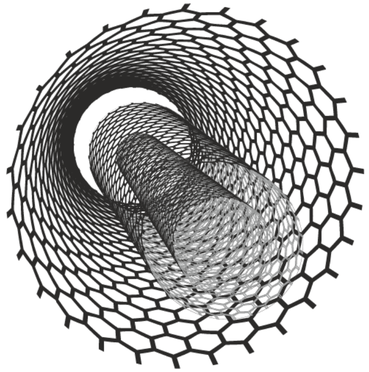
Depth Profile of the Hydrogenation of Multi Walls Carbon Nanotubes with Soft-to-Hard X-ray Photoemission Spectroscopy

FisMat2025, Jul 9th 2025

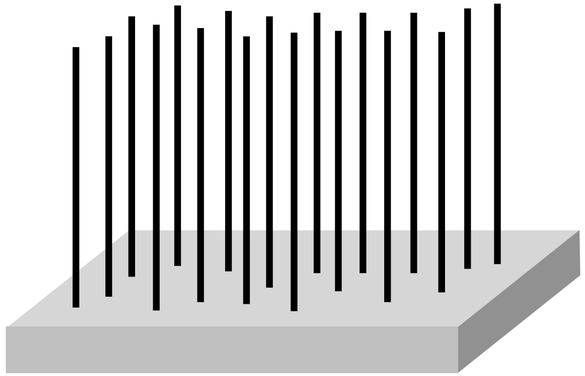
Orlando Castellano, Alice Apponi, Daniele Paoloni, Luca Cecchini, Francesco Pandolfi, Ilaria Rago, Carlo Mariani, Gianluca Cavoto, Tien-Lin Lee, Pardeep Kumar Thakur, Francesco Offi, Alessandro Ruocco

CNTs and Structural Changes Upon Hydrogenation

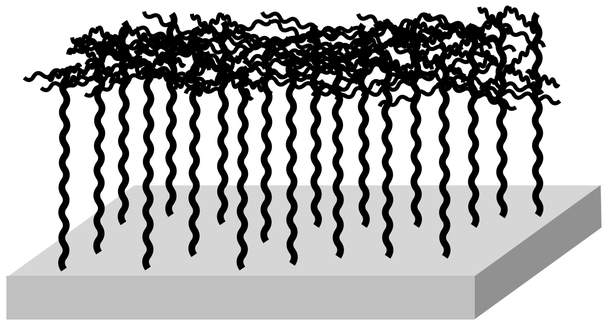
Multi wall CNT



Carbon Nanotubes (CNTs) are rolled-up sheets of graphene forming cylinders with nanometer-scale diameter

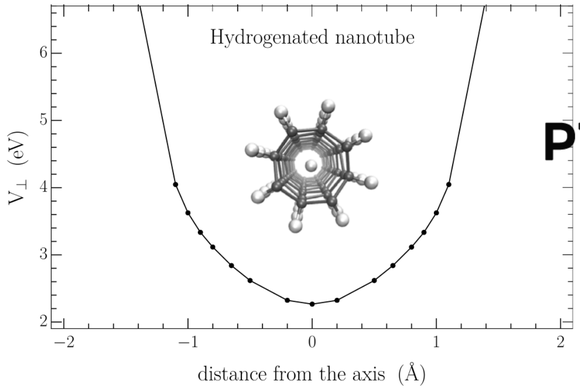


Ideal vs realistic Vertically Aligned CNT forest



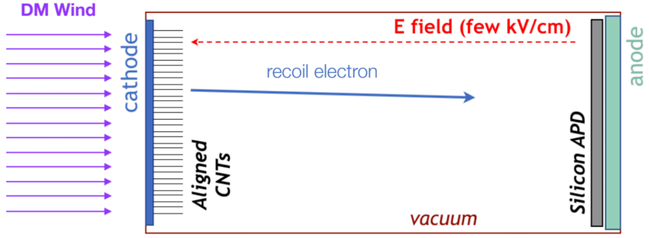
Why Hydrogenate CNTs?

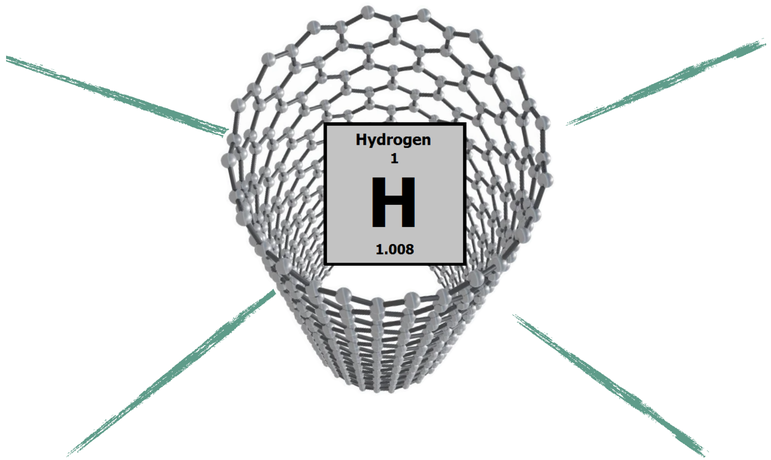
Solid Tritium target for Neutrino Mass Measurement



PTOLEMY

Directional Dark Matter Detector





Tunability of Electronic Properties

Hydrogen Storage

Two Samples and a Plasma Recipe for Hydrogenation

CNT pristine

Annealing

Used as a reference

Two samples from the same batch

Annealing 650 °C

TITAN LAB

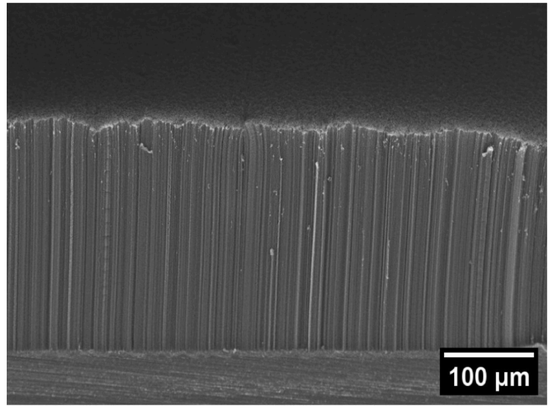
TECHNOLOGY INNOVATION THROUGH ADVANCED NANOSTRUCTURES

LAboratorio di Spettroscopie Elettroniche e di Correlazione

LASEC

diamond

I09 beamline



CNT plasma H

Exposed to hydrogen plasma:

- 100 W
- 0.7 mbar H_2, 300 sccm
- 1 h

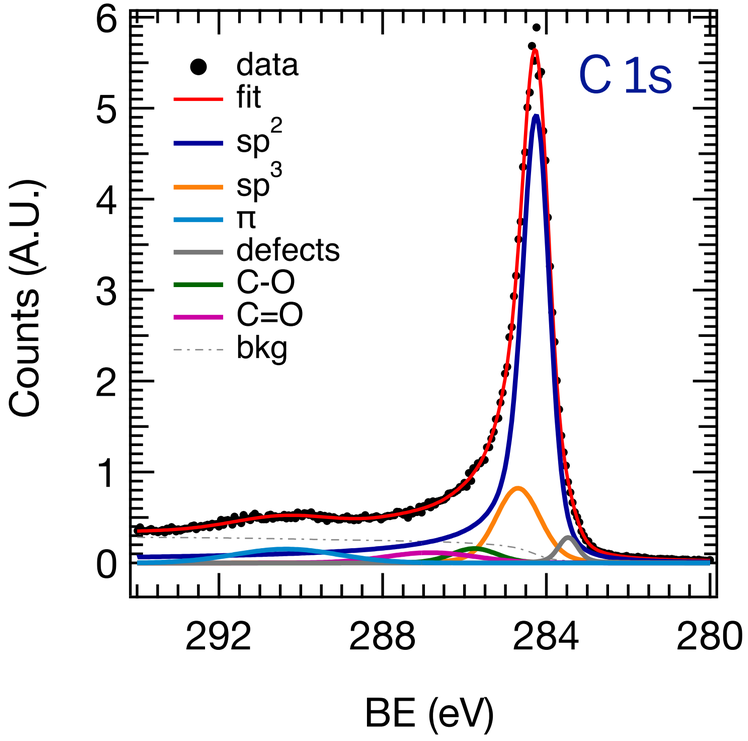
Kept in low vacuum during transfer

Annealing at T < 300 °C

XPS

Monochromatized Al Kα = 1487.6 eV

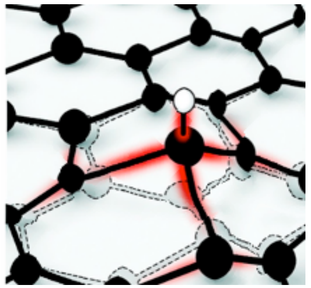
CNT pristine



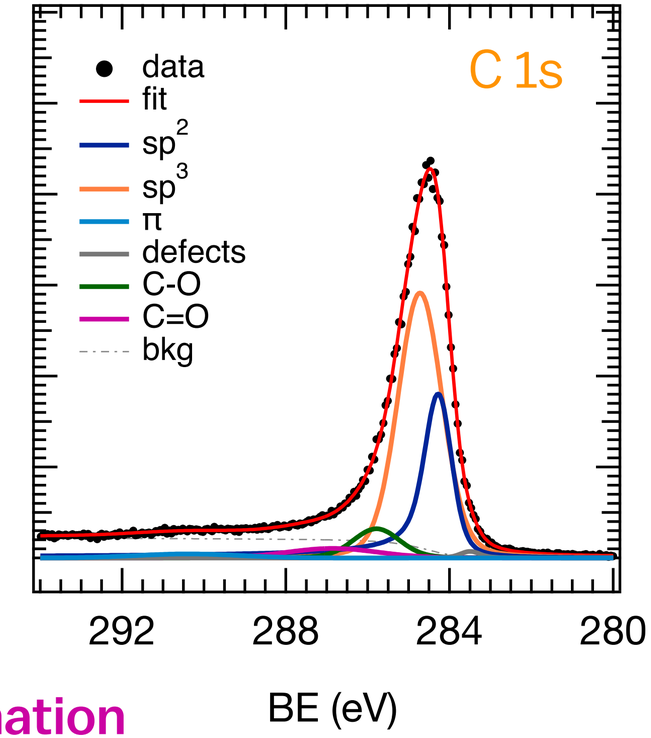
- **sp²** -to-**sp³** carbon hybridization

$$\frac{I_{sp^3}}{I_{sp^3} + I_{sp^2}} = 0.67$$

- Hydrogenation causes **sp²** to **sp³** transitions



CNT plasma H

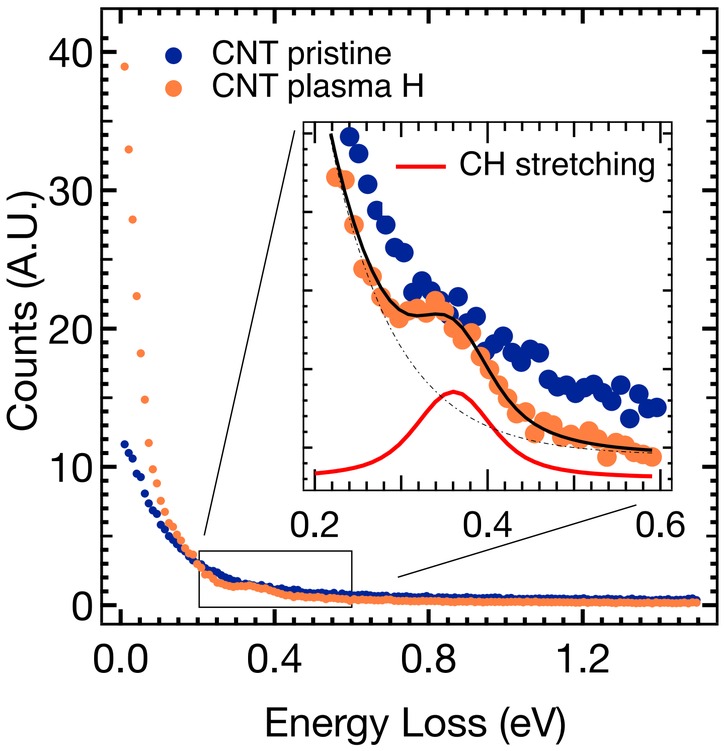


- Negligible increase of **oxides contamination**
- 0.5 eV lower **Work function** in H-CNT

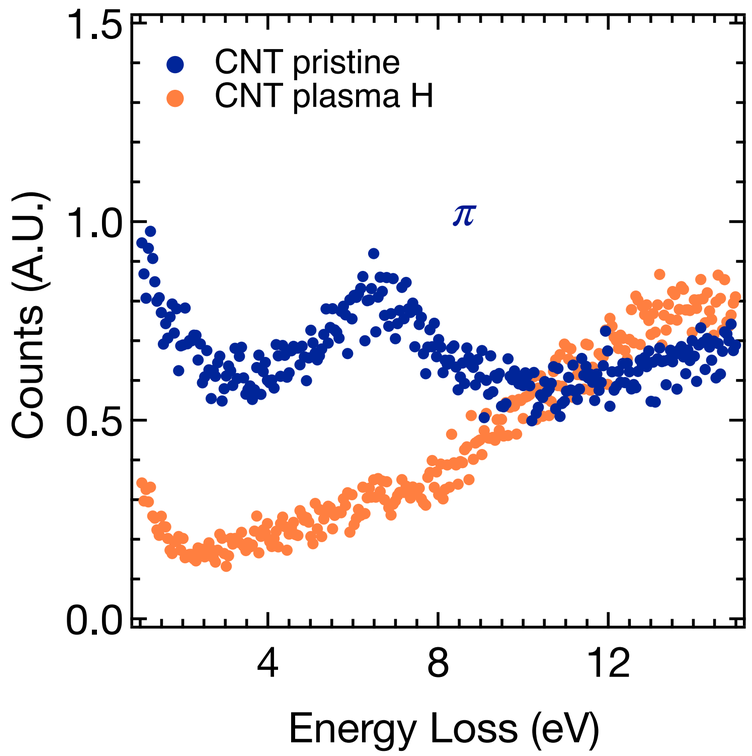
Electron Energy Loss Confirms Hydrogenation

EELS

$E_{primary}$ = 90 eV



- **C-H** stretching
- **π plasmon** quenching
- **Band Gap** opening



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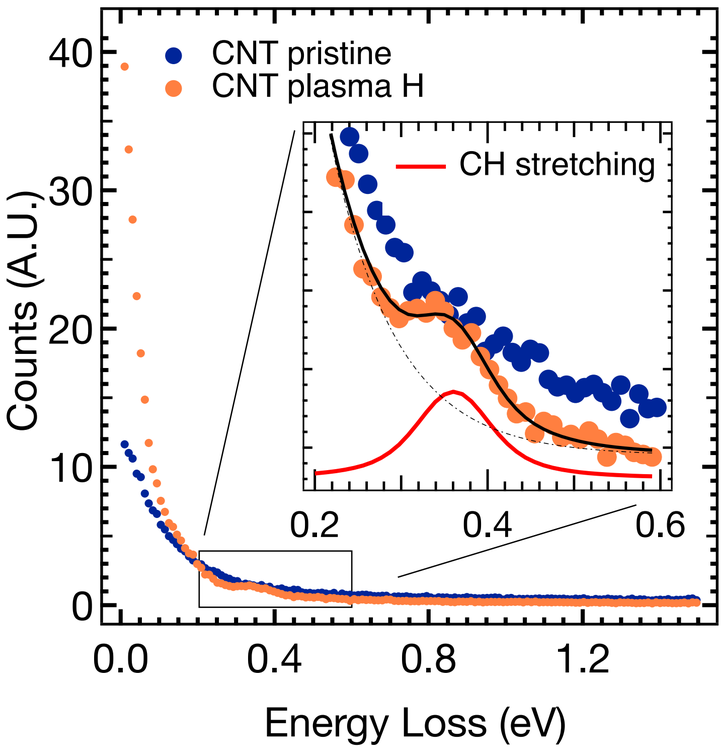

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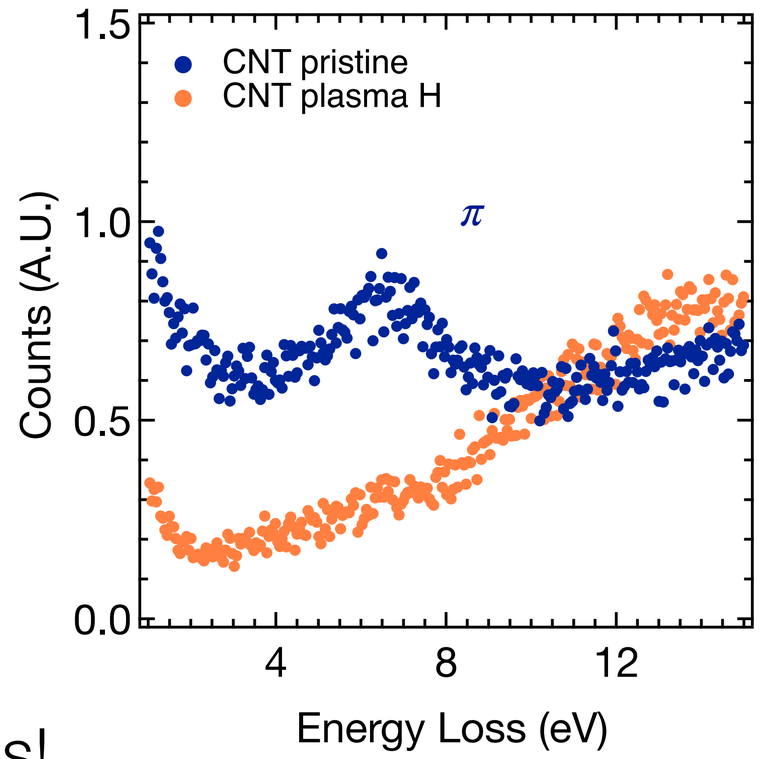
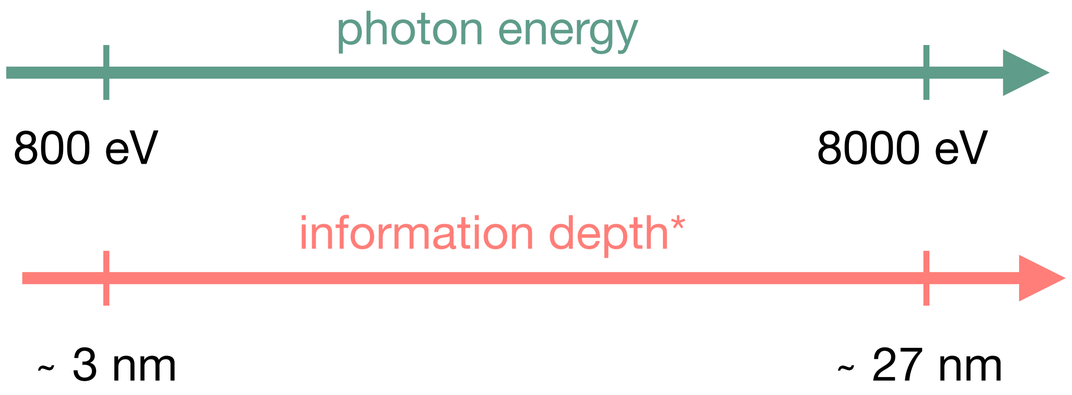


Surface sensitive techniques!

How Deep Does the Hydrogenation Go?

- **Variable photon energy** allows probing from surface to inner layers
- Lineshape changes provide insight into **sp^2** vs **sp^3** carbon hybridization

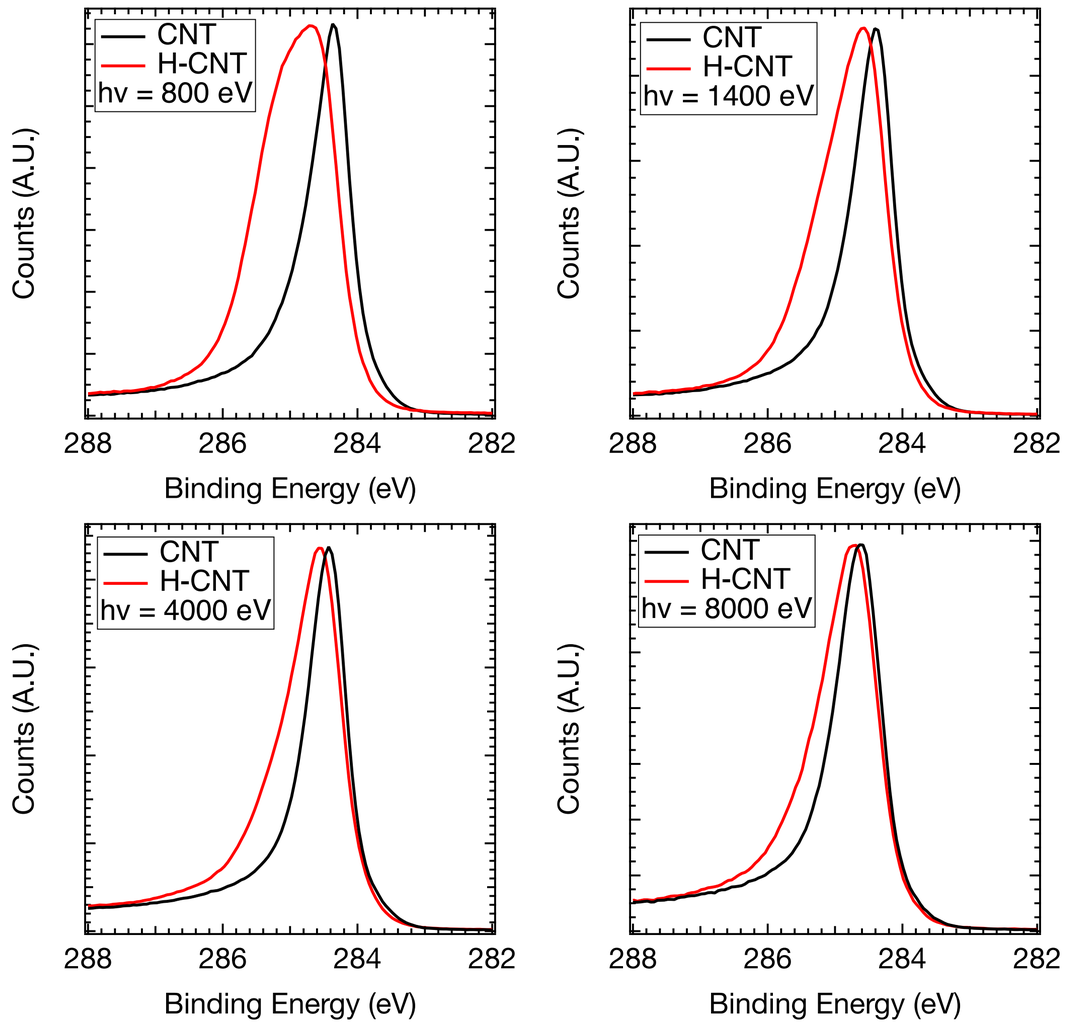


*3 x electron Inelastic Mean Free Path in graphite

Not surface-limited, not fully bulk…

diamond
I09 beamline

C 1s



Inelastic Mean Free Path

hv (eV)	$\lambda_{graphite}$ (nm)
800	1
1400	2
4000	4.7
8000	9.1

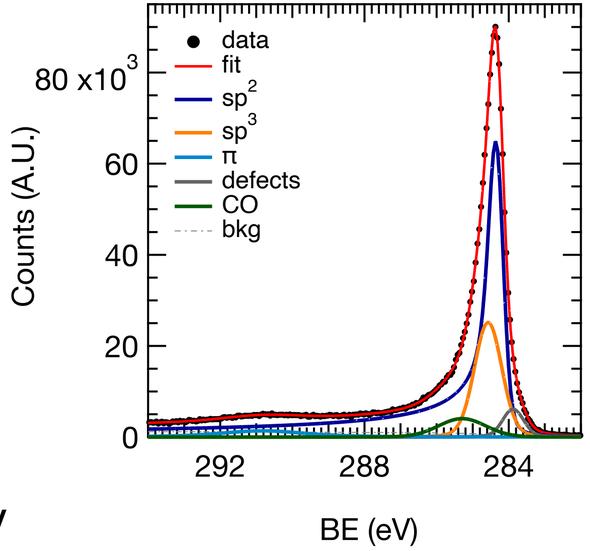
- Line shape differences between CNT and H-CNT **decrease with depth sensitivity**
- With **8 keV** photon **there is still a sign of hydrogenation**

Quantifying the Sp^3 Content with Soft Photons

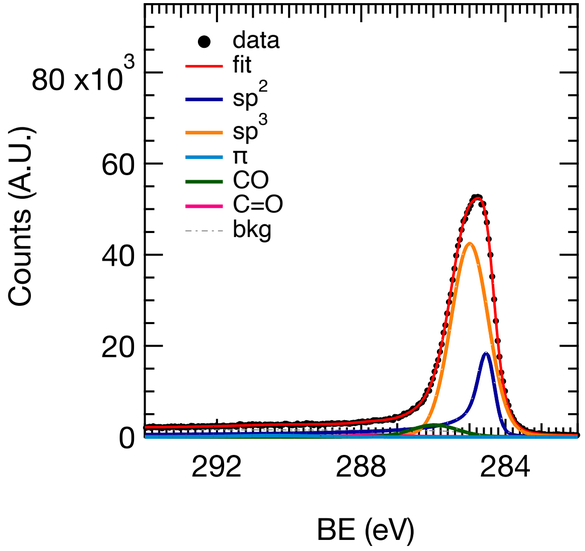
diamond
I09 beamline

hv = 800 eV
λ = 1 nm

CNT pristine

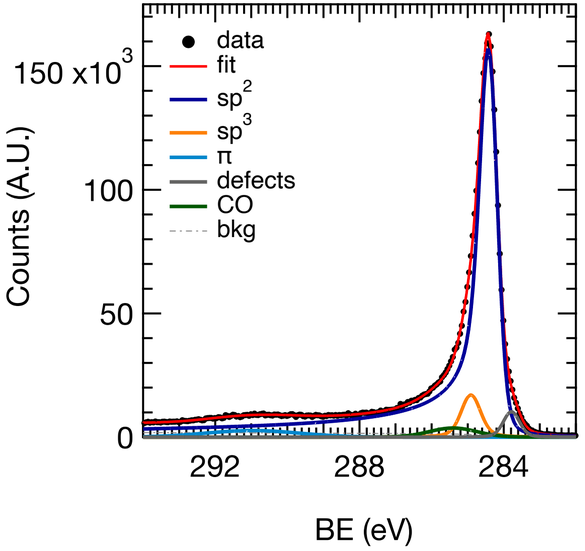


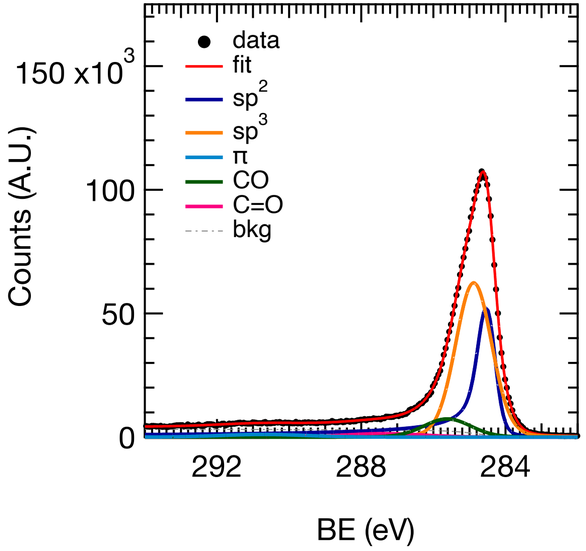
CNT plasma H



$$\frac{I_{sp^3}}{I_{sp^3} + I_{sp^2}} = 0.74$$

hv = 1400 eV
λ = 2 nm





$$\frac{I_{sp^3}}{I_{sp^3} + I_{sp^2}} = 0.61$$

Lineshape Changes due to Recoil Effects in HAXPES

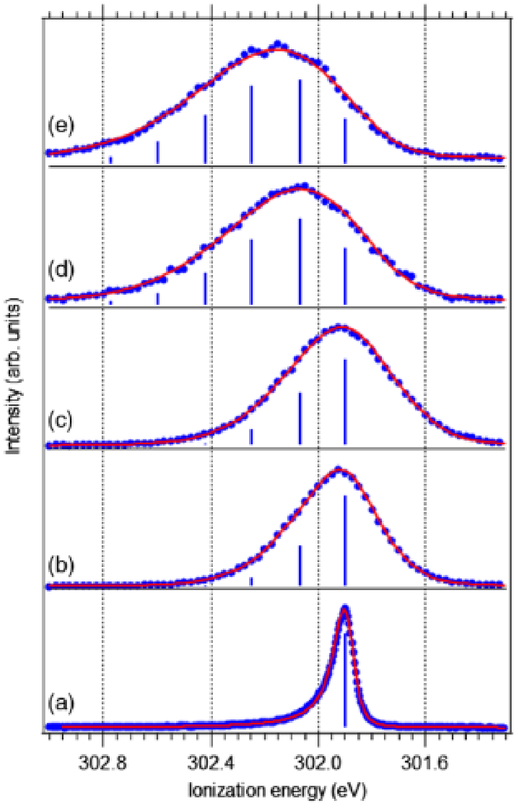
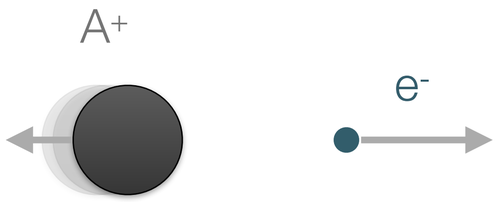


FIG. 1. Carbon 1*s* photoelectron spectra of CF_4, measured at different photon energies: (a) 330 eV, (b) 2.3 keV, (c) 3.0 keV, (d) 6.9 keV, and (e) 8.5 keV. Dots, experimental data points; continuous red line, least-squares curve-fitting result; vertical sticks, positions and relative intensities of the vibrational peaks.

gaseous molecule

Kukk *et al.*, Phys. Rev. Lett. 121, 073002 (2018)

Free Atom Recoil



- Recoil: average energy shift
- Vibrational modes: asymmetric broadening

solid sample

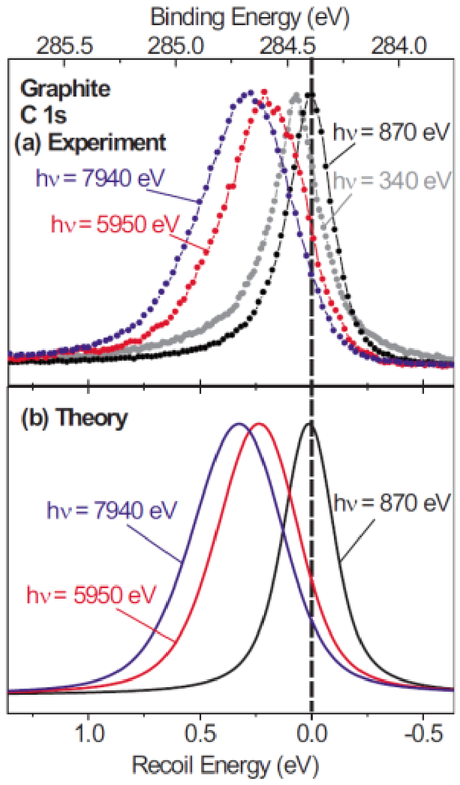
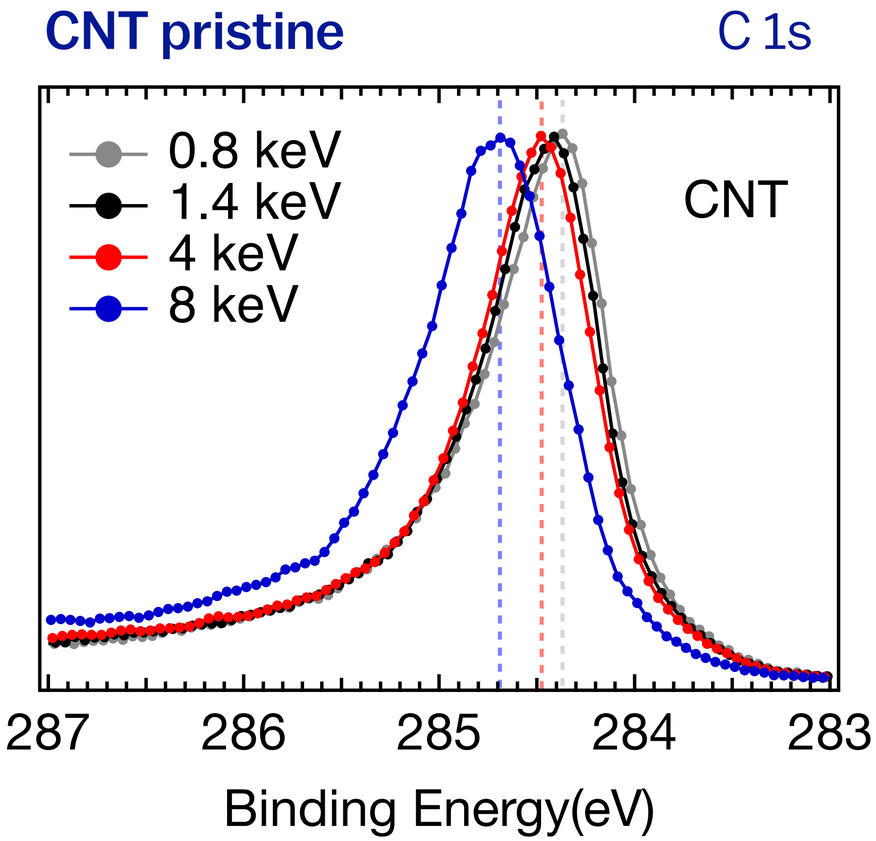


FIG. 1. (Color online) (a) Photon energy dependence of C 1*s* core-level spectra of graphite. The soft x ray ($h\nu$=340 and 870 eV) and hard x ray ($h\nu$=5950 and 7940 eV) are measured at the emission angles of 90° and 85° relative to the sample surface. (b) Theoretically obtained spectra taking into account the recoil effect in a Debye model with $\hbar\omega_{b,D}$=75 meV.

Takata *et al.*, Phys. Rev. B 75, 233404 (2007)

Hit Me (Photon) One More Time



Measured energy shift wrt C1s at hv = 800 eV:

- hv 4000 eV: ~ 100 meV
- hv 8000 eV: ~ 300 meV

Free Atom Recoil: $E_r = \frac{m_e}{M} E_k$ $\frac{m_e}{M_C} \sim 4.6 \times 10^{-5}$

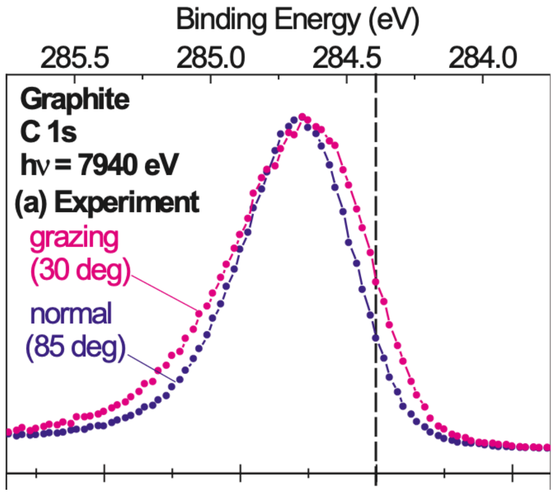
hv 800 eV	$E_r \sim 0.02$ eV
hv 4 KeV	$E_r \sim 0.17$ eV
hv 8 KeV	$E_r \sim 0.37$ eV

Bending vs Stretching Modes Angular Dependence

Graphite

Grazing emission: in plane stretching mode, broader peak

Normal emission: out-of-plane bending mode



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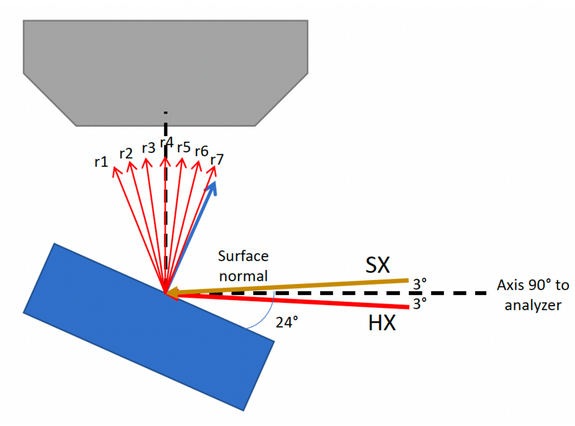
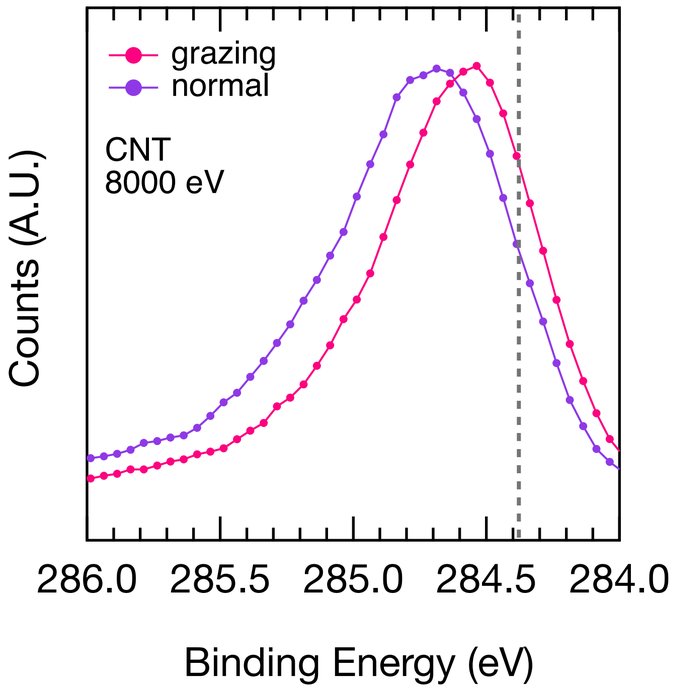
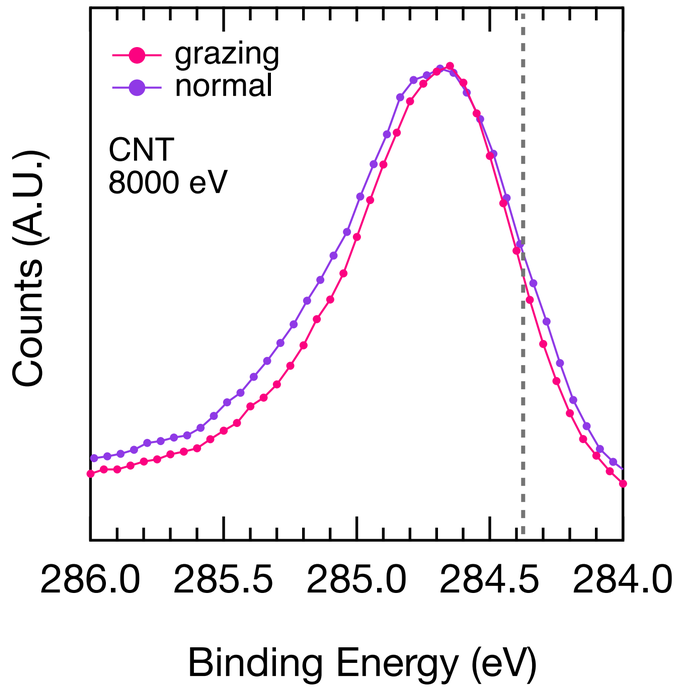


VA-CNT

- **Normal emission**: broader peak
- Average shift changes with emission angle



manually aligned



Wrapping Up

- ✓ **Highly hydrogenated CNTs** with minimal oxygen contamination

- ✓ **Hydrogenation** involves mainly the **outer layers**, but is **not limited to the very surface**

Can we quantify hydrogen distribution in depth?

- ✓ **Recoil effects observed in pristine CNTs**, average energy shift consistent with graphite

How can we explain the angular dependence?
What about H-CNTs? Can we study C-H vibrations?

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Work in progress!

Aknowledgements

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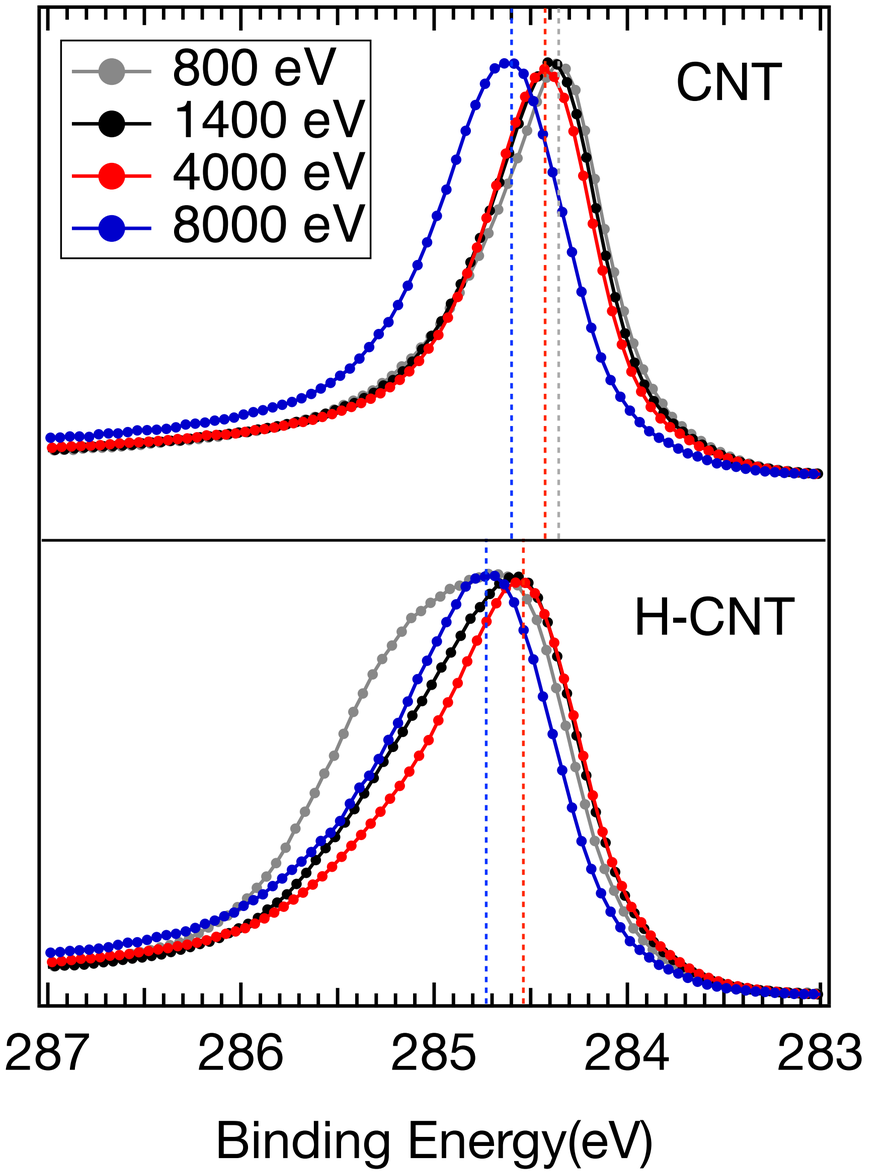


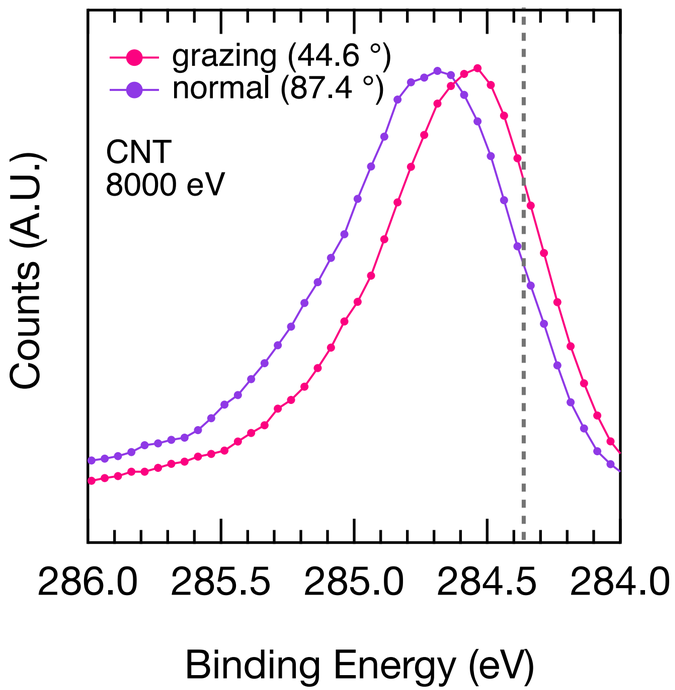
- 800 eV ~ 1400 eV no major C-C recoil effect
- 4000 eV energy shift ~ 100 meV
- 8000 eV energy shift ~ 250 meV

- Mix of depth inhomogeneous and recoil effect hard to disentangle

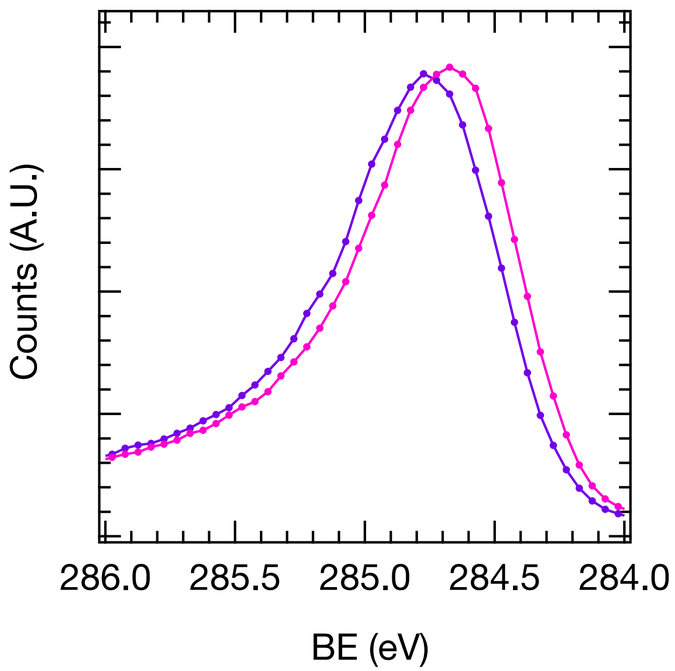
Sp3 lower at higher information depth, effective sharper line shape and shift to lower BE

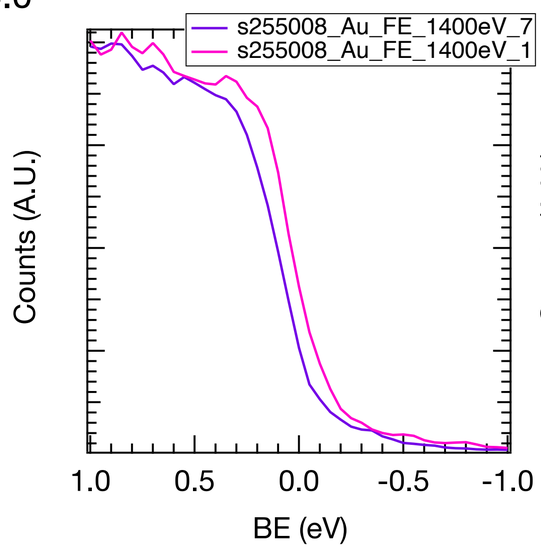
Recoil increase with photon energy, peak shift to lower KE, higher BE

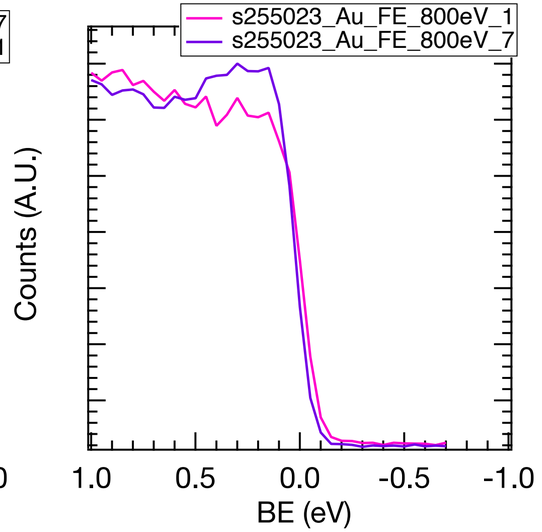
VA-CNT


grazing (44.6 °)
normal (87.4 °)
CNT
8000 eV
Counts (A.U.)
286.0
285.5
285.0
284.5
284.0
Binding Energy (eV)

NPG


Counts (A.U.)
286.0
285.5
285.0
284.5
284.0
BE (eV)


s255008_Au_FE_1400eV_7
s255008_Au_FE_1400eV_1
Counts (A.U.)
1.0
0.5
0.0
-0.5
-1.0
BE (eV)


s255023_Au_FE_800eV_1
s255023_Au_FE_800eV_7
Counts (A.U.)
1.0
0.5
0.0
-0.5
-1.0
BE (eV)

Uniform overlayer sp3 over substrate sp2

(c) Semi-infinite substrate with uniform overlayer of thickness t—Peak k from substrate with $E_{\mathrm{kIn}} \equiv E_{\mathrm{k}}$:

$$N_k(\theta) = I_0 \Omega_0(E_k) A_0(E_k) D_0(E_k) \rho \, \mathrm{d}\sigma_k/\mathrm{d}\Omega \, \Lambda_{\mathrm{e}}(E_k) \times \exp\left(-t/\Lambda_{\mathrm{e}}'(E_k) \sin\theta\right) \quad (117)$$

Peak l from overlayer with $E_{\mathrm{kIn}} \equiv E_l$:

$$N_l(\theta) = I_0 \Omega_0(E_l) A_0(E_l) D_0(E_l) \rho' \, \mathrm{d}\sigma_l/\mathrm{d}\Omega \, \Lambda_{\mathrm{e}}'(E_l) \times \left[1 - \exp\left(-t/\Lambda_{\mathrm{e}}'(E_l) \sin\theta\right)\right] \quad (118)$$

where

$\Lambda_{\mathrm{e}}(E_k)$ = an attenuation length in the substrate

$\Lambda_{\mathrm{e}}'(E_k)$ = an attenuation length in the overlayer

ρ = an atomic density in the substrate

ρ' = an atomic density in the overlayer.

$$\frac{I_{sp3}}{I_{sp3} + I_{sp2}} = \frac{I_{\text{overlayer}}}{I_{\text{overlayer}} + I_{\text{substrate}}} = \frac{1 - e^{-d/\lambda \cos\theta}}{1 - e^{-d/\lambda \cos\theta} + e^{-d/\lambda \cos\theta}} = 1 - e^{-d/\lambda}$$

Uniform overlayer model does not work well for both 800 and 1400 photons

hv = 800 eV

$$\lambda = 1nm, \frac{sp3}{sp3 + sp2} = 0.74$$

$$1 - e^{-d/1} = 0.74 \Rightarrow d = -\ln(0.26) = 1.35\,\text{nm}$$

hv = 1400 eV

$$\lambda = 2nm, \frac{sp3}{sp3 + sp2} = 0.61$$

$$1 - e^{-d/2} = 0.61 \Rightarrow d = -2\ln(0.39) = 1.88\,\text{nm}$$

((1.88+1.35)/2=1.615

2*(1.88-1.35)/(1.88+1.35) =0.328

Exponential density of sp3 overlayer

$$f_{sp3}(z) = f_0 \cdot e^{-z/d_0}$$

$$f_{sp2}(z) = 1 - f_{sp3}(z)$$

sp^3 is 100% at the surface

d_0 characteristic sp^3 length

$$I_{sp3} \propto \int_0^\infty f_{sp3}(z) \cdot e^{-z/\lambda}\, dz = \int_0^\infty e^{-z/d_0} \cdot e^{-z/\lambda}\, dz = \int_0^\infty e^{-z(1/d_0+1/\lambda)}\, dz I_{sp3} \propto \frac{1}{(1/d_0 + 1/\lambda)} = \frac{d_0\lambda}{d_0+\lambda}$$

$$I_{sp2} \propto \int_0^\infty \left[1 - f_{sp3}(z)\right] \cdot e^{-z/\lambda}\, dz = \int_0^\infty \left(1 - e^{-z/d_0}\right) \cdot e^{-z/\lambda}\, dz = \lambda\left(1 - \frac{d_0}{d_0+\lambda}\right) = \lambda\left(\frac{\lambda}{d_0+\lambda}\right) = \frac{\lambda^2}{d_0+\lambda}$$

Exponential density of sp3 overlayer is better

$$f_{sp3}(z) = f_0 \cdot e^{-z/d_0}$$

$$f_{sp2}(z) = 1 - f_{sp3}(z)$$

sp^3 is 100% at the surface

d_0 characteristic sp^3 length

$$\frac{I_{sp3}}{I_{sp3} + I_{sp2}} = \frac{d_0\lambda/(d_0+\lambda)}{d_0\lambda/(d_0+\lambda) + \lambda^2/(d_0+\lambda)} = \frac{d_0}{d_0+\lambda}$$

hv = 800 eV

$$\lambda = 1nm, \frac{sp3}{sp3+sp2} = 0.74$$

$$d_0 = \frac{0.74}{1-0.74} = 2.85\,\text{nm}$$

(3.13+2.85)/2=2.99

hv = 1400 eV

$$\lambda = 2nm, \frac{sp3}{sp3+sp2} = 0.61$$

$$d_0 = \frac{0.61}{1-0.61} = 3.13\,\text{nm}$$

2*(3.13-2.85)/(3.13+2.85) =0.0936

Sp3 in equivalent layers of graphite

Layer separation in graphite = 0.35 nm

d = 1.61 (uniform model)

1.61/0.35 = 4.6

d_0 = 2.99 (exponential model)

2.99/0.35 = 8.5

Hydrogen surface density uniform model a spanne

$$n_C \approx 3.82 \times 10^{13} \text{ atomi/mm}^2$$

$$N_H = 4.6 \cdot n_C = 4.6 \cdot 3.82 \times 10^{13} = 1.7572 \times 10^{14} \text{ atomi H/mm}^2$$

$$m_H = 1.0078 \text{ u} = 1.0078 \cdot 1.6605 \times 10^{-24} \text{ g} \approx 1.6736 \times 10^{-24} \text{ g}$$

$$m_H \approx 29 \text{ ng/cm}^2$$

1 ug Hydrogen (uniform model)

$m_H = 1\,\text{ug} \approx 60$  *

* 30 cm^2 in total

Hydrogen surface density exponential model a spanne

$$n_0 = \frac{3.82 \times 10^{13}}{0.335} \approx 1.14 \times 10^{14} \text{ atomi/mm}^2\text{/nm}$$

$$N_H = \int_0^\infty n_H(z)\, dz = \int_0^\infty n_0 \cdot e^{-z/d_0} dz = n_0 \cdot d_0 = 1.14 \times 10^{14} \cdot 3 = 3.42 \times 10^{14} \text{ atomi/mm}^2$$

$$m_H \approx 57 \text{ ng/cm}^2$$

1 ug Hydrogen (exponential model)

Layer separation as in graphite = 0.35 nm

Electron IMFP as in graphite

$$\frac{sp3}{sp3 + sp2} = \quad \text{H:C stoichiometry}$$

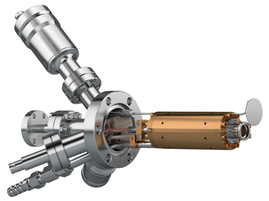
Characteristic penetration depth: 8.5 layers

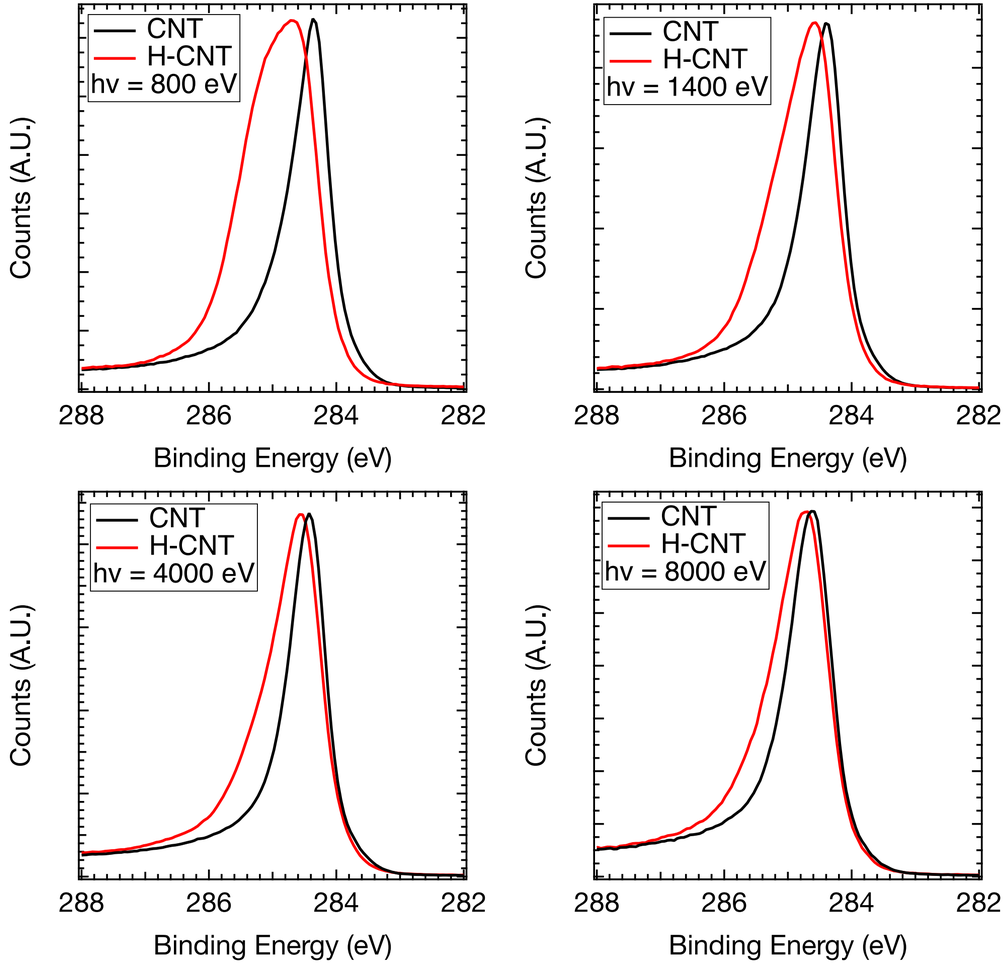
$m_H \approx 57$ ng/cm^2

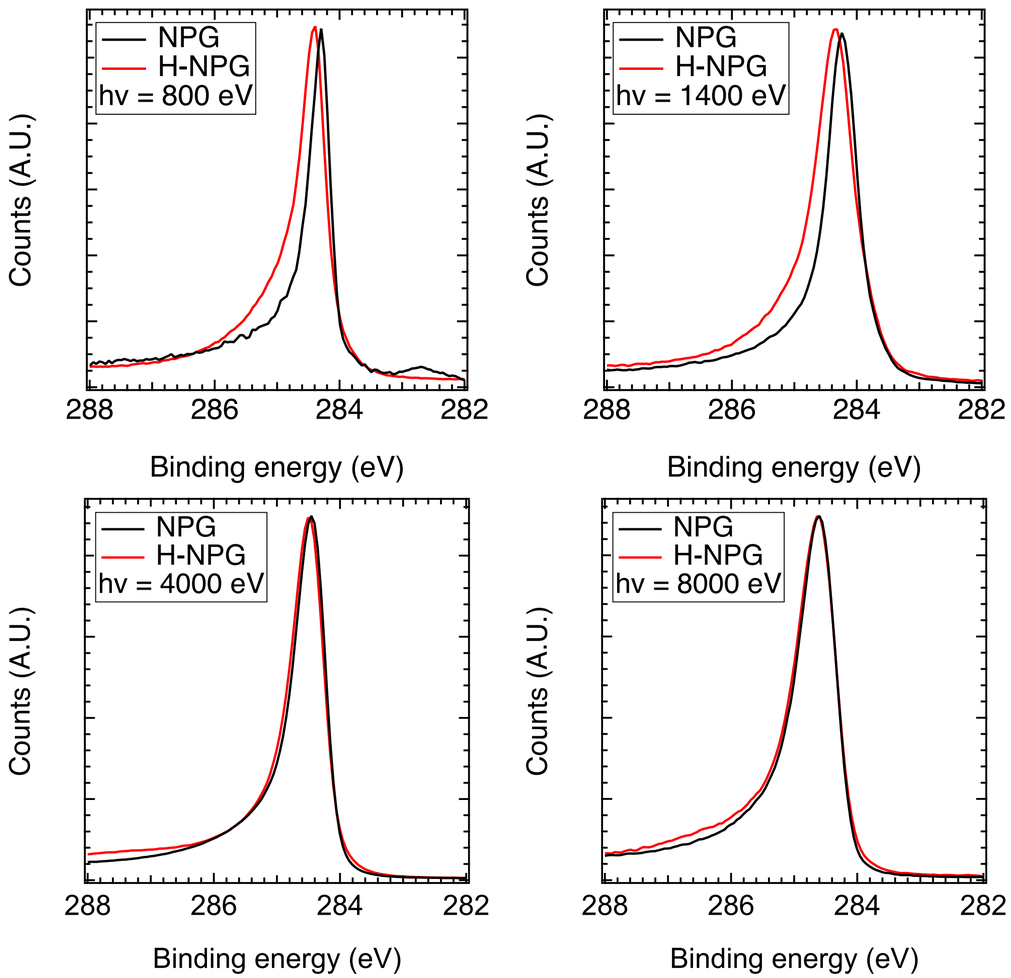
$m_H = 1$ ug ≈ 30  *

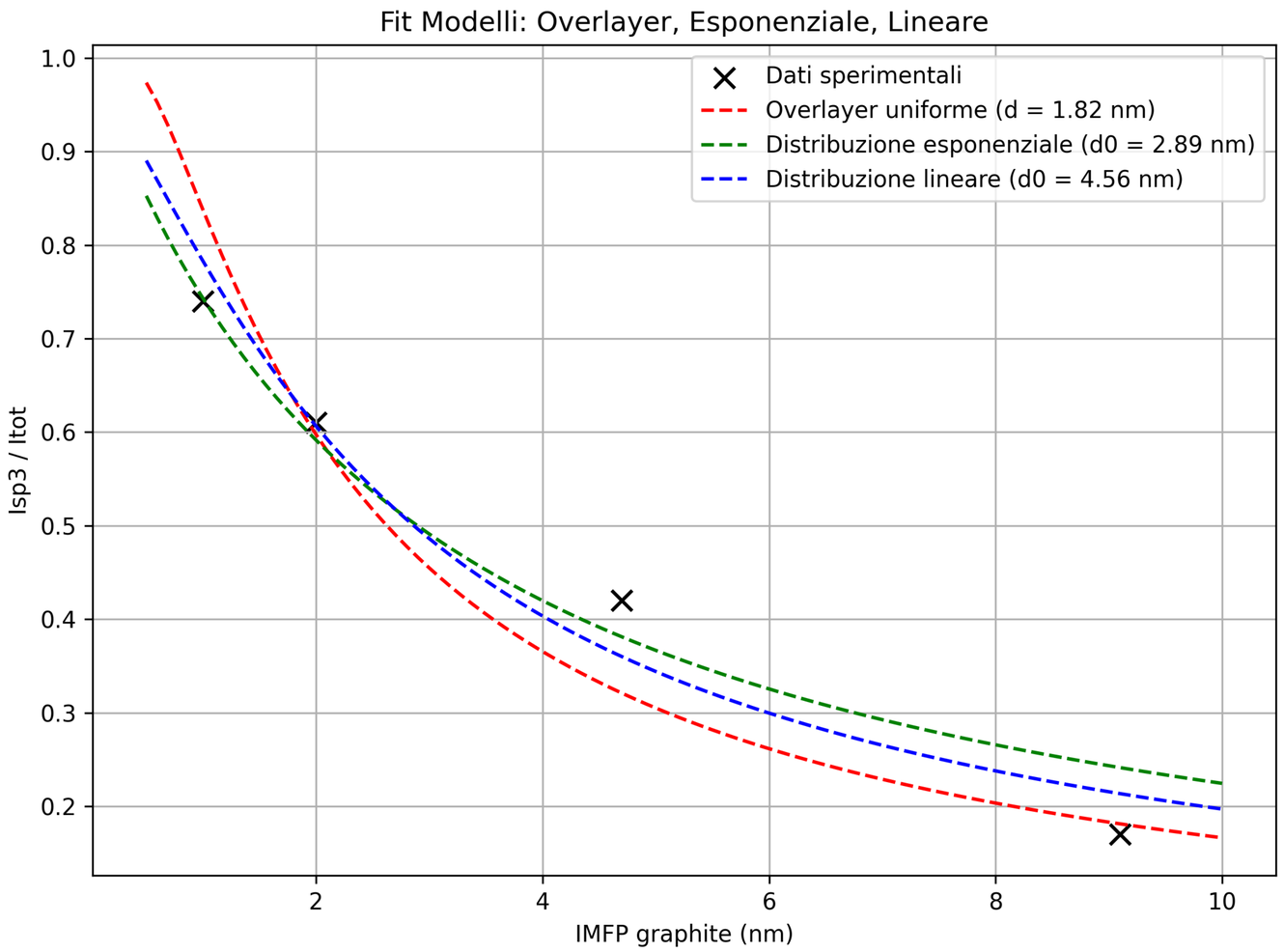
* 15 cm^2 total

Not surface-limited, not fully bulk… but more H than in nano-porous graphene

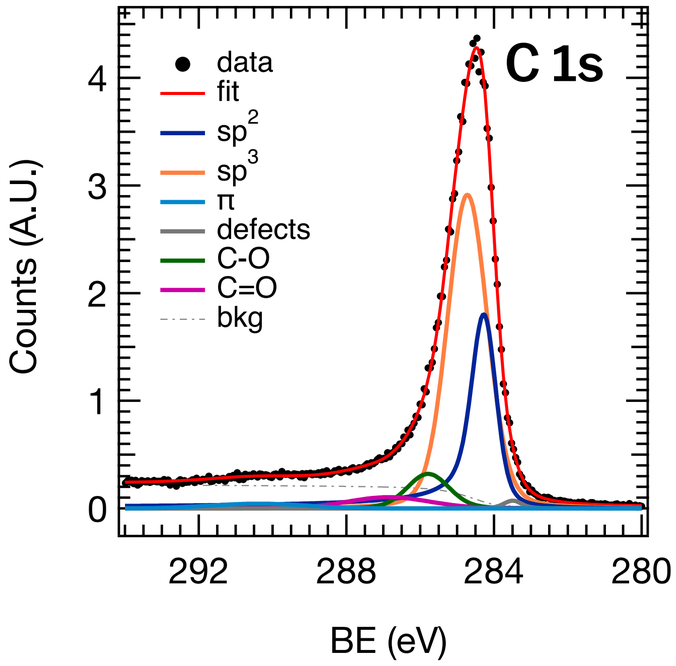







Fit Modelli: Overlayer, Esponenziale, Lineare
Dati sperimentali
Overlayer uniforme (d = 1.82 nm)
Distribuzione esponenziale (d0 = 2.89 nm)
Distribuzione lineare (d0 = 4.56 nm)
Isp3 / Itot
IMFP graphite (nm)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
2
4
6
8
10

Hydrogen Plasma *vs* Thermal Cracking Hydrogenation



$I_{sp3} / (I_{sp2} + I_{sp3}) \simeq 67\%$

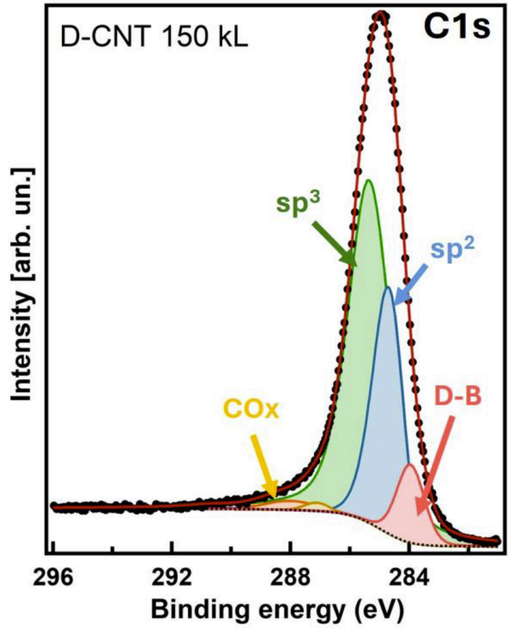
WF = 3.81 ± 0.05 eV

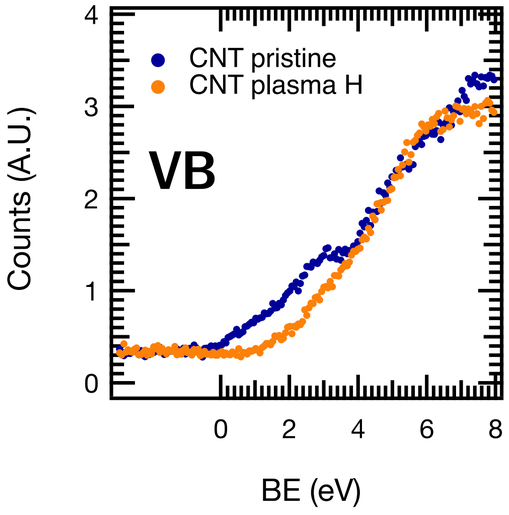
Atomic Deuterium bonding to Multi-Walled Carbon Nano Tubes

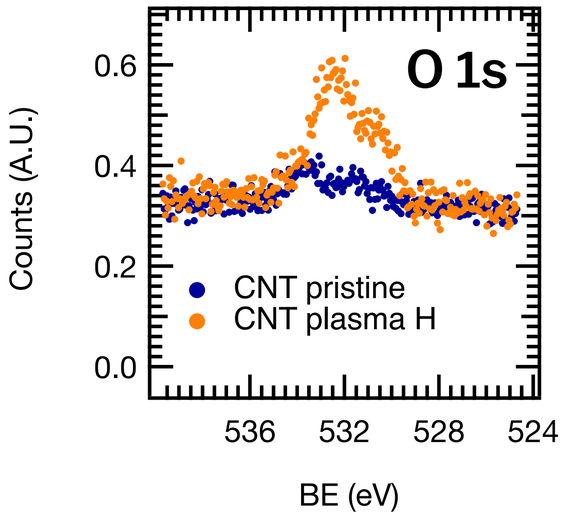
Sammar Tayyab et al., to be published

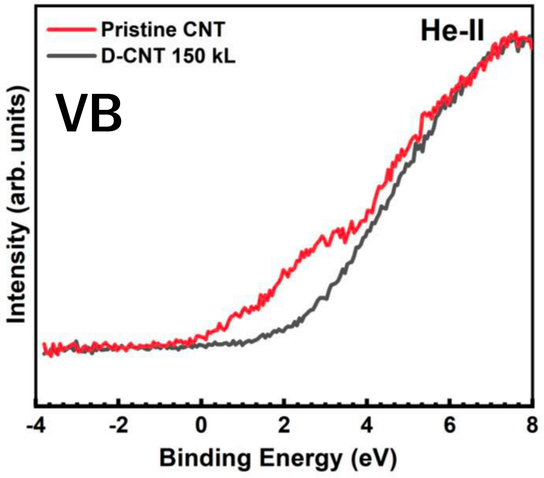
$I_{sp3} / (I_{sp2} + I_{sp3}) \simeq 70\%$

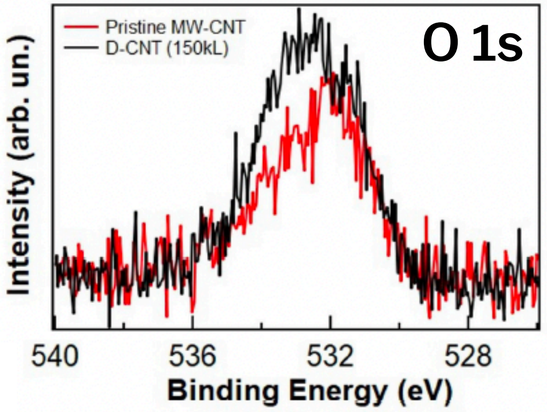
WF = 3.84 ± 0.05 eV





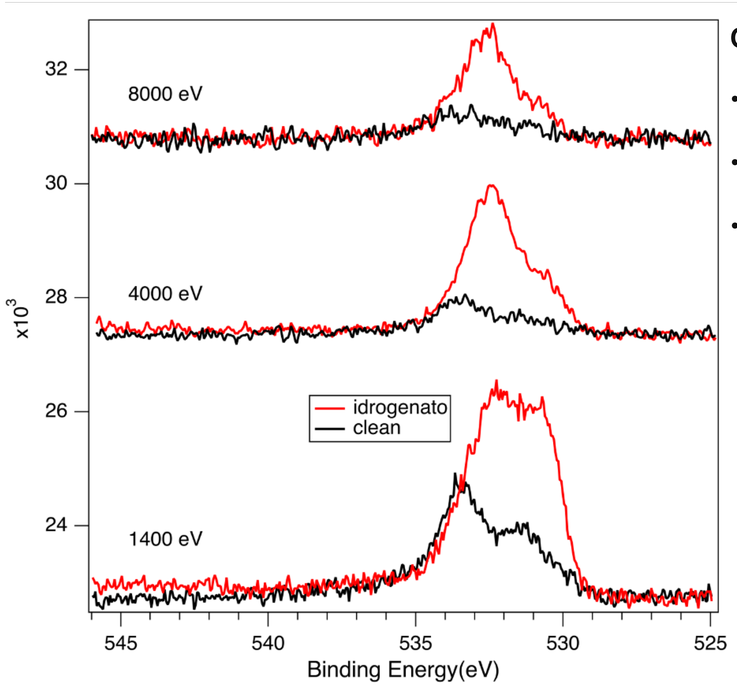






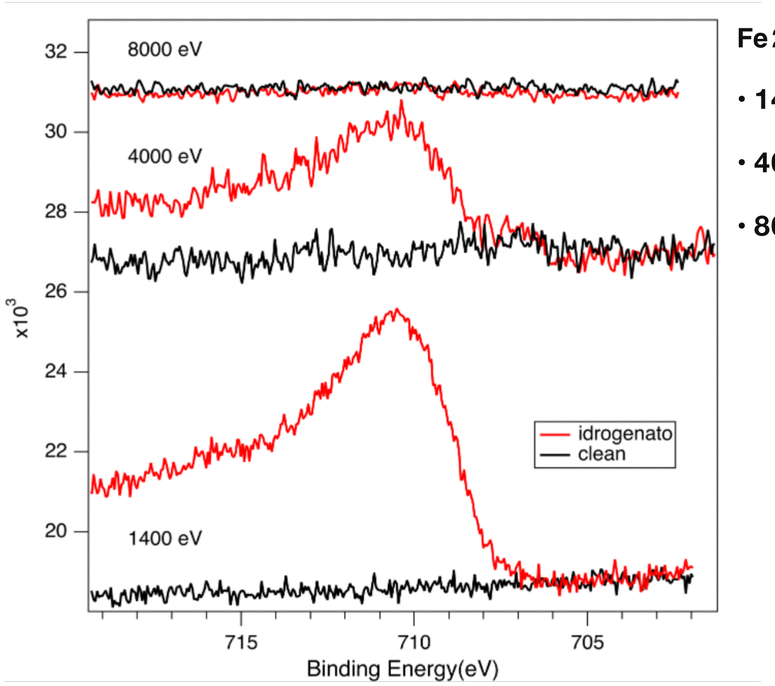
O1s and Fe 2p content

Cross section values
Yeh & Lindau (1985)
Scofield (1973)



O 1s

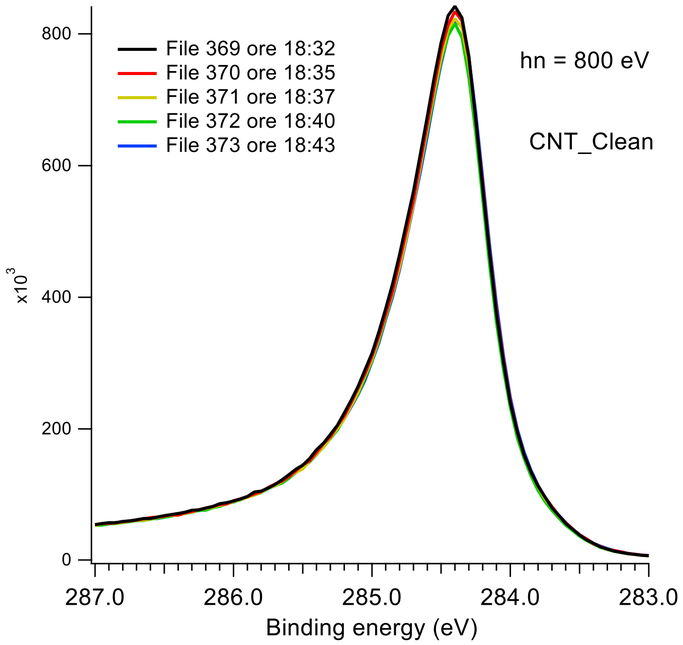
- **1400eV**: ≈0.15 Mb
- **4000eV**: ≈0.02 Mb
- **8000eV**: ≈0.005 Mb

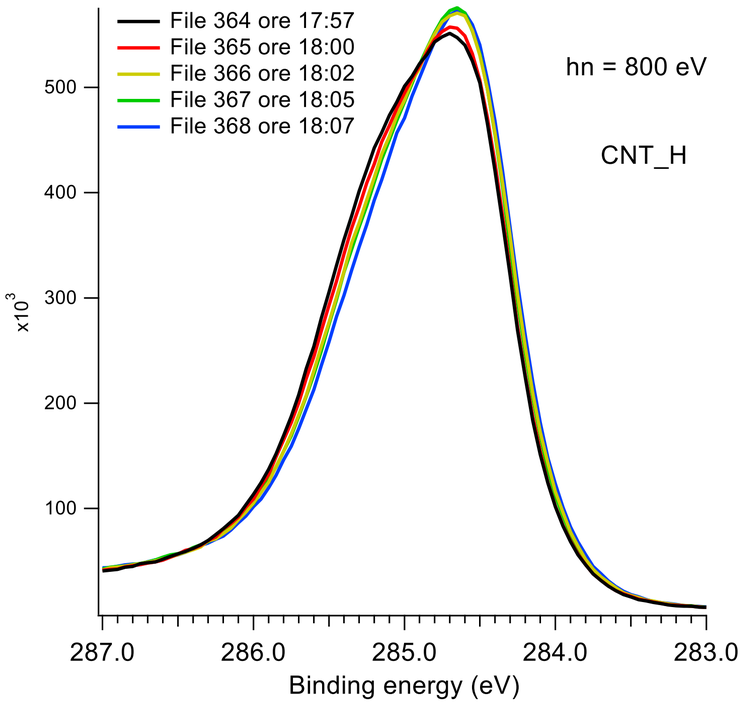


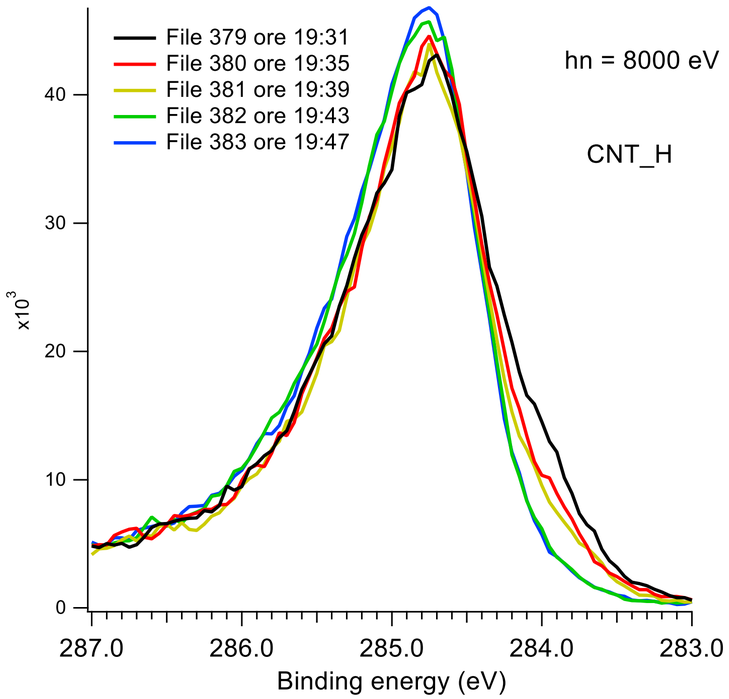
Fe 2p

- **1400eV**: ≈0.5 Mb
- **4000eV**: ≈0.08 Mb
- **8000eV**: ≈0.02 Mb

Beam makes hydrogen desorbs

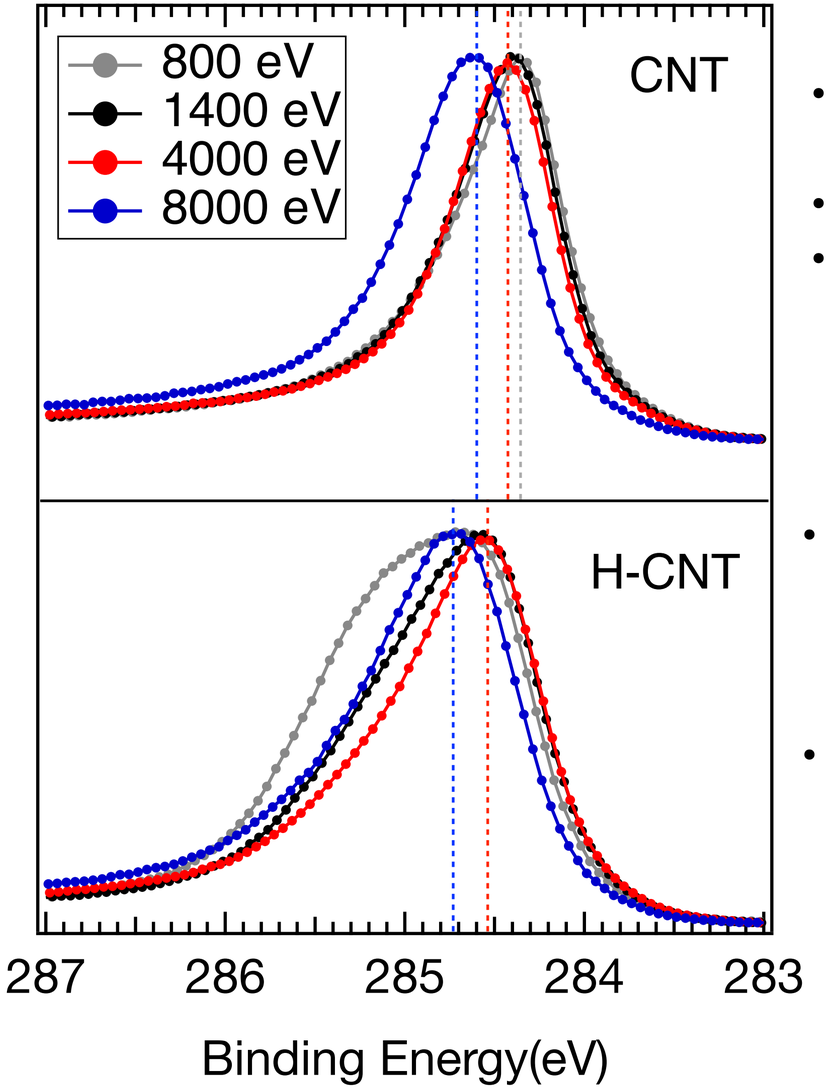






Recoil Effects in Photoemission: Hit Me (Photon) One More Time

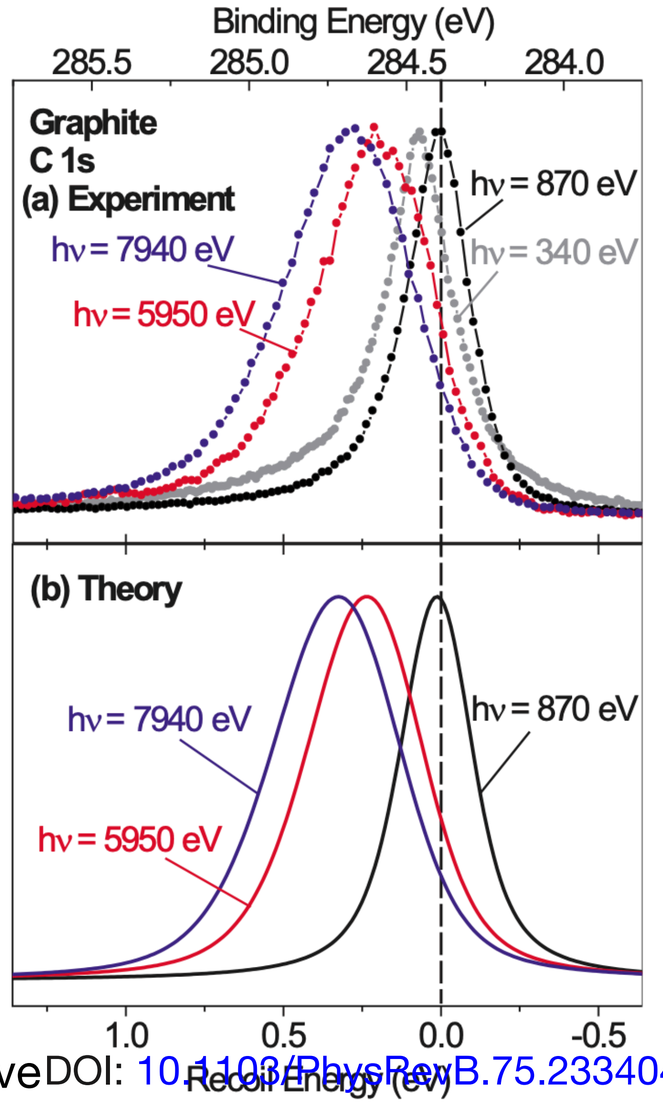
- Recoil: shift
- Kind/number of phonon excitations: asymmetric broadening



- 800 eV ~ 1400 eV no major C-C recoil effect
- 4000 eV energy shift ~ 100 meV
- 8000 eV energy shift ~ 250 meV

- prominent sp3 component gradually decreases with photon energy

- From 4000 eV to 8000 eV increasing recoil effect

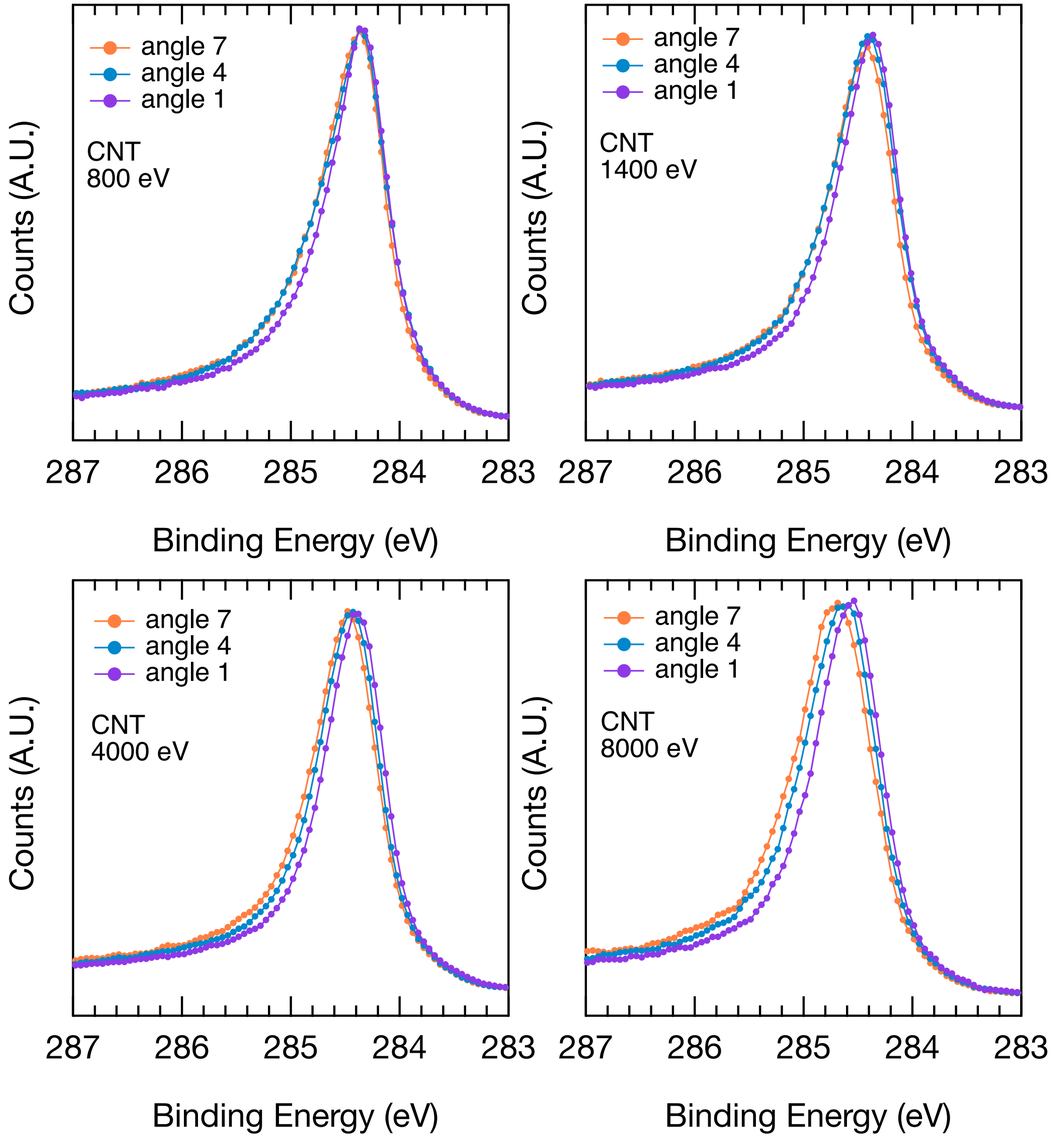


- Modello semiclassico
- Armonico (no dissipaz)
- Single phonon
- No coupling elettronico (curve simmetriche no coda di drude)

DOI: 10.1103/PhysRevB.75.233404

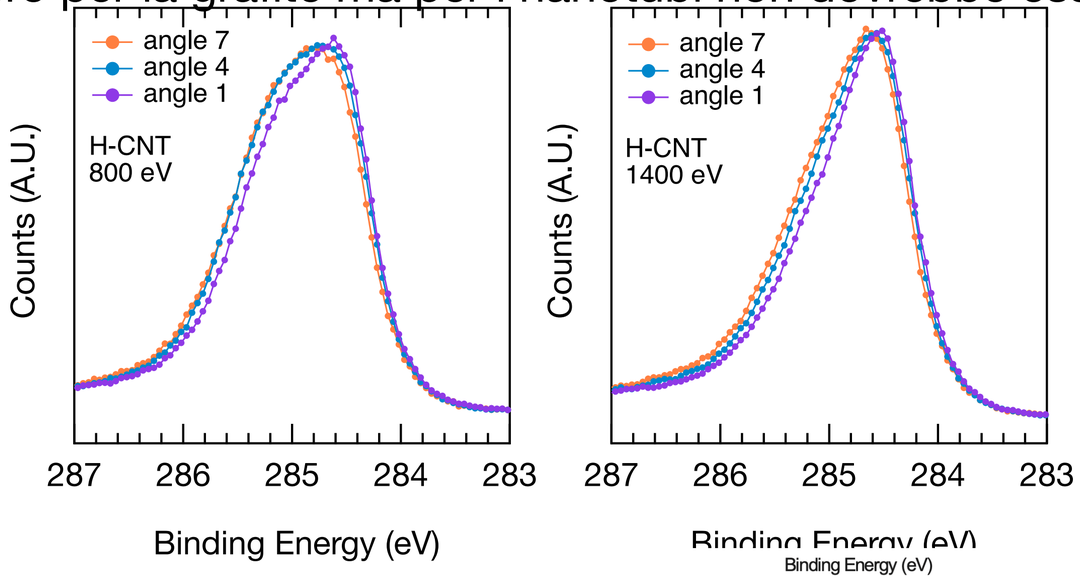
Bending vs Stretching modes with High Energy ARPES

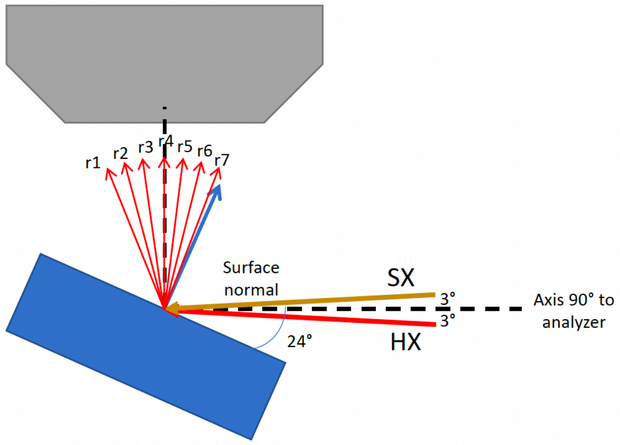
- Angle 7: normal emission

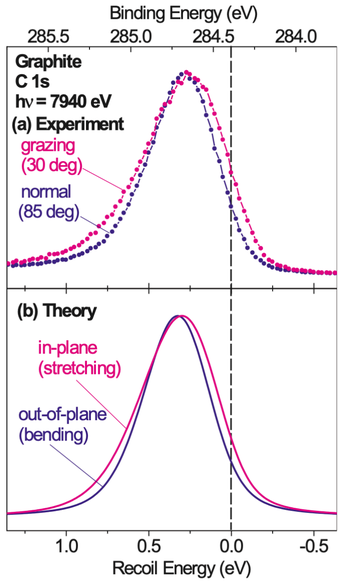


- Out of plane (normal emission): higher recoil energy

È vero per la grafite ma per i nanotubi non dovrebbe essere l'opp

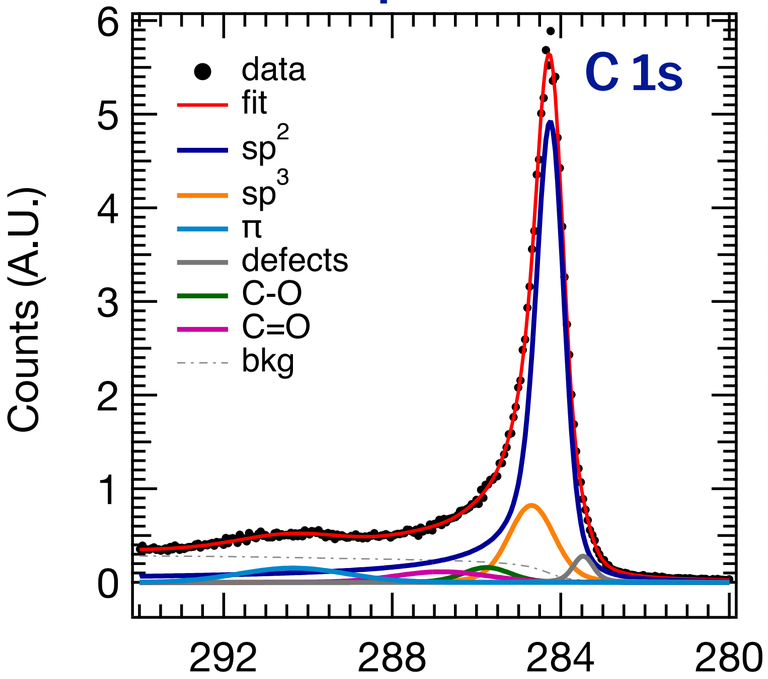






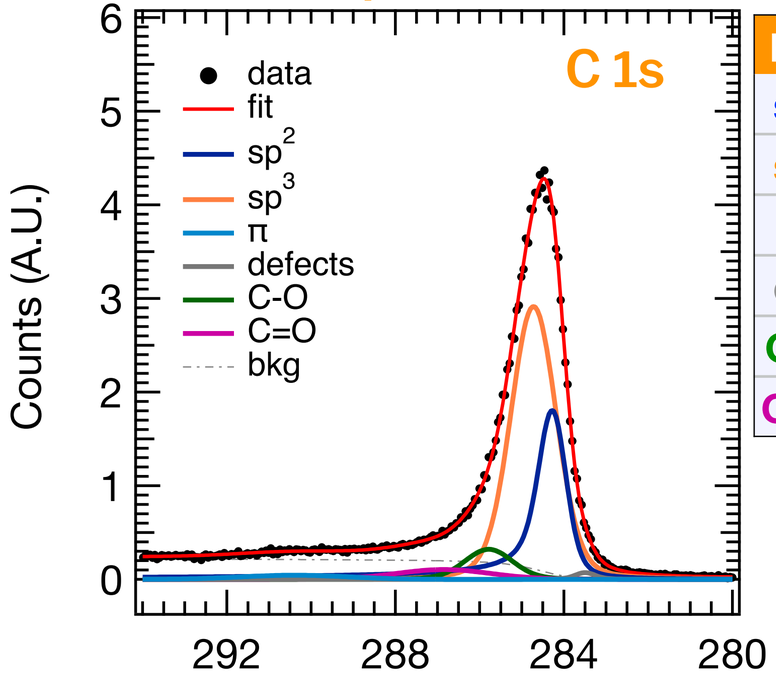
XPS analysis: from sp² towards sp³

CNT pristine

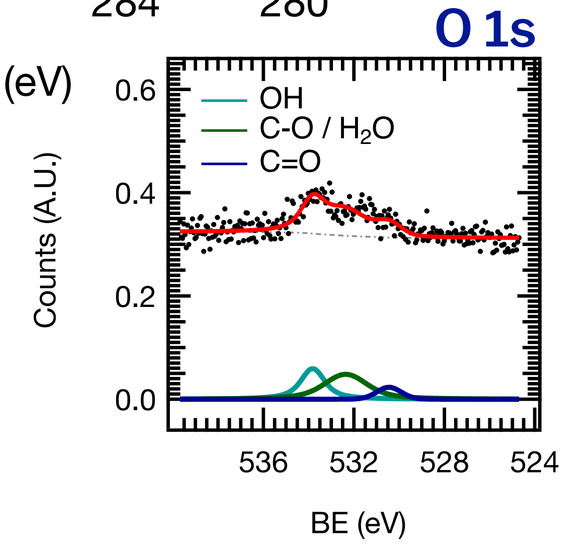


Rel intensity (I_x / I_{tot})	
sp²	0.66 ± 0.02
sp³	0.14 ± 0.02
π	0.06 ± 0.03
def	0.02 ± 0.004
C-O	0.03 ± 0.02
C=O	0.04 ± 0.02

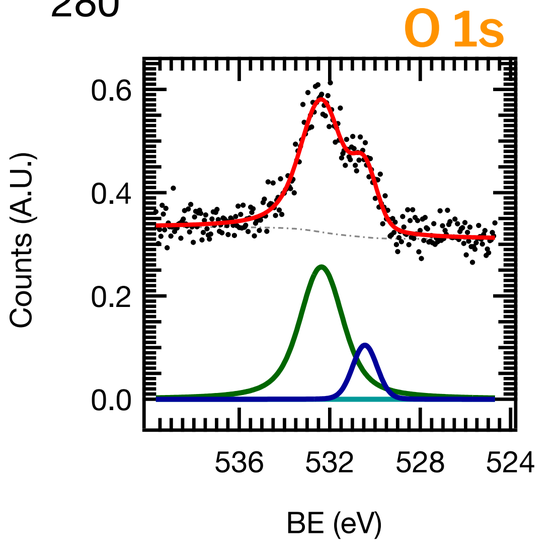
CNT plasma H



Rel intensity (I_x / I_{tot})	
sp²	0.28 ± 0.03
sp³	0.56 ± 0.04
π	0.02 ± 0.01
def	0.01 ± 0.003
C-O	0.06 ± 0.03
C=O	0.04 ± 0.02

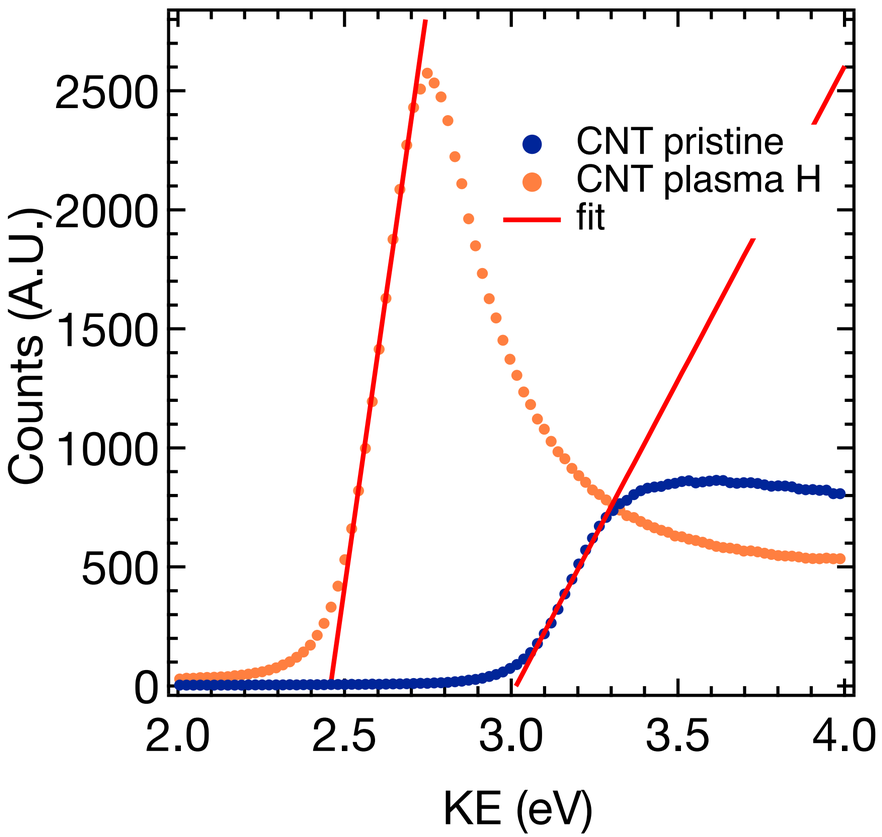


- **sp²** decreases, **sp³** increases (x4)
- **C-O** and **C=O** increases



UPS: Work Function Changes and Band Gap Opening

Secondary Electron onset (SE)



V_{BIAS} = - 3 V

Work Function measure: $\phi_{sample} = h\nu - \Delta E_k = h\nu - (FL - SE)$

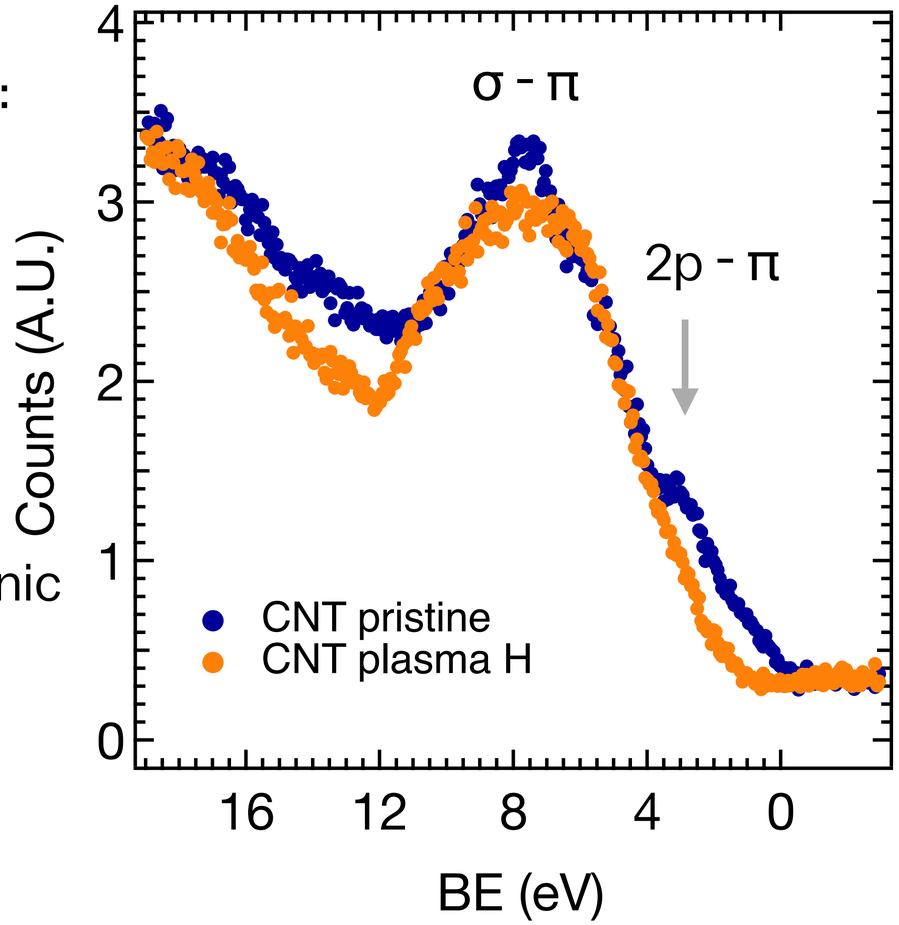
Surface dipole changes:

- **WF lowers** from 4.33 ± 0.05 eV to 3.81 ± 0.05 eV

Depletion of the electronic levels near Fermi level

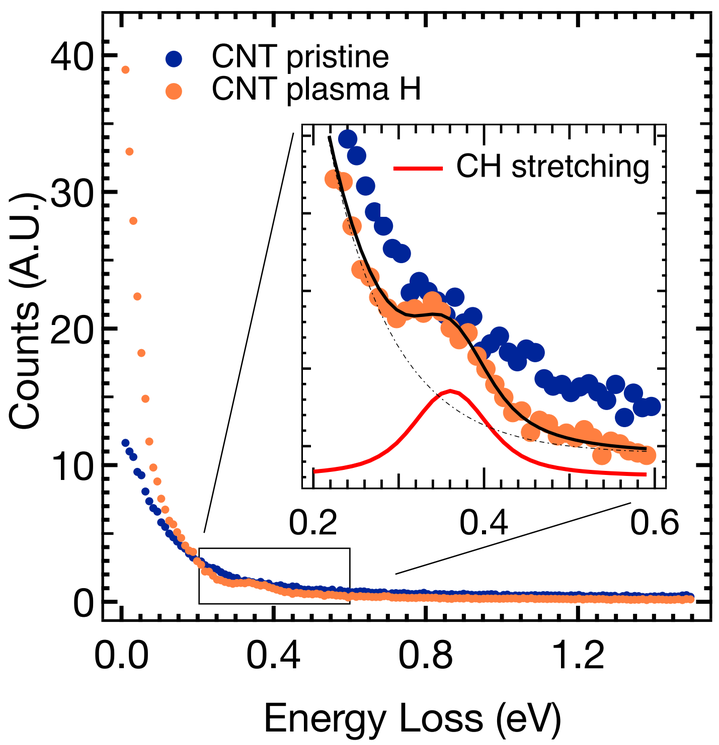
- **Gap opening**

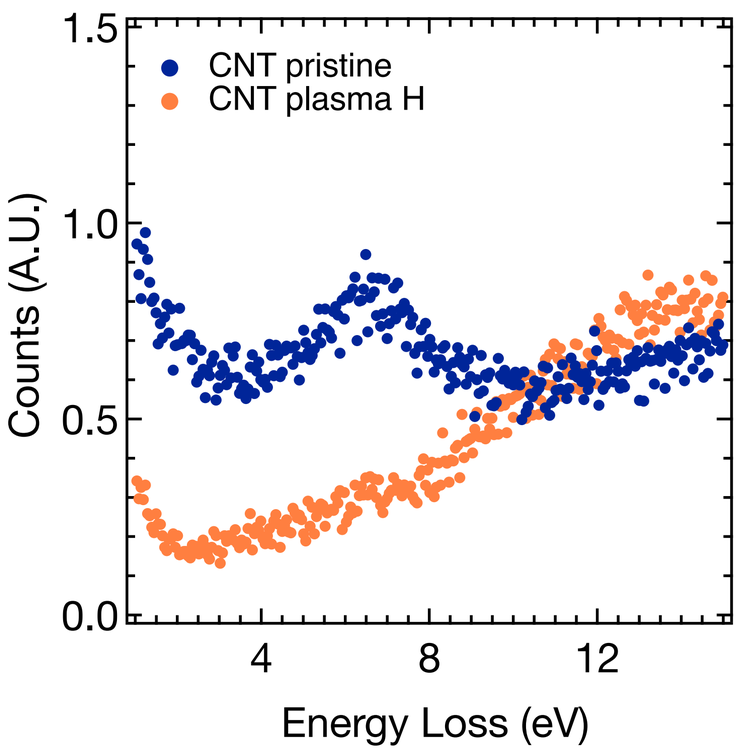
Valence Band He II

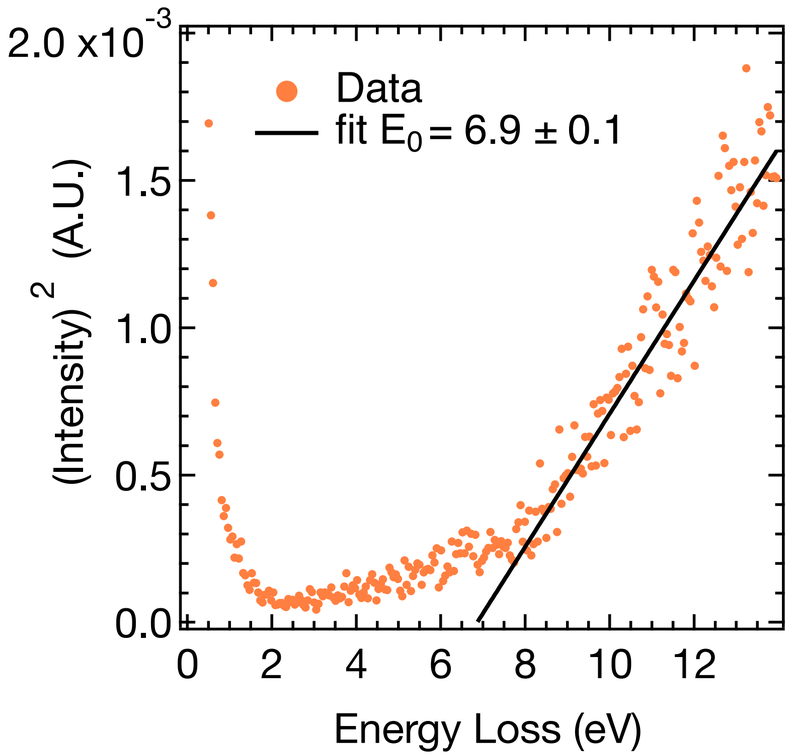


Hydrogenation Signatures in Energy Loss Spectroscopy

Electron Energy Loss Spectroscopy







- **CH stretching** appears at ~ 0.36 eV
- Quenching of the **π plasmon** and low energy losses
- Wide **band gap** opening ~ 6.9 eV