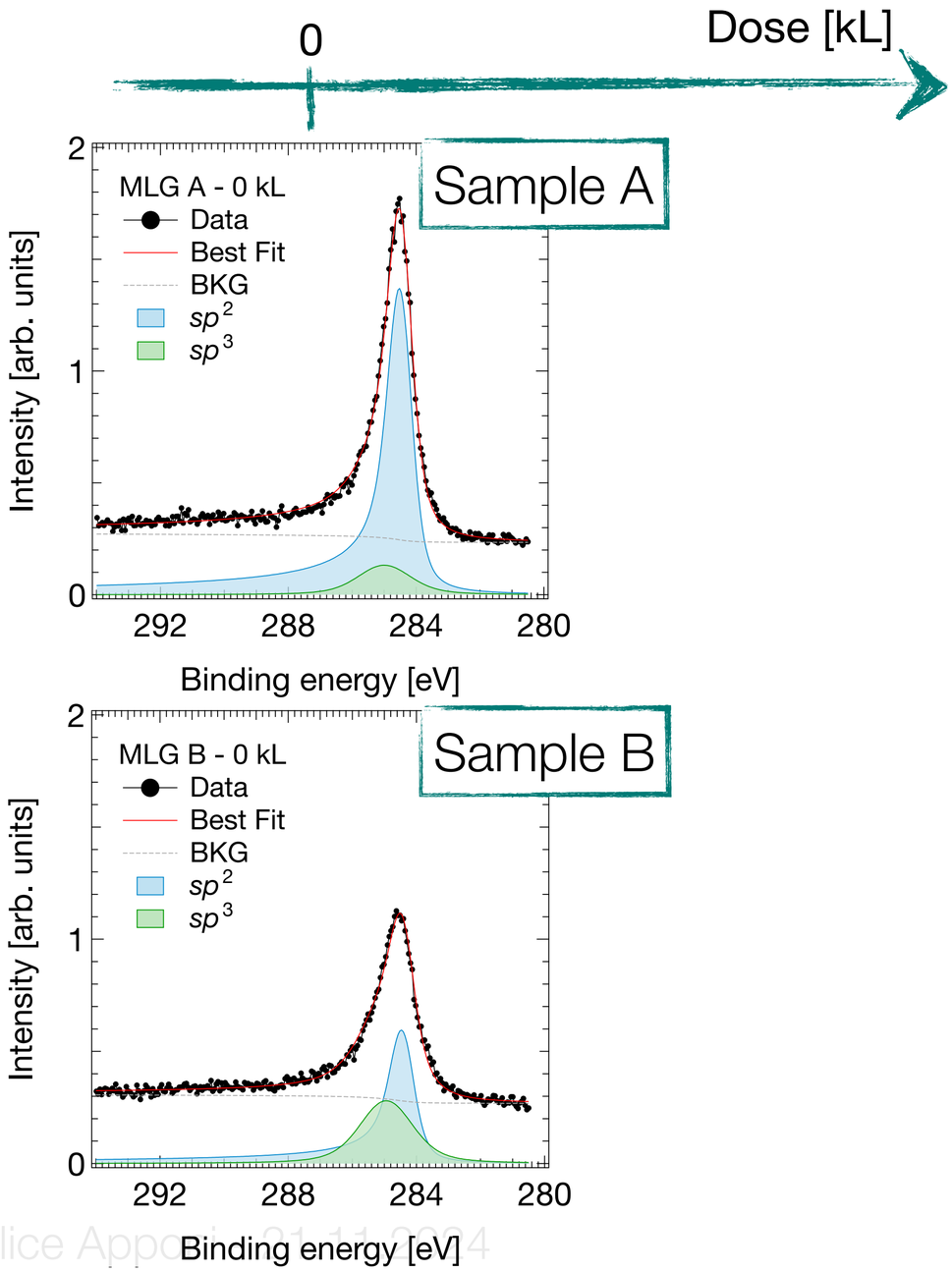
Stability of Hydrogenated Graphene

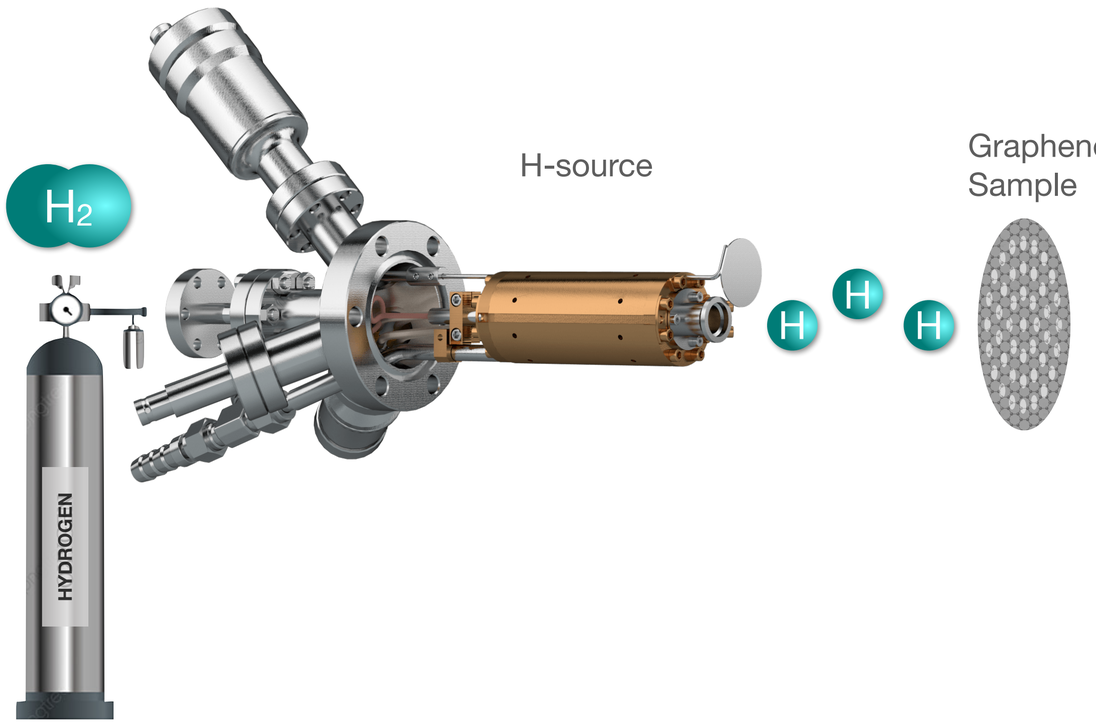
Alice Apponi, Daniele Paoloni, Orlando Castellano,

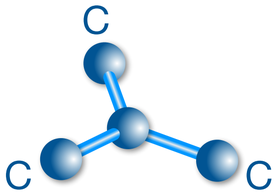
Alessandro Ruocco, Francesco Offi, Carlo Mariani

Ptolemy General Meeting 21.11.24 - Genova

Remeber These Two Guys? Hydrogenated Graphene on TEM

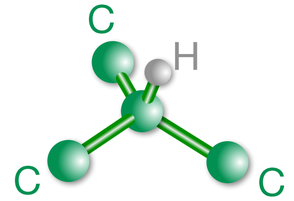




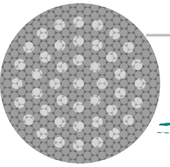


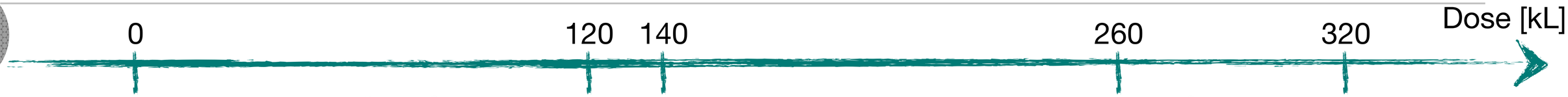
Carbon hybridization

changing from sp^2 to sp^3

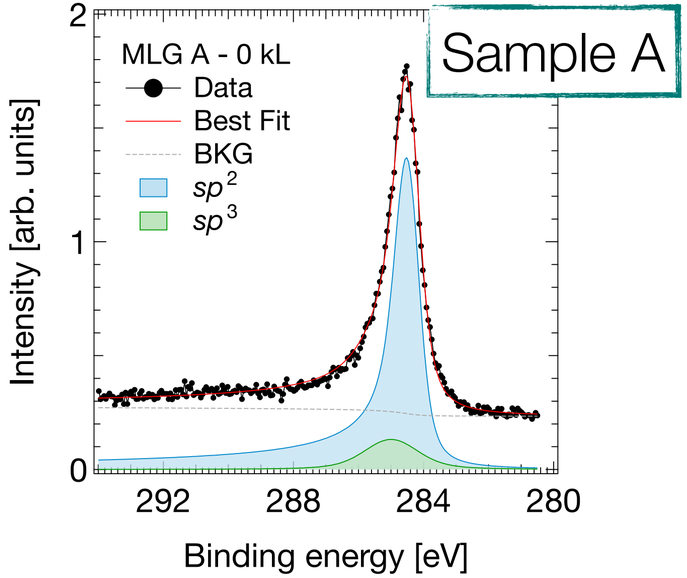


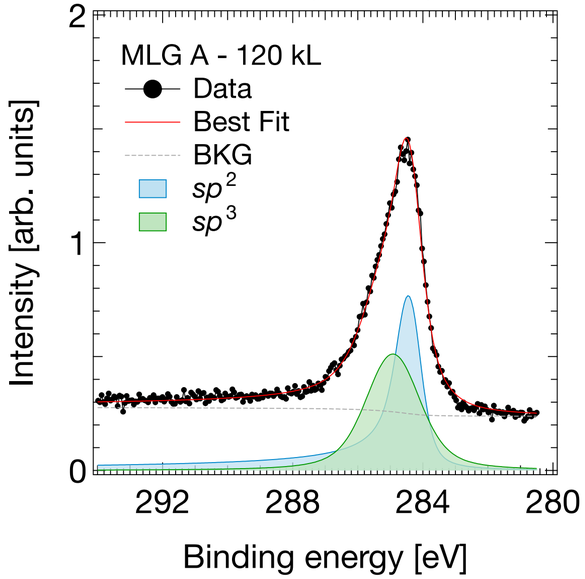
Remeber These Two Guys? Hydrogenated Graphene on TEM

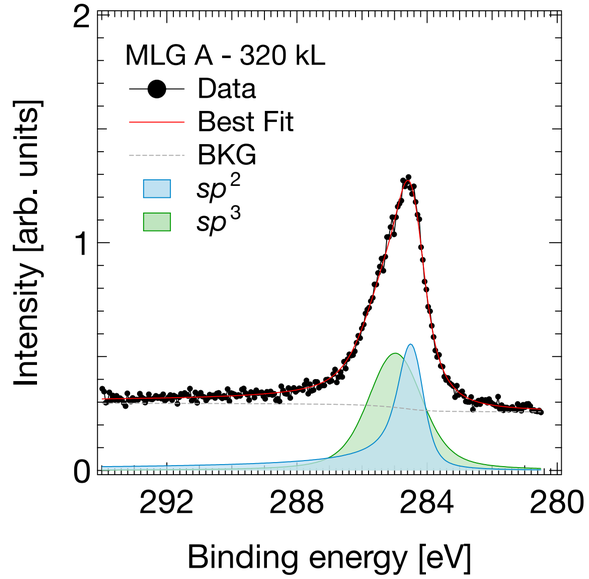




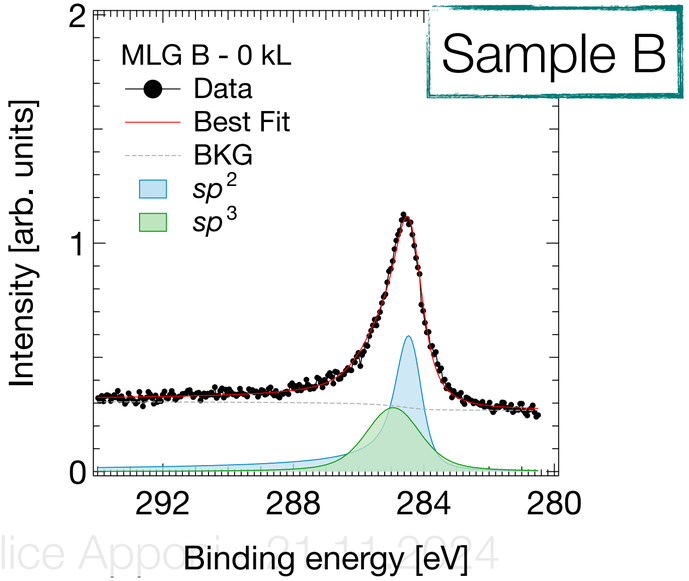
Sample A

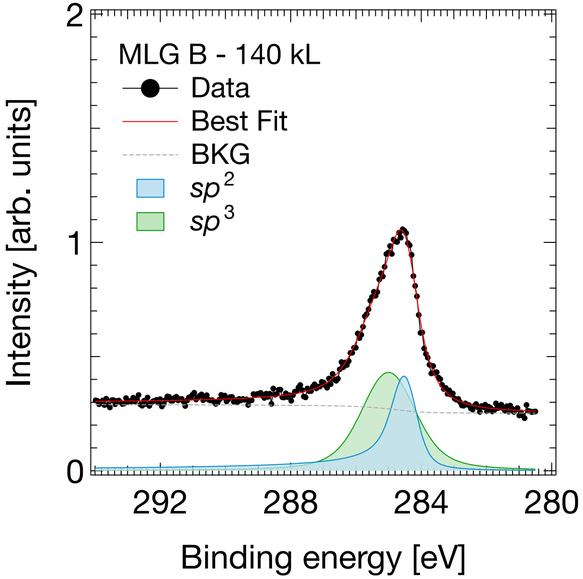


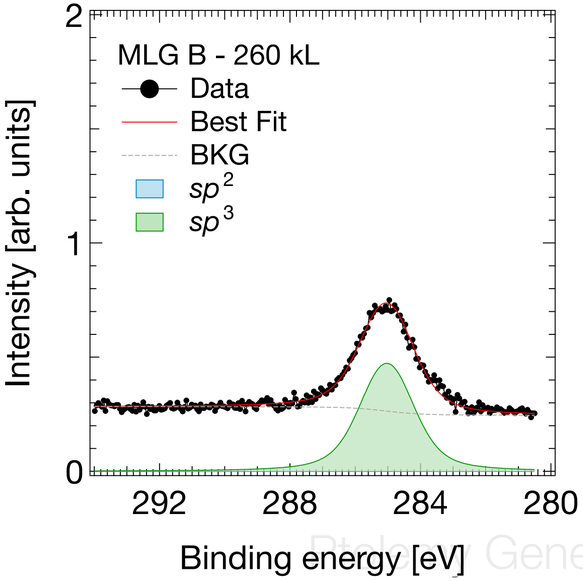




Sample B

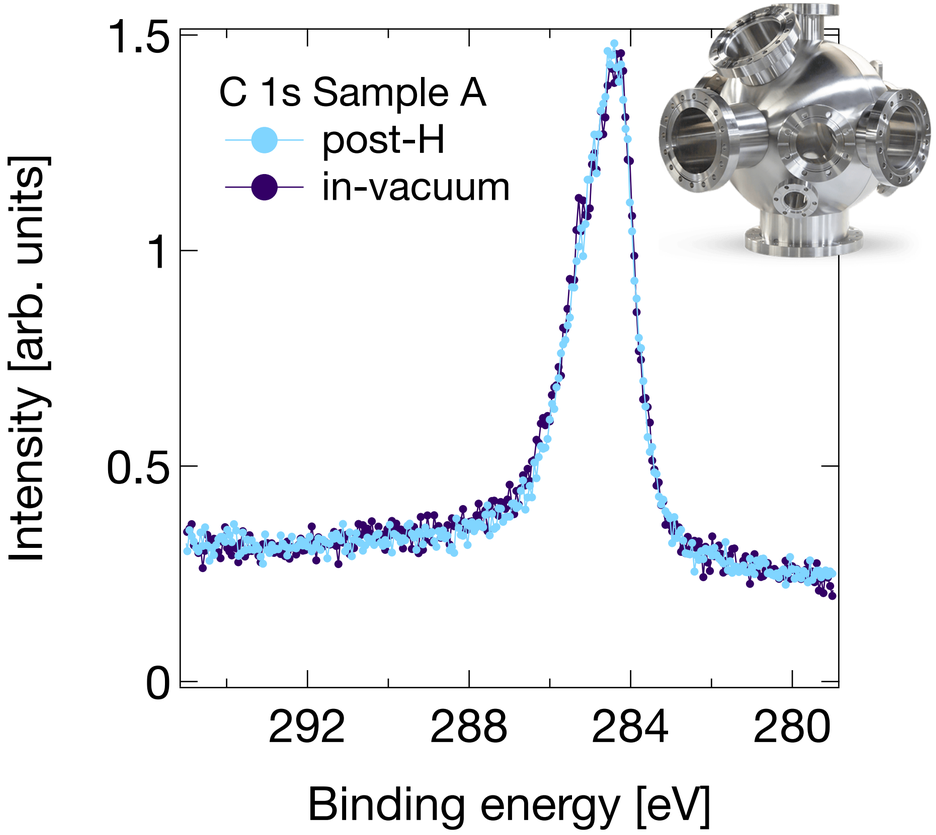


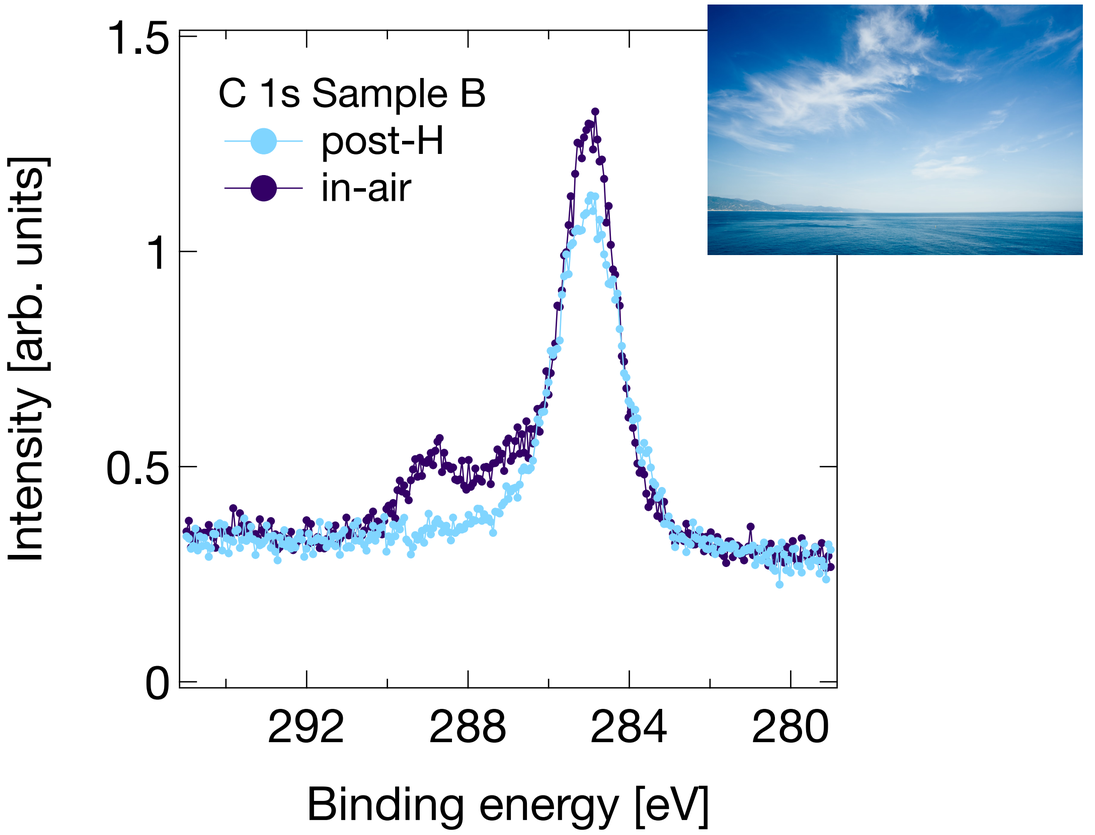




A few months later…

Hydorgenation Stability: Good in UHV, Oxidation in Air





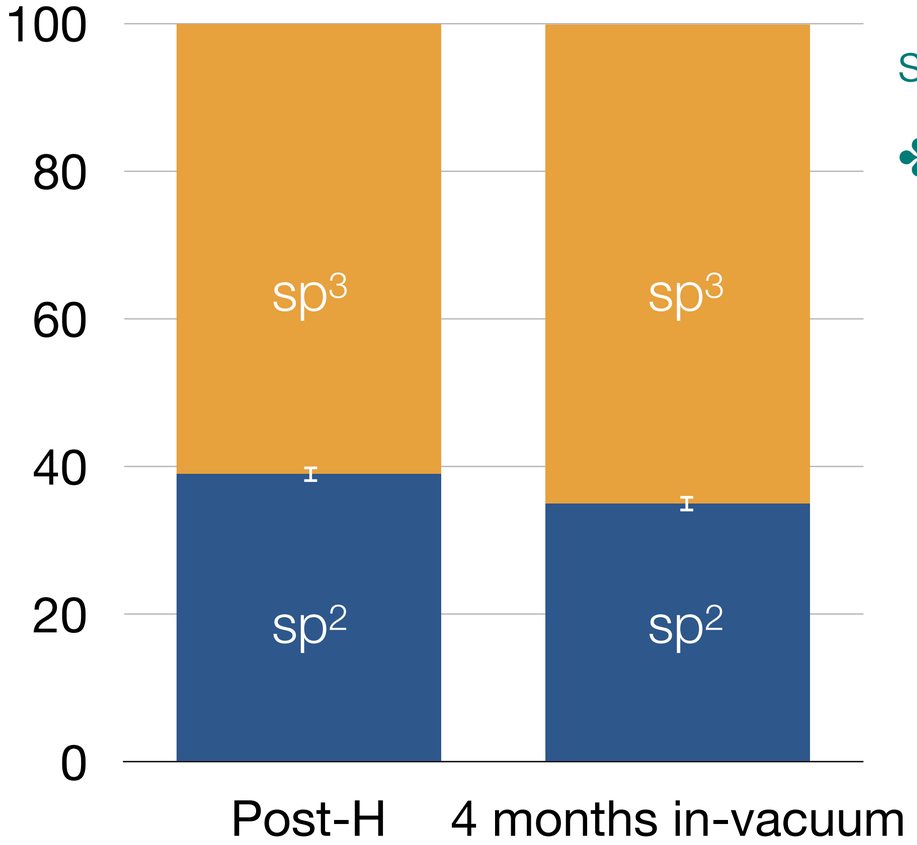
Sample A:

- 4 months in ultra-high vacuum (10^{-10} mbar)
- Almost unchanged

Sample B:

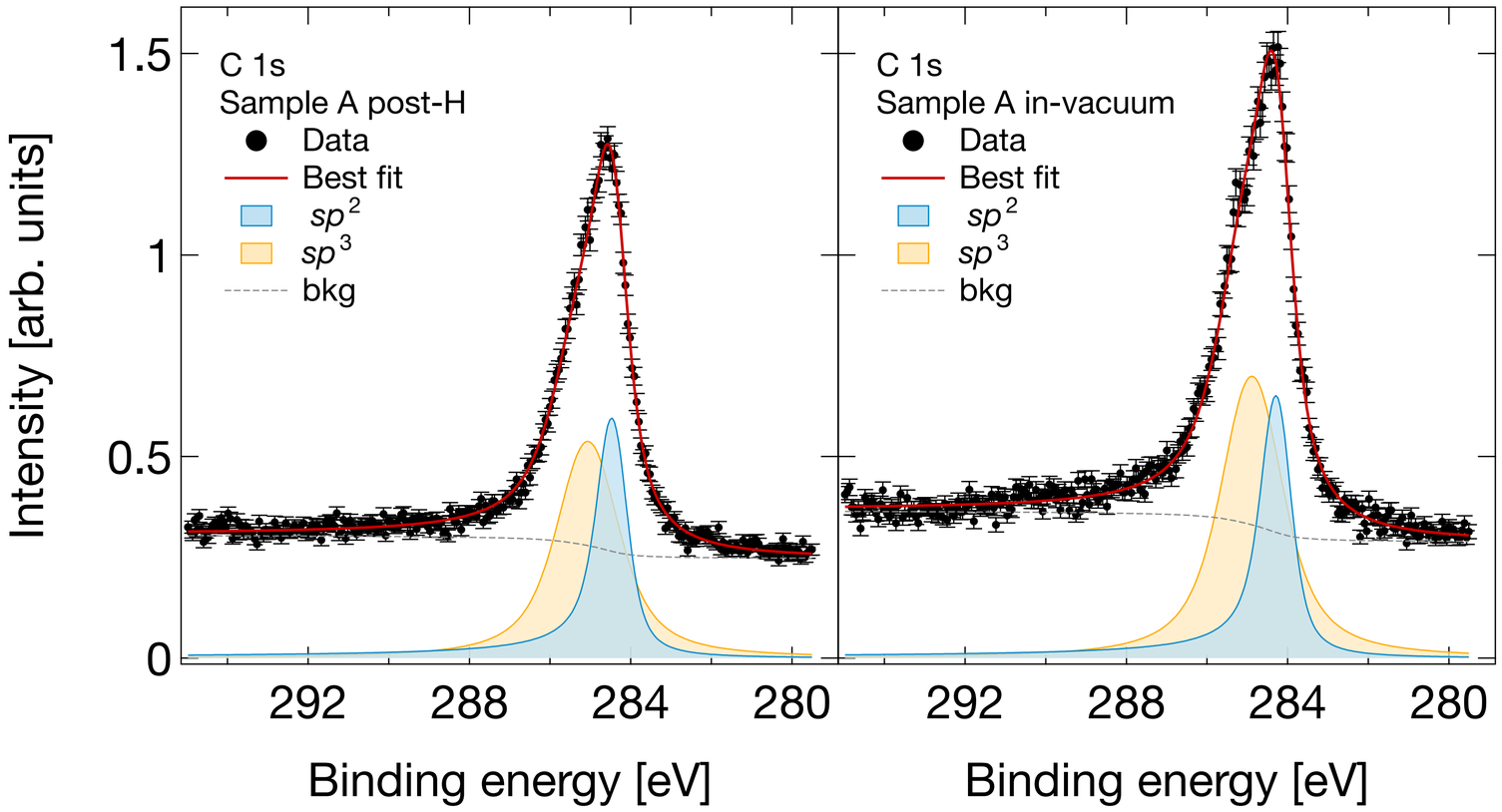
- 11 months in air
- Significant oxidation

Hydrogenation Very Stable in UHV

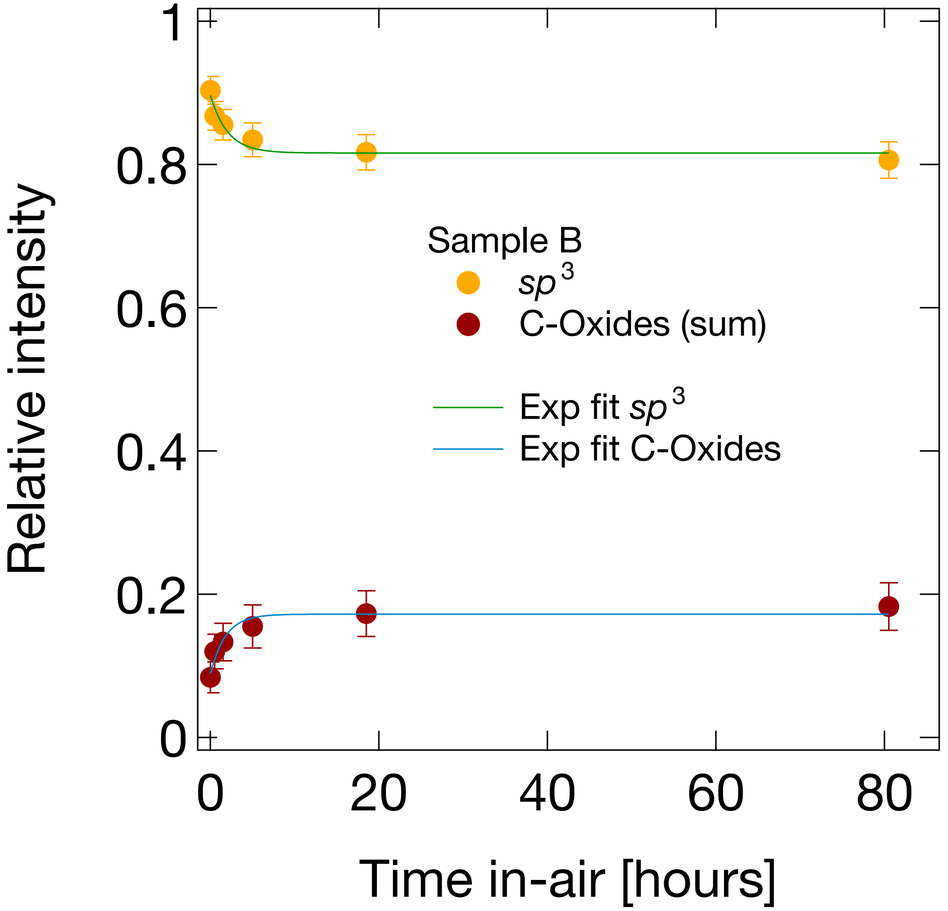


sp^3 relative variation:

- 4 ± 2 %



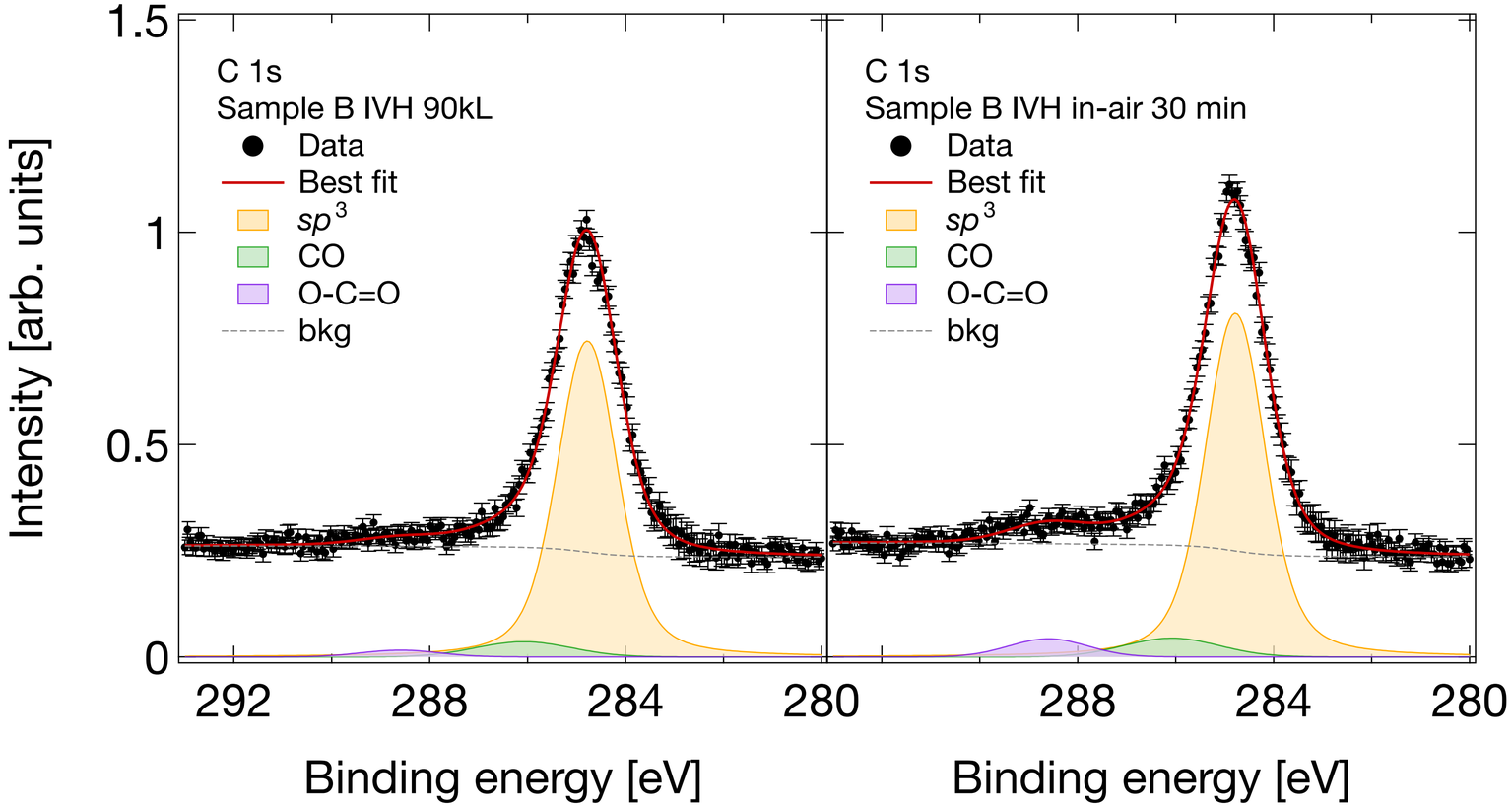
Time-Scale of Oxidation is ~30 min



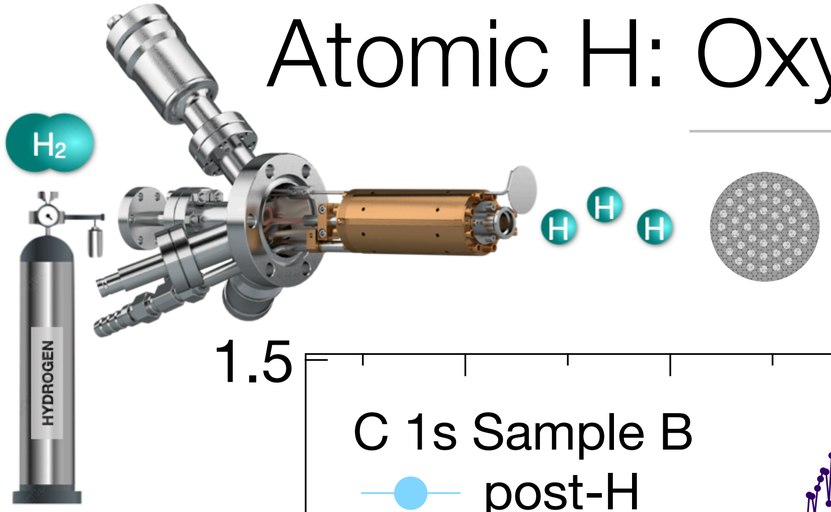
Exponential fit C-Oxides:

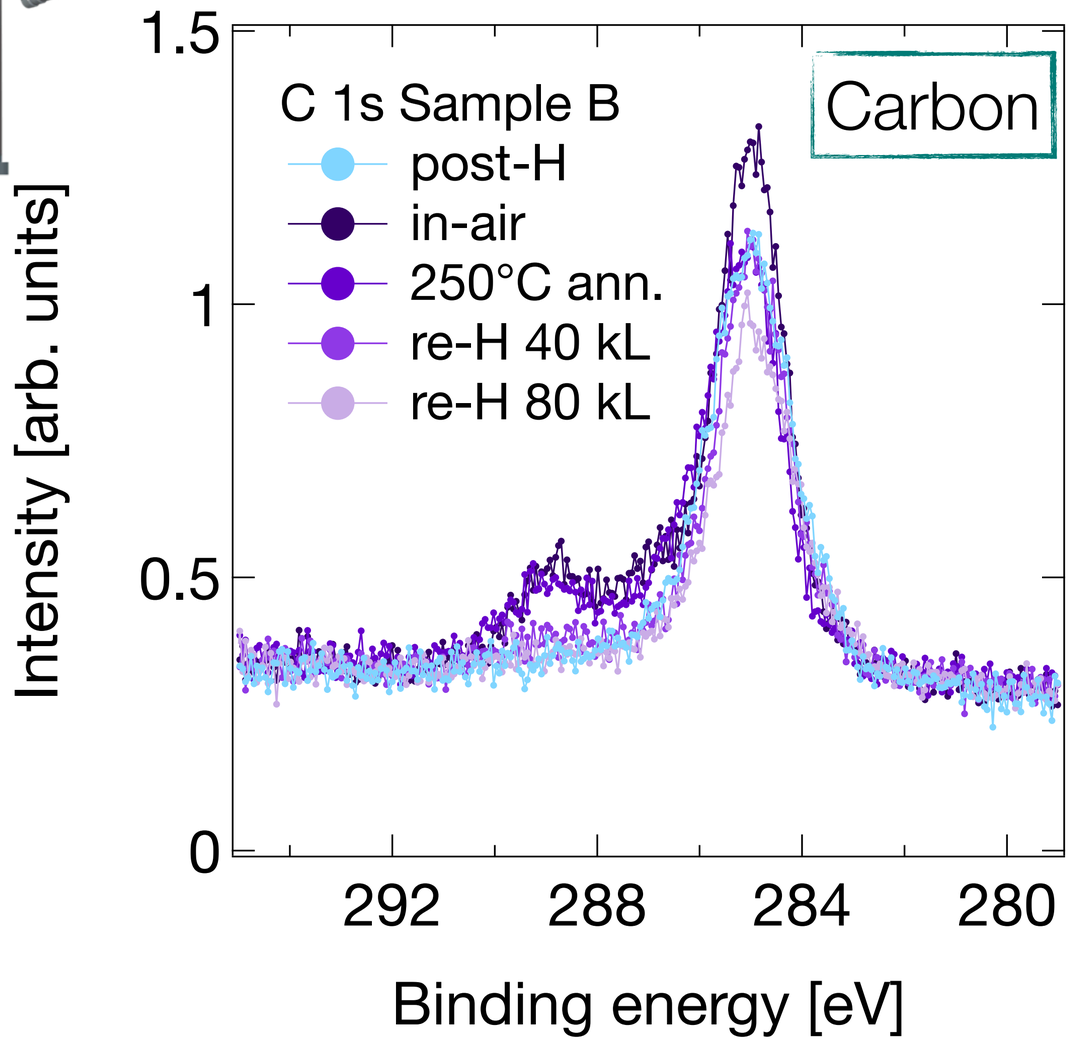
- $1/\tau = 0.55 \pm 0.53$ hours

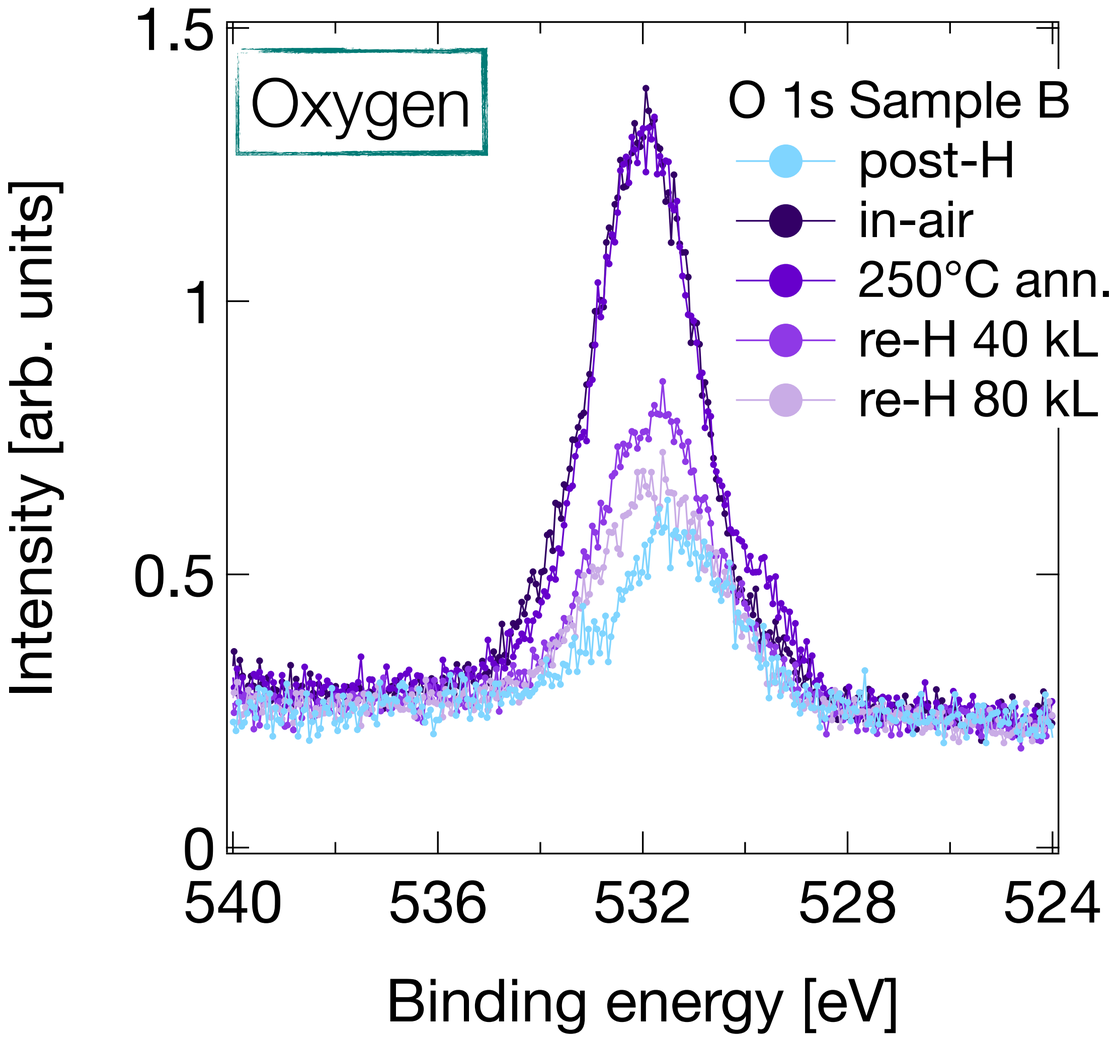
30 min



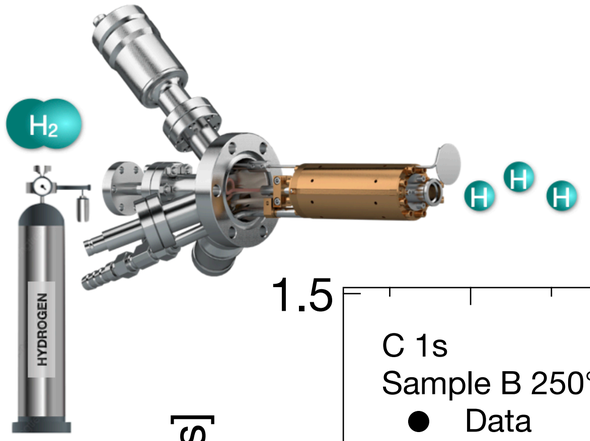
Atomic H: Oxygen Substitution and Re-Hydrogenation

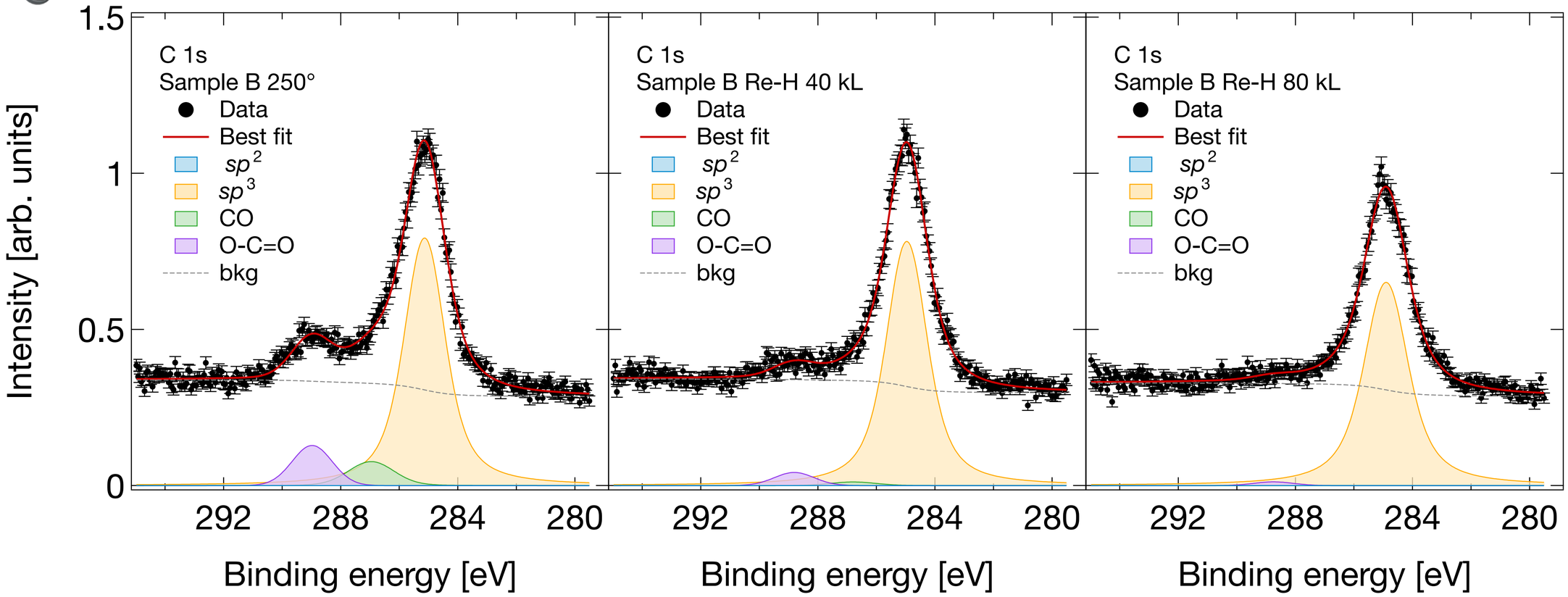






The sp^3 Is the Only Component Left Again

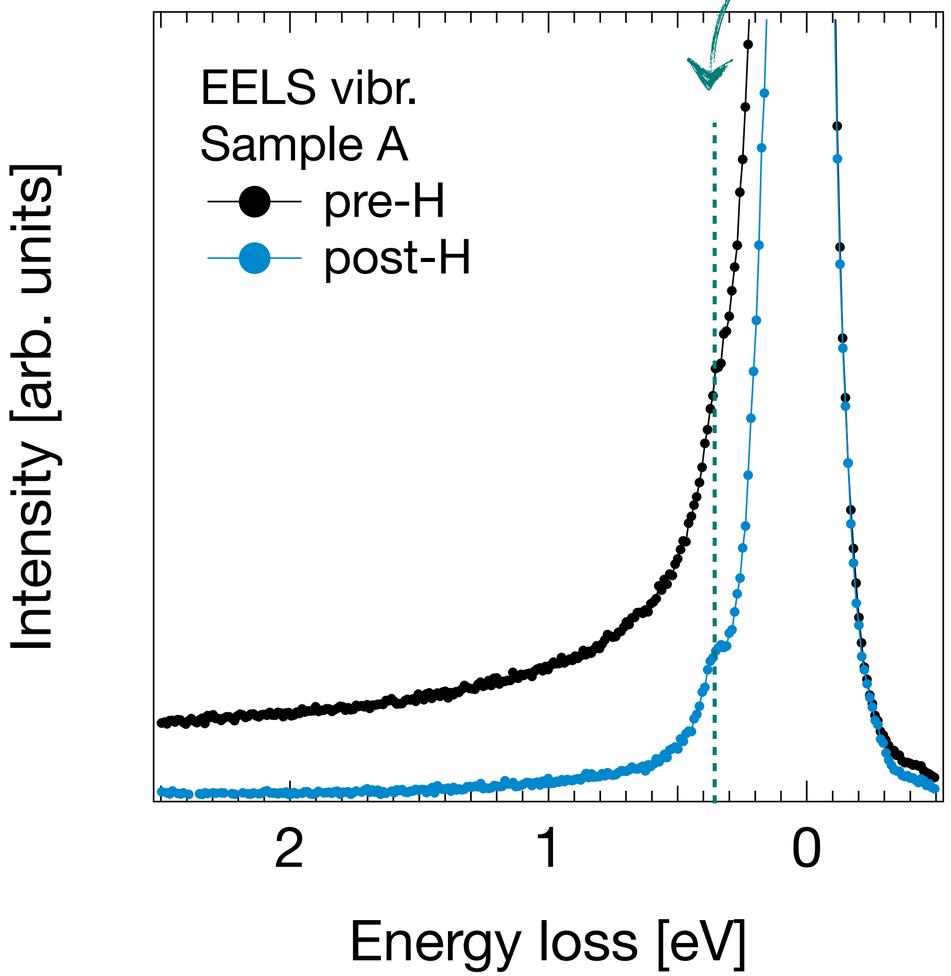


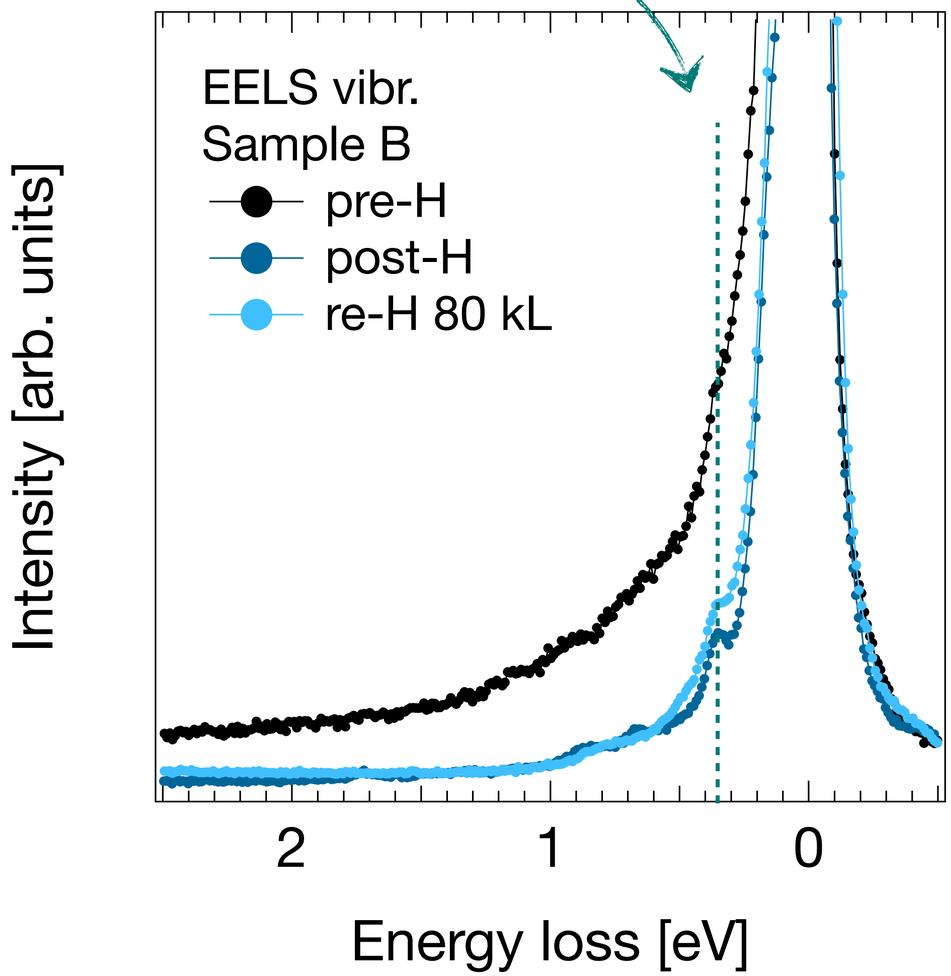


EELS Confirms Hydrogenation and Re-Hydrogenation

DIRECT H FOOTPRINT!

C-H stretching
~360 meV



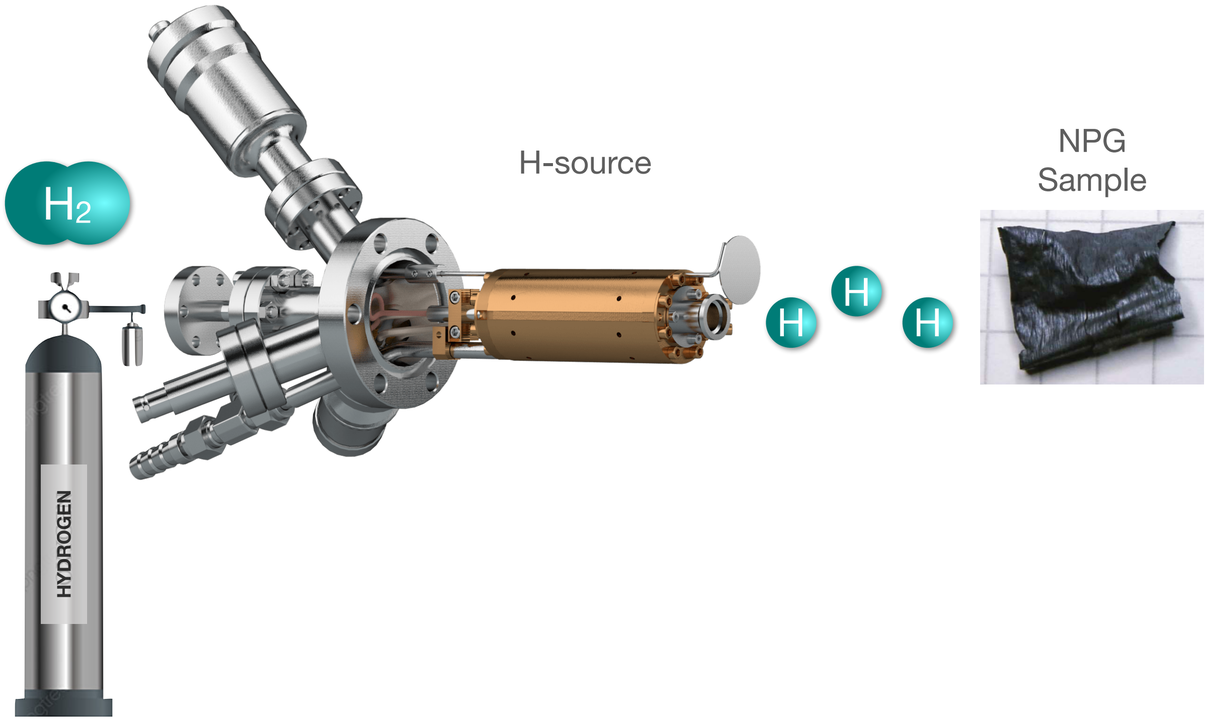


In-Depth Study at Synchrotron Facility

LAboratorio di Spettroscopie Elettroniche e di Correlazione

LASEC

diamond



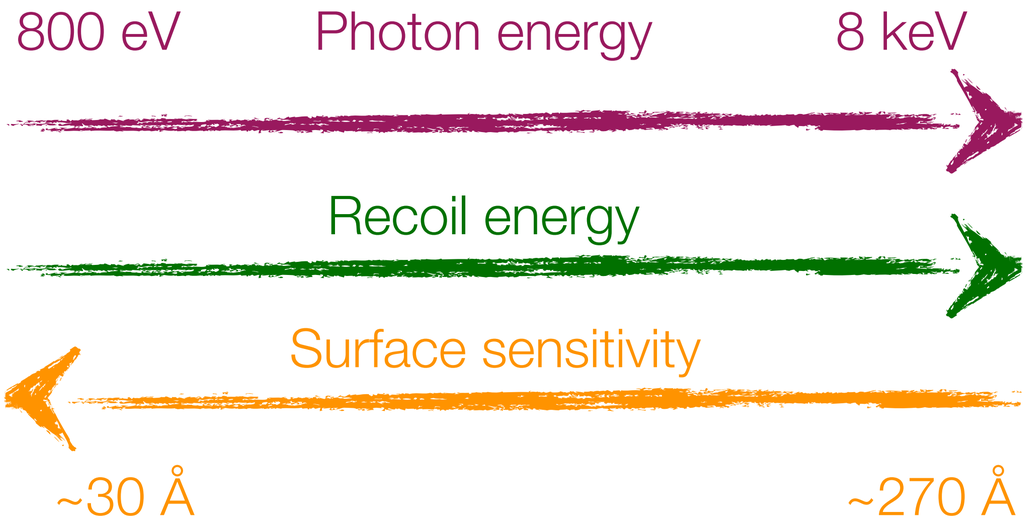
Diamond Light Source XPS experiment:

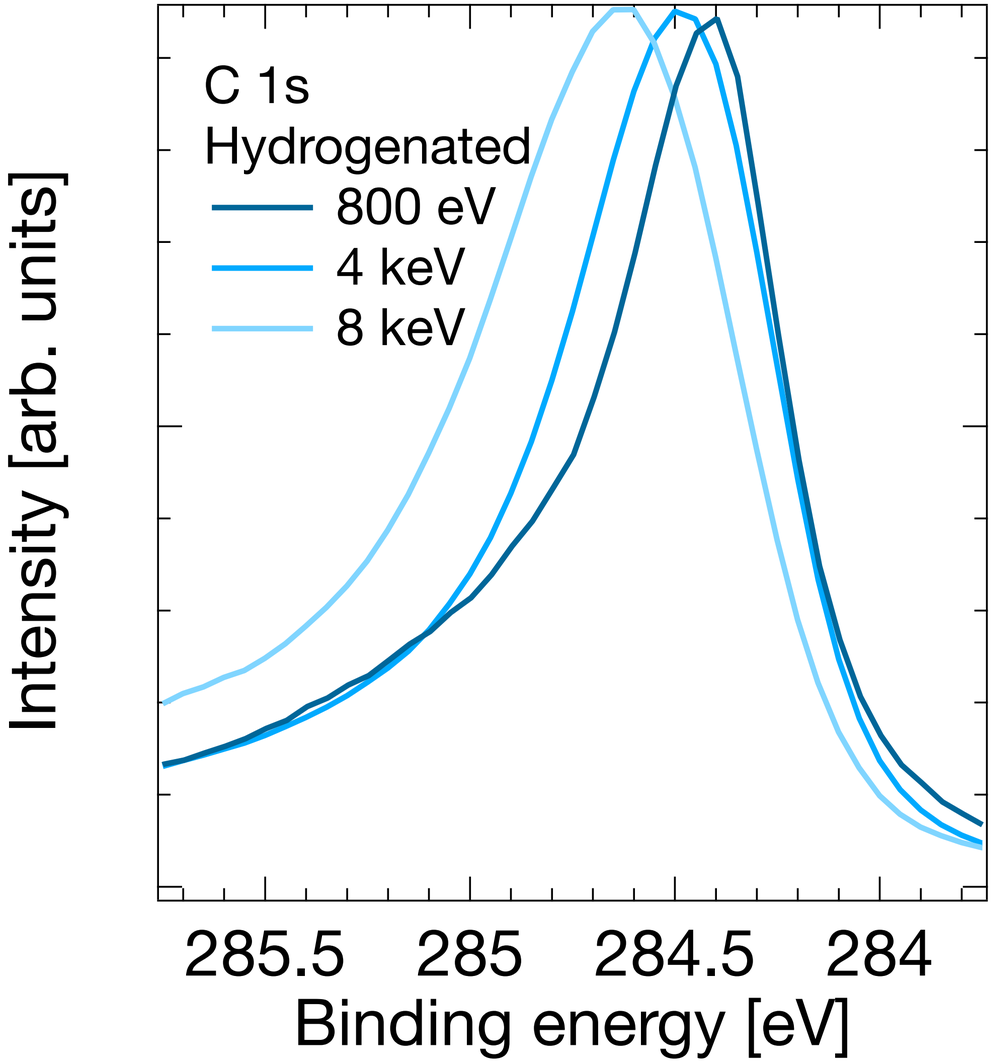
- NPG clean VS hydrogenated
- Increasing hv 0.8 → 8 keV
- In-depth hydrogenation
- Recoil effect to study C-C and C-H vibrational modes

Recoil Effects Visible in NPG Too but C-C Vibrations Only

Recoil in NPG:

- Well visible for NPG hydrogenated
- Unfortunately only superficial hydrogenation
- C-H vibrational effects can not be studied



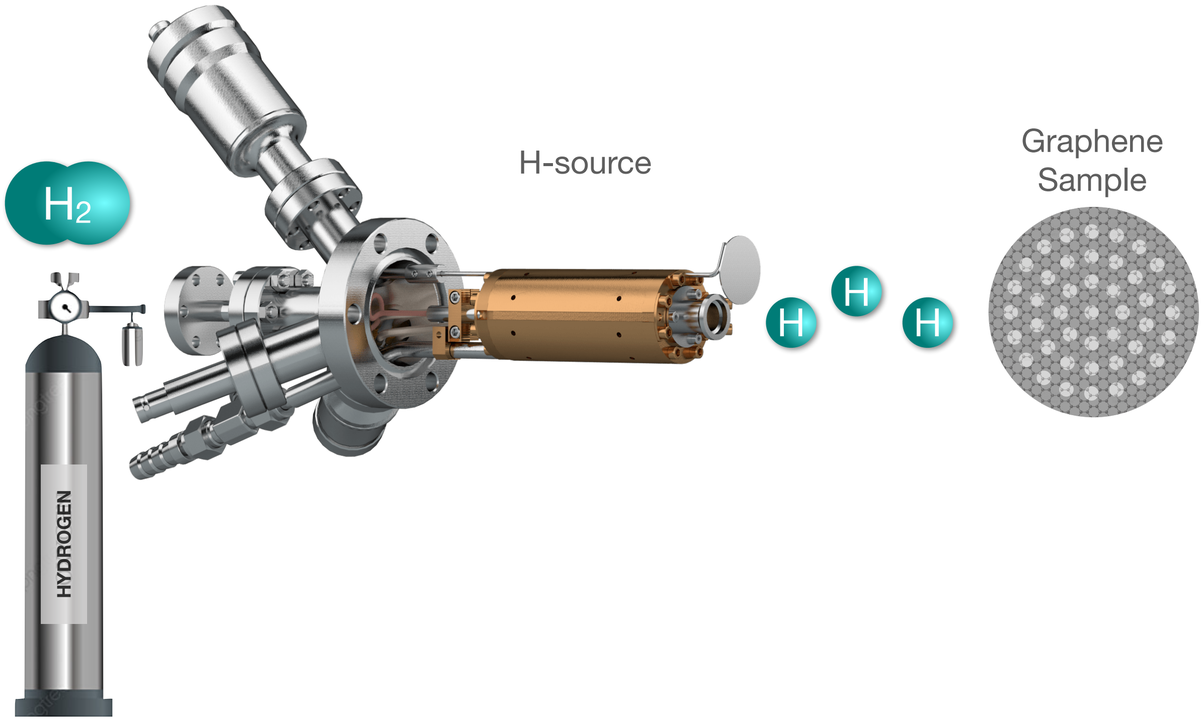


Beamtime Assigned 7-10 December 2024

LAboratorio di Spettroscopie Elettroniche e di Correlazione

LASEC

diamond



STAY TUNED!

To Conclude

Hydrogenation stability:

- Long-lasting hydrogenation in ultra-high vacuum
- Oxygen-to-hydrogen substitution in air (30 min time-scale)
- Good news: it is reversible!

PAPER IN PREPARATION!

Hard X-rays photoemission:

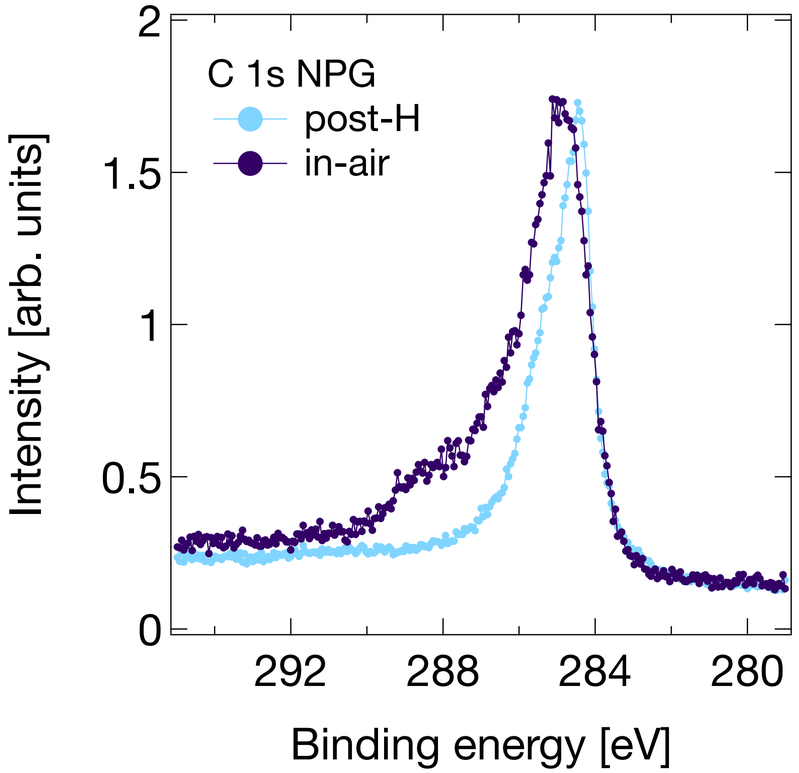
- Recoil effects can be used to study vibrational properties
- C-H modes not visible in NPG because too superficial
- Beamtime in two weeks for hydrogenated graphene

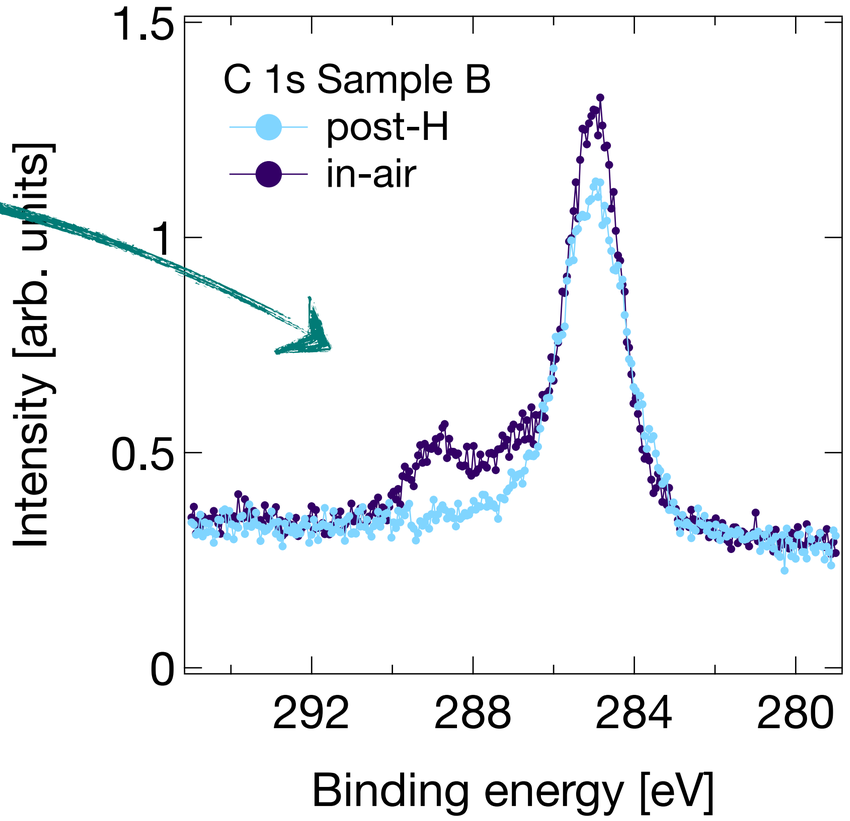
BACKUP

Hydorgenation Stability: Good in UHV, Oxidation in Air

We saw something like this also

for NPG after 4 months in air!

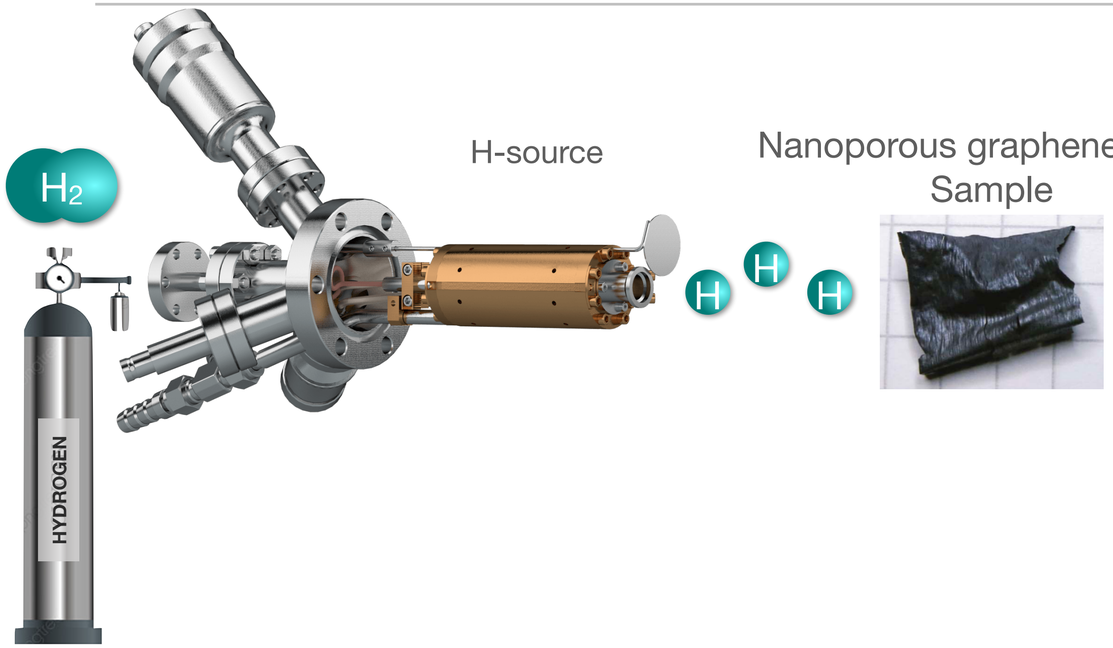




Sample B:

- Hydrogenation ~100 % sp^3
- 11 months in air
- Significant oxidation

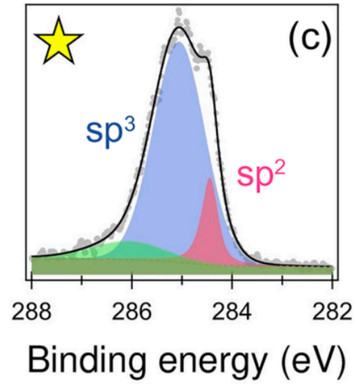
Hydrogenation of NPG: Different Depth Sensitivity

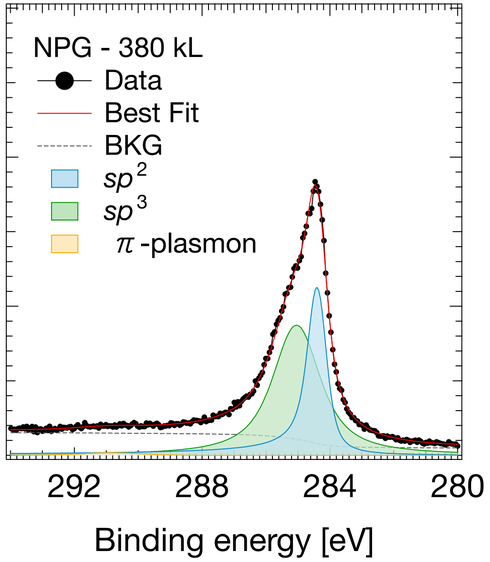


Synchrotron micro-XPS experiment:

- hv = 350 eV (C 1s E_K = 60 eV)
- $sp^3/(sp^2+sp^3)$ ≈ 90% achieved

Betti, M.G. *et al.*, *Nano Letters (2022)*,
https://doi.org/10.1021/acs.nanolett.2c00162





Lab. XPS experiment:

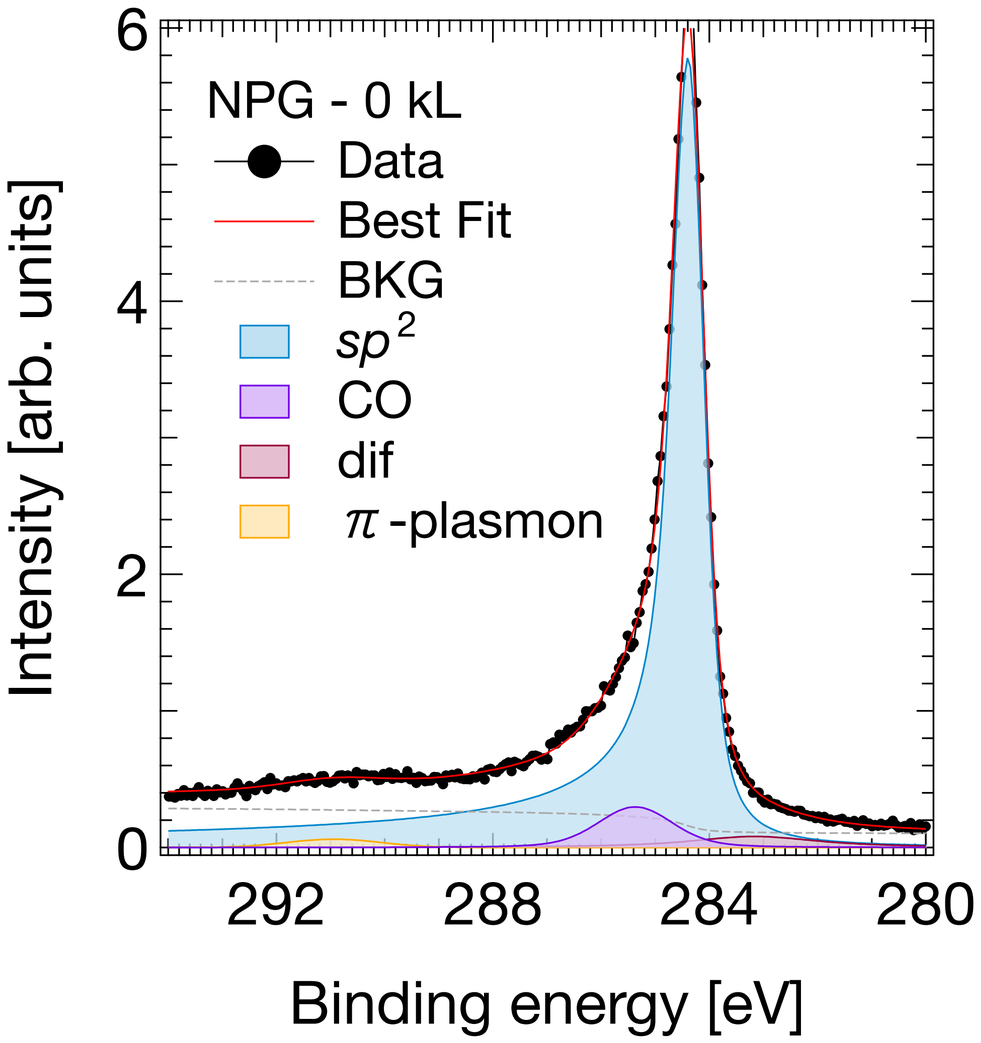
- hv = 1486.7 eV (C 1s E_K = 1200 eV)
- $sp^3/(sp^2+sp^3)$ ≈ 64% achieved

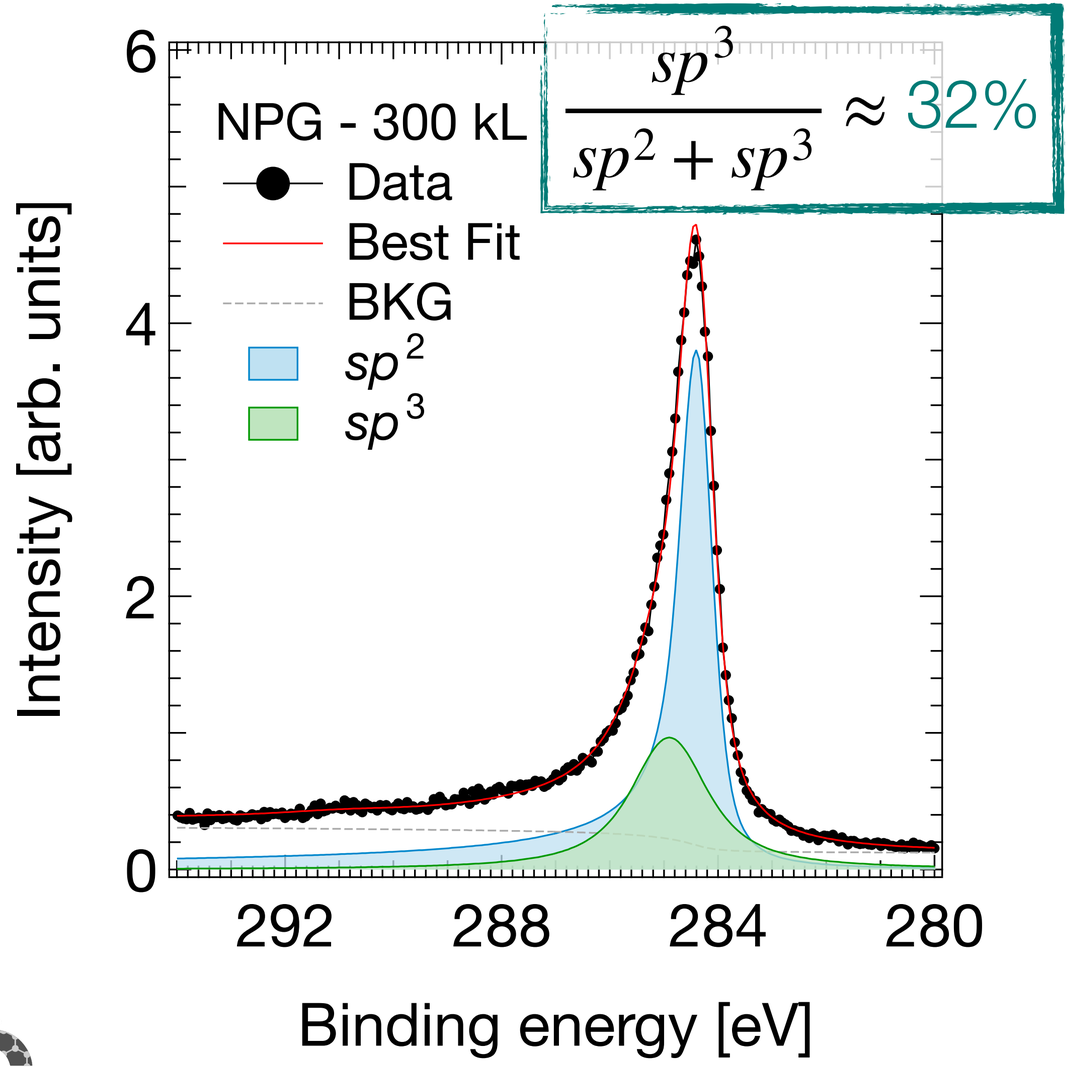
Different depth sensitivity

E_K = 60 eV depth ~ 9 Å

E_K = 1200 eV depth ~ 90 Å

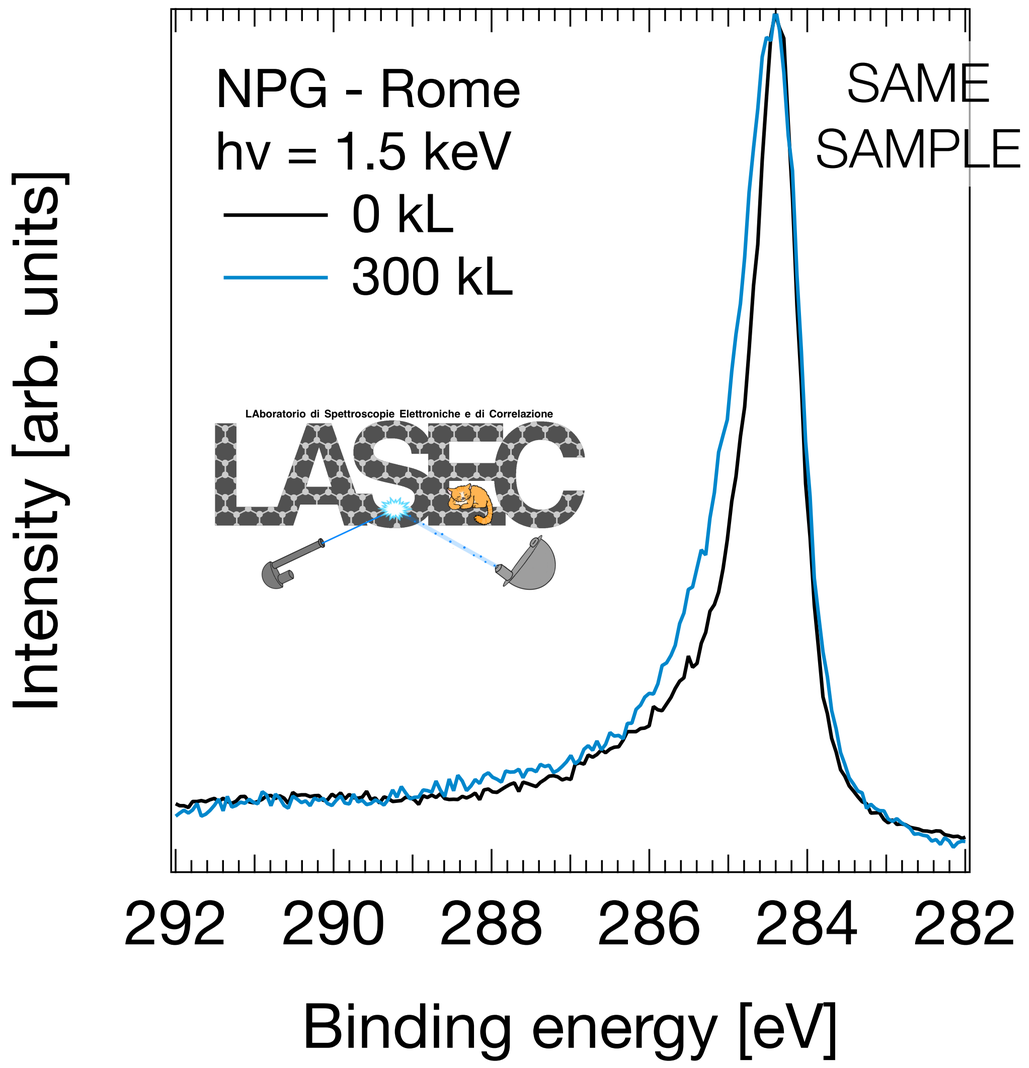
After 300 kL of Hydrogen 32% sp3 at LASEC

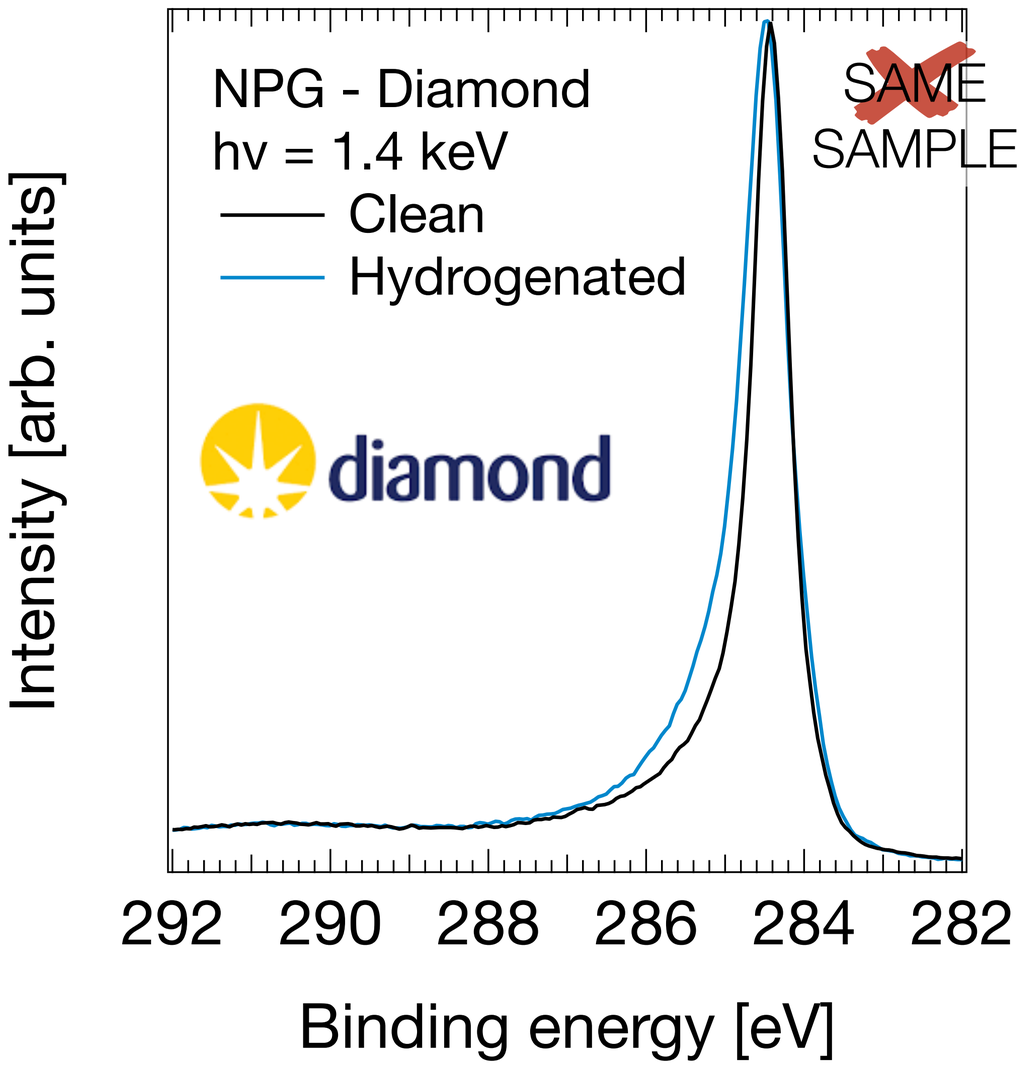




Stable Hydrogenation From Rome to Diamond

Food vacuum
(a few mbar)



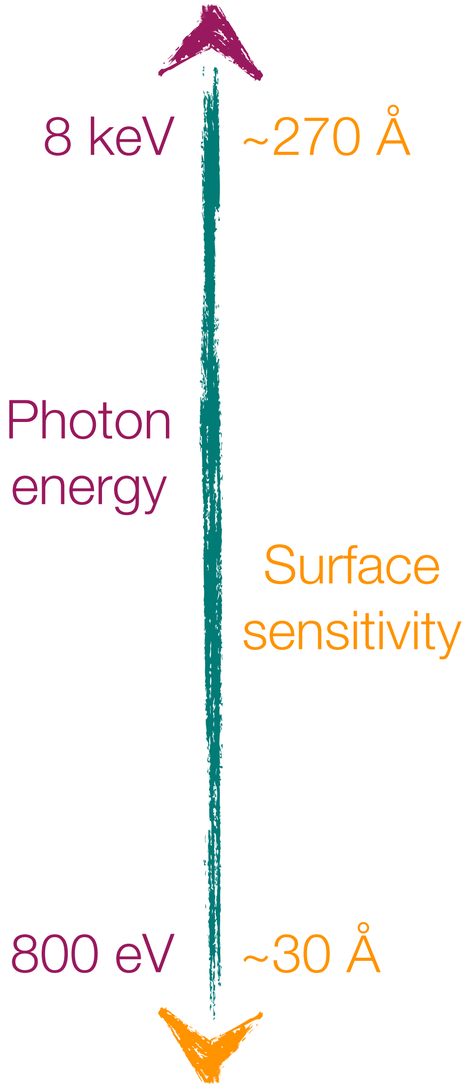


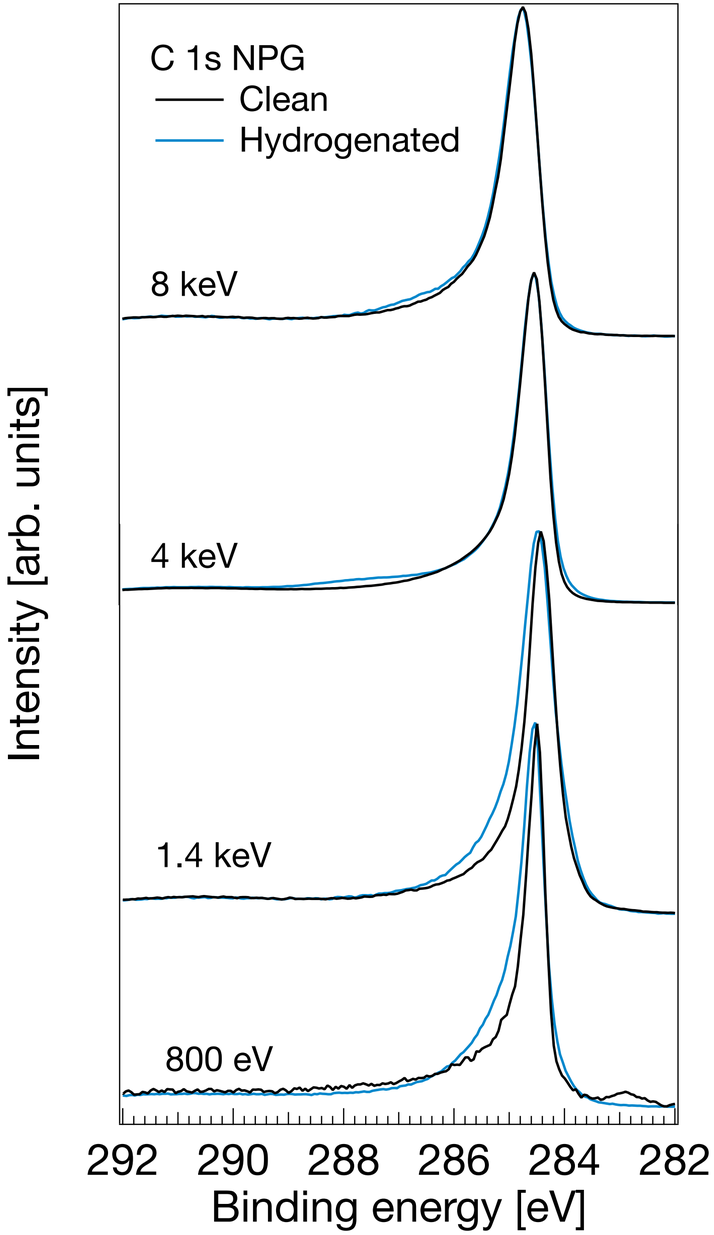
Hydrogenation Only on Surface

Diamond Light Source XPS experiment:

- NPG clean VS hydrogenated
- Increasing hv 0.8 → 8 keV
- In-depth information increases
- Hydrogenation reaches only superficial layers

Be careful with H-uptake evaluation when talking about sp^3 % !

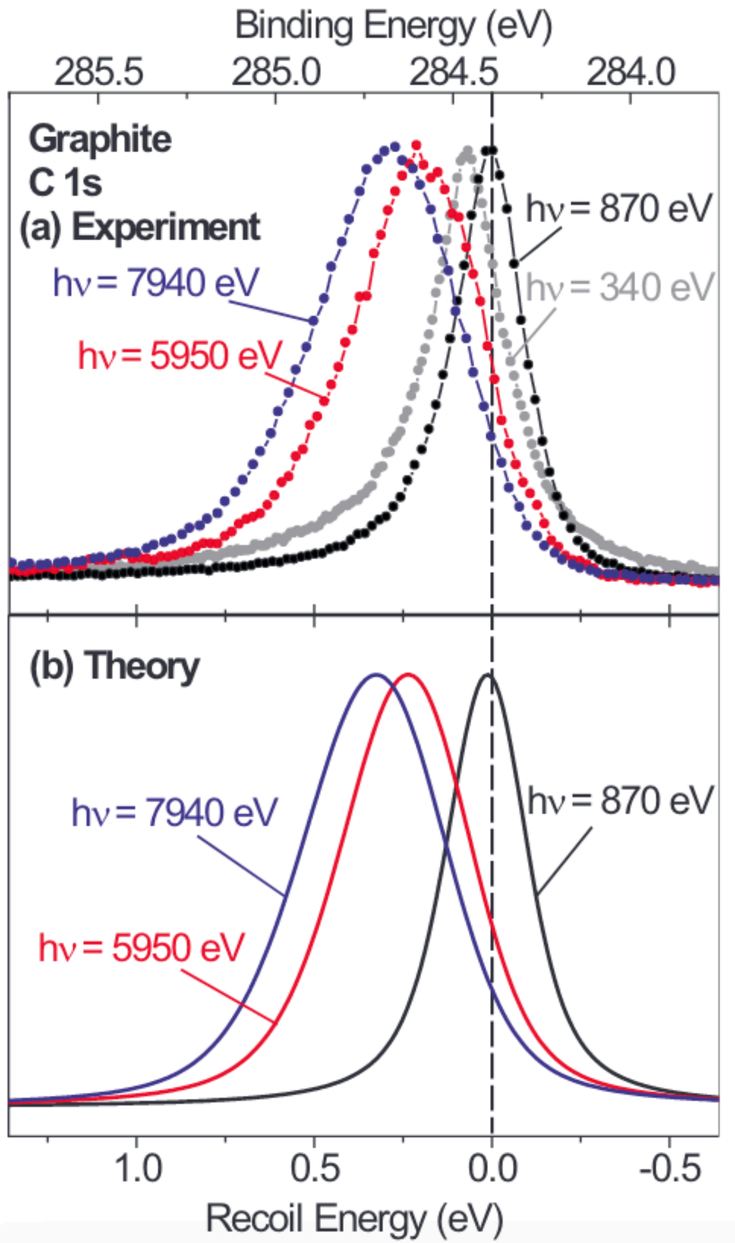




Recoil Effect Visible With Hard X-Rays in Graphite

Recoil effect:

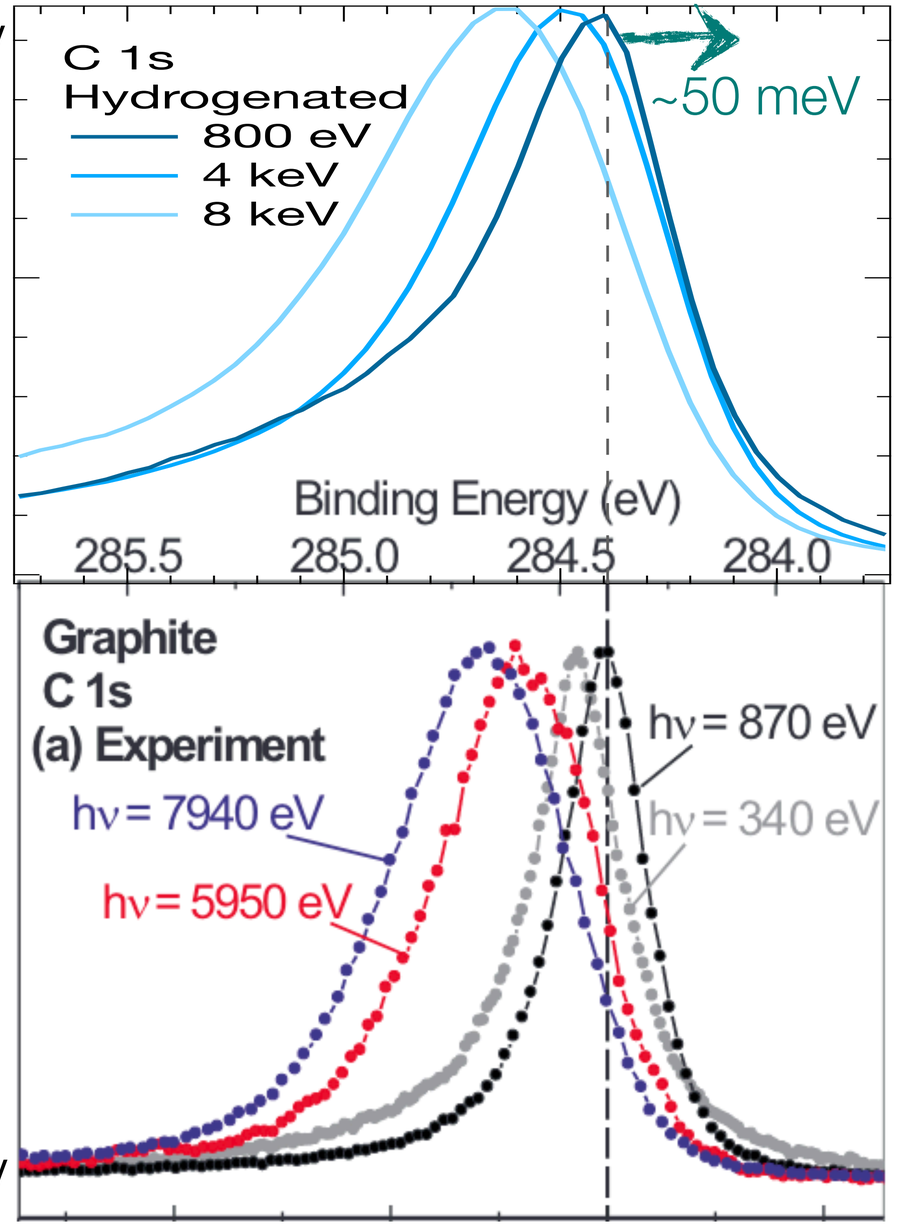
- $E_r = \frac{m}{M} E_k$
- Carbon recoil $\frac{m}{M} = 4.6 \cdot 10^{-5}$
- In hard X-ray regime become sizeable ($E_r = 370$ meV for hν = 8 keV)
- In solids:
  - rigid shift (free atom recoil)
  - asym. broadening (phonon excitation)



PRB **75**, 233404 2007 doi:10.1103/PhysRevB.75.233404

Shift Compatible With Graphite, Ask Theoreticians for Differences :)

ΔE = 120 meV @ 800 eV
ΔE = 250 meV @ 4 keV
ΔE = 270 meV @ 8 keV



NPG-Graphite Comparison:

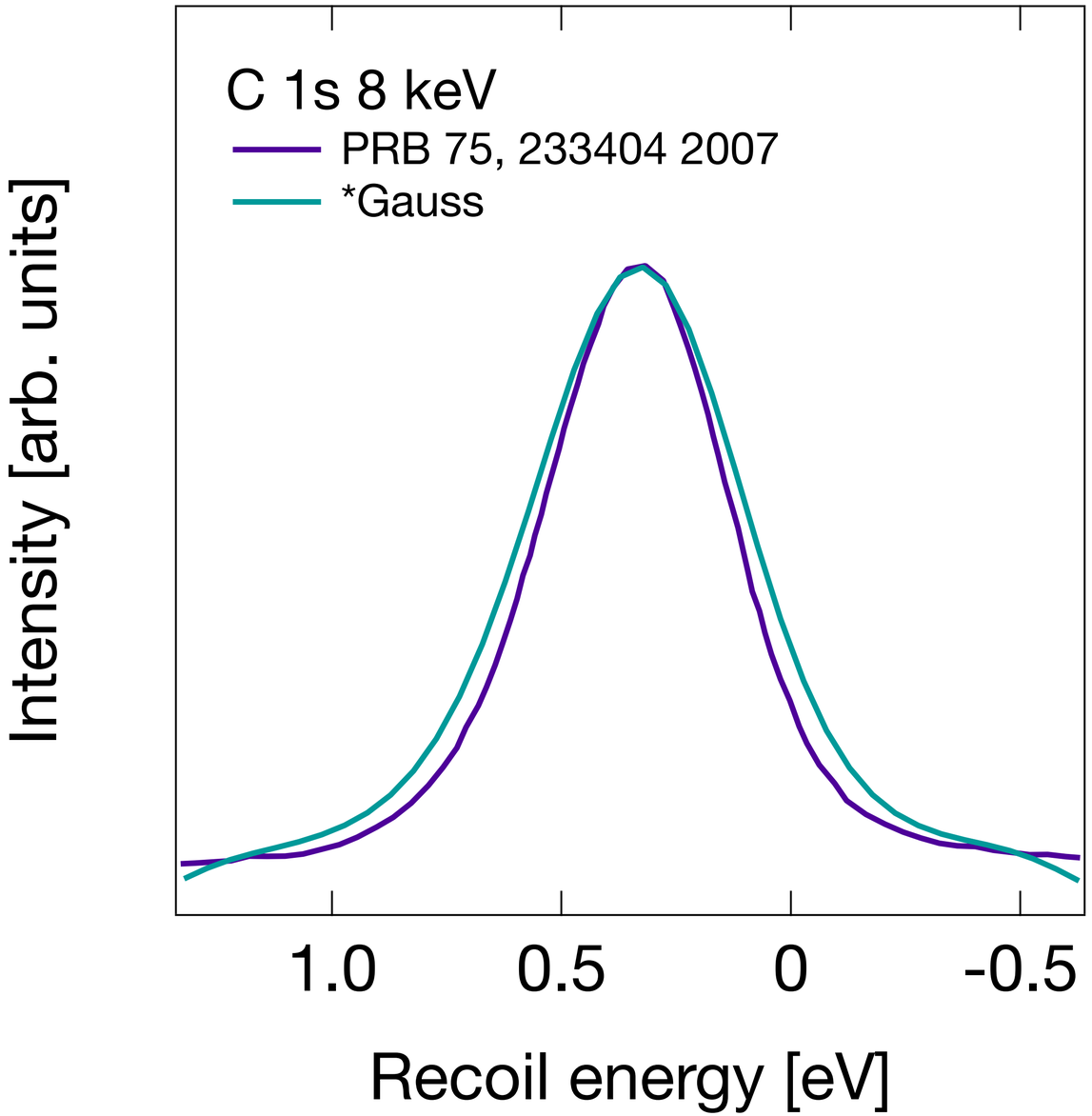
- Different resolution to be taken into account
- NPG shifts ~230 meV @ 8 keV
- Graphite shifts ~280 meV @ 8 keV

ΔE = 100 - 120 meV

Let’s Try to Apply Theo. Model to NPG Data

To apply theo. model with our data:

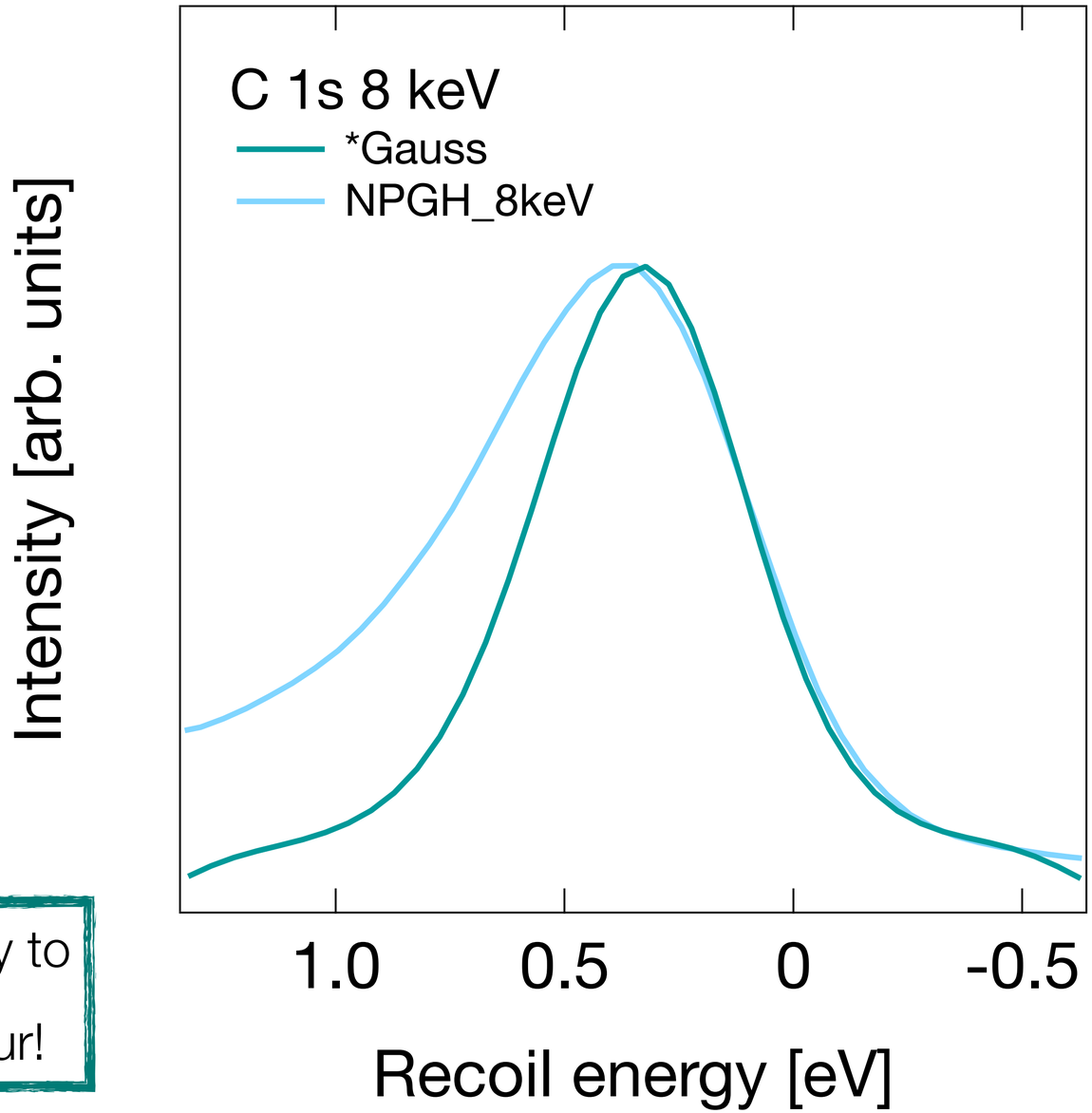
- Energy resolution difference into account
- Convlute graphite theo. model with a gaussian



Energy Resolution Not Enough to Explain the Broadening

NPG hydrogenated data at 8 keV:

- Graphite theo. model convoluted with gaussian accounting for resolution difference
- The energy resolution is not enough to explain the broadening
- Recoil effects seem *larger* for graphene wrt graphite



A specific theoretical model is necessary to explain nanoporous graphene behaviour!

Borrowed From Angelo

SOME IDEAS

- One could avoid working with a "potential" altogether
- Only quantity we really need to know:

$$S(\mathbf{q}_f, \omega_f) = \sum_f \left| \langle \psi_f | \Psi_{\text{bef}} \rangle \right|^2 \rho(\omega_f)$$

- Can we compute from DFT directly this quantity?
- Can we measure it from an experiment with similar momentum exchanged to the system, $\mathbf{q} \sim 100$ keV?

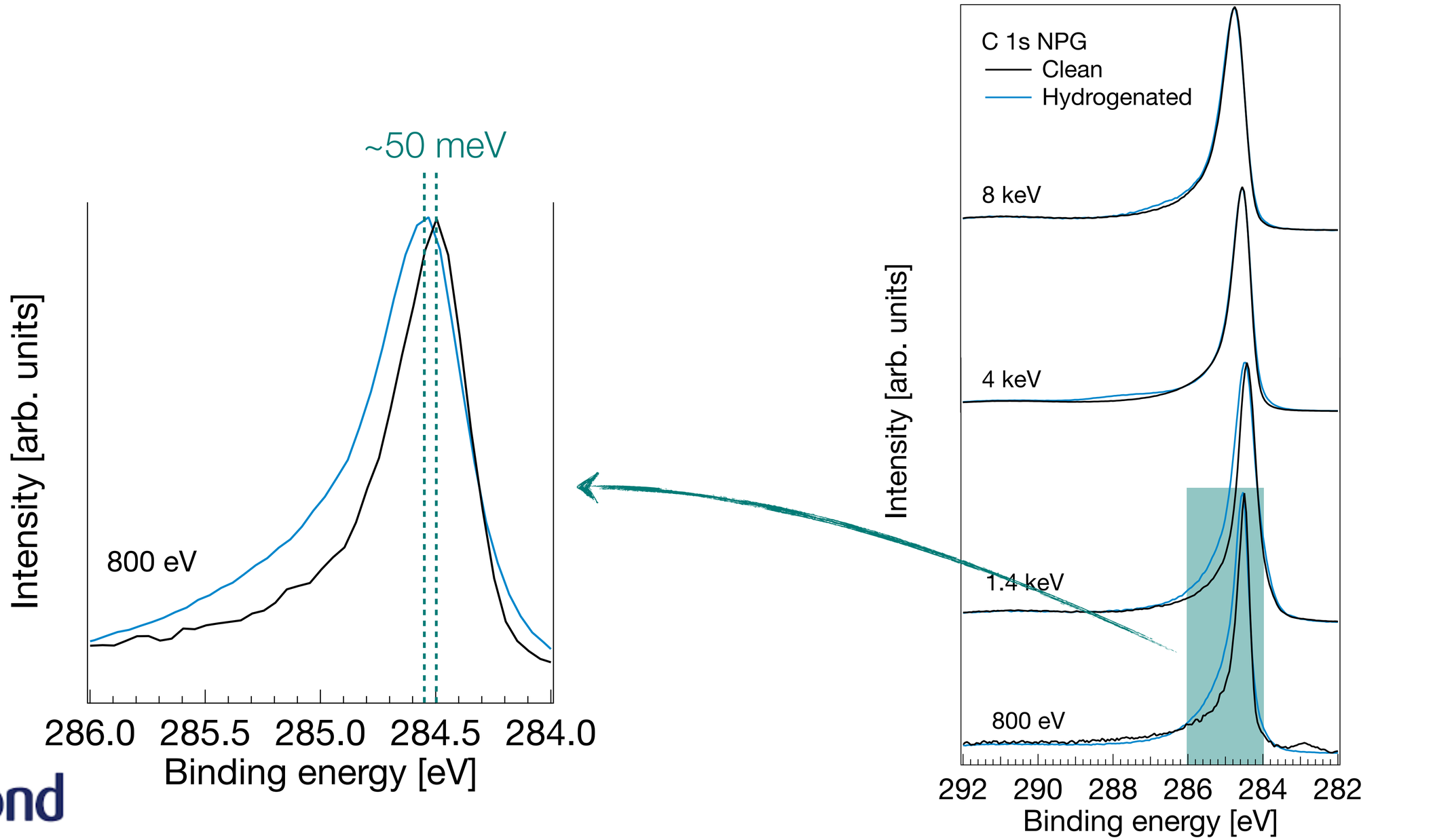
Angelo Esposito SAPIENZA UNIVERSITÀ DI ROMA INFN Istituto Nazionale di Fisica Nucleare 15/22 PPC, May 2024

The answer is YES:

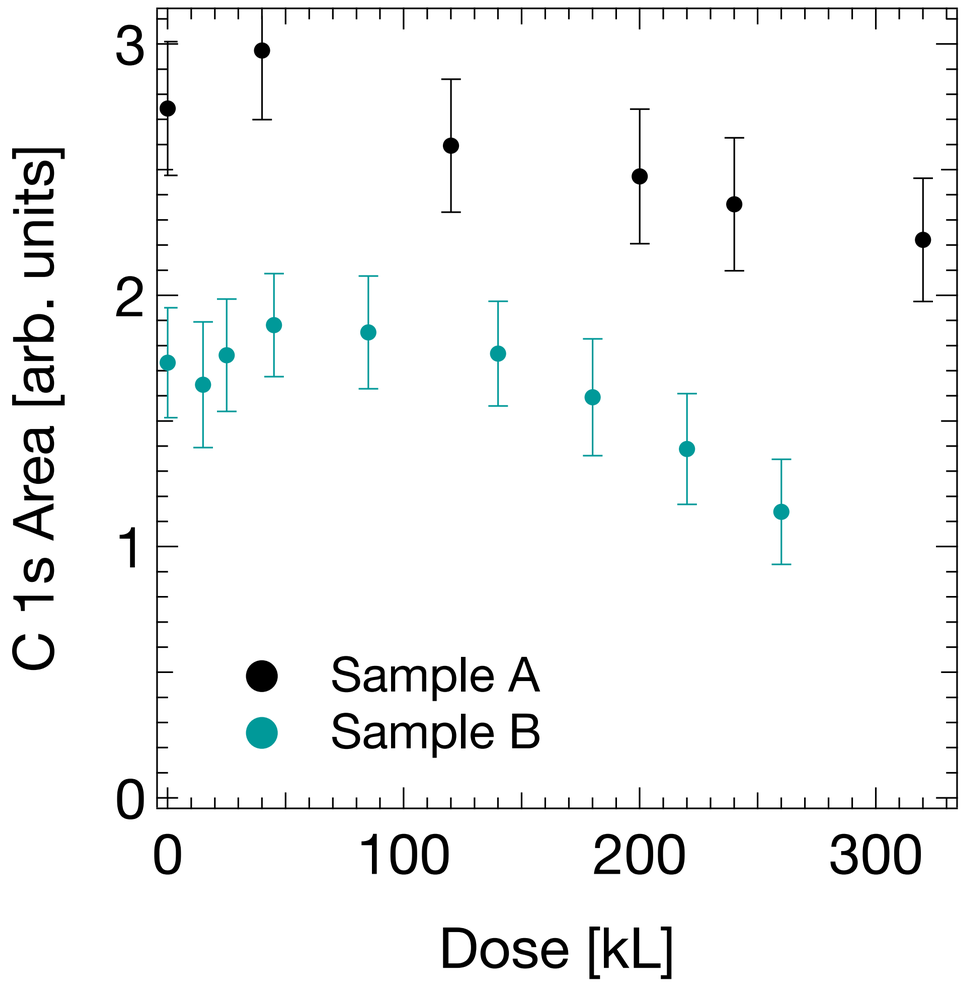
- This is exactly what we do with Hard-XPS
- Lower energy 8 keV
- Slightly different system only carbon without H
- Proposal submitted for hydrogenated monolayer graphene to study the C-H system

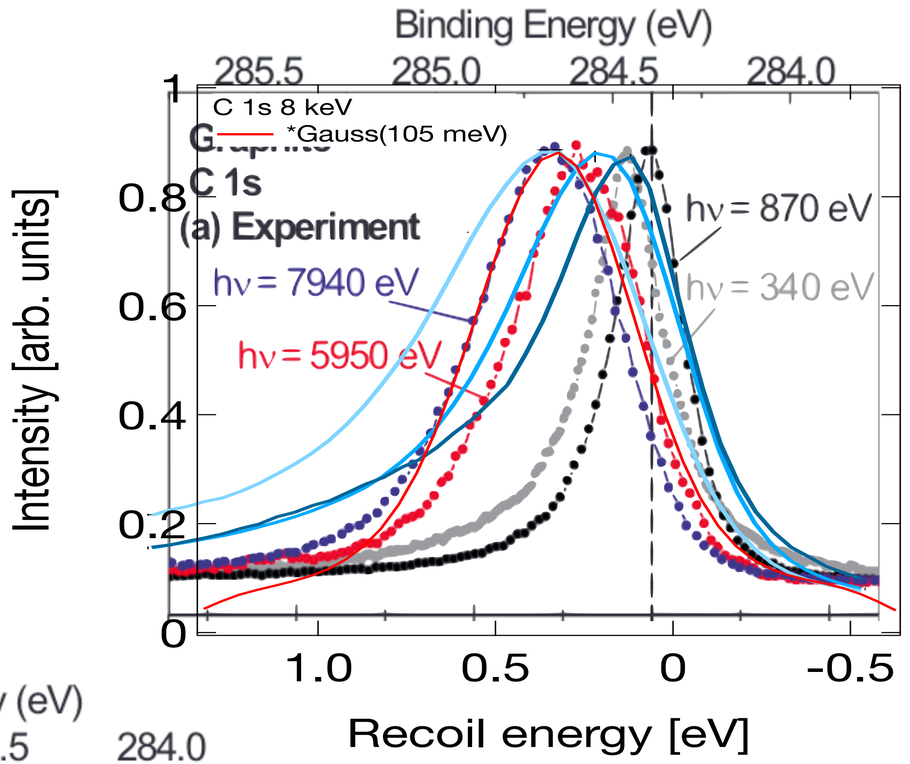
NPG DATA ARE A PROMISING GYM FOR THEORY!

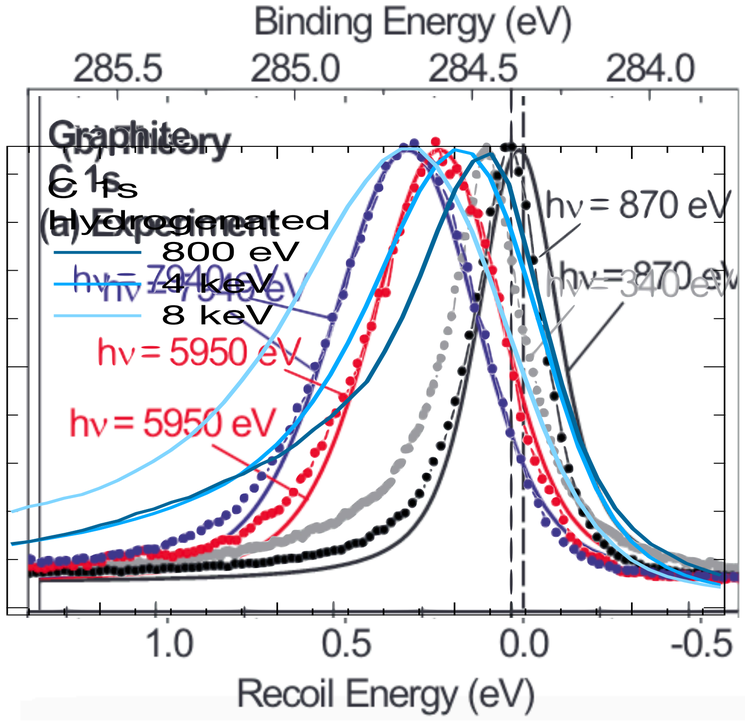
Remember This 50 meV Shift for Later!



Total C 1s Area Decreases With H Exposure




Binding Energy (eV)
285.5
285.0
284.5
284.0
C 1s 8 keV
*Gauss(105 meV)
Graphite
C 1s
(a) Experiment
hν = 7940 eV
hν = 5950 eV
hν = 870 eV
hν = 340 eV
Intensity [arb. units]
1
0.8
0.6
0.4
0.2
0
1.0
0.5
0
-0.5
Recoil energy [eV]


Binding Energy (eV)
285.5
285.0
284.5
284.0
Graphite
C 1s
(a) Experiment
(b) Theory
800 eV
4 keV
8 keV
hν = 7940 eV
hν = 5950 eV
hν = 5950 eV
hν = 870 eV
hν = 870 eV
1.0
0.5
0.0
-0.5
Recoil Energy (eV)