X-RAY RAMAN SCATTERING

SIMO HUOTARI
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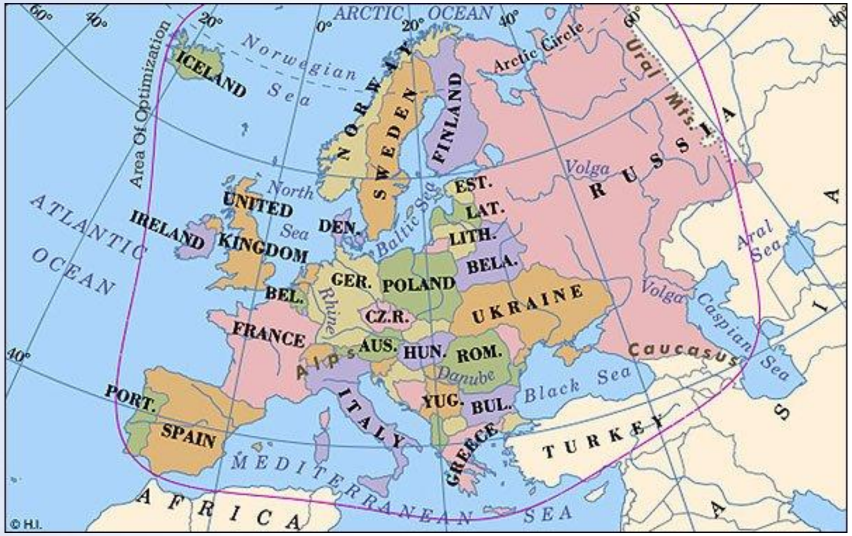
HELSINKI ELECTRONIC STRUCTURE & INELASTIC X-RAY SCATTERING = **HELIXS**



Finland (population 5,5 million)

Helsinki (capital of Finland)

Simo Huotari, M. Hakala, K. Hämäläinen,
J. Niskanen, S. Galambosi, J. Hashemi, A. Akbari,
M. Aramini, K. Ruotsalainen, J. Inkinen,
A. Kallonen, J. Koskelo, A.-P. Honkanen, A. Musazay

ESRF, Grenoble, France

http://helixs.physics.helsinki.fi
http://www.fsruo.fi

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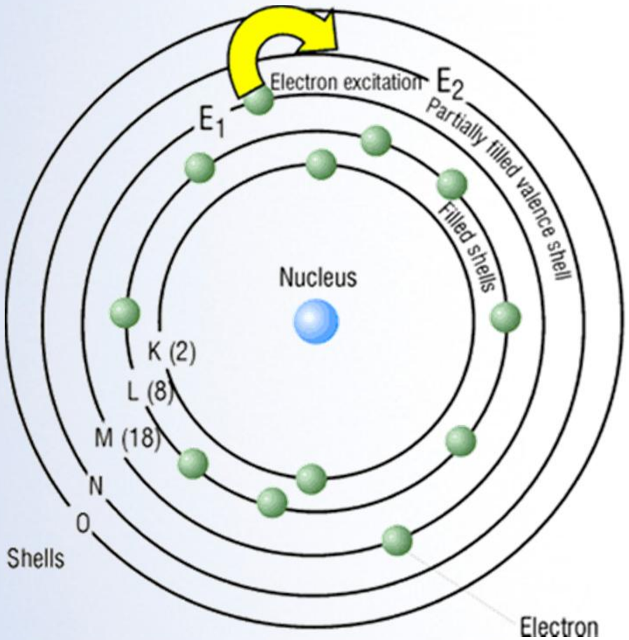
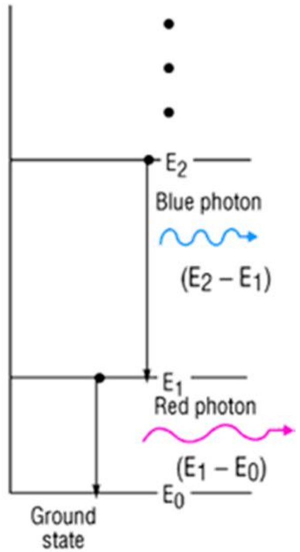
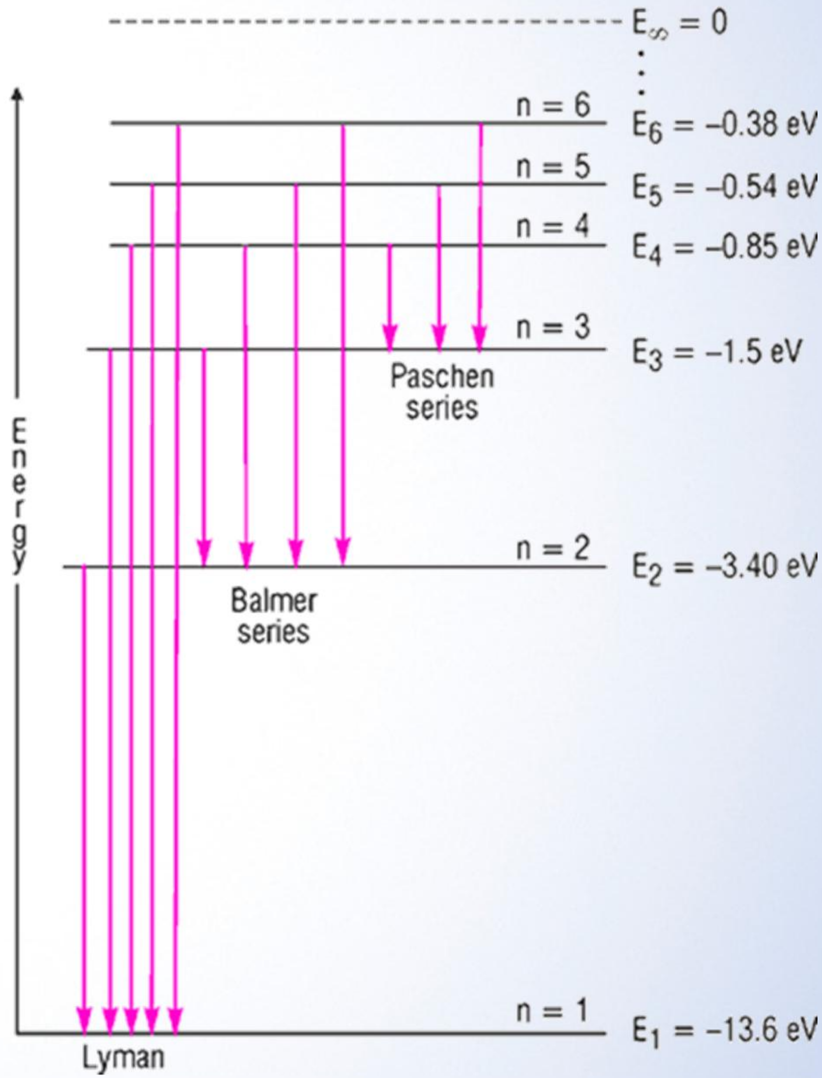
ENERGY LEVELS IN ATOM







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CONTENT

1. X-ray absorption spectroscopy
2. Compton scattering
3. X-ray Raman scattering
4. Equivalence of absorption & X-ray Raman

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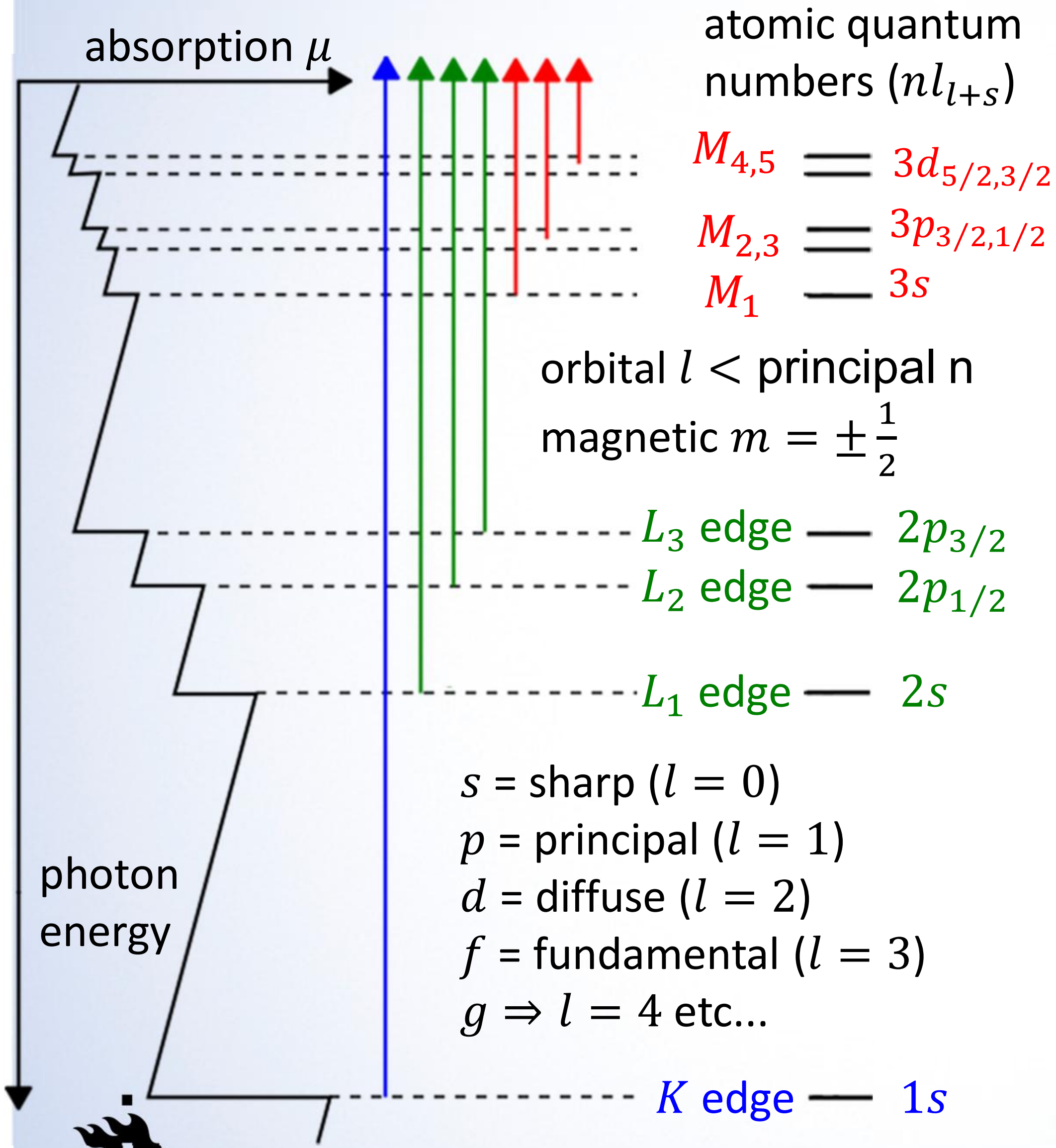
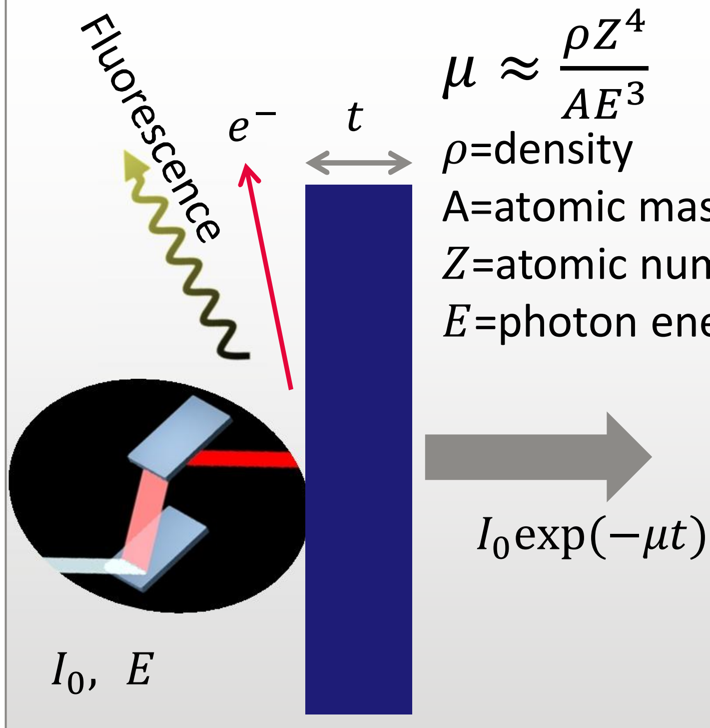
ABSORPTION EDGES



absorption coefficient:

$$\mu \approx \frac{\rho Z^4}{AE^3}$$

ρ=density
A=atomic mass
Z=atomic number
E=photon energy



Measure at least one of:
- transmission
- fluorescence yield
- electron/ion yield
- electron current

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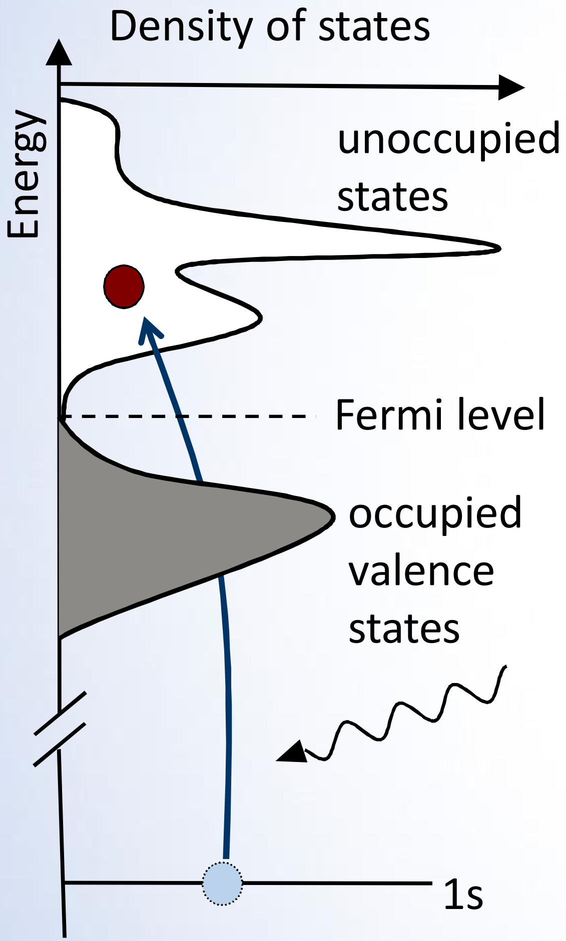
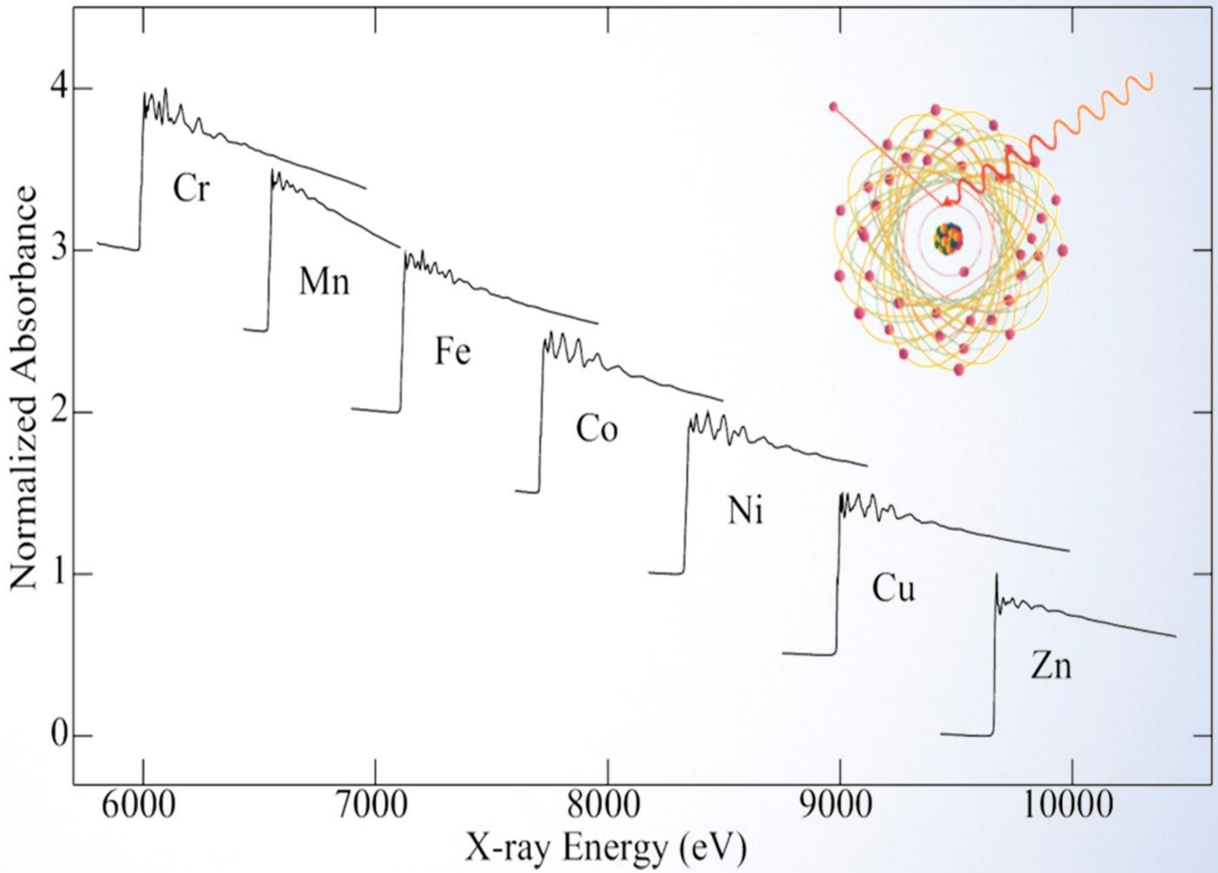
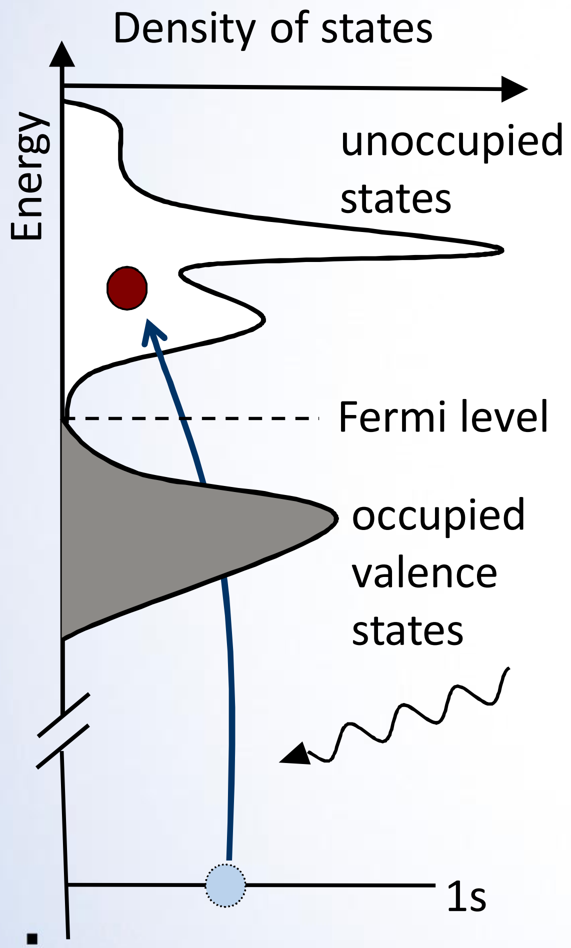
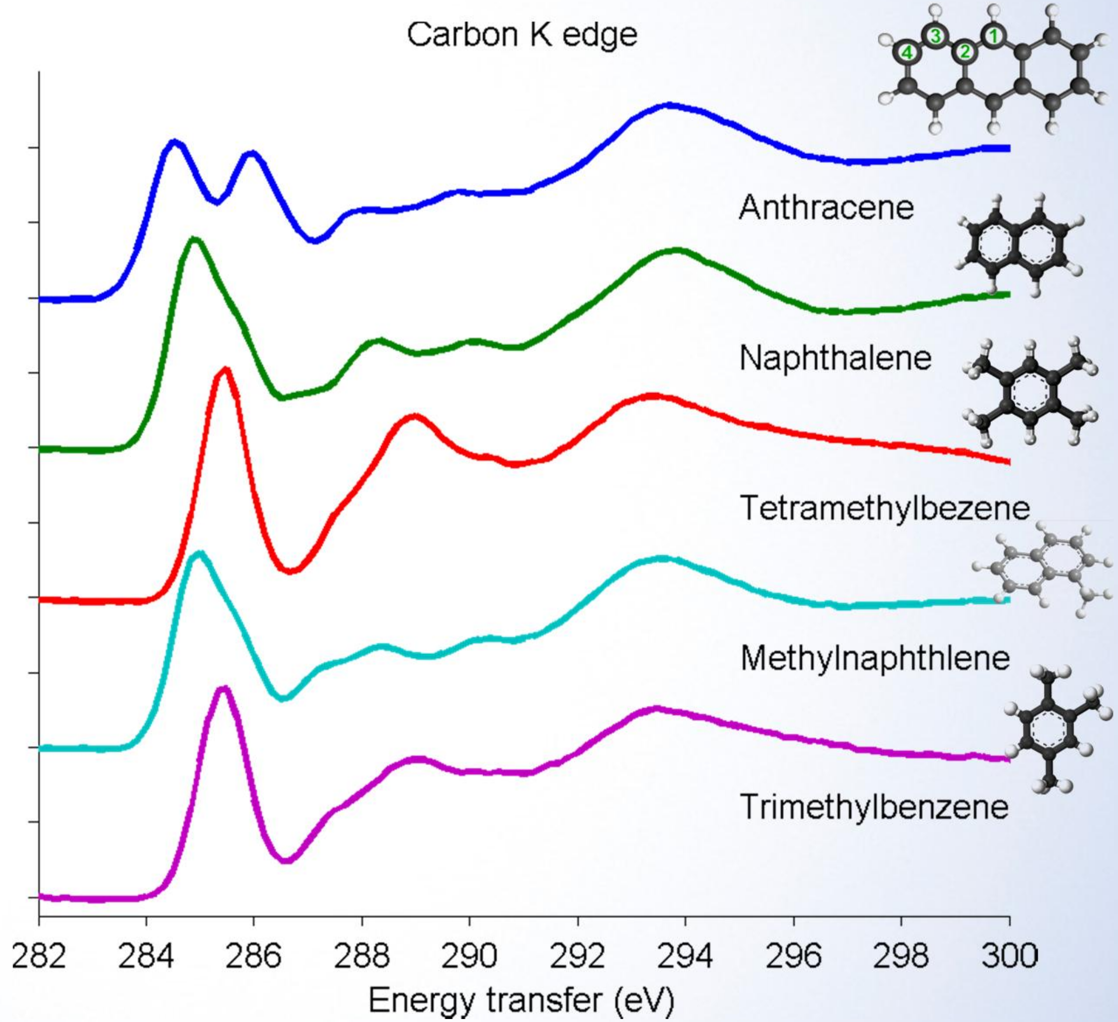
HARD X-RAY EDGES





SOFT X-RAY EDGES





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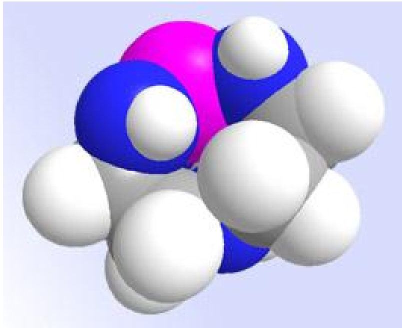
SOFT AND HARD X-RAYS

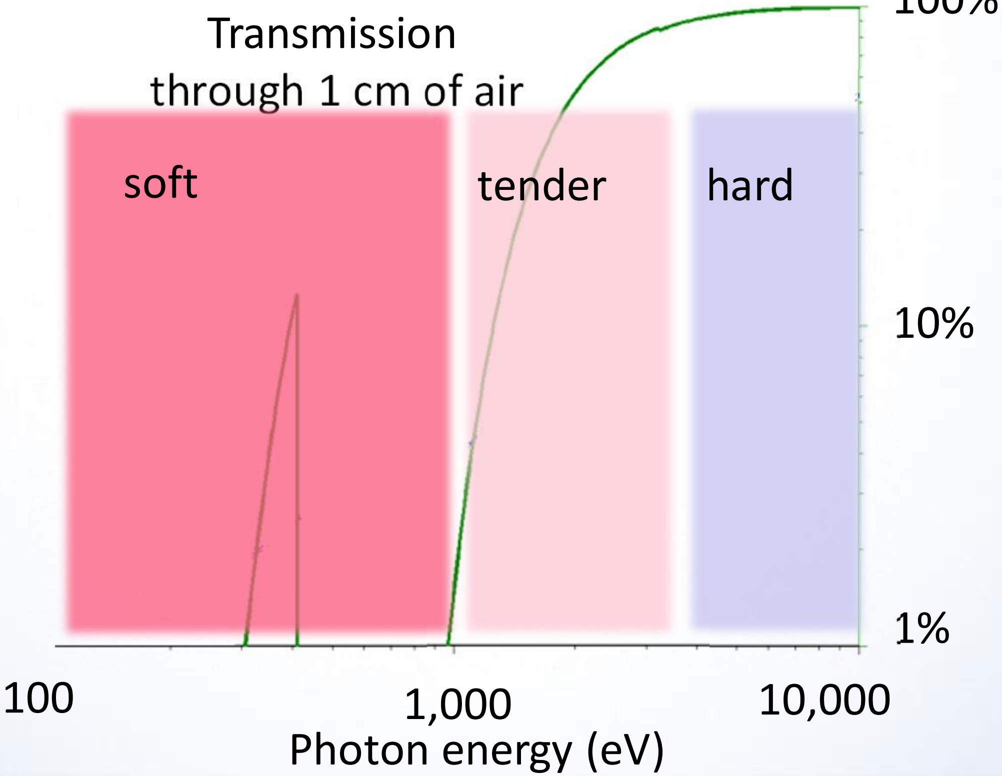
Soft x-rays



Hard x-rays

Ideal for spectroscopies of gases, clusters, surfaces

Ideal for in situ environments, atmospheric and higher pressures

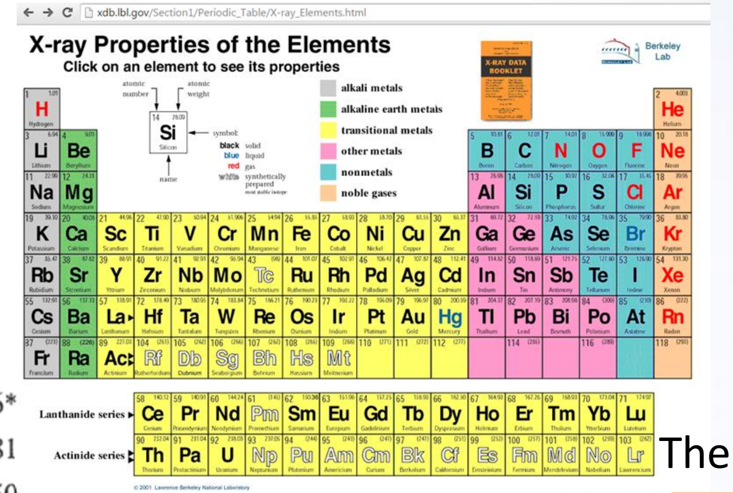


”tender” x-rays

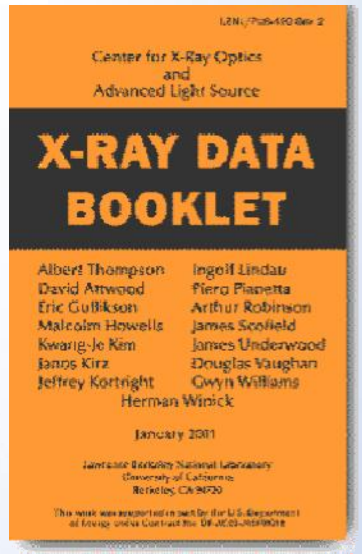
ABSORPTION EDGE ENERGIES

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 $3p_{3/2}$
1 H	13.6						
2 He	24.6*						
3 Li	54.7*						
4 Be	111.5*						
5 B	188*						
6 C	284.2*						
7 N	409.9*	37.3*					
8 O	543.1*	41.6*					
9 F	696.7*						
10 Ne	870.2*	48.5*	21.7*	21.6*			
11 Na	1070.8†	63.5†	30.65	30.81			
12 Mg	1303.0†	88.7	49.78	49.50			
13 Al	1559.6	117.8	72.95	72.55			
14 Si	1839	149.7*b	99.82	99.42			
15 P	2145.5	189*	136*	135*			
16 S	2472	230.9	163.6*	162.5*			
17 Cl	2822.4	270*	202*	200*			
18 Ar	3205.9*	326.3*	250.6†	248.4*	29.3*	15.9*	15.7*
19 K	3608.4*	378.6*	297.3*	294.6*	34.8*	18.3*	18.3*
20 Ca	4038.5*	438.4†	349.7†	346.2†	44.3 †	25.4†	25.4†
21 Sc	4492	498.0*	403.6*	398.7*	51.1*	28.3*	28.3*
22 Ti	4966	560.9†	460.2†	453.8†	58.7†	32.6†	32.6†

in electron volts (eV)



The ”orange book”



http://xdb.lbl.gov/Section1/Periodic_Table/X-ray_Elements.html

http://xdb.lbl.gov/

$1,000,000 QUESTION

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 $3p_{3/2}$
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22 Ti	4966	560.9†	460.2†	453.8†	58.7†	32.6†	32.6†

in electron volts (eV)

Q: Is there any way to measure these soft-x-ray absorption edges in a way that is not surface sensitive, require a vacuum, or could be used with complex sample environments?

THEN YOU COULD DO ALL THIS...

...and more!

PRL 109, 046401 (2012) PHYSICAL REVIEW LETTERS week ending 27 JULY 2012

Determining the In-Plane Orientation of the Ground-State Orbital of $CeCu_2Si_2$

T. Willers,[1] F. Strigari,[1] N. Hiraoka,[2] Y. Q. Cai,[3] M. W. Haverkort,[4] K.-D. Tsuei,[2] Y. F. Liao,[2] S. Seiro,[5] C. Geibel,[5] F. Steglich,[5] L. H. Tjeng,[5] and A. Severing[1]

PNAS

Electronic structure of carbon dioxide under pressure and insights into the molecular-to-nonmolecular transition

Sean R. Shieh[a,1], Ignace Jarrige[b], Min Wu[c,d], Nozomu Hiraoka[e], John S. Tse[d], Zhongying Mi[a,2], Linada Kaci[a], Jian-Zhong Jiang[c], and Yong Q. Cai[b]

[a]Departments of Earth Sciences, and Physics and Astronomy, University of Western Ontario, London, ON, Canada N6A 5B7; [b]Photon Sciences, Brookhaven National Laboratory, Upton, NY 11973; [c]International Center for New Structured Materials and Laboratory of New Structured Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China; [d]Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, SK, Canada S7N 5E2; and [e]National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan

LETTERS

The formation of sp^3 bonding in compressed BN

YUE MENG*[1,2], HO-KWANG MAO[2], PETER J. ENG[3], THOMAS P. TRAINOR[3†], MATTHEW NEWVILLE[3], MICHAEL Y. HU[1,2], CHICHANG KAO[4], JINFU SHU[2], DANIEL HAUSERMANN[1,2] AND RUSSELL J. HEMLEY[2]

SCIENTIFIC REPORTS

OPEN

Structure and Properties of Dense Silica Glass

Min Wu[1,2], Yunfeng Liang[2,3], Jian-Zhong Jiang[1] & John S. Tse[1,2]

PNAS

Microscopic structure of water at elevated pressures and temperatures

Christoph J. Sahle[a,b,1], Christian Sternemann[a], Christian Schmidt[c], Susi Lehtola[b], Sandro Jahn[c], Laura Simonelli[d], Simo Huotari[b], Mikko Hakala[b], Tuomas Pylkkänen[b], Alexander Nyrow[a], Kolja Mende[a], Metin Tolan[a], Keijo Hämäläinen[b], and Max Wilke[c]

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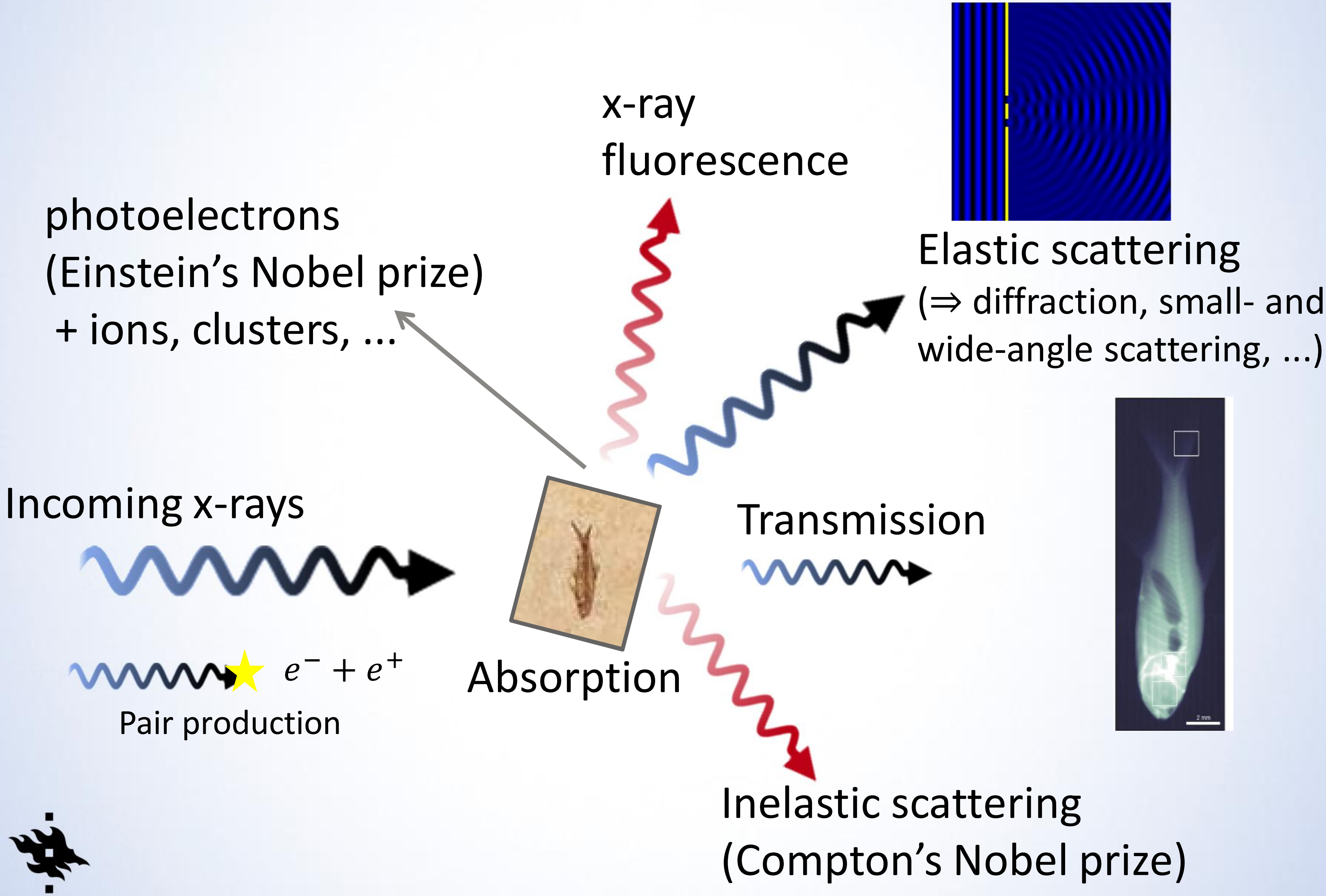
X-RAY / MATTER INTERACTION



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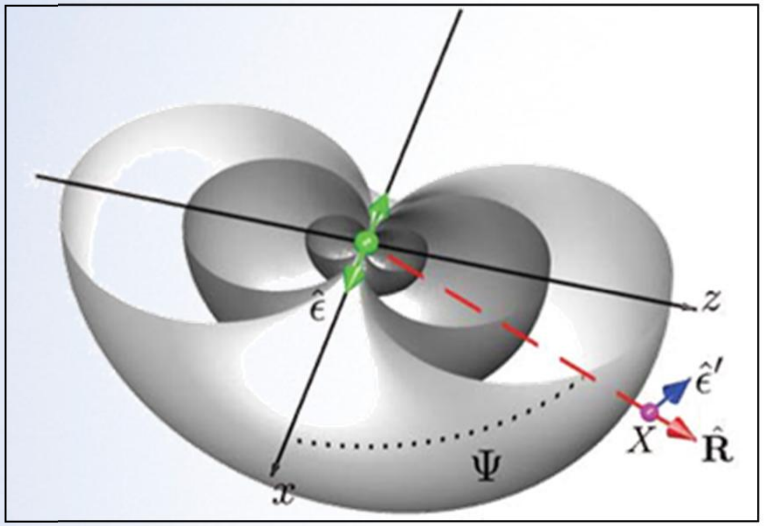
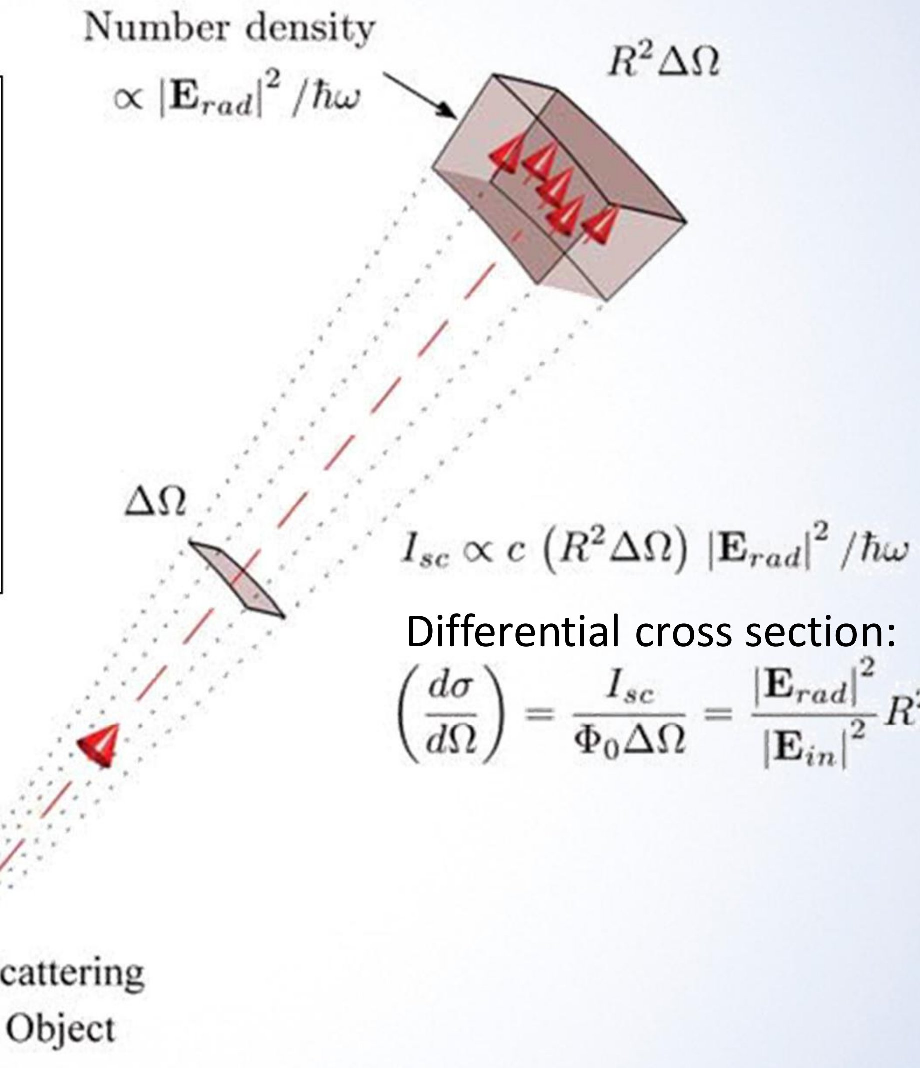
X-RAY SCATTERING



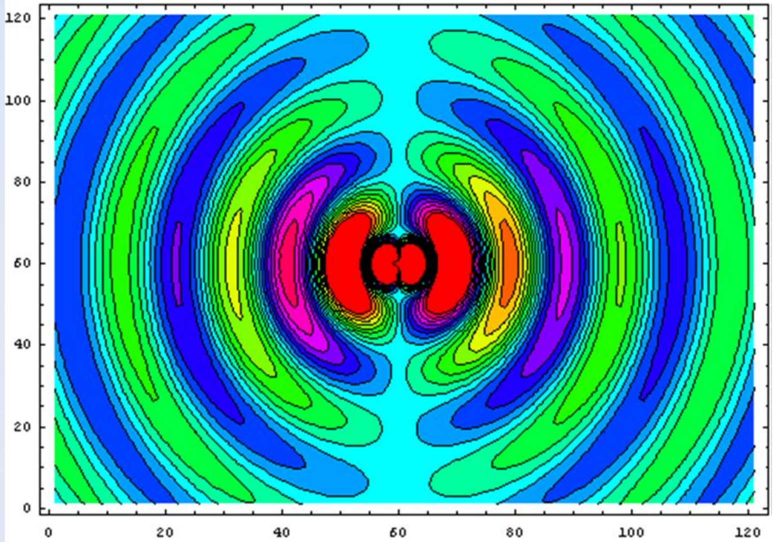


Differential cross section:

$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{I_{sc}}{\Phi_0 \Delta\Omega} = \frac{|\mathbf{E}_{rad}|^2}{|\mathbf{E}_{in}|^2} R^2$$

From Als-Nielsen & McMorrow:
Elements of Modern X-ray Physics (Wiley)

ELASTIC SCATTERING FROM AN ELECTRON (CLASSICAL)



Thomson cross section

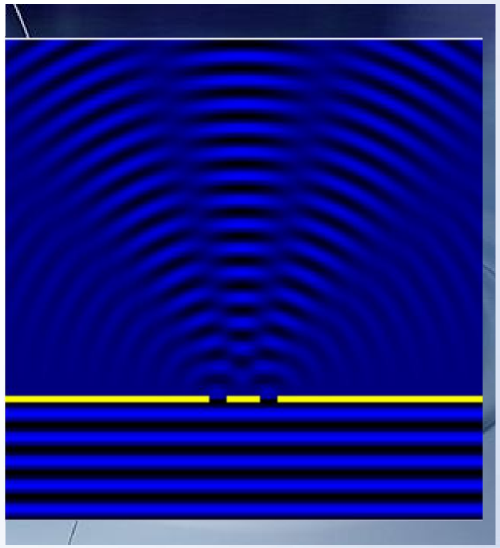
$$\left(\frac{d\sigma}{d\Omega}\right)_{TH} = r_0^2 \,|\, \hat{e}_1 \cdot \hat{e}_2 |^2 = r_0^2 \left(\frac{1+\cos^2 2\theta}{2}\right)$$

Unpolarized radiation

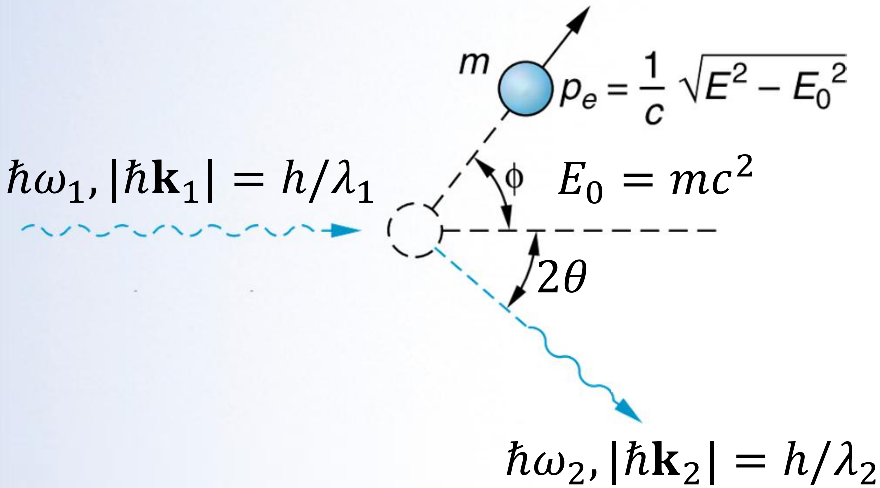
(THOMSON)

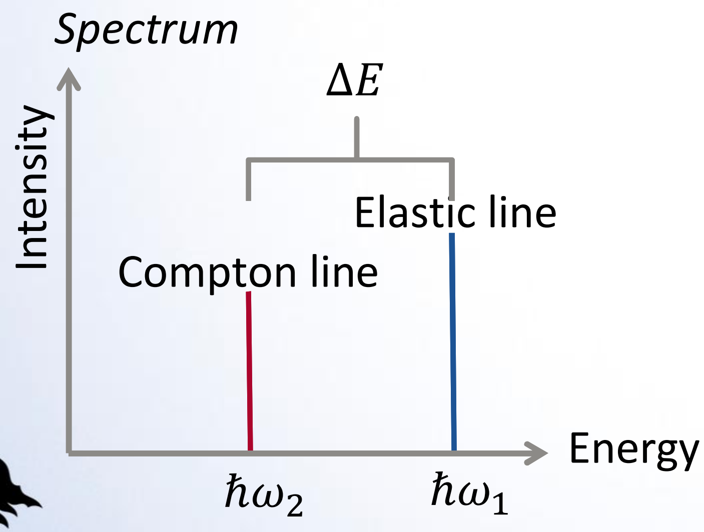
$$\begin{cases} r_0 = 2.8 \cdot 10^{-15}\,\mathrm{m} \\ r_0^{\;2} = 0.079\ \mathrm{barn} \end{cases}$$

1 barn = 10^{-24} cm^2 (cross section of a uranium nucleus)



INELASTIC SCATTERING FROM AN ELECTRON (CLASSICAL)





1. Particle (photon) scatters off another particle (electron). Collision is inelastic ⇒ loss of energy

2. Laws of energy and momentum concervation hold:

$$\hbar c|\mathbf{k}_1| - \hbar c|\mathbf{k}_2| = \sqrt{E_0^2 + p_e^2 c^2} - E_0$$

$$\hbar\mathbf{k}_1 - \hbar\mathbf{k}_2 = \mathbf{p}_e$$

3. This leads to a well defined red-shift of the photon energy upon scattering ⇒ the so-called ***Compton shift***

Arthur Holly Compton, Nobel prize 1927

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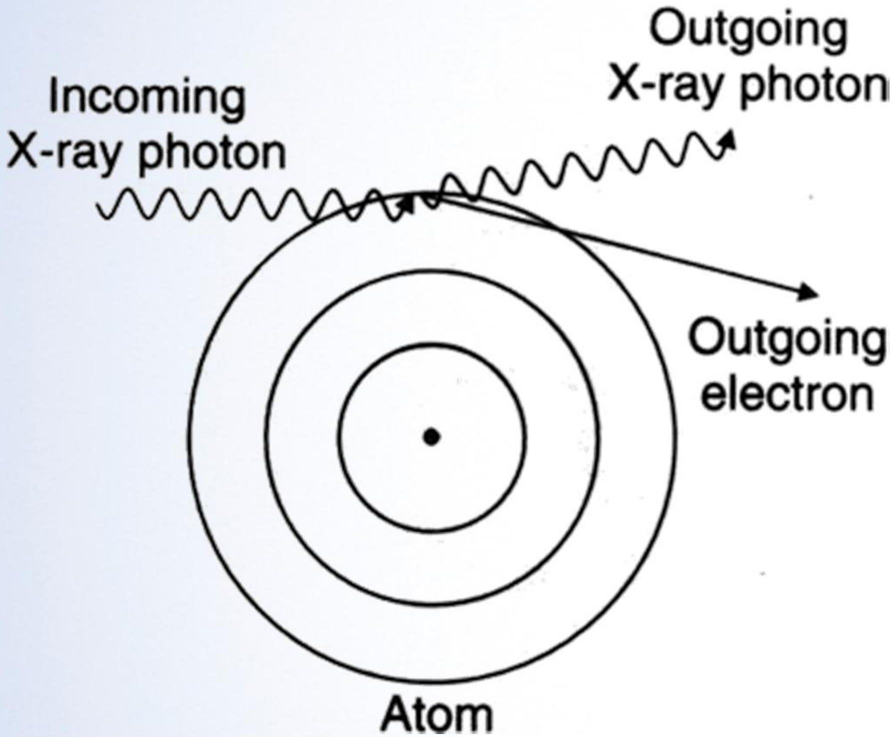
EXERCISE: COMPTON SCATTERING

1. Derive the wavelength change $\Delta\lambda$ in Compton scattering for an electron that is initially at rest, photon scattering angle 2θ.

2. How does $\Delta\lambda$ depend on the initial wavelength?

3. Bonus question: What is the Compton shift in energy as a function of momentum transfer q?

INELASTIC SCATTERING FROM AN ATOM (CLASSICAL)



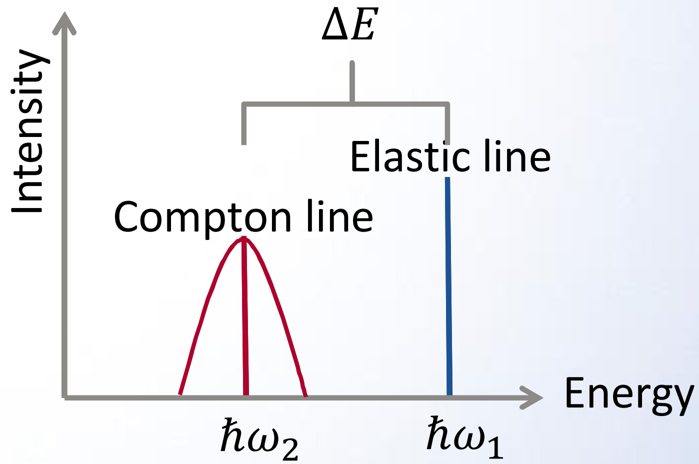
$$\left(\frac{d\sigma}{d\Omega}\right) = \left(\frac{d\sigma}{d\Omega}\right)_{\mathrm{Th}} \times S$$

S = Incoherent atomic scattering factor

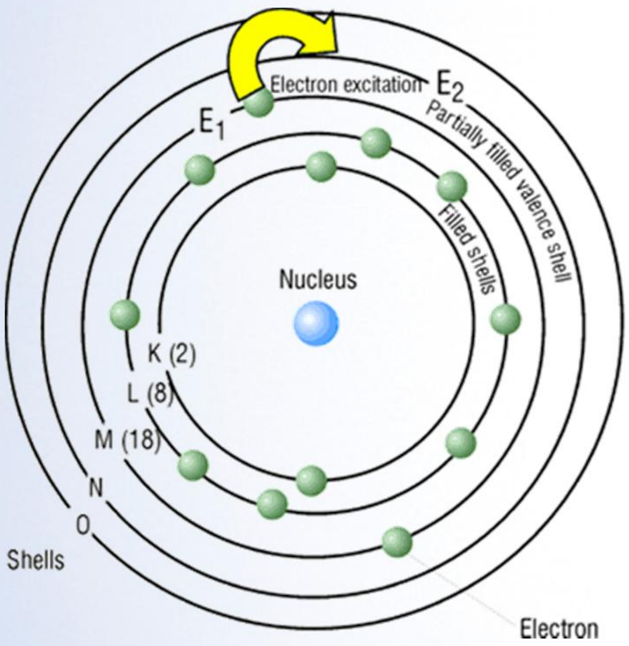
Electrons bound to atoms are constantly on the move!

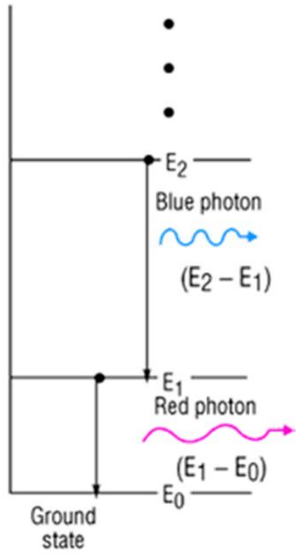
Initially electrons are not at rest in general ⇒ Doppler shift (from the laws of conservation of energy and momentum)

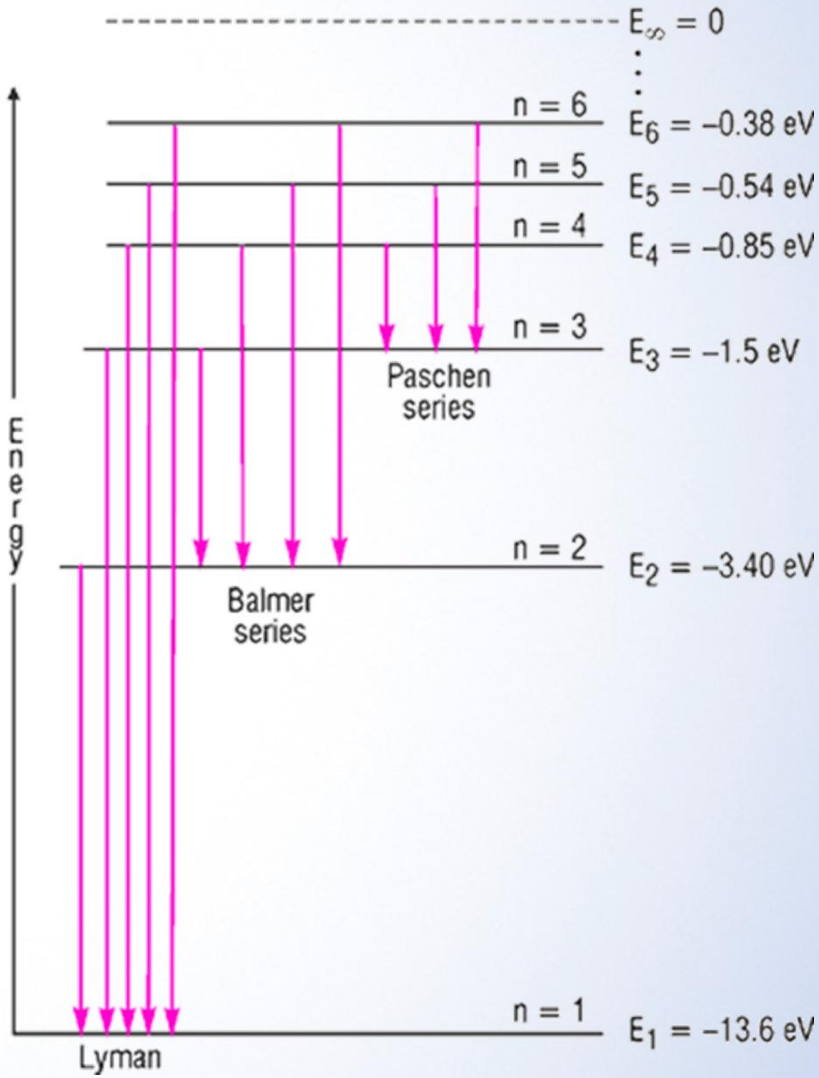
Spectrum



ENERGY LEVELS IN ATOM







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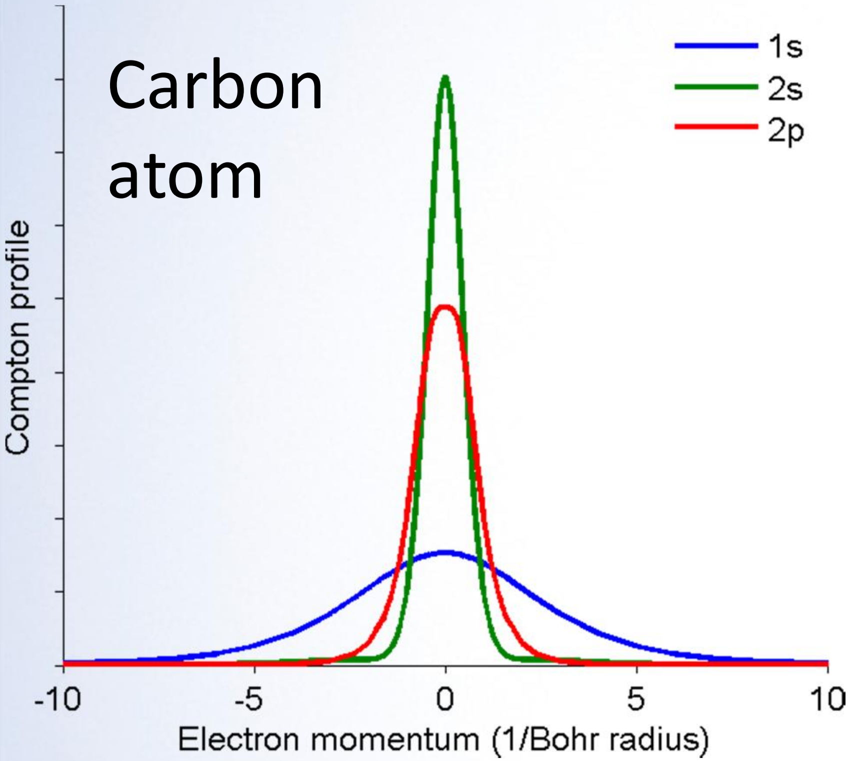
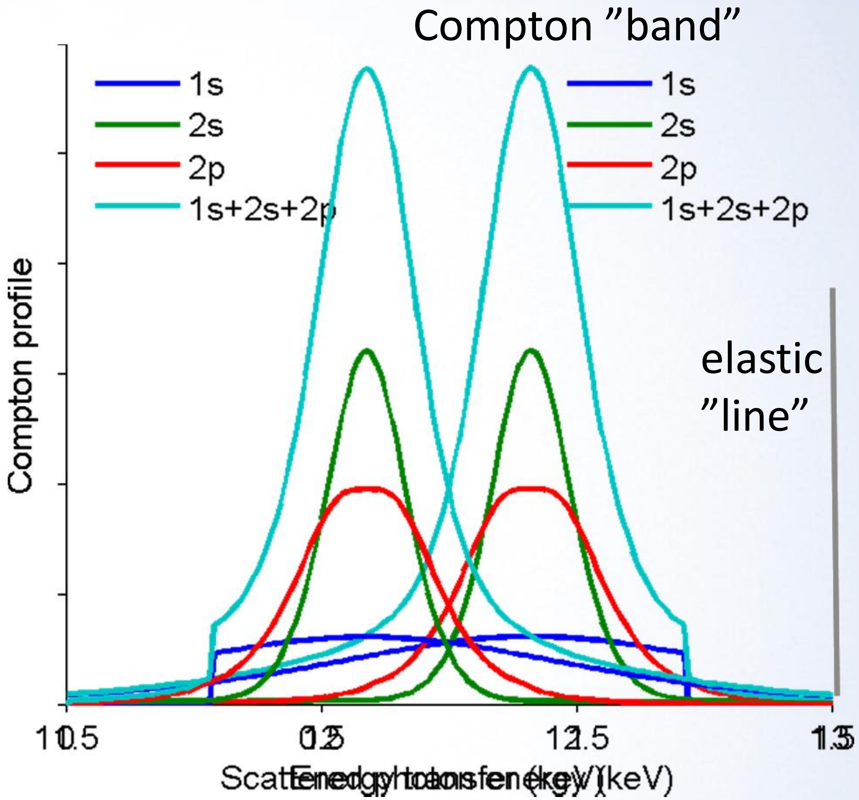
COMPTON PROFILE OF AN ATOM





- Compton profile peak appears at energy transfer of $\hbar\omega_1 - \hbar\omega_2 \approx q^2/2m$

- X-ray Raman edge appears at the corresponding electron shell’s binding energy

In our example: carbon atom
$\hbar\omega_1 = 13$ keV
$2\theta = 150^\circ$

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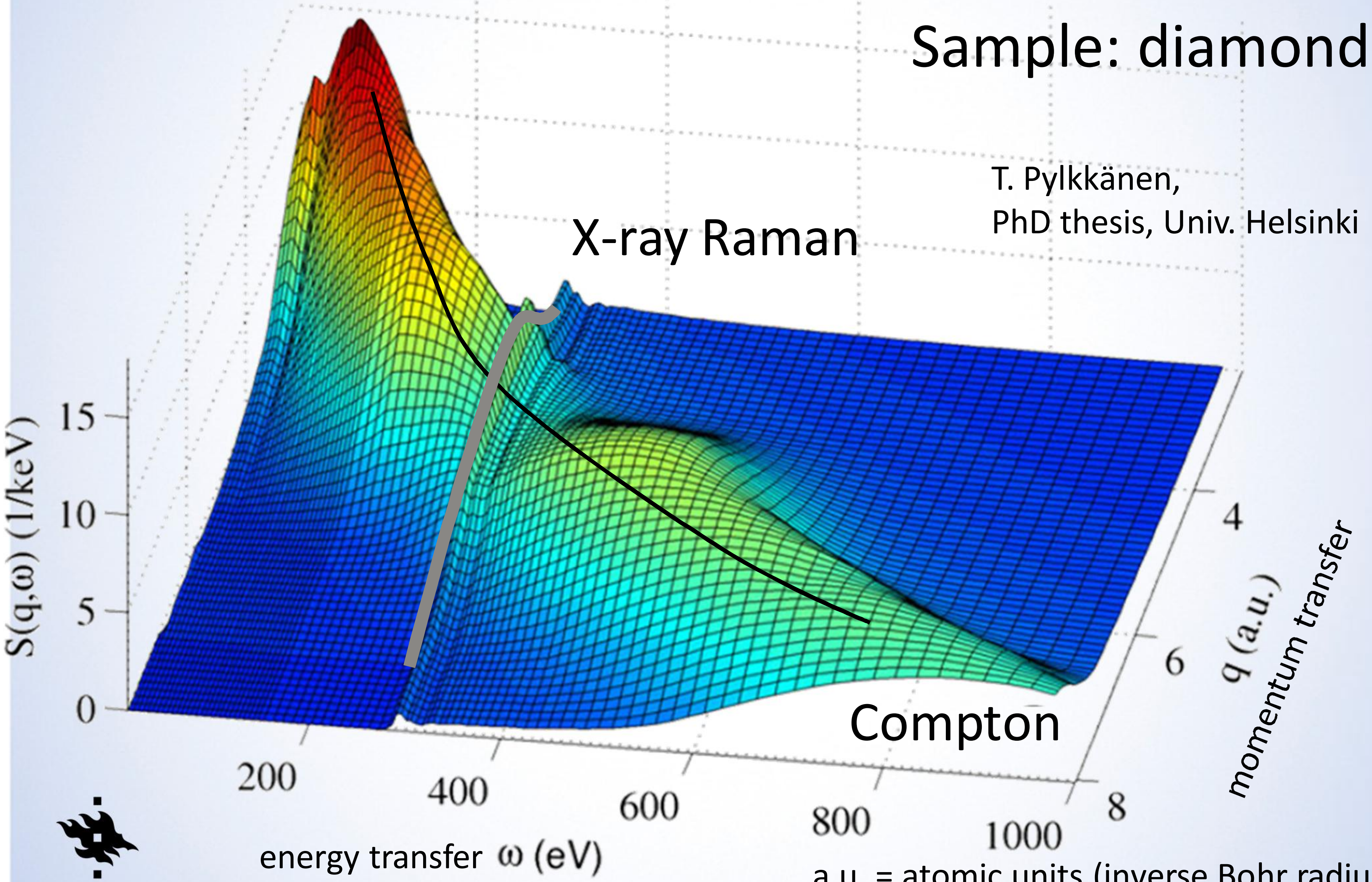
TYPICAL SPECTRUM

Sample: diamond

T. Pylkkänen,
PhD thesis, Univ. Helsinki



a.u. = atomic units (inverse Bohr radius)

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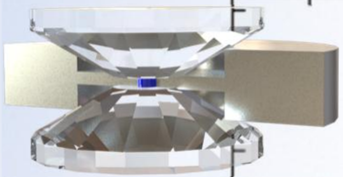
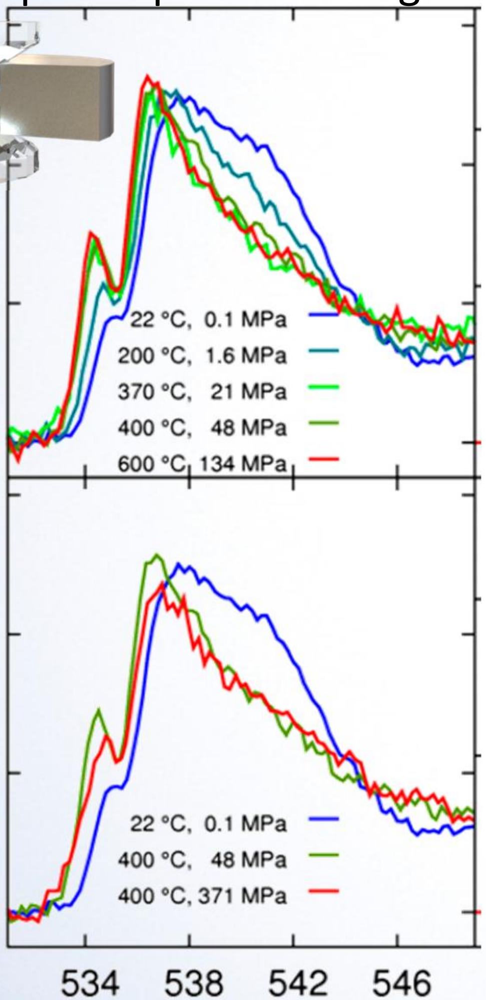
X-RAY RAMAN SPECTRA

Oxygen K edge in water
up to supercritical regime



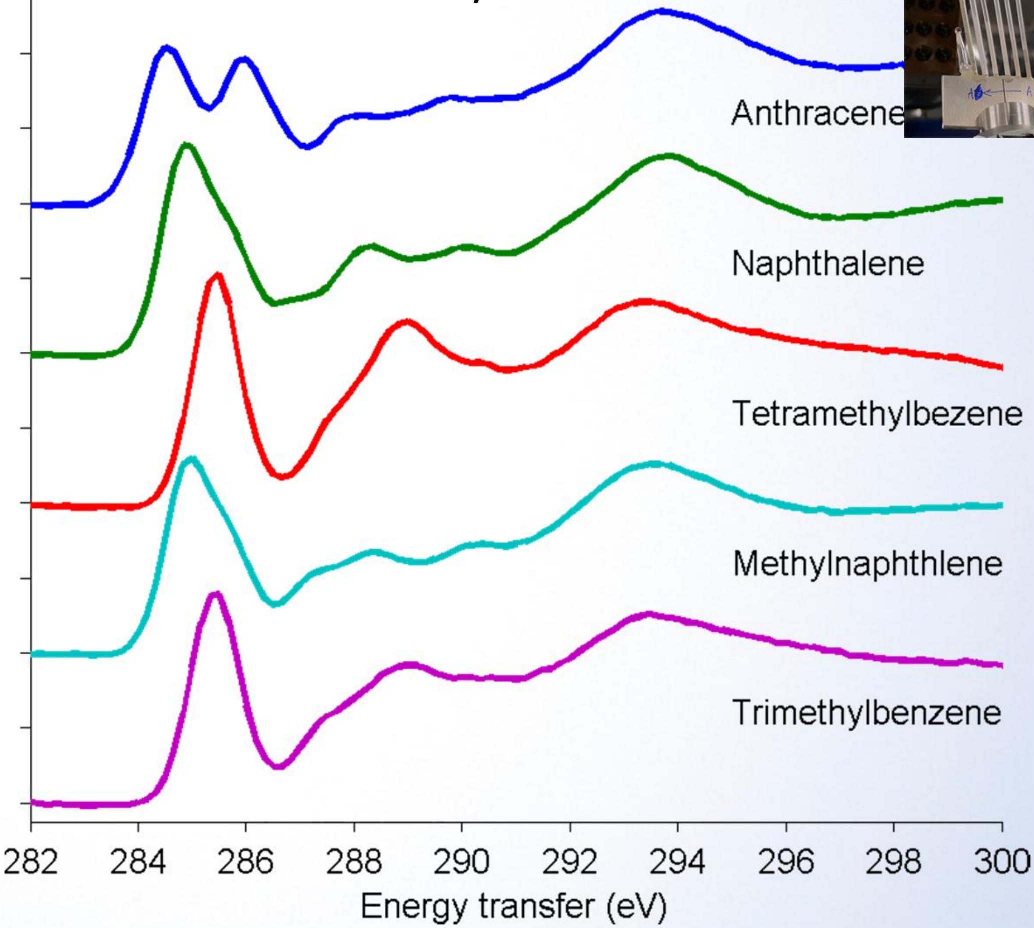


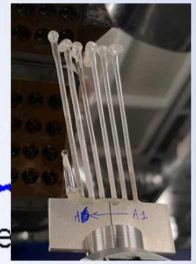
Energy transfer (eV)

Sahle et al. PNAS 2013

Using 10 keV x-radiation!

Carbon K edge
aromatic hydrocarbons





Ruiz-Martinez et al. to be published

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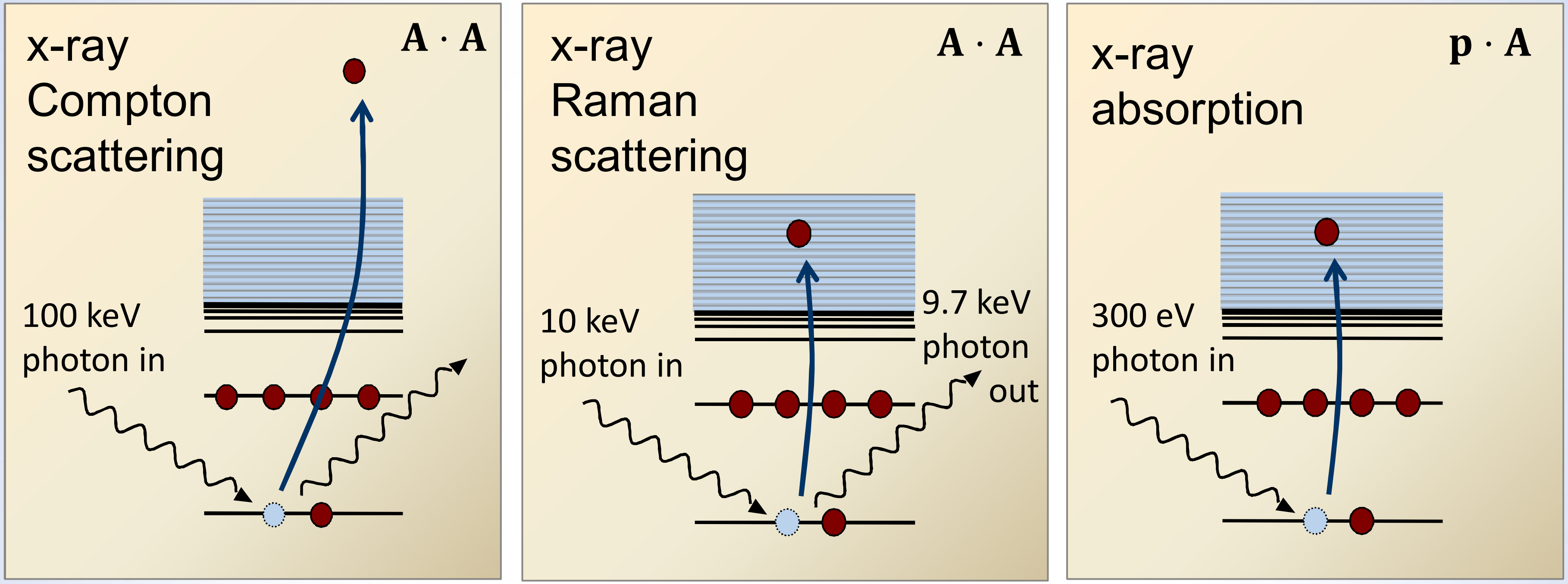
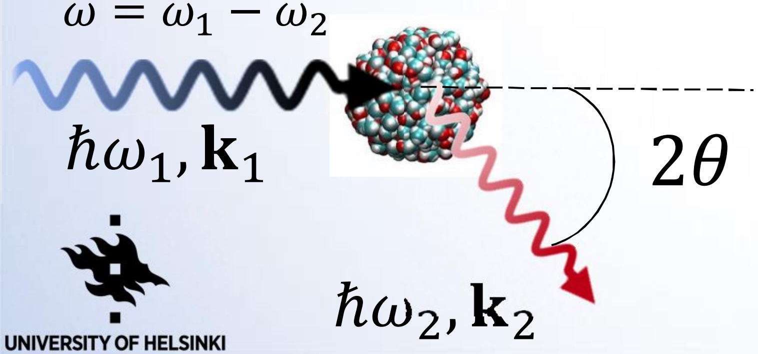
X-RAY RAMAN SCATTERING



$\mathbf{Q} = \mathbf{k}_1 - \mathbf{k}_2$

$\omega = \omega_1 - \omega_2$



In Compton & XRS we measure the dynamic structure factor

$$S(\mathbf{Q},\omega) \propto \sum_f |\langle f|\exp(i\mathbf{Q}\cdot\mathbf{r})|i\rangle|^2$$

$$e^{i\mathbf{Q}\cdot\mathbf{r}} = 1 + i\mathbf{Q}\cdot\mathbf{r} - (\mathbf{Q}\cdot\mathbf{r})^2/2 + \cdots$$

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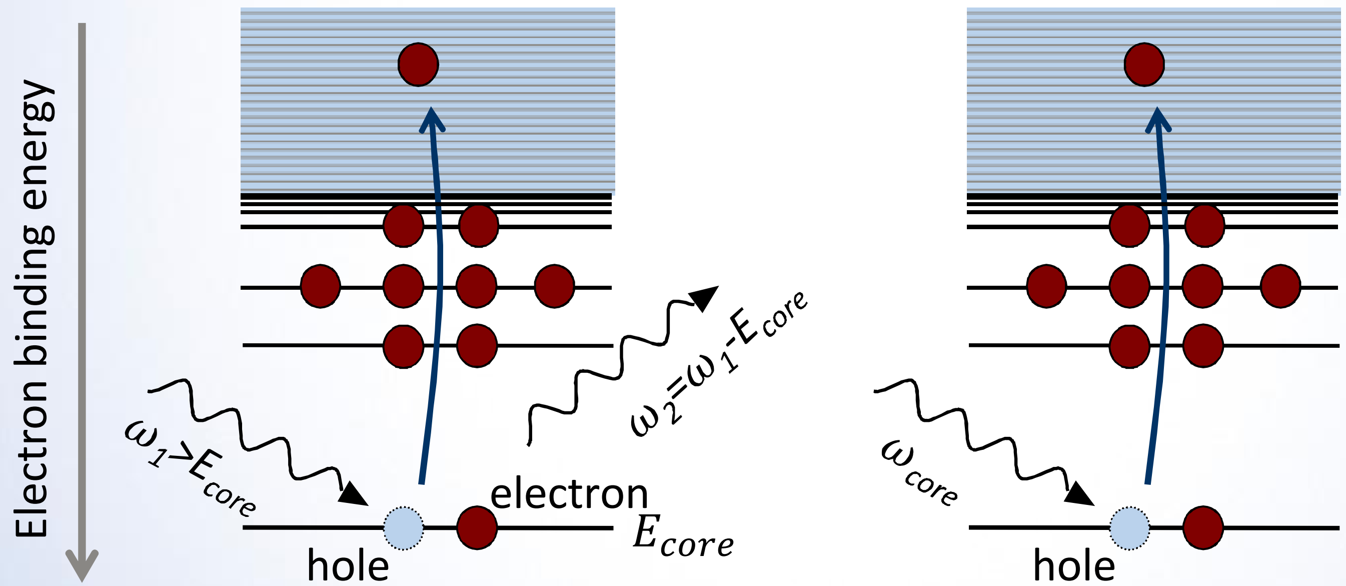
INELASTIC SCATTERING

Equivalence of:

Scattering	Absorption	Excitations
optical Raman	infrared absorption	vibrational (meV)
x-ray Raman	soft x-ray absorption	core-electrons (eV, keV)



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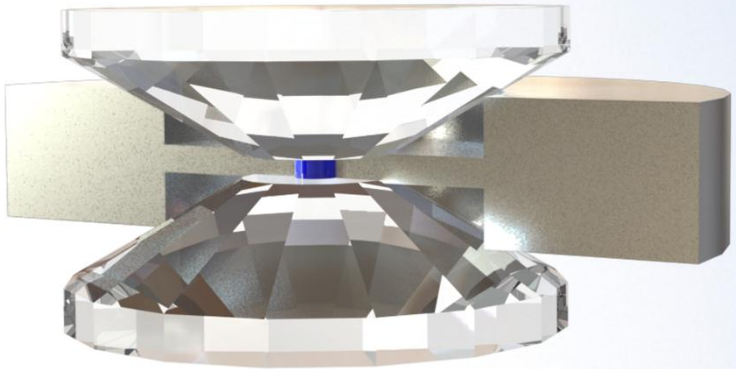
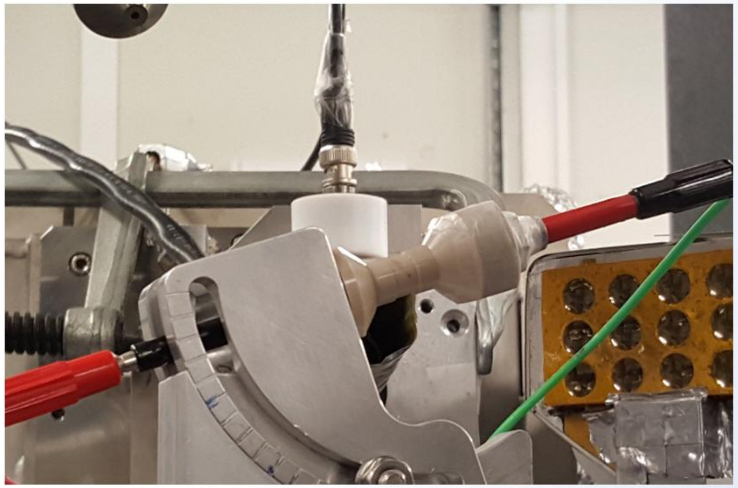
HARD X-RAYS: BENEFITS

Access to extreme conditions and in-situ environments (chemical reactors, etc)



Diamond anvil cell: high pressure

Bulk sensitivity



Li-ion battery: electrochemistry

Not limited to dipolar transitions

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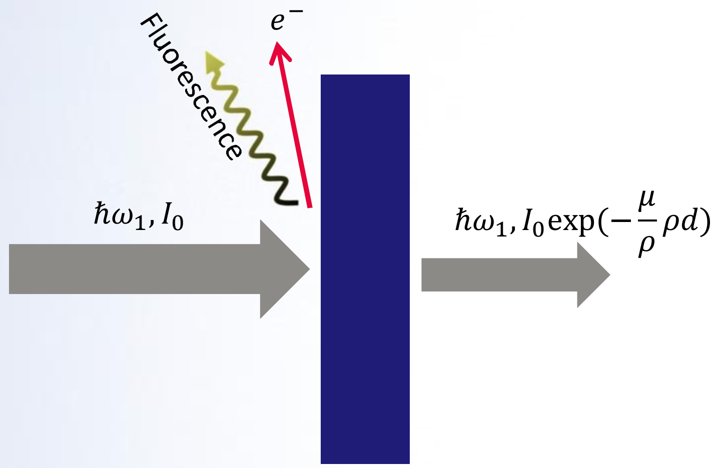
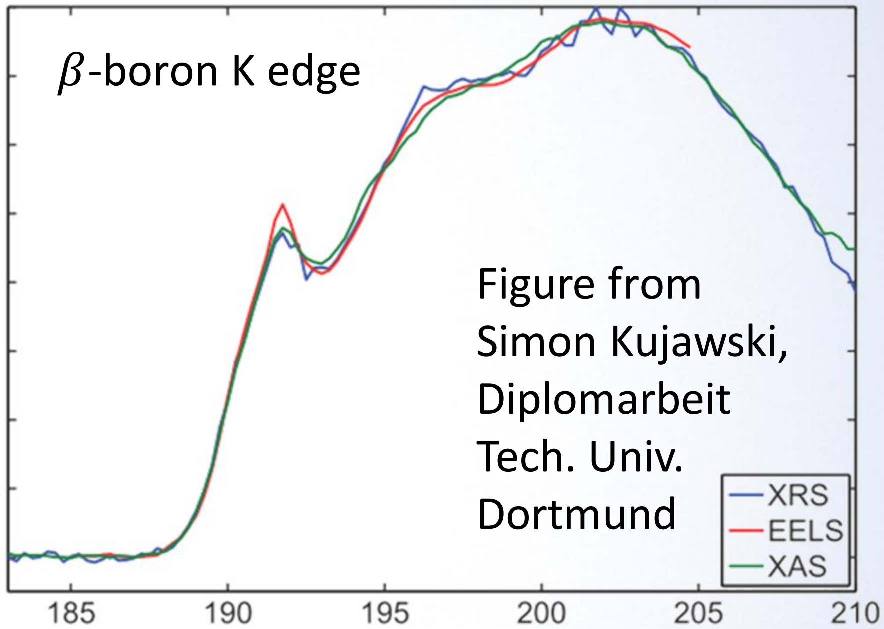
COMPLEMENTARY TECHNIQUES

- Soft x-ray absorption (XAS, XANES, EXAFS)





- Electron scattering (EELS, ELNES)

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WHY IS IT CALLED X-RAY "RAMAN"

Indian J. Phys. **2** 387–398 (1928)

A new radiation*

C V RAMAN, F.R.S.

[Plate 1]

1. Introduction

I propose this evening to speak to you on a new kind of radiation or light-emission from atoms and molecules. To make the significance of the discovery clear, I propose to place before you the history of the investigations made at Calcutta which led up to it. Before doing so, however, a few preliminary remarks regarding radiation from atoms and molecules will not be out of place.

8. Possible X-ray analogies

If a quantum of radiation can be absorbed in part and scattered in part in the optical region of the spectrum, should not similar phenomena also occur in X-ray scattering? The type of scattering discovered by Prof. Compton may possibly be only one of numerous other types of scattering with modified frequencies, some with a line spectrum and some in the nature of continuous radiation. The extreme ultra-violet region of the spectrum may also furnish us with numerous examples of the new type of radiation, which clearly occupies a position intermediate between scattering and fluorescence.

BELOVED CHILD HAS MANY NAMES (FINNISH PROVERB)

(Non-resonant) X-ray Raman scattering (XRS)

Non-resonant inelastic x-ray scattering (NRIXS or NIXS)

Not to be confused with:
- Nuclear resonant inelastic x-ray scattering (NRIXS or NIXS)
- Raman scattering (RS) (i.e., as is done with lasers for vibrational spectroscopy)
- Resonant X-ray Raman scattering (RRS) (older name for resonant x-ray emission spectroscopy, RXES)

We must do something to clear this nomenclature up...

The Finnish brown bear (*Ursus arctos):*
Karhu, otso, mesikämmen, metsän kuningas, kontio, oksi, nalle, ohto, ...

UNIVERSITY OF HELSINKI

REFRESH

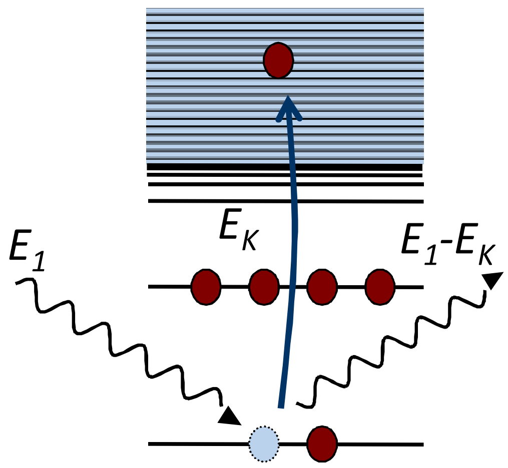
X-ray Raman scattering is inelastic x-ray scattering from core electrons

Powerful technique rapidly growing in popularity with 3rd generation synchrotrons

Use hard x-rays to study soft x-ray edges

⇨ **bulk-sensitive** measurements
easy access to **extreme environments**

Additionally **momentum-transfer** gives access to non dipole transitions



energy transfer E_K
momentum transfer **q**