# Soft X-ray Fluorescence Spectroscopy for Materials Science and Chemical Physics

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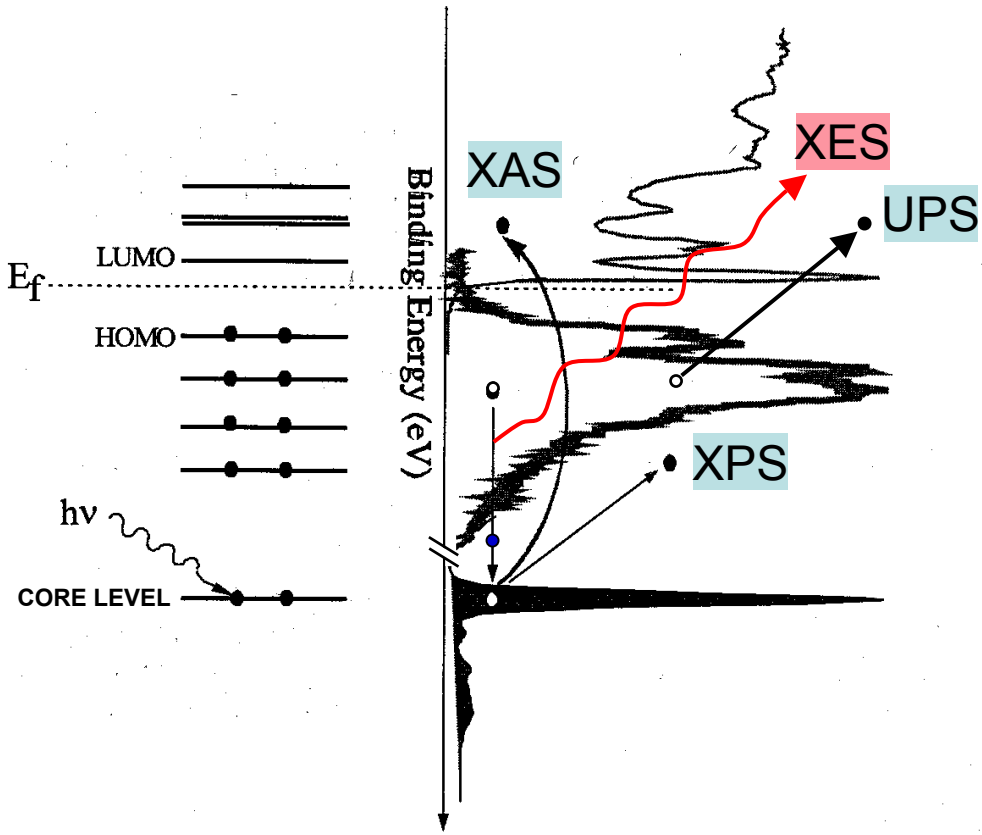
## Outline

- **Soft X-ray emission/inelastic scattering**
  - **probing capabilities**
  - **new application areas**
- **Experimental developments**

# VUV / Soft X-ray Spectroscopies

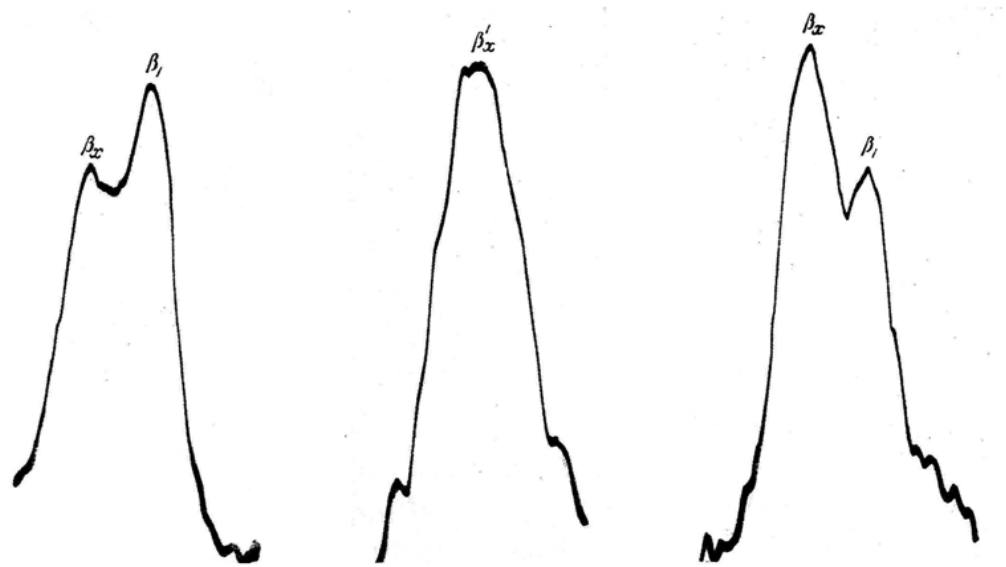
**Spectroscopies probe:**

- **UPS:** filled valence band
- **XPS:** core states, valence band indirectly
- **XAS :** unfilled valence band
- **XES:** filled valence band, element selective, in resonant mode site selective



# Chemical effects in X-ray emission

S $K_\beta$ emission of various Sulphur compounds

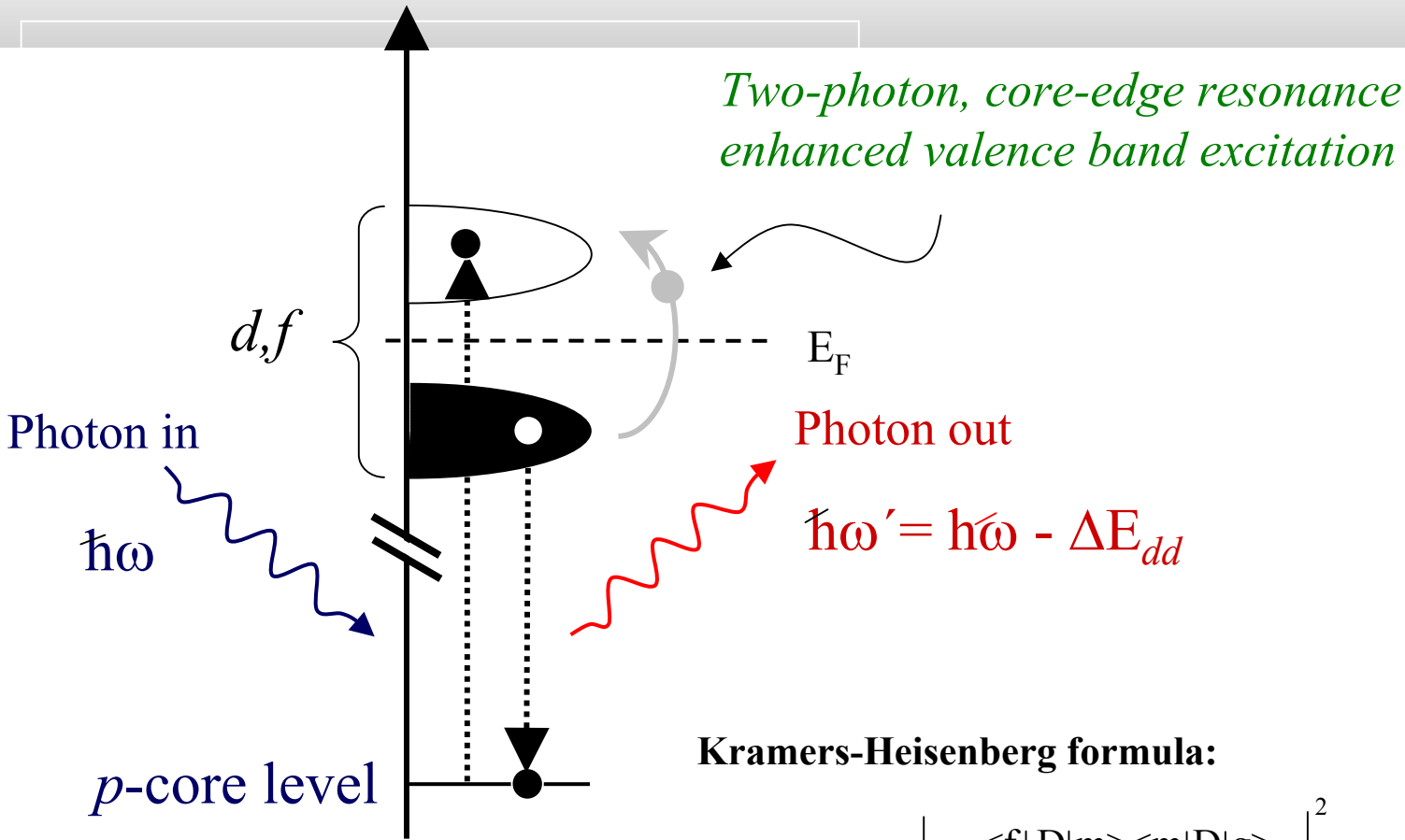



$Ag_2S$ auf Kupferantikathode. $Ag_2S$ auf Eisenantikathode. $Ag_2S$ auf Aluminiumantikathode.

Abb. 146. (Aus LINDH und LUNDQUIST, Ark. f. Mat., Astr. o. Fysik 18.)

**A. Lindh, Ark. Fys. 18, 35 (1924)**

# Resonant Inelastic X-ray Scattering (RIXS)




**Kramers-Heisenberg formula:**

$$F(\omega,\omega') = \sum_f \left| \sum_m \frac{\langle f|D|m\rangle\langle m|D|g\rangle}{E_g + \omega - E_m - i\Gamma_m} \right|^2 \delta(E_g + \omega - E_f - \omega')$$

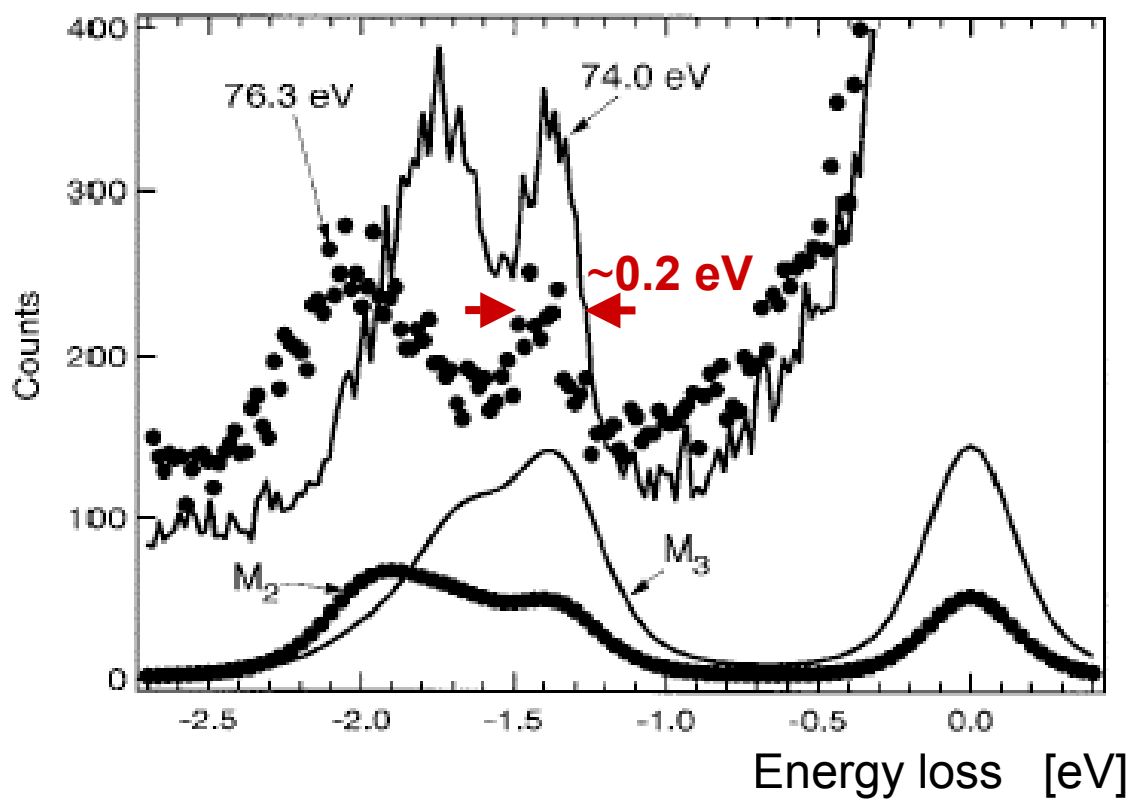
Appl. to *d* and *f* systems, see e.g.:
S. Butorin, *et al.*, Phys. Rev. Lett., **77**, 574 (1996)

# Additional characteristics of RIXS

- Low energy excitations in neutral system
- Two-photon process
- Dispersion through momentum conservation
- Site selectivity due to core resonance
- No core state broadening
- Localization dependence
- Femtosecond dynamics by detuning

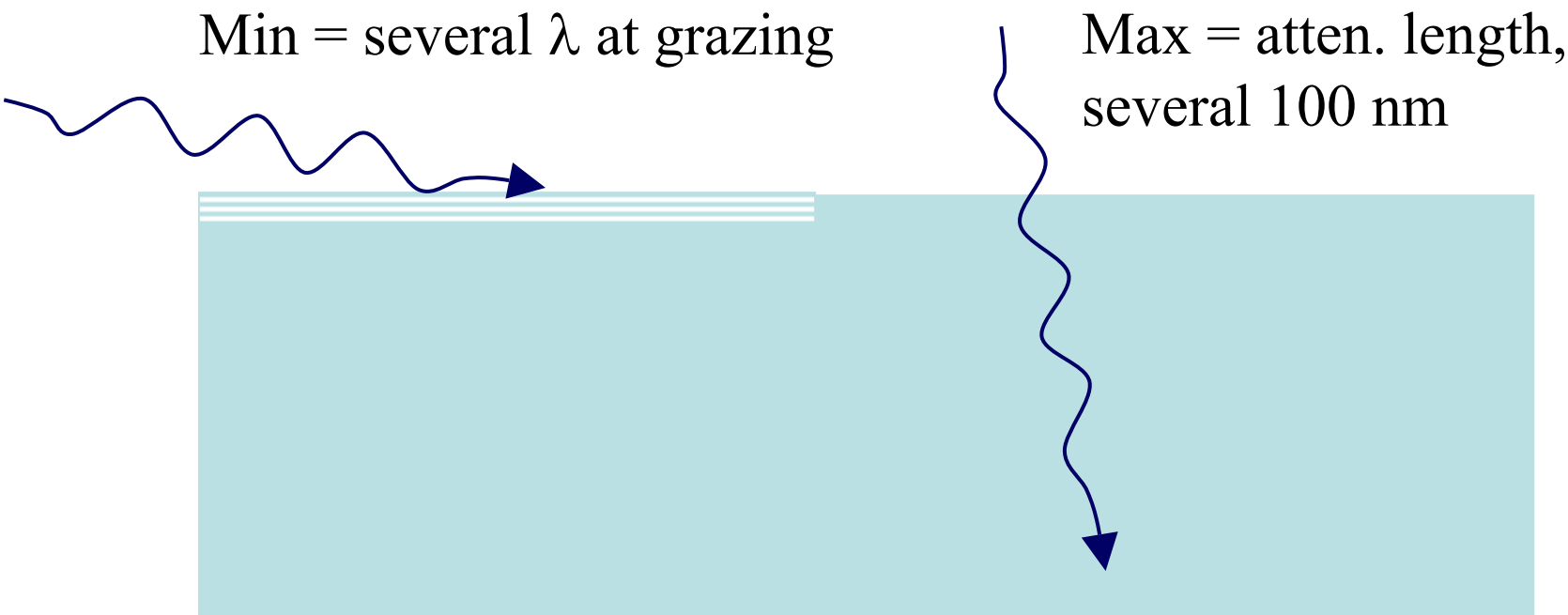
# Sub-natural lifetime broadening in resonant Cu M emission

**Cu M XPS width =**
**= 1.5 eV**



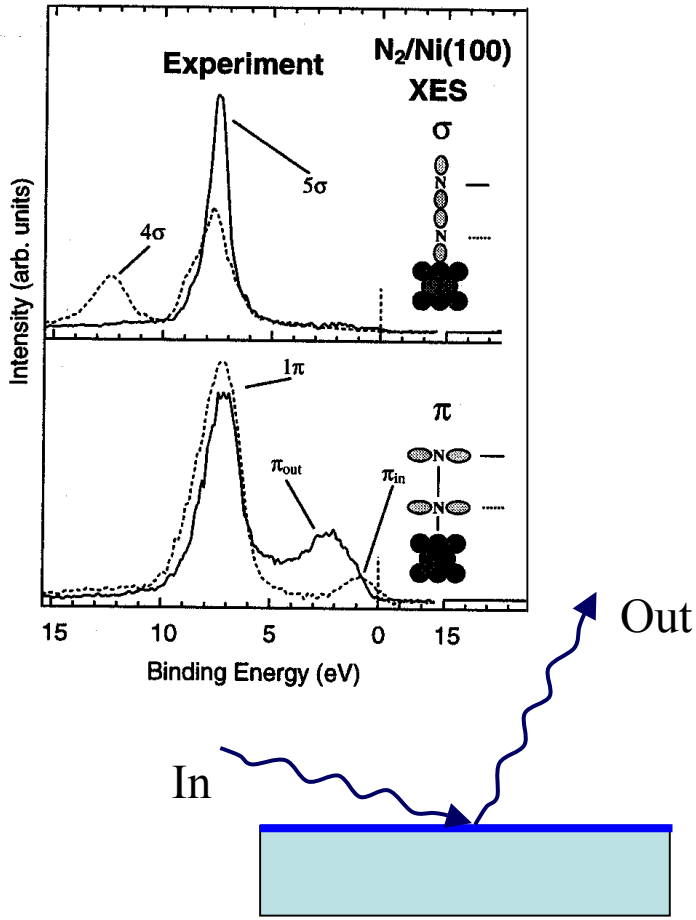

P. Kuiper *et al*., Phys.Rev.Lett., **80**, 5204 (1998)

# Penetration of soft X-rays



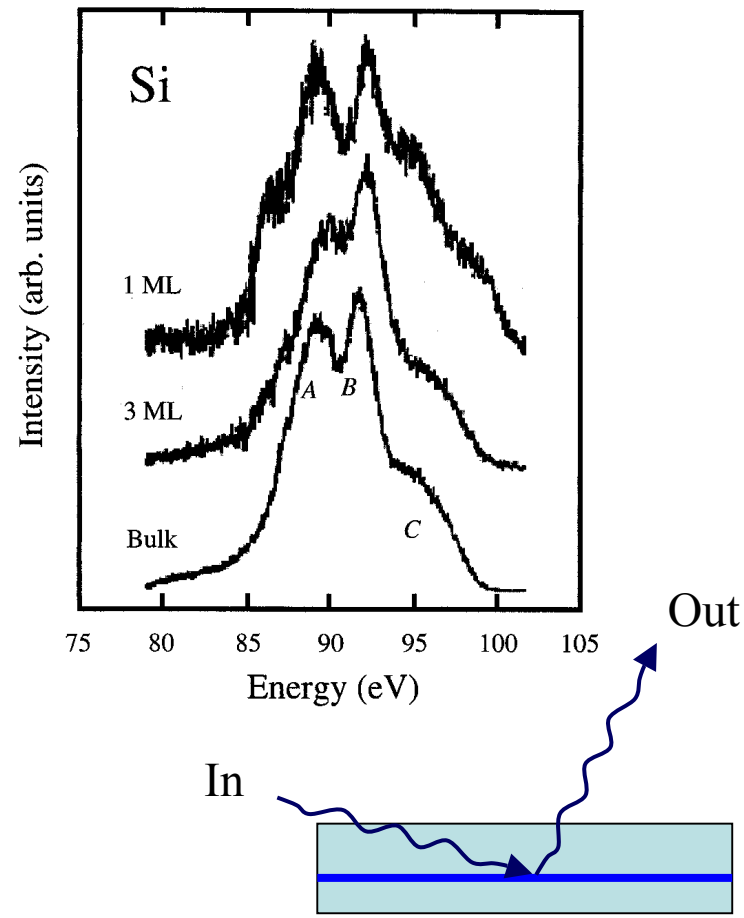
# SXES of very thin layers

Surface overlayer




A. Nilsson *et al*., Phys. Rev. Lett., **87**, 2847 (1997)

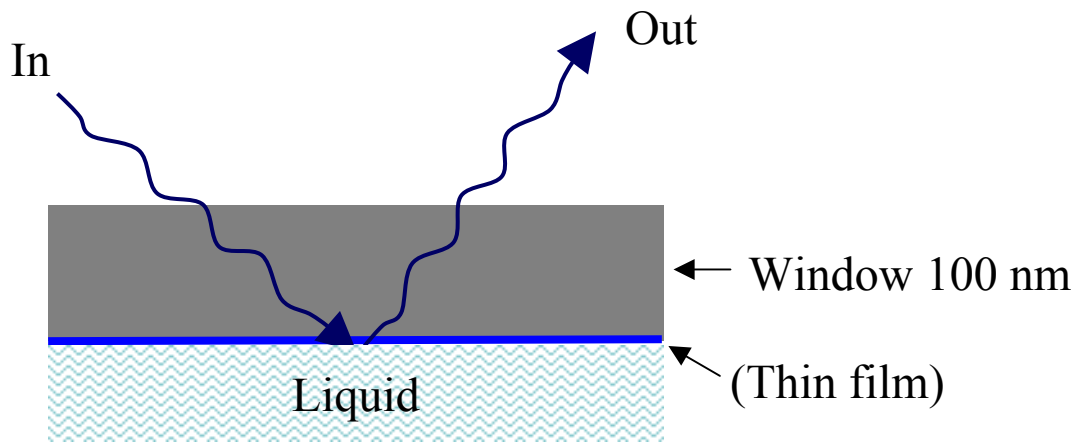
Buried layer



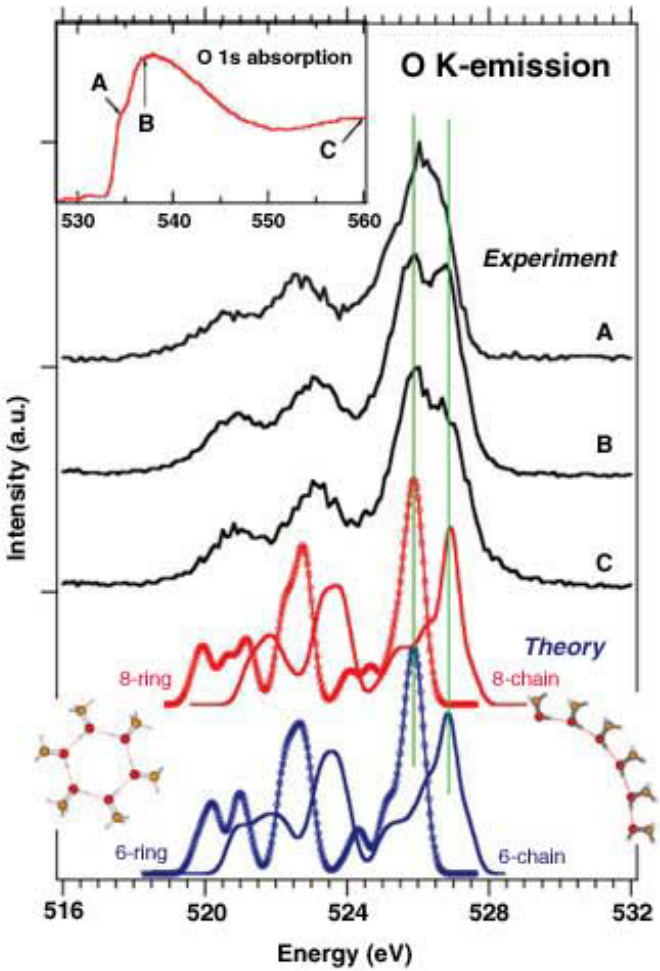

P.-O. Nilsson *et al*., Phys. Rev. **B 52**, 8643 (1995)

# SXES on liquid systems

Liquid wetting window

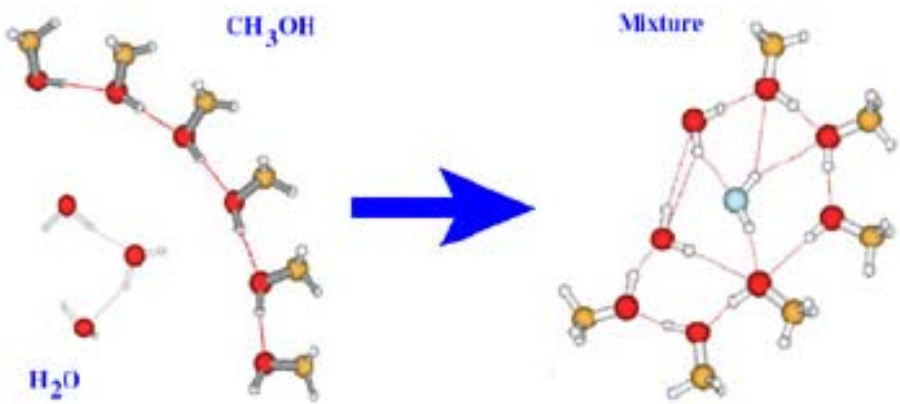


# Why do not alcohol and water want to mix completely?



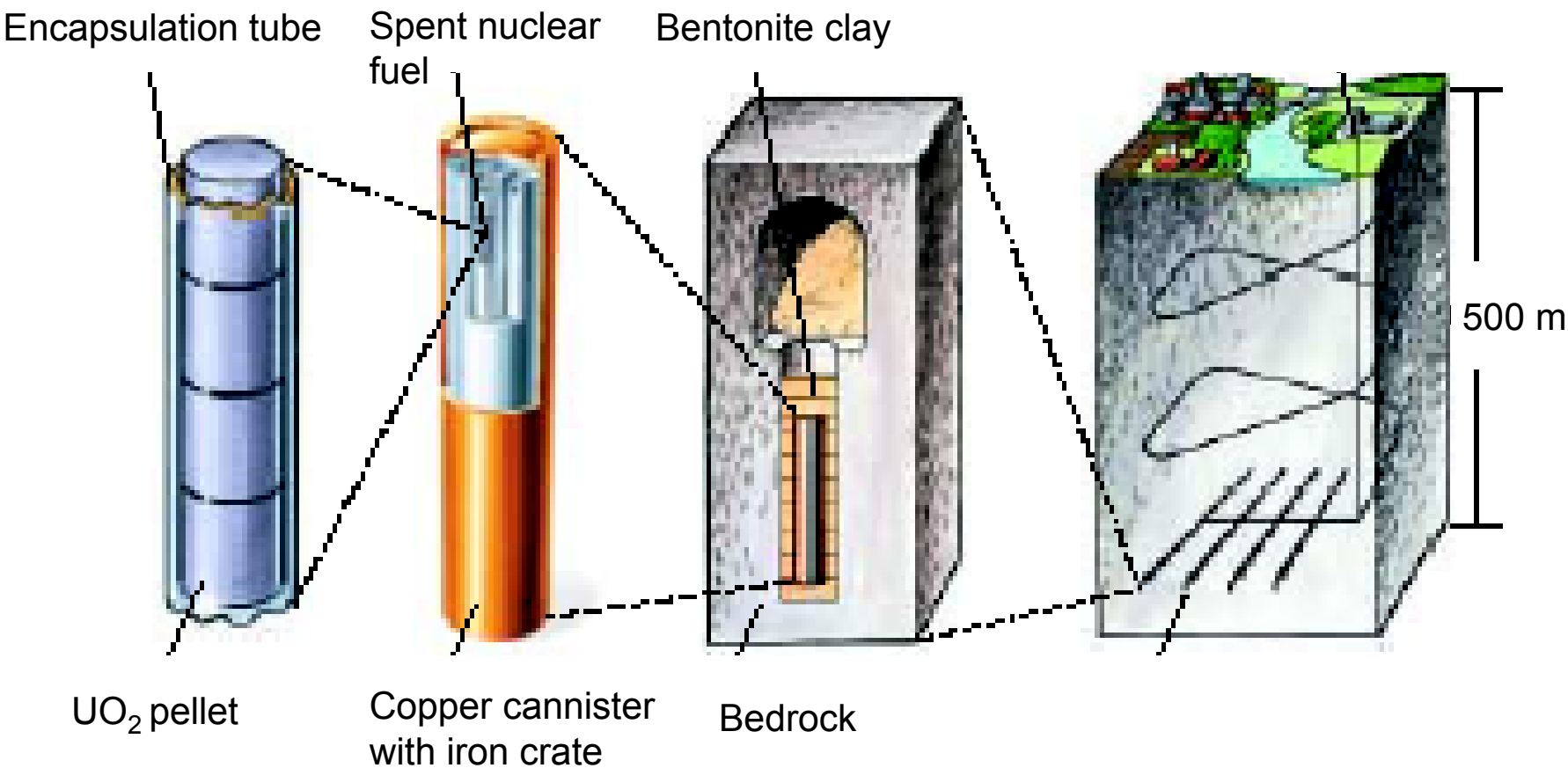

**Soft X-ray spectra reveal local molecular structure:**

***Water molecules bridge alcohol molecular chains***

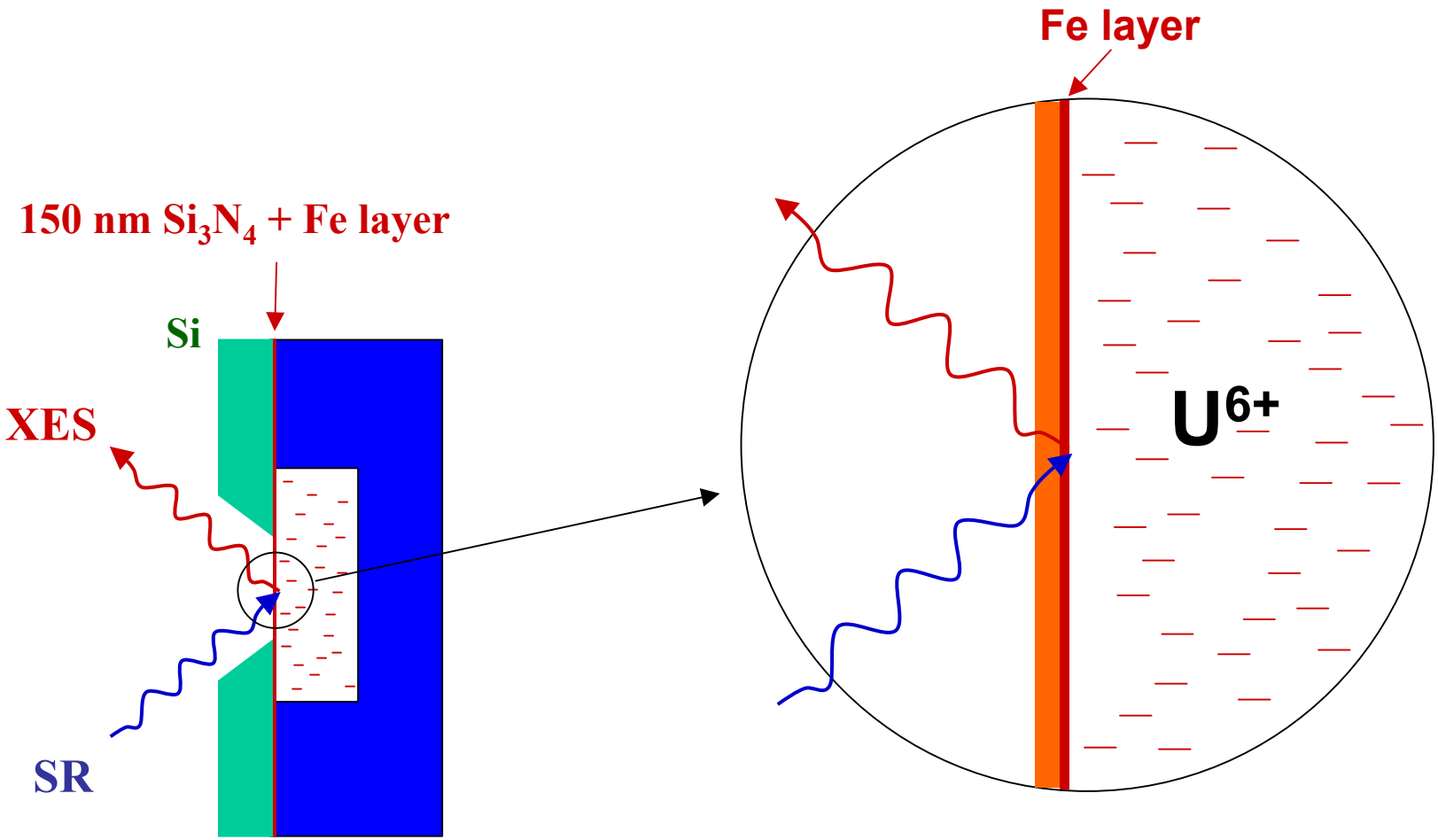



J.-H. Guo, *et al*., Phys. Rev. Lett. **91**, 157401 (2003)

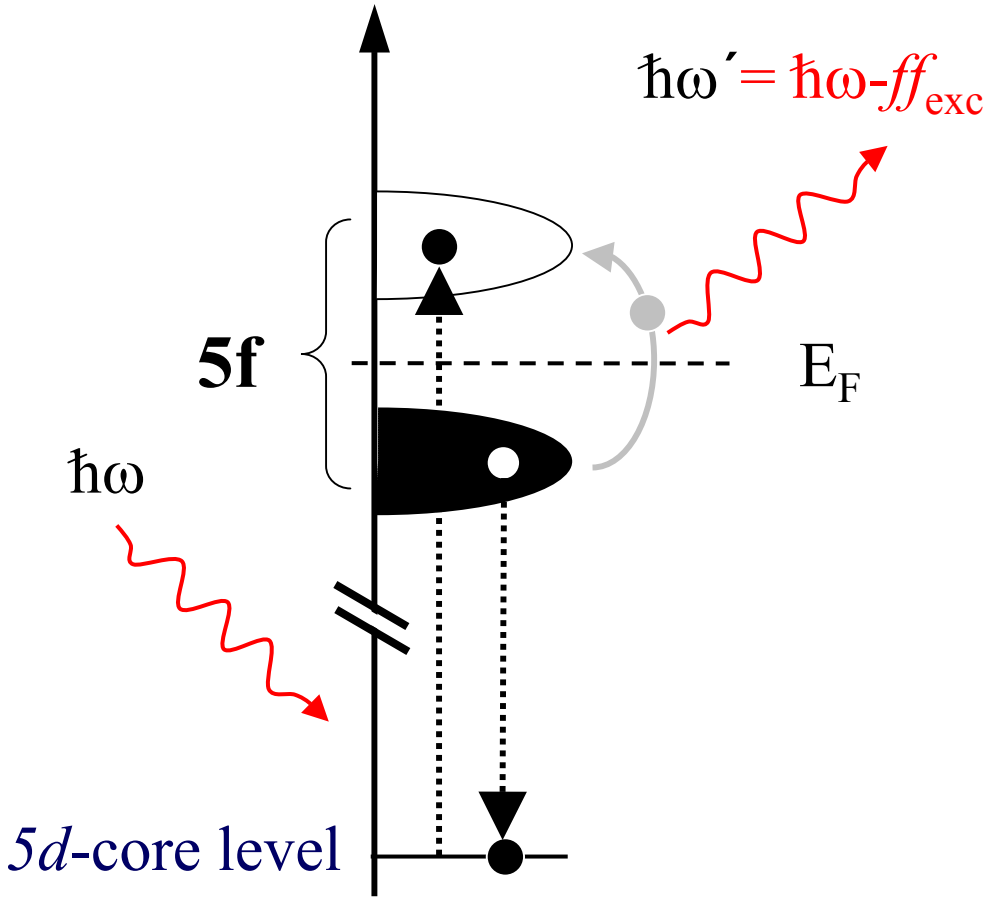
# Repository for nuclear waste

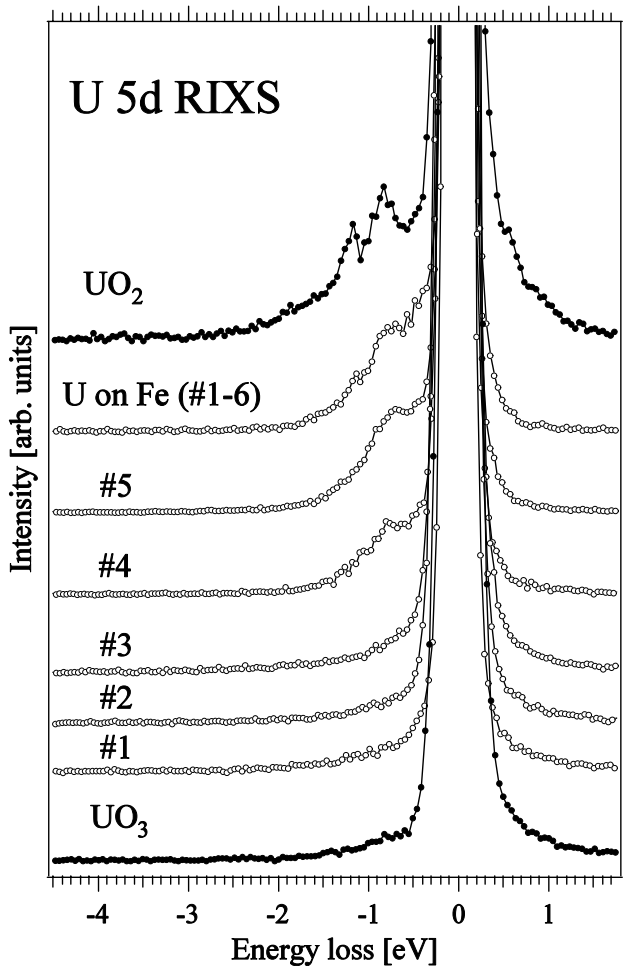


# *In situ* RIXS study of iron-induced reduction of Uranium 6+ in liquid phase

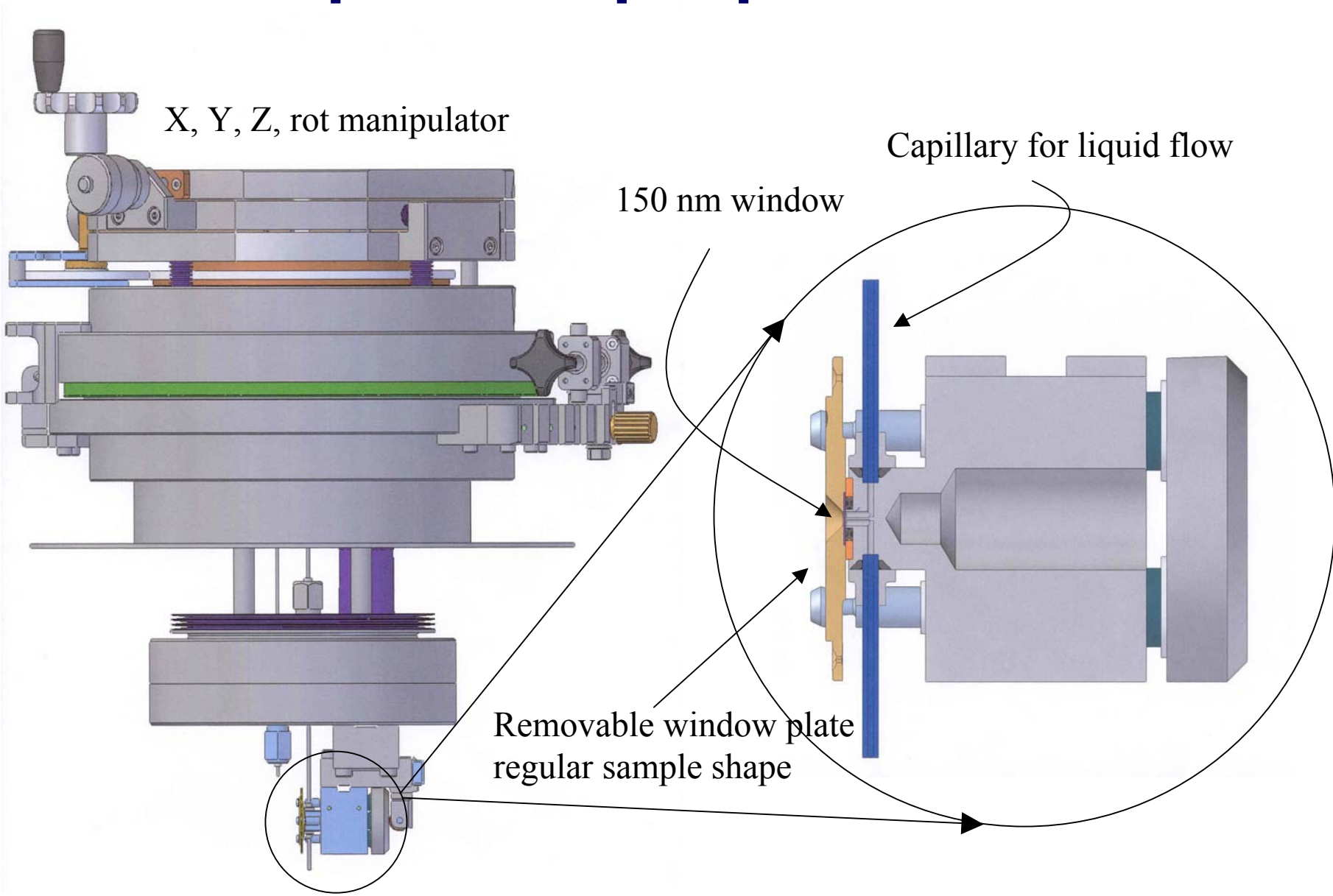


# Determination of oxidation states of actinides in spent nuclear fuel by RIXS



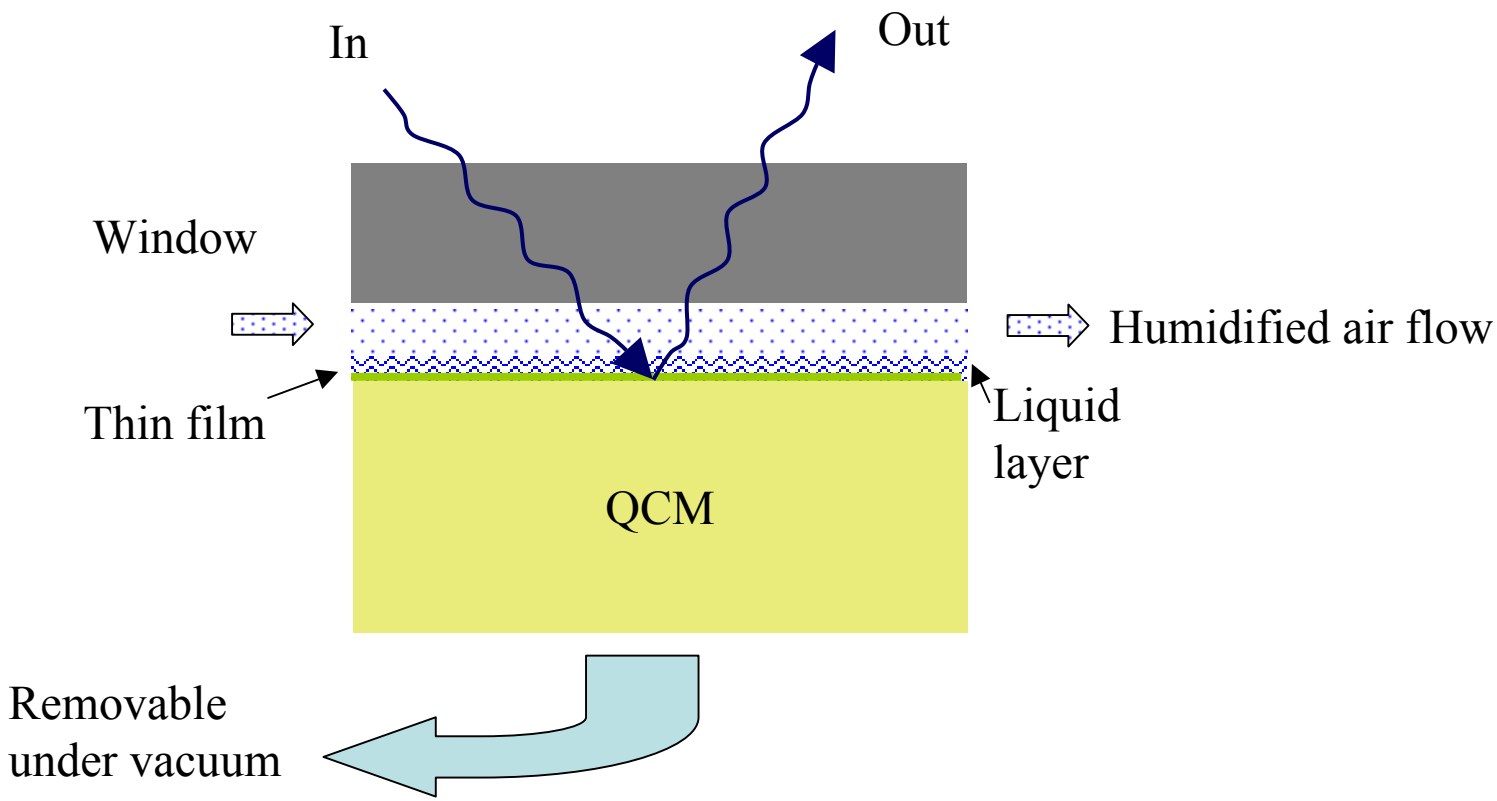



# Liquid sample platform

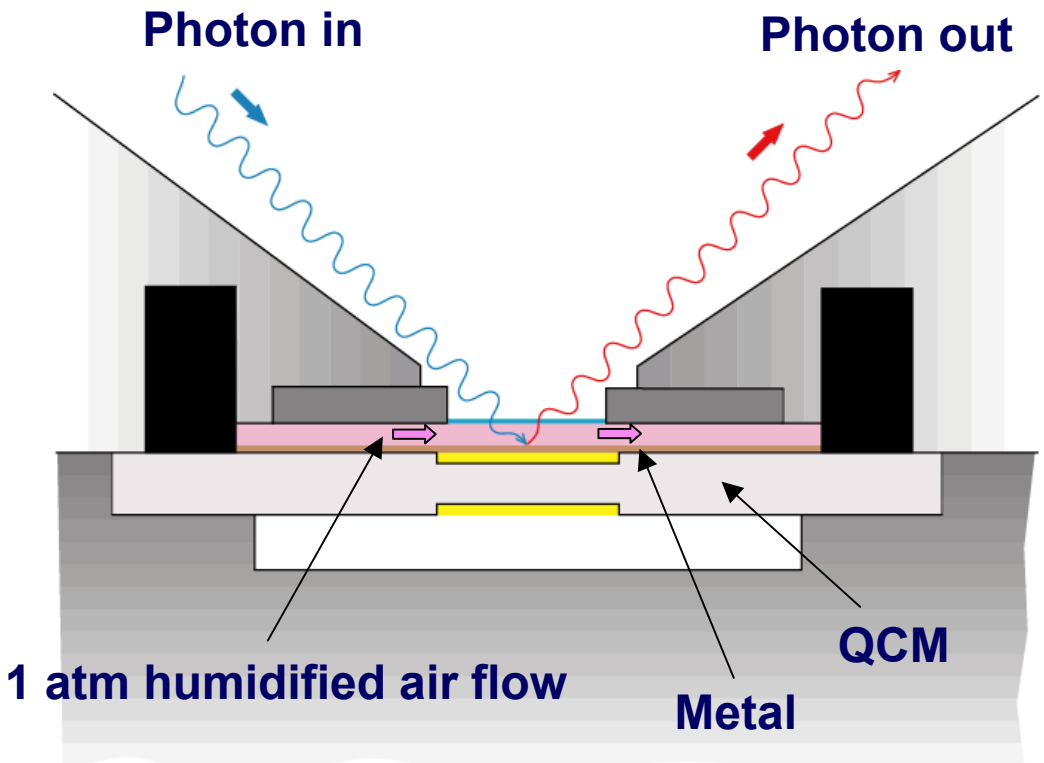


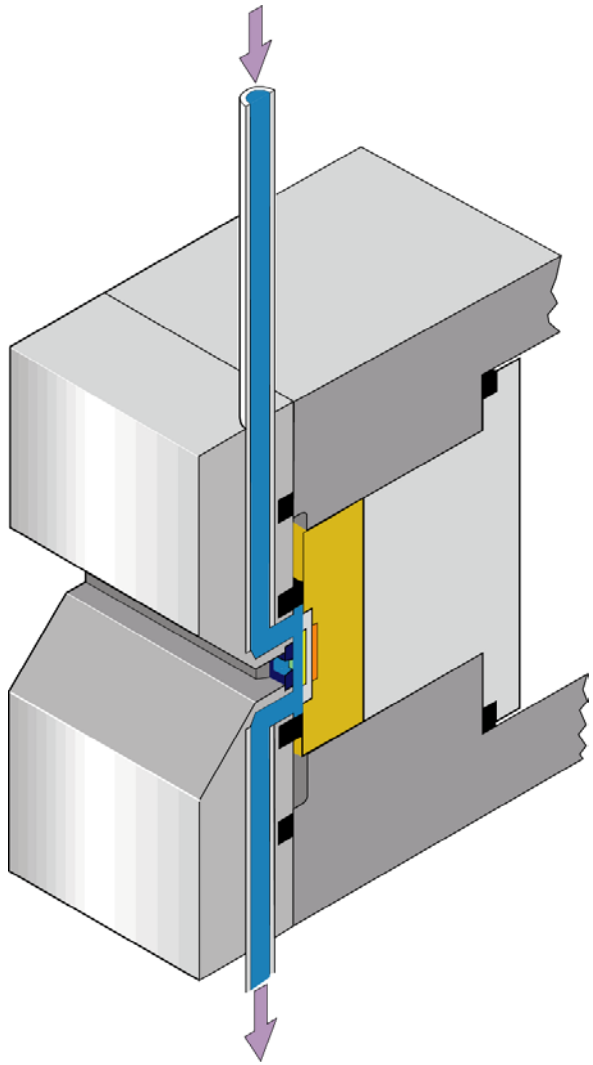
# SXES on liquid systems

Liquid layer on substrate at ambient conditions

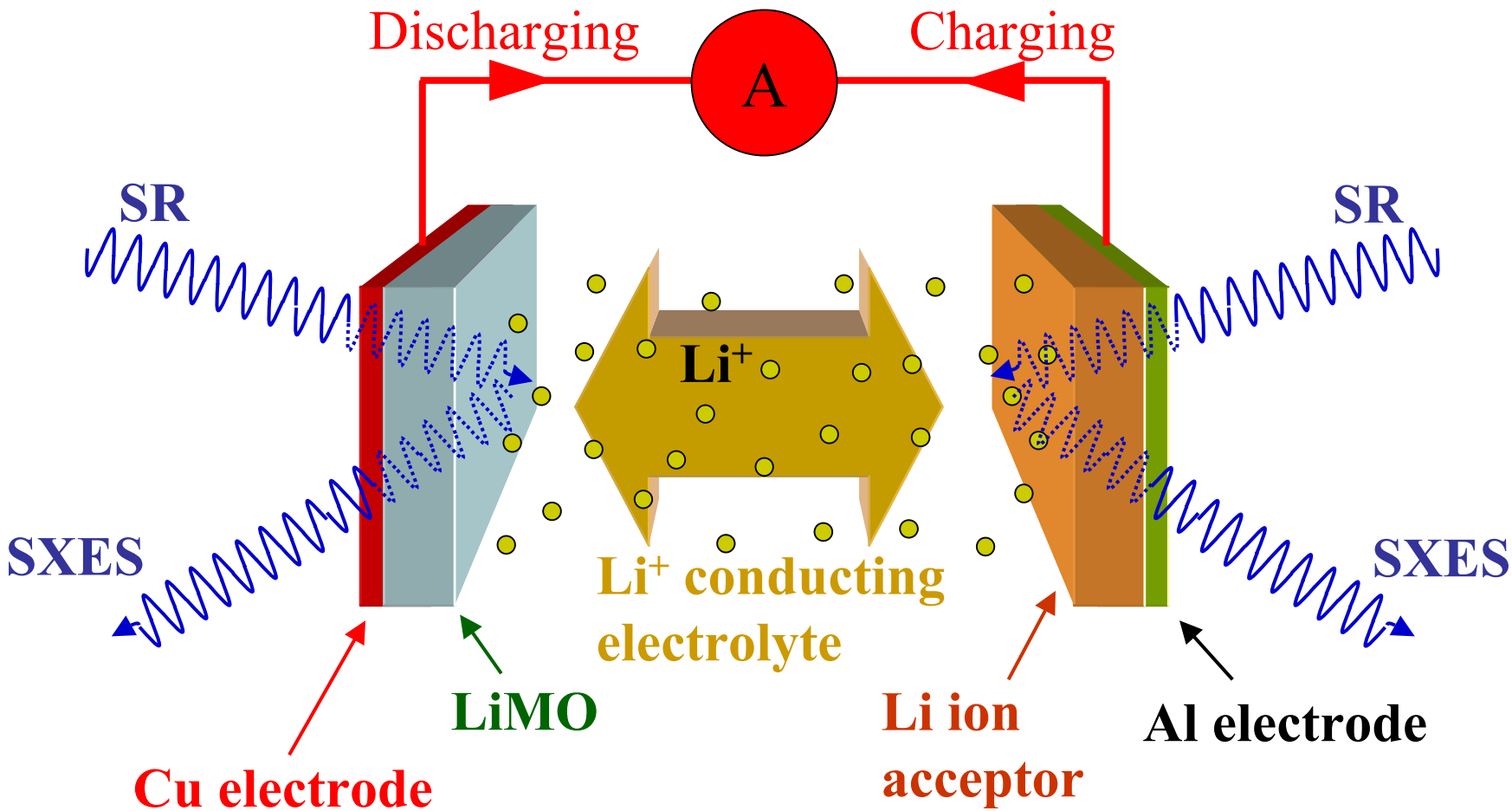


# RIXS gas/liquid cell for corrosion studies

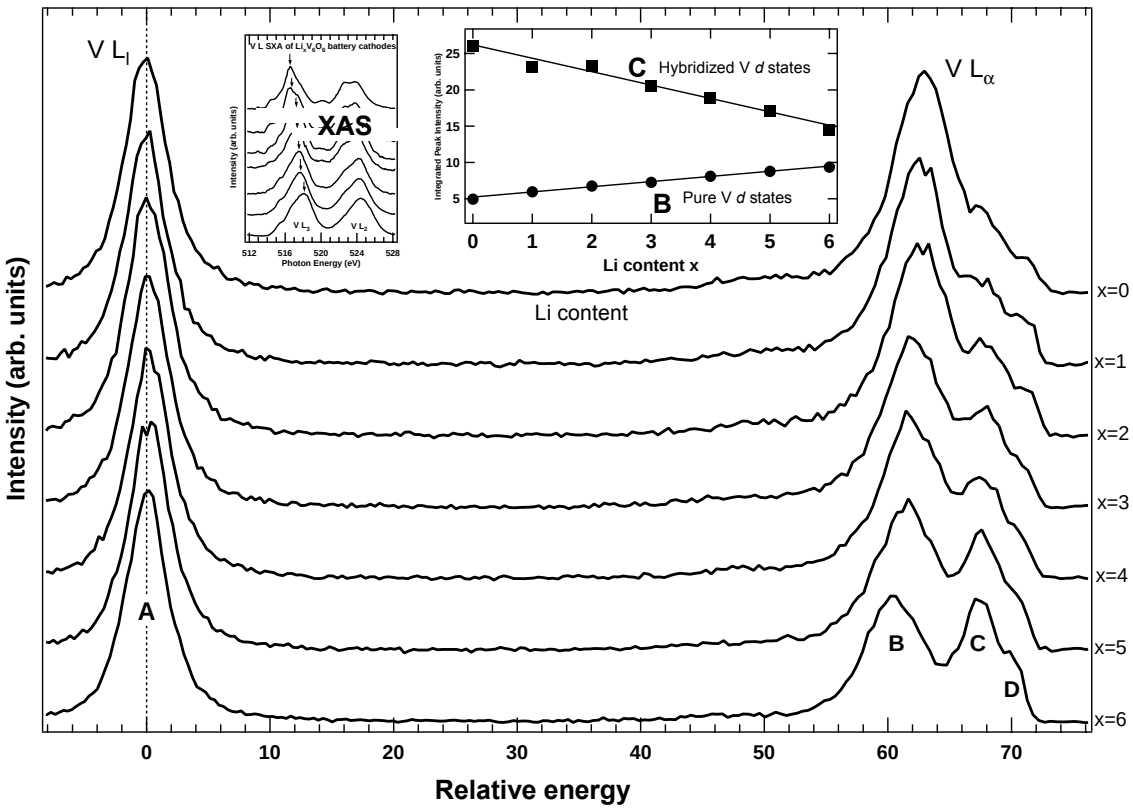


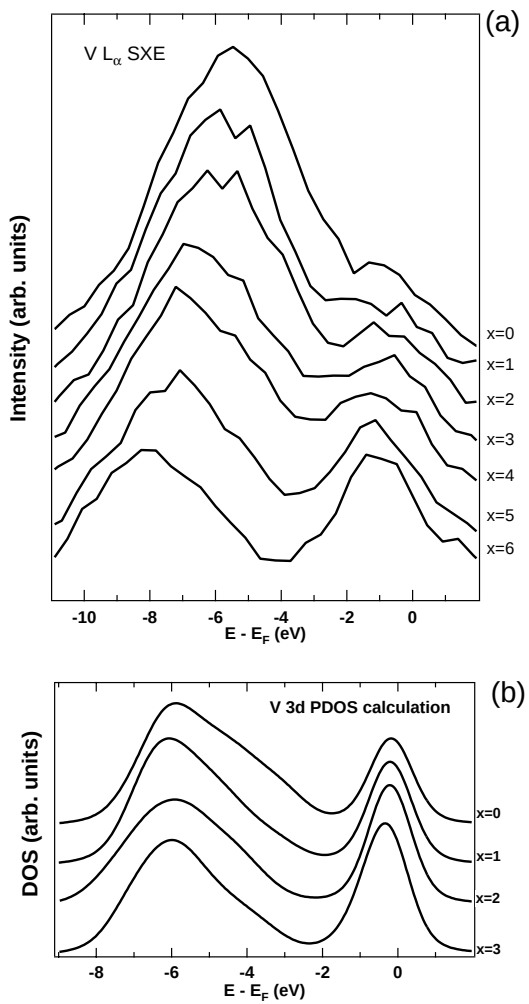



# *In situ* study of electrochemical processes by SXES

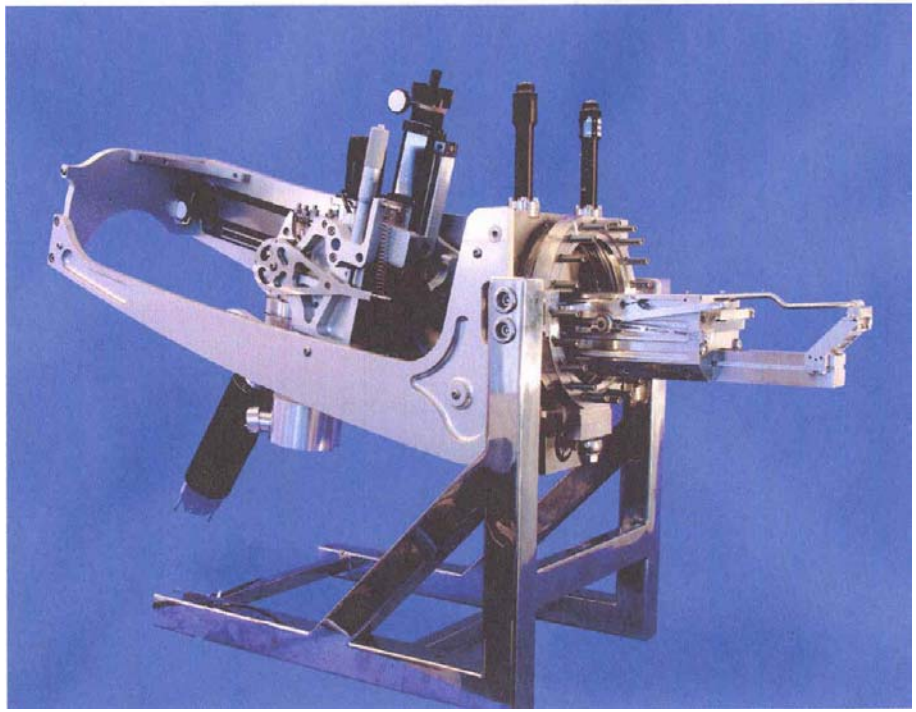


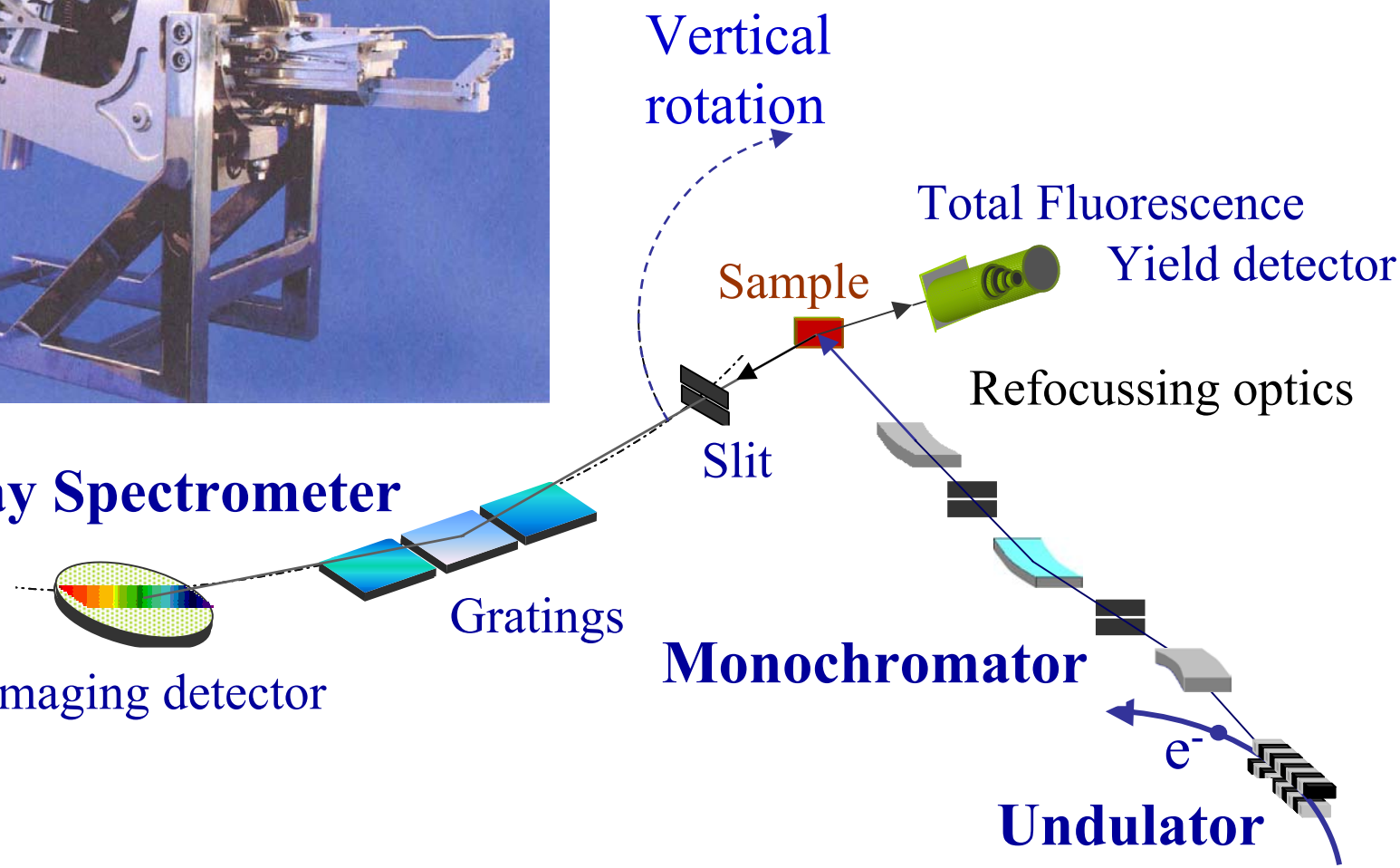
# Soft X-ray spectra of Li-inserted $V_6O_{13}$



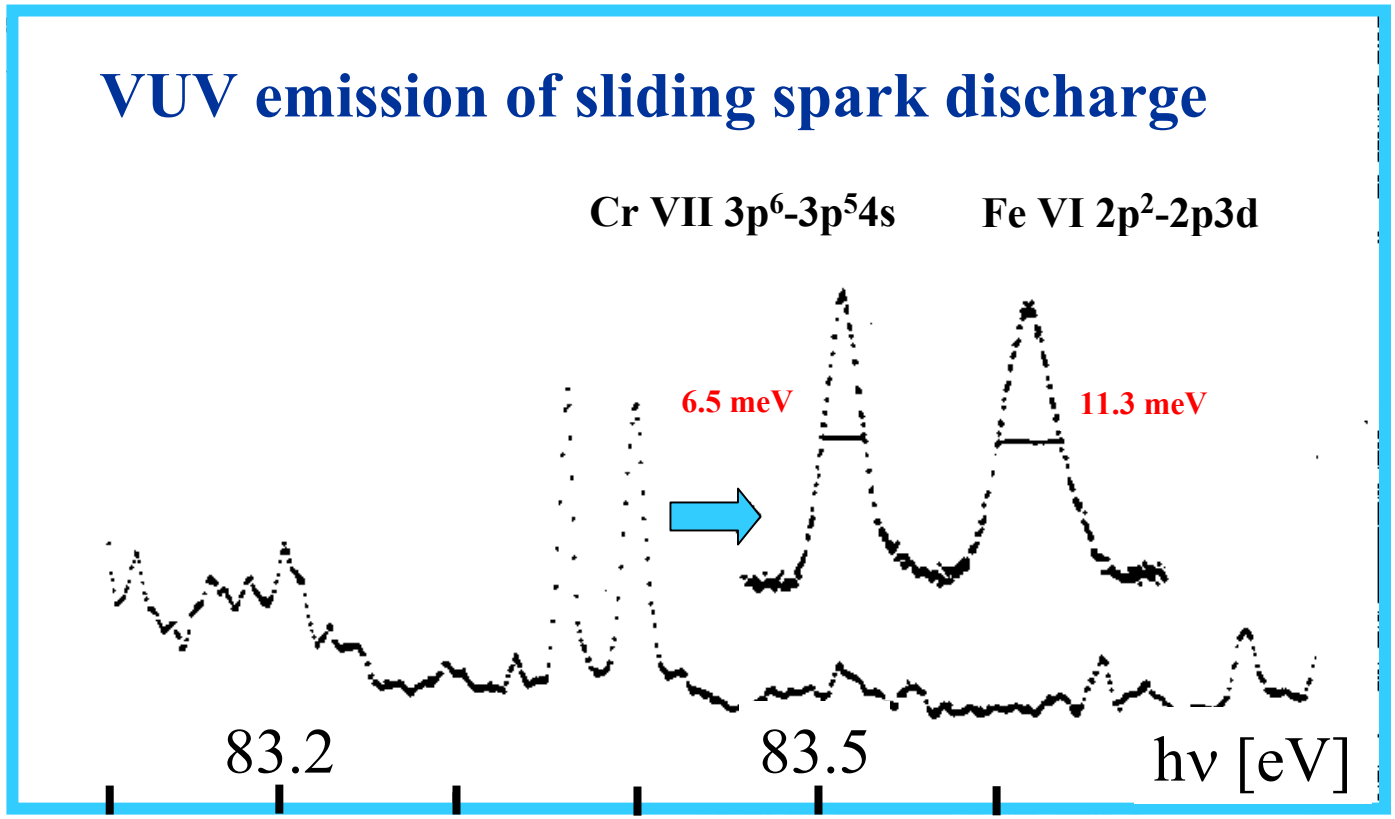




T. Schmitt, *et al*., J. Appl. Phys., **95**, 6444 (2004)



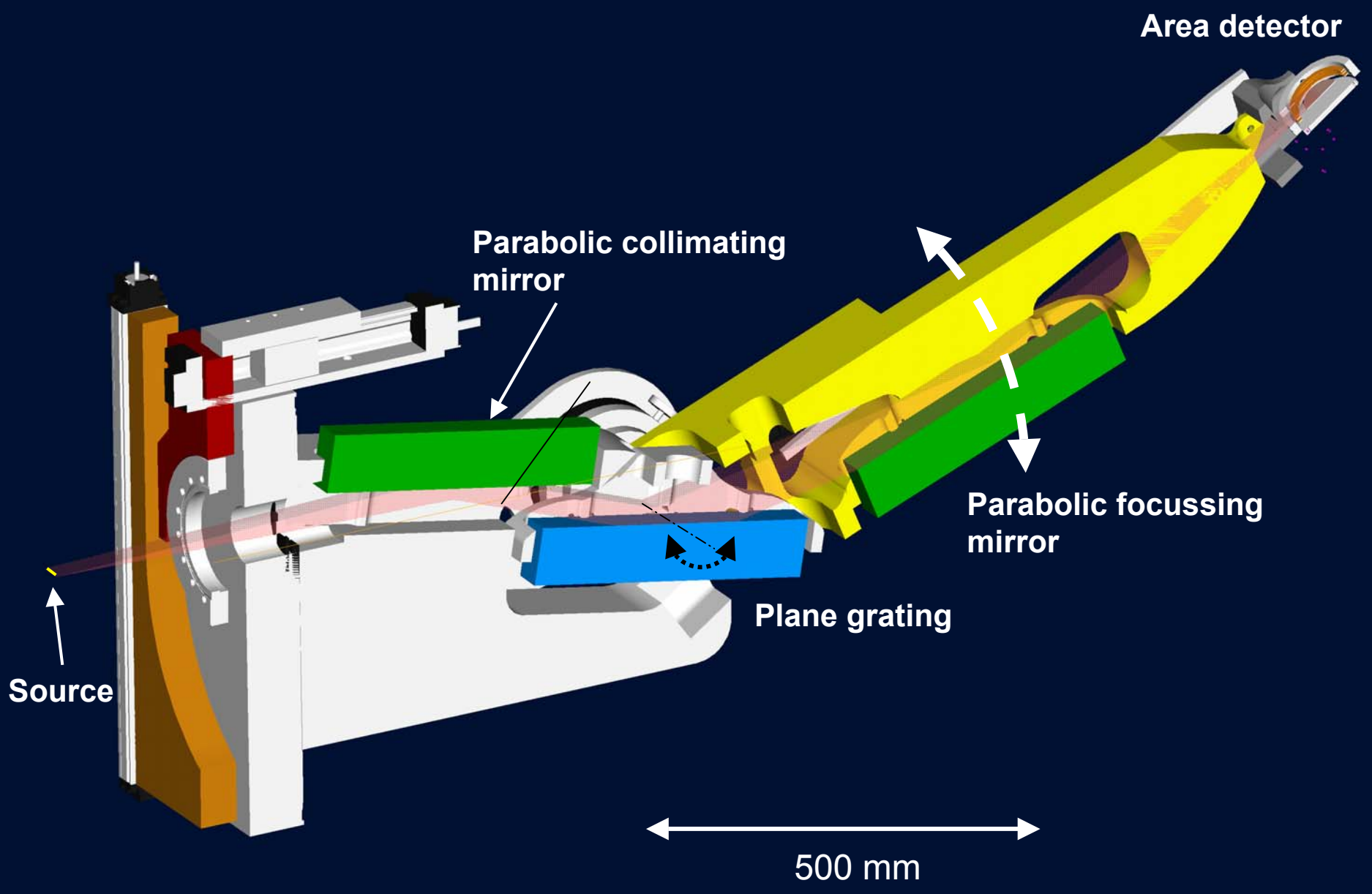

Vertical
rotation
Total Fluorescence
Yield detector
Sample
Refocussing optics
Slit
Soft X-Ray Spectrometer
Gratings
Monochromator
Imaging detector
e-
Undulator

# Very high resolution ultra-soft X-ray emission spectra



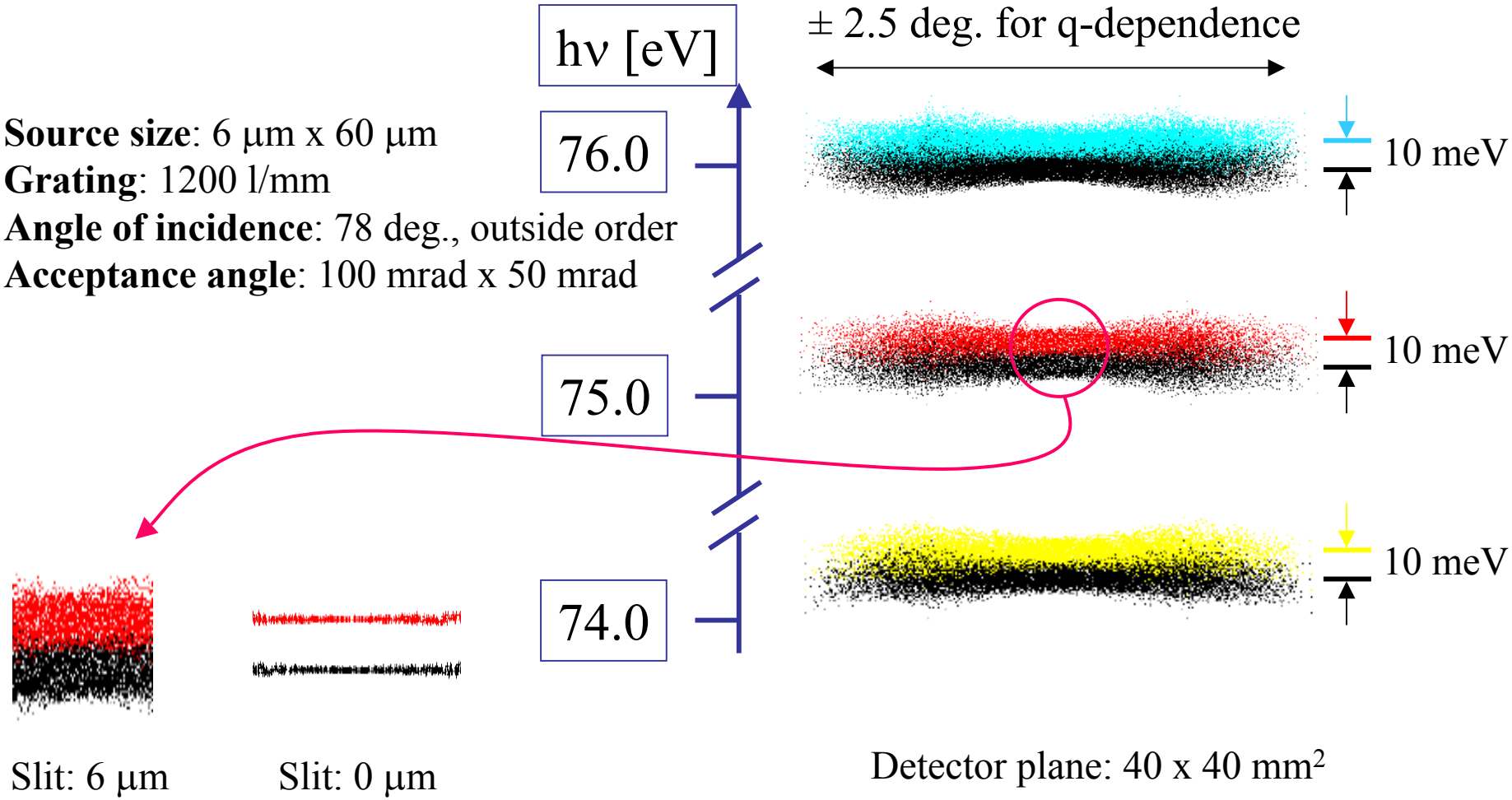

M. Bäckström, *et al*., Phys. Scripta, **29**, 568 (1984)

# Parabolic plane grating SX spectrometer

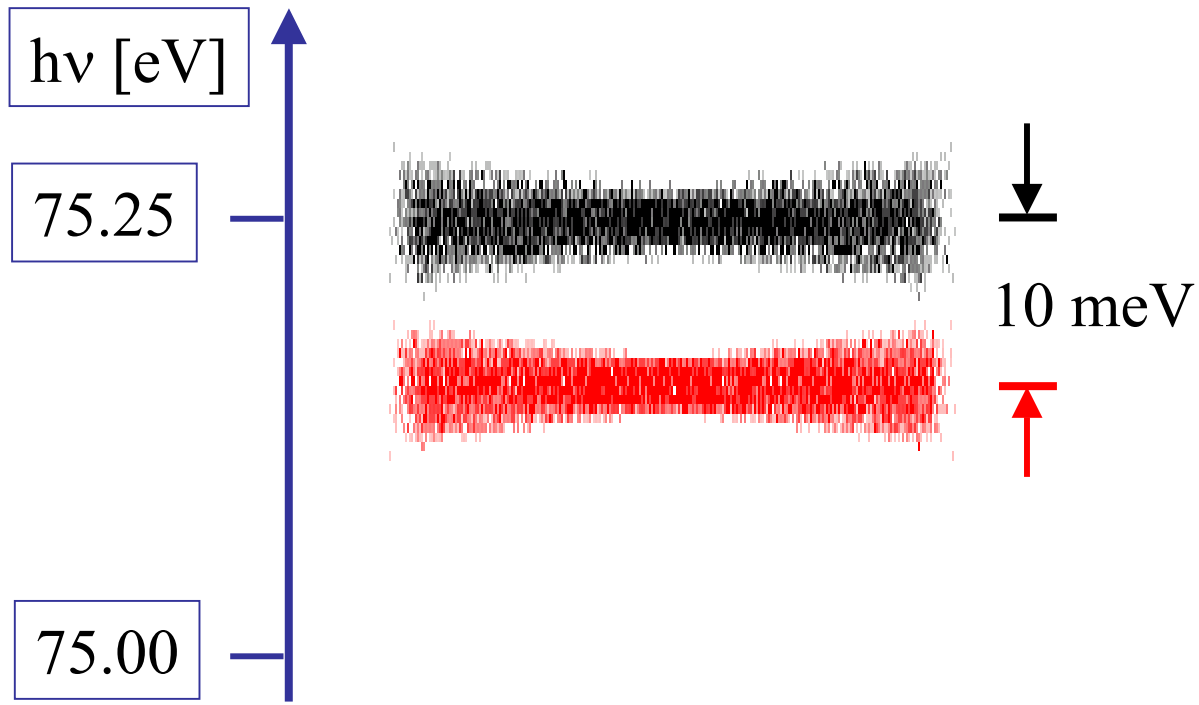


# Raytracing of Double Paraboloidal Mirror Plane Grating Spectrometer

**Source size**: 6 μm x 60 μm
**Grating**: 1200 l/mm
**Angle of incidence**: 78 deg., outside order
**Acceptance angle**: 100 mrad x 50 mrad



# Maximizing resolution for plane grating spectrometer




**Source size**: 6 μm x 60 μm
**Grating**: 1800 l/mm
**Angle of incidence**: 85 deg., inside order
**Acceptance angle**: 20 mrad x 50 mrad

# Acknowledgement

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