Exploring VACNT Anisotropy through Angle Resolved Electron Emission

Do the nanotubes tube?

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ROMA TRE UNIVERSITÀ DEGLI STUDI

ANDROMEDA

Aligned Nanotube Detector for Research On MeV Darkmatter

INFN Istituto Nazionale di Fisica Nucleare

Experimental setups

Photoemission

UV photon source: He I: 21.22 eV
He II: 40.8 eV

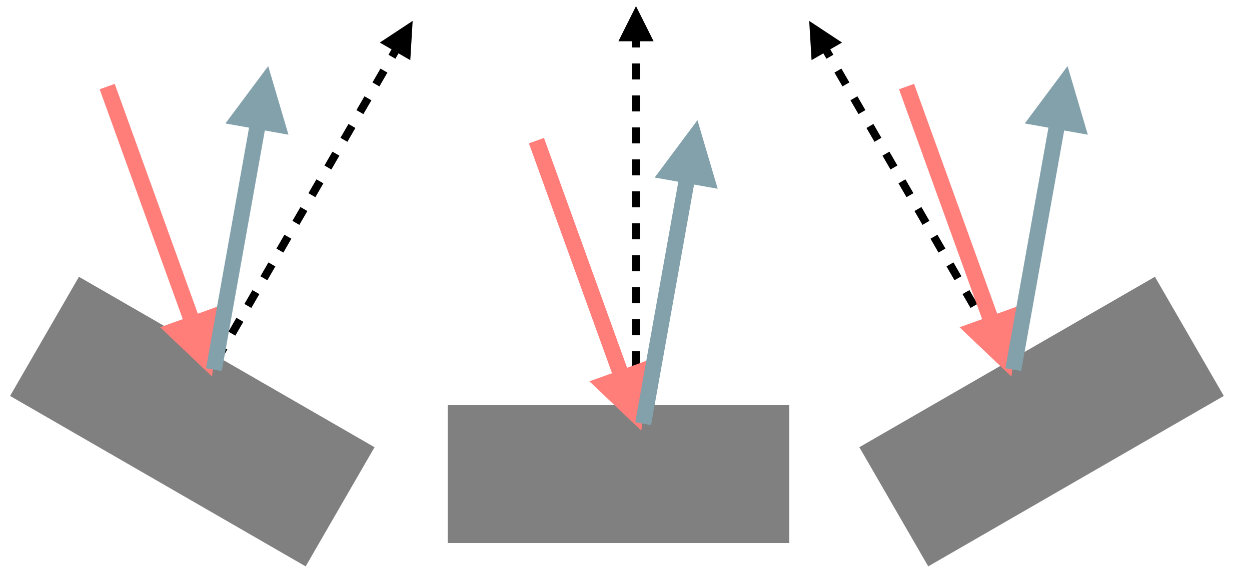
Hemispherical Electron Analyzer

Collects photoemitted electrons

Selected in E_k

Spectrum

The sample rotates



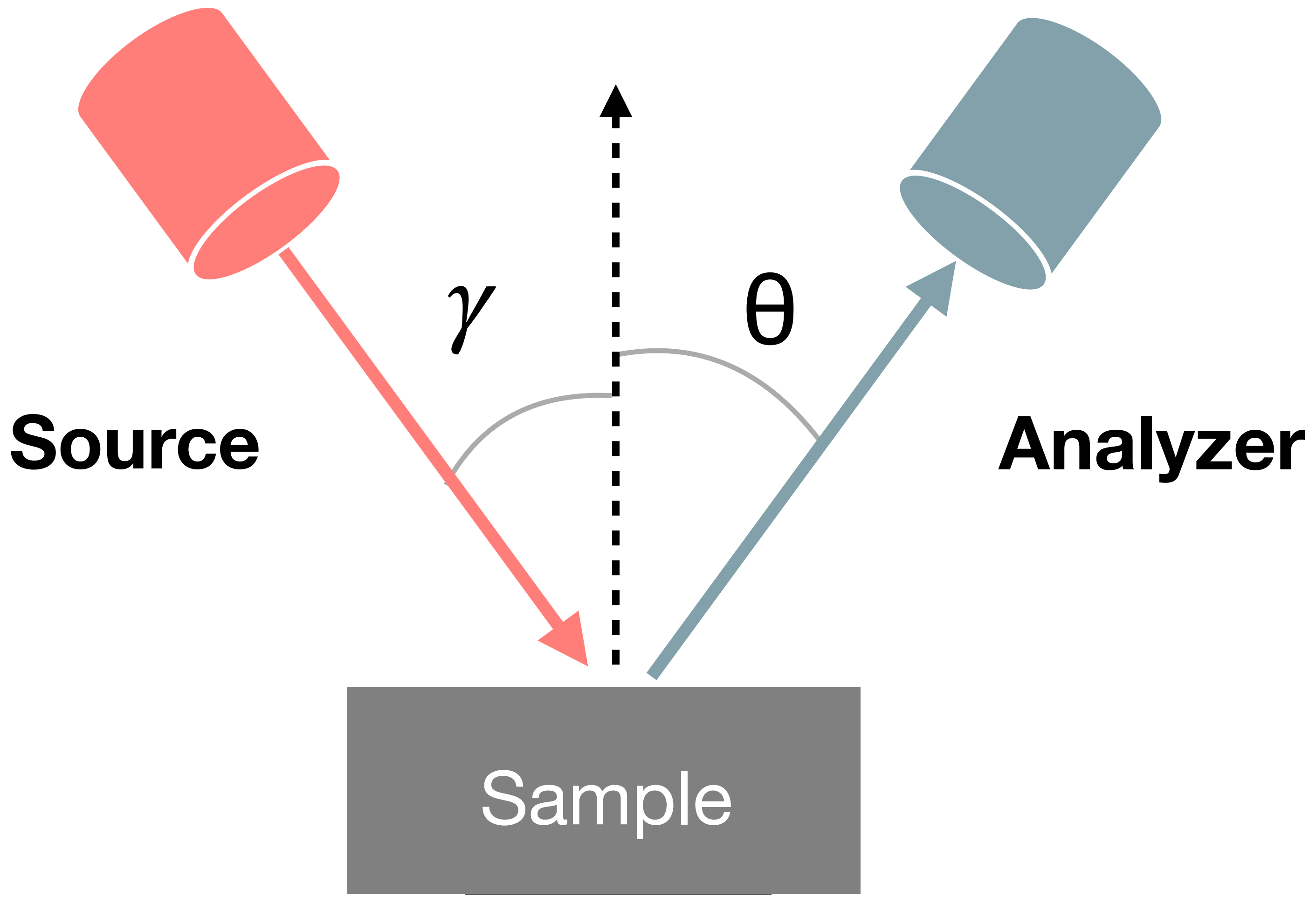
Electron scattering

Monochromatic electron gun

Primary electrons:
KE 90 ± 0.05 eV

Hemispherical Electron Analyzer

Collects elastically backscattered electrons:
KE 90 ± 0.09 eV



Source and Analyzer are at a fixed angle:

$$\gamma + \theta = 30\,°$$

Compare VA-CNTs to isotropic samples

RO-Graphite

Randomly oriented graphite sheets

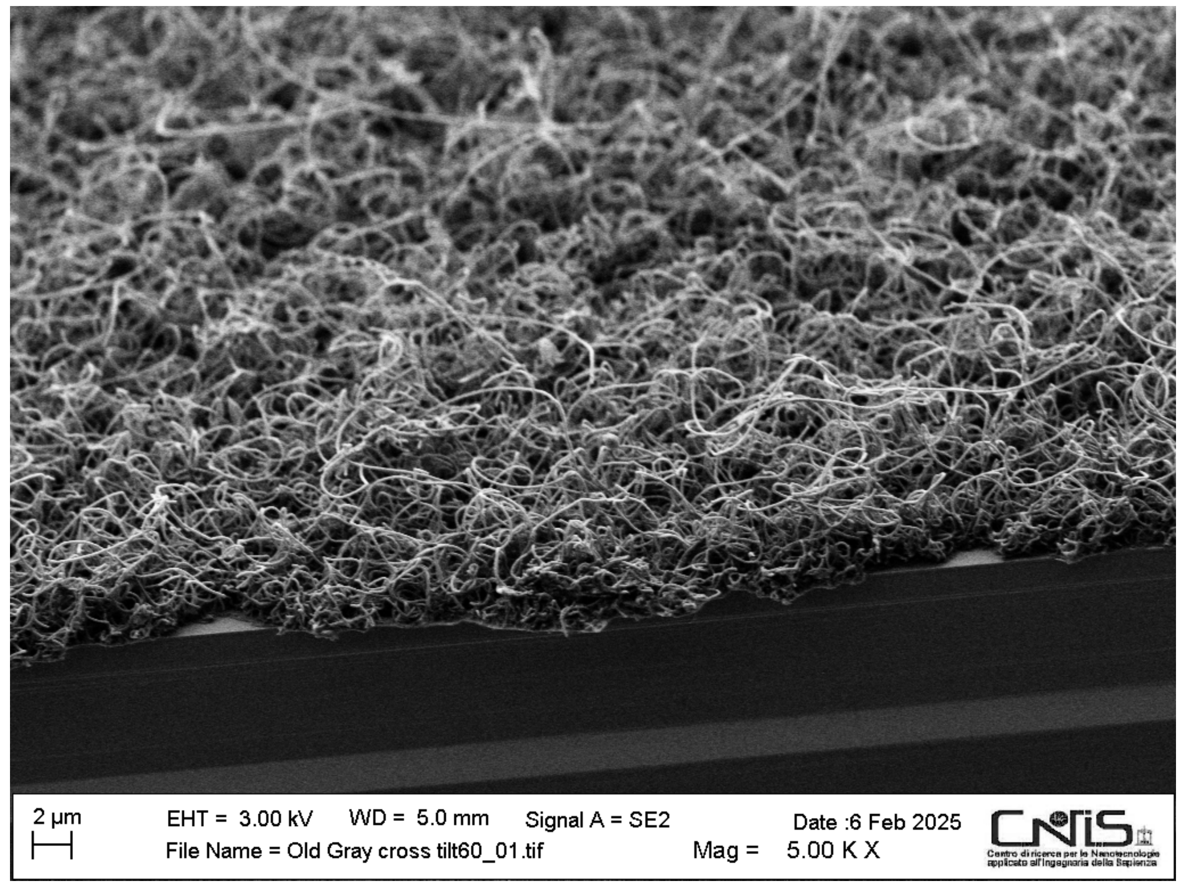
(TAAB c107 colloidal graphite, Aquadag)

\+ bonus **ARCAP** sample holder

(amorphous Copper / Nickel alloy)

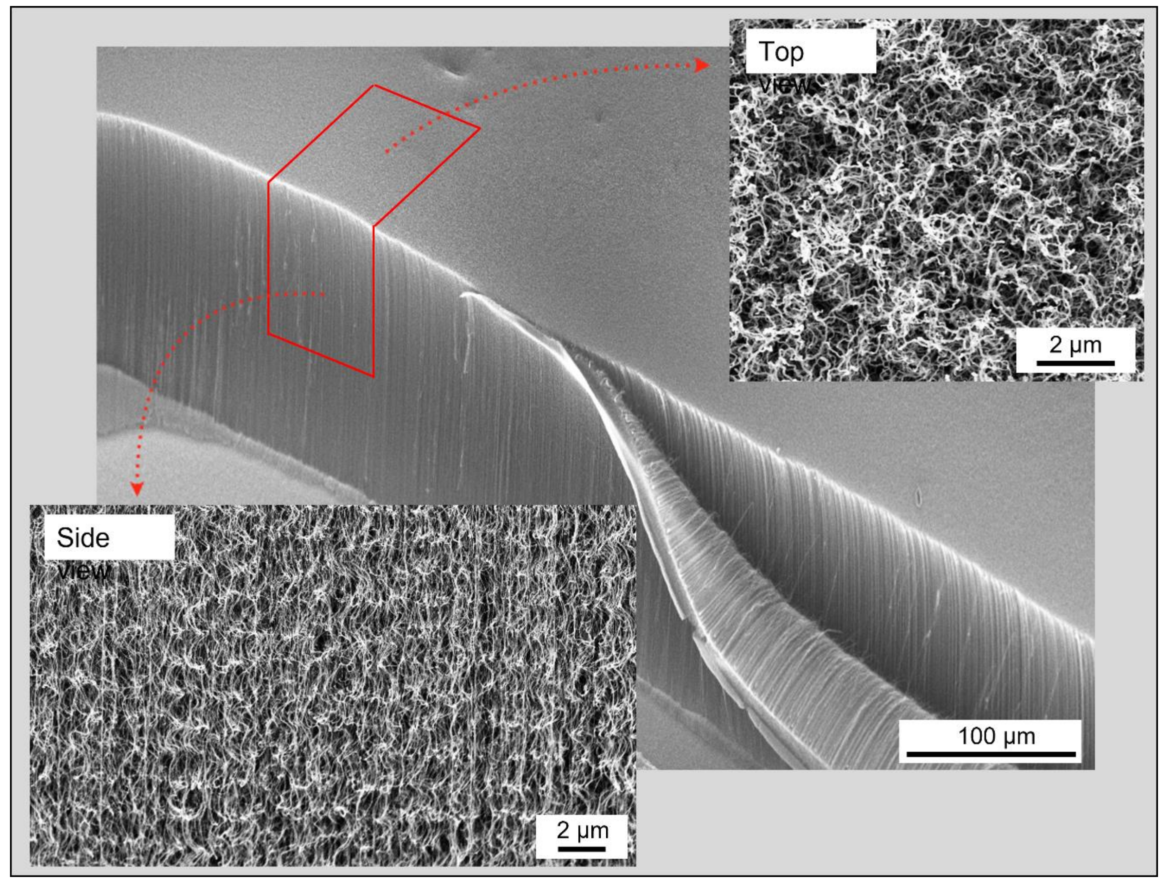
RO-CNT

Randomly oriented carbon nanotubes

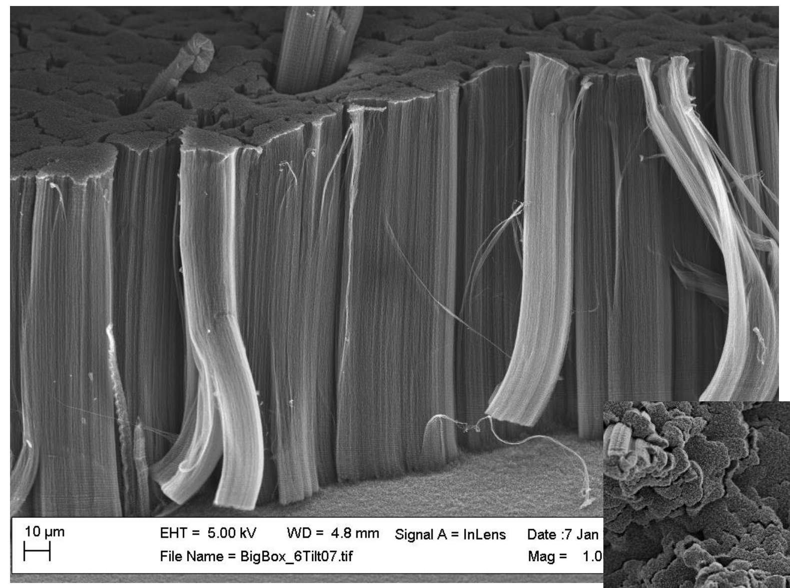


VA-CNT

- As grown

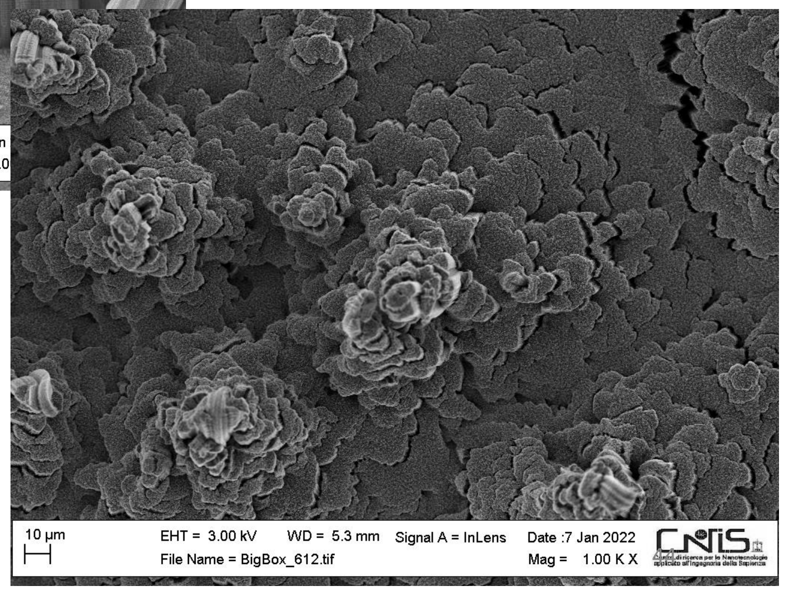


- Mild Etched

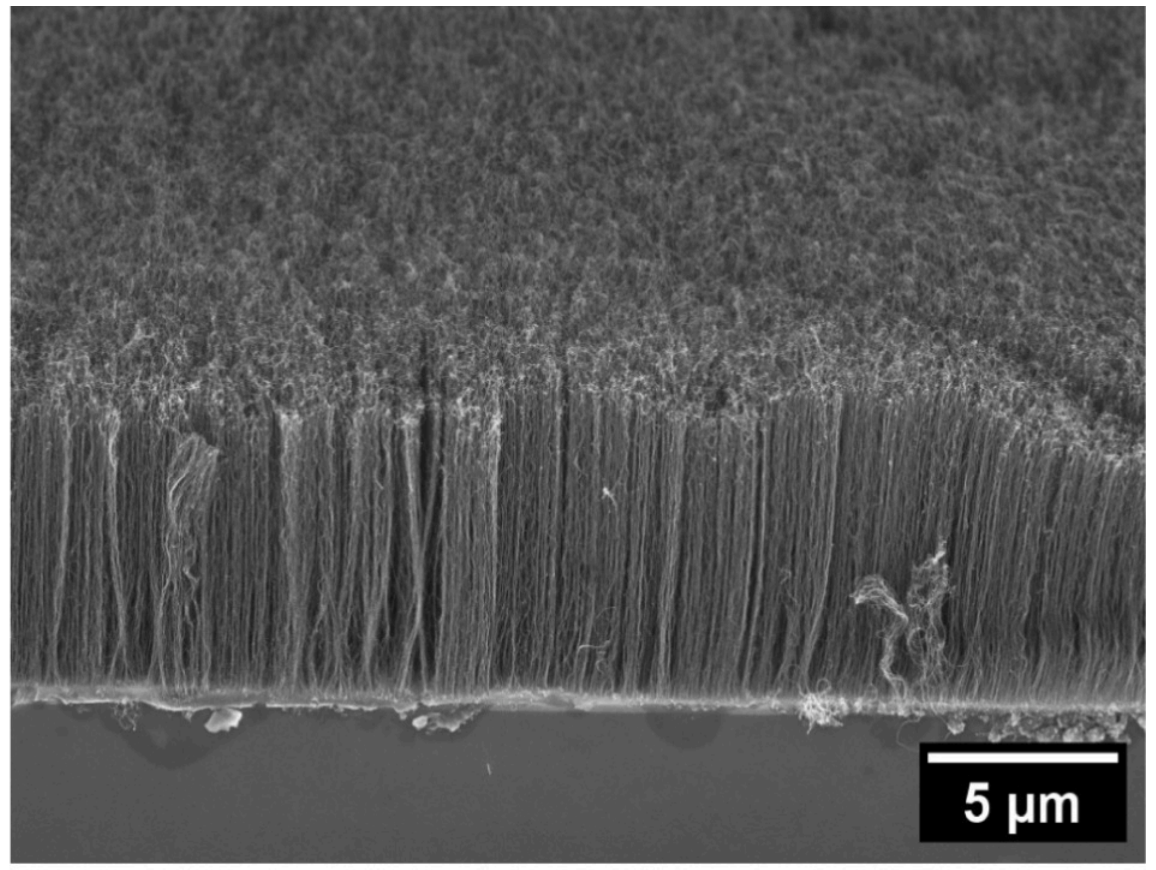


Ar/O_2 Etching parameters:

Ar: 10 sccm
O_2: 2 sccm
Pressure: 200 mTorr
Power: 35 W
Time: 5 min

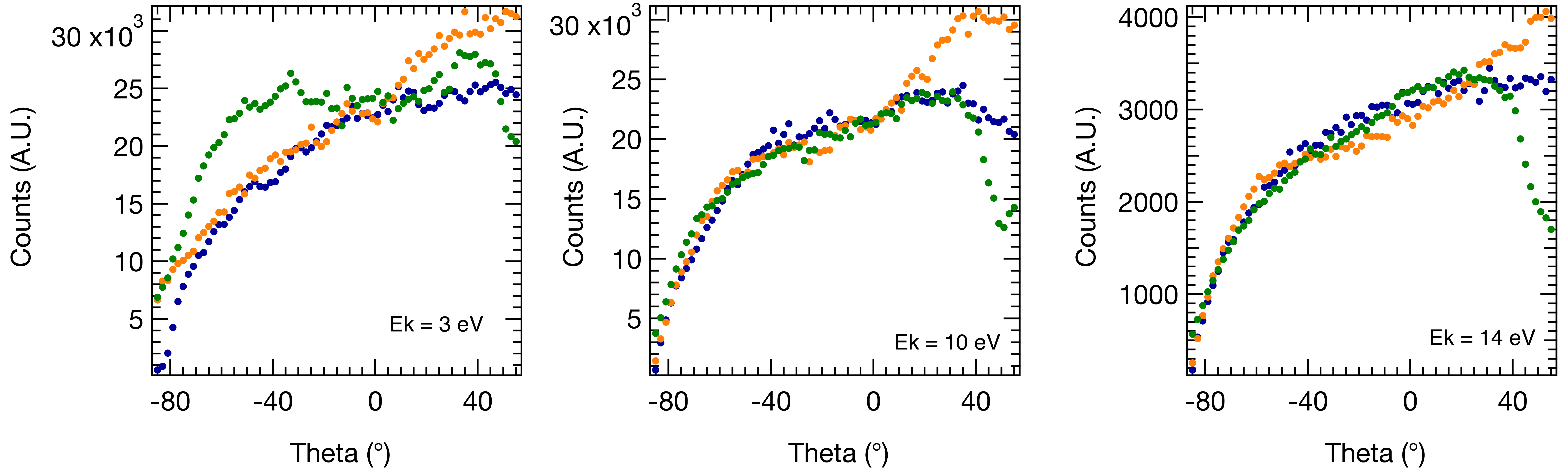


- Plasma Enhanced



Photoemission from Randomly Oriented (RO) carbon and Vertically Aligned (VA) CNTs

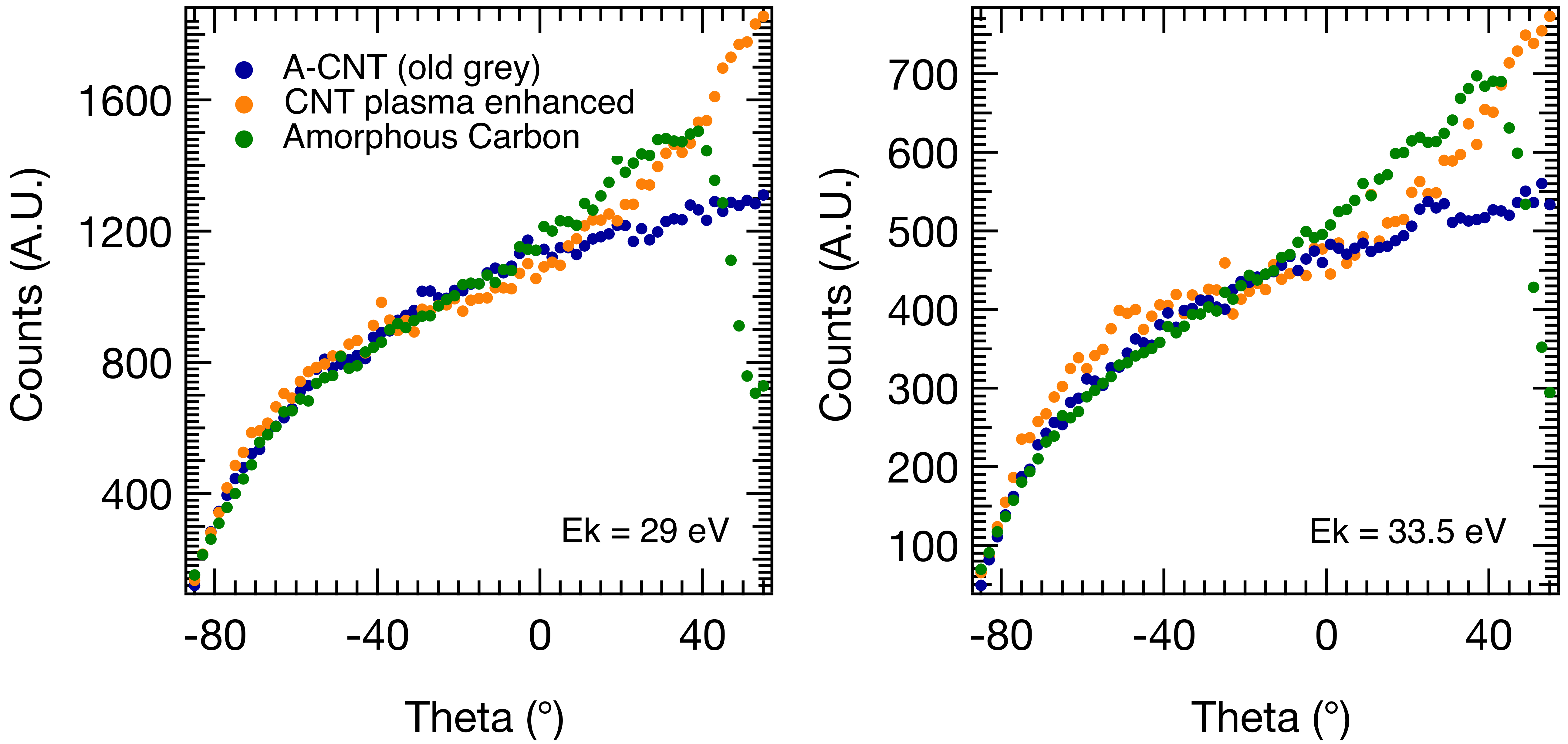
Measurements are not so simple to read



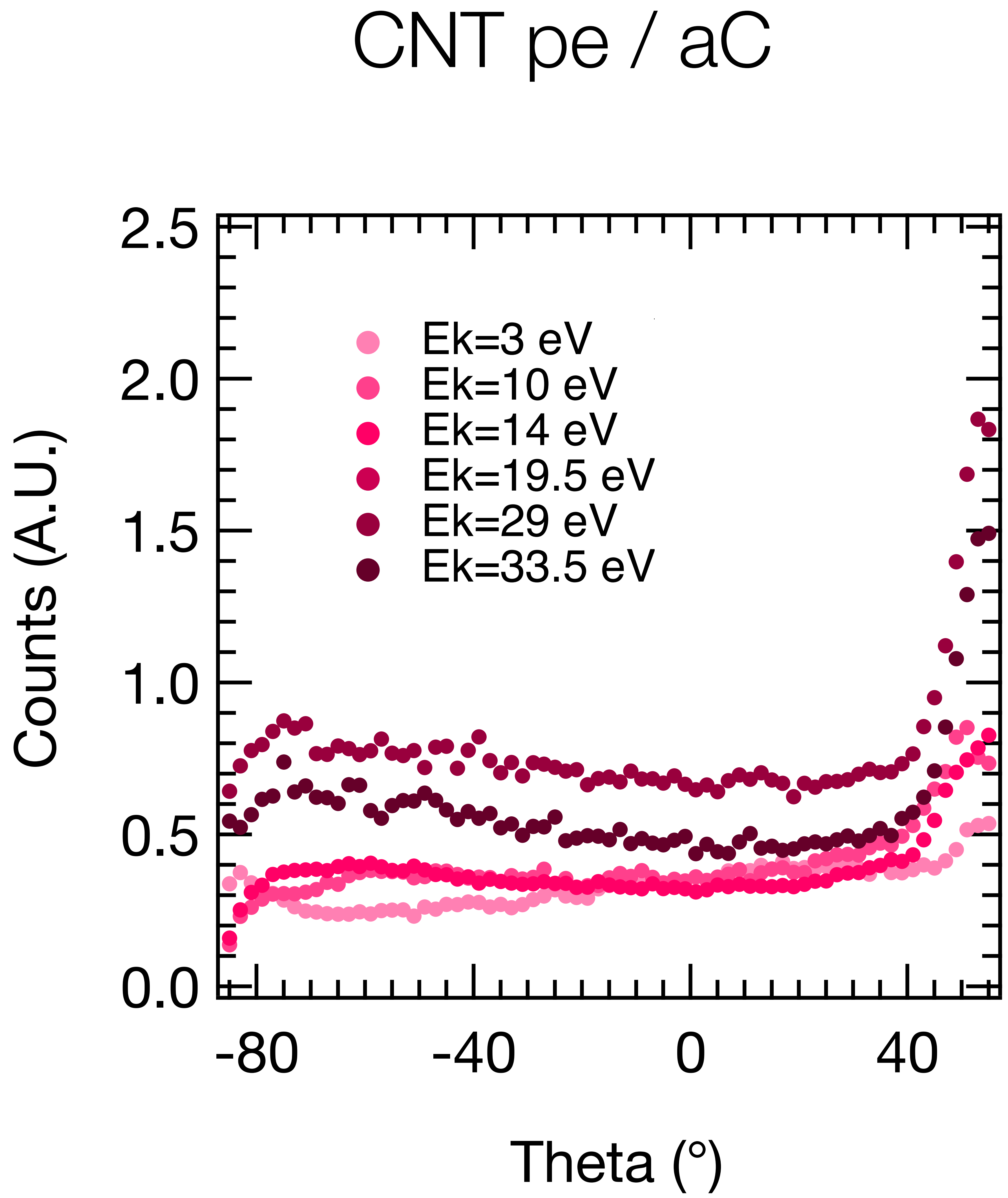
Not symmetric with respect to θ=0

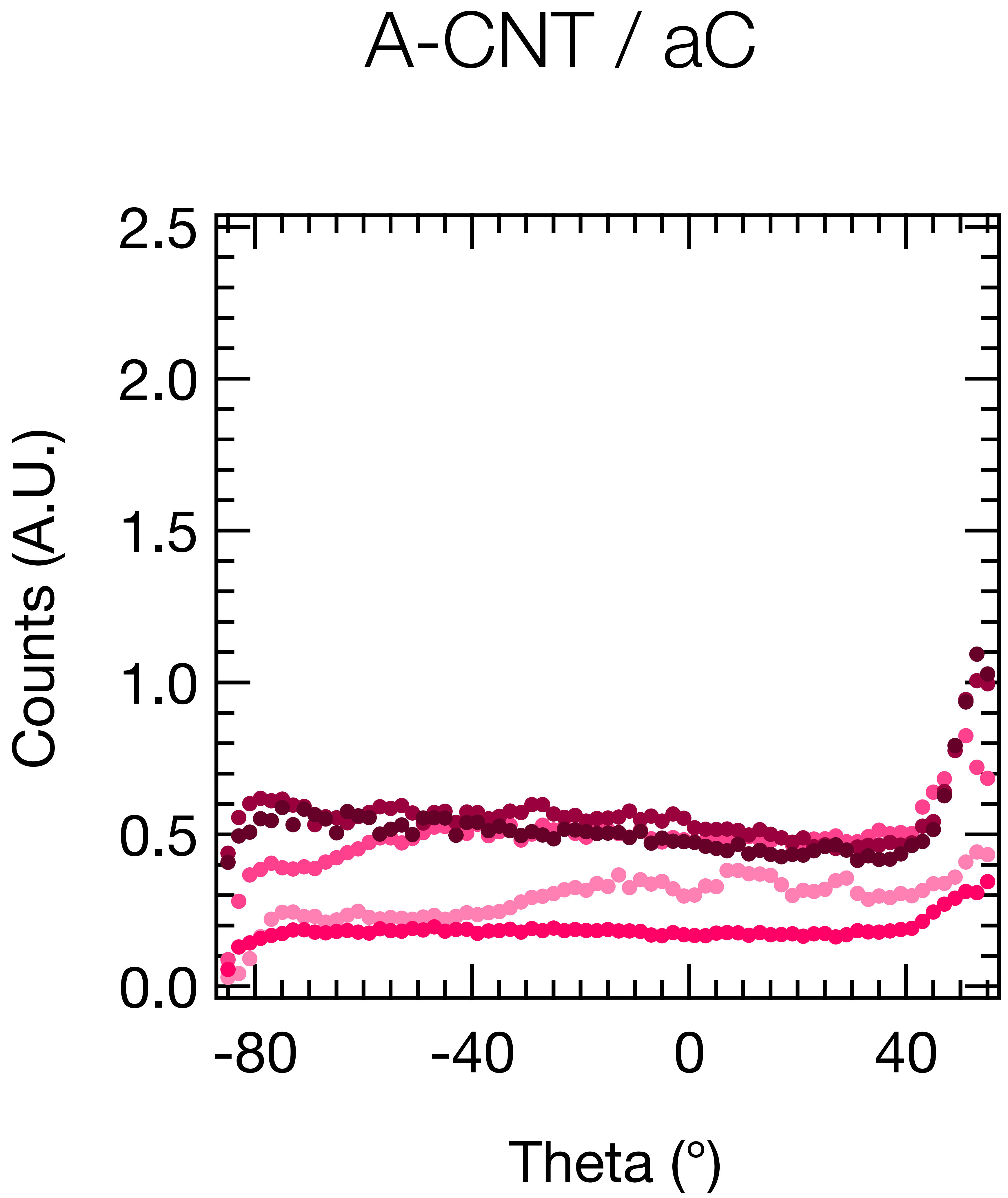
At θ -> θ_{max}
(grazing photon incidence)

- Graphite decreases
- A-CNT slowly increase
- CNT pe have an enhancement



CNTs have a grazing incidence enhancement wrt amorphous Carbon

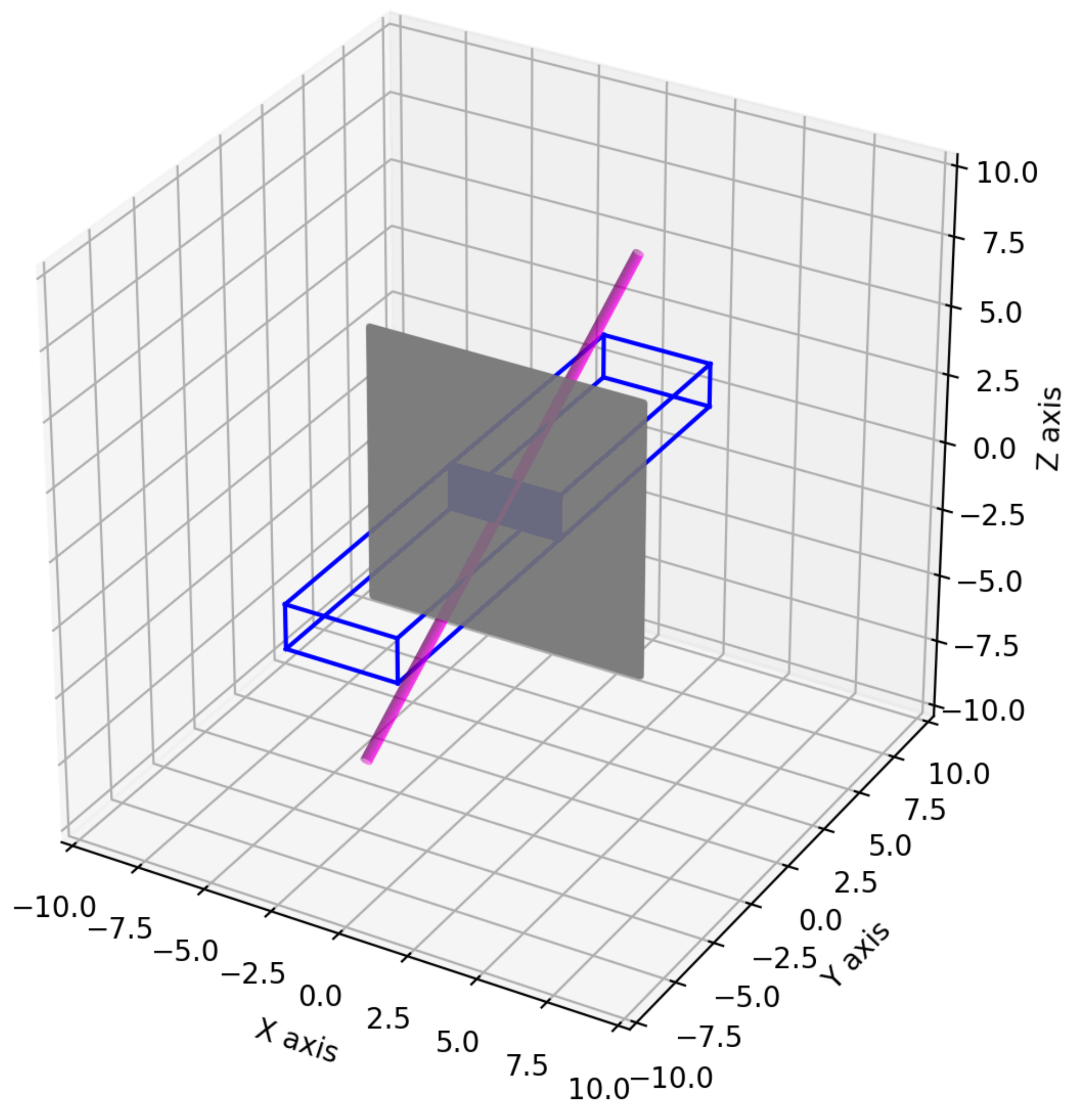




Ingredients for a theoretical model

Geometry

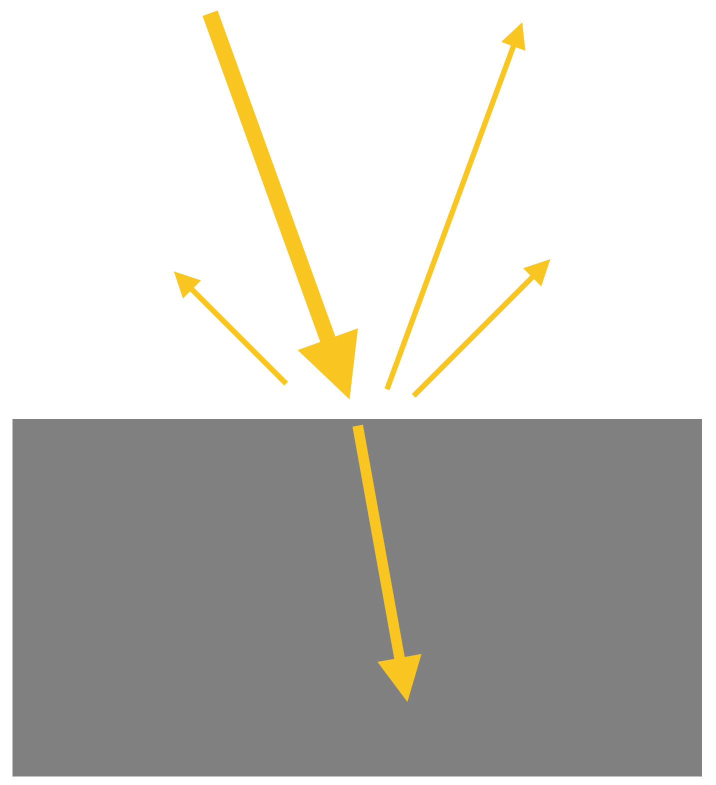
UV beam - Sample - Field Of View Intersections



Physics

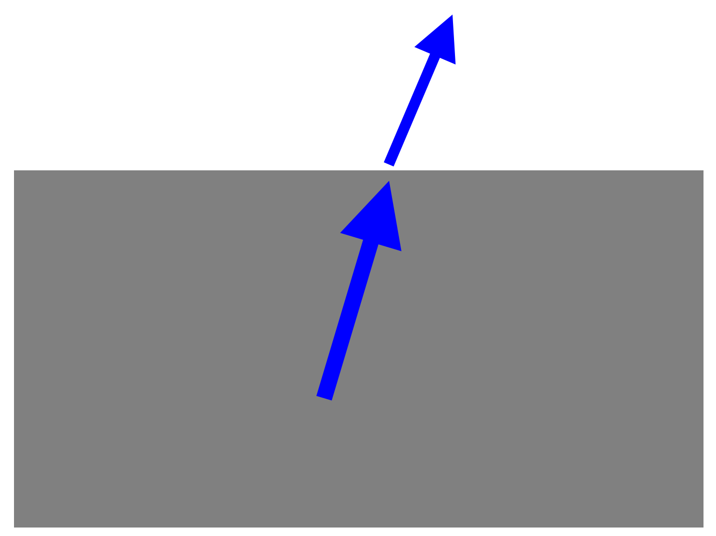
Interaction of UV photons with matter

- Reflection / surface diffusion
- Refraction
- Transmission



Interaction of photoelectrons with matter

- Transmission
- Refraction



Trying to get rid of photon dependence

$$\frac{I^1_{pe}(\theta)}{I^2_{pe}(\theta)}$$

with 1, 2 different sample depends on both reflection, UV and e^- transmission

$$\frac{I^1_{pe}(\theta)}{I^{1'}_{pe}(\theta)}$$

For E_k, $E_{k'}$ different electron energy is simpler

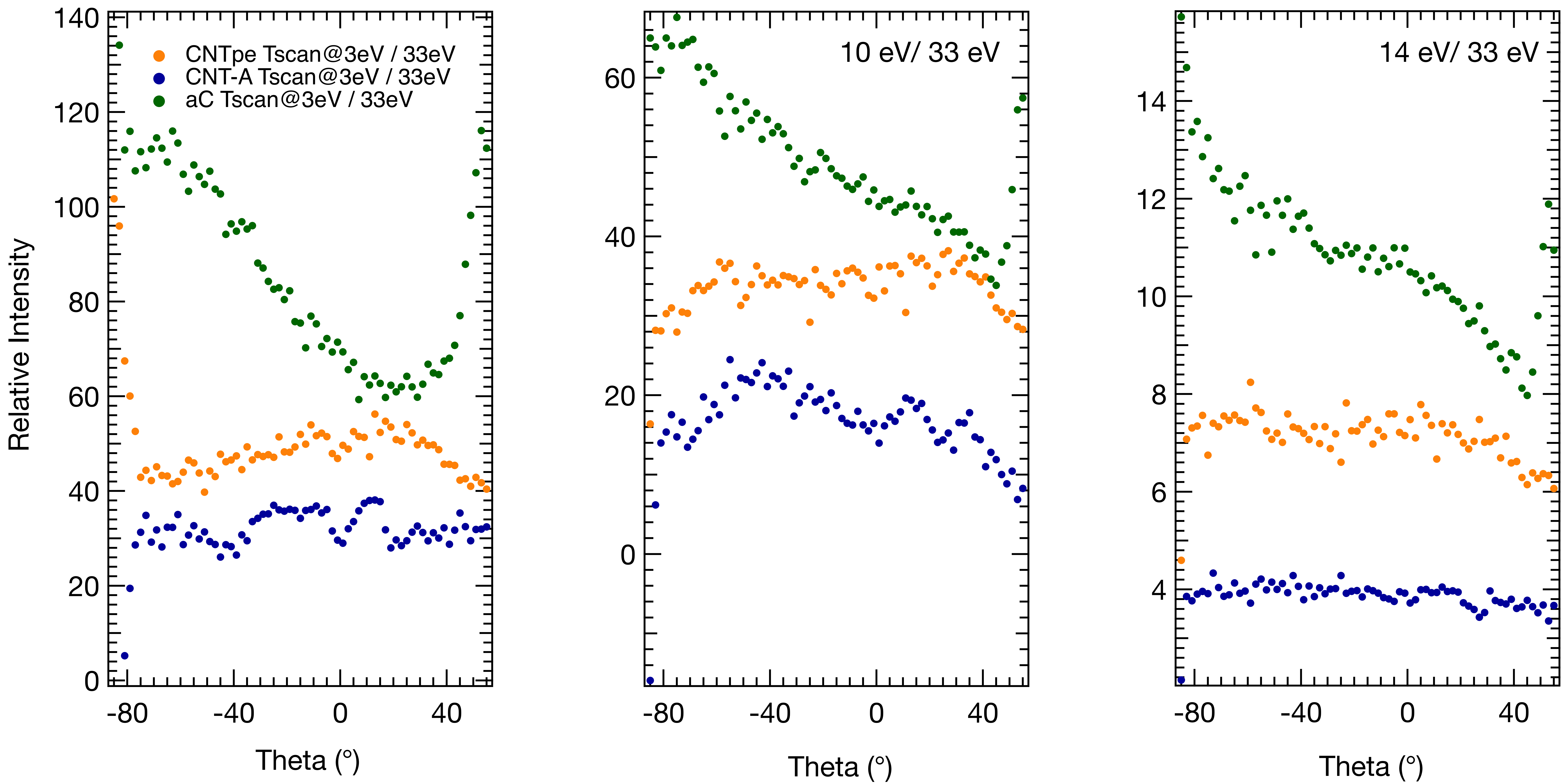
$$\propto \frac{V}{V'} \cdot \frac{\lambda'_e(\lambda_{\gamma,\mathrm{eff}} + \lambda_e \cos\theta)}{\lambda_e(\lambda_{\gamma,\mathrm{eff}} + \lambda'_e \cos\theta)}$$

FoV dimension is not the same (for these measurements…)

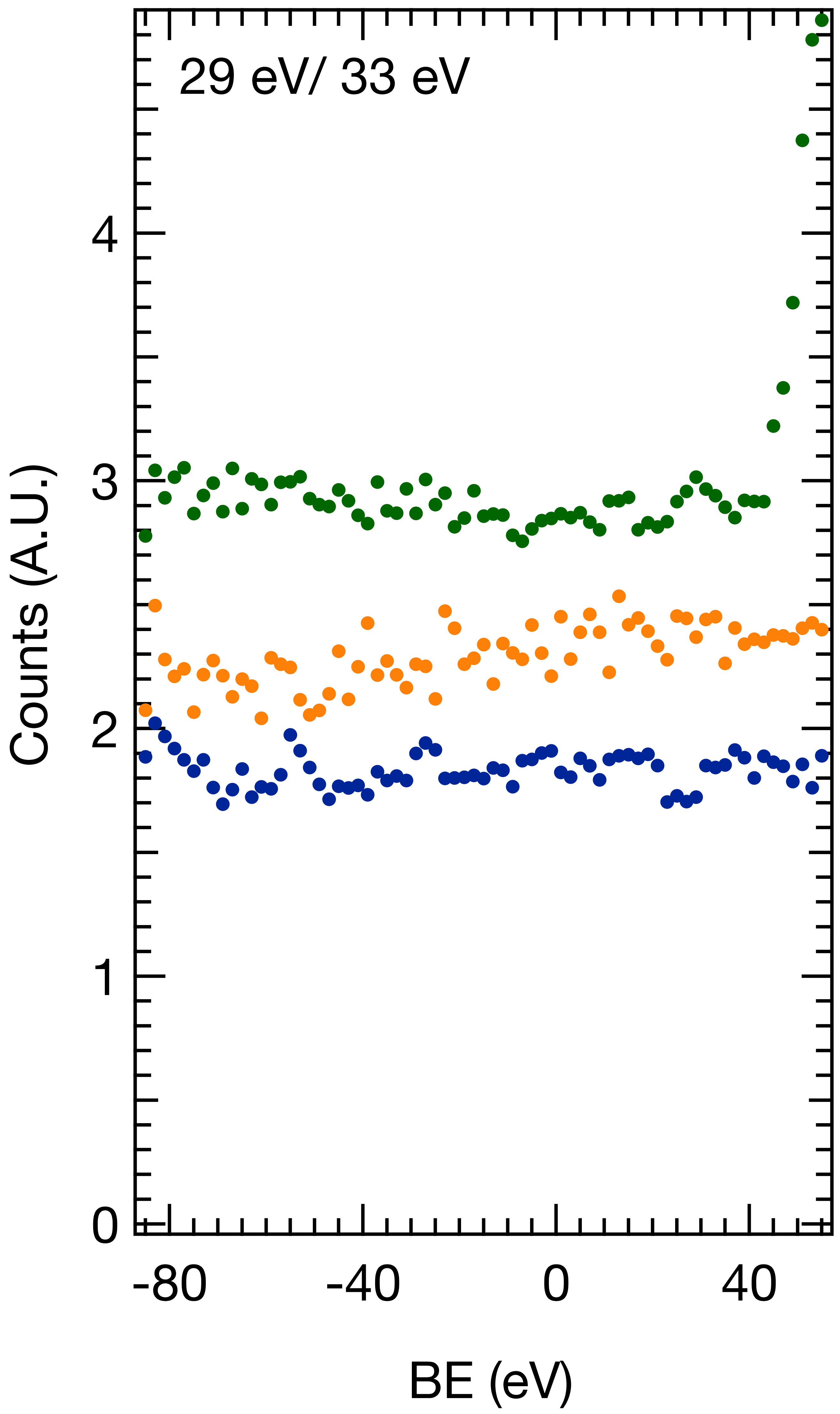
The angular dependence which is energy independent is eliminated

CNTs seems both different from amorphous carbon*

* for $E_k < 16$ eV, hv = a*20.21 + b*40.8 (Mixture of He I and He II photons, a and b are each time different)



For $E_k \sim E_{k'}$ no information on the angular dependence



At $E_k > 16$ eV (Fermi Level fo He I) only He II photon contribution

$$\frac{I^{1}_{pe}(\theta)}{I^{1'}_{pe}(\theta)}$$

Do not depends on photon flux

(It depends on photoemission cross section and detector efficiency)

Obviously for $E_k \sim E_{k'}$

$$\frac{\lambda'_e(\lambda_{\gamma,\mathrm{eff}} + \lambda_e \cos\theta)}{\lambda_e(\lambda_{\gamma,\mathrm{eff}} + \lambda'_e \cos\theta)} \sim 1$$

What about secondary electrons?

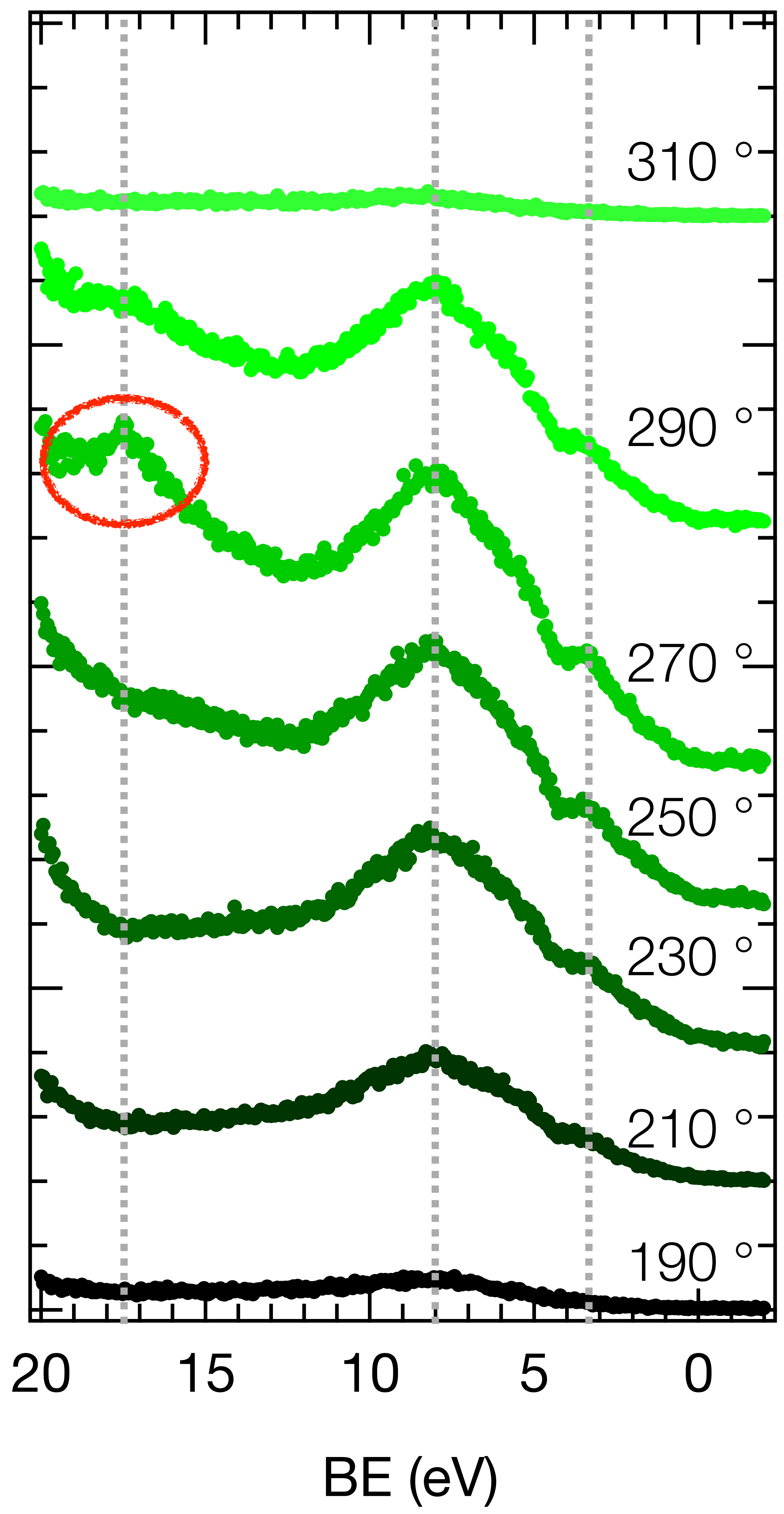
Are we measuring them?

Do they have angular dependence

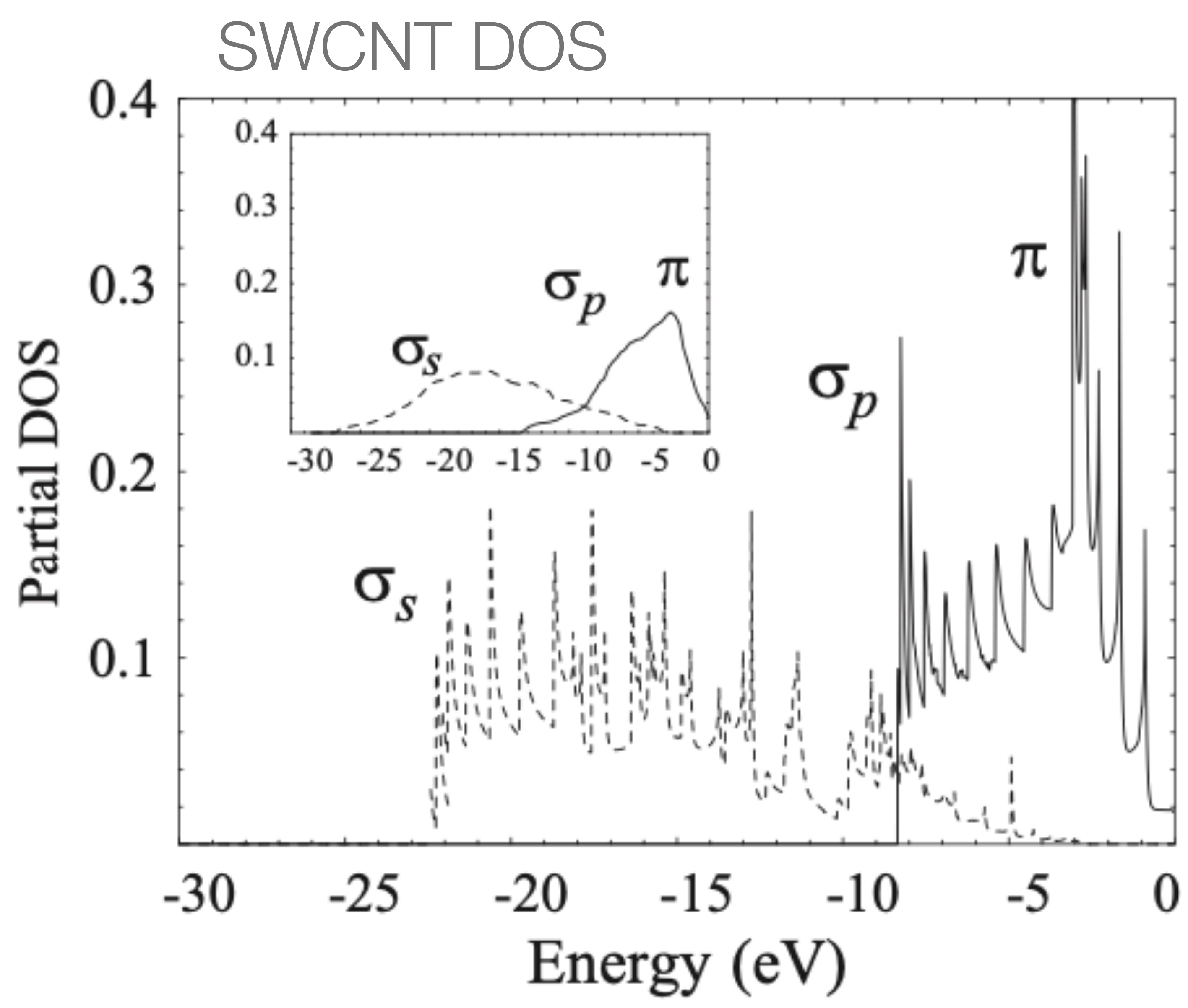
Can we disentangle them from
“primary” photoelectrons?

ARPES: CNT as grown vs CNT plasma etched

CNT plasma etched

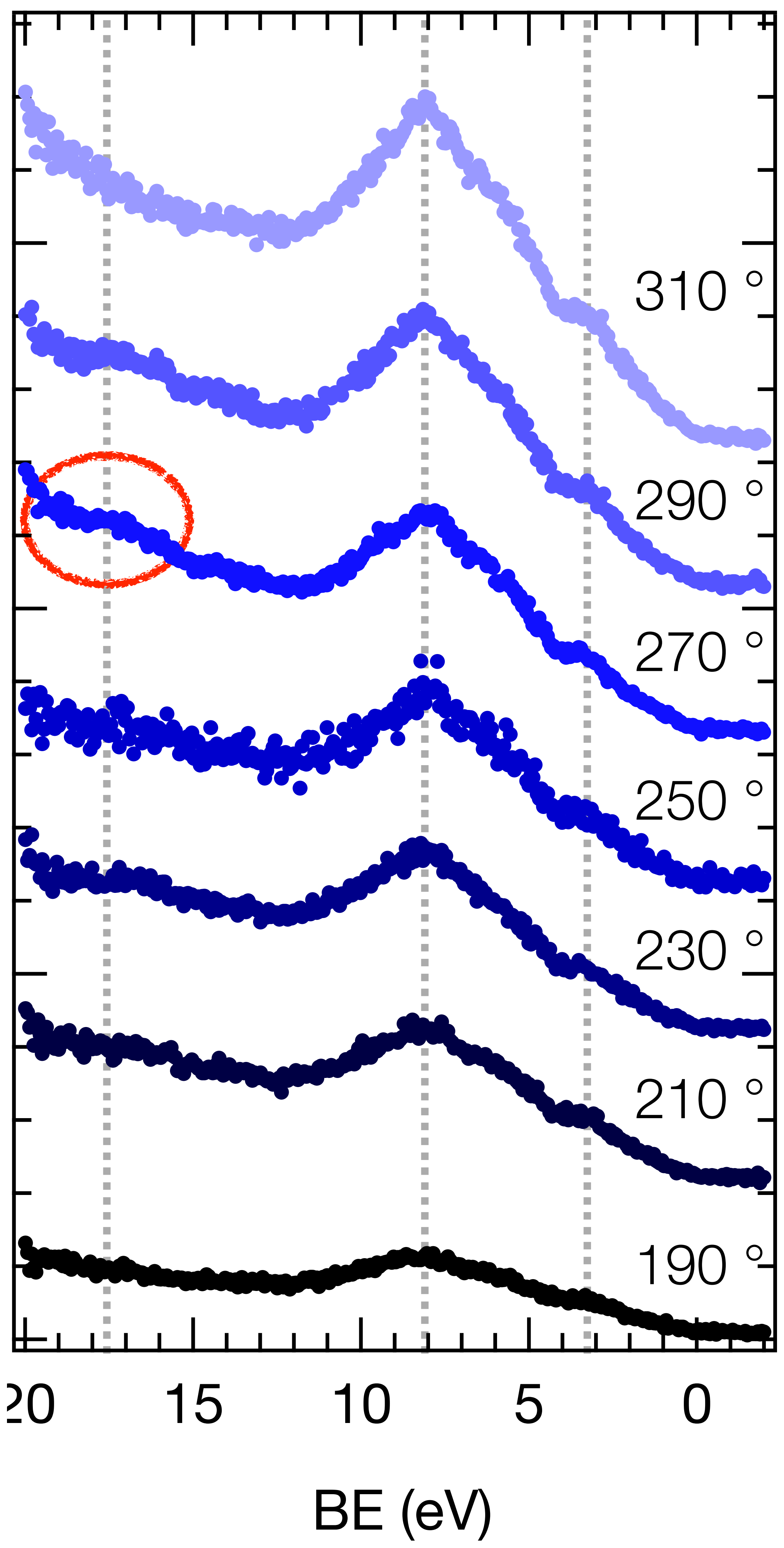


- No clear band dispersion for BE < 10 eV
- At BE = 17.5 eV a component rises near normal emission condition

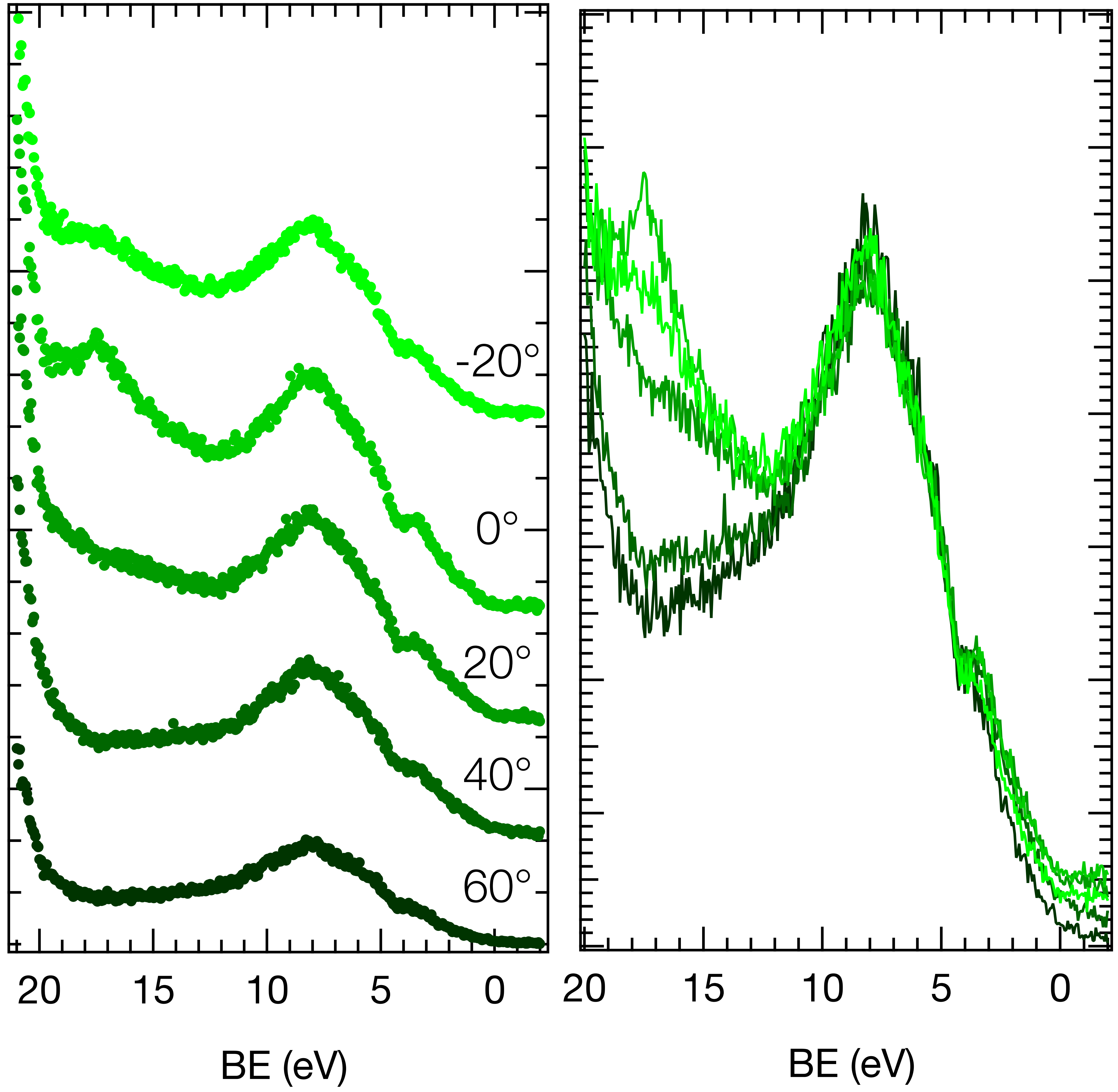


DOI: 10.1103/PhysRevB.76.233408

CNT as grown



State dispersion has been observed in literature



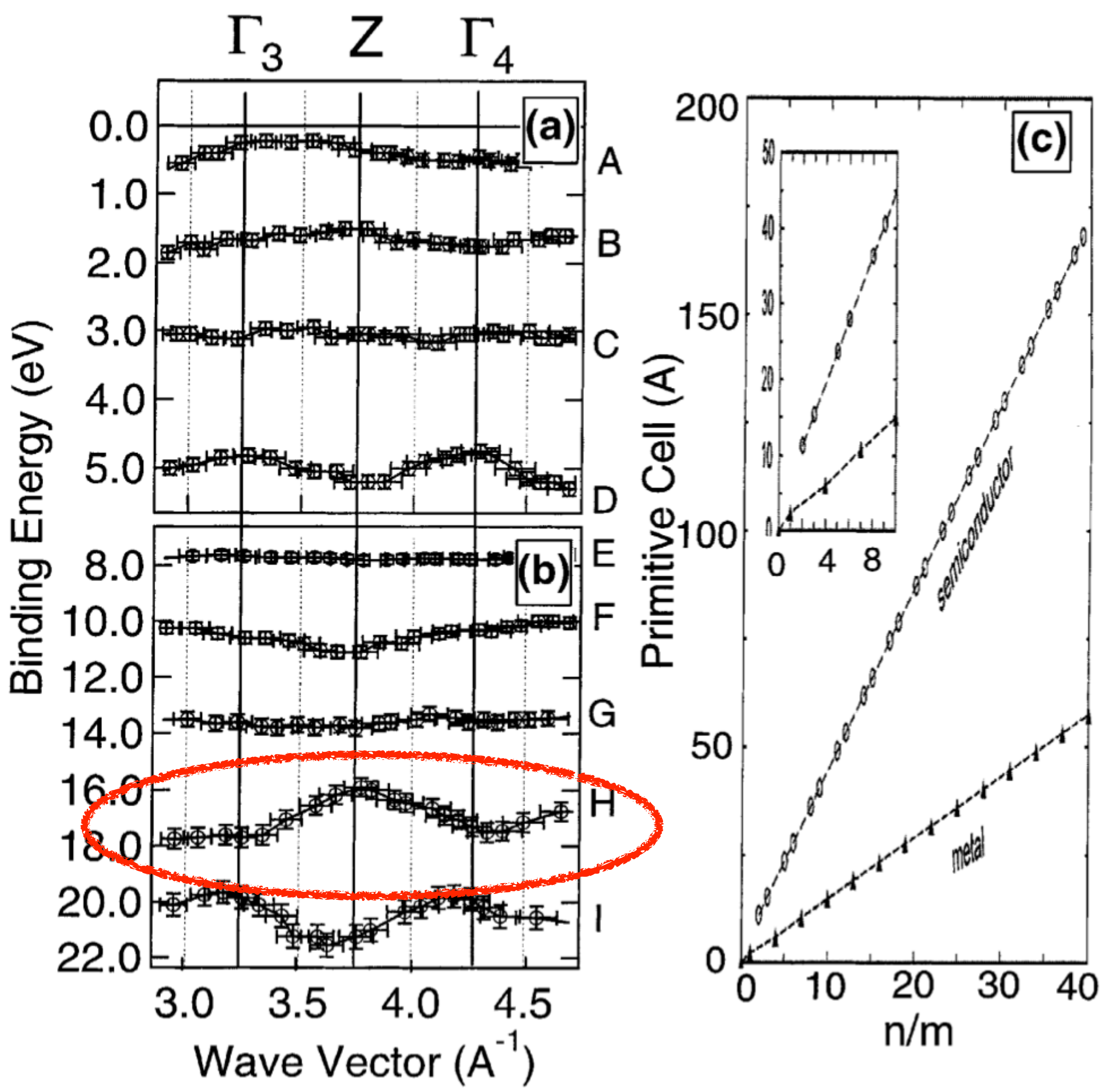


Fig. 4. Electronic band dispersion as a function of *k*-parallel momentum to the tube axis for: (a) first four low binding energy features (A, B, C, and D) near Fermi level; (b) the next five higher binding energy features (E, F, G, H, and I); (c) length of a primitive cell as a function of integer n/m in (n, m) nanotubes. Note that the scale of y-axis in (a) is different from that of (b).

Electron elastic backscattering from Randomly Oriented (RO) carbon and Vertically Aligned (VA) CNTs

Model for electron backscattering on isotropic media

Elastic Peak Electron Spectroscopy (EPES) Theory

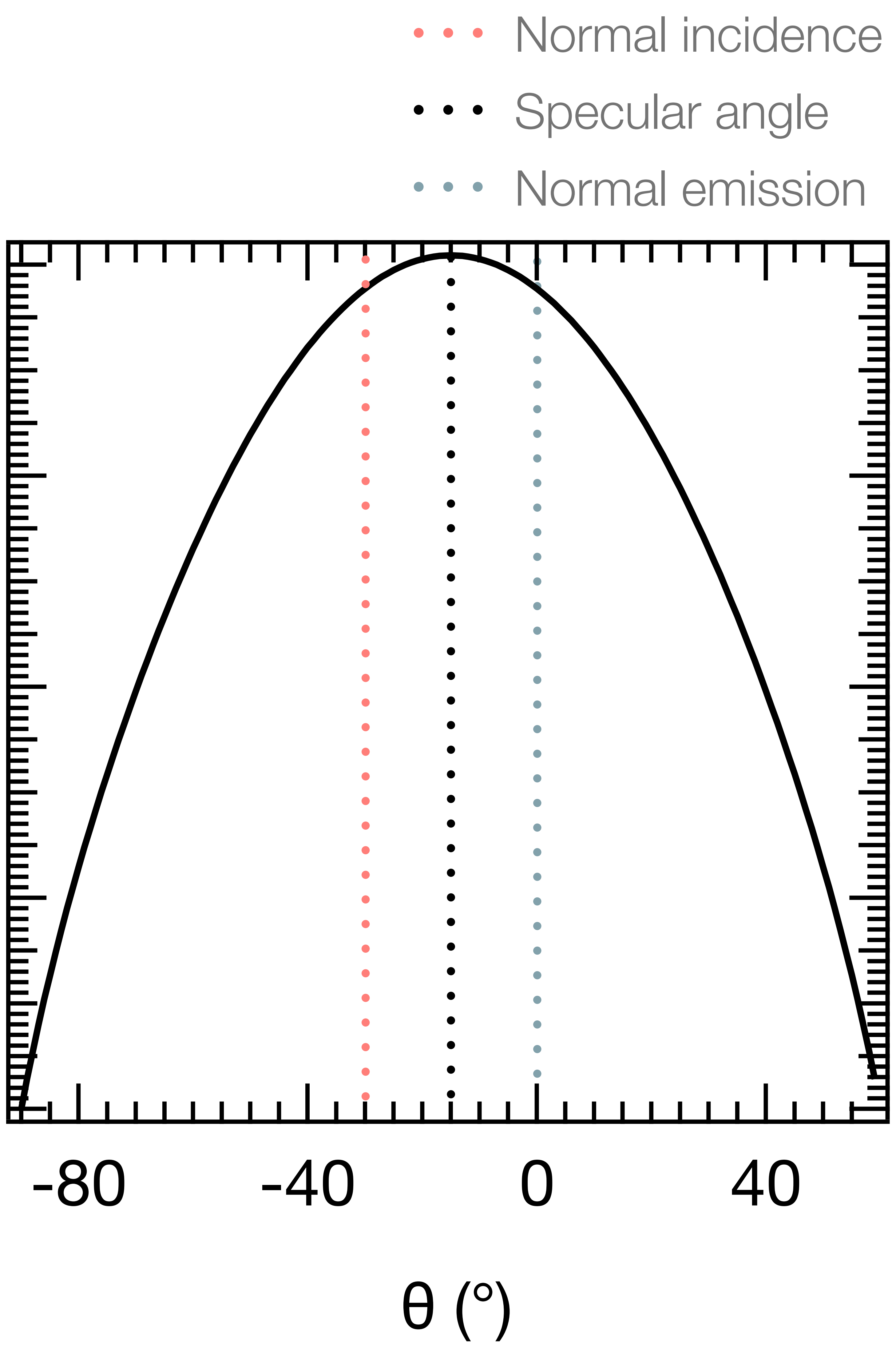
Gergely, G. (1986). Elastic peak electron spectroscopy. Scanning, 8(5), 203–214. doi:10.1002/sca.4950080503

- Single electron scattering approximation
- Transmission follows Lambert beer law

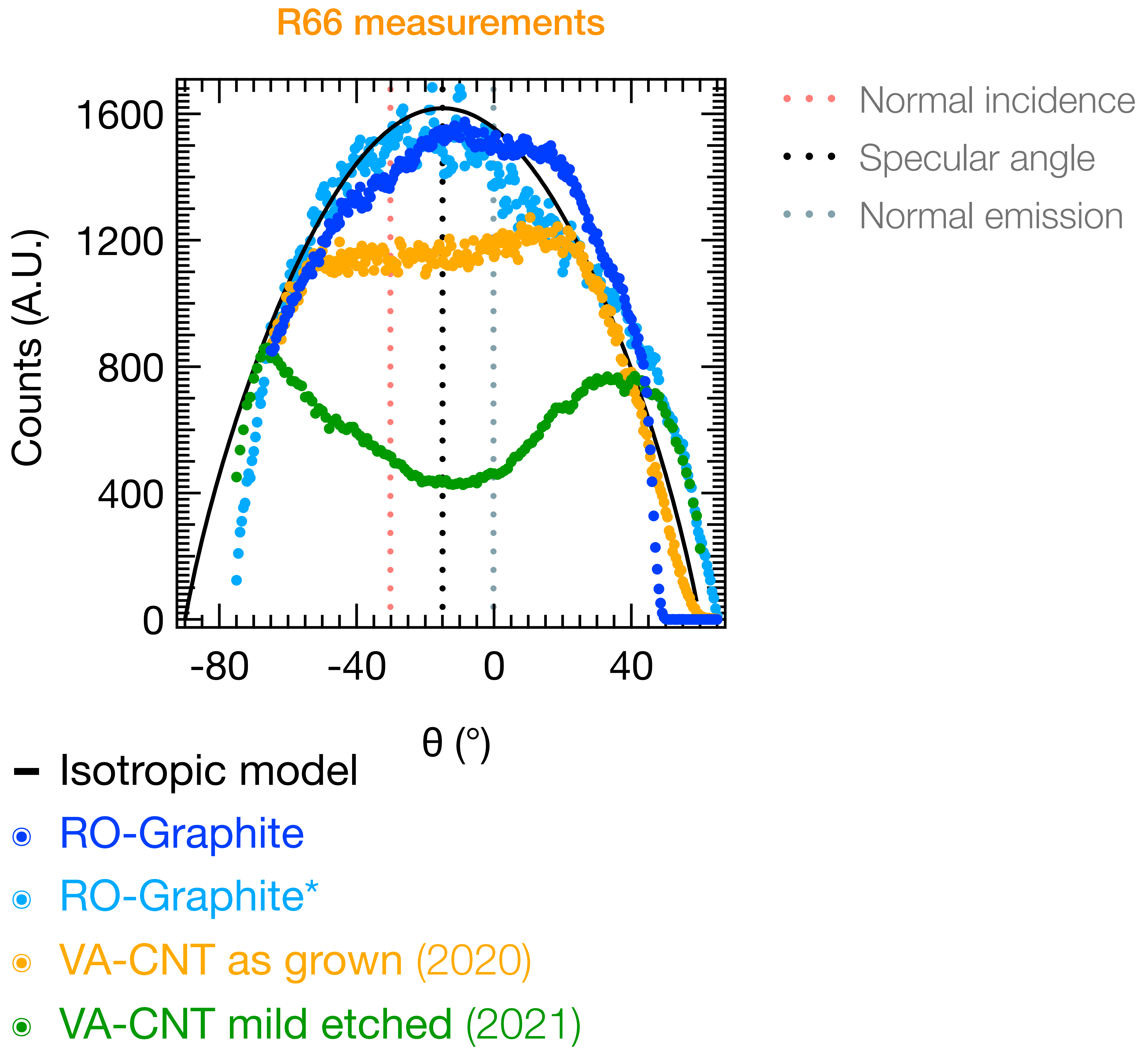
$$I(z) = I_0\, e^{-\frac{z}{\lambda \cos\alpha}}$$

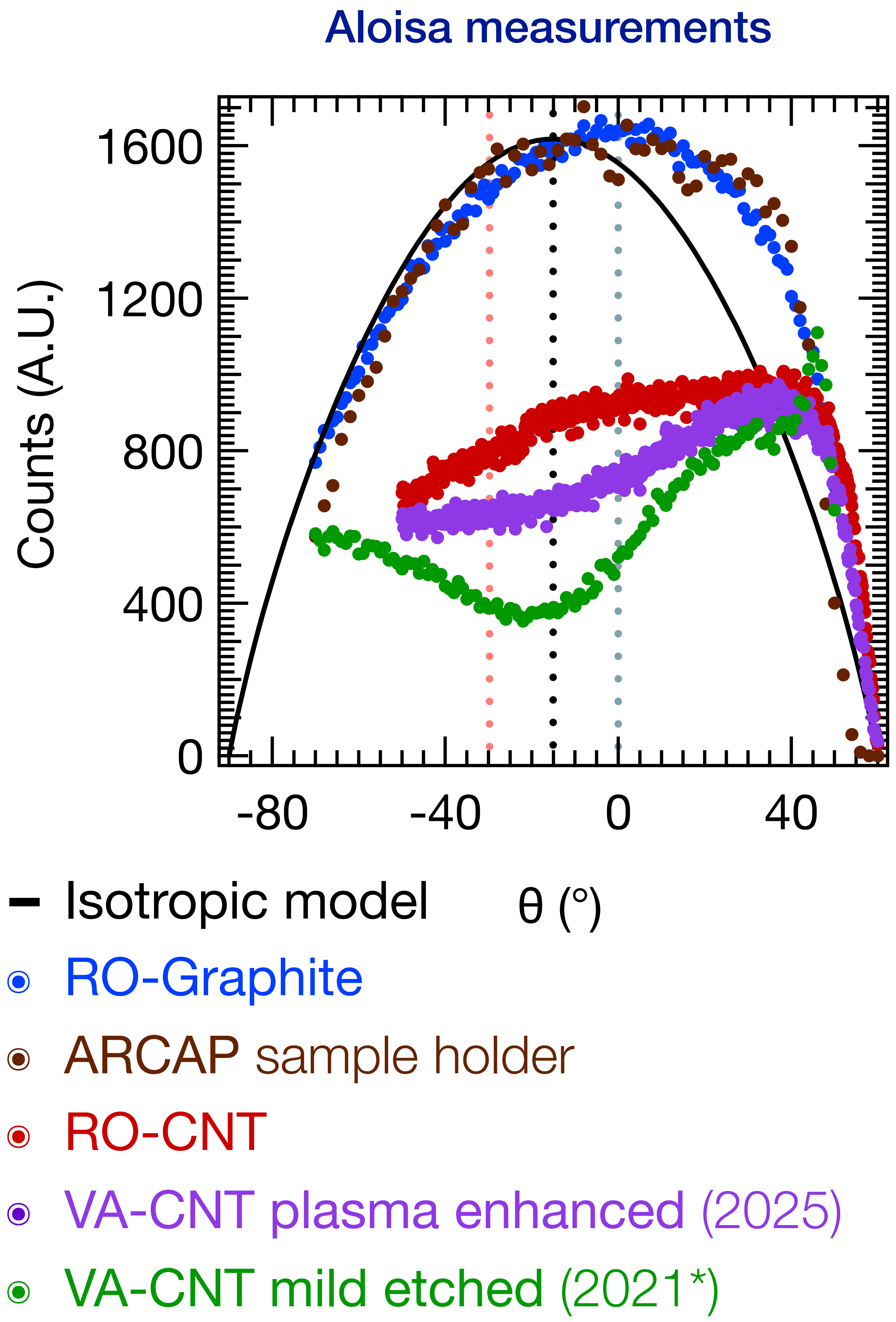
- Flat surface (no roughness)
- Ideal isotropic = no diffraction / structure factor

$$I_{EBS}(\theta, \gamma) = I_0 \cdot n \cdot \frac{d\sigma}{d\Omega} \cdot \Delta\Omega \cdot \frac{\lambda \cos\gamma \cos\theta}{\cos\theta + \cos\gamma}$$

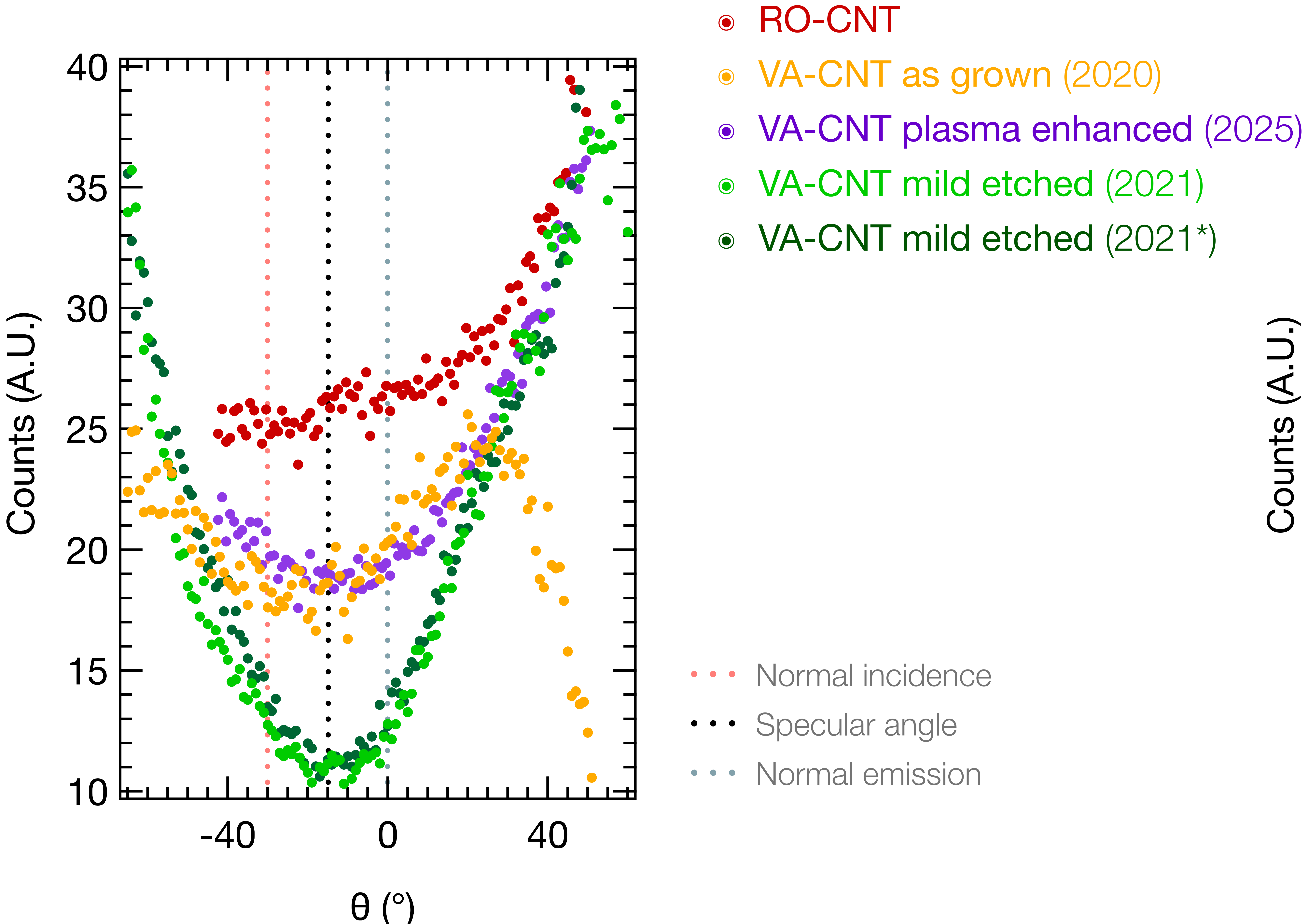


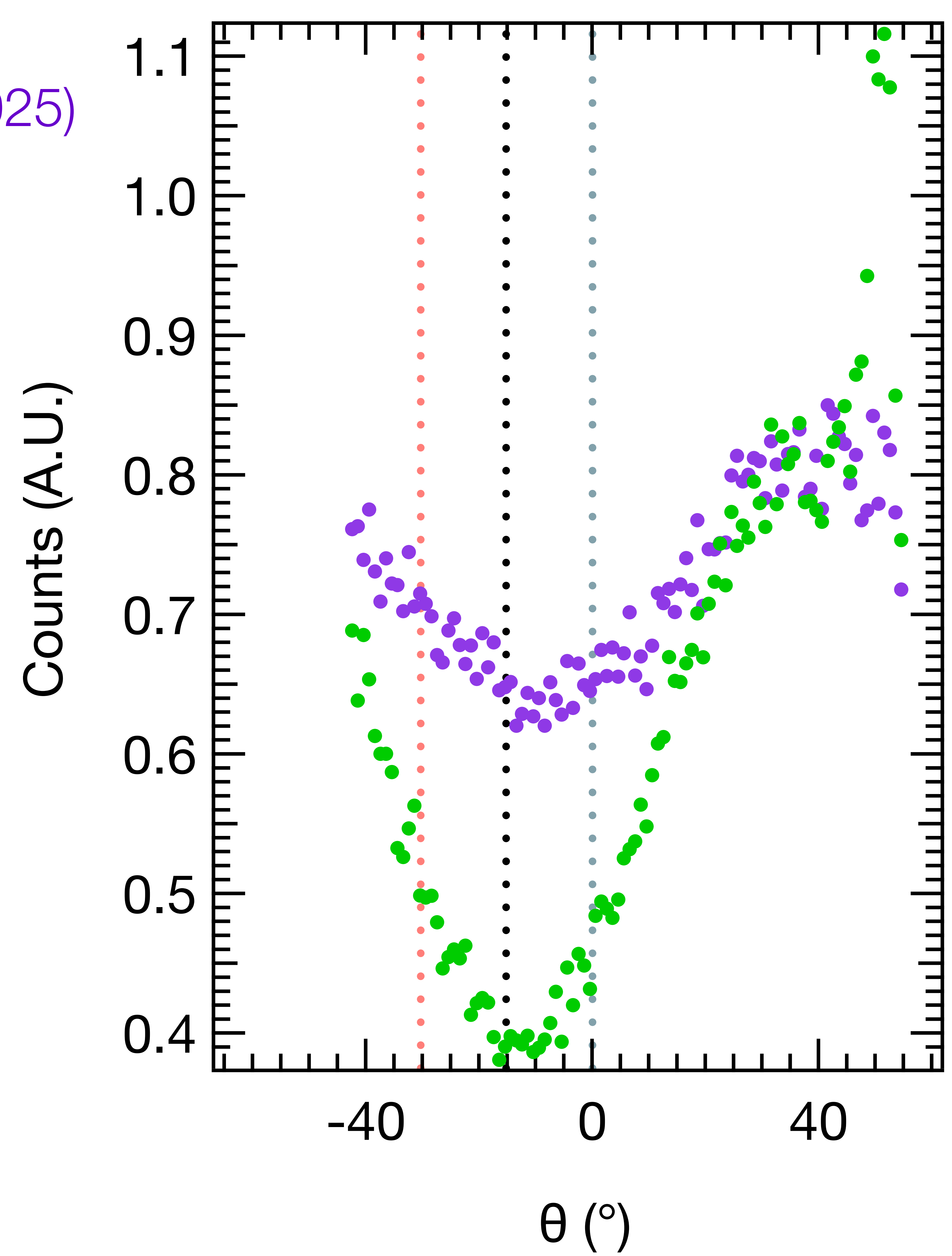
Only random oriented graphite behave as an ideal isotropic medium





Mild etched VA-CNT are more anisotropic

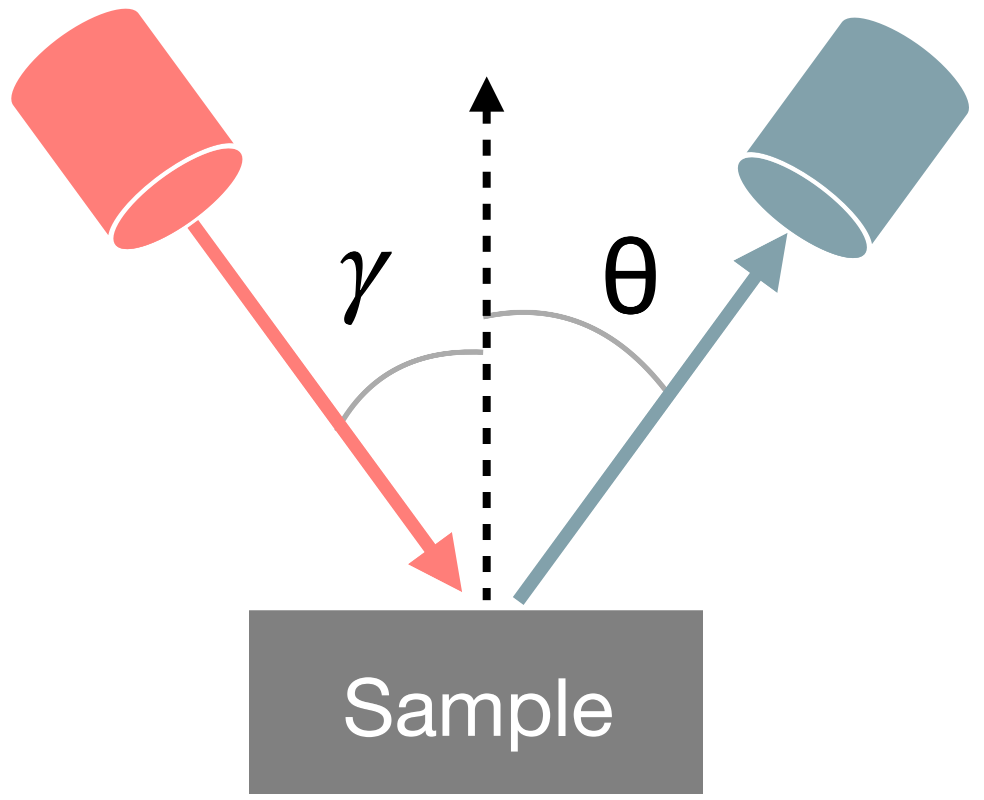




What we have learned so far

- Only RO-Graphite behave as an **ideal isotropic medium**
- RO-CNT have no clear angular dependence
- **VA-CNT have a valley** centered at the specular angle

Specular angle: $\gamma = \theta$



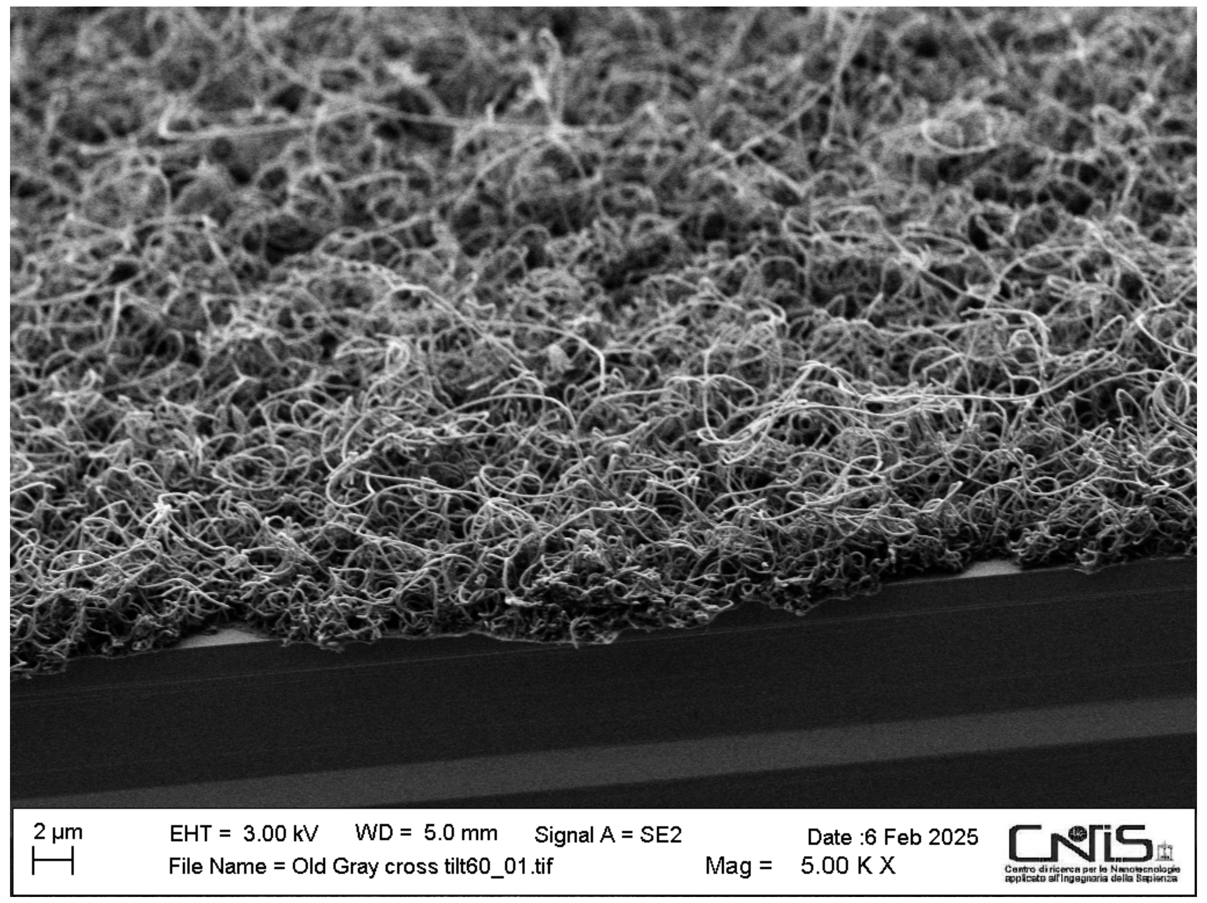
VA-CNT mild etched > VA-CNT plasma enhanced, VA-CNT as grown

CNT have a rough surface

Totally random

There is no normal surface direction

→ Flat angular dependence



The dark side of the CNTs

Geometric toy model for aligned nanotubes

CNT = 2D filled rectangle

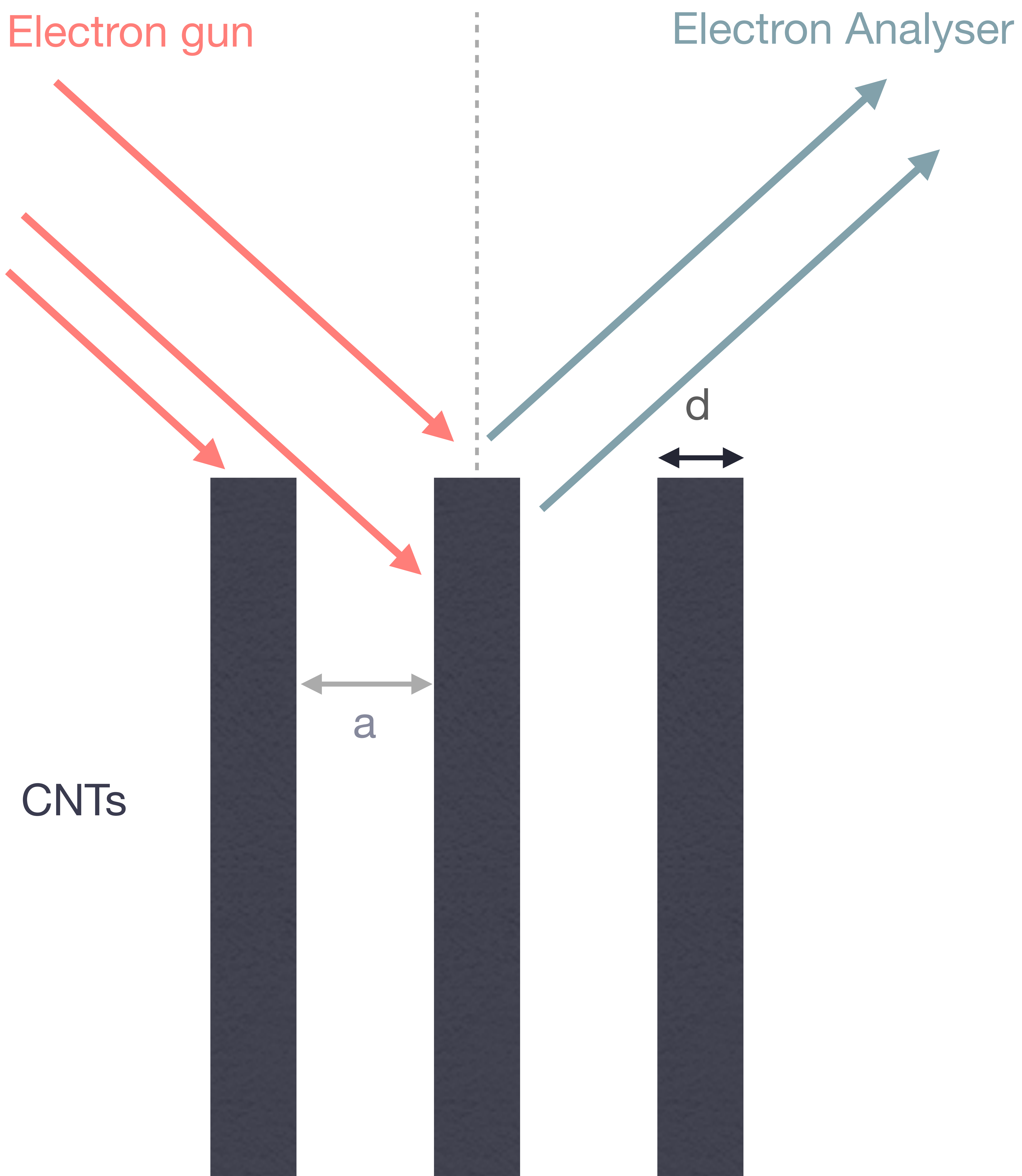
2 lateral sides, 1 top side

Infinite height

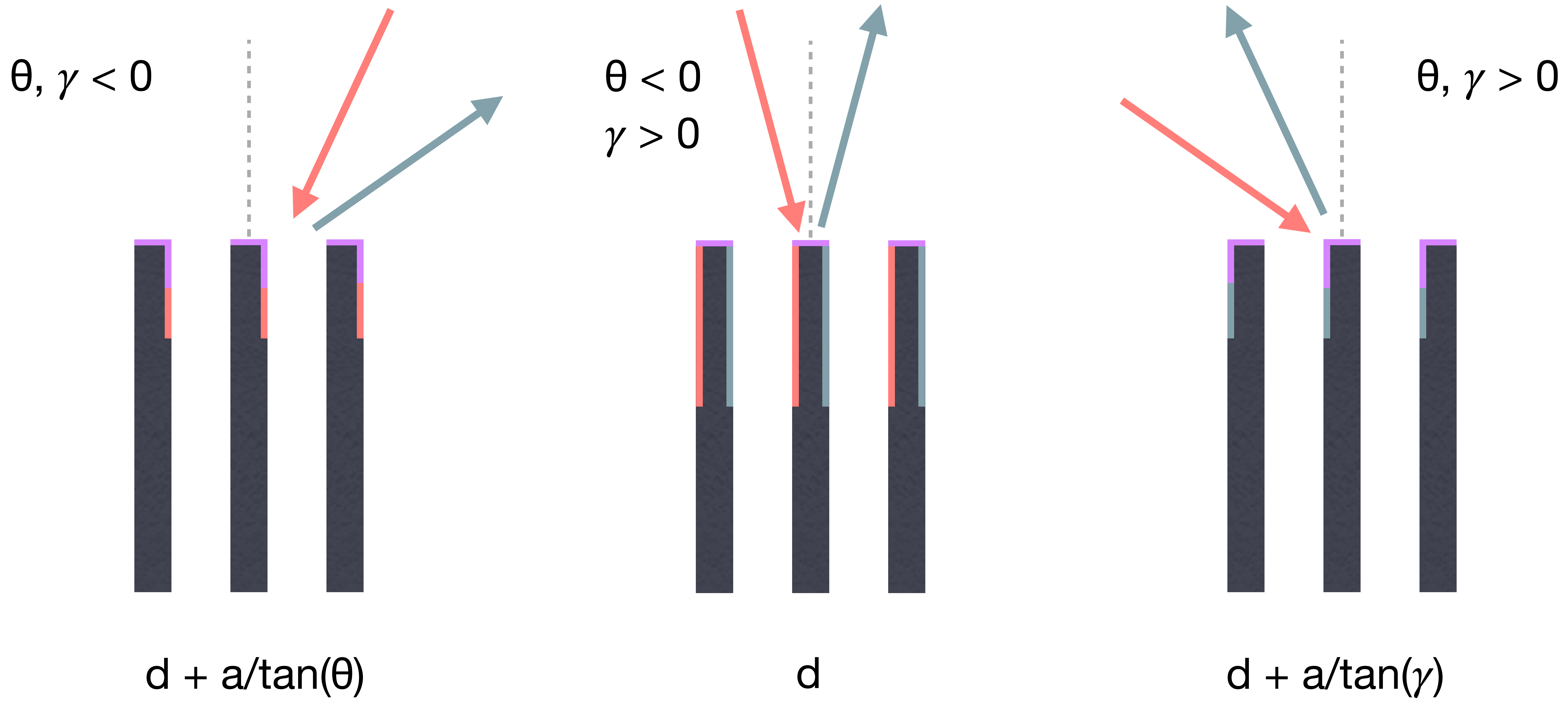
Impinging outgoing electrons rays are stopped at the surface

d: CNT external diameter

a: CNTs spacing



Cross section area has a minimum on the specular

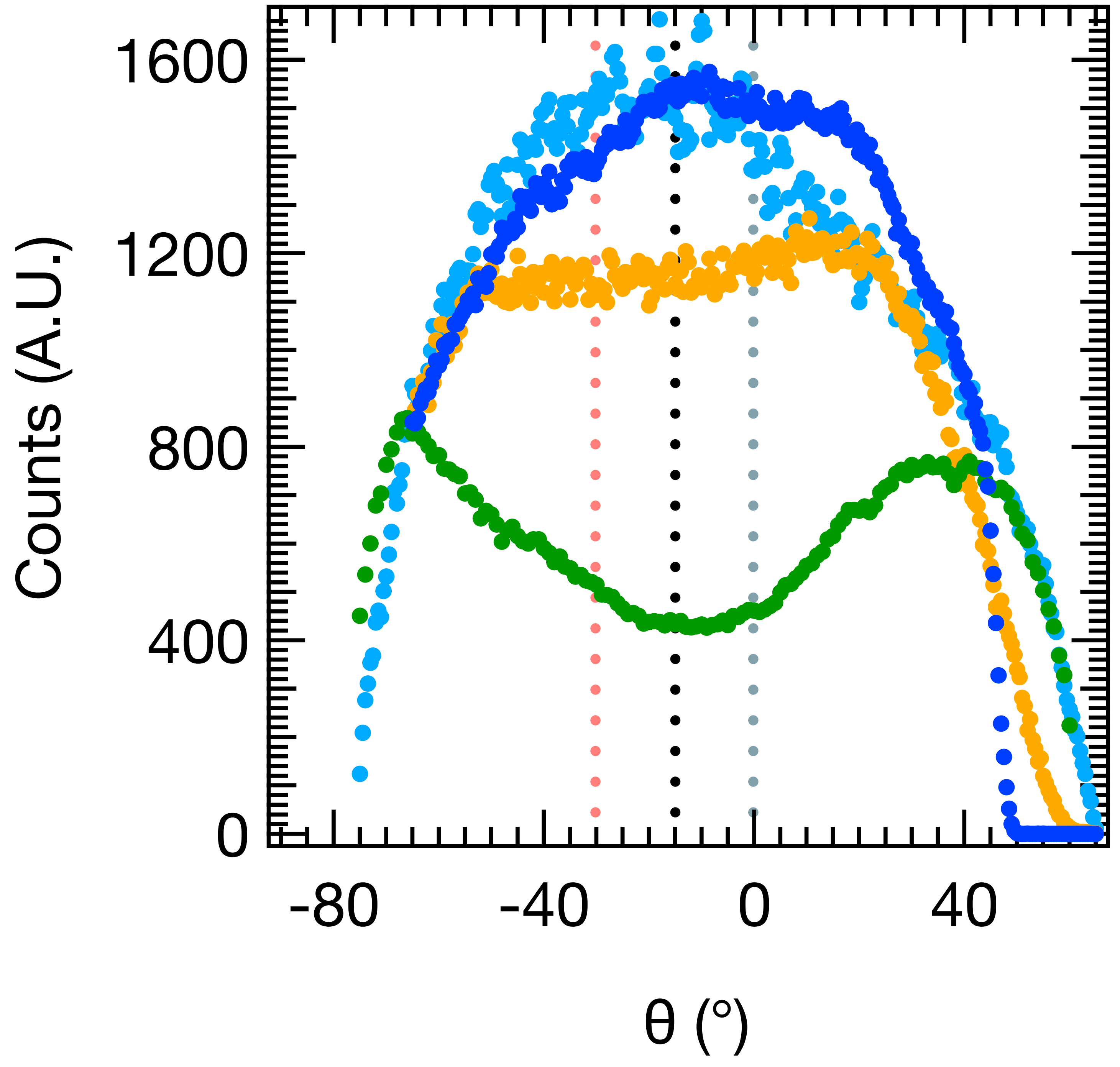


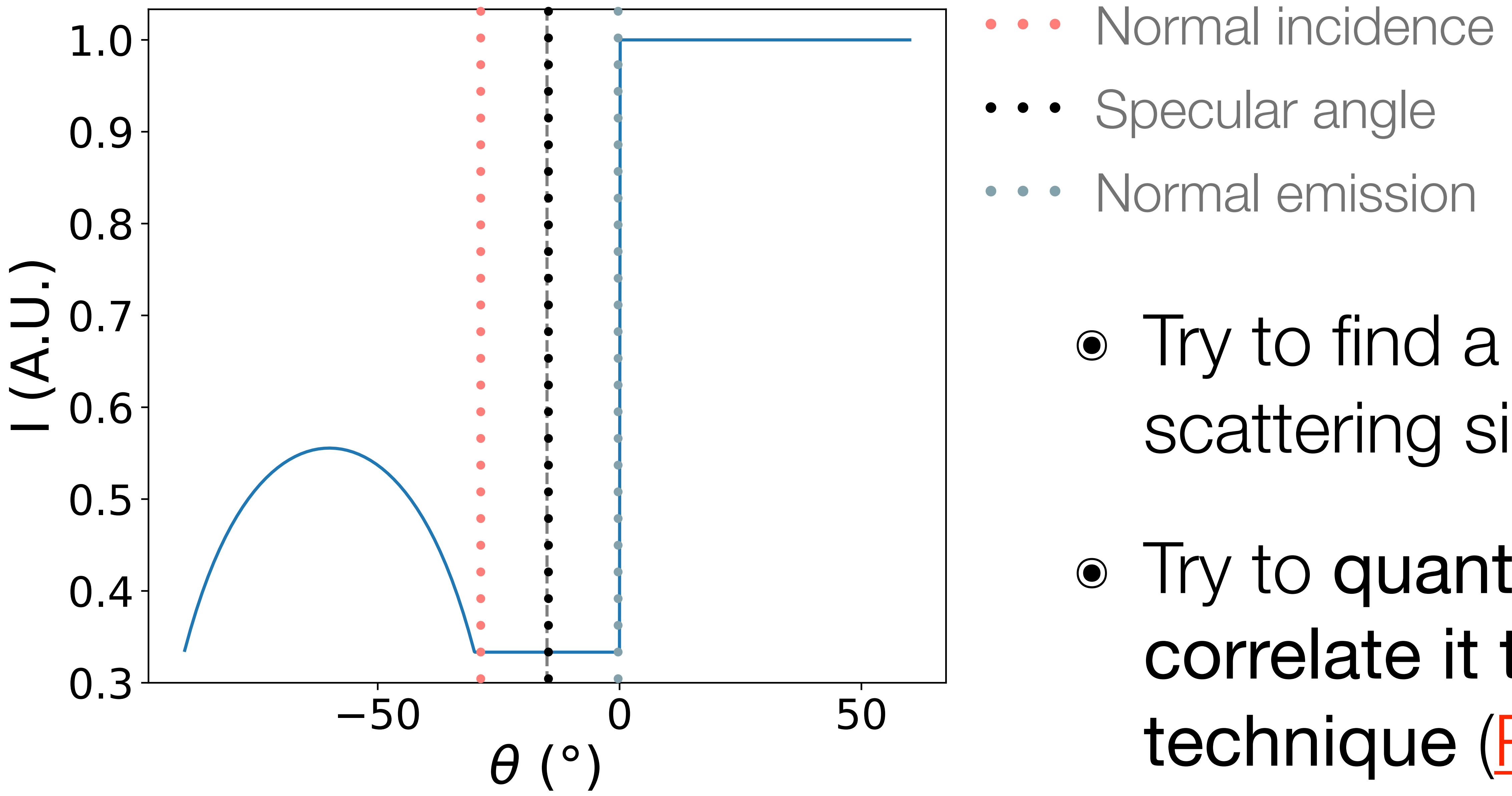
Trying a mathematical formulation…

$$A_i \cap A_S = \begin{cases} d + \min\left(\frac{a}{|\tan(\theta)|}, \frac{a}{|\tan(\gamma)|}\right) & \text{if } \theta \cdot \gamma > 0 \\ d & \text{else} \end{cases}$$

To conclude

- **VA-CNT valley** centered at the specular angle **can be explained** due to simple geometrical considerations **for an ideally vertically aligned sample**
- The **asymmetry** of the model function is **not observed in data**
- Experiment and model give info on the morphology of the tips





- Try to find a more **refined theoretical model** based on electron scattering simulations (Nebula)
- Try to **quantify valley depth** (degree of anisotropy) and **to correlate it to CNT alignment measured with another technique** (Polarized Raman, SEM image analysis)