Unit 6.2 Rotational, Vibrational and Raman Spectroscopy (Marks 20)

Rotational spectra of diatomic molecules – rigid rotator concept – determination of bond length – effect of isotopic substitution – spectra of non-rigid rotator. Vibrational spectra of diatomic molecules – harmonic and anharmonic oscillator model – Morse potential - calculation of force constants – effect of isotope - vibrations of polyatomic molecules, overtone and combination bands (H_2O, CO_2). Diatomic vibrating rotor – vibration rotation spectrum of CO. Principle of Raman spectroscopy – rotational and vibrational Raman spectra of linear molecules – rule of mutual exclusion.

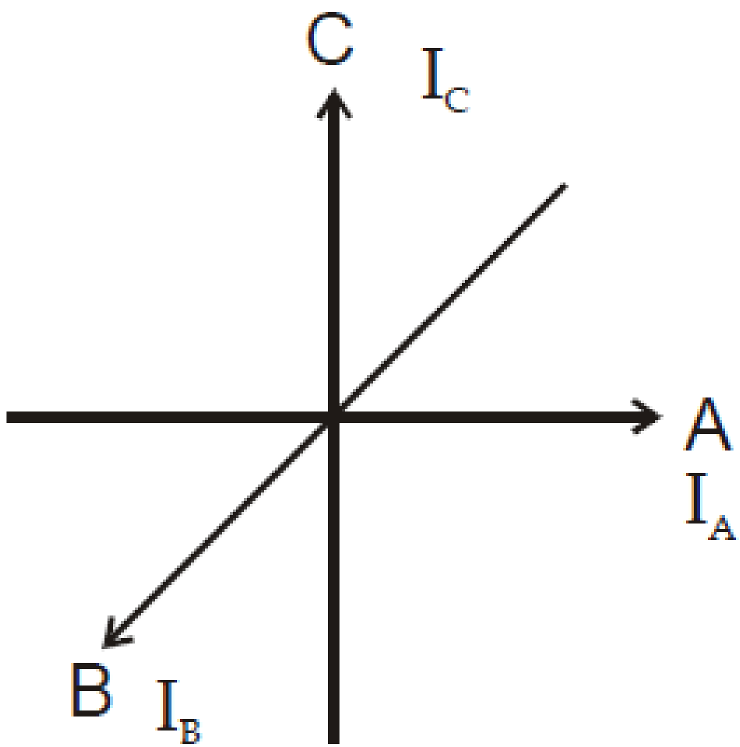
Structure elucidation by IR spectroscopy – finger print region and group frequencies – effect of hydrogen bonding (alcohol, keto-enol) and coordination to metal.

Classification of Molecules

Spectroscopy in the microwave region is concerned with the study of pure rotational motion of molecules. The condition for a molecule to be microwave active is that the molecule must possess a permanent dipole moment, *for example, HCl, CO etc. The* rotating dipole then generates an electric field which may interact with the electrical component of the microwave radiation. Rotational spectra are obtained when the energy absorbed by the molecule is so low that it can cause transition only from one rotational level to another within the same vibrational level. Microwave spectroscopy is a useful technique and gives the values of molecular parameters such as bond lengths, dipole moments and nuclear spins etc.

Classification of Molecules

The rotation of a three dimensional body may be quite complex and it is convenient to resolve it into rotational components about three mutually perpendicular direction through the centre of gravity - the principal axes of rotation. Thus a body has three principal moments of inertia, one about each axis, usually disignated I_A, I_B and I_C.



Classification of Molecules

Polyatomic molecules are broadly divided into four classes:

(i) Linear Molecules

(ii) Spherical Top Molecules

(iii) Symmetric Top Molecules

(iv) Asymmetric Top Molecules

Classification of Molecules

1. Linear molecules

As the name suggests, in this case, all the atoms of the molecules are arranged in a straight line. Some of the molecules of this category are HCl, CO2, OCS, HCN, C2H2 etc. The three directions of rotation may be taken as

(a) about the bond axes

(b) end-over-end roation in the plane of the paper and

(c) end-over-end rotation at right angles to the plane. As the nuclei of the atoms which give the main contribution to the mass are situated in the axis A, the moment of inertia about this axis is approximately zero. *i.e.* $I_A = 0$. *The moments of inertia* I_B *and* I_C correspond to the end- over-end rotation of the molecule and therefore they are equal. Thus, for a linear molecule $I_A = 0$ and $I_B = I_C$.

Classification of Molecules

2. Symmetric tops

In a symmetric top, two of the principal moments of inertia are equal and all the three are non zero. Examples CH_4, CH_3Cl etc in which the carbon has a tetrahedral coordination. The C–Cl bond axis (in CH_3Cl) having a three fold axis of symmetry in the A-axis and on this the centre of gravity of the molecules lies. The two mutually perpendicular B and C axis lie in a plane perpendicular to the A-axis. It is obvious $I_B=I_C$. A molecule of this type spinning about the A-axis resembles a spinning top and hence the name symmetric top. The molecule in this class are further subdivided into the groups prolate symmetric top and the oblate symmetric top. In prolate $I_B = I_C > I_A$ (e.g. CH_3Cl, CH_3F, CH_3CN, NH_3 etc.) and in oblate $I_B = I_C < I_A$ (e.g. BF_3, BCl_3 etc.)

Classification of Molecules

3. Spherical tops

When all the three principal moments of inertia of a molecule are equal, it is called a spherical top (e.g. CH4, OsO4, SF6, CCl4 etc.) *i.e.* $I_A = I_B = I_C$

4. Asymmetric tops

These molecules, to which the majority of substance belong, have all three moments of inertia different is $I_A \neq I_B \neq I_C$. Some of the example are H2O, CH3OH, CH2 = CHCl etc.

Classification of Molecules