Chapter 4

OPTICAL-BASED SENSORS FOR ENVIRONMENTAL MONITORING

Reference textbooks

- W. Demtroder – “*Laser spectroscopy, Vol. 1, Basic principles*”, Springer (2008)
- J. Hodgkinson, R.P. Tatam – *“Optical gas sensing: a review”*, Meas. Sci. Technol. 24 (2013) 012004

4.1 ABSORPTION AND EMISSION OF LIGHT

Emission and absorption spectra

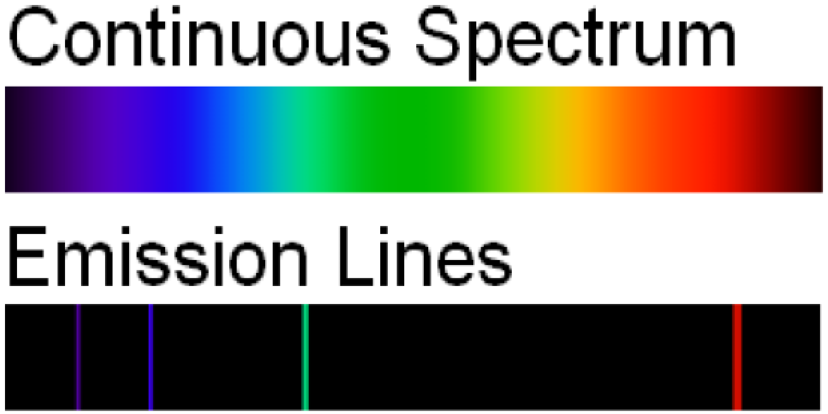
The spectral distribution of radiant flux (the energy emitted per unit of time) from a source is called as the **emission spectrum**.

An emission spectrum can have a **continuous or discrete** spectral distribution**.**

An example of **continuous** spectral distribution is the **blackbody** emission spectrum.

In **discrete spectral distributions**, the radiant flux of a source has **distinct maxima at certain frequency values ν_{ik}**, and are generated by transitions of atoms and molecules between two bound states of energy E_k and E_i ($E_k > E_i$) by the relation:

$$h\nu_{ik} = E_k - E_i \tag{4.1}$$



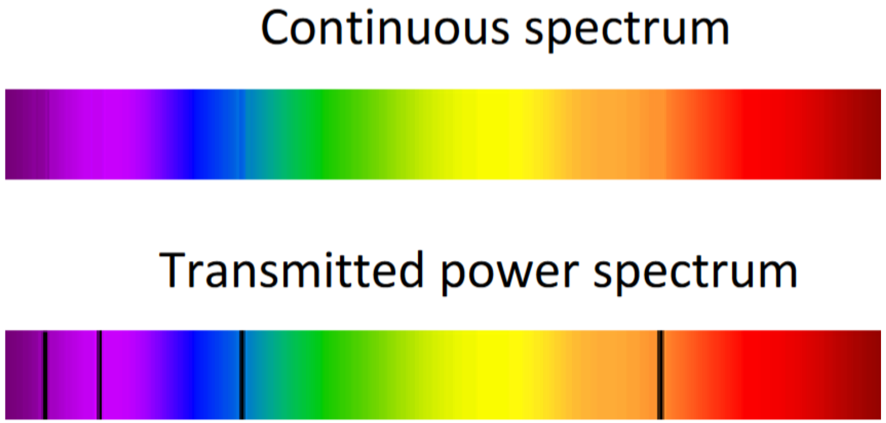
4.1 ABSORPTION AND EMISSION OF LIGHT

Emission and absorption spectra

If a continuous spectrum radiation passes through a gas sample, **molecules in the lower energy state E_i can absorb radiant power at eigenfrequencies**:

$$\nu_{ik} = (E_k - E_i)/h \tag{4.2}$$

which will cause spectral "**holes**“ on the distribution of the transmitted power.



Continuous spectrum

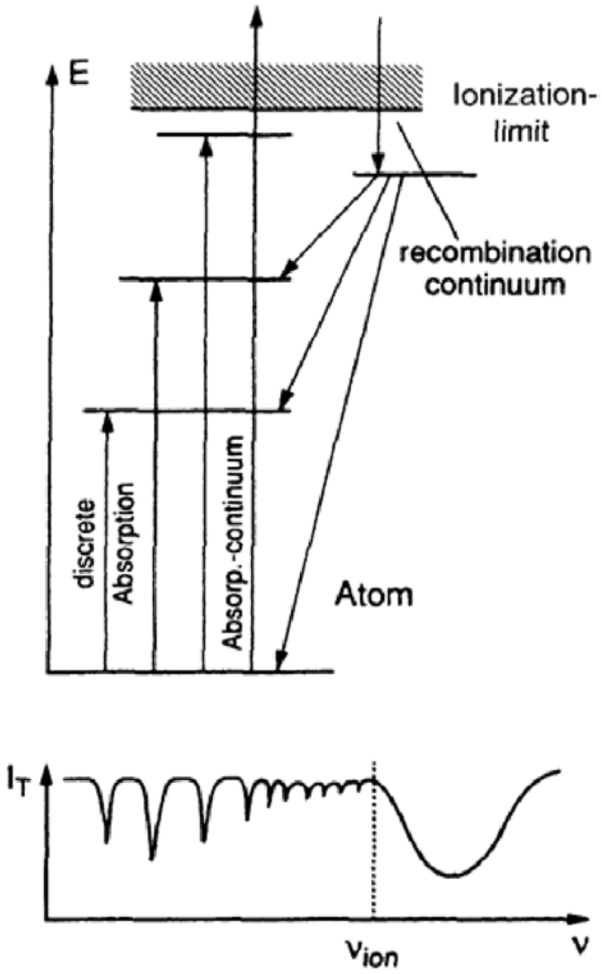
Transmitted power spectrum

4.1 ABSORPTION AND EMISSION OF LIGHT

Emission and absorption spectra

The difference between the incident spectral distribution on the sample and the transmitted one is called as the absorption spectrum of the gas sample.

- The absorbed energy will excite the molecules to the state E_k.
- If these states are energy levels, the resulting spectrum will be a discrete absorption spectrum.
- If E_k is above the ionization energy, the absorption spectrum will be continuous.



4.1 ABSORPTION AND EMISSION OF LIGHT

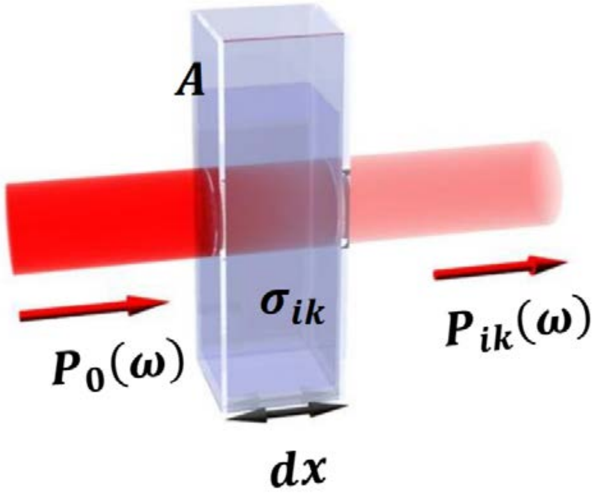
Emission and absorption spectra

Let’s suppose a radiant flux incident on a sample, which absorbs part of the radiation.

The fraction of power absorbed within the spectral interval $d\omega$ at angular frequency ω as a result of the transition $|k\rangle \rightarrow |i\rangle$ within the volume $\Delta V = A \cdot dx$ can be expressed as:

$$dP_{ki}(\omega)d\omega = P_0(\omega)\left(N_k - \frac{g_k}{g_i} N_i\right)\sigma_{ki}\, dxd\omega = P_0(\omega)\alpha_{ik}dxd\omega \qquad (4.4)$$

Where, $P_0(\omega)$ is the incident power, σ_{ki} the absorption cross-section, $N_k - \frac{g_k}{g_i} N_i$ is the difference of the population density of absorbing molecules in the two energy levels (g_i and g_k are the number of degenerate states for energy levels E_i and E_k, respectively). **α_{ik} is the absorption coefficient for the selected energetic transition.**



4.1 ABSORPTION AND EMISSION OF LIGHT

Emission and absorption spectra

At thermal equilibrium, the population of the levels is given by the Boltzmann distribution, namely:

$$N_i = N\frac{g_i}{Z}e^{-\frac{E_i}{KT}}$$

$$N_k = N\frac{g_k}{Z}e^{-\frac{E_k}{KT}} \tag{4.5}$$

where N is the total density of molecules and $Z = \sum_q e^{-\frac{qh\nu}{KT}}$ is the partition function defined as a summation over all of the allowed states. Integrating Eq (4.4) within the overall frequency range emitted by the source:

$$P_{ki} = \frac{N}{Z}g_k\left(e^{-\frac{E_k}{KT}} - e^{-\frac{E_i}{KT}}\right)dx \int P_0(\omega)\sigma_{ki}\, d\omega \tag{4.6}$$

4.1 ABSORPTION AND EMISSION OF LIGHT

Emission and absorption spectra

In the case of a monochromatic source, i.e., a laser, results: $P_0(\omega) = P_0\delta(\omega - \omega_0)$. Thus, the transmitted power becomes:

$$P_{ki} = \frac{N}{Z} g_k \left(e^{-\frac{E_k}{KT}} - e^{-\frac{E_i}{KT}}\right) P_0(\omega)\sigma_{ki}dx \tag{4.7}$$

From this formula, two main conclusions can be drawn:

- Absorption lines can be measured only if the absorbed power is high enough, or if the density of molecules N or the optical pathlength dx are sufficiently large.
- The first Boltzmann factor in the round bracket must be larger than the second one. This means that $\boldsymbol{E}_k < \boldsymbol{KT}$ but $\boldsymbol{E}_i > \boldsymbol{KT}$.

Therefore, the gas absorption lines at thermal equilibrium are intense only for transitions starting from energy levels E_k that are thermally populated towards poorly populated thermally states E_i

4.1 ABSORPTION AND EMISSION OF LIGHT

Emission and absorption spectra

However, according to Eq. (4.4) **the intensity of the spectral lines depends not only on the population density of the molecules in the levels involved but also on the probability of transition of the corresponding molecular transitions** $(\boldsymbol{\sigma_{ik}})$**.**

If these probabilities are known, population density can be calculated by measuring the intensities of absorption lines.

- The measurement of the intensity of the absorption or emission lines allows **the estimation of the concentration of the elements in the samples** (useful also in stellar atmospheres or interstellar space)
- **Comparing the intensities of different lines** of the same gaseous species (for example, transitions $E_i \rightarrow E_k$ and $E_j \rightarrow E_k$, that is, from two different higher levels E_i and E_j to the same lower level E_k) **the temperature of the light source can be determined** starting from population densities N_i and N_j of levels E_i and E_j, at the thermal equilibrium.

4.1 ABSORPTION AND EMISSION OF LIGHT

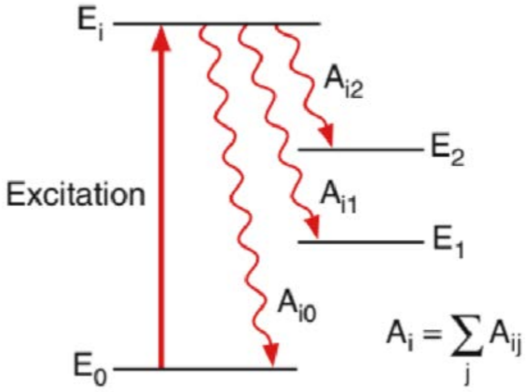
Transition probabilities

Let us consider a simple **two-level system**.

The probability of transition $\wp_{ik}$ that an excited molecule in the level E_i make a transition to the lower level E_k by spontaneous emission of a quantum of energy $h\nu_{ik} = E_i - E_k$ is determined by the **Einstein coefficient of spontaneous emission A_{ik}** by the relation:

$$\frac{d\wp_{ik}}{dt} = A_{ik} \tag{4.8}$$

When there are several possible transitions from E_i to different energy levels lower E_k, the probability of transition is given by $A_i = \sum_k A_{ik}$



4.1 ABSORPTION AND EMISSION OF LIGHT

Transition probabilities

The decrease dN_i of population density N_i in the time interval dt will be:

$$dN_i = -A_i N_i dt \tag{4.9}$$

Resulting in:

$$N_i(t) = N_0 e^{-A_i t} \tag{4.10}$$

where N_0 is the population density at t = 0.

Therefore, the **population density decreases exponentially**. After a time $\boldsymbol{\tau_i}$ **= 1/**$\boldsymbol{A_i}$, the population density N_i has decreased by a value of 1/e from its initial value at t = 0.

Thus, τ_i can be defined as the **average lifetime for decay by spontaneous emission of the level** $\boldsymbol{E_i}$**.**

4.1 ABSORPTION AND EMISSION OF LIGHT

Transition probabilities

Spontaneous emission is not the only spontaneous decay mechanism for the energy level E_i, as the energy level can be depopulated by means of collision-induced, non radiative transitions.

The probability $\wp_{ik}^{coll}$ can be written as:

$$\frac{d\wp_{ik}^{coll}}{dt} = \overline{v_{AB}}\, N_B \sigma_{ik}^{coll} \tag{4.11}$$

being N_B **the density of molecules B** with which it can collide, $\overline{v_{AB}}$ **the average relative speed** between molecules A and B, and σ_{ik}^{coll} the cross-section for inelastic collisions inducing the transition $E_i \rightarrow E_k$.

Assuming a Maxwell-Boltzmann distribution for speeds of the molecules at the thermal equilibrium, at temperature T in a volume V, the average relative speed results:

$$\overline{v_{AB}} = \sqrt{\frac{8KT}{\mu\pi}} \tag{4.12}$$

With μ the effective mass of the system composed by molecules A and B.

4.1 ABSORPTION AND EMISSION OF LIGHT

Transition probabilities

The density of molecules N_B can be expressed as a function of pressure P and temperature T, assuming an ideal gas law:

$$N_B = \frac{N}{V} = \frac{P}{KT} \tag{4.13}$$

Therefore, the effective average lifetime of the excited state can be expressed as a function of measurable parameters:

$$\frac{1}{\tau_i^{eff}} = \frac{1}{\tau_i^{spont}} + \sigma_{ik}^{coll} \sqrt{\frac{8KT}{\mu\pi}}\, P = \frac{1}{\tau_i^{spont}} + \frac{1}{\tau_i^{coll}} \tag{4.14}$$

However, the energy level can be depopulated not only in a spontaneous way, but also in a stimulated way.

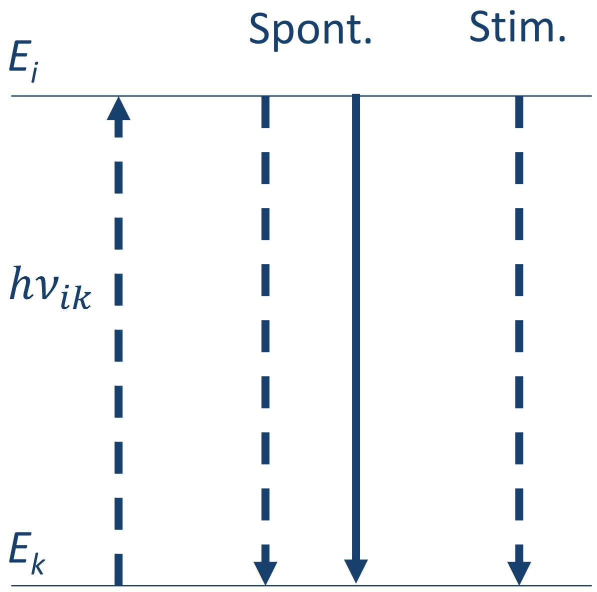
4.1 ABSORPTION AND EMISSION OF LIGHT

Transition probabilities

With an intense radiation field, the stimulated emission becomes no longer negligible, contributing to the depopulation of the level E_i through the transition $|i\rangle \rightarrow |k\rangle$ with a probability given by:

$$\frac{d\wp_{ik}^{stim}}{dt} = \rho(\nu_{ik})B_{ik} \tag{4.15}$$

being $\rho(\upsilon_{ik})$ the energy density of the radiation field at frequency υ_{ik}, **and B_{ik} the Einstein coefficient of the stimulated emission.**



In this case, the overall probability of transition determining the actual average lifetime of the level $\boldsymbol{Ei}$ will be given by the sum of the three contributions: spontaneous emission, stimulated emission and inelastic collisions.

$$\frac{1}{\tau_i^{eff}} = \sum_k \left(\frac{1}{\tau_i^{spont}} + \sigma_{ik}^{coll}\sqrt{\frac{8KT}{\mu\pi}}\,P + \rho(\nu_{ik})B_{ik} \right) \tag{4.16}$$

4.2 ROTO-VIBRATIONAL SPECTROSCOPY

Molecules and their energy levels

It is clear that **the absorption and emission processes depends on the energy levels distribution** of the target molecule. From a physical point of view, the energy of a system can be described by means of its **Hamiltonian within the Schrödinger equation: $\boldsymbol{H\psi = E\psi}$**.

The Hamiltonian H of a diatomic or polyatomic molecule is the sum of the kinetic energy T and the potential energy V, considering electrons, nuclei and their interaction.

In a molecule the kinetic energy T consists of contributions T_e and T_n from the motions of the electrons and nuclei, respectively. The potential energy comprises two terms, V_{ee} and V_{nn} due to coulombic repulsions between the electrons and between the nuclei, respectively, and a third term V_{en} due to attractive forces between the electrons and nuclei.

So, the Hamiltonian H has the form:

$$H = T + V = T_e + T_n + V_{ee} + V_{nn} + V_{en} \tag{4.17}$$

4.2 ROTO-VIBRATIONAL SPECTROSCOPY

Molecules and their energy levels

In the **Born–Oppenheimer approximation** proposed in 1927, it is assumed that vibrating nuclei move so slowly compared with electrons.

In other words, **the electrons "adjust“ instantaneously to any nuclear motion**: they are said to follow the nuclei.

For this reason, we can **factorize the total wave function $\boldsymbol{\psi}$** as:

$$\psi \ = \psi_e(q, Q)\psi_n(Q) \tag{4.19}$$

Where q represents the electron coordinates and Q the nuclei coordinates. Imposing Eq. (4.19) as solution to the Schrödinger equation, results:

$$E = E_e + E_n \tag{4.20}$$

4.2 ROTO-VIBRATIONAL SPECTROSCOPY

Molecules and their energy levels

The wave function ψ_n can be further **factorized into a vibrational part ψ_v and a rotational part ψ_r:**

$$\psi_n = \psi_v \psi_r \tag{4.21}$$

It follows that the energy of the nuclei can be expressed as:

$$E_n = E_v + E_r \tag{4.22}$$

In summary, the wave function of a molecule can be factorized as:

$$\psi = \psi_e \psi_v \psi_r \tag{4.23}$$

and its energy eigenvalues as:

$$E = E_e + E_v + E_r \tag{4.24}$$

Namely, we can treat electronic, vibrational and rotational spectroscopy separately.

4.2 ROTO-VIBRATIONAL SPECTROSCOPY

Rotational spectroscopy: the rigid rotor

Optical-based detection techniques exploit the rotational and vibrational energy to identify and quantify target concentrations.

Molecules in gas phase are characterized by several configurations, depending on the number and the type of atoms composing the molecule itself.

A useful approximate model for the end-over-end rotation of a molecule is that of the rigid rotor in which the bond joining the nuclei is regarded as a rigid, weightless rod.

To study the rotational spectra of molecules, it is useful to classify them according to the main **moments of inertia $\boldsymbol{I}$**.

$$I = \sum_i m_i r_i^2 \tag{4.25}$$

4.2 ROTO-VIBRATIONAL SPECTROSCOPY

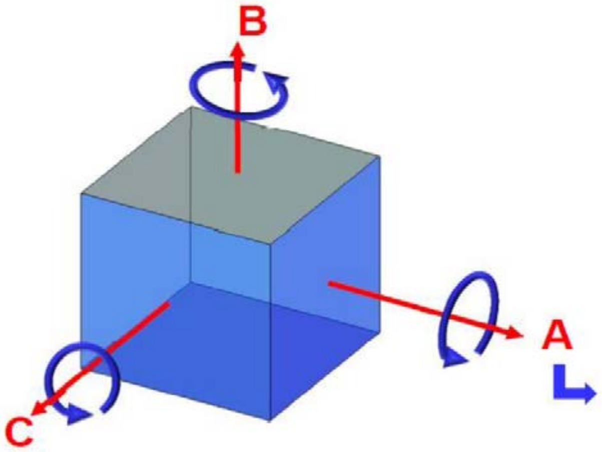
Rotational spectroscopy: the rigid rotor

In a rigid rotor can be always found one axis, called the $c - axis$, **about which the moment of inertia has its maximum value**, and another axis, labeled the $a - axis$, **about which I has its minimum value**. It can be shown that the two must be mutually perpendicular.

These two axes, together with another axis that is perpendicular to both ($b - axis$), constitute the principal axes of inertia referred to the principal moments of inertia I_a, I_b and I_c.

Thus, according to convention, the principal axes are ordered as $I_c \geq I_b \geq I_a$.

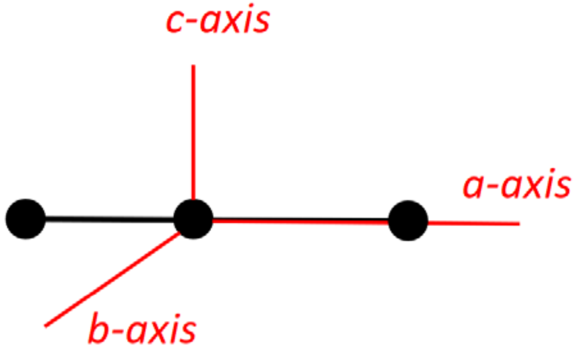
Depending on the relative size of the inertia moments, I_a, I_b and I_c, rotors can de divided into four classes: **linear rotors, symmetric tops, spherical tops and asymmetric rotors**.



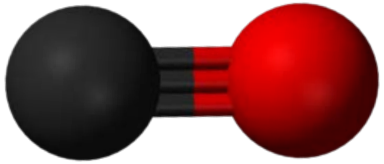
4.2 ROTO-VIBRATIONAL SPECTROSCOPY

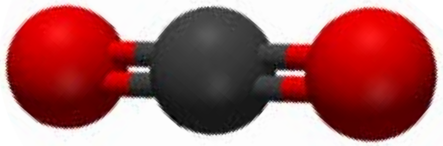
Linear rotors

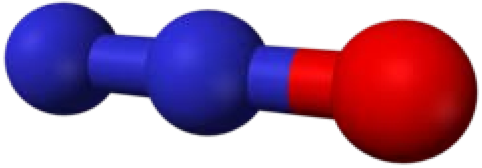
In a linear rotor results: I_b = I_c and I_a = 0, where $b - axis$ and c $- axis$ may be in any direction perpendicular to the internuclear a $- axis$.



Examples of linear rotors are all the **diatomic molecules** (carbon monoxide (CO), nitric oxide (NO), etc..) and **linear molecules** carbon dioxide (CO_2), nitrous oxide (N_2O), etc.



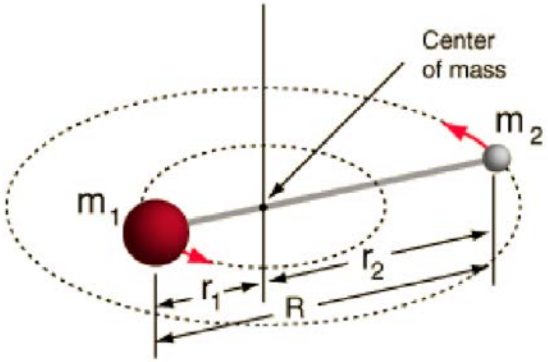




4.2 ROTO-VIBRATIONAL SPECTROSCOPY

Linear rotors

This kind of rotors can be easily described considering their effective mass μ, thus reducing the motion to a rotation around the center of mass of the molecule. For ease of description, we will consider a heteronuclear diatomic molecule.



In this case, the wave function describing the molecule can be split in a radial part $R(r)$ and an **angular part $\Upsilon(\theta, \varphi)$.**

Assuming the radial coordinate *r* fixed, to find the rotational energy we can solve the angular part of Schrödinger equation:

$$\Lambda^2 \Upsilon(\theta, \varphi) = \mathcal{E} \Upsilon(\theta, \varphi) \tag{4.26}$$

Where Λ is the Legendre operator and $\mathcal{E}$ **are the energy eigenvalues of the angular part.**

4.2 ROTO-VIBRATIONAL SPECTROSCOPY

Linear rotors

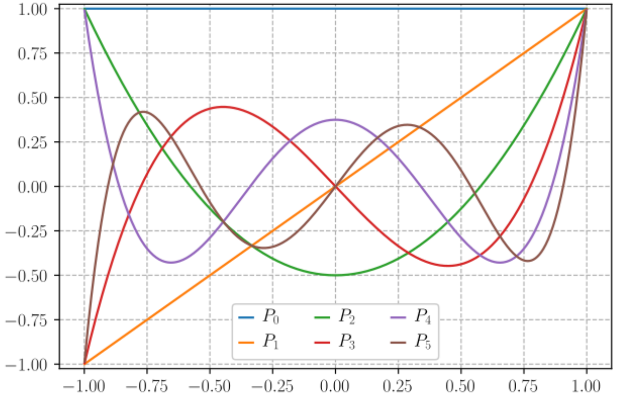
This is the equation typically solved for the angular momentum operator in spherical coordinates, and the eigenfunctions are spherical harmonics:

$$Y_j^m(\theta,\varphi) = A_{j,m}\, e^{im\varphi}\, P_j(\cos\theta) \tag{4.27}$$

where $P_j(cos\theta)$ are Legendre polynomials in sine and cosine terms, and J and m are integers.

Fixed $J = 0, 1, 2, \dots$, the integer m assumes only the following values: $-J + 1\ \dots, J, J + 1$.

Here J **is the total angular momentum** and m **is the z-component** of angular momentum.



4.2 ROTO-VIBRATIONAL SPECTROSCOPY

Linear rotors

Solving Eq. (4.26) using the expression of Eq. (4.27), the eigenvalues of the rotational part are:

$$\mathcal{E} = J(J+1) \tag{4.28}$$

Including the solutions for the radial part of the Schrödinger equation, the **total rotational energy** are:

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1) = \frac{\hbar^2}{2I} J(J+1) \tag{4.29}$$

For spectroscopic applications, it is convenient to express the energy in frequency, as these are easier to be measured.

$$F(J) = \frac{E_r}{\hbar} = \frac{\hbar}{2I} J(J+1) = BJ(J+1) \tag{4.30}$$

B is known as the **rotational constant**, and has the unit of angular frequency, as $F(J)$.

4.2 ROTO-VIBRATIONAL SPECTROSCOPY

Selection rules

Are all the energetic transitions among rotational levels allowed? **The answer is, no.**

To determine if a transition is or not allowed, we can determine some **selection rules**. A selection rule, or transition rule, formally constrains the possible transitions of a system from one quantum state to another.

A selection rule consists of two parts: a **general and a specific one**.

The general selection rule constrains the requirements for a given spectrum to be observable. Once the general selection rule is verified, the specific selection rule is applied to the atom or molecules to determine whether a certain transition within the spectrum can occur.

Selection rules determine all possible transitions between quantum levels as a result of the absorption or emission of electromagnetic radiation.

(n.b. selection rules are meant to be broken…)

4.2 ROTO-VIBRATIONAL SPECTROSCOPY

Selection rules for rotational energies

In the case of radiation absorption, the selection rules rely on the **electrical dipole moment** of the molecule.

As general selection rule, a molecule must have a permanent dipole moment to have a rotational spectrum.

Therefore, **heteronuclear** diatomic molecules (CO, NO, HF) have a rotational spectrum, while **homonuclear** diatomic molecules (H_2, N_2, O_2) **cannot have a rotational spectrum**.

Similarly, **asymmetric polyatomic linear molecules** such as $O = C = S$, $H - C \equiv N$ (namely, without a center of inversion) **can have rotational transitions**, while **symmetrical polyatomic linear molecules** (with inversion center) such as $O = C = O$ e $H - C \equiv C - H$ (with a center of inversion) **cannot not have a "pure" rotational spectrum**.

However, these molecules can still be "IR active" due pseudo-rotational or "induced" dipole moment, following a symmetry breaking, as occurs for CO_2 (spoiler: vibrations).

4.2 ROTO-VIBRATIONAL SPECTROSCOPY

Selection rules for rotational energies

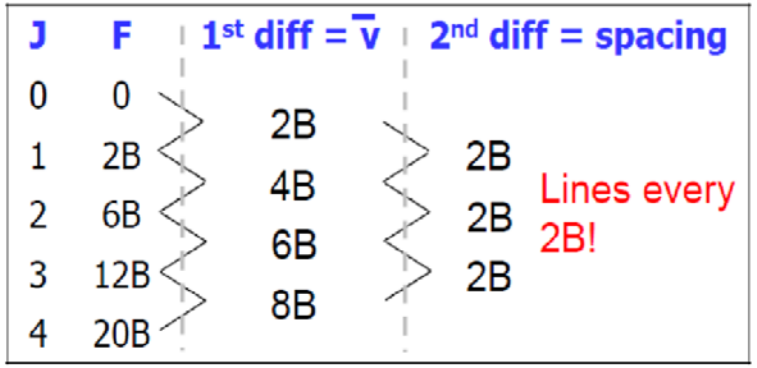
For rotational levels, **the specific selection rules** are:

$$\Delta J = \pm 1\,;\ \Delta m = 0 \tag{4.31}$$

and the transition angular frequencies are:

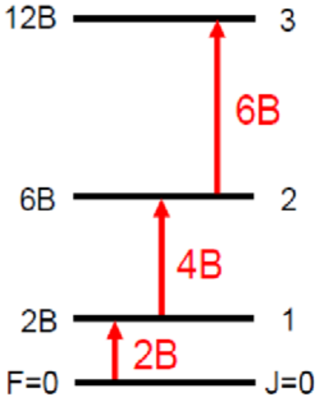
$$\omega = F(J+1) - F(J) = 2B(J+1) \tag{4.32}$$

As a result, the rotational spectra of heteronuclear diatomic molecules are the easiest to be recognized and analyzed because they consist of equally spaced absorption lines.



J	F	1st diff = $\bar{v}$	2nd diff = spacing
0	0		
		2B	
1	2B		2B
		4B	
2	6B		2B
		6B	
3	12B		2B
		8B	
4	20B		

Lines every 2B!



4.2 ROTO-VIBRATIONAL SPECTROSCOPY

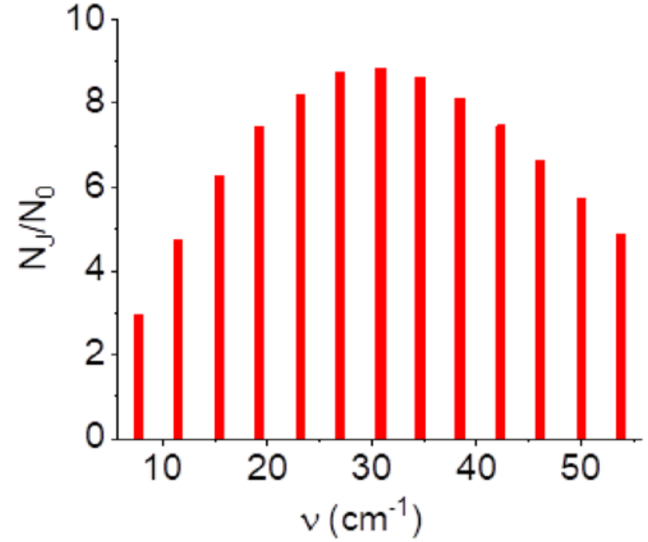
Intensity of the rotational energy for linear rotor

The intensities of the rotational lines depend on the population of the lowest energy state of the transition. **The population N_J of the J-th level respect to N_0 is given by the Boltzmann distribution:**

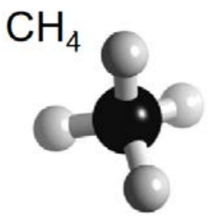
$$\frac{N_J}{N_0} = (2J + 1)e^{-\frac{E_r}{KT}} \qquad (4.33)$$

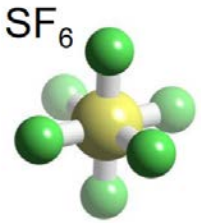
where $(2J + 1)$ represents the degeneration of the J-th level, resulting from the number of possible values for m which still corresponds to the same energy eigenvalue, and E_r were calculated in Eq. (4.29) $\left(E_r = \frac{\hbar^2}{2I} J(J + 1)\right)$.

Two competing terms thus determines the intensity of the rotational absorption. At small values of J, the $(2J + 1)$ term dominates: N_J/N_0 increases as J increases. Then a maximum is reached as a trade-off; after that, the exponential term becomes dominant and N_J/N_0 goes quickly to zero.



4.2 ROTO-VIBRATIONAL SPECTROSCOPY





Spherical rotor molecules

In spherical rotor molecules three principal moments of inertia are the same: $\boldsymbol{I_a = I_b = I_c}$

Examples of spherical rotor are **methane (CH_4) and sulfur hexafluoride (SF_6).** In principle, **spherical rotor molecule are symmetric**, thus do not have a permanent dipole moment and, therefore, a rotational spectra.

However, rotation about any of the C3 axes (i.e., any of the four axes in methane containing a C–H bond) results in a **centrifugal distortion** in which the other three hydrogen atoms are thrown outwards slightly from the axis. This corresponds to a symmetry-break inducing a pseudo-rotational spectra.

Neglecting centrifugal distortion, the rotation term values for a spherical rotor can be calculated as:

$$F(J) = B(J+1) \qquad (4.34)$$

Which is an identical expression to that for a diatomic or linear polyatomic molecules. Being characterized by the same specific transition rules, the transition frequencies are again:

$$\omega = F(J+1) - F(J) = 2B(J+1) \qquad (4.35)$$

4.2 ROTO-VIBRATIONAL SPECTROSCOPY

Asymmetric rotor molecules

Asymmetric rotor molecules have three different moments of inertia: $\boldsymbol{I_a \neq I_b \neq I_c}$

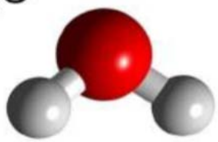
Examples of asymmetric rotors are the molecules water vapor (H_2O) or nitric dioxide (NO_2).

These molecules form one of the largest group, however the exact determination of their rotational spectra is nontrivial. In fact, there are no closed formulae for their rotational term values.

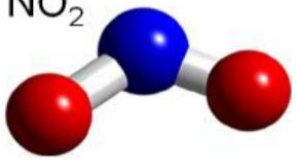
Instead, these term values can be determined accurately only by a matrix diagonalization for each value of J, which remains a good quantum number.

However, their rotational frequencies $F(J)$ can be still calculated starting from Eq. (4.30), considering some corrective terms depending on the selected molecule.

H_2O



NO_2



4.2 ROTO-VIBRATIONAL SPECTROSCOPY

Vibrational energy: harmonic oscillator

A model to describe the **vibrations of a diatomic molecule** is to consider the interatomic chemical bond as a **harmonic oscillator with spring constant k**. In quantum physics this system is described by a Schrödinger equation whose energy eigenvalues are:

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \tag{4.36}$$

With n = 0,1,2,…, and $\omega = \sqrt{\frac{k}{\mu}}$. Therefore, the vibrational levels are equispaced by $\hbar\omega$ and the lowest energy level corresponding to n = 0 has energy $E_0 = \hbar\omega/2$.

As done for rotations, it is convenient to use term values instead of energy levels. Vibrational term values $G(n)$ have dimensions of wavenumber, so we have:

$$G(n) = \frac{E_n}{\hbar}\left(n + \frac{1}{2}\right) \tag{4.37}$$

4.2 ROTO-VIBRATIONAL SPECTROSCOPY

Selection rules for vibrational energies

As discussed for rotational transitions, the **general selection rule** still applies to vibrational transitions as a **net dipole moment different from zero** is required to the molecules to allow energy transfer.

For vibrational energies, the specific selection rule is:

$$\Delta n = \pm 1 \tag{4.38}$$

In this case, no degeneration is present in the energy levels, thus at the thermal equilibrium, the population N_n of the n-th vibrational level is related to N_0 of the lowest energy level by the Boltzmann factor:

$$\frac{N_n}{N_0} = e^{-\frac{E_n}{KT}} \tag{4.39}$$

4.2 ROTO-VIBRATIONAL SPECTROSCOPY

Selection rules for vibrational energies

It is worth noticing that the selection rule expressed in Eq. (4.38) is the result of calculations operated performing a first-order approximation on the electrical dipole moment.

If we include the effect of **higher terms, known as anharmonicity,** these results in additional selection rules:

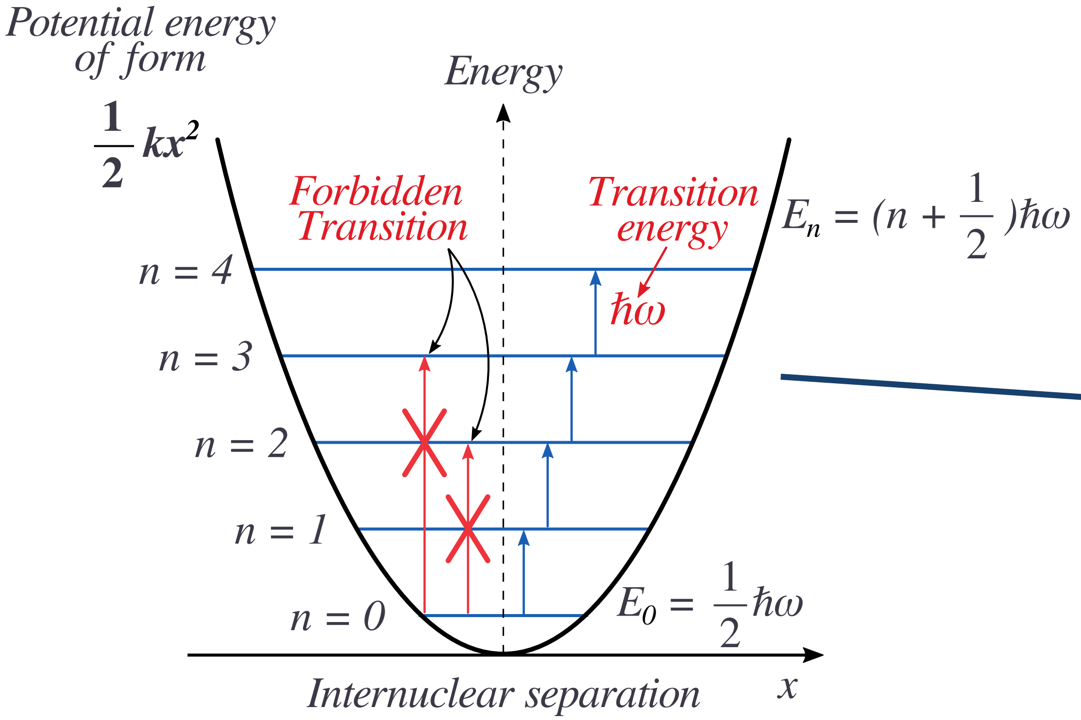
$$\Delta n = \pm 1, \pm 2, \pm 3, \ldots \tag{4.40}$$

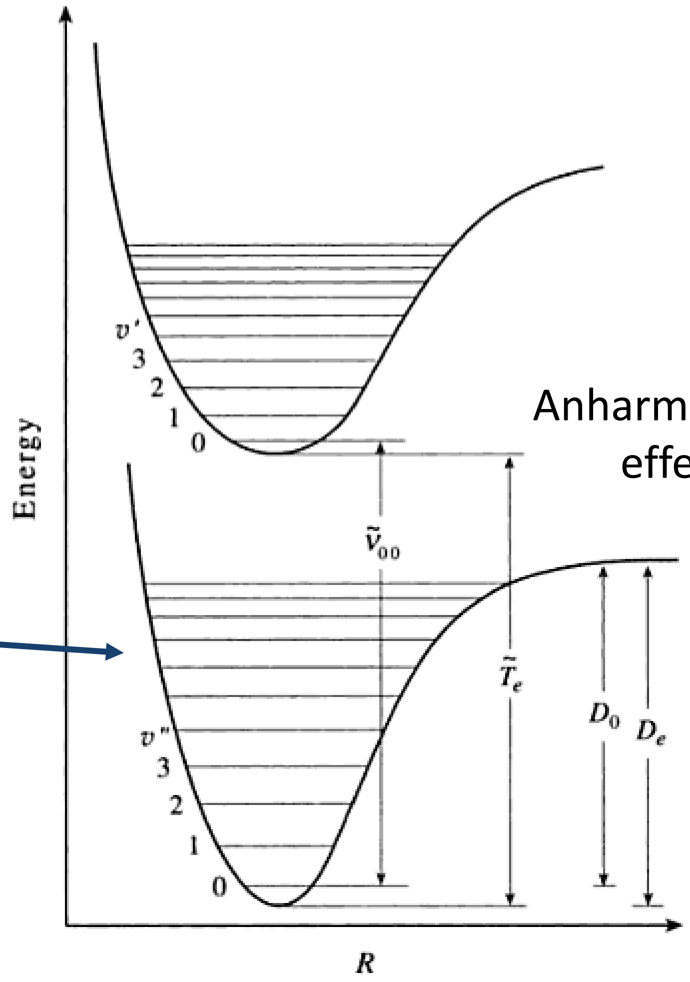
However, electrical anharmonicity is usually small, the effect is to make only a very small contribution to the intensities of $\Delta n = \pm 2, \pm 3, \ldots$ and these transitions are known as **vibrational overtones.**

Energetic transitions obeying to the selection rule $\Delta n = \pm 1$ are known as fundamental vibrational band.

4.2 ROTO-VIBRATIONAL SPECTROSCOPY

Selection rules for vibrational energies





Anharmonicity effect

4.2 ROTO-VIBRATIONAL SPECTROSCOPY

P-, R- and Q-branch structures

Each vibrational transition observed in the gas phase gives rise to what is called a '**band**' in the spectrum. The word '**line**' is reserved for describing a transition between rotational levels associated with the two vibrational levels giving rise to the fine structure of a band.

In roto-vibrational spectroscopy, considering the selection rules $\Delta \upsilon = \pm 1$ e $\Delta J = \pm 1$, **transitions can occur between stacks of rotational energy levels associated with two different vibrational levels**. The rotational part of the transition is subject to the same selection rules as pure rotational transitions.

When a molecule has both vibrational and rotational energy the total term values S are given by the sum of the rotational term values $F(J)$ and the vibrational term values $G(n)$:

$$S = G(n) + F(J) \cong \omega \left(n + \frac{1}{2}\right) + BJ(J+1) \tag{4.41}$$

Therefore, in absorption ($\Delta \upsilon = +1$), you will have two possible set of transitions:

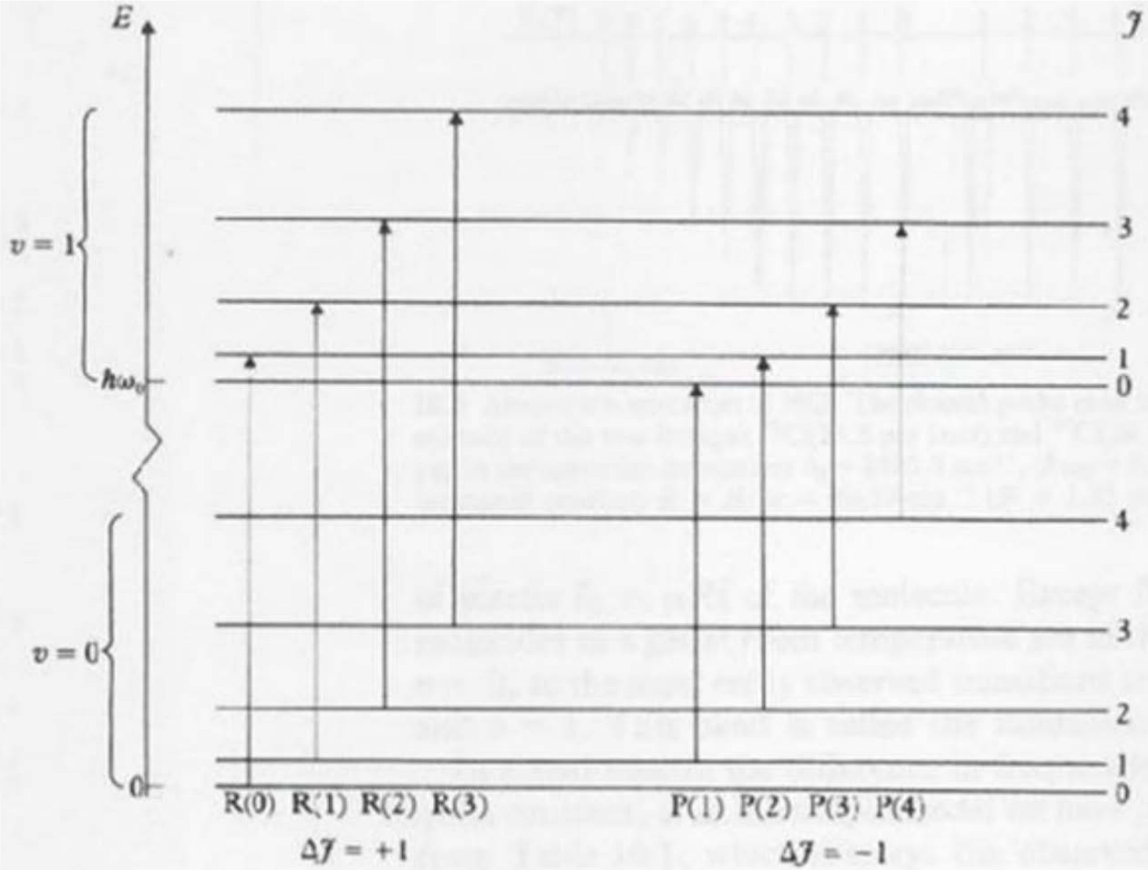
- **$\Delta J = -1$, called the P-branch**
- **$\Delta J = +1$, called the R-branch**

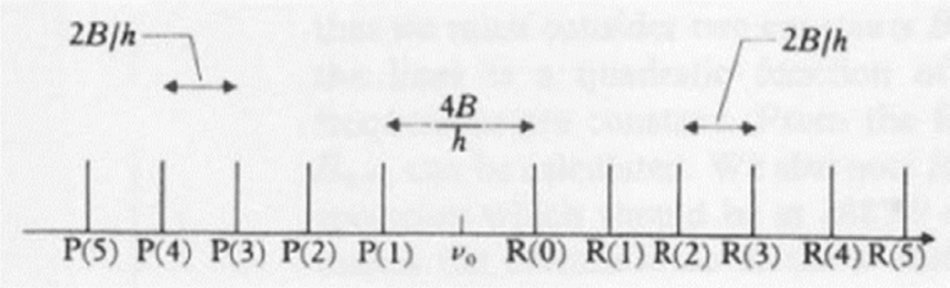
4.2 ROTO-VIBRATIONAL SPECTROSCOPY

P-, R- and Q-branch structures

Each transition of the $\boldsymbol{R-branch}$ is labelled $R(J)$ while each transition of $\boldsymbol{P-branch}$ with $P(J)$, where J represents the lowest state value.

The **spacing between adjacent** *R-branch* lines and also between adjacent *P-branch* lines **is $\boldsymbol{2B}$**. The **spacing between the first *P-branch*** transition, $P(1)$, **and the first *R-branch* transition,** $R(0)$, is equal to $\boldsymbol{4B}$.



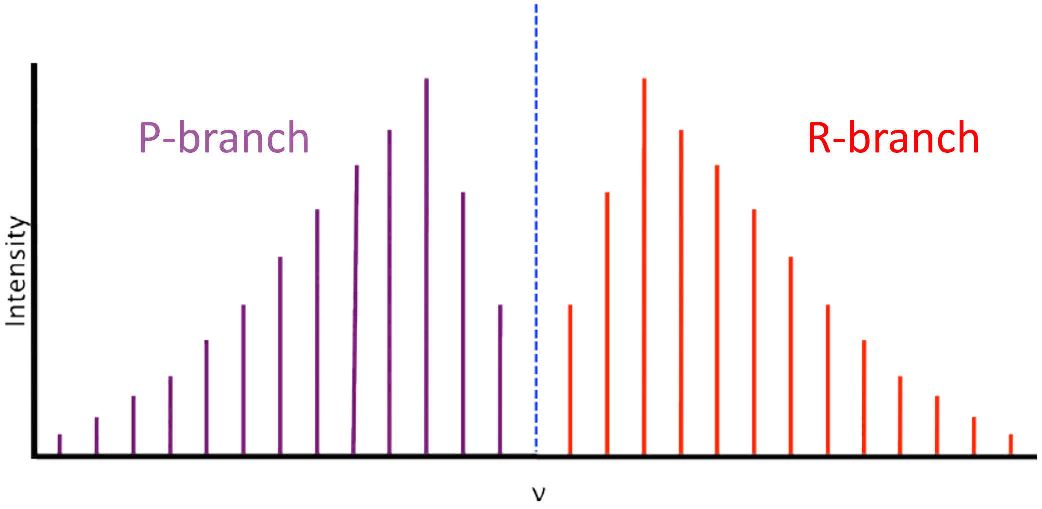


4.2 ROTO-VIBRATIONAL SPECTROSCOPY

P-, R- and Q-branch structures

The **intensity distribution** among rotational transitions in a vibration–rotation band is governed by the **Boltzmann distribution** of population among the initial states, as described in Eq.(4.33):

$$\frac{N_J}{N_0} = (2J+1)e^{-\frac{B\hbar J(J+1)}{KT}} \qquad (4.33)$$



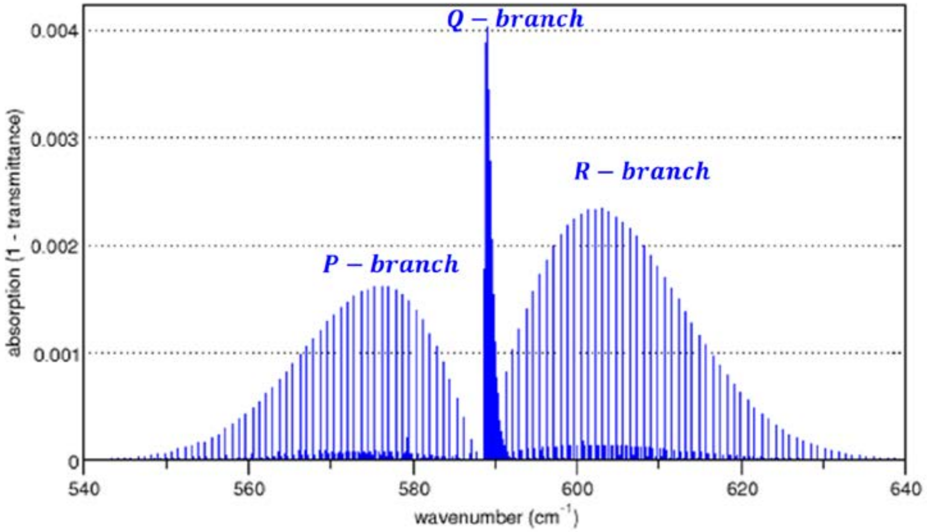
4.2 ROTO-VIBRATIONAL SPECTROSCOPY

P-, R- and Q-branch structures

Since transitions with $\Delta J = 0$ **are forbidden** means that **purely vibrational transitions are not allowed.** If they were allowed, they would all be at the center of the gap between P- and R- branches.

This branch is called **Q-branch.** The molecules characterized by a Q-branch have a rotational selection rule $\Delta J = 0, \pm 1.$

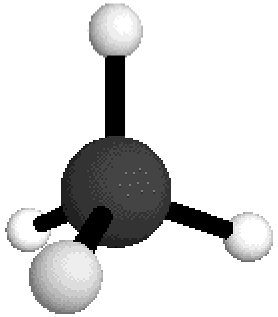
Q-branch can be found in polyatomic molecules and also in diatomic molecules having an electronic angular momentum in the ground electronic state. One of these molecules is nitric oxide (NO).



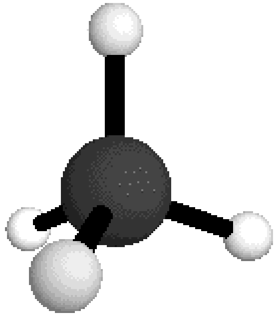
4.2 ROTO-VIBRATIONAL SPECTROSCOPY

Methane (CH_4)

$o_1 = 3025.5$ cm^{-1}
A_1 Symmetry

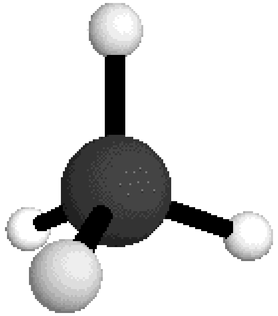


$o_2 = 1582.7$ cm^{-1}
E Symmetry

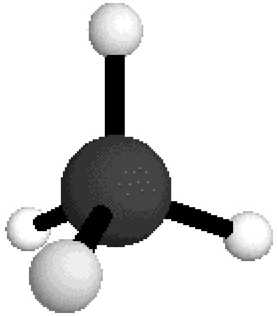


Symmetric:
Not IR active

$o_3 = 3156.8$ cm^{-1}
F_2 Symmetry



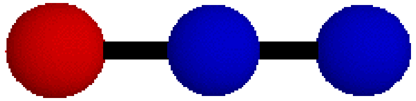
$o_4 = 1367.4$ cm^{-1}
F_2 Symmetry



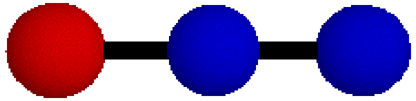
Asymmetric:
IR active

Nitrous Oxide (N_2O)

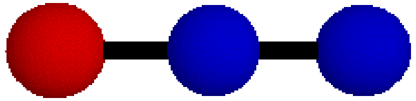
$o_1 = 1298.3$ cm^{-1}
R^+ Symmetry



$o_2 = 596.3$ cm^{-1}
P Symmetry

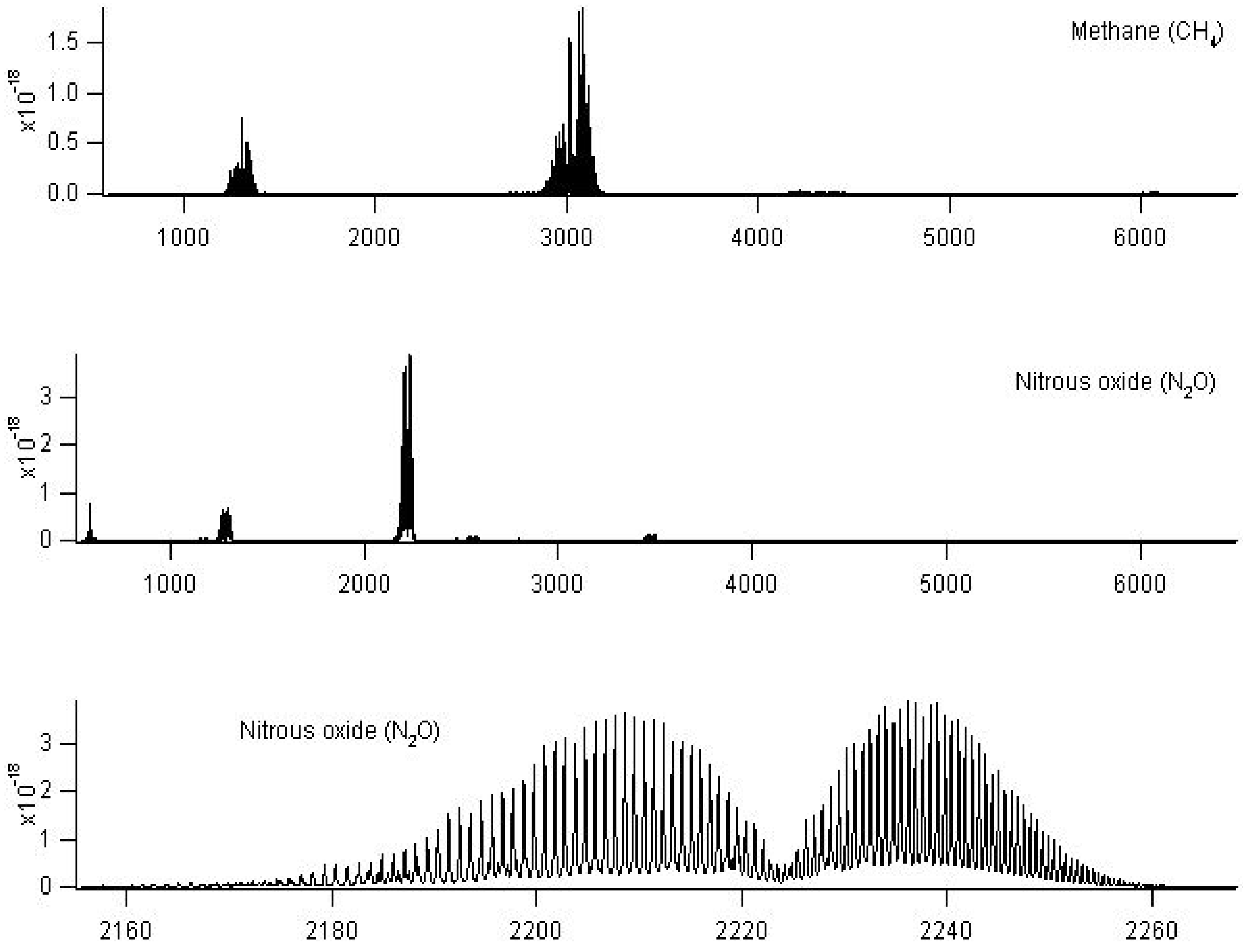


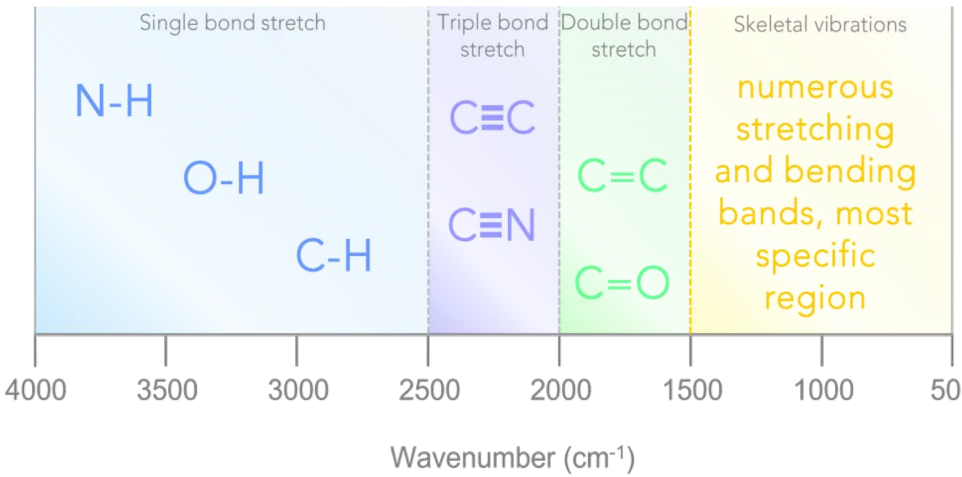
$o_3 = 2282.2$ cm^{-1}
R^+ Symmetry



4.2 ROTO-VIBRATIONAL SPECTROSCOPY

Molecular fingerprint





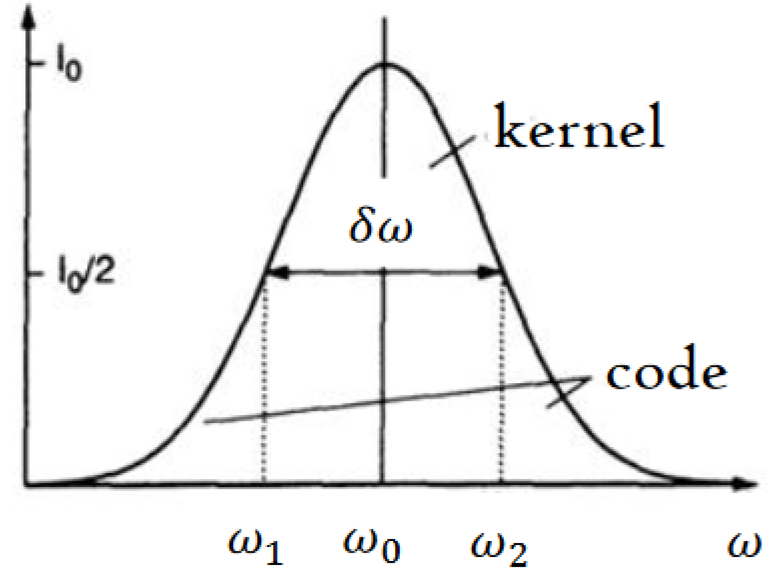
4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Lineshapes

Spectral lines in discrete absorption or emission spectra **are never strictly monochromatic**. Even with the very high resolution of interferometers, one observes a **spectral distribution $I(\upsilon)$** of the absorbed or emitted intensity around the central frequency $\omega_0 = \frac{(E_b - E_a)}{\hbar}$ corresponding to a molecular transition with the energy difference $\Delta E = E_b - E_a$ between upper and lower levels.

The function $I(\omega)$ in the vicinity of ω_0 is called the **line profile**.

The frequency interval $\delta\omega = \omega_2 - \omega_1$ between the two frequencies ω_2 and ω_1 for which $I(\omega_1) = I(\omega_2) = I(\omega_0)/2$ is the **Full-Width Half-Maximum (FWHM)** of the line, often shortened to the **linewidth**.



4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Lineshapes

Lineshape depends on the occurring broadening effects. The main broadening effects can be divided in:

- **Natural broadening**
- **Collisional broadening**
- **Thermal motion broadening**, known as **Doppler** broadening

Natural and collisional broadening effects are also referred as **homogenous broadening**, as the increase the optical linewidth equally affects different radiating or absorbing atoms, ions or molecules.

Conversely, the Doppler broadening is an **inhomogeneous broadening** effect, depending on the different velocities of the atoms of a gas .

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Natural broadening

Let's consider to irradiate a sample of molecules with monochromatic radiation resonant with the transition $E_a \rightarrow E_b$ and the following spontaneous emission of transition $E_b \rightarrow E_a$.

The excited atomic electron can be described by the classical model of a **damped harmonic oscillator** with frequency ω, mass m and restoring force constant k.

The radiative energy loss results in a damping of the oscillation described by the damping constant γ_n.

Because the amplitude $x(t)$ of the oscillation decreases gradually, the **frequency of the emitted radiation is no longer monochromatic** as it would be for an oscillation with constant amplitude. **Instead, it shows a frequency distribution.**

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

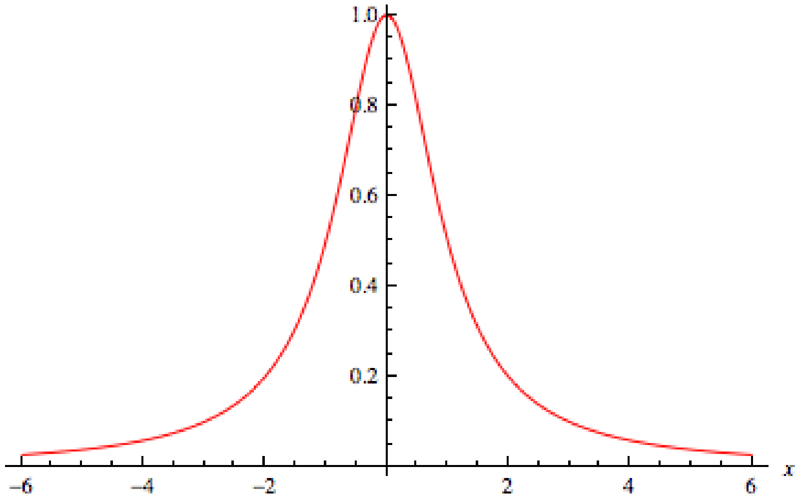
Natural broadening

As a result, the intensity profile of the spectral line becomes:

$$I(\omega-\omega_0) \simeq \frac{I_0}{2\pi}\frac{\gamma_n}{(\omega-\omega_0)^2+\left(\frac{\gamma_n}{2}\right)^2} \tag{4.34}$$

with a FWHM of $\boldsymbol{\delta\nu} = \boldsymbol{\frac{\gamma_n}{2\pi}}$ and peak intensity $I(\omega_0) = \frac{2I_0}{\pi\gamma_n}$, $I_0 = \int I(\omega)d\omega$.

This is referred as **Lorentzian lineshape.**



4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Doppler broadening

Generally, the Lorentzian line profile with purely natural linewidth cannot be observed without special techniques, because it is completely concealed by other broadening effects.

Besides collisional broadening, the major contributions to the spectral linewidth in gases at low pressures is the **Doppler width, which is due to the thermal motion of the absorbing or emitting molecules.**

Consider an excited molecule with a velocity $\boldsymbol{v}$ = $\{v_x,\ v_y, v_z\}$ relative to the rest frame of the observer. The central frequency of a molecular emission line that is ω_0 in the coordinate system of the molecule is Doppler shifted to:

$$\omega = \ \omega_0 + \vec{\boldsymbol{k}} \cdot \vec{\boldsymbol{v}} \tag{4.35}$$

for an observer looking toward the emitting molecule. The same process occurs for a molecule that is absorbing the radiation.

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Doppler broadening

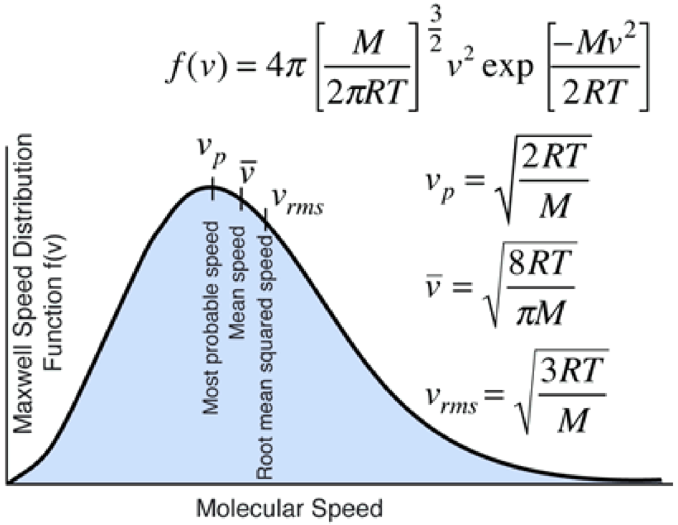
If we choose the z −direction to coincide with the light propagation, with $\boldsymbol{k}$ ={0,0, k_z} and $k = \frac{\omega_0}{c}$, then Eq. (4.35) becomes:

$$\omega' = \omega_0 \left(1 + \frac{v_z}{c}\right) \tag{4.36}$$

At thermal equilibrium, the molecules of a gas follow a **Maxwellian velocity distribution** (see Eq. (2.10)). This can be expressed in terms of number of molecules with absorption frequencies shifted from ω_0 into the interval [ω, ω + $d\omega$]:

$$n_i(\omega)d\omega = N_i \frac{c}{\omega_0 v_p \sqrt{\pi}}\, e^{-\left[\frac{c(\omega-\omega_0)}{\omega_0 v_p}\right]^2} d\omega \tag{4.37}$$

Where $v_p = \sqrt{\frac{2KT}{m}}$ is the most probable velocity.



4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

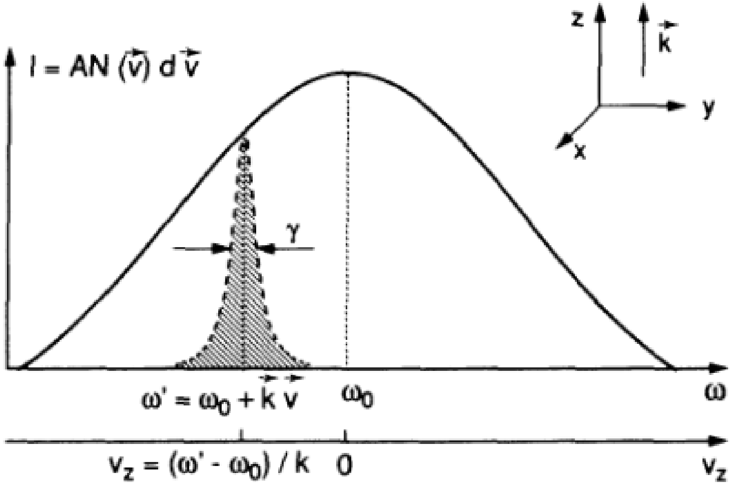
Doppler broadening

The emitted or absorbed radiant power $P(\omega)d\omega$ is proportional to density $n_i(\omega)d\omega$ of molecules emitting or absorbing in the interval $d\omega$, thus the **intensity profile of a Doppler-broadened spectral line** becomes:

$$I(\omega) = I_0 e^{-\left[\frac{c(\omega-\omega_0)}{\omega_0 v_p}\right]^2} \tag{4.38}$$

Which is a Gaussian profile. The FWHM of this lineshape is $\delta\omega_D = 2\sqrt{ln2}\,\frac{\omega_0 v_p}{c} = \frac{\omega_0}{c}\sqrt{\frac{8kTln2}{m}}$.

This is known as Doppler width, and generally results $\boldsymbol{\delta\omega_D \gg \delta\omega_n}$



4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Collisional broadening

When an atom A with energy levels E_i and E_k approaches another atom or molecule B, **the energy levels of A are shifted because of the interaction between A and B**. This shift depends on the electron configurations of A and B and on the distance $R(A,B)$, between both collision partners, which we define as the distance between the centers of mass of A and B.

The energy shifts ΔE are, in general, different for the levels E_i and E_k and may be positive as well as negative. The energy shift ΔE is positive if the interaction between A and B is repulsive, and negative if it is attractive. **The shift $\Delta\omega = \omega_0 - \omega_{ik}$ depends on how differently the two energy levels E_i and E_k are shifted at a distance $R(A, B)$ where the emission probability has a maximum.**

If no internal energy of the collision partners is transferred during the collision by nonradiative transitions, the **collision is elastic**.

Conversely, if the excitation energy E_i of atom A is either partly or completely transferred into internal energy of the collision partner B, or into translational energy of both partners, the **collision is inelastic**.

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Collisional broadening

Both elastic and inelastic collisions cause a spectral broadening of the line profile. Elastic collisions also cause a peak shift.

The spectral broadening can be calculated from the transition probability for the depopulation of level E_i. The collisional transition probability is:

$$A_i^{coll} = N_B \sigma_i v \tag{4.39}$$

Where N_B of collisional partner B, σ_i the collision cross section and *v* the mean relative velocity. Inserting the relations at the thermal equilibrium:

$$\bar{v} = \sqrt{\frac{8kT}{\pi\mu}} \;\; ; \;\; \mu = \frac{M_A \cdot M_B}{M_A + M_B} \;\; ; \;\; p_B = N_B kT \tag{4.40}$$

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Collisional broadening

It follows that this pressure-dependent transition probability causes a corresponding pressure-dependent linewidth $\delta\omega$, which can be described by a sum of two damping terms:

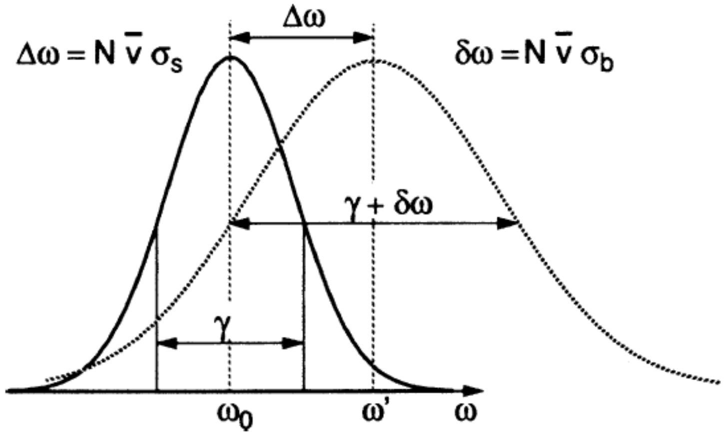
$$\delta\omega = \delta\omega_n + \delta\omega_{coll} = \gamma_n + \gamma_{coll} = \gamma_n + 2\sigma_B\sqrt{\frac{2}{\pi\mu KT}} \cdot p_B \tag{4.41}$$

Therefore, **the collisional broadening is also referred as pressure broadening. It is the dominant broadening effect at room temperature and pressure > 100 Torr .**

Ultimately, we can write the line profile as:

$$I(\omega - \omega_0) \simeq \frac{I_0}{2\pi}\frac{\gamma_n + N_B\sigma_B\bar{v}}{(\omega-\omega_0-N_B\sigma_S\bar{v})^2+\left(\frac{\gamma_n}{2}+N_B\sigma_B\bar{v}\right)^2} \tag{4.42}$$

where the shift $N_B\sigma_B\bar{v}$ and the broadening $N_B\sigma_S\bar{v}$ of the line profile are determined by the number density N_B of collisional partner B and by the collision cross sections σ_s for the line shift, and σ_B for broadening.



4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Voigt profile

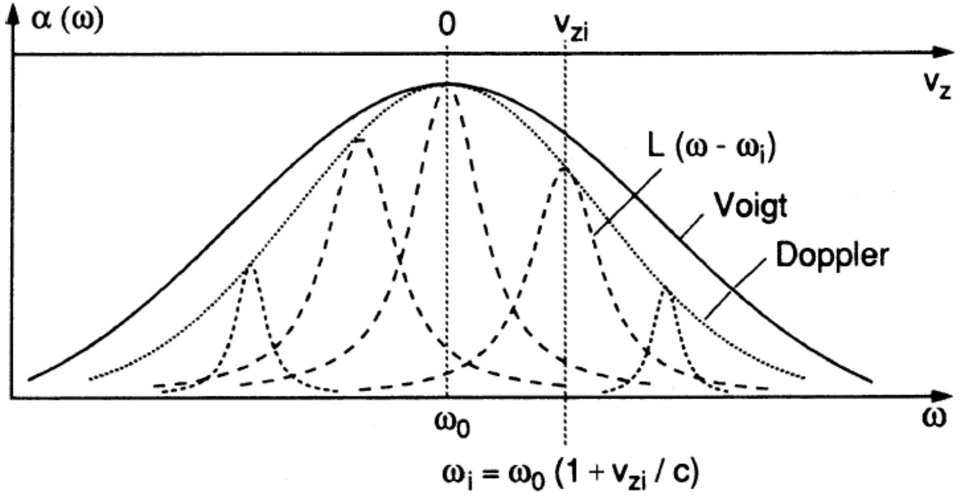
The combined contribution of Lorentzian and Gaussian profile can be accounted evaluating the convolution of these profiles:

$$I(\omega) = C \cdot \int_0^{\infty} \frac{e^{-\left[\frac{c}{v_p}\cdot\frac{(\omega_0-\omega')}{\omega_0}\right]^2}}{(\omega-\omega')^2+(\gamma/2)\hat{}2}\, d\omega' \tag{4.43}$$

With $C = \frac{\gamma N_i c}{2 v_p \pi^{\frac{3}{2}} \omega_0}$.

This intensity profile, is called **Voigt profile**.

Voigt profiles play an important role in the spectroscopy of stellar atmospheres, where accurate measurements of line wings allow the contributions of Doppler broadening and natural linewidth or collisional line broadening to be separated.

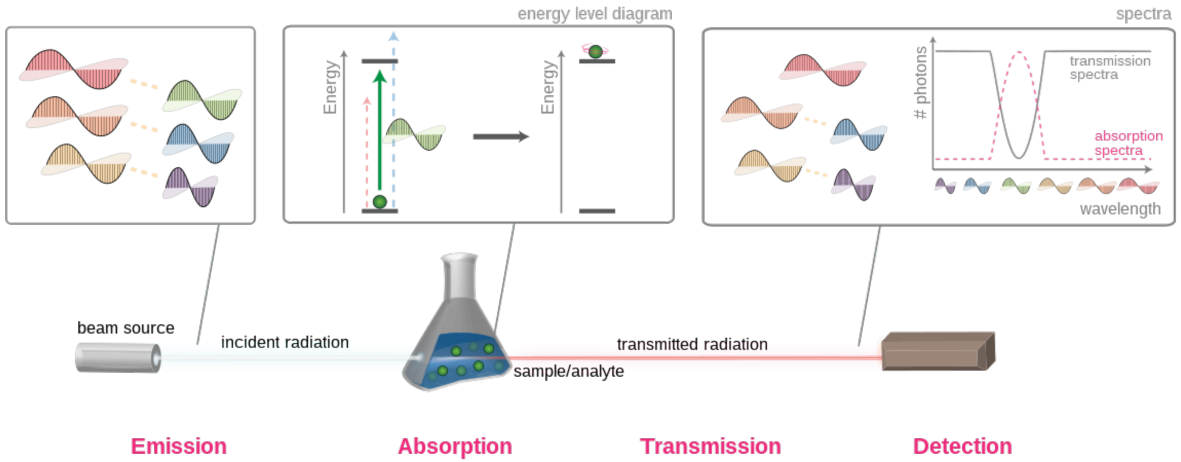


4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Absorption spectroscopy

Gas sensors based on optical absorption offer fast responses, minimal drift and high gas specificity, with zero cross-response to other gases as long as their design is carefully considered. Measurements can be made in **real time and in situ** without disturbing the gas sample, which can be important in process control.

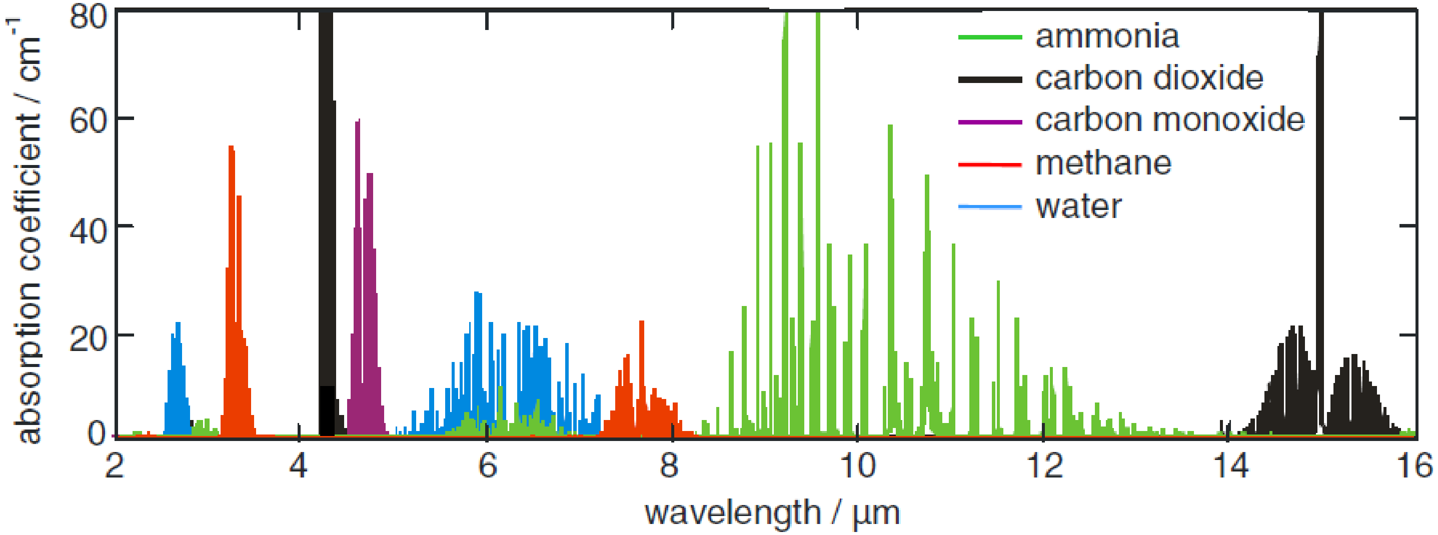
Because the transduction method makes a direct measurement of a molecule’s physical properties (its **absorption at a specific wavelength**), drift is reduced and, because the incident light intensity can be determined, measurements are self-referenced, making them inherently reliable.



4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Absorption spectroscopy

Many chemical species exhibit strong absorption in the **UV/visible, near infrared or mid infrared regions of the electromagnetic spectrum**. The absorption lines or bands are specific to each species, and this forms the basis for their detection and measurement. In the so-called **fingerprint region** of the infrared, gas phase absorption spectra exhibit narrow lines as a result of molecular vibrations at discrete energy levels. These can be measured at high resolution, resolving the line, or at lower resolution, measuring the absorption band.

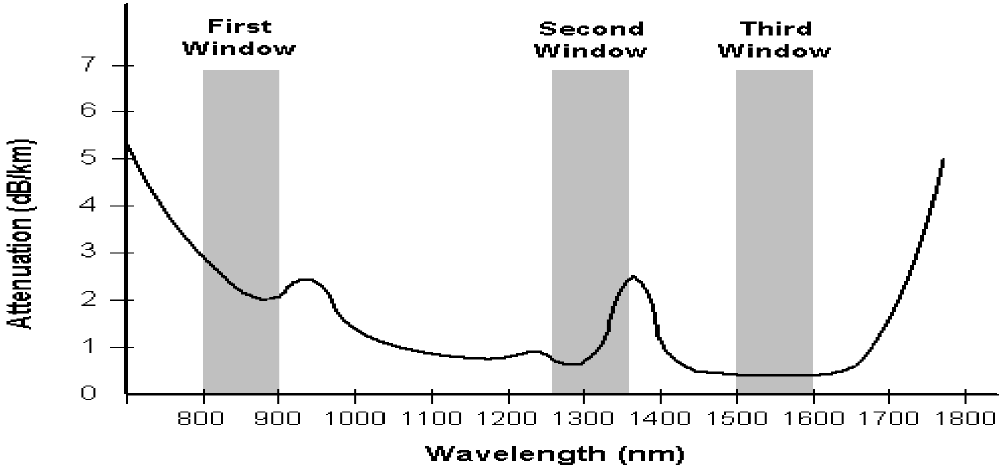


4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Absorption spectroscopy

Near IR spectra are typically overtones of fundamental vibrations in the mid IR and hence can be significantly weaker (e.g. around 100 times weaker for methane).

However, the availability of high-quality sources and detectors, primarily derived from telecommunications applications, can counteract this disadvantage and signal: noise ratios can be relatively high.



4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Absorption spectroscopy

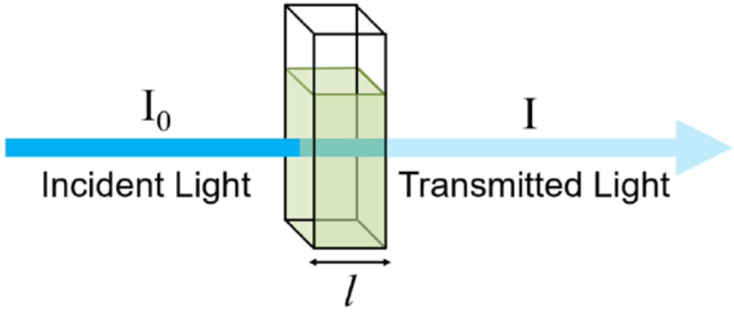
The simplest method for measuring the absorption spectrum of a gas species is to determine the absorption coefficient $\alpha(\omega)$ using the **Lambert-Beer law**:

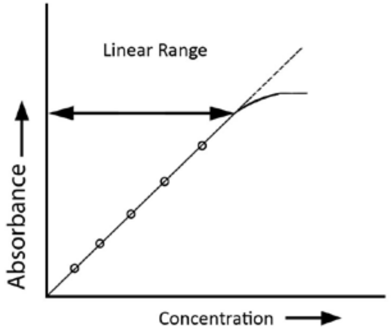
$$I_T\,(\omega) = I_0 e^{-\alpha(\omega)x} \tag{4.44}$$

which allows to calculate the radiation transmitted I_T after passing through an optical path of length x.

In the approximation of small absorptions $\alpha(\omega)x \ll 1$, using the approximation $e^{-\alpha(\omega)x} \ll 1 - \alpha(\omega)x$, Lambert-Beer's law can be reduced to:

$$I_T(\omega) \simeq I_0[1 - \alpha(\omega)x] \tag{4.45}$$





4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Absorption spectroscopy

An absorption spectrum is a plot of α as a function of wavelength (e.g. in µm) or its reciprocal, wavenumber (in cm^{-1}).

Public-domain quantified spectra are available from

- US National Institute of Standards and Technology - *https://www.nist.gov/pml/atomic-spectra-database*
- Pacific Northwest National Laboratory (PNNL) – *https://vpl.astro.washington.edu/spectra/allmoleculeslist.htm*
- Hitran database - *https://hitran.org/*

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Direct absorption

By measuring the intensity I_0, the absorption coefficient can be retrieved as:

$$\alpha(\omega) = \frac{I_0 - I_T(\omega)}{x \cdot I_0} = \frac{\Delta I}{x \cdot I_0} \tag{4.46}$$

where $\Delta I = I_0 - I_T(\omega)$.

Starting from Eq. (4.4), the **absorption coefficient $\alpha(\omega)$** of an energetic transition with **absorption cross section $\sigma(\omega)$** is determined is determined by the density of the **absorbing molecules N_{abs}**:

$$\alpha(\omega) = N_{abs} \cdot \sigma(\omega) = N_{tot} \cdot \sigma(\omega) \cdot c \tag{4.47}$$

Where N_{tot} is the molecular density of the sample, and **c is the gas target concentration**.

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Direct absorption

Therefore, it is possible to calculate the minimum detectable concentration over an optical absorption path L as :

$$c_{min} \geq \frac{\Delta I}{I_0} \cdot \frac{1}{\alpha\, L\, N_{tot}} \tag{4.48}$$

The minimum detectable density of absorbers directly depends on:

a. the absorption coefficient α

b. the length of the optical path L

c. the minimum detectable change in intensity $\Delta I/I_0$ caused by absorption.

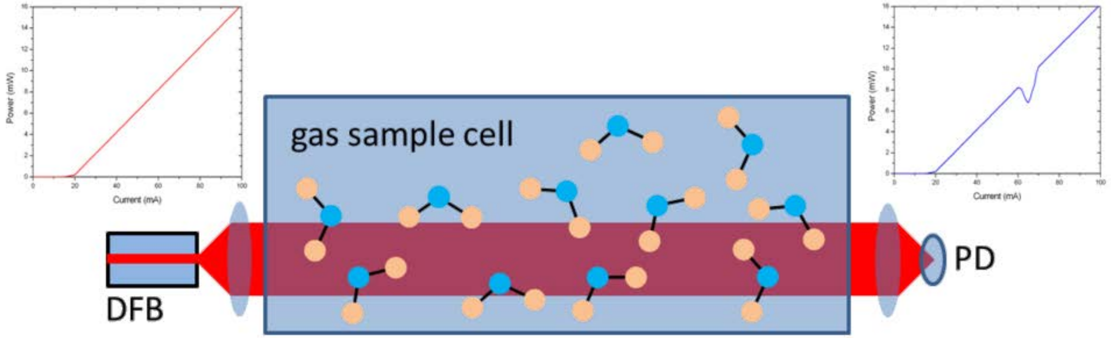
To achieve high detection sensitivities, L must be as large as possible and the minimum detectable value $\Delta I/I_0$ as small as possible.

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Direct absorption

In the case of small absorptions, measuring $\Delta I/I_0$ involves estimating small differences $I_0 - I_T$ of two large quantities I_0 and I_T. The two main contributions that negatively affect the accuracy of the measurement of $\Delta I/I_0$:

- **Fluctuations in I_0**
- **The noise level of the photodetector**



For these reasons, different detection methods have been developed to reduce impact of these limitations and increase detection sensitivities.

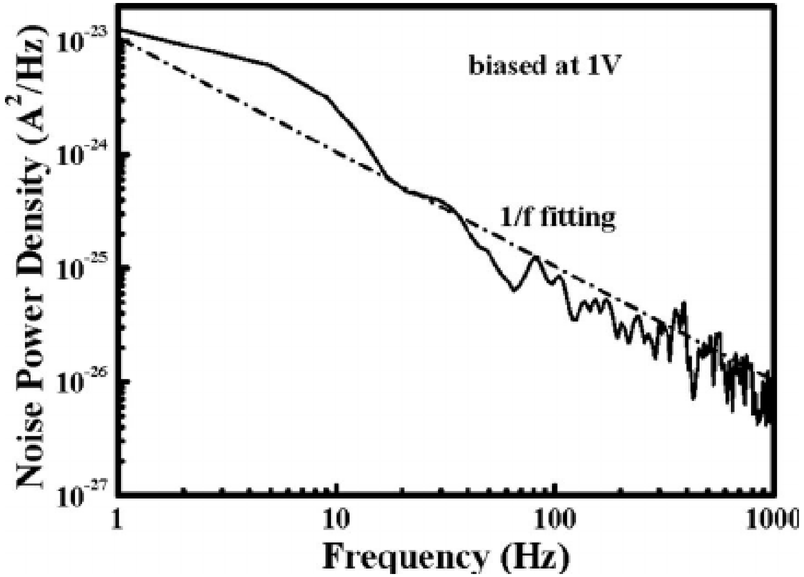
4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Amplitude modulation

The noise level of a photodetector is actually a **noise spectrum of a photodetector**, i.e., the noise level as a function of the working frequency.

The noise level significantly decreases when the photodetector operates at higher frequencies.

For example, it is reduced by several orders of magnitude when moving from frequencies of the order of Hz up to frequencies of the order of kHz, following indicatively the **Flicker noise trend 1/**f.



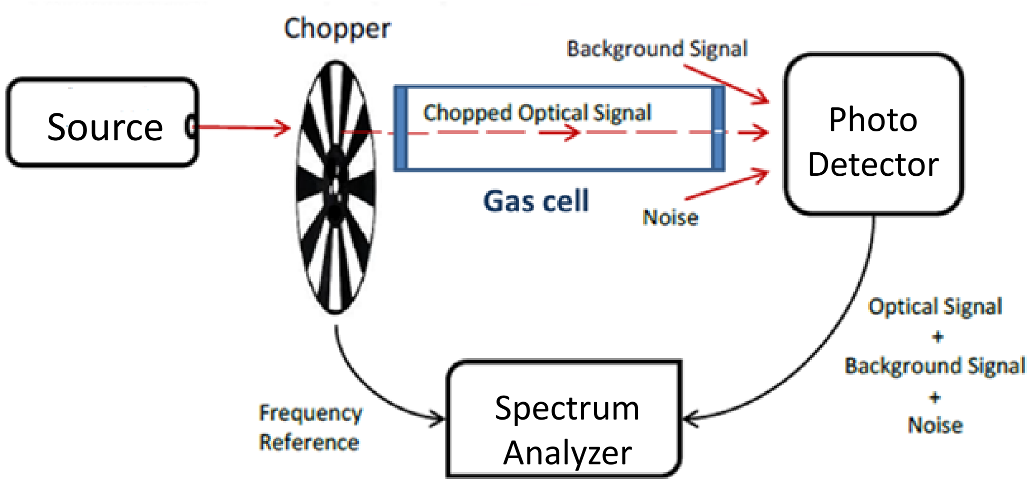
4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Amplitude modulation

For this reason, rather than working with a continuous-wave (CW) light sources, it is more convenient to modulate the light intensity at a certain frequency, and then to filter the signal from the photodetector to extract only the spectral component at the working frequency.

This approach is called Amplitude Modulation Spectroscopy.

The light beam with continuous emission is modulated in intensity using a mechanical modulator (chopper) with a duty-cycle, typically, of 50 %. The light transmitted by the cell containing the absorbent gas sample is sent to a photodetector, which generates an electrical signal proportional to the concentration of the absorbent gas.



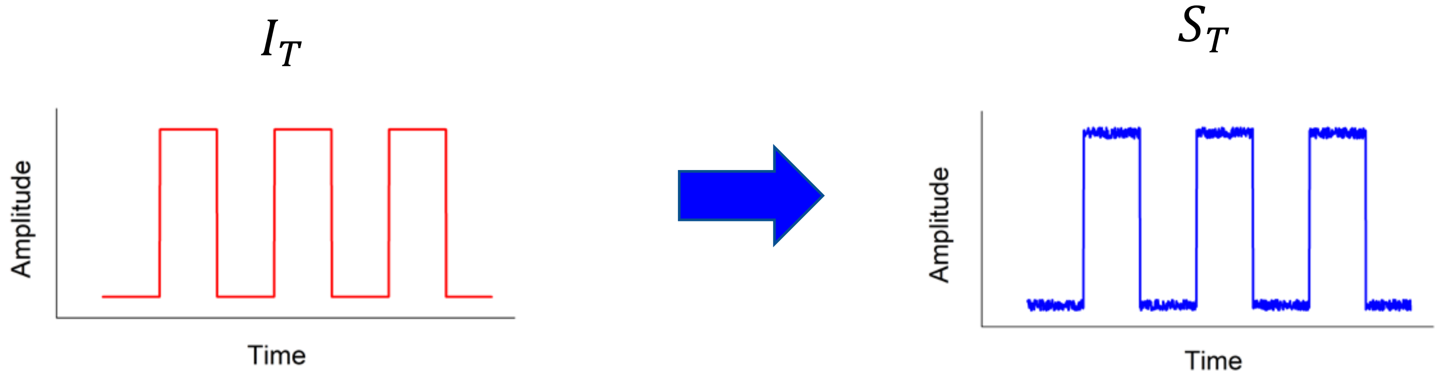
4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Amplitude modulation

The signal is then sent to a spectrum analyzer that extracts the spectral component at the frequency of modulation of the beam by a Fourier analysis of the input signal. An alternative to the spectrum analyzer is a lock-in amplifier.

Being Ω the modulation frequency, the light intensity incident on the gas sample can be represented as a square wave at the Ω frequency.

This means that in the Lamber-Beer equation for small absorptions, $I_T(\omega) = I_0\,[1 - \alpha(\omega)x]$, I_0 has itself a square wave shape. If the wavelength of the laser is fixed on the peak of the absorption line, I_T will also be a square wave in the time domain as well as the signal S_T acquired by the detector.



4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Amplitude modulation

The detector signal S_T is sent to a **spectrum analyzer to extract only the component at the Ω frequency**, i.e., at the modulation frequency of the light intensity.

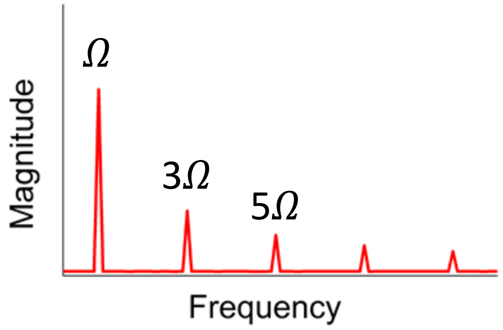
In the frequency domain, square waves with a duty cycle of 50% can be expressed as a **Fourier series**:

$$\psi_{square} = \frac{4}{\pi}\sum_{k=1}^{\infty}\frac{sen[(2k-1)\Omega t]}{(2k-1)} = \frac{4}{\pi}\left[sen(\Omega t) + \frac{1}{3}sen(3\Omega t) + \frac{1}{5}sen(5\Omega t) + \cdots\right] \qquad (4.49)$$

Only the odd harmonics are present: the third one with amplitude equal to one third of the fundamental, the fifth harmonic with amplitude equal to one fifth of the fundamental, and so on.

Therefore, in the acquired spectrum there will be unwanted contributions even to the higher harmonics.

If only the spectral component of I_T at the Ω frequency is extracted, I_T/I_0 as a function of the frequency of the light will follow the trend of the absorption coefficient $\alpha(\omega)$, as in the case of direct absorption with the advantage of a significantly lower photodetector noise level.



4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Frequency modulation

Amplitude modulation involves the use of a mechanical modulator that hardly allows to reach modulation frequencies > 5 KHz. At such frequencies, mechanical choppers tend to suffer from frequency instabilities. In addition, they are bulky and noisy.

Operating with laser sources, a simpler alternative is to modulate the laser injection current. If the injection current is modulated with an amplitude such as to alternate at a frequency Ω the condition of laser on with that of laser off (laser below threshold), the result will be identical to that of a mechanical modulator.

However, this condition is not advisable as abrupt variations in the current injected at such high frequencies can lead to instability of the source generated by the alternation of heat accumulation and subsequent dissipation.

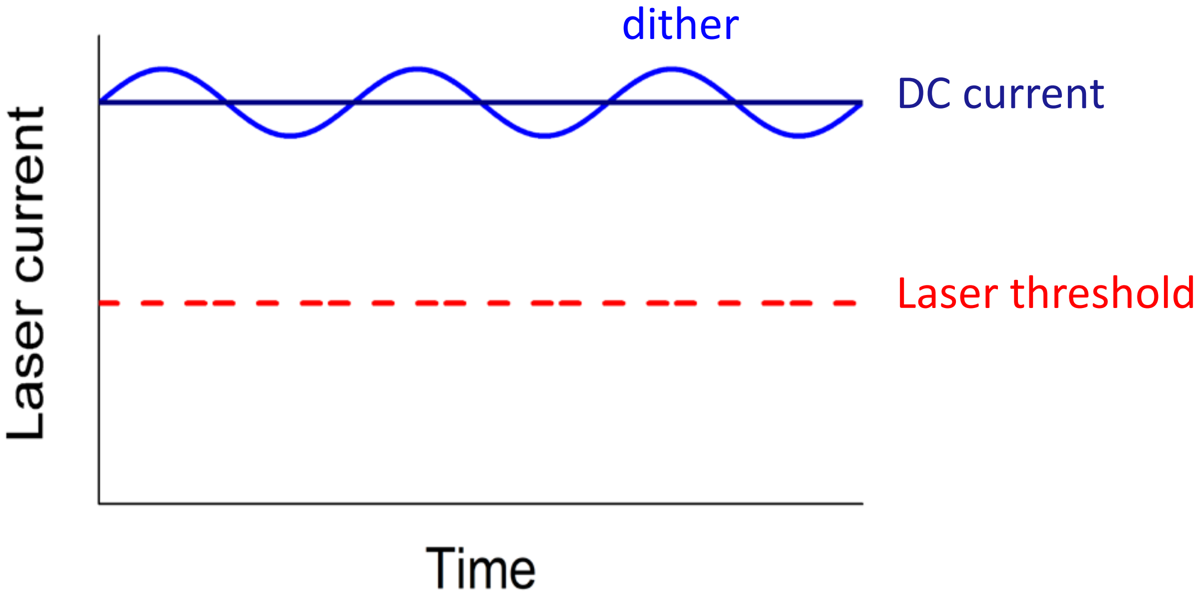
To overcome this issue, it is preferred to polarize the laser with a direct current above the threshold and apply a modulation with an amplitude such that the laser is always above the threshold. This condition is known in the literature as **dithering**.

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Frequency modulation

When a dither is applied, **the square wave is not the best solution** as we have seen that there will be unwanted contributions to the **higher harmonics** as well.

For this reason, it is preferred to apply a **sinusoidal dither at a frequency *Ω***, to have only one contribution in frequency, without distortions due to higher harmonics.

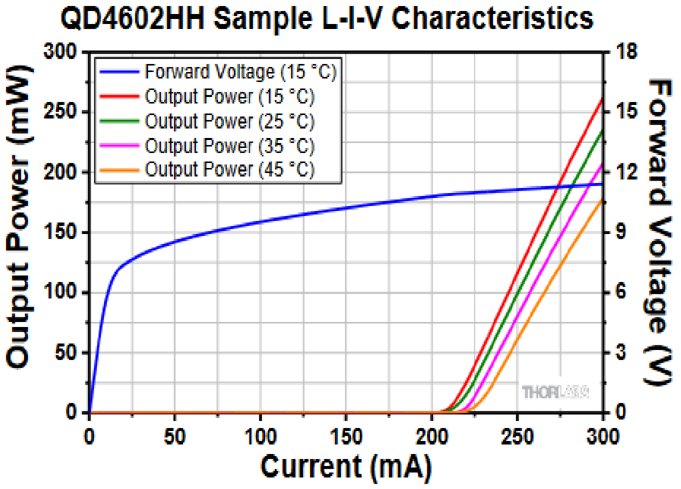


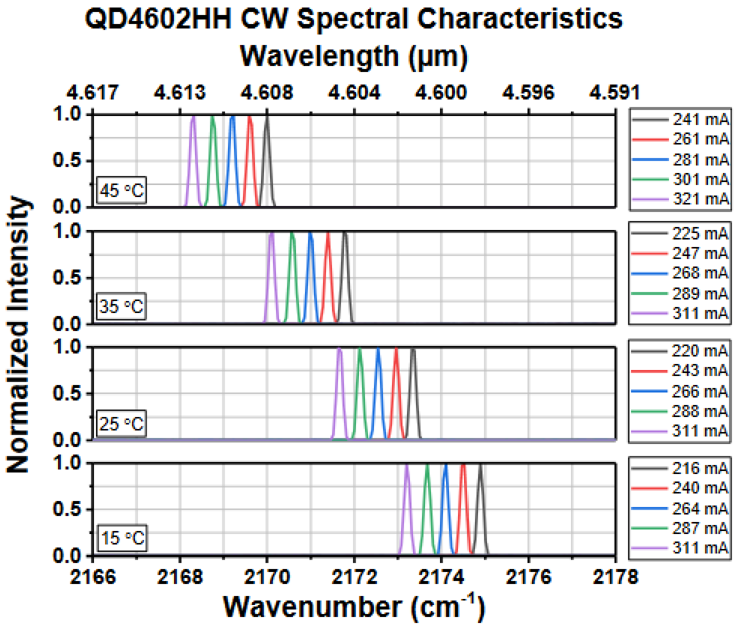
4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Frequency modulation

If the intensity of the laser varies linearly with the electric current, a sinusoidal dither applied to the current will correspond to a modulation of the current at the same frequency, without distortion. This is the case with laser diodes, in which above the lasing threshold, the light intensity varies linearly with the injected current.

Unfortunately, for diode lasers, the **emission wavelength also varies linearly with the electric current**, as a result of the dependence of the refractive index on the temperature of the active medium.





4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Frequency modulation

So, if we apply a dither of amplitude Δi at the frequency Ω to the DC current i_{DC}, with $\Delta i \ll i_{DC}$, the instantaneous current will be (we neglect any type of phase shift):

$$i(t) = i_{\mathrm{DC}} + \Delta \mathrm{i} \cos(\Omega t) \tag{4.50}$$

and the laser intensity will vary with the same trend:

$$I_0(t) = I_{\mathrm{DC}} + \Delta \mathrm{I} \cos(\Omega t) \tag{4.51}$$

and simultaneously the emission frequency will be modulated at the same frequency Ω:

$$\omega(t) = \omega_0 + \Delta\omega \cos(\Omega t) \tag{4.52}$$

This technique is known as Frequency Modulation. In the literature, it is usually referred a **Frequency Modulation if Ω is in the range of MHz**, while it is known as **Wavelength Modulation if Ω < 100 kHz**.

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Frequency modulation

In the case of **small absorptions**:

$$I_T(\omega) = I_0[1 - \alpha(\omega)x] \tag{4.53}$$

Since the absorption coefficient is a function of frequency:

$$\alpha(\omega) \propto \frac{\left(\frac{\gamma}{2}\right)^2}{(\omega-\omega_0)^2+\left(\frac{\gamma}{2}\right)^2} \tag{4.54}$$

If $\frac{\Delta\omega}{\omega_0} \ll 1$, a **Taylor expansion around the central frequency ω_0 can be performed**, with the addiction of a contribution α_0 that does not depend, or weakly depends, on the frequency of the laser (for example, absorption by optical surfaces) such that it can be considered constant:

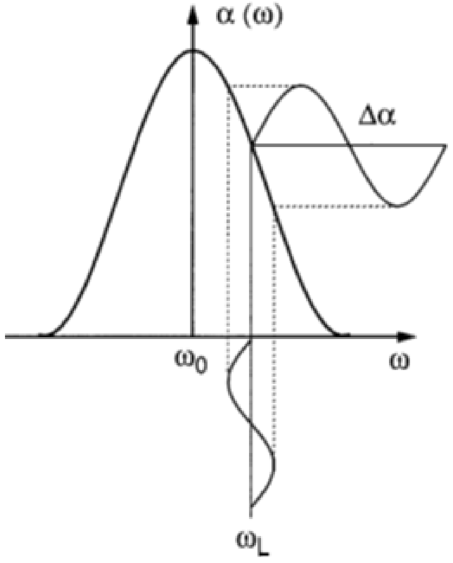
$$\alpha[\omega(t)] = \alpha_0 + \left.\frac{\partial\alpha}{\partial\omega}\right|_{\omega=\omega_0} \Delta\omega\cos(\Omega t) + \frac{1}{2}\left.\frac{\partial^2\alpha}{\partial\omega^2}\right|_{\omega=\omega_0} (\Delta\omega)^2\cos^2(\Omega t)+\ldots \tag{4.55}$$

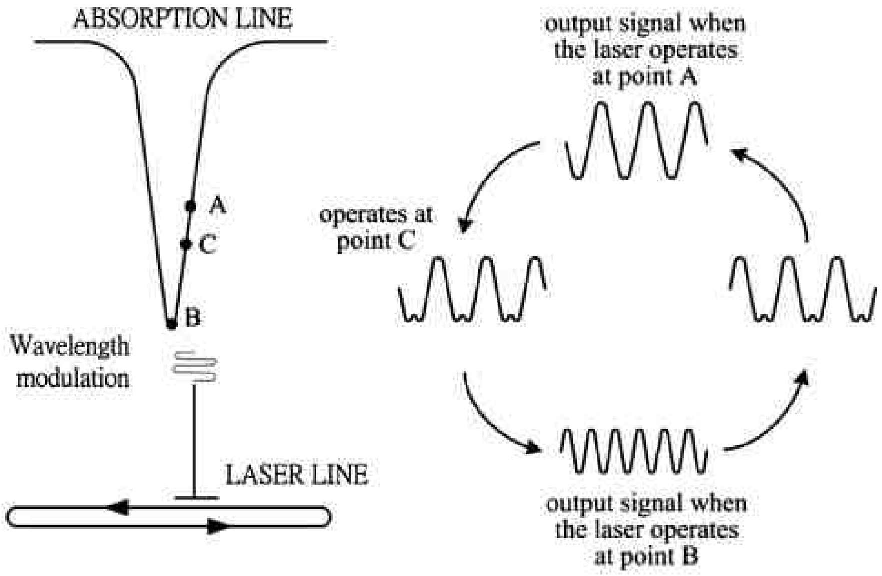
4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Frequency modulation

Inserting $I_0(t)$ (Eq. 4.51) and the Taylor series expansion of $\alpha[\omega(t)]$ into the Lambert-Beer law for small absorptions, we get:

$$I_t(t) = [I_{DC} + \Delta I cos(\Omega t)]\left[1 - L\left(\alpha_0 + \left.\frac{\partial\alpha}{\partial\omega}\right|_{\omega=\omega_0} \Delta\omega\, cos(\Omega t) + \frac{1}{2}\left.\frac{\partial^2\alpha}{\partial\omega^2}\right|_{\omega=\omega_0} (\Delta\omega)^2\, cos^2(\Omega t) + \ldots\right)\right] \tag{4.56}$$





4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Frequency modulation

By developing the product, you get:

$$\begin{aligned} I_t(t) &= I_{\mathrm{DC}} - L I_{\mathrm{DC}} \alpha_0 - L I_{\mathrm{DC}} \left.\frac{\partial \alpha}{\partial \omega}\right|_{\omega=\omega_0} \Delta\omega \cos(\Omega t) \\ &- L I_{\mathrm{DC}} \frac{1}{2} \left.\frac{\partial^2 \alpha}{\partial \omega^2}\right|_{\omega=\omega_0} (\Delta\omega)^2 \cos^2(\Omega t) + \Delta \mathrm{I} \cos(\Omega t) - \mathrm{L} \alpha_0 \Delta \mathrm{I} \cos(\Omega t) \\ &- L \Delta \mathrm{I} \Delta\omega \left.\frac{\partial \alpha}{\partial \omega}\right|_{\omega=\omega_0} \cos^2(\Omega t) + O[\cos^3(\Omega t)] \end{aligned} \tag{4.57}$$

We observe that the intensity transmitted has three types of contribution:

- one not dependent on the frequency Ω
- one proportional to $\cos(\Omega t)$
- one proportional to $\cos^2(\Omega t)$

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Frequency modulation

If we acquire the only spectral component at the frequency Ω of the signal $I_t(t)$ and suppose we filter all the others, we will have that:

$$I_t(t)|_{cos\Omega \mathrm{t}} = \Delta \mathrm{I}(1-\mathrm{L})\alpha_0 - L I_{\mathrm{DC}} \Delta\omega \left.\frac{\partial\alpha}{\partial\omega}\right|_{\omega=\omega_0} \tag{4.58}$$

By linearly varying i_{DC} to spectrally scan the absorption line, we will have that $I_t(t)|_{cos\Omega \mathrm{t}}$ will consists of two contributions:

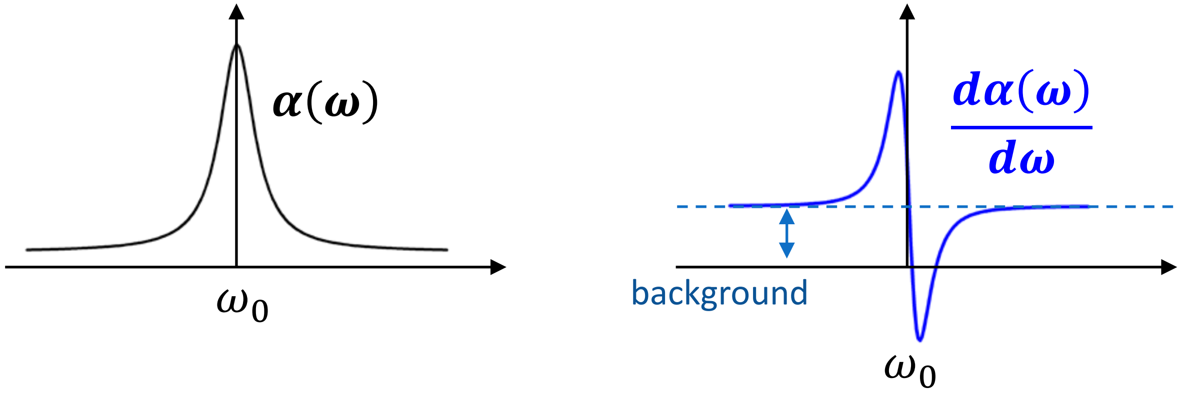
- a constant contribution, $\Delta \mathrm{I}(1-\mathrm{L})\alpha_0$, not dependent on the shape of the absorption line,
- a constant contribution proportional to the derivative before the absorption line.

This technique is known as **wavelength modulation and 1f detection**, as you **acquire the signal at the same frequency at which you modulate it.**

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Frequency modulation

Assuming a Lorentzian lineshape, $I_t(t)|_{cos\Omega t}$:



Working in these conditions, there are **three major disadvantages**:

1. The acquired **line shape is heavily distorted**
2. It is **not background-free**, which means that post-processing techniques must be adopted to remove the contribution due to the background
3. Once the background contribution is removed, $\boldsymbol{I_t(t)|_{cos\Omega t} = 0}$ **at the maximum absorption**. This is not particularly useful for extracting information about the concentration of the absorbent gas.

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Frequency modulation

Let's consider the **components of $I_t(t)$ proportional to $\cos^2(\Omega t)$.**

From the trigonometry, we know that $cos^2(\Omega t) = \frac{1+\cos(2\Omega t)}{2}$, so $\mathbf{cos^2(\Omega t)}$ **-component are proportional to the first harmonic (2Ω)**.

Therefore, **if we modulate the current of a laser diode at Ω, $\mathrm{I_t(t)}$ will have components at the fundamental and components at the first harmonic.**

If we acquire only the components at the first harmonic, going to filter the fundamental ones, the signal be in the form of:

$$I_t(t)|_{cos2\Omega\mathrm{t}} = -L\Delta \mathrm{I}\Delta\omega \left.\frac{\partial\alpha}{\partial\omega}\right|_{\omega=\omega_0} - LI_{\mathrm{DC}}(\Delta\omega)^2 \frac{1}{2}\left.\frac{\partial^2\alpha}{\partial\omega^2}\right|_{\omega=\omega_0} \tag{4.59}$$

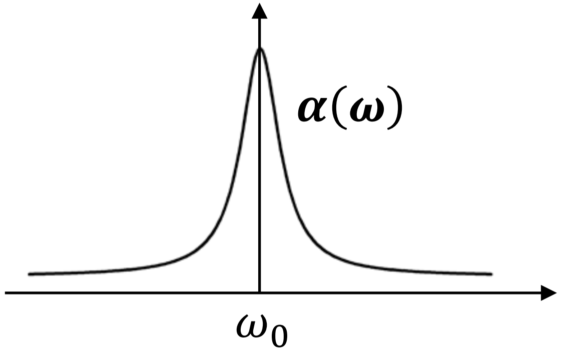
4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

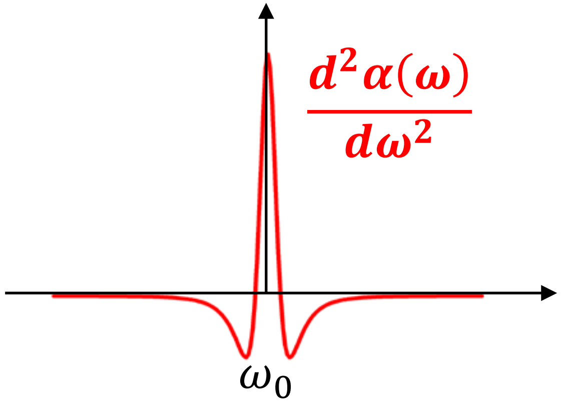
Frequency modulation

By scanning the absorption line of the absorbing gas, $I_t(t)|_{cos2\Omega t}$ will have two contributions: one proportional to the first derivative of the lineshape and the other one proportional to the second derivative.

This technique is known as **wavelength modulation and 2f detection**: the **laser is modulated at a frequency Ω and the signal acquired at the first harmonic 2Ω**.

Assuming that the absorption lineshape is Lorentzian one, the second derivative will have this form:



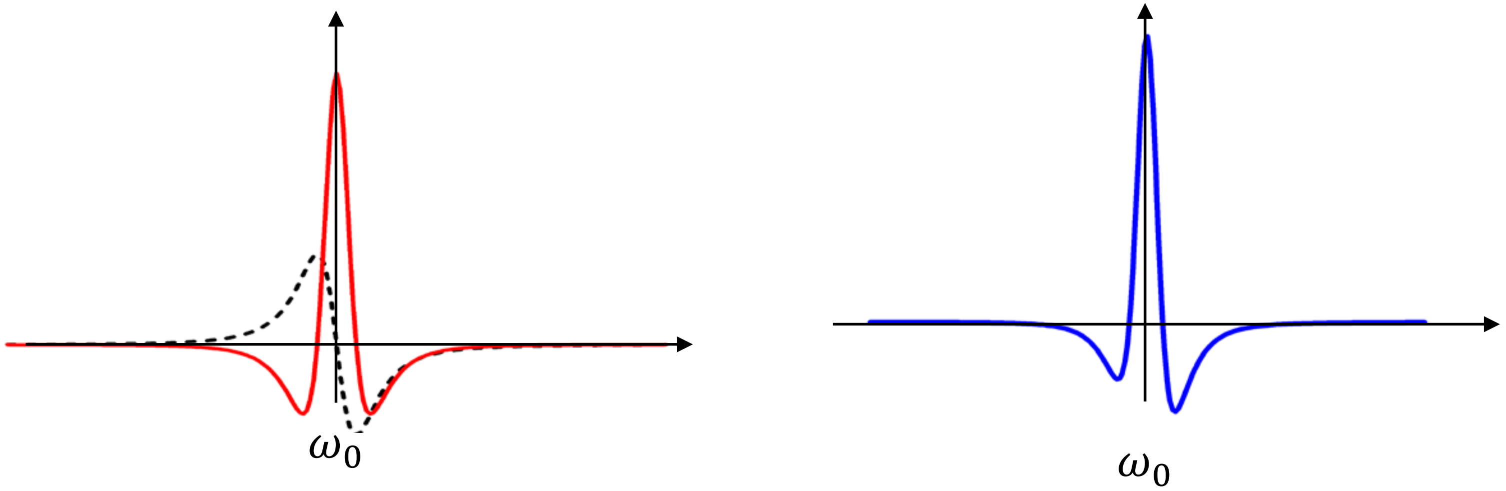


- The central peak is at the maximum of the absorption
- there are two symmetrical lobes of opposite sign on two sides with respect to the central peak, no background

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Frequency modulation

Adding the **contribution due to the first derivative**, it is easy to verify that the resulting effect will be to **make the two lateral lobes asymmetrical**, without altering the intensity of the central peak, since the first derivative before a Lorentzian function is zero at the maximum absorption, and changes sign depending on the side.



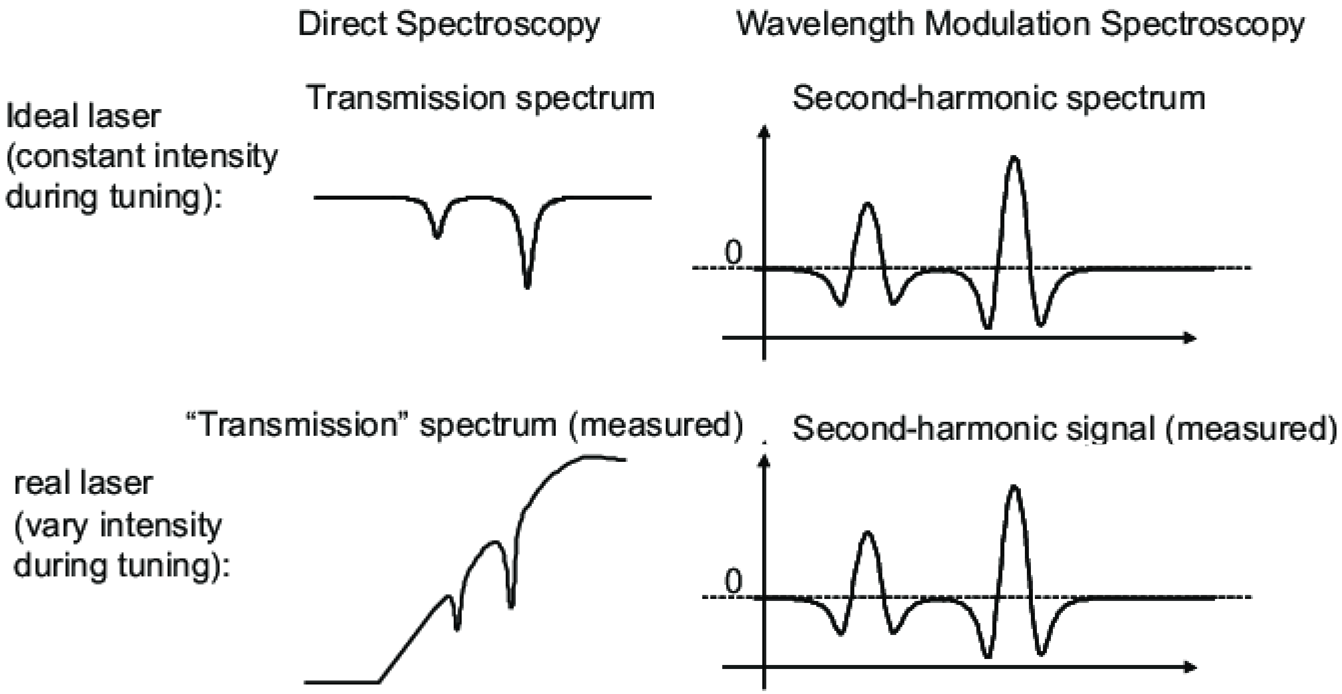
For this reason, the contribution due to the first derivative is known as **Residual Amplitude Modulation (RAM).**

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Frequency modulation

In conclusion, working in wavelength modulation and **2f detection alters the shape of the absorption** line, but **the maximum signal is still at the maximum absorption**.

The **great advantage lies in the fact that the technique is background-free**, eliminating all the inconvenient introduced in post-processing to remove the background contribution from the signal.



4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Lock-in detection

Working in amplitude or frequency modulation requires that the signal acquired by the photodetector is sent to a spectrum analyzer to extract the desired component (the fundamental or the first harmonic).

Spectrum analyzers are expensive and require complex computational processing, based on the Fourier transform. The same functions of filtering a single component from an analog signal can be performed using a **lock-in amplifier**.

A lock-in amplifier is an instrument used for the analysis of AC signals of low intensity, up to nV or characterized by high background noise, which can sometimes be even higher than the intensity of the signal itself.

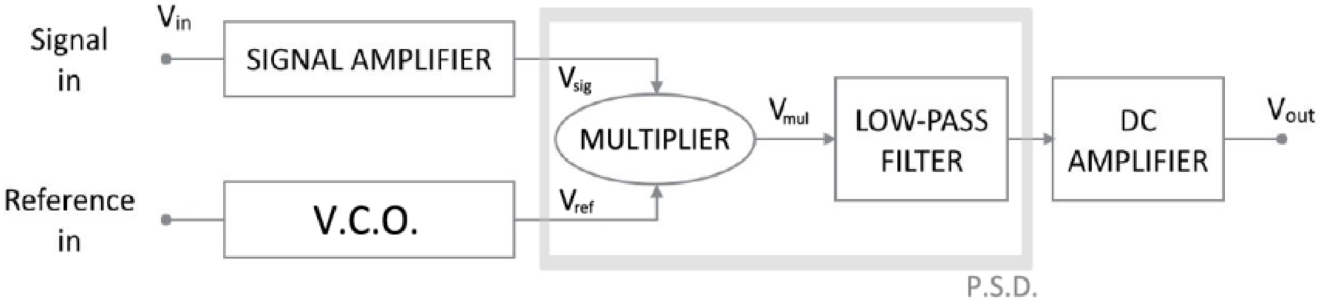
The principle of operation is based on the extraction from the input signal, typically noisy, only the component with the desired frequency and phase, going to filter the remaining components, whose contribution of noise is then canceled. The technique is therefore called **Phase-Sensitive Detection (PSD)** and allows to measure the amplitude of the only desired component.

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Lock-in detection

The typical structure of a lock-in amplifier consists of:

- **Voltage Controlled Oscillator (V.C.O.)**: Typically, an oscillator, or waveform generator, adjustable in frequency and phase and used to generate the reference signal (in commercial amplifiers it is usually integrated).
- **Phase-Sensitive Detector (P.S.D.)**: composed of the multiplier of electrical signals (Multiplier) and the low-pass filter with adjustable threshold;
- **DC amplifier**: DC signal amplifier used to amplify the output signal from the PSD in a controlled way.



4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Lock-in detection

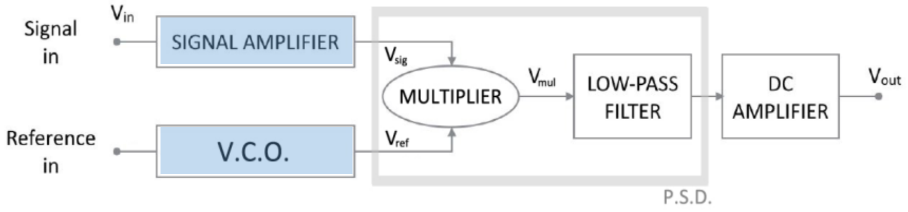
To evaluate the principle of operation of the PSD, the heart of the lock-in technique, let us consider the **reference signal $\mathbf{V_{ref}}$** as a periodic signal that can be represented as a sine wave of frequency Ω_{ref}

$$V_{ref} = A_{ref} cos\left(\Omega_{ref} t + \varphi_{ref}\right) \qquad (4.60)$$

and the **signal to be measured $\mathbf{V_{sign}}$** as:

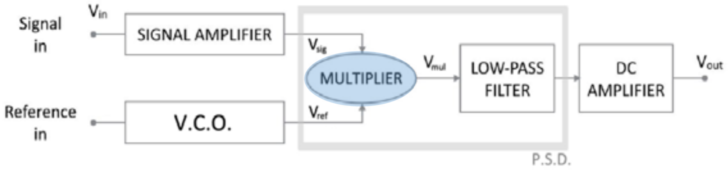
$$V_{sig} = A_{sig} cos\left(\Omega_{sig} t + \varphi_{sig}\right) + \sum_{\Omega_{noise}} A_{noise} cos(\Omega_{noise} t + \varphi_{noise}) \qquad (4.61)$$

which can be expanded in the Fourier series as the **superposition of a sinusoidal signal** at the frequency Ω_{sig}, to be extracted, **with all the other spectral components** that are the background noise to be subtracted.



4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Lock-in detection



The signals V_{ref} and V_{sig} are then multiplied each other:

$$V_{ref} \times V_{sig} =$$

$$A_{ref} A_{sig} cos\left(\Omega_{ref} t + \varphi_{ref}\right) cos\left(\Omega_{sig} t + \varphi_{sig}\right) +$$

$$A_{ref} cos\left(\Omega_{ref} t + \varphi_{ref}\right) \sum_{\omega_{noise}} A_{noise} cos\left(\Omega_{noise} t + \varphi_{noise}\right) \qquad (4.62)$$

Using the **trigonometric relation** $cos\alpha \cdot cos\beta = \frac{1}{2}[\cos(\alpha + \beta) + \cos(\alpha - \beta)]$:

$$V_{ref} \times V_{sig} =$$

$$\frac{1}{2} A_{ref} A_{sig} \left\{\cos\left[\left(\Omega_{sig} + \Omega_{ref}\right)t + \left(\varphi_{sig} + \varphi_{ref}\right)\right] + \cos\left[\left(\Omega_{sig} - \Omega_{ref}\right)t + \left(\varphi_{sig} - \varphi_{ref}\right)\right]\right\} +$$
$$\frac{1}{2} A_{ref} \left\{\sum_{\omega_{noise}} A_{noise} \left[\cos\left[\left(\Omega_{ref} + \Omega_{noise}\right)t + \left(\varphi_{ref} + \varphi_{noise}\right)\right] + cos\left[\left(\Omega_{ref} - \Omega_{noise}\right)t +\right.\right.\right.$$
$$\left.\left.\left.\left(\varphi_{ref} - \varphi_{noise}\right)\right]\right]\right\} \qquad (4.63)$$

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Lock-in detection

The final result at the output of the **low-pass filter** $(\Omega_{sig} - \Omega_{ref} = 0)$ will be:

$$V_{PSD} = \frac{1}{2} A_{ref} A_{sig} \cos\left(\varphi_{sig} - \varphi_{ref}\right) + \frac{1}{2} A_{ref} A_{noise} \cos\left(\varphi_{ref} - \varphi_{noise}\right) \quad (4.64)$$

As a result, **the system is sensitive to the phase difference between the signal to be measured and the reference signal**. In addition, the generated signal $\boldsymbol{V_{PSD}}$ **is affected only by the noise component at the reference frequency**.

By knowing the amplitude of the reference signal (A_{ref}) it is possible to retrieve the A_{sig} measurement; in addition, it is possible to determine the phase of the signal with respect to the reference.

Thus, the **output of the lock-in amplifier** will be:

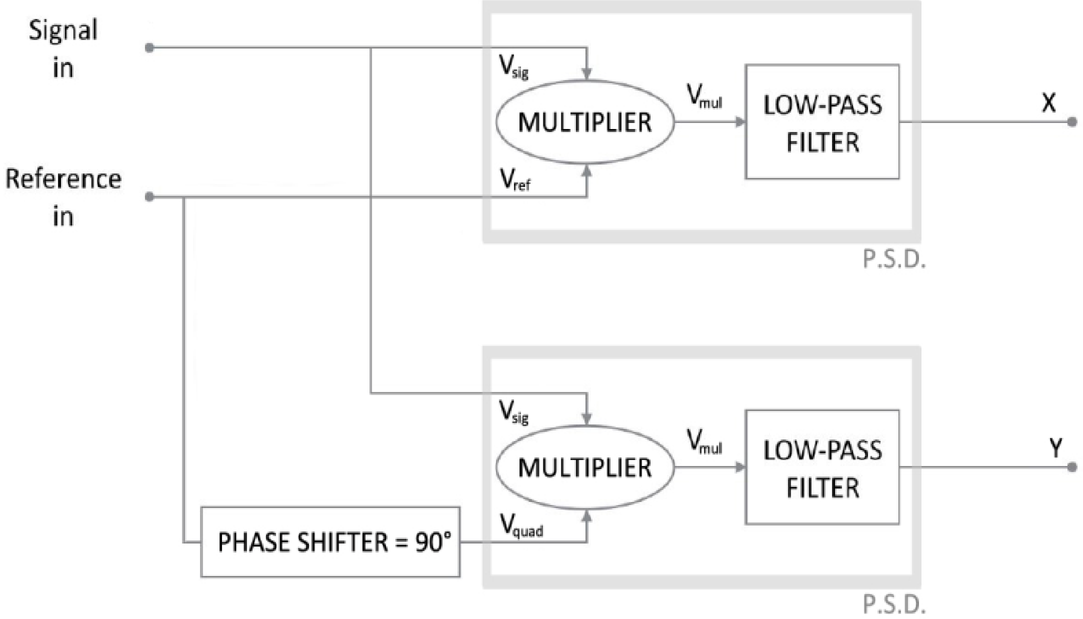
$$\boldsymbol{V_{out} \propto A_{sig} cos\varphi} \quad (4.65)$$

where $\varphi = \varphi_{sig} - \varphi_{ref}$

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Lock-in detection

This dependence on the phase difference between the two signals can be eliminated by **using a dual-phase lock-in amplifier.**



A dual-phase lock-in has an additional PSD that measures the quadrature component of the signal , i.e. the signal component at 90° compared to that measured by the first channel.

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Lock-in detection

In this way, **simultaneous measurement of the amplitude and phase of the signal is possible**. Assuming then that the quadrature component has the form:

$$V_{quad} = A_{quad} cos\left(\Omega_{ref}t + \varphi_{ref} + \frac{\pi}{2}\right) \qquad (4.66)$$

Repeating the same steps made previously, the output signal from the second PSD will be:

$$V_{quad} \times V_{sig} =$$

$$\frac{1}{2}A_{sig}A_{quad}\left\{\cos\left[\left(\varphi_{sig} - \varphi_{ref} + \frac{\pi}{2}\right)\right]\right\} + \frac{1}{2}A_{quad}A_{noise}\left\{\cos\left(\varphi_{ref} - \varphi_{noise} + \frac{\pi}{2}\right)\right\} =$$

$$\frac{1}{2}A_{sig}A_{quad}\{\mathrm{sen}(\varphi_{sig} - \varphi_{ref})\} + \frac{1}{2}A_{quad}A_{noise}\{\mathrm{sen}(\varphi_{ref} - \varphi_{noise})\} \qquad (4.67)$$

4.3 FUNDAMENTALS OF ABSORPTION SPECTROSCOPY

Lock-in detection

At the output of the low-pass filter the overall signal will be:

$$V_{PSD2} = \frac{1}{2} A_{quad} A_{sig} \operatorname{sen}(\varphi_{sig} - \varphi_{ref}) + \frac{1}{2} A_{quad} A_{noise} \operatorname{sen}(\varphi_{ref} - \varphi_{noise}) \qquad (4.68)$$

Finally, at the **output of the dual-phase lock-in amplifier**, neglecting the contribution of noise, two signals are obtained:

$$\begin{gathered} X \propto A_{sig} \cos\varphi \\ Y \propto A_{sig} \operatorname{sen}\varphi \end{gathered} \qquad (4.69)$$

the first is called a **in-phase signal**, since it is maximized when the phase difference φ is zero, while the second represents the **quadrature component**. The, the amplitude R of the signal and the phase φ can be easily calculated by using the relations:

$$R = \sqrt{X^2 + Y^2} \propto A_{sig} \;\; ; \;\; \varphi = arctg\left(\frac{Y}{X}\right) \qquad (4.70)$$

R is proportional to the amplitude of the component Ω_{sig} of the acquired signal.