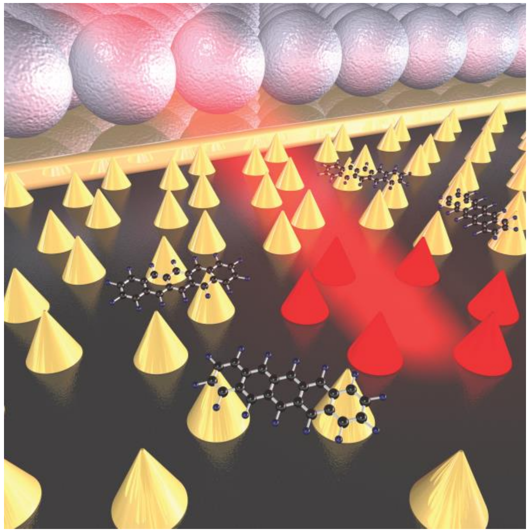
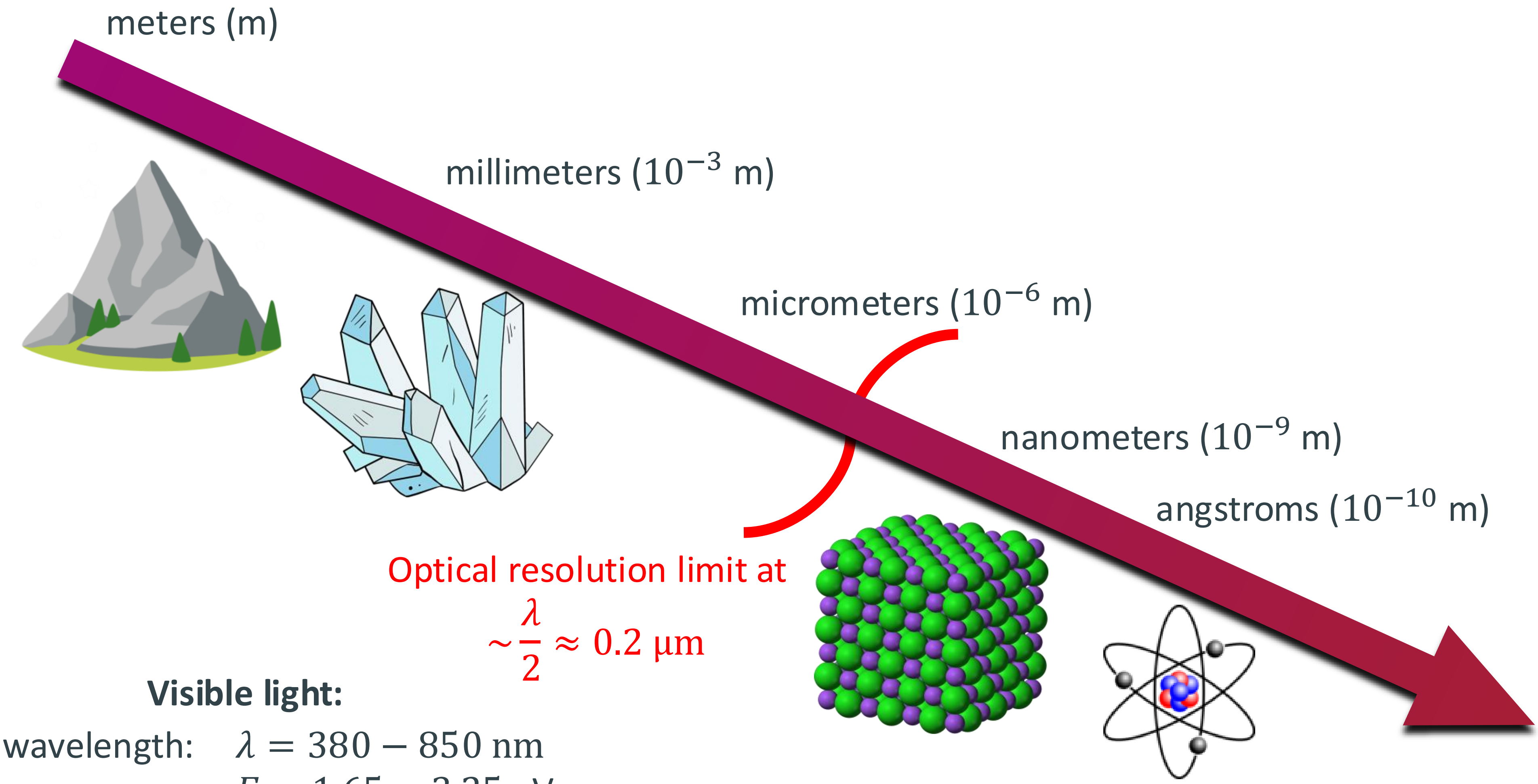
Basic module
Physics of Nanostructures

Summer term 2025



J. Meyer, D. Kölle, I. Zaluzhnyy,
Exercices: R. Löffler

How to see nanoobjects



meters (m)

millimeters (10^{-3} m)

micrometers (10^{-6} m)

nanometers (10^{-9} m)

angstroms (10^{-10} m)

Optical resolution limit at

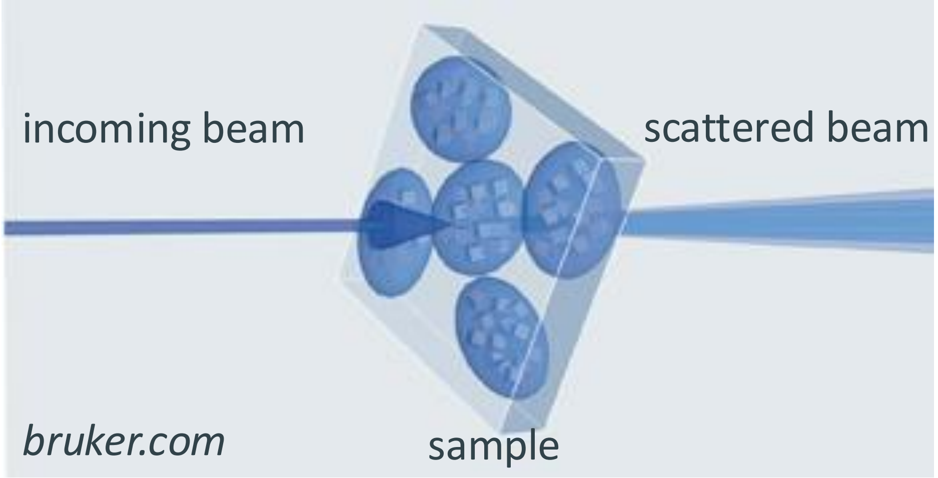
$\sim \frac{\lambda}{2} \approx 0.2\ \mu\mathrm{m}$

Visible light:

wavelength: $\lambda = 380 - 850\ \mathrm{nm}$

energy: $E = 1.65 - 3.25\ \mathrm{eV}$

Concept of scattering techniques



bruker.com

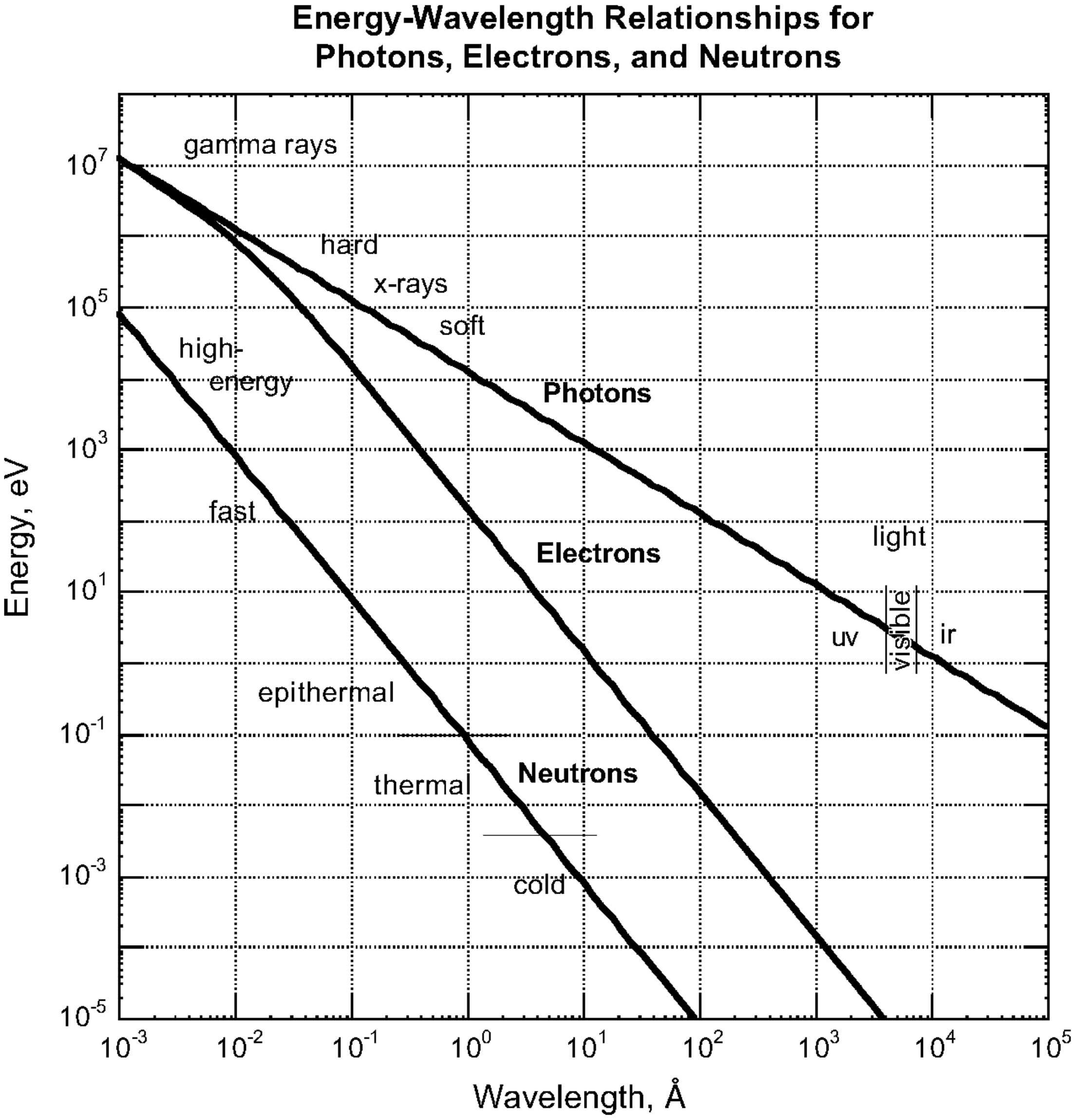
Advantages:

- non-invasive
- statistically significant
- detailed structural information on nanoscale
- applicable *in situ* and in real time
- direct analysis possible (predominantly for single-scattering scenarios)

Examples of structural "inhomogeneities" that can be studied by scattering:

- atomic lattices
- structural domains, nanoparticles, agglomerates, superlattices, etc.
- interfaces and surfaces

Scattering of X-rays, Electrons and Neutrons



Photons (X-rays):

$$E = \frac{2\pi\hbar c}{\lambda} \qquad E[eV] = \frac{12398}{\lambda[\text{Å}]}$$

Neutrons:

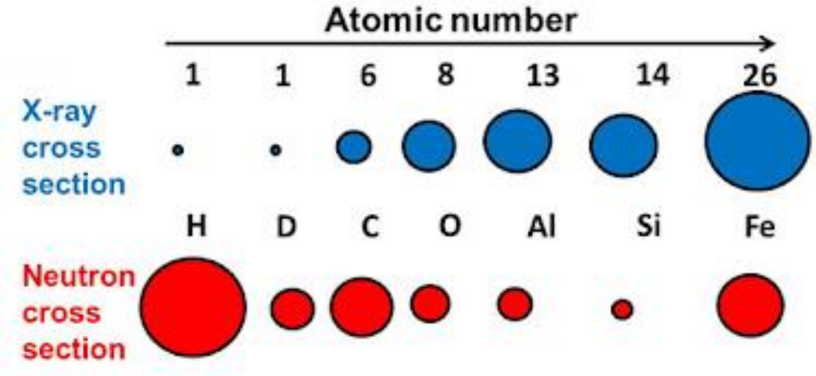
$$E = \frac{2\pi^2\hbar^2}{m_n\lambda^2} \qquad E[eV] = \frac{81.8204}{\lambda^2[\text{Å}^2]}$$

Electrons (non-relativistic):

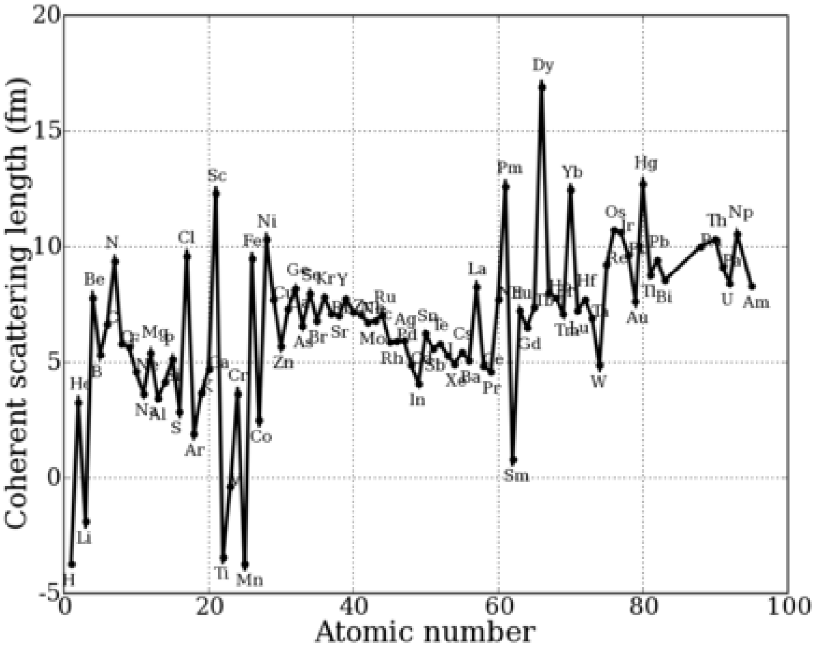
$$E = \frac{2\pi^2\hbar^2}{m_e\lambda^2} \qquad E[eV] = \frac{150.442}{\lambda^2[\text{Å}^2]}$$

Carpenter & Loong, Elements of slow-neutron scattering (2015)

Scattering of X-rays and Neutrons

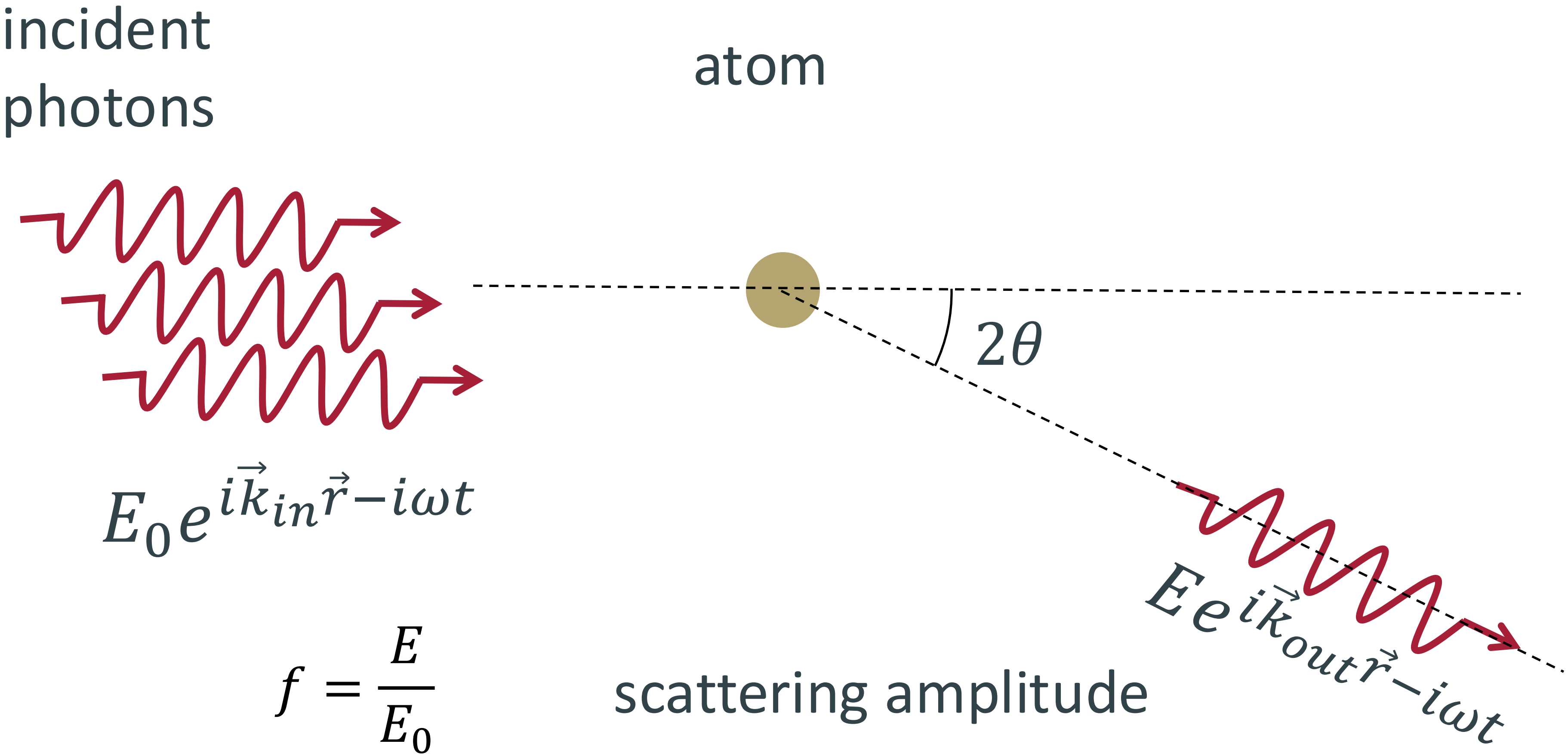


http://worldsciencereport.blogspot.com/



https://www.ncnr.nist.gov/resources/n-lengths/

Scattering by a single atom



incident photons

atom

2θ

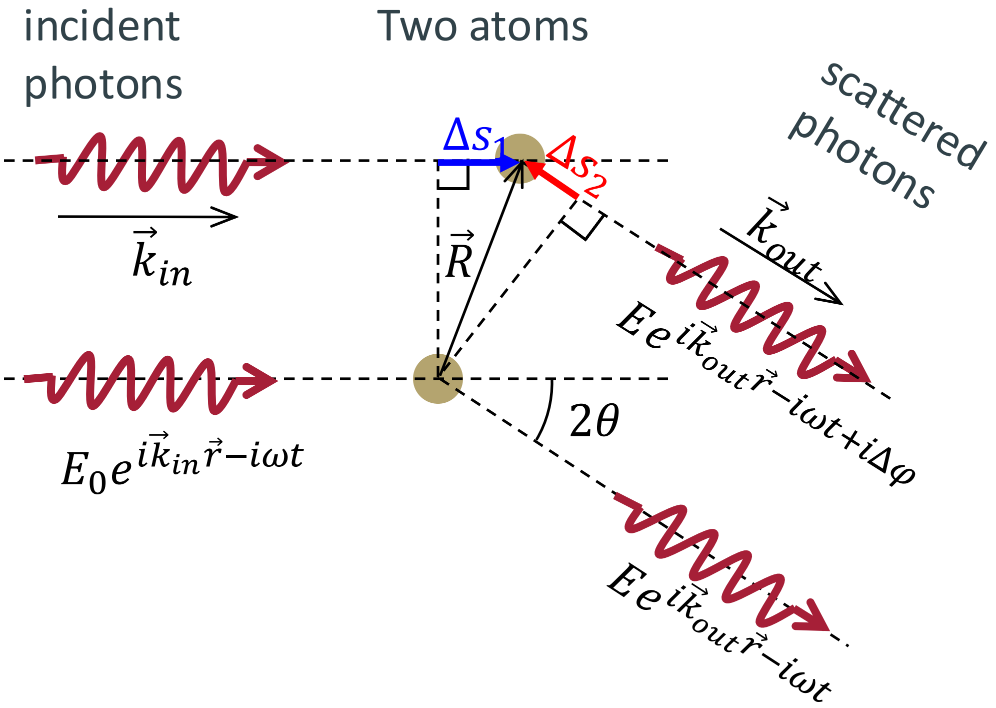
$E_0 e^{i\vec{k}_{in}\vec{r}-i\omega t}$

$E e^{i\vec{k}_{out}\vec{r}-i\omega t}$

$$f = \frac{E}{E_0}$$ scattering amplitude

$$\frac{\partial\sigma}{\partial\Omega} = |f(\Omega)|^2$$ differential cross section

Scattering by two atoms



Phase difference between the waves scattered by two electrons

$$\Delta\varphi = k\Delta s = \frac{2\pi}{\lambda}(\Delta s_1 + \Delta s_2)$$

$$= k_{in}\Delta s_1 + k_{out}\Delta s_2$$

$$= \vec{k}_{in}\vec{R} - \vec{k}_{out}\vec{R} = -(\vec{k}_{out} - \vec{k}_{in})\vec{R}$$

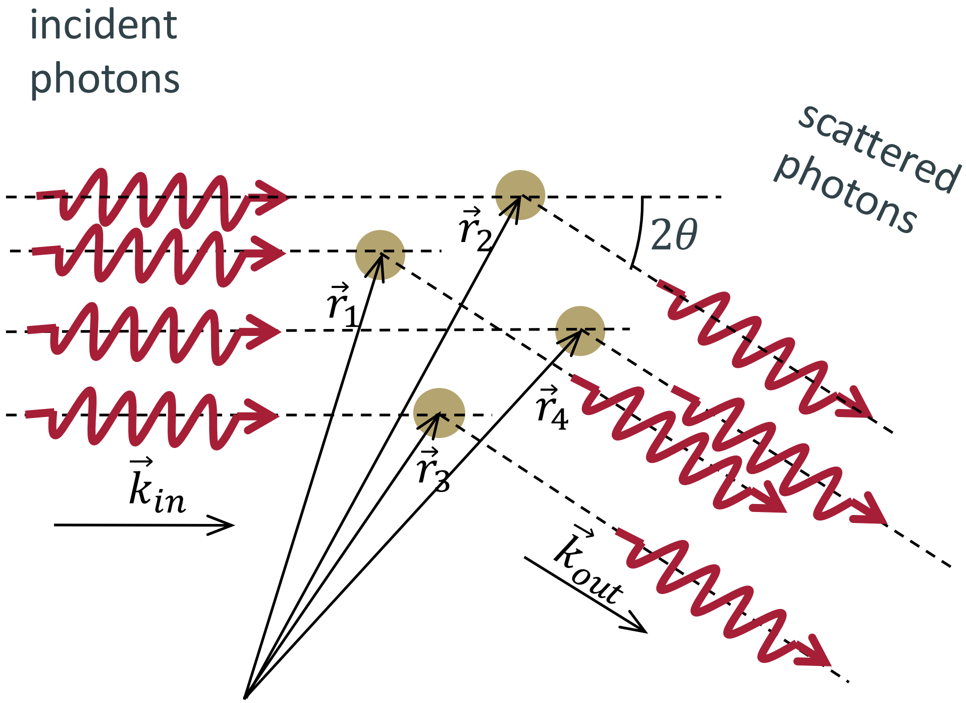
$$= -\vec{q}\vec{R}$$

Resulting scattered field at point $\vec{r}$

$$E \propto E_0\, e^{i\vec{k}_{out}\vec{r}-i\omega t} + E_0\, e^{i\vec{k}_{out}\vec{r}-i\omega t-i\vec{q}\vec{R}}$$

$$\propto E_0\left(1 + e^{-i\vec{q}\vec{R}}\right)$$

Scattering by many atoms



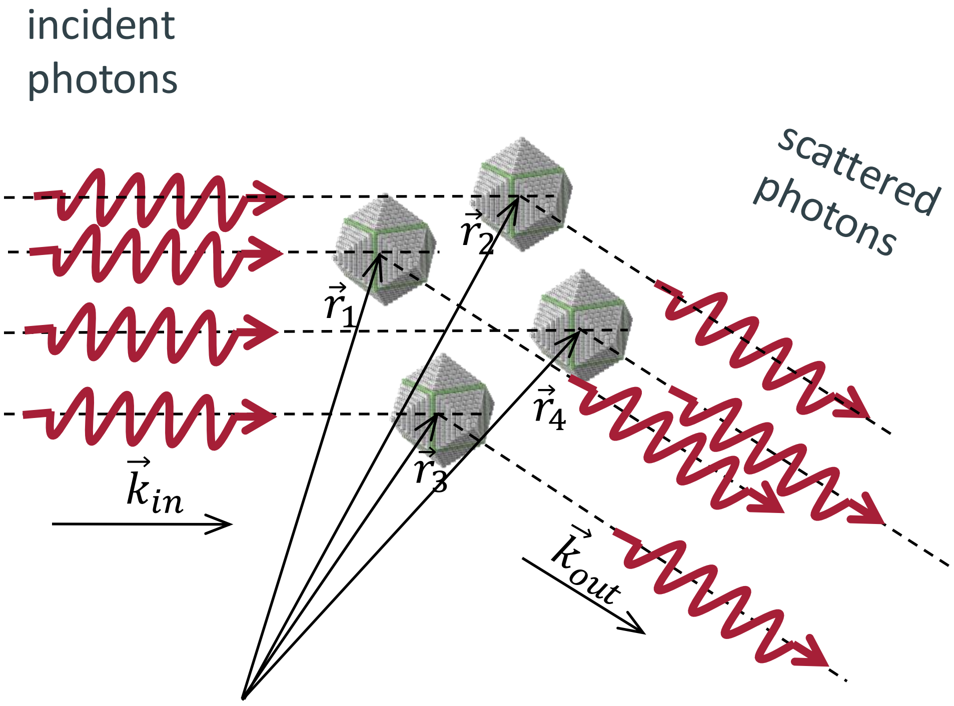
$$\vec{q} = \vec{k}_{out} - \vec{k}_{in}$$

Resulting scattered field:

$$E \propto \sum_{n=1}^{N} E_0 f_n(q) e^{i\vec{k}_{out}\vec{r} - i\omega t - i\vec{q}\vec{r}_n} \propto E_0 \underbrace{\sum_{n=1}^{N} f_n(q) e^{-i\vec{q}\vec{r}_n}}$$

Interference between photons scattered from different atoms

Scattering by nanoparticles



$$\vec{q} = \vec{k}_{out} - \vec{k}_{in}$$

Resulting scattered field:

Interference between photons scattered from different atoms

- Many nanoparticles

$$E \propto E_0 \sum_{n=1}^{N} \underbrace{f_n(q)} \overbrace{e^{-i\vec{q}\vec{r}_n}}$$

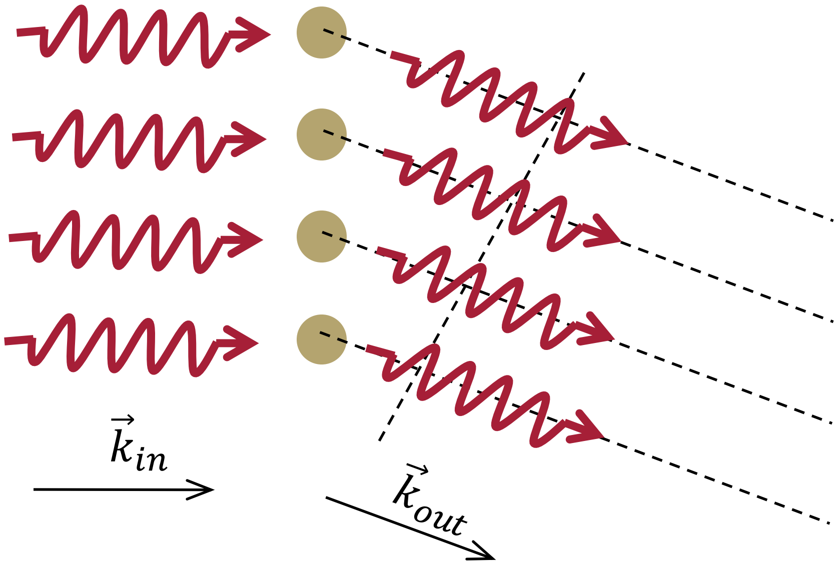
scattering form factor of a nanoparticle

$$f(q) = \int \rho_{el}(\vec{r}) e^{-i\vec{q}\vec{r}} d\vec{r}$$

scattering form factor of a nanoparticle

Scattering by a 1D periodic array of atoms

Scattering in phase:

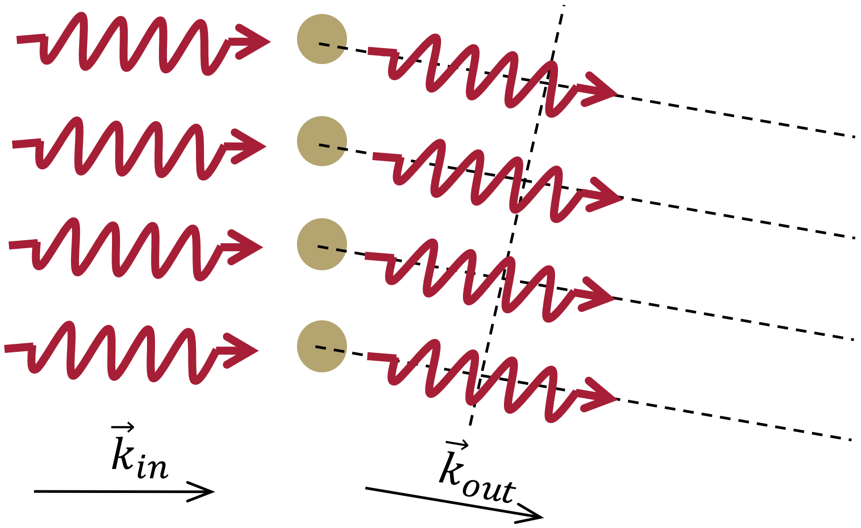


$$E \propto f(q)\sum_{n=1}^{N} e^{-i\vec{q}\vec{r}_n} = f(q)\sum_{n=1}^{N} 1 \propto N\cdot f(q)$$

If for all atoms, $\vec{q}\vec{r}_n = 2\pi\cdot m$

sharp and intense diffraction peak
(Bragg peak)

Scattering out of phase:



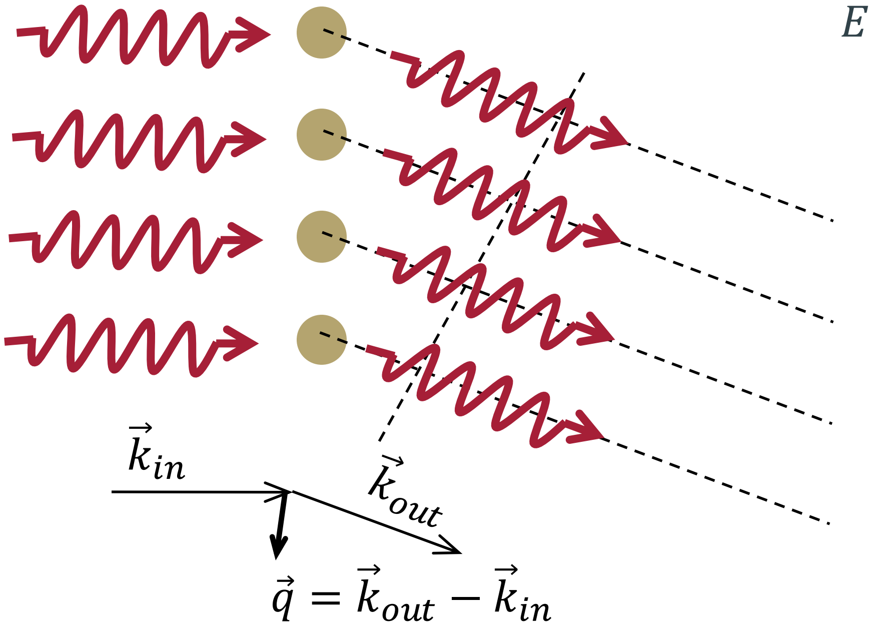
$$E \propto f(q)\sum_{n=1}^{N} e^{-i\vec{q}\vec{r}_n} = f(q)\sum_{n=1}^{N} (\pm 1) \approx 0$$

If for all atoms, $\vec{q}\vec{r}_n = \pi\cdot m$

very weak scattering signal
between the diffraction peaks

Scattering by a 1D periodic array of atoms

Scattering in phase:

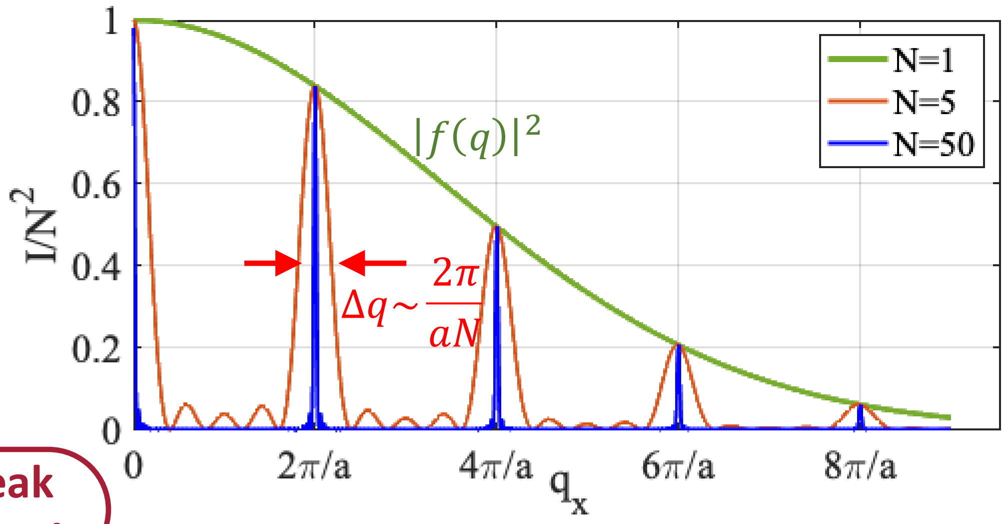


For a periodic array of atoms: $x_n = n \cdot a$

$$E \propto f(q) \sum_{n=1}^{N} e^{-iq_x x_n} = f(q) \sum_{n=1}^{N} e^{-iq_x a \cdot n}$$

$$= f(q) e^{-iq_x a} \frac{1 - e^{-iq_x a \cdot N}}{1 - e^{-iq_x a}}$$

$$I \propto |E|^2 \propto |f(q)|^2 \cdot \left| \frac{\sin\left(\frac{q_x a}{2} \cdot N\right)}{\sin\left(\frac{q_x a}{2}\right)} \right|^2$$



Size of a crystal → Width of the Bragg peak
Shape of a crystal → Shape of the Bragg peak

Strain of the atomic lattice

- Perfect crystal lattice

$$I \propto \left| \sum_{n=1}^{N} e^{-iq \cdot a \cdot n} \right|^2$$

Diffraction peaks at $q = \frac{2\pi}{a} m = q_m$

- Compressive strain $\varepsilon < 0$

Diffraction peaks at $q = \frac{2\pi}{a-\Delta a} m$

$$\approx q_m \left(1 + \frac{\Delta a}{a}\right)$$

- Tensile strain $\varepsilon > 0$

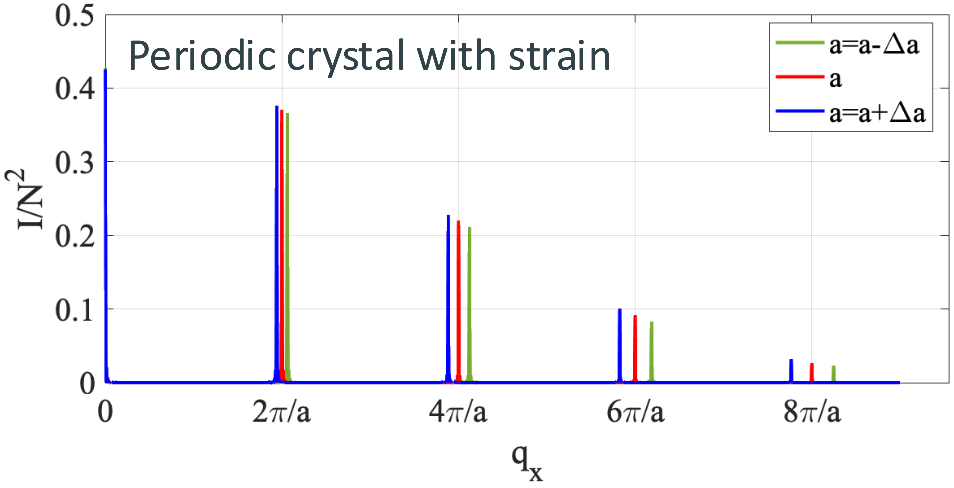
Diffraction peaks at $q = \frac{2\pi}{a+\Delta a} m$

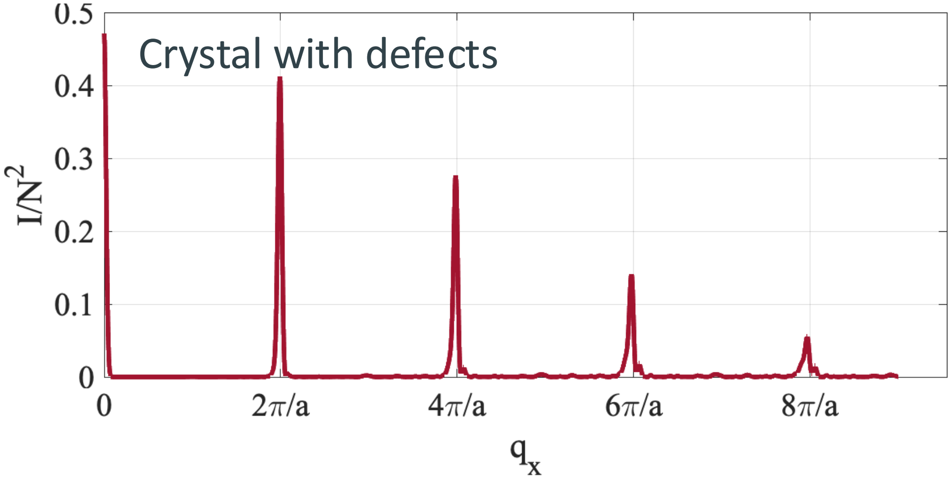
$$\approx q_m \left(1 - \frac{\Delta a}{a}\right)$$

- Real crystal with defects

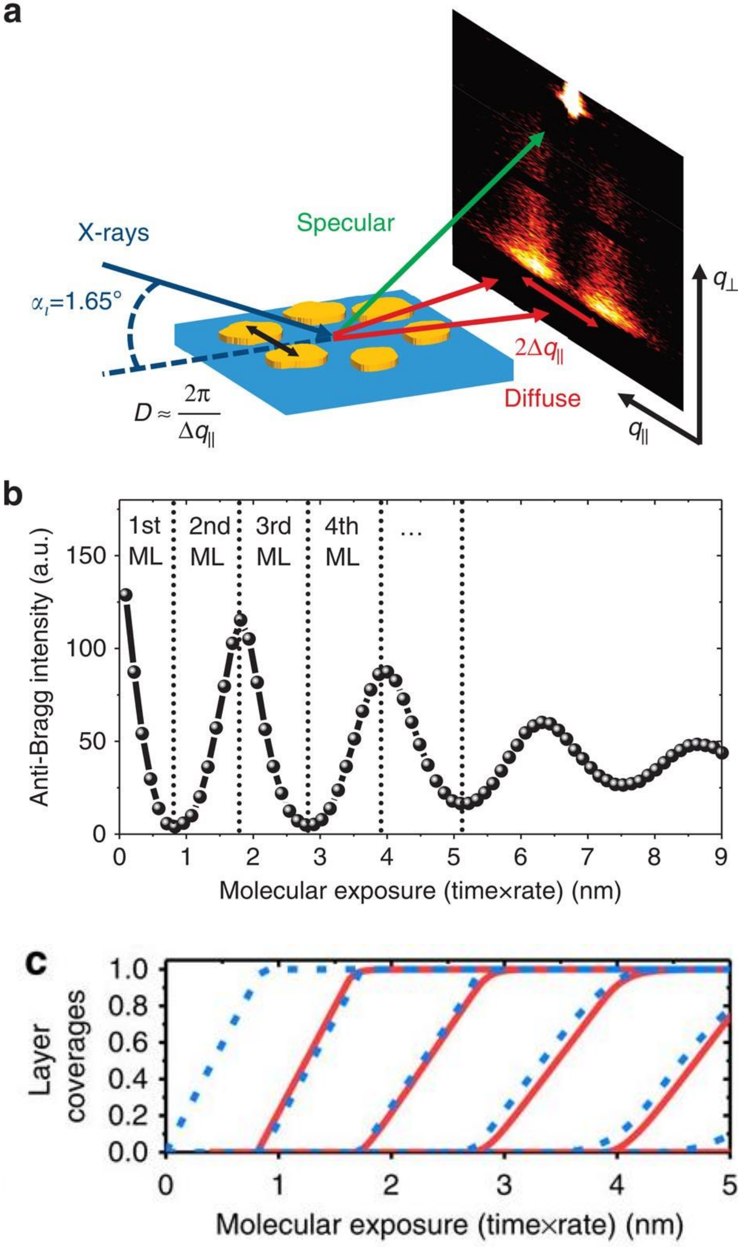
Diffraction peaks at $q = \frac{2\pi}{\langle a \rangle} m$

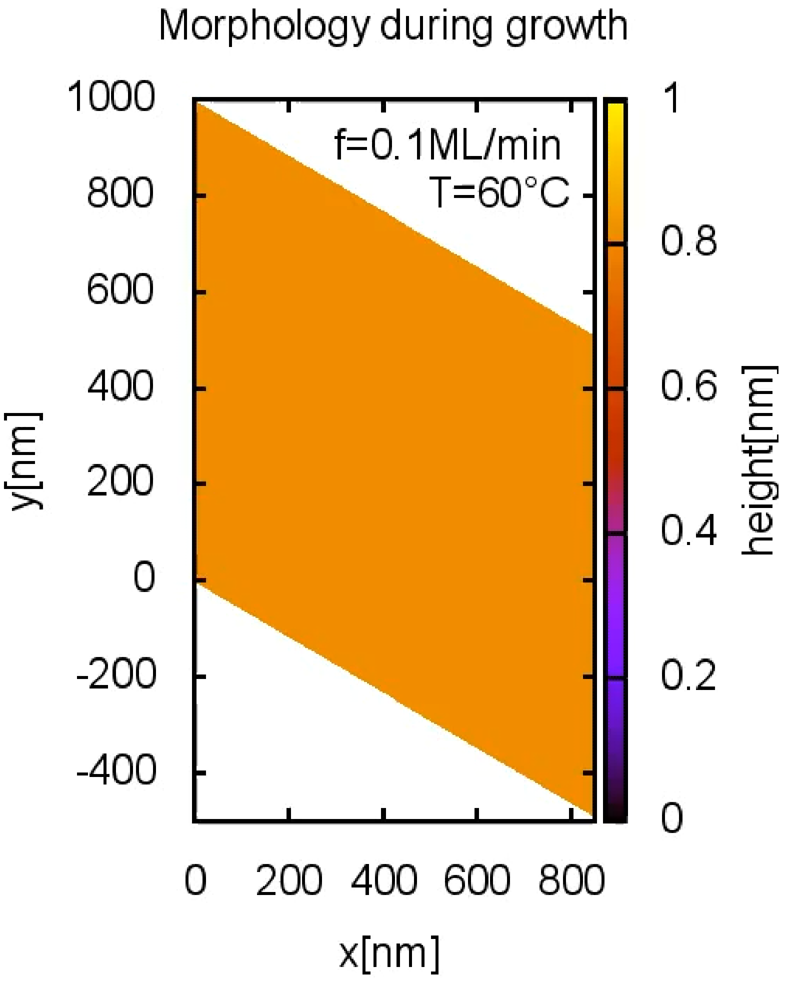
Width of the peaks $\Delta q = q_m \frac{\Delta a}{\langle a \rangle}$





Deposition of C_{60} on mica





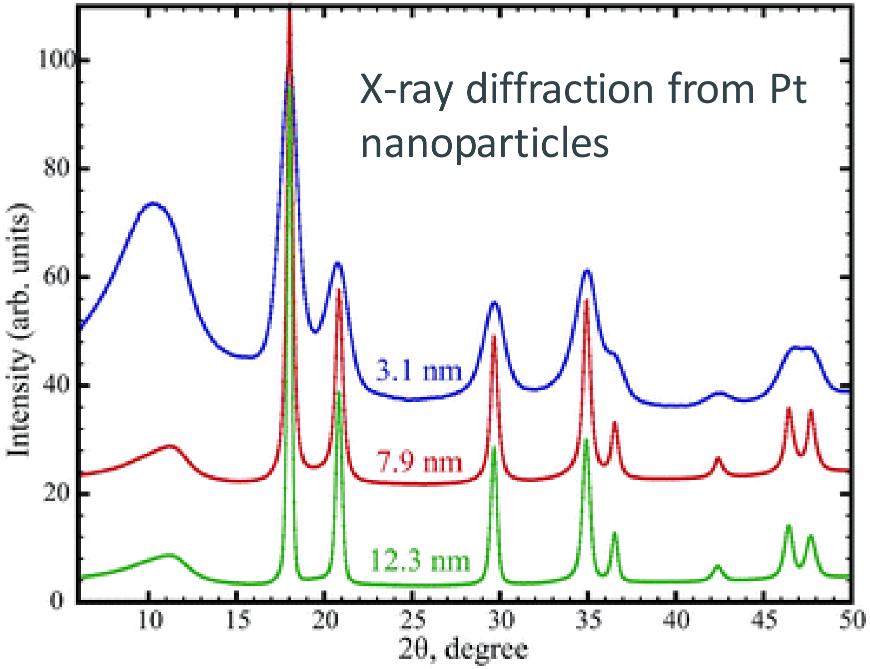
S. Bommel, *et al. Nat. Commun* **5**, 5388 (2014)

Scherrer's broadening

The smaller is the sample, the broader are the Bragg reflections:

$$B(2\theta) = \frac{K\lambda}{L\cos\theta},$$

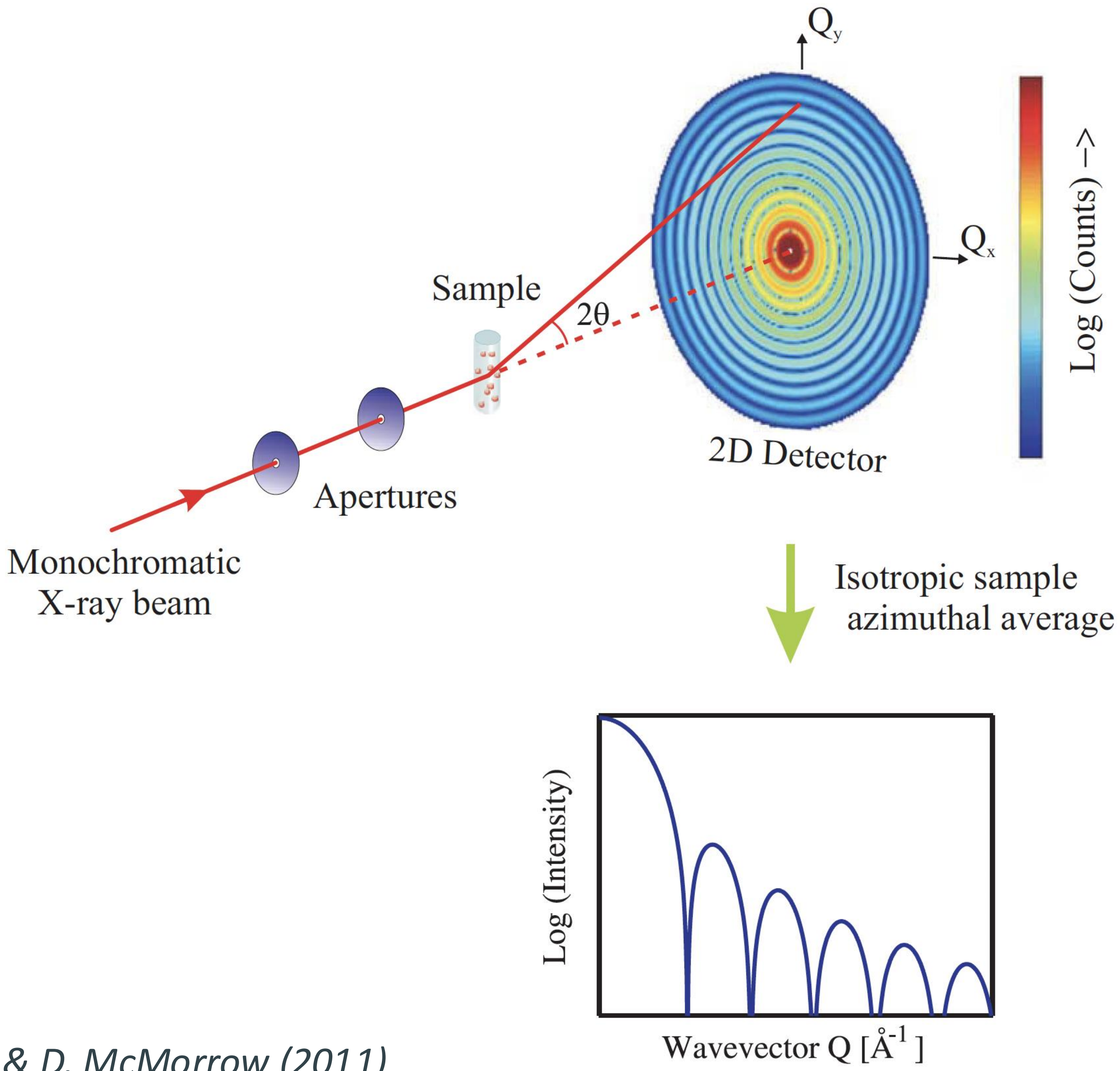
where $B(2\theta)$ is the width (FWHM) of the diffraction peak in radians and $K \sim 1$ is the shape factor.



Leontyev et al., RSC Adv., **2014** 35959-35965

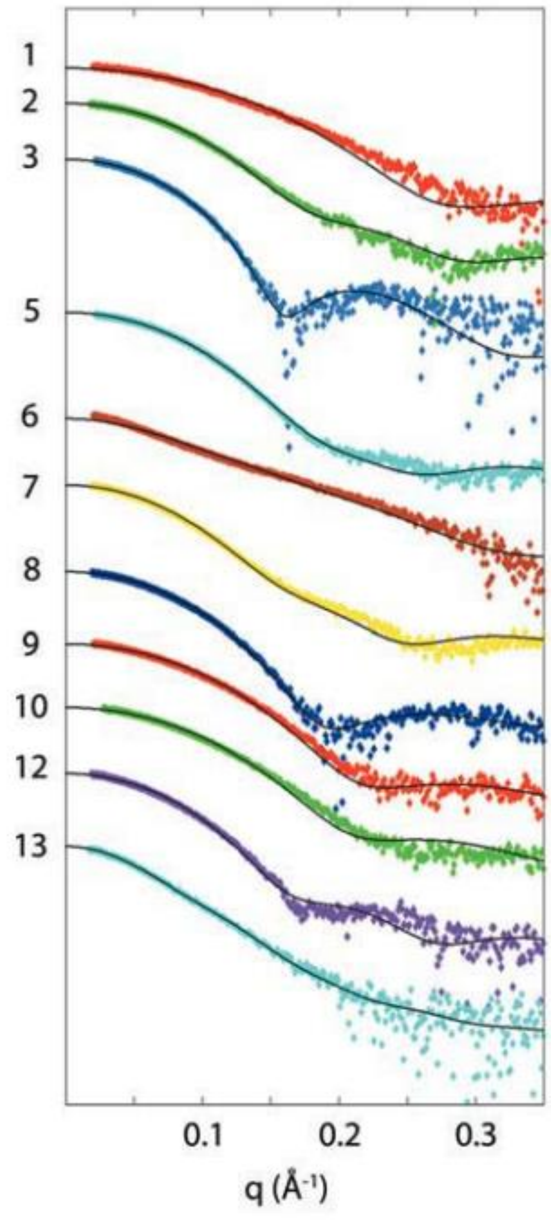
$a_{Pt} = 3.9231$ Å (bulk crystal)

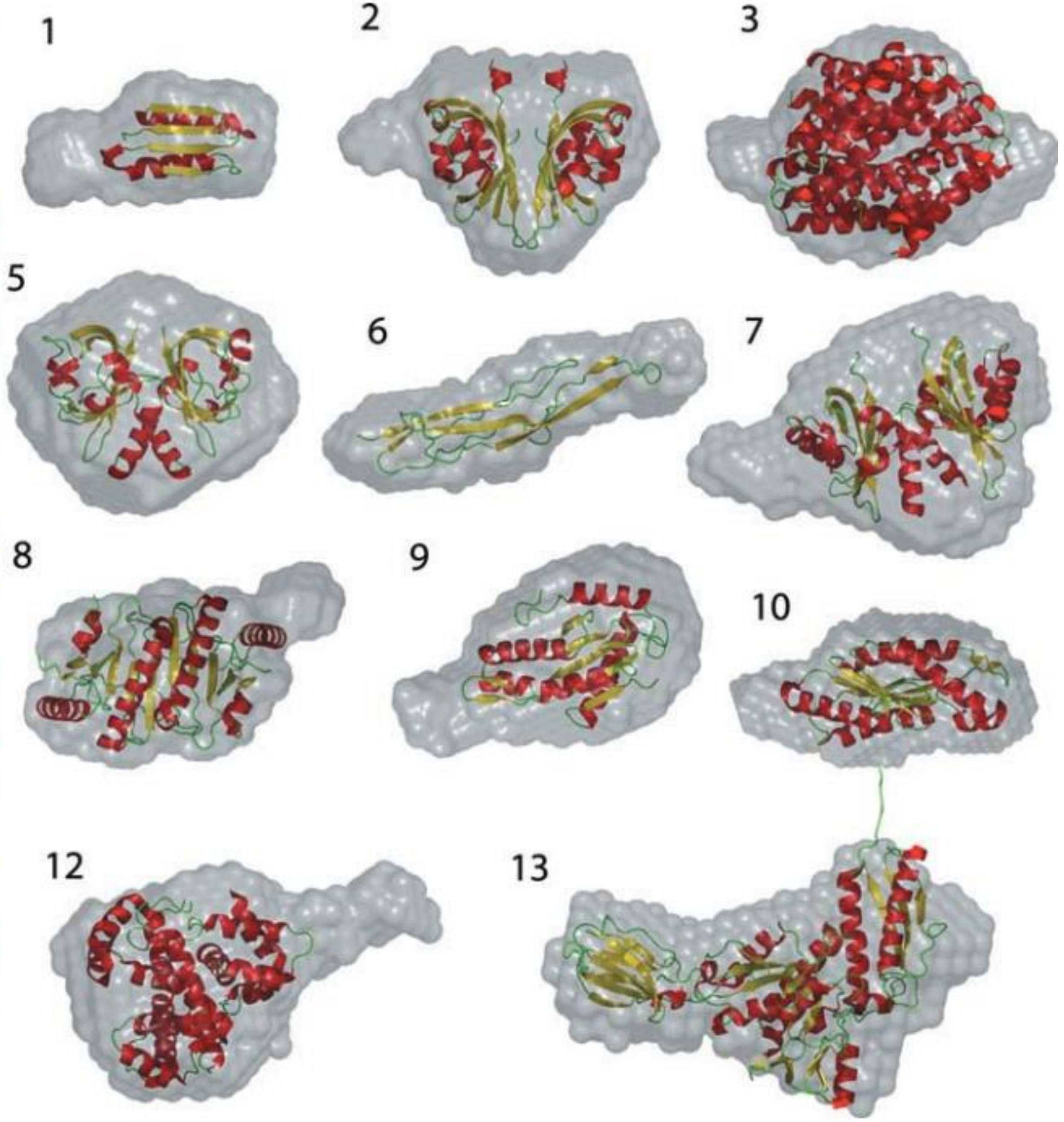
Small Angle X-ray Scattering (SAXS)



J. Als-Nielsen & D. McMorrow (2011)

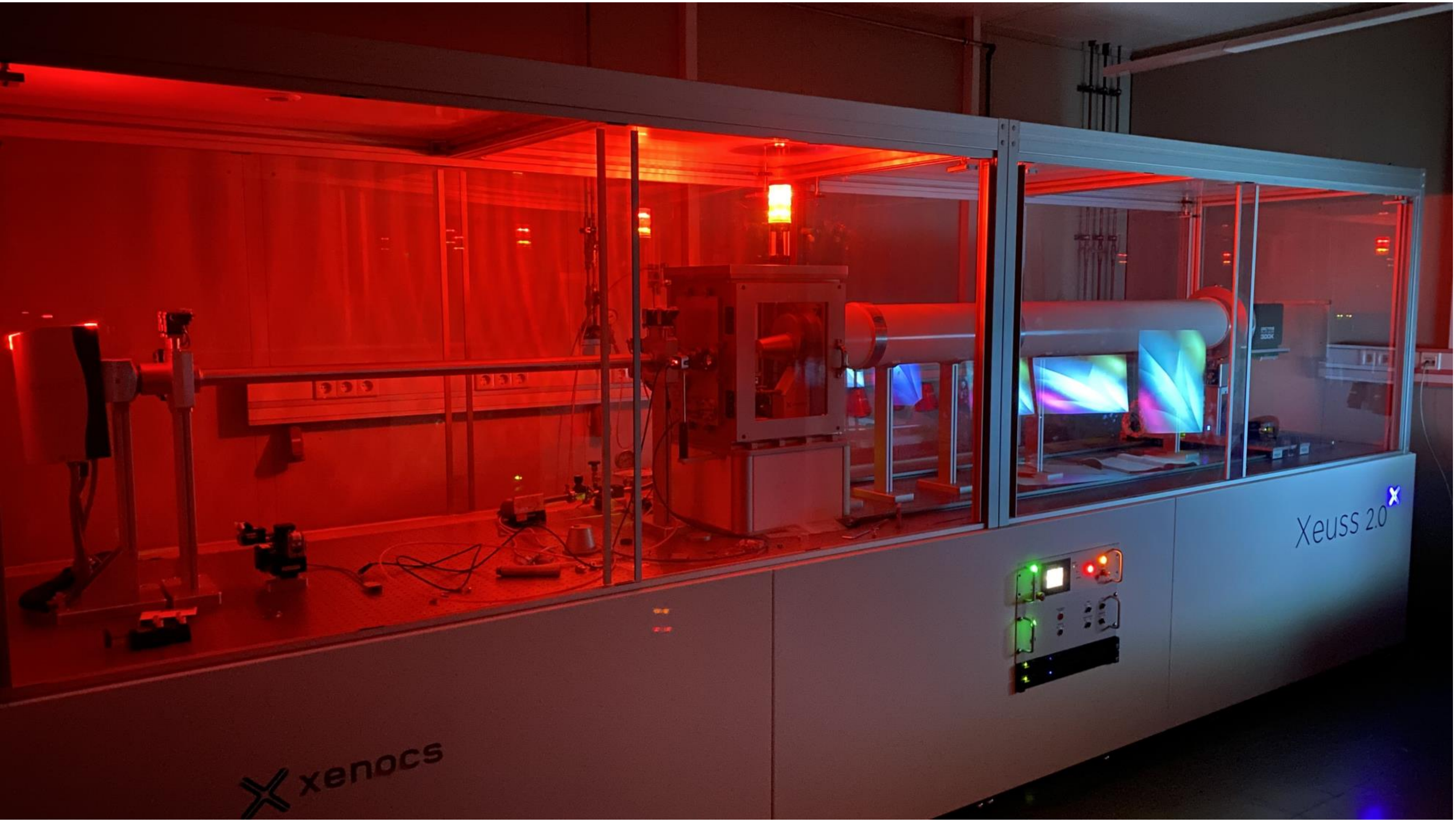
SAXS on proteins



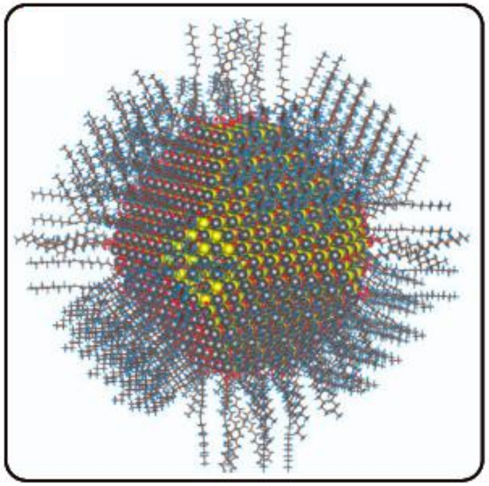


*T.D. Grant et al. Biopolymers **95** 517 (2011)*

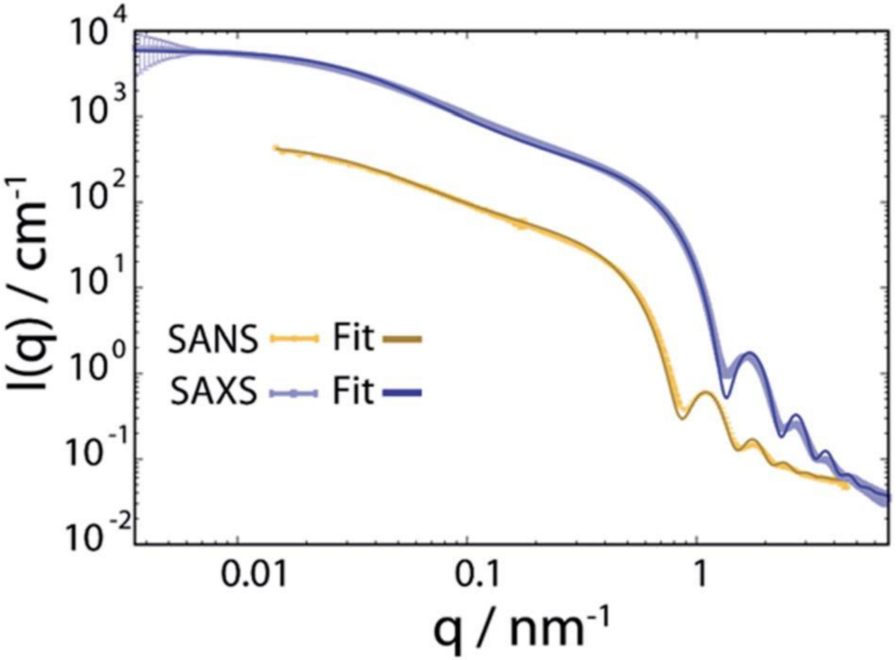
Small Angle X-ray Scattering (SAXS)

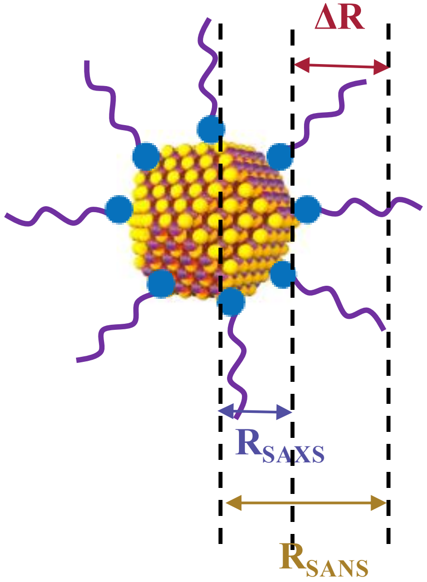


Neutrons / X-rays contrast



PbS nanoparticle
coated with oleic acid



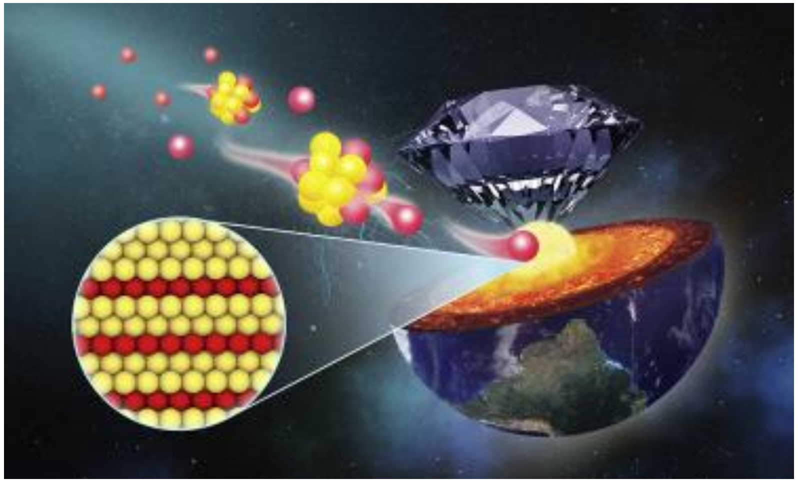


X-rays ”see” almost exclusively the PbS core
Neutrons “see” both the PbS core and OA shell

T. Seydel et al., Chem. Sci. **11**, 8875 (2020)

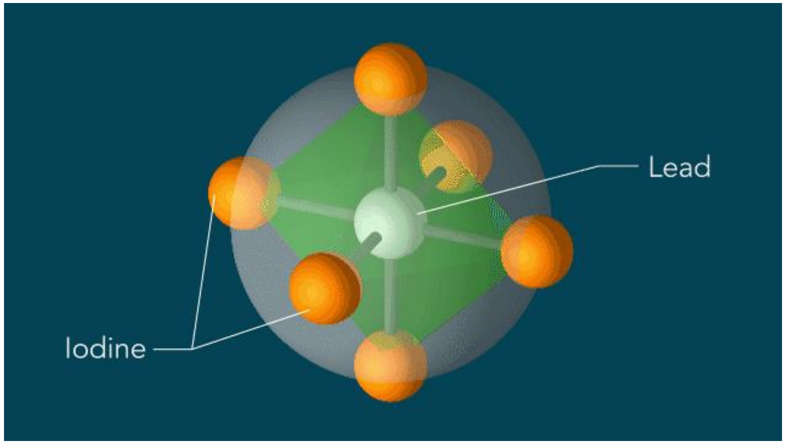
Possibilities for *in situ* experiments

1. X-ray diffraction in extreme conditions (high pressure, high/low temperatures, etc)



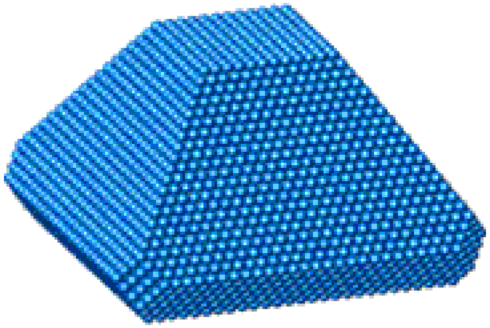
Liu et al., The Innovation 4 100354 (2023)

2. X-ray diffraction with time resolution (tracking chemical reactions)



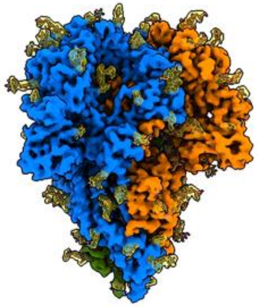
SLAC National Accelerator Laboratory

3. X-ray diffraction *in operando* (catalysis, voltage-induced changes, etc)

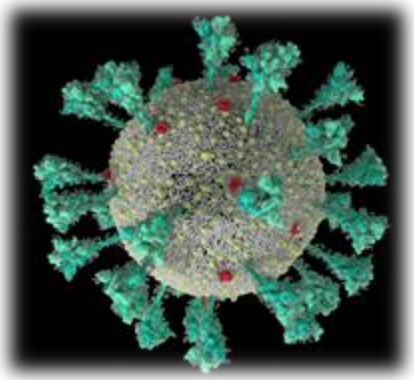


DESY

4. X-ray diffraction of biologically important systems

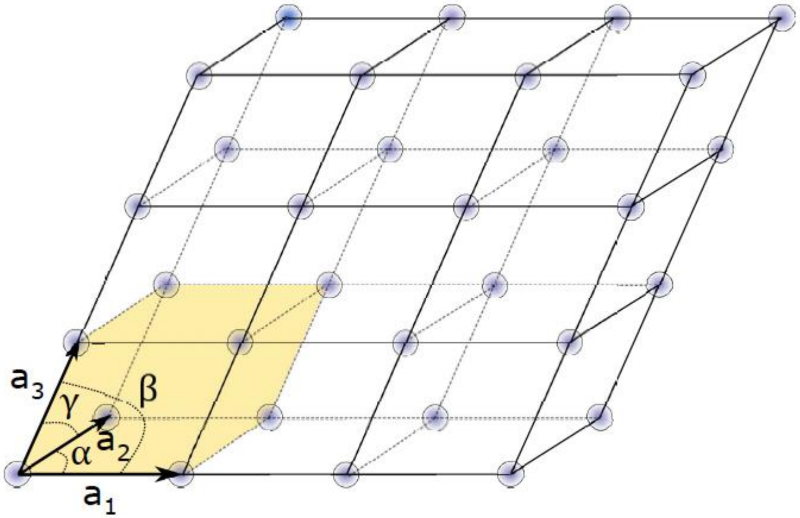


SLAC National Accelerator Laboratory



Scattering by a 3D periodic array of atoms

In a crystal lattice, $\vec{r}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$



We observe a diffraction peak, if for all atoms, $\vec{q}\vec{r}_n = 2\pi \cdot m$

$$E \propto f(q) \sum_{n=1}^{N} e^{-i\vec{q}\vec{r}_n} = f(q) \sum_{n=1}^{N} 1 \propto N \cdot f(q)$$

A reciprocal lattice: $\vec{G}_{hkl} = h\vec{a}_1^* + k\vec{a}_2^* + l\vec{a}_3^*$ with the reciprocal unit vectors

$$\vec{a}_1^* = \frac{2\pi[\vec{a}_2 \times \vec{a}_3]}{\vec{a}_1 \cdot [\vec{a}_2 \times \vec{a}_3]}$$

$$\vec{a}_2^* = \frac{2\pi[\vec{a}_3 \times \vec{a}_1]}{\vec{a}_2 \cdot [\vec{a}_3 \times \vec{a}_1]}$$

$$\vec{a}_3^* = \frac{2\pi[\vec{a}_1 \times \vec{a}_2]}{\vec{a}_3 \cdot [\vec{a}_1 \times \vec{a}_2]}$$

Note that

$$\vec{a}_1^* \cdot \vec{a}_1 = 2\pi$$
$$\vec{a}_2^* \cdot \vec{a}_2 = 2\pi$$
$$\vec{a}_3^* \cdot \vec{a}_3 = 2\pi$$

All mixed products are zero

$$\vec{a}_i^* \cdot \vec{a}_j = 0$$

For any atom of the real lattice

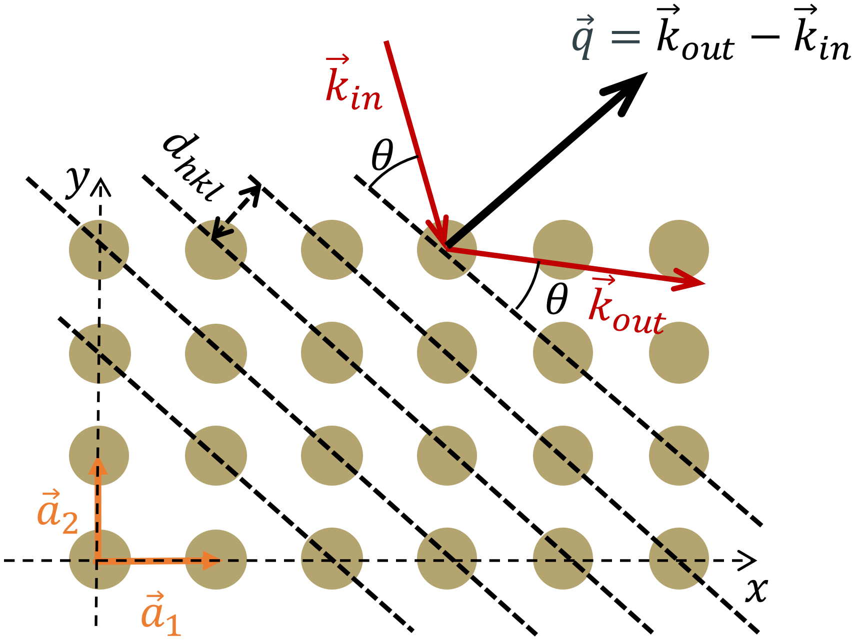
$$\vec{G}_{hkl}\vec{r}_n = 2\pi \cdot (hn_1 + kn_2 + ln_3) = 2\pi \cdot m$$

The condition to observe a Bragg peak

$$\vec{q} = \vec{k}_{out} - \vec{k}_{in} = \vec{G}_{hkl}$$

Real space and reciprocal space

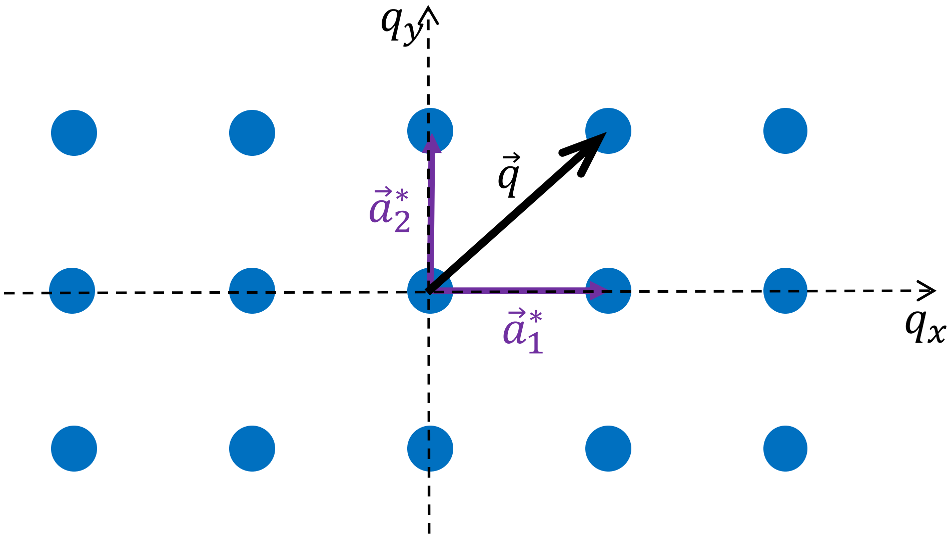
Scattering in real space



The scattering can be seen as specular reflection from a set of parallel atomic planes. The interference between the photons scattered from different planes will be constructive if the Bragg condition is satisfied:

$$2d_{hkl}\sin\theta = \lambda$$

Scattering in reciprocal space

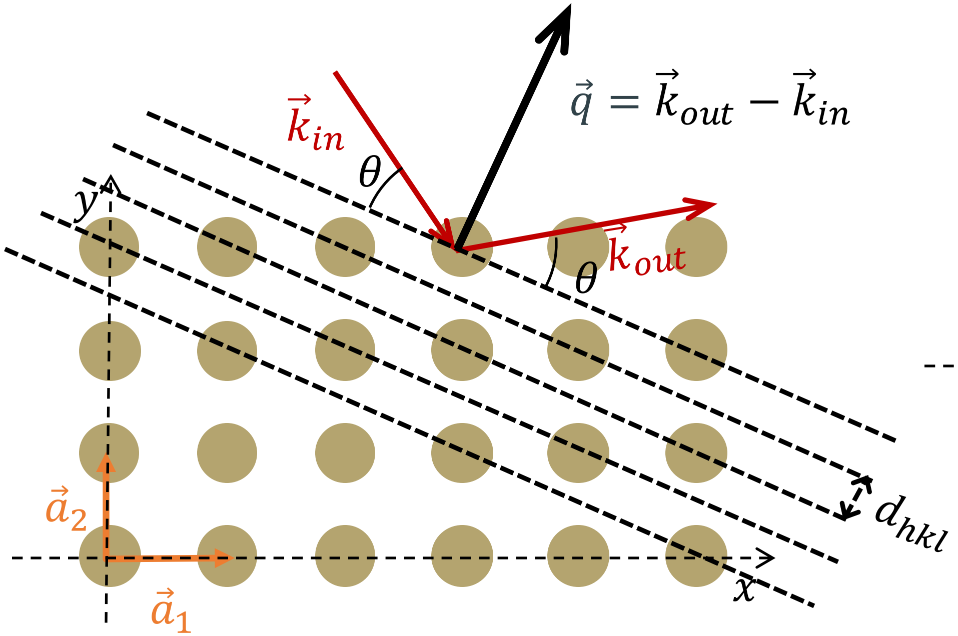


$$\vec{q} = \vec{a}_1^* + \vec{a}_2^* = \vec{G}_{hkl}$$

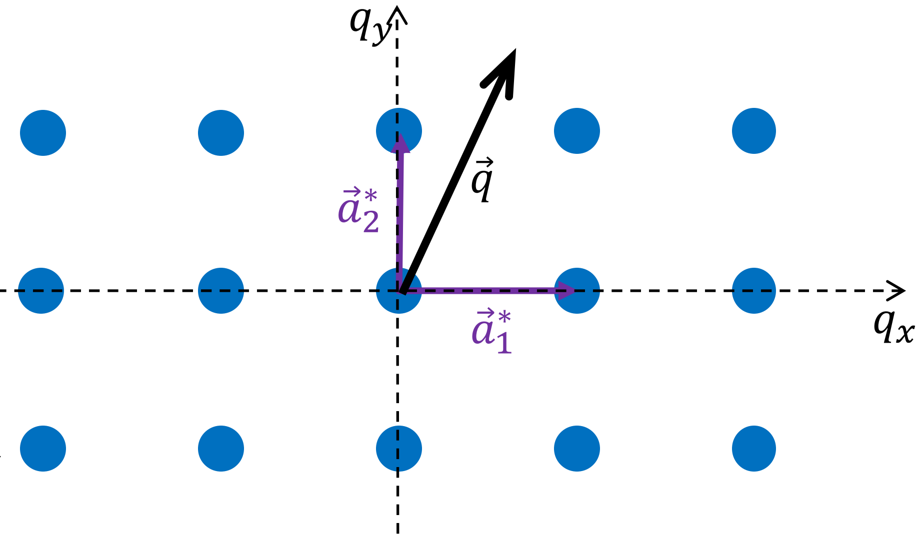
Laue condition is satisfied, so we will see a diffraction peak in this experiment.

Real space and reciprocal space

Scattering in real space



Scattering in reciprocal space



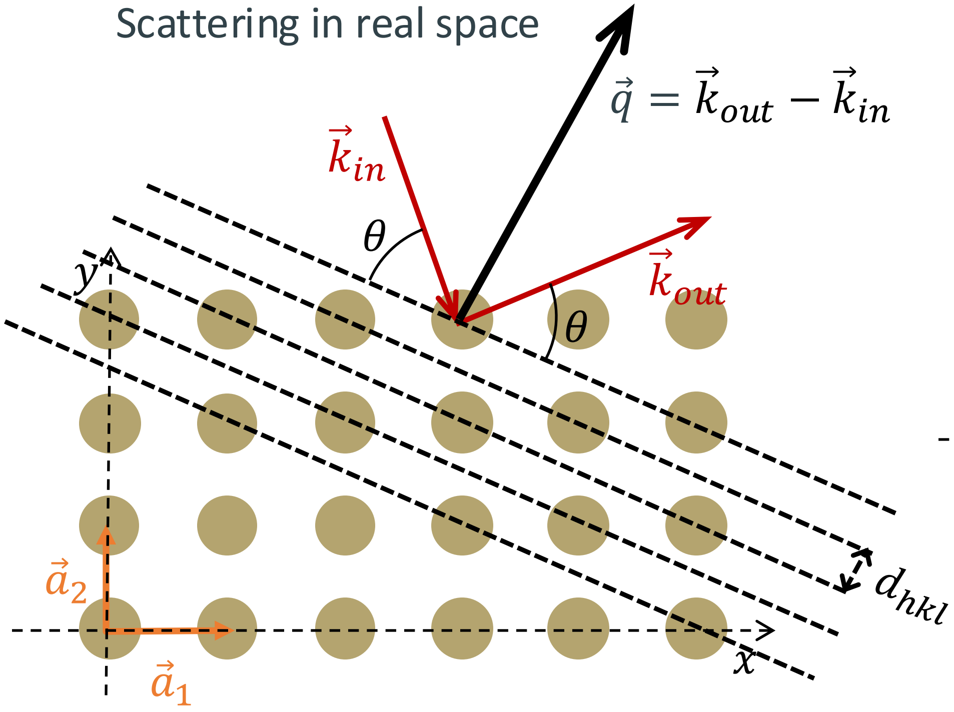
$\vec{q} \neq \vec{G}_{hkl}$

Bragg condition is not satisfied:
$2d_{hkl} \sin\theta \neq \lambda$

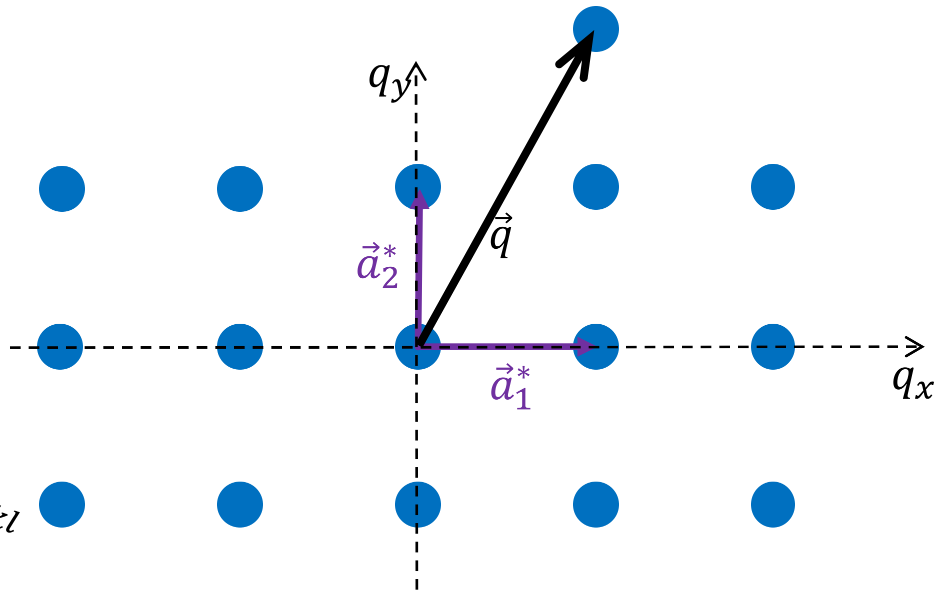
Laue condition is not satisfied, so we will not see a diffraction peak in this experiment.

Real space and reciprocal space

Scattering in real space



Scattering in reciprocal space



$$\vec{q} = \vec{a}_1^* + 2\vec{a}_2^* = \vec{G}_{hkl}$$

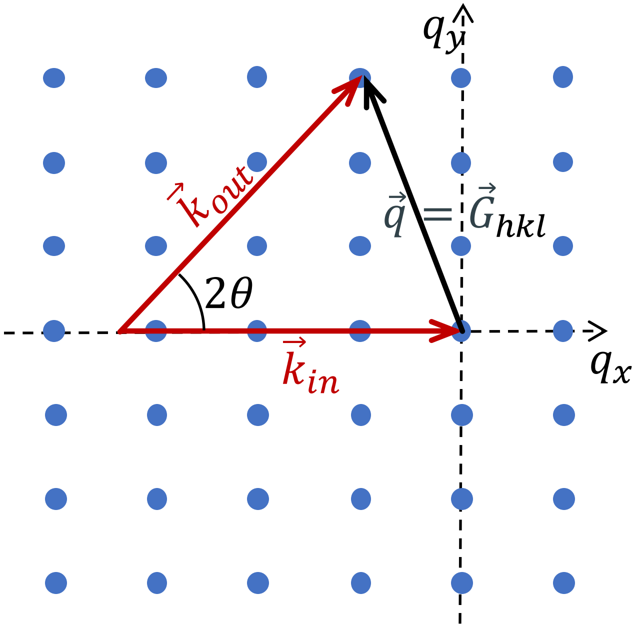
By adjusting the incidence angle, Bragg condition is satisfied again, so we can see the diffraction peak

$$2d_{hkl}\sin\theta = \lambda$$

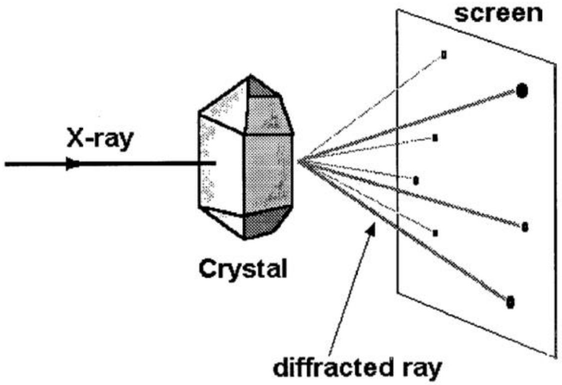
Laue condition is satisfied

The Ewald sphere

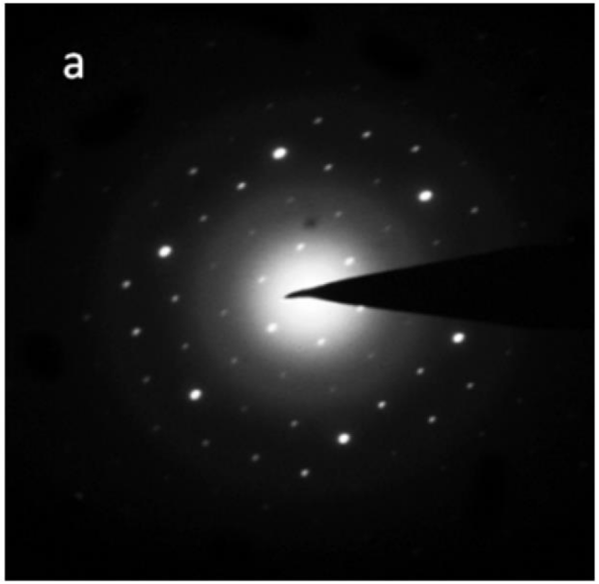
For elastic scattering, $|\vec{k}_{in}| = |\vec{k}_{out}| = \frac{2\pi}{\lambda}$. It means, that all possible scattering vectors $\vec{q} = \vec{k}_{out} - \vec{k}_{in}$ form a sphere of radius $\frac{2\pi}{\lambda}$ in reciprocal space. A diffraction pattern, measured with a 2D detector, is a cross section of reciprocal space with the Ewald sphere.



Ewald's sphere in reciprocal space

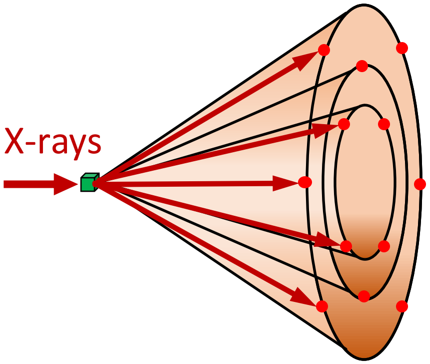


Single crystal diffraction experiment

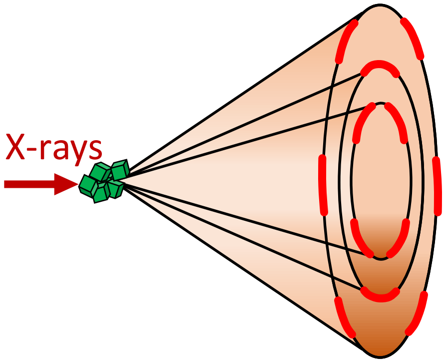


Diffraction pattern

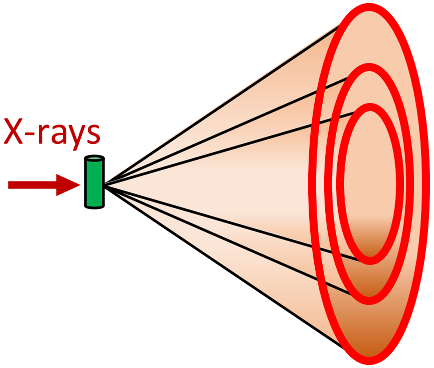
Powder diffraction



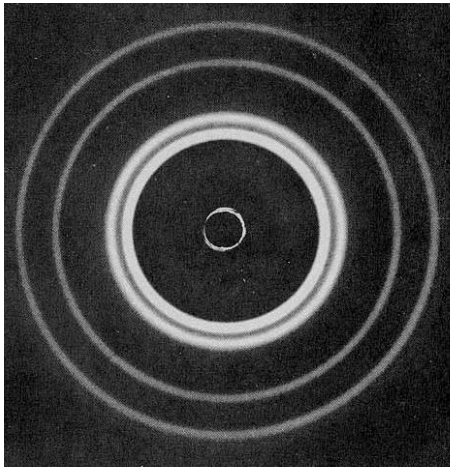
Single crystal diffraction (Bragg reflections)



Polycrystalline sample with preferred orientation of crystal grains

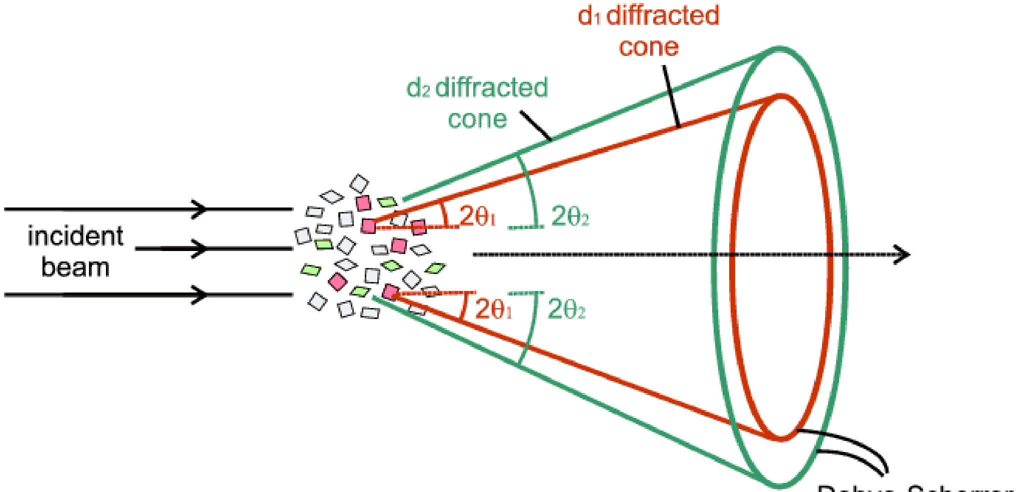


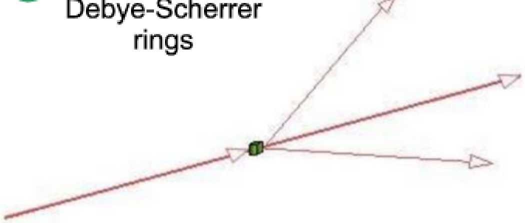
Perfect powder diffraction (Debye-Scherrer rings)



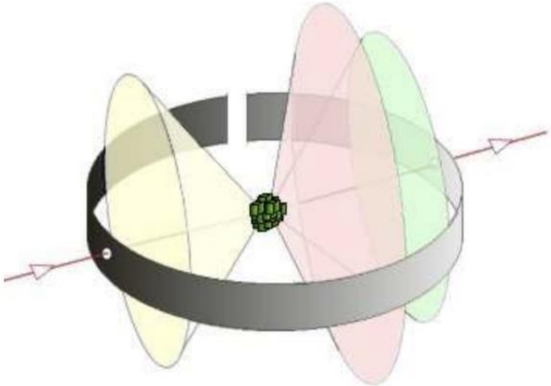
Debye-Scherrer diffraction rings from aluminum foil

Powder diffraction

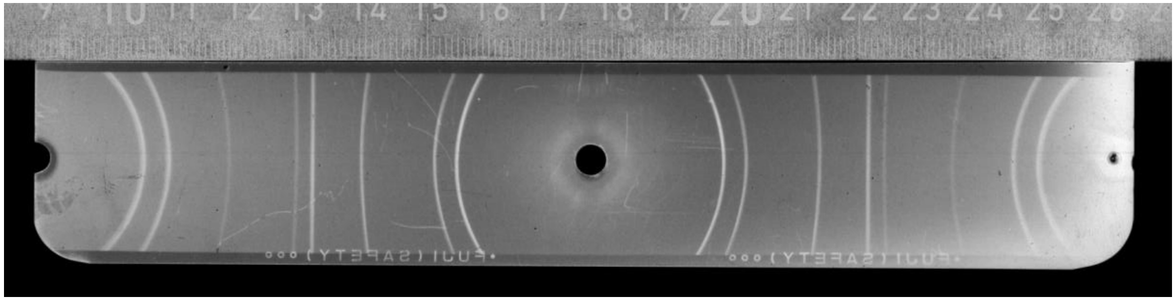




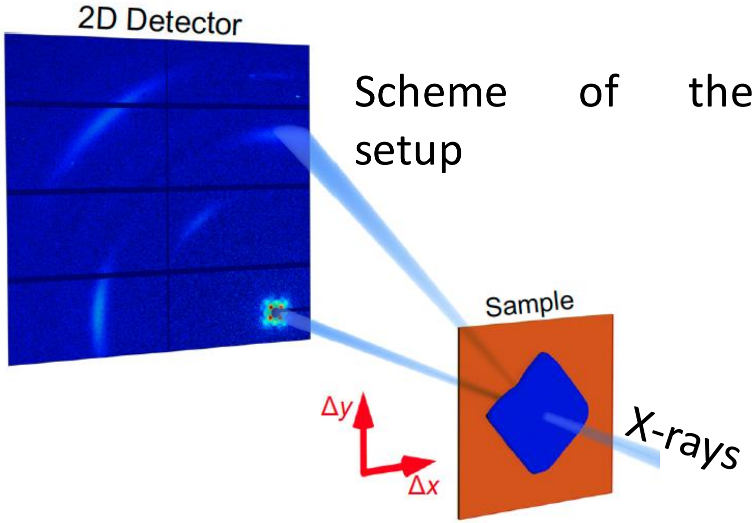
Single Crystal



Polycrystalline Powder

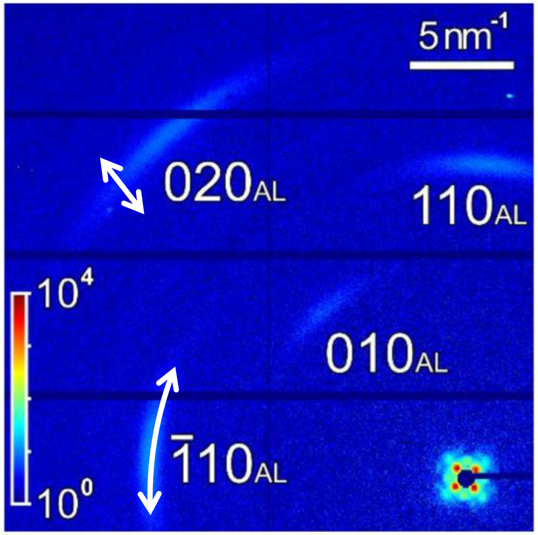


Mosaic spread (azimuthal broadening)

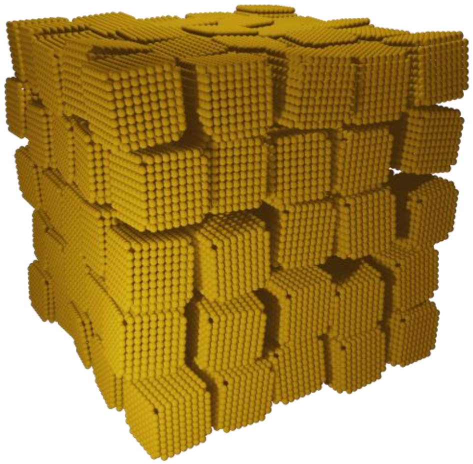


Scheme of the setup

Diffraction pattern

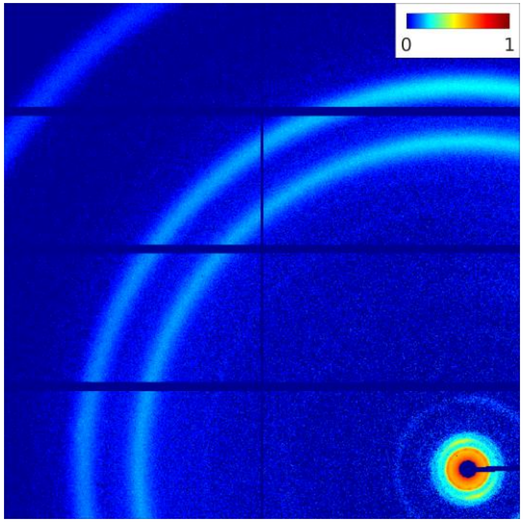


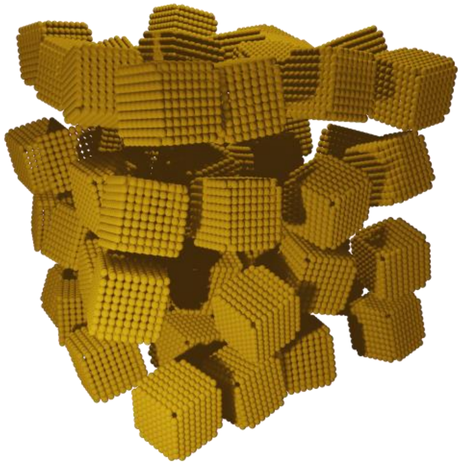
Structure of mesocrystal



Radial width of the peak (Scherrer's broadening) – size of a nanoparticle

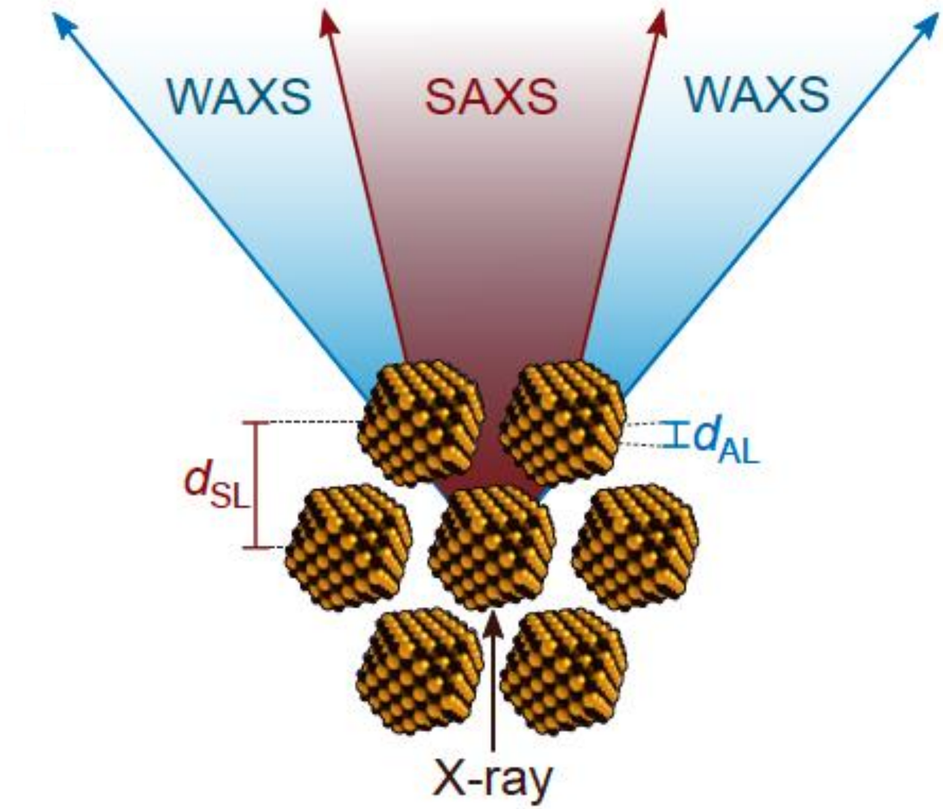
Azimuthal width of the peak – orientational distributions of nanoparticles



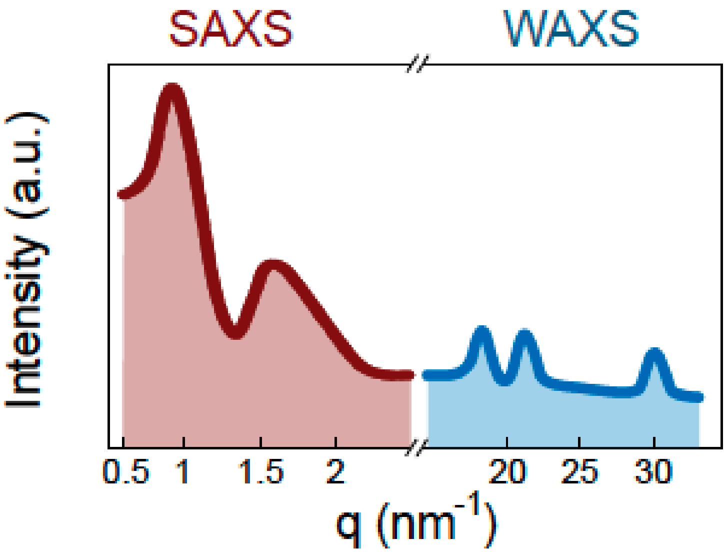


D. Lapkin et al., Nat. Commun. ***13*** *892 (2022)*

Diffraction from quantum dot solids



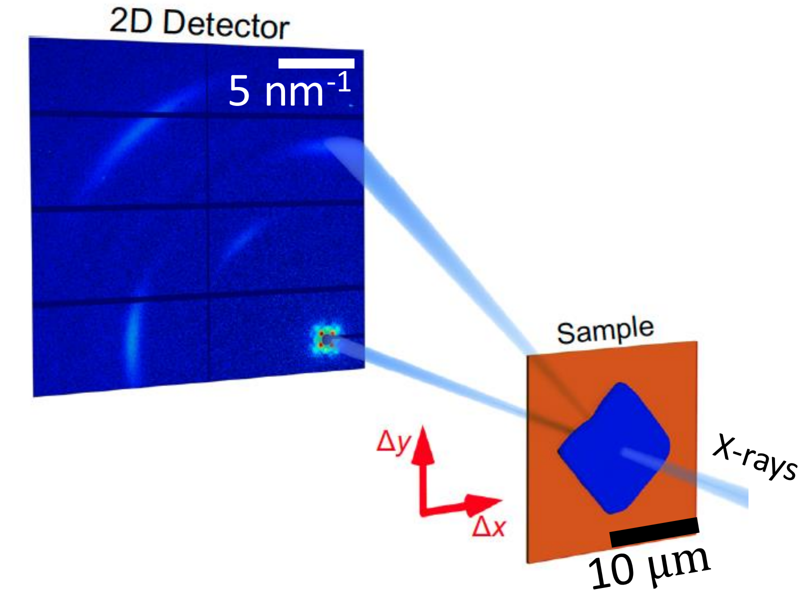
- Small Angle X-ray Scattering (SAXS) is sensitive to the distance between the nanoparticles (superlattice)
- Wide Angle X-ray Scattering (WAXS) is sensitive to the distance between atoms (atomic lattice of nanoparticles)

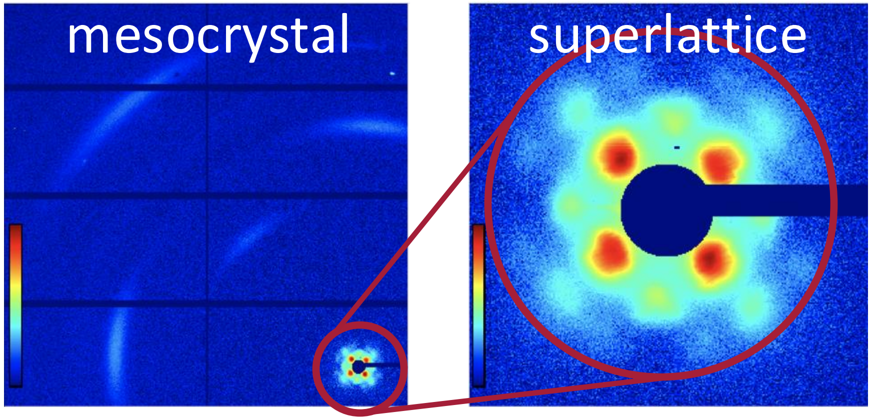


with X-ray diffraction one can simultaneously "see" the structure on two length scales: atomic lattice and superlattice

A. Maier, PhD thesis (2021)

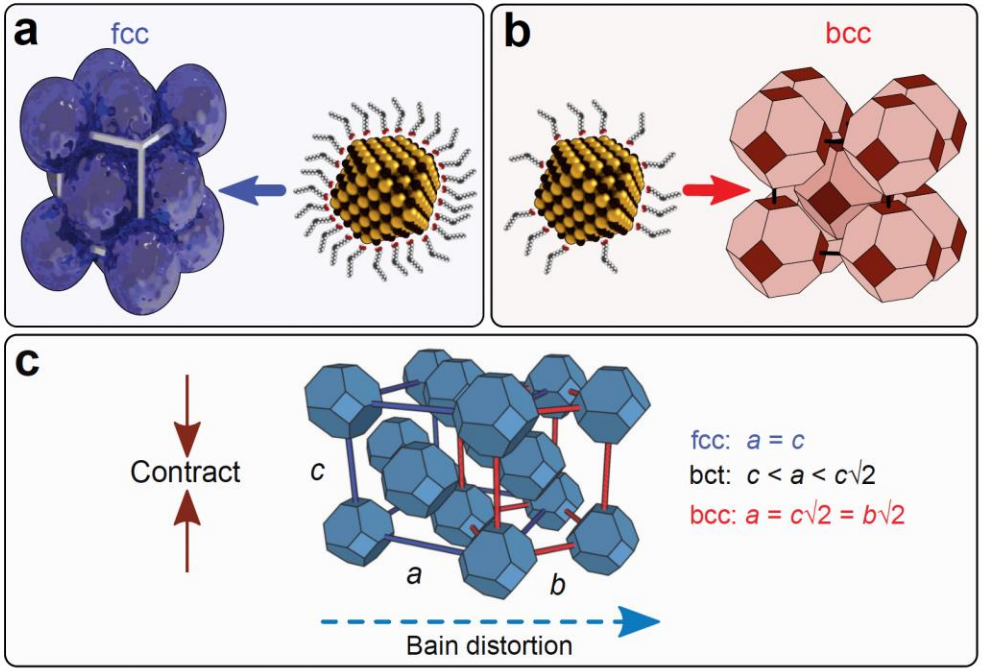
Structure of superlattice





D. Lapkin et al., Nat. Commun. ***13*** *892 (2022)*

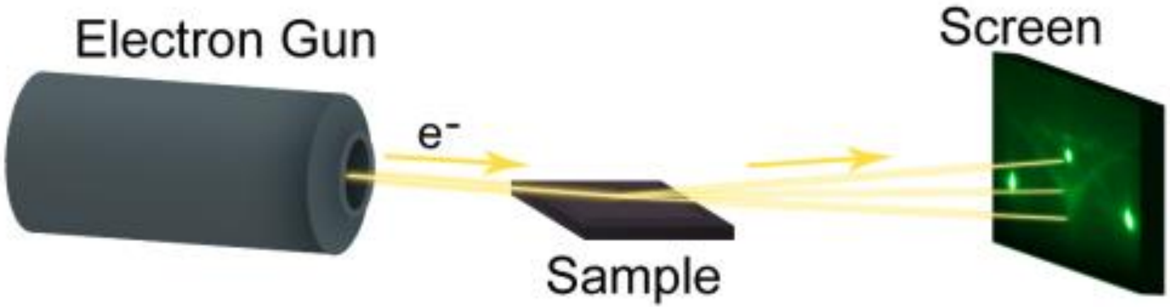
Structure of the superlattice



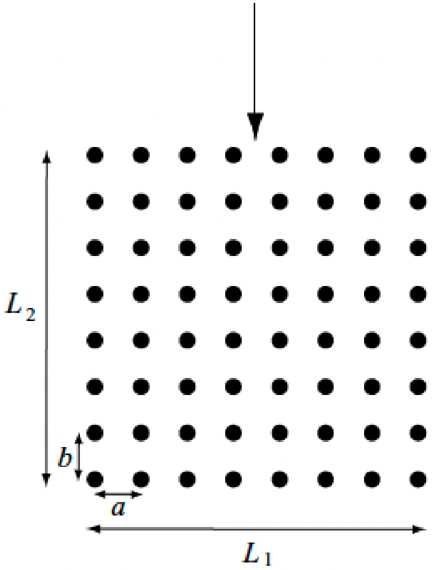
J. Novák et al., ACS Appl. Mater. Interfaces ***8****, 22526 (2016)*

A. Maier, PhD thesis (2021)

Reflection High-Energy Electron Diffraction (RHEED)



N. Derriche, *et al.* (2019).



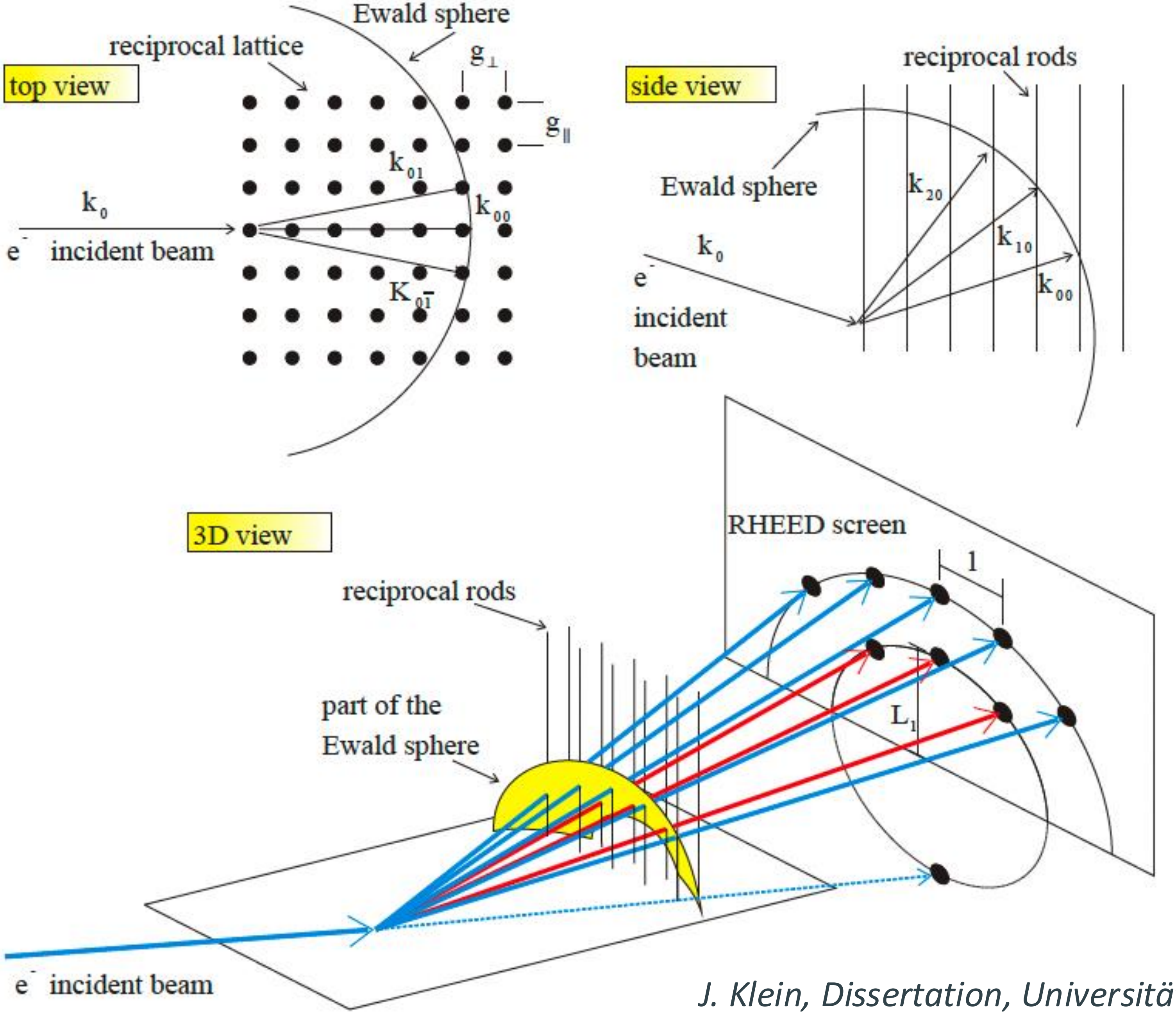
Scattering from atoms on a surface (scattering from a 2D crystal)

$$A \propto \sum_{n=1}^{N} e^{-i\vec{q}\vec{r}_n} = \sum_{n=1}^{N} e^{-i(q_x x_n + q_y y_n + q_z z_n)} \underset{\substack{\uparrow \\ z_n = 0}}{=} \sum_{n=1}^{N} e^{-i(q_x x_n + q_y y_n)}$$

Scattering will occur (constructive interference) for certain values of q_x and q_y and all values of q_z (reciprocal rods). For example, for a simple rectangular lattice:

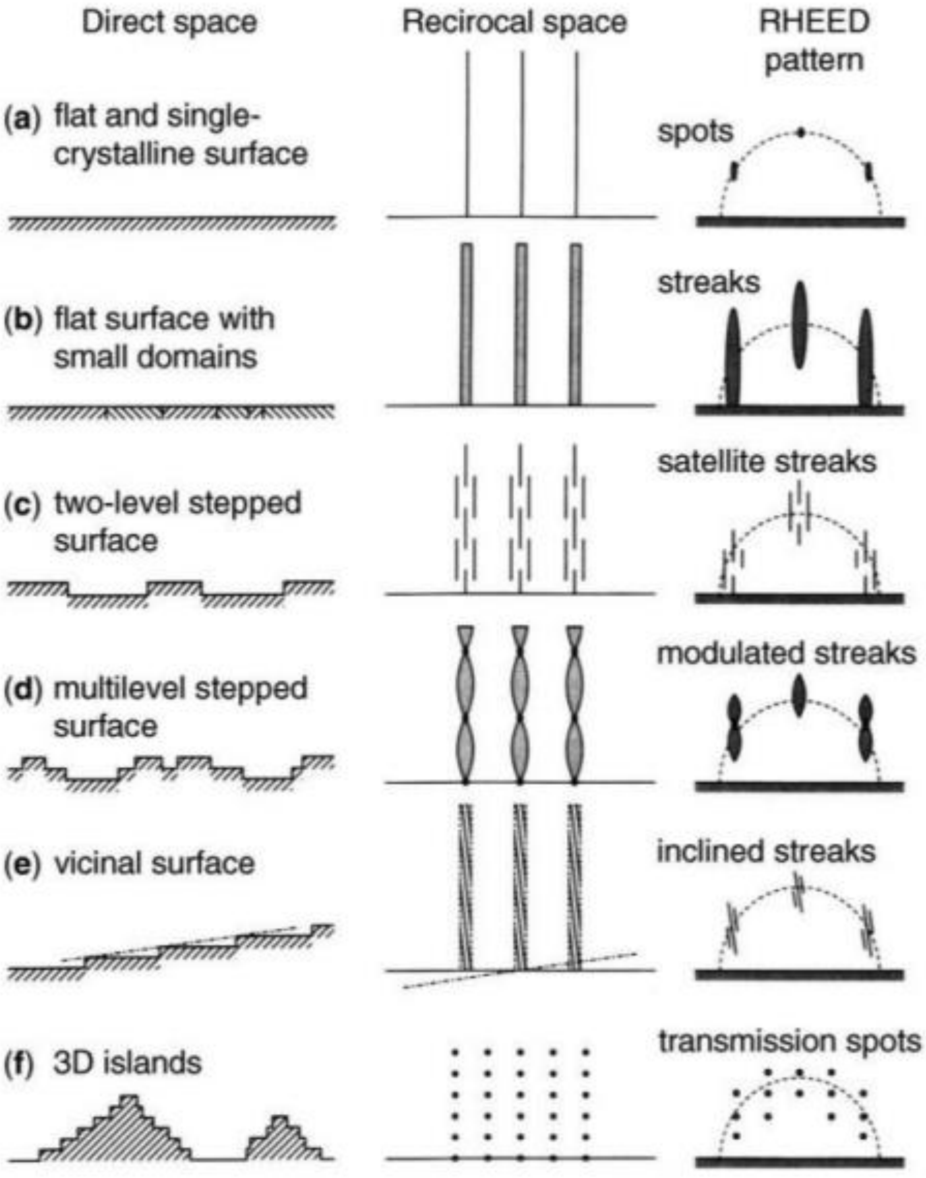
$$q_x = \frac{2\pi}{a} h, \qquad (h, k \ - integers)$$
$$q_y = \frac{2\pi}{b} k,$$

Reflection High-Energy Electron Diffraction (RHEED)

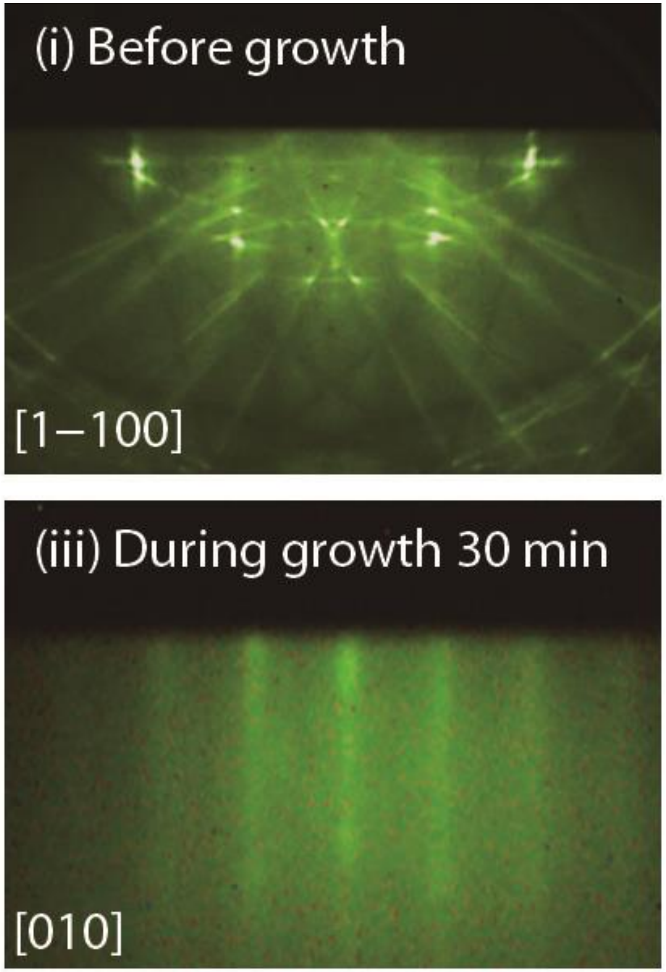


J. Klein, Dissertation, Universität zu Köln (2001)

Reflection High-Energy Electron Diffraction (RHEED)



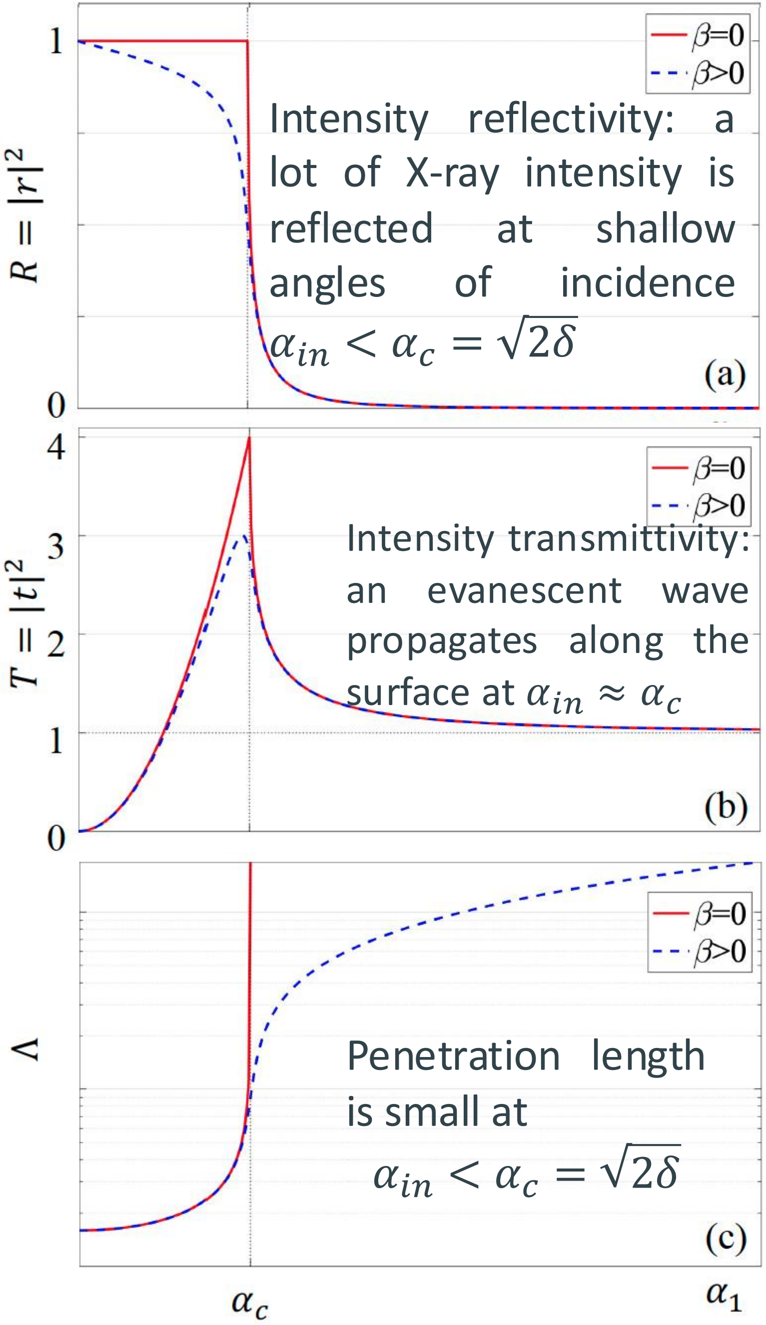
A. Ichimiya, P. Cohen (2004)



Growth of β-Ga_2O_3 on sapphire (0001-Al_2O_3)

J. Wei et al., J. Semicond. ***40*** *012802 (2019)*

Surface sensitivity



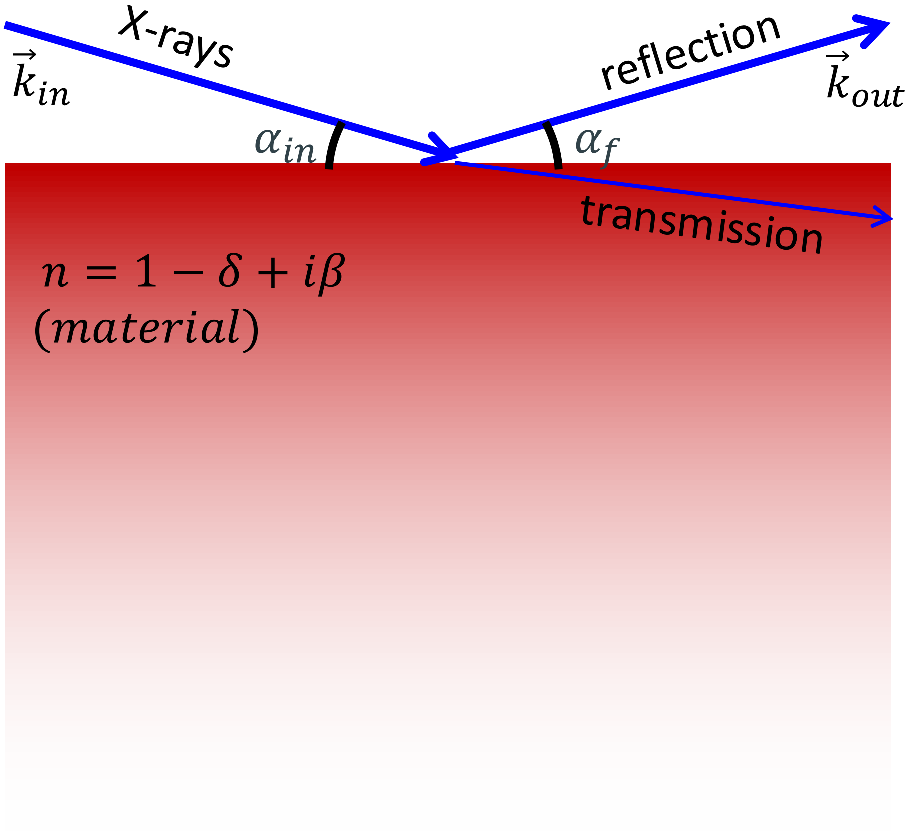
Intensity reflectivity: a lot of X-ray intensity is reflected at shallow angles of incidence $\alpha_{in} < \alpha_c = \sqrt{2\delta}$

Intensity transmittivity: an evanescent wave propagates along the surface at $\alpha_{in} \approx \alpha_c$

Penetration length is small at

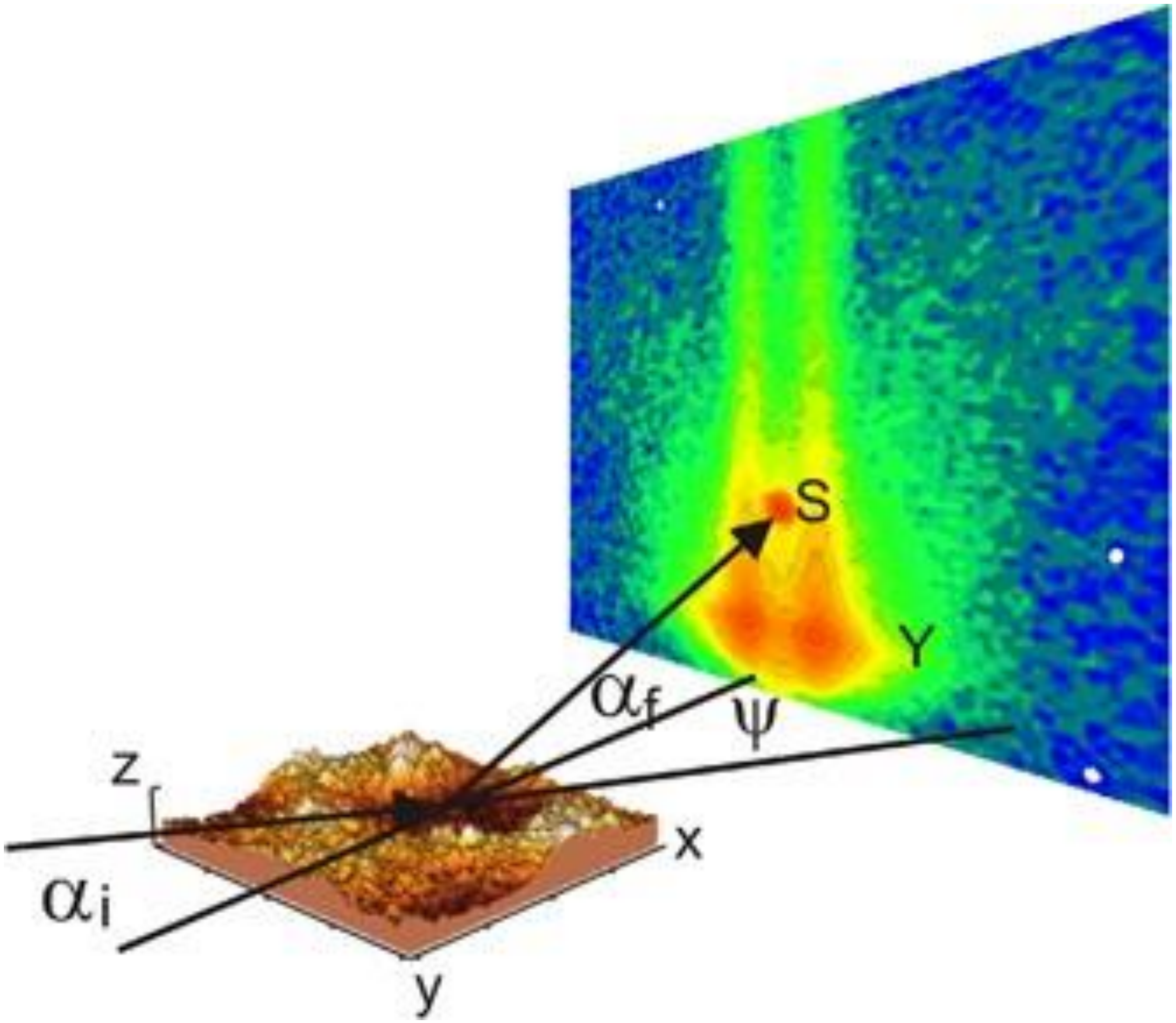
$$\alpha_{in} < \alpha_c = \sqrt{2\delta}$$

$n = 1\ (vacuum)$



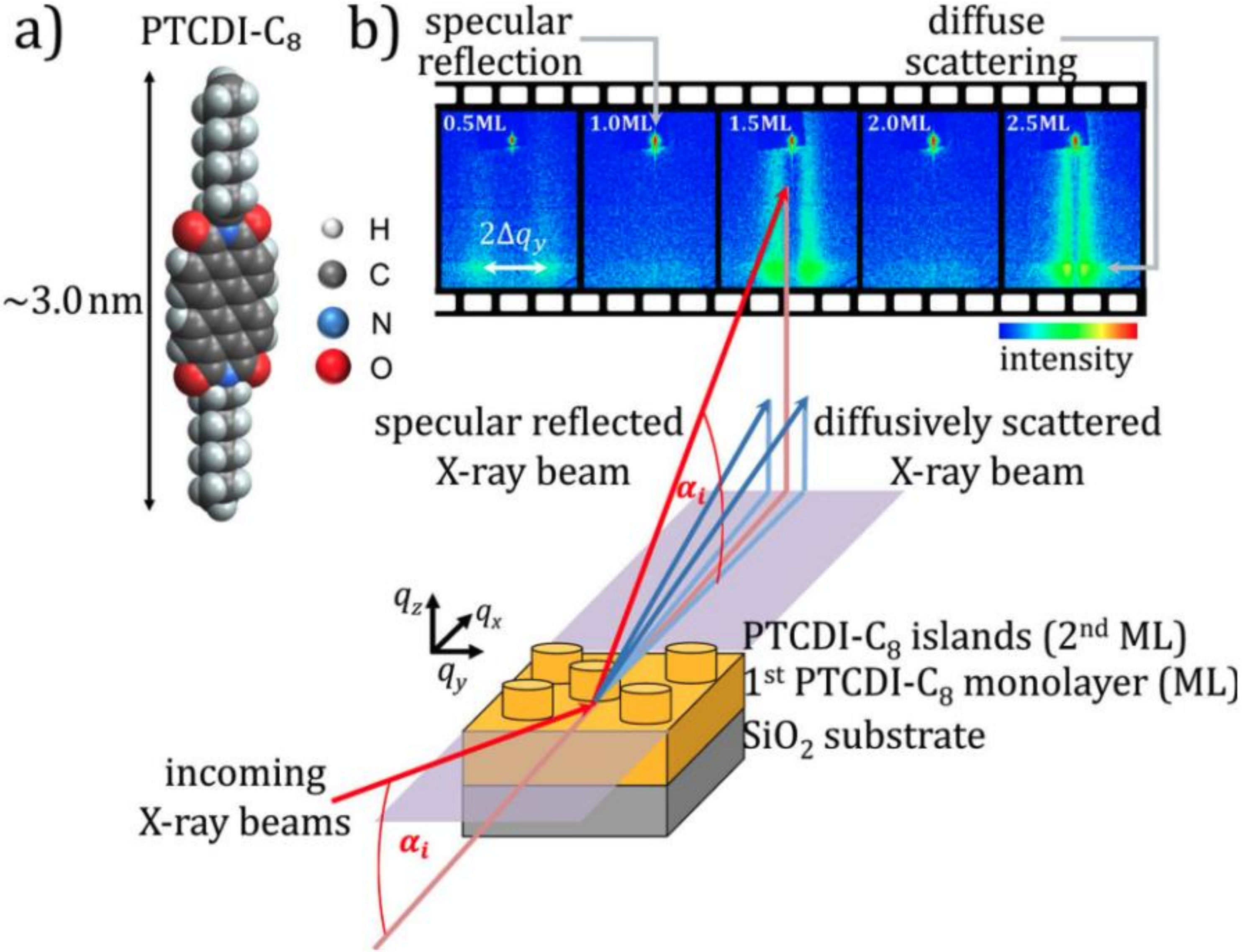
$n = 1 - \delta + i\beta$
$(material)$

Scattering from rough surfaces



*P. Müller-Buschbaum, Polymer Journal **34** 892 (2013)*

Scattering from rough surfaces



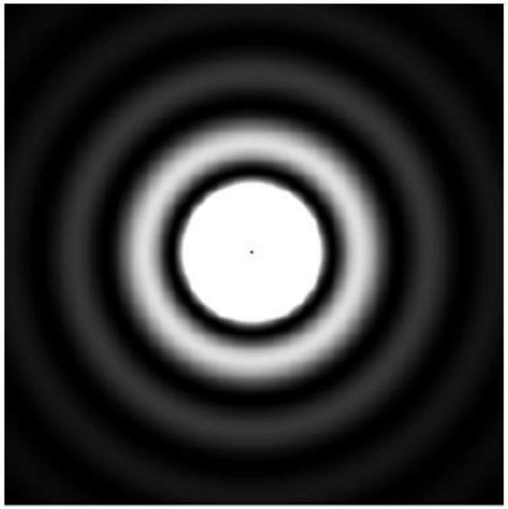
A. Zykov et al, J. Chem. Phys. ***146****, 052803 (2017)*

Light microscopy

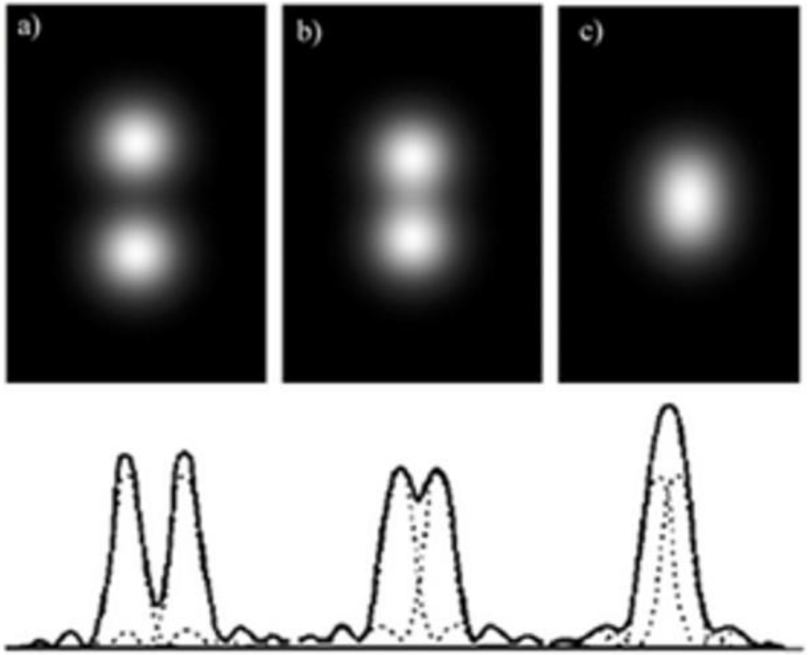
Rayleigh criterion equation (resolution): $\Delta= k_1 \cdot \frac{\lambda}{NA} \sim \frac{\lambda}{n \cdot \sin\theta}$

Due to diffraction effects (Airy disc), the minimal distance between to objects is $\lambda/2$, so that the objects can be still resolved.

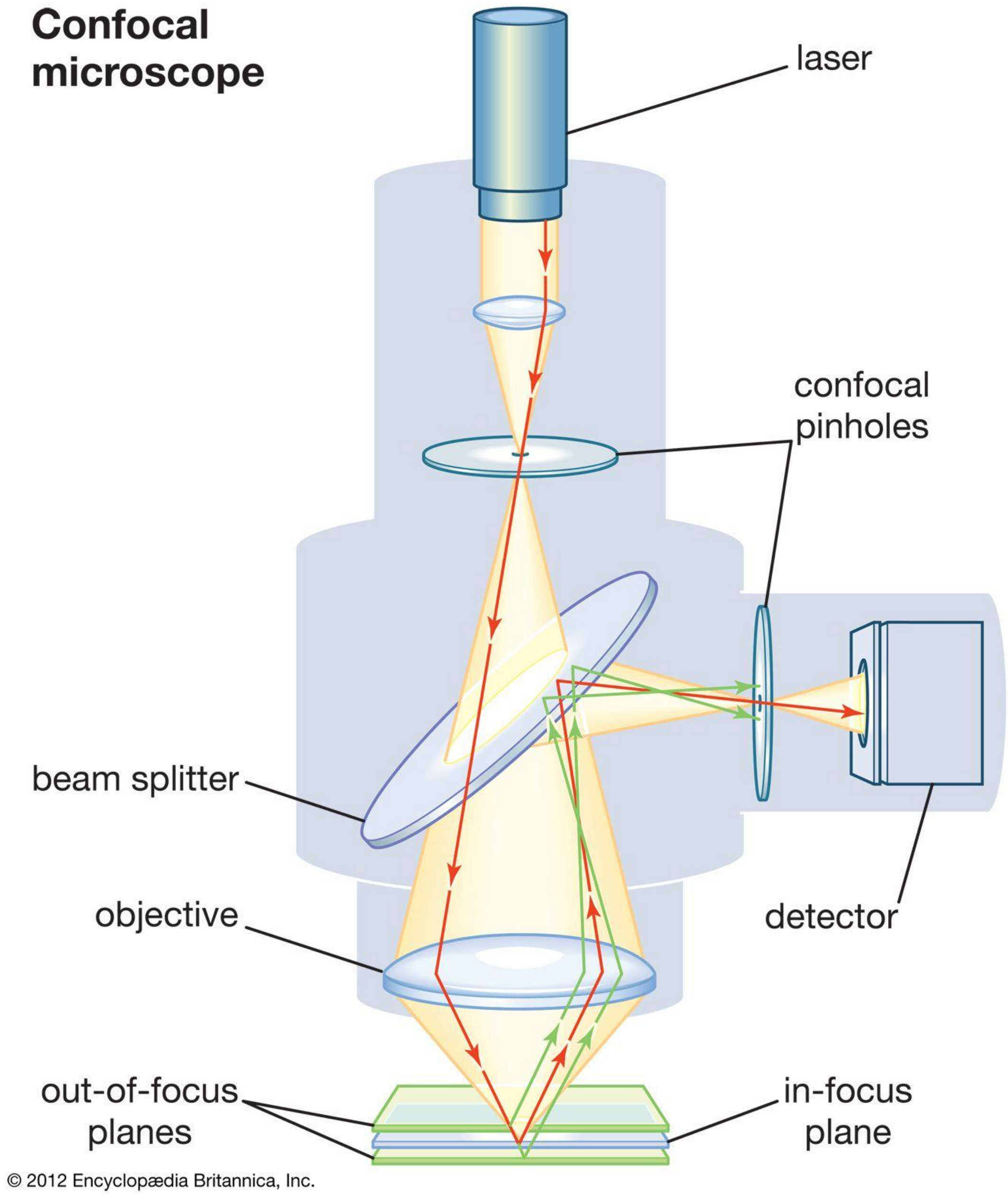
(a)



(b)



Confocal microscopy



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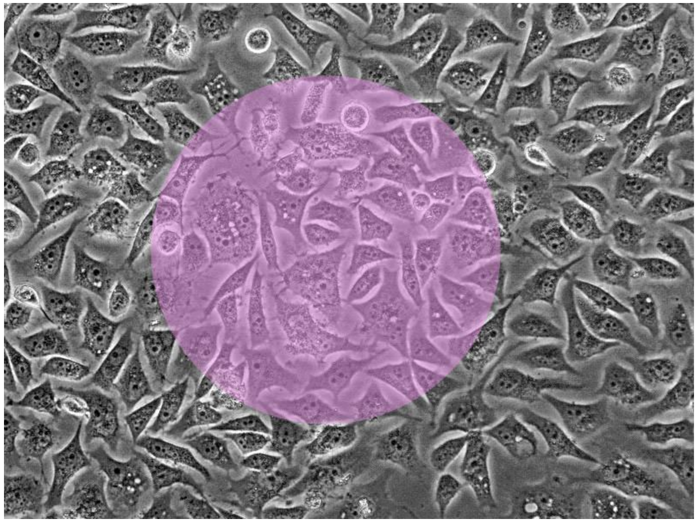
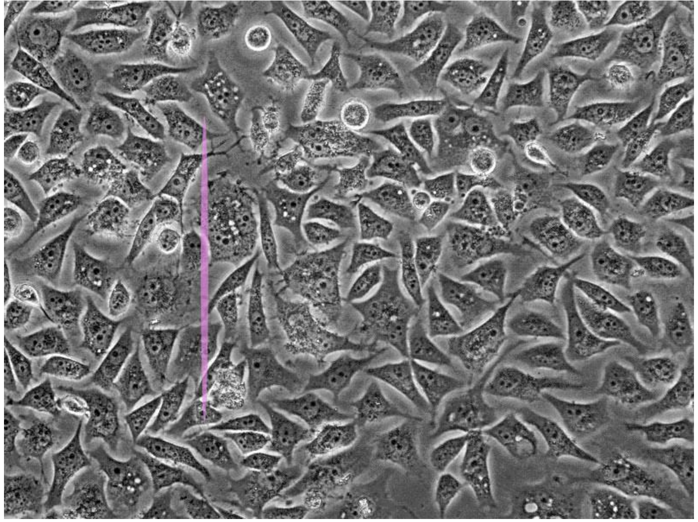
Standard fluorescence microscopy

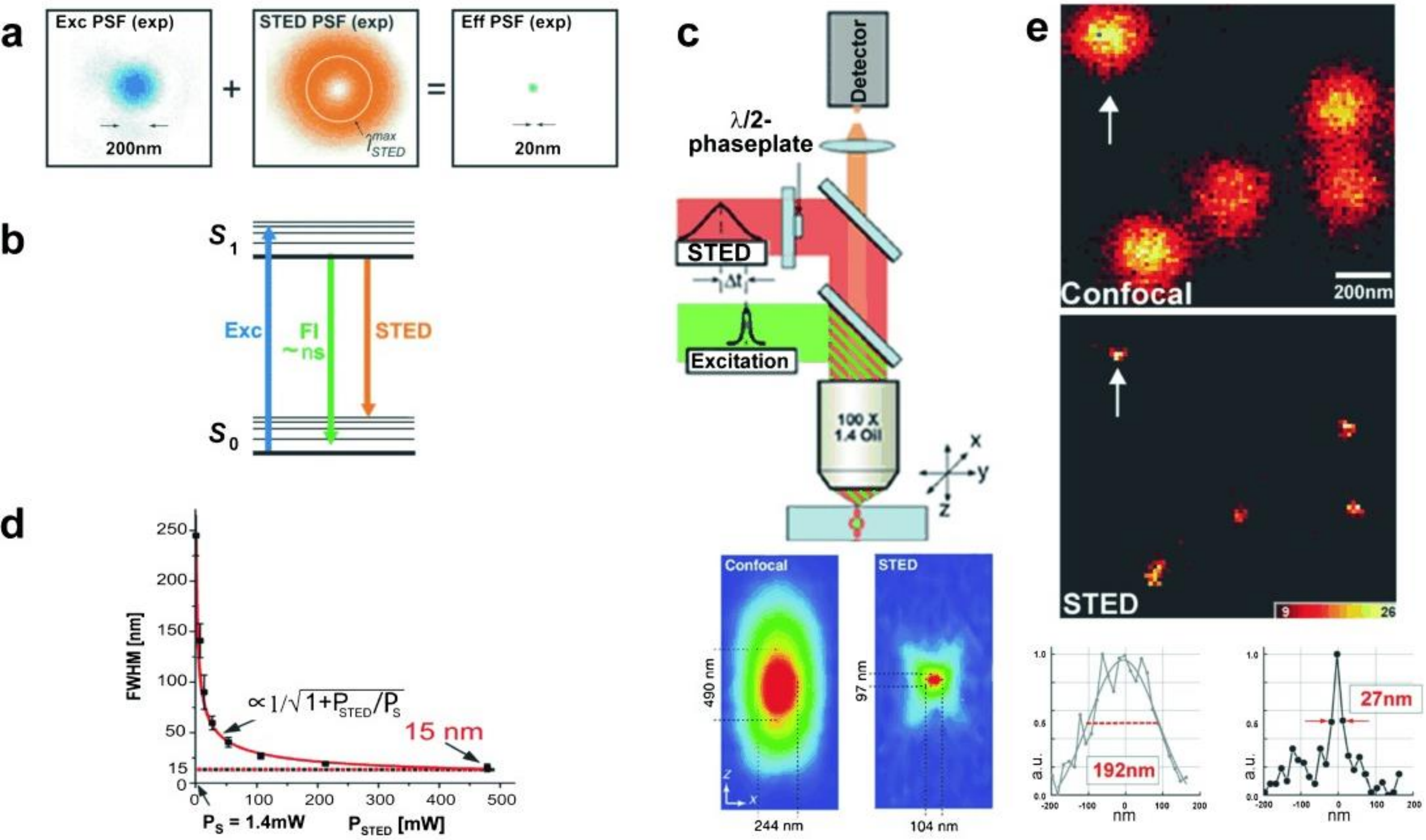


Confocal microscopy



www.cherrybiotech.com

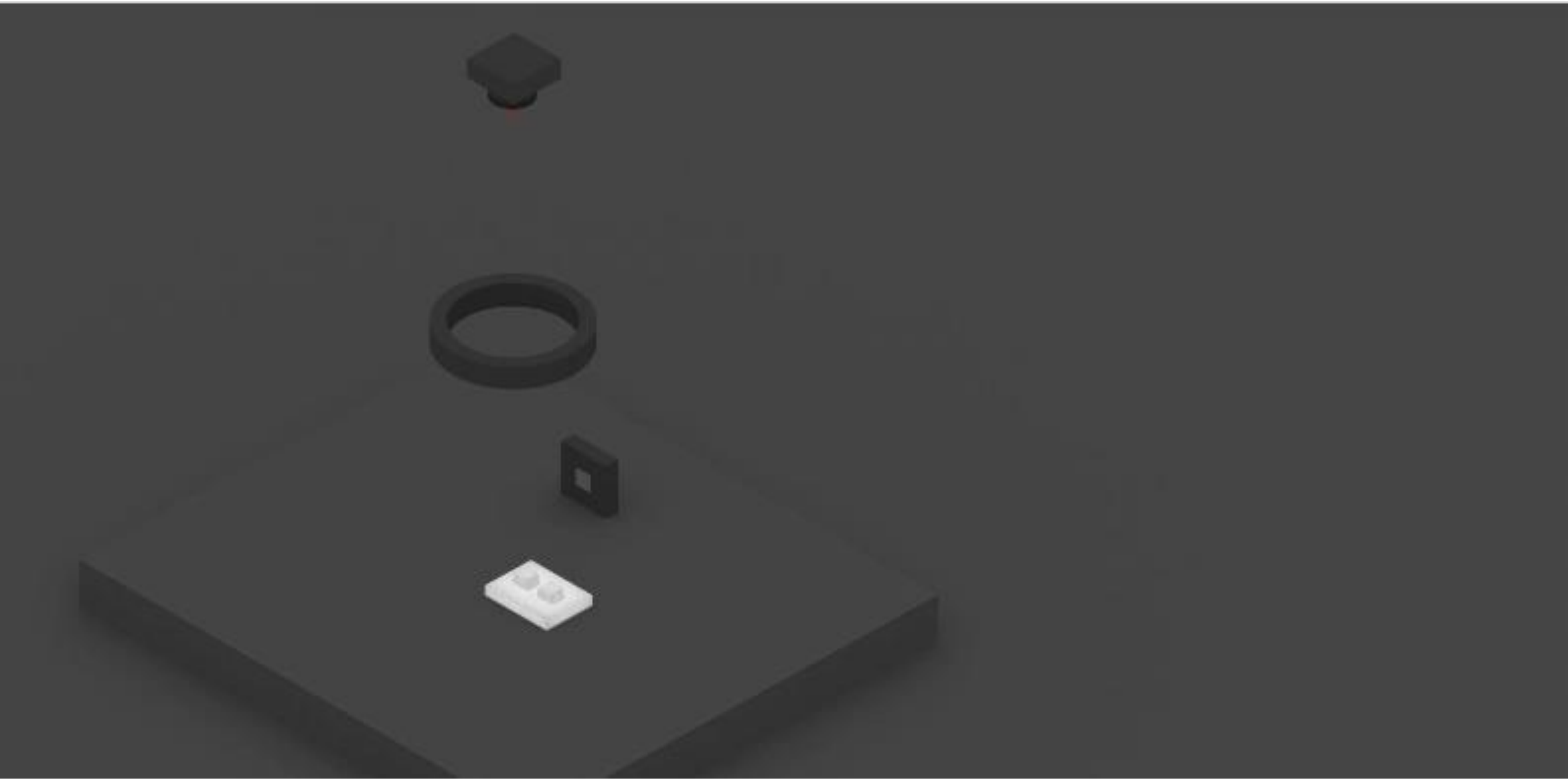
Stimulated emission depletion microscopy



Möckl et al., Angew. Chem. Int. Ed. 53, 13972 (2014)

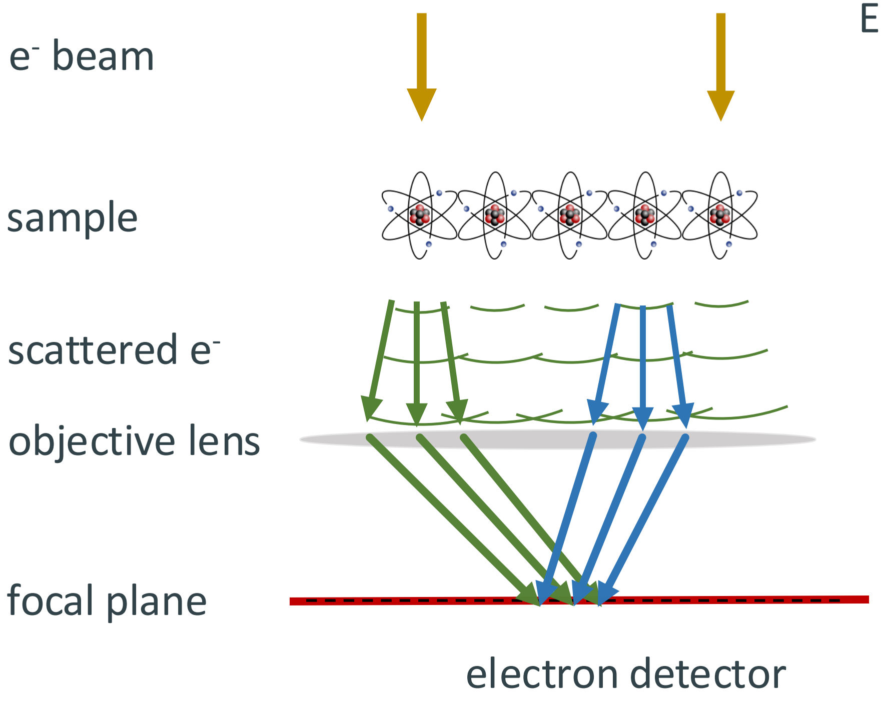
Scanning electron microscopy (SEM)

Electrons (E=5-15 keV) are focused to a spot of 1-2 nm. The beam scans the sample's surface and the scattered electrons are recorded by a detector.



Transmission electron microscopy (TEM)

Diffraction mode



e^- beam

sample

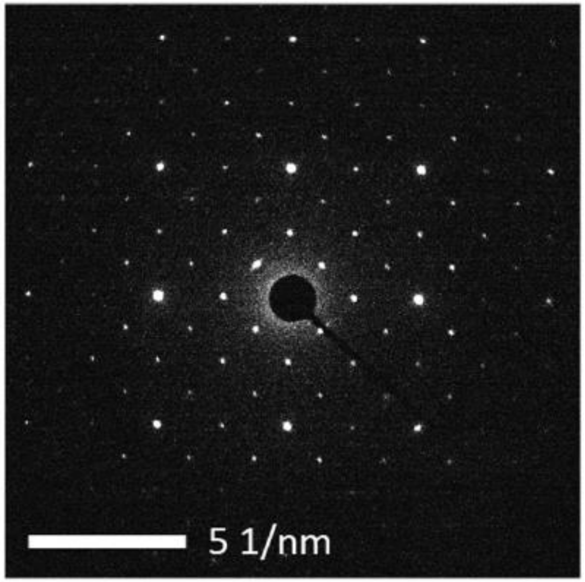
scattered e^-

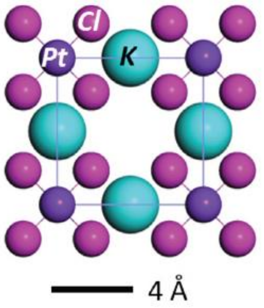
objective lens

focal plane

electron detector

Electron diffraction from K_2PtCl_4 nanoparticle

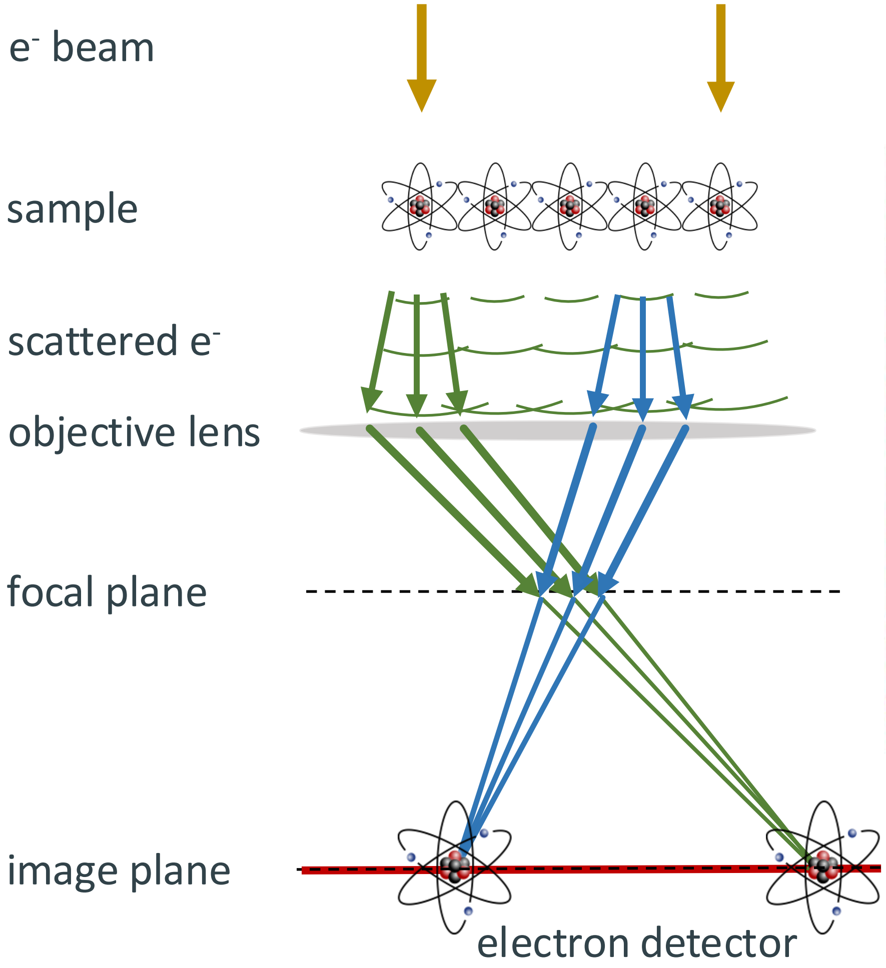




Gao et al., Sci. Adv. 2019; **5** : eaau9590

Transmission electron microscopy (TEM)

Imaging mode



e^- beam

sample

scattered e^-

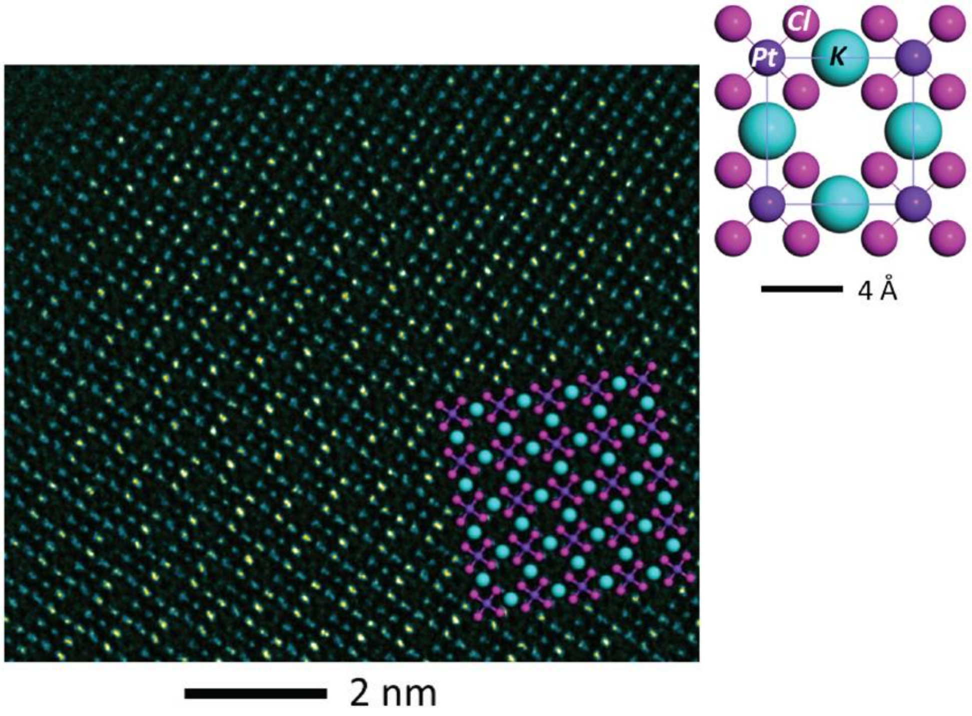
objective lens

focal plane

image plane

electron detector

Real-space image of K_2PtCl_4 crystal lattice with an overlaid atomic model



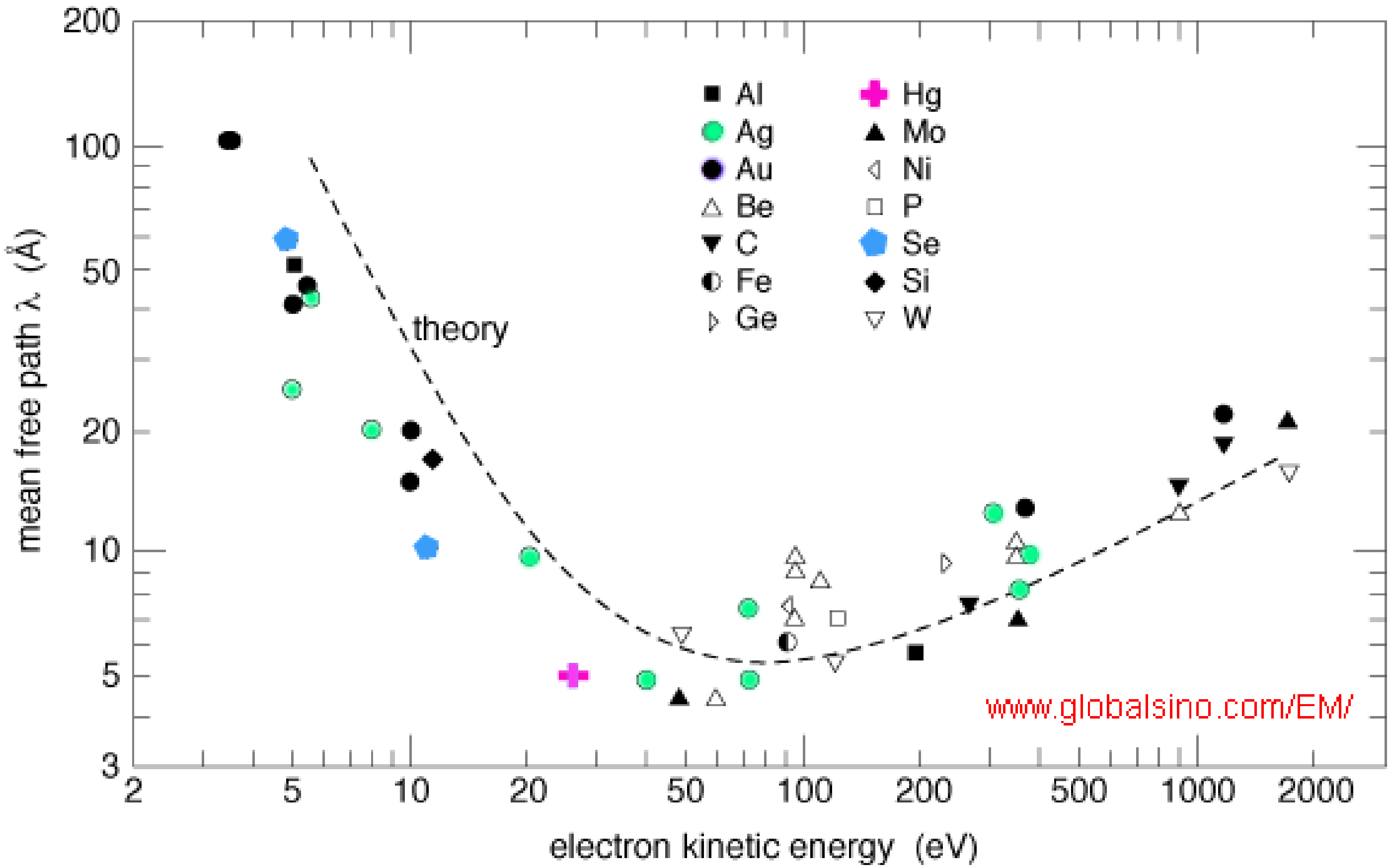
Gao et al., Sci. Adv. 2019; **5** : eaau9590

Electron inelastic mean free path (IMFP)

$$I(d) = I_0 \exp\left(-\frac{d}{\lambda(E)}\right)$$

Decay of the electron intensity in the media due to inelastic scattering

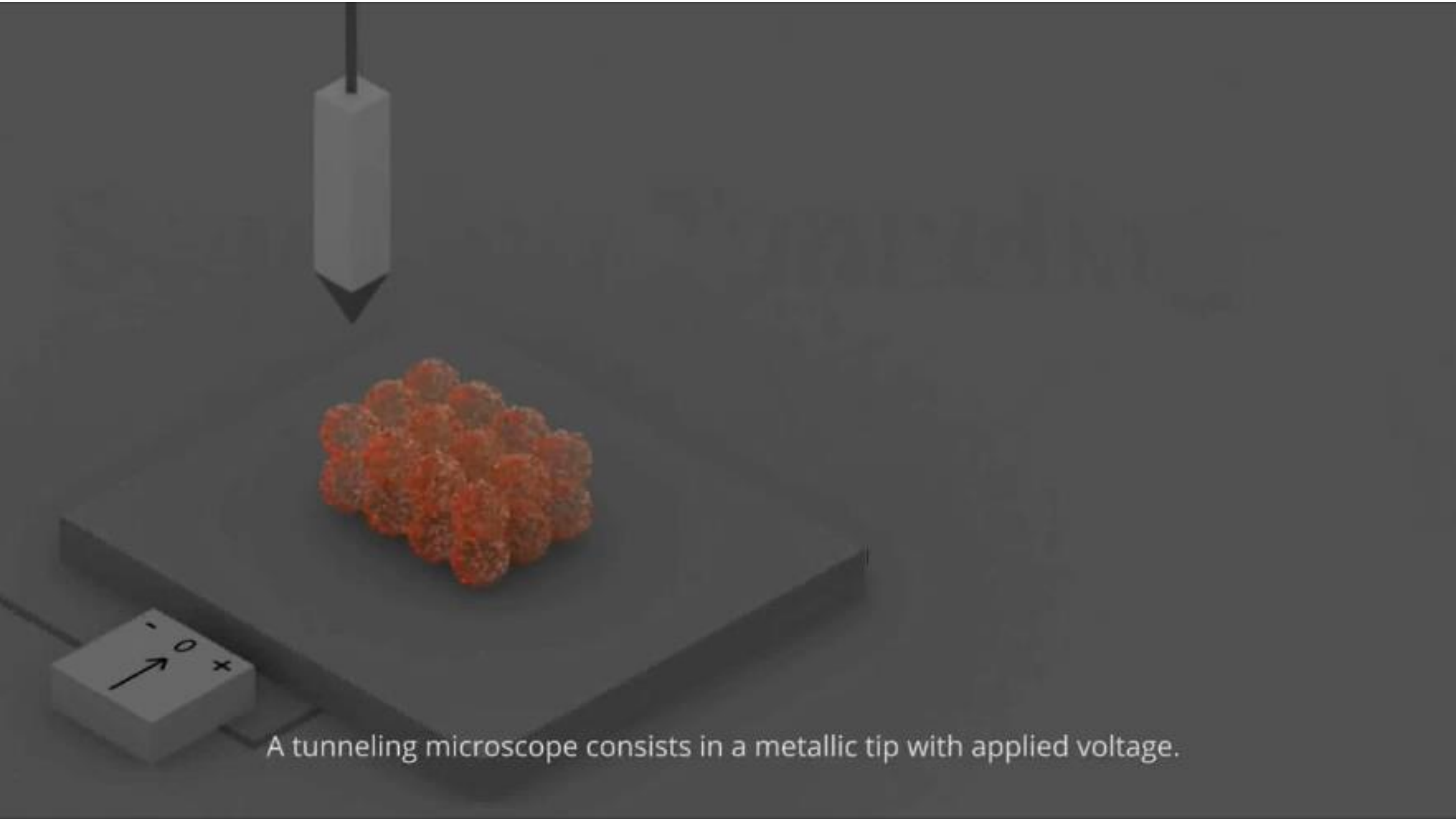
$$\lambda[monolayers] = \frac{538}{E^2[eV^2]} + 0.41\sqrt{a[nm]E[eV]}$$



M. Seah and W. Dench, Surf. Interface Anal., **1** 2-11 (1979)

Scanning tunneling microscopy (STM)

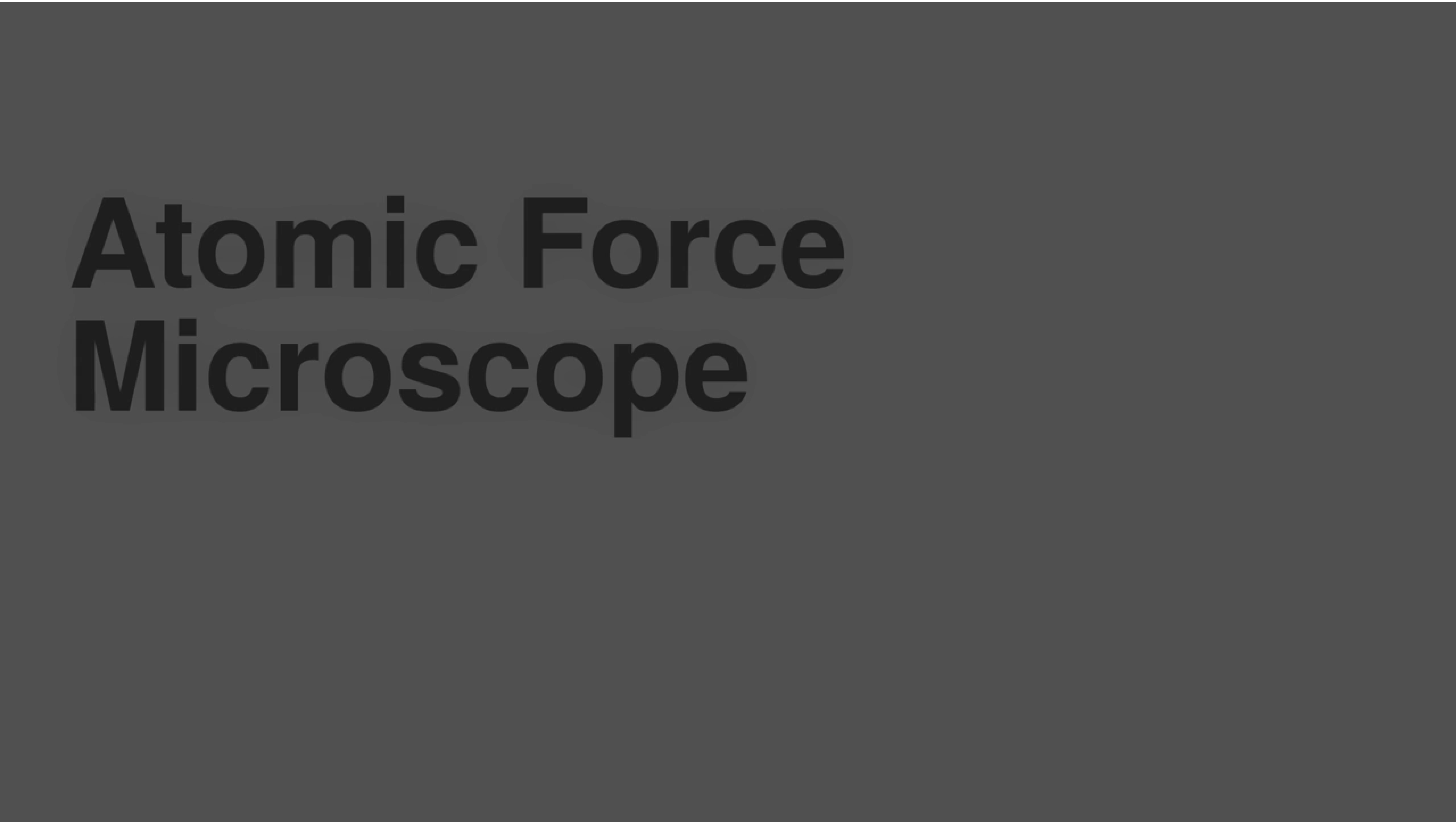
Measures quantum tunneling current between the atom and the tip.



A tunneling microscope consists in a metallic tip with applied voltage.

quantummadesimple.com

Atomic Force Microscopy (AFM)



Atomic Force Microscope

Incomplete list of microscopy techniques

Large field of view

Visible light microscopy
Transmission electron microscopy (TEM) in imaging mode

Small field of view

Confocal microscopy
Stimulated emission depletion (STED) microscopy
Scanning electron microscopy (SEM)
Scanning tunneling microscopy (STM)
Atomic force microscopy (AFM)
Magnetic force microscopy (MFM)
Electrostatic force microscopy (EFM)
Scanning near-field optical microscopy (SNOM)

Scanning probe microscopy (SPM)

Diffraction + microscopy

(imaging in reciprocal space + scanning)

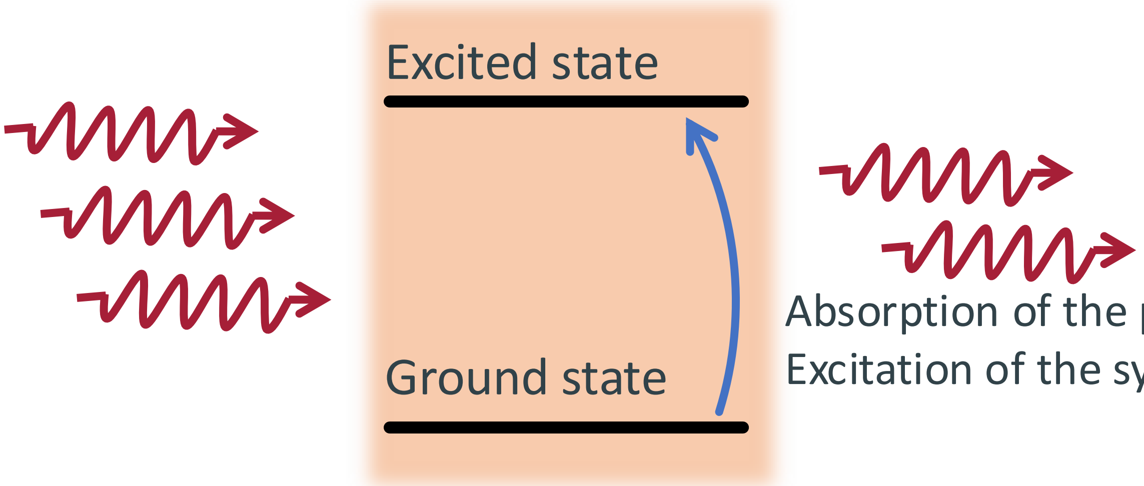
Scanning Transmission Electron Microscopy (STEM)
Scanning Transmission X-ray Microscopy (STXM)

Absorption spectroscopy

Probe

System

Measured spectrum



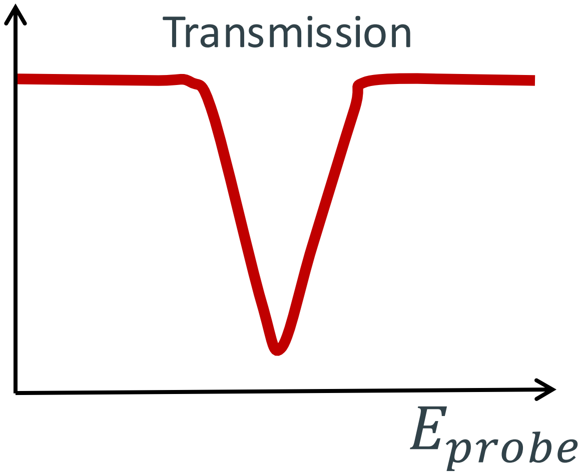
Excited state

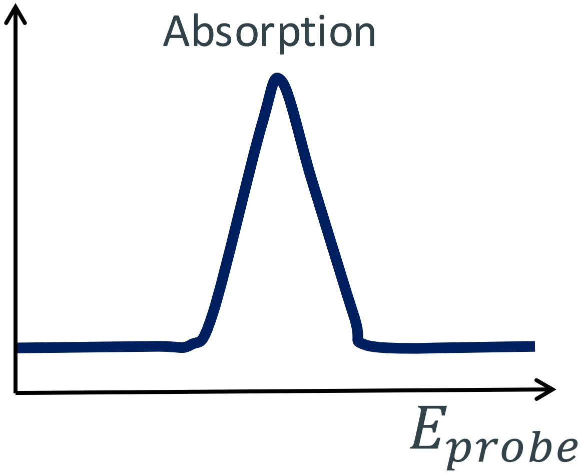
Ground state

Absorption of the probe

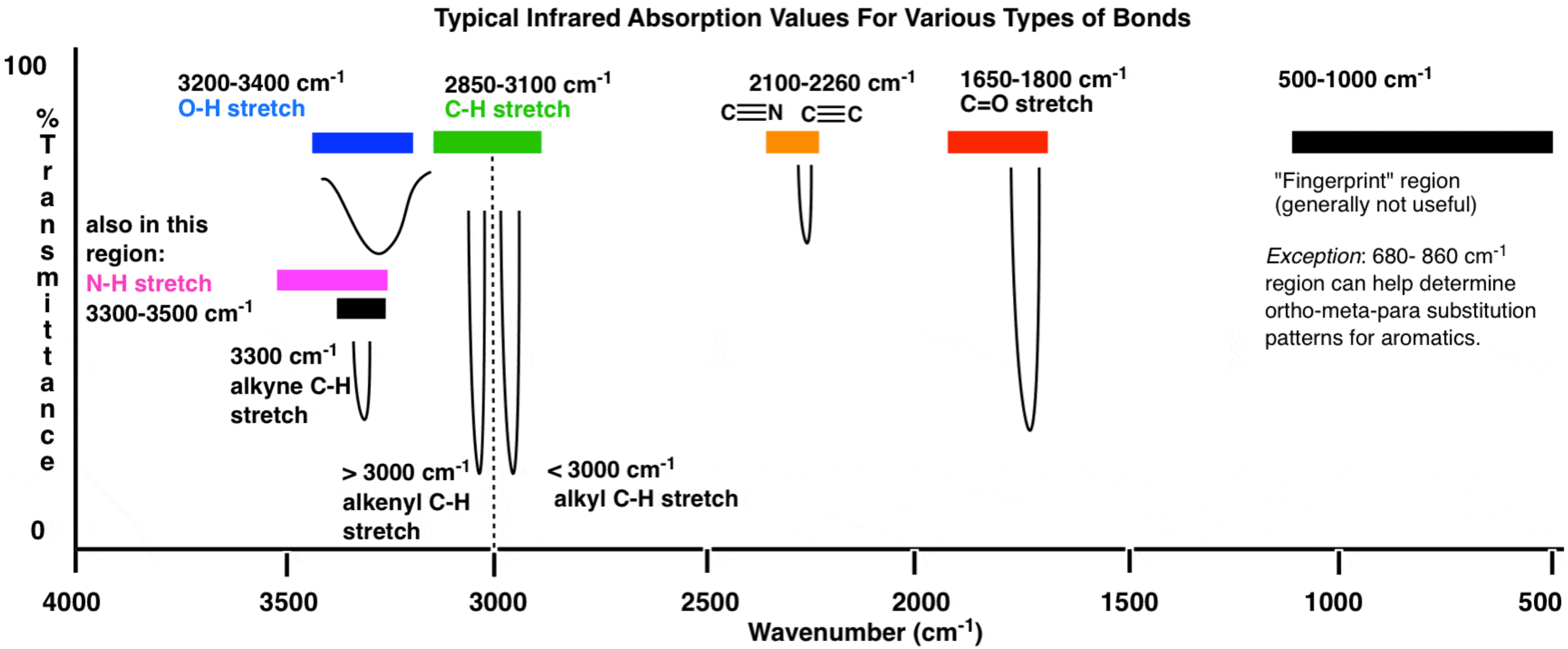
Excitation of the system

- Electromagnetic wave



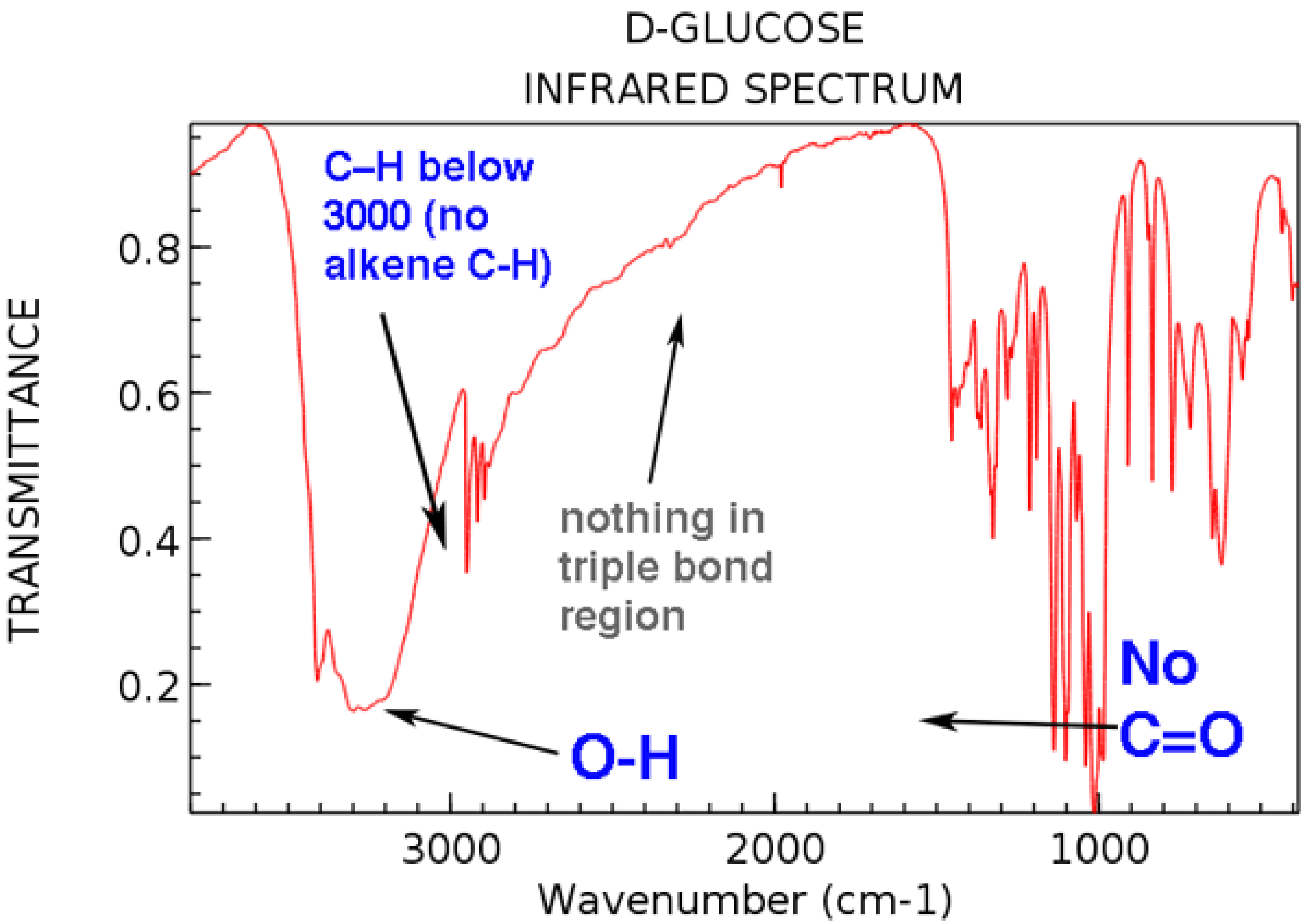


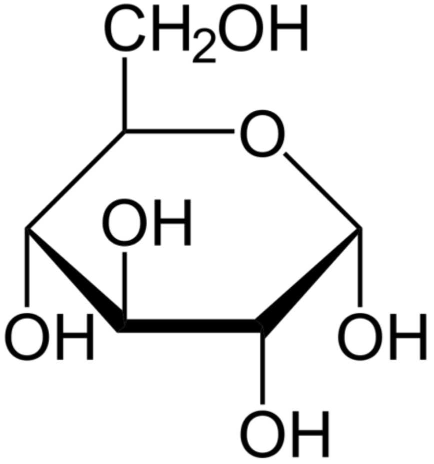
Infrared spectroscopy



https://www.masterorganicchemistry.com/2016/11/23/quick_analysis_of_ir_spectra/

Infrared spectroscopy



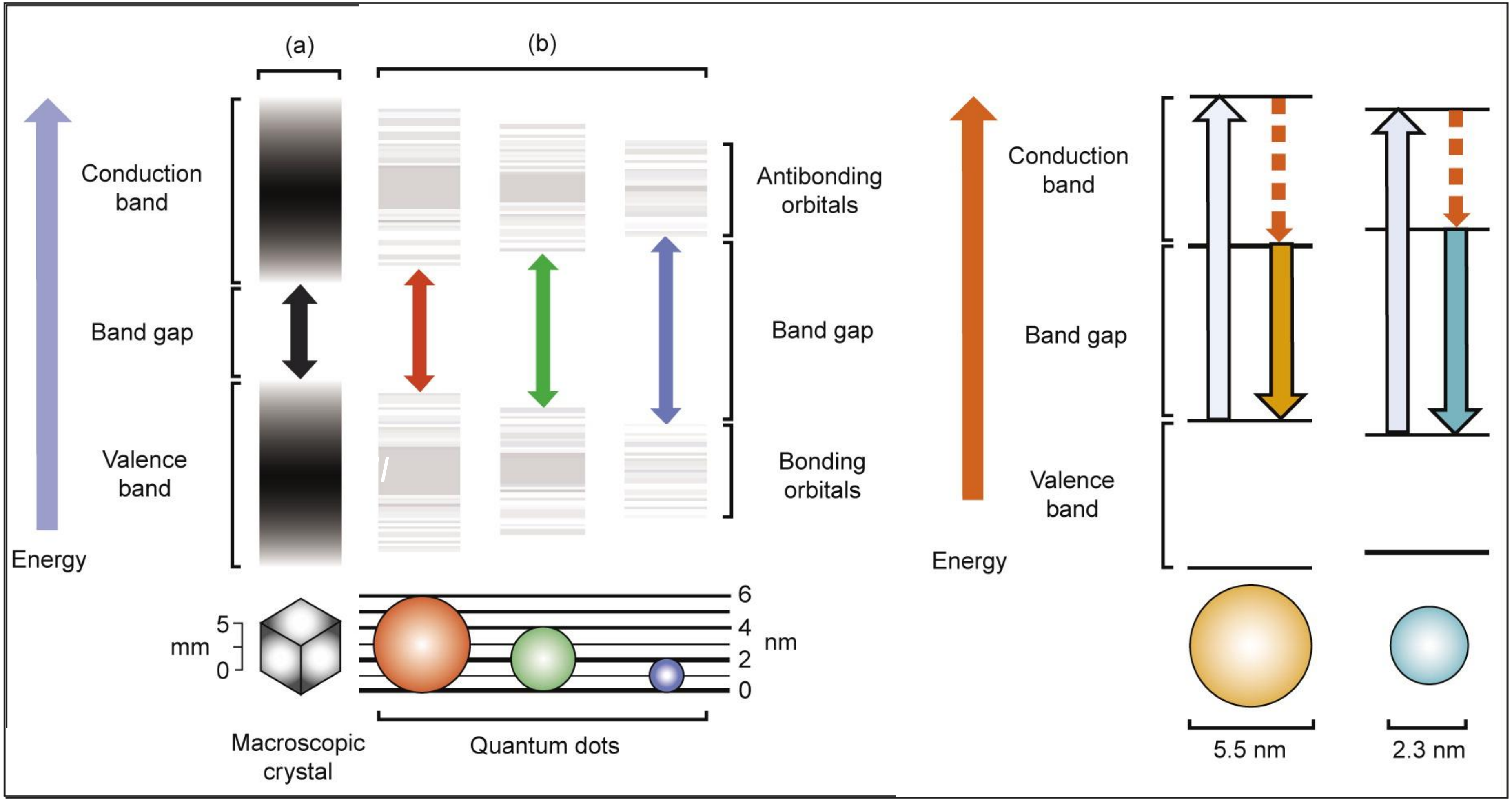


https://www.masterorganicchemistry.com/2016/11/23/quick_analysis_of_ir_spectra/

Ultraviolet-visible spectroscopy

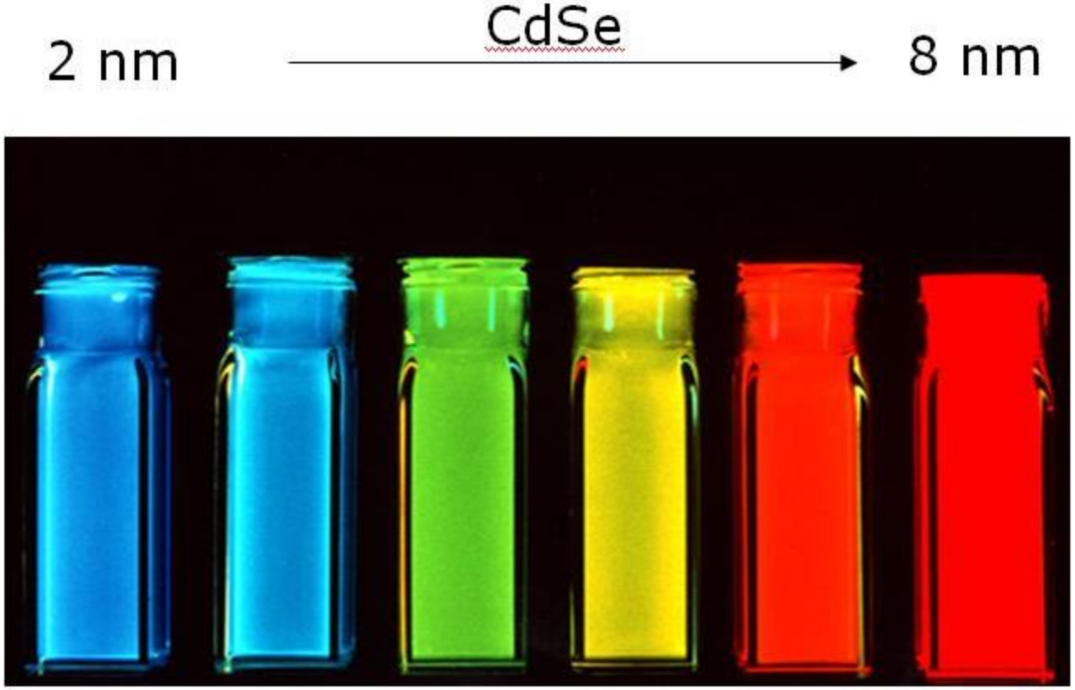
Probes electronic transitions; can be used for qualitive and quantitative analysis.

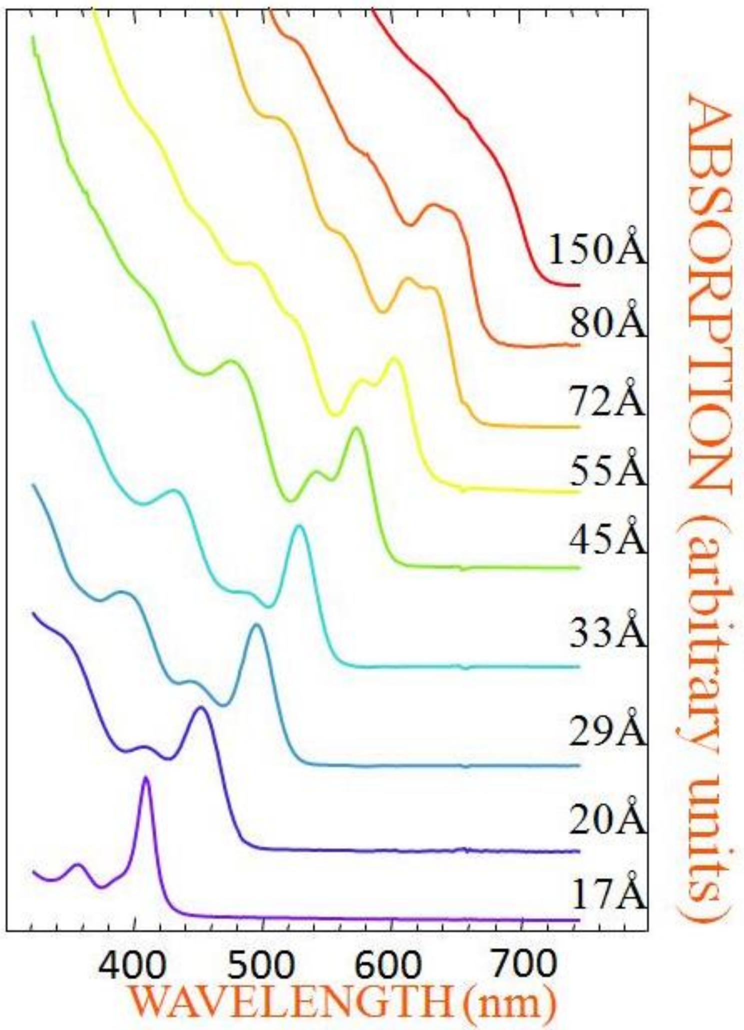
Example: determination of nanoparticle size by absorption and/or fluorescence



D. Ioannou and D. K. Griffin , *Nano Rev.*, **1** , 5117 (2010)

Ultraviolet-visible spectroscopy



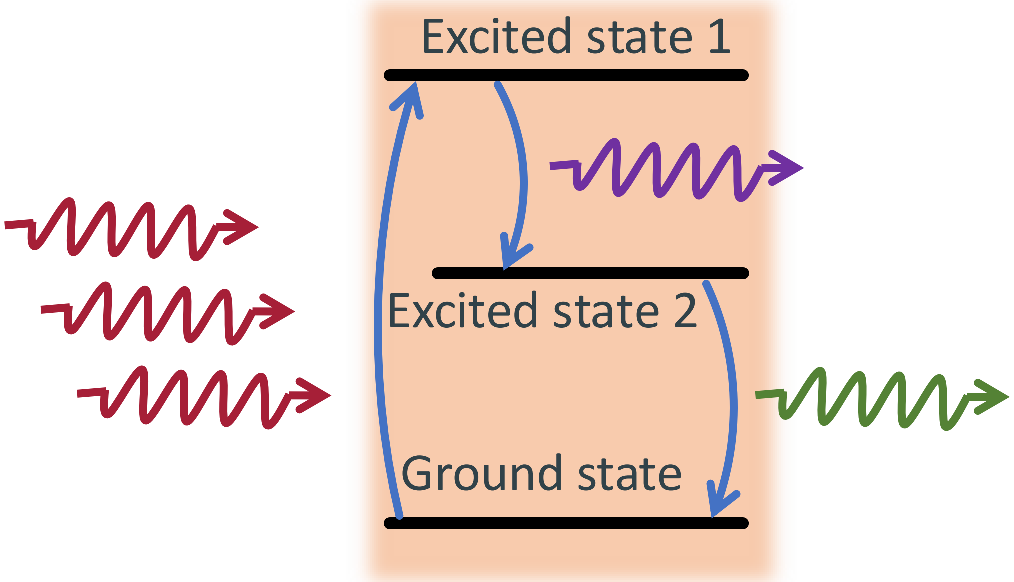


https://serc.carleton.edu/details/images/180093.htm

Emission spectroscopy

Probe

System

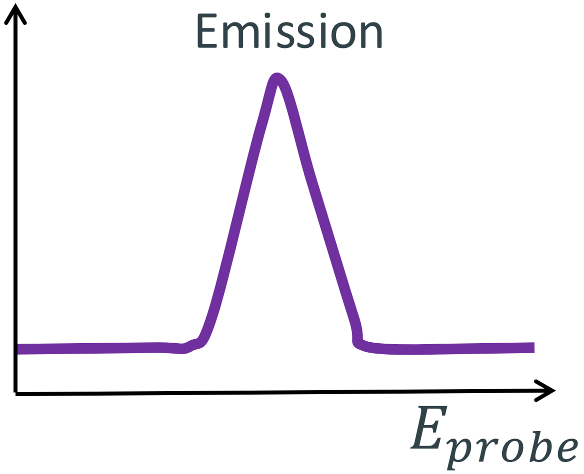


Excited state 1

Excited state 2

Ground state

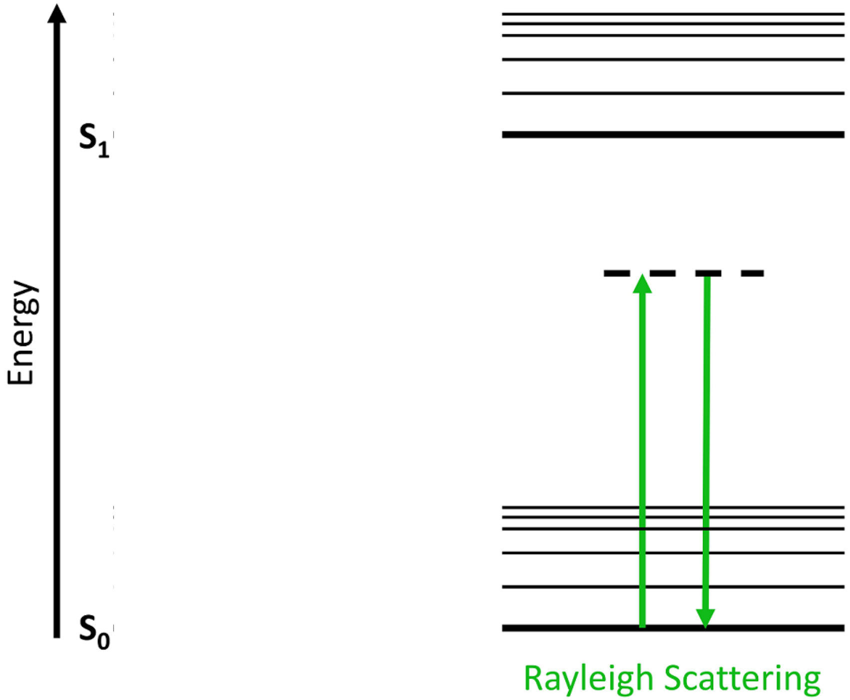
Measured spectrum

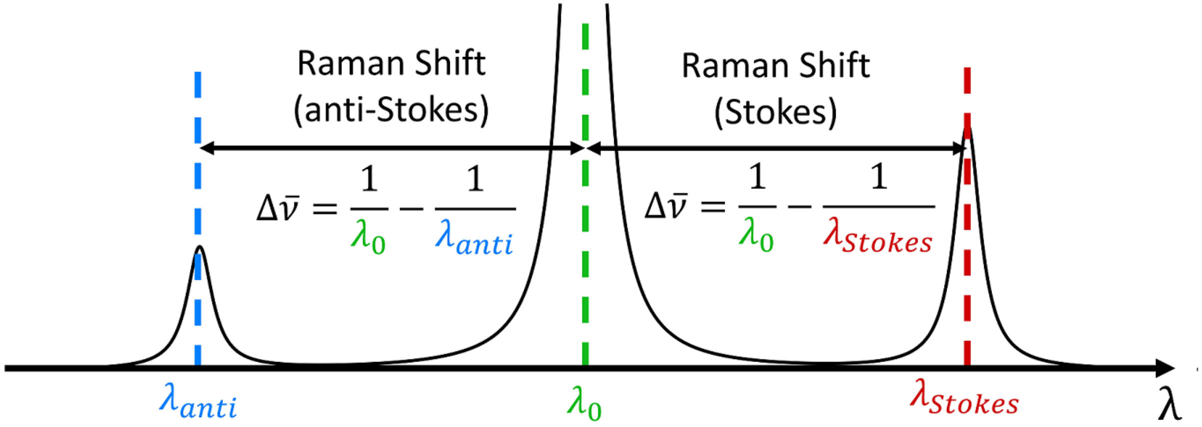


Emission is not necessary of the same nature as the probe.
For example, it can be:

- incoming probe: x-ray
- emission: photoelectron

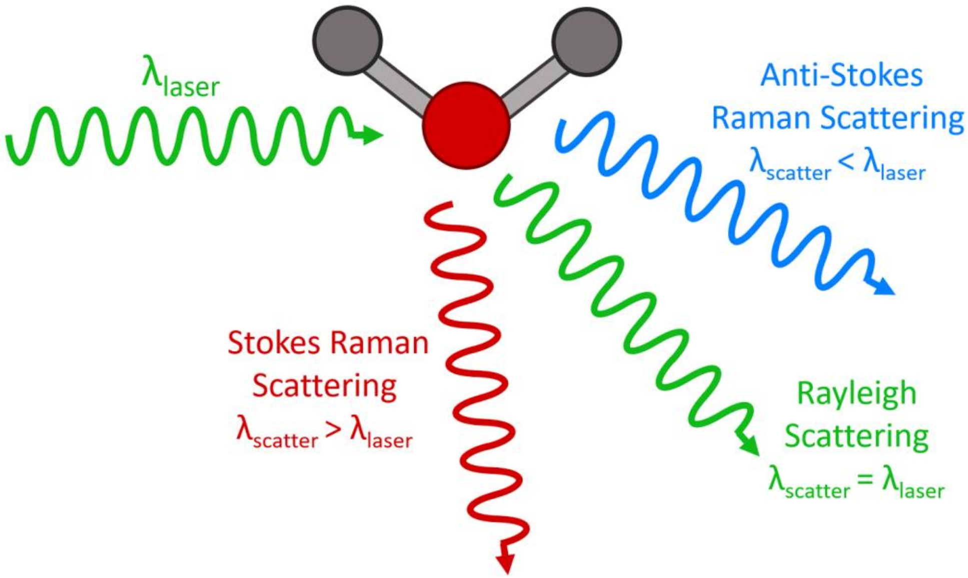
Raman spectroscopy

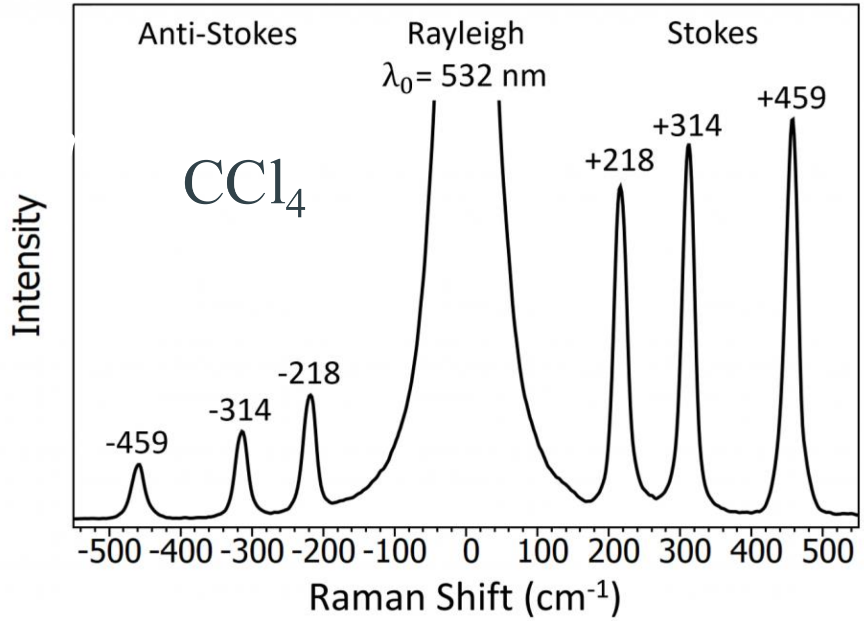


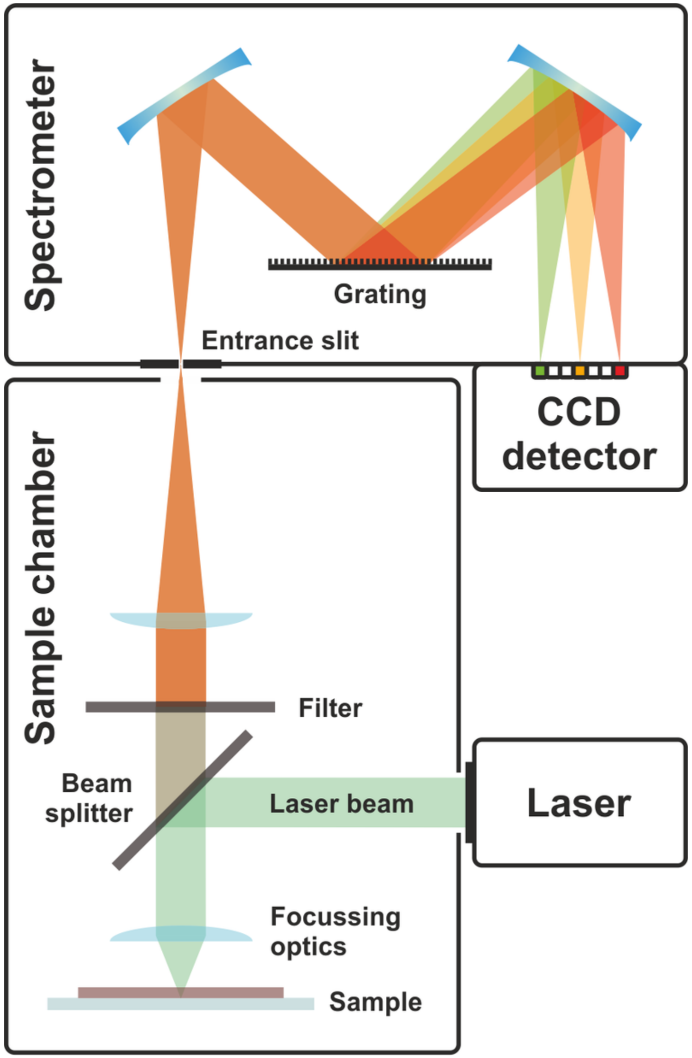


https://www.edinst.com/blog/what-is-raman-spectroscopy/

Raman spectroscopy





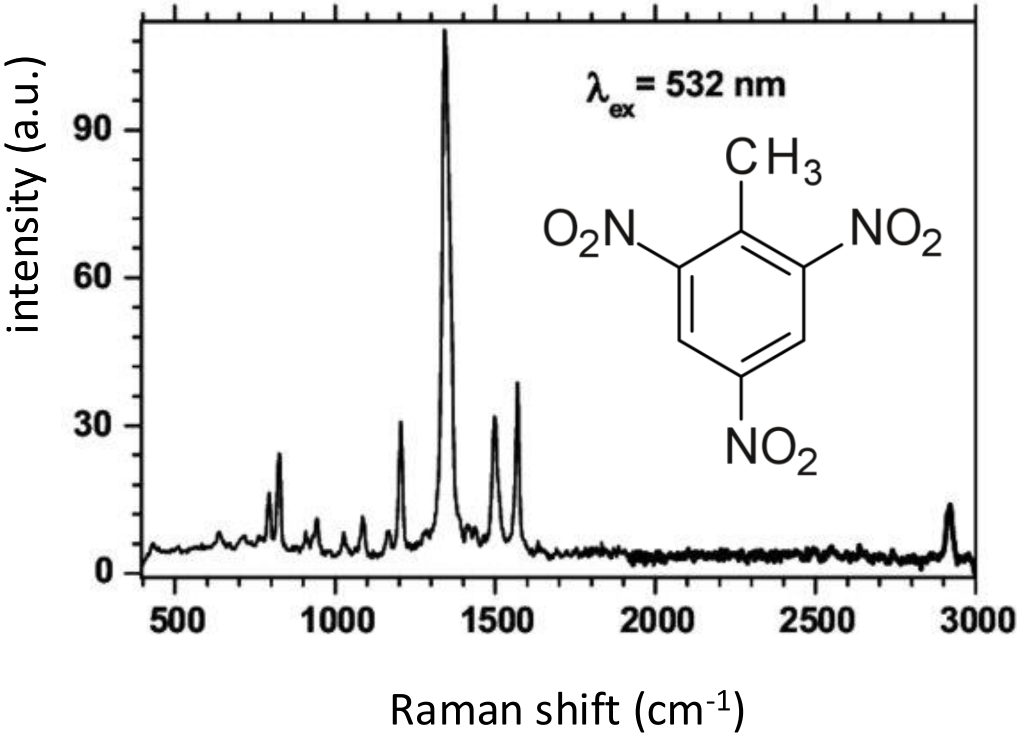


T. Schmidt, P. Dariz, Heritage **2** 1662 (2019)

Raman spectroscopy

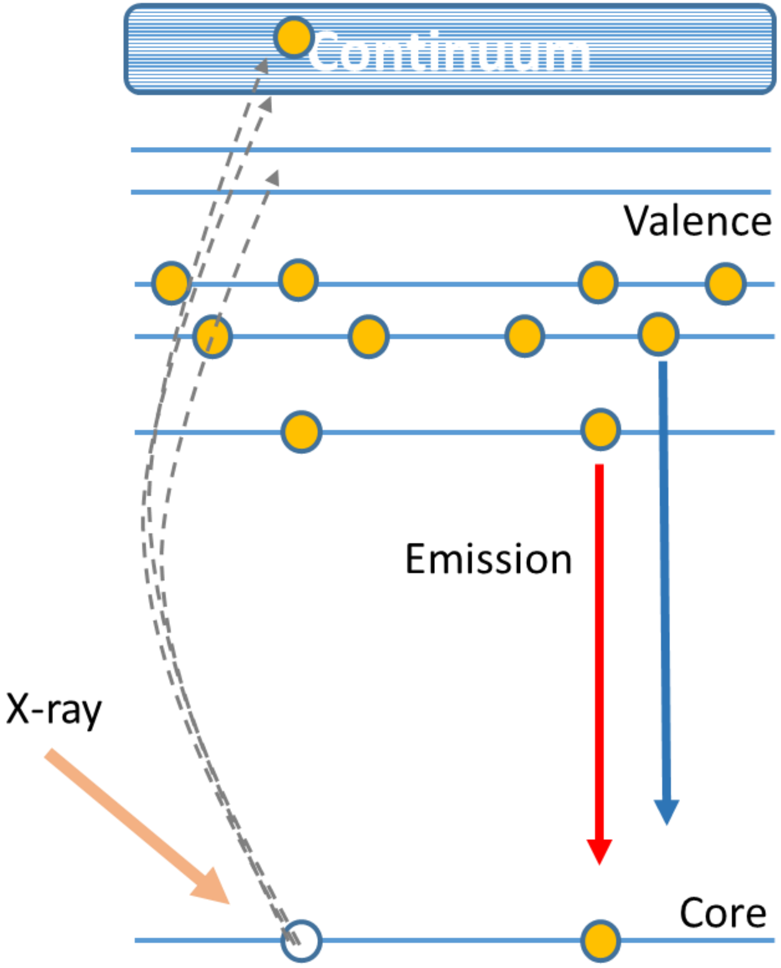
Functional group	Raman Shift (cm^{-1})
O-H	3600-3000
N-H	3500-3100
C-H	3100-2800
C≡C	2200-2100
C=O	1750-1700
C=C	1675-1600
C-C	1300-700
Aromatic Ring	1000-900
O-O	900-800
C-Cl	850-650

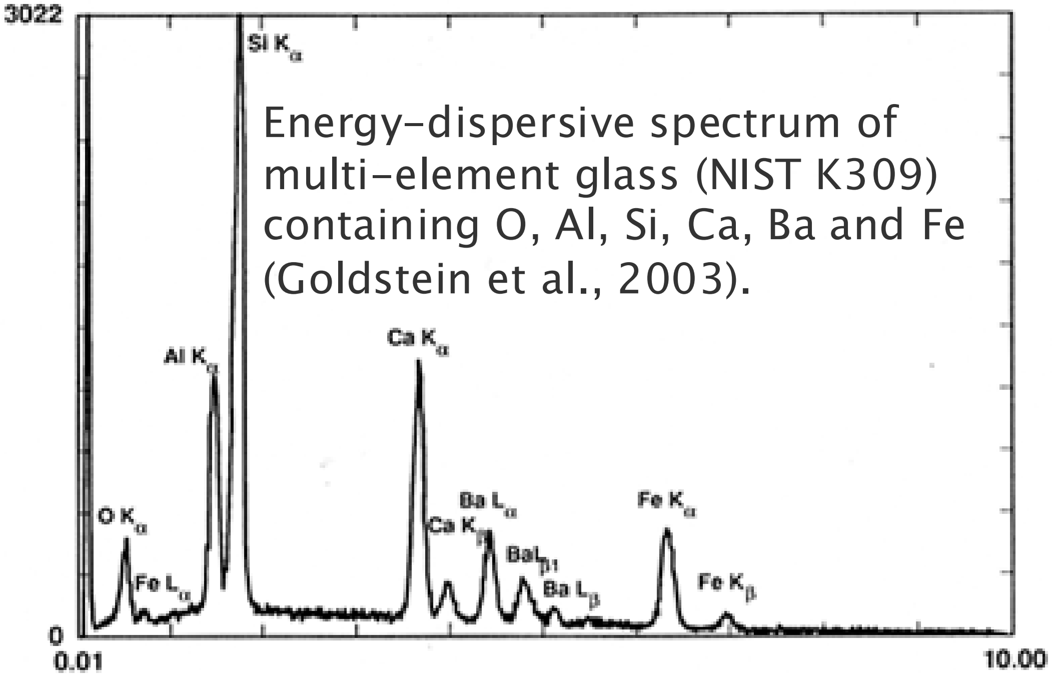
Raman spectrum for TNT



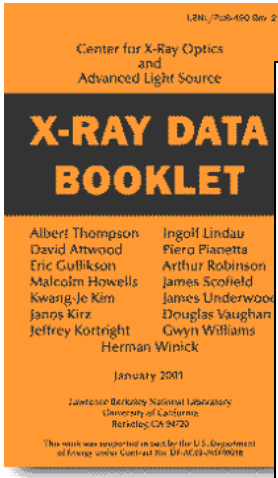
L. Nagli et al., Opt. Mater. **30** 1747 (2008)

X-ray fluorescence (XRF)





Energy-dispersive spectrum of multi-element glass (NIST K309) containing O, Al, Si, Ca, Ba and Fe (Goldstein et al., 2003).



Center for X-Ray Optics
and
Advanced Light Source

X-RAY DATA BOOKLET

Albert Thompson
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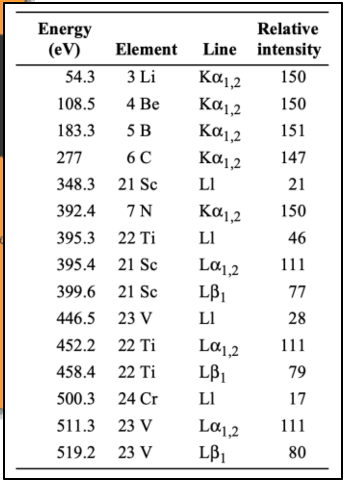
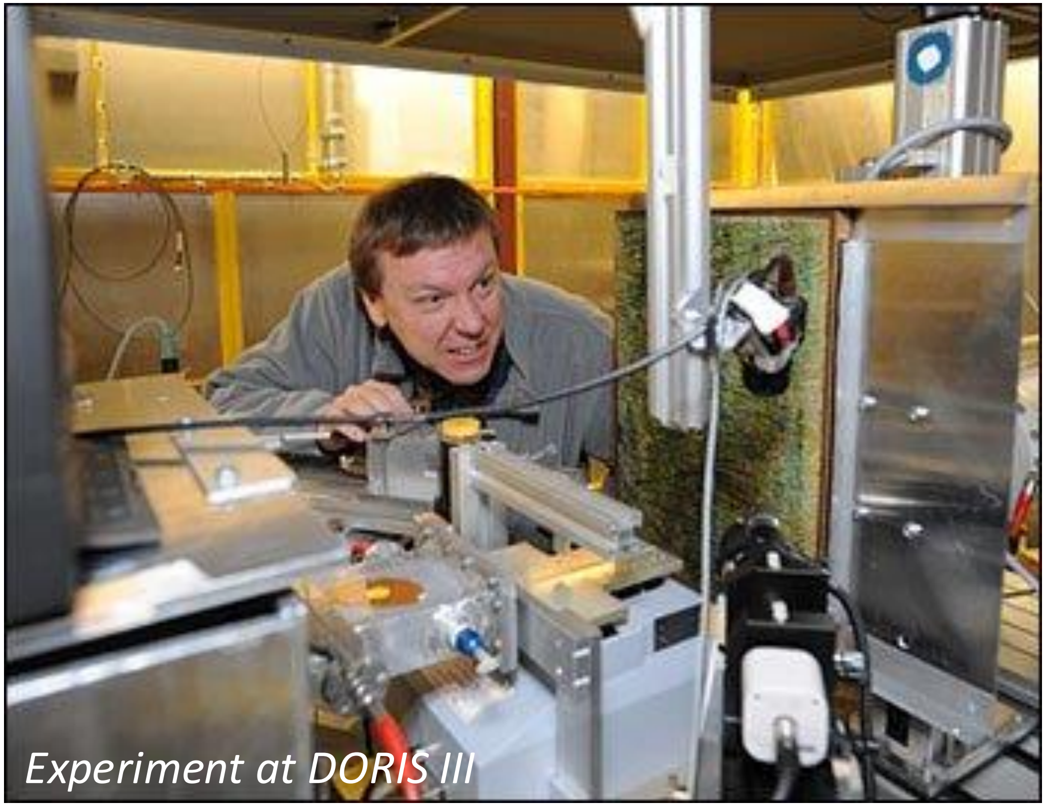


Energy (eV)	Element	Line	Relative intensity
54.3	3 Li	$K\alpha_{1,2}$	150
108.5	4 Be	$K\alpha_{1,2}$	150
183.3	5 B	$K\alpha_{1,2}$	151
277	6 C	$K\alpha_{1,2}$	147
348.3	21 Sc	Ll	21
392.4	7 N	$K\alpha_{1,2}$	150
395.3	22 Ti	Ll	46
395.4	21 Sc	$L\alpha_{1,2}$	111
399.6	21 Sc	$L\beta_1$	77
446.5	23 V	Ll	28
452.2	22 Ti	$L\alpha_{1,2}$	111
458.4	22 Ti	$L\beta_1$	79
500.3	24 Cr	Ll	17
511.3	23 V	$L\alpha_{1,2}$	111
519.2	23 V	$L\beta_1$	80

X-ray fluorescence (XRF)


Experiment at DORIS III

- Different paints contain different elements. For example, there is cobalt in «cobalt blue», mercury in «vermillion», antimony in «naples yellow», lead in «lead white».
- Using X-ray fluorescence one can measure the elemental map of a painting, and hence reconstruct the colors. Sometimes it reveals hidden pictures under the outer layer of the painting.

https://colourlex.com/project/x-ray-fluorescence/

X-ray fluorescence (XRF)

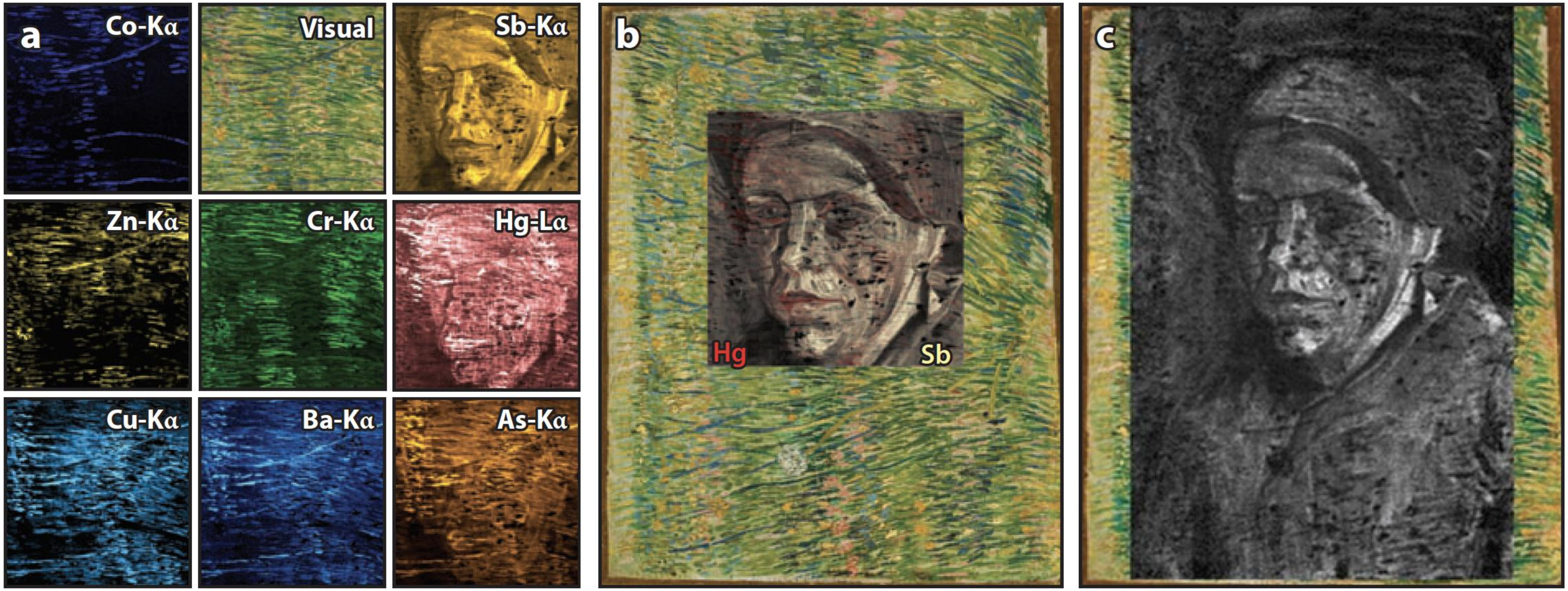


Figure 7

(*a*) Elemental maps recorded from Van Gogh's *Patch of Grass* (Kröller–Müller Museum, Otterlo, Netherlands) with macroscopic X-ray fluorescence (MA-XRF) scanning at beam line L (DORIS III synchrotron facility, Hamburg, Germany). (*b*) Reconstruction of the flesh tones of the hidden head of a woman, obtained by combining the Sb (*off-white*) and Hg (*red*) distributions mounted on a photograph of the painting. (*c*) Sb distribution obtained by mobile MA-XRF of (almost) the entire painting.

K. Janssens et al., Annual Review of Analytical Chemistry (2008) 6(1):399-425
J. Dik et al., *Anal. Chem.* 2008, 80, 16, 6436–6442

X-ray photoemission spectroscopy (XPS)

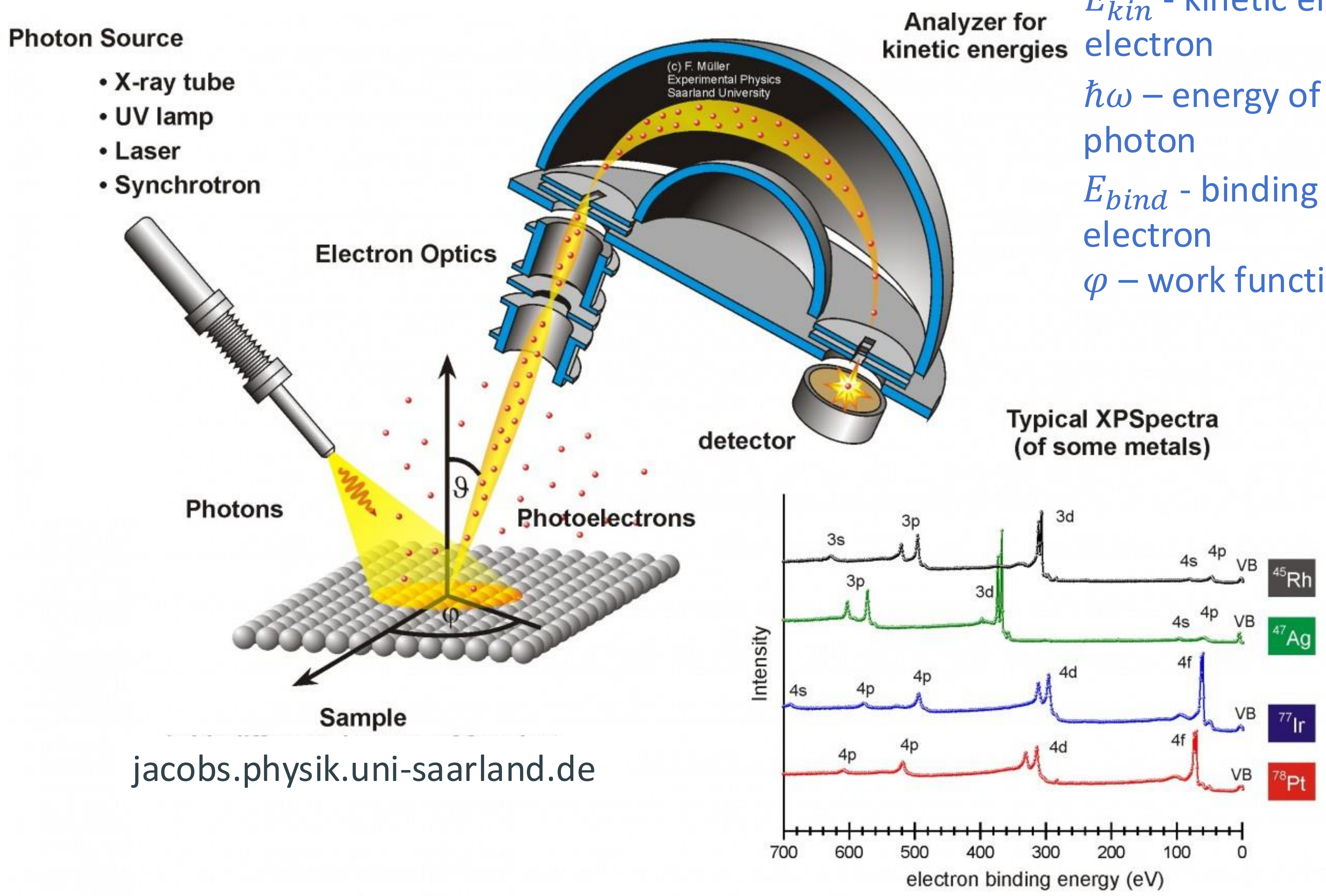
$$E_{kin}^{e} = \hbar\omega - E_{bind} - \varphi$$

E_{kin}^{e} - kinetic energy of an electron

$\hbar\omega$ – energy of an incident photon

E_{bind} - binding energy of an electron

φ – work function



jacobs.physik.uni-saarland.de

Chemical shift

$$E_{kin}^{e} = \hbar\omega - E_{bind} - \varphi$$

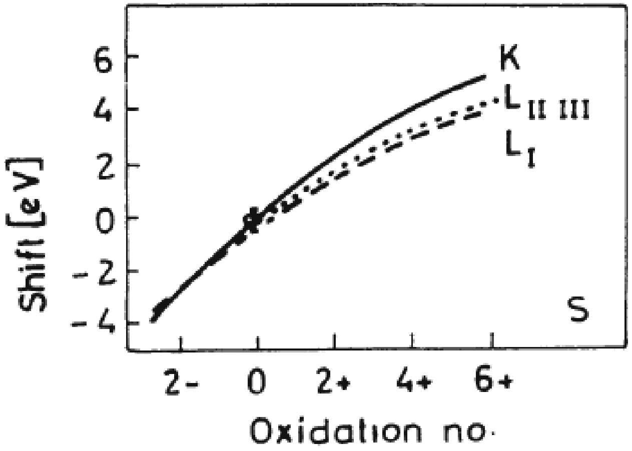
It is possible to determine the oxidation state of the elements and even the type of chemical bonds.

E_{kin}^{e} - kinetic energy of an electron

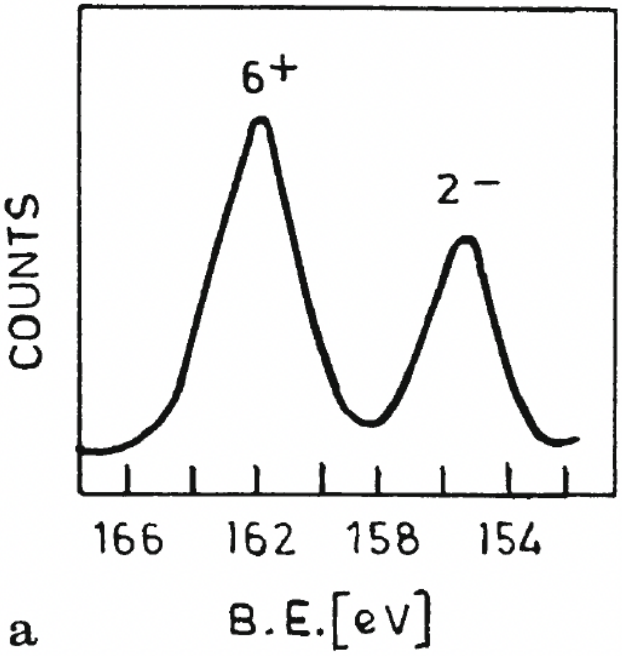
$\hbar\omega$ – energy of an incident photon

E_{bind} - binding energy of an electron

φ – work function

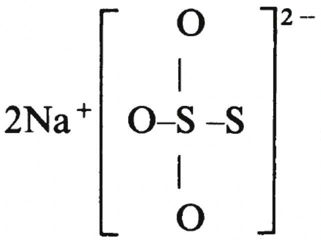


Chemical shifts of the K , L_1, $L_{2,3}$ levels of sulfur for different oxidation numbers, by photoelectron spectroscopy.



Sulphur spectrum from sodium thiosulphate by a photoelectron (2p level, Mg Kα line as source)

sodium thiosulphate



$$2Na^{+}\left[\begin{array}{c} O \\ | \\ O{-}S{-}S \\ | \\ O \end{array}\right]^{2-}$$

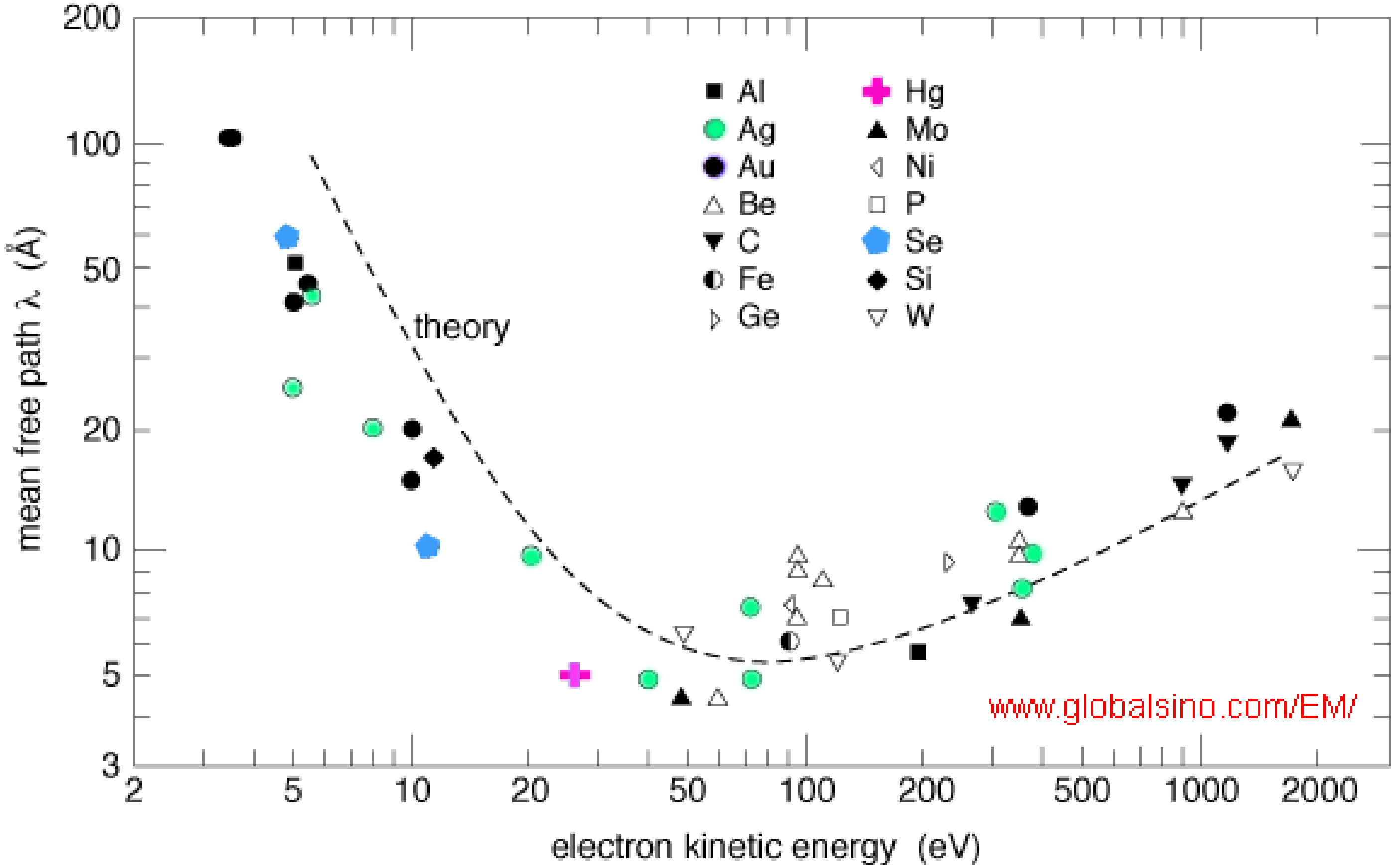
Agarwal, X-ray spectroscopy (1991)

Electron inelastic mean free path (IMFP)

$$I(d) = I_0 \exp\left(-\frac{d}{\lambda(E)}\right)$$

Decay of the electron intensity in the media due to inelastic scattering

$$\lambda[monolayers] = \frac{538}{E^2[eV^2]} + 0.41\sqrt{a[nm]E[eV]}$$



M. Seah and W. Dench, Surf. Interface Anal., **1** 2-11 (1979)

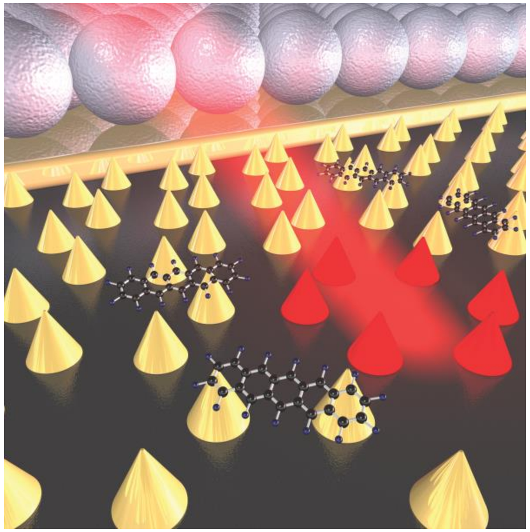
Final remarks

Preparation:

- growth of thin films: statistical growth, layer-by-layer growth
- Formation of nanoclusters: islands (Wulff construction, diffusion-limited aggregation)
- Experimental techniques: PVD, CVD, lithography

Characterization:

- Scattering techniques: scattering from atomic layers of thin films, scattering from nanoparticles, scattering from surfaces and interfaces
- Microscopy: visible light, electron microscopy, SPM
- Spectroscopy: absorption & emission (VIS, UV, IR, X-ray)



More on scattering in WiSe2025:

Advances topics in physics of condensed matter

Good luck at the exam!

Lectures: J. Meyer, D. Kölle, I. Zaluzhnyy; Exercises: R. Löffler