2017

光物性物理学

Optical Properties and Spectroscopy of Materials

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Lecture Note 4

X-ray Absorption spectroscopy
and
X-ray emission spectroscopy

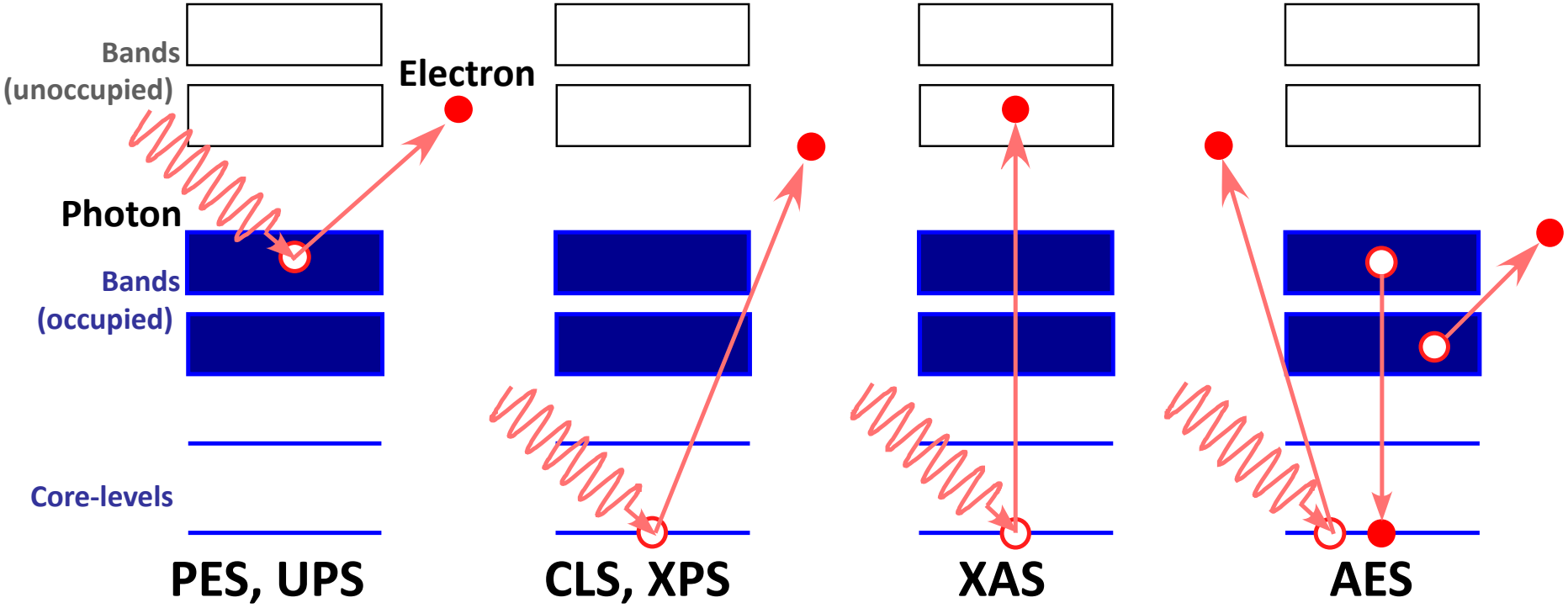
Photon-in / Particle-out

Photoemission Spectroscopy (PES), Ultraviolet Photoelectron Spectroscopy (UPS)

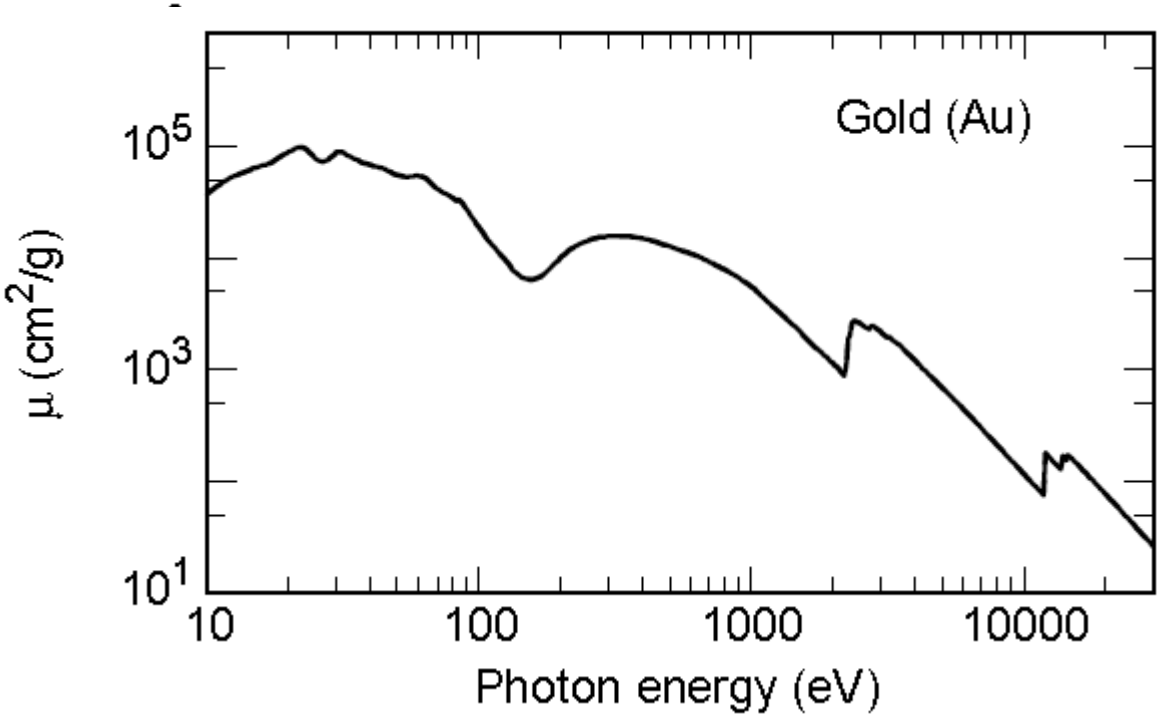
Core-level Spectroscopy (CLS), X-ray Photoelectron Spectroscopy (XPS)

X-ray Absorption Spectroscopy (XAS)

Auger Electron Spectroscopy (AES)

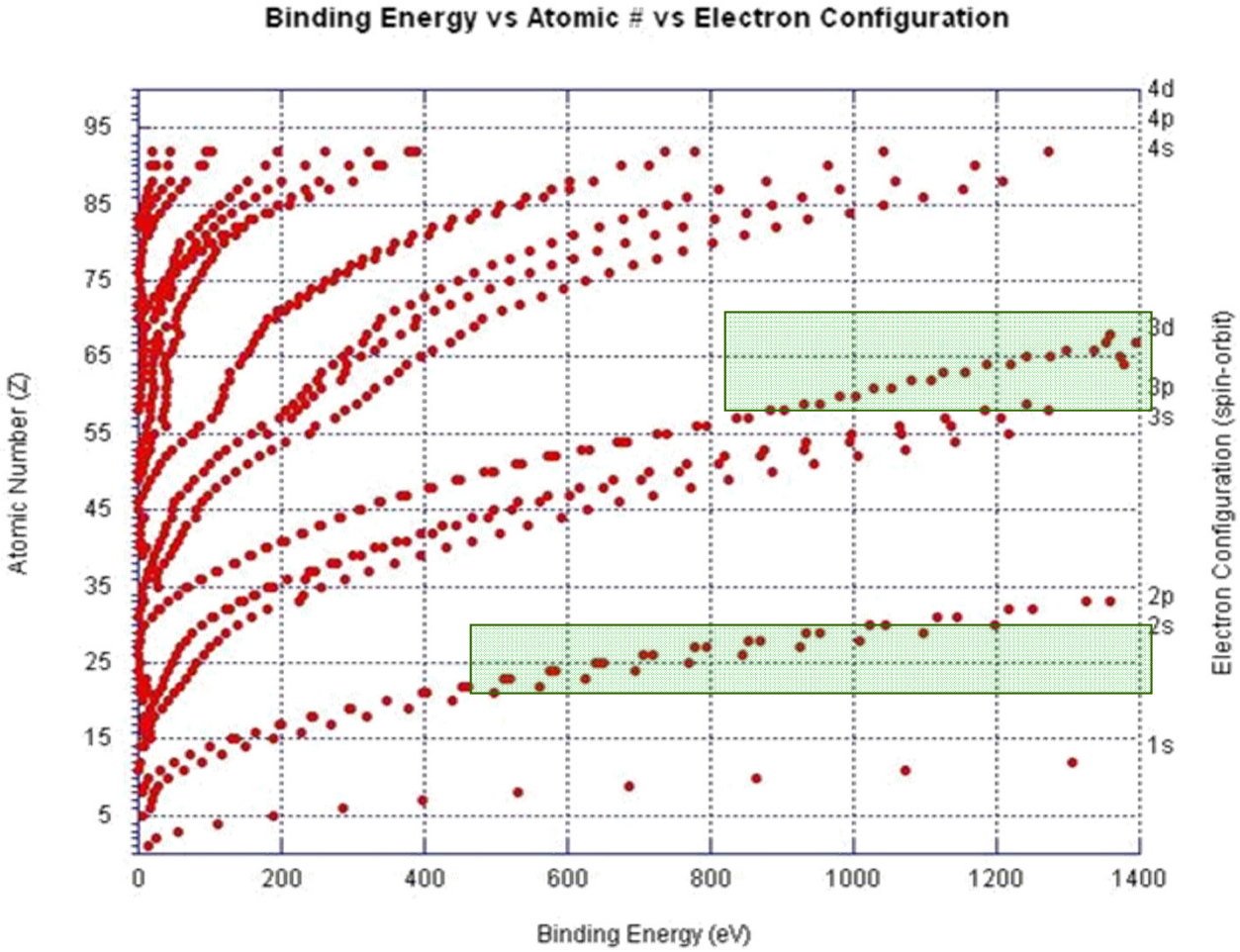


質量吸収係数：μ（cm^2/g）



Spectroscopy with VUV~SX

- Absorption edge, resonance effect



lanthanoid
（**M-edge**）

transition metal
（**L-edge**）

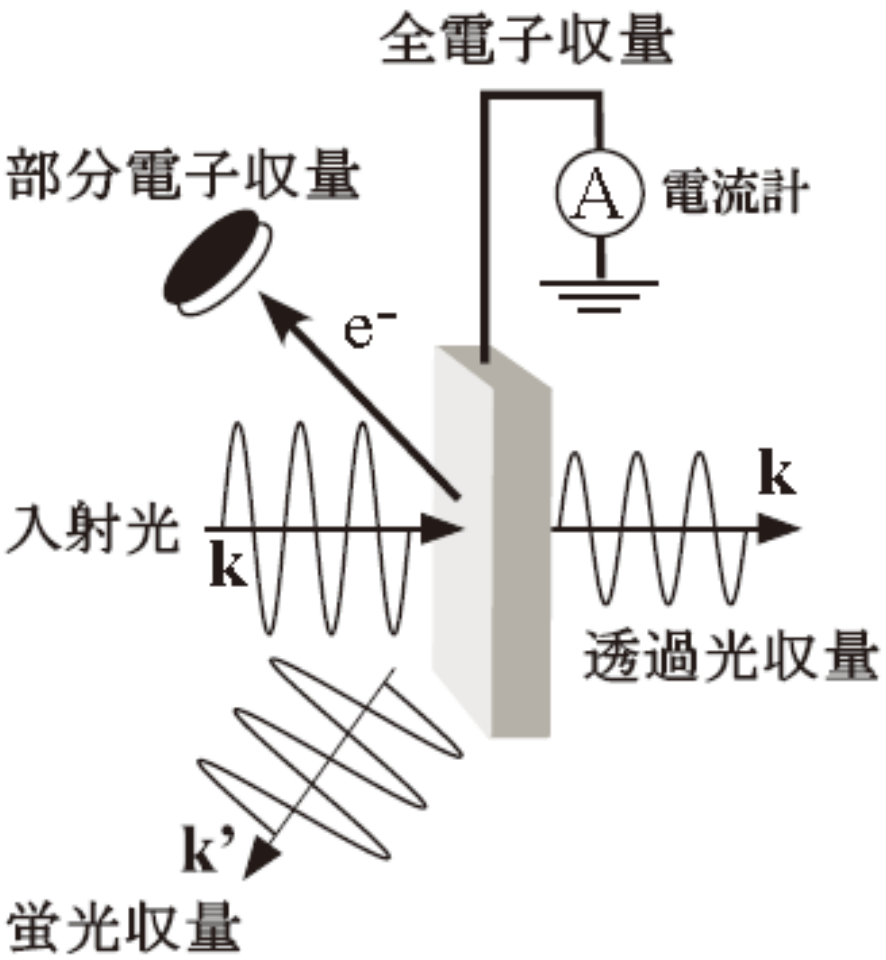


FIG. 19: X線吸収分光実験の様子。

Transmission yield (透過光収量)

$I_t = I_0\, e^{-\mu t}$

- Direct measurement
- Sample thickness limit (≦100nm)

Electron yield （電子収量）

$I_e = I_0 \mu L_e$

- Indirect measurement
- Rather surface sensitive (probing depth ~ 5nm)

Fluorescence yield (蛍光収量)

$I_f = I_0 \mu L_f$

- Indirect measurement
- Rather bulk sensitive
- Self-absorption problem

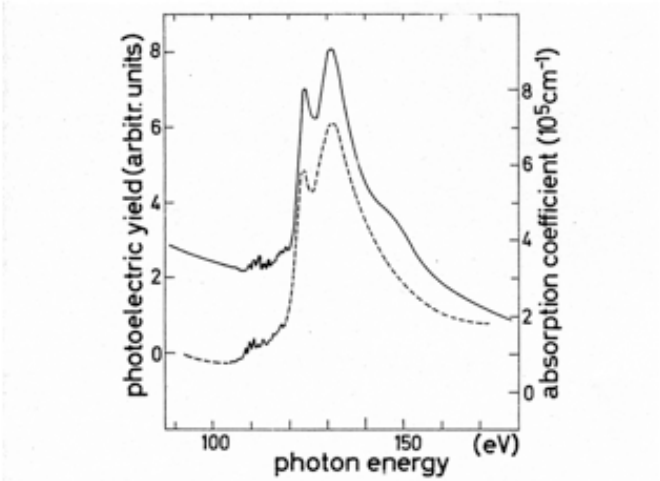


FIG. 1. Comparison of photoelectric yield (solid curve) and absorption (dashed curve) spectra for Pr.

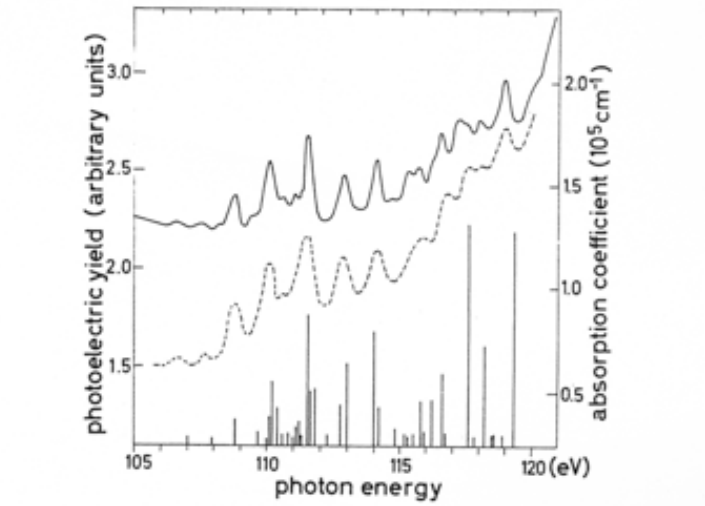
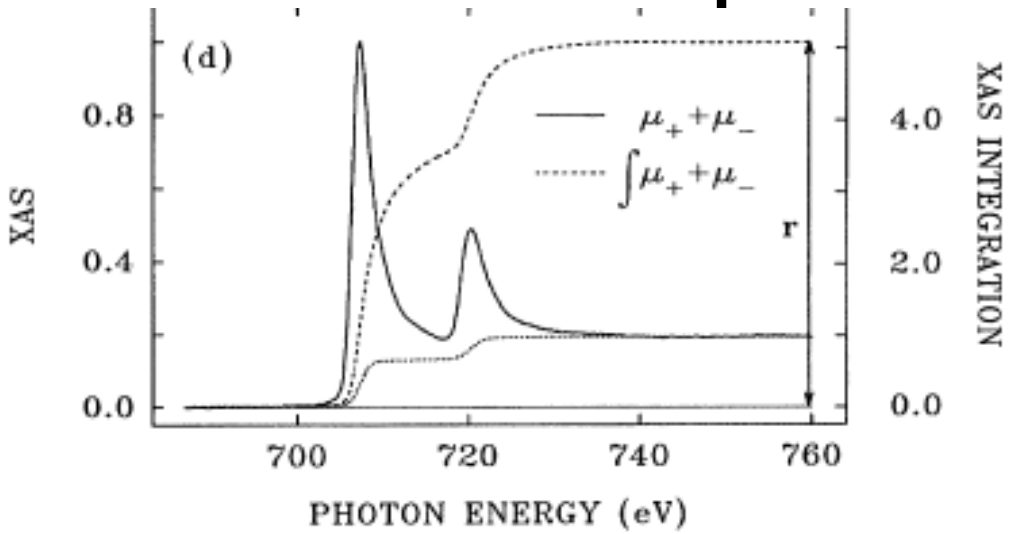


FIG. 2. Energy region of fine structure, yield (solid curve) and absorption (dashed curve) for Pr. The vertical lines are the result of an atomic calculation (Ref. 19); the length of the lines represents the oscillator strength.

透過法と電子収量法で測定したプラセオジウムの軟X線吸収スペクトル。

[W. Gudat and C. Kunz, *Phys. Rev. Lett.*, 29, 169-172 (1972)]

Example Fe and FeO



Fe:
C.T. Chen *et al*., Phys. Rev. Lett. **75**, 152 (1995).

Fe_2O_3:
P. Kuiper *et al*., Phys. Rev. Lett. **70**, 1549 (1993).

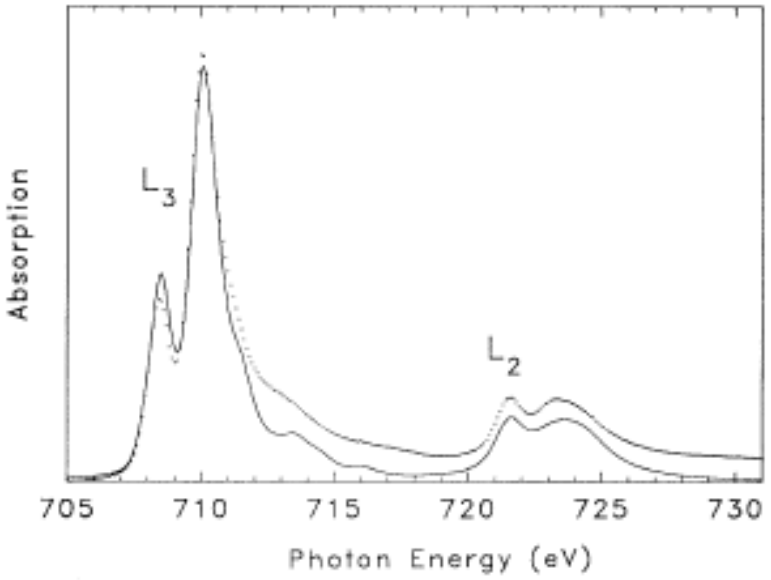
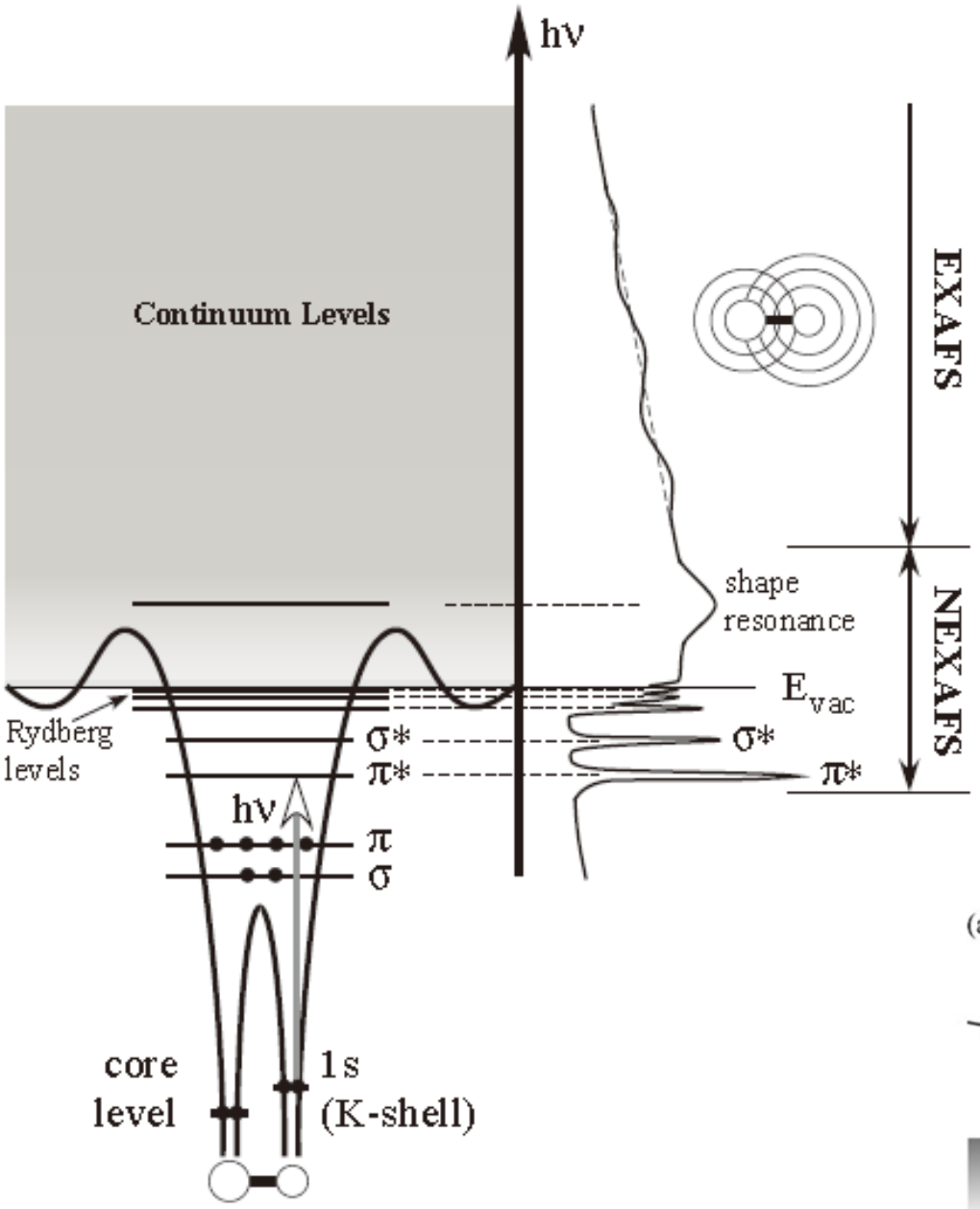


FIG. 1. Comparison of the Fe $2p$ absorption spectrum of Fe_2O_3 powder (points) with a calculation for Fe^{3+} $(3d^5)$ in octahedral symmetry (line).



Extended
X-ray Absorption Fine Structure

Near-Edge
X-ray Absorption Fine Structure

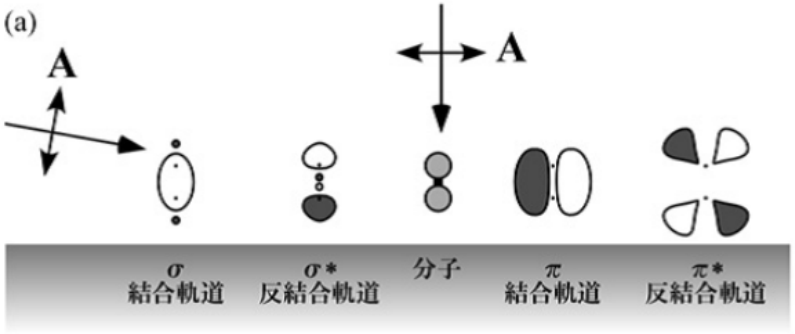


図 0.27　吸収端近傍における吸収スペクトルの様子。

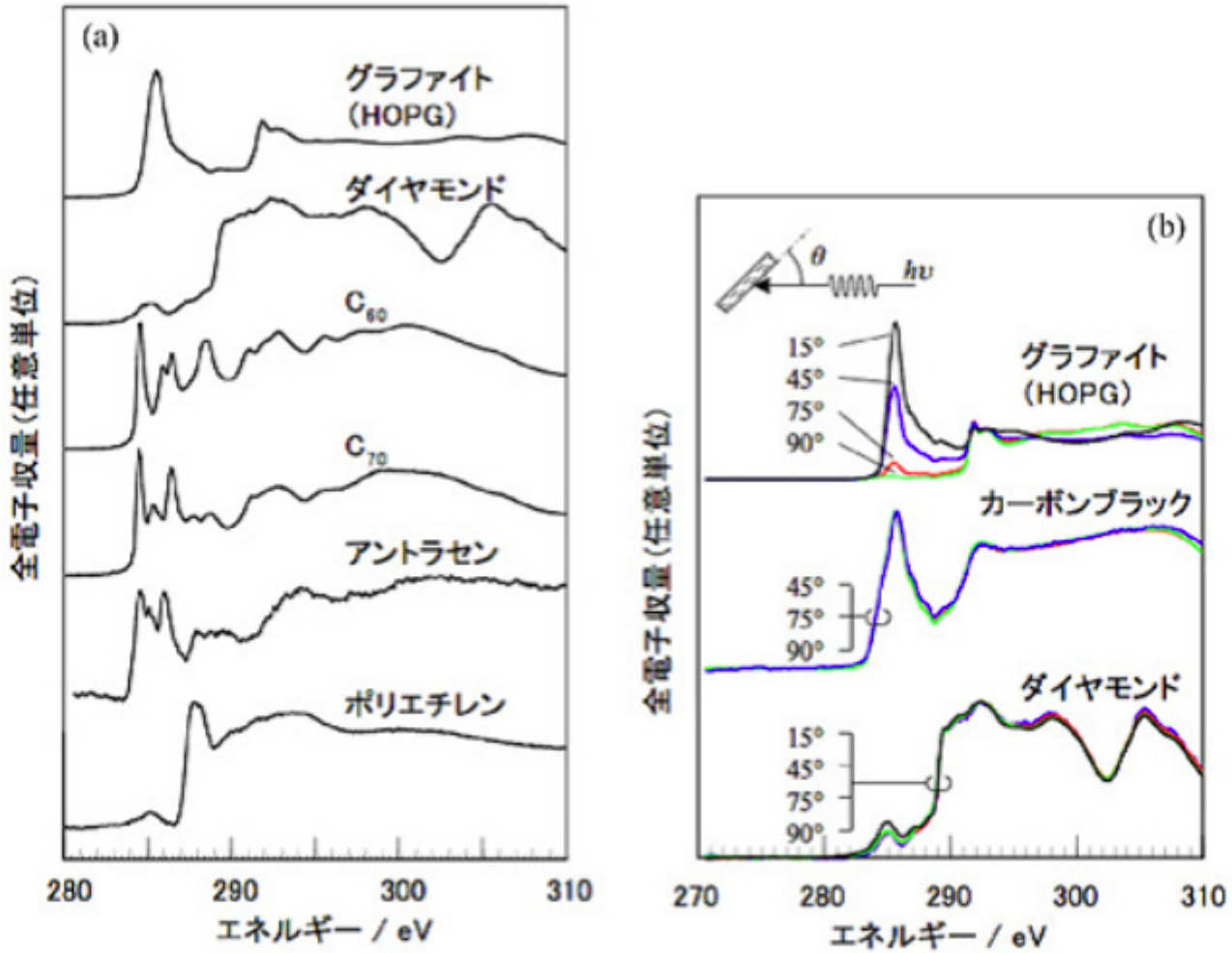
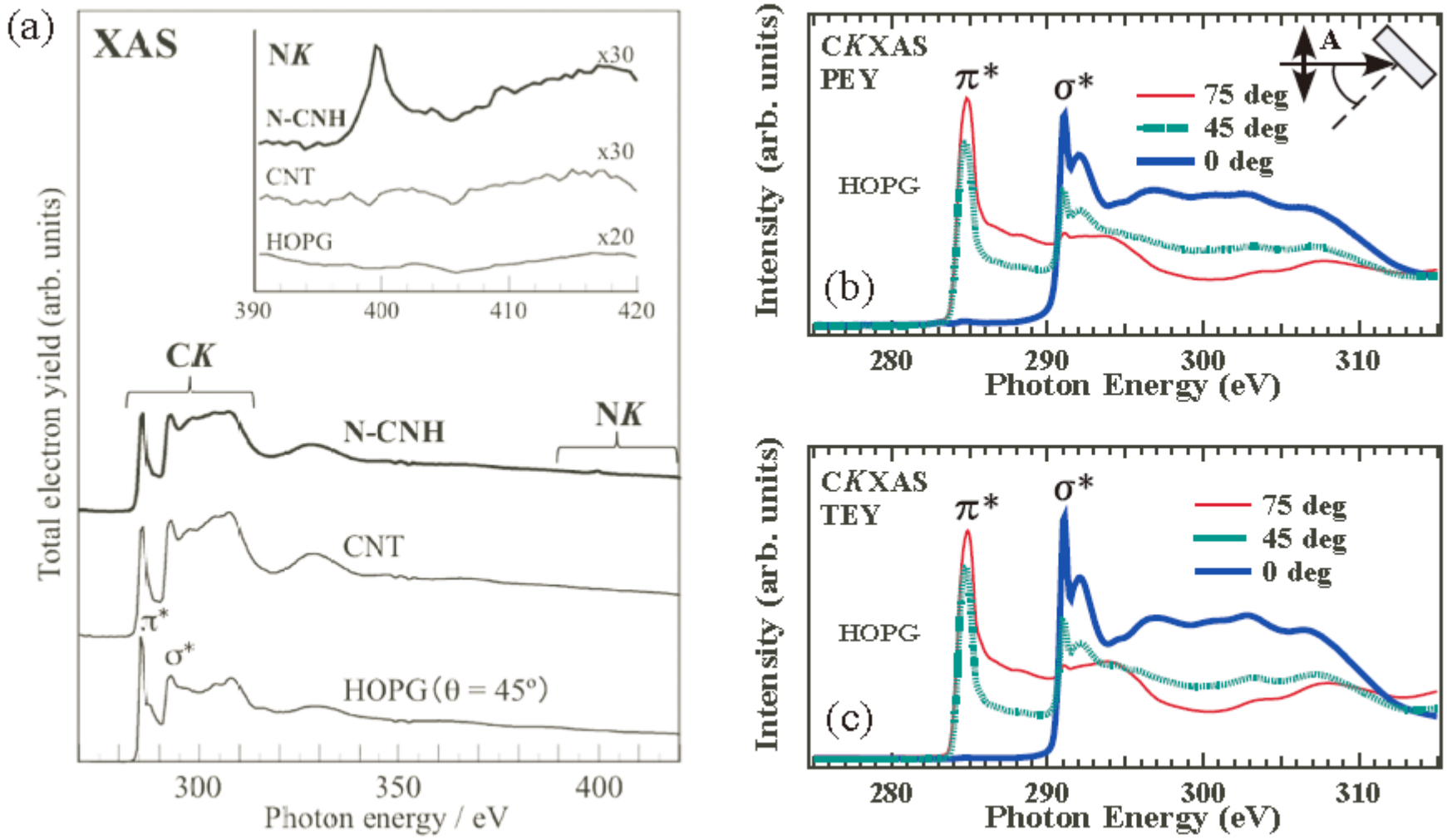
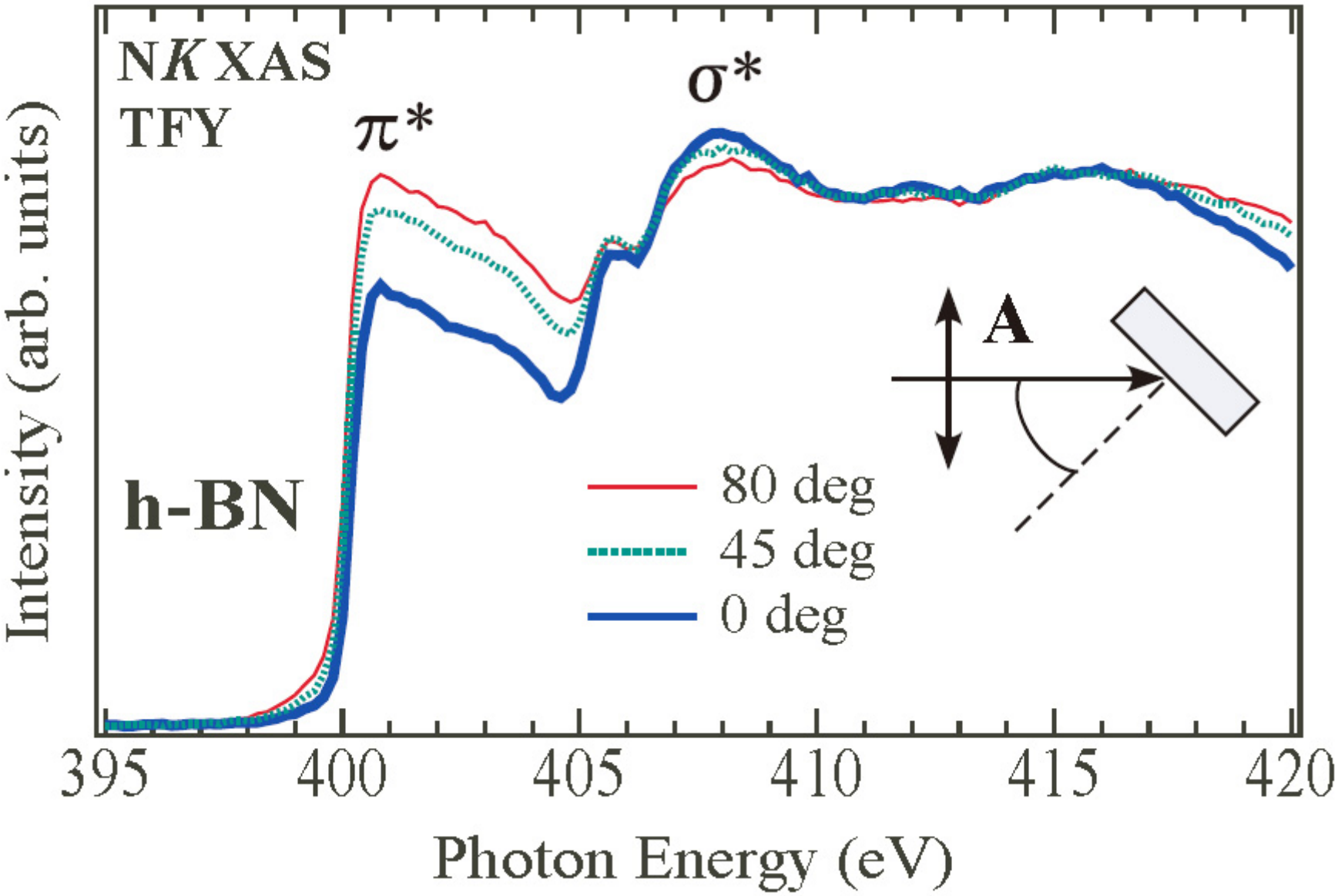
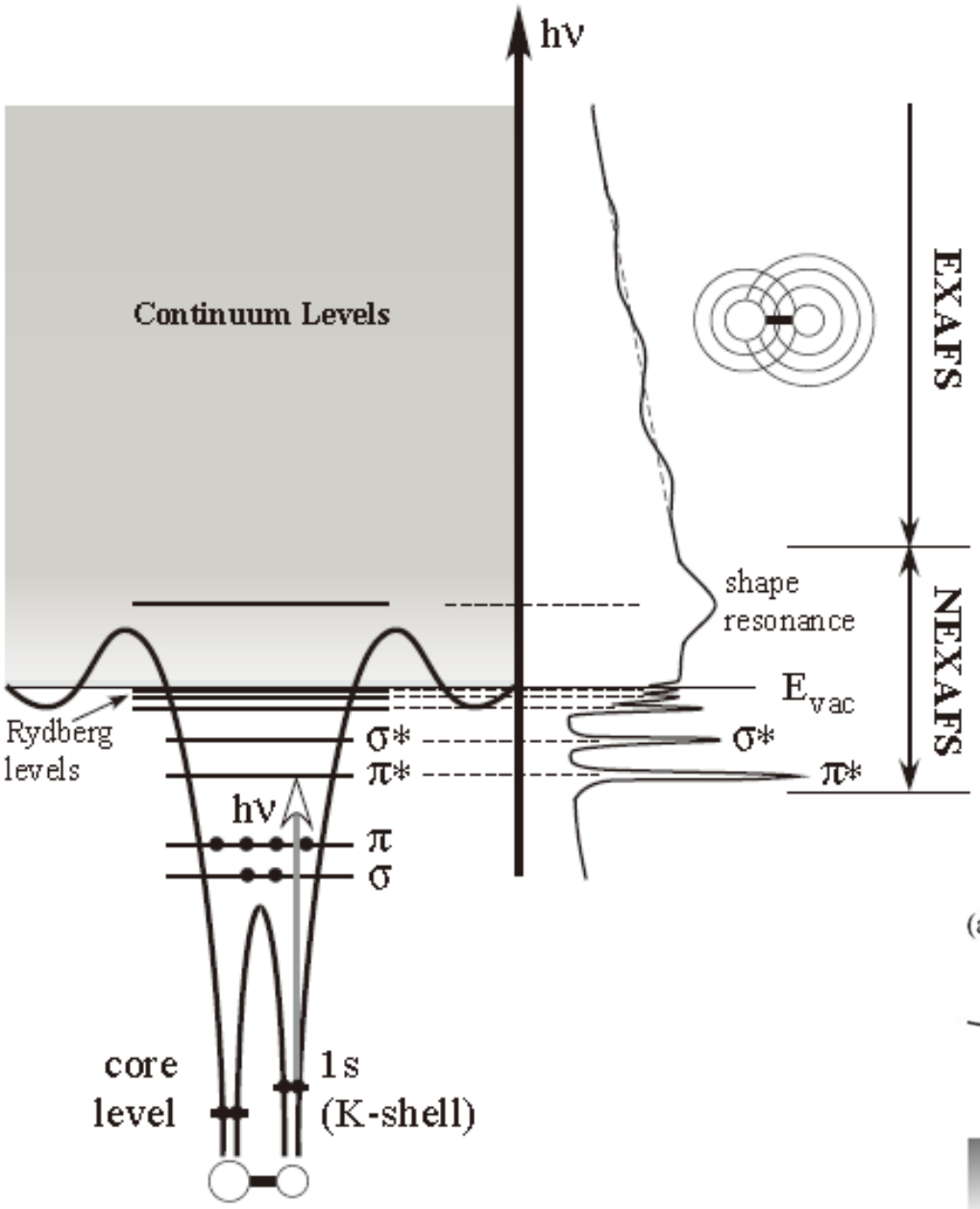


FIG. 20: (a) C K 吸収端における典型的炭素化合物の全電子収量軟X線吸収スペクトル。(b) 入射角θを変化させて測定したグラファイト，カーボンブラック，ダイヤモンドの軟X線吸収スペクトル。（兵庫県立大：村松康司教授より提供）


(a)
XAS
NK
N-CNH
x30
CNT
x30
HOPG
x20
390
400
410
420
CK
NK
N-CNH
CNT
π*
σ*
HOPG (θ = 45°)
Total electron yield (arb. units)
300
350
400
Photon energy / eV
CKXAS
PEY
π*
σ*
75 deg
45 deg
0 deg
A
HOPG
(b)
Intensity (arb. units)
280
290
300
310
Photon Energy (eV)
CKXAS
TEY
π*
σ*
75 deg
45 deg
0 deg
HOPG
(c)
Intensity (arb. units)
280
290
300
310
Photon Energy (eV)


NK XAS
TFY
π*
σ*
h-BN
80 deg
45 deg
0 deg
A
Intensity (arb. units)
395
400
405
410
415
420
Photon Energy (eV)



Extended
X-ray Absorption Fine Structure

Near-Edge
X-ray Absorption Fine Structure

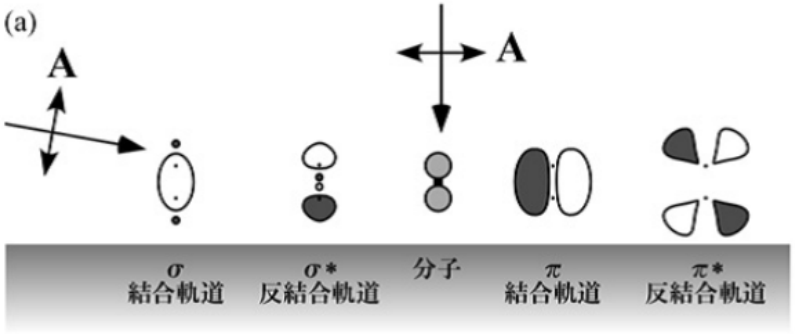


図 0.27　吸収端近傍における吸収スペクトルの様子。

EXAFS解析の流れ　(Flow of EXAFS analysis)

１．測定 (Measurement)

２．実験データよりχ(E)を取り出す (Extracting χ(E))

３．波数スペクトルに変換して、重みを付けたk^nχ(k)をフーリエ変換し、大まかに原子構造を捉える。
(Conversion to wave vector spectra and Fourier transform k^nχ(k) to determine atomic structure roughly)

４．　χ(k)を原子構造モデルを元にフィッティングする。
(Determine the accurate atomic structure by fitting χ(k))

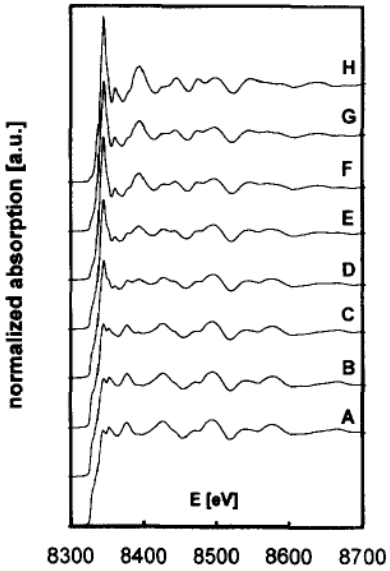


Fig. 1. Representative pre-edge background subtracted XAFS data (truncated at 8700 eV for clarity). A, B, D, F: CEY data. C, E, G, H: TEY data. NiO overlayer thicknesses: native oxide ≈ 25 Å (A), 50 Å (B/C), 235 Å (D/E), 1275 Å (F/G), 3000 Å (H).

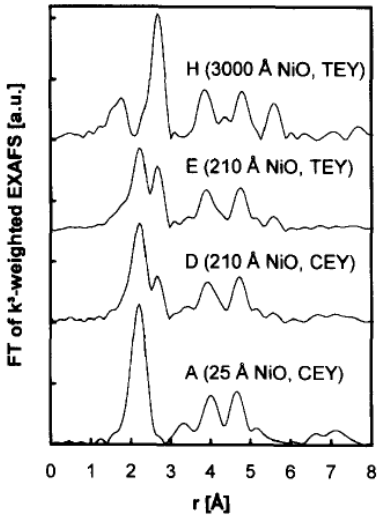


Fig. 2. Fourier transforms of k^3-weighted EXAFS from spectra A, D, E and H of Fig. 1.

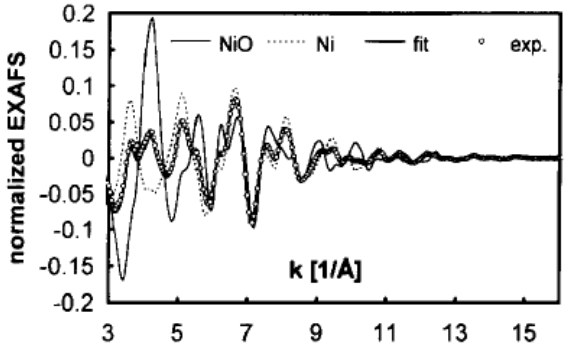


Fig. 3. Unweighted EXAFS from spectra A (dotted line), H (thin full line) and D (white circles) in Fig. 1. Thick full line: spectrum generated by linear combination of the EXAFS of A (35%) and H (65%).

S.L.M. Schroeder et al. / Surface Science 324 (1995) L371–L377

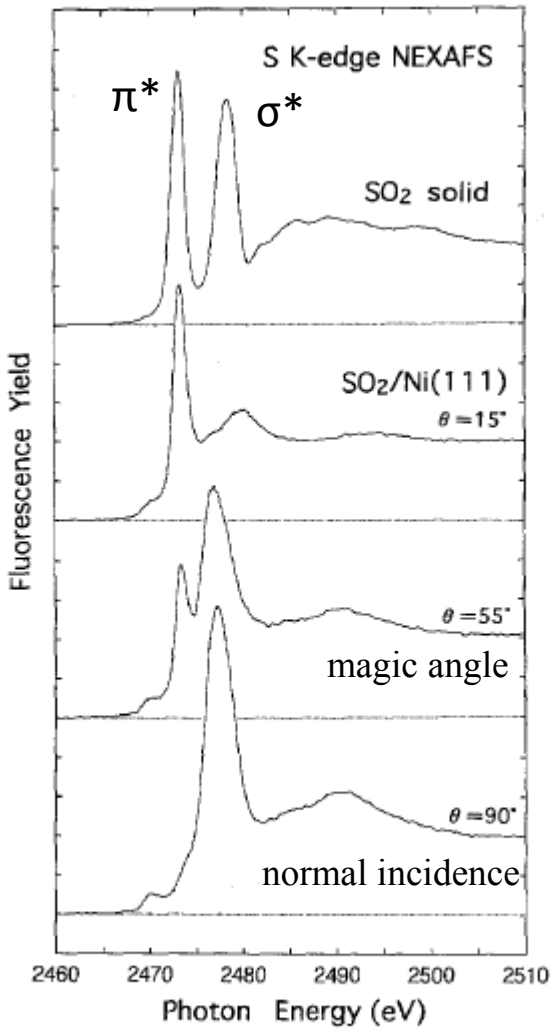


Fig. 1. S K-edge NEXAFS spectra of submonolayer SO_2 /Ni(111) taken at X-ray incidence angles of $\theta = 90°$, 55° and 15° at a temperature of 92 K, together with that of solid SO_2.

- Suppression of the π* peak

=> Partial occupation of the π* orbital

⇒ Charge transfer from the Ni d-band

⇒ The strong mixing of SO_2 π*- Ni d-band

A flat-lying orientation
of the molecular plane on a surface

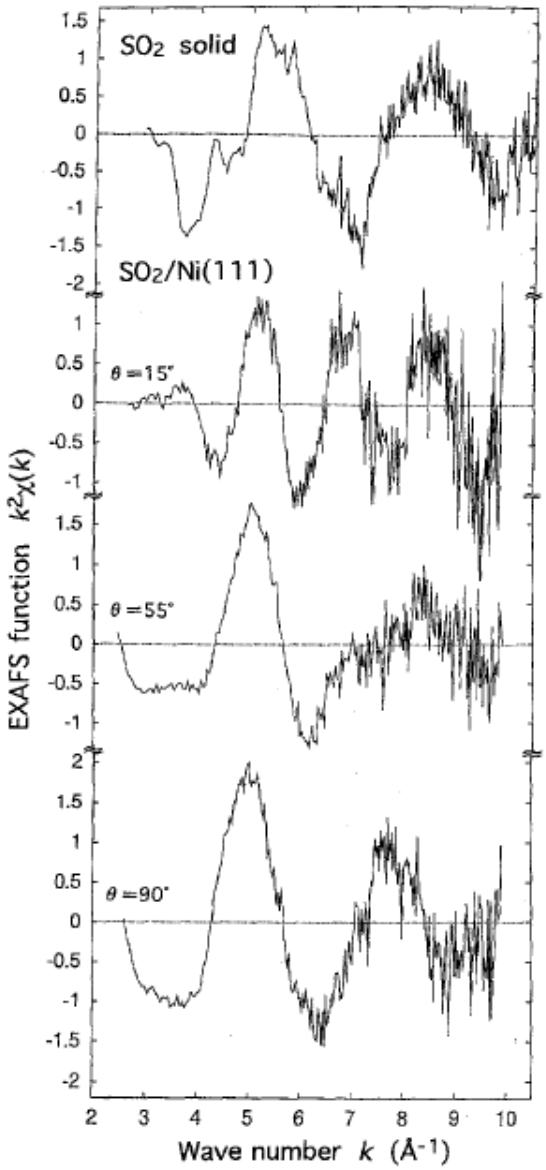


Fig. 4. S K-edge SEXAFS oscillation functions $k^2\chi(k)$ of submonolayer SO_2/Ni(111) taken at X-ray incidence angles of $\theta = 90°$, 55° and 15° at a temperature of 92 K, together with that of solid SO_2 at 92 K.

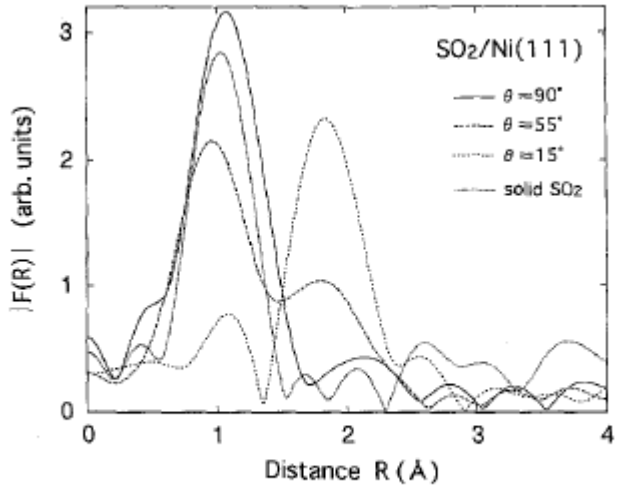


Fig. 6. Fourier transforms of $k^2\chi(k)$ of submonolayer SO_2/Ni(111) and solid SO_2 shown in Fig. 4.

Note: S-O bond length : 1.43 Å (solid SO_2)

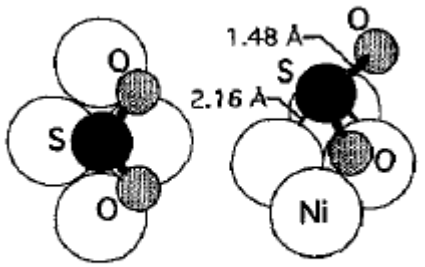
Using phase shift values from the references
and to determine the structure by fitting

$$\chi(k) \propto \sum_j N_j \frac{1}{kr_j^2} exp\{-2r_j/\lambda(k)\} sin(2kr_j + \delta)$$ (fitting)

Table 1
The ratio of the effective coordination numbers, $\eta = N^*(55°)/N^*(15°)$, for the S–Ni shells of SO_2/Ni(111) and SO_2/Ni(100), together with calculated values of η for typical adsorption sites on unreconstructed surfaces

Surface	Experimental	Calculated		
		Hollow	Bridge	Atop
Ni(111)	0.53(5)	0.626	0.523	0.353
Ni(100)	0.51(5)	0.966	0.522	0.353

For the calculations of η, S–Ni distances of 2.16 Å on Ni(111) and 2.18 Å on Ni(100) were used.



Ni(111)

X-ray Magnetic Circular Dichroism (X線磁気円2色性)

$$\Delta\mu = \mu_+(+\mathrm{B}) - \mu_+(\text{-B}) = \mu_-(\text{-B}) - \mu_-(+\mathrm{B}) = \mu_-(\text{-B}) - \mu_+(\text{-B}) \qquad (33)$$

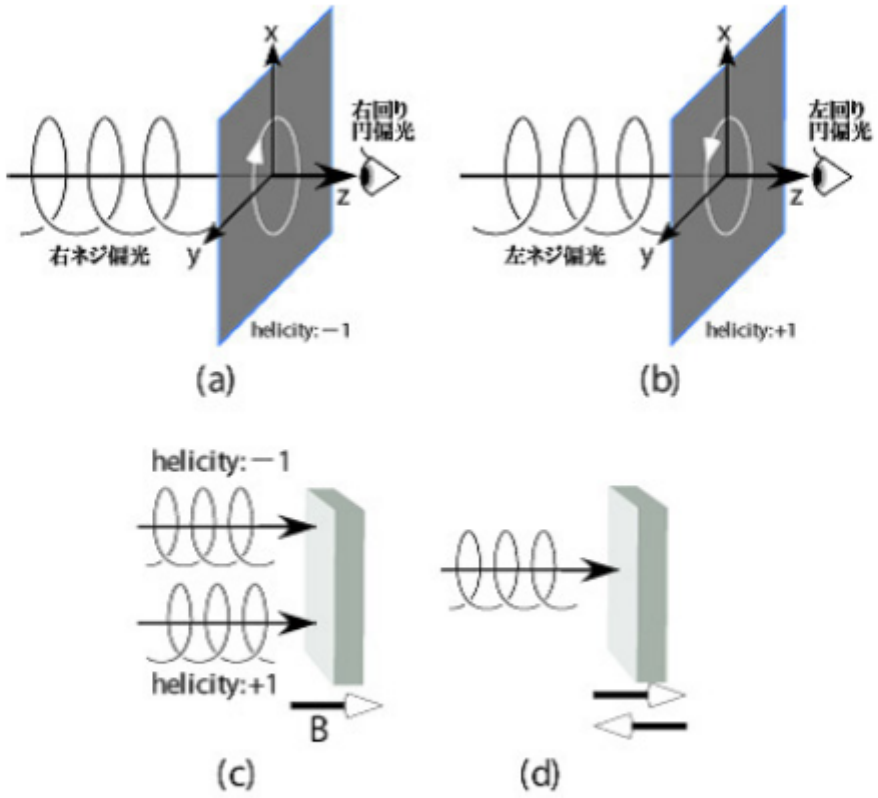


FIG. 21: (a,b) 円偏光の定義:(a) 右ネジ偏光、右回り円偏光、helicity=-1; (b) 左ネジ偏光、左回り円偏光、helicity=+1。(c,d) XMCD の測定：(c) 円偏光の切換；(d) 印加磁場の向きの切換。

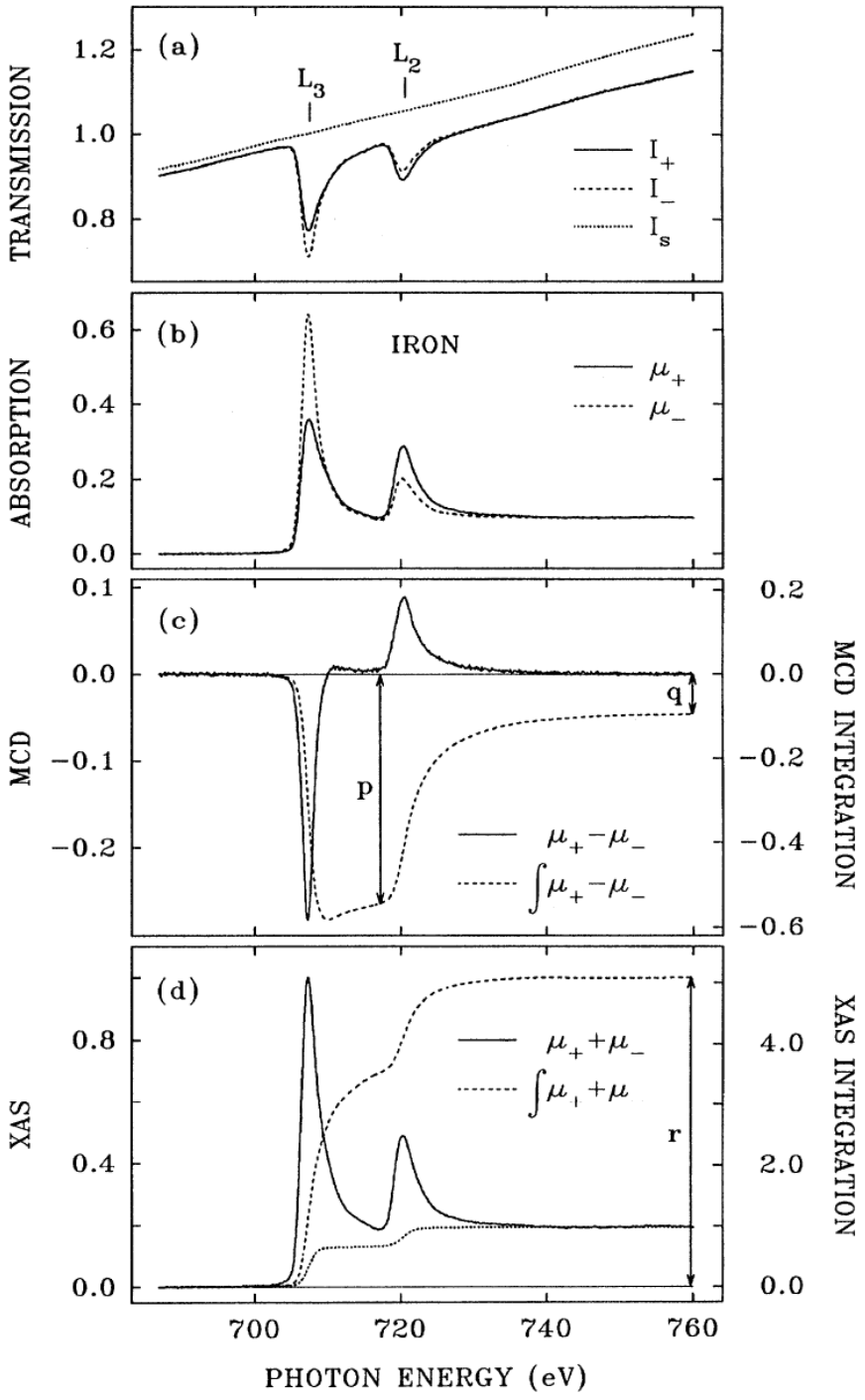


FIG. 1. $L_{2,3}$-edge XAS and MCD spectra of iron: (a) transmission spectra of Fe/parylene thin films, and of the parylene substrates alone, taken at two opposite saturation magnetizations; (b) the XAS absorption spectra calculated from the transmission data shown in (a); (c) and (d) are the MCD and summed XAS spectra and their integrations calculated from the spectra shown in (b). The dotted line shown in (d) is the two-step-like function for edge-jump removal before the integration. The p and q shown in (c) and the r shown in (d) are the three integrals needed in the sum-rule analysis.

FIG. 24: Fe 試料における $L_{2,3}$-吸収端 (edge) の XAS 及び XMCD スペクトル (積分)。(a) 実験で得られた透過スペクトル、(b)(a) から求めた XAS スペクトル、(c)XMCD スペクトルとその積分、(d) XAS スペクトルとその積分 [41]。p,q,r を求めるための各積分は (d) の edge-jump を含むバックグラウンド (two-step-like function) を引いてから行われています。

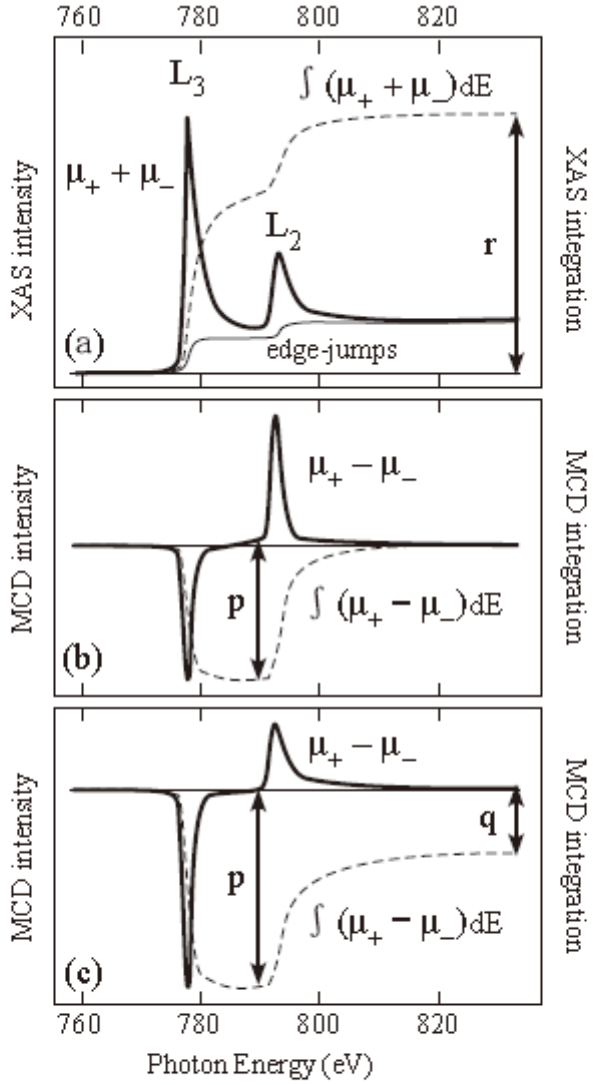
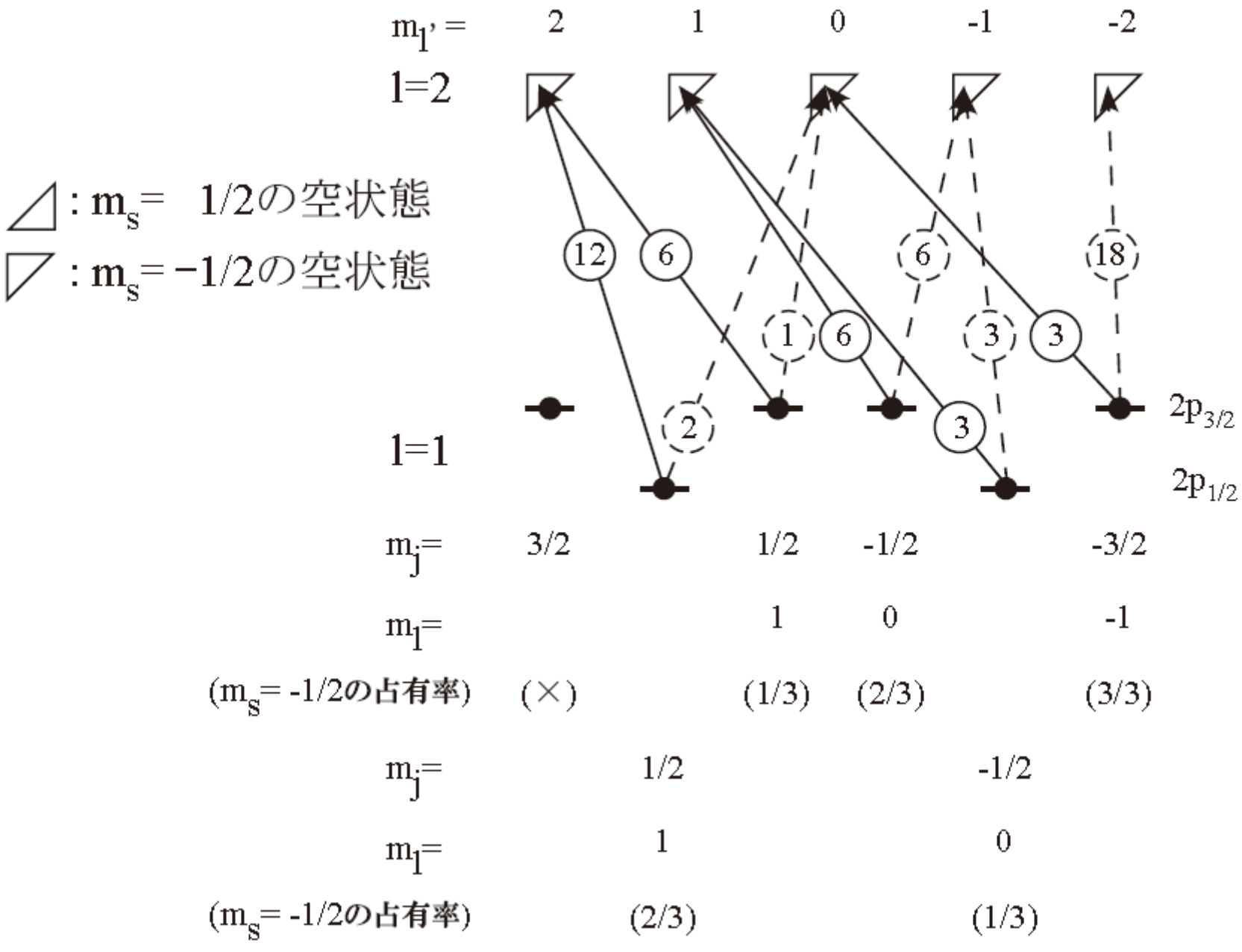
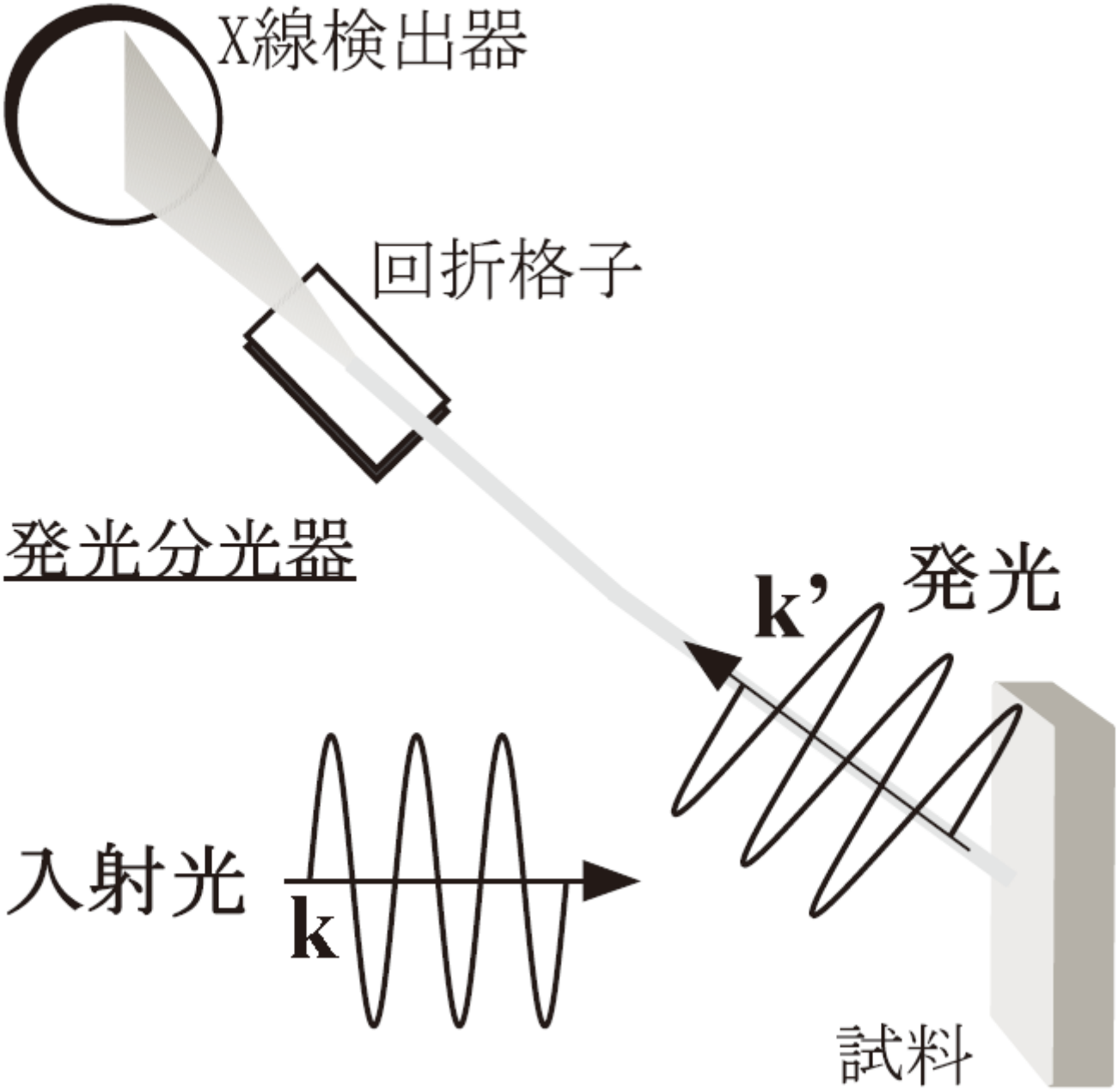
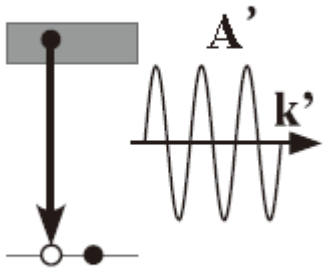


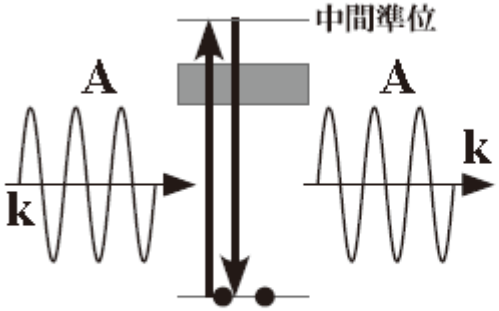
FIG. 23: $L_{2,3}$-吸収端 (edge) のXAS及びXMCD スペクトル（積分）と μ_+,μ_- の関係。p,q,r を求めるための各積分は (a) の edge-jump を含むバックグラウンドを引いてから行われています。(a)$L_{2,3}$-吸収端 (edge) のXAS スペクトルとその積分。(b) $L_{2,3}$-吸収端 (edge) のXAS スペクトルとその積分 (軌道磁気モーメントが0の場合)。(c) $L_{2,3}$-吸収端 (edge) のXAS スペクトルとその積分 (軌道磁気モーメントがある場合)。


m_l' = 2 1 0 -1 -2
l=2
△ : m_s= 1/2の空状態
▽ : m_s= −1/2の空状態
12 6 6 18
1 6 3 3
2 3
l=1
$2p_{3/2}$
$2p_{1/2}$
m_j= 3/2 1/2 -1/2 -3/2
m_l= 1 0 -1
(m_s= -1/2の占有率) (×) (1/3) (2/3) (3/3)
m_j= 1/2 -1/2
m_l= 1 0
(m_s= -1/2の占有率) (2/3) (1/3)

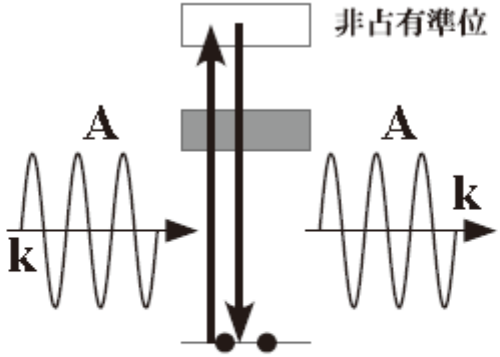

X線検出器
回折格子
発光分光器
k'
発光
入射光
k
試料



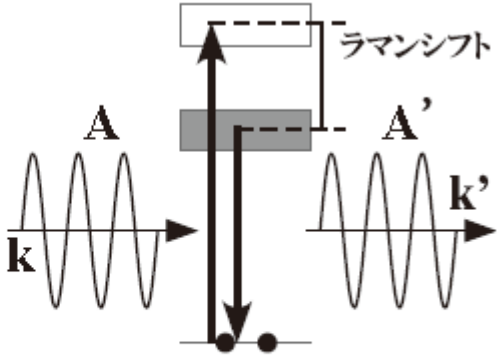
(c) 吸収：2次過程
(蛍光過程)



(f) 弾性X線散乱
(レイリー散乱)



(g) 共鳴弾性X線散乱



(h) 共鳴非弾性X線散乱
(共鳴ラマン散乱)

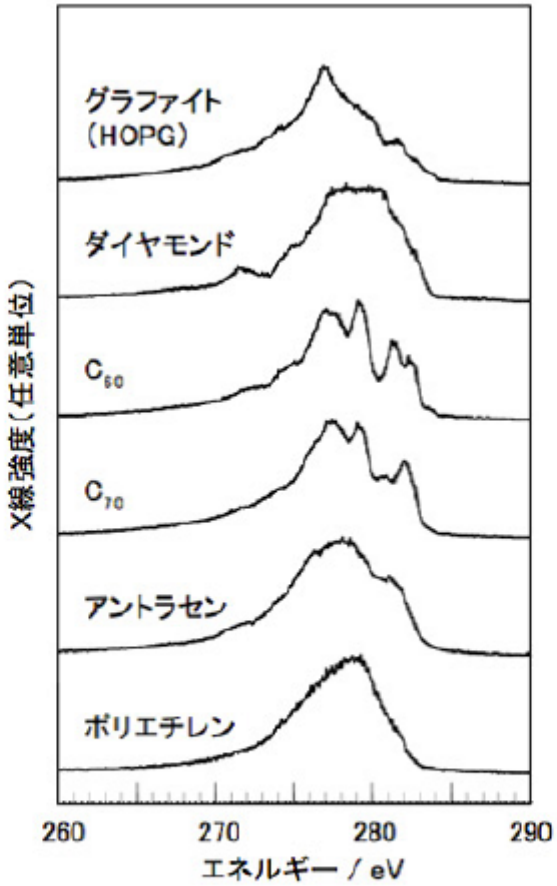


FIG. 26: 典型的な炭素化合物の放射光励起 CK X線発光 (蛍光) スペクトル。(兵庫県立大：村松康司教授より提供)

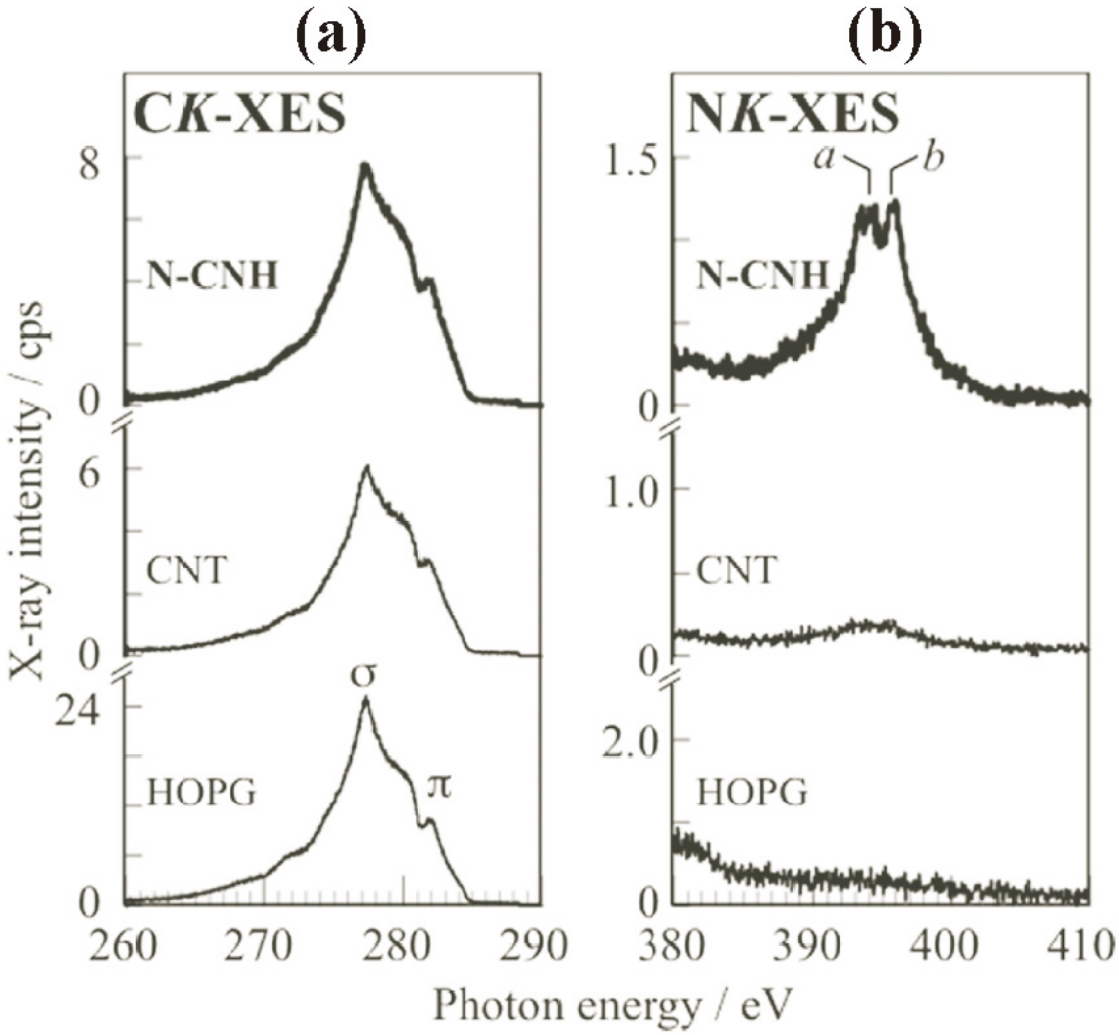


図 0.36 グラファイト (HOPG, Highly Oriented Pyrolytic Graphite)、カーボンナノチューブ (CNT, Carbon Nanotube)、窒素含有カーボンナノホーン (N-CNH、N-Carobon Nanohorn) の (a) 炭素及び (b) 窒素の K 殻の軟 X 線発光スペクトル[35]。励起光のエネルギーはそれぞれ 320 と 430eV である。

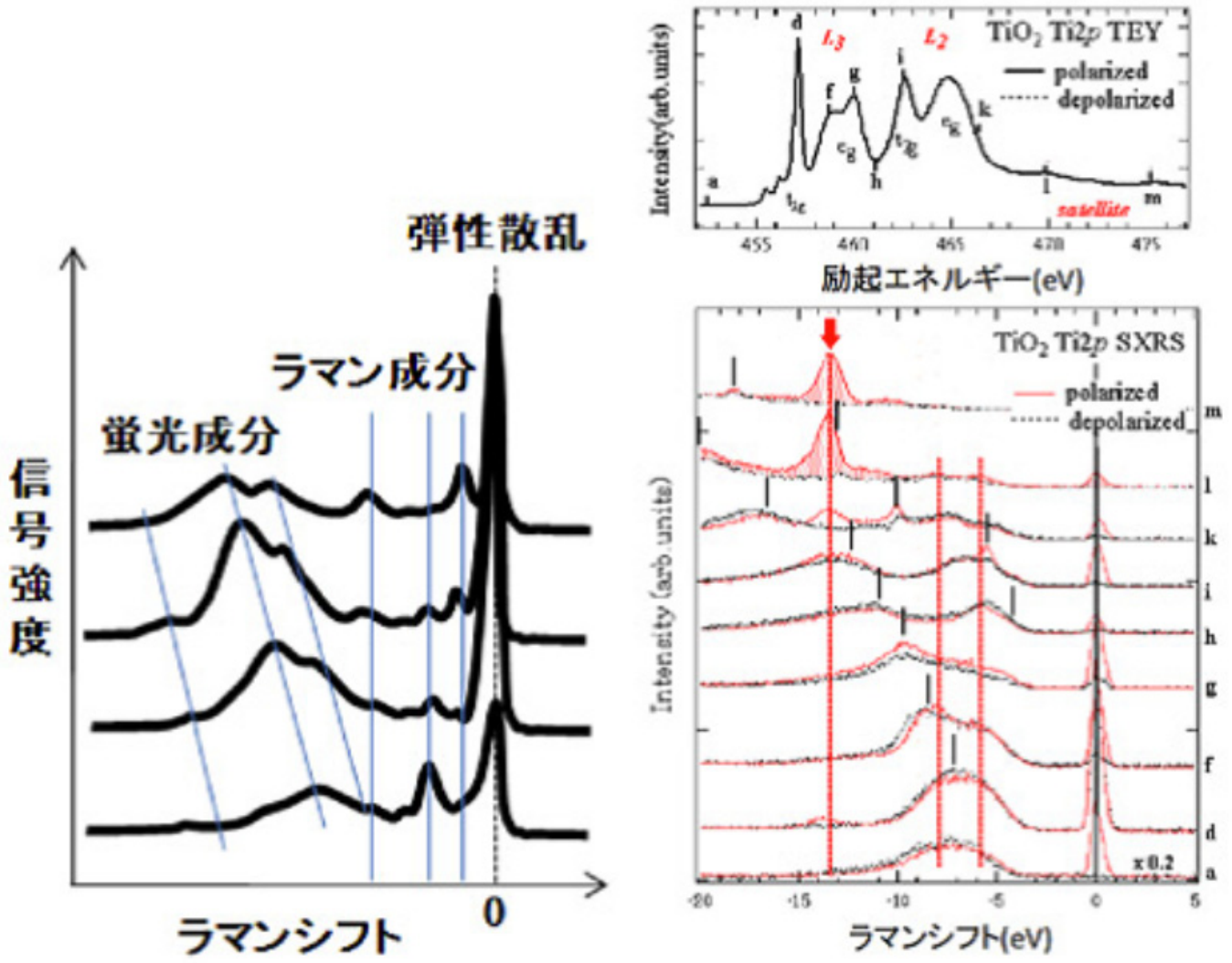
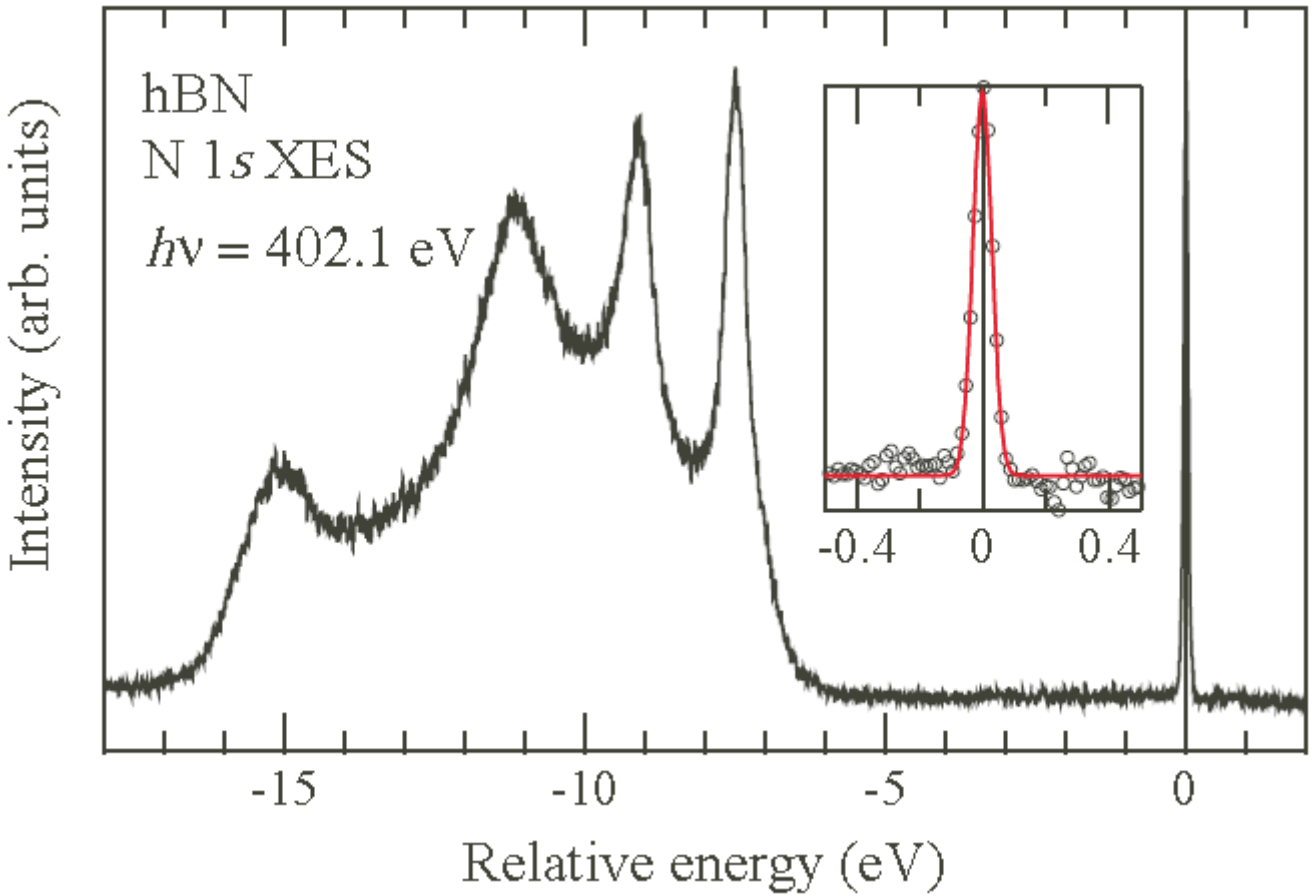


FIG. 27: (左) 共鳴励起発光の共鳴発光スペクトルのラマンシフト表示。(右)TiO2 の Ti 2p 共鳴発光スペクトル [47]。


hBN
N 1s XES
hν = 402.1 eV
Intensity (arb. units)
-15
-10
-5
0
Relative energy (eV)
-0.4
0
0.4

Advantages of the resonant inelastic X-ray scattering(RIXS)

1. Exploiting both the energy and momentum dependence of the photon scattering cross section.
2. Element and orbital specific:
3. Bulk sensitive:
4. Needs only small sample volumes:
5. Utilize the polarization of the photon:

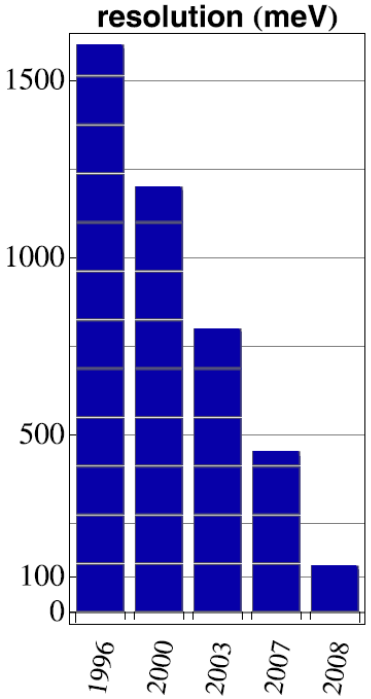
The main limitation is that the process is photon hungry;

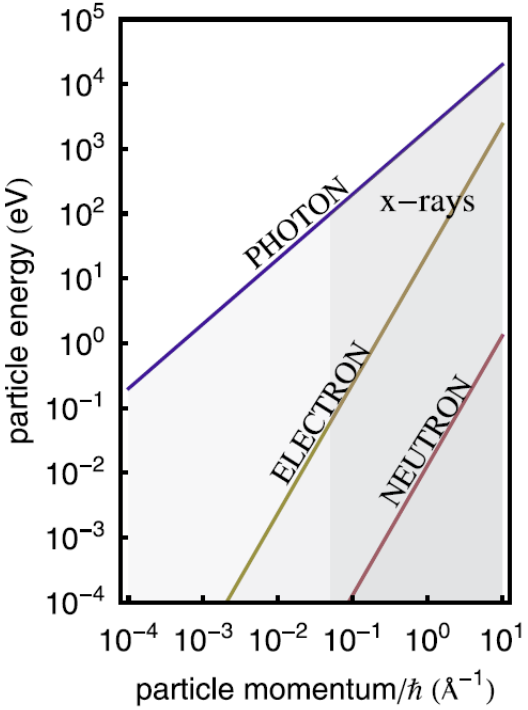
L. J. P. Ament *et al*., Rev. Mod. Phys. **83**, 705 (2011).

▪ 共鳴非弾性X線散乱 ・共鳴軟X線ラマン散乱

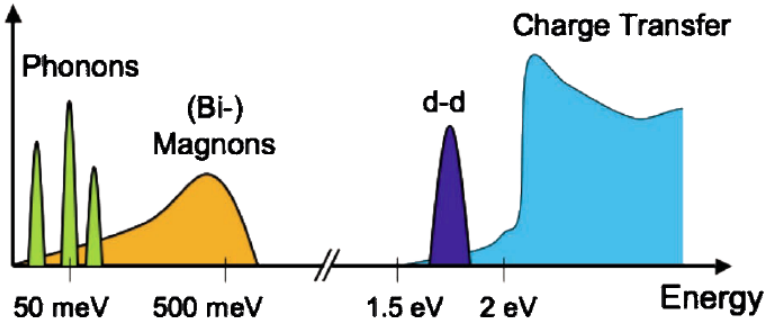
光源の高輝度化 → エネルギーの高分解能化

Soft x−ray regime: Cu L−edge





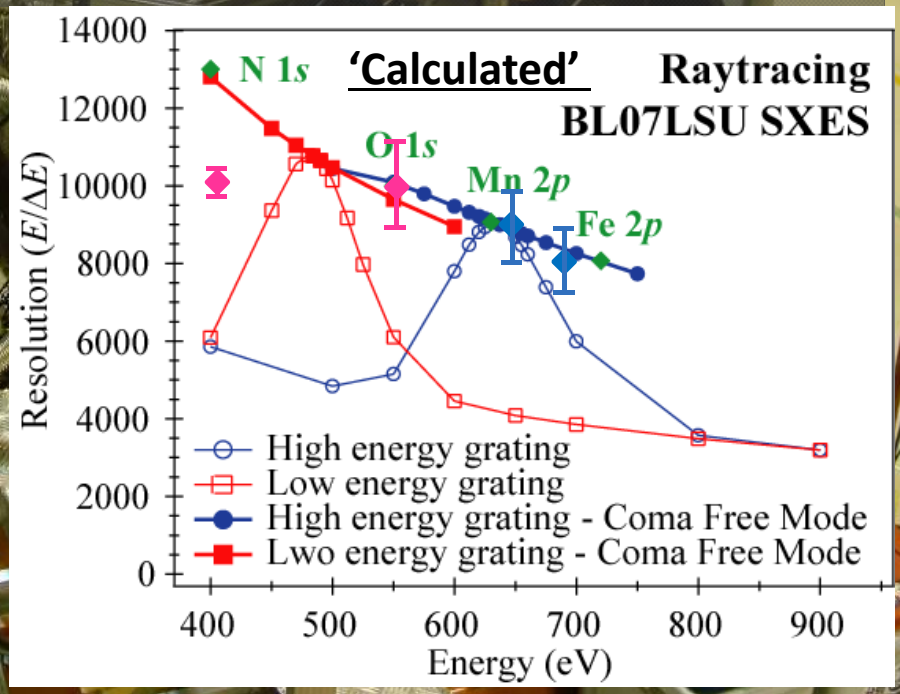
Different elementary excitations in condensed matter systems and their approximate energy scales in strongly correlated electron materials such as transition-metal oxides.



L. J. P. Ament *et al*., Rev. Mod. Phys. **83**, 705 (2011).

HORNET: Ultrahigh resolution XES station@SPring-8 BL07LSU

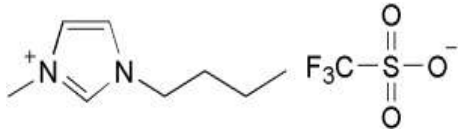
2009.10 コミッショニング
2010.7　分解能E/ΔE>5000
2010.12 分解能E/ΔE>10000 (N 1*s*)
2011.1~ ユーザー実験（G課題）開始
始



HORNET: Ultrahigh resolution XES station
@SPring-8 BL07LSU

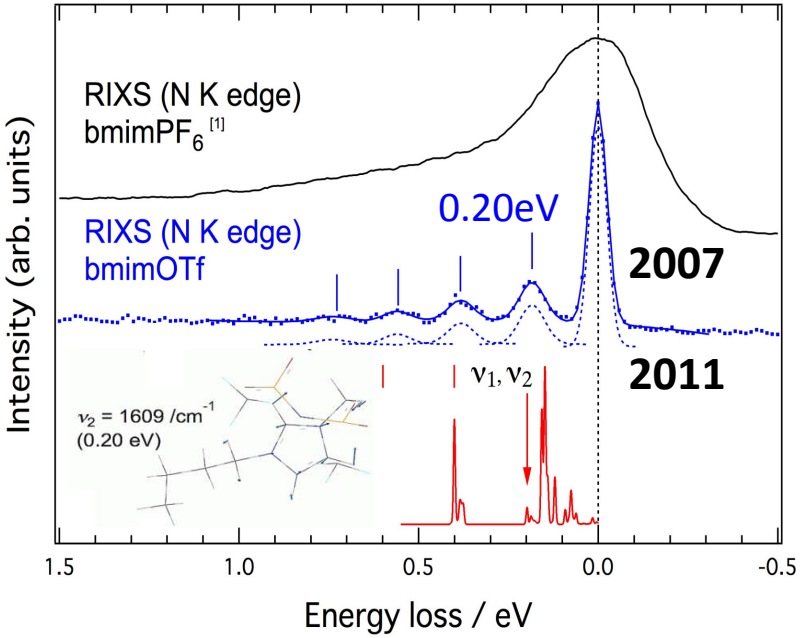
UltraHigh-resolution

i) Ionic liquids

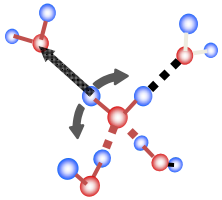


(a) [bmim]⁺ cation (b) OTf anion

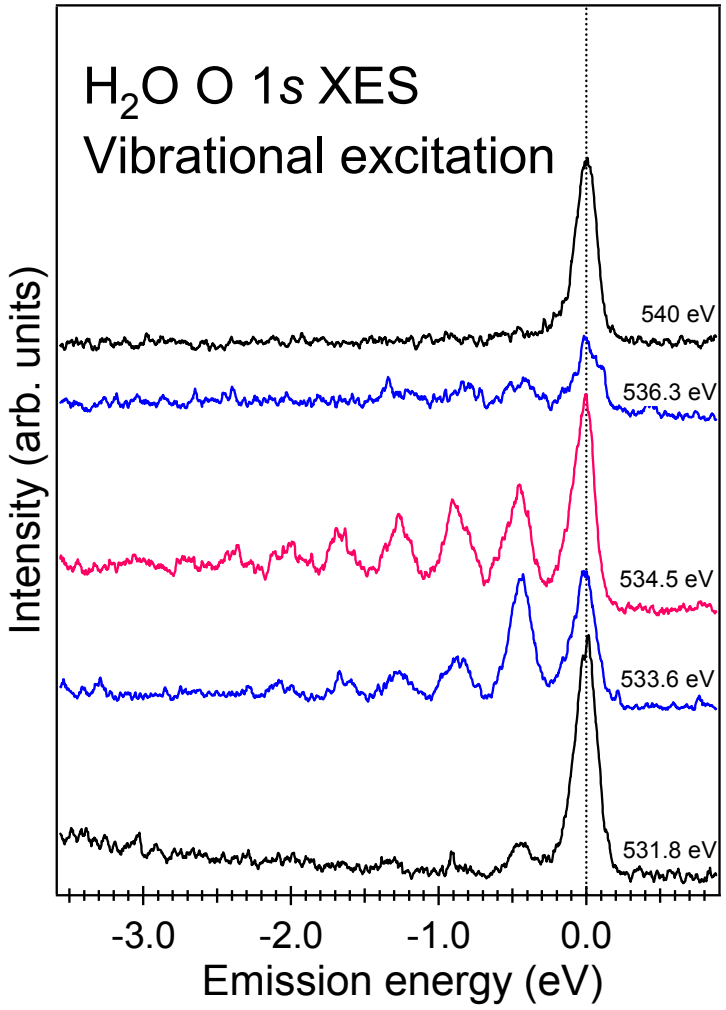
窒素周辺の多重振動スペクトル
→局所的な配位構造の情報



ii) liquid water



水の多重振動スペクトル
→水素結合による非線形
ポテンシャルの解析



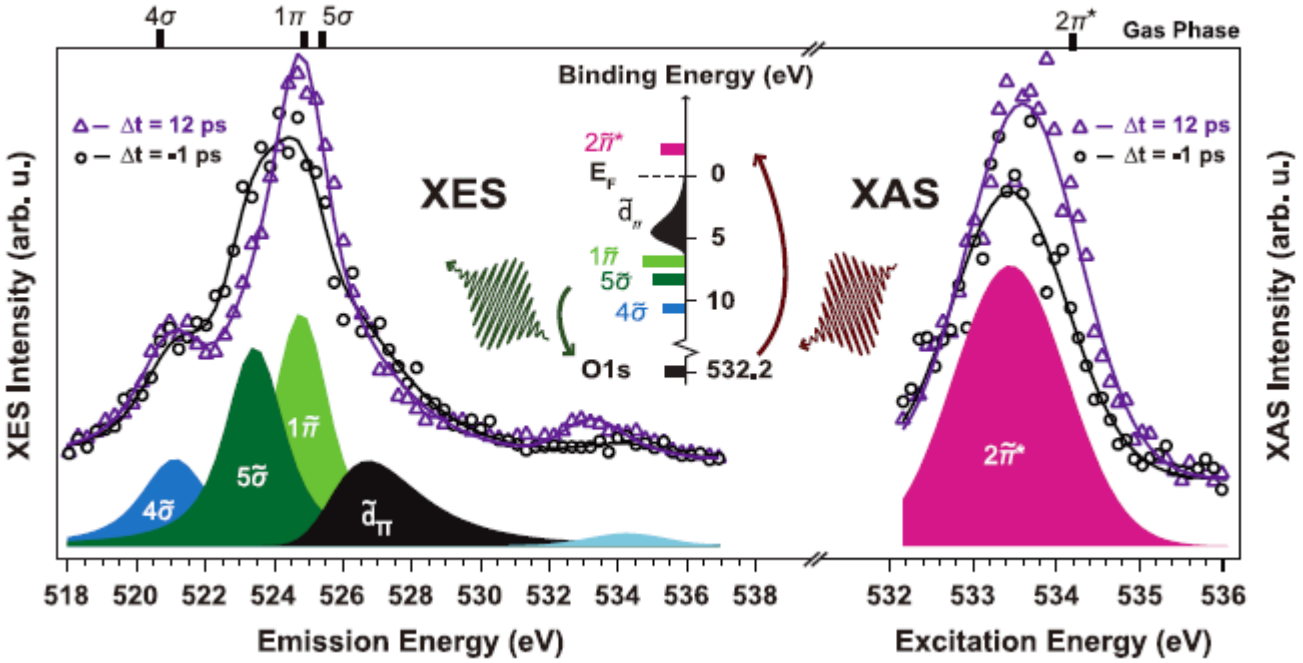
Synchrotron radiation facilities on the earth

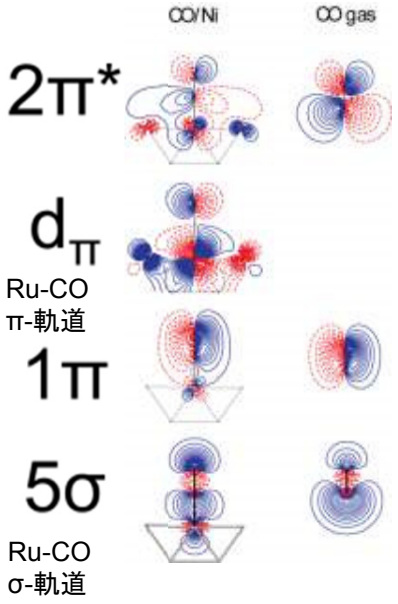
http://www.lightsources.org/

XFEL facilities on the earth

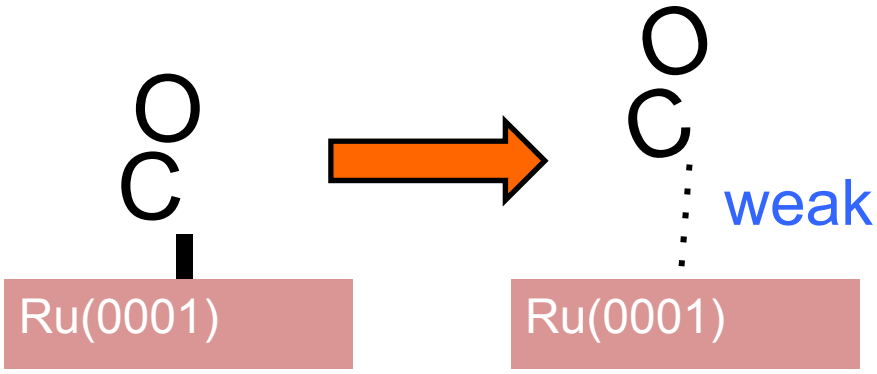
XES and XAS with XFEL
CO desorption from Ru(0001)Pump-probe XES

LCLS@SLAC　　M. Dell'Angela *et al.,* Science **339**, 1302 (2013).





Direction observation during chemical bond breaking !



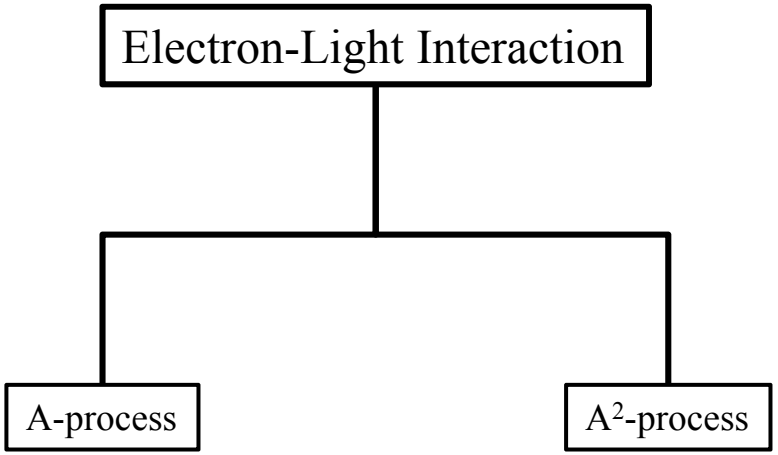
光物性物理学

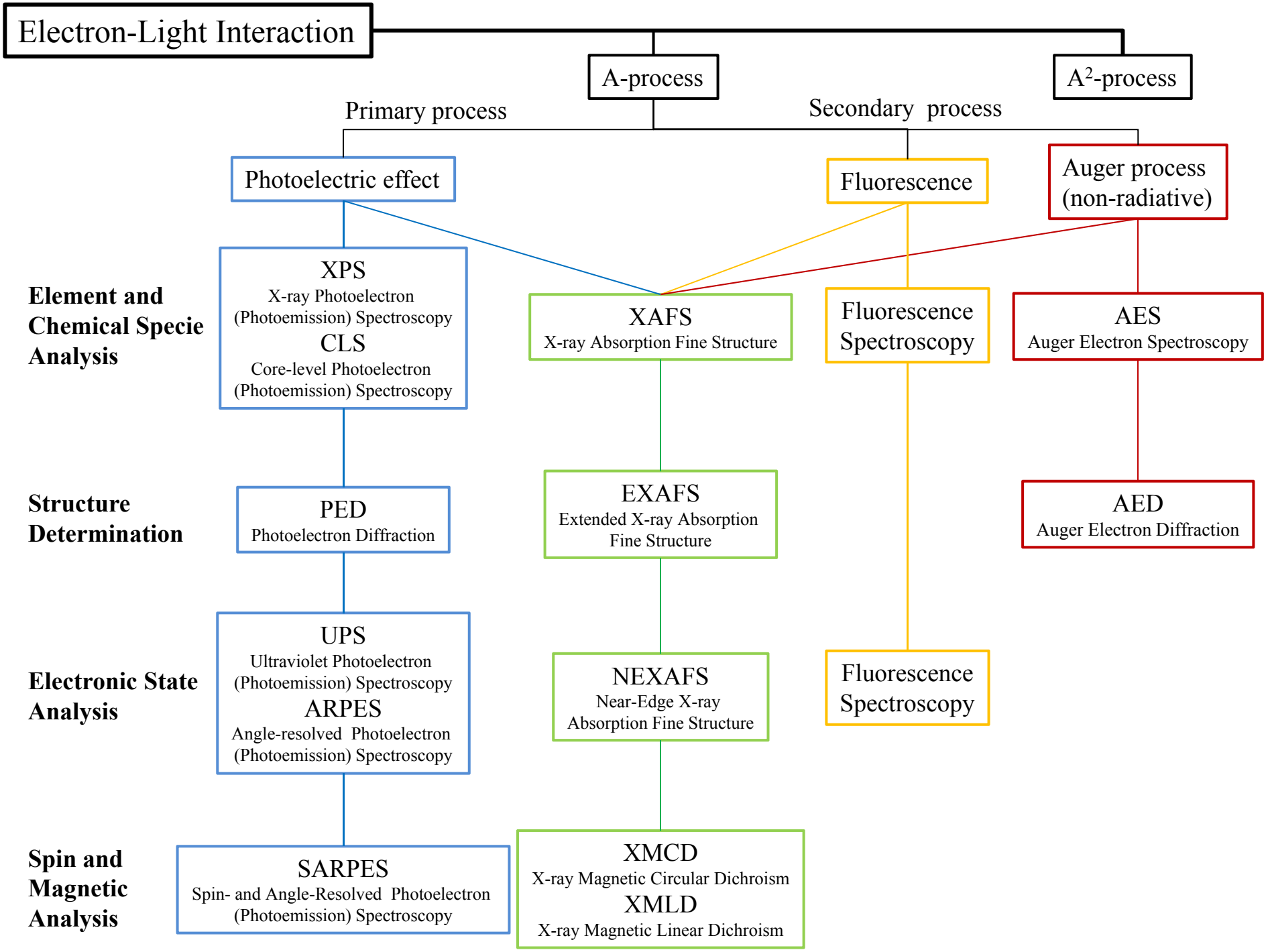
Optical Properties and Spectroscopy of Solids

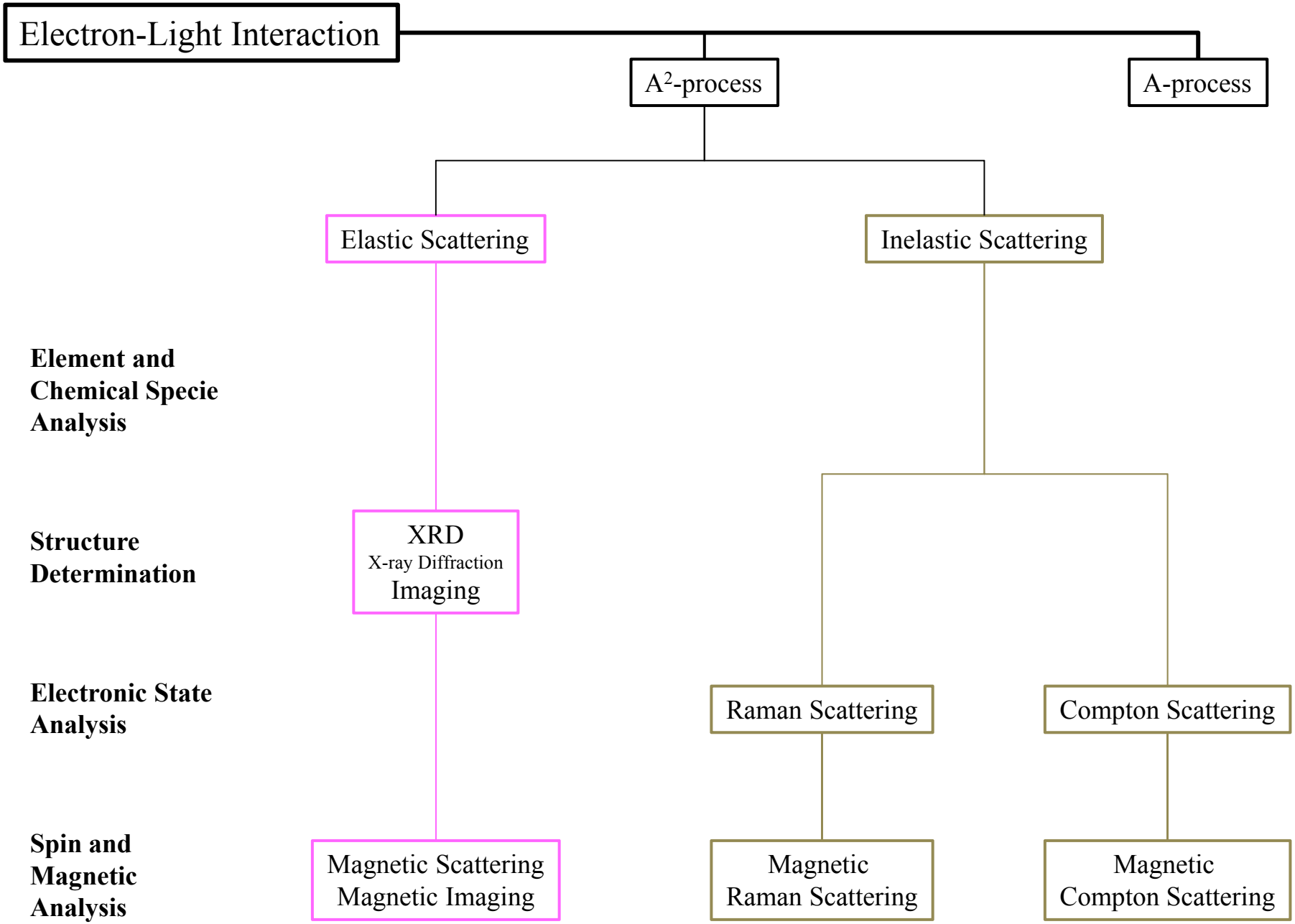
Light and Matter

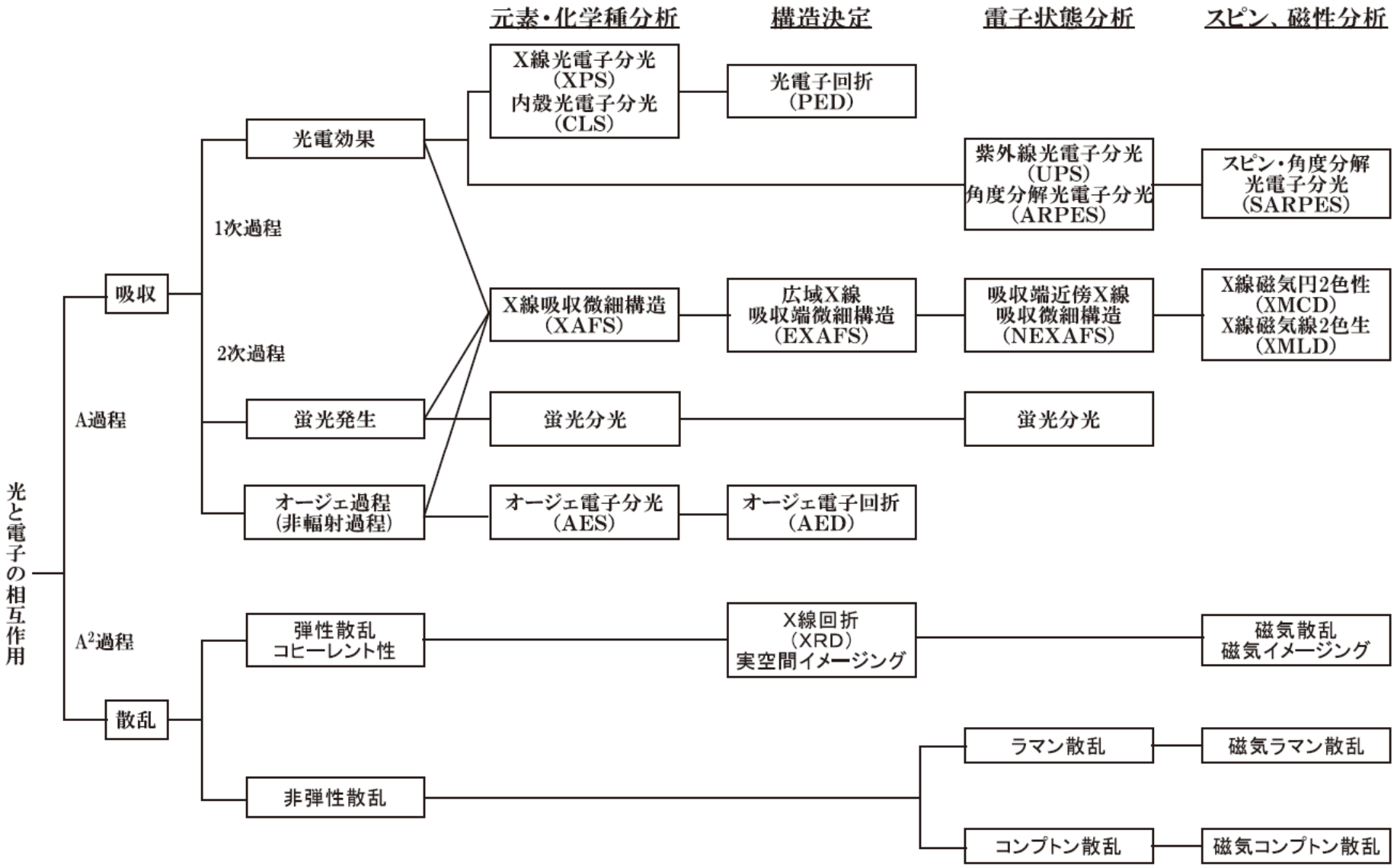
Synchrotron radiation
Free Electron Laser

Solid (bulk and surface)



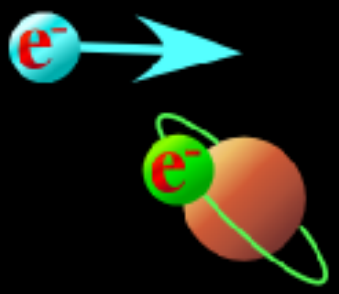

Electron-Light Interaction
A-process
A²-process
Primary process
Secondary process
Photoelectric effect
Fluorescence
Auger process (non-radiative)
Element and Chemical Specie Analysis
XPS
X-ray Photoelectron (Photoemission) Spectroscopy
CLS
Core-level Photoelectron (Photoemission) Spectroscopy
XAFS
X-ray Absorption Fine Structure
Fluorescence Spectroscopy
AES
Auger Electron Spectroscopy
Structure Determination
PED
Photoelectron Diffraction
EXAFS
Extended X-ray Absorption Fine Structure
AED
Auger Electron Diffraction
Electronic State Analysis
UPS
Ultraviolet Photoelectron (Photoemission) Spectroscopy
ARPES
Angle-resolved Photoelectron (Photoemission) Spectroscopy
NEXAFS
Near-Edge X-ray Absorption Fine Structure
Fluorescence Spectroscopy
Spin and Magnetic Analysis
SARPES
Spin- and Angle-Resolved Photoelectron (Photoemission) Spectroscopy
XMCD
X-ray Magnetic Circular Dichroism
XMLD
X-ray Magnetic Linear Dichroism


Electron-Light Interaction
A2-process
A-process
Elastic Scattering
Inelastic Scattering
Element and Chemical Specie Analysis
Structure Determination
XRD
X-ray Diffraction
Imaging
Electronic State Analysis
Raman Scattering
Compton Scattering
Spin and Magnetic Analysis
Magnetic Scattering
Magnetic Imaging
Magnetic
Raman Scattering
Magnetic
Compton Scattering

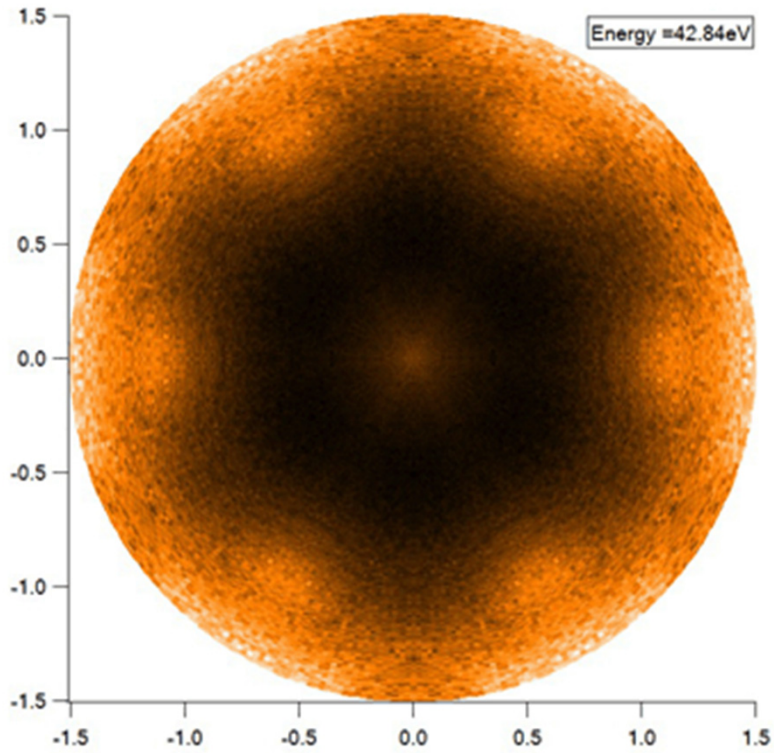


物質による軟X線の
吸収、散乱、発光を用いた
様々な分析法が存在し、
まとめるとこうなります。

みなさんが知りたい
物質情報は軟X線で
分かりそうですか？



Electrons emitted from a sample tell us about it.



Enjoy your research ♪