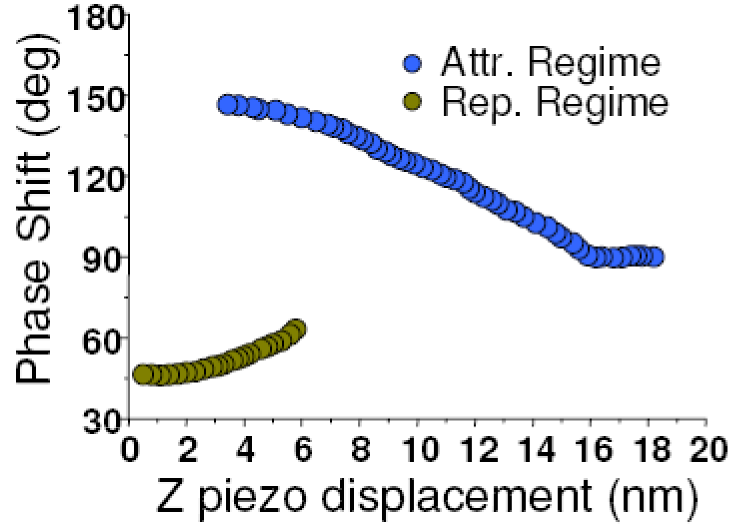


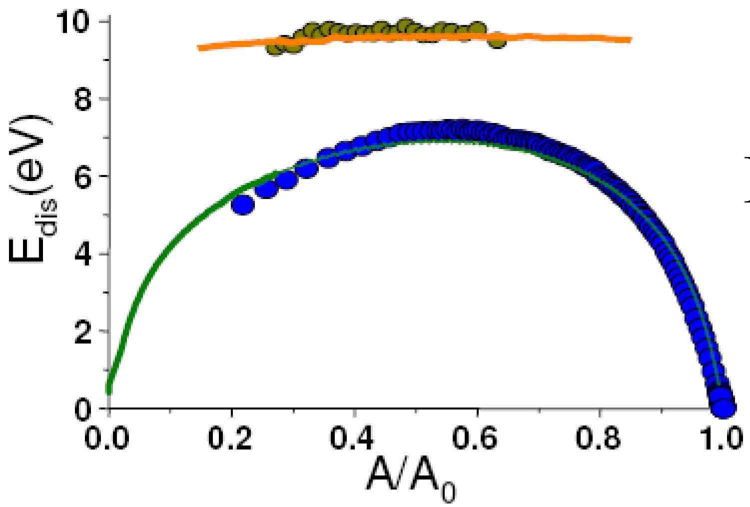
Dynamical Simulations based on continuum mechanics models:

- DMT (contact) + long-range attractive interactions (vdW-like)
- hysteresis: different strength (α, γ) for approach/retraction

Experiments (RT): Dynamic dissipation curves

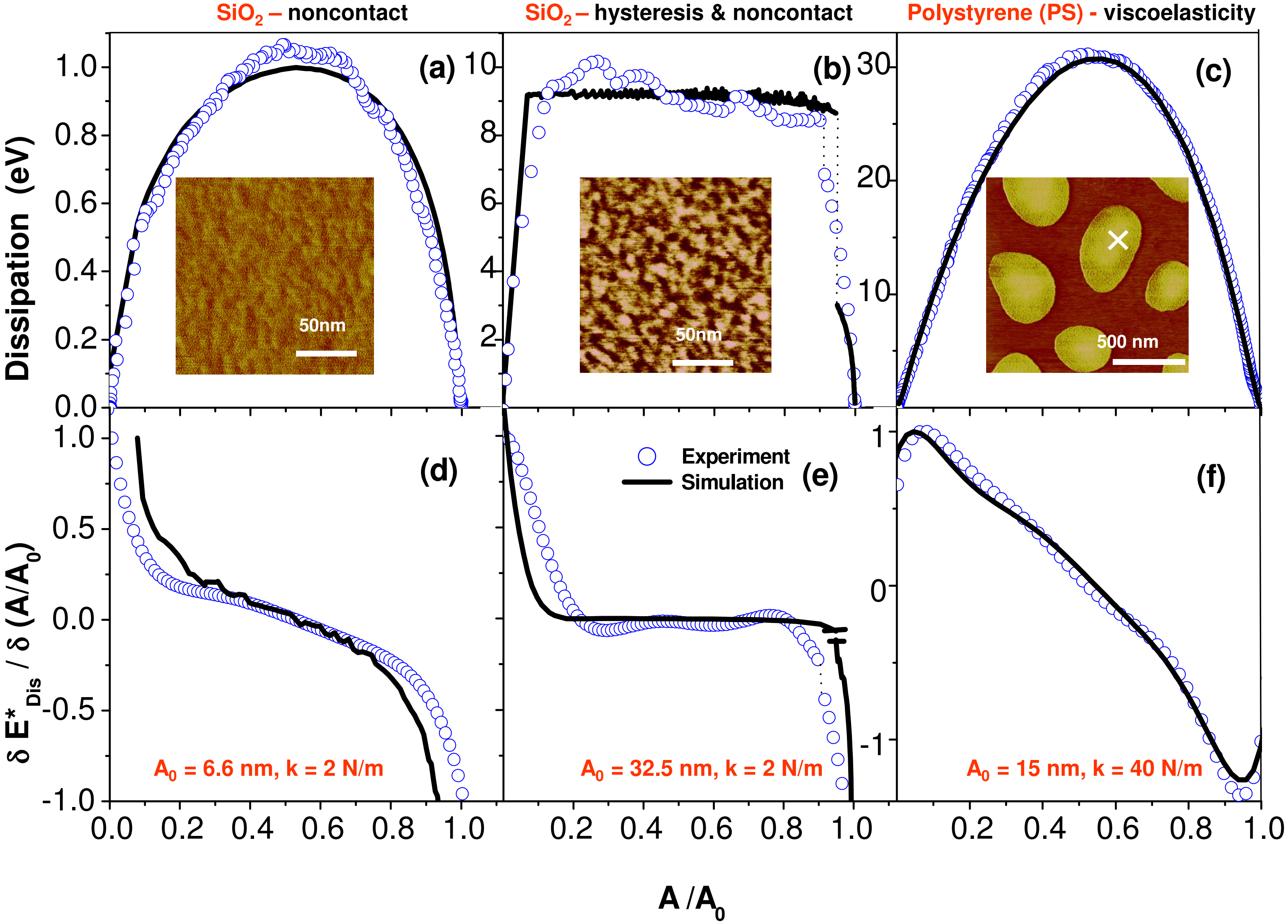






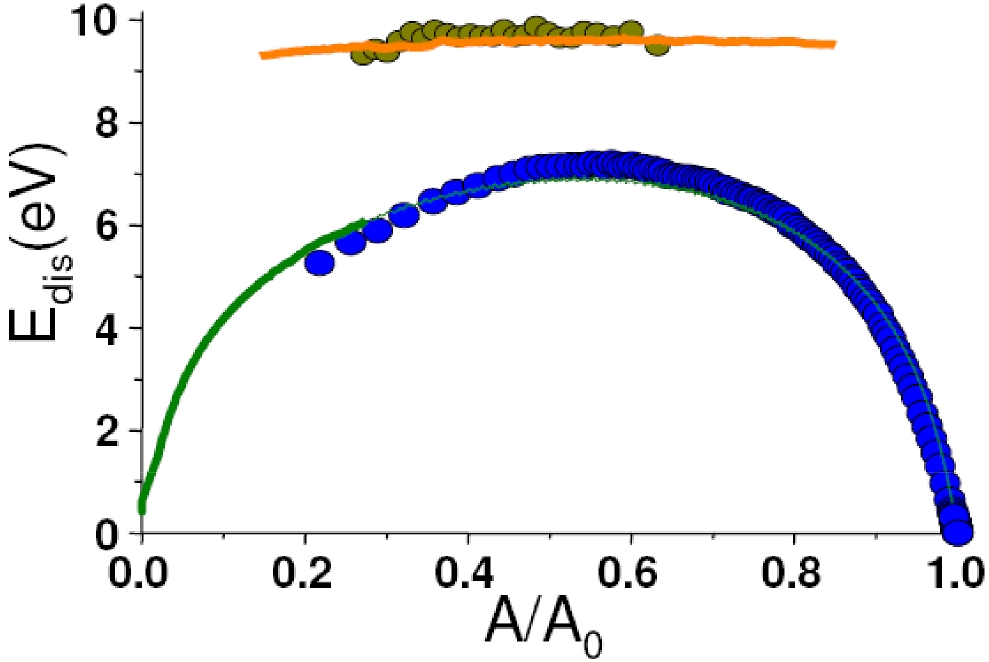
$$E_{dis} = \left(\sin\varphi - \frac{A}{A_0}\right)\frac{A}{A_0}\frac{\pi k A_0^2}{Q}$$

Identification of dissipation processes



R. García et al., *Phys. Rev. Lett.* **97**, 016103 (2006)

Experiments & simulations: DMT (contact) + vdW (LR)



$$F_{\rm DMT} = Y^* R^{1/2} \delta^{3/2} - 4\pi R \gamma,$$

$$F_i = -\frac{\alpha(t)}{d^2}$$

indentation 2 Å ⇒ E_{dis} ≈ 2.5 eV

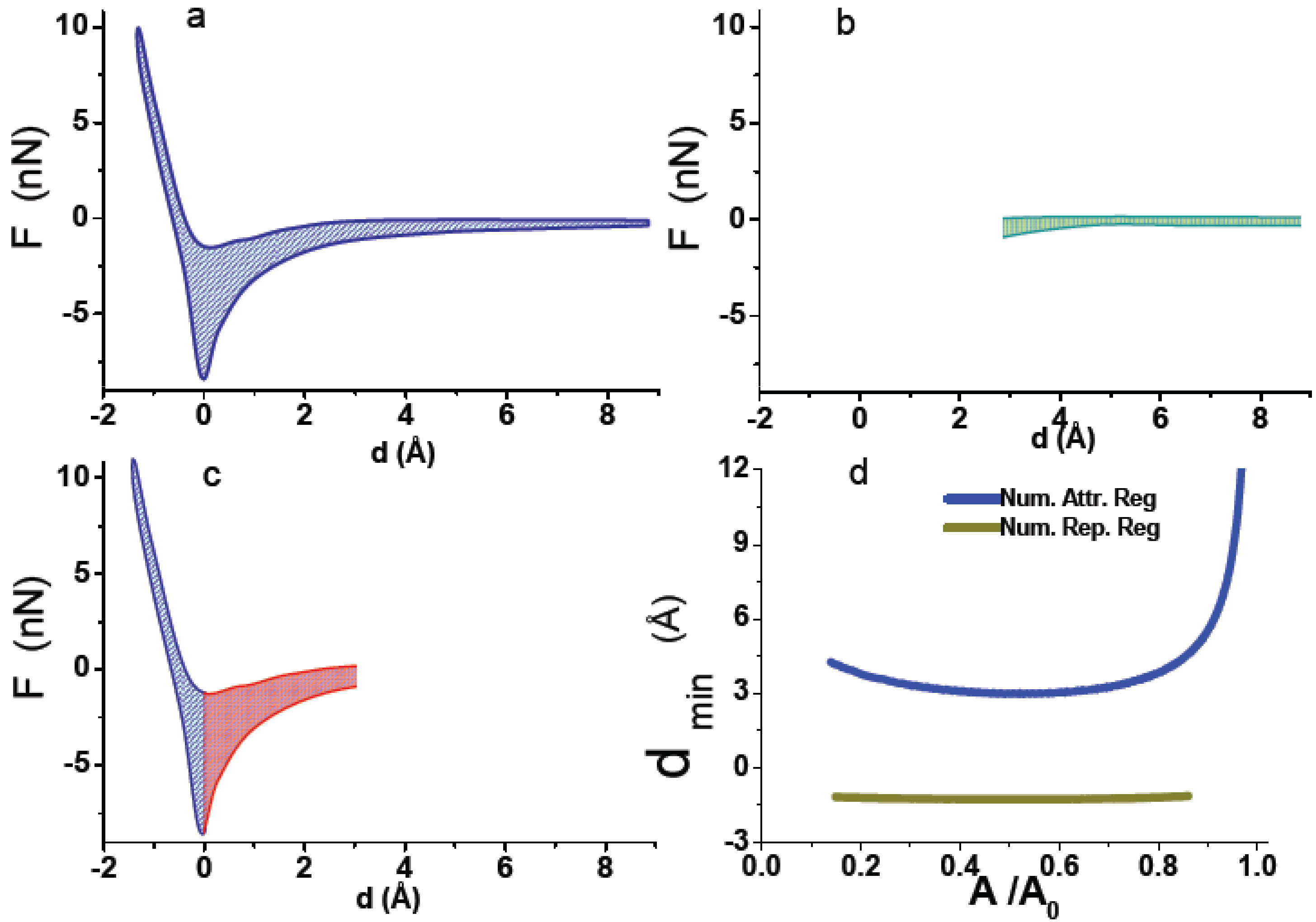
R = 7 nm, Y *= 60 GPa (T6) (Si: 170 GPa)

$\alpha_a = 7 \text{x} 10^{-28}$ Jm, $\gamma_a = 50$ mJ/m^2

$\alpha_r = 3\ \alpha_a$, $\gamma_r = 57$ mJ/m^2

Fitted to a single point
(A_i , ϕ_i)

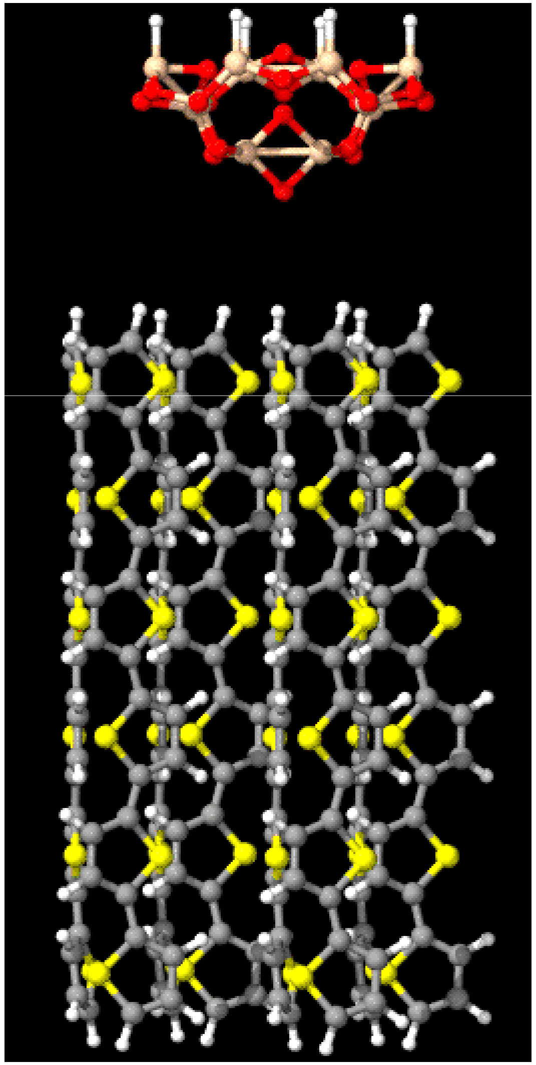
Extracting the short-range dissipation….



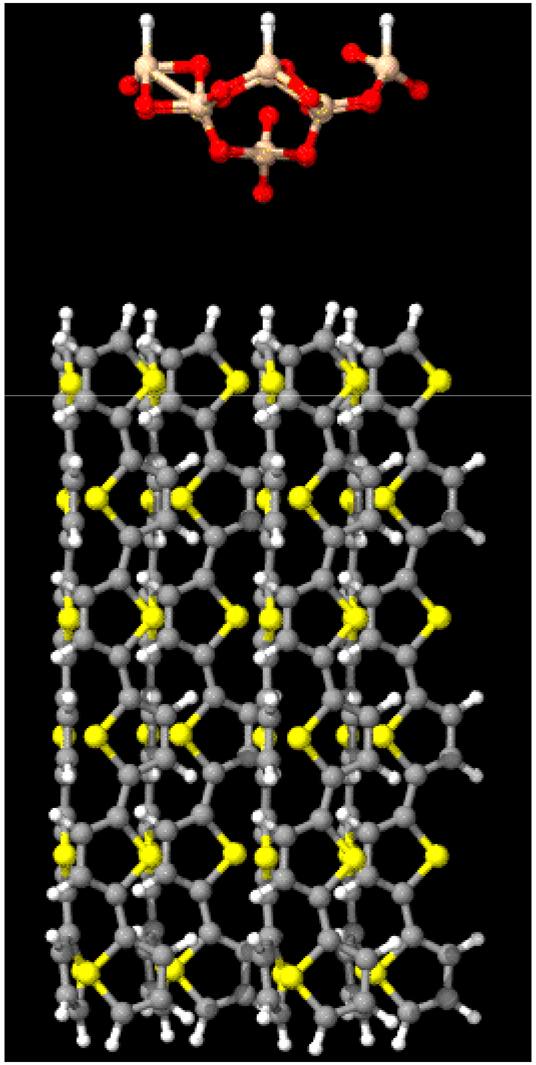
Short-range energy dissipation ~ 1.4 eV !!!

Si Oxide tip on T6: first-principles simulations

- S rotate

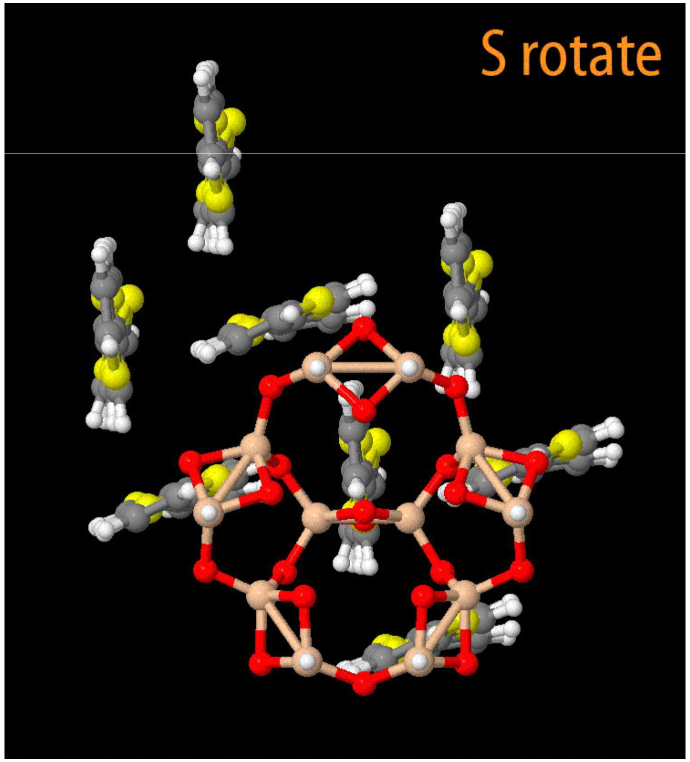


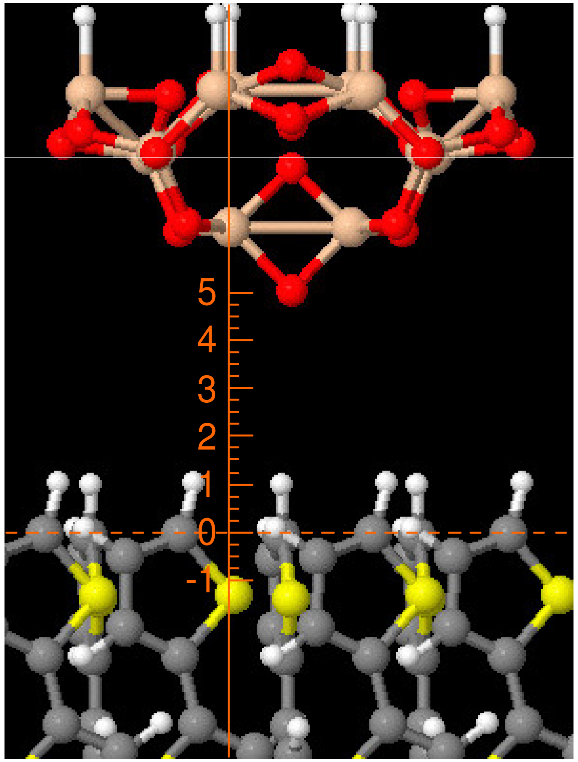
- C position



Different positions of the tip and lengths of simulations

- Five different positions of the Si-O tip: S rotate, S, H, C and hollow
- Three different distances of approaching the tip towards the surface:
  short: 5 Å → 2 Å → 5 Å middle: 5 Å → 0 Å → 5 Å long: 5 Å → -1 Å → 5 Å

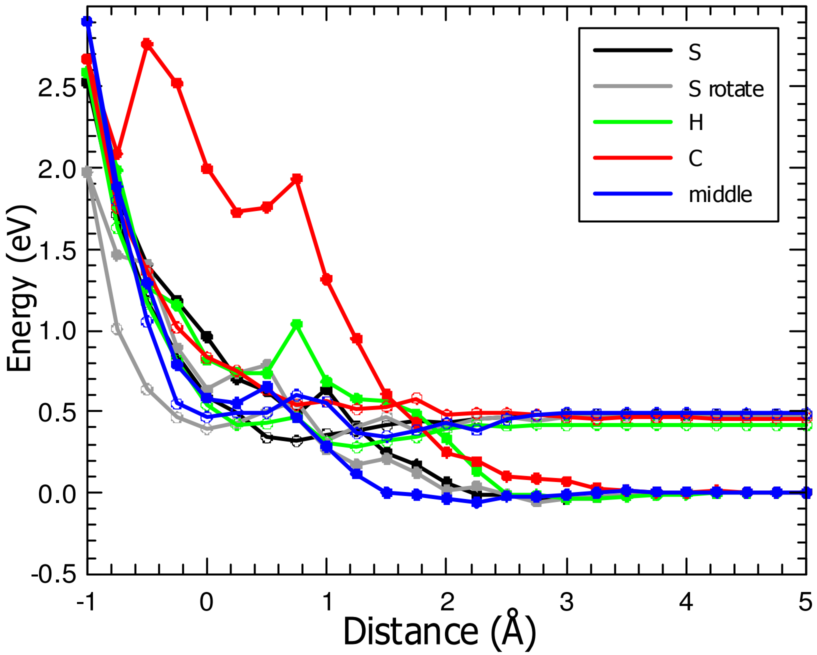




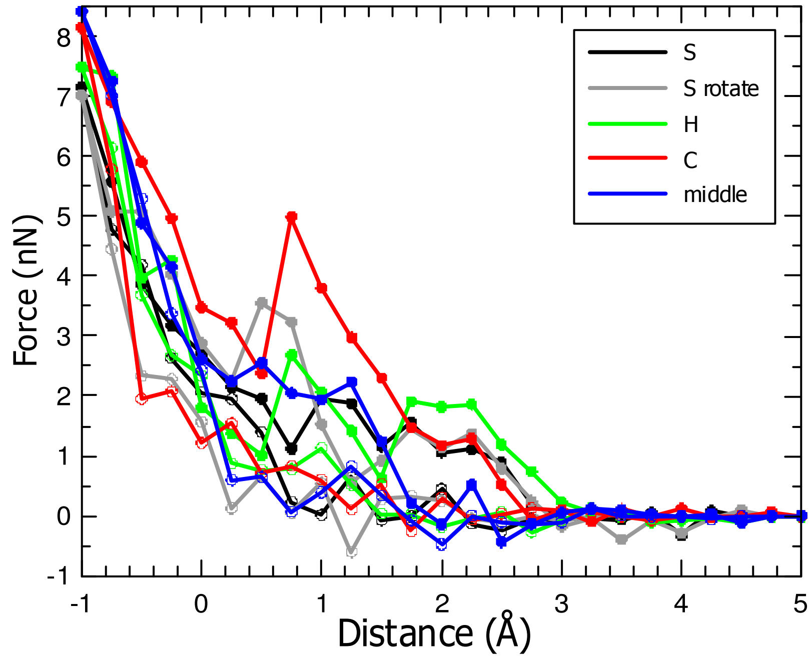
Long simulation: approach & retraction of the tip

- approach: 5 Å → -1 Å ●——●——●
- retraction: -1 Å → 5 Å ⊙-----⊙-----⊙

- Energy vs. distance



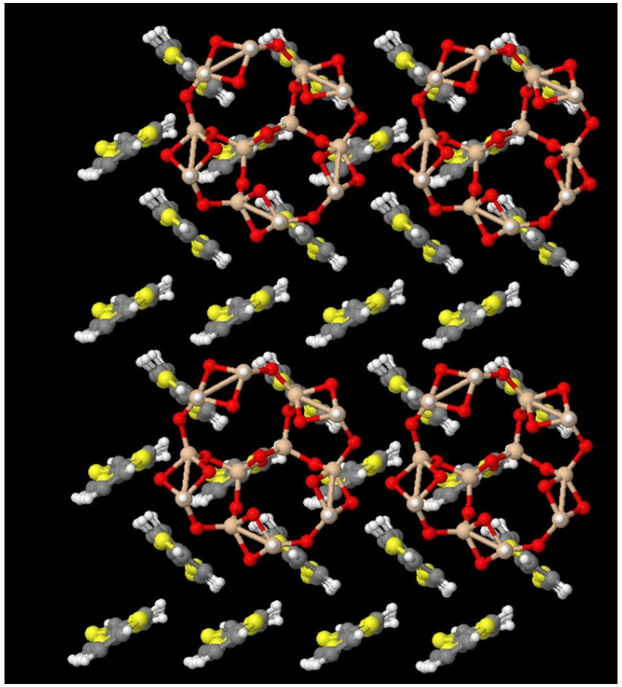
- Force vs. distance



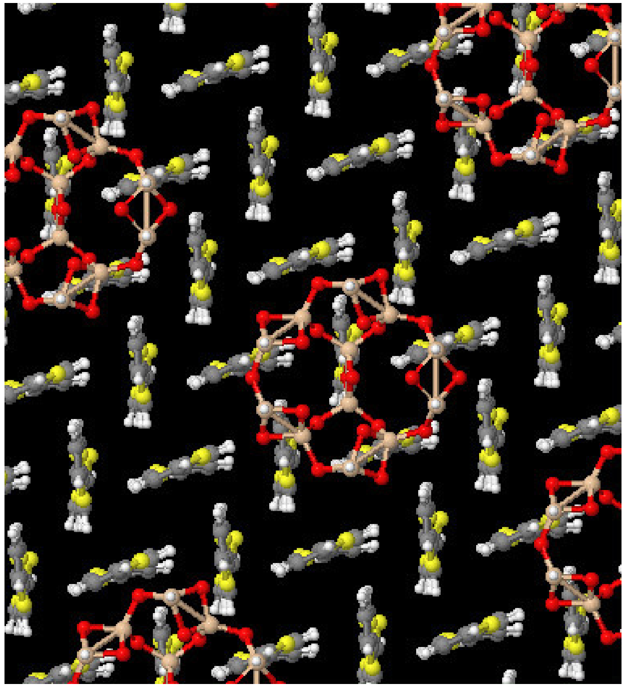
Limitations of our 4×2 quasi-static simulations?

- Spureous confinement due to the supercell approach?

4×2



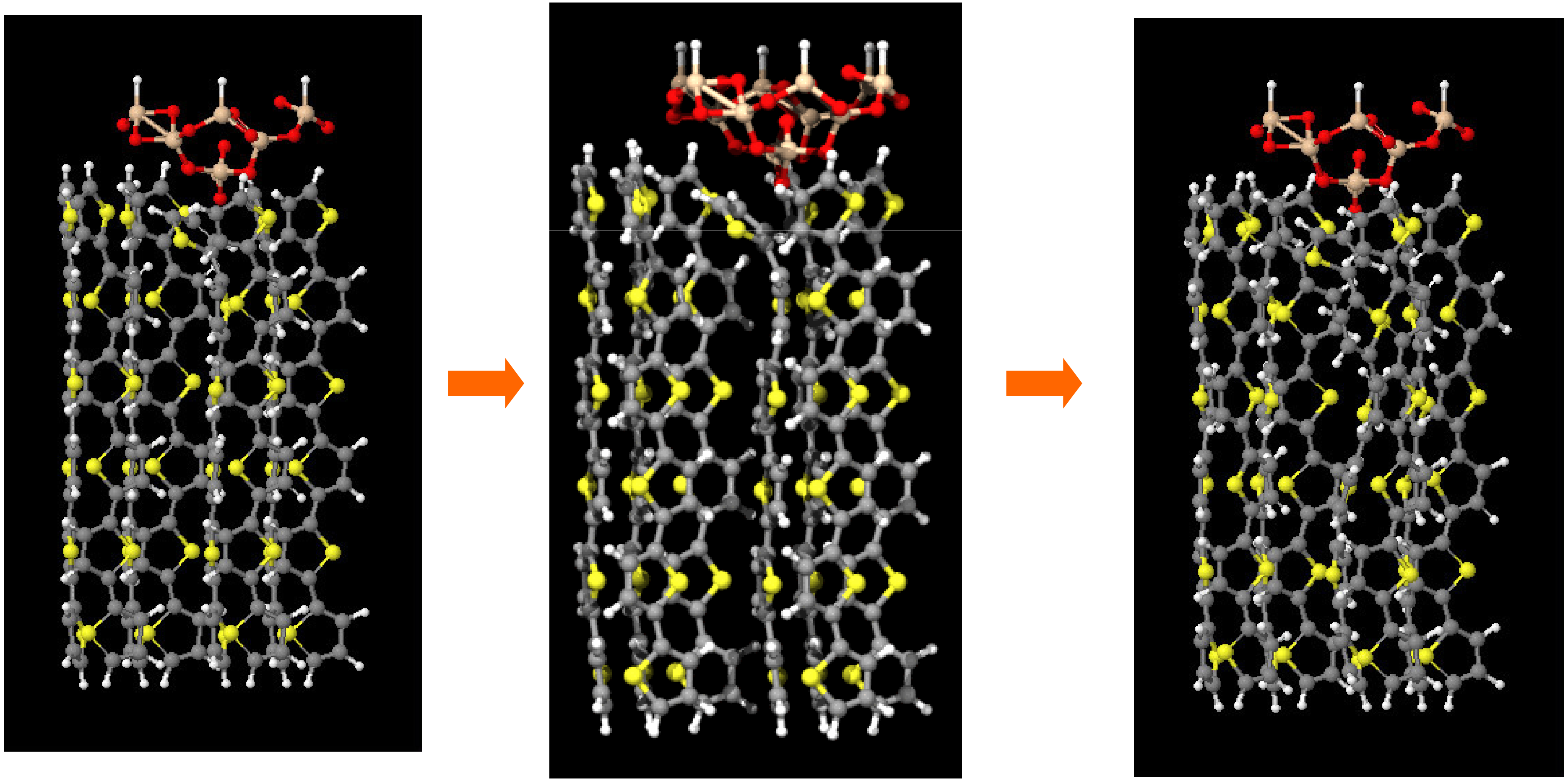
4×3



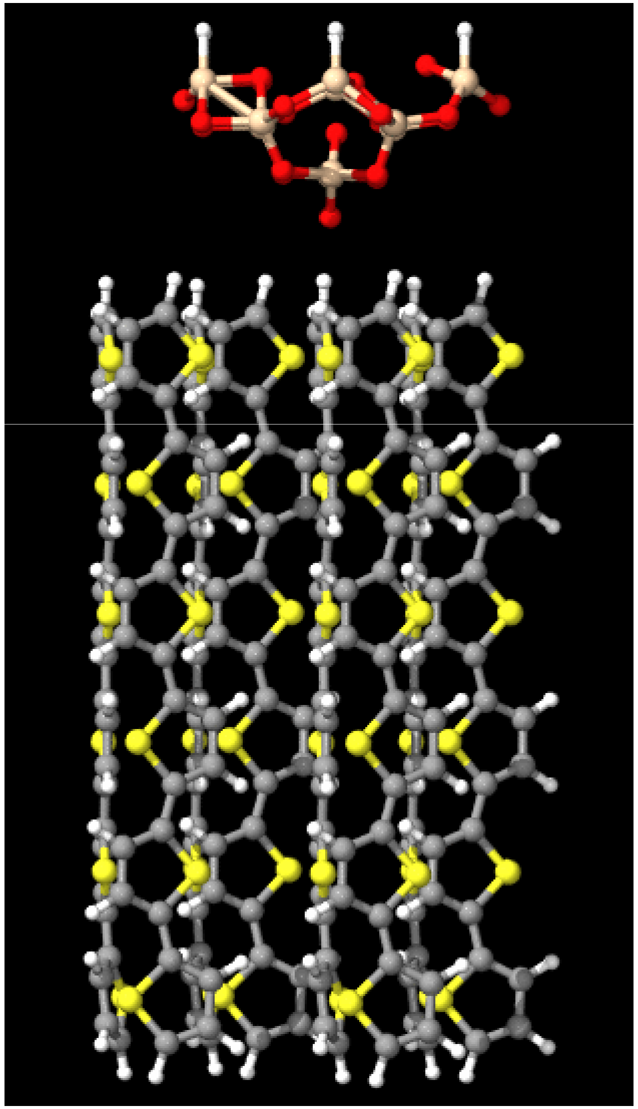
- Complicated energy landscape: Temperature effects?

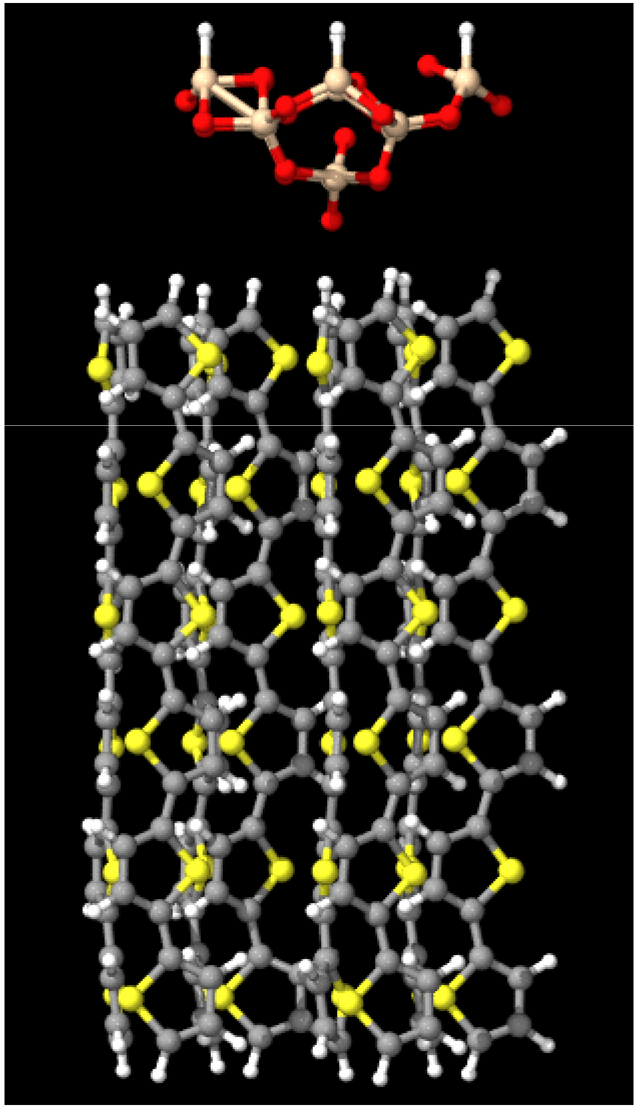
Simulated annealing: MD simulation step: 300 K

- Only for one tip position (above S atom) and 4x2 system.
- Short (350 fs) MD simulation (microcanonical, T ≈ 300 K) + relaxation using Dynamical Quenching (energy minimization "cooling down" the system).



Quasi-static versus MD simulations

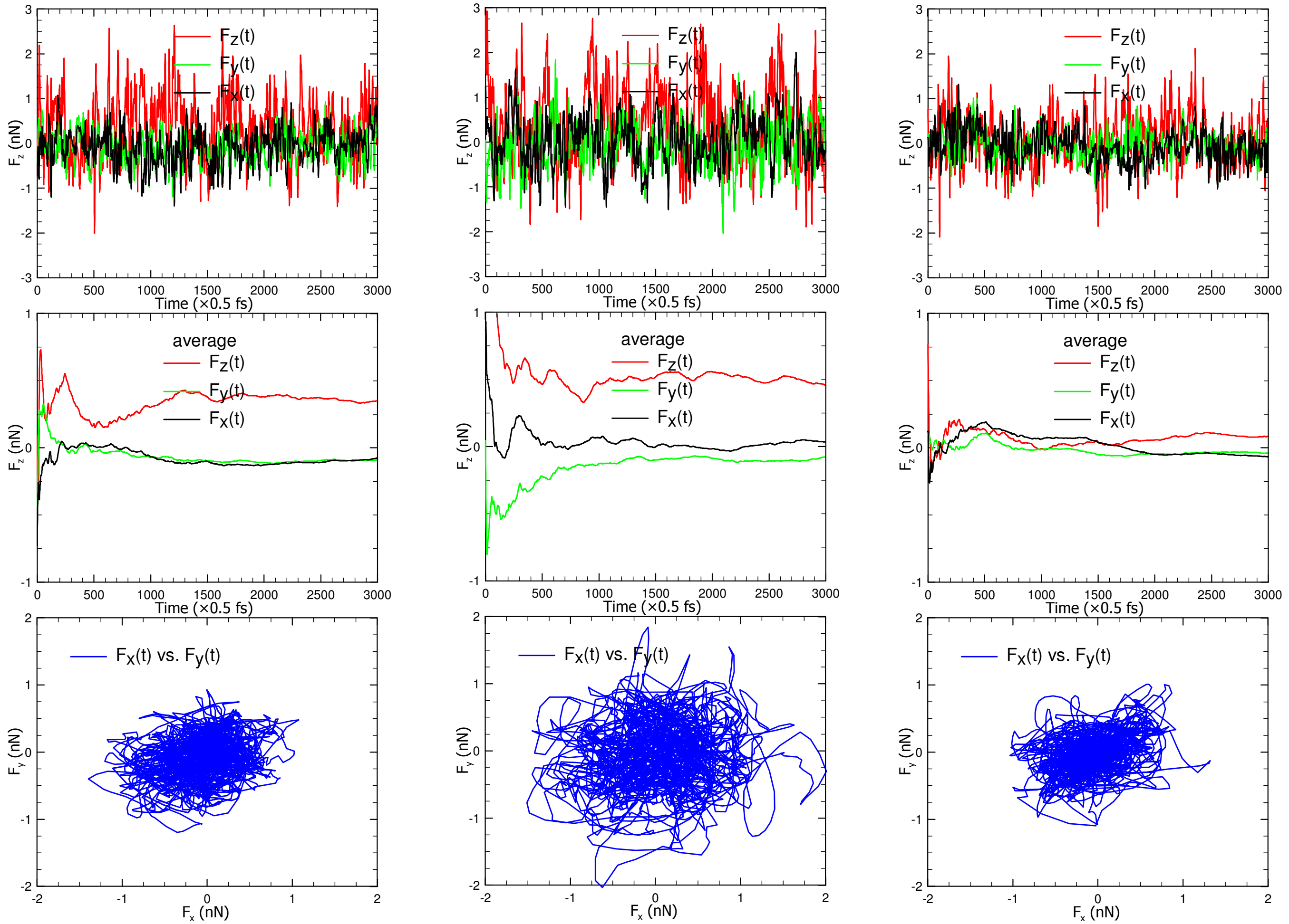




MD at 300 K – forces

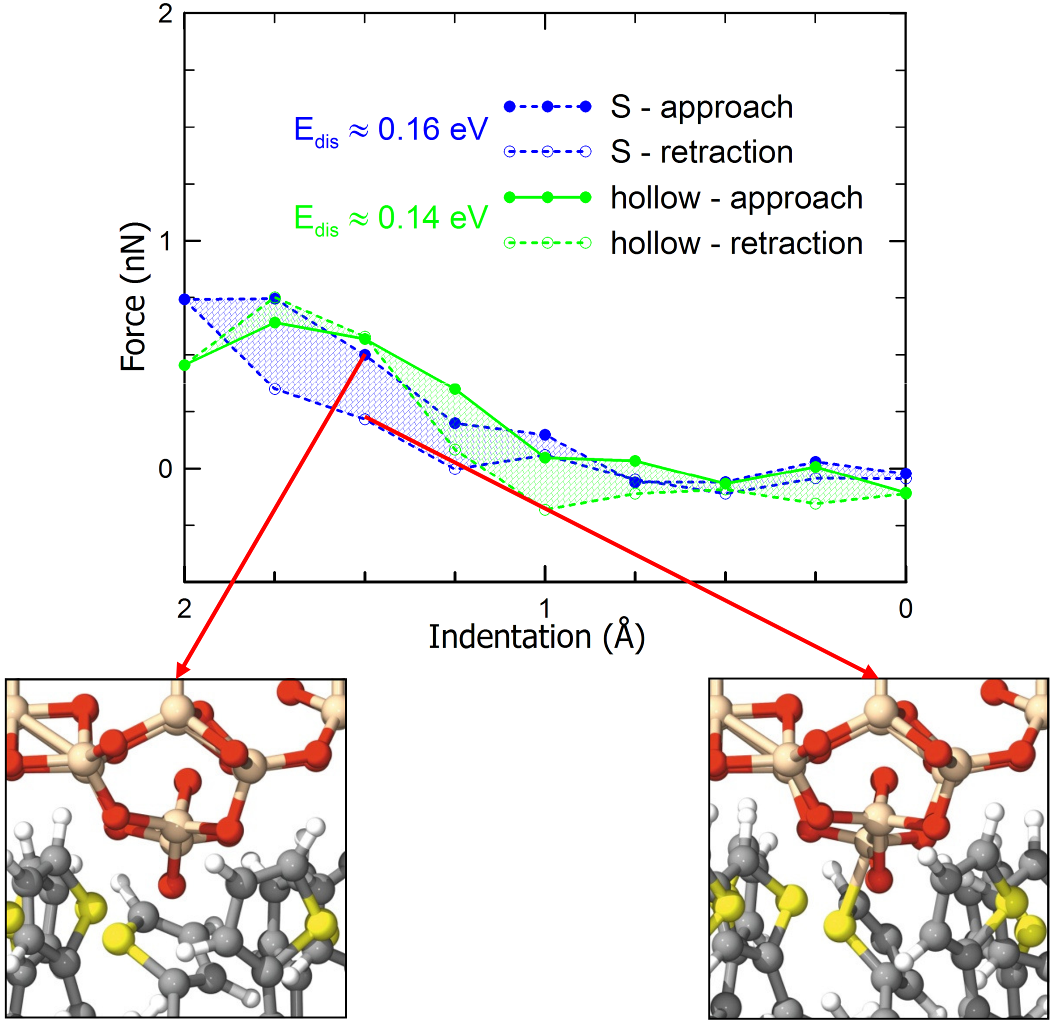
- hollow position

$Z_{tip\text{-}appr} = 1.75$ | $Z_{tip} = 1$ | $Z_{tip\text{-}retr} = 1.75$



MD simulations at 300 K – 3000 time steps

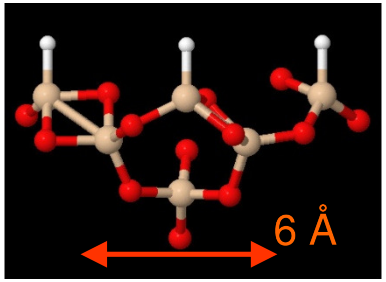
- $E_{dis} \approx 0.15$ eV



Experiments: a multi-asperity contact….

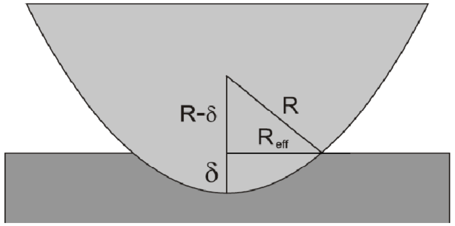
- **$E_{dis} \approx 0.15$ eV**

$R_{eff} \sim 3$ Å

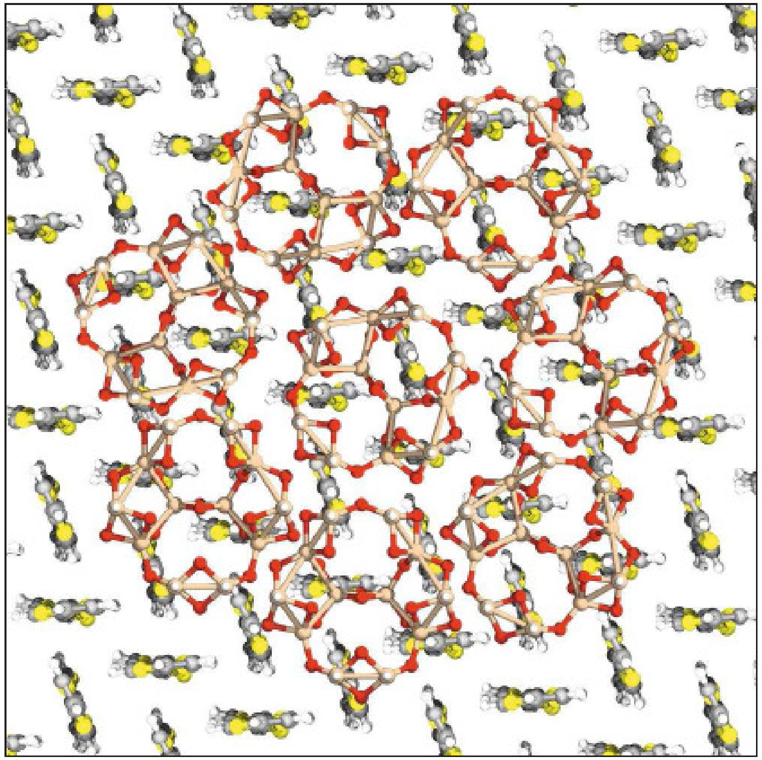


- **$E_{dis} \approx 1.4$ eV**

R = 7 nm, δ = 1.4 Å $\Rightarrow$ contact: 3.1 nm^2



$$a = \sqrt{\delta R}$$



- deformation mechanisms are very local

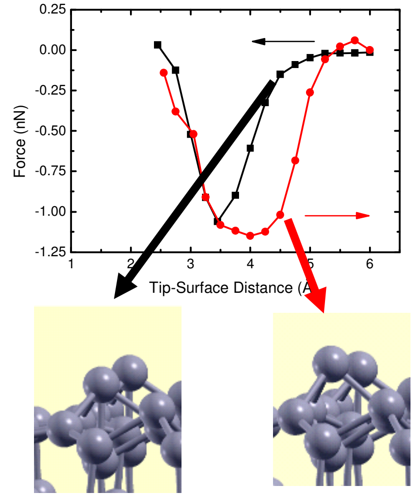
- dissipated energy is very similar for the different tip positions

Conclusions

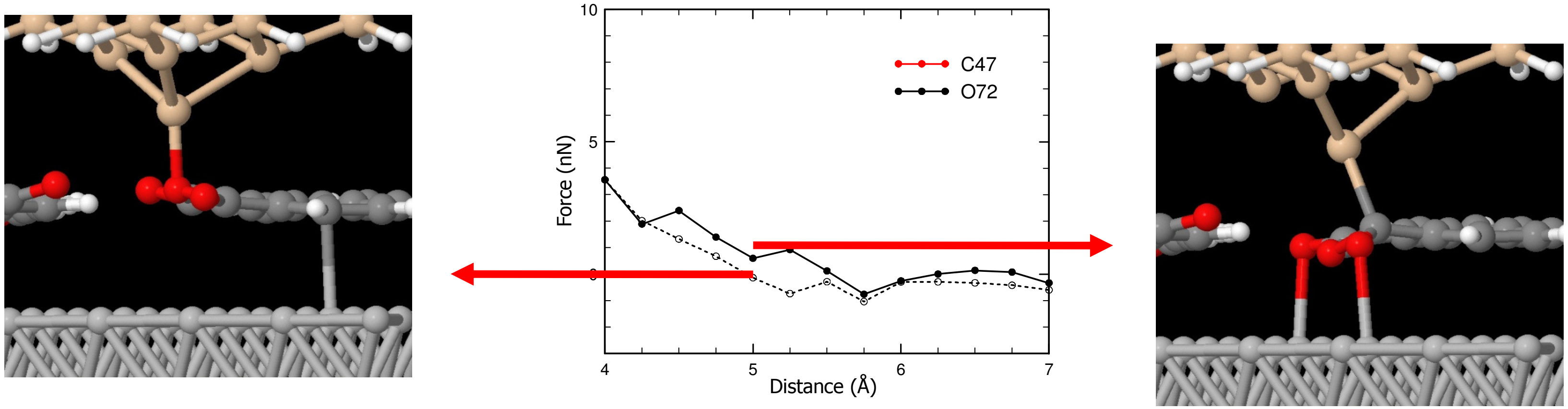
theory & experiment identify adhesion hysteresis as the leading energy dissipation mechanism at near contact

1. FM-AFM: Identification of a dissipation channel due to single atomic contact adhesion on semiconductor surfaces.

N. Oyabu et al. Phys. Rev. Lett. 96, 106101 (2006).



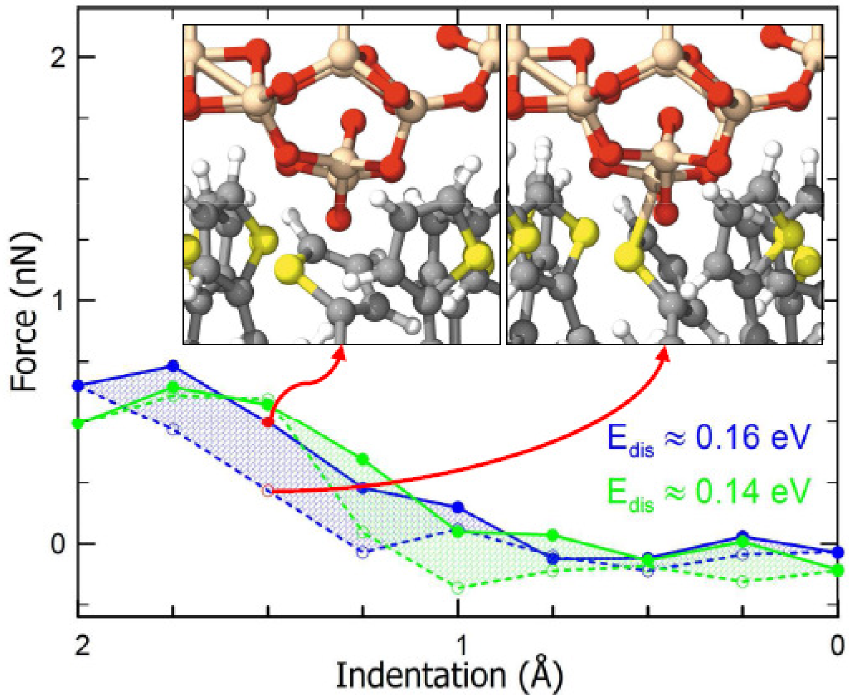
2. FM-AFM: submolecular resolution in the dissipation images for PTCDA on Ag(111)



Conclusions

theory & experiment identify adhesion hysteresis as the leading energy dissipation mechanism at near contact

3. AM-AFM: Combining continuum models and large scale *ab initio* MD simulations to understand the dissipation mechanisms in a sexithiophene ML deposited on SiO_x



R. García, R. Magerle and R.P., Nature Materials **6**, 405 (2007)

N.F. Martinez et al, Nanotechnology 20, 434021 (2009)
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