1.1 Origin of microwave spectrum.

Spectroscopy in the region of wavelengths of a few cm to a few mm has been usually referred to as 'Microwave Spectroscopy'. In recent years the techniques of microwave spectroscopy have been widely applied for the determination of molecular parameters and also to derive a variety of other associated information. The advantages in this branch of spectroscopy are the great sensitivity and resolution of electronic apparatus that are used. The radiation under observation is always polarised owing to the very nature of its generation. This is an additional facility.

Broadly speaking, a microwave spectrum may be atomic or molecular in origin. Atomic microwave spectra are rare. When present, as in the case of hydrogen, they originate from the energy differences of the many fine and hyperfine structures of the electronic energy levels. When molecular in origin, microwave spectra may be due to any of the three reasons given below:

(a) Inversion in a molecule capable of existing in two mirror-image structures with nearly equal energy in either position.

(b) Existence of a permanent magnetic dipole moment of a molecule.

(c) Rotation of the molecule either as a whole (pure rotation) or as one part of the molecule relative to another (internal rotation).

Some molecules are structurally asymmetric but possess two equilibrium mirror-image positions. They will spontaneously pass from one equilibrium position to the other. So far only NH_3 (and its isotope substituted derivatives) has been observed to give a microwave inversion spectrum. However, it has importance of giving high intensity lines and also of being historically studied first.

Some molecules do not have any net electric dipole moment but have, on the other hand, a non-zero magnetic dipole moment. Such a case is not common but, if it occurs, the molecule interacts with the incoming electromagnetic field through its magnetic dipole moment. So far only oxygen has been observed to give a microwave spectrum by virtue of magnetic dipole moment. It gives both non-resonant and resonant lines. The former is due to pure rotational transition, whereas the latter is believed to be due to fine structure in a rotational level arising from interaction between overall rotation and electronic spin momentum.

Lines of microwave transition due to molecular rotation largely outnumber those due to the other two reasons. In general, if a molecule has high enough moments of inertia it is likely to have a low frequency spectrum and a part occasionally falls in the microwave region. There have been detailed studies of molecular microwave spectra due to either overall rotation of the molecule or due to internal rotation.

1.2 Diatomic and Linear Polyatomic Molecules.

For a diatomic molecule, the frequencies of rotational transition can be approximately given by a formula of the type

$$\nu = 2B(J+1) - 4D(J+1)^3, \quad . \quad . \quad . \qquad (1.1)$$