Hydrogen reactivity on a graphite surface

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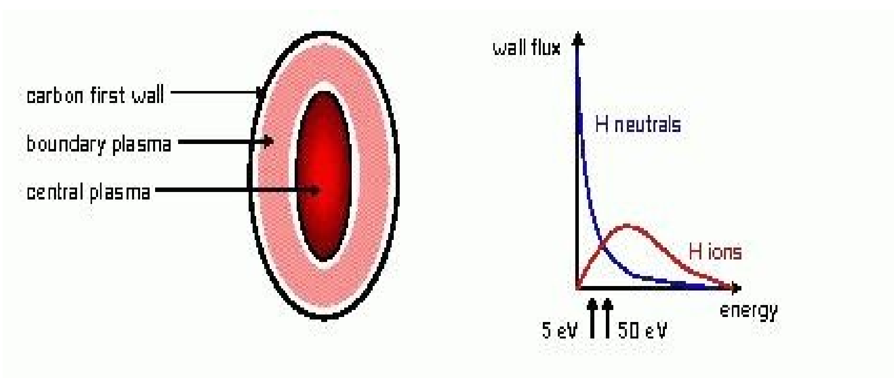
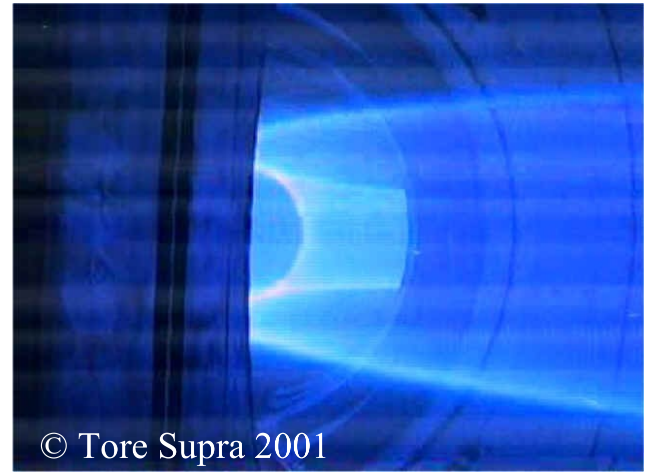
Motivations

- ITER Plasma surface interactions (PSI)
- Experimental modeling of PSI by simple systems:
  - Walls: HOPG,
  - Plasma : atoms & ions.
- Discrimination of effects due to neutrals and ions
- Variations of incident energy and fluxes

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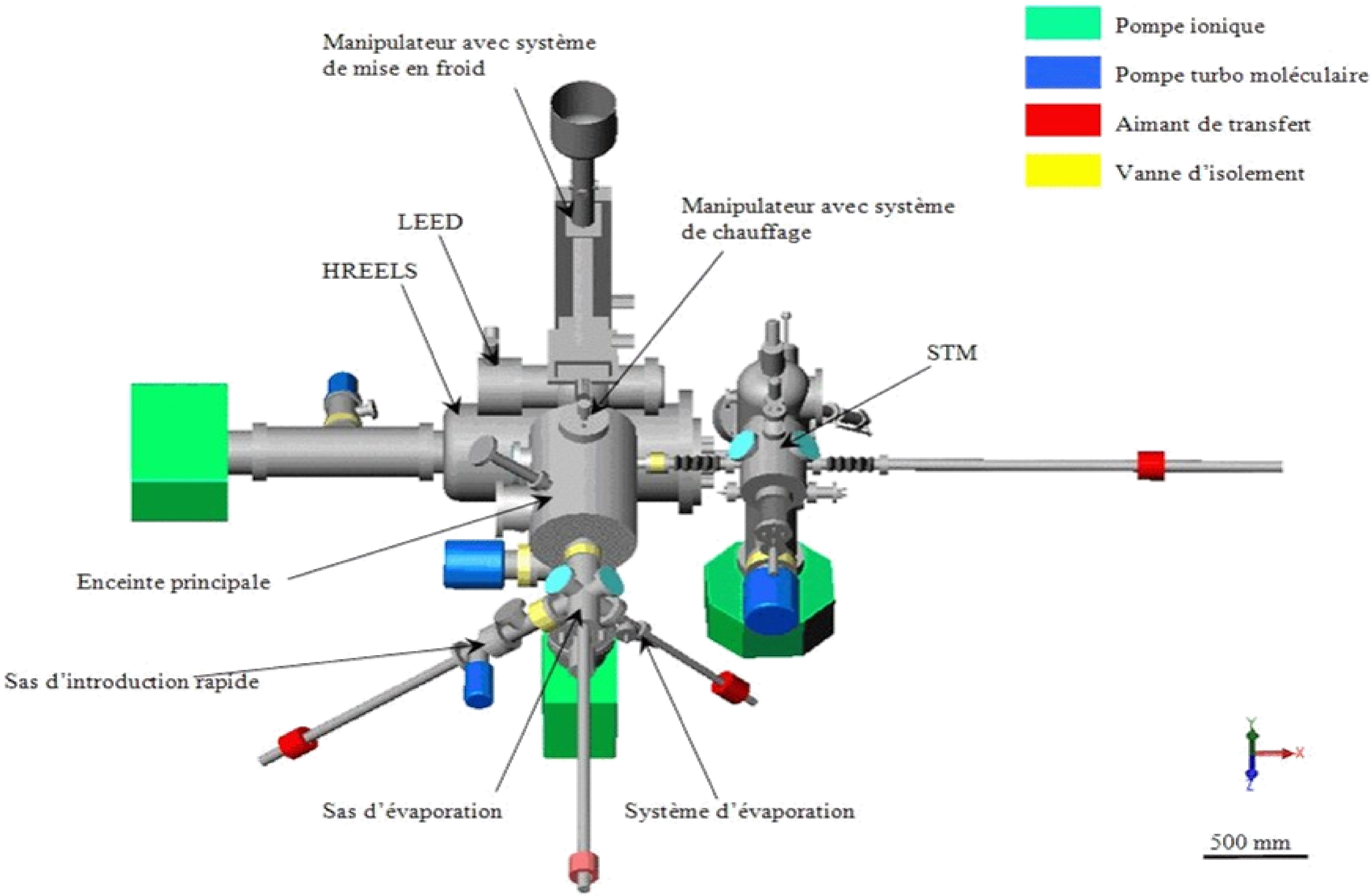
Fundamental studies in labs (e.g.: PIIM)

neutrals ions plasma

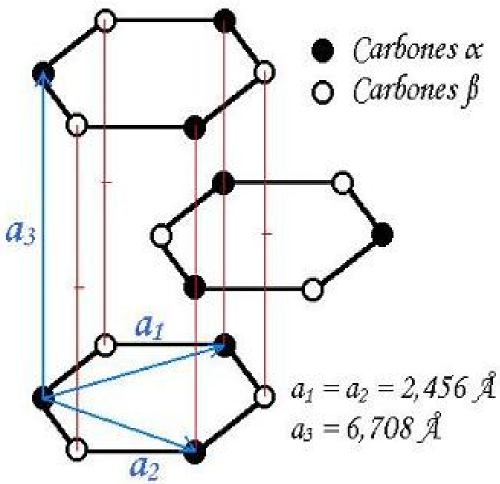
Outlines

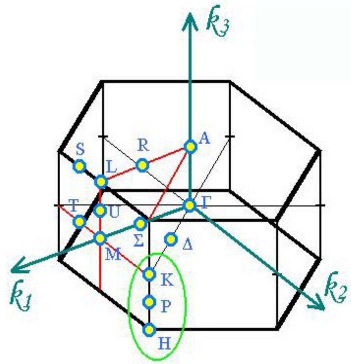
- Motivations
- Experimental setup
- Graphite background
- Adsorption of atomic hydrogen:
  - HREELS study
  - STM study
- Bombardment with hydrogen ions:
  - HREELS study
  - STM study
- Abstraction of H(D) by D(H) on clean surface and bombarded surface
- Plasma-surface interaction
- Conclusion and prospects

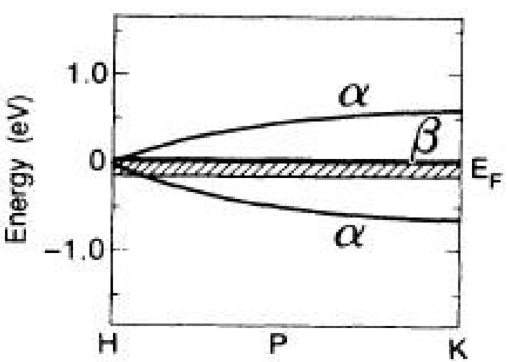
Experimental set-up



Band structure of graphite

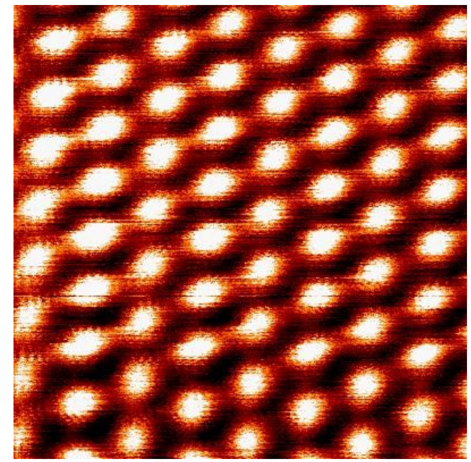




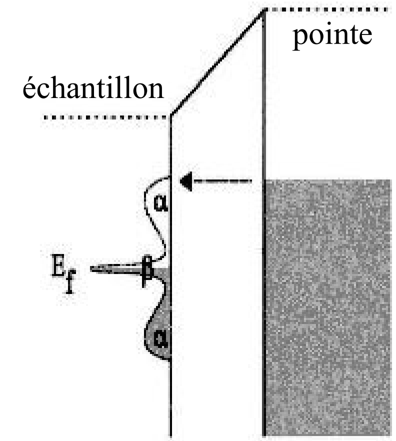


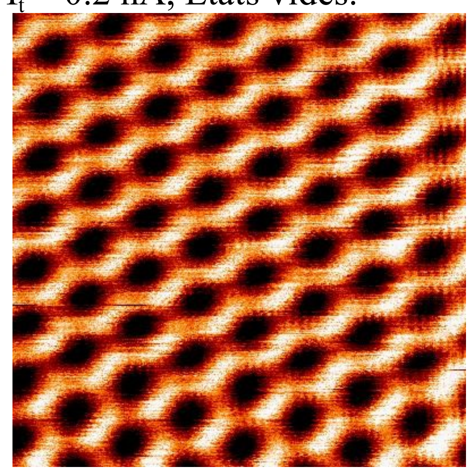
Wallace P.R., *Physical Review*, 71, 622, (1947)

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

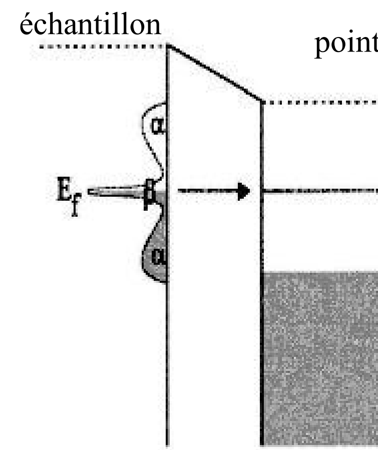


2 nm x 2 nm, V_{bias} = + 66 mV, I_t = 0.2 nA, États vides.

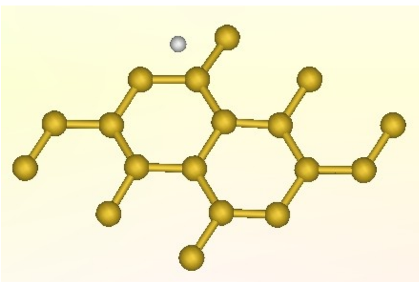


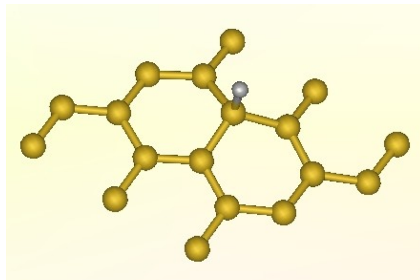


2 nm x 2 nm, V_{bias} = - 66 mV, I_t = 0.2 nA, États pleins.

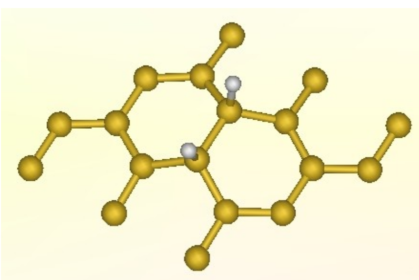


Adsorption model of atomic hydrogen

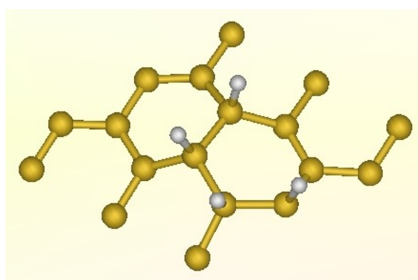




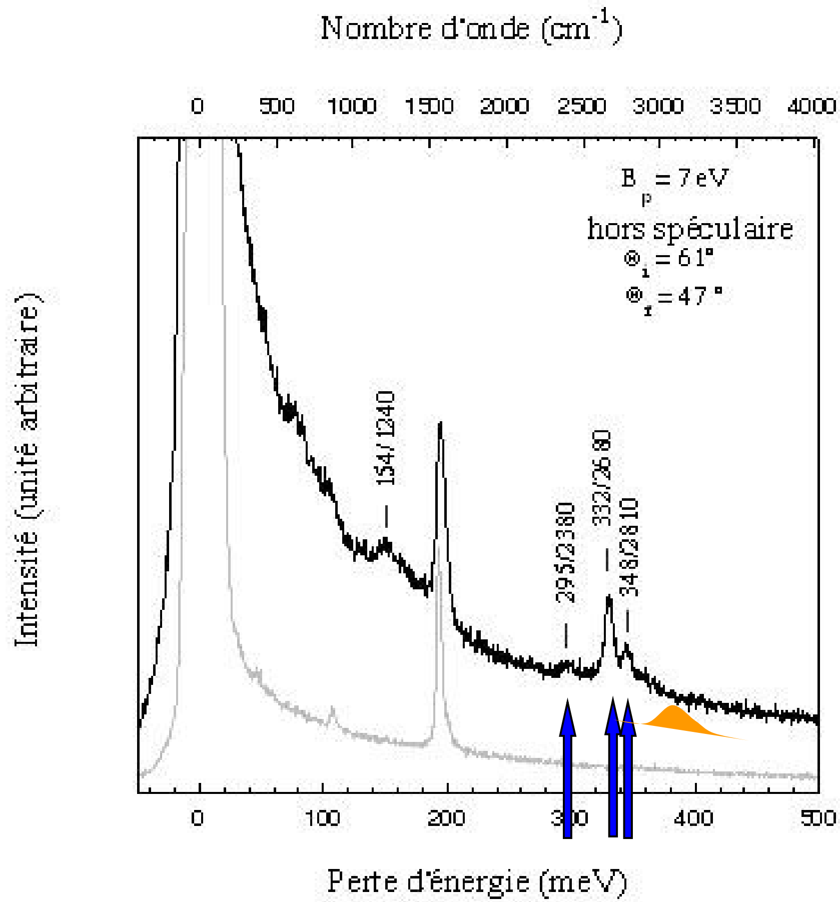
monomer



dimer



Quartet - cluster

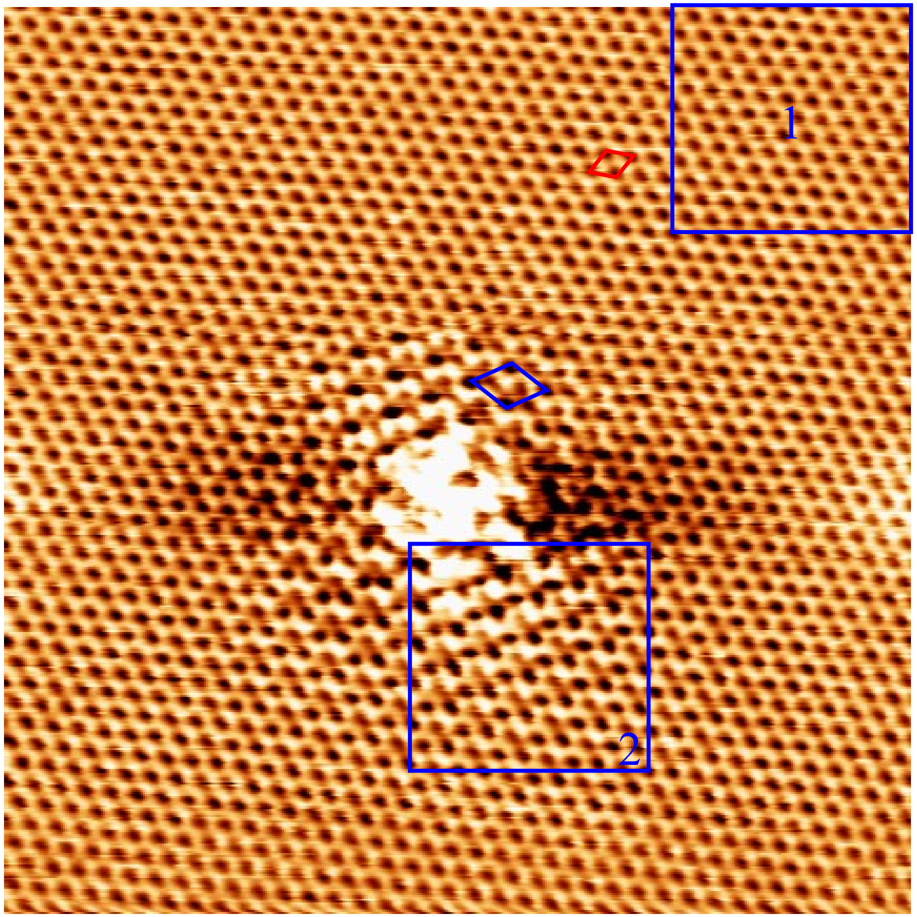


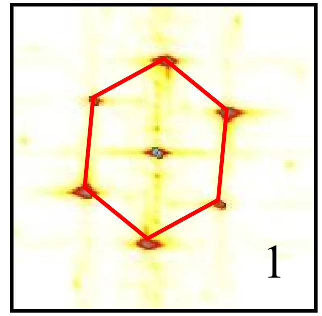
- C-H « weak » bond
- weak sp^3 character

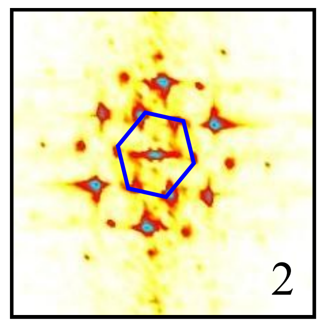
Allouche A., Ferro Y., Angot T., Thomas C., Layet J.-M., *J. Chem. Phy.*, 123, 124701, (2005)

LDOS pertubation

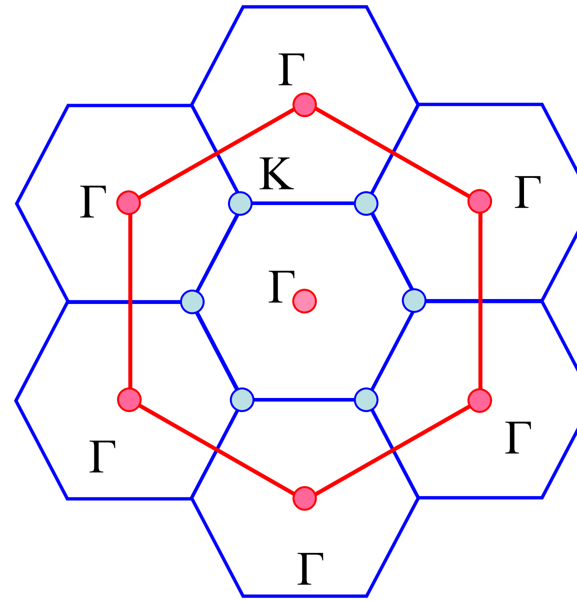
Exposure : 3 Langmuir atomic hydrogen







Reciprocal space unit cell

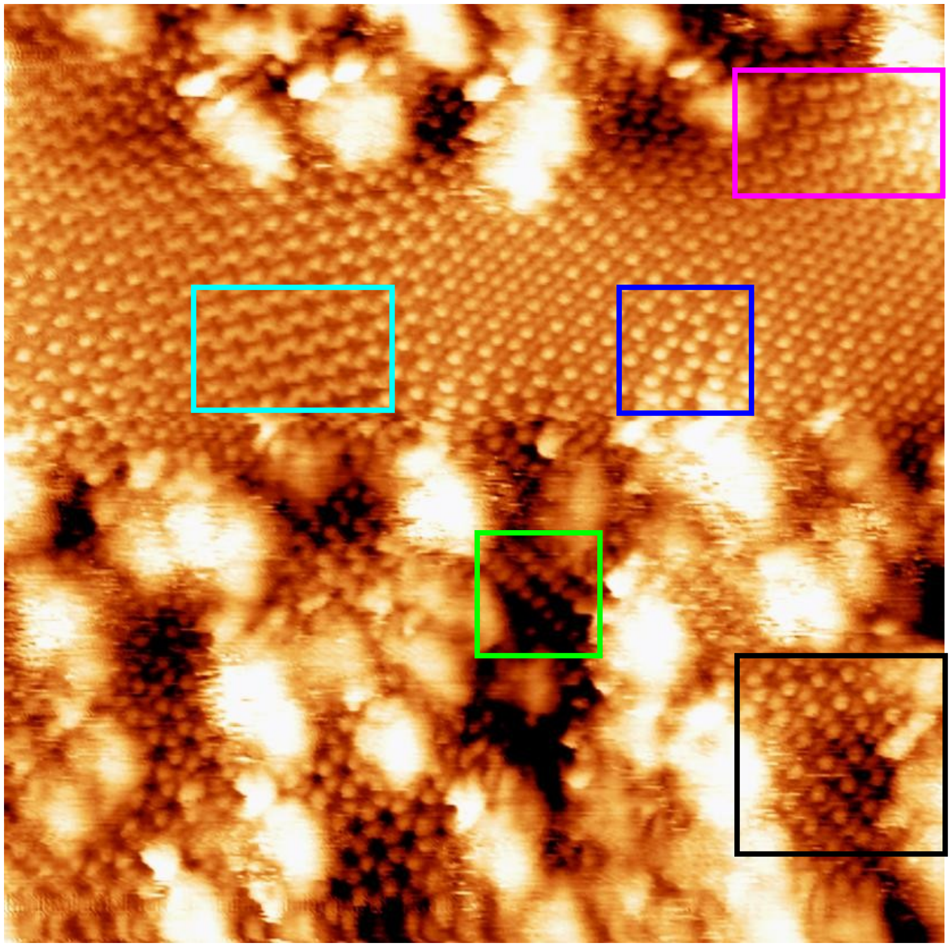


2D Brillouin zone

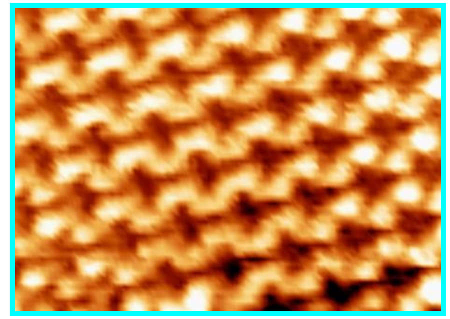
10,3 nm x 10,3 nm, V_{bias} = 30 mV, I_t = 0.250 nA.

Superstructure : $\left(\sqrt{3}\times\sqrt{3}\right)R30^o$

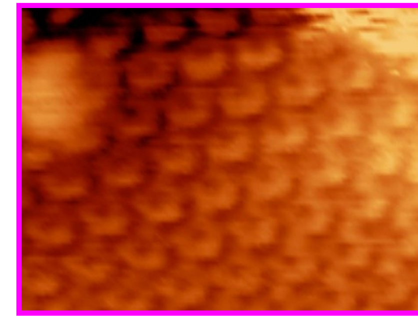
Standing Charge Density Waves



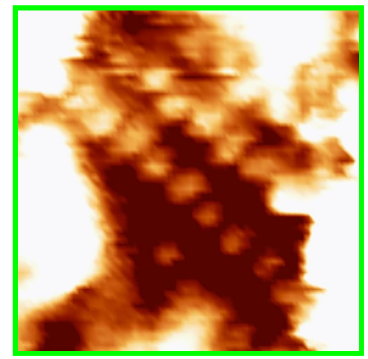
15 nm x 15 nm, V_{bias} = 50 mV, I_t = 0.35 nA.
Exposure : 12 Langmuir atomic hydrogen



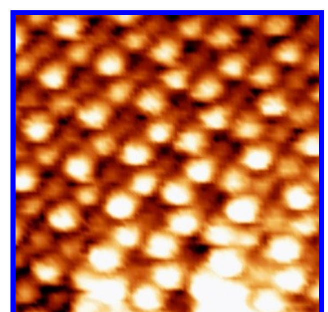
3.5 nm x 2.5 nm



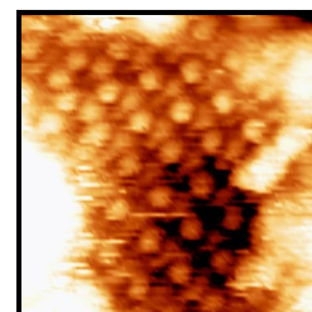
3.6 nm x 2.7 nm



2.3 nm x 2.3 nm



2.6 nm x 2.6 nm

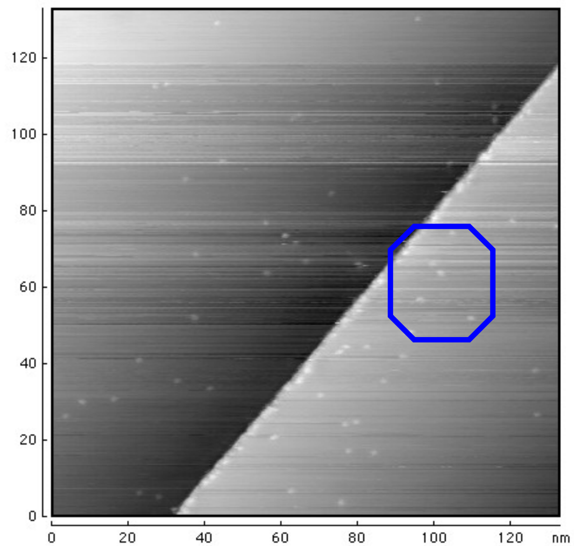


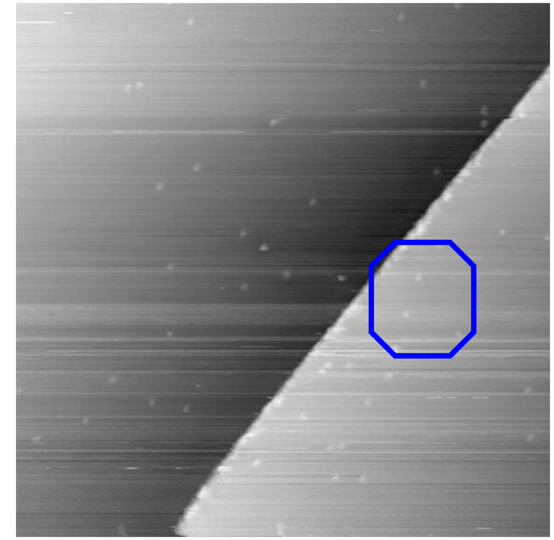
3.5 nm x 3.5 nm

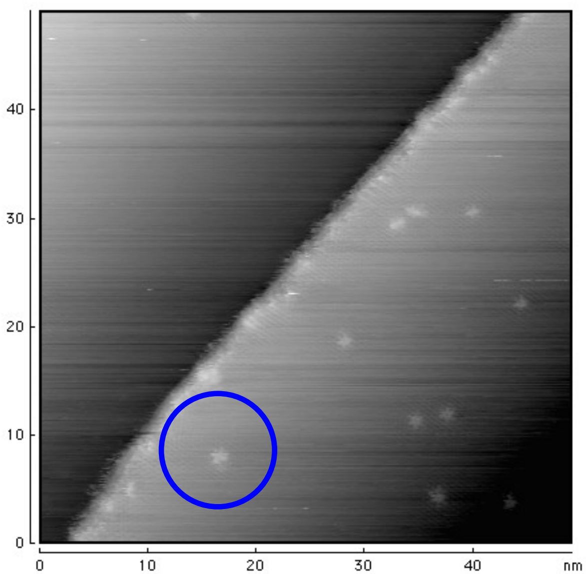
Desorption

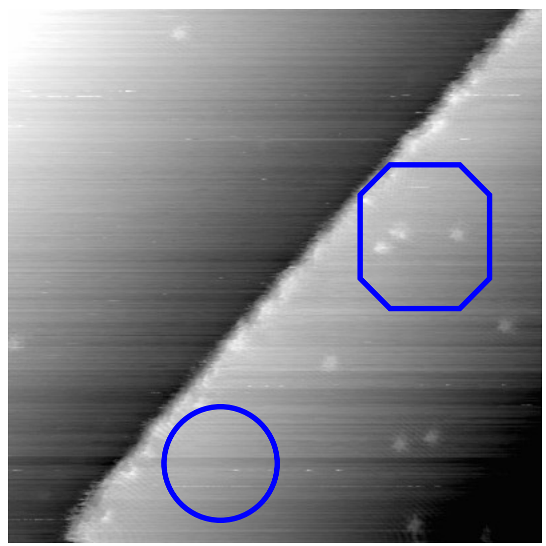
3 Langmuir atomic hydrogen

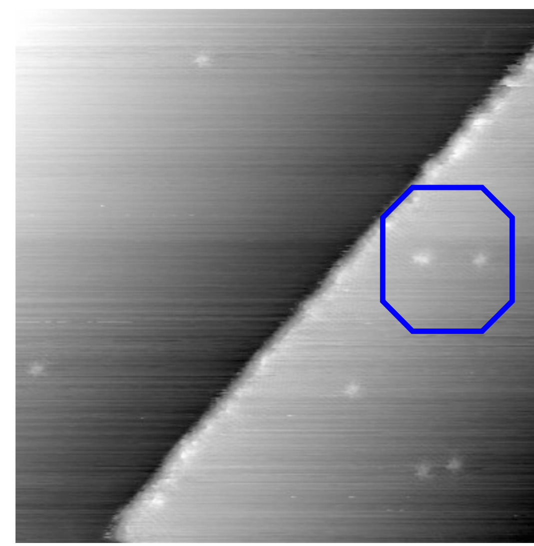
V_{bias}=100 mV
I=0.35 nA,
120 nm x 120 nm

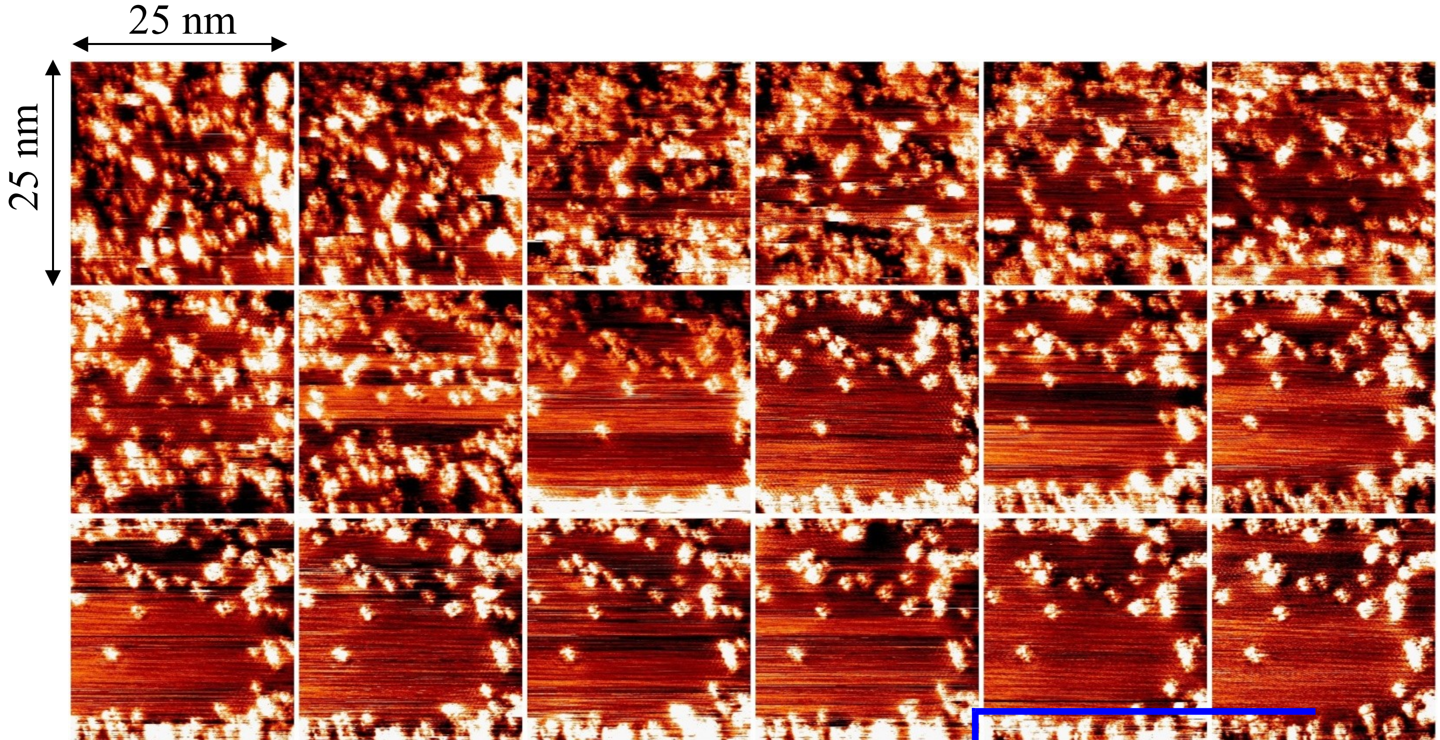










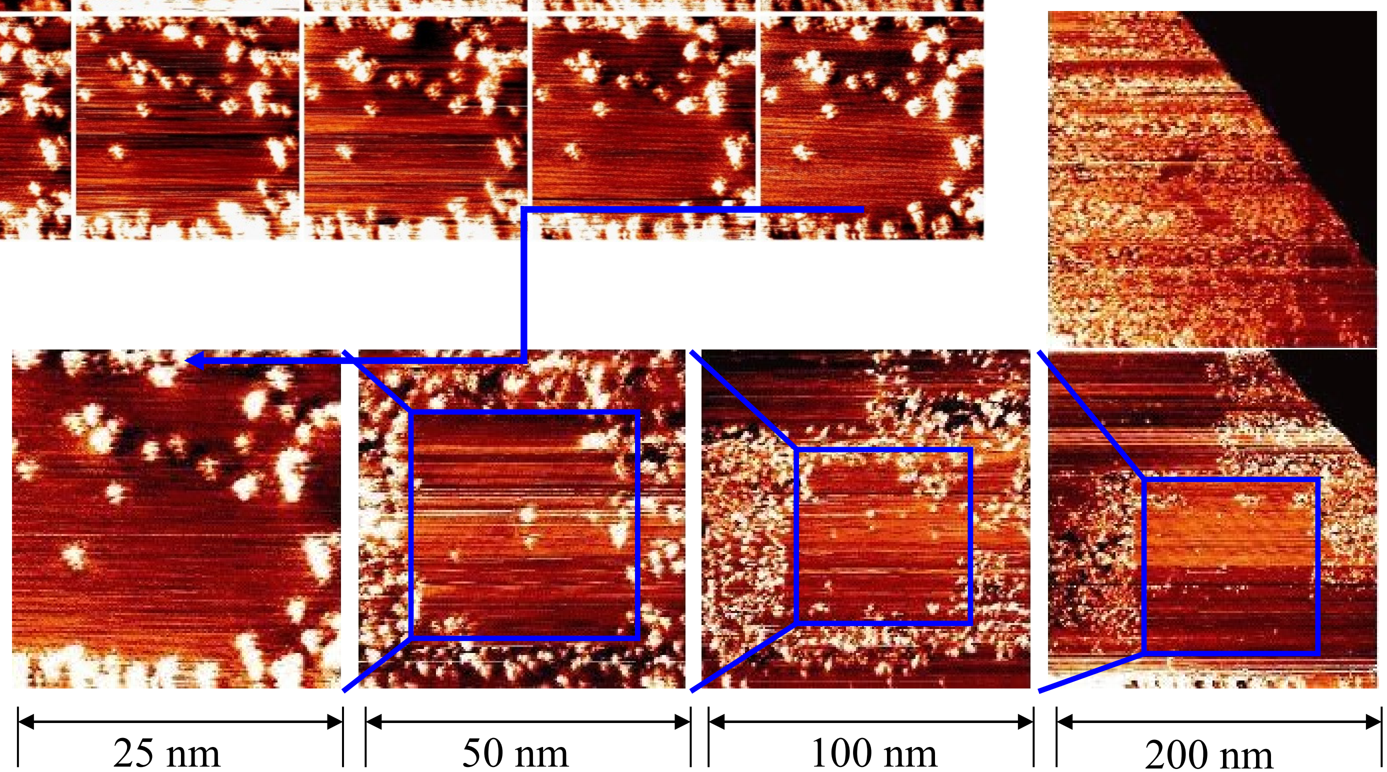


V_{bias} = 90 mV

I = 0.30 nA

<u>Exposure :</u>

18 Langmuir atomic H



Mechanical interaction between tip and graphene sheet

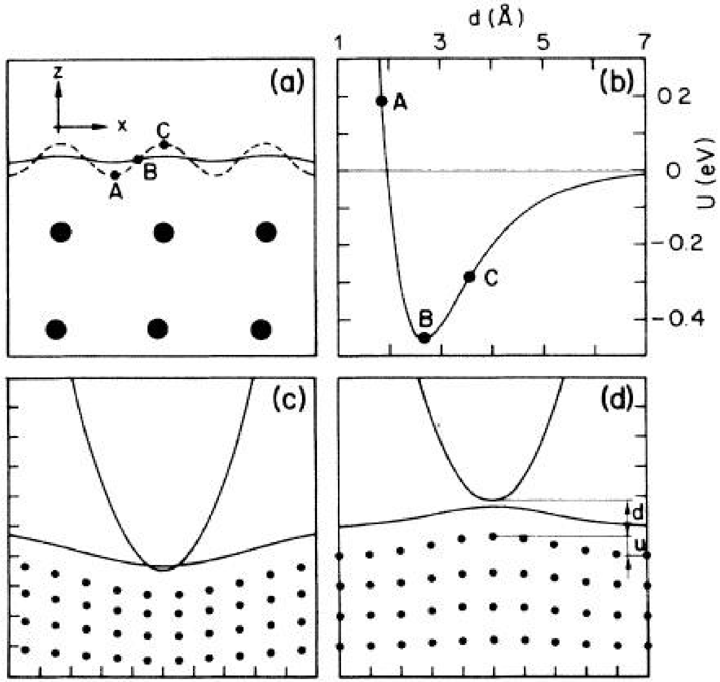


FIG. 2. (a) Contour of constant local density of states (dashed line), and contour of total charge density (solid line). Filled circles indicate the positions of carbon atoms of the top two layers. (b) Potential used for the interaction of tip and surface. Schematic (c) compression and (d) expansion of graphite for the tip at points A and C, respectively, of (a).

Soler et *al.*, *Phys. Rev. Letters*, 57, 444, (1986)

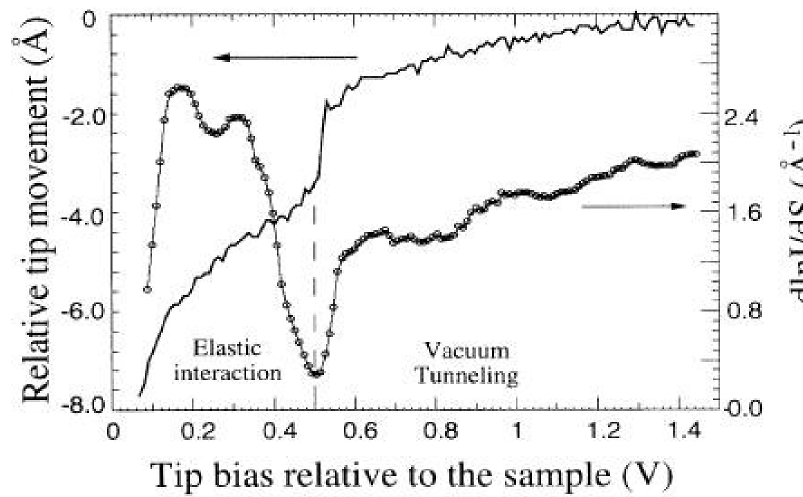
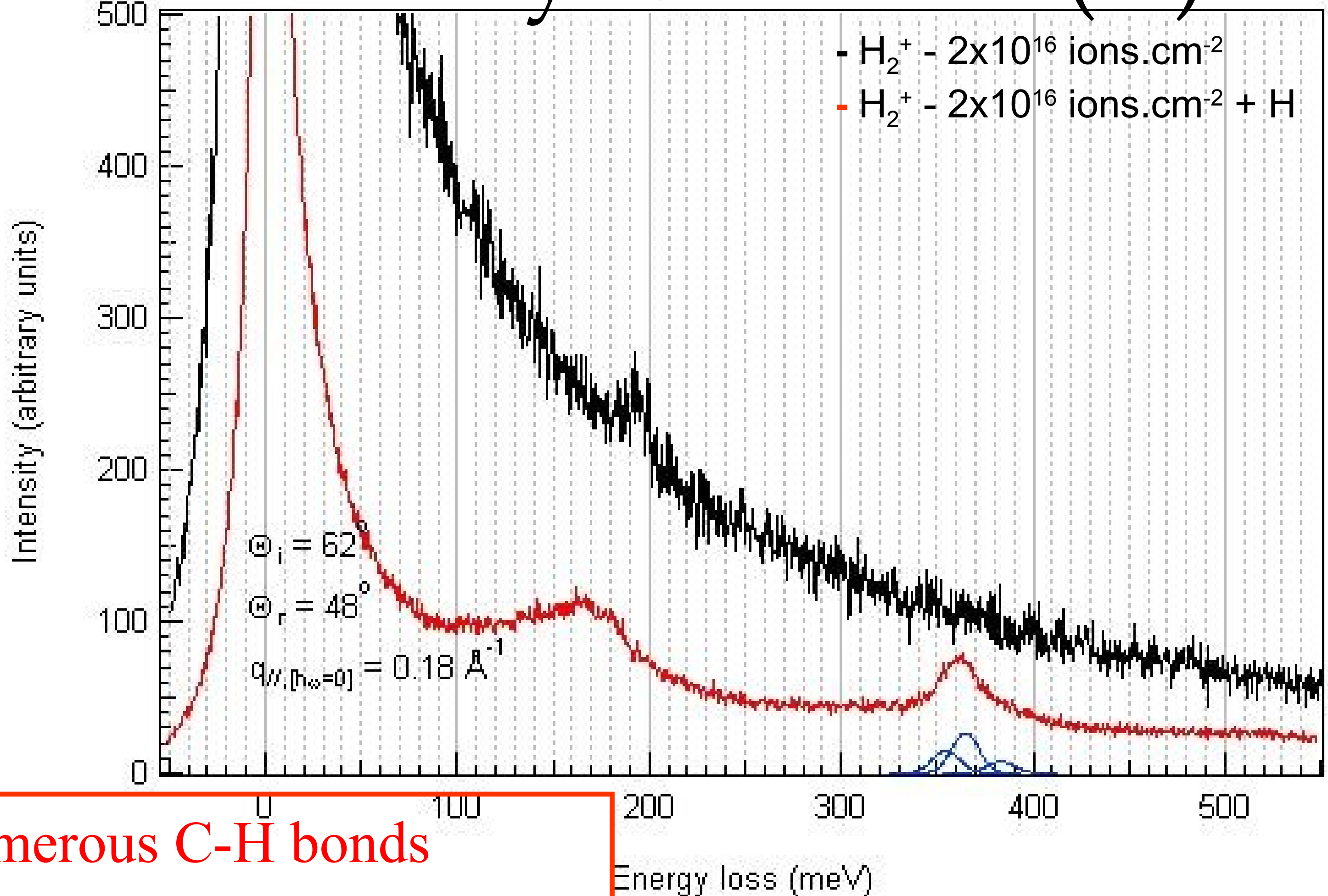


FIG. 2. Measurement of the relative tip movement and $d \ln I/dS$, as a function of the tip bias at a constant tunneling current of 1 nA. In this measurement, the relative tip movement was directly recorded from the *z*-piezovoltage. $d \ln I/dS$ was measured by a lock-in amplifier with a *z*-modulation amplitude of 0.08 Å at a frequency of 1 kHz.

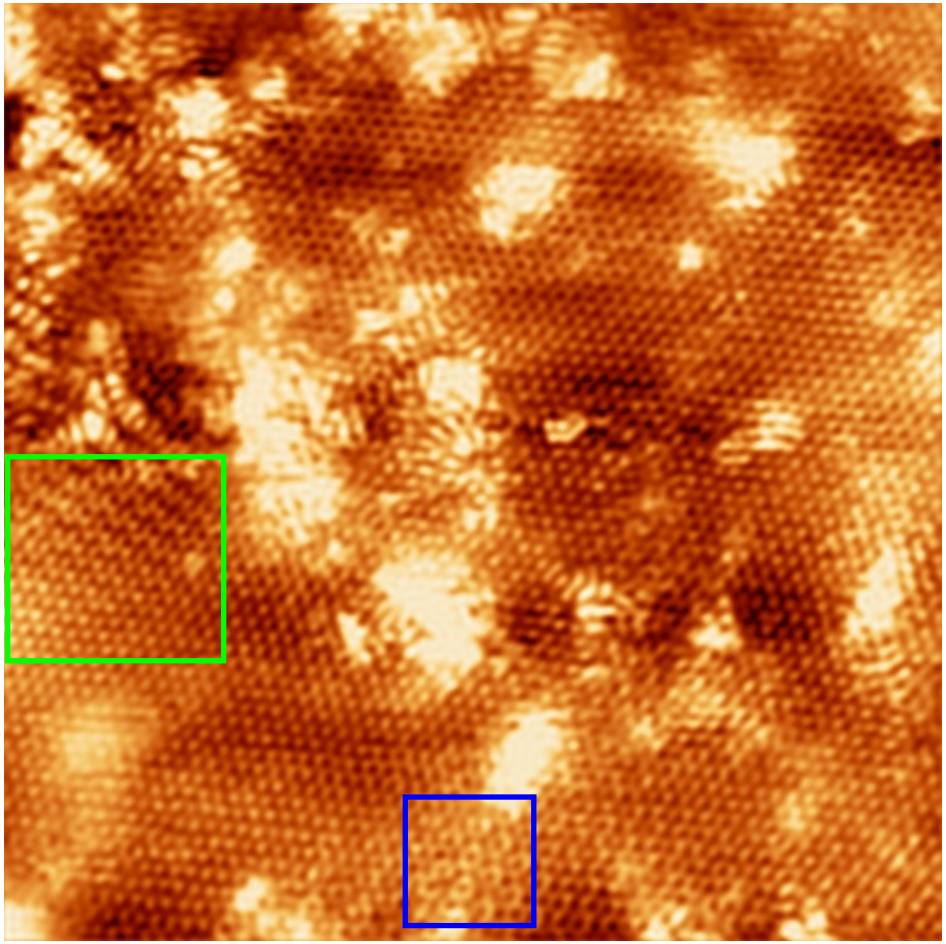
Gwo S. and Shih C.K., *Phys. Rev. B*, 47, 3059,(1993)

Bombardment by ions $H_2^+(D_2^+)$ & reactivity towards H(D).

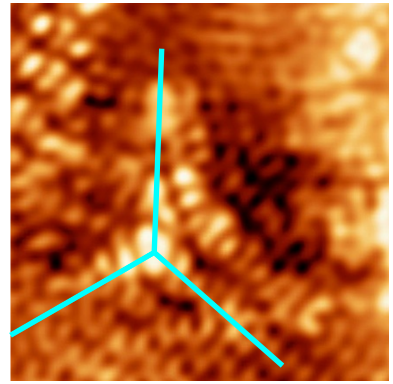


- Numerous C-H bonds
- Strong sp^3 character

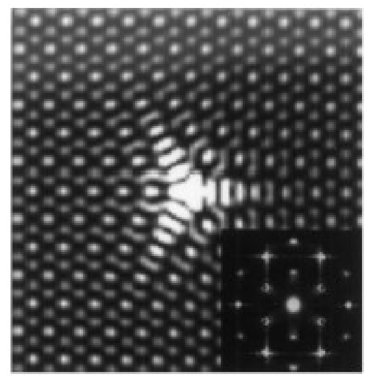
« Low » ion flux



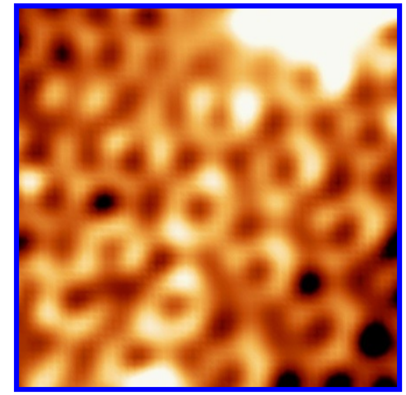
Fluence ≈ 10^{14} ions.cm^{-2} et E_{ions} = 300 eV.
16.5 nm x 16.5 nm, V_{bias} = 8.46 mV, I_t = 0.5 nA.



4.2 nm x 4.2 nm

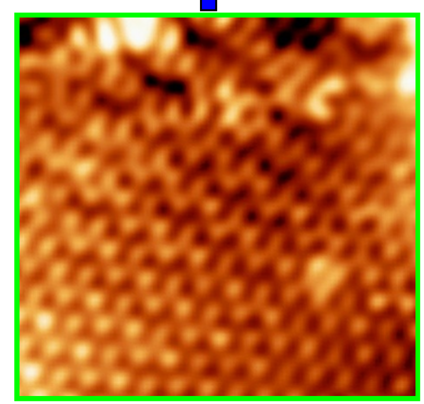


Kelly K.F., Halas N.J., *Surface Science*, 416, L1085, (1998)



2.2 nm x 2.2 nm

Atomic hydrogen



3.8 nm x 3.6 nm

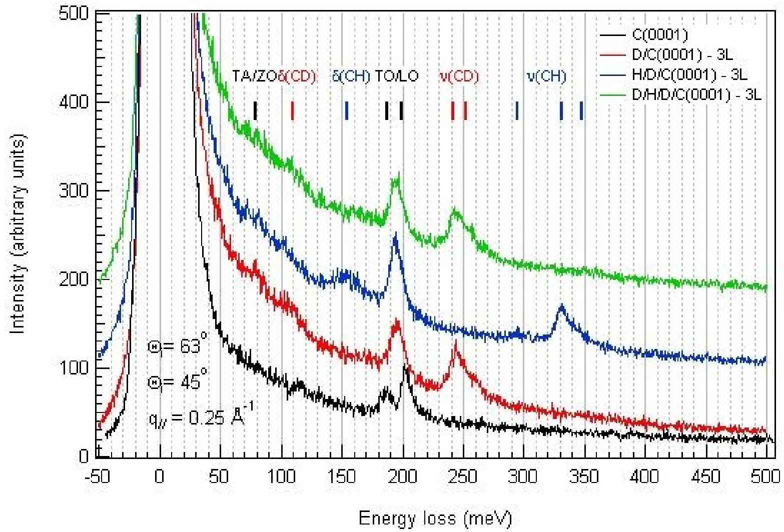
Summary H(D) & $H_2^+(D_2^+)$

- Atomic H(D) sur HOPG
  - C-H « weak » bond
  - weak sp^3 character

- Atomic H(D) on bombarded HOPG
  - numerous C-H bonds
  - strong sp^3 character

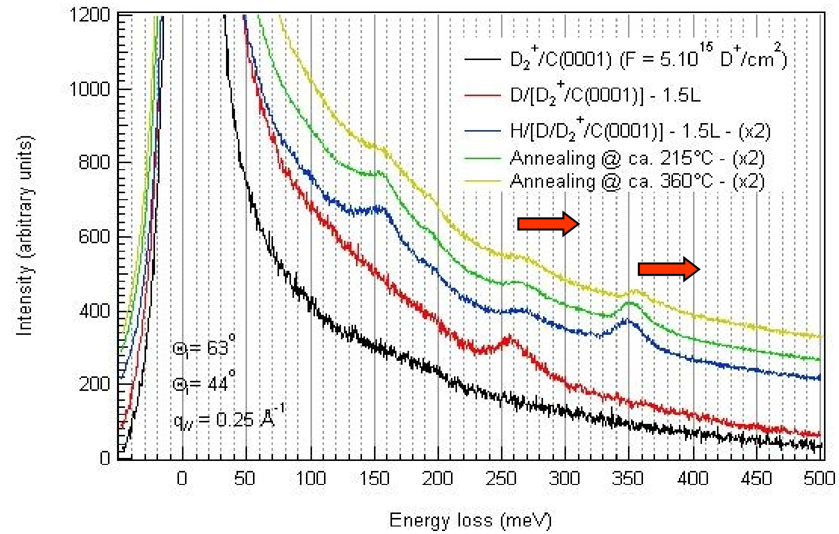
Abstraction of H(D) by D(H)

- Clean surface



	ν(CD)$_1$	ν(CD)$_2$	ν(CH)$_1$	ν(CH)$_2$	ν(CH)$_3$
D/C	244.8	259.2	x	x	x
H/D	x	x	298.4	330.9	345.6
D/H	244.0	256.7	X	x	x
	Pairs	clusters	monom ers	Pairs	clusters

- Bombarded surface



- **after bombardment:**

Larger peak due to D adsorbed on defects

- **abstraction :**

ν(CD) still visible

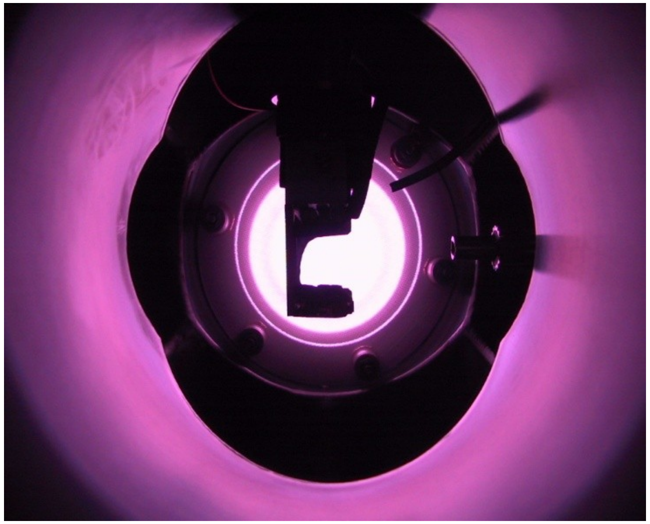
- **annealing:**

When Θ increases, only H(D) related to defects still present

Utility: abstraction can discriminate sp^2 & sp^3

RF source

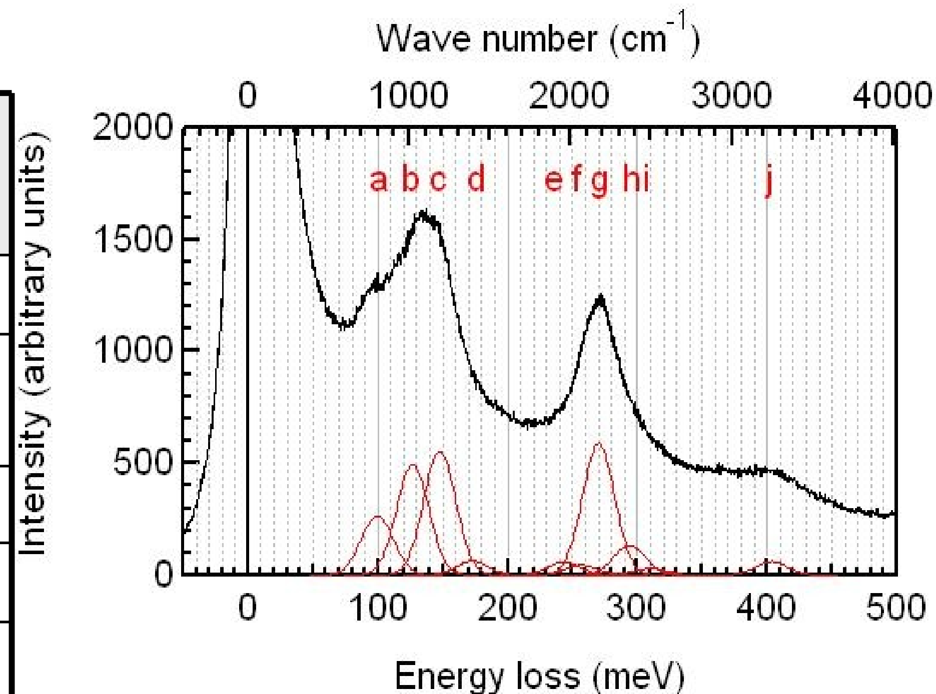
- « home made »
- P ~ 20 mbar (Ar, H_2, D_2)
- 100 W < P_{inj} < 300 W
- Inductively coupled
  - $V_p - V_f \sim 20$ V
  - $n_e \sim 10^{9}$ cm^{-3}, $T_e \sim 5$ eV
  - $n_0 \sim 10^{14} - 10^{15}$ cm^{-3}
- Fluxes:
  - Ions : $\Gamma_i \sim 10^{13}$ cm^{-2}.s^{-1}
  - Neutrals: $\Gamma_n \sim 10^{16}$ cm^{-2}.s^{-1}
- Energy:
  - Ions: ~ 20 eV
  - Neutrals: RT => 26 meV

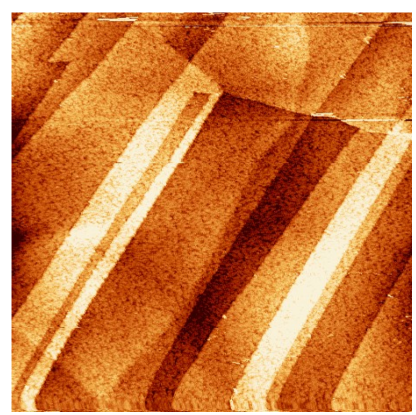


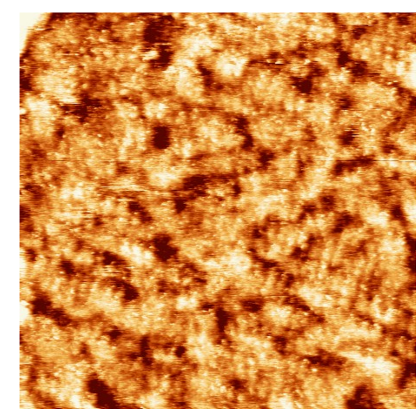
Preliminary results

- Plasma D_2 – 7 s

Name	Position		Assignation
	(meV)	(cm^{-1})	
a	99.7	805	$\delta(CD_x)$, x=1,2,3, sp^3
b	127.1	1025	$\delta(CD_x)$, x=2,3, sp^3 ν(C-C)
c	147.9	1190	ν(C-C)
d	174.1	1405	ν(C=C) aromatic
e	244.6	1970	ν(CD) paires
f	256.8	2070	ν(CD) clusters
g	269.7	2175	ν(CD), x=1,2,3, sp^3
h	294.1	2370	$\nu(CD_x)$, x=1,2, sp^2
i	310.0	2500	ν(CD), sp
j	403.3	3250	[(b,c) + g]




1µm x 1µm


42nm x 42nm

Conclusion and prospects

- Conclusions
  - Vibrational study (HREELS) :
    - proposition of adsorption model
    - abstraction of H(D) by D(H)
  - Microscopic study (STM):
    - LDOS perturbations,
    - Standing waves patterns,
    - STM-tip induced hydrogen desorption
  - Comparison between neutrals, ions & plasmas.
- Prospects
  - Plasma studies,
  - Hydrogen manipulation,
  - Studies of hydrogen/tungsten, hydrogen/B (or O) doped graphite…

Thank you for your attention