D.P.VIPRA P.G. COLLAGE BILASPUR CG

M.Sc. 1st Semester

Department of chemistry an assignment report

Spectroscopy unit - 01

Topic – intensities of spectral lines

Session : 2021-22

Guidance by

Deepak Tiwari

Topic :- INTENSITY OF SPECTRAL LINES

INTENSITY OF SPECTRAL LINES AND TRANSITION PROBABILITY

The intensity of spectral line can be determined by considering the three main factors.

1. The transition probability, i.e., the probability of a system in one state changing to another state.

2. The population, i.e., the number of atoms or molecules initially in the state from which the transition occurs.
3. Concentration or path length of the sample, i.e., the amount of material present giving rise to the spectrum.

1. Transition Probability.- Transition probability indicates the probability of transition between two given energy levels. Light can be absorbed or emitted if a change in the vibrational state is accompanied by a change in the dipole moment of the molecule. dipole transitions are the strongest transitions that account for most of the molecular and atomic spectroscopic transitions. Magnetic dipole transitions occur in magnetic resonance spectroscopy. The detailed calculation of absolute transition probabilities involves precise quantum mechanical wave functions of the two states between which the transition occurs.

Quantum Mechanical Expression for the Calculation of Transition Probability.

(i) Consider transition probability for electric dipole transitions. The probability for absorption of radiation for a transition to take place from state m to state n is proportional to the number of photons with frequency Vmn The number of photons is proportional to the radiation density U(v mn). The rate of absorption is given by

$$N_m \; B_{mn} \; U(\nu_{mn})$$

(ii) where Nm is the number of molecules in the state m and Bmn is a proportionality constant known as Einstein's coefficient for induced (or stimulated) absorption, which is given as

$$B_{mn} = \frac{8\pi^2}{3h^2}\left(\int \psi_n \, \mu \, \psi_m \, d\tau\right)^2$$

(iii) where is the molecular electric dipole moment operator. The absorption intensity of a transition can thus be obtained from a consideration of the possible non-zero values of Ban Integrals represented below are known as transition moment integrals

$$[\mu] = \left[\int_{-\infty}^{+\infty} \psi_n \, \mu \, \psi_m \, d\tau\right]$$

(iv) Hence the probabilities of the electric dipole induced transitions between the vibrational states Wm and wn of the same electronic state of a polyatomic molecule are proportional to the square of the magnitude of the appropriate transition moment integral, that is,

$$\left(\int_{-\infty}^{+\infty} \psi_n \, \mu \, \psi_m \, d\tau\right)^2$$

The integration is carried over the entire range of nuclear coordinates. The integral represents charge migration during the transition. Same expression can be written for each of the three Cartesian components of the dipole moment vector.

$$[\mu_x]_{mn} = \int \psi_m \mu_x \psi_n \, d\tau$$

$$[\mu_y]_{mn} = \int \psi_m \mu_y \psi_n \, d\tau, \quad [\mu_z]_{mn} = \int \psi_m \mu_z \psi_n \, d\tau$$

These three equations can be shown more simply as

$$[\mu] = \int \psi_m \mu \psi_n \, d\tau$$

where [u] is the expectation value and u is the dipole moment operator. At a much lower level of sophistication, it is often possible to decide whether a particular transition is forbidden or allowed (i.e., whether the transition probability is zero or non-zero). This process is essentially the deduction of selection rules, which allow us to decide between which levels transitions will give rise to spectral lines.

The quantum mechanical formulation of the selection rule is that if a molecule undergoes a transition from a vibrational state m to a vibrational state n, light can only be absorbed or emitted if the integral,

$$[\mu] = \int_{-\infty}^{+\infty} \psi_m \mu \psi_n \, d\tau \text{ is not equal to zero}$$

A transition is forbidden if [u]= 0. This is the basic infrared selection rule. Thus the transition moment determines the intensity of the absorption (or emission) of radiatio A transition is allowed, i.e., the integral is non-zero, if the direct product of the fact defining the transition moment contains the totally symmetric representation and s forbidden otherwise. Also transitions will be allowed if the following factors have a appreciable symmetry relationship.

(a) Geometry of the molecule or orbital in the ground and excited
(b) Orientation of the electric dipole of the incident light that might induce t transition.

Thank You