Optical absorption
Theory, implementation and applications

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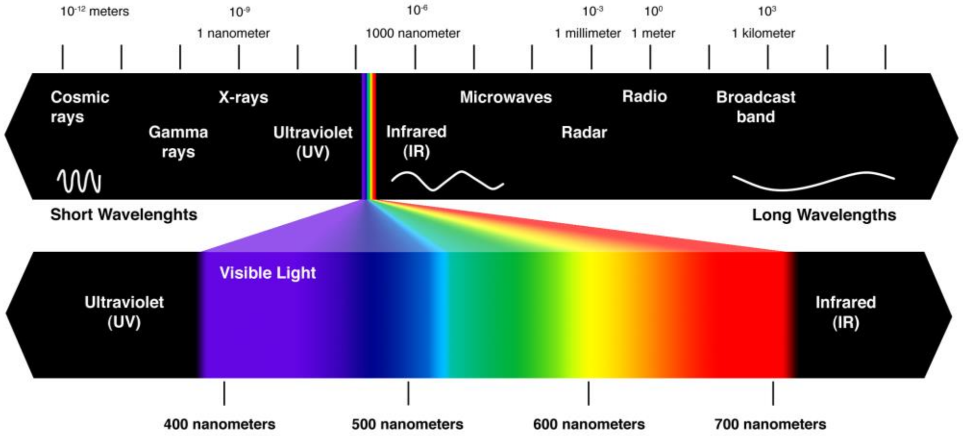
What is optical absorption

- All materials are made up of protons, neutrons and electrons
- Light (photons) interact with charged species i.e. protons and electrons
- In some cases a photon transfer all its energy to a proton or electron – this is absorption. The photon is 'absorbed' and ceases to exist.
- At optical wavelengths (i.e. the colours we see) photons normally interact with electrons. This lecture focuses on this



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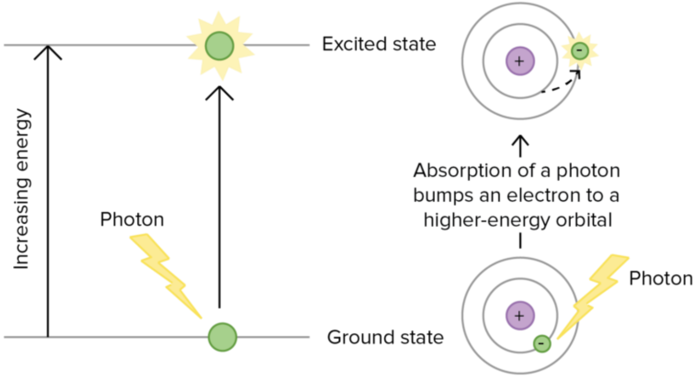
Two measurements

- We can’t measure something that has ceased to exist
- Measuring the energy change of the electron directly is difficult
- We measure the number of photons not absorbed, typically by those reflected and those transmitted
- Photons not reflected or transmitted are those absorbed



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Applications

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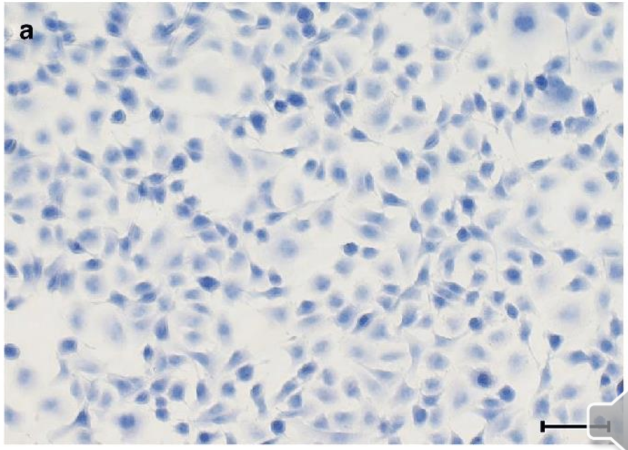
- Sight is partly based on reflection and transmission
- Understanding biological cells
- Observing chemical reactions
- Calculating the potential of solar cells
- X-rays
- The composition of stars
- ......



Hammoudeh, S.M., Hammoudeh, A.M. & Hamoudi, R. *Histochem Cell Biol* **152**, 75–84 (2019). https://doi.org/10.1007/s00418-019-01775-7

Sections

- Transmission and reflection measurements
- The theory of transmission and reflection
- Practical examples

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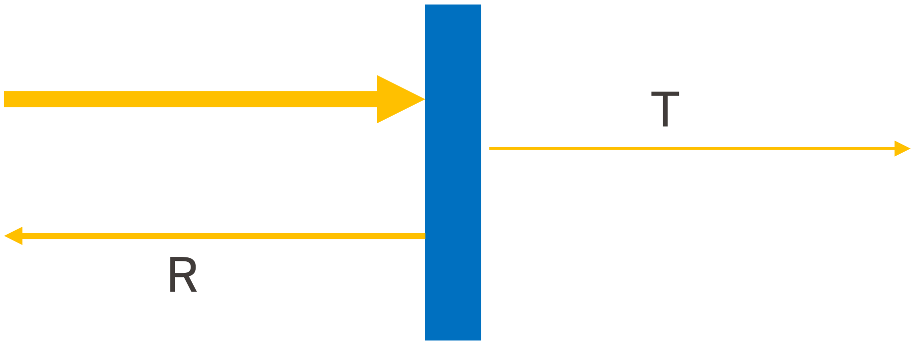
The simple picture

- Light comes from a light source
- We measure the light reflected (R) and transmitted (T)
- The absorption is A=1-R-T



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An example to do at home

- Ambient light and cameras can be used to measure transmission and reflection
- Here is a simple example of looking at the effect of making tea
- Most phone cameras automatically adjust exposure settings

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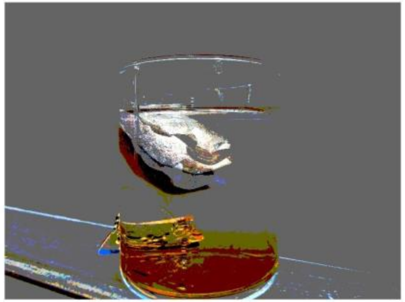
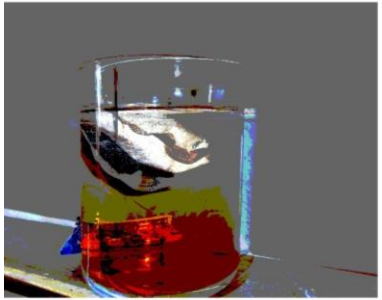
An example to do at home

- Here I calculate the % change in transmission $\frac{New\ image}{Original\ image}$



100s



200s

300s

400s

- For this sample I know change in transmission is due to absorption

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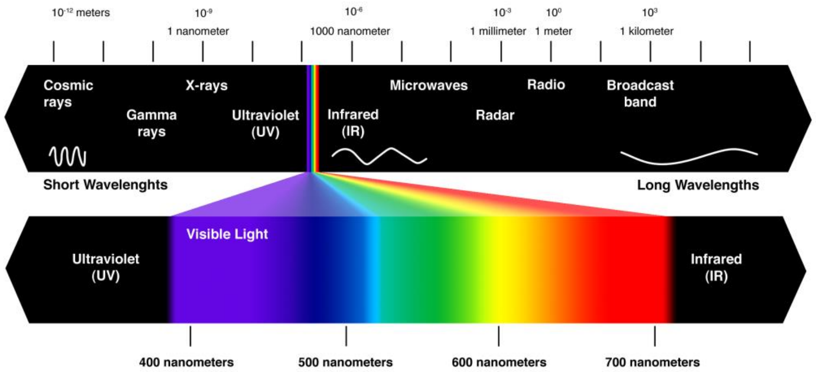
Limitations of the tea experiment

- Ambient light can change (e.g. the sun moves)
- We can't be sure all the signal is due to transmission and not reflection
- We don't have wavelength resolution i.e. we just measure some average absorption



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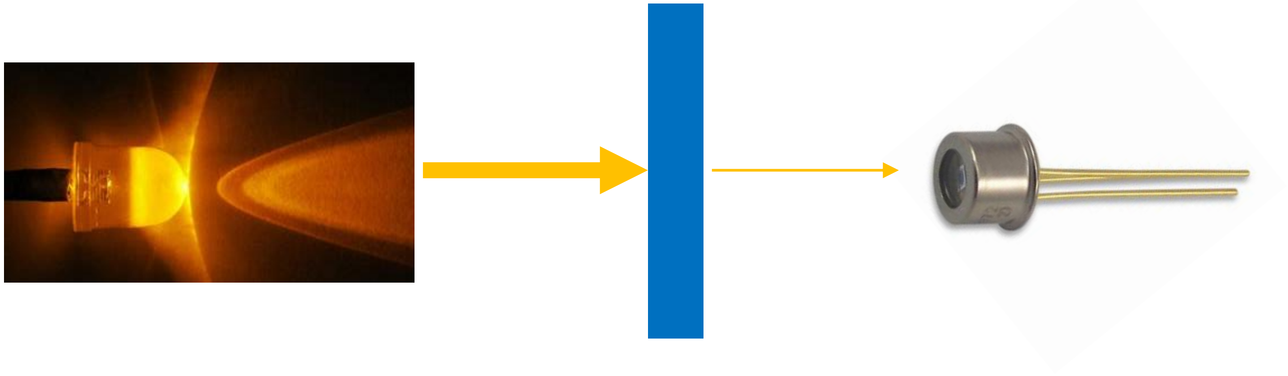
Equipment to measure transmission and reflection well – monochromatic measurement

- Monochromatic light source (LED, laser pointer)
- Detector (typically a ‘photodiode’, though can be a camera)
- Can only measure one wavelength



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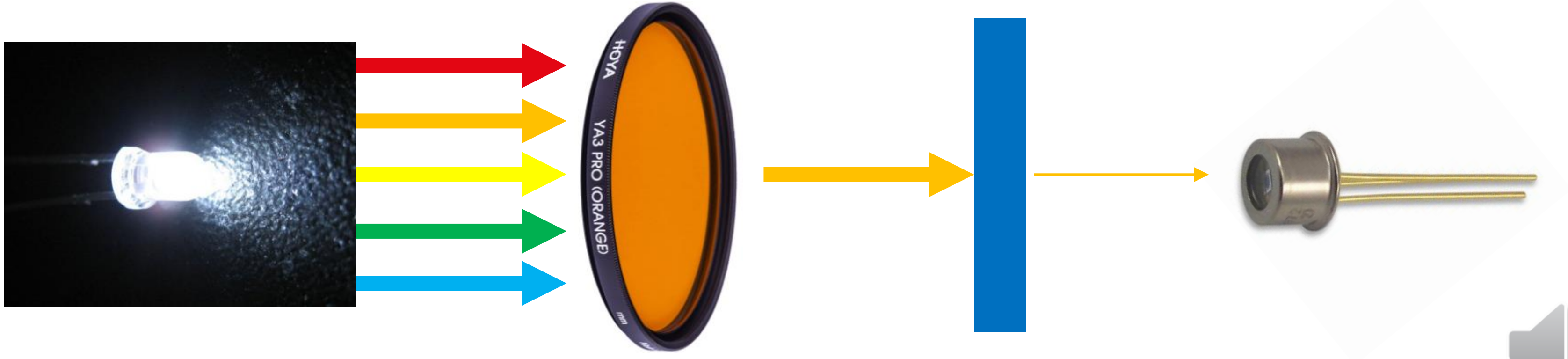
Equipment to measure transmission and reflection well – UV-Vis measurement

- Broadband white light source (lightbulb, Xenon arc lamp…)
- Single wavelength selector (bandpass filter or diffraction grating)
- Detector (typically a ‘photodiode’, though can be a camera)



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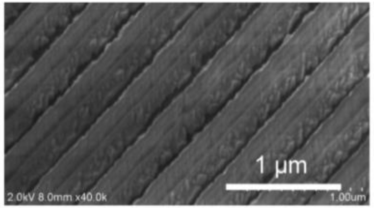
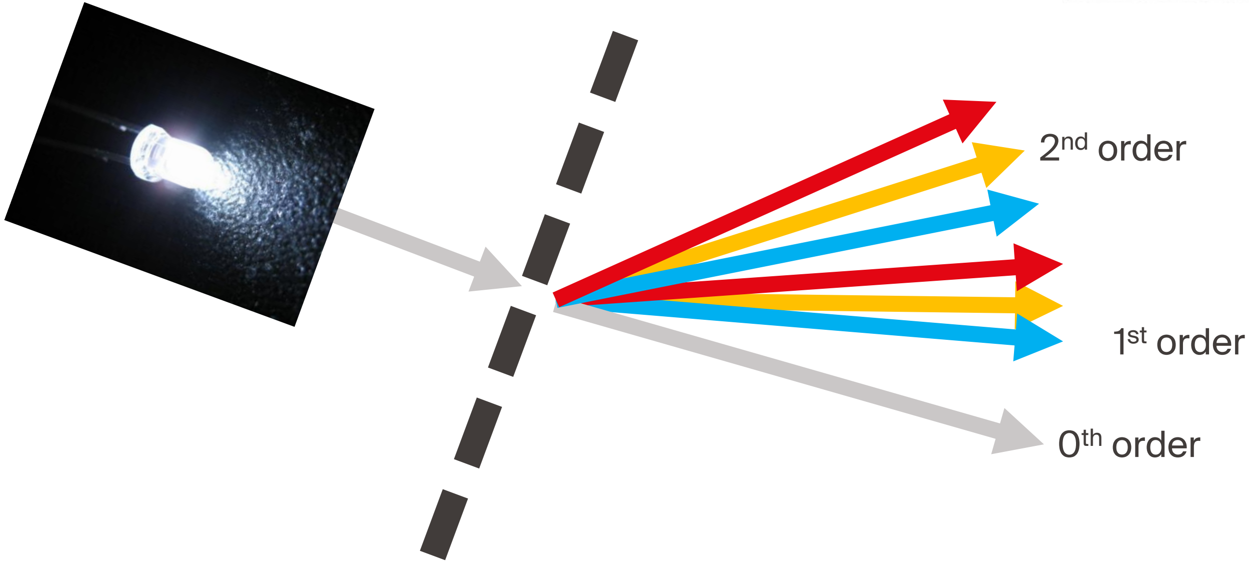
Diffraction gratings

- Microscale repeating unit
- Spread colours of light over many angles





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Equipment to measure transmission and reflection well – UV-Vis measurement

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- Broadband white light source (lightbulb, Xenon arc lamp…)
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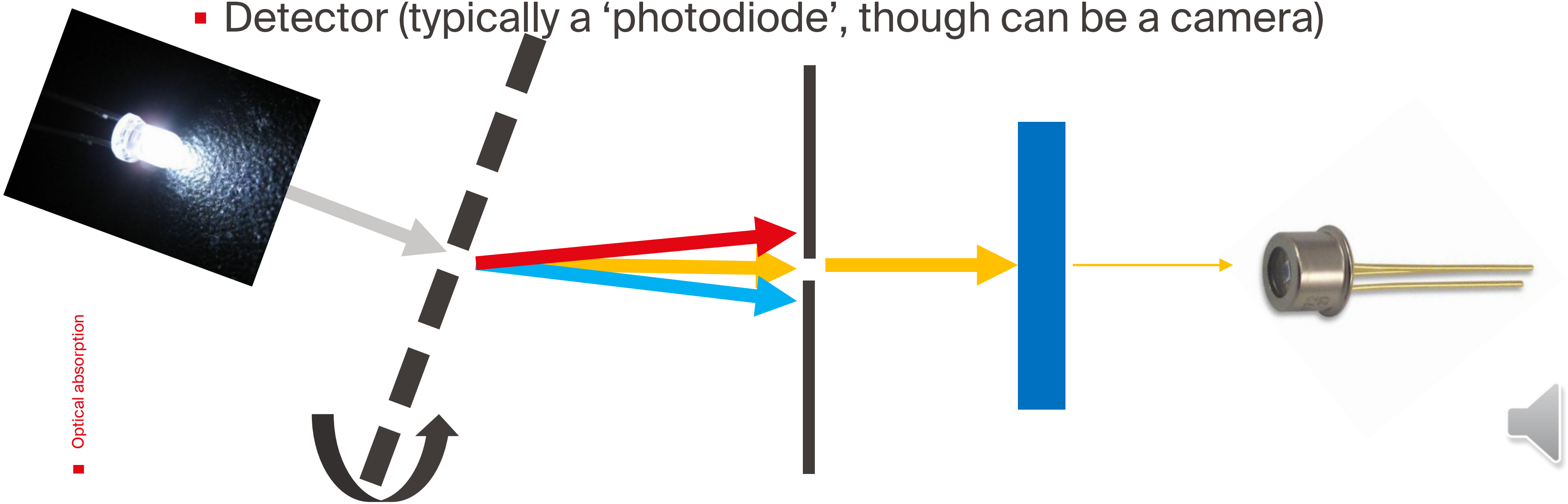
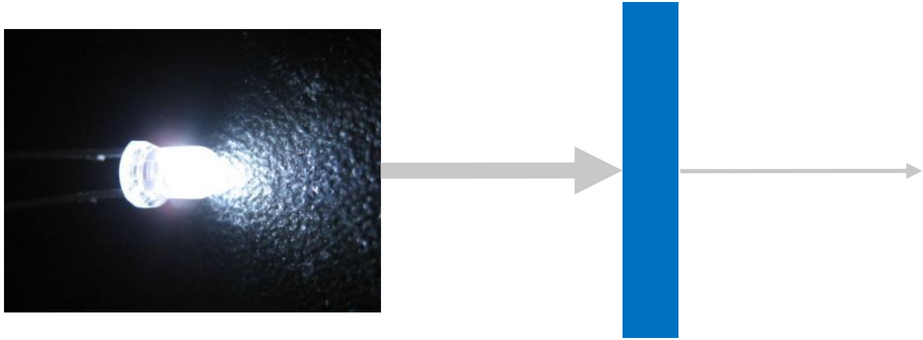
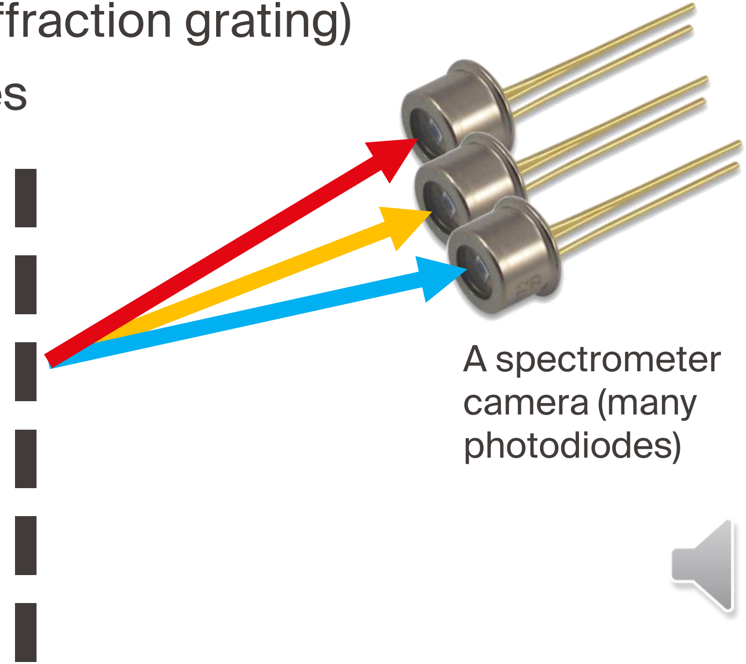


Equipment to measure transmission and reflection well – Spectrometer measurement

- Broadband white light source (lightbulb, Xenon arc lamp…)
- Single wavelength selector (filter or diffraction grating)
- Camera made up of many photodiodes





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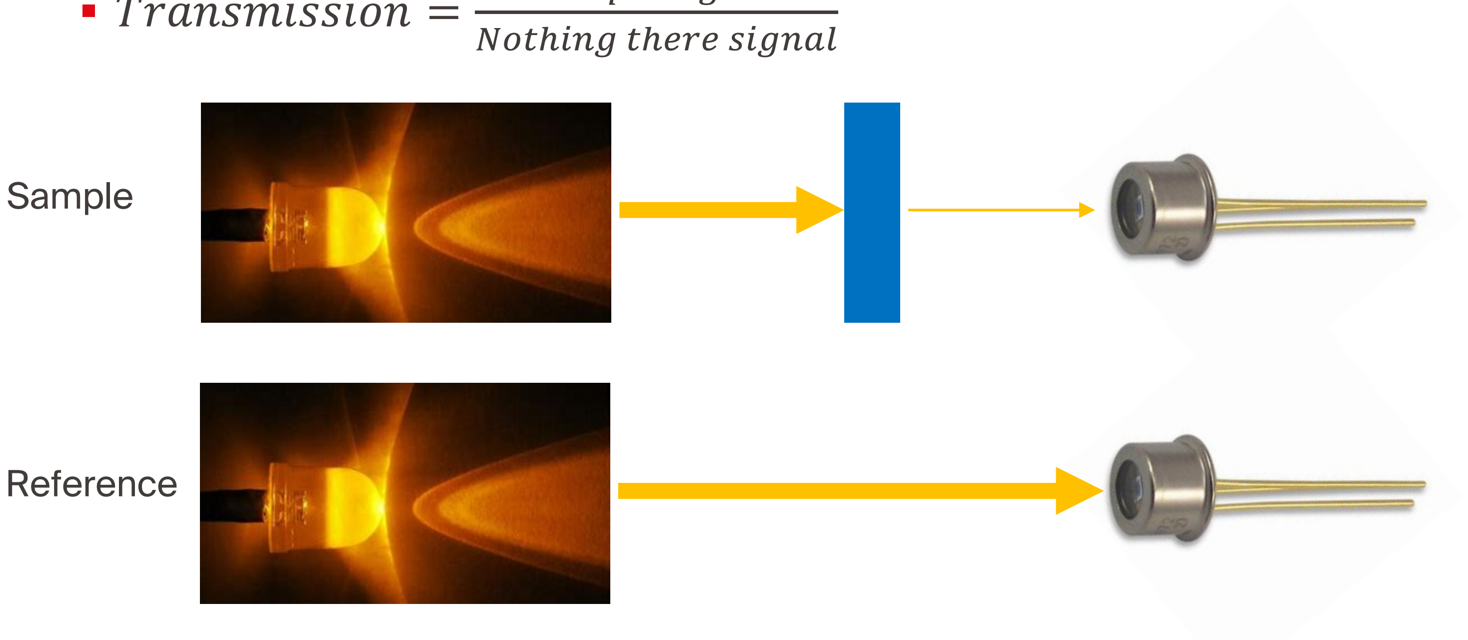
Experimental layout to measure transmission

- Everything is in one line
- $Transmission = \dfrac{Sample\ signal}{Nothing\ there\ signal}$



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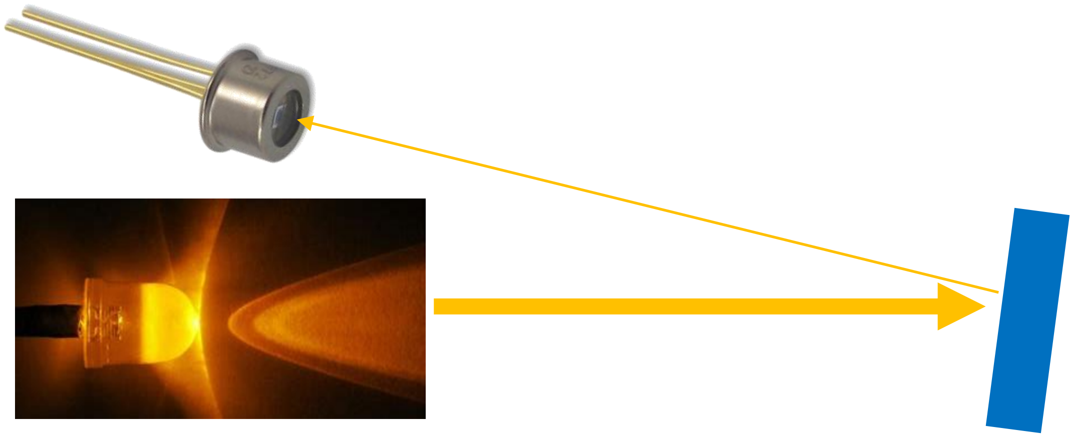
Experimental layout to measure reflection

- Keep everything as close to one line as possible
- Need a mirror (or similar) with known reflection spectrum (see later)
- $Reflection = \frac{Sample\ signal}{Reference\ signal \div Reflection\ strength\ of\ reference}$



Sample and reflection reference both have same position

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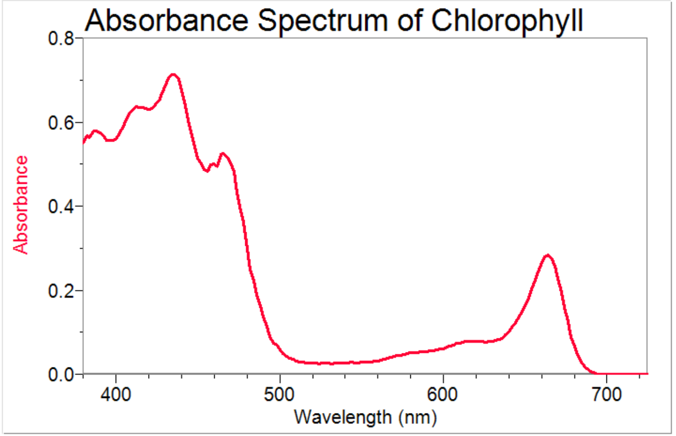
How to do a measurement and the sample

- Make sure that the substrate/glass/liquid your sample is on/in does not have a strong optical response
- $Absorption = 1 - Transmission - Reflection$



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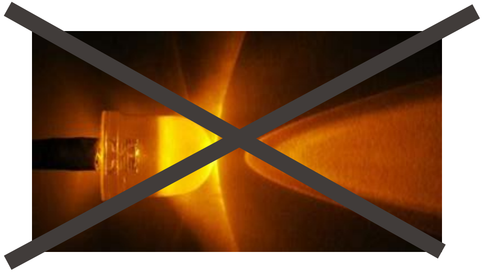
Background signals

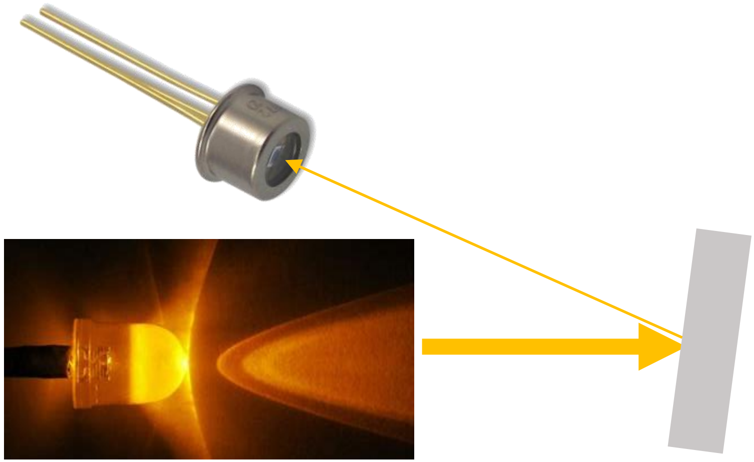
- In any measurement there is a background signal (when the light source is turned off)
- $Transmission = \frac{Sample\ signal - Background\ signal}{Nothing\ there\ signal - Background\ signal}$
- $Reflection =$

$$\frac{Sample\ signal - Background\ signal}{(Reference\ signal - Background\ signal) \div Reflection\ strength\ of\ reference}$$



References and how to calibrate them

- Here I discuss the process for a mirror
- Often companies will publish this data
- $Reflection\ reference\ strength = \frac{Reflected\ signal - Background\ signal}{Direct\ signal - Background\ signal}$



Mirror, want light as close to perpendicular as possible

Nothing there (raw light source counts)

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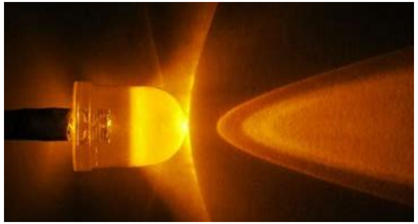
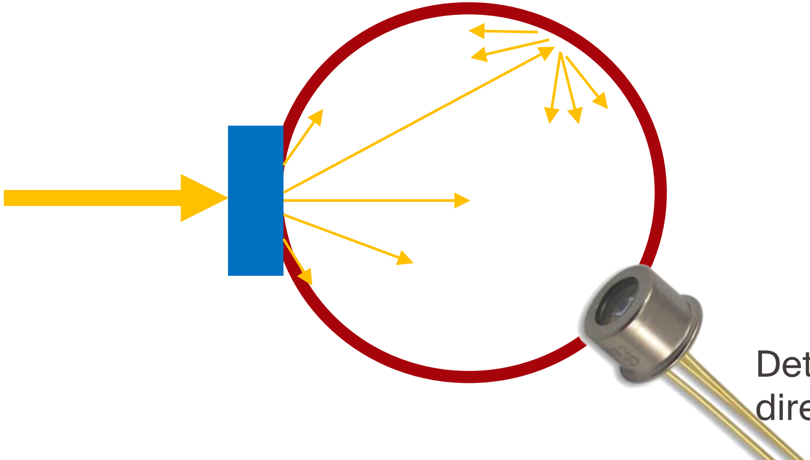
Light scattering – direct and diffuse measurements

- In reality light doesn’t just travel in straight lines
- Rough samples scatter light in many directions
- We use ‘integrating spheres’ to measure this
- Integrating spheres randomise the direction of light inside

Sample





Detector not in the direct light path

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Light scattering – direct and diffuse measurements

- Direct reflection/transmission/absorption is without an integrating sphere
- Diffuse reflection/transmission/absorption is with an integrating sphere
- Both definitions can be useful for answering different questions
- If scattering is strong

$$Absorption = 1 - direct\ transmission - direct\ reflection - scattering$$
$$= 1 - diffuse\ transmission - diffuse\ reflection$$

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Optical absorption as a function of angle

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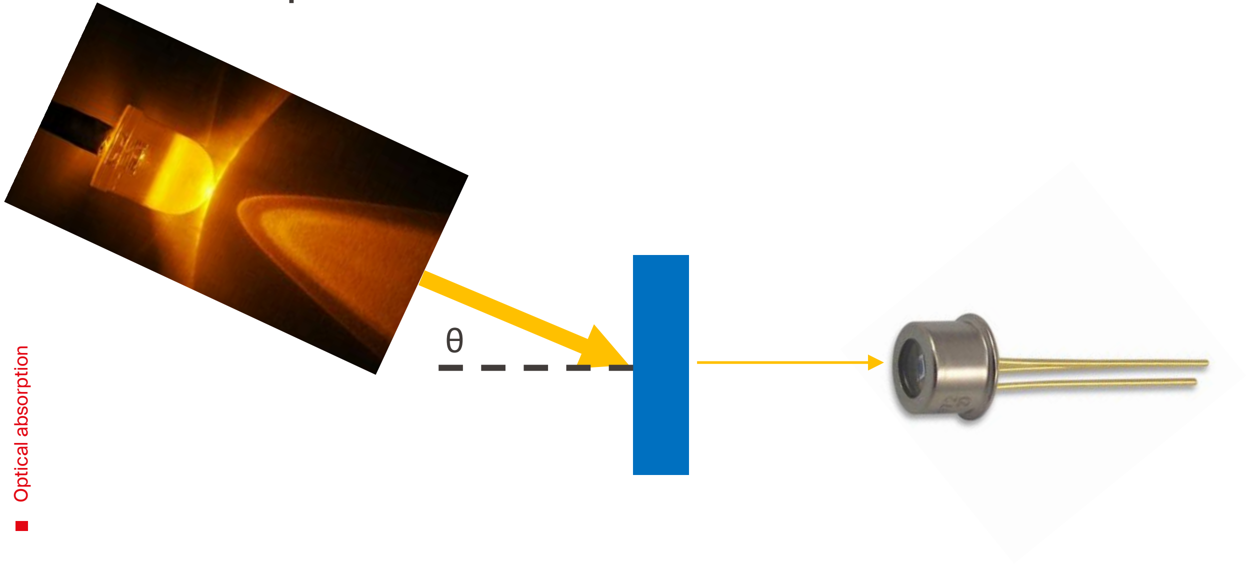
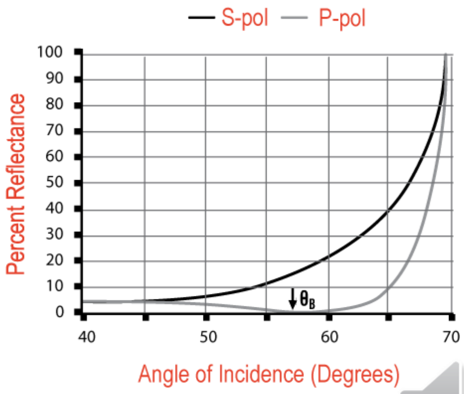
- Direct measurements are a function of angle of the incident light
- If not stated, it's assumed the incident light is perpendicular to the sample





Sections

- Transmission and reflection measurements
- The theory of transmission and reflection
- Practical examples

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Optical constants

- All materials have optical constants
- Different fields call these different terms
- The real refractive index (n) determines the speed of light in the material
- The extinction coefficient/imaginary refractive index (k) determines how strongly the sample absorbs
- Often the total refractive index is written as N=n+ik
- Some groups use relative permittivity, ε, which has real and imaginary parts. For a non-magnetic material $N = \sqrt{\varepsilon}$.
- These constants are available online for many materials, e.g. https://refractiveindex.info

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Beer-Lambert Law 1

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- The absorption coefficient, α, is defined as the fraction of light intensity absorbed per unit length
- $\alpha = \frac{4\pi k}{\lambda}$, where λ is wavelength
- Consider light travelling in a medium. We can state that

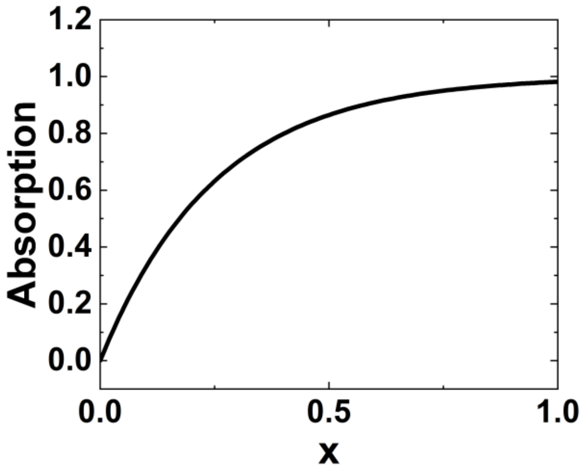
$$I(x + dx) - I(x) = -\alpha I(x)dx$$

where I is the intensity of light and x the position in the material.

- This can be solved to give $I(x) = I_0 e^{-\alpha x}$, where I_0 is the intensity at $x = 0$

Beer-Lambert Law 2

- $I(x) = I_0 e^{-\alpha x}$
- Light is absorbed by an exponential function within a material
- The absorption between $x = 0$ and x is given by that not present at x, $Absorption = I_0(1 - e^{-\alpha x})$



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Calculating transmission and reflection for a thick object - 1

- For thick objects we only need to consider the intensity of light
- All materials start and end somewhere – at these surfaces reflect and transmit light
- The intensity reflection coefficient between two materials is given by $R_{12} = \left|\frac{N_1 - N_2}{N_1 + N_2}\right|^2$ (not derived here)
- Within a material there are many reflections, these must all be accounted for

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Calculating transmission and reflection for a thick object - 2

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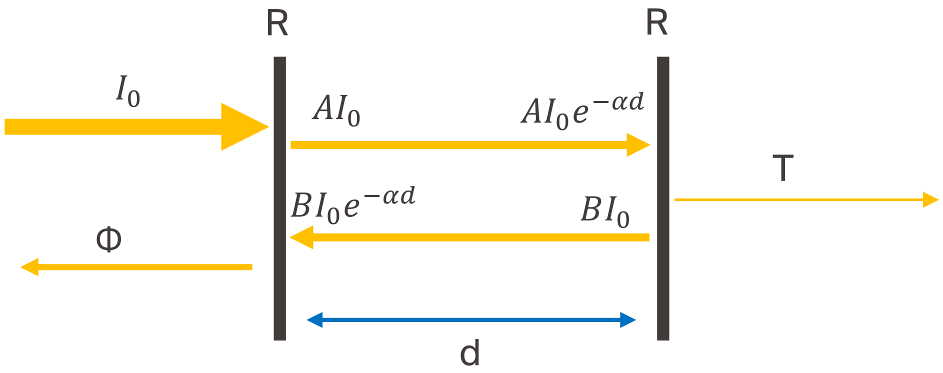
- Consider the following situation (no scattering)



- We can say:

$$AI_0 = (1-R)I_0 + RBI_0e^{-\alpha d}$$
$$BI_0 = RAI_0e^{-\alpha d}$$
$$T = (1-R)AI_0e^{-\alpha d}$$
$$\Phi = (1-R)BI_0e^{-\alpha d}$$

Calculating transmission and reflection for a thick object - 3

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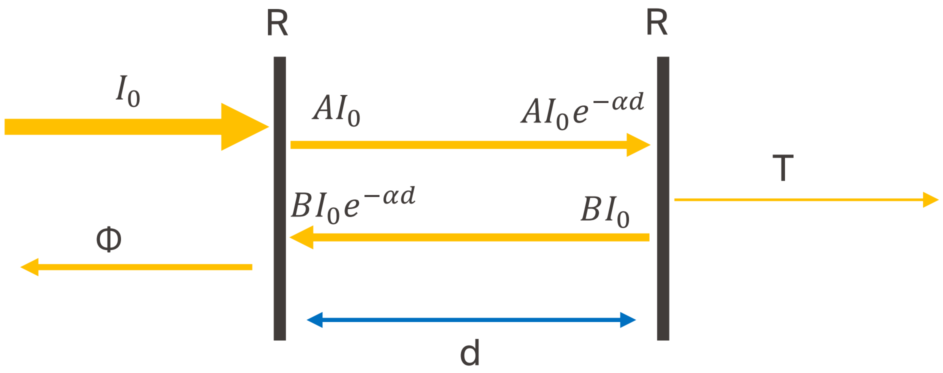
- Consider the following situation (no scattering)



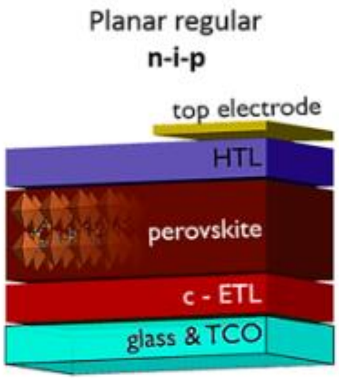
- Can solve to give

$$T = \frac{I_0(1-R)^2e^{-\alpha d}}{1-R^2e^{-2\alpha d}}; \; \Phi = \frac{I_0R(1-R)^2e^{-2\alpha d}}{1-R^2e^{-2\alpha d}}$$

$$Absorption = 1 - T - \Phi$$

Calculating transmission and reflection for a thick object - 3

- Many materials have lots of layers – this becomes a headache!
- Thankfully there is a good mathematical approach to this, called the 'Transfer Matrix Method'
- I will not give details here but several excellent (and short) tutorials exist e.g. https://www.youtube.com/watch?v=XuSxmb9-viY



Saliba, M. et al. Chem. Mater. 30, 13, 4193–4201 (2018)

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Calculating transmission and reflection for a thin object - 1

- The picture becomes more complicated for thin objects
- Good evidence for this is thin film interference
- It depends on your light source and sample, but typically thin film interference should be considered for samples <100μm thick
- Need to model the electric field of light instead of its intensity

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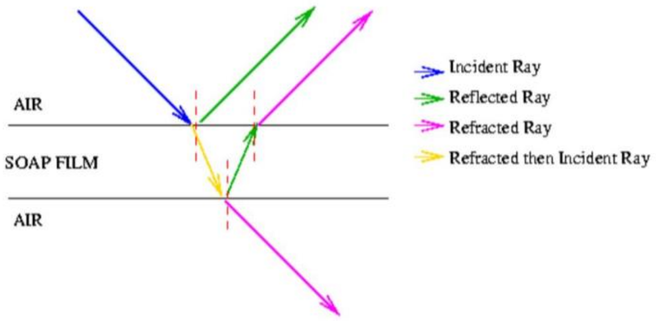
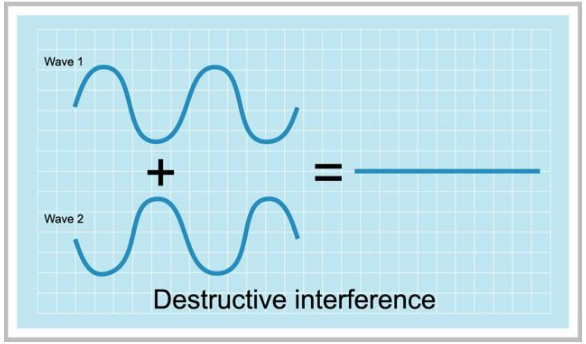
Calculating transmission and reflection for a thin object - 2

- Thin film interference is due to multiple rays interacting
- Can get unexpected effects in transmission and reflection
- The transfer matrix model can also be applied in this situation, but with electric fields instead of light intensities



http://laser.physics.sunysb.edu/~hilary/graphics/interference.gif



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Rough materials

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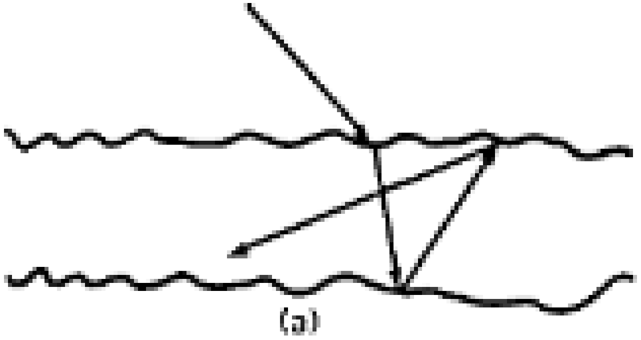
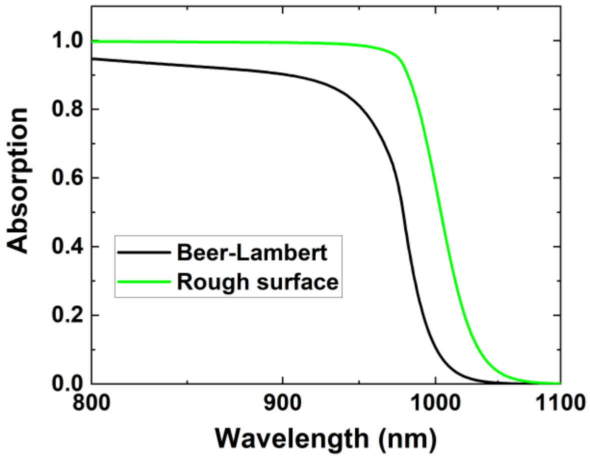
- Light often doesn't travel in straight lines
- Can increase absorption beyond the Beer Lambert law significantly with rough films



Eli Yablonovitch, "Statistical ray optics," J. Opt. Soc. Am. 72, 899-907 (1982)



Scattering theory

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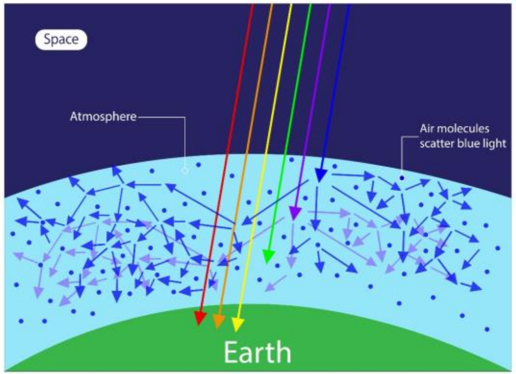
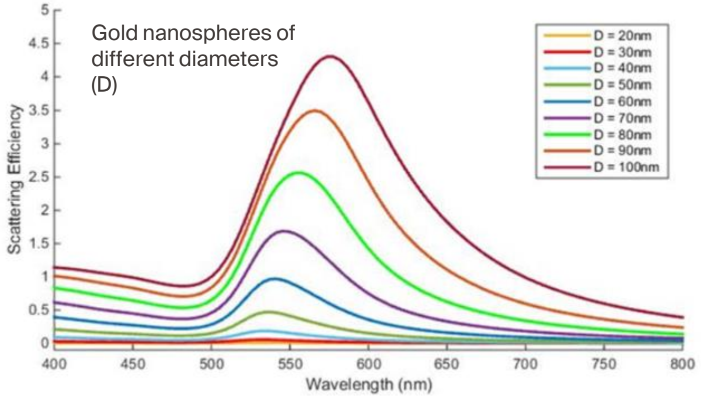
- As well as rough films, small objects scatter light
- Often small objects strongly scatter one particular wavelength
- One of the effects of this is the sky being blue
- Scattering theory is a huge area of research!





A.R. Shafiqa et al 2018 J. Phys.: Conf. Ser. 1083 01204

Sections

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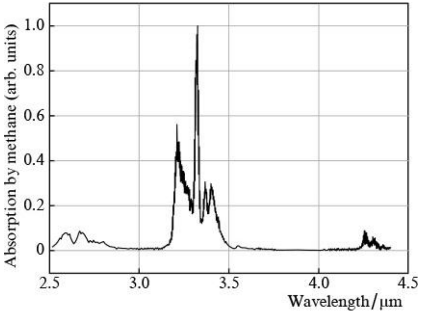
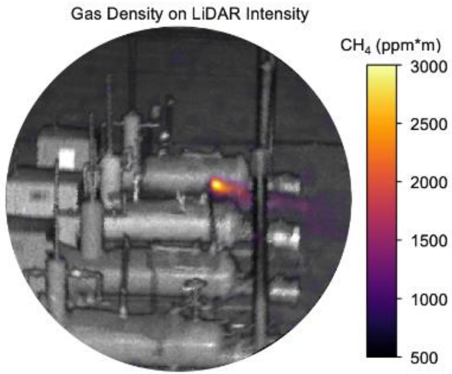
Identifying chemicals in solution

- Every material has its own optical constants
- We can tell the difference between materials by measuring absorption
- One application of this is identifying chemicals in the air



I.V. Sherstov and D.B. Kolker 2020 *Quantum Electron.* **50** 1063



https://qlmtec.com/

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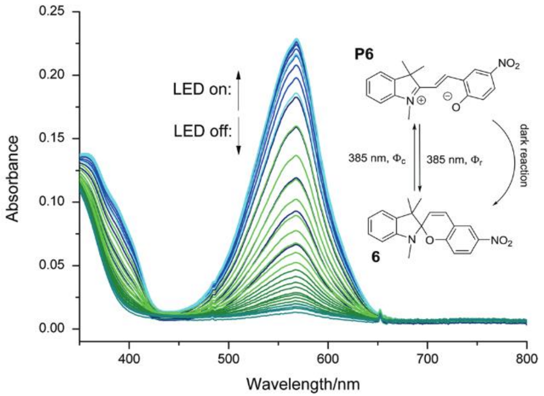
Monitoring chemical reactions quantitatively

- We can monitor the rate of chemical reactions by measuring absorption
- By measuring absorption at different wavelengths we can monitor different parts of the reaction



Photochem. Photobiol. Sci., 2018, 17, 660

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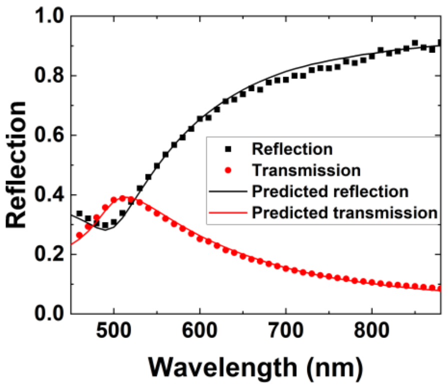
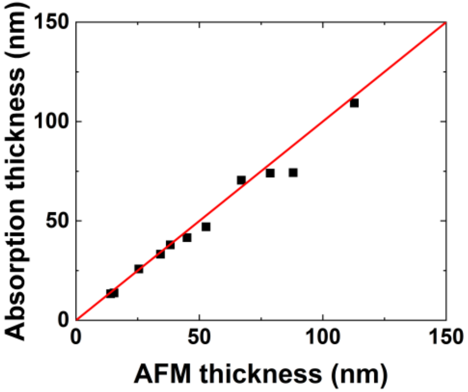
Calculating material thicknesses

- Can fit absorption measurements to transfer matrix method calculations, to calculate the thickness of samples (here gold)
- Excellent agreement with thickness measured by other techniques ('AFM thickness' below)





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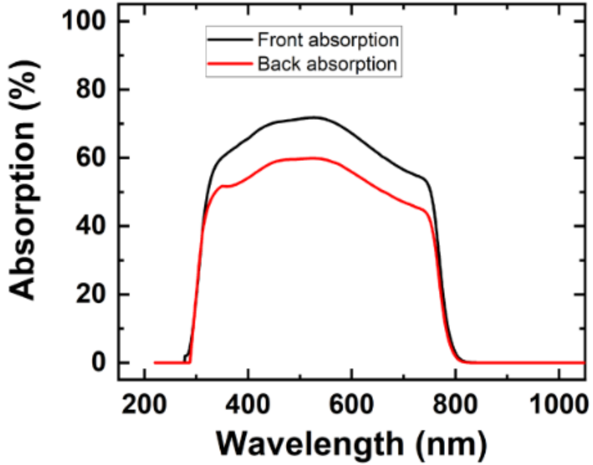
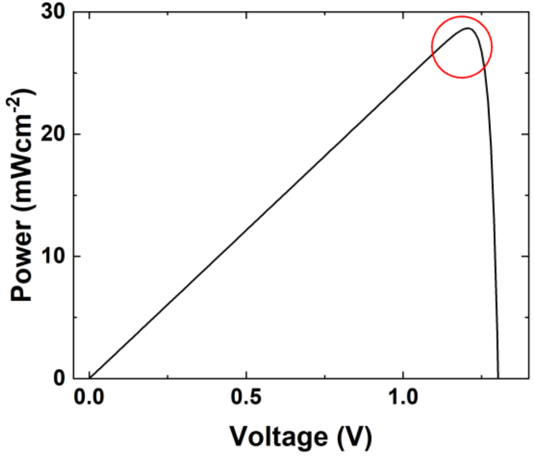
Measuring absorption to calculate maximum solar cell efficiency

- We need to know how much light is absorbed in solar cells
- From this data we can calculate the maximum efficiency of a solar cell





Phys. Rev. Applied. 17, 044026 (2022)

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Conclusions

- Optical absorption is a very powerful but simple technique
- It is possible to carry out simple measurements, or more complicated wavelength/angle resolved approaches
- Even a thorough absorption measurement only requires readily available equipment
- There are a very wide range of applications

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