Probing nanostructures with forces and currents: From atomic-scale contrast on graphene and carbon nanotubes to heterofullerene synthesis with planar aromatic precursors

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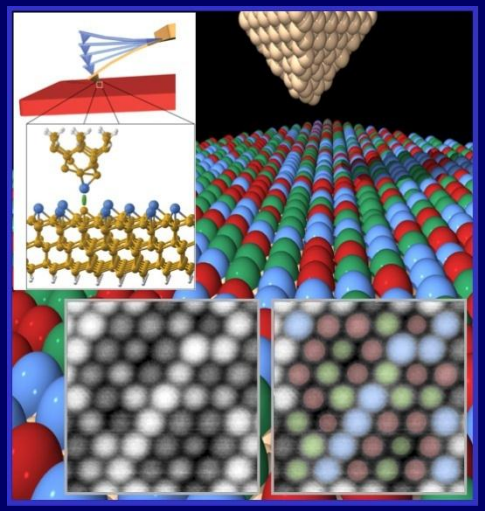
http://www.uam.es/spmth



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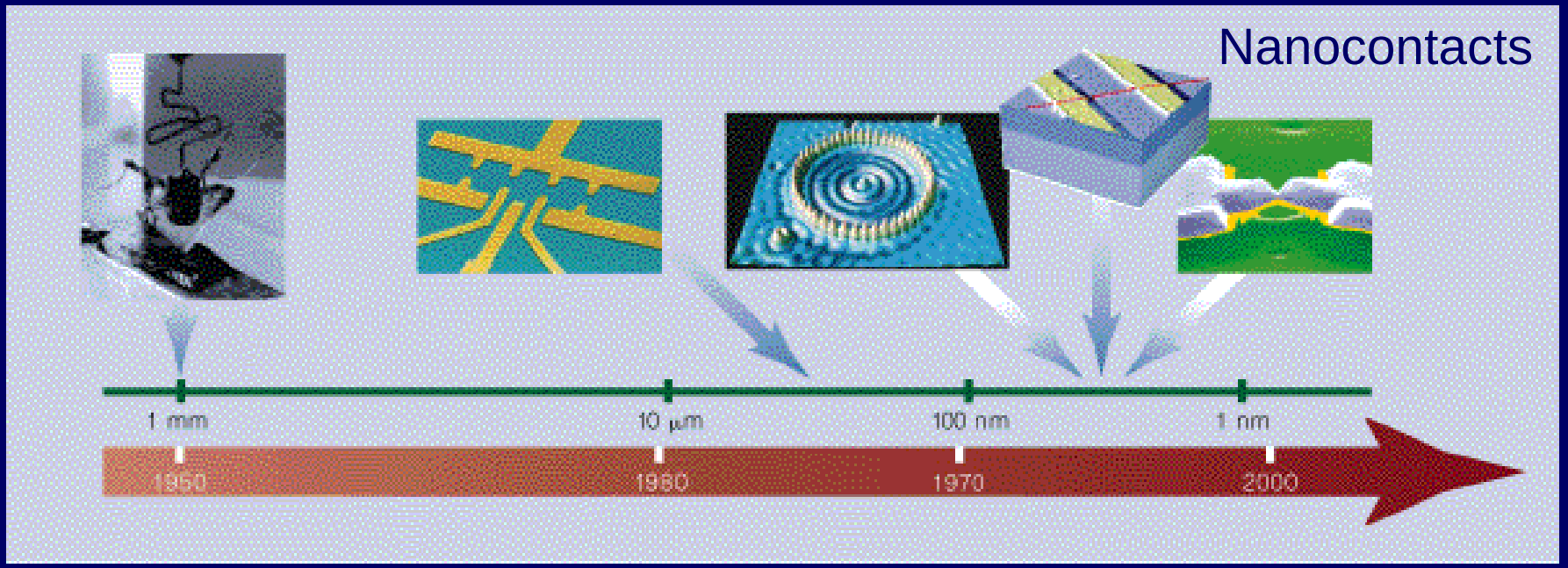
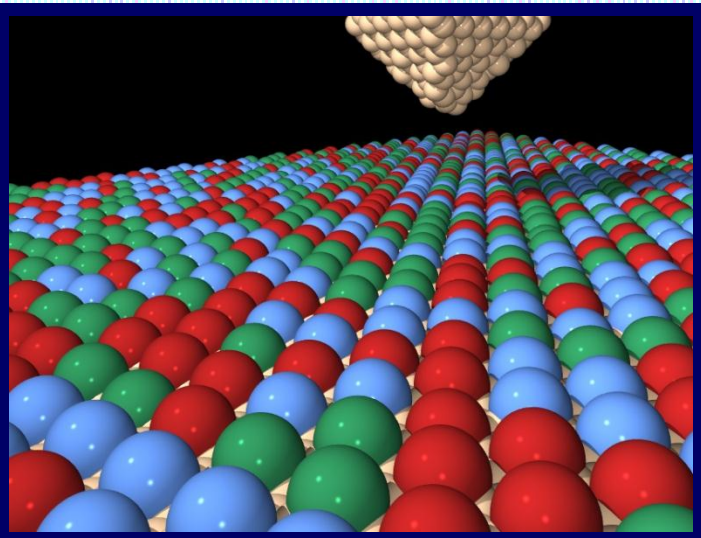
Seminar Dresde 30/06/2011

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

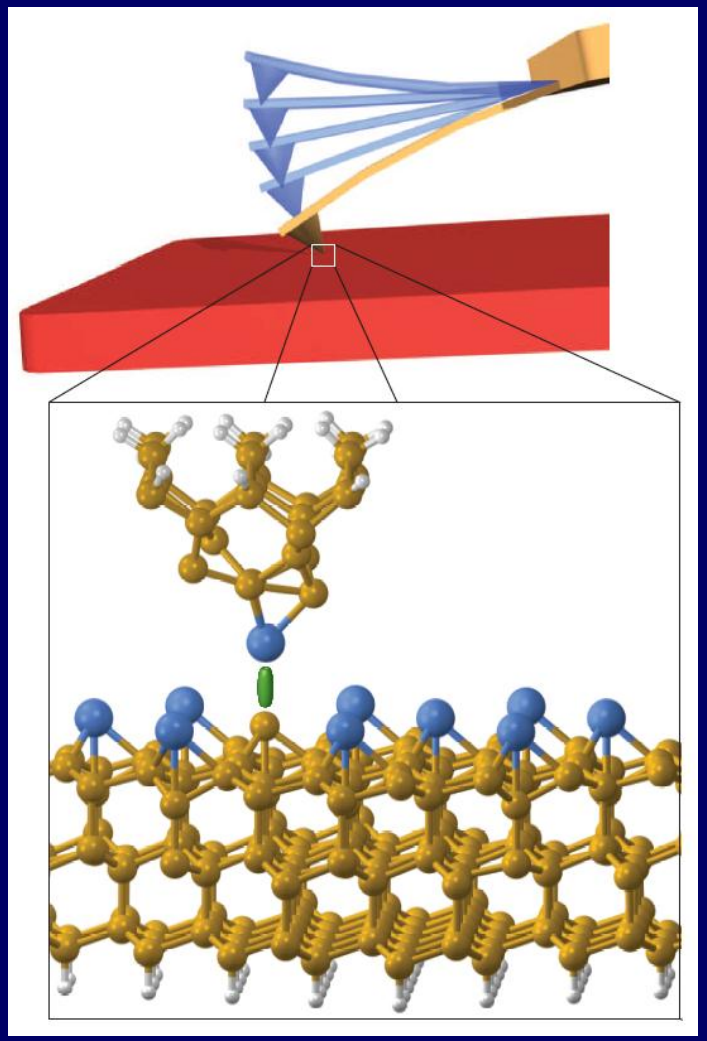


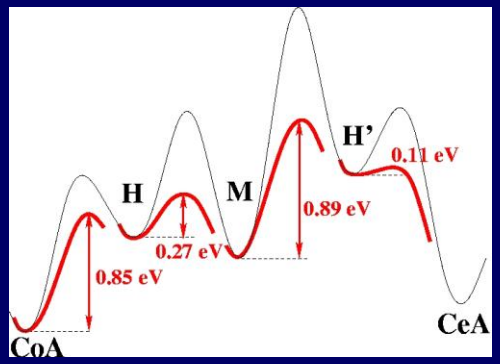
Scanning Probe Microscopes (SPMs):

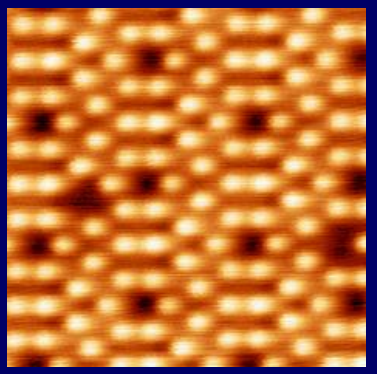
- Scanning Tunneling Microscope (STM)
- Atomic Force Microscope (AFM)
- …

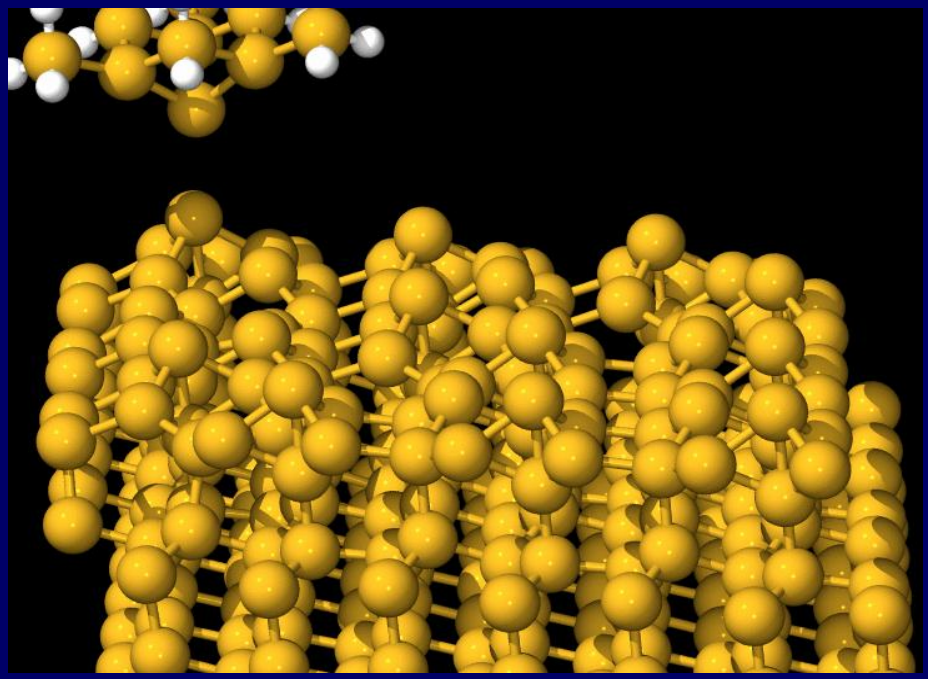


Forces & Transport in Nanostructures: First-principles calculations









STM & AFM Imaging

Single-atom manipulation

Methodology

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

Ab-initio total energy methods

(based in Density Functional Theory)

Non-equilibrium Green's Functions

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

Linked with the local orbital description

Structure + electronic properties

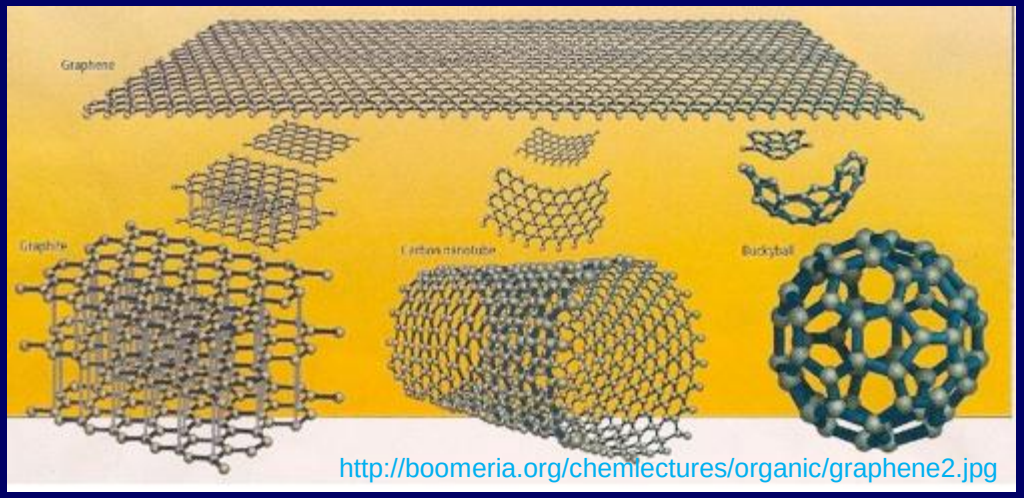
Electronic transport

FIREBALL, OPENMX
CASTEP, VASP + vdW corrections

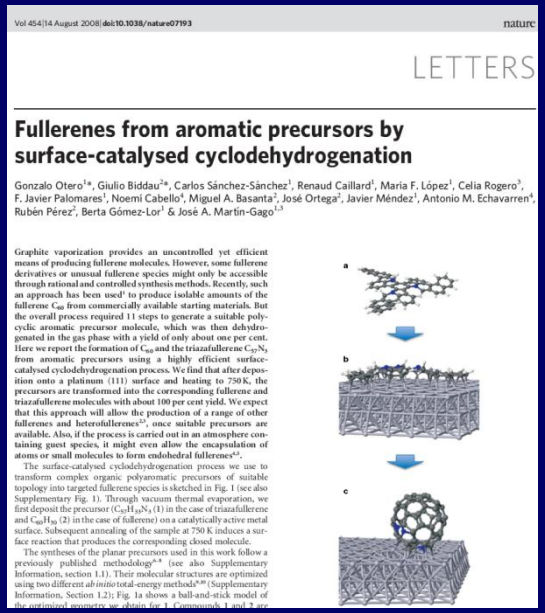
Low-dimensional carbon materials

outstanding electronic and mechanical properties

- Graphene and graphene nanoribbons (2D)
- Carbon Nanotubes (1D)
- Fullerenes (0D)



http://boomeria.org/chemlectures/organic/graphene2.jpg


Vol 454|14 August 2008|doi:10.1038/nature07193 nature

LETTERS

Fullerenes from aromatic precursors by surface-catalysed cyclodehydrogenation

Gonzalo Otero[1]*, Giulio Biddau[2]*, Carlos Sánchez-Sánchez[1], Renaud Caillard[1], María F. López[1], Celia Rogero[3], F. Javier Palomares[1], Noemí Cabello[4], Miguel A. Basanta[2], José Ortega[2], Javier Méndez[1], Antonio M. Echavarren[4], Rubén Pérez[2], Berta Gómez-Lor[1] & José A. Martín-Gago[1,3]

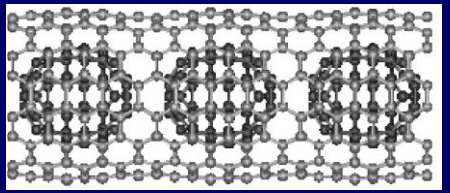
Graphite vaporization provides an uncontrolled yet efficient means of producing fullerene molecules. However, some fullerene derivatives or unusual fullerene species might only be accessible through rational and controlled synthesis methods. Recently, such an approach has been used[1] to produce isolable amounts of the fullerene C_{60} from commercially available starting materials. But the overall process required 11 steps to generate a suitable polycyclic aromatic precursor molecule, which was then dehydrogenated in the gas phase with a yield of only about one per cent. Here we report the formation of C_{60} and the triazafullerene $C_{57}N_3$ from aromatic precursors using a highly efficient surface-catalysed cyclodehydrogenation process. We find that after deposition onto a platinum (111) surface and heating to 750 K, the precursors are transformed into the corresponding fullerene and triazafullerene molecules with about 100 per cent yield. We expect that this approach will allow the production of a range of other fullerenes and heterofullerenes[2,3], once suitable precursors are available. Also, if the process is carried out in an atmosphere containing guest species, it might even allow the encapsulation of atoms or small molecules to form endohedral fullerenes[4,5].

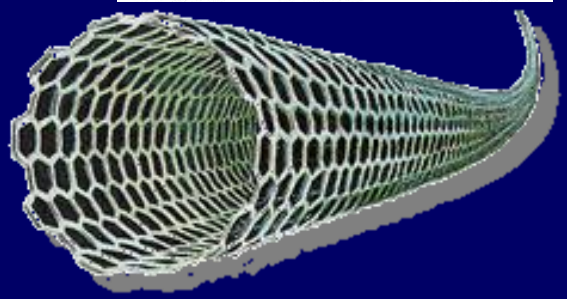
The surface-catalysed cyclodehydrogenation process we use to transform complex organic polyaromatic precursors of suitable topology into targeted fullerene species is sketched in Fig. 1 (see also Supplementary Fig. 1). Through vacuum thermal evaporation, we first deposit the precursor ($C_{60}H_{28}N_4$ (1) in the case of triazafullerene and $C_{60}H_{30}$ (2) in the case of fullerene) on a catalytically active metal surface. Subsequent annealing of the sample at 750 K induces a surface reaction that produces the corresponding closed molecule.

The syntheses of the planar precursors used in this work follow a previously published methodology[6,7] (see also Supplementary Information, section 1.1). Their molecular structures are optimized using two different *ab initio* total-energy methods[8,9] (Supplementary Information, Section 1.2); Fig. 1a shows a ball-and-stick model of the optimized geometry we obtain for 1. Compounds 1 and 2 are

And more: Controlled doping of carbon materials:

- Endo & exofullerenes, heterofullerenes, doped nanotubes and graphene nanoribons, peapods,…





Tools to visualize, characterize and manipulate at the atomic scale: key step in turning these expectations into real devices

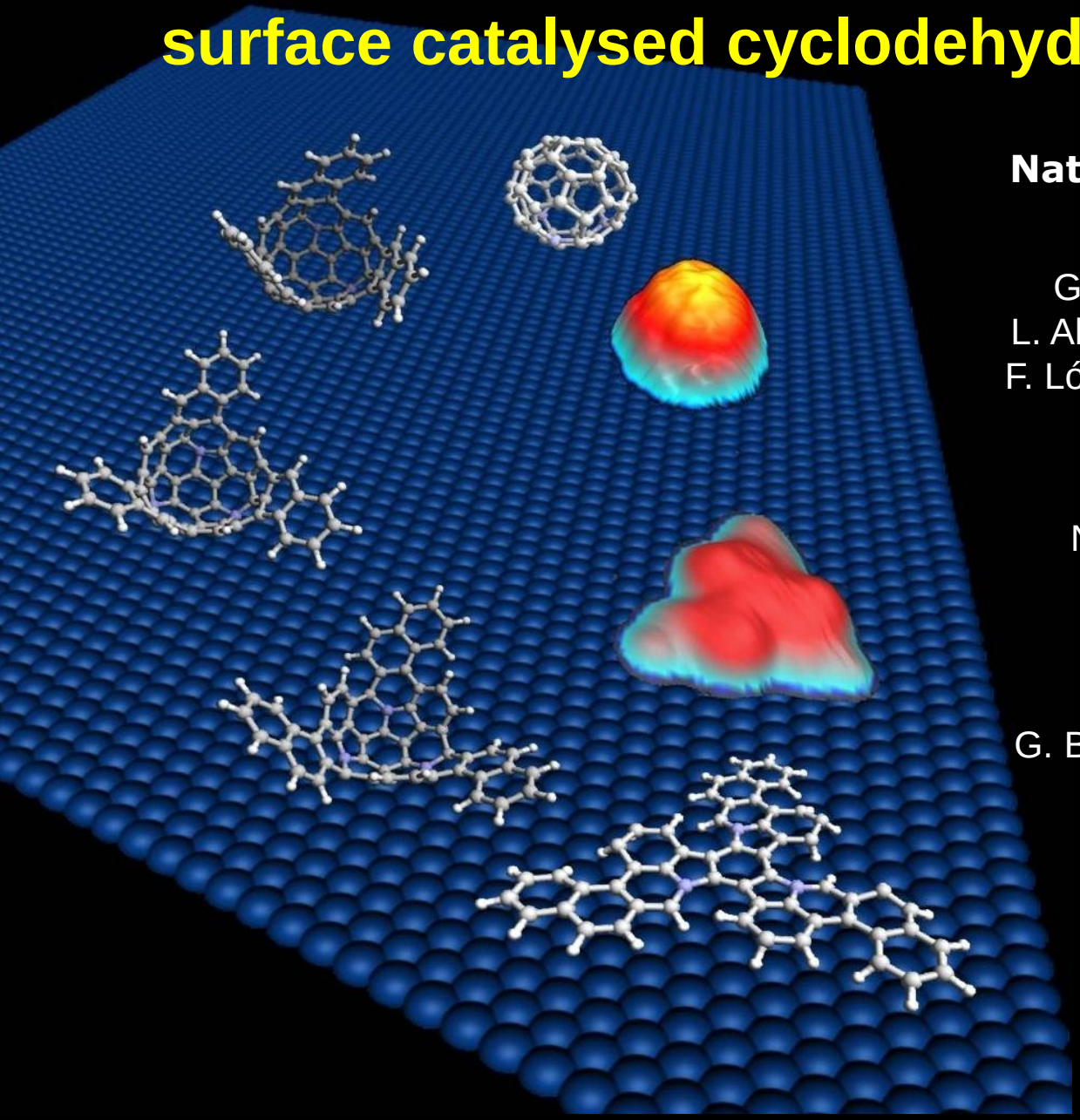
Outline

1. **Frequency Modulation (FM) -AFM in a nutshell**

2. **Forces and currents in carbon nanostructures**
   Atomic contrast: PRL (29/04/2011, Editors' suggestion)
   Vacancies on Graphene/Pt(111): PRL (accepted)
   Are these defects magnetic?

3. **Heterofullerenes from planar precursors:**
   Atomic-scale Origami: Nature 454, 865 (2008)
   Surface induced enantiomeric recognition:
   Chem. Euro.J. 6, 3920 (2010)
   Vacancy network in Pt induced by C_{60}
   Nature Materials (submitted)

Fullerenes from aromatic precursors by surface catalysed cyclodehydrogenation



Nature 454, 865 (2008)

G. Otero, C. Sánchez-Sánchez, L. Alvarez, R. Caillard, C. Rogero, M. F. López, F. J. Palomares, J. Méndez, José A. Martín-Gago
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(ICIQ, ICMM)

G. Biddau, M. A. Basanta, J. Ortega, R. Pérez
(UAM)

2. Frequency Modulation-AFM in a nutshell

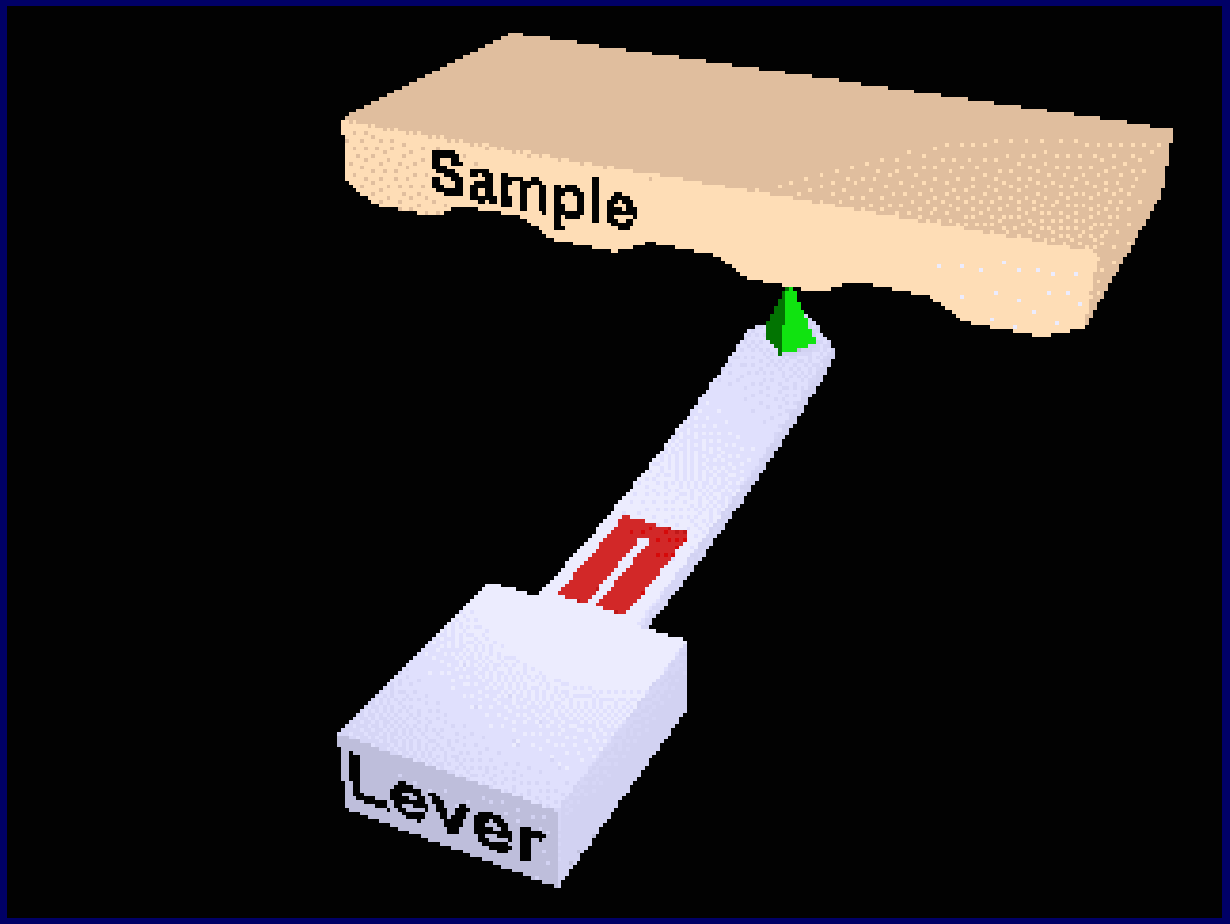
Developing new capabilities for the FM-AFM

Chemical identification: Nature 446, 64 (2007)

Atom Manipulation: Science 322, 413 (2008)

ATOMIC FORCE MICROSCOPY (AFM)

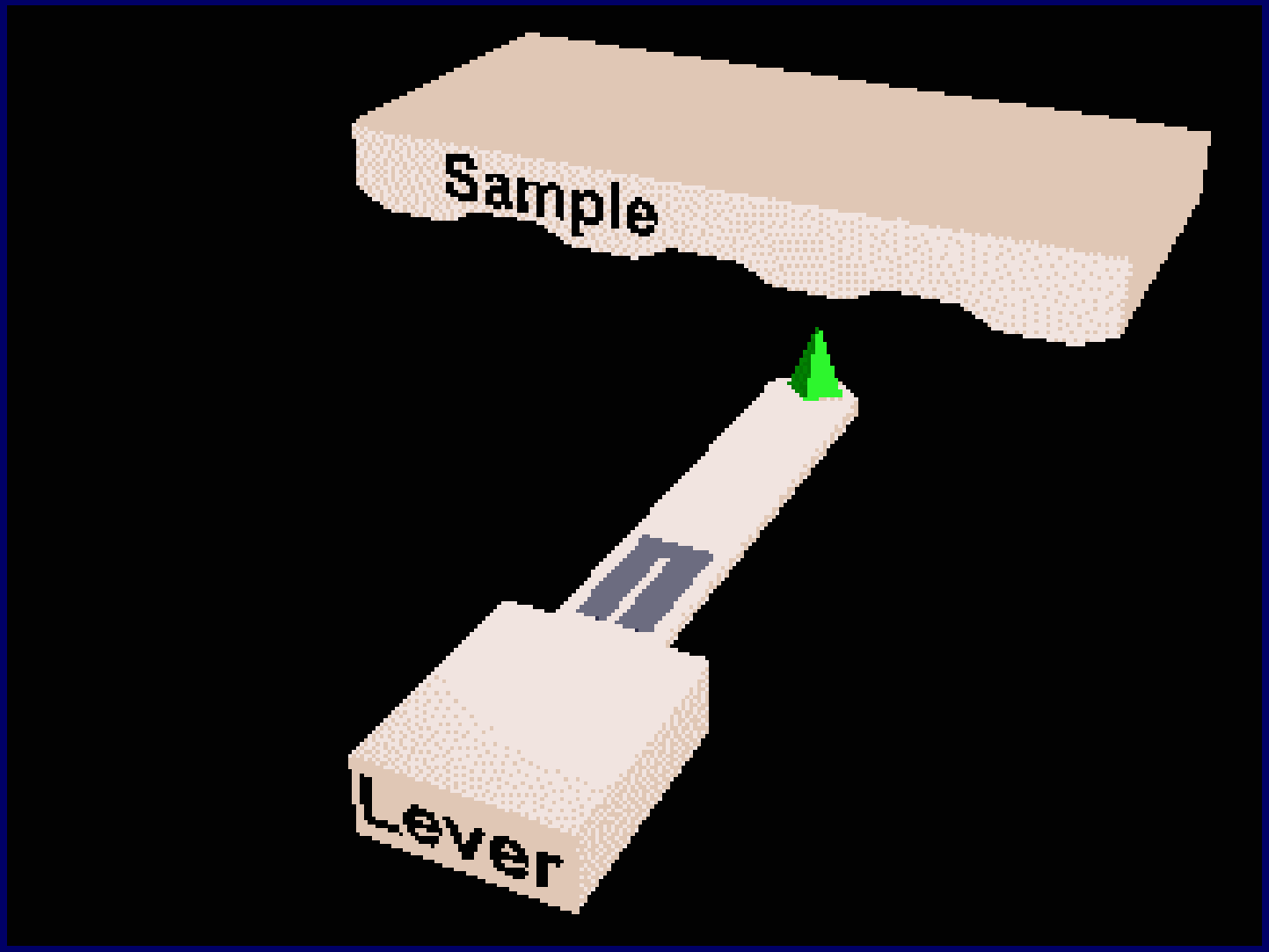
G. Binnig, C. Gerber & C. Quate, PRL 56 (1986) 930



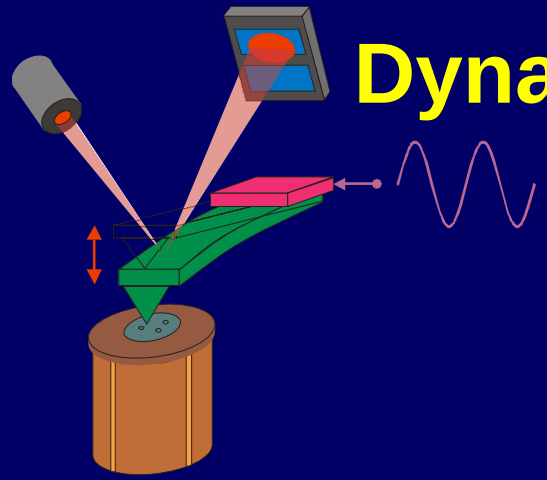
2nd most cited PRL: +5000 citations !!!

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

Dynamic AFM

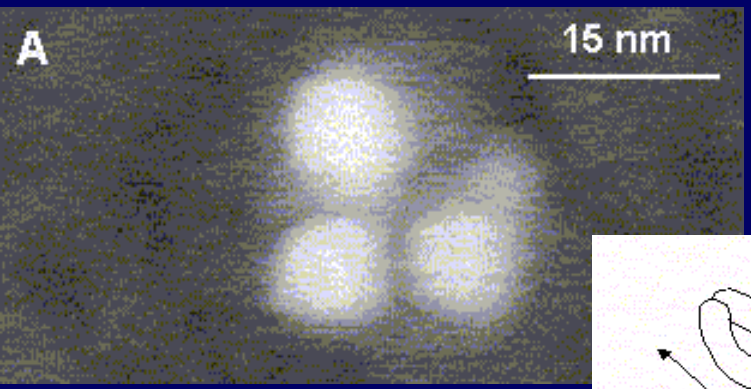


http://monet.physik.unibas.ch/famars/afm_prin.htm

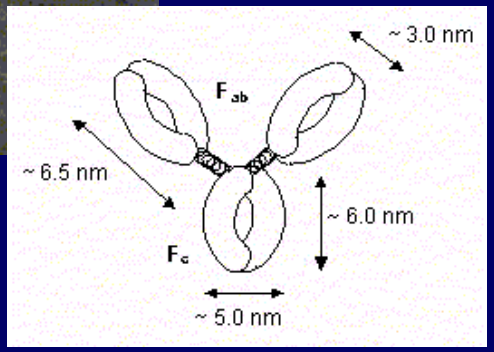


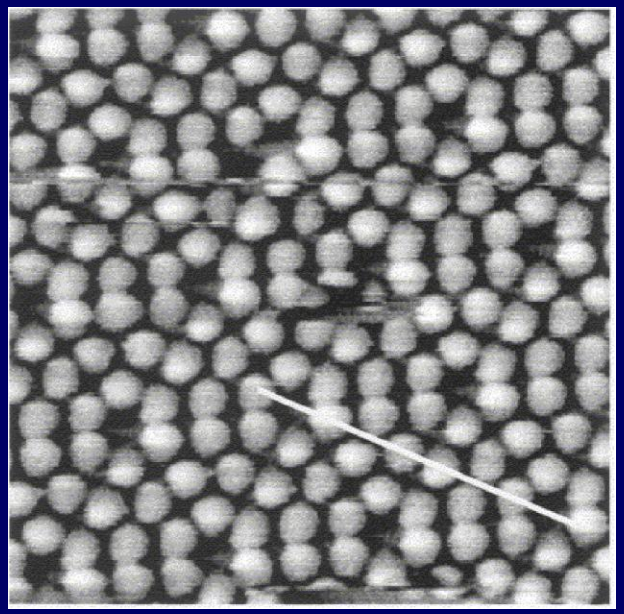
Dynamic AFM: Our Goal

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.

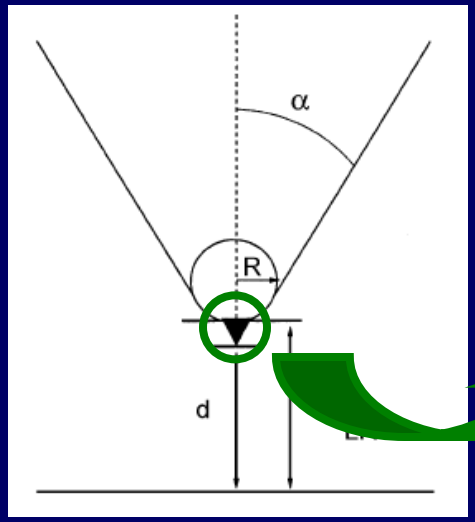
•Resolve atomic-scale defects in UHV.

FM-dAFM

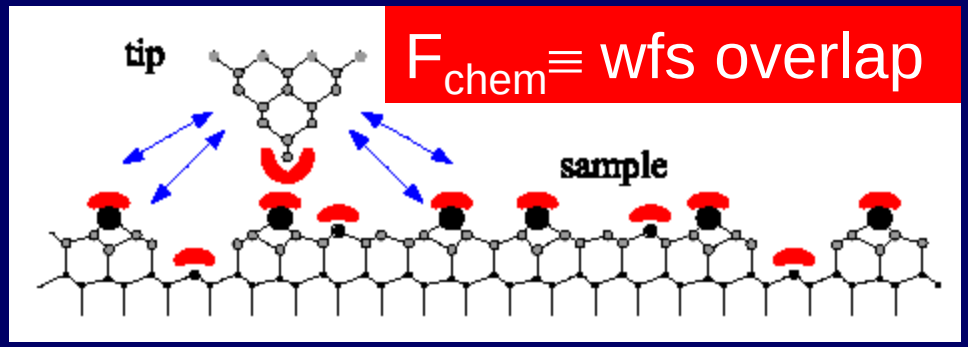
R. García and R. Pérez, Surf. Sci. Rep. 47, 197 (2002)

Tip-sample Interaction: $F_V + F_{vdW} + F_{chem}$

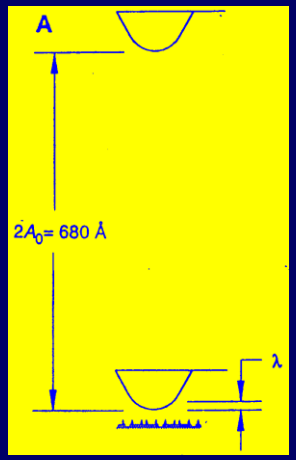
$$F_{\mathrm{V}} = -\pi\epsilon_0 (V_{\mathrm{s}} - V_{\mathrm{c}})^2 \left\{ \frac{R}{d_{\mathrm{LR}}} + s(\alpha) \left[\ln\left(\frac{L}{d_{\mathrm{LR}} + R_\alpha} \right) - 1 \right] - \frac{R[1 - s(\alpha)\cos^2\alpha/\sin\alpha]}{d_{\mathrm{LR}} + R_\alpha} \right\}$$

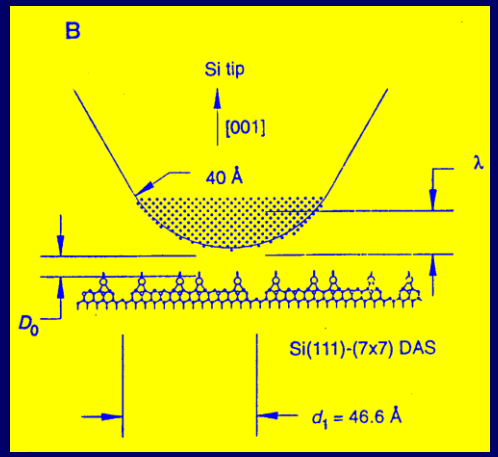


$$F_{\mathrm{vdW}} = -\frac{H}{6} \left\{ \frac{R}{d_{\mathrm{LR}}^2} + \frac{\tan^2\alpha}{d_{\mathrm{LR}} + R_\alpha} - \frac{R_\alpha}{d_{\mathrm{LR}}(d_{\mathrm{LR}} + R_\alpha)} \right\}$$



F_{chem}≡ wfs overlap





Exp: A = 340 Å !!!, R = 40 Å

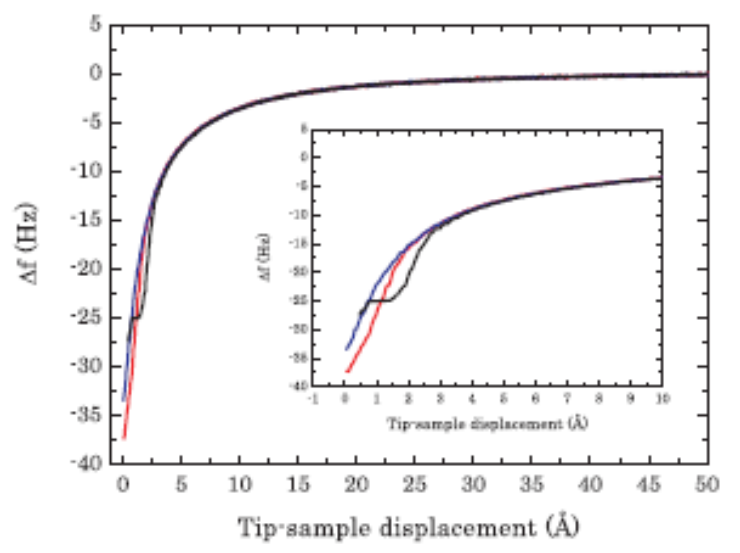
Sensitivity to Short-Range Forces?

$$\Delta f(d) = \frac{f_0}{\pi k a_1} \int_{-1}^{1} F_{\mathrm{ts}}[d + a_1(1+u)] u \frac{\mathrm{d}u}{\sqrt{1-u^2}}$$

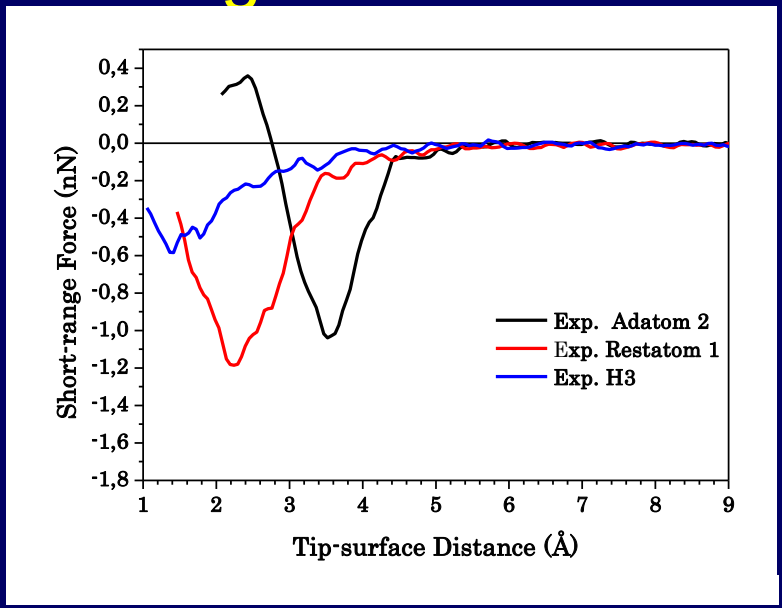
$$u = \cos(\omega t)$$

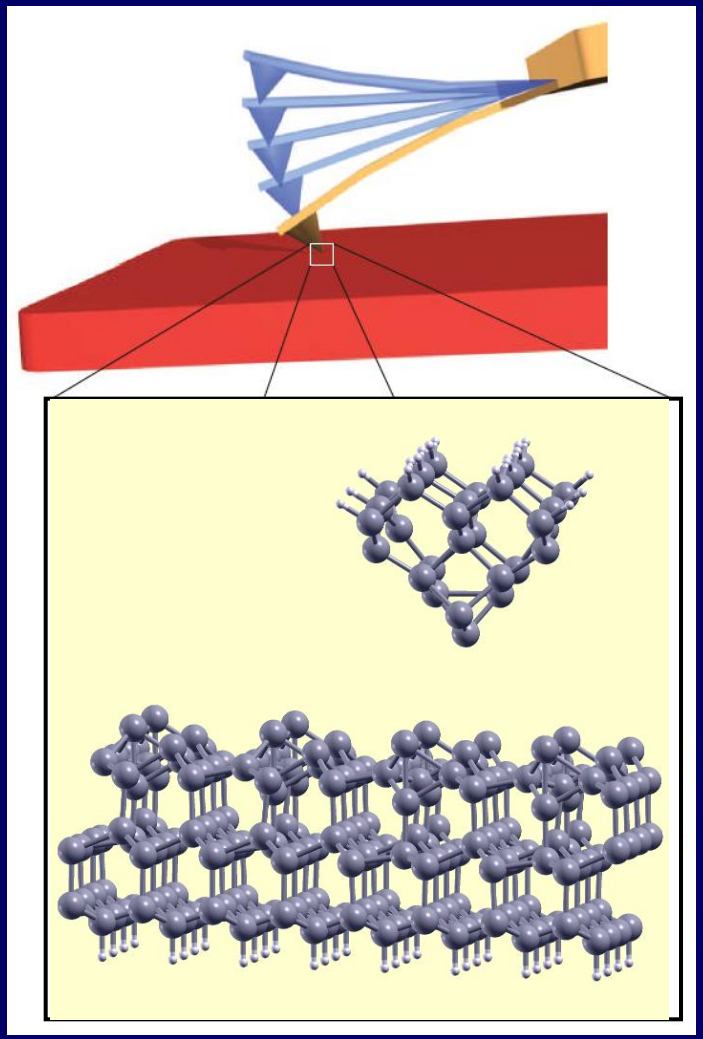
Weak singularity at turning points !!!!

Dynamic Force Spectroscopy: Access to F_{ts}



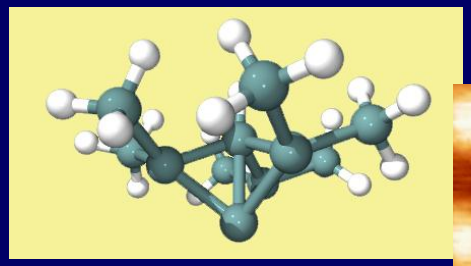
Inversion algorithms



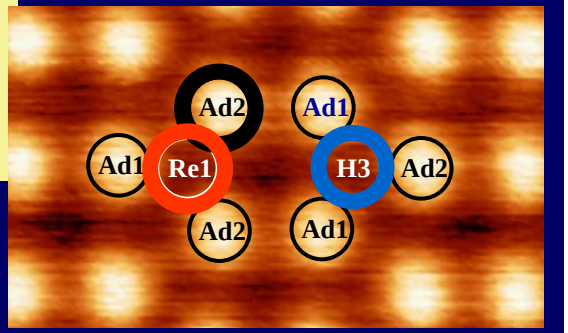


SR forces amenable to ab initio calculations

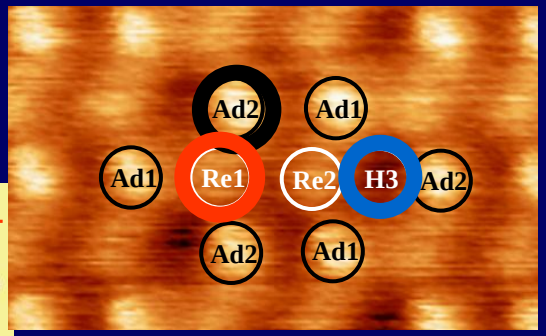
Force spectroscopy: Tip identification

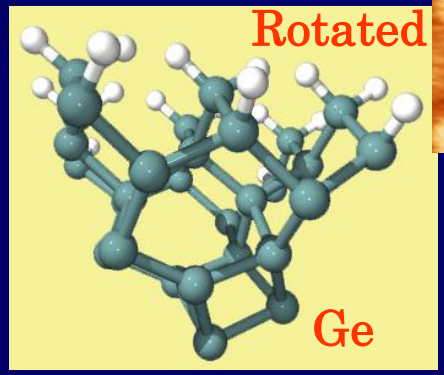


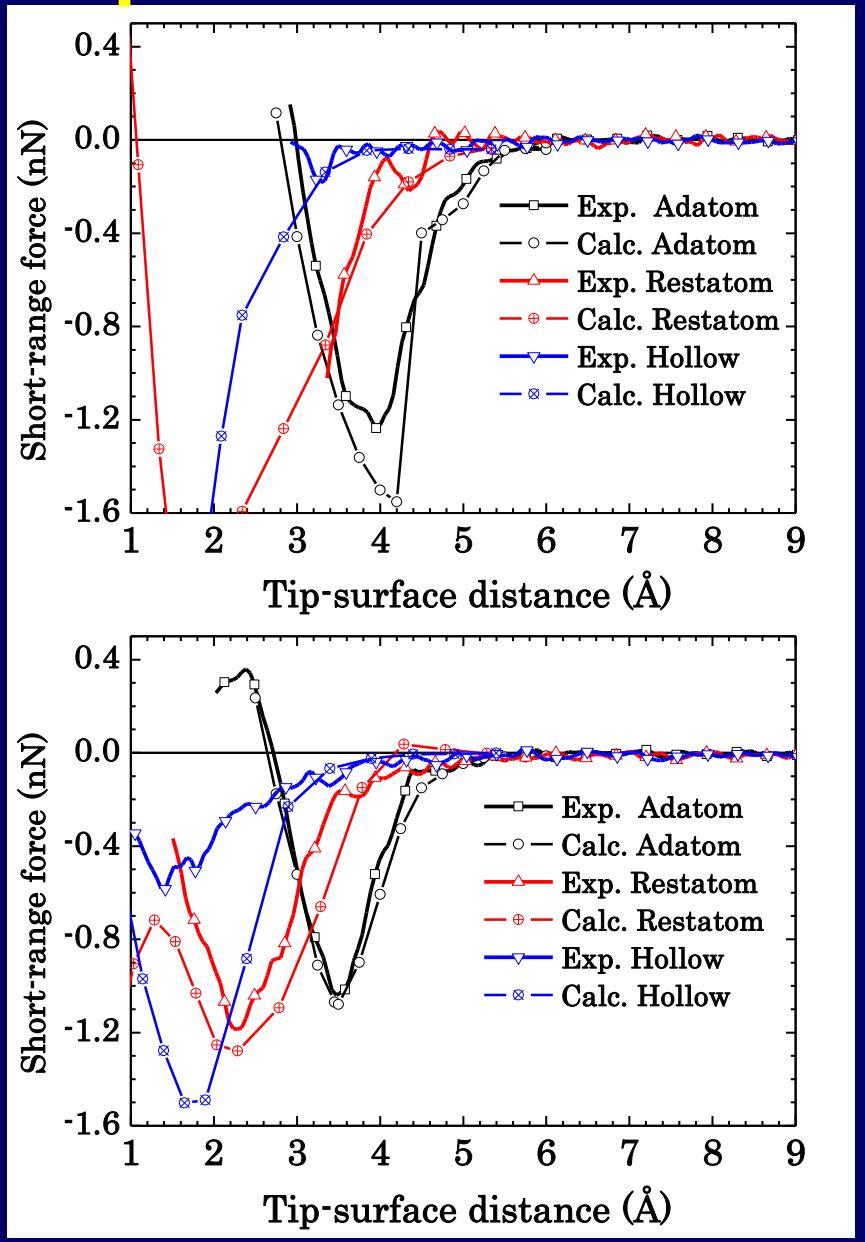
Tip A



Tip B

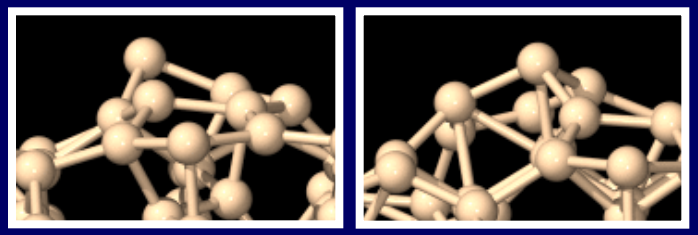




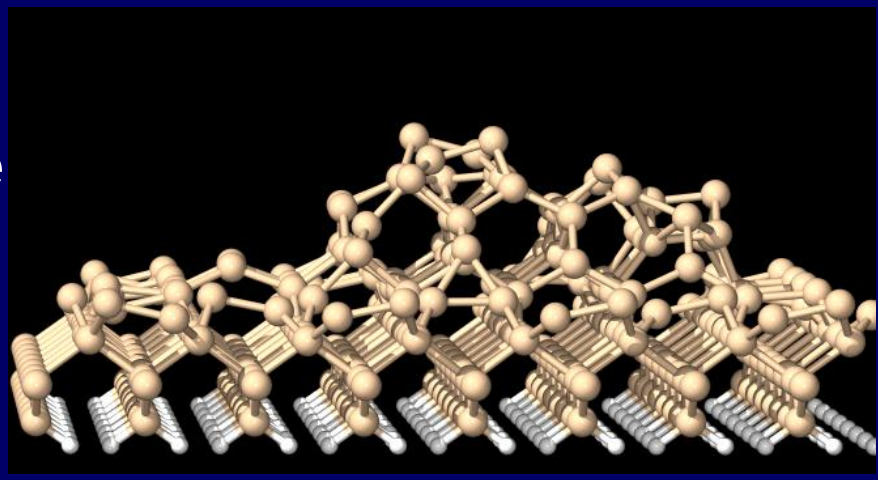


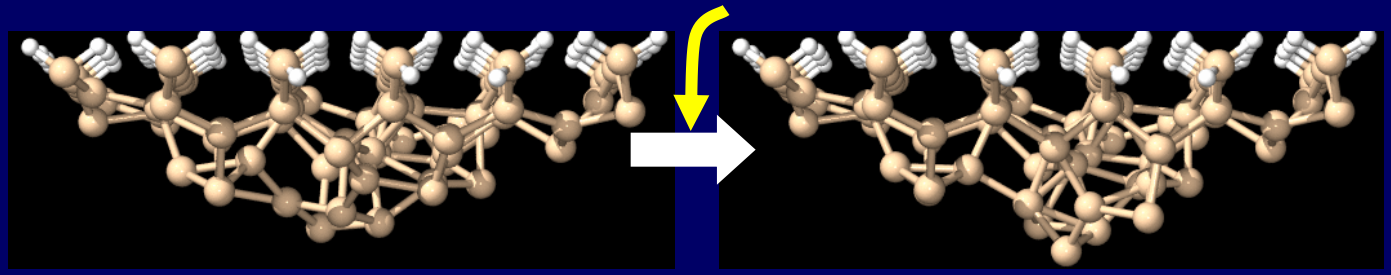
N. Oyabu et al. Phys. Rev. Lett. 96, 106101 (2006).

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.)

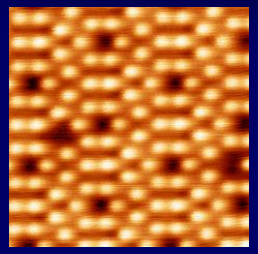


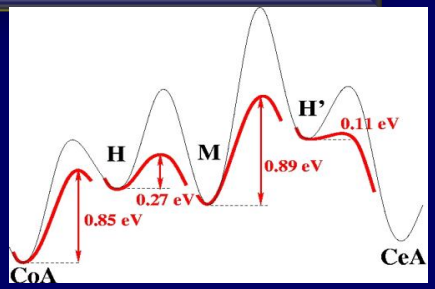


P. Pou, S.A. Ghasemi, P. Jelinek, T. Lenosky, S. Goedecker & R. P.
Nanotechnology 20, 264015 (2009)

FM-AFM: Atomic contrast with SR Forces

Lateral Manipulation



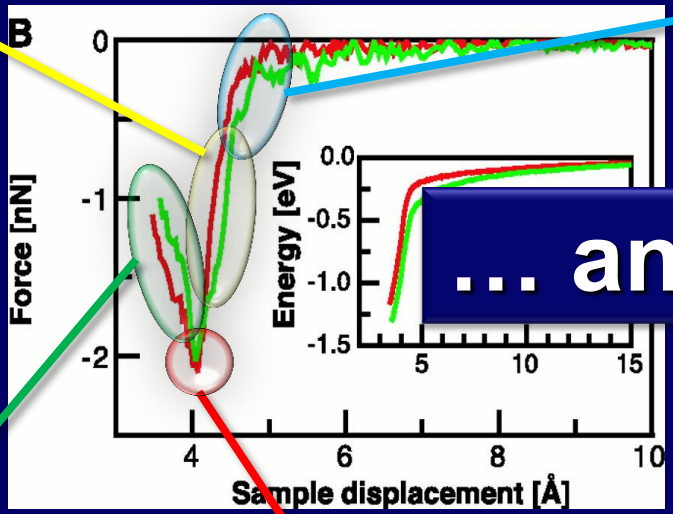


Y. Sugimoto et al PRL 98, 106104 (2007).

Imaging

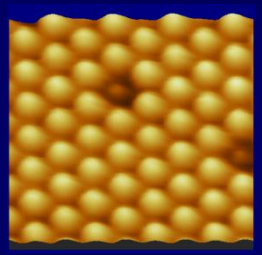
access to the real surface structure

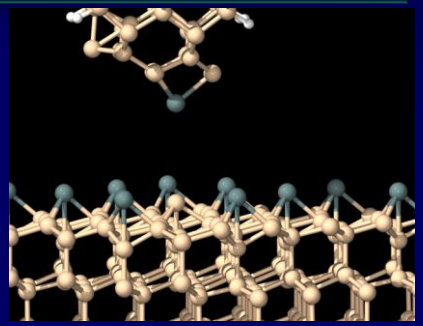
… and currents



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

Vertical Manipulation

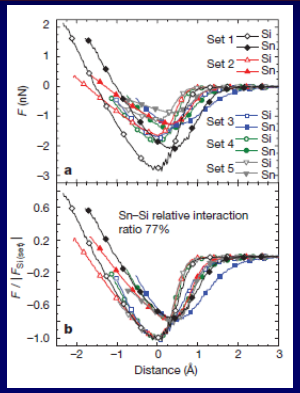


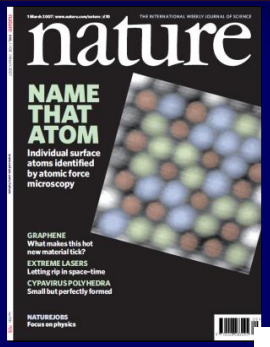


Y. Sugimoto et al, Science 322 (2008) 413

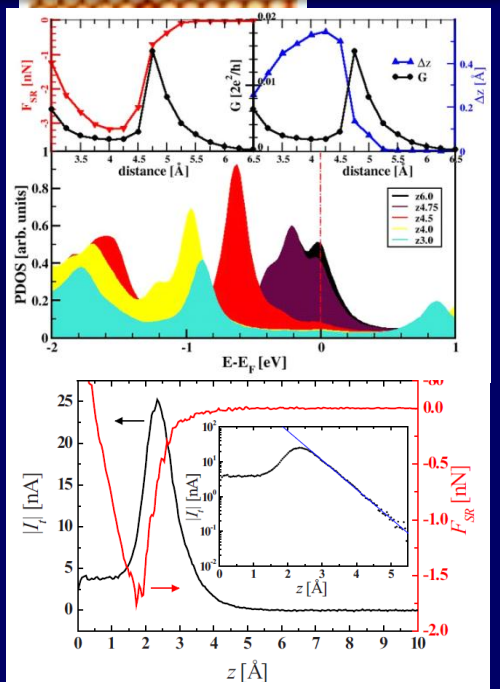
O. Custance et al, Nat. Nano 4 (2009) 803

Chemical Identification





Y. Sugimoto e
Nature 446 (20



P. Jelinek,et al, PRL 101 (2008) 176101

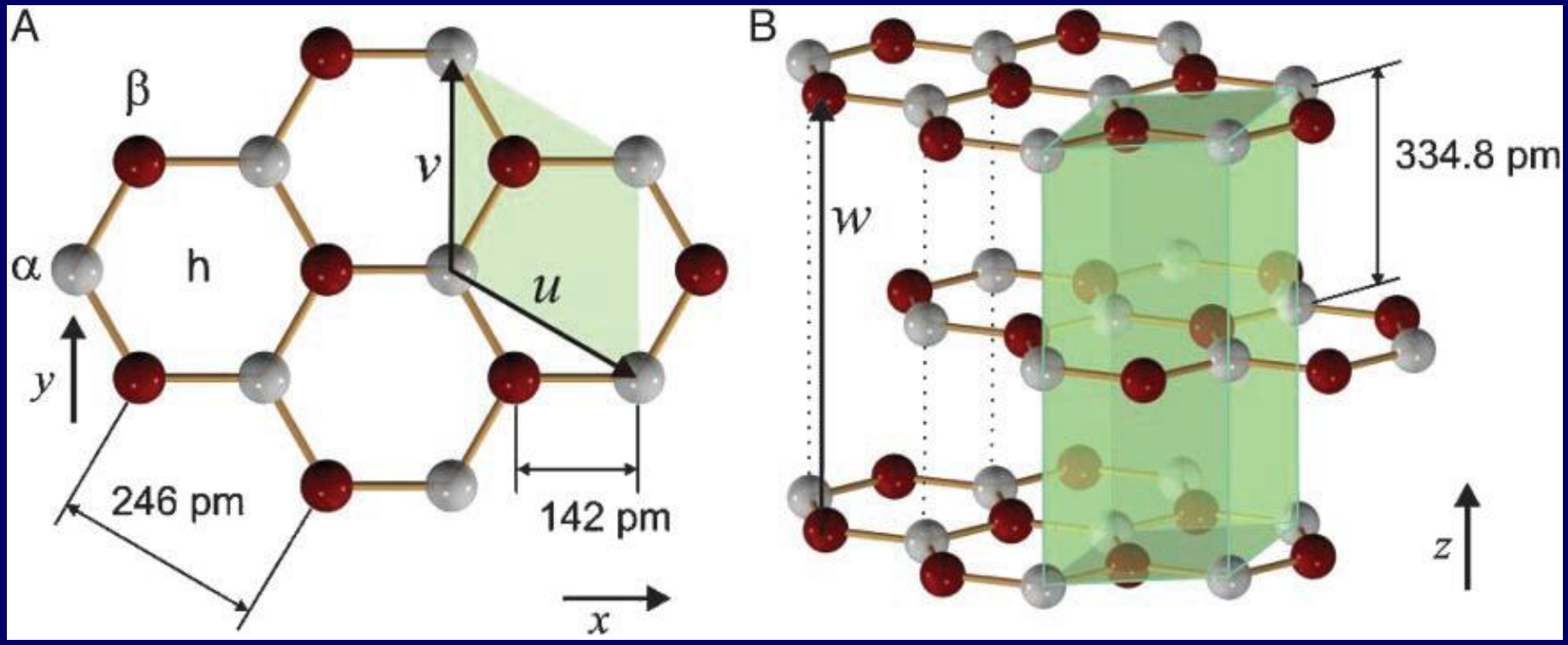
D. Sawada et al, APL (2009) 173117

3. Forces and currents in Carbon Nanostructures: Are we imaging atoms?

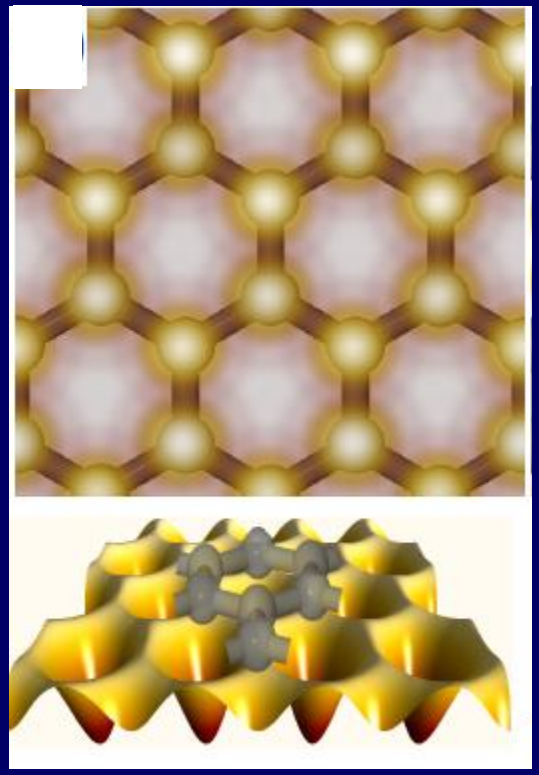
Atomic contrast: PRL 106 (2011) 176101(Editors' suggestion)

Vacancies on Graphene/Pt(111): PRL (accepted)

Graphite: Bernal stacking

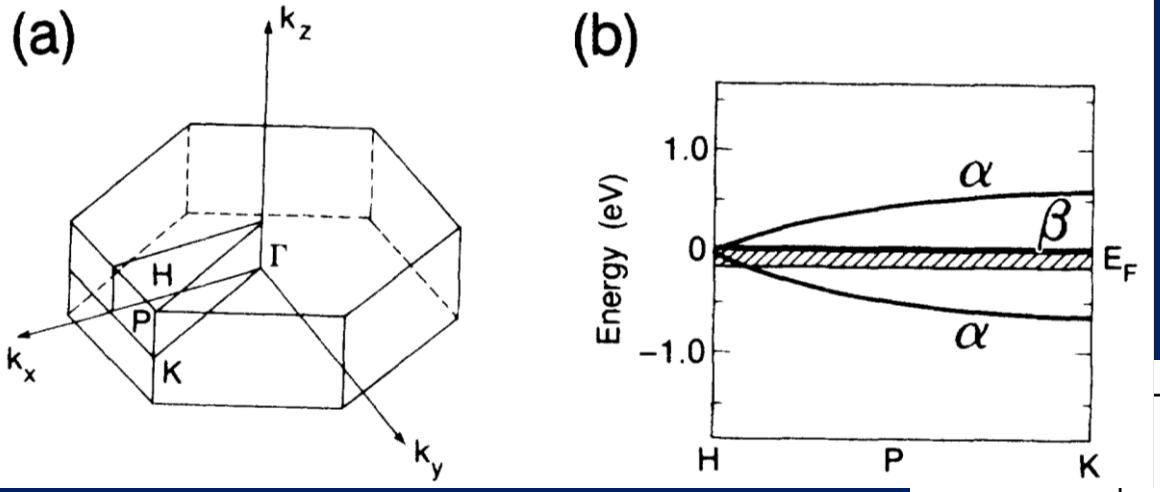


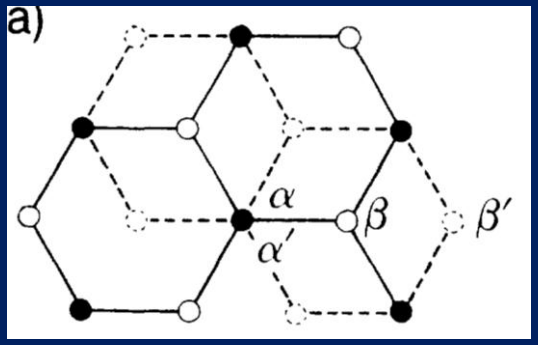
Atomic-scale contrast: maxima on the atoms ⇒ honeycomb image



STM Experiments:
bright protrusions form
an hexagonal lattice !!

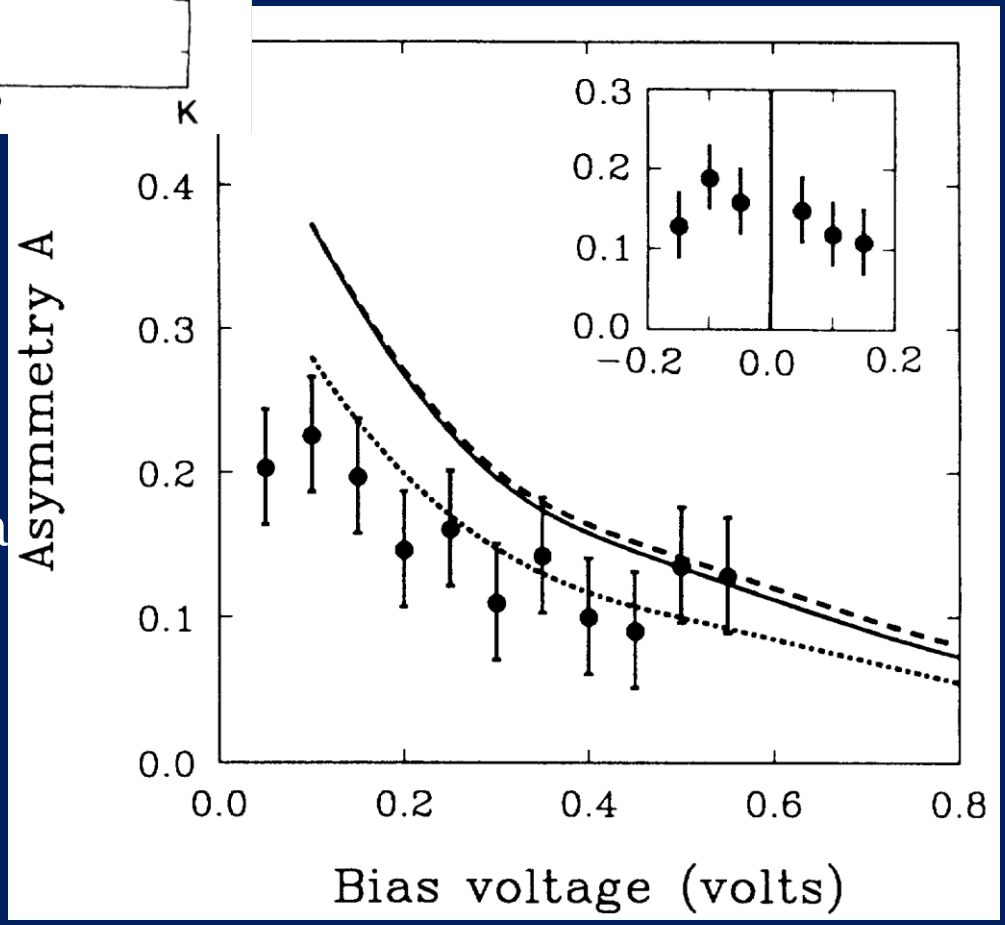
Low-bias STM: Imaging of the β sublattice





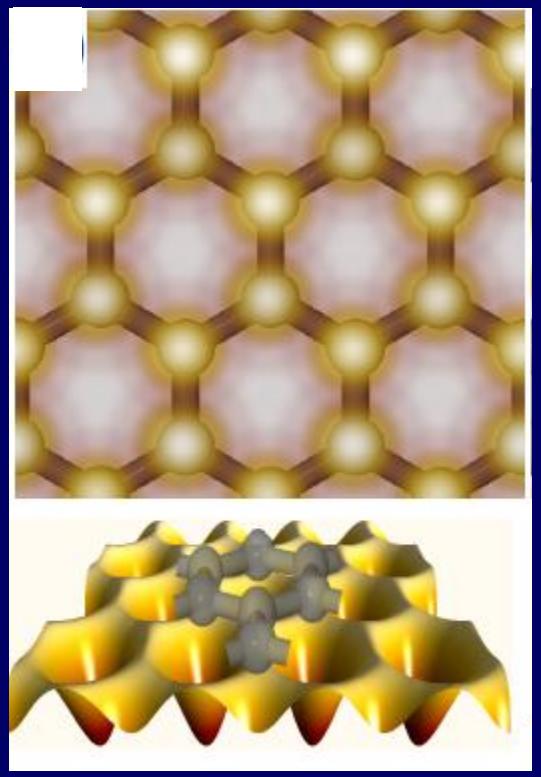
$$A = \frac{I(\beta) - I(\alpha)}{I(\beta) + I(\alpha)}$$

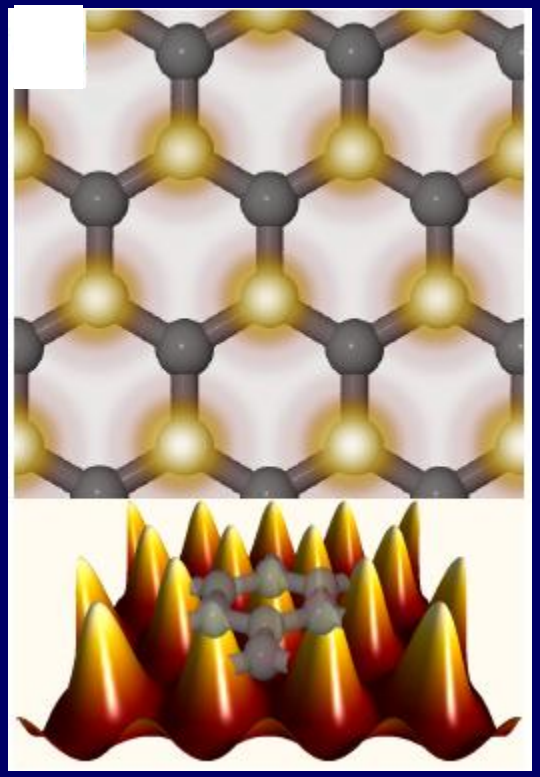
* Experiments: contact resistance data
* Theory: Calculations for tip-surface distance= 0.5 and 1 Å



D. Tomanek et al.,
Phys. Rev. B 35, 7790 (1987).

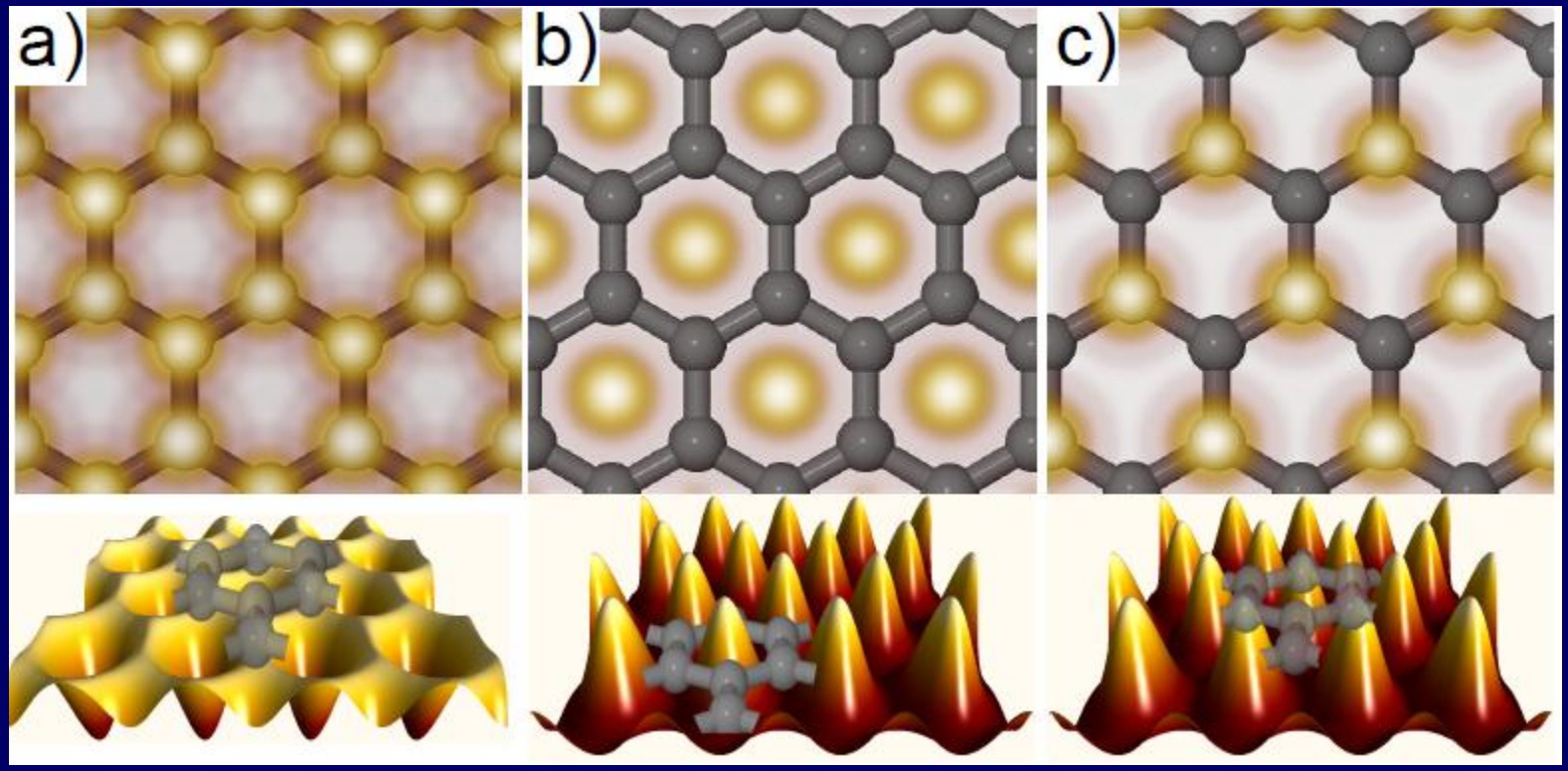
Atomic-scale contrast: honeycomb vs hexagonal





Atomic-scale contrast: maxima on the atoms or hollow sites?

honeycomb hexagonal hexagonal



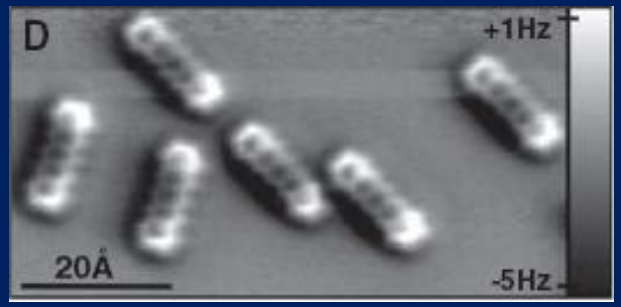
STM images taken with very different operation conditions and bias voltages show always an hexagonal symmetry…

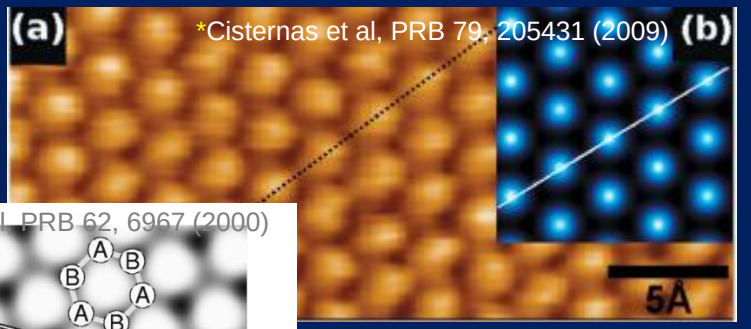
SPM on low dimension carbon materials

STM: Graphite **(>25 years ago)**

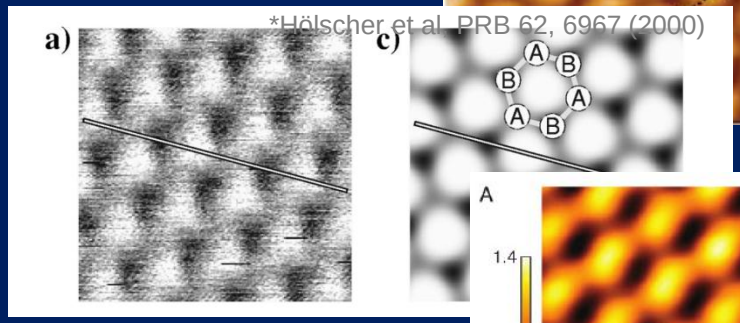
FM-AFM (>10 years):

- Graphite
  - Albers et al, Nature Nano 2009; Hembacher et al, PRL 2005; Hembacher et al, PNAS 2003; Hölscher et al, PRB 2000;…
- Carbon Nanotubes
  - Ashino et al, PRL 2004; Ashino et al nanotech 2005;…
- PAHs: Pentacene
  - Gross et al, Science 2009

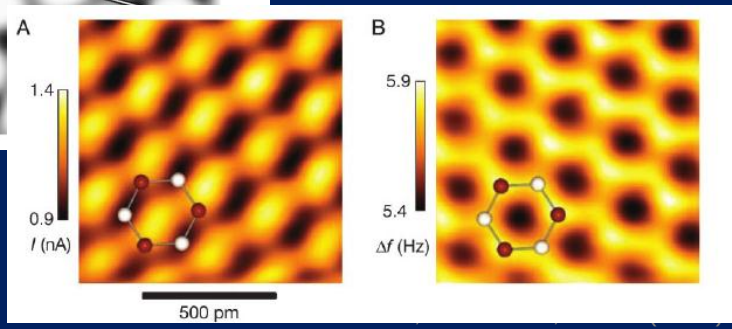


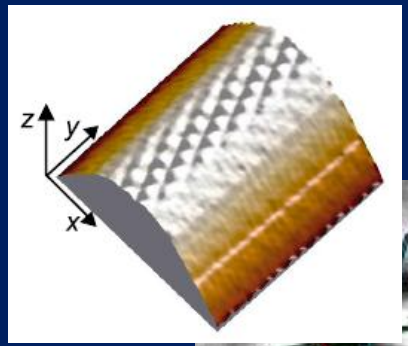


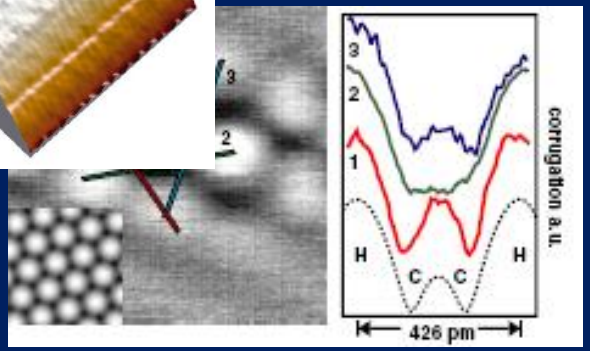
*Cisternas et al, PRB 79, 205431 (2009)

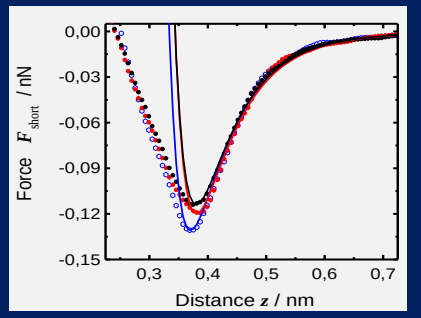


*Hölscher et al, PRB 62, 6967 (2000)



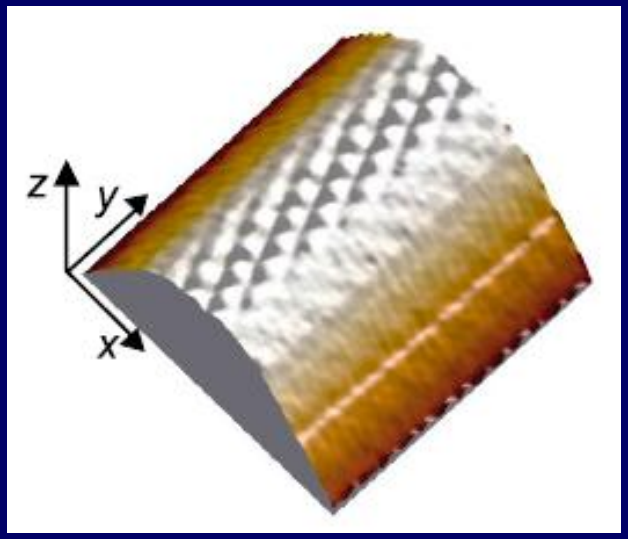


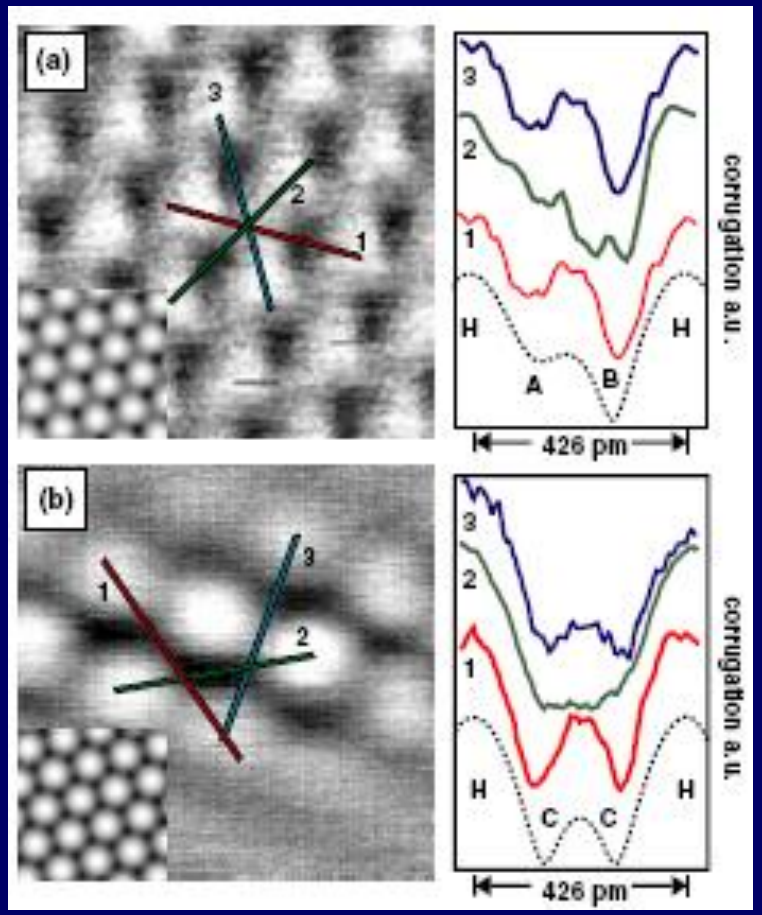




*Ashino et al, Nanotec. 16, S134 (2005)

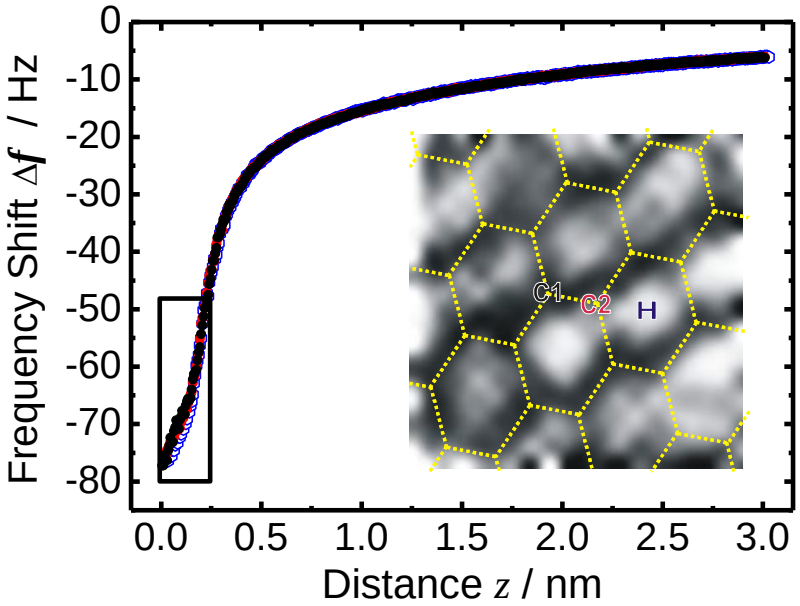
Imaging nanotubes with FM-AFM

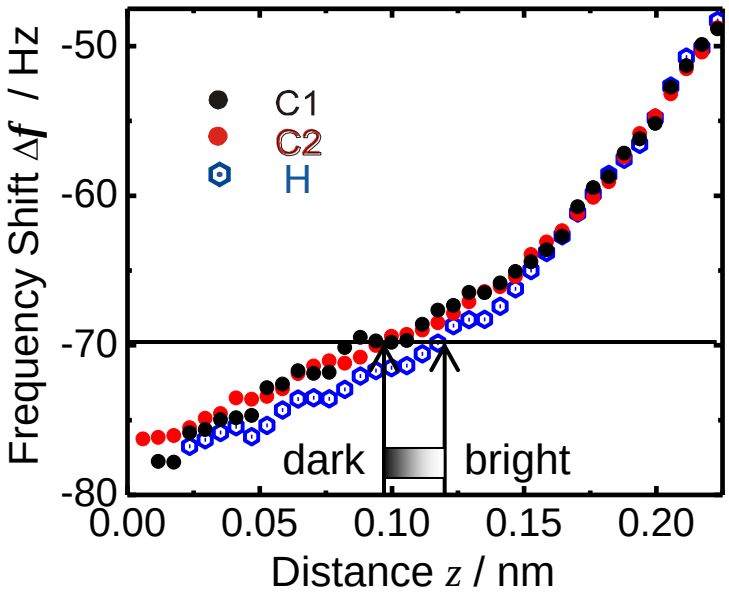


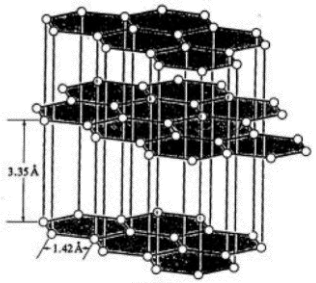


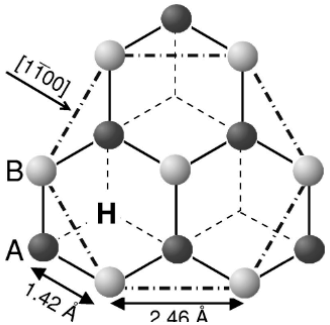
M. Ashino et al, Phys. Rev. Lett. 93, 136101 (2004).
M. Ashino et al., Nat. Nanotechnol. 3, 337 (2008).

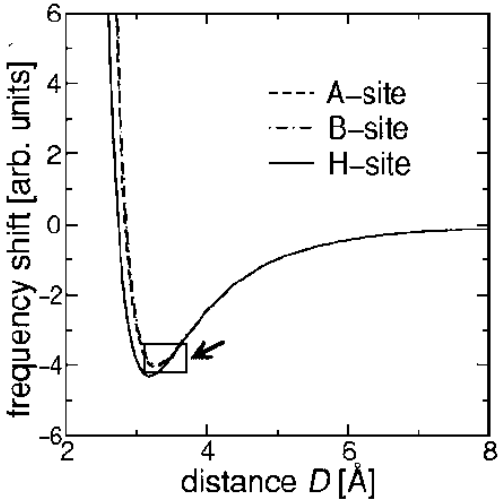
Frequency Shift vs Distance Curves @ Individual Atomic Lattice Sites

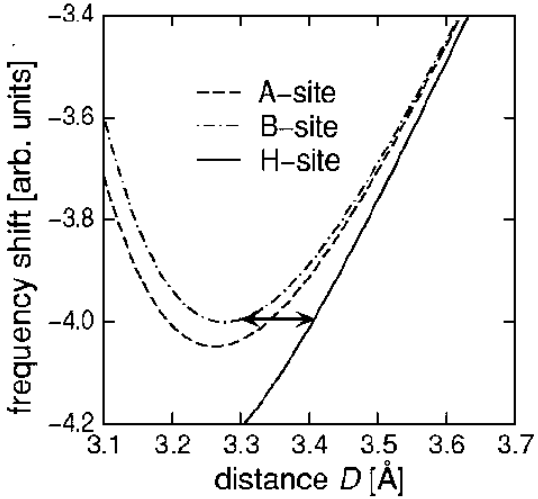








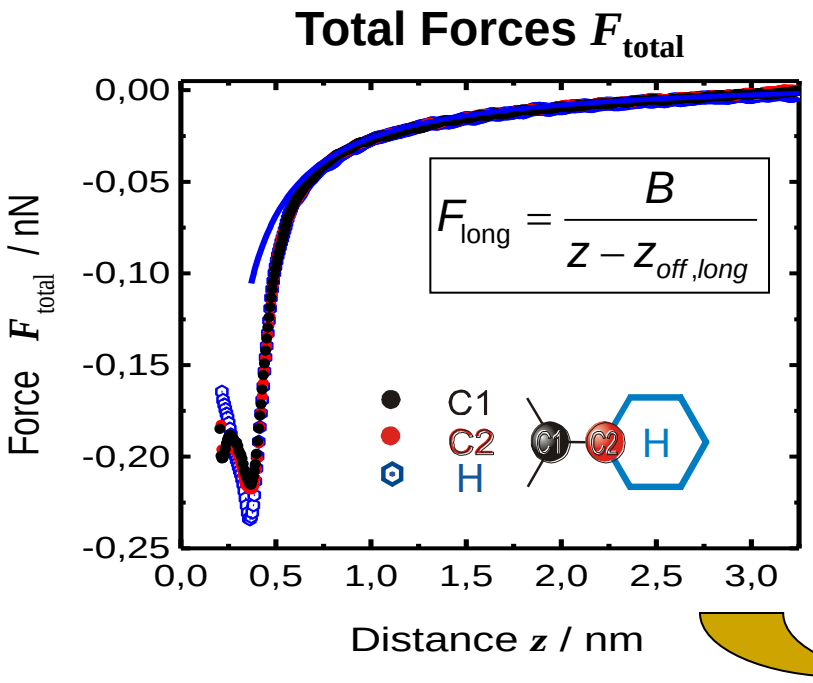


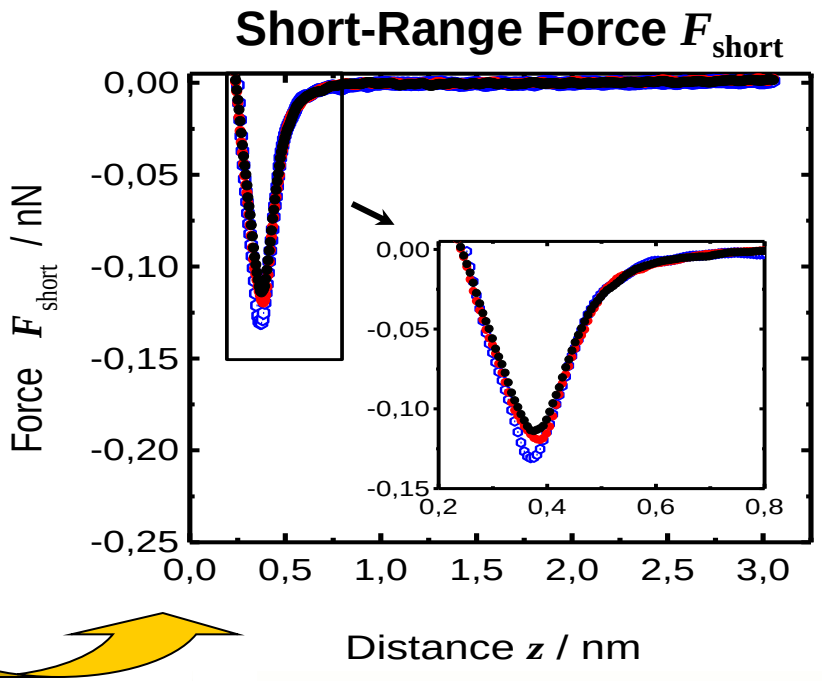


📖 H. Hölscher *et al.*, PRB **62**, 6967 (2000).

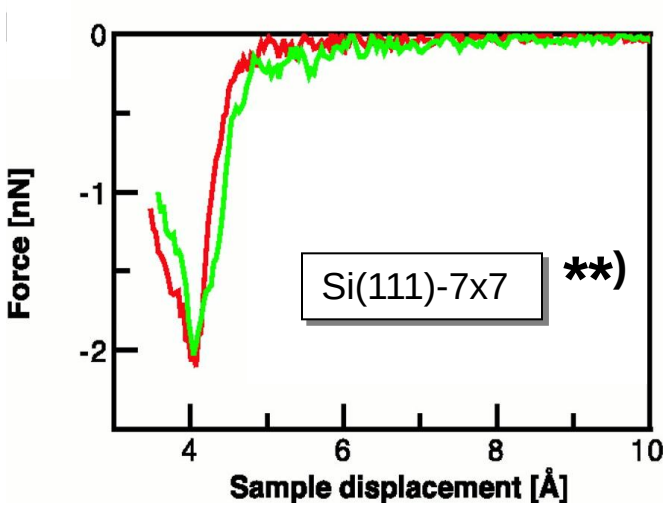
M. Ashino

Analysis of Short-Range $F_{short}(z)$ Curves





$$F_{short} = F_{total} - F_{long}$$ *)

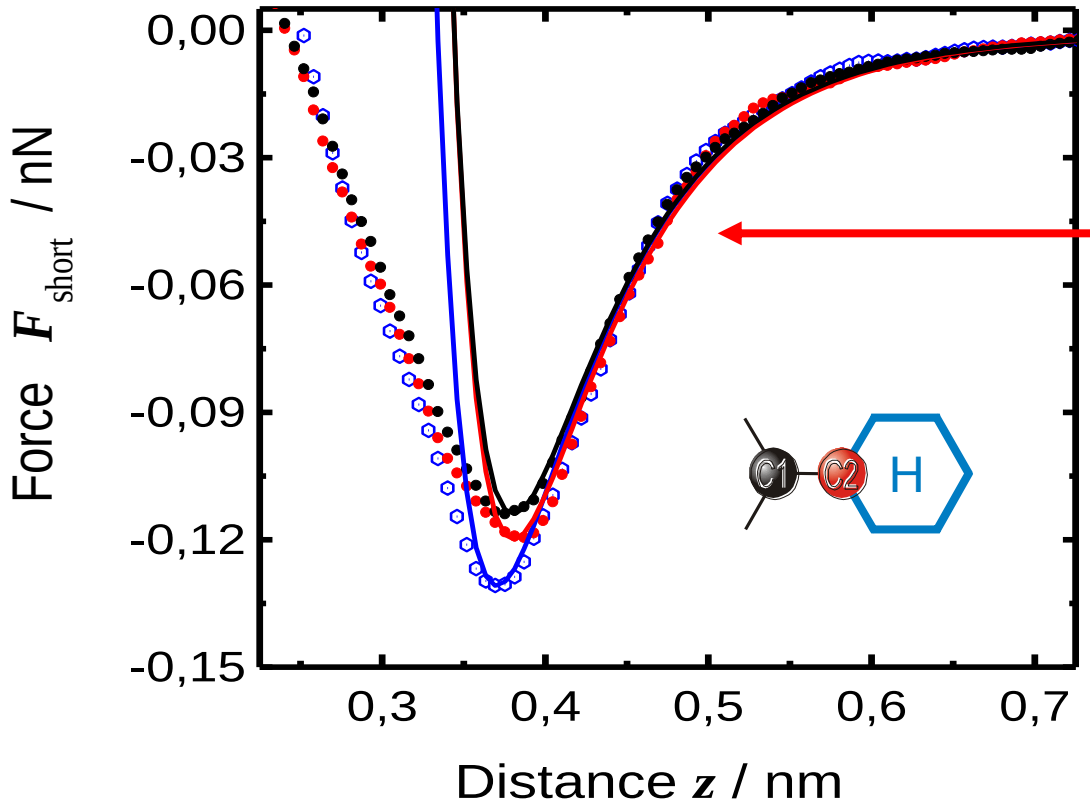


*) Guggisberg *et al.*, PRB **61**, 11151 (2000).

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

M. Ashino

Analysis of Short-Range $F_{short}(z)$ Curves

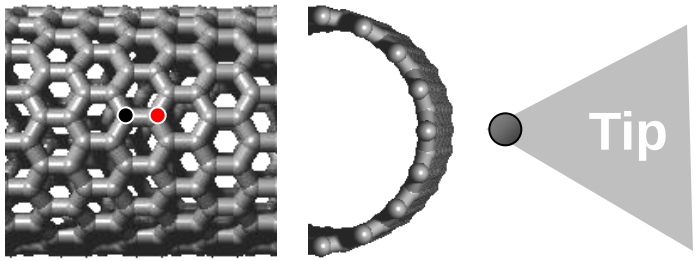


Forces derived from
Lennard—Jones Potential

$$F_{L-J}(z) = \frac{12E_0}{z_0}\left[\left(\frac{z_0}{z}\right)^{13} - \left(\frac{z_0}{z}\right)^{7}\right]$$

- E_0 = **Binding Energy**
- z_0 = Equilibrium Distance

($z_0 \equiv 0.334$ nm)



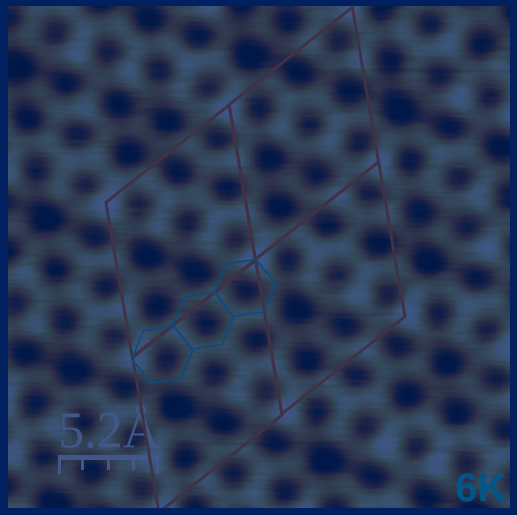
E_0(C1) ≈ **87.4 meV**
E_0 (C2) ≈ **91.8 meV**
E_0 (H) ≈ **101 meV**

M. Ashino

Origin of the atomic contrast?

- FM-AFM: DFT+vdW Forces on SWCNT and graphite (0001)
  - Is vdW providing atomic resolution?
  - atomic contrast versus tip reactivity
- Does STM always image atoms?: multiple scattering effects

- Graphene on Pt(111): Moire patterns



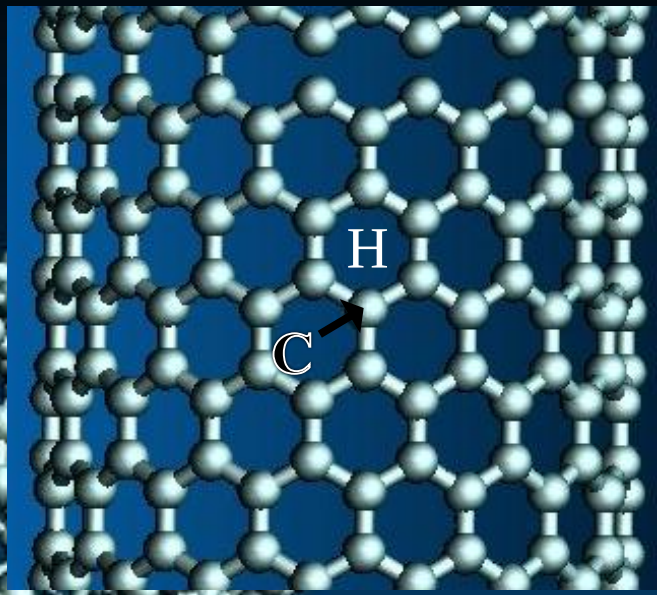
- Vacancies on Gr/Pt(111): Are the localized states on the vacancy preserved?

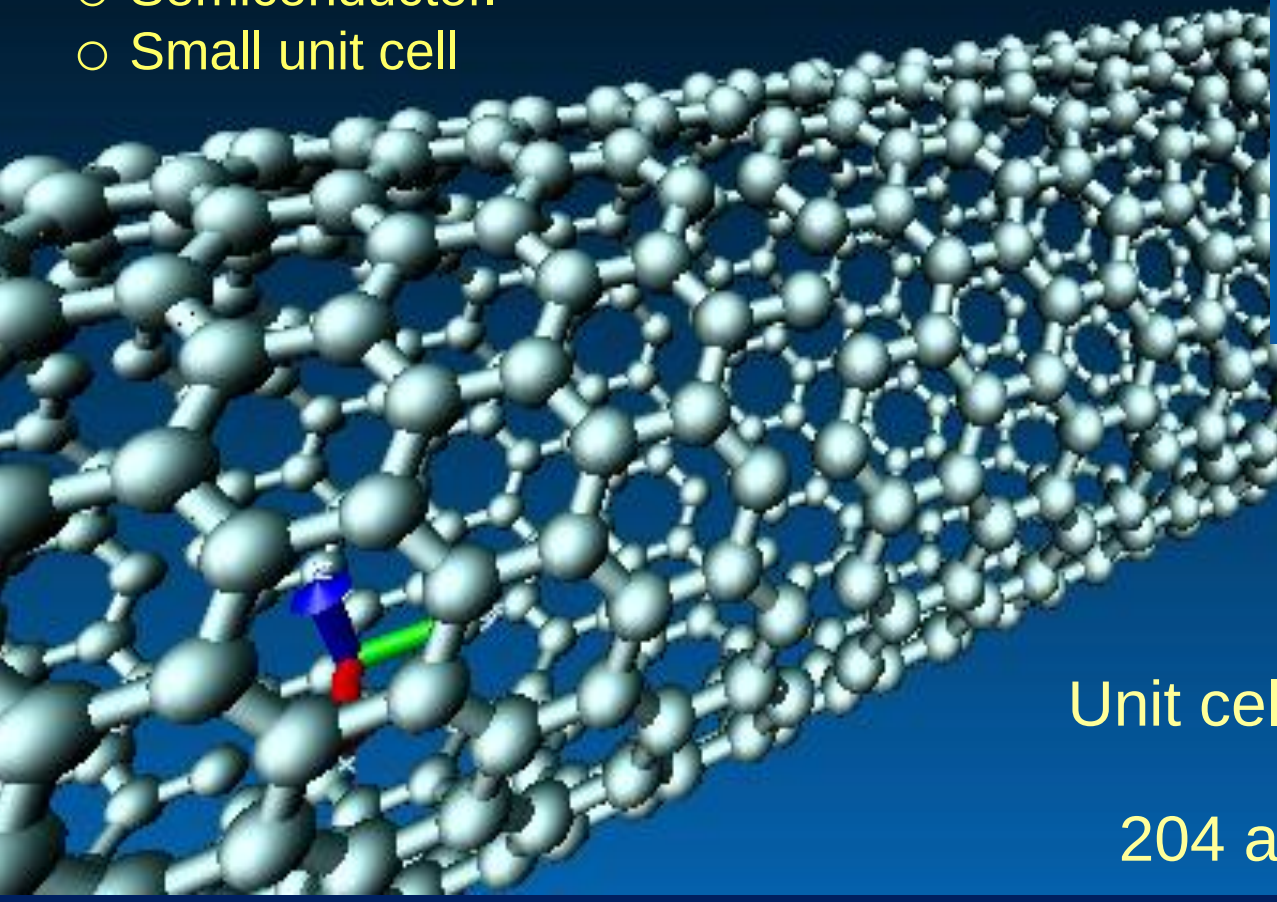
M. M. Ugeda et al, PRL 104, 096804 (2010)

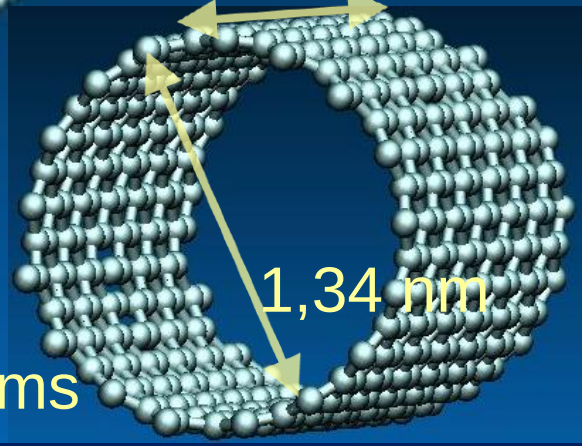
DFT+vdW calculations on CNT: system

Nanotube (17,0)

- Similar diameter to the NT used in experiments (1,34 nm vs 1,38 nm).
- Semiconductor.
- Small unit cell





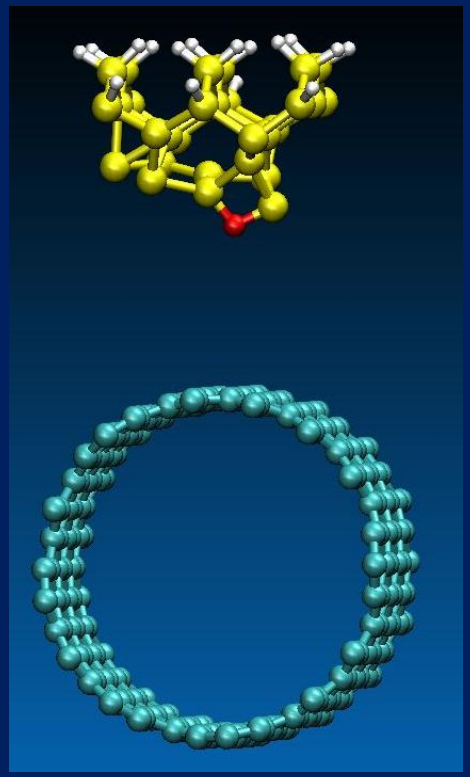


Unit cell:

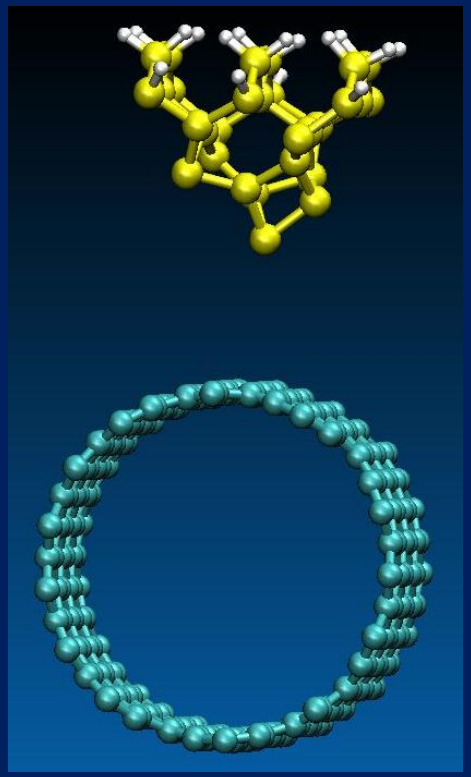
204 atoms

DFT+vdW calculations on CNT: Tips

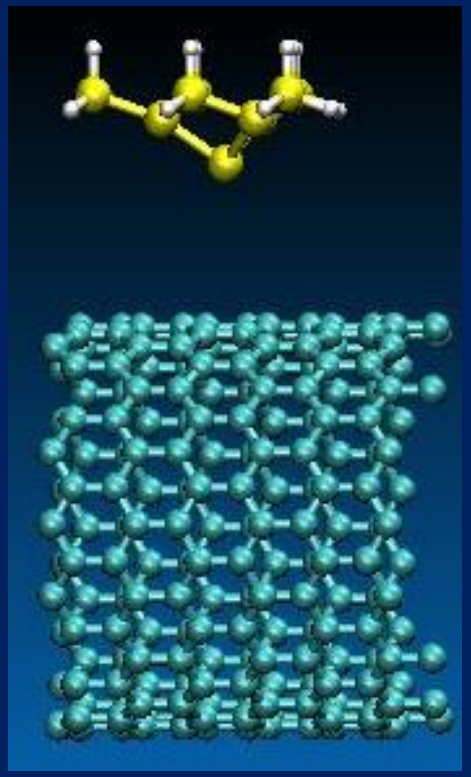
CHEMICAL REACTIVITY



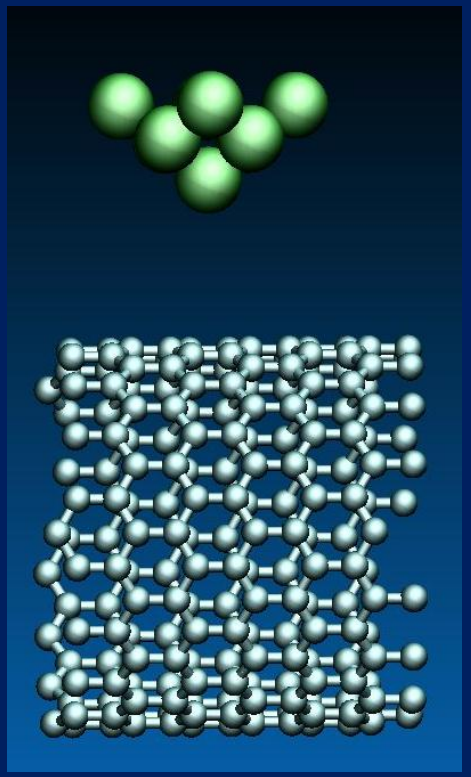
O apex atom in a Si tip



Dimer Si tip



H3 Si tip



Metallic W tip

DFT+vdW calculations on NT: method

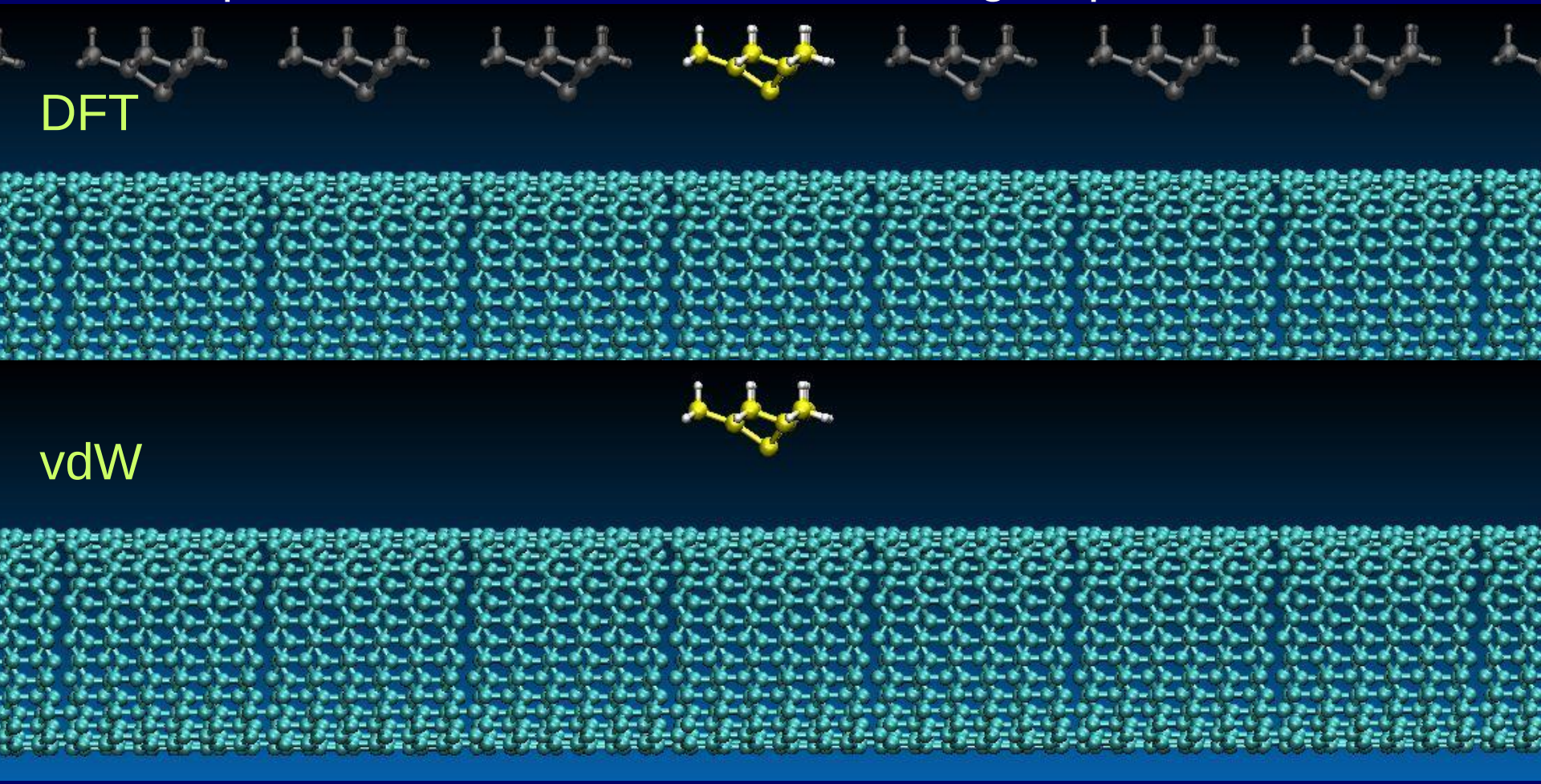
Atomistic simulations with DFT + vdW:

- DFT calculation:
  - VASP: PW + PAW pseudopotentials
  - Electronic exchange correlation: PBE (also LDA)
  - Supercell calculation, 1x4x1 Monkhorst–Pack (MP) E_k-sampling mesh. Convergence criteria: Ecut = 500 eV. Forces < 0.01 eV/Å
- vdW calculation:
  - Grimme approach [S. Grimme, *J. Comp. Chem.,* **25** 1463 (2004)]
  - Atomic relaxations included
  - Calculation taking into account the Tip and a large NT fragment (not supercell approach)

$$E_{TOTAL} = E_{DFT} + E_{vdW}$$

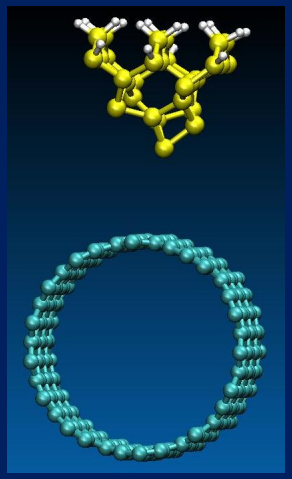
DFT+vdW calculations on NT: method

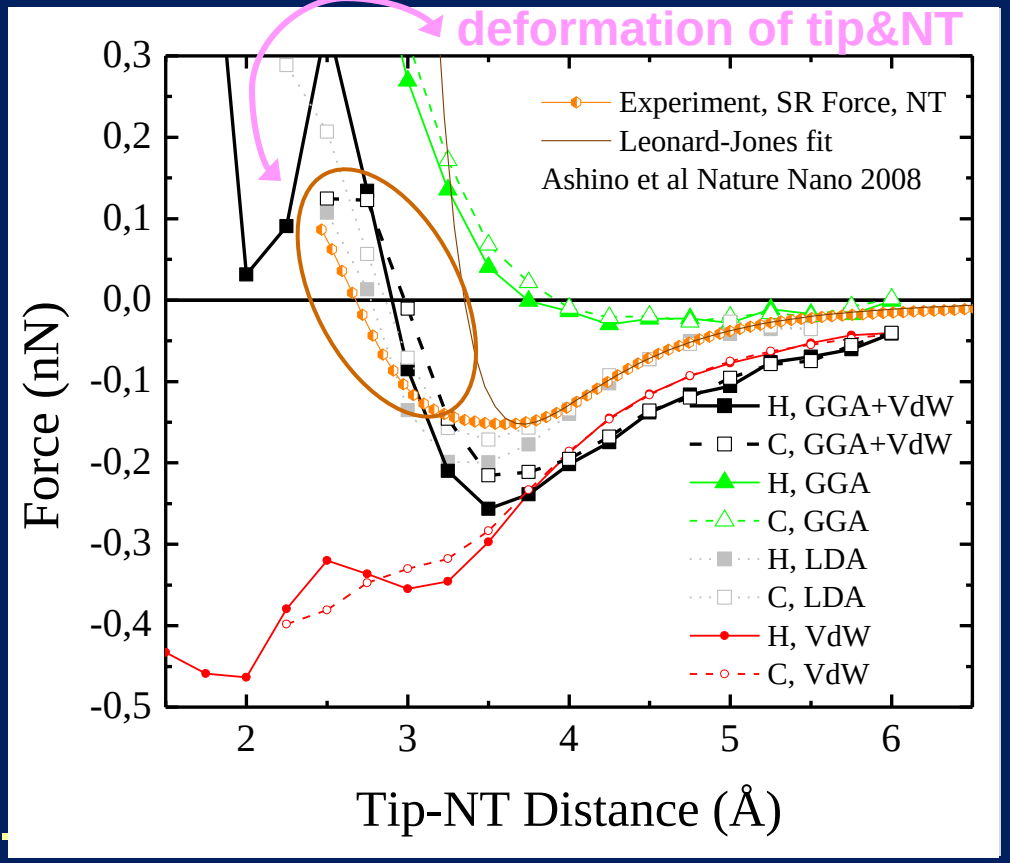
Supercell for DFT vs nanotube + single tip for vdW



DFT+vdW calculations on NT: Results

Dimer Si tip





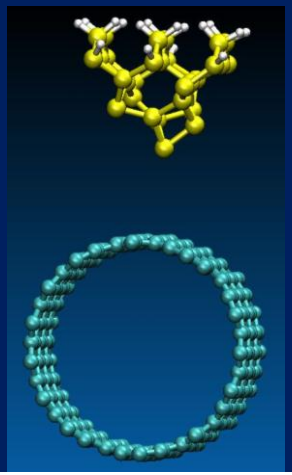
Forces vs experiments:

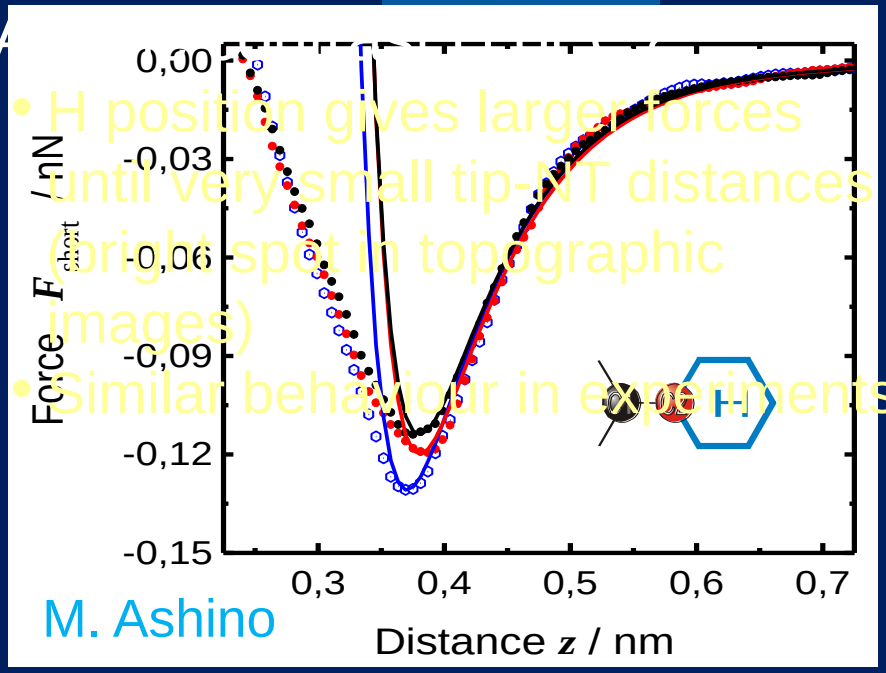
- GGA gives very small forces
- GGA+vdW yields the correct order of magnitude ~ -0.25 nN, but forces are larger than the experimental values, < 0.15 nN (tip model or vdW parameters?).

- LDA provides a surprisingly good agreement with GGA+vdW

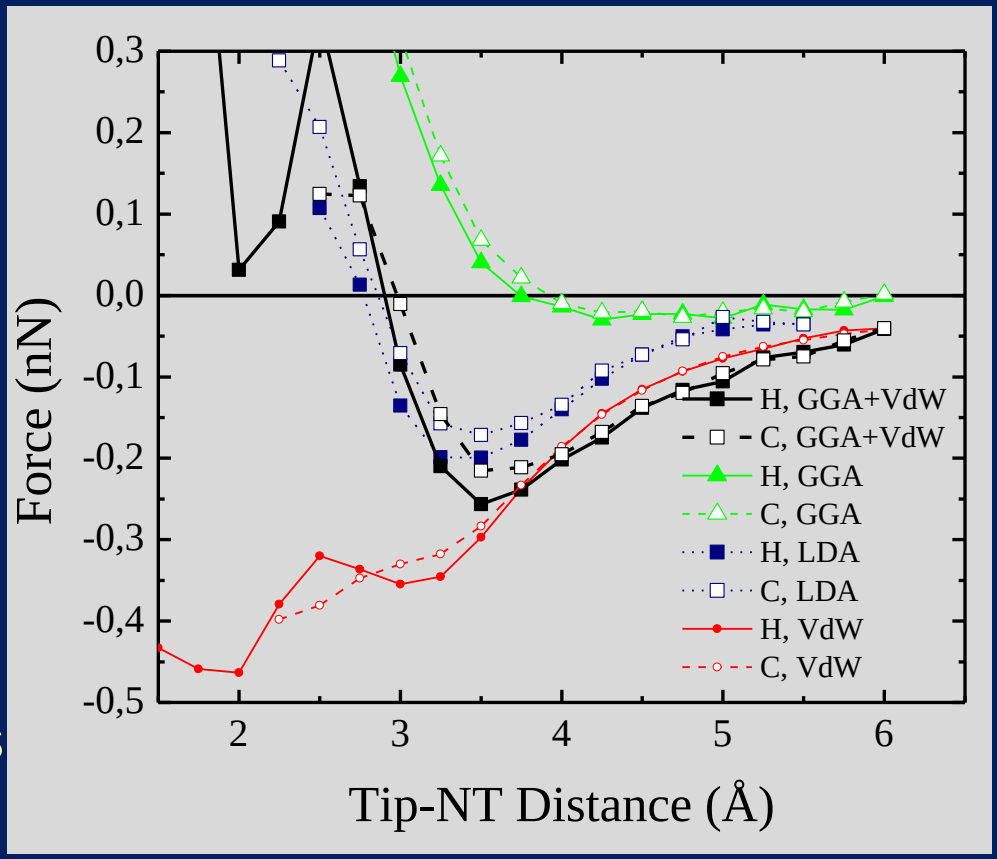
DFT+vdW calculations on NT: Results

Dimer Si tip



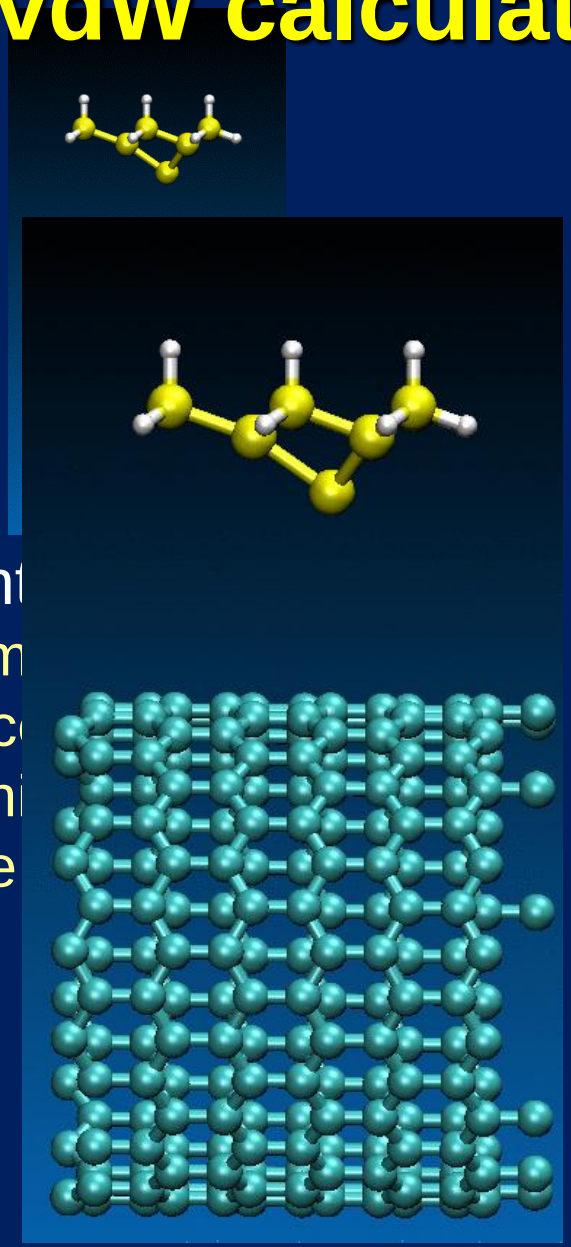


- H position gives larger forces until very small tip-NT distances (bright spot in topographic images)
- Similar behaviour in experiments

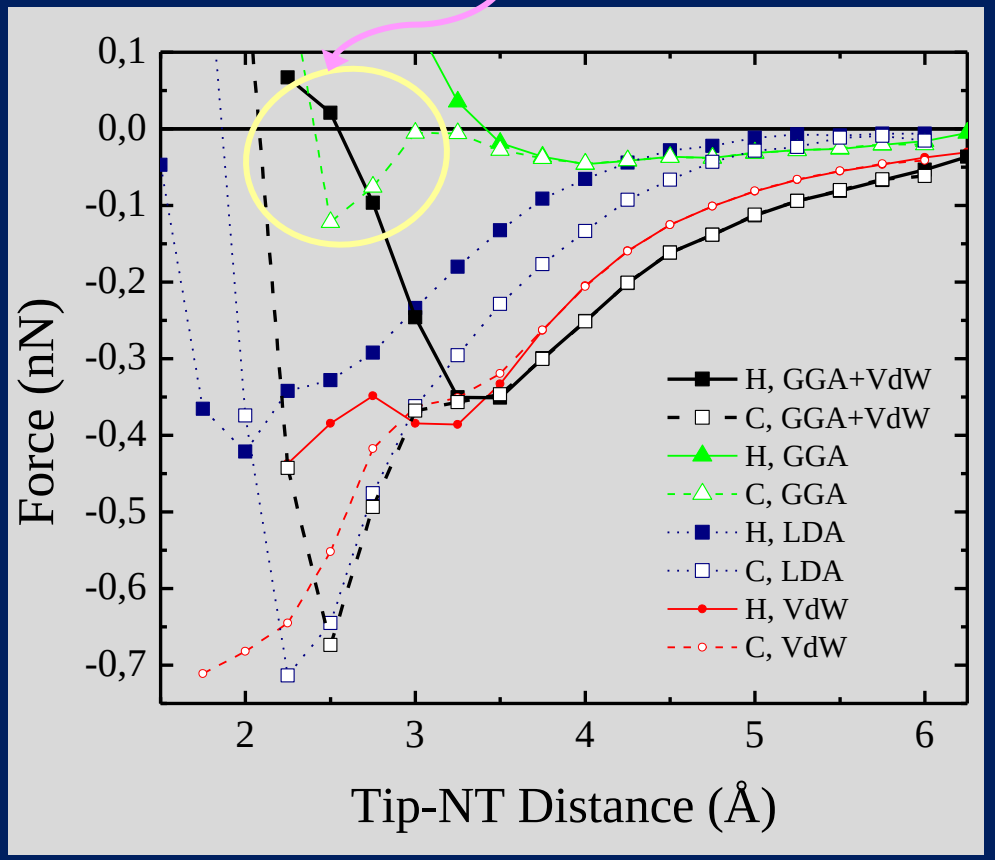


DFT+vdW calculations on NT: H3 Si tip

H3 Si tip



Atomic cont
- H3 tip is m
  larger forc
  topographi
- Very large



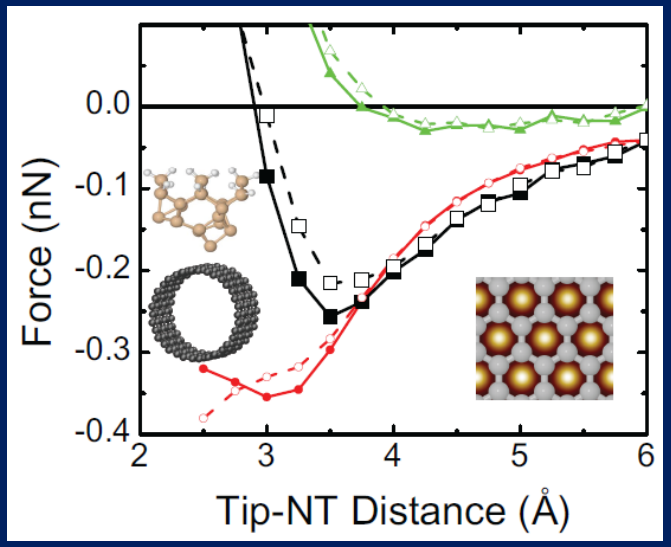
Atomic contrast vs tip reactivity

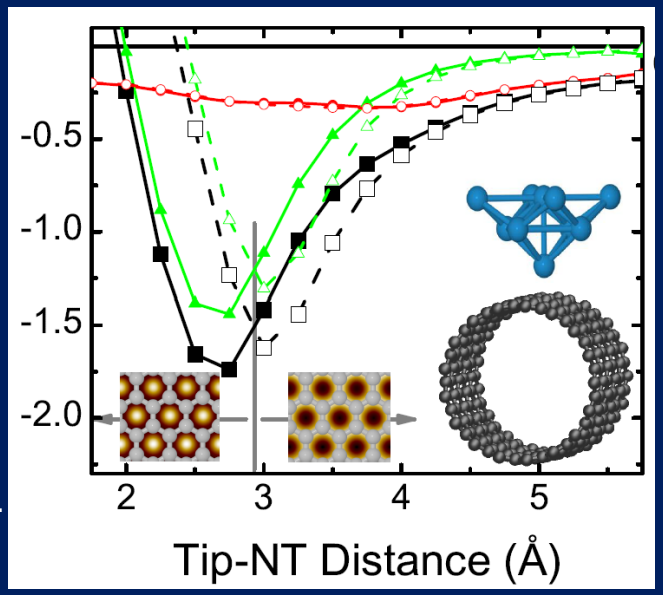
For weakly reactive tips, vdW sets the absolute force scale but **atomic contrast is always controlled by SR Chemical forces**

Weakly reactive tips: Pauli repulsion (smaller on areas of low electronic density) → larger attractive forces on the hollow site: **hexagonal pattern** of bright spots

Strongly interacting Tip: attractive interaction dominates → larger forces on atoms (local change of hybridization) → **honeycomb pattern**

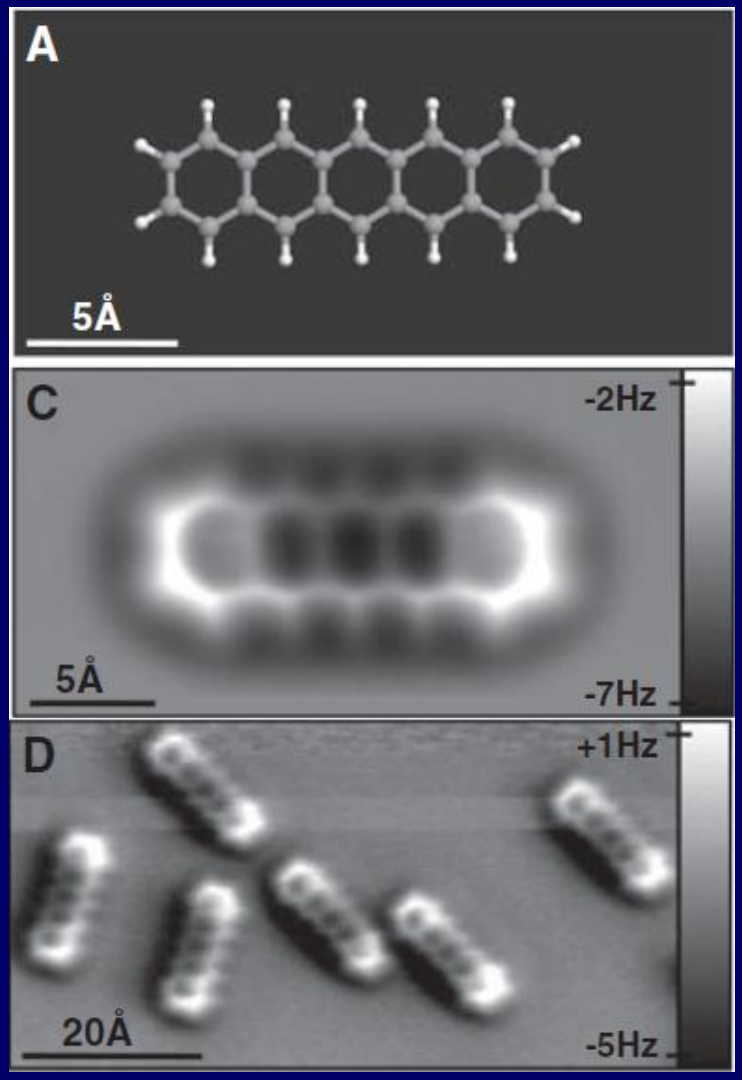
Inverted contrast on the repulsive regime

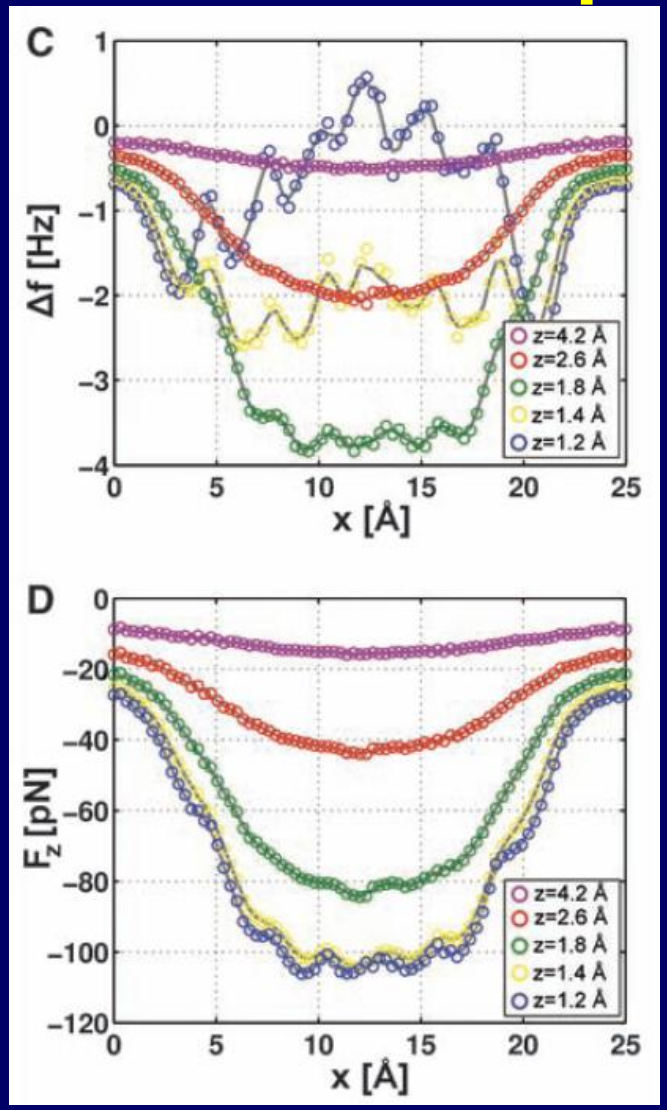




M. Ondracek et al , Phys. Rev. Lett. 106 (2011) 176101
(Editors' Suggestion, 29/04/2011 & ViewPoint)

The Chemical Structure of a Molecule Resolved by FM-AFM with a CO tip !!

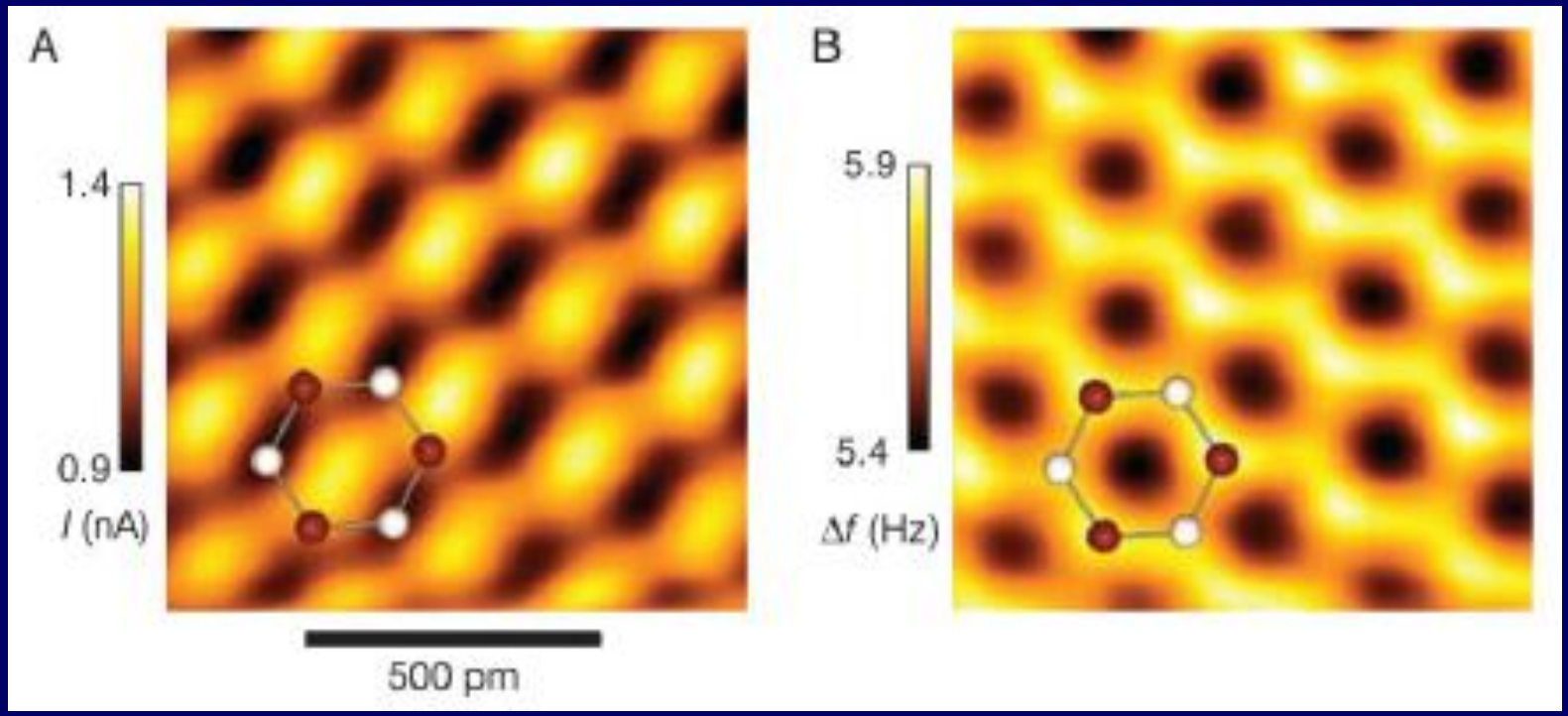




L. Gross et al, Science 325, 1110 (2009)

Does STM provides a clear identification of the maxima?

STM AFM



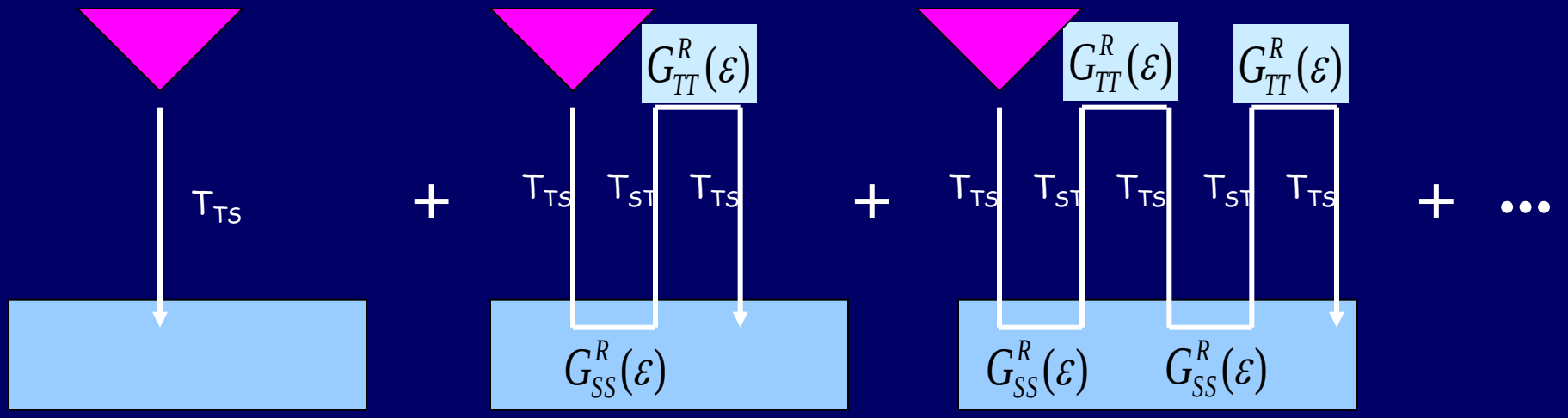
Hembacher et al, PRL 2005; Hembacher et al, PNAS 2003;

STM Simulations: KELDYSH-GREEN'S FUNCTION METHOD

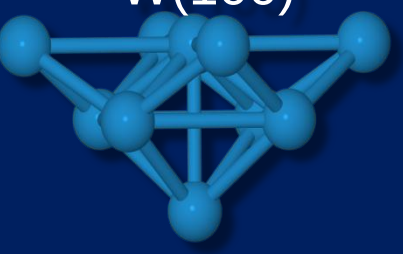
Exact solution to all orders in the tip-sample hoppings !!

$$I_{tunnel} = 4\pi e/\hbar \int_{-\infty}^{+\infty} Trace\left\{\hat{T}_{TS}^{eff}\,\hat{\rho}_{SS}\hat{T}_{ST}^{eff}\,\hat{\rho}_{TT}\right\}\left[f_T(\varepsilon) - f_S(\varepsilon)\right]d\varepsilon$$

$$\hat{T}_{TS}^{eff} = \left\{1 - \hat{G}_{SS}^{R}\hat{T}_{ST}\hat{G}_{TT}^{R}\hat{T}_{TS}\right\}^{-1}\hat{T}_{TS} = \hat{T}_{TS} + \hat{T}_{TS}\hat{G}_{SS}^{R}\hat{T}_{ST}\hat{G}_{TT}^{R}\hat{T}_{TS} + ...$$

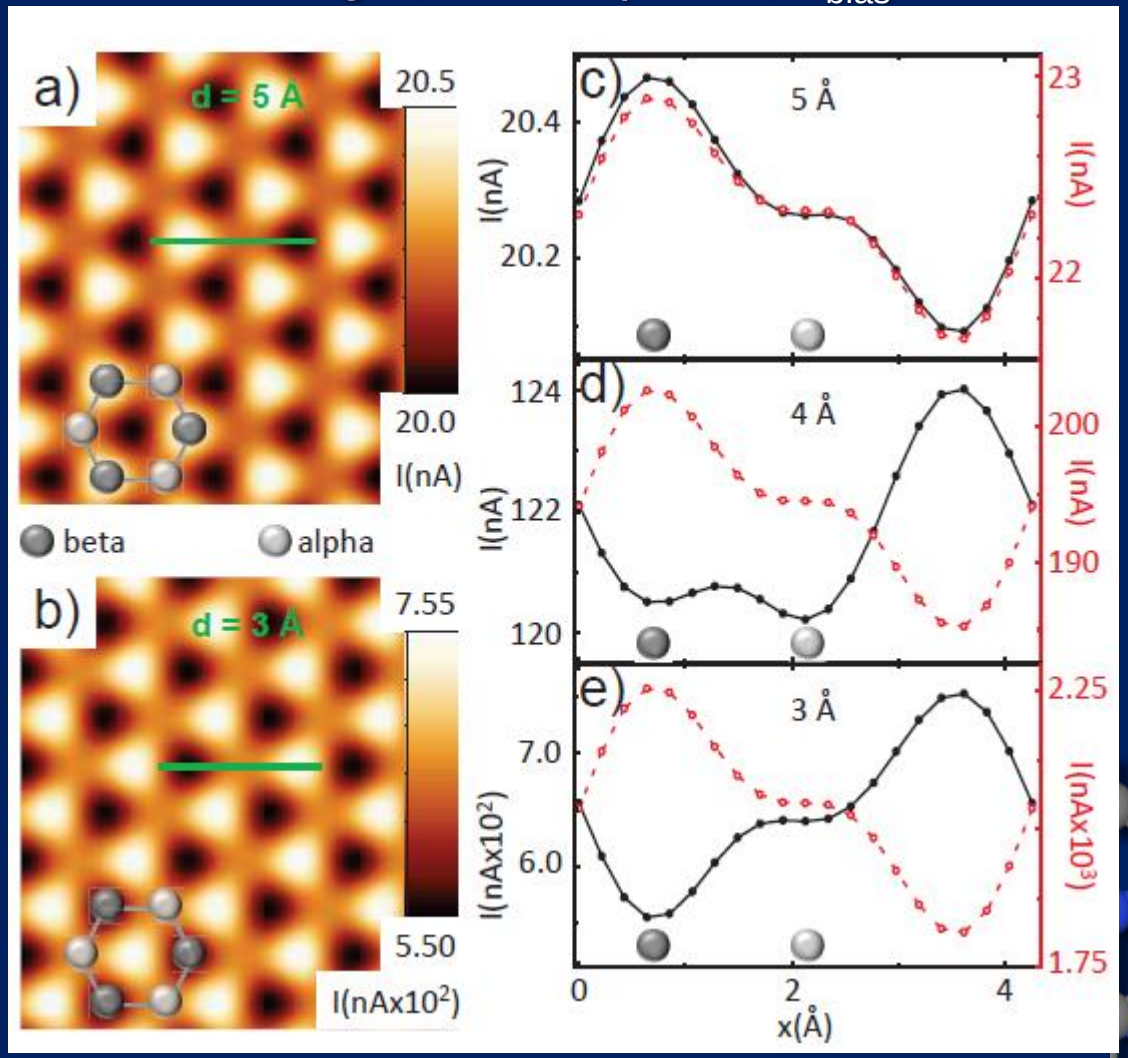


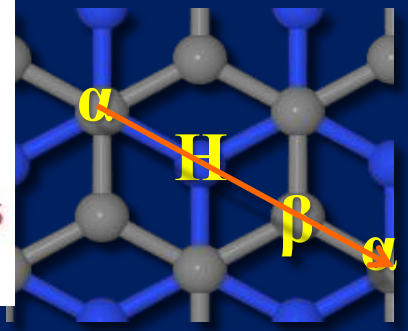
JM. Blanco, F. Flores and R. P., Progress in Surface Science 81, 403-443 (2006)



“Static” STM: results

constant height; 1024 k-points, V_{bias} = -0.3 V





- **change in the contrast with the distance**
- **inverted contrast for distances < 4 Å due to the multiple scattering effect**

Conclusions: Are we imaging atoms?

- FM-AFM: The atomic contrast is controlled by the Short Range Chemical forces. vdW interaction sets the absolute force scale.

- Topographic images yield bright spots on H or C positions depending on the Tip apex: less reactive tips favours the hollow position, more reactive apexes or metallic tips would yield the C atoms as bright spots.

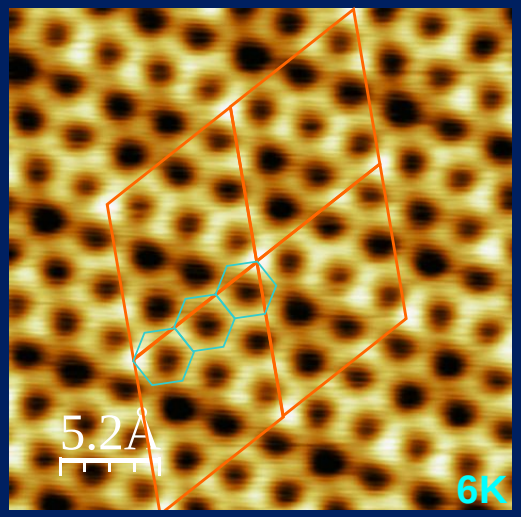
- STM contrast changes with distance: Bright spots located on hollow sites for close distances. Multiple Scattering required!.

- AFM is an excellent experimental tool to check the theoretical vdW approaches!

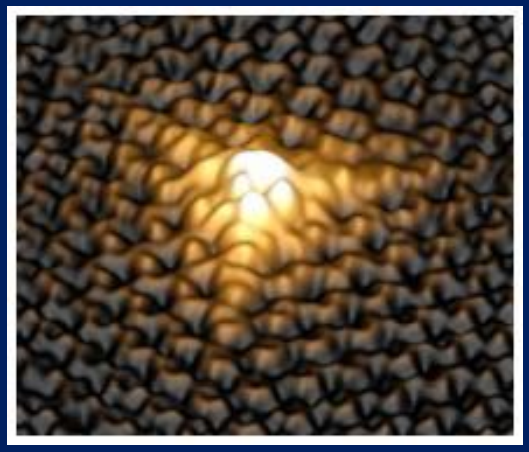
Origin of the atomic contrast?

- FM-AFM: DFT+vdW Forces on SWCNT and graphite (0001)
  - Is vdW providing atomic resolution?
  - atomic contrast versus tip reactivity
- Does STM always image atoms?: multiple scattering effects

- Graphene on Pt(111): Moire patterns



- Vacancies on Gr/Pt(111): Are the localized states on the vacancy preserved?



M. M. Ugeda et al, PRL 104, 096804 (2010)

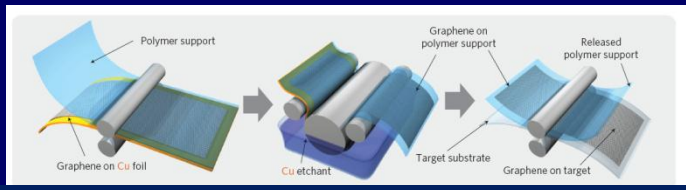
Graphene on metals

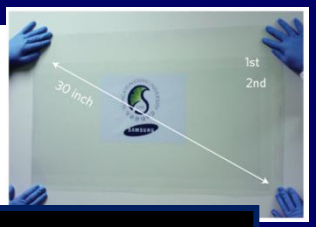
Highly perfect graphene sheets can be grown on various metals

ML graphene on: Co, Ni, Ru, Rh, Pd, Ir, Pt, Cu

see J. Wintterlin *et al.*, Surf. Sci. **603**, 1841 (2009) for a review

Macroscopic-sized graphene films recently transferred to arbitrary substrates



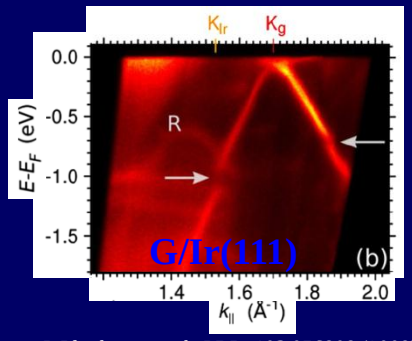


How does the presence of a metallic substrate modify the properties of an atomically tailored graphene layer

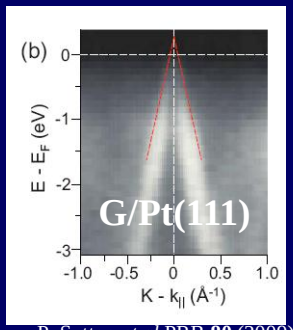
G. Giovannetti *et al.*, PRL **101** 026803 (2008).

A. B. Preobrajenski *et al.* PRB **78,** (2008)

In the weakly interacting systems the electronic structure of ideal graphene is basically preserved.



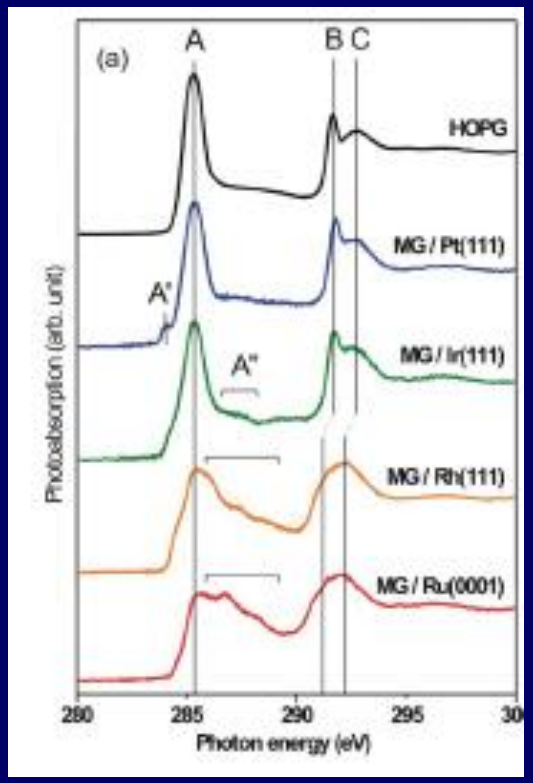
I. Pletikosic *et al.*, PRL. **102** 056808 (2009)

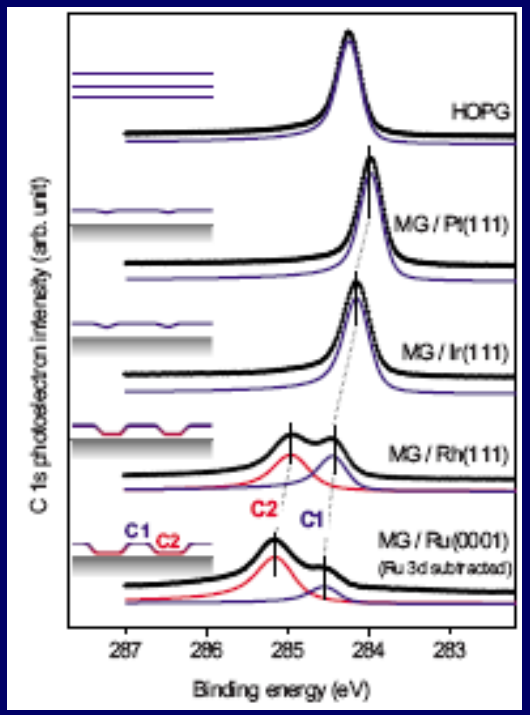


P. Sutter, *et al* PRB **80** (2009)

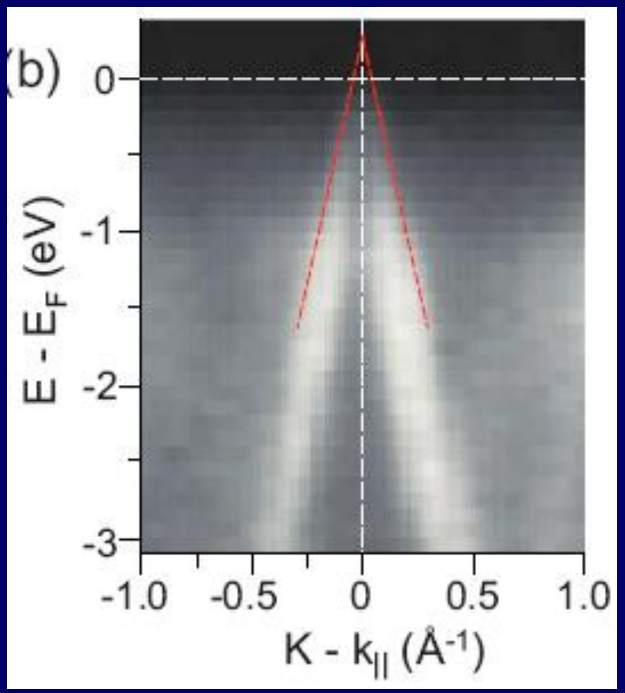
Pristine graphene adsorbed on Pt(111) surfaces

Graphene monolayer adsorbed on Pt(111)
one of the weakest interacting graphene-metal systems





$v_F = 10^6$ m/s

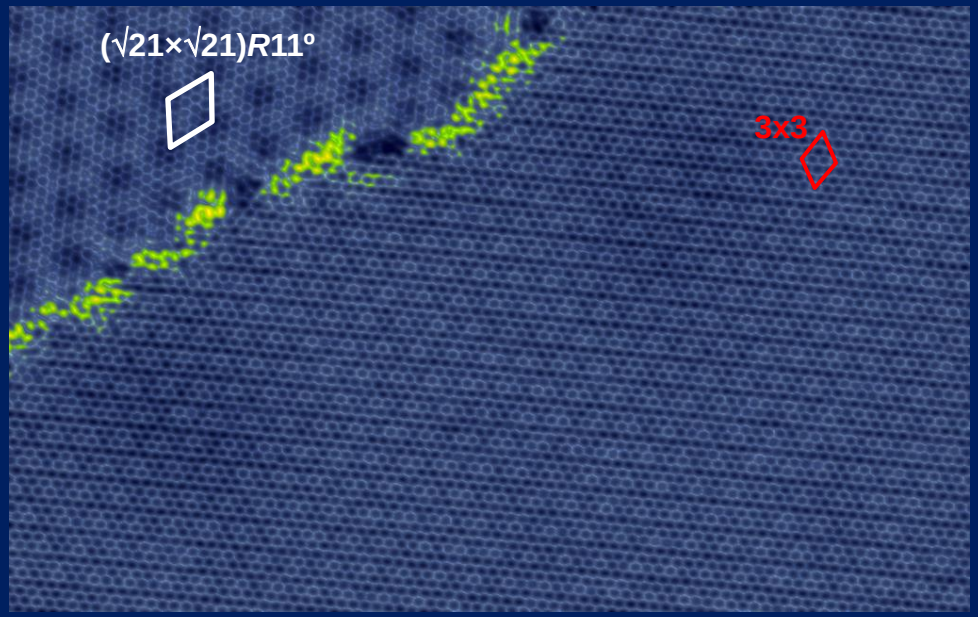


A. B. Preobrajenski *et al*. PRB **78,** 073401 (2008)

P. Sutter, *et al*., PRB **80,** 245411 (2009).

Pristine graphene adsorbed on Pt(111) surfaces

Formed by chemical vapor deposition of ethylene in UHV at temperatures above 1275K



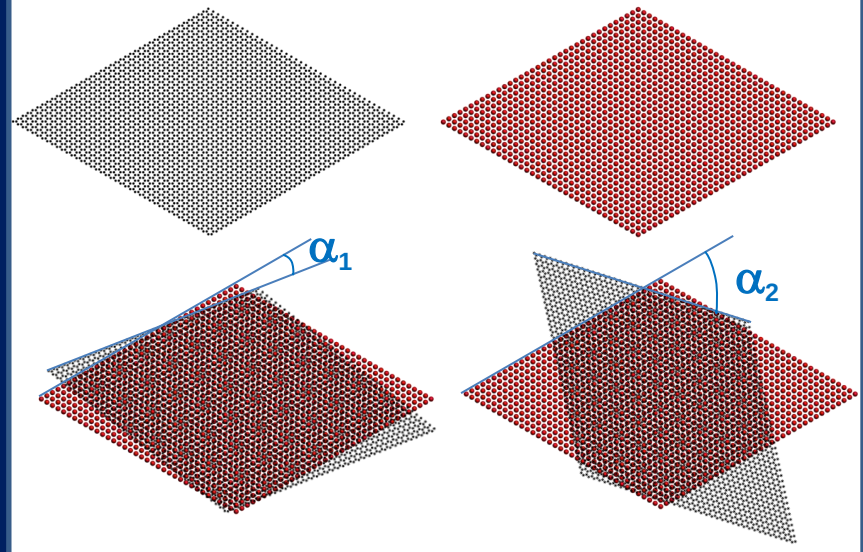
Various moirés patterns are formed

T. A. Land et al., Surf. Sci. **264** 261 (1992).
M. Enachescuet al., Phys. Rev. B **60**, 16913 (1999).
P. Sutter, *et al*., PRB. B **80,** 245411 (2009).
G. Otero et al. Phys. Rev. Lett. **105**, 216102 (2010).

Moiré periodicity

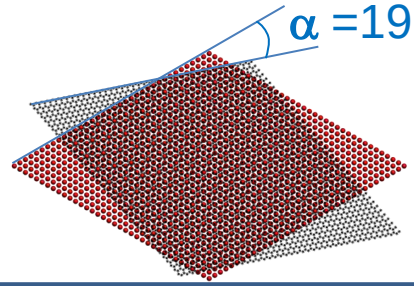
ML Graphene (a=2.46 Å)

Pt(111) surface (a=2.78 Å)



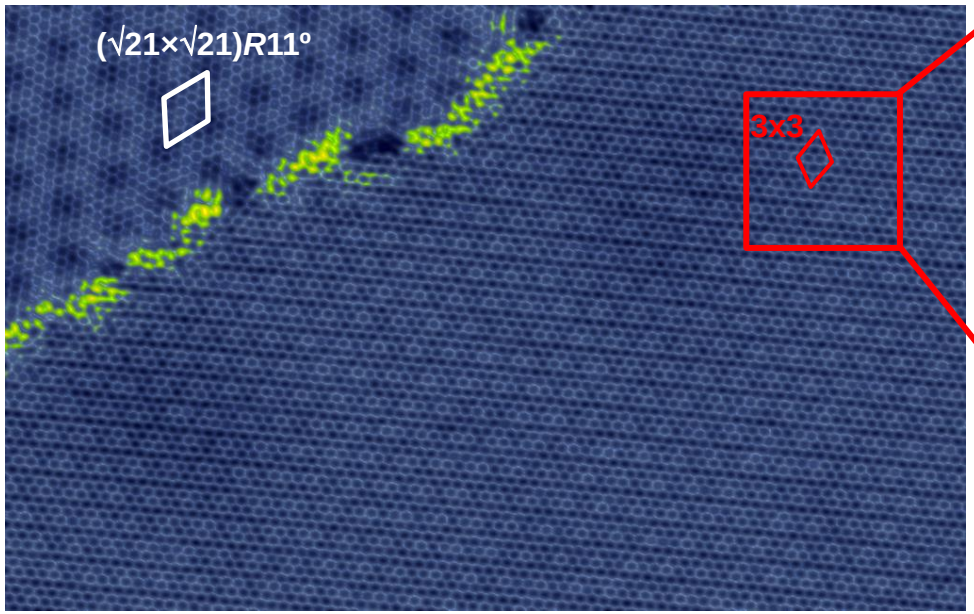
Our results are basically independent of the moiré superstructure

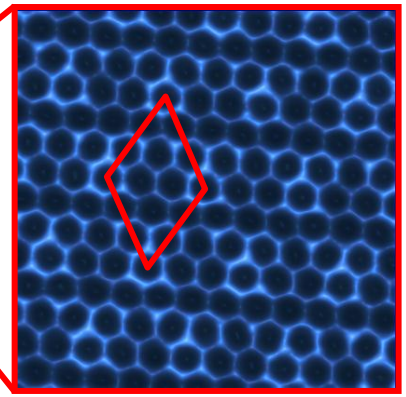
=> 3x3

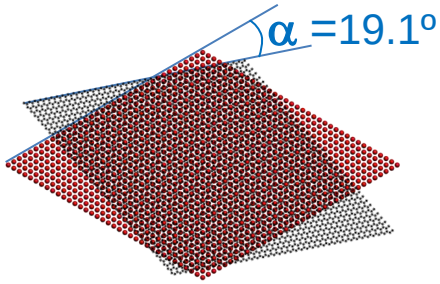


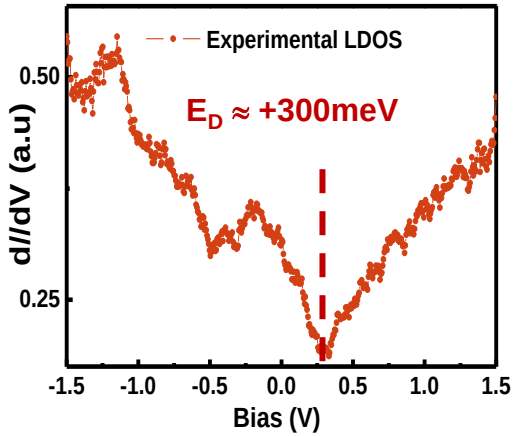
Pristine graphene adsorbed on Pt(111) surfaces

3x3 moiré









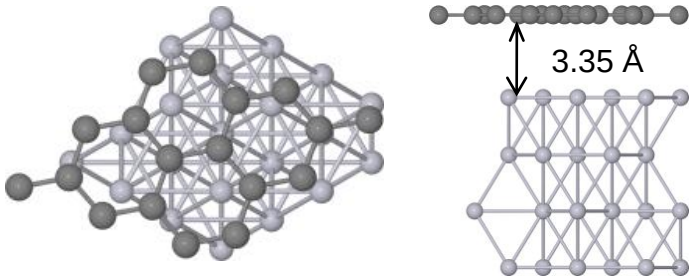
Dirac point at +300 meV

In agreement with theoretical predictions and photoemission estimations

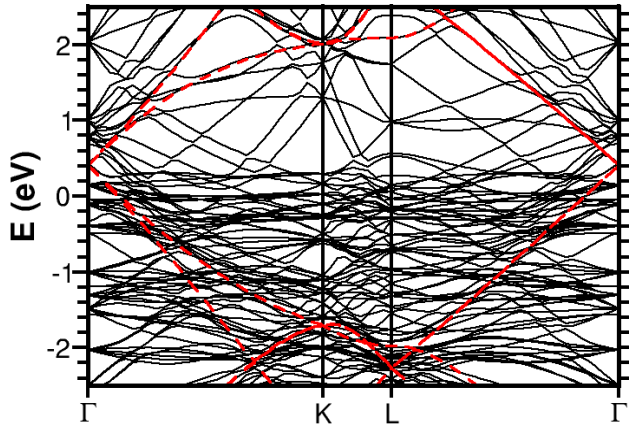
G. Giovannetti *et al*., PRL **101** 026803 (2008).
P. Sutter, *et al* PRB **80,** 245411 ,(2009)

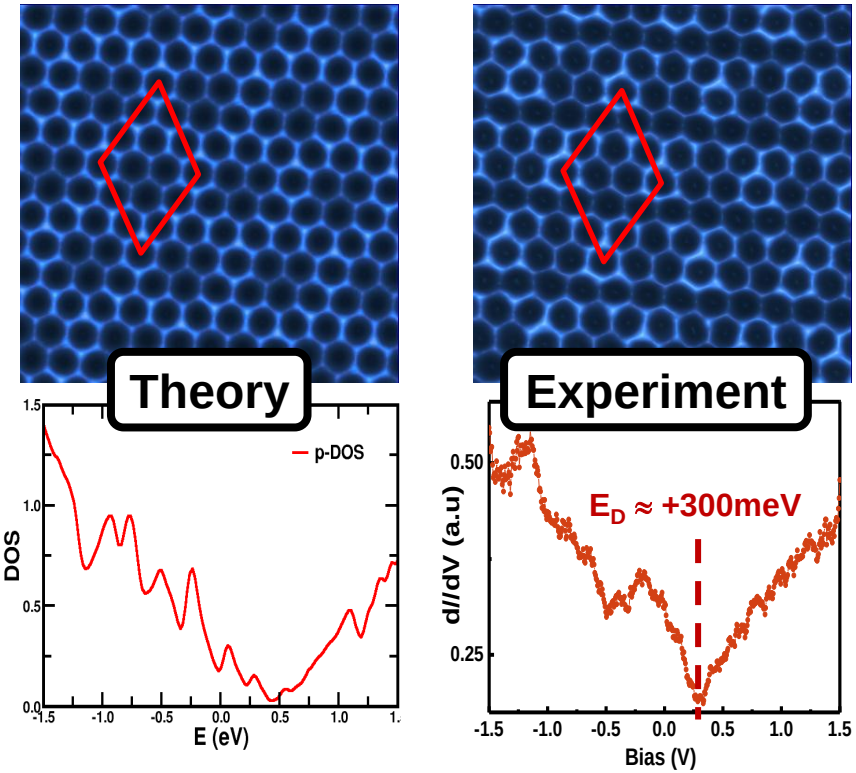
Graphene on Pt(111): DFT calculations

3x3 moiré



Optimal Pt – graphene distance !!





Calculation details:

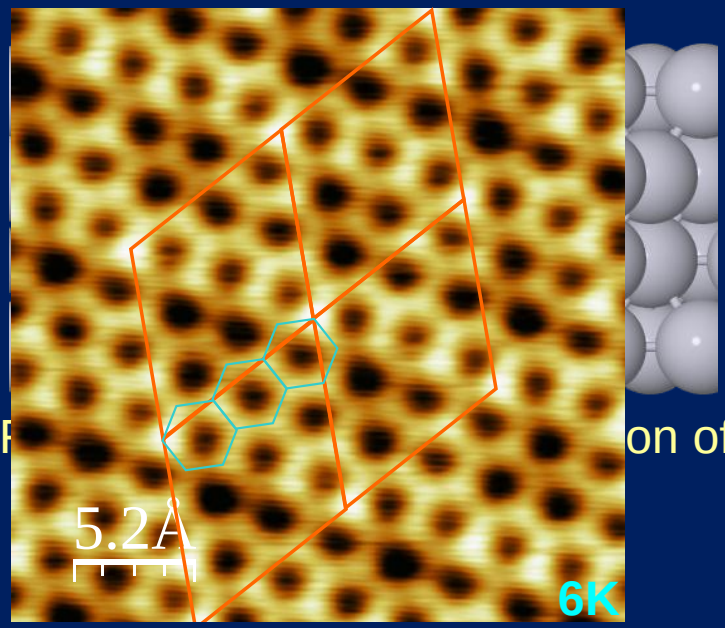
- DFT- VASP code
- **PBE functional + van der Waals interactions**
- Planewave cutoff: 400 eV
- STM images: OpenMX code

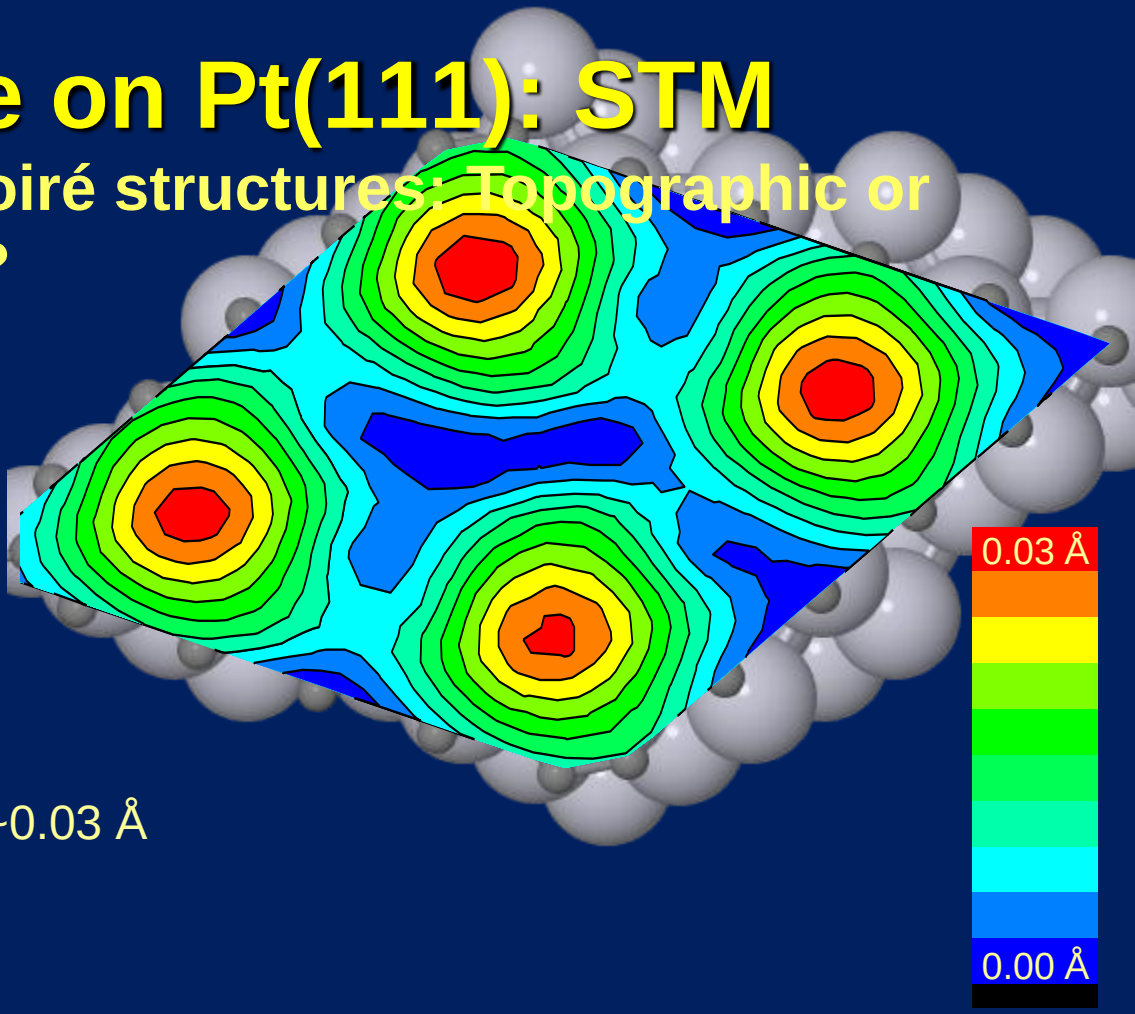
STM corrugation can be explained as a purely electronic effect

Calculations reinforce the association of the dip in the DOS with E_D position

Graphene on Pt(111): STM

- Graphene on metals: Moiré structures: Topographic or purely electronic effect?

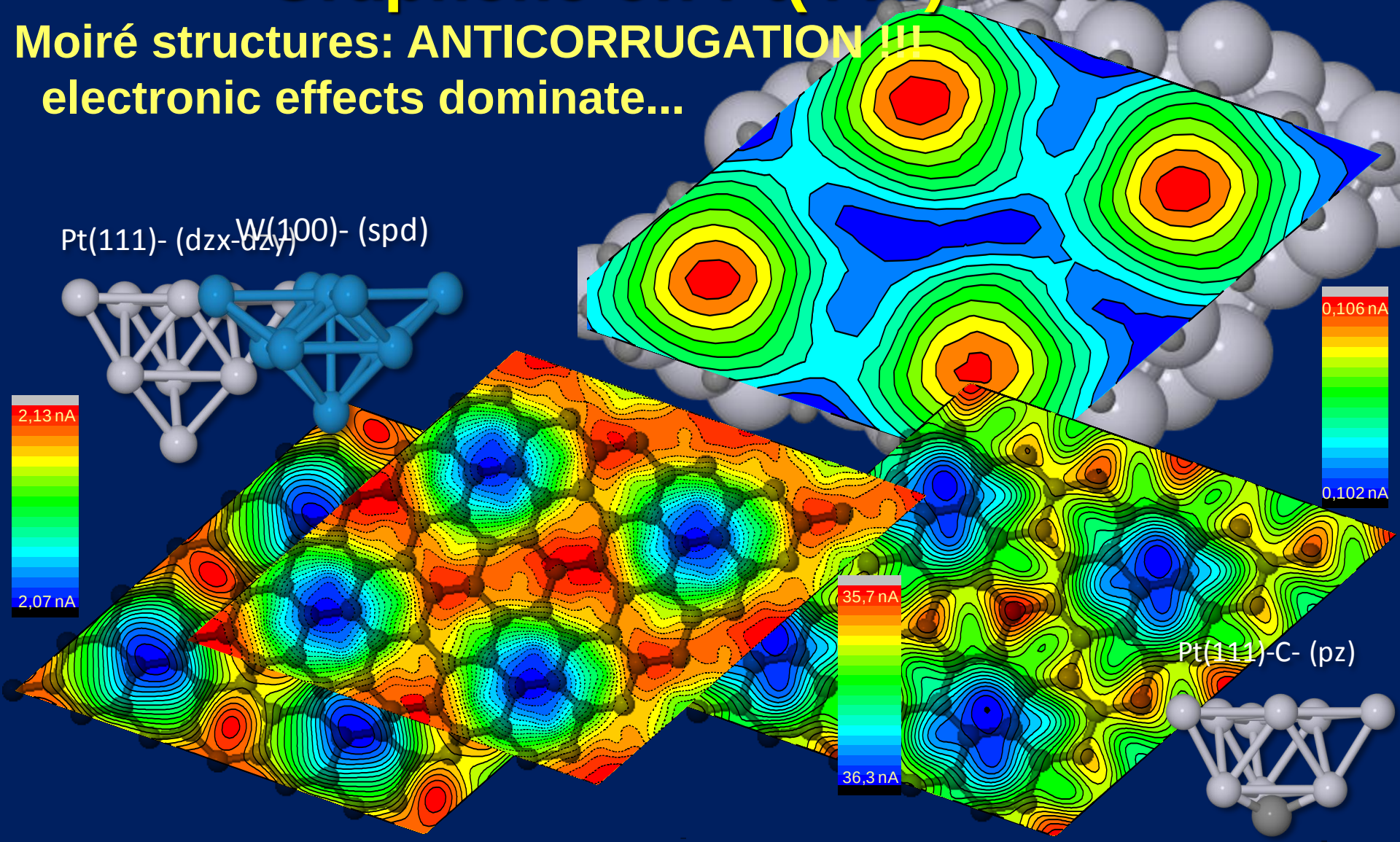




on of ~0.03 Å

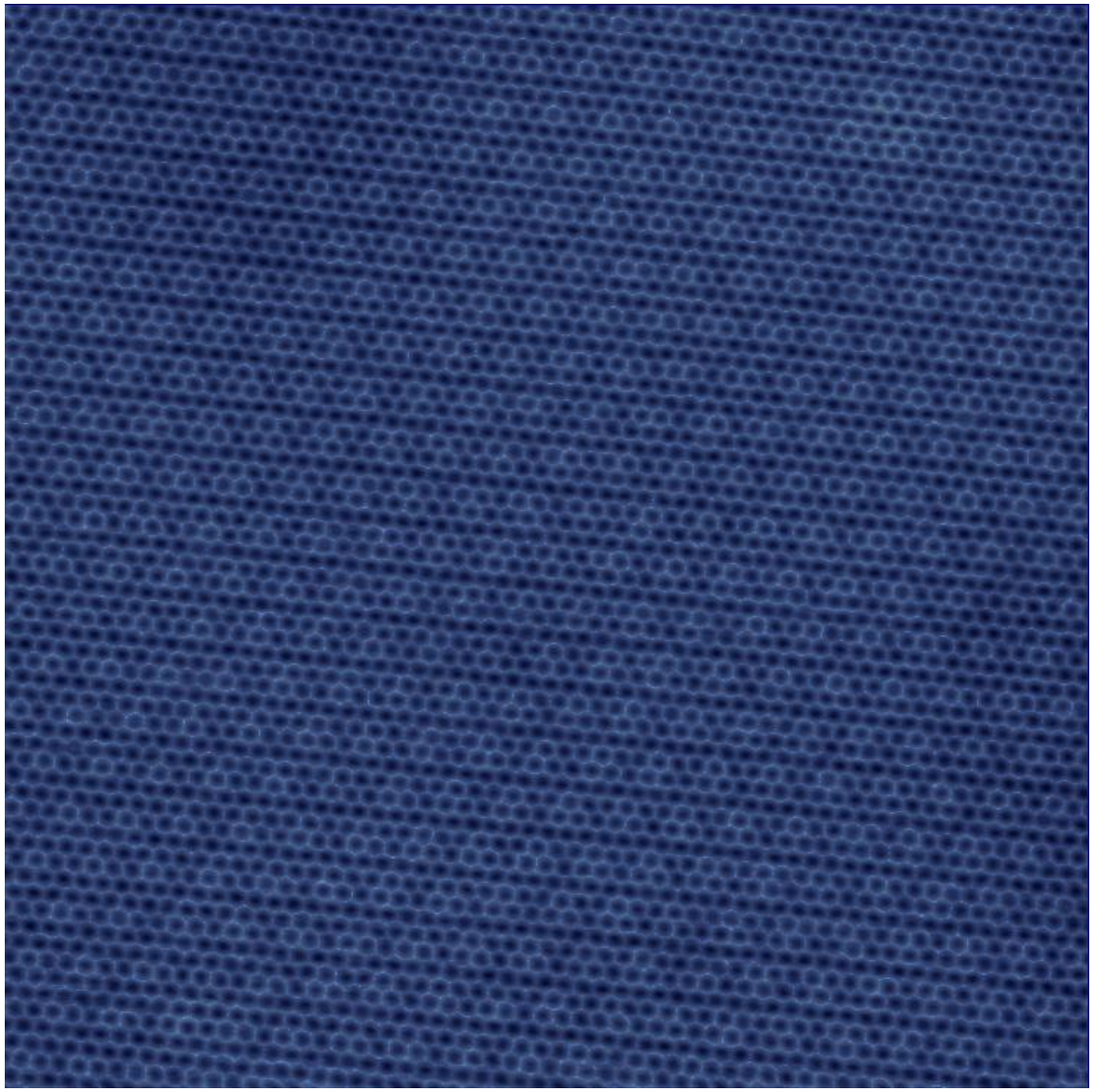
Graphene on Pt(111): STM

Moiré structures: ANTICORRUGATION !!!
electronic effects dominate...



Vacancies on Graphene/Pt(111)

- ✓ Creation of single vacancies by Ar^+ irradiation at RT (same parameters as in HOPG)



Vacancies on Graphene/Pt(111)

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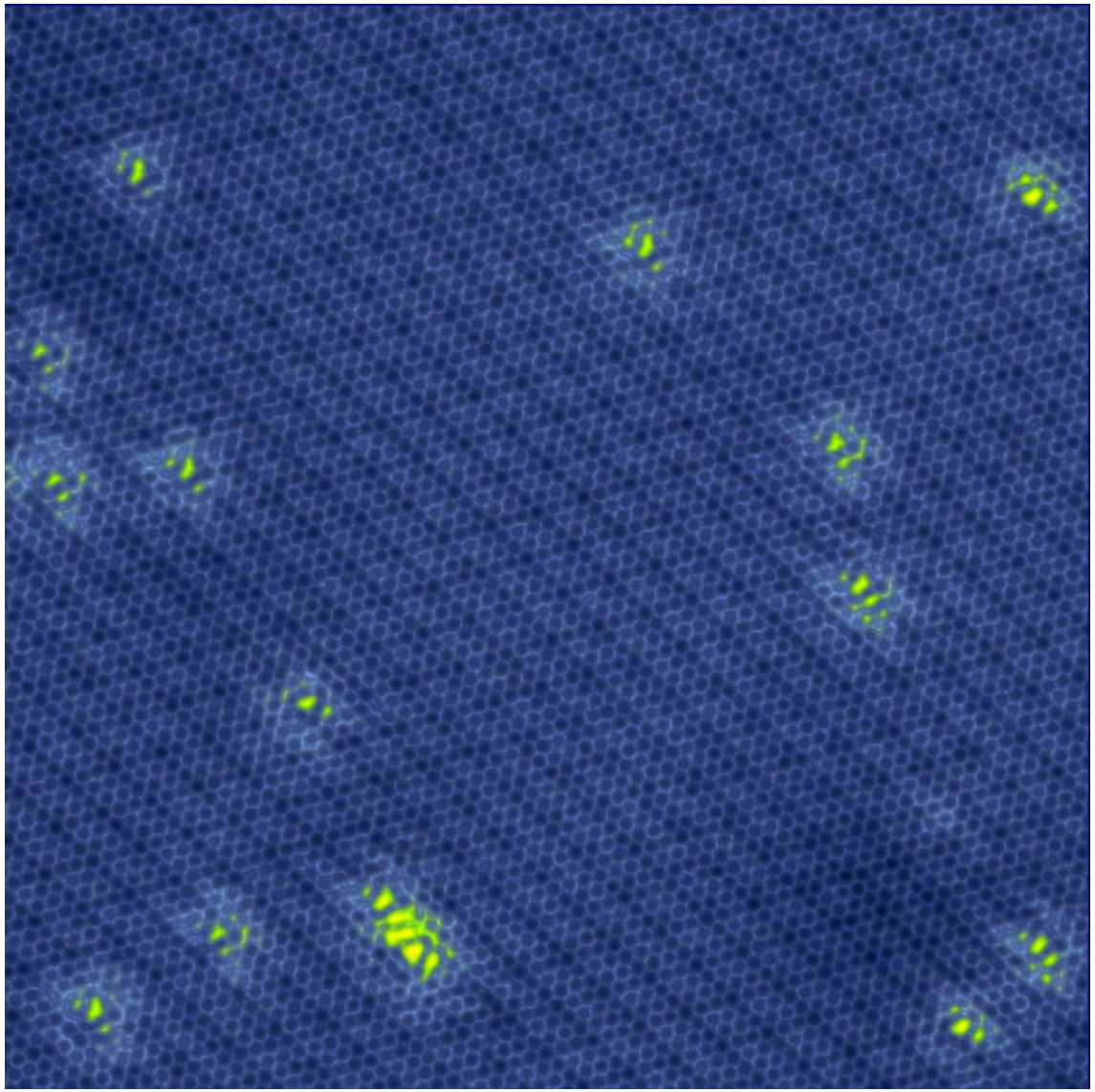
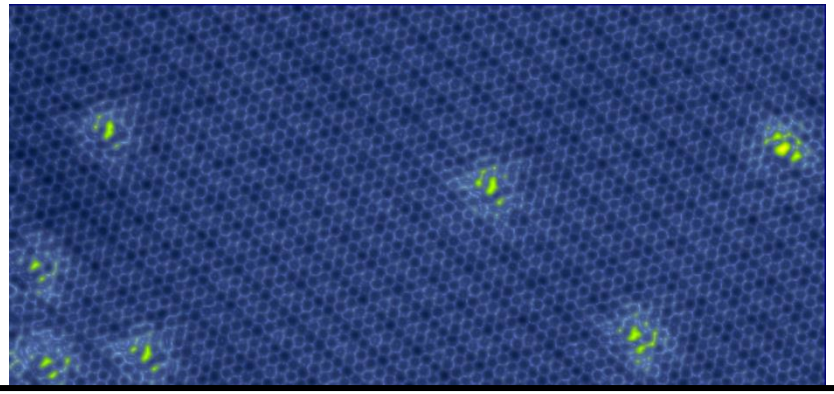
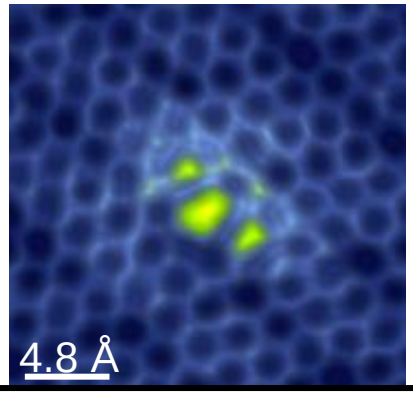
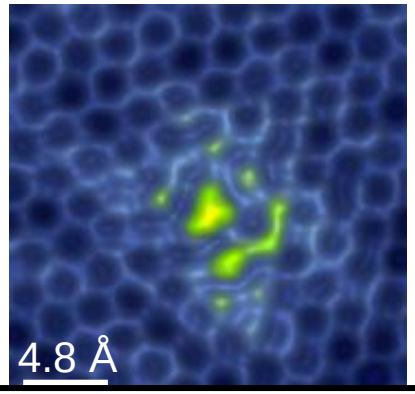


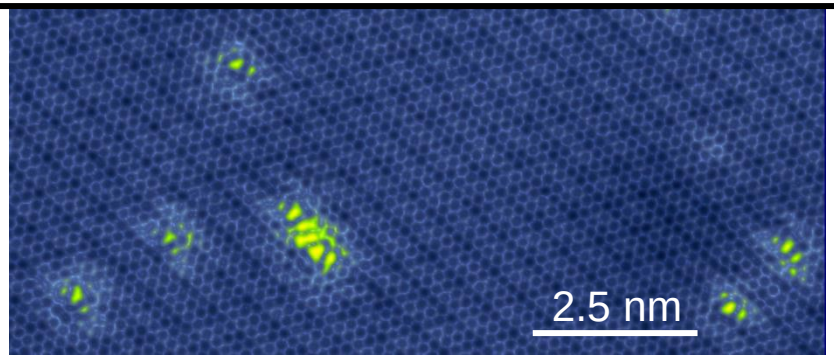
Vacancies on Graphene/Pt(111)

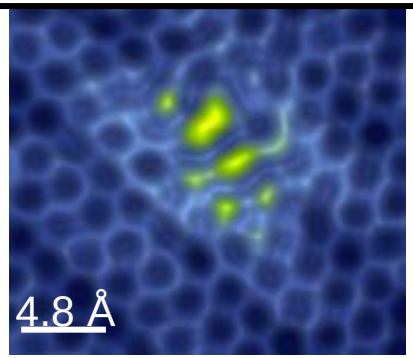


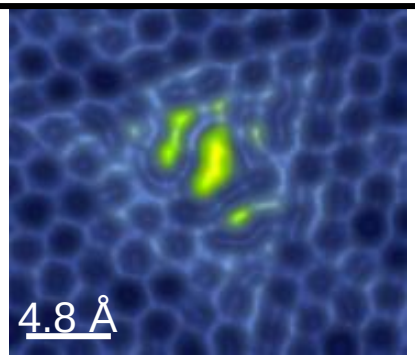




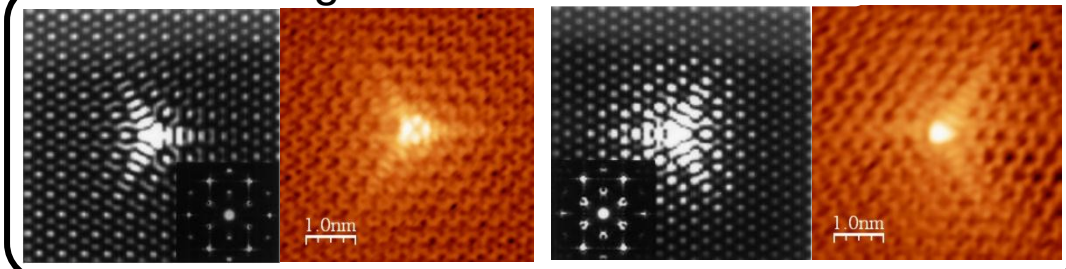
Almost identical features showing non trivial pattern of high LDOS intensity







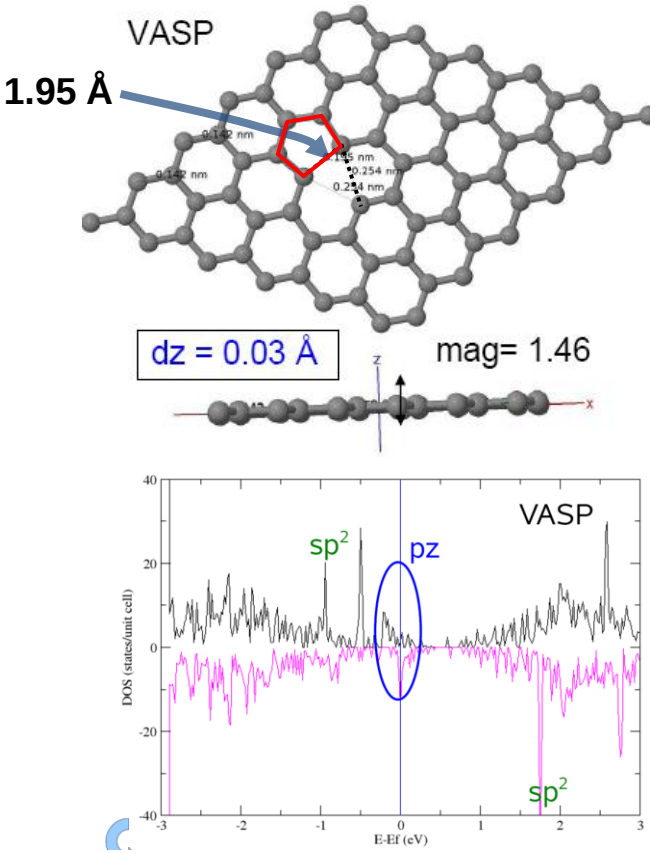
Single C vacancies in HOPG



We need bring into play DFT calculations in order to unravel its nature

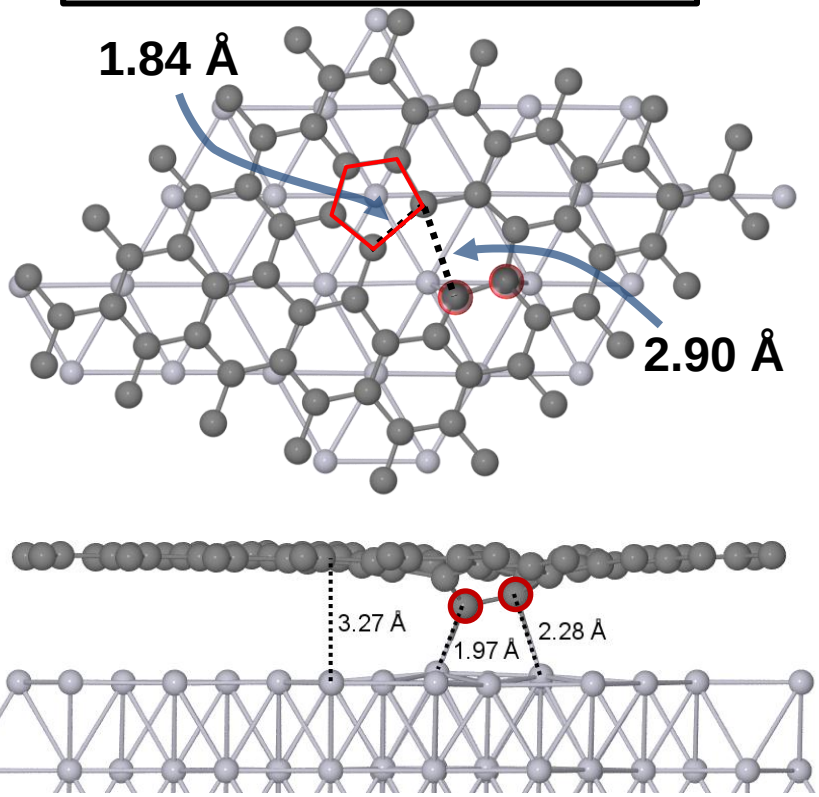
Vacancies on Graphene/Pt(111)

Free standing graphene (6x6)



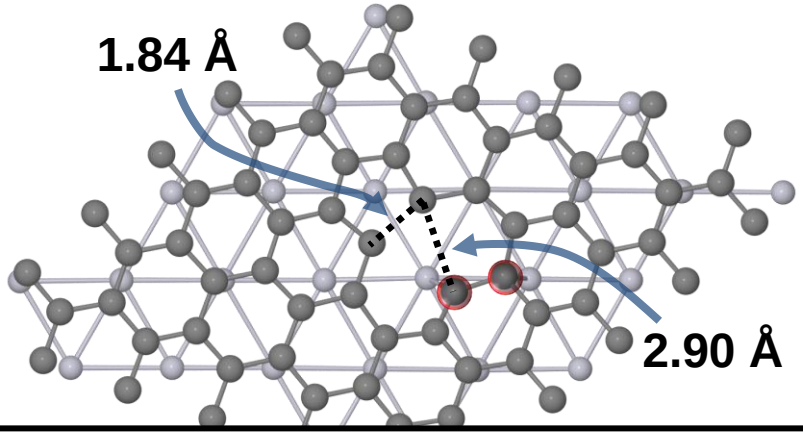
Calculations show a magnetic moment for vacancy in FSG in agreement with O. Yazyev et al, Phys. Rev. B. 75, 125408 (2007)

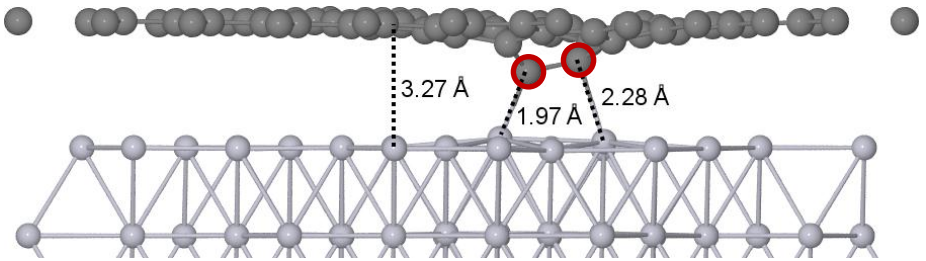
Graphene on Pt(111) (6x6)



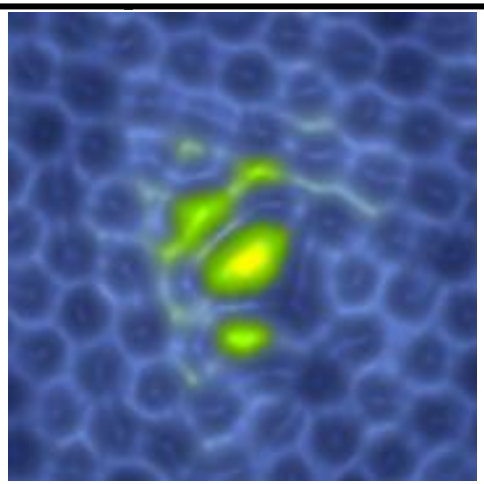
Graphene interaction with the metal strongly increases due to vacancies, giving rise to the quenching of the magnetic moment of the system

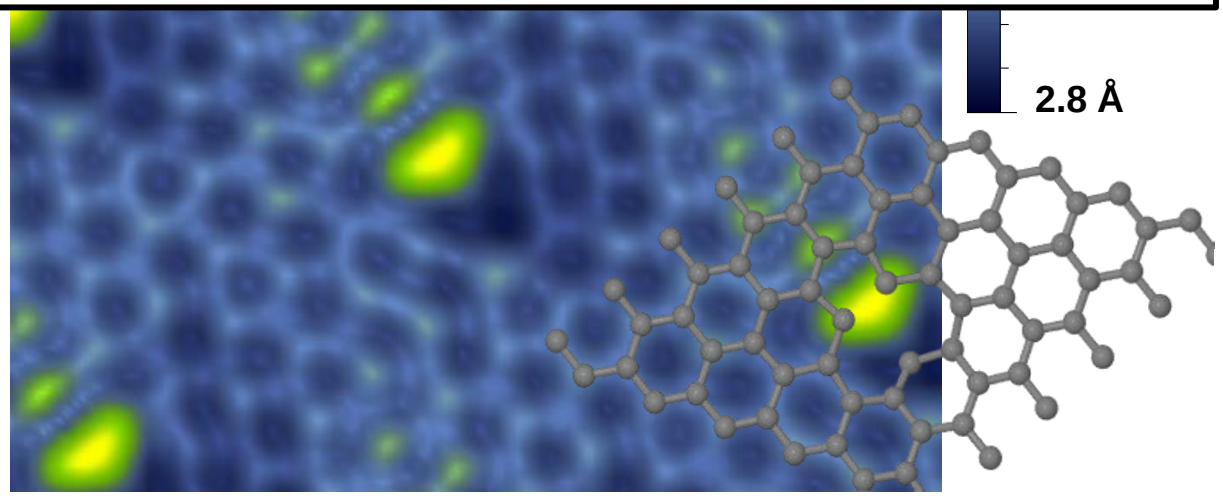
Vacancies on Graphene/Pt(111)



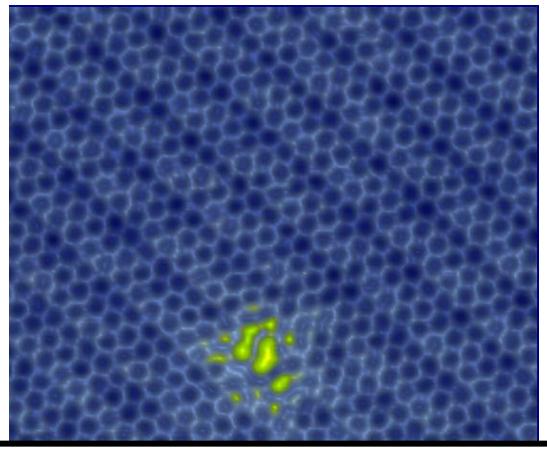


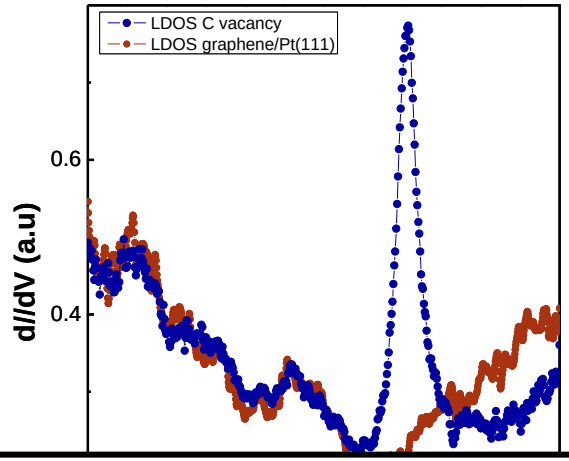
Calculations show that each of the bright features found in the STM images after the ion bombardment is due a missing C atom

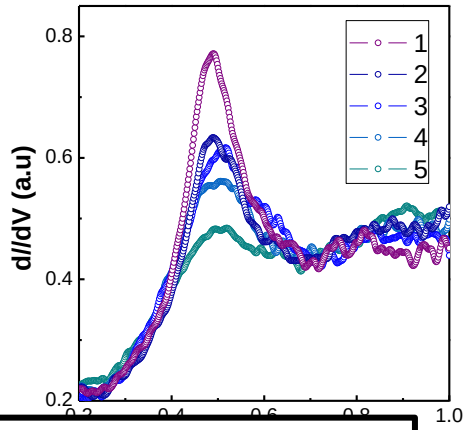




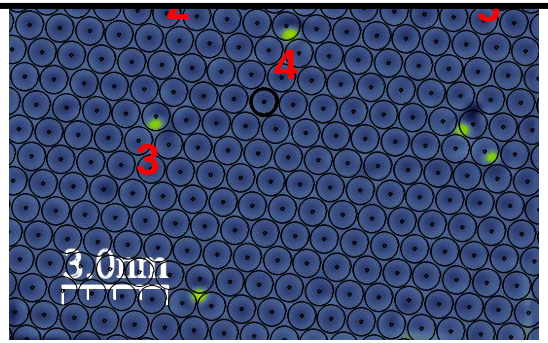
Tunneling Spectroscopy

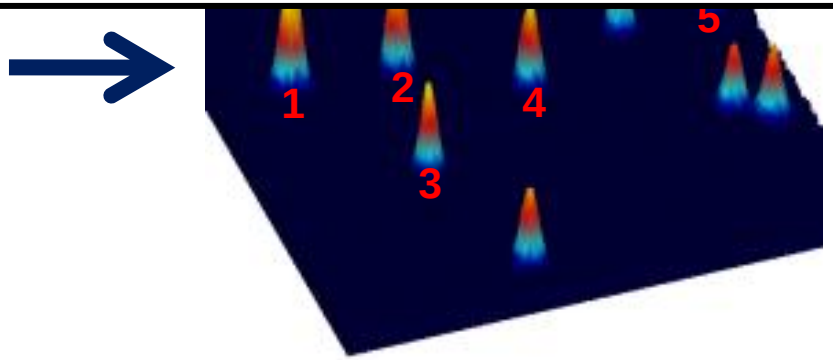


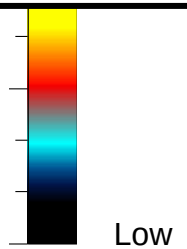




Even in weakly coupled graphene/metal systems, the presence of the metal has to be seriously taken into account in order to controllably tune graphene properties by locally modifying its structure

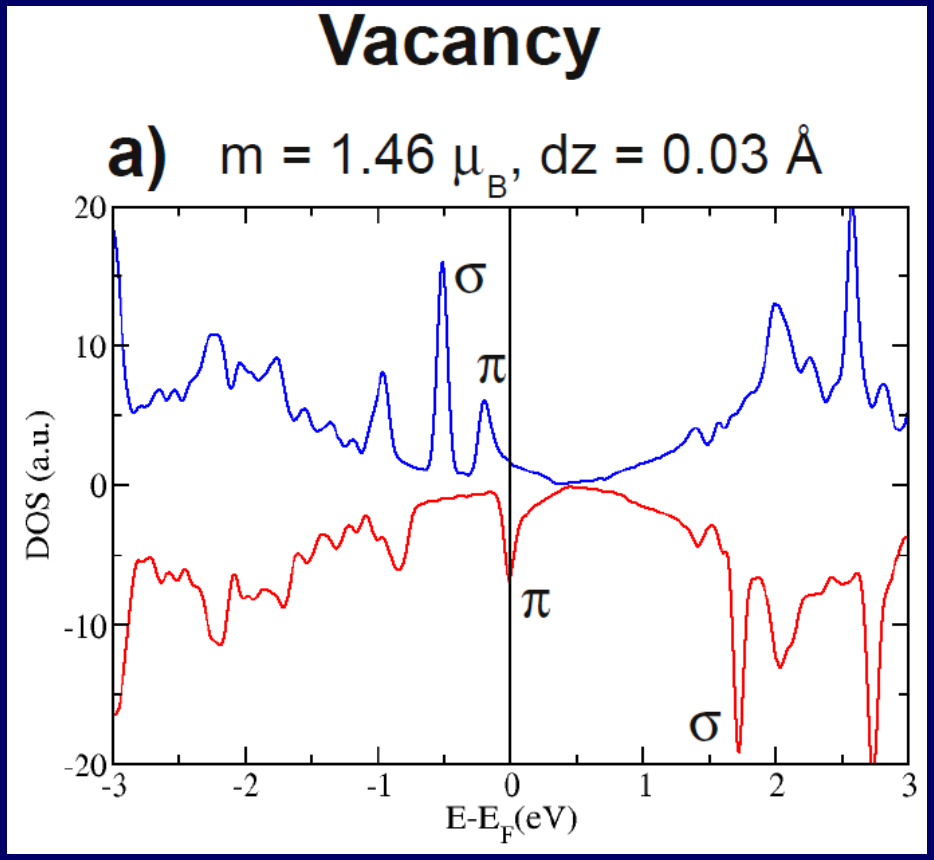


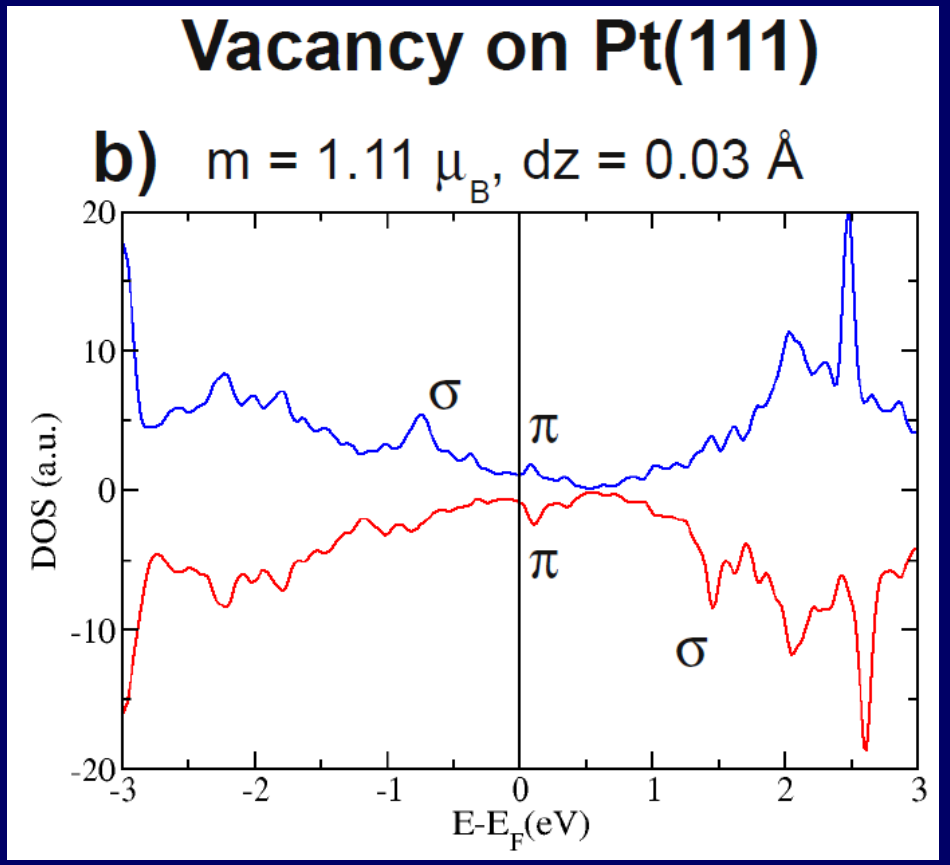




Quenching of the magnetism (1): doping

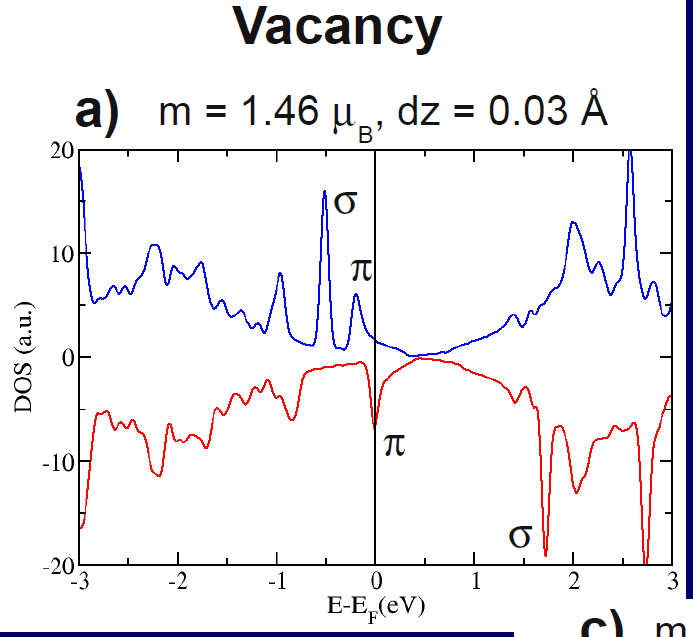
The doping effect induced by the metal pushes the C π states of both spins above the Fermi level !!

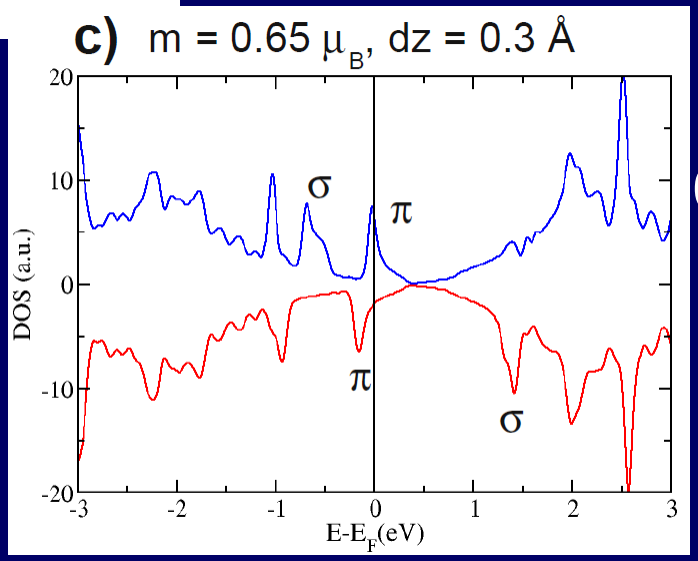




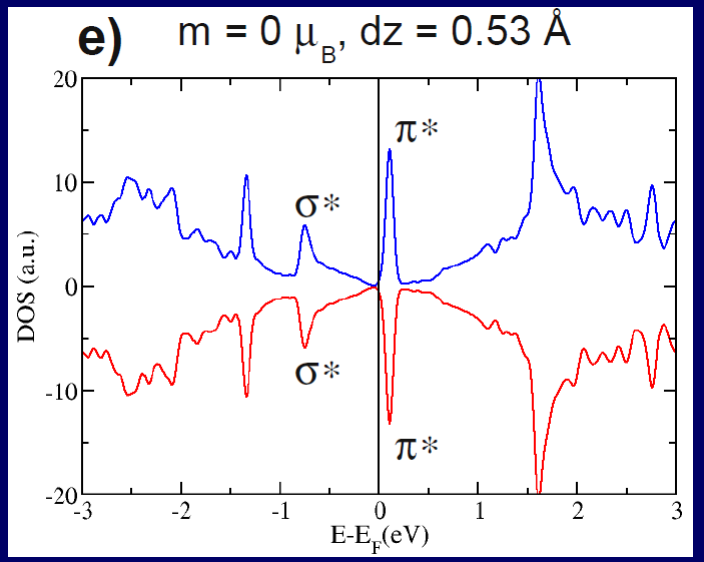
A planar structure, like the one of the vacancy in isolated graphene, would be still magnetic !!

Quenching of the magnetism (2): relaxation of the unpaired C atom out of graphene plane



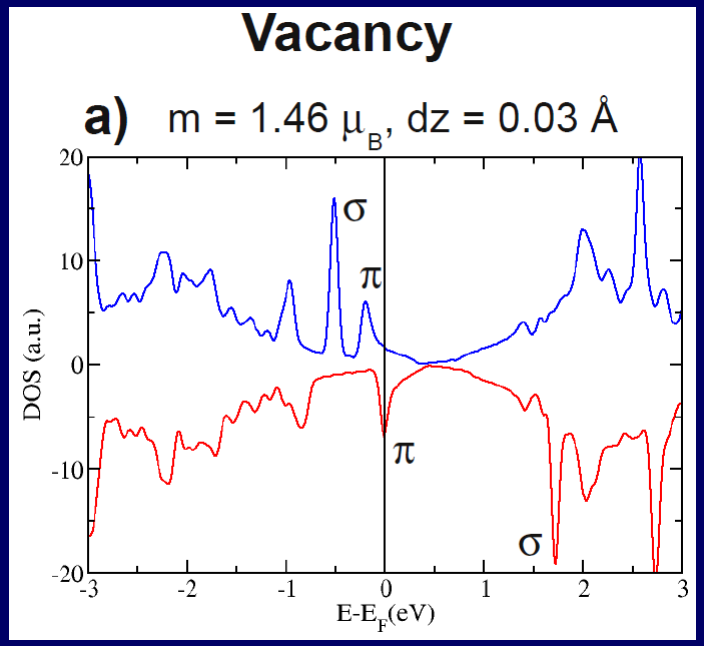


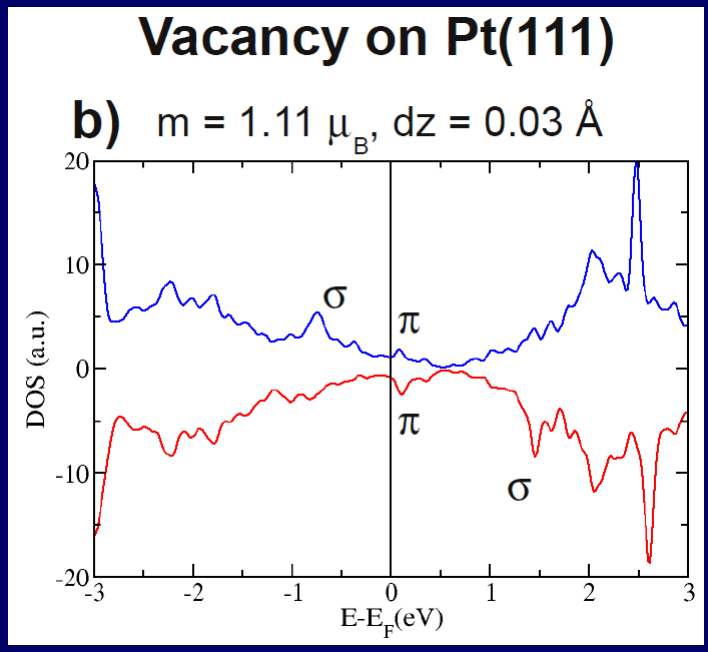
0.1 eV above magnetic GS

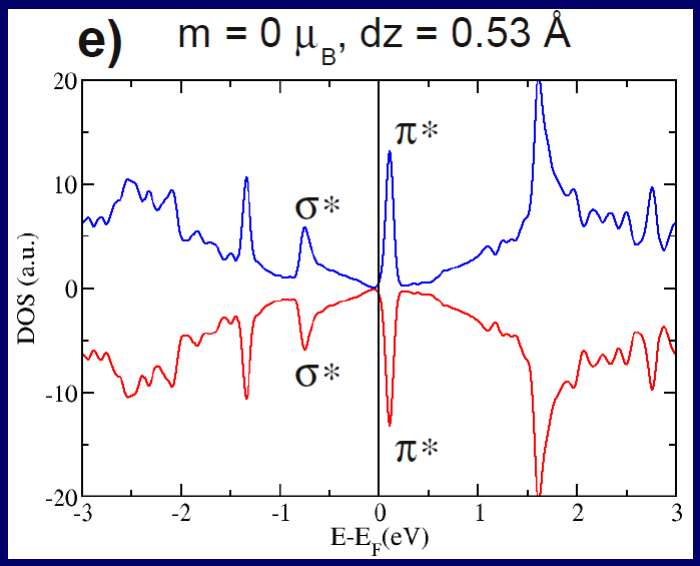


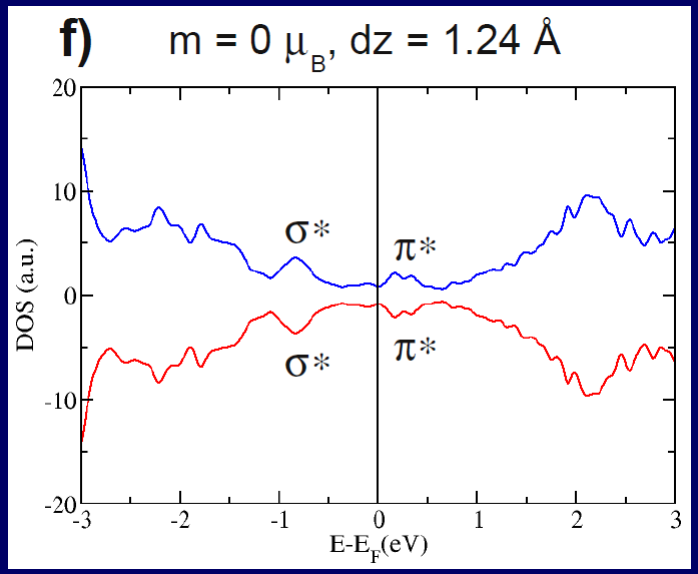
The outward displacement mixes the σ and π states and changes the hybridization of the atom

Quenching of magnetism: Gr/Pt(111)





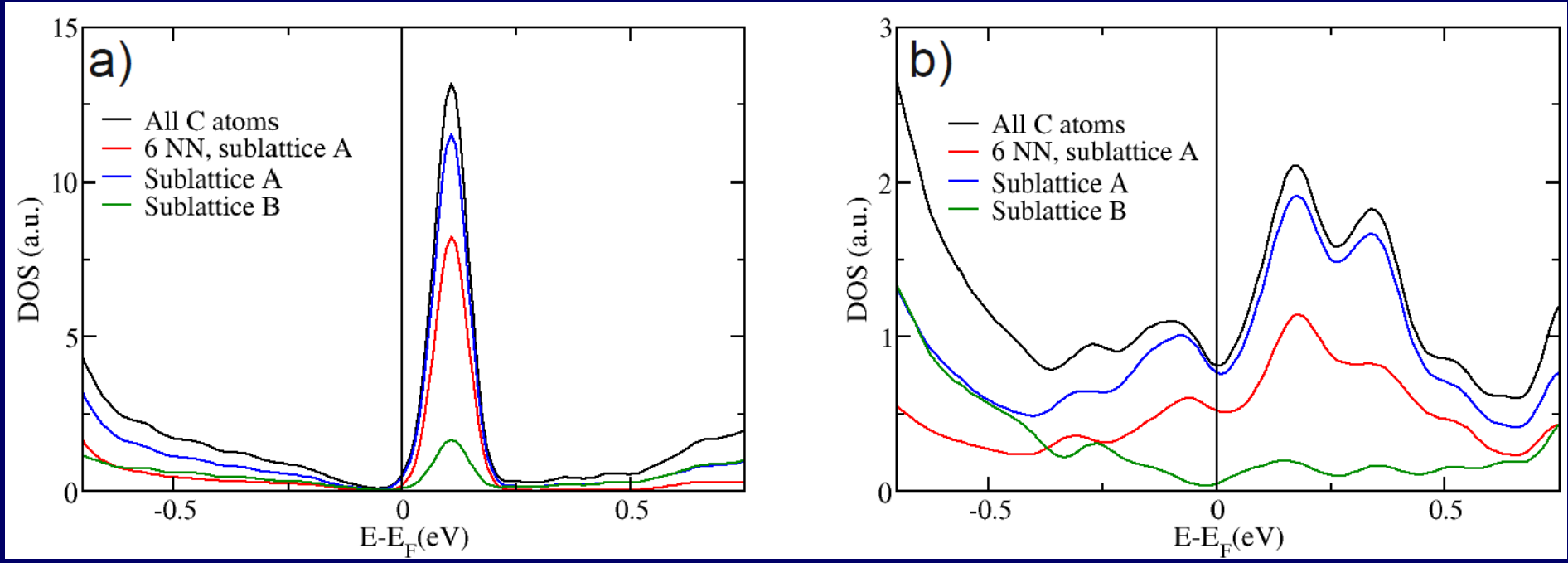




Character of the DOS resonance above E_F

Vacancy on Graphene

Vacancy on Gr/Pt(111)



The PDOS has esentially a p-character in this energy range

Conclusions

1. **Forces & Transport in Nanostructures with ab initio methods: a perfect tool to extract information from STM and AFM experiments**

2. **FM-AFM: single-atom imaging, manipulation, and chemical identification on all kind of surfaces.**

3. **Forces and currents in carbon nanostructures**
   AFM contrast controlled by tip apex reactivity
   STM contrast depends on distance: inversion !!
   Graphene/Pt(111): interaction modifies significantly the properties of the defects

4. **Heterofullerenes from planar precursors:**
   Atomic-scale Origami (2D chemistry+ surface catalyzed cyclization)

Same ideas applied to the production of graphene nanoribbons (Jao et al., Nature 458, 877 (2010))

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Thank you for your attention !!

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