An introduction to Monte Carlo methods in XRF analysis

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Outline

1. Introduction to Monte Carlo methods
2. Monte Carlo simulation of energy dispersive X-ray fluorescence (ED-XRF) spectrometers
3. Overview of available codes

Monte Carlo method: definition

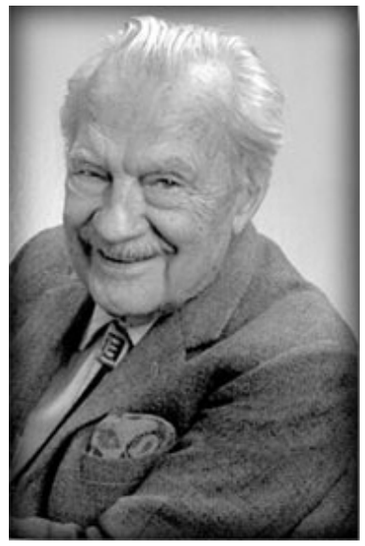
Refers to any technique of statistical sampling, employed to approximate solutions to quantitative problems which may be too complex to solve analytically

Origins of the Monte Carlo method

Developed twice independently

1. Enrico Fermi: moderation of neutrons

2. Metropolis, Ulam and Von Neumann: Manhattan project and ENIAC



The beginning of the Monte Carlo method by N. Metropolis, 1987

Monte Carlo simulation method

- Widespread statistical simulation tool based on the use of random numbers
- A given problem is converted to its probabilistic analogue
- Used in mathematics, physics, engineering, biology, artificial intelligence, economy etc.

Monte Carlo simulation method

- Phenomena occurring in the examined system must be characterized by probability density function (pdfs)
- Perform simulations by random sampling from the pdfs
- Desired result is taken as an average over a number of observations
- Engine is most often a pseudo random number generator

Generating random variables with a specified distribution

- Continuous random variable: $x_{min} \leq X \leq x_{max}$
- Probability density function: $f(x) \geq 0$
  with: $\int_{x_{min}}^{x_{max}} f(x)dx = 1$
- Cumulative distribution function: $F(x) = \int_{x_{min}}^{x} f(u)du$

- Monotonously increasing, $F(x_{min}) = 0$, $F(x_{max}) = 1$
  $x = F^{-1}(R)$ inverse cdf, with $0 \leq R \leq 1$

  The values selected using the inverse cdf will reproduce the distribution $f(x)$ in the interval $[x_{min}, x_{max}]$

Generating random variables with a specified distribution

- Discrete random variables: $X = \{x_1,...,x_n\}$
- Corresponding probabilities of events $\{x_1,...,x_n\}$: $\{P_1,...,P_n\}$ $\quad \sum_{i=1}^{n} P_i = 1$
- R: uniform random number in [0,1]
- Select event for index k={1,...,n}:

$$\sum_{i=1}^{k-1} P_i < R \leq \sum_{i=1}^{k} P_i$$

Random number generators

- Critical component of all Monte Carlo simulations!
- Initially performed using lists of "true" random numbers
- Von Neumann: first pseudo random number generator (middle-square method)
- Properties: speed, period length, uniformity, coverage

A Million Random Digits with 100,000 Normal Deviates by the RAND corporation

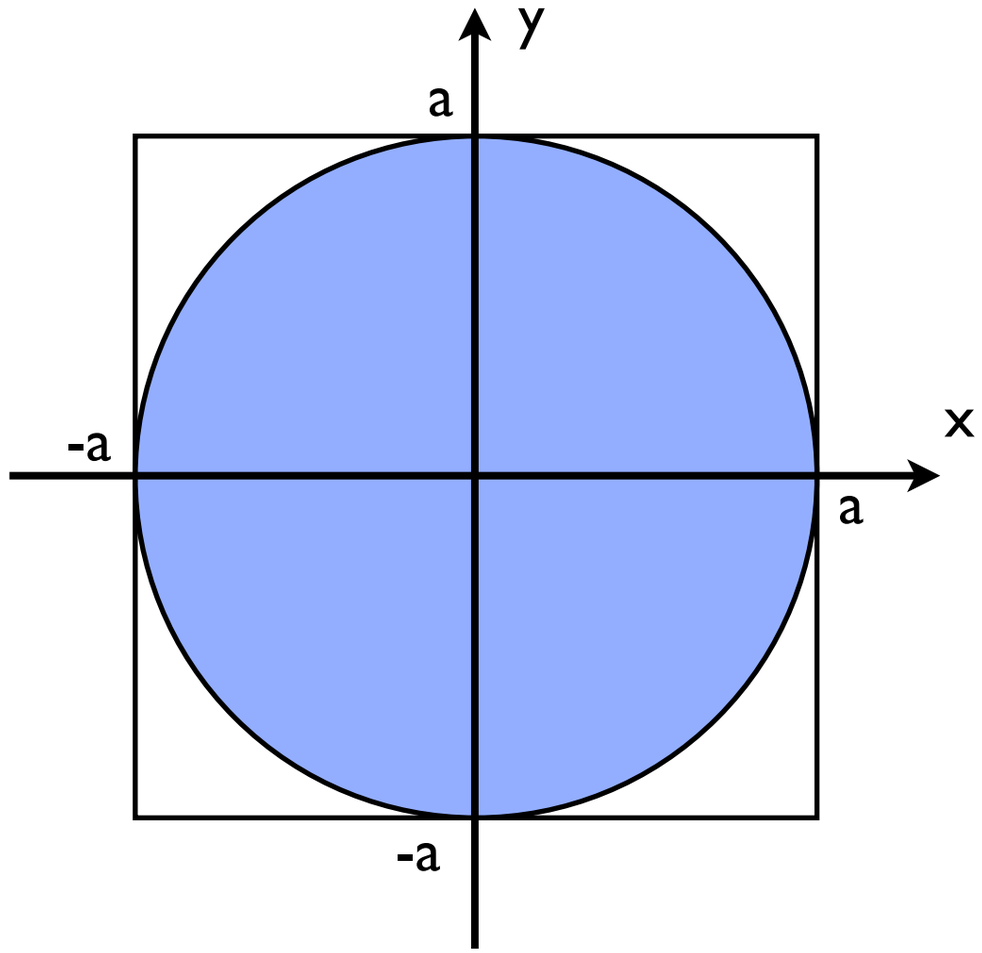
Pseudo random number generators

1. Linear congruential generators
   - Short period: maximum 2^{32} or 2^{64}
   - Easily implemented
   - $X_{n+1} = (aX_n + b) \bmod m$
2. Mersenne twister
   - Most commonly used PRNG nowadays
   - Period: $2^{19937}-1$
   - Passes the Diehard test package
   - GPU implementation available (MTGP)

Pseudo random number generators

3. /dev/random
   - special device file on Unix(-like) operating systems
   - very high quality randomness (for cryptographic applications!)
   - entropy pool fed with noise produced by device drivers, network interfaces etc.
   - blocks → slow!
   - non-blocking version: /dev/urandom (Linux only)
   - Windows alternative: CryptGenRandom and rand_s

Example: estimation of π

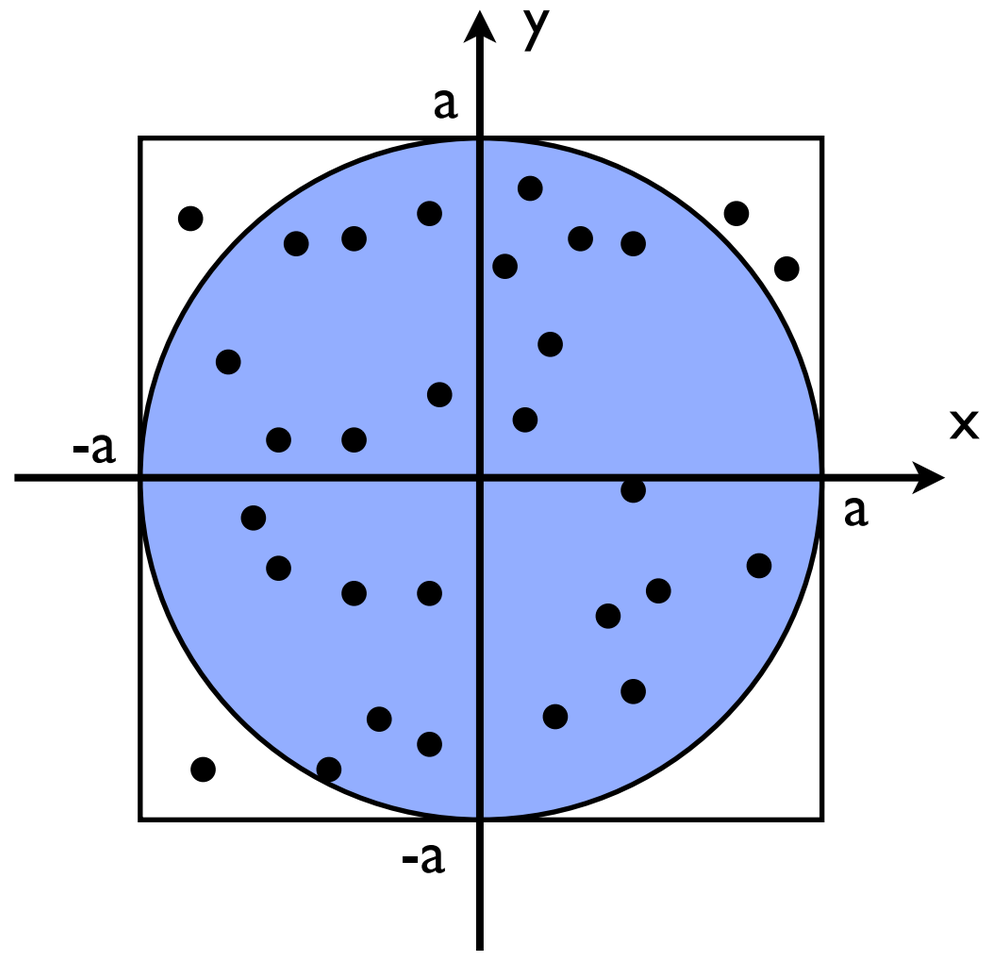


Random selection of points within a square of $2a \times 2a = 4a^2$ area

$$\pi = 4\left(\frac{a^2\pi}{4a^2}\right) = 4\left(\frac{A_{circle}}{A_{square}}\right) \approx 4\left(\frac{N_{circle}}{N_{total}}\right)$$

Example: estimation of π

Random selection of points within a square of $2a \times 2a = 4a^2$ area



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Monte Carlo simulation of X-ray fluorescence spectrometers

Brute force algorithm

A general Monte Carlo simulation of ED-XRF spectrometers

- Basic idea: predict the response of X-ray imaging and spectroscopy experiments
- Optimize and design experimental setups *in silico*
- Dose calculation
- Estimation of detection limits
- Quantification

A general Monte Carlo simulation of ED-XRF spectrometers

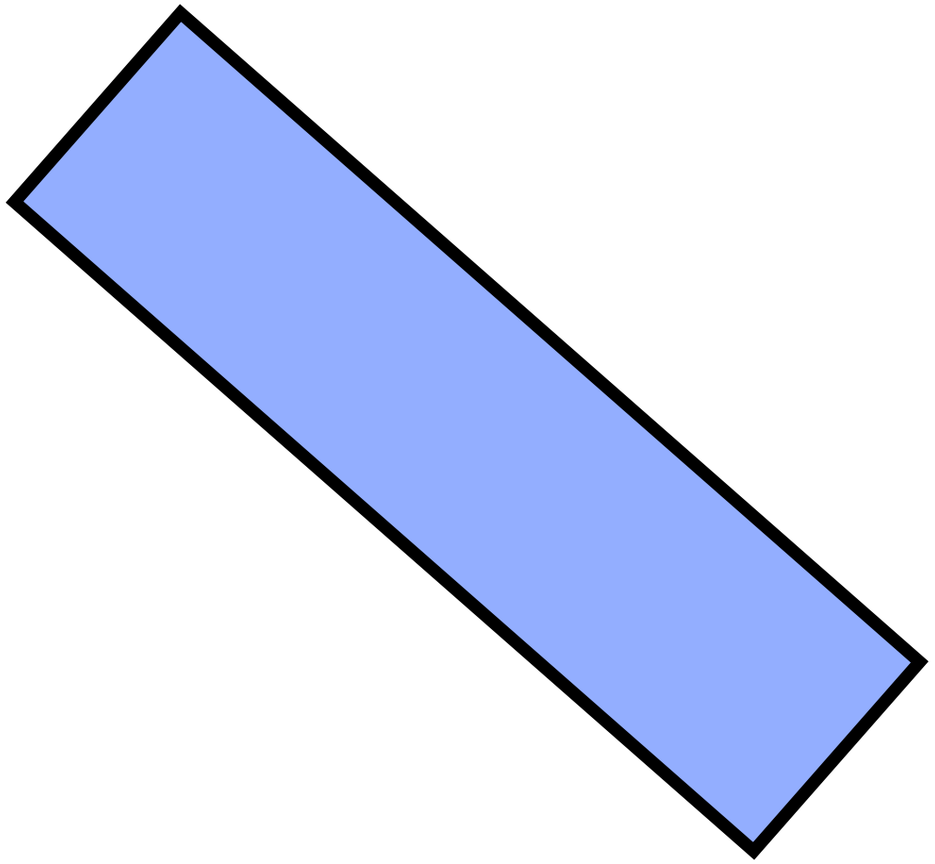
- Simulates the fate of individual photons
- Trajectories are modeled as consisting of a number of straight steps.
- At the end of each step, an interaction will occur, leading to a change in direction and energy

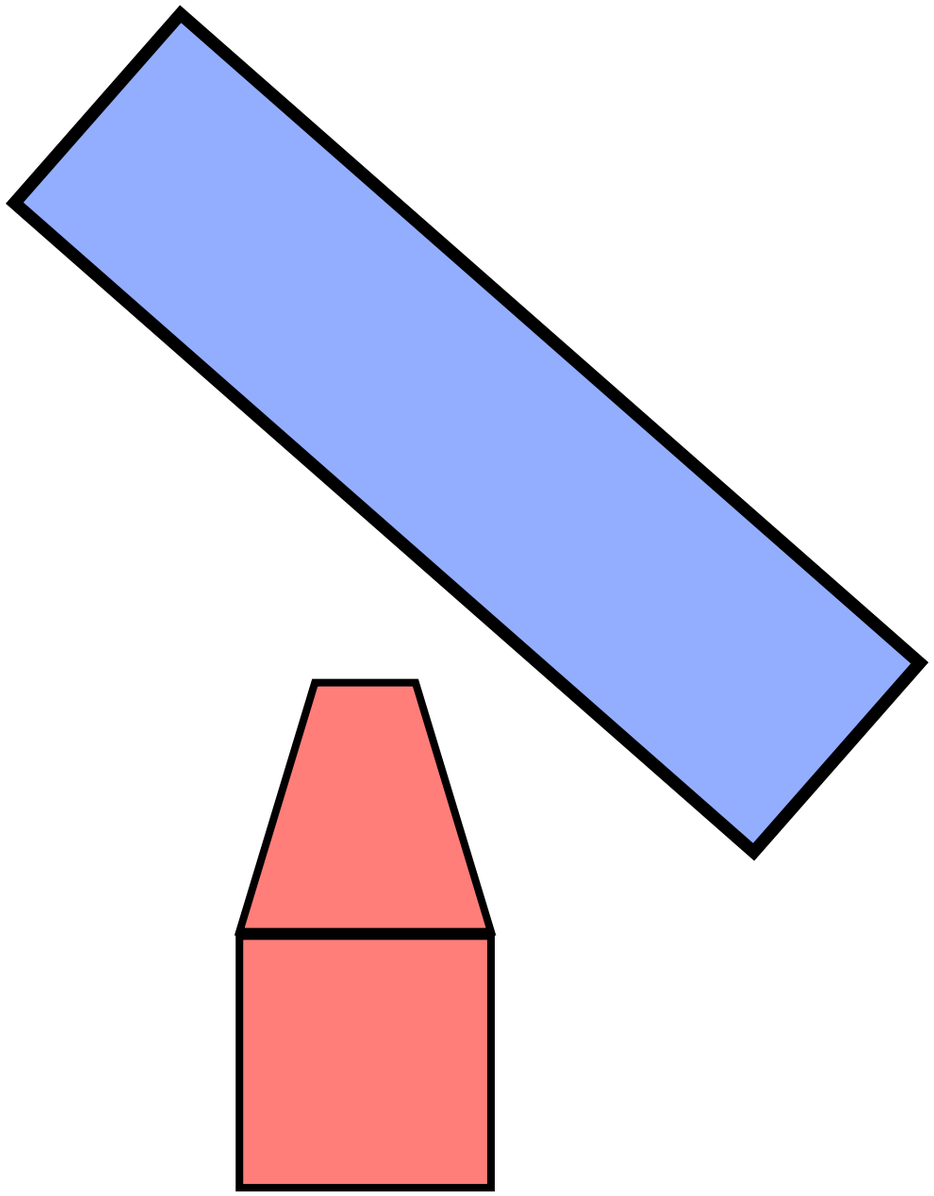
Initial photon properties:

- Energy
- Degree of linear polarization
- Intensity (weight)
- Point or Gaussian source
- Discrete or continuous

Sample properties:

- position and orientation
- *n* parallel layers
- Thickness
- Density
- Composition

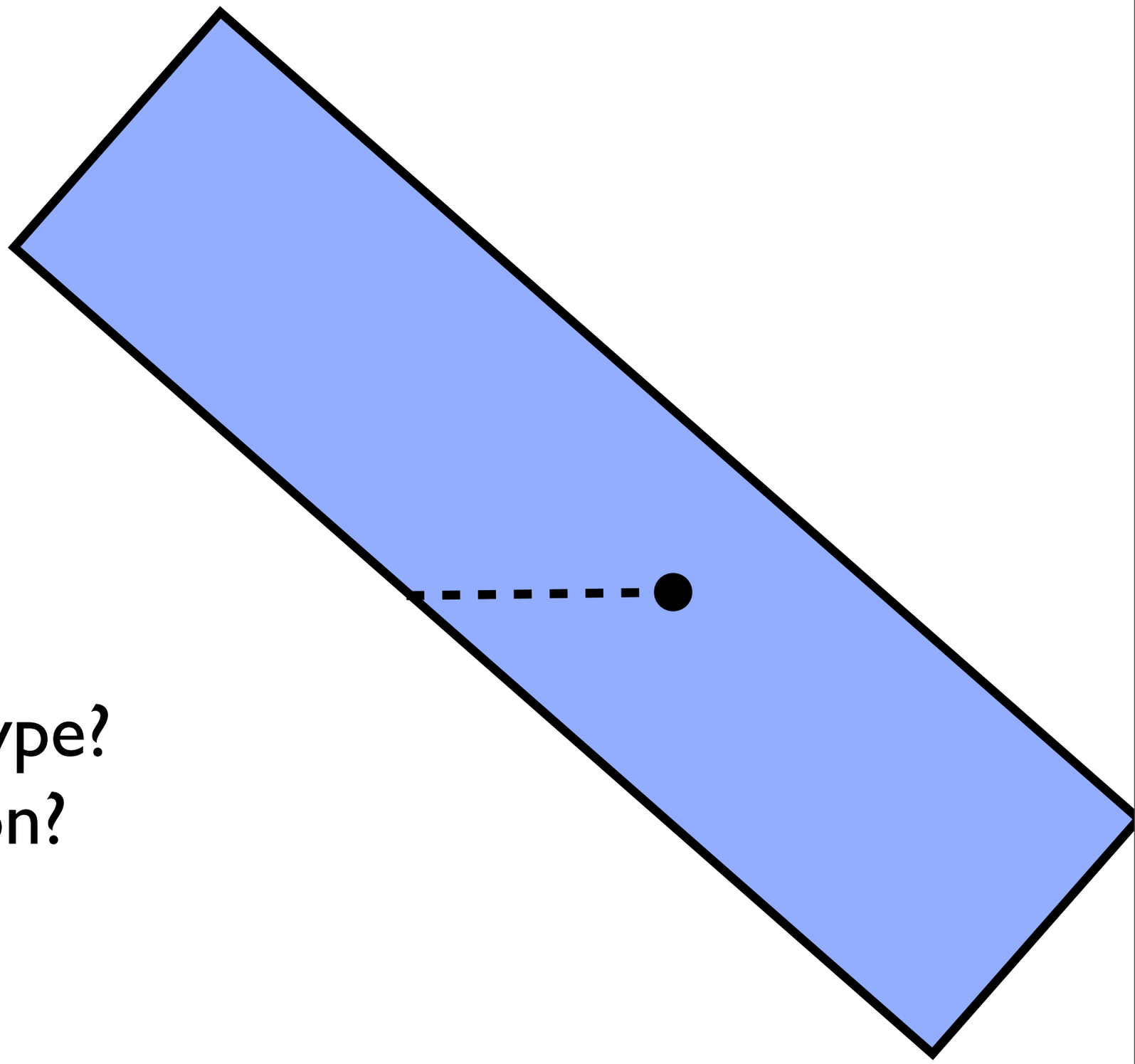




Detector properties:

- position and orientation
- crystal
- window
- zero/gain
- Collimator (optional)

Stepsize?
Atom type?
Interaction type?
New direction?



Selection of the step length

- Determined by the density, thickness and the absorption coefficients of the sample layers
- Inverse cdf is based on the Bouguer-Lambert-Beer equation:

$$f(x) = \mu\rho \exp(-\mu\rho x)$$

$$F(x) = \int_0^x \mu\rho \exp(-\mu\rho t)dt = 1 - \exp(-\mu\rho x) \equiv R \Rightarrow x = -\frac{1}{\mu\rho}\ln(1-R) \Leftrightarrow x = -\frac{1}{\mu\rho}ln(R)$$

Selection of atom type

Current layer contains n_e different elements, each element present with a weight fraction w_i

$$\sum_{i=0}^{k} w_i m_i \leq R < \sum_{i=0}^{k+1} w_i m_i \qquad \text{with} \qquad m_i = \frac{\mu_i}{\sum_{i=0}^{n_e} w_i \mu_i}$$

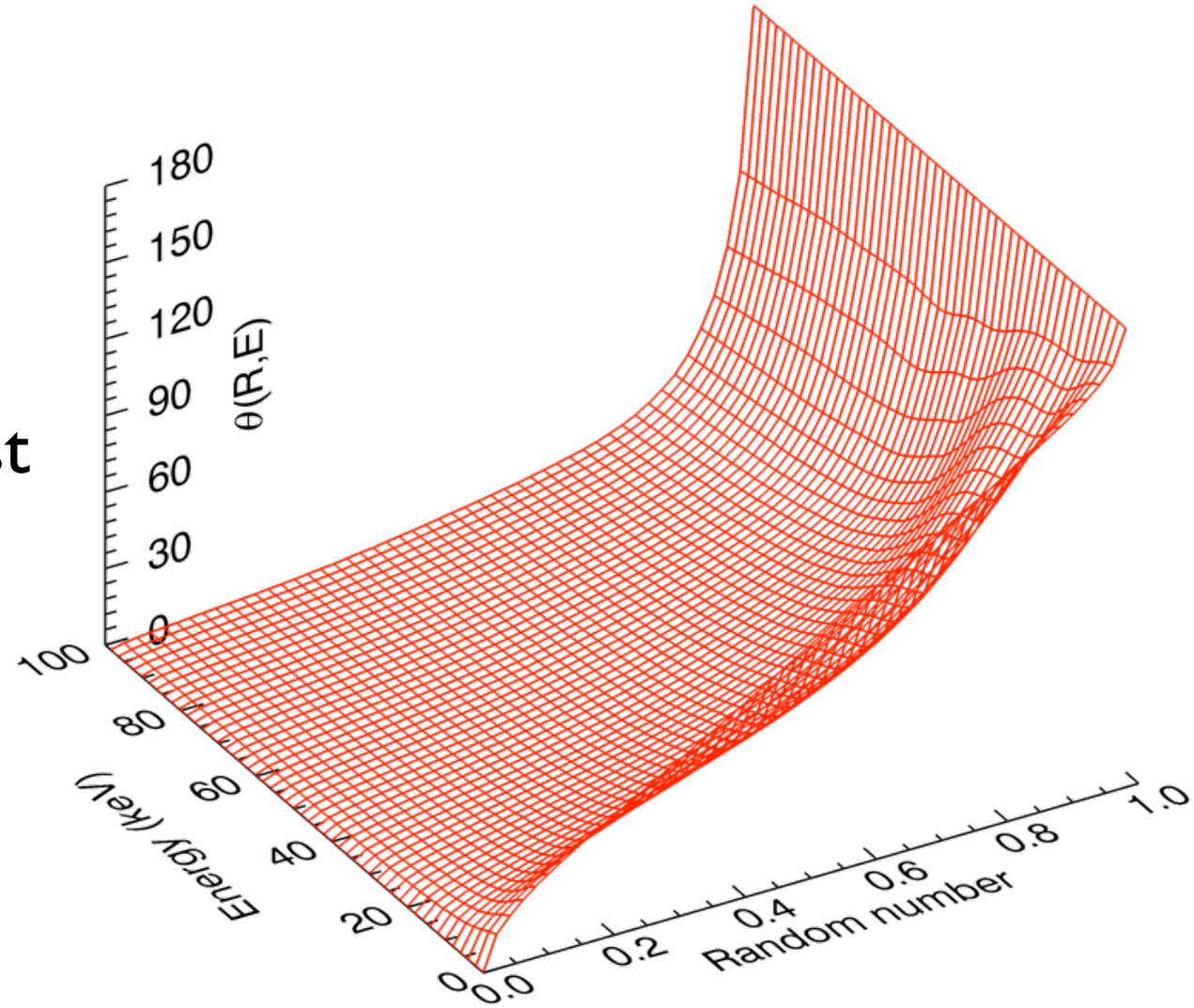
Selection of interaction type

Three possibilities:

1. Rayleigh scattering: $0 \leq R \leq \frac{\sigma_{RZ}}{\mu_Z}$
2. Compton scattering $\frac{\sigma_{RZ}}{\mu_Z} < R \leq \frac{\sigma_{RZ} + \sigma_{CZ}}{\mu_Z}$
3. Photoelectric effect $\frac{\sigma_{RZ} + \sigma_{CZ}}{\mu_Z} < R \leq 1$

Rayleigh scattering

- Energy remains unchanged
- Scattering angle θ_i and azimuthal angle φ_i must be selected in accordance with the appropriate differential Rayleigh cross section.
- Inverse CDFs are calculated numerically



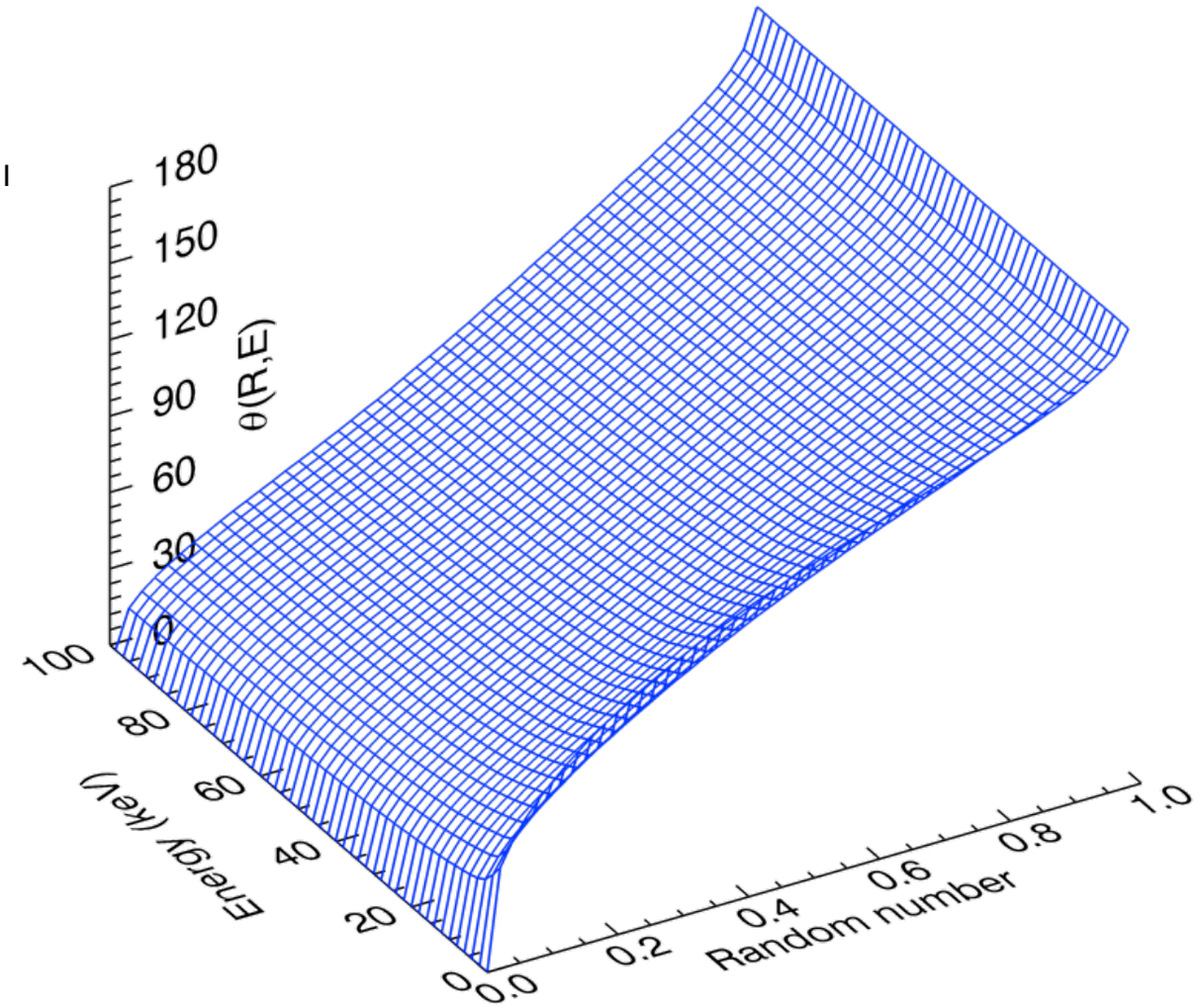
Compton scattering

- Energy-loss according to Compton formula:

$$E_{i+1} = E_i \left(1 + \frac{E_i}{m_e c^2} (1 - \cos\theta_i) - \frac{2p_z}{m_e c} \sin\frac{\theta_i}{2} \right)^{-1}$$

- Scattering angle θ_i and azimuthal angle φ_i must be selected in accordance with the appropriate differential Compton cross section.

- Takes into account the influence of the momentum p_z of the scattering electron on the energy-transfer



Photoelectric effect

Which shell experienced effect?

$$\text{shell} = \begin{cases} K \text{ shell: } 0 \le R < \dfrac{\tau_K}{\tau} \\ L1 \text{ shell: } \dfrac{\tau_K}{\tau} \le R < \dfrac{\tau_K + \tau_{L1}}{\tau} \\ L2 \text{ shell: } \dfrac{\tau_K + \tau_{L1}}{\tau} \le R < \dfrac{\tau_K + \tau_{L1} + \tau_{L2}}{\tau} \\ L3 \text{ shell: } \dfrac{\tau_K + \tau_{L1} + \tau_{L2}}{\tau} \le R < \dfrac{\tau_K + \tau_{L1} + \tau_{L2} + \tau_{L3}}{\tau} \\ \ldots \end{cases}$$

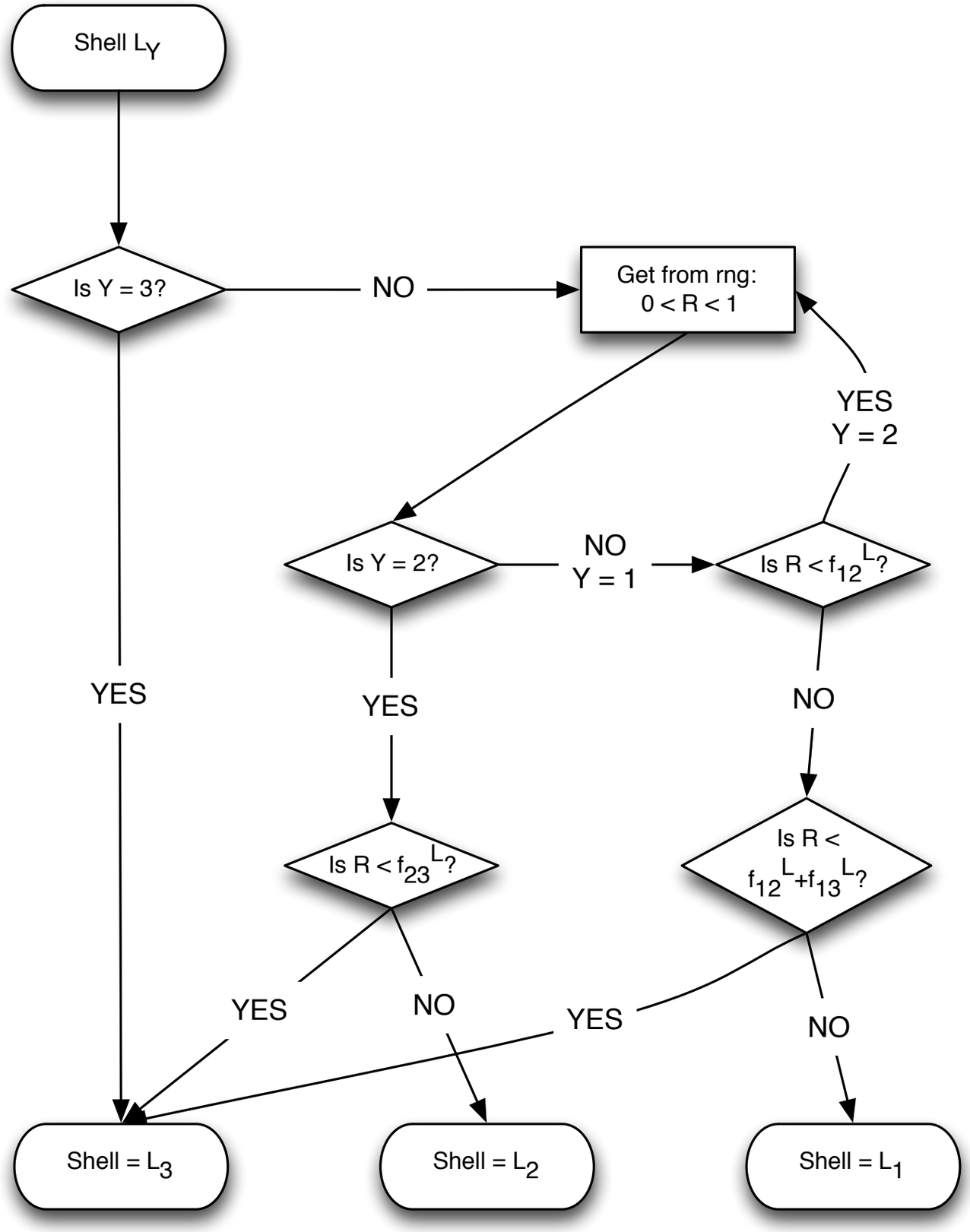
Photoelectric effect

Fluorescence yield: fluorescence or Auger effect?

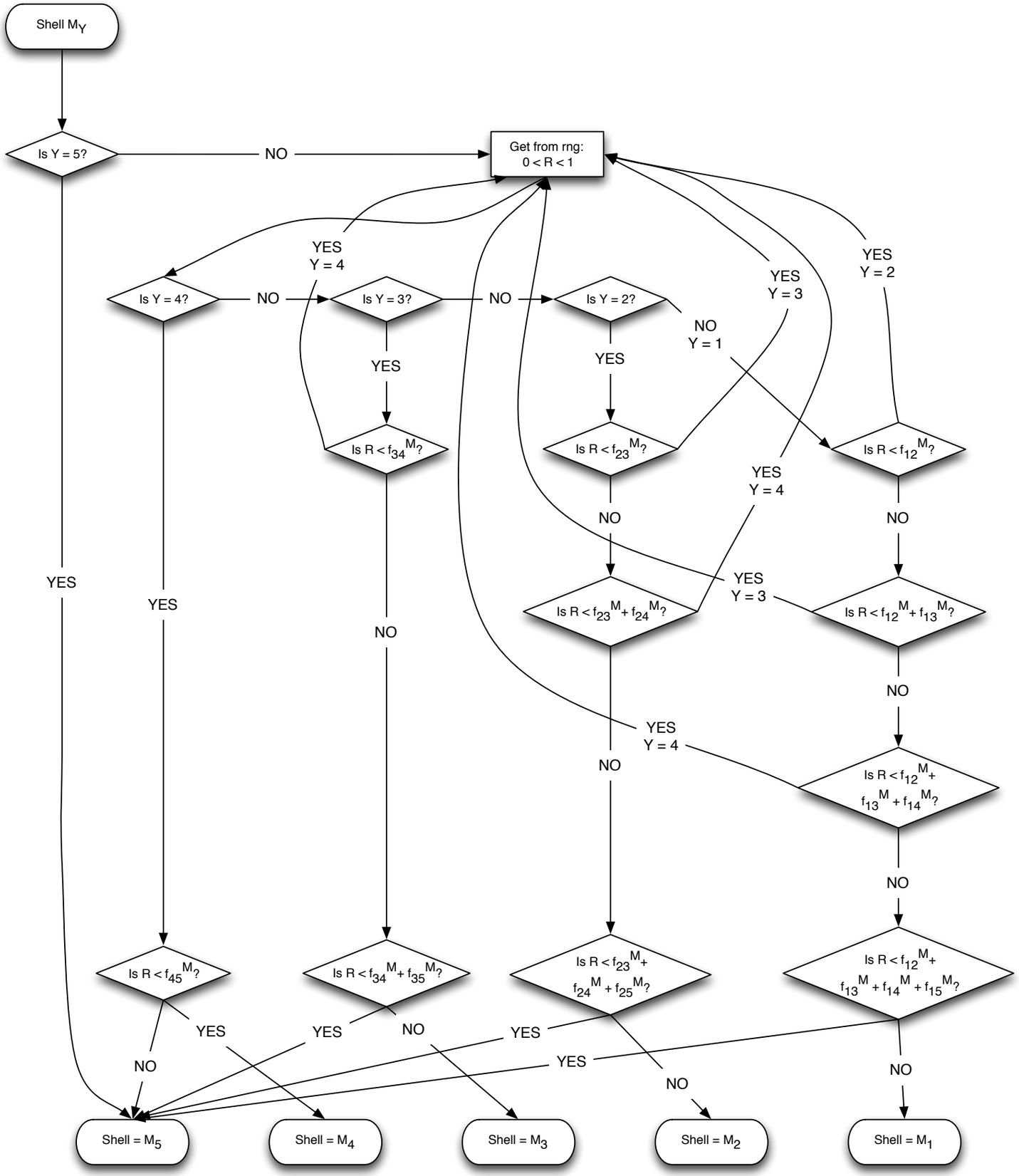
Using yields for *primary* vacancies!

Fluorescence if: $0 \leq R < \omega_{\text{shell}}$

Take into account Coster-Kronig transitions!



Definitive selection of L-shell to be involved in transition



Definitive selection of M-shell to be involved in transition

Photoelectric effect

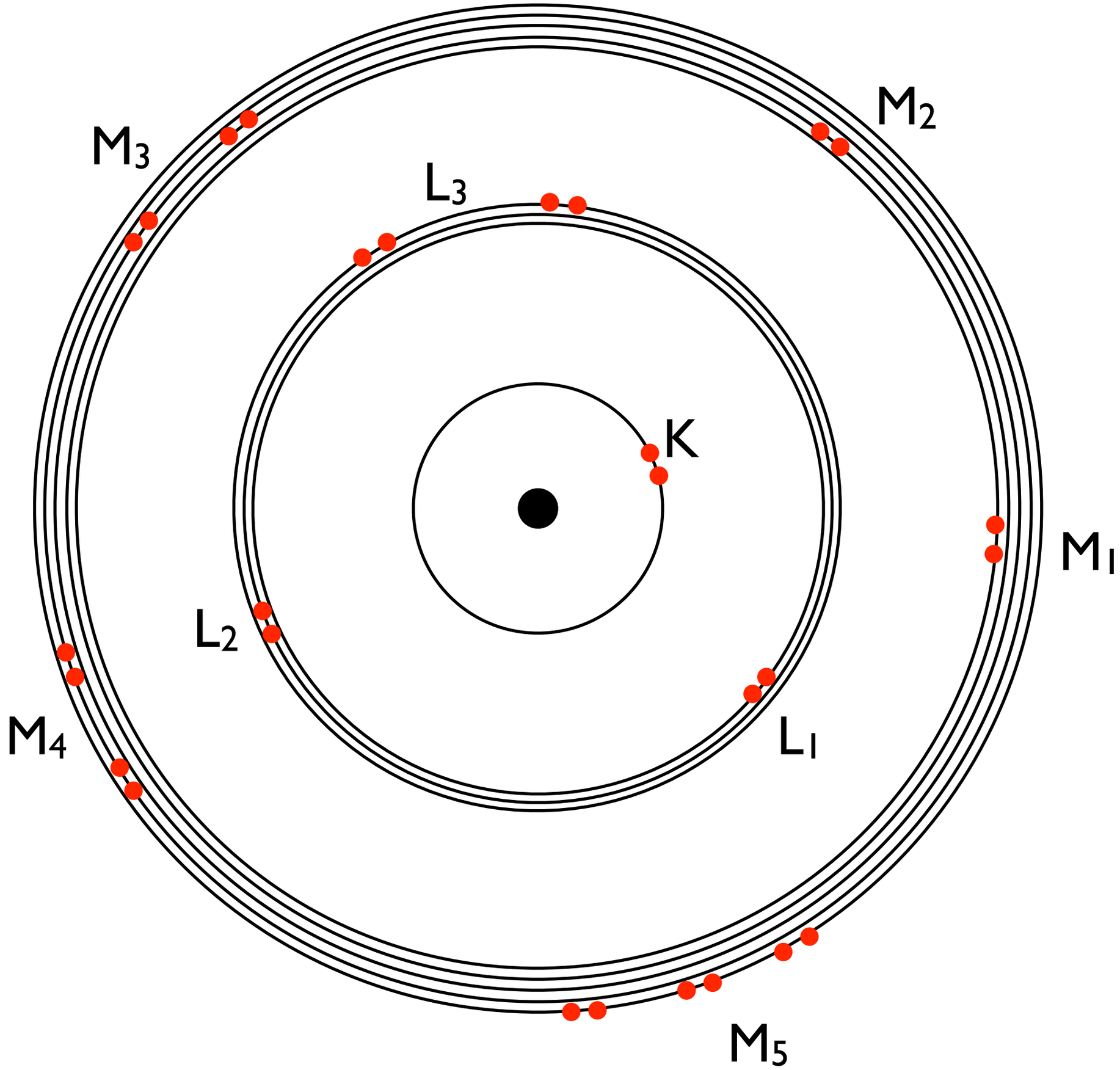
Which fluorescence line?

Determine using the shell's radiative rates:

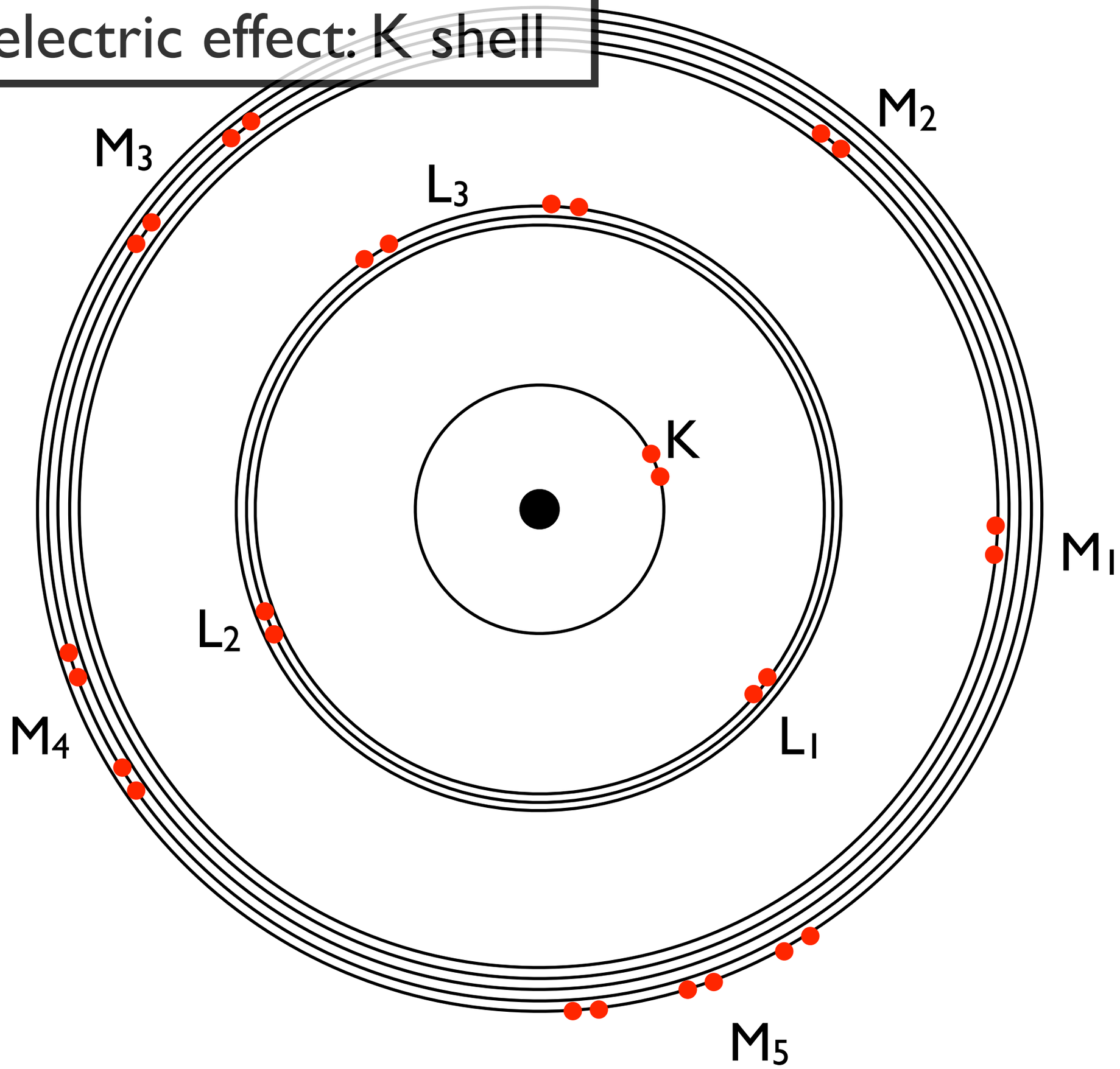
$$\text{line} = \begin{cases} KL_2\text{line: } 0 \le R < p_{KL_2} \\ KL_3\text{line: } p_{KL_2} \le R < p_{KL_2} + p_{KL_3} \\ KM_2\text{line: } p_{KL_2} + p_{KL_3} \le R < p_{KL_2} + p_{KL_3} + p_{KM_2} \\ KM_3\text{line: } p_{KL_2} + p_{KL_3} + p_{KM_2} \le R < p_{KL_2} + p_{KL_3} + p_{KM_2} + p_{KM_3} \\ \ldots \end{cases}$$

Scattering angle θ_i and azimuthal angle φ_i are chosen random: $\cos\theta_i = (2R - 1)$

$$\varphi_i = 2\pi R$$


M3
L3
M2
K
L2
M1
M4
L1
M5

Photoelectric effect: K shell



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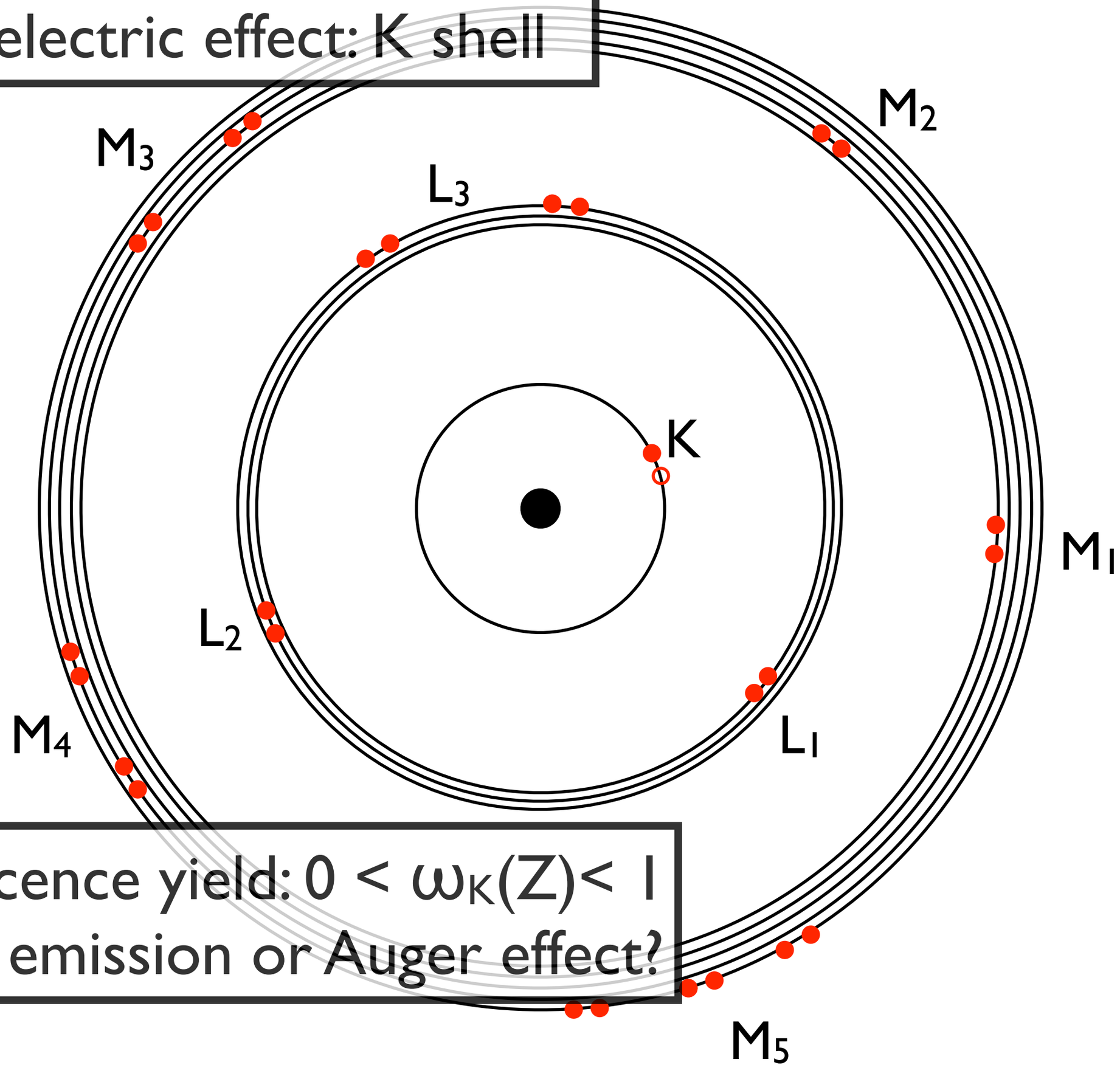
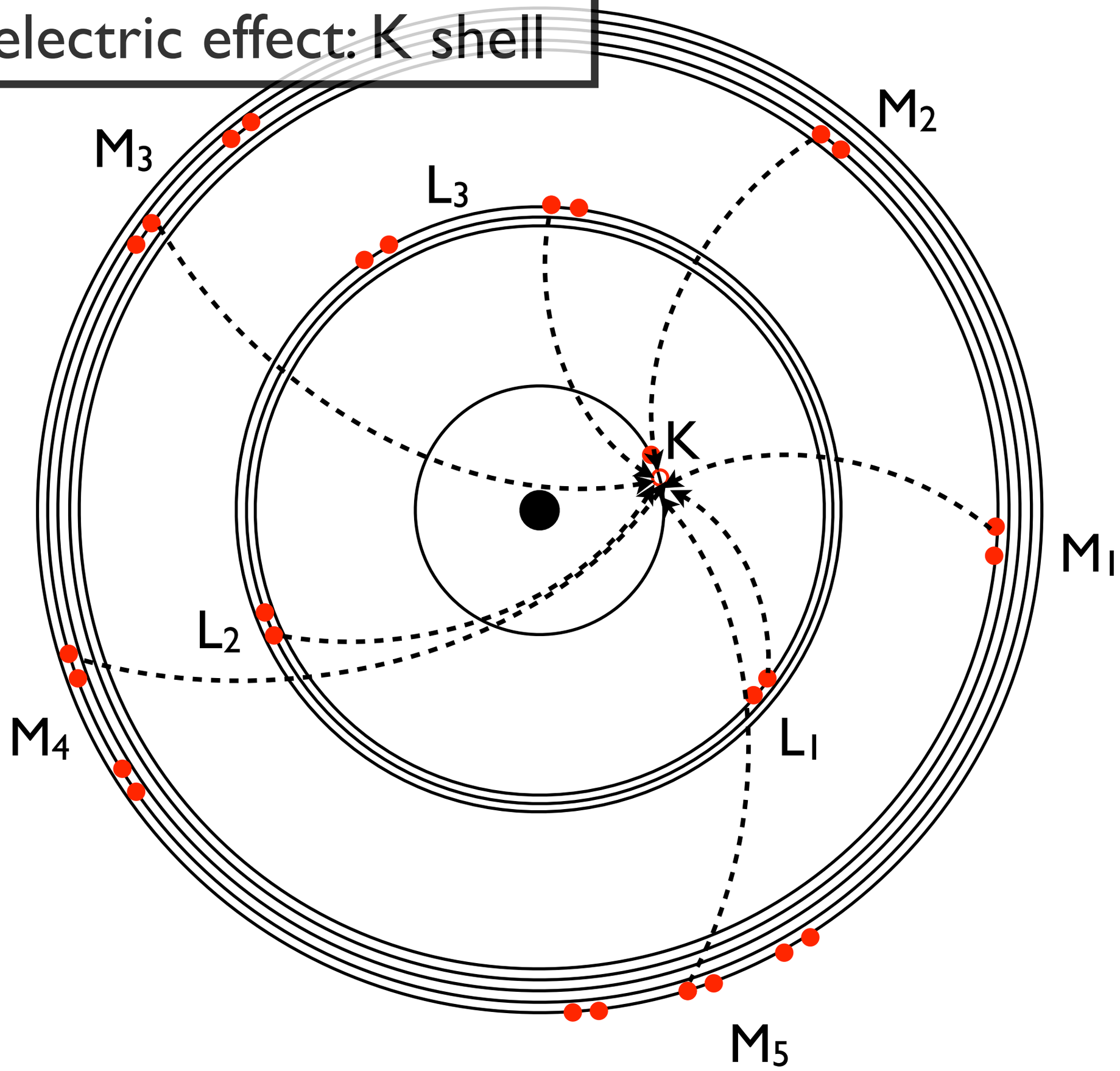


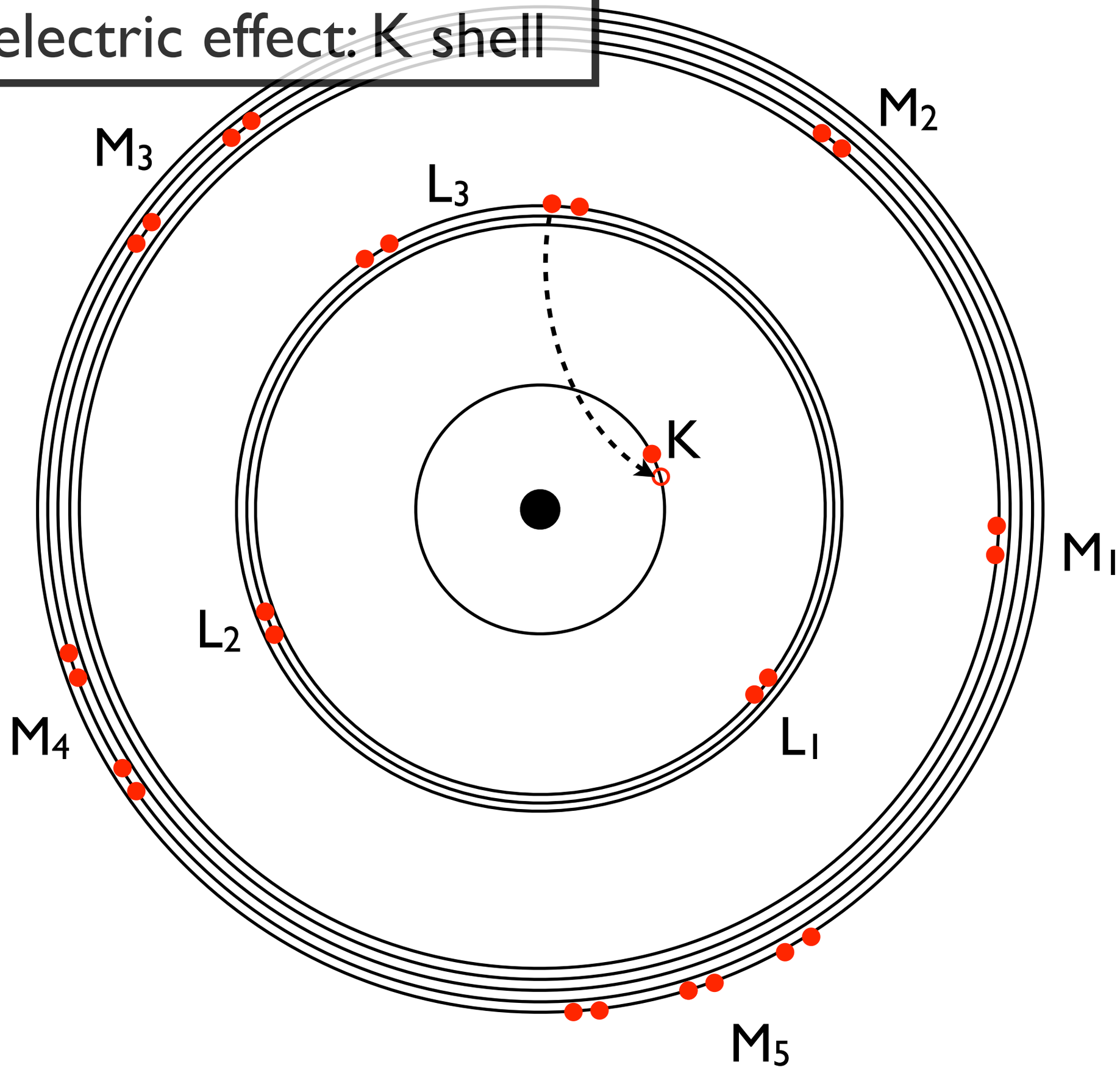
Fluorescence yield: $0 < \omega_K(Z) < 1$

Photon emission or Auger effect?

Photoelectric effect: K shell



Photoelectric effect: K shell



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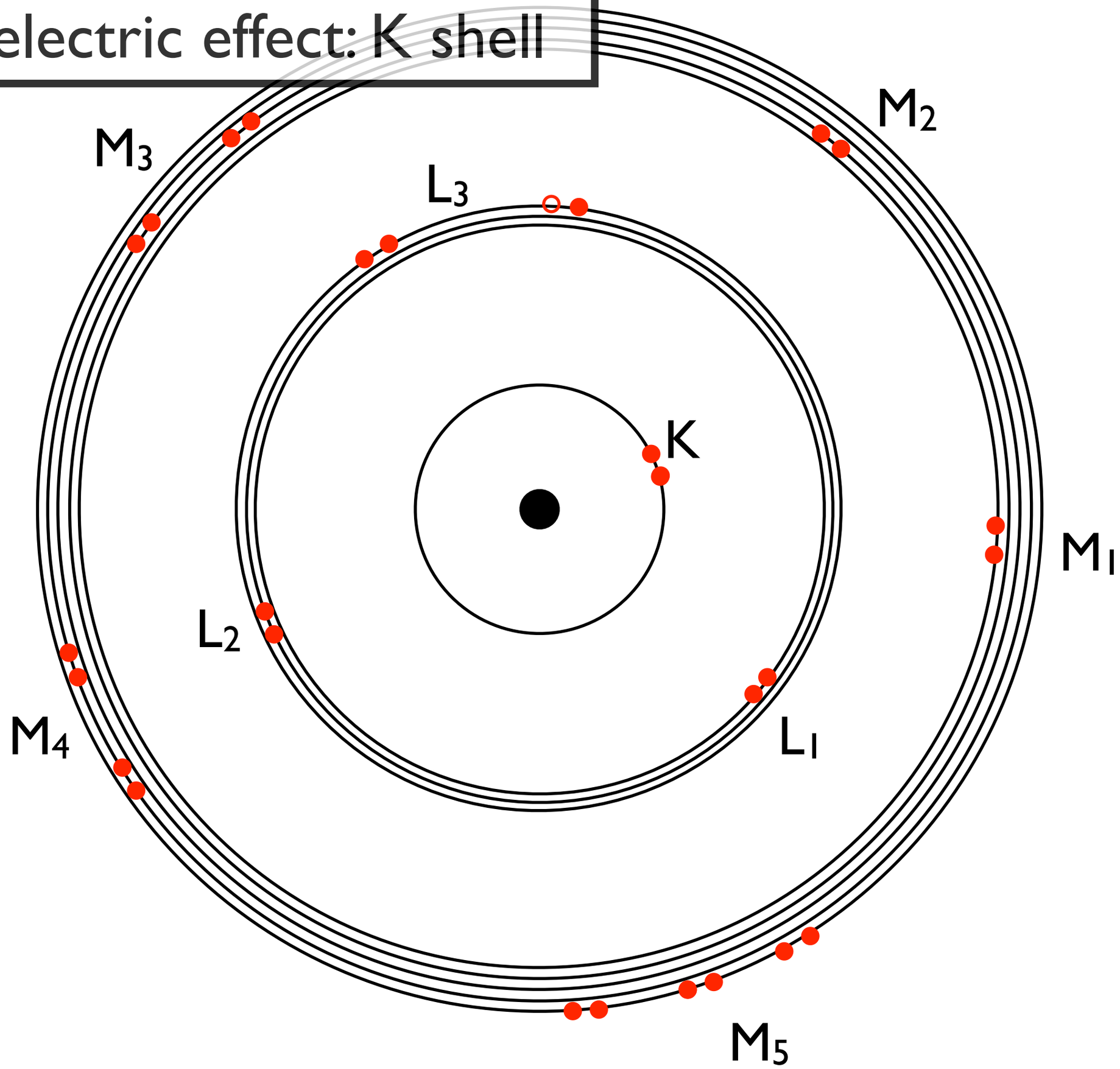
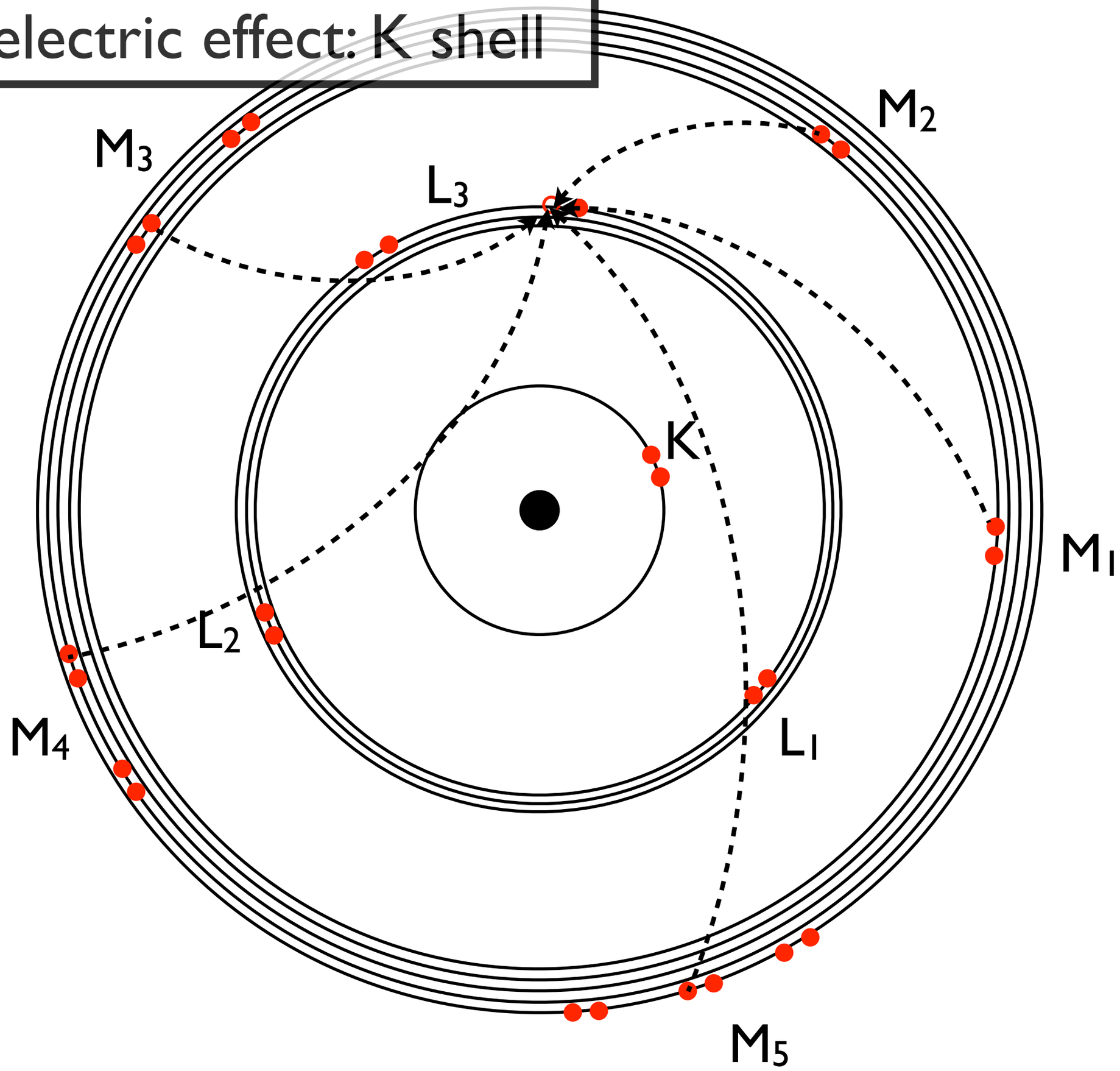
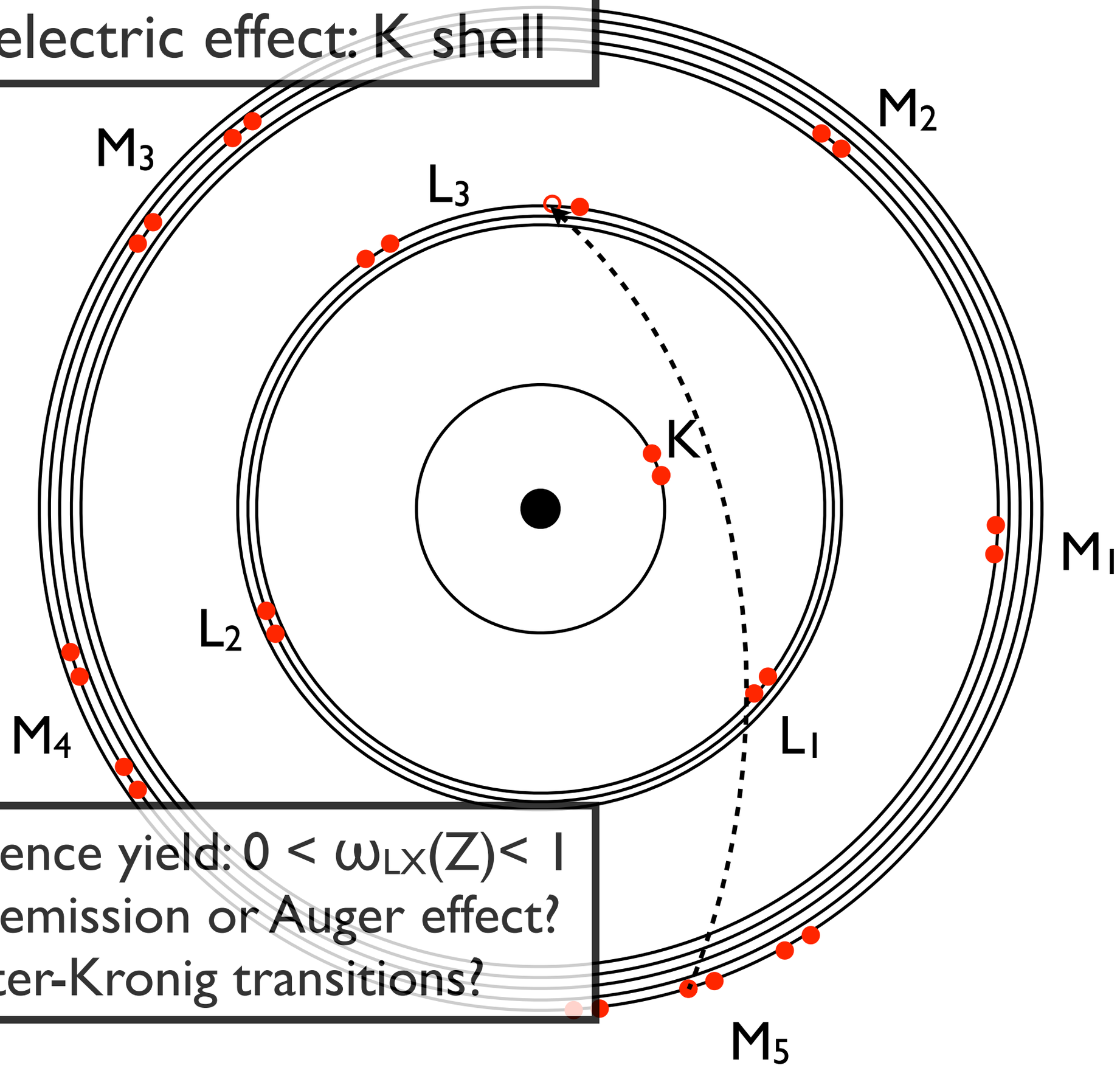


Photoelectric effect: K shell



Photoelectric effect: K shell

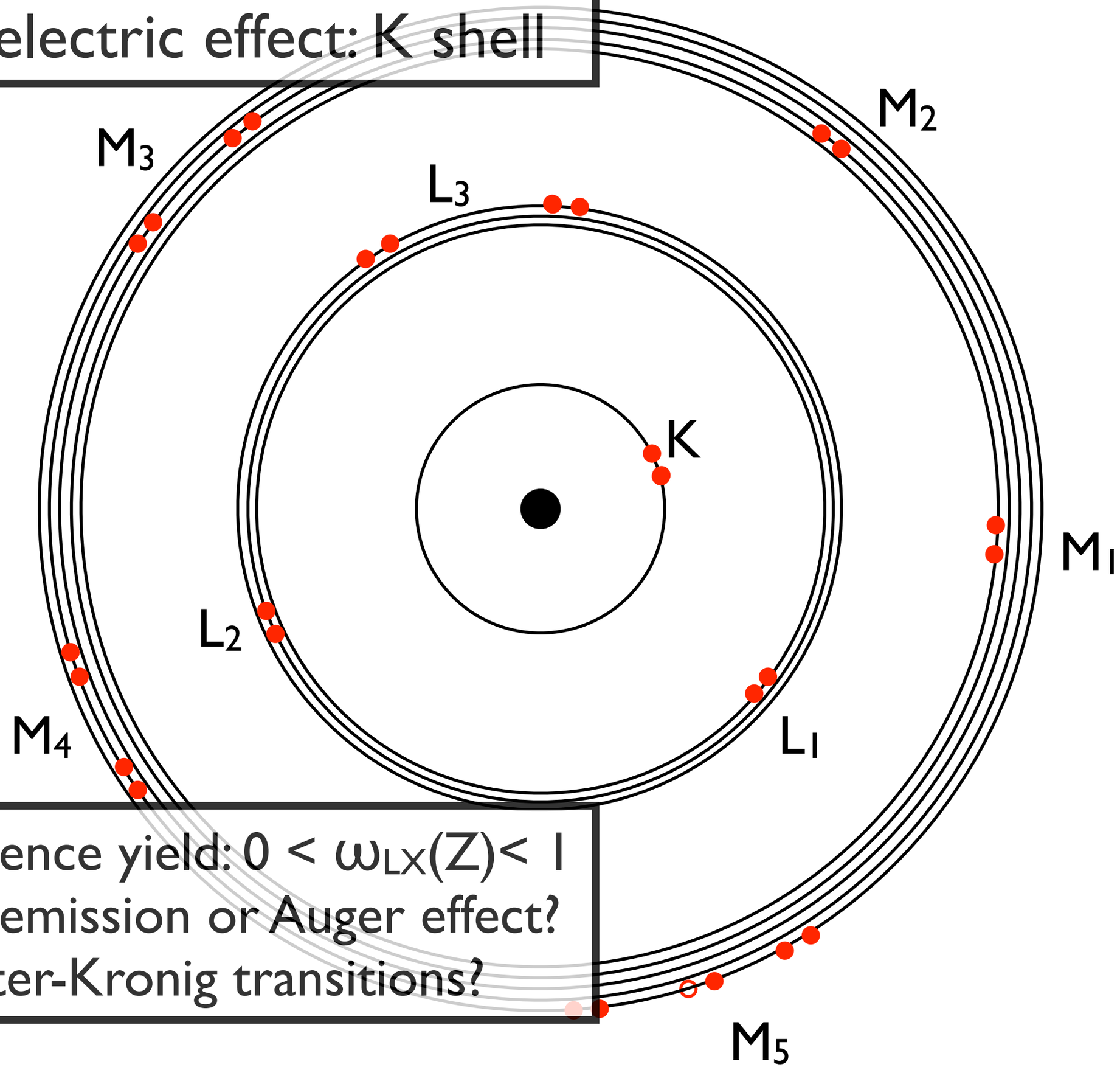


Fluorescence yield: $0 < \omega_{LX}(Z) < 1$

Photon emission or Auger effect?

Coster-Kronig transitions?

Photoelectric effect: K shell



Fluorescence yield: $0 < \omega_{LX}(Z) < 1$

Photon emission or Auger effect?

Coster-Kronig transitions?

XRF cross sections: cascade effect

- Occurs whenever multiple shells of a particular element can be excited
- Two components: radiative and non-radiative
- Leads to considerable boost in the observed intensity of L- and M-lines: several times larger than intensity through primary excitations
- Very obvious when using monochromatic excitations
- Very often neglected in quantification and simulations
- Complex implementation
- Many fundamental parameters involved → accuracy?

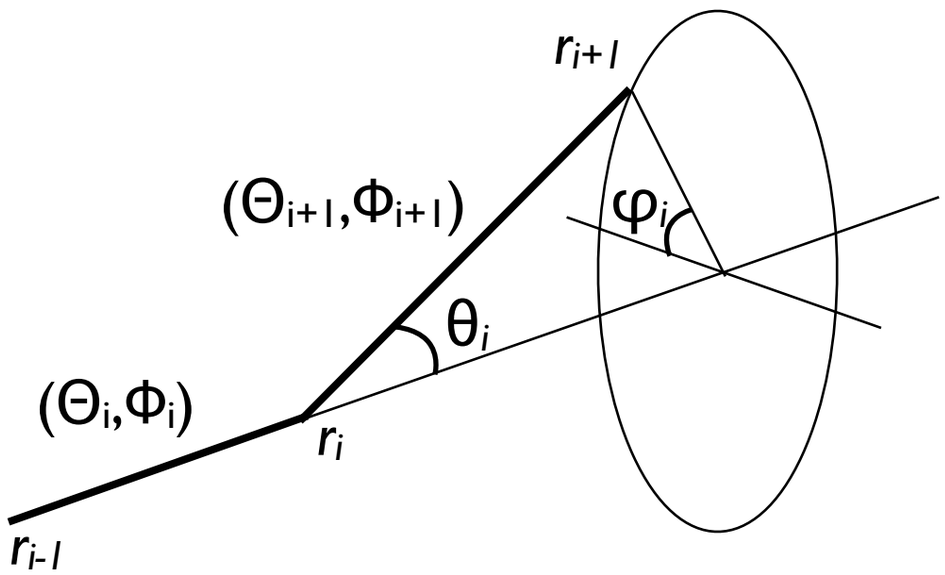
New photon coordinates

Photon direction:

$$\begin{bmatrix} \sin\Theta_{i+1}\cos\Phi_{i+1} \\ \sin\Theta_{i+1}\sin\Phi_{i+1} \\ \cos\Theta_{i+1} \end{bmatrix} = \begin{bmatrix} \cos\Theta_i\cos\Phi_i & -\sin\Phi_i & \sin\Theta_i\cos\Phi_i \\ \cos\Theta_i\sin\Phi_i & \cos\Phi_i & \sin\Theta_i\sin\Phi_i \\ -\sin\Theta_i & 0 & \cos\Theta_i \end{bmatrix} \begin{bmatrix} \sin\theta_i\cos\phi_i \\ \sin\theta_i\sin\phi_i \\ \cos\theta_i \end{bmatrix}$$

Photon coordinates:

$$x_{i+1} = x_i + S_i \sin\Theta_{i+1}\cos\Phi_{i+1}$$
$$y_{i+1} = y_i + S_i \sin\Theta_{i+1}\sin\Phi_{i+1}$$
$$x_{i+1} = x_i + S_i \cos\Phi_{i+1}$$



Photon termination

- After each interaction, a new step length will be calculated and so on...
- The procedure stops when either the photon is absorbed by the sample or leaves it.
- Upon leaving the sample, a check is performed to determine whether or not the photon hits the detector

Brute force algorithm: inefficient

- Very large number of photons must be simulated
- Possible loss of photons due to thin, low absorbent samples, low fluorescence yields, and detector geometry
- Usually requires supercomputer

Code optimizations: variance reduction

Selection of the step length

- Force photons to stay within the system
- Largest index *m* is found according to:

$$\sum_{i=1}^{m} \mu_i S_i < -\ln\left(1 - RP_{abs}\right) \quad \text{with} \quad P_{abs} = 1 - \exp\left(-\sum_{i=1}^{n} \mu_i S_i\right)$$

- Step length calculated as:

$$S = \sum_{i=1}^{m} \left(1 - \frac{\mu_i}{\mu_{m+1}}\right) S_i - \frac{1}{\mu_{m+1}} \ln\left(1 - RP_{abs}\right)$$

- Photon weight multiplied with P_{abs}

Forced detection

- For each photon at each interaction point
- Calculate the probabilities of all possible *pathways* of the photon to reach a random point on the detector
- Fractional photons added to virtual MCA

$$P = P_{conv} P_{dir} P_{esc}$$

Fluorescence yield

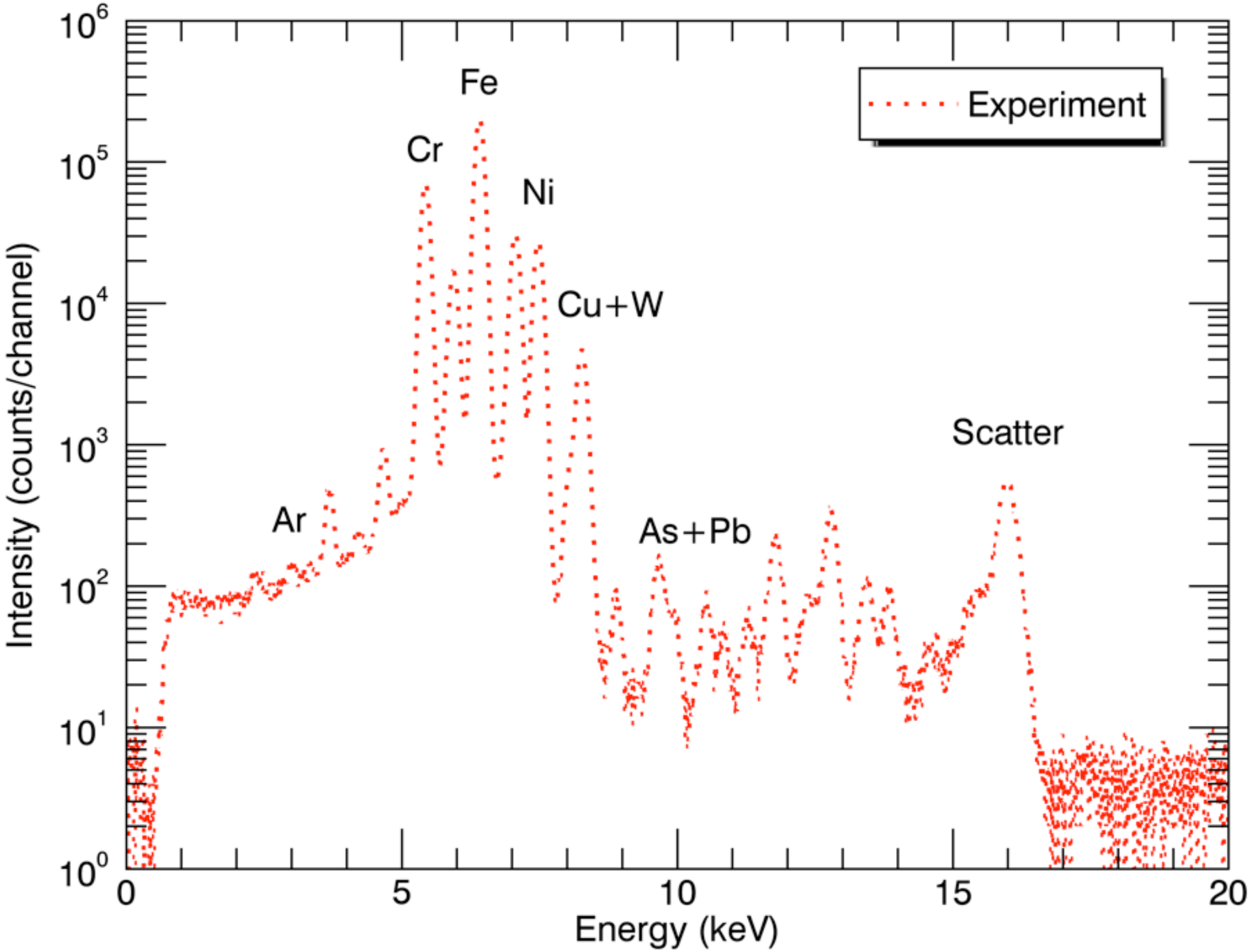
- Multiply photon weight with fluorescence yield of selected sub-shell
- Avoids the loss of simulated photons to low energy cascade photons
- Cascade effect simulation taken into account by variance reduction through corrected XRF production cross sections

Detector response function

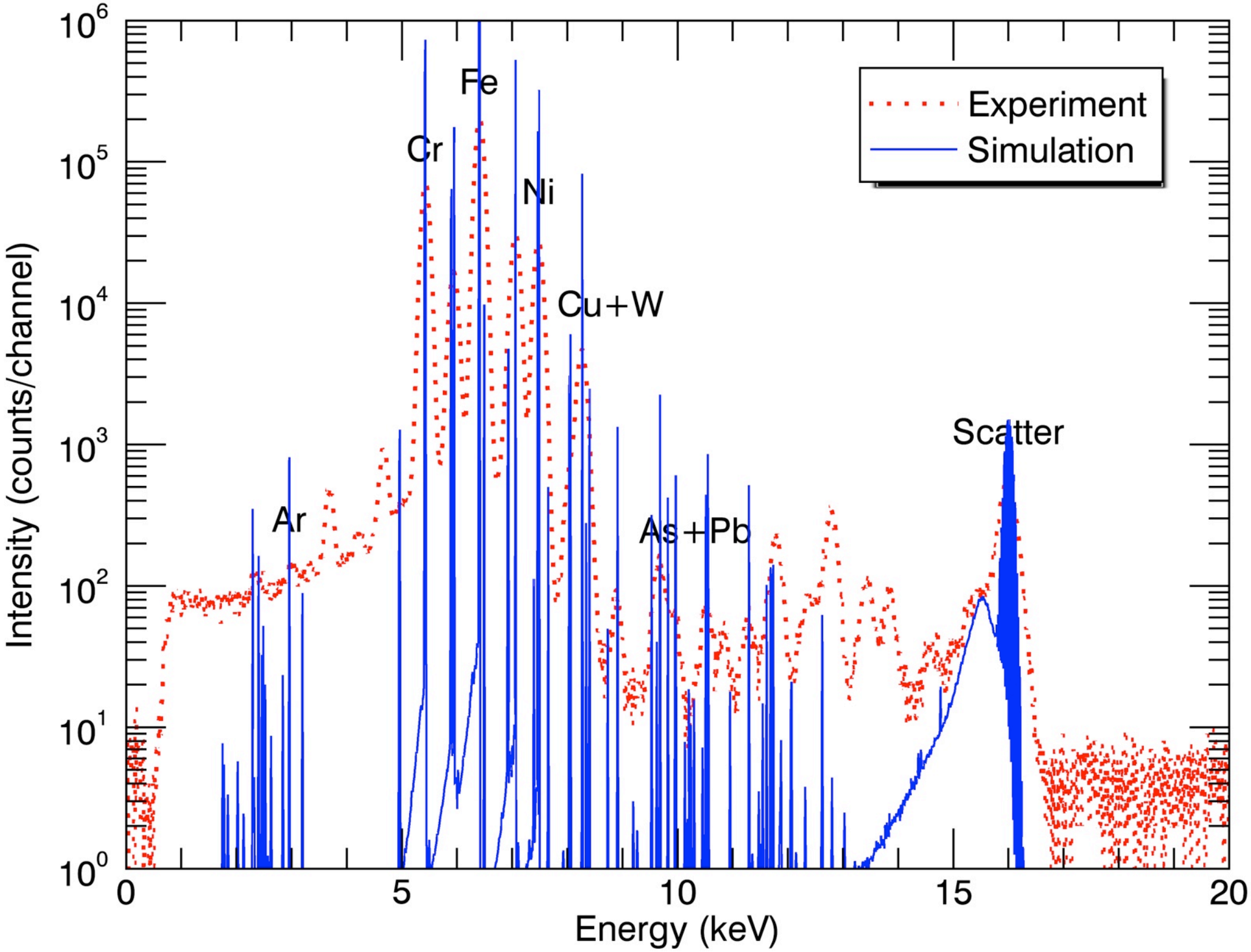
Case study: NIST SRM 1155

- Stainless steel Cr18Ni12
- HASYLAB Beamline L
- Excitation energy: 16 keV
- Exposure: 300 s RT
- Degree of polarization ~ 92 %
- Beam-size: 10 x 10 μm^2

Cr	18.37%
Ni	12.35%
Mo	2.386%
Mn	1.619%
Cu	0.1734%
Co	0.1052%
V	0.0508%
C	0.0445%
S	0.0175%



Experimental data



Raw simulation result

Semiconductor detectors

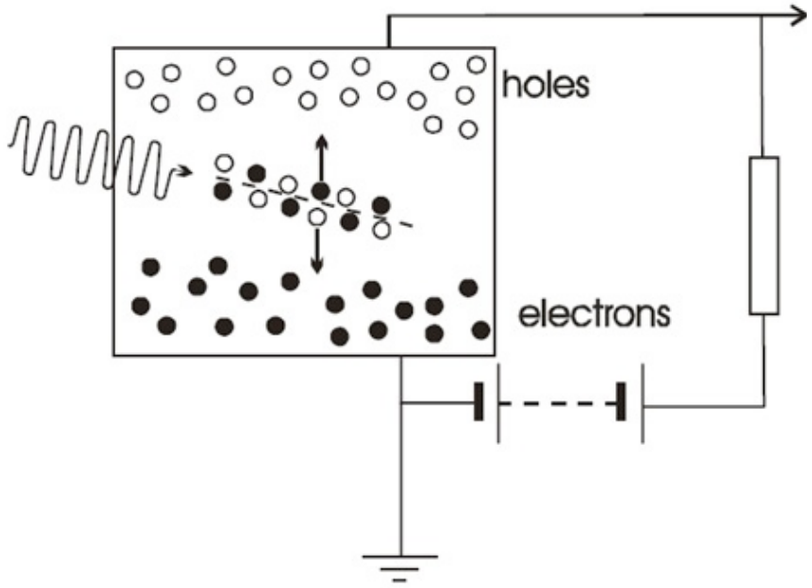
- Incident X-rays will ionize the semiconductor material, leading to the production of electron-hole pairs

- The number of pairs is proportional the energy of the incoming photon

- Influenced by an electric field, the electrons and holes migrate to the electrodes

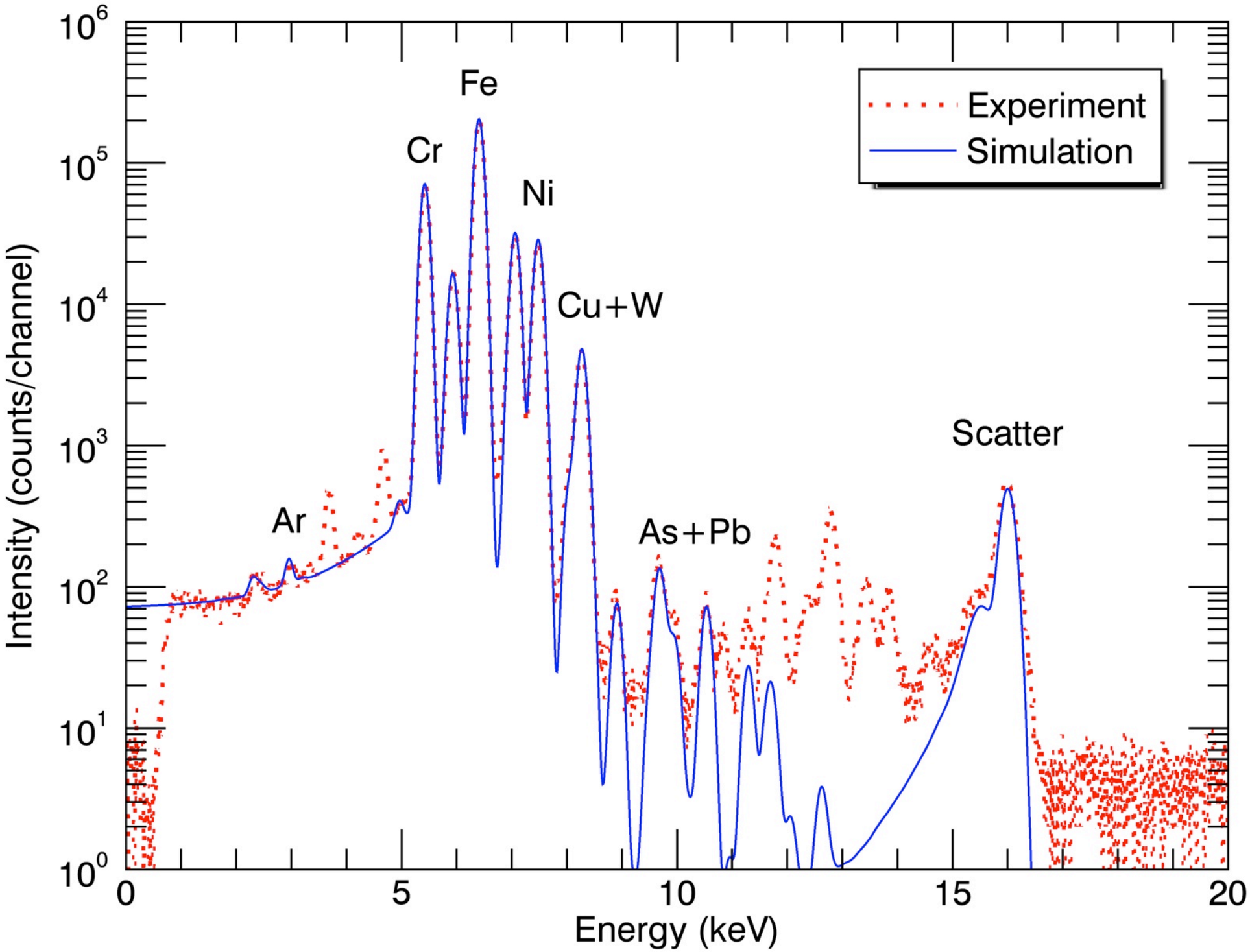
- Results in a pulse that will be measured in the outer circuit

- Dead time leads to some photons not being counted

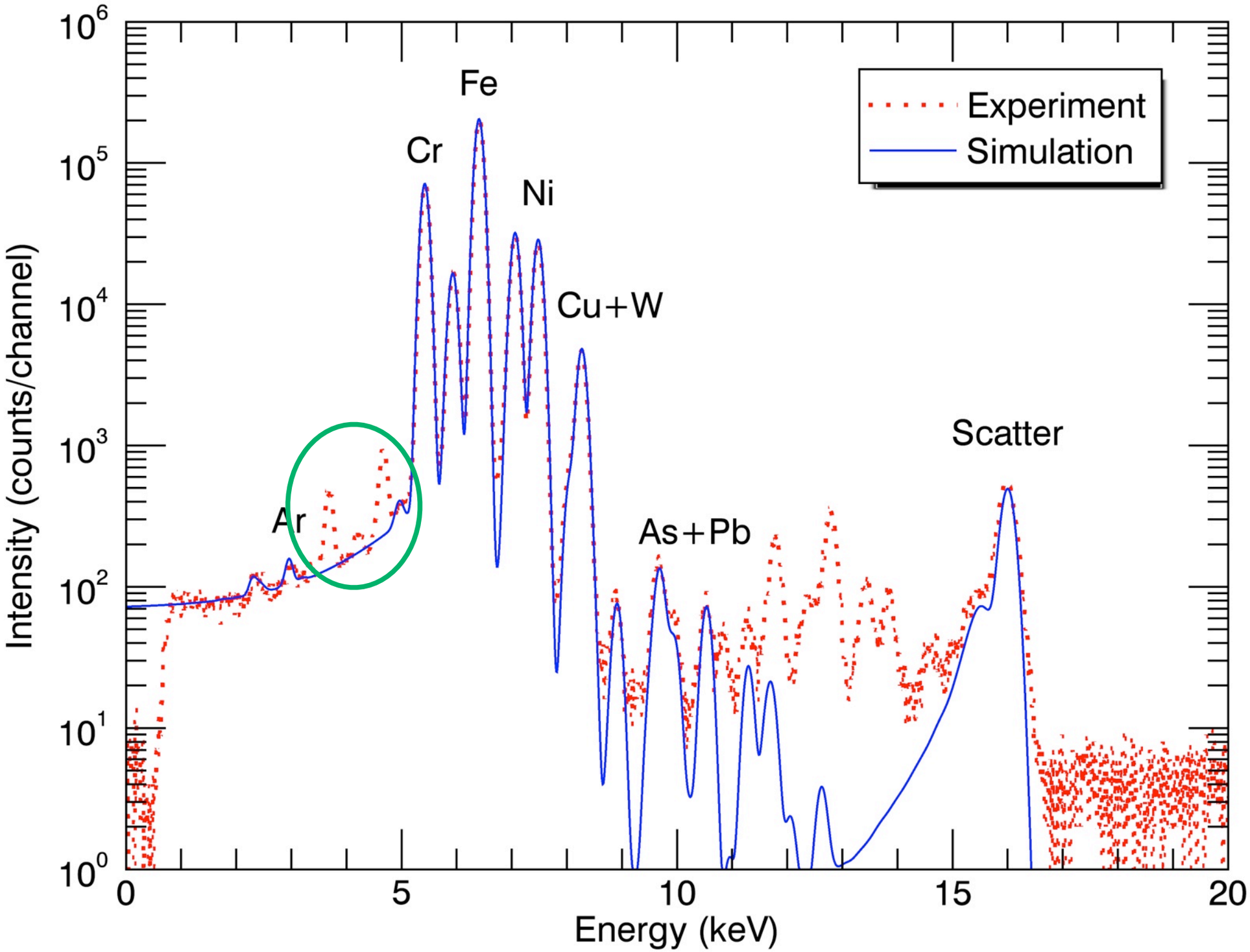


Spectral artifacts: peak broadening

- XRF lines experience Gaussian peak-broadening, due to the statistical nature of the photon-charge conversions and to electronic noise
- Incoming lines are not discrete, but have a Lorentzian profile
- Spectral peaks follow a Voigt profile, a convolution of a Gaussian and a Lorentzian distribution
- Usually approximated as Gaussians or pseudo-Voigt functions



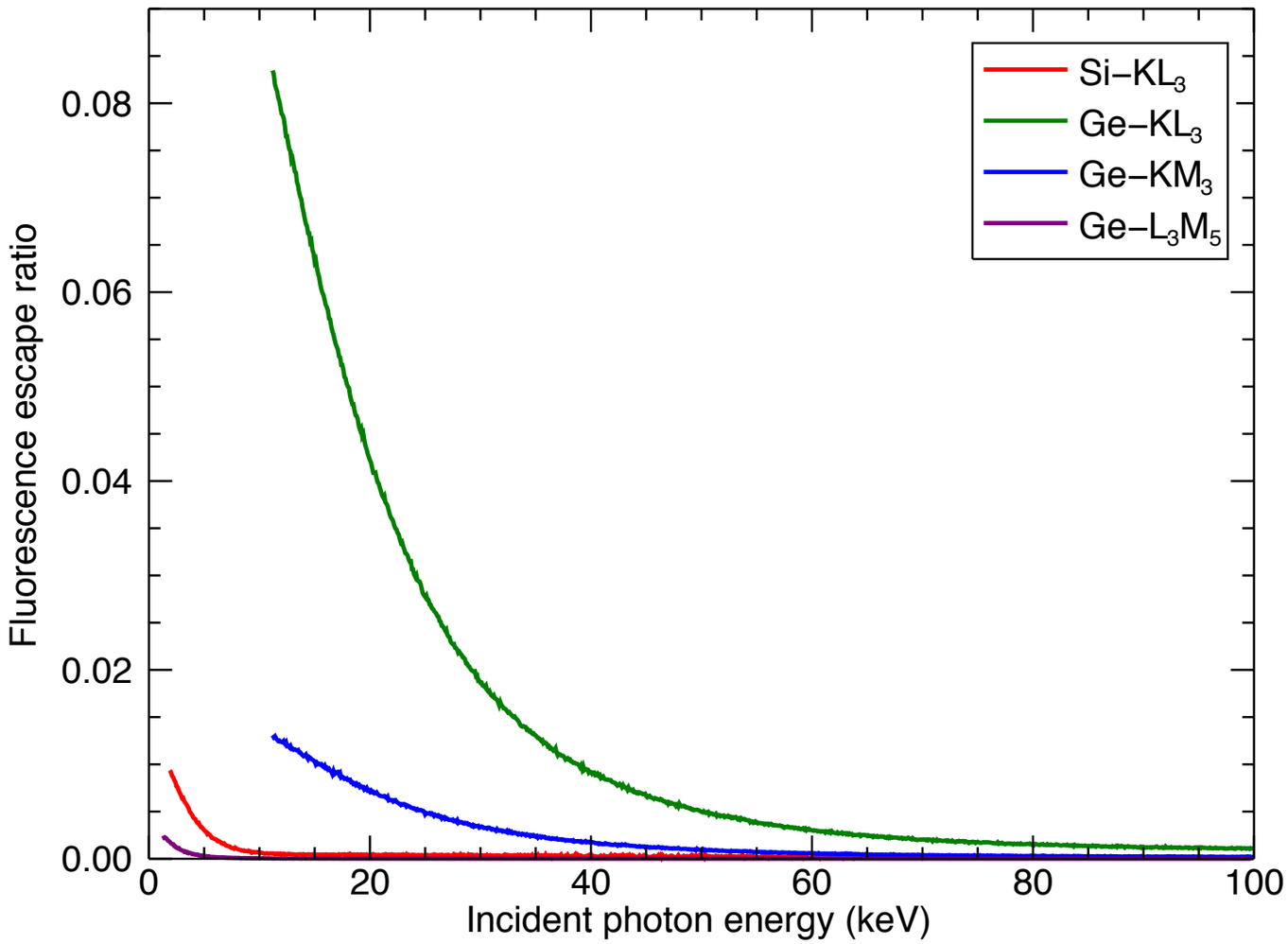
After Gaussian convolution



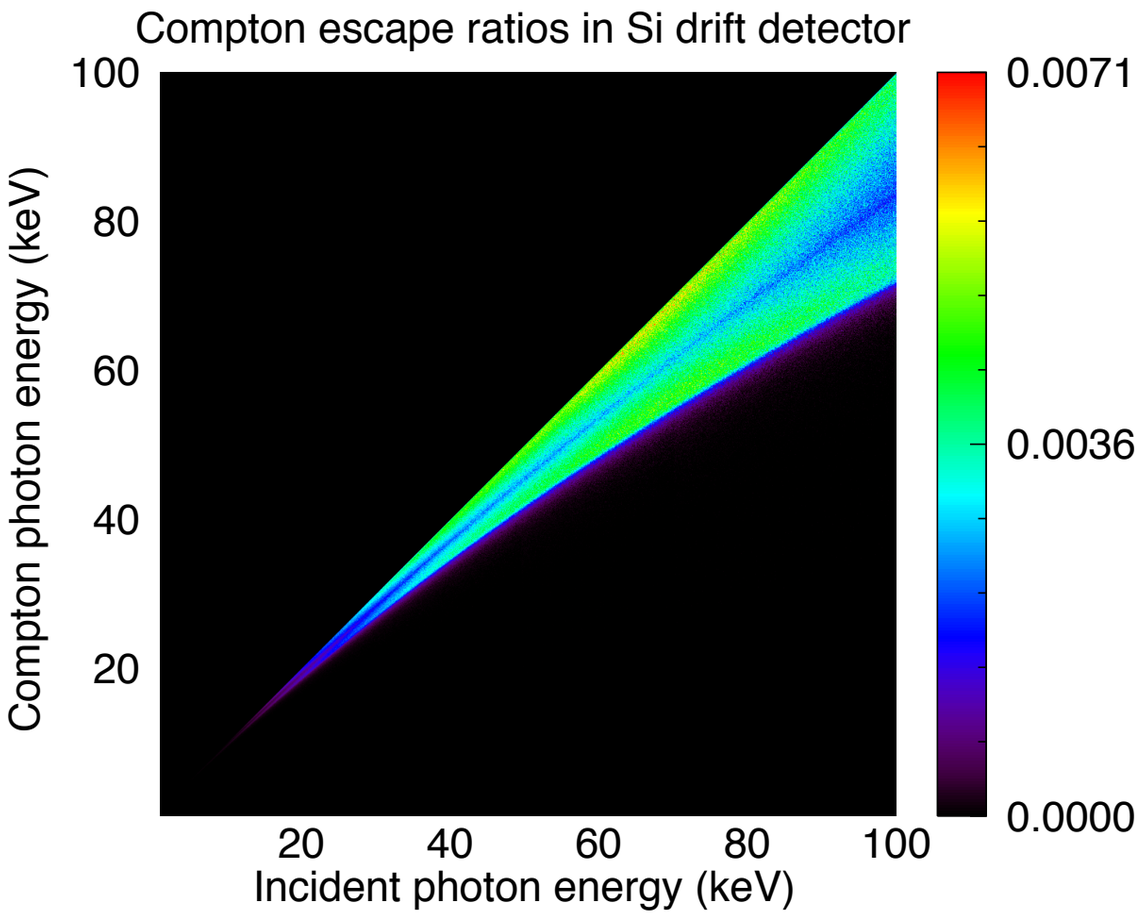
After Gaussian convolution

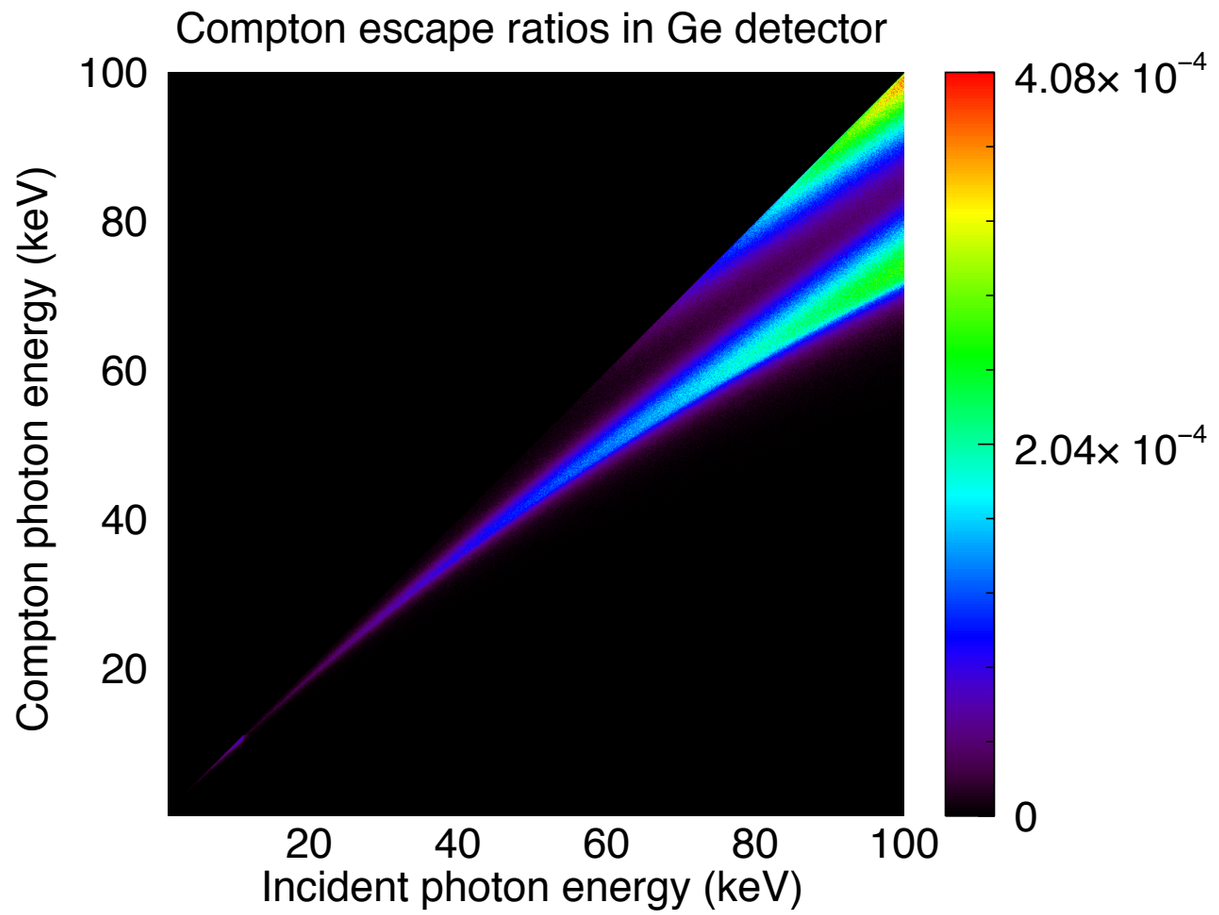
Detector escape peaks

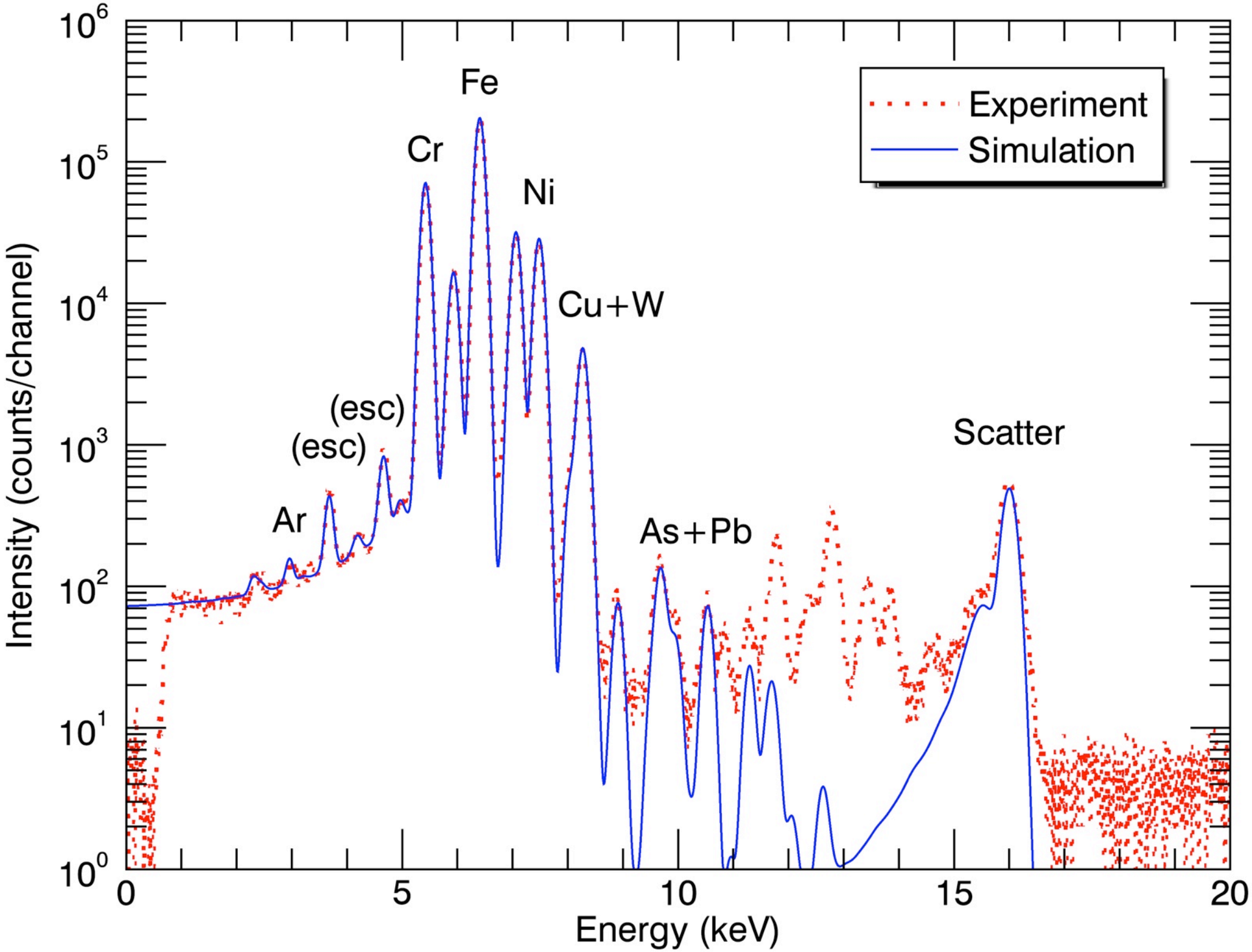
- Photons produced in detector crystal through XRF or Compton scattering may leave detector
- Results in detection of a pulse with energy lower than expected
- Escape peak ratios calculated based on crystal composition and thickness
- Calculated analytically or with Monte Carlo simulation



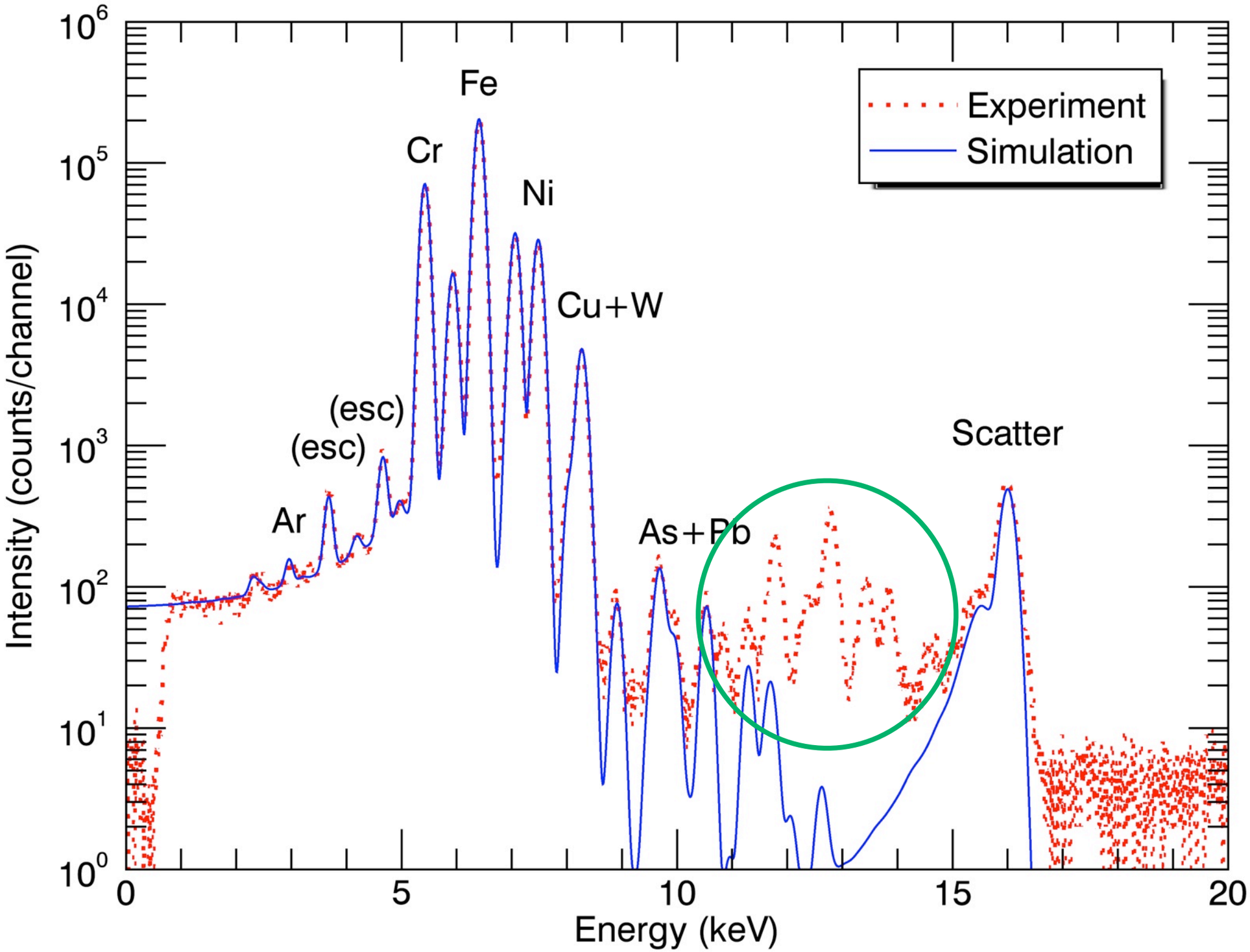
Detector escape peaks







With escape peaks

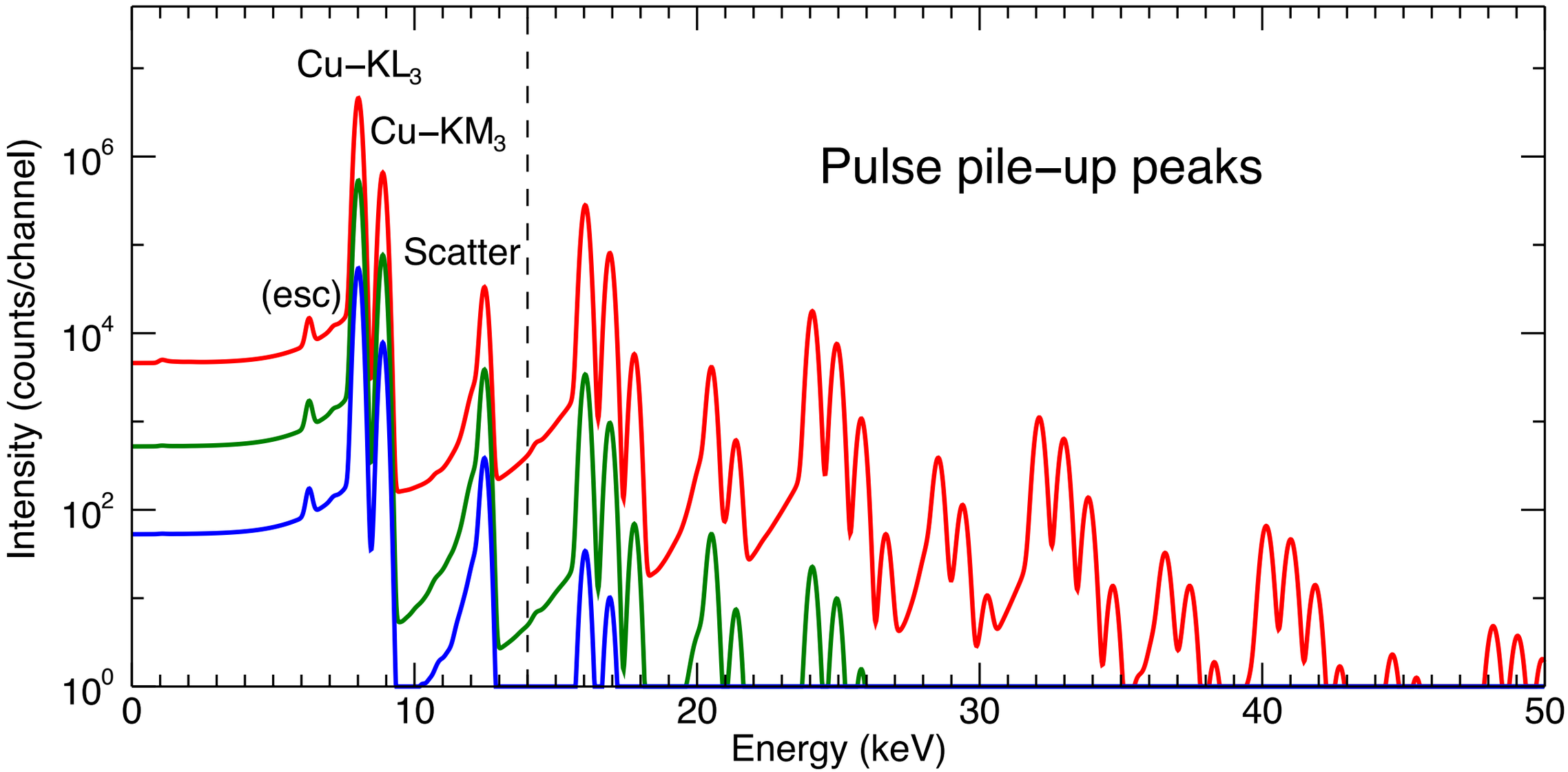


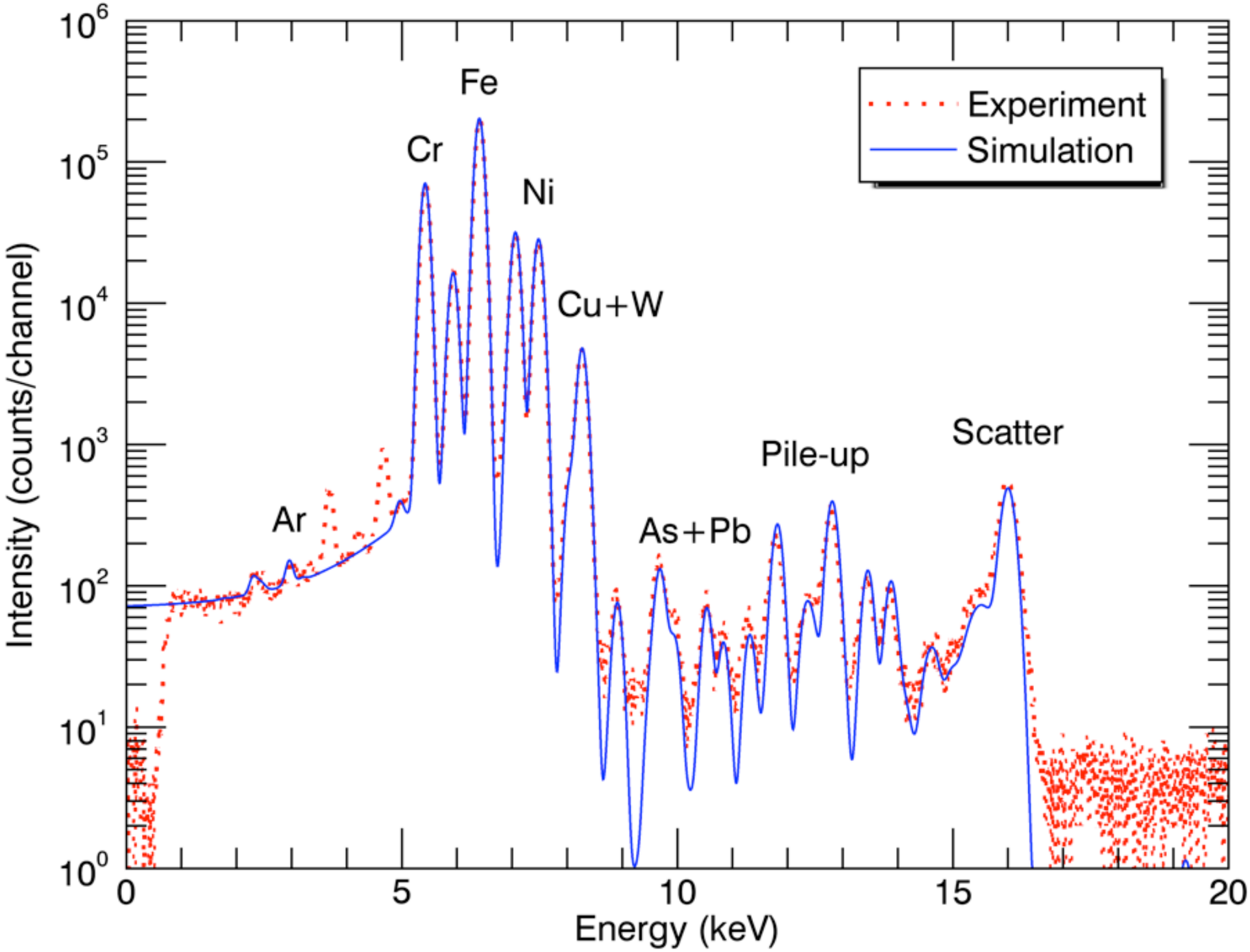
With escape peaks

Detector pulse pile-up simulation

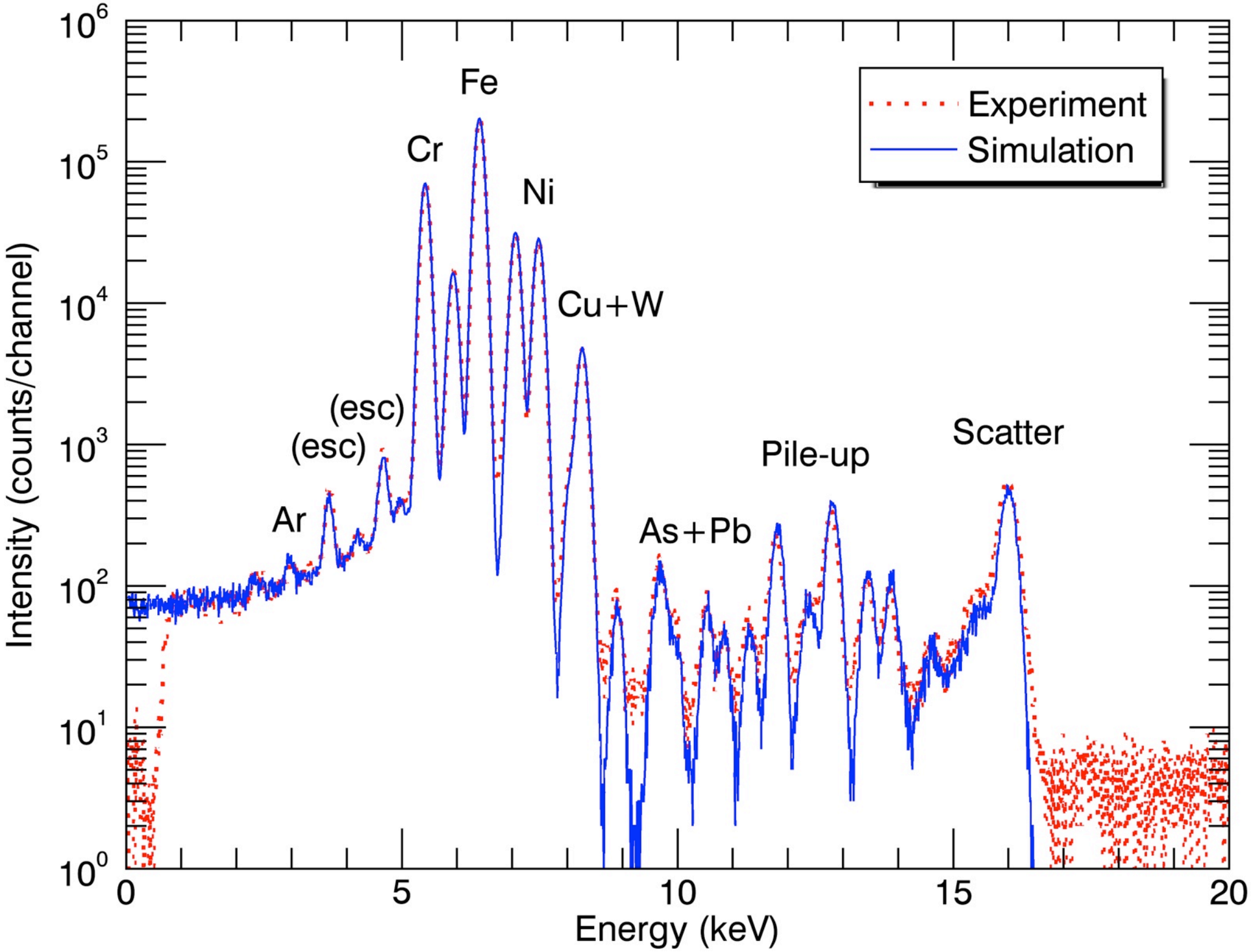
- Emergence of peaks at energy values corresponding to the sum of XRF peaks
- Due to the limitations of the electronics connected to the detector
- Magnitude strongly correlated to beam intensity
- Monte Carlo simulation using exponential pulse interval distribution

Detector pulse pile-up simulation

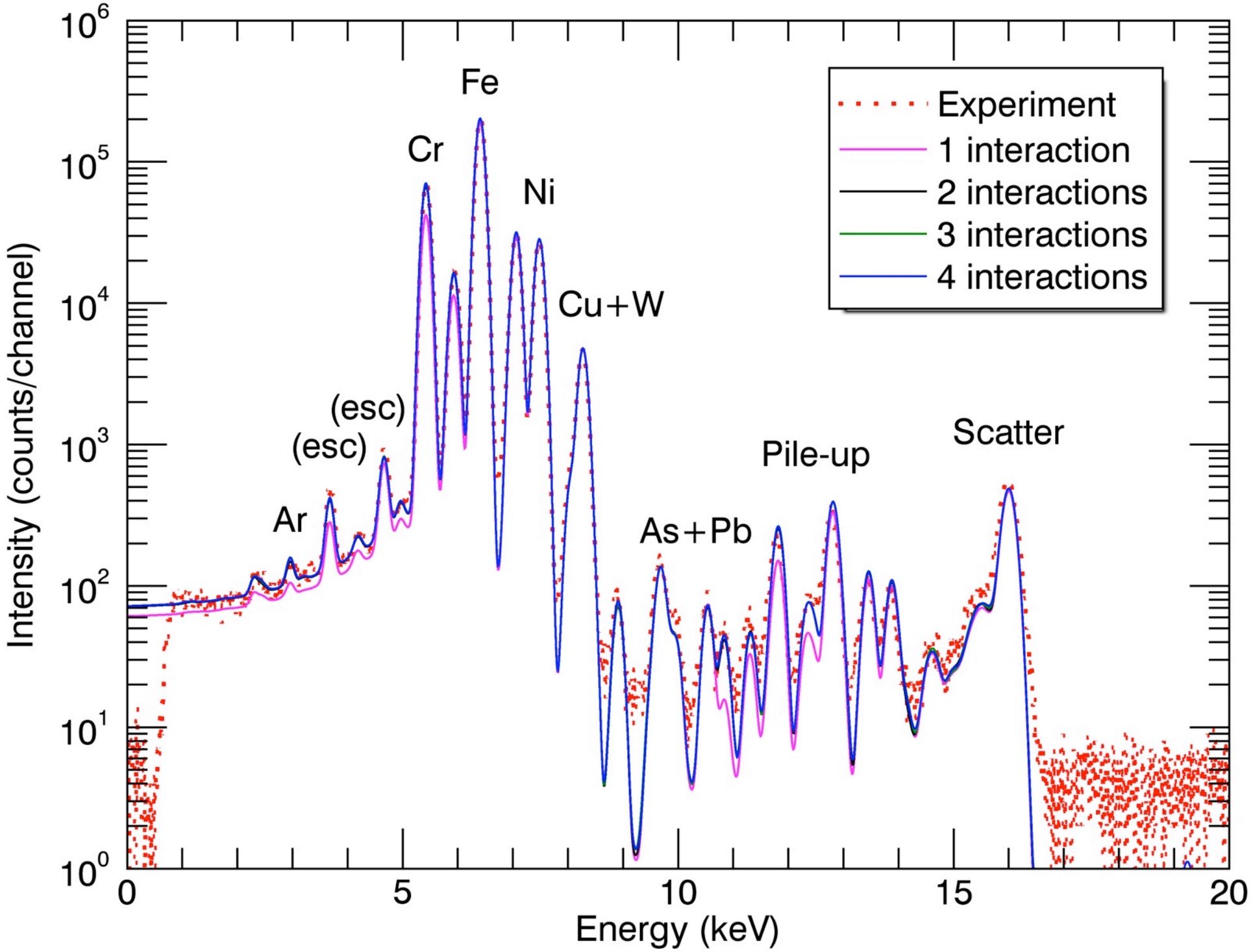




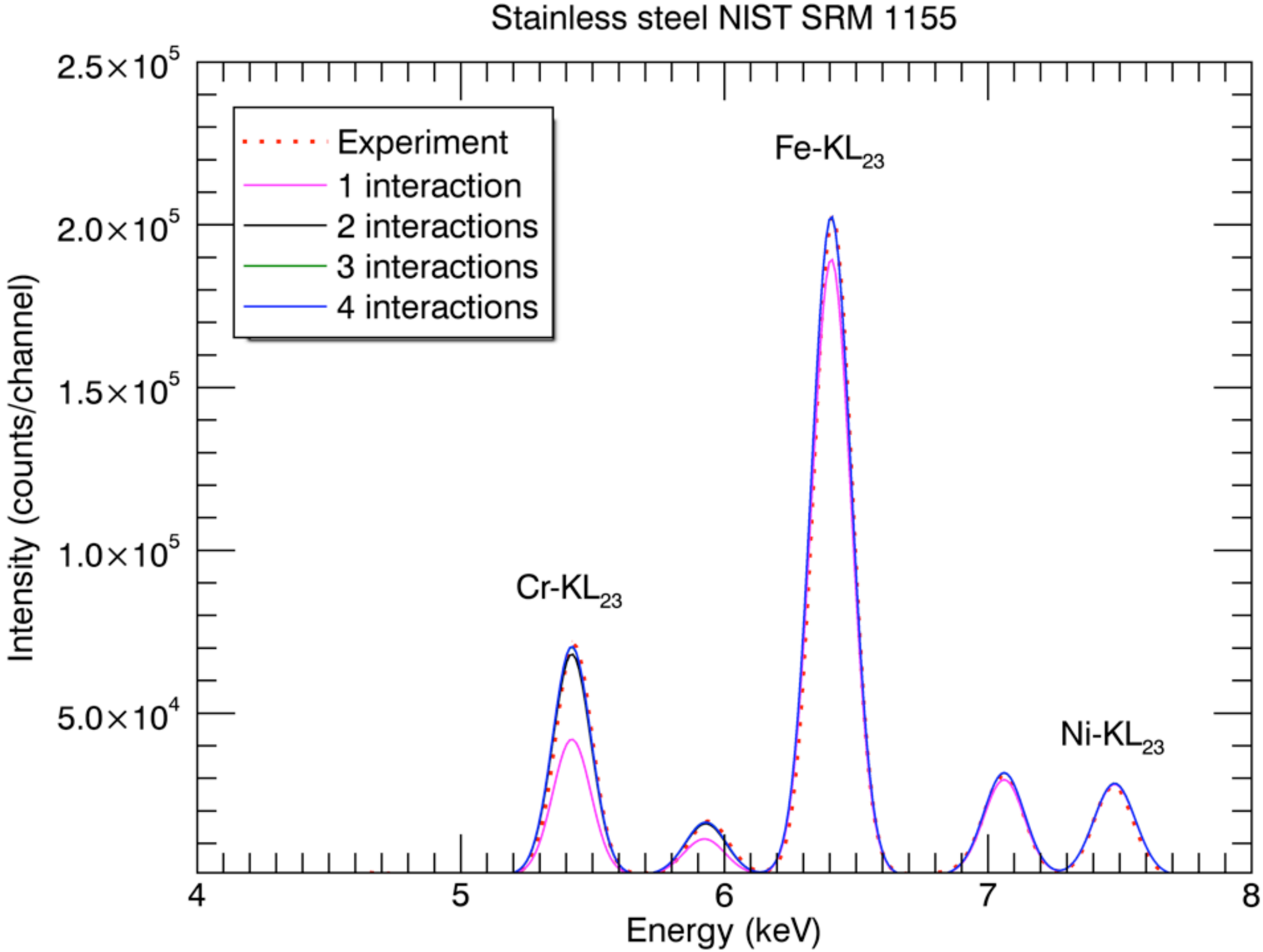
With pulse pile-up...



...and some Poisson noise



Higher order interactions



Higher order interactions

Individual interaction contributions to intensity

- XRF CS of Cr-KL_{23}
  @16 keV: 8.3116287
  @Ni-KL_{23}: 70.221933
  @Fe-KL_{23}: 109.02429!!

- XRF CS of Fe-KL_{23}
  @16 keV: 12.699491
  @Ni-KL_{23}: 97.242868

- XRF CS of Ni-KL_{23}
  @16 keV: 18.460541

  Expressed in cm^2/g

#	Cr-KL_{23}	Fe-KL_{23}	Ni-KL_{23}
1	655007	3084620	482088
2	406554	194120	3066
3	29652	2558	28
4	706	27	< 1

Overview of available codes

Geant4

- Low energy electromagnetic package
- Support for cascade effect
- Toolkit, not a finalized program
- Allows for very complex geometries
- Electron-matter interactions
- Open source

MCSHAPE

- Dedicated XRF code
- Advanced modeling of electrons produced by Compton, Auger and photoelectric effect
- University of Bologna: Jorge Fernandez and Viviana Scot
- Source code not distributed, binaries only

XRMC

- X-ray spectroscopy and imaging experiments
- Complex sample geometries using quadrics
- Highly extensible
- University of Sassari
- Open source: GPLv3

References

- L. Vincze et al. *Spectrochim. Acta Part B*, 48(4): 553–573, 1993.
- L. Vincze et al. *Spectrochim. Acta Part B*, 50(2): 127–147, 1995.
- T. Schoonjans et al. *Spectrochim. Acta Part B*, 70:10–23, 2012.

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