

Spectroscopy

Intensity of Spectral Lines:

The intensity of spectral line depends on three important factors. These are —

1. **Transition Probability** : Suppose a transition takes place between a pair of states i and j with wave function ϕ_i and ϕ_j , then transition probability is defined as,

$$R_{ij} = \int \phi_i \hat{A} \phi_j \delta\tau$$

The integral is called the transition moment integral and \hat{A} is an operator (electric dipole moment operator or magnetic dipole moment operator or polarizability operator). The transition probability can be calculated from knowledge of quantum mechanical wave function of the two states involved in the transition. Alternatively, we can use symmetry and predict whether the transition moment integral will be zero or not. Rules restricting transition between energy levels are called selection rules. Whenever $\hat{A} = 0$ is called forbidden transition because no transition is occurs in this condition and whenever $\hat{A} \neq 0$, then the spectral line will be strong and it will be allowed transition.

$\hat{A} = 0$, Forbidden transition

$\hat{A} \neq 0$, Allowed transition

2. **Population State**: If we have two levels from which transitions to third are equally probable, then obviously the most intense spectral line will arise from the level which initially has the greater population, There is simple statistical rule governing the population of a set of energy levels.

The population of any state can be calculated from the Maxwell-Boltzmann distribution formula —

$$n_j/n_i = e^{-\Delta E/kT}$$

when several states have same energy, the population increases correspondingly. Then, if g is the number of state with energy E_j and lowest energy level E_i is a single state, the ratio

$$n_j/n_i = g e^{-\Delta E/kT}, \text{ where } g \text{ is the degeneracy factor.}$$

3. **Path length of the sample**: Clearly if a sample is absorbing energy from a beam of radiation, the more sample the beam traverses the more energy will be absorbed from it. We might expect that twice as much sample would give twice the absorption, but a very simple argument shows that this is not so. Consider two identical samples of the same material, S_1 and S_2 , and assume that S_1 and S_2 alone absorb 50% of the energy falling on them, allowing the remaining 50% to pass through. If we pass a beam of initial intensity I_0 through S_1 , 50% of I_0 will be absorbed and the intensity of the beam leaving S_1 will be $(1/2)I_0$; if we then pass this beam through S_2 a further 50% will be absorbed, and $1/2 \times (1/2)I_0 = (1/4)I_0$ will be leave S_2 . Thus two 50% absorption in



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succession do not add up to 100% but only to 75% absorption. An exactly similar relationship exist between the concentration of a sample and the amount of energy absorption- a doubling of the concentration produces something less than a doubling of the absorption,

The relationship between concentration (c), path length (l), and the incident and transmitted intensities of radiation, (I_0 and I, respectively) can be expressed in many ways,, all based on the Lambert –Beer law, which is often written as :

$$I/I_0 = \exp(-kcl) \dots\dots\dots(1)$$

where k is a constant for the particular spectroscopic transition under investigation. To remove the inconvenience of using an exponential function, the above equation can be recast as:

$$I/I_0 = 10^{-\epsilon cl} = T, \dots\dots\dots(2)$$

where we have introduced the symbol T for transmittance, defined simply as the ratio I/I_0 : ϵ is called the molar absorption coefficient.

When spectroscopy used to measure concentration of material it is convenient to have a relationship which, unlike the above two equation, is linear in concentration. Inverting Eq.2 and taking logarithms we have:

$$I_0/I = 10^{\epsilon cl} \text{ or } \log(I_0/I) = \epsilon cl = A$$

Where we defined the important quantity A,, called the absorbance, or optical density. A is directly proportional to concentration and , because of its convenience in this respect, some spectrometer are constructed to record spectra directly in absorbance.