

# **Modeling X-ray photoelectron diffraction forcing/accelerating convergence**

Shin Yasuda<sup>1</sup>,

Mariko Terao-Dunseath<sup>2</sup>, Kevin Dunseath<sup>2</sup>, Sylvain Tricot<sup>1</sup>, Didier Sébilleau<sup>1</sup>

<sup>1</sup>Department of Material and nanoscience, Institut of Physics, University of Rennes, France

<sup>2</sup>Department of molecular physics, Institut of Physics, University of Rennes, France

**MaMaSELF<sup>2</sup>**



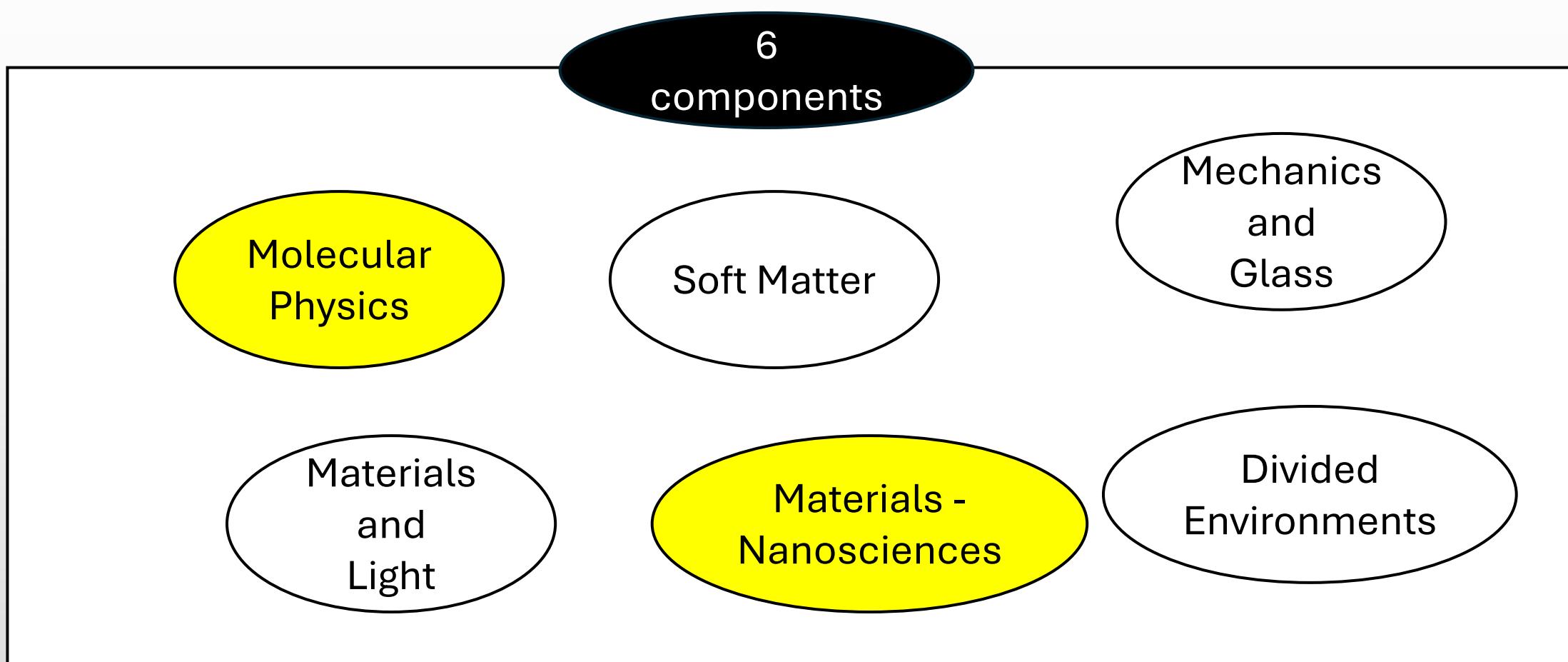
5<sup>th</sup> September 2024



Modeling of X-ray photoelectron diffraction

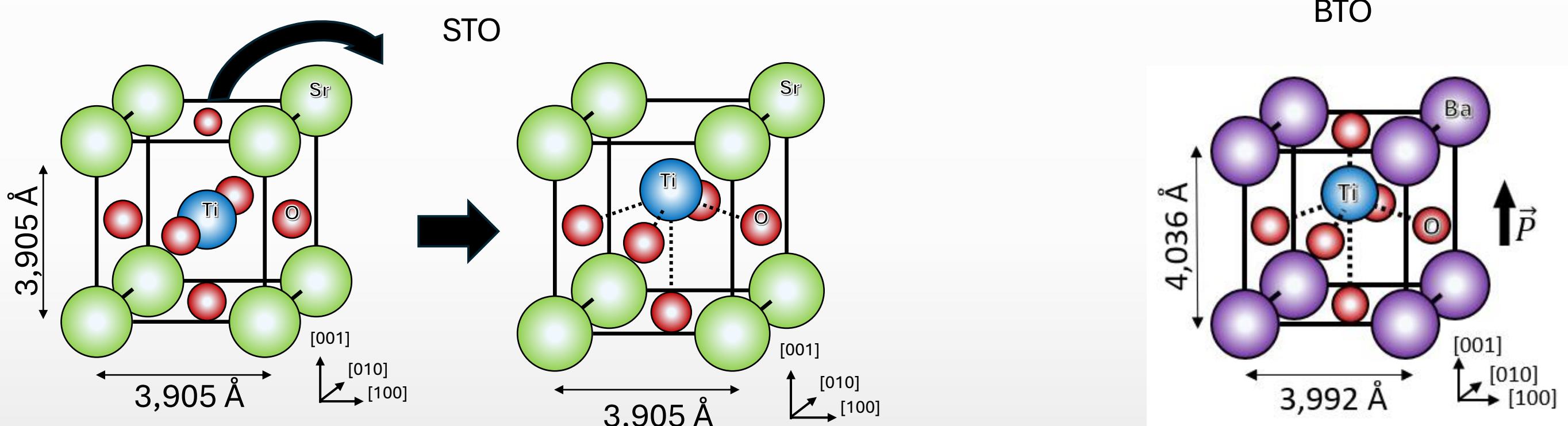


- research unit affiliated with the University of Rennes and the CNRS
- fundamental and applied physics with various interdisciplinary fields and operates on the Beaulieu campus with six research departments
- partnering with industry, employing about 120 permanent staff and around 40 non-permanent staff, including doctoral students and post-doctoral fellows



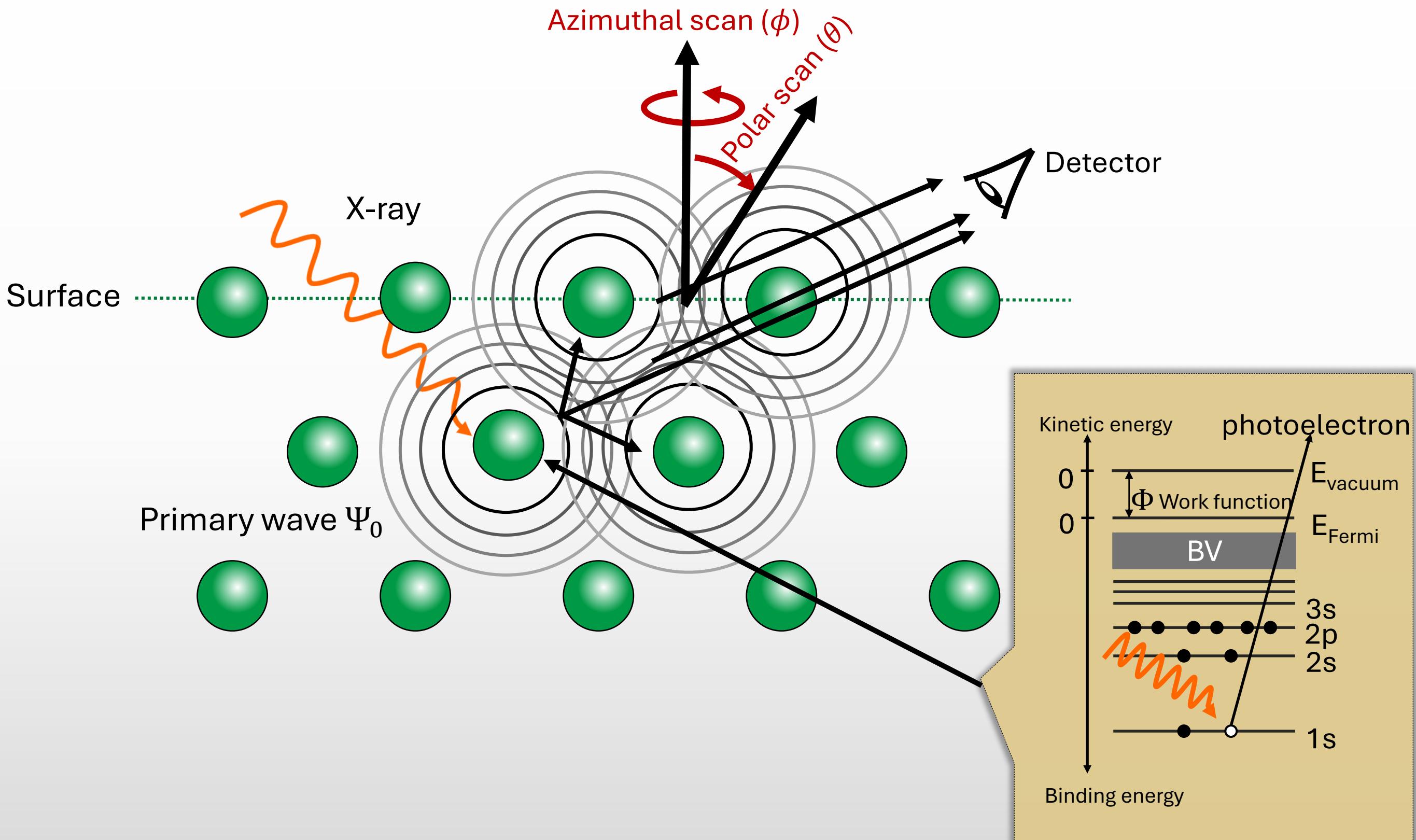
# Application importance: SrTiO<sub>3</sub>

- Small changes in structure responsible for essential properties in **perovskites**
- **Perovskites** are of great technological importance (*Resistance switching, Blue-light emission, Photo-catalysis, 2DEG...*)



- To understand and/or control these properties, we need:
  - ✓ Accurate crystallographic information,
  - ✓ Chemical resolution,
  - ✓ Surface sensitivity

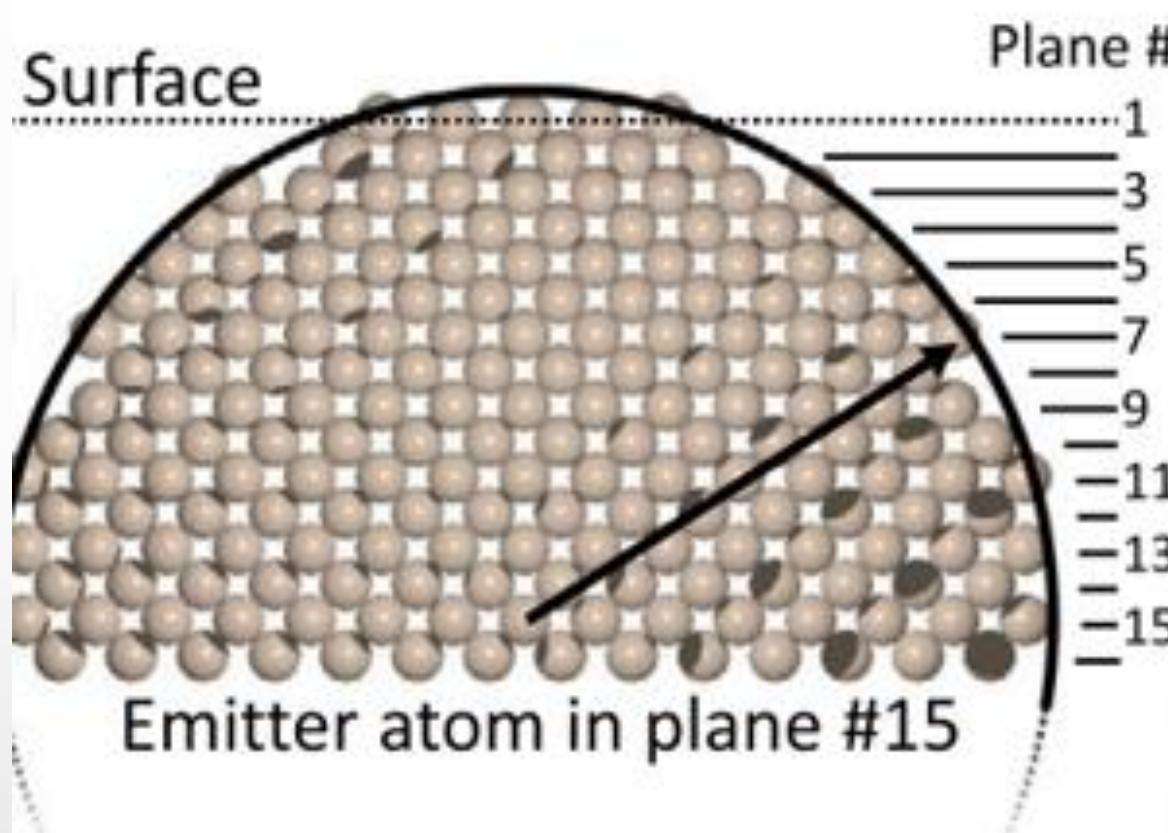
# Principle of Photo Electron Diffraction



- ✓ All the information we seek is inside the spectrum but we have no direct way to retrieve it.
- ✓ This information can only be extracted accurately through comparison to a theoretical model
- **MsSpec ([1])**
  - ✓ Python-Fortran combined package to compute the differential cross-section for PED
- **MsSpec has:**
  - ✓ Matrix inversion: Exact solution but with much memory then almost impossible for large clusters
  - ✓ Series expansion: perturbative solution, usually applicable for large clusters

[1]: Website of MsSpec: <https://msspec.cnrs.fr/index.html>

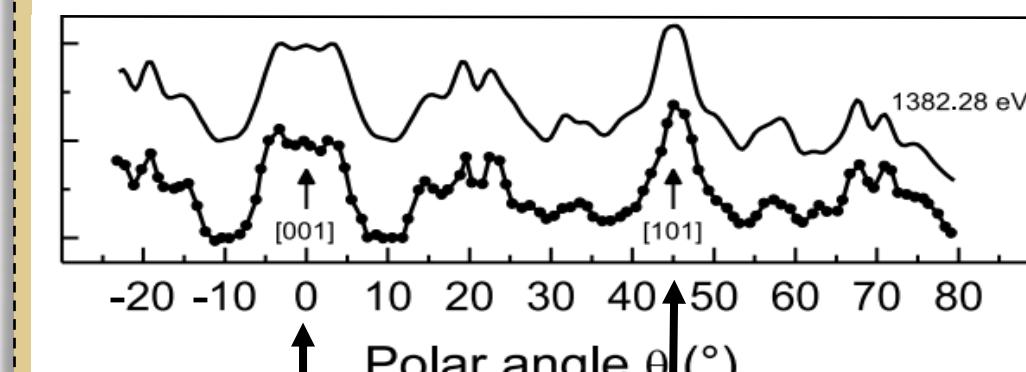
# e.g.: Comparison with experimental data - Si -



Si(2p) in Si(001) substrate

Peaks of intensity along dense atomic directions

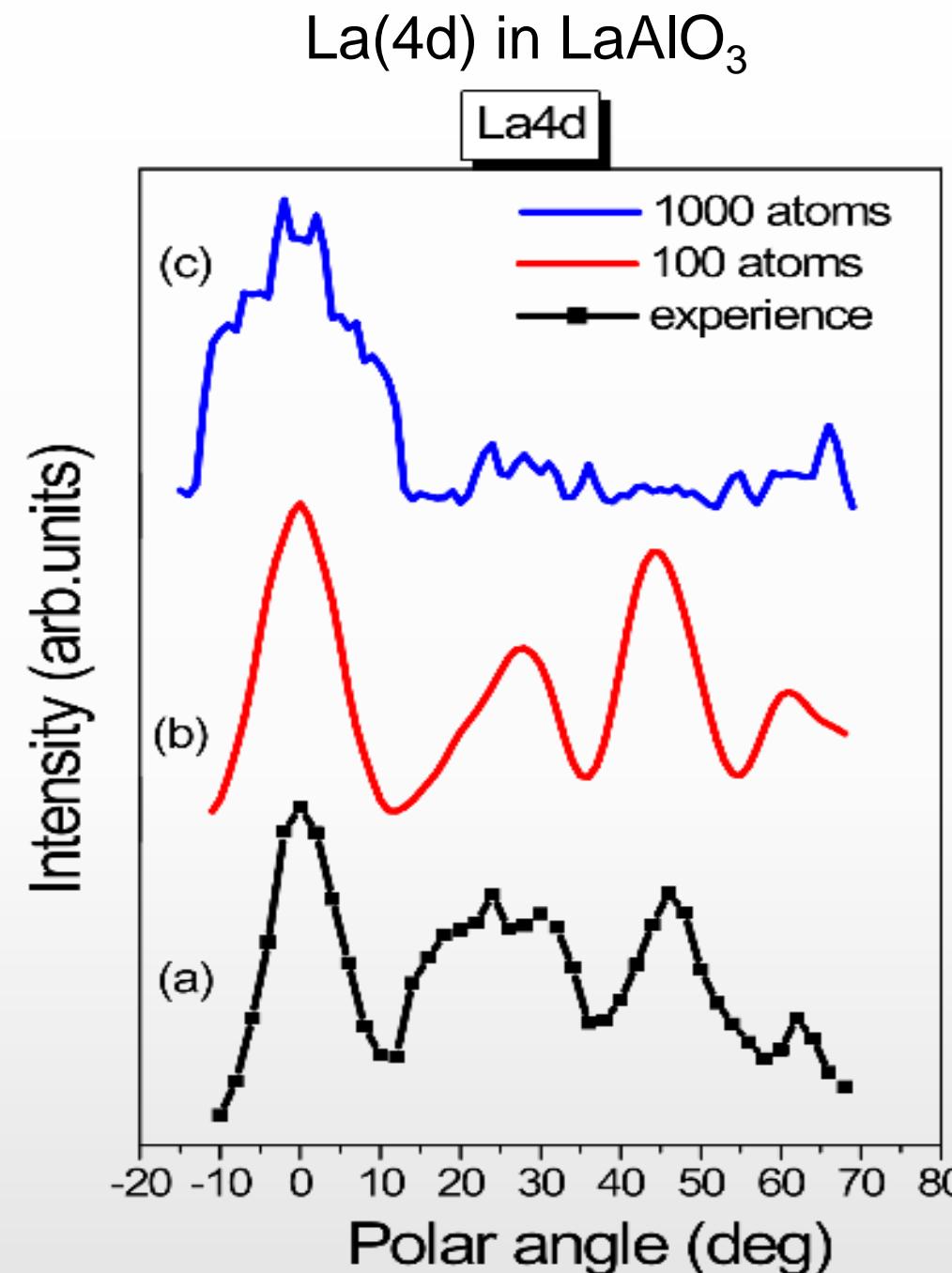
Polar scan of Si(2p) in Si(001) substrate



[001] [101]

Simulation needed for complete interpretation  
and quantitative information

S. Tricot, T. Jaouen, D. Sébilleau, P.  
Schieffer, *J. Electron. Spectrosc.*, **256**,  
147176 (2022)



PED calculation for  $\text{LaAlO}_3$  (Mohamed Zanouni,  
Faculty of Sciences, Tangiers, Morocco)

Where divergence comes from and how to avoid it ?

**Taylor expansion**

$$(1 - x)^{-1} = 1 + x + x^2 + \dots$$

**converges if  $|x| < 1$**

$$(I - K)^{-1} = I + K + K^2 + \dots$$

**converges if  $\rho(K) < 1$**

- ✓ We look at spectra radius,  $\rho$  to clarify when we have divergence:
- ✓  $\rho(K)$  is the largest eigenvalue in modulus.
- ✓ If  $\rho(K) > 1$ , divergence appears in SE.

- SE

$$(I - K)^{-1} = I + K + K^2 + \dots \text{diverges}$$

- Idea [2]

- ✓ Mix **I** and **K** with parameter  $\omega$ :

$$G_1 = (1 - \omega)I + \omega K \Rightarrow (I - K)^{-1} = \omega(I - G_1)^{-1}$$

- We hope for some  $\omega$  parameter

$$\rho(G_1) < 1$$

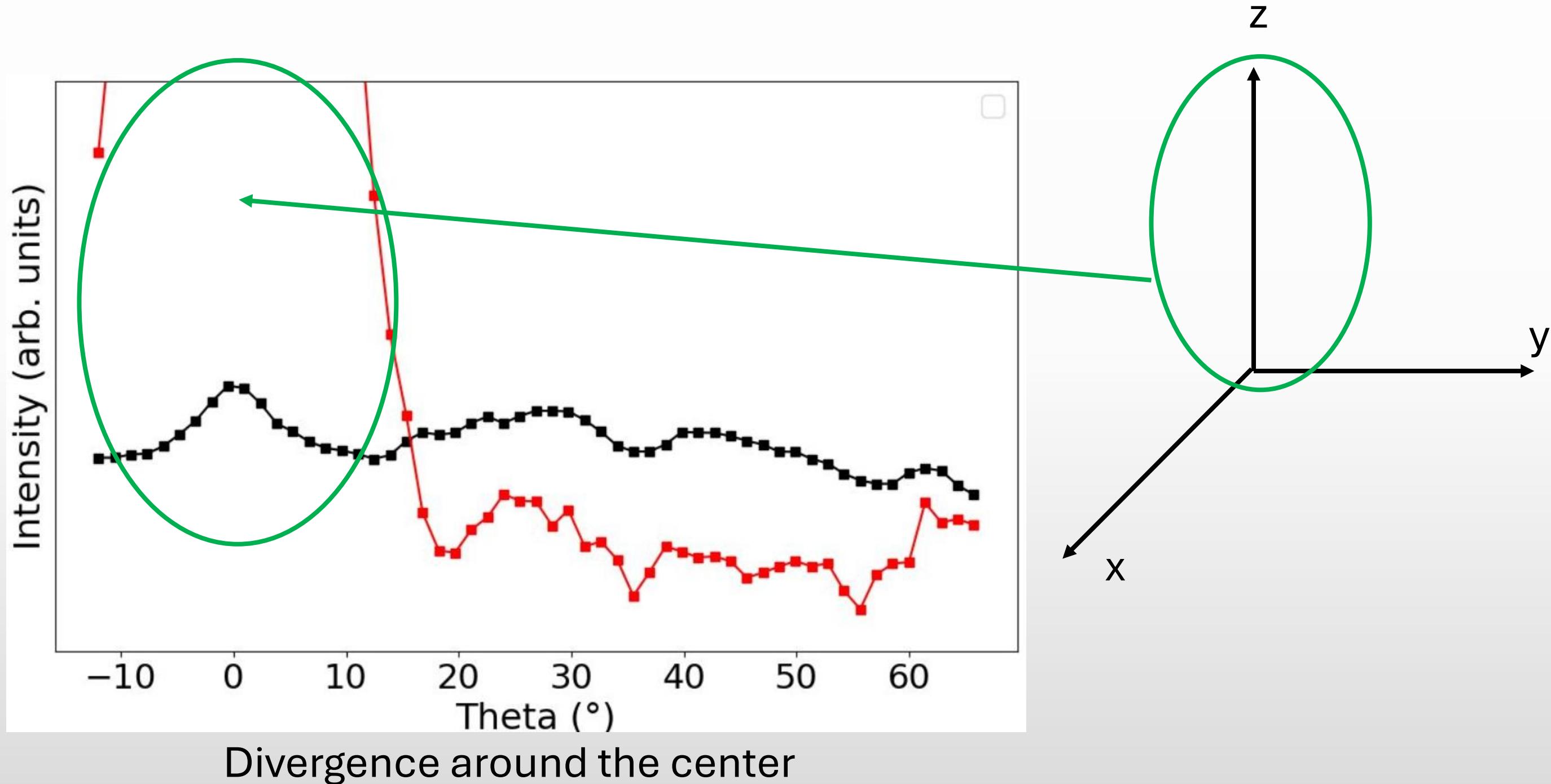
- The calculation is as heavy as MI.

- ✓ For 1000 atoms, around 3 weeks !

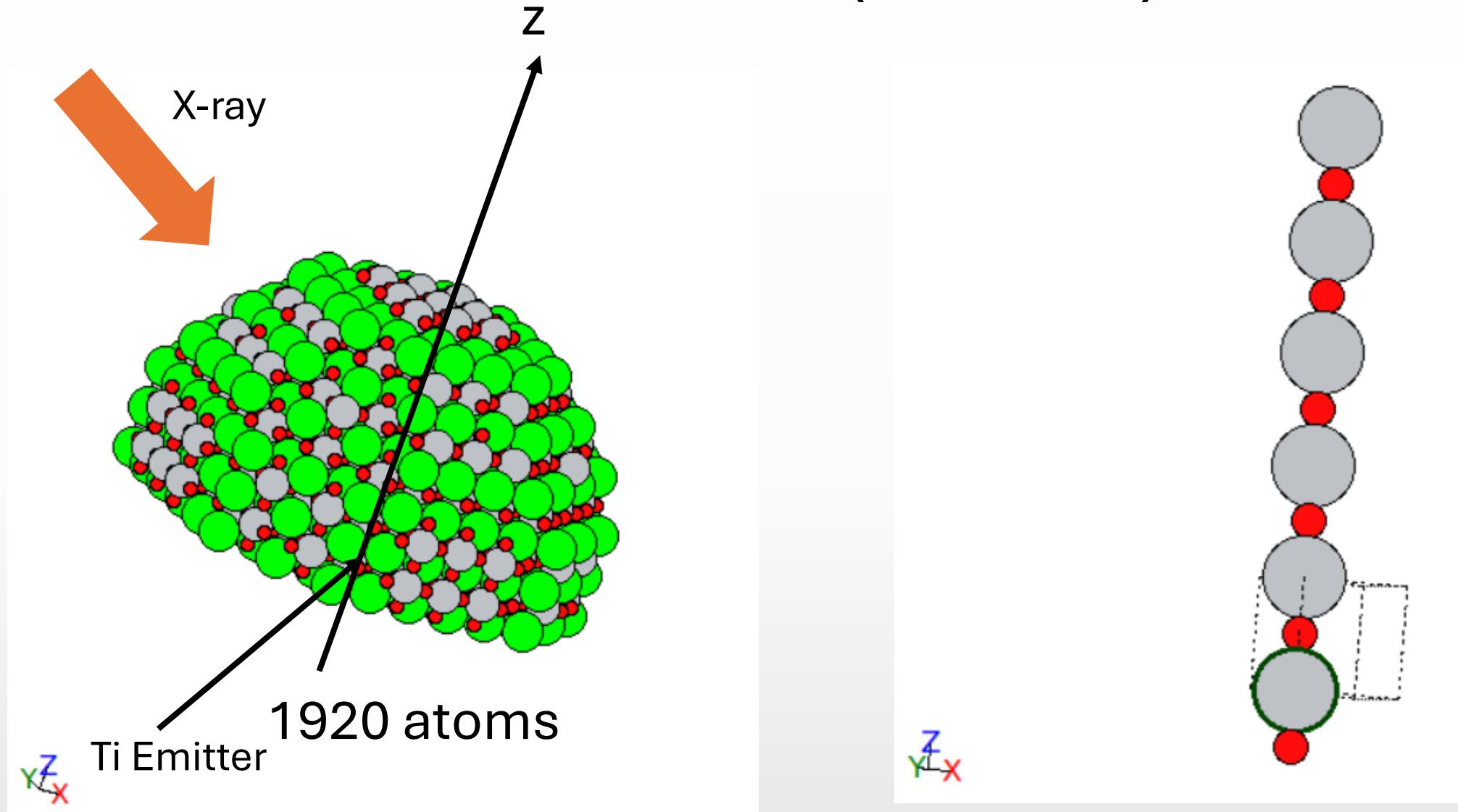
- ✓ Increasing Series truncation order by 1, CPU time is multiplied by 1000.

[2] Takatsu, A. et al., Simple renormalization schemes for multiple scattering series expansions, Phys. Chem. Chem. 24 5658–5668 (2022)

- Let's look at a real experiment;



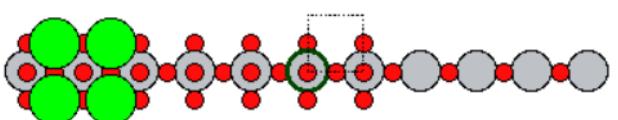
- STO cluster with Ti emitter (1019 eV)



$$\begin{aligned}\rho_{SE} &= 1.135 \\ \omega &= 0.813 + 0.241j \\ \rho_{G_1} &= 0.706\end{aligned}$$

- Number of planes: 12
- Radius of the semisphere: 21 Å
- Ti emitter at the second plane from the bottom

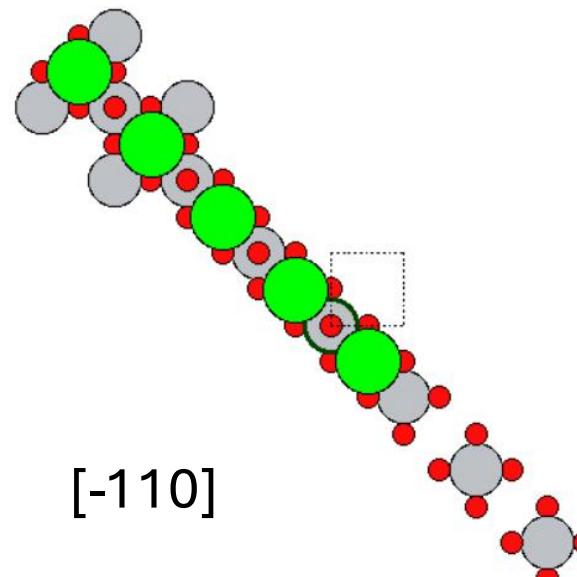
- Atomic cones that diverge



[-100]

Y  
Z  
X

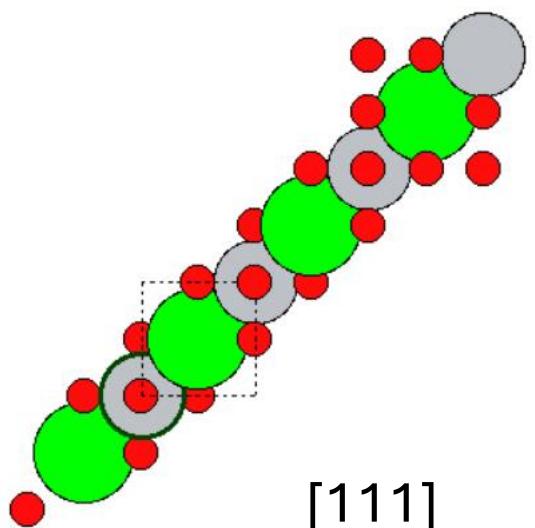
$$\begin{aligned}\rho_{SE} &= 1.818 \\ \omega &= 0.600 + 0.284j \\ \rho_{G_1} &= 0.820\end{aligned}$$



[-110]

Y  
Z  
X

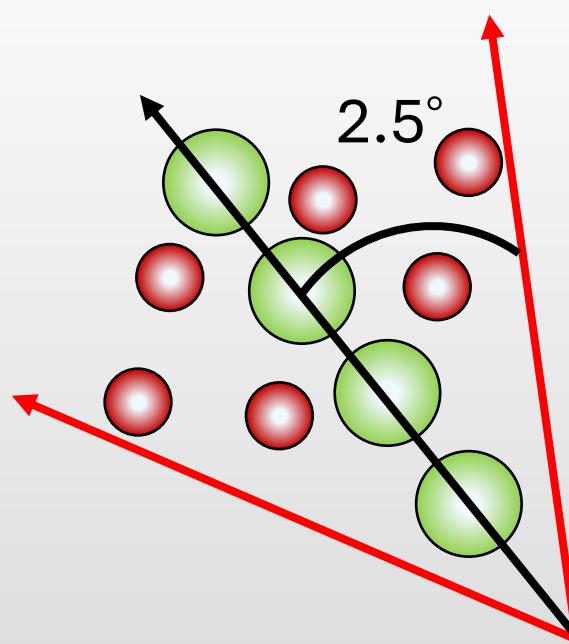
$$\begin{aligned}\rho_{SE} &= 1.005 \\ \omega &= 0.842 + 0.230j \\ \rho_{G_1} &= 0.655\end{aligned}$$



[111]

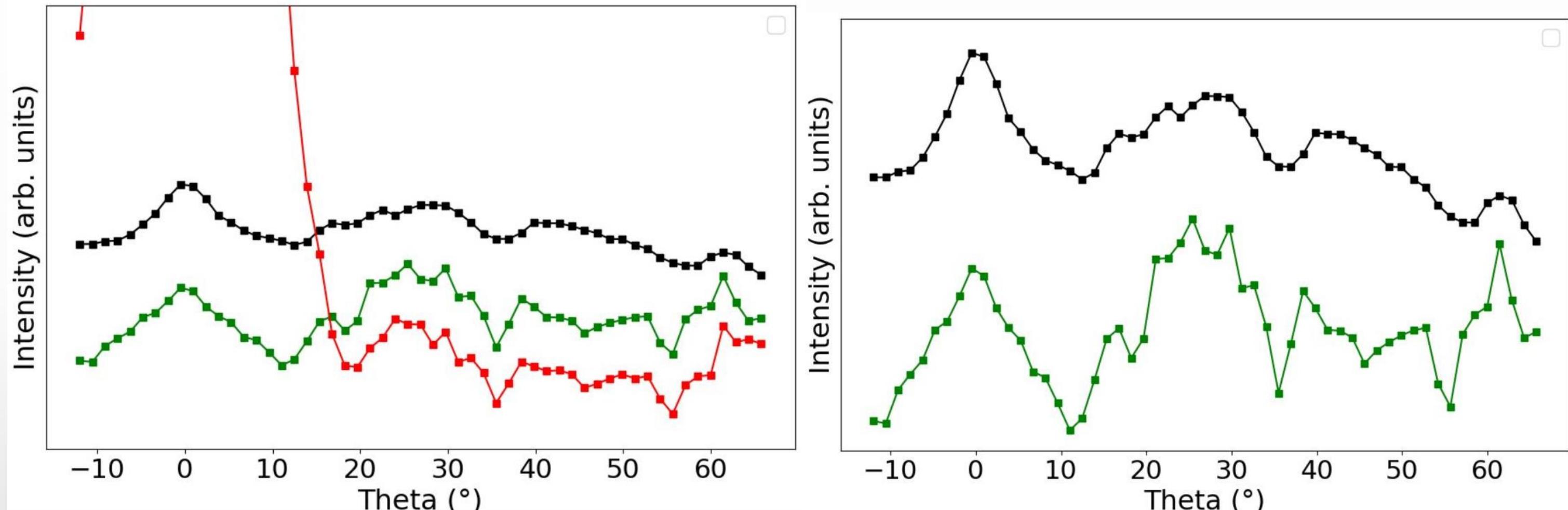
Y  
Z  
X

$$\begin{aligned}\rho_{SE} &= 1.026 \\ \omega &= 0.780 + 0.114j \\ \rho_{G_1} &= 0.646\end{aligned}$$



$$\tilde{\omega} = 0.757 + 0.192j$$

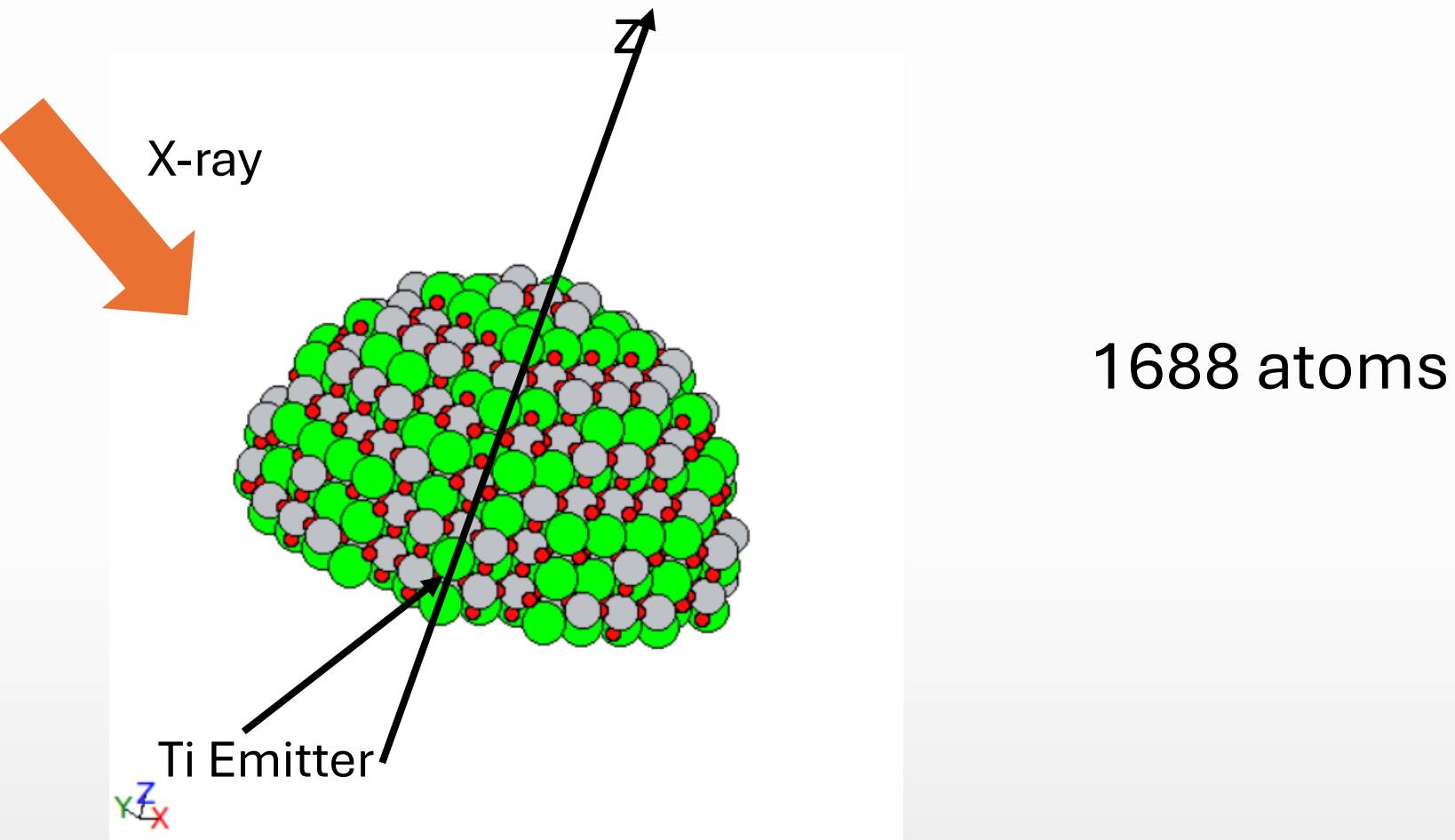
- Simulation and Experiment



Black: Experiment.  
Green: Simulation with  $G_1$   
Red: Simulation without  $G_1$

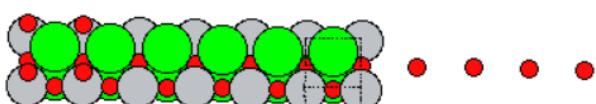
# Simulating clusters: STO, O emitter

- STO cluster with O emitter (948 eV)



- Number of planes: 10
- Radius of the semisphere: 21 Å
- O emitter at the second plane from the bottom

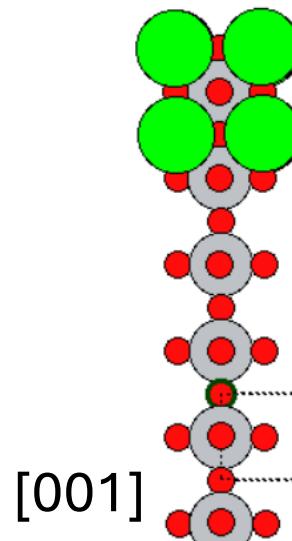
- Atomic cones that diverge



[-100]

Y  
X  
Z

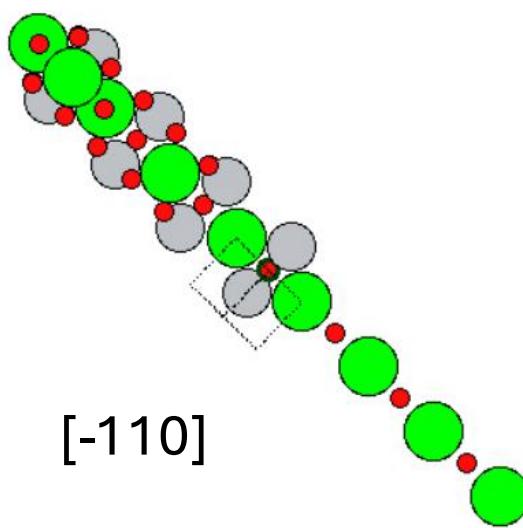
$$\begin{aligned}\rho_{SE} &= 1.277 \\ \omega &= 0.722 + 0.256j \\ \rho_{G_1} &= 0.762\end{aligned}$$



[001]

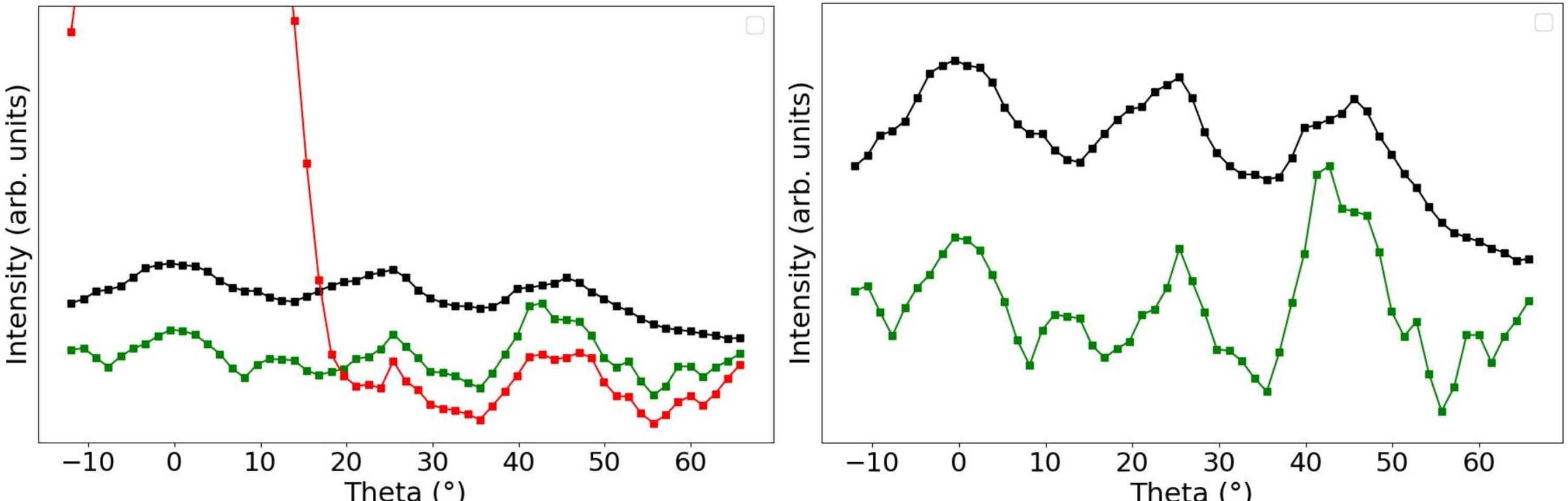
Z  
Y  
X

$$\begin{aligned}\rho_{SE} &= 1.212 \\ \omega &= 0.784 + 0.246j \\ \rho_{G_1} &= 0.720\end{aligned}$$



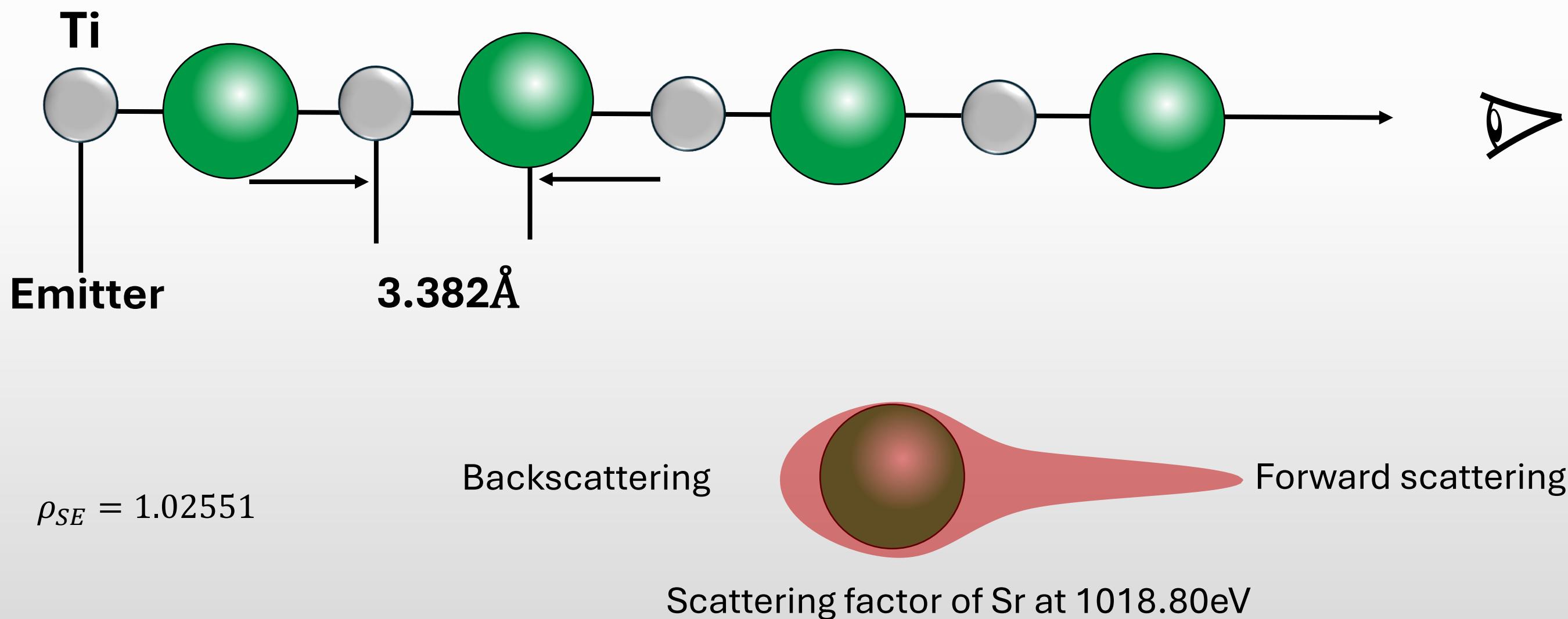
[-110]

- Simulation and Experiment

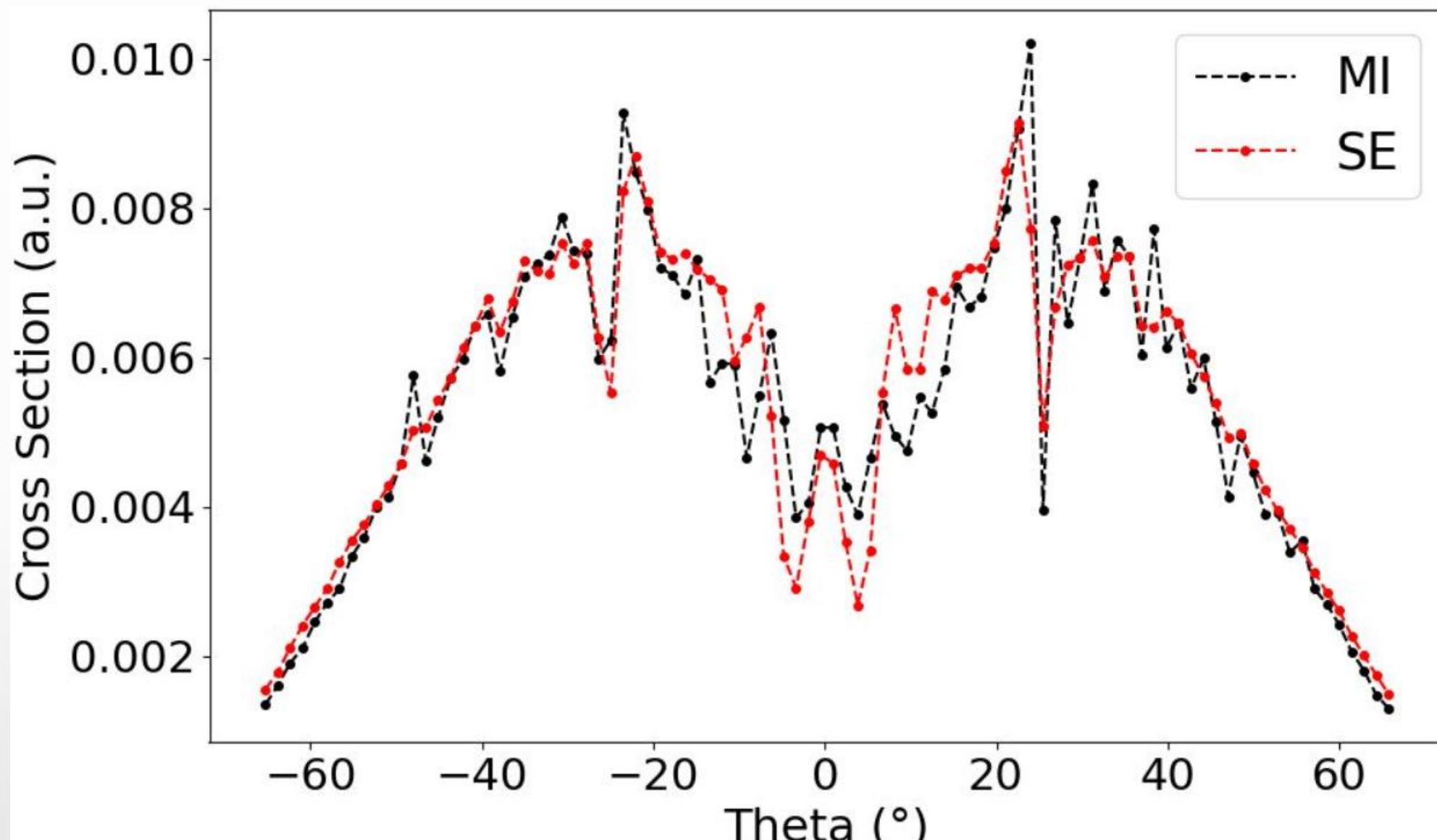


Black: Experiment.  
Green: Simulation with  $G_1$   
Red: Simulation without  $G_1$

## 8\_TiSr-atomic chain at 1018.80eV

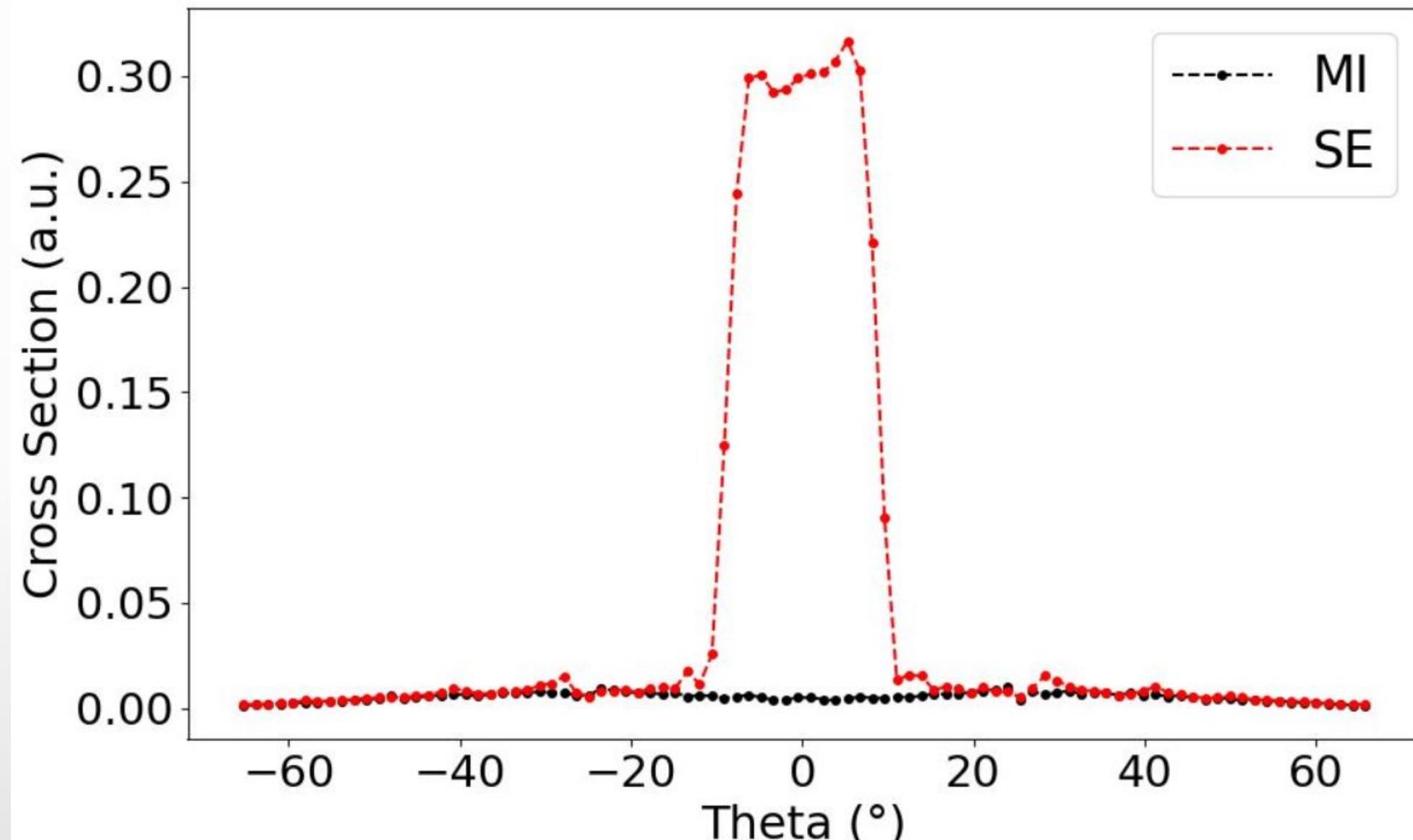


# Result: Ti-Sr chain, without backscattering



- Removing all backscattering
- Almost agrees with MI

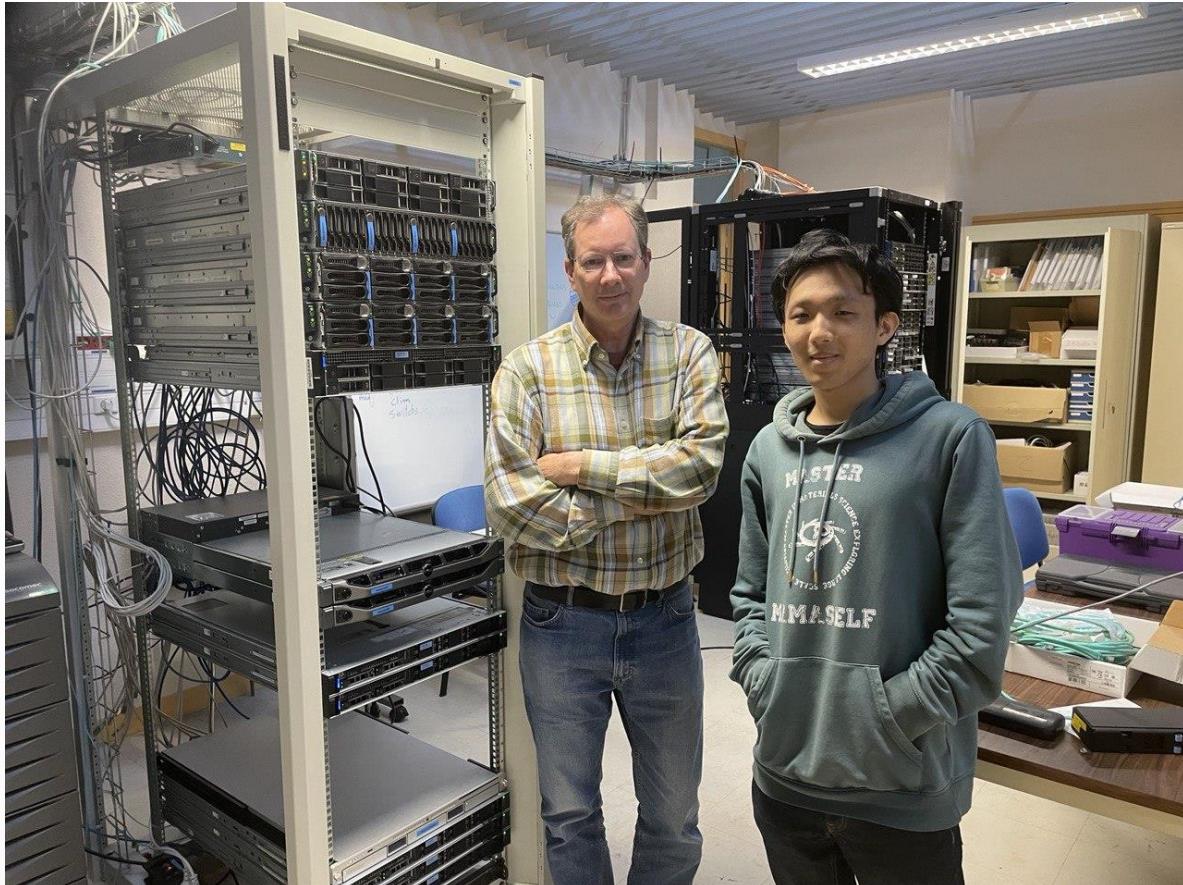
# Result: Ti-Sr chain, with backscattering



Taylor truncation order  $n = 7$   
Central peak ten times more than MI

# Summary

- **So far:**
  - ✓ We have found out divergence effect on an atomic chain.
  - ✓ The divergence effect seems to happen due to backscattering.
  - ✓ We demonstrated our methodology simulating theta scans for STO based on atomic chains.
  - ✓ More perovskites are to be tested (CTO, BTO,...etc, experimental data are available at the IPR.)



**Thank you very much for all  
and thank you for listening.**

- New properties of materials: related to the perfect control of their crystallographic properties
- Accurate crystallographic information, Chemical resolution, Surface sensitivity...
- Differential cross section: Angular distribution of a detected electron at device

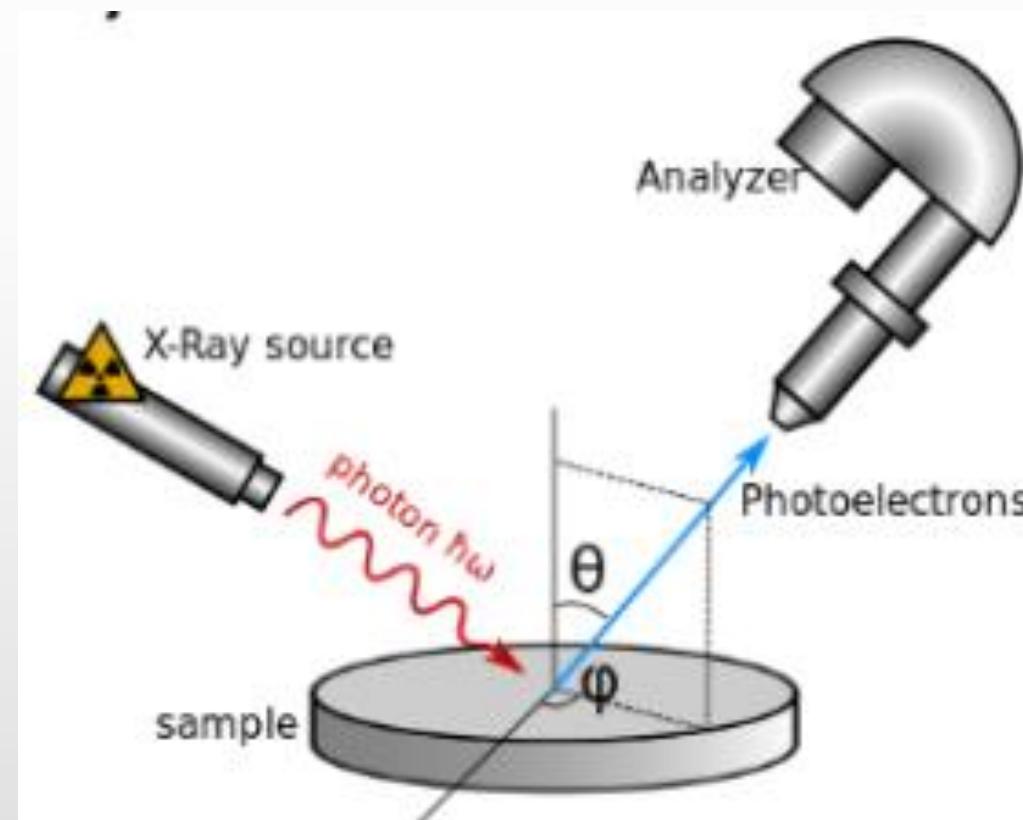


Fig.2: PED experimental setup, cited from [1].

[1] Website of MsSpec: <https://msspec.cnrs.fr/index.html>

# State of the art and PED

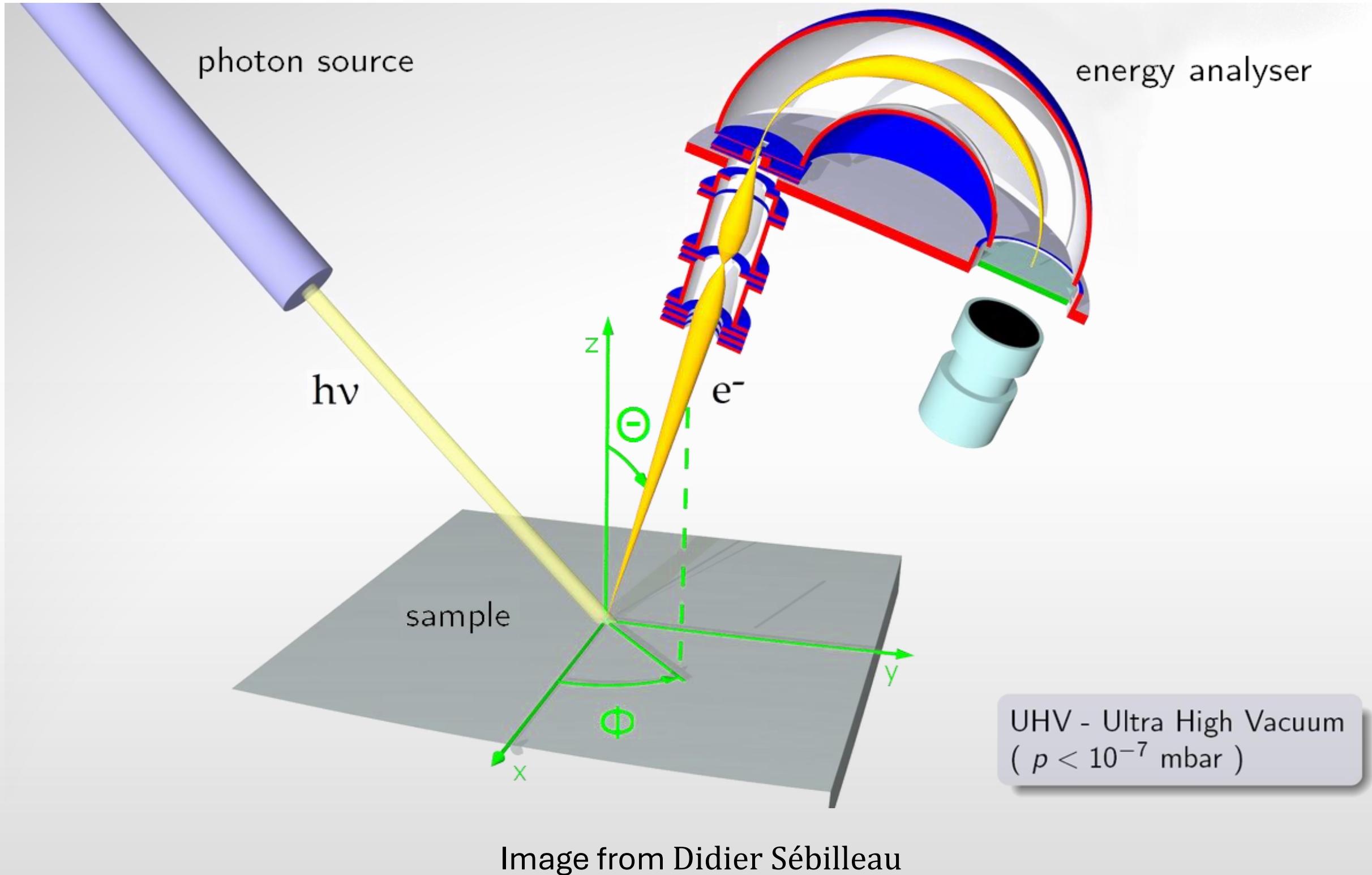


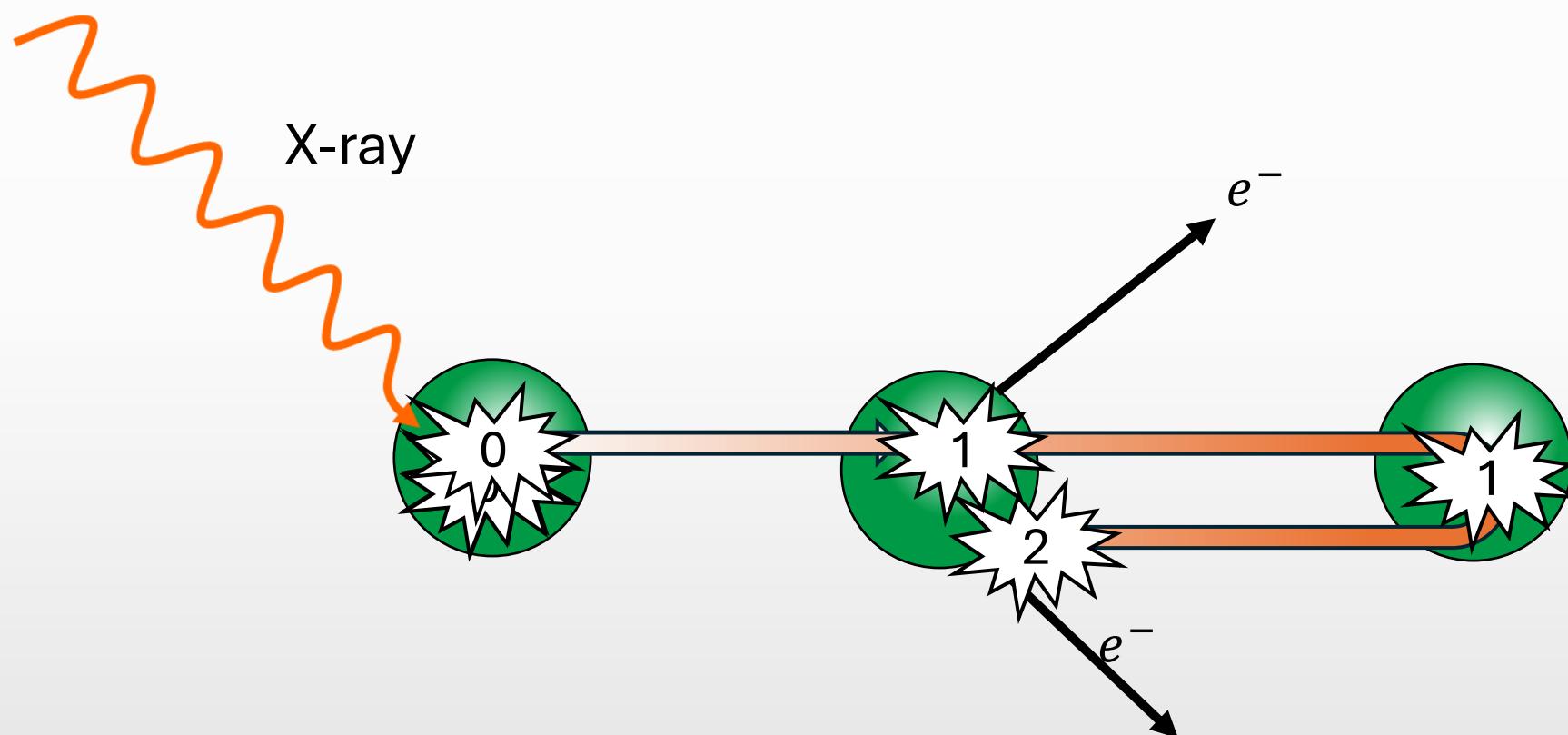
Image from Didier Sébilleau

- $N \sim N_{\text{at}} * (l_{\text{max}} + 1)^{**2}$
- $E_k = 40\text{eV}, l_{\text{max}} = 4$
- $E_k = 1000\text{eV}, l_{\text{max}} = 15$
- $E_k = 8000\text{eV}, l_{\text{max}} = 50$

- High truncation order of scattering paths
  - ✓ High kinetic energy for photo electron ( $\sim 1000\text{eV}$ ) (lab condition)
  - ✓ Electron Mean Free Path is large (19Å: larger clusters)
- High consumption of scattering orders
  - ✓ Sr has higher backscattering factor than Ti and O
  - ✓ Forward scattering factor > lattice parameter

## Calculation time

- Calculation time is proportional to the number of paths taken into account (not the atomic species and structure,...purely geometric way !):
- ✓ E.g. 1: 3 Sr atoms, scattering order = 2



Some other scatterings taken into account...  
Totally... 7 !  
It doesn't take even 1 minutes to calculate !

- In PED, we focus on differential cross section. (reflecting the structure of material)
- It's associated with the scattering path operator:

$$\tau = \mathbf{T}(\mathbf{I} - \mathbf{G}_0 \mathbf{T})^{-1}$$

✓ Physic is easy !

- $\mathbf{T}$ : scattering by individual atom with potential

- $\mathbf{G}_0$ : free propagation of an electron from atom to atom

✓ We need to solve the eigenvalue equation of  $\tau$ :

✓ We have to inverse the matrix,  $(\mathbf{I} - \mathbf{G}_0 \mathbf{T})^{-1}$  → **Matrix inversion method**

✓ It is mostly impossible because the matrix size is huge for clusters.

- Instead of it:

$$\bar{\tau}^{ji} = \bar{T}_i \delta_{ij} + \bar{T}_j G_o \bar{T}_i + \sum_{k \neq i,j} \bar{T}_j G_o \bar{T}_k G_o \bar{T}_i + \dots$$

- ✓ This is looking like:

$$(1 - x)^{-1} = 1 + x + x^2 + \dots$$

where  $x \cong G_0 T$  (don't check your math !)

- ✓ It diverges at  $x > 1$ .

- In this regard, we have divergence if  $\text{spec}(G_0 T) > 1$ ; absolute value of some eigenvalue is above 1.

- We introduce spectral radius:

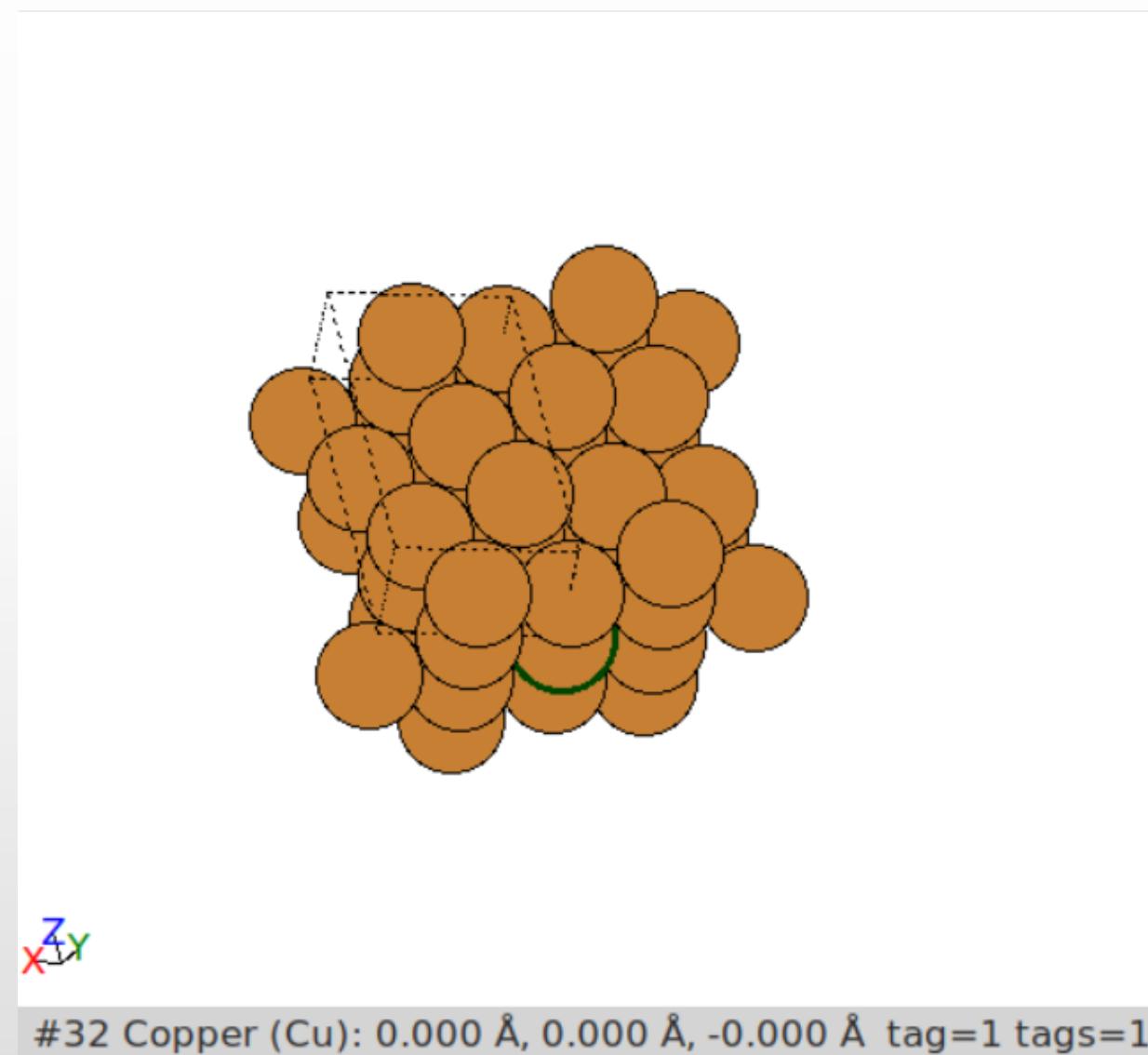
$$\rho = \max_{\lambda} \text{abs}(\lambda)$$

- Then we may say:

$$\rho > 1 \stackrel{\text{def}}{\iff} (\text{Divergence appears})$$

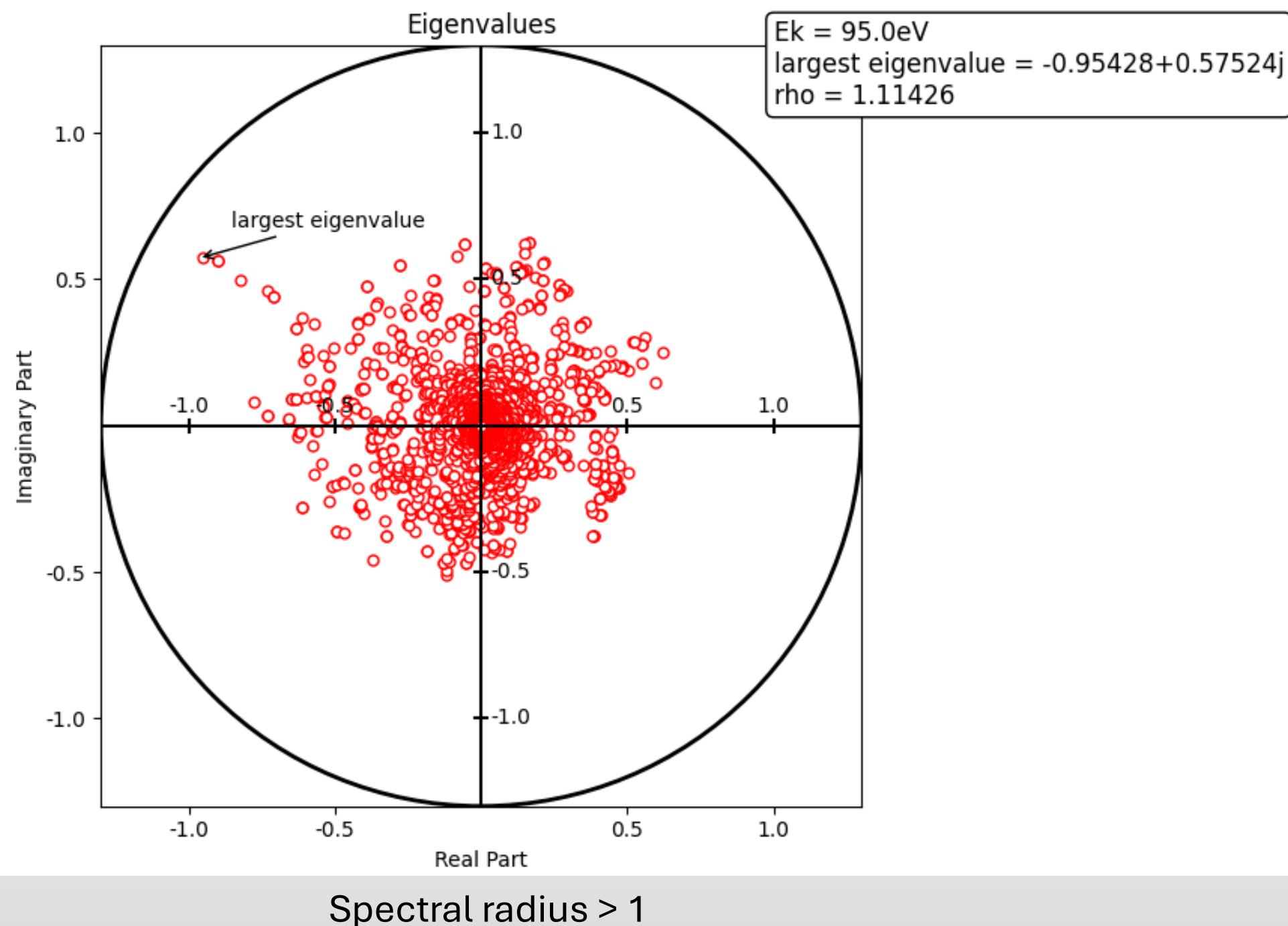
# Success of Renormalization methods

- Mainly, three methods have been proposed and successful to break the divergence !
  - ✓ E,g.: G\_1 (approximation at n=1, enough for most of cases...)



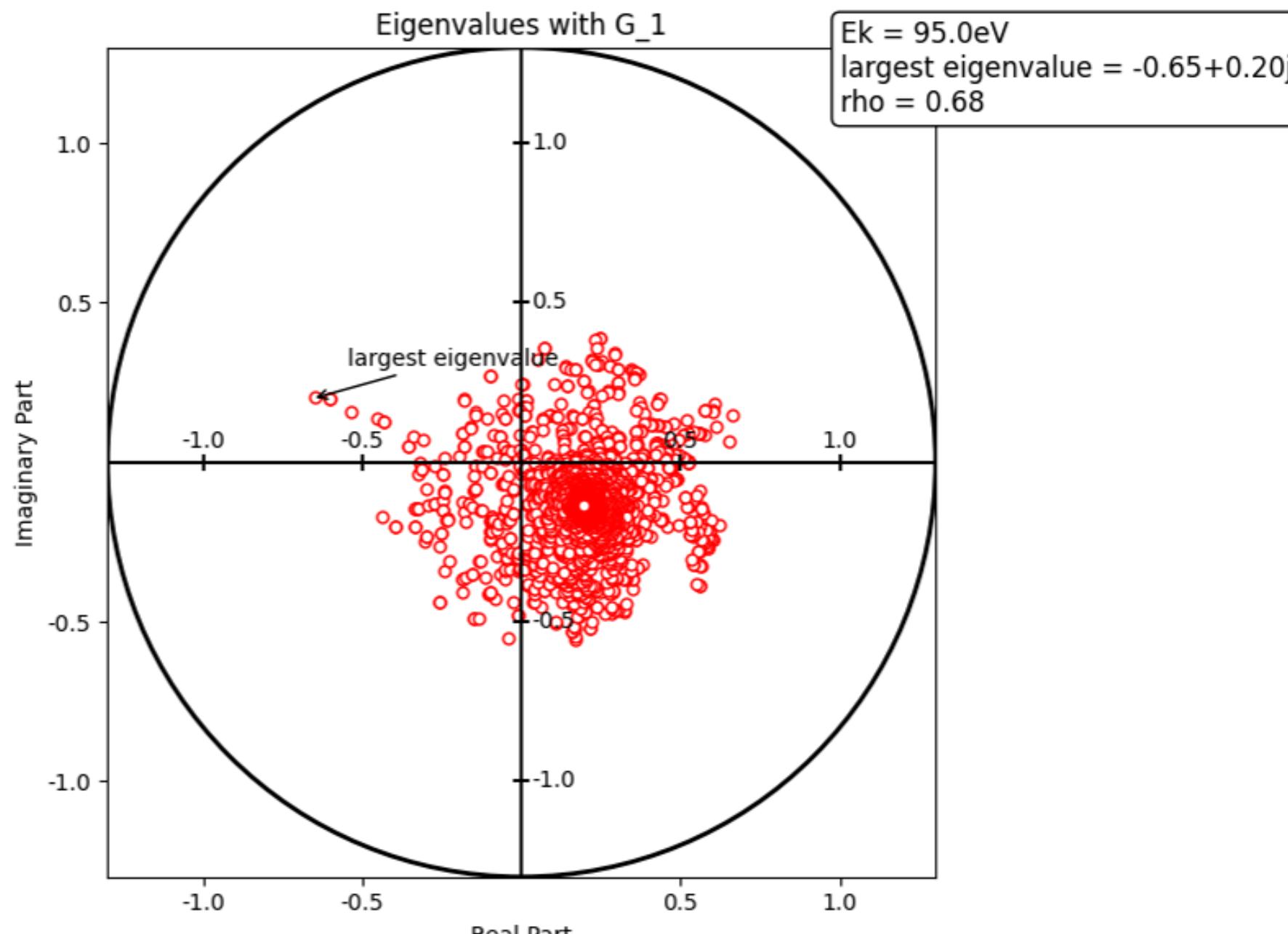
# Success of Renormalization methods

- All spectra are:



# Success of Renormalization methods

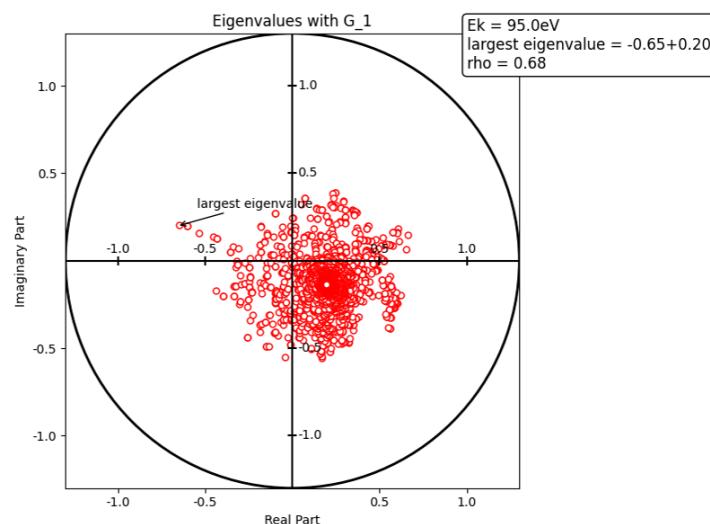
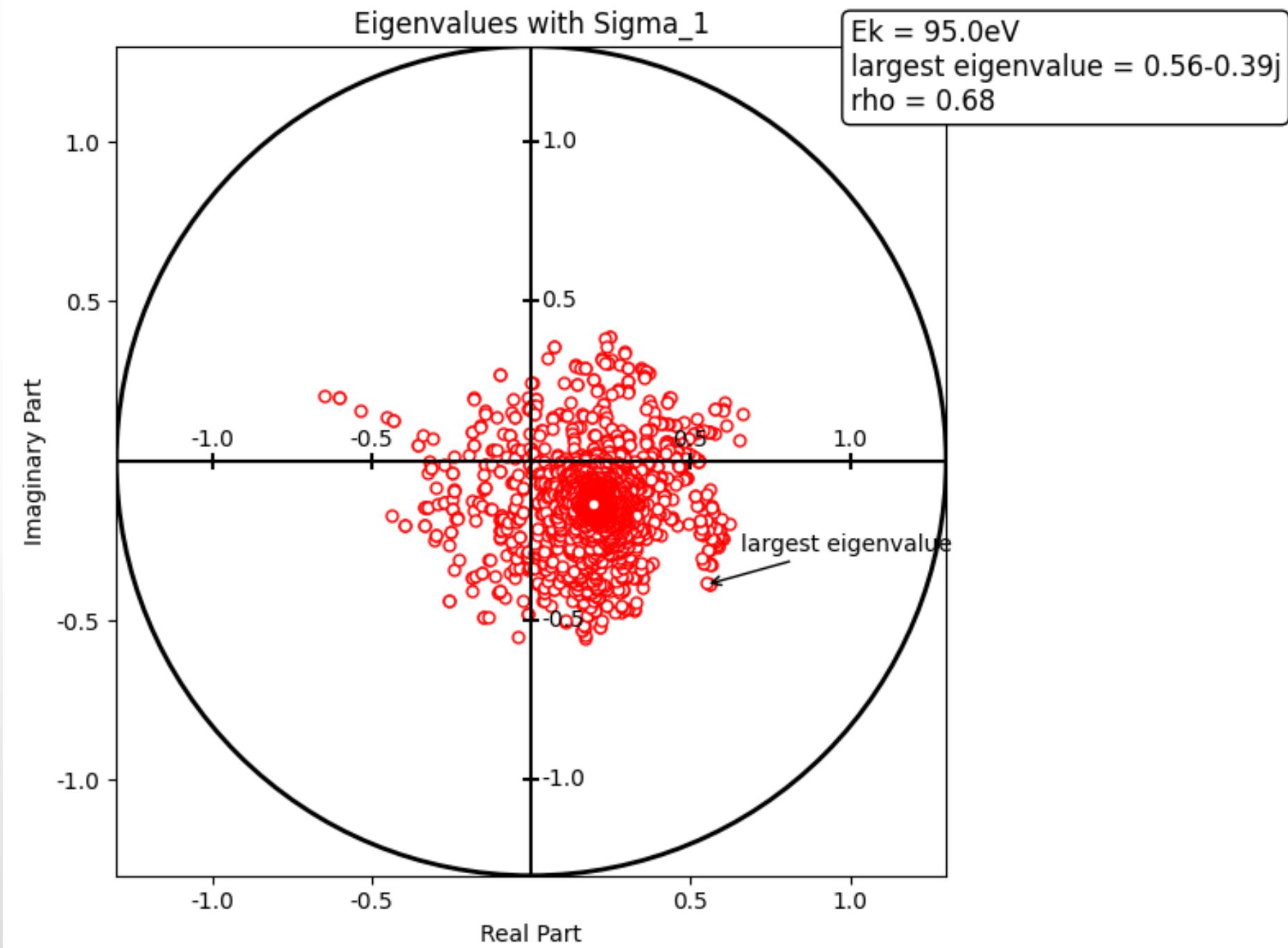
- Using G\_1 is good:



Spectral radius < 1

# Success of Renormalization methods

- Others:

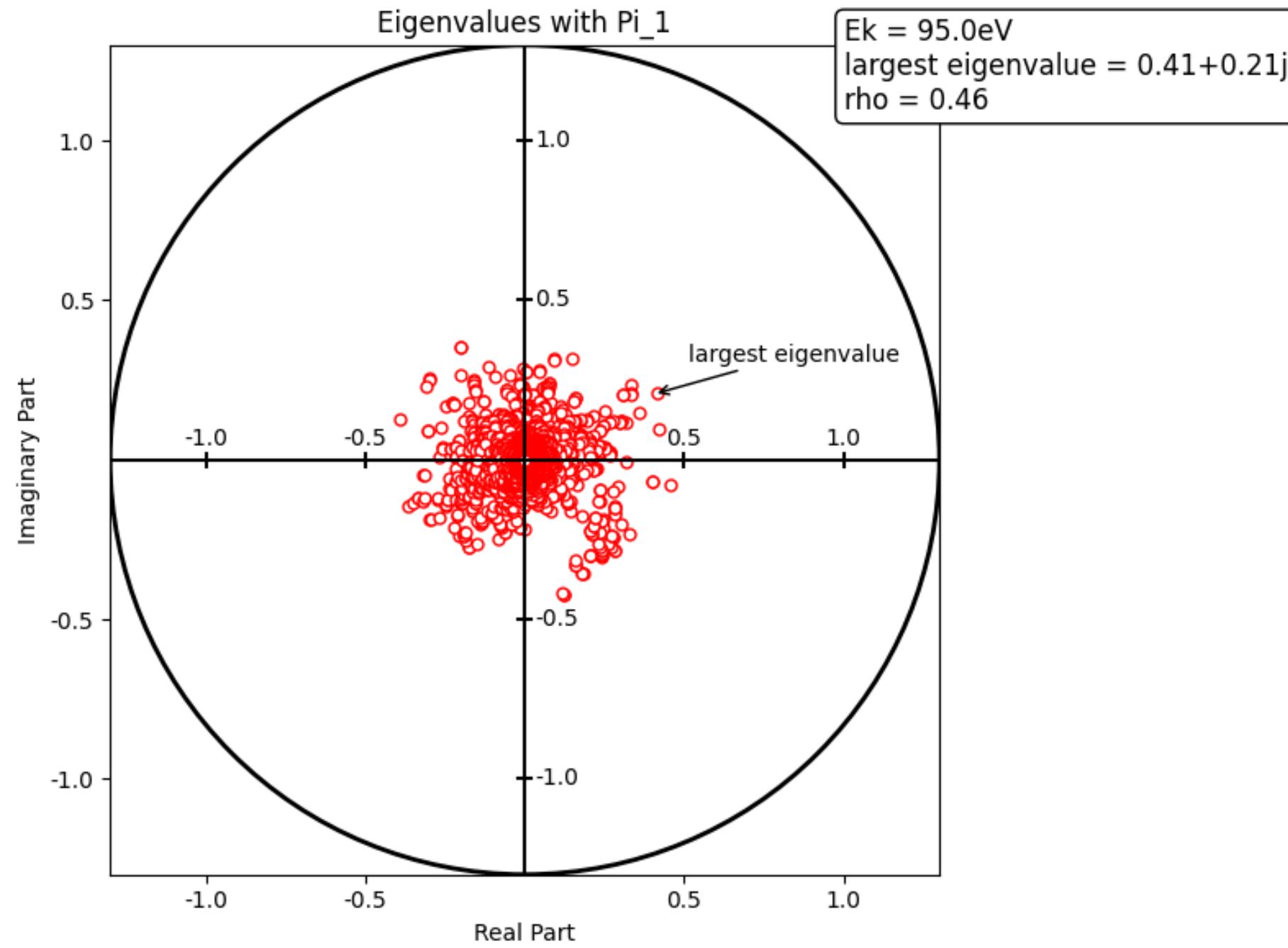


G\_1

Around the same distribution and same spectral radius as G\_1 !

# Success of Renormalization methods

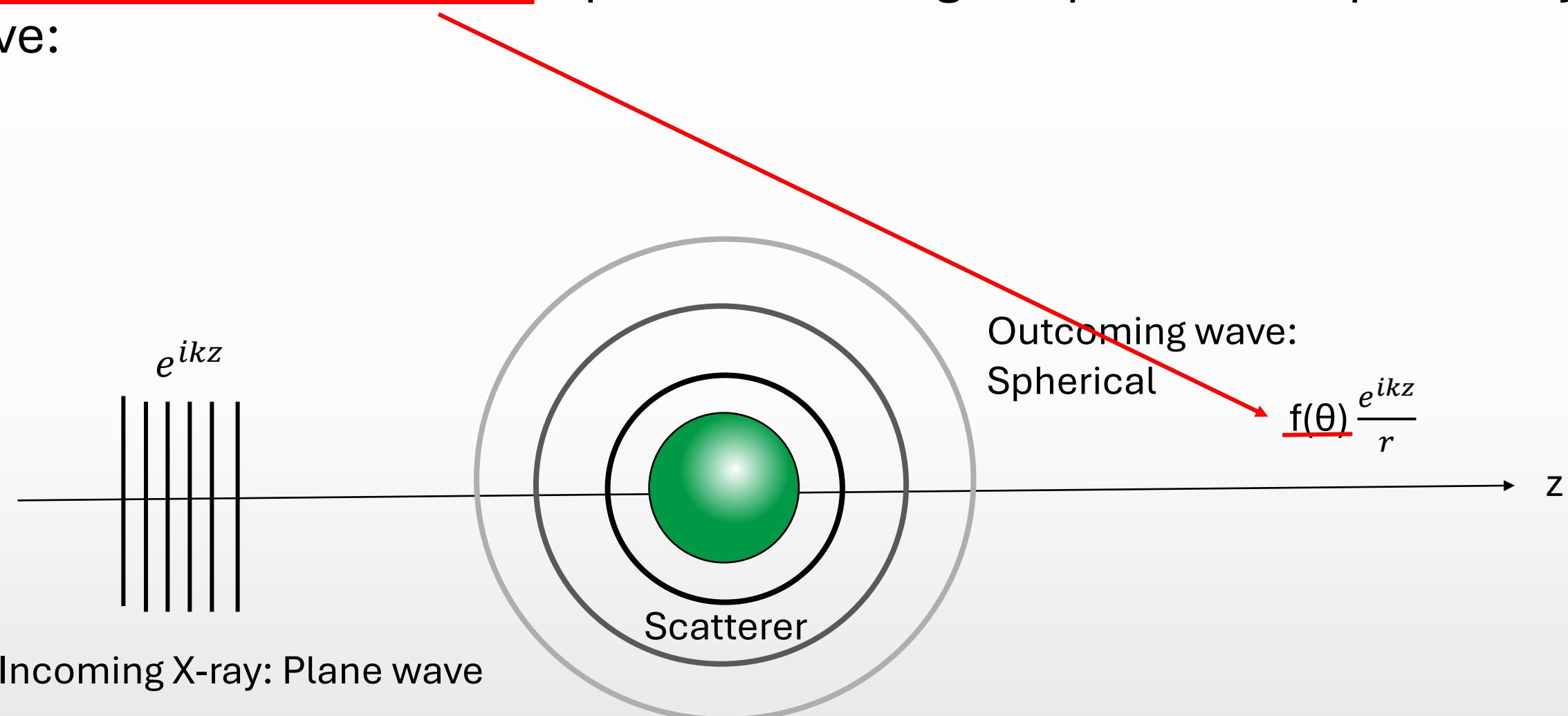
- Others:



Most condensed around the center; expected to converge fastest !

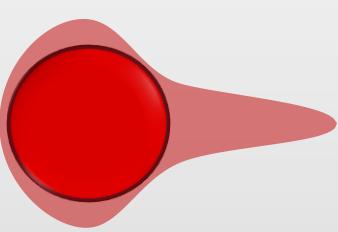
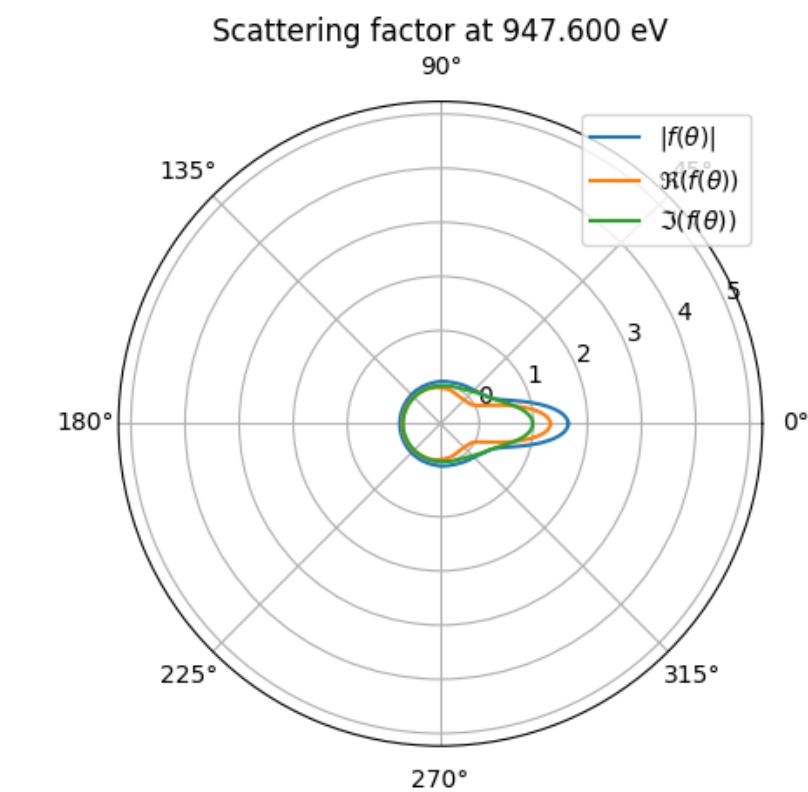
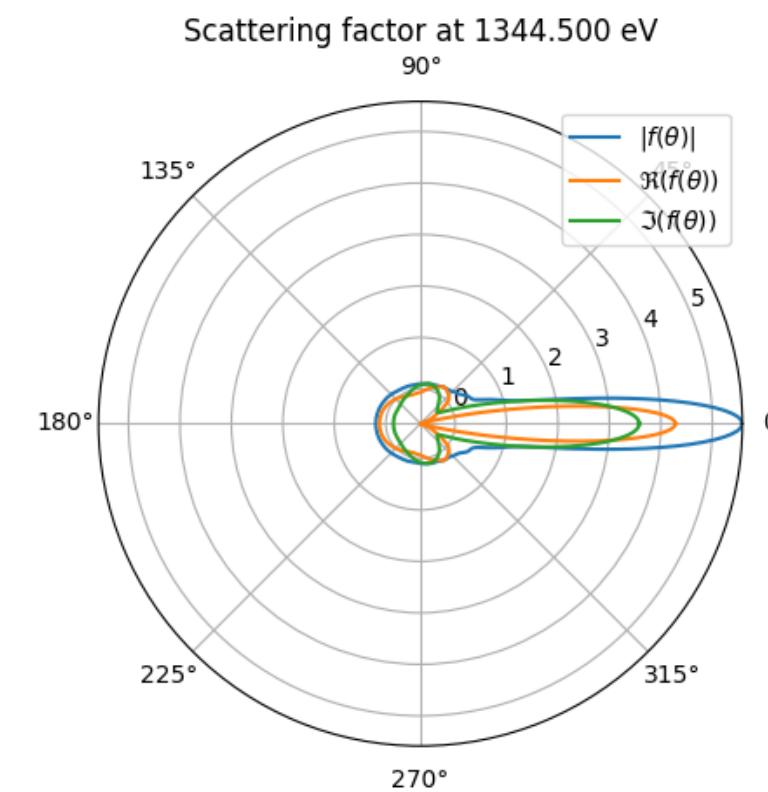
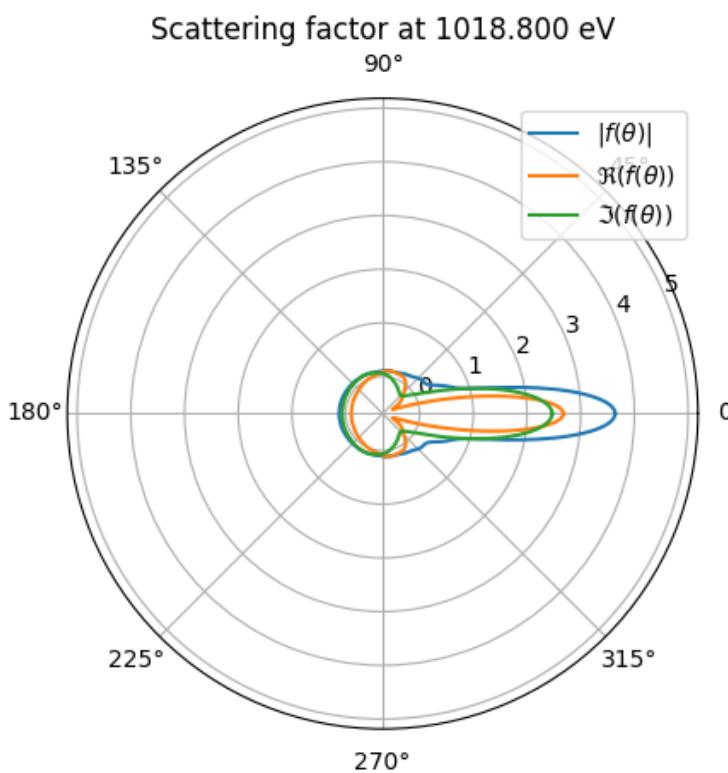
# Scattering factor

- Scattering amplitude,  $f(\theta)$  represents an angular part of the spherically scattering wave:



# Scattering factor

- Scattering factor is the largest in forward and backward for Sr

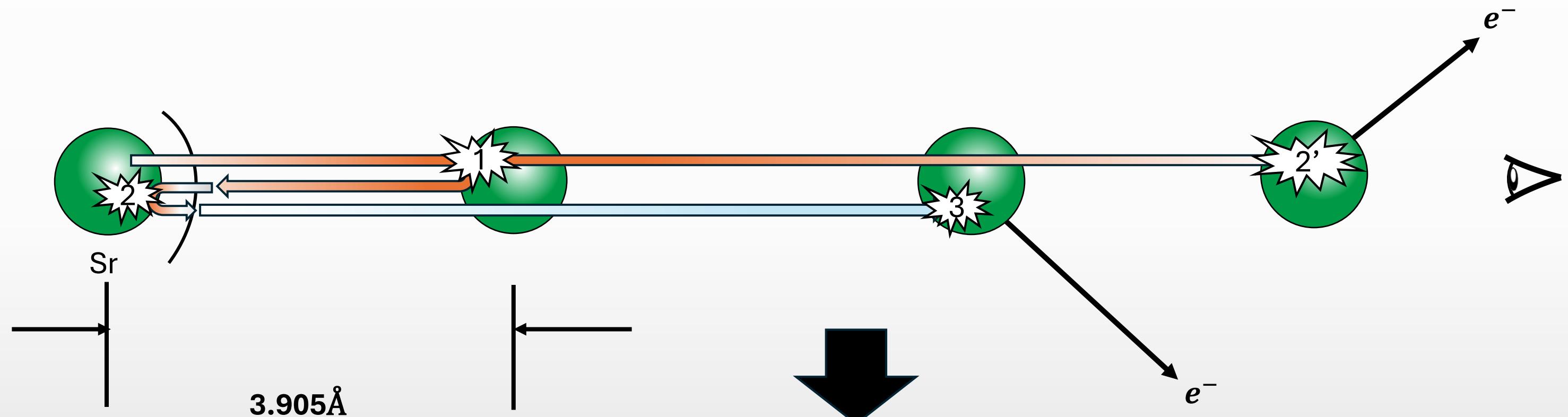


# Scattering factor

- High consumption of scattering orders:

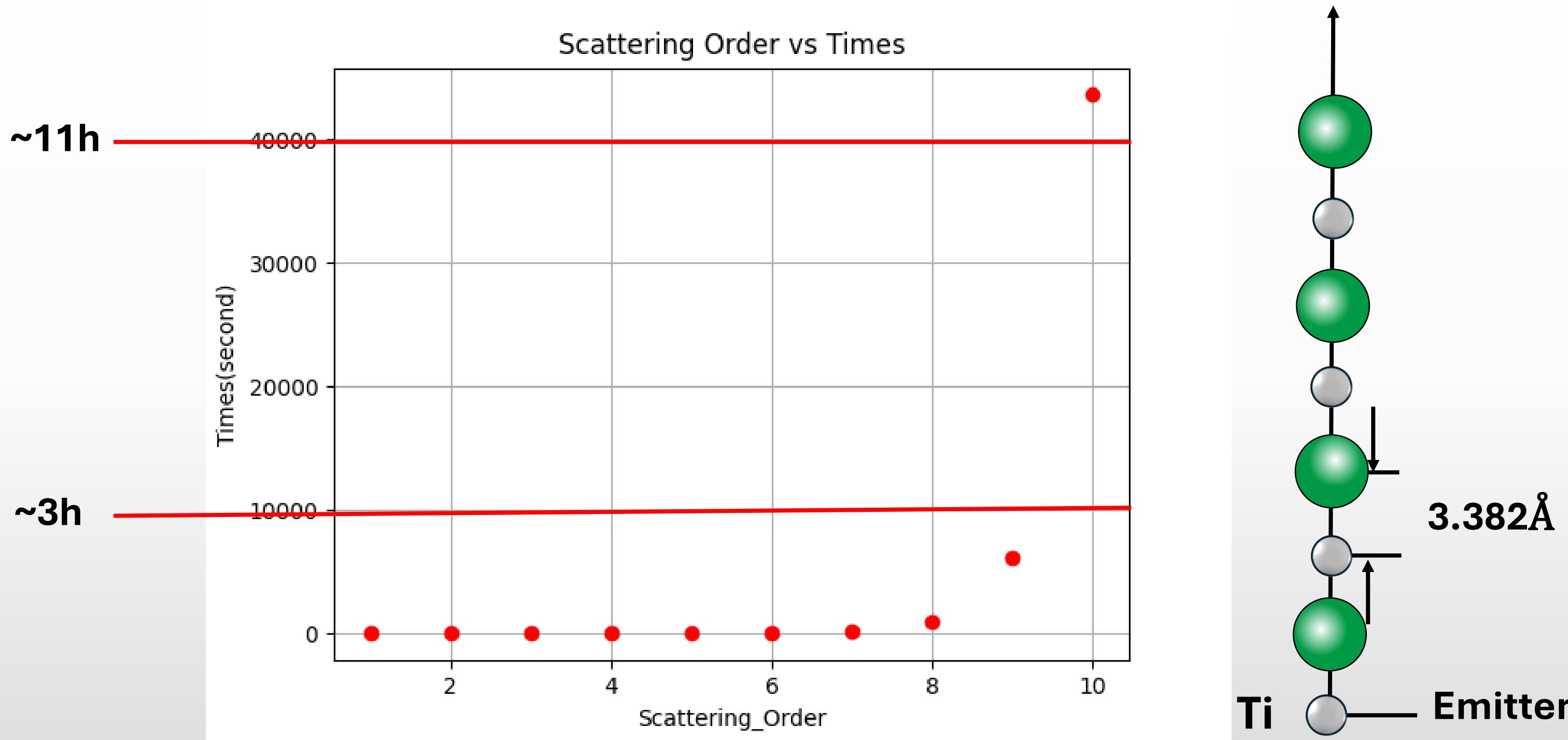
E.g.: 4 Sr atoms, scattering order = 3

We can do a few scattering events in PC, but it's not few for back scatterings !



Certain error per each scattering  
High error accumulation

# Scattering vs calculation time



## Experimental setup

- Energy Source
- ✓ The energy of X-ray source should be higher than the orbital energy

$$\underline{E_e} = \underline{h\nu}_{\text{Source energy}} - \underline{E_o}_{\text{Orbital energy}} - \underline{W}_{\text{Work function } \sim 4 - 5 \text{ eV, negligible}}$$

Kinetic energy of  $e^-$

- Geometry
- ✓ Cluster orientation, angles of X-ray Source, etc...
- Cluster detail
- ✓ Orbital energy for an emitter (For STO, Sr Ti and O applies)

## Experimental setup - Energy Source – [3]

- We have two considerations:
  - ✓ Line width must not limit the energy resolution
  - ✓ Energy must be high enough
- In general, two types of materials are used for energy source, Al and Mg.
  - ✓ Line width less than 1.0eV
  - ✓ High energy
  - ✓ Moreover, ease of fabrication and stability under electron bombardment

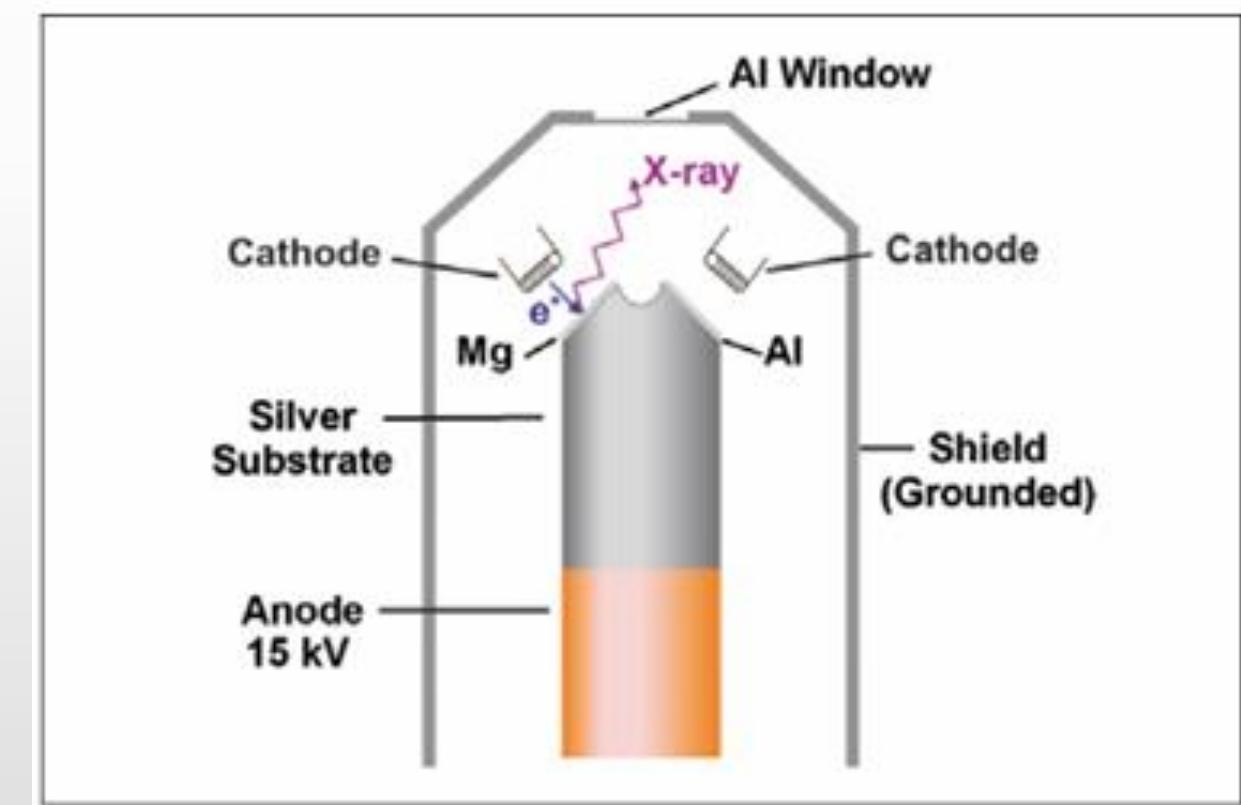
Energies and widths of some characteristic soft X-ray lines (excerpted from )

Line	Energy,eV	Width,eV
Mg Ka	1253.6	0.7
Al Ka	1486.6	0.85

[3] D.Briggs and M.P.Seath PRACTICAL SURFACE ANALYSIS SECOND EDITION VOLUME 1 – Auger and X-ray-Photoelectron Spectroscopy (1990) (p51 - 54)

## Experimental setup - Energy Source – [3]

- Two thin films are deposited on Cu anode ( $10\mu\text{m}$  in typical).
- ✓ Both are switched simply, in a couple of minutes.
- Two cathodes eject electrons into the anode nearby.
- Water flowing inside the anode to cool it under the electron bombardment.
- X-ray passes out through Al window.
  - ✓ screen the sample from stray electrons
  - ✓ // heating effects
  - ✓ // contamination in the source



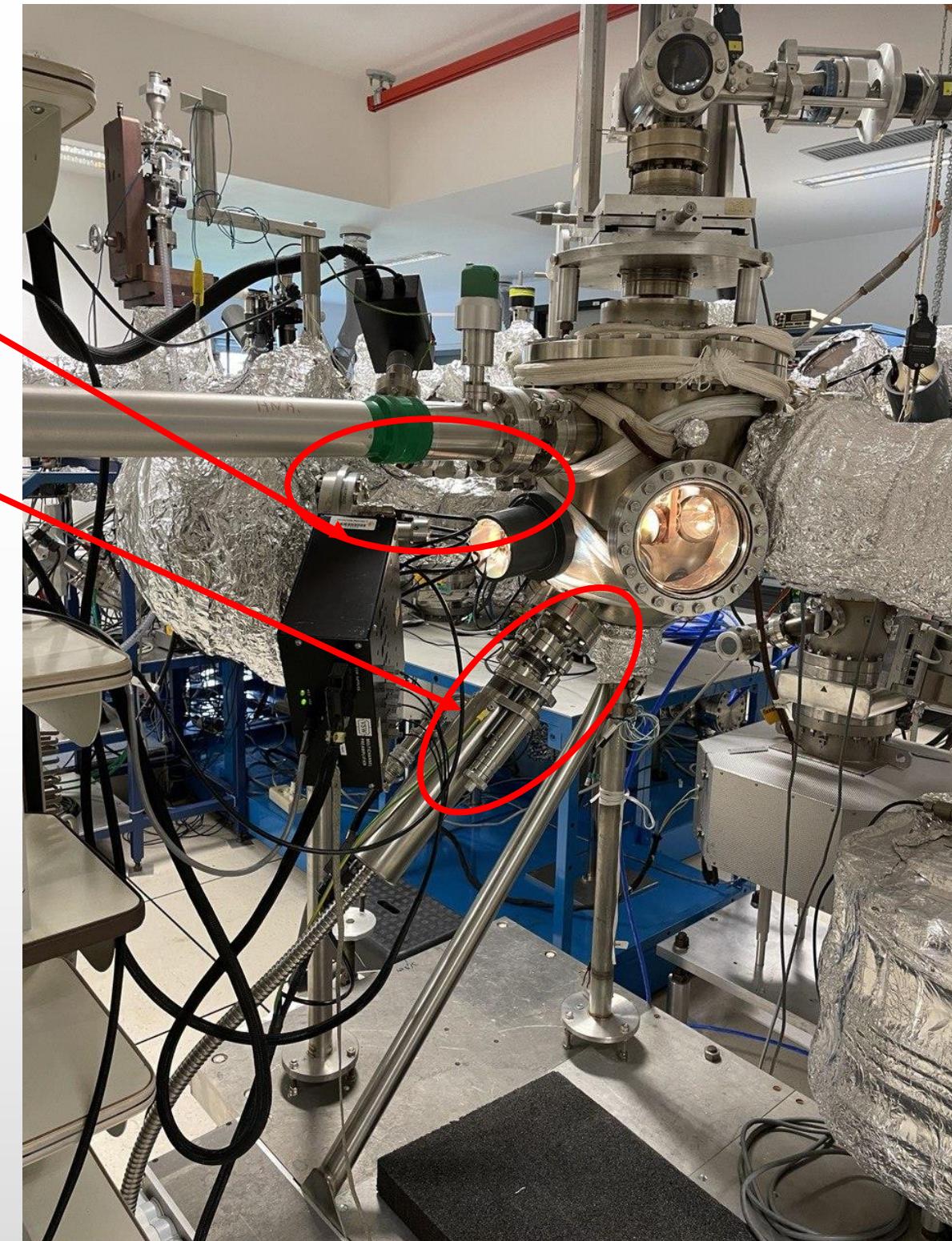
Twin X-ray anode sources

[3] (p54 - 56)

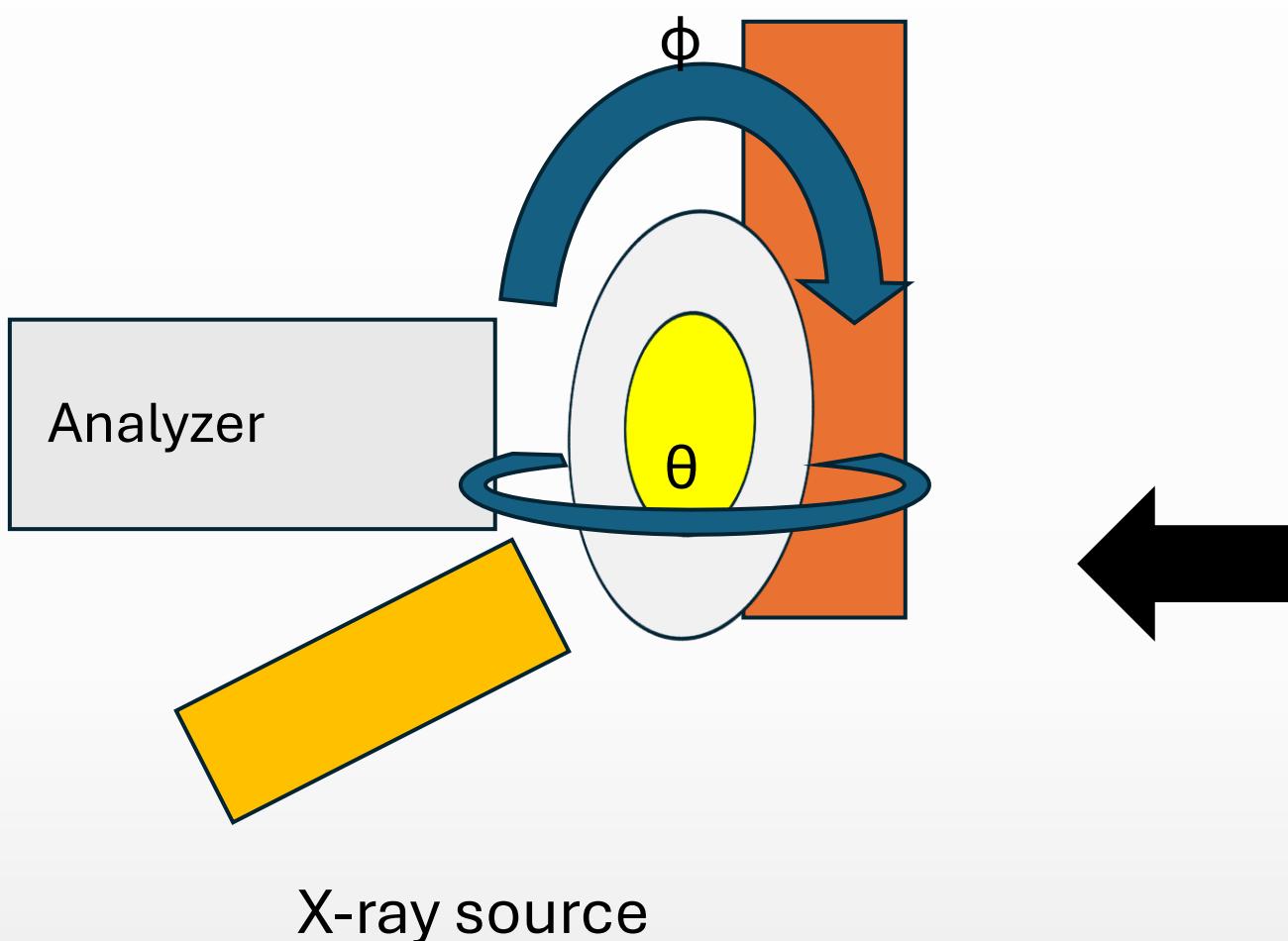
<https://www.thermofisher.com/fr/fr/home/materials-science/learning-center/surface-analysis/x-ray-generation.html>

# Experimental setup - Geometry -

Analyzer  
X-ray tube  
Description for XPD

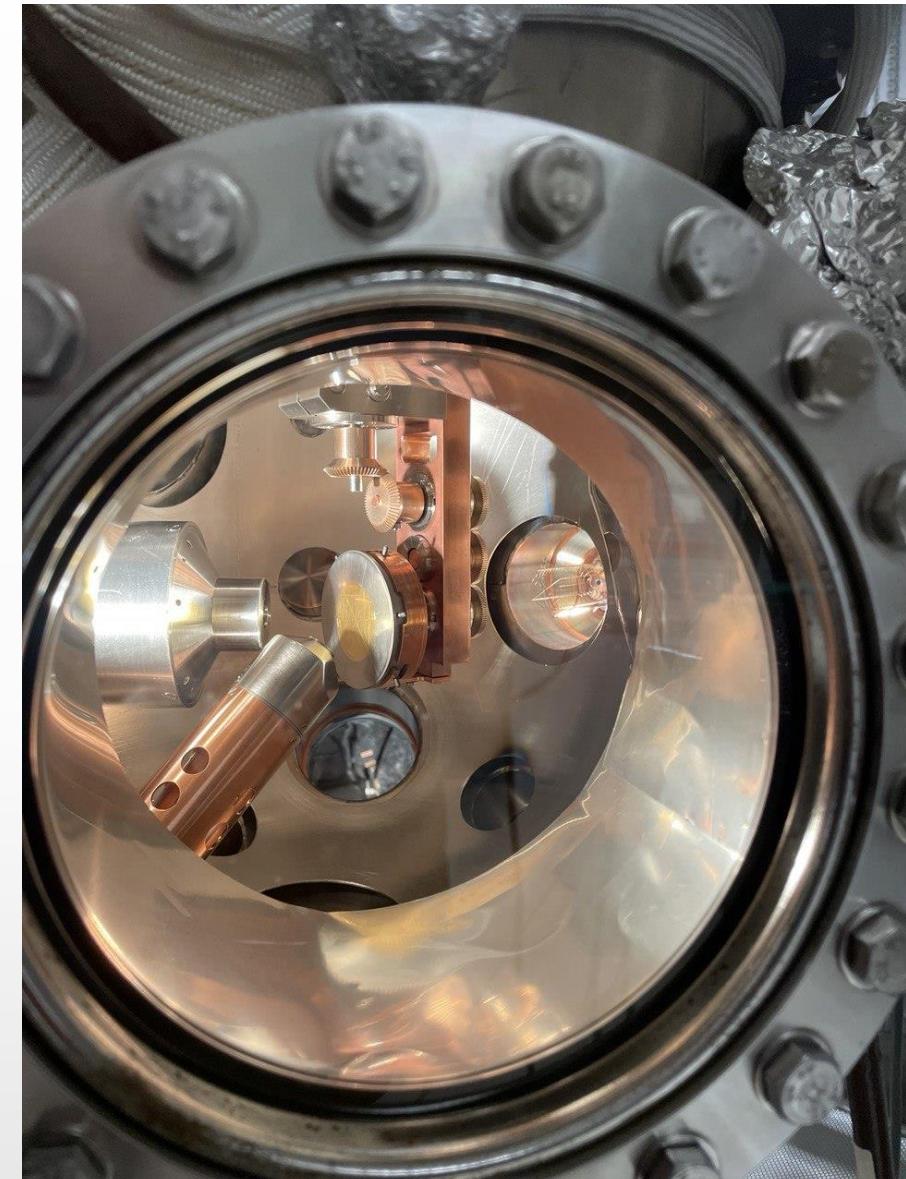


# Experimental setup - Geometry -

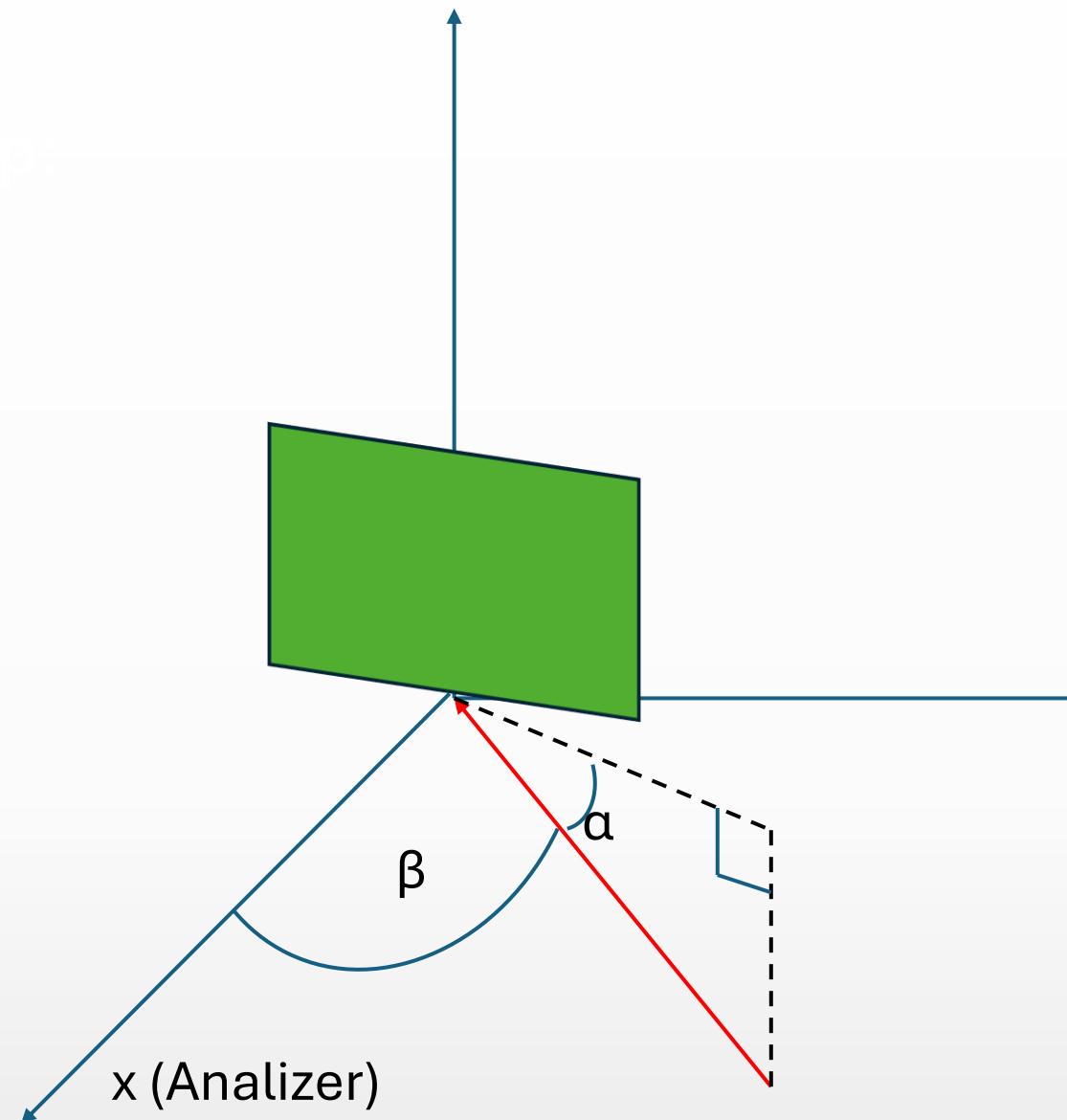


Theta scan possible only from -  
 $10^\circ$  to  $\sim 60^\circ$

(less than  $-10^\circ$ , the sample would  
hit the X-ray source)

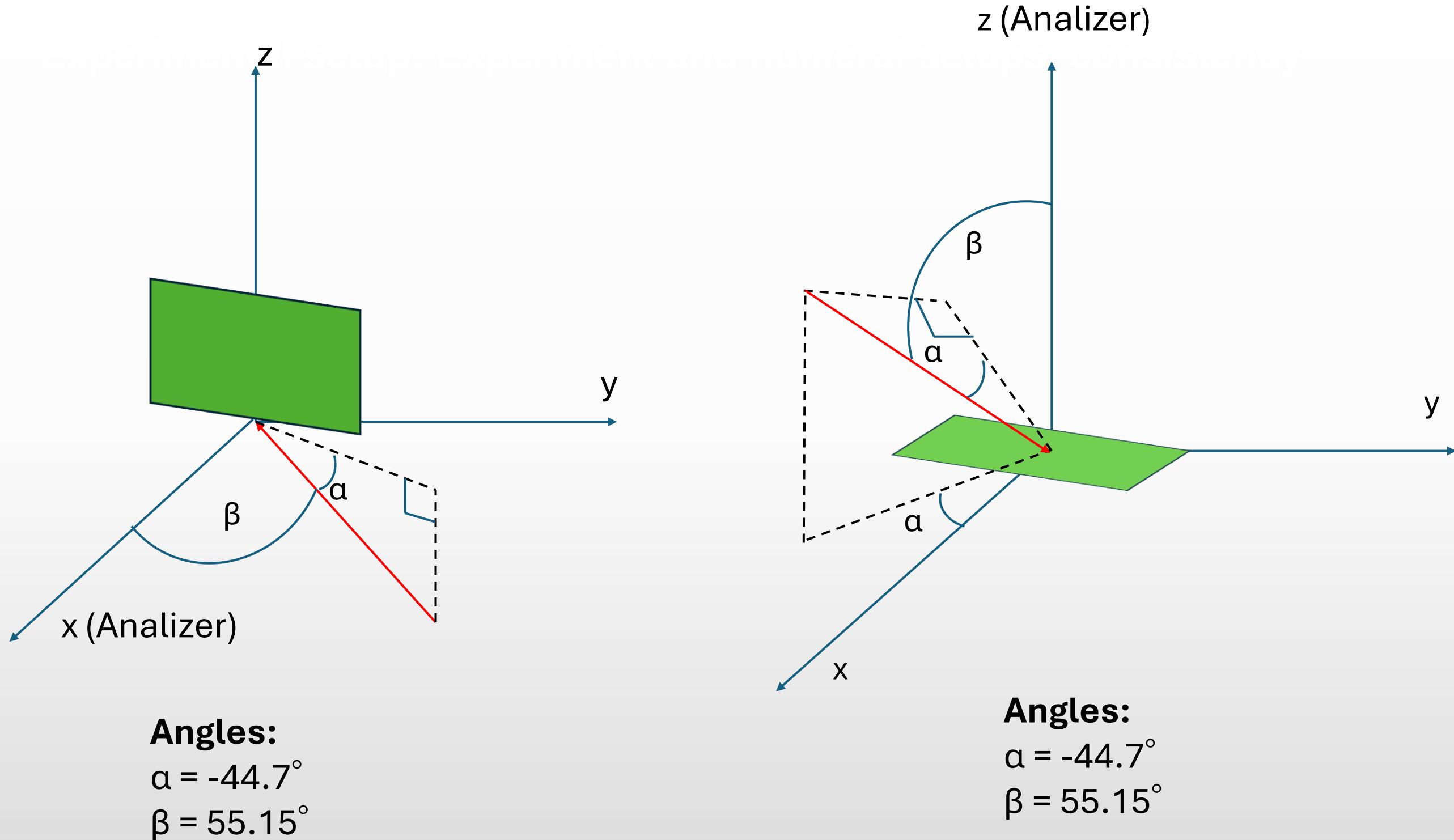


## Experimental setup - Geometry -



- Analyzer axis is normal to the surface and fixed during the experiment.
- Angle between the analyser axis and x-ray Axis =  $\beta = 55.15^\circ$  ( $\alpha = -44.7^\circ$  )

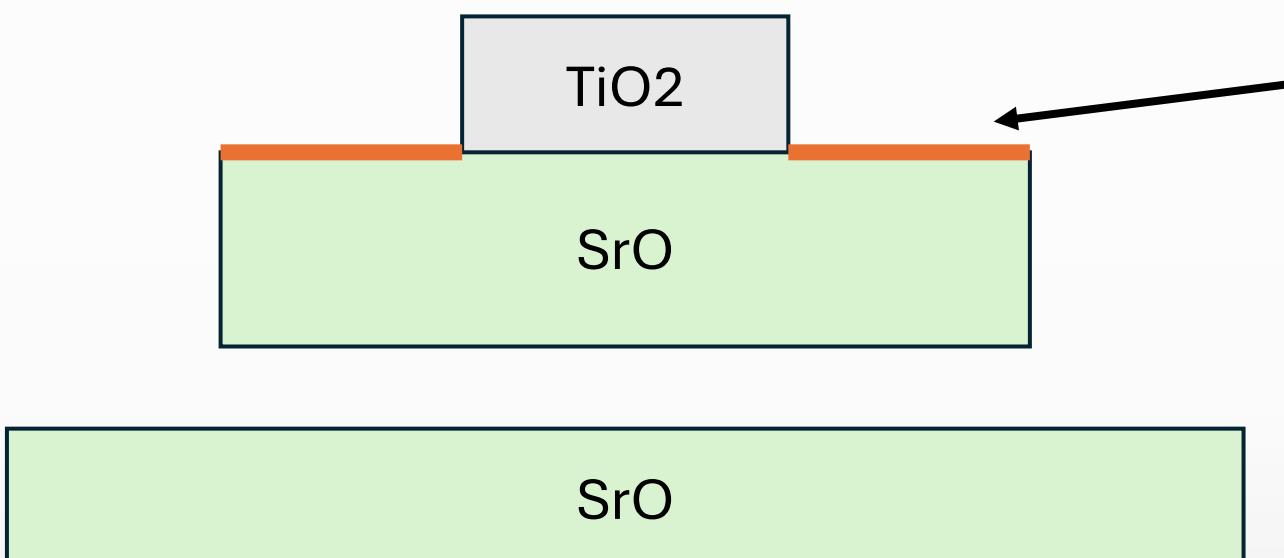
# Experimental setup - Geometry -



# Experimental setup

- **About surface...**

- ✓ Usually, the surface is preferred to be TiO<sub>2</sub> side.



Oxidized:  
 $\text{SrO} \rightarrow \text{Sr(OH)}_2$   
+carbon contaminate

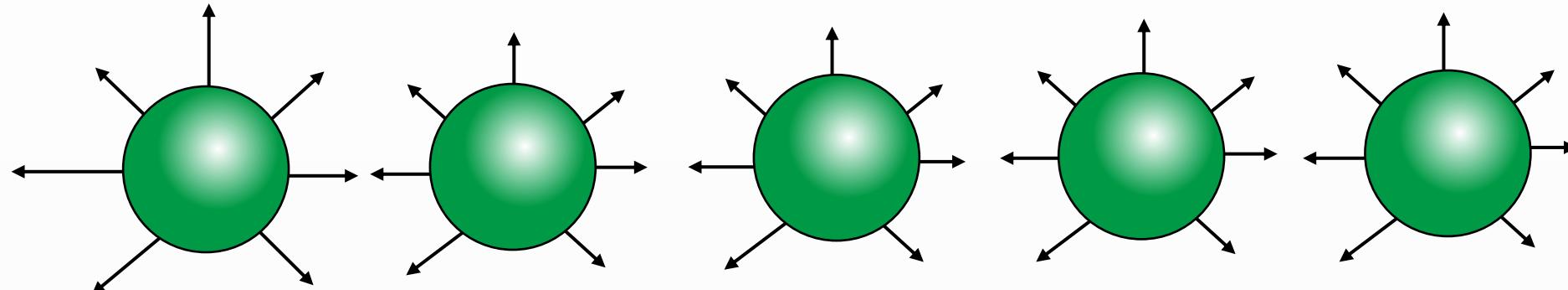
The effect is tiny...

- **About emitter...**

- ✓ **Sr:** 3d5/2 (1344.5 eV), 3d3/2 (1344.5+1.74 eV)
- ✓ **Ti:** 2p3/2 (1018.8eV)
- ✓ **O:** 1s (947.6eV)

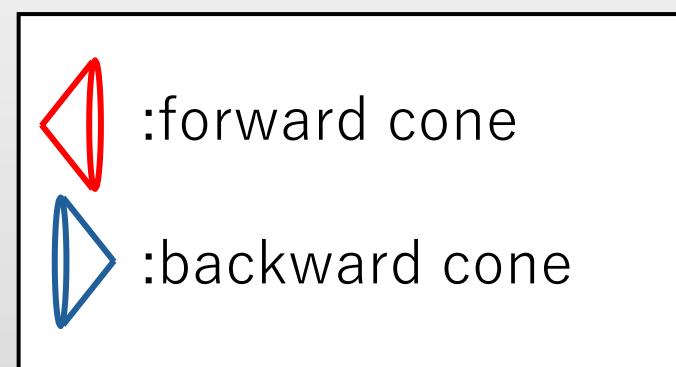
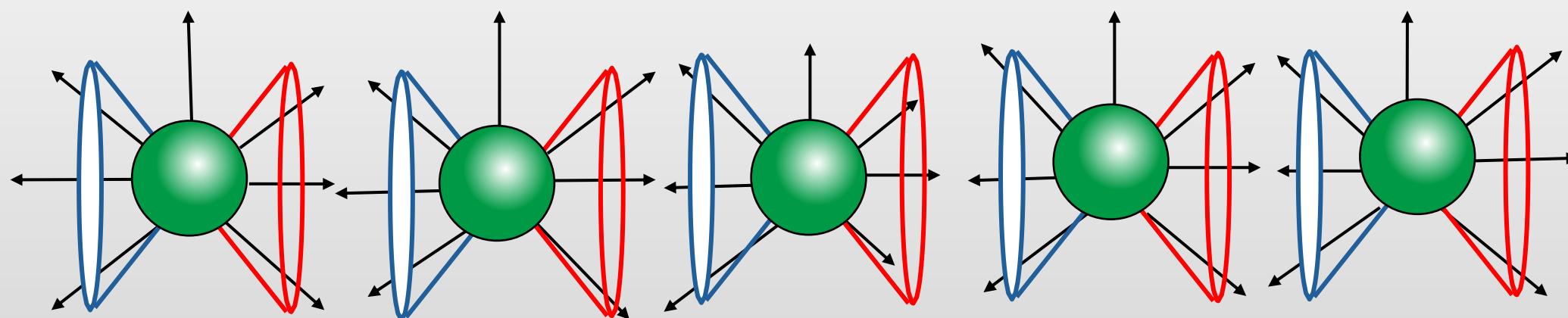
## Another technical method - Path Filtering -

- Usually: huge number of scattering paths



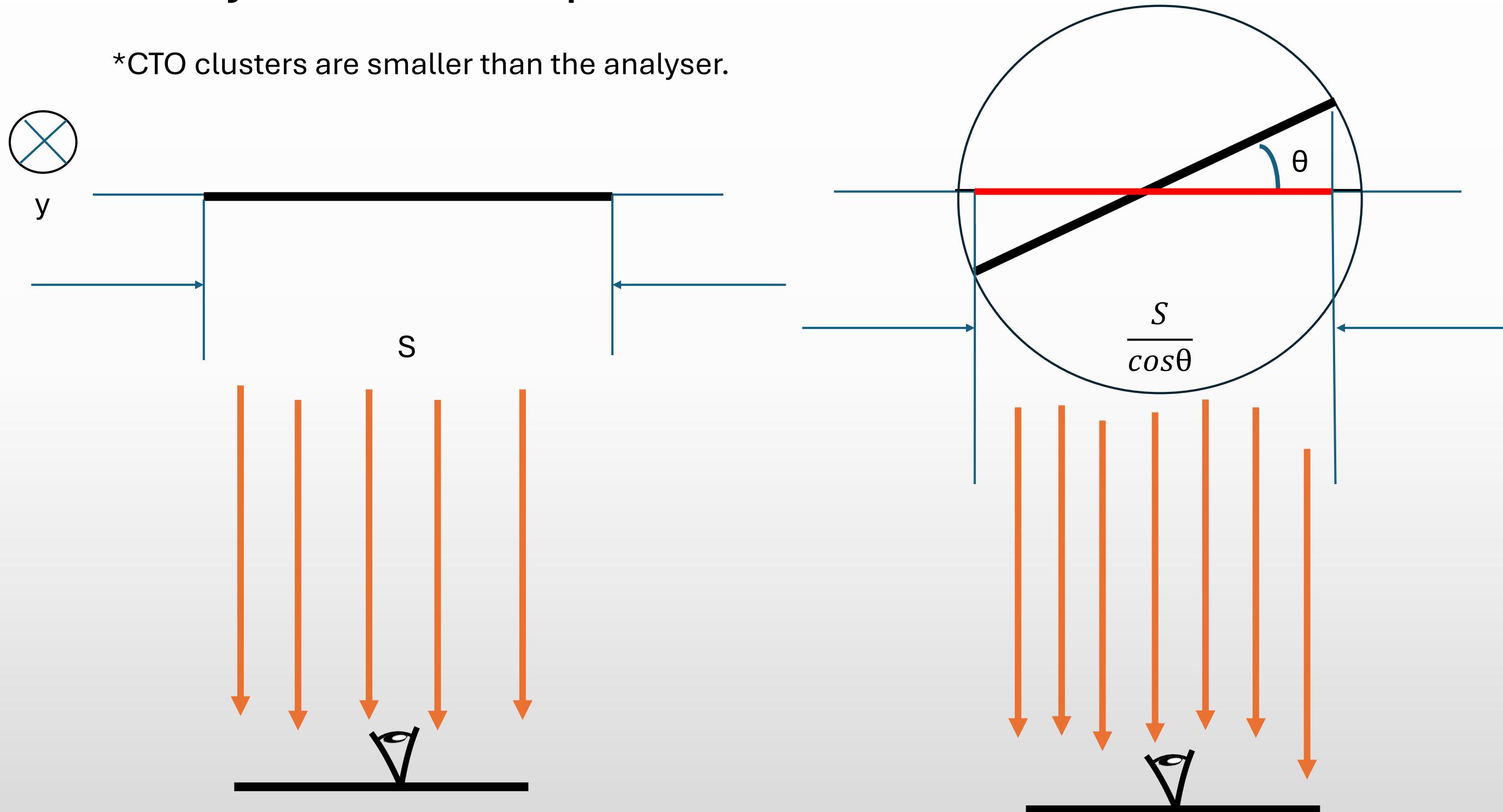
**Key**  
 $(\text{Calculation time}) \propto (\text{Number of paths})$

- Forward or Backward Filterings:



- Analyzer and sample areas

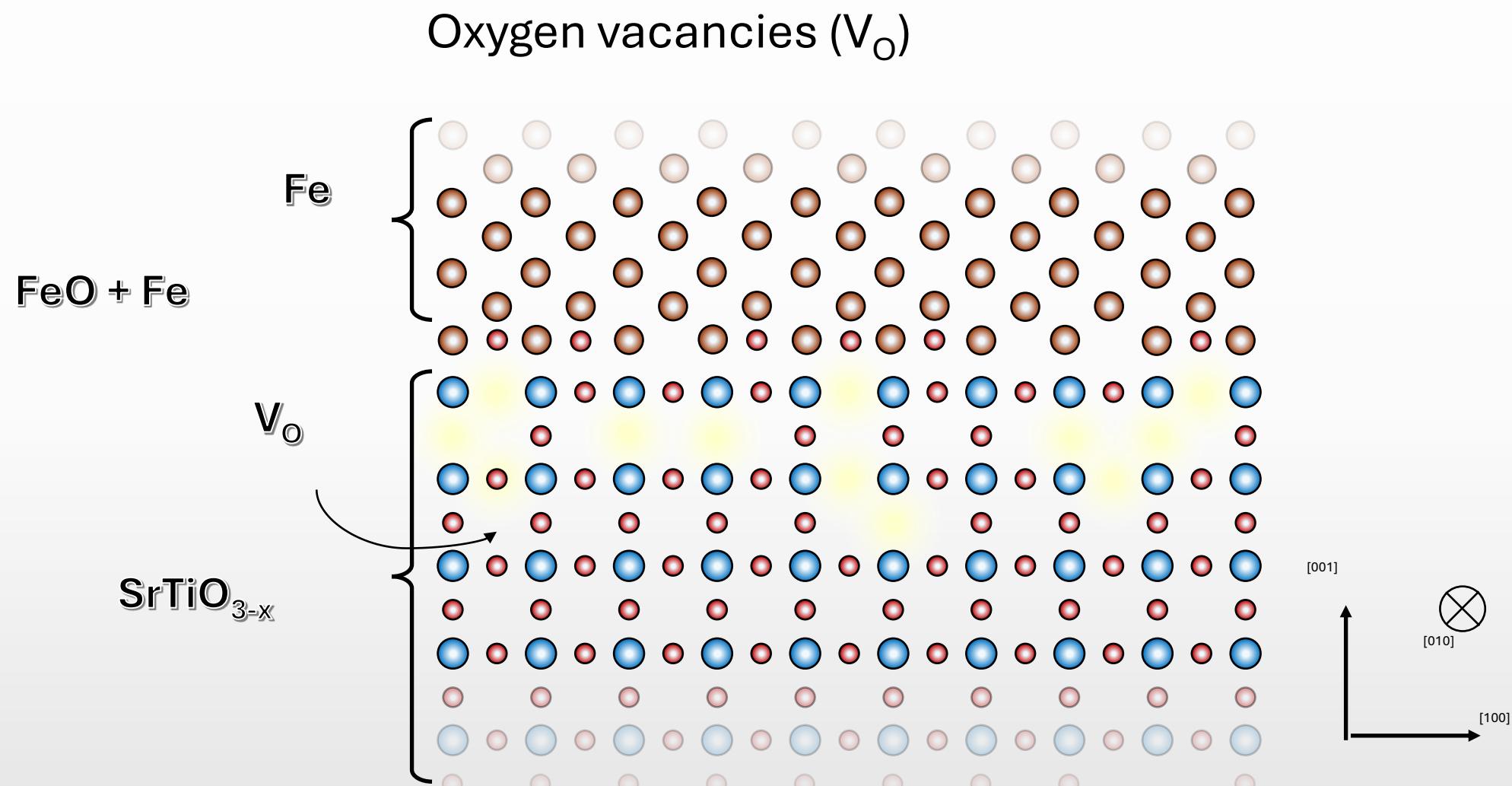
\*CTO clusters are smaller than the analyser.



- Just for having the decrease of the intensity, we have other factors...
- Sensitivity change to the surface
- Pollution of the surface
- Photon flux onto the surface

Etc...

# Oxygen vacancy



# Matrix inversion

- Storage requirements scale as:

$$[(N * (l_{max}))^2]^2$$

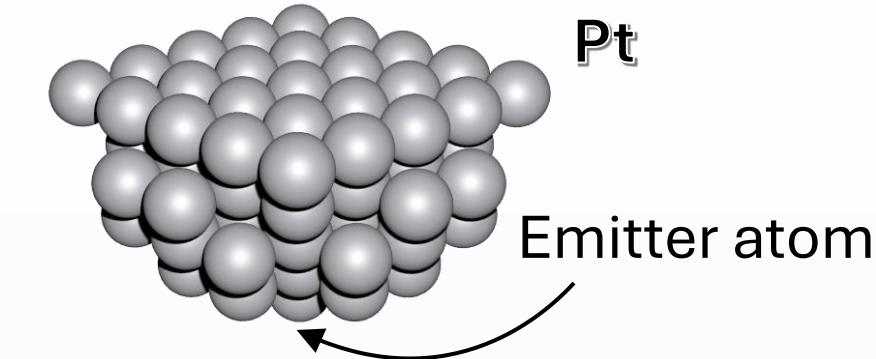
e.g.:

A few Tb of RAM for a cluster of 1000 atoms @ 1000 eV

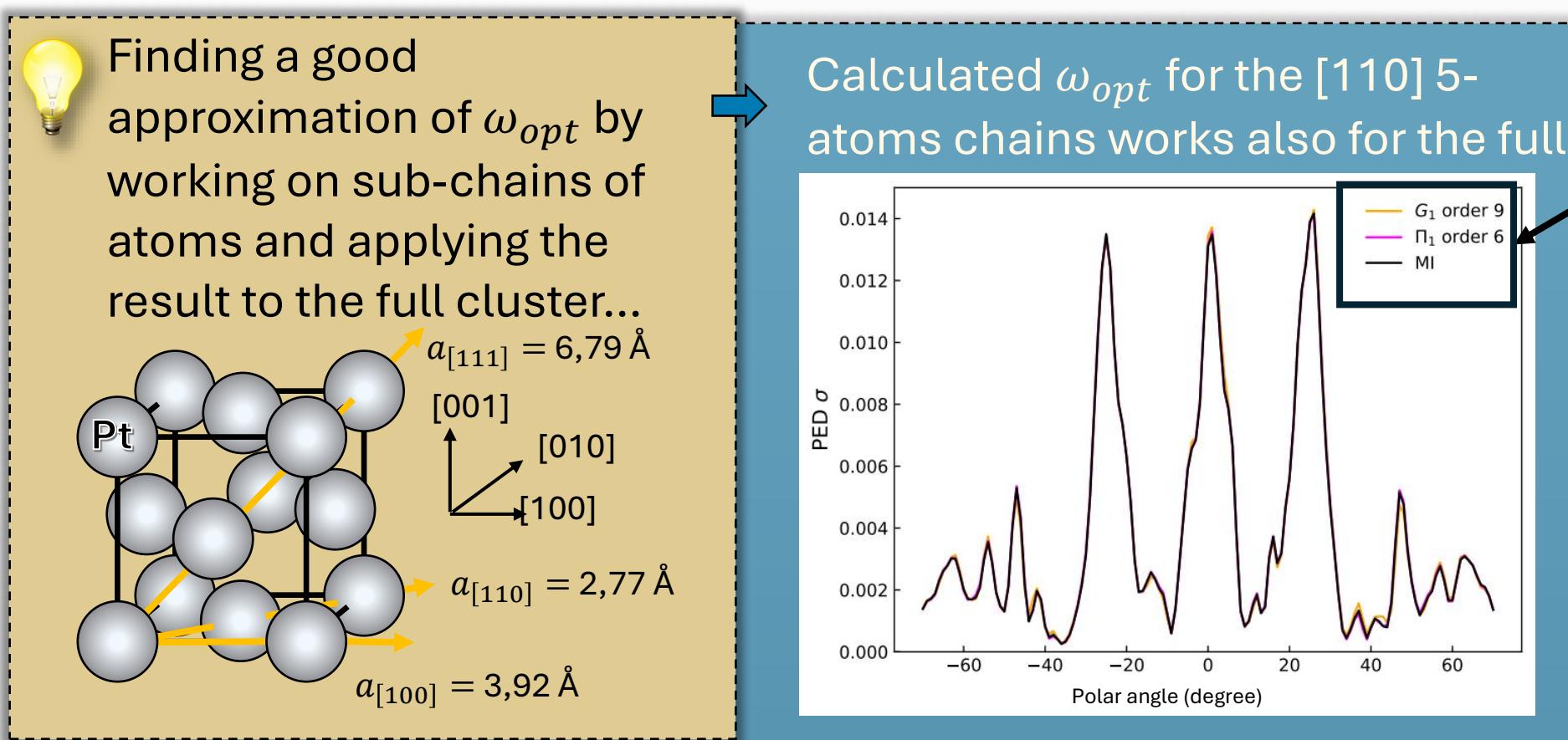
# Methodology for atomic chains

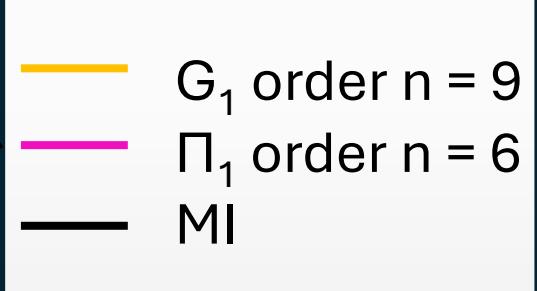
- Methodology: calculate  $\omega$  only for dense atomic chains and then use it for the full cluster.

84 atoms cluster of Pt  
Spectral radius = 1,09 @ 410 eV



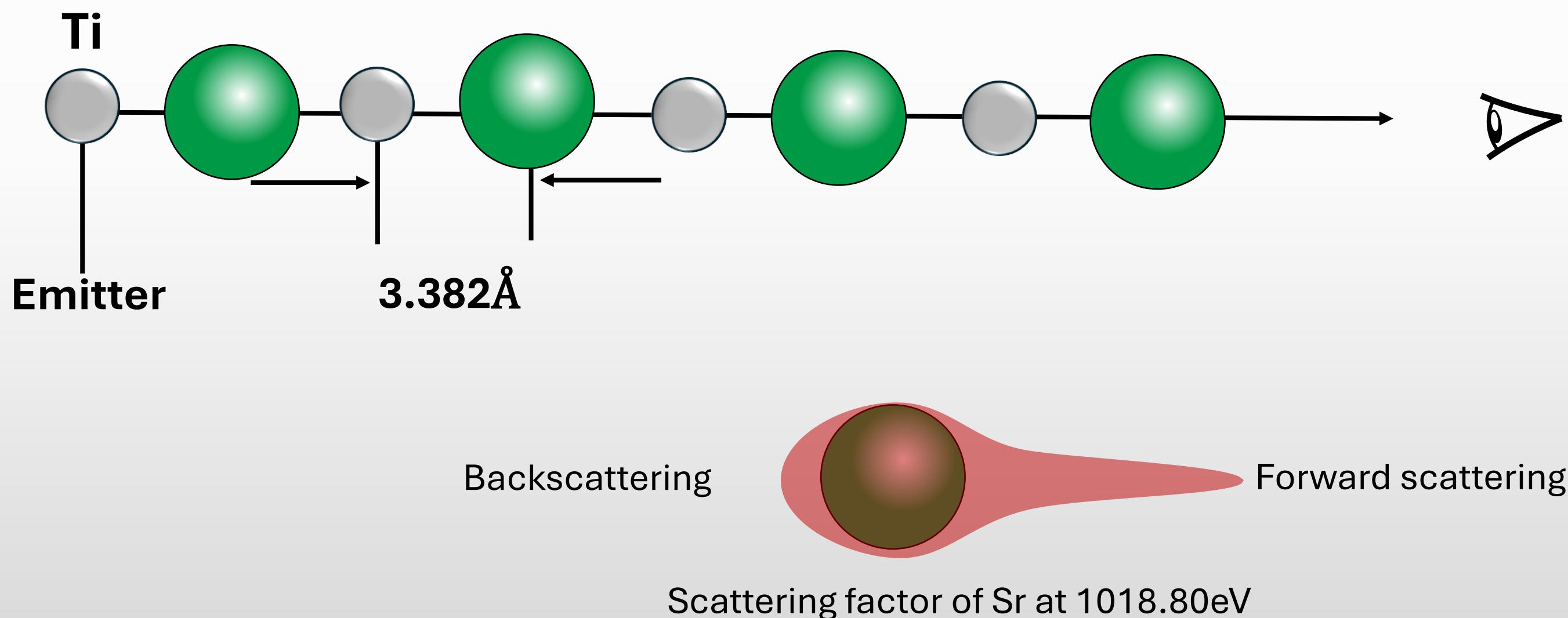
- E,g.:
  1. Spectral radius follows the same trend than Perovskites
  2. Can still be computed by MI to aid comparison



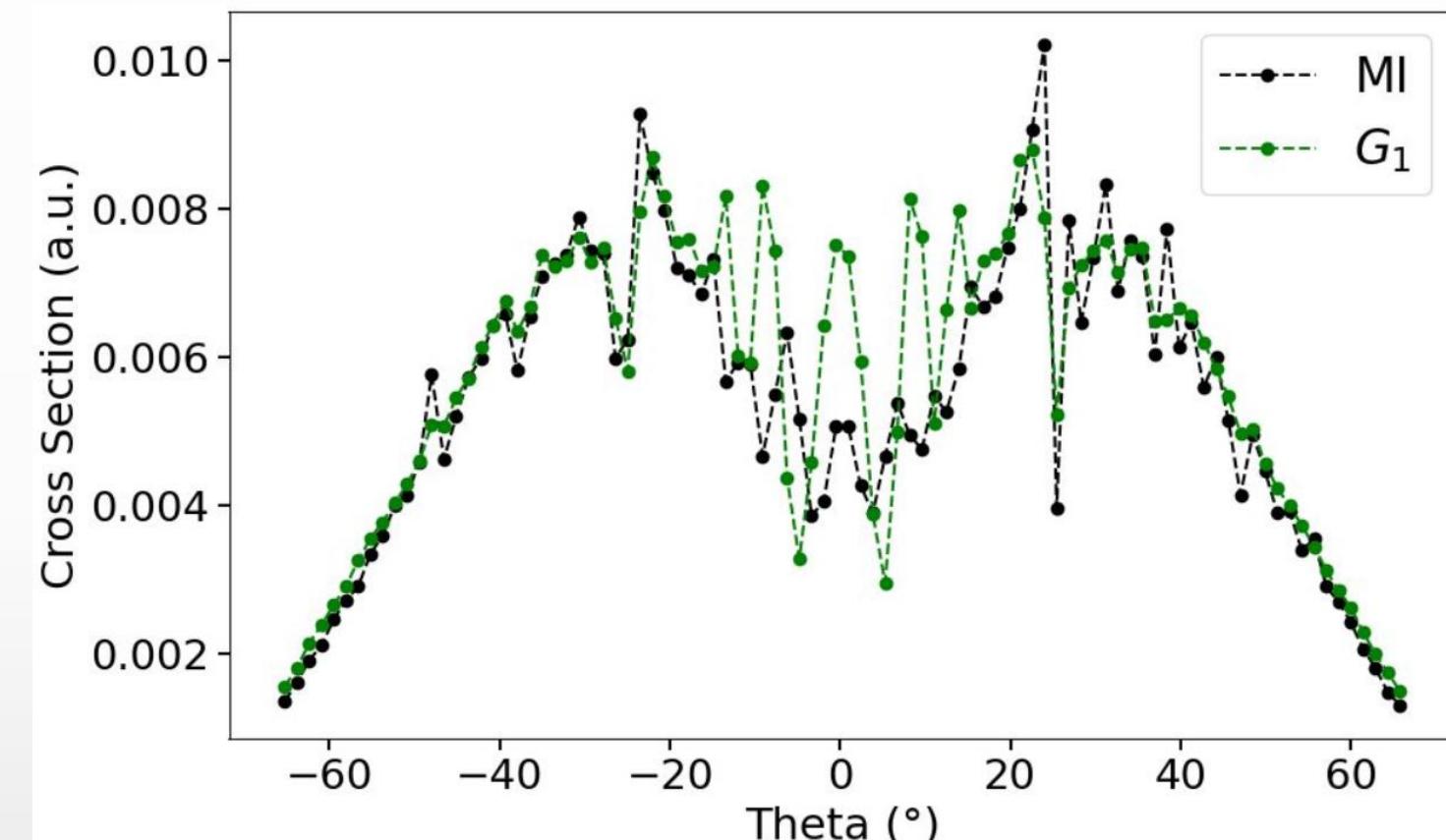
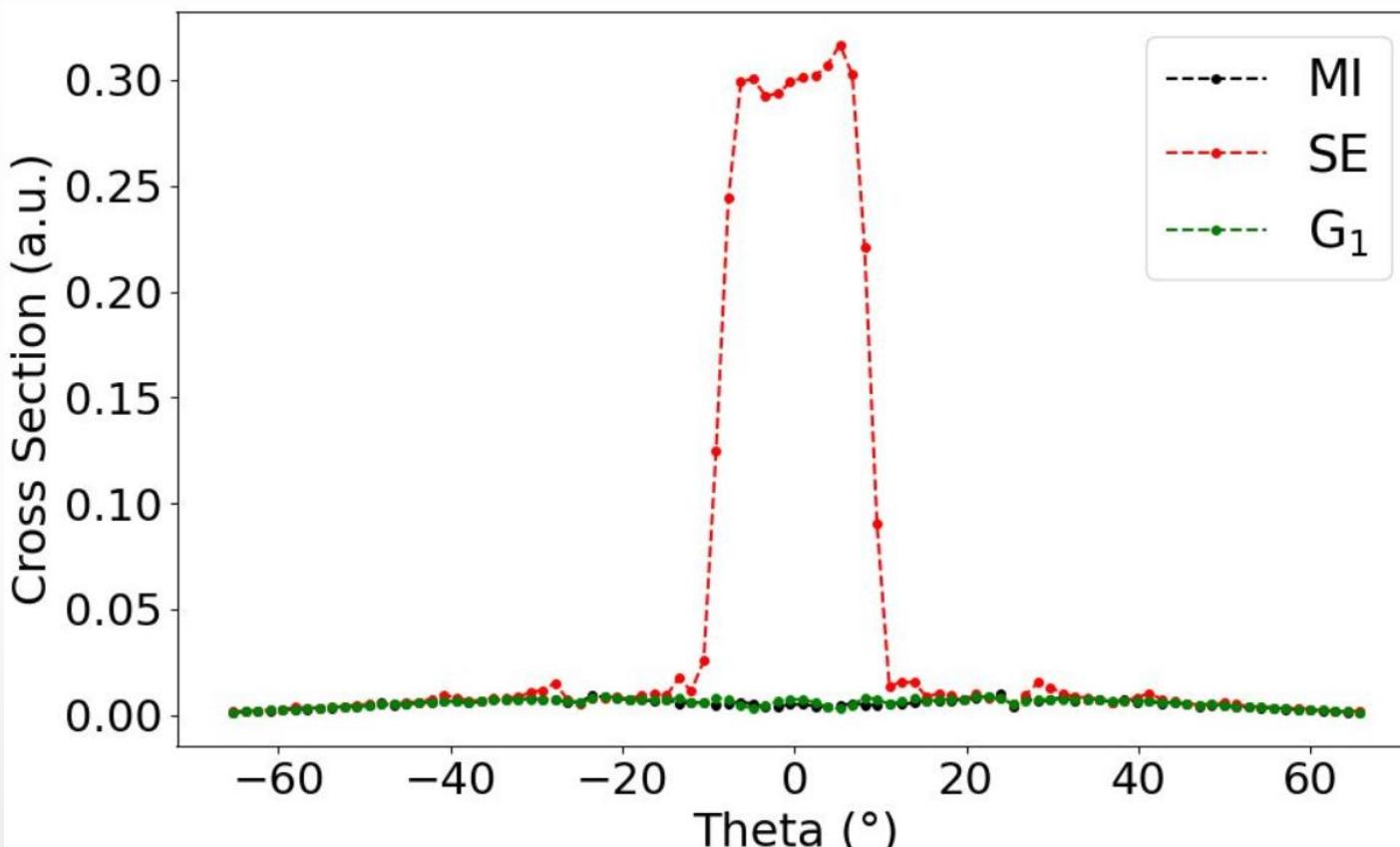

  
 — G<sub>1</sub> order n = 9  
 — Π<sub>1</sub> order n = 6  
 — MI

$\Pi_1$  is faster than  $G_1$   
 $CPU \propto (N_{at}-1)^n$

# 8\_TiSr-atomic chain at 1018.80eV

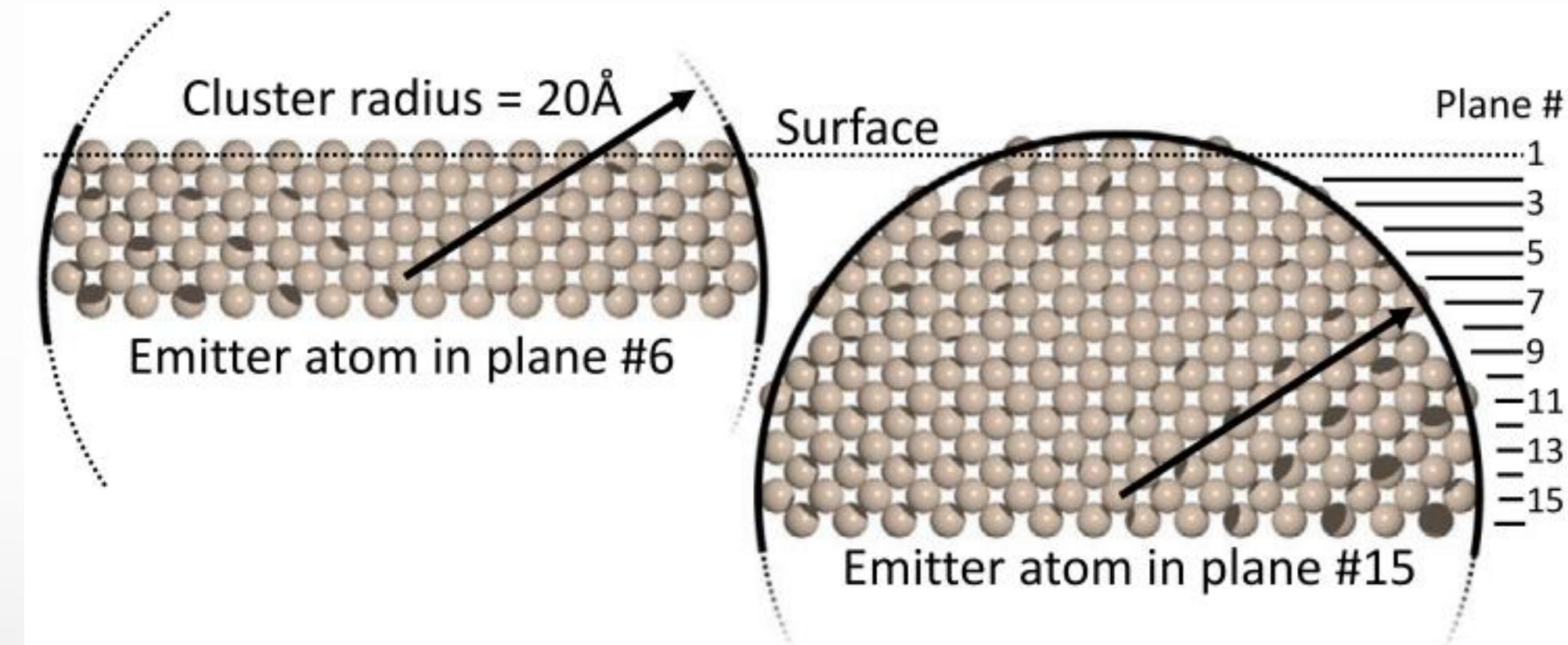


# Result: PED scan with renormalization



- Renormalization with  $G_1$  ( $n=7$ )
- Almost agrees with MI

- Recipe for creating clusters

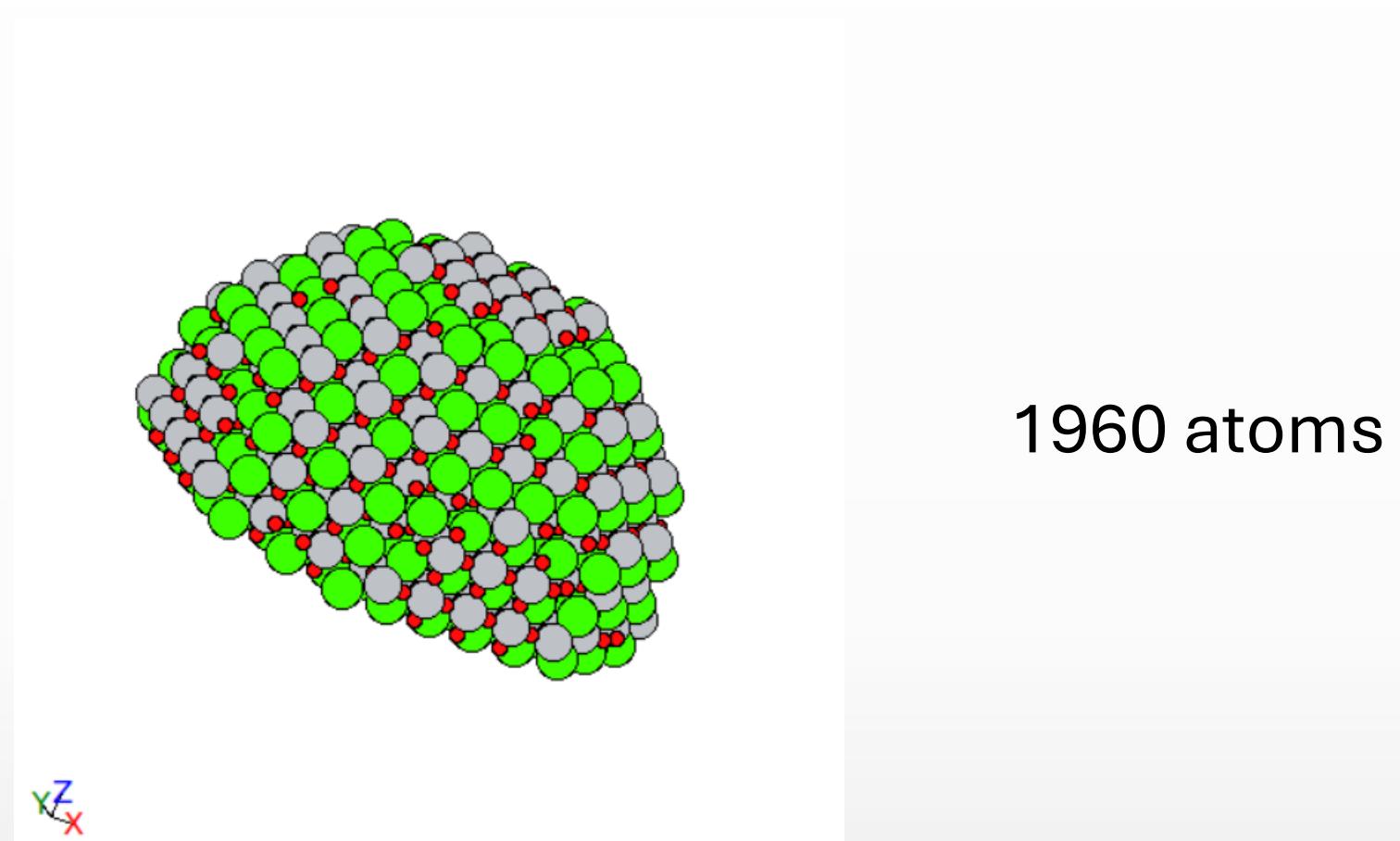


This figure is cited from [1].

The cluster tested is shaped like a semisphere (right) based on a sphere.

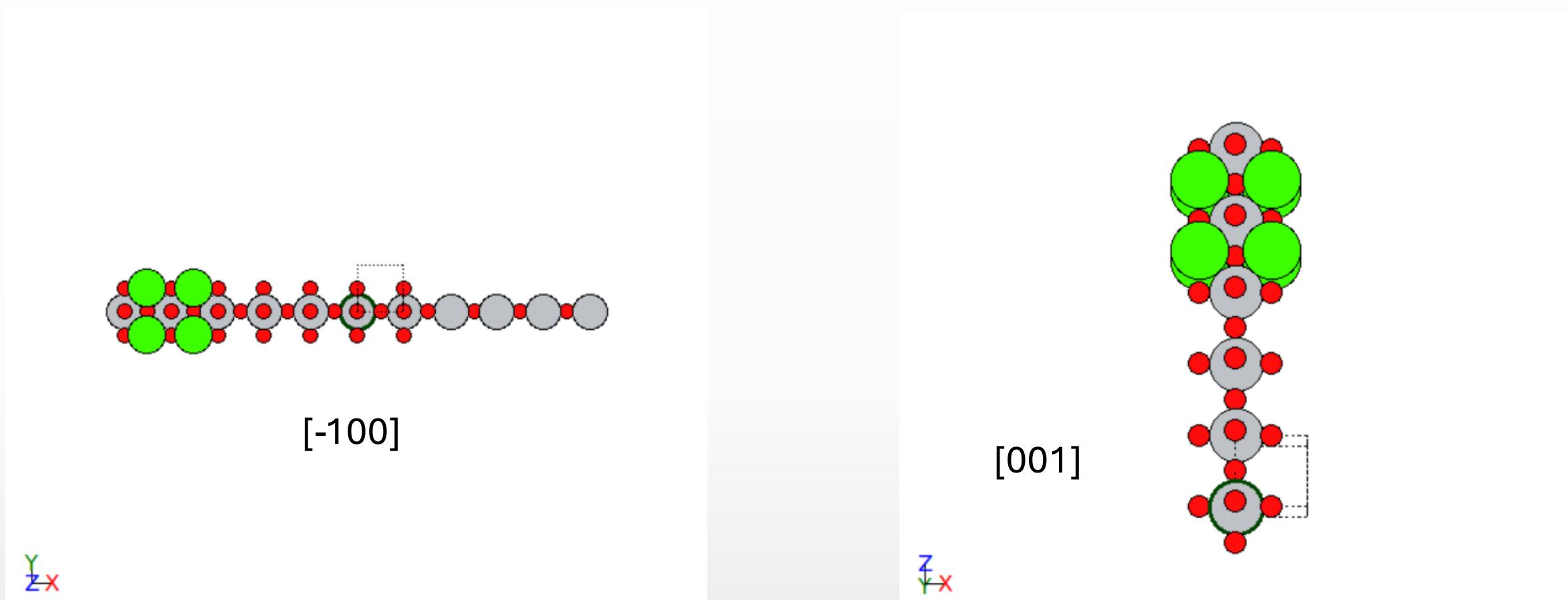
I created a cylinder-shaped cluster with a large number of atoms, eliminated all atoms out of a sphere given a radius, and cut the part below a given z coordinate.

- CTO cluster with Ti emitter



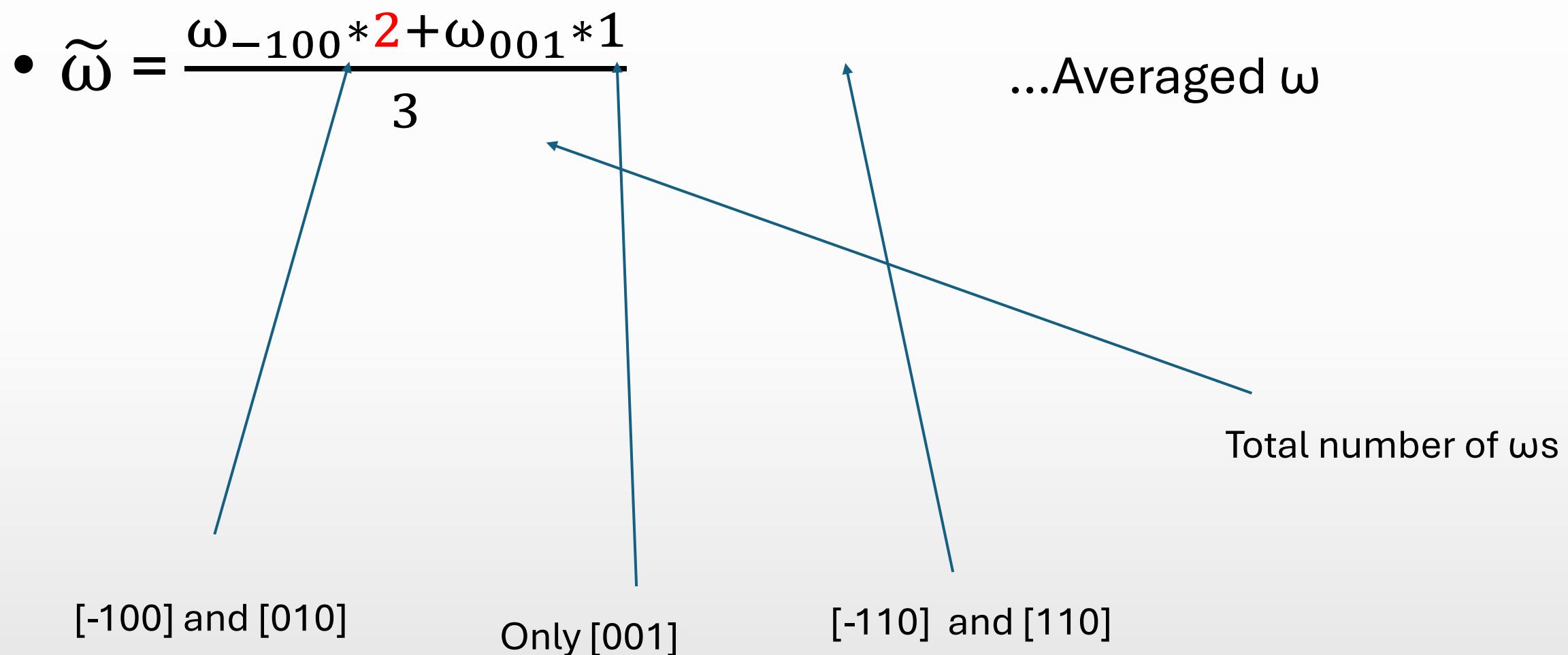
- Number of planes: 12
- Radius of the semisphere: 21 Å
- Cutting sphere in z any below  $z = -1.1 * 3.905 / 2$
- Ti emitter at the second plane from the bottom

- Atomic cones that diverge

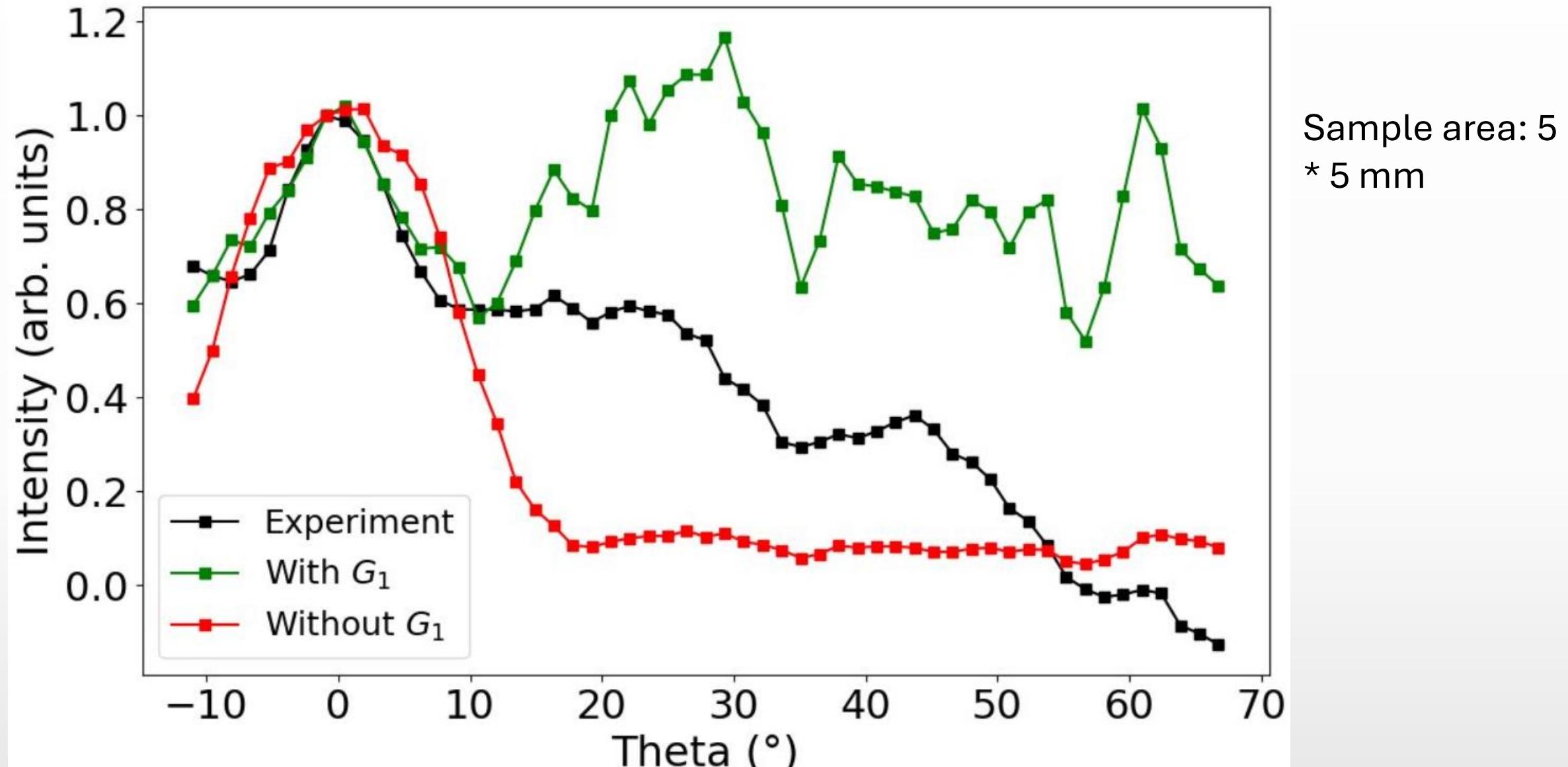


# Simulating clusters: STO

- Approximation for  $\omega$



## • Simulation and Experiment

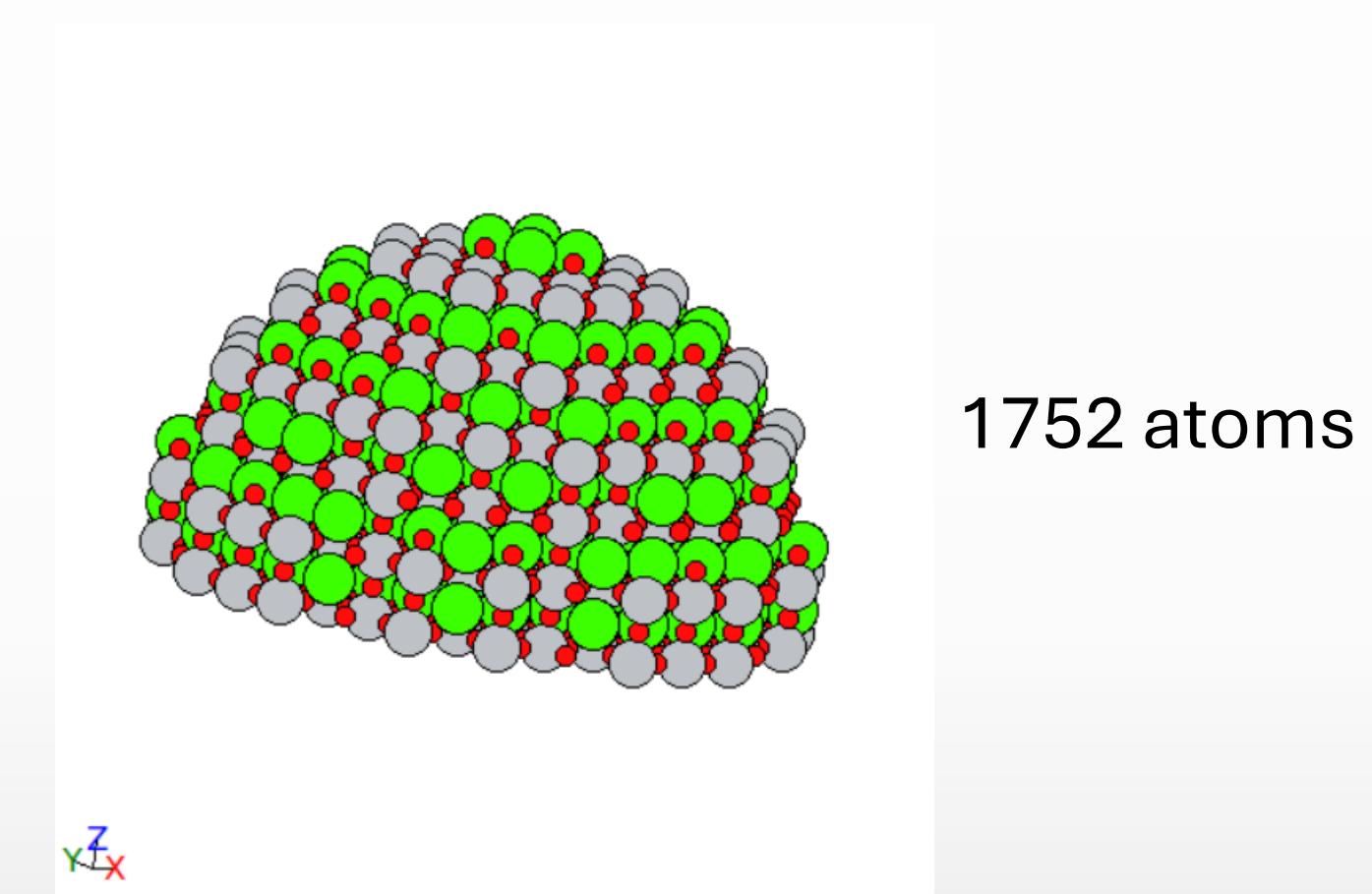


Black: Higher angle peaks are not clear. The intensity much reduces along theta because the sample is four times smaller than STO in area and more influenced by the size effect.

Green: Cross section at  $\phi=0^\circ$  **with  $G_1$**

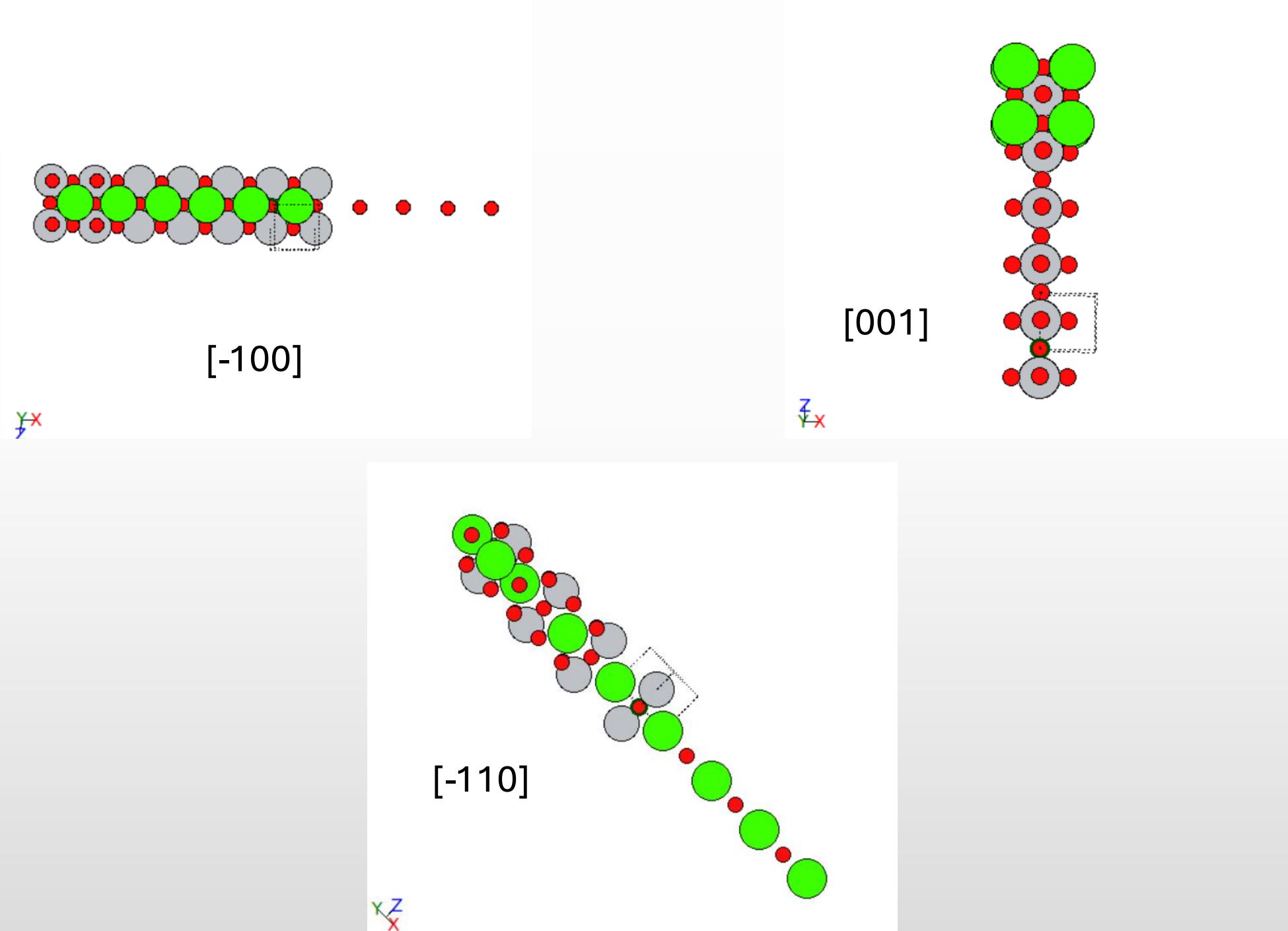
Red: Cross section at  $\phi=0^\circ$  **without  $G_1$**

- CTO cluster with O emitter

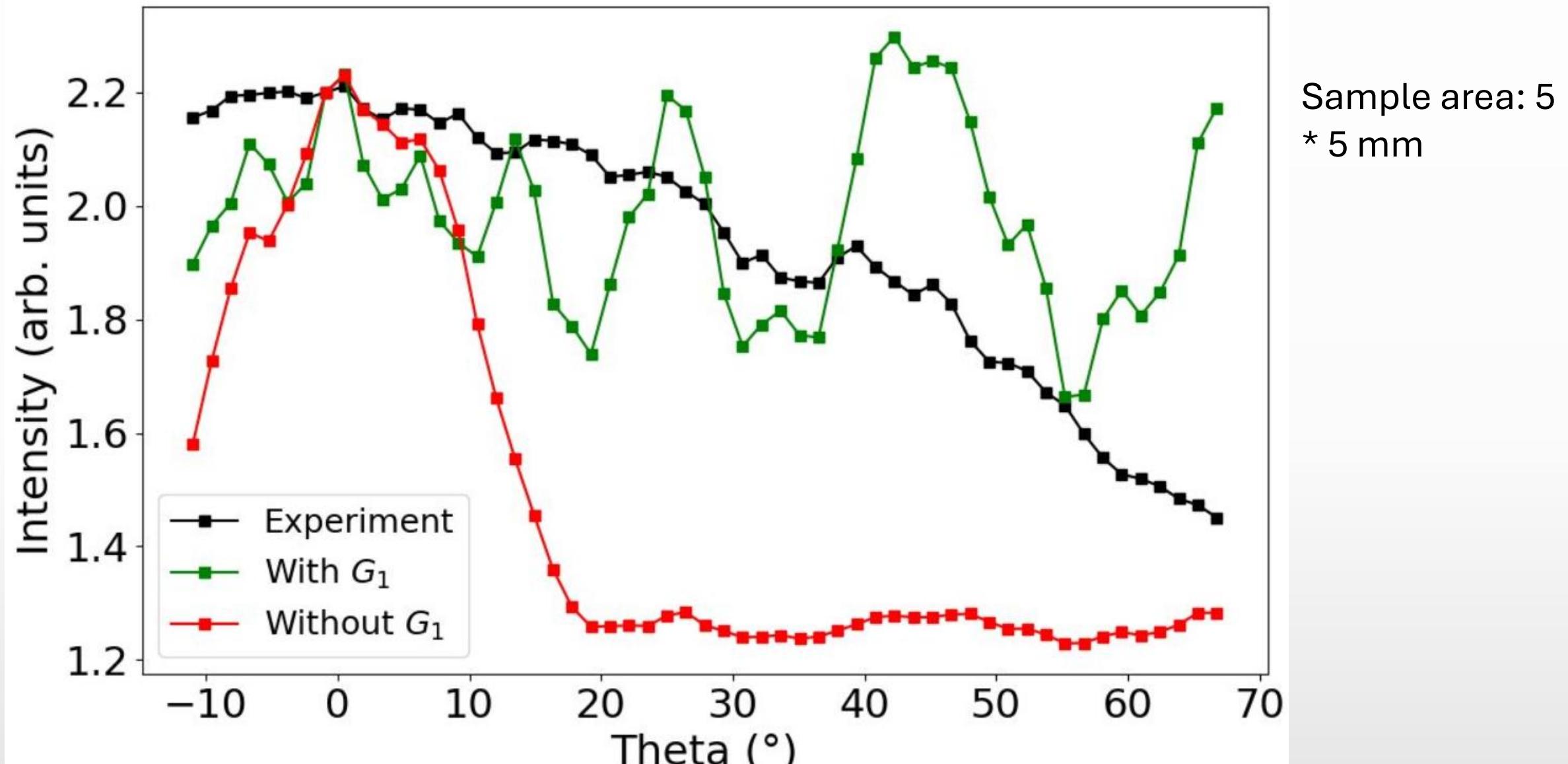


- Number of planes: 10
- Radius of the semisphere: 20Å
- Cutting sphere in z any below  $z = -1.1 * 3.905 / 2$
- O emitter at the second plane from the bottom

- Atomic cones that diverge



- Simulation and Experiment



Black: every peaks are not clear. The intensity much reduces along theta because it is more influenced by the size effect.

Green: Cross section at  $\phi=0^\circ$  **with  $G_1$**

Red: Cross section at  $\phi=0^\circ$  **without  $G_1$**