

Responsive Functional Materials

Ass.-Prof. Dr. Heidi A. Schwartz

Photoactive Hybrid Materials

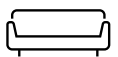
Universität Innsbruck



<https://www.uibk.ac.at/en/aatc/ag-schwartz/>



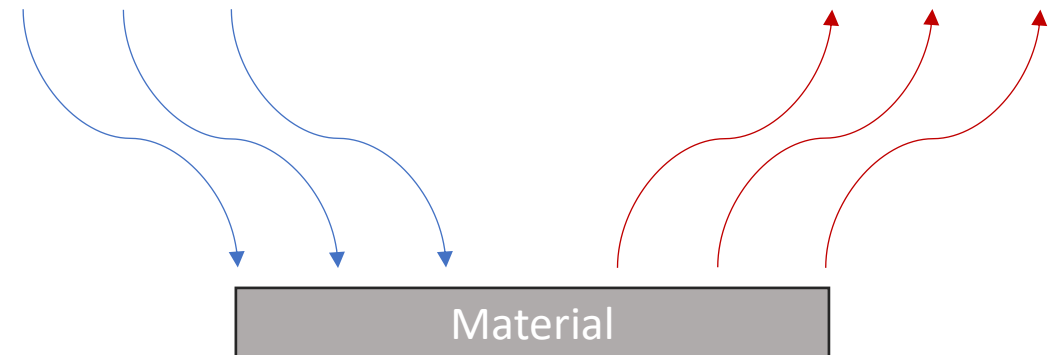
heidi.schwartz@uibk.ac.at



L01.063

External stimuli

Functionality



Outline for today's lecture

1. Short conclusion of last lecture

2. Learning objectives

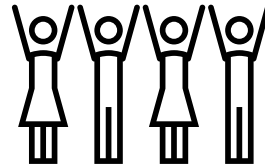
- Analyzation tools and characterization methods II
- Next time: Porous Materials I

Diffraction / no change in electronic structure



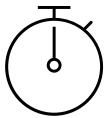
- X-ray diffraction
- Neutron diffraction
- Pair Distribution Function (PDF)





Group-/Tandem-Work

For this week, set up a table with method, sample requirement, information gained and limitations.



During the whole lecture

Characterization methods – there are so many...

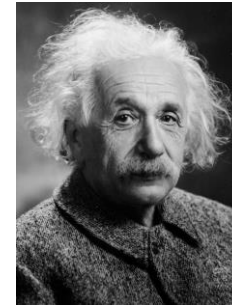
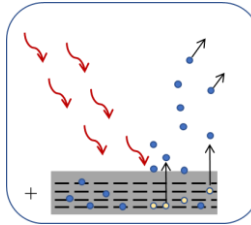
There are various methods to determine the average and the local structure: diffraction and spectroscopic methods.

Diffraction / no change in electronic structure



- X-ray diffraction
- Neutron diffraction
- Pair Distribution Function (PDF)

Photoelectric effect

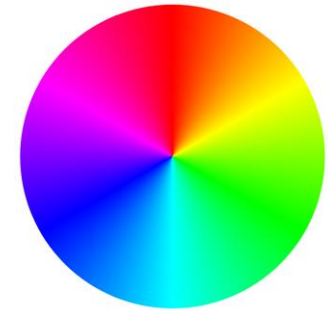


- XAS, XPS (AES) & UPS

Vibrations and Rotations

- IR and Raman

Electronic, nuclear transitions



- UV/Vis spectroscopy
- NMR spectroscopy

Further methods: EDX, mass spectrometry, DSC-TGA, BET.

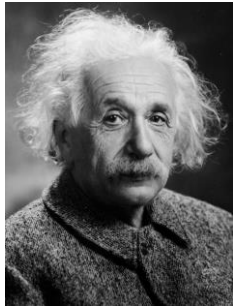
Fundamentals of spectroscopic methods

Photoelectric & photovoltaic effect

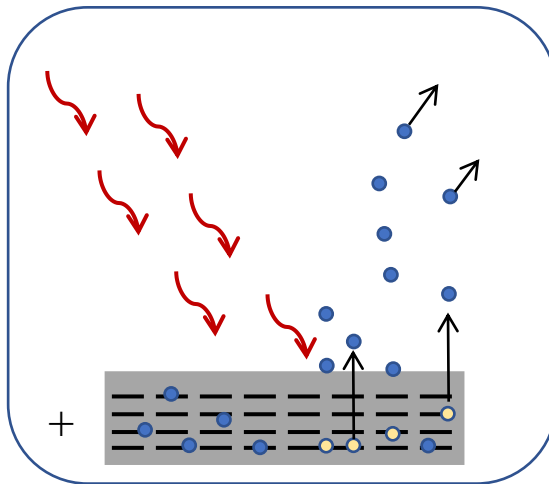
“excitation of electrons to a higher-energy state, when a material is exposed to electromagnetic radiation”



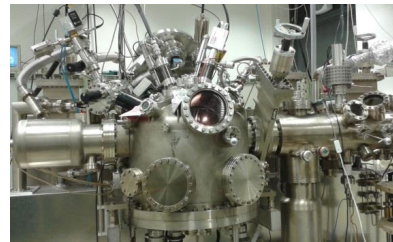
Short reminder from
last time!



A. Einstein



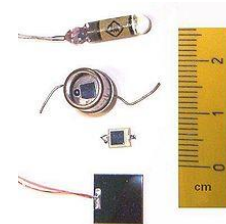
Electrons leave the
material.



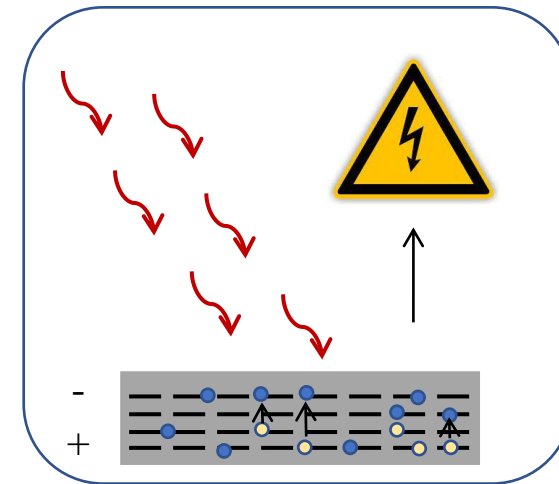
XPS.



Solar cell.



Photodiode.



Electrons stay within the
material.



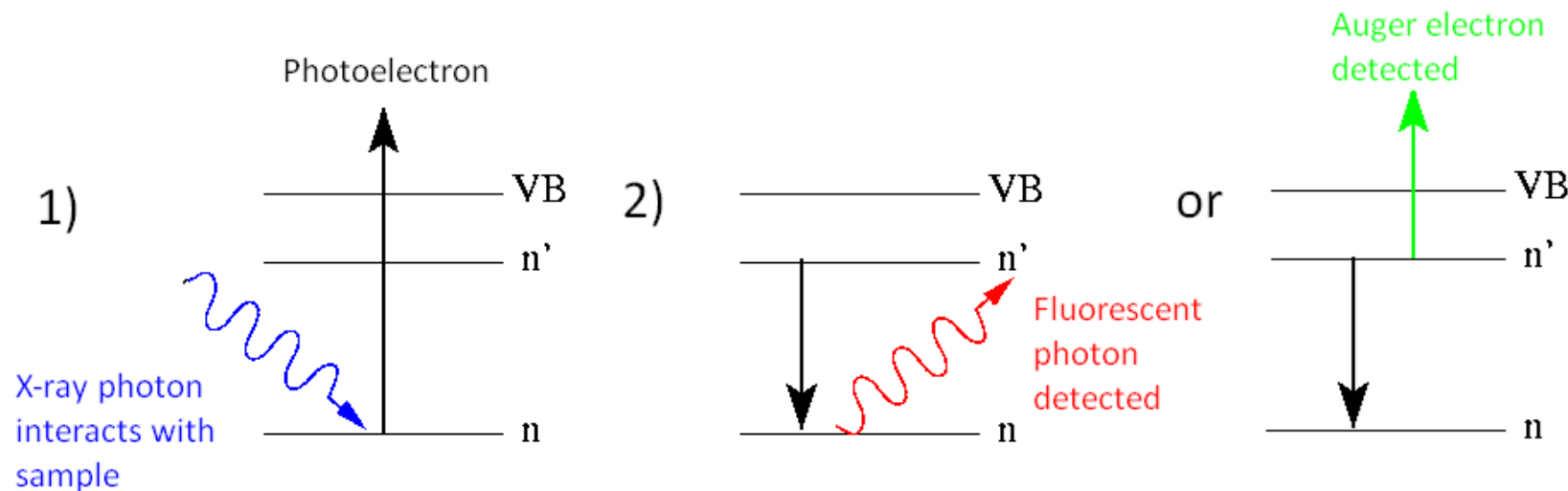
E. Becquerel

Photovoltaic effect is also called the inner photoelectric effect.

XAS – X-ray Absorption Spectroscopy

Generic term for several X-ray spectroscopic measurement methods: XANES or NEXAFS (X-ray absorption near-edge structure) and EXAFS (extended X-ray absorption fine structure).

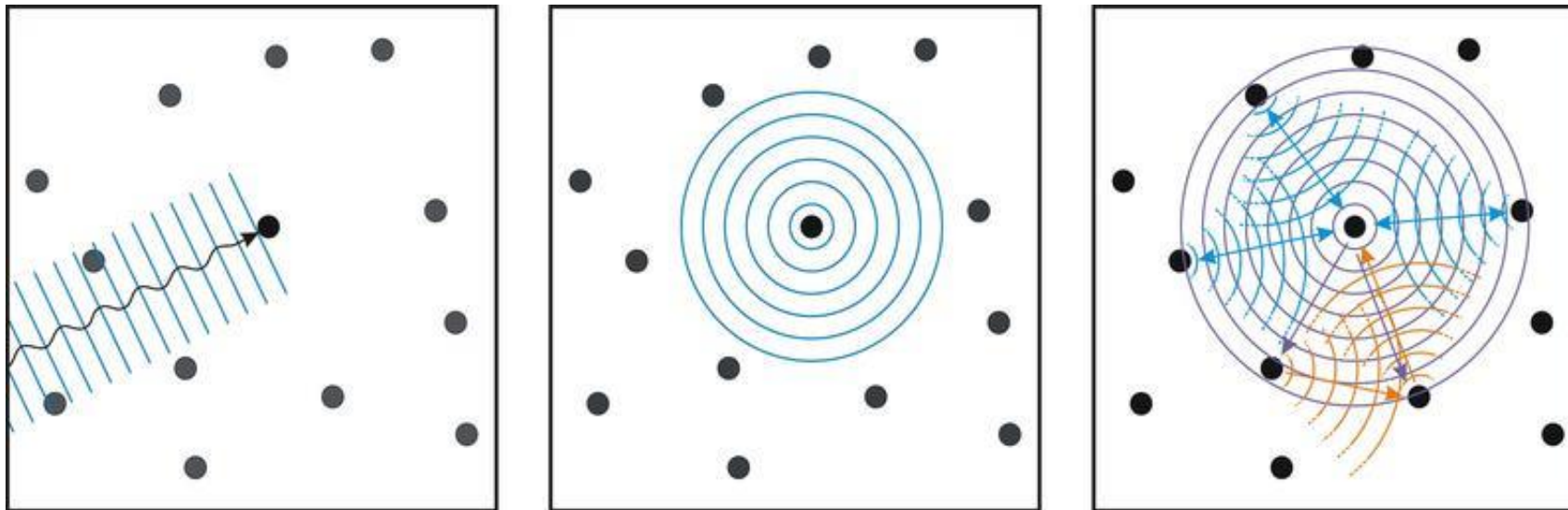
Sample requirements: Gas, liquid or solid state.



Absorption of X-ray in the area of an absorption edge

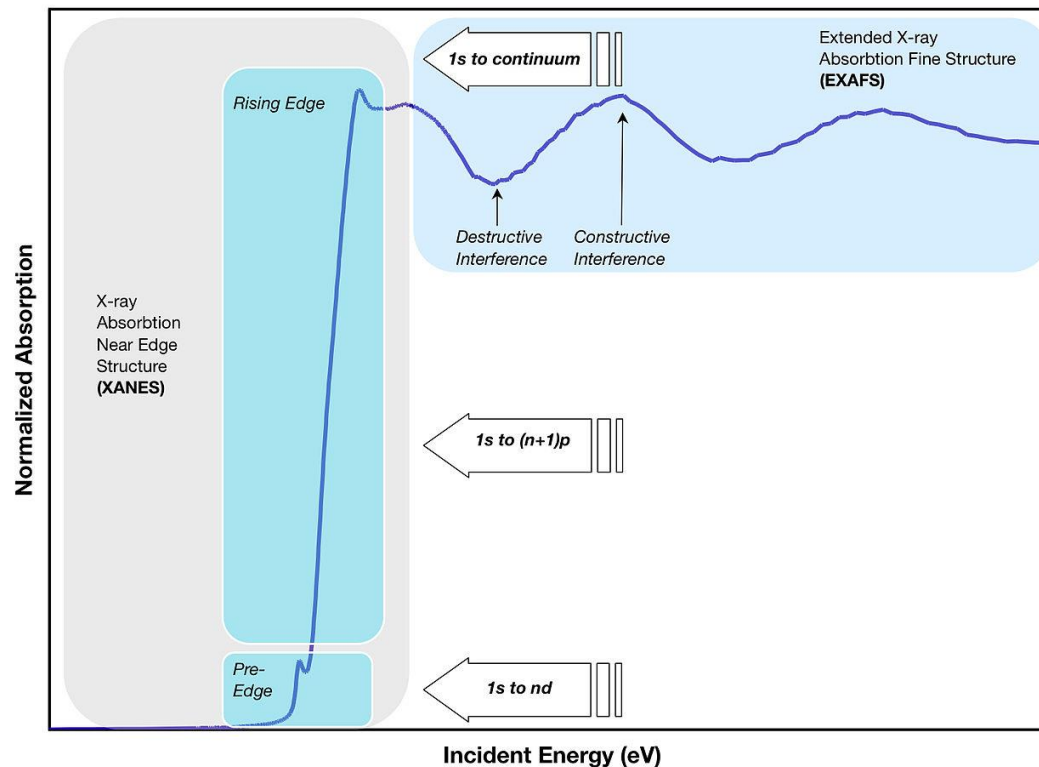
XAS – X-ray Absorption Spectroscopy

- X-ray quantum of sufficient energy can eject electron from near-nuclear orbital
(Absorption increases → **absorption edge**)
- absorbing atom emits spherical photoelectron wave:
 - i) Single scattering processes: blue (EXAFS)
 - ii) Multiple scattering processes: orange (NEXAFS/XANES)



XAS – X-ray Absorption Spectroscopy

- Mainly determined by intra-atomic absorption bands (excitation of near-nuclear electrons into unoccupied states) / XANES.



XANES:

- Valence
- Electronic structure

EXAFS:

- Chemical environment
- Coordination

XPS – X-ray Photoelectron Spectroscopy

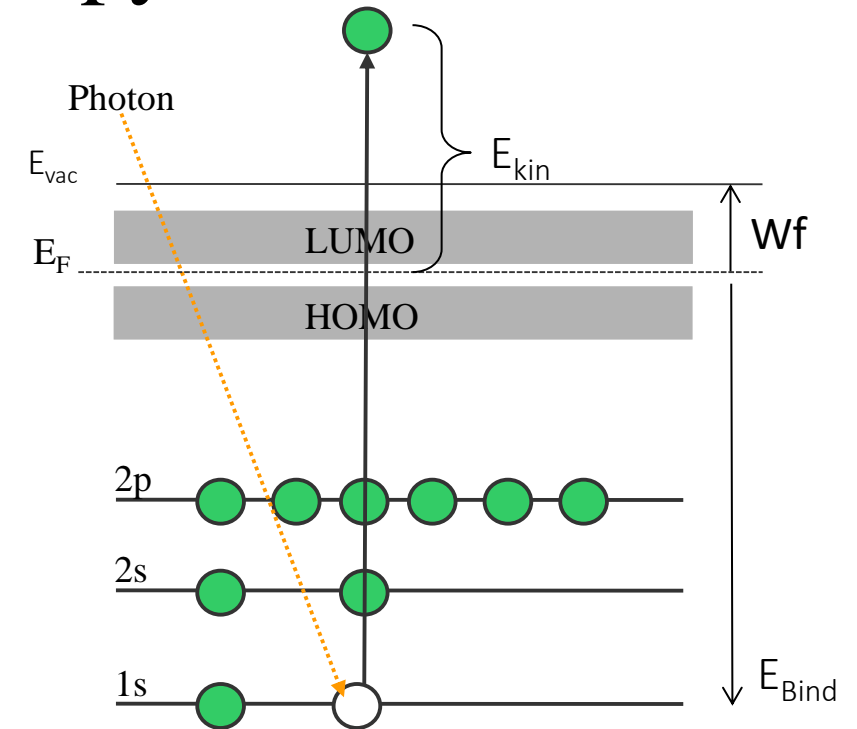
Sample requirements: Solid state, preferably conductive and thin film.

- incident photon ejects an electron, which leaves the solid body
- the higher the photon energy or lower the binding energy, the higher is the kinetic energy of electron

Photons:

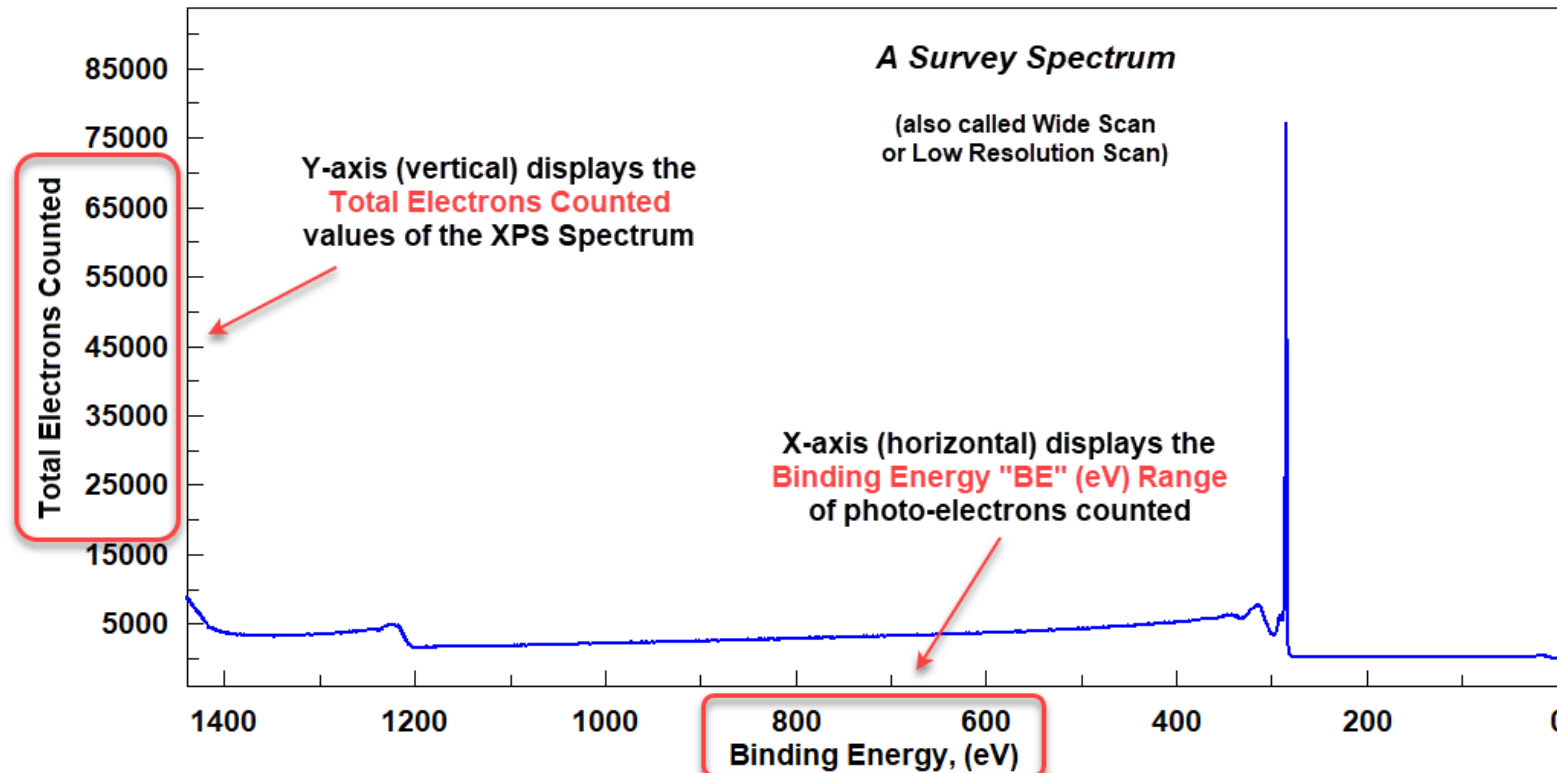
- Energy around 1-2 k eV is necessary (X-rays of a Mg or Al source)
- Monochromatic excitation is obligatory

Information on: Oxidation state, composition and chemical environment.

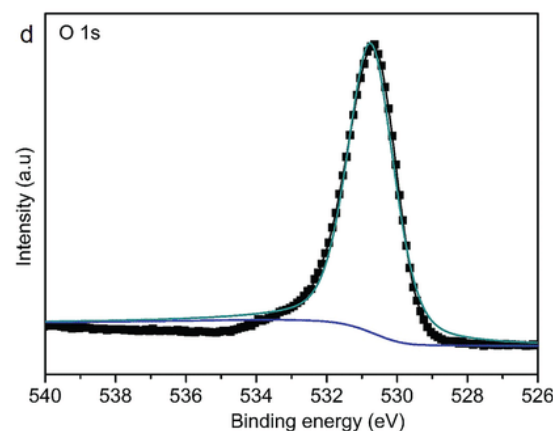
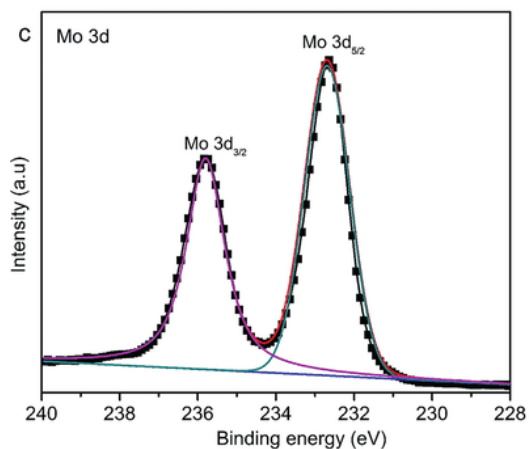
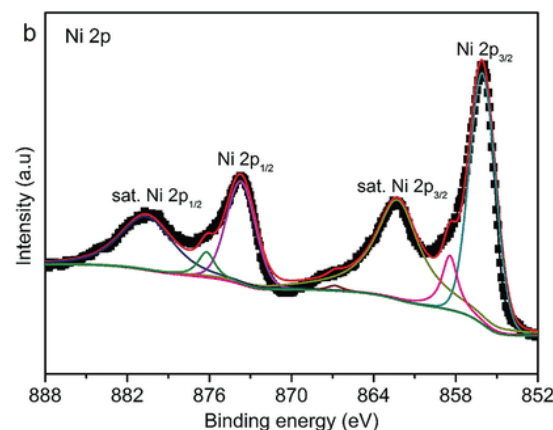
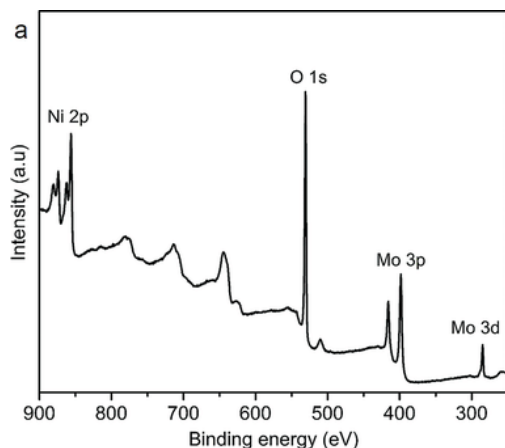


XPS – X-ray Photoelectron Spectroscopy

A **survey spectrum** is collected for a first and fast analysis. It has a low resolution because of the high pass energy E_{pass} used for this fast scan. Information: Which elements are present or absent?



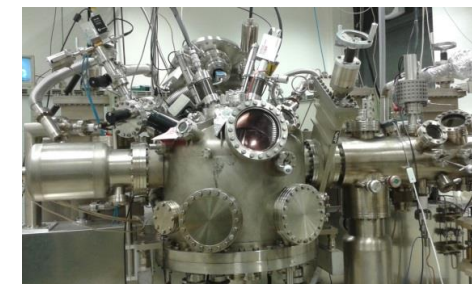
XPS – X-ray Photoelectron Spectroscopy



Spin-Orbit Splitting or $j-j$ coupling of peaks

<i>Subshell</i>	<i>j values</i>	<i>Area ratio</i>
s	1/2	n/a
p	1/2 3/2	1:2
d	3/2 5/2	2:3
f	5/2 7/2	3:4

FWHM and L:G are equal for these spin-orbit doublets and a specific peak separation.



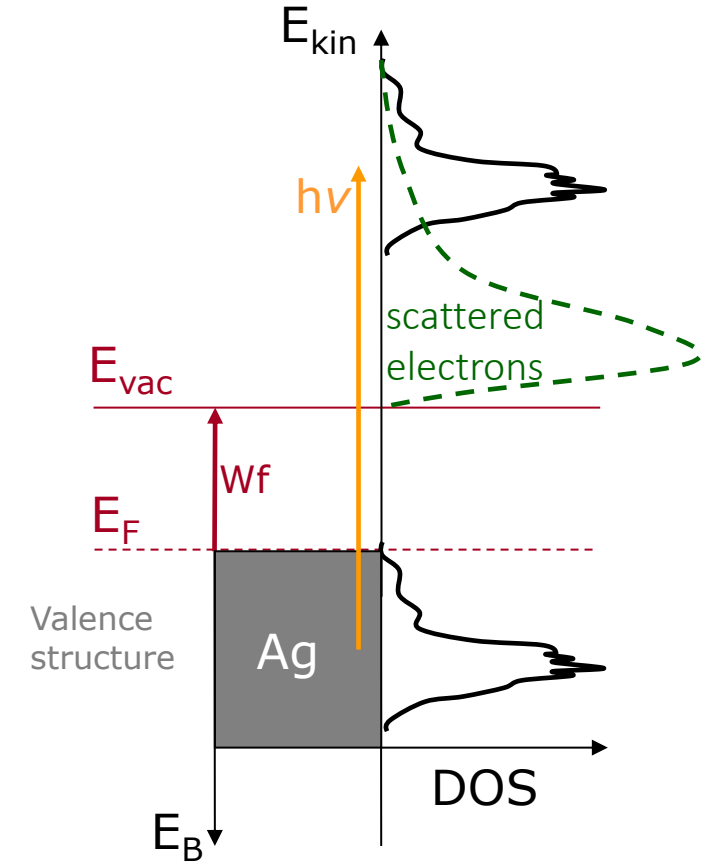
UPS – Ultraviolet Photoelectron Spectroscopy

Sample requirements: Solid state, conductive and thin film.

Same principle as XPS, but:

- UV light is used (He plasma lamp): is only capable of releasing VE
- Serves to determine the valence band structure
- kinetic energy of the photoelectrons gives the density of states (DOS)
- minimal energy differences of MOs or even physical surfaces are resolved

Information on: Valence band structure and density of states (DOS).



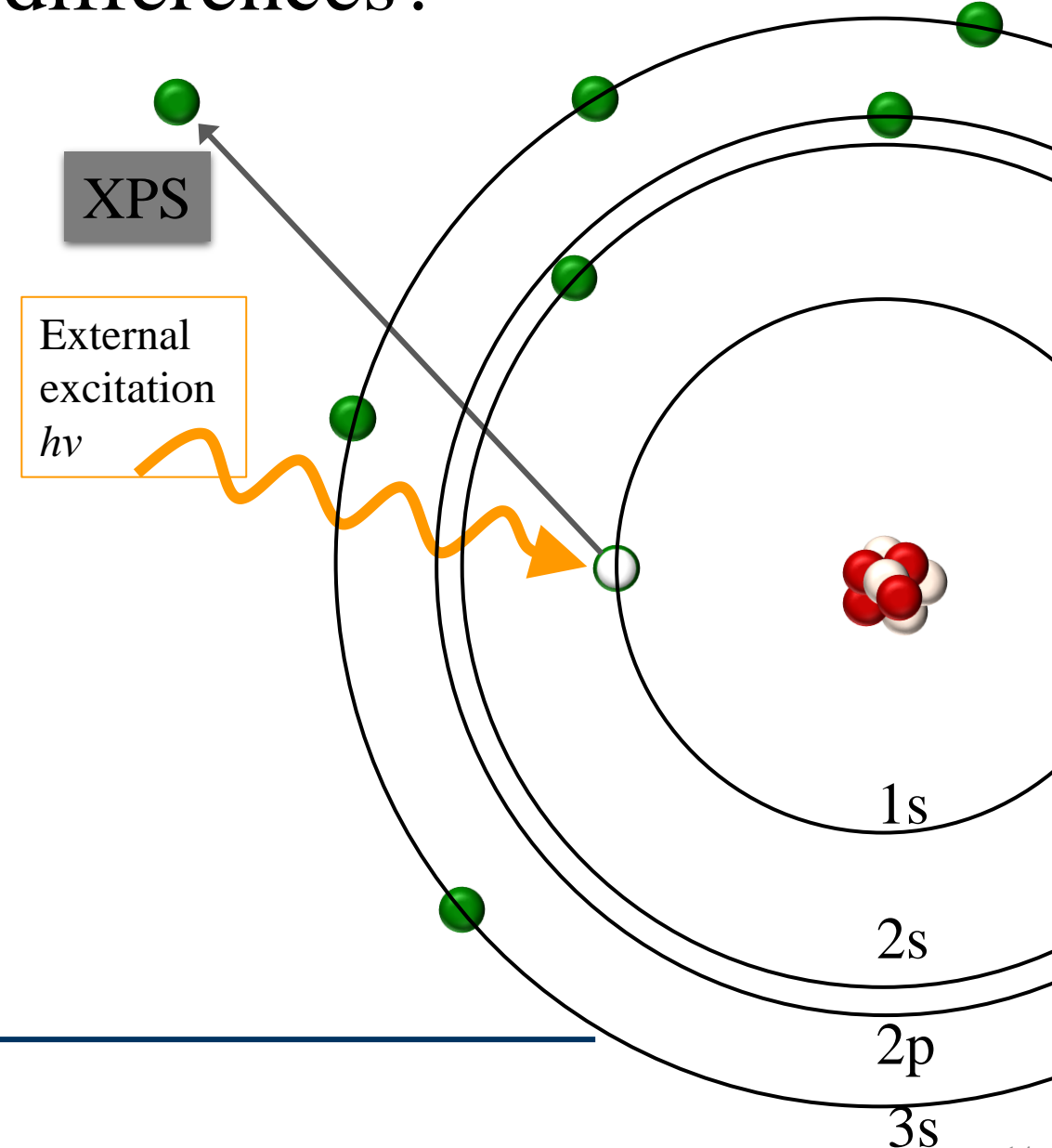
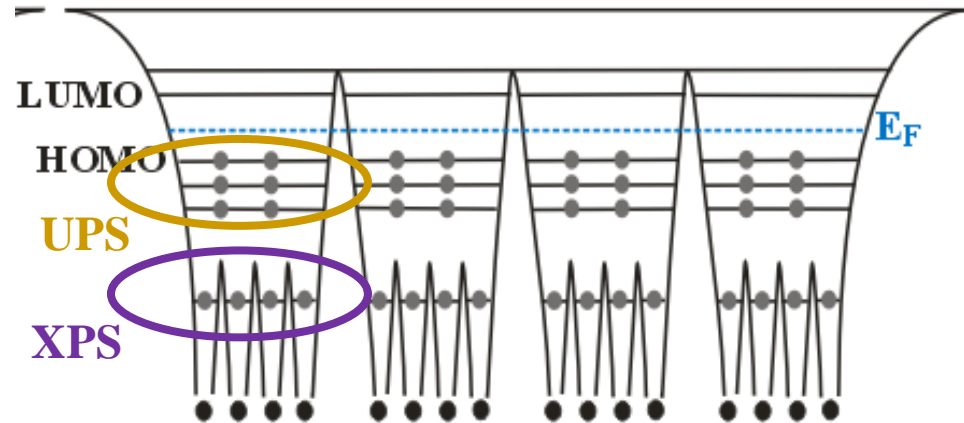
XPS versus UPS – what are the differences?

XPS:

- Ejects electrons from inner orbitals
- X-rays are used

UPS:

- Serves to determine valence band structure
- UV light is used



IR Spectroscopy – utilizing low energy radiation

Sample requirements: Gas, liquid or solid state.

Generation of IR radiation

- i) Nernst lamp (ZrO_2)
- ii) Globar (SiC)



Vibrations in which the **dipole moment changes** are **IR active**.

N. Banwell, E. M. McCash, Molekülspektroskopie, Oldenbourg Verlag, München, 1999.

M. Hesse, H. Meier, B. Zeeh, Spektroskopische Methoden in der Organischen Chemie, Thieme-Verlag, Stuttgart, 2002.

www.chemgapedia.de (10th +11th June 2018)

IR Spectroscopy – utilizing low energy radiation

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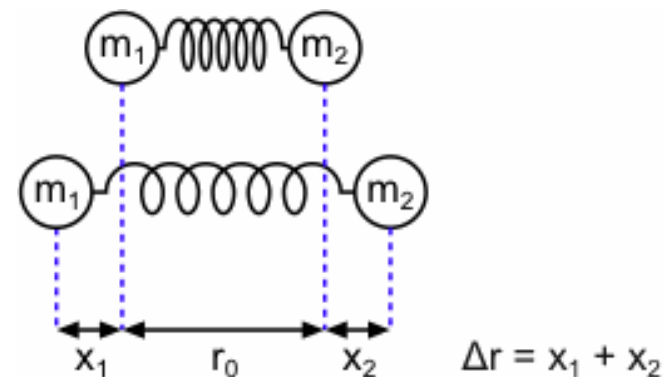
Generation of IR radiation

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Vibrations in which the **dipole moment changes** are **IR active**.

Modell of a two-atomic molecule



Hook's law + involvement of anharmonic oscillator:

- the stronger the bond, the higher the frequency
- the higher the red. mass, the lower the frequency

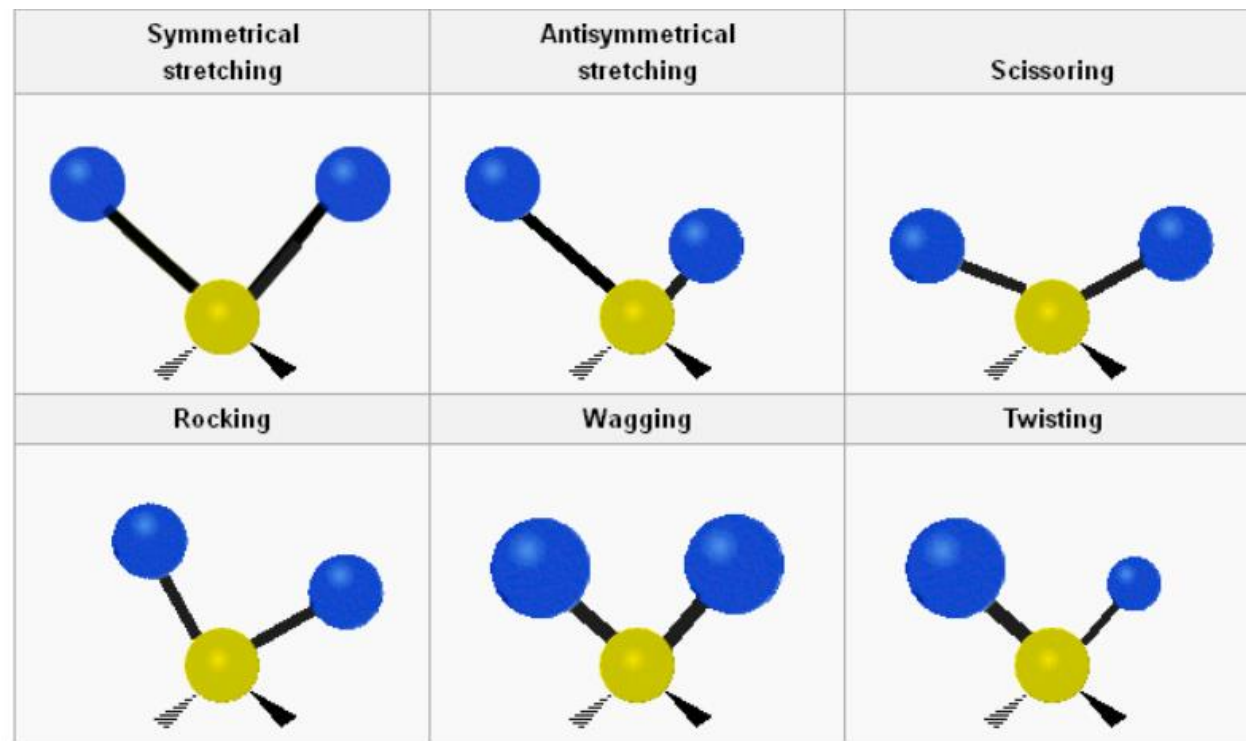
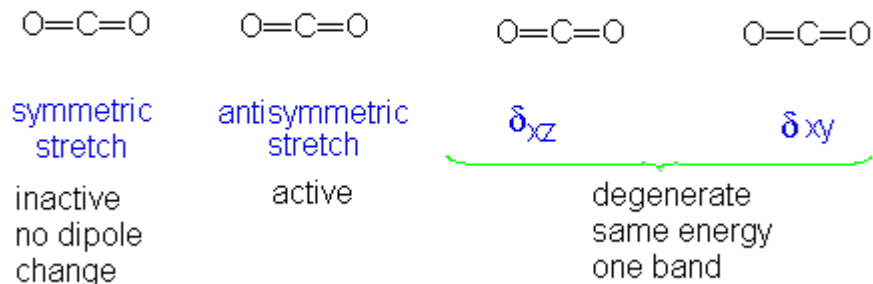
IR Spectroscopy

IR detects molecular vibrations and rotations directly as absorption.

Molecules with symmetry centre

- symmetric vibrations - not IR active
- asymmetric vibrations - IR active

Example: CO₂



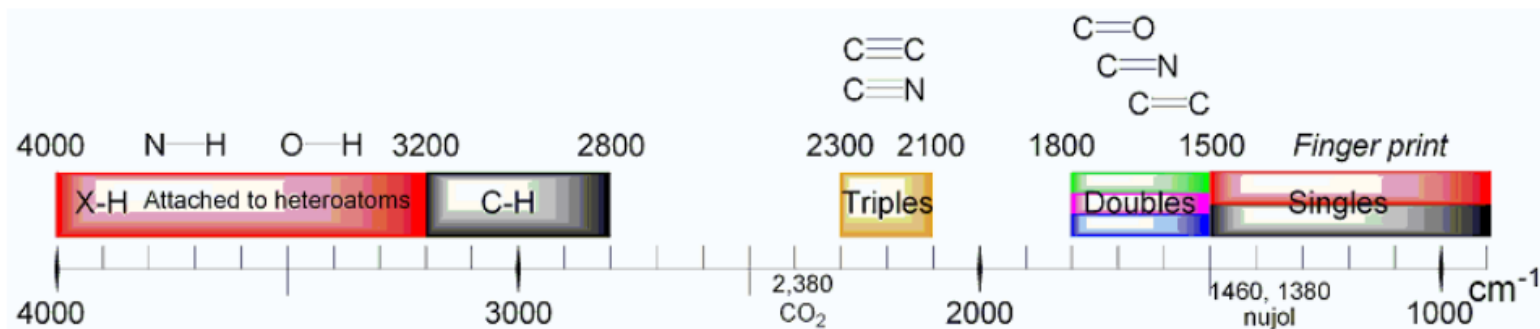
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[Infrared Spectroscopy \(usp.br\)](https://usp.br) and [Introduction to Vibrations - Chemistry LibreTexts](https://chem.libretexts.org) (27th March 2023)

IR Spectroscopy

IR detects molecular vibrations and rotations directly as absorption.



Wavenumbers listed in cm^{-1} .

Information from the IR spectrum

- functional groups
- bond types / bond strength
- atomic distances

ν = valence vibration

δ = deformation vibrations / bending vibrations

γ = deformation vibrations (out-of-plane)

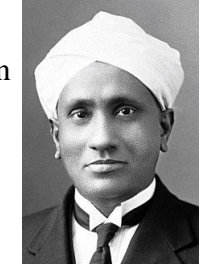
τ = torsional vibrations

Raman Spectroscopy

Raman measures molecular vibrations and rotations indirectly as **scattered** radiation (excitation with laser (usually $\lambda = 1064 \text{ nm}$)).



A. Smekal
Theoretical prediction
1923



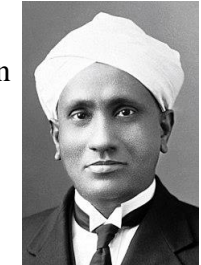
C. V. Raman
Experimental proof
1928

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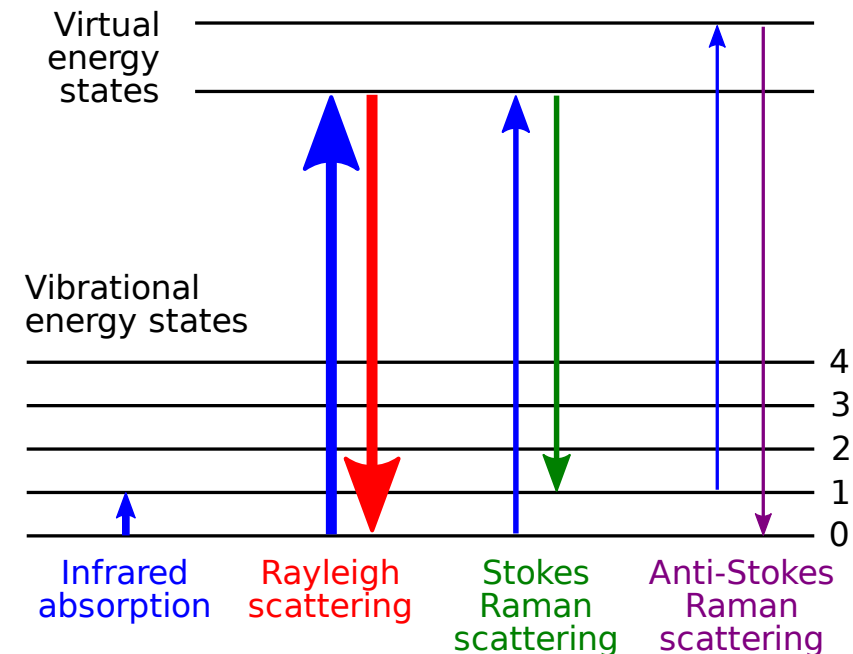
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Exploiting the Raman effect - scattering phenomenon

- *Rayleigh* radiation / scattering (elastic impact)
 - I. Scattered radiation has the same energy as incident light
- *Raman* scattered radiation (inelastic collision)
 - I. Stokes lines (lower frequency than *Rayleigh*)
 - II. Anti-Stokes lines (higher frequency than *Rayleigh*) (rare, low I at RT)

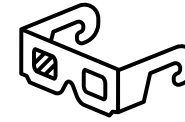


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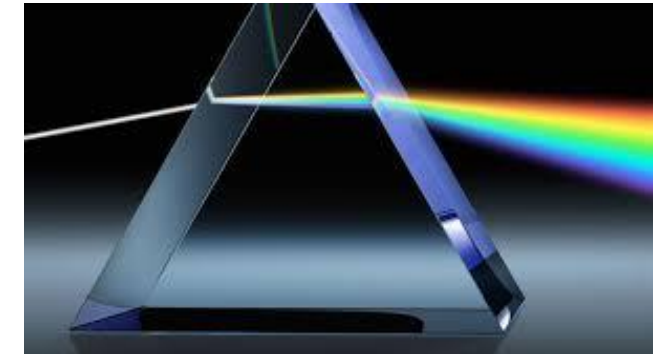
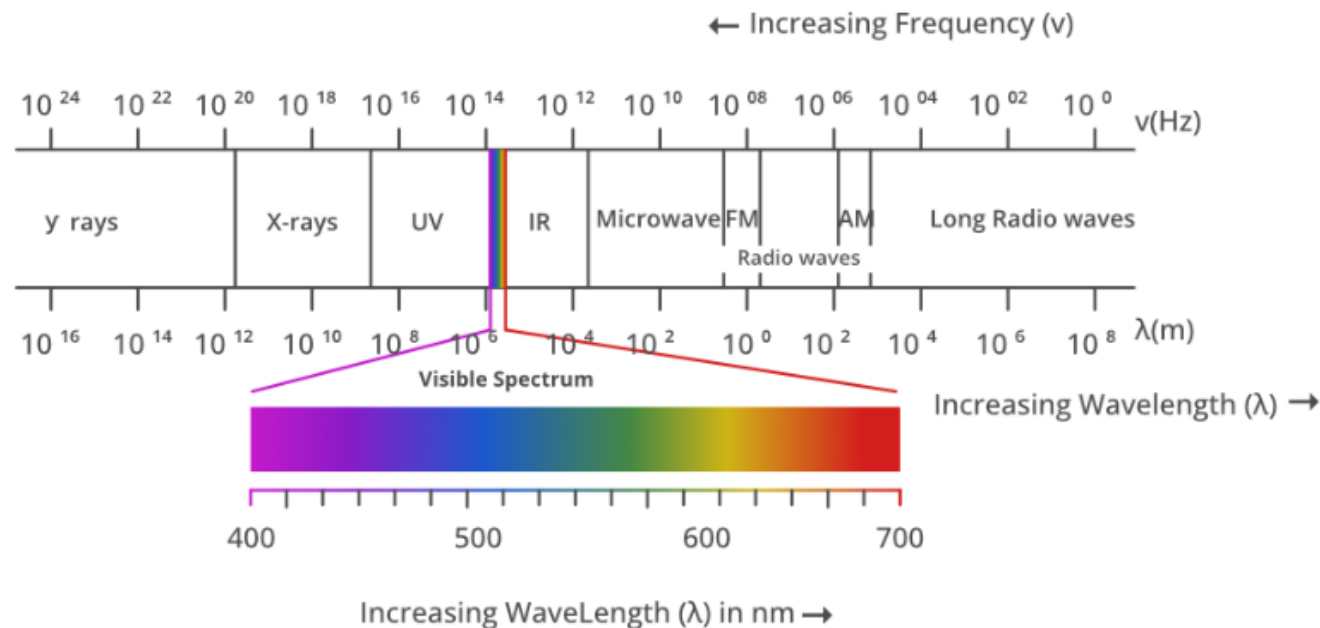
M. Hesse, H. Meier, B. Zeeh, Spektroskopische Methoden in der Organischen Chemie, Thieme-Verlag, Stuttgart, 2002.

[Raman spectroscopy – Wikipedia](#) (29th March 2023)

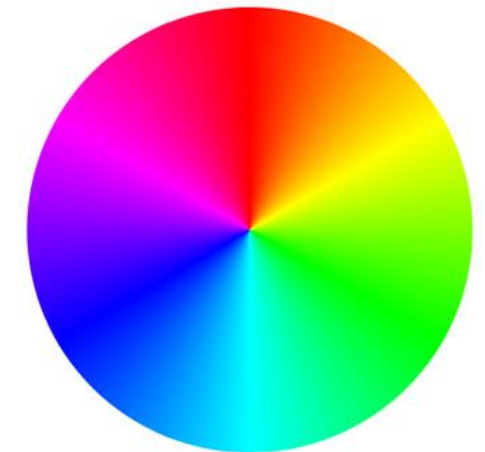
What the human eye can see



We can only perceive a portion of electromagnetic light. We call this the visible light or Vis range between 400 - 800 nm.



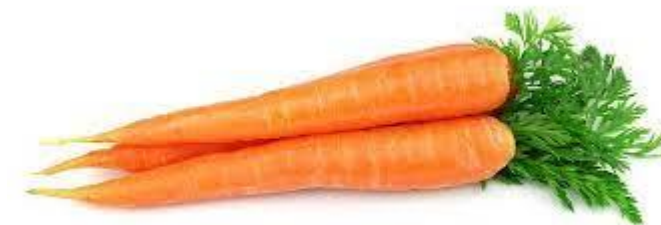
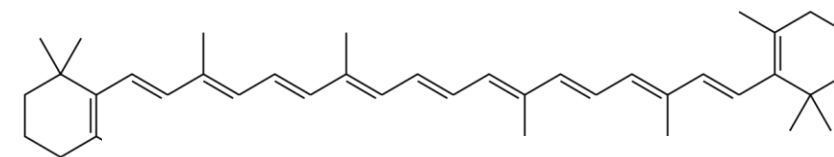
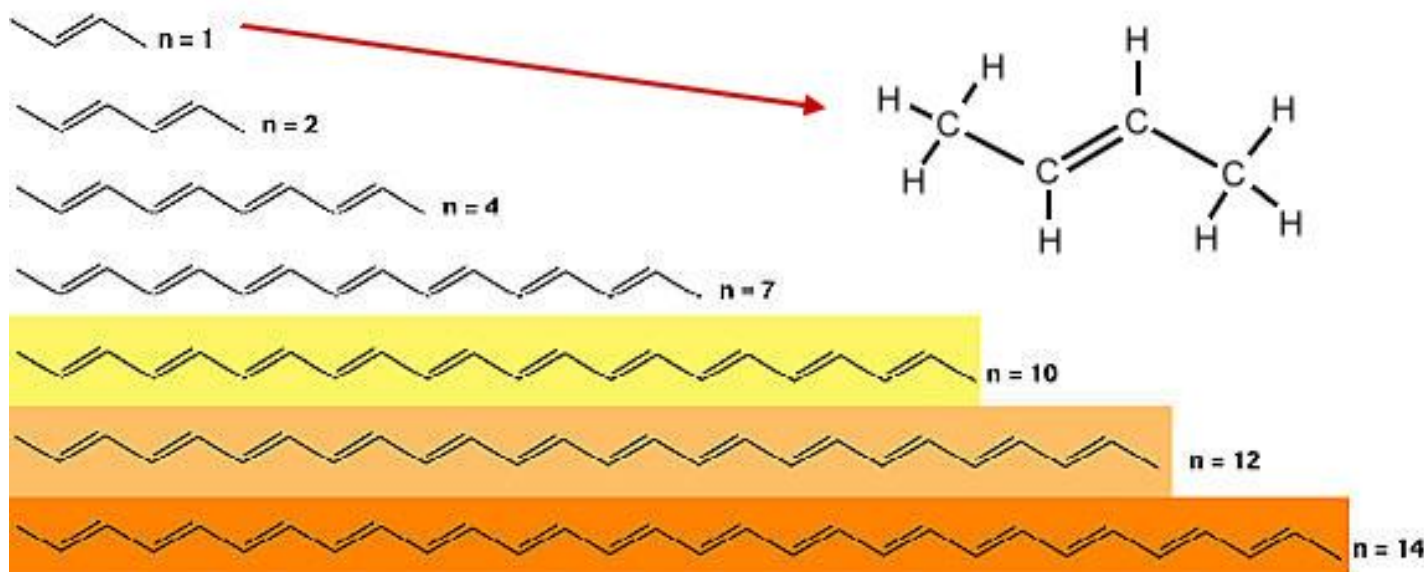
The non-absorbed part of the light, the complementary color, is visible!



A substance is perceived as coloured if it absorbs a wavelength from this range.

The origin of color

Organic compounds: The reason for the colorfulness are electron transitions between occupied and unoccupied molecular orbitals - MO theory!



We perceive polyenes with more than **nine** conjugated double bonds as colored!

Single bonds: $\sigma \rightarrow \sigma^*$

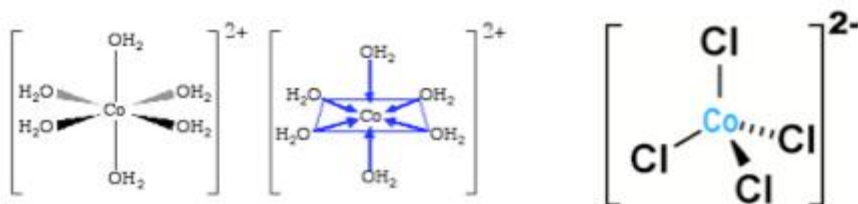
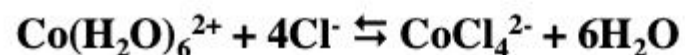
Double or triple bonds: $\pi \rightarrow \pi^*$

Non-bonding MO free electron pair in antibonding orbital : $n \rightarrow \pi^*$

The origin of color

Coordination compounds: The reason for the colorfulness are electron transitions between occupied and unoccupied d-orbitals - MO theory!

The Co^{2+} ion and CoCl_4^{2-} ion equilibrium



What is the electron configuration of Co^{2+} ?

What does ligand field splitting look like in an octahedral/tetrahedral ligand field?

Which transition requires more energy?

Ligand field theory
is the explanation!

The origin of color

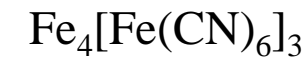
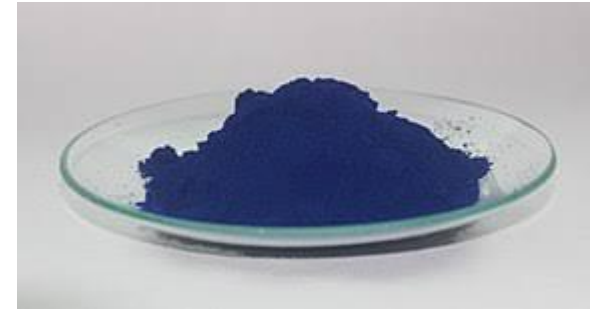
Charge transfer compounds: The reason for the colorfulness are electron transitions between different species of a compound!

Transition **ligand** to **metal**: KMnO_4

Transition **metal** to **ligand**: Fe^{2+} complexes with bipyridine

Transition **metal** to **metal**: Berlin blue

Transition **ligand** to **ligand**

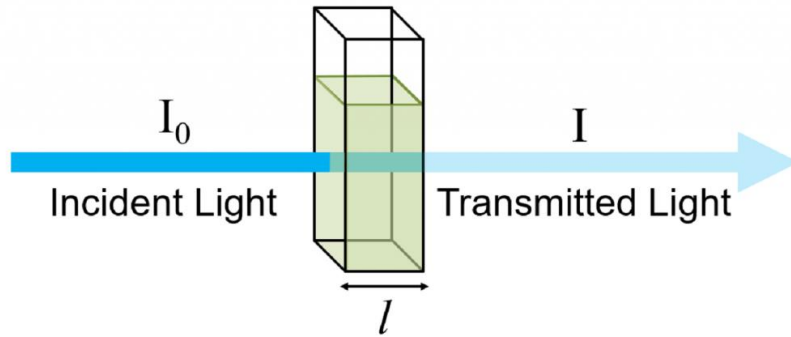


If one dissolves these charge-transfer complexes, color shifts occur depending on the solvent!

Solvatochromism

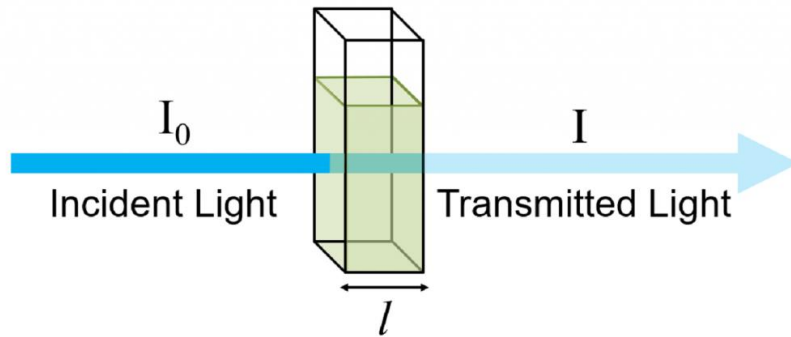
UV/Vis spectroscopy

Fundamental process is the absorption of a specific part of electromagnetic radiation. What is measured, is the non-absorbed part I of the initial light I_0 .



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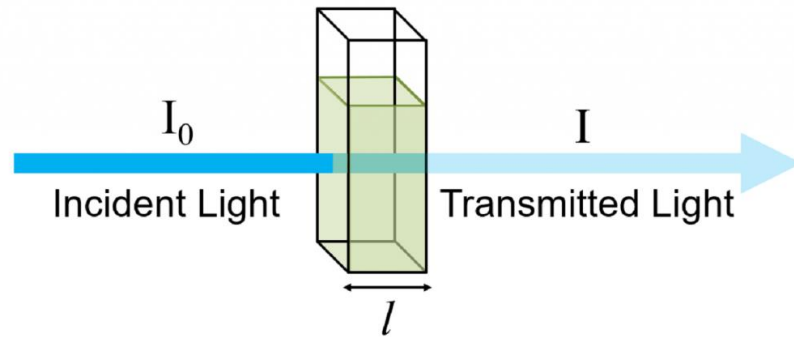


Transmittance is defined as the ratio of the transmitted intensity I over the incident intensity I_0 :

$$T = \left(\frac{I}{I_0}\right), \text{ with values from 0 to 1}$$

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Lambert-Beer law: It describes the linear relationship between absorbance A and the concentration c , molar absorption coefficient ϵ and the optical path length l . Further, it is related to the negative log of the transmission:

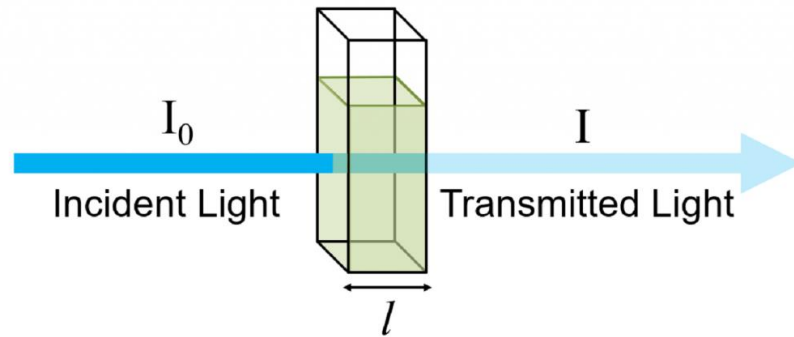
$$A = \epsilon \cdot c \cdot l = -\log(T) = \log\left(\frac{I_0}{I}\right)$$

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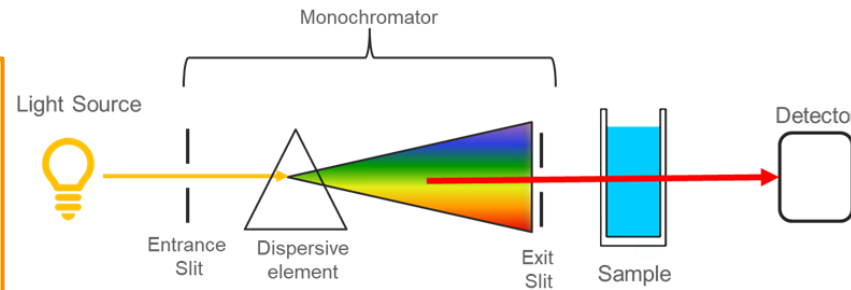


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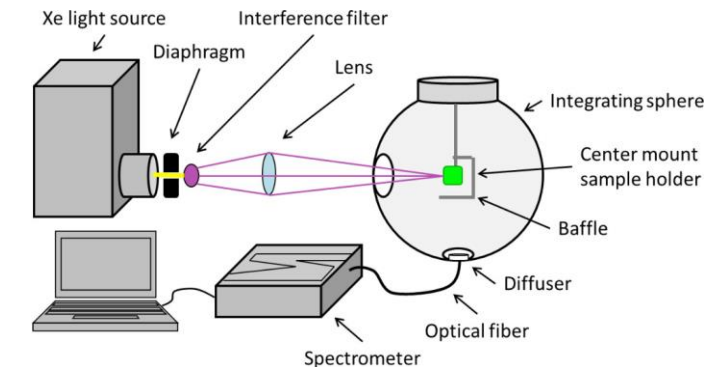
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Absorption mode of an UV/Vis spectrometer.



Reflection mode of an UV/Vis spectrometer.

Questions?

