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1. Learning Outcomes

In this module, you shall be learning about the classification of polyatomic molecules on the basis of the shape of their momental ellipsoid and the interpretation of their pure rotation spectra.

2. Introduction

Polyatomic molecules have complex rotational spectra. In order to interpret their spectra, molecules are divided into four classes based on the shape of their moment of inertia ellipsoids. In the next section, we discuss the various classes of molecules and their rotational spectra.

3. Classification of Molecules

Molecular shapes are classified by reference to the relative values of the moments of inertia about **three axes at right angles** (Fig. 1)**.**

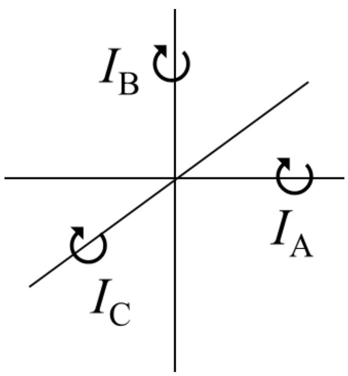

Figure 1. Principal moments of inertia

Polyatomic molecules are broadly divided into four classes:

(i) Linear Molecules
(ii) Spherical Top Molecules
(iii) Symmetric Top Molecules
(iv) Asymmetric Top Molecules

3.1 Linear Molecules

Diatomic molecules belong to this class of molecules. These molecules either belong to $C_{\infty v}$ (heteronuclear) or $D_{\infty h}$ (homonuclear) point groups. In any case, their main axis is a C_∞ axis along the bond axis (Fig. 2).

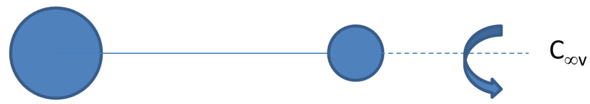

Figure 2. Diatomic molecule

Along this axis, the moment of inertia is zero since no atoms contribute to it (both lie along this axis). Thus, this is the I_A axis since it is the smallest. The other two inertial axes lie perpendicular to this one and to each other and both are equal in magnitude. Since we are plotting $1/\sqrt{I}$ to obtain the moment of inertia ellipsoid, the major axis is along the bond axis and this is of infinite length. The moment of inertia ellipsoid is a cylinder of infinite length (Fig. 3).

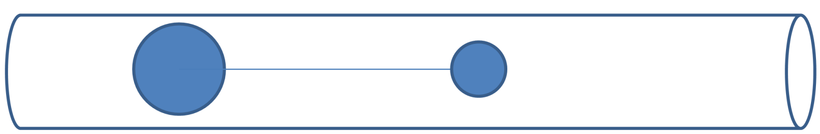

Figure 3. Moment of inertia ellipsoid of a linear molecule

3.2 Spherical Top Molecules

The next category of molecules is the spherical top molecules and this is the most symmetrical of all categories. All molecules shaped like spheres, such as SF_6, CH_4 and CCl_4, i.e. those which have O_h and T_d (and also I_h) symmetry belong this category. Because of their spherical symmetry, they have zero dipole moment and they are microwave inactive.

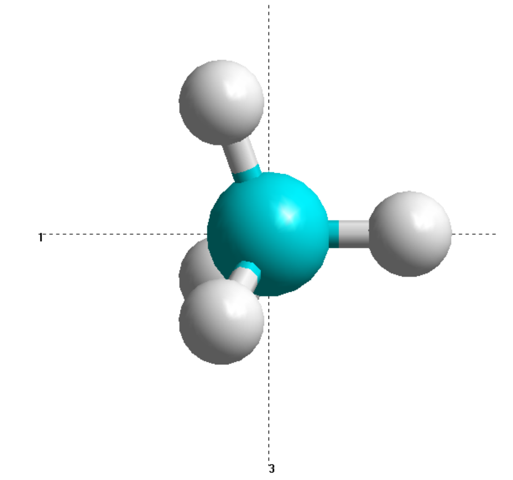

Figure 4. The spherical top methane molecule

3.3 Symmetric Top Molecules

The next category of molecules is the symmetric top molecules, which have two equal principal moments of inertia and the third is unique. They are further subdivided into two categories:

(i) Prolate symmetric tops

Let us consider the molecule CH_3I, obtained by replacing a hydrogen of methane by iodine, reducing the symmetry from T_d to C_{3v} (Fig. 5).

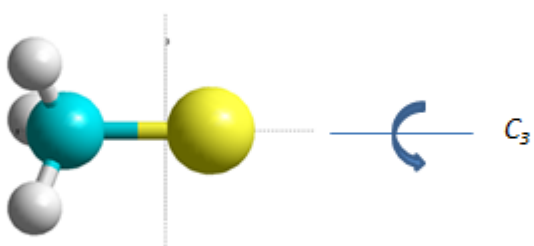

Figure 5. The CH_3I molecule

Along the C_3 axis, the only atoms that contribute are the light hydrogens, and hence the moment of inertia is smallest along this axis. Therefore, this must be the '*a*' axis, since by convention, the smallest component of the moment of inertia is labelled I_A. The other two axes are perpendicular to this axis and to each other and are also equal.

Hence, for this molecule, we may write

$$I_A < I_B = I_C$$

and, because of the reciprocal relationship,

$$A > B = C$$

Molecules of this type are called **Prolate Symmetric Top** molecules. Their shape resembles that of a shuttlecock (Fig. 5).

Linear molecules are a special case of prolate symmetric tops, since their $I_A = 0$.

The other possibility is that the unique axis could be the largest (I_C) and such molecules are called **oblate symmetric top** molecules.

(ii) Oblate symmetric top molecules

For these molecules,

$$I_A = I_B < I_C$$

Such molecules are flat, saucer shaped and resemble a Frisbee. An example is the planar D_{3h} molecule BF_3 (Fig. 6).

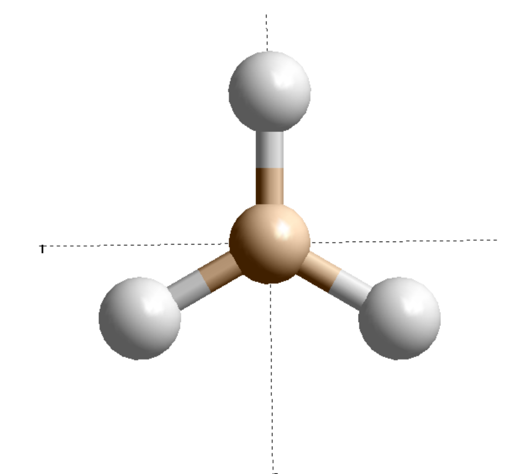

Figure 6. The BF_3 molecule

Here, too, the unique axis is C_3, but this is perpendicular to the plane of the molecule. It passes through the centre of mass at the boron atom. All three fluorine atoms contribute to the moment of inertia along this axis, and hence it is the highest I_C. The other two moment of inertia axes also pass through boron. One lies along a B-F bond, and the other is perpendicular to it (see Fig. 6).

Let us evaluate the three moments of inertia. Along the C_3 axis is I_C. If m_F is the mass of a fluorine atom and m_B that of boron (Fig. 7), we may write

$$I_C = 0 \times m_B + 3m_F r_{BF}^2$$
$$I_A = 0 \times m_B + m_F r_{BF}^2 + 2m_F (r_{BF} \sin 30)^2 = m_F r_{BF}^2 + \frac{1}{2} m_F {r_{BF}}^2 = \frac{3}{2} m_F {r_{BF}}^2 \qquad (1)$$

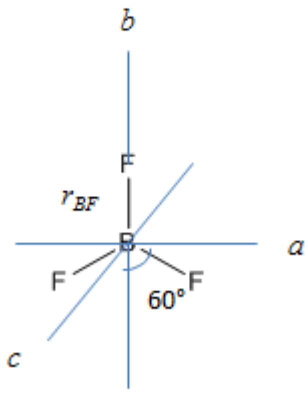

Figure 7. Moment of inertia components for BF_3

For I_A, we have considered the perpendicular distance of the two fluorine atoms from the '*a*' axis and we observe that $I_A = ½\, I_C$.

Similarly, for I_B, we write

$$I_B = 0 \times m_B + 0 \times m_F + 2m_F (r_{BF} \sin 60)^2 = 2m_F r_{BF}^2 \left(\frac{\sqrt{3}}{2} \right)^2 = \frac{3}{2} m_F {r_{BF}}^2 \qquad (2)$$

Comparison with equation (1) tells us that

$$I_A = I_B = ½\, I_C$$

Another oblate top molecule is the also planar molecule, benzene (D_{6h}).

All molecules that have a single C_n rotation axis with $n \geq 3$ are symmetric top molecules. One of the exceptions is allene (D_{2d}), which has an S_4 axis, though its highest order proper rotation axis is only C_2 (Fig. 8).

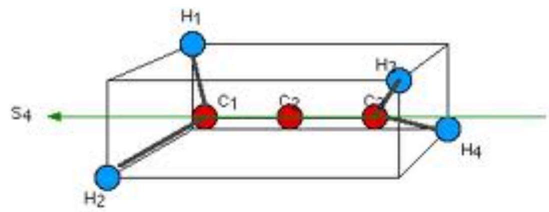

Figure 8. The S_4 axis of allene

If the molecule has its highest order rotation axis as C_2 or there is no proper rotation axis, the molecule is an asymmetric top molecule. This is the least symmetric class of molecules, for which

$$I_A \neq I_B \neq I_C$$

Their spectra are the most difficult to interpret. The vast majority of molecules, e.g. H_2O, $C_2H_2F_2$, etc. falls in this category.

Example 1

Determine the point group symmetry of the following molecules in their electronic ground states: H_2O, C_2H_2, C_2H_4, *cis* and *trans*-CHFCHF, CCl_4, BF_3, XeF_4, CH_3F, and C_6H_6.
Determine for each molecule whether it is a symmetric top, a linear rotor, a spherical top, or an asymmetric top.

Solution

Molecule	**Point Group**	**Classification**
H_2O	C_{2v}	Asymmetric top
C_2H_2	$D_{\infty h}$	Linear
C_2H_4	D_{2h}	Asymmetric top
cis-CHFCHF	C_{2v}	Asymmetric top
trans-CHFCHF	C_{2h}	Asymmetric top
CCl_4	T_d	Spherical top
BF_3	D_{5h}	Symmetric top (oblate)
XeF_4	D_{4h}	Symmetric top (oblate)
CH_3F	C_{3v}	Symmetric top (prolate)
C_6H_6	D_{6h}	Symmetric top (oblate)

Fortunately, their spectra resemble either that of prolate symmetric tops or oblate symmetric tops, depending on the geometry. Several formulae have been used to evaluate their degree of symmetry, and one that is frequently used is Ray's asymmetry parameter, κ, defined as

$$\kappa = \frac{2B - A - C}{A - C} \qquad (3)$$

Consider first a prolate symmetric top, for which $A > B = C$. Substituting for B in equation (3), we obtain

$$\kappa = \frac{2C - A - C}{A - C} = -1$$

Similarly, for an oblate top, $A = B > C$. Again substituting for B, we obtain

$$\kappa = \frac{2A - A - C}{A - C} = 1$$

Thus, an asymmetric top molecule, which has a negative κ value close to -1 is called *near prolate* and one with a positive value close to +1 is called *near oblate.* A value close to zero signifies the largest degree of asymmetry.

Example 2

Consider the molecule thioformaldehyde, H_2CS. The rotational constants are A = 291291.641 MHz, B = 17699.628 MHz and C = 16651.83 MHz. This molecule is a near symmetric top. Which one (oblate or prolate)?

Solution

$$\kappa = \frac{2B - A - C}{A - C} = \frac{2 \times 17699.628 - 291291.641 - 16651.83}{291291.641 - 16651.82} = -0.99237$$

Since this value is close to -1, the molecule is near prolate.

4. Summary

- In order to interpret rotational spectra, molecules are classified, according to the shapes of their moment of inertia ellipsoids, into four categories.
- Linear molecules have a moment of inertia ellipsoid that resembles an infinite cylinder.
- Polyatomic linear molecules with N atoms have N-1 bond lengths to be determined, but only one moment of inertia can be extracted from the spectra. The answer is isotopic substitution that gives more equations. Up to four isotopic substitutions can be done. More often, this need not be done, since many isotopic species are present in natural abundance.
- Spherical top molecules are the most symmetrical but lack a dipole moment, and are thus microwave inactive.
- Symmetric top molecules have one proper rotation axis C_n with $n \geq 3$. They have two moments of inertia equal to each other. They are further subdivided into prolate tops or oblate tops, depending on whether the unique axis is the smallest or the largest.
- Prolate tops molecules are shaped like shuttlecocks, and oblate tops like Frisbees.
- The most asymmetrical class is of the asymmetric top molecules. All their principal components of moment of inertia are different. Their spectra resemble either those of prolate or those of oblate top molecules.