

ROTATION SPECTROSCOPY

ELECTROMAGNETIC RADIATION

Electromagnetic radiations can interact with matter in various ways. Each interaction gives us insights about certain properties of the matter and use of electromagnetic radiations of different energies can give different information about the matter under study. Different regions of electromagnetic spectrum have different kinds of spectroscopic techniques associated with them (Figure 1 & 2).

Radiowaves : ESR and NMR spectroscopy

Microwaves : Rotational spectroscopy.

Infrared waves : IR spectroscopy

UV/ VIS waves : UV/VIS spectroscopy

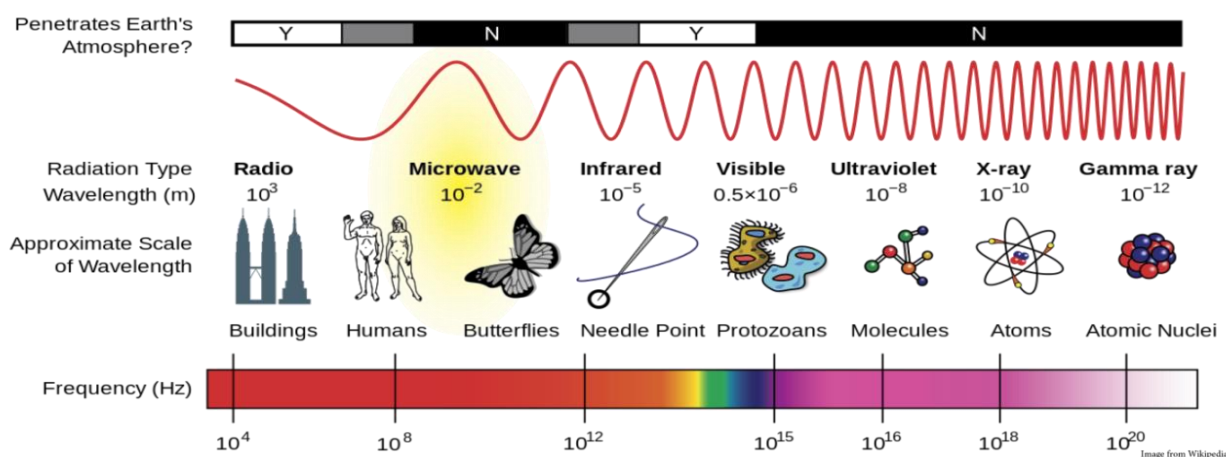


Figure 1. Electromagnetic spectrum

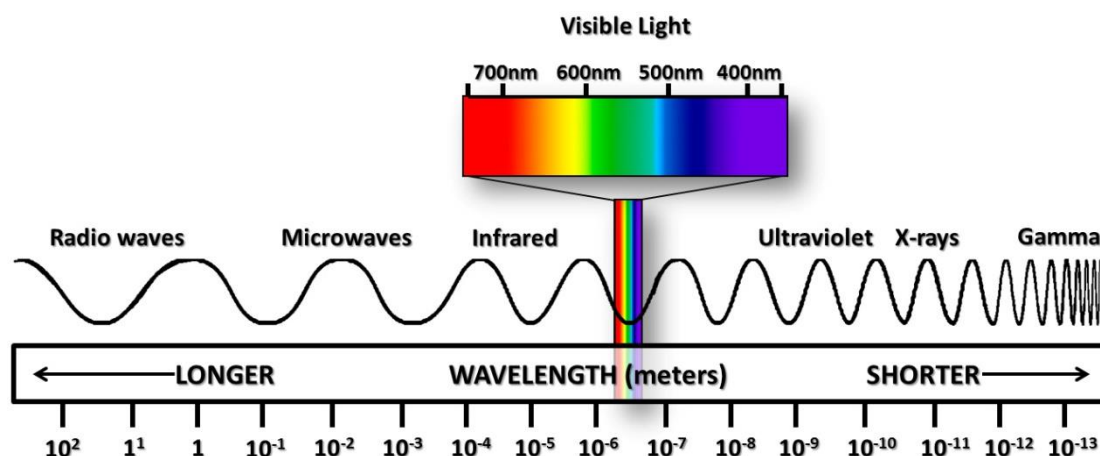


Figure 2. Electromagnetic spectrum

The visible light is merely a part of the whole spectrum of electromagnetic radiation, extending from the radio waves to cosmic rays. All these apparently different forms of electromagnetic radiations travel at the same velocity but characteristically differ from each other in terms of frequencies and wavelength.

The propagation of these radiations involves both electric and magnetic forces which give rise to their common class name electromagnetic radiation. In spectroscopy, only the effects associated with electric component of electromagnetic wave are important. Therefore, the light wave travelling through space is represented by a sinusoidal trace (Figure 3). A wave is an oscillating displacement that depends on position and time. A region of positive displacement is called a *crest*, and a region of negative displacement is called a *trough*. A location where the displacement of a wave equals zero is called a *node*. The distance from one crest to the next is called the *wavelength* λ . The distance A is known as the maximum amplitude of the wave. The *period* τ of a wave is the time for the first return of the oscillating object to an initial state. The *frequency* (ν) is the reciprocal of the period, or the number of oscillations per second. Although a wave is frequently characterized in terms of its wavelength λ , often the terms such as wavenumber ($\bar{\nu}$), frequency (ν), cycles per second (cps) or hertz (Hz) are also used.

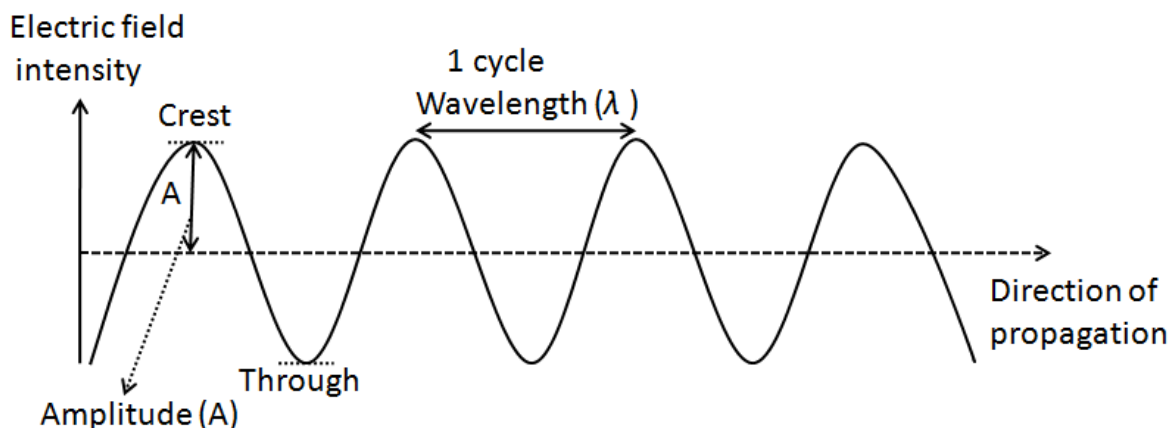


Figure 3. Wave like propagation of light (λ = wavelength, A = amplitude)

$$1 \text{ \AA} = 10^{-1} \text{ nm} = 10^{-8} \text{ cm}$$

The four quantities wavelength, wavenumber, frequency and velocity can be related to each other by following relationships

$$\text{Wavelength } (\lambda) = 1 / \bar{\nu} = c / \nu$$

$$\text{Wave-number } (\bar{\nu}) = 1 / \lambda = \nu / c$$

$$\text{Frequency } (\nu) = c / \lambda = c \bar{\nu}$$

$$\text{Velocity } (c) = \nu \lambda = \nu / \bar{\nu}$$

ULTRAVIOLET-VISIBLE SPECTROSCOPY

UV-Visible spectroscopy deals with the study of the electronic transitions of molecules as they absorb light in the UV (190-400 nm) and visible regions (400-800 nm) of the electromagnetic spectrum. The absorption of ultraviolet or visible radiation lead to transition among electronic energy levels, hence it is also often called electronic spectroscopy.

UV absorptions of molecules are generally broad because vibrational and rotational levels are "superimposed" on top of the electronic levels (Figure 4). In addition to undergoing electronic transitions the atoms can rotate and vibrate with respect to each other. These vibrations and rotations also have

discrete energy levels. This large number of available levels produces multiple absorptions and appearance of broad bands in an UV/VIS spectrum, rather than narrow peaks. For this reason, the wavelength of maximum absorption (λ_{\max}) is usually reported.

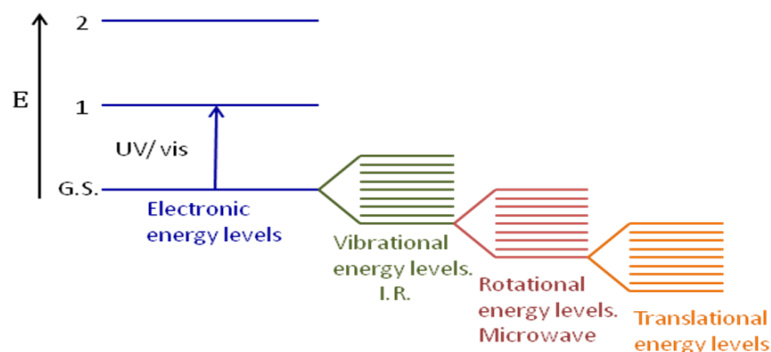


Figure 4. Electronic transitions with vibrational, rotational, translational transitions superimposed

ELECTRONIC TRANSITIONS

When a radiation passes through a material and radiation is absorbed. If it occurs and yields a spectrum with gaps in it, called an **absorption spectrum**. As a result of energy absorption, atoms or molecules pass from a state of low energy or ground state to a state of higher energy state or excited state (Figure 5). The absorbed energy is exactly equal to the energy difference between the excited and ground states. Generally, most probable transition is from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

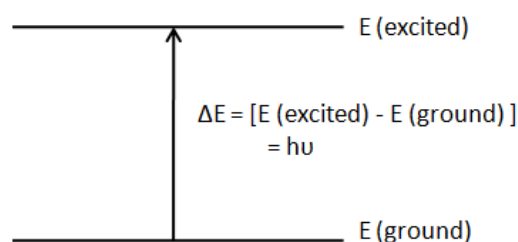


Figure 5. The excitation process.



ROTATIONAL SPECTROSCOPY

When the transition of a molecule takes place from one rotational level to another rotational level in the same vibrational states, the energy differences between two rotational states appears due to emission or absorption of a quantum of radiation. The resulting spectra will consist of a series of closely spaced lines. This spectrum is known as pure rotational spectra.

RIGID ROTATOR

Application of **quantum theory** shows that the rotational energy possessed by a molecule is **quantized**, in the same way that all energy is quantized. In general, the rate of rotation of a molecule is sufficiently slow compared with the rate of vibration of the bonds, that the molecule can be considered as a **rigid rotator** rotating with fixed internuclear separations given by the average of the vibrational displacements. So, the rigid rotor is a model system that consists of two nuclei with fixed internuclear distance equal to r_e . No vibration is possible.

DIATOMIC MOLECULE

The simplest type of rigid rotor is the linear rotor of a diatomic molecule.

ROTATIONAL SPECTROSCOPY: SELECTION RULES AND TRANSITIONS

For a molecule to interact with an electromagnetic field, and undergo a transition between two energy levels, requires an **electric dipole** (μ) to be associated with the motion giving rise to the energy levels. Since rotational motion does not change the electric dipole of a molecule, the **physical selection rule** for rotational energy transitions is:

the molecule must possess a permanent electric dipole ($\mu \neq 0$) (i.e. the molecule must be polar)

Symmetric molecules with a center of inversion, for example **homonuclear diatomics** (H_2 , O_2 , Cl_2 , F_2 , I_2 , O_3) and **symmetric polyatomic molecules** (CO_2 , H_2O_2 , CH_4 and SF_6) do not have permanent electric dipoles and therefore do not give rise to rotational spectra. **Heteronuclear diatomics** (e.g. HCl) and polyatomic molecules with no center of inversion (e.g. NH_3) do have rotational spectra.



$\text{SO}_2 = \text{Rotationally active}$

$\text{HD} = \text{Rotationally inactive}$

Of the molecules N_2 , CO_2 , OCS , H_2O , $\text{CH}_2=\text{CH}_2$, C_6H_6 , only OCS and H_2O are polar, so only these two molecules have microwave spectra.

Illustration: Identifying infrared active molecules

Of the molecules N_2 , CO_2 , OCS , H_2O , $\text{CH}_2=\text{CH}_2$, C_6H_6 , only OCS and H_2O are polar, so only these two molecules have microwave spectra.

Self-test Q1. Which of the following molecules may show a pure rotational microwave absorption spectrum: (a) H_2O , (b) H_2O_2 , (c) NH_3 , (d) N_2O ?

Self-test Q2. Which of the following molecules may show a pure rotational Raman spectrum: (a) H_2 , (b) HCl , (c) CH_4 , (d) CH_3Cl ?

Self-test Q3. Which of the following molecules may show a pure rotational Raman spectrum: (a) CH_2Cl_2 , (b) CH_3CH_3 , (c) SF_6 , (d) N_2O ?

The **specific selection rules** summarizing allowed transitions between rotational energy levels are:

$$\Delta J = \pm 1 \quad \text{or} \quad J_f - J_i = \pm 1$$

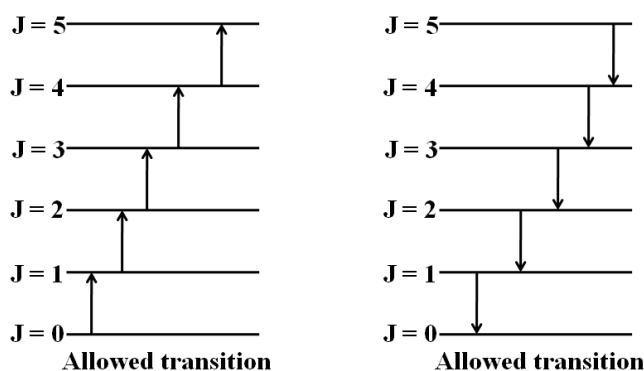


Fig. 6. The allowed rotational energy levels of a rigid diatomic molecule

ROTATIONAL ENERGY EXPRESSION

Solving the Schrödinger equation and applying appropriate boundary conditions we have,



Rotational Energy (E_J), $E_J = \frac{h^2}{8\pi^2 I} J(J+1)$ in Jule unit

I = moment of inertia

J = Rotational quantum number = 0,1,2,3,4,5,6..etc

$$\varepsilon_J = \frac{E_J}{h} = \frac{h}{8\pi^2 I} J(J+1) \quad \text{in Sec}^{-1} \text{ i.e. in frq. unit}$$

$$\bar{\varepsilon}_J = \frac{E_J}{c} = \frac{h}{8\pi^2 I c} J(J+1) \quad \text{in cm}^{-1} \text{ i.e. in wave no. Unit}$$

For, UV/Vis light energy expressed in unit of wavelength (cm)

For, I.R. light energy expressed in unit of wave number (cm^{-1})

For, Microwave light energy expressed in unit of wave number (cm^{-1})

$$\text{Wave number} = \frac{1}{\lambda} \text{ cm}^{-1}$$

$$= \frac{\nu}{c} \text{ cm}^{-1}$$

$$= \frac{E}{hc} \text{ cm}^{-1}$$

$$\text{Wave number} = \bar{\varepsilon}_J = \frac{E_J}{c} \text{ cm}^{-1} = \frac{h}{8\pi^2 I c} J(J+1) \text{ cm}^{-1}$$

For a given species of molecules, $\frac{h}{8\pi^2 I c}$ is a constant and it is substituted by B . B is termed as rotational constant.

$\therefore B = \frac{h}{8\pi^2 I c}$ $\therefore \bar{\varepsilon}_J = BJ(J+1)$ or transition from rotational quantum J (lower en. State) to one of higher quantum number ($J+1$), the energy differences between these two neighboring states will be,

$$\begin{aligned}
 E_{J+1} - E_J &= B(J+1)(J+1+1) - BJ(J+1) \\
 &= B(J+1)(J+2) - BJ(J+1) \\
 &= 2B(J+1) \\
 \bar{\nu}_J &= 2B(J+1), \quad B \text{ is in wave no (cm}^{-1}\text{) unit.}
 \end{aligned}$$

ROTATIONAL PEAKS

We have, $\bar{\epsilon}_J = BJ(J+1)$, Bin cm^{-1} unit,

We know, $\bar{\nu}_J = 2B(J+1)$, J= Rotational quantum no of the lower energy state.

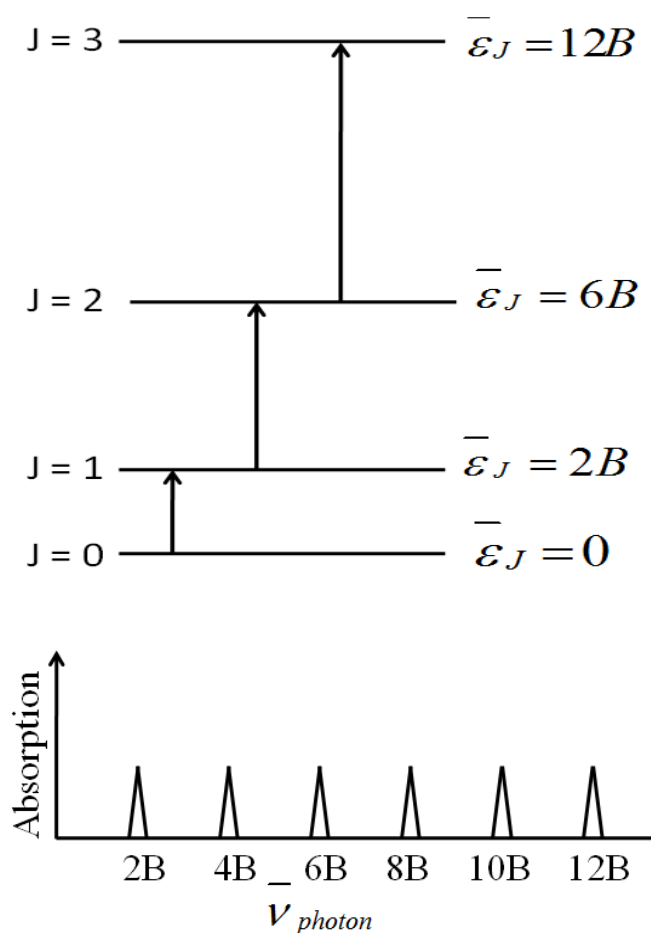


Figure 7. Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum which arises for them



For the transition from $J = 0$ to $J = 1$ level, $\bar{\nu} = 2B(0+1) = 2B$

For the transition from $J = 1$ to $J = 2$ level, $\bar{\nu} = 2B(1+1) = 4B$

For the transition from $J = 2$ to $J = 3$ level, $\bar{\nu} = 2B(2+1) = 6B$

Therefore, the rotational energy levels are not equispaced. But, the rotational lines or the peaks in the rotational spectra are equispaced and the spacing is $2B \text{ cm}^{-1}$.

References-

- ✓ William Kemp. (2002) Organic Spectroscopy. PAIGRAVE
- ✓ [Y. R. SHARMA](#). (2013) Elementary Organic Spectroscopy (Principles And Chemical Applications). S. Chand Limited.
- ✓ Pavia, D. L., Lampman, G. M., & Kriz, G. S. (1979). Introduction to spectroscopy: a guide for students of organic chemistry. Philadelphia, W.B. Saunders Co.

[The information, including the figures, are collected from the above references and will be used solely for academic purpose.]