

TYPES OF ROTATORS

1. Introduction

Rotational spectroscopy deals with the study of the rotational transitions of molecules when they absorb or emit electromagnetic radiation in the microwave region (1–300 GHz).

The energy levels and transition patterns depend strongly on the shape and mass distribution of the molecule — which are described by its moments of inertia.

Thus, molecules are classified into different types of rotors, depending on how their moments of inertia are distributed along the three principal axes.

2. Moment of Inertia & Rotational Constant

For a molecule, the moment of inertia about an axis is given by:

$$I = \sum m_i r_i^2$$

Where, m_i = mass of atom i

r_i = radius of atom i

The rotational constant B in (cm^{-1}) is related to I as:

$$B = \frac{h}{8\pi^2 c I}$$

Where h = Planck's constant

I = moment of Inertia

c = speed of light

The Quantum Mechanical Approach to Molecular Rotation

In classical mechanics, a molecule can rotate freely about any axis. However, at the quantum mechanical level, the rotational energy of a molecule is **quantized**, meaning it can only exist at specific discrete energy levels. These energy levels are determined by the molecule's **moment of inertia**, which in turn depends on its mass distribution and geometry.

To simplify our understanding, we treat molecules as **rigid rotors**, meaning their bond lengths and angles are fixed during rotation.

The key to classifying rotors lies in comparing their **principal moments of inertia**. We label these moments of inertia as I_a , I_b and I_c , by convention, in increasing order: $I_a \leq I_b \leq I_c$

Based on the relationships between these three principal moments of inertia, we categorize molecules into four main types of rotors:

1. Linear Rotors

Linear molecules have all their atoms arranged along a straight line.

Characteristics:

- The moment of inertia about the internuclear axis I_a is essentially zero.
- The two principal moments of inertia perpendicular to the molecular axis are equal and non-zero:

$$I_a=0 \text{ \& } I_b=I_c \neq 0$$

- **Examples:** HCl, CO, CO₂, HCN, N₂

Energy Levels and Spectrum:

- The rotational energy levels for a rigid linear rotor are given by the equation: $E_J = BJ(J + 1)$

Where B is the rotational constant and J is the rotational quantum number (0, 1, 2, ...).

- The selection rule is $\Delta J = \pm 1$
- **Result:** A series of **equally spaced lines** in the spectrum, with the spacing equal to 2B.

2. Symmetric Top Rotors

Symmetric top rotors have two equal principal moments of inertia, with the third being different.

Characteristics:

- They must have at least a three-fold (C_3) axis of symmetry.
- Prolate Symmetric Tops ("Cigar-shaped"): The unique moment is smallest.

$$I_a < I_b = I_c$$

*Examples: Methyl fluoride, chloroform, ammonia.

- Oblate Symmetric Tops ("Disc-shaped"): The unique moment is largest.

$$I_a > I_b = I_c$$

*Examples: Benzene, boron trifluoride.

Energy Levels and Spectrum:

- The energy levels depend on two quantum numbers, J & K (rotation about the unique axis).

$$E_{J,K} = BJ(J + 1) + (A - B)K^2 \text{ (for prolate)}$$

- The selection rules are $\Delta J = \pm 1$ & $\Delta K = 0$

- **Result:** Due to $\Delta K = 0$, the spectrum remains a series of **equally spaced lines** (spacing $2B$), but each line may correspond to **multiple overlapping transitions** for different K values.
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3. Spherical Top Rotors

Spherical top rotors have all three principal moments of inertia equal, possessing high symmetry.

Characteristics:

- All three principal moments of inertia are equal:

$$I_a = I_b = I_c \neq 0$$

- **Examples:** Methane, carbon tetrachloride, sulfur hexafluoride.
- **No permanent electric dipole moment.**

Rotational Spectrum:

- Spherical top molecules **do not exhibit a pure rotational spectrum** in the microwave region because the absence of a permanent electric dipole moment means they cannot interact with the electromagnetic field.
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4. Asymmetric Top Rotors

Asymmetric top rotors are the most common type and have three distinct principal moments of inertia.

Characteristics:

- All three principal moments of inertia are different:

$$I_a \neq I_b \neq I_c$$

- They do not have a principal axis of rotation that is an axis of three-fold or higher symmetry.
- **Examples:** Water, formaldehyde, most organic molecules.

Energy Levels and Spectrum:

- The energy levels cannot be expressed by a simple analytical formula and depend on complex quantum numbers J_KaKc .
- **Result:** The rotational spectrum is typically **very complex**, consisting of a dense forest of **unequally spaced lines**.

Conclusion

Understanding the types of rotors is the foundational step in comprehending rotational spectroscopy. By classifying molecules based on their moments of inertia, we can predict the general appearance of their rotational spectra and begin to extract valuable structural parameters like bond lengths and bond angles.