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Laser spectroscopy for gas sensing

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The term **SPECTROSCOPY** denotes methods where the interaction of light with matter is utilized.

The strength of some interaction (e.g. absorption of light) is measured as a function of the photon energy *E* = *h*ν, or wavelength λ, or wavenumber $\tilde{\nu} = \frac{1}{\lambda}$

Some quantities

	photon energy eV	wavelength μm	wavenumber cm^{-1}
Ultraviolet	6.2–3.1	0.2–0.4	50000–25000
Visible	3.1–1.55	0.4–0.8	25000–12500
Near IR	1.55–0.41	0.8–3.0	12500–3300
Mid IR	0.41–0.025	3.0–50	3300–200

SOME USEFUL RELATIONS

ν = photon frequency

$\omega = 2\pi\nu$ = angular frequency

$E = h\nu$ = photon energy

$\lambda = c/\nu$ = photon wavelength

c = speed of light in vacuum $\approx 3 \cdot 10^{-8}$ m/s

h = Planck's constant = $4.14 \cdot 10^{-15}$ eV·s

1 eV = $1.6 \cdot 10^{-19}$ J

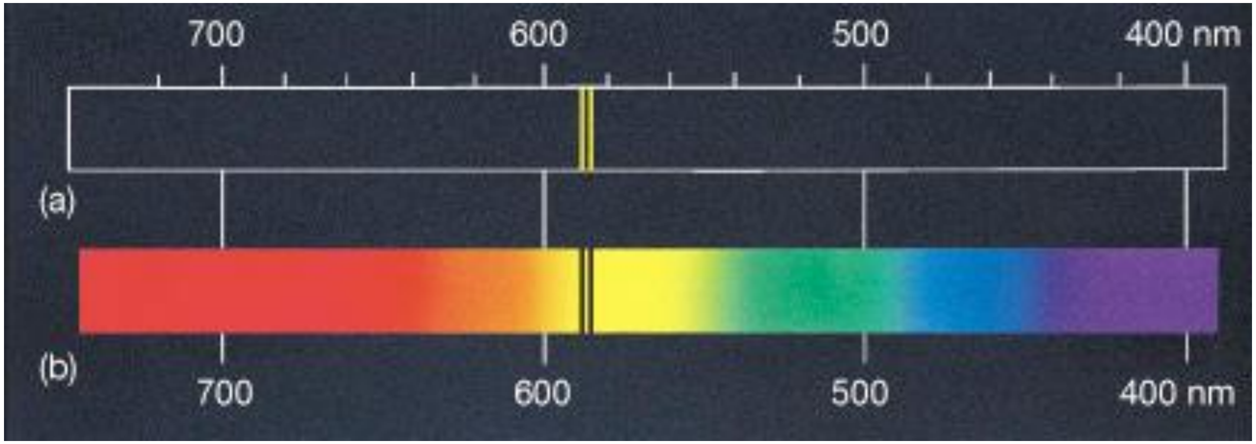
$$\lambda(\mu\text{m}) = 1.24 / E(\text{eV})$$

$$\tilde{\nu}\,(\text{cm}^{-1}) = 10000 / \lambda(\mu\text{m})$$

ATOMIC ABSORPTION IN ATOMS

Wave-matter interaction in atoms ⇒ transfer of energy from photons to electrons ⇒ excitation of electrons from one atomic orbital to another

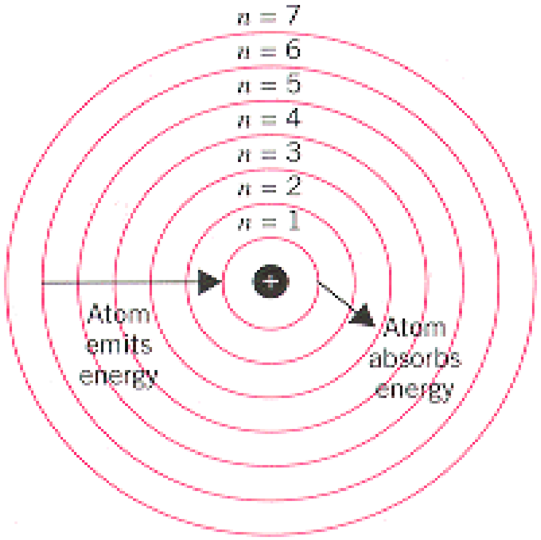
Since the atomic orbitals have *discrete specific energies*, transitions among them have discrete specific energies. Therefore, ***atomic absorption spectra consist of a series of "lines" at the wavelengths of radiation that correspond in energy to each allowable electronic transition***.

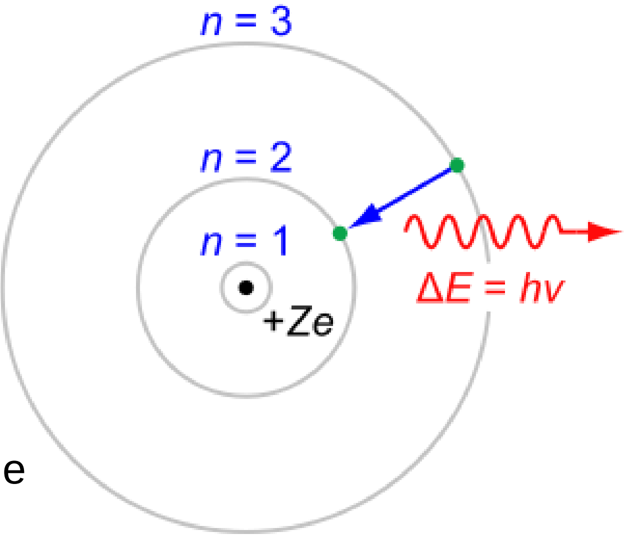


Emission and absorption spectrum of sodium: D-lines at 588.995 and 589.592 nm (yellow)

BOHR ATOMIC MODEL

- Negatively charged electron orbits a positively charged nucleus
- The electrons can only orbit stably, without radiating, in certain "stationary orbits" at a discrete set of distances from the nucleus. These orbits are associated with definite energies and are also called energy levels. In these orbits, the electron's acceleration does not result in radiation and energy loss as it would be required by classical electromagnetism.
- Quantum jump between orbits with help from an absorbed amount of electromagnetic radiation





The Bohr model of the Hydrogen Atom

$$m\frac{v^2}{r} = \frac{Ze^2}{r^2} \Rightarrow v = e\sqrt{\frac{Z}{mr}}$$

Electron speed (from Newton law **F**=m**a**)

$$E = \frac{1}{2}mv^2 - \frac{Ze^2}{r} = -\frac{Ze^2}{2r}$$

Energy of the system

Discretization of the electron orbits

$$mr_n v = n\frac{h}{2\pi} = n\hbar \qquad (n = 1,2,3,\ldots)$$

The electron angular momentum is quantized

$$\Rightarrow r_n = n^2\frac{\hbar^2}{e^2 mZ} = n^2 0.053 \text{ nm}$$

$$\Rightarrow E_n = -Z^2\frac{Rhc}{n^2} \quad \text{with } R = \frac{2\pi^2 e^4 m}{h^3 c} = 109737 \text{ cm}^{-1}$$

Energy levels

$$E_n \approx -13.6\frac{Z^2}{n^2}\text{ eV}$$

Emission or absorption of energy ($\Delta E = h\nu$)

$$\nu = \frac{E_n - E_{n'}}{h}$$

$$\tilde{\nu} = \frac{E_n - E_{n'}}{hc}$$

For the H atom (Z = 1)

$$\nu = Rc\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$$

$$\tilde{\nu} = R\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$$

EXERCISE

Calculate the emission lines for the hydrogen atom (Z = 1) for the transitions from level n’ = 1

Answer:

$$\tilde{\nu} = R\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$$

$R(1-1/2^2) = 109737 \cdot 0.75 = 82303\ \mathrm{cm}^{-1} \Rightarrow \lambda_1 = 121.5$ nm

$R(1-1/3^2) = 109737 \cdot 0.89 = 97666\ \mathrm{cm}^{-1} \Rightarrow \lambda_2 = 102.4$ nm

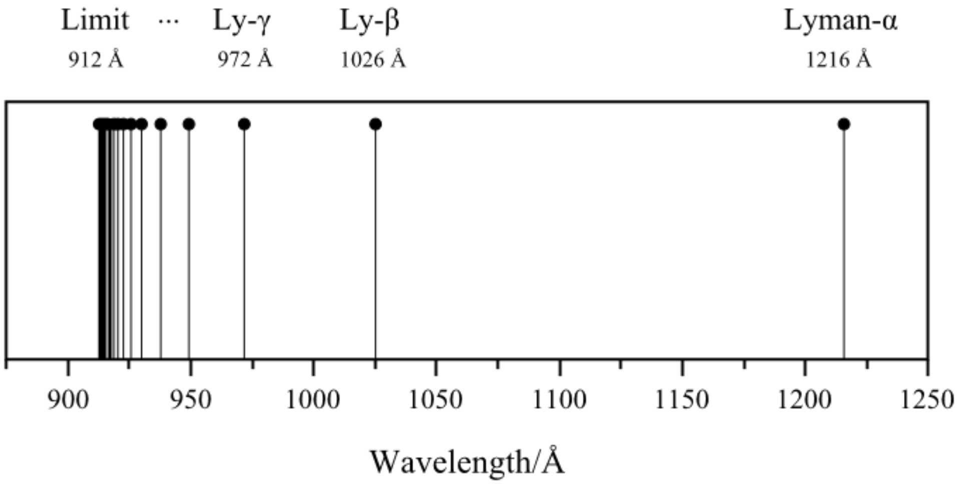
$R(1-1/4^2) = 109737 \cdot 0.94 = 103153\ \mathrm{cm}^{-1} \Rightarrow \lambda_3 = 97$ nm

……

Limit for $n \to \infty$ $R(1-0) = 109737\ \mathrm{cm}^{-1} \Rightarrow \lambda_\infty = 91.2$ nm

This is called ***Lymann series***

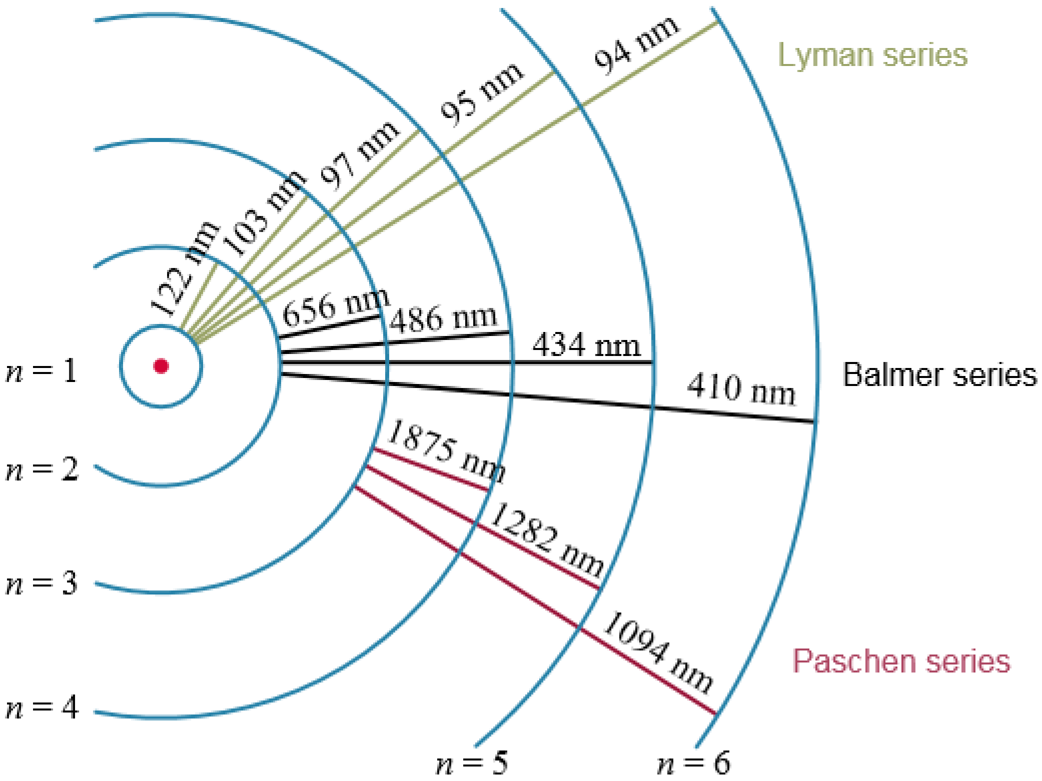
Atomic Hydrogen emission



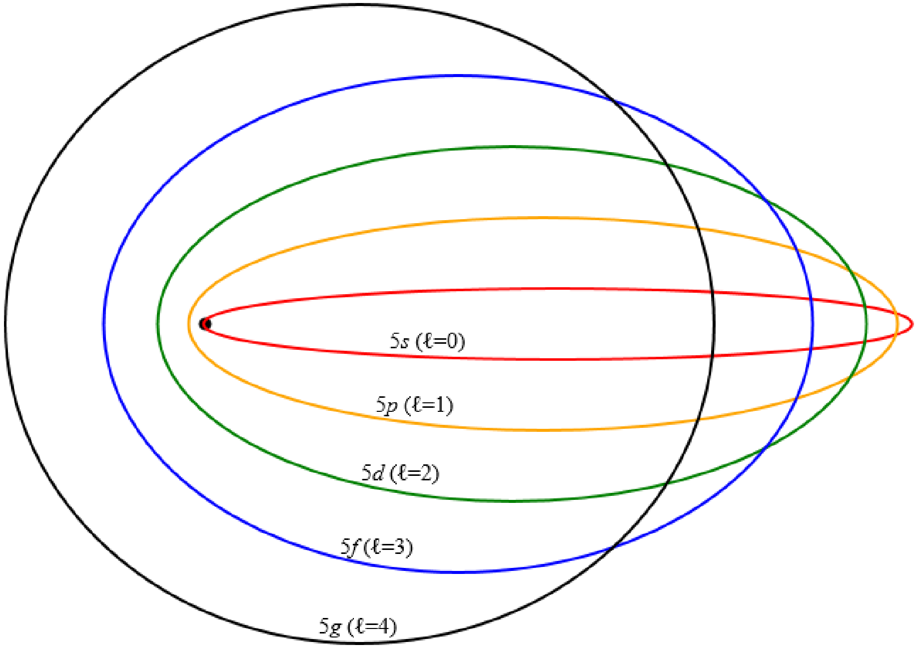
Lyman series
n’=1,   n=2,3,4,…..

Balmer series
n’=2,   n=3,4,5,…..

ATOMIC HYDROGEN EMISSION



ATOMS WITH MORE ELECTROS



Generalized Bohr's model

- Elliptical orbits ⇒ two quantum numbers to define an ellipse
- Energy levels depend on two quantum numbers ⇒ more energy levels than the single atom

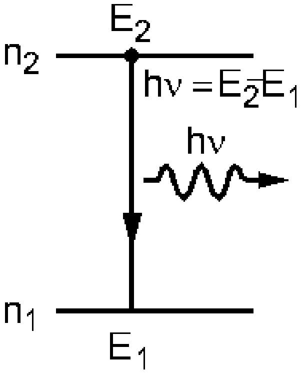
SPONTANEOUS EMISSION

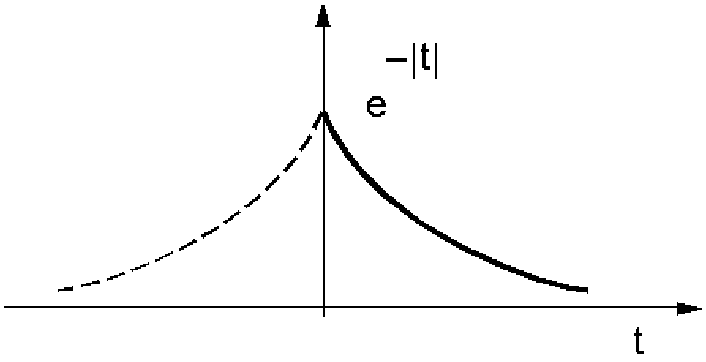
The atom decays from level E2 to level E1 with a certain probability A(2,1) and emits a corresponding photon at frequency ν

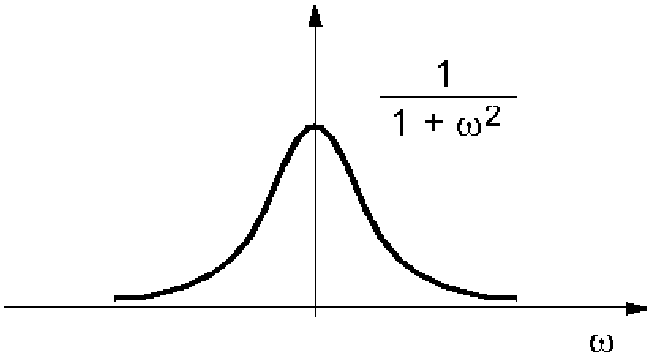
A(2,1) = Einstein coefficient for spontaneous emission from level E2 to level E1

Starting from a level *n*, the atom can decay to lower levels with a total probability γ_n. The decay speed is proportional to the numbers of atoms in the level *n*.

$$\frac{dN_n}{dt} = -N_n\gamma_n \rightarrow N_n = N_n^0 e^{-\gamma_n t}$$







Time domain: exponential

Spectral line profile: lorentzian

Fourier transform

LINE PROFILE

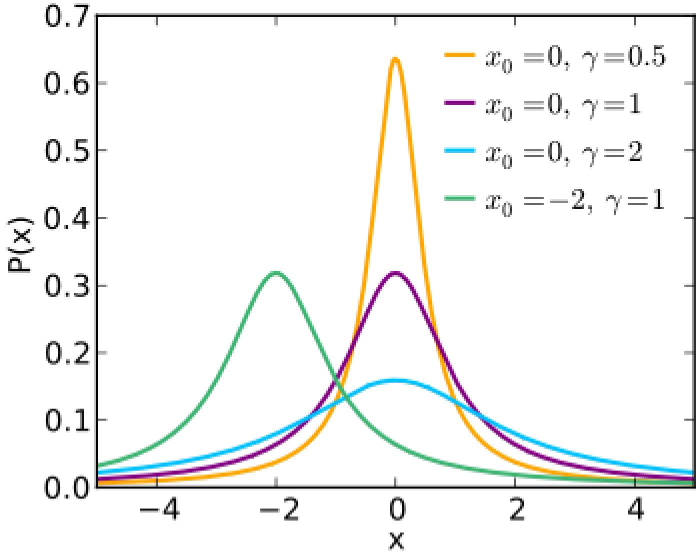
Natural broadening in brief

The uncertainty principle $\Delta E \cdot \Delta t \approx h/2\pi$ (h is the Planck constant) relates the lifetime of an excited state with the uncertainty of its energy. A short lifetime will have a large energy uncertainty and a broad emission. As the excited state decays exponentially in time, this effect produces a line with ***Lorentzian profile***.

$$\delta\nu \approx \frac{\Delta E}{h} \approx \frac{1}{2\pi\Delta t}$$

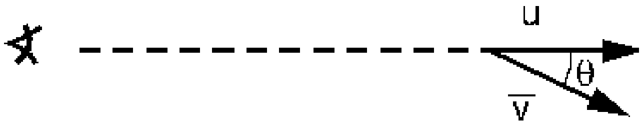
$$g(\nu) = \frac{\gamma}{4\pi^2} \frac{1}{(\nu-\nu_0)^2 + (\gamma/4\pi)^2}$$

where Γ is the total transition probability for the excited level



DOPPLER EFFECT

Relative speed between atom and observer



Frequency shift $$\frac{\nu-\nu_0}{\nu_0}=\frac{\delta\nu}{\nu_0}=\frac{\nu\cos\theta}{c}=\frac{u}{c}$$

Maxwellian distribution of atoms ⇒ it describes the particle speeds at thermodynamic equilibrium in idealized gases where the particles move freely inside a container without interacting with one another, except for very brief collisions

$$dw \propto \exp\left\{-\frac{m}{2kT}u^2\right\}du$$

Distribution of atoms within a speed interval du

The Doppler shift at a certain frequency is proportional to the particles (atoms/molecules) that are moving at a velocity u giving $\delta\nu/\nu = u/c$

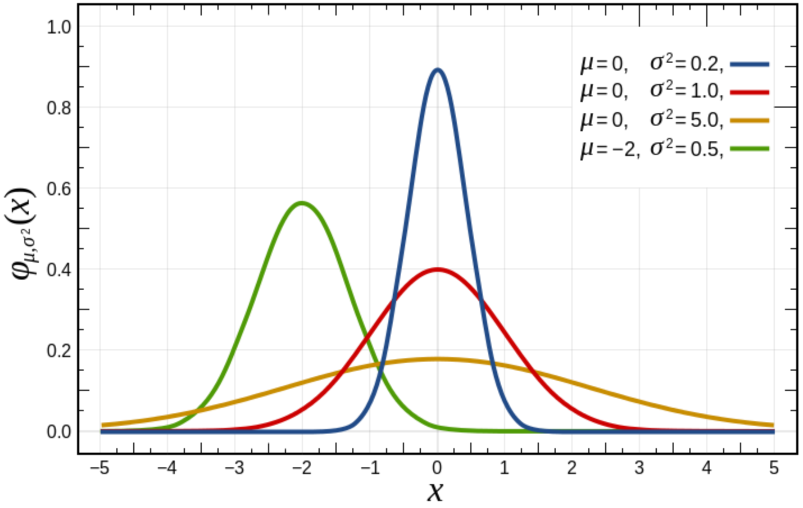
Doppler broadening in brief

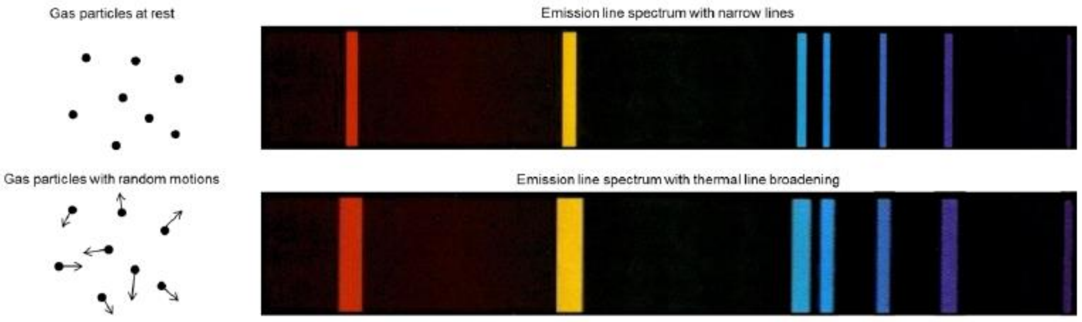
The atoms in a gas have a distribution of velocities. Each photon emitted will be shifted in frequency by the Doppler effect depending on the velocity of the atom relative to the observer. The higher the temperature of the gas, the wider the distribution of velocities in the gas. Since the spectral line is a combination of all of the emitted radiation, the higher the temperature of the gas, the broader the spectral line emitted from that gas. This broadening effect is described by a **Gaussian profile**.

$$I(\nu) \propto \exp\left\{-\frac{mc^2}{2kT}\frac{\delta\nu^2}{\nu_0^2}\right\}$$

$$\delta_d^{\nu} = \frac{\nu_0}{c}\sqrt{\frac{8kT\ln 2}{m}} \qquad \delta_d^{\lambda} = \frac{\lambda_0}{c}\sqrt{\frac{8kT\ln 2}{m}}$$

m = atomic mass
k = Boltzmann constant





EXERCISE

Calculate the natural broadening and the Doppler broadening for the H atom at the transition Lymann-α at 121.5 nm at T = 1000 K (electric discharge).
The average life of the excited state is $\tau = 0.16\cdot10^{-8}$ s

Natural broadening
$\delta\nu \approx 1\cdot10^{8}$ Hz = 0.1 GHz

$$\delta\nu \approx \frac{1}{2\pi\Delta t}$$

Doppler broadening
$\delta\nu_d = 1/(121.5\cdot10^{-9}) \cdot [(5.55 \cdot 1.3\cdot10^{-23} \cdot 500/(1.8\cdot10^{-27})]^{0.5} = 5.6\cdot10^{10}$ Hz = 56 GHz

$$\delta_d^{\nu} = \frac{\nu}{c}\sqrt{\frac{8kT\ln 2}{m}} = \frac{1}{\lambda}\sqrt{\frac{8kT\ln 2}{m}}$$

where
K = Boltzmann constant = $1.3\cdot10^{-23}$ J/K
m = hydrogen mass = $1.8\cdot10^{-27}$ kg

Doppler broadening is 1-3 orders of magnitude higher than the natural broadening (depending on element, transition, temperature)

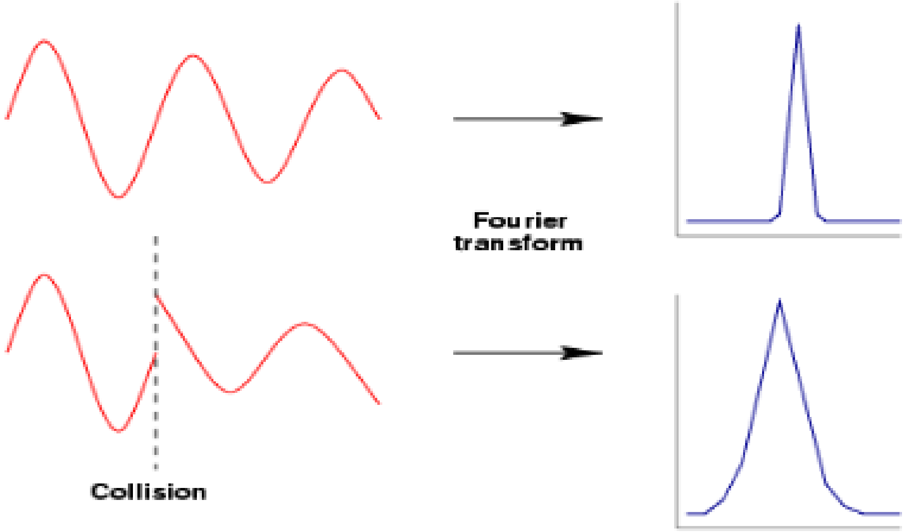
COLLISION EFFECT

Natural emission from an atom is disturbed by collisions ⇒ phase and amplitude of the emitted radiation change ⇒ the duration of the unperturbed emission is reduced ⇒ the line width is increased

$$I(\nu) \propto \frac{1}{(\nu_0-\nu)^2+(1/2\pi\tau_0)^2}$$

τ_0 average time between collisions

$$\delta_c^\nu = 1/2\pi\tau_0$$



From kinetic gas theory

$$\delta_c^\nu = \frac{\sigma n}{2\pi}\sqrt{\frac{2kT}{m}} \propto p$$

σ = cross section for collisions (m^2)

n = density of particles (m^{-3})

m = mass

Pressure broadening in brief

The collision of other particles with the emitting particle interrupts the emission process, and by shortening the characteristic time for the process, increases the uncertainty in the energy emitted. This effect depends on the density of the gas, hence on pressure. The broadening effect is described by a **Lorentzian profile**.

EXERCISE

Calculate the collisional broadening for the H atom, 1 atm, atom density *n* = $7.2 \cdot 10^{24}$ m^{-3} at the transition Lymann-α at 121.5 nm at T = 1000 K (electric discharge).
The collisional cross section at 121.5 nm is $\sigma = 10^{-19}$ m^2

Collisional broadening
$\delta\nu_c \approx 5 \cdot 10^8$ Hz = 0.5 GHz

$$\delta_c^\nu = \frac{\sigma n}{2\pi}\sqrt{\frac{2kT}{m}} = \frac{p\sigma N_A}{2\pi R}\sqrt{\frac{2k}{Tm}}$$

where
K = Boltzmann constant = $1.3 \cdot 10^{-23}$ J/K
m = hydrogen mass = $1.8 \cdot 10^{-27}$ kg

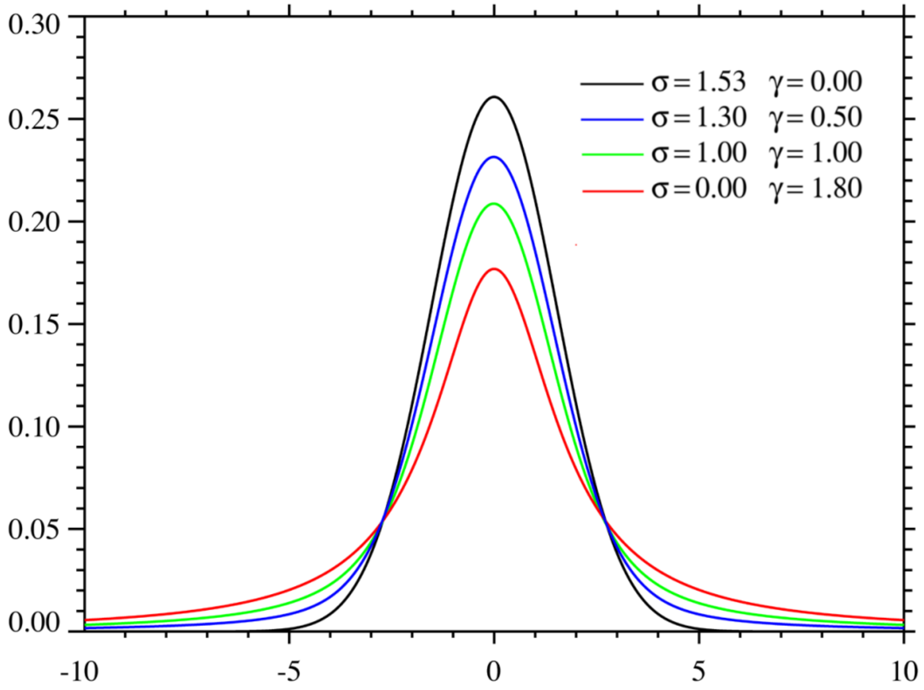
$$n = \frac{N_A d}{M} = \frac{pN_A}{RT}$$

Collisional broadening is higher than natural broadening and depends on gas pressure.

Total broadening

A combination of the different causes gives a **Voigt profile** $\Rightarrow$ convolution between a Gaussian and a Lorentzian

The Voigt profile is dominated by the Gaussian in the center and by the Lorentzian in the wings



LINE PROFILES IN GASES

For gas absorption lines in standard conditions (atmospheric pressure and ambient temperature), the line profile is dominated by collision broadening (lorentzian profiles).

Example

Pressure broadening at room temperature for the oxygen lines in the A band (760 nm or 13122 cm^{-1}) accounts for a typical broadening of 0.05 cm^{-1}/atm.

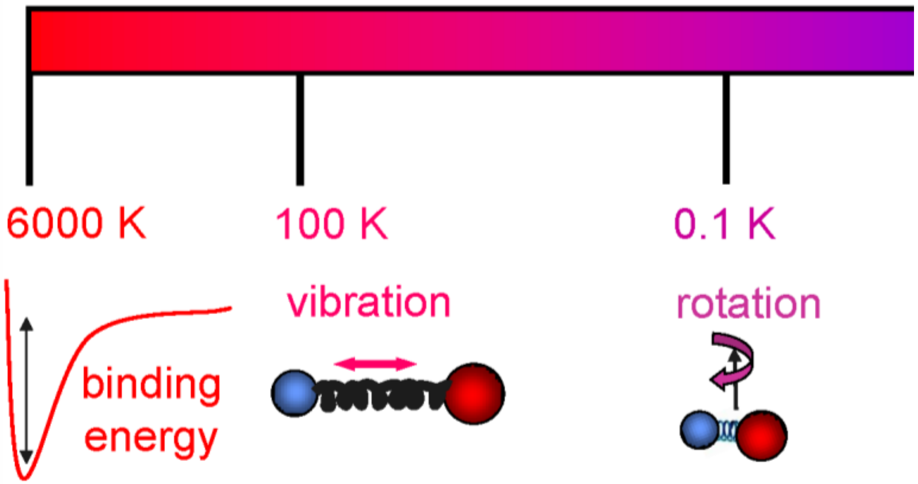
At room temperature and ambient pressure, the measured linewidth is around 2 GHz with a line profile that is largely lorentzian.

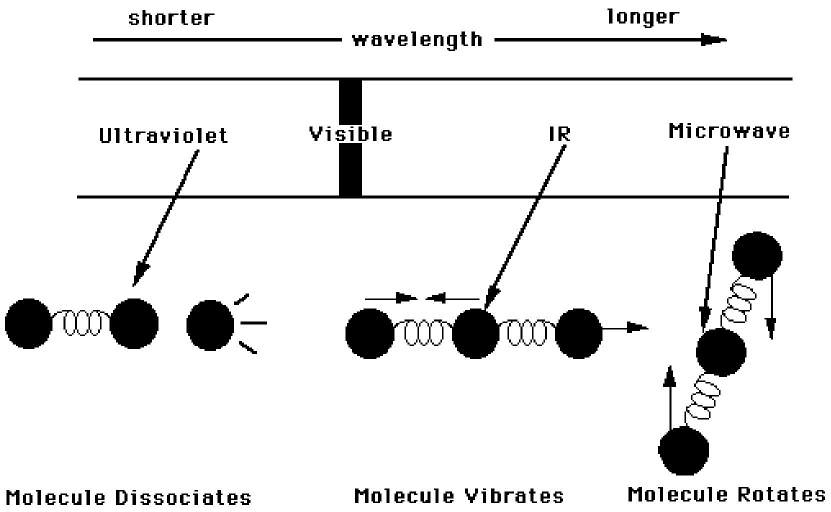
ABSORBTION SPECTRA IN MOLECULES

For molecules, there are two other important processes to consider besides the excitation of electrons from one molecular orbital to another.

The first is that **molecules vibrate**. Molecular vibrations or vibrational transitions occur in the infrared portion of the spectrum and are therefore lower in energy than electronic transitions.

The second is that **molecules rotate**. Molecular rotations or rotational transitions occur in the microwave portion of the spectrum and are therefore lower in energy than electronic and vibrational transitions.





MOLECULES ARE PUT IN RESONANCE BY LIGHT

What is resonance ?

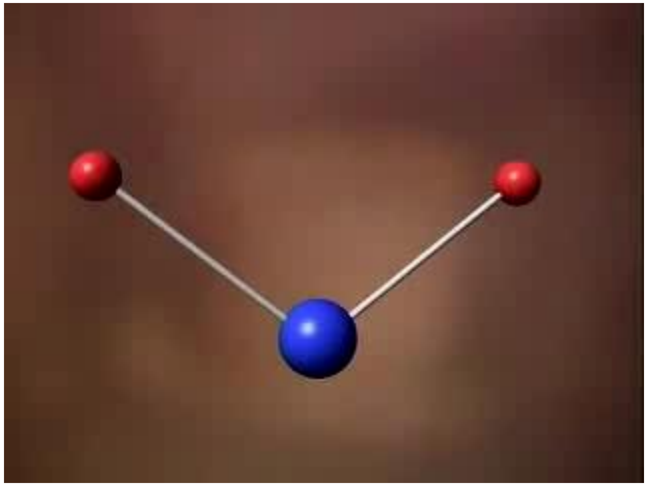
It is a phenomenon that occurs when an external force drives a system to oscillate with greater amplitude at a specific preferential frequency.

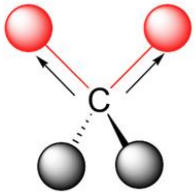
Frequencies at which the response amplitude is a relative maximum are known as the **resonance frequencies**. At resonant frequencies, small periodic driving forces have the ability to produce large amplitude oscillations. This is because the system stores vibrational energy.

Tacoma bridge disaster, Washington state (1940)

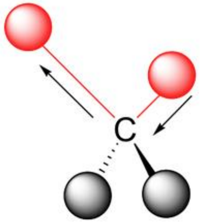
Covalent molecular bonds behave like **springs**. At room temperature, organic molecules are always in motion (**vibrational modes**).

The energy of molecular vibration is *quantized*, meaning that a molecule can only stretch and bend at certain 'allowed' frequencies. If a molecule is exposed to e.m. radiation that matches the frequency of one of its vibrational modes, it will absorb energy from the radiation and jump to a higher vibrational energy state. The difference in energy between the two vibrational states is equal to the energy associated with the wavelength of radiation that was absorbed.

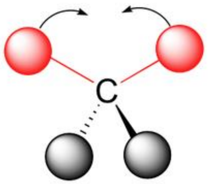




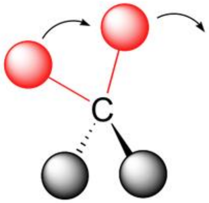
symmetric stretching



asymmetric stretching



scissoring



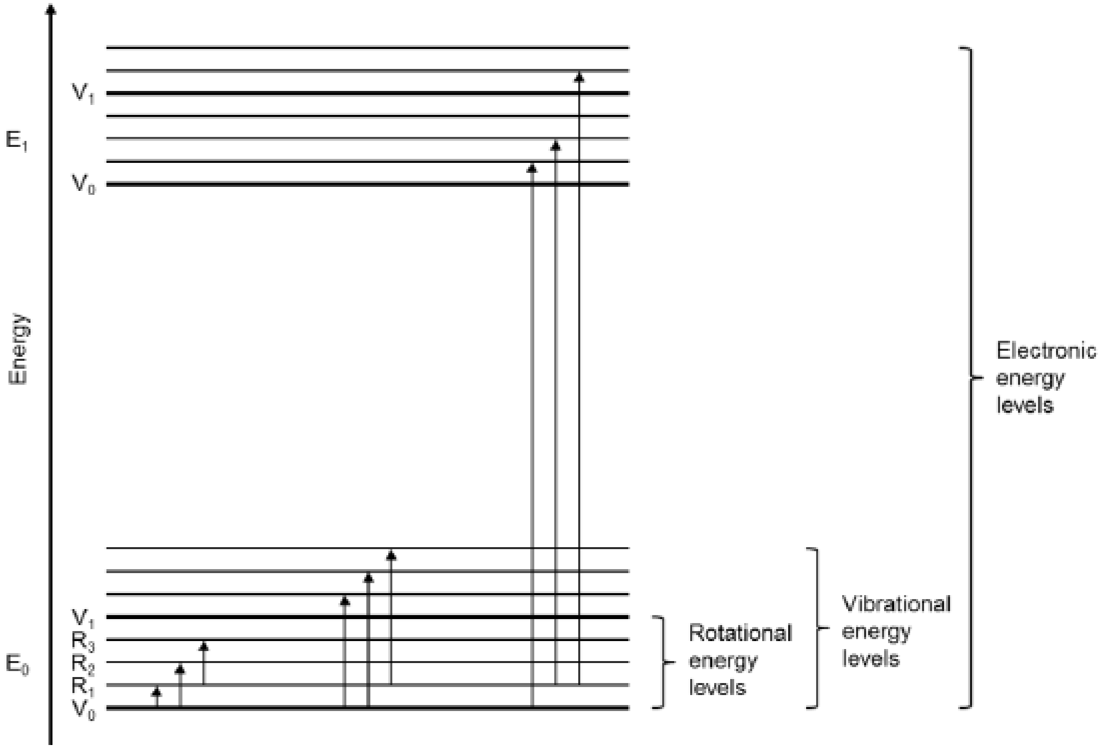
rocking

Roto-vibrational levels

A molecular vibration is excited when the molecule absorbs a quantum of energy, *E*, corresponding to the vibration's frequency, ν, according to the relation $E = h\nu$.

Simultaneous excitation of a vibration and rotations gives rise to **vibrational-rotational spectra**.

Order of magnitude of is 1000 cm^{-1} for vibration frequencies, 10 cm^{-1} for rotation frequencies ⇒ spacing of rotational levels is 1/100 of vibrational



Energy level diagram for a molecule showing electronic, vibrational and rotational states. Arrows represent possible absorption transitions.

MOLECULAR LEVELS

Electronic energy δE$_e$

$$\delta p\,\delta x \geq \frac{\hbar}{2} \rightarrow \delta p \approx \frac{\hbar}{a} \rightarrow \delta E_e \approx \frac{\hbar^2}{ma^2} \qquad \left(E_e = \frac{p^2}{2m} \right)$$

m = electron mass

a = molecule size

δE$_e$ ≈ (1÷10 eV) $\tilde{\nu} \approx 10^5 \;\; cm^{-1}$

Vibrational energy δE_v

Elastic oscillator

$$F = M\ddot{x} = -K_0 \mathrm{x} \qquad \omega_v = \sqrt{\frac{K_0}{M}}$$

M = molecular mass

$$\delta E_v \cdot \delta t_v = \hbar \qquad \delta t_v \approx \frac{1}{\omega_v} \qquad \delta E_v = \hbar\omega_v = \hbar\sqrt{\frac{K_0}{M}}$$

If the atoms are moved by *a*, energy levels are distorted $\delta E_e = K_0 a^2$

$$\delta E_\mathrm{v} = \sqrt{\frac{m}{M}}\delta E_e \qquad \tilde{\nu} \approx 10^3\ \mathrm{cm}^{-1}$$

Rotational energy δE$_r$

Quantum mechanical rigid rotor

$$E_r = \frac{\hbar^2 J(J+1)}{2Ma^2} \qquad J = 1,2,\ldots$$

Energy difference between level 0 and 1

$$\delta E_r \approx \frac{\hbar^2}{Ma^2} \approx \sqrt{\frac{m}{M}}\delta E_\mathrm{v} \quad \rightarrow \; 10\,\mathrm{cm}^{-1}$$

BIATOMIC MOLECULE (H_2)

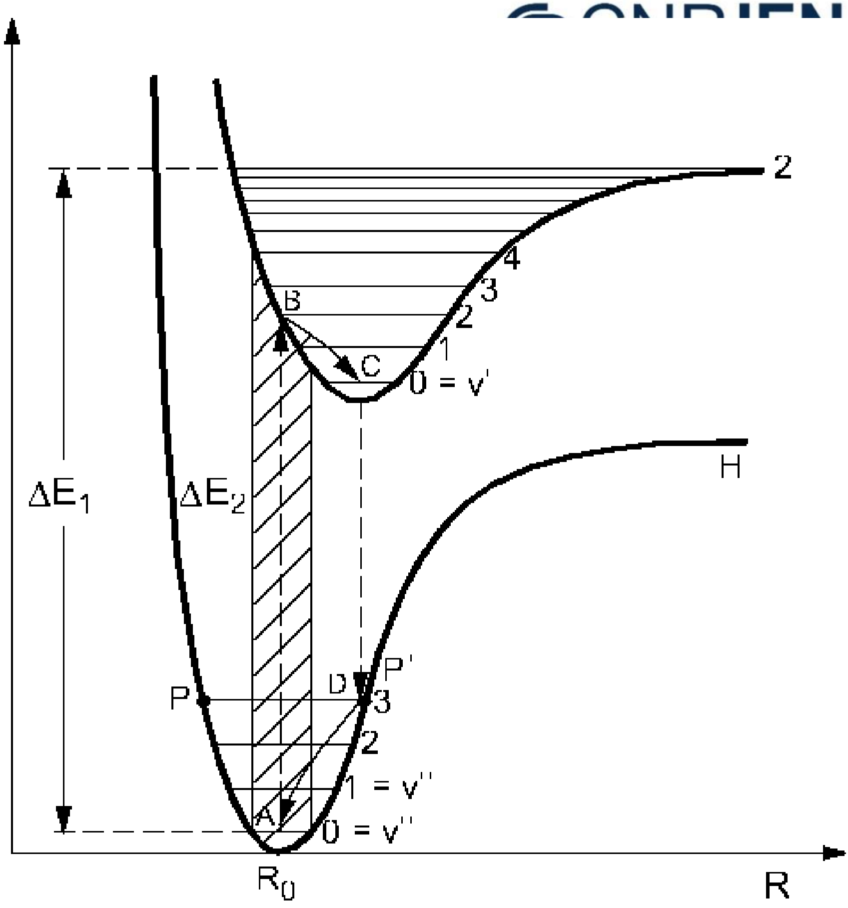
Two states: fundamental and excited

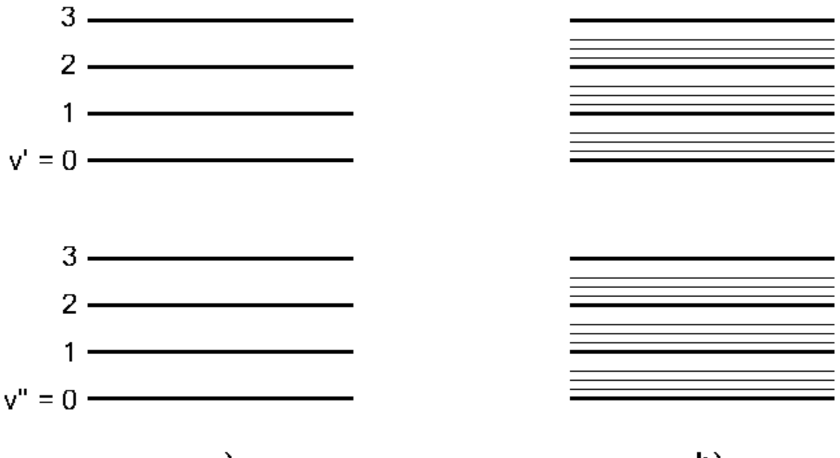
For R decreasing, the strength is attractive ($R > R_0$), then has a minimum ($R = R_0$), then it becomes repulsive ($R < R_0$)

The two atoms, without oscillations, are in the condition $R = R_0$

If they oscillate with small amplitude around R_0, they form a harmonic oscillator

$$\frac{\partial E}{\partial r} = F \qquad \delta E_{\mathrm{v}} = \hbar\sqrt{\frac{K_0}{M}}$$





a) b)

MOLECULAR TRANSITIONS

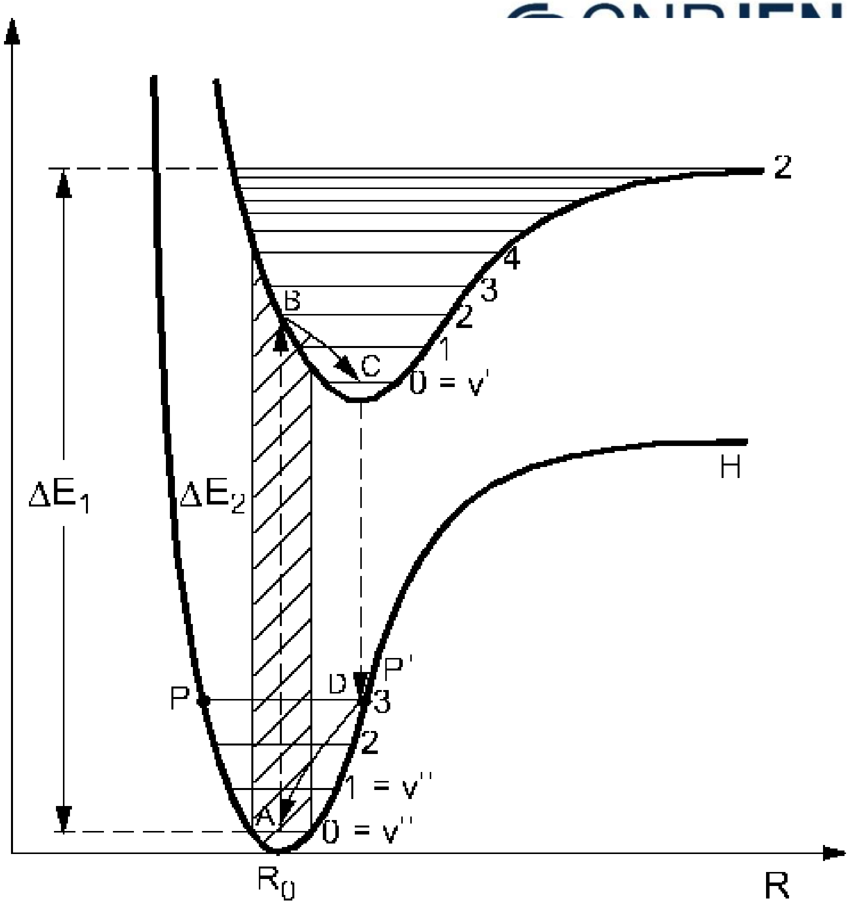
Molecule excited by radiation ΔE_2.

It will move from vibrational level A to level B.

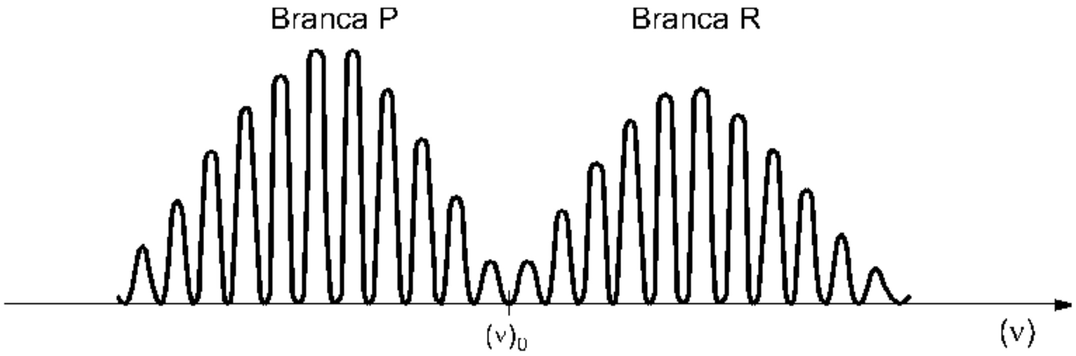
Then, due to collisions, it will decay to level C.

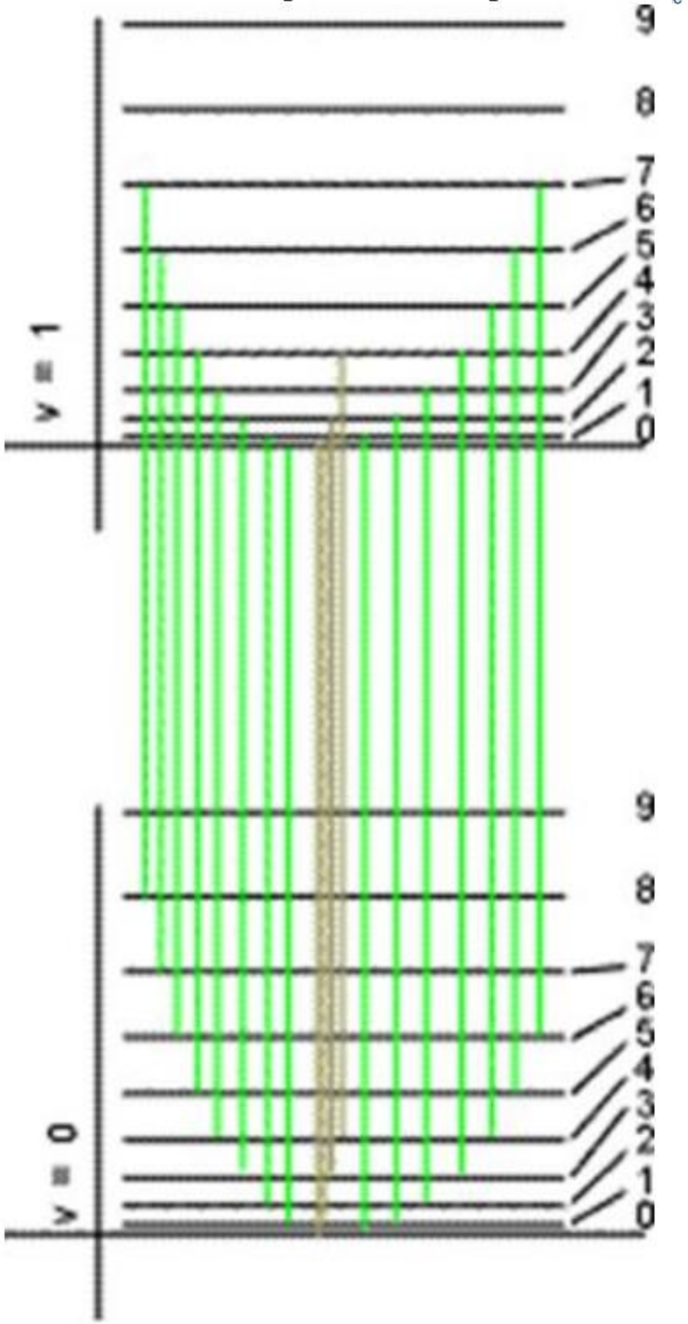
Finally, it will decay for spontaneous emission to level D, then to level A.

In reality, molecule will transit from a rotational level, inside a vibrational level, to another rotational level, inside another vibrational level.

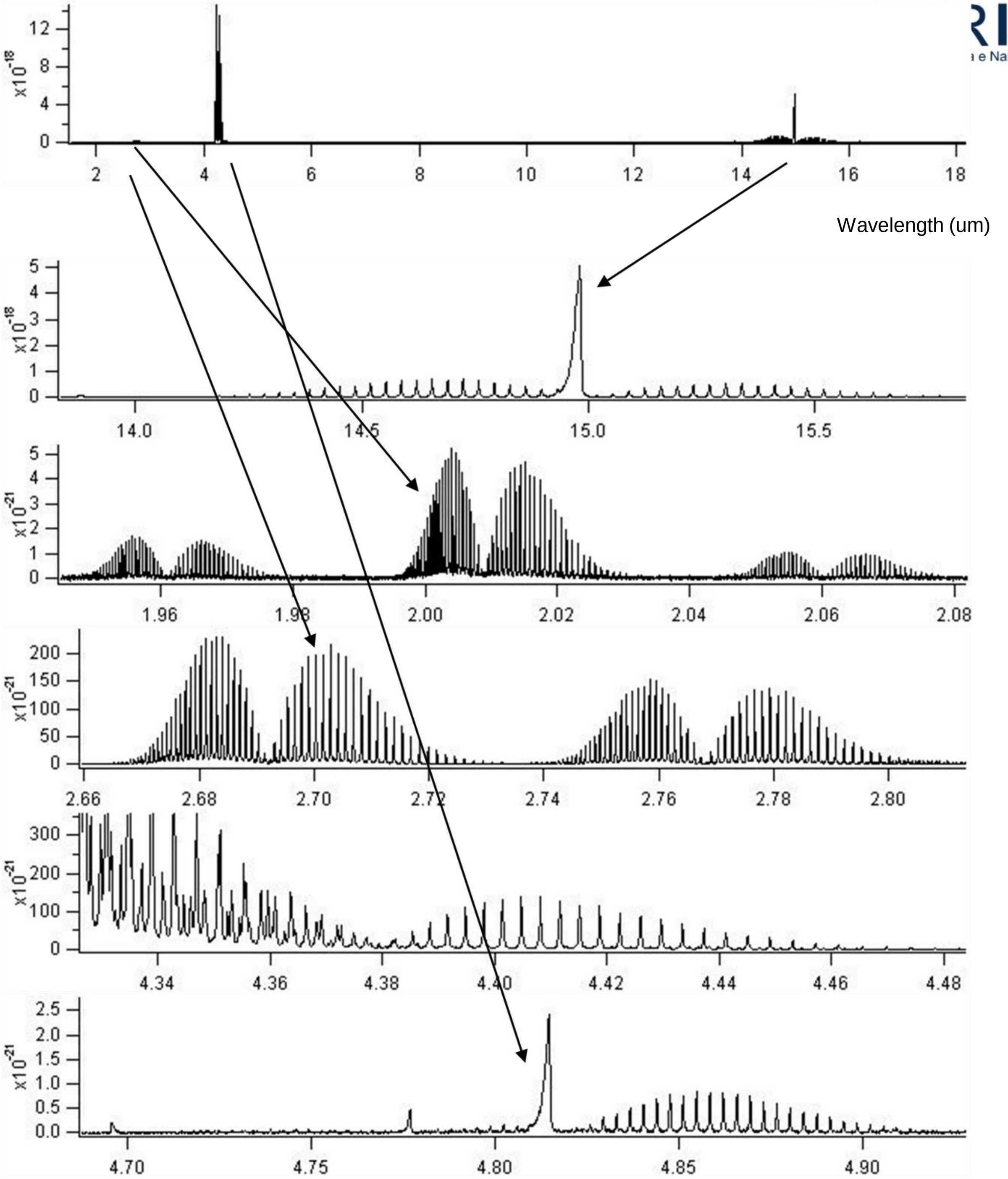


Due to the selection rules, two branches appear on a vibrational line: ***branch p*** (lower frequencies) and ***branch r*** (higher frequencies).
The distribution of the intensities in the two branches depends on the distribution of the population of several atoms on the levels.





CO2 absorption spectrum



MOLECULAR SPECTROSCOPY

In a spectroscopy experiment, e.m. radiation of a specified range of wavelengths is allowed to pass through a sample containing a compound of interest. The sample molecules absorb energy from some of the wavelengths, and as a result jump from a low energy ‘ground state’ to some higher energy ‘excited state’.
Other wavelengths are *not* absorbed by the sample molecule, so they pass on through.

A given molecule will specifically absorb only those wavelengths which have energies that correspond to the energy difference of the transition that is occurring.

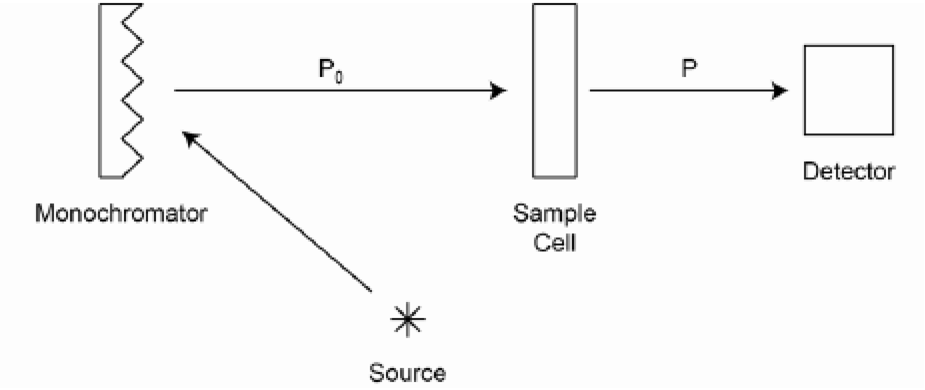
WHY SPECTROSCOPY IS USED ?

Spectroscopy in analytical chemistry is used: (1) **to identify a species** and (2) **to quantify a species**.

Identification of a species involves recording the absorption or emission of a species as a function of the wavelength to obtain a spectrum (i.e., a plot of the absorbance or emission intensity as a function of wavelength). The features in the spectrum provide a signature for a molecule that may be used for identification.

Quantification of a species using a spectroscopic method involves measuring the absorbance or intensity of the emission and relating that to the concentration.

ABSORBANCE MEASUREMENTS



P_0 = power from the radiation source at wavelength λ

P = power transmitted through the sample at wavelength λ

Trasmittance $T = P/P_0$

Absorbance $A = -\log(T) = \log(P_0/P)$

Beer-Lambert law $A = k\,b\,c$

k = extinction coefficient (function of the wavelength)

b = path length

c = concentration

GAS DETECTION

Absorption spectra of IR gases display a range of fine line structures and broad peaks, and cover a wide range between **1.0 to 20 µm**.
An apparatus used to plot the spectra is called '**DISPERSIVE**' and serves as a **spectrometer.** In many IR gas sensing applications, spectrometry is not really needed, since users want to measure the concentration of known gas species.

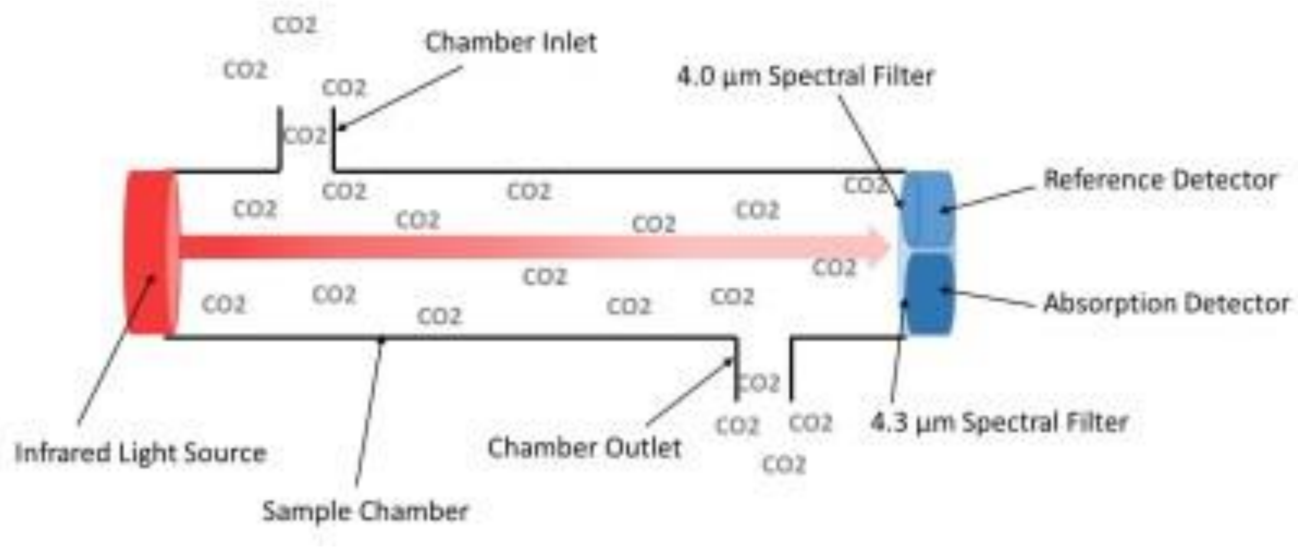
In a **NON-DISPERSIVE INFRARED** (NDIR) sensing method, fixed narrow-band filters are used with separate IR detectors to detect a few gas absorption lines across a restricted wavelength range. The concentration of gas can be obtained measuring the **absorption** through the filter.

Non-dispersive spectroscopy is typically used around 3-5 um, since the absorption lines in such a region are very strong than at shorter wavelengths, therefore a high signal-to-noise ratio can be achieved.

OPTICAL ABSORPTION SPECTROSCOPY: NON DISPERSIVE INFRARED SPECTROSCOPY (NDIR)

An IR beam passes through the sampling chamber. By measuring the amount of absorbed IR the concentration of the gas component can be determined.

The optical filter is centered on an absorption band of the gas to be detected (e.g., 4.81 um for CO_2) and is typically mounted in front of the detector to eliminate all light except the wavelength which the selected gas molecules can absorb.



IR source
IR active detector with suitable filter
Absorption cell with gas admission
IR reference detector with neutral filter for background monitoring

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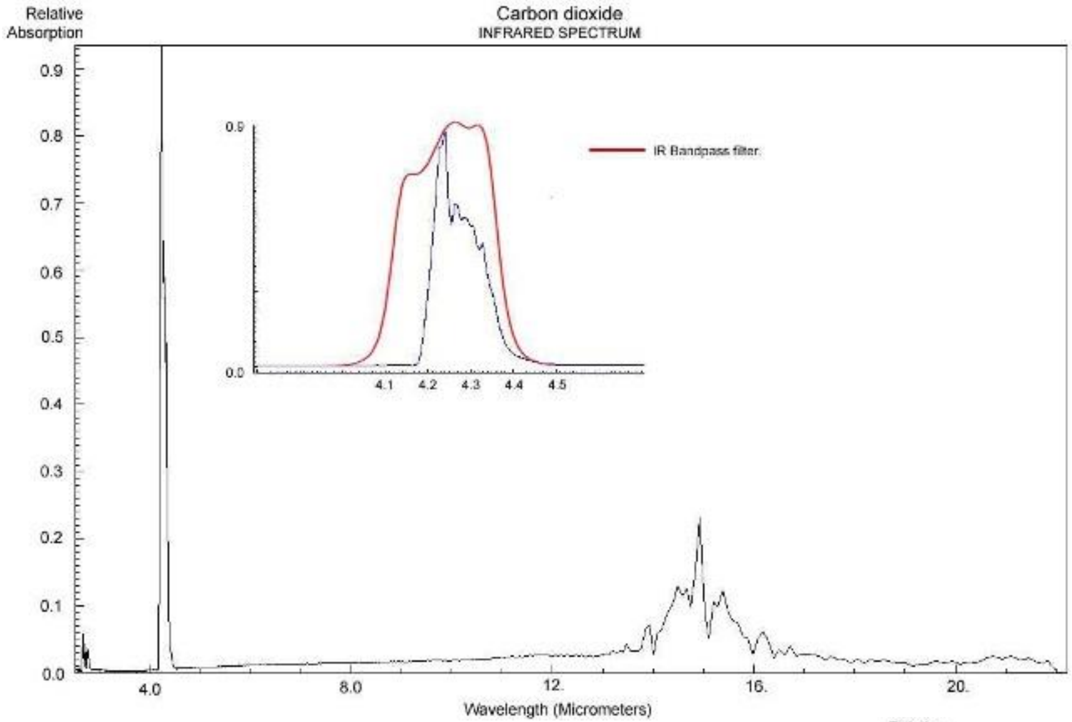
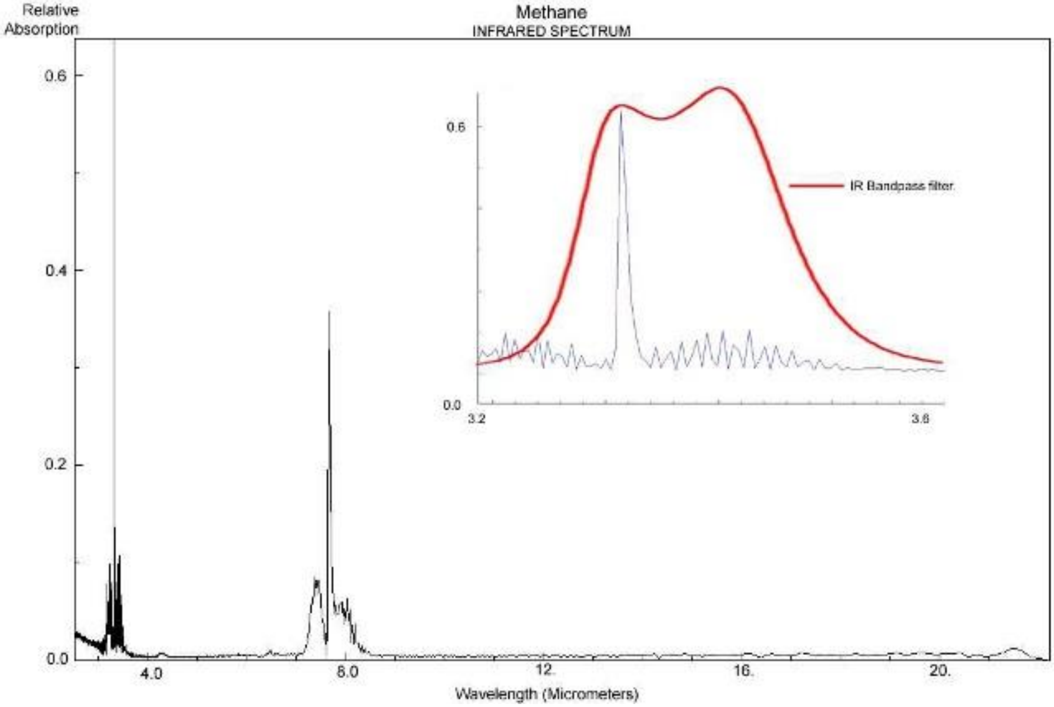
INFRARED SPECTRUM OF GASES



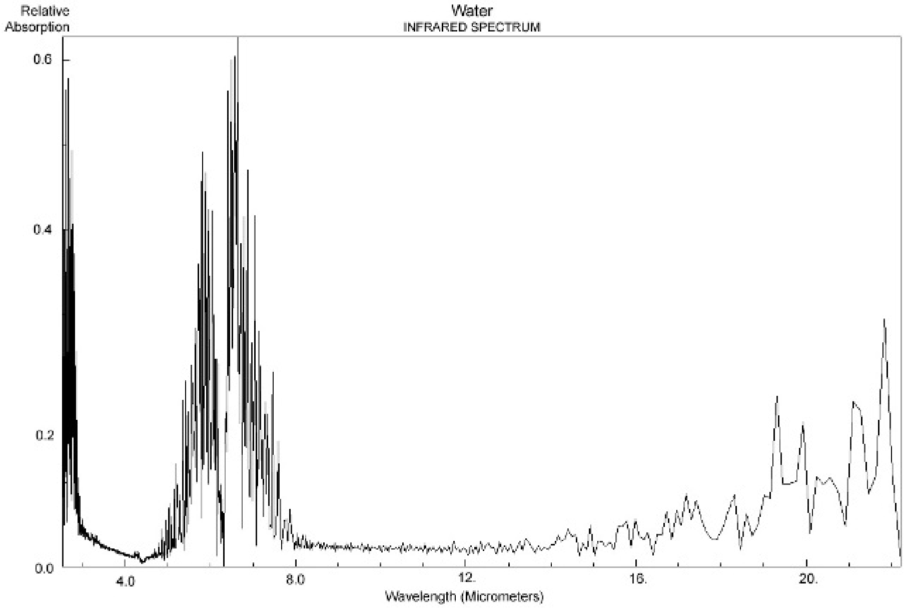


CHOICE OF SENSING WAVELENGTHS

The choice of sensing wavelengths is controlled by the availability of IR sources and also the need to work within the ***'water windows***'.

The water absorption spectrum displays strong absorptions less then 3 µm, from 5-8 µm and beyond 16 µm. Broad-band spectroscopy in these regions will be very noisy, since it would be subject to strong interference from humidity.

Hence, it is better to operate in the **8-16 micron** or **3-5 micron windows** where a number of practical gas lines exist.

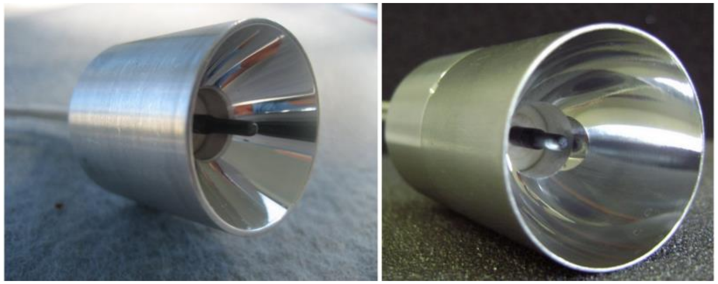


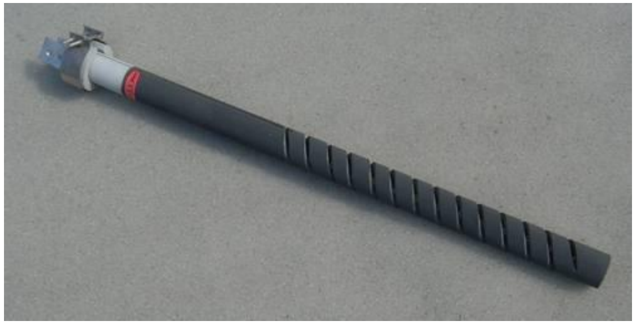
INFRARED SOURCES

These sources operate through the heating of an element so that it emits in the infrared range. As these devices are broadband, some energy is released at visible wavelengths.

- Globar: silicon carbide rod, electrically heated to 1300 °C, radiation between 1-40 μm
- Coiled resistance wires
- LED (Light Emitted Diodes) based on GaSb, In As

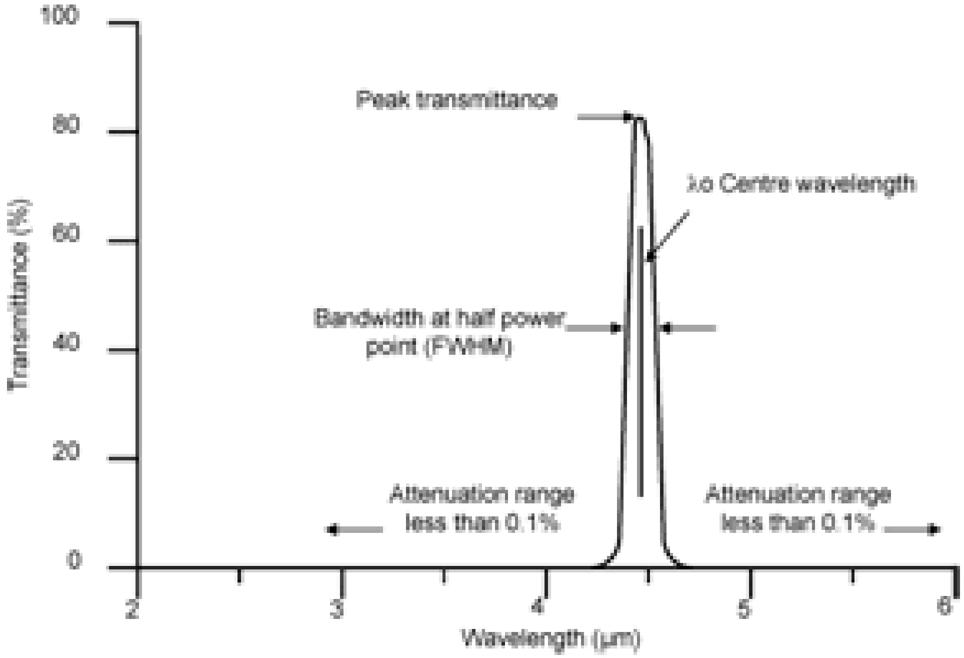
A reflector can be added to the source to increase the output power





FILTERS

Optical filters have a very narrow bandwidth, typically of few tens of micron at several microns (e.g., 0.2 um bandwidth at 4.2 um)



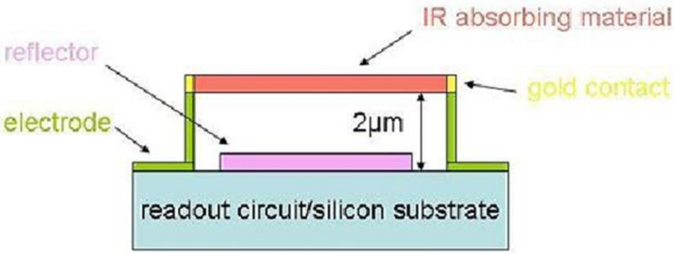
INFRARED DETECTORS

1. THERMAL

Based on phenomena depending on temperature

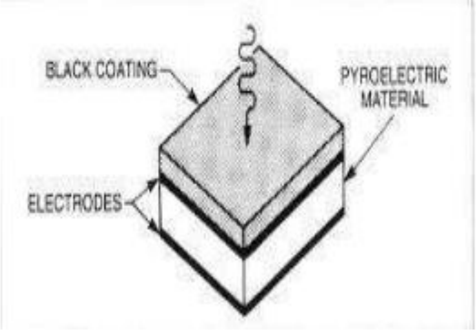
Bolometers

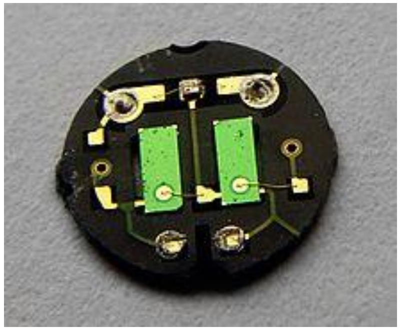
It consists of an absorptive element (semiconductor), such as a thin layer of material. A temperature change of the detector is detected when IR radiation is absorbed.



Pyro electric

Single crystalline wafer of a pyro electric material, such as triglycerine sulphate. Material exhibit electrical polarization. When the temperature is altered, the polarization changes, therefore an electric signal (voltage) is measured.



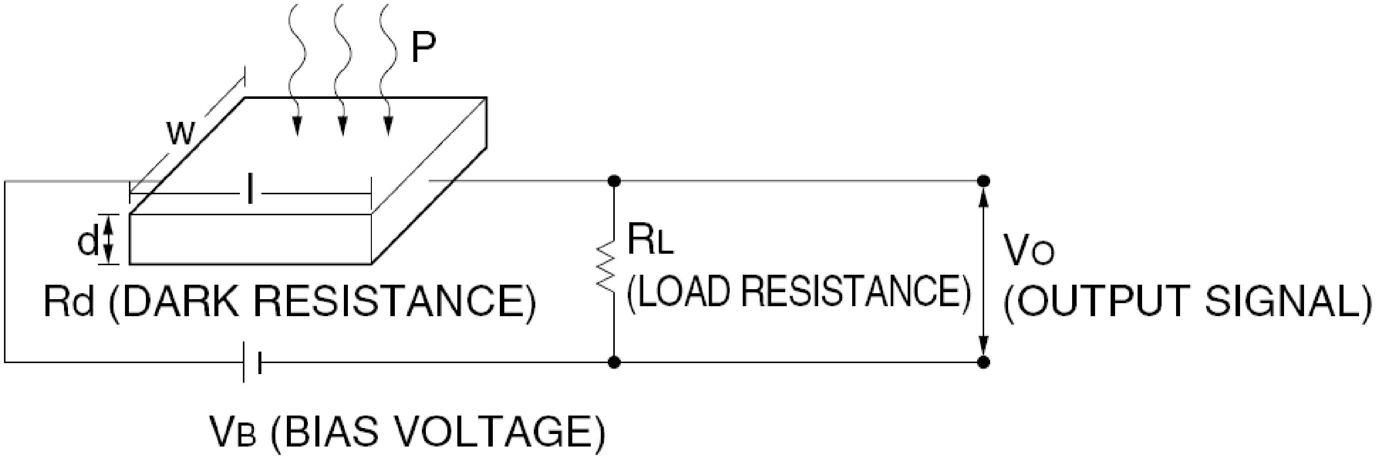


2. PHOTONIC DETECTORS

They are based on semiconductors with low band gap, to interact with the low-energy photons:

⇒ InGaAs: 0.7-2.6 um
⇒ Ge: 0.8-1.7 um
⇒ PbS: 1.3-2.0 um
⇒ PbSe: 1.5-5.2 um
⇒ InAs: 1.0-3.8 um
⇒ InSb: 1.0-6.0 um
⇒ HgCdTe: 0.8-25 um

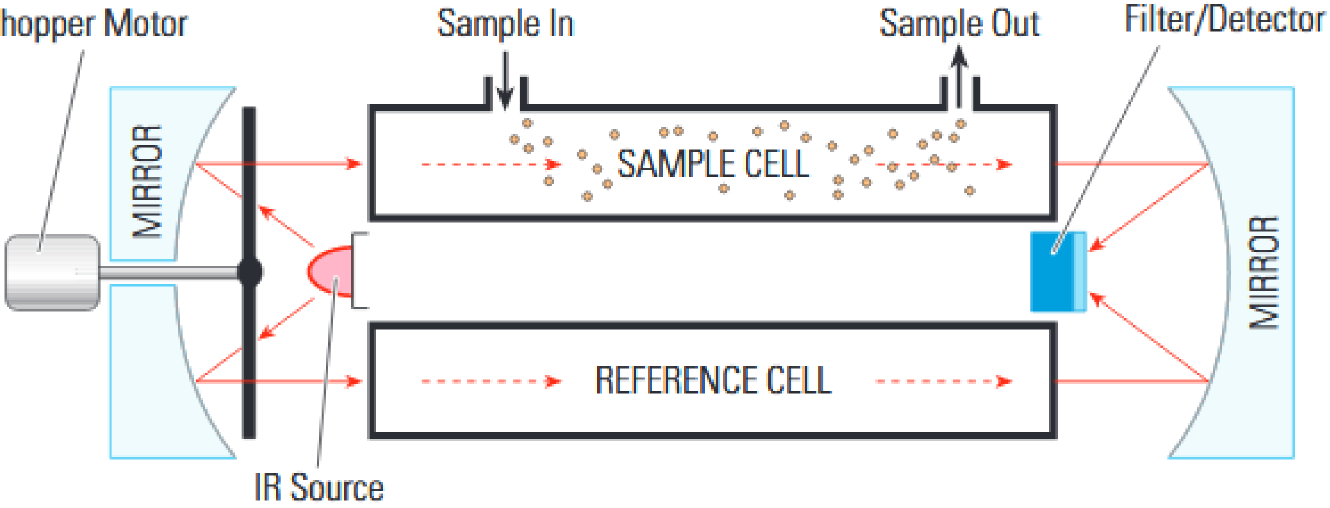
They are cooled to decrease the thermal noise.



Instrument setup

The detector has normally two channels:

- The measuring channel, with the sample cell and a filter centered in the absorption band of the gas to be detected
- The reference channel, whit a reference cell that is filled with nitrogen and is used to measure the background
- A chopper is used to illuminate consecutively the two cells: it is a rotating wheel with a hole



Double Beams with Chopper Layout

List of gases that can be detected

Here is a partial list of gases that can be detected through ND IR spectroscopy:

- Carbon dioxide and carbon monoxide
- Nitrogen oxides (NOx)
- Alkanes or saturated hydrocarbons such as methane, ethane, propane, butane, pentane
- Alkenes or unsaturated hydrocarbons such as ethylene, propylene, etc.
- Aromatics such as benzene and toluene
- Alcohols such as methanol, ethanol, propanol
- Ketones such as acetone
- Aldehydes

Benefits of NDIR Technique

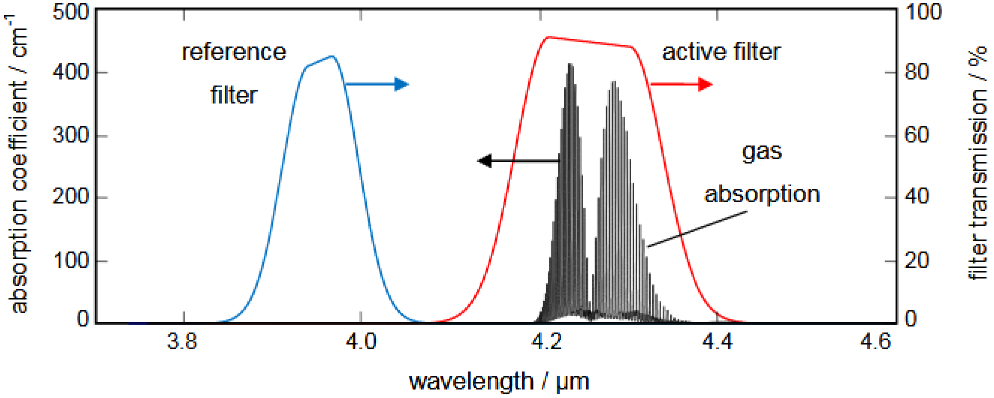
- Not affected by hazardous chemical environments
- NDIR gas sensors do not suffer from any poisoning effects (unlike catalytic sensors)
- CO_2 is detected without major interference from other gases
- No sensor burn-out or deterioration upon exposure to high gas concentrations
- Stable and long-term operation
- Minimum recalibration procedures
- Optically simple

Example: carbon dioxide detection for air quality monitoring

Carbon dioxide concentration in atmosphere is 400 ppm (0.04 %)

20-30 ppm accuracy is normally achieved
10 ppm accuracy is achieved for high performance

Hand-held or stationary devices available



Example: leak detection with 2D imaging camera

The leak is monitored by a 2D camera with an infrared filter centered on the using the background radiation as a light source.

False-color image of ethane leaking from a polyethylene plant

ABSORPTION TO BE MEASURED

Beer-Lambert law $$P(\lambda) = P_0(\lambda)\exp(-\sigma_\lambda Nl)$$

$P_0(\lambda)$ = power emitted by the source at wavelength λ
σ_λ = cross section at the wavelength λ
N = concentration of absorbing particles (absorbing molecules per unit volume)
l = optical path

Example

CO_2 NDIR spectroscopy at 4.1 um, 400 ppm = $4\cdot10^{-4}$ concentration
$\sigma_\lambda = 10^{-17}$ cm^2 (intense absorption)
N = $2.4\cdot10^{25}$ (molecules density at 1 atm) · $4\cdot10^{-4}$ (concentration) $\approx 10^{22}$ m^{-3} = 10^{16} cm^{-3}

l = 1 cm (compact cell)
$\exp(-\sigma_\lambda N l) = 0.90 \Rightarrow$ 10% absorption

l = 20 cm
$\exp(-\sigma_\lambda N l) = 0.14 \Rightarrow$ 86% absorption

A strong absorption signal can be measured at low concentration in a rather short optical path

Comparison with other absorption bands

CO_2 absorption at 2 um, 400 ppm = $4 \cdot 10^{-4}$ concentration
$\sigma_\lambda = 5 \cdot 10^{-21}$ cm^2
N = 10^{16} cm^{-3}
l = 20 cm
$\exp(-\sigma_\lambda N l) = 0.999 \Rightarrow 0.1\%$ absorption (to be compared with 86% at 4 um)

The absorption signal is very weak due to the lower cross section of the absorption lines.
Non-dispersive spectroscopy cannot be applied.

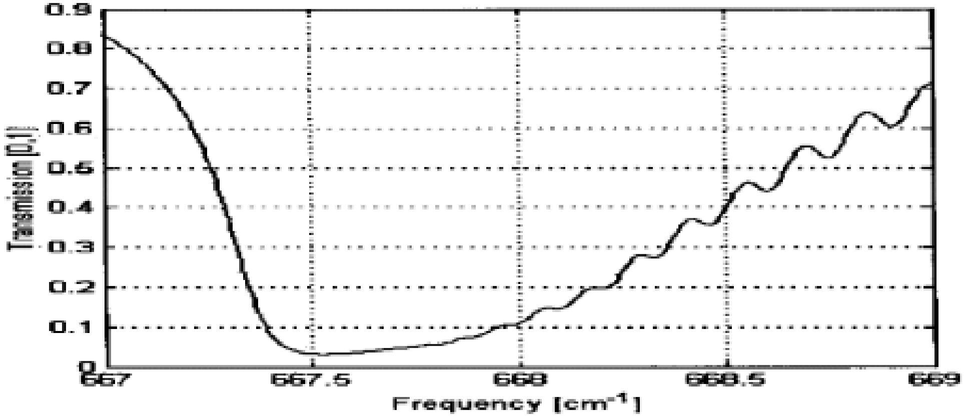
OPTICAL ABSORPTION SPECTROSCOPY: TUNABLE DIODE LASER SPECTROSCOPY (TDLAS)

In non dispersive infrared spectroscopy (NDIR) the signal is acquired integrated on the spectral region defined by the filter bandwidth.

No information is provided on the line profile, **in NDIR only the gas absorption is measured**, therefore the **gas concentration** is obtained.

Measurements on **line profile** can give important parameters other than **concentration**, such as the gas **pressure** and **temperature**

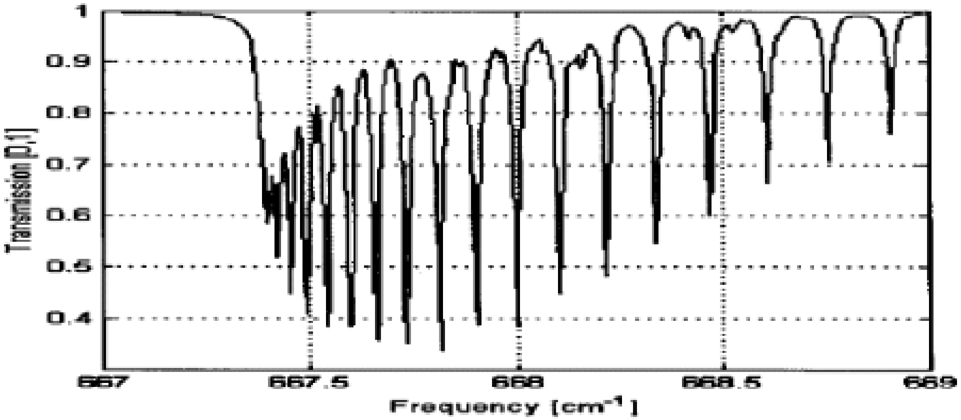
To measure the line profile we need a **monochromatic light** $\Rightarrow$ we have to illuminate the sample with a light having a bandwidth much smaller than the line bandwidth p = 1000 mb



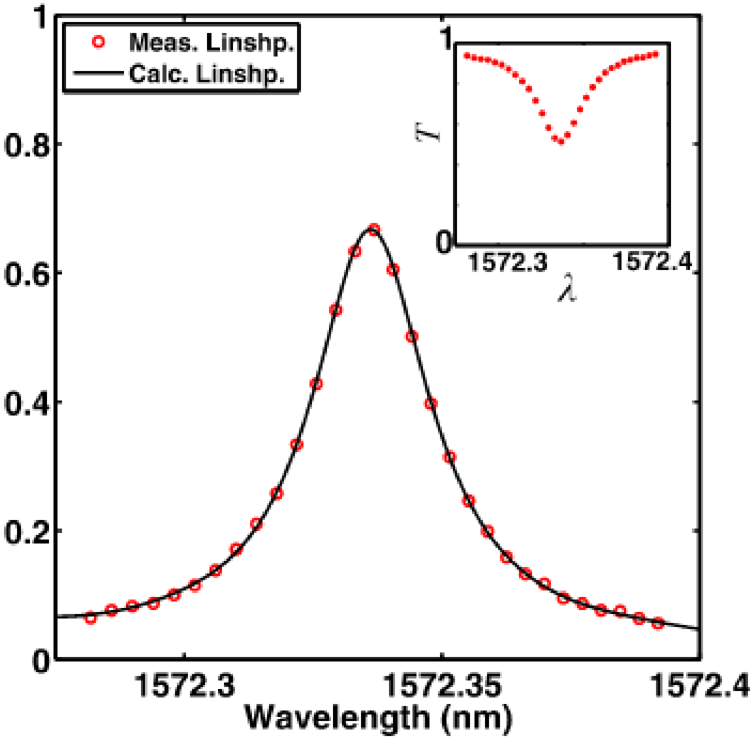
Example: transmission of CO_2, air concentration (400 ppm = 0.04%), 1 m path, atmospheric pressure (top) and 100 mbar (down), ambient temperature, 15 um wavelength (668 cm^{-1})

Pressure broadening is decreasing

p = 100 mb



To measure the line profile even at low temperatures, a light with a bandwidth lower than the line broadening is needed. A resolution better than 0.10 nm at 15 um is required



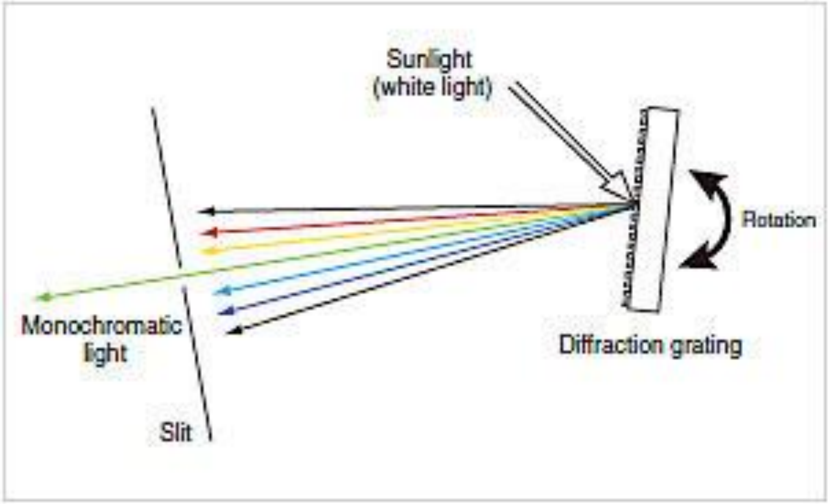
Example: typical lineshape of carbon dioxide (CO_2) in the atmosphere, 4.5 km altitude, 1.57 um

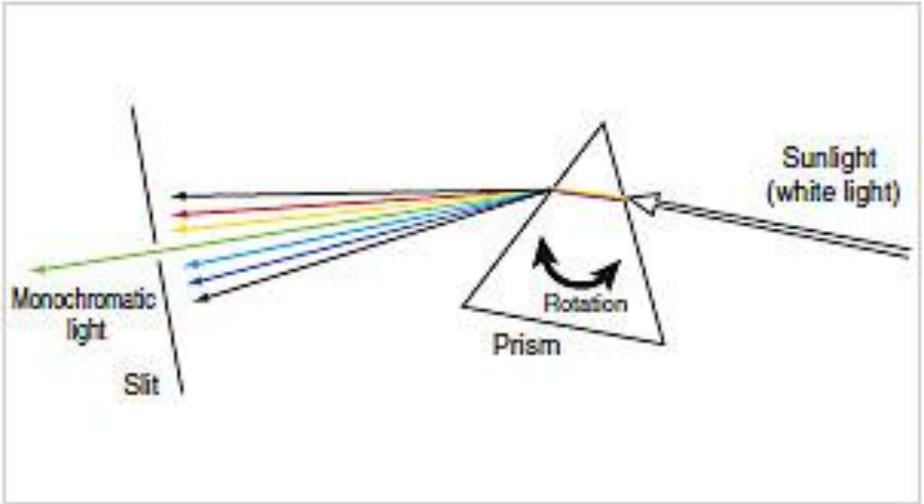
The sampling of the line profile has been done with 30 points on ≈0.1 nm ⇒ source bandwidth < 0.003 nm

HOW CAN BE OBTAINED A MONOCHROMATIC SOURCE TO BE USED FOR GAS SPECTROSCOPY ?

1. MONOCHROMATOR

A monochromator is an optical device that transmit a narrow band of wavelengths of light.





AND WHAT ELSE ?

2. LASER

A laser emit intrinsically monochromatic light with a very high resolution.
If the laser is operating in single mode, the emission linewidth is very narroq.

Example
The He:Ne laser emission is centered at 633 nm (red), single mode operation, bandwidth of 1700 MHz (Doppler dominated)

Calculate the line width in nm

$$\nu = \frac{c}{\lambda} \Rightarrow \Delta\nu = \frac{c}{\lambda^2}\Delta\lambda \Rightarrow \frac{\Delta\nu}{\nu} = \left(\frac{c}{\lambda^2}\Delta\lambda\right) \Big/ \left(\frac{c}{\lambda}\right) = \frac{\Delta\lambda}{\lambda} \Rightarrow \frac{\Delta\nu}{\nu} = \frac{\Delta\lambda}{\lambda}$$

$\nu = c/\lambda = 3\cdot10^{8}/633\cdot10^{-9} = 4.74\cdot10^{14}$ Hz
$\Delta\nu/\nu = 1700\cdot10^{6} / 4.74\cdot10^{14} = 3.6\cdot10^{-6}$
$\Delta\lambda = \lambda\,(\Delta\nu/\nu) = 633\cdot10^{-9}\cdot 3.6\cdot10^{-6} \approx 2.3\cdot10^{-12}$ m = 2.3 pm

For applications to molecular spectroscopy, the laser can be considered as a pure monochromatic source.

THE MONOCHROMATIC SOURCE HAS TO BE TUNABLE

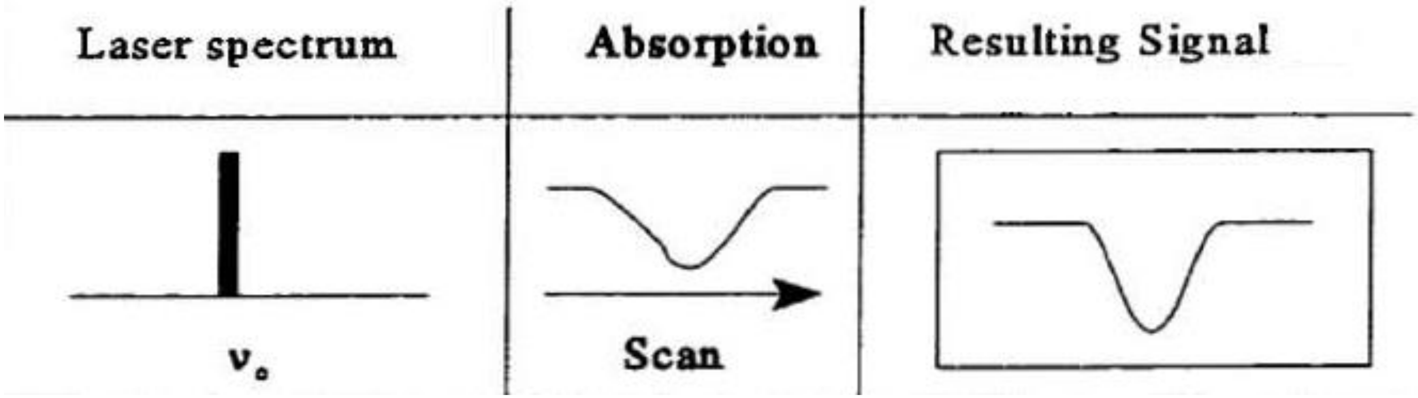
To scan the line shape, the laser wavelength has to be changed over the line bandwidth ⇒ **a single-mode tunable laser is needed**

Which single-mode tunable lasers are available ?

SEMICONDUCTOR LASERS

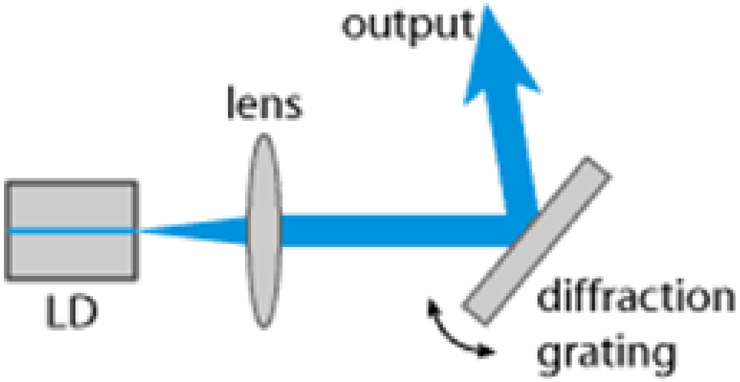
They can be realized single mode

The emission wavelength can be tuned depending on current or temperature



TUNABLE EXTERNAL CAVITY DIODE LASERS

Tunable external-cavity diode lasers use a ***diffraction grating*** as the wavelength-selective element in the external resonator.
The Littrow configuration contains a collimating lens and a diffraction grating as the end mirror. The first-order diffracted beam provides optical feedback to the laser diode chip. The emission wavelength can be tuned by rotating the diffraction grating.



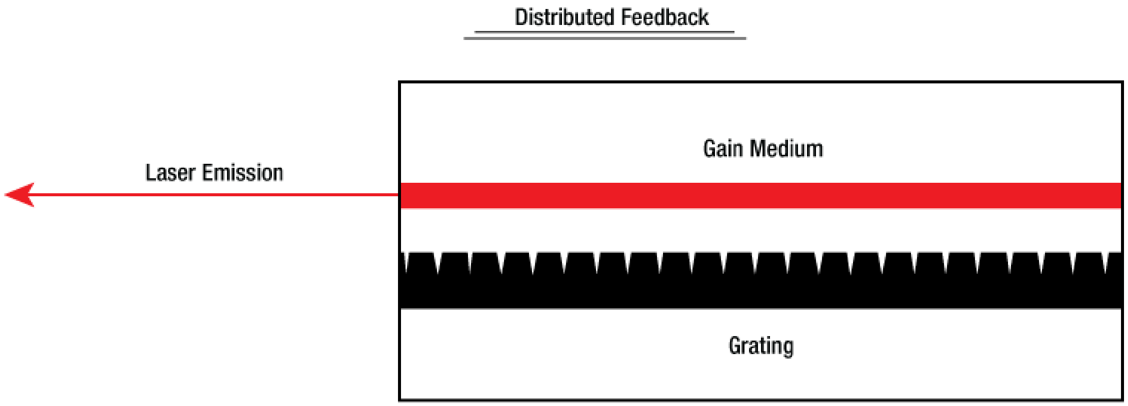
Littrow configuration

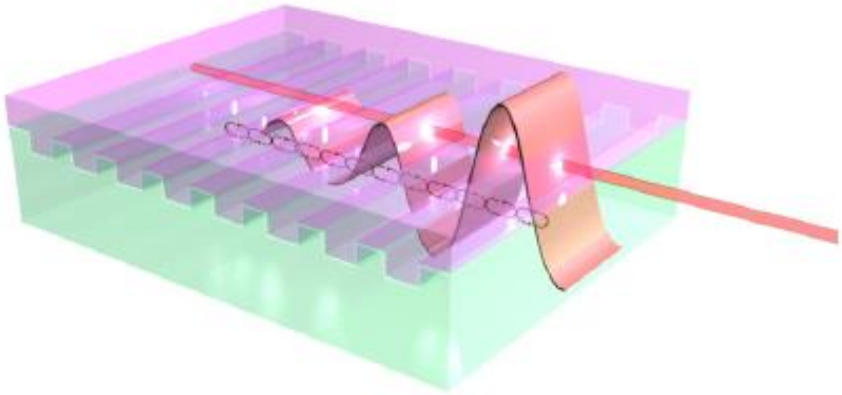
DISTRIBUTED FEEDBACK LASERS (DFB LASERS)

The resonator consists of a periodic structure (a grating), which acts as a distributed reflector in the wavelength range of laser action, and contains a gain medium.

Maximum emitted power is in the range 30-50 mW.

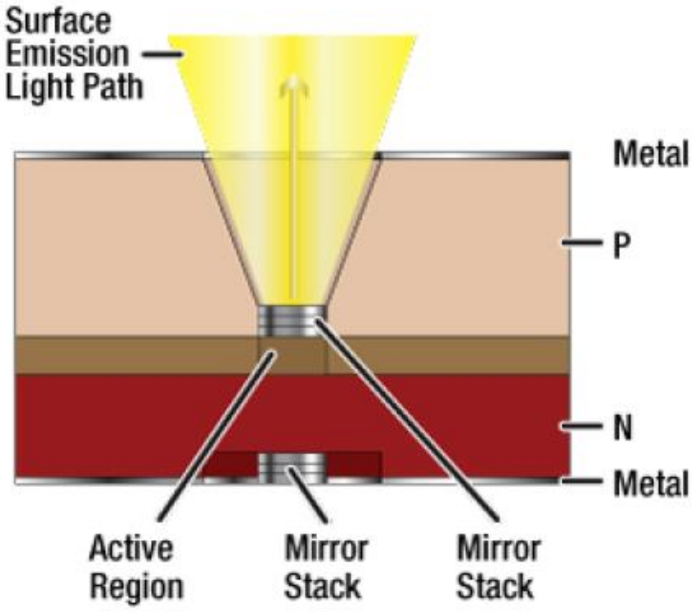
Linewidth is few to several MHz.

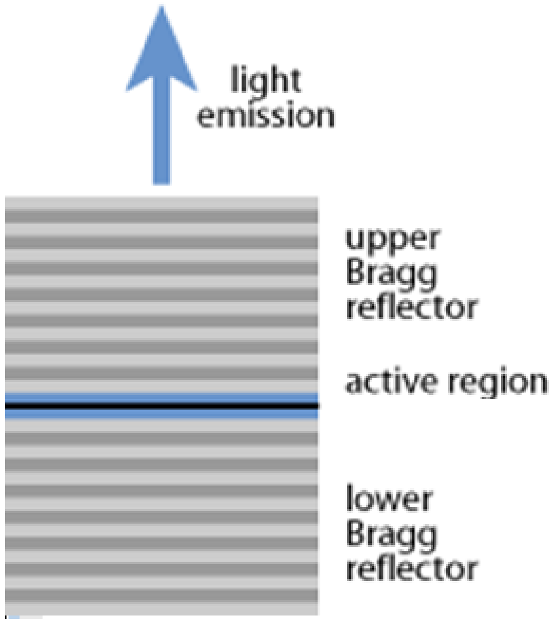




VERTICAL CAVITY SURFACE EMITTING LASERS (VCSEL)

VCSELs are are laser diodes with a monolithic laser resonator, where the emitted light leaves the device in a direction perpendicular to the chip surface. The resonator is realized with two semiconductor Bragg mirrors (alternating sequence of layers of two different optical materials). Between those, there is the active region having a total thickness of few micrometers.
Maximum emitted power is in the range 0.5–5 mW.
Linewidth is 10 to 80 MHz.





HOW MUCH CAN WE SCAN ?

Example: VCSEL laser

Current $2 \div 10$ mA

Temperature $15 \div 35$ °C

Output power is changing with the current

$\Delta P/\Delta I = 0.05 \div 0.5$ mW/mA

Tunability in current $\Delta\lambda/\Delta I = 0.2 \div 0.9$ nm/mA

Tunability in temperature $\Delta\lambda/\Delta T = 0.08 \div 0.2$ nm/°C

Wavelength tunability

Current $\Delta\lambda = (\Delta\lambda/\Delta I)\cdot\Delta I = 0.5 \cdot 10 = 5$ nm

Temperature $\Delta\lambda = (\Delta\lambda/\Delta T)\cdot\Delta T = 0.15 \cdot 20 = 3$ nm

Example: DFB laser

Current range	70 mA typical range, 100÷150 mA max
Temperature	10 ÷ 50 °C

Output power is changing with the current

$\Delta P/\Delta I = 0.05 \div 0.5$ mW/mA

Tunability in current	$\Delta\lambda/\Delta I = 0.003$ nm/mA
Tunability in temperature	$\Delta\lambda/\Delta T = 0.06$ nm/°C

Wavelength tunability

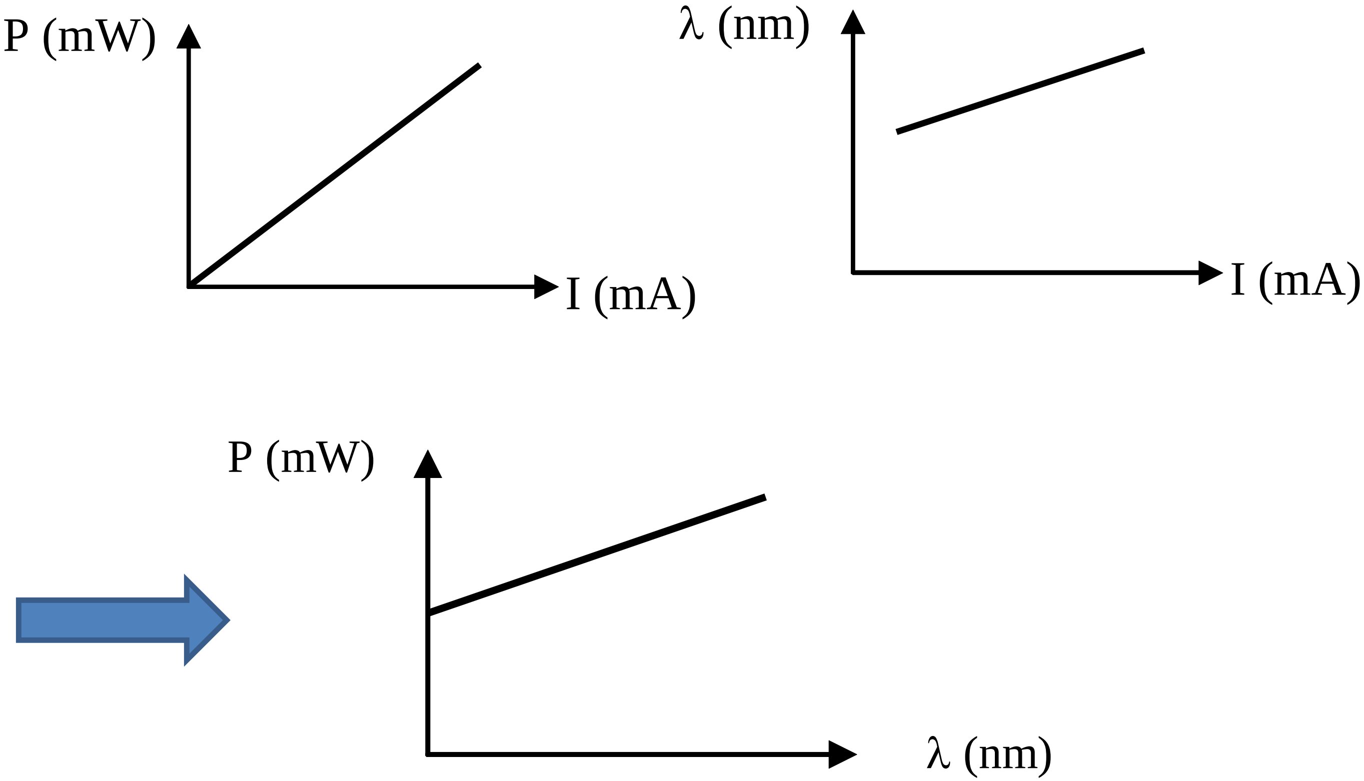
Current	$\Delta\lambda = (\Delta\lambda/\Delta I)\cdot\Delta I = 0.003 \cdot 70 = 0.2$ nm
Temperature	$\Delta\lambda = (\Delta\lambda/\Delta T)\cdot\Delta T = 0.06 \cdot 40 = 2.4$ nm

HOW IS WAVELENGTH SCANNING PERFORMED ?

Scanning in temperature is slow, for thermal inertia

Scanning in current is normally used, since it is very fast

When the wavelength is scanned, the current is varied ⇒ output power is changing

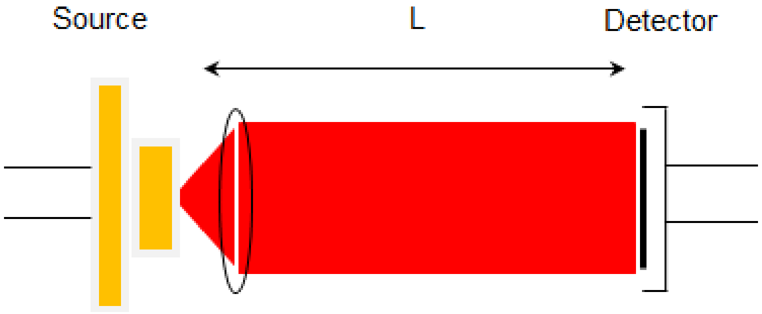


OPTICAL ABSORPTION SPECTROSCOPY: TUNABLE DIODE LASER SPECTROSCOPY (TDLAS)

A tunable semiconductor laser is used as the light source. The light is tuned in wavelength to scan the profile of one (or more) absorption line of the gas to be analyzed.
The line profile gives information on concentration, pressure and temperature.

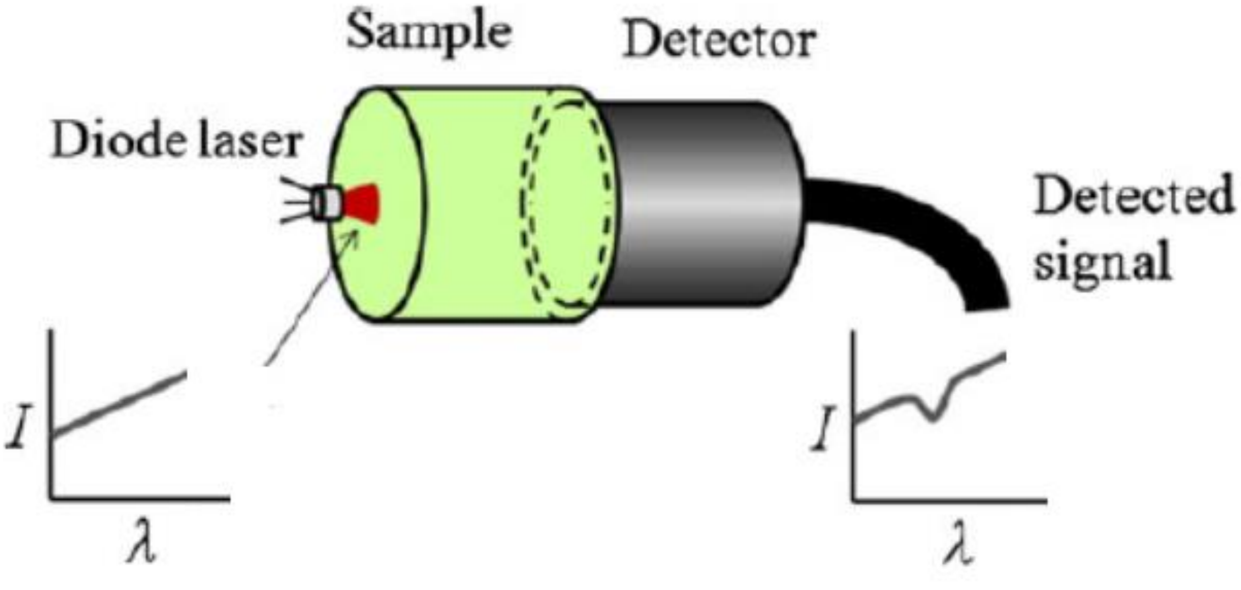
A basic TDLAS setup consists of:

1) tunable diode laser light source
2) transmitting optics
3) optically absorbing medium
4) receiving optics
5) detector



DIRECT ABSORPTION SPECTROSCOPY

The laser is tuned to scan a line profile of the gas to be measured.
The laser temperature is fixed.
A triangular driving wave (in current) is used to tune the wavelength around one of the absorption lines. The photodiode measures an increasing power, since when the wavelength is tuned also the power is changed.



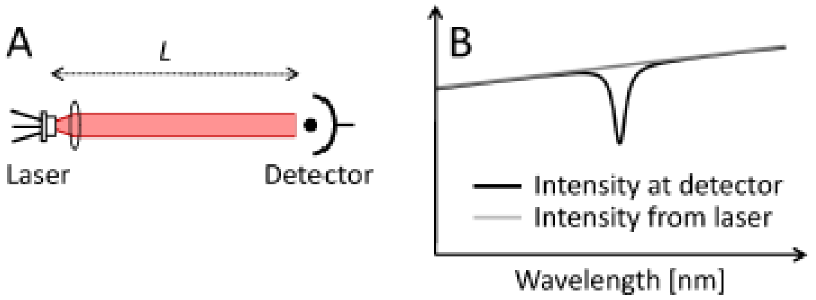
Nomenclature: I – Intensity (a.u.), λ – Wavelength (nm)

SIGNAL PROCESSING

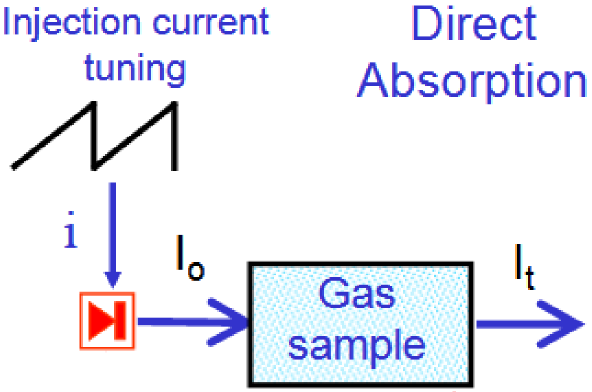
The driving signal has saw-tooth profile.

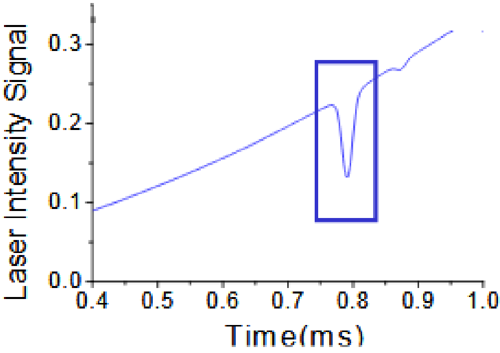
Several measurements are taken to do an average and increase the signal-to-noise ratio.

The laser background has to be subtracted (obtained by a “best fit” procedure).

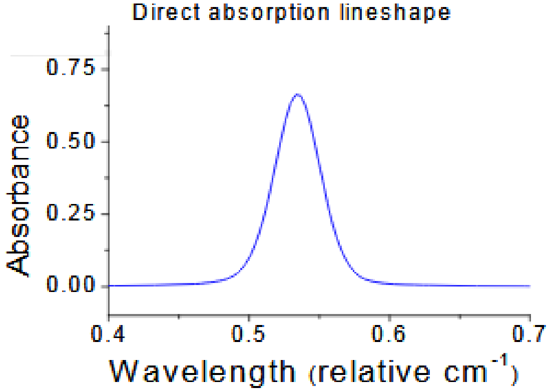


(A) Optical channel. (B) Direct absorption signal.





Baseline fit for I_o



Direct absorption spectroscopy is applied when the absorption lines are quite strong (e.g., CO_2, H_2O, CH_4)

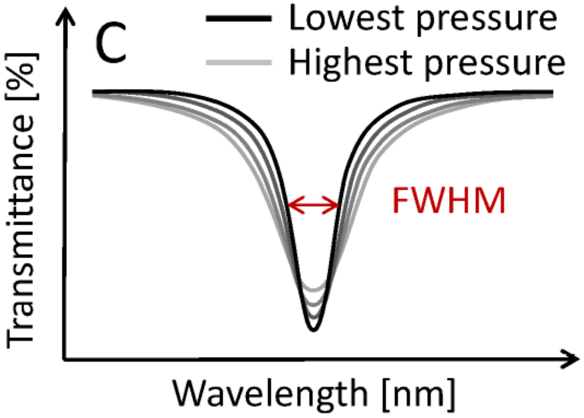
Example: CO2 is measured at 2 um

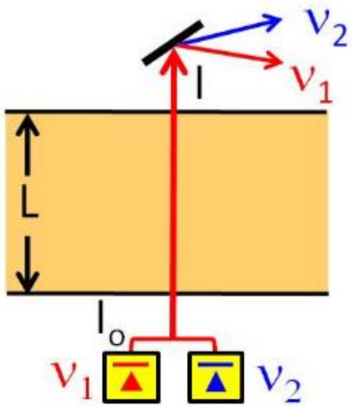
WHAT IS MEASURED

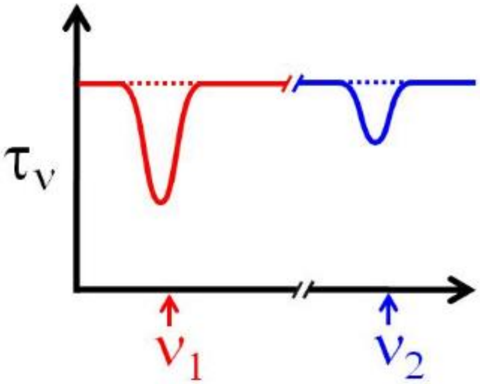
- ***Gas concentration***: total absorption of the line (integral)

- ***Gas pressure***: width of the line

- ***Gas temperature***: Temperature is not measured by looking at the line width, since at ambient temperature pressure is the dominating factor.
  Temperature is measured by acquiring the absorption on two lines at two wavelengths and measuring the relative signal between the two. The ratio is proportional to the temperature.

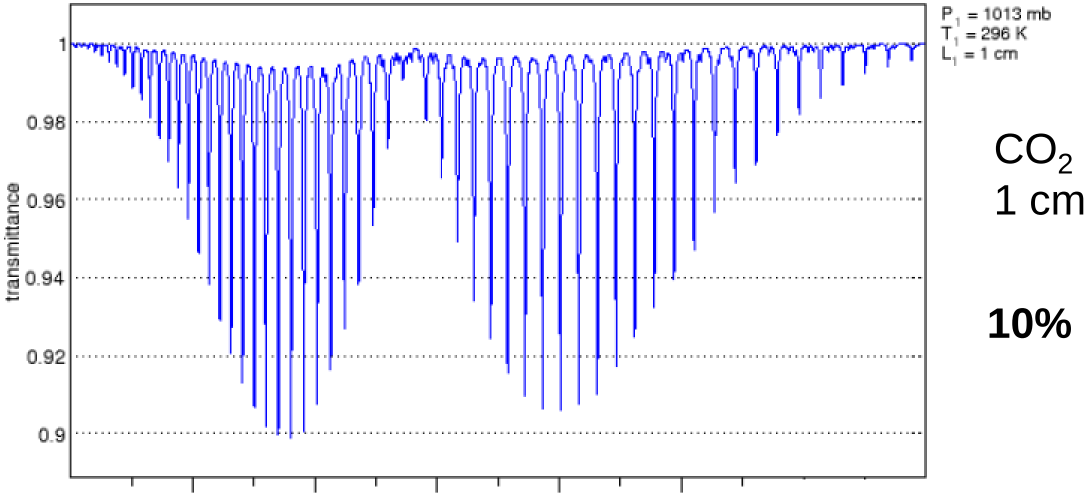






WHAT FOR WEAK ABSORPTION LINES ?

Direct absorption spectroscopy is applied when the absorption lines are quite strong (e.g., CO_2, H_2O, CH_4).
For weak absorption, the signal obtained by the direct spectroscopy is very noisy.

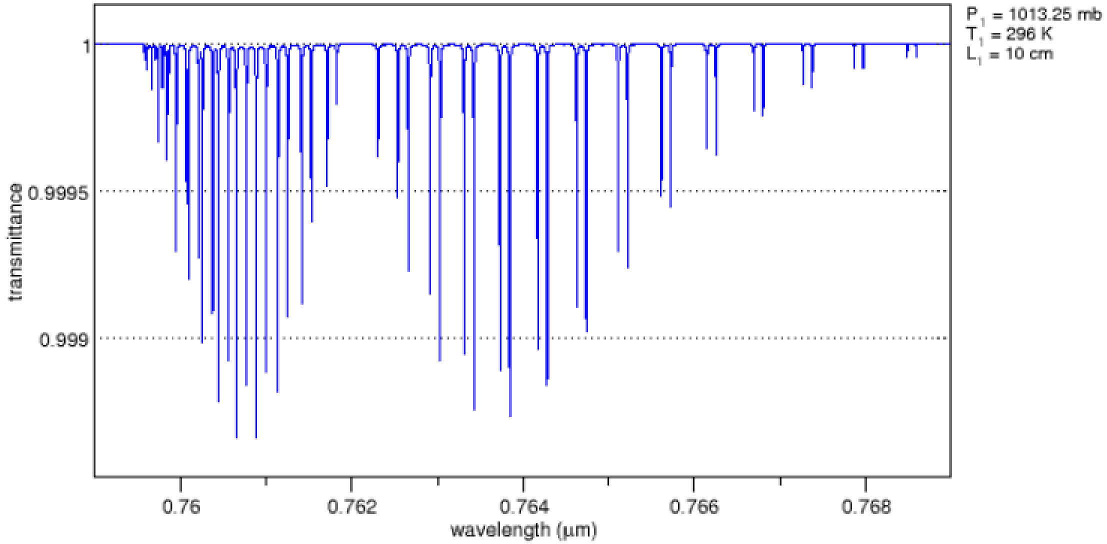


CO_2 absorption, 100% concentration,
1 cm path length

10%

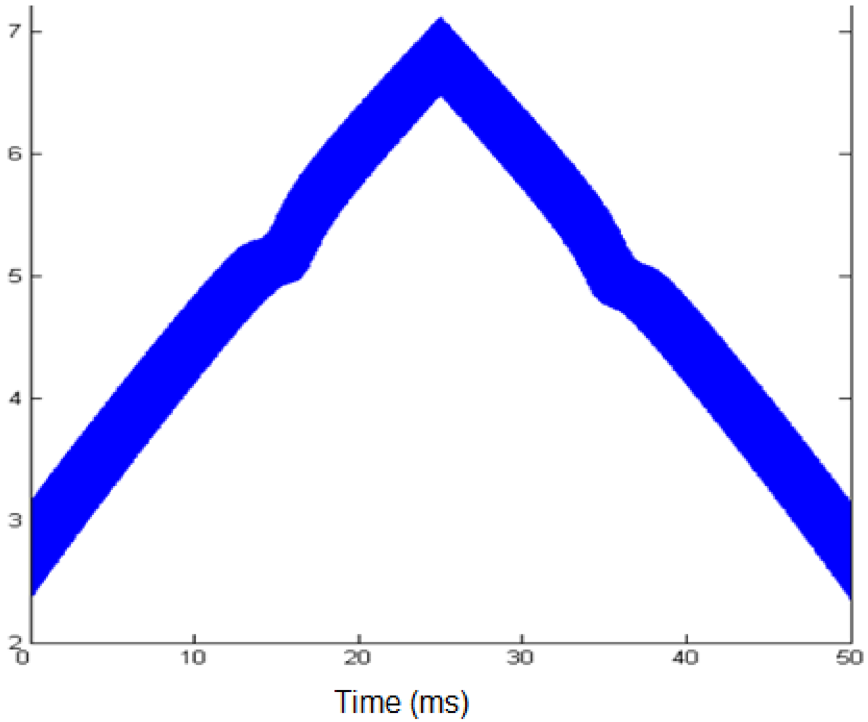
O_2 absorption, 100% concentration,
1 cm path length

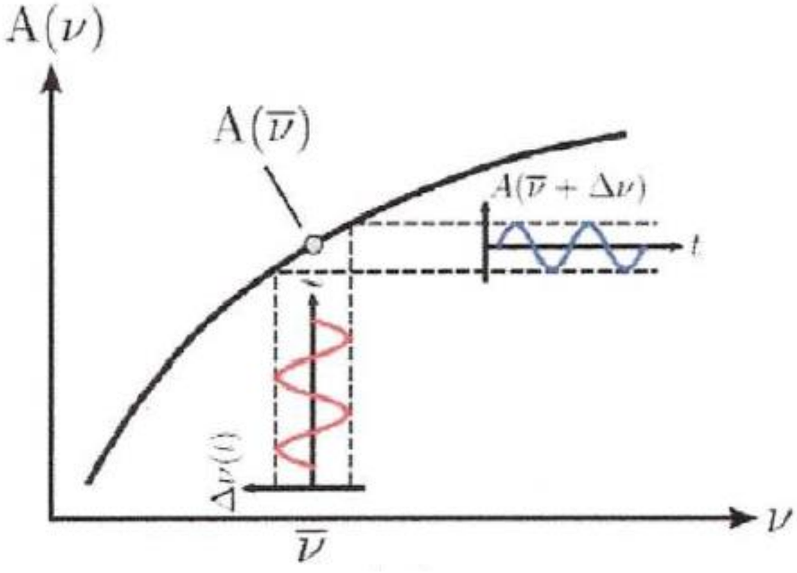
10^{-4}



WAVELENGTH MODULATION SPECTROSCOPY (WMS)

In WMS the laser is modulated with a triangular wave with frequency ω_{scan} and by an overlapping sinusoidal wave with frequency $\omega_{mod} >> \omega_{scan}$

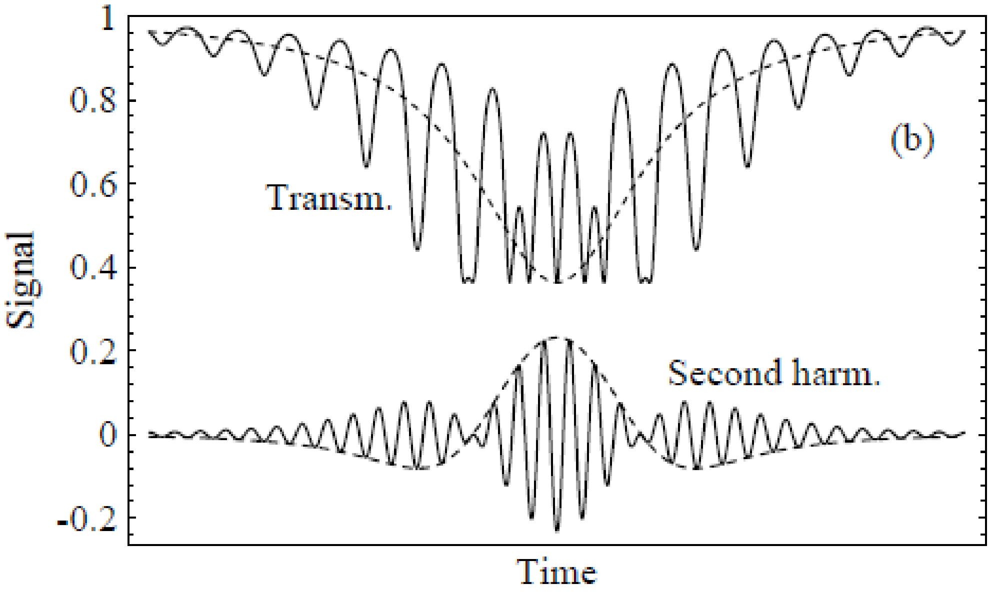




An arbitrary non-linear signal $A(\nu)$ [dark] is modulated at the frequency $\underline{\nu}$ with a signal $a \cdot \cos(\omega_{mod} t)$ [red]. Due to non linearity of $A(\nu)$, the resulting signal $A(\underline{\nu} + \Delta\nu)$ [blue] has components to ω_{mod} and its harmonics $2\omega_{mod}$, $3\omega_{mod}$, …

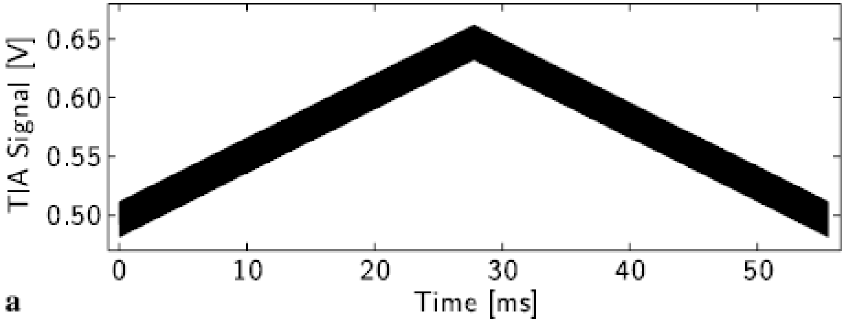
SIGNAL PROCESSING

Low-frequency scan (triangular wave)	100–1000 Hz
High-frequency modulation	100–200 kHz

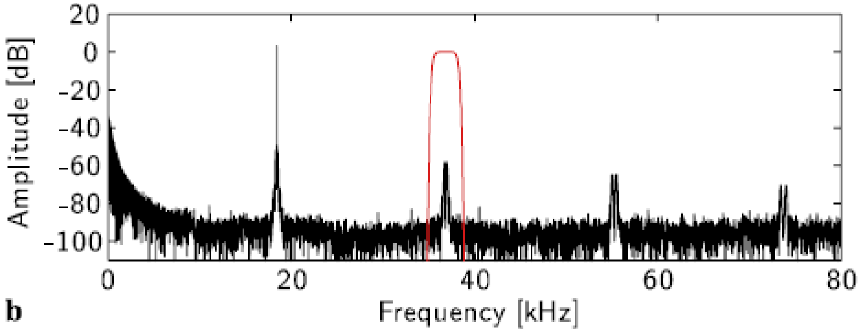


The envelope of the second harmonic signal is used for gas detection

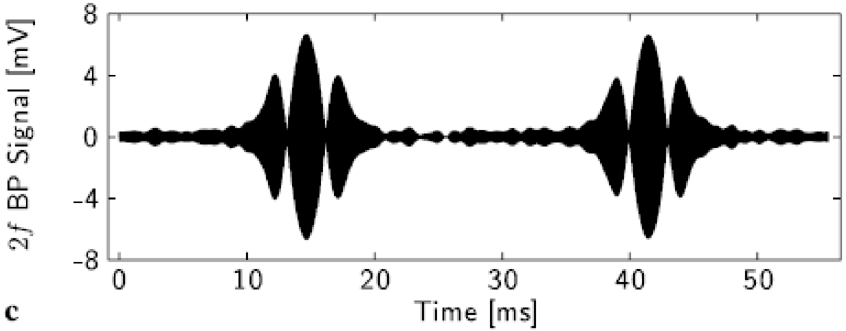
All is done digitally



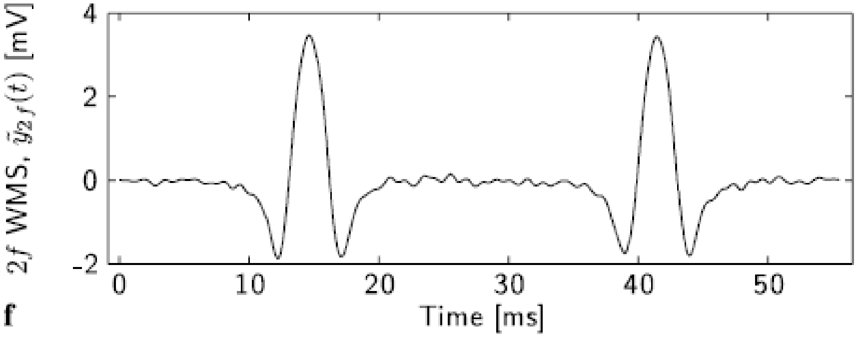
- Acquired signal



- Fourier transform on acquired signal
- Filtering of the second harmonic



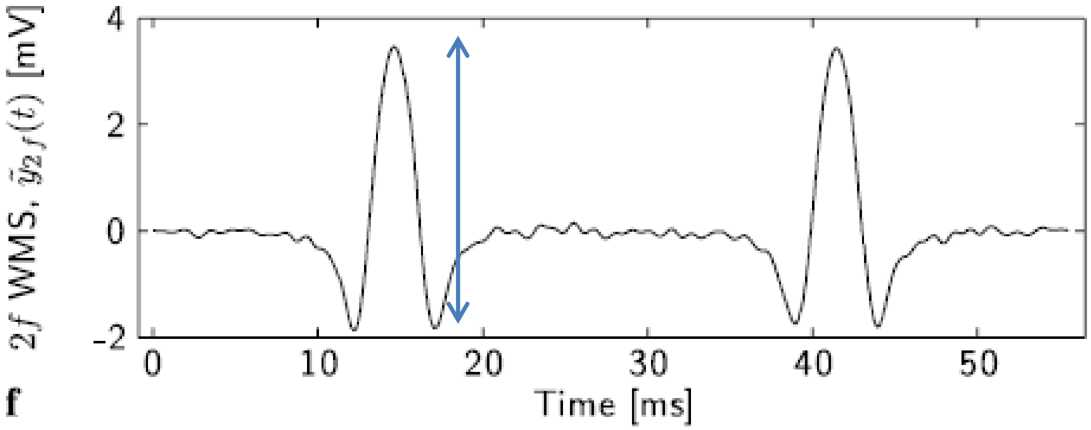
- Band-passed filtered signal on the time domain



- Signal envelope

CALCULATION OF THE CONCENTRATION

The concentration is proportional to the peak-to-peak signal

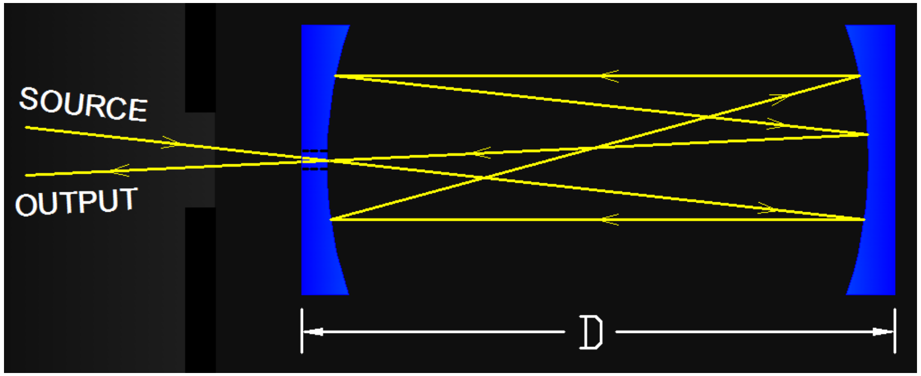


Since most of the noise is filtered out, the WMS is much more sensitive than the direct absorption.

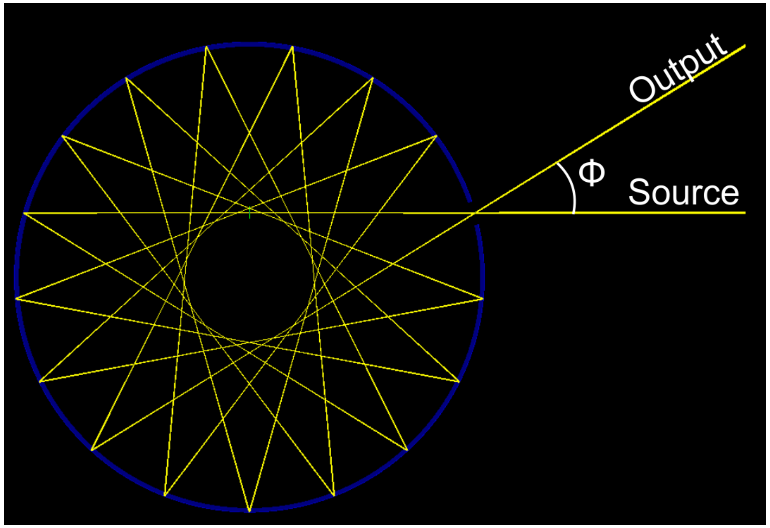
Minimum detectable absorption is of the order of 10^{-5}

HOW TO INCREASE THE OPTICAL PATH

Multi-pass cells: improve detection sensitivity by increasing the path length of light that travels through a small and constant gas volume



Herriott cell
Two opposing spherical mirrors, hole machined into one of the mirrors to allow the beams to enter and exit the cavity



Circular multipass cell
Circular arrangement of spherical or toroidal mirrors

WHICH GASES CAN BE DETECTED IN THE NEAR IR

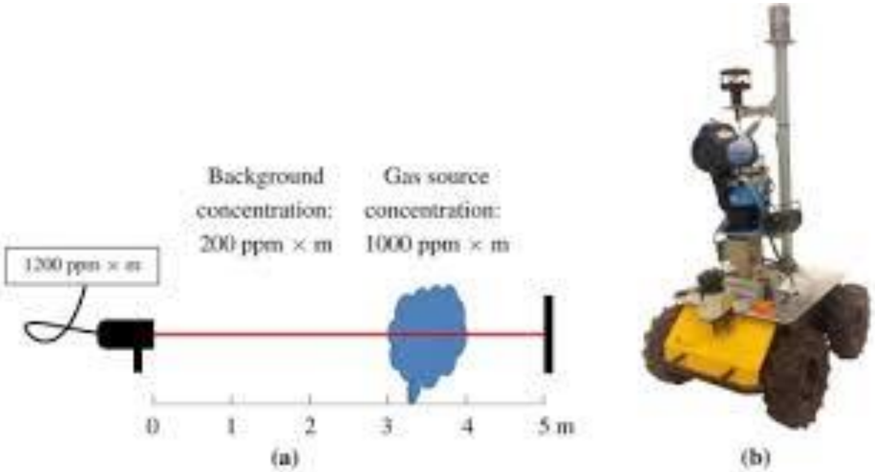
Oxygen, O2	760 nm
Hydrogen fluoride, HF	1278 nm
Water vapour, H_2O	1392 nm, 1854 nm
Ammonia, NH_3	1512 nm
Carbon monoxide, CO	1560 nm, 2350 nm
Hydrogen sulfide, H_2S	1580 nm
Methane, CH_4	1654 nm, 1689 nm
Hydrocloridric acid, HCl	1742 nm
Carbon dioxide, CO_2	2004-2012 nm

……….

Industrial application of laser spectroscopy
ENVIRONMENTAL MONITORING

TDLAS is applied to ambient monitoring and pollution monitoring for different gases (SO_2, NO, NO_2, ammonia,…..).

Applications include measuring the pollution in atmosphere as well as monitoring industrial processes or leak detection

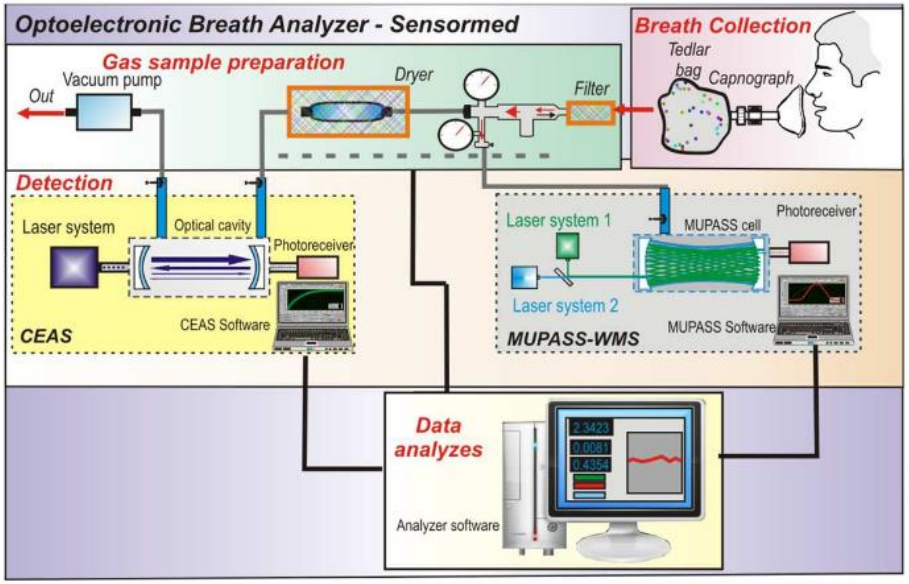


Industrial application of laser spectroscopy
PHARMACEUTICAL APPLICATIONS

- In-line detection of oxygen and water vapour inside pharmaceutical vials
- This measurement is useful to check closure tightness as well as drying process

BREATH ANALYSIS

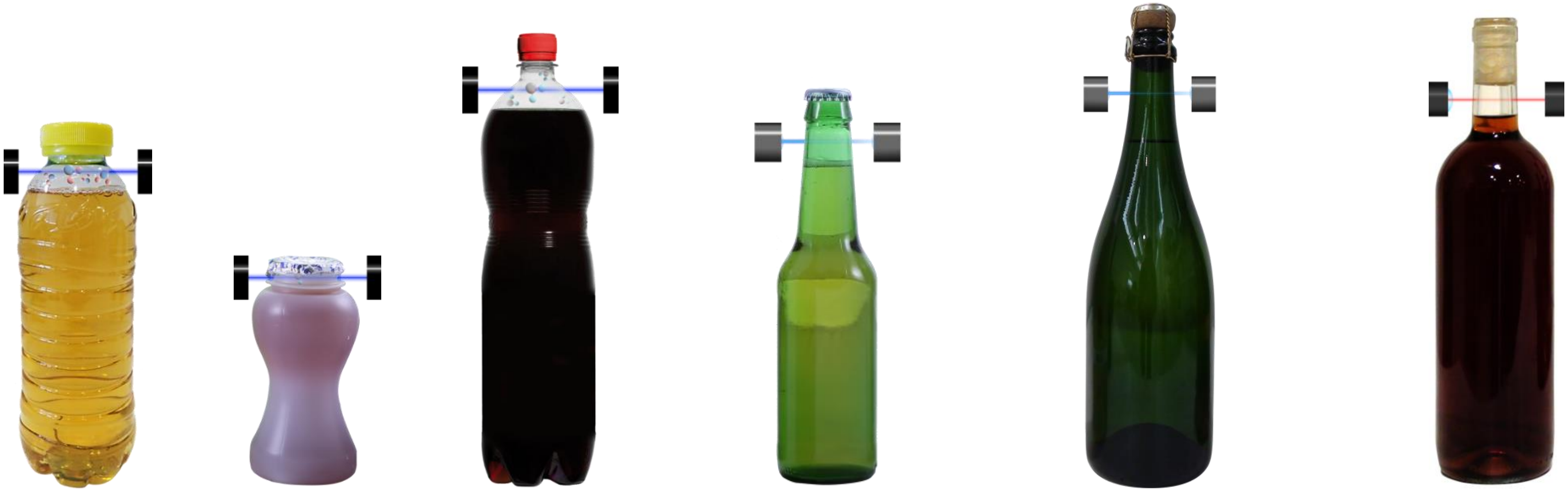
Medical diagnostics by breath trace gas analysis (acetaldehyde, ammonia, carbon dioxide, carbon monoxide, carbonyl sulfide, ethane)



Industrial application of laser spectroscopy
BOTTLING INDUSTRY

- Both oxygen and carbon dioxide sensors have been developed for lab testing applications
- Carbon dioxide content and pressure measurement are needed in the sparkling wine industry, while oxygen concentration data is interesting for aging still wines; both are useful in the soft drink industry.

Applications to different liquid products (such as wine, beer, soft drinks) in containers with different materials (such as glass or plastic bottles) and transmission properties (such as almost transparent bottles or dark bottles)



Industrial application of laser spectroscopy
BOTTLING INDUSTRY

TDLAS is applied to in-line measurement of gas pressure in bottling lines.
It measures the pressure of CO_2 or H_2O in partially transparent close containers (e.g. bottles). The measurements are done in real time on 100% of the samples.
The measurement time is 10 ms per sample, the processing speed is up to 1200 bottles/min.

Food packaging in modified atmosphere

Food packed under controlled atmosphere represents a large market that is growing in number and value: meat, fish, vegetebles, bread and bakery products, cheese and dairy products, each requiring different gases and composition for optimal conservation.

MODIFIED ATMOSPHERE PACKAGING (MAP)

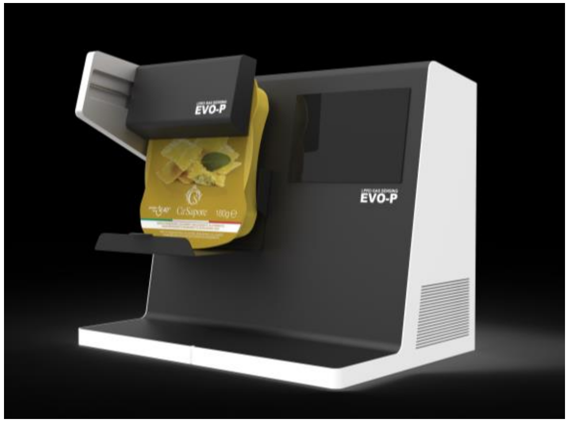
- ATMOSPHERE WITHIN THE FOOD PACKAGE CONTAINS AN INERT GAS (typically a mixture of N_2 and CO_2)

- OXYGEN CONTENT KEPT UNDER A CERTAIN THRESHOLD

FOOD	AIR PACKAGED LIFETIME DAYS	MAP LIFETIME DAYS
BEEF	4	12
PORK	4	9
POULTRY	6	18
BRED	7	21
COFFEE	1	350

Food products

- Different stand-alone devices using TDLAS have been designed to analyze modified atmosphere packages, in order to address many kinds of samples.
- Oxygen and carbon dioxide can be sensed.
- The instruments can be operated in transmission or backreflection mode.



LPRO, Italy

Gasporox, Sweden

More information on:
http://www.safetypack-project.eu/

IN-LINE ANALYSIS ON PACKAGES IN MODIFIED ATMOSPHERE

SHELF LIFE

☑ identify sealing defect or micro-leakages within the package

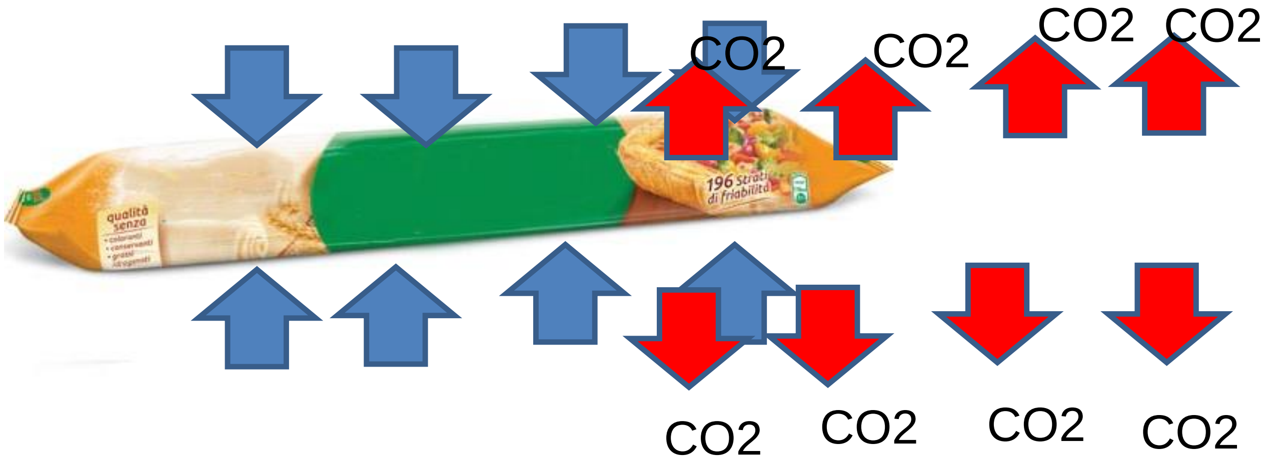
FOOD SAFETY

☑ prevent the presence on the market of deteriorated products

BRAND PROTECTION

☑ prevent dispute on the product

IN-LINE MEASUREMENT: how this can be done ?



Apply a light pressure on the sample to facilitate the possible leakage from micro-holes. In presence of any leakage, carbon dioxide (typically 20-30% inside the package) is released outside, where it can be measured over the ambient concentration (0.4% typical) through absorption spectroscopy.

CONCLUSIONS

Laser spectroscopy is a very powerful method for the non-invasive analysis of gases with several industrial and scientific applications.

“A splendid light has dawned on me”

Albert Einstein