Spectroscopy from experimentalist's viewpoint

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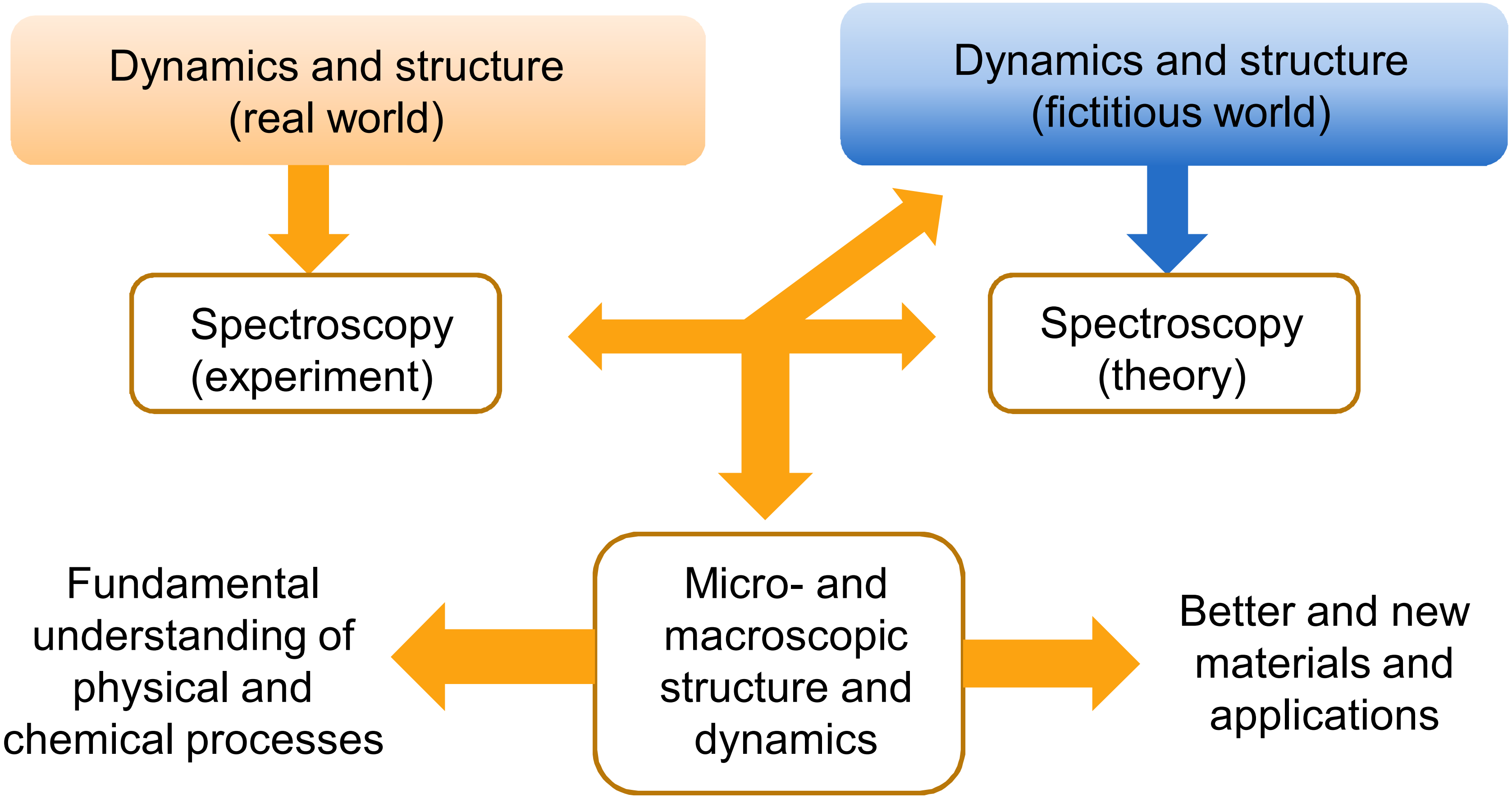
Motivation: why theory



Dynamics and structure
(real world)

Dynamics and structure
(fictitious world)

Spectroscopy
(experiment)

Spectroscopy
(theory)

Fundamental
understanding of
physical and
chemical processes

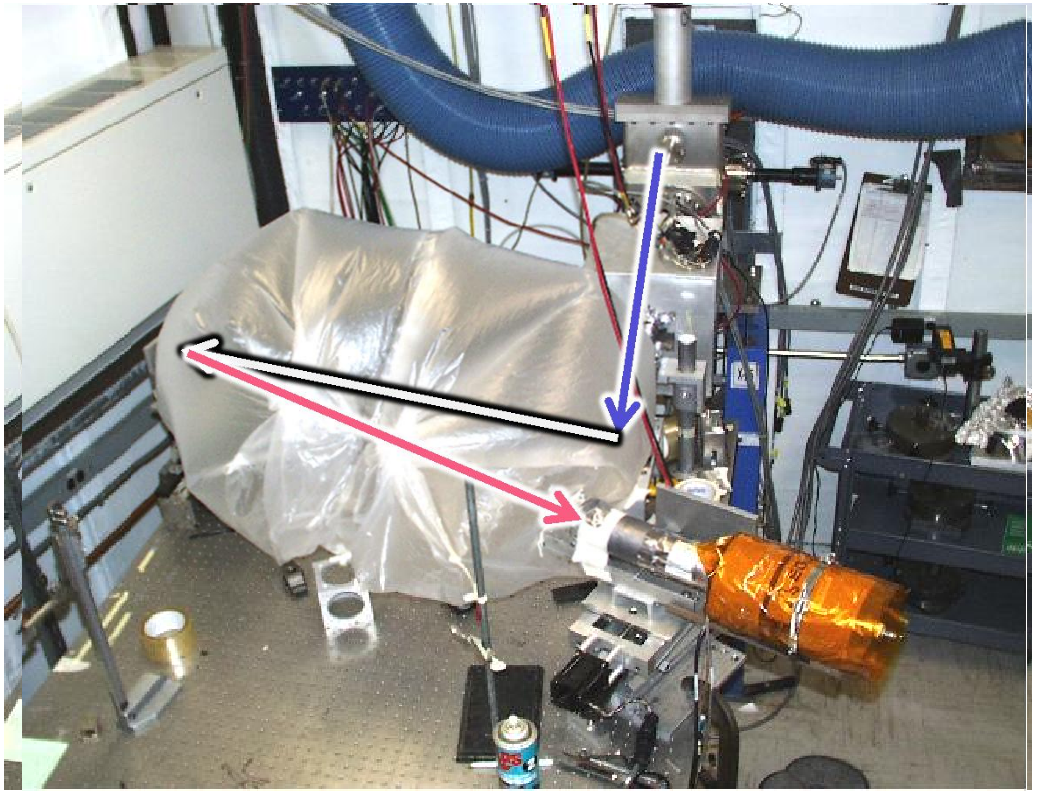
Micro- and
macroscopic
structure and
dynamics

Better and new
materials and
applications

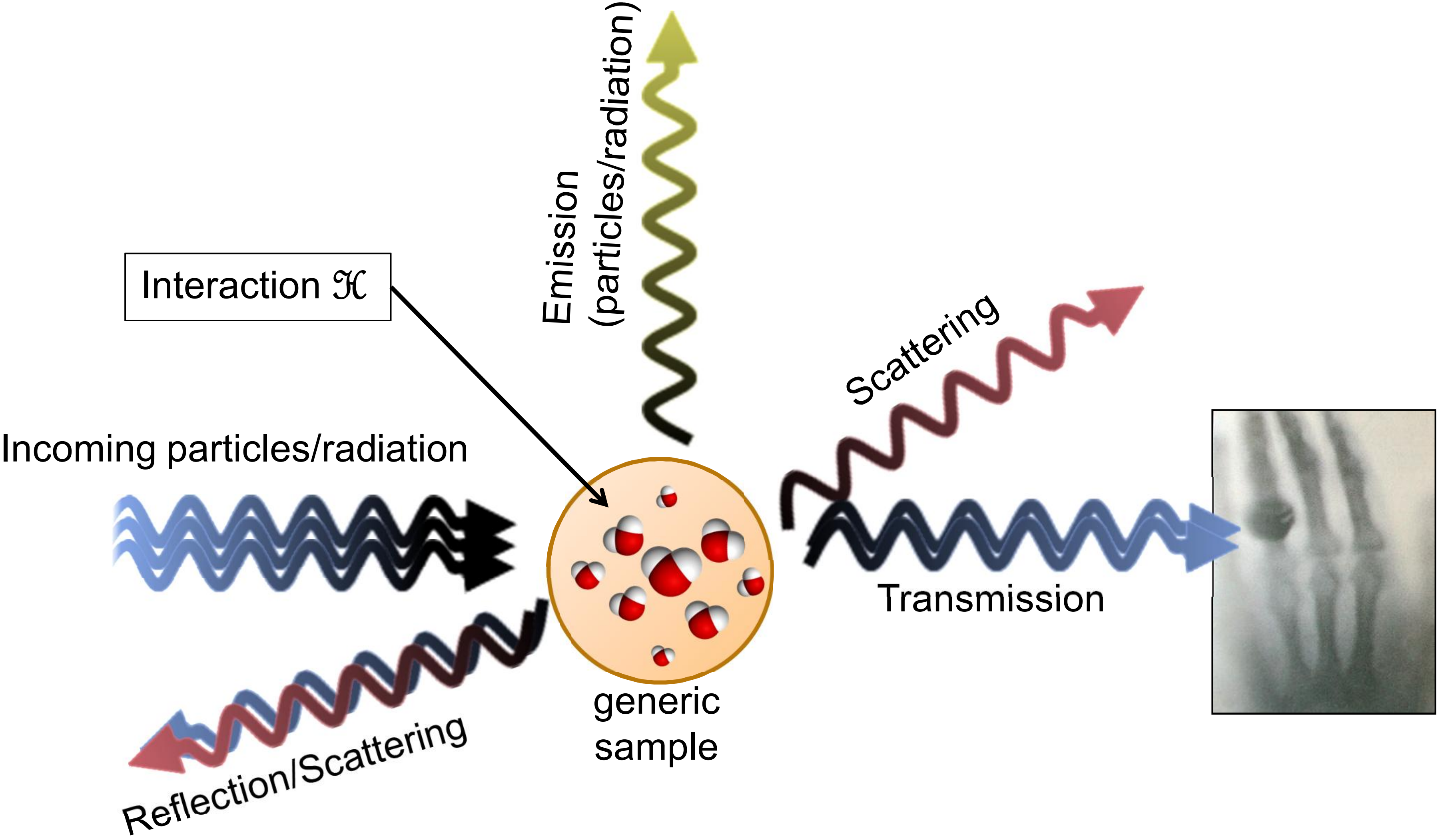
Measurement vs. experiment

Equipment for measurements

Equipment for experiments



Probes and messengers



Properties of particles

Polarization: linear, circular

- photons
- electrons (how?)
- linear and circular dichroism become possible

Probing depth

- surface vs. bulk sensitivity
- e.g., what is surface enhanced Raman scattering, SERS?

Element or site selectivity

- what methods can selectively probe properties of selected atom in a large system?

Access of dynamic ranges

- energy, momentum, time, space
- resolving power / applicable range

(non-exhaustive)

Classification of excitations

	Collective	**”Single particle”**
Vibrational	Sound waves (phonons)	Molecular bending, stretching...
Spin	Magnons, spin waves	Spin flip
Charge	Plasmons, polarons	Excitons, momentum density, electron removal
Orbital	Orbiton	Crystal-field excitation

+ multiples (bimagnons, double plasmons, ...)
+ coupling (important!)

Electron response to electromagnetic field

Macroscopic **dielectric function** $\varepsilon_M(Q,E) = \varepsilon_1(Q,E) + i\,\varepsilon_2(Q,E)$

Complex refractive index $\tilde{n} = \sqrt{\varepsilon} = n + i\kappa$

Reflectivity $R = \frac{(n-1)^2+\kappa^2}{(n+1)^2+\kappa^2}$ — Reflectivity measurements

Absorption coefficient $\alpha = 4\pi\kappa/\lambda$ — UV/Vis absorption, x-ray absorption (XAS), ...

Loss function $-\mathrm{Im}[\varepsilon_M{}^{-1}(\mathbf{Q},E)]$ — Electron energy loss, inelastic x-ray scattering

Dynamic structure factor $S(\mathbf{Q},E) = -\left(\frac{Q^2}{4\pi^2e^2n}\right)\,\mathrm{Im}[\varepsilon_M{}^{-1}(\mathbf{Q},E)]$

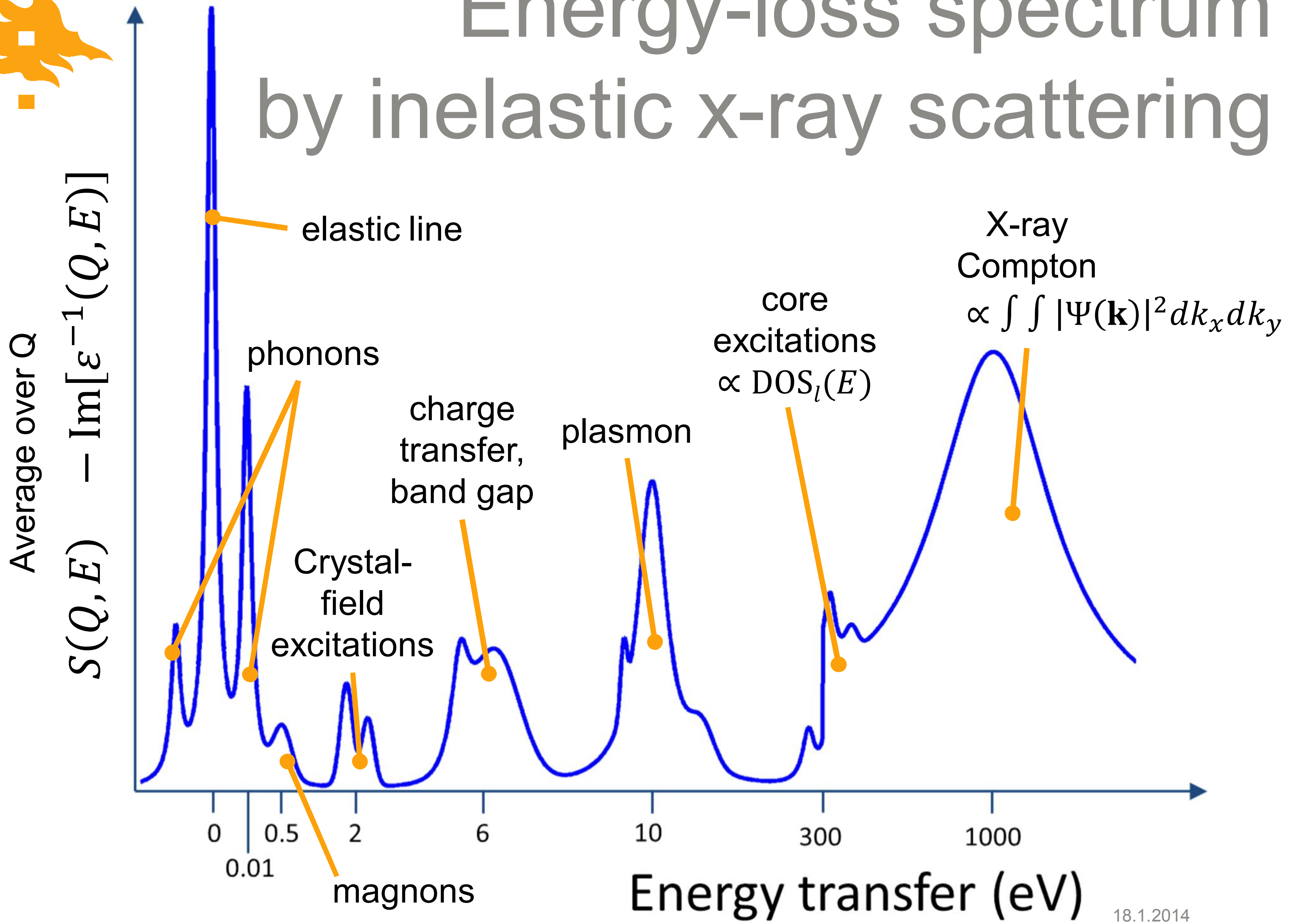
Spectral density function $A(k,\omega)$

Resonant Raman spectra

Dynamic structure factor is also the Fourier transform of the **density correlation function**

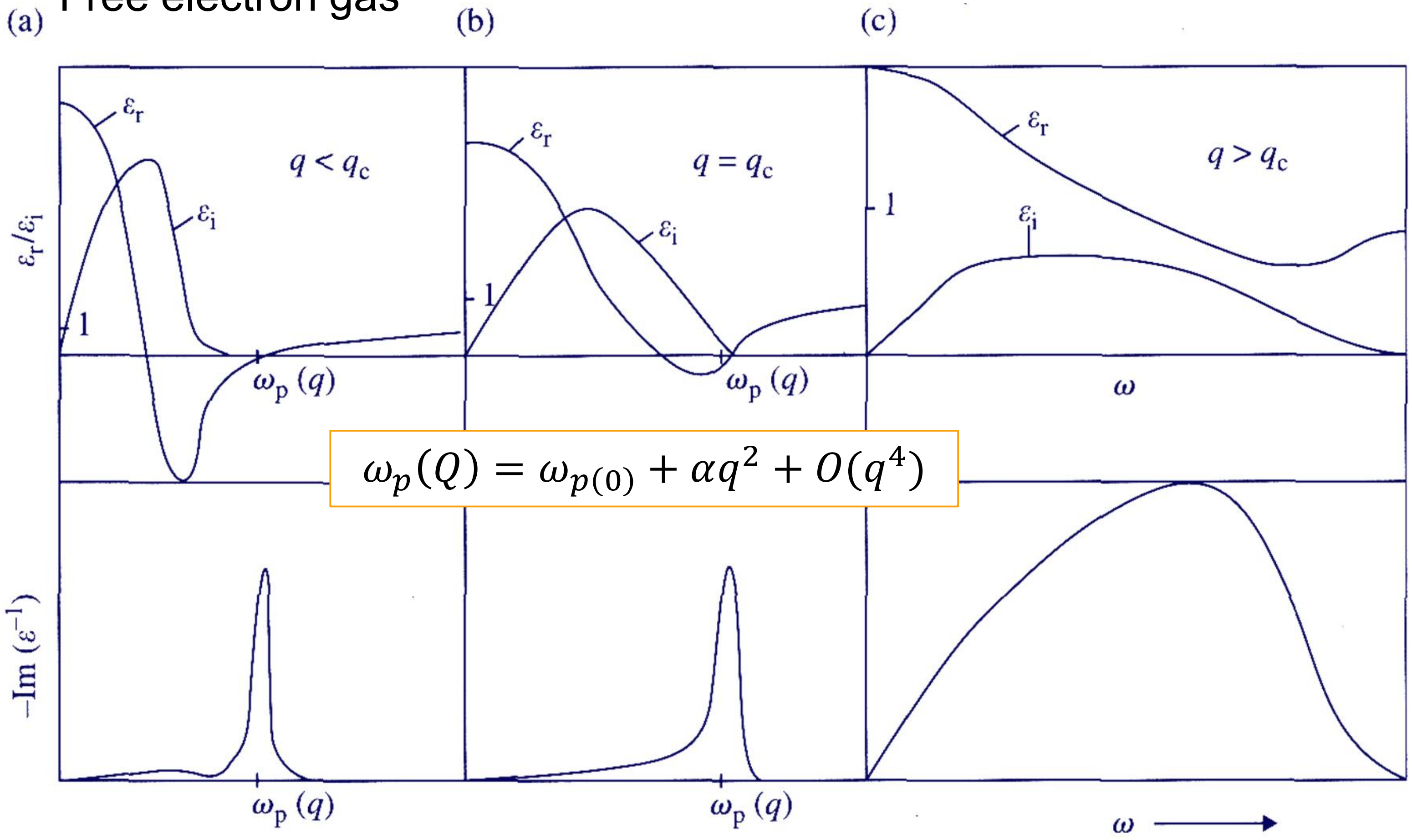
i

Energy-loss spectrum by inelastic x-ray scattering



Plasmons

Dielectric function from the Lindhard polarization function (RPA)
Free electron gas



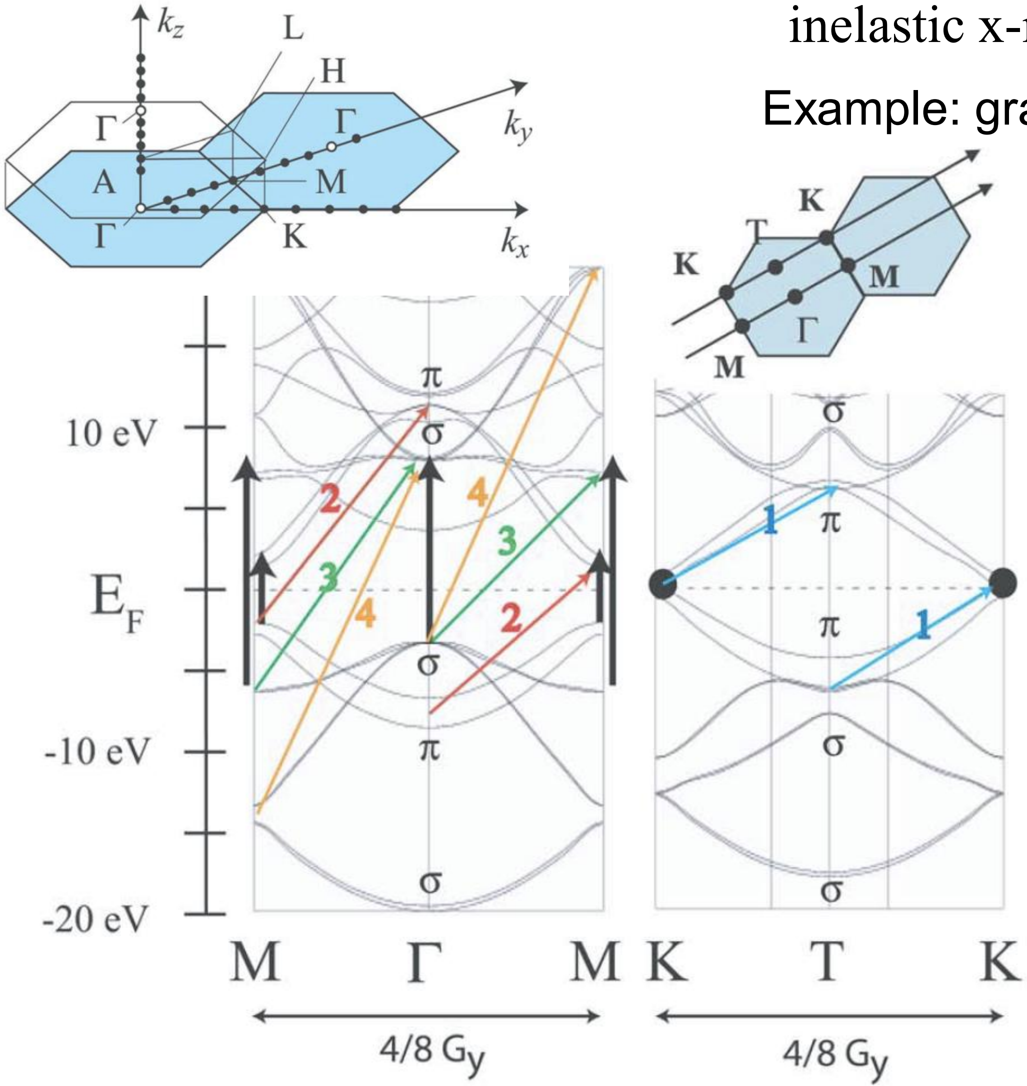
$$\omega_p(Q) = \omega_{p(0)} + \alpha q^2 + O(q^4)$$

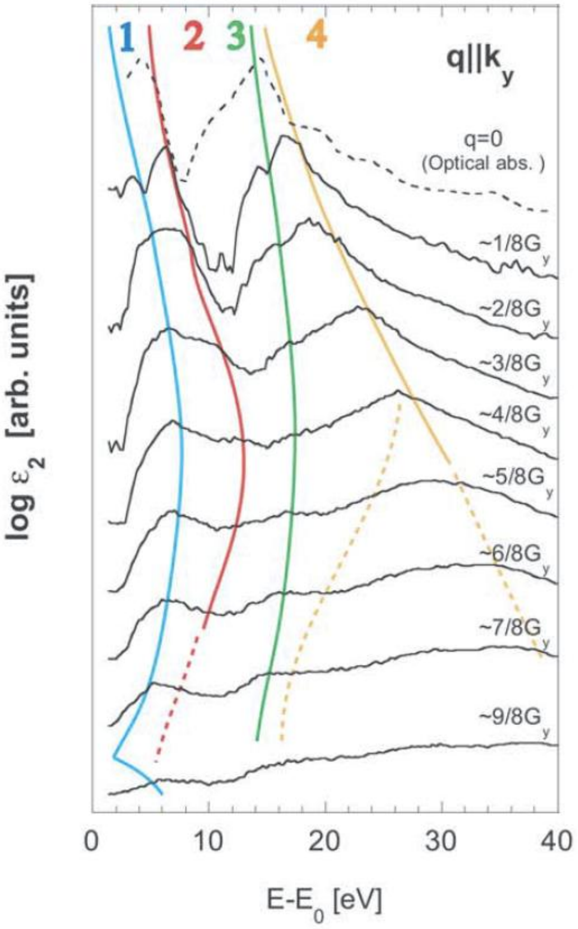
W. Schülke: Electron dynamics by inelastic x-ray scattering (Oxford Univ. Press)

Inter-and intraband excitations

Both ***energy*** and ***momentum*** can be controlled in inelastic x-ray scattering spectroscopy

Example: graphite





N. Hiraoka et al., PRB 72, 075103 (2005)

Outgoing particle

Incoming particle

	Nothing	Photon	Electron
Nothing	Skiing at the Pyrenees	Light emission, photoluminescence	Electron emission
Photon	Absorption (IR, UV/vis, vacuum UV, x-ray..) CD; XMCD	Ellipsometry, reflectometry, Raman, Brillouin, x-ray scattering, Compton scattering	Photoemission Auger spectroscopy
Electron	Electron absorption	Inverse photoemission Cathodoluminescence	Electron energy loss Tunneling

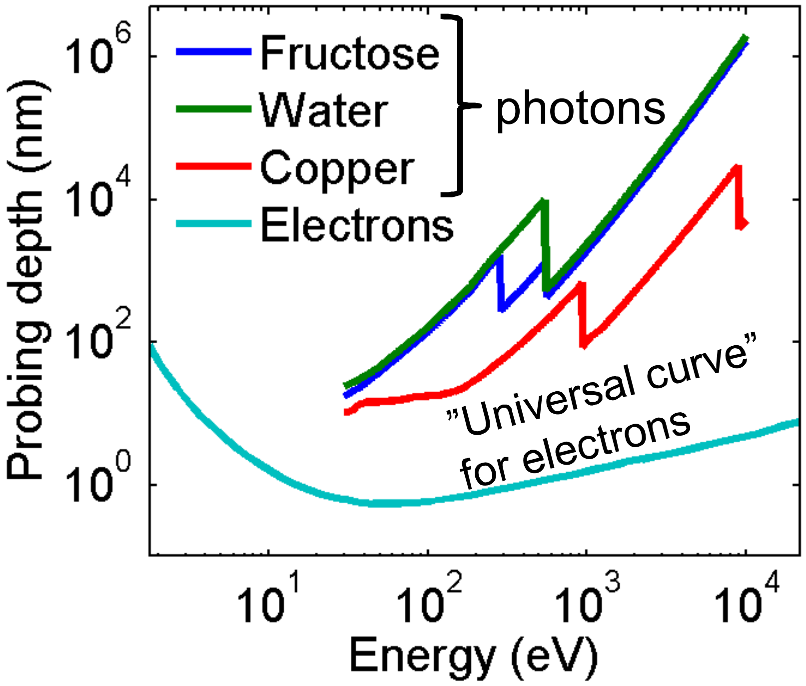
+ Time-of-flights
+ Non-linear phenomena

Differences in:
- Dynamic range of Q and E, coupling to spin, nuclei, …
- Bulk or surface sensitivity
- Resolving power in energy, momentum, time, space…
- Element specifity (useful for complicated systems)

Particle probing depth

Large probability for interaction ⇒ higher surface sensitivity

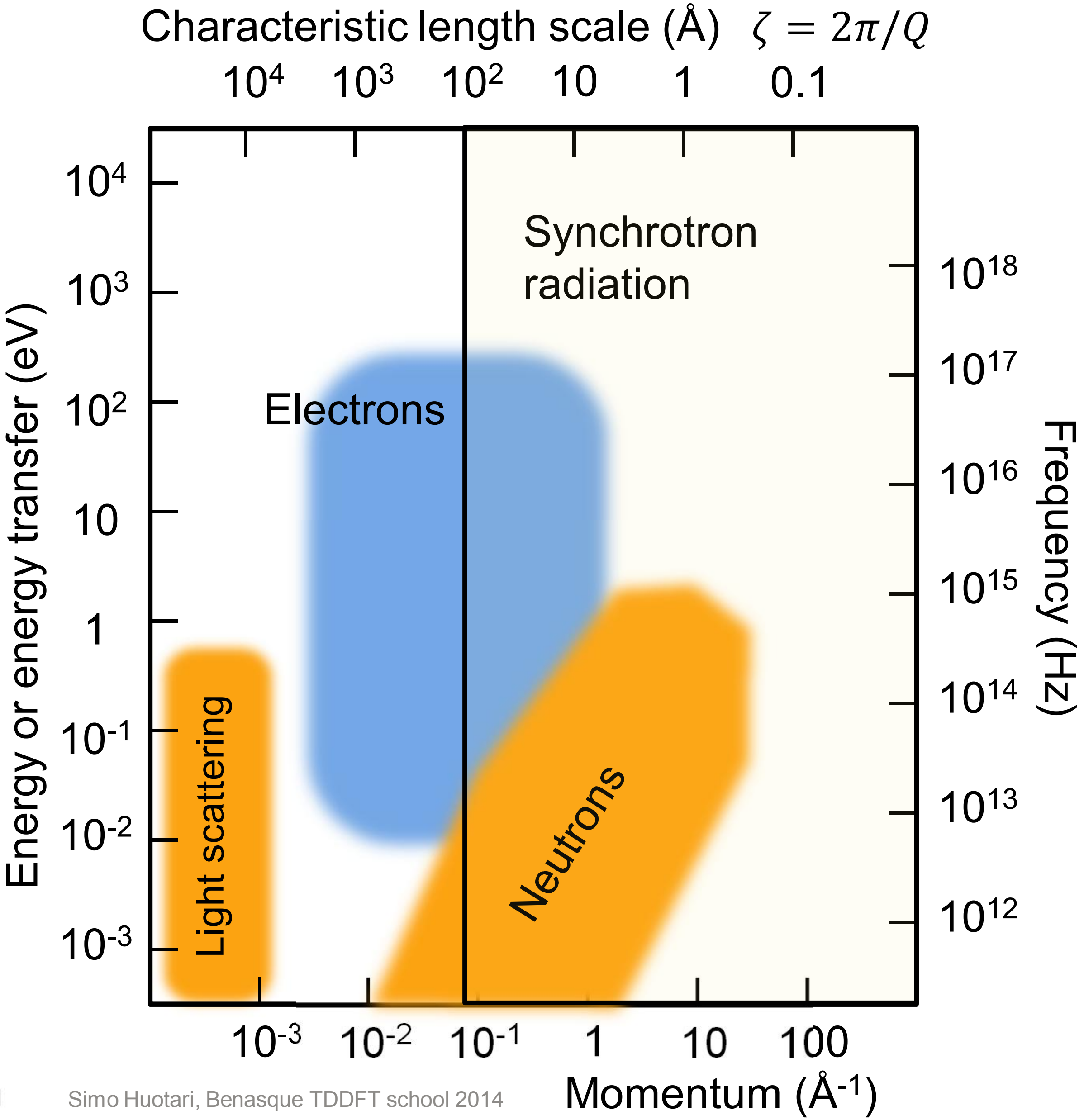
Dependence on atomic number ⇒ elemental sensitivity



Question: why it is useful to do transmission microscopy of organic matter using photon energies of 400 eV?

Advanced question:
Which of the techniques are sensitive to bulk and which are sensitive to surface?

Dynamic ranges for scattering

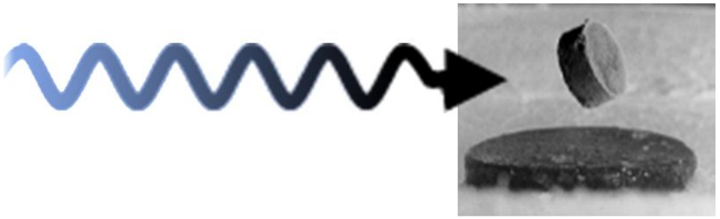


Spectroscopy - interaction

Photon-electron
$$H = \frac{e^2}{2mc^2}\mathbf{A}^2 + \frac{e}{mc}\mathbf{A}\cdot\mathbf{p}$$

Scattering

Absorption and emission in first order, resonant scattering in second order



Electron-electron
$$V = e^2/|\mathbf{r} - \mathbf{r}_i|$$

Transition rate from state |A> to state |B> is given by the Fermi's Golden Rule:

$$W_{BA} = \frac{2\pi}{\hbar}\left|\langle B|H|A\rangle + \sum_I \frac{\langle B|H|I\rangle\langle I|H|A\rangle}{E_A - E_I + i\Gamma/2}\right|^2 \delta(E_B - E_A) + O(H^3)$$

Kramers-Heisenberg formula

From $\mathbf{A}\cdot\mathbf{A}$ - Non-resonant scattering (Raman, inelastic x-ray, ...)

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}\omega_2} = r_0^2\left(\frac{\omega_2}{\omega_1}\right)\Bigg|\boxed{<\Psi_f|e^{i\mathbf{Q}\cdot\mathbf{r}}|\Psi_i>(\boldsymbol{\epsilon}_1\cdot\boldsymbol{\epsilon}_2)}$$
$$+\frac{1}{m}\sum_n\Bigg[\boxed{\frac{\langle\Psi_f\mid\boldsymbol{\epsilon}_2\cdot\mathbf{p}\;e^{-i\mathbf{k}_2\cdot\mathbf{r}}\mid\Psi_n\rangle\langle\Psi_n\mid\boldsymbol{\epsilon}_1\cdot\mathbf{p}\;e^{i\mathbf{k}_1\cdot\mathbf{r}}\mid\Psi_i\rangle}{E_i-E_n+\omega_1+i\Gamma_n}}$$
$$+\frac{\langle\Psi_f\mid\boldsymbol{\epsilon}_1\cdot\mathbf{p}\;e^{i\mathbf{k}_1\cdot\mathbf{r}}\mid\Psi_n\rangle\langle\Psi_n\mid\boldsymbol{\epsilon}_2\cdot\mathbf{p}\;e^{-i\mathbf{k}_2\cdot\mathbf{r}}\mid\Psi_i\rangle}{E_i-E_n-\omega_2}\Bigg]\Bigg|^2\delta(E_i-E_f+\omega)$$

From $\mathbf{p}\cdot\mathbf{A}$ - Resonant scattering (Resonant Raman, resonant inelastic x-ray scattering)

Dynamic structure factor

Average density-density correlation function

$$G(\mathbf{r},t)=\frac{1}{N}\int\langle\rho(\mathbf{r}'-\mathbf{r},t)\rho(\mathbf{r}',0)\rangle d\mathbf{r}'$$

Dynamic structure factor

$$S(\mathbf{Q},E)=\int\int G(\mathbf{r},t)e^{i\mathbf{Q}\cdot r}e^{-iEt}$$

Small *Q*
interference effects are important
(collective excitations)

Large *Q*
independent particle excitations

Absorption and scattering

Absorption $$P(\omega) \propto \sum_f \left|\langle \Psi_f | \mathbf{p} \cdot \mathbf{A} | \Psi_i \rangle\right|^2 \delta\left(E_i - E_f + \omega\right)$$ **Dipole rule**

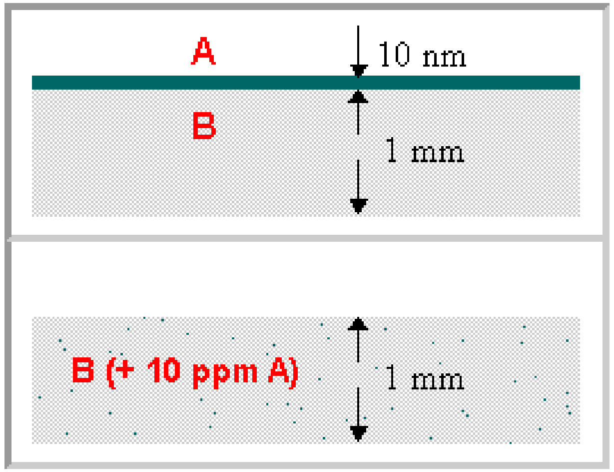
Scattering $$S(\mathbf{Q}, \omega) \propto \sum_f \left|\langle \Psi_f | \, e^{i\,\mathbf{Q}\cdot\mathbf{r}} | \Psi_i \rangle\right|^2 \delta\left(E_i - E_f + \omega\right)$$

What happens with the momentum transfer dependence of the scattering matrix element?

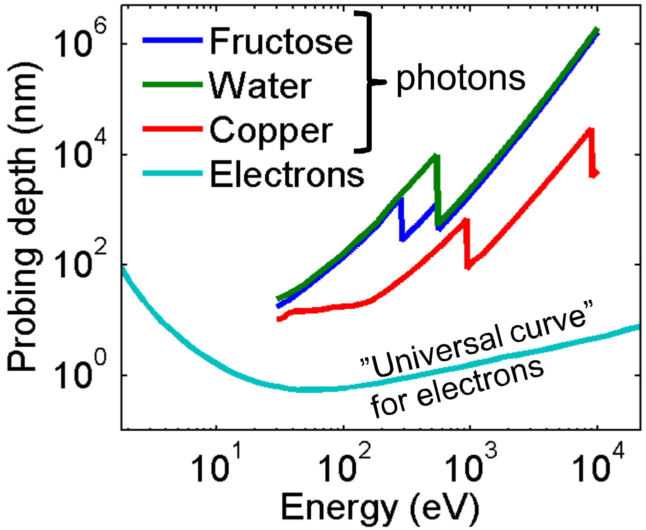
$$e^{i\mathbf{Q}\cdot\mathbf{r}} = 1 + \underbrace{i\mathbf{Q}\cdot\mathbf{r}}_{\text{dipole}} - \underbrace{(\mathbf{Q}\cdot\mathbf{r})^2/2 + \cdots}_{\text{higher order multipoles}}$$

dipole **higher order multipoles**

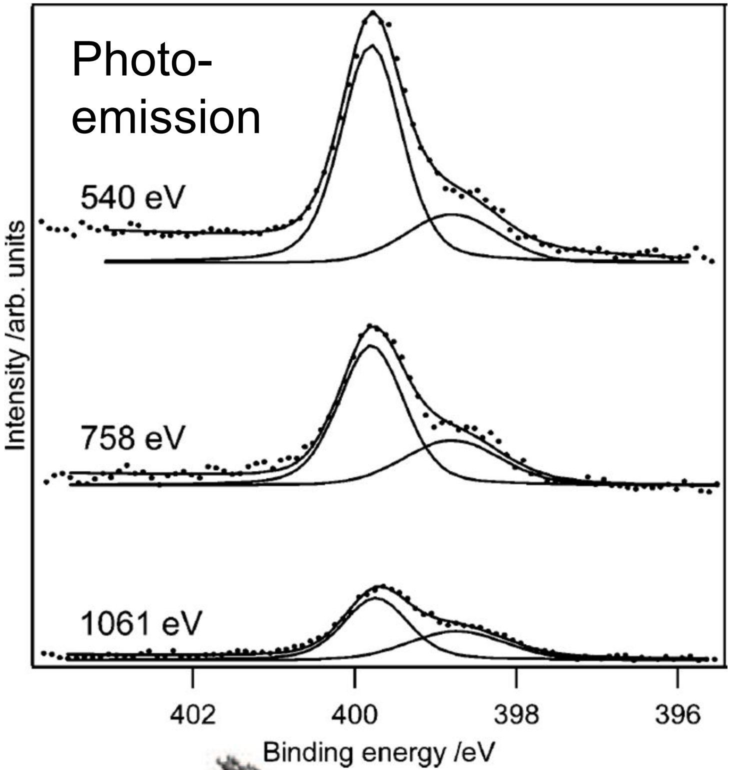
Surface sensitivity: molecular orientation

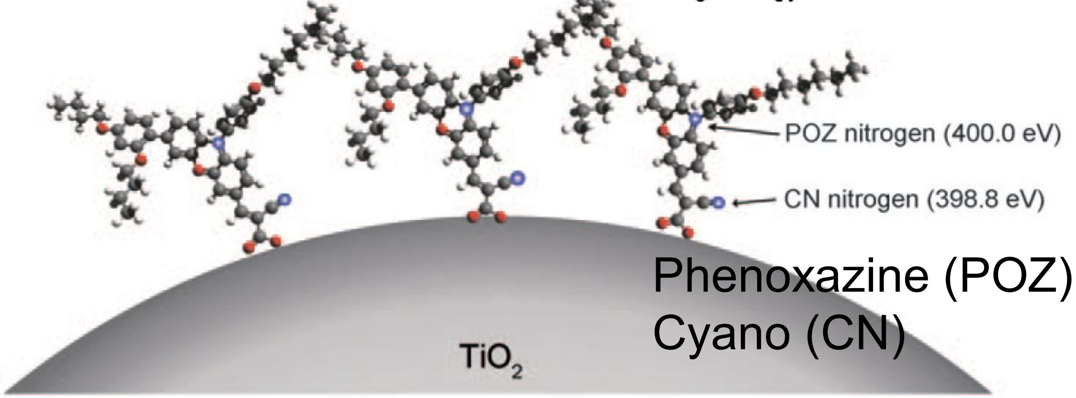


http://www.chem.qmul.ac.uk/surfaces/scc/scat5_1.htm



E.M.J. Johansson et al.
J. Phys. Chem. C 111, 8580 (2007)





Phenoxazine (POZ)
Cyano (CN)

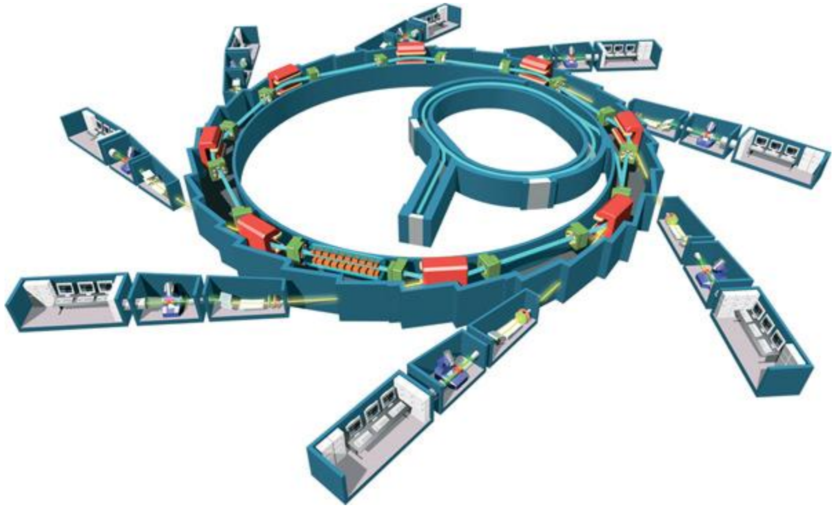
K.M.Karlsson et al. Chem. Eur. J. 17, 6415 (2011)

Modern 3rd generation synchrotrons

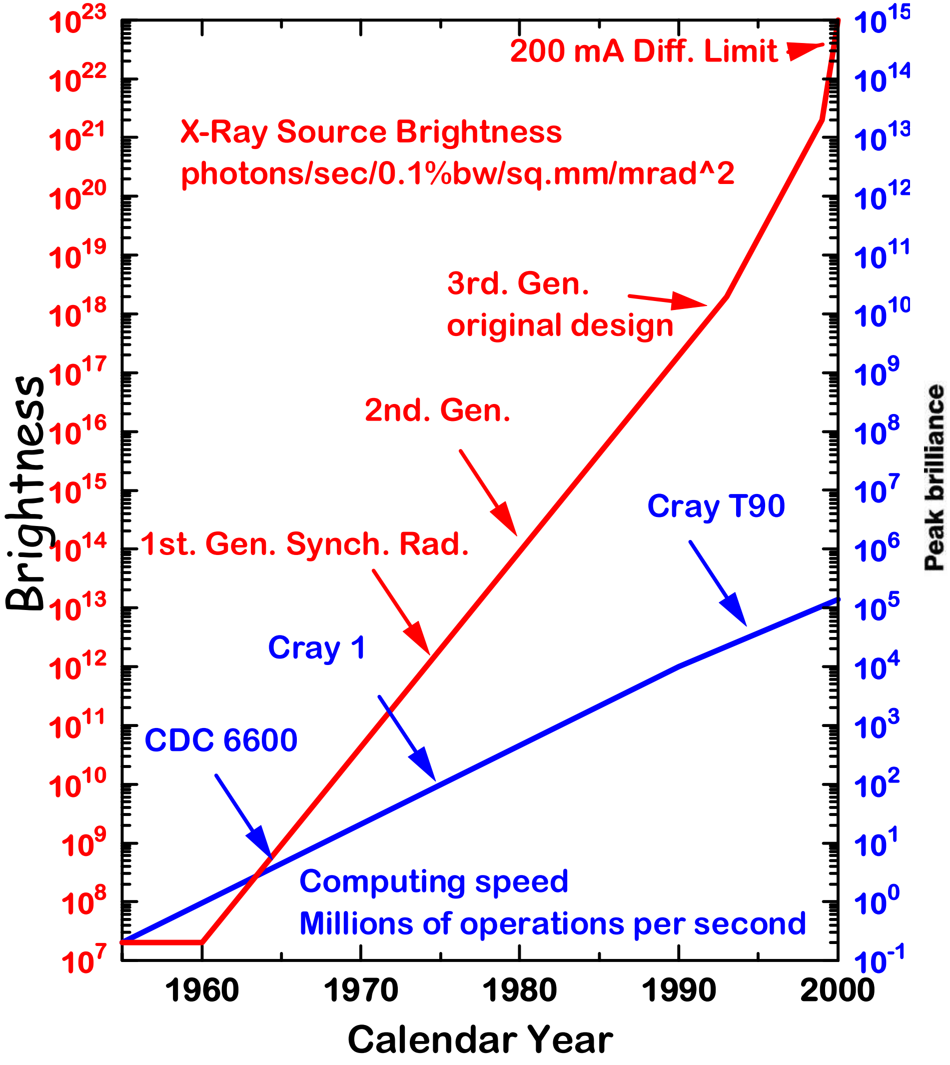
Advanced Photon Source, USA

Super Photon Ring 8 (Spring-8), Japan

European Synchrotron Radiation Facility, France



Moore’s law


200 mA Diff. Limit
X-Ray Source Brightness
photons/sec/0.1%bw/sq.mm/mrad^2
3rd. Gen.
original design
2nd. Gen.
1st. Gen. Synch. Rad.
Cray T90
Cray 1
CDC 6600
Computing speed
Millions of operations per second
Brightness
Peak brilliance
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1980
1990
2000
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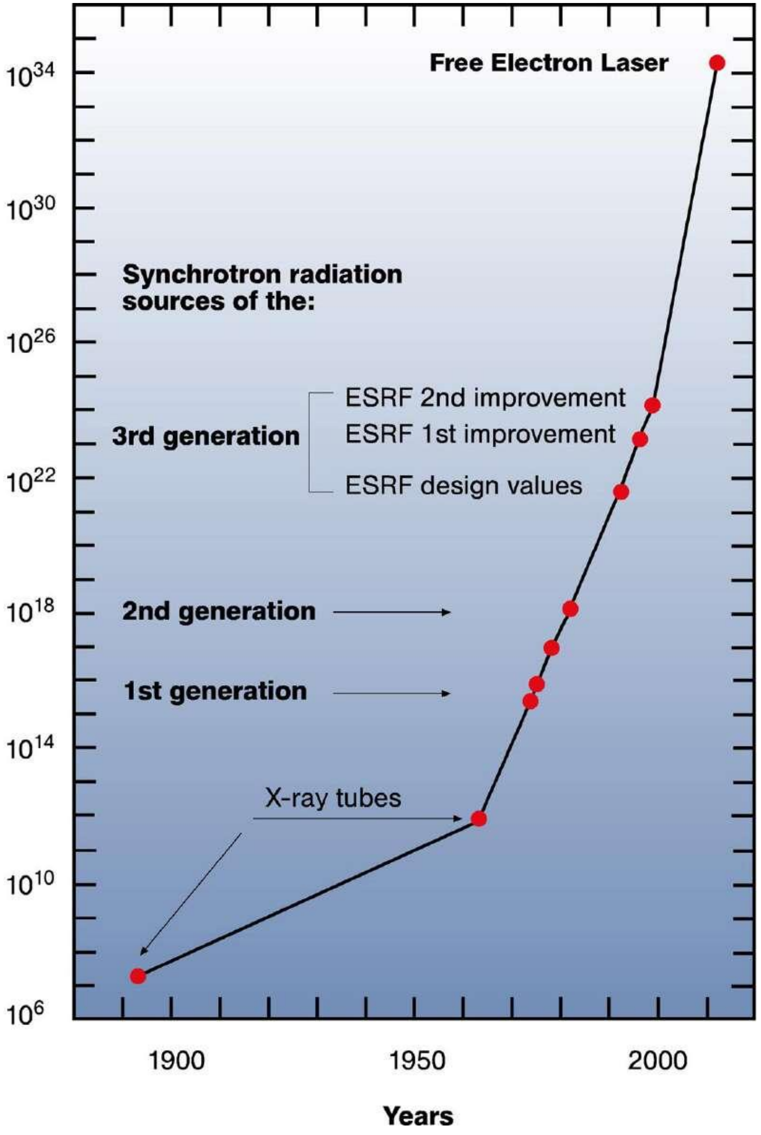
Free Electron Laser
Synchrotron radiation
sources of the:
3rd generation
ESRF 2nd improvement
ESRF 1st improvement
ESRF design values
2nd generation
1st generation
X-ray tubes
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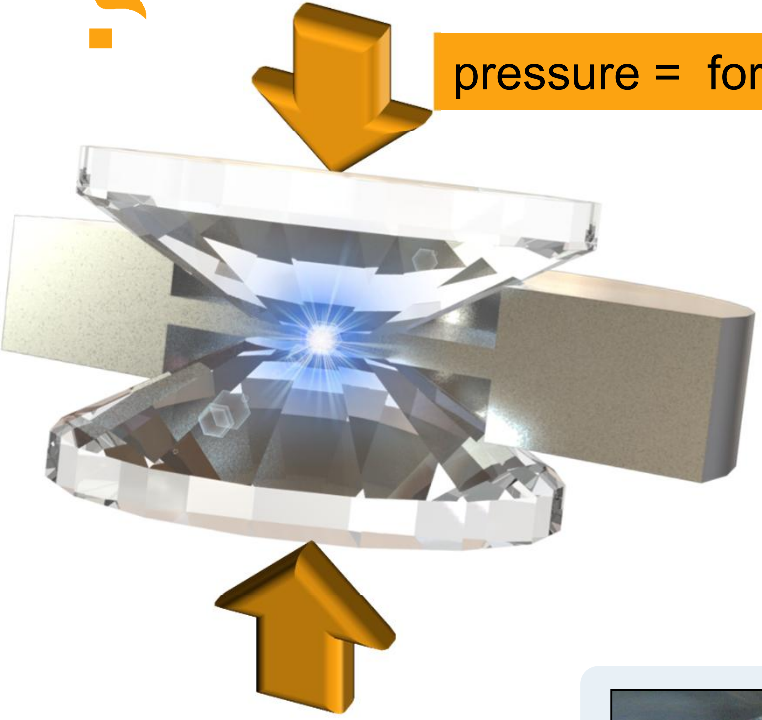
10^{30}
10^{26}
10^{22}
10^{18}
10^{14}
10^{10}
10^{6}
1900
1950
2000
Years

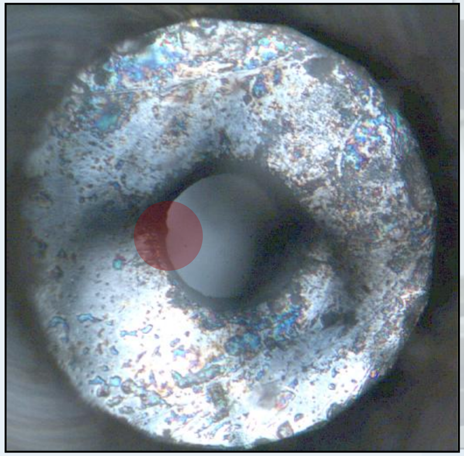
Extremely high pressures

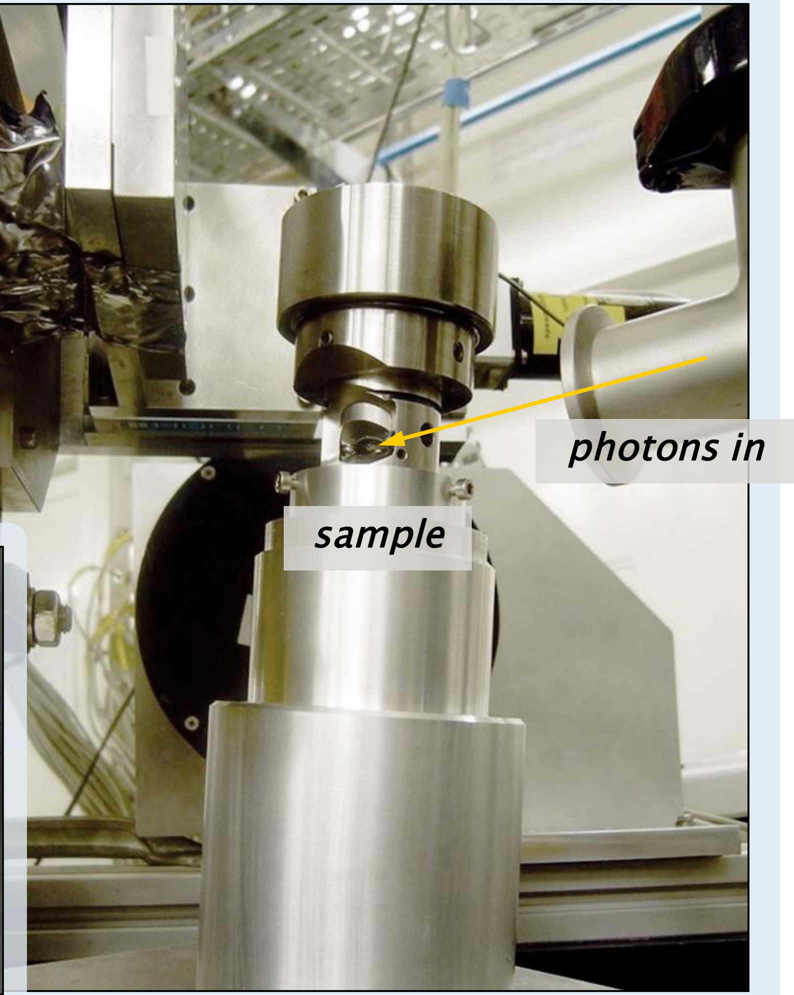


Experimental details

- 1 mm diamond tip (culet)
- ∅ 5 mm Be gasket
- ∅ 350 micron sample size
- X-ray beam 100 × 50 µm^2
- Ruby chip for *P* calibration

V.M.Giordano, T. Pylkkänen et al. ESRF ID16



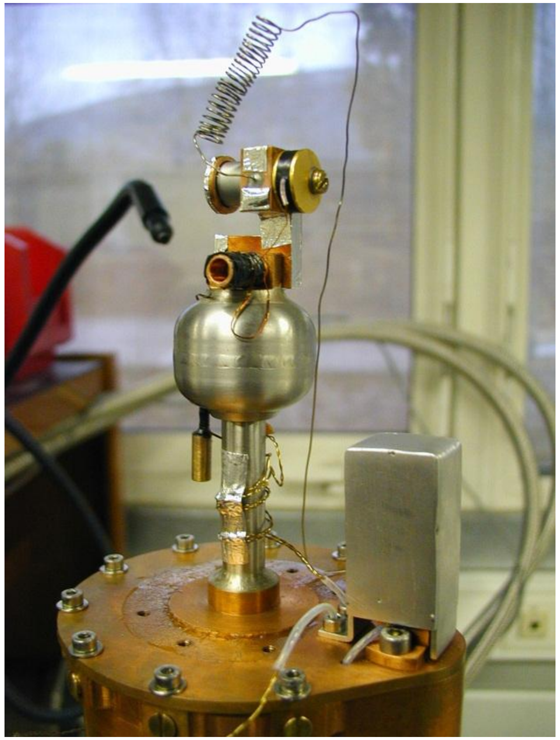


Low temperatures

Liquid nitrogen cryo-jet (77 K)

Liquid He Cryostat (4 K)

He sorption pump (1 K)

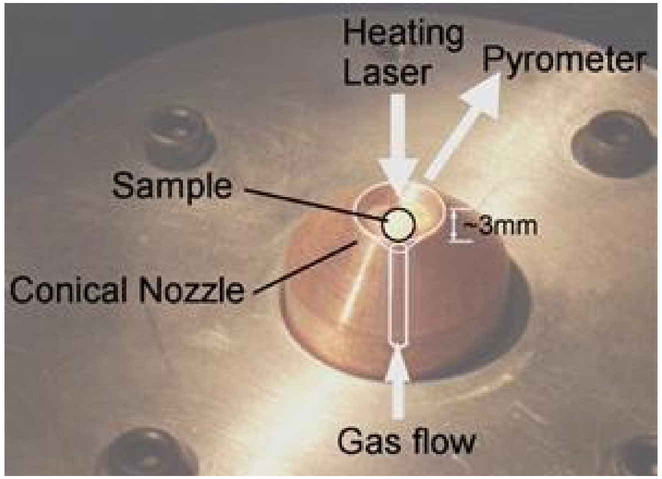


F. Albergamo et al., ESRF

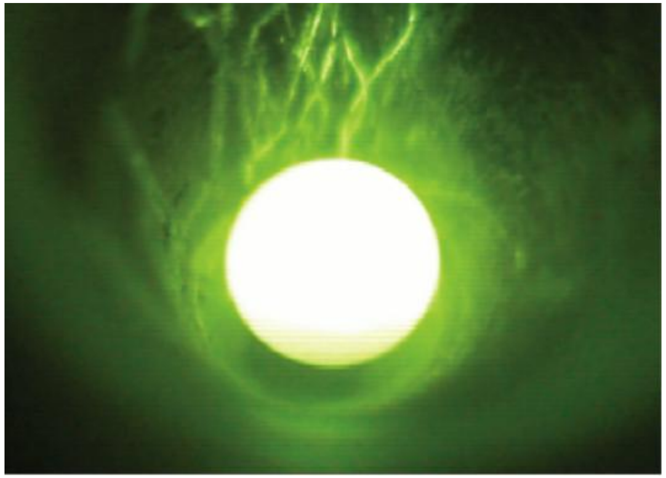
Extremely high temperatures (thousands of deg): Laser heating and aerodynamic levitation

High temperatures (up to 1000 deg C): furnaces, hot air guns

ESRF, Sample group



Wikipedia: Aerodynamic levitation



Droplet of liquid basalt BCR-2 during levitation. The sample was heated from the top using a CO_2-laser. The diameter of the sphere was ~2 mm. A. Pack et al., Geochemical transactions 2010, 11:4