



Lectures of Molecular spectroscopy  
Scholar year 2024-2025  
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## **Lecture No. 2: Microwave Spectroscopy**

### **1-Introduction**

#### **What is the main features of Microwave spectroscopy (pure rotational spectrum)?**

- Molecules have a fixed point, is the center of mass when atoms held together by chemical bonds.
- The rotational energies correspond to the microwave region of electromagnetic radiation ( $3 \times 10^{10}$  to  $3 \times 10^{12}$  Hz; energy range around 10 to 100 J/mol) and energy range around 10 kJ/mol) of the electromagnetic radiation.
- Pure rotation motion is for rigid rotor system, there is no vibration during rotation motion.
- In real life, molecules rotate and vibrate is occurs simultaneously.

### **2-Advantages:-**

#### **What is the main scientific advantage of Microwave spectroscopy (pure rotational spectrum)?**

- Determine the molecular structure of molecules in gas phase.
- Establish energetic barriers to internal rotation that associated with the rotation of the chemical compounds.

- Observation of hyperfine structure and provides information on the electronic structures of molecules.
- Understanding of the nature of weak molecular interactions such as van der Waals, hydrogen and halogen bonds through rotational spectroscopy.
- Achieved the measurement of bond length, mass of atoms, and mass of isotopes.

### **3-Rotator molecules.**

A molecule in the gas phase is free to rotate relative to a set of mutually orthogonal axes of fixed orientation in space, centered on the center of mass of the molecule.

**Q// Why Free rotation is not possible for molecules in liquid or solid phases? The free rotation is not possible for molecules in liquid or solid phases due to the presence of intermolecular forces.**

Rotation about each unique axis is associated with a set of quantized energy levels dependent on the moment of inertia about that axis and a quantum number.

Linear molecules the energy levels is describe by a single moment of inertia and a single quantum number,  $J$ , which defines the magnitude of the rotational angular momentum.

Nonlinear molecules which are symmetric rotors (or symmetric tops, there are two moments of inertia and the energy also depends on a second rotational quantum number,  $K$ , which defines the vector component of rotational angular momentum along the principal symmetry axis.

Analysis of spectroscopic data are expressed detailed results in quantitative determination of the values of the moments of inertia. From these precise values of the molecular structure and dimensions may be obtained. The rotational energy of a linear molecule, approximated as a rigid rotor is:  $E = BJ(J+1) \text{ -----1, } \epsilon = BJ(J+1)$

Energy value will be in joule units and becomes in  $\text{Cm}^{-1}$  after divided on light velocity.

Since J, is rotational quantum number and takes  $J = 0, 1, 2, 3 \dots n$ , and

$$B = \frac{h}{8\pi^2 cI} \text{ is the rotational constant } \text{cm}^{-1} \text{ units.}$$

For molecules other than hydrides, the moment of inertia I is such that  $B \leq 1 \text{ cm}^{-1}$ , and the rotational levels are so close together. Only “optical” spectrographs or spectrometers of the highest resolving power are capable of detecting the rotational structure on vibrational or vibronic transitions; and even these instruments fail when  $B \ll 1 \text{ cm}^{-1}$  as is the case for most molecules containing four or more heavy atoms.

Multiplication of  $B(\text{cm}^{-1})$  by the velocity of light c shows that in frequency units B is of the order or less than 30 GHz .

This places transitions between the pure rotational energy states of most molecules in the microwave region of the spectrum, where resolution of rotational structure is much better than that in the optical region. Just as in the classical problem where an oscillatory electrical field can cause an electric dipole to rotate with the frequency of the impressed field, the oscillatory electric vector of electromagnetic radiation can similarly “drive” a quantum mechanical rotor possessing a permanent electric dipole moment.

Similarly, the magnetic vector of the electromagnetic wave can interact with a rotor possessing a permanent magnetic moment. Thus molecules

such as OCS and BrCN, having electric moments, and O<sub>2</sub>, having a magnetic moment, have rotational spectra in the microwave region, while a molecule such as Carbon dioxide does not.

For a quantum mechanical rotor, the energy of the electromagnetic field is absorbed only when the frequency of the field is near that corresponding to the energy difference between two discrete energy states of the rotor.

The resulting absorption lines for the quantum oscillator constitute the microwave spectrum that one observes. Working backward from the spectrum then, one can ascertain the rotational energy states of the molecule, the moments of inertia of the molecule, and therefore some information about the dimensions of the molecule.

In certain cases, one can obtain sufficient information to obtain all the bond distances in the molecule, or for a nonlinear molecule, all the bond distances, bond angles, mass of isotopes (according to reduced mass) and moment of inertia. This is one of the primary goals of microwave spectroscopy.

#### **4- Intensities of Transitions and Selection Rules:**

The polar molecules (active microwave molecules) are interacted with electric vectors associated with electromagnetic radiation. The selection rules for pure rotational transitions in a linear rotor. These are  $\Delta J = \pm 1$ , since rotational energy levels have constant distance between each two rotation levels that equal to  $2B$ , this come out by differences of two levels through energy value as following:

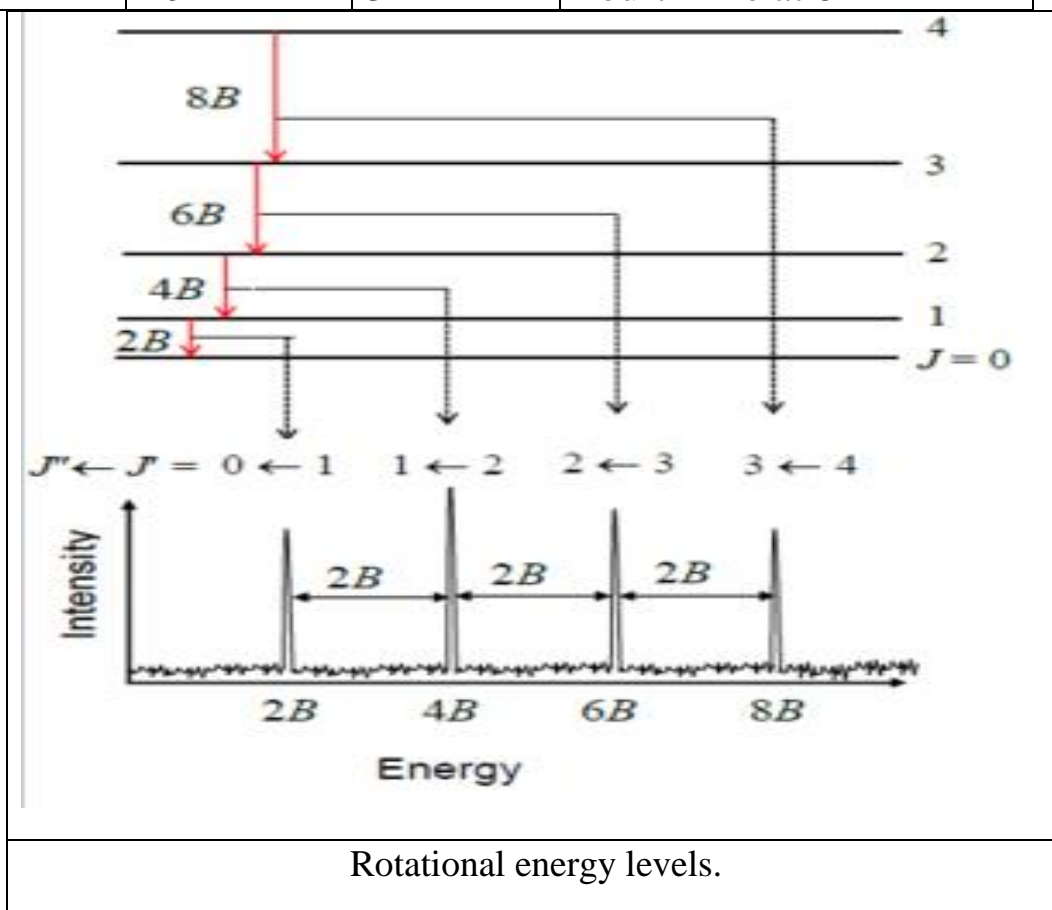
$$\Delta \epsilon = \epsilon_{J+1} - \epsilon_J - 2$$

$$\Delta \epsilon = B J+1(J+1+1) - B J(J+1)$$

$$\Delta \epsilon = 2B(J+1) \text{-----} 3$$

There are constant distance between rotational levels  $2B$ ,  $4B$ ,  $6B$ , and so on.... Can be make a table of energy measurements for several values of rotational quantum numbers:-

J	Energy/ $\epsilon_j$	Transition $J \rightarrow J'$	Absorption spectral line $\text{cm}^{-1}$
0	0	-----	----- ground state
1	$2B$	$0 \rightarrow 1$	First line at $2B$
2	$6B$	$1 \rightarrow 2$	Second line at $4B$
3	$12B$	$2 \rightarrow 3$	Third line at $6B$
4	$20B$	$3 \rightarrow 4$	Fourth line at $8B$



## 4-Classification of molecules.

### General Classification of Molecules

Back to the moment of inertia

Recall Definition: The **moment of inertia**  $I$  of a system about an axis passing through the centre of mass is given by;

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

We classify **polyatomic molecules** on the basis of their moments of inertia about three mutually perpendicular axes through the centre of mass (principal axes).

Call these axes  $a, b, c$  and (and thus  $I_a, I_b, I_c$ ) such that  $I_c = I_{max}$  and

$$I_a \leq I_b \leq I_c$$

### General Classification of Molecules

I. **Spherical tops:**

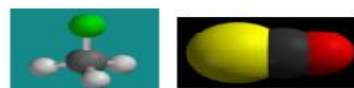
$$I_a = I_b = I_c$$



II. **Symmetric tops:** (two identical  $I_i$ )

a) **Prolate tops:**

$$I_a < I_b = I_c$$



b) **Oblate tops:**

$$I_a = I_b < I_c$$



III. **Asymmetric tops:**

$$I_a < I_b < I_c$$



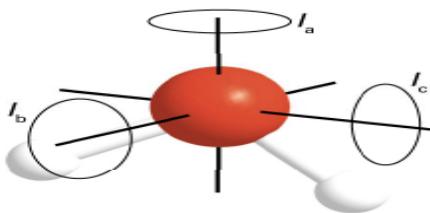
### Rotational terms

For diatomics we defined a rotational constant  $\tilde{B} \propto \frac{1}{I} = \frac{1}{\mu R^2}$

In general we require three such rotational constants:

as wavenumbers:  $\tilde{A} = \frac{h}{8\pi^2 c I_a}$   $\tilde{B} = \frac{h}{8\pi^2 c I_b}$   $\tilde{C} = \frac{h}{8\pi^2 c I_c}$

$$\tilde{A} \geq \tilde{B} \geq \tilde{C}$$



**H<sub>2</sub>O molecule**

$$\tilde{A} = 27.9 \text{ cm}^{-1}$$

$$\tilde{B} = 14.5 \text{ cm}^{-1}$$

$$\tilde{C} = 9.3 \text{ cm}^{-1}$$

But, we can no longer relate these constants explicitly to individual bond lengths within the molecule.

## 5-Applications.

Q1//Rotation spectrum of  ${}_{76}\text{Br}_{19}\text{F}$  has a series of lines in equal distance from each other ( $0.71433\text{cm}^{-1}$ ). Calculate the rotation constant, moment of inertia, and length bond of molecule.

Answer //

1-Equal distance=  $2B = 0.71433\text{cm}^{-1}$  Rotation constant= $B=0.35717\text{ cm}^{-1}$

2- Moment of inertia= $h/8\pi^2BC \Rightarrow I=7.83 \times 10^{-96}\text{ kg.m}^2$

3- Length bond of molecule=  $r = \sqrt{I/\mu} = 0.1755\text{nm}$

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Q2//The microwave spectrum of  ${}^{39}\text{K}{}^{127}\text{I}$  is consisted of a series of lines whose spacing is almost constant at 3634 MHz . Calculate the bond length of Potassium iodide, if you know that 1 AMU= $1.67 \times 10^{-27}\text{ kg}$ .

Answer//???? The rotational spacing for KI is given in Hz, a unit of frequency.

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Q3//Calculate the value of  $I$  and  $r$  of  ${}^{12}\text{C}{}^{16}\text{O}$ . If you know that rotation, transition occurs at  $0.92118\text{ cm}^{-1}$ .

$$\begin{aligned}\text{Answer// } I &= h/(8\pi^2 BC) = 6.626 \times 10^{-34}/(8 \times 3.14152 \times 0.92118 \times 3 \times 10^{10}) \\ &= 1.45579 \times 10^{-46}\text{ kg m}^2\end{aligned}$$

Since the value of  $B$  is in  $\text{cm}^{-1}$ , the velocity of light  $C$  is taken in  $\text{cm/s}$ .

$I = \mu r^2$ . The atomic mass of  $\text{C} \equiv 12.0000\text{ AMU}$ ,  $\text{O} \equiv 15.9994\text{ AMU}$ .

1 AMU =  $1.6604 \times 10^{-27}\text{ kg}$ . The reduced mass of CO can be calculated to be  $1.13836 \times 10^{-27}\text{ kg}$ . Therefore  $r^2 = I/\mu = 1.45579 \times 10^{-46}/1.13826 \times 10^{-27}\text{ m}^2$  and  $r = 1.131\text{ \AA}$ .