Atomic and Molecular Physics

Course Code: PHYS4009

Lecture Topic

Molecular Spectroscopy

By

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Please see the video lecture at
https://www.youtube.com/watch?v=A2DQ_OxJ2Og

Outline

Questions that comes in our mind ?

What is the term Spectroscopy?

What does light do to the molecules?

How can you produce a molecular spectrum?

What information does the molecular spectrum give?

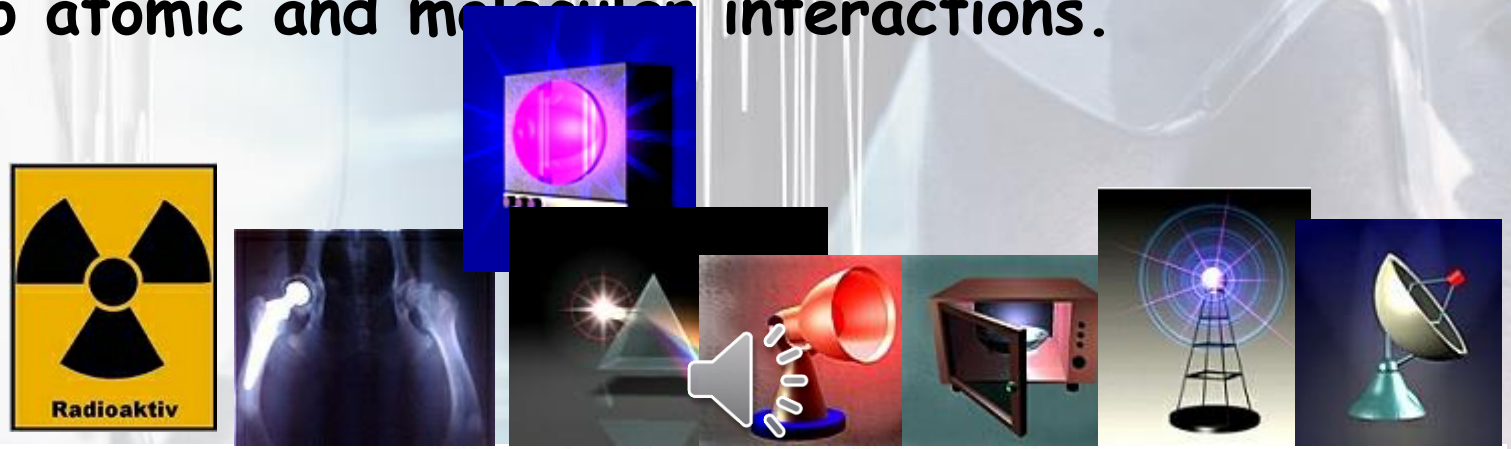
What we achieve?

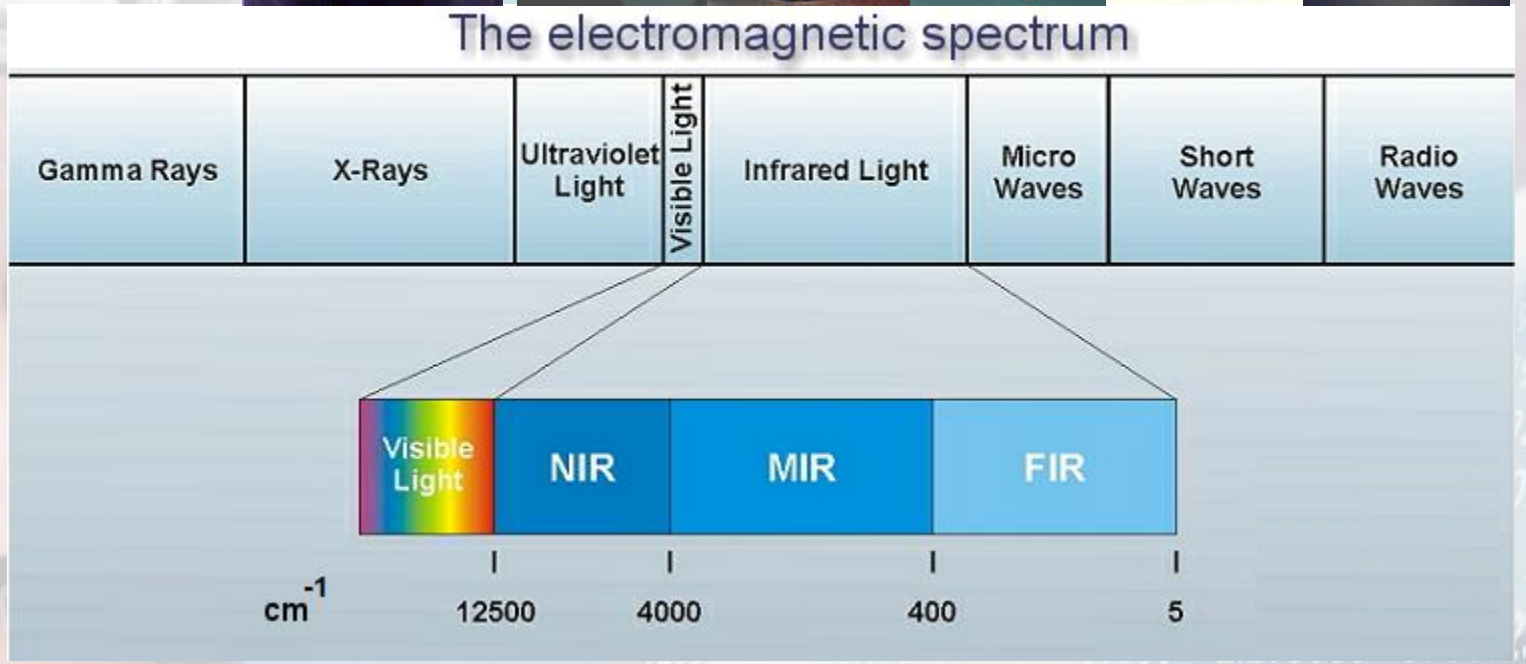
Understanding of:

- *How light interacts with molecules*
- *Molecular Energy States*
- *How to use spectroscopy to quantitatively characterize molecule*
- *How to extract molecular information*

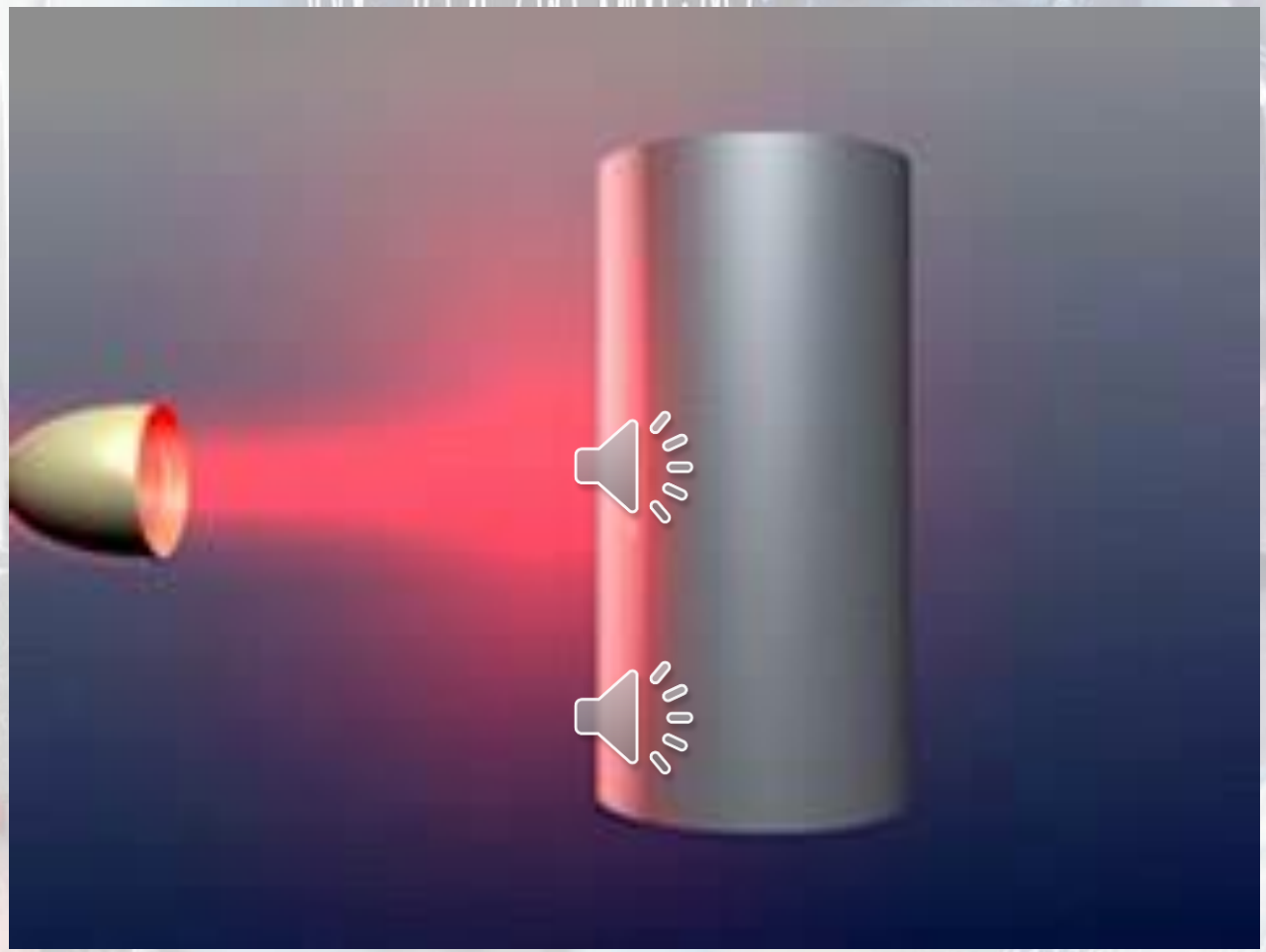
SPECTROSCOPY

Spectroscopy is the study of electromagnetic spectra – the wavelength composition of light – due to atomic and molecular interactions.



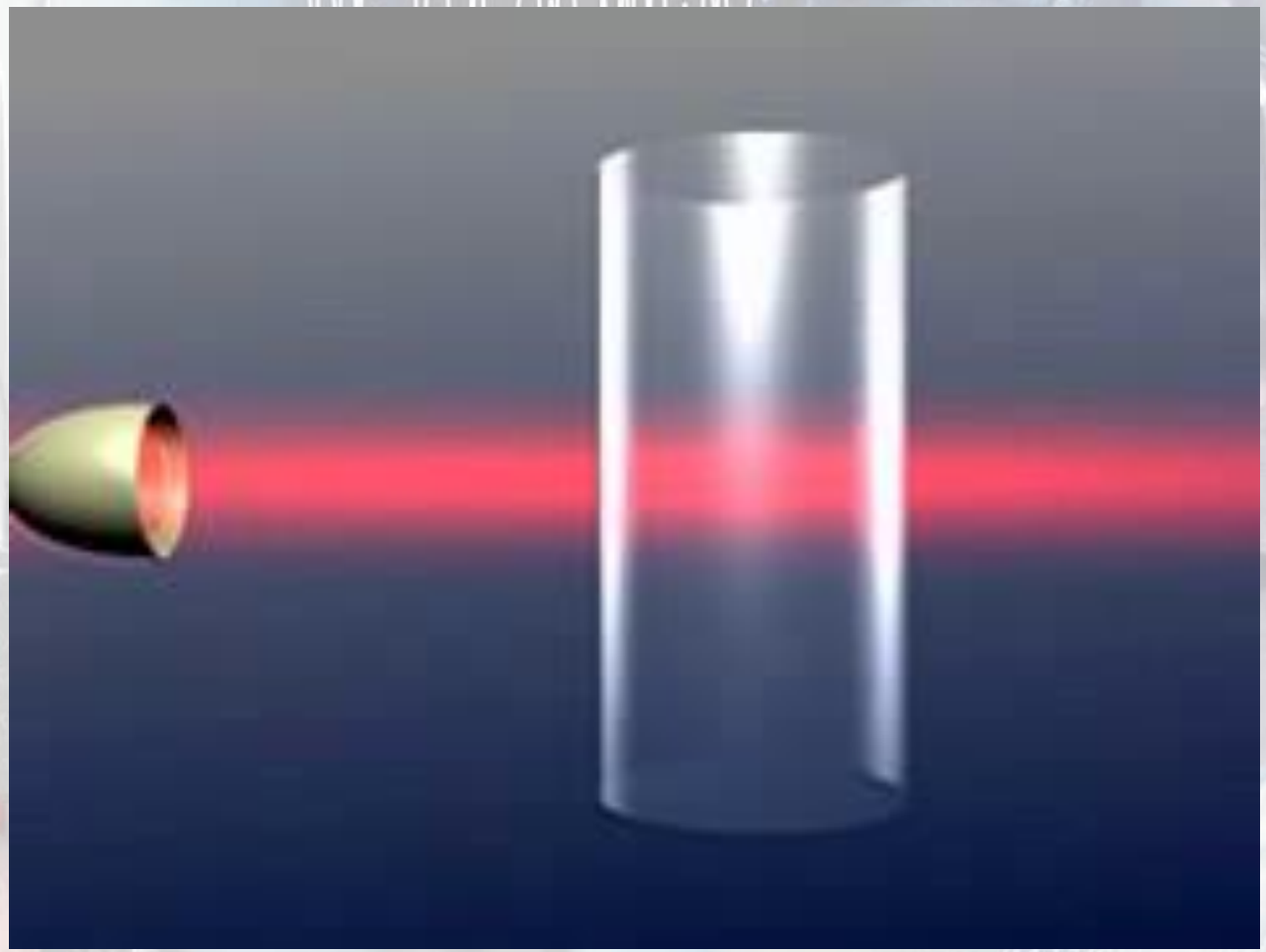


Interaction of radiation with matter



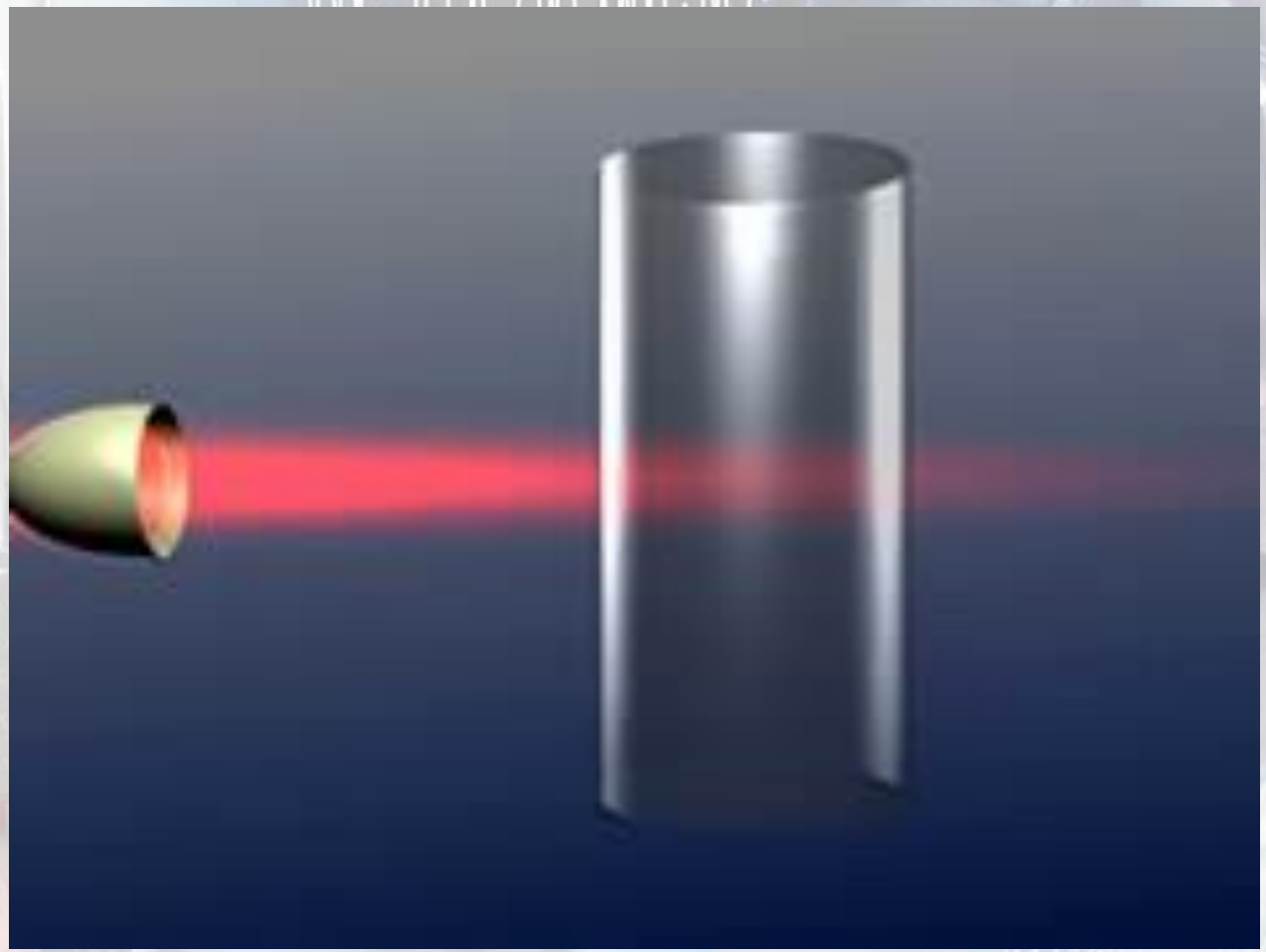
Reflection

Interaction of radiation with matter



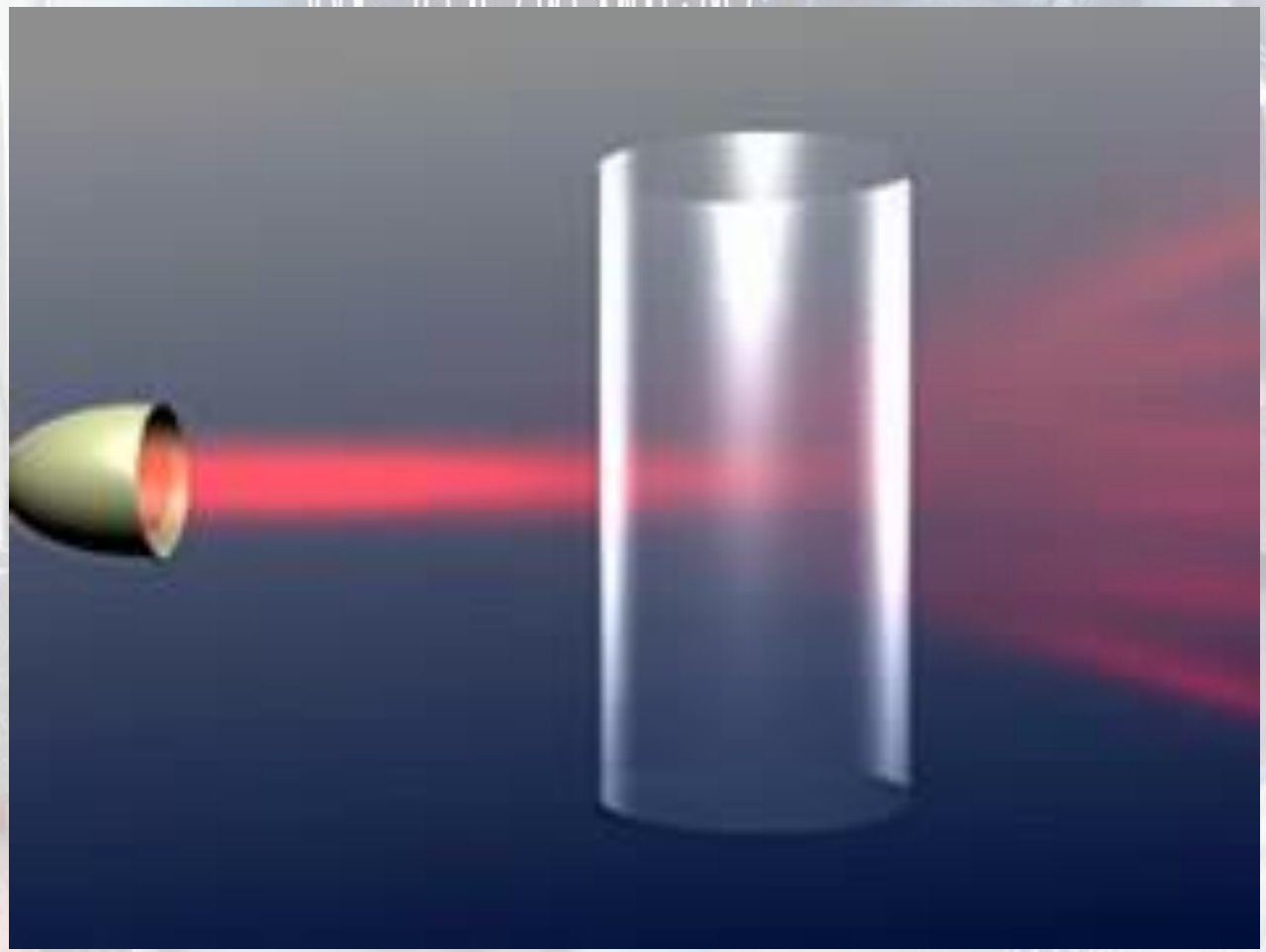
Transmission

Interaction of radiation with matter



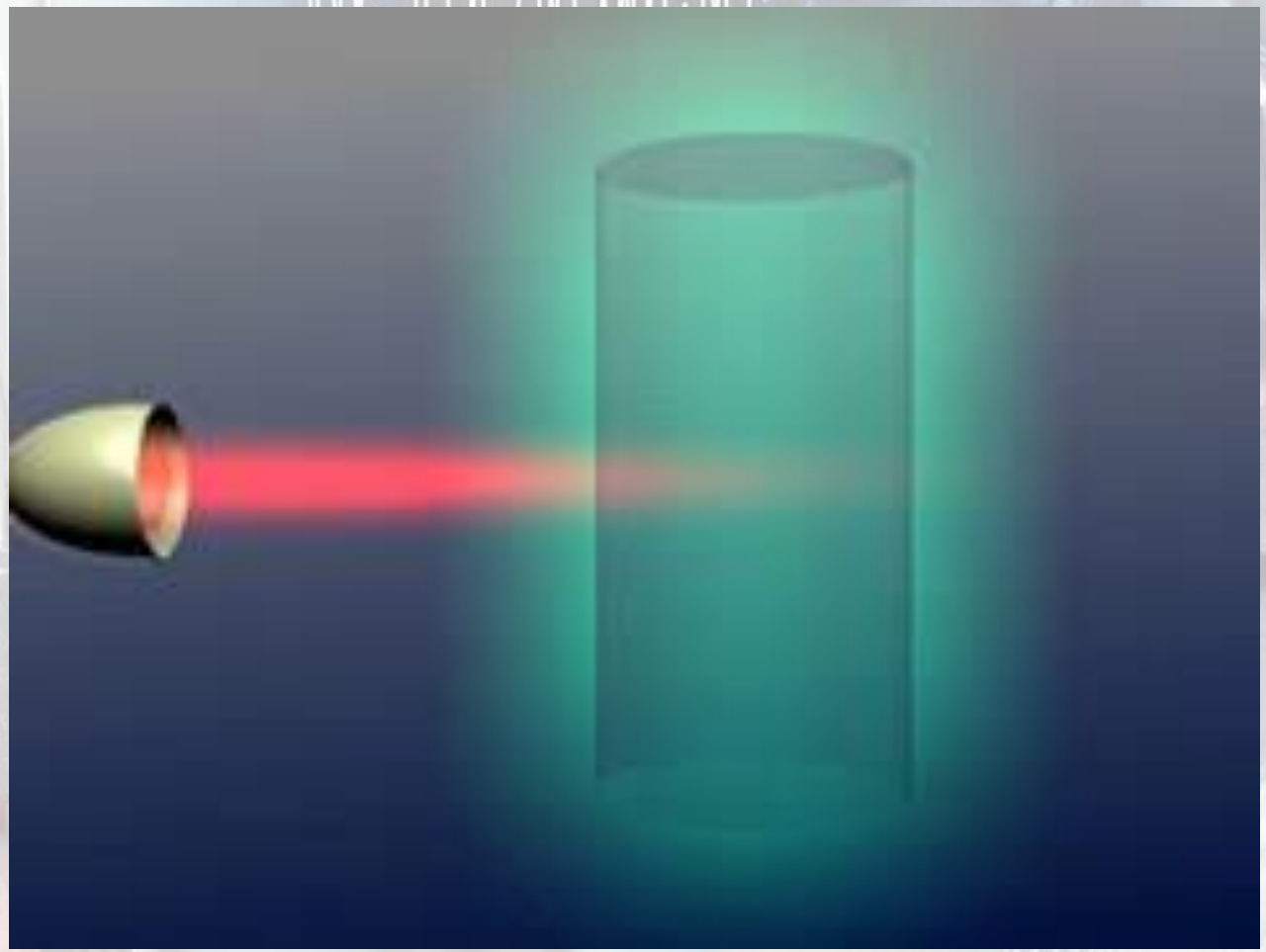
Absorption

Interaction of radiation with matter



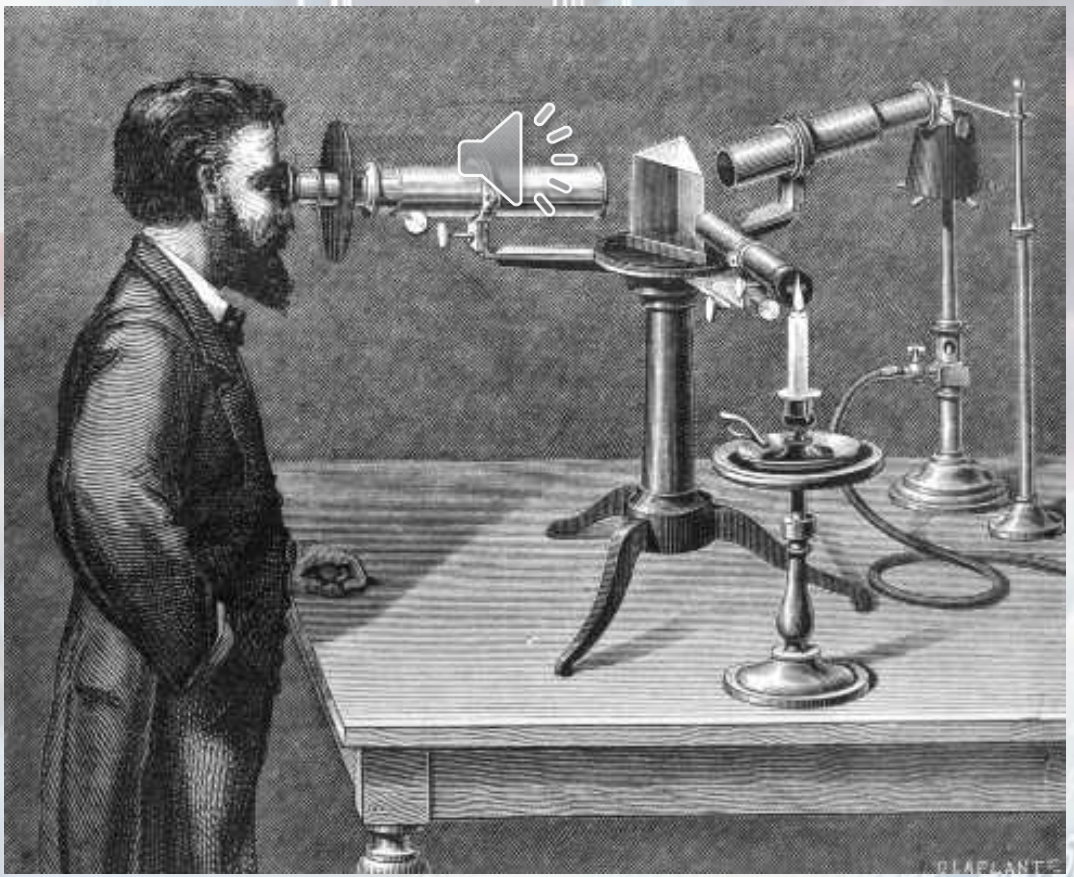
Scattering

Interaction of radiation with matter

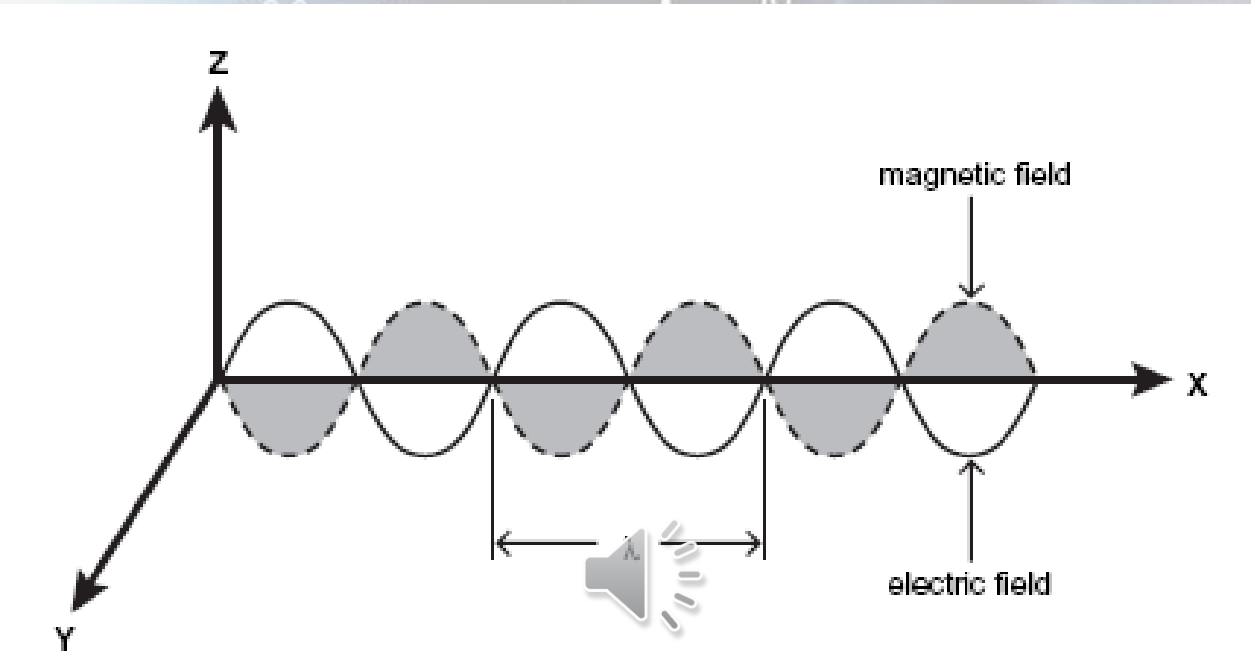


Photoluminescence

Spectroscopy is the study of matter (atom or molecule or any substance) by investigating light, sound, or particles that are absorbed, emitted or scattered by the matter under investigation with the help of spectroscopic instruments



Light : Electromagnetic Radiation



$$E = E_0 \sin(kx - \omega t)$$

$$B = B_0 \sin(kx - \omega t)$$

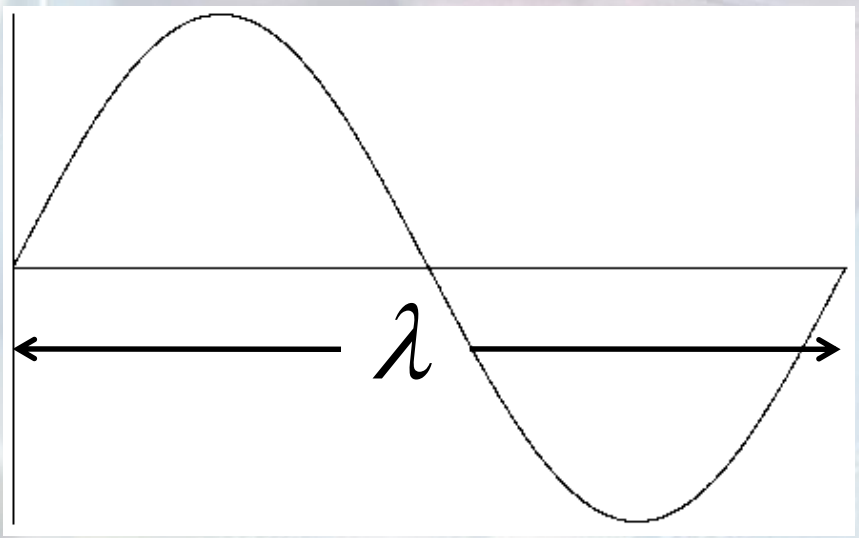
$$k = \frac{2\pi}{\lambda} \qquad \omega = 2\pi\nu$$

Energy of Photon

$$E = h\nu = h\frac{c}{\lambda} = hc\tilde{\nu}$$

$h = 6.626 \times 10^{-34}\, js$ $\quad$ $c = 2.997 \times 10^{8}\, m/s$

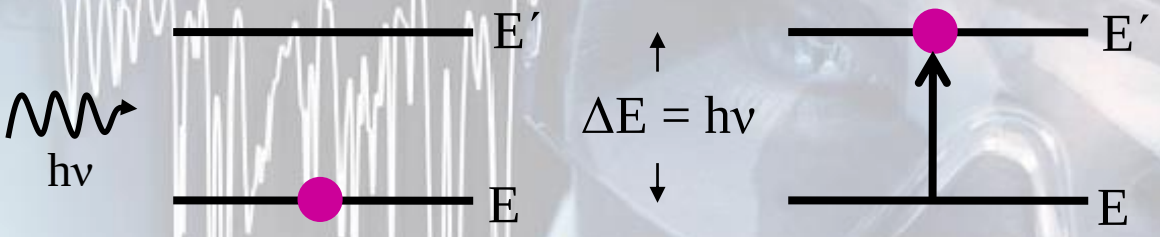
$$Wave\ frequency \quad \nu = \frac{c}{\lambda}$$



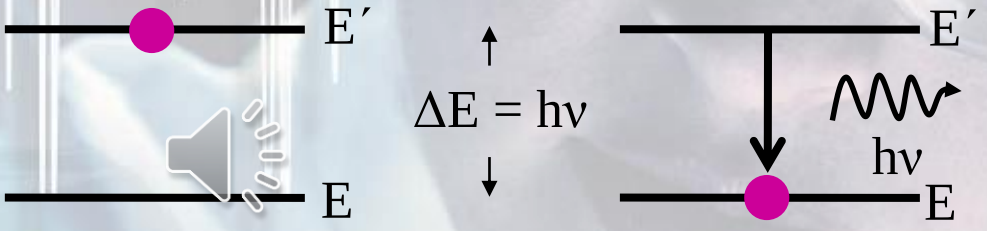
$$Wavenumber\ (cm^{-1}) \quad \tilde{\nu} = \frac{1}{\lambda(cm)}$$

Molecular Interaction with Light

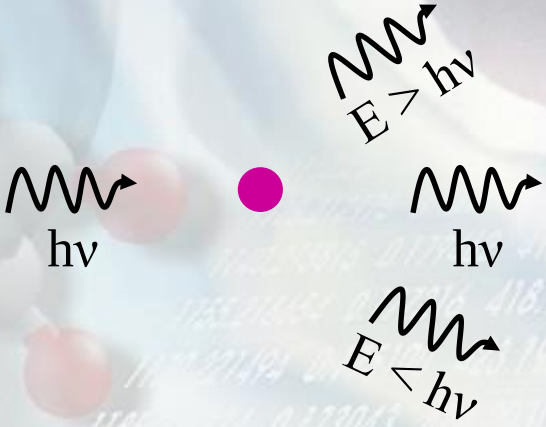
Absorption



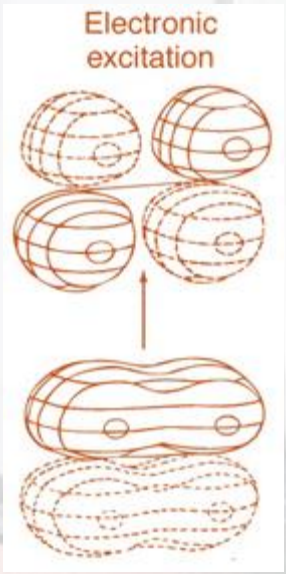
Emission

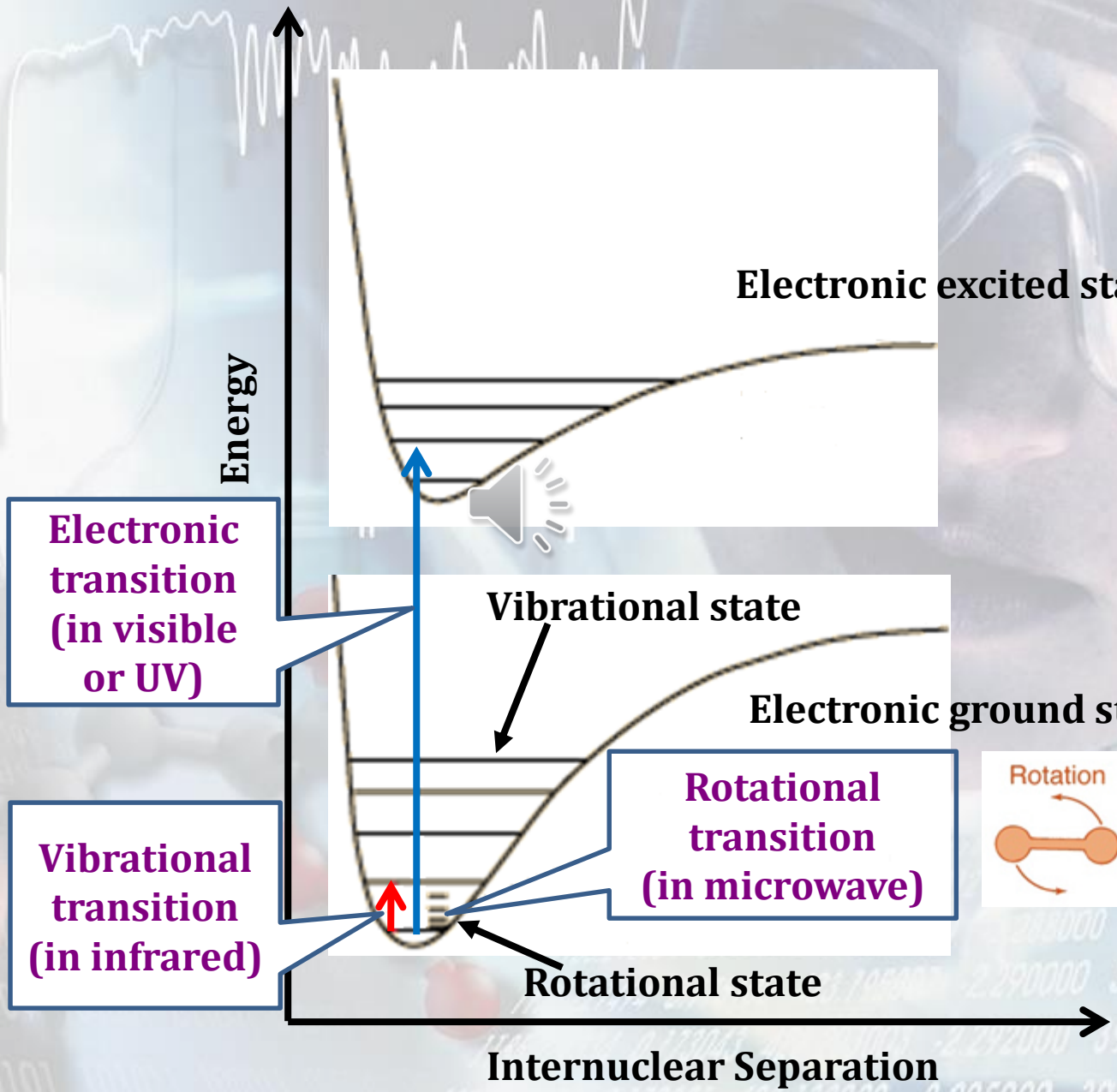


Scattering

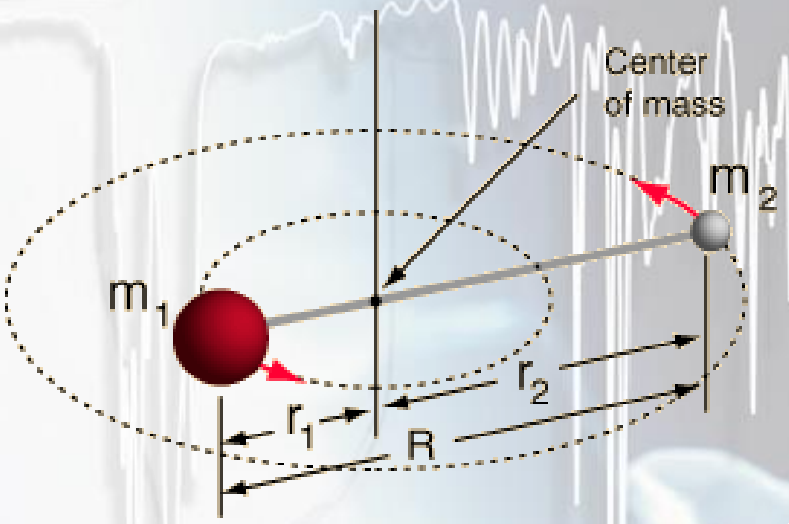


Molecular Energy States



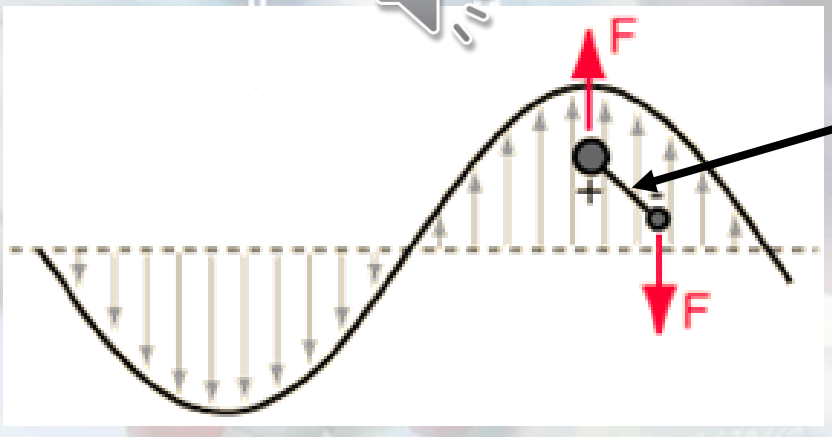


Molecular Rotation in Diatomic Molecule



$$I = \mu R^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$



Permanent dipole moment

The electric field of an electromagnetic wave exerts a torque on a electric dipole

Molecular Rotational Energy

$$E = \frac{1}{2} I\omega_x^2 + \frac{1}{2} I\omega_y^2 + \frac{1}{2} I\omega_z^2$$

Angular momentum $L = I\omega$

$$E = \frac{L_x^2}{2I_x} + \frac{L_y^2}{2I_y} + \frac{L_z^2}{2I_z}$$

$$H\psi = \frac{L^2}{2I}\psi = \frac{J(J+1)\hbar^2}{2I}\psi$$

J is Rotational Quantum Number

$$E = \frac{J(J+1)\hbar^2}{2I}$$

$$F(J) = \frac{E}{hc} = BJ(J+1)\ \ cm^{-1}$$

For rigid rotor

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

$$F(J) = \frac{E}{hc} = BJ(J+1) - DJ^2(J+1)^2 + \cdots \ \ cm^{-1}$$

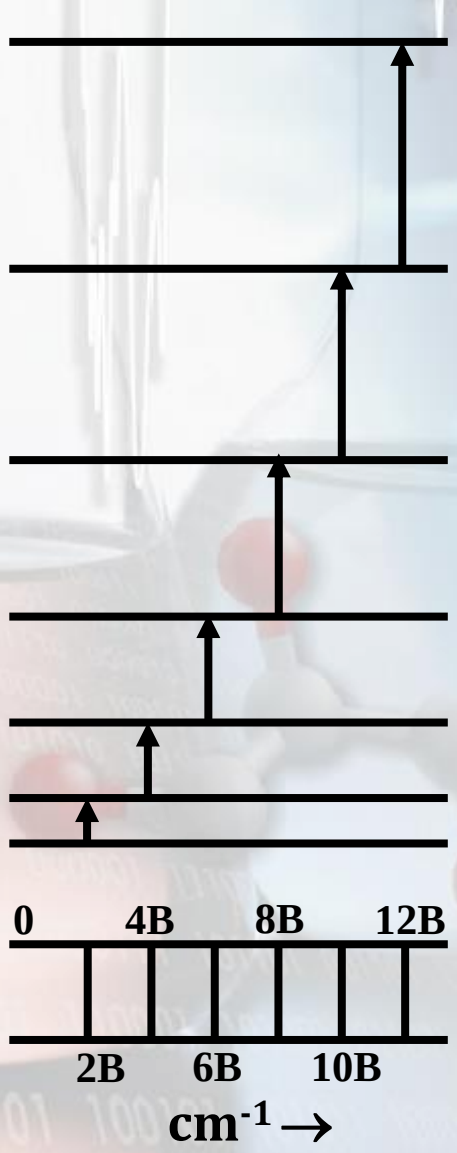
For non-rigid rotor

B is Rotational constant and ***D*** is centrifugal distortion constant

Rotational Energy Level

Rigid Rotor

$F(J) = BJ(J+1)\ cm^{-1}$



Selection rule

$\Delta J = \pm 1$

Non-Rigid Rotor

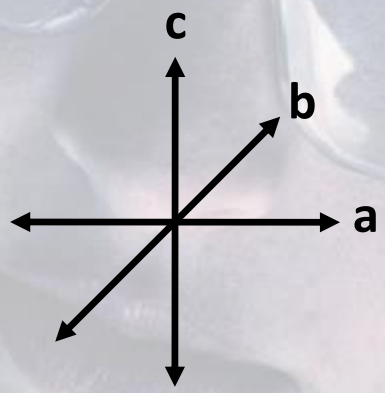
$F(J) = BJ(J+1) - DJ^2(J+1)^2 \ldots . cm^{-1}$

Molecular Rotation in Polyatomic Molecule

The rotational spectra of molecules can be classified according to their principal moments of inertia

$$I = \sum_i M_i R_i^2$$

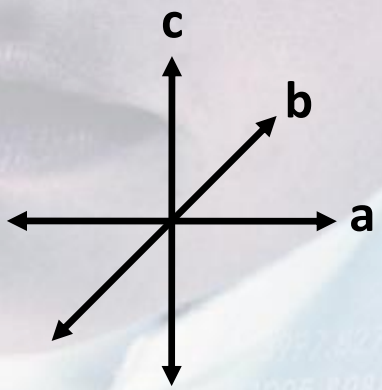
$$I_c \geq I_b \geq I_a$$

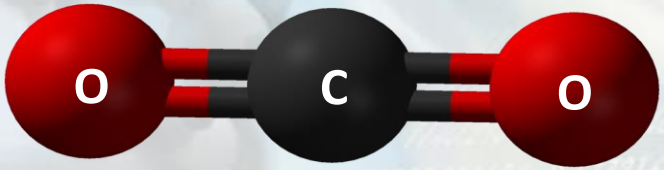


The particular pattern of energy levels and hence the transitions in the rotational spectrum for a molecule is determined by its symmetry. Based on the symmetry of their structure, molecules are divided into four different classes.

Linear molecules

$$I_c = I_b \geq I_a = 0$$

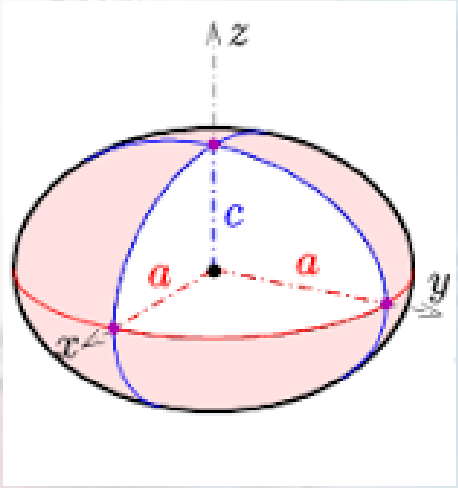


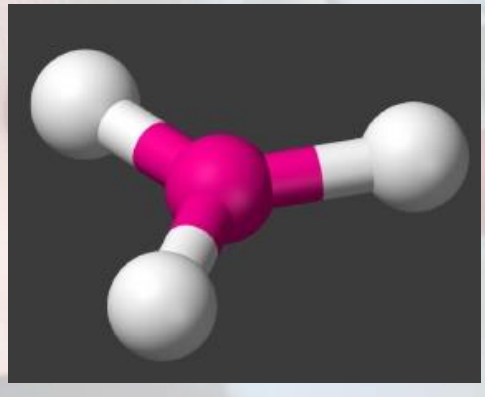


Symmetric top

$$I_c > I_b = I_a$$

Oblate

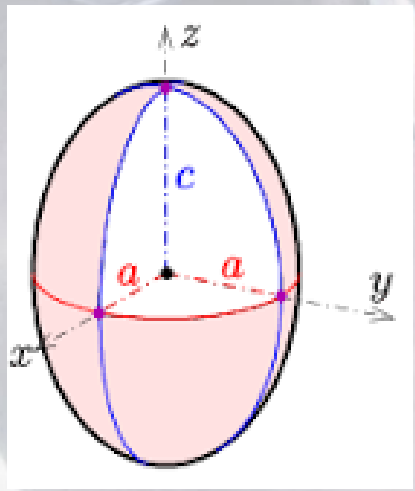


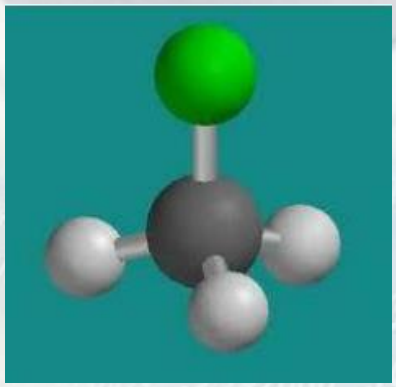


BF_3

$$I_c = I_b > I_a$$

Prolate

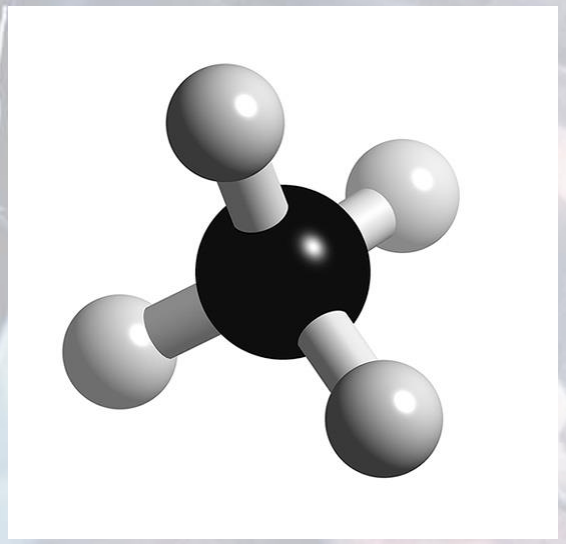




CH_3Cl

Spherical top

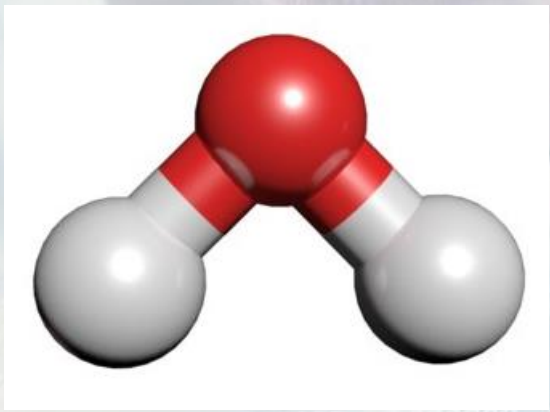
$$I_c = I_b = I_a$$



CH_4

Asymmetric top

$$I_c \neq I_b \neq I_a$$



H_2O

Books for Further Reading

1. Fundamentals of Molecular Spectroscopy by C. N. Banwell (McGraw Hill)

2. Basic Atomic & Molecular Spectroscopy by J. M. Hollas (Royal Society of Chemistry)

References:

http://hyperphysics.phy-astr.gsu.edu/hbase/index.html

Bruker application notes


Thank you