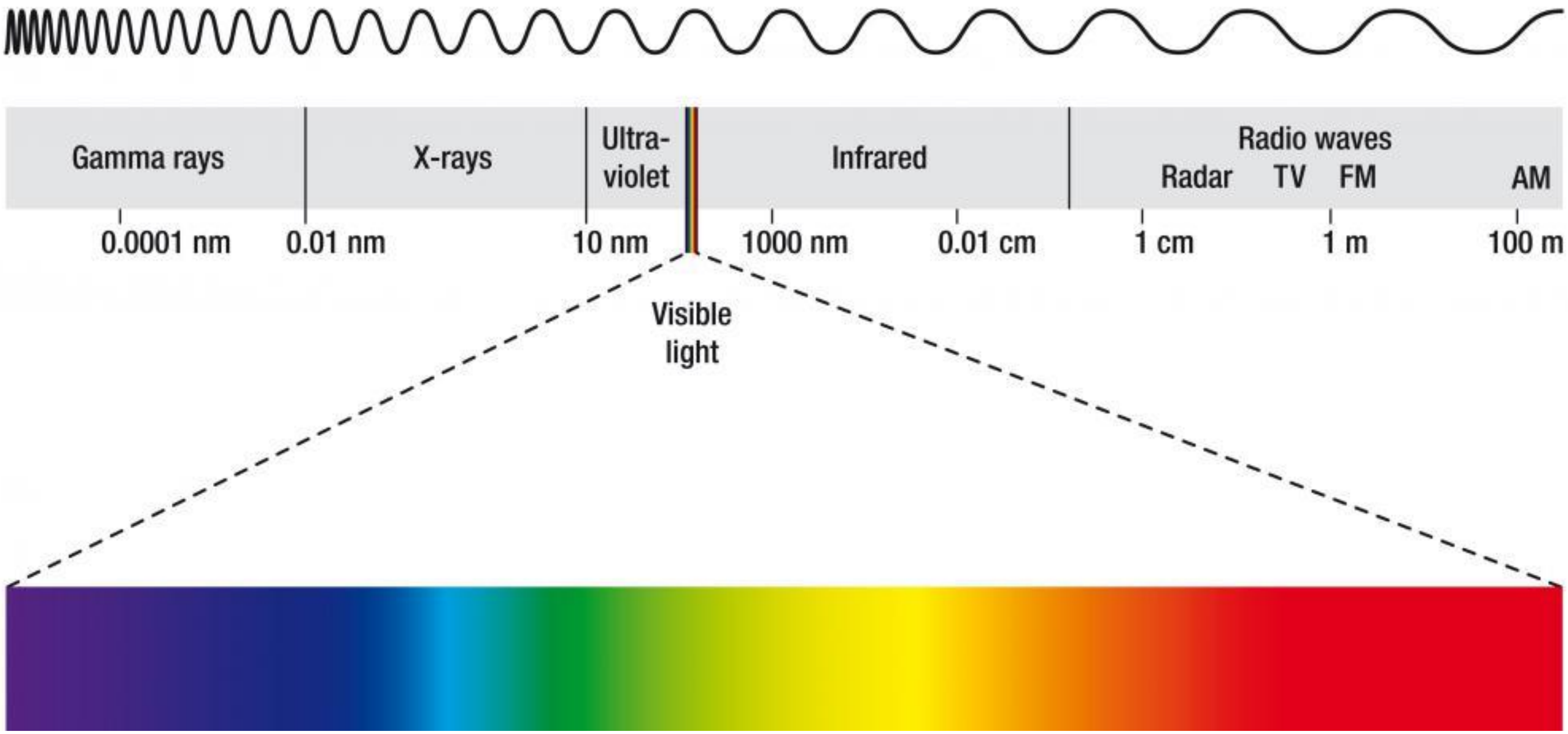
Aalto University
School of Electrical
Engineering

Spectroscopy

ELEC-E5710 Sensors and Measurement Methods

Spectroscopy

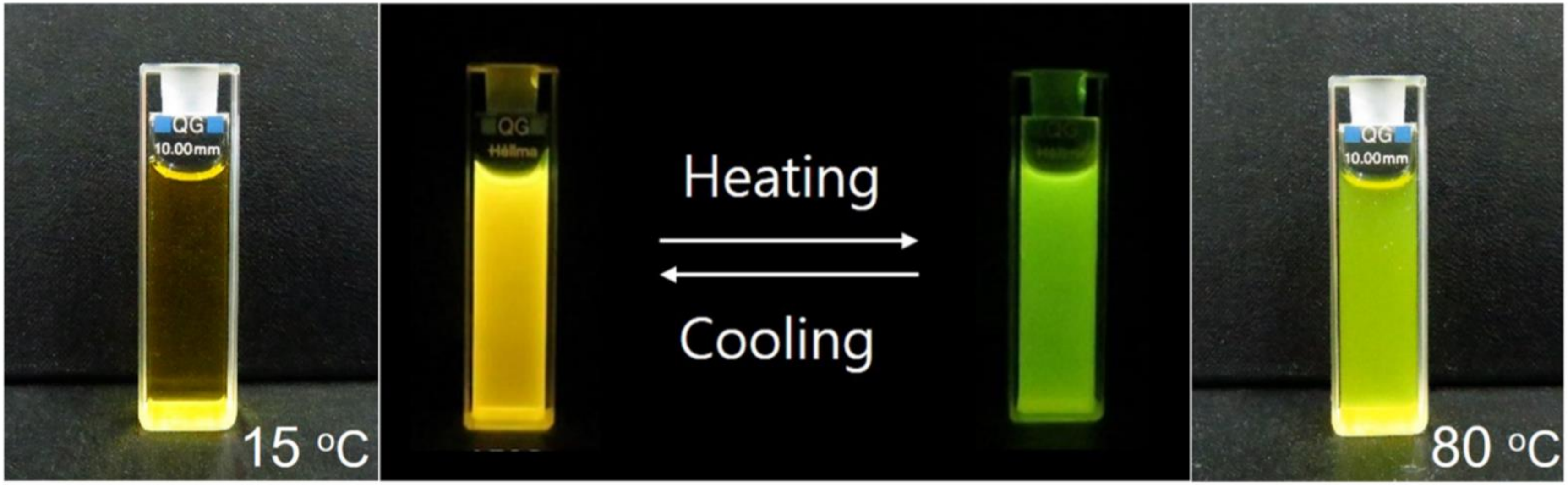
- Meaning in the most general sense: study of the interaction between matter and any form of radiative energy (such as acoustic wave, electron flux, x-ray radiation, etc.)
- More commonly, however, the term is limited to mean the study of the interaction between **matter** and **electromagnetic radiation**



Spectroscopy

- Spectroscopy is a fundamental tool in the fields of physics, chemistry, and astronomy
- Also widely applied in fields of pharmaceuticals, cosmetics, food and agriculture, mining, waste sorting, pollution monitoring etc.
- Enables the investigation of the (elemental) composition and physical structure of matter
- Can also be used to estimate ambient condition, such as temperature, pressure or electric field

Cui, Junjie, et al. "Smart fluorescent nanoparticles in water showing temperature-dependent ratiometric fluorescence color change." ACS applied materials & interfaces 9.3 (2017): 2883-2890.



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Most important types of matter and electromagnetic radiation interaction

+ practical examples of measurements

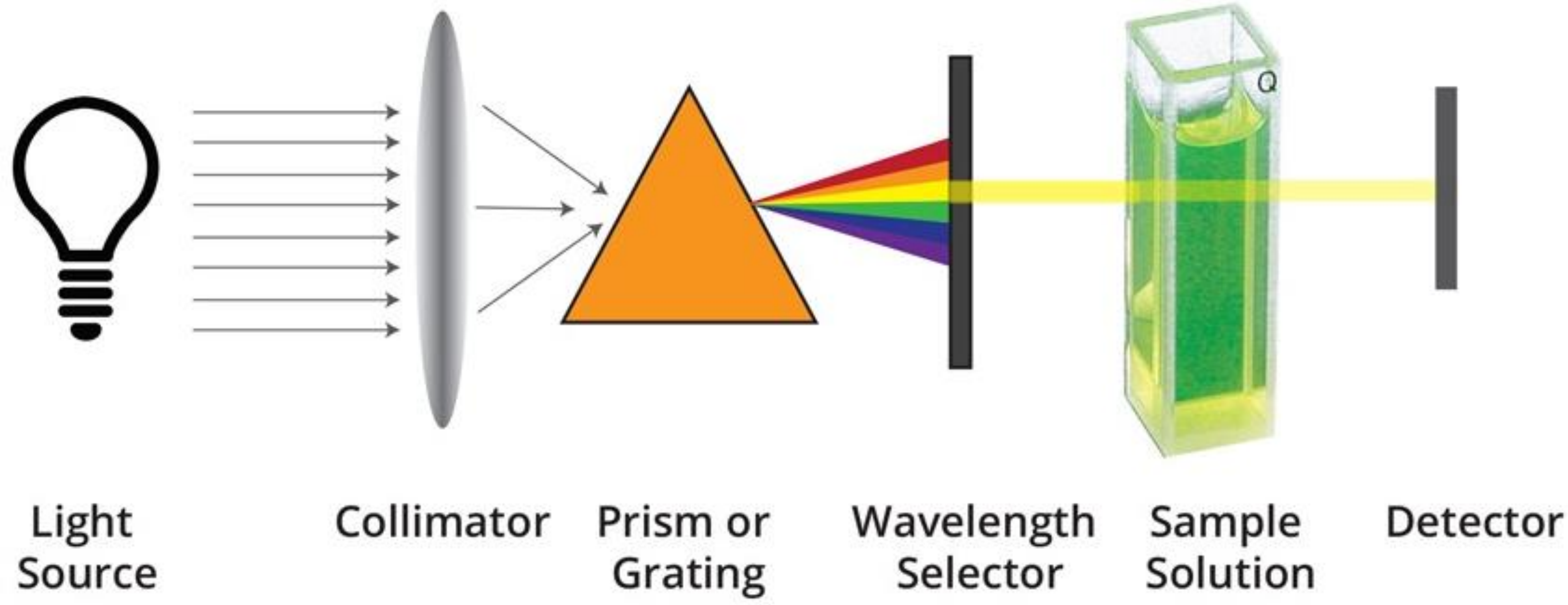
Unfortunately we can only scratch the surface…

Partial list of methods taken from wikipedia

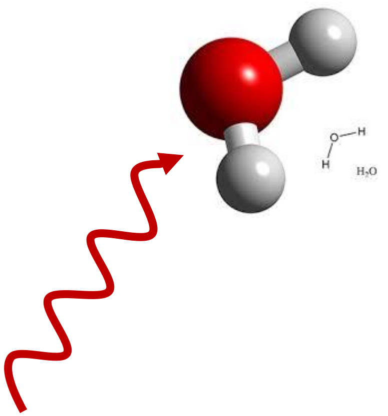
- Acoustic resonance spectroscopy
- Auger electron spectroscopy
- Cavity ring-down spectroscopy
- Circular Dichroism spectroscopy
- Coherent anti-Stokes Raman spectroscopy
- Cold vapour atomic fluorescence spectroscopy
- Two-dimensional NMR spectroscopy
- Deep-level transient spectroscopy
- Dielectric spectroscopy
- Dual-polarization interferometry
- Electron energy loss spectroscopy
- Electron phenomenological spectroscopy
- Electron paramagnetic resonance spectroscopy
- Force spectroscopy
- Fourier-transform spectroscopy
- Hadron spectroscopy
- Hyperspectral imaging
- Inelastic electron tunneling spectroscopy
- Inelastic neutron scattering
- Laser-induced breakdown spectroscopy
- Laser spectroscopy using tunable lasers
- Mass spectroscopy
- Mössbauer spectroscopy
- Multivariate optical computing
- Neutron spin echo spectroscopy
- Perturbed angular correlation
- Photoacoustic spectroscopy
- Photoemission spectroscopy
- Photothermal spectroscopy
- Pump-probe spectroscopy
- Raman optical activity spectroscopy
- Raman spectroscopy
- Saturated spectroscopy
- Scanning tunneling spectroscopy
- Spectrophotometry
- Spin noise spectroscopy
- Time-resolved spectroscopy
- Time-stretch spectroscopy
- Thermal infrared spectroscopy
- Transient grating spectroscopy
- Ultraviolet photoelectron spectroscopy
- Ultraviolet–visible spectroscopy
- Vibrational circular dichroism spectroscopy
- Video spectroscopy
- X-ray photoelectron spectroscopy

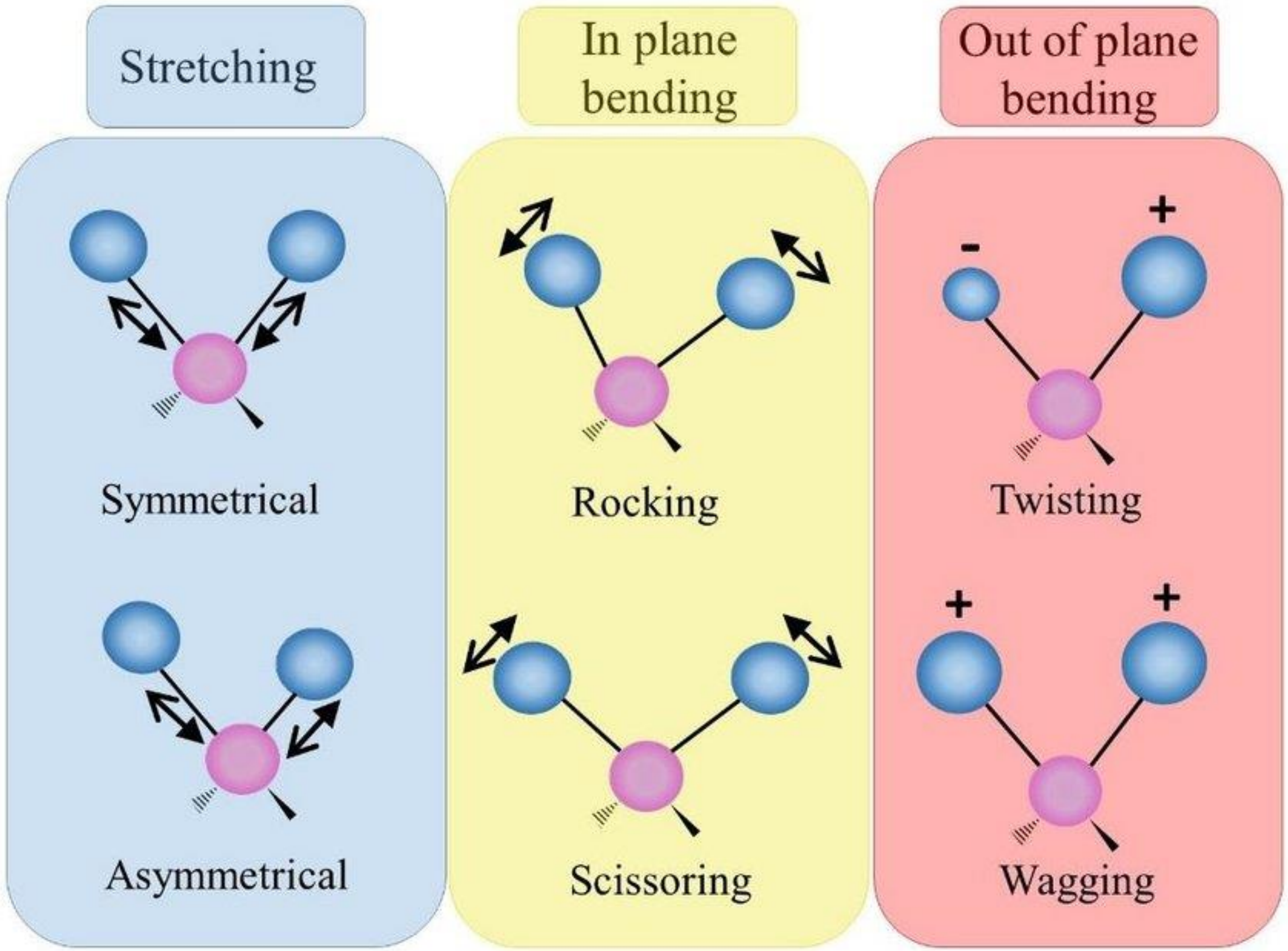
Absorption spectroscopy

- Measurement the absorption of radiation, as a function of wavelength (or energy or frequency)
- Features in absorption spectra due to interaction with the sample
- The absorption spectrum is primarily determined by the atomic and molecular composition of the material
- Radiation is more likely to be absorbed at wavelengths that match the energy difference between two quantum mechanical states of the molecules or atoms



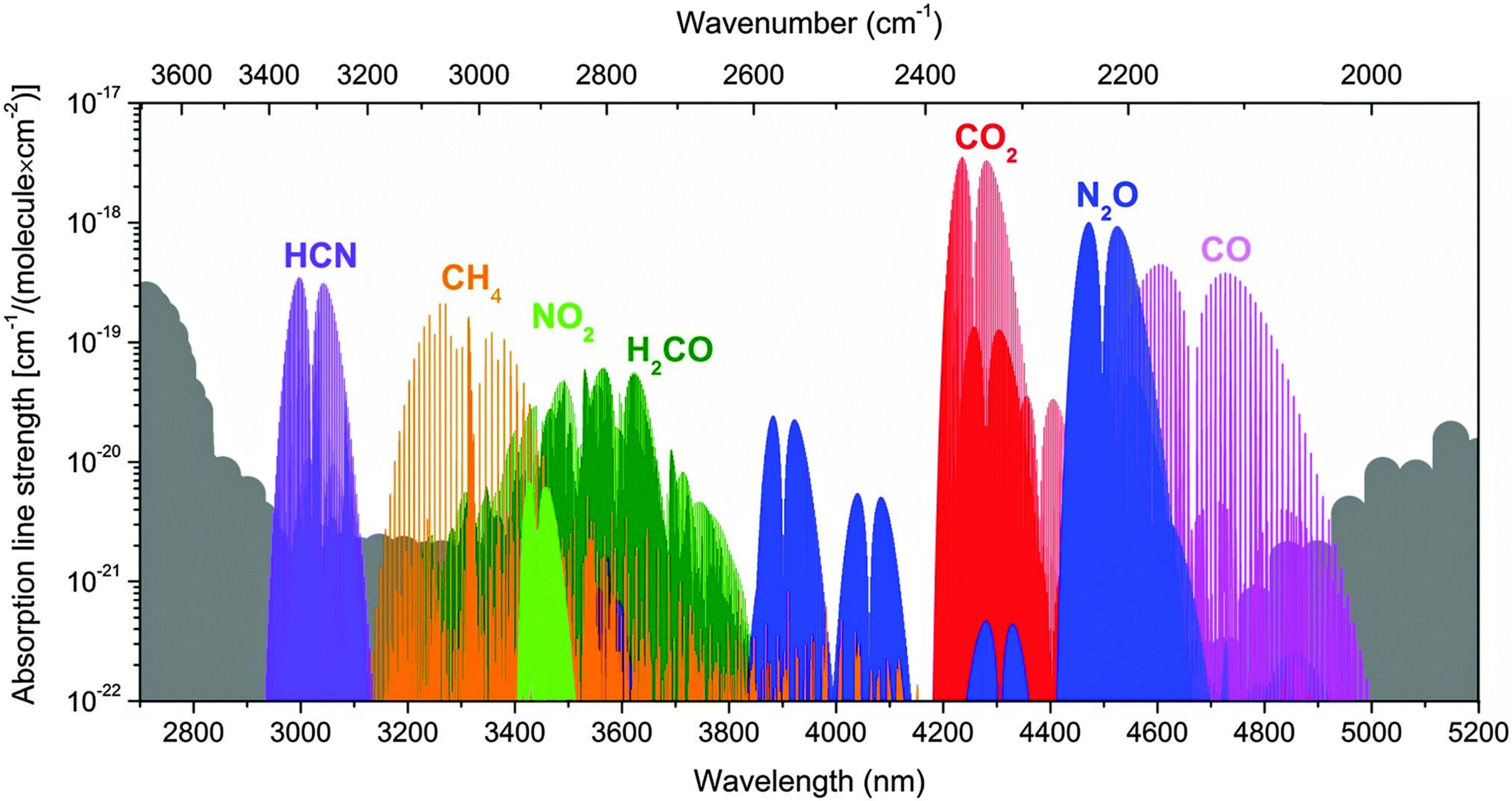
Vibration modes of molecules





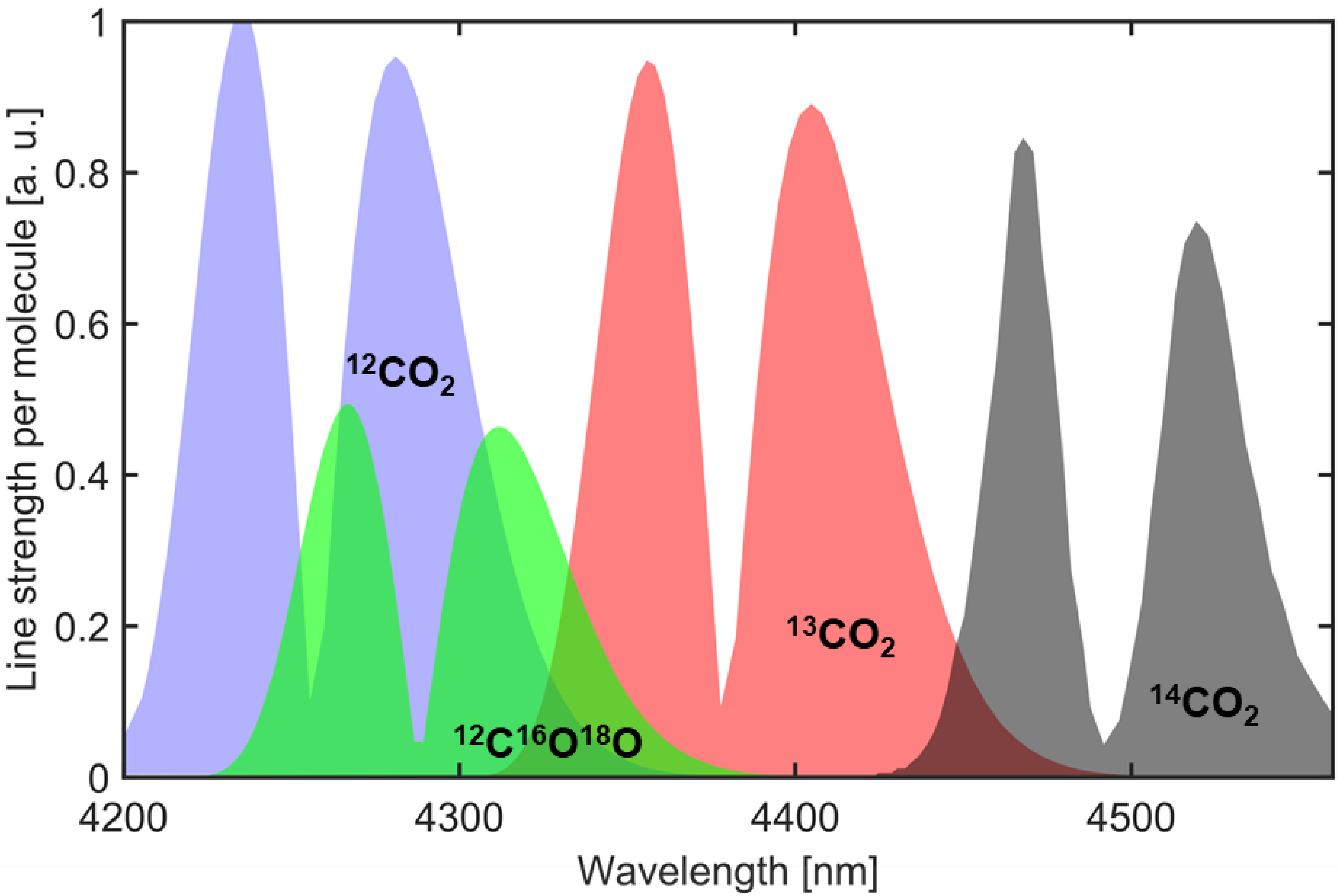
Vibration modes of molecules

- Each chemical has specific absorption "fingerprint"

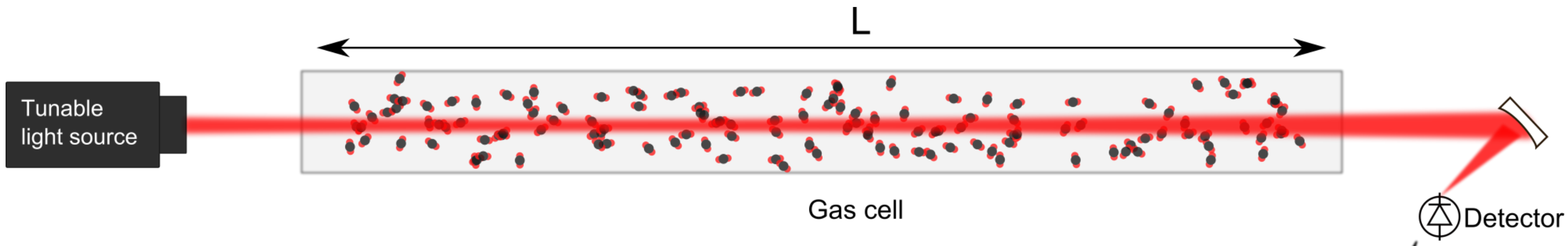


Vibration modes of molecules

- Even different isotopes can be distinguished



Practical measurement setup for gasses

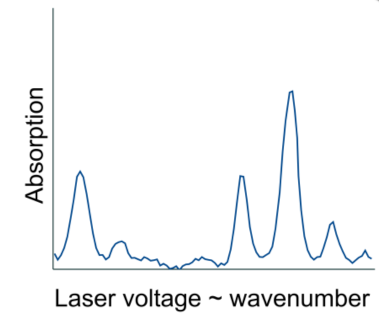


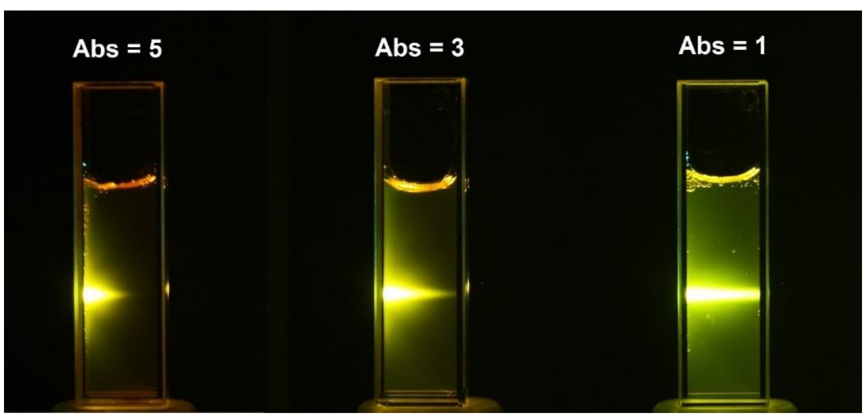
Beer-Lambert law:

$I_{out} = I_{in} e^{-\sigma L N}$

σ = Attenuation cross section [m²]
L = Material thickness [m]
N = Volume number density [1/m³]

$$\frac{I_{out}(\lambda)}{I_{in}(\lambda)} \rightarrow$$

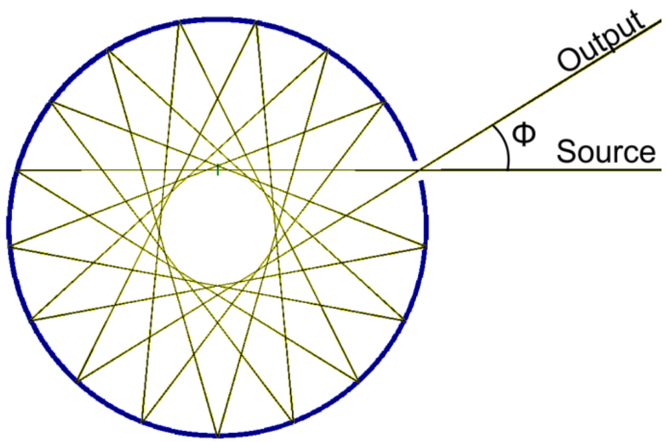


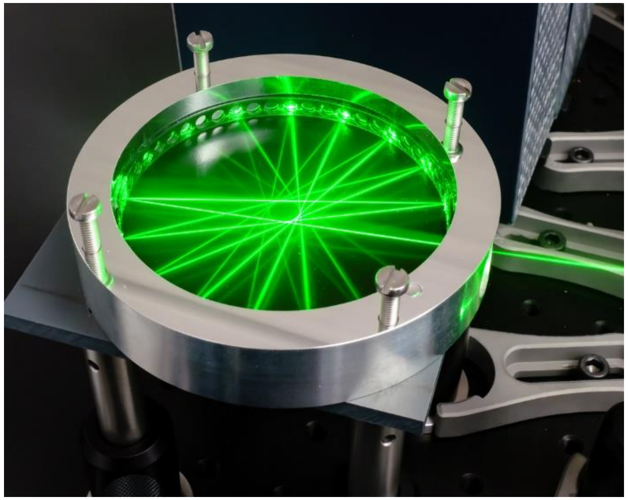


Multipass cells

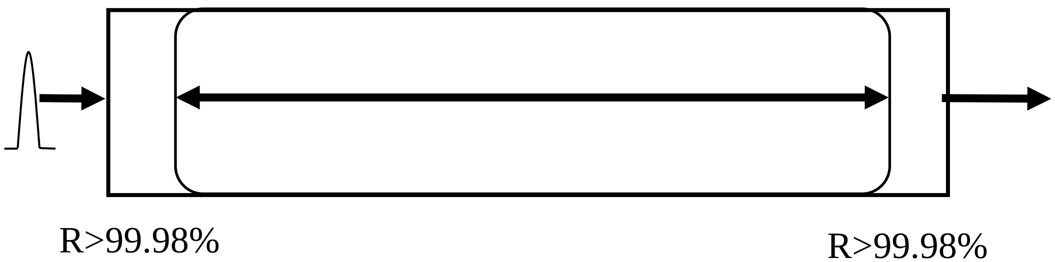
- Herriott Cells

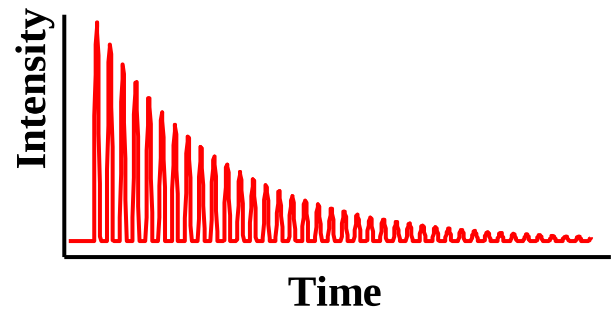
- Circular multipass cell





Cavity Enhanced Absorption



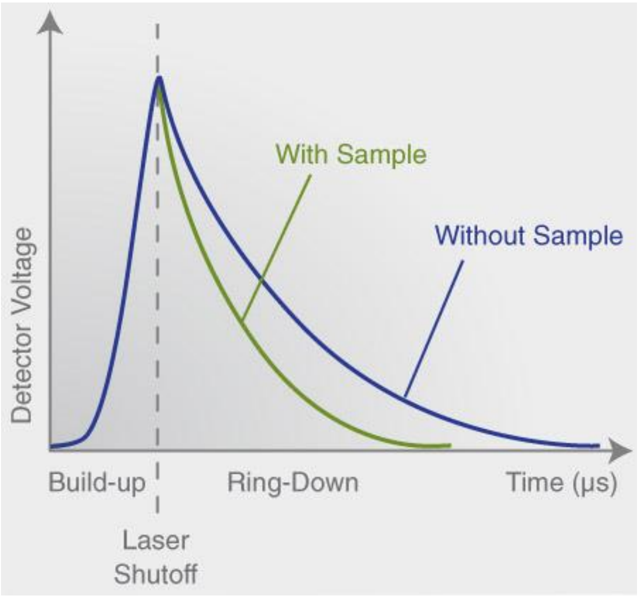


- Measure time integrated intensity

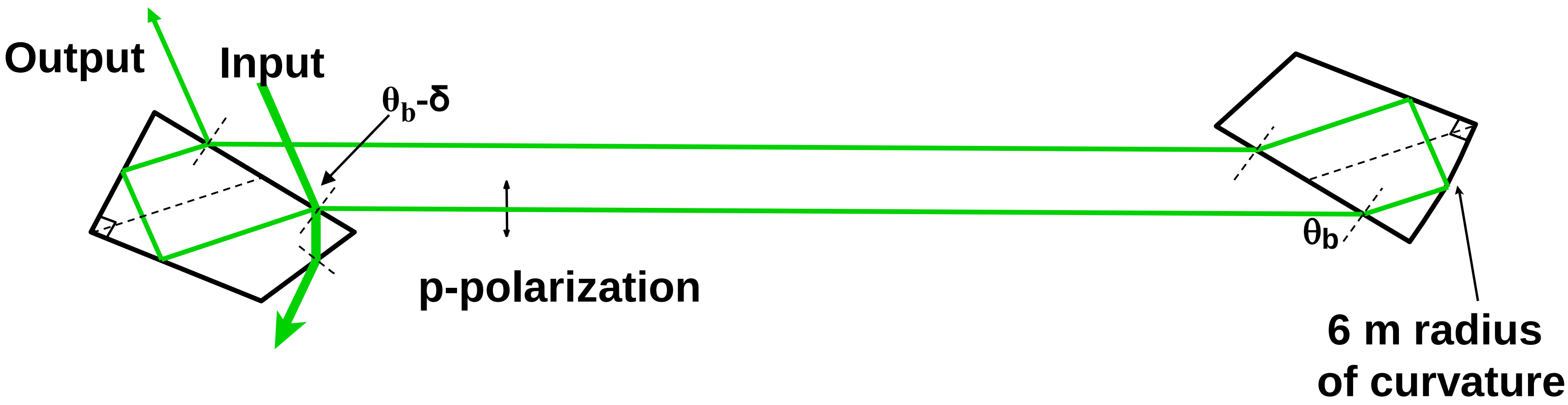
$$\alpha(\upsilon) = \left(\frac{I_o(\upsilon)}{I(\upsilon)} - 1 \right) \frac{1}{\tau c}$$

$I(\nu)$ = time integrated intensity with absorbing species

$I_o(\nu)$ = time integrated intensity of empty cavity



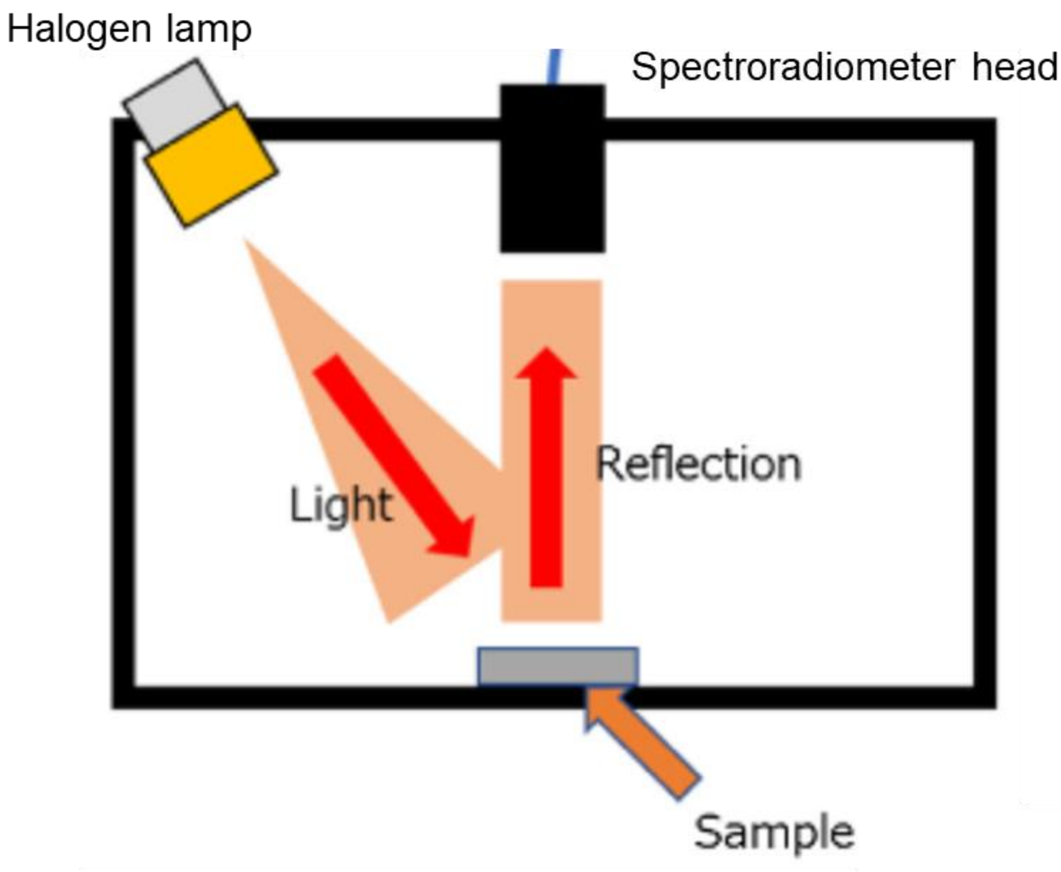
Prism cavity

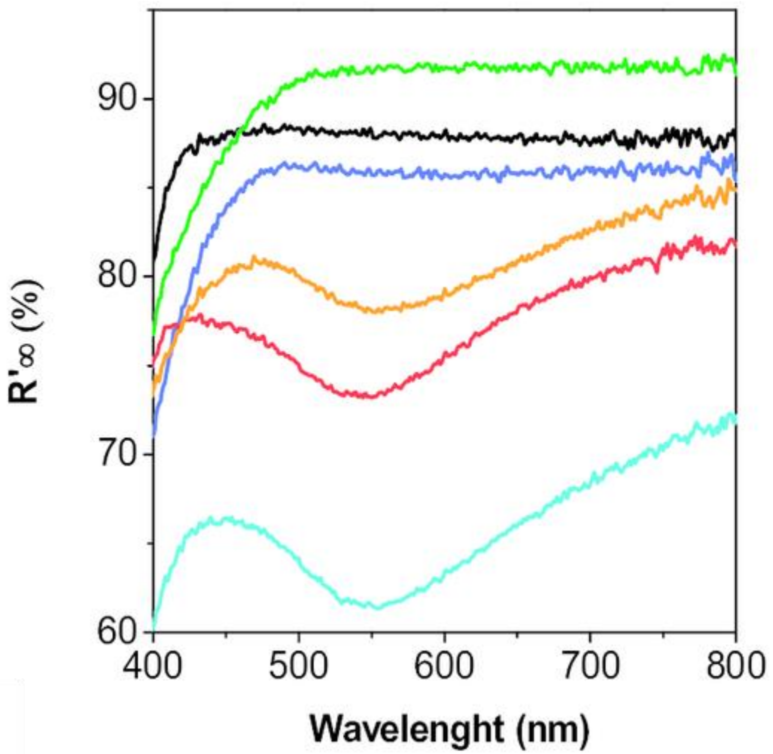


- Wider spectral coverage
- No dielectric coatings (suitable for harsh environments)

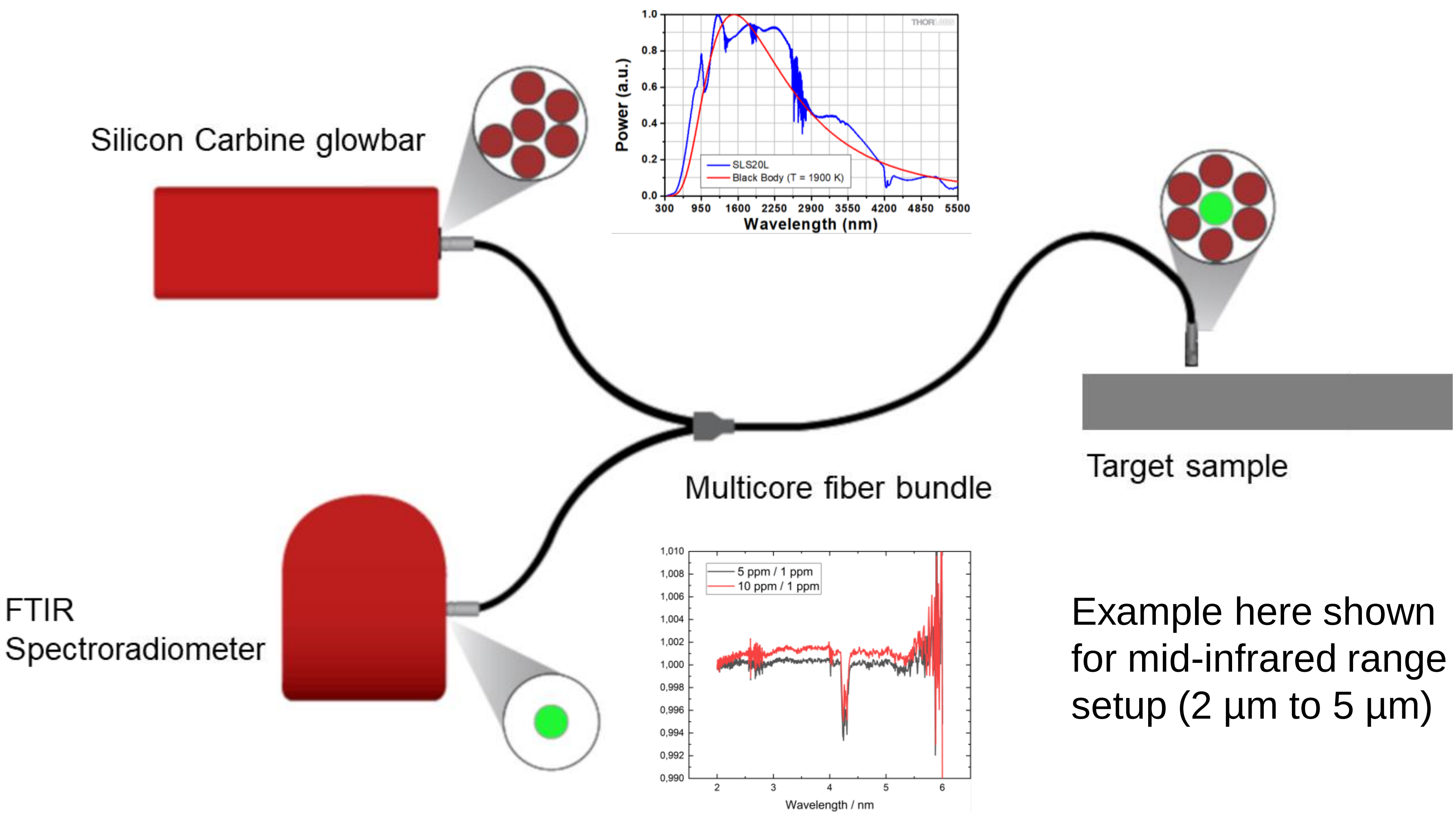
Reflection spectroscopy

- Measurement the reflectance of radiation, as a function of wavelength (or energy or frequency)
- Very similar to absorption spectroscopy
- Surface properties





Fiber based reflectance measurement

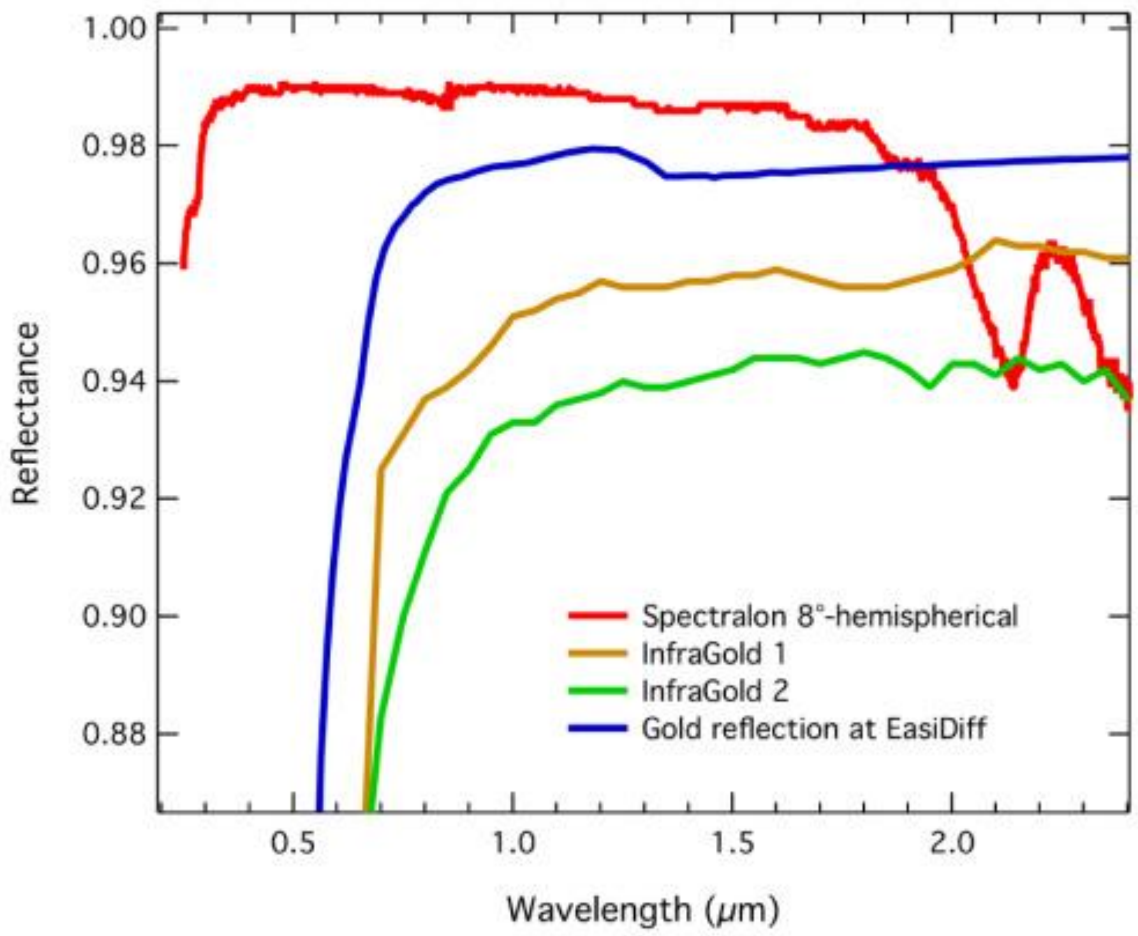


Example here shown for mid-infrared range setup (2 µm to 5 µm)

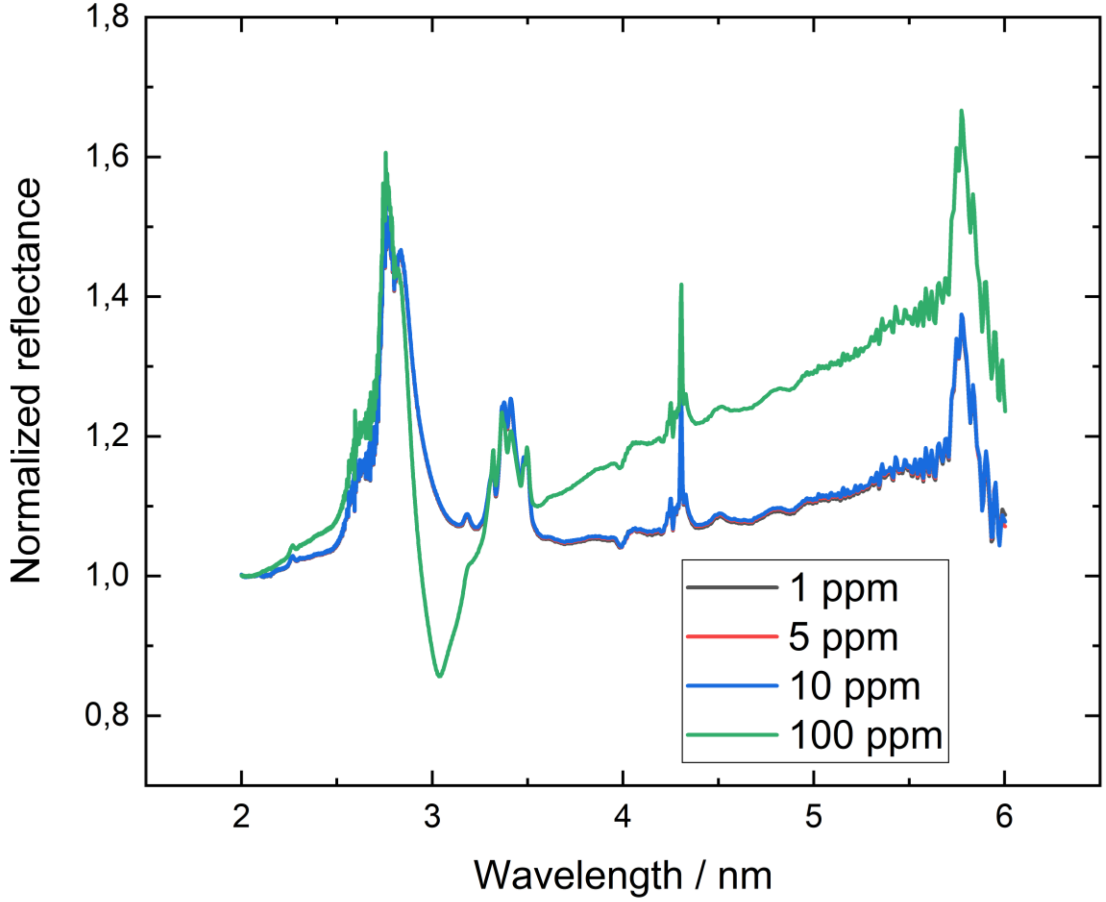
Reflectance calibration targets

Spectralon calibration target

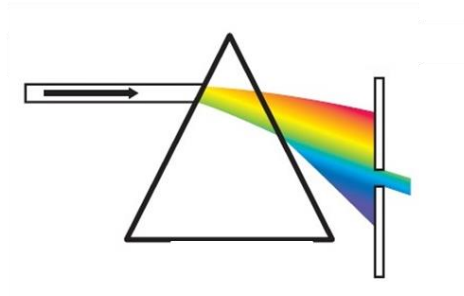
Gold calibration target

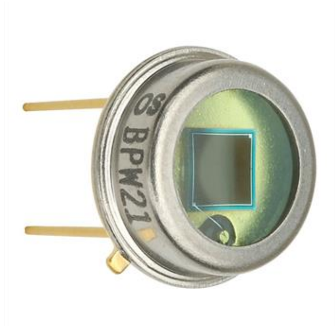


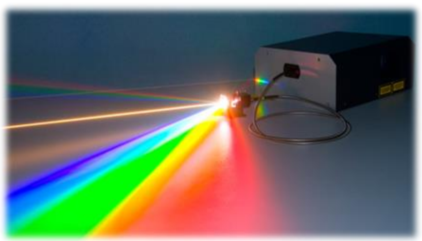
Example: detecting traces of cleaning agents on medical surfaces



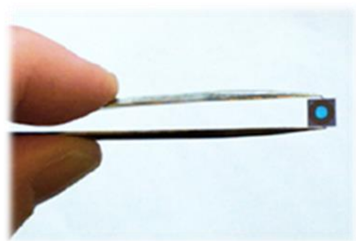
Long distance measurement of reflectance spectra using supercontinuum laser and tunable MEMS filter







Supercontinuum laser

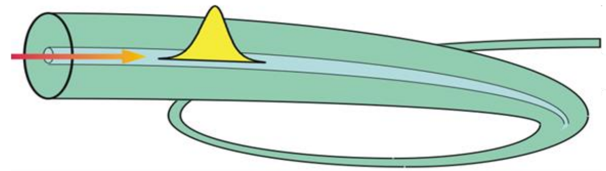


Tunable MEMS filter

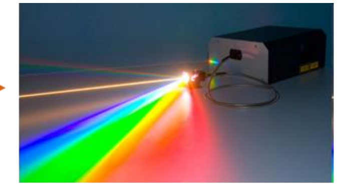
Long distance optics

Supercontinuum laser

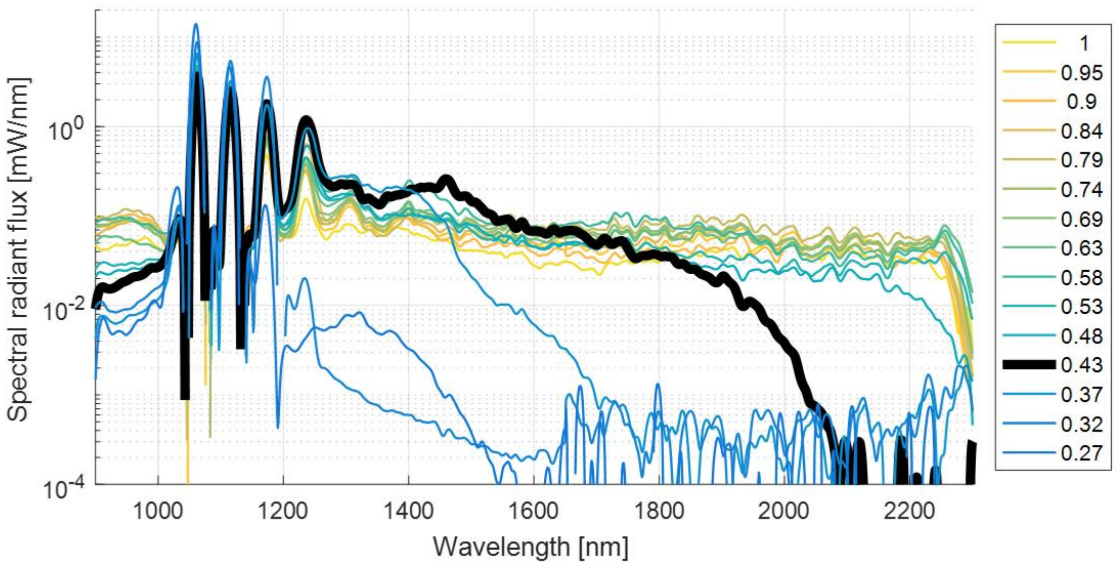
Monochromatic diode pump laser



Nonlinear optical fibre



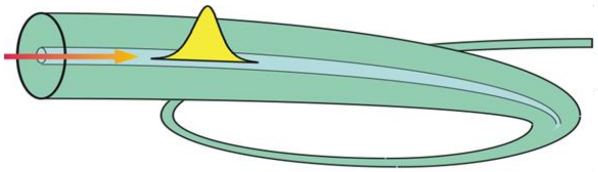
Supercontinuum generation



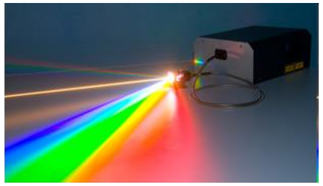
Broadband light source with laser propagation properties

Supercontinuum laser

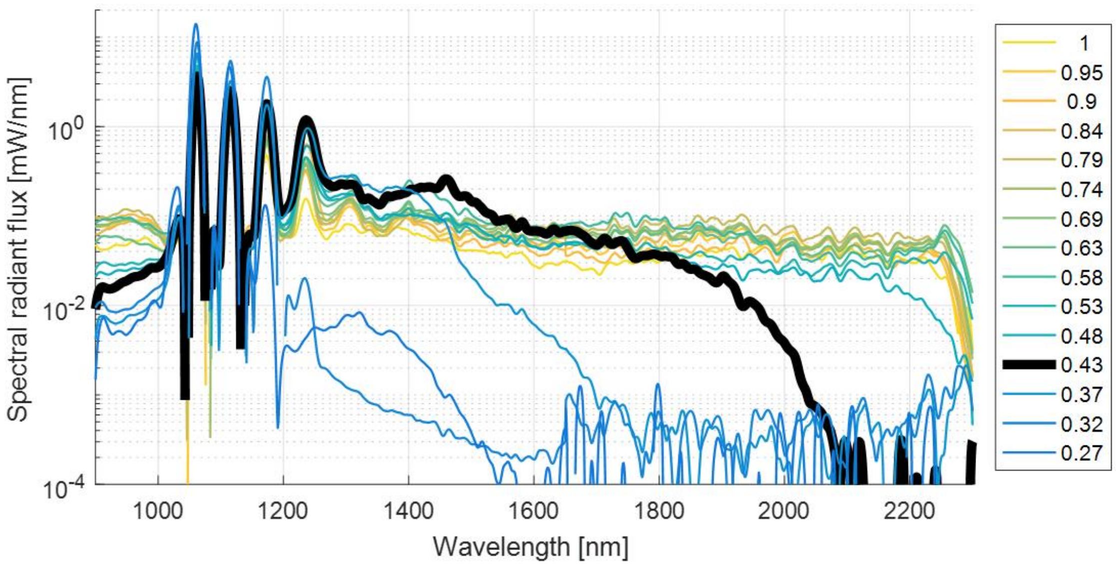
Monochromatic diode pump laser



Nonlinear optical fibre



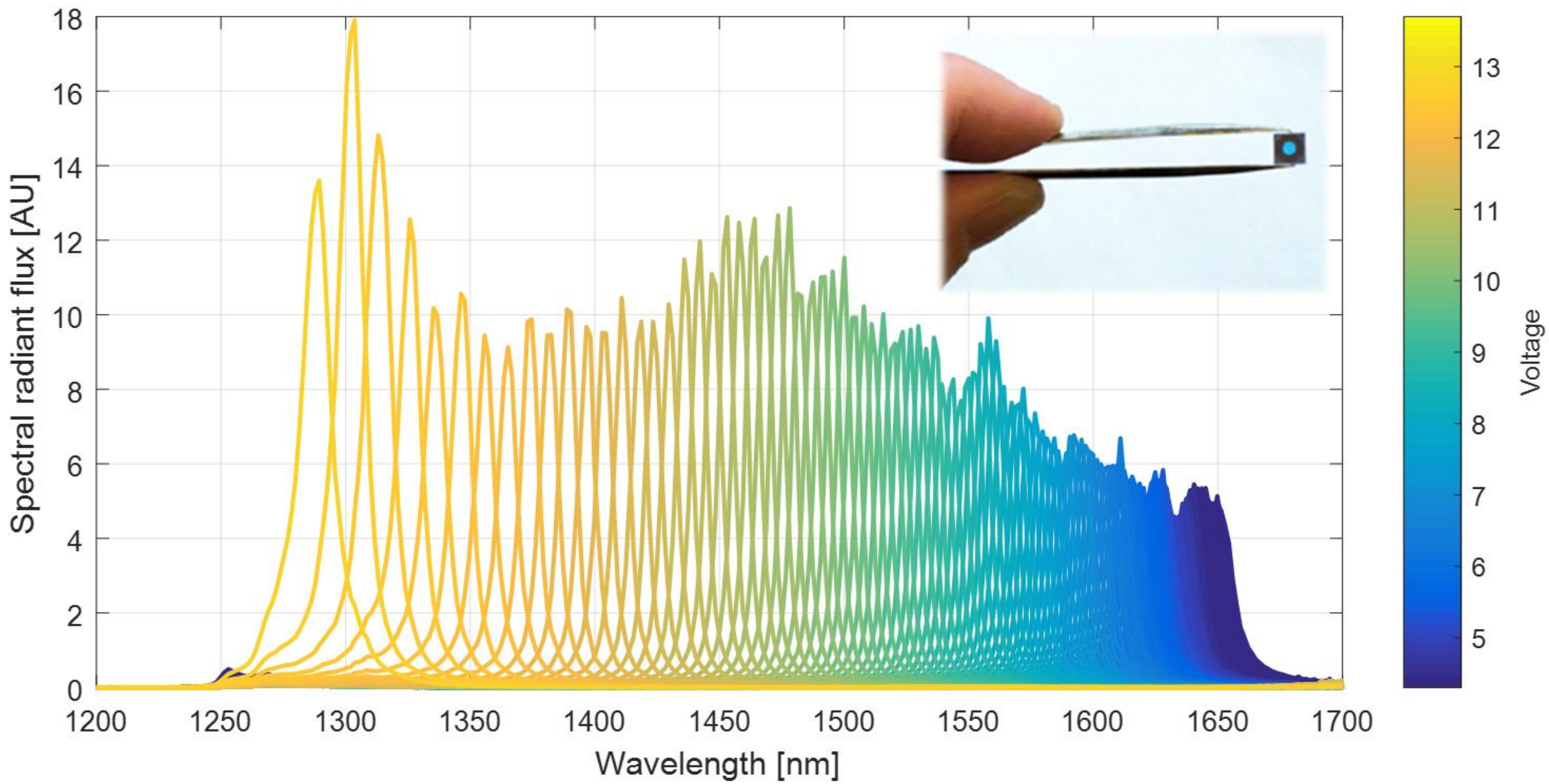
Supercontinuum generation



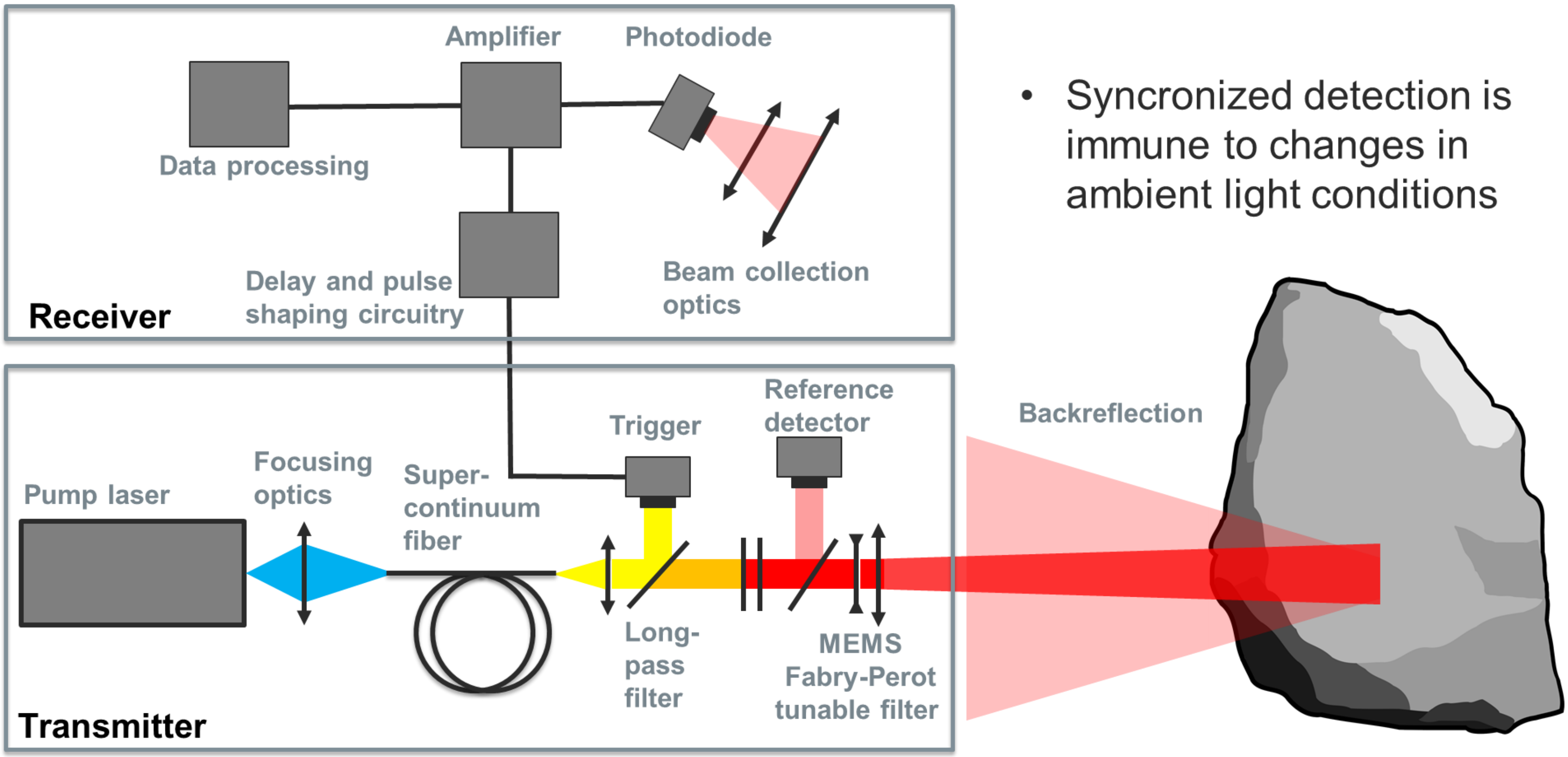
Broadband light source with laser propagation properties

MEMS-based tunable filter

- Narrow optical band-pass filter that can be tuned with control voltage
- Scan speed up to 1 MHz

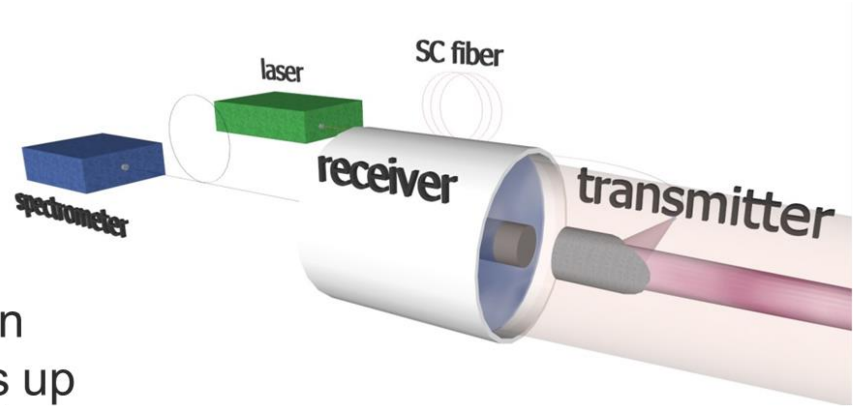


Full detection system

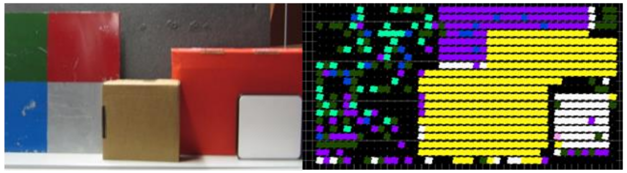


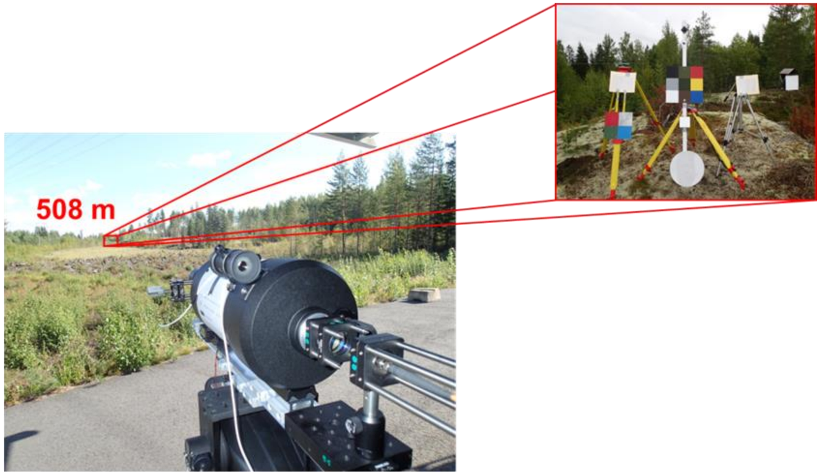
- Syncronized detection is immune to changes in ambient light conditions

High power version



- Coaxial transmitter and receiver
- Output power 16 W
- Irradiance up to 1 000 000 x the sun
- Spectral measurement at distances up to **1.5 km**



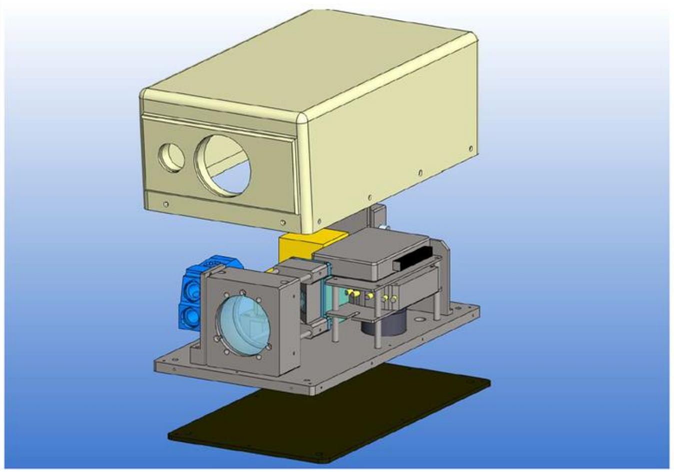


A. Manninen et al. Optics Express **22** (2014)

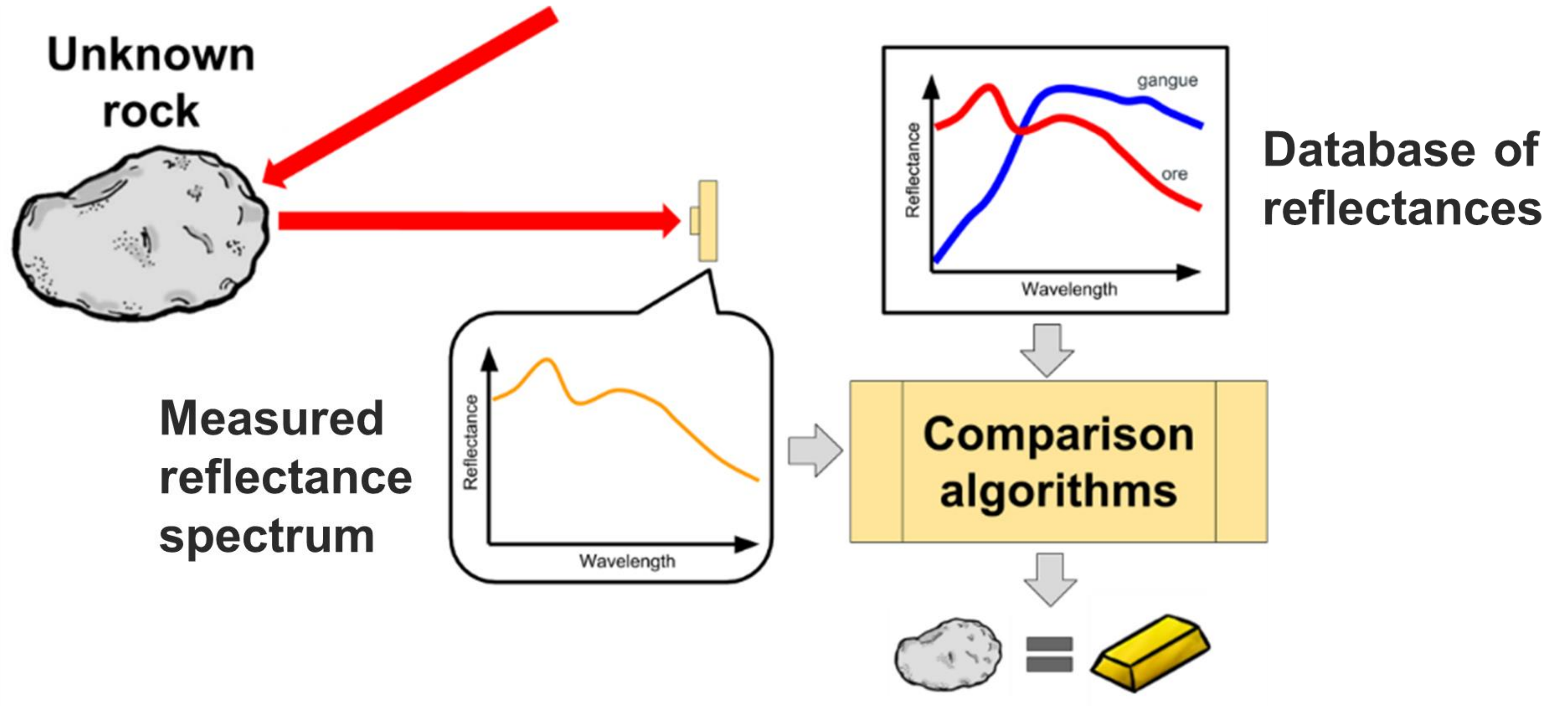
Low power (eye-safe) versio

- Compact: footprint 400x220 mm
- Eye-safe
- Operating distance up to 100 m
- Wireless communication
- Camera for targeting and situational awareness
- Design driven by the requirements of mining applications

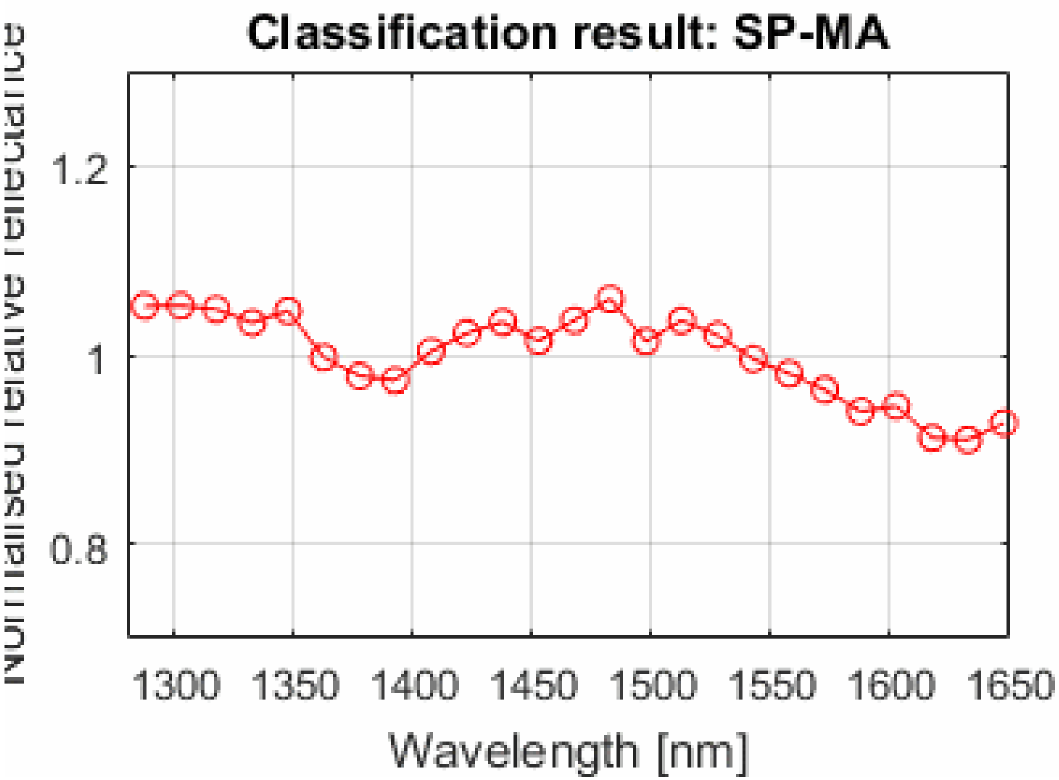
T. Kääriäinen et al. Sensors **19** (2019)

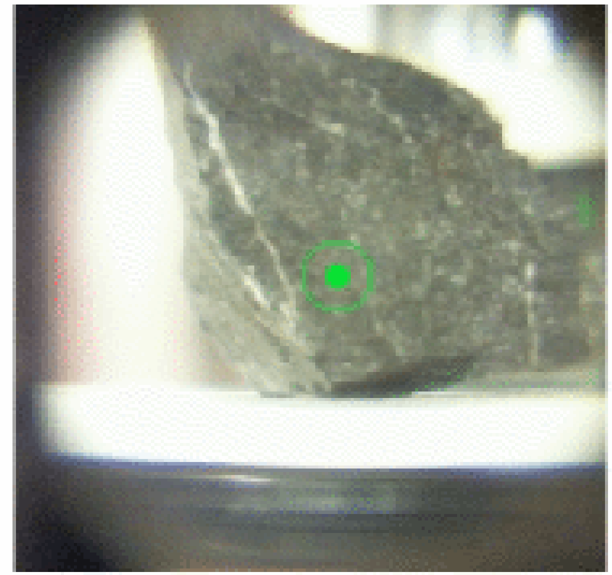


Machine learning based automated ore detection



Mineral classification in real time

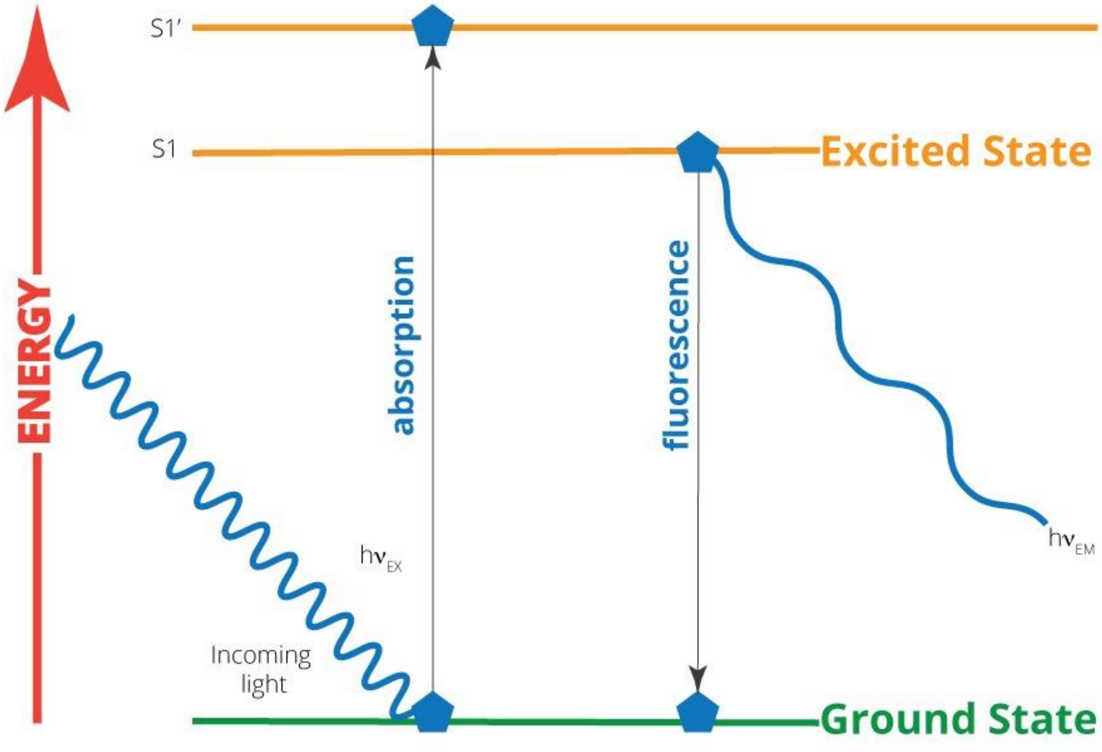




90 % of the measured spectra are classified correctly in real time

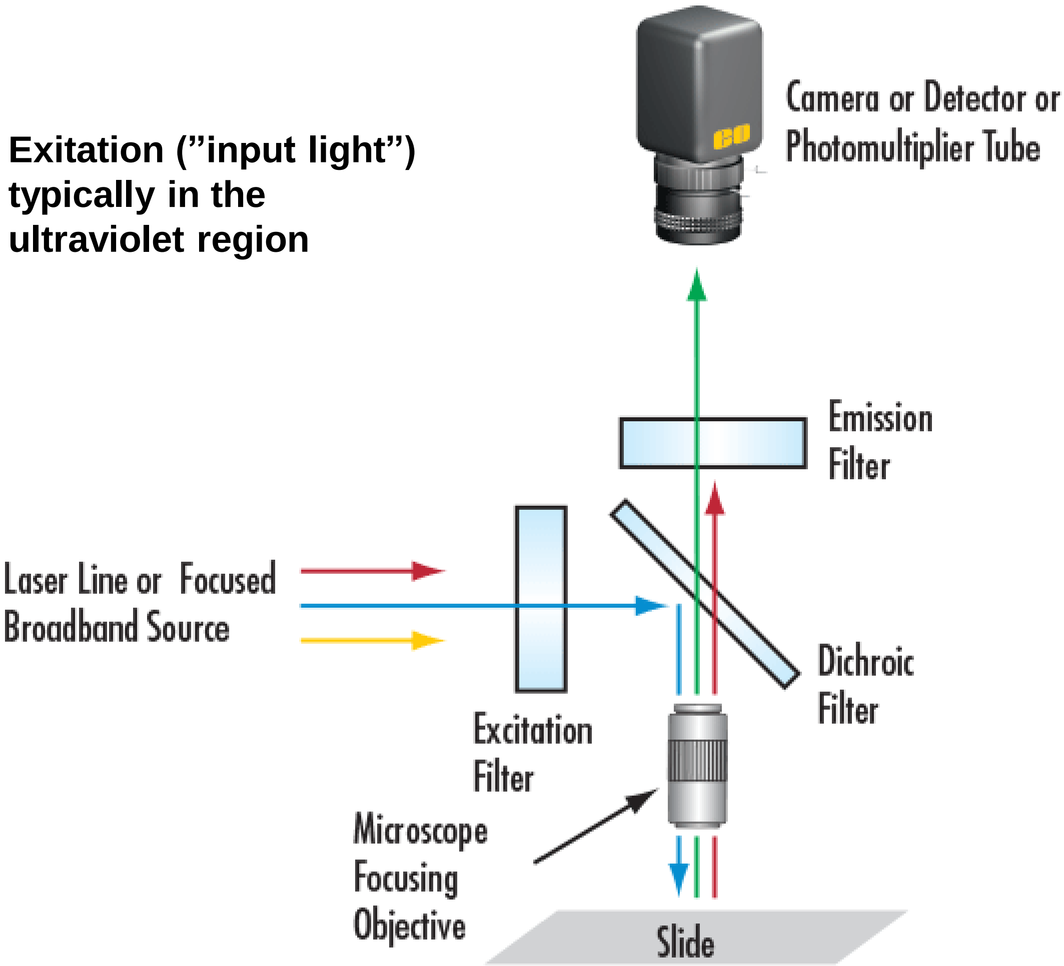
Fluorescence

- Fluorescence is the emission of light by a substance that has absorbed light (or other electromagnetic radiation)



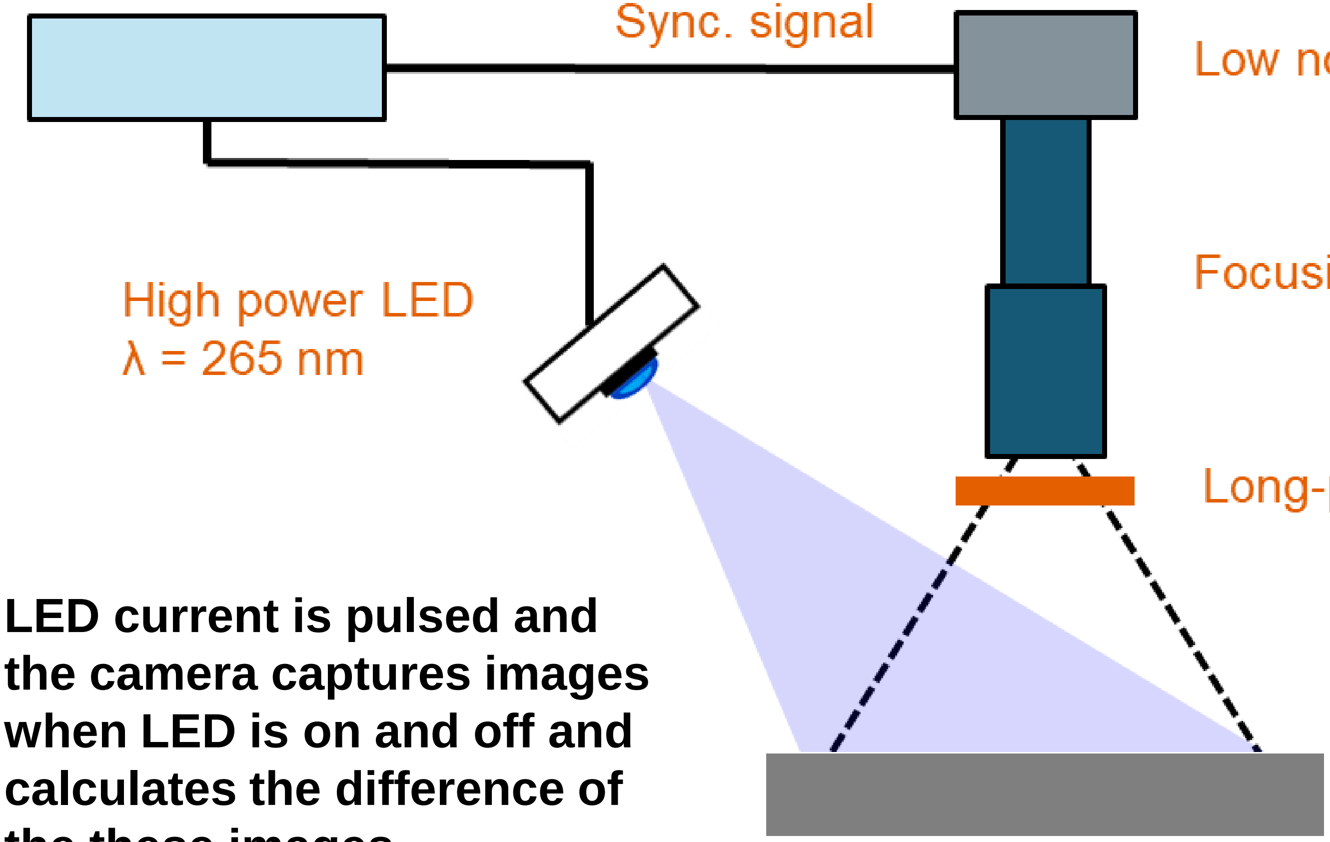
Fluorescence – example setup

Exitation (”input light”) typically in the ultraviolet region



A dichroic filter passes selectively a small range of wavelengths while reflecting other colors

Fluorescence – example setup 2

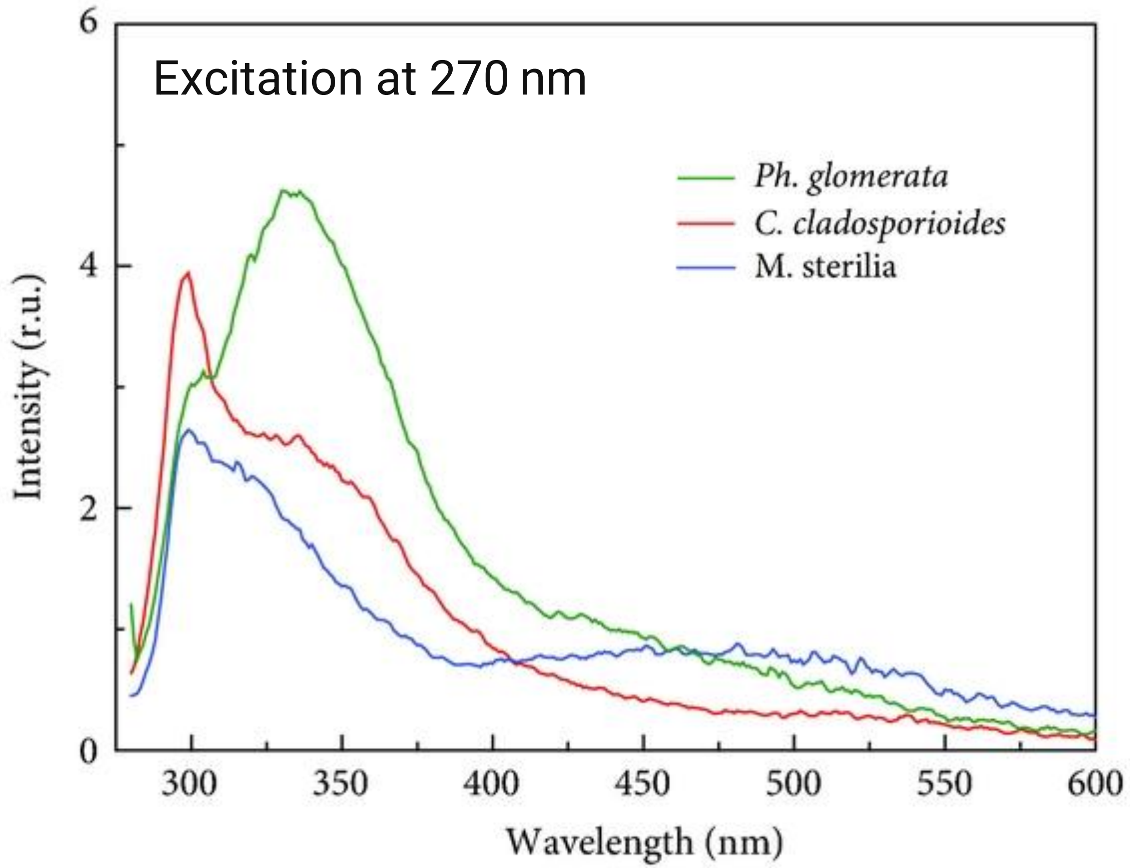


LED current is pulsed and the camera captures images when LED is on and off and calculates the difference of the these images

Example: Fluorescence spectra as identification tool

- Fluorescent spectra can also be used for identification
- For example: metabolytes of various bacteria and fungi are fluorescent, with unique spectral ”fingerprint”

Example: Fluorescence spectra as identification tool



Khundzhua, D. A., et al. "Spectral characterization of fungal metabolites in aqueous medium with humus substances." *Journal of Spectroscopy* 2013 (2012).