7.Mechanical broadening of the spectral line

When a radiation falls on a certain atom, it will deal with it not at one wavelength or at one frequency but with a spectral distribution given by the function $\mathbf{g}(\Delta\boldsymbol{\omega})$

Also, when the atom moves from an energy level to another energy level that does not emit or absorb one wavelength or frequency, but a narrow band of frequencies is usually described as a function that gives the spectral pattern of emission or absorption. The shape of the spectral line and the causes of broadening are not different, whether resulting from emission or absorption.

The broadening of the spectral line can be classified into two main forms:

1. Homogeneous broadening
2. Heterogeneous broadening

Below are three different processes that cause the broadening of the spectral line and represent models for both types of broadening. These combined processes give a spectral line with a specific width centered on the transfer frequency $\boldsymbol{v_0}$ called the resonant frequency. Where the spectral line width is usually determined by the width of the shape at the point where the transition intensity drops to half of its value i.e. $\boldsymbol{I = \frac{1}{2} I_0}$

This range ($\Delta\boldsymbol{v_0}$) is called the full width at half maximum (FWHM). Fig (1-6) shows the spectral line intensity as a function of the frequency due to the emission and absorption.

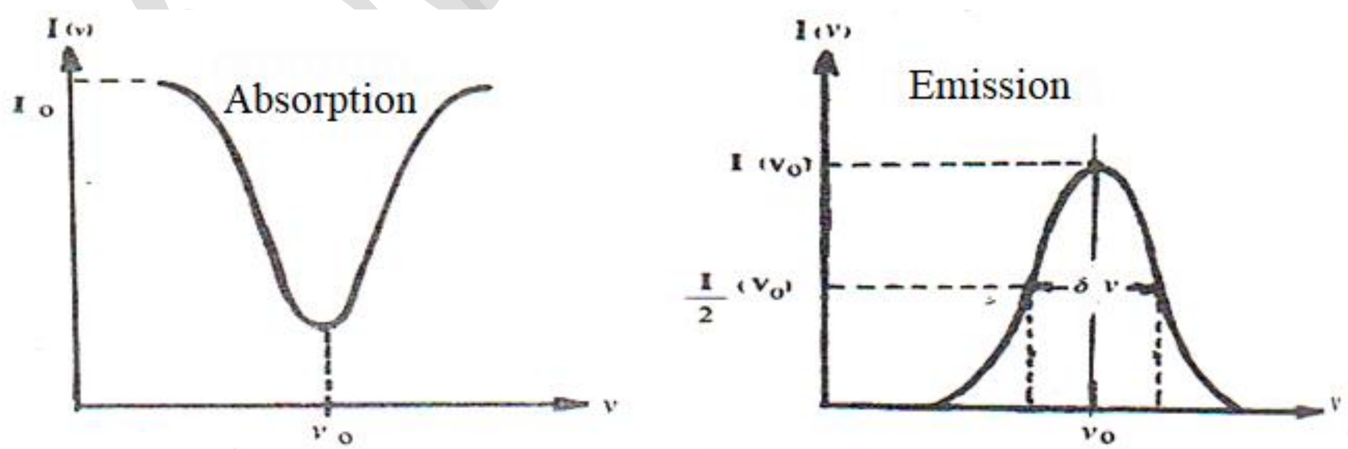

Fig (1-6)

7.1 Natural Broadening

It represents a homogenous broadening and occurs as a result of the limited life time of the energy levels τ_2 , τ_1, which is related to the transition process. The energy level can not take a specific energy value E_2 but in fact it has a narrow distribution of energy centered around this value (usually described as ΔE) according to the uncertainty principle

$$\Delta \boldsymbol{E}\ .\ \Delta \boldsymbol{t} \approx \hbar$$

$$\Delta \boldsymbol{E} \approx \frac{\hbar}{\Delta \boldsymbol{t}}$$

Where $\Delta \boldsymbol{t}$ represents a probability at the time of finding the atom at the energy level E and this probability is measured by the average life time of that level τ. The frequency $\Delta \boldsymbol{v}$ is associated with the energy distribution $\Delta \boldsymbol{E}$ by

$$\Delta \boldsymbol{E} = \boldsymbol{h}\, \Delta \boldsymbol{v}$$

$$\therefore \quad \frac{h}{2\pi\ \Delta \boldsymbol{t}} = \boldsymbol{h}\, \Delta \boldsymbol{v} \therefore \frac{\hbar}{\Delta \boldsymbol{t}} = \boldsymbol{h}\, \Delta \boldsymbol{v} \qquad \boldsymbol{but} \quad \hbar = \frac{h}{2\pi}$$

$$\boxed{\Delta \boldsymbol{v_0} = \frac{\mathbf{1}}{\mathbf{2}\boldsymbol{\pi}\ \boldsymbol{\tau}}}$$

$\Delta \boldsymbol{v_0}$ represents the total line width at FWHM as shown in Fig(1-7), where the natural broadening of the spectral line (has frequency $\boldsymbol{v_0}$) between the energy level E_1 and E_2 as follows:

$$\Delta \boldsymbol{v_0} = \Delta \boldsymbol{v_1} + \Delta \boldsymbol{v_2} = \frac{\mathbf{1}}{\mathbf{2}\boldsymbol{\pi}\ \boldsymbol{\tau_1}} + \frac{\mathbf{1}}{\mathbf{2}\boldsymbol{\pi}\ \boldsymbol{\tau_2}}$$

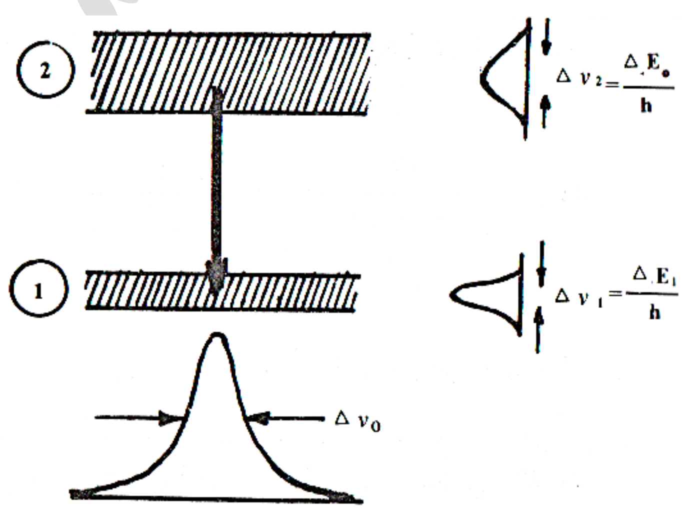

Fig (1-7)

Example 3:

Calculate natural broadening of the red neon line with a 632.8 nm wavelength (in the helium-neon laser) between the energy levels $3s_2$ ($\tau_2 = 19.6\, n\, sec$) and $3p_4$ ($\tau_1 = 18.7\, n\, sec$).

Solution:

$$\Delta v_0 = \frac{1}{2\pi\ \tau_1} + \frac{1}{2\pi\ \tau_2} = \frac{1}{2 \times 3.14 \times 18.7 \times 10^{-9}} + \frac{1}{2 \times 3.14 \times 19.6 \times 10^{-9}} = 16.6\ MHz$$

7.2 Collision Broadening

It is a homogeneous broadening to the spectral line caused by the collision of the radioactive or absorbed atom with neighboring molecules and atoms. For example, in the case of gas, the atom collides with other or similar atoms, or with neutral or charged particles, and even with the walls of the vessel that contains them.

The collision process, which has a very short time, affects the radiation and makes a sudden change in the phase (see Fig 1-8), which causes the broadening for spectral line. The width of the line is at the middle of the intensity.

$$\Delta v_0 = \frac{1}{\pi\ \tau_c}$$

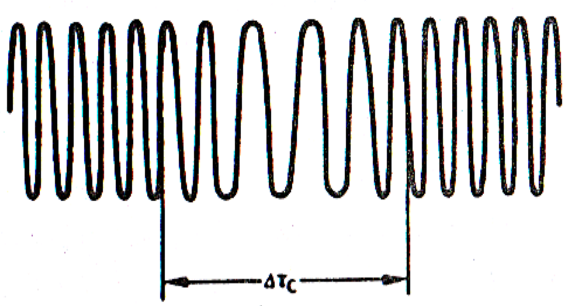

Fig: (1-8)

The collision time τ_c can be calculated from kinetic theory of gases by

$$\tau_c \cong \frac{(mkT)^{1/2}}{(8\pi)^{1/2}\, Pd^2}$$

Where P: gas pressure d: atom diameter (Molecule) T: absolute temperature m :particle mass

It is clear that the τ_c is inversely proportional to the pressure and therefore the line broadening Δv_0 is increased by increasing the gas pressure, The collision process also often causes the shift of the spectral line to be red (longer wave) or blue (shorter wave).

Example 4: Calculate the collision broadening at FWHM of a helium-neon laser, where the gas pressure is usually 0.67 milliard bar and the diameter d of neon atom about 2.7×10^{-10}meters. $\tau_c = 0.5 \times 10^{-6}$ **sec** at room temperature.

Solution : Inhomogeneous broadening

$$\text{MHz}\Delta v_0 = \frac{1}{\pi\ \tau_c} = 0.64$$

7.3 Doppler broadening

It is a heterogeneous broadening to the spectral line where the emission frequencies are distributed on a narrow scale centered around the v_0. The Doppler broadening is caused by the random movement of the atom that is moving towards the electromagnetic radiation or its opposite. Thus, the frequency at which the atom is exposed is more or less than v_0 according to the Doppler phenomenon.

$$v_0 = v(1 \mp \frac{V}{c})$$

Where V : speed of atom c: speed of light

$$\Delta v_0 = \frac{2v_0}{c}\ (\frac{2kT}{m}\ ln\ 2)^{1/2}$$

Where T: absolute temperature of the medium, K: Boltzmann constant, m: Mass of atom or molecule.

$$\mathbf{V}_P = \left(\frac{2kT}{m}\right)^{1/2} = \left(\frac{2RT}{M}\right)^{1/2}$$

Where $\mathbf{V_P}$**:** Speed Particle , ***R = 8.31 J · K^-1^ · mol^-1^*** universal gas constant and M : Molecular mass

$$\Delta v_0 = \frac{2v_0 V_p}{c} \; (\ln 2)^{1/2}$$

$$\Delta v_0 = 7.16 \times 10^{-7} \, v_0 \sqrt{\frac{T}{M}}$$

Example 5: Calculate the Doppler exposure of a Neon gas spectrometer at room temperature, noting that the waveform of the laser is 632.8 nm.

Solution :

$$\Delta v_0 = 1.3 \; GHz$$

If we compare this value to that resulting from natural and collision broadening, we find that Doppler exposure is the largest, but it becomes negligible at low temperatures (gas cooling), while collision broadening is greater at the high pressure of gas.

1. Energy levels of the molecule

A molecule is a structure consisting of two (or more) similar or different atoms. The total energy of the molecule consists of:

1. Electrons energy Ee: occupy the last unsaturated orbits. Transitions between levels are in the range between nearby infrared are extended to visible range as well as ultraviolet waves.
2. Vibration energy Ev: Transitions between levels are in the range of infrared waves
3. The rotational energy Er: The transitions between levels are in the range of microwaves.
4. Random transitions energy Et:

When studying the molecular spectrum, the first three energies are based on quantum laws, While kinetic energy is based on classical laws.

At room temperature of 300 Kelvin, Ee and Ev are much larger than KT. This means that the molecule in the equilibrium state takes the lowest level of oscillation.