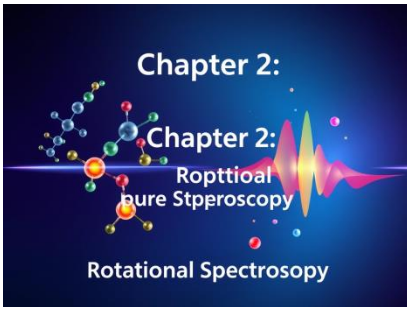
Chapter II:

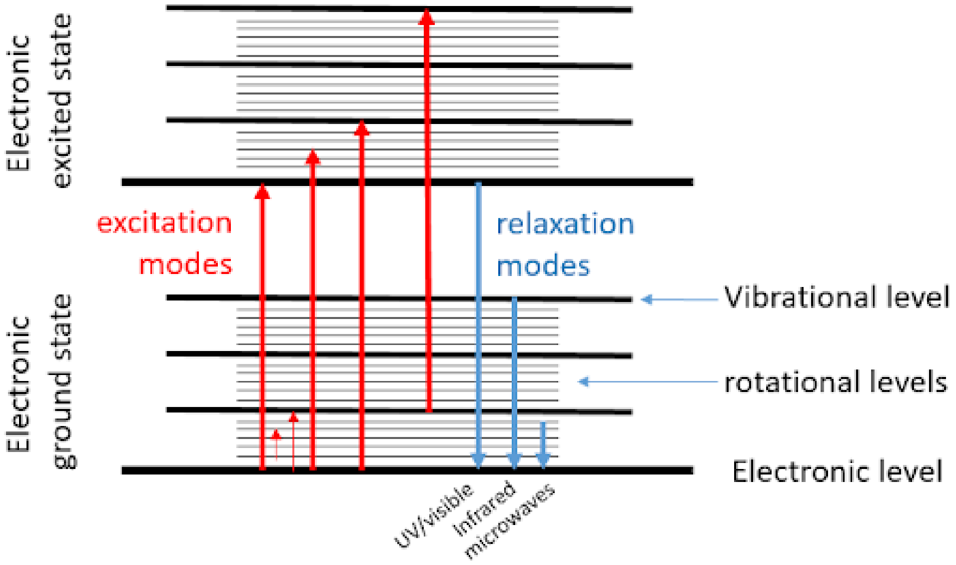
Pure Rotational Spectroscopy



II.1. Introduction:

Pure rotational spectroscopy is an essential method for probing the structure and dynamics of molecules in their gaseous state. It provides valuable information on the spatial distribution of atoms within a molecule, particularly on **bond lengths** and **valence angles,** through the analysis of energy transitions associated with rotational motions.

In this approach, molecules are considered **quantum rotators** , whose energy levels are quantized according to theoretical models. The **rigid rotator model** constitutes the first approximation, in which the interatomic distance is assumed to be constant. This simple model allows us to describe the **rotational energy levels** and the **selection rules** that govern the transitions observable in the microwave range. However, real molecules undergo **centrifugal distortion** during rapid rotation, leading to the more realistic **non-rigid rotator model** . Furthermore, isotopic substitution results in measurable **isotopic effects** on the spectra, providing detailed structural information.



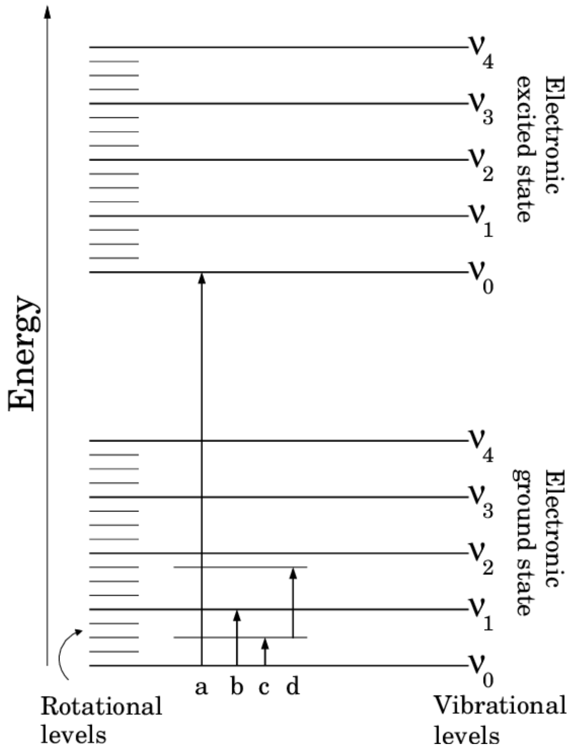


Fig. II.1. Schematic representation of rotational and vibrational energy levels

Thus, pure rotational spectroscopy offers a bridge between quantum theory and experimental molecular structure, allowing direct access to the fundamental geometric and dynamic parameters of molecules.

Pure rotational spectroscopy is primarily applied **to molecules in the gaseous state** .

Case of gases (gaseous state) → Yes, observable: In the gaseous state, molecules **can rotate freely** around their axes.

- Transitions between (quantized) **rotational energy levels** are therefore possible and **detectable** .
- The corresponding spectra are in the **microwave range (1–100 cm^{-1}) .** It **is in this case that pure rotational spectroscopy is best observed.**

Case of liquids → No, blurred transitions

- In a liquid, molecules **frequently collide** and intermolecular interactions **disrupt** rotations.
- These collisions cause **the fine structure of rotational lines to disappear** : the transitions become too broad or merge. **Pure rotational spectra are therefore practically invisible in liquids.**

Case of solids → No, rotation is blocked

- In a solid, molecules are **fixed in a crystalline lattice** or strongly bonded.

- They cannot **perform free rotation** , only **vibrations** around an equilibrium position. **No pure rotation is observable.**

Comparison: Pure rotational spectroscopy, infrared, Raman and UV-Visible

Features	**Pure rotational spectroscopy (microwaves)**	**Infrared (IR) spectroscopy**	**Raman Spectroscopy**	**UV-Visible Spectroscopy**
Type of transition observed	**rotational** transition between rotational energy levels	**Vibrational** transition (often accompanied by rotational changes)	**Vibrational and rotational** transition through **inelastic** light diffusion	**Electronic** transition (change of electronic state)
spectral domain	**Microwave** : 1 – 100 cm^{-1} (long wavelengths)	**- infrared** : 4000 – 400 cm^{-1}	**Visible or near-IR light** (laser radiation scattering, ~100–4000 cm^{-1} Raman shift)	**UV and visible** : 200 – 800 nm
Energy level involved	Very weak (10^{-3} eV)	Average (10^{-1} eV)	Average (10^{-1} eV , like IR)	High (1–10 eV)
Molecular movement studied	**Rotation** of molecules	**Vibration** of the joints (stretching, deformation)	**Vibration** (and sometimes rotation) detected via light scattering	**Electronic transitions** of valence electrons
Experimental conditions	Applies **to gases** only (free rotation)	Applicable to **gases, liquids and solids**	Applicable to **gases, liquids and solids**	Applicable to all states
Type of spectrum obtained	Very thin and evenly spaced lines	Vibration bands with superimposed rotational structure	Symmetrical bands in the incident radiation (Stokes and anti-Stokes lines)	Broadband (electronic absorption)
Sensitivity to molecular structure	Provide the **molecular geometry** (bond lengths, moments of inertia)	Describe the **nature of the chemical bonds** and **functional groups.**	Provides information on **active Raman vibration modes** (polarizability changes)	Provides information on **electronic levels** and $\pi\to\pi$, $n\to\pi$ *transitions* **

Transition selection	ΔJ = ±1 (pure rotation)	Δv = ±1 and ΔJ = ±1 (rotation-vibration)	Δv = ±1; active transitions if **polarizability** changes	Transition is permitted if the electronic transition moment is non-zero (symmetry rules)

Simplified comparative summary:

Spectroscopy type	What she studies primarily	Suitable material state	Information obtained
Microwave (pure rotation)	Rotation of molecules	Gas	Interatomic distances
Infrared (IR)	Vibrations of the connections	Gas, liquid, solid	Functional groups
Raman	Vibrations (due to light diffusion)	Gas, liquid, solid	Symmetry of vibrations, complementary to IR
UV-Visible	Electronic transitions	All states	structure , chromophores

Conclusion:

- **Pure rotational spectroscopy** is the most precise: it provides information on **molecular geometry** .
- **Infrared and Raman spectroscopy** provide vibrational **information** (nature of the bonds).
- **UV-Visible spectroscopy** explores electronic **transitions** , linked to molecular orbitals.
- Together, these techniques provide a **complete view** of molecular behavior (rotation → vibration → electronics).

II.2. Definition:

Pure rotational spectroscopy is a spectroscopic technique that studies the **transitions between the rotational energy levels** of molecules. These transitions occur when molecules absorb or emit **electromagnetic radiation in the microwave region** (approximately **1 to 100 cm^{-1} , or** 10–1000 **GHz**).

It provides precise information on **molecular geometry** (bond lengths, angles, moments of inertia) and the **distribution of atomic masses** within the molecule.

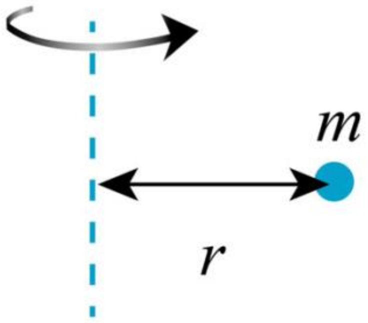
These transitions appear in the far-infrared from 20 to 250 $\propto\mu$ or from 250 to 40 cm^{-1}

II.3. Molecular rotational movement

II.3.1. Rotation of a particle:

Let υ_{rot} The rotational frequency (number of revolutions per second) and ω angular velocity (radians per second) are given by: $\omega = 2\pi\upsilon_{rot}$

Kinetic energy: $E_c = \frac{1}{2} m v^2$ can be expressed as a function of r (distance of the particle from the center of gravity) and $v = r\omega$



Either: $E_c = \frac{1}{2} m v^2 = \frac{1}{2} m (r\omega)^2 = \frac{1}{2} I \omega^2$

With: I being the moment of inertia, $I_c = m r^2$

II.3.2. Rotation of the diatomic molecule: the case of the rigid rotator

Let's examine a simple mechanical model. Consider a diatomic molecule as a rigid system consisting of two spheres: a rigid rotator

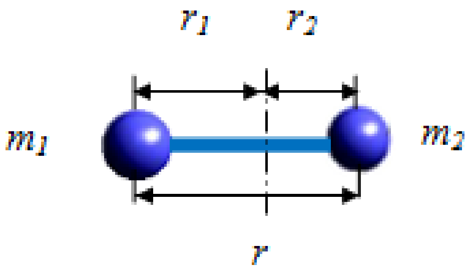


Fig. II.2: Mechanical model of the rigid rotator

According to this model, each of the two atoms with masses m1 and m2 is assumed to have a material point

a) Expression of the moment of inertia; In the general case, we have :

$$I_c = \sum_i m_i r_i^2$$

In the case of two particles: $I = m_1 r_1^2 + m_2 r_2^2$

Where r1 and r2 are the respective distances of atom 1 and 2 from the center of gravity .

Let's express I as a function of r, the bond length of the diatomic molecule:

$r = r_1 + r_2$ and $r_1 = r - r_2 \mapsto r_2 = r - r_1$

On the other hand, the position of the center of gravity (center of mass) of a diatomic molecule is such that: $m_1 r_1 = m_2 r_2$

We can write: $m_1 r_1 = m_2 (r - r_1)$ and $m_2 r_2 = m_1 (r - r_2)$

From this we can deduce: $r_1 = \frac{m_2}{m_1 + m_2} r$ and $r_2 = \frac{m_1}{m_1 + m_2} r$

Substituting $I = m_1 r_1^2 + m_2 r_2^2$ the expressions for r1 and r2 in terms of r into the equation, we obtain:

$$I = m_1 \left[\frac{m_2}{m_1 + m_2} r \right]^2 + m_2 \left[\frac{m_1}{m_1 + m_2} r \right]^2$$

Hence: $I = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2$, where $\mu = \frac{m_1 m_2}{m_1 + m_2}$; reduced mass of the molecule

This relationship means that, from a mechanical point of view, the diatomic molecule can be studied as a single volume of mass ⌠ rotating from a point located at a fixed distance r equal to the internuclear distance:

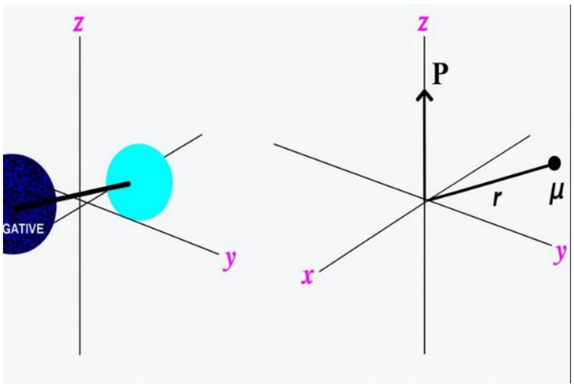


Fig. II.3: Mechanical equivalent of the rigid diatomic rotator

b) Expression of kinetic energy:

$$\mathbf{E_C = \frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 \Rightarrow \frac{1}{2}\omega^2\left(m_1r_1^2 + m_2r_2^2\right) = \frac{1}{2}\omega^2 I}$$

$$\mathbf{I = m_1r_1^2 + m_2r_2^2}$$

$$\mathbf{v_1 = \omega r_1 \quad and \quad v_2 = \omega r_2}$$

By analogy with momentum equal to **mv²** , we also define angular momentum P: $P = I\varpi$

In summary, we therefore have the following equations:

$$\mathbf{E_C = \frac{1}{2}I\omega^2 \leftrightarrow I = \mu r^2 \leftrightarrow \mu = \frac{m_1m_2}{m_1 + m_2} \leftrightarrow P = I\omega}$$

c) Rotational energy:

For a microscopic system, the solution to the energy problem is obtained by solving the ***Schrödinger equation,*** and the mathematical solution of this equation introduces quantum numbers and the quantization of energy:

In the case of rotational motion, quantum restrictions are expressed as a function of angular momentum. The allowed values of angular momentum are multiples of $\hbar$. The angular momentum operator has the following eigenvalue:

$$P = I\varpi = \hbar\sqrt{J(J+1)} \qquad J = 0,1 \ldots\ldots\ldots\ldots\ldots\ldots$$

The integer **J** is called the rotational quantum number. The expression for the rotational kinetic energy is:

$$E_c = \frac{1}{2}I\varpi^2 = \frac{(I\varpi)^2}{2I} = \frac{\hbar^2}{2I}\left[J(J+1)\right] \qquad J = 0,1 \ldots\ldots\ldots\ldots\ldots$$

Finally, the rotational energy denoted **E** $_{\mathbf{j}}$ East :

$$E_J = \frac{h^2}{8\pi^2 I}\left[J(J+1)\right] \quad J = 0,1 \ldots\ldots\ldots\ldots\ldots$$

With : $A = \frac{h^2}{8\pi^2 I}$, constant for a given molecule

$$E_0 = 0\,, E_1 = 2A\,, E_2 = 6A,\ E_3 = 12A, \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$E_1 - E_0 = 2A\,, E_{21} - E_1 = 4A\,, E_2 = 6A,\ E_3 - E_2 = 6A, \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

The energy level diagram of the rotating molecule appears as a series of horizontal lines moving further and further apart.

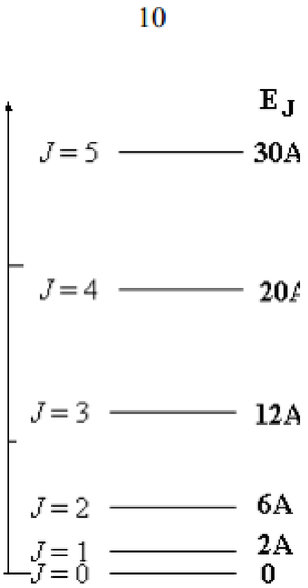


Fig. II.4: Position of rotational energy levels

d) Selection rule:

Since rotational momentum is linked to dipole moment, molecules with zero electric dipole moment (such as homonuclear diatomic molecules H_2 , N_2 , or O_2) exhibit neither rotational absorption nor emission. In contrast, heteronuclear molecules possessing a dipole moment can undergo rotations corresponding to quantized energy levels. These levels are described by the **rotational quantum number** , and the transitions between them obey **selection rules** specifying which transitions are allowed.

Selection rule for rotation: $\Delta J = \pm 1$**; [allowed transitions between a level J and a level J +1 in absorption or between a level J and J -1 in emission]**

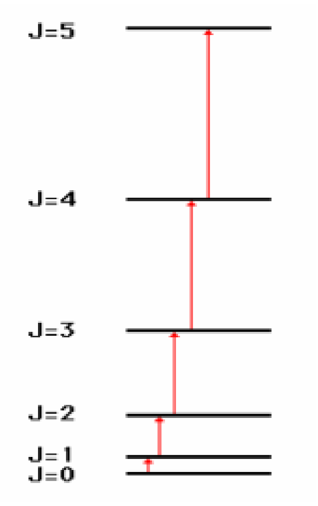


Fig. II.5: Possible transitions between rotational energy levels in the case of absorption

Note : Molecules such as **H_2** , **N_2** , **O_2 ,** or **CO_2** do not possess a **permanent dipole moment** . Consequently, they **do not absorb radiation in the microwave region** , the domain where rotational transitions occur. This lack of absorption is of great practical importance: if these molecules were capable of absorbing in this region, **the operation of radars** , which emit in the microwave range, **would be significantly disrupted** , as **a substantial portion of the signal intensity would be absorbed by the atmosphere .**

II.4. Positions of the rotation lines

On the **energy level diagram** , **possible rotational transitions** are represented by arrows. Each arrow corresponds to a **transition between two quantized energy levels** , resulting in **the appearance of a line** in the microwave absorption spectrum. A **rotational line** therefore corresponds to a **transition between two successive levels** , denoted **J** and **J + 1** .

The **energy difference** between these two successive levels is given by the following relationship:

$$\Delta E_{J\rightarrow J+1}=E_{J+1}-E_{J}=2\frac{h^2}{8\pi^2 I}(J+1)=h\upsilon=hc\bar{\upsilon}$$

$$\bar{\upsilon}=2\frac{h}{8c\pi^2 I}(J+1)$$

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

$$\bar{\upsilon}=2B(J+1)$$

The following line corresponds to the J+1 →to J+2 transition: $\bar{\upsilon}=2B(J+2)$

The wavenumber interval between two consecutive lines is constant:

$$\Delta\bar{\upsilon}=2B=\bar{\upsilon}_{J+1}-\bar{\upsilon}_{J}$$

In the rigid rotator approximation, the rotation lines of a diatomic molecule are equidistant

We thus observe a spectrum that can be schematically represented as shown in the figure:

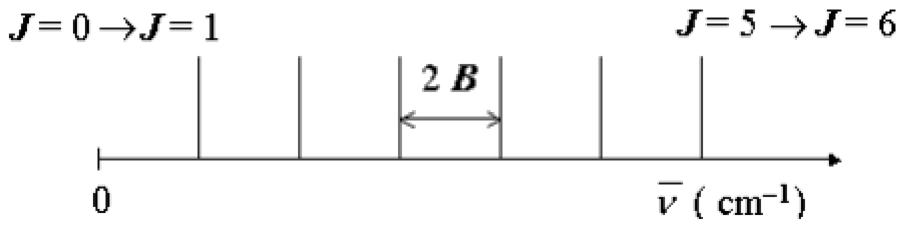


Fig. II.6. Schematic of the rotation spectrum

From the **experimental value of** $\Delta\bar{\upsilon}$, it is possible to **determine the rotation constant B** , and then deduce **the moment of inertia** of the molecule under study. Knowing the **masses of the atoms** constituting the molecule, one can then **calculate the internuclear distance,** that is, the average distance between the two nuclei.

II.5. Rotation line intensities

The **rotational spectrum** of a diatomic molecule actually shows that **not all the spectral lines have the same intensity.** Contrary to the simplified theoretical model, the **intensities of the lines vary** according to the **population of energy levels,** which depends on the **temperature according to the Boltzmann** distribution. The real appearance of such a spectrum is illustrated by the case of the **HCl molecule,** often used as a representative example in rotational spectroscopy.

(HCl): It possesses a permanent dipole moment. Unlike homonuclear molecules such as H_2 , N_2 , or O_2 , HCl **is heteronuclear** (two different atoms: hydrogen and chlorine). This means that there is a **difference in electronegativity** between the two atoms, which creates a **separation of charges** → therefore a **permanent dipole moment** .

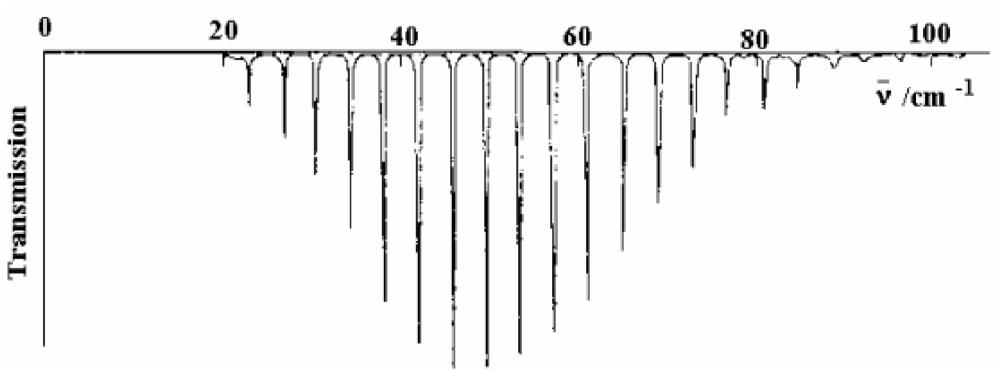


Fig. II.7. Pure rotational spectrum of the HCl molecule in the gaseous state

II.6. Rotation of polyatomic molecules

Molecules are classified (after analysis of their symmetry elements) into four categories:

- Linear molecules.
- Spherical spinning tops.
- Symmetrical spinning tops.
- Asymmetrical spinning tops.

a) V.1 Linear polyatomic molecules

The relationship giving the possible rotational energy levels for the linear polyatomic molecule is identical to that corresponding to diatomic molecules:

$$E_J == \frac{h^2}{8\pi^2 I} J(J+1); J=0,1,2,..........$$

Where I is the moment of inertia of the system (it is unique for a given molecule).

The energy levels have the same arrangement as for diatomic molecules, but they are closer together due to a higher moment of inertia.

Example: $H-Cl$: B = 20.68 cm^{-1}

- $H-{}^{12}C \equiv {}^{14}N$: B = 1.48 cm^{-1}

The selection rule is still and like $\Delta J = \pm 1$ homonuclear diatomic molecules, symmetric molecules (CO_2, C_2H_2) do not exhibit a pure rotation spectrum.

However, a different problem arises. The molecule has at least two internuclear distances [(n-1) bonds for a molecule containing n atoms].

How can these bond lengths be determined from the rotation spectrum?

Let us then consider the simplest case: the linear triatomic molecule.

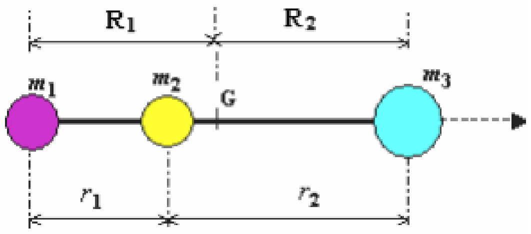


Fig. II. 8. linear triatomic molecule

We know that the moment of inertia of a rigid polyatomic molecule with respect to a given axis is given by the relation:

$I = \sum m_i R_i{}^2 I$

where m_i is the mass of particle iii, and r_i is the distance R from this axis, which is often the distance to gravity.

A mathematical solution to the problem leads to:

$$\mathbf{I} = \frac{\mathbf{m_2 m_1 r_1^2 + m_2 m_3 r_2^2 + m_3 m_1 (r_1 + r_2)^2}}{\mathbf{m_1 + m_2 + m_3}}$$

Where : r1 , r2 and r3 are the lengths of the two bonds of the linear triatomic molecule.

It should be noted that, in order to determine isotopic molecules, one must take into account the bond lengths, which requires a complete knowledge of the properties of isotopes.

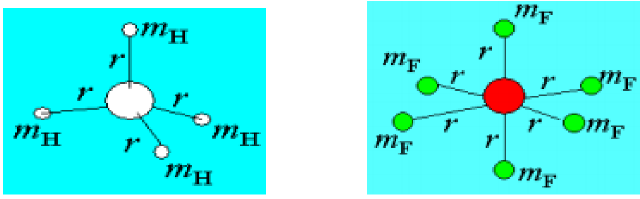
Interatomic distances vary only slightly due to isotopic substitution.

The problem relates to solving two equations with two unknowns...

b) Nonlinear or spatially distributed polyatomic molecules:

A nonlinear or spatial molecule possesses three moments of inertia along three perpendicular axes called principal axes: these molecules are divided into three categories according to the values of these moments:

- **In the case of spherical molecules:** these are molecules whose three moments are equal: for example, CH_4 and SF_6:

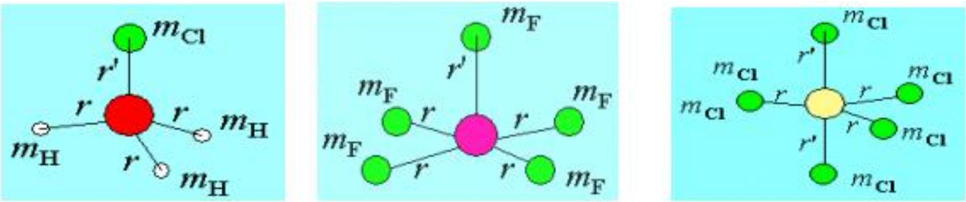


CH_4 **SF_6**

Fig. II.9. Spherical molecules

- **Case of symmetrical top-type molecules:**

Molecules with two equal moments of inertia are said to be of the symmetrical top type; example: NH3 , CH3Cl , and PCl5



CH_3Cl **BrF_5** **PCl_5**

Fig. II. 10. Symmetrical top-type molecules

In the case of introducing two distinct moments of inertia into the *Schrödinger equation,* this leads to the definition of two quantum numbers: we keep the quantum number J and add a quantum number K: K = J, J-1, J-2, ……-(J-1), -J

Energy can be written as:

$$\mathbf{E}=\frac{\mathbf{K}^2\mathbf{h}^2}{2\left(4\pi^2\right)\mathbf{I}_\mathbf{A}}+\left[\mathbf{J}\left(\mathbf{J}+1\right)-\mathbf{K}^2\right]\frac{\mathbf{h}^2}{4\pi^2\mathbf{I}_\mathbf{B}}$$

The applicable selection rules are as follows: $\Delta J=\pm 1;\Delta K=0$.

II.7. Detailed principle of pure rotational spectroscopy:

II.7.1. Rigid Rotor Model: The molecule is assumed to behave like a **rigid body** where the atoms are linked by bonds of fixed length.

A **rigid body** is a system made up of several material points (atoms or masses) whose **relative distances remain constant** during motion. In other words, the atoms **do not move relative to each other** : the shape and dimensions of the body **do not change.**

- **Molecules have a quantized rotational energy:**

- At ordinary temperature, molecules in the gas phase **rotate freely** around their center of mass.
- In quantum mechanics, their **rotational energy** can only take **certain discrete values** :

  $E_J=BJ(J+1)$

  Or :

  - J: rotational quantum number (0, 1, 2, 3, …),
  - $B=\frac{h}{8\pi^2 Ic}$ = rotational constant,
  - I: moment of inertia = μr^2, depending on the distance r between atoms and the reduced mass μ.

Each molecule therefore possesses well-defined rotational energy levels.

- **Interaction with microwave radiation**

- **electromagnetic radiation** is passed into the **microwave range** (wavelength of a few millimeters), it can be **absorbed** by the molecule.
- **absorption** to occur , the photon's energy must **correspond exactly to the difference** between two rotational levels:

  $\Delta E=E_{J+1}-E_J=2B(J+1)$

- And the **selection rule** dictates: $\Delta J=\pm 1$

  (The molecule goes from level J to level J+1).

  Each absorption corresponds to a **line in the microwave spectrum** .

- **Condition for observing a rotational transition**

- The molecule must possess a **permanent dipole moment** ($\mu \neq 0$). This dipole moment interacts with the **electric field** of the radiation.
- If the molecule is **non-polar** (like N_2 , O_2 , Cl_2) , it **cannot absorb** microwave radiation: its pure rotational spectrum is **invisible.**

  Examples of active molecules: HCl , CO, HF, H_2O , NH_3 . Examples of **inactive molecules:** N_2 , O_2 , CH_4, CO_2 .

How the molecule absorbs radiation

1. The **oscillating electric field** of the microwave wave exerts a **torque** on the **electric dipole** of the molecule.
2. This couple tends to **align the dipole** with the field.
3. If the **frequency of the radiation** corresponds to the **natural transition frequency** between two levels J and J+1, there is **resonance** → the molecule **absorbs** the energy of the photon.
4. The molecule then moves to a **higher rotational state,** meaning it **rotates faster** .

Spectrum observation

- By scanning the frequency of microwave radiation, we observe a **series of regularly spaced absorption lines** .
- The spacing between two successive lines is:

$$\Delta\bar{\upsilon}=2B$$

- From this distance, we can **calculate the rotation constant** B, then the **moment of inertia** , and finally the **link length** r:

$$r=\sqrt{\frac{h}{8\pi^2 c\mu B}}$$

In summary (logical diagram of the principle)

Stage	Phenomenon	Result
1	Rotating molecule (quantized levels)	$E_J = BJ(J+1)$
2	Application of microwave radiation	Field-dipole interaction
3	Absorption ($\Delta J = +1$) if frequency = $\Delta E/h$	Rotational transition
4	Observation of absorption lines	Determination of B, I, and r

II.7.2. Non-rigid rotator model:

A **non-rigid rotator** is a more realistic model than a rigid rotator. It takes into account the fact that, in reality, **chemical bonds are not perfectly rigid** : when a molecule spins rapidly, **centrifugal force** tends to **slightly lengthen the bonds** , which modifies the **moment of inertia** and therefore the **rotational energy levels** .

- **Physical principle:**

- When a molecule rotates, each atom experiences an outward **centrifugal force.**
- This force causes an **increase in the interatomic distance** r.
- Since the **moment of inertia,** $I = \mu r^2$ depends on r, it **increases** with the rotational speed.
- As a result, the **energy levels** become slightly **less spaced out** than in the rigid case.

The rotational energy of the non-rigid rotator is written as:

$$E_J = BJ(J+1) - BJ^2(J+1)^2$$

Or:

- B: rotational constant (as for the rigid rotator),
- D: **centrifugal distortion constant,** very small, which corrects the rigid model.

A **non-rigid rotator** is a model of a rotating molecule that takes into account **centrifugal distortion:** the bonds lengthen slightly as the rotational speed increases. This results in a **non-perfectly regular spacing** of the lines in the rotational spectrum.

- **Conclusion:**

- If she keeps her arms fixed → **rigid rotator.**
- If it spreads them apart by rotating quickly → **non-rigid rotator** (centrifugal distortion).
- If it receives a small "boost of energy" at the right time → it **spins faster,** like a molecule that **absorbs a microwave photon.**