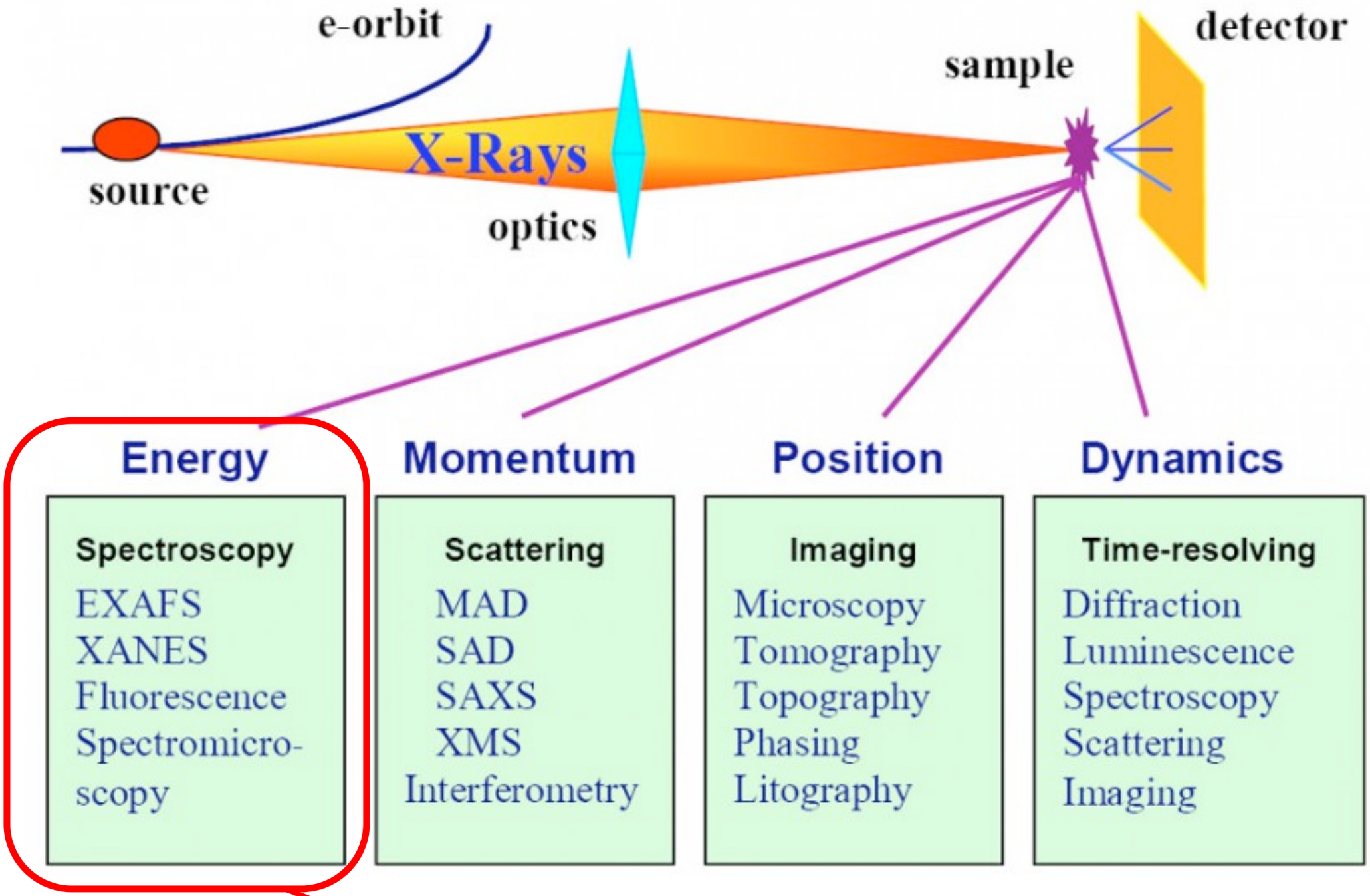
Generic SR experiment

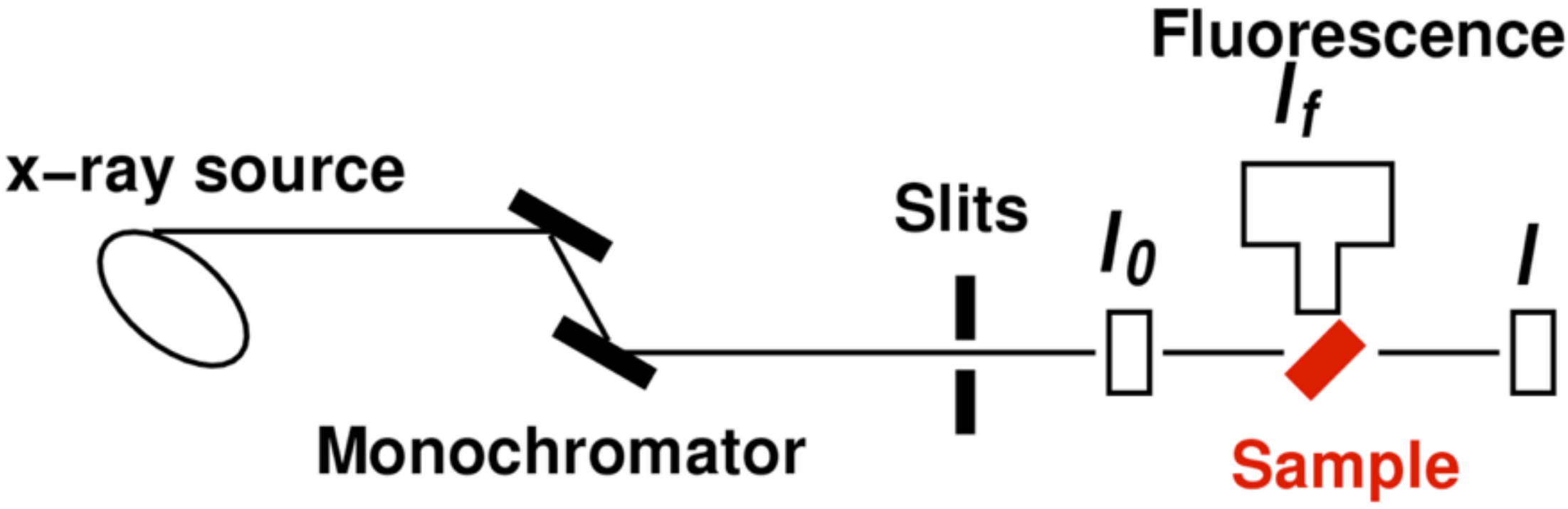


Radiation Absorption

Electrons NOT leaving the sample:

XAFS
(X-ray Absorption Fine Structure)

XAFS measurement scheme



We want to measure the energy dependence of the x-ray absorption coefficient μ(E). It can be measured:

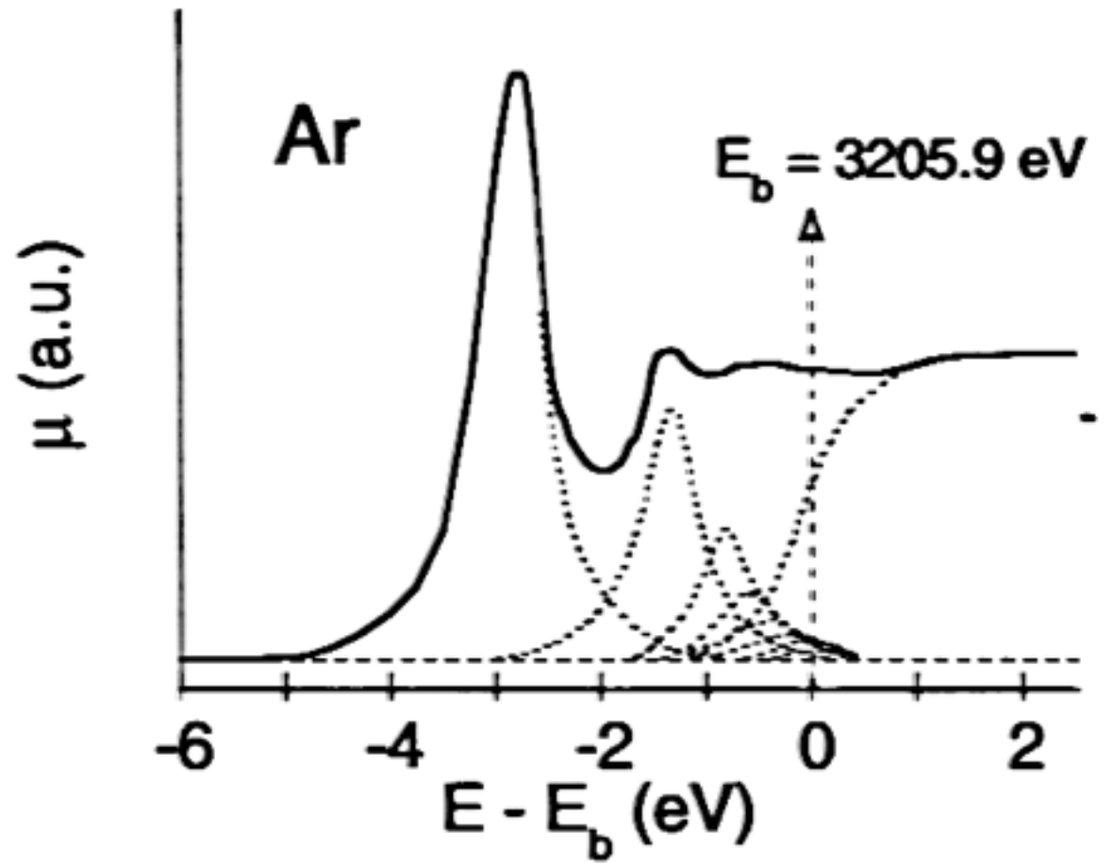
- Directly by measuring I and I_0:

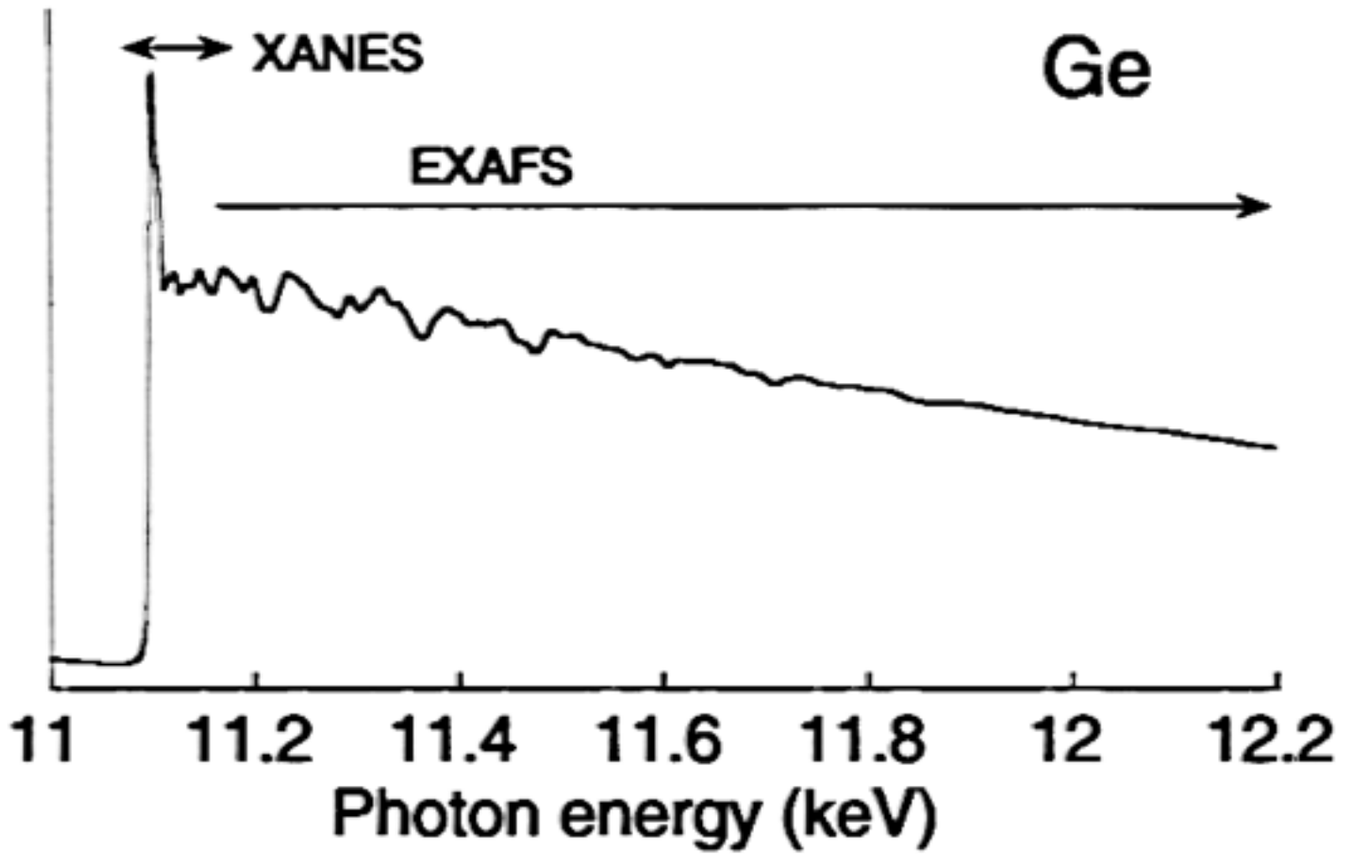
$$\mu(E) = -\frac{1}{d}\ln\left[\frac{I}{I_0}\right]$$

- By measuring the signal from a recombination process of the core-hole, i.e. by measuring the fluorescence yield or the Auger yield. In this case:

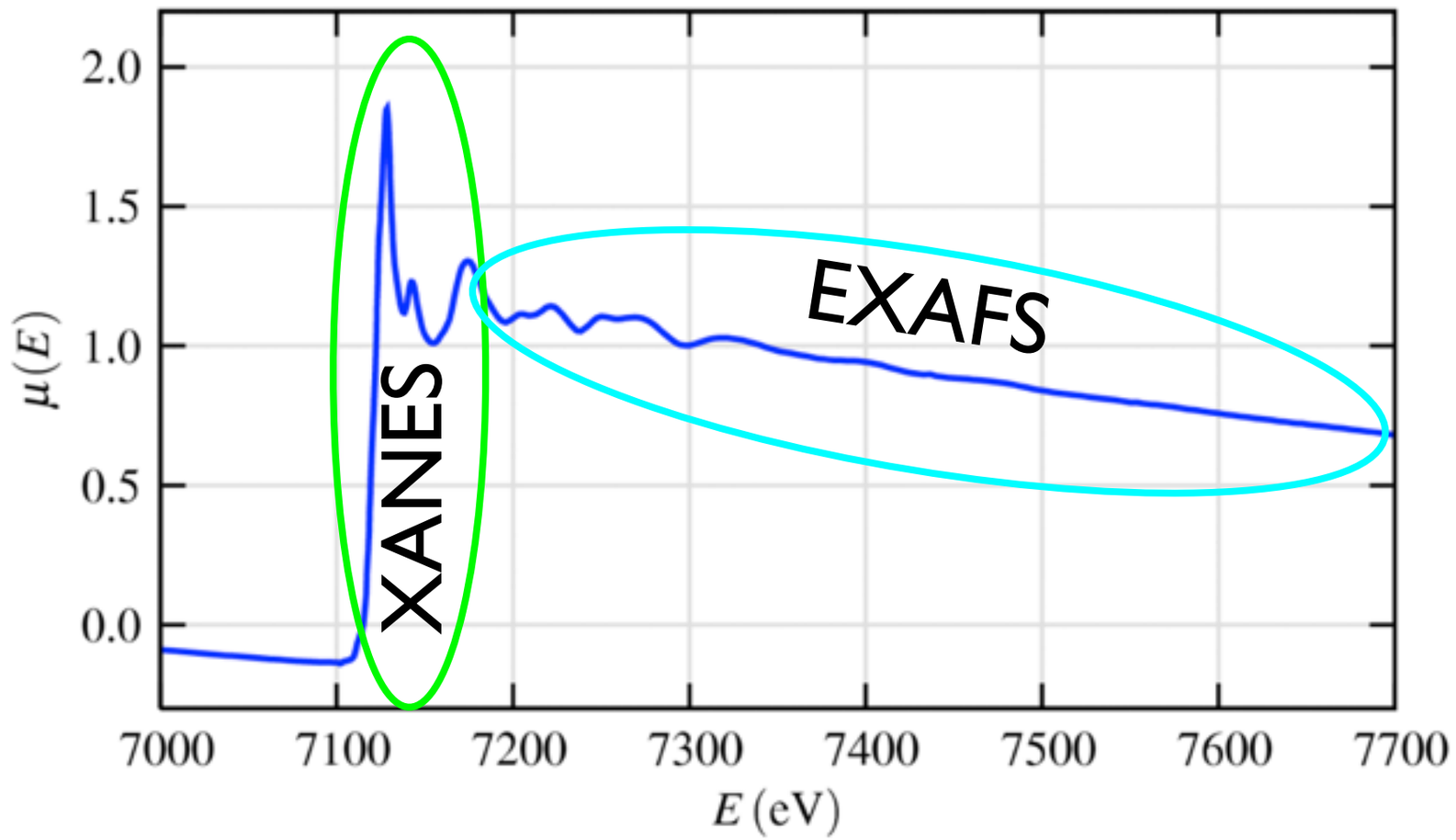
$$\mu(E) \propto \frac{I_f}{I_0}$$

The k-edge absorption in isolated atoms and in a solid





A typical (FeO) solid state k-edge spectrum.

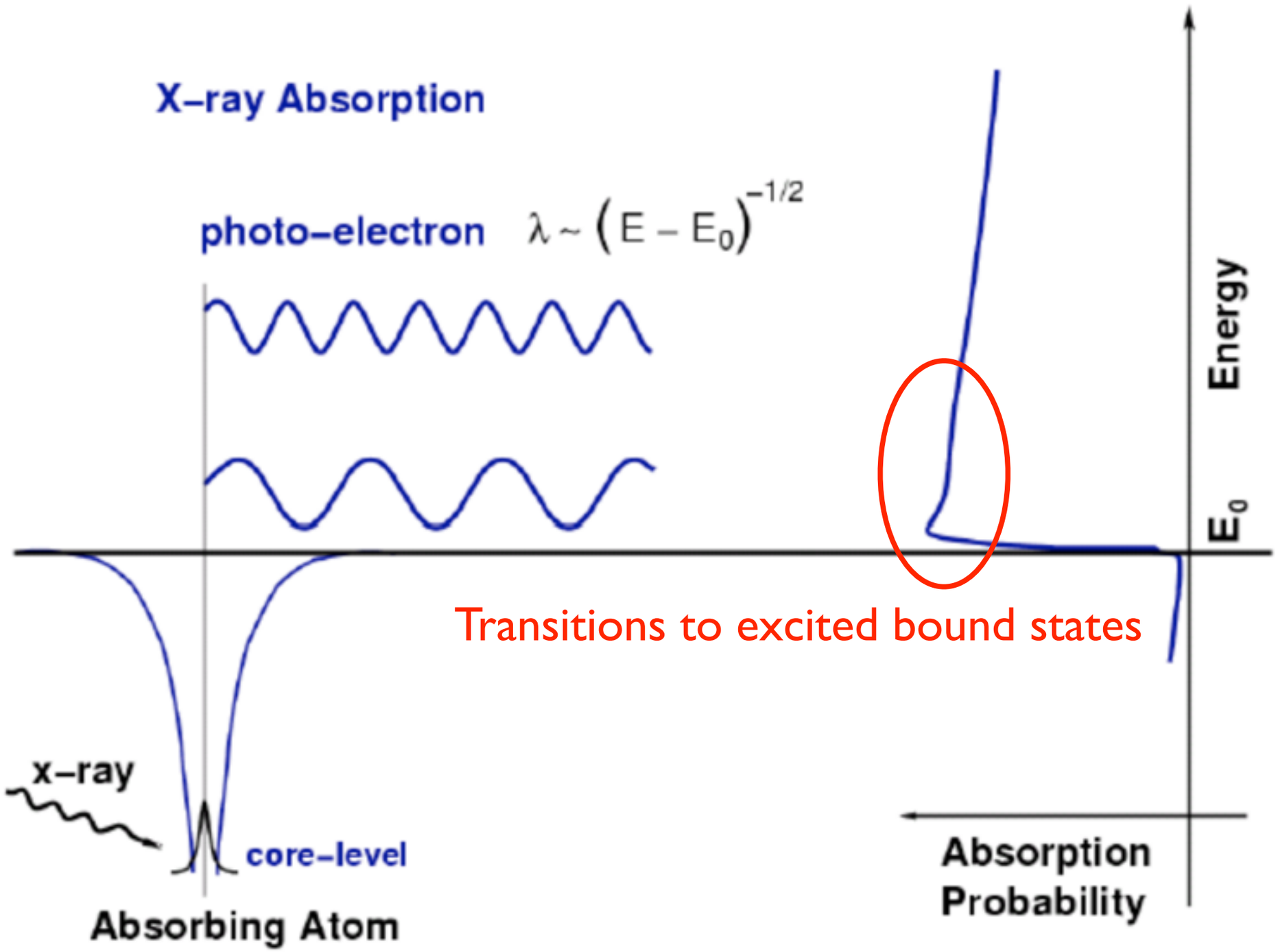


The absorption coefficient in the dipole approximation and for wavelengths >>r_0 is given by:

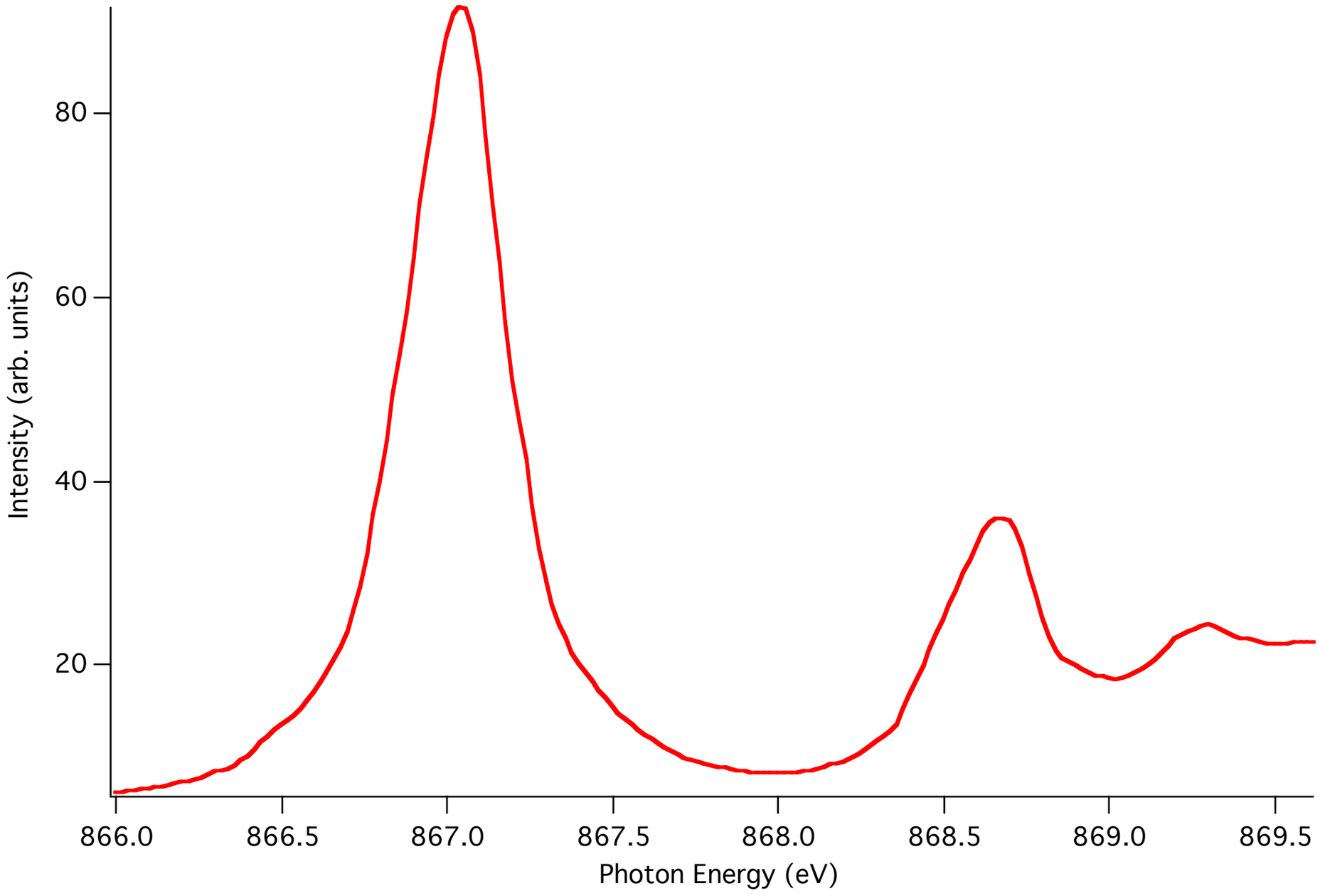
$$\mu(\hbar\omega) = \frac{4\pi^2 e^2}{nm^2 c\omega} \sum_{if} |\hat{e} \cdot \langle f| \vec{p} |i\rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

For an isolated atom

$$\mu(\hbar\omega) = \frac{4\pi^2 e^2}{nm^2 c\omega} \sum_{if} |\hat{e} \cdot \langle f | \vec{p} | i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

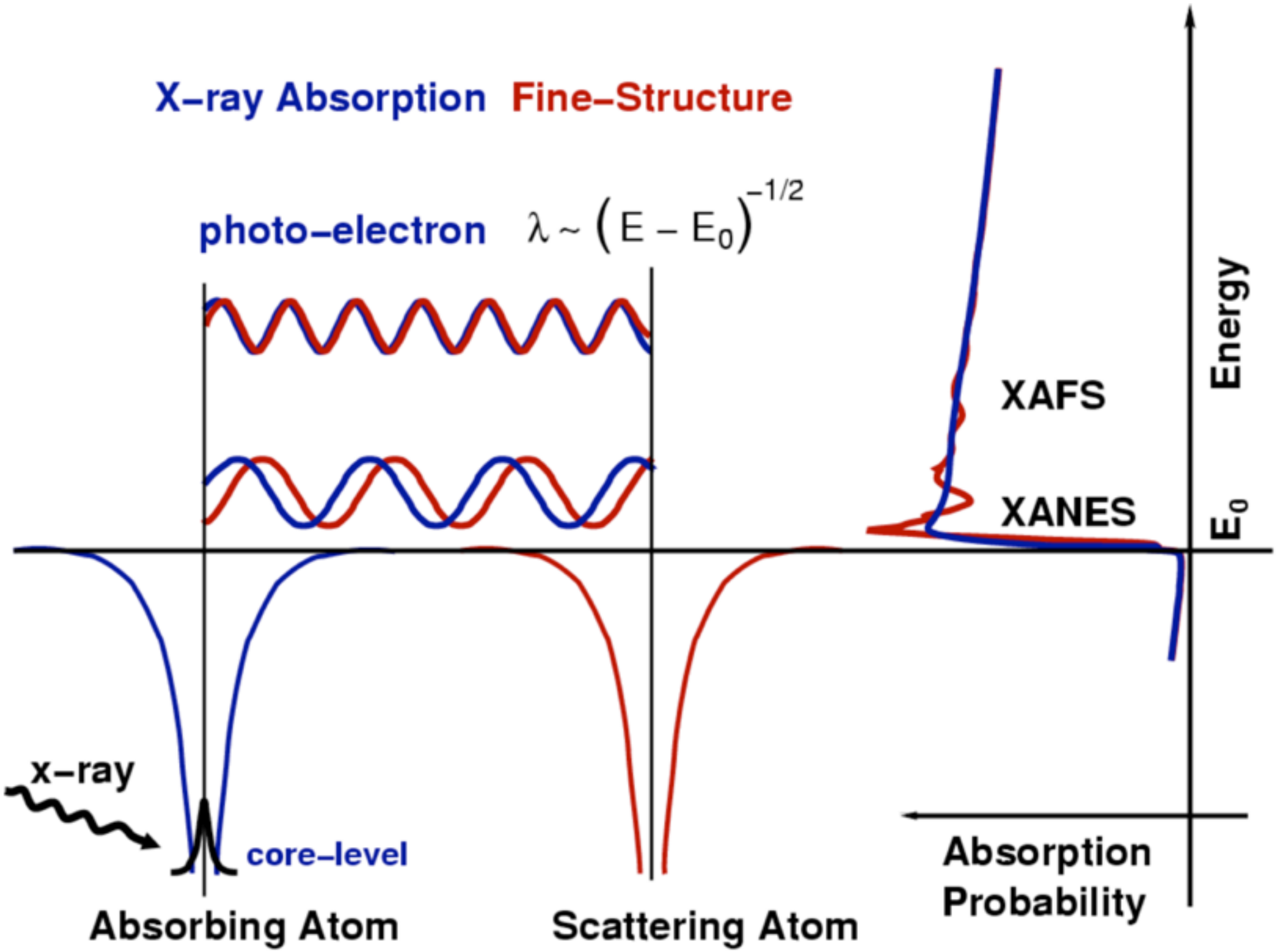


Isolated atoms: the Ne K-edge excitation



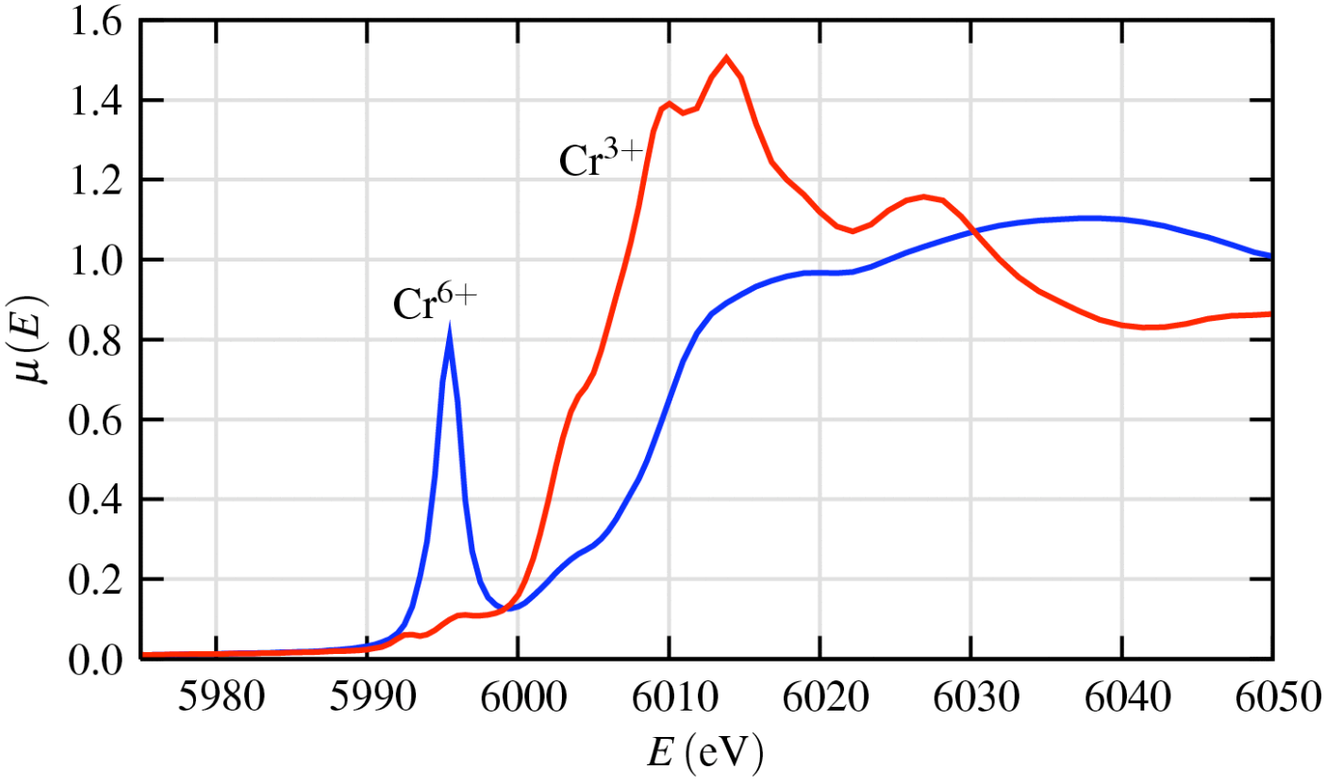
For a two atom system

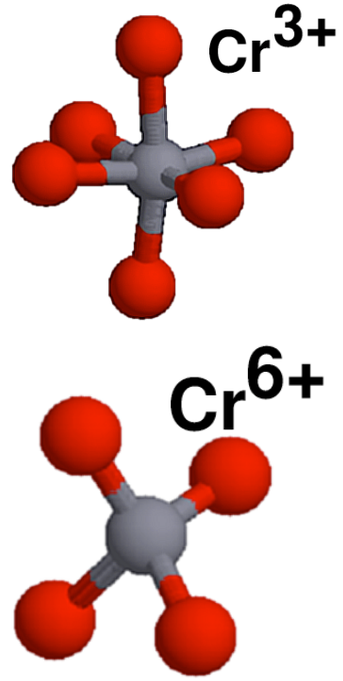
$$\mu(\hbar\omega) = \frac{4\pi^2 e^2}{nm^2 c\omega} \sum_{if} |\hat{e} \cdot \langle f | \vec{p} | i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$



XANES

XANES Analysis: Oxidation State and Coordination Chemistry



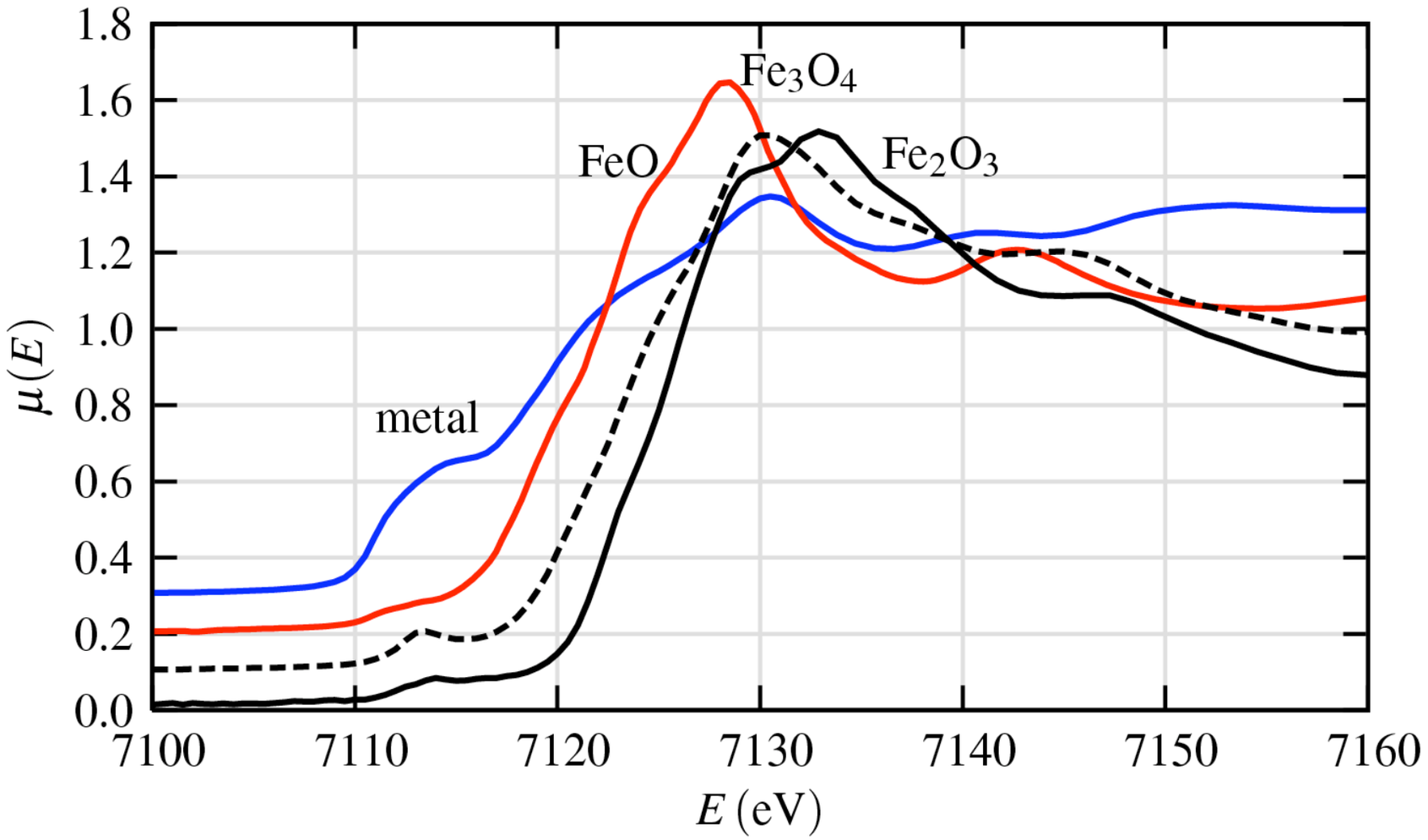


The XANES of Cr^{3+} and Cr^{6+} shows a dramatic dependence on oxidation state and coordination chemistry.

For ions with partially filled d shells, the p-d hybridization changes dramatically as *regular octahedra* distort, and is very large for *tetrahedral* coordination.

This gives a dramatic *pre-edge peak* – absorption to a localized electronic state.

Edge Shifts and Pre-edge Peaks in Fe oxides

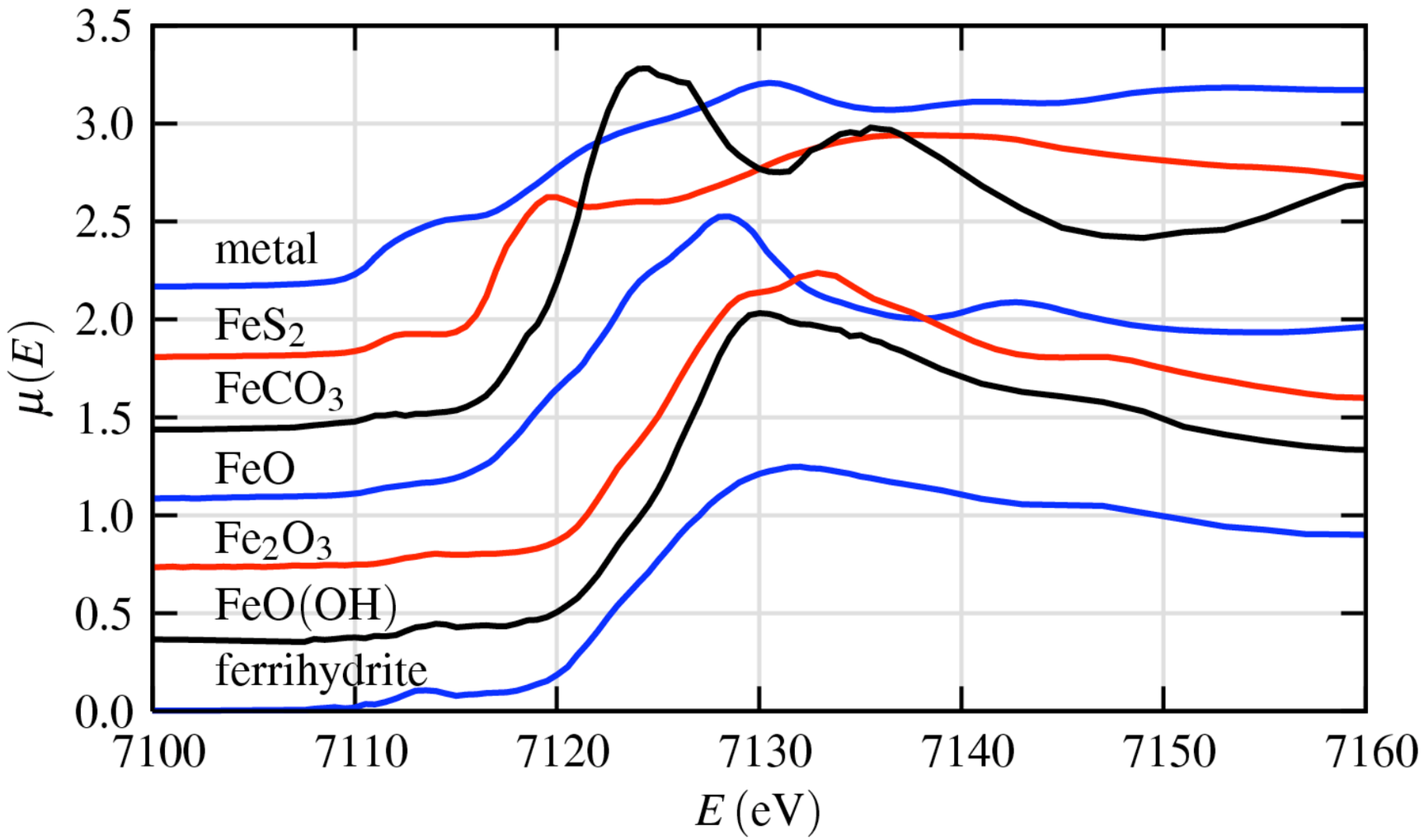


XANES for Fe oxides and metal. **The shift of the edge position can be used to determine the valence state.**

The heights and positions of pre-edge peaks can also be reliably used to determine Fe^{3+}/Fe^{2+} ratios (and similar ratios for many cations).

XANES Analysis: Oxidation State

The Normalized XANES from several Fe compounds:

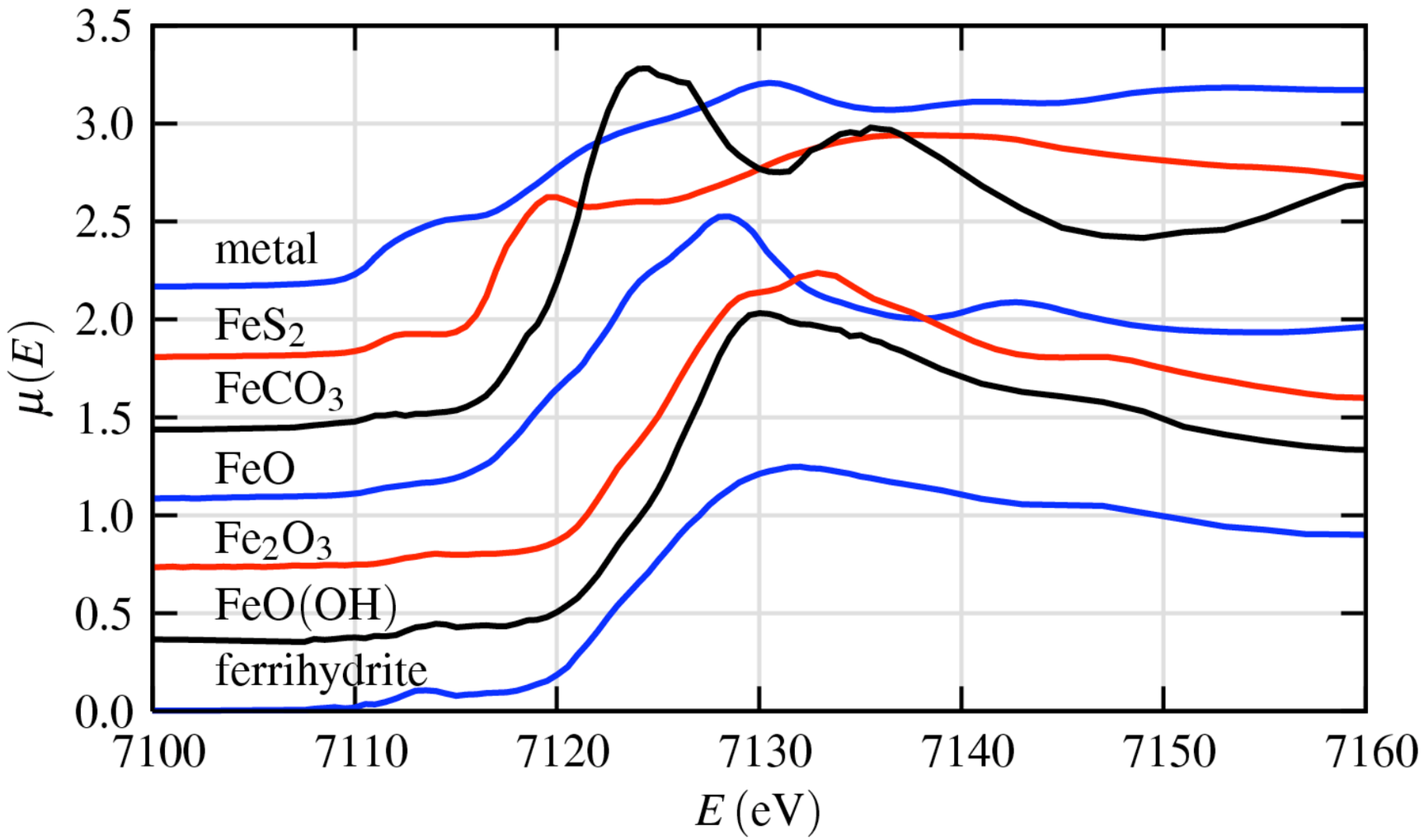


XANES can be used simply as a fingerprint of phases and oxidation state.

XANES Analysis can be as simple as making linear combinations of "known" spectra to get compositional fraction of these components.

XANES Analysis: Oxidation State

The Normalized XANES from several Fe compounds:



XANES can be used simply as a fingerprint of phases and oxidation state.

XANES Analysis can be as simple as making linear combinations of "known" spectra to get compositional fraction of these components.

XANES: Conclusions

XANES is a much larger signal than EXAFS

XANES can be done at lower concentrations, and less-than-perfect sample conditions.

XANES is easier to crudely interpret than EXAFS

For many systems, the XANES analysis based on linear combinations of known spectra from "model compounds" is sufficient.

XANES is harder to fully interpret than EXAFS

The exact physical and chemical interpretation of all spectral features is still difficult to do accurately, precisely, and reliably.

This situation is improving, so stay tuned to the progress in XANES calculations . . . .

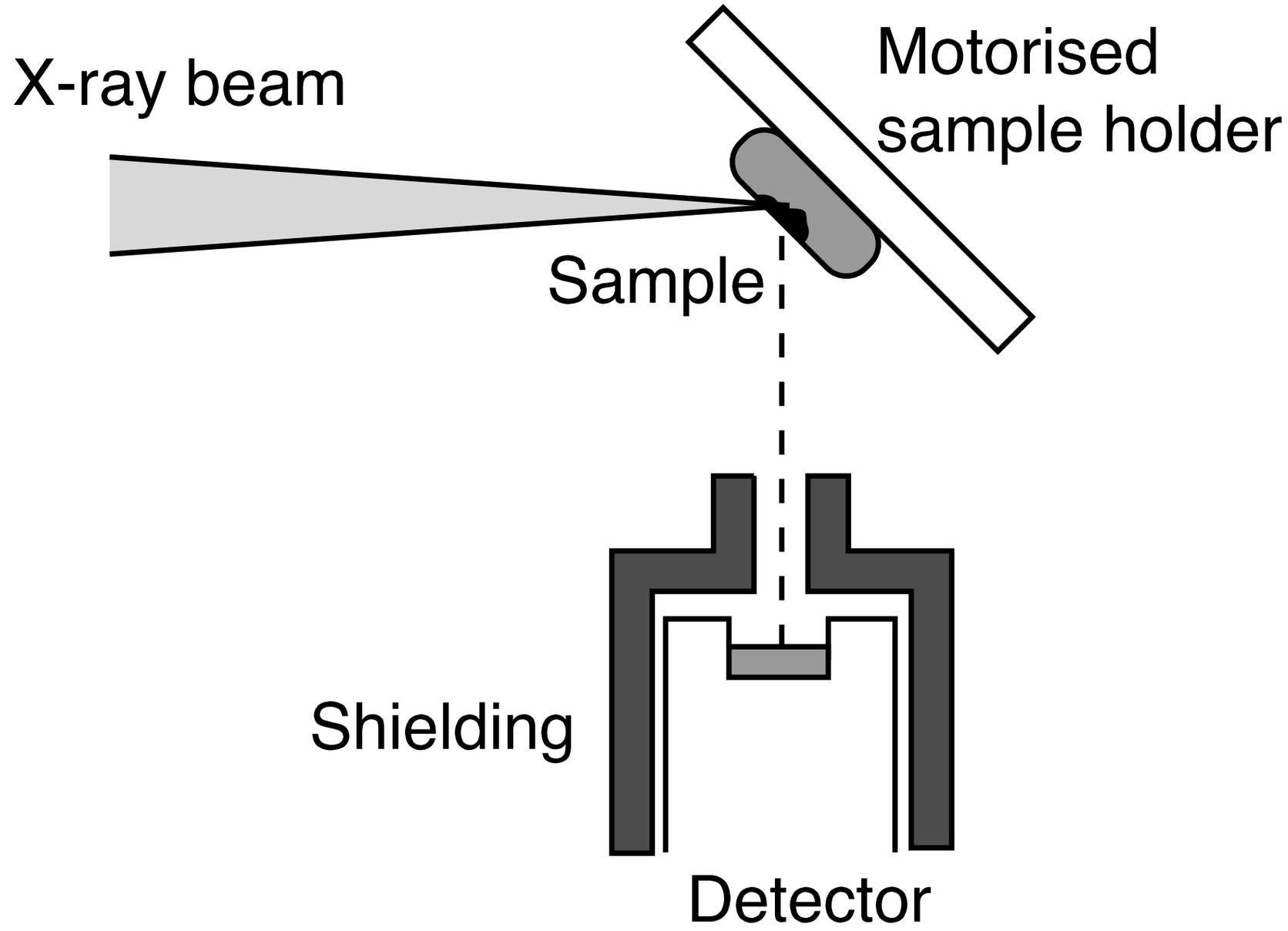
Anal. Chem. **2008,** *80,* 6436–6442

Visualization of a Lost Painting by Vincent van Gogh Using Synchrotron Radiation Based X-ray Fluorescence Elemental Mapping

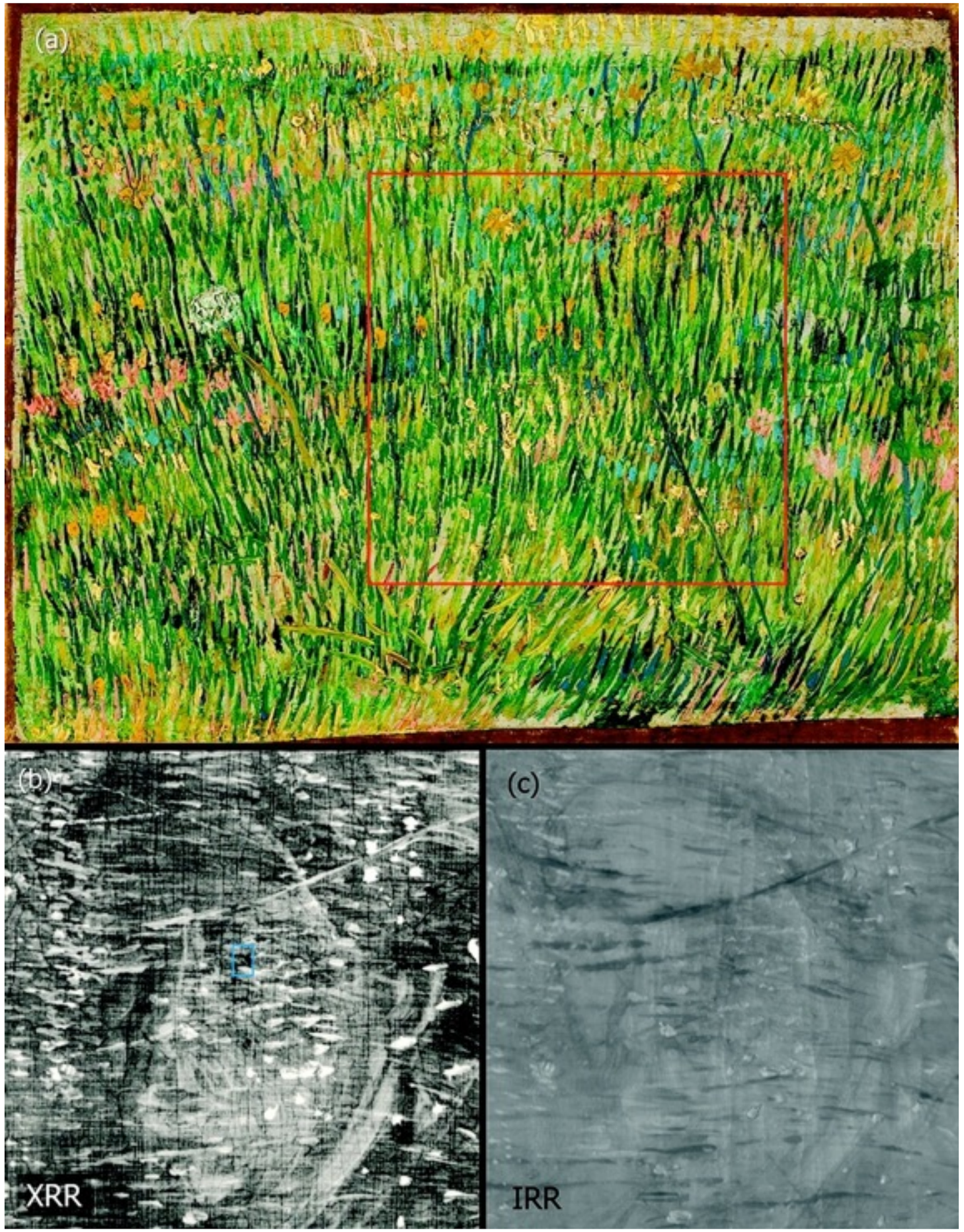
Joris Dik,[*,†] Koen Janssens,[‡] Geert Van Der Snickt,[‡] Luuk van der Loeff,[§] Karen Rickers,[||] and Marine Cotte[⊥,⊗]

Department of Materials Science, Delft University of Technology, Mekelweg 2, 2628CD Delft, The Netherlands, Centre for Micro- and Trace Analysis, Department of Chemistry, Universiteit Antwerpen, Universiteitsplein 1, 2610 Antwerp, Belgium, Kröller-Müller Museum, Houtkampweg 6, P.O. Box 1, 6730 AA Otterlo, The Netherlands, Deutsches Elektronen-Synchrotron (DESY), Notkestrasse 85, 22603 Hamburg, Germany, Centre of Research and Restoration of the French Museums, UMR-171-CNRS, Palais du Louvre, Porte des Lions, 14 quai François Mitterrand, 75001 Paris, France, and European Synchrotron Radiation Facility BP220, 38043 Grenoble Cedex, France

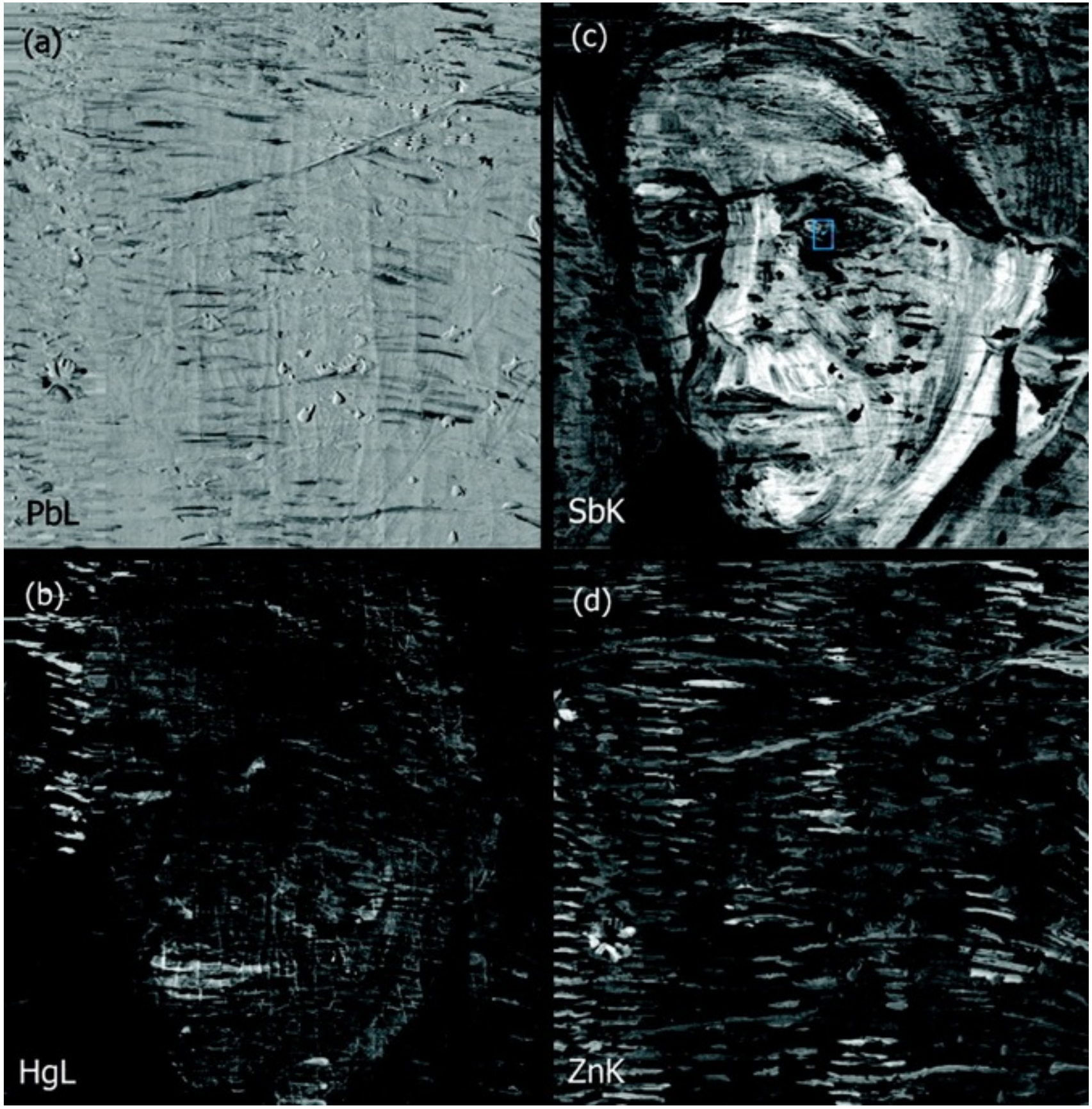
Schematic representation of set-ups of X-ray absorption (XANES, EXAFS) experiments in reflection geometry

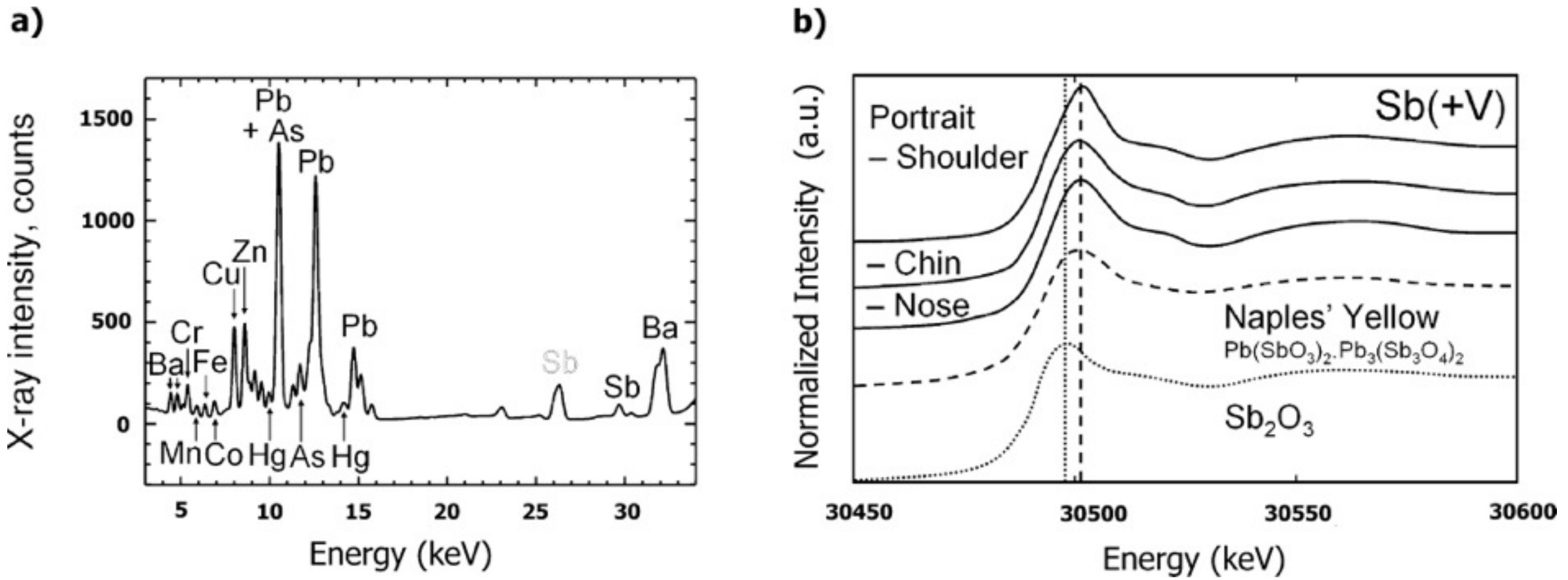


(a) Vincent van Gogh, Patch of Grass, Paris, Apr-June 1887, oil on canvas, 30 cm × 40 cm, Kröller-Müller Museum, Otterlo, The Netherlands (KM 105.264; F583/JH1263). The red frame indicates the field of view in images b and c (rotated 90° counter-clockwise). (b) X-ray radiation transmission radiograph (XRR), paint sample location indicated in the blue frame (Figure 4). (c) Infrared reflectograph (IRR).



(a) Distribution of Pb L measured with SR-based XRF (black, low intensity; white, high intensity). (b) Hg L showing distribu- tion of vermillion. (c) Sb K showing distribution of Naples yellow, paint sample location indicated in the blue frame (Figure 4). (d) Zn K showing distribution of zinc white, mostly corresponding with surface painting but some overlap with concentrations of SbK (nose, ear, neck).

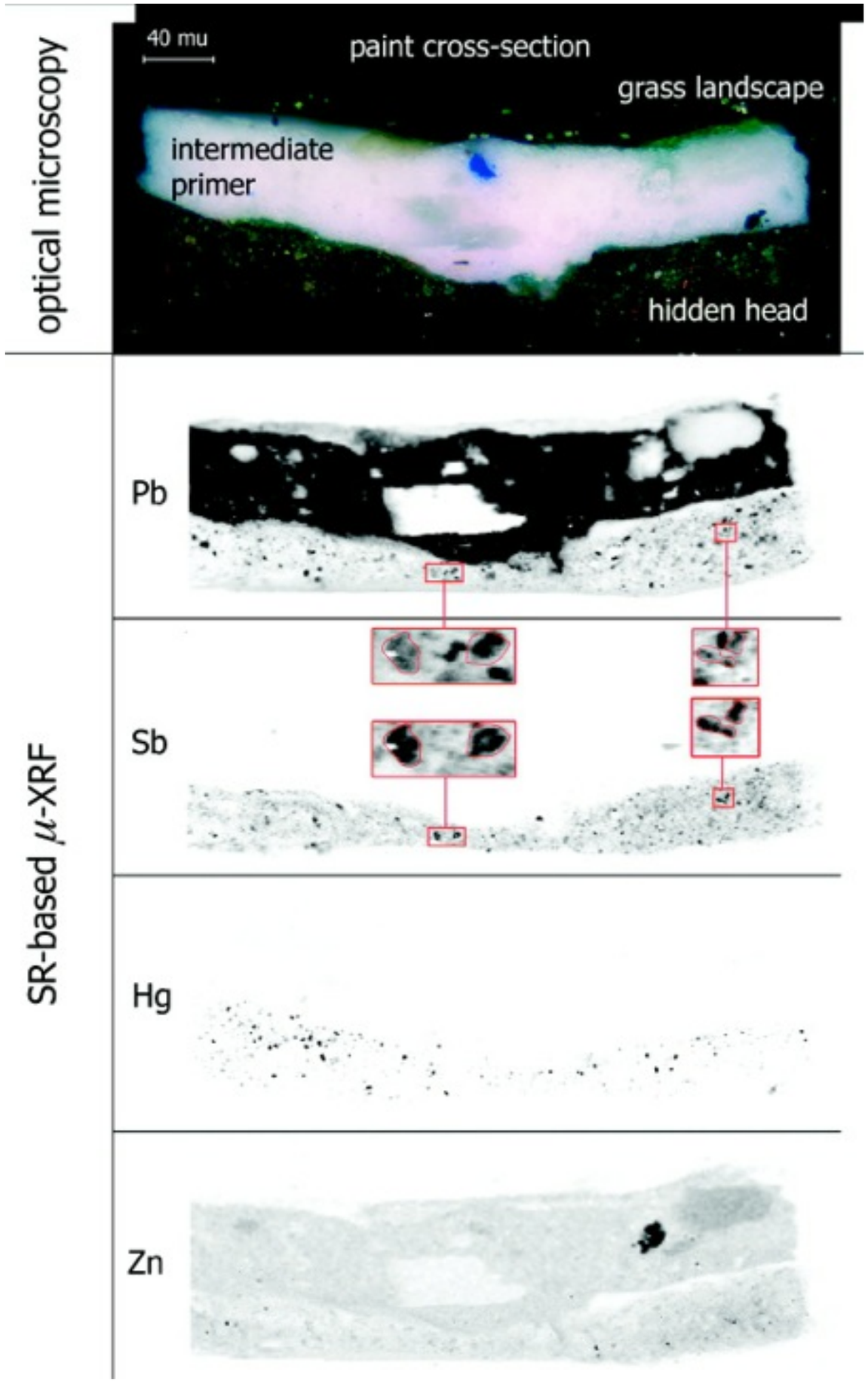




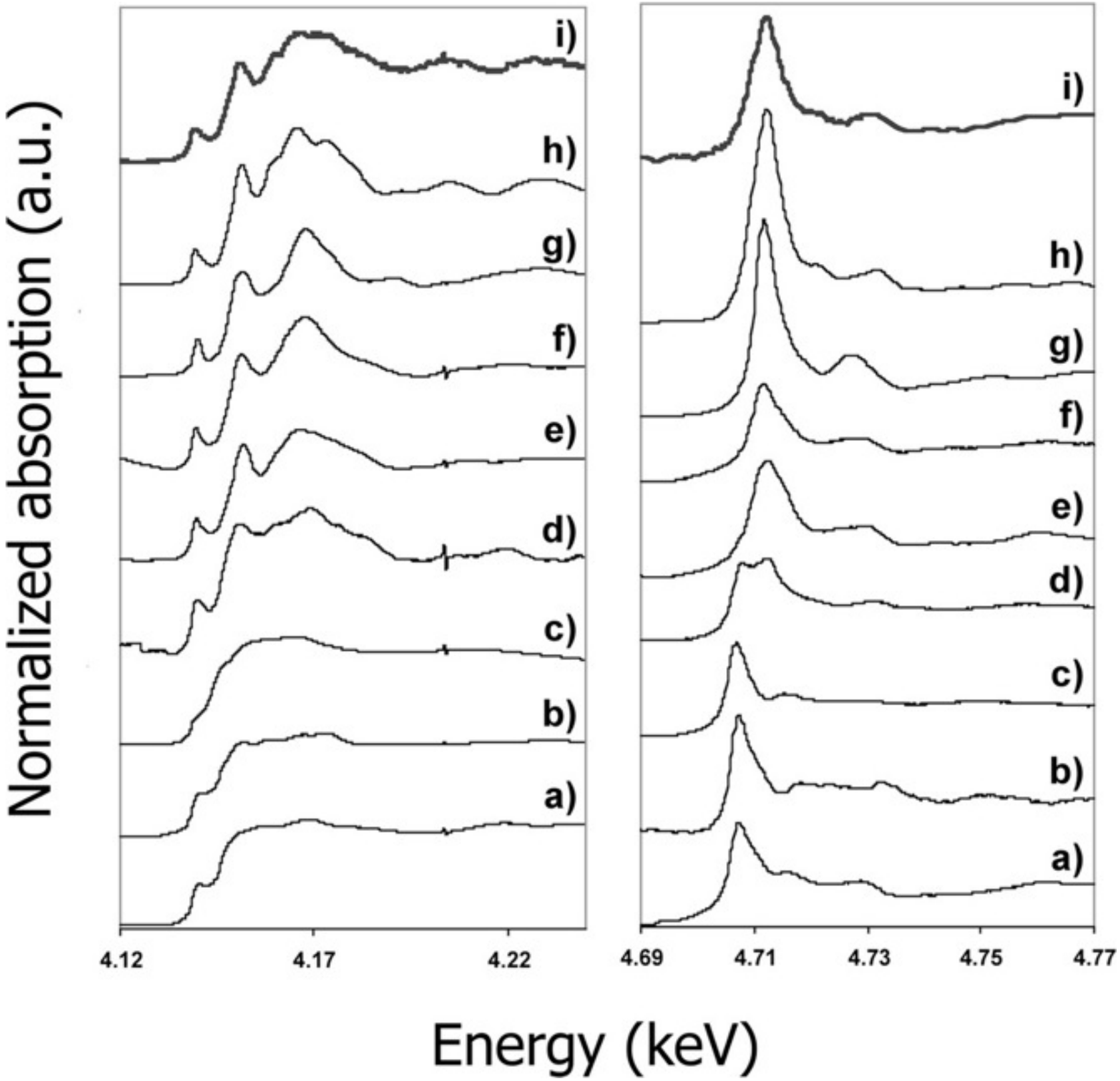
(a) Example of a X-ray fluorescence spectrum, derived from one location on the painting, showing the presence of Sb; (b) Comparison of Sb K- edge XANES spectra from three positions on the painting to reference XANES spectra of Naples yellow [Pb(SbO3)2 · Pb3(Sb3O4)2] and antimony white (Sb2O3). All spectra were recorded in the fluorescent mode.

View on sample location indicated in Figures 1b and 2c (rotated 90° counter clockwise). The red frame indicates the location of the sample before removal. The insets show photographs of both sides of the unembedded sample before cross-sectioning.

Cross section of paint sample measured with SR-based μ-XRF showing elemental distributions of Pb, Sb, Hg, and Zn (black, high intensity; white, low intensity). Insets show the correlation of Sb and Pb on the pigment grain level.



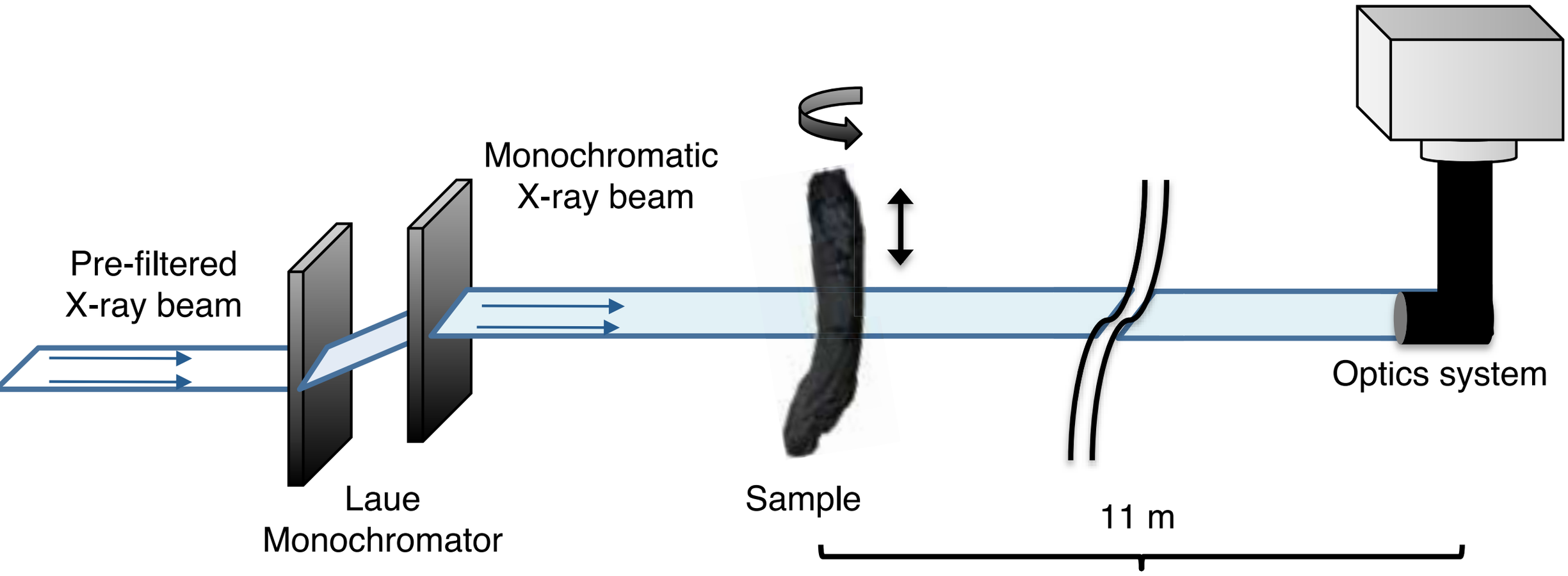
XANES spectra at the Sb-LIII edge (upper spectrum) and at the Sb-LI edge (lower spectrum). Reference antimony compounds: Sb_2O_3 as (a) valentinite and as (b) senarmontite; (c) Sb_2S_2O, kermesite; (d) Sb_2O_4; (e) Sb_3O_6OH, stibiconite; (f) $KSbO_3 \cdot 3H_2O$; (g) $NaSbO_3OH \cdot 3H_2O$; (h) Naples yellow; and (i) Sb pigment in the cross section of the Van Gogh painting (Figure 5).



(a) Tritonal color reconstruction of Sb (yellowish white) and Hg (red) representing the flesh color of the hidden face. (b) Detail from Vincent van Gogh, *Head of a Woman*, Nuenen, winter 1884-85, oil on canvas, 42 cm × 33 cm, Kro¨ller-Mu¨ller Museum, Otterlo (KM 105.591; F154/JH608). (c) Detail from Vincent van Gogh, *Head of a Woman*, Nuenen, winter 1884-85, oil on canvas, 42 cm × 34 cm, Van Gogh Museum, Amsterdam (F156/JH569).

Tomography

Tomography



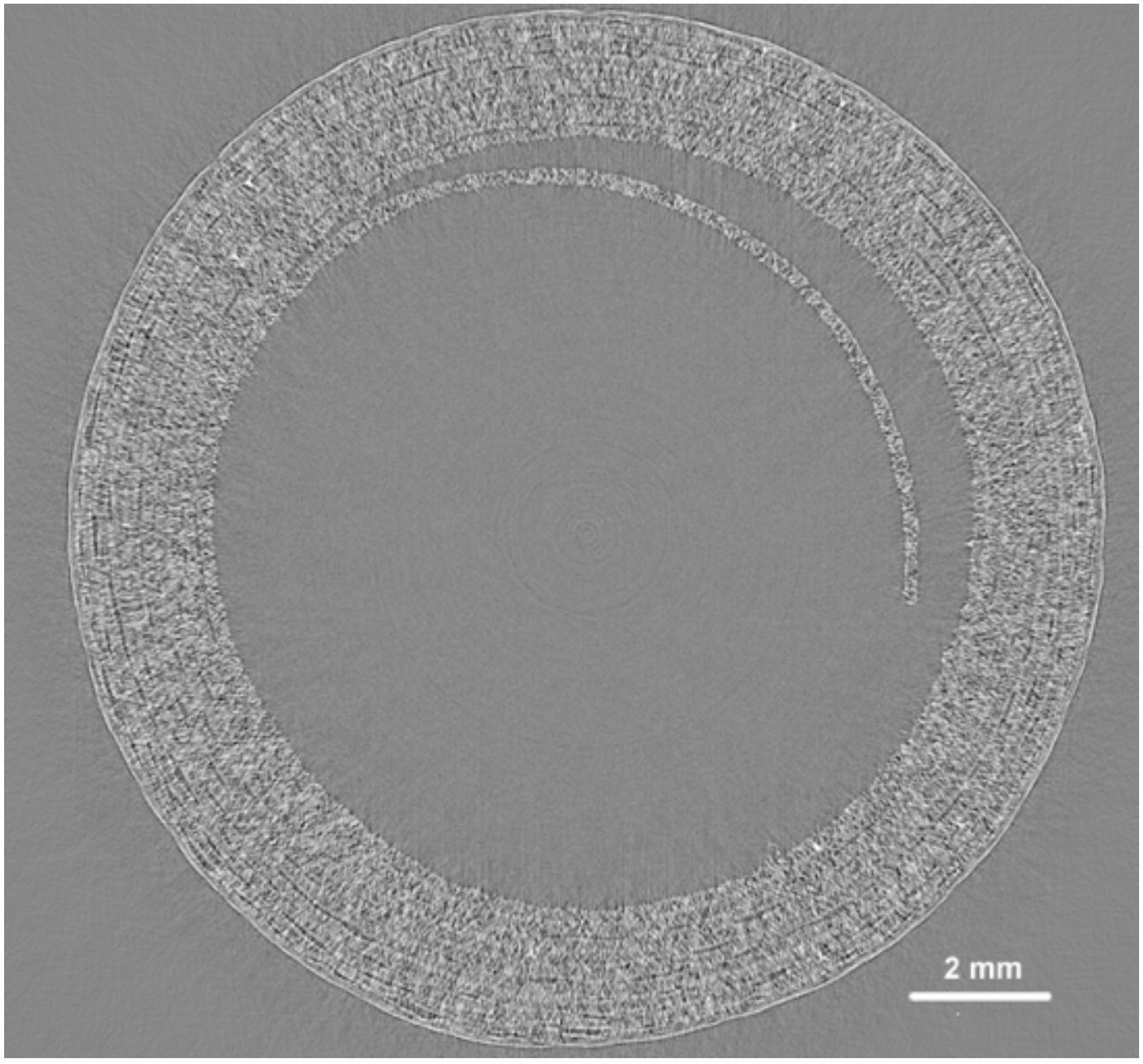
The experimental set-up

The organ by Lorenzo da Pavia

Organ by Lorenzo Gusnasco (1494)
Pipes made with rolled and glued carton
Structural characterization of the paper pipes to define strategies for restoration, conservation and possible substitution
Instrument of great historical and artistic relevance

Cultural Heritage

The organ by Lorenzo da Pavia

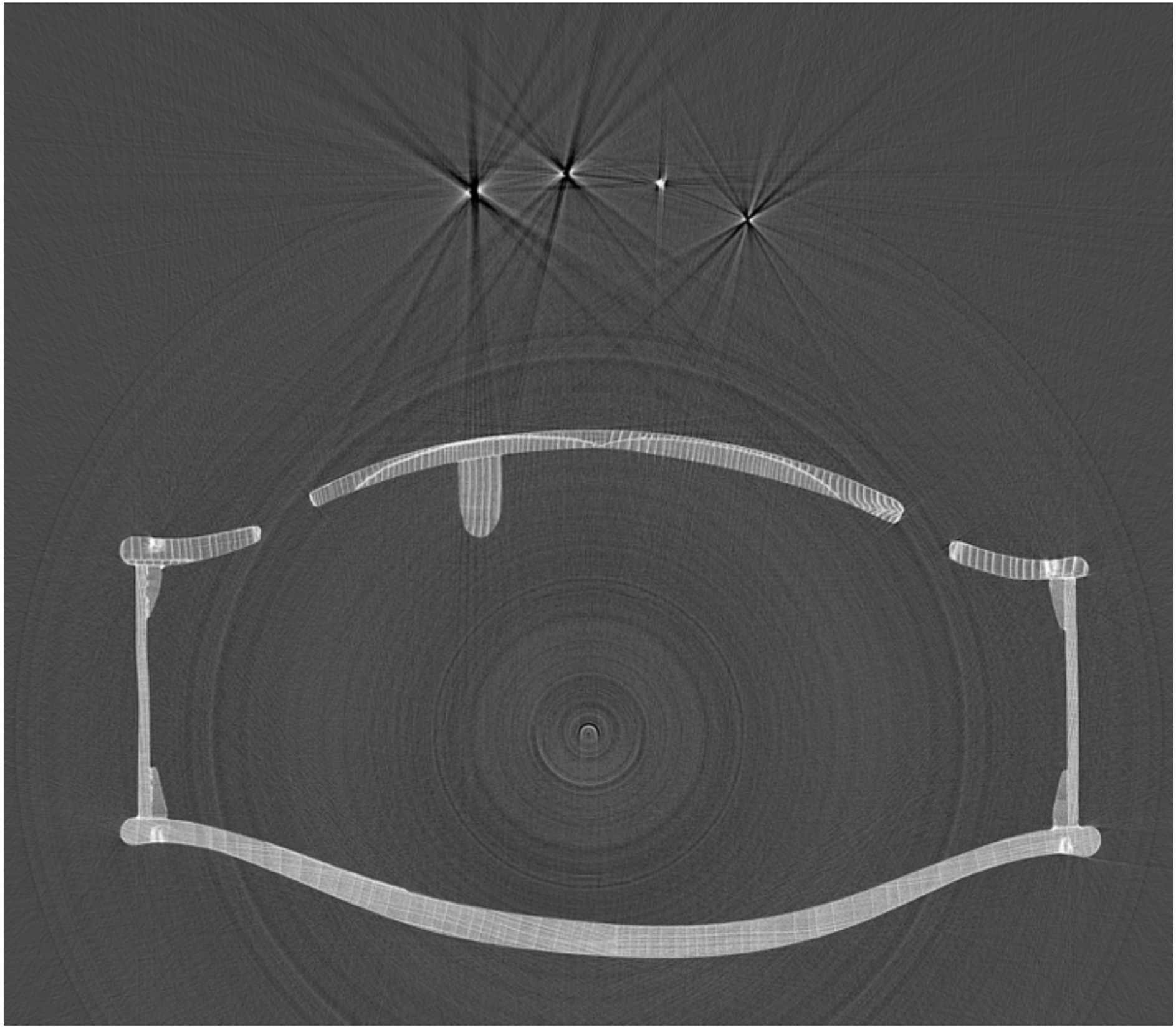


Virtual slice of a paper pipe with a spatial resolution of 9 microns

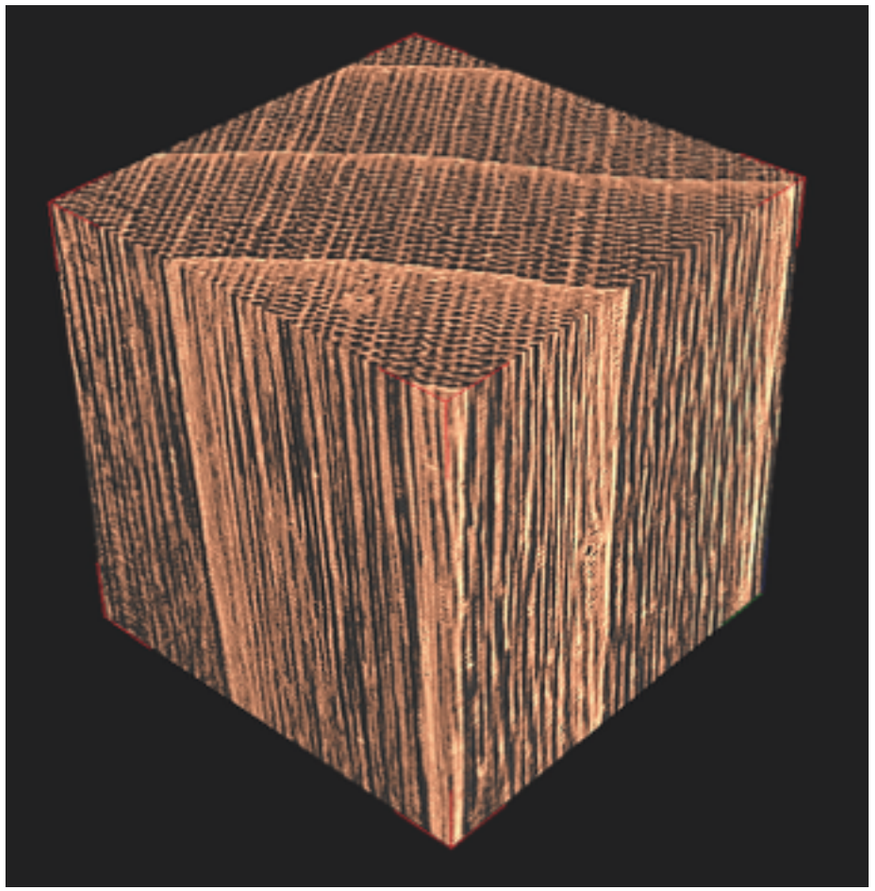
The Guadagnini violin (1753) (owned by Peter Herresthal)

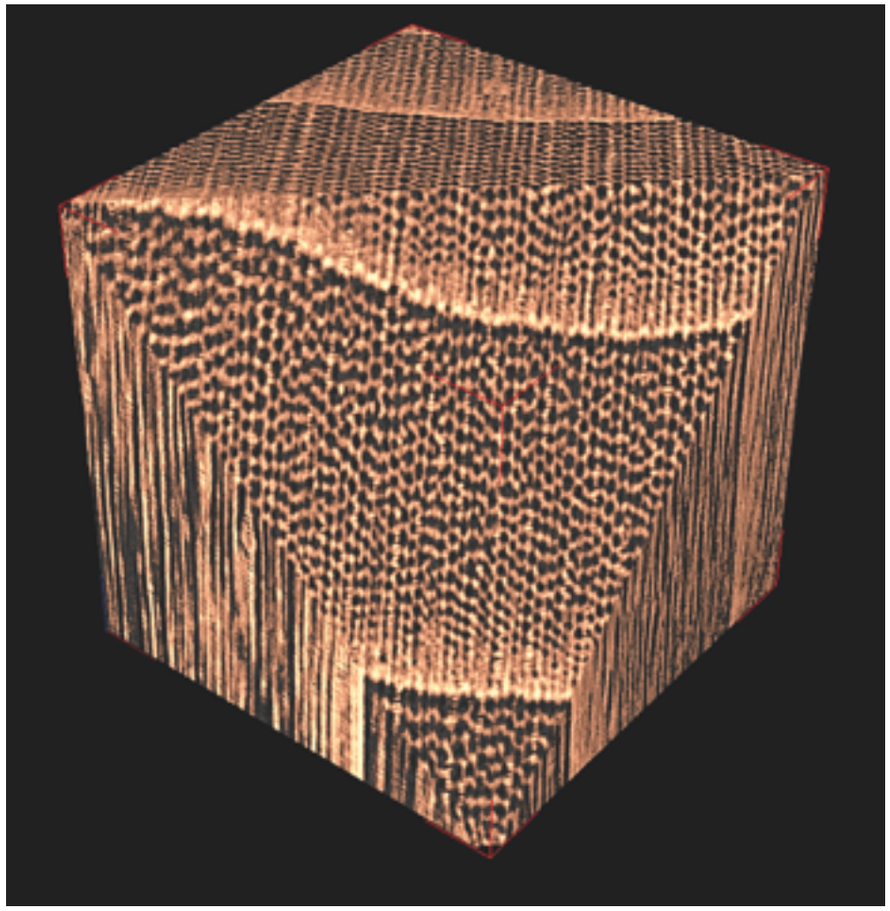
SR & Cultural Heritage

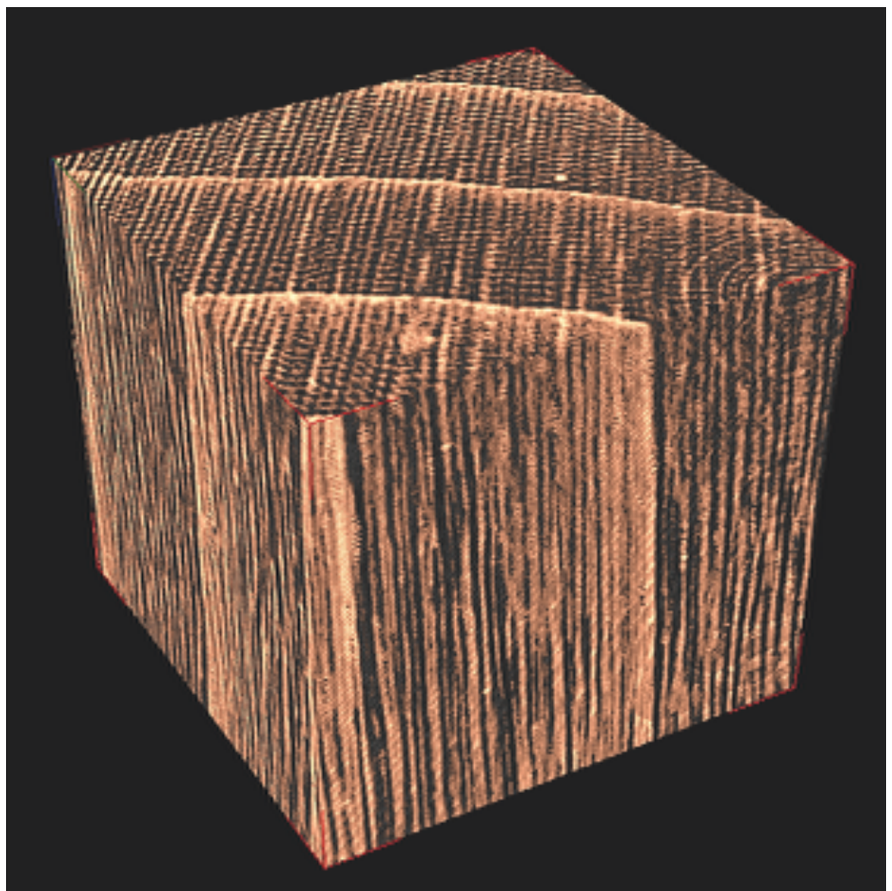
The Guadagnini violin (1753) (owned by Peter Herresthal)



SR & Cultural Heritage







Preservation of an ancient Roman ship: diffusion of Polyethylene glycol into the wood fibres

nature COMMUNICATIONS

ARTICLE

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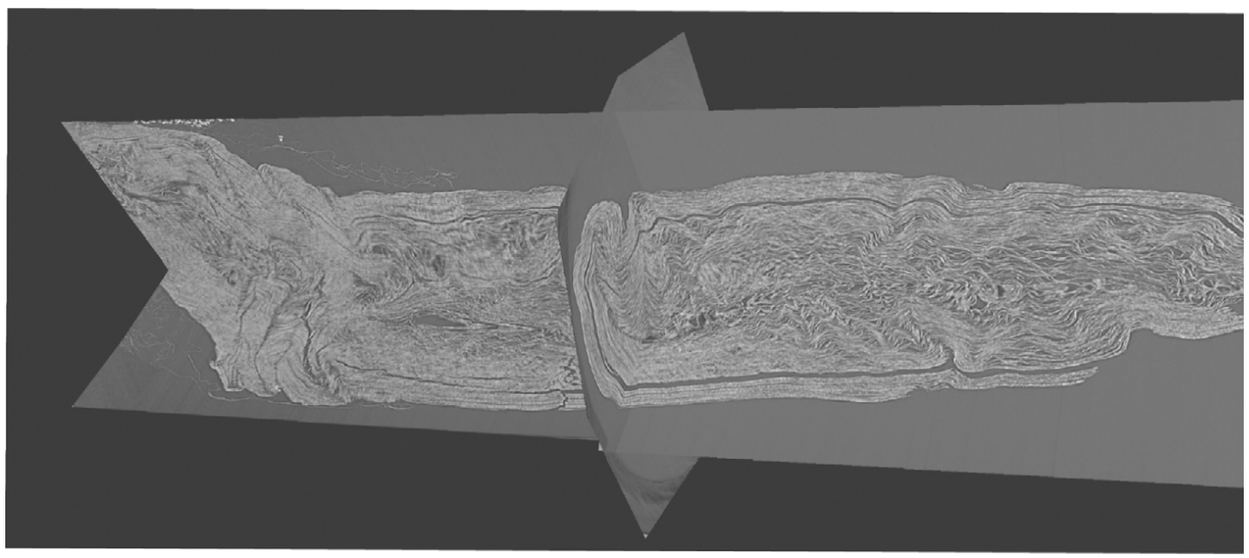
Tomography and Cultural Heritage

Revealing letters in rolled Herculaneum papyri by X-ray phase-contrast imaging

Vito Mocella[1,*], Emmanuel Brun[2,3,*], Claudio Ferrero[2] & Daniel Delattre[4]

Hundreds of papyrus rolls, buried by the eruption of Mount Vesuvius in 79 AD and belonging to the only library passed on from Antiquity, were discovered 260 years ago at Herculaneum. These carbonized papyri are extremely fragile and are inevitably damaged or destroyed in the process of trying to open them to read their contents. In recent years, new imaging techniques have been developed to read the texts without unwrapping the rolls. Until now, specialists have been unable to view the carbon-based ink of these papyri, even when they could penetrate the different layers of their spiral structure. Here for the first time, we show that X-ray phase-contrast tomography can reveal various letters hidden inside the precious papyri without unrolling them. This attempt opens up new opportunities to read many Herculaneum papyri, which are still rolled up, thus enhancing our knowledge of ancient Greek literature and philosophy.

b



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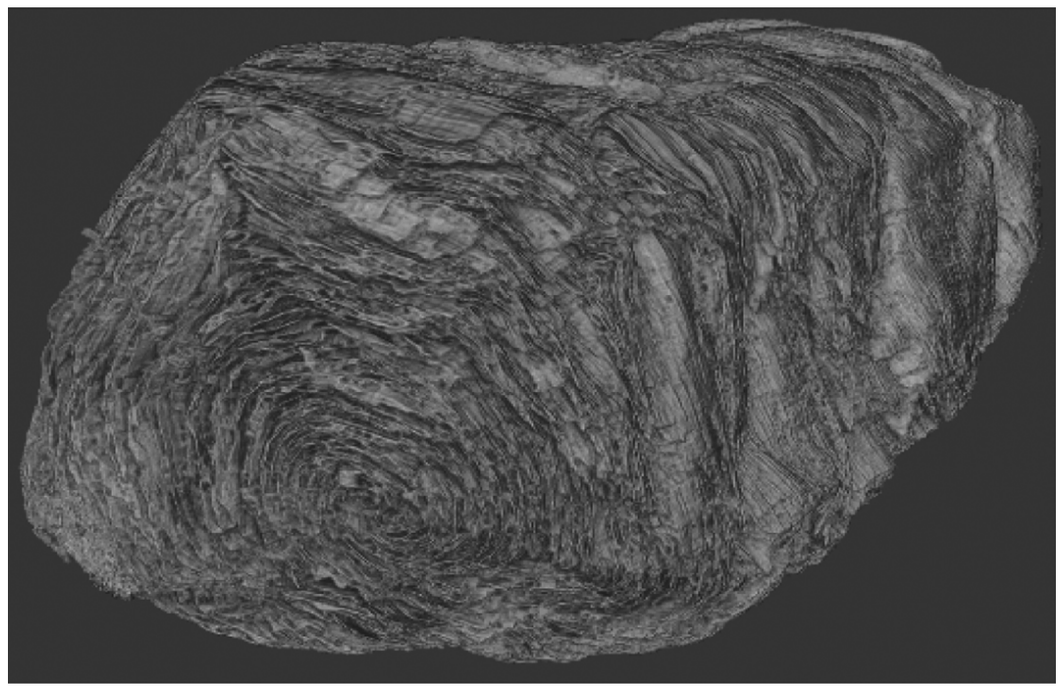
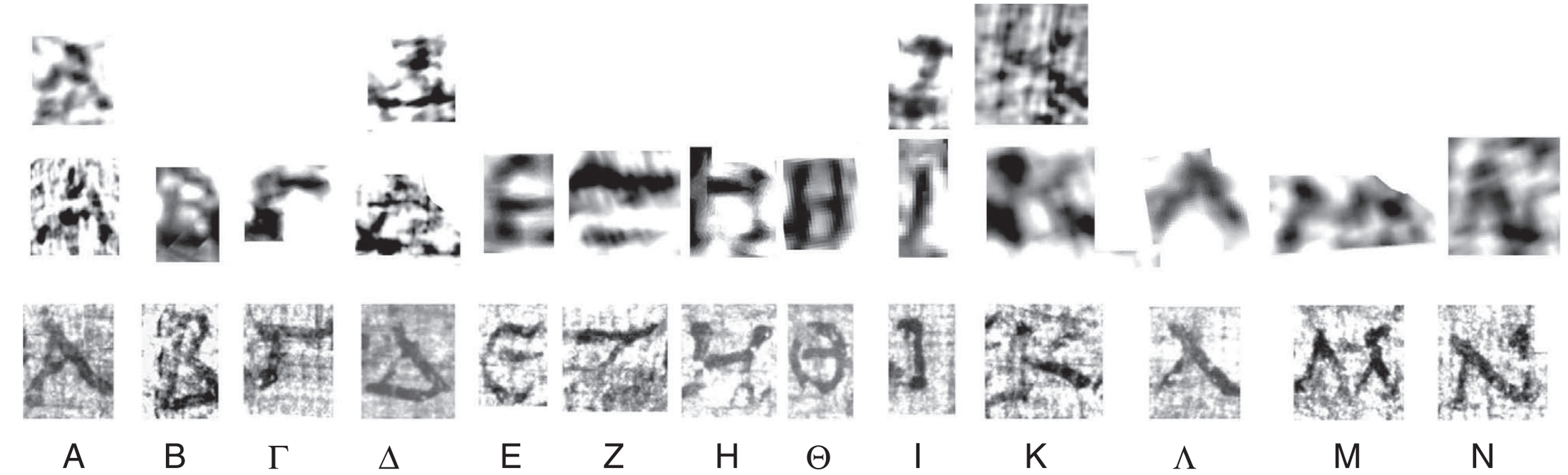
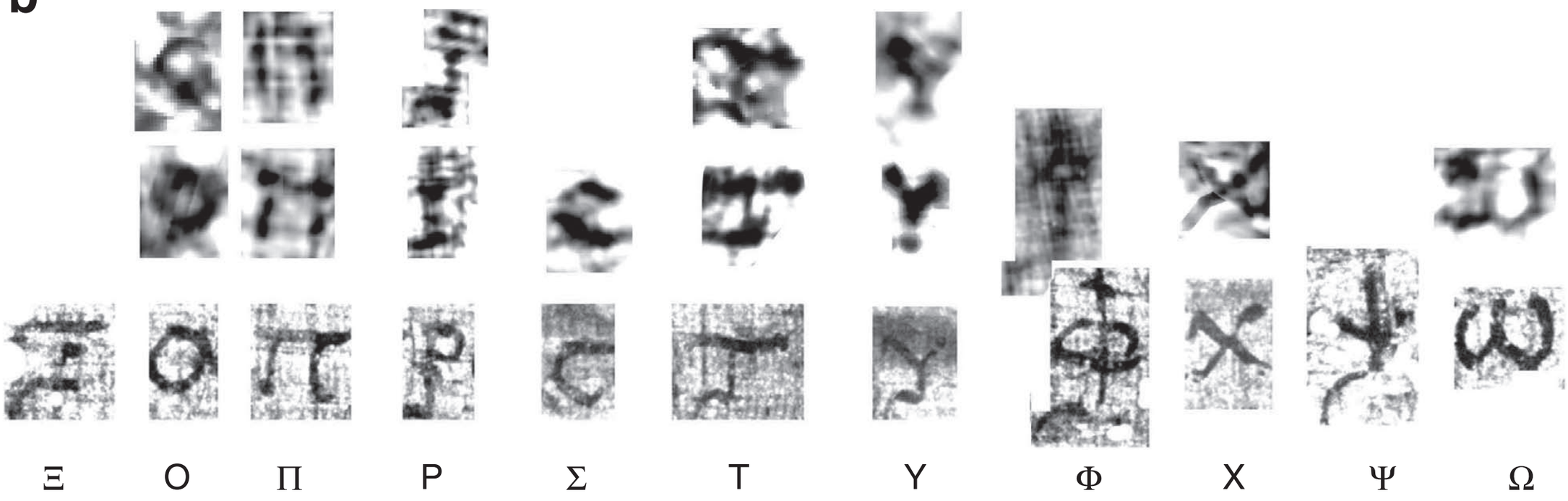


The Herculaneum papyrus scroll PHerc.Paris. 4. (**a**) A picture of the PHerc.Paris. 4 lying in its transport holder, fabricated by means of a three-dimensional scan of the external papyrus shape profile (B16 cm length). The carbonized papyrus is extremely fragile. Its deformation was caused mechanically by the eruptive material;
(**b**) three orthogonal slices, and
(**c**) a volume rendition of the reconstructed papyrus, which highlights the huge complexity inside the scroll, where the papyrus convolutions were exposed to tremendous stresses.





(a) The alphabet letters from A to N (alpha to nu) as revealed by the XPCT experiment, primarily from the innermost region of the papyrus, where the individual coils are more distinguishable, are reported on lines 1 and 2; on line 3 the infrared images of the same letters from the unrolled papyrus PHerc. 1471, which was used as a reference for the writing style of the scroll PHerc.Paris. 4. Printed capital letters of the ancient Greek alphabet are given below line 3. (b) The alphabet letters revealed by the XPCT experiment from Ξ to Ω (xi to omega).