The Abdus Salam
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IAEA
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# Introduction to X-ray microscopy and ray microscopy and spectro-microscopy

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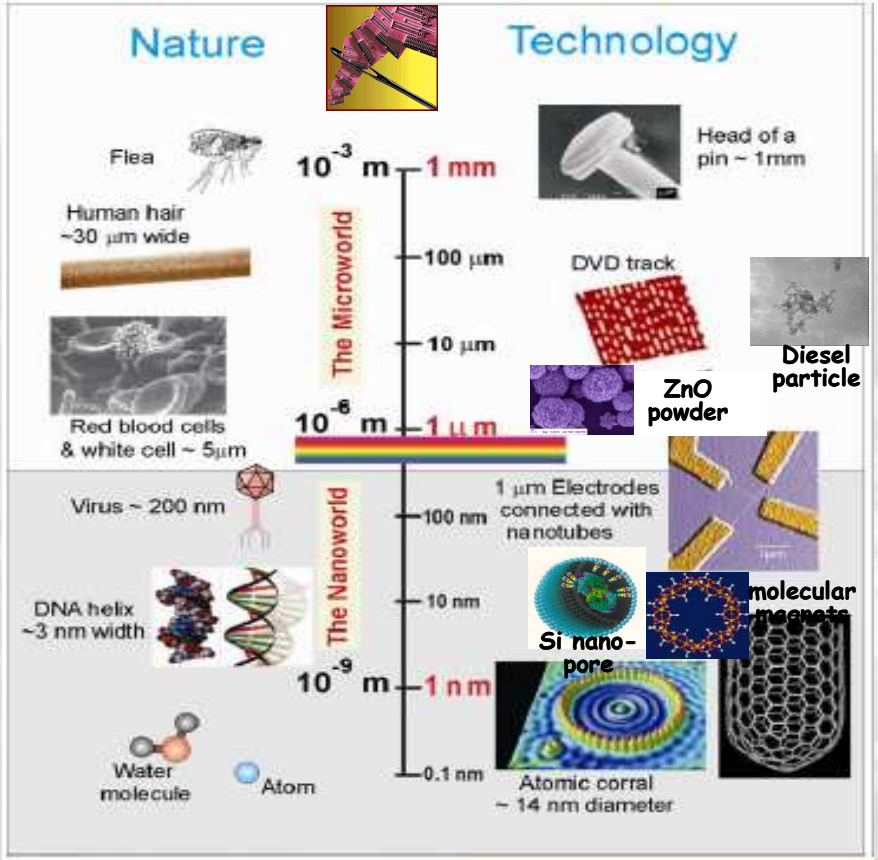
# Introduction to X-ray microscopy and spectro-microscopy

Maya Kiskinova, Sincrotrone Trieste, Italy



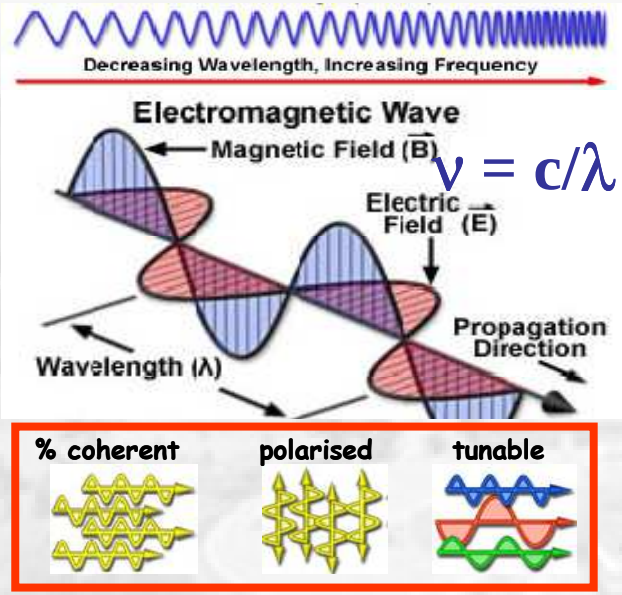

- Materials have properties varying at various depth and length scales.
- Structure and chemical composition usually is different at the surface and in the bulk.
- New properties expected with decreasing their dimensions.

**What we NEED:**

Spatial resolution & chemical sensitivity, morphology & structure, varying probing depth, temporal resolution..

# Why using synchrotrons for microscopy?

**Only 'LIGHT' with comparable wavelength, λ, can visualize the micro- and nano-structured world**




## Synchrotron Light

- High brightness.
- Tunability
- Polarization.
- Time structure.
- Coherence.

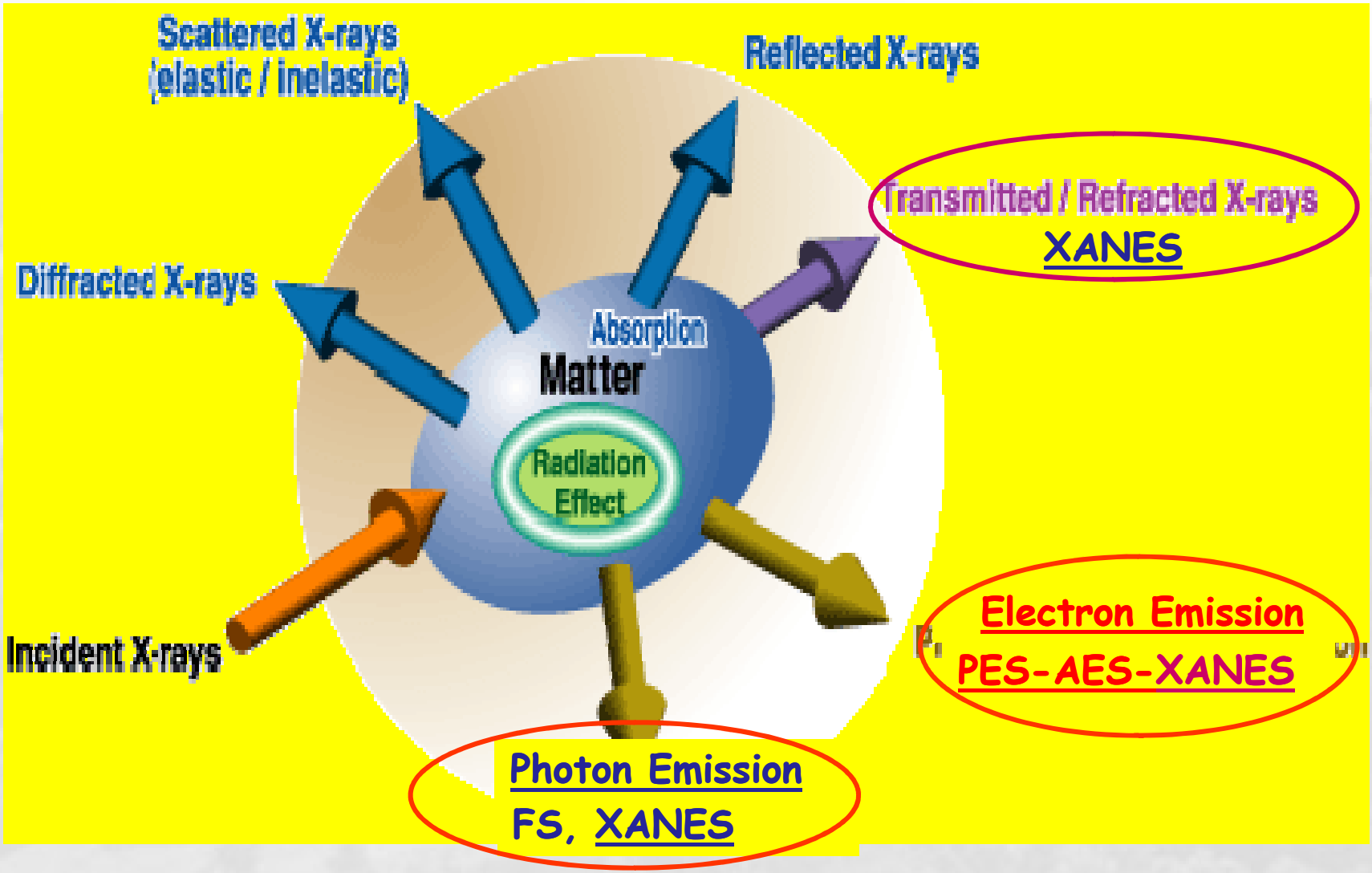
## Modern technology

- ✓ X-ray focusing optics.
- ✓ X-ray or electron detectors.

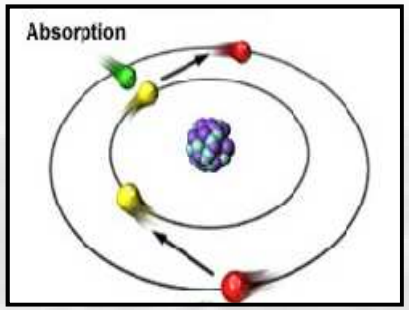
## X-Rays compared to charged particles:

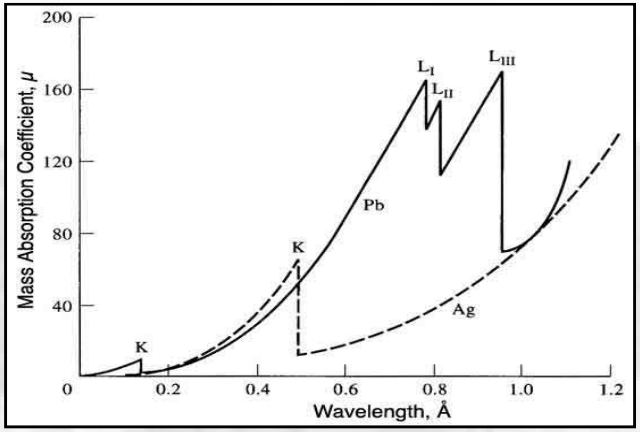
- Higher penetration power: wave-lenght controlled.
- Great variety of spectroscopies-elemental, chemical etc information.
- Variety of imaging contrasts with diffraction limited resolution.
- Less sensible to sample environment.

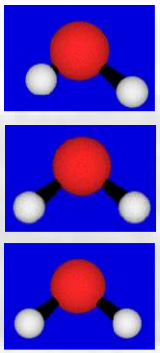
# Interactions of x-rays with the matter:
## redirection & absorption ⇒ x-ray transmission and x-ray or electron emission

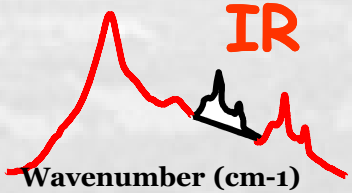


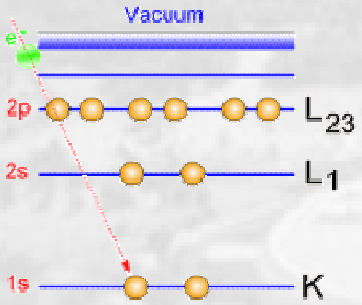
# Synchrotrons offer a variety of spectroscopy and imaging approaches

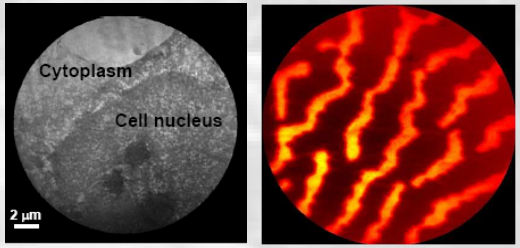


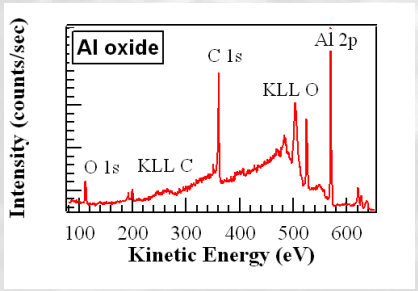



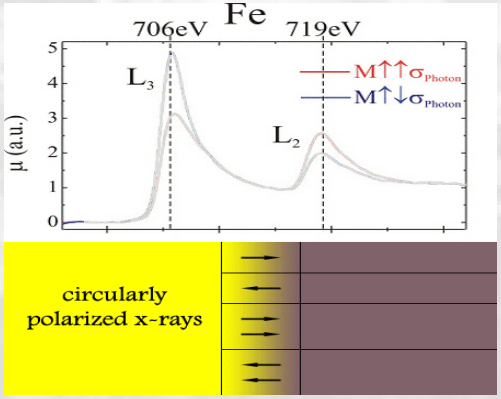





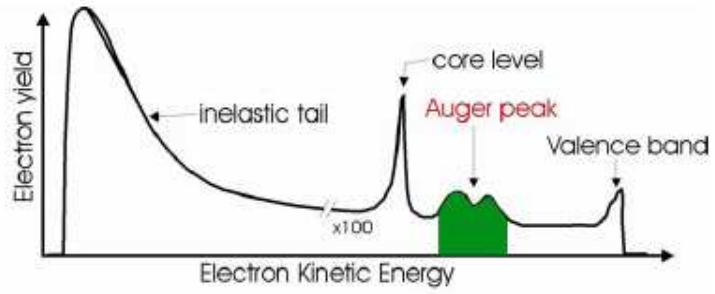



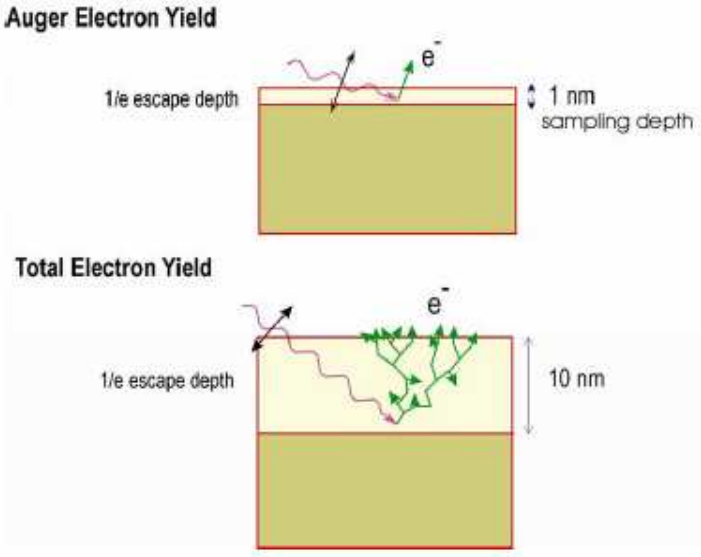




**Imaging:** morphology (absorption and scattering) or composition (spectroscopy)

# Sampling depths depend on the detected signal (electrons or photons)

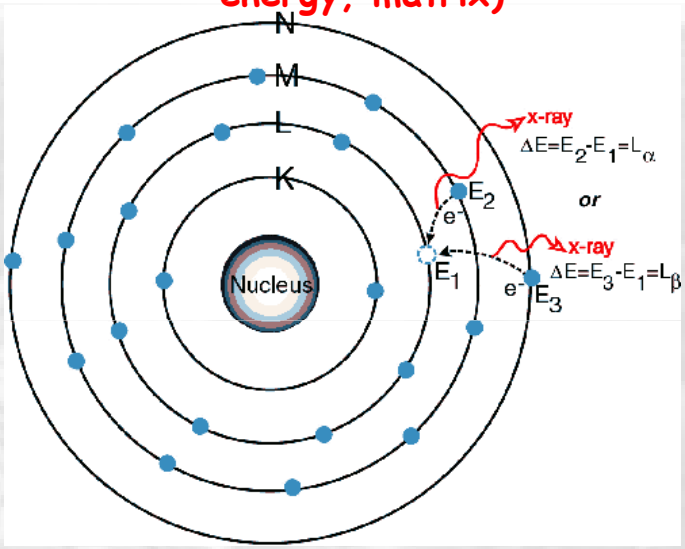
## TEY, core, valence and Auger electron emission

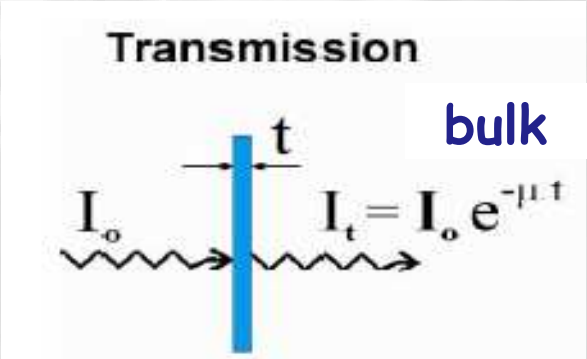



## Fluorescence emission:

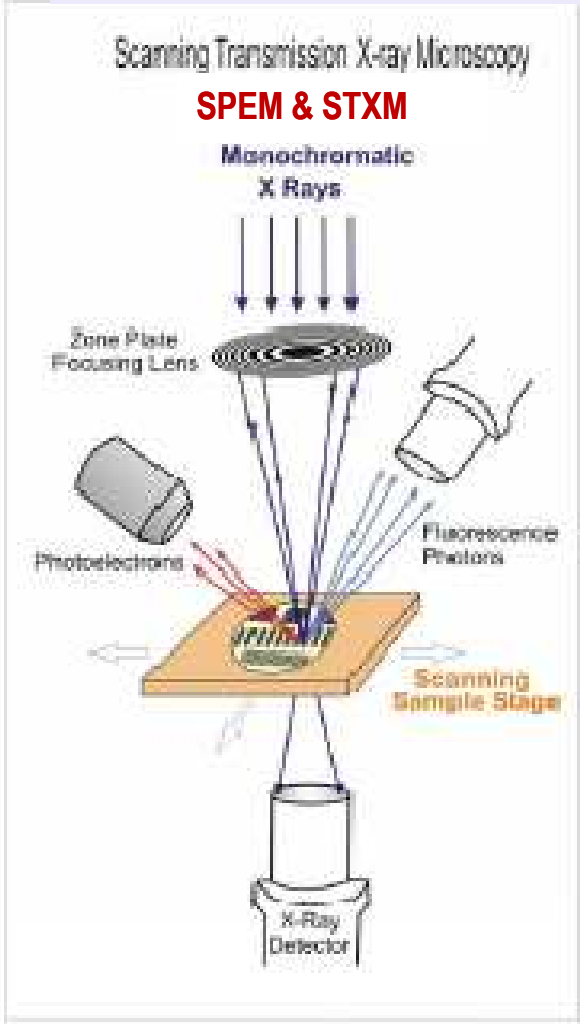
Probe depth- > 100 nm = f(photon energy, matrix)

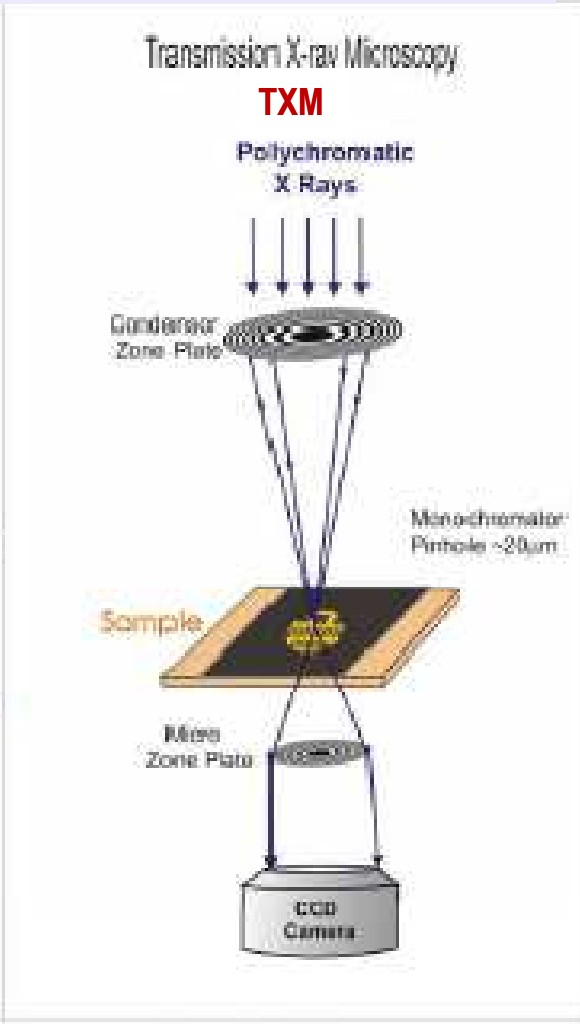


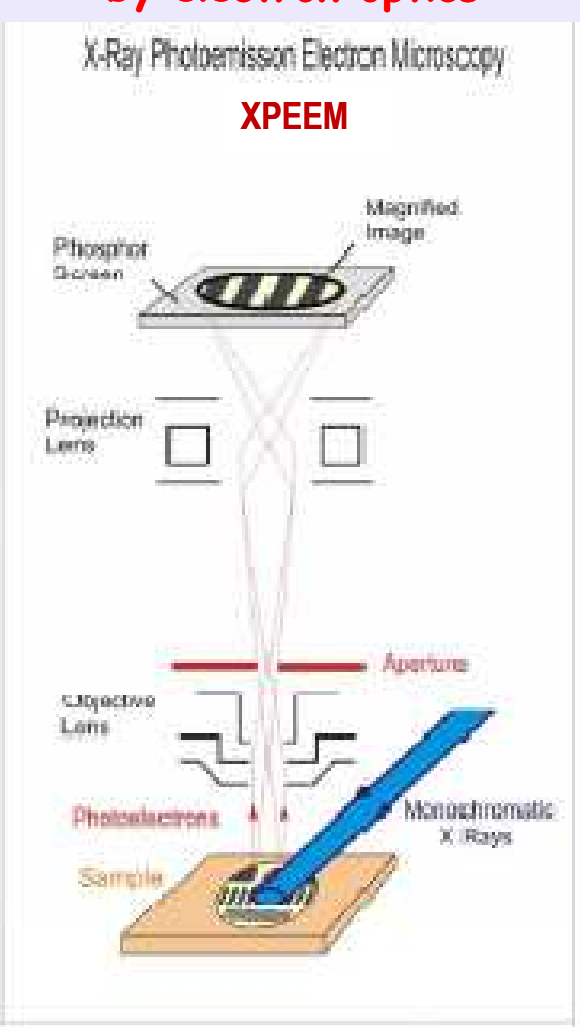
# X-ray microscopes using photon or electron optics

## Lateral resolution provided by photon optics

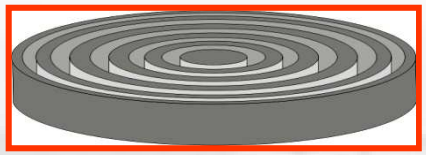


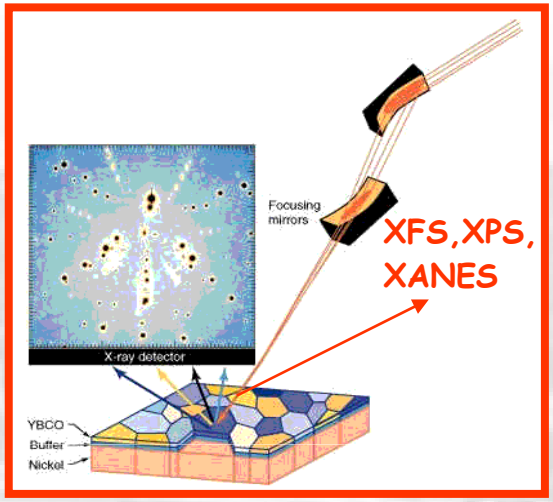

## Lateral resolution provided by electron optics



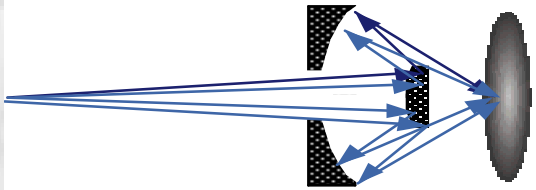
# X-ray focusing optics:
## zone plates, mirrors, capillaries



Zone Plate optics: from ~ 200 to ~ 10000 eV
Resolution: 20 nm in transmission

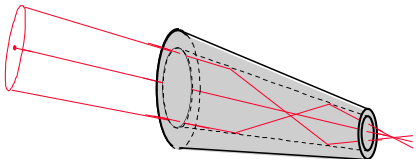



KP-B mirrors each focusing in one direction: soft & hard: ~ 1000 nm
Soft & hard x-rays!
chromatic focal point, easy energy tunability, comfortable working distance
Resolution ≤ 100 nm



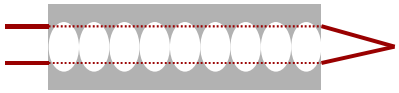
Normal incidence: spherical mirrors with multilayer interference coating (Schwarzschild Objective)
not tunable, E < 100 eV
Resolution: best ~ 100 nm

Capillary: multiple reflection concentrator



Hard x-rays ~ 8-18 keV
Resolution: > 3000 nm

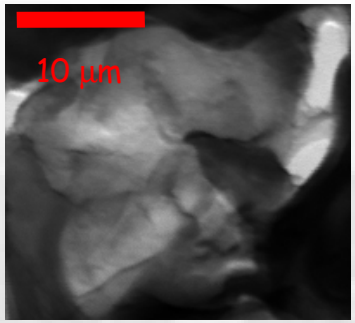
Refractive lenses



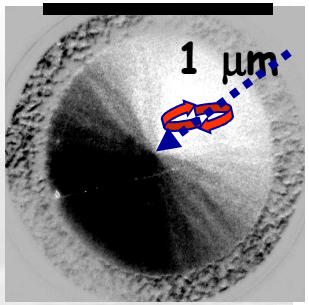
Hard x-rays ~ 4-70 keV
Resolution: > 1000 nm

# Imaging and μ-spectroscopy

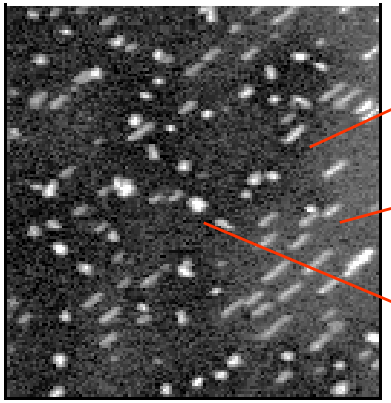
Illy coffee cells

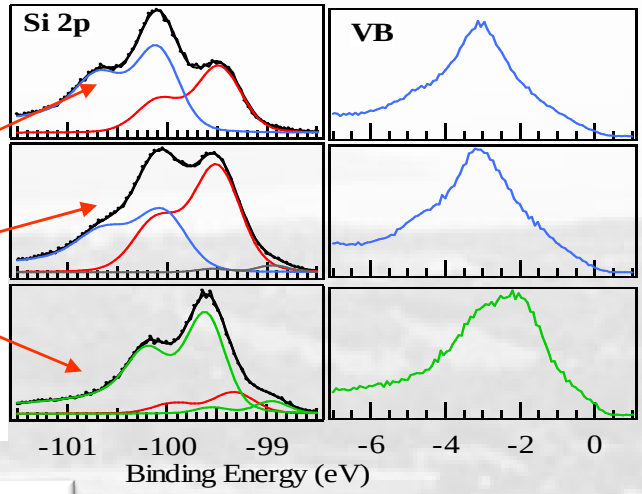



Permaloy NS




Ni/Si-Ni3p map





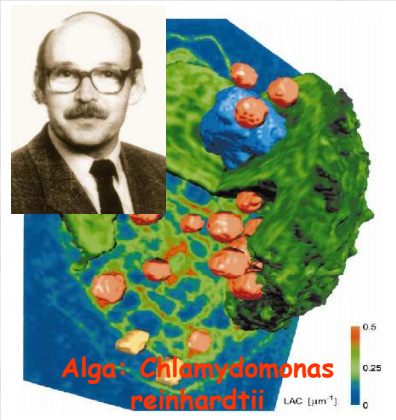

Emitted electrons (XPS,XANES),
Transmitted/emitted photons (XANES,FS)
IMAGE **contrast reflects:**

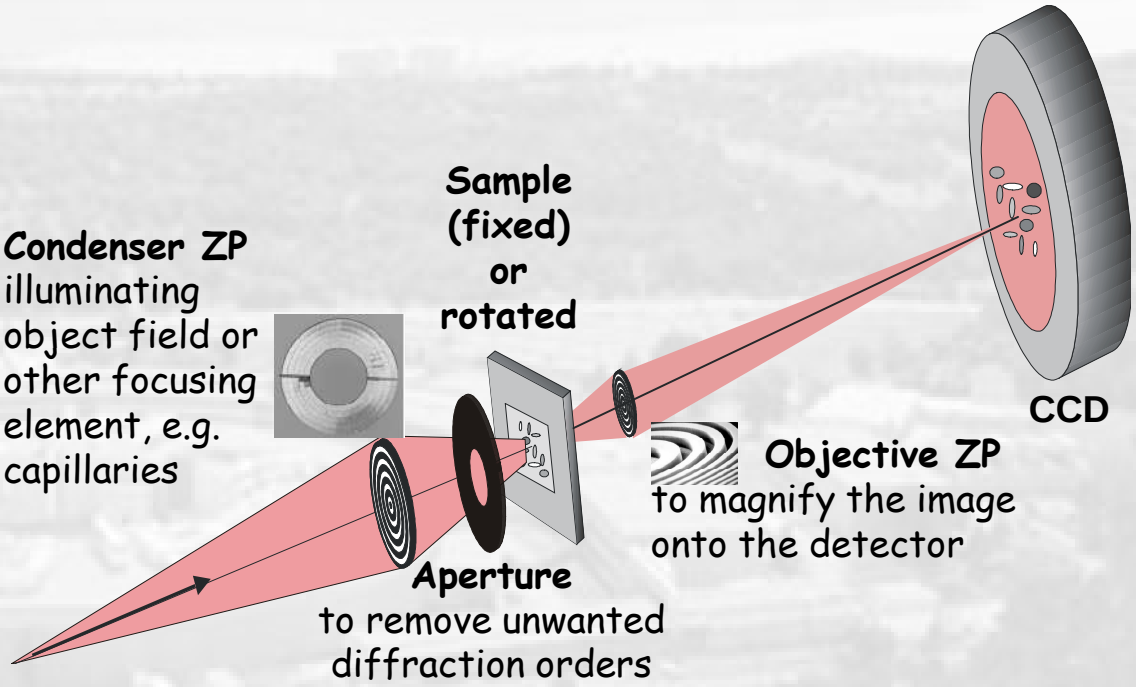
1) morphology (x-ray contrast based on absorption, scattering, refraction etc);
2) elemental composition;
3) chemical states;
4) magnetic spin or bonding orientation;
5) band bending, charging, etc.

Detailed characterization of the chemical and electronic structure of the coexisting micro-phases: μ-PES, XANES & FS

# Imaging x-ray transmission microscope (TXM)

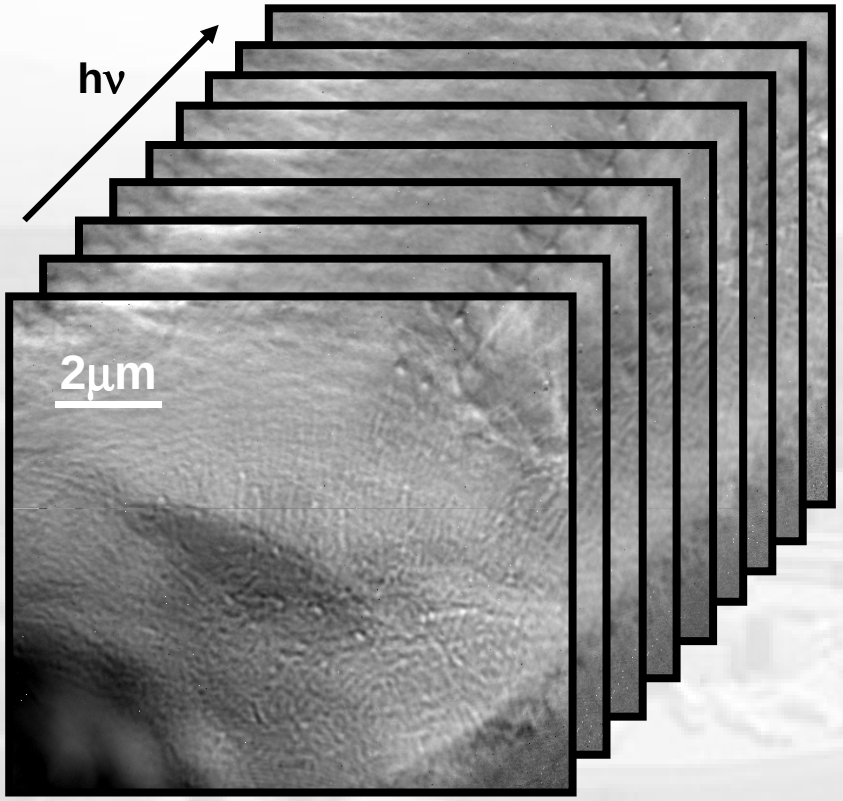
History: 1st experiments at DESY, 1976
Uni Göttingen, Günther Schmahl & Co
The first operating XTM – 1979 ACO, 1983 - BESSY I.




2009 - XTM (10+3): - ALS (2), APS (2), BESSY II (1), ELETTRA (1), ESRF (1), ASTRID (1), SPRING'8 (1), AURORA (1), DIAMOND(1), SOLEIL (1), ALBA (1). Resolution achieved 15 nm.

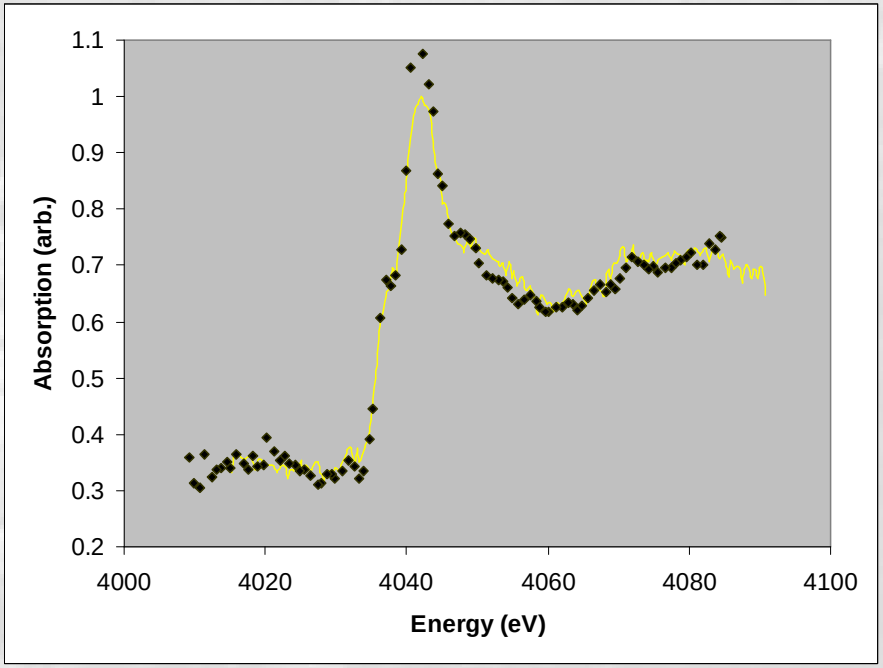
# Imaging and spectro-microscopy with FFIM




Trabecular bone of a mouse femur sample (10μm thick);
Image field is 27 x 21 $\mu m^2$

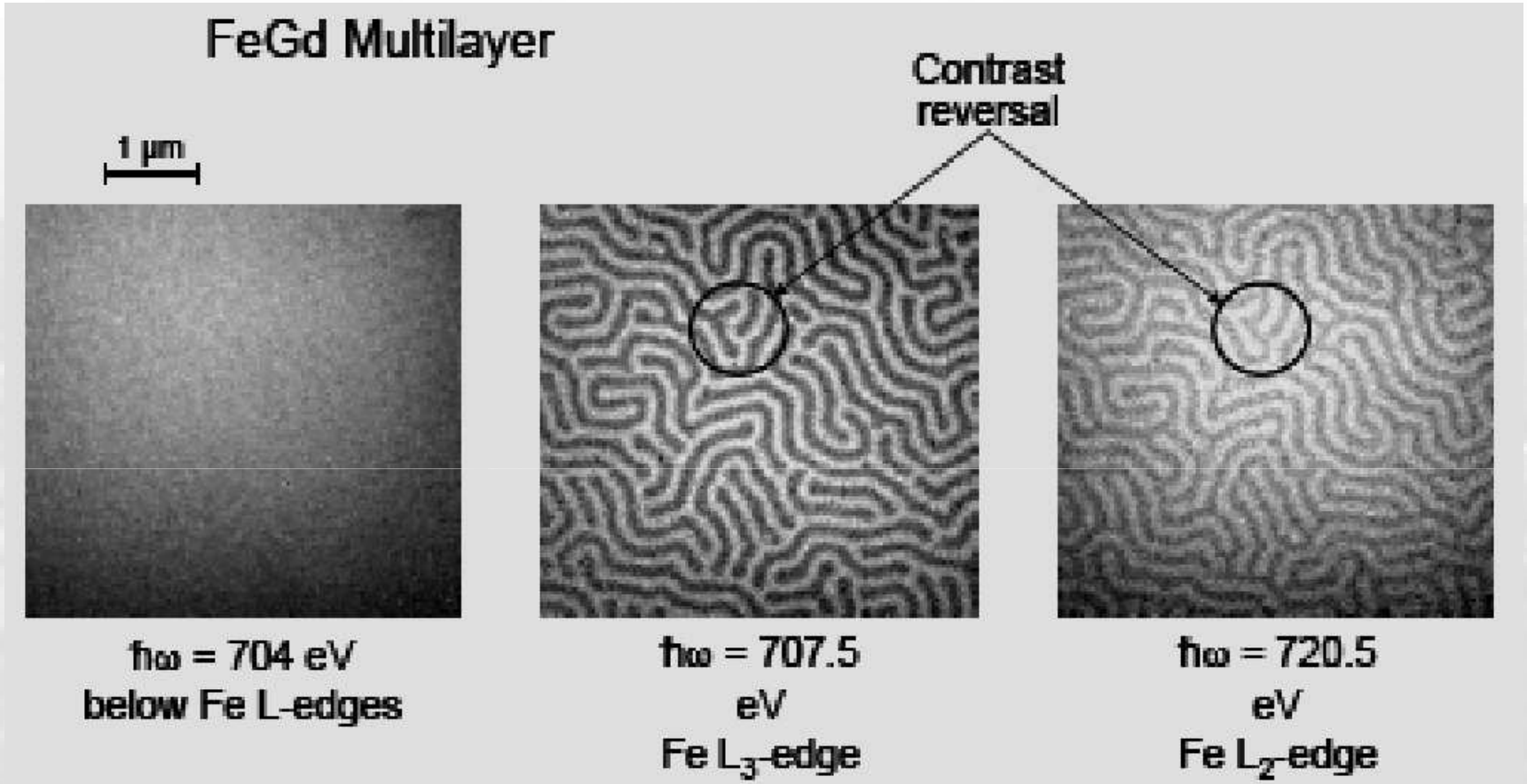
Study dealing with genetic determinism of immobilization induced bone loss with the FFIM at ID21, ESRF, France

*M.Salome et al.*

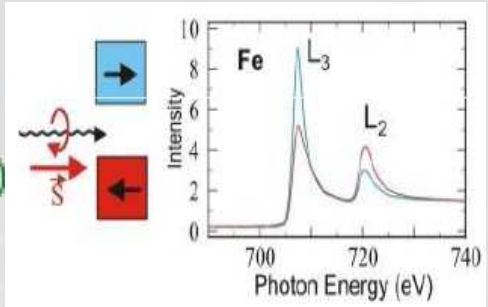



Hydroxy-apatite spectrum recovered from a stack of 200 images

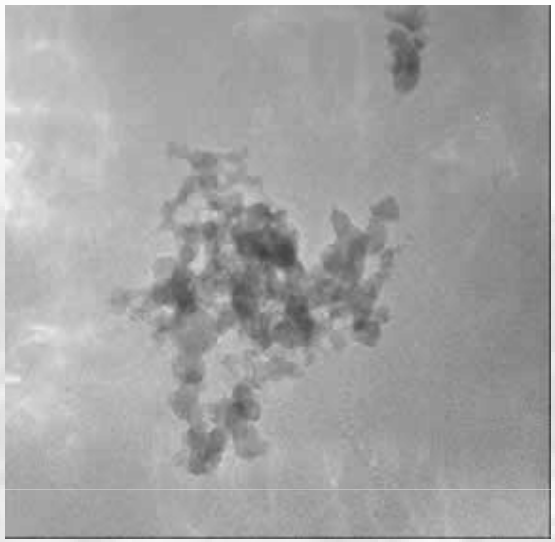
# Magnetic imaging (XCMD) with FFIM: domain sizes and spatial distribution

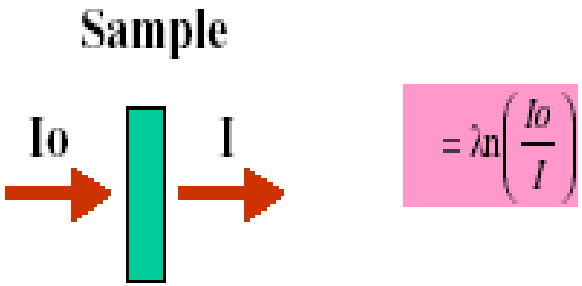


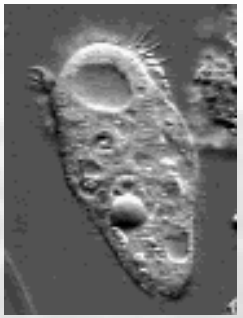

P. Fischer, T. Eimuller, M. Koehler (U. Wuerzberg)
S. Tsunashima (U. Nagoya) and N. Tagaki (Sanyo)
G. Denbeaux, L. Johnson, A. Pearson (CXRO-LBNL)



# FFIM and Cell Biology: morphological information





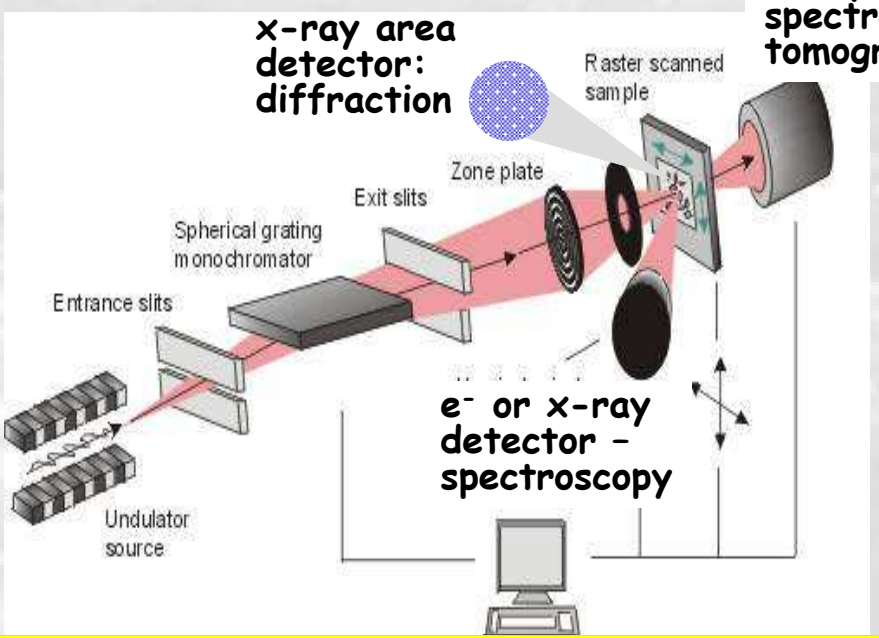
**Cell imaging in their natural environment: the cells contain C and N and absorb an order of magnitude more strongly than the surrounding water when using x-rays below the O edge (540 eV, 'water window'). The resulting natural contrast generates unprecedented views of the internal cellular architecture in a natural, albeit frozen, state, information crucial for understanding the cellular function: Tomography!!!**

# X-ray Scanning Microscopy: uses focusing x-ray optics (preferred zone plates)

**History:** The 1st experiments with lab source at SSR late 1970s

NSLS-Stony Brook: Janos Kirz & Co.

The first operating STXM - 1983, SPEM – 1990.

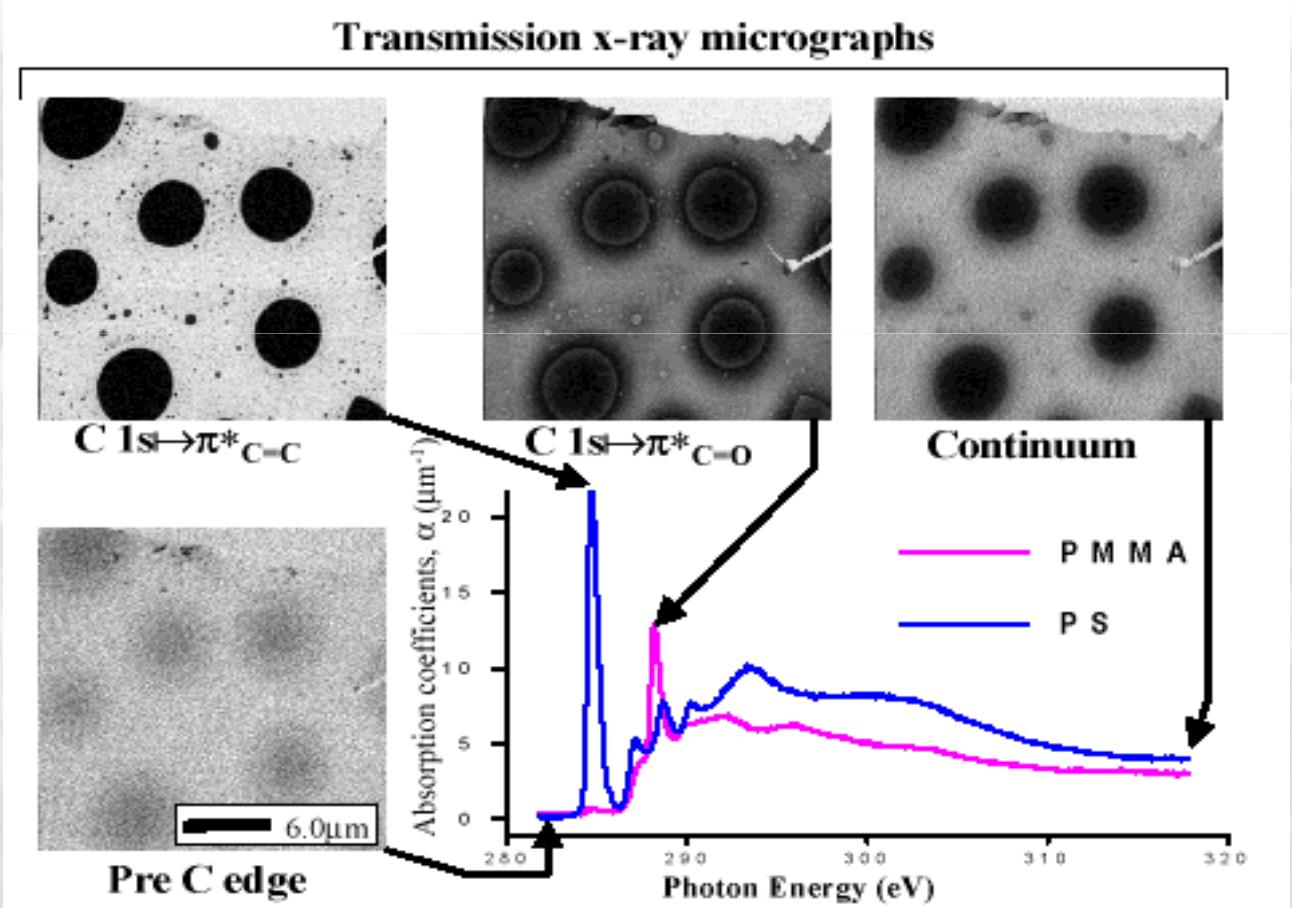



x-ray detectors: spectroscopy & tomogrpahy

2008 - STXM and/or SPEM (17): - ALS (3), APS (2), BESSY2 (1), ELETTRA (3), ESRF (1), PLS (1), NSLS (1), SLS (1), SPRING'8 (1), SRRC (1), CLS (1), DIAMOND (1), Soleil (1). Resolution achieved 25 nm.

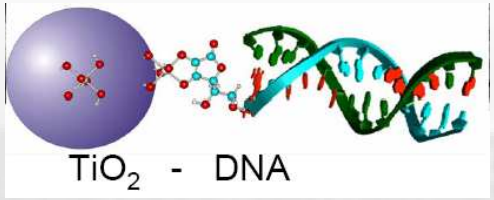
# XANES imaging and spectroscopy with STXM

## Polymer science: outlining the lateral distribution of PS/PMMA using the XANES fingerprints



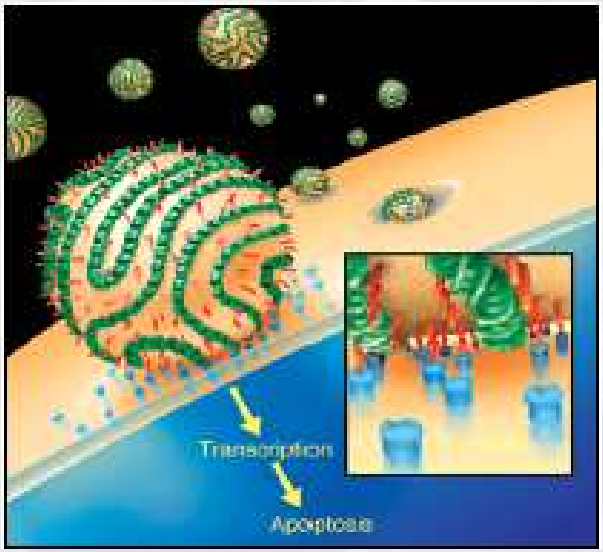

H. Ade et al, STXM at NSLS

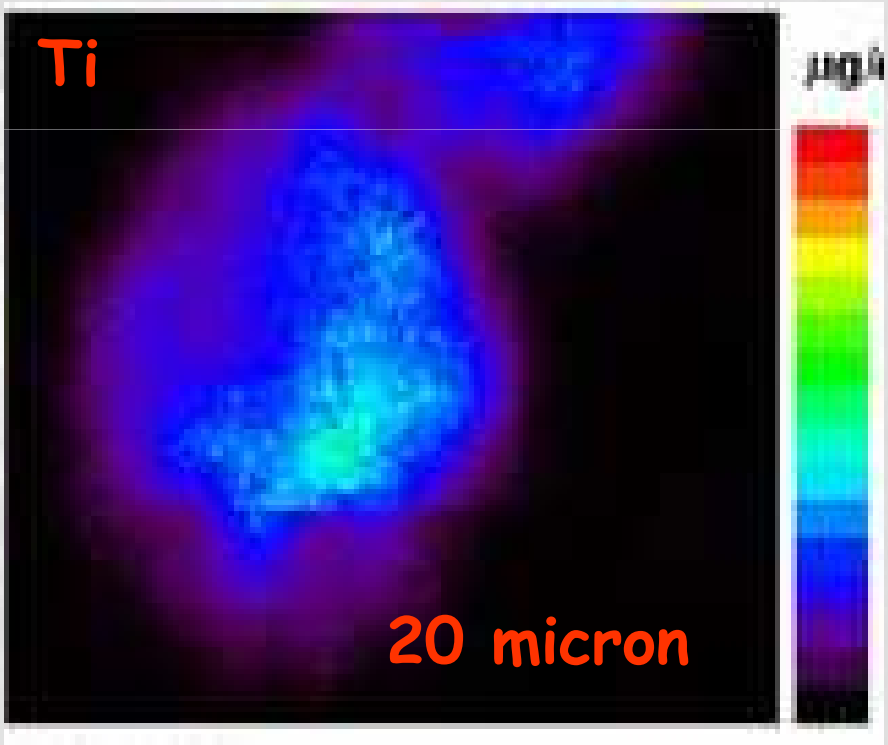
# TiO2-DNA nano-composites for in-vivo Gene Surgery: XRF maps




**Chemical FS imaging is crucial to quantify the success rate and reveal the location of the single stranded nanoparticle in the cell chromosome**

**DNA-TiO2 particle crossing cell walls**

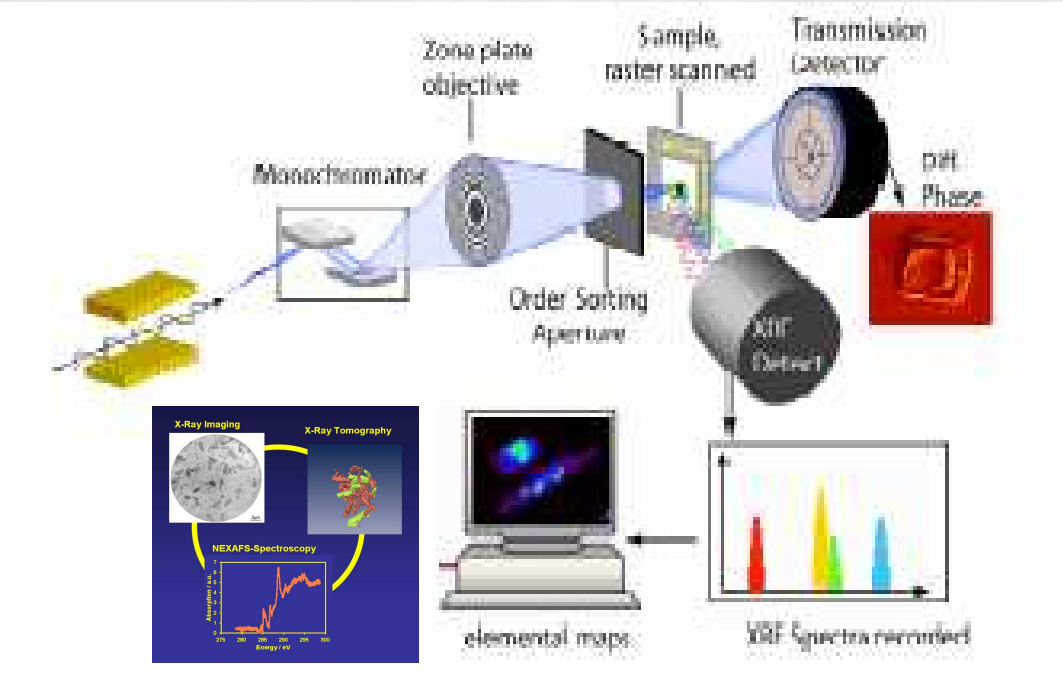


# X-ray contrast based on photon detection

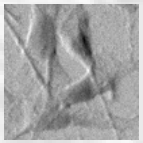
**CHEMICAL SENSITIVITY, VARYING PROBING DEPTH, MORPHOLOGY & STRUCTURE, VERSATILE SPECIMEN ENVIRONMENT**

**COMPLEMENTARY: transmission & XRF + XANES**




## X-ray Absorption

- Bright-field imaging - morphology
- Chemical and magnetic contrast: XAS and XFS



## X-ray Scattering: morphology

- Phase contrast
- Dark-field imaging
- Ptycography

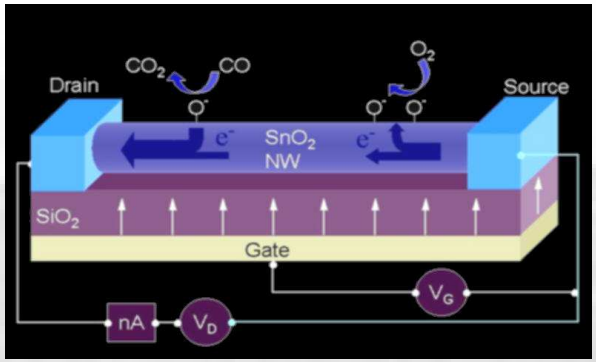
**More details for the FFIM and STXM + XRF techniques and applications in the forthcoming lectures of Burkhard Kaulich**

# Low-dimensional materials and their unique properties

**There's Plenty of Room at the Bottom**

*An Invitation to Enter a New Field of Physics & Material Science*

*Richard P. Feynman - 1959!!!*




Surface 'geometric' structure

**Increased surface-to-volume ratio: the surface status controls physical and chemical properties**

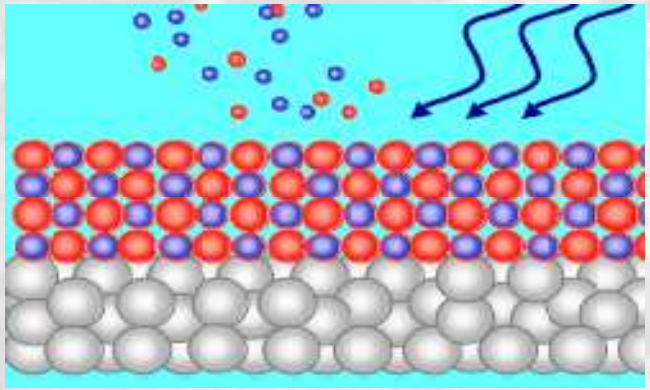
Surface chemistry

Electronic properties and confinement effects

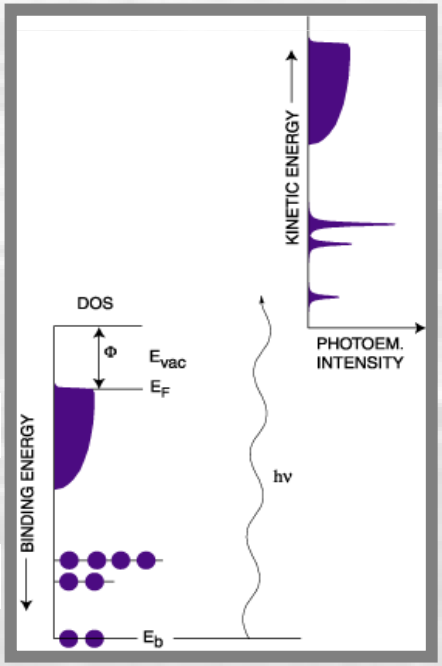
**Spatial resolution with chemical and structural surface sensitivity are needed.**

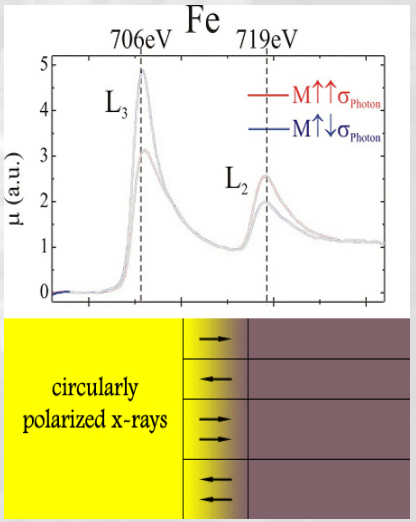
# All information of PES at microscopic scales

- Qualitative and quantitative elemental information: CL
- Chemical composition and chemical bonding:CL & VB
- Electronic and magnetic structure (VB, ARUPS, PED, XMCD-XMLD with secondary electrons (XANES).
- Information depth < 10 nm (surface sensitive)

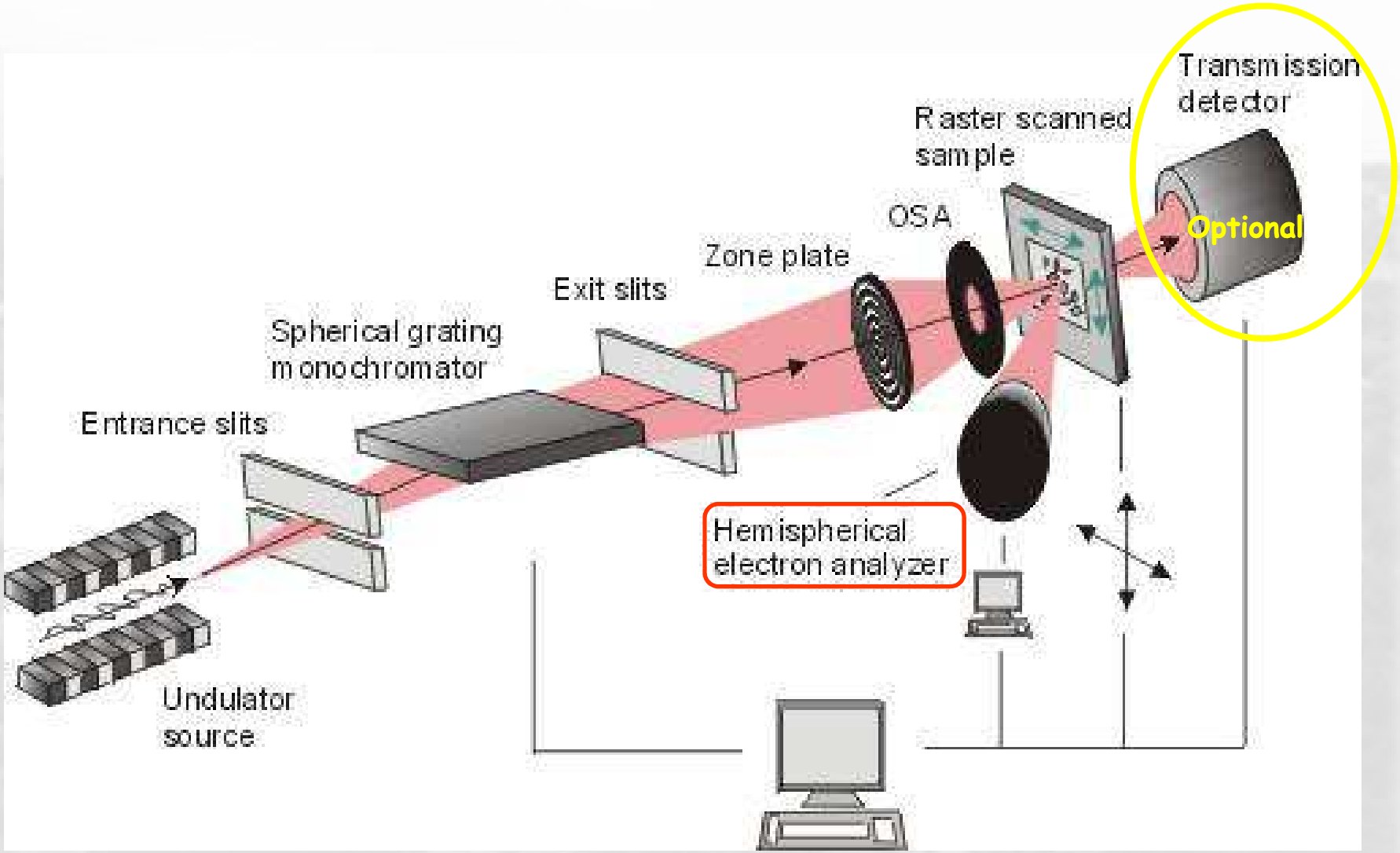


*Information depth = dsin$\theta$*
*d = Escape depth ~ 3 $\lambda$*
*$\theta$ = Emission angle relative to surface*
*$\lambda$ = Inelastic Mean Free Path*



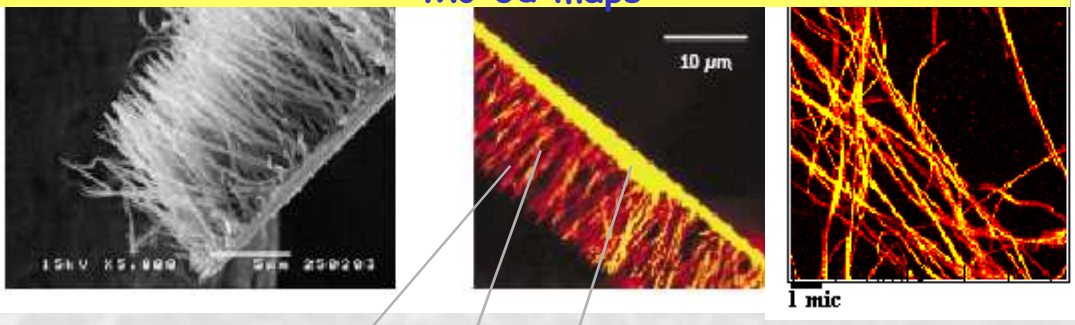



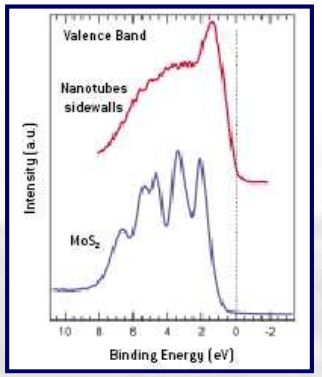
# Scanning photoelectron microscopy: PES and XANES

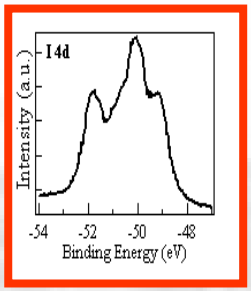


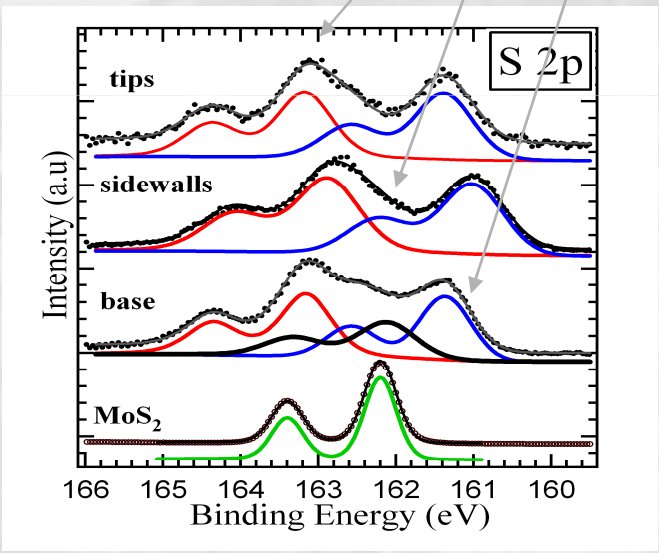
# SPEM characterization of $MoS_2$-nanotubes

**Twisted chiral bundles of Mo-S individual cylinders: Mo 3d maps**



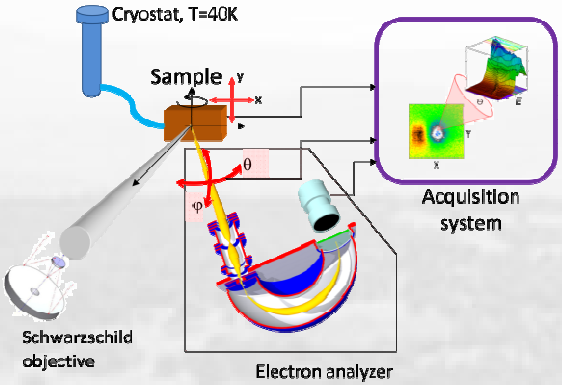



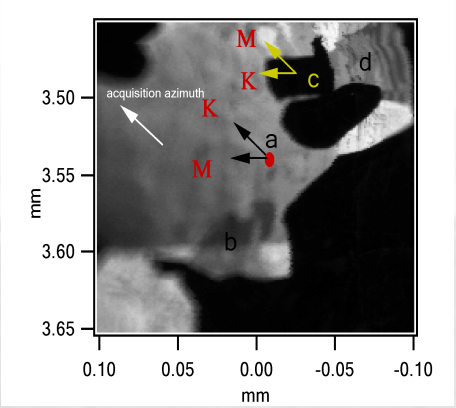

**SPEM revealed I (used as a carrier) in interstitial positions between the tubes bonded to the outer S atoms.**

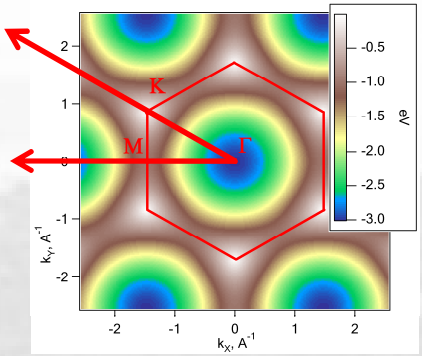
**Due to the low dimensionality the S 2p, Mo 3d and VB spectra are position-dependent and reflect electronic properties significantly different those of the $MoS_2$ crystal.**

**More details for the SPEM technique and applications in the forthcoming lectures of Luca Gregoratti**

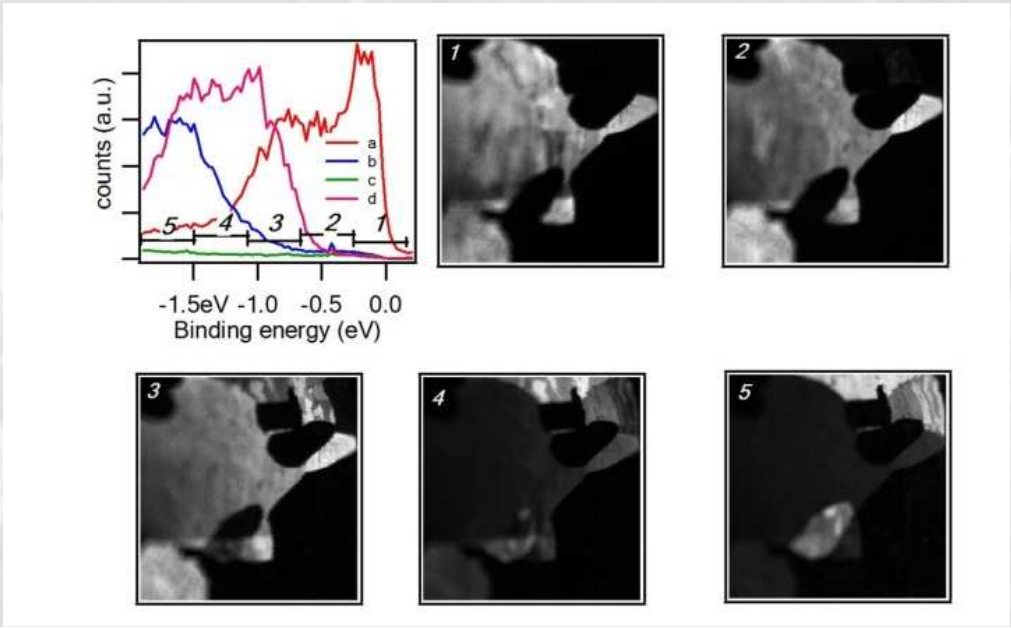
# Scanning photoelectron microscopy with ARUPS at Elettra



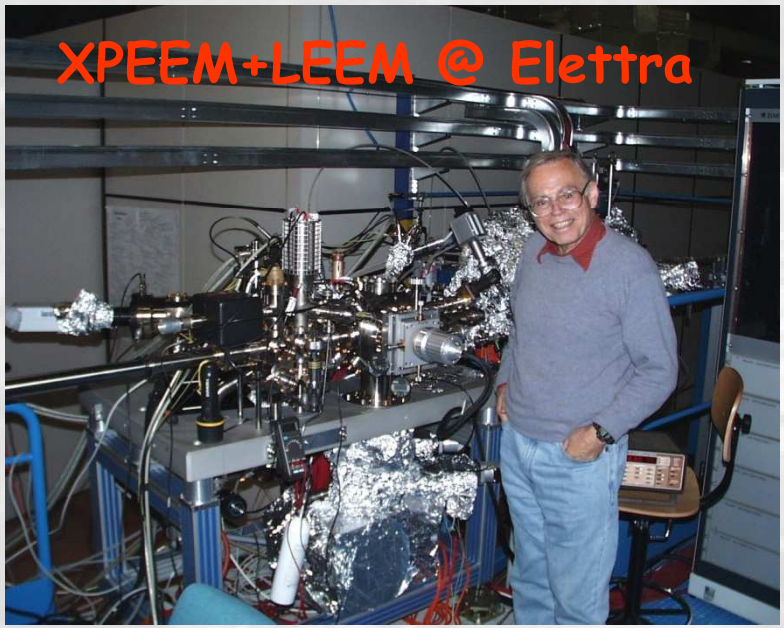

π-band dispersion of HOPG

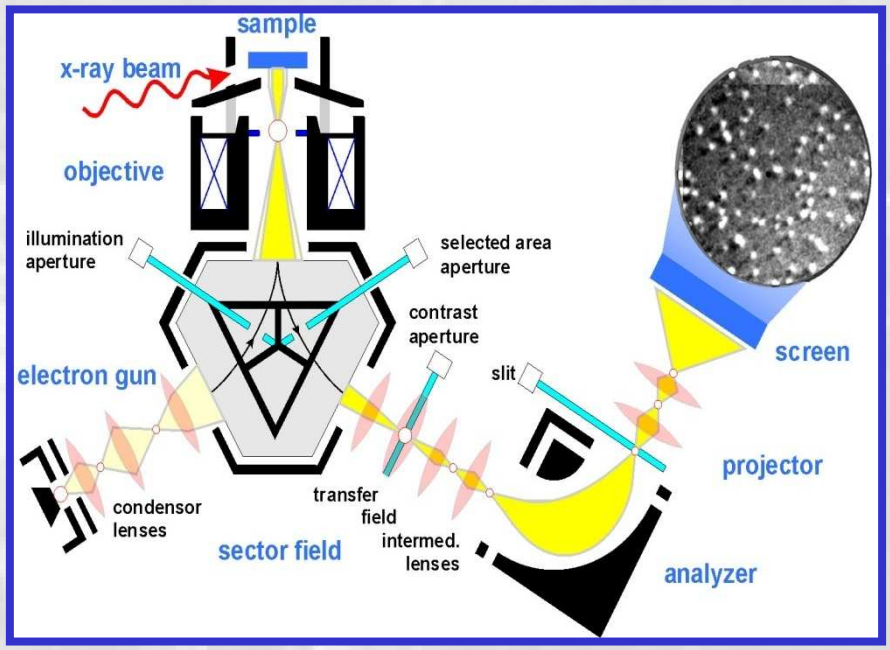



## ARPES microscope: orientation disorder of graphite flakes

# X-ray Imaging PhotoEmission Electron Microscopy (XPEEM) (+ LEEM)

History: PEEM-early 1930s, XPEEM late 1980s
Ernst Bauer (Uni Claustal), W. Engel (FHI-Berlin).B. Tonner (SRC)
The 1st XPEEM with energy analyser (XPS&XAS) – early 1990s

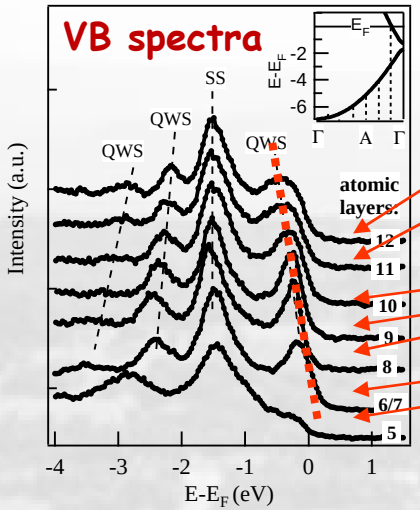


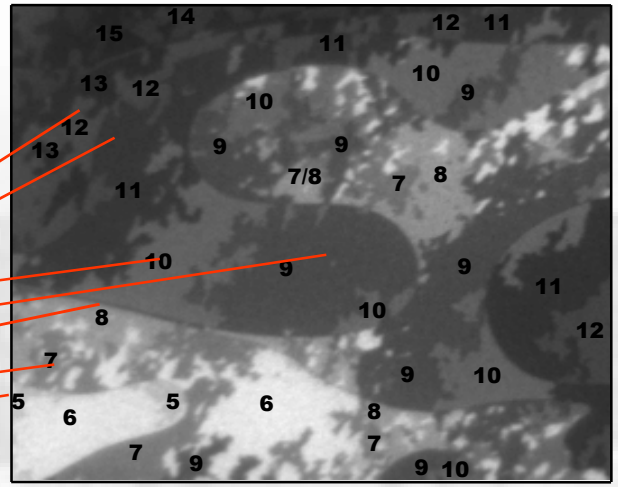

2006- XPEEM (19): ALS(1), APS(1), BESSY II (2), ELETTRA (1), NSLS (1), PLS (1), SPRING'8 (2), SLS (1*), SRRC (1), SRS(1), MAXLab (1*), CLS (1*), SOLEIL(1), DIAMOND (1), APS (1), Alba (1). Resolution achieved 20 nm.

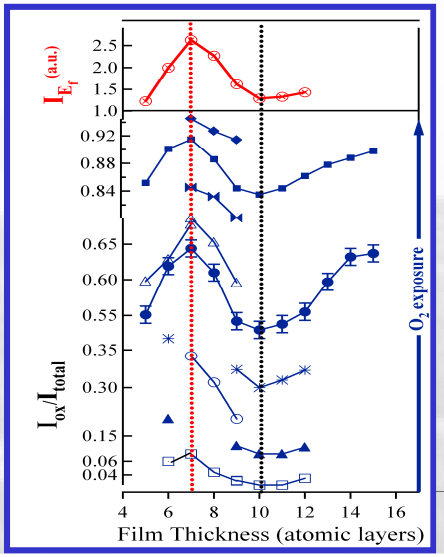
# LEEM-XPEEM: Mg Films on W(110)

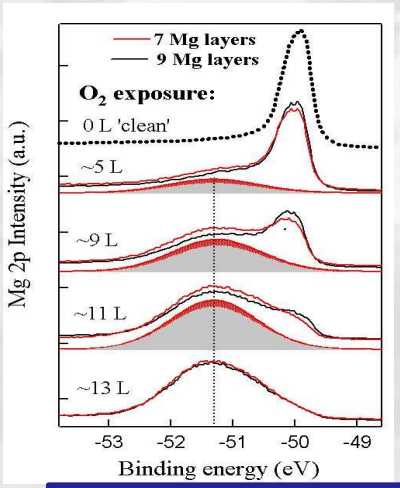
## Thickness-Electron Confinement-Oxidation rate



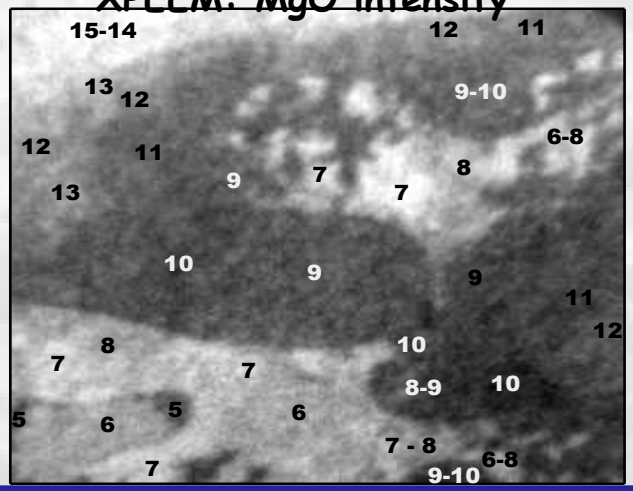

LEEM - thickness






XPEEM: MgO intensity

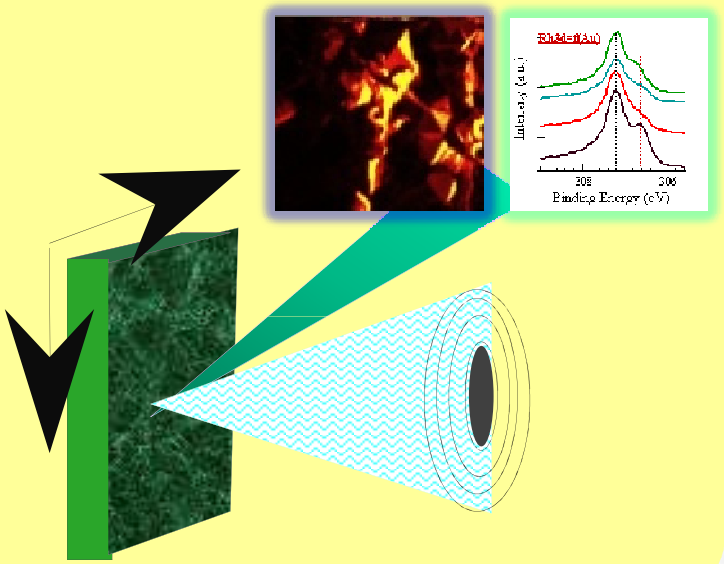


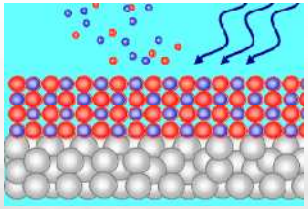
Oxidation rate quantitatively correlates to the oscillations in the electron density at the Fermi level

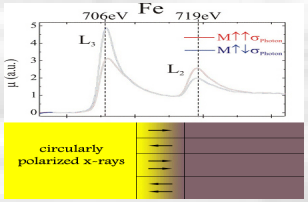
**More details for the XPEEM-LEEM technique and applications in the forthcoming lectures of Andrea Locatelli**

# Synchrotron-based photoelectron microscopes: they are complementary

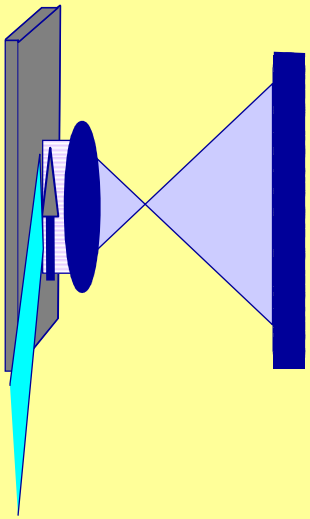
## SPEM

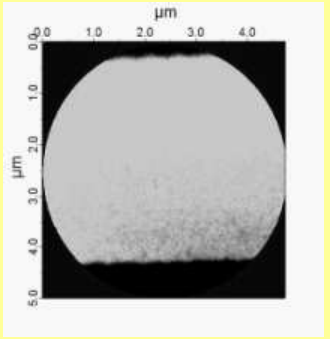





## XPEEM-LEEM

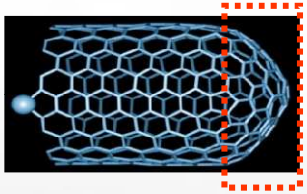





+ Full power of XPS
+ Spectro-imaging.
+ Flexible sample geometry and FOV.
+ Insensitive to sample roughness;
- Fast processes or XANES.
- Lateral resolution (50 nm).

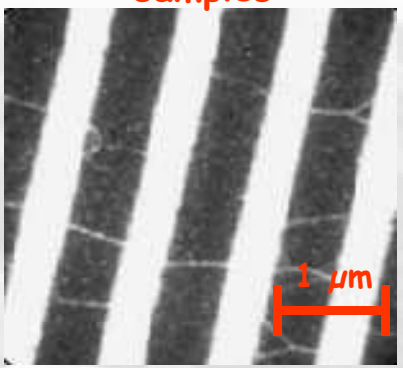
+ Lateral resolution (<5nm imaging)
+ Dynamic studies;
+ XANES, PED&ARUPS.
+ LEEM & m-LEED: structure
- XPS spectral resolution
- sample roughness and size.

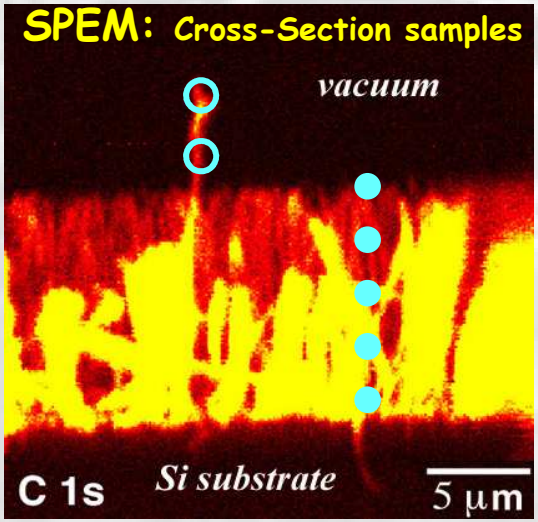
# Carbon nanotubes with SPEM and XPEEM: C 1s images and spectroscopy

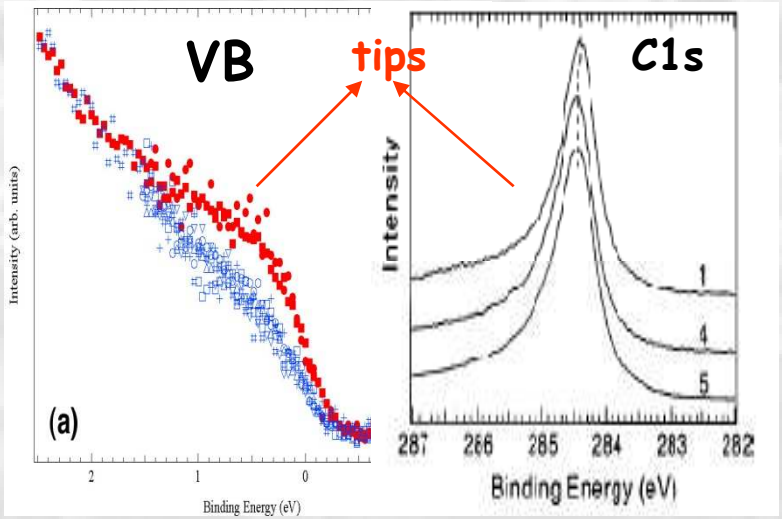


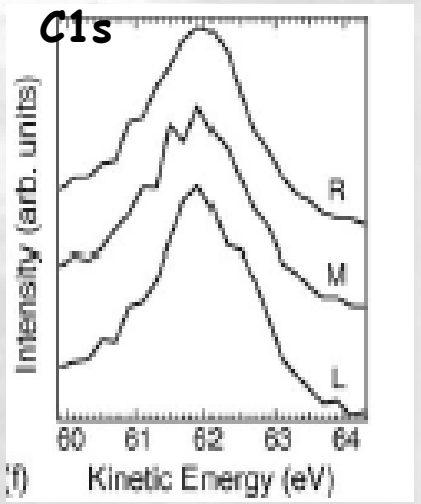
**Valence band and C1s spectra evidence different local electronic structures at the sidewalls and at the tips of MWCT: higher DB density on spherically curved tips & defects?**

XPEEM: only flat samples




S. Suzuki et al, Phys. Rev B66, 35413 Carbon 42, 559, 35413, JESRP 144, 357

# Classical X-ray imaging and spectromicroscopy: brief outline

| SURFACES & INTERFACES: XPEEM and SPEM | BULK SAMPLES STXM-SPEM-TXM |
|---|---|
| PHOTON IN/ ELECTRON OUT | PHOTON IN/PHOTON OUT |
| (probing depth=f($E_{el}$) max ~ 20 nm) | (probing depth = f ($E_{ph}$) > 100 nm) |
| Spectroscopy (XPS-AES-XANES) ONLY CONDUCTIVE SAMPLES | (Spectroscopy – XFS or XANES) |
| Total $e^-$ yield (sample current) | XANES: Total hν yield, Transmitted x-rays |
| ➢ Chemical surface sensitivity: Quantitative μ-XPS (0.01 ML) | Chemical bulk sensitivity Quantitative μ-XFS |
| ➢ Chemical & electronic (VB) structure | Trace element mapping |

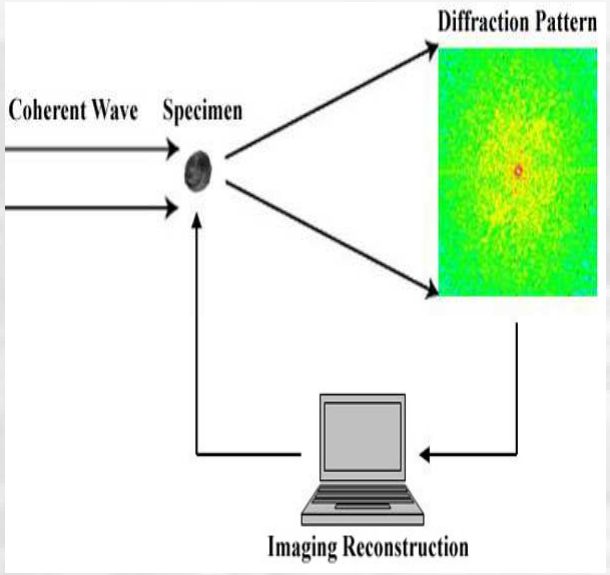
# Imaging – resolution - depth penetration

- X-ray microscopes monitoring electrons - limited to surfaces and resolution depending on the focusing or electron optics
- X-ray microscopes monitoring photons (scanning, full field imaging microscopes) – depth information but limited in lateral and depth resolution by the optical elements: repetition rate and coherence to be considered.
- Electron microscopes, e.g TEM can resolve even atoms but are limited in penetration (samples thinner than ~ 30 nm).

The depth-resolution limitations can in principle be overcome by image reconstruction from measured coherent X ray diffraction pattern: the pattern of the sample is recorded with no optics-imposed resolution limits, i.e. the resolution is only diffraction (wavelength) limited.

# Exploiting the coherence: Coherent Diffraction Imaging

**Based upon the principle of coherent scattering in combination with a method of direct phase recovery called oversampling.**




- The scattered amplitude is a Fourier transform of (complex) electron density f(r): $F(k) = \int f(r)\, e^{-2\pi i\, k \cdot r}\, dr$

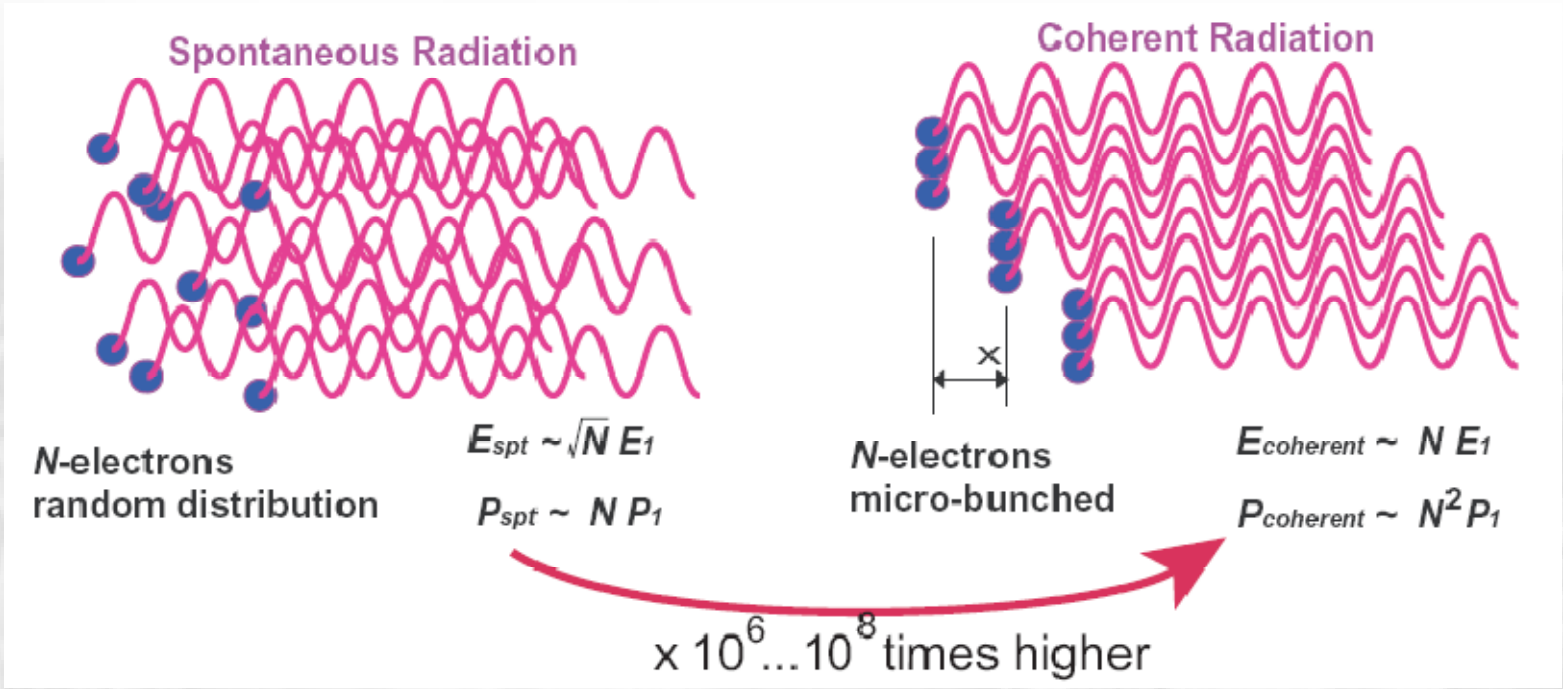
  J. Miao et al, *J. Opt. Soc. Am. A* 15, 1662.

- Phase information retrieved by iterative algorithms applied to oversampled diffraction pattern, or through a mask-based holographically formed interference pattern.

❖ Avoids ~100x signal loss of lenses and can go beyond numerical aperture limit of available optics.

❑ Challenge: algorithms for reconstruction of the holography patterns.

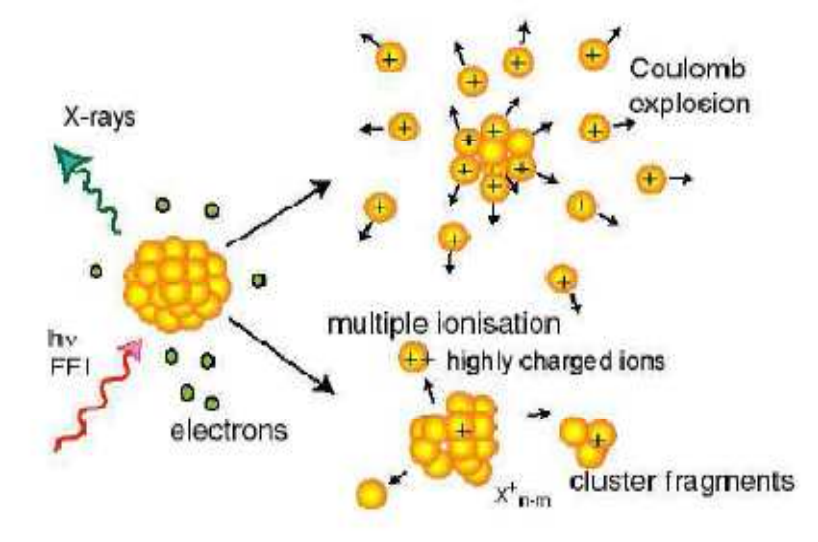
# Synchrotron vs Laser Radiation

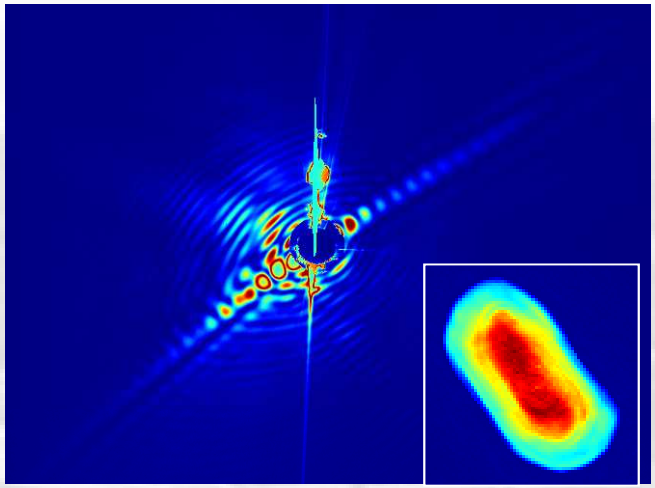



**Synchrotron undulator radiation:** pinhole and monochromators are used for spatial and spectral filtering, but the at the expense of intensity!

**FEL:** natural coherence each electron emits spontaneous emission that overlap each other in phase

# Time scales for 'non-destructive' flash imaging: get information in a single shot!

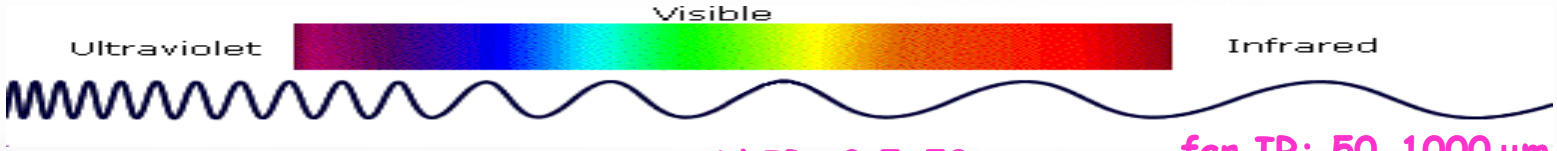


⇒ With an of pulse length < 50 fs and 3 x $10^{12}$ photons focused down to a spot of ~ 0.1 μm, a 2D diffraction pattern can be recorded before the radiation damage manifests itself.

**More details for the CDI technique and applications using synchrotrons and FELs in the forthcoming lectures of Janos² Kirz and Hajdu**

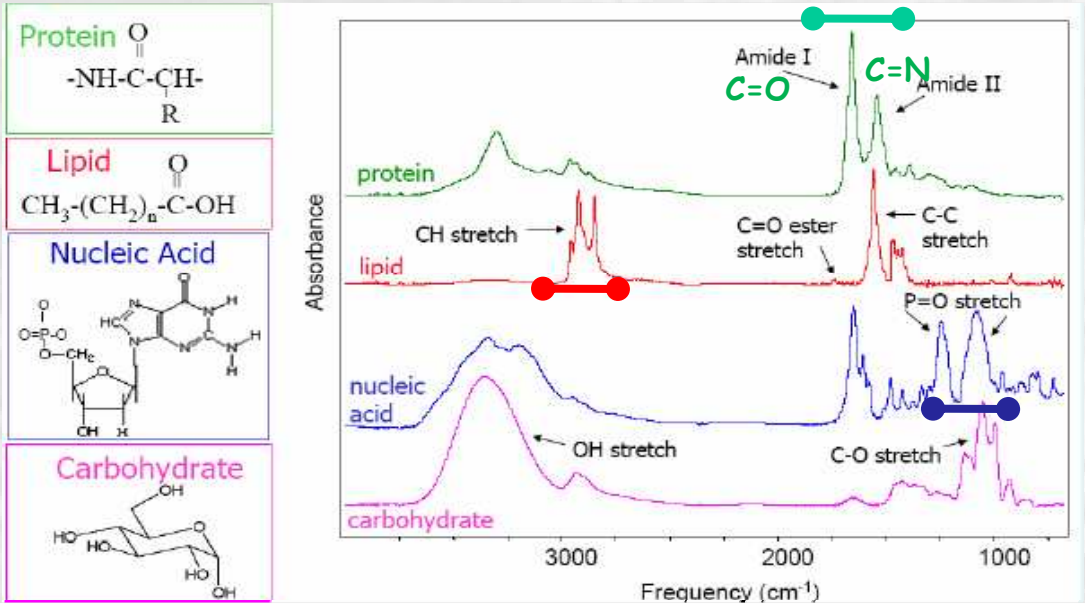
# Infrared Specromicroscopy

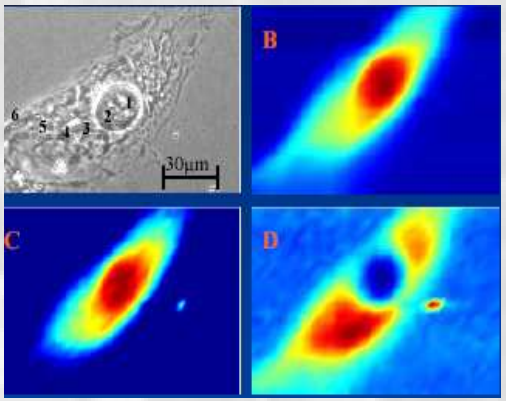



near IR: 0.8-2.5 μm
Phonons,
Molecular Rotations

mid IR: 2.5-50 μm
Molecular Vibrations
Electronic excitations

far IR: 50-1000 μm
Molecular Overtones
Bands combinations,
Excitons

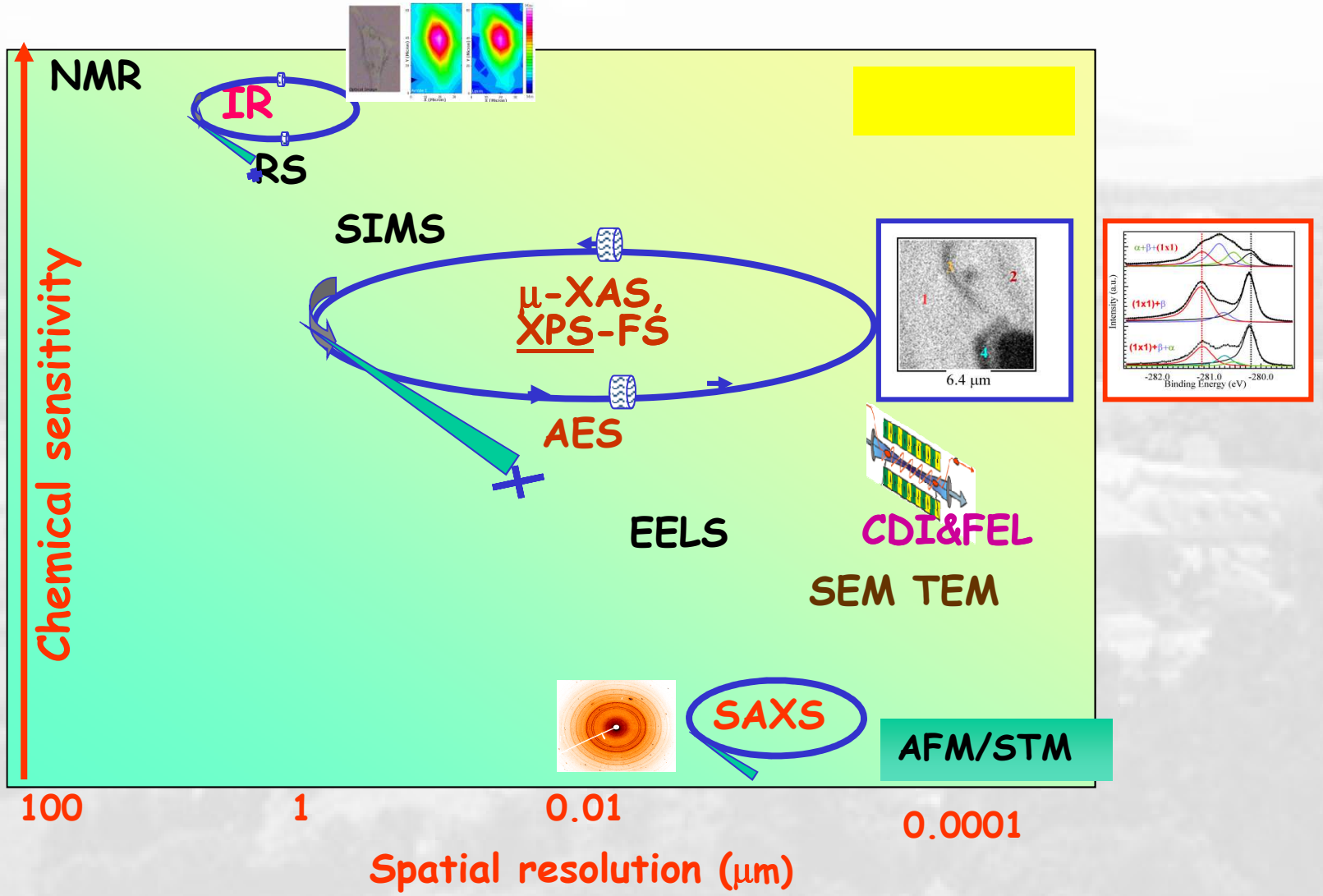



Band components (intensity, position, width and shape) are sensitive to chemical changes and physical properties

More details for the IRMS technique and applications in the forthcoming lectures of Paul Dumas, Lisa Vaccari and Andrea Perucchi

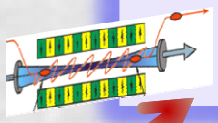
# Chemical specificity and resolution using SR



# Enjoy the following Lectures

**X-ray microscopy: absorption & phase contrast**
**(lectures Kaulich)**
- 2D/ 3D morphology
- High resolution.
- Density mapping.

**X-ray (Coherent) Scattering**
**(lectures Kirz-Hajdu)**
- Structure: stress/strain/texture 2D/3D mapping.
- Chemistry at resonances



**Photoelectron Spectromicroscopy:**
**(lectures Gregoratti-Locatelli)**
- Chemical state
- Chemical mapping.
- Surface sensitive.

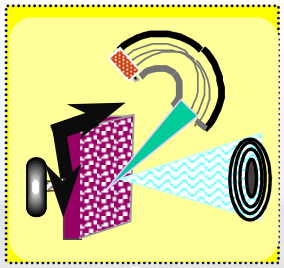
**Fluorescence spectromicroscopy**
**(lectures Kaulich)**
- Elemental quantification
- Elemental mapping
- Bulk sensitive

**X-ray Absorption Spectromicroscopy**
**(lectures Locatelli-Kaulich)**
- Short range structure.
- Electronic and magnetic structure.
- Chemical mapping.
- Depth information determined by the collected signal – electrons or photons

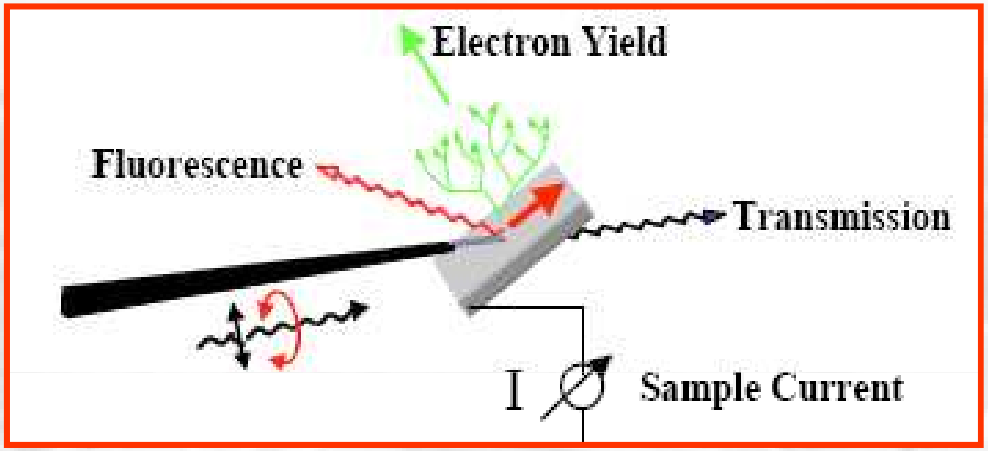
**Infrared Spectromicroscopy**
**(lectures Dumas-Vaccari-Perucchi)**
- Molecular groups and structure
- High S/N for organic matter
- Functional group imaging.
- Modest resolution but non-destructive radiation.

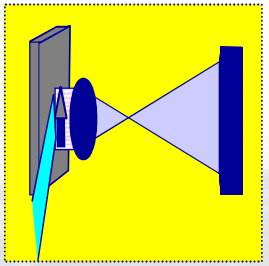
# Microscopy @ Elettra: visit May 6th

## hν-in/e⁻-out: PE & XAS

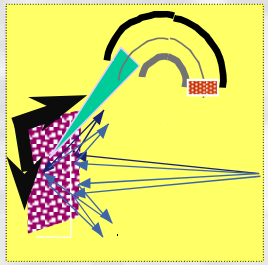


**SPEM-ZP:**
ESCA microscopy
1995 -



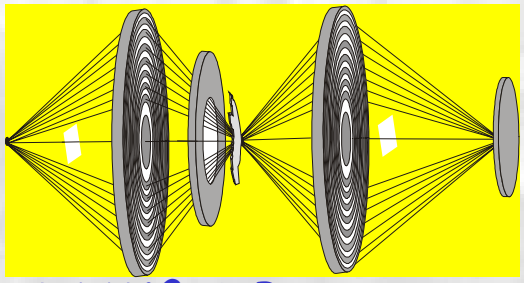



**XPEEM:**
Nanospectroscopy
2001 -

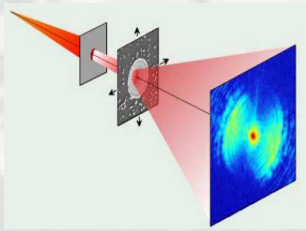


**SPEM-SO:**
Spectromicroscopy
1998 -
now developed as
μ-ARPES

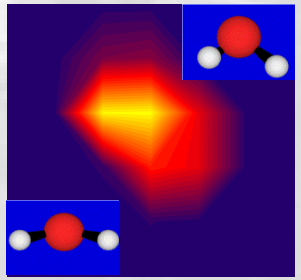
## hν-in/hν-out: XAS (FS), CDI & IRAS



**TXM²-ZP:** TwinMic
2005 -



**DiProI@Fermi**
**commissioning**



**IRAS:** SISSI
2005