Towards real materials: Mechanical properties from first-principles simulations

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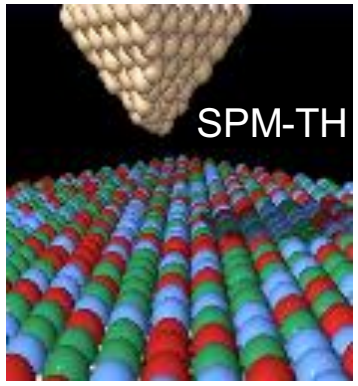
Theory of Condensed Matter Department &

Condensed Matter Physics Center (IFIMAC)

http://www.uam.es/spmth



UNIVERSIDAD AUTONOMA DE MADRID

IfiMAC Condensed Matter Physics Center

EXCELENCIA SEVERO OCHOA

Mike Payne's 60th birthday Symposium, Cambridge, 11/01/2020

"The mechanical properties of materials are ultimately determined by events occurring on the atomic scale."

Fracture of Brittle Solids - Brian R. Lawn

- QM is needed to describe the breaking and remaking of bonds that lies behind.

(You can go quite far –thousands of atoms- ... BUT...)

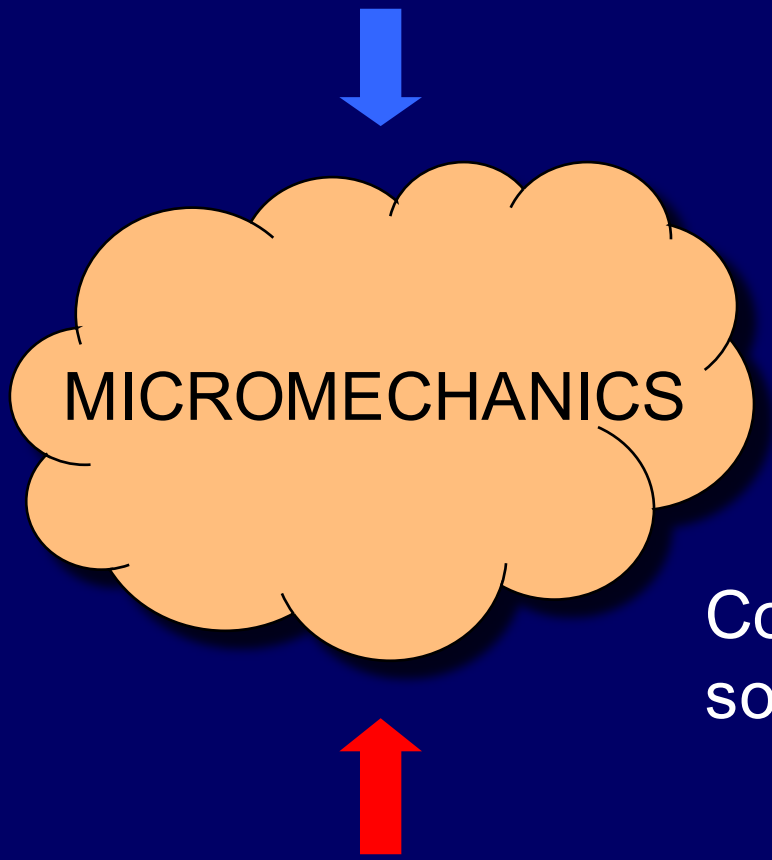
- The correct boundary conditions have to be imposed...

(Long-range interactions are present: Elasticity, Electrostatics)

Technical developments + increase in computer power

⇒ Approaching the size that matters for material science

Is ab-initio really necessary?

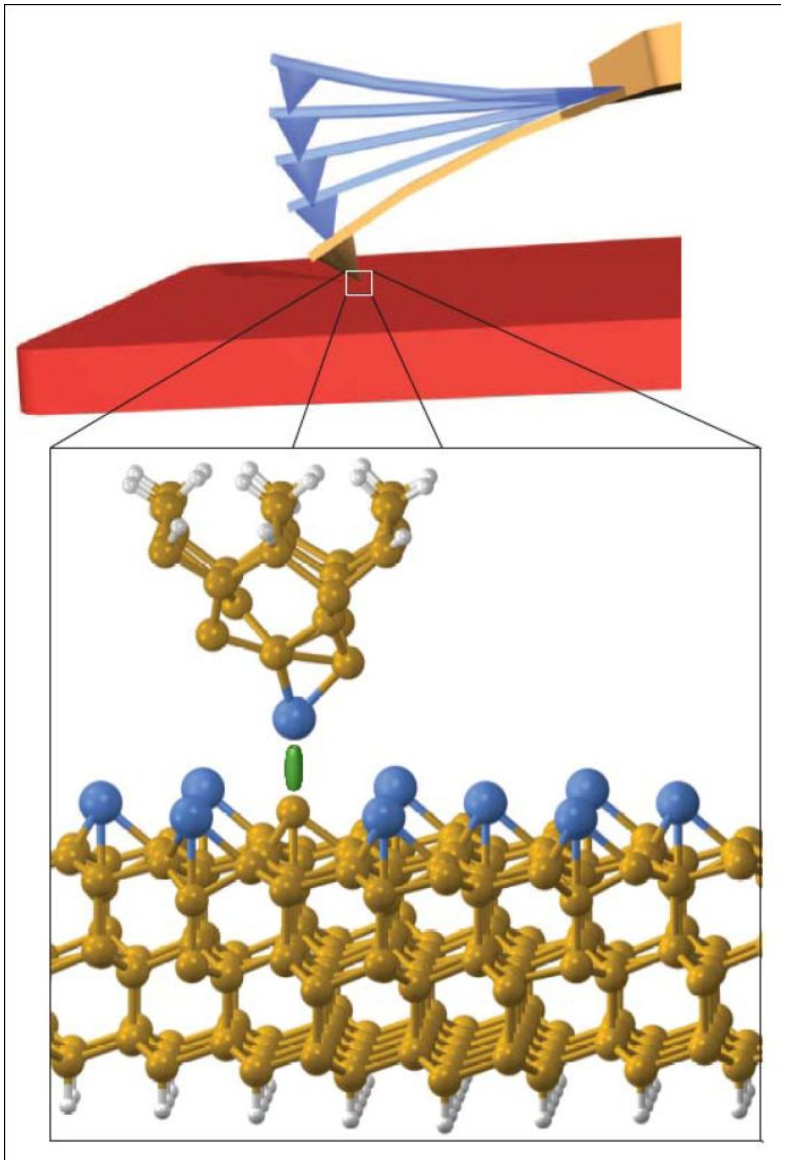


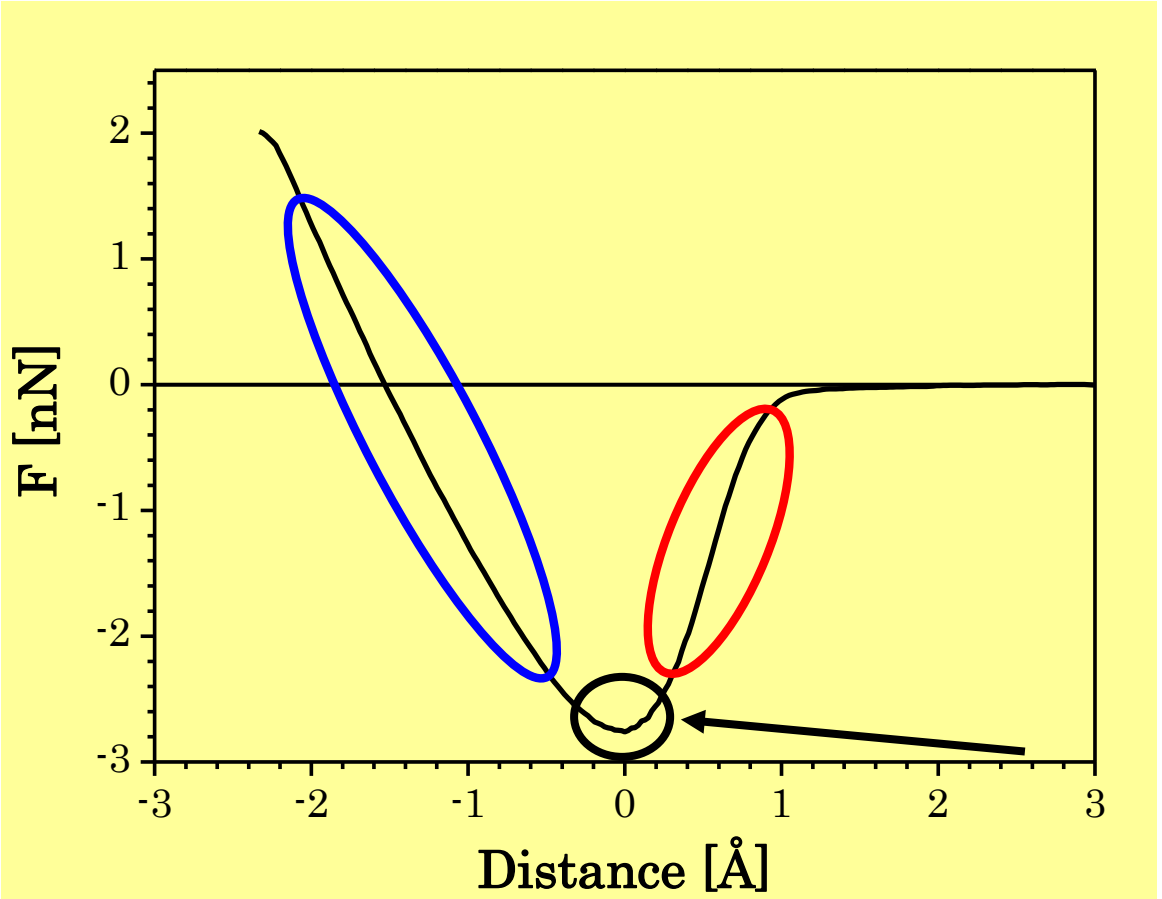
Could we do something useful?

Experiments probing matter on shorter scales

(scanning probes: STM,AFM,Nanoindentation)

Tip-sample interaction: from wear to near-contact





VOLUME 75, NUMBER 26 PHYSICAL REVIEW LETTERS 25 DECEMBER 1995

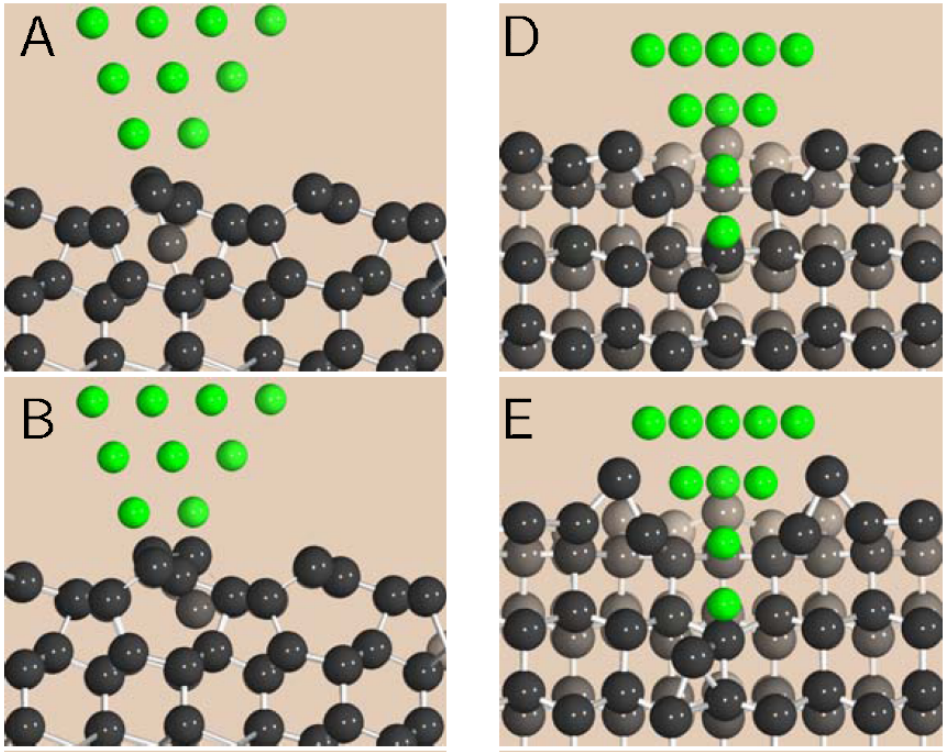
First Principles Simulations of Silicon Nanoindentation

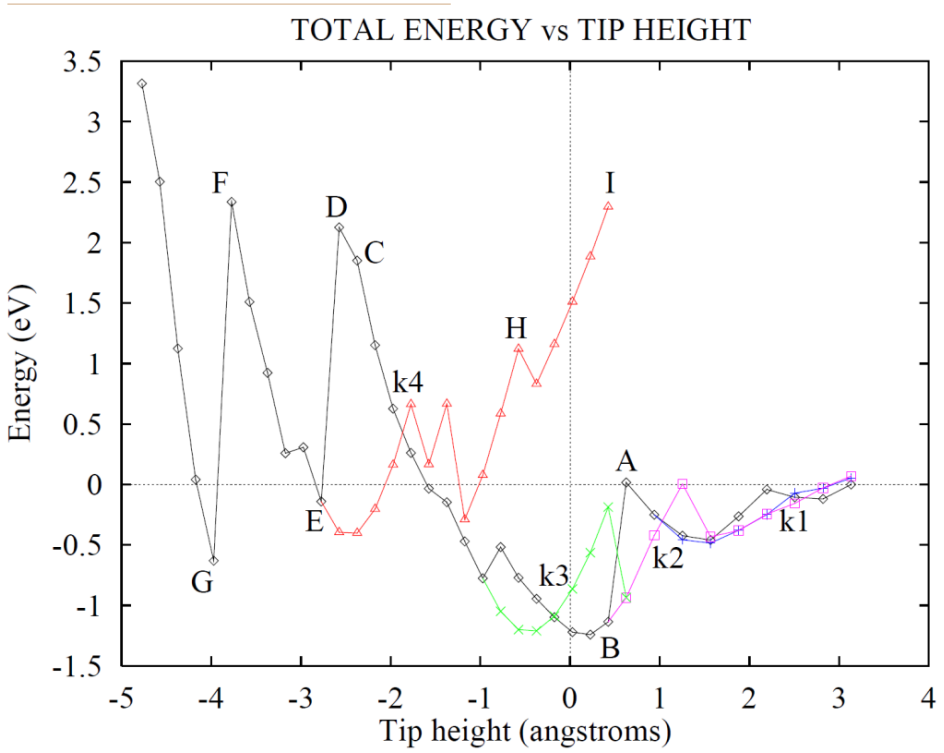
Rubén Pérez and Michael C. Payne

TCM, Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 OHE, United Kingdom

Alan D. Simpson

Edinburgh Parallel Computer Centre, University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, United Kingdom





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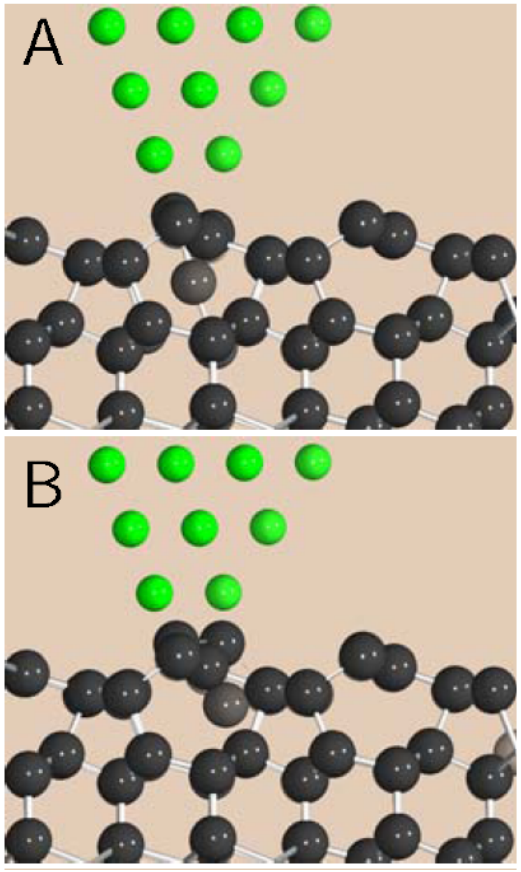
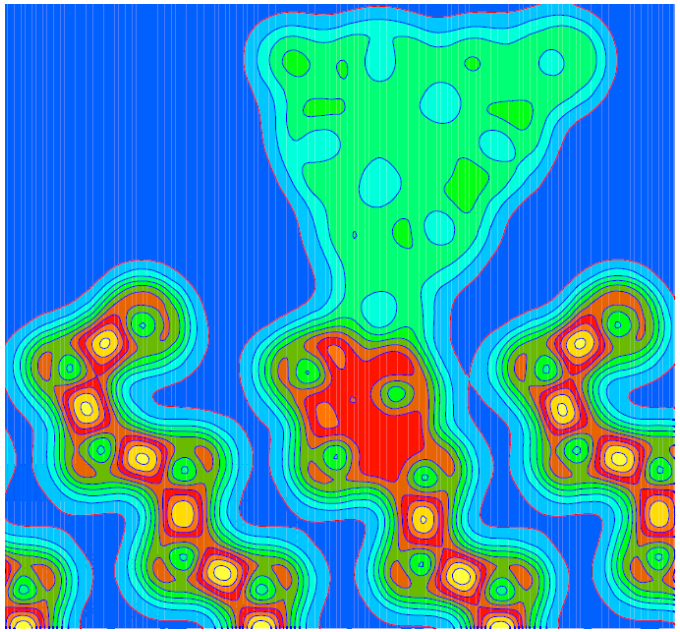
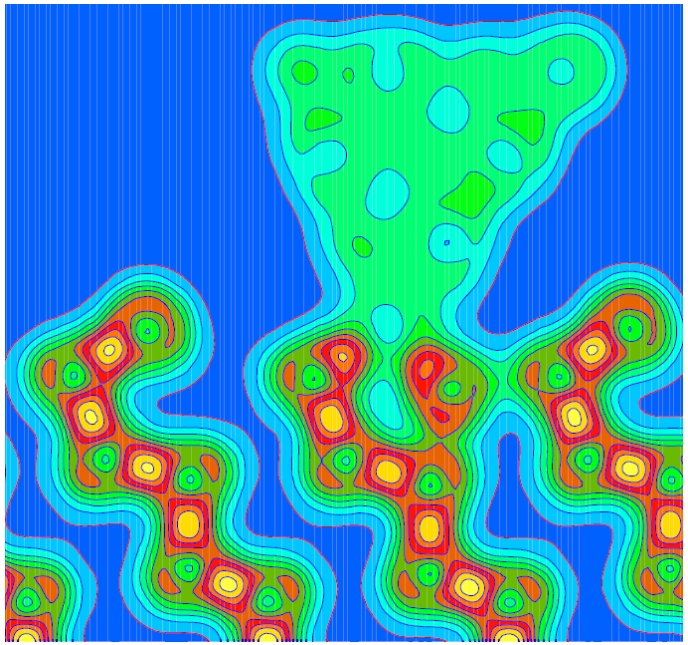




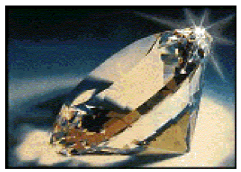


Can Atomic Force Microscopy Achieve Atomic Resolution in Contact Mode?

M. R. Jarvis,[1] Rubén Pérez,[2] and M. C. Payne[1]
[1]*Theory of Condensed Matter, Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 OHE, United Kingdom*
[2]*Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain*
(Received 9 June 2000)

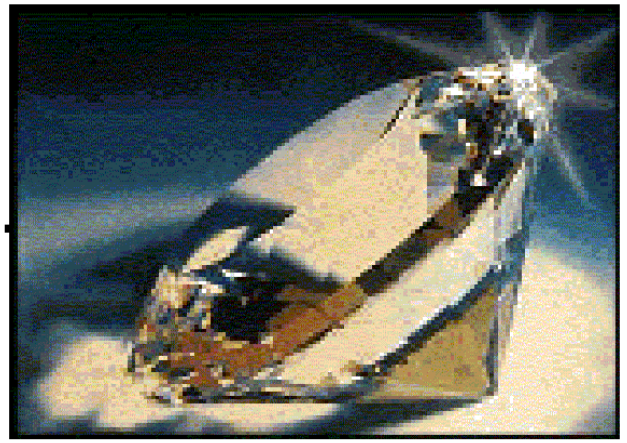
Maximum force: 30 nN !! Contamination effects Resolution limits in c-AFM

Microscopic Mechanism for Mechanical Polishing of Diamond (110) Surfaces



M. R. Jarvis,[1] Ruben Pérez,[2] F. M. van Bouwelen,[3] and M. C. Payne[1]
[1]*Theory of Condensed Matter, Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 OHE, United Kingdom*
[2]*Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain*
[3]*Applied Physics, Faculty of Science, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands*

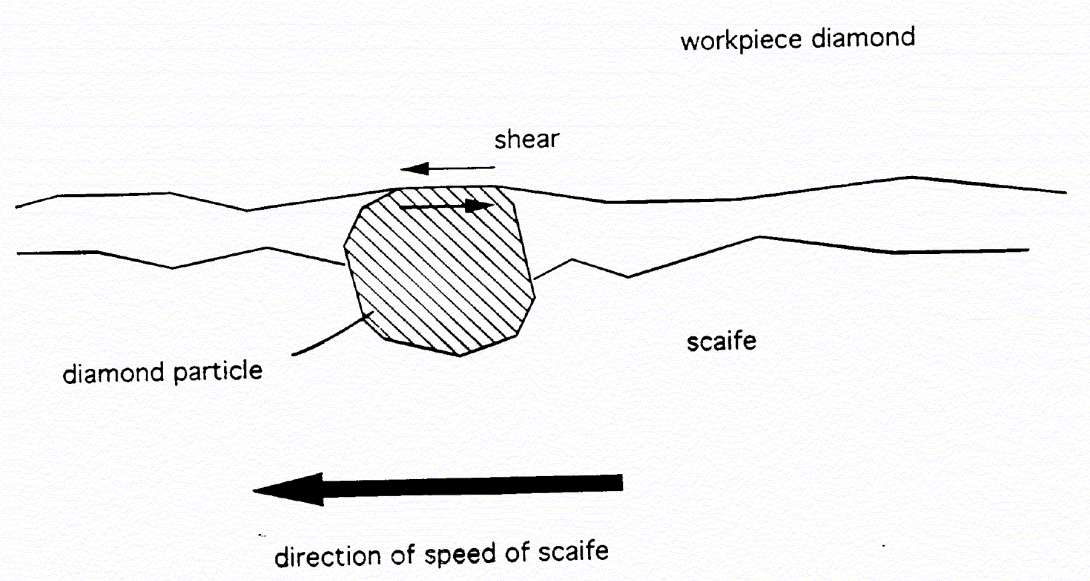
Diamond Polishing



Dealing with the boundary conditions…

Atomic scale mechanism for wear?

Industrial Polishing of Diamonds



- Scaife rotates at ~ 50 RPS

Radius 15-20 cm ⇒ v ~ 30 m/s

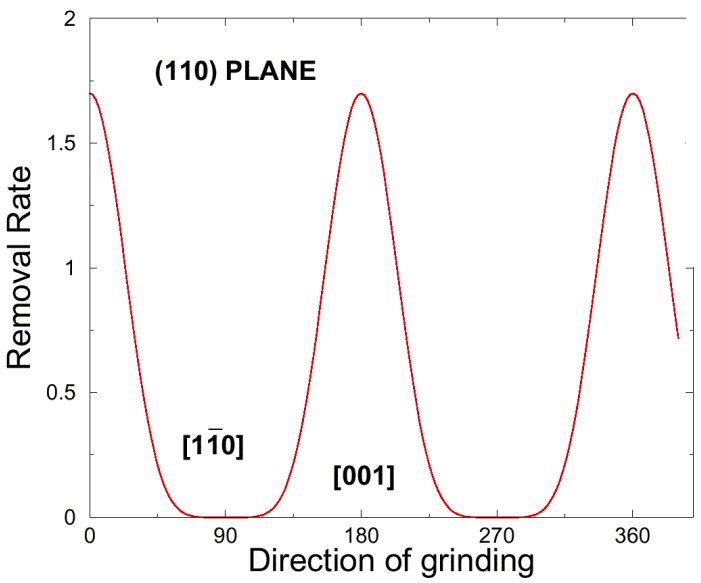
- Ratio of material lost

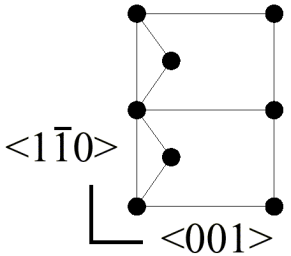
  diamond/scaife ~ 10

- Rate of removal proportional to scaife speed (same amount of material removed per rotation)

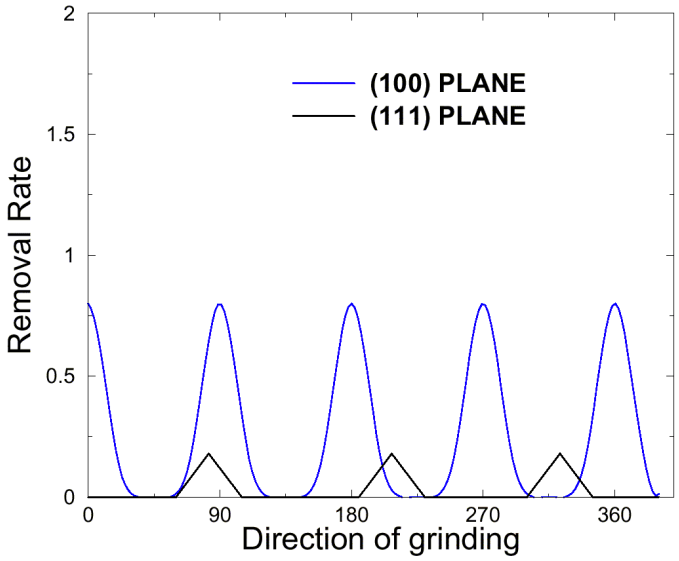
No thermally activated!!!

Strong Anisotropy in Diamond Polishing: microscopic wear mechanism?





10:1 ratio between the removal rate for ⟨001⟩ and the ⟨1-10⟩ in the (110) surface



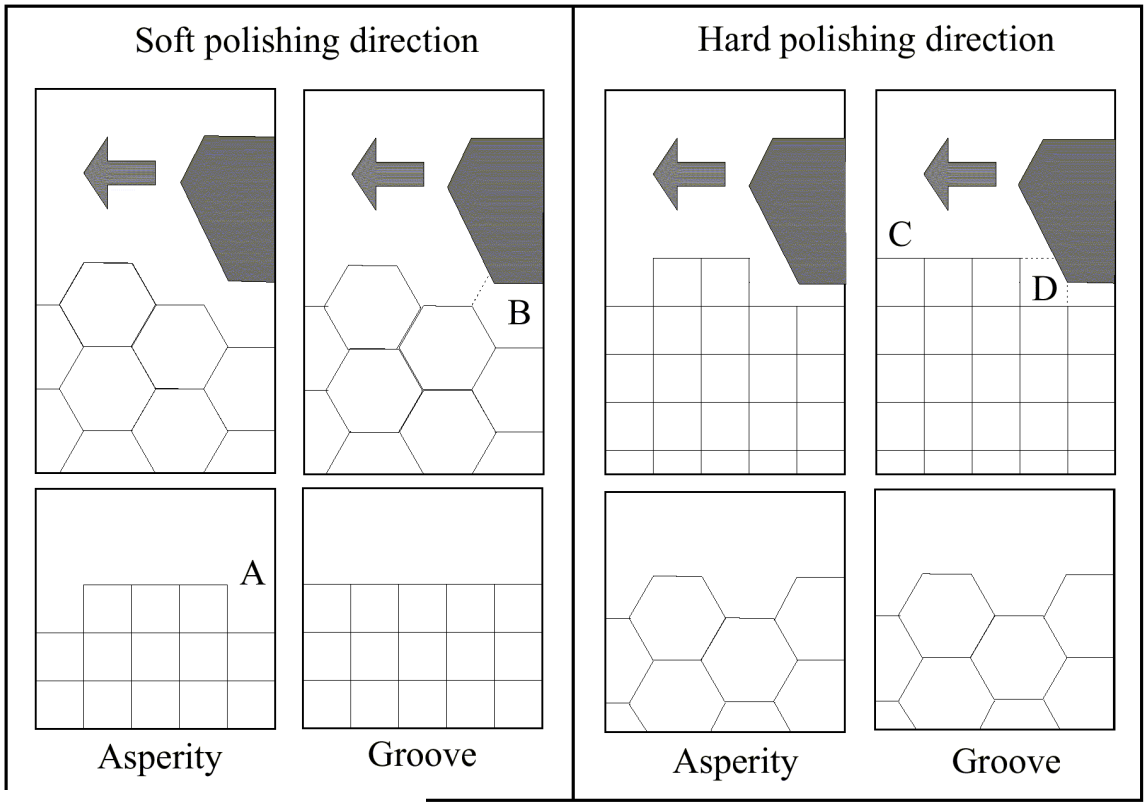
New experimental evidence:
(STM, AFM, EELS,...)

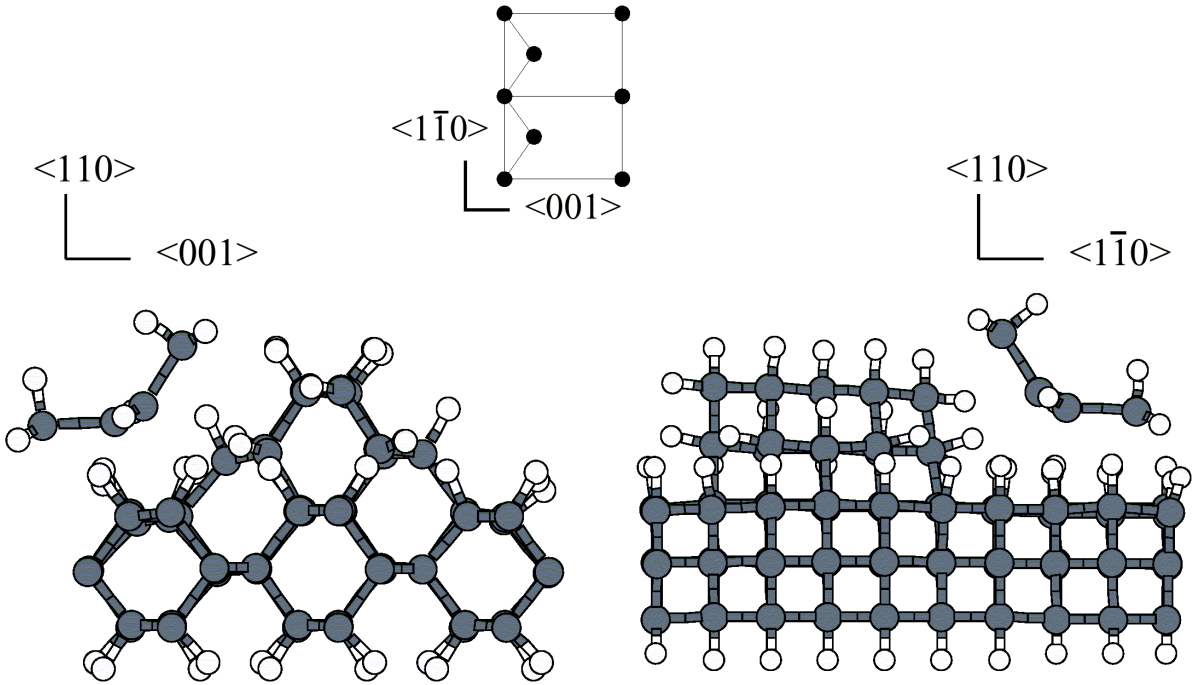
- Inconsistent (surface morphology, residue) with the accepted (111) microcleavage theory.
- Mechanism in which only a few carbons are removed in each tribological event.

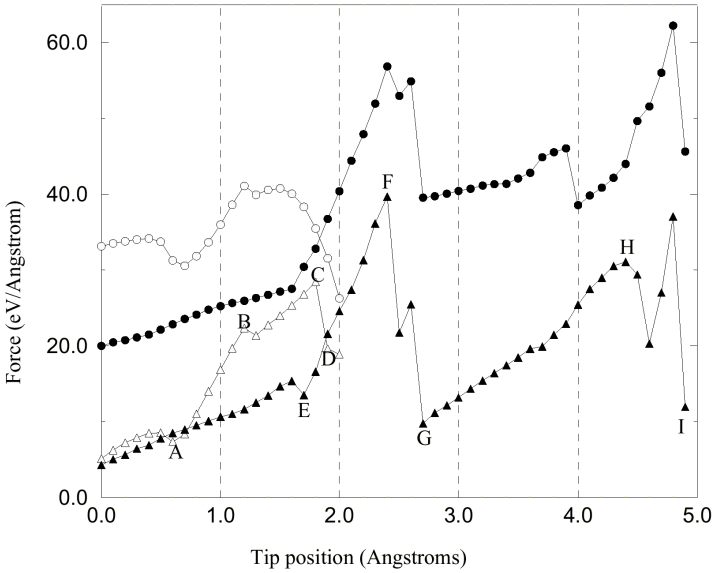
Nanogrooving?

F.M. Van Bouwelen, L.M. Brown, J.E. Field (Cambridge)
J. Couto, W.J.P. Van Enckevort, M. Seal (Nijmegen)

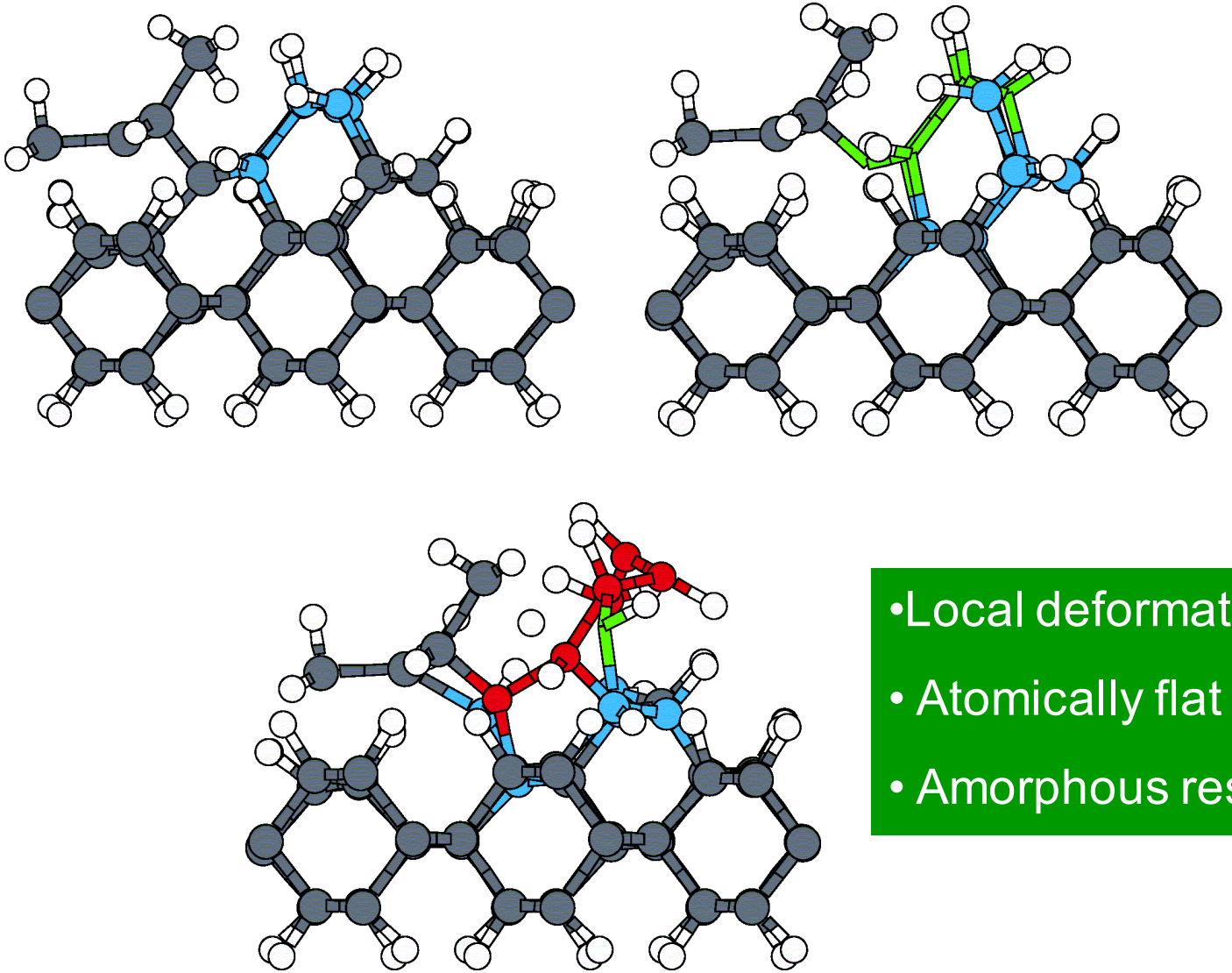
Relating nanogrooving to removal of a single nanoasperity





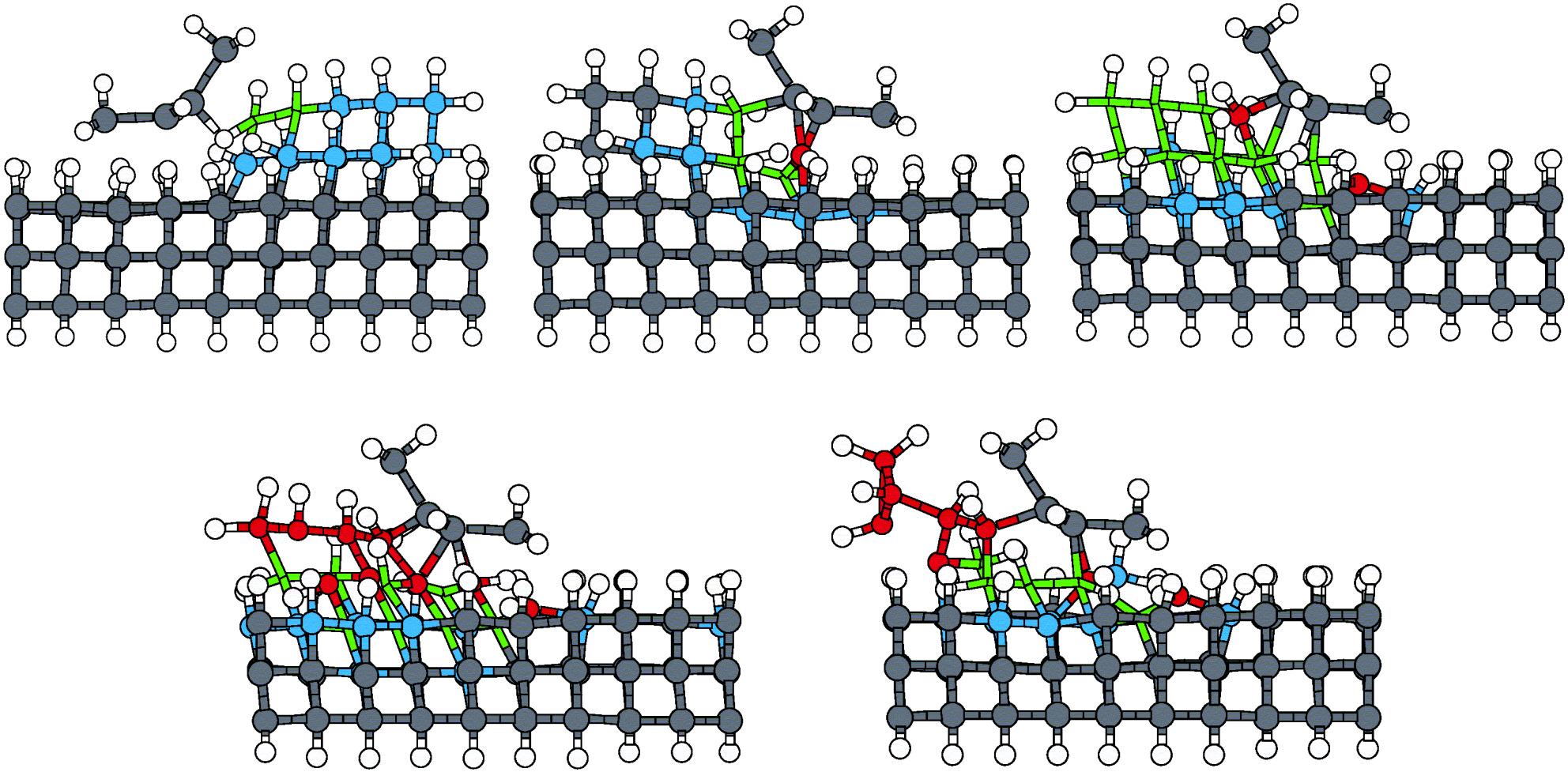


Nanoasperity removal in the “soft” ⟨001⟩ direction: Extend of deformation



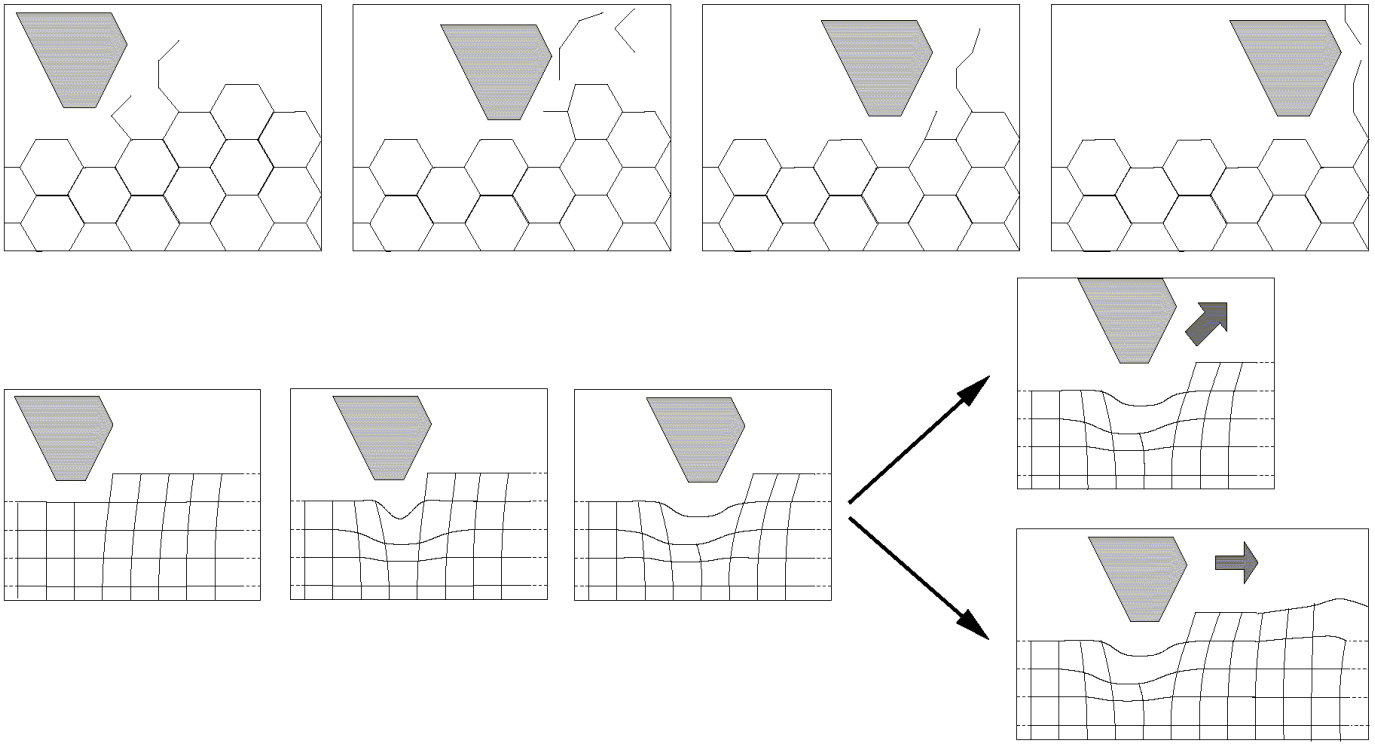
- Local deformation.
- Atomically flat surface.
- Amorphous residue

Nanoasperity removal in "hard" ⟨1$\bar{1}$0⟩ direction: Non-local deformation



Non-local deformation + sub-surface damage

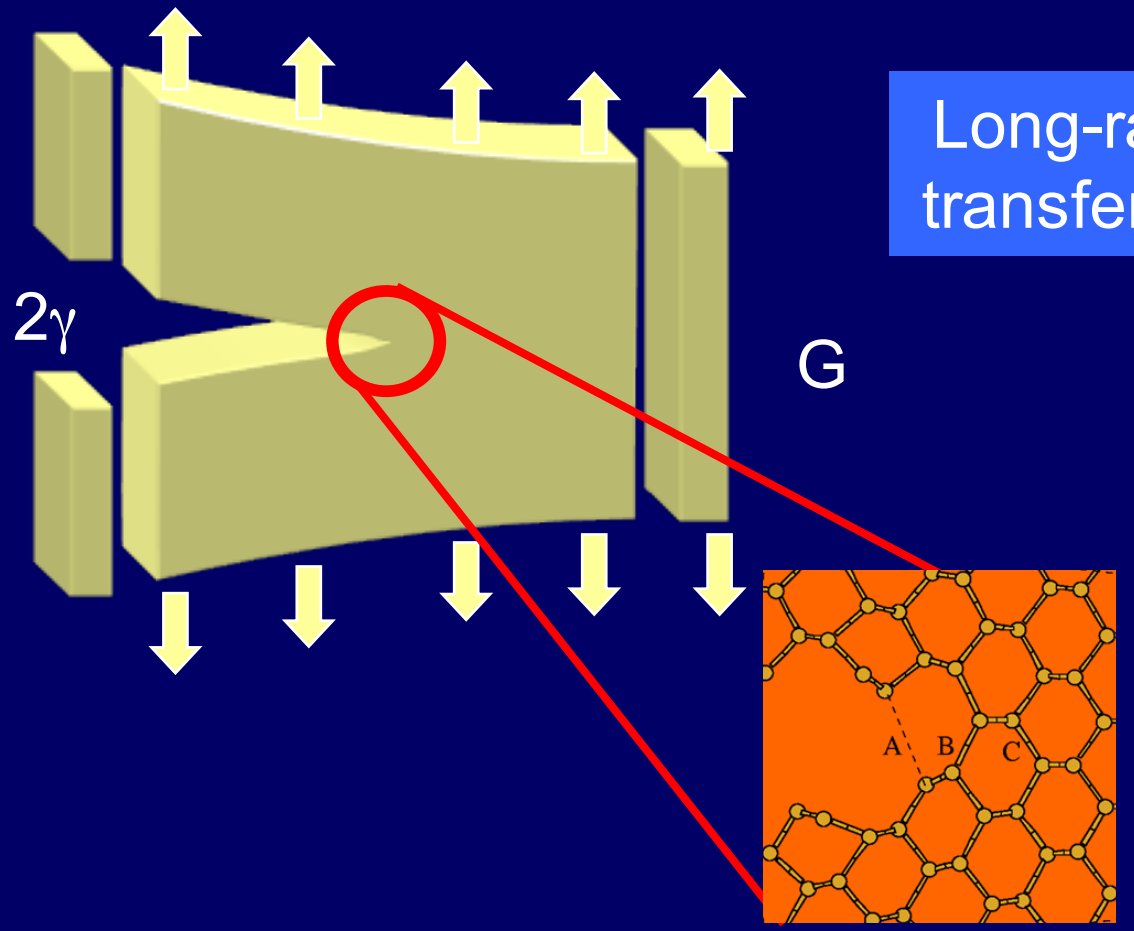
Nanogroove formation vs asperity removal



• “soft” direction: local deformation ⇒ Forces and mechanism as in the isolated asperity.

• “hard” direction: Non-local deformation ⇒ Greater resistance: subsurface damage or tip deflection.

Fracture: a multiscale problem



Long-range elastic interactions transfer the load to the crack tip

The breaking/remaking of bonds that controls crack propagation requires a quantum-mechanical description

VOLUME 84, NUMBER 23 PHYSICAL REVIEW LETTERS 5 JUNE 2000

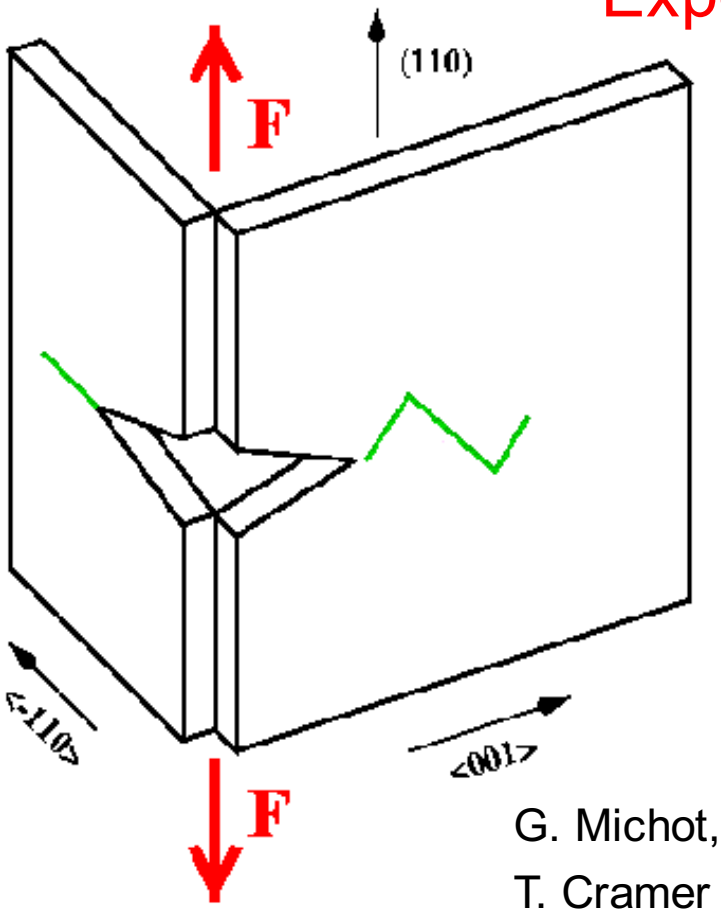
Directional Anisotropy in the Cleavage Fracture of Silicon

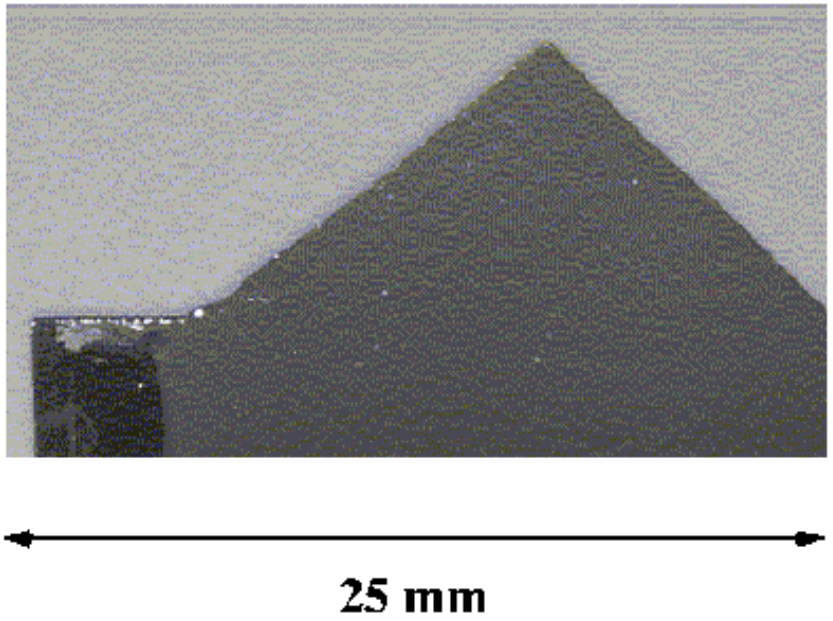
Rubén Pérez [1,2] and Peter Gumbsch [2]

[1] *Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain*

[2] *Max Planck Institut für Metallforschung, Seestrasse 92, 70174 Stuttgart, Germany*

Experiments: Directional Anisotropy

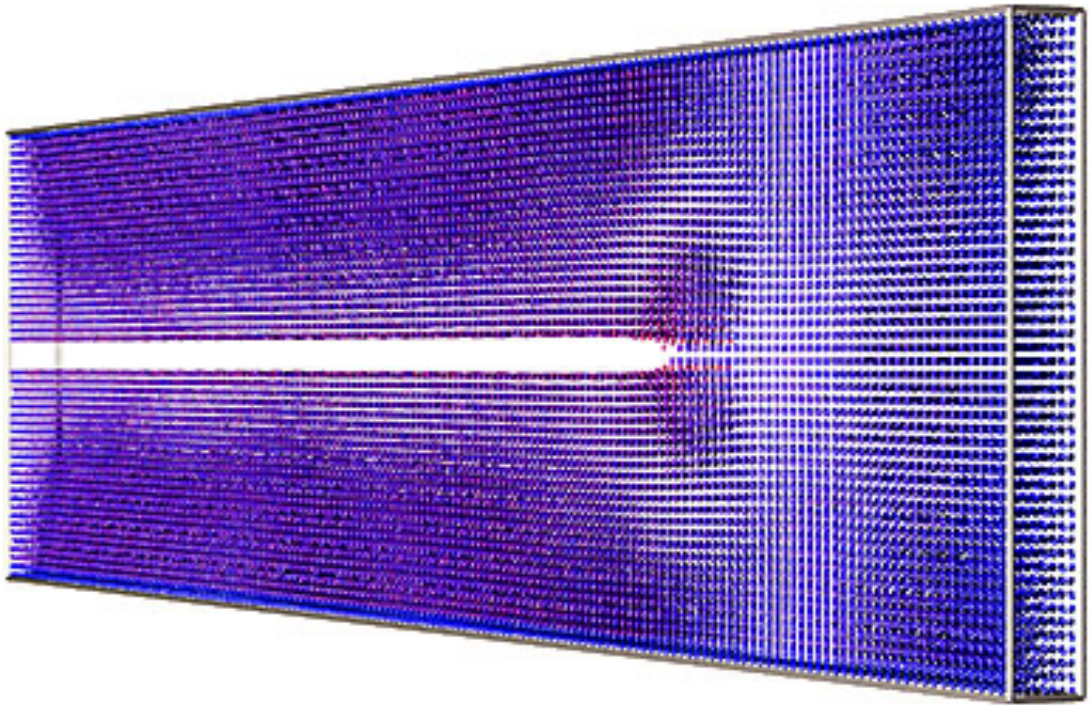




G. Michot, Crystal Properties & Preparation, 17-18, 55 (1988)

T. Cramer et al, PRL 85, 788 (2000)

Are first-principles methods necessary?



D. Holland and M. Marder

PRL 80, 746 (1998).

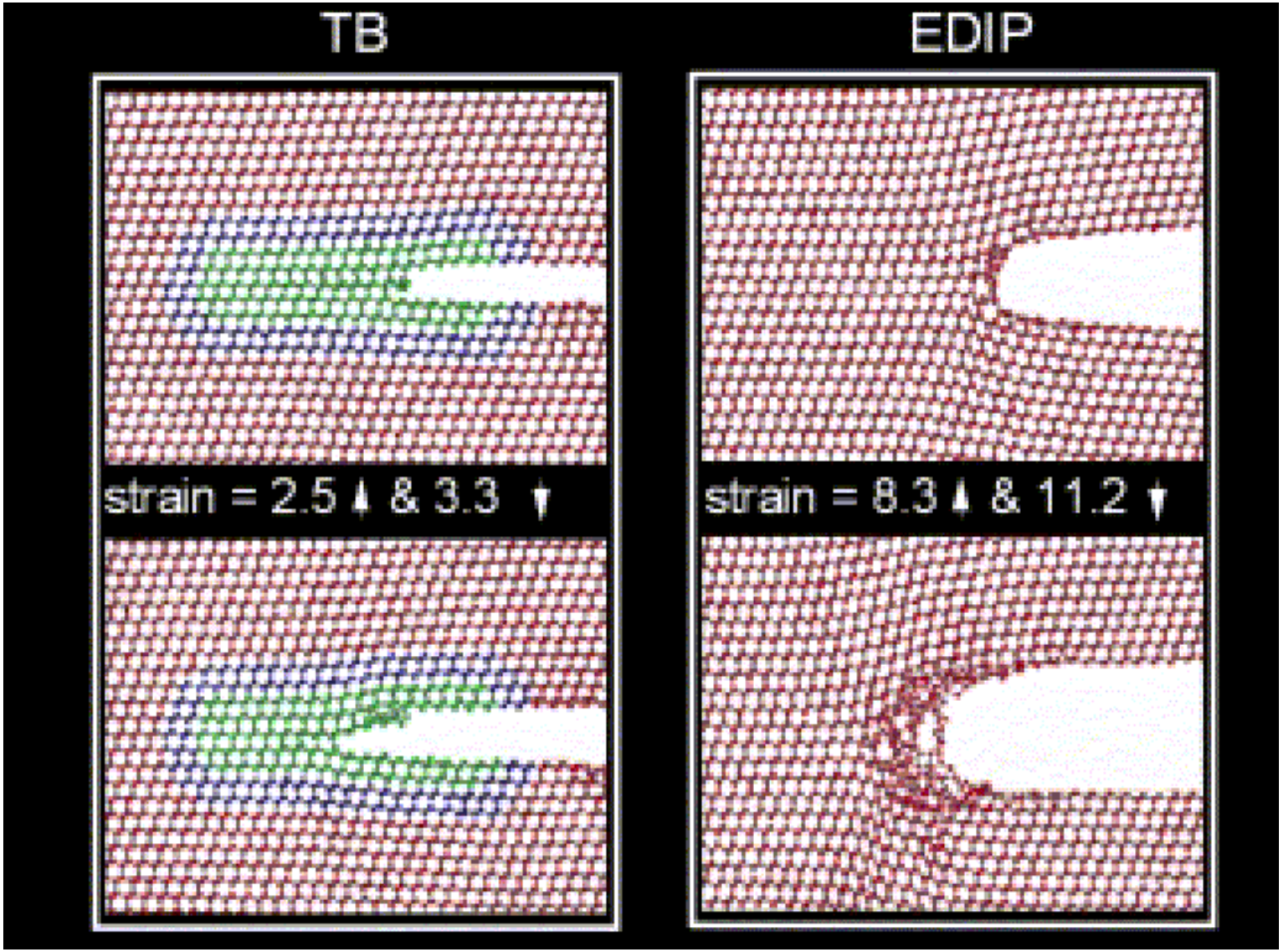
10^5 atoms + 10 ns

Stillinger-Weber

In our Letter we stated that we used Stillinger-Weber potentials in our simulations. The statement is incorrect. Our potentials are of the Stillinger-Weber form but the parameter λ, a coefficient governing the stiffness of angle-dependent forces, should have had the value $\lambda = 21$, while we used $\lambda = 42$. One consequence of increasing λ is that the melting temperature of silicon increases to approximately 3500 K, while the correct value is 1683 K. Upon reducing λ to the correct value, cracks in Stillinger-Weber silicon emit blunting dislocations and refuse to move further until given an energy on the order of 4 times the experimentally known value. With $\lambda = 42$ the phenomenology of fracture agrees with experiment. Neither the Stillinger-Weber potential nor our modification can be regarded as giving a satisfactory description of fracture.

D. H. & M. M., PRL 81, 4029 (1998) (ERRATUM)

Classical Potentials vs Tight-Binding



F. Abraham et al, MRS Bull (May 2000)

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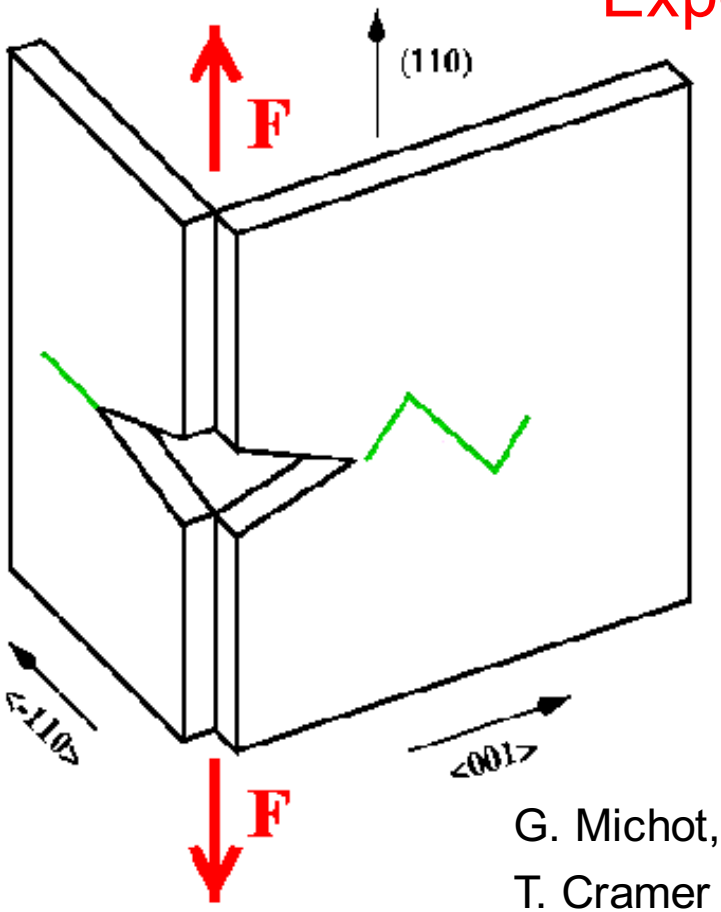
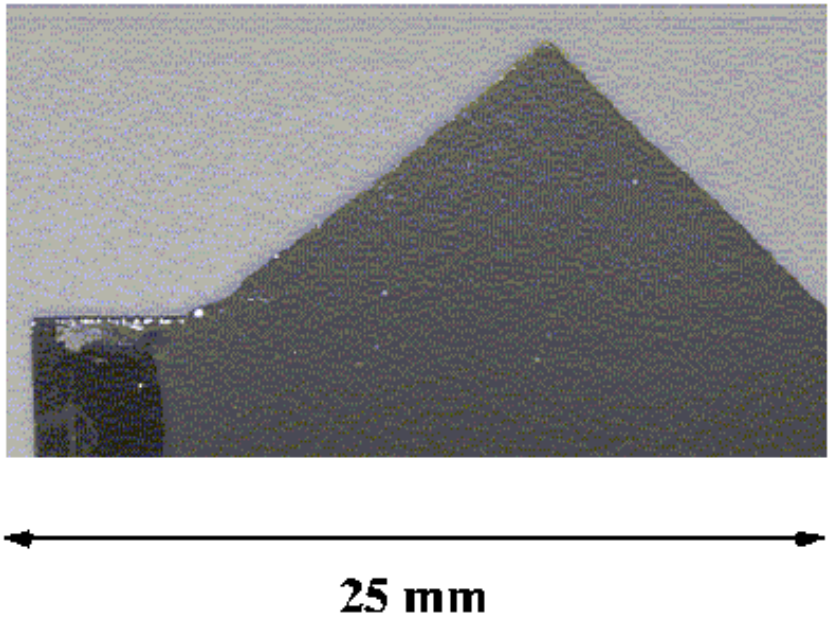


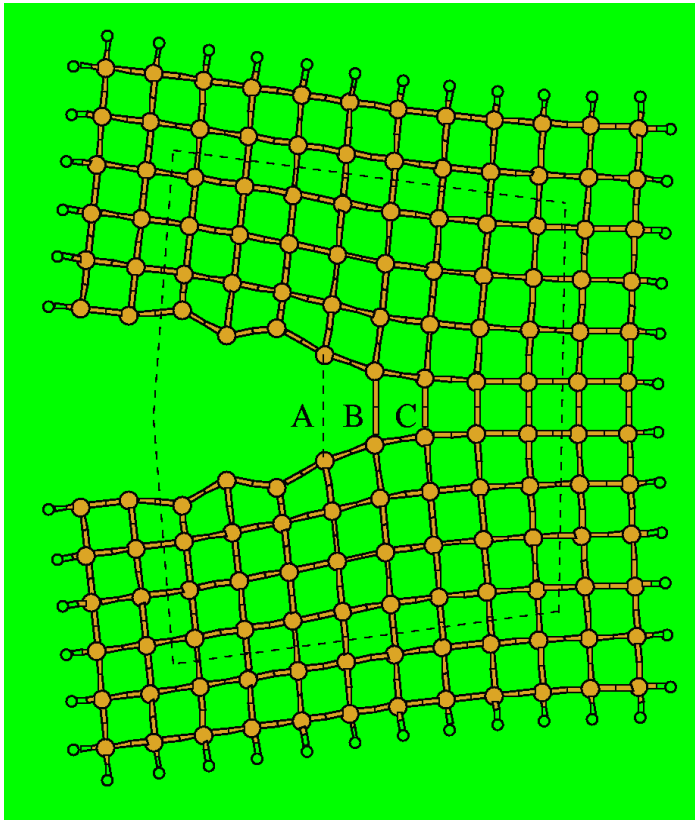


G. Michot, Crystal Properties & Preparation, 17-18, 55 (1988)

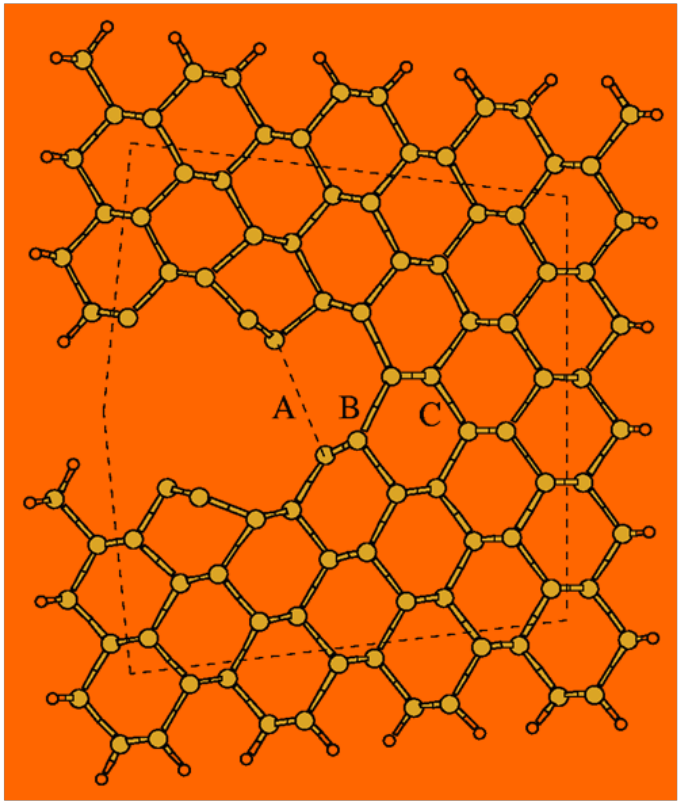
T. Cramer et al, PRL 85, 788 (2000)

Our approach: **Boundary Conditions** + Scaling

[-110](110) Easy



[001](110) Difficult

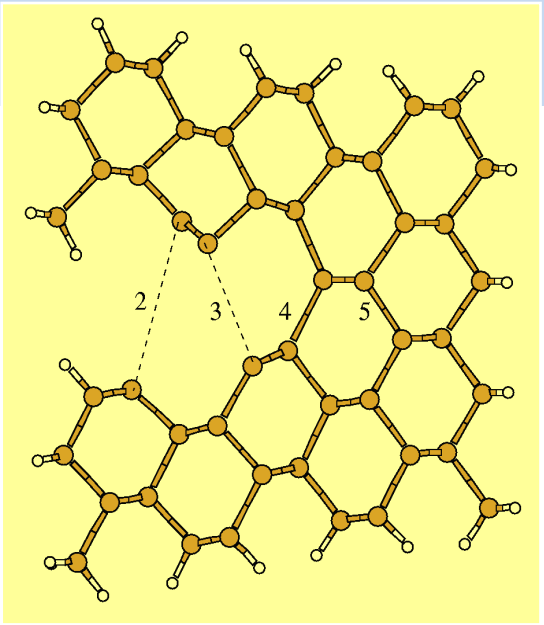


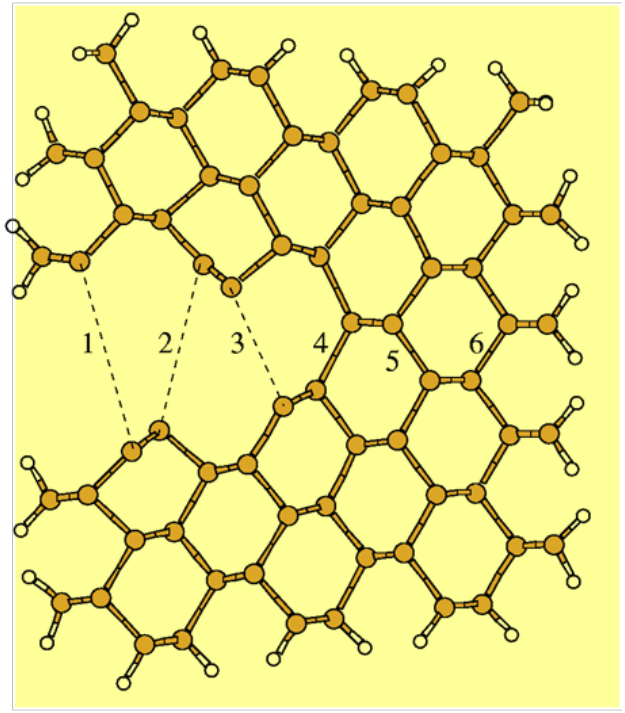
- Outer atoms fixed at positions predicted by anisotropic linear elasticity.
- Inner atoms relaxed with QM.

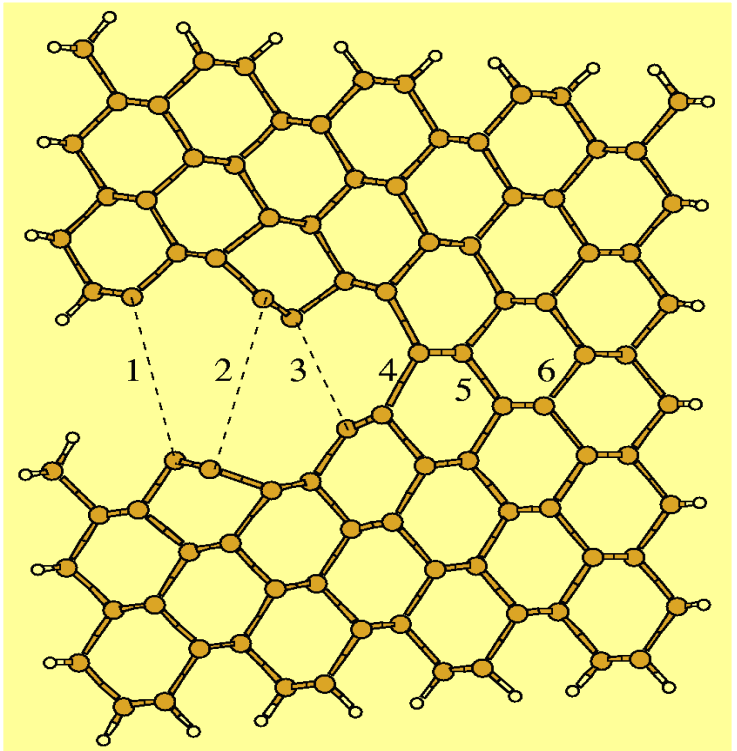
Our approach:

Boundary Conditions

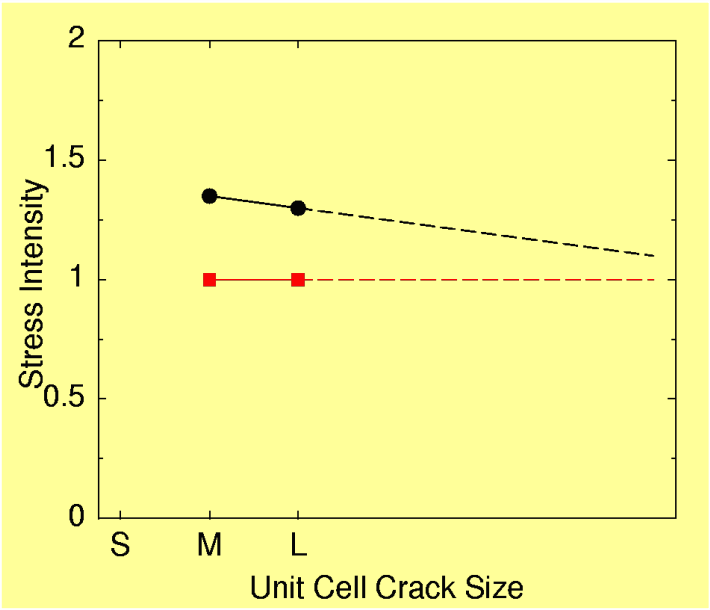
+ **Scaling**

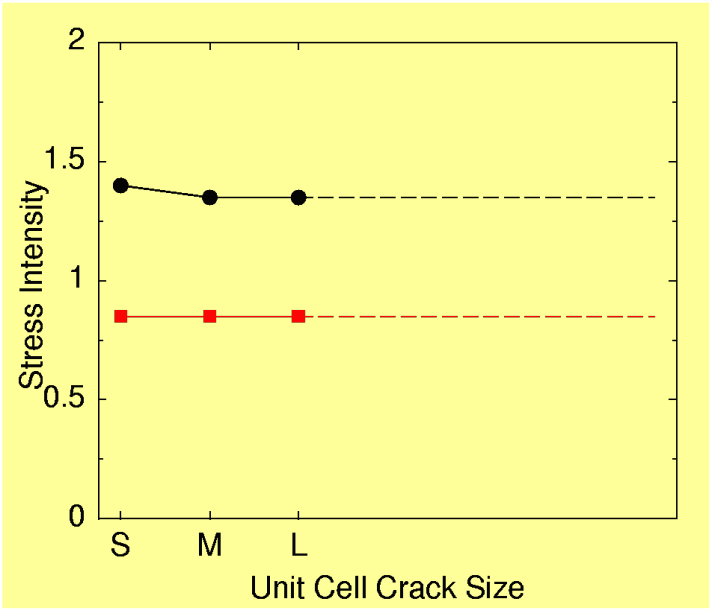






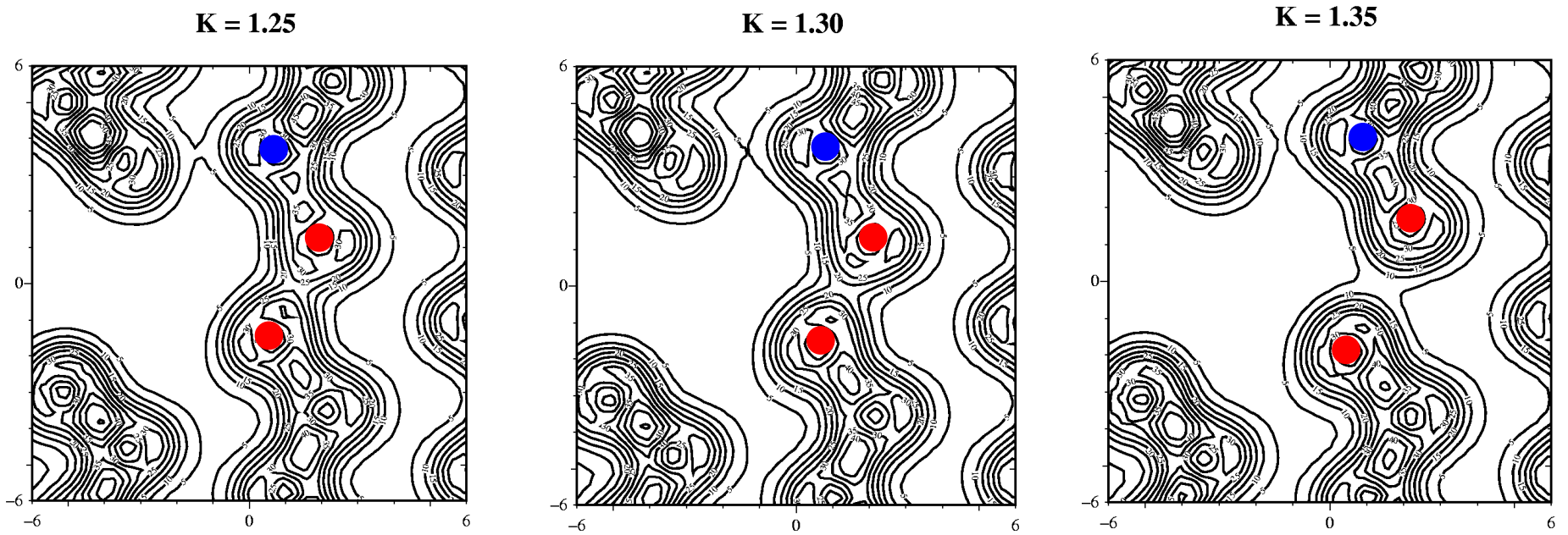
Bond breaking vs Lattice trapping

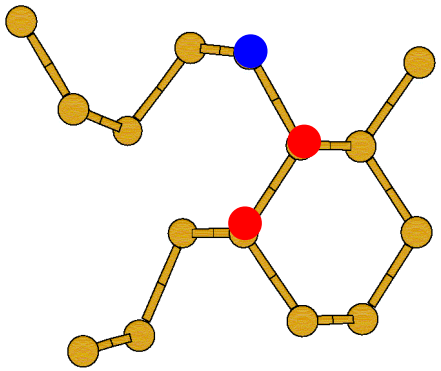




	$(110)[001]$	$(110)[1\bar{1}0]$
bond breaking	continuous (mimics continuum mechanics)	discontinuous (rearrangements of few atoms at crack tip)
lattice trapping	small	large
variation with system size	decreases	no change
propagation	easy	difficult $\Longrightarrow$ higher fracture toughness

Origin of lattice trapping: load sharing





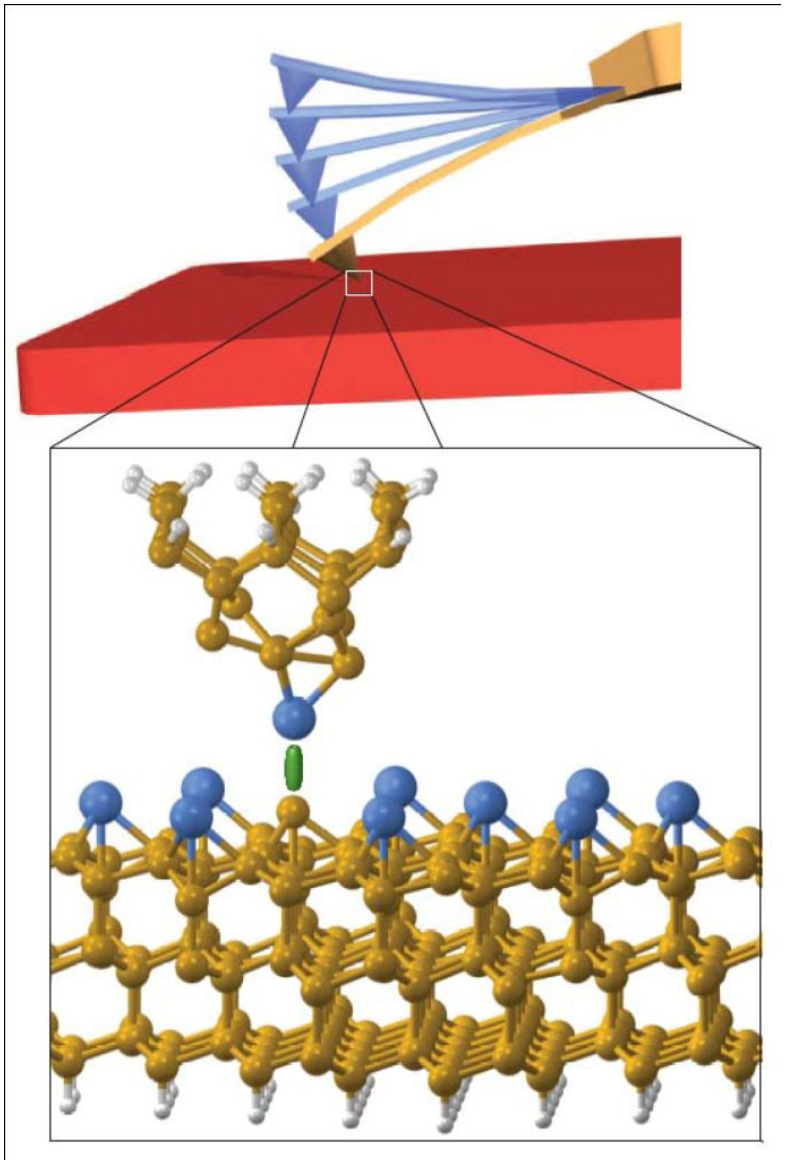
- Propagation at experimental loads
- Anisotropy: “lattice trapping”

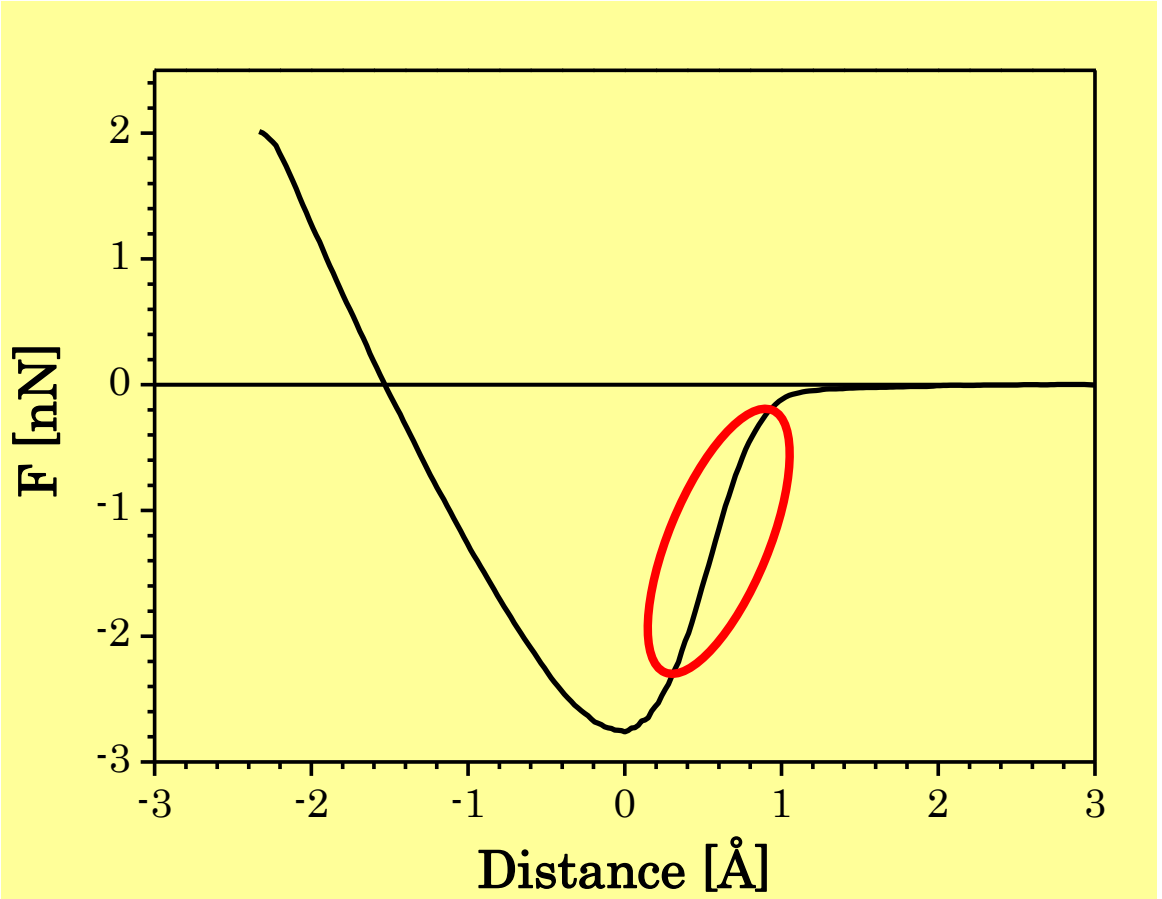
(two types of atomic processes)

Phys. Rev. Lett. 84 (2000) 5347

Acta Mater. 48 (2000) 4517

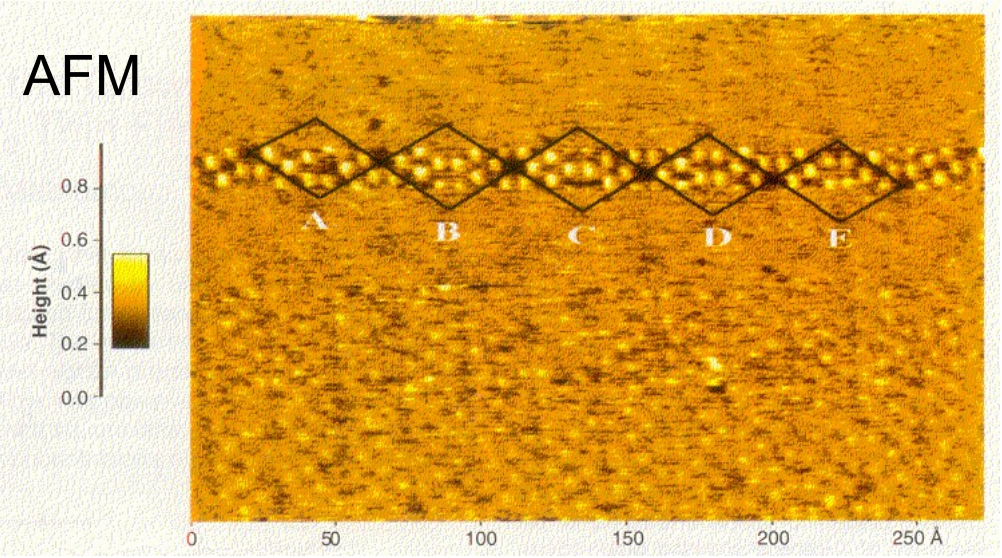
Atomic-scale AFM: a single atomic contact

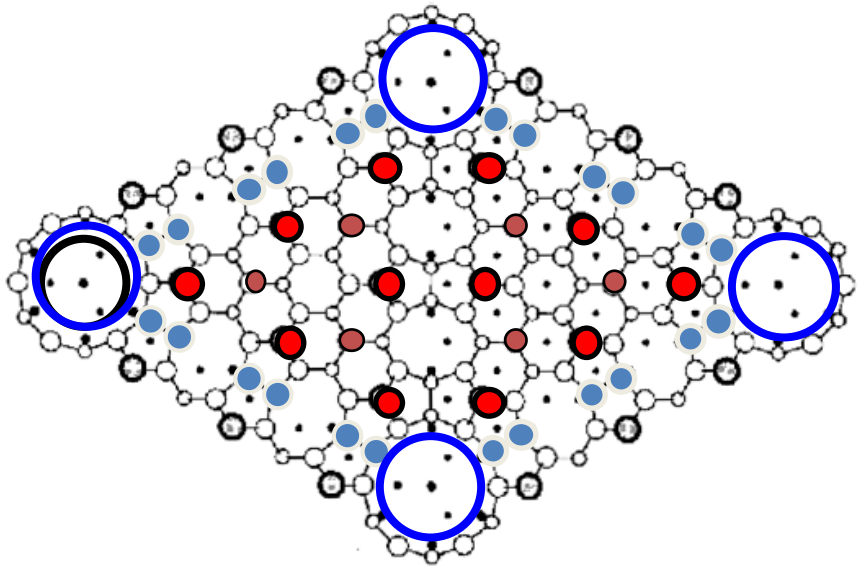




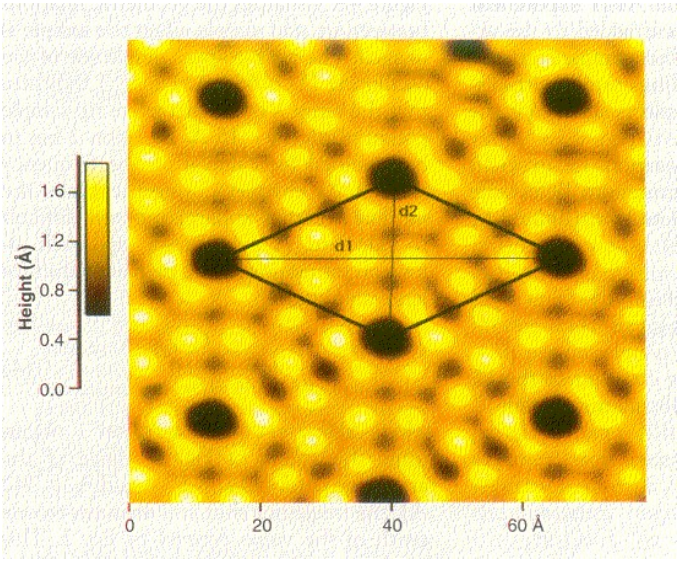
Atomic resolution in FM-AFM:Si(111)-7x7

AFM

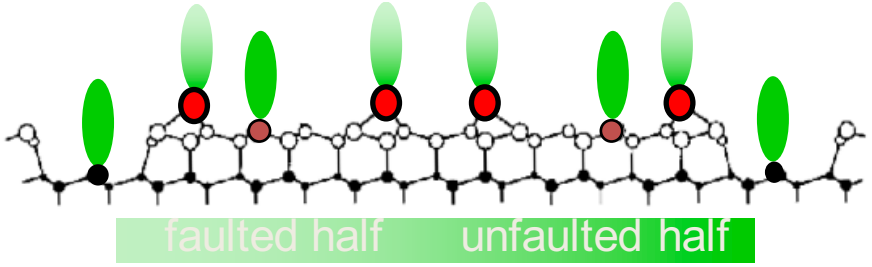




STM



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



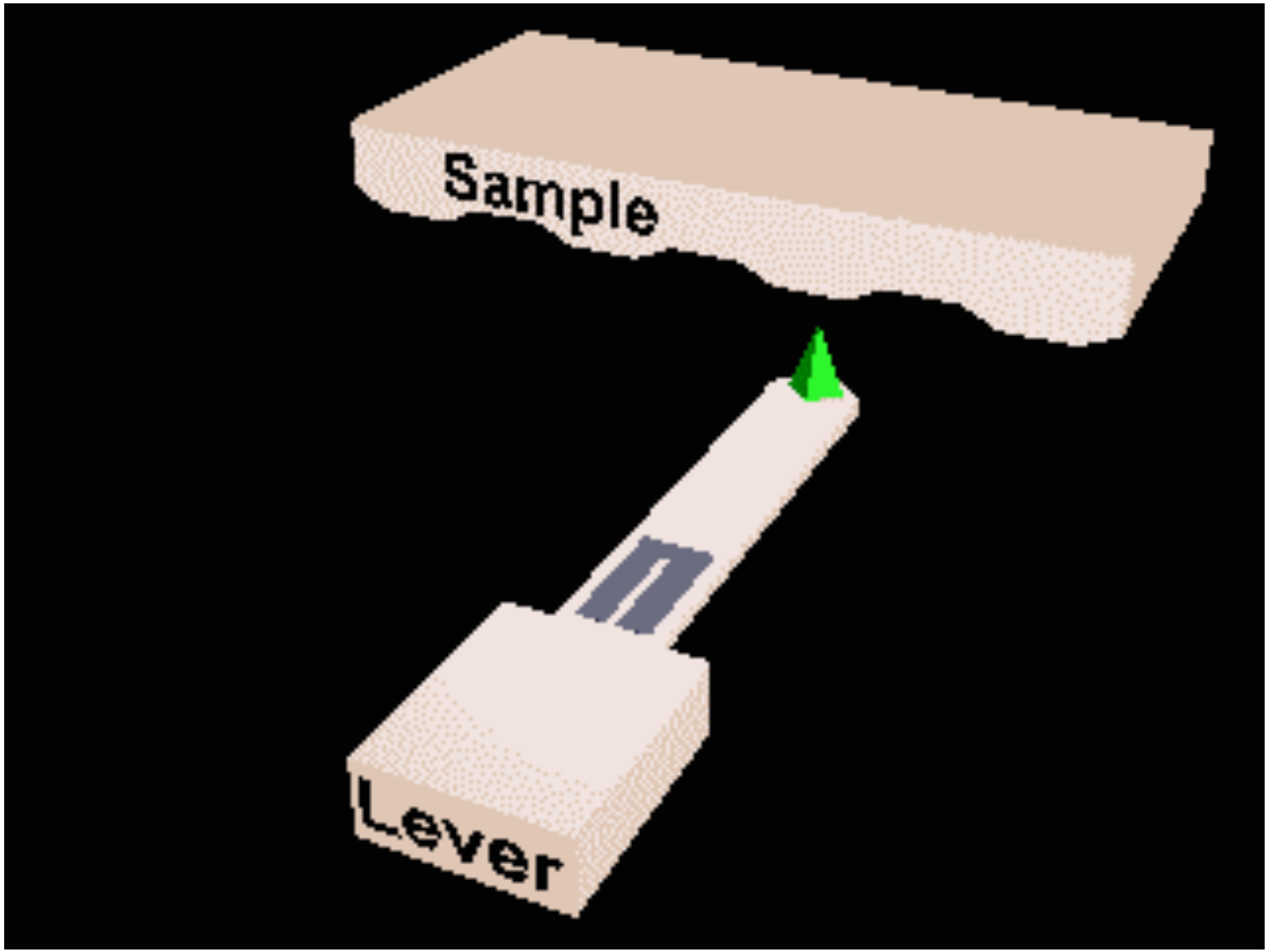
12 adatoms

6 rest atoms

corner hole

dimers

Dynamic AFM



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

Understanding the contrast in FM-AFM

VOLUME 78, NUMBER 4 PHYSICAL REVIEW LETTERS 27 JANUARY 1997

Role of Covalent Tip-Surface Interactions in Noncontact Atomic Force Microscopy on Reactive Surfaces

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Surface-tip interactions in noncontact atomic-force microscopy on reactive surfaces: Si(111)

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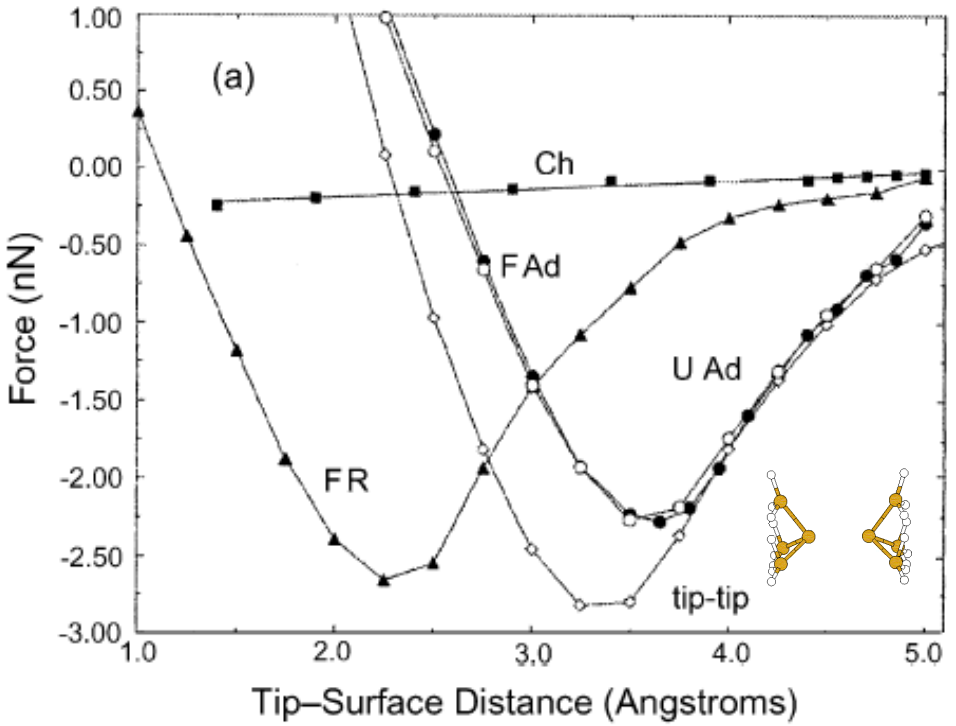
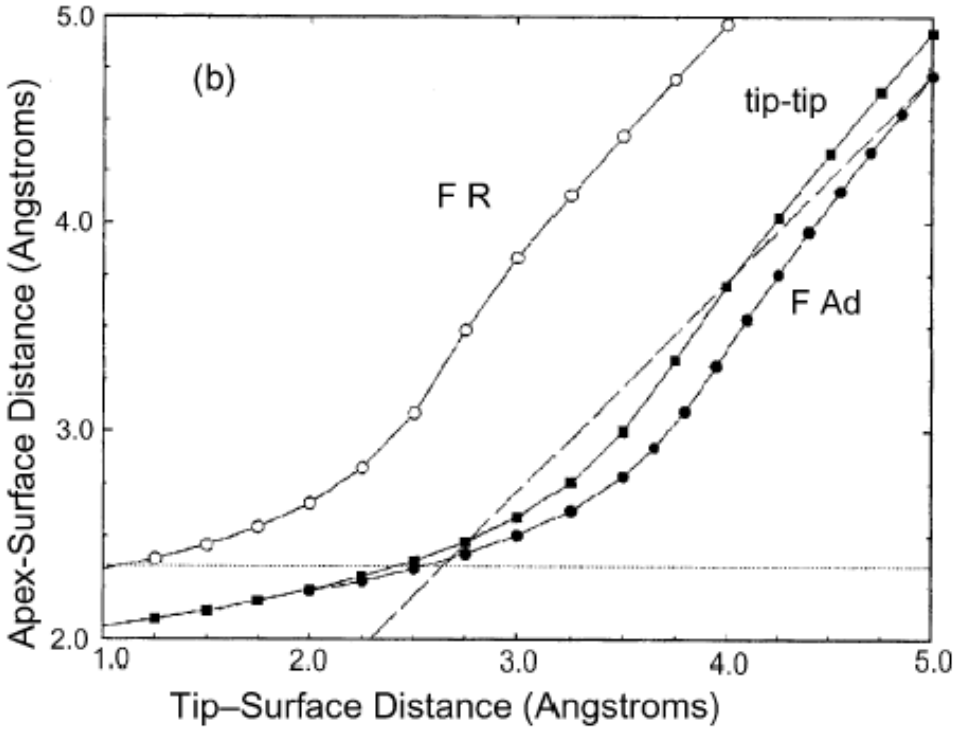
(Received 9 March 1998; revised manuscript received 11 May 1998)

Force-distance curves & Atomic relaxations

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

atomic relaxations due to tip-surface interactions!!

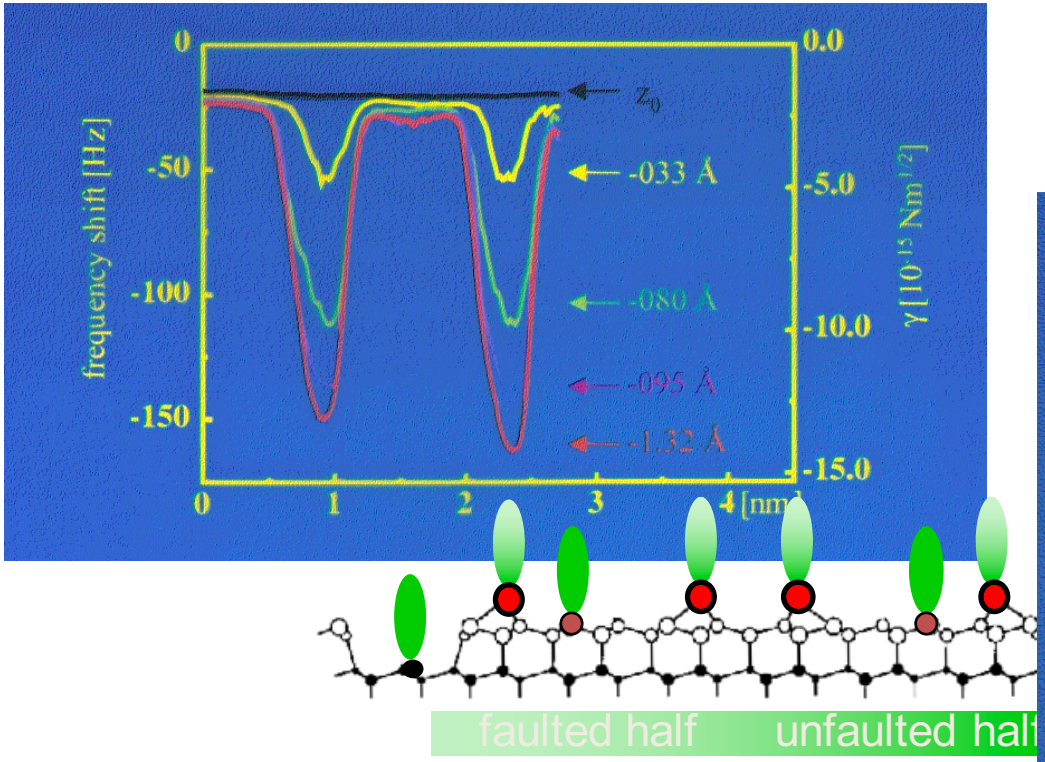




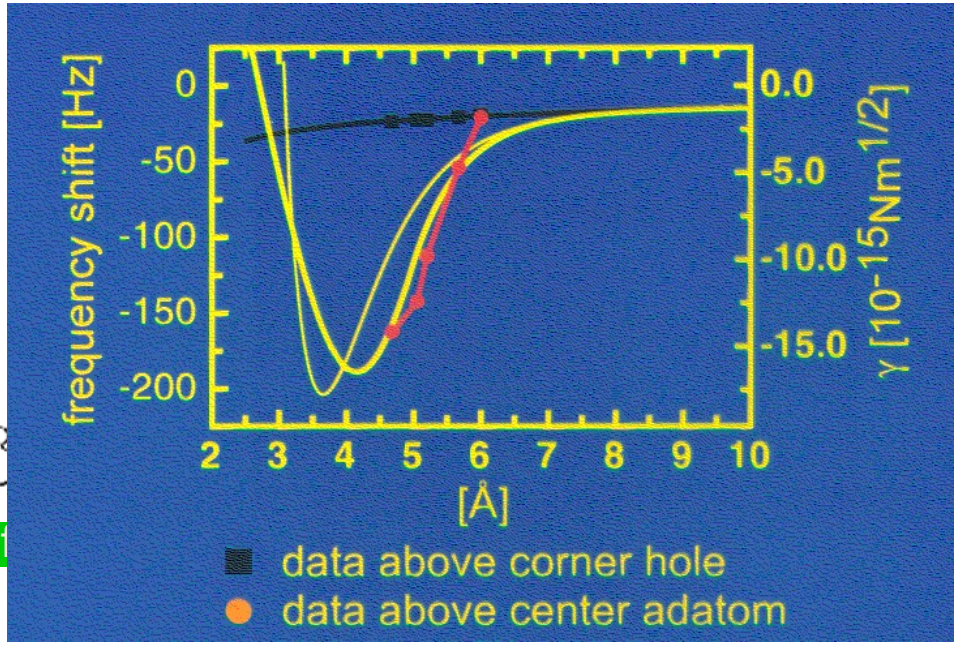
Force vs distance curves ➡ prediction for Δf vs distance

$$\Delta f\,(d) = -\frac{1}{2\pi}\frac{f_0}{kA_0}\int_0^{2\pi} F_{ts}\left[d + A_o(1+\cos\varphi)\right]\cos\varphi\, d\varphi$$

Comparison between theory and low-temperature FM-AFM experiments



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

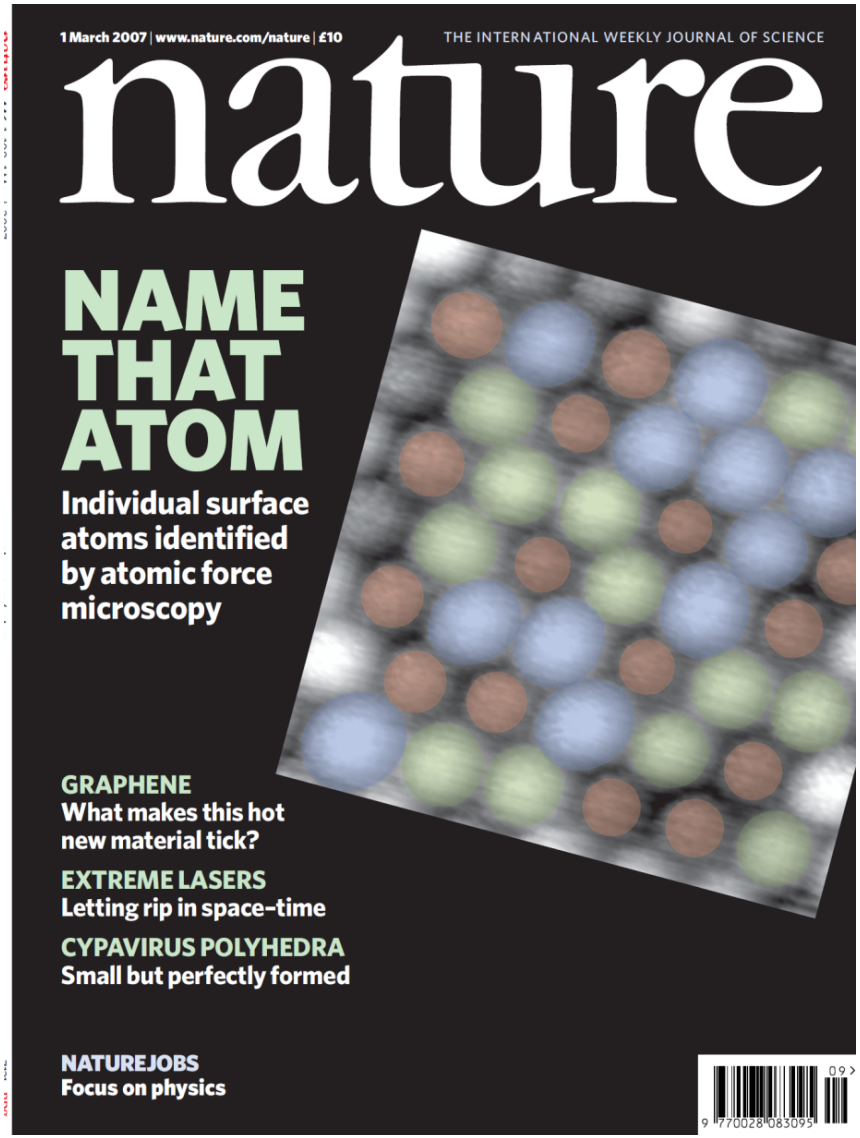
R. Pérez et al , PRL 78, 678 (1997)
R. Pérez et al , PRB 58, 10835 (1998)

nature Vol 446|1 March 2007|doi:10.1038/nature05530

Chemical identification of individual surface atoms by atomic force microscopy

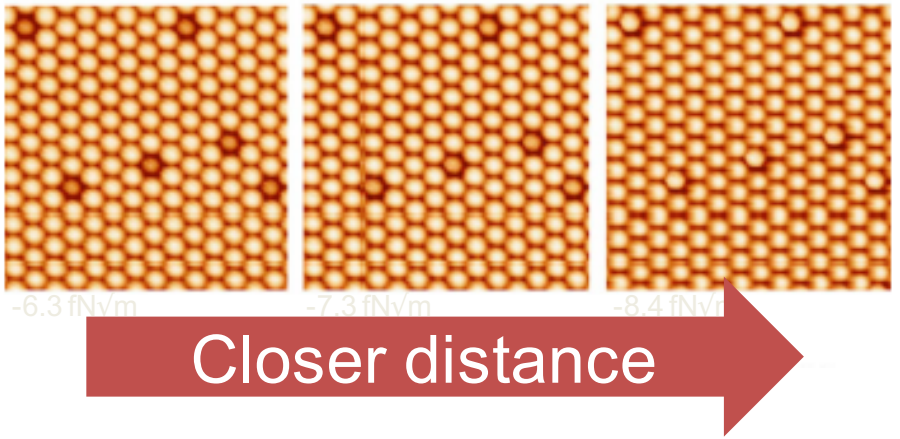
Y. Sugimoto et al Nature 446, 64 (2007).

Yoshiaki Sugimoto[1], Pablo Pou[2], Masayuki Abe[1,3], Pavel Jelinek[4], Rubén Pérez[2], Seizo Morita[1] & Óscar Custance[1]

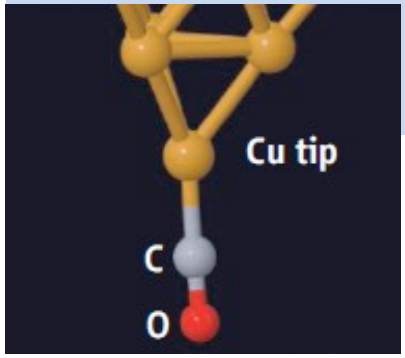


based on the relative interaction ratio of the maximum attractive force measured by dynamic force spectroscopy

HINT: changes in the topography of defects with the distance: access to the real surface structure?

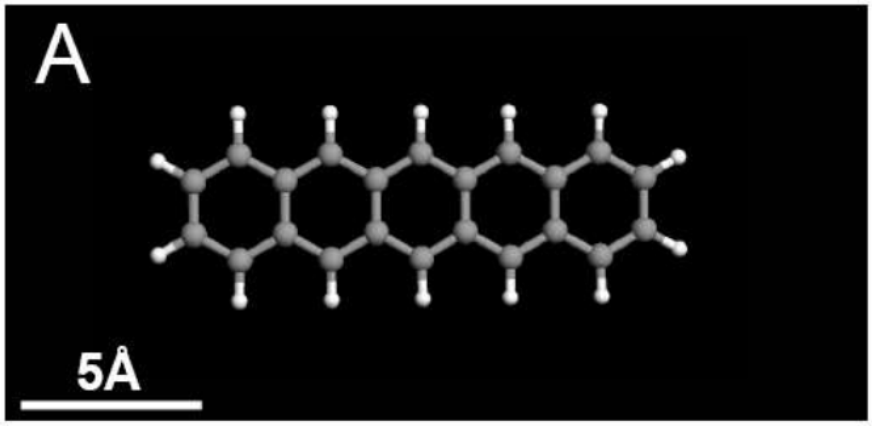


Y. Sugimoto et al Phys. Rev. B 73, 205329 (2006).

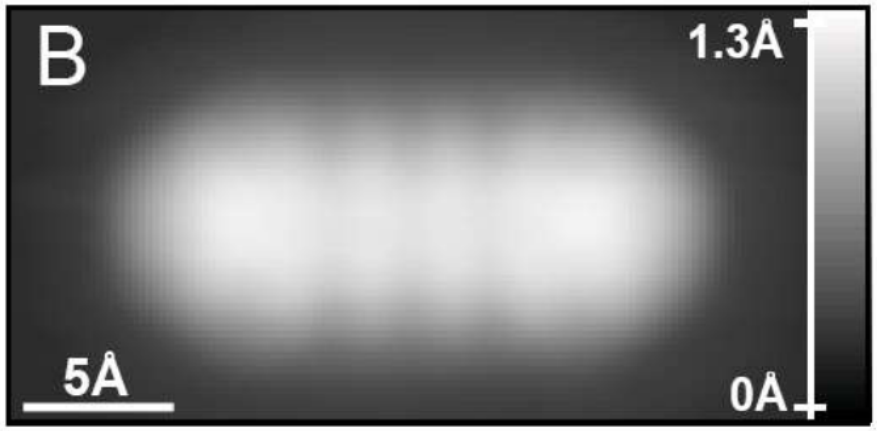


Chemical Structure Resolved by AFM

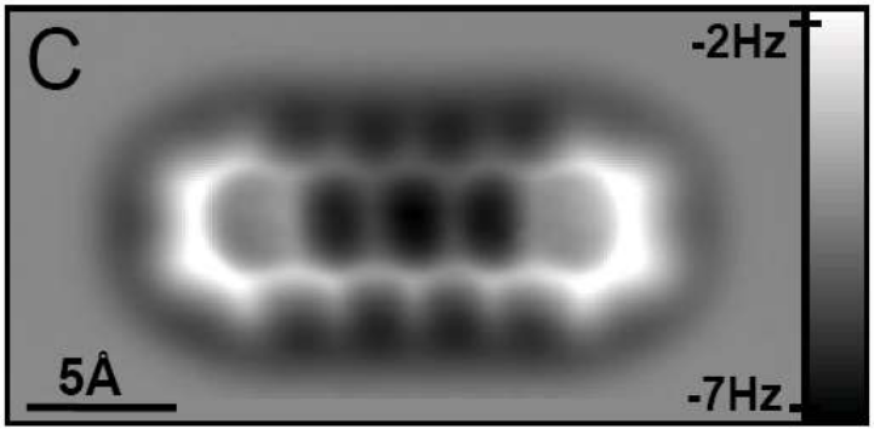
Pentacene/2(NaCl)/Cu(111) imaged with a CO Tip



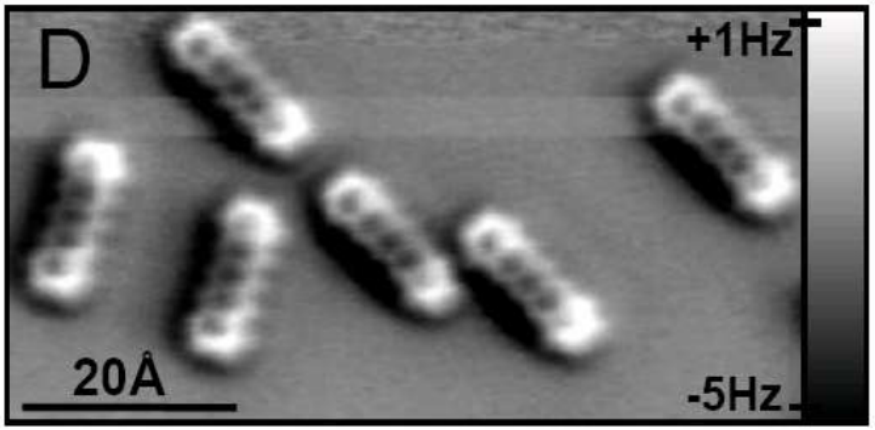
Model



STM (I = 110 pA, V = 170 mV)



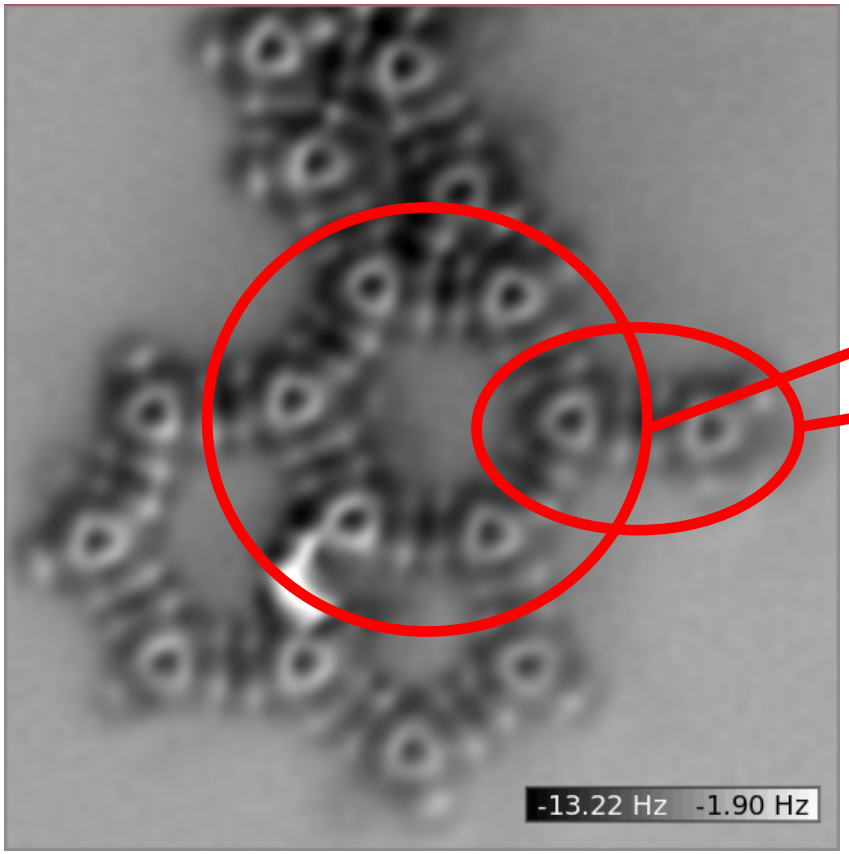
AFM (z = -0.1 Å, A = 0.2 Å)

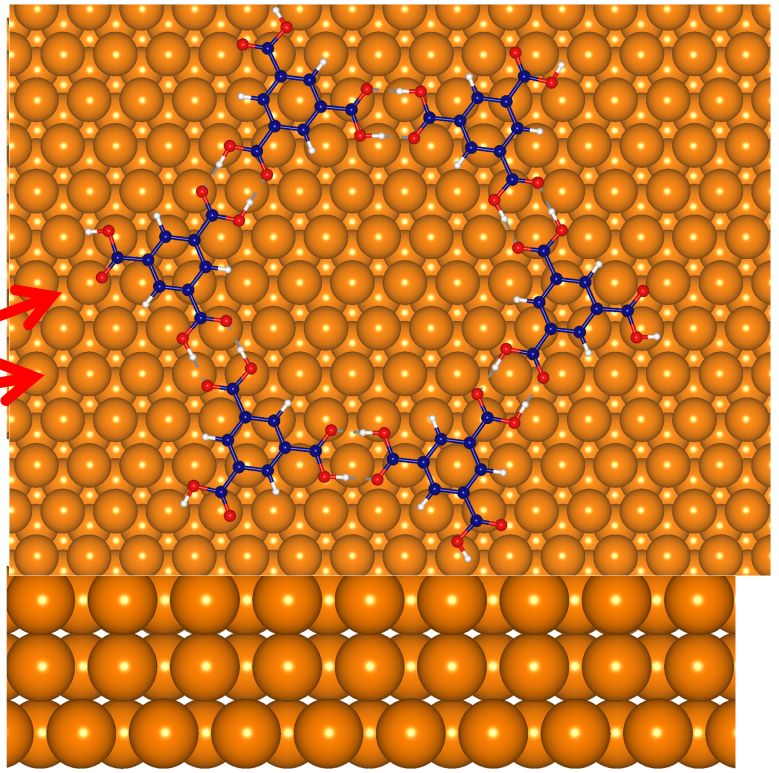


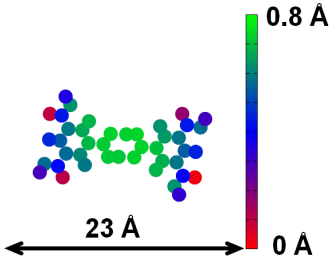
AFM (z = 0.0 Å, A = 0.8 Å)

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

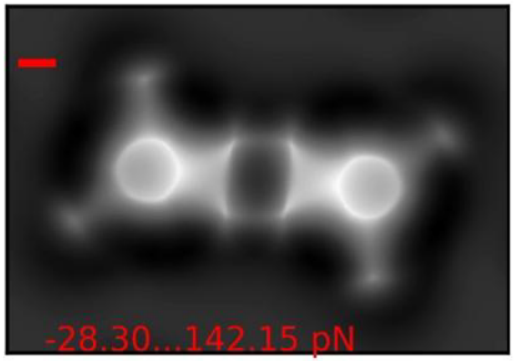
TMA networks on Cu(111)

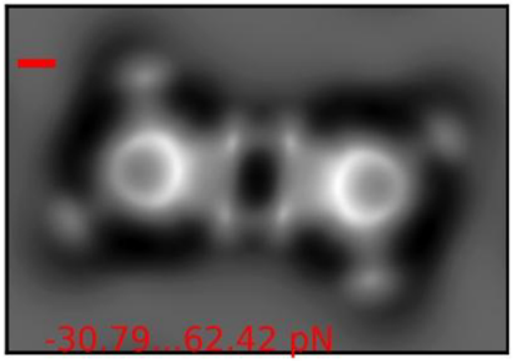


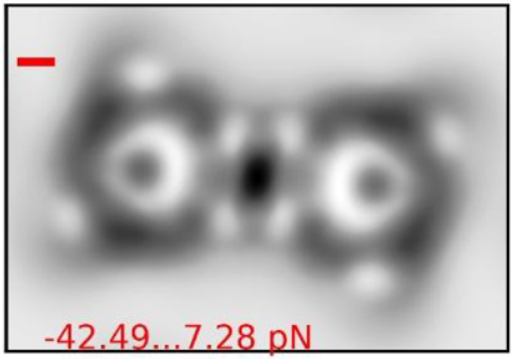




Z_{max} = 3.29 Å
Z_{min} = 2.58 Å
Z_{av} = 3.08 Å
ΔZ = 0.71 Å







Our approach for HR-AFM simulations

A total potential split in four contributions:

$$V(R_{\mathrm{tip}}, \theta, \varphi) = V_{\mathrm{ES}} + V_{\mathrm{SR}} + V_{\mathrm{vdW}} + V_{\mathrm{tilt}}$$

(1) electrostatic:

$$V_{\mathrm{ES}} = \int \rho^{\mathrm{tip}}(\mathbf{r}, R_{\mathrm{tip}}, \theta, \varphi)\phi^{\mathrm{sam}}(\mathbf{r})d\mathbf{r}$$

(2) short range:

$$V_{\mathrm{SR}} = V_0 \int [\rho^{\mathrm{tip}}(\mathbf{r}, R_{\mathrm{tip}}, \theta, \varphi)\rho^{\mathrm{sam}}(\mathbf{r})]^{\alpha} d\mathbf{r}$$

Two DFT inputs
Charge density ρ^{tip} ρ^{sam}
Local potential ϕ^{sam}

Two (universal) fitting parameters
α V_0

(3) van der Waals: → From DFT (D2/D3)

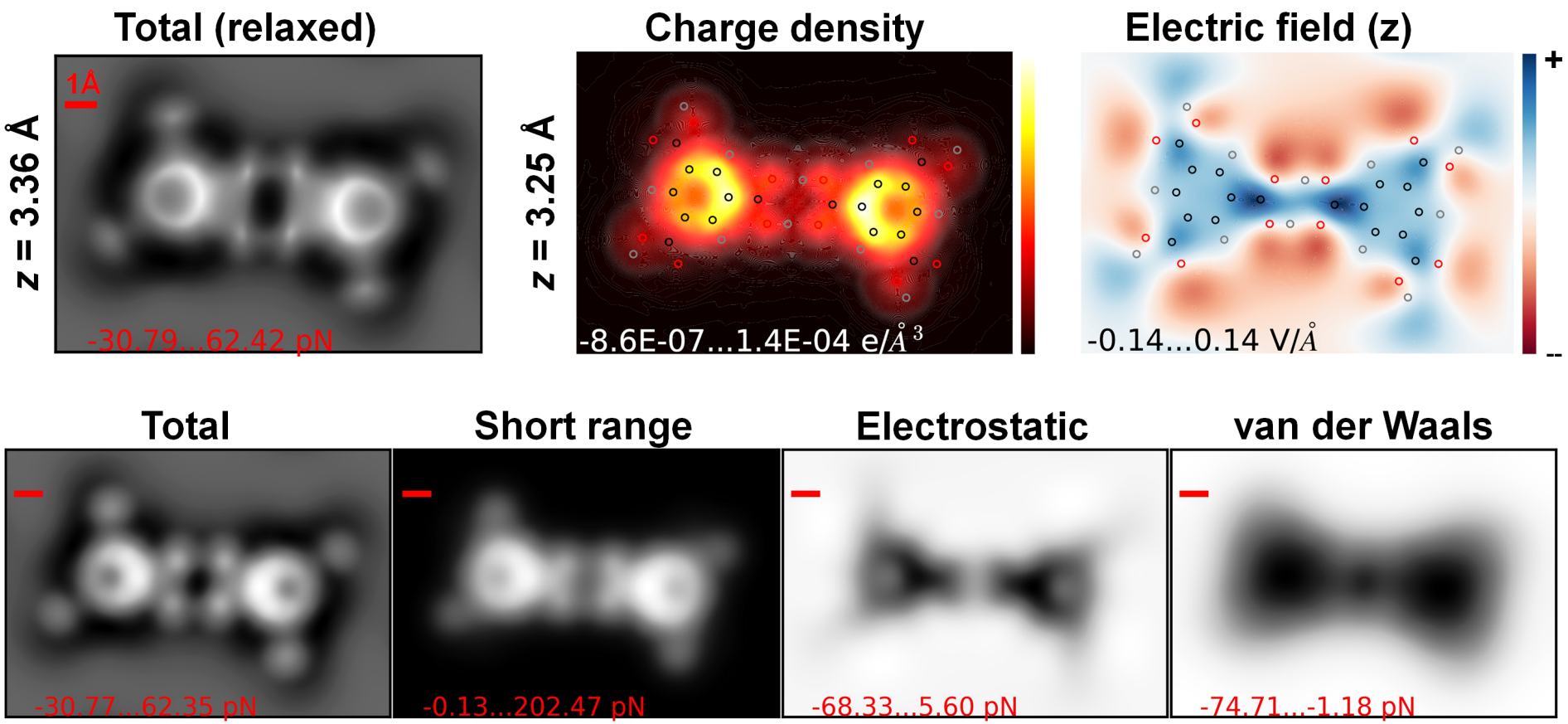
(4) tilting: $V_{\mathrm{tilt}} = \frac{1}{2}\kappa\theta^2$ Spring constant ≈ 0.01 Ha/rad^2

M. Ellner, et al., Nanoletters 16, 1974 (2016)

M. Ellner, P. Pou, RP, PRB 76, 075418 (2017)

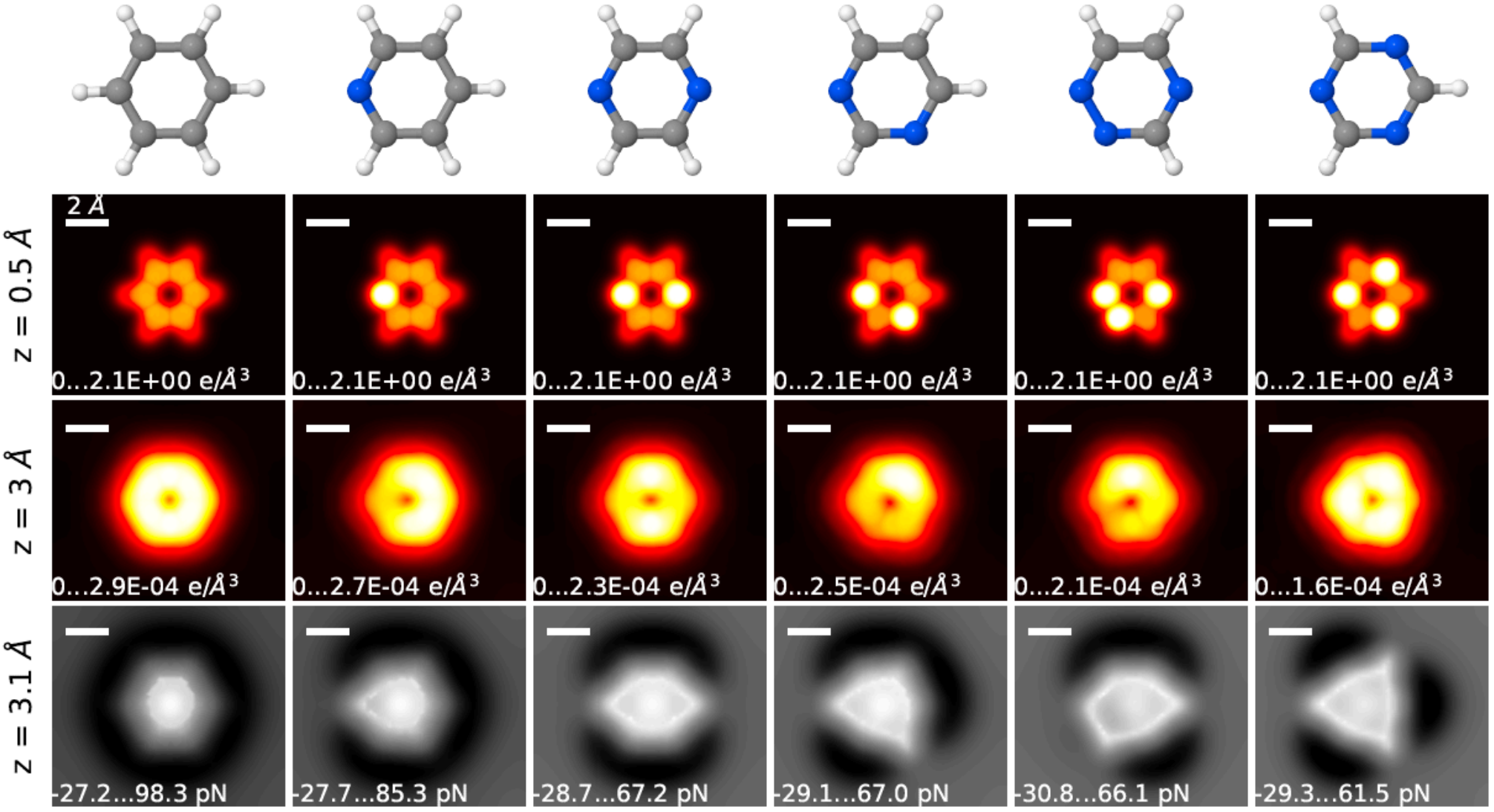
M. Ellner, P. Pou, RP, ACS Nano **13** (2019) 786

AFM imaging analysis



Six-membered rings with N heteroatoms

fingerprints for molecular ID



M. Ellner, P. Pou, R. Perez, ACS Nano 13, 786 (2019)

Gaining insight into the mechanical response...

- Nanoindentation. PRL 75 (1995) 4748

  defect nucleation

  permanent damage

- Wear: diamond polishing. PRL 80 (1998) 3428

- Mechanical resistance of diamond tips and surfaces. PRL 86 (2001) 1287

  Maximum force: 30 nN !!

  Contamination effects PRL 78 (1997) 0678

- Atomic contrast in FM-AFM. PRB 58 (1998) 10835

"The mechanical properties of materials are ultimately determined by events occurring on the atomic scale."