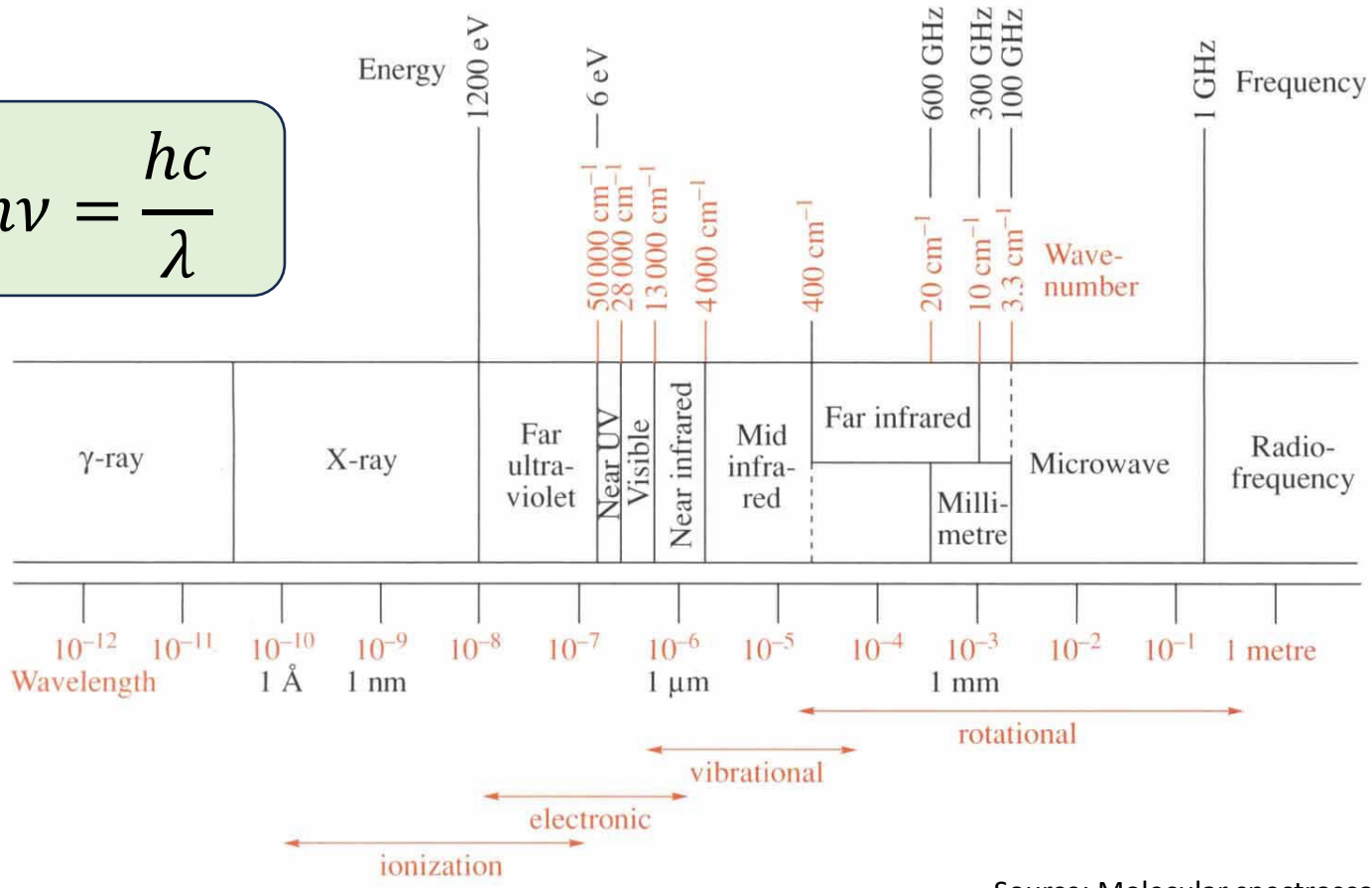
Absorption and emission

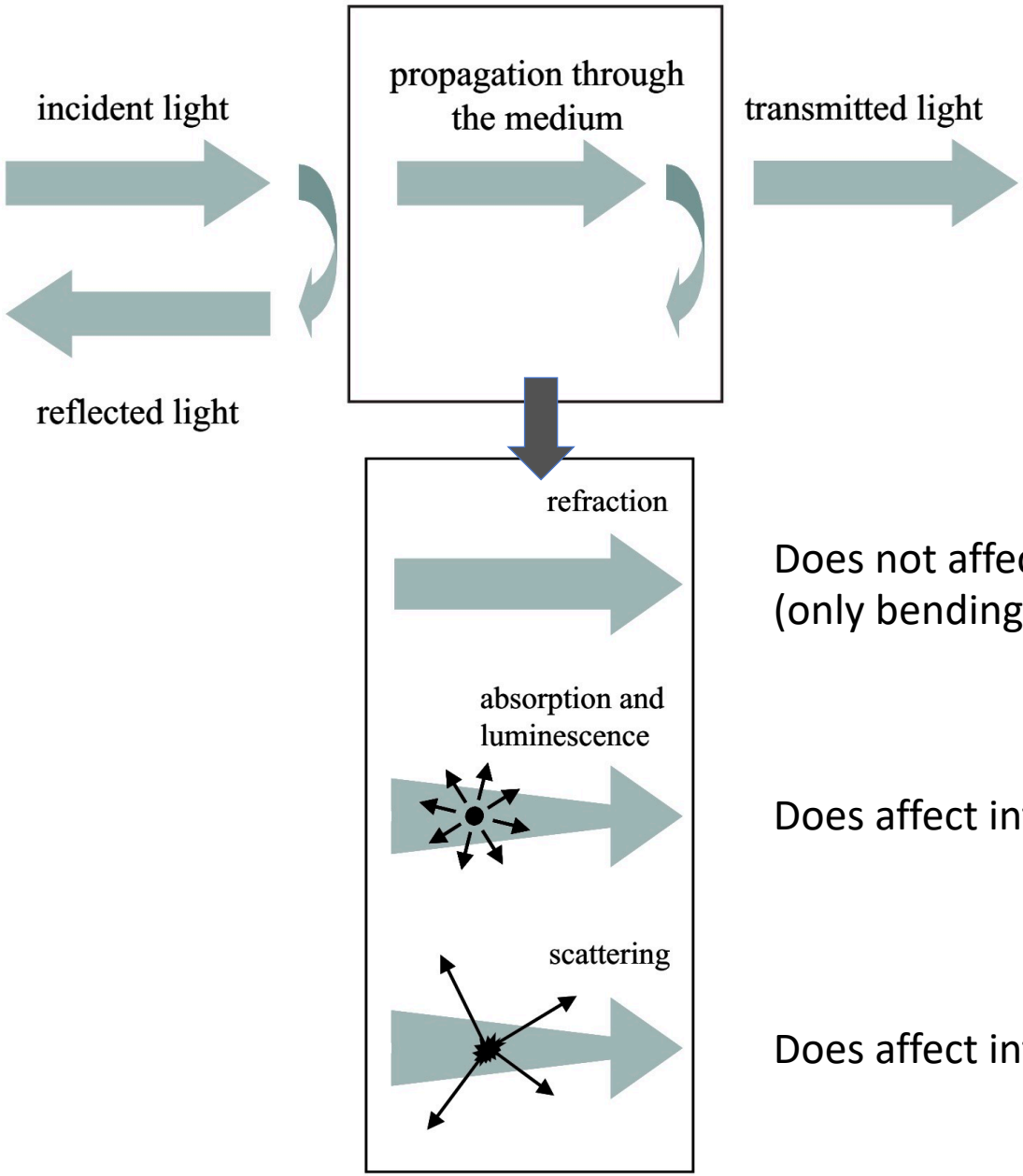
The Electromagnetic Spectrum

$$E = h\nu = \frac{hc}{\lambda}$$



Source: Molecular spectroscopy, Hallas

Optical Processes



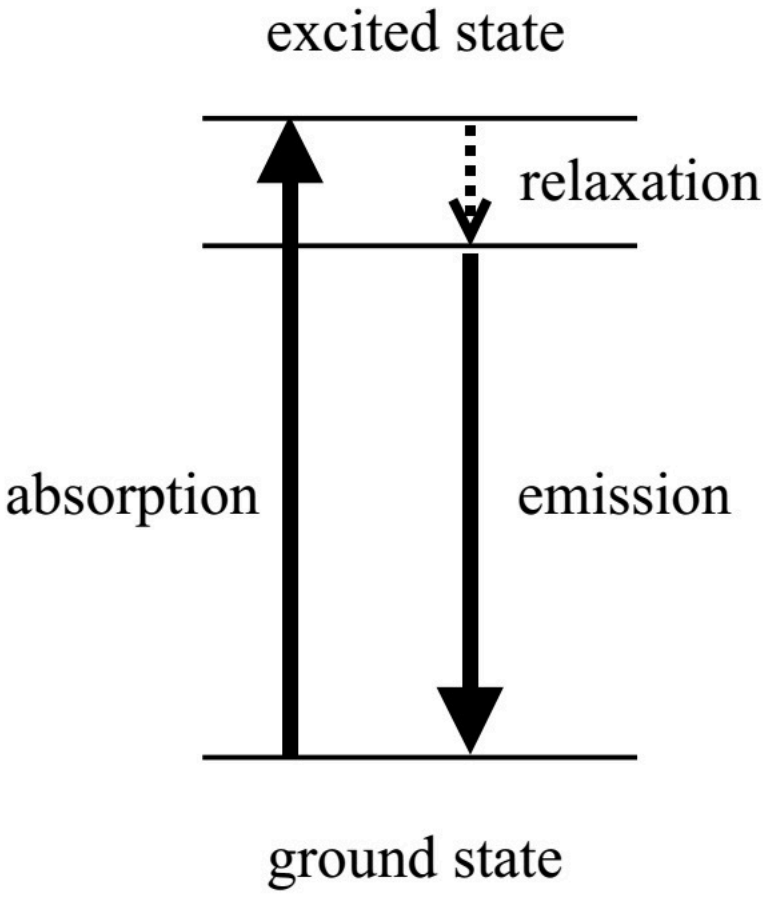
Does not affect intensity
(only bending of light ray)

Does affect intensity

Does affect intensity

Absorption and emission

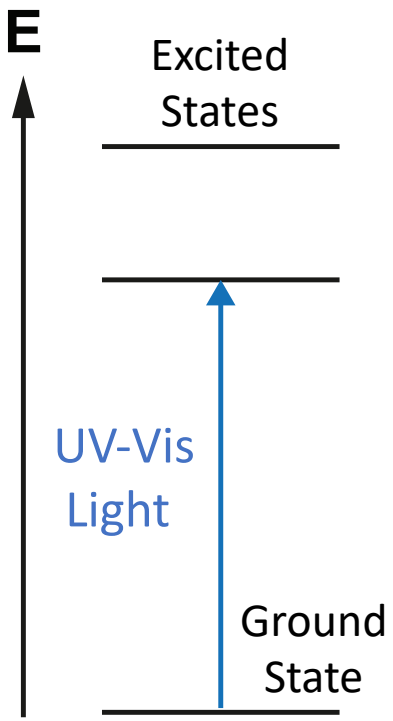
The most simplified picture:



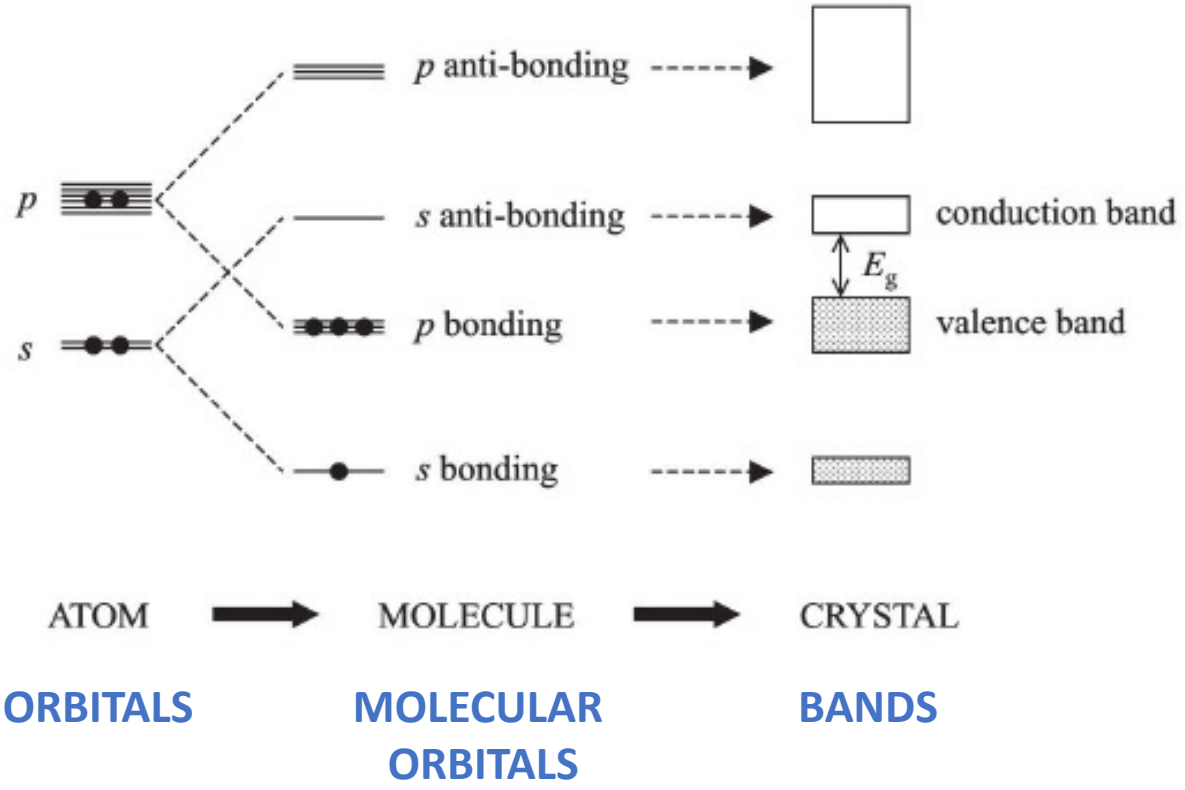
What are the ground states/excited states?
What energy is associated to these processes?

Absorption

Electronic transitions

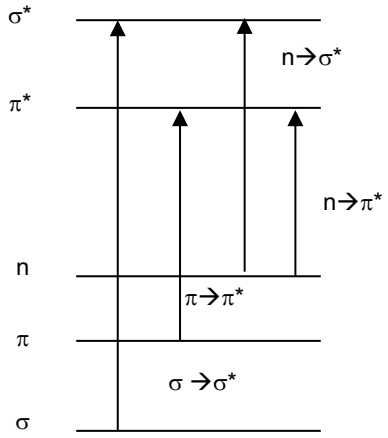


Quantized levels
Convert E
as orbital motion



Electronic transitions

- In organic molecules we are concerned mostly with orbitals originating from the overlap of atomic **s** and **p** orbitals or their hybrids
- These can be classified as **s** and **p** bonding orbitals and **s*** and **p*** antibonding orbitals, as well as nonbonding orbitals, **n**
- Most organic molecules are closed-shell molecules in which the highest occupied molecular orbital (HOMO) are bonding **s**, **p** or nonbonding orbitals.
- On excitation, an electron may be promoted into the lowest unoccupied molecular orbital (LUMO), which is usually an antibonding s* or p* orbital.



Occurrence of the different transitions in typical molecular classes:

p →p*: alkenes, alkynes and aromatic molecules
n →p*: compounds with carbonyl, thiocarbonyl, nitro, azo and imine goups
n →s*: amines, alcohols and haloalkanes
s →s*: alkanes

Electronic transitions

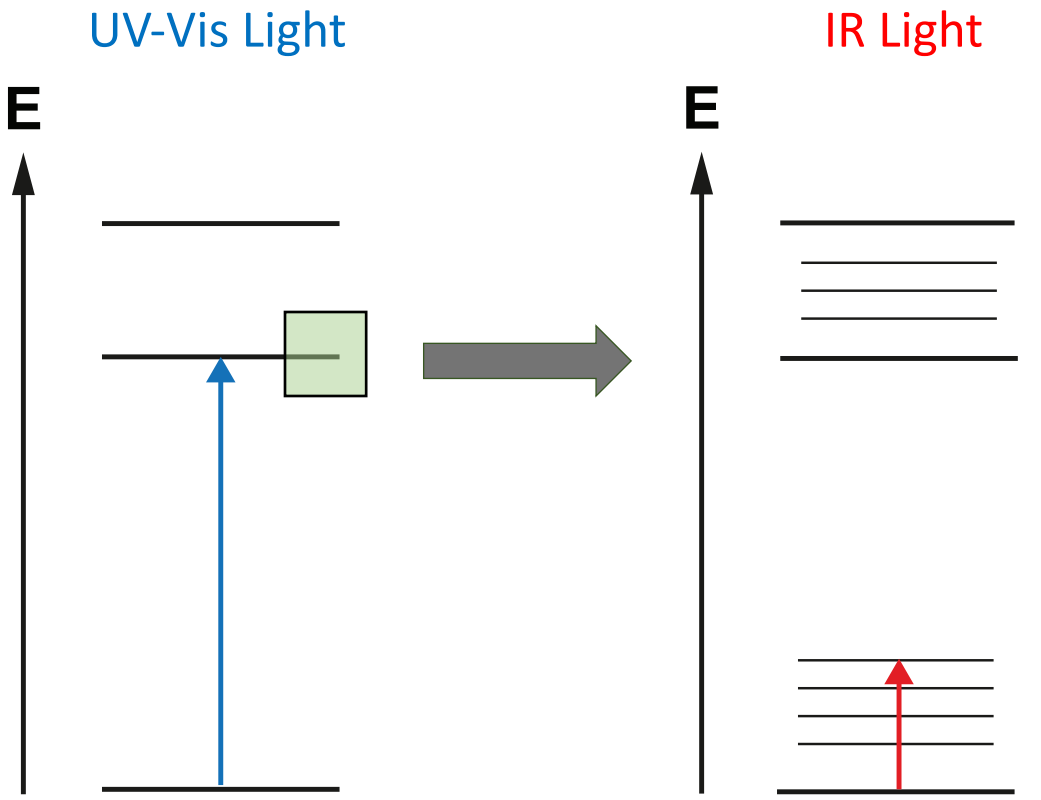
- Not all the electrons of a molecule are involved in optical transitions, but only those electrons belonging to the relevant orbitals.
- The **chromophore** represents that group or part of an organic molecule that is primarily responsible for its photochemical activity
- By classifying an organic molecule according to the type of chromophore it contains, we can group molecular electron systems
- This list enumerates only the most simple groups. Typically, dyes and pigments exhibit an immense variety of chromophores

Table 3.1 Absorption properties of some common chromophores

Chromophore	Transition	$\lambda_{max}^{(a)}$/nm	ε_{max}/dm^3 mol^{-1} cm^{-1}
N=O	n→π*	660	200
C=S	n→π*	520	100
N=N	n→π*	350	100
C=C–C=O	n→π*	350	30
C=O	n→π*	280	20
NO_2	n→π*	270	20
Benzene	π→π*	260	200
C=N	n→π*	240	150
C=C–C=O	π→π*	220	2×10^5
C=C–C=C	π→π*	220	2×10^5
S=O	n→π*	210	1.5×10^3
C=C	π→π*	180	1×10^5
C–C	σ→σ*	<180	1×10^3
C–H	σ→σ*	<180	1×10^3

[a] Approximate.

Vibrational transitions



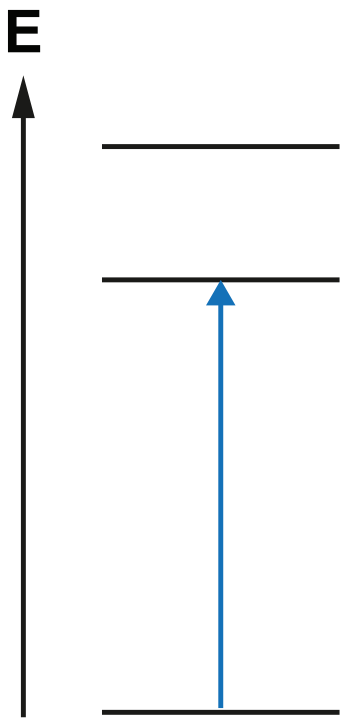
Quantized levels
Convert E
as orbital motion

Quantized levels
Convert E as
vibrational motion

Rotational transitions

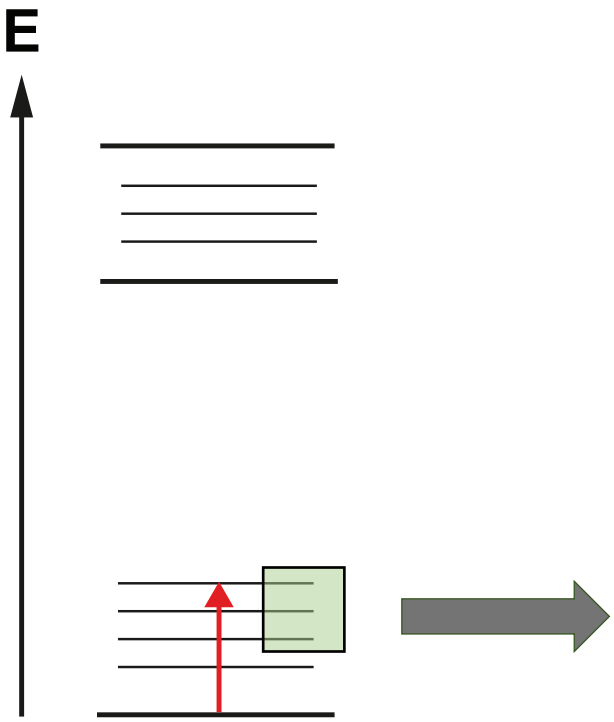
$$h\nu = E_{total} = E_{el} + E_{vib} + E_{rot}$$

UV-Vis Light



Quantized levels
Convert E
as orbital motion

IR Light

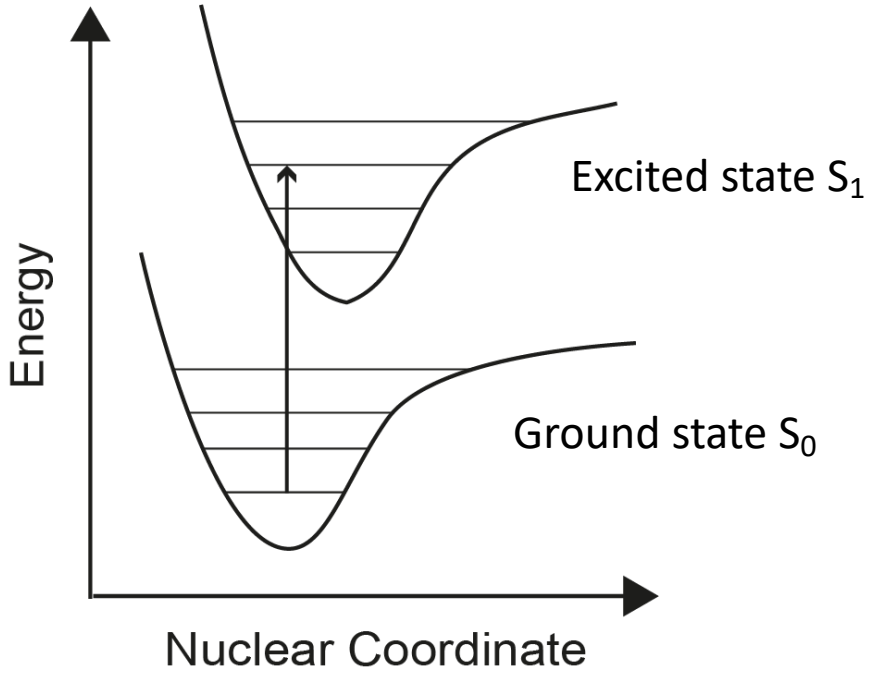


Quantized levels
Convert E as
vibrational motion

Microwave

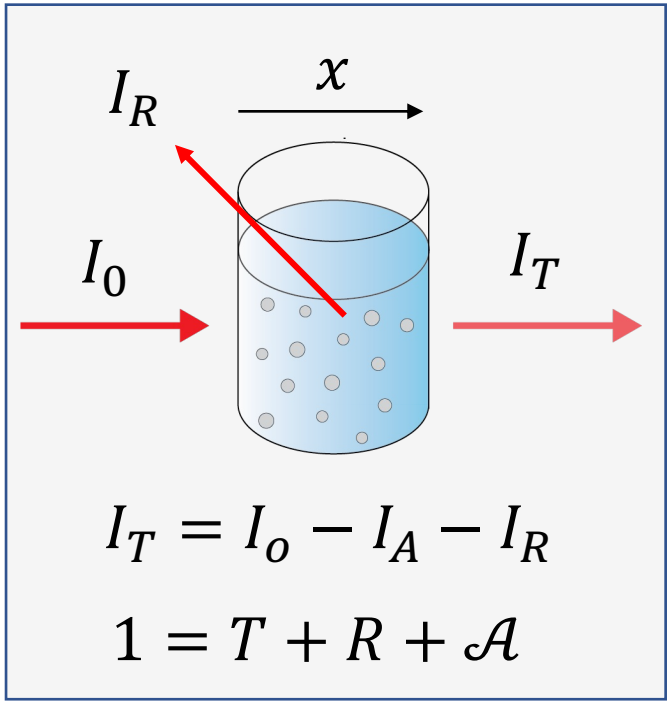
Quantized levels
Convert E as
rotational motion

Absorption timescales



Vertical transition (Franck-Condon)
10^{-16} s (sub-femtosecond)

Laws of Light Absorption



$$\frac{I_T}{I_o} = Transmittance = T$$

$$\frac{I_R}{I_o} = Reflectance = R$$

$$\frac{I_A}{I_o} = Absorptance = \mathcal{A}$$

Strict definition of **absorbance** A: $\mathrm{A} = -\log(T + R) = -\log(1 - \mathcal{A})$

Usual definition of **absorbance** A: $\mathrm{A} = -\log T = -\log\left(\frac{I_T}{I_o}\right)$

Laws of Light Absorption

Intensity (= optical power per unit area) decay through the medium neglecting scattering/reflection:

$$dI = -\propto dx \cdot I(x)$$

$$ln\frac{I(x)}{I_0} = -\propto x$$

$$I(x) = I_0 \exp(-\propto x)$$ **Beer's Law**

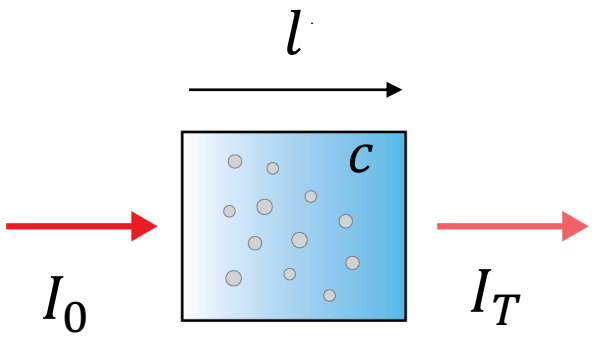
Link with the medium's complex refractive index: $\tilde{n} = n + ik$

Absorption coefficient $\propto$ (cm^{-1})

$$\propto = \frac{2\omega}{c}k = \frac{4\pi}{\lambda}k$$

Extinction coefficient k (-), Im($\tilde{n}$)

Beer – Lambert law



$$A = -\log\left(\frac{I_T}{I_o}\right) = -\log T = \varepsilon c l \ [-]$$

ε = molar decadic extinction coefficient [l mol^{-1} cm^{-1}]

c = molar concentration [mol l^{-1}]

l = optical pathlength [cm]

A often given as optical density (OD), decadic

Example:

c = 10^{-3} M and ε = 10^{4} l mol^{-1} cm^{-1}

T = 0.01, A = 2 ⇒ 99% of the light is absorbed within the first 2 mm of the solution

(OD = 2 allows 1% of light to be transmitted through the sample)

Superimposition of absorbing systems:

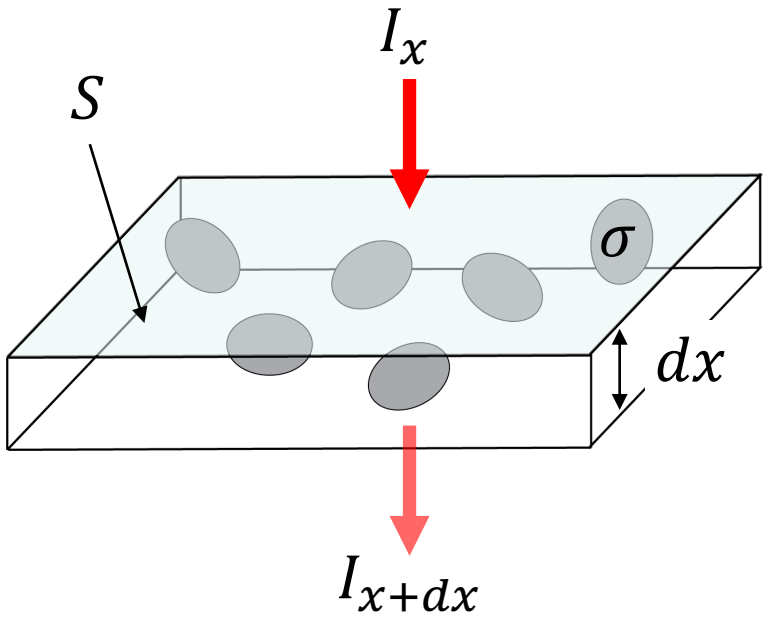
Transmittance is multiplicative: $T_{tot} = \prod_i T_i$

Absorbance is additive : $A_{tot} = \sum_i A_i$

Justification of Beer – Lambert law

Assumptions:

- Individual molecules totally block light within a characteristic cross-section σ
- Monochromatic light
- Molecules do not cast any shadow on each other (only true if the concentration *c* is low)
- **Neglect scattering/reflection**

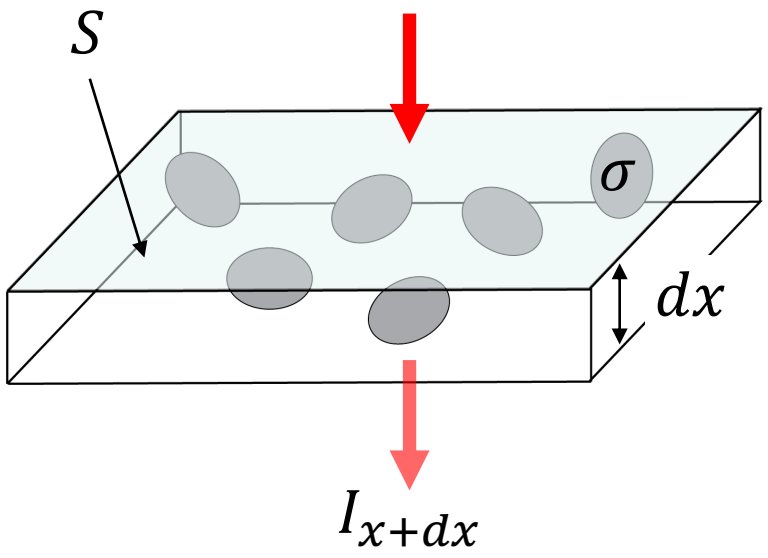


Going back to absorptance: $\mathcal{A} = \frac{I_A}{I_o}$ and $I_A = I_o - I_T$

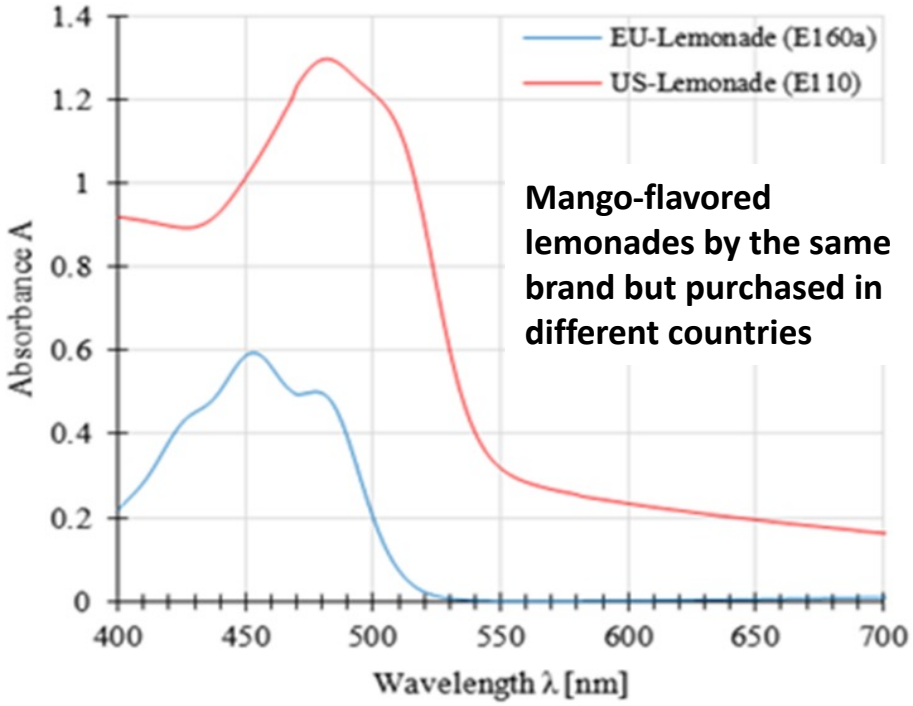
$$\Rightarrow \frac{I(x) - I(x+dx)}{I(x)} = \frac{dI}{I(x)} = -\propto \cdot dx$$

How to get $-\frac{dI}{I(x)}$ of a solution volume S · dx containing ***N*** molecules?

$$-\frac{dI}{I(x)} = \frac{Blocked\ surface}{Total\ surface}$$



What do we learn from absorption spectroscopy?



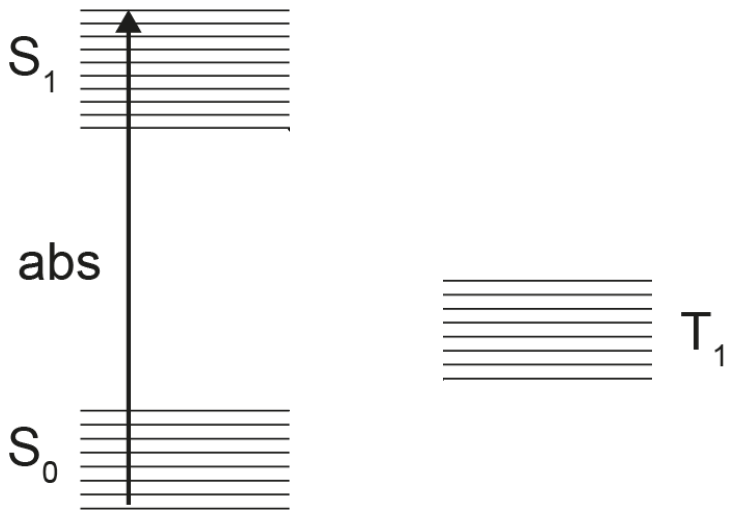
Gräb et al. , World J. Chem. Edu. **2019**, *7*, 136-144

From an absorption spectrum it is possible to determine the chemical or physical properties of a sample

- Identify molecules in a solid or liquid sample
- Determine the concentration of a particular molecule in solution
- Characterize the absorbance or transmittance through a liquid or solid vs. wavelength (example: protective glasses, filters)
- Characterize the reflectance properties of a surface
- Measure the color of a material
- Study chemical reactions or biological processes
- Nanoparticles: determine the size

Emission

Jablonski Diagrams



Process	Timescale (approx.)
Absorption	10^{-16} s (sub-femto)
Vibrational relaxation	10^{-12} s (pico)
Internal conversion	10^{-9} -10^{-6} s (nano-micro)
Fluorescence	10^{-9} (nano)
Intersystem crossing	10^{-9} -10^{-6} s (nano-micro)
Phosphorescence	s to h (forbidden transition)

Kasha's rule:
Photon emission occurs in appreciable yield only from the lowest excited state!

From **photoluminescence**, we can learn many things about excited states of molecules and materials!

Photoluminescence lifetimes

- The lifetime of radiative processes depends on the probability for the transition and thus on the Einstein coefficient for spontaneous emission
- The lifetime of the excited state is defined by the **average time** the molecule spends in the excited state prior to return to the ground state
- For $M + h\upsilon \rightarrow M^* \rightarrow M' + h\upsilon'$, concentration decrease of excited molecules in time:
- The lifetime of the fluorophore **in the absence of nonradiative processes** is called the intrinsic or natural lifetime (in practice not easy to obtain…)

Quantum yield Φ_{PL}

$$M + h\upsilon \rightarrow M^* \rightarrow M' + h\upsilon'$$

$$\Phi_{\mathrm{PL}} = \frac{N(h\nu')}{N(h\nu)}$$

Numbers of photons emitted (by unit of time, volume…)

Numbers of photons absorbed (by unit of time, volume…)

Can use the rate constants (s^{-1}) to express the quantum yield:

$$\Phi_{\mathrm{PL}} = \frac{k_{PL}}{k_{PL} + k_{isc} + k_{ic} + k_q[Q]}$$

Quenching:
Energy transfer,
collisional quenching,
excited-state reactions
(***electron transfer***!)…

Note: PL refers either to fluorescence, or to phosphorescence

Can be simplified using k_{nr}:

$$\Phi_{PL} = \frac{k_{PL}}{k_{PL} + k_{nr}}$$

Lifetimes and QY

- The quantum yield can be close to unity if the nonradiative decay rate is much smaller than the rate of radiative decay
  → Decrease internal conversion, inter-system crossing and quenching

- Natural lifetime τ_{PL} can be calculated from measured lifetime τ and QY: $\tau_{PL} = \frac{\tau}{\Phi_{PL}}$

- A simple atomic substitution can greatly change the emission

- Heavy atoms usually result in larger intersystem crossing and larger internal conversion

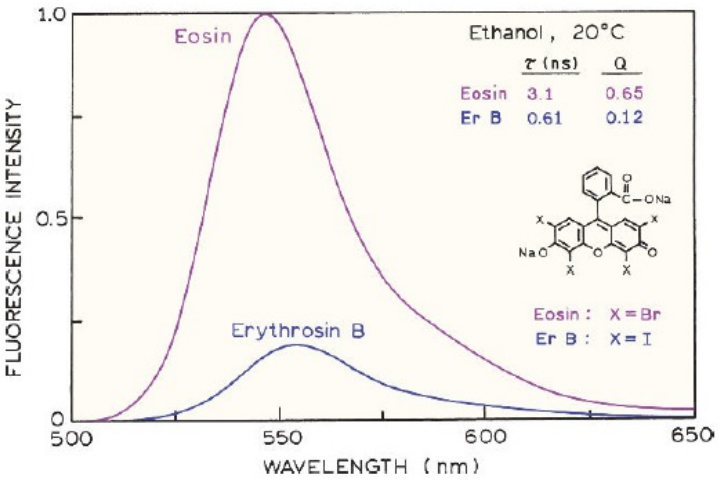
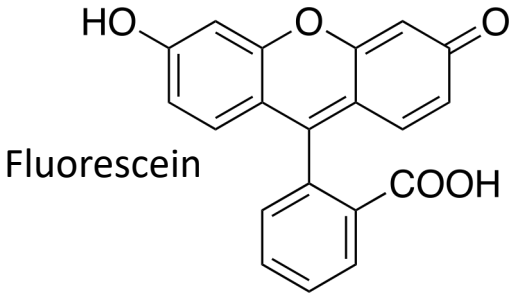


Figure 1.13. Emission spectra of eosin and erythrosin B (ErB).

PL is everywhere…

- Organic molecules with π-conjugated electrons

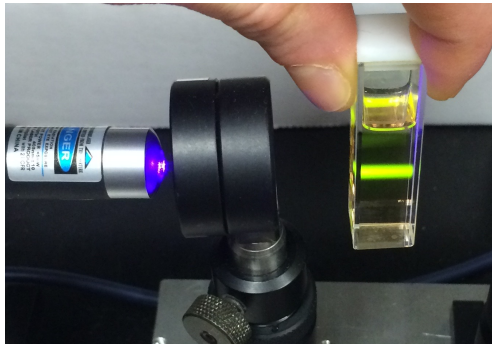
→ Depending on their size and structure, organic dyes can emit from the UV out into the near-IR



- Molecules in nature: amino acids, chlorophylls, and natural pigments

https://commons.wikimedia.org/w/index.php?curid=31042238

- Semiconductors
- Quantum dots

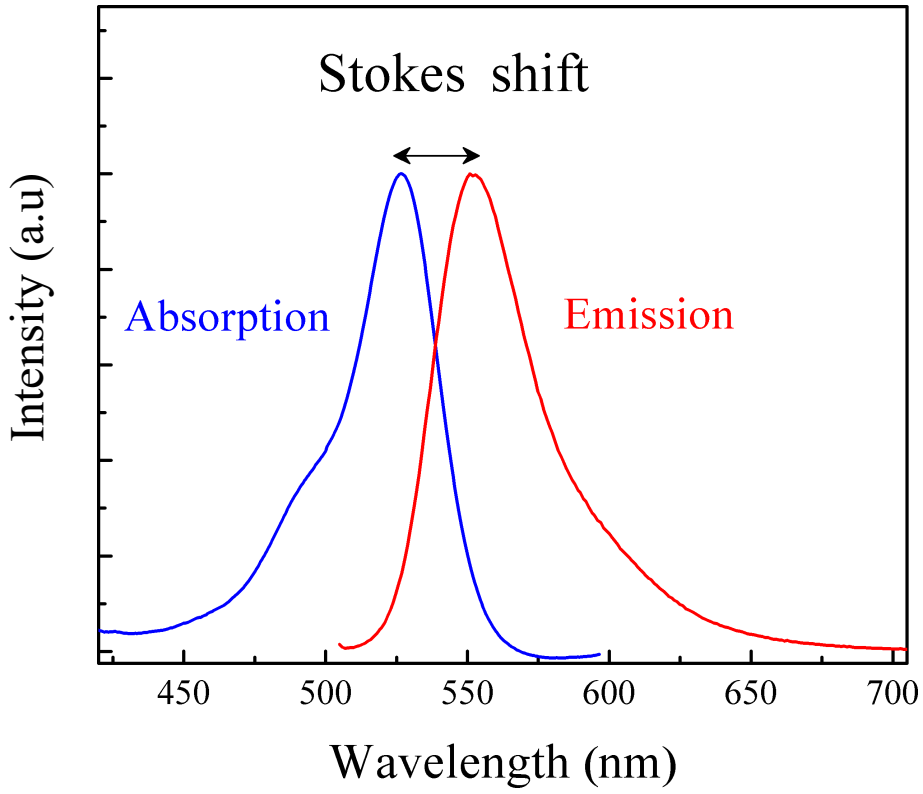


Bünzli, Trends in Chemistry, November, Vol. 1, No. 8

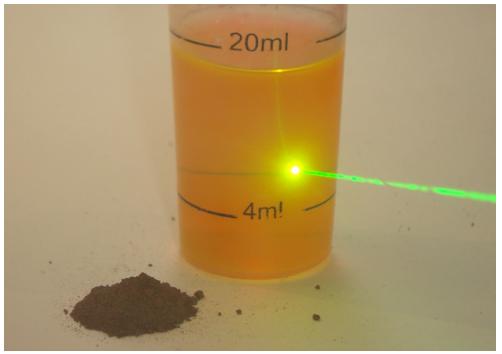
- Rare earth elements, or lanthanides

PL spectrum

- Steady state PL spectra = molecules excited by a constant source of light emit PL. The emitted photons, or intensity, are detected as a function of wavelength
- PL emission spectrum = excitation wavelength is fixed and the emission wavelength is scanned to get a plot of intensity vs. emission wavelength



Rhodamine 6G in methanol



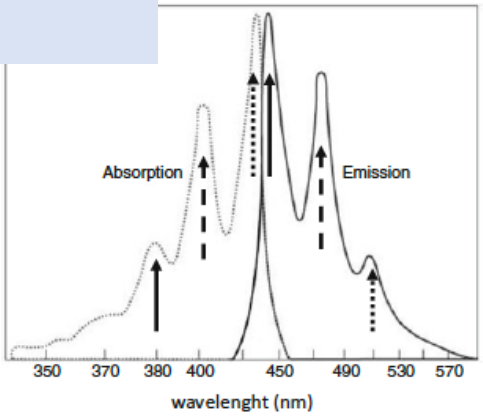
Green: 510-550 nm
Yellow ~ 560–590 nm

https://commons.wikimedia.org/w/index.php?curid=29474504
https://commons.wikimedia.org/w/index.php?curid=7423205

Absorption vs. emission spectrum

Molecules

The mirror image rule



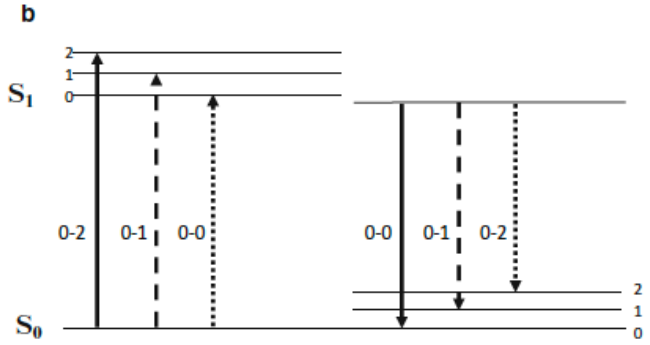
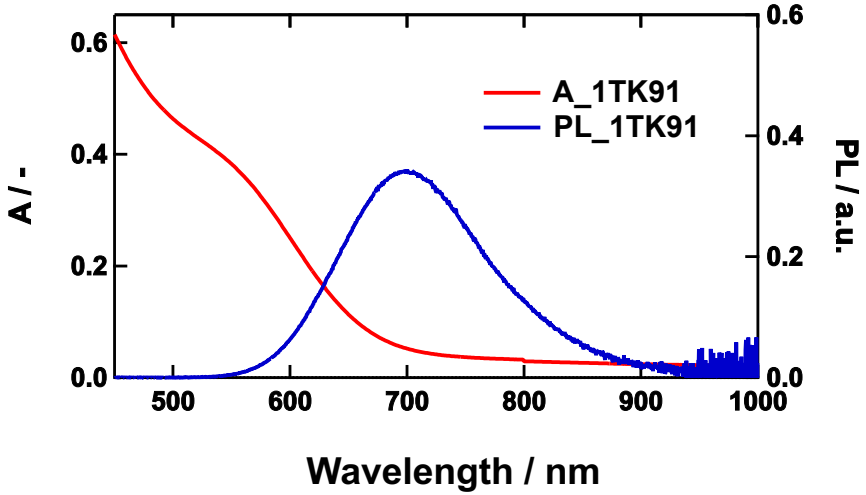


Fig. 2.5 (a) Normalized absorption and emission spectra of perylene in benzene. (b) Simplified Perrin-Jablonski diagram illustrating the mirror image rule

Bagatolli, Fluorescence Spectroscopy: Basic Foundations and Methods

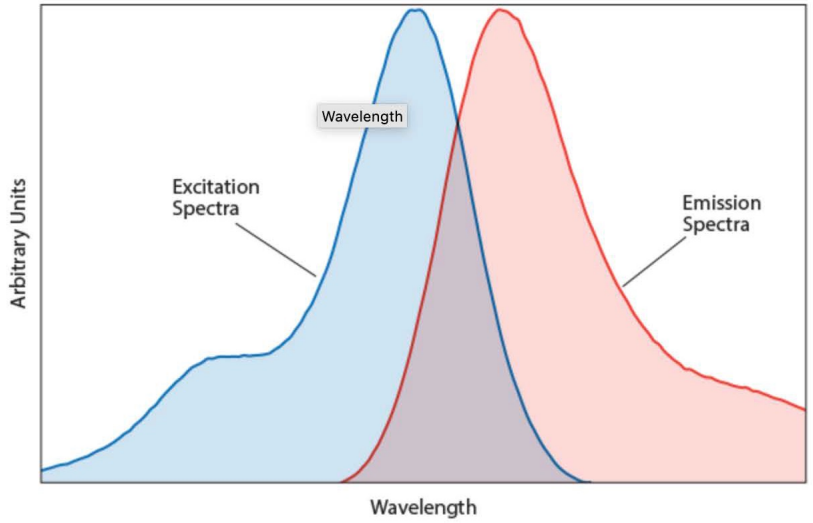
Semiconductor nanocrystals (quantum dots)



$CuInS_2/CdS$

Excitation vs. emission spectrum

PL excitation spectrum = detection of fixed emission wavelength while the excitation monochromator wavelength is scanned



Source: Chroma

- Gives information about the wavelengths at which a sample will absorb in order to emit at the single emission wavelength chosen for observation
- Analogous to absorbance spectrum, but much more sensitive technique (limits of detection and molecular specificity)
- Excitation spectra = specific to a single emitting wavelength/species as opposed to an absorbance spectrum, which measures all absorbing species in a solution or sample.
- Emission and excitation spectra of a given fluorophore are mirror images of each other (or close to)

What do we learn from PL spectroscopy?

- **Concentrations:**

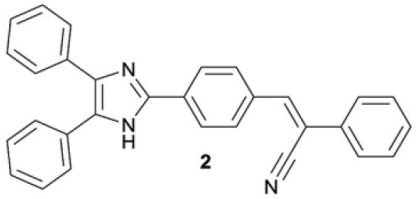
Standard concentration curves can be used to determine concentrations of the same luminescent molecule in unknown samples

- **Recombination mechanisms:**

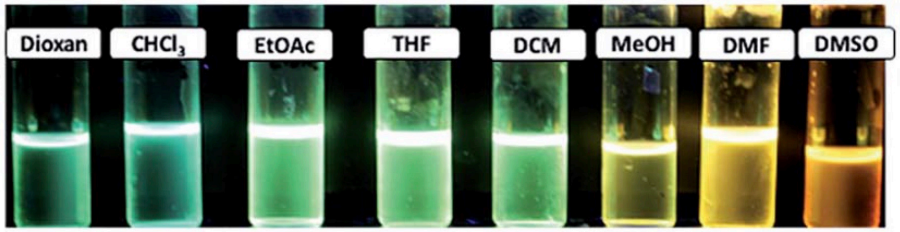
Ex: Radiative rate constants are weakly dependent on T, while non-radiative rate constant is strongly affected and will increase with increasing T

- **Solvent properties**

Ex: pH, polarity, and ion concentration



Solvatochromism of a π-conjugated luminophore for OLED



Anandhan et al., *RSC Adv.* **2019**, *9*, 12085-12096

- **Interactions with other molecules around it:**

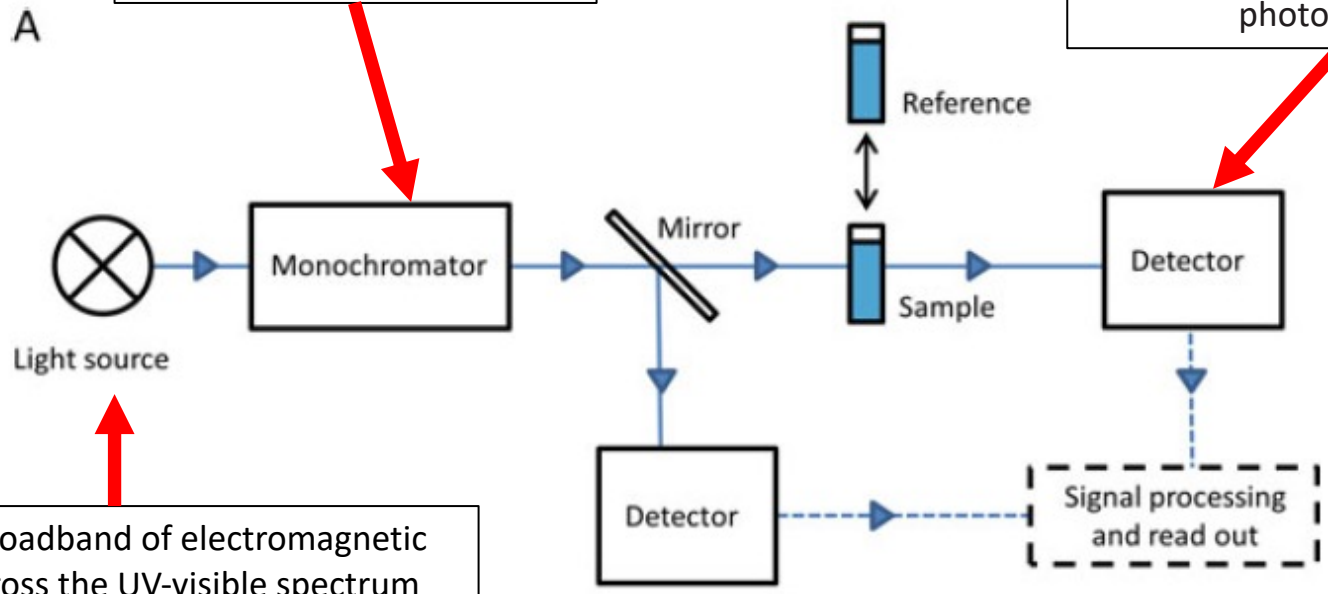
Quencher molecules and molecules or materials that involve energy transfer

How to measure an absorption spectrum?

UV-Vis spectrophotometer: Single-Beam optical layout

Separate the broadband radiation into monochromatic light

Measure the intensity of the reflected or transmitted radiation (specific for certain wavelengths, PMT or photodiodes)



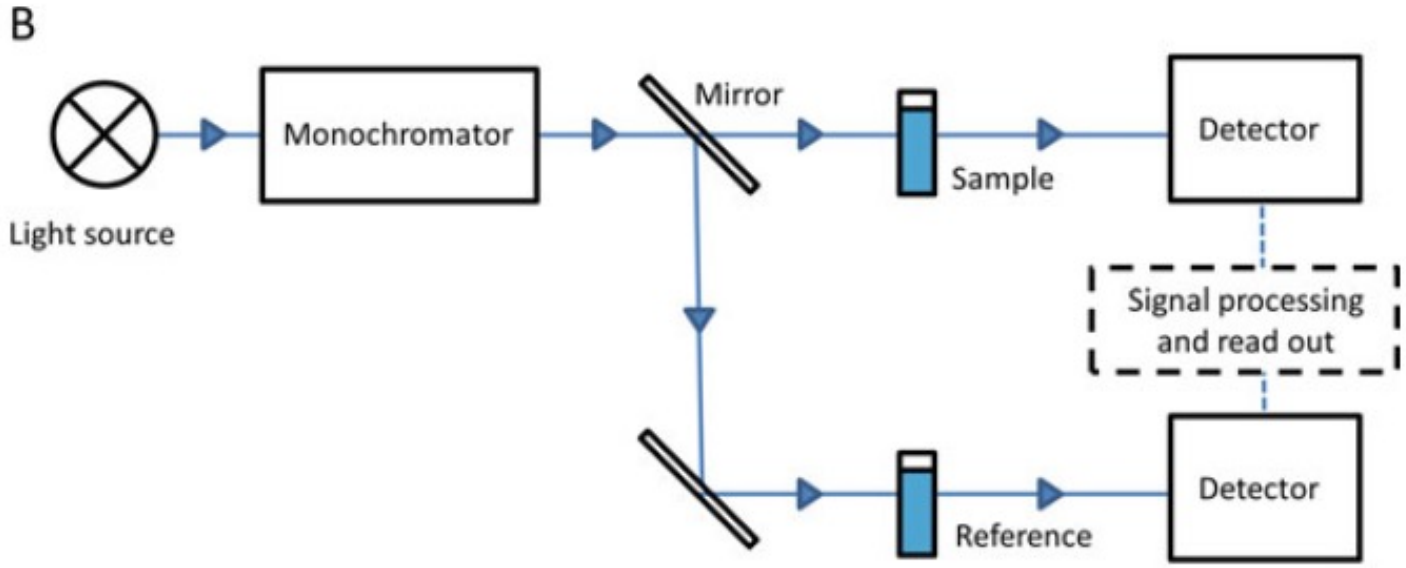
Generates broadband of electromagnetic radiation across the UV-visible spectrum

A deuterium arc lamp: good intensity continuum in the UV region and some intensity in the visible region
A tungsten-halogen lamp: good intensity over the entire visible range and NIR

Corrects for light source fluctuations

Østergaard, UV/Vis Spectrophotometry and UV Imaging

UV-Vis spectrophotometer: Double-beam optical layout



Reference and sample measured at the same time

OR

Reference detector is used to correct lamp brightness fluctuations for each measurement, while the solvent or blank (in the case of a solid sample) is measured in the sample position and then subtracted from the sample spectrum after collection

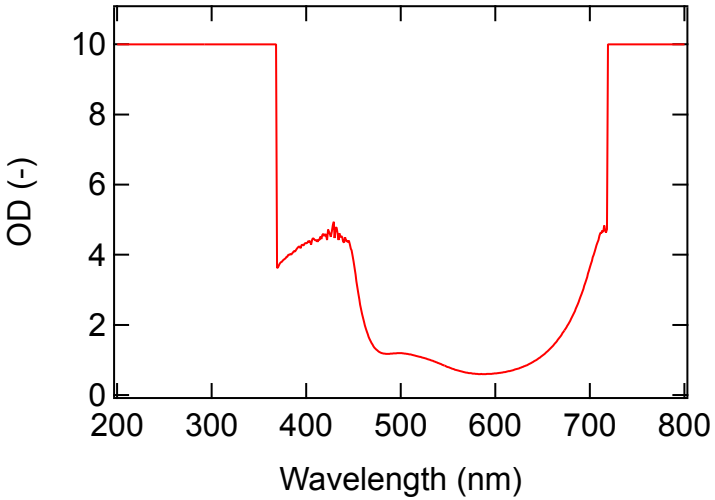
Other layouts: Pulsed white light + prism to disperse intensity at once on CCD (no monochromator)

→ Rapid because no scanning of wavelengths, better to follow kinetics

→ For sample that can degrade quickly (photosensitive)

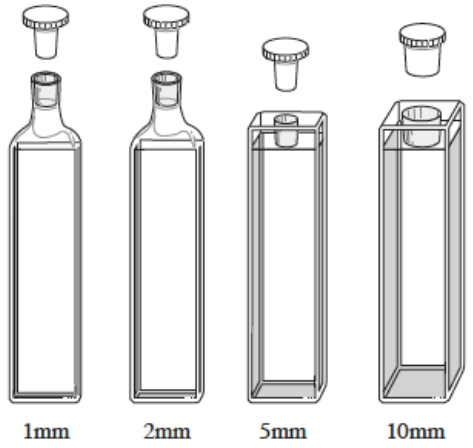
Measurement of liquid samples

- Cuvettes are important: use same face and matching pairs, remove fingerprints (absorption in the UV)



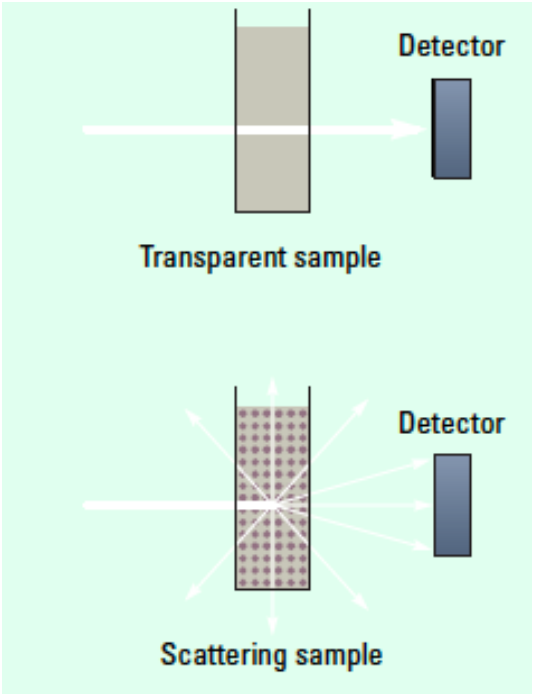
- Make a blank before (if not double beam design)

- Optimum OD around 1 to avoid noise and be able to calculate concentrations – dilute or adapt cuvettes
  - Concentrated samples with high absorbance (OD>3): short pathlength cuvette (≤ 5 mm) – or they need to be diluted
  - Short pathlength cuvettes can be used to compensate for solvents with high absorbance
  - Dilute samples with low absorbance (OD <0.2) need a long pathlength cell to help reduce the level of error (> 10 mm)



Scattering

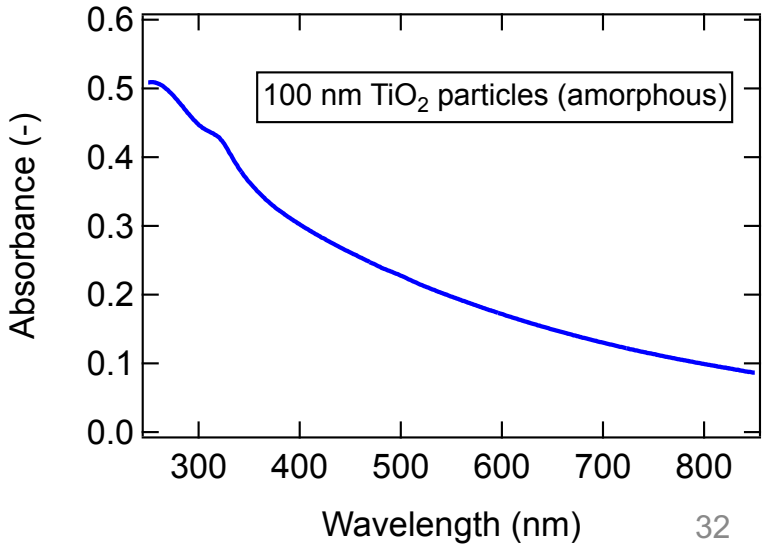
- Filtering samples prior to measurement may help reducing scattering (dust, impurities…)
- But may not always be practicable, especially if dealing with colloidal suspensions



Example: 100 nm TiO_2 particles
TiO_2 bandgap: 3.2 eV (390 nm)

Why does the absorption spectrum show absorption in the visible?

Scattering results in an apparent background absorbance!



Rayleigh and Tyndall scattering

In the UV-visible part of the spectrum, two types of scattering can be observed:

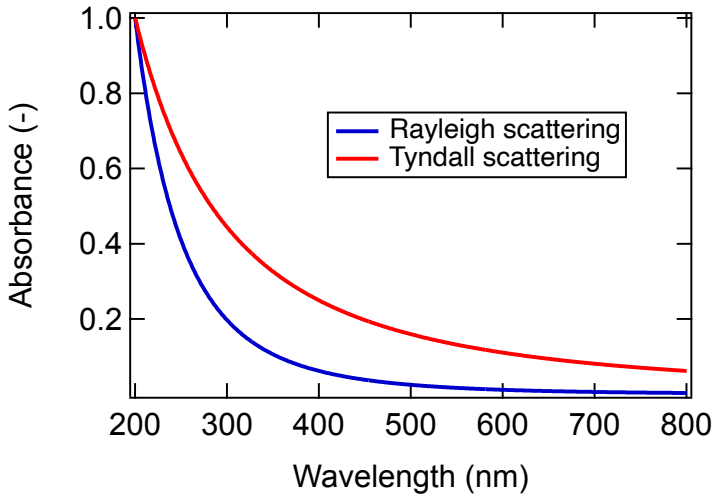
Rayleigh scattering:

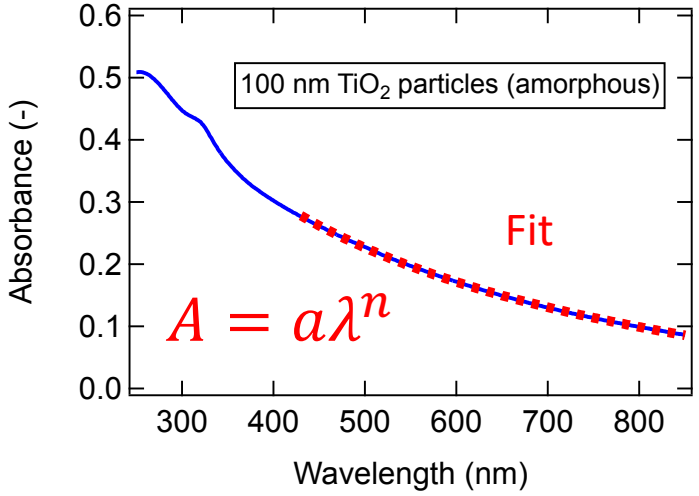
- Particles are small relative to the wavelength of light
- Proportional to λ^{-4}

Tyndall scattering:

- Particles are large relative to the wavelength of light (typically some colloids)
- Can have a more complicated wavelength dependence, but approx. to λ^{-2}

In practice, may range from λ^{-4} to λ^{-2}, depending on the distribution of particle sizes: fit with open parameter n





Rayleigh and Tyndall scattering

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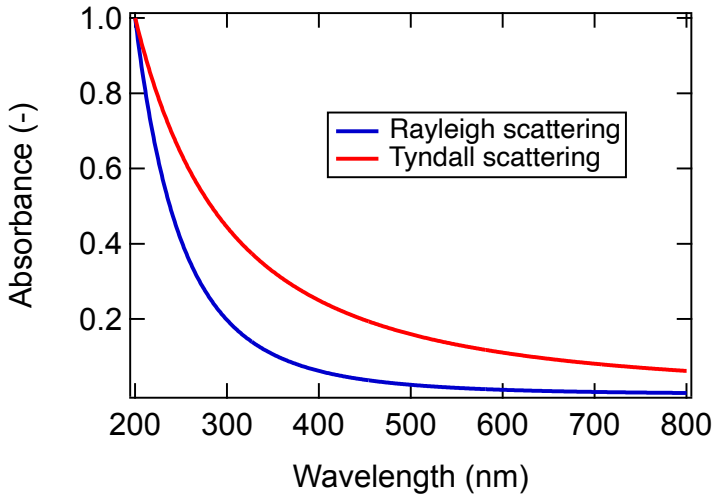

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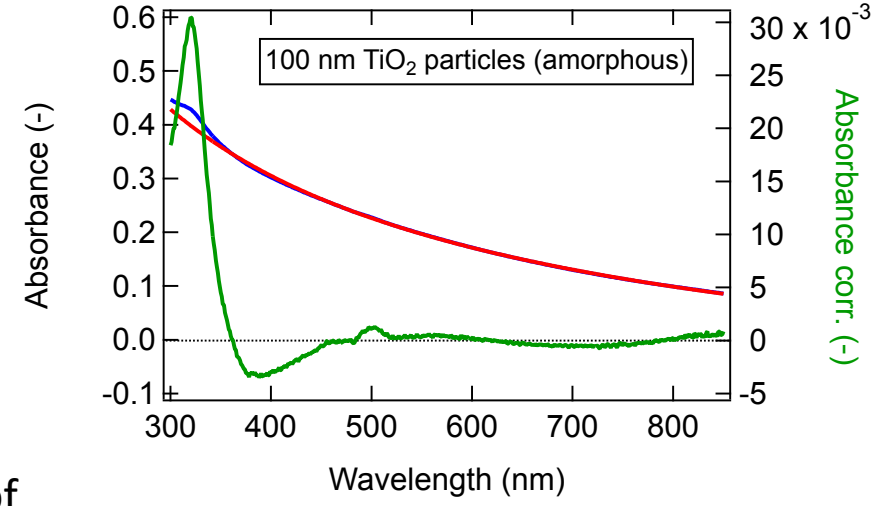
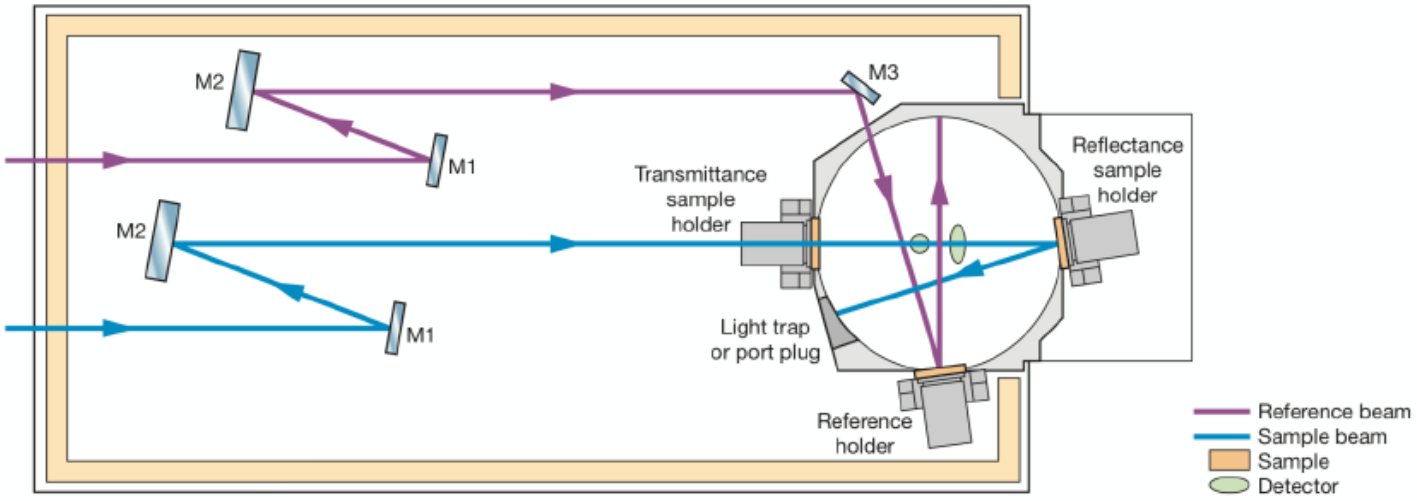


Note: If scattering results from aggregation of compound, it will be difficult/not possible to correct

Measurement of (thin) films

- As long as scattering, optical density and interferences are not a big problem…Then same precautions as a liquid scattering

- More accurate: Absorptance can be measured with an integrating sphere

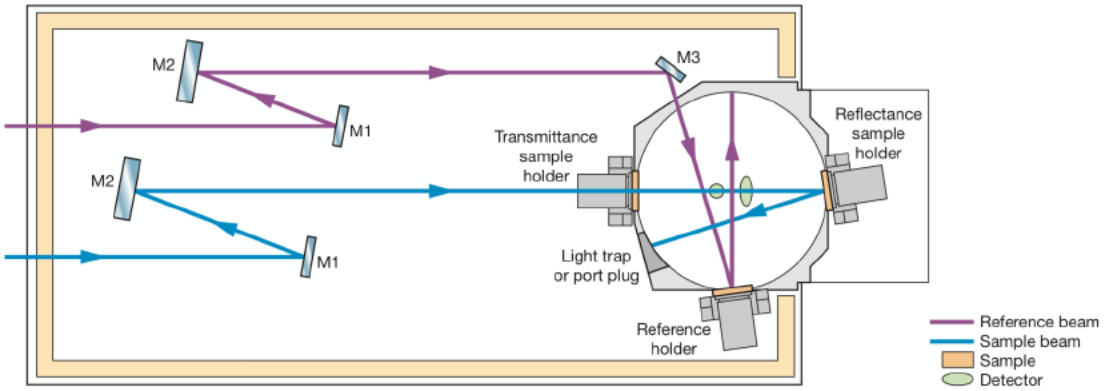


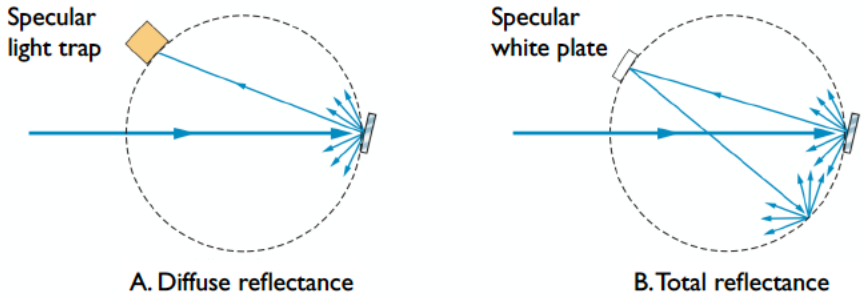
Integrating sphere is coated with an all-reflective surface such as (barium sulfate-based materials or Spectralon®) to capture all the light in the sphere

Measurement of (thin) films

- To calculate the attenuation coefficient of a thin film the **total transmittance** and **total reflectance** spectra of the material need to be acquired → $\mathcal{A} = 1 - (T + R)$

- The material cannot be opaque!





T: Measure all the transmitted light (use a specular light trap) = Specular transmittance + Diffuse transmittance

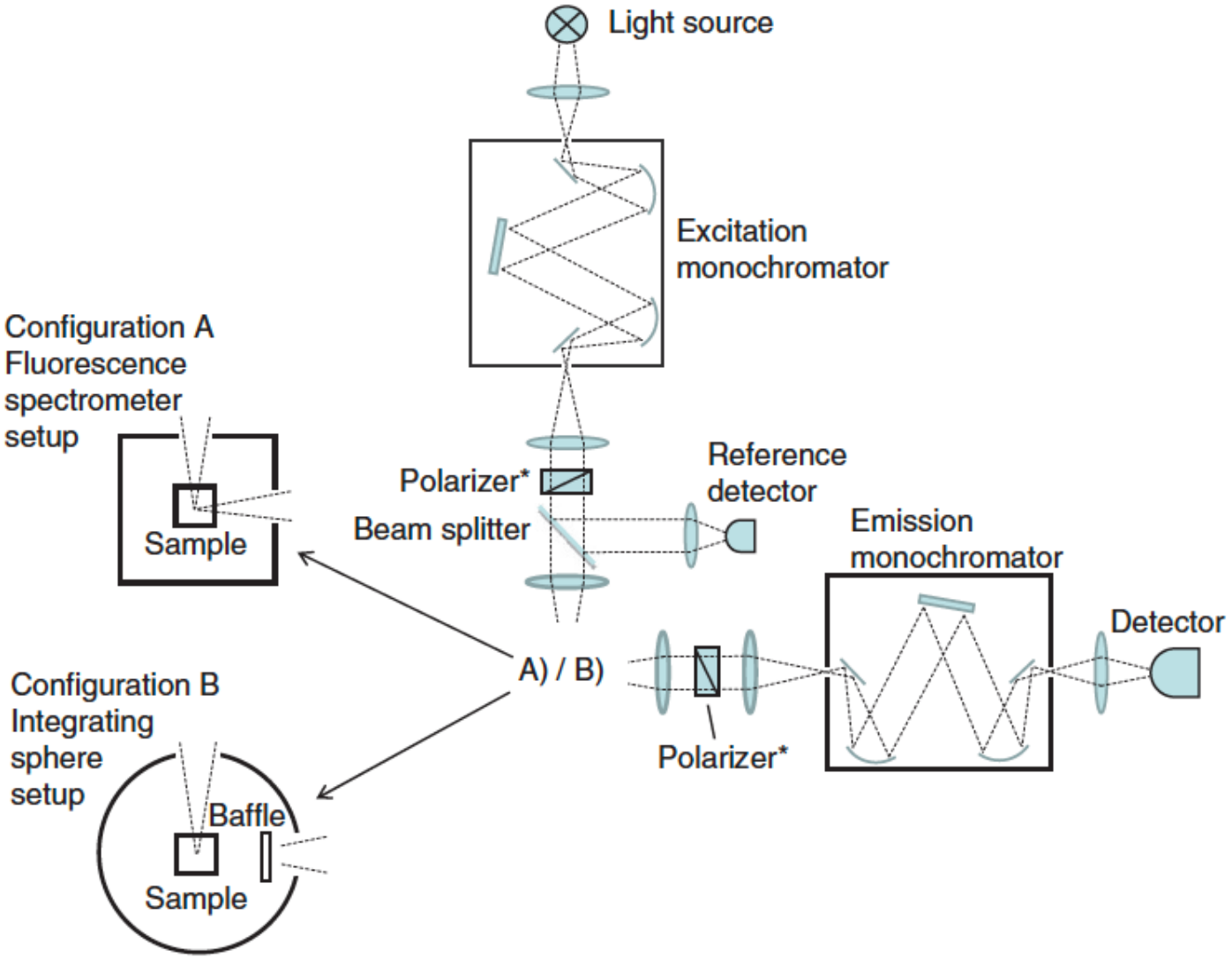
R: Measure all the reflected light (use a a specular white plate) = Specular reflectance + Diffuse reflectance

Specular = Total - Diffuse

Note: We will treat diffuse reflection later on!

How to measure a PL spectrum?

Steady-state measurement

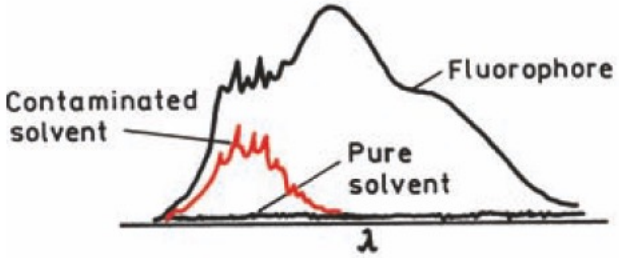


Würth et al., Nature Protocols, 2013, 8, 1535–1550

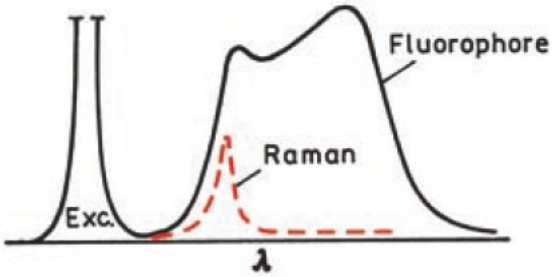
Common problems

Fluorophore concentration too high

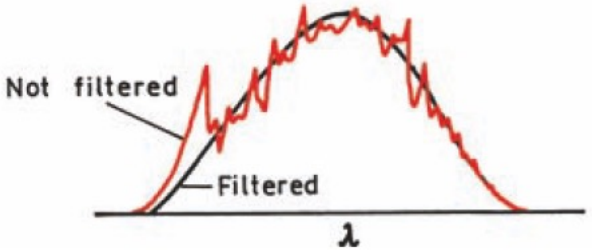
Contaminated solvent and / or cuvette



Scattered light

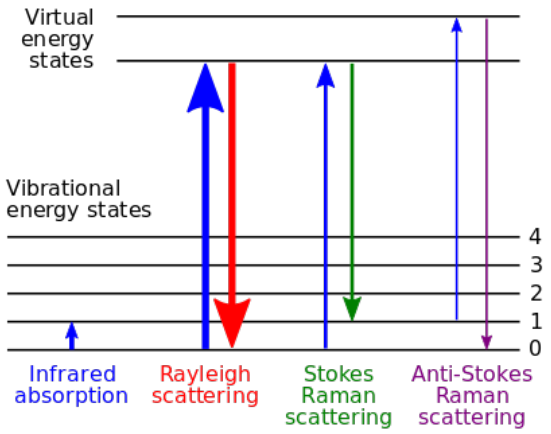


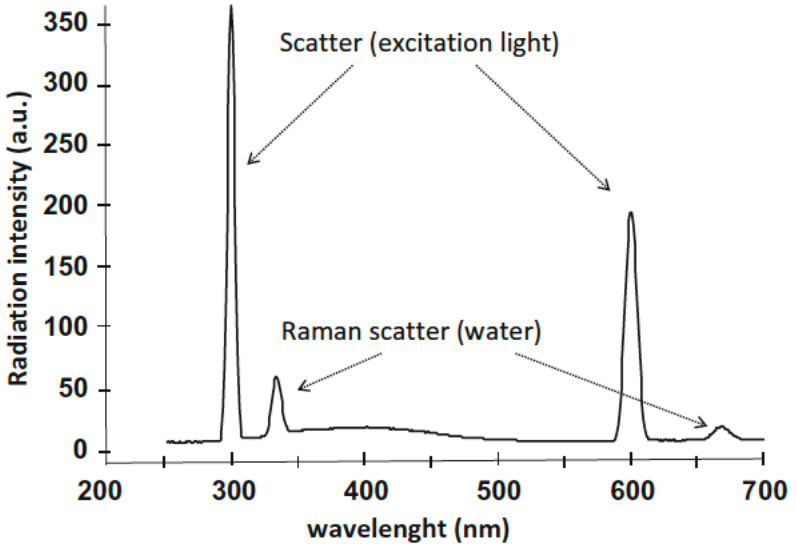
Particles in solution



Importance of blank measurement

- If the PL intensity is weak, Raman peaks can be seen in a PL spectrum
- The spectrum of a blank solvent can be measured under the same conditions as the sample, then subtracted from the sample spectrum
- Position of Raman peak changes with excitation wavelength but Raman shift remains the same
- Raman peak of water (shift) can be used for calibration





Bagatolli, Fluorescence Spectroscopy: Basic Foundations and Methods

Fig. 2.10 Emission scan from 250 to 700 nm with excitation at 300 nm, peaks correspond (from *left* to *right*) to Rayleigh scatter (300 nm), Raman scatter (334 nm), second order Rayleigh (600 nm) and second order Raman (668 nm)

Measuring quantum yields

- **PLQY** = number of photons emitted as a fraction of the number of photons absorbed

→ This characteristic property of a fluorophore or fluorescent molecule is important for understanding molecular behavior and interactions for many key materials

- **ELQY** = the number of photons emitted divided by the electron current of a device

→ This is important for lighting, display devices…

Two main methods for measuring QY:

1) Relative method:

- Compare the integral of the emission spectra of a sample to a known sample (ex.: fluorescein) under identical measurements conditions
- Requires only a fluorimeter and a spectrometer
- Rather used for samples in solution

2) Absolute method:

- Uses an integrating sphere and which is applicable to both solutions and solid samples
- Three measurements are required for the determination of the fluorescence quantum yield.

Timescales

- Reminder: Natural lifetime τ_f can be calculated from measured lifetime τ and QY:

$$\tau_f = \frac{\tau}{\Phi_f}$$

We saw how to obtain the quantum yield
But how do we measure τ of fluorescence/phosphorescence?

1) For strongly luminescent compounds and relatively slow τ :
Measures fluorescence intensity at specific time intervals after the excitation pulse by opening a gate

2) For weakly luminescent compounds and relatively fast τ :
Time-correlated single photon counting → We will see this later on in the course