X-ray Absorption/Emission and Optical Photons
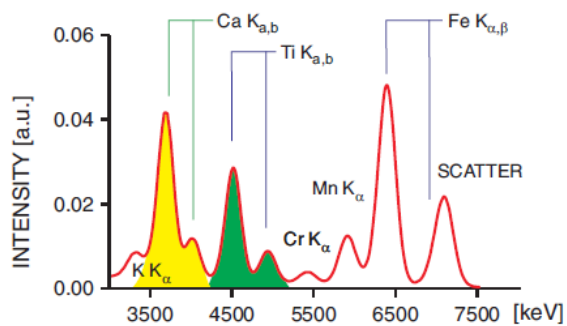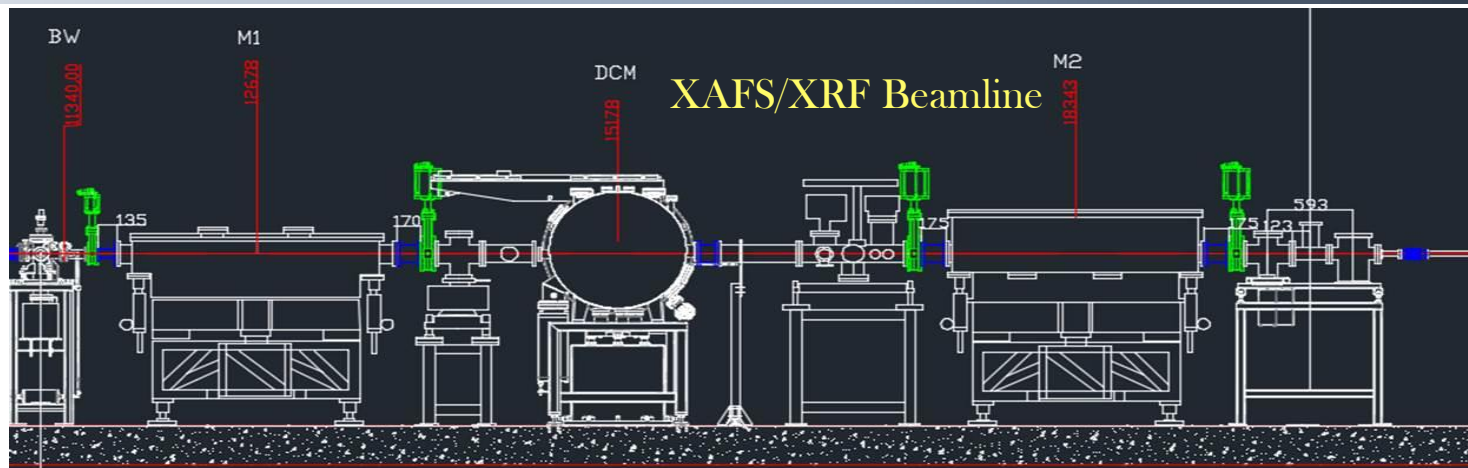
Latif Ullah Khan
XAFS/XRF Beamline Scientist

Email: latifullah.khan@sesame.org.jo
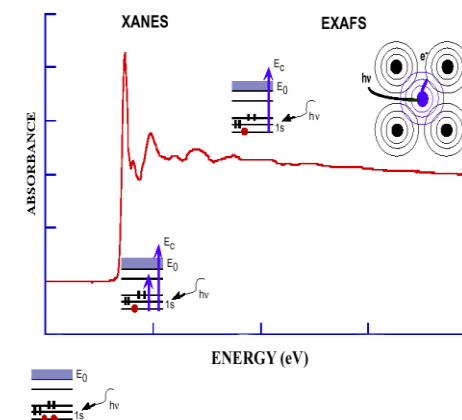
Date: January 26, 2023

Natural Synchrotron Source
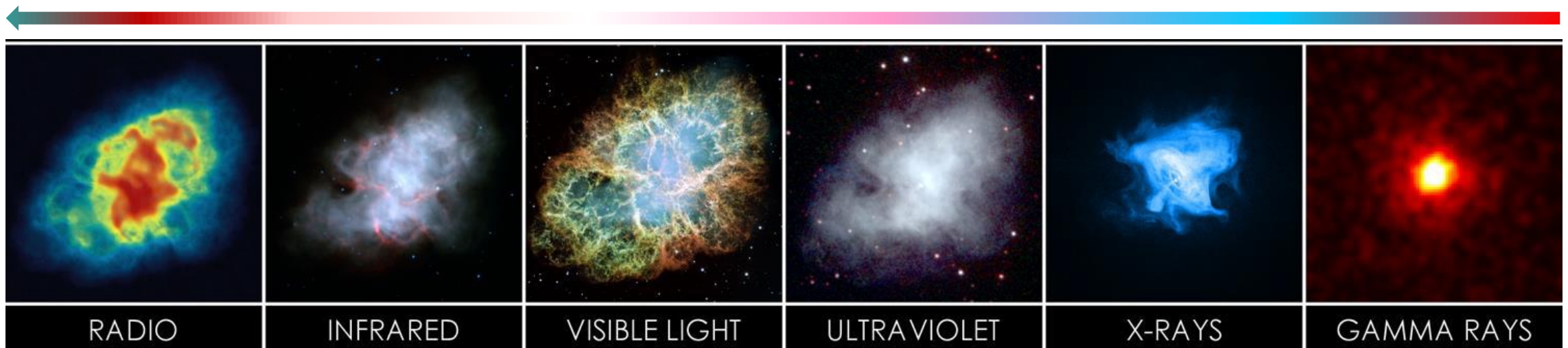
Crab Nebula
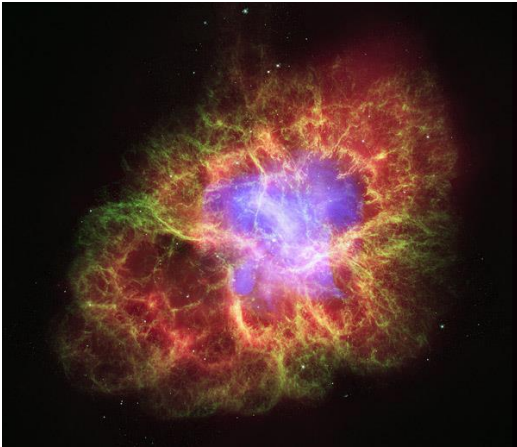
Crab pulsar

❏ **Crab pulsar** emits pulses of radiation from gamma rays to radio waves

❏ **Crab Nebula** is generally the brightest persistent gamma-ray source in the sky.
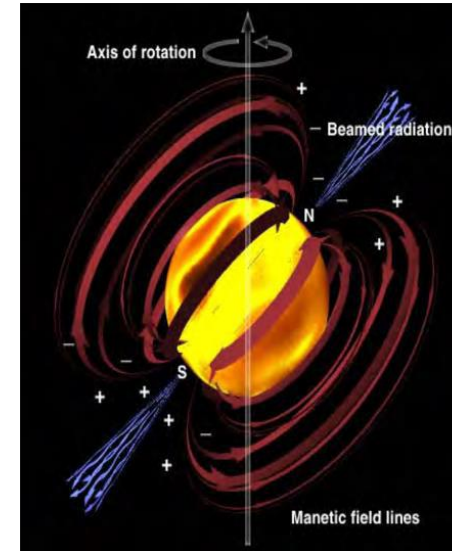
- *Neutron star*
- *30 Km diameter*
- *30 Hz rotation*
- *108T magnetic field*

Images at different frequencies

| RADIO | INFRARED | VISIBLE LIGHT | ULTRAVIOLET | X-RAYS | GAMMA RAYS |

SESAME Synchrotron Light Source

SESAME Light Source

Storage Ring
2.5 GeV

Booster
800 MeV

Microtron
22 MeV

SESAME Accelerator

- Circumference: 133.2 m
- Operation current: 300 mA
- Natural emittance: 26 nmrad

World Maps
Synchrotron Light Sources
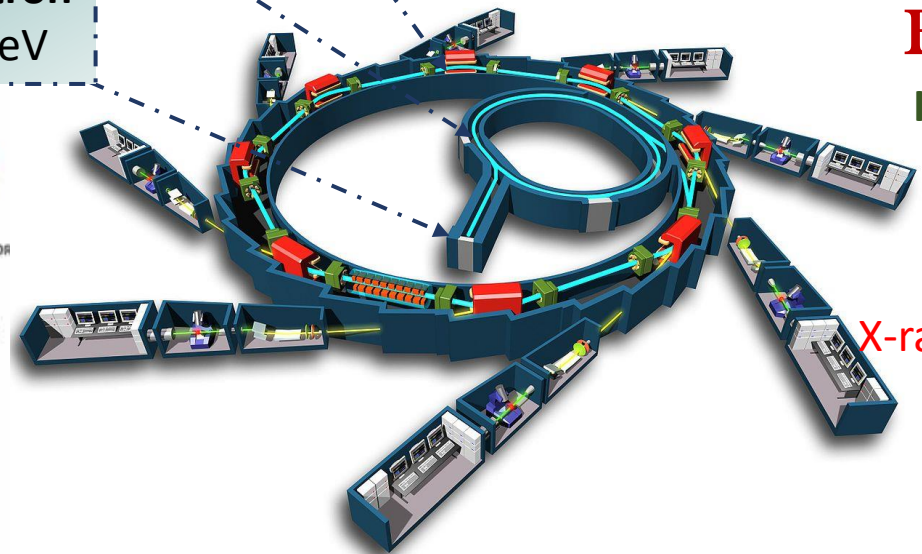
Beamlines

IR
XAFS/XRF
XRD
Soft X-ray
X-ray Tomography

❑ **There are now more than 60 synchrotrons and FELs around the world**

XAFS/XRF Beamline Optics

VFM (M2)
(18328)

DCM
(15178)

Source (D08)
Bending Magnet

CVD Window
(11340)

VCM (M1)
(12678)

BENDING MAGNET
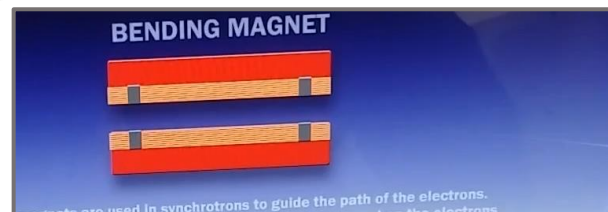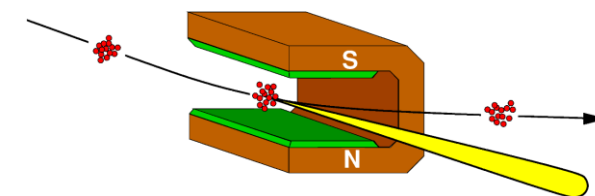
Harfouche, M.; Abdellatief, Khan, L.U.; Paolucci, G. et al. Emergence of the first XAFS/XRF beamline in the Middle East: providing studies of elements and their atomic/electronic structure in pluridisciplinary research fields. *J. Synchrotron Rad.* 29, 1-7, 2022.

Beamline Specifications

| Parameter	Value
Magnetic field (BM)	1.4554 T
Energy Range	4.7 keV – 30 keV
Energy Resolution **Si (111)** **Si (311)**	10^{-4}
Flux	5×10^{11} Ph/s @ 8 keV
Beam size (Horizontal x Vertical)	determined by slits "H x V" (max: 20 x 5 mm^2) (min: 1 x 1 mm^2)

Specifications of the Collimating and Focusing Mirrors

Specification	VCM (M1)	VFM (M2)
Dimensions (mm)	1200 x 70	1200x150
Coatings	Si, Pt	Si, Pt
Angle of incidence	Variable	Variable
Substrate	Silicon single crystal	ZERODUR
Cooling	Water cooled	Uncooled
Flatness	Cylindrical	Cylindrical
Type of bender	Pneumatic	Pneumatic
Minimum radius (km)	5.3	5.3
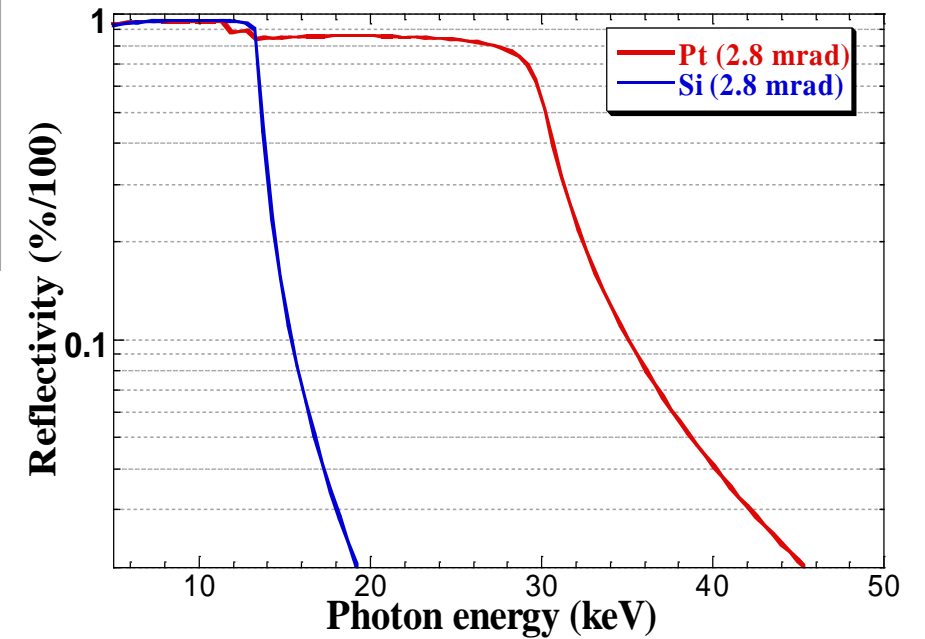
Mirrors reflectivity at 2.8 *mrad* incident beam angle for Pt and Si coatings

End Station

XAFS/XRF Experimental Station
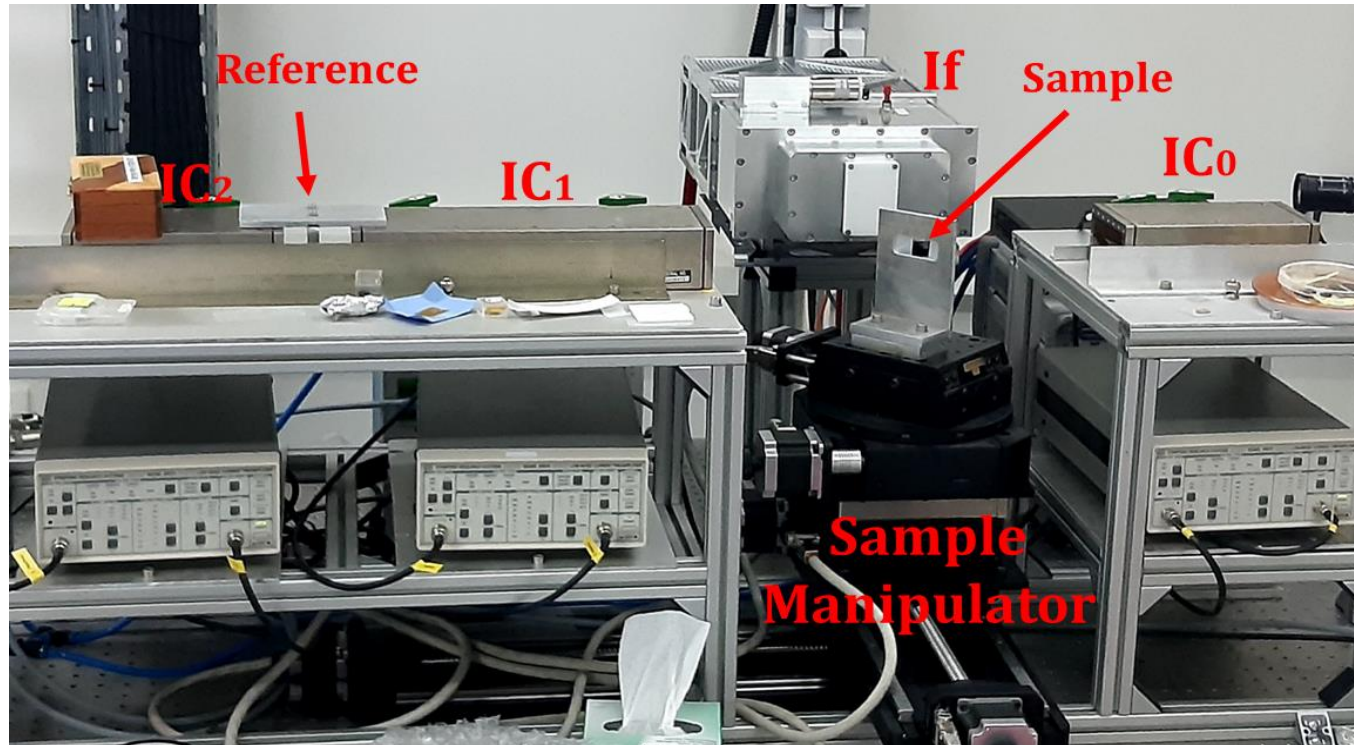
Cryojet for cooling sample (~95 K)

Techniques available

➢ **XAFS**

➢ **XRF**

➢ **XEOL** (In Progress)

XAFS measurement

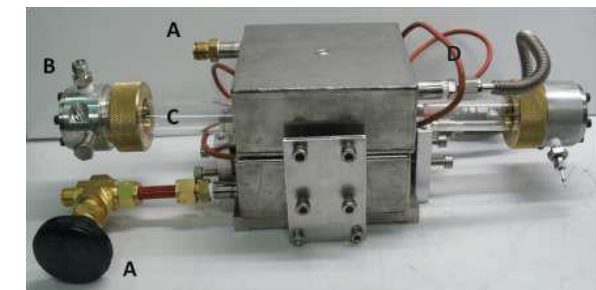**Transmission mode:** $\mu(E) = \log(I_0 / I)$

Fluorescence mode: $\mu(E) \propto I_f / I_0$

Sample Environment - Tubular Furnace/Reactor (Prototype)

6

X-ray Discovery and XAS/Luminescence

- X-ray absorption spectroscopy (XAS) adventure was started about one hundred years ago, after a while the discovery of X-rays in 1895 by Wilhelm Conrad Röntgen (German mechanical engineer and physicist).

- Röntgen discovered the X-ray from the LUMINESCENCE (Optical Photons) produced by screen of barium platinocyanide as a result of X-ray Absorption (Excitation).
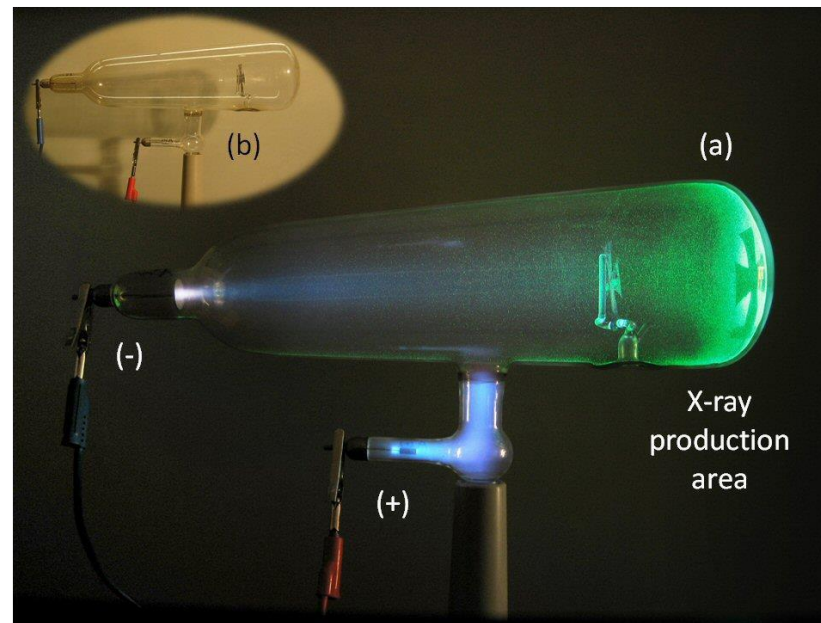
Wilhelm Röntgen discovered X-rays using the Crookes tube.
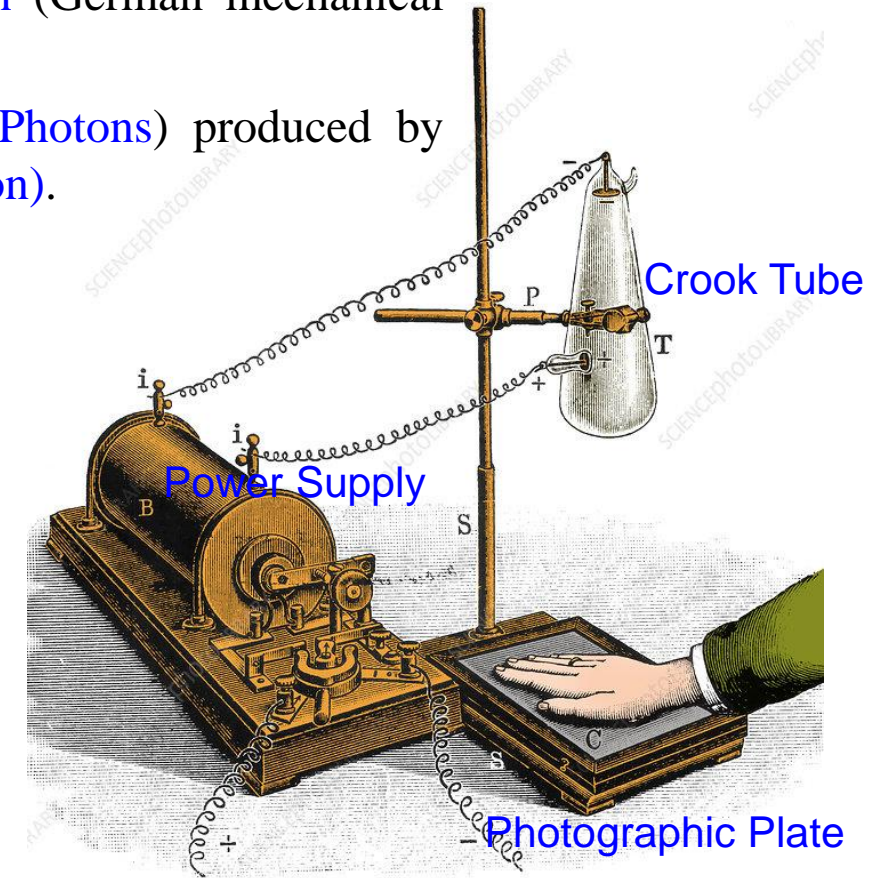
Drawing of the X-ray machine used by Wilhelm Roentgen to produce images of the hand.

W. C. Rontgen, Nature 53, 274 (1896). English translation by A. Stanton.

- The first X-ray absorption spectrum was observed by de Broglie in 1913, after a while the discovery of X-rays by Röntgen (1895). In his X-ray absorption experiment, de Broglie used X-ray tube as a source and mounted a single crystal on the cylinder of a recording barometer, employing a clockwork mechanism to rotate the crystal around its vertical axis at a constant angular speed. As the crystal was rotated, the X-rays scattered at all angles between the incident beam and the diffraction planes, according to the Bragg law, and consequently change the X-ray energy E:

$$2d_{hkl} \text{ sine } \theta = \lambda = hc/E$$

  c: Speed of light (c = 2.9979 10^{+8} m/s)
  h: Planck constant (h = 6.626 × 10^{-34} J s)
  Thus, hc = 12.3984 Å keV

- He recorded the X-rays of varying intensities on a photographic plate and observed two distinct discontinuities on the film, proving to be the K-edge absorption spectra of silver and bromine atoms present in photographic emulsion.

- This experiment provided a foundation for the modern monochromatic beam (Monochromator)

As Solid   As Vapor
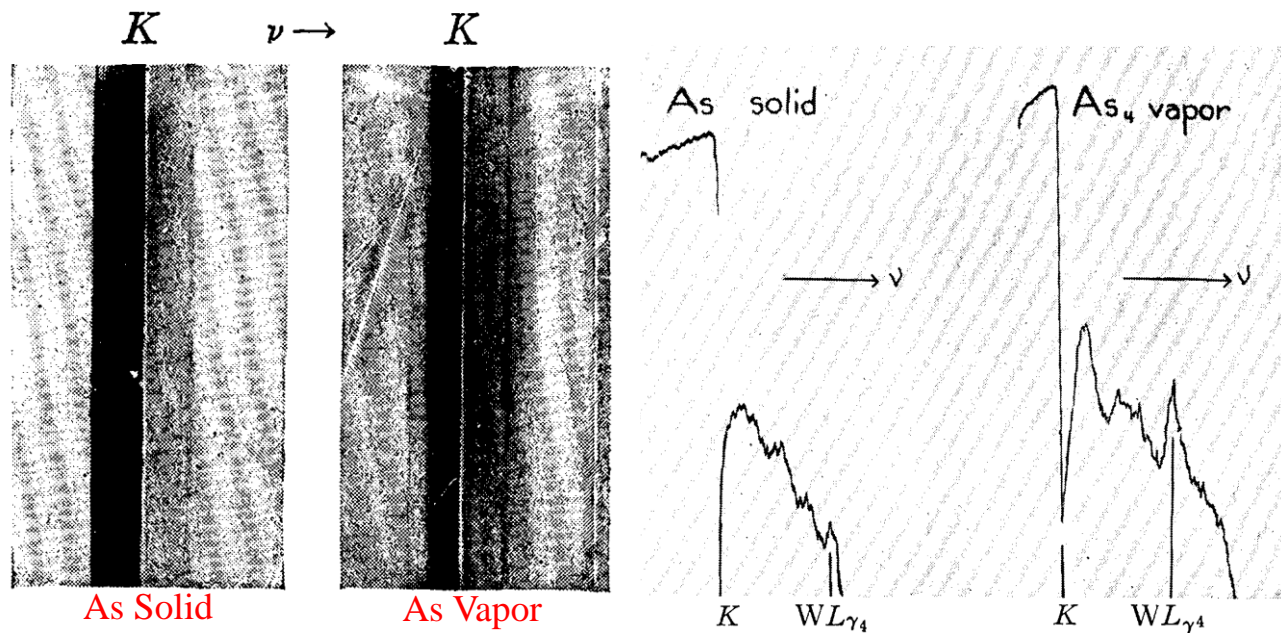
J. D. Hanawalt, The Dependence of X-ray Absorption Spectra upon Chemical and Physical State. *Phys. Rev.* 1931, *37*, 715.

Jeroen A. Van Bokhoven and Carlo Lamberti, X-Ray Absorption and X-Ray Emission Spectroscopy: Theory and Applications. Wiley Online Lib. 2016.
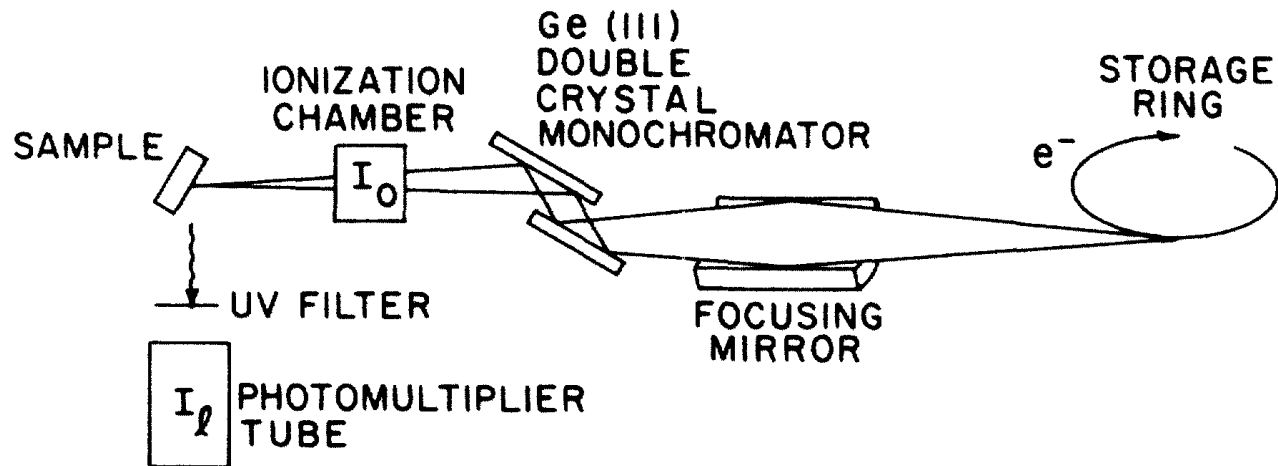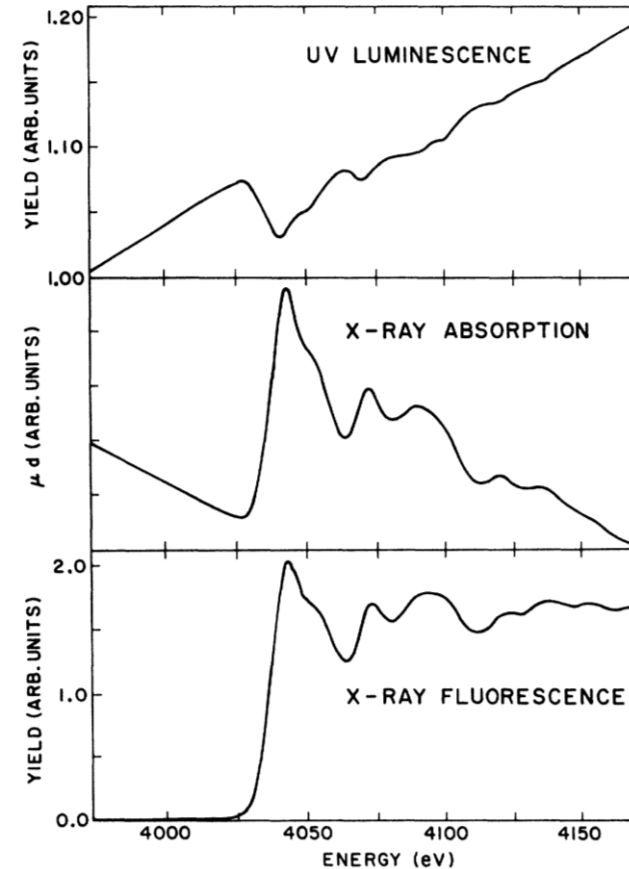
XEOL

❑ A crucial relation between the X-ray photon and optical photon is manifested by X-ray Excited Optical Luminescence (**X**E**O**L).

❑ **X**E**O**L demonstrates the fundamental mechanism of the conversion of X-ray energy absorbed by the system to optical photons.

❑ XEOL was successfully exploited over the past decades for a quantitative detection of rare earth ions at the ultra-trace level (part per billion) in high purity inorganic hosts.

❑ **X**E**O**L is often used together with XANES/NEXAFS to provide site specificity and reveal the electronic structure and optical properties of the wide range of materials, such as rare earth phosphors, semiconductors, quantum dots etc., applying in display/lighting technologies (e.g., LED lamps, TV, smartphone screen etc.), scintillators (X-ray/Gamma rays detectors) and energy conversion devices (Photovoltaic cells).

❑ Now a days mostly synchrotron light sources have **X**E**O**L facility (Applications: **X**E**O**L Spectra, XAFS in **X**E**O**L mode, **X**E**O**L imaging or element selective mapping of heterogeneous materials with submicron resolution.

X-ray Excited Optical Luminescence Spectroscopies, Chapter 15, In Chemical Applications of Synchrotron Radiation (by T.K. Sham)

First XAFS in XEOL Mode

➢ First XAFS in X-ray excited optical luminescence (XEOL) mode by Antonio Bianconi at Stanford Synchrotron Radiation Project 1978

Experimental Setup

XAFS in XEOL mode

XAFS in Transmission mode

XAFS in Fluorescence mode

Ca K-edge XAFS of CaF_2

Antonio Bianconi, D. Jackson, K. Monahan, Intrinsic luminescence excitation spectrum and extended x-ray absorption fine structure above the K edge in CaF_2. *Physical Review B* 17(4), 1978.

10

Rare Earths

Tm – least abundant of the RE (0.5 ppm) → It is more abundant than Cd, Ag, Pt, Au, Se…

Rare Earths Applications

Aplicacations of Phosphors
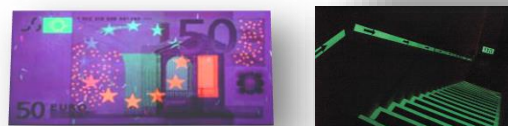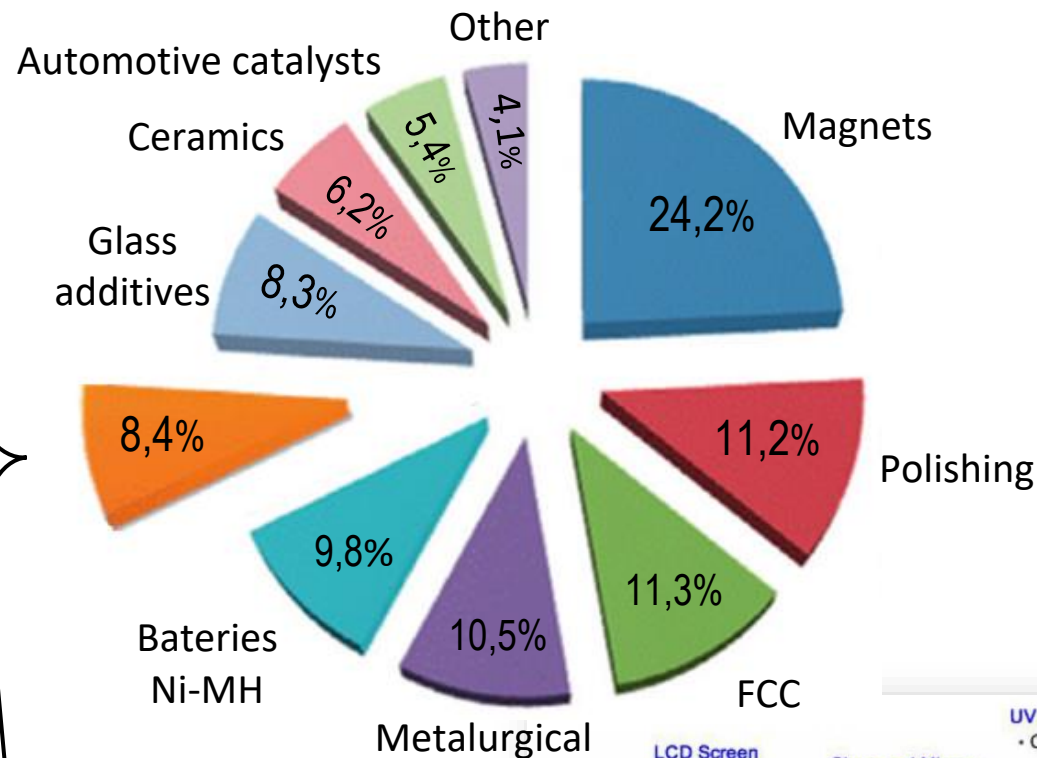
Lighting and Display
97% volume (9500T)

Y 69,6%   Ce 10,9%   La 8,3%
Eu 4,9%   Tb 4,5%   Gd 1,8%

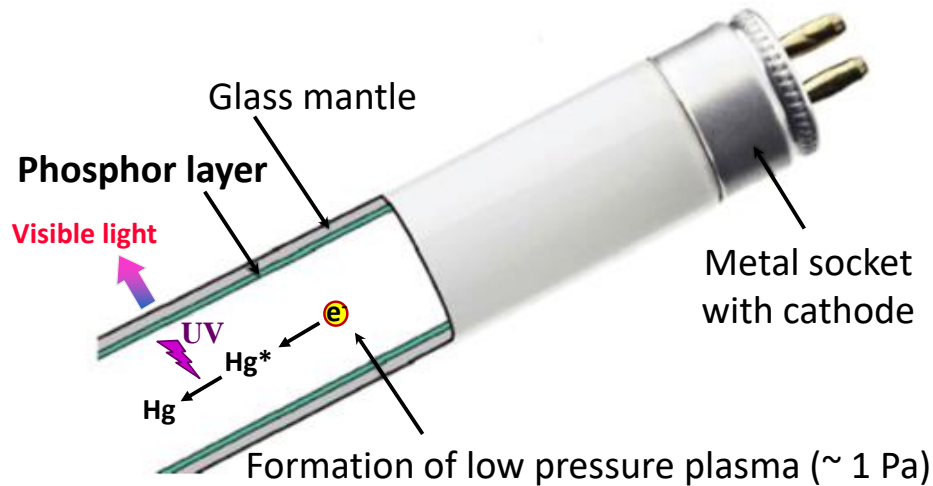**Other**   Laser and Scintillator
Medical

Optical Markers   Persistant luminescent

Pie chart:
- Magnets 24,2%
- Polishing 11,2%
- FCC 11,3%
- Metalurgical 10,5%
- Bateries Ni-MH 9,8%
- Glass additives 8,4%
- Glass additives 8,3%
- Ceramics 6,2%
- Automotive catalysts 5,4%
- Other 4,1%

Toyota Prius
- LCD Screen: Europium, Yttrium, Cerium
- Glass and Mirrors Polishing Powder: Cerium
- UV Cut Glass: Cerium
- Diesel Fuel Additive: Cerium, Lanthanum
- Component Sensors: Yttrium
- Hybrid NiMH Battery: Lanthanum, Cerium
- Hybrid Electric Motor/Generator: Neodymium, Praseodymium, Dysprosium, Terbium
- Headlight Glass: Neodymium
- 25+ Electric Motors: Neodymium magnets
- Catalytic Converter: Cerium, Lanthanum

J. Lucas, P. Lucas, T. Le Mercier, A. Rollat, W. Davenport, in:, Rare Earths, Elsevier, 2015

12

Evolution of Lighting Technology

How fluorescent lamp work?

Glass mantle

Phosphor layer

Visible light

UV

Hg*

Hg

e

Metal socket with cathode

Formation of low pressure plasma (~ 1 Pa)

Phosphor		Emission
Y_2O_3:Eu^{3+}	(YOE)	Red
$(Ce^{3+},Tb^{3+})MgAl_{11}O_{19}$	(CAT)	Green
$BaMgAl_{10}O_{17}$:Eu^{2+}	(BAM)	Blue

White LED lamp

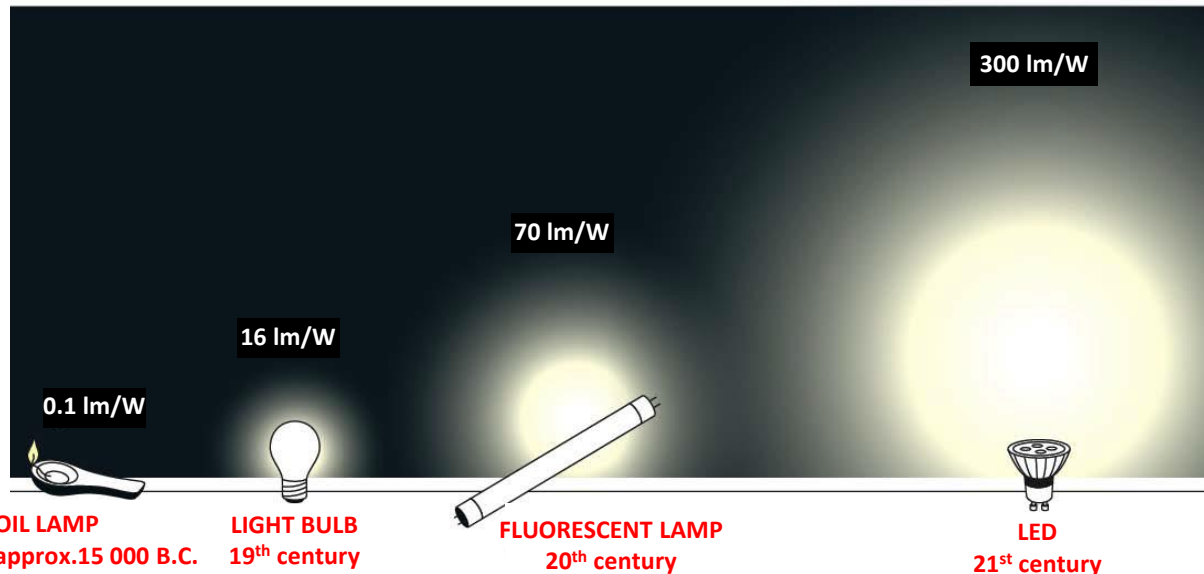Phosphor

Light extracting dome

Blue LED chip
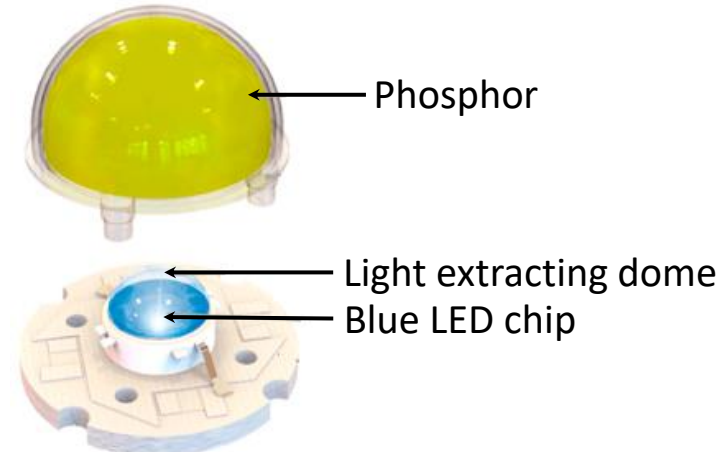
Phosphor: $Y_3Al_5O_{12}$:Ce^{3+} (YAG:Ce)
Emission color: Yellow

Energy Savings Impact

- ➢ **~ 40 % Electricity Savings (261 TWh)** in USA in 2030 due to LEDs
- ➢ **Eliminates** the need for **30+** 1000 MW **Power Plants** by 2030
- ➢ **Avoids Generating ~ 185 million tons of CO_2**

(SHUJI NAKAMURA Nobel Prize 2014)

300 lm/W

70 lm/W

16 lm/W

0.1 lm/W

OIL LAMP
approx.15 000 B.C.

LIGHT BULB
19th century

FLUORESCENT LAMP
20th century

LED
21st century

13

Global Rare Earths Mines Reserves

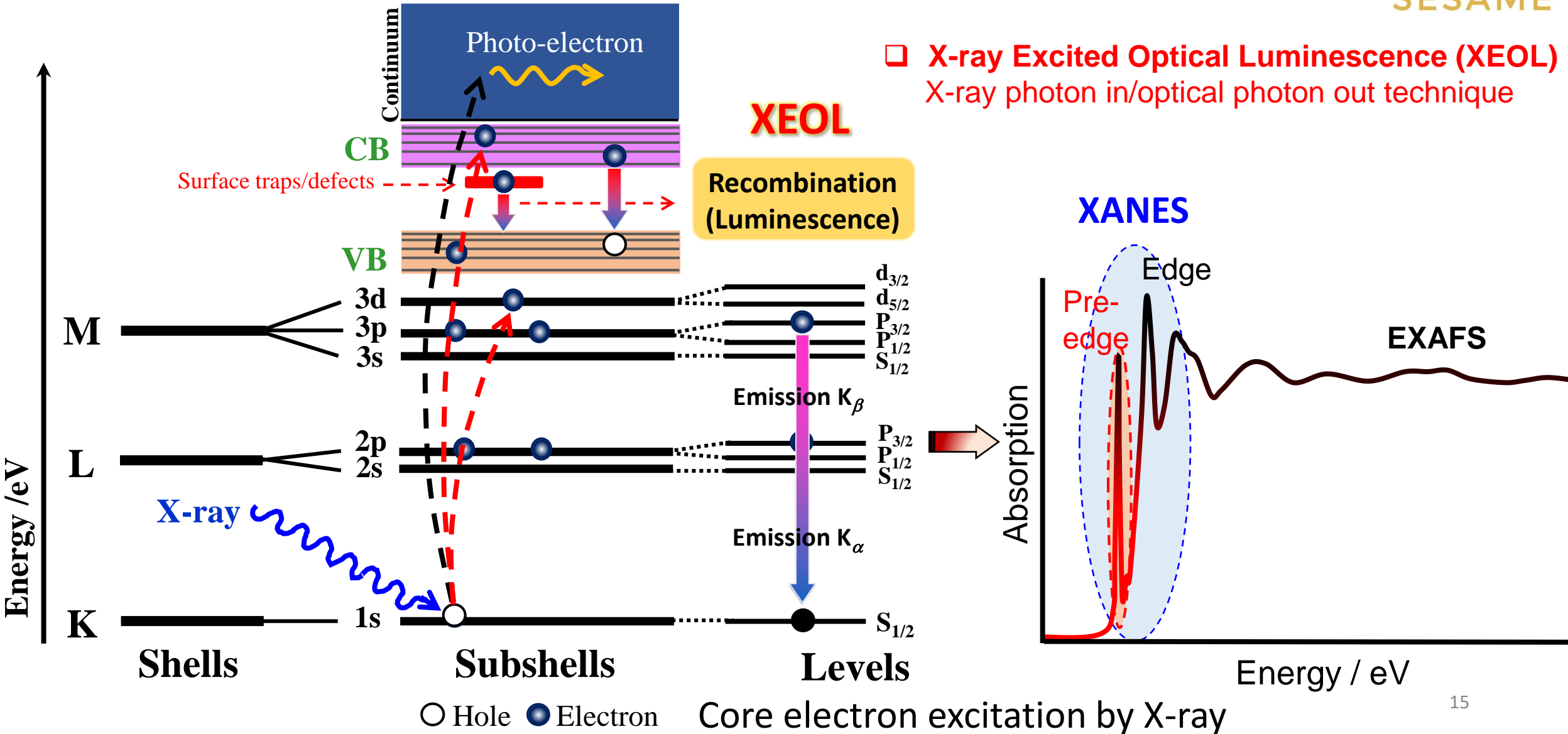- World total reserves (rounded about): 120,000,000 tons (120 million metric tons)
- China: 44,000,000 tons or 44 million metric tons (36%)

Global Rare Earths Mines Reserves 2020

Legend:
- United States
- Australia
- Brazil
- Canada
- China
- Greenland
- India
- Malawi
- Malaysia
- Russia
- South Africa
- Vietnam

X-ray Absorption and Electron Excitation Mechanism

Core electron excitation by X-ray

Persistent Luminescence Mechanism

- For full understanding of luminescence in a **solid state materials** (phsophors), the energy level structures need to be studied for:
  - The host.
  - The luminescent ions.
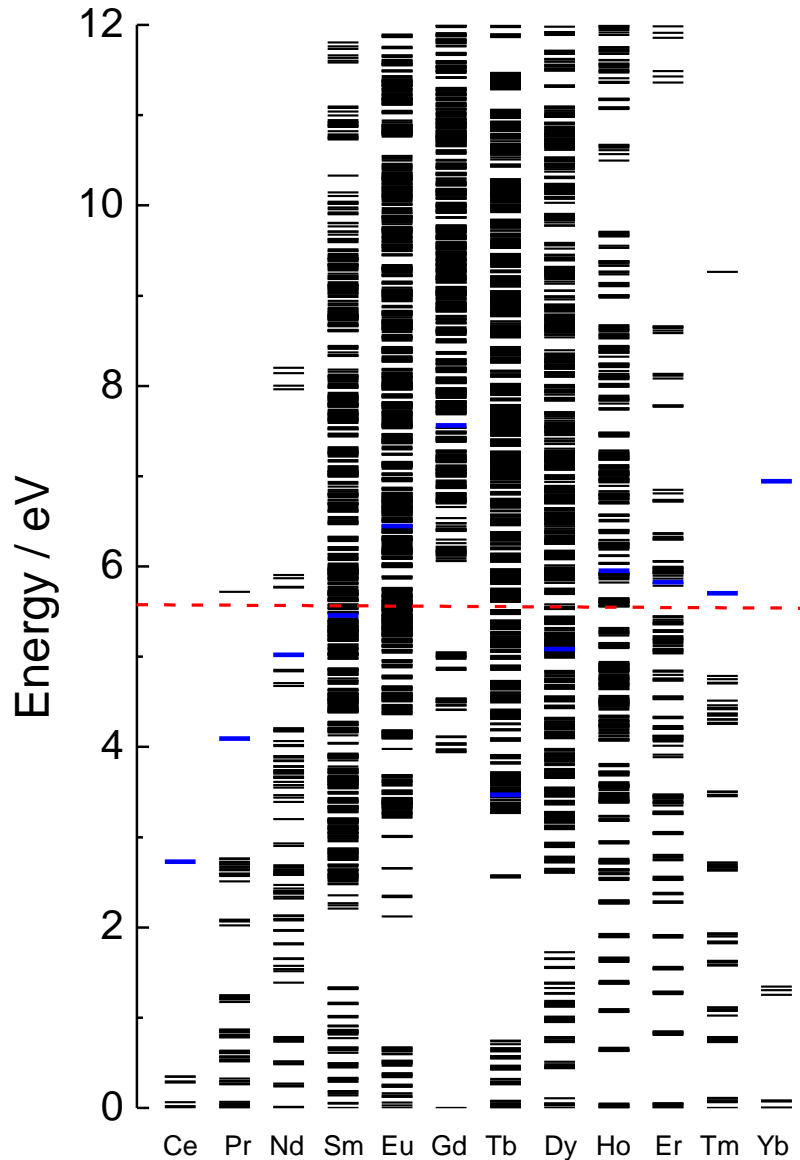   (Emission center)
  - Structural defects.
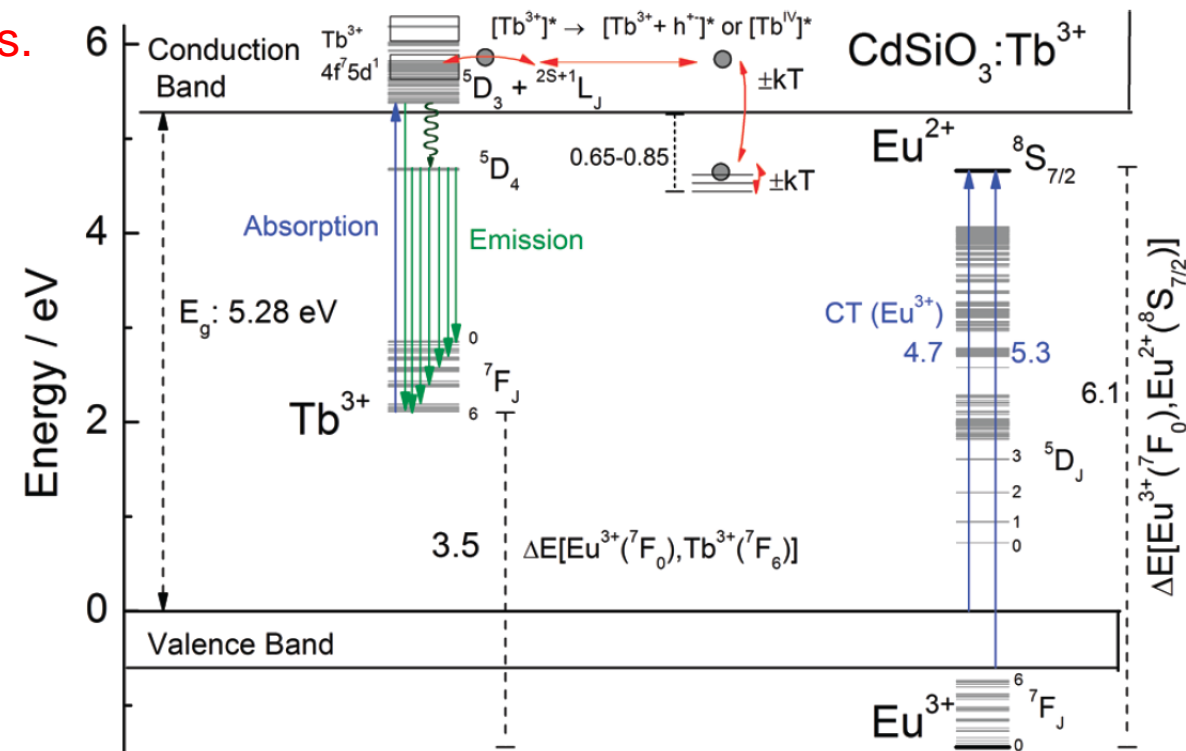
Persistent luminescence mechanism of Tb^{3+} in $CdSiO_3$.

- Goal: models for predicting the luminescence properties of materials.
  - Combining experimental (optical) and theoretical methods.
  - Probing metal ions (emission center) by X-ray absorption.

Lanthanides (Ln^{3+}) Energy Levels: 4-10 eV Energy Range

Energy levels structure of trivalent lanthanides ions.

Energy range 4-10 eV needed for:

- Host band gap energy (E$_g$) determination.
  - Essential for *e.g.* persistent luminescence materials.
    - Example: 7.1 eV for Sr$_2$MgSi$_2$O$_7$:Eu^{2+},Dy^{3+}.
- Study of dopant energy levels structure in the **VUV** range (> 6 eV).
  - High 4f levels and 5d levels.
    - Quantum cutting materials (*e.g.* KMgF$_3$:Pr^{3+}).
- Higher photon flux needed than with lab equipment.
  - High sensitivity.
- Measuring fast kinetics (ns) and time resolution.
- Synchrotron light sources offer a better temporal stability in terms of the duration, amplitude and repetition rate of the pulses than the most sophisticated pulsed lasers.

High energy limit of laboratory set-ups: 5.6 eV.
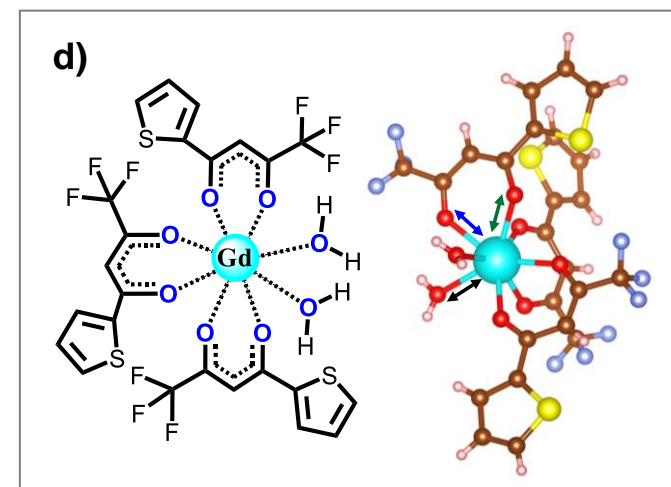
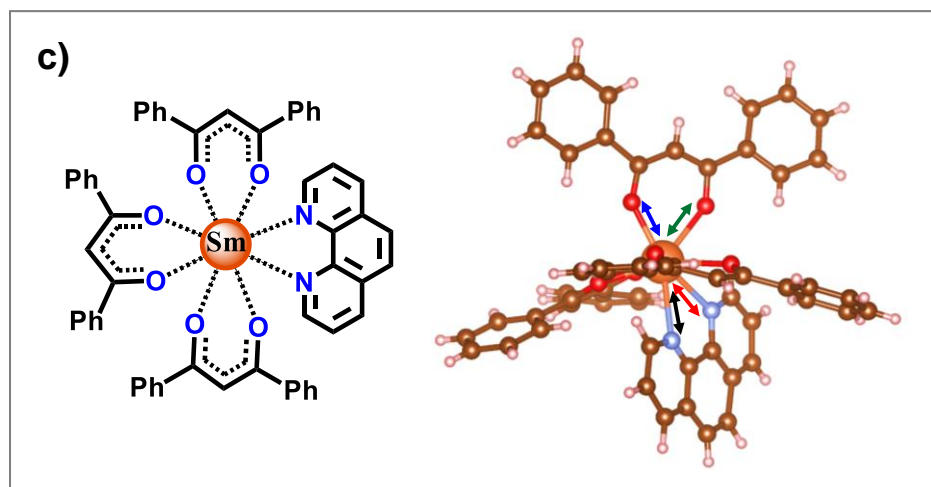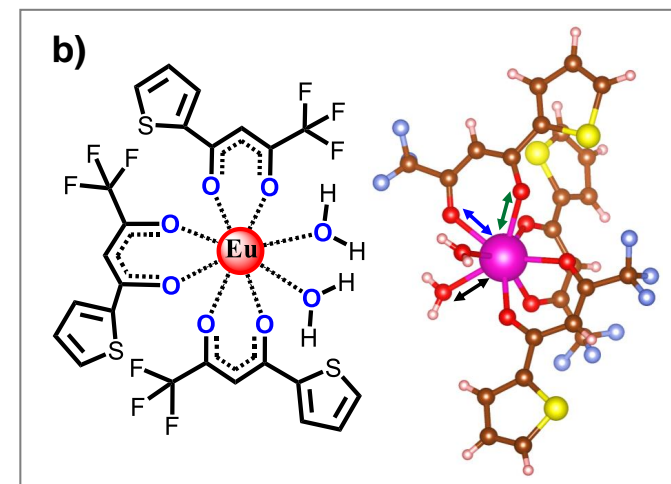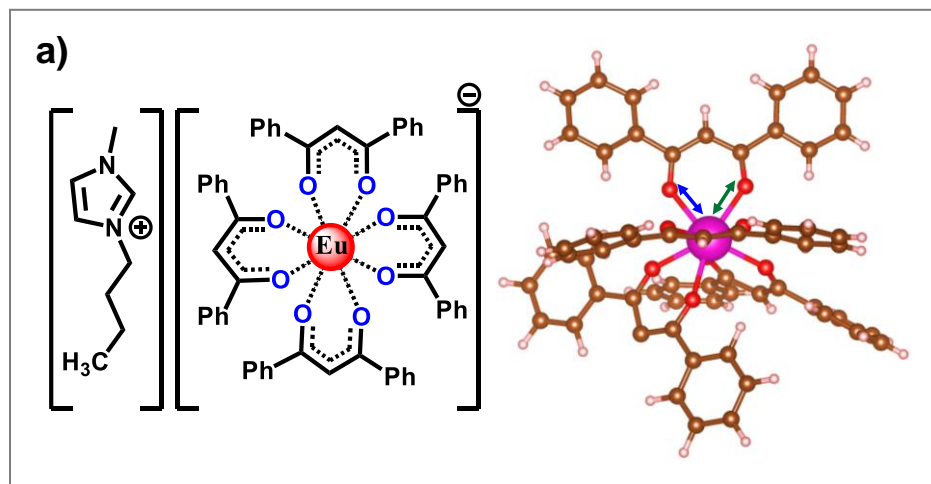# RE³⁺ β-Diketonates

- **Sm³⁺, Gd³⁺ and Eu³⁺ β-diketonates**
- Fabrication of single-layer organic light-emitting memory devices
- Modern optical quantum memories
- Organic light emitting diodes (OLEDs).
- Gd (III) complex, an excellent T_1 contrast agents in MRI imaging

Samples provided by Prof. Hermi F. Brito, Laboratory of *f*-block elements, Institute of Chemistry University of Sao Paulo Brazil.
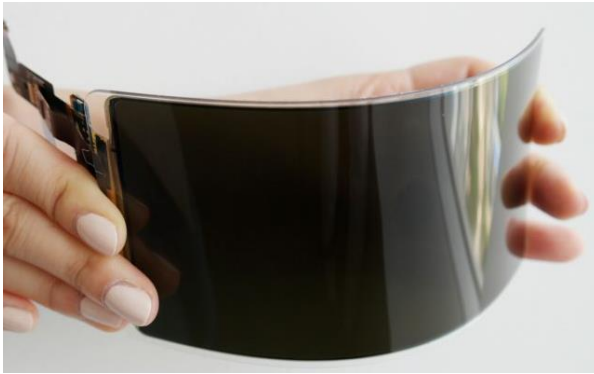
Phosphors in Display Technologies

Unbreakable OLED Display

Rare Earth Phosphors in TV Display

OLED Display

cathode

electron beam

accelerating anodes

focus anode

deflection coils

phosphorescent screen
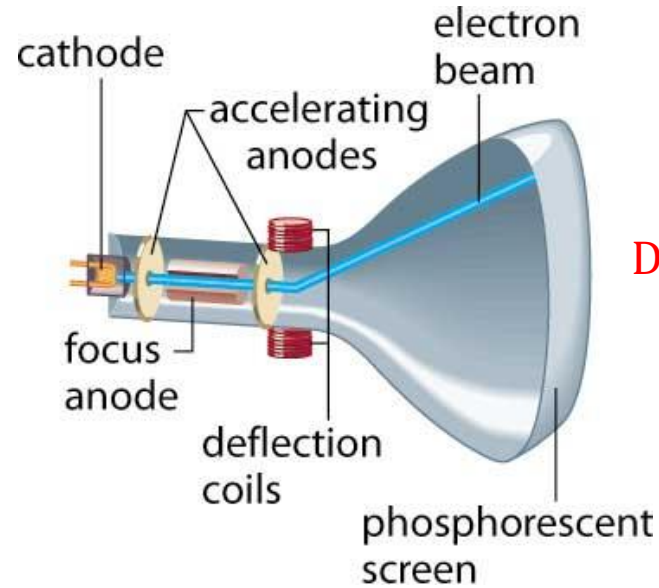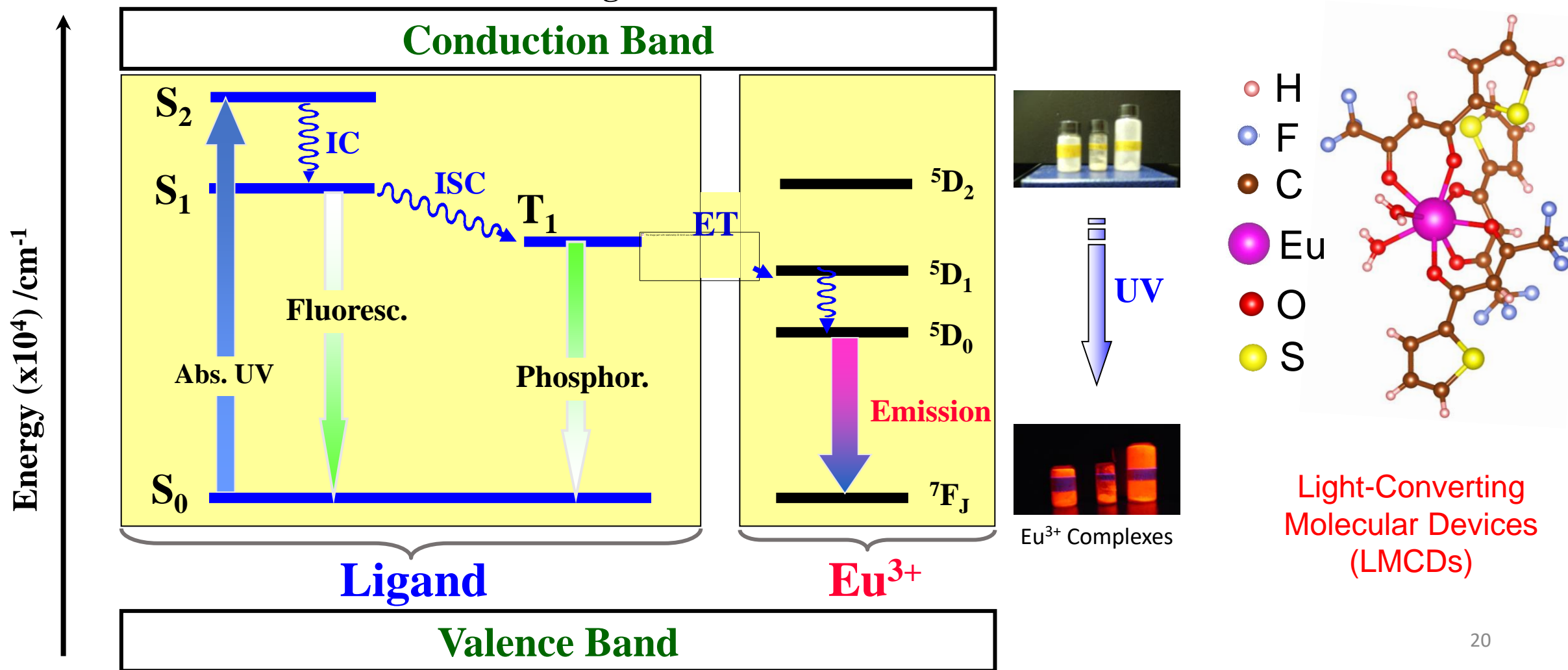
(Phosphors)

Development

LG OLED TV AI ThinQ

Samsung

Intramolecular Energy Transfer

Efficient: Absorption (L) → **Transfer of energy Ligand-Eu^{3+}** **→ Emission (Eu)**

Eu^{3+} Complexes

Light-Converting Molecular Devices (LMCDs)

Eu³⁺ Complex: X-ray Scintillator (Optical Photons)

6980 eV

Rising edge
$^2p_{3/2} \rightarrow 5d$ (Eu³⁺)

7100 eV

7300 eV

Eu L₃-edge (6977 eV)

6950 eV

X-ray Scintillator
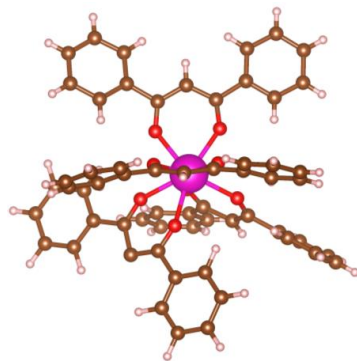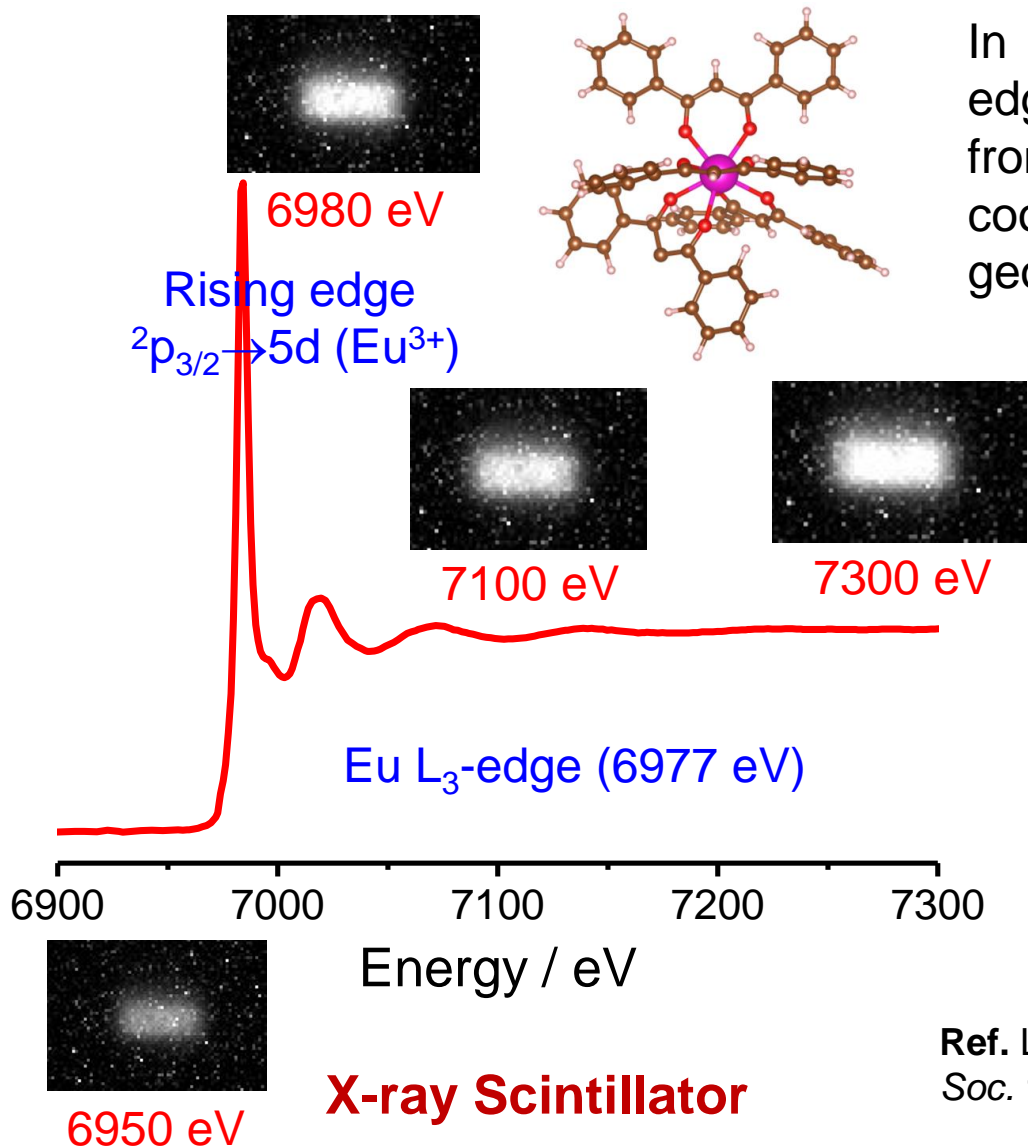
In d-transition metals, rising edge has strong contribution from 1s→4p, dependent on coordination number and geometry (ligand field effect).

Ligand field effect
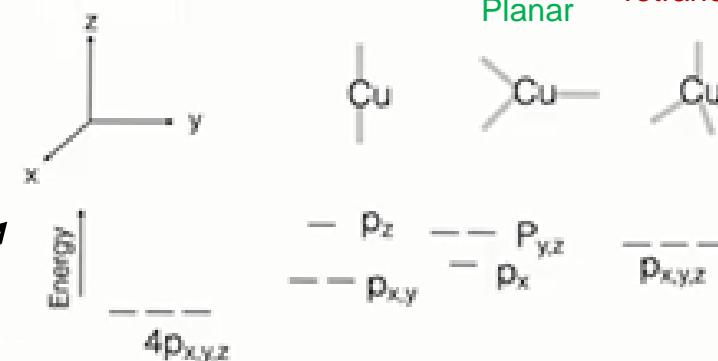
Conf.	Ligand field (cm⁻¹)
3dᴺ	15000
4dᴺ	20000
5dᴺ	25000
4fᴺ	**300**
5fᴺ	**2000**

Ref. Lung-Shan Kau et al. *J. Am. Chem. Soc.* 1987, *109,* 6433-6442.

Cu K-edge

2-Coord Cu(I)
3-Coord Cu(I)
4-Coord Cu(I)
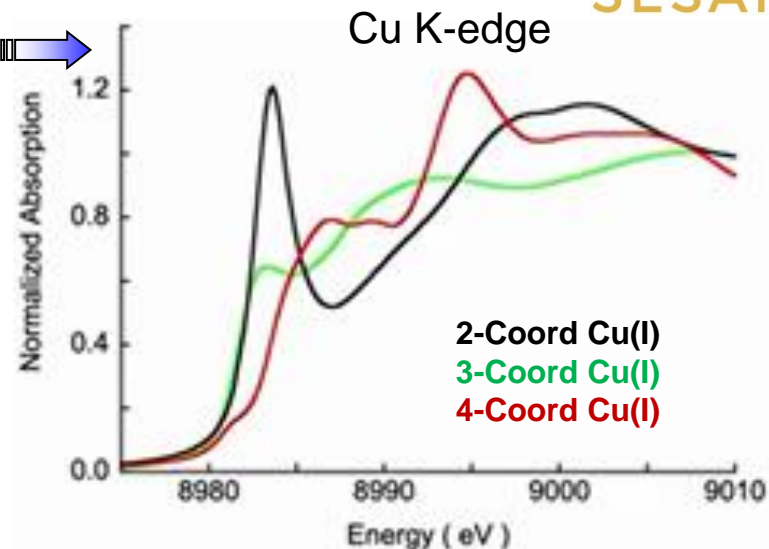
Coordination No: **2**   **3**   **4**
                      Linear   Trigonal   Tetrahedral
                                 Planar

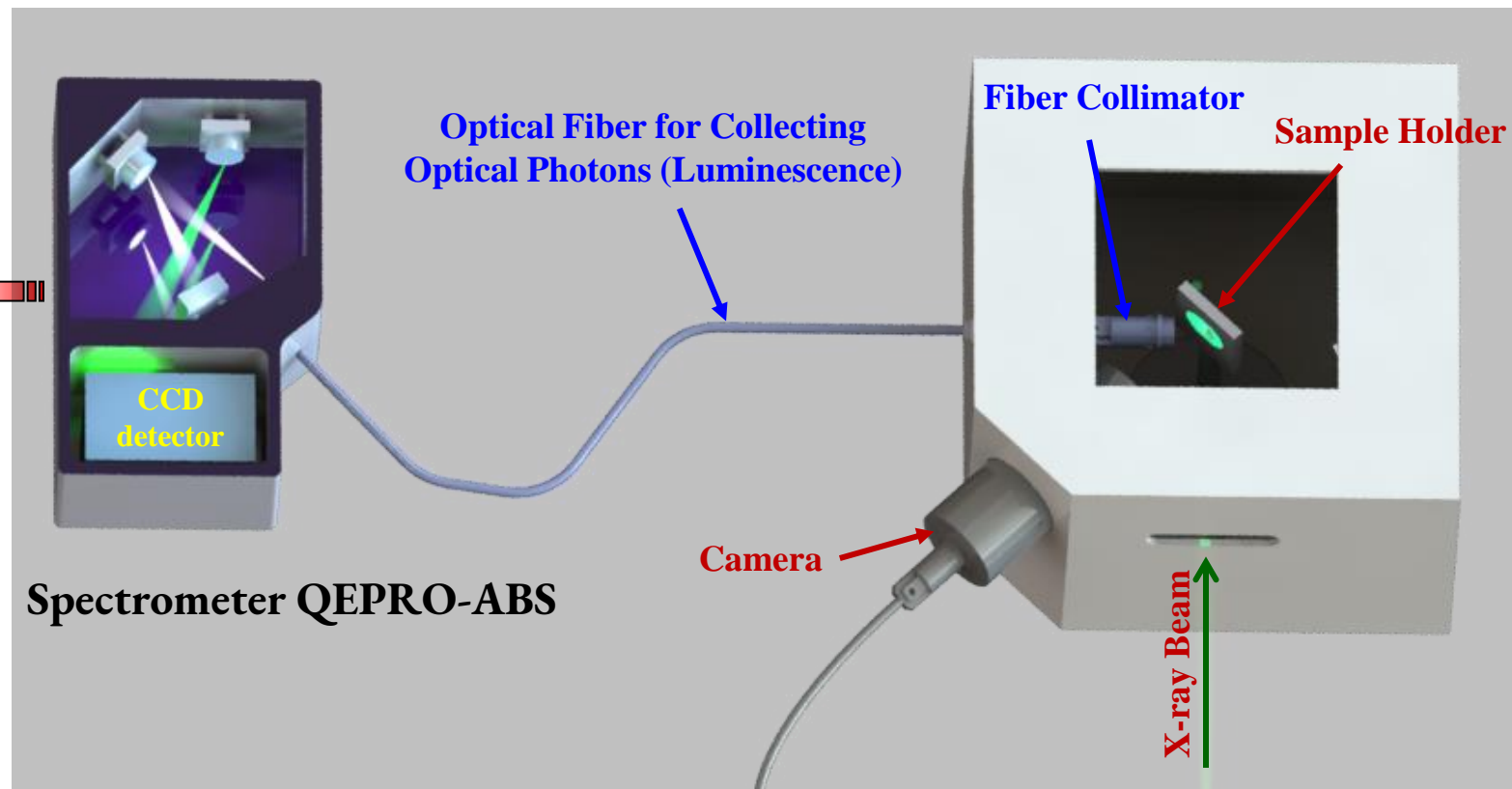Ligand field splitting of copper 4p orbitals as a function of site geometry.

21

XEOL Setup
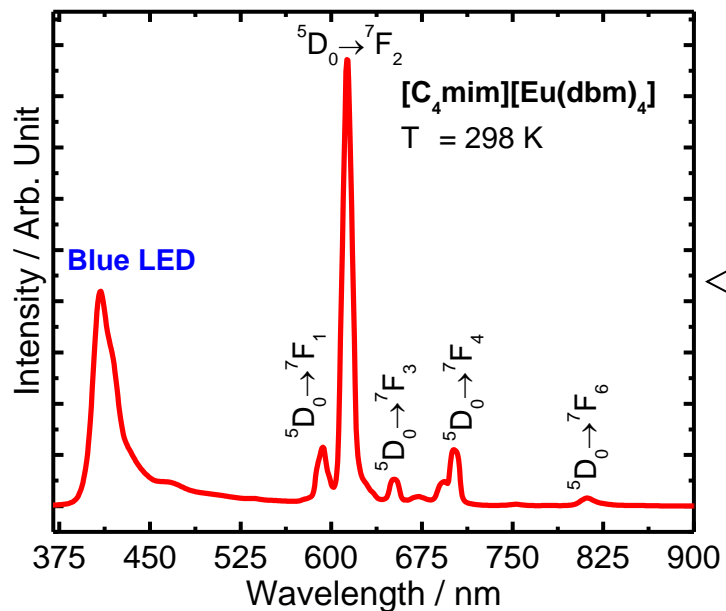
Emission Spectrum of Eu^{3+} complex
Measured with QEPRO-ABS (Exc. LEDs)

Spectrometer QEPRO-ABS

Optical Fiber for Collecting Optical Photons (Luminescence)

Fiber Collimator

Sample Holder

CCD detector

Camera

X-ray Beam

Abid Ur Rehman Mechanical Engineer

❑ X-ray Excited Optical Luminescence (XEOL) Spectroscopy

❑ Luminescence (λ: 200 - 920nm)

❑ XANES in XEOL mode

Project Grant from IAEA

IAEA
International Atomic Energy Agency

Machine Learning: XANES Simulation

❑ The modern data science-based machine learning is very attractive among the XAFS community to explore the X-ray absorption spectroscopy data of metals across the science.

❑ The quantitative structural determination from the XANES is largely demanded in catalysis, energy storage materials and metal complexes (XANES simulation by machine learning PyFitIt package).
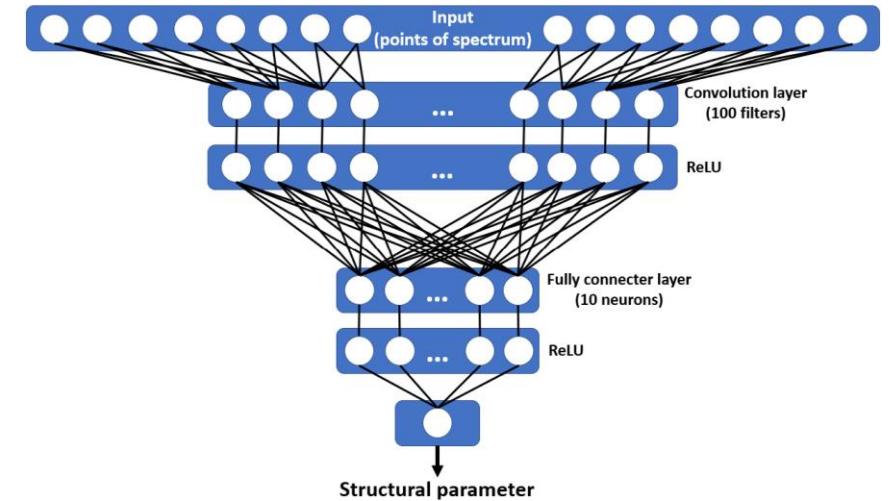
Machine Learning: PyFitit Inverse method

00 Fitting Smooth ⟹ Input data: Crystal structure (XYZ), experimental XANES and define FDMNES convolution parameters

10 Create a project ⟹ Photoabsorber selection, define geometry deformation within allowed limit (degrees of freedom) and FDMNES parameters for *ab-initio* XANES calculation

20 Calculate XANES for a set of geometries ⟹ Train a model on input data (100 samples), parallel calculations of theoretical XANES, needs multicores clusters [SESAME server 24 cores (CPUs)]

30 Inverse approach ⟹ Calculated spectrum from the step 20 and employ Euclidean (L_2) norm, integral of the squared difference between the theoretical & experimental XANES spectrum

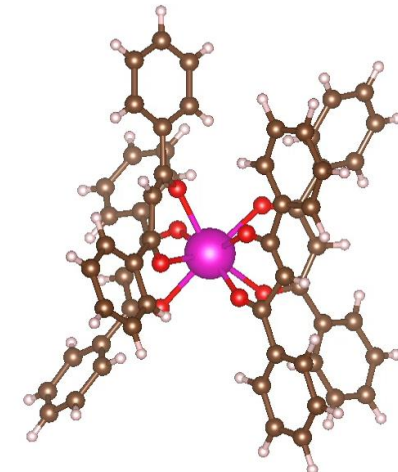**50 Fitting XANES by sliders** ⟹ Fit by sliders within allowed limit of deformation

A. Martini, S.A. Guda, A.A. Guda et al. PyFitit: The software for quantitative analysis of XANES spectra using machine-learning algorithm. *Computer Physics Communications* 250 (2020) 107064.

PyFitIt Package: Machine Learning

- **PyFitIt**, a machine learning (*i.e.*, implementing neural network) based XANES simulation technique, exploiting the PyFitIt Python library with Python codes in Jupyter notebooks.

- Direct (prediction of a XANES spectrum for a given set of structural parameters) and indirect (prediction of a set of structural parameters for a given XANES spectrum) approaches for the XANES prediction and the corresponding 3D structural refinement.

- FDMNES or FEFF or ADF codes to calculate the *ab initio* theoretical XANES.

- Euclidean (L_2) norm, integral of the squared difference between the theoretical & experimental XANES spectrum (like the Levenberg-Marquardt algorithm in Artemis Demeter, GNXAS etc., for EXAFS fit) .

- These methods developed for the Big Data or multidimensional data tasks and appropriate to run on the multicore's clusters (local computer very long time).

- 3D structure (XYZ) as input data and sampling points P_1, P_2, . . . , P_N for the training set can be selected by grid and improved Latin hypercube sampling (IHS).

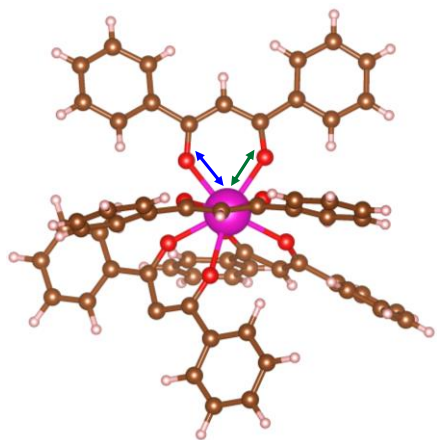
Neural network implemented in PyFitIt

3D Structure

A. Martini, S.A. Guda, A.A. Guda et al. PyFitit: The software for quantitative analysis of XANES spectra using machine-learning algorithm. *Computer Physics Communications* 250 (2020) 107064.

PyFitIt XANES Simulation: Eu³⁺ *Tetrakis* Complex

- **PyFitIt, indirect** approach to simulate the experimental XANES spectrum of Eu³⁺ tetrakis complex .

- **FDMNES** code to calculate the *ab initio* theoretical XANES.

- **3D structure (XYZ)** with **experimental XANES** were used as an input data.

Project: Accessible Modern Data Science based Data Analysis Platform for Diverse Users of X-Ray Absorption and Fluorescence Spectroscopy

Grant Award: RSC UK

ROYAL SOCIETY OF CHEMISTRY

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PyFitIt XANES Simulation: Structure Refinement

> **Eu³⁺ tetrakis β-diketonate complex [Eu(dbm)₄(C₄mim)]**
> dbm: dibenzoylmethane and C₄mim: 1-butyl-3-methylimidazolium bromide
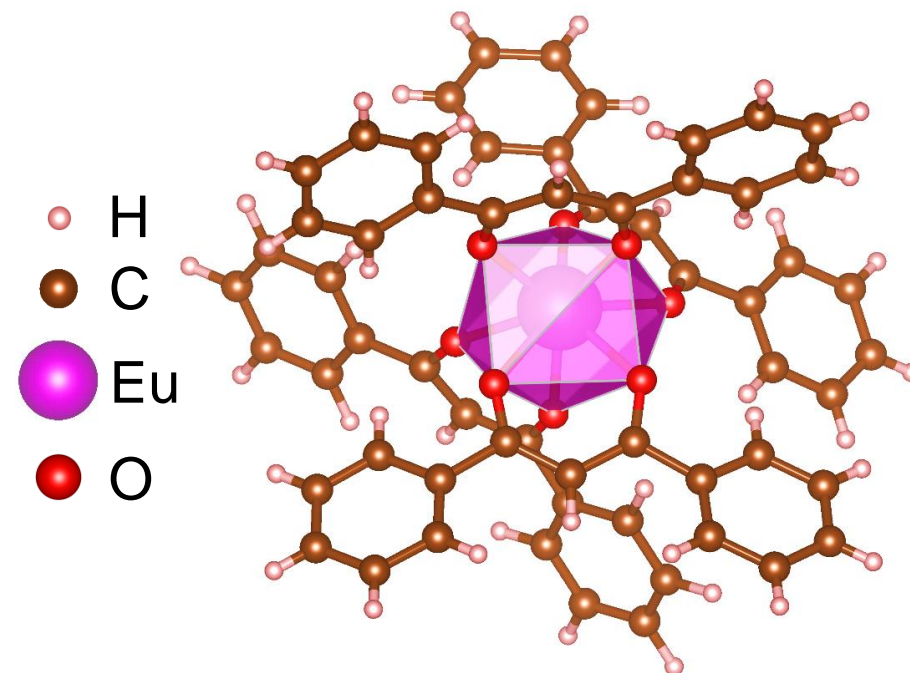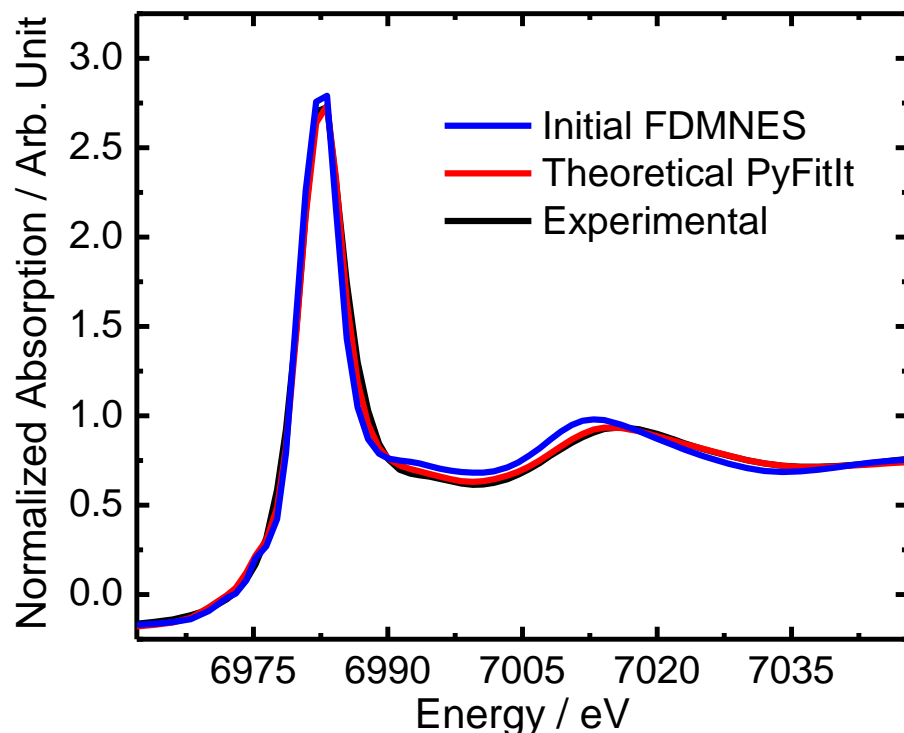
Experimental and theoretical XANES calculated at the Eu L_3-edge using the FDMNES code directly and pyFitIt inverse method (left), and corresponding generated distorted square antiprismatic structure (right) for the Eu³⁺ tetrakis complex [Eu(dbm)₄(C₄mim)].

Applying Wavelet Transform - EXAFS Equation

EXAFS Oscillation:
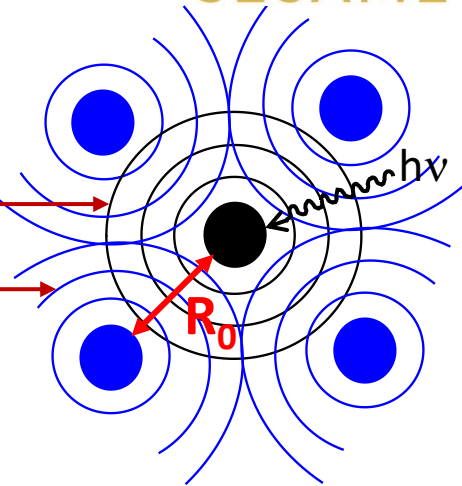
$$\chi(k) = \sum_i \chi_i(k)$$

k is the photoelectron wavenumber

Each path can be written as:

$$\chi_i(k) = \left(\frac{(N_i S_0^2) F_i(k)}{k R_i^2} \sin(2kR_i + \varphi_i(k)) \exp\left(-2\sigma_i^2 k^2\right) \exp\left(-\frac{2R_i}{\lambda(k)}\right) \right)$$
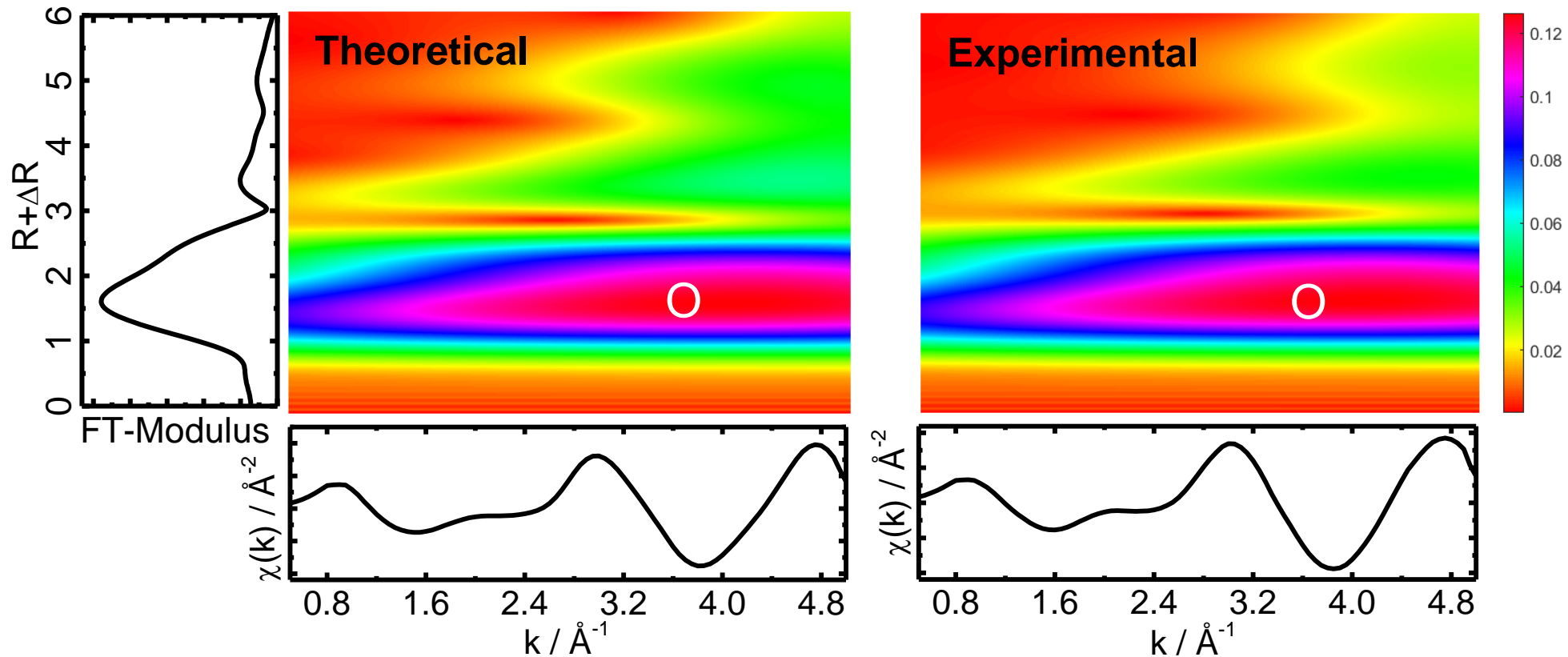
Photo-electron wave

Back-scattered wave

R_0

$h\nu$

- CCWT modulus visualizes the coordination shells of the neighboring atoms around the photoabsorber in form of RGB colored maps in the 2D and 3D CCWT images, simultaneously analyzing the input EXAFS data into respective two-dimensional k and R spaces.

- the lower atomic number atoms, such as O, more effectively backscatterers at lower k values, and high atomic numbers ones at higher k values, owning to the contribution of backscattering amplitude functions (F_i (k)) of the neighboring atoms, associated with the number of repulsive electrons in their electronic clouds.

Muñoz, M.; Argoul, P.; Farges, F. Continuous Cauchy Wavelet Transform Analyses of EXAFS Spectra: A Qualitative Approach. *Am. Mineral*. 2003, 88 (4), 694–700.

# Applying Wavelet Transform

Continuous Cauchy wavelet transform analyses of theoretical (left) and experimental (right) XANES, showing the localization of O backscatterer as a pinkish red color map in similar pattern two-dimensional CCWT images.

XANES Simulation: Eu³⁺ *Tris β*-Diketonate Complex

> **Eu³⁺ tris *β*-diketonate complex [Eu(tta)₃(H₂O)₂]**
> **tta: 3-thenoyltrifluoroacetonate**

> **Typical crystal structure**

- Experimental and theoretical XANES calculated at the Eu L_3-edge using the PyFitIt inverse method (a)

- Corresponding square antiprismatic 3D structure for the [Eu(tta)₃(H₂O)₂] complex (b) .

- Continuous Cauchy wavelet transform analyses of theoretical (c) and experimental (d) XANES, showing the localization of O backscatterer as a dark-red color map in similar pattern two-dimensional CCWT images.
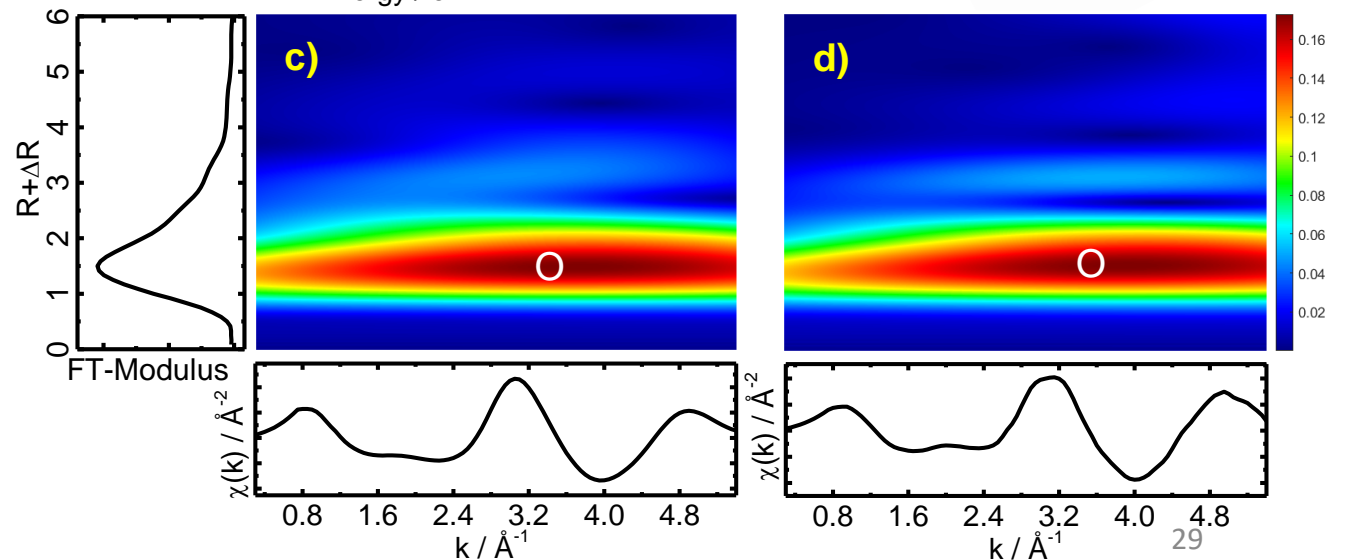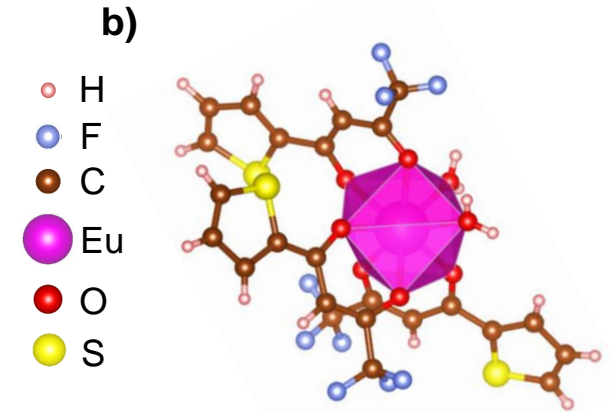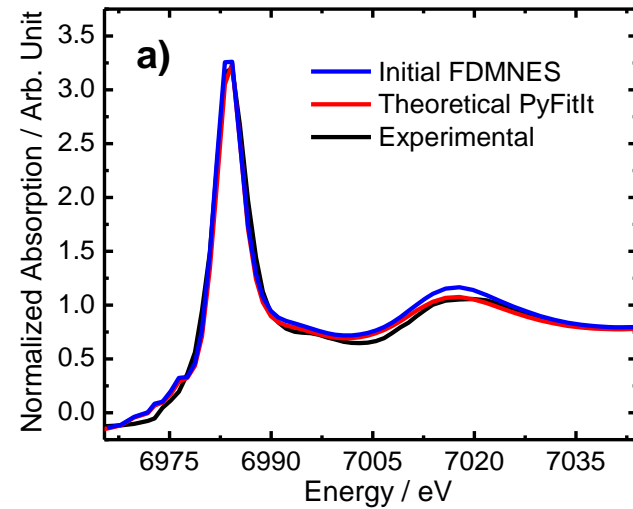
XANES Simulation: Gd^{3+}/Sm^{3+} β-Diketonates
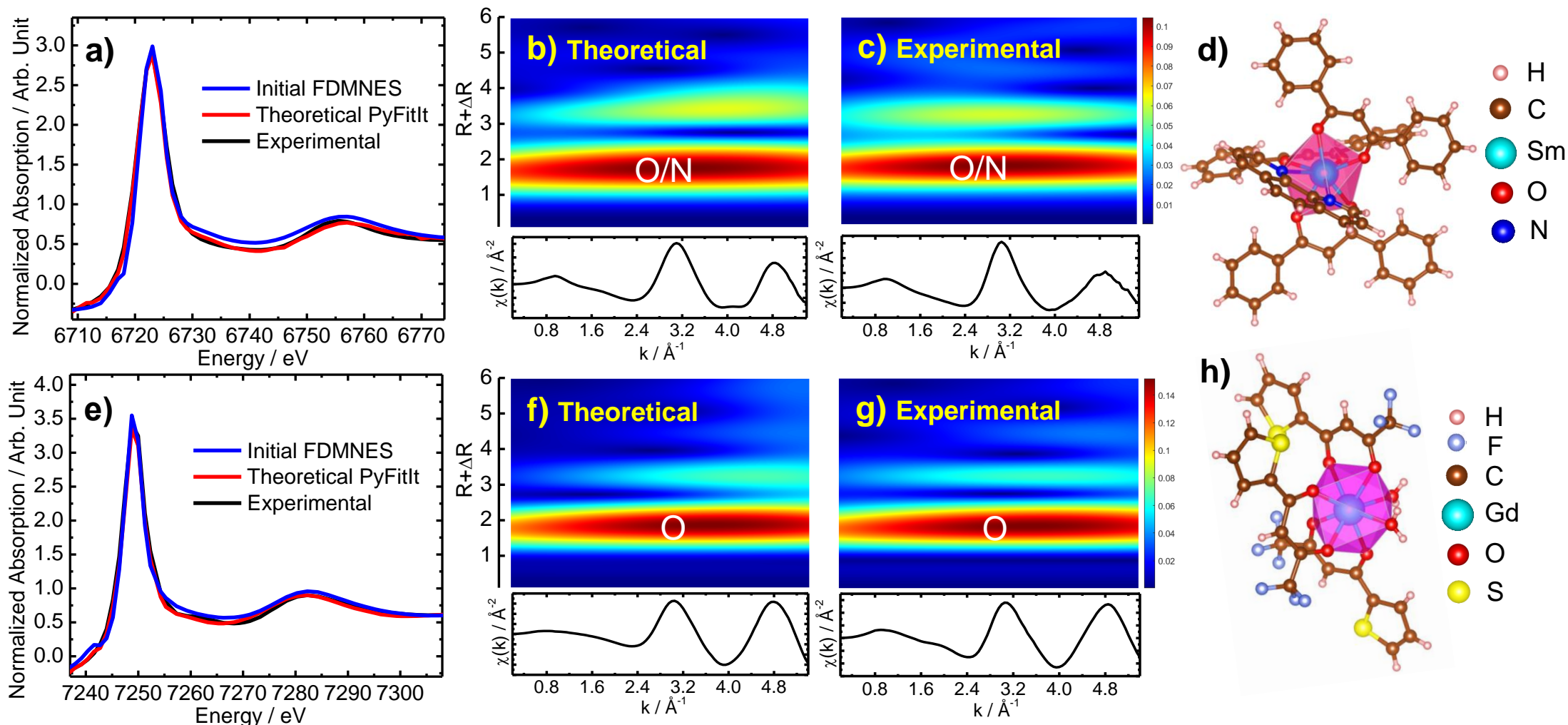
Sm^{3+} β-diketonate: [Sm(dbm)$_3$(phen)]
dbm: dibenzoylmethane, phen: phenanthroline

Gd^{3+} β-diketonate: [Gd(tta)$_3$(H$_2$O)$_2$]
tta: 3-thenoyltrifluoroacetonate

EXAFS Fit

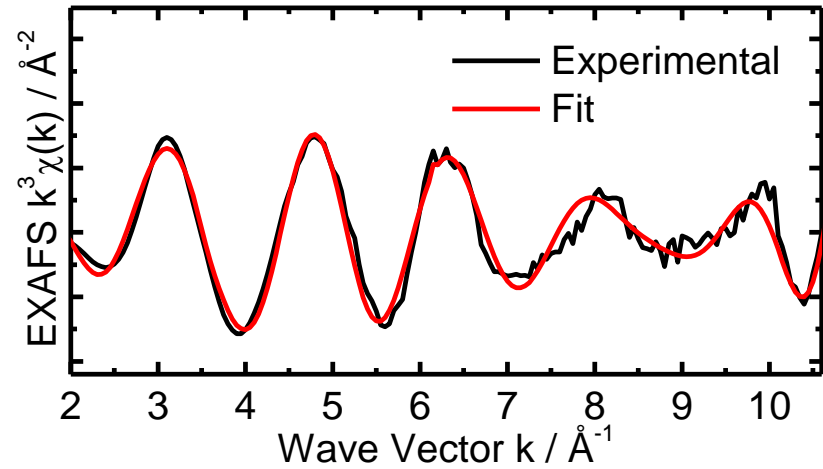- **EXAFS Fit: Artemis from Demeter**

- $[C_4mim][Eu(dbm)_4]$ complex (left)

- $[Eu(tta)_3(H_2O)_2]$ complex (right)

- The XYZ 3D structures obtained from the PyFitIt XANES simulation were used in EXAFS fit

- feff input files were generated from the corresponding 3D structures in MOLDRAW software
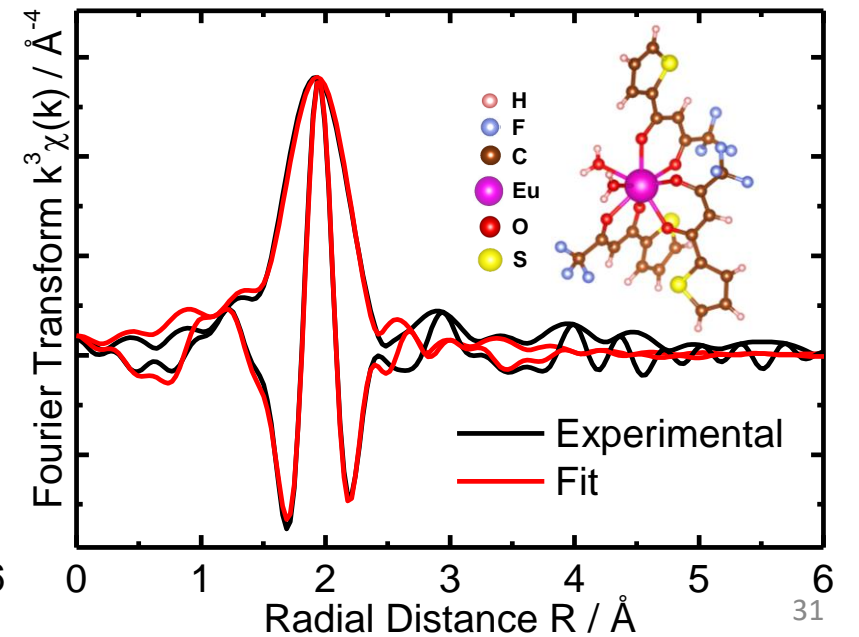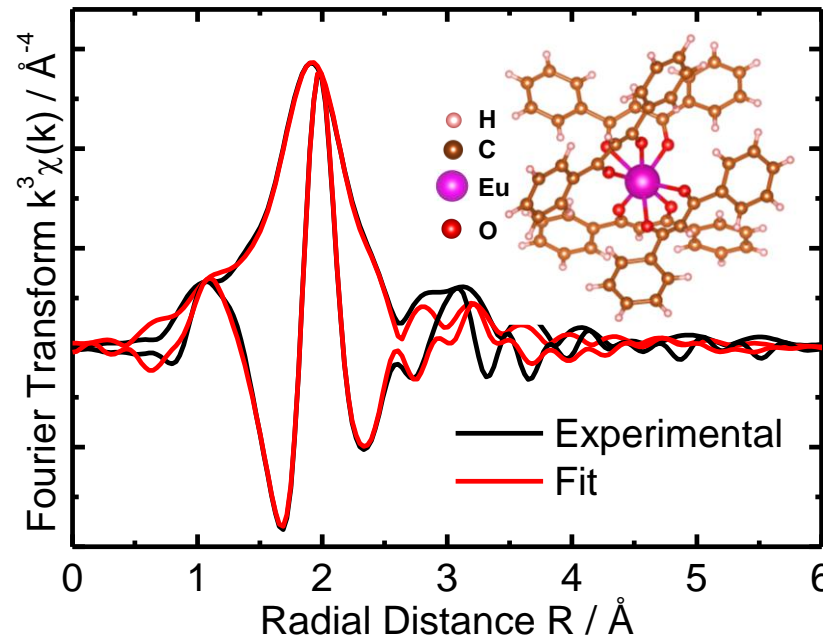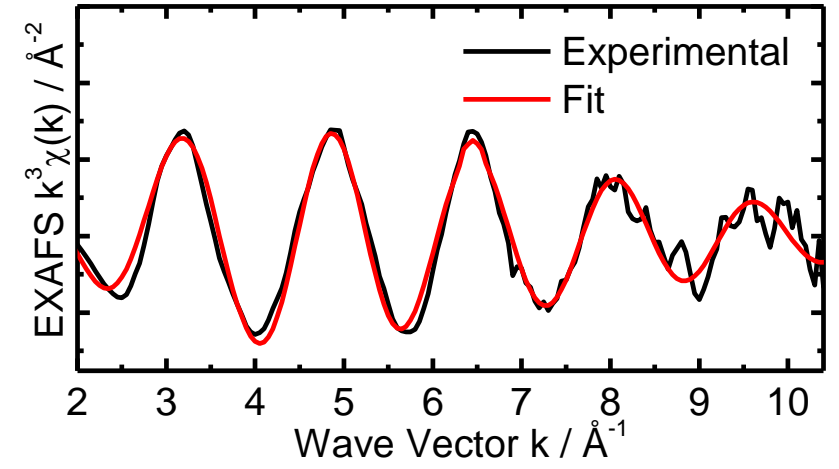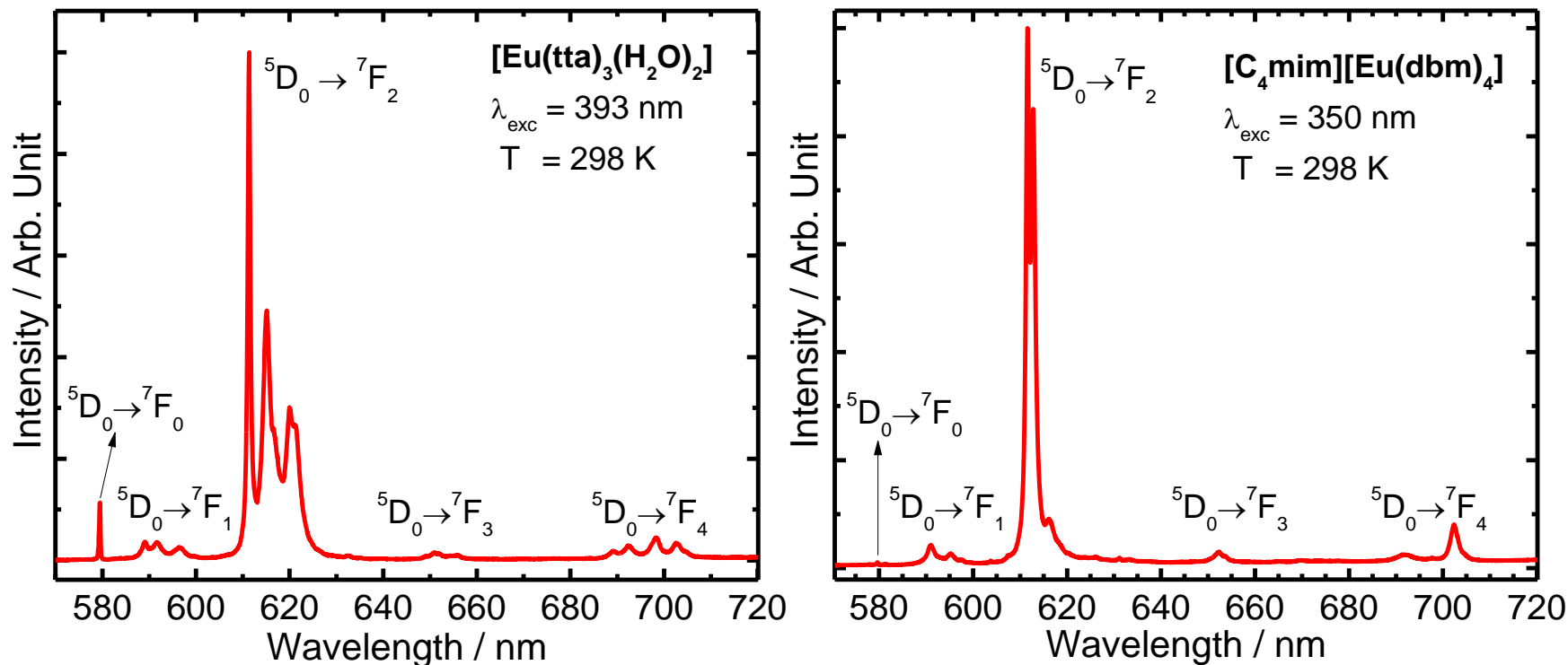
EXAFS Fit

➤ **Artemis** employs FEFF8-lite code to calculate the values of the $F_i(k)$ (effective scattering amplitude), $\phi_i(k)$ (effective scattering phase shift) and λ (mean free path of the photoelectron).

➤ **IFEFFIT** in **Artemis** use Levenberg-Marquardt (algorithm) method of nonlinear least-squares minimization to minimize the standard χ^2 fitting metric:

$$\chi^2 = \frac{N_{idp}}{\varepsilon N_{data}} \sum_{i=min}^{max} \left[Re\left(\chi_d(r_i) - \chi_t(r_i) \right)^2 + Im\left(\chi_d(r_i) - \chi_t(r_i) \right)^2 \right]$$

EXAFS fitting parameters: N_{degen}: degeneracy of the path, R: mean coordination shell radii, σ^2: mean square relative displacements (MSRDs) or Debye–Waller factor, S_0^2: passive electron reduction factor E_0: photoelectron energy and R_{factor}: goodness of the fit for the $[C_4mim][Eu(dbm)_4]$ and $[Eu(tta)_3(H_2O)_2]$ complexes.

Complex	Bond	N_{degen}	R(Å)	σ^2(Å^2)	S_0^2	E_0 (eV)	R_{factor}
	Eu-O$_1$	2	2.287±0.009	0.0105±0.0020	0.89	9.8	0.0074
$[C_4mim][Eu(dbm)_4]$	Eu-O$_2$	3	2.434±0.007	0.0122±0.0021	0.89	9.8	0.0074
	Eu-O$_3$	3	2.540±0.008	0.0091±0.0021	0.89	9.8	0.0074
	Eu-O$_1$	4	2.357±0.007	0.0058±0.0009	1.01	10	0.0040
$[Eu(tta)_3(H_2O)_2]$	Eu-O$_2$	2	2.436±0.007	0.0058±0.0009	1.01	10	0.0040
	Eu-O$_3$	2	2.492±0.007	0.0077±0.0055	1.01	10	0.0040

Khan, L. U. et al. A Strategy to Probe the Local Atomic Structure of Luminescent Rare Earth Complexes by XANES Simulation Using Machine Learning Based PyFitIt Approach. *Inorganic Chemistry (ACS),* 2023 (Accepted - In Press).

Validating PyFitIt XANES Simulation *via* Optical Properties

Emission spectra of the [Eu(tta)$_3$(H$_2$O)$_2$] (left) and [C$_4$mim][Eu(tta)$_4$] (right) complexes recorded in solid state at 298 K temperature under excitations corresponded to the S$_0$→S$_n$ transitions of the corresponding organic ligands.

4f-4f Intensity Parameters (Ω_λ)

Refractive index

$$A_{0 \to J'}(\text{exp.}) = \frac{4e^2 \omega_{0 \to J'}}{3\hbar c^3 (2J+1)} \left[\frac{n(n^2+2)^2}{9} \right] \left\langle {}^5D_0 \left\| U^{(\lambda)} \right\| {}^7F_\lambda \right\rangle^2 \Omega_\lambda(\text{exp.})$$

Lorentz local field correction (χ)

Reduced element matrix

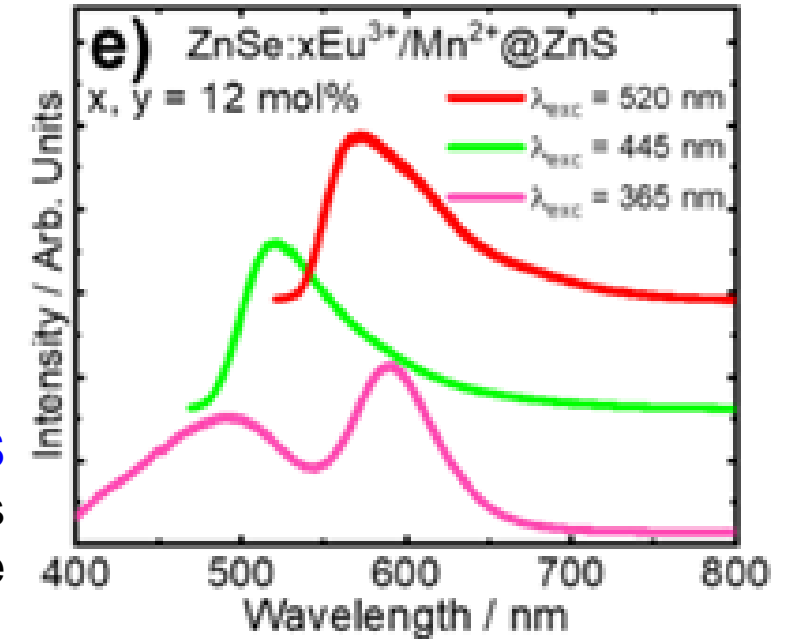Experimental and theoretical intensity parameters (Ω_λ, λ = 2 and 4) for the $[Eu(tta)_3(H_2O)_2]$ and $[C_4mim][Eu(tta)_4]$ complexes.

The spontaneous emission coefficients ($A_{0 \to J}$) are given by

$$A_{0 \to J} = \left(\frac{S_{0 \to J}}{S_{0 \to 1}} \right) A_{0 \to 1}$$

Complex	Ω_2		Ω_4	
	Experimental	PyFitIt	Experimental	PyFitIt
$[C_4mim][Eu(dbm)_4]$	29 ± 1	28.99 ± 0.08	5.8 ± 0.7	5.80 ± 0.14
$[Eu(tta)_3(H_2O)_2]$	32 ± 1	32.00 ± 0.01	6.8 ± 0.8	7.07 ± 0.01

Oscar L. Malta et al. JOYSpectra: A web platform for luminescence of lanthanides. Optical Materials: X 11 (2021) 100080.

Wide Visible-Range Fluorescence QDs
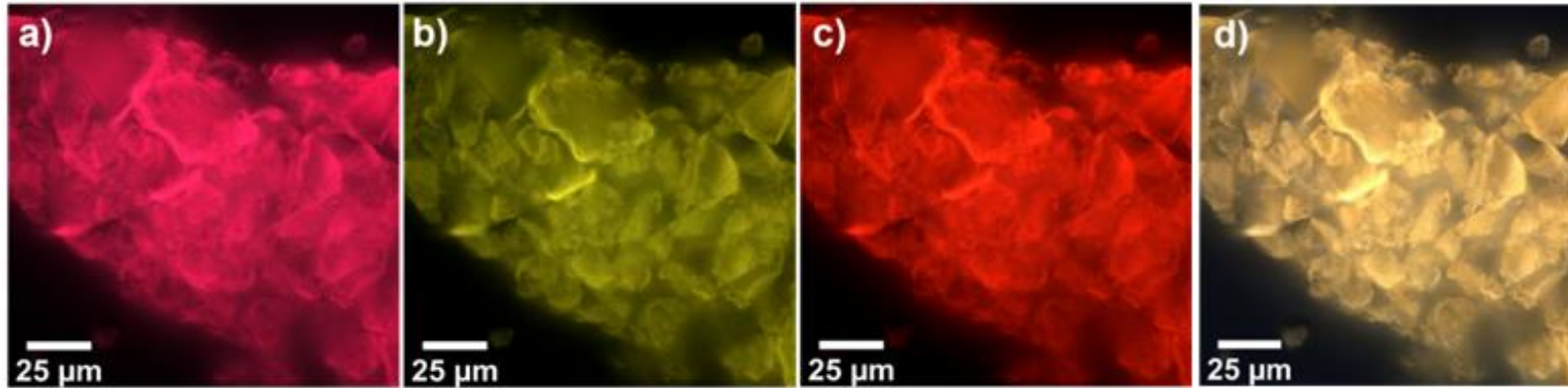
CytoViva dual-mode fluorescence images of aqueous ZnSe:Eu^{3+},Mn^{2+}@ZnS core/shell QDs dispersion, measured at different excitation wavelengths (λ_{exc}): 390 nm (a), 445 nm (b), 520 nm (c), white light (d), and the corresponding emission spectrum (e).

- **Unraveling the excitation wavelength dependent tunable emission color:**
  - Energy transfer mechanism among metal ions dopants and host lattice.
  - X-ray absorption spectroscopy (XAFS) to probe metals local structure and oxidation states with optical properties needed.
  - XEOL in combination with XANES may ideal.

Images Courtesy: Dr. Zahid Ullah Khan Institute of Biomedical Sciences, University of Sao Paulo, Brazil

Probing Local Structure of QDs by XAFS

Normalized XANES spectra (a,b) and the Fourier transforms of their k^2-weighted EXAFS [$\chi(k)$] (c,d) for the ZnSe:Eu^{3+},Mn^{2+} core and ZnSe:Eu^{3+},Mn^{2+}@ZnS core/shell QDs collected at the Eu L$_3$-edge (6977 eV) and Zn K-edge (9659 eV).

- K-edge of Zn in sulfides exhibited three well-defined peaks till 50 eV above the edge, and only two peaks in selenides, because the *p*-like densities of states mainly determined by the type of counter anion, Se and S in ZnSe and ZnS lattice, respectively.

- Eu^{3+} ion occupy sites in both ZnSe and ZnS cubic lattice.
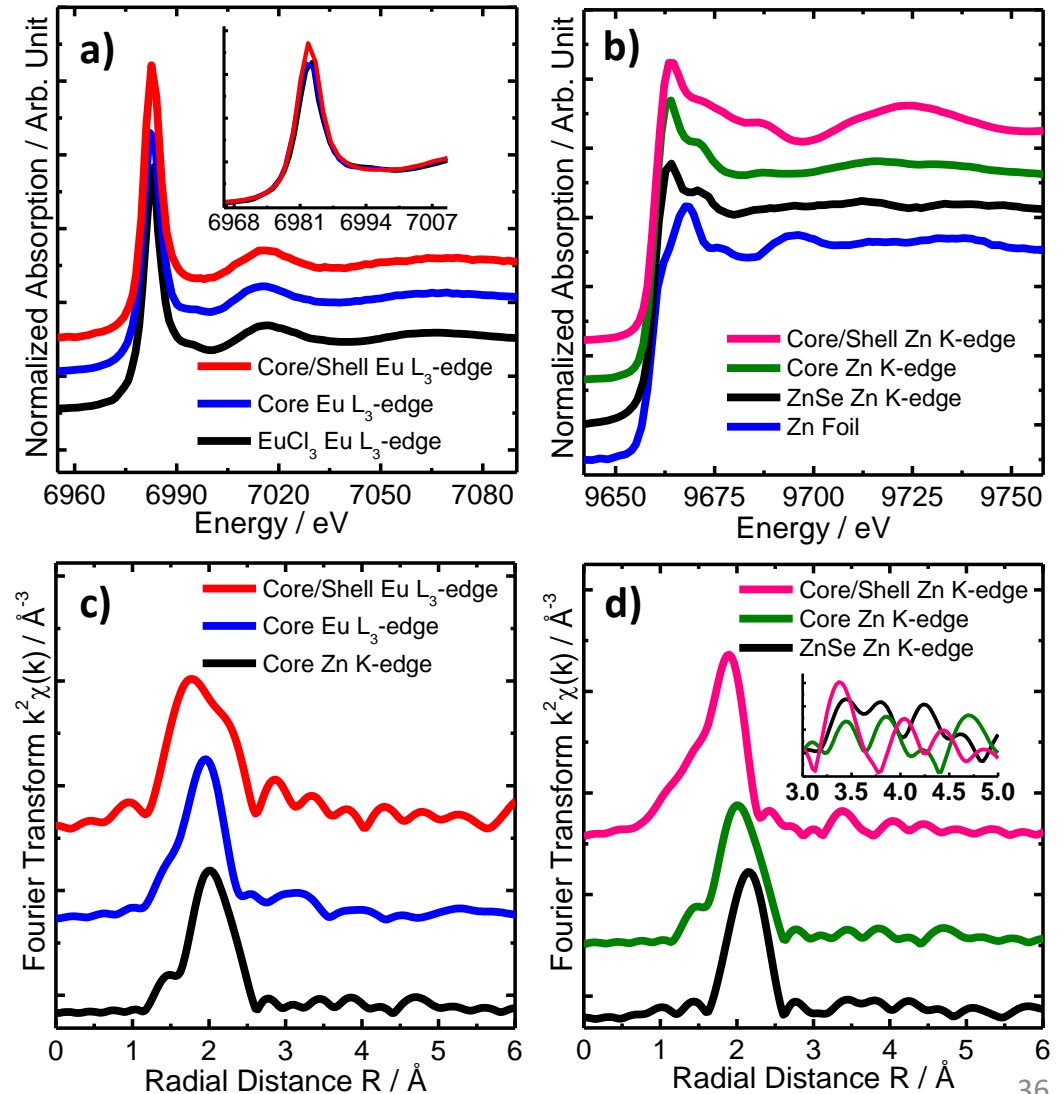
Optical Properties of QDs

UV-visible absorption spectra (a), excitation spectra (b) and emission spectra (c) of ZnS passivated ZnSe:Eu^{3+},Mn^{2+} and ZnSe:Eu^{3+} core/shell QDs, and schematic representation of energy level diagram (d).

Wide Visible-Range Activatable Fluorescence ZnSe:Eu^{3+}/Mn^{2+}@ZnS Quantum Dots: Local Atomic Structure Order and Application as a Nanoprobe for Bioimaging

Check for updates

Zahid Ullah Khan, Mayara Klimuk Uchiyama, Latif Ullah Khan, Koiti Araki, Hiro Goto, Maria Cláudia F. C. Felinto, Ana Olívia de Souza, Hermi Felinto Brito and Magnus Gidlund
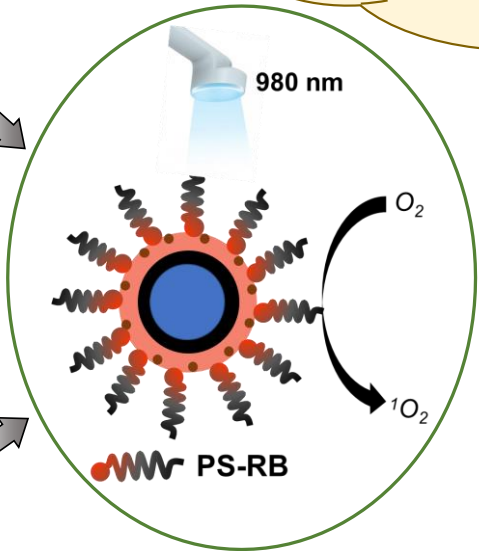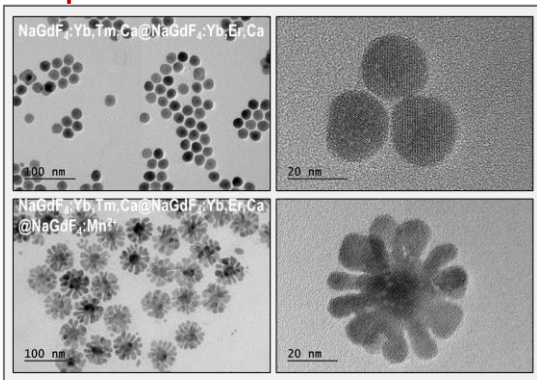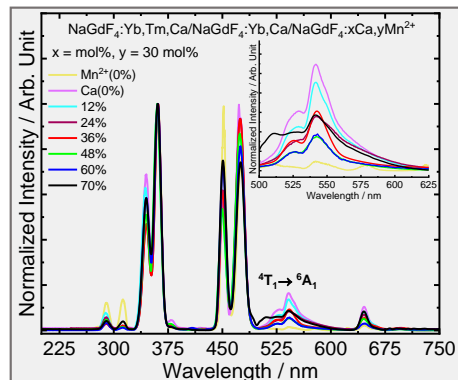
INSTITUTO DE QUÍMICA
Universidade de São Paulo
USP
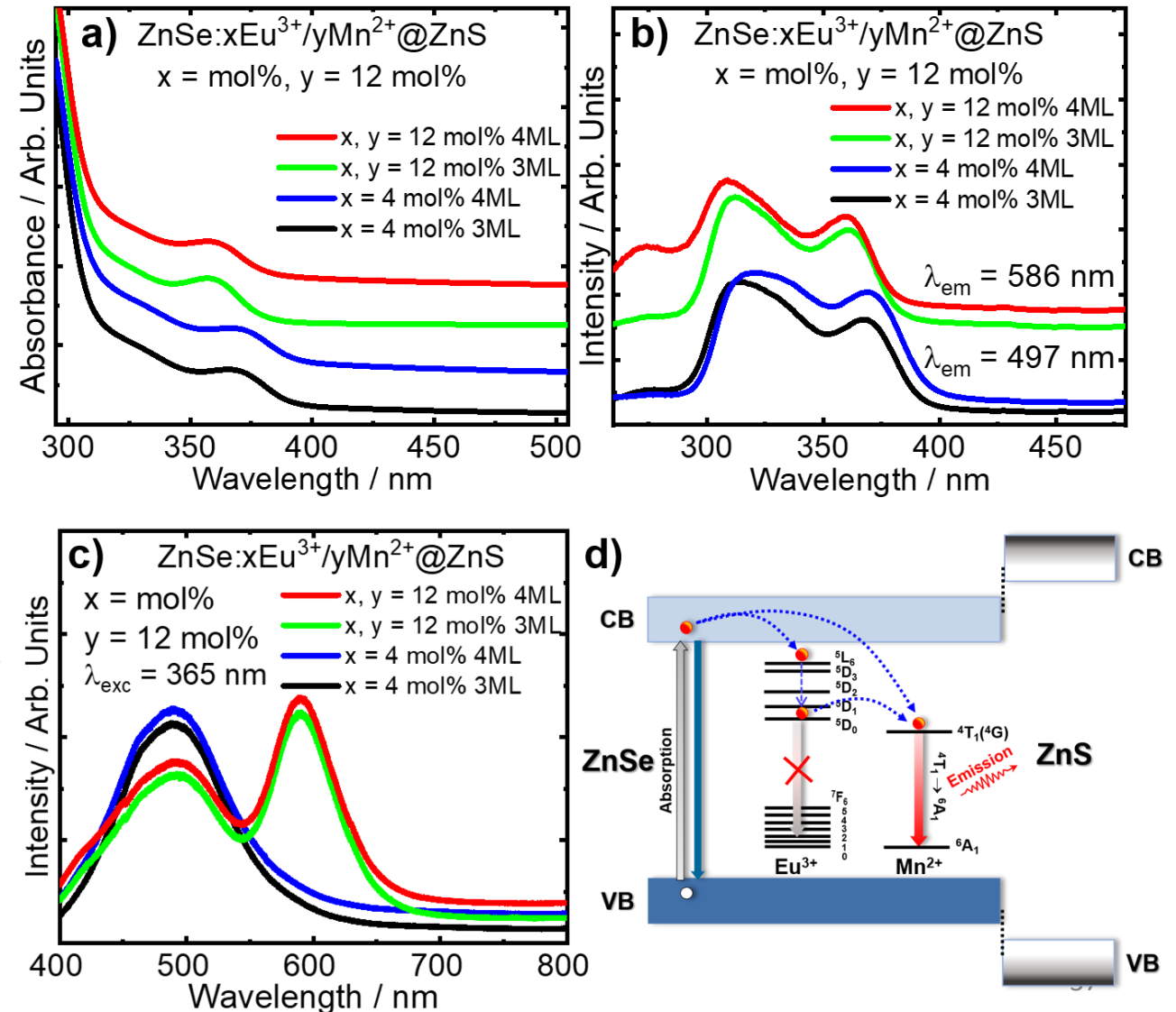
Singlet Oxygen ($^1O_2$) Generation: Luminescence NPs as Amplifiers/Sensitizers

Upconversion Nanoparticles

Quantum Dots (QDs)

XANES in combination with **UC/DC-**Luminescence/**XEOL** can provide deep insight on local electronic structure and energy levels structure of metals ions to probe the energy transfer and luminescence mechanism in nanophosphors, acting as amplifiers for singlet oxygen ($^1O_2$) generation.
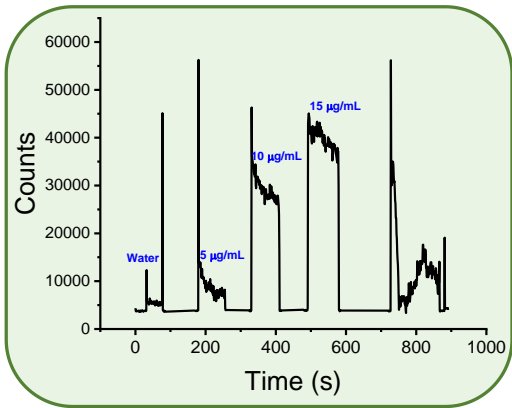
The spherical and flowers shapes visible luminescence nanophosphors act as efficient amplifiers for singlet oxygen ($^1O_2$) generation, under irradiation with UV-vis and near-IR (980 nm) laser.

980 nm

O_2

$^1O_2$

PS-RB
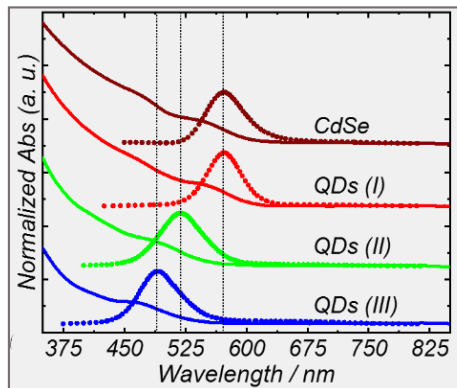
Emission Color-Tunable CdSe/ZnS QDs as Photosensitizers for $^1O_2$ Generation

Yellow - QDs (I)   **Green - QDs (II)**   **Blue - QDs (III)**

Anion exchange at interface alloying

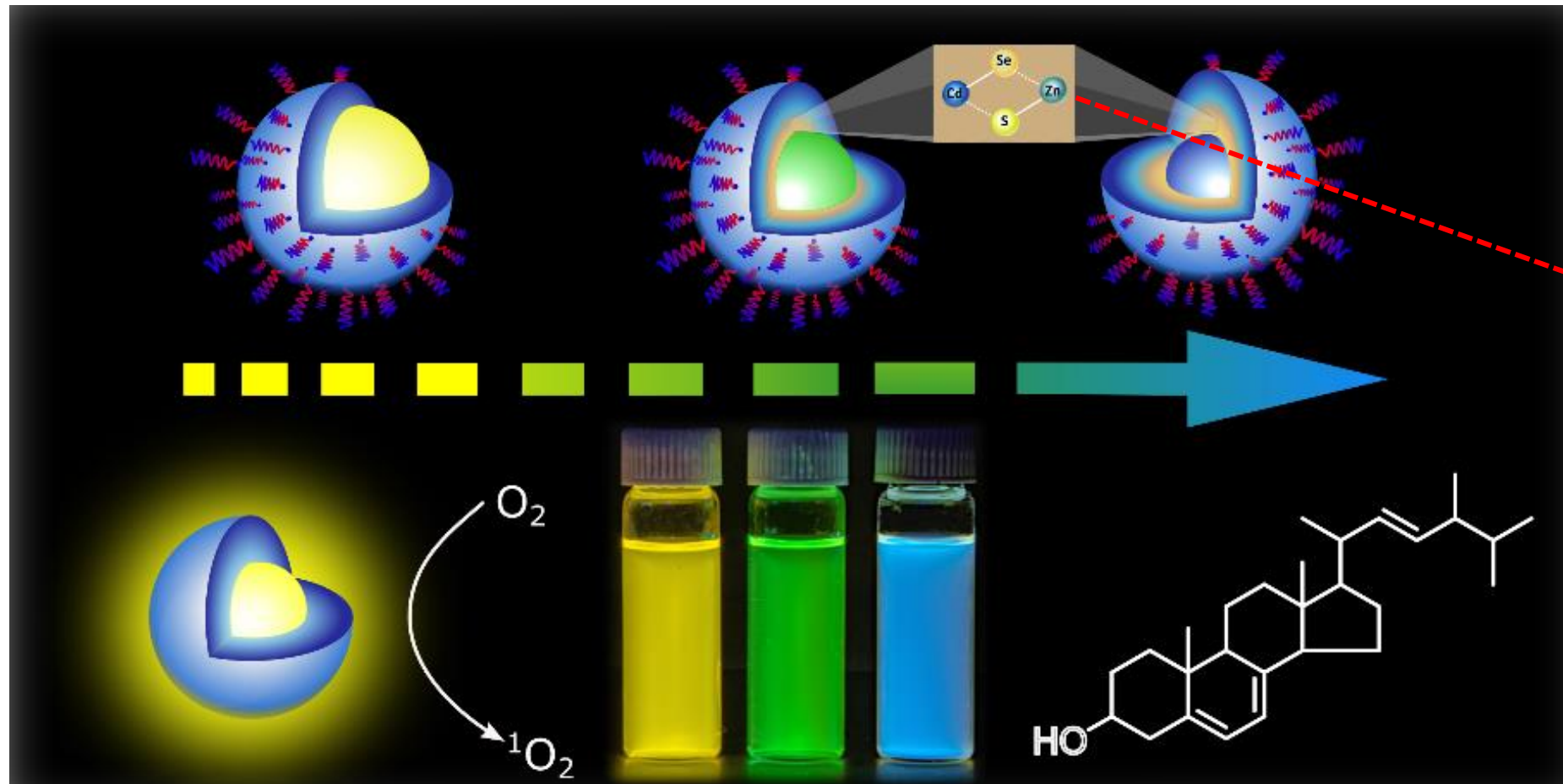Khan, Z.U. et al. Singlet Molecular Oxygen Generation *via* Unexpected Emission Color-Tunable CdSe/ZnS Nanocrystals. *ACS Appl. Nano Mater.* 2023 (Under revision)

Probing Anion Exchange in Core/Shell QDs by XAFS
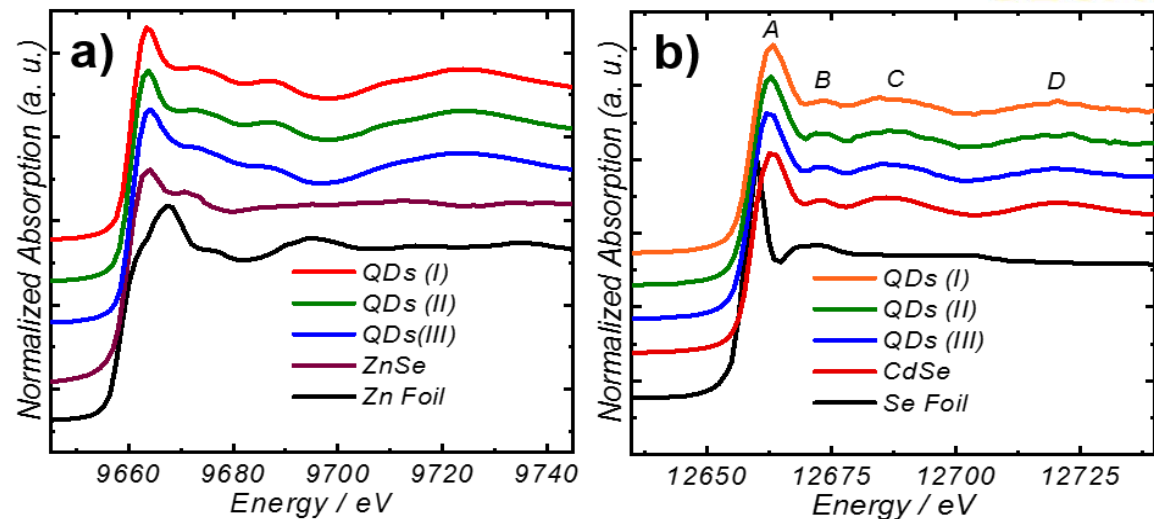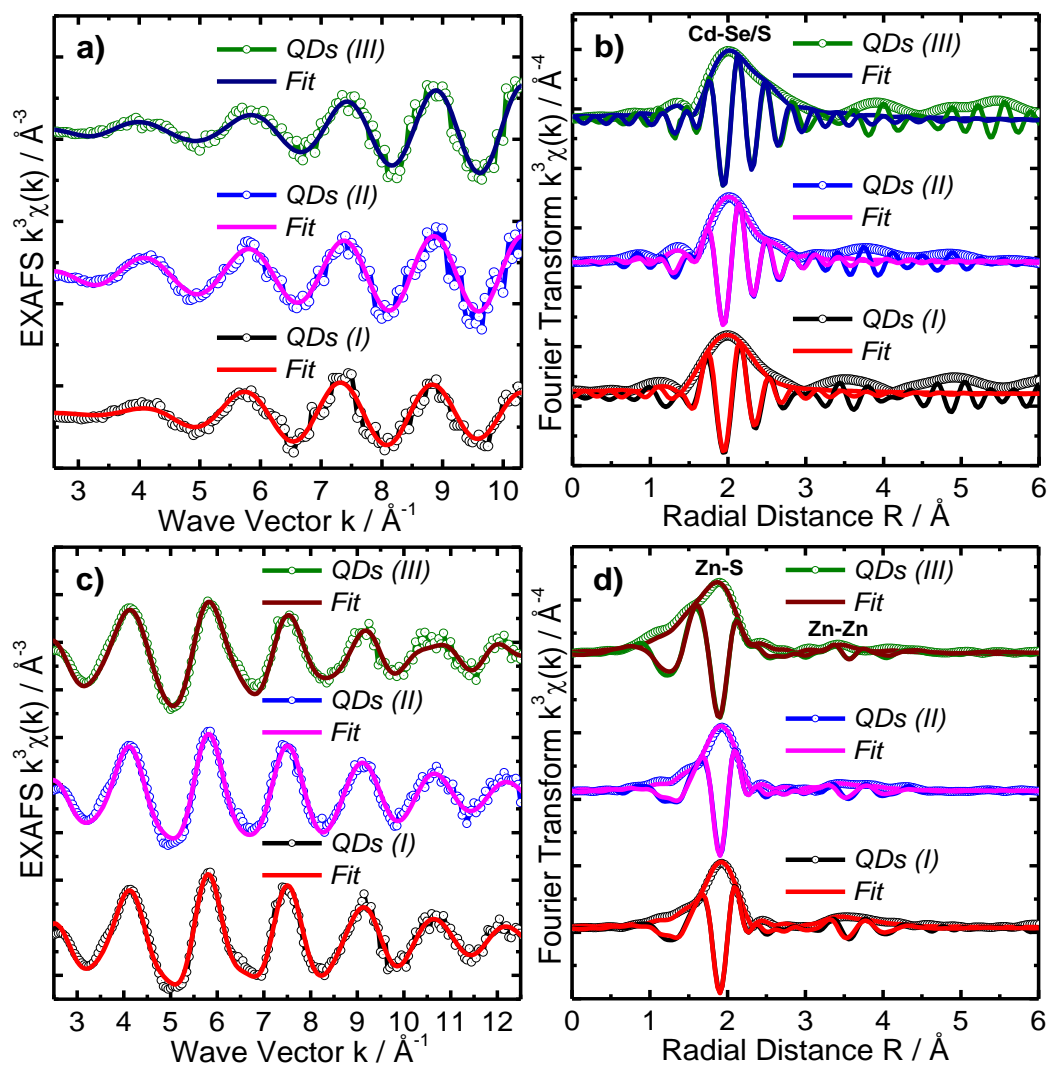
Table 1. Derived EXAFS fitting parameters, including N: number of neighboring atoms, R: distance between absorbing atom and its neighbors, σ^2: mean square relative displacements (MSRDs) or Debye–Waller factor, S^0_2: amplitude reduction factor and R_{factor}: goodness of fit for the QDs (**I**), QDs (**II**), and QDs (**III**).

Material	Bond Type	N	R(Å)	σ^2(Å²)	S^2_0	R_{factor}
QDs (I)	Cd-Se	4	2.531±0.008	0.01048±0.00088	1.0	0.0310
QDs (II)	Cd-S	2	2.494±0.009	0.00189±0.00055	0.9	0.0092
	Cd-Se	2	2.567±0.009	0.01368±0.00710	0.9	0.0092
QDs (III)	Cd-S	2.7	2.516±0.005	0.00929±0.00334	0.7	0.0211
	Cd-Se	1.3	2.589±0.005	0.00160±0.00092	0.7	0.0211

Energy Conversion and Storage Devices - Renewable Energy

- Nickel ion-implanted Coblat (II) Oxides thin films deposited on the Fluorine-doped Tin Oxide (FTO) glass (Fixed fluence: 1×10^{15} cm^{-2}), using Pelletron Tandem Accelerator (Energy: 700 KeV).

Pelletron Tandem Accelerator

National Center of Physics Pakistan

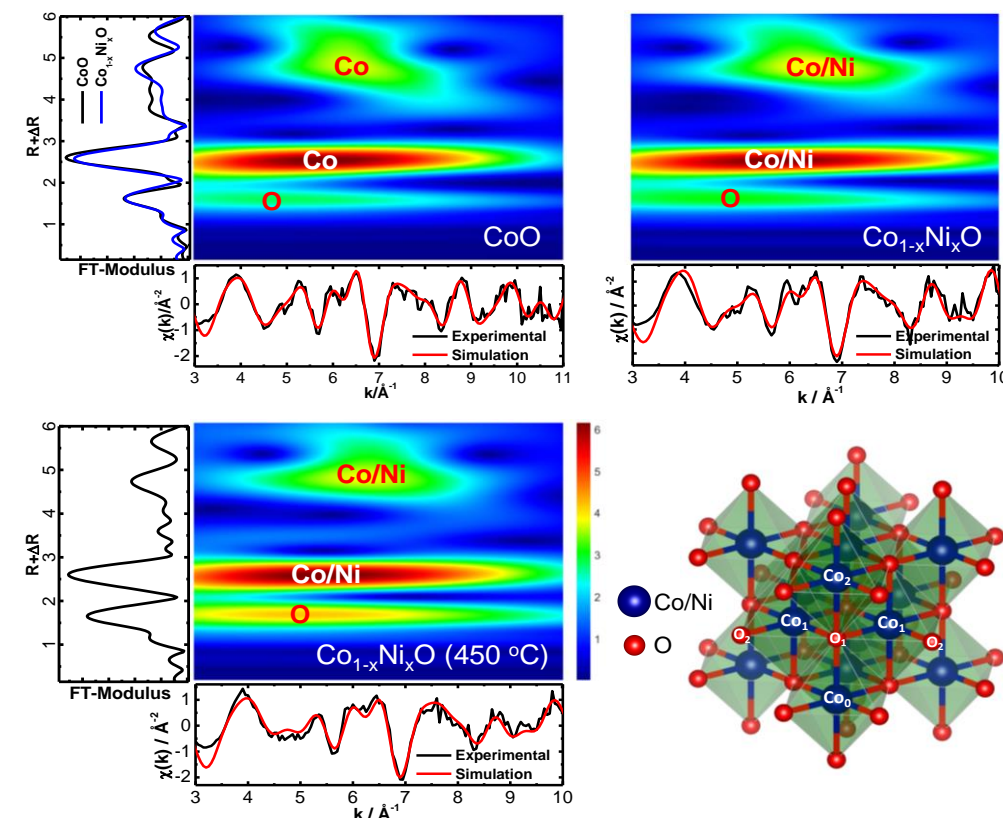**Energy:** 700 keV-35 MeV
Beam spot: 0.5 to 8 mm

Ion beams : H, He, B, P, C, Si, P, Ni, Cu, Fe, Au

- Exploring defects/oxygen vacancies in these samples *via* XAFS to enhance their efficiencies for application as electrocatalysts in Hydrogen Evolution Reaction - HER (Fuel Cells).

Dr. Naila Jabeeen Rresearch Group from National Center of Physics Pakistan

EXAFS Simulation by Evolutionary Algorithm Implemented in Reverse Monte Carlo method (EA-RMC).

Sample Environment - Tubular Furnace/Reactor

❑ Tubular Furnace/Reactor: A Sample Environment for In-Operando X-ray Absorption Studies (Catalysis)

Temperature (°C)	Sample Holder Ø mm	Atmospheres	Controller
Up to 800	8	Gases, Vapors and Vacuum	Programmable Logic Controller (PLC), SEASME
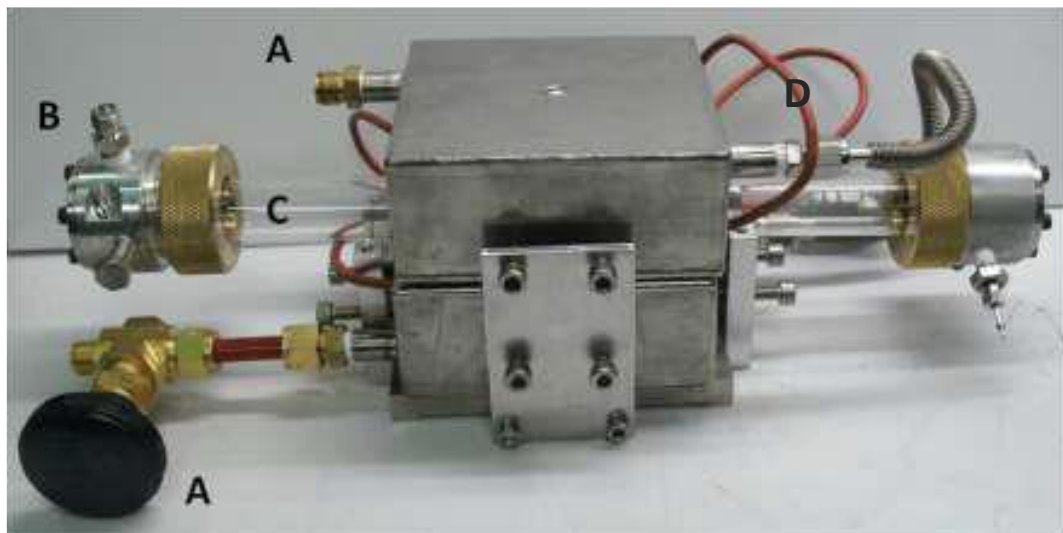
A: Inlet and outlet for water cooling
B: Inlet and outlet for gases with Kapton windows
C: Quartz glass tube
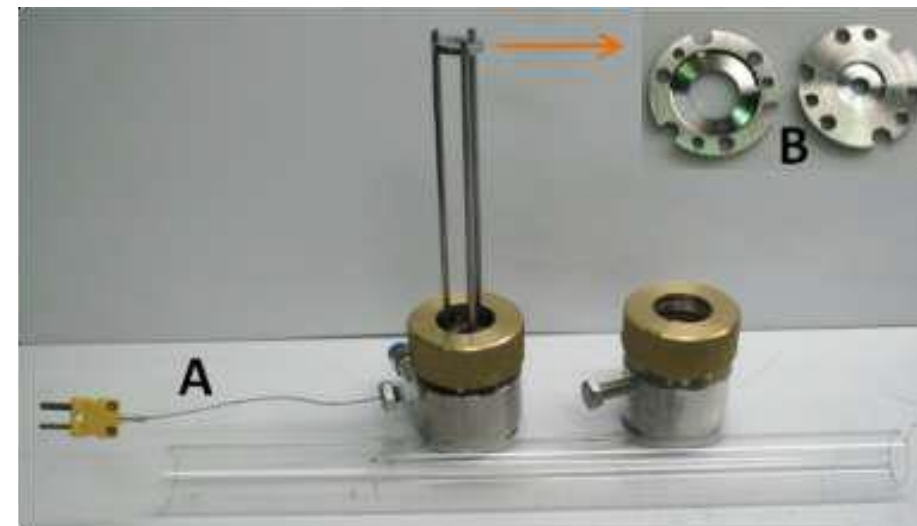
A: Thermocouple on the sample
B: End sample holder

Collaboration: Dr. Santiago J. A. Figueroa QUATI Beamline

LNLS Brazilian Synchrotron Light Laboratory
+ sirius

Sample Environment For Catalysis

SESAME

❑ **In-House Preparation of Tubular Furnace**
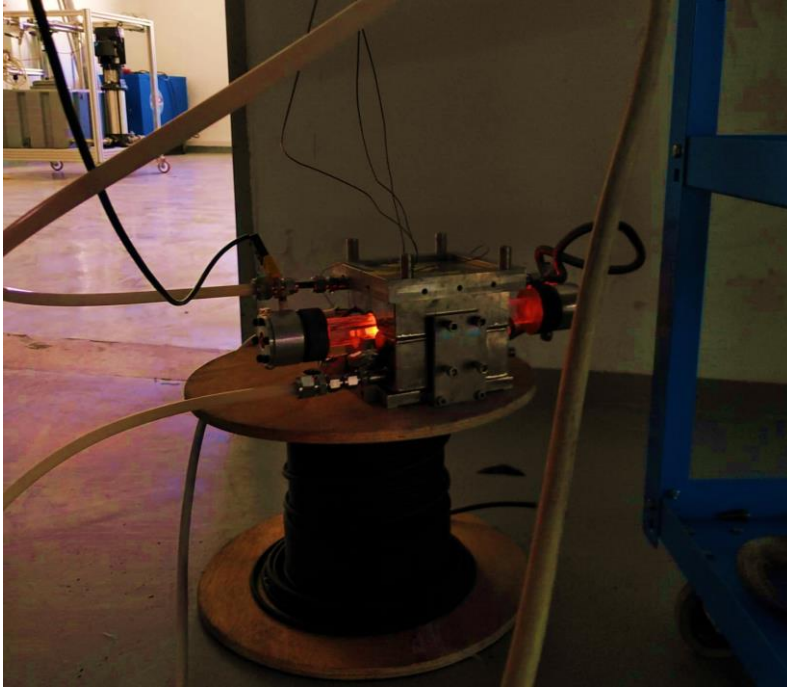
❑ Main steel chamber *In-house* design

Cooled Water channel

Quartz tube

K type thermocouple ~ 1370 °C

Kapton window

Atmosphere Inlet

Sample
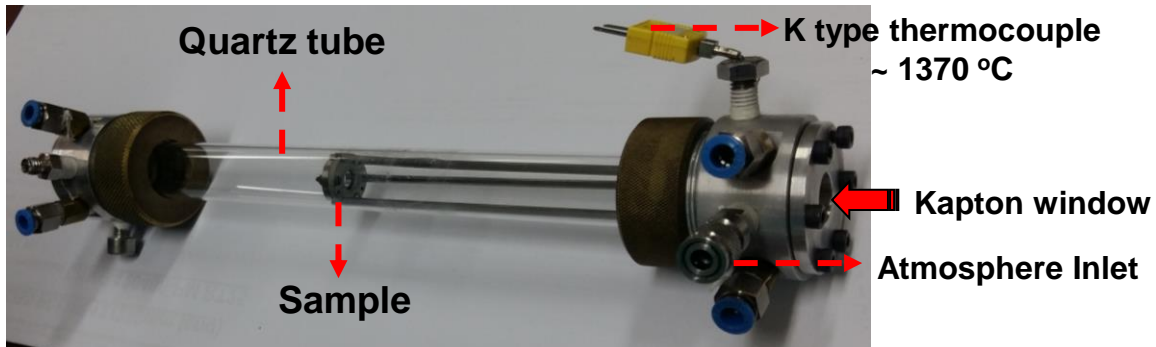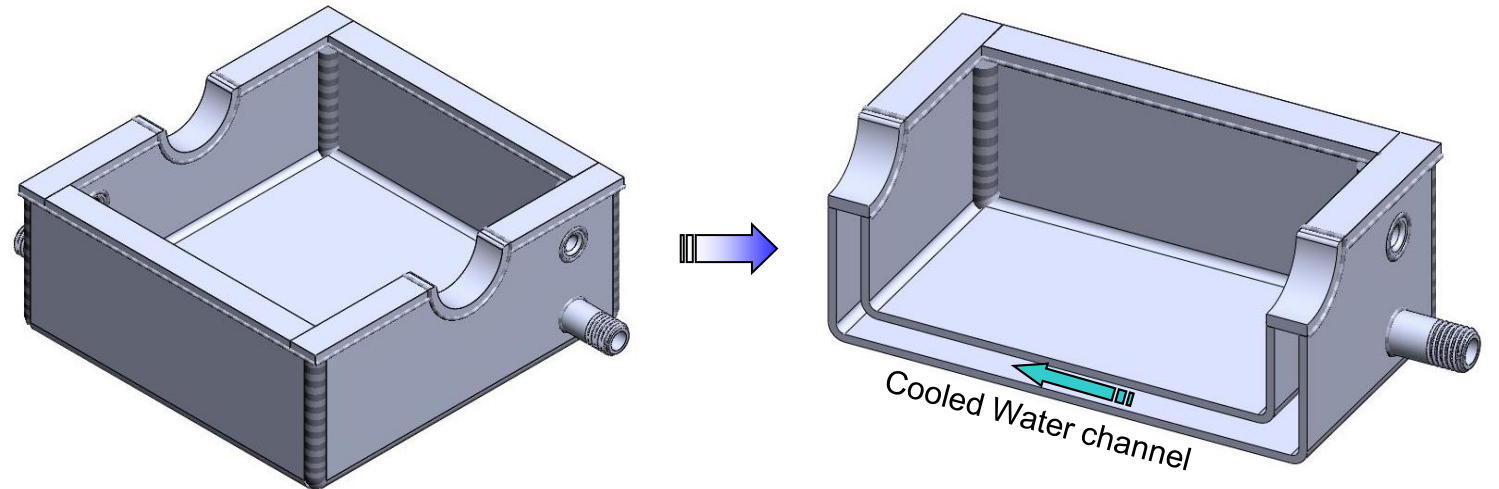
➤ Highly stable temperature response (400-800 °C)

➤ Efficient cooling

➤ Two models: *i*) 25-400 °C and *ii*) 400-800 °C range

➤ Installation of thermal and water flow switches

Publications (2022-2023)

1) Harfouche, M. et al. Emergence of the first XAFS/XRF beamline in the Middle East: providing studies of elements and their atomic/electronic structure in pluridisciplinary research fields. *J. Synchrotron Rad.,* 29, 1-7, 2022.

Nanophosphors

1) Rehman, A.U.; Khan, L.U.; Brito, H.F.; Khan, Z.U. and Khan, A.M. Surfactant-based synthesis of optically active colloidal GdF_3:Ce^{3+}(5%),Eu^{3+}(x%) and GdF_3:Ce^{3+}(5%),Eu^{3+}(5%)/SiO_2 phosphor nanocomposites. *Applied Nanoscience (Springer),* 12, 2183–2193, 2022.

2) Khan, Z.U.; Uchiyama, M.K.; Khan, L.U.; Araki, K.; Goto, H.; Felinto, M.C.F.C.; De Souza, A.O.; Brito, H.F.; Gidlund, M. Wide Visible-Range Activatable Fluorescence ZnSe:Eu^{3+}/Mn^{2+}@ZnS Quantum Dots: Local Atomic Structure Order and Application as a Nanoprobe for Bioimaging. *J. Mater. Chem. B* (RSC), 10, 247-261, 2022.

3) Khan, L.U.; Khan, Z.U.; Blois, L; Tabassam, L.; Brito, H.F. and Figueroa, S.J.A. A New Strategy to Probe the Local Atomic Structure of Luminescent Rare Earth Complexes by XANES Simulation Using Machine Learning Based PyFitIt Approach. *Inorganic Chemistry* (ACS), 2023 (Accepted InPress).

4) Khan, Z.U.; Khan, L.U. et al. Singlet Molecular Oxygen Generation via Unexpected Emission Color-Tunable CdSe/ZnS Nanocrystals. *ACS Applied Nano Materials* (ACS), 2023 (In Revision).

Catalysis

1) Sajid, F.; Jabeen, N.; Khan, L.U. et al. Local atomic structure order and electrochemical properties of NiO based nano-catalysts for ethanol sensing at room temperature. *Journal of Physics and Chemistry of Solids* (Elsevier), 175, *111201,* 2023.

2) Qadeer, N.; Jabeen, N.; Khan, L.U.; Sohail, M.; Zaheer, M.; Vaqas, M.; Kanwal, A.; Sajid, F.; Qamar, S. and Akhter, Z. Hydrothermal Synthesis and Characterization of Transition Metal (Mn/Fe/Cu) Co-Doped Cerium Oxide-Based Nano-Additives for Potential Use in the Reduction of Exhaust Emission from Spark Ignition Engines. *RSC Adv. (RSC),* 12, 15564-15574, 2022.

3) Rubab, A.; Baig, N.; Sher, M.; Ali, M.; Ul-Hamid, A.; Jabeen, N.; Khan, L.U.; Sohail, M. Synthesis and Characterization of a Carbon-Supported Cobalt Nitride Nano-Catalyst. *ChemNanoMat. (Wiley Online Library)* e202100428, 2022.

4) Jamil, S.; Jabeen, N.; Khan, L.U.; Akhter, Z. et al. Synthesis and Comparative Evaluation of Optical and Electrochemical Properties of Efficacious Heterostructured-Nanocatalysts of ZnSe with Commercial and Reduced Titania. *Journal of Alloys and Compounds* (Elsevier), 879, 160449, 2021.

5) Khan, L.U.; Jabeen, N.; et al. Investigating Local Structure of Ion-Implanted (Ni^{2+}) and Thermally Annealed Rocksalt CoO film by EXAFS Simulation Using Evolutionary Algorithm. *ACS Appl. Energy Mater. (ACS),* 4, 2049–2055, 2021.

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(DQF-UFPE)

Prof. Marcelo Knobel
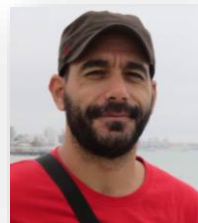Nanomagnetism Physics IFGW
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(SIRIUS LNLS)

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(IFGW-UNICAMP)

Prof. Kleber
Magnetism Physics
(IFGW-UNICAMP)

Dr. Maria C.F.C. Felinto
Rare Earths (IPEN)

Dr. Vronica Teixeira
XEOL - Carnauba BL
(SIRIUS LNLS)

Dr. Muhammad Usman
Ion Beam Accelator
(NCP Islamabad)

Dr. Naila Jabeen
Catalysis Nanotecnology
(NCP Islamabad)

Prof. Magnus
Immune Physiopathology
(ICB-USP)

Dr. Zahid Khan
Nanobiotechnology
(ICB-USP)

Thanks

Thanks