

Rotation Spectra of Polyatomic Molecules

(16)

(i) Linear Molecules We consider first molecules such as carbon oxysulphide OCS , or Chloroacetylene $\text{HC}\equiv\text{CCl}$ \rightarrow all the atoms lie on a straight line, this type gives rise to a particularly simple spectra in the microwave region.

Since $I_B = I_C$; $I_A = 0$, as for diatomic molecules, the energy levels are given by

$$E_J = BJ(J+1) - DJ^2(J+1)^2 + \dots \text{ cm}^{-1} \quad \text{--- (1)}$$

Spectrum will show the same $2B$ separation modified by the distortion constant.

The whole of the discussions on diatomic molecules applies equally to all linear molecules.
Three important points:

1. Moment of inertia for the end-over-end rotation of a polyatomic linear molecule is greater than that of a diatomic molecule, the B values are much smaller, spectral lines are more closely spaced. B values for diatomic molecule $\sim 10 \text{ cm}^{-1}$ for triatomic $\sim 1 \text{ cm}^{-1}$ and still less for larger molecules.
2. The molecule as usual possess a dipole moment if it is to exhibit a rotational spectrum.
 OCS is microwave active, while OCO (CO_2) will not.

Isotopic substitution does not lead to a dipole moment since the bond lengths and atomic charges are unaltered by the substitution. (17)

→ $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ is microwave inactive.

3. A non-cyclic polyatomic molecule containing N atoms has altogether $N-1$ individual bond lengths to be determined. In triatomic molecule OCS, there is r_{CO} and r_{CS} . There is only one moment of inertia for the end-over-end rotation of OCS, and this one value can be determined from the spectrum.

Taking $B = 0.2027 \text{ cm}^{-1}$

$$I_B = \frac{h}{8\pi^2 B c} = 137.95 \times 10^{-47} \text{ kg m}^2$$

→ From this one observation, it is impossible to deduce the two unknowns, r_{CO} and r_{CS} .

This difficulty is overcome, if we study a molecule with different atomic masses but the same bond lengths - i.e. an isotopically substituted molecule, since this will have a different moment of inertia.

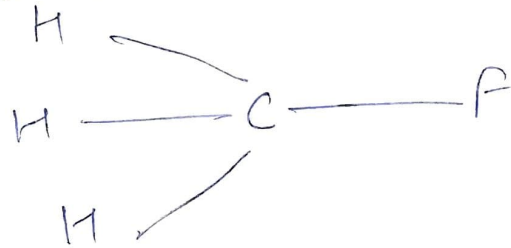
(ii) Spherical Top Molecules: The moment of inertia of spherical top molecule is independent of the orientation of the rotational axis in the molecule $I_A = I_B = I_C = I$

Thus there is again only one value of the moment of inertia in spherical top molecule. The energy level pattern → identical with that of a linear molecule.

(11) Symmetric Top Molecules: Rotational energy (18)

Levels are more complicated than those of linear molecules, but due to their symmetry, their pure rotational spectra are still relatively simple.

Consider a molecule such as methyl fluoride, the three hydrogen atoms are bonded tetrahedrally to the carbon.



As in the case of linear molecules, the end-over-end rotation in and out of the plane of paper are still identical and we have $I_B = I_C$. The moment of ~~inertia~~ 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

Symmetric tops: $I_B = I_C \neq I_A$, $I_A \neq 0$ — (2)

(i) $I_B = I_C > I_A$, prolate symmetric top
Ex. methyl fluoride

(ii) $I_B = I_C < I_A$; oblate symmetric top
Ex. boron trichloride
 $I_A = 2I_B = 2I_C$