X-ray Spectroscopy

A Critical Look at Past Accomplishments and Future Prospects

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Lecture plan

1. Fundamental principles of x-ray – matter interactions: x-ray absorption and emission
2. Principles of EXAFS and XANES data analysis
3. Applications of x-ray spectroscopy to inorganic chemistry
4. Advanced methods in x-ray spectroscopy

Fundamental principles

1. Techniques for studying metals
2. Interactions of x-rays with matter
3. XAS – EXAFS and XANES
4. Data collections
   a) Generation of x-rays
   b) Measurement of x-rays
   c) Transmission vs. Fluorescence measurements
   d) Sensitivity

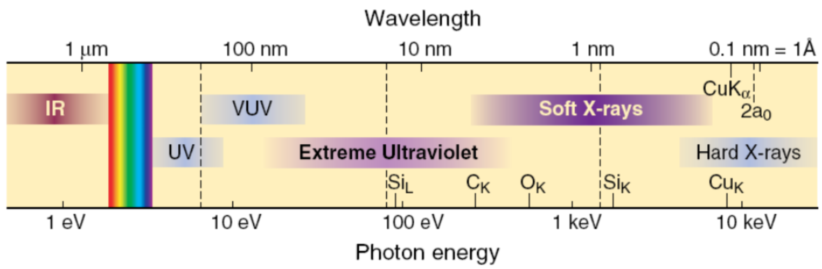
Techniques for studying metal sites (proteins, materials, etc.)

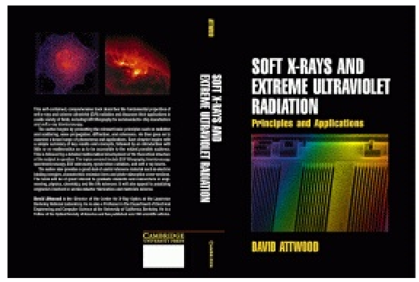
- UV-visible spectroscopy
- EPR spectroscopy
- Magnetic susceptibility
- MCD

Require open d shell

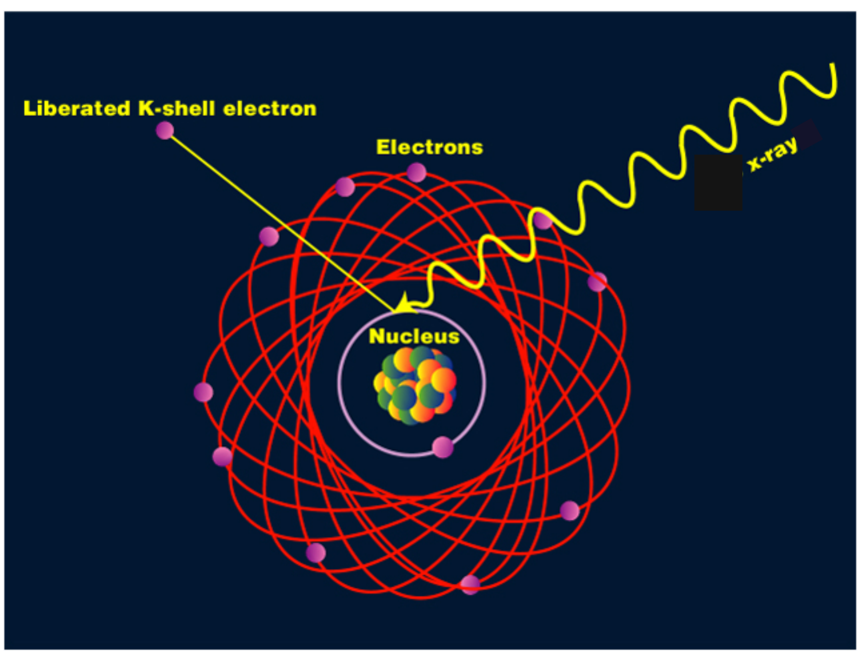
- NMR spectroscopy — Requires I=1/2 nucleus
- X-ray crystallography — Requires crystals

- X-ray spectroscopy

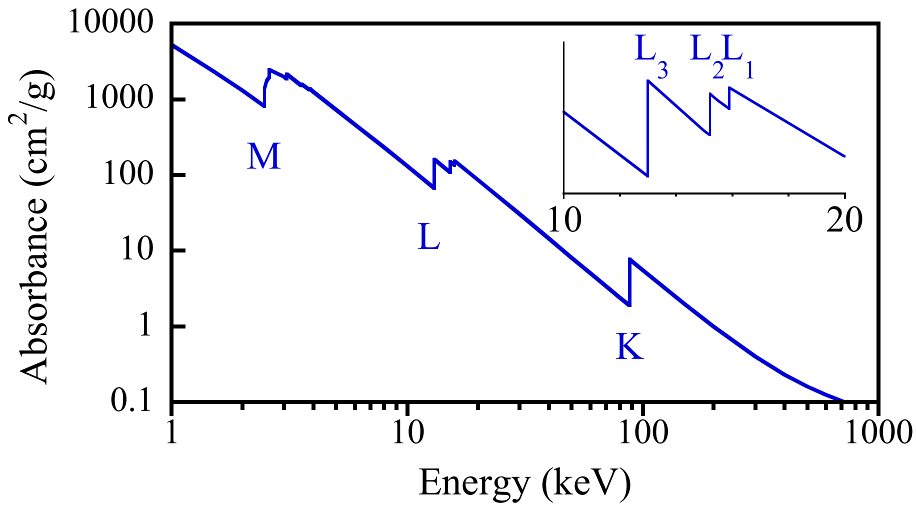




http://www.coe.berkeley.edu/AST/sxreuv



Absorption of x-rays by Pb



Electron binding energies of the elements

Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$	M_4 $3d_{3/2}$	M_5 $3d_{5/}$
1 H	13.6								
2 He	24.6[b]								
3 Li	54.7[b]								
4 Be	111.5[b]								
5 B	188[b]								
6 C	284.2[b]								
7 N	409.9[b]	37.3[b]							
8 O	543.1[b]	41.6[b]							
9 F	696.7[b]								
10 Ne	870.2[b]	48.5[b]	21.7[b]	21.6[b]					
11 Na	1070.8[c]	63.5[c]	30.4[c]	30.5[b]					
12 Mg	1303.0[c]	88.6[b]	49.6[c]	49.2[c]					
13 Al	1559.6	117.8[b]	72.9[b]	72.5[b]					
14 Si	1838.9	149.7[b]	99.8[b]	99.2[b]					
15 P	2145.5	189[b]	136[b]	135[b]					
16 S	2472	230.9[b]	163.6[b]	162.5[b]					
17 Cl	2822.4	270.2[b]	202[b]	200[b]					
18 Ar	3205.9[b]	326.3[b]	250.6[b]	248.4[b]	29.3[b]	15.9[b]	15.7[b]		
19 K	3608.4[b]	378.6[b]	297.3[b]	294.6[b]	34.8[b]	18.3[b]	18.3[b]		
20 Ca	4038.5[b]	438.4[c]	349.7[c]	346.2[c]	44.3[c]	25.4[c]	25.4[c]		
21 Sc	4492.8	498.0[b]	403.6[b]	398.7[b]	51.1[b]	28.3[b]	28.3[b]		
22 Ti	4966.4	560.9[c]	461.2[c]	453.8[c]	58.7[c]	32.6[c]	32.6[c]		
23 V	5465.1	626.7[c]	519.8[c]	512.1[c]	66.3[c]	37.2[c]	37.2[c]		
24 Cr	5989.2	695.7[c]	583.8[c]	574.1[c]	74.1[c]	42.2[c]	42.2[c]		
25 Mn	6539.0	769.1[c]	649.9[c]	638.7[c]	82.3[c]	47.2[c]	47.2[c]		
26 Fe	7112.0	844.6[c]	719.9[c]	706.8[c]	91.3[c]	52.7[c]	52.7[c]		
27 Co	7708.9	925.1[c]	793.3[c]	778.1[c]	101.0[c]	58.9[c]	58.9[c]		
28 Ni	8332.8	1008.6[c]	870.0[c]	852.7[c]	110.8[c]	68.0[c]	66.2[c]		
29 Cu	8978.9	1096.7[c]	952.3[c]	932.5[c]	122.5[c]	77.3[c]	75.1[c]		
30 Zn	9658.6	1196.2[b]	1044.9[b]	1021.8[b]	139.8[b]	91.4[b]	88.6[b]	10.2[b]	10.1[b]

International XAFS Society

http://www.ixasportal.net/ixas/

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  - Scientific Trends
  - XAFS 15 (2012)
  - XAFS 16 (2015)

Databases

- X-Ray Interactions With Matter
- NIST: X-Ray Transition Energies Database
- NIST: X-Ray Mass Attenuation Coefficients
- Database of Raman spectroscopy, X-ray diffraction and chemistry of minerals
- The EELS Data Base :: Home
- Online Materials Information Resource – MatWeb
- Crystal Lattice Structures
- Crystal Structure Databases
- American Mineralogist Crystal Structure Database
- Superconducting Materials Database
- Superconductivity Papers Database

Links

Facilities

America

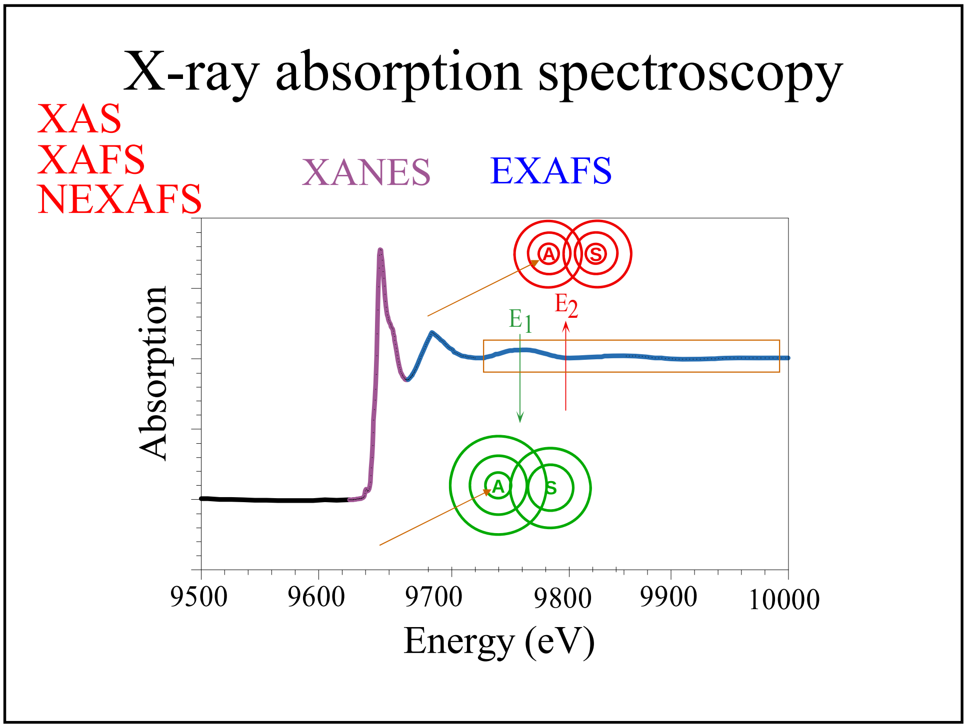
- ALS - Advanced Light Source, USA
- APS - Advanced Photon Source, USA
- CAMD - Center for Advanced Microstructures & Devices, USA
- CHESS - Cornell High Energy Synchrotron Source, USA
- CLS - Canadian Light Source, Canada
- CTST - UCSB Center for Terahertz Science and Technology, U
- DFELL - Duke Free Electron Laser Laboratory, USA
- Jlab - Jefferson Lab, USA
- LCLS - Linac Coherent Light Source, USA
- LNLS - Laboratorio Nacional de Luz Sincrotron, Brazil
- NSLS - National Synchrotron Light Source, USA
- SRC - Synchrotron Radiation Center, USA
- SSRL - Stanford Synchrotron Radiation Lightsource, USA
- SURF - Synchrotron Ultraviolet Radiation Facility, USA
- VU FEL - W. M. Keck Vanderbilt Free-electron Laser Center, U

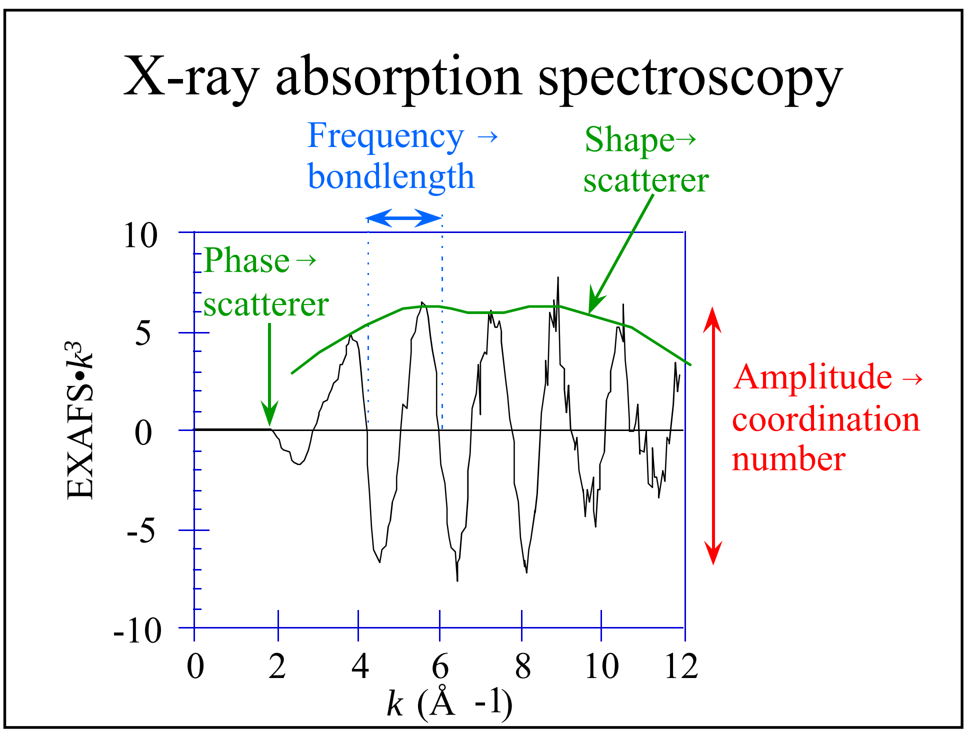
US DOE Nanoscale Science Research Centers

- CFN - Center for Functional Nanomaterials, USA
- CNM - Center for Nanoscale Materials, USA
- FOUNDRY - The Molecular Foundry, USA

Asia

- BSRF - Beijing Synchrotron Radiation Facility, P.R. China
- CANDLE, Armenia
- HSRC - Hiroshima Synchrotron Radiation Center, Japan
- iFEL - Institute of Free Electron Laser, Japan
- INDUS 1/INDUS 2, India
- IR FEL Research Center - FEL-SUT, Japan
- Medical Synchrotron Radiation Facility, Japan
- NSRL - National Synchrotron Radiation Laboratory, P.R. China
- NSRRC - National Synchrotron Radiation Research Center, Taiwan
- NSSR - Nagoya University Small Synchrotron Radiation Facility, Japan
- KSR - Nuclear Science Research Facility, Japan
- PAL - Pohang Accelerator Laboratory , Korea
- PF - Photon Factory, KEK, Japan
- Ritsumeikan University (Rits) Synchrotron Radiation Center, Japan
- SAGA-LS - Saga Light Source, Japan
- SESAME, Jordan
- SLRI - Synchrotron Light Research Institute, Thailand
- SPring-8, Japan
- SSLS - Singapore Synchrotron Light Source, Singapore
- SSRC - Siberian Synchrotron Research Center, Russian Federation
- SSRF - Shanghai Synchrotron Radiation Facility, P.R. China
- SuperSOR - SuperSOR Synchrotron Radiation Facility, Japan


X-ray absorption spectroscopy
XAS
XAFS
NEXAFS
XANES
EXAFS
Absorption
E1
E2
A
S
9500
9600
9700
9800
9900
10000
Energy (eV)


X-ray absorption spectroscopy
Frequency → bondlength
Shape→ scatterer
Phase→ scatterer
Amplitude → coordination number
EXAFS•k3
10
5
0
-5
-10
0
2
4
6
8
10
12
k (Å -1)

Information Content of EXAFS

- Bond length ± 0.02 Å (accuracy)
- Bond length ±0.005 Å (precision)
- Coordination number (lower limit) ± 1
- Ligation type (Z) ± 10

R_{max} < ~ 4 Å

Scott, R. A. "Measurement of Metal-Ligand Distances by EXAFS" *Methods Enzymol.* **1985**, *117*, 414-459.

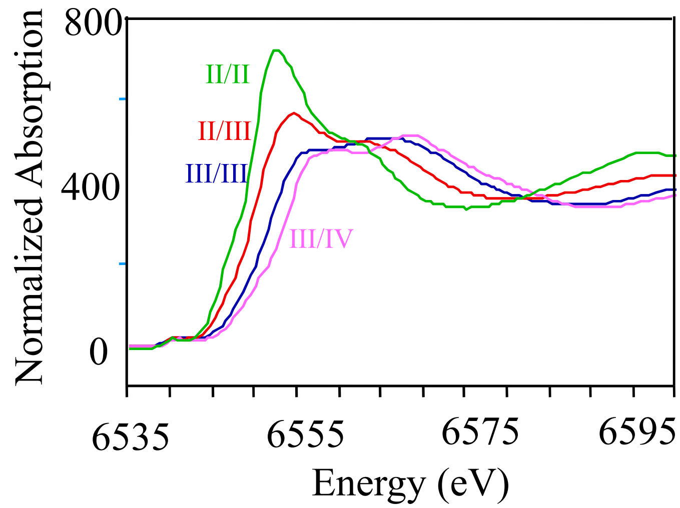
Teo, B. K. *EXAFS: Basic Principles and Data Analysis*; Springer-Verlag: New York, **1986**.

Scott, R.A., "X-Ray Absorption Spectroscopy" in *Physical Methods in Bioinorganic Chemistry*, Que, L. (Ed)., **2000**, University Science Books.

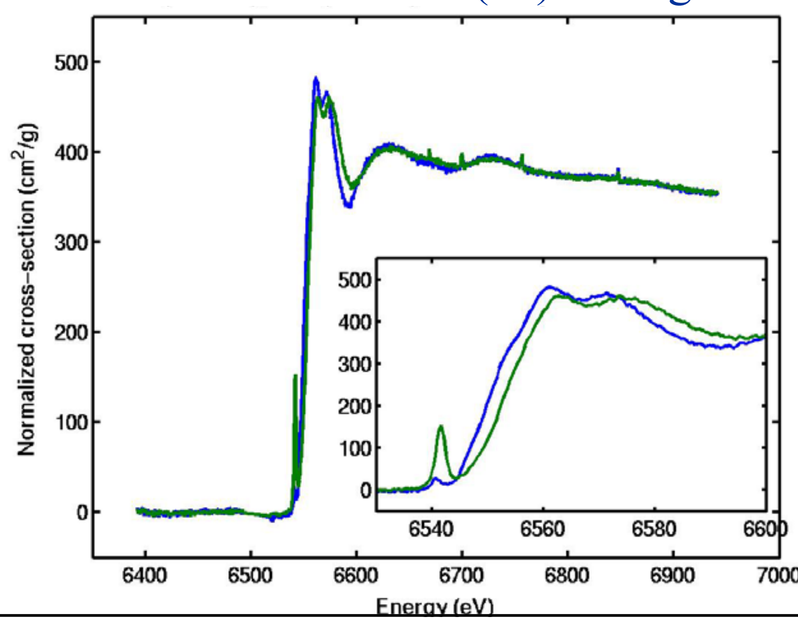
Penner-Hahn, J.E., "X-Ray Absorption Spectroscopy", in Comp. Coord. Chem. II, Vol. 2, **2004**.

Levina A, Armstrong R.S., Lay P.A., "Three-dimensional structure determination using multiple-scattering analysis of XAFS: applications to metalloproteins and coordination chemistry" *Coord. Chem. Rev.* **2005**, *249*, 141-160.

Dependence of XANES on Oxidation State



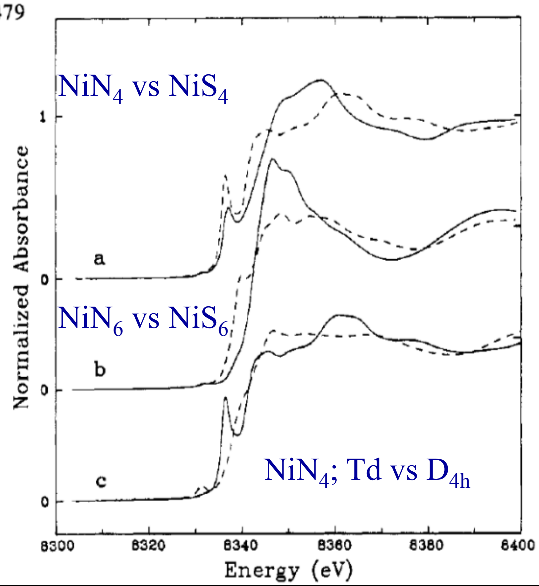
Mn(V)=O has intense pre-edge transition, not seen in Mn(III) analog



X-ray Absorption Spectroscopic Evidence for a Unique Nickel Site in *Clostridium thermoaceticum* Carbon Monoxide Dehydrogenase

Stephen P. Cramer,*[1a,b] Marly K. Eidsness,[1c,d] W.-H. Pan,[1a] Thomas A. Morton,[1e] Steve W. Ragsdale,[1e,f] Daniel V. DerVartanian,[1e] Lars G. Ljungdahl,[1e] and Robert A. Scott*[1g]

Inorg. Chem. **1987**, *26*, 2477–2479



Advantages of XAFS

Direct structural determination for:

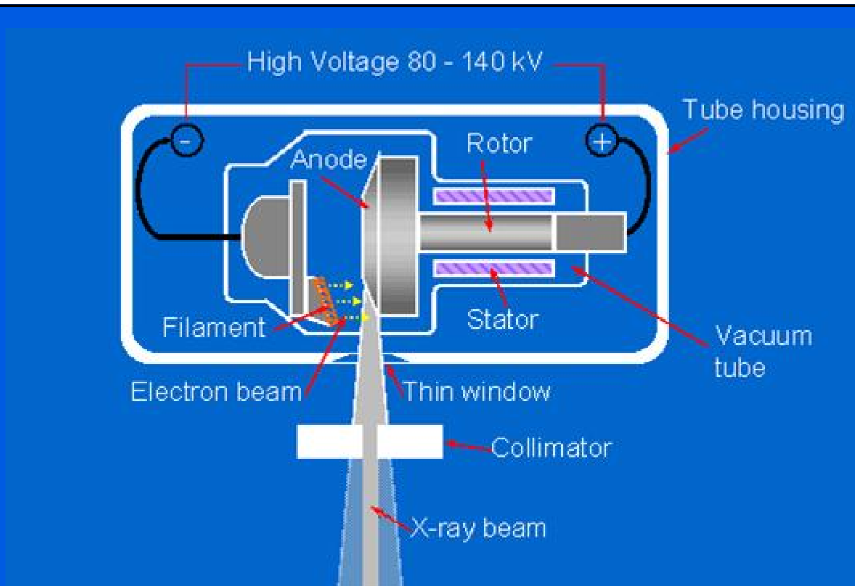
- Any form of matter
- Any isotope
- Any spin state

Direct determination of oxidation state

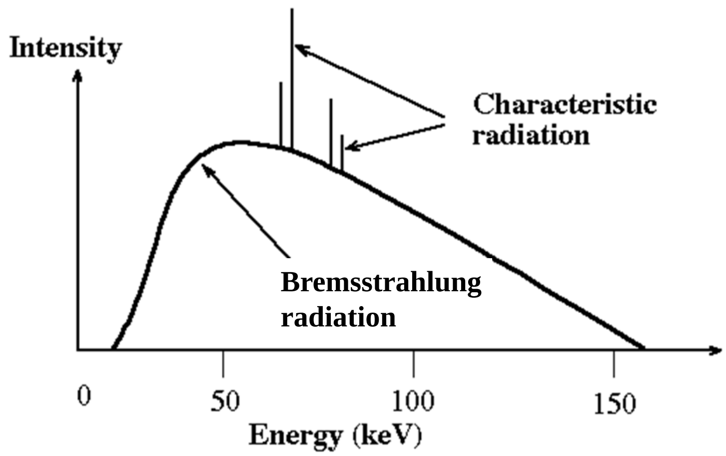
Disadvantages of XAFS

- Bulk spectroscopy (average structure)
- Little angular information
- Gives only *local* structural information
- Limited sensitivity

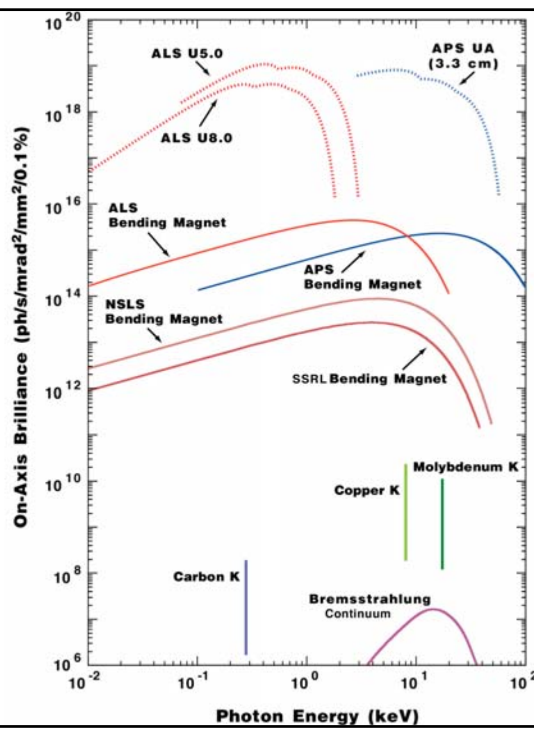
- Requires synchrotron x-ray source



http://learntech.uwe.ac.uk/radscience/x-ray_tube



Synchrotrons produce intense, tunable x-ray beams



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- Spectroscopy
- Diffraction

This article elsewhere

Published online 6 May 2009 | *Nature* **459**, 16-17 (2009) | doi:10.1038/459016a

News

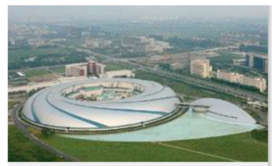
China joins world-class synchrotron club

Nation's costliest science facility is unveiled.

David Cyranoski

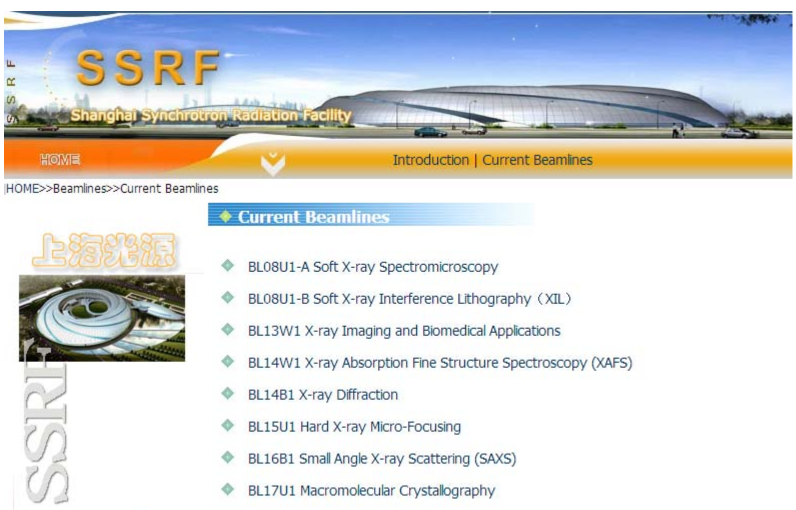
<dateline> **Shanghai** </dateline>

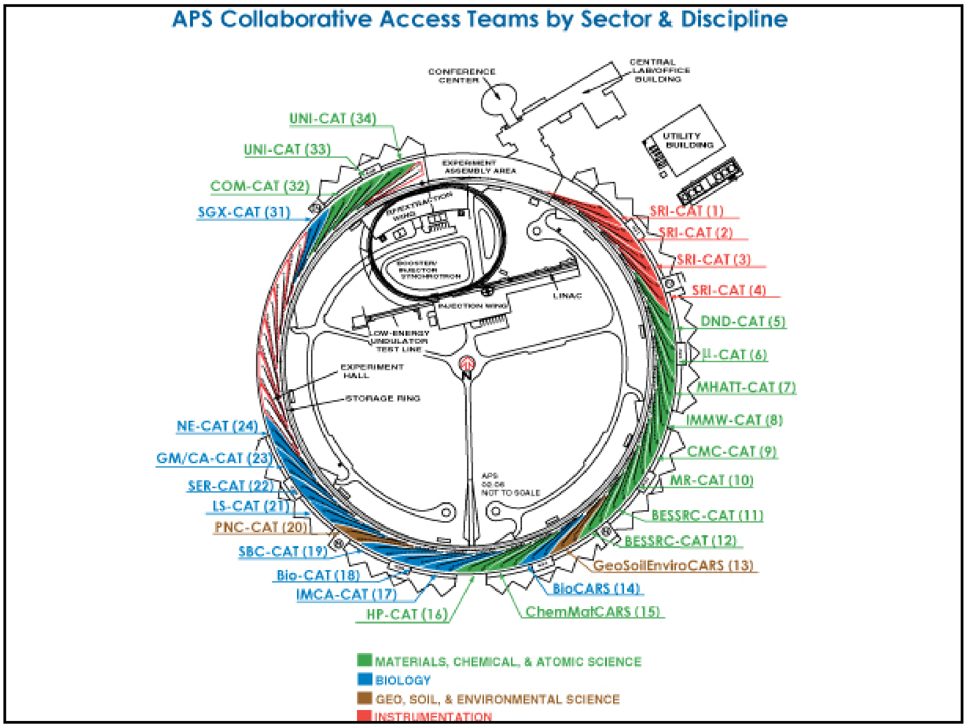
The Shanghai Synchrotron Radiation Facility (SSRF) officially opened its doors last week to a queue of scientists waiting hungrily for beamline time. The 1.2-billion renminbi (US$176-million) light source is China's biggest investment in a single science facility to date, says Zhao Zhentang, an accelerator physicist and the facility's

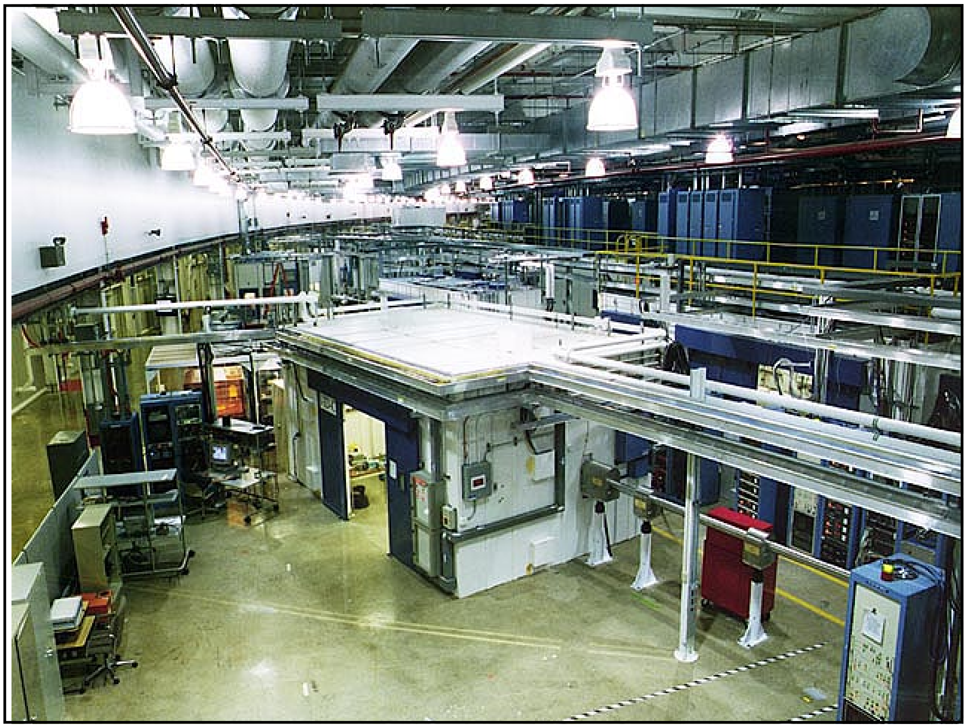


The Shanghai synchrotron is drawing Chinese scientists back from abroad.

SHANGHAI INST. APPL. PHYS.

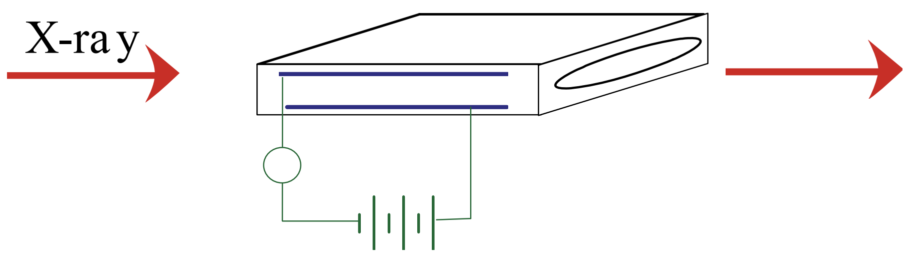

SSRF
Shanghai Synchrotron Radiation Facility
HOME
Introduction | Current Beamlines
HOME>>Beamlines>>Current Beamlines
Current Beamlines
上海光源
BL08U1-A Soft X-ray Spectromicroscopy
BL08U1-B Soft X-ray Interference Lithography（XIL）
BL13W1 X-ray Imaging and Biomedical Applications
BL14W1 X-ray Absorption Fine Structure Spectroscopy (XAFS)
BL14B1 X-ray Diffraction
BL15U1 Hard X-ray Micro-Focusing
BL16B1 Small Angle X-ray Scattering (SAXS)
BL17U1 Macromolecular Crystallography


APS Collaborative Access Teams by Sector & Discipline
CONFERENCE CENTER
CENTRAL LAB/OFFICE BUILDING
UTILITY BUILDING
EXPERIMENT ASSEMBLY AREA
BOOSTER/ INJECTOR SYNCHROTRON
LINAC
INJECTION WING
LOW-ENERGY UNDULATOR TEST LINE
EXPERIMENT HALL
STORAGE RING
NOT TO SCALE
UNI-CAT (34)
UNI-CAT (33)
COM-CAT (32)
SGX-CAT (31)
SRI-CAT (1)
SRI-CAT (2)
SRI-CAT (3)
SRI-CAT (4)
DND-CAT (5)
µ-CAT (6)
MHATT-CAT (7)
IMMW-CAT (8)
CMC-CAT (9)
MR-CAT (10)
BESSRC-CAT (11)
BESSRC-CAT (12)
GeoSoilEnviroCARS (13)
BioCARS (14)
ChemMatCARS (15)
HP-CAT (16)
IMCA-CAT (17)
Bio-CAT (18)
SBC-CAT (19)
PNC-CAT (20)
LS-CAT (21)
SER-CAT (22)
GM/CA-CAT (23)
NE-CAT (24)
MATERIALS, CHEMICAL, & ATOMIC SCIENCE
BIOLOGY
GEO, SOIL, & ENVIRONMENTAL SCIENCE
INSTRUMENTATION



Detection of x-rays

X-rays are ionizing radiation – need to collect (and count) ionizations



Transmission measurements

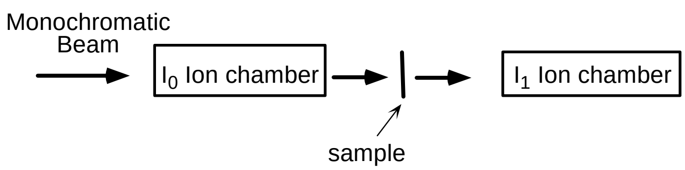
Beer-Lambert law I_0=incident, I_t=transmitted

$$I_t = I_0 10^{-\varepsilon C l} \qquad I_t = I_0 e^{-\mu t}$$

$$I_t = I_0 e^{-\mu_m \rho t}$$

- t sample thickness (cm)
- μ absorption coefficient (cm^{-1})
- μ_m mass absorption coefficient ($cm^2 g^{-1}$)
- ρ Density ($g\ cm^{-3}$)

Absorbance



$$A = \varepsilon C l = \log\left(\frac{I_0}{I_t}\right) \qquad A = \mu t = \ln\left(\frac{I_0}{I_t}\right)$$

X-ray absorption coefficients

http://csrri.iit.edu/periodic-table.html

http://physics.nist.gov/PhysRefData/XrayMassCoef/cover.html

http://csrri.iit.edu/periodic-table.html

Periodic Table

Click on any button with element name to get its x-ray properties. If you give an energy value in the box at the top of the table then you also get x-ray cross-sections at that energy. The original subroutine (mucal.f or mucal.c) used to calculate x-ray cross-sections is available from here.

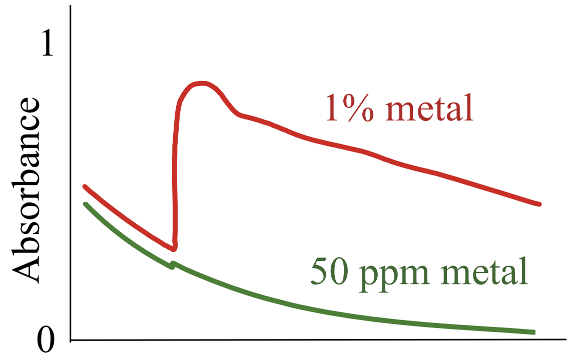
Energy: 7.2 keV

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe

Element		Edge Energies (keV)		Edge jumps		Fluorescence yield	
Symbol	Fe	K	7.11199999	K	8.0714798	K	0.340000004
Z	26	L1	0.842000008	L1	1.1567719	L1	0.00100000005
Atomic Weight	55.8499985	L2	0.719900012	L2	2.09867859	L2	0.0939999968
Density	7.86000013	L3	0.706799984	L3	0.	L3	6.40299988
		M	0.0939999968				
		K-alpha	6.40299988				
		K-beta	7.05700016				
		L-alpha	0.				
		L-beta	0.				

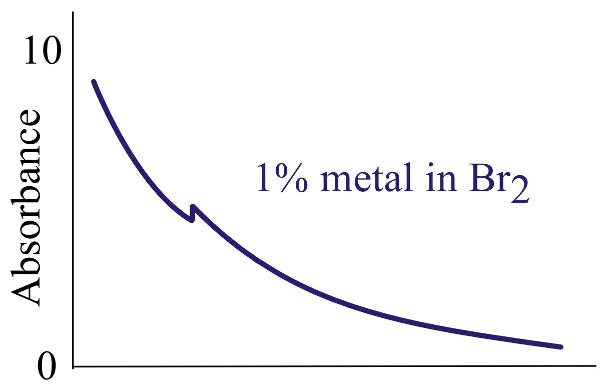
Cross-sections at E = 7.19999981 keV (cm^2/gm)		
Photoelectric	393.506775	
Coherent	1.797014	
Incoherent	0.0686381012	
Total	395.372406	
Conversion factor (C) {(Barns/Atom) = C * (cm^2/gm)}	92.7399979	
Absorption coefficient	3107.6272	1/cm
1/mu (element)	3.21788907	microns

Absorbance is great for concentrated samples,

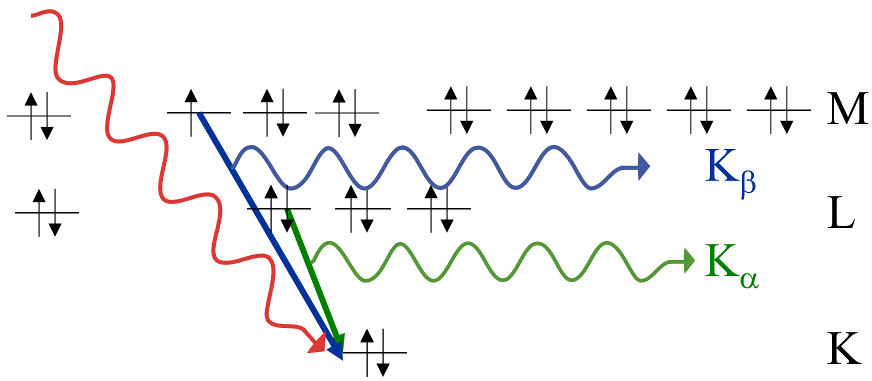


but not for dilute samples.

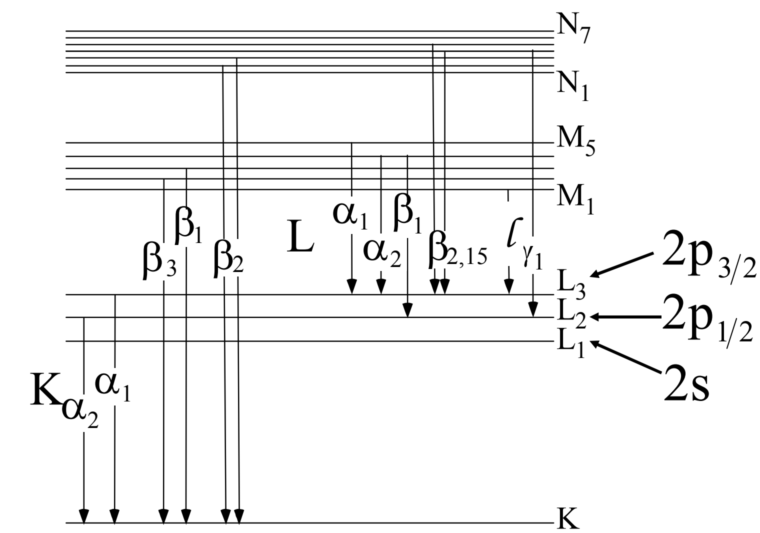
Transmission is also sensitive to background absorption



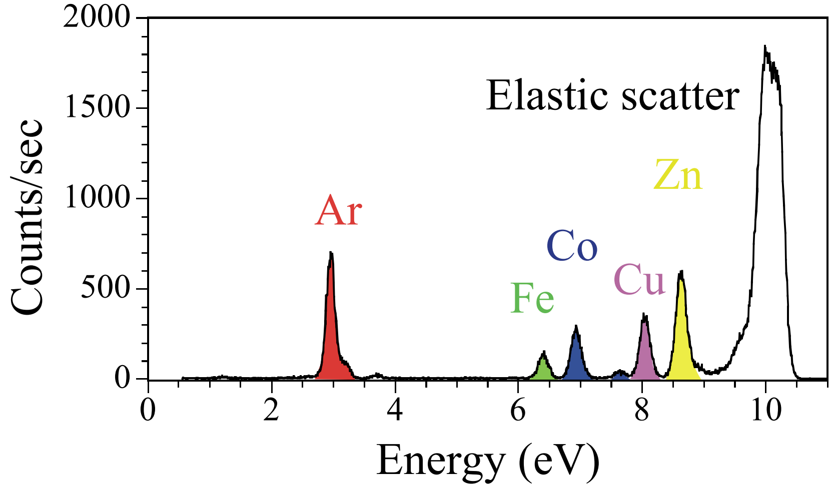
X-ray Fluorescence



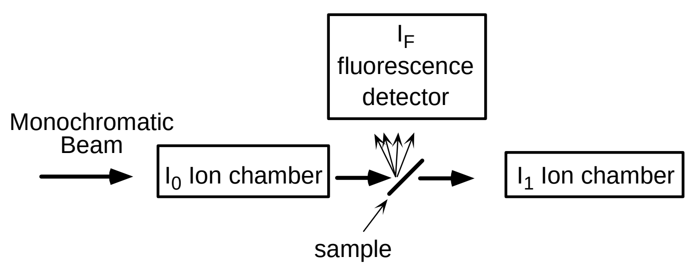
X-ray fluorescence lines



X-ray fluorescence spectra give element sensitivity



Fluorescence excitation spectra



Measure fluorescence intensity as excitation energy is scanned

Self-absorption

$$I_F = I_0 \frac{\Omega}{4\pi} \varepsilon \frac{\mu_X(E)}{\mu_T(E) + \mu_T(E_{fl})} \left(1 - e^{-[\mu_T(E) + \mu_T(E_{fl})]t}\right)$$

$$\mu_T = \mu_X + \mu_B$$

Reduces to $I_f \propto \mu_X$ if $\mu t \ll 1$ (thin)

If $\mu t \gg 1$ (thick)

$$I_F \approx \frac{\mu_X(E)}{\mu_T(E) + \mu_T(E_{fl})} = \frac{\mu_X(E)}{\mu_X(E) + \mu_B(E) + \mu_T(E_{fl})}$$

Goulon J, et al. "On Experimental Attenuation Factors Of The Amplitude Of The EXAFS Oscillations In Absorption, Reflectivity And Luminescence Measurements", *J de Physique* **43**, 539-548 1982

Self-absorption continued

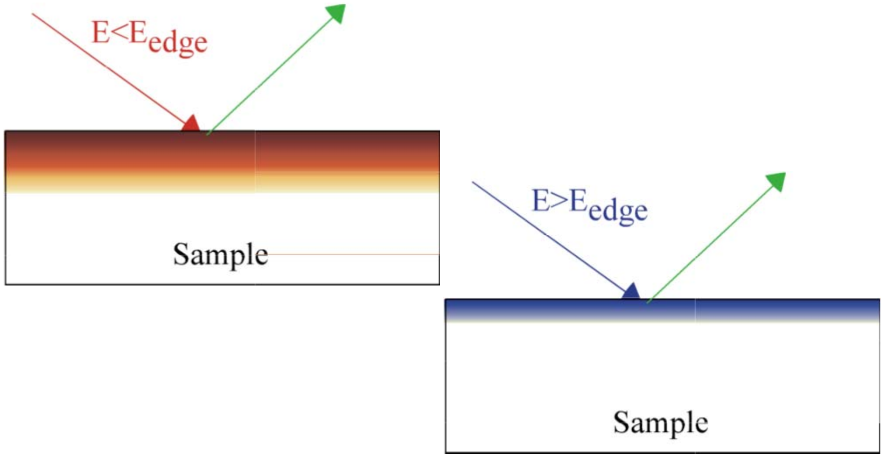
$$\frac{\mu_X(E)}{\mu_X(E) + \mu_B(E) + \mu_T(E_{fl})} \approx \mu_X(E)$$

Only if $\mu_X \ll \mu_B$ (dilute)

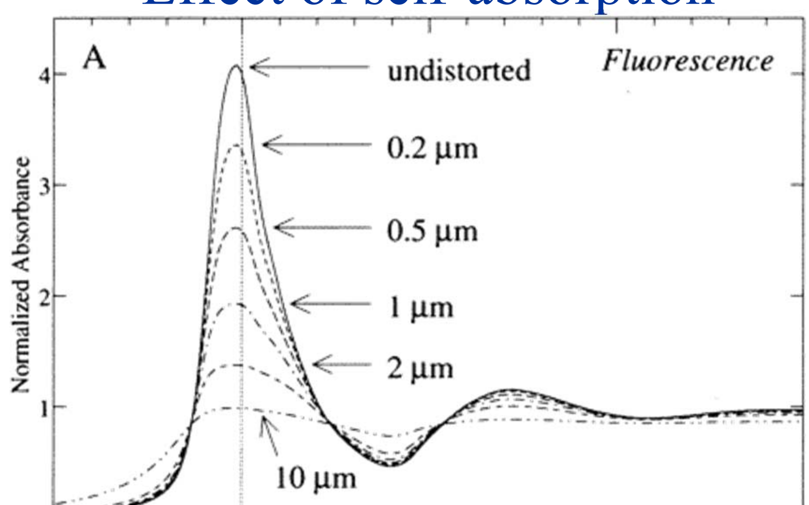
Fluorescence excitation spectra only give accurate μ_X if samples are thin or dilute. Otherwise, need to correct.

Waldo GS, Carlson RMK, Moldowan JM, Peters KE, Penner-Hahn JE "Sulfur Speciation In Heavy Petroleums - Information From X-ray Absorption Near-edge Structure " Geochim Cosmochim Acta **55** 801-814 (1991)

If samples are not either thin or dilute, will have self-absorption



Effect of self-absorption



Pickering IJ, et al. "Analysis of sulfur biochemistry of sulfur bacteria using X-ray absorption spectroscopy" *Biochemistry* **40** 8138-8145 (2001)

Self-absorption

If a sample gives a reasonable transmission signal, it is too concentrated to measure by fluorescence (unless sample is very thin)

Signal/Noise concerns in XAS

Counting statistics – uncertainty ~ $(\text{counts})^{1/2}$

If there is no background, S/N= $(\text{counts})^{1/2}$

Typical fluorescence 10^4 sec^{-1} to 10^5 sec^{-1}

Transmission ion-chambers – typical currents ≥10 nA ~ 10^{10} electrons/s Negligible noise from counting statistics.

Important noise sources: electronic, microphonic, beam problems (below)

Sensitivity

EXAFS amplitude falls of ≈ $1/k^3$

10% effect at k=2 Å^{-1}; 0.03% at k=14 Å^{-1}

For EXAFS S/N=3 at 14 Å^{-1} need absorption S/N=3/0.0003=10^4

Therefore need 10^8 counts at k=14 Å^{-1}

What is required to have 10^8 fluorescent photons

Incident flux ≈ $2 \cdot 10^{13}$ sec^{-1} in 10^{-8} m^2

Fluorescence yield ≈ 0.5 → need absorbance of 10^{-5} to give 10^8 fluorescent photons in 1 second

Absorbance = $3 \cdot 10^4$ barns/atom

= $3 \cdot 10^{-16} \cdot$N

Need N ≈ $3 \cdot 10^{10}$

50 fmole, 50 μM if sample is (100 μm)^3

Reality

Detected solid angle is 1-5% (i.e., 10^6 sec^{-1}) but – count times of 100 sec/pt are realistic → total measurement time ~6 hrs (vs. 3 minutes)

However

Effective count rate is often detector-limited: if scatter:fluorescence is 100:1, N_{max}~10^4 (10^2-fold lower than optimum).

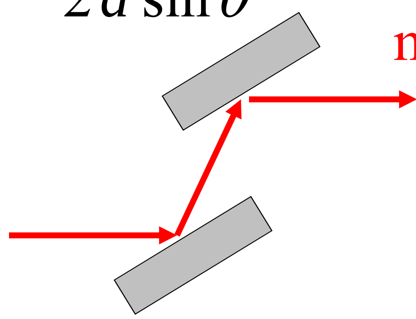
- Solids
  - If absorbance of element of interest > background absorbance use transmission
  - If absorbance of element of interest << background absorbance use fluorescence
  - Samples need to be optically thin – often requires dilution
- Solutions
  - If concentrated, treat like a solid
  - If dilute (negligible edge jump) use fluorescence
  - Typical limits
    - ~ 100 µM Zn in 50 µL aqueous solution (5 nmole)
    - ~1.0 mM V in 10 µL aqueous solution (10 nmole)
    - 10 µM Mo in 200 µL aqueous solution (2 nmole)

Bragg's Law

$$n\lambda = 2d\sin\theta ; E = hc/\lambda$$

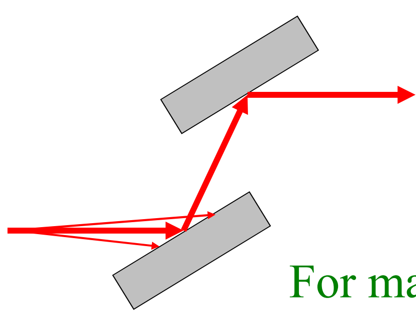
$$E = \frac{nhc}{2d\sin\theta}$$

Double-crystal monochromator



Energy resolution

$$n\lambda = 2d\sin\theta$$



Angular divergence gives spread in energy. Vertical slits decrease $\Delta\theta$, and thus ΔE.

For many 3rd generation sources, angular divergence of beam is small compared to intrinsic width of reflection

Energy calibration

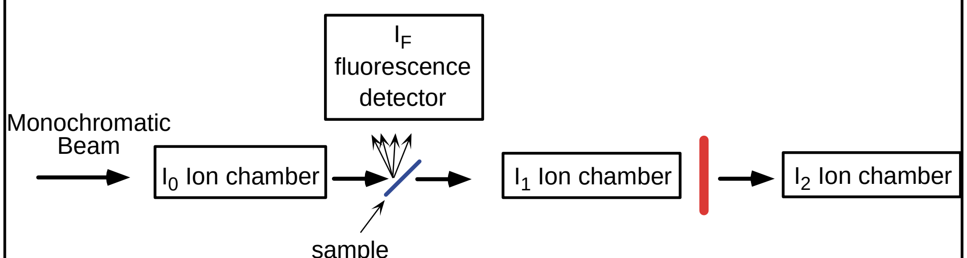
$$n\lambda = 2d\sin\theta$$

Want to know E to ~0.1 eV (1 part in 10^5)
Accurate absolute energy determination is hard. Typically, settle for precise relative energy.

For absolute calibration, see:

Pettifer RF, Hermes C "Absolute energy calibration of x-ray-radiation from synchrotron sources" *J Appl Crystallogr* **18**, 404-412 (1985)

Internal energy calibration



$$A_{sample} = \ln\left(\frac{I_0}{I_1}\right) \qquad A_{foil} = \ln\left(\frac{I_1}{I_2}\right)$$

Harmonic contamination

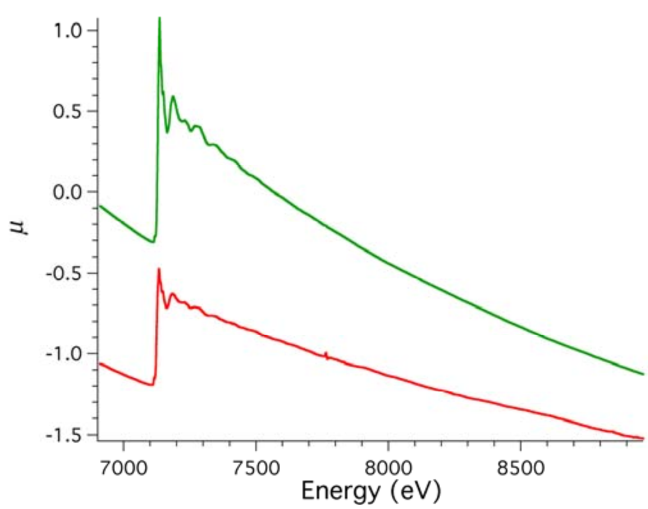
$$n\lambda = 2d\sin\theta$$

$$I_0 = I_0 + \beta I_{0,2E}$$

$$I_t = e^{-\mu t} I_0 + \beta I_{0,2E}$$

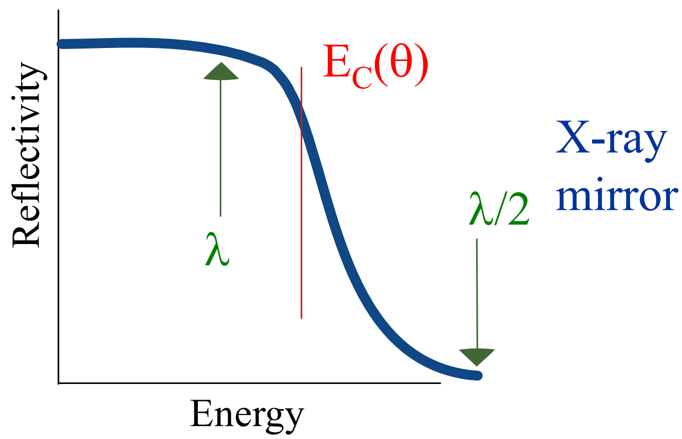
$$A = \ln\left(\frac{I_0}{I_1}\right) = \ln\left(\frac{I_0 + \beta I_{0,2E}}{e^{-\mu t} I_0 + \beta I_{0,2E}}\right)$$

Experimental consequence of harmonic contamination

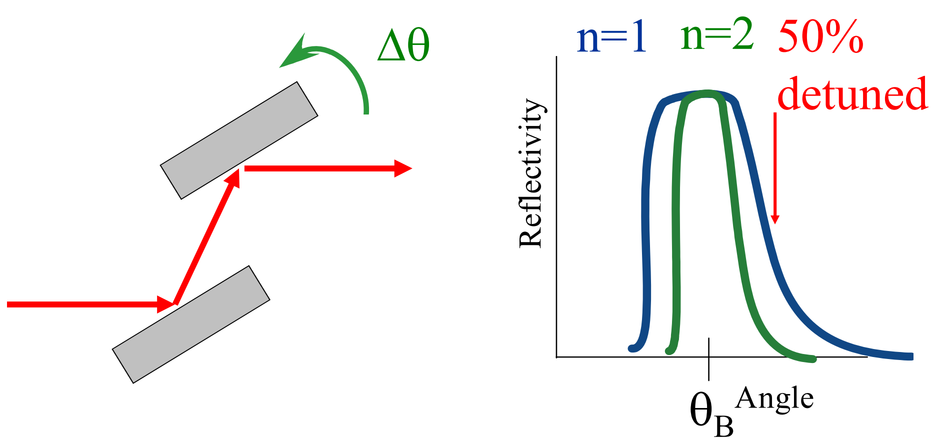


pinholes and self-absorption cause similar effect – amplitudes are too small

Harmonic rejection mirror



"Detuning" monochromator



Fluorescence Detectors

- Energy resolving
  - Energy dispersive – Ge or Si(Li)
  - Wavelength dispersive
  - Exotic
- Non-energy resolving
  - Ion chamber
  - PIN diode

Energy-dispersive detectors

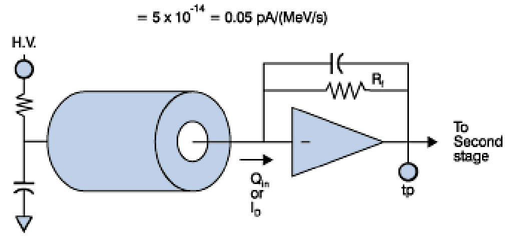
Charge carriers produced by Ge per unit energy deposited = 1/2.98

$$\text{Detector Current} = \text{Energy Rate}\left(\frac{eV}{s}\right) \times \frac{\text{charge (Q)}}{\text{energy (eV)}} \times 1.6 \times 10^{-19}\ \frac{\text{Coulombs}}{Q}$$

Charge per charge carrier

$$\frac{\text{Detector Current (A)}}{\text{Energy Rate (MeV/s)}} = 10^{6} \times \frac{1.6 \times 10^{-19}}{2.98}$$

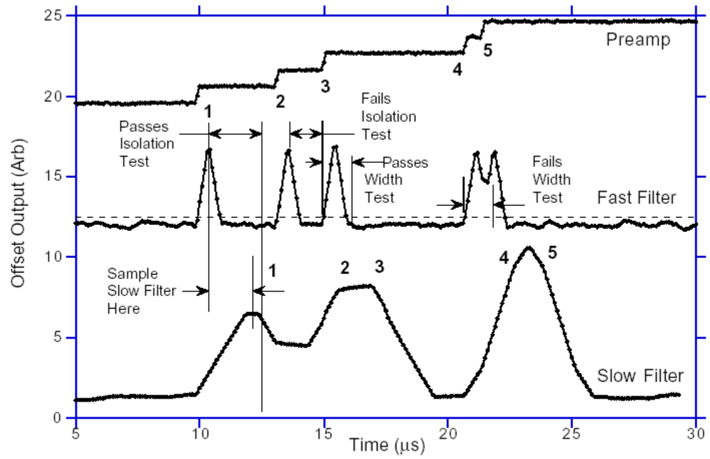
$$= 5 \times 10^{-14} = 0.05\ \text{pA/(MeV/s)}$$



The energy rate limit of RC preamplifiers is a function of feedback resistor value (Rf) and dynamic range.

http://www.canberra.com/products/491.asp

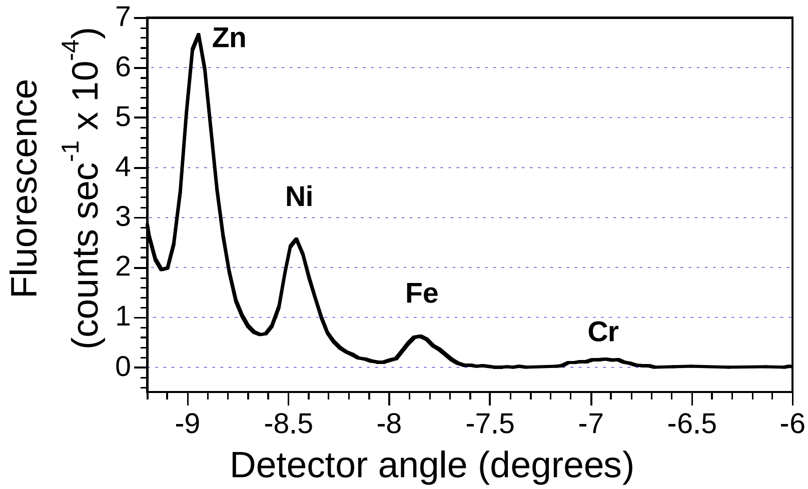
Solid-state detectors have relatively low maximum count rates



http://www.xia.com/AppNotes/DXP_Pile.pdf

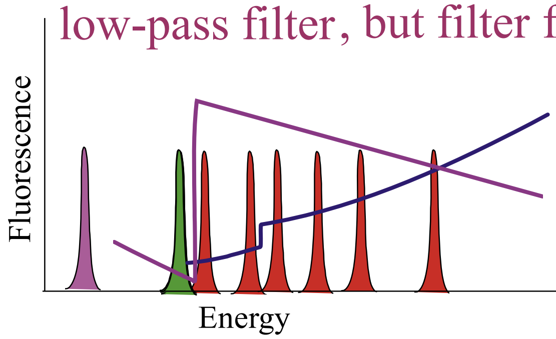
Wavelength-dispersive detectors

Reasonable solid angle results in low resolution, but unlimited count rate



Non-energy resolving detectors

Z-1 element functions as
low-pass filter, but filter fluorescences



Fluorescence Excitation

Soller slits + Z-1 filter improve fluorescence