Rotational Spectroscopy

Introduction

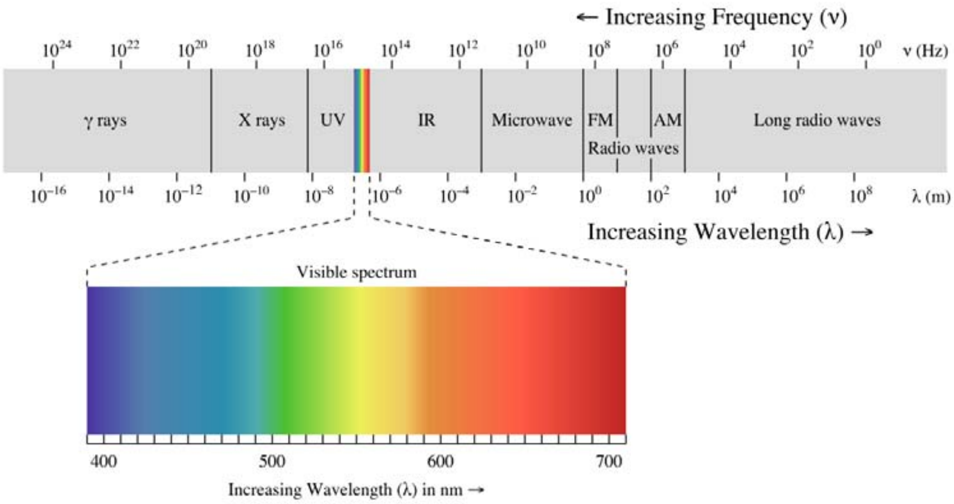


Figure 1: The electromagnetic Spectrum

Pure rotational (Microwave) spectra

If the energy absorbed by the molecules is so low that it can cause transition only from one rotational level to another within the same vibrational level, the result obtained is called the rotational spectrum. These spectra are, therefore, observed in the far infra-red region or in the microwave region whose energies are extremely small ($\bar{\upsilon}$) 1-100 $cm^{-}1$ and wavelength 1cm-100μm and frequency $3x10^{10}$-$3x10^{12}$.

Criteria to be Microwave active for Molecules

A molecule such as hydrogen chloride, HCl, in which one atom (the hydrogen) carries a permanent net positive charge and the other a net negative, is said to have a permanent electric dipole moment. H_2 or Cl_2, on the other hand, in which there is no such charge separation, have a zero dipole. If we consider the rotation of HCl (Figure2, where it can be noticed that if only a pure rotation takes place, the centre of gravity of the molecule must not move), it can be seen that plus and minus charges places periodically, and the component dipole moment in a given direction (say upward in the plane of the paper) fluctuates regularly. This fluctuation is plotted in the lower half of the figure2, and it is seen to be exactly similar in form to be fluctuating electric field of radiation. Thus, interaction can occur, energy can be absorbed or emitted, and the radiation gives rise to a spectrum. ***All molecules having a permanent moment are said to be 'microwave active'. If there is no dipole, as in H_2 or Cl_2, no interaction can take place and the molecule is 'microwave inactive'.*** This impose a limitation on the applicability of microwave spectroscopy.

Absorption of Electromagnetic Radiation - The Coupling Mechanism

An electromagnetic wave is an oscillating electrical field and interacts only with molecules that can undergo a change in dipole moment.

The oscillating dipole can be provided by the rotation of a permanent dipole like for example HCl. This type of interaction leads to microwave spectra

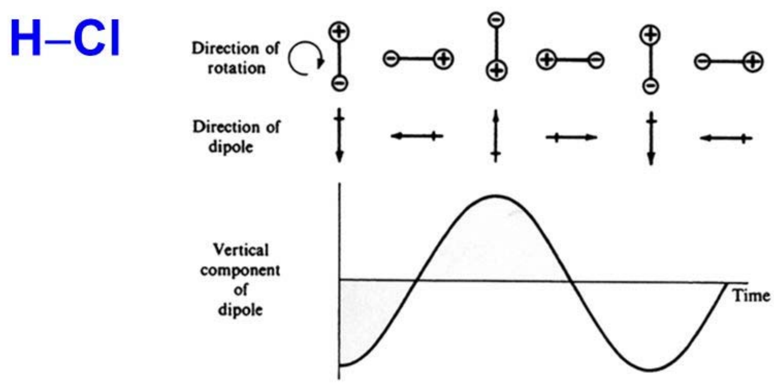


Fig. 2: The rotation of a polar diatomic molecule, showing the fluctuation in the dipole moment measured in a particular direction

The Rotation of Molecules

The spectroscopy in the microwave region is concerned with the study of rotating molecules. The rotation of a three-dimensional body may quite complex and it is convenient to resolve it into rotational components about three mutually perpendicular directions through the centre of gravity- the principal axes of rotation. Thus, a body has three principal moments of inertia, one about each axis, usually designated I_A, I_B and I_C.

Molecules may be classified into groups according to the relative values of their three principal moments of inertia -which, it will be seen, is tantamount to classifying them according to their shapes. The different types of such molecules are classified as:

1.Linear Molecule: These, as the name implies, are molecules in which all the atoms are arranged in a straight line, such as hydrogen chloride HCl or Carbon oxysulphide OCS, illustrated below

H—Cl

O—C—S

The three directions of rotation may be taken as

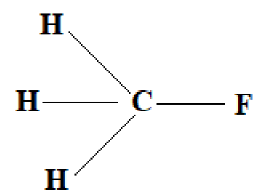
(a) about the bond axis, (b) end-over-end rotation in the plane of the paper and (c) end-over-end rotation at right angles to the plane

It is self-evident that the moments of (b) and (c) are the same (that is $I_B = I_C$) while that of (a) is very small. As an approximation it may be said that I_A=0, although it should be noted that this is only an approximation.

Thus, for linear molecules:

$$I_B = I_C \qquad I_A=0$$

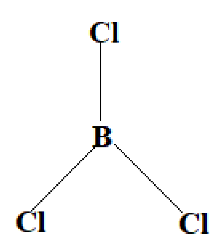
2. Symmetric Top Molecule: Consider a molecule such as methyl fluoride, where the three hydrogen atoms are bonded tetrahedrally to the carbon, as shown below:



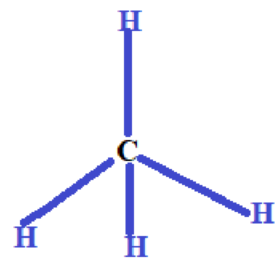
As in the case of linear molecules, the end-over-end rotation in, and out of, the plane of the paper is still identical and the condition is $I_B = I_C$. The moment of inertia about the C—F bond axis (chosen as the main rotational axis since the centre of gravity lies along it) is now not negligible, however, because it involves the rotation of three comparatively massive hydrogen atoms off this axis. Such a molecule spinning about this axis can be imagined as a top, and hence the name of the class.

Now the condition for the Symmetric tops is: $I_B = I_C \neq I_A$ $\qquad$ $I_A \neq 0$

There are two subdivisions of this class. If, as in methyl fluoride above, $\mathbf{I_B = I_C > I_A}$, then the molecule is called a ***prolate symmetric top***; whereas if $\mathbf{I_B = I_C < I_A}$, then the molecule is called a ***oblate symmetric top.*** An example of the later type is boron trichloride, which is shown, is planar and symmetrical. In this case, $\mathbf{I_B = 2I_C = 2I_A}$,



3.Spherical Top Molecules: When a molecule has all three moments of inertia identical, it is called a spherical top. A simple example is the tetrahedra molecule methane CH_4.



Simple tops: $I_B = I_C = I_A$

Since these molecules can have no dipole moment owing to their symmetry, rotation alone can produce no dipole change and hence no rotational spectrum is observable.

4.Assymmetric Tops Molecules: These molecules, to which the majority of substances belong, having all three moments of inertia different:

$$I_B \neq I_C \neq I_A$$

Simple examples are water and vinyl Chloride CH_2=CHCl