

Electronics And Instrumentation

8th Semester

Subject: Analytical Instrumentation

Subject code: BT 808

Unit-3

Flame Photometers

3.2 Intensity of the Signal

The intensity of a signal depends on the population of the energy level from which the transition is originating and the probability of such a transition. You would recall from Unit 1 that according to the Boltzmann statistical distribution, the population of the ground state i.e., the number of species in the ground state is highest and it keeps on decreasing as we go to higher energy levels. In case of the atoms the population of any excited state relative to that of the ground state is given by the following formula.

$$\frac{N^*}{N_0} = \frac{g^*}{g_0} e^{-\frac{\Delta E}{kT}}$$
$$\text{Or } N^* = N_0 \frac{g^*}{g_0} e^{-\frac{\Delta E}{kT}}$$

where,

N^* and N_0 = Number of atoms in excited state and ground state, respectively,

ΔE = Energy difference between ground and excited state (in J),

g^* and g_0 = Statistical factors that depend on the degeneracies of the levels involved,

k = Boltzmann constant ($= 1.28 \times 10^{-23} \text{ J K}^{-1}$), and

T = Absolute temperature.

According to above Eq., after the ground state, the lowest energy excited state will be most populated and the population of the higher excited states would decrease progressively. Eq. can be used to determine the population of an excited state with respect to the ground state. Let us illustrate this with the help of an example.

Example 7.1

The characteristic yellow emission of sodium vapours consists of a pair of lines at 589 nm and 589.6 nm. These arise from the emission of radiation by the gaseous sodium atoms in the $3p$ excited state to $3s$ ground state. Compute the ratio of the sodium atoms in the excited state to the ground state.

Solution

As per Eq. 7.1 we have, $\frac{N^*}{N_0} = \frac{g^*}{g_0} e^{-\frac{\Delta E}{kT}}$

Therefore, to evaluate the ratio of the atoms in the excited state to that in the ground state we need to know the statistical factors g^* and g_0 and ΔE .

As the $3s$ and $3p$ levels have two and six quantum states i.e., the statistical factors are 2 and 6 respectively, the ratio of g^* and g_0 comes out to be $6/2 = 3$

The change in energy, ΔE , can be calculated by using the formula, $\Delta E = \frac{hc}{\lambda}$

$$\Delta E = \frac{6.626 \times 10^{-34} \text{ Js} \times 3.0 \times 10^8 \text{ ms}^{-1}}{589.3 \times 10^{-9} \text{ m}}$$

The wavelength is taken as an average of the two, i.e., $\left(\frac{589.0 + 589.6}{2} \right)$

$$\Delta E = 3.37 \times 10^{-19} \text{ J}$$

Substituting the value of ΔE in the above equation, we get the following.

$$\frac{N^*}{N_0} = \frac{6}{2} e^{-\frac{-3.37 \times 10^{-19} \text{ J}}{1.38 \times 10^{-23} \text{ JK}^{-1} \times 3000 \text{ K}}}$$

$$\frac{N^*}{N_0} = 3e^{\frac{-3.37 \times 10^{-19}}{4.14 \times 10^{-20}}} = 3e^{-8.08} = 3.096 \times 10^{-4}$$

You have learnt above that the intensity of a signal depends on the population of the level from which the transition originates and the probability of such a transition. These are the intrinsic parameters of the analyte being determined. In addition to these, the intensity of a signal does depend on an important external parameter, viz., the concentration of the analyte. This, in fact is the basis of quantitative aspect of the spectroscopic methods. Let us see how the intensity depends on the concentration of the analyte for an emission spectrum.

Intensity Concentration Relationship

The intensity of the emitted radiation (P) is proportional to the number of excited atoms N^* .

$$P \propto N^*$$

$$P = a. N^* \text{ (where } a \text{ is the proportionality constant)}$$

Again, from Eq. 7.1, we see that the number of atoms in the excited state, N^* , at a given temperature are proportional to N_0 . Therefore, we can write the following.

$$P = a. N_0 \frac{g^*}{g_0} e^{-\frac{\Delta E}{kT}} \text{ (as } N^* = N_0 \frac{g^*}{g_0} e^{-\frac{\Delta E}{kT}} \text{)}$$

$$P = K. N_0 \text{ (} K = a. \frac{g^*}{g_0} e^{-\frac{\Delta E}{kT}} \text{)}$$

$$P = K'. C \text{ (as, } N_0 \text{ is directly proportional to metal concentration)}$$

Thus, the intensity of the emitted light will be directly proportional to the concentration of the element introduced into the flame.

3.3 Spectral Line Width

The lines are generally symmetric around the λ_{max} , the wavelength at which the intensity of emitted radiation is maximum. The absorbance is also the maximum at the same wavelength. The **line width** is defined as the width of the signal measured at one half the height of the maximum signal. It is expressed as $D\lambda_{1/2}$ and is measured in the

units of wavelength. This full width is measured at one half of the maximum (*FWHM*) is also called as **effective line width**. Fig. 3 shows the schematic diagram defining the atomic line width. The line width resulting from a transition of an electron between two discrete, single valued energy states is expected to be zero.

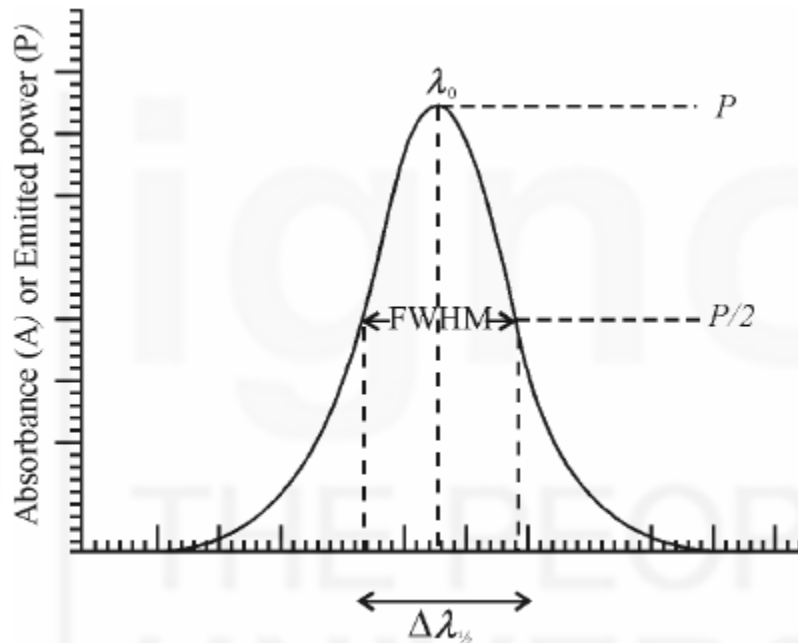


Fig. 3: A schematic diagram defining the atomic line width

You may be wondering that if the transitions leading to the atomic spectrum are amongst the discrete energy levels, then how do we get width or broadness in the signal? Your apprehension is quite justified. This ‘**finite**’ or the **natural width** of the atomic spectrum results from a number of phenomena. These are given below.

- **Uncertainty or Heisenberg broadening:** This arises due to the uncertainty in the energies of the excited state.
- **Collisional broadening:** It is due to the distortion of the outer energy levels arising as a consequence of the collision with other atoms.

- **Doppler broadening:** It is due to the shift in the frequencies of the emitted photon due to relative motion with respect to the detector. The details of these phenomena can be obtained from any of the standard text books on spectroscopy. Some of the books are listed at the end of the Block.