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

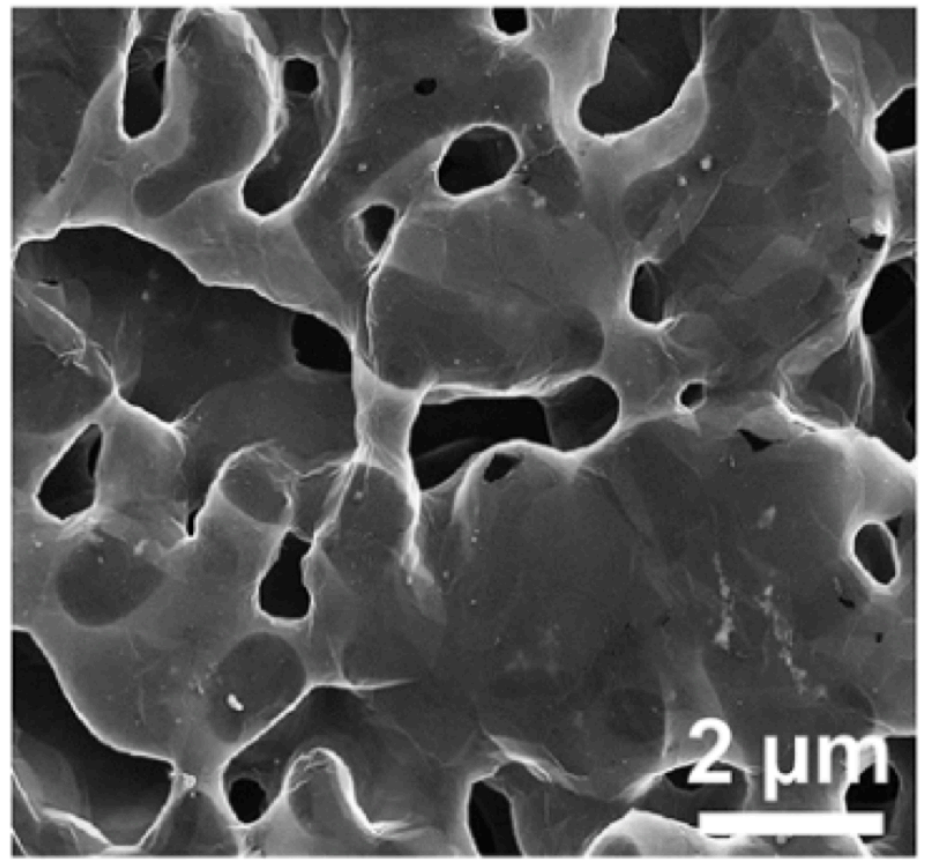
Ptolemy Collaboration Meeting, July 1-2, 2025

Orlando Castellano, Alice Apponi, Daniele Paoloni, Luca Cecchini, Francesco Pandolfi, Ilaria Rago, Carlo Mariani, Gianluca Cavoto, Francesco Offi, Alessandro Ruocco

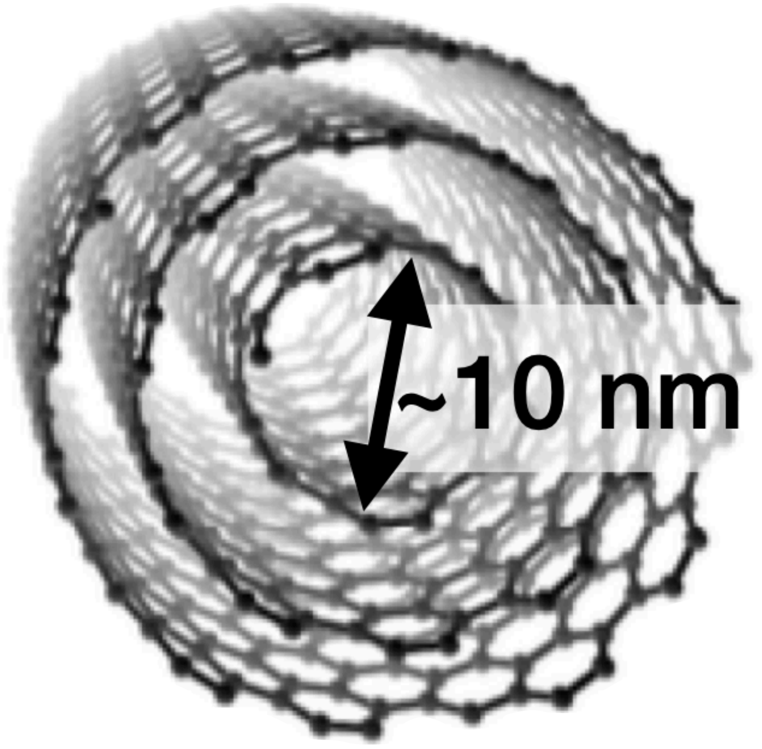
ROMA TRE UNIVERSITÀ DEGLI STUDI
LAboratorio di Spettroscopie Elettroniche e di Correlazione LASEC
PTOLEMY
ANDROMeDA Aligned Nanotube Detector for Research On MeV Darkmatter
INFN Istituto Nazionale di Fisica Nucleare

Possible Tritiated Target Solutions

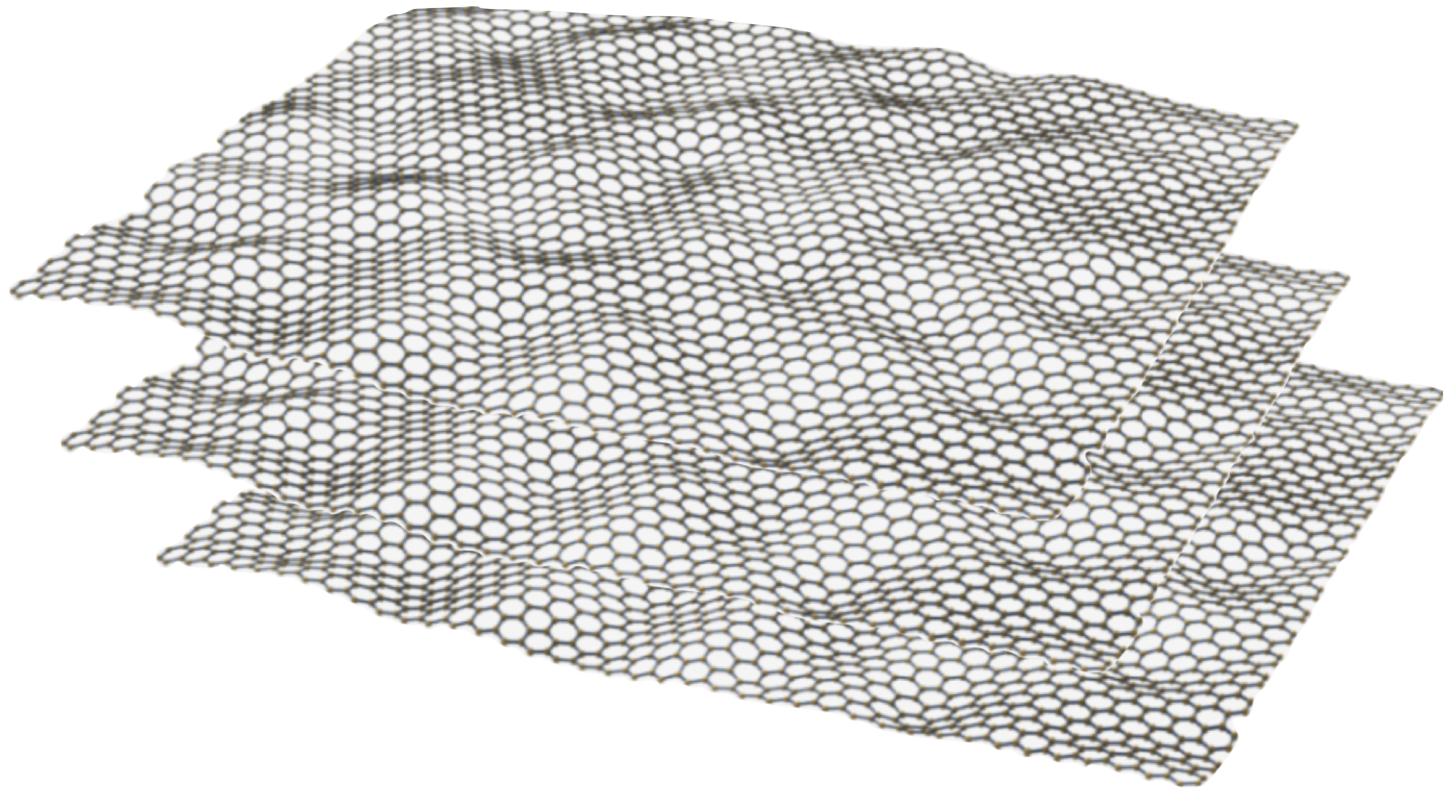
Tritium in a solid-state target



Nano-porous graphene



Carbon Nanotubes



Stacked graphene layers

Two Samples and a Plasma Recipe for Hydrogenation

CNT pristine

Annealing

Used as a reference

<u>Two samples</u> from the same batch

Annealing 650 °C

TITAN LAB
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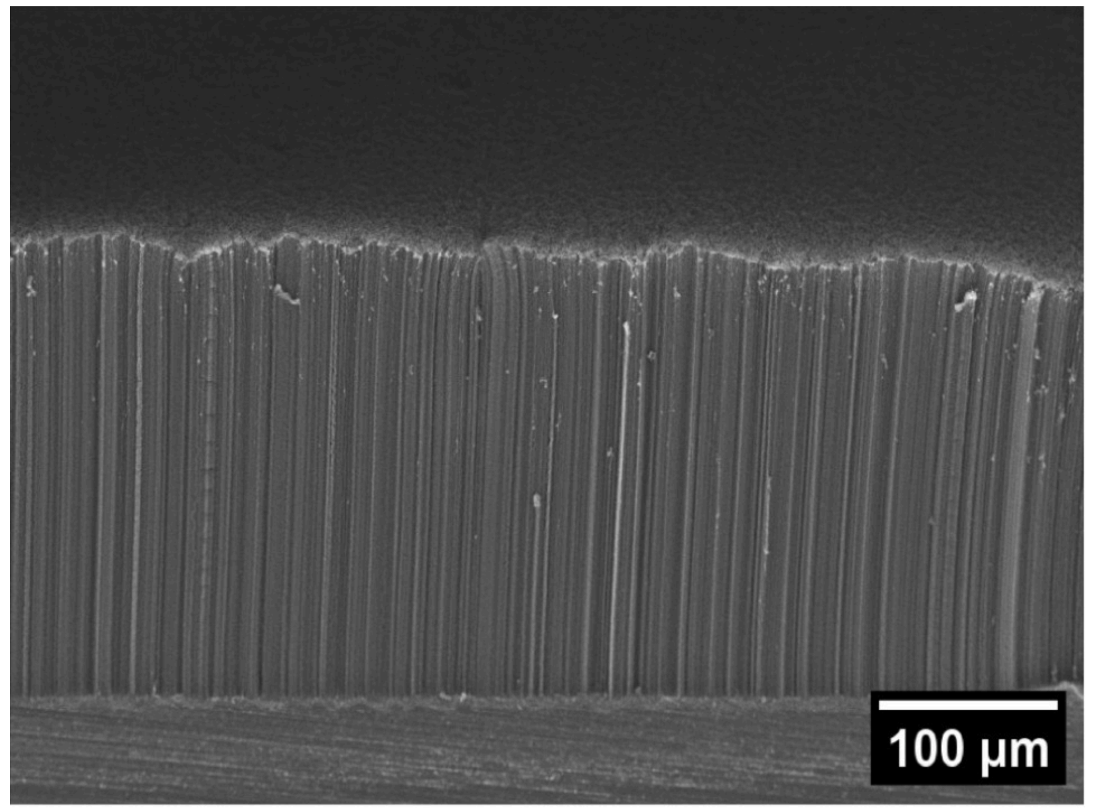
diamond



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

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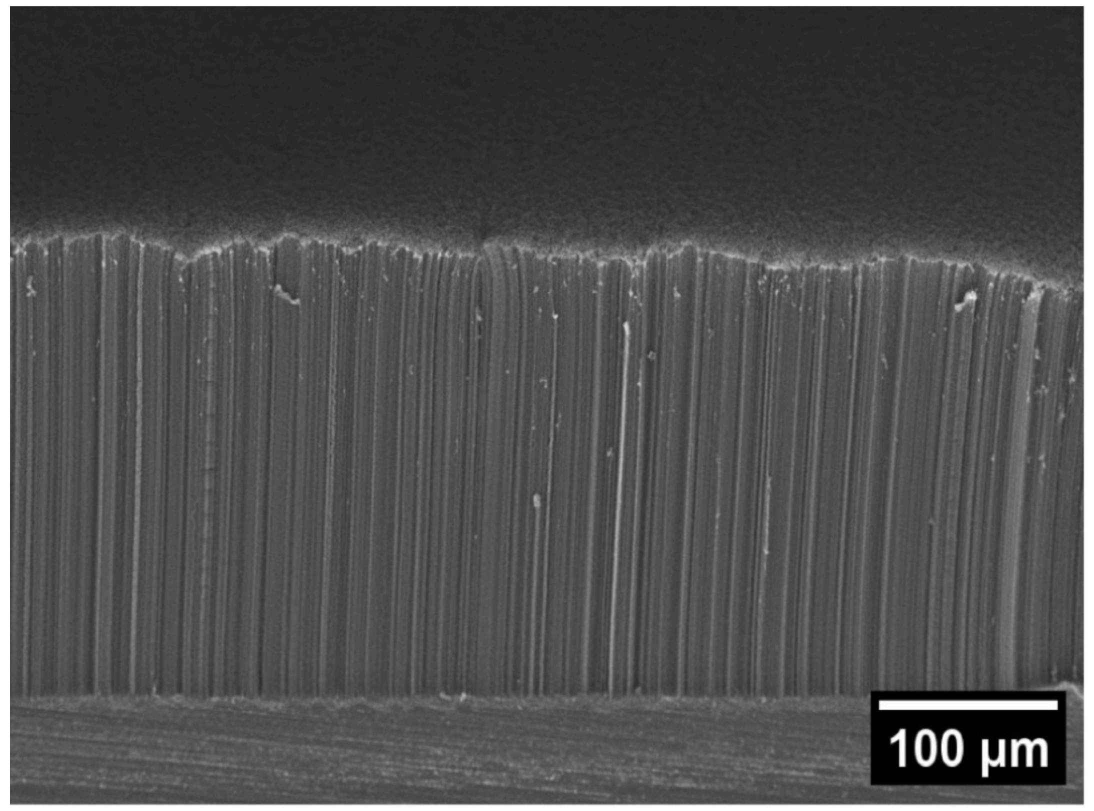


CNT plasma H

Exposed to hydrogen plasma:

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

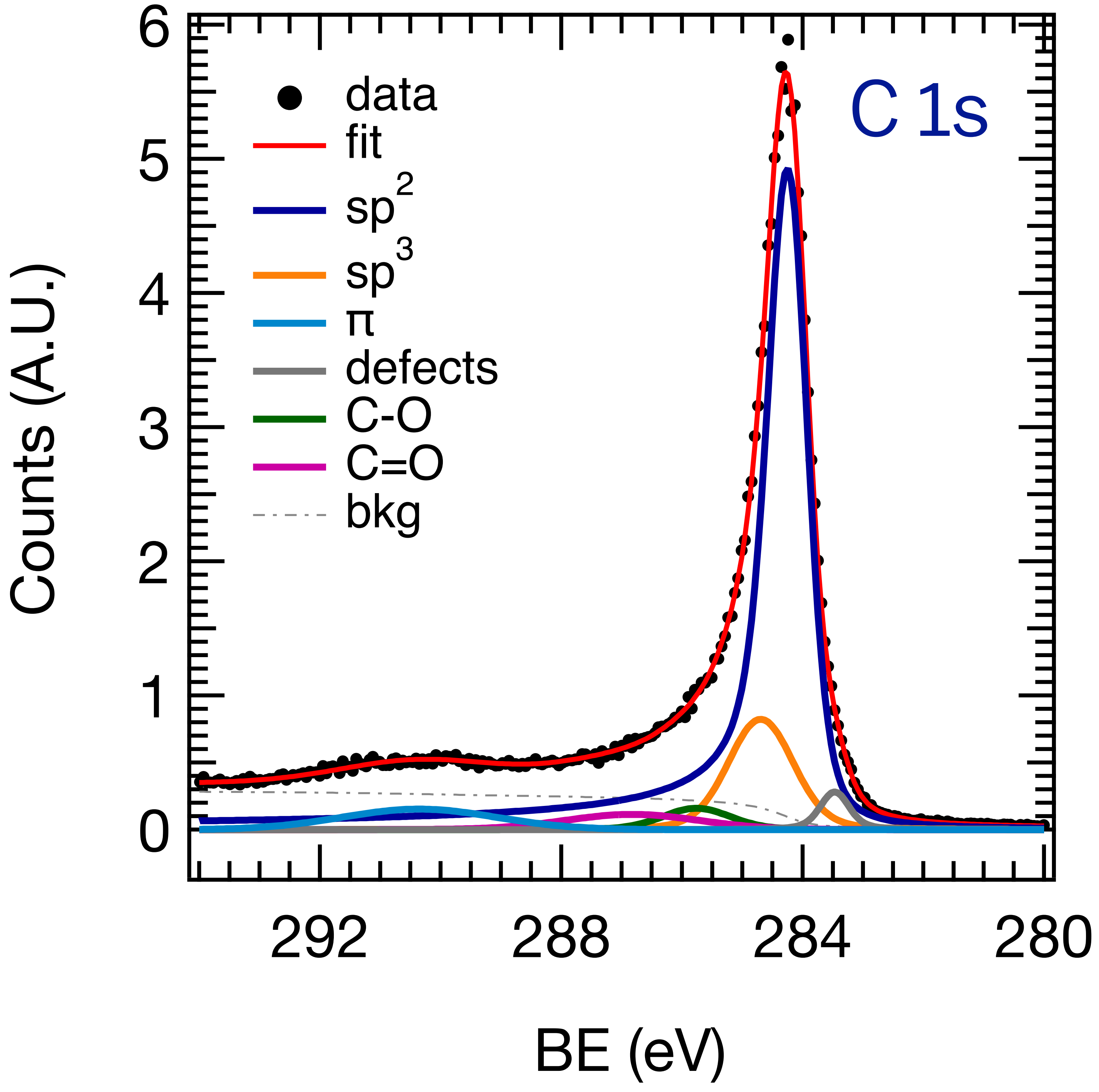
Kept in low vacuum during transfer

Annealing at T < 300 °C

XPS

Monochromatized Al Kα = 1487.6 eV

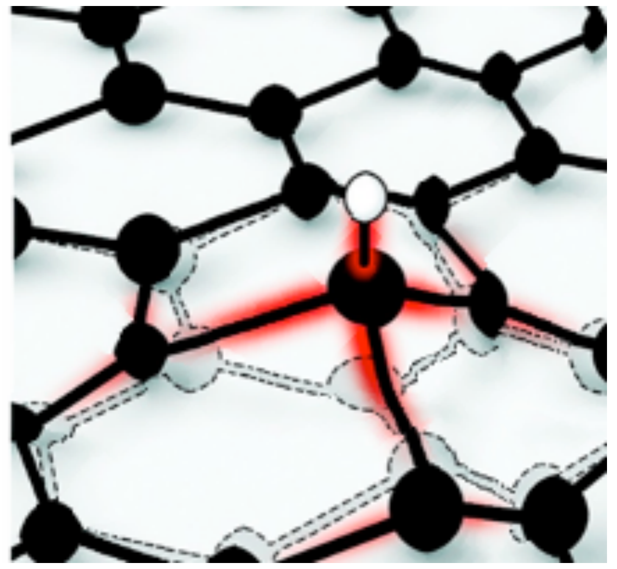
CNT pristine



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

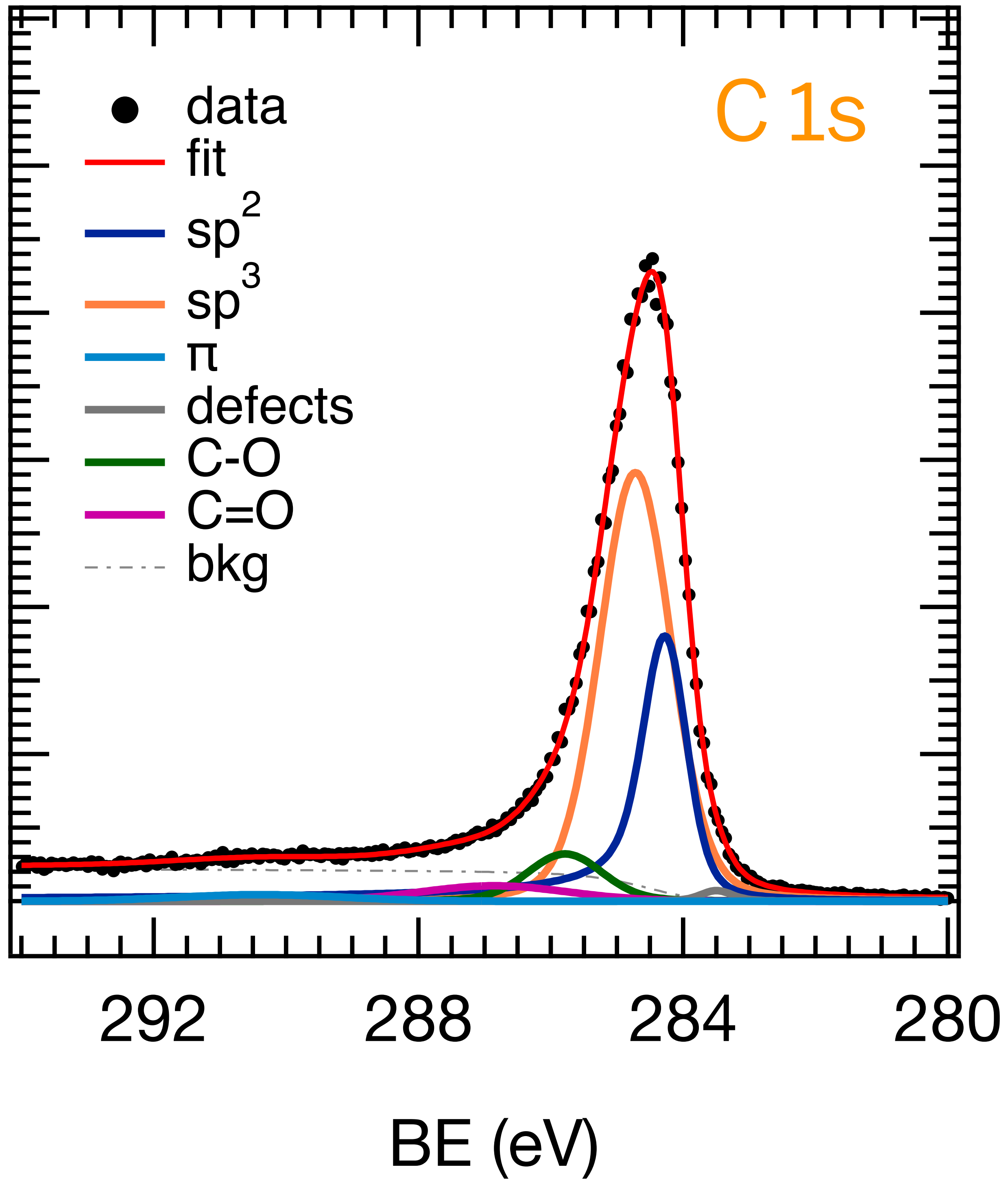
I_{sp3} / (I_{sp2} + I_{sp3})= 0.67

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



- 0.5 eV lower **Work function** in H-CNT

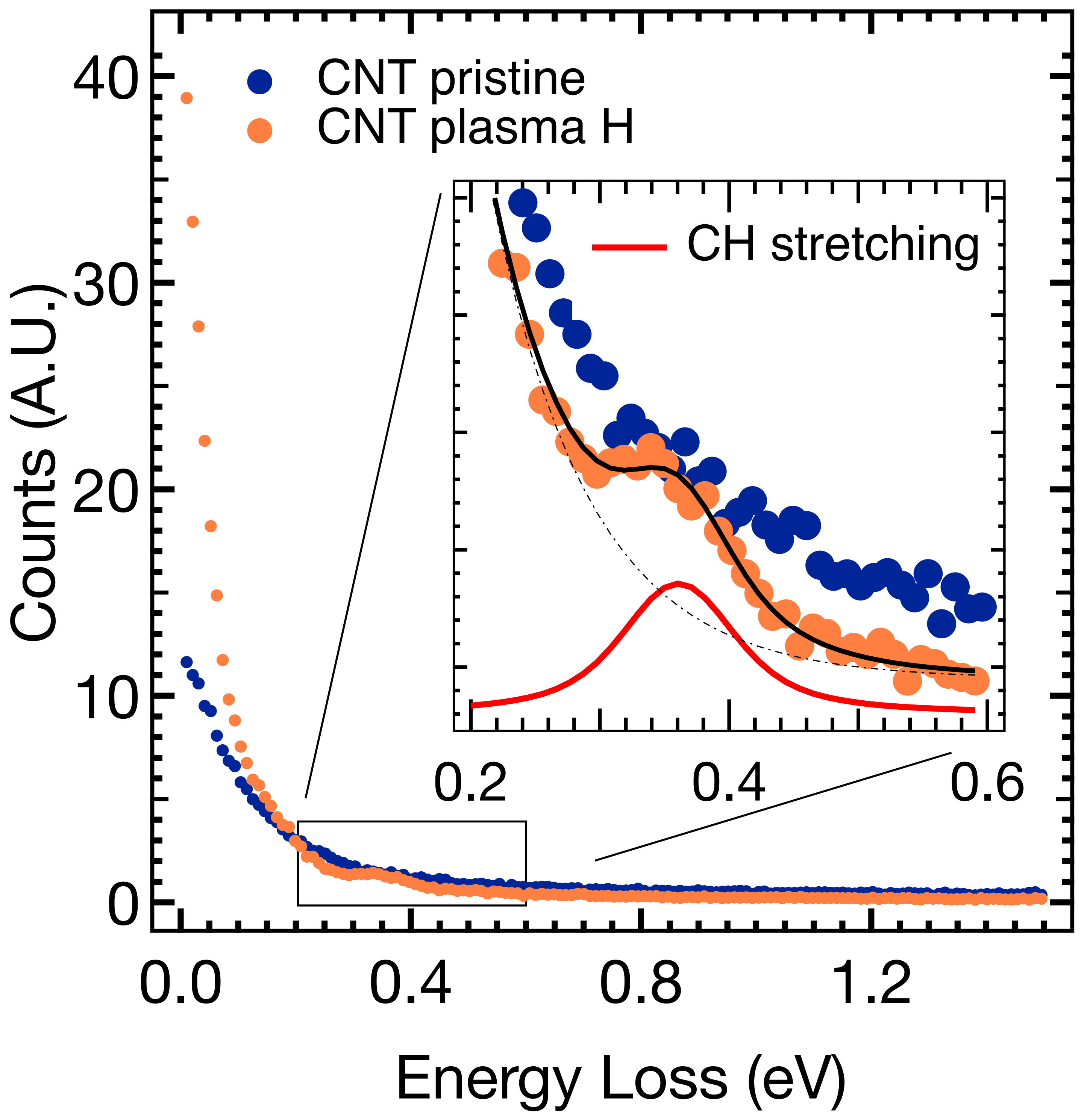
CNT plasma H



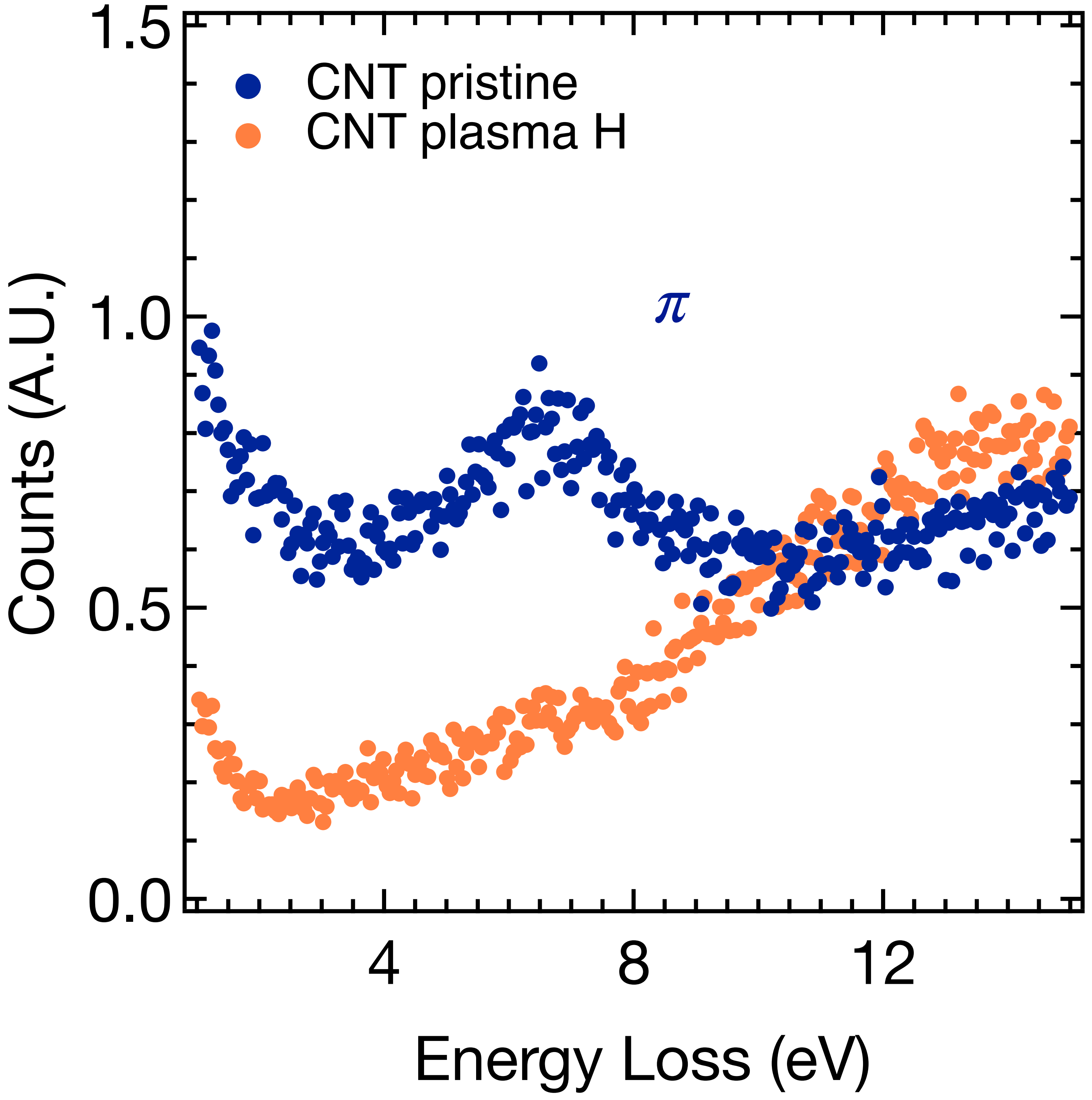
Electron Energy Loss Confirms Hydrogenation

EELS

$E_{primary}$ = 90 eV



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



Electron Energy Loss Confirms Hydrogenation

EELS

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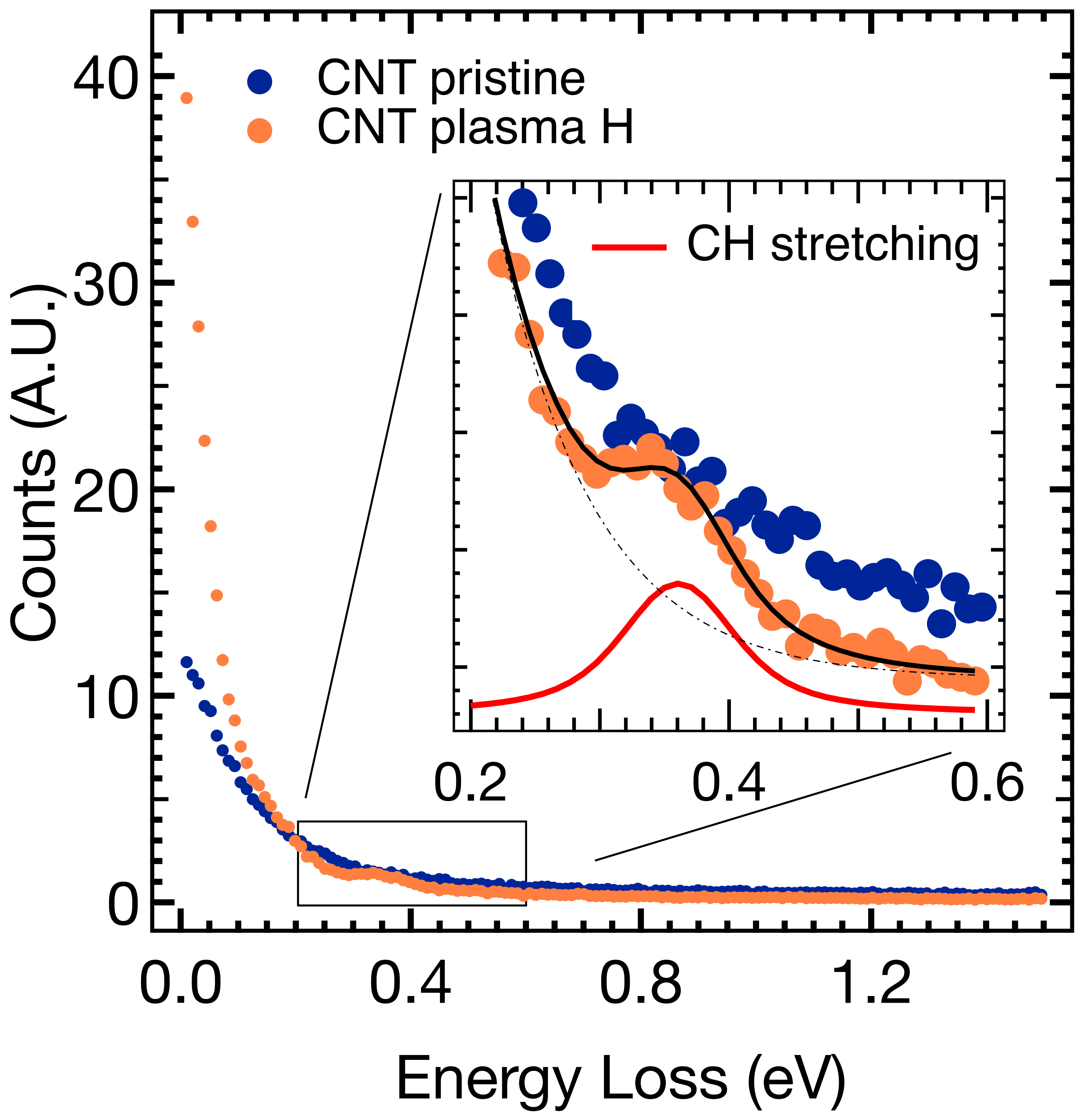

- **C-H** stretching
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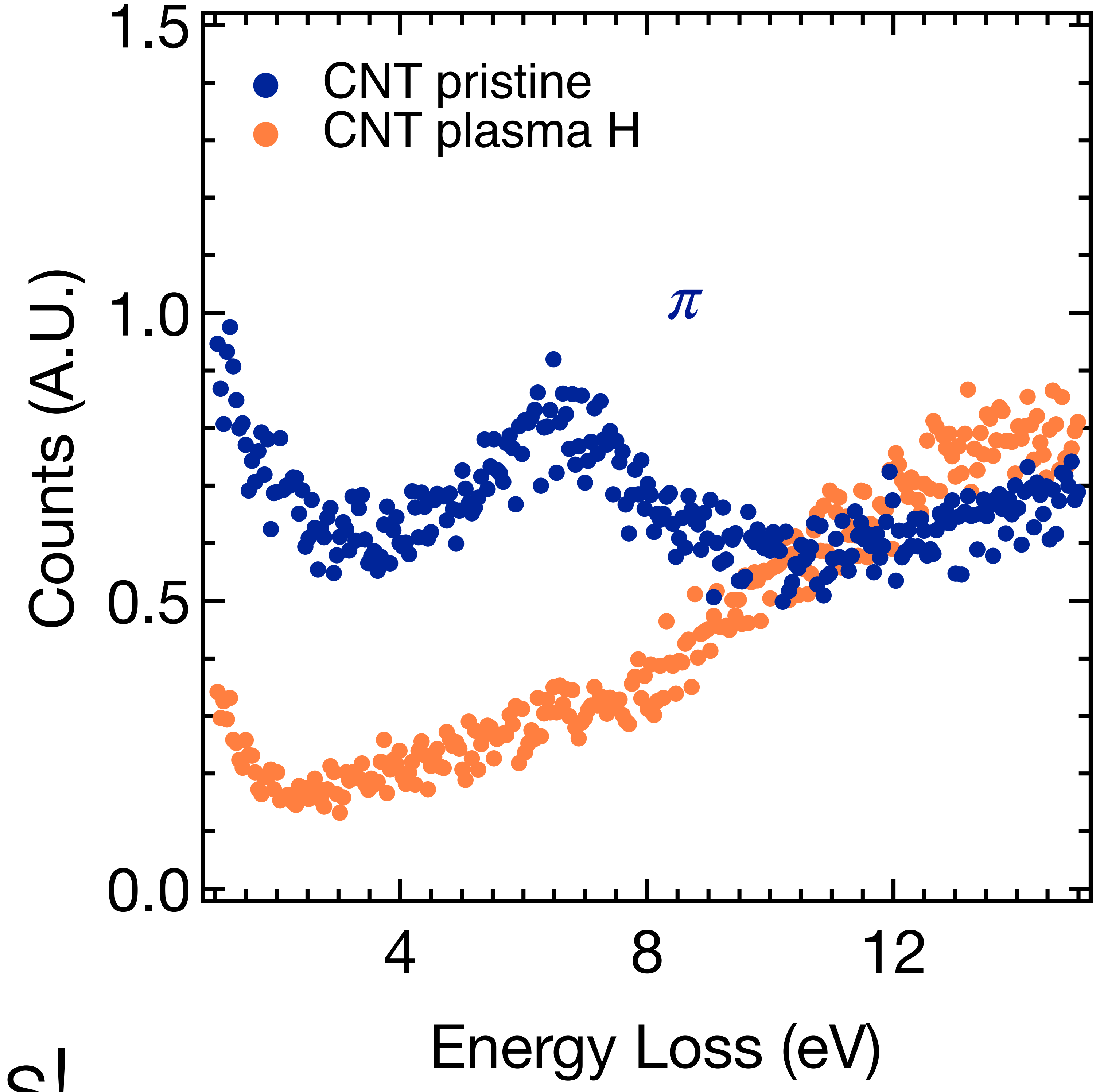
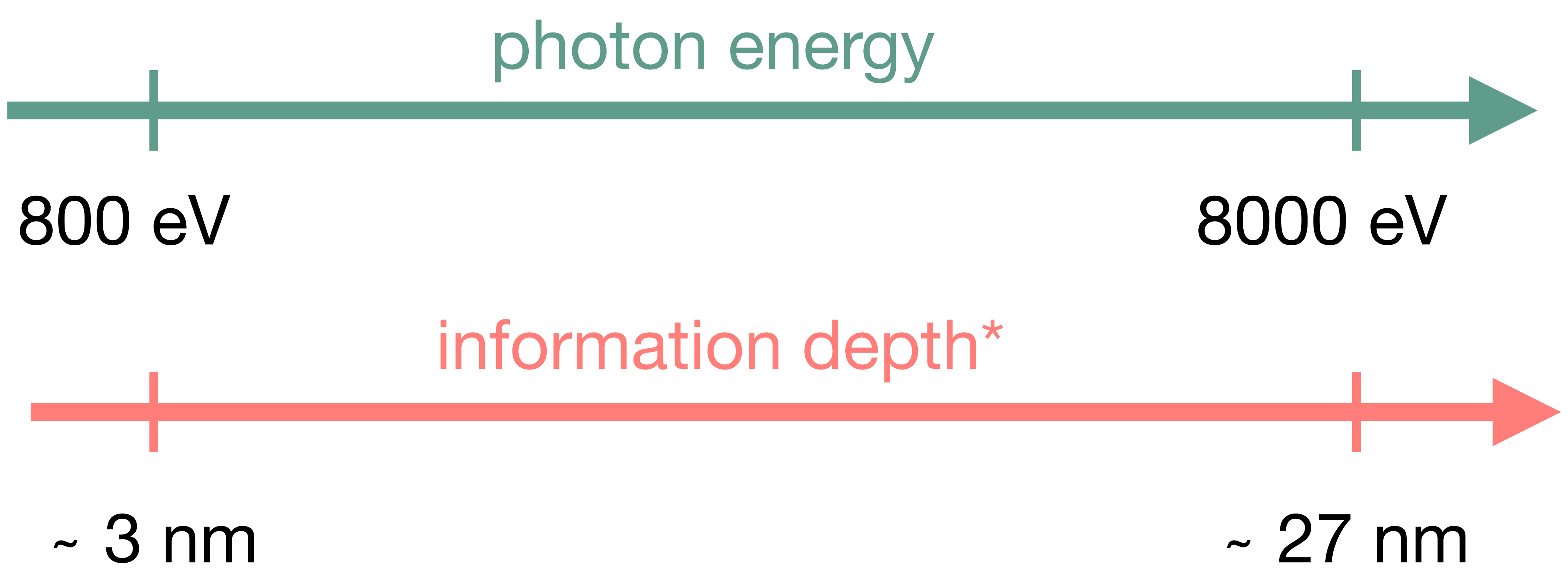


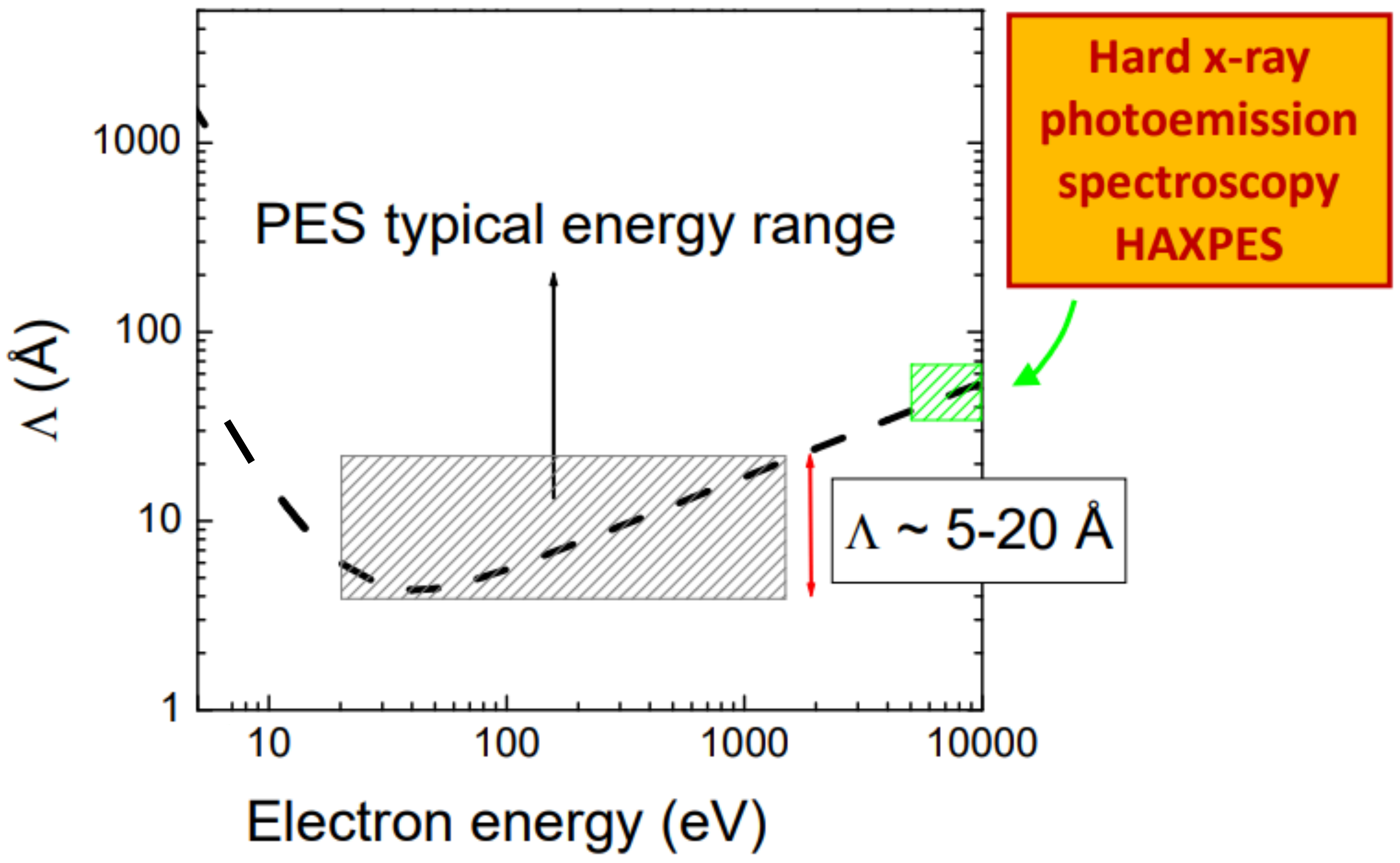
Surface sensitive techniques!

How Deep Does the Hydrogenation Go?

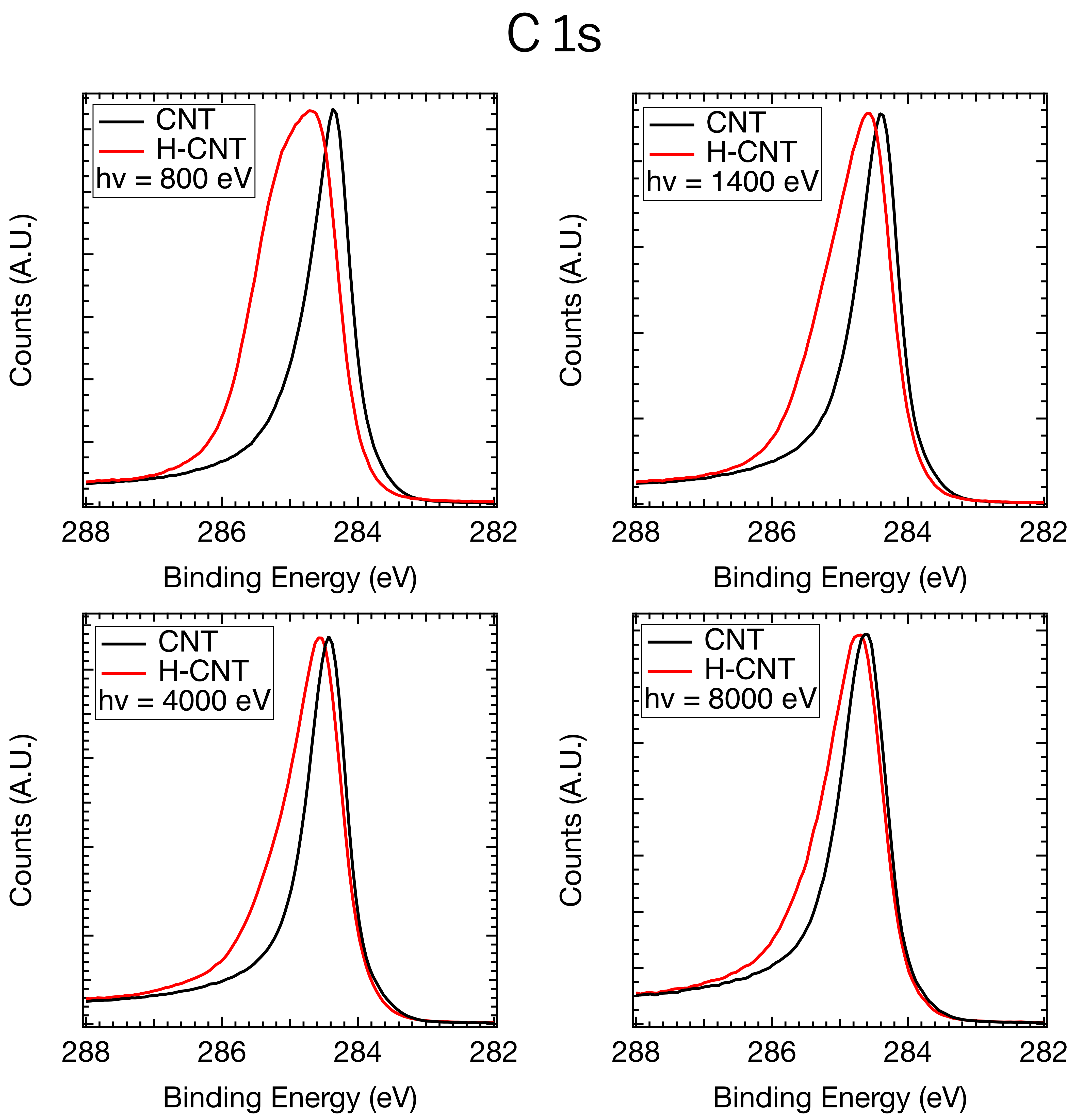
- **Variable photon energy** allows probing from surface to inner layers
- Lineshape changes provide insight into **sp²** vs **sp³** carbon hybridization



*3 x electron Inelastic Mean Free Path in graphite



Not surface-limited, not fully bulk…

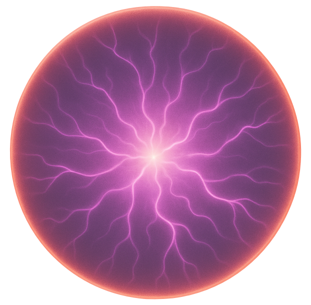


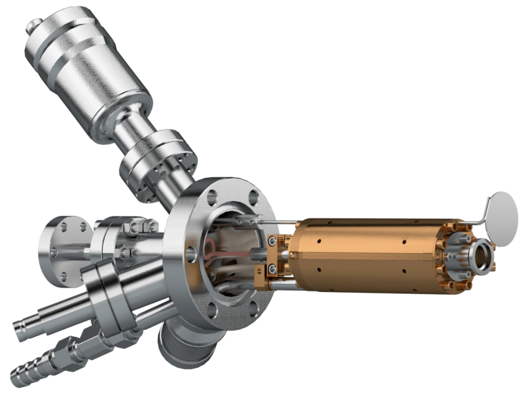
Inelastic Mean Free Path

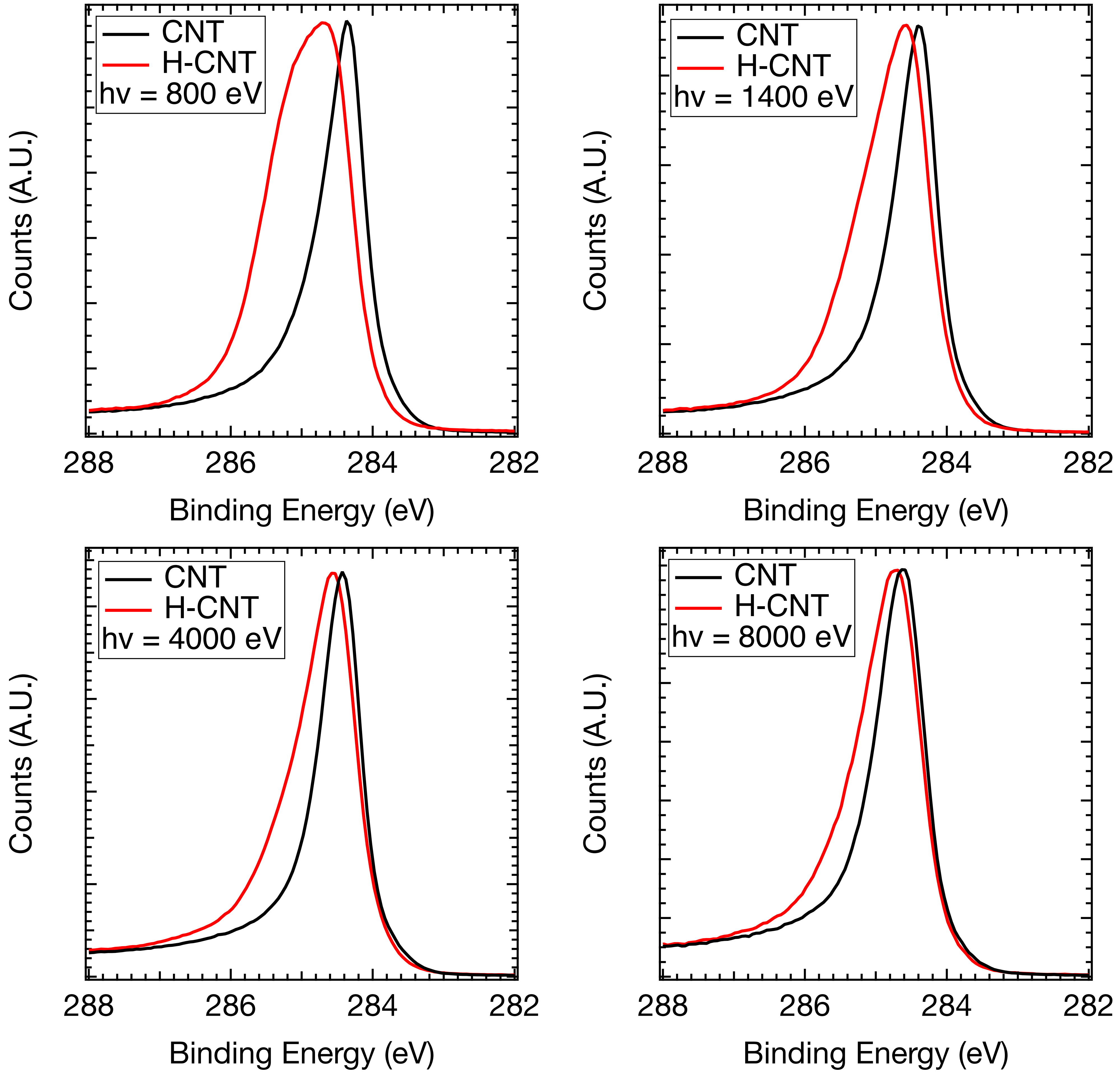
$h\nu$ (keV)	$\lambda_{graphite}$ (nm)
350	0.5
800	1.0
1400	2.0
4000	4.7
8000	9.1

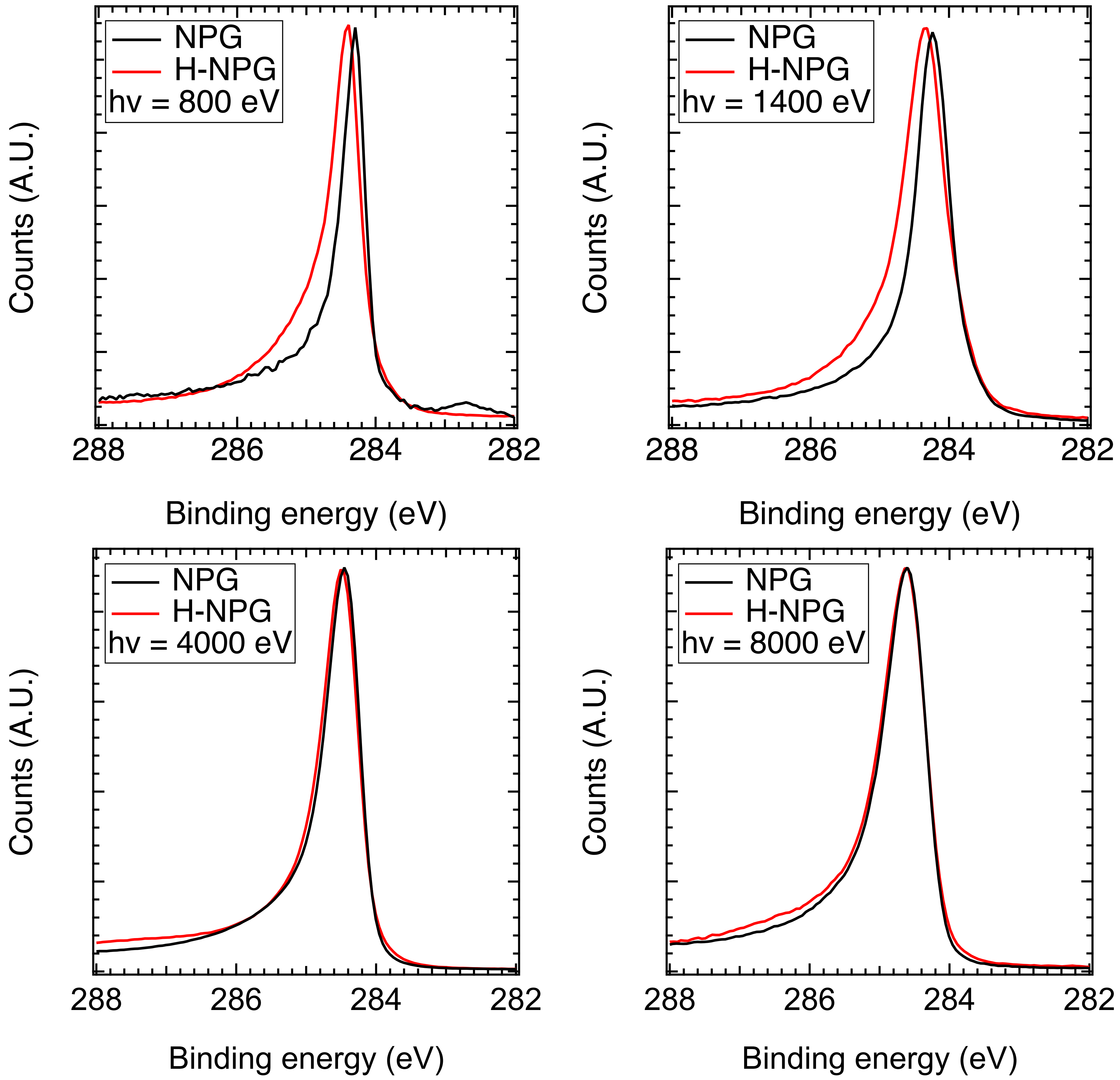
- Line shape differences between CNT and H-CNT **decrease with depth sensitivity**
- With **8 keV** photon **there is still a sign of hydrogenation**

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









Quantifying the Sp³ Content with Soft Photons

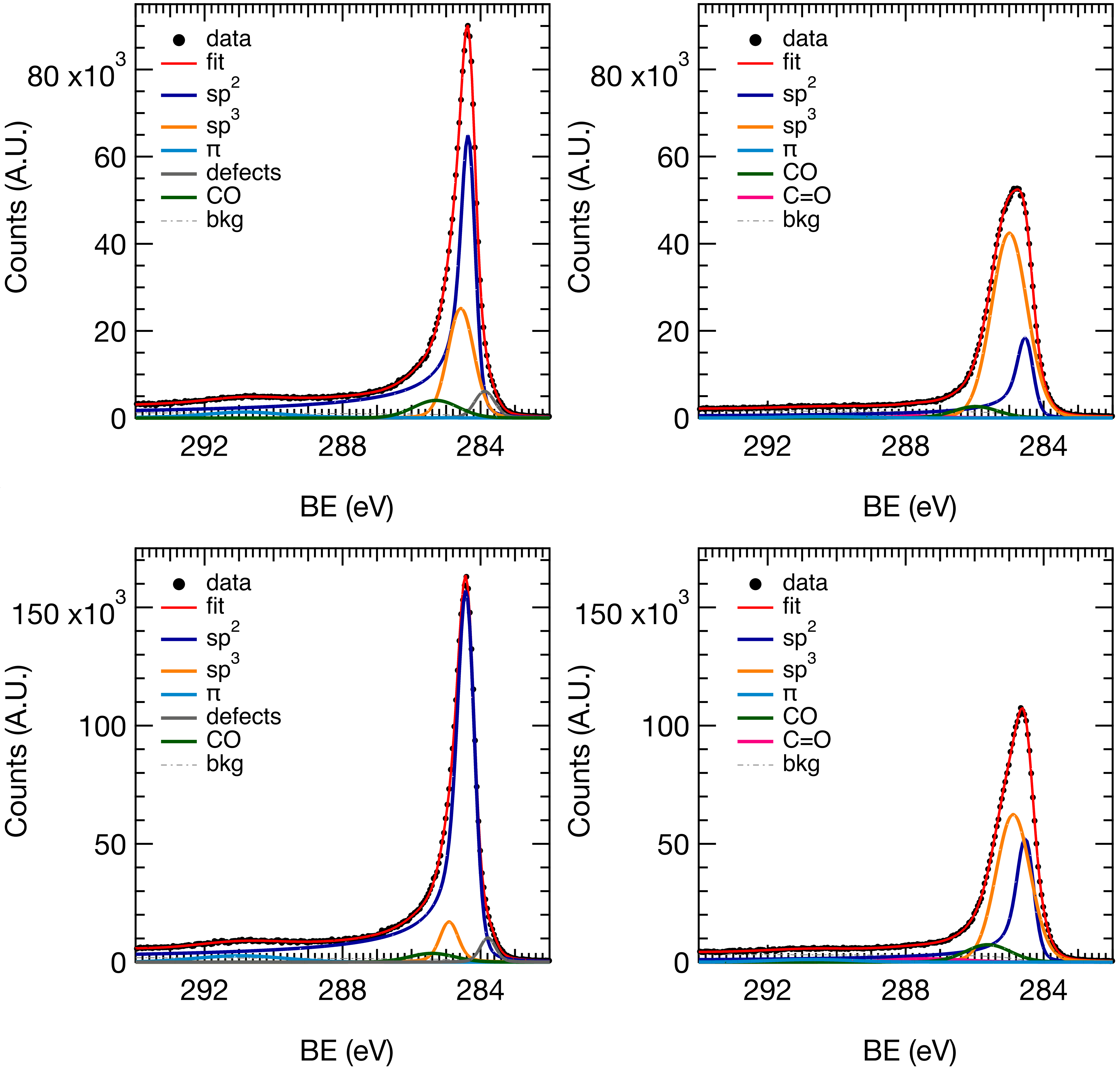
hv = 800 eV

λ = 1 nm

hv = 1400 eV

λ = 2 nm

CNT pristine **CNT plasma H**



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

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

Lineshape Changes due to Recoil Effects in HAXPES

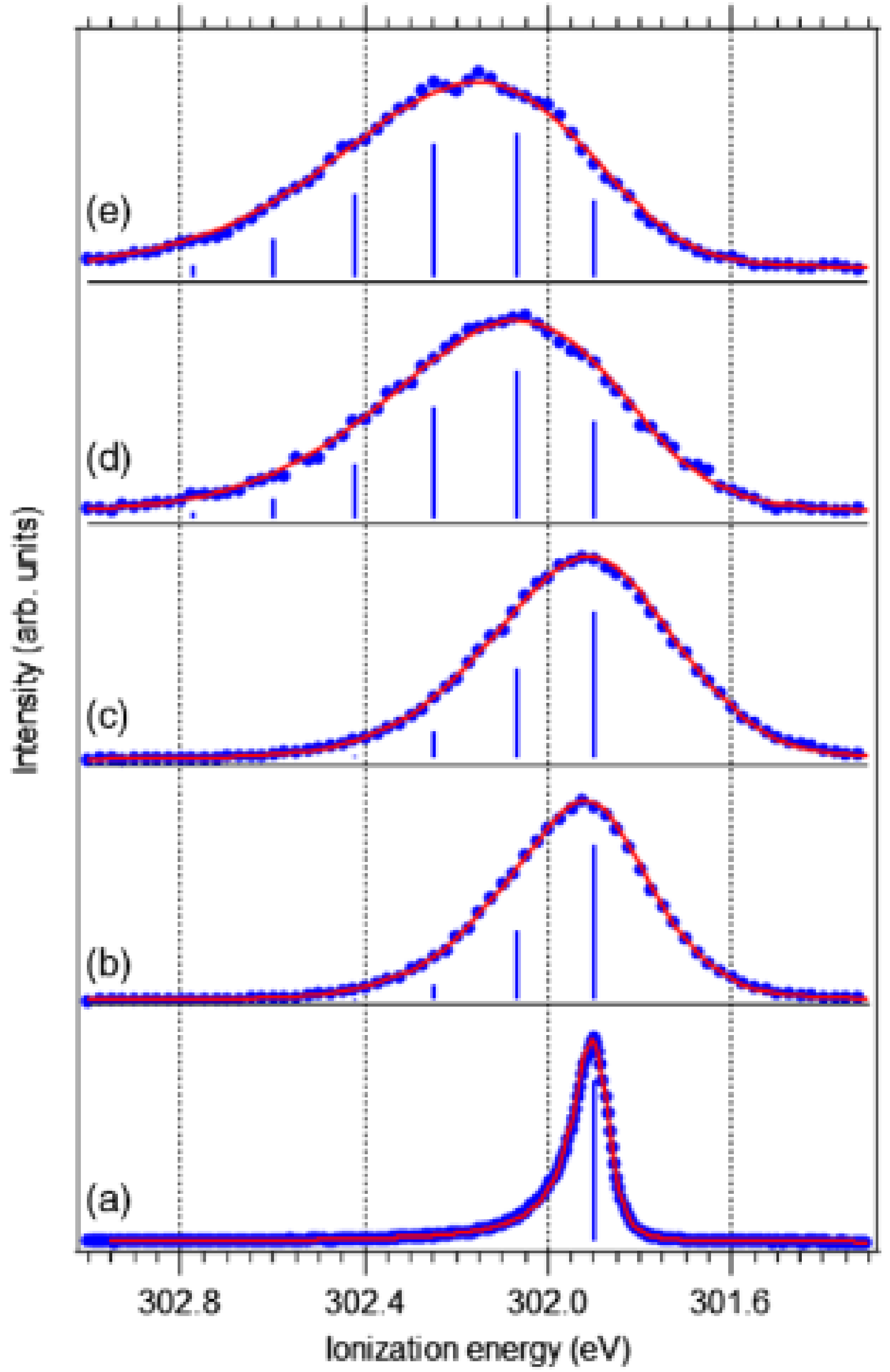
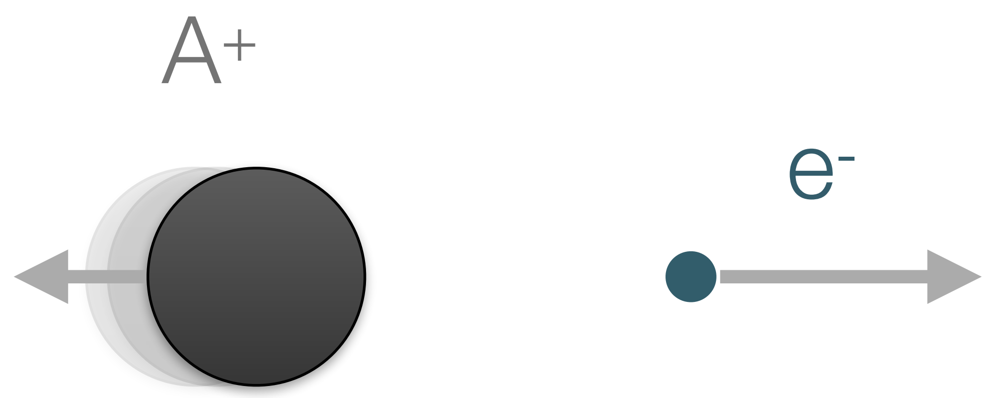


FIG. 1. Carbon 1s photoelectron spectra of CF_4, measured at different photon energies: (a) 330 eV, (b) 2.3 keV, (c) 3.0 keV, (d) 6.9 keV, and (e) 8.5 keV. Dots, experimental data points; continuous red line, least-squares curve-fitting result; vertical sticks, positions and relative intensities of the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

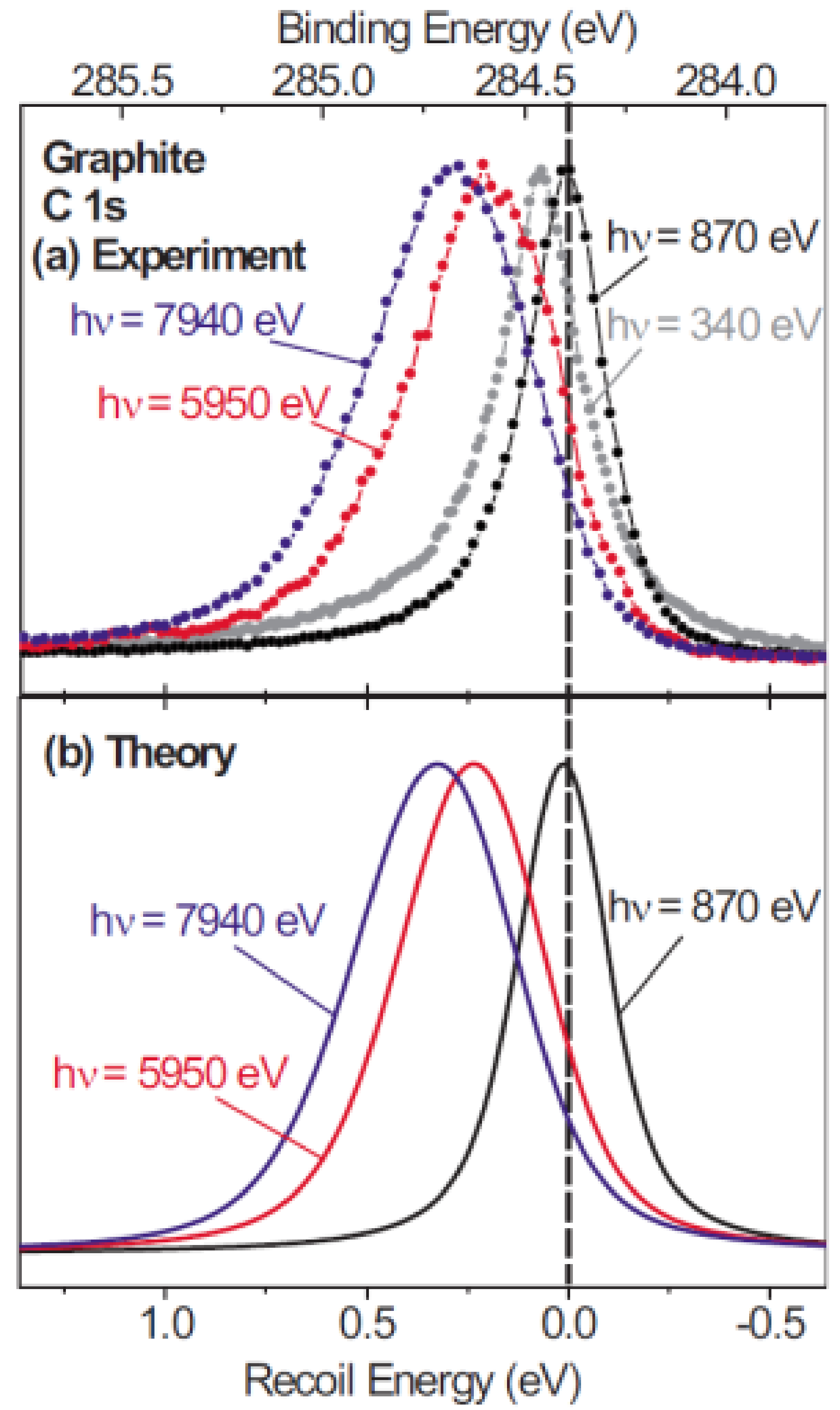
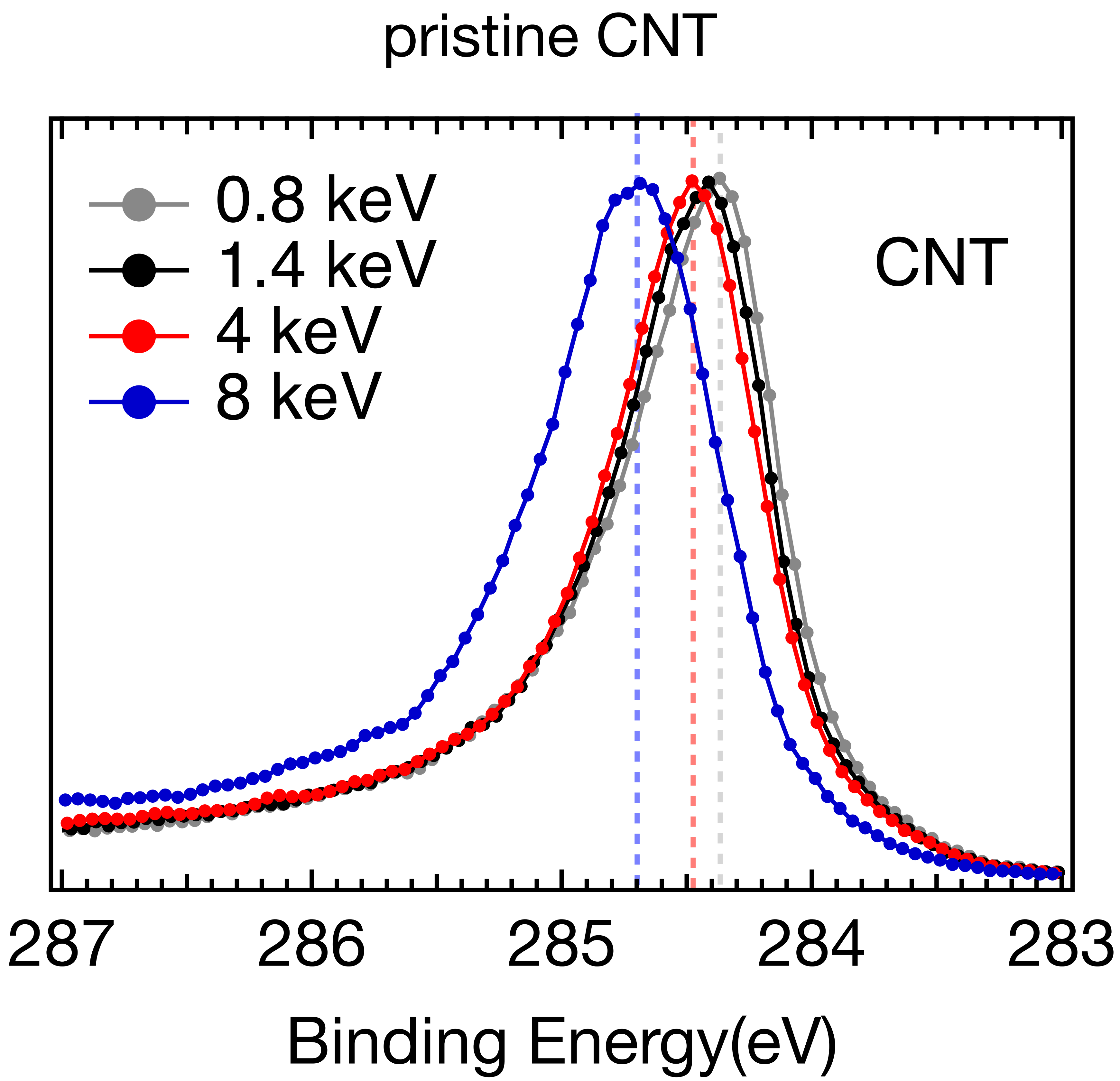


FIG. 1. (Color online) (a) Photon energy dependence of C 1s core-level spectra of graphite. The soft x ray ($h\nu$=340 and 870 eV) and hard x ray ($h\nu$=5950 and 7940 eV) are measured at the emission angles of 90° and 85° relative to the sample surface. (b) Theoretically obtained spectra taking into 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 hv = 800 eV

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

Free Atom Recoil

$$E_r = \frac{m_e}{M} E_k \qquad \frac{m_e}{M_C} \sim 4.6 \times 10^{-5}$$

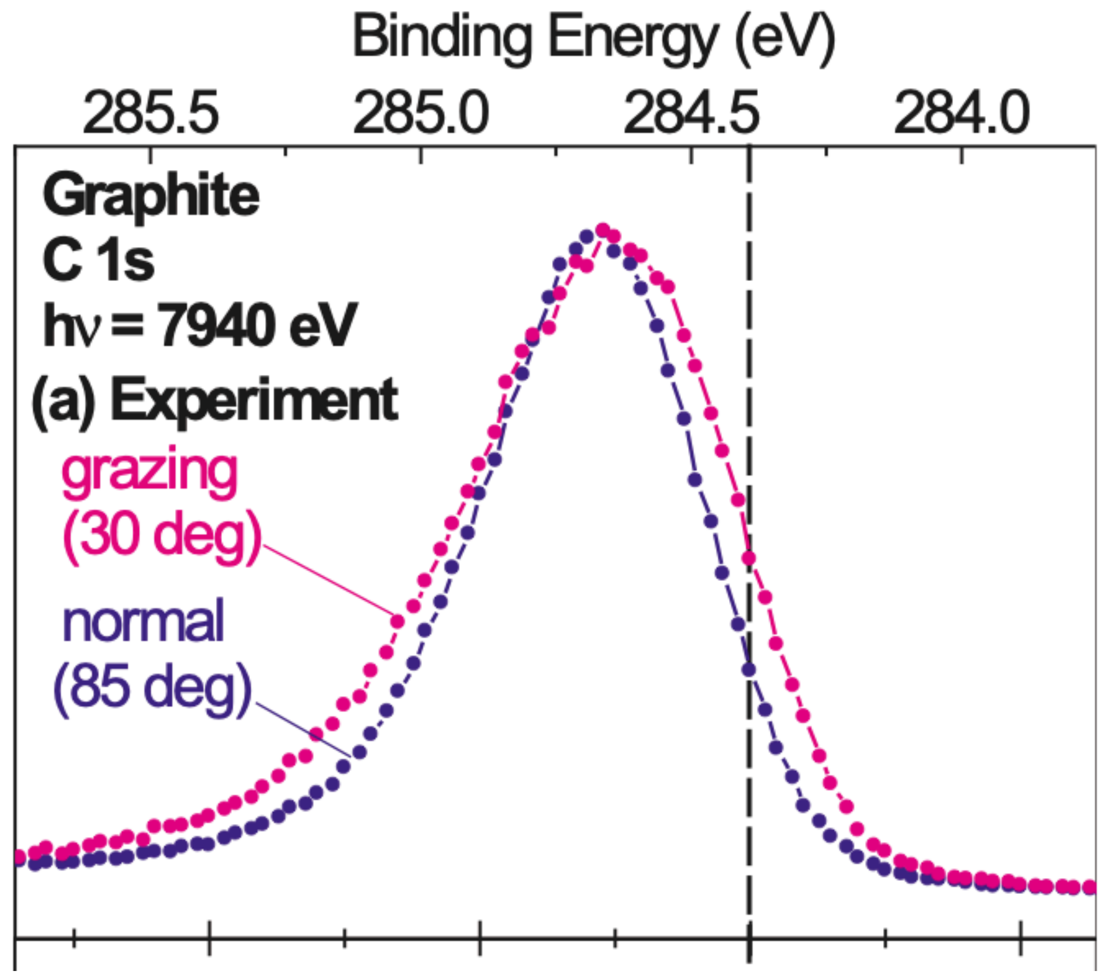
hv 800 eV	$E_r \sim 0.02$ eV
hv 4 KeV	$E_r \sim 0.17$ eV
hv 8 KeV	$E_r \sim 0.37$ eV

Bending vs Stretching Modes Angular Dependence

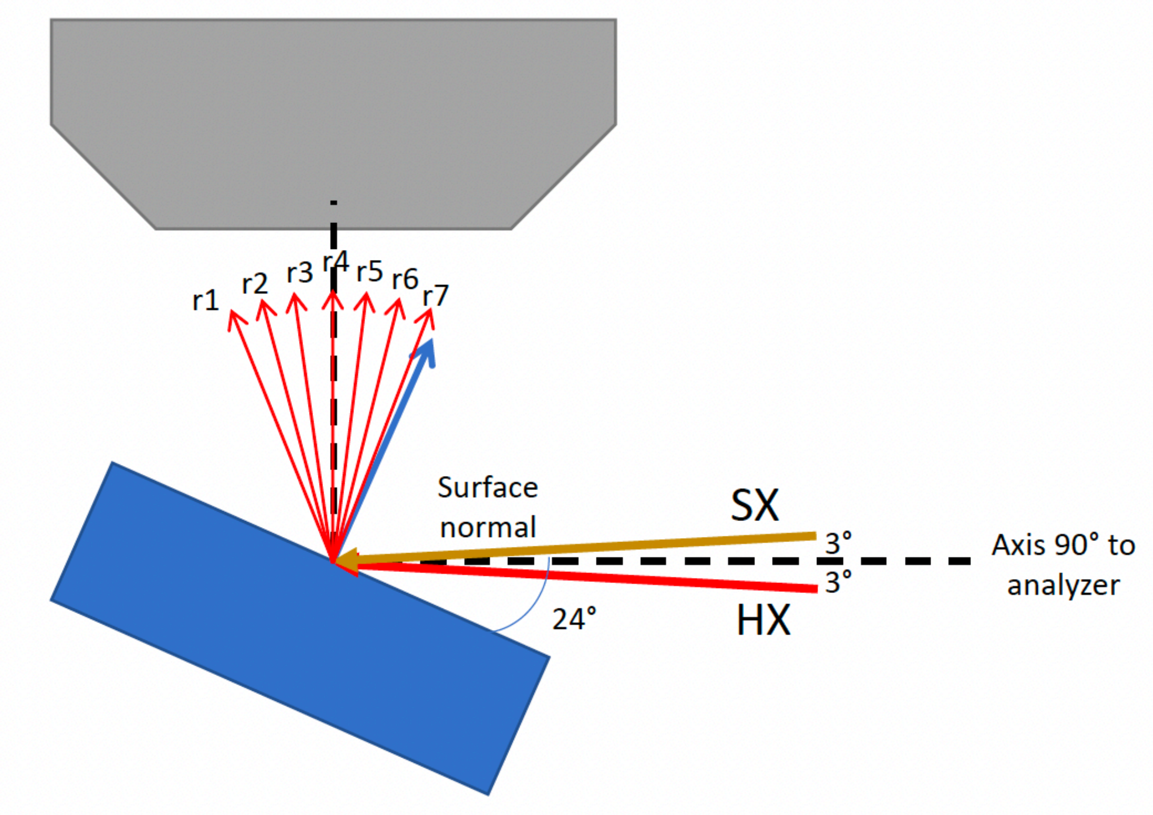
Graphite

Grazing emission: in plane stretching mode, broader peak

Normal emission: out-of-plane bending mode

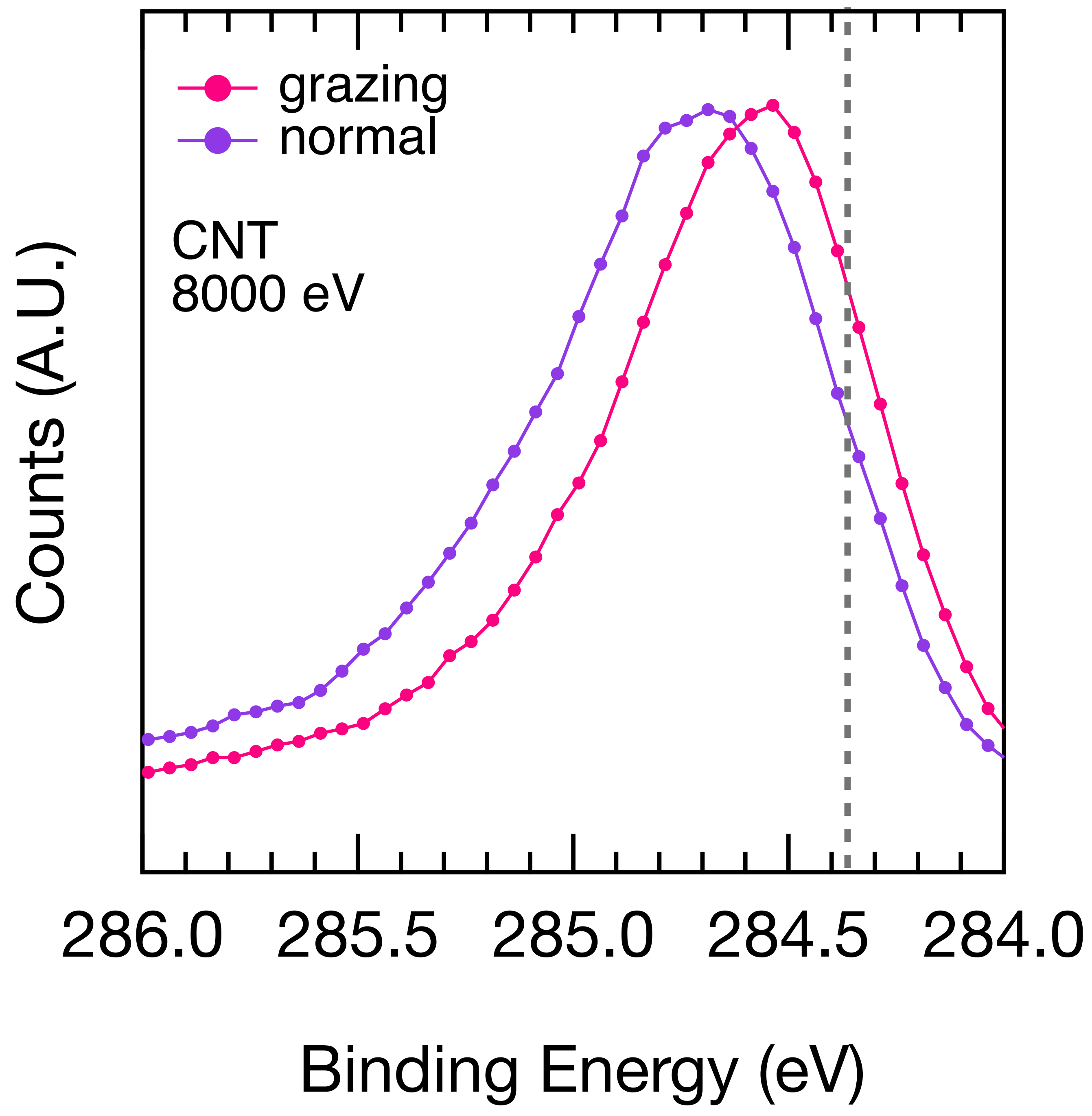


Takata *et al.*, Phys. Rev. B 75, 233404 (2007)

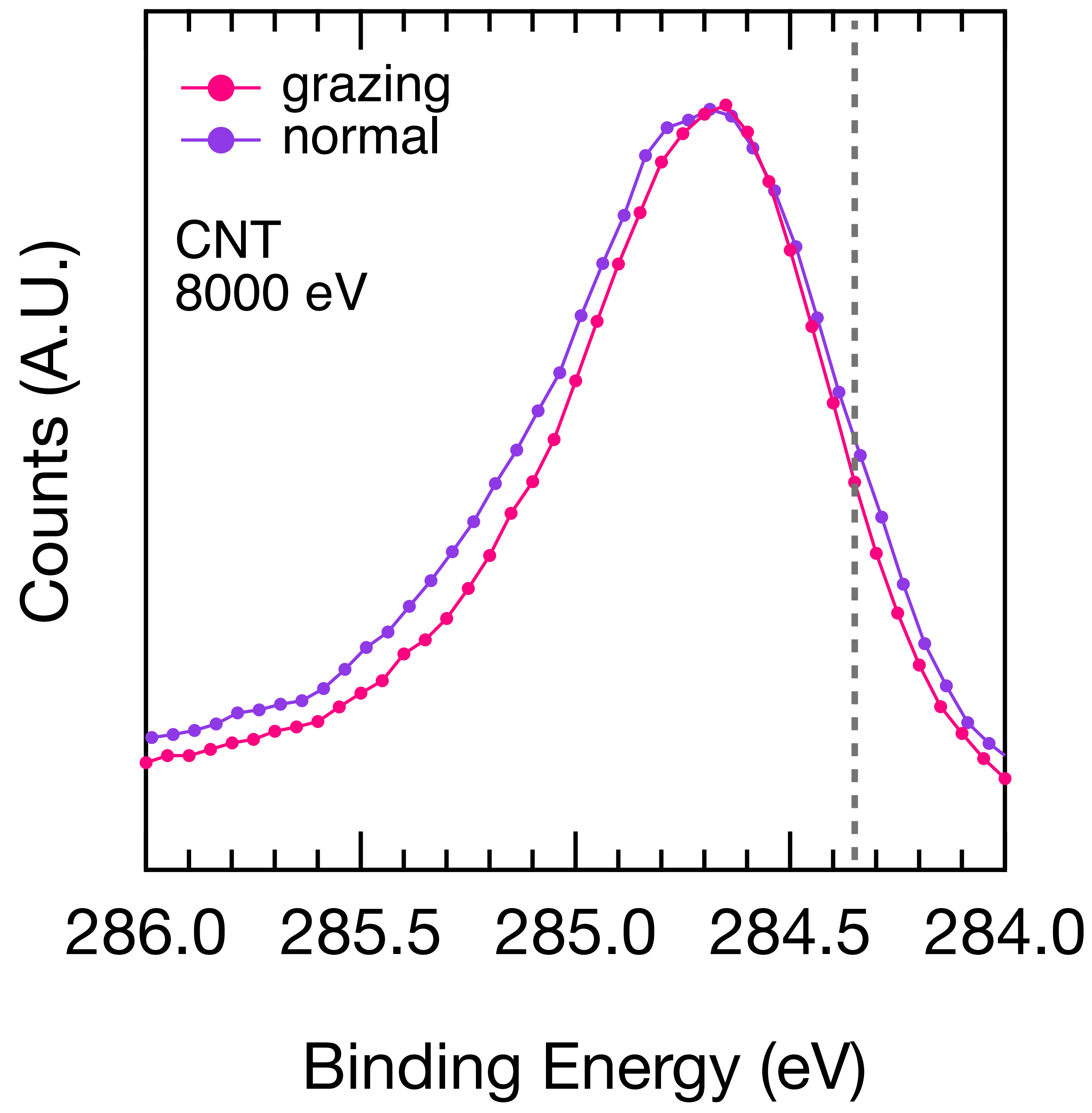


VA-CNT

- **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?

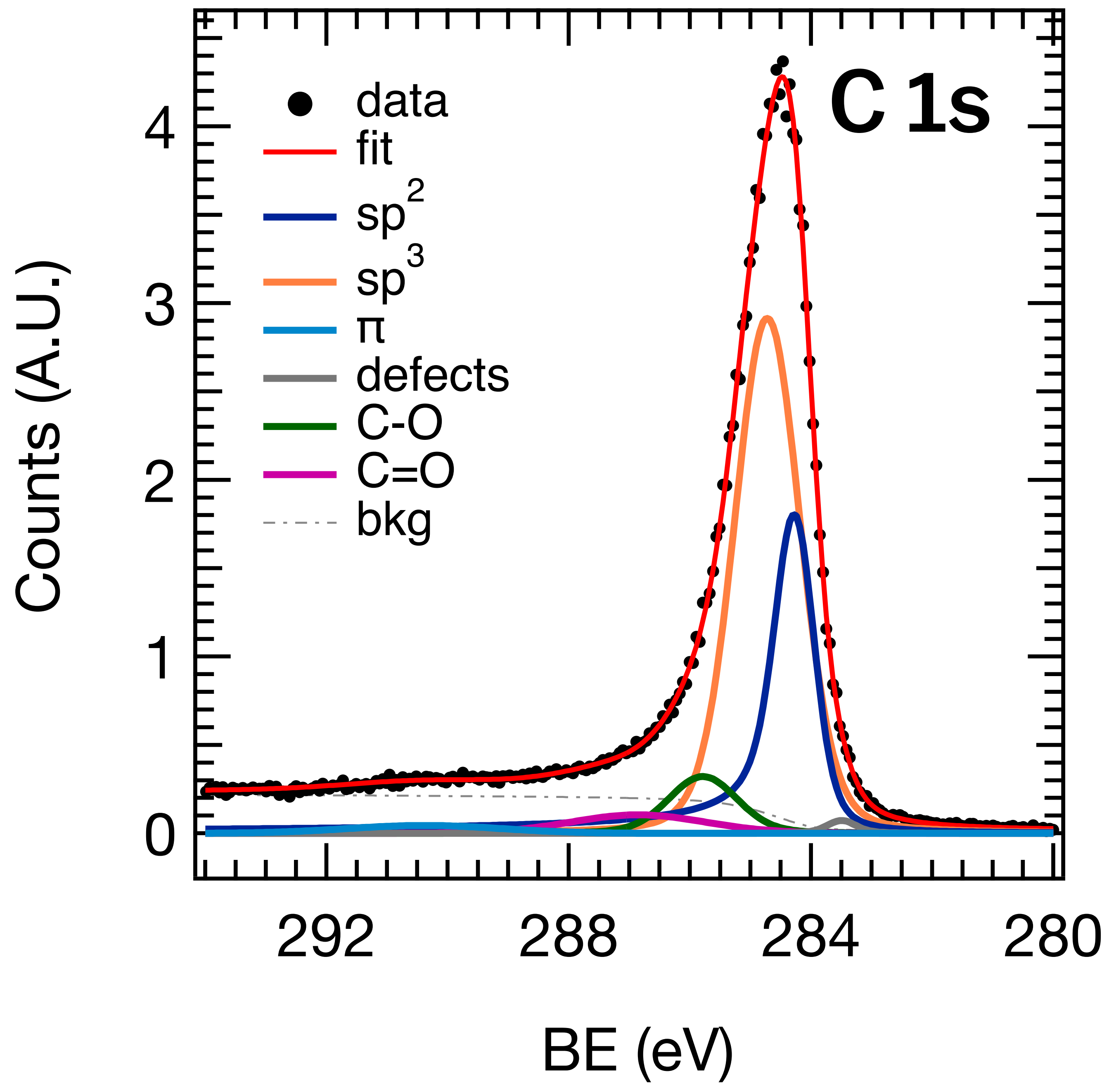
Update on Tritiation feasibility

We have started measurements of the residual gas composition during hydrogenation (deuteration)

- Check for (heavy) water and light hydrocarbons as secondary products

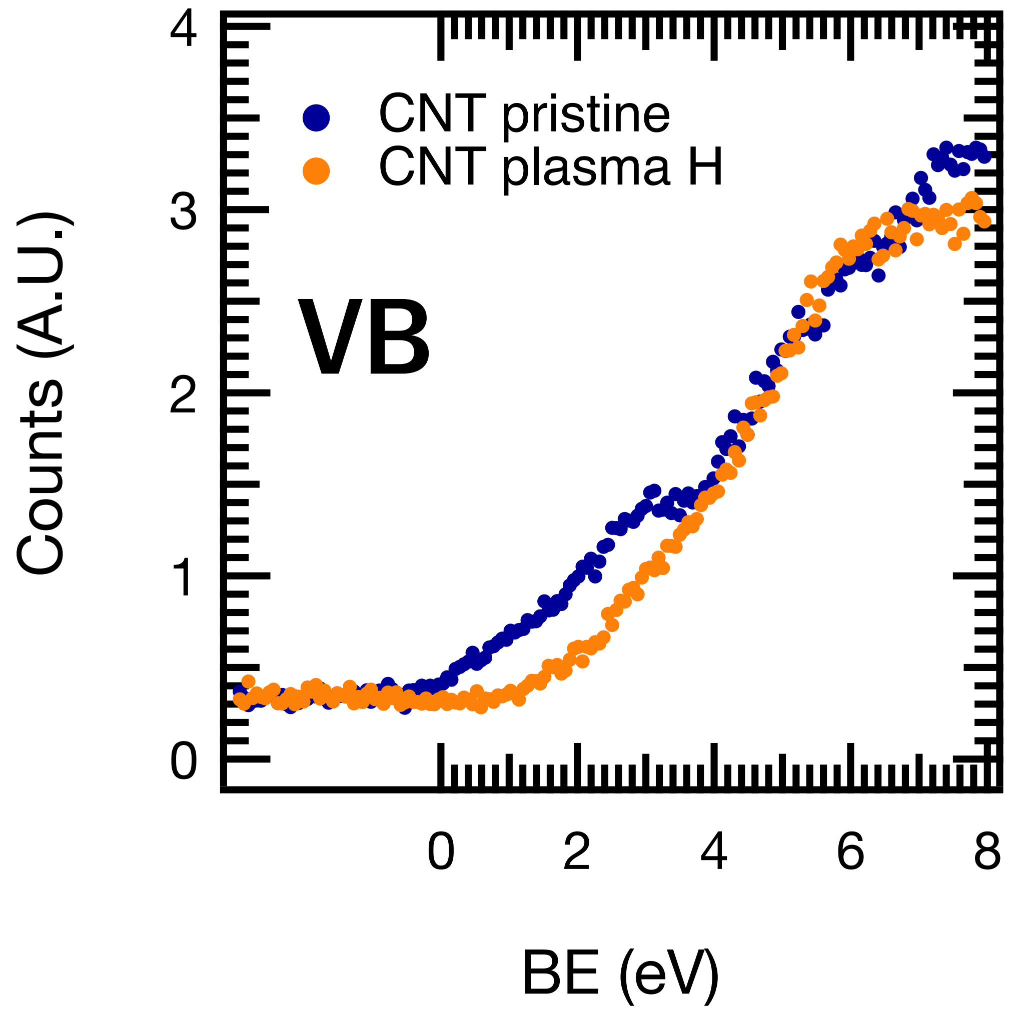
Stay tuned!

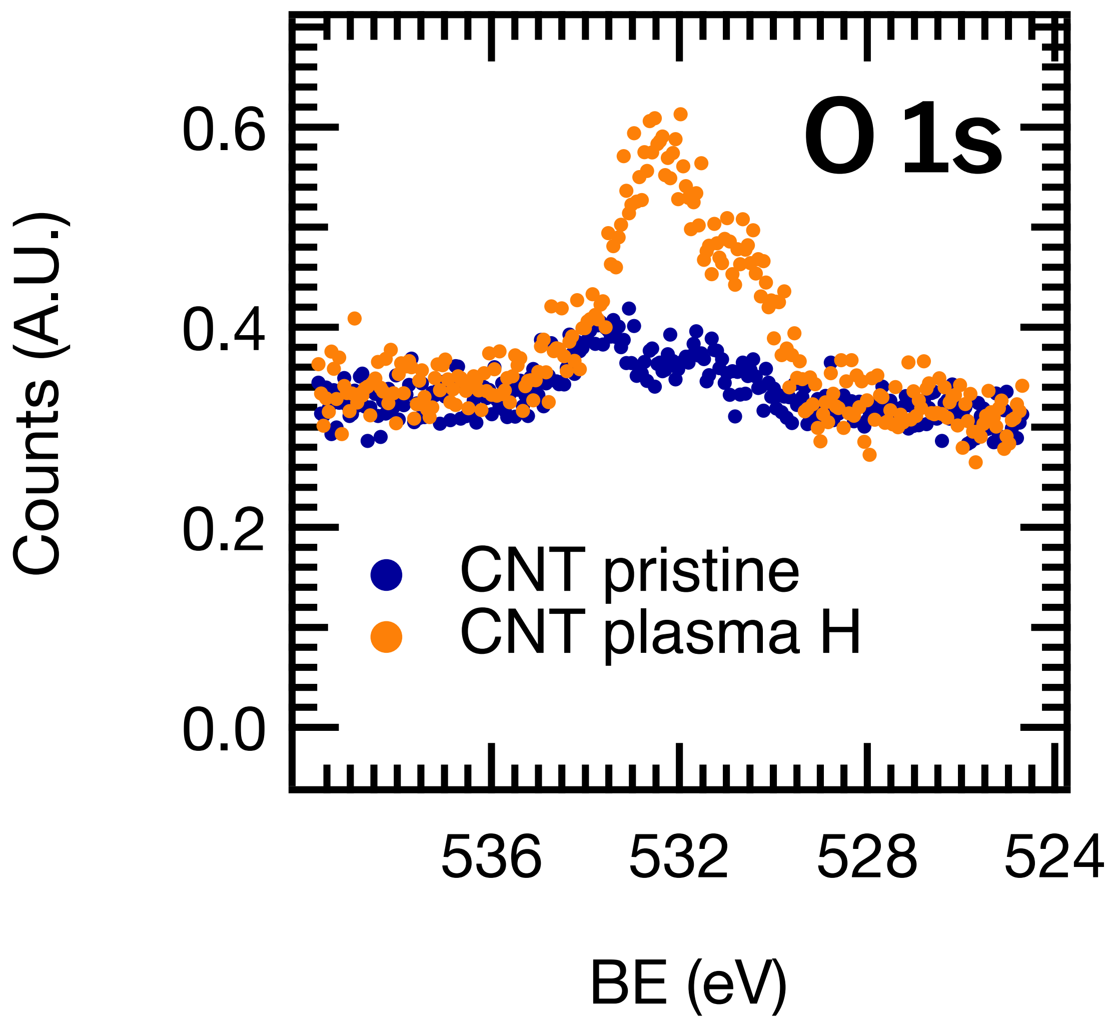
Hydrogen Plasma *vs* Thermal Cracking Hydrogenation



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

WF = 3.81 ± 0.05 eV



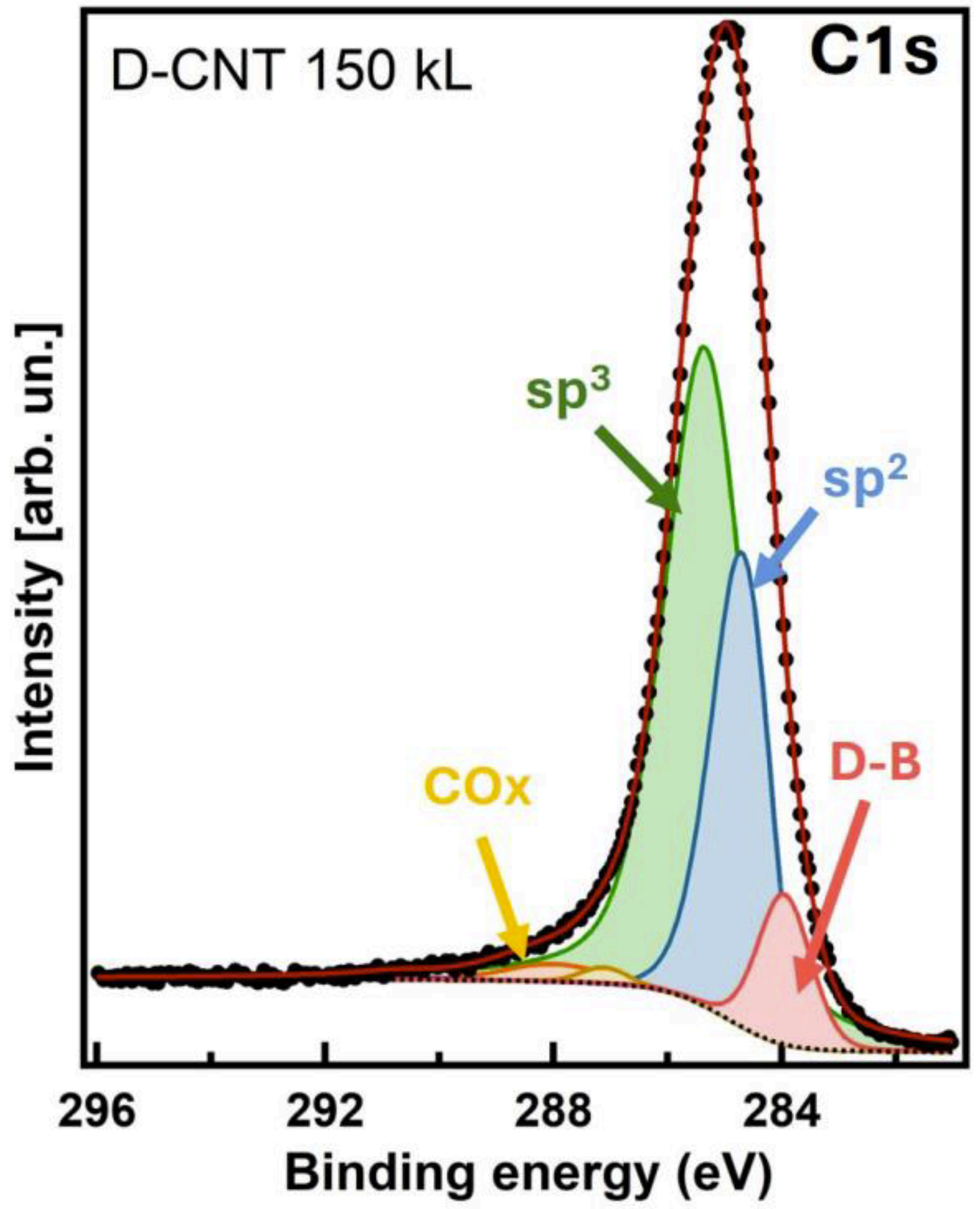


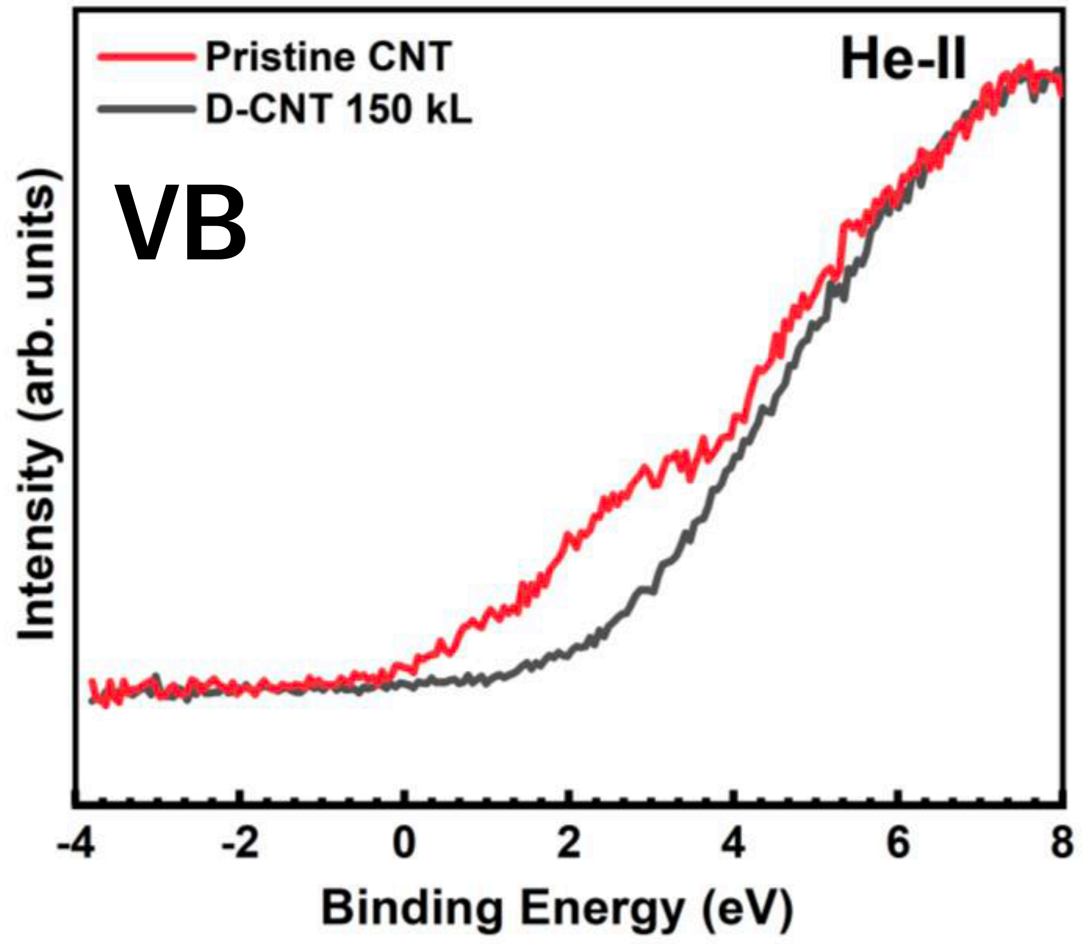
Atomic Deuterium bonding to Multi-Walled Carbon Nano Tubes

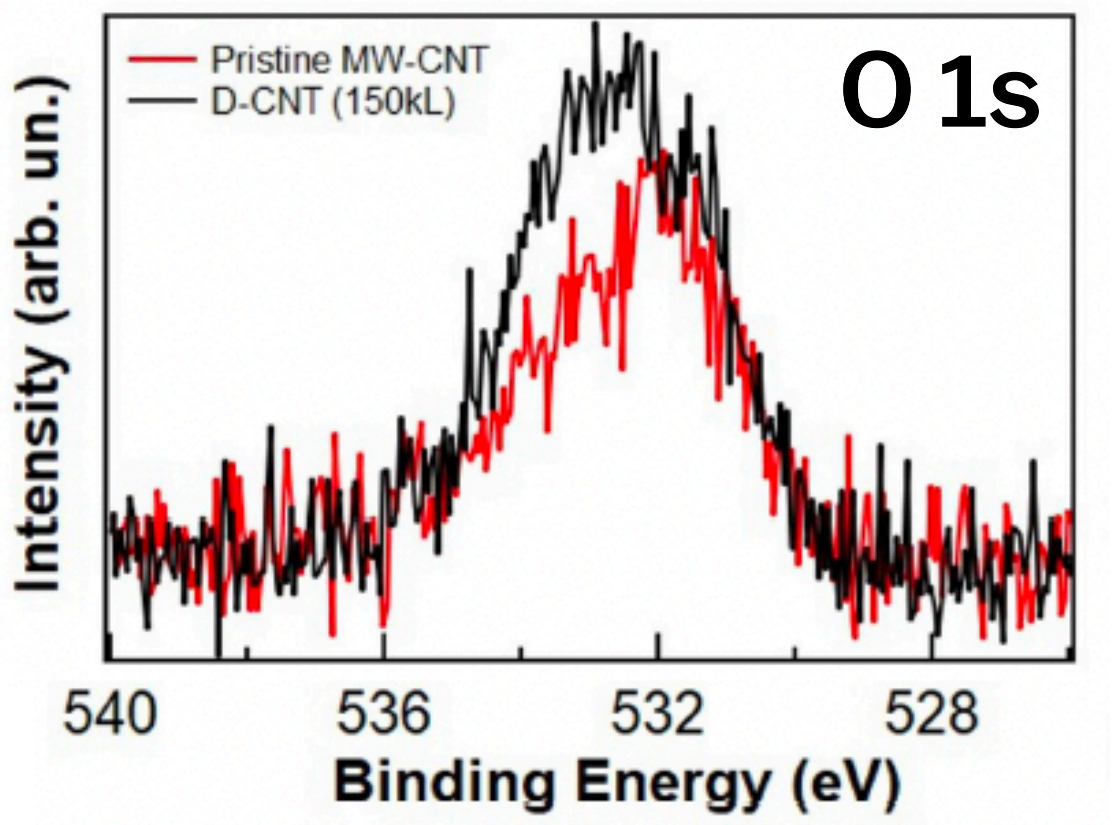
Sammar Tayyab et al., to be published

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

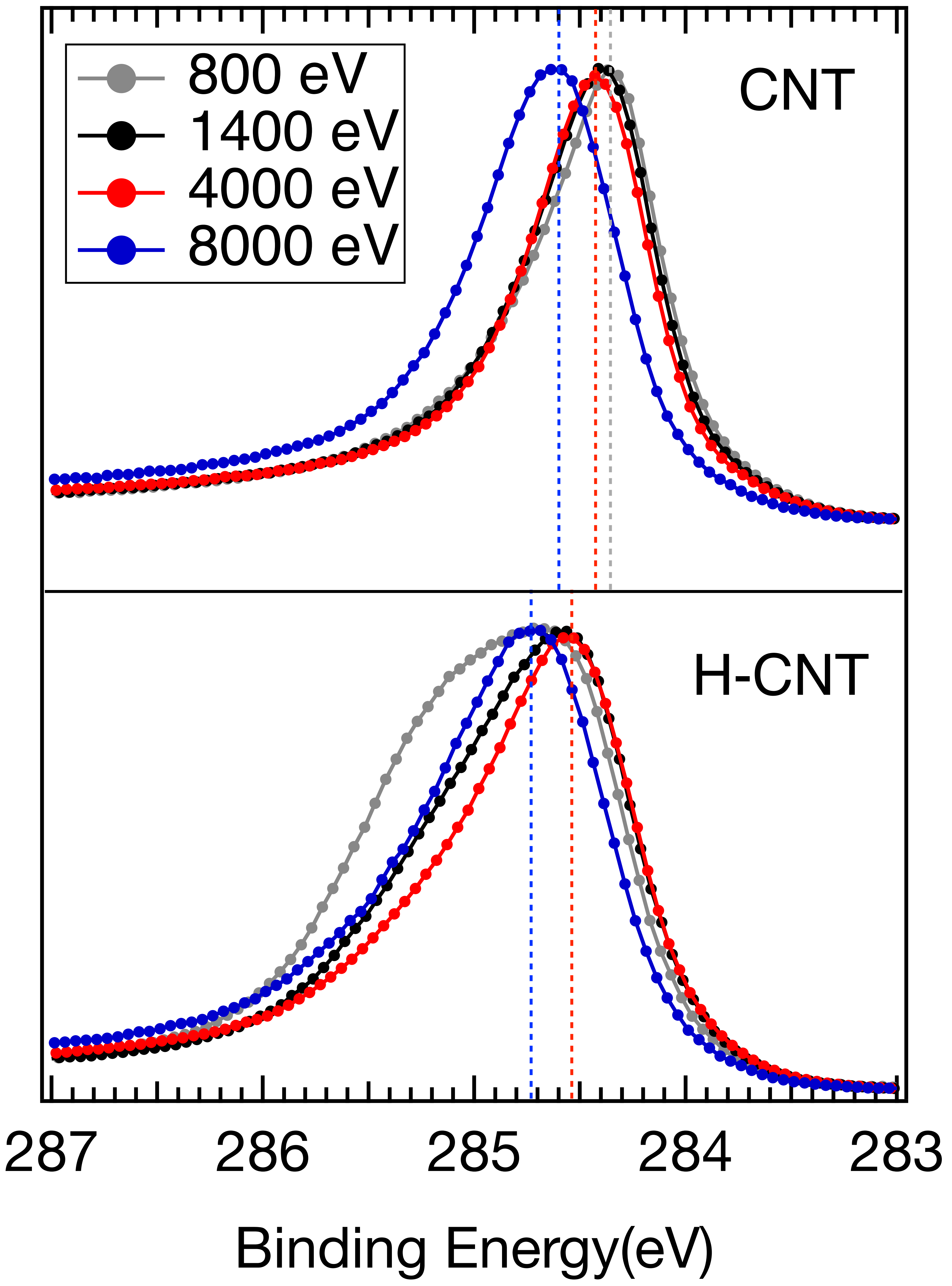
WF = 3.84 ± 0.05 eV







Hit Me (Photon) One More Time



- 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 inhomogeniusness 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

1 ug Tritium

Characteristic penetration depth: 8.5 layers

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

assumptions

- Layer separation as in graphite = 0.35 nm
- Electron mean free path equals to IMFP as in graphite

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

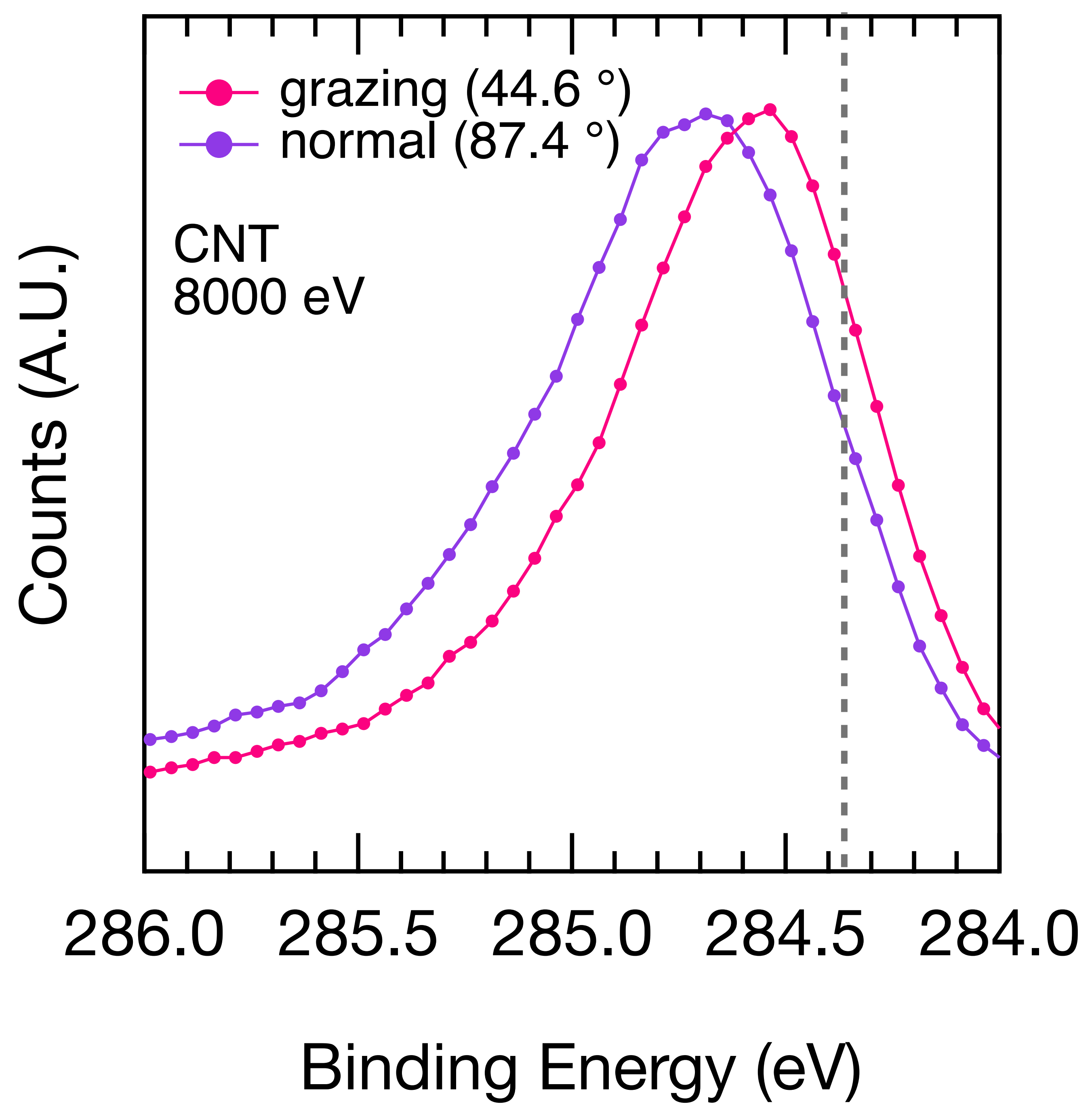
- Exponential decaying hydrogen distribution in depth

$$1\,\text{ug}\, m_{H^3} = 0.33\,\text{ug}\, m_H = \approx 10$$

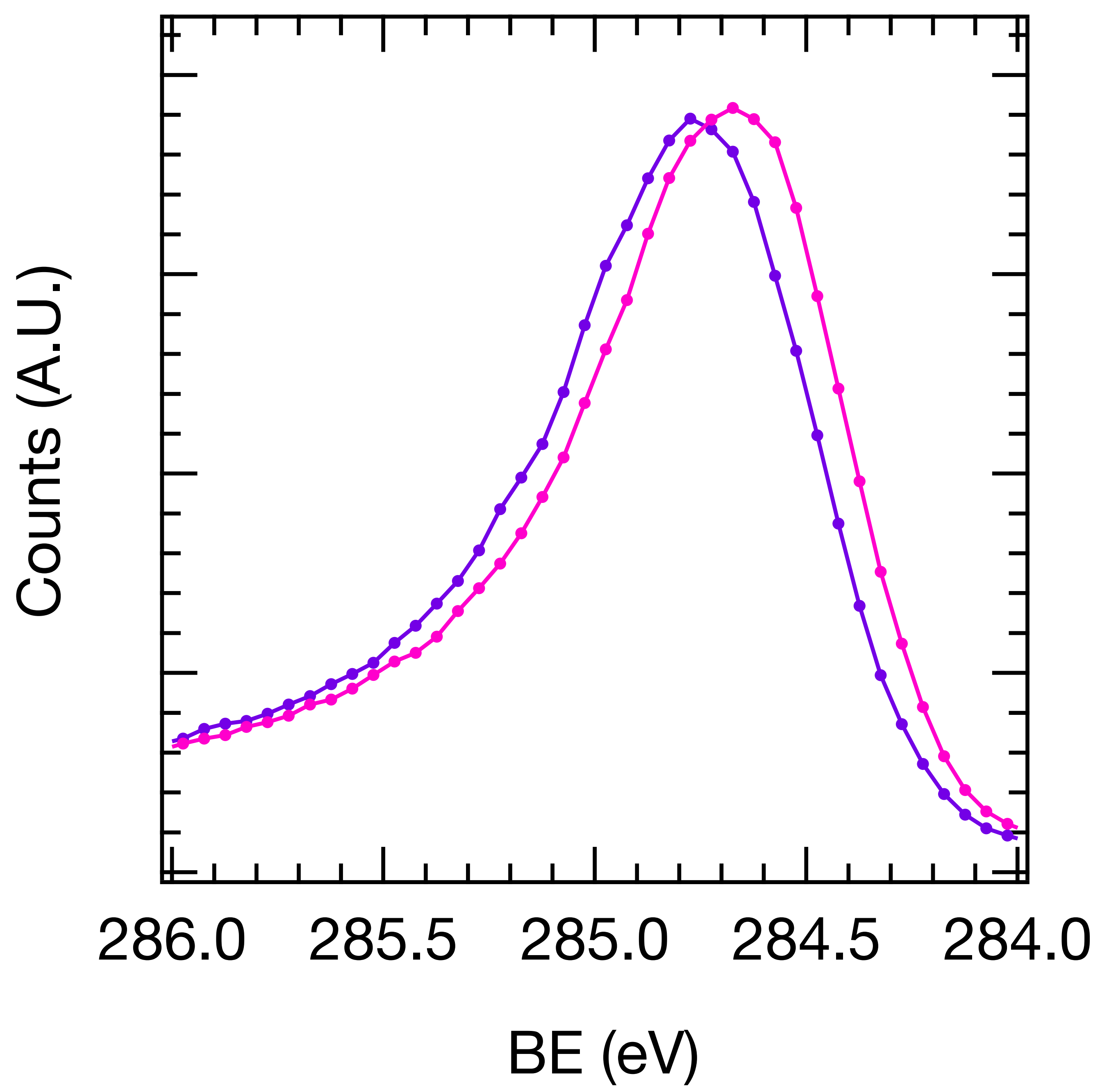
*

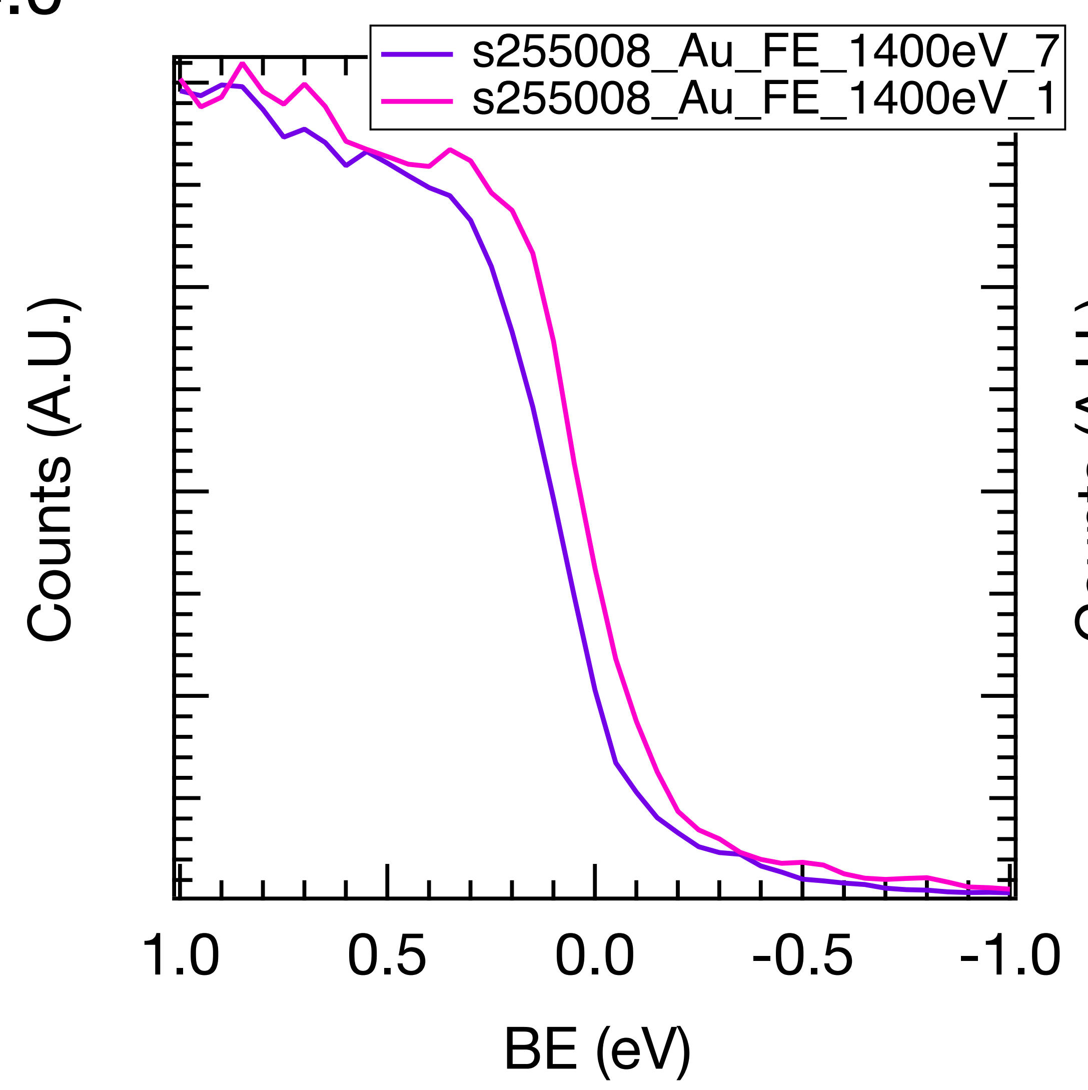
* 5 cm² total

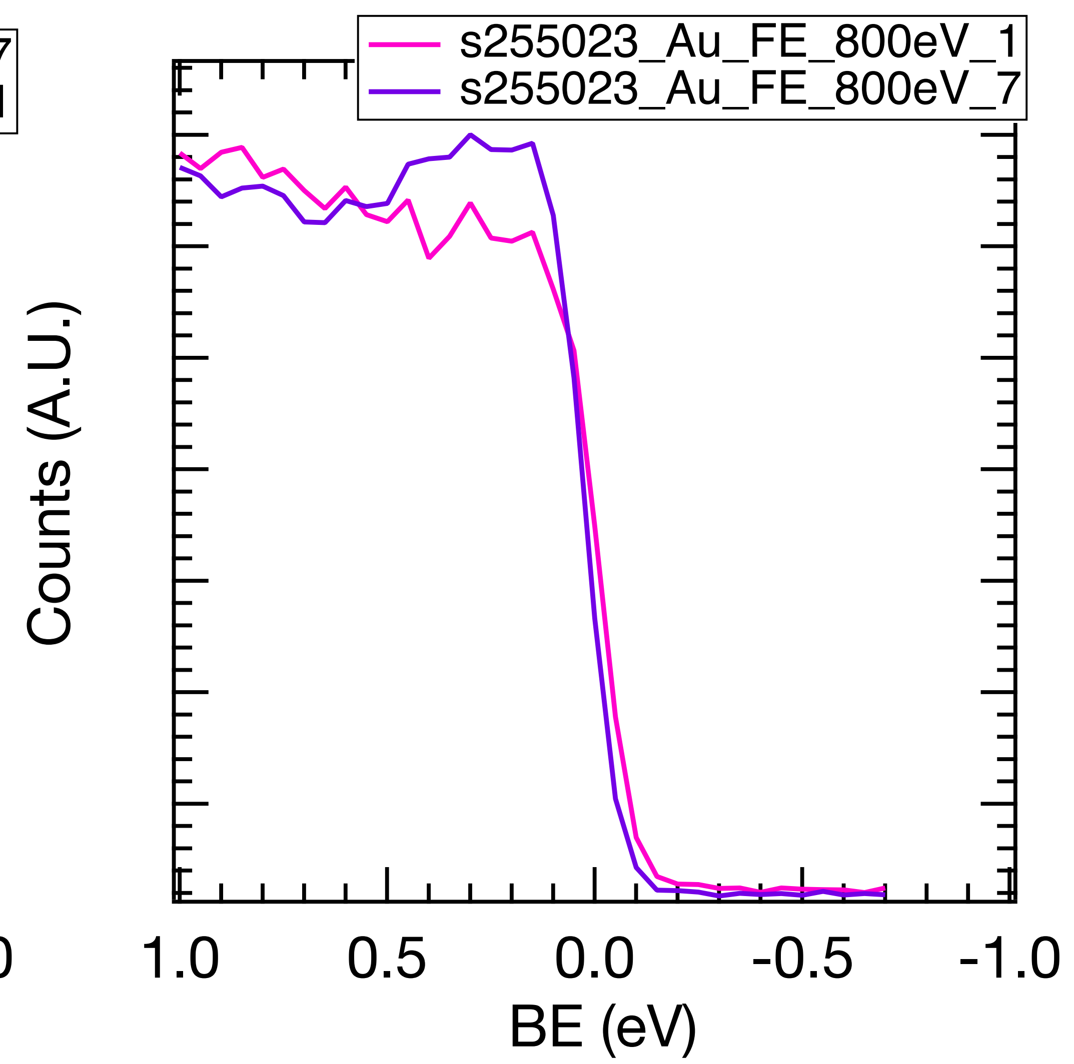
VA-CNT


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 $E_{\mathrm{kln}} \equiv E_{\mathrm{k}}$:

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

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

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

where

$\Lambda_e(E_k)$ = an attenuation length in the substrate
$\Lambda_e'(E_k)$ = 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

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

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

hv = 1400 eV

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

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

(3.13+2.85)/2=2.99

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

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

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

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

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

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 (uniform model)

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

* 30 cm^2 in total

1 ug Hydrogen (exponential model)

$m_H = 1\,\text{ug} \approx 30$  *

* 15 cm² total

1 ug Tritium (exponential model)

Layer separation as in graphite = 0.35 nm

Electron IMFP as in graphite

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

Characteristic penetration depth: 8.5 layers

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

$$1\,\text{ug}\,m_{H^3} = 0.33\,\text{ug}\,m_H = \approx 10$$  *

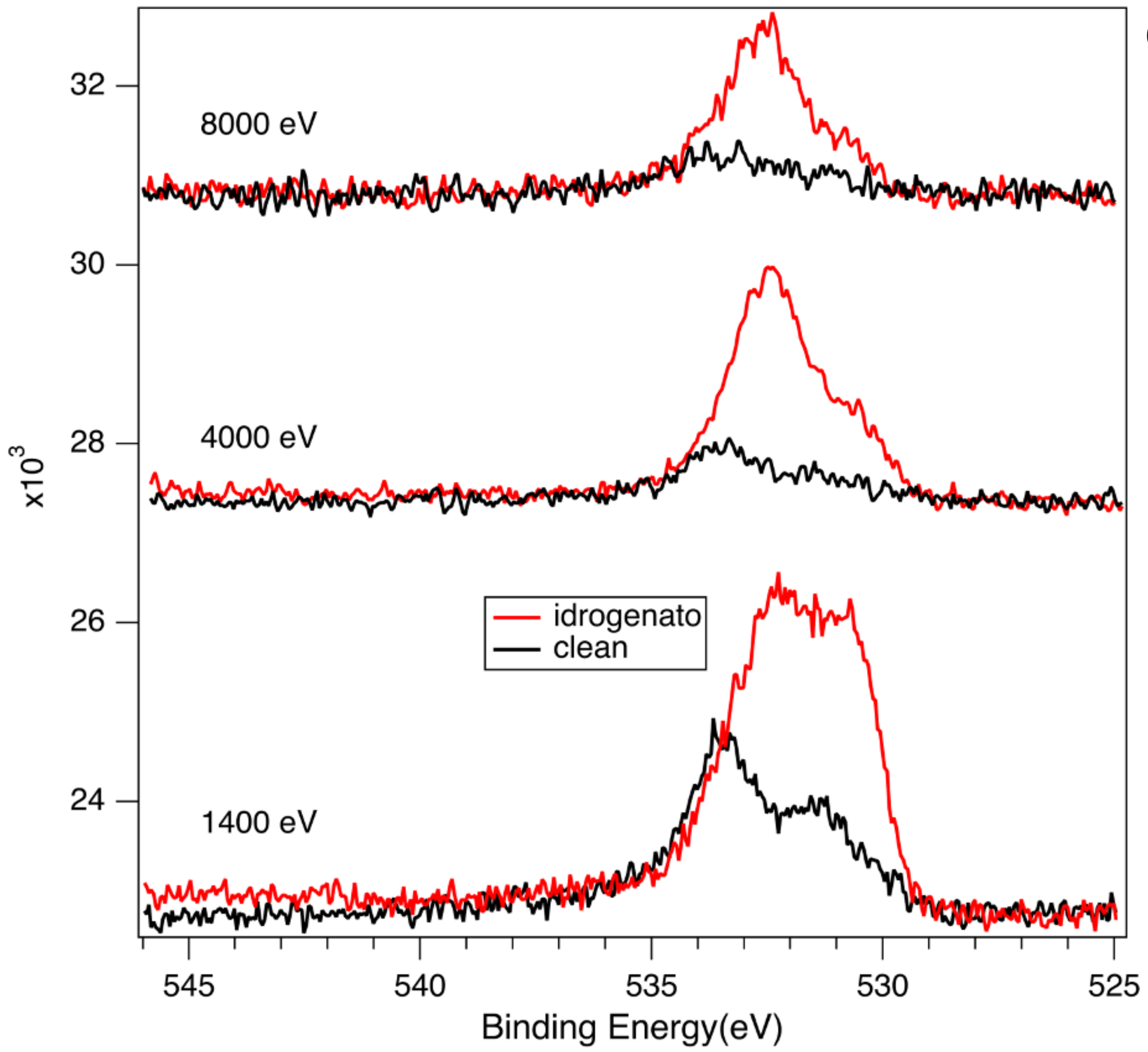
* 5 cm^2 total

O1s and Fe 2p content

Cross section values

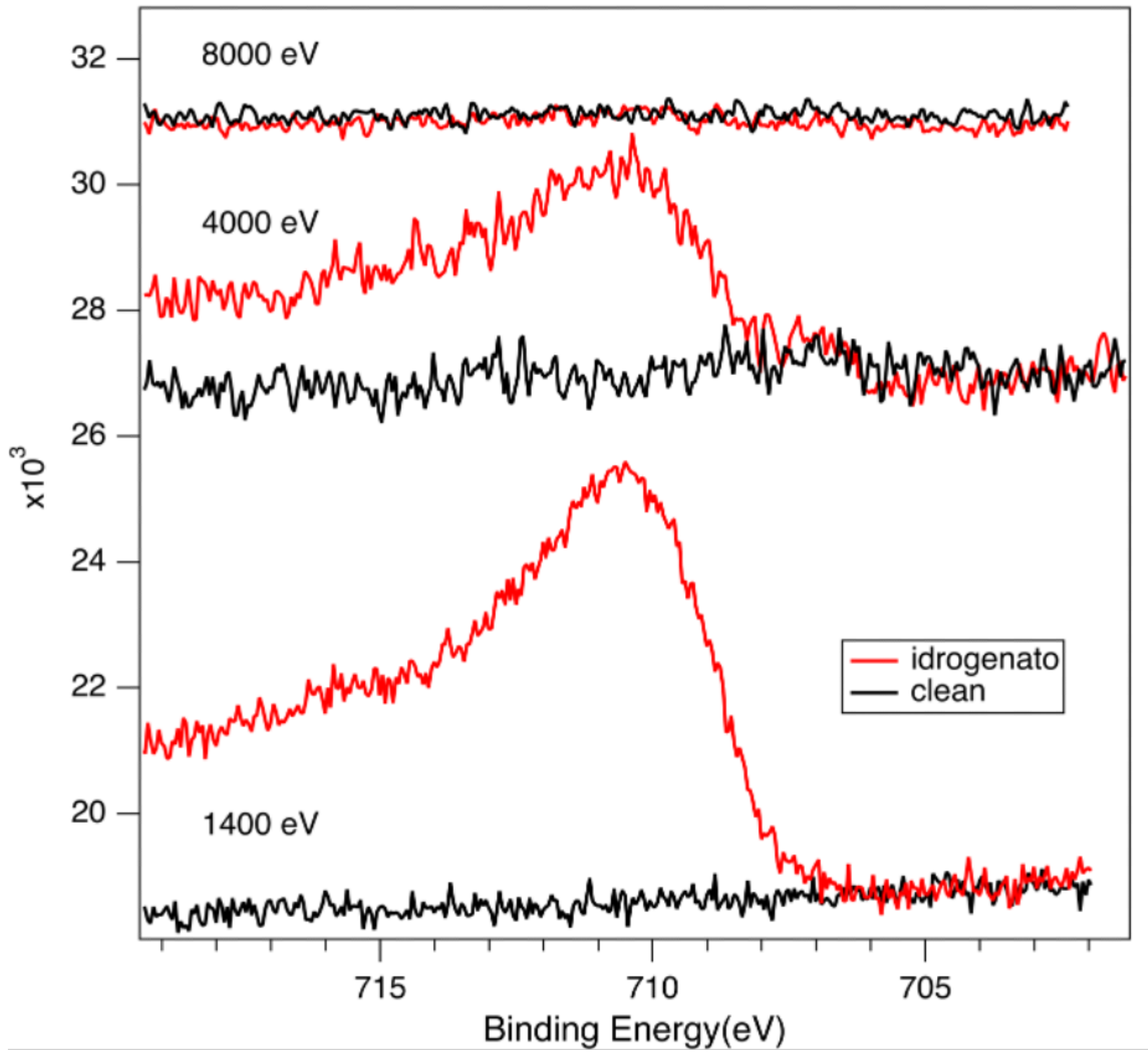
Yeh & Lindau (1985)

Scofield (1973)



O 1s

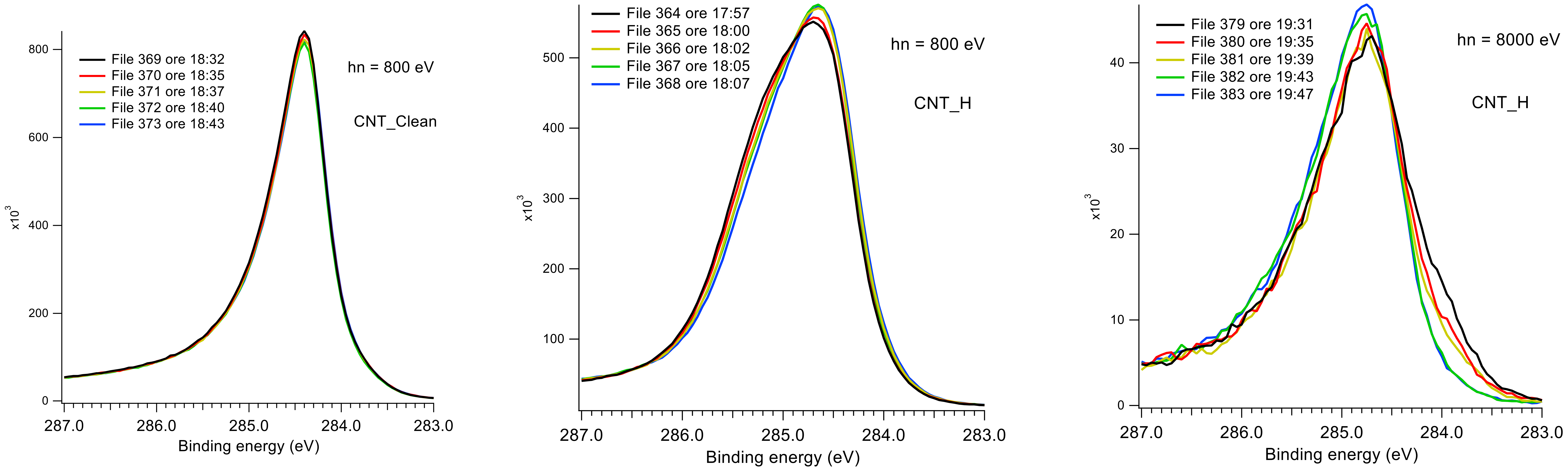
- **1400eV**: ≈0.15 Mb
- **4000eV**: ≈0.02 Mb
- **8000eV**: ≈0.005 Mb



Fe 2p

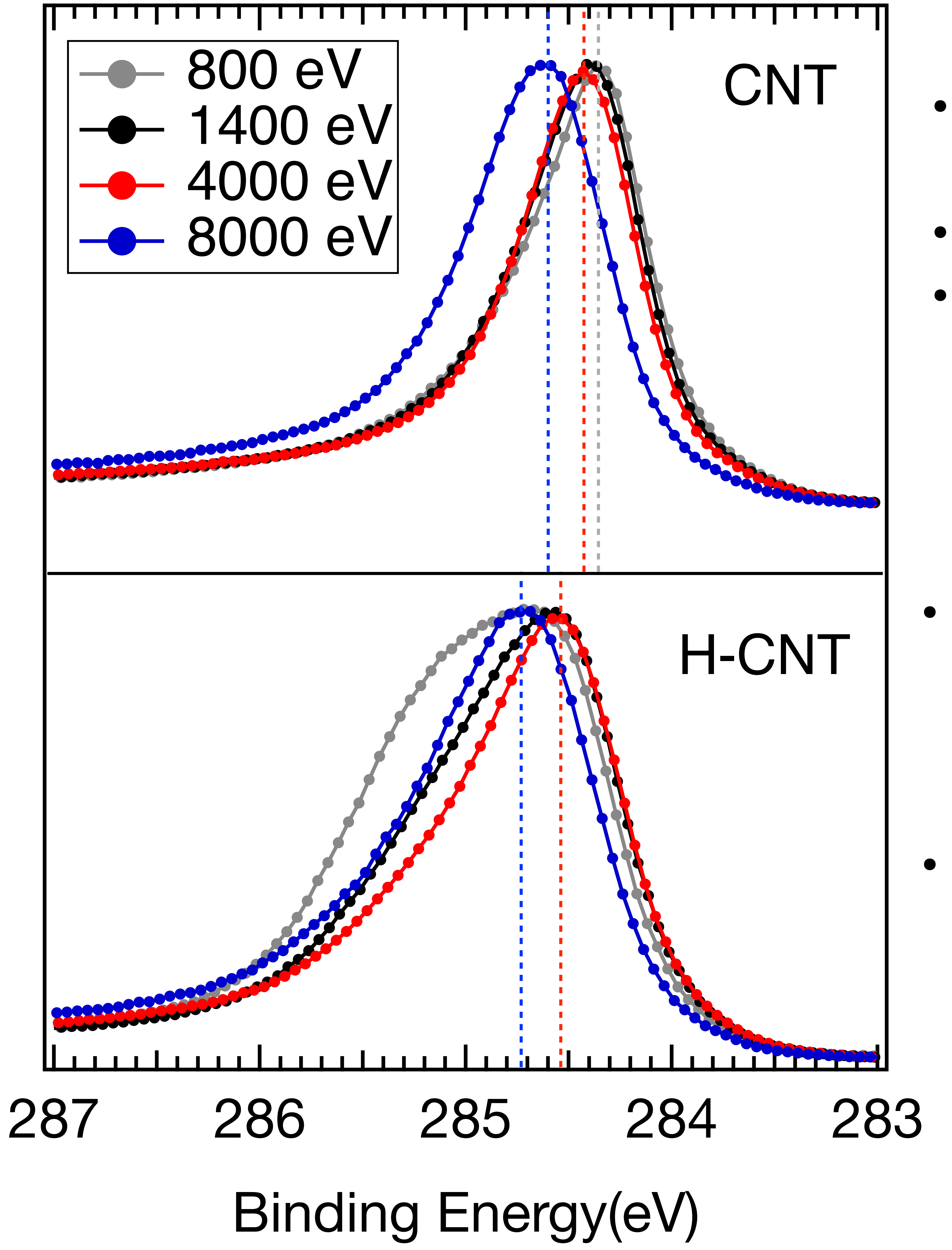
- **1400eV**: ≈0.5 Mb
- **4000eV**: ≈0.08 Mb
- **8000eV**: ≈0.02 Mb

Beam makes hydrogen desorbs

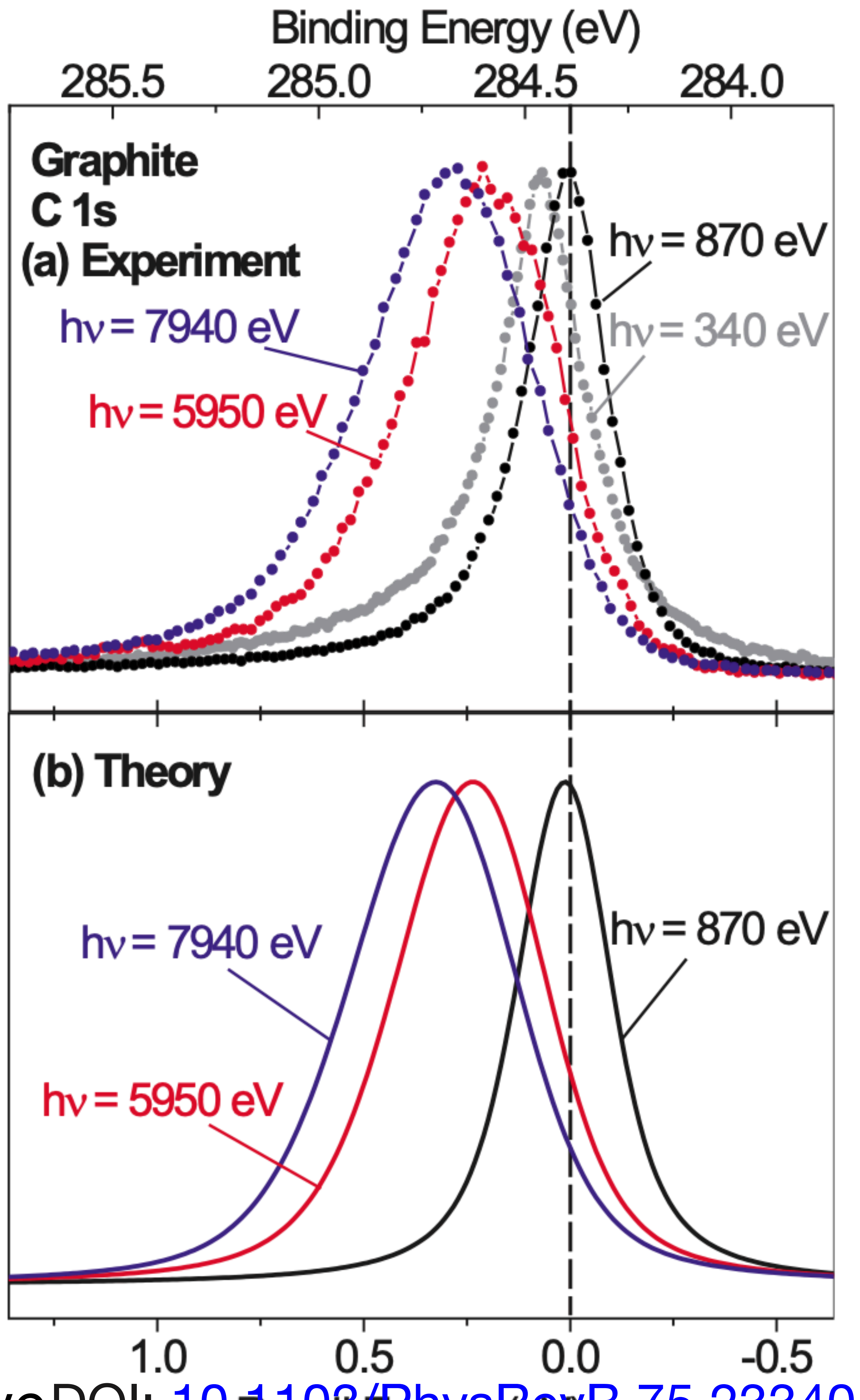


Recoil Effects in Photoemission: Hit Me (Photon) One More Time

- 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)

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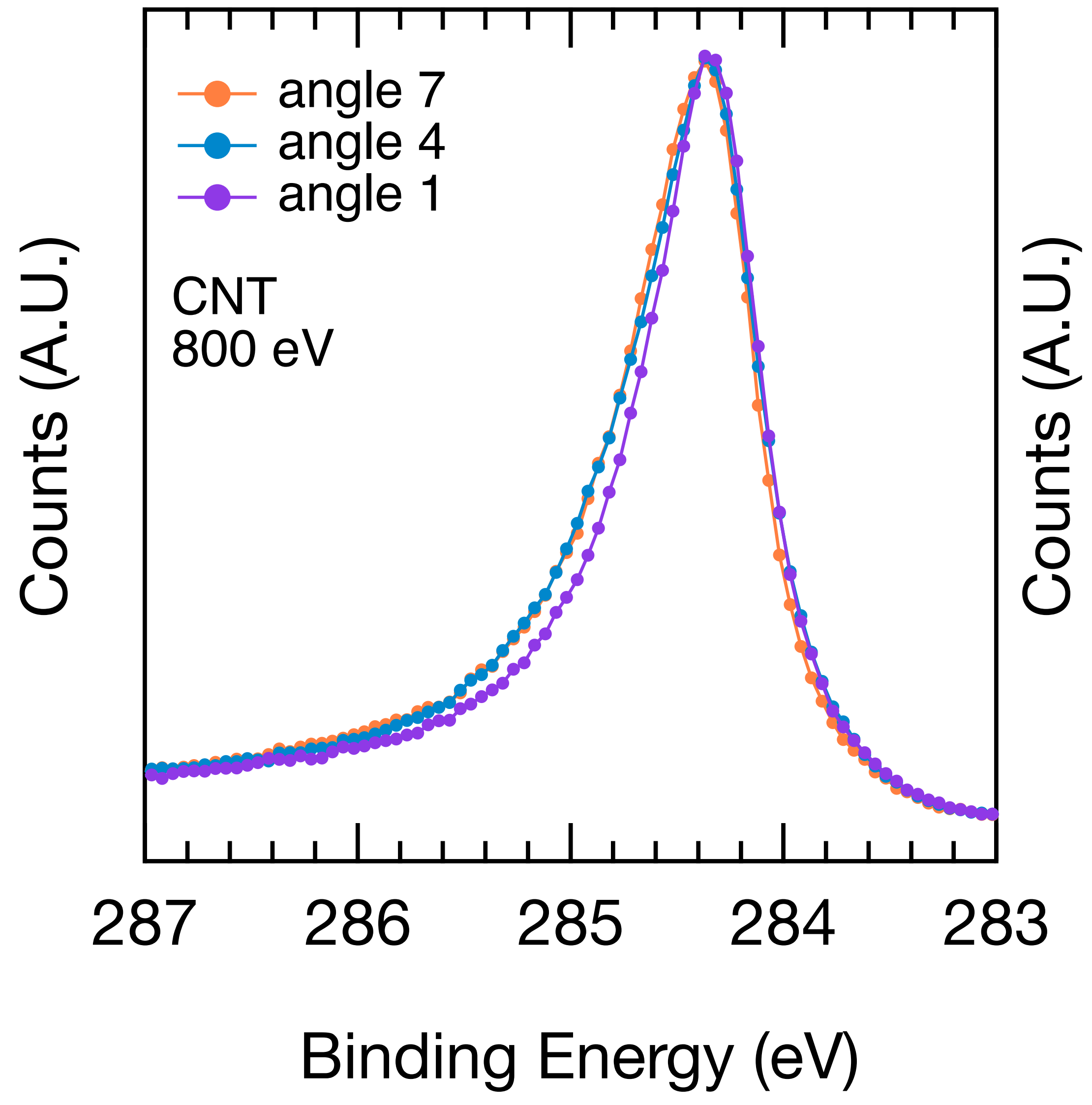
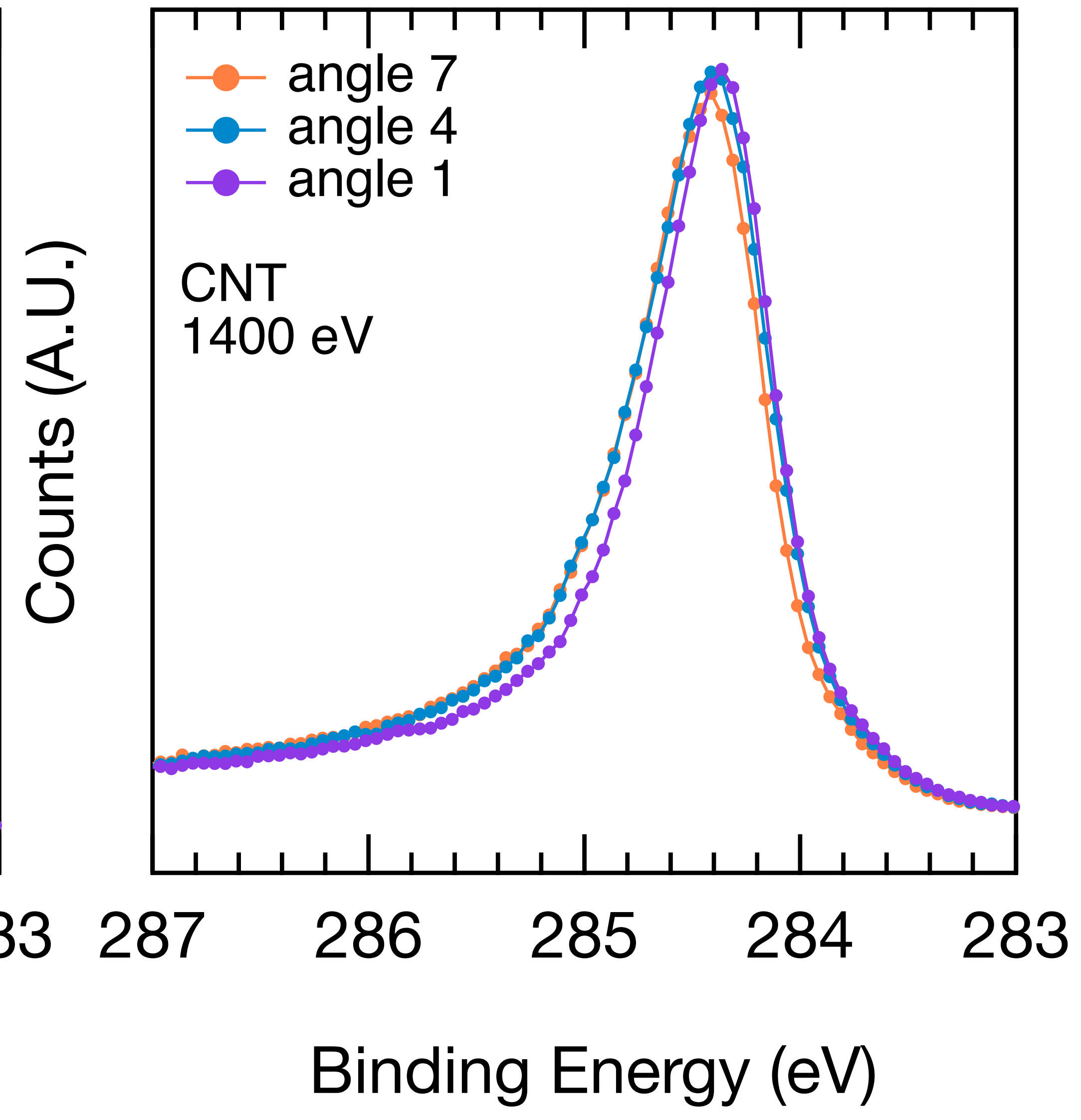
Bending vs Stretching modes with High Energy ARPES

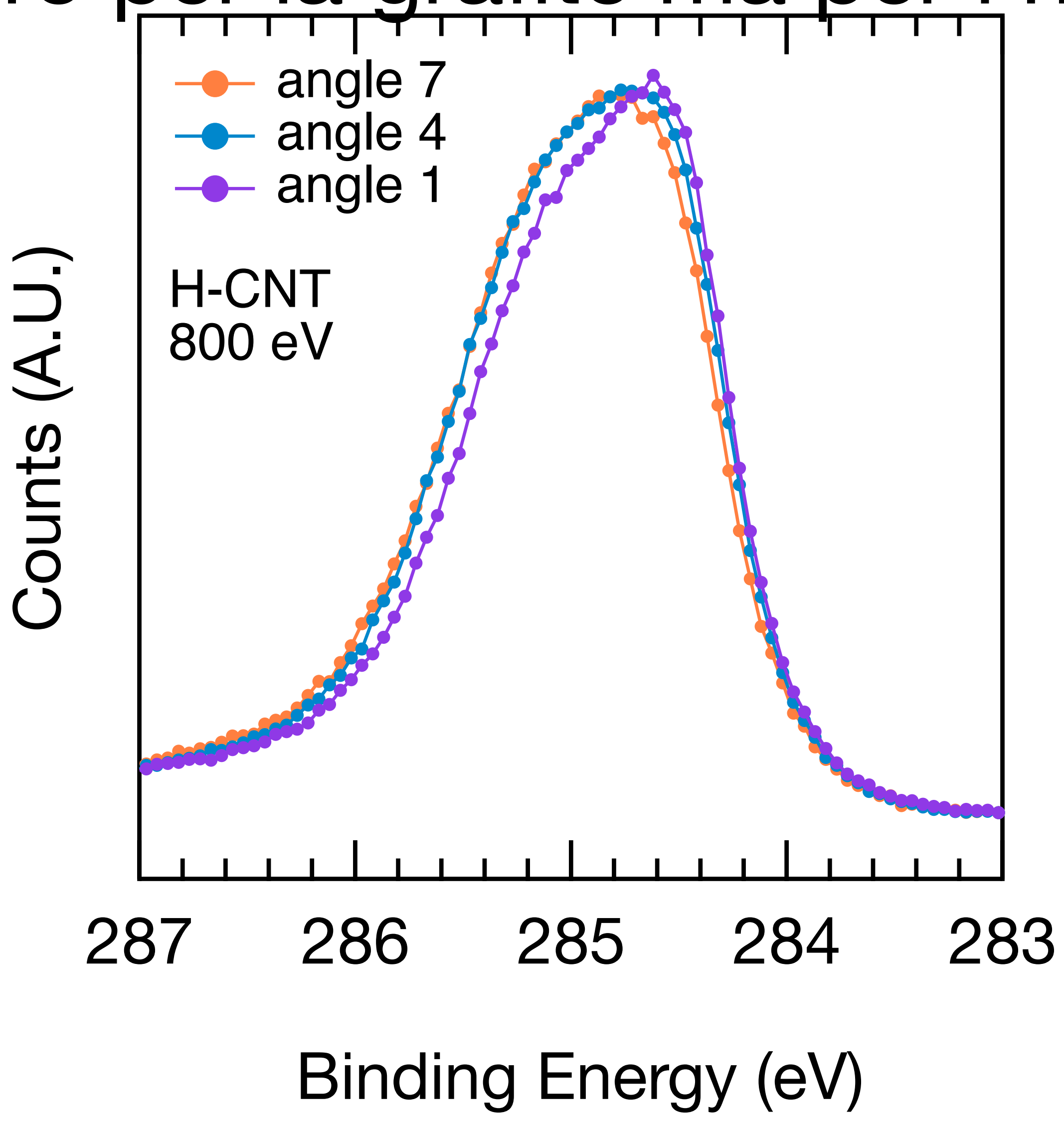
- Out of plane (normal emission): higher recoil energy

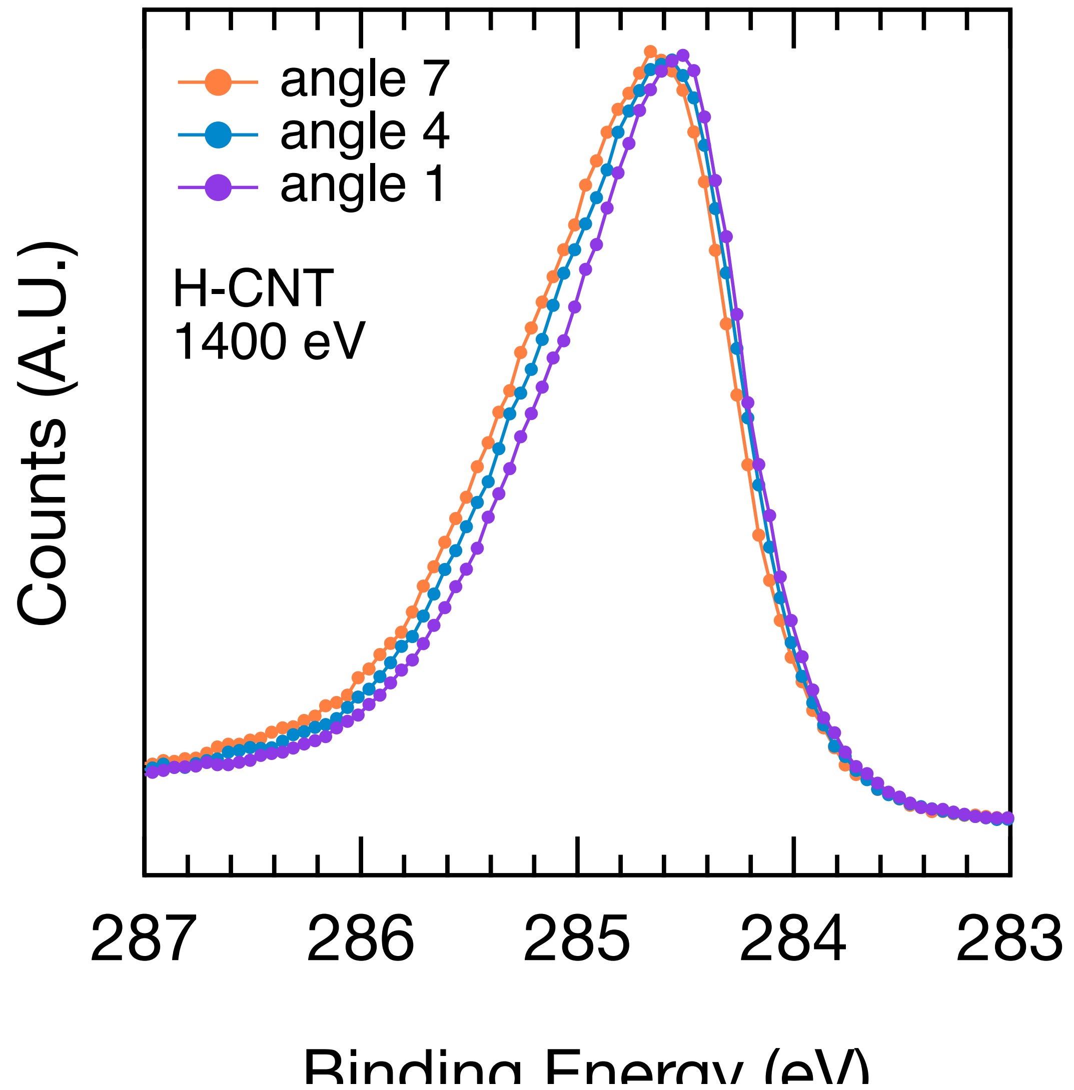
È vero per la grafite ma per i nanotubi non dovrebbe essere l'opp

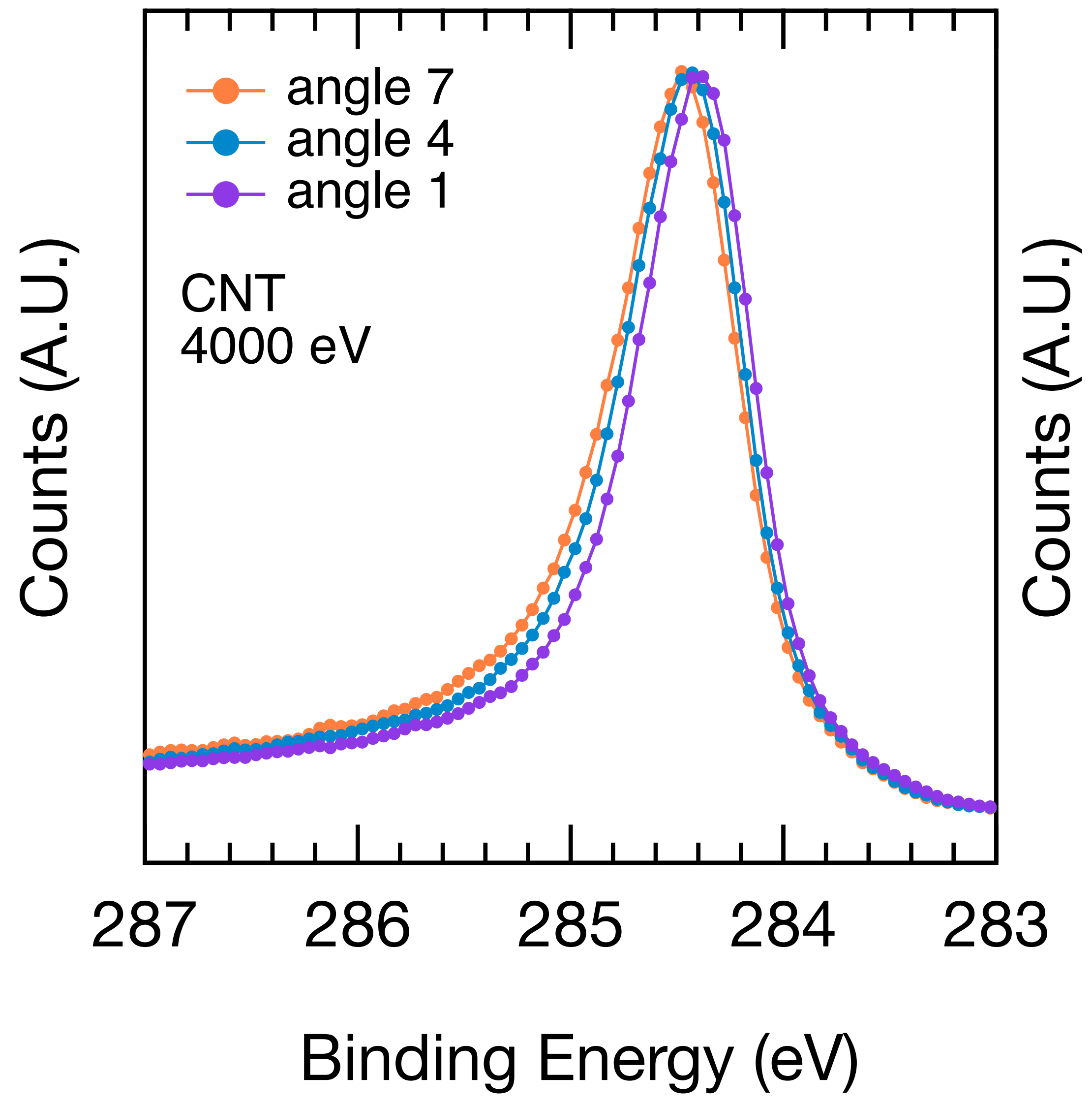
- Angle 7: normal emission

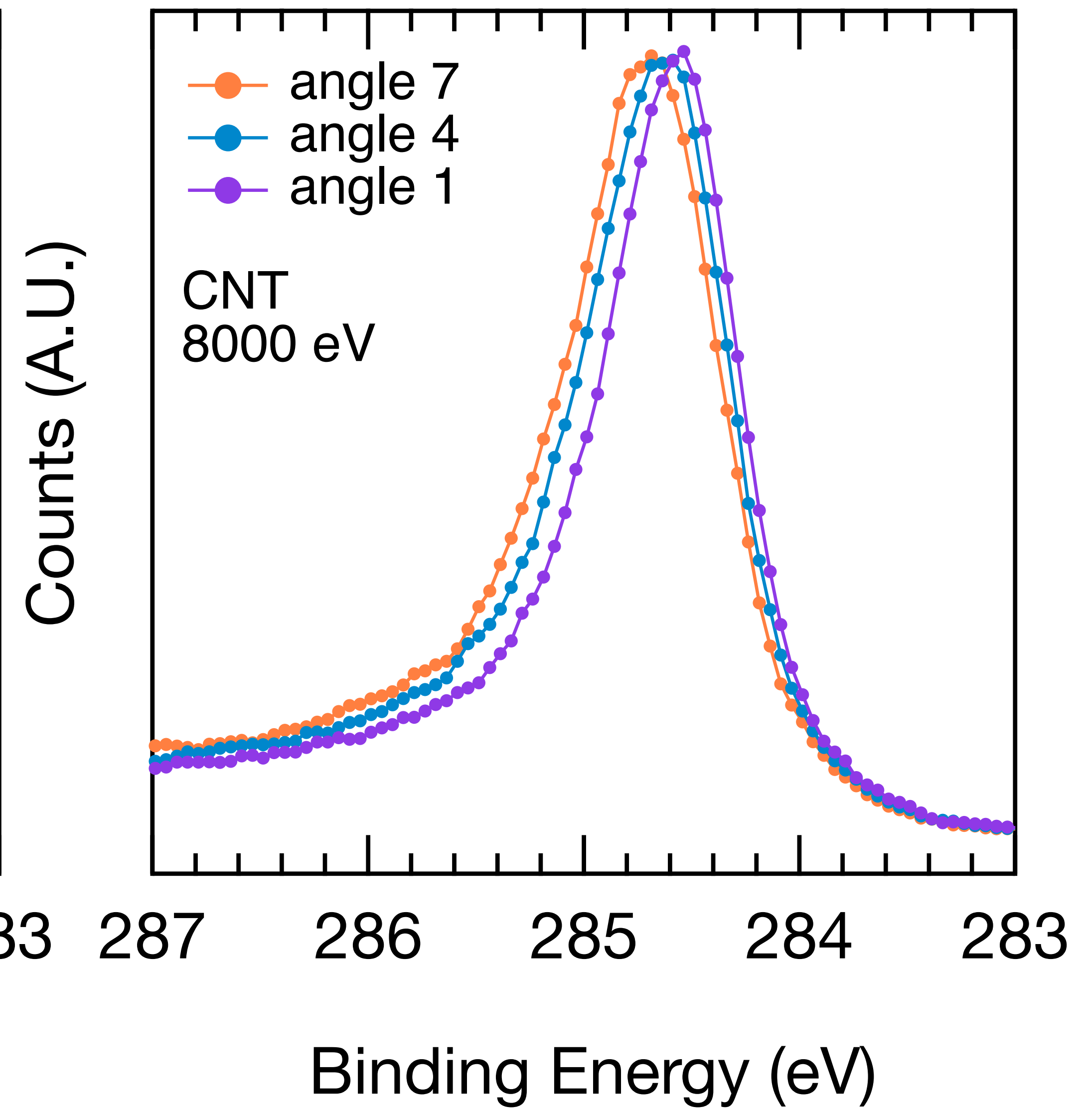


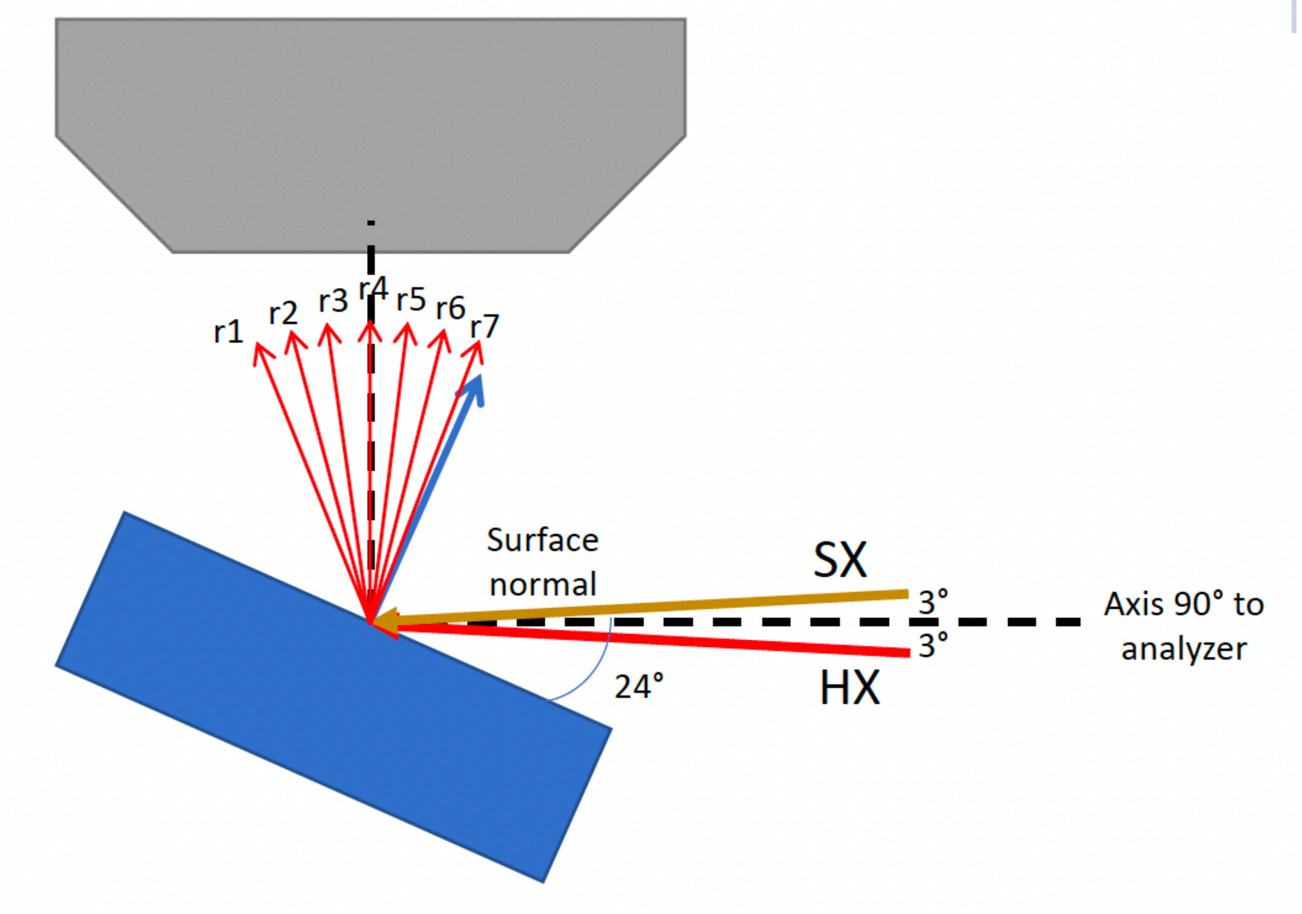


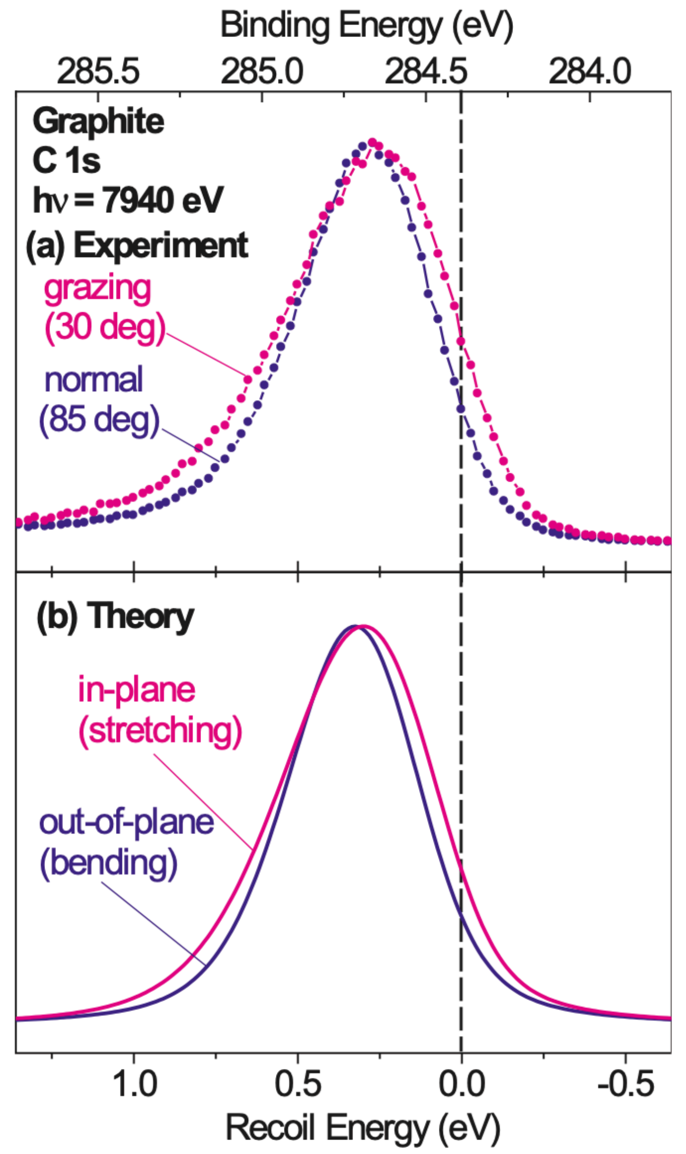






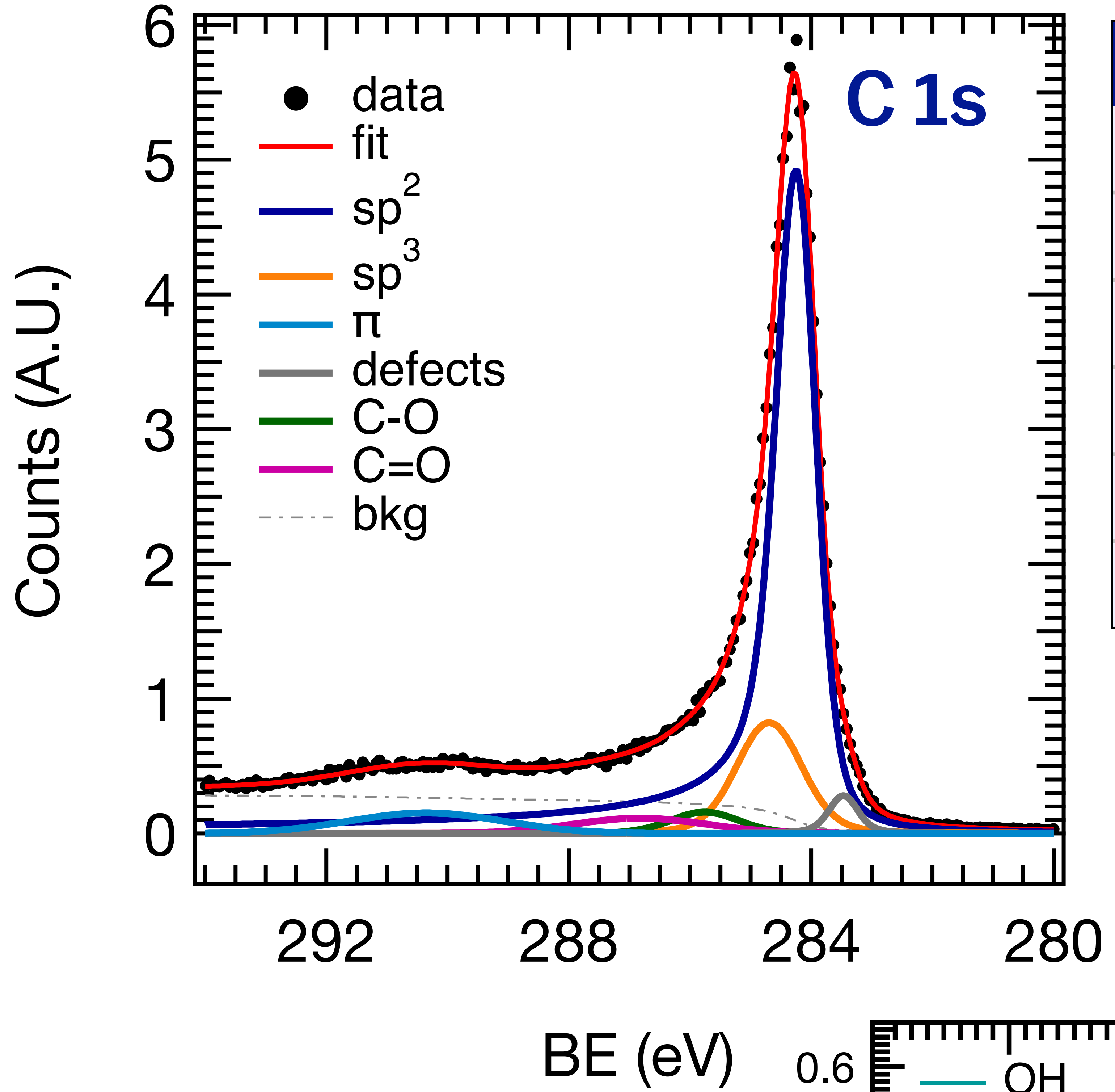




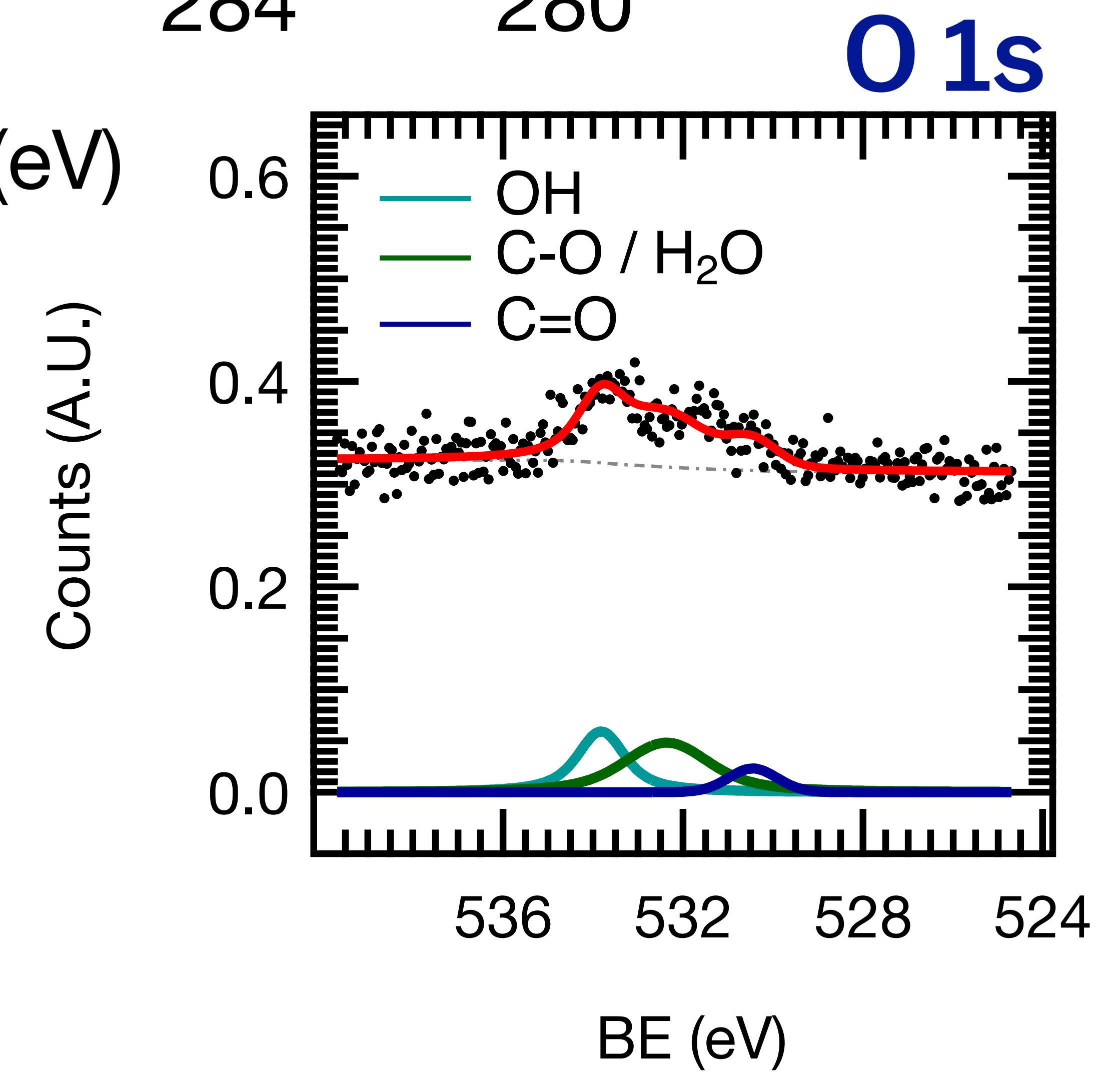


XPS analysis: from sp² towards sp³

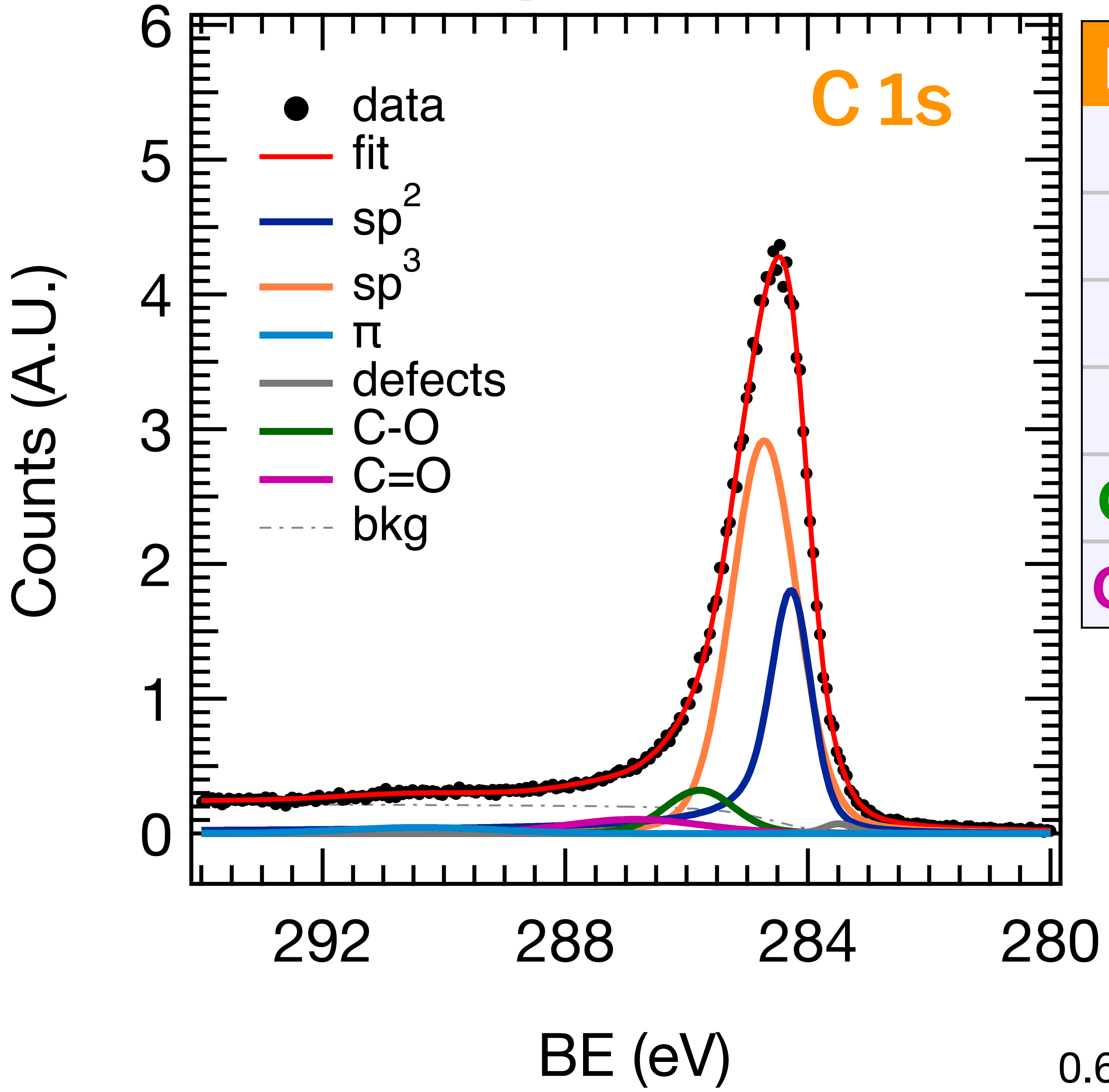
CNT pristine



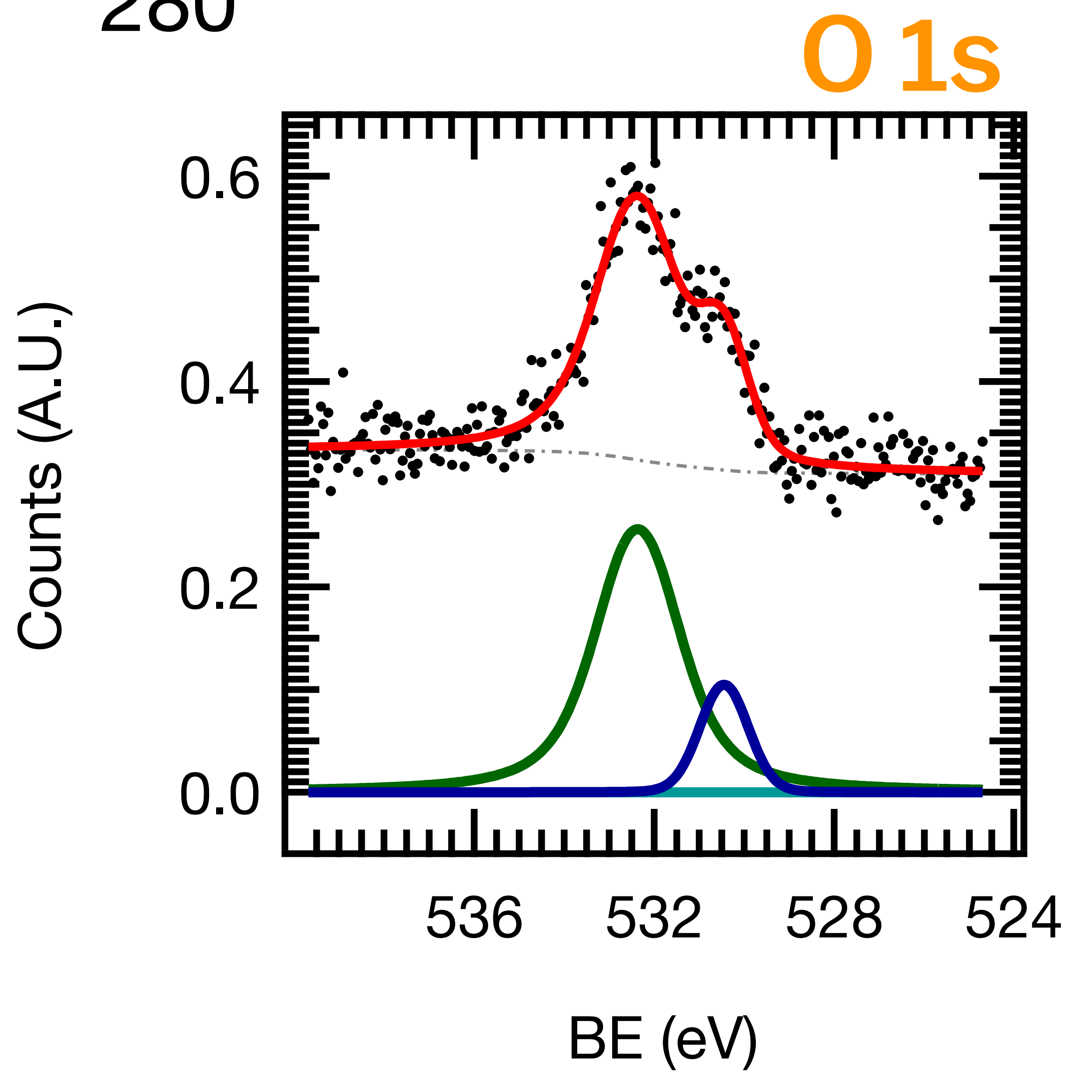
Rel intensity (I_x / I_{tot})	
sp^2	0.66 ± 0.02
sp^3	0.14 ± 0.02
π	0.06 ± 0.03
def	0.02 ± 0.004
C-O	0.03 ± 0.02
C=O	0.04 ± 0.02



CNT plasma H



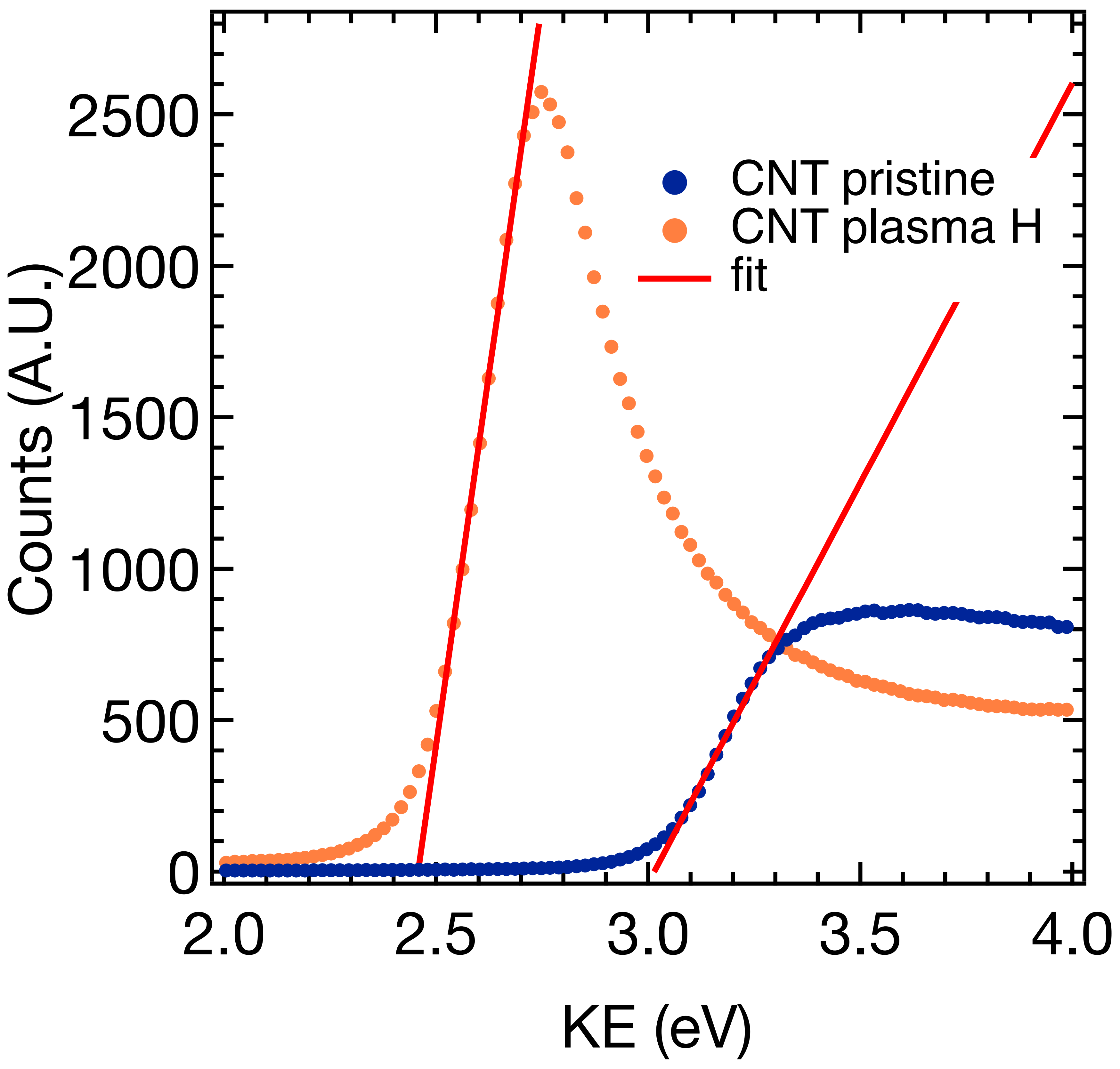
Rel intensity (I_x / I_{tot})	
sp^2	0.28 ± 0.03
sp^3	0.56 ± 0.04
π	0.02 ± 0.01
def	0.01 ± 0.003
C-O	0.06 ± 0.03
C=O	0.04 ± 0.02



- **sp^2** decreases, **sp^3** increases (x4)
- **C-O** and **C=O** increases

UPS: Work Function Changes and Band Gap Opening

Secondary Electron onset (SE)



V_{BIAS} = - 3 V

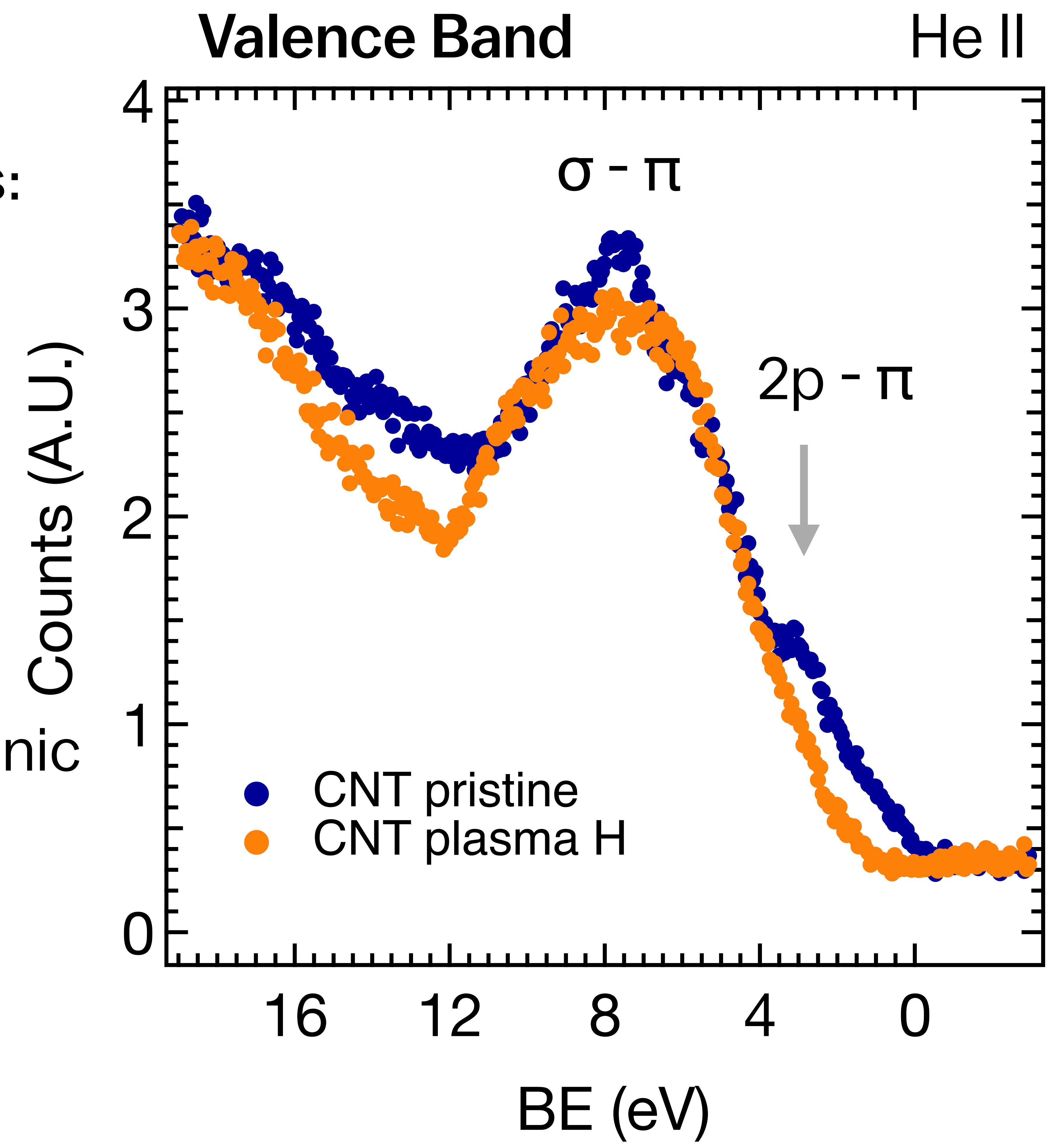
Work Function measure: $\phi_{sample} = h\nu - \Delta E_k = h\nu - (FL - SE)$

Surface dipole changes:

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

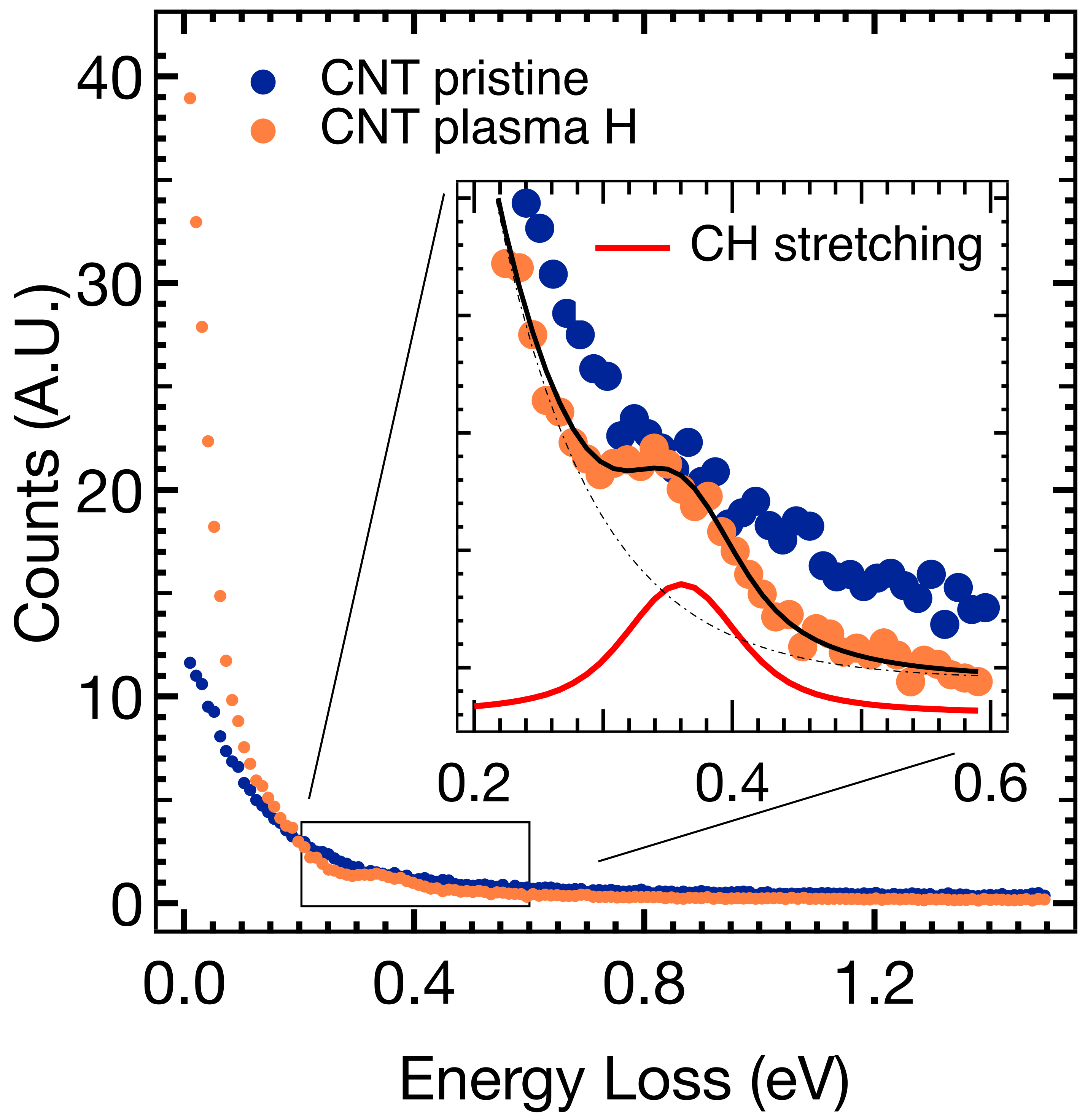
Depletion of the electronic levels near Fermi level

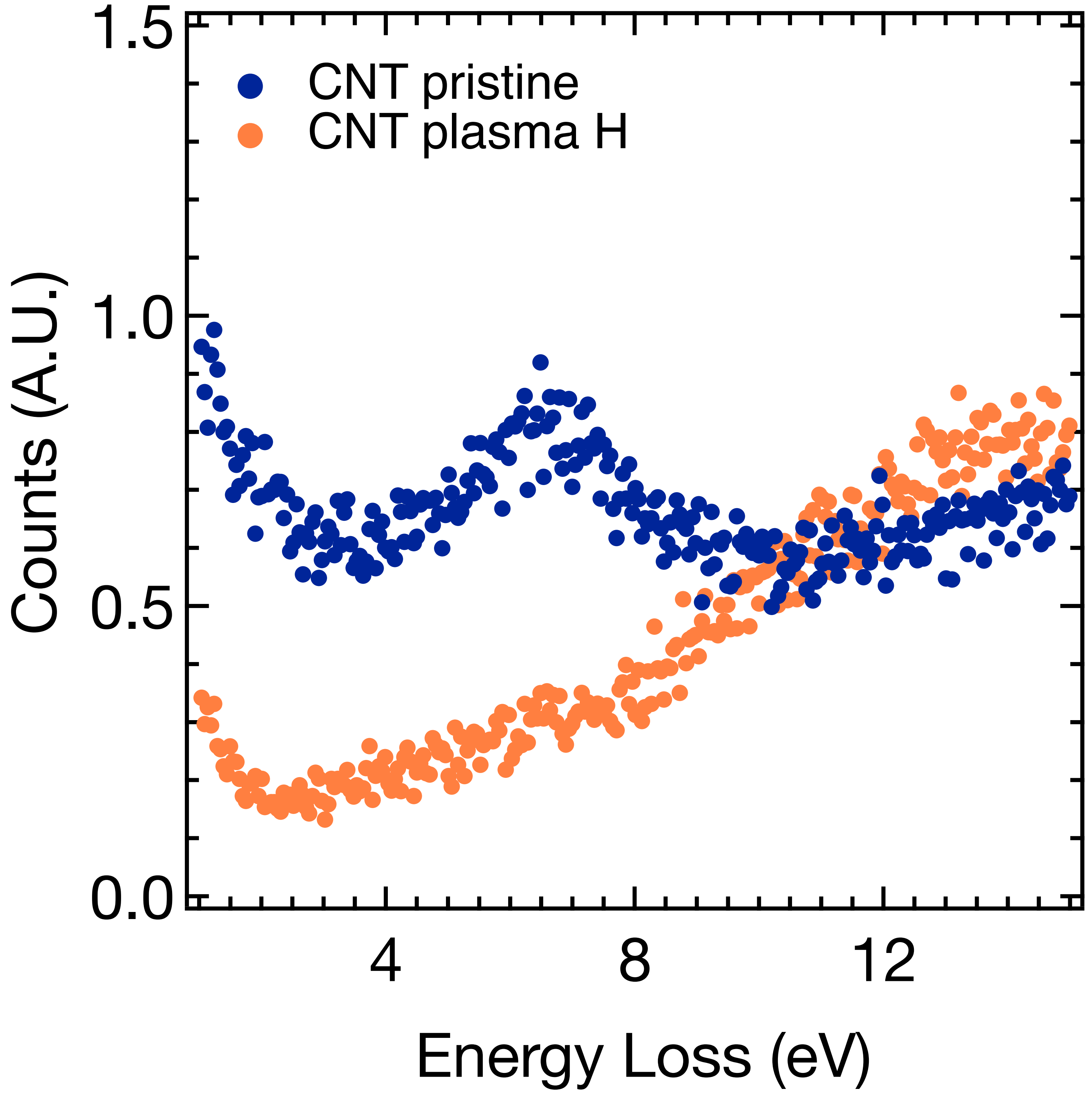
- **Gap opening**

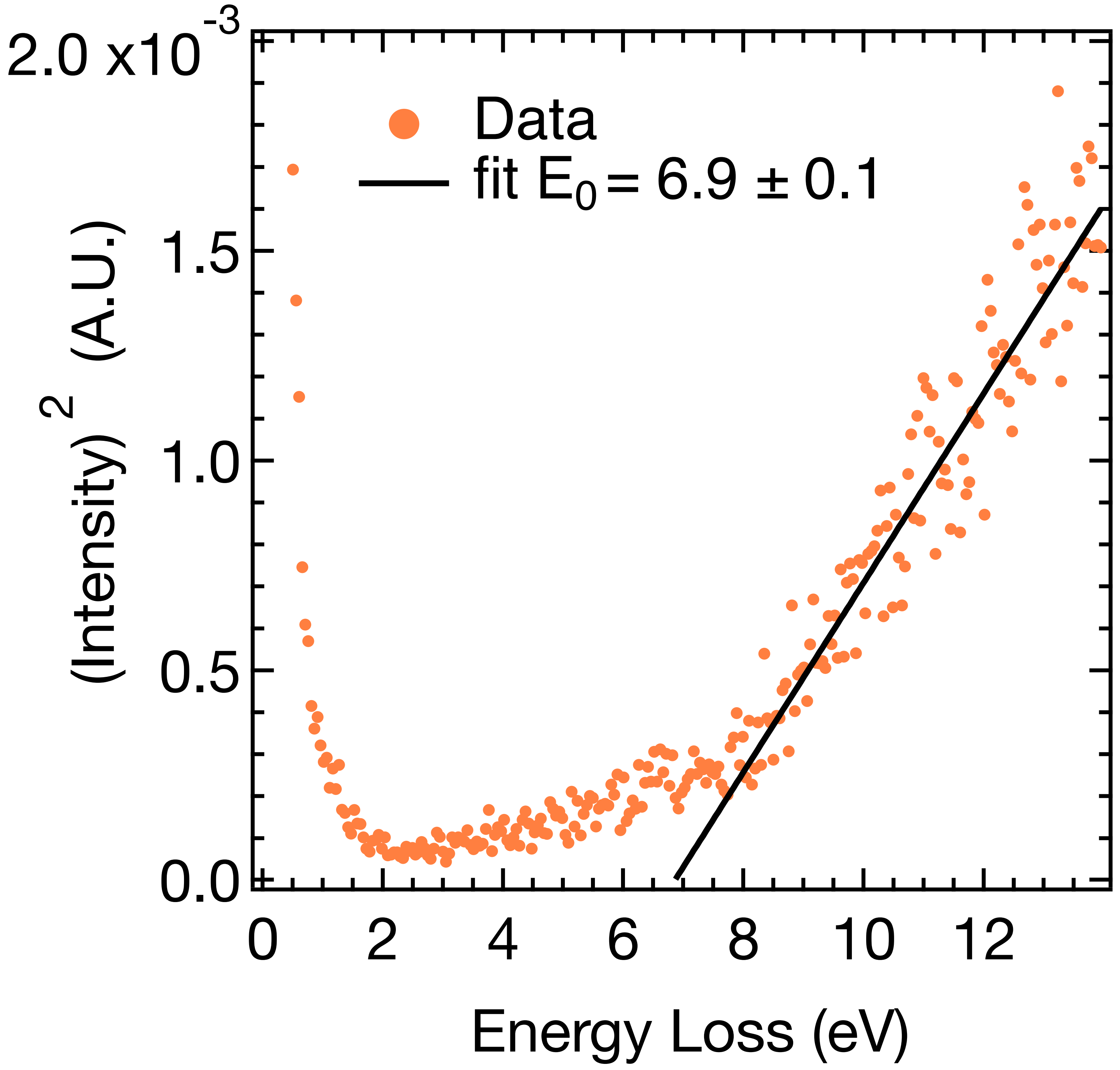


Hydrogenation Signatures in Energy Loss Spectroscopy

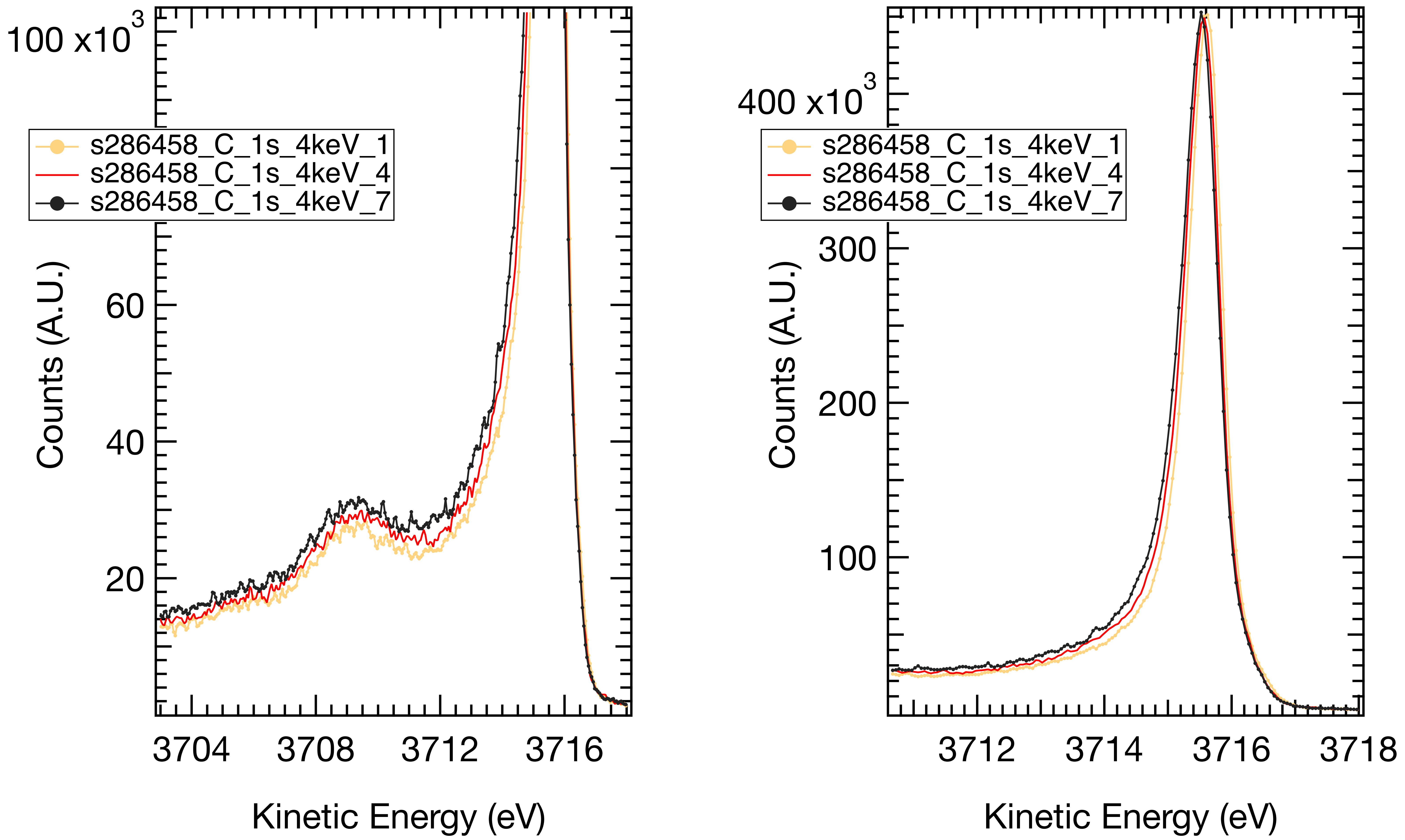
Electron Energy Loss Spectroscopy







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


100 x10^3
60
40
20
s286458_C_1s_4keV_1
s286458_C_1s_4keV_4
s286458_C_1s_4keV_7
Counts (A.U.)
3704
3708
3712
3716
Kinetic Energy (eV)
400 x10^3
300
200
100
s286458_C_1s_4keV_1
s286458_C_1s_4keV_4
s286458_C_1s_4keV_7
Counts (A.U.)
3712
3714
3716
3718
Kinetic Energy (eV)