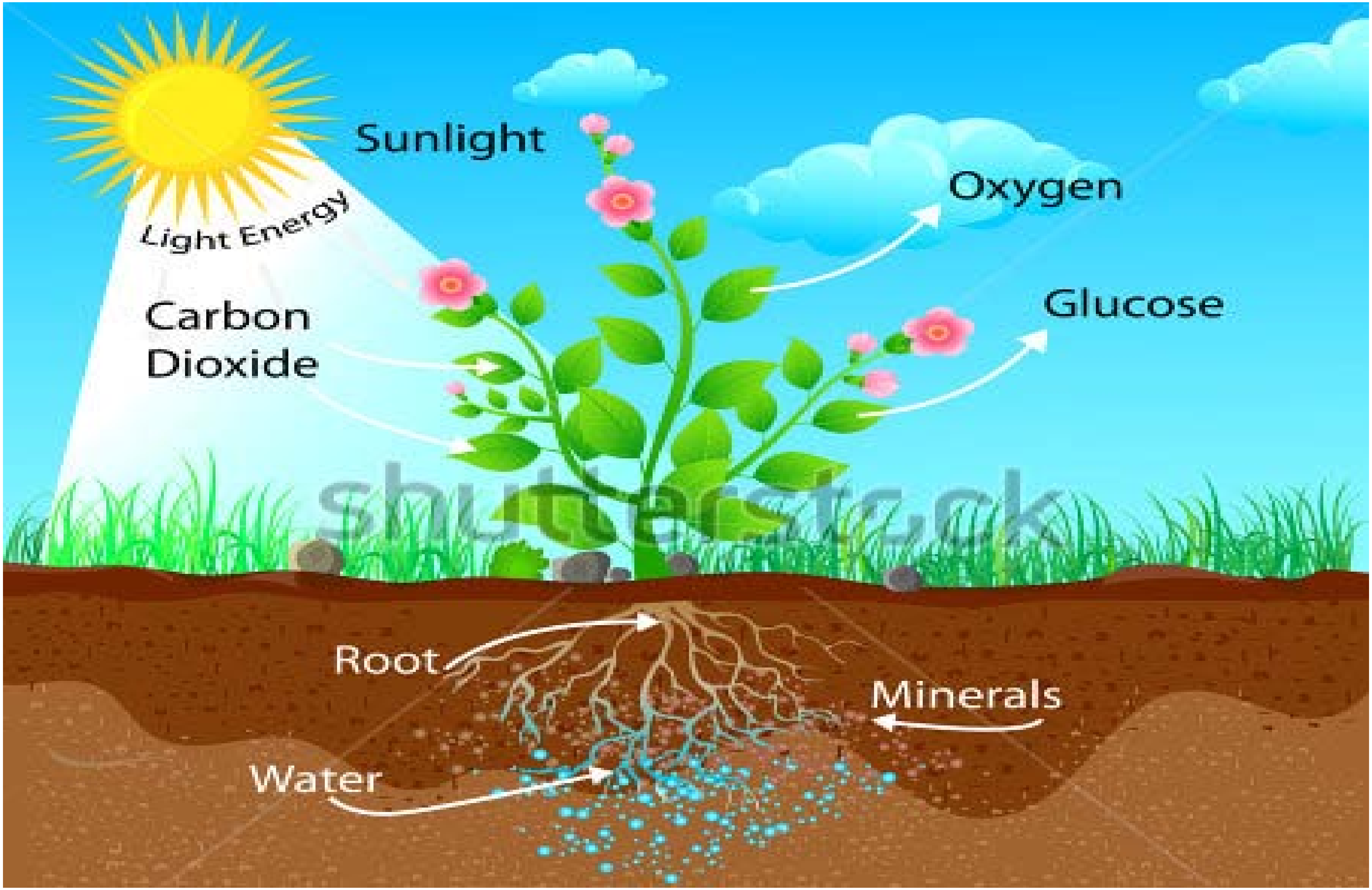
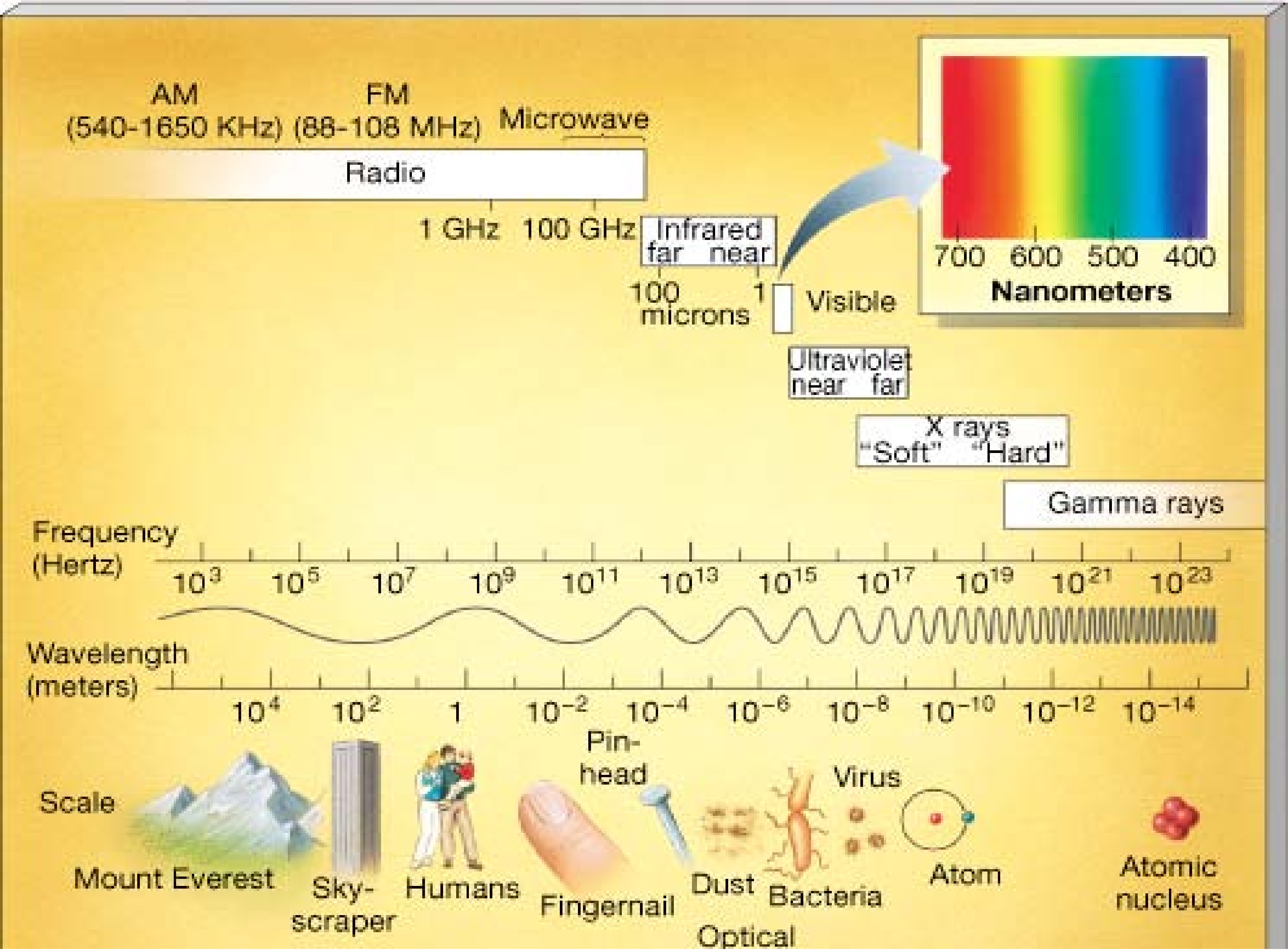
Electromagnetic Spectrum and Electromagnetic Radiation


Sunlight
Light Energy
Oxygen
Glucose
Carbon Dioxide
Root
Minerals
Water


AM
(540-1650 KHz)
FM
(88-108 MHz)
Microwave
Radio
1 GHz
100 GHz
Infrared
far near
100 microns
1
Visible
700
600
500
400
Nanometers
Ultraviolet
near far
X rays
"Soft" "Hard"
Gamma rays
Frequency (Hertz)
10^3
10^5
10^7
10^9
10^{11}
10^{13}
10^{15}
10^{17}
10^{19}
10^{21}
10^{23}
Wavelength (meters)
10^4
10^2
1
10^{-2}
10^{-4}
10^{-6}
10^{-8}
10^{-10}
10^{-12}
10^{-14}
Scale
Mount Everest
Sky-scraper
Humans
Fingernail
Pin-head
Dust
Optical
Bacteria
Virus
Atom
Atomic nucleus

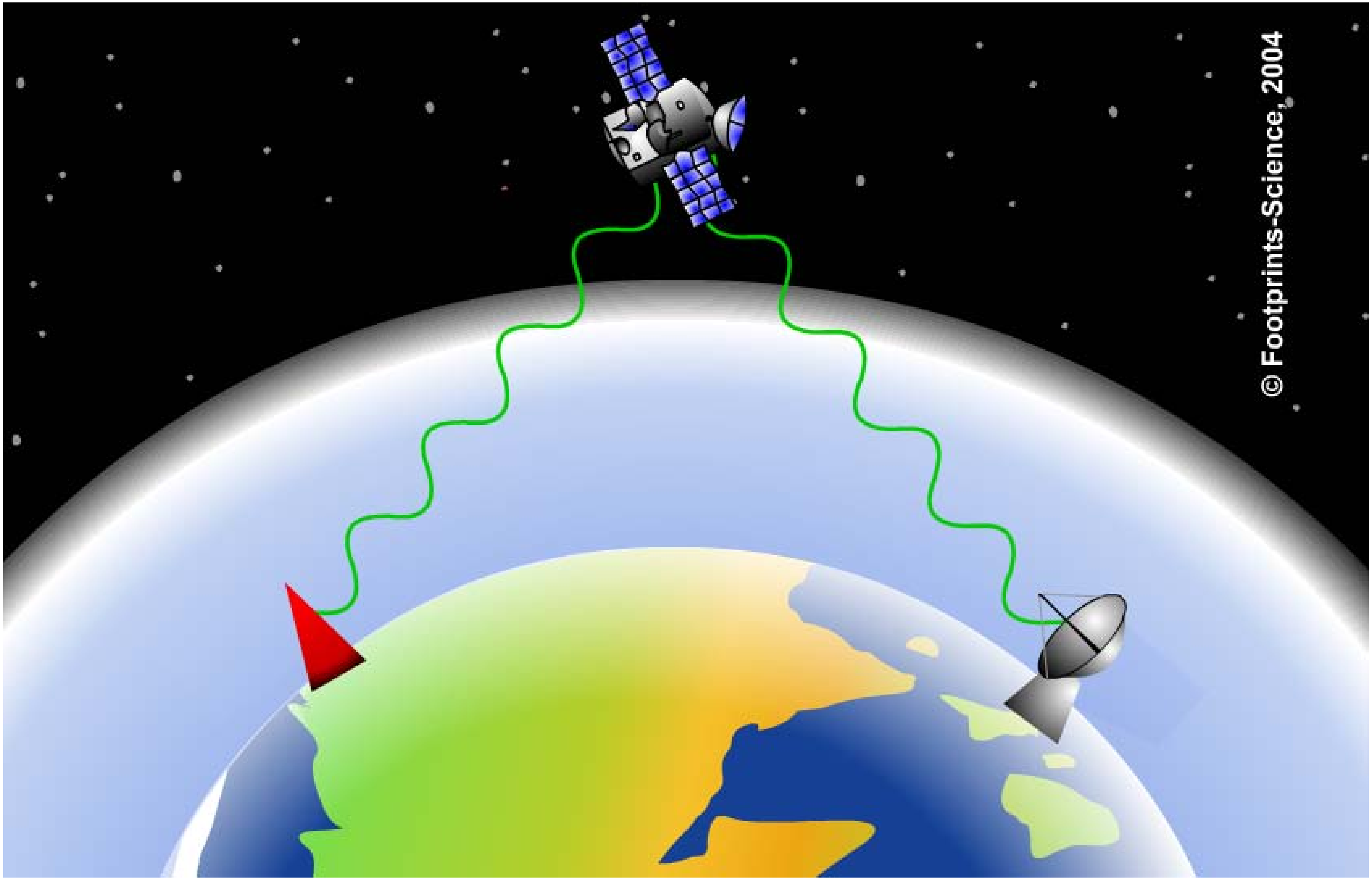
Apple iPhone 5

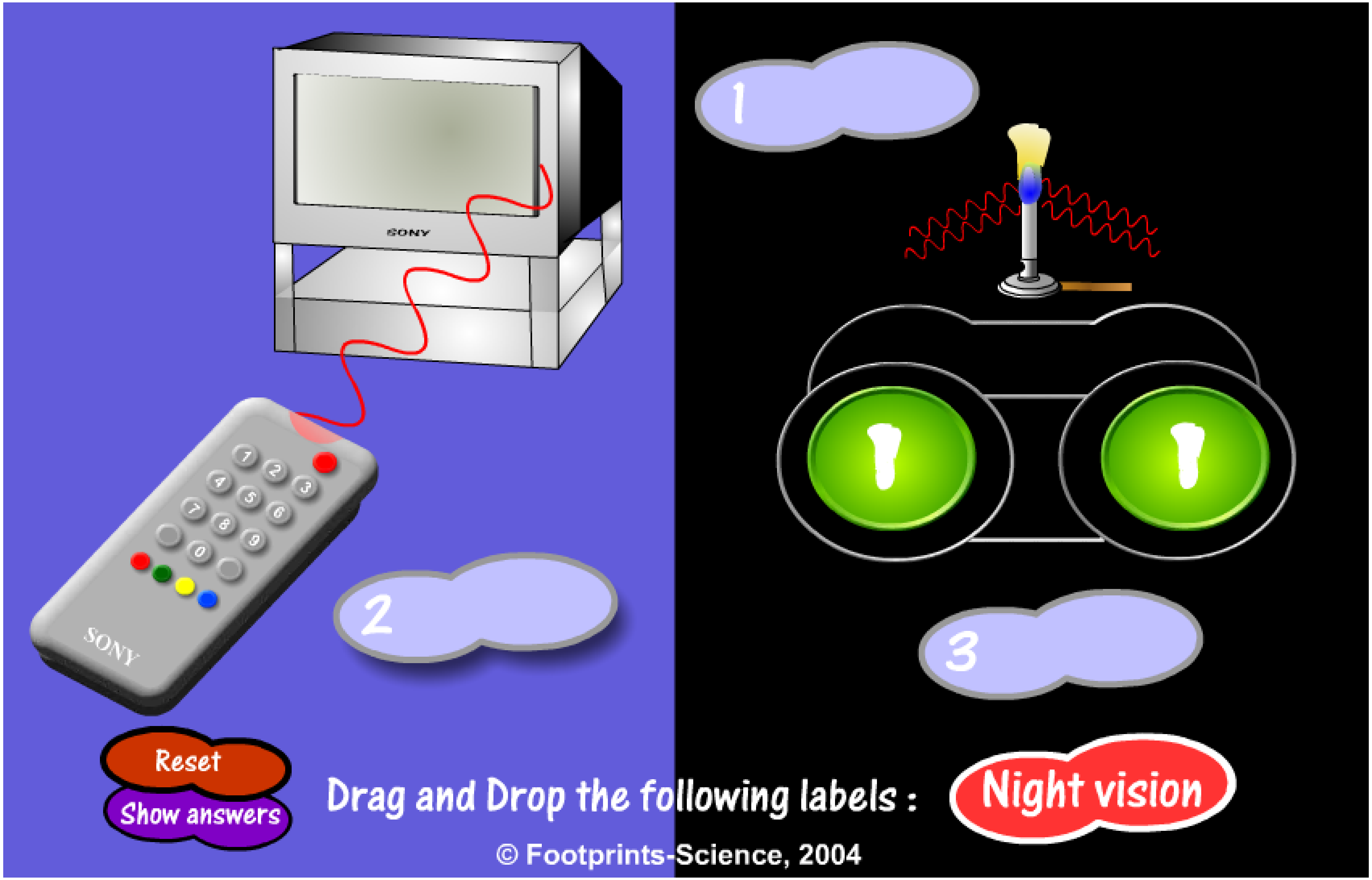
How do cordless phones work?

- Cell phones and cordless telephones are ***transceivers,*** device that transmits one signal & receives another radio signal from a base unit.
- You can talk and listen at the same time because the two signals are at different frequencies.

Communications Satellites

- Thousands of satellites orbit Earth. A radio or TV station sends microwave signals to the satellite which amplifies the signal and sends it back to a different place on Earth. Satellite uses dif freq to send & receive.


© Footprints-Science, 2004



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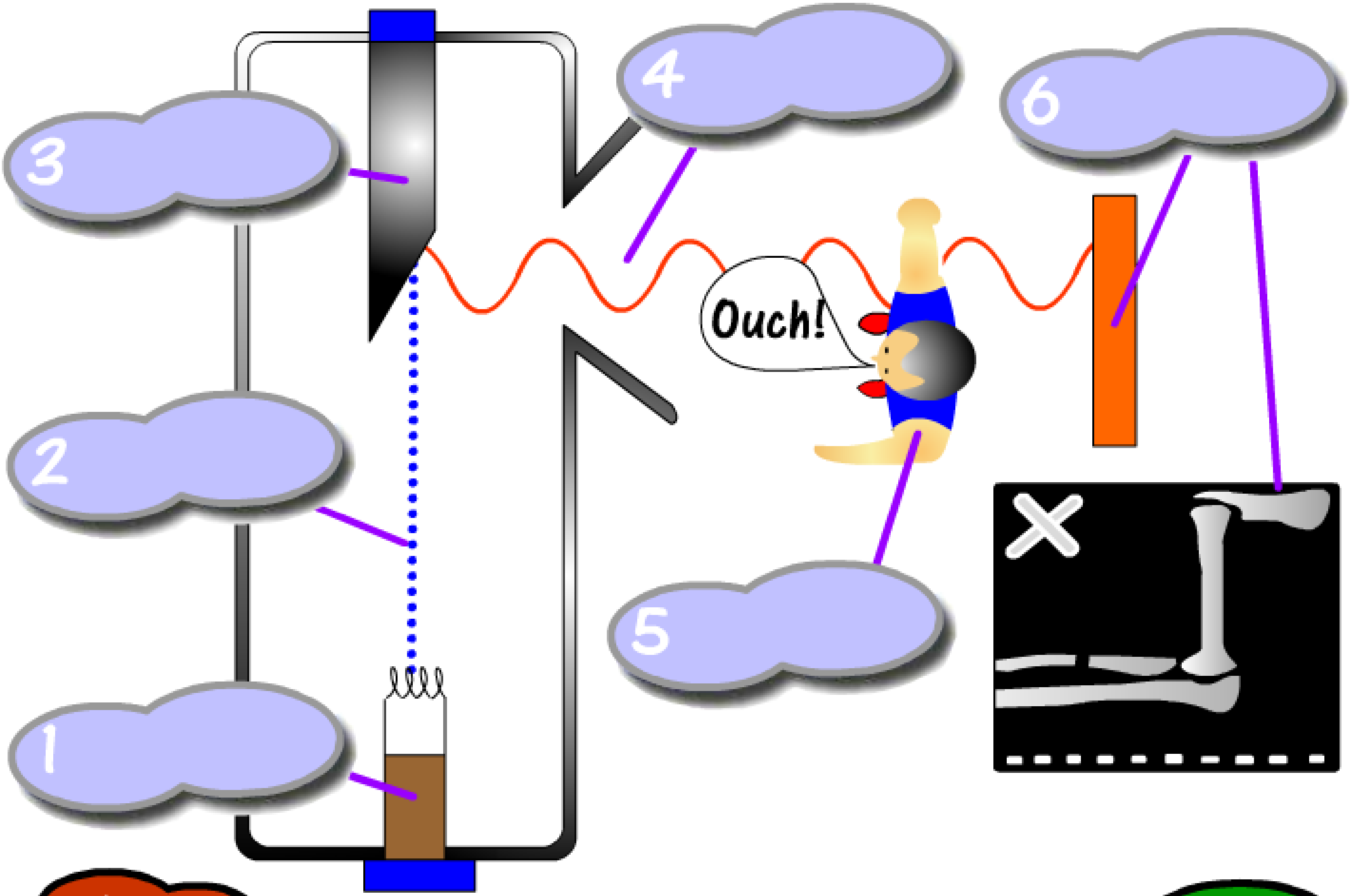

Reset

Show answers

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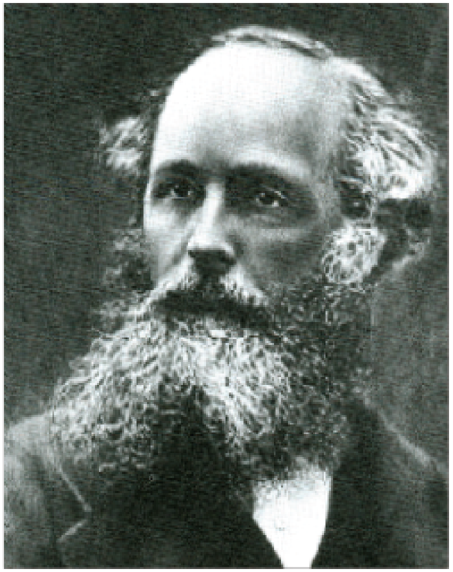
Electron beam

Information about galaxy:

Electromagnetic Theory

Electromagnetic radiation: wave model



- James Clerk Maxwell (1831-1879) – Scottish mathematician and physicist
- Wave model of EM energy
  - Unified existing laws of electricity and magnetism (Newton, Faraday, Kelvin, Ampère)
  - Oscillating electric field produces a magnetic field (and vice versa) – propagates an EM wave
  - Can be described by 4 differential equations
  - Derived speed of EM wave in a vacuum

Maxwell's Equations

- Four equations relating electric (**E**) and magnetic fields (**B**) – vector fields

- ε_0 is electric permittivity of free space (or vacuum permittivity - a constant) – *resistance to formation of an electric field in a vacuum*

- $\varepsilon_0 = 8.854188 \times 10^{-12}$ Farad m^{-1}

- μ_0 is magnetic permeability of free space (or magnetic constant - a constant) – *resistance to formation of a magnetic field in a vacuum*

- $\mu_0 = 1.2566 \times 10^{-6}$ T.m/A (T = Tesla; SI unit of magnetic field)

$$\nabla \bullet E = \frac{\rho}{\varepsilon_0}$$

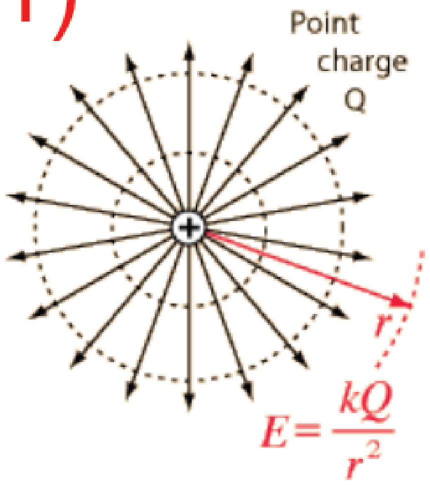
$$\nabla \bullet B = 0$$

$$\nabla \times E = -\frac{\partial B}{\partial t}$$

$$\nabla \times B = \mu_0 J + \varepsilon_0 \mu$$

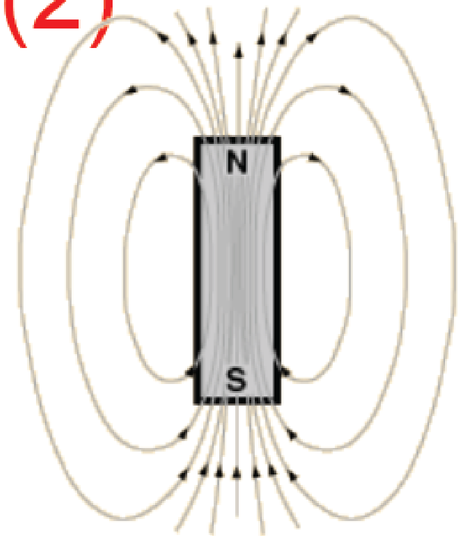
Maxwell’s Equations (1)

$$\nabla \bullet E = \frac{\rho}{\varepsilon_0}$$



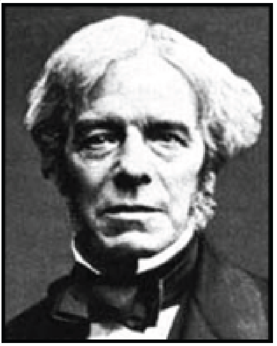
- Gauss’ law for electricity: the electric flux out of any closed surface is proportional to the total charge enclosed within the surface; i.e. a charge will radiate a measurable field of influence around it.
- **E** = electric field, ρ = net charge inside, ε_0 = vacuum permittivity (constant)
- Recall: divergence of a vector field is a measure of its tendency to converge on or repel from a point.
- Direction of an electric field is the direction of the force it would exert on a positive charge placed in the field
- If a region of space has more electrons than protons, the total charge is negative, and the direction of the electric field is negative (inwards), and vice versa.

Maxwell’s Equations (2)



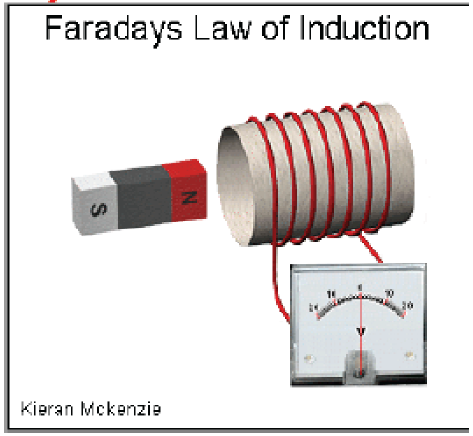
$$\nabla \bullet B = 0$$

- Gauss’ law for magnetism: the net magnetic flux out of any closed surface is zero (i.e. magnetic monopoles do not exist)
- **B** = magnetic field; magnetic flux = **B**A (A = area perpendicular to field **B**)
- Recall: divergence of a vector field is a measure of its tendency to converge on or repel from a point.
- Magnetic sources are dipole sources and magnetic field lines are loops – we cannot isolate N or S ‘monopoles’ (unlike electric sources or point charges – protons, electrons)
- Magnetic monopoles *could* exist, but have never been observed



Maxwell’s Equations (3)

$$\nabla \times E = -\frac{\partial B}{\partial t}$$



Faradays Law of Induction

Kieran Mckenzie

- Faraday’s Law of Induction: the curl of the electric field (**E**) is equal to the negative of rate of change of the magnetic flux through the area enclosed by the loop
- **E** = electric field; **B** = magnetic field
- Recall: curl of a vector field is a vector with magnitude equal to the maximum ‘circulation’ at each point and oriented perpendicularly to this plane of circulation for each point.
- Magnetic field weakens ➔ curl of electric field is positive and vice versa
- Hence changing magnetic fields affect the curl (‘circulation’) of the electric field – basis of electric generators (moving magnet induces current in a conducting loop)

Maxwell's Equations (4)

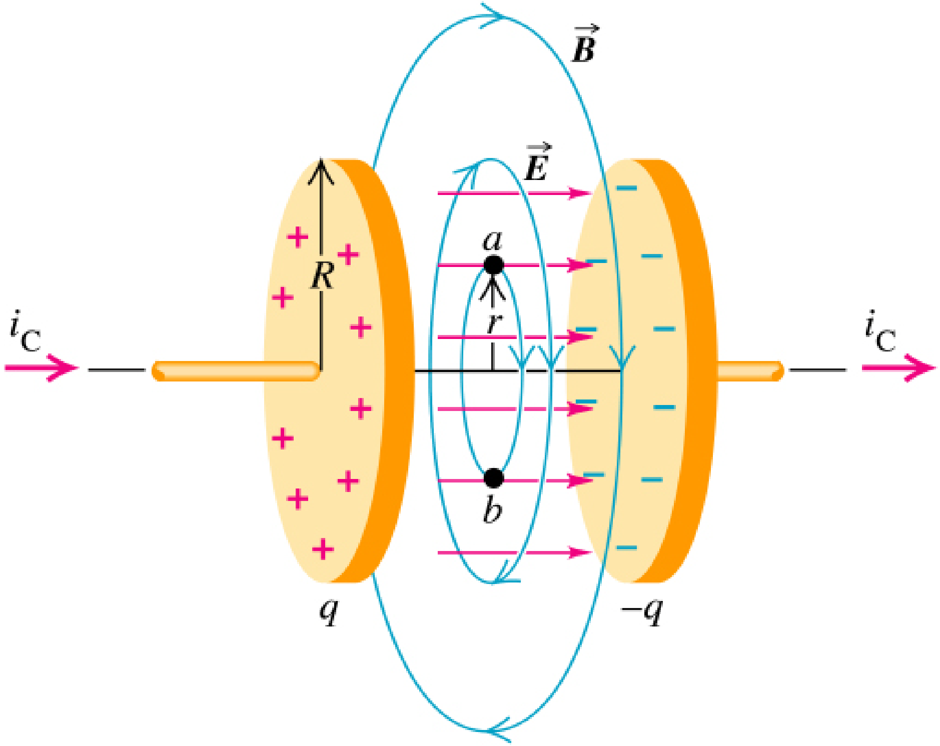
$$\nabla \times B = \mu_0 J + \varepsilon_0 \mu_0 \frac{\partial E}{\partial t}$$

- Ampère's Law: the curl of the magnetic field (**B**) is proportional to the electric current flowing through the loop

AND to the rate of change of the electric field. 🡐 added by Maxwell

- **B** = magnetic field; J = current density (current per unit area); **E** = electric field
- The curl of a magnetic field is basically a measure of its strength
- First term on RHS: in the presence of an electric current (J), there is always a magnetic field around it; **B** is dependent on J (*e.g., electromagnets*)
- Second term on RHS: a changing electric field generates a magnetic field.
- Therefore, generation of a magnetic field does not require electric current, only a changing electric field. An oscillating electric field produces a variable magnetic field (as dE/dT changes)

Charging of a capacitor



Putting it all together….

- An oscillating electric field produces a variable magnetic field. A changing magnetic field produces an electric field….and so on.
- In 'free space' (vacuum) we can assume current density (J) and charge (ρ) are zero i.e. there are no electric currents or charges
- Equations become:

$$\nabla \bullet E = 0$$

$$\nabla \bullet B = 0$$

$$\nabla \times E = -\frac{\partial B}{\partial t}$$

$$\nabla \times B = \varepsilon_0 \mu_0 \frac{\partial E}{\partial t}$$

Solving Maxwell's Equations

Take curl of: $\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$

$$\vec{\nabla} \times [\vec{\nabla} \times \vec{E}] = \vec{\nabla} \times [-\frac{\partial \vec{B}}{\partial t}]$$

Change the order of differentiation on the RHS:

$$\vec{\nabla} \times [\vec{\nabla} \times \vec{E}] = -\frac{\partial}{\partial t}[\vec{\nabla} \times \vec{B}]$$

Solving Maxwell's Equations (cont'd)

But (Equation 4):

$$\vec{\nabla} \times \vec{B} = \mu\varepsilon \frac{\partial \vec{E}}{\partial t}$$

Substituting for $\vec{\nabla} \times \vec{B}$, we have:

$$\vec{\nabla} \times [\vec{\nabla} \times \vec{E}] = -\frac{\partial}{\partial t}[\vec{\nabla} \times \vec{B}] \Rightarrow \vec{\nabla} \times [\vec{\nabla} \times \vec{E}] = -\frac{\partial}{\partial t}[\mu\varepsilon \frac{\partial \vec{E}}{\partial t}]$$

Or:

$$\vec{\nabla} \times [\vec{\nabla} \times \vec{E}] = -\mu\varepsilon \frac{\partial^2 \vec{E}}{\partial t^2}$$

assuming that μ and ε are constant in time.

Solving Maxwell's Equations (cont'd)

Identity: $\vec{\nabla} \times [\vec{\nabla} \times \vec{f}] \equiv \vec{\nabla}(\vec{\nabla} \cdot \vec{f}) - \nabla^2 \vec{f}$

Using the identity, $\vec{\nabla} \times [\vec{\nabla} \times \vec{E}] = -\mu\varepsilon \frac{\partial^2 \vec{E}}{\partial t^2}$

becomes: $\vec{\nabla}(\vec{\nabla} \cdot \vec{E}) - \nabla^2 \vec{E} = -\mu\varepsilon \frac{\partial^2 \vec{E}}{\partial t^2}$

Assuming zero charge density (free space; Equation 1):

$$\vec{\nabla} \cdot \vec{E} = 0$$

and we're left with: $\nabla^2 \vec{E} = \mu\varepsilon \frac{\partial^2 \vec{E}}{\partial t^2}$

Solving Maxwell's Equations (cont'd)

$$\nabla^2 \vec{E} = \mu\varepsilon \frac{\partial^2 \vec{E}}{\partial t^2} \qquad \nabla^2 \vec{B} = \mu\varepsilon \frac{\partial^2 \vec{B}}{\partial t^2}$$

The same result is obtained for the magnetic field B.

These are forms of the 3D wave equation, describing the propagation of a sinusoidal wave:

$$\nabla^2 u = \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2}$$

Where v is a constant equal to the propagation speed of the wave

So for EM waves, $v = \dfrac{1}{\sqrt{\mu\varepsilon}}$

Solving Maxwell's Equations (cont'd)

So for EM waves, $v = \dfrac{1}{\sqrt{\mu\varepsilon}}$,

Units of μ = T.m/A

The Tesla (T) can be written as kg A^{-1} s^{-2}

So units of μ are kg m A^{-2} s^{-2}

Units of ε = Farad m^{-1} or A^2 s^4 kg^{-1} m^{-3} in SI base units

So units of $\mu\varepsilon$ are m^{-2} s^2

Square root is m^{-1} s, reciprocal is m s^{-1} (i.e., velocity)

$\varepsilon_0 = 8.854188 \times 10^{-12}$ and $\mu_0 = 1.2566371 \times 10^{-6}$

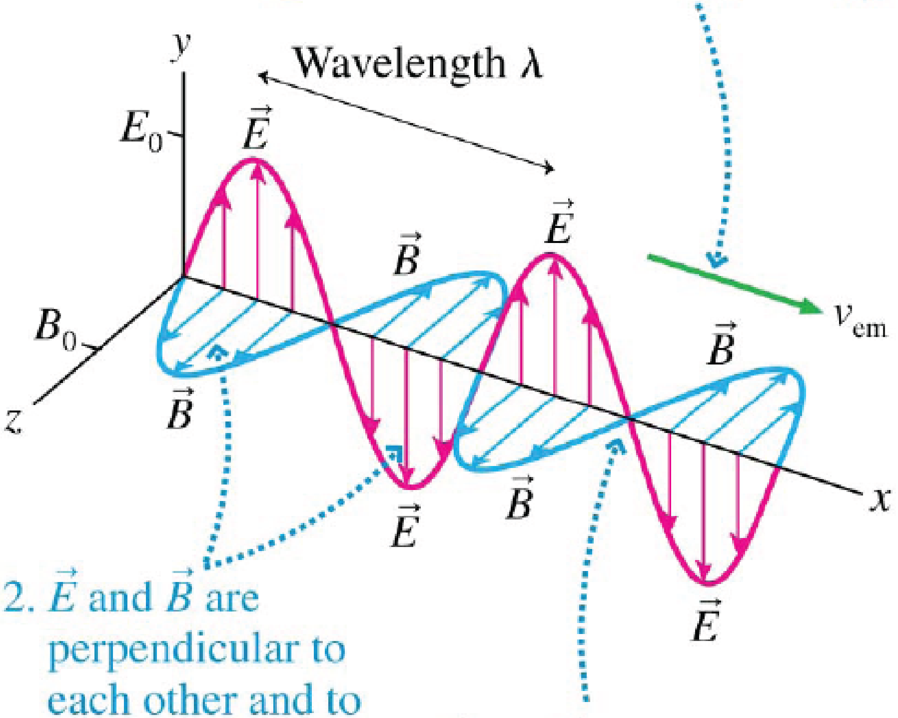
Evaluating the expression gives 2.998×10^8 m s^{-1}

Maxwell (1865) recognized this as the (known) speed of light – confirming that light was in fact an EM wave.

The propagation direction of a light wave

FIGURE 35.19 A sinusoidal electromagnetic wave.

1. A sinusoidal wave with frequency f and wavelength λ travels with wave speed v_{em}.



2. $\vec{E}$ and $\vec{B}$ are perpendicular to each other and to the direction of travel. The fields have amplitudes E_0 and B_0.

3. $\vec{E}$ and $\vec{B}$ are in phase. That is, they have matching crests, troughs, and zeros.

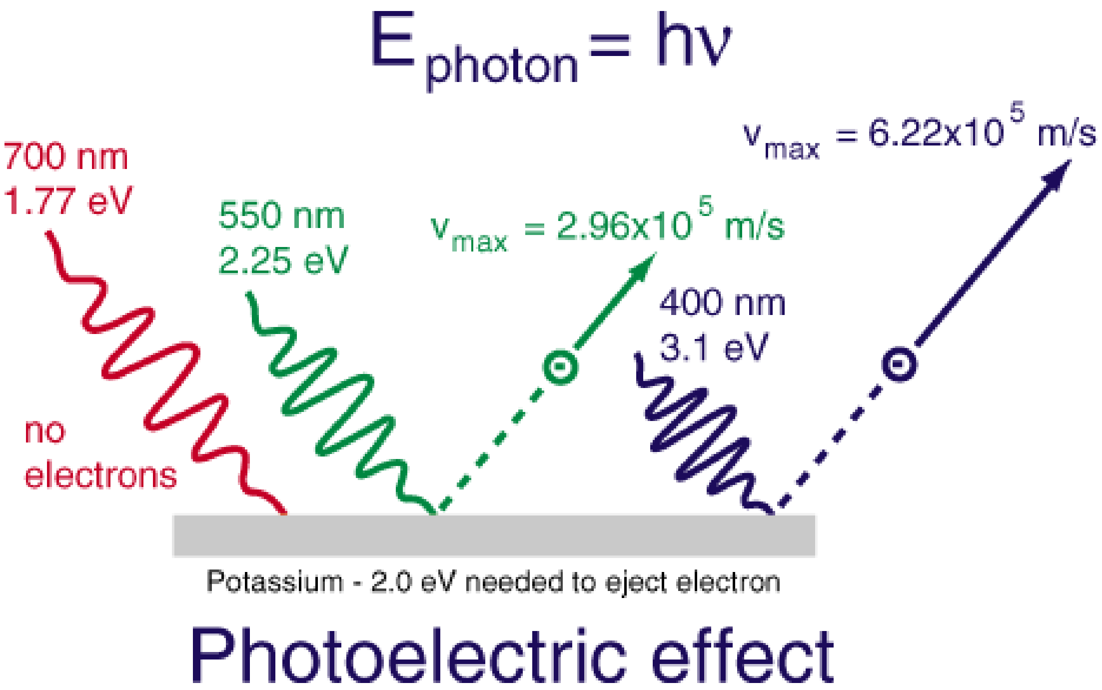
$$\vec{v} = \vec{E} \times \vec{B}$$

Right-hand screw rule

Video On Electromagnetic Field Generation

Particle Nature of EM Wave??

PhotoElectric Effect



$$T = h\nu - W$$

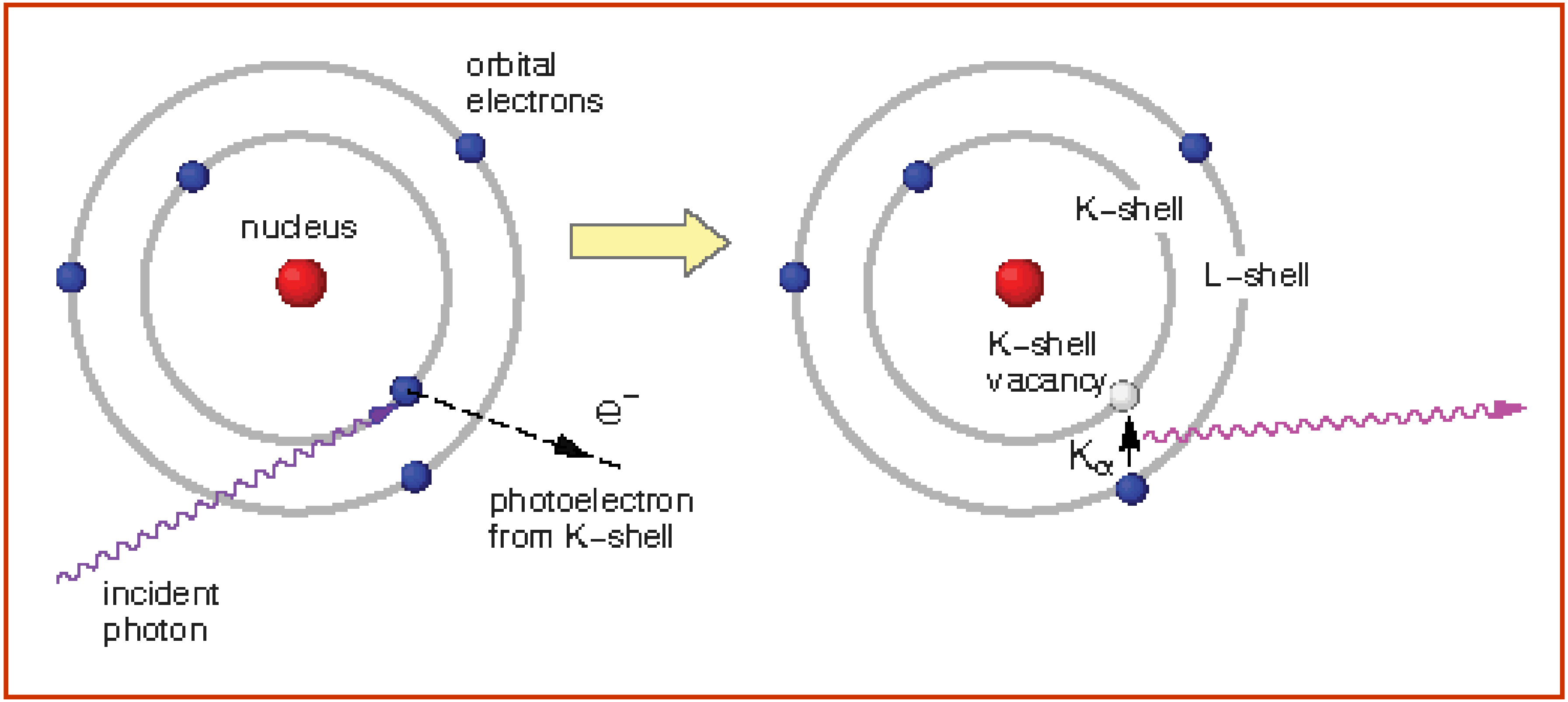
Photoelectric Effect

- When an incident photon ejects an electron, the process is called “photoelectric” effect. It is a photon-electron interaction rather than a charged particle interaction.

- The photon transfers all its energy to the electron in a single cataclysmic event after which the photon ceases to exist and the ejected electron retains all the energy originally possessed by the photon except for the energy required to overcome the binding energy of the electron.

- since an electron has been ejected, a vacancy exists in the K shell and thus one or more characteristic x-rays will be produced as the vacancy is filled by electrons from higher orbits.

Photoelectric Effect



Photons

- **The light absorbed or emitted must be in "packets" of electromagnetic radiation containing a specific amount of energy.**

- **These packets are called "PHOTONS."**

- **The energy of a photon is related to the frequency of the electromagnetic energy absorbed or emitted.**

Frequency and Energy

The energy of a photon is related to the frequency of light emitted or absorbed by

$$E = h\nu$$

where h = Planck's constant

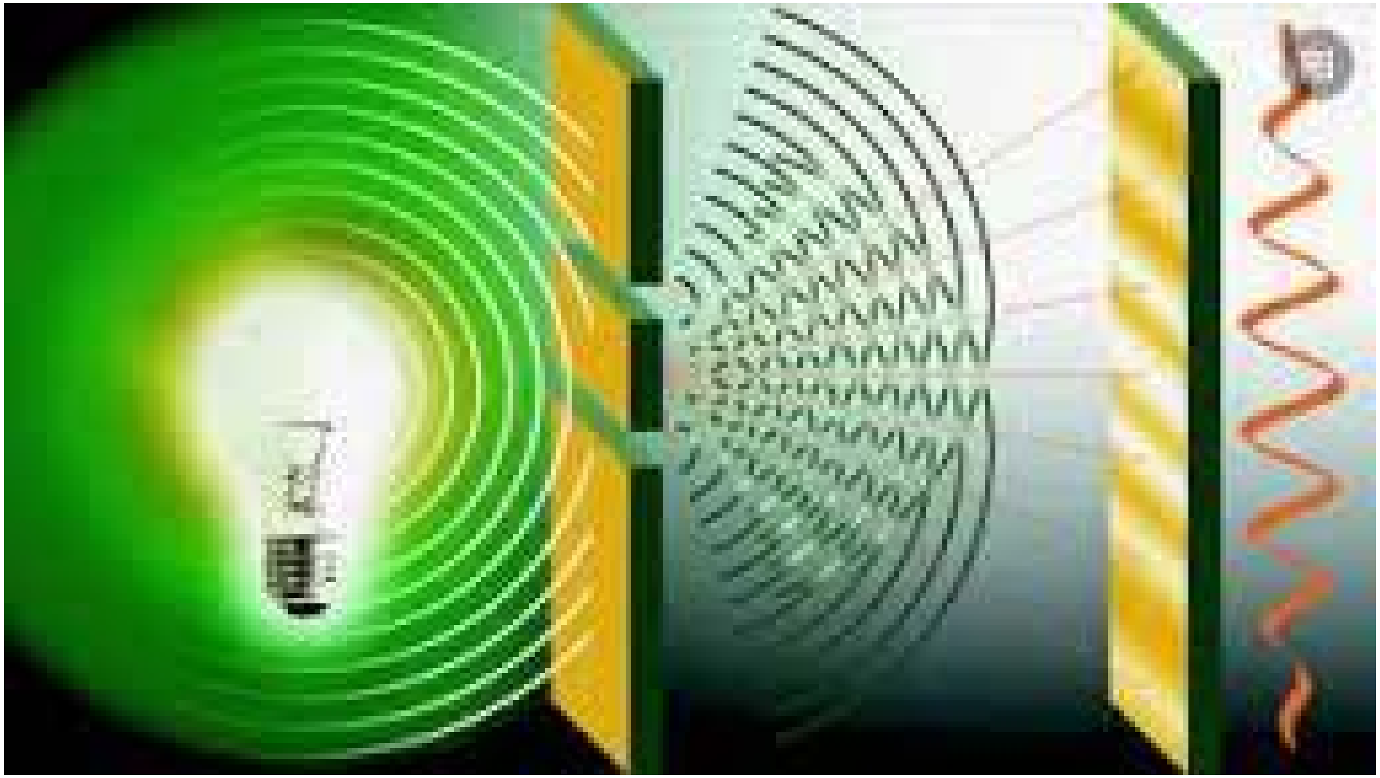
$$\nu = C/\lambda$$

so, $E \alpha\ 1/\lambda$

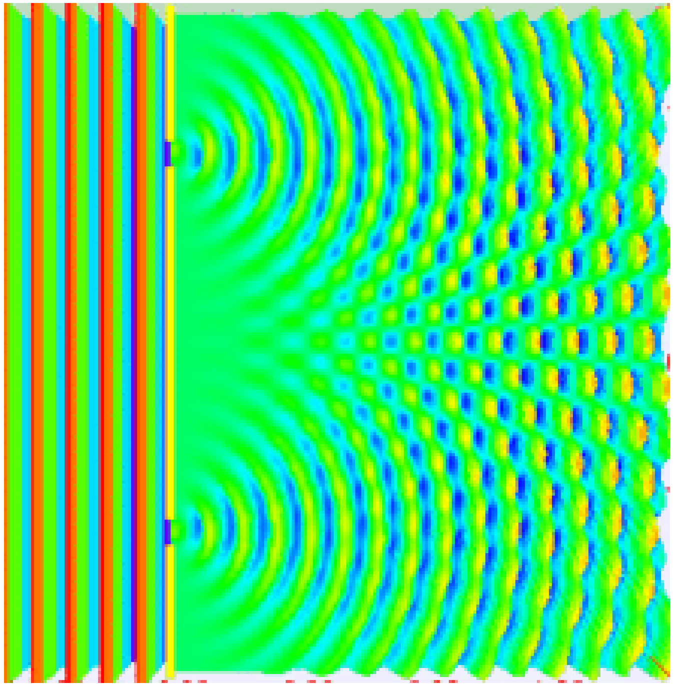
“Every physicist thinks he knows what a photon is.
I spent my life to find out what a photon is and I still don’t know.”

Albert Einstein

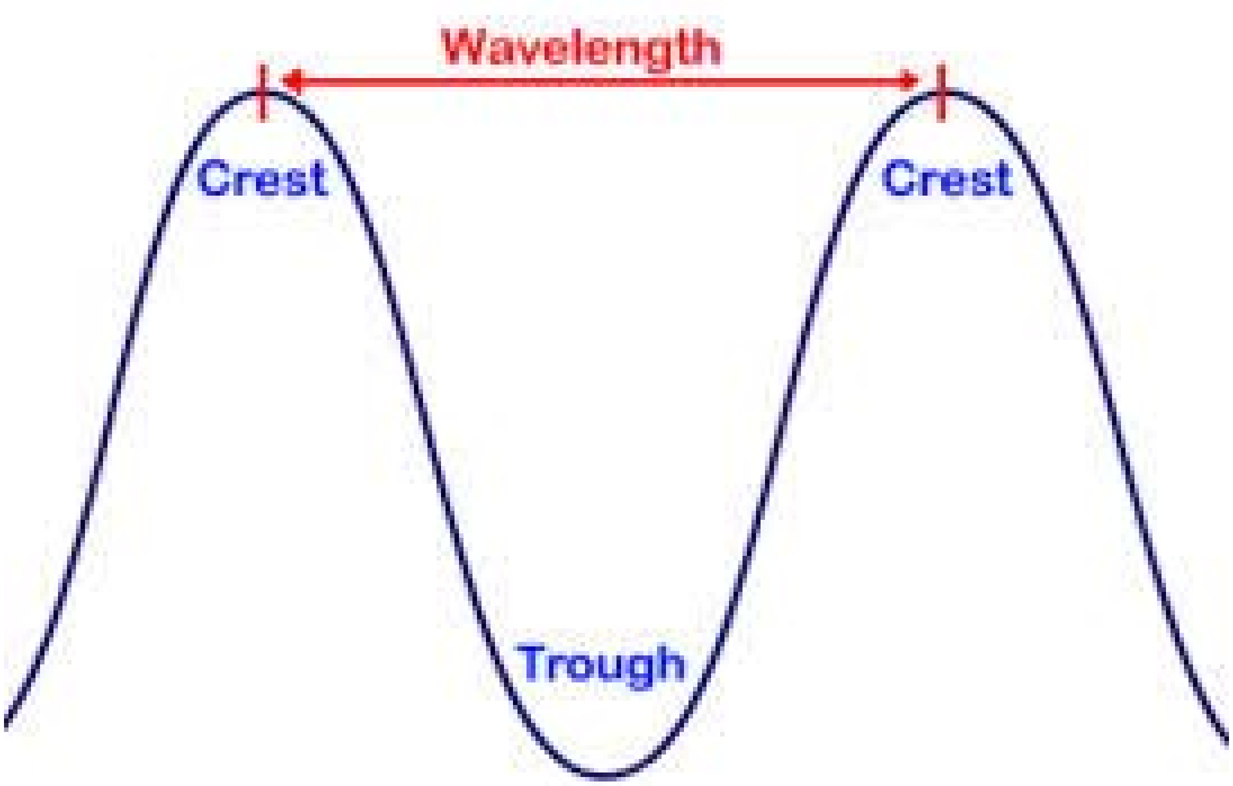
Wave Nature of Light

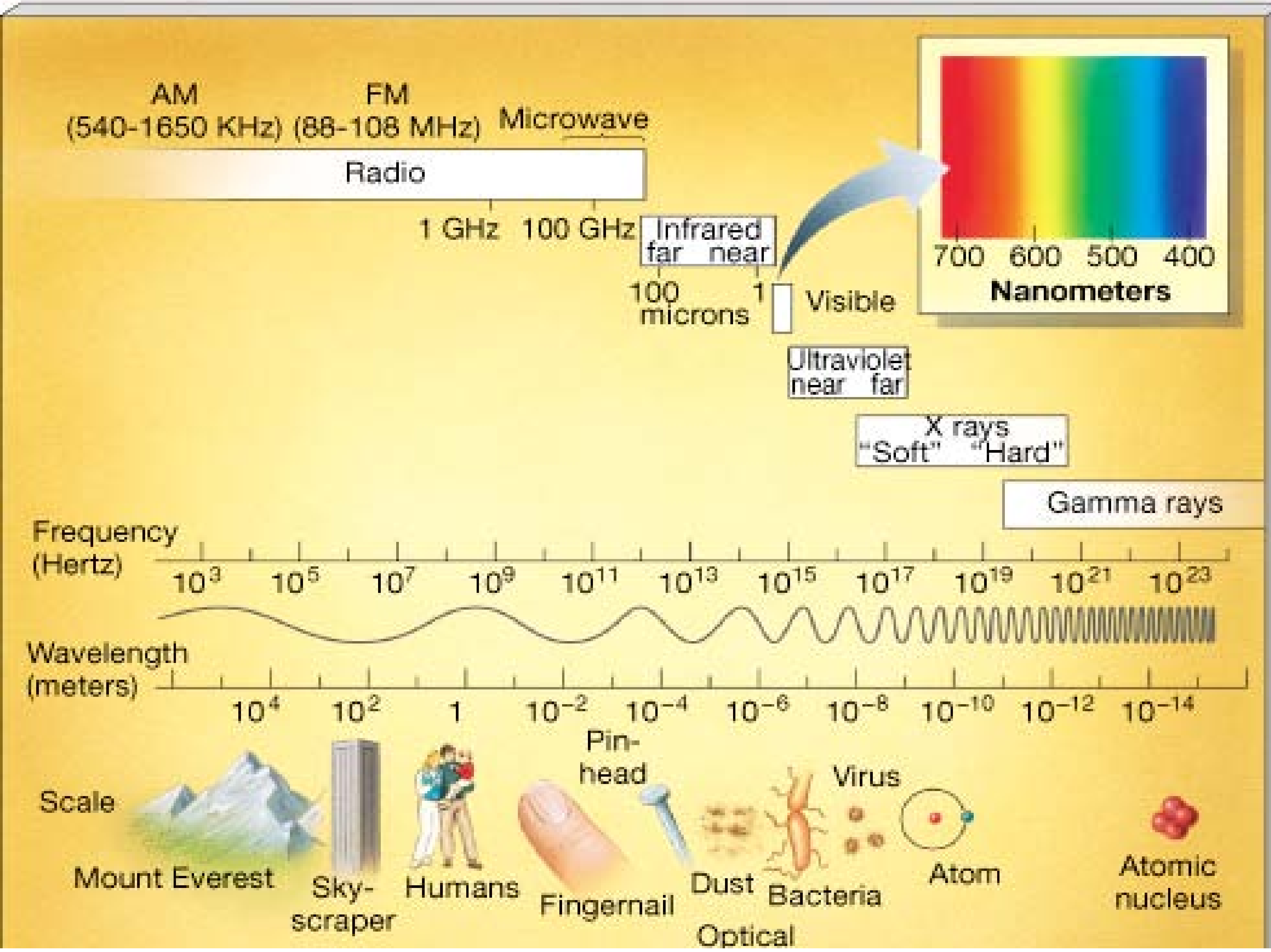


Diffraction Pattern of light



Definition of wavelength

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10^{-14}
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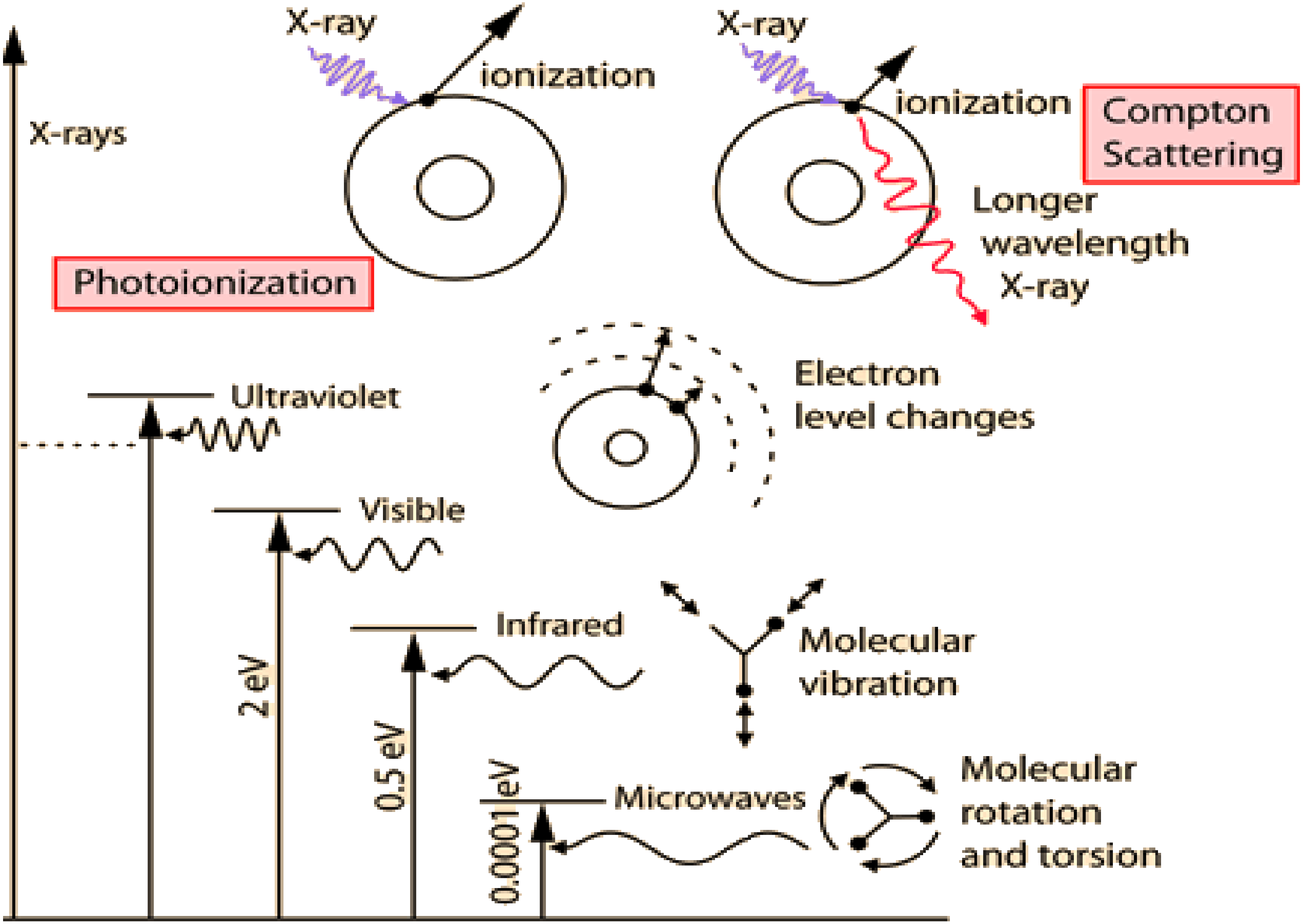
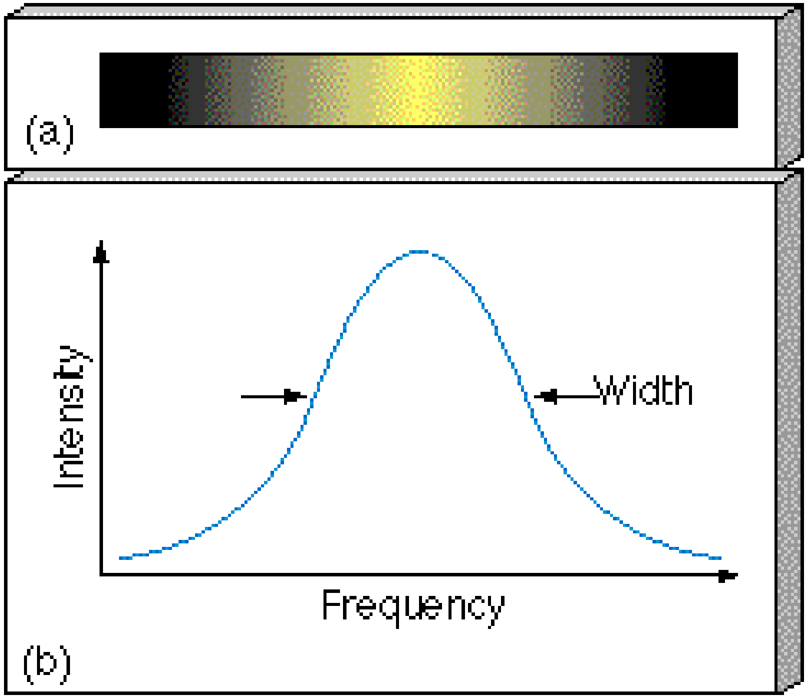
Sky-scraper
Humans
Fingernail
Pin-head
Dust
Optical
Bacteria
Virus
Atom
Atomic nucleus

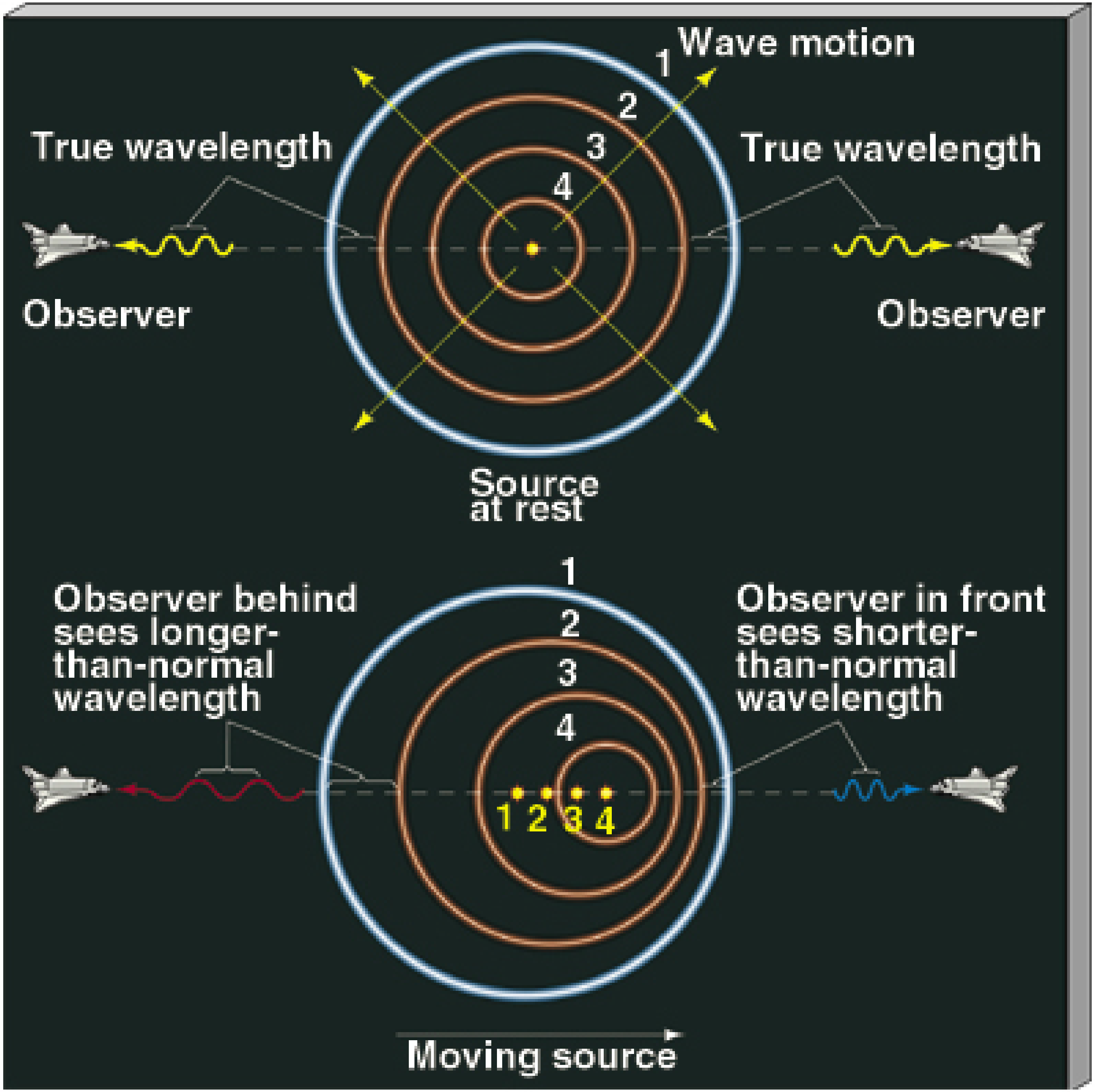
Different ways molecules can interact with E-M radiation



Spectral Linewidth

- **Physical mechanisms can broaden spectral lines.**
  - **Doppler Effect**
    - **Thermal motion**
    - **Rotation**
  - **Collision Broadening**
  - **Heisenberg Uncertainty Principle**

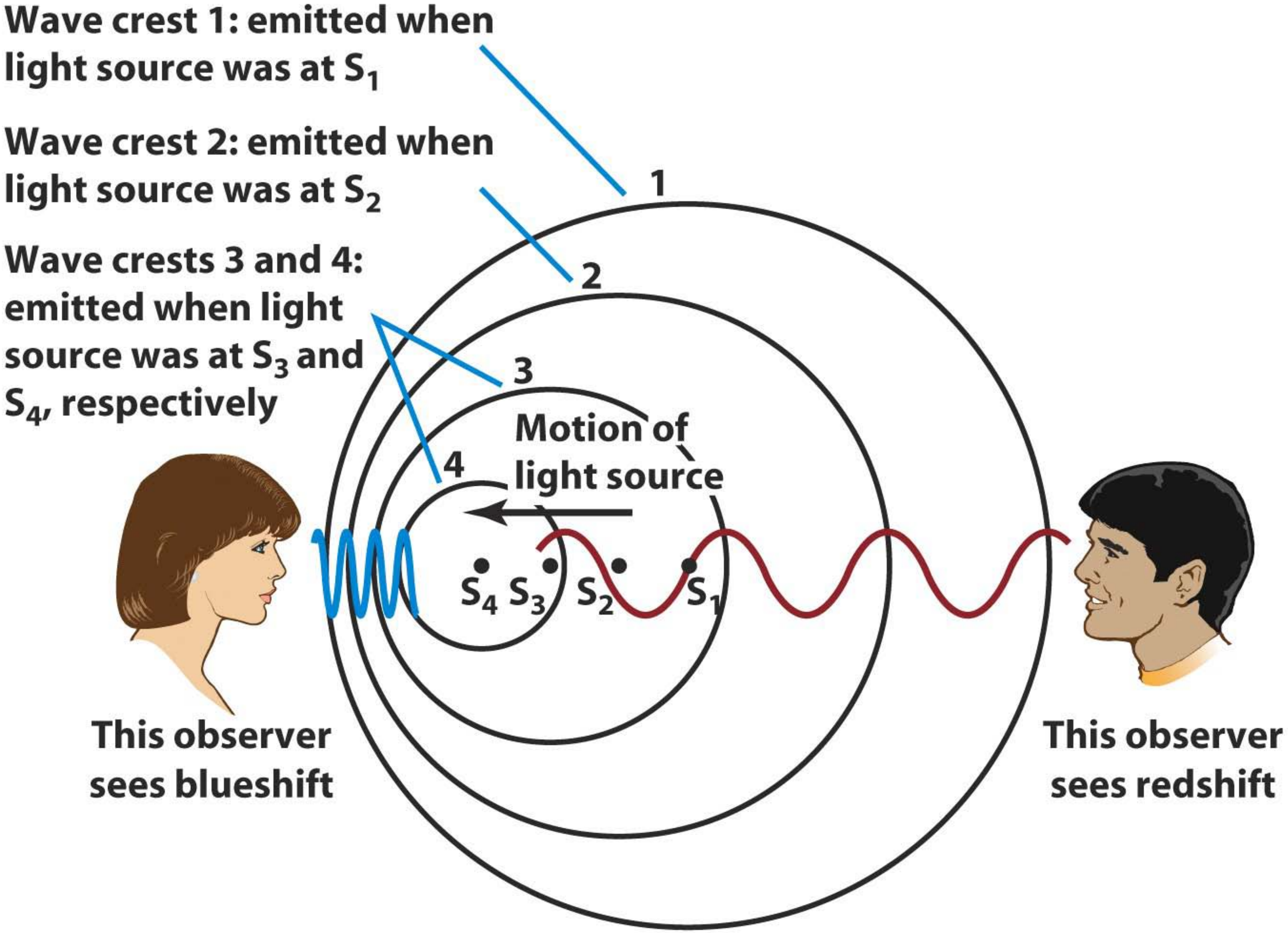




Doppler Shift

- The greater the velocity the greater the shift.

The wavelength of a spectral line is affected by the relative motion between the source and the observer



Doppler Shifts

- **Red Shift**: The object is moving away from the observer
- **Blue Shift**: The object is moving towards the observer

$$\Delta\lambda/\lambda_o = v/c$$

$\Delta\lambda$ = wavelength shift

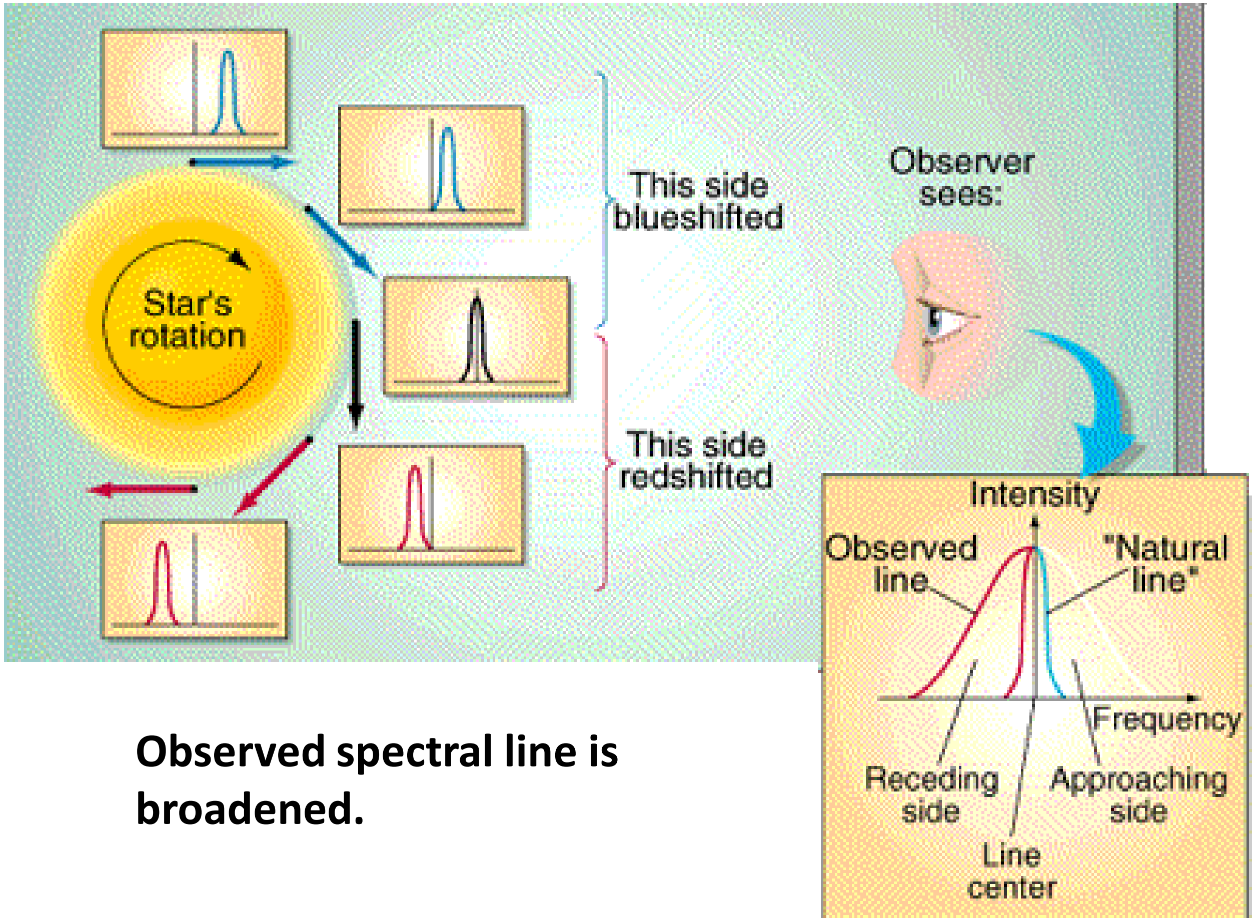
λ_o = wavelength if source is not moving

v = velocity of source

c = speed of light

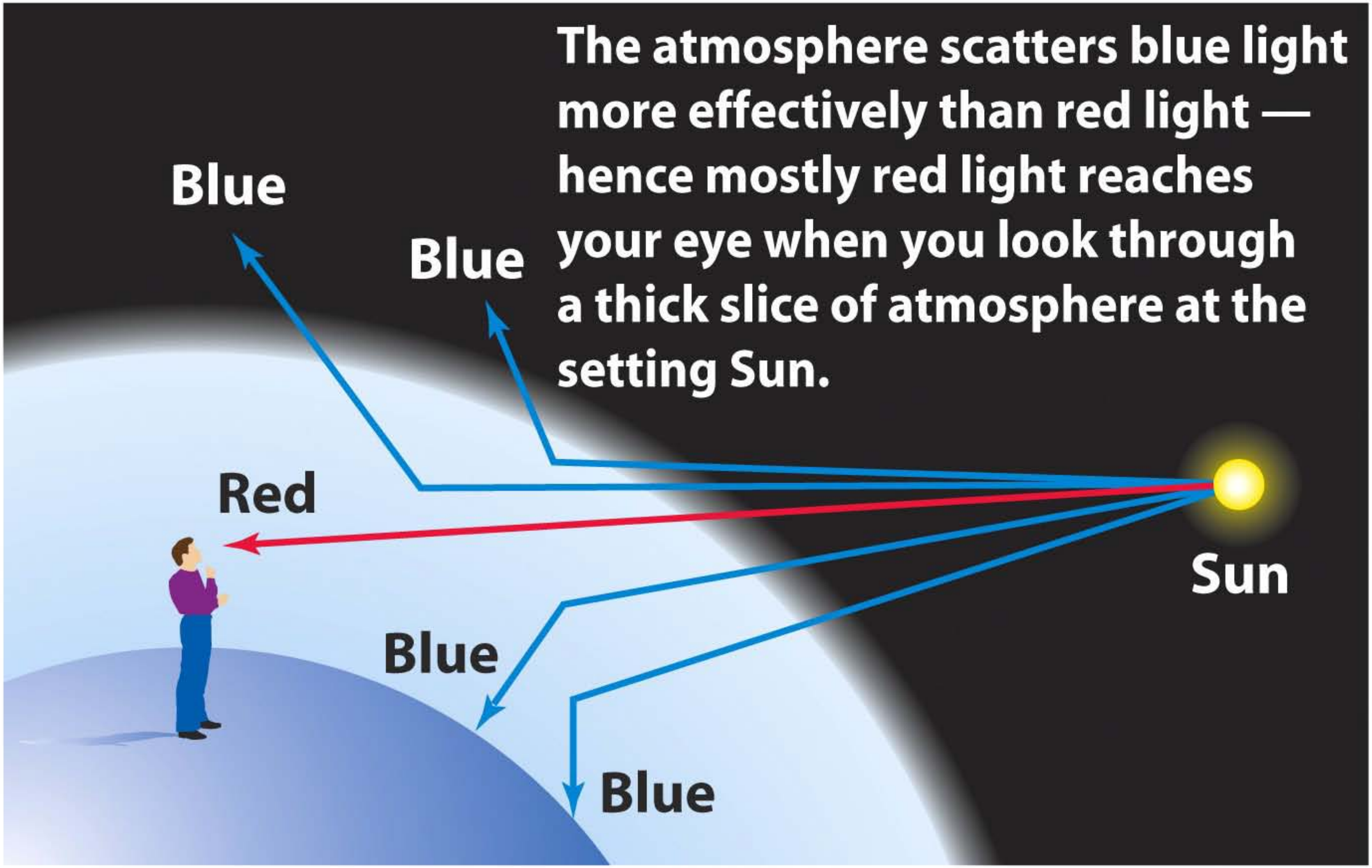
Doppler Effect: Rotation

- **Rotation of star/gas will produce a broadening of spectral lines.**
- **Photons emitted from side *spinning toward us*, *blueshifted*.**
- **Photons emitted from side *spinning away from us*, *redshifted*.**

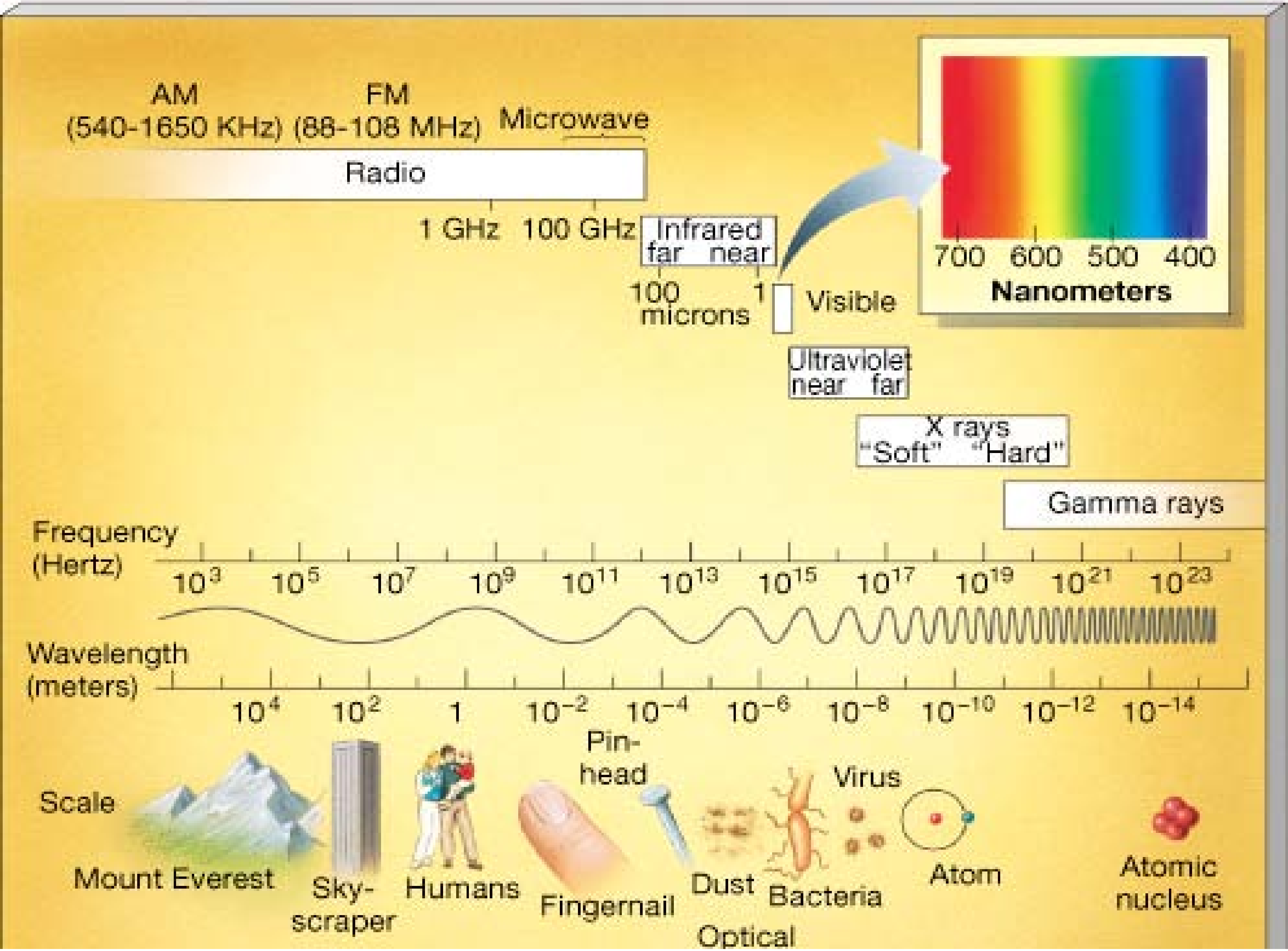


Observed spectral line is broadened.

END



(b) Why the setting Sun looks red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10^9
10^{11}
10^{13}
10^{15}
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10^{-8}
10^{-10}
10^{-12}
10^{-14}
Scale
Mount Everest
Sky-scraper
Humans
Fingernail
Pin-head
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Virus
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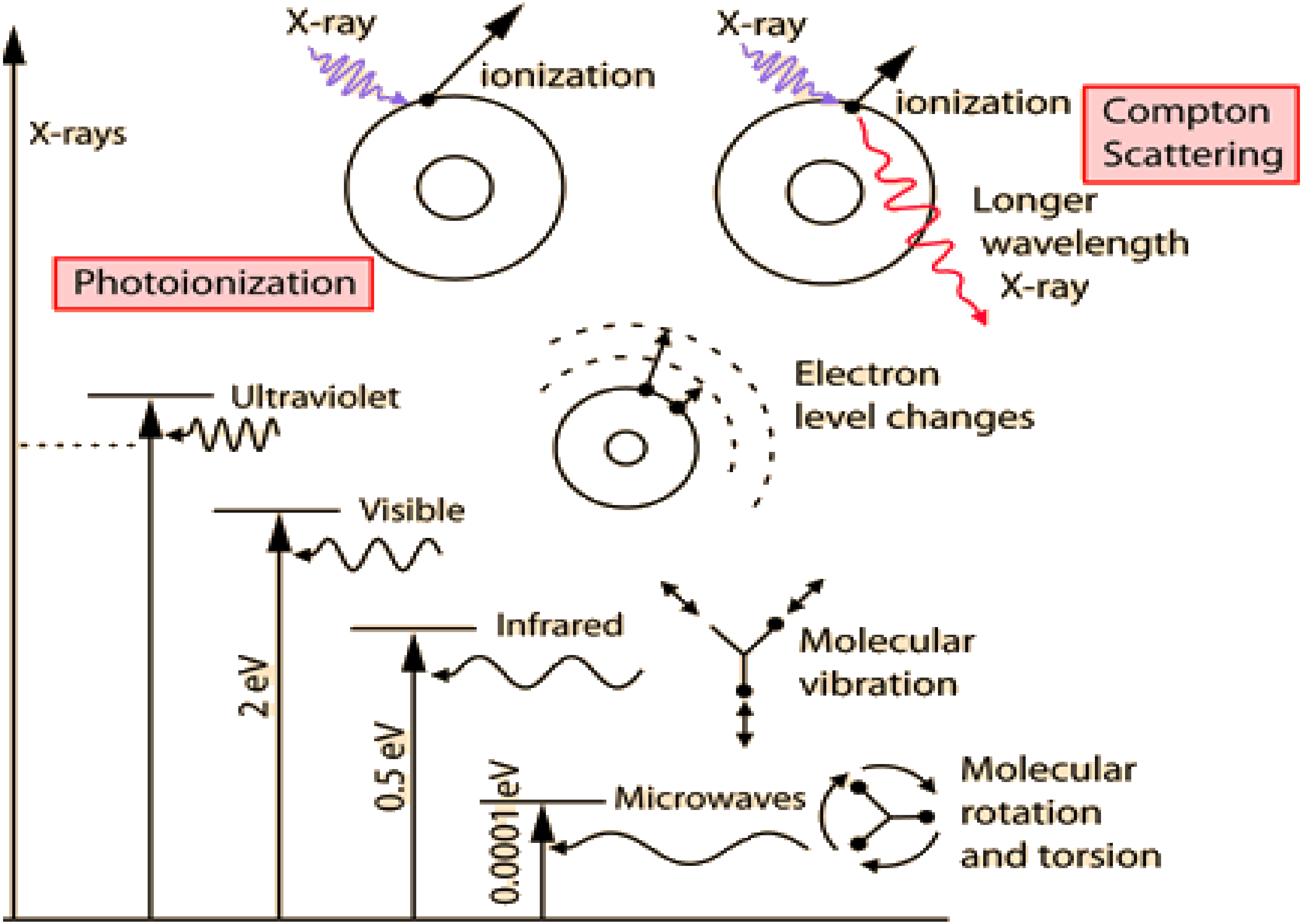
Different ways molecules can interact with E-M radiation



Microwave Spectroscopy

or

Rotational Spectroscopy

Molecular Energy

➔ Molecules can have the following types of energy

Translational or kinetic (due to motion)

Electronic (PE and KE of electrons)

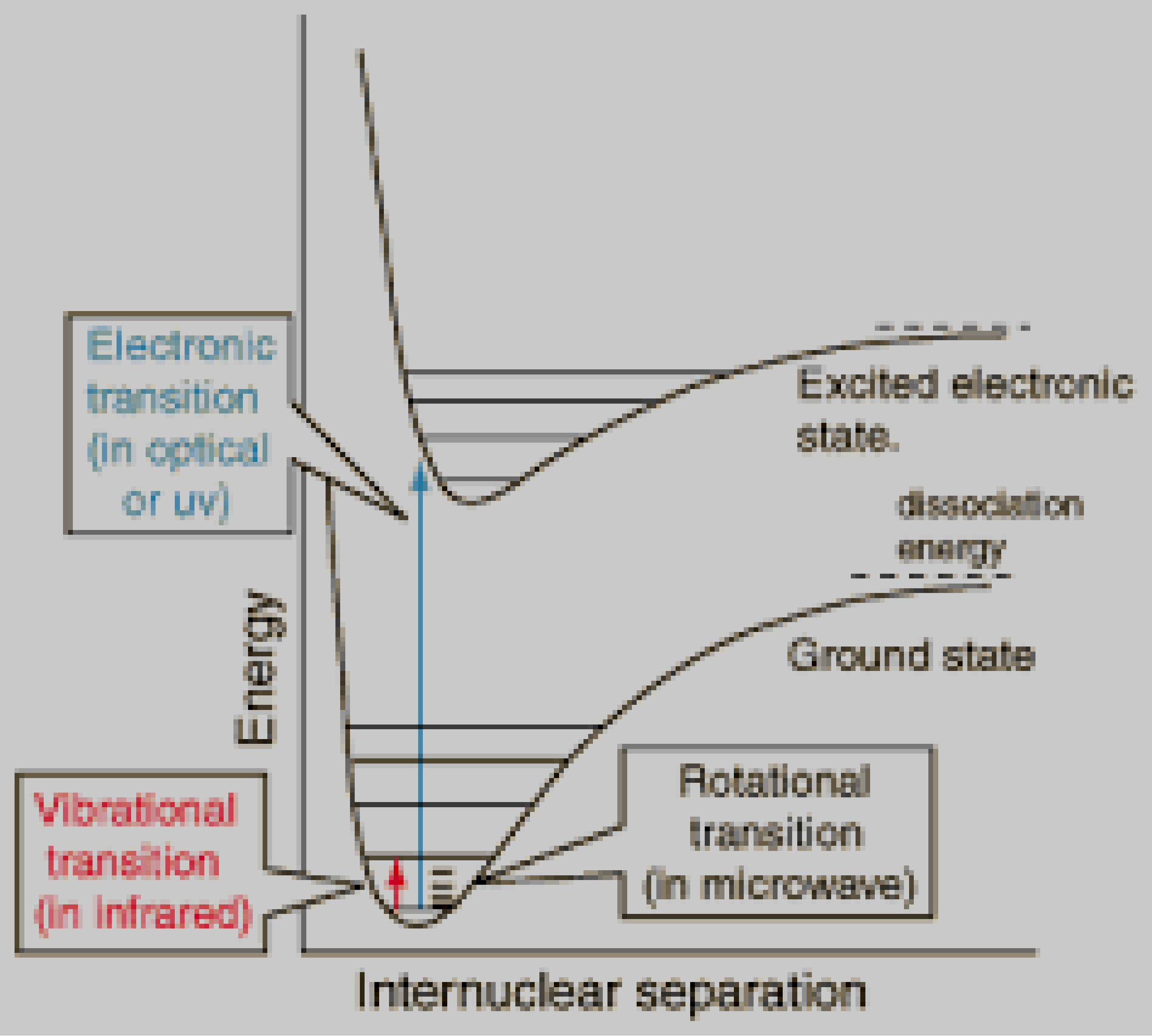
Vibrational (oscillation of atoms in bonds)

Rotational

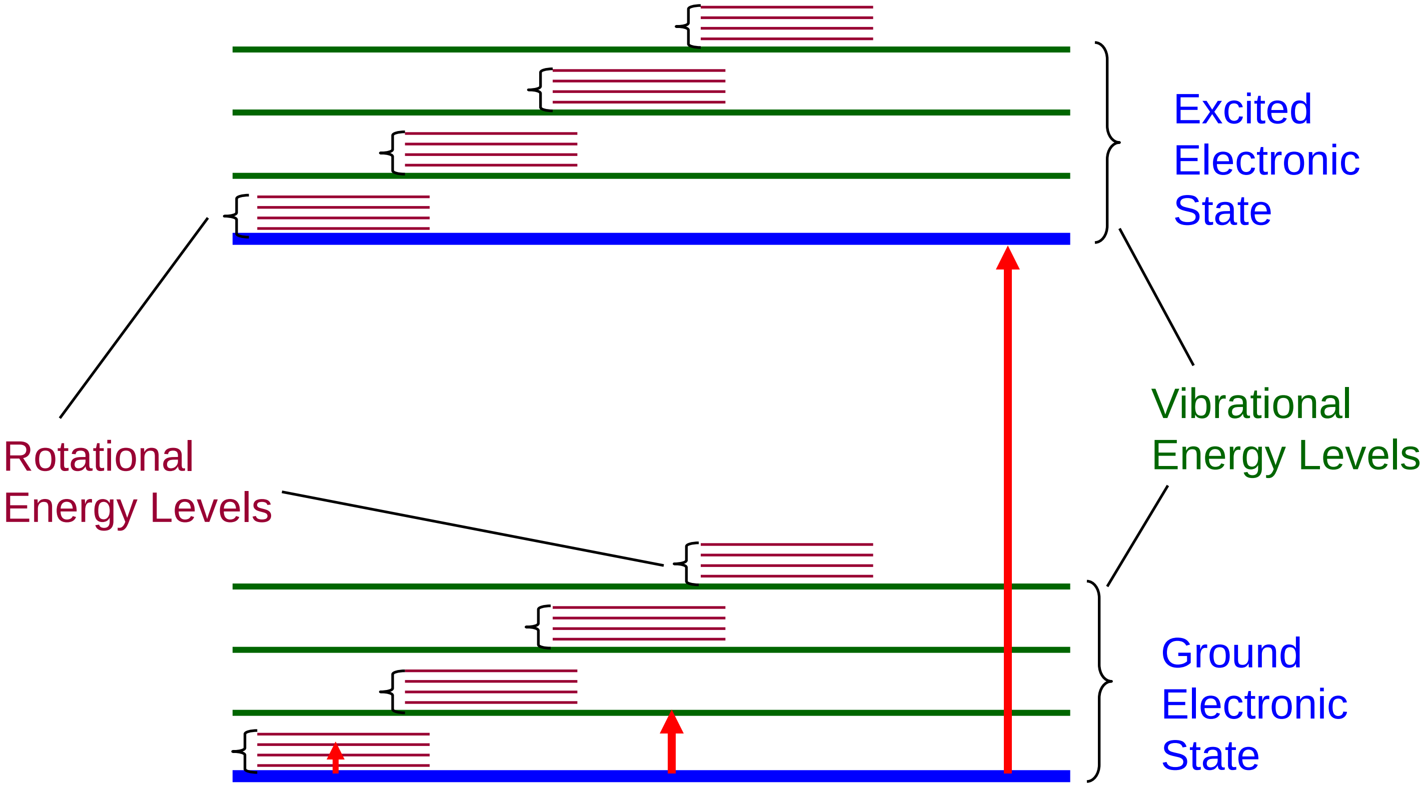
➔ All except the KE are quantized

$$E_{\text{molecule}} = E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{electronic}}$$

Molecular Energy Levels



Molecular Energy Levels



Rotational Transition	Vibrational Transition	Electronic Transition
1-20 cm^{-1}	2000-4000 cm^{-1}	10000-50000 cm^{-1}
Microwave	Infrared	UV-Visible

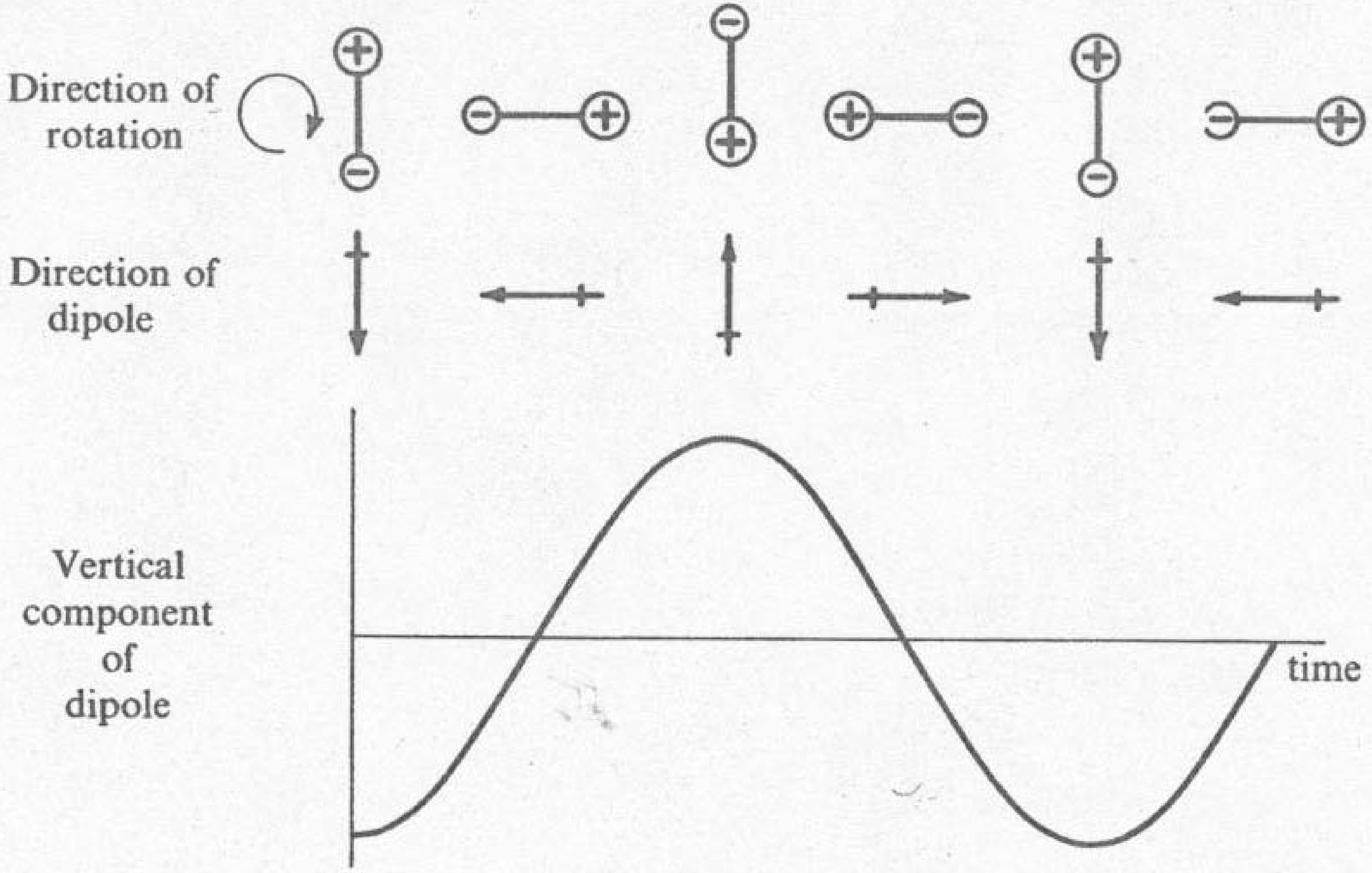
Molecular Energy Levels

The relative energy of the spacing between energy levels for various types of transitions in a molecule are in the order:

Rotational Transition		Vibrational Transition		Electronic Transition
	<<		<<	
1-20 cm^{-1}		2000-4000 cm^{-1}		10000-50000 cm^{-1}

Thus, the various types of energy transitions occur in different regions of the EMR spectrum and do not overlap.

Rotational motion of a Diatomic Molecule



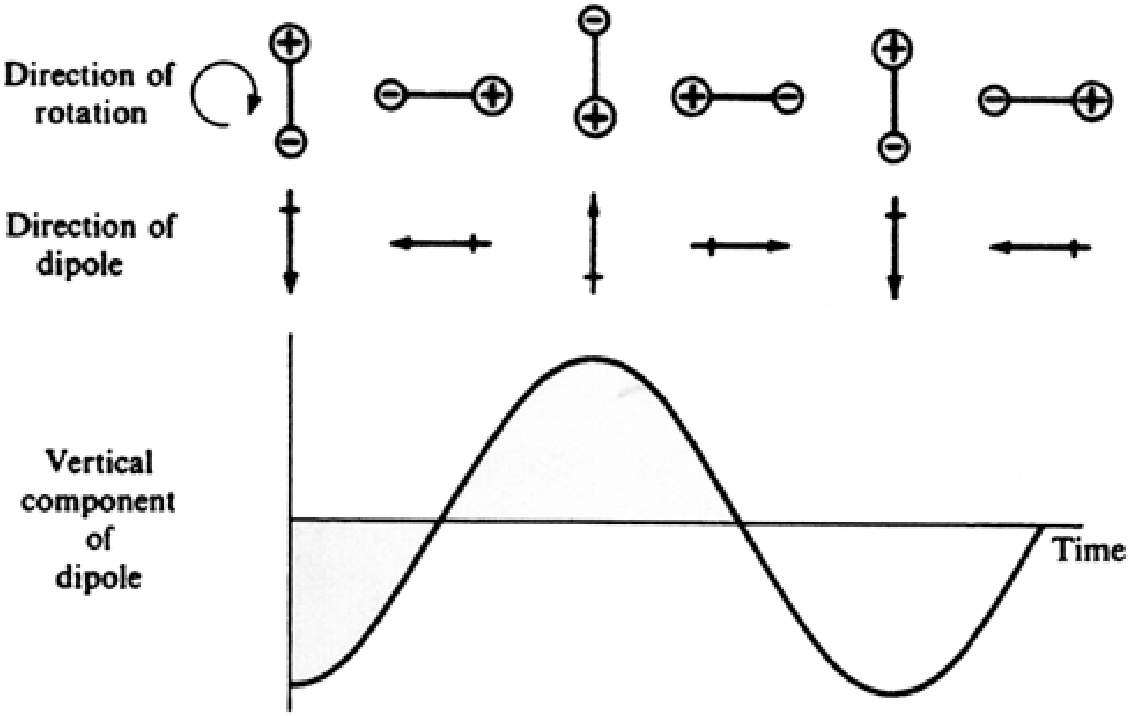
The rotation of a diatomic molecule, HCl, *showing the fluctuation in the dipole moment measured in a particular direction.*

Absorption of Electromagnetic Radiation - The Coupling Mechanism

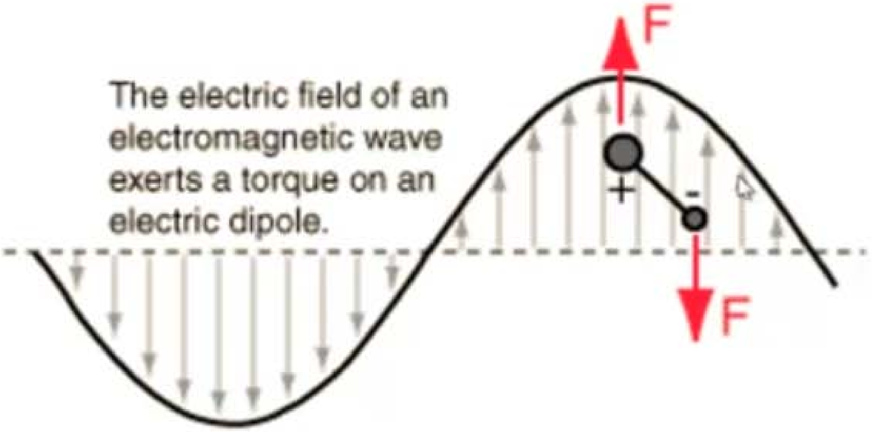
✸ An electromagnetic wave is an oscillating electrical field and interacts only with molecules that can undergo a change in **dipole moment**.

✸ The oscillating dipole can be provided by the rotation of a permanent dipole like for example **HCl**. This type of interaction leads to microwave spectra.

H–Cl



- How can electromagnetic radiation lead to changes in the rotational state of a molecule?

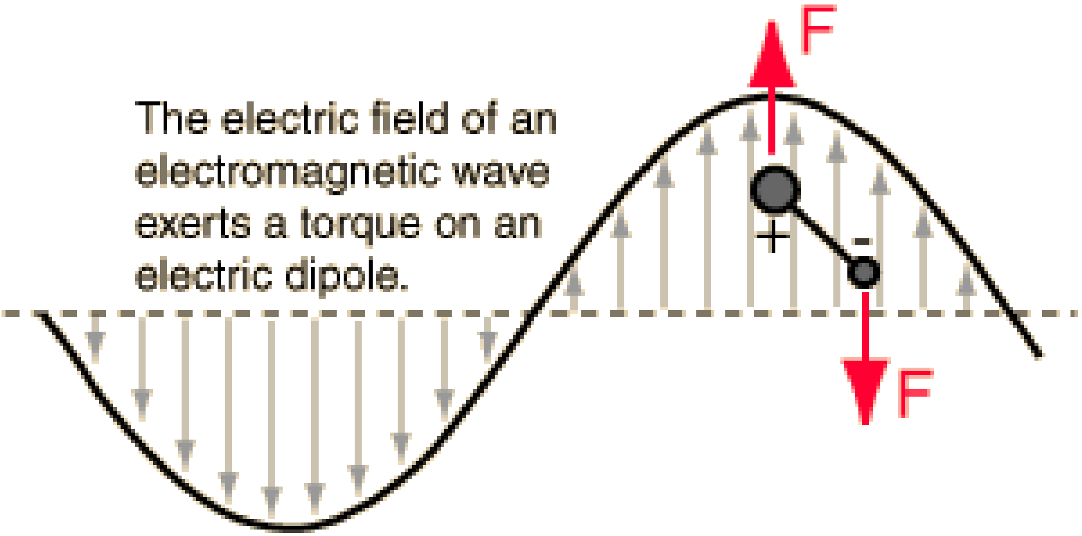


The electromagnetic field exerts a **torque** on the molecule.

Origin of Microwave Spectroscopy

✸ Incident electromagnetic waves can excite the rotational levels of molecules provided they have an **electric dipole moment**. The electromagnetic field exerts a **torque** on the molecule.

✸ The spectra for rotational transitions of molecules is typically in the **microwave region** of the electromagnetic spectrum.


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

- **Absorption of microwave radiation causes heating due to increased molecular rotational activity....**

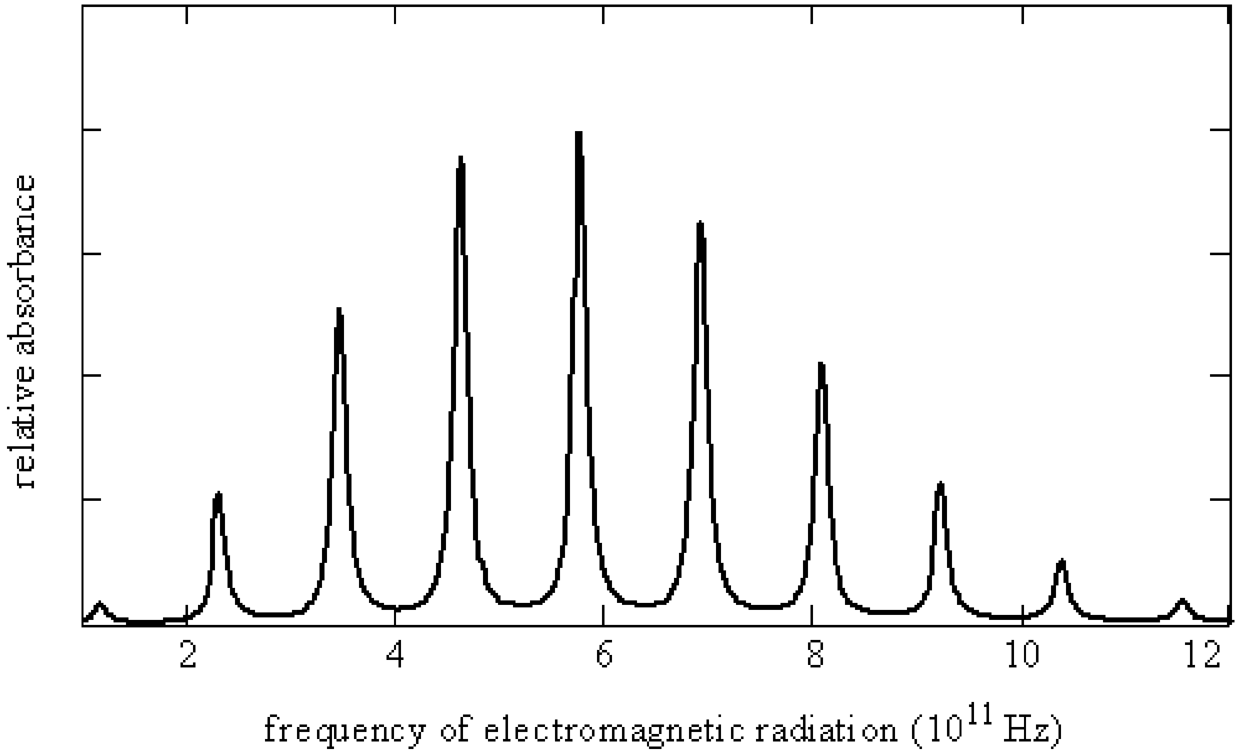
Micro-wave ACTIVE molecules

Incident electromagnetic waves can excite the rotational levels of molecules provided they have an **electric dipole moment**. The electromagnetic field exerts a **torque** on the molecule.

- **Homonuclear diatomic molecules (such as H_2, O_2, N_2 , Cl_2) – have zero dipole (non polar) -- have zero change of dipole during the rotation – hence NO interaction with radiation -- hence homonuclear diatomic molecules are microwave inactive**

- **Heteronuclear diatomic molecules (such as HCl, HF, CO) – have permanent dipolemoment (polar compound) -- change of dipole occurs during the rotation – hence interaction with radiation takes place – Therefore, heteronuclear diatomic molecules are microwave active.**

The rotation spectrum of $^{12}C^{16}O$

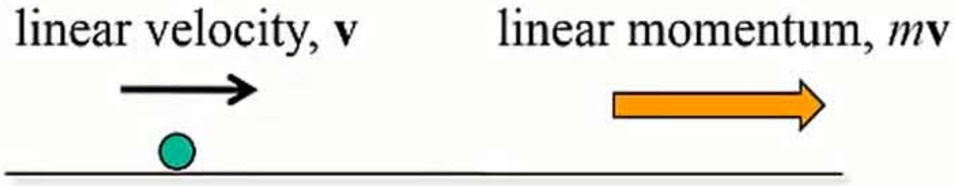


- **The lines are nearly equally spaced and vary in intensity.**

- **We also will learn why the lines are nearly equally spaced and vary in intensity. Such spectra can be used to determine bond lengths, and even bond angles in polyatomic molecules.**

Angular Velocity and Angular Momentum

- Linear motion

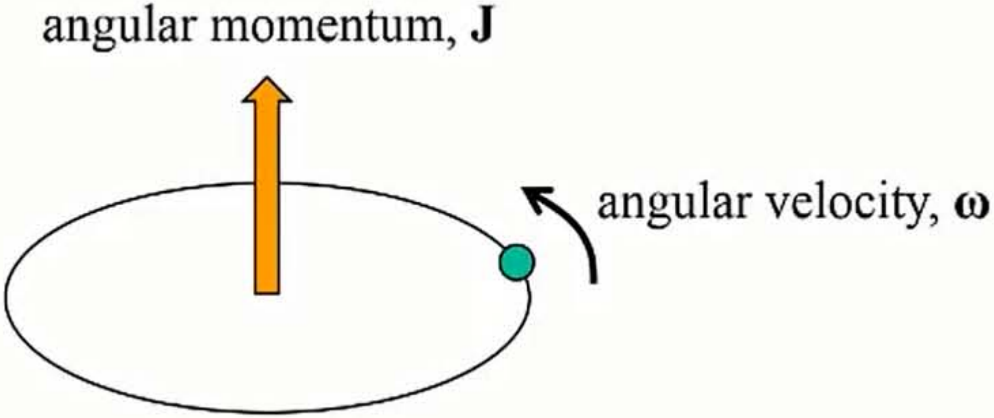


linear velocity, **v**

linear momentum, *m***v**

- Circular motion

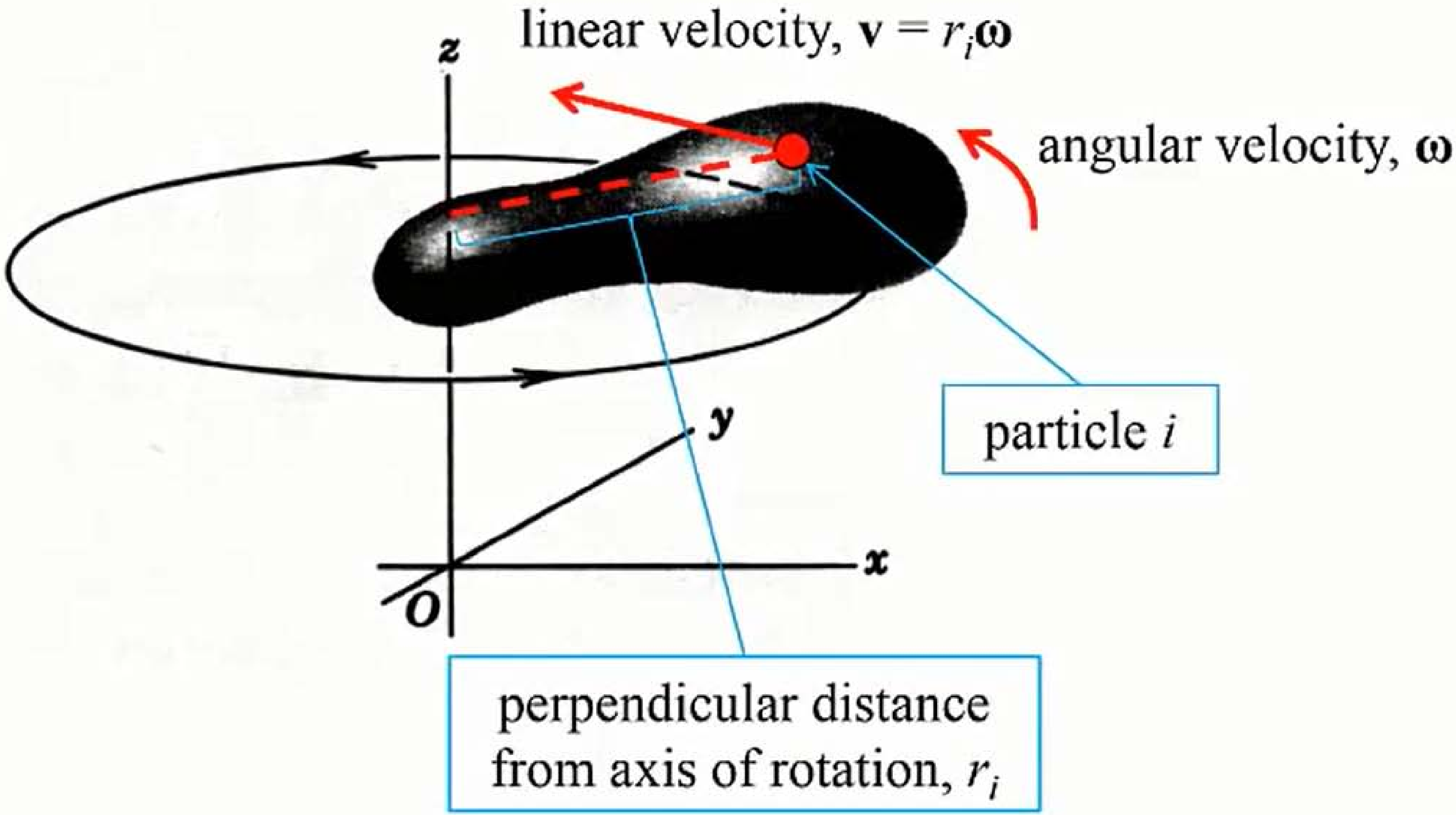
The angular momentum **J** of a particle is represented by a vector along the axis of rotation and perpendicular to the plane of rotation



angular momentum, **J**

angular velocity, **ω**

What is the Moment of Inertia?



linear velocity, $\mathbf{v} = r_i\boldsymbol{\omega}$

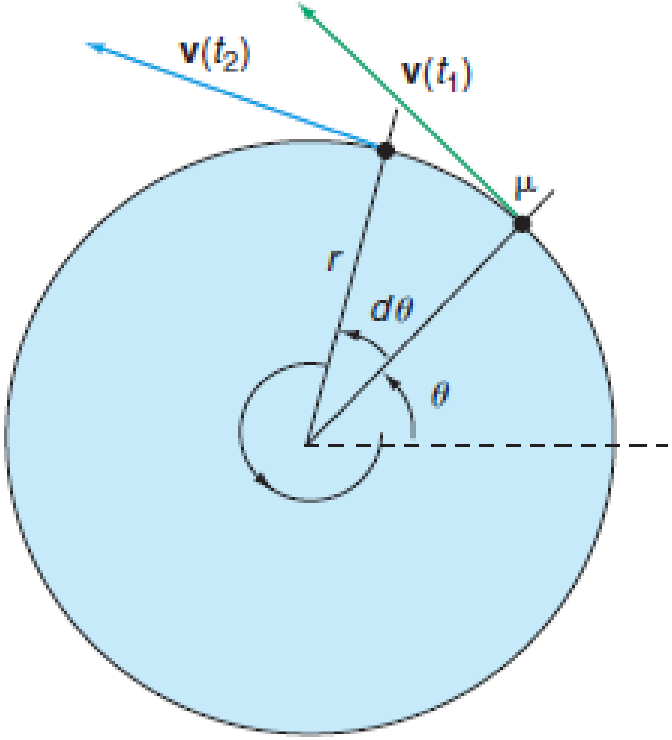
angular velocity, $\boldsymbol{\omega}$

particle i

perpendicular distance from axis of rotation, r_i

Kinetic energy of each particle $i = \frac{1}{2}\, m_i \mathbf{v}_i^2 = \frac{1}{2}\, m_i r_i^2 \boldsymbol{\omega}^2$

Angular velocity (ω) & Linear Velocity



	Linear	Angular	Relationship
Velocity	$v = \frac{r\,d\theta}{dt}$	$\omega = \frac{d\theta}{dt}$	$v = \omega\, r$

Moment of Inertia

- Total kinetic energy of the rotating body

$$\text{Kinetic energy, } T = \sum_i \left(\tfrac{1}{2} m_i r_i^2 \boldsymbol{\omega}^2\right)$$

$$= \sum_i \left(\tfrac{1}{2} m_i r_i^2\right) \boldsymbol{\omega}^2$$

$$= \tfrac{1}{2} I \boldsymbol{\omega}^2$$

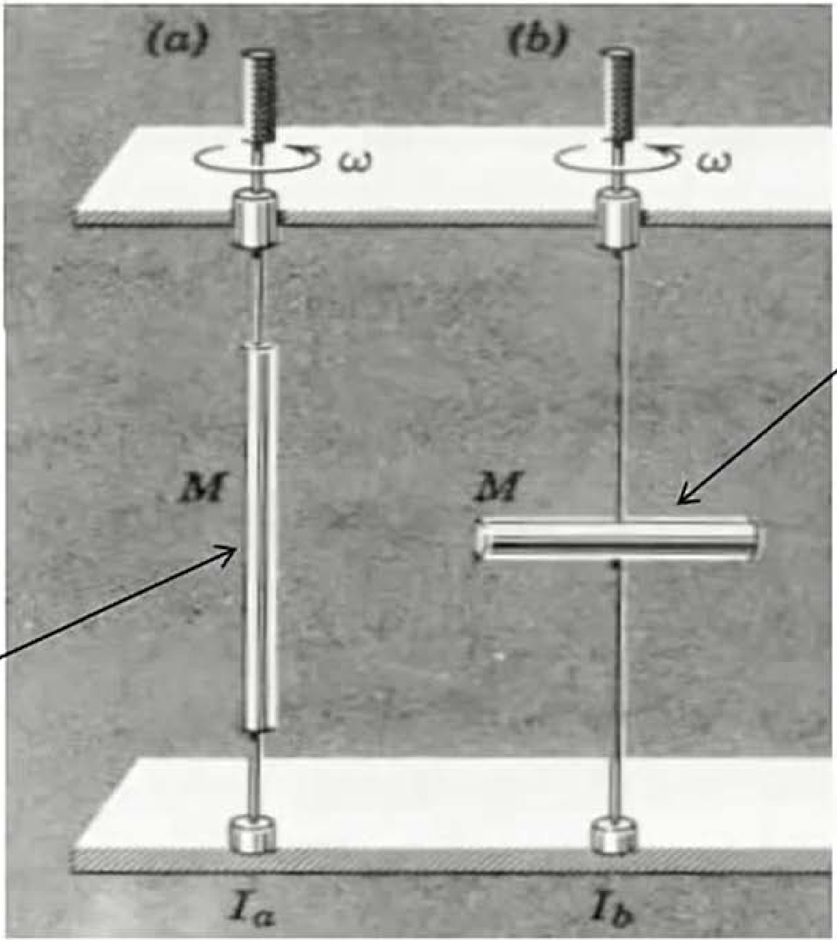
- Compare this to the kinetic energy of a body undergoing linear motion = ½ $m\mathbf{v}^2$

$$\text{Moment of Inertia, } I = \sum_i m_i r_i^2$$

The resistance of the rotating body to a change in its rotational motion about a given axis

Which has the higher *I*?

$$\boxed{I = \sum_i m_i r_i^2}$$



The average distance of each particle in the rod to the axis of rotation is small

The average distance of each particle in the rod to the axis of rotation is larger

Role of Moment of Inertia towards Angular Momentum

Rotational period

$$\tau_{\text{rot}} = \frac{2\pi \text{ radians/revolution}}{\omega \text{ (radians/sec)}}$$

$$\begin{aligned} K_{\text{rot}} &= \frac{1}{2}\frac{m_A m_B}{m_A + m_B} r_e^2\omega^2 \\ &\equiv \frac{1}{2}\mu r_e^2\omega^2 \\ &\equiv \frac{1}{2}I\omega^2 \end{aligned}$$

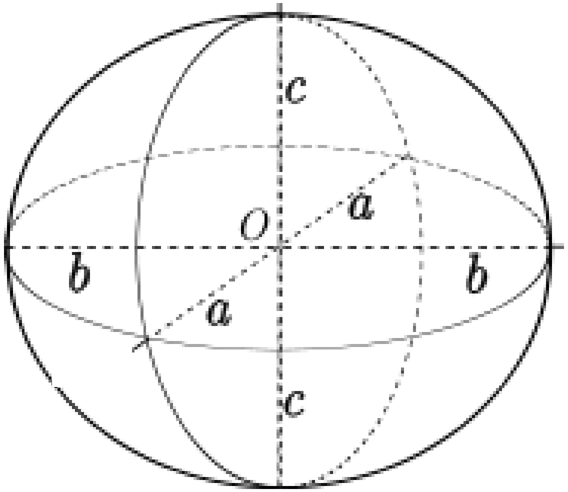
For $K_{rot} = k_B T$

$$\tau_{\text{rot}} = 2\pi\sqrt{\frac{I}{2k_B T}} = 2\pi\sqrt{\frac{\mu r_e^2}{2k_B T}}$$

For a typical molecule at room temperature

$$\tau_{rot} \approx 10^{-12} s = 1 ps$$ *(one picosecond)*

Classes of Rotating Molecules

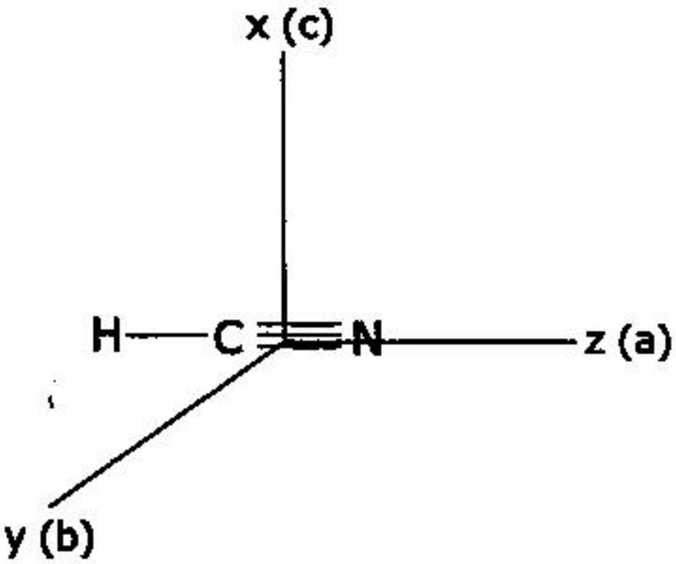


b should be replaced by a

★ Molecules can be classified into five main groups depending on their moments of inertia.

1.	$I_C = I_B\ , I_A = 0$	Linear molecules
2.	$I_C = I_B = I_A$	Spherical top
3.	$I_C = I_B > I_A$	Prolate symmetric top
4.	$I_C > I_B = I_A$	Oblate symmetric top
5.	$I_C > I_B > I_A$	Asymmetric top

Linear Molecules



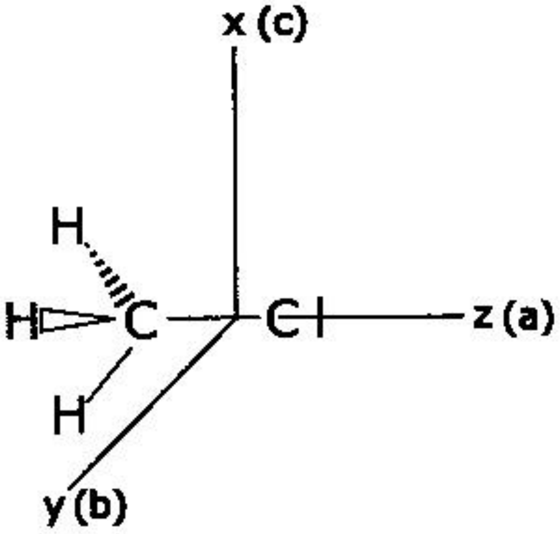
Other examples:

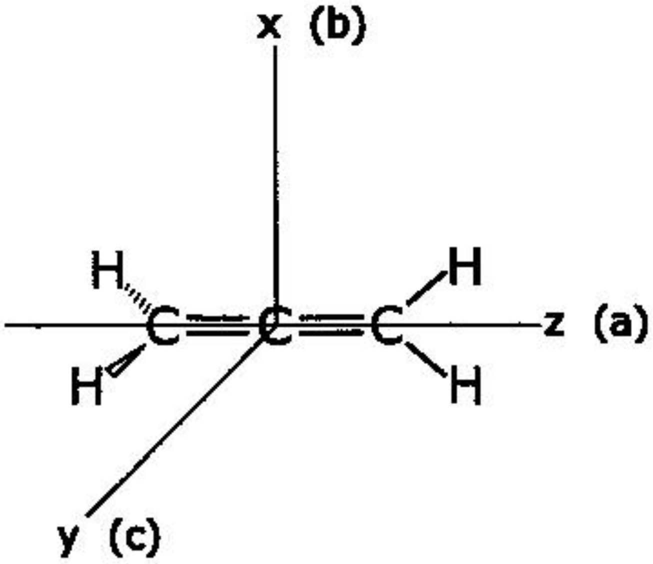
- HCl
- CO_2
- H–C≡C–H
- H–C≡C–C≡C–C≡C–H
- LiF

$$I_C = I_B \, , I_A = 0$$

Linear molecules

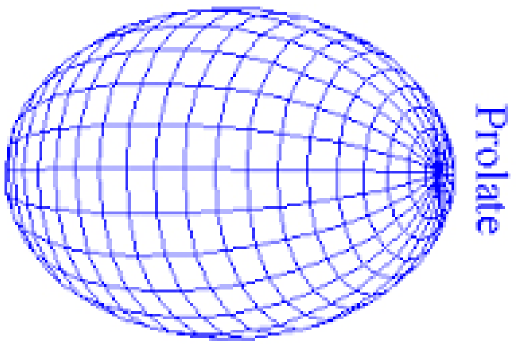
Prolate Symmetric Top Molecules



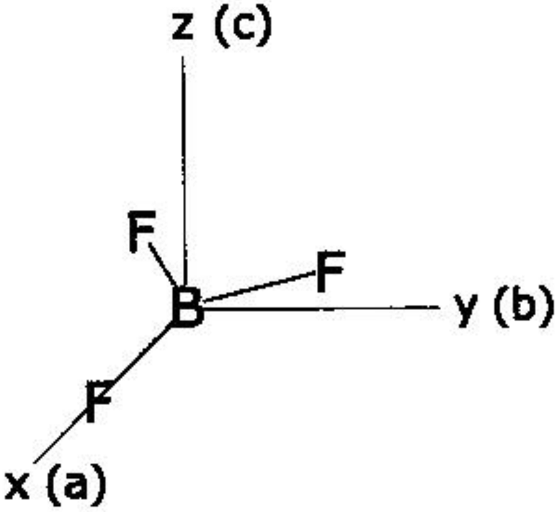


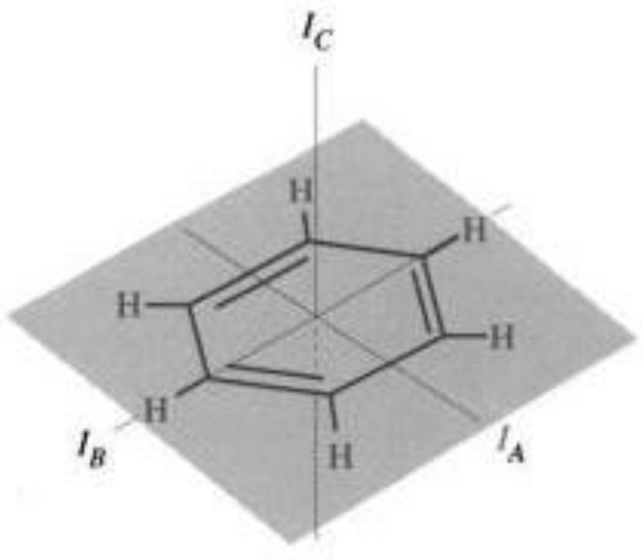
$$I_C = I_B > I_A$$

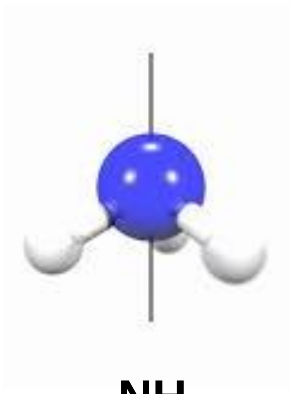
Prolate symmetric top



Oblate Symmetric Top Molecules



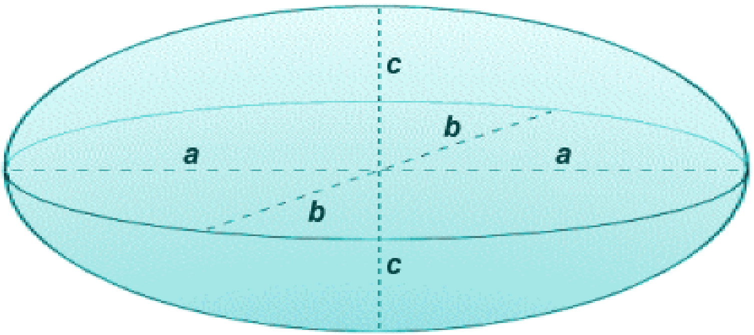


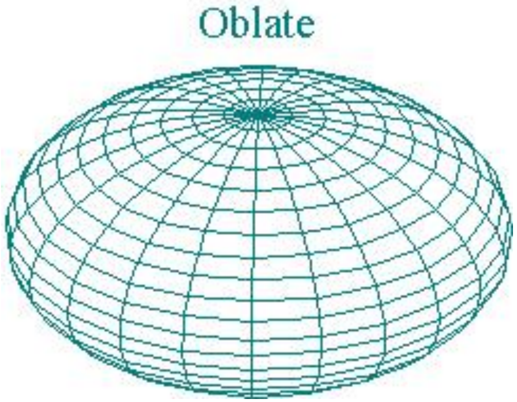


NH_3

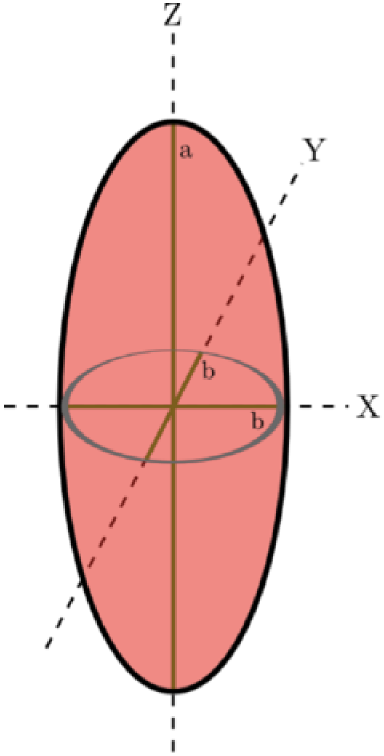
$$I_C > I_B = I_A$$

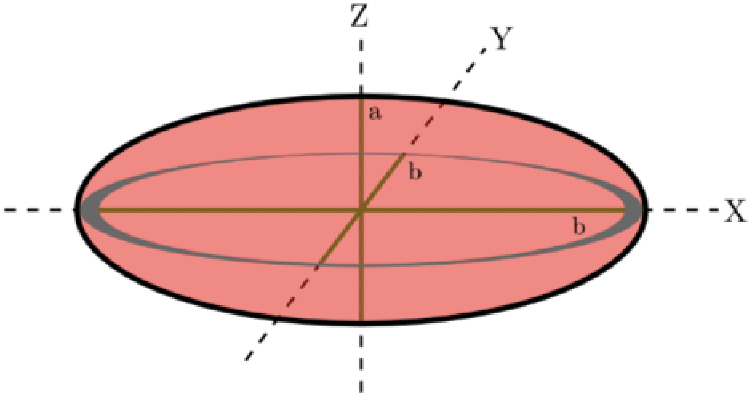
Oblate symmetric top



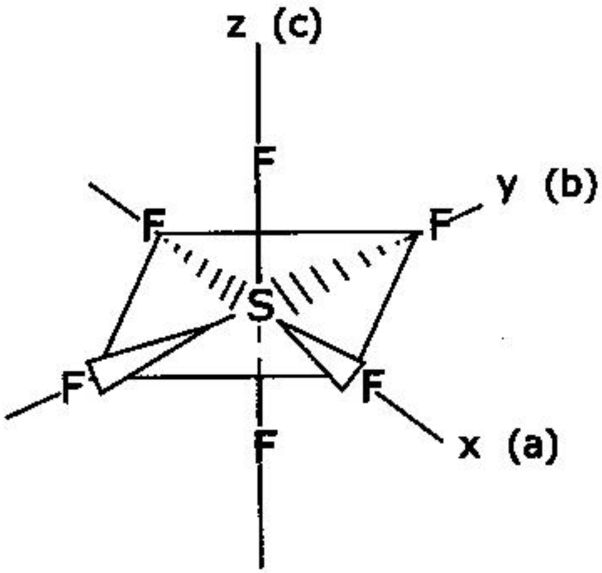


Prolate and Oblate





Spherical Top Molecules



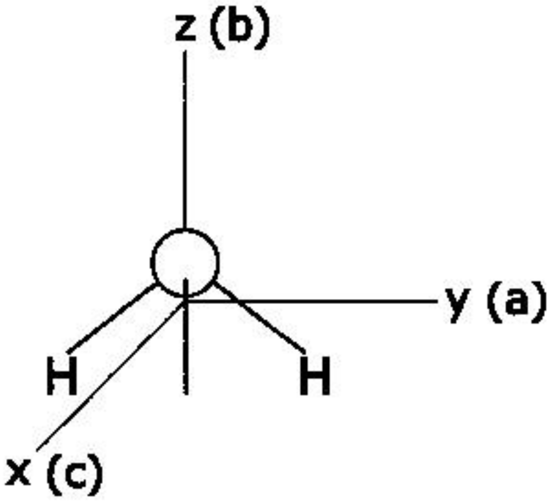
$I_C = I_B = I_A$

Spherical top

Other examples:

- CH_4
- CCl_4
- Generally, molecules with O_h, T_d, or I_h point groups are considered spherical top molecules.

Asymmetric Top Molecules

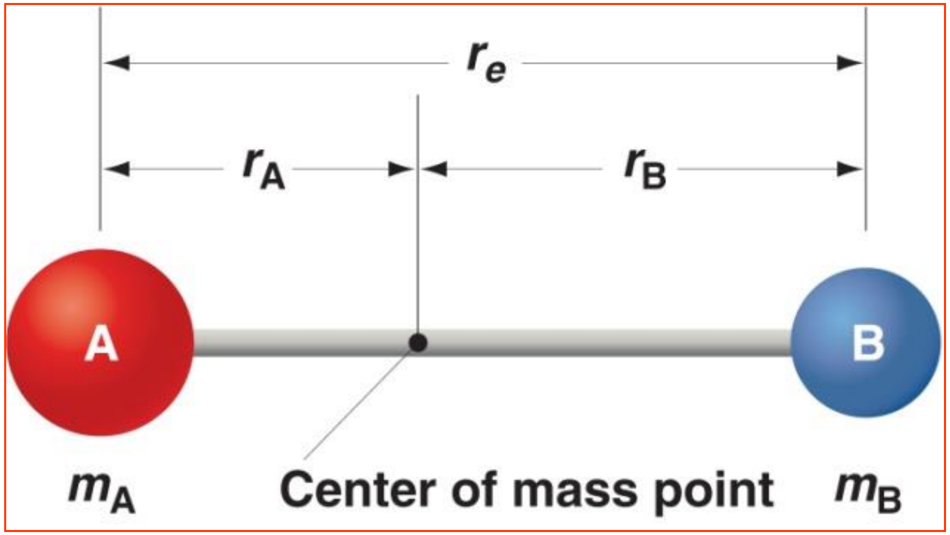


$$I_C > I_B > I_A$$

Asymmetric top

Most of the molecules are asymmetric top.

Rotational Motion: Rigid Rotator Model



$$r_e = r_A + r_B$$

$$m_A r_A = m_B r_B$$

$$r_A = \frac{m_B}{m_A + m_B} r_e$$

$$r_B = \frac{m_A}{m_A + m_B} r_e$$

Rotational Kinetic Energy (K_{rot})

$$K_{\text{rot}} = \tfrac{1}{2} m_A v_A^2 + \tfrac{1}{2} m_B v_B^2$$

$$= \tfrac{1}{2} m_A (r_A \omega)^2 + \tfrac{1}{2} m_B (r_B \omega)^2$$

where ω is angular velocity, dθ/dt

Rotational Kinetic Energy (K_{rot})

$$K_{\text{rot}} = \tfrac{1}{2}\frac{m_A m_B}{m_A + m_B} r_e^2 \omega^2$$

$$\equiv \tfrac{1}{2}\mu r_e^2 \omega^2$$

$$\equiv \tfrac{1}{2} I \omega^2$$

reduced mass

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

moment of inertia

$$I = m_A r_A^2 + m_B r_B^2 = \mu r_e^2$$

(*compare this with* $K) = \frac{1}{2} mv^2$

Using angular moment

$$J = I\omega \quad \text{or} \quad L = I\omega$$

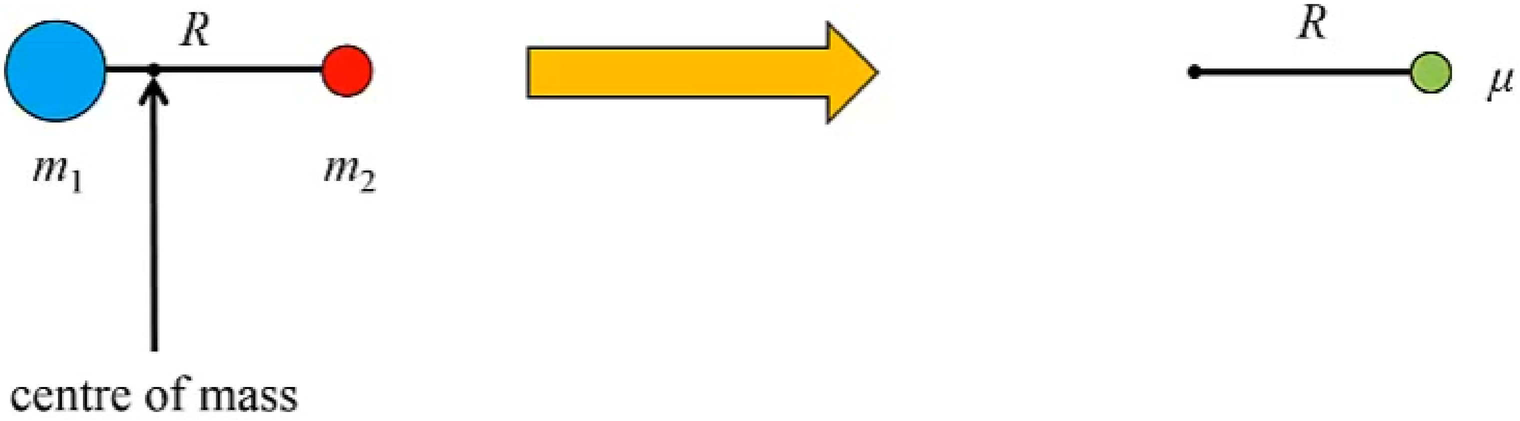
(compare this with $p = mv$ **)**

the rotational kinetic energy becomes

$$\boxed{K_{\text{rot}} = \frac{J^2}{2I}} \quad \text{or} \quad \boxed{K_{\text{rot}} = \frac{L^2}{2I}}$$

(*compare this with* $K) = \frac{p^2}{2m}$

Reduced Mass



Quantum mechanics of rigid rotor rotation

To solve the Schrödinger equation

$$H\psi = E\psi$$

We need to set up the Hamiltonian:

$$H \text{ or } \hat{H}_{total} = T + V$$

One needs to define the kinetic and potential energy

ASSUMPTION

The potential energy of rigid rotor diatomic molecule is zero:

$V = 0$ ⇦ IMPORTANCE ASSUMPTION

The Hamiltonian operator of rigid rotor diatomic molecule corresponds to the kinetic energy operator:

$$\hat{H}_{total} = \hat{T} = -\frac{\hbar^2}{2\mu}\nabla^2 = \frac{\hat{L}^2}{2I}$$

Rotational operators:

$$I = m_1 r_1^2 + m_2 r_2^2 = \mu r_0^2 \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$v = \omega r_0$$

$$L = I\omega \qquad V = 0$$

$$\hat{H}_{total} = \hat{T} + \hat{V} = \left[-\frac{\hbar^2}{2\mu} \nabla^2 + \cancelto{0}{\hat{V}} \right]$$

where ∇^2 is the Laplacian Operator

In Cartesian coordinates

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Rigid Diatomic Molecules

- Set up the Schrödinger equation for the rigid rotor model:

$$\hat{H}\Psi = E\Psi$$

$$-\frac{\hbar^2}{2I}\nabla^2\Psi_{\mathrm{rot}} = E_{\mathrm{rot}}\Psi_{\mathrm{rot}}$$

$$-\frac{\hbar^2}{2I}\left(\frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{r\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\Psi_{\mathrm{rot}} = E_{\mathrm{rot}}\Psi_{\mathrm{rot}}$$

- Solving this equation reveals that the rotational energy levels are quantised

Rotational Energy

- Quantised rotational energy levels:

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

Joules

- $J = 0, 1, 2, \ldots$ are the set of possible rotational quantum numbers

- For each quantum number J there is a corresponding wavefunction and energy level

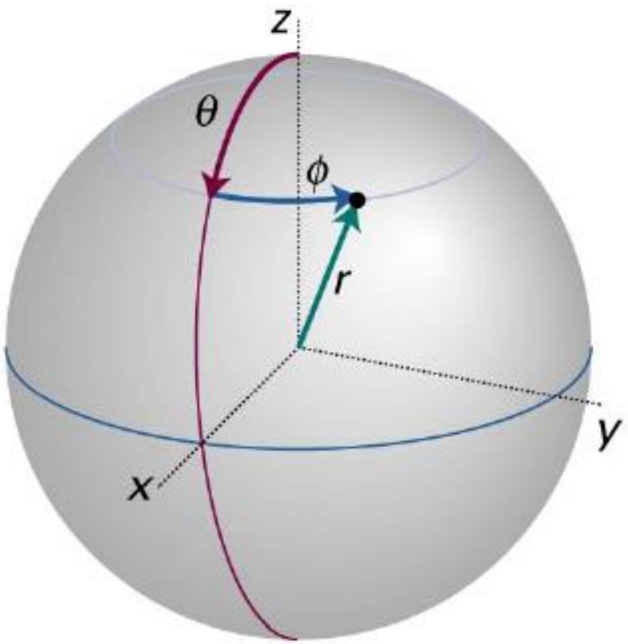
$$\tilde{F}(J) = \frac{E_J}{h\tilde{c}} = \frac{J(J+1)h}{8\pi^2 I\tilde{c}} = \tilde{B}J(J+1)$$

cm^{-1}

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

Transformation to spherical polar coordinates

For rigid rotor model, we usually transform the ∇^2 Cartesian coordinates into spherical polar coordinates .



Cartesian coordinates		**Spherical polar coordinates**
$\psi(x,y,z)$	⇨	$\psi(r,\theta,\phi)$
$-\infty < x < \infty$		$0 \le \cancel{r \le} \infty$
$-\infty < y < \infty$	⇨	$0 \le \theta \le \pi$
$-\infty < z < \infty$		$0 \le \phi < 2\pi$
$z = r\cos\theta$		$r = \sqrt{x^2 + y^2 + z^2}$
$x = r\sin\theta\cos\phi$		$\theta = \cos^{-1}\dfrac{z}{r}$
$y = r\sin\theta\sin\phi$		$\phi = \tan^{-1}\left(\dfrac{y}{x}\right)$

Transform the ∇^2 Cartesian coordinates into spherical polar coordinates

$$\frac{\partial \psi}{\partial r} = 0$$

$$\nabla^2 = \cancel{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \phi^2}$$

$$= \frac{1}{r_0^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right)$$

Because of rigid bond (fixed bond length)

$$r = r_0$$

$$\hat{H} = \hat{T} = -\frac{\hbar^2}{2\mu}\nabla^2 = -\frac{\hbar^2}{2\mu r_0^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right)$$

$$= -\frac{\hbar^2}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right)$$

$$I = \mu r_0^2$$

After transformation, we get:

$$\hat{T} = -\frac{\hbar^2}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

Because $\hat{T} = \frac{\hat{L}^2}{2I}$

The square of angular momentum operator becomes

$$\hat{L}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

L^2 is important operator in the solution for energy levels and wavefunctions of rigid rotor in the Schrödinger equation.

Another importance of the angular momentum is L_z (the z-component)

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

Thus, the Hamiltonian operator in the Schrödinger equation

$$H = \frac{L^2}{2I}$$

Another implication of the rigid rotor (fixed bond length) is the wave function depends on θ and ϕ :

$$\psi(r,\theta,\phi) = \psi(\theta,\phi)$$

$$H\psi(\theta,\phi) = E\psi(\theta,\phi)$$

Rigid rotor wavefunctions

$$H\psi(\theta,\phi)=E\psi(\theta,\phi) \qquad 0<\theta<\pi \ : \ 0<\phi<2\pi$$

$$\hat{H}=-\frac{\hbar^2}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

The full wavefunctions $\psi(r,\theta,\phi)=R(r)Y(\theta,\phi)$

Reduce to $\psi(\theta,\phi)=Y(\theta,\phi)$

Consider only the angular part of the wavefunctions

$$-\frac{\hbar^2}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)Y(\theta,\phi)=EY(\theta,\phi)$$

Set the Schrödinger Equation equal to zero and $\times\left(-2I\sin^2\theta/\hbar^2\right)$

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right)+\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}+\frac{2I}{\hbar^2}\sin^2\theta E Y(\theta,\phi)=0$$

From the previous slide

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right)+\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}+\frac{2I}{\hbar^2}\sin^2\theta E Y(\theta,\phi)=0$$

Rearranging the differential equation separating the θ-dependent terms from the θ-dependent terms:

$$\underbrace{\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{2I}{\hbar^2}\sin^2\theta E\right]}_{\text{Only }\theta}Y(\theta,\phi)=-\underbrace{\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}}_{\text{Only }\phi}$$

the Schrödinger equation can be solved using separation of variables.

$$Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$$

From the previous slide

$$\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\beta\sin^{2}\theta\right]\Theta(\theta)\Phi(\phi)=-\frac{\partial^{2}\Theta(\theta)\Phi(\phi)}{\partial\phi^{2}}$$

$$\beta=\frac{2IE}{\hbar^{2}}$$

LHS operator does not operate on Φ(ϕ) and RHS operator does not operate on Θ(θ).

$$\Phi(\phi)\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\beta\sin^{2}\theta\,\Theta(\theta)\Phi(\phi)=-\Theta(\theta)\frac{\partial^{2}\Phi(\phi)}{\partial\phi^{2}}$$

Devide by Φ(ϕ) Θ(θ)

$$\underbrace{\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right)+\beta\sin^{2}\theta}_{\text{Only }\theta}=-\underbrace{\frac{1}{\Phi(\phi)}\frac{\partial^{2}\Phi(\phi)}{\partial\phi^{2}}}_{\text{Only }\phi}$$

Each side of the equation must be equal. Let give it to m^2

From the previous slide

$$\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right)+\beta\sin^2\theta=-\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=m^2$$

$$\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right)+\beta\sin^2\theta=m^2 \qquad \text{(I)}$$

$$-\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=m^2 \qquad \text{(II)}$$

Let solve Eq.(II)

$$-\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=m^2$$

$$\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=-m^2\frac{1}{\Phi(\phi)}$$

$$\Phi(\phi)=A_m e^{im\phi}\ \text{or}\ \ A_{-m}e^{-im\phi}$$

Consider periodicity conditions $\Phi(\phi+2\pi)=\Phi(\phi)$

The solution for Φ(ϕ) is :

$$\Phi(\phi)=\frac{1}{\sqrt{2\pi}}e^{im\phi}\ ;\ \ \mathrm{m}=0,\pm 1,\pm 2,..$$

Normalization constant

The Legendre Equation

For solving Eq.(I),

$$\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right)+\beta\sin^2\theta=m^2$$

Change variables: $x=\cos\theta\,,\quad \Theta(\theta)=P(x),\quad \frac{dx}{-\sin\theta}=\mathrm{d}\theta$

Since: $0\le\theta\le\pi \;\Rightarrow\; -1\le x\le +1$

$$\sin^2\theta=1-\cos^2\theta=1-x^2$$

The eq(I) is transformed into:

$$(1-x^2)\frac{d^2}{dx^2}P(x)-2\frac{d}{dx}P(x)+\left[\beta-\frac{m^2}{1-x^2}\right]P(x)=0$$

The Legendre Equation

Associated Legendre polynomials

The solutions of the Legendre Eq. are :

$$\Theta(\theta) = A_m P_J^{|m|}(\cos\theta)$$

$P_J^{|m|}(\cos\theta)$ The Associated Legendre polynomials

Normalization constant

$$A_m = \sqrt{\left(\frac{2J+1}{2}\right)\frac{(J-|m|)!}{(J+|m|)!}}$$

$$\Theta(\theta) = \sqrt{\left(\frac{2J+1}{2}\right)\frac{(J-|m|)!}{(J+|m|)!}}P_J^{|m|}(\cos\theta)$$

The Associated Legendre polynomials

$$P_J^{|m|}(\cos\theta) \qquad ; \;\; \mathrm{J} = 0, 1, 2, ... \;\; \text{and } \mathrm{m} = 0, \pm 1, \pm 2, ..$$

$$P_0^0(\cos\theta) = 1$$

$$P_1^0(\cos\theta) = \cos\theta$$

$$P_1^{\pm 1}(\cos\theta) = \sin\theta$$

$$P_2^0(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$$

$$P_2^{\pm 1}(\cos\theta) = 3\sin\theta\cos\theta$$

$$P_2^{\pm 2}(\cos\theta) = 3\sin^2\theta$$

Spherical harmonic wavefunctions

$$Y(\theta,\phi) = Y_J^m(\theta,\phi) = \Theta(\theta)\Phi(\phi)$$

$$= \underbrace{\sqrt{\left(\frac{2J+1}{2}\right)\frac{(J-|m|)!}{(J+|m|)!}}P_J^{|m|}(\cos\theta)}_{\Theta(\theta)}\ \underbrace{\frac{1}{\sqrt{2\pi}}e^{im\phi}}_{\Phi(\phi)}$$

$$Y_J^m(\theta,\phi) = \sqrt{\left(\frac{2J+1}{4\pi}\right)\frac{(J-|m|)!}{(J+|m|)!}}P_J^{|m|}(\cos\theta)\, e^{im\phi}$$

$$;\ \ \mathrm{J} = 0, 1, 2, \ldots \text{ and } \mathrm{m} = 0, \pm 1, \pm 2, ..$$

The wavefunctions for J = 0, 1, 2

$$Y_0^0(\theta,\phi)=\frac{1}{(4\pi)^{1/2}}$$

$$Y_1^0(\theta,\phi)=\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$$

$$Y_1^{\pm1}(\theta,\phi)=\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm i\phi}$$

$$Y_2^0(\theta,\phi)=\left(\frac{5}{16\pi}\right)^{1/2}\left(3\cos^2\theta-1\right)$$

$$Y_2^{\pm1}(\theta,\phi)=\left(\frac{5}{16\pi}\right)^{1/2}\sin\theta\cos\theta\, e^{\pm i\phi}$$

$$Y_2^{\pm2}(\theta,\phi)=\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\, e^{\pm 2i\phi}$$

Rotational energy levels of rigid rotor

The Hamiltonian (Laplacian) operator:

$$\hat{H} = T = -\frac{\hbar^2}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

The spherical harmonic wave functions:

$$-\frac{\hbar^2}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)Y(\theta,\phi) = EY(\theta,\phi)$$

$$Y_J^m(\theta,\phi) = \sqrt{\left(\frac{2J+1}{4\pi}\right)\frac{(J-|m|)!}{(J+|m|)!}}P_J^{|m|}(\cos\theta)\, e^{im\phi}$$

Because $Y_J^m(\theta,\phi)$ are Eigenfunct ions of $\hat{\mathrm{H}}$

solving for this Schrödinger gives the quantized J(J+1) result :

$$\hat{H}Y_J^m(\theta,\phi) = \frac{\hbar^2}{2I}J(J+1)\,Y_J^m(\theta,\phi)$$

$$,\quad \mathrm{J} = 0,1,2,\ldots$$

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

J is Rotational quantum number

Rotational Energy of Rigid Diatomic molecule

Rotational Energy Levels for rigid rotor:

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ joules} \qquad \text{where } J = 0, 1, 2, \ldots$$

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1) \text{ cm}^{-1} \qquad (J = 0, 1, 2, \ldots)$$

$$\boxed{\varepsilon_J = \bar{B} J(J+1) \text{ cm}^{-1}} \qquad (J = 0, 1, 2, \ldots)$$

where $\bar{B}$, the *rotational constant*, is given by $\bar{B} = \frac{h}{8\pi^2 I_B c} \text{ cm}^{-1}$

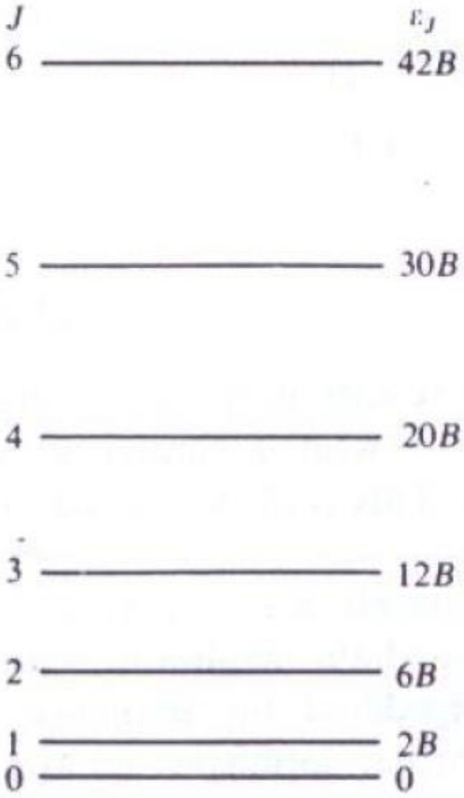
Where $I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2$

Rotational Spectra of Rigid Diatomic Molecule

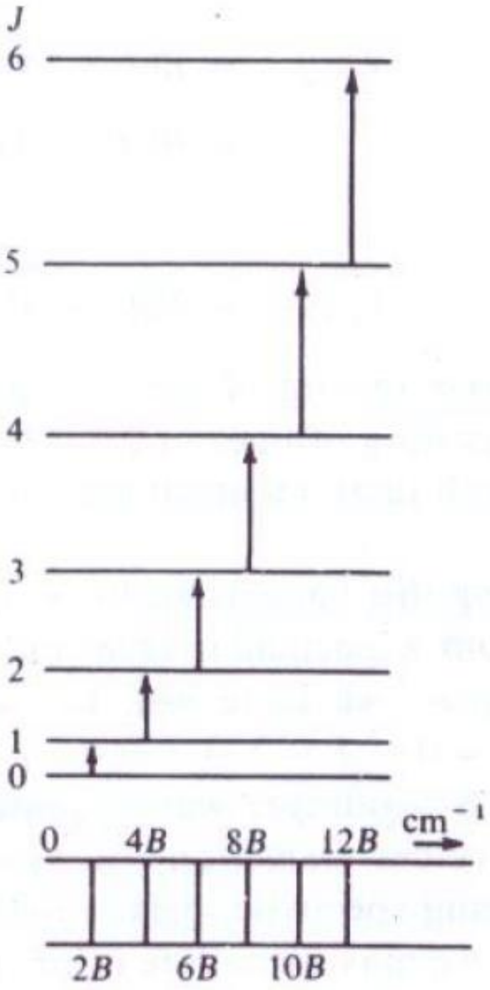
For rigid rotor, J → J + 1,

$$\bar{\nu}_{J \rightarrow J+1} = 2B(J + 1)\ \text{cm}^{-1}$$

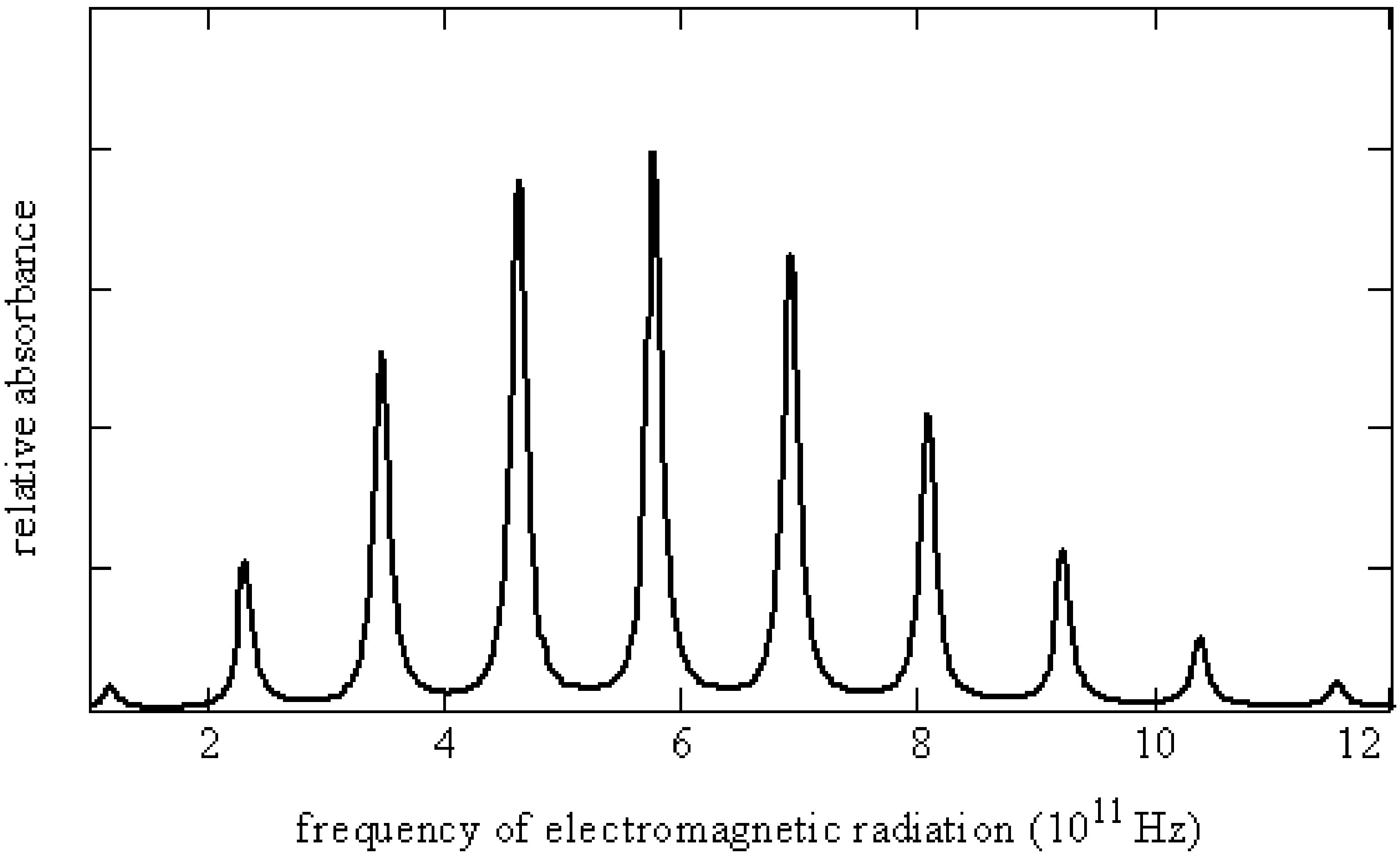
Selection rule: $\Delta J = \pm 1$



The allowed rotational energy levels of a rigid diatomic molecule



Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum


relative absorbance
2
4
6
8
10
12
frequency of electromagnetic radiation (10^{11} Hz)

Selection Rule for Rotational Transition

Transition dipole moment

$$\mu_{fi} = \int \Psi_f \mu \Psi_i d\tau$$

initial state

final state

⇒ only if this integral is nonzero, the transition is allowed; if it is zero, the transition is forbidden

$$\Delta J = \pm 1$$

Example: Using the following total energy eigenfunctions for the three-dimensional rigid rotor, **show that the J=0 → J=1 transition is allowed**, and that the **J=0 → J=2 transition is forbidden**:

Providing the notation $Y_j^{M_j}$ is used for the preceding functions.

$$Y_0^0(\theta,\phi)=\frac{1}{(4\pi)^{1/2}} \qquad Y_1^0(\theta,\phi)=\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$$

$$Y_2^0(\theta,\phi)=\left(\frac{5}{16\pi}\right)^{1/2}\left(3\cos^2\theta-1\right)$$

Assuming the electromagnetic field to lie along the *z*-axis, $\mu_z=\mu\cos\theta$

the transition dipole moment integral takes the form

$$\mu_z^{10}=\mu\int_0^{2\pi}d\phi\int_0^{\pi}Y_1^0(\theta,\phi)(\cos\theta)Y_0^0(\theta,\phi)\sin\theta d\theta$$

For the J=0 → J=1 transition,

$$Y_0^0(\theta,\phi)=\frac{1}{(4\pi)^{1/2}} \quad\Rightarrow\quad Y_1^0(\theta,\phi)=\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$$

$$\mu_z^{10}=\mu\int_0^{2\pi}d\phi\int_0^{\pi}Y_{J=1}^0(\theta,\phi)(\cos\theta)Y_{J=0}^0(\theta,\phi)\sin\theta d\theta$$

$$=\mu\int_0^{2\pi}d\phi\int_0^{\pi}\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta(\cos\theta)\frac{1}{(4\pi)^{1/2}}\sin\theta d\theta$$

$$=\mu\frac{\sqrt{3}}{4\pi}\int_0^{2\pi}d\phi\int_0^{\pi}\cos^2\theta\sin\theta d\theta$$

$$\boxed{\int_0^{2\pi}d\phi=[\phi]_0^{2\pi}=2\pi-0}$$

$$=\mu\frac{\sqrt{3}}{4\pi}(2\pi)\int_0^{\pi}\cos^2\theta\sin\theta d\theta$$

$$=\mu\frac{\sqrt{3}}{2}\int_0^{\pi}\cos^2\theta\sin\theta d\theta$$

For the *J*=0 → *J*=1 transition,

Now consider $\int_0^{\pi} \cos^2\theta \sin\theta d\theta$

Use reduction or substitution method

$$x = \theta, \quad z = \cos x, \qquad \frac{dz}{dx} = -\sin x, \quad dx = -\frac{1}{\sin x}dz$$

$$\int \cos^2 x \sin x dx = \int z^2 \sin x dx = \int z^2 \sin x\left(-\frac{1}{\sin x}\right)dz = -\int z^2 dz$$

$$= -\frac{1}{3}z^3 = -\frac{1}{3}\cos^3 x$$

Replace the result into the original integration

$$\int_0^{\pi} \cos^2\theta \sin\theta d\theta = \left[-\frac{1}{3}\cos^3\theta\right]_0^{\pi} = -\frac{1}{3}(-1^3 - 1^3) = \frac{2}{3}$$

For the *J*=0 → *J*=1 transition,

From the previous derivation:

$$\mu_z^{10} = \mu \frac{\sqrt{3}}{2} \int_0^{\pi} \cos^2\theta \sin\theta d\theta$$

$$\int_0^{\pi} \cos^2\theta \sin\theta d\theta = \frac{2}{3}$$

$$\mu_z^{10} = \mu \frac{\sqrt{3}}{2}\left(\frac{2}{3}\right) = \mu \frac{\sqrt{3}}{3}$$

Thus:

$$\mu_z^{10} = \mu \frac{\sqrt{3}}{3} \neq 0$$

The *J*=0 → *J*=1 transition is allowed.

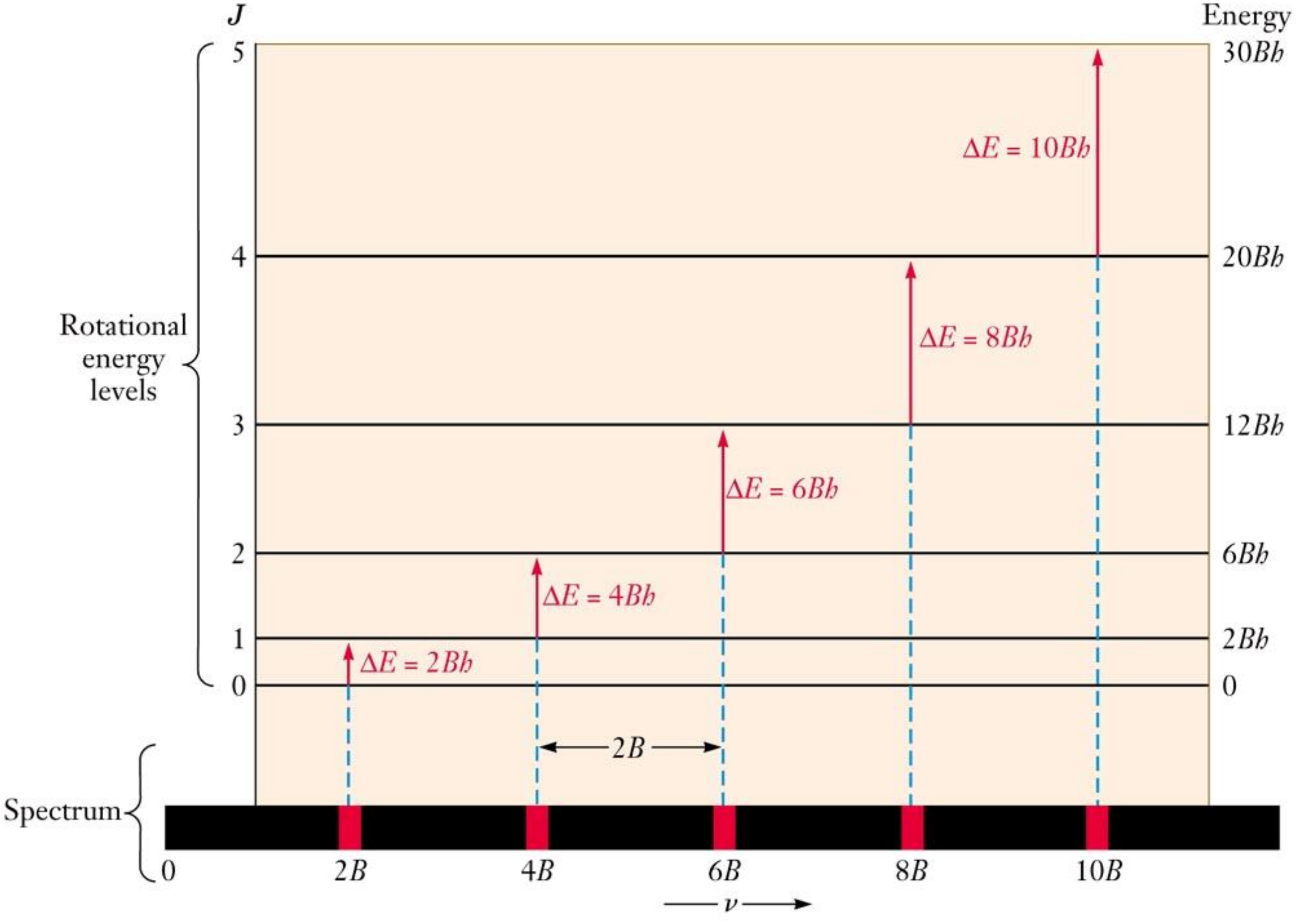
Home Assignment

Using transition moment integral and Spherical Harmonic wave functions for the *J*=0 and *J* =2 energy levels, show that *J*=0 → *J* =2 transition is forbidden.

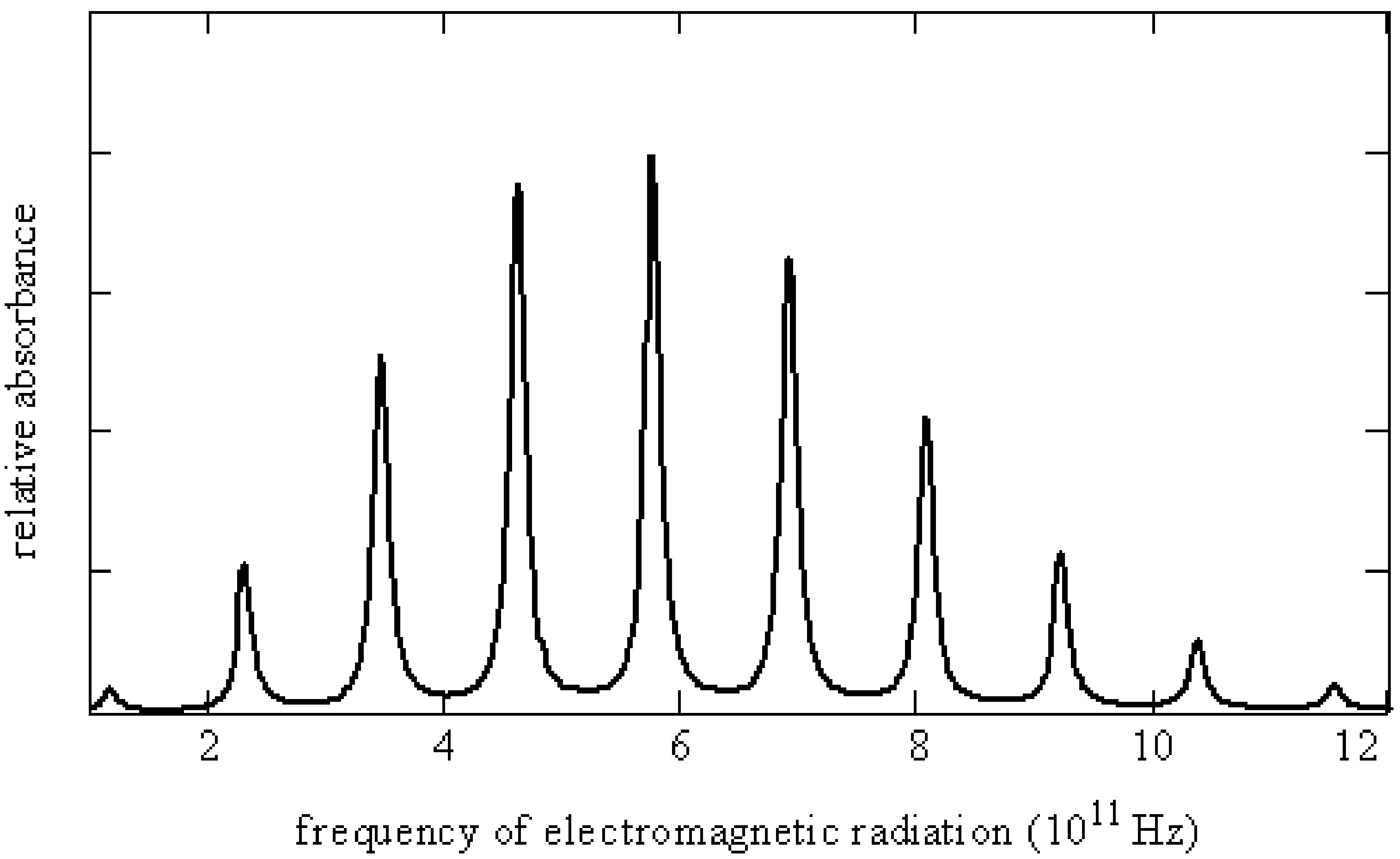
Rotational Spectra of Rigid Rotor

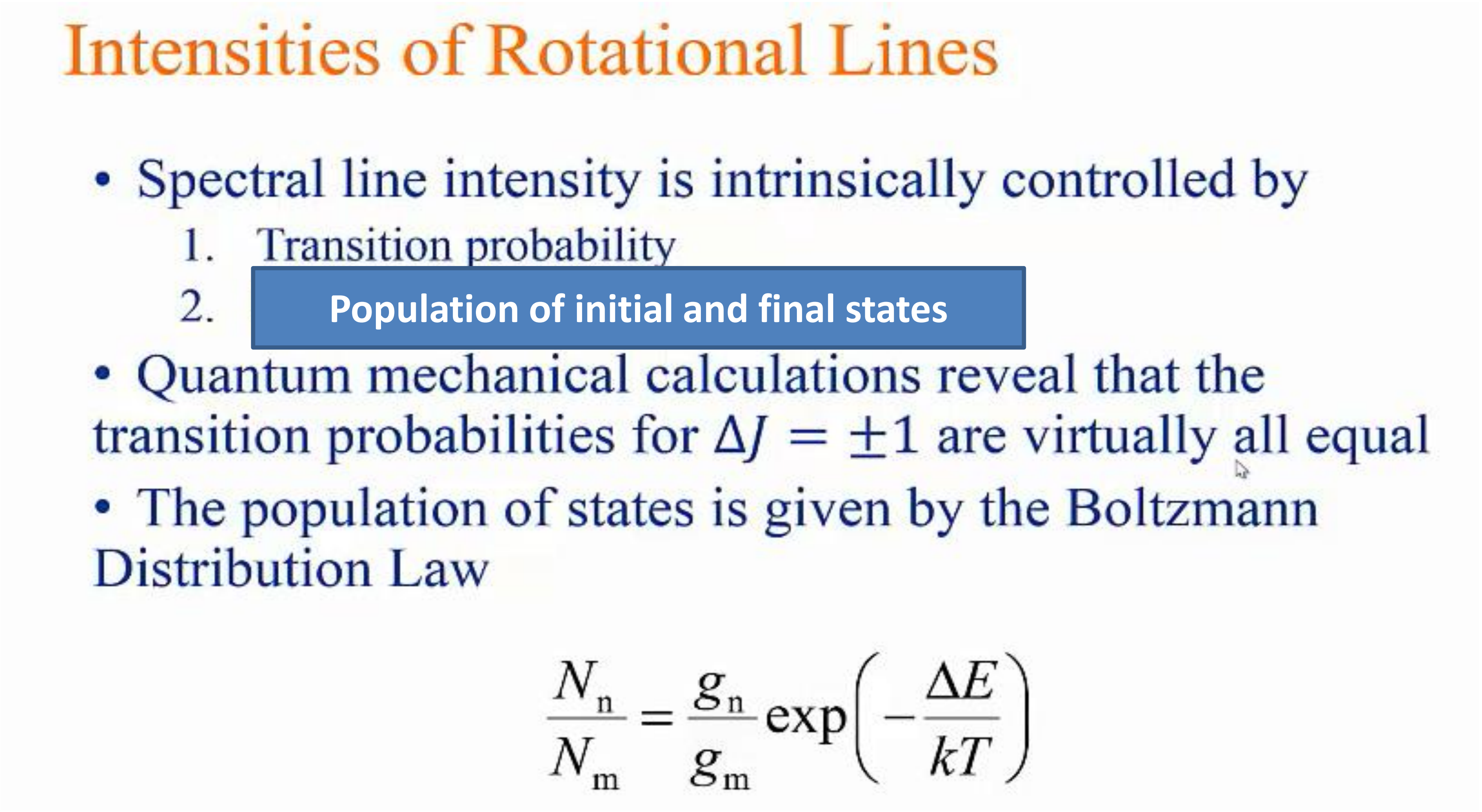
Selection Rule: Apart from **Specific rule, ΔJ= ±1,** Gross rule- the molecule should have a **permanent electric dipole moment, μ .** Thus, **homonuclear diatomic molecules do not have a pure rotational spectrum. Heteronuclear diatomic molecules do have rotational spectra.**

$$\Delta j = \pm 1$$
$$\Delta j = +1 \ (absorption)$$
$$\Delta j = -1 \ (emission)$$



© 2003 Thomson-Brooks/Cole


relative absorbance
2
4
6
8
10
12
frequency of electromagnetic radiation (10^{11} Hz)



Intensities of Rotational Lines

- Spectral line intensity is intrinsically controlled by
  1. Transition probability
  2. Population of initial and final states
- Quantum mechanical calculations reveal that the transition probabilities for $\Delta J = \pm 1$ are virtually all equal
- The population of states is given by the Boltzmann Distribution Law

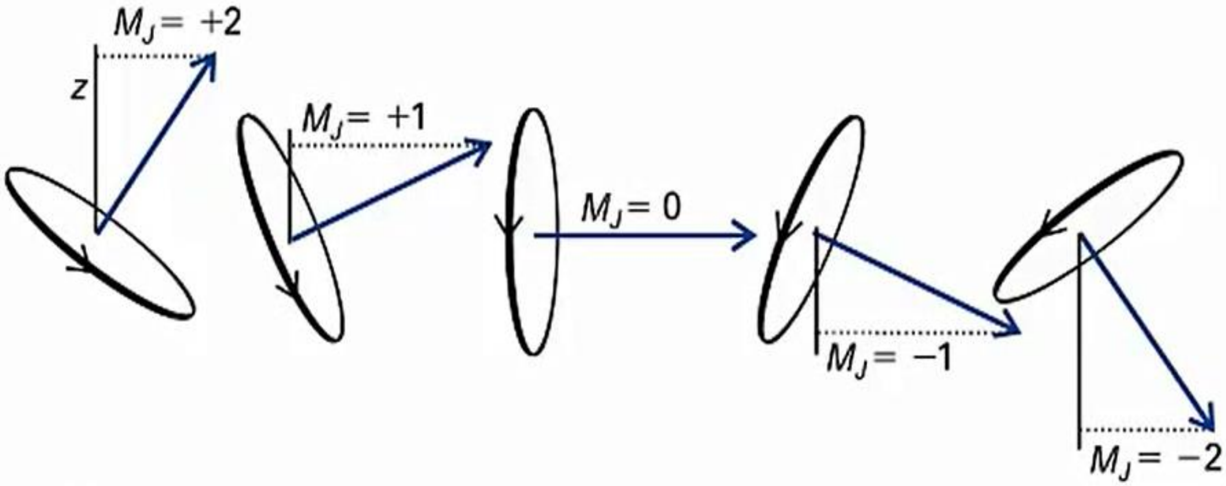
$$\frac{N_{\mathrm{n}}}{N_{\mathrm{m}}} = \frac{g_{\mathrm{n}}}{g_{\mathrm{m}}} \exp\left(-\frac{\Delta E}{kT}\right)$$

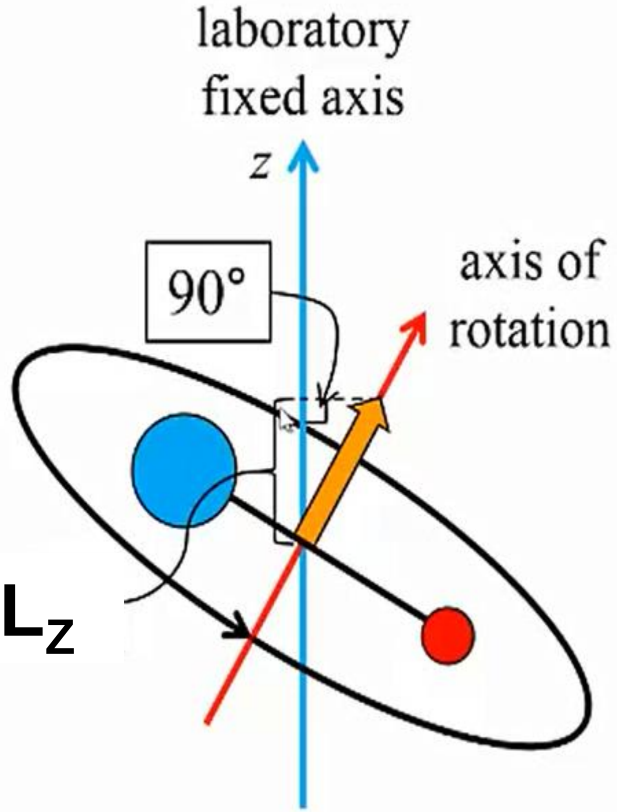
Spatial Orientation

- How is the molecule orientated with respect to a reference (laboratory) fixed axis?
    - Project J onto the reference axis z

$$\mathbf{L} = \sqrt{J(J+1)}\,\hbar$$

$$\mathbf{L_Z} = M_J\hbar, \qquad \text{where } M_J = 0, \pm 1, \pm 2, \ldots, \pm J$$





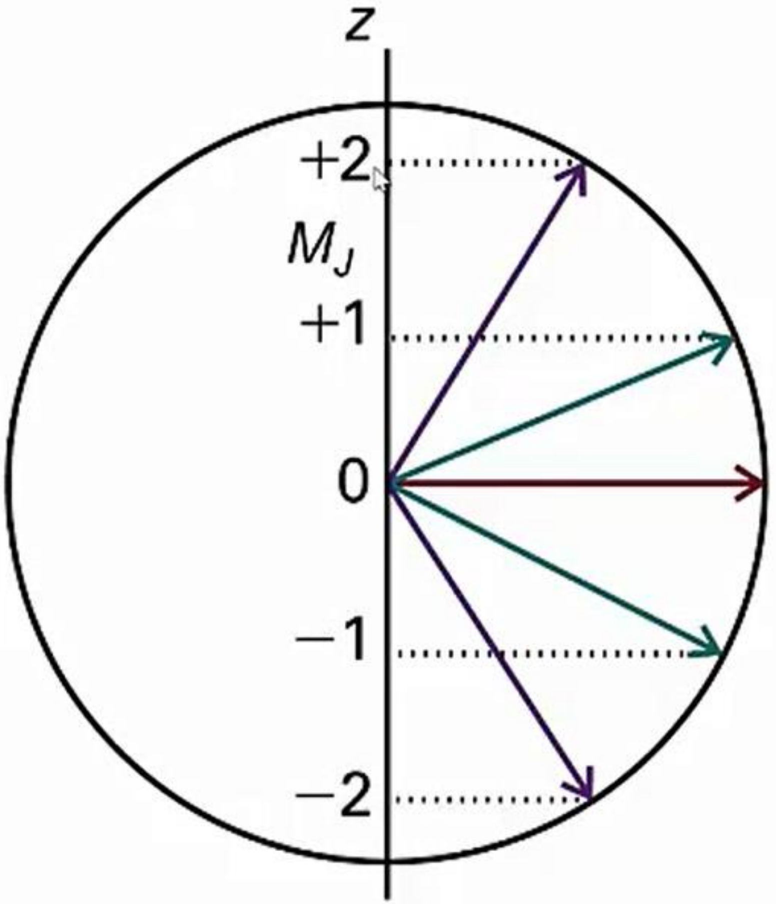


Figure 9-40a
Atkins Physical Chemistry, Eighth Edition

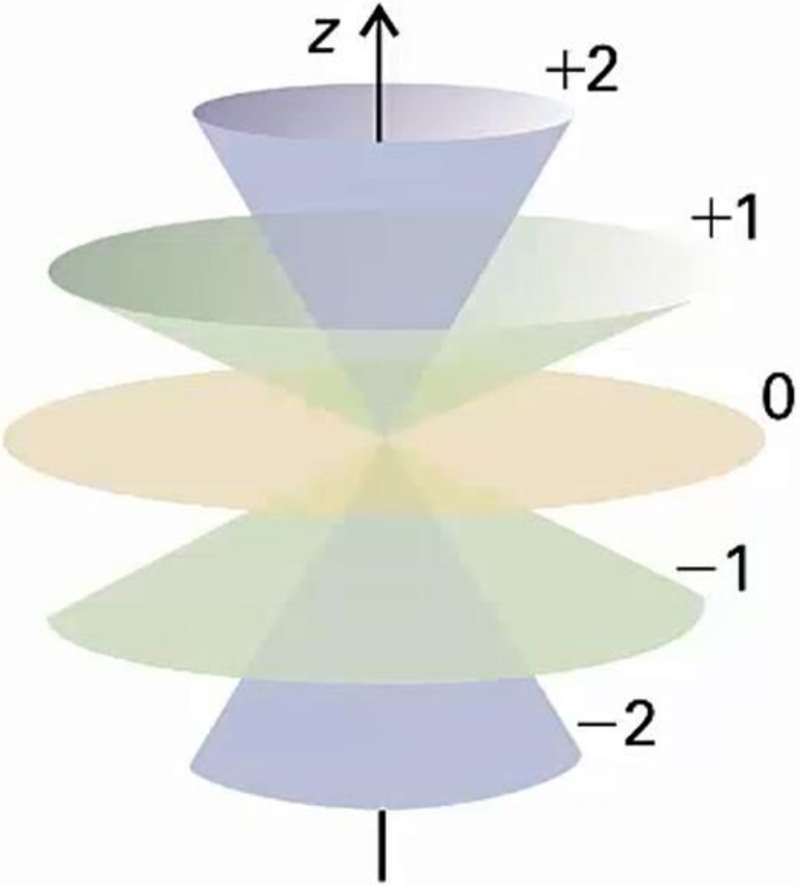


Figure 9-40b
Atkins Physical Chemistry, Eighth Edition

Degeneracy of Rotational Energy Levels

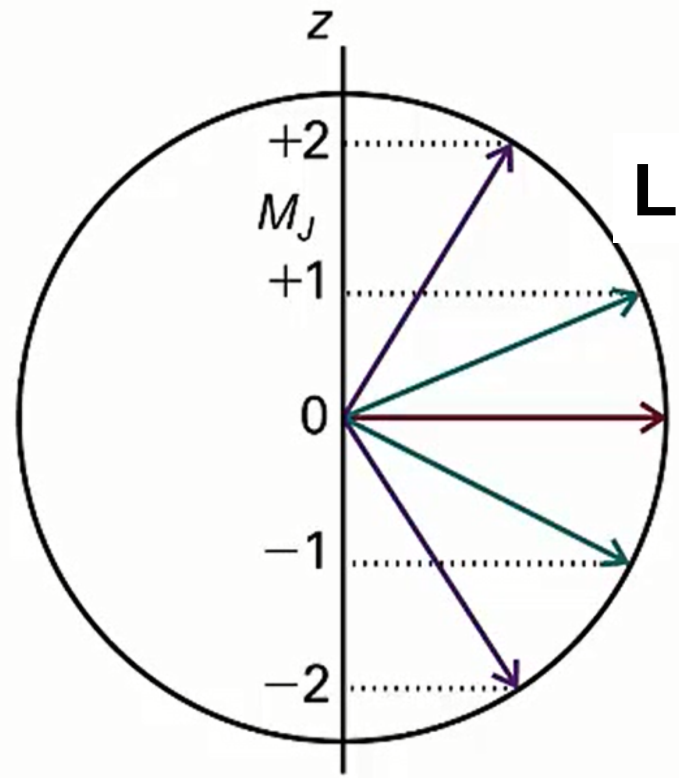


Figure 9-40a
Atkins Physical Chemistry, Eighth Edition
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$$\mathbf{L} = \sqrt{J(J+1)}\,\hbar$$

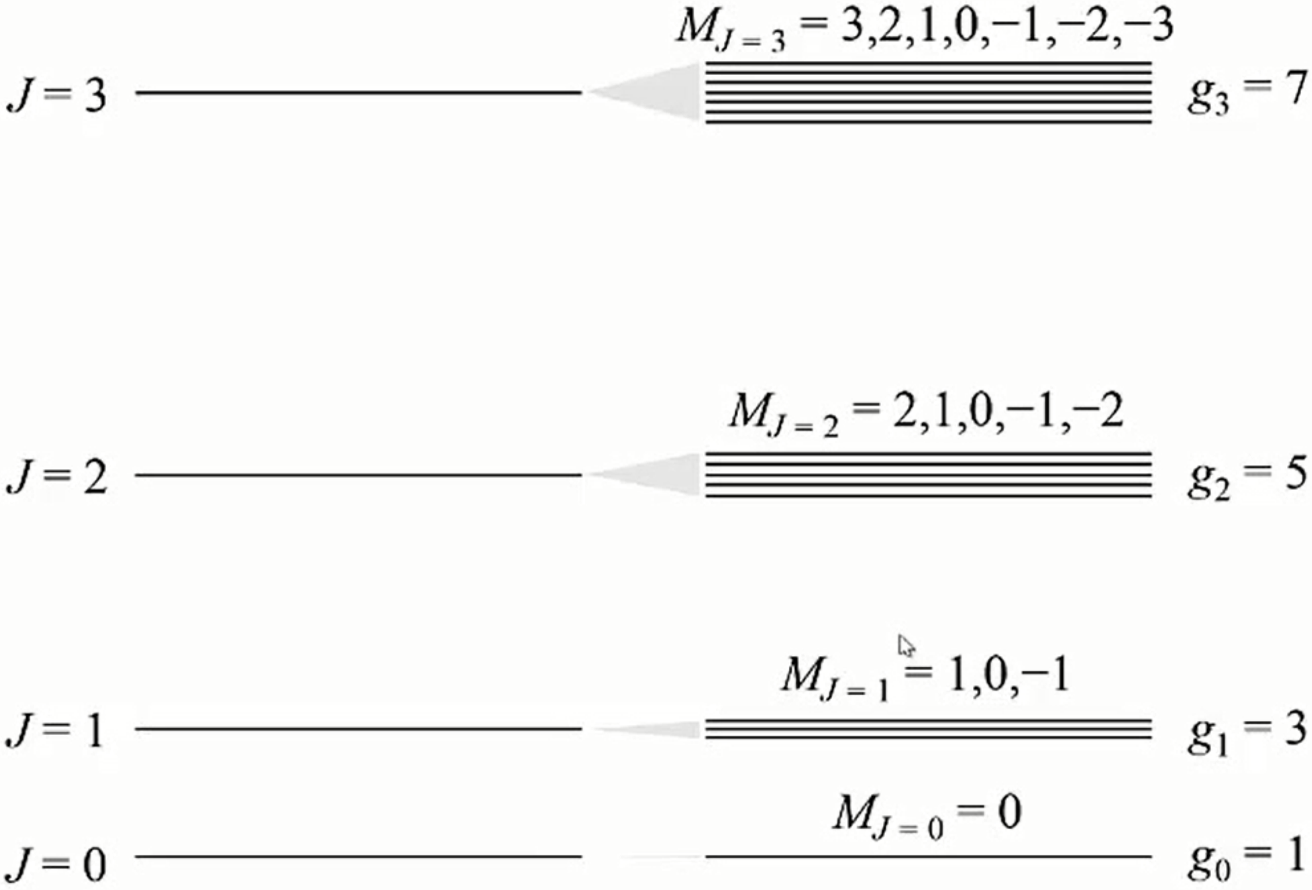
$$\mathbf{L_z} = M_J\hbar, \quad \text{where } M_J = 0, \pm 1, \pm 2, \ldots, \pm J$$

$$J = 0, \quad M_J = 0$$

$$J = 1, \quad M_J = 1, 0, -1$$

$$J = 2, \quad M_J = 2, 1, 0, -1, -2$$

Each rotational energy level is
$(2J + 1)$-fold degenerate



$M_{J=3} = 3,2,1,0,-1,-2,-3$

$J = 3$ $\quad g_3 = 7$

$M_{J=2} = 2,1,0,-1,-2$

$J = 2$ $\quad g_2 = 5$

$M_{J=1} = 1,0,-1$

$J = 1$ $\quad g_1 = 3$

$M_{J=0} = 0$

$J = 0$ $\quad g_0 = 1$

Degeneracy:

$$g_J = 2J + 1$$

Summary

- Rotational energy, E_J, is quantised

$$E_J = \frac{J(J+1)\hbar^2}{2I}, \qquad J = 0,1,2,\ldots$$

- Angular momentum, J, is quantised

$$\mathbf{J} = \sqrt{J(J+1)}\,\hbar$$

- The component of J on an arbitrary axis, J_z, is quantised

$$J_z = M_J\hbar, \qquad \text{where } M_J = 0, \pm 1, \pm 2, \ldots, \pm J$$

- A rotating body may not take up an arbitrary orientation with respect to some specific axis

Intensities of Rotational Lines

- Spectral line intensity is intrinsically controlled by
  1. Transition probability
  2. Population of initial and final states
- Quantum mechanical calculations reveal that the transition probabilities for $\Delta J = \pm 1$ are virtually all equal
- The population of states is given by the Boltzmann Distribution Law

$$\frac{N_{\mathrm{n}}}{N_{\mathrm{m}}} = \frac{g_{\mathrm{n}}}{g_{\mathrm{m}}} \exp\left(-\frac{\Delta E}{kT}\right)$$

Population Distribution

- The number of rotational levels with a particular energy E_J increases with J

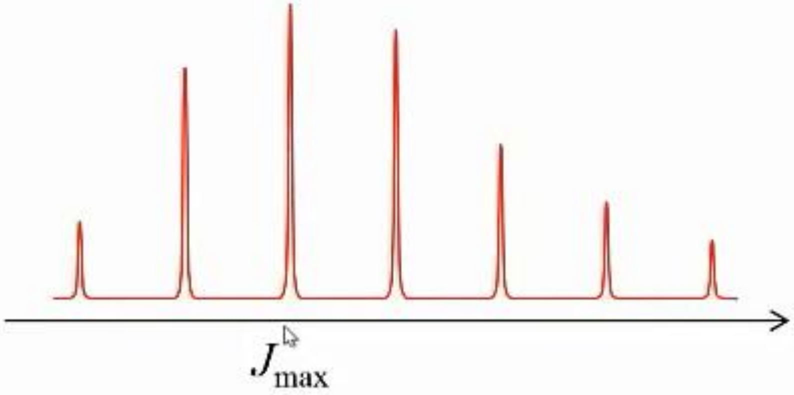
$$\boxed{\text{Degeneracy, } g_J = 2J+1}$$

- With respect to the ground rotational state, $J = 0$,

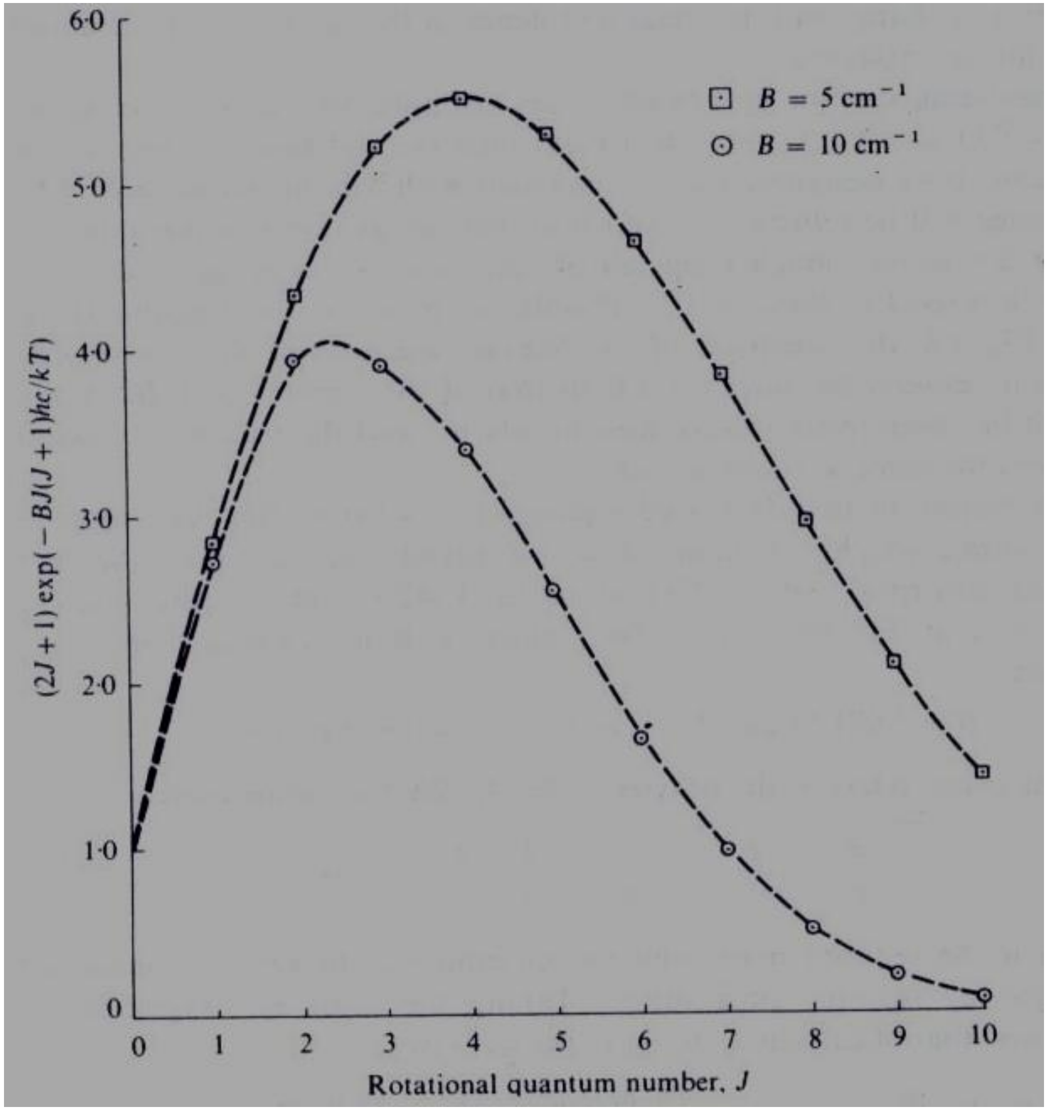
$$\boxed{\frac{N_J}{N_0} = (2J+1)\exp\left(-\frac{J(J+1)hc\tilde{B}}{kT}\right)}$$

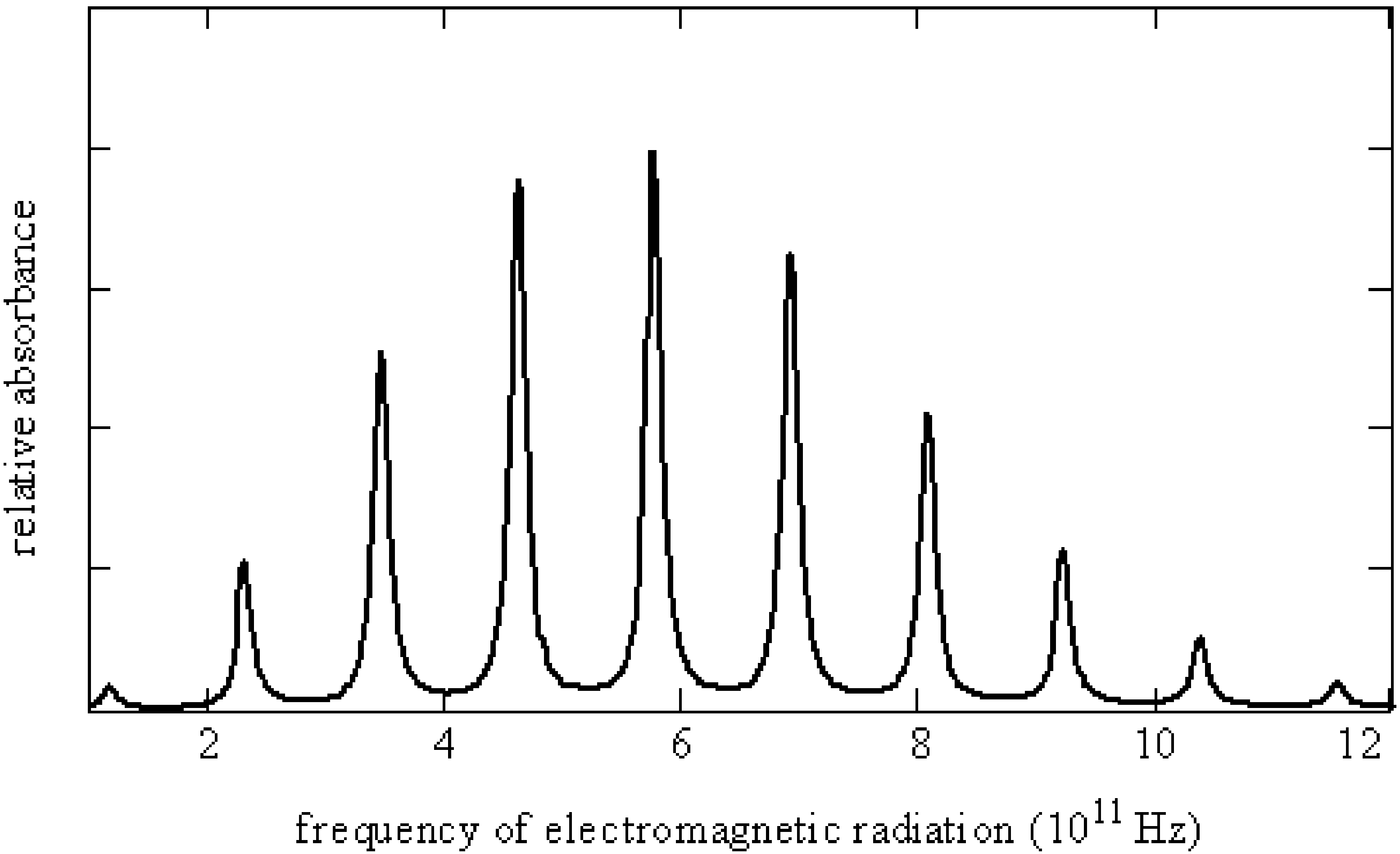
$$\frac{d(N_J/N_0)}{dJ} = 0 \quad \Rightarrow \quad J_{\max} \approx \sqrt{\frac{kT}{2hc\tilde{B}}} - \frac{1}{2}$$

Population Distribution



$$\boxed{J_{\text{max}} \approx \sqrt{\frac{kT}{2hc\tilde{B}}} - \frac{1}{2}}$$



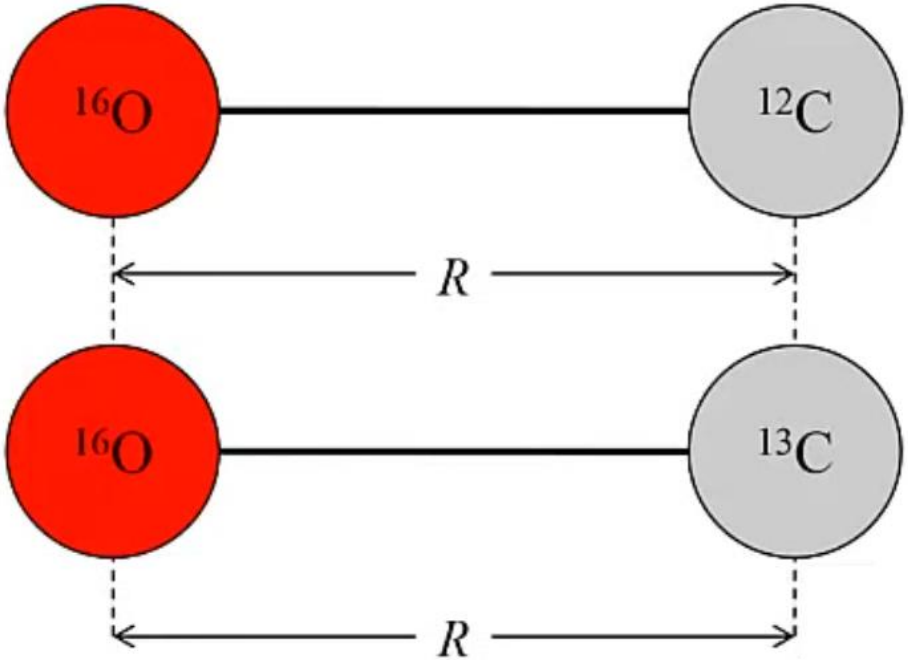

relative absorbance
2
4
6
8
10
12
frequency of electromagnetic radiation (10^{11} Hz)

18.01.2017

Effect of Isotopic Substitution

Isotopic Substitution

- Does $^{13}C^{16}O$ rotate the same as $^{12}C^{16}O$?

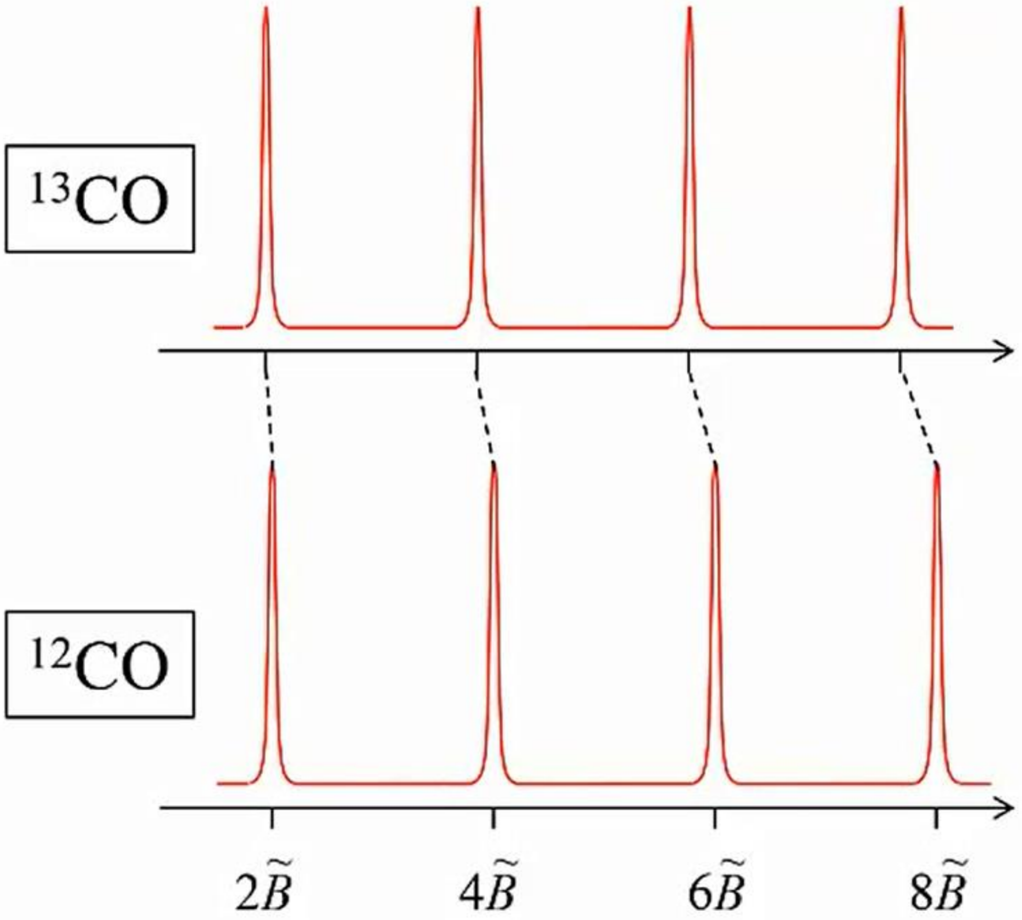


- No significant change in bond length upon isotopic substitution

Effect of Isotope Substitution

- Consider change in atomic mass

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



$$\tilde{B}(^{13}C^{16}O) = 1.83669\ \mathrm{cm}^{-1}$$

$$\tilde{B}(^{12}C^{16}O) = 1.92118\ \mathrm{cm}^{-1}$$

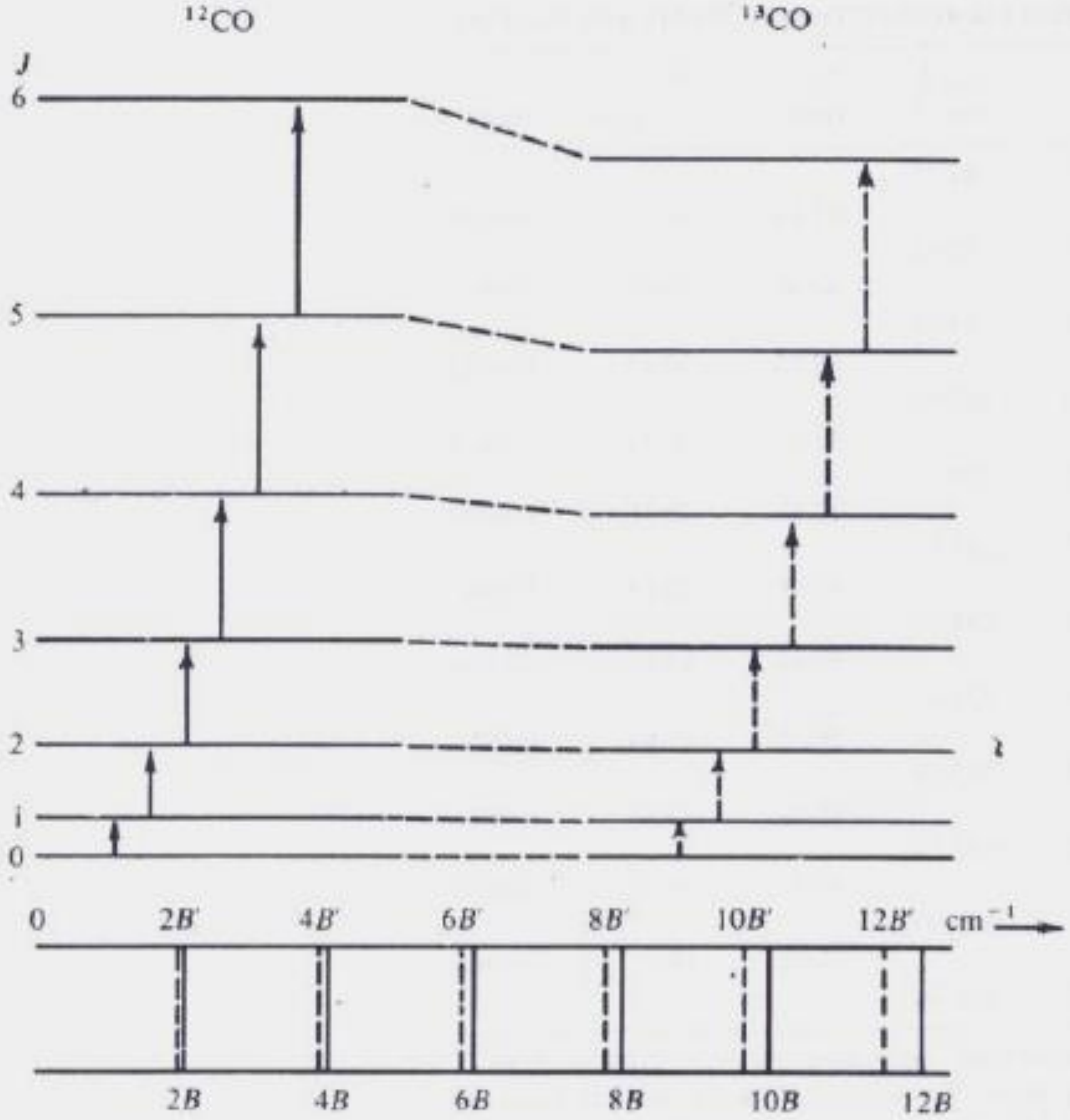
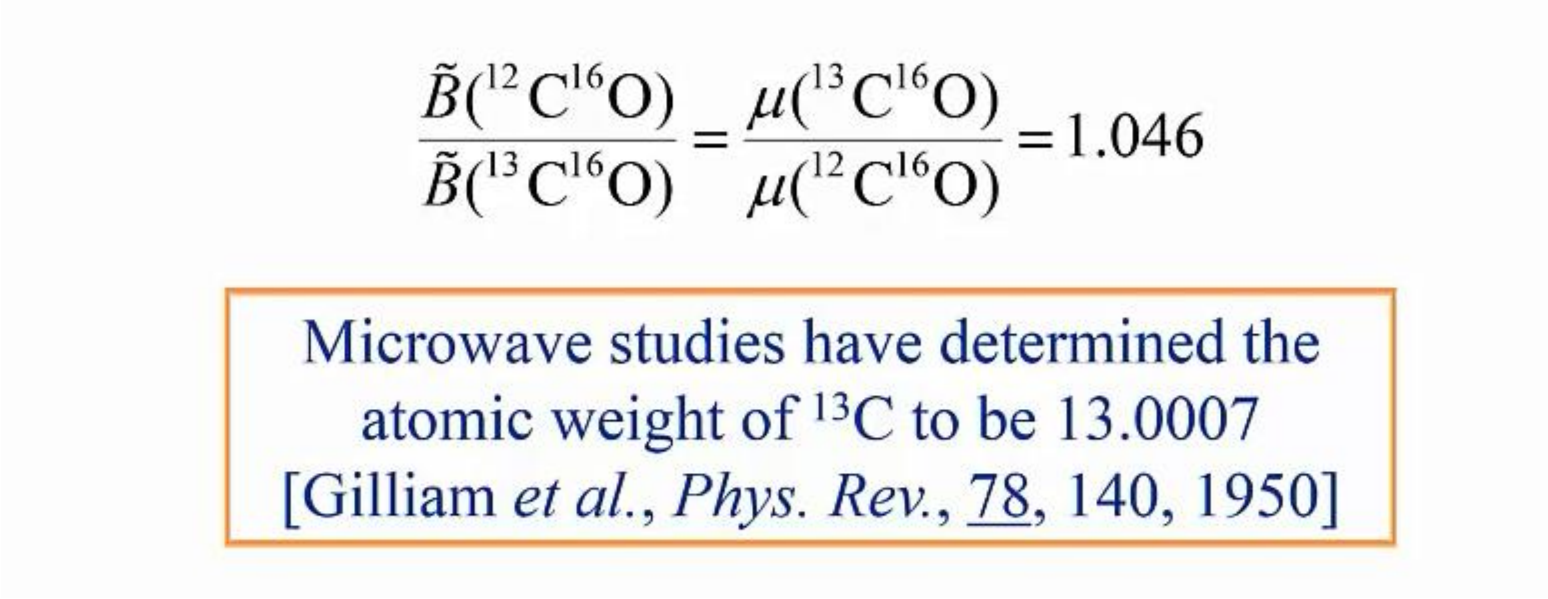


Figure 2.8 The effect of isotopic substitution on the energy levels and hence rotational spectrum of a diatomic molecule such as carbon monoxide.

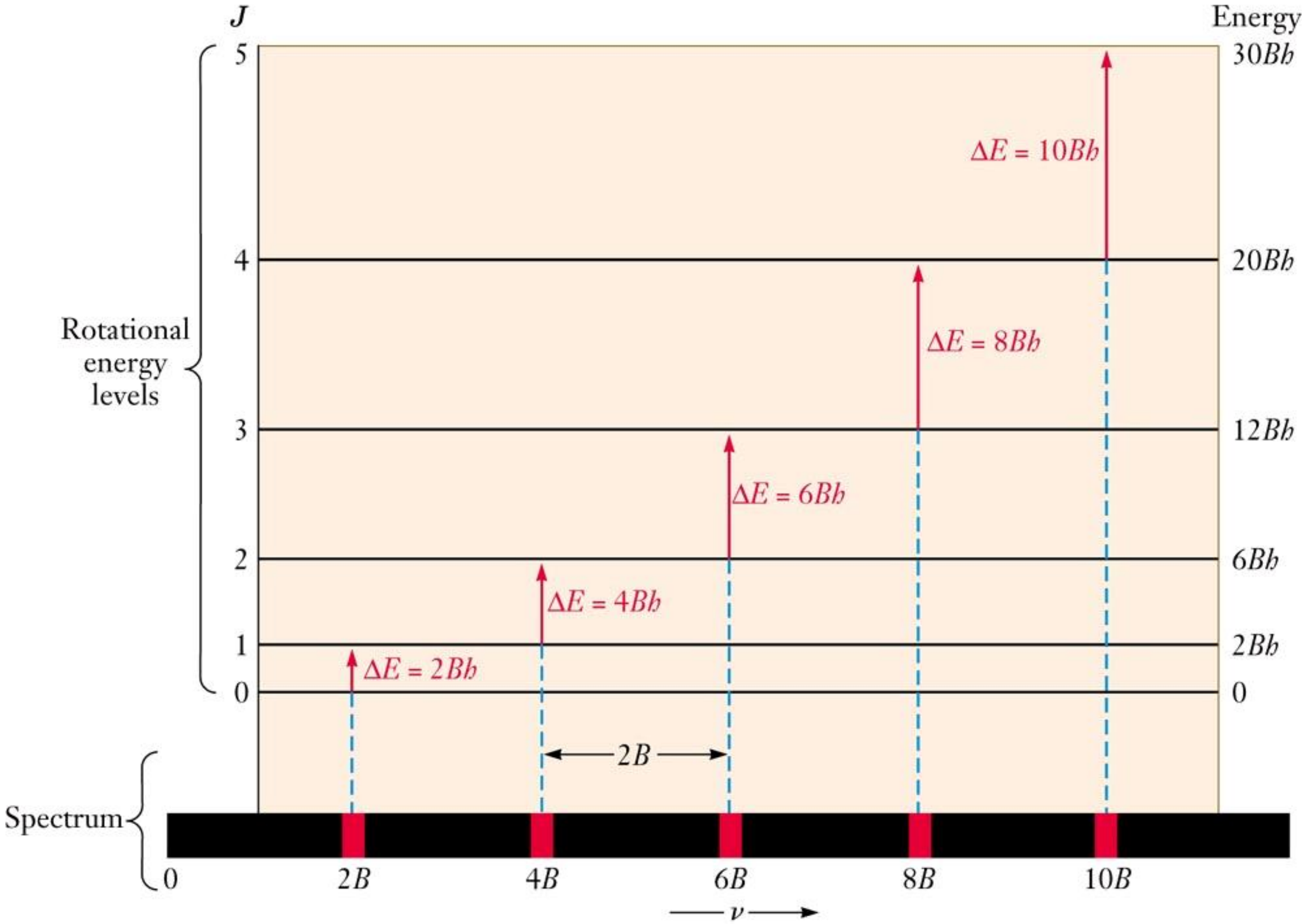
1. Determination of Accurate Atomic weights



$$\frac{\tilde{B}(^{12}\mathrm{C}^{16}\mathrm{O})}{\tilde{B}(^{13}\mathrm{C}^{16}\mathrm{O})} = \frac{\mu(^{13}\mathrm{C}^{16}\mathrm{O})}{\mu(^{12}\mathrm{C}^{16}\mathrm{O})} = 1.046$$

Microwave studies have determined the atomic weight of ^{13}C to be 13.0007 [Gilliam *et al.*, *Phys. Rev.*, 78, 140, 1950]

2. Determination of natural abundance of isotope from the comparison of intensities of spectra.



J
Energy
5
30Bh
ΔE = 10Bh
4
20Bh
ΔE = 8Bh
Rotational energy levels
3
12Bh
ΔE = 6Bh
2
6Bh
ΔE = 4Bh
1
2Bh
ΔE = 2Bh
0
0
2B
Spectrum
0
2B
4B
6B
8B
10B
ν

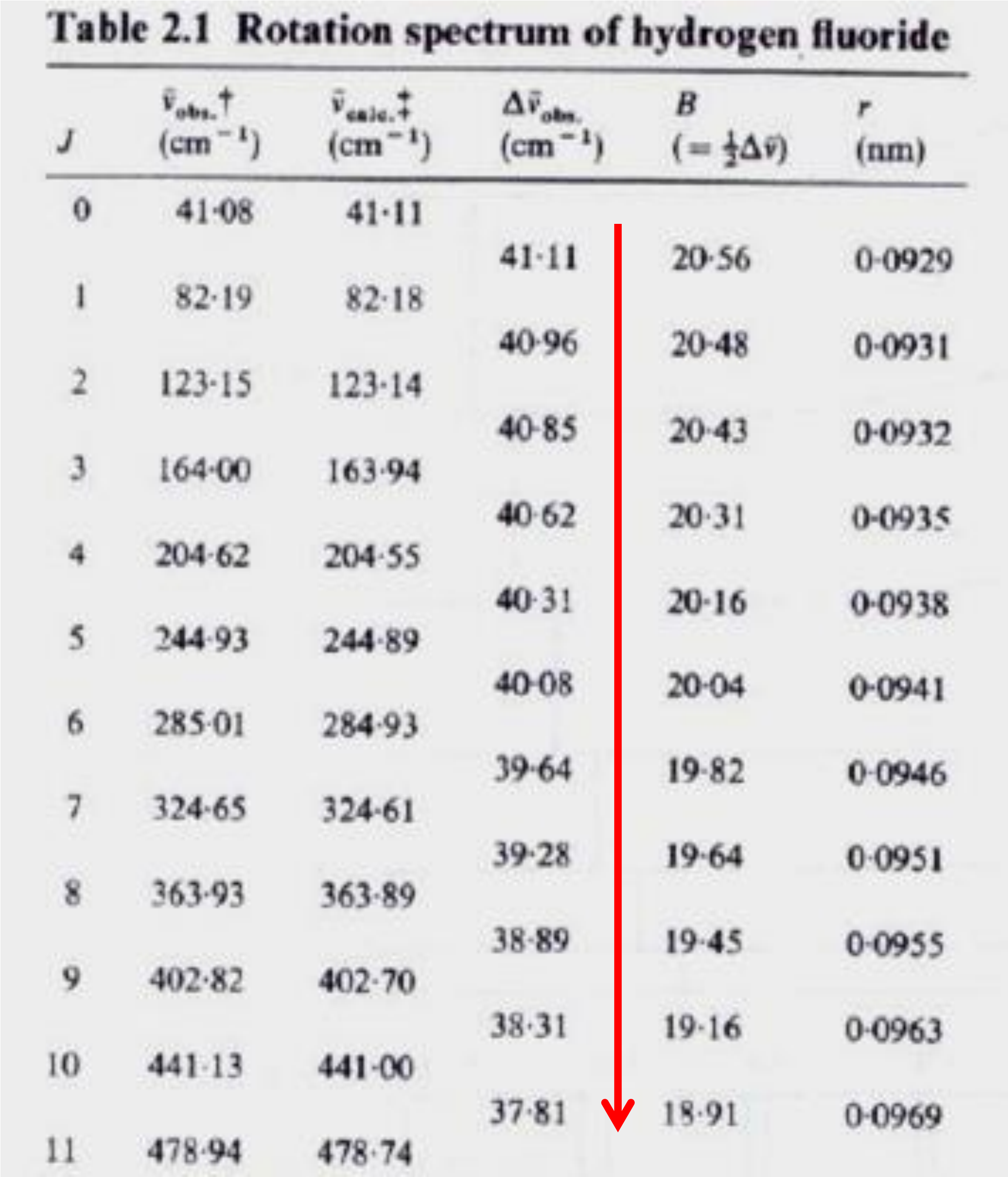


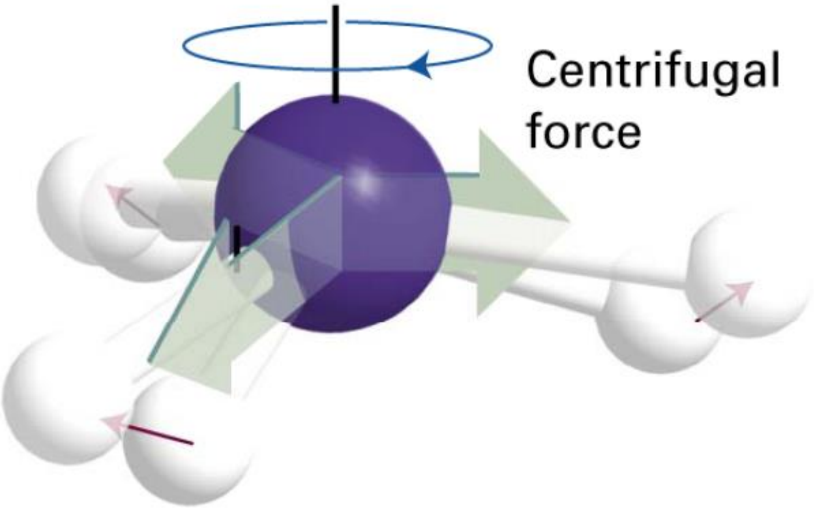
Table 2.1 Rotation spectrum of hydrogen fluoride

J	$\bar{\nu}_{\text{obs.}}$† (cm^{-1})	$\bar{\nu}_{\text{calc.}}$‡ (cm^{-1})	$\Delta\bar{\nu}_{\text{obs.}}$ (cm^{-1})	B $(=\frac{1}{2}\Delta\bar{\nu})$	r (nm)
0	41·08	41·11			
			41·11	20·56	0·0929
1	82·19	82·18			
			40·96	20·48	0·0931
2	123·15	123·14			
			40·85	20·43	0·0932
3	164·00	163·94			
			40·62	20·31	0·0935
4	204·62	204·55			
			40·31	20·16	0·0938
5	244·93	244·89			
			40·08	20·04	0·0941
6	285·01	284·93			
			39·64	19·82	0·0946
7	324·65	324·61			
			39·28	19·64	0·0951
8	363·93	363·89			
			38·89	19·45	0·0955
9	402·82	402·70			
			38·31	19·16	0·0963
10	441·13	441·00			
			37·81	18·91	0·0969
11	478·94	478·74			

The non-rigid rotator

The rigid rotor model holds for, well, rigid rotors.

Molecules, unfortunately, are *not* rigid rotors – their bonds stretch during rotation.



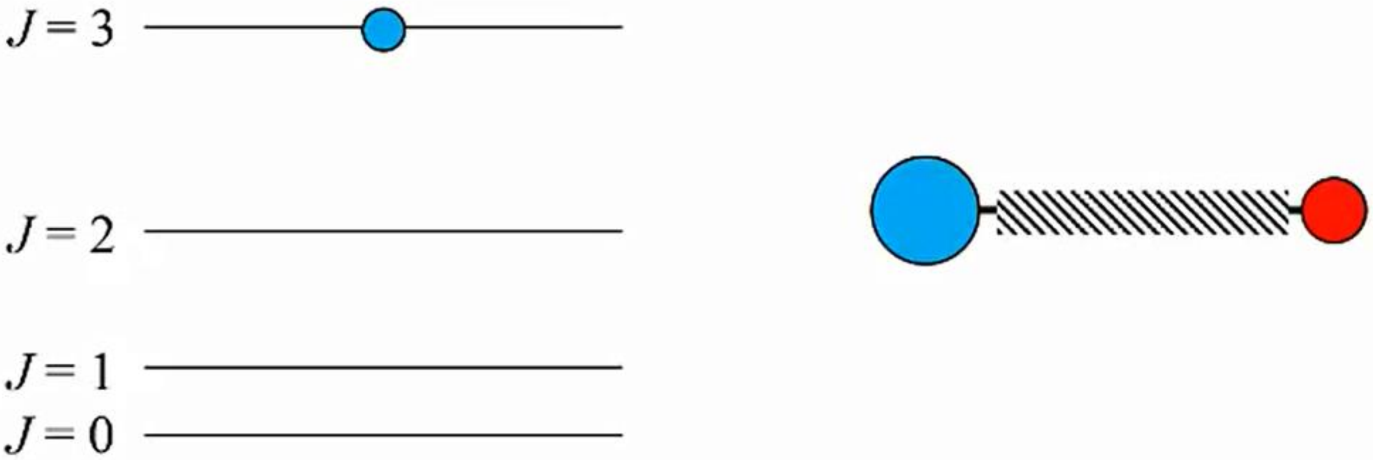
As a result, the various I (and thus rotational constants) *change* with J.

It is more convenient (*i.e.*, easier) to treat centrifugal distortion as a perturbation to the rigid rotor terms.

$$k = 4\pi^2\bar{\omega}^2c^2\mu$$

Non-rigid Rotor

- Chemical bonds are elastic



- The centrifugal force arising from rotation distorts the molecule, stretching the bond slightly
- As the rate of rotation increases,
  - The bond length increases
  - The moment of inertia increases
  - The rotational constant decreases

Improved Model

- Solving the Schrödinger equation gives

$$E_J = \frac{h^2}{8\pi^2 I}J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k}J^2(J+1)^2$$

Joules

$$\tilde{F}(J) = \frac{E_J}{h\tilde{c}} = \tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2$$

cm^{-1}

$$\tilde{B} = \frac{h}{8\pi^2 I\tilde{c}} \quad \text{and} \quad \tilde{D} = \frac{h^3}{32\pi^4 I^2 r^2 k\tilde{c}}$$

centrifugal distortion constant

k: force constant

Simple Harmonic Model

- The simple harmonic oscillator model gives

$$\tilde{\nu} = \frac{1}{2\pi\tilde{c}}\sqrt{\frac{k}{\mu}}$$

- Thus it can be shown that within this approximation

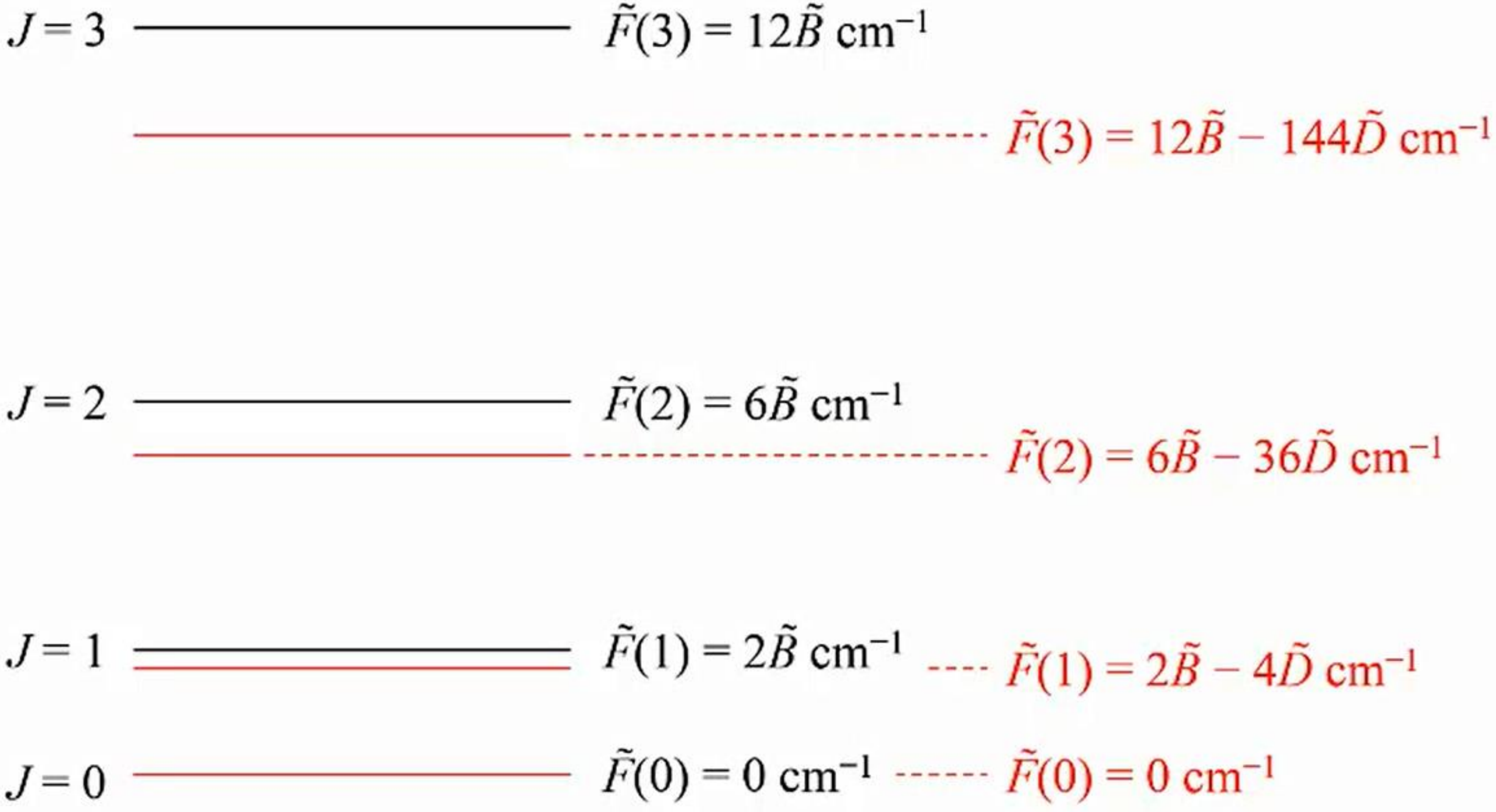
$$\tilde{D} = \frac{4\tilde{B}^3}{\tilde{\nu}^2} \quad \boxed{\text{cm}^{-1}}$$

- Hence from $\tilde{D}$, we can estimate the vibrational frequency of the bond

We will return to this point when we discuss Vibrational Spectroscopy

$$\tilde{F}(J) = \tilde{B}J(J+1)$$

$$\tilde{F}(J) = \tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2$$



$J = 3$ $\tilde{F}(3) = 12\tilde{B}\ \mathrm{cm}^{-1}$

$\tilde{F}(3) = 12\tilde{B} - 144\tilde{D}\ \mathrm{cm}^{-1}$

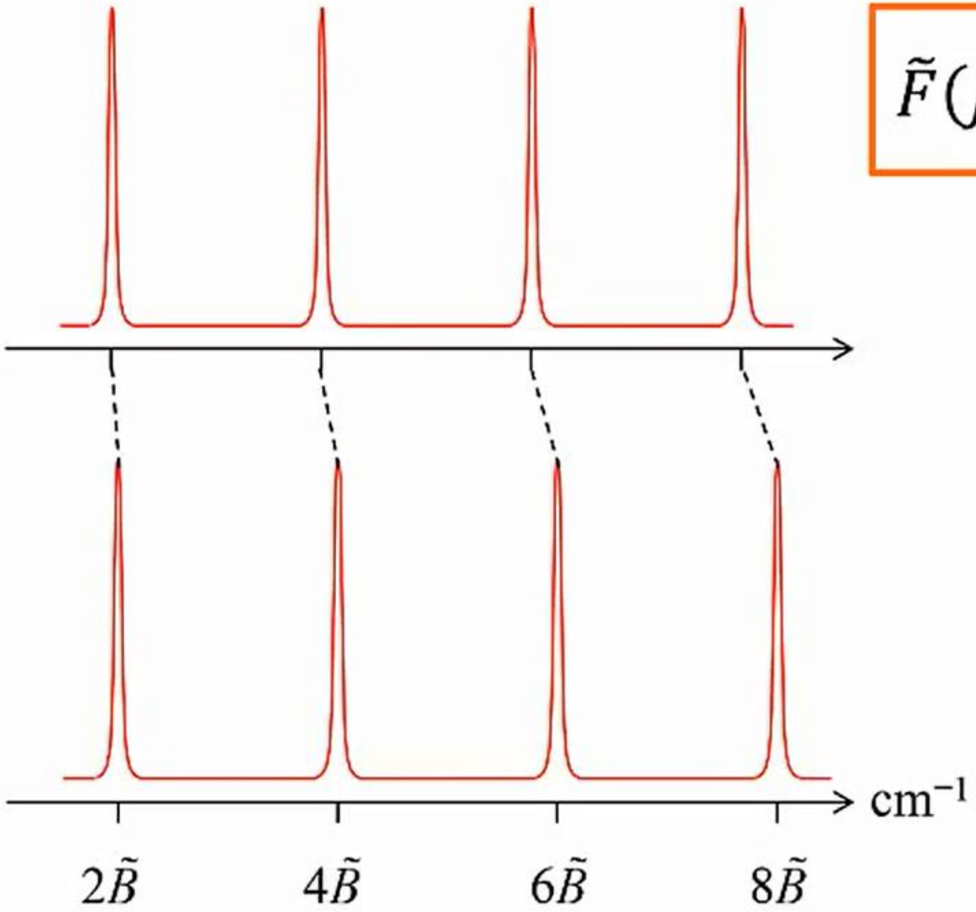
$J = 2$ $\tilde{F}(2) = 6\tilde{B}\ \mathrm{cm}^{-1}$

$\tilde{F}(2) = 6\tilde{B} - 36\tilde{D}\ \mathrm{cm}^{-1}$

$J = 1$ $\tilde{F}(1) = 2\tilde{B}\ \mathrm{cm}^{-1}$ $\tilde{F}(1) = 2\tilde{B} - 4\tilde{D}\ \mathrm{cm}^{-1}$

$J = 0$ $\tilde{F}(0) = 0\ \mathrm{cm}^{-1}$ $\tilde{F}(0) = 0\ \mathrm{cm}^{-1}$

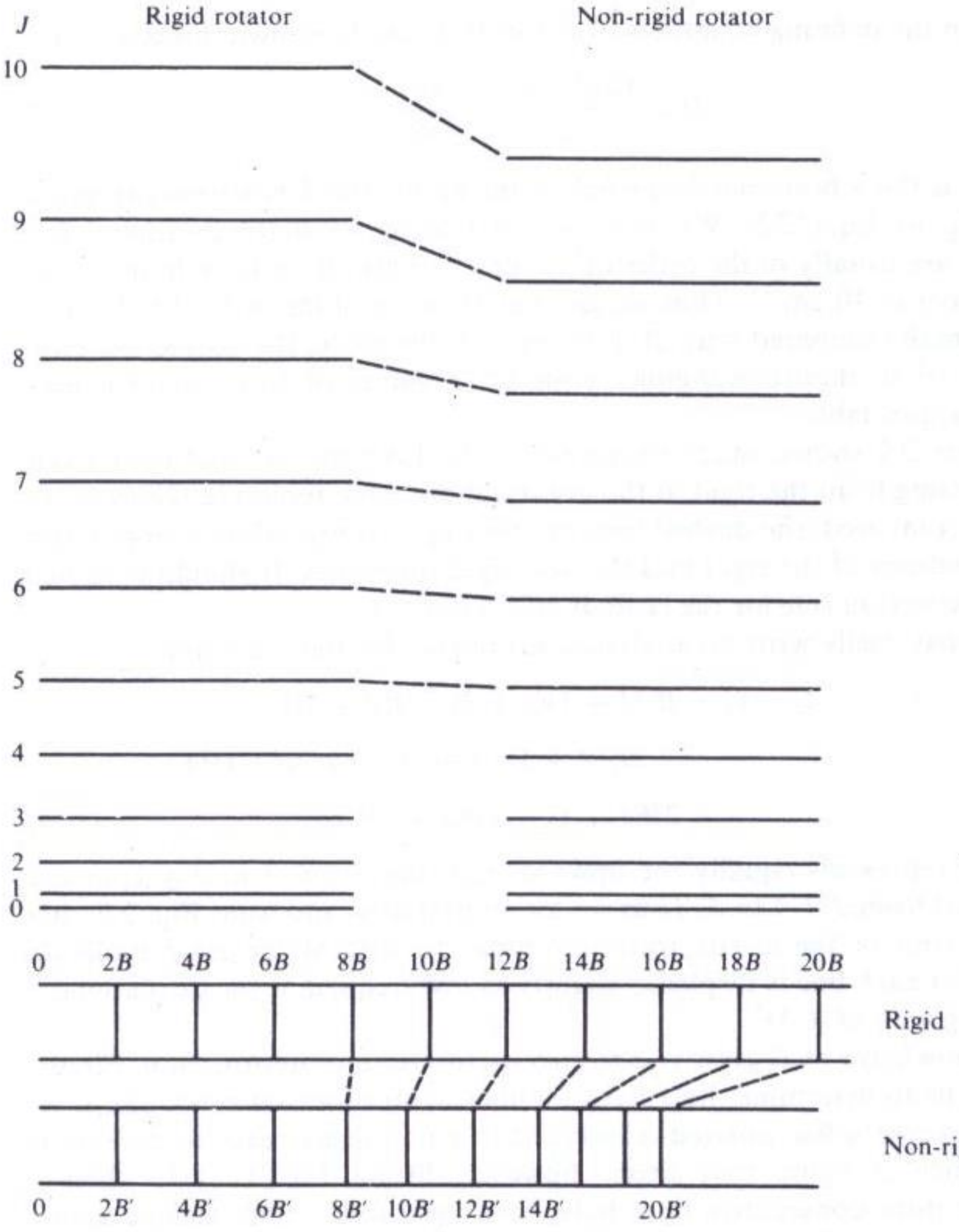
Rotational Transitions for a Non-rigid Rotor



$$\boxed{\tilde{F}(J) = \tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2}$$

$$\begin{aligned}\tilde{\nu} &= \tilde{F}(J+1) - \tilde{F}(J) \\ &= 2\tilde{B}(J+1) - 4\tilde{D}(J+1)^3\end{aligned}$$

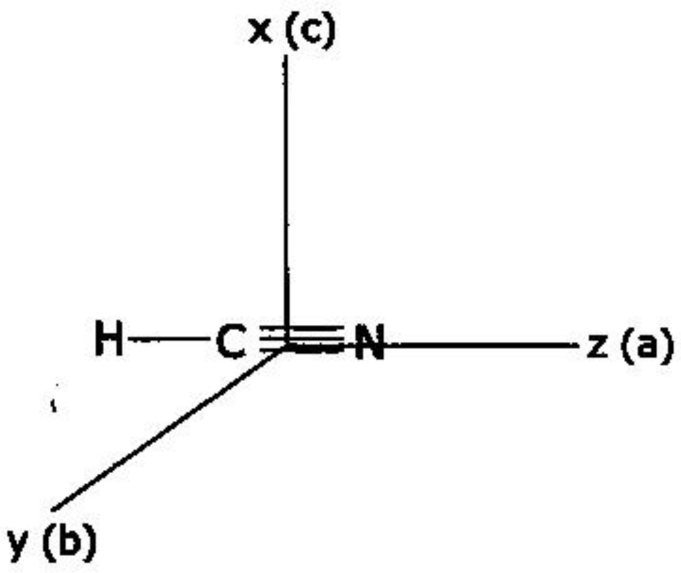
- Spectral line spacing decreases with J as $(J+1)^3$


J
Rigid rotator
Non-rigid rotator
10
9
8
7
6
5
4
3
2
1
0
0
2B
4B
6B
8B
10B
12B
14B
16B
18B
20B
Rigid
Non-rigid
0
2B′
4B′
6B′
8B′
10B′
12B′
14B′
20B′

Summary

- Centrifugal distortion leads to rotational energy levels that are closer together as J increases
    - *C.f.* particle-in-a-box
- Selection rules and intensity pattern do not change
- $\tilde{B}$ is of the order 1–10 cm^{-1}
- $\widetilde{D}$ is of the order 10^{-3} cm^{-1}
- The correction term $\widetilde{D}J^2(J+1)^2$ may be negligible when J is small

Linear Molecules



Other examples:

- HCl
- CO_2
- H–C≡C–H
- H–C≡C–C≡C–C≡C–H
- LiF

$$I_C = I_B = I\ ,\ I_A = 0$$

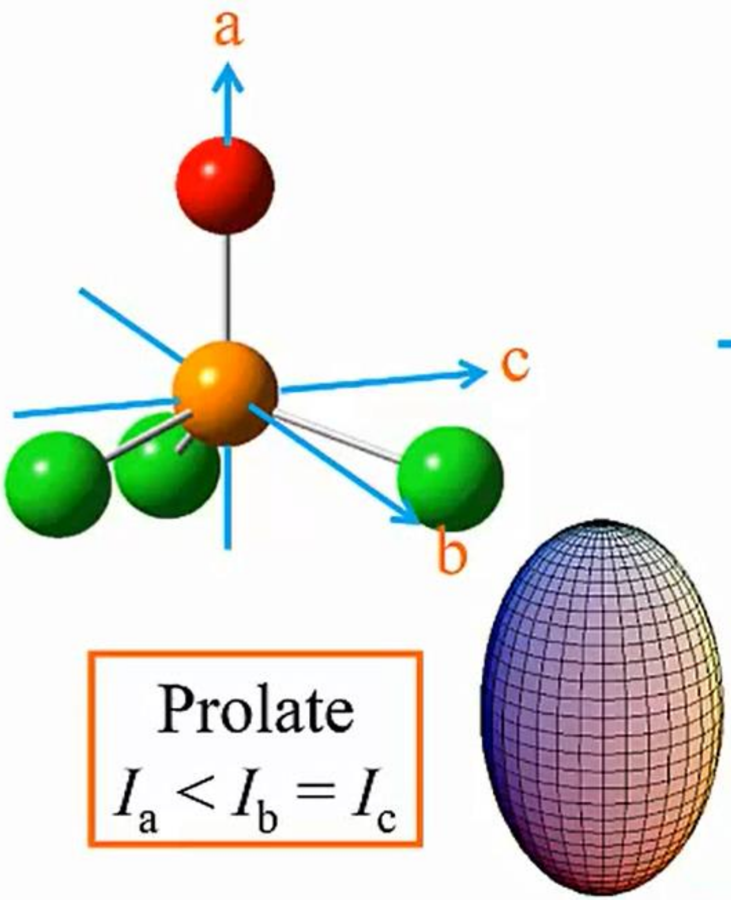
Linear molecules

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

(3) Symmetric Top Molecules

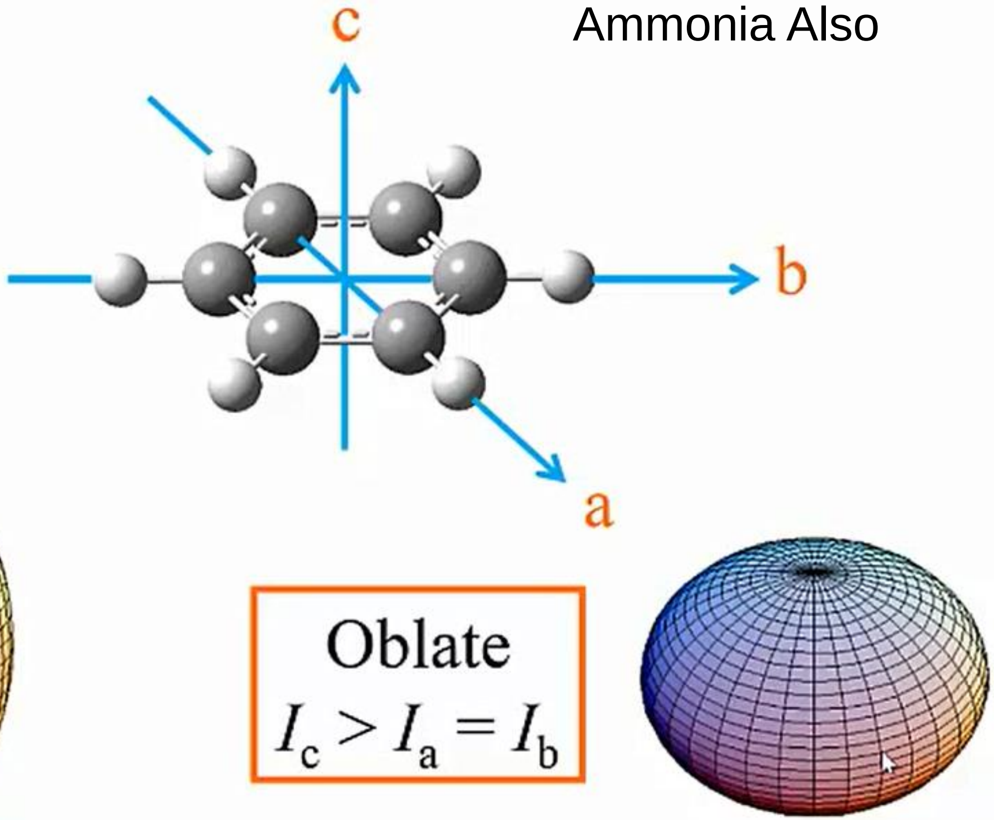
$I_a < I_b = I_c$ (prolate)
$I_a = I_b < I_c$ (oblate)

- Permanent dipole moment, $\mu \neq 0$ and so rotational transitions are observed



Prolate
$I_a < I_b = I_c$

Ammonia Also



Oblate
$I_c > I_a = I_b$

Rigid Symmetric Top (Prolate)

- Solving the Schrödinger equation gives

$$\tilde{F}(J,K) = \frac{E_{J,K}}{h\tilde{c}} = \tilde{B}J(J+1) + \left(\tilde{A} - \tilde{B}\right)K^2 \quad \boxed{\mathrm{cm}^{-1}}$$

$$\tilde{B} = \frac{h}{8\pi^2 I_b \tilde{c}}, \tilde{A} = \frac{h}{8\pi^2 I_a \tilde{c}} \text{ (prolate)}$$

- $J = 0, 1, 2, \ldots$
- $K = 0, \pm 1, \pm 2, \ldots \pm J$ are the set of possible quantum numbers from the projection of the angular momentum on the a axis (prolate)

Rigid Symmetric Top (Oblate)

- Solving the Schrödinger equation gives

$$\tilde{F}(J,K) = \frac{E_{J,K}}{h\tilde{c}} = \tilde{B}J(J+1) + (\tilde{C} - \tilde{B})K^2 \qquad \boxed{\text{cm}^{-1}}$$

$$\tilde{B} = \frac{h}{8\pi^2 I_b \tilde{c}}, \quad \tilde{C} = \frac{h}{8\pi^2 I_c \tilde{c}}$$

oblate

- $J = 0, 1, 2, \ldots$

- $K = 0, \pm 1, \pm 2, \ldots \pm J$ are the set of possible quantum numbers from the projection of the angular momentum on the c axis (oblate)

Physical Significance of K

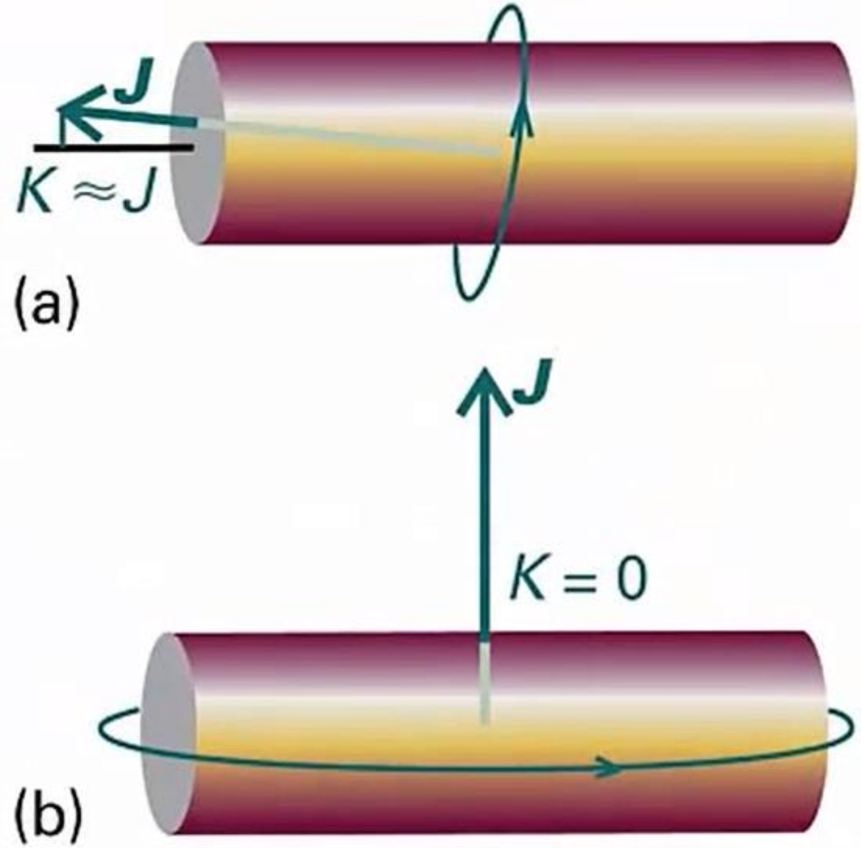


Figure 13-13
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

Picture Taken from Hollas

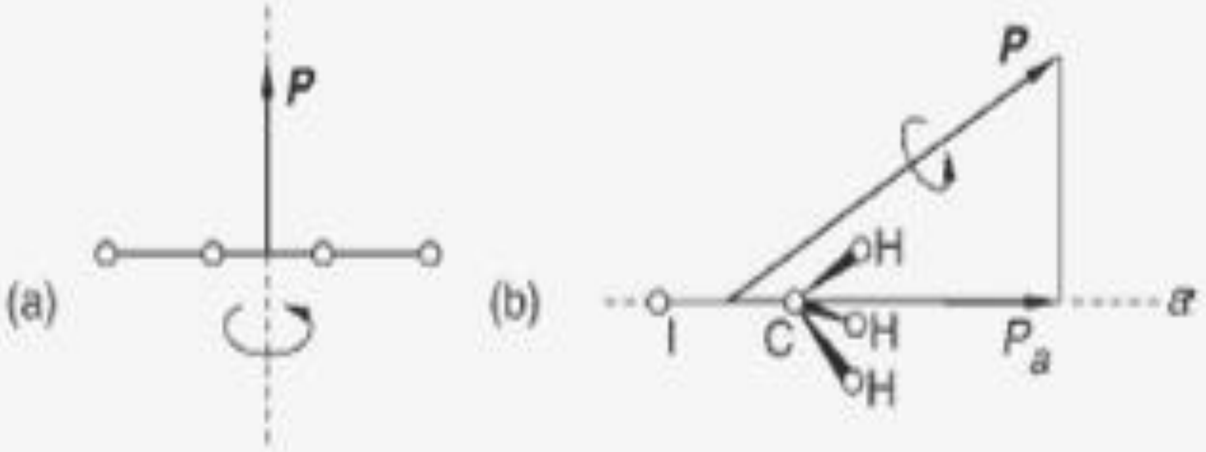


Figure 5.5 The rotational angular momentum vector *P* for (a) a linear molecule and (b) the prolate symmetric rotor CH$_3$I where P_a is the component along the *a* axis

Here, P is equivalent to L (total angular momentum vector)

P_a is considered to be La = Kħ

Quantum Numbers, J, K, M_J

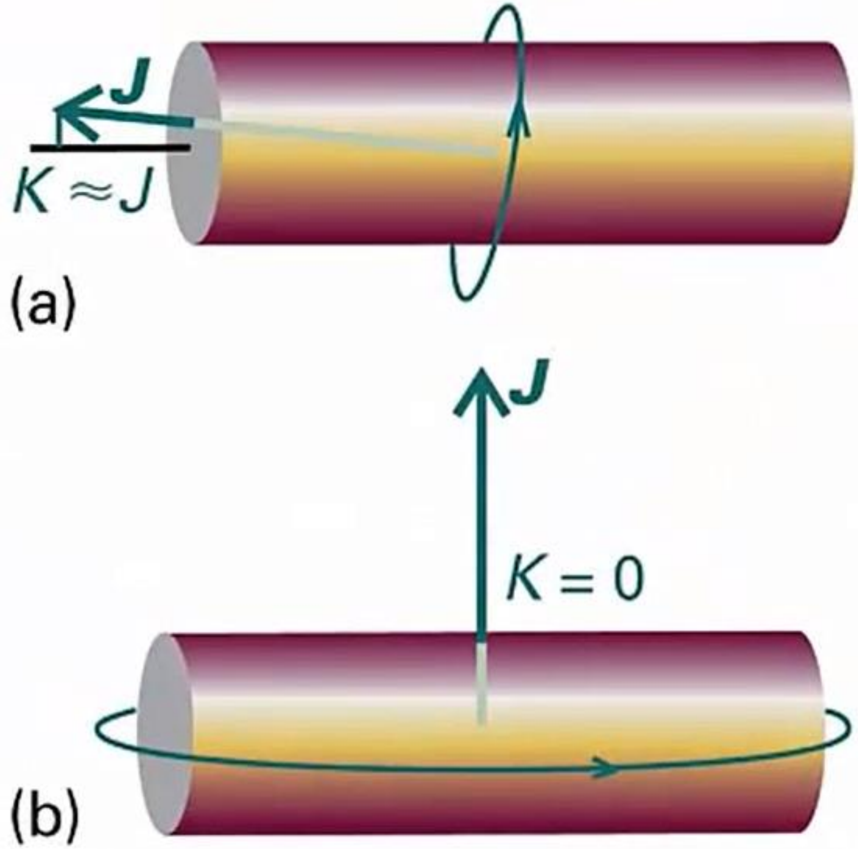
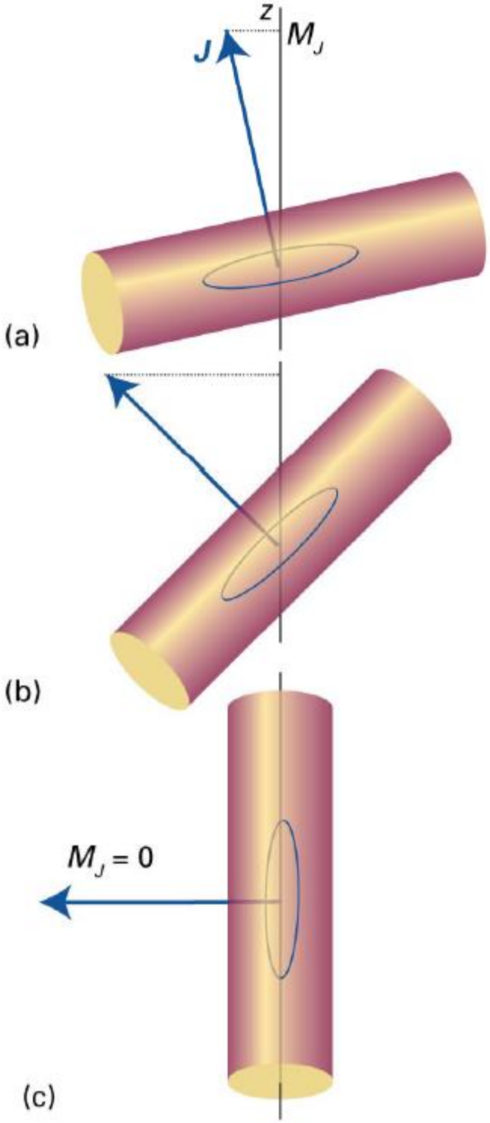


Figure 13-13
Atkins Physical Chemistry, Eighth Edition

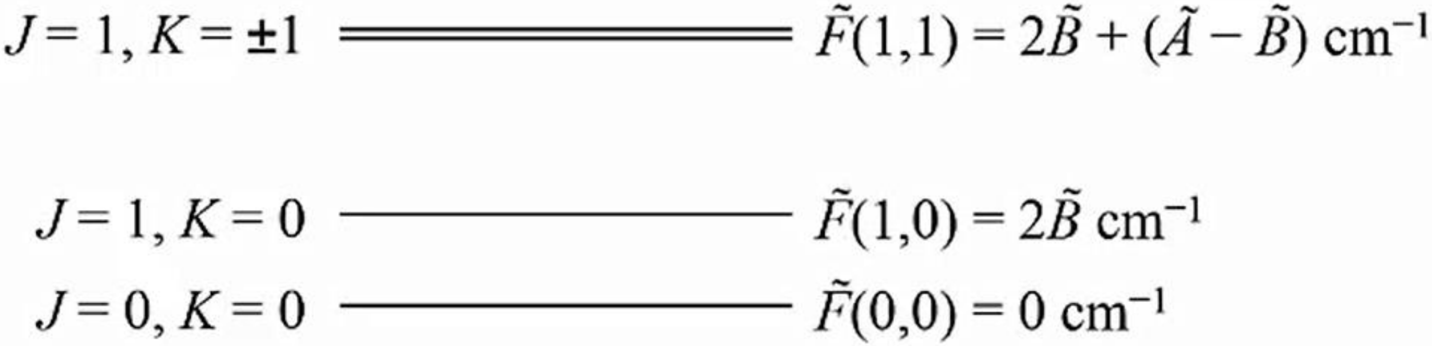


Rotational Energy Level Diagram

$$\tilde{F}(J,K) = \tilde{B}J(J+1) + \left(\tilde{A} - \tilde{B}\right)K^2$$

where $J = 0, 1, 2, \ldots$

$K = 0, \pm 1 \pm 2, \ldots, \pm J$



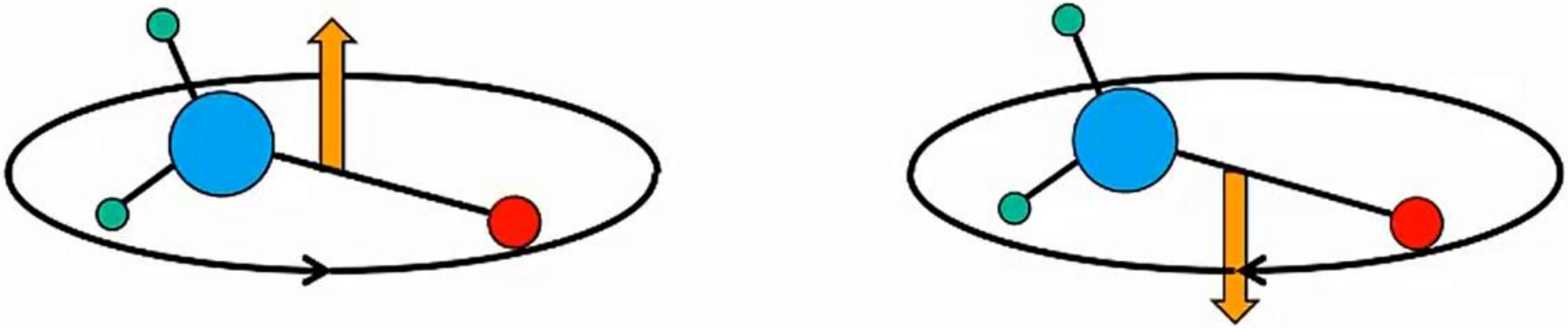
$J = 1, K = \pm 1$ — $\tilde{F}(1,1) = 2\tilde{B} + (\tilde{A} - \tilde{B})\ \text{cm}^{-1}$

$J = 1, K = 0$ — $\tilde{F}(1,0) = 2\tilde{B}\ \text{cm}^{-1}$

$J = 0, K = 0$ — $\tilde{F}(0,0) = 0\ \text{cm}^{-1}$

Sign of *K* Quantum Number

- Opposite signs of *K* correspond to the opposite senses of rotation



Degeneracy of rotational levels:

$$g_{J,K} = 2J + 1 \text{ for } K = 0$$

$$g_{J,K} = 2(2J + 1) \text{ for } K \neq 0$$

- All levels with $K > 0$ are doubly degenerate

Rotational Spectrum of Symmetric Tops

$$\boxed{\tilde{F}(J,K) = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2}$$

- The selection rules are

$$\boxed{\Delta J = \pm 1, \qquad \Delta K = 0}$$

- Thus for the $J \longrightarrow J + 1$ transition

$$\boxed{\begin{aligned} \tilde{\nu} &= \tilde{F}(J+1,K) - \tilde{F}(J,K) \\ &= 2\tilde{B}(J+1) \end{aligned}}$$

- The spectrum is independent of K and similar to that of a linear molecule

Energy Levels and Selection Rule for Prolate Symmetric Top Molecules

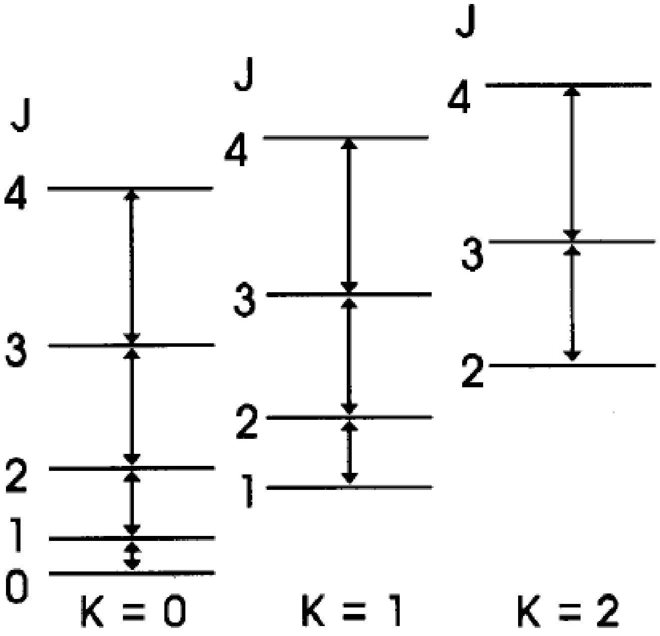
Selection rules and rotational spectra for symmetric tops

$\Delta J=+/-1$

$\Delta M=0, +/- 1$

$\Delta K=0$

The transitions are confined to lie within a K-stack



The allowed electric dipole transitions of a prolate symmetric top.

Spectra of Symmetric tops

	prolate	**oblate**
Terms:	$F_{J,K} = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2$	$F_{J,K} = \tilde{B}J(J+1) + (\tilde{C} - \tilde{B})K^2$

Allowed transitions:

$$\tilde{\nu} = F_{J+1,K} - F_{J,K}$$

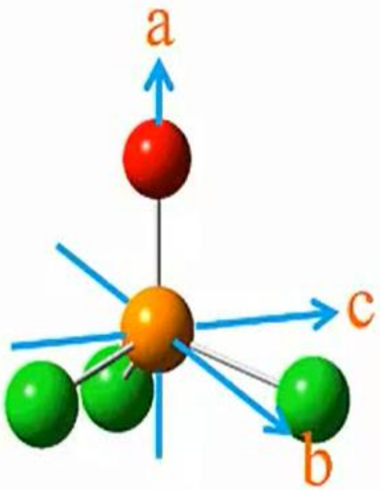
$$\boxed{i.e., \quad \tilde{\nu} = 2\tilde{B}(J+1)}$$

Within the rigid rotor approximation spectra of prolate & oblate tops are the same as for linear molecules (and indeed spherical tops):

***i.e.*, Equally spaced lines with separation =** $2\tilde{B}$

We thus obtain no information on the unique axis (*a* for prolate, *c* for oblate) *i.e.*, nothing about the other rotational constants.

- Only I_b ($= I_\mathrm{c}$) can be obtained from the rotational spectrum

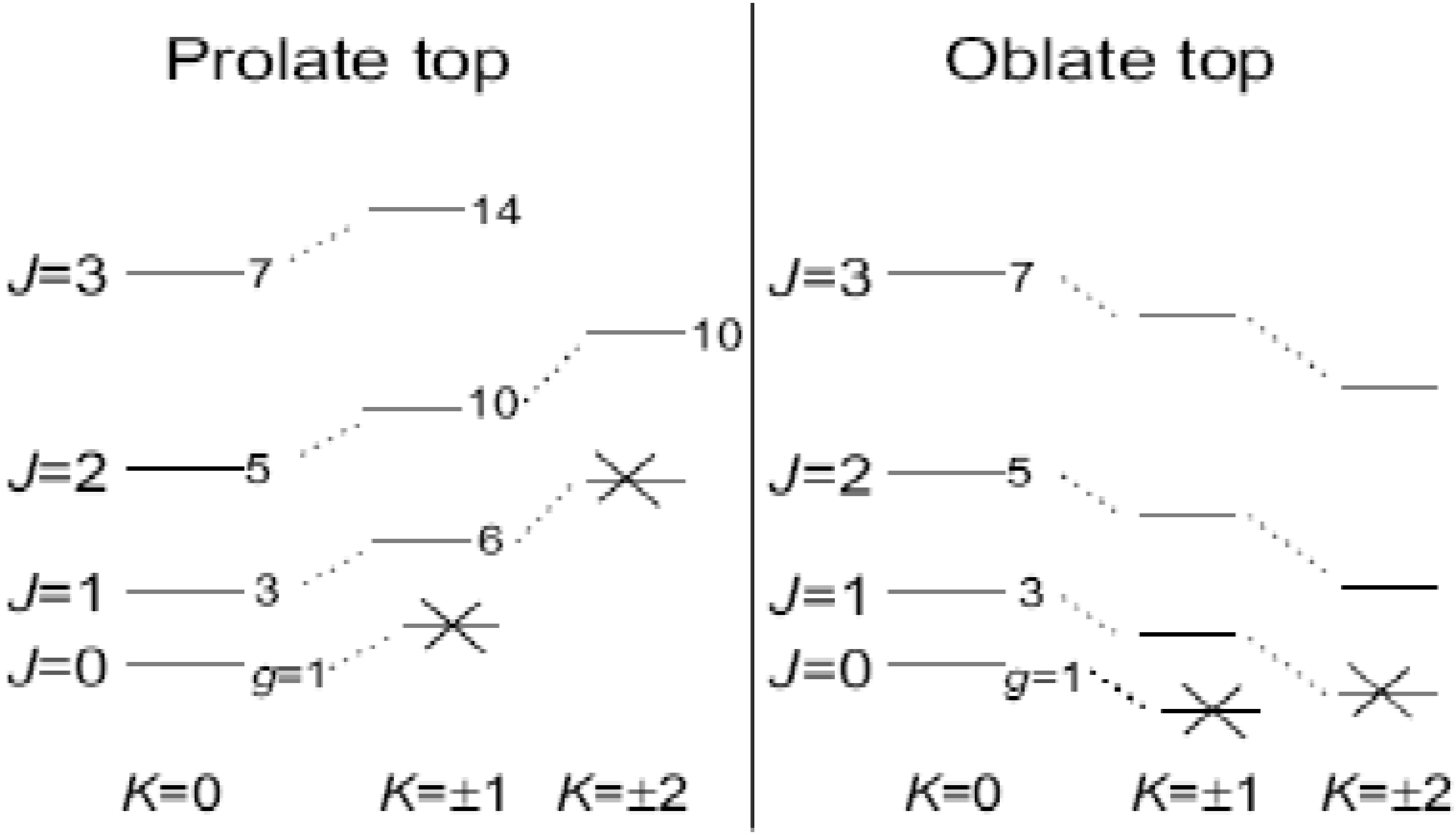


- Value of $\tilde{A}$ is not obtainable from the rotational spectrum
  - The electric dipole lies parallel to this axis, hence rotation about this axis will not be excited by interaction with electromagnetic radiation

Linear *vs.* Symmetric Rotors

- Ignoring centrifugal distortion

	Linear Rotors	**Symmetric Rotors**
Moments of Inertia	$I_a = 0, I_b = I_c$	$I_a < I_b = I_c$ (prolate)
Energy Levels	$F(J) = \tilde{B}J(J+1)$	$F(J,K) = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})\mathrm{K}^2$
Quantum Numbers	$J = 0, 1, 2, \ldots$	$J = 0, 1, 2, \ldots$ $K = 0, \pm1, \pm2, \ldots, \pm J$
Selection Rules	$\Delta J = \pm1$	$\Delta J = \pm1$ $\Delta K = 0$
Separation between levels	$2\tilde{B}\,(J+1)$	
Spacing between spectral lines	$2\tilde{B}$	

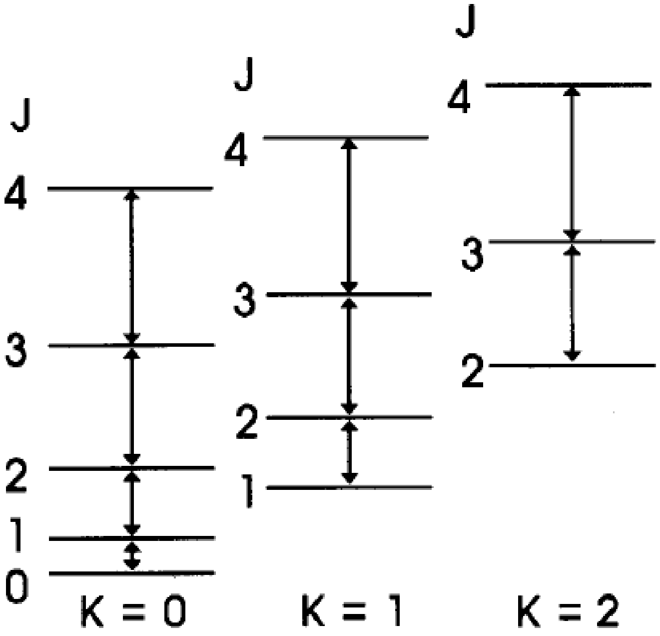


Since the energy is independent of the sign of K, levels with the same absolute magnitude of K coincide, so that all levels for which K is greater than zero are doubly degenerate, and there are only J + 1 distinct energy values for each possible value of J. For each particular value of K, there is an infinite series of levels with different values of J. These are identical in spacing with the linear molecule levels except that the series must start with J = K rather than J = 0.

Selection rules and rotational spectra for symmetric tops

$\Delta J = +/-1$
$\Delta M = 0, +/- 1$
$\Delta K = 0$

The transitions are confined to lie within a K-stack



The allowed electric dipole transitions of a prolate symmetric top.

Effect of Centrifugal Distortion on Spectra for Prolate Symmetric top Molecules:

$$\begin{aligned}\nu_{J+1,K\leftarrow J,K} &= F(J+1, K) - F(J, K)\\ &= 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2.\end{aligned}$$

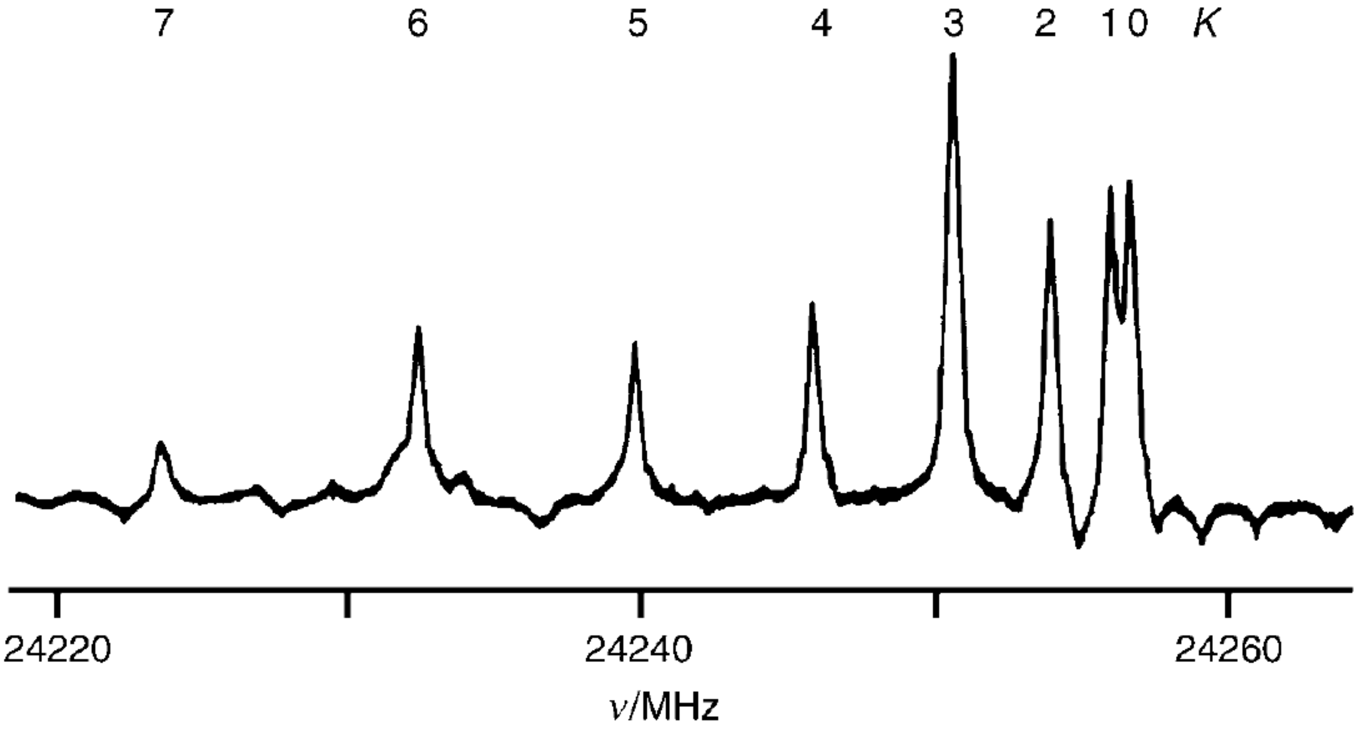
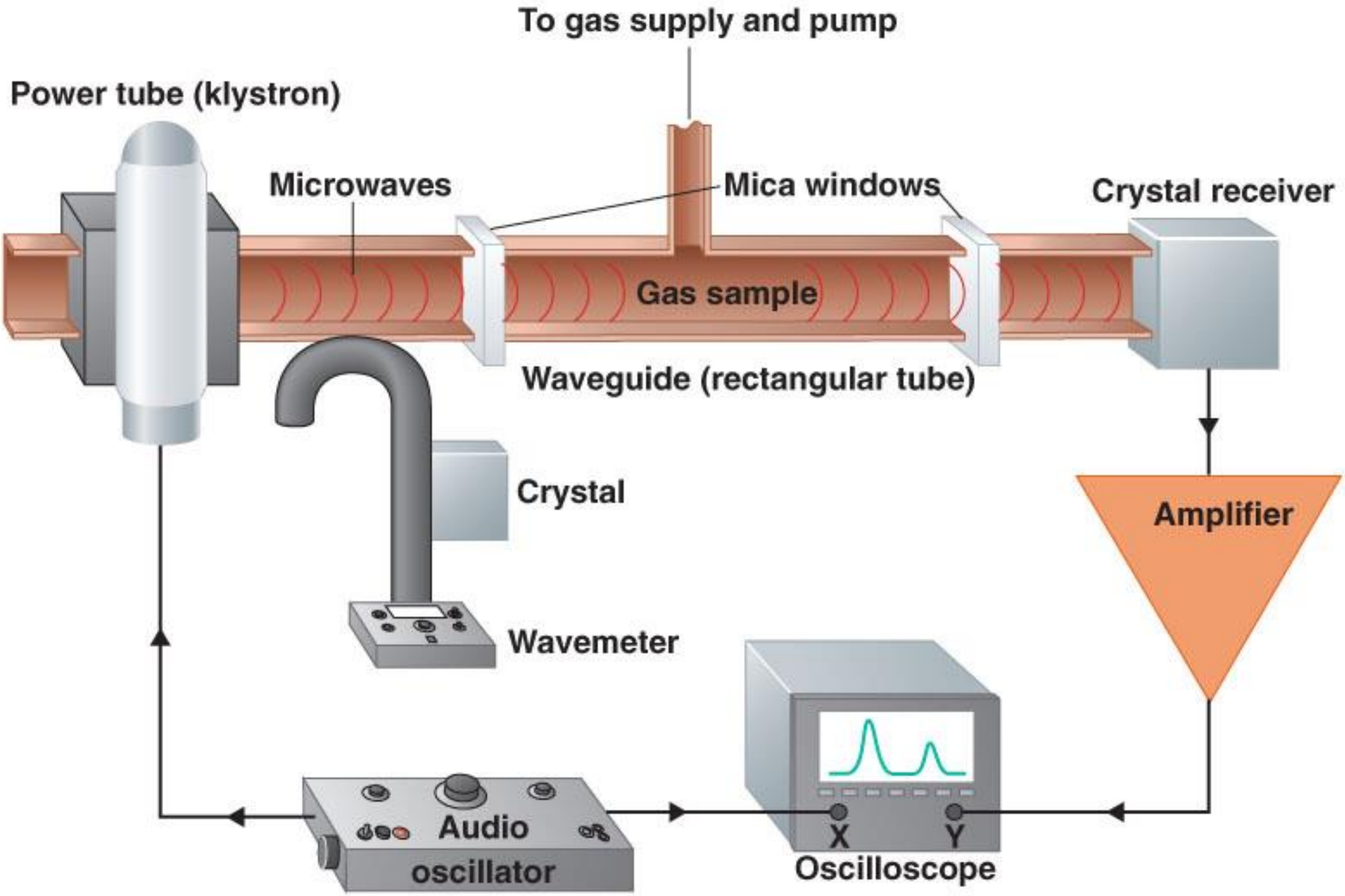


Figure 5.7 Eight components, with $K = 0$ to 7 and separated by centrifugal distortion, of the $J = 8 - 7$ microwave transition of SiH_3NCS

Microwave Instrument



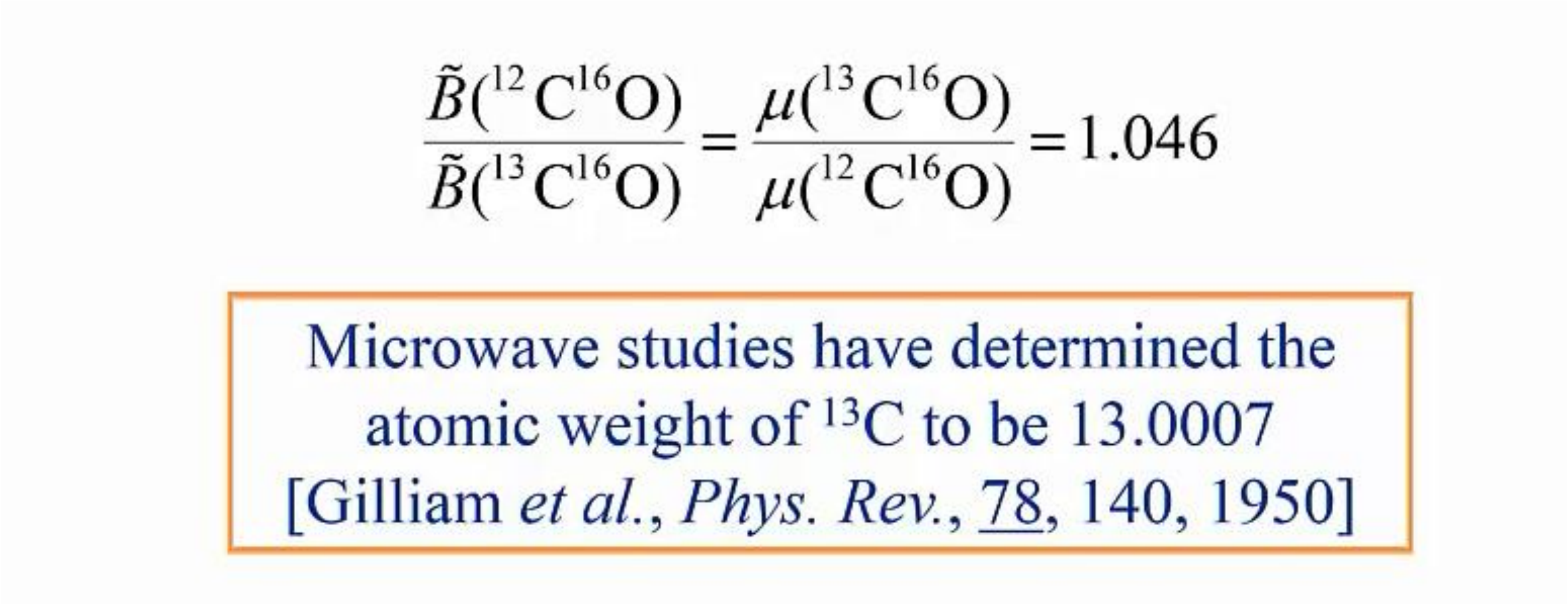
Application of Microwave Spectroscopy

Applications

- Provides an accurate determination of bond lengths and bond angles of molecules

Molecule	Bond Angle (°)	Bond Length (Å)
CH_3Br	$\angle HCH = 110.80$	$CH = 1.011$ $CBr = 1.938$
CH_3F	$\angle HCH = 110.00$	$CH = 1.109$ $CF = 1.385$
$CH_3C{\equiv}CH$	$\angle HCH = 108.23$	CH (methyl) = 1.097 $CC = 1.460$ $C{\equiv}C = 1.207$ $\equiv CH = 1.056$

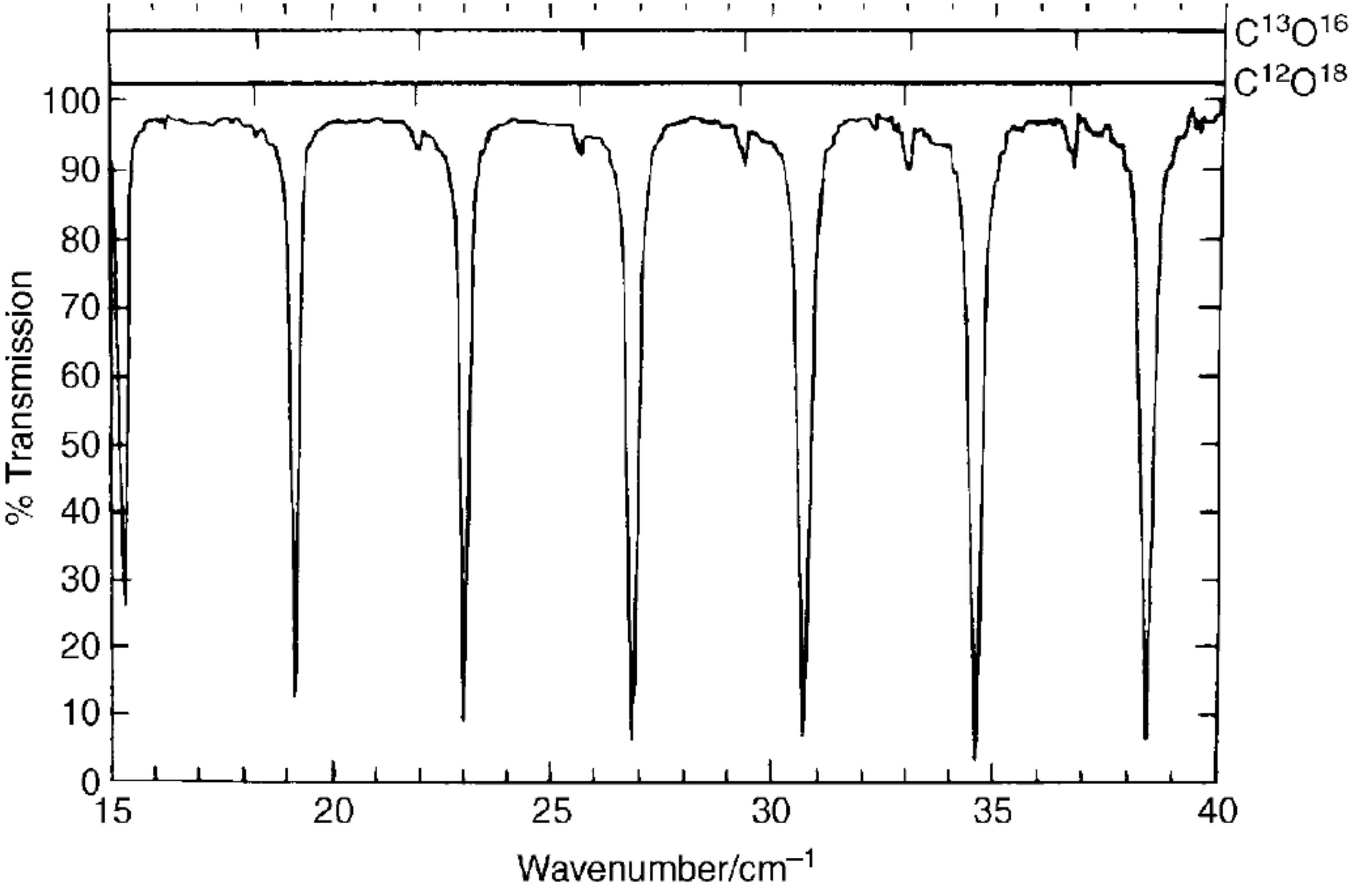
Determination of Accurate Atomic weights



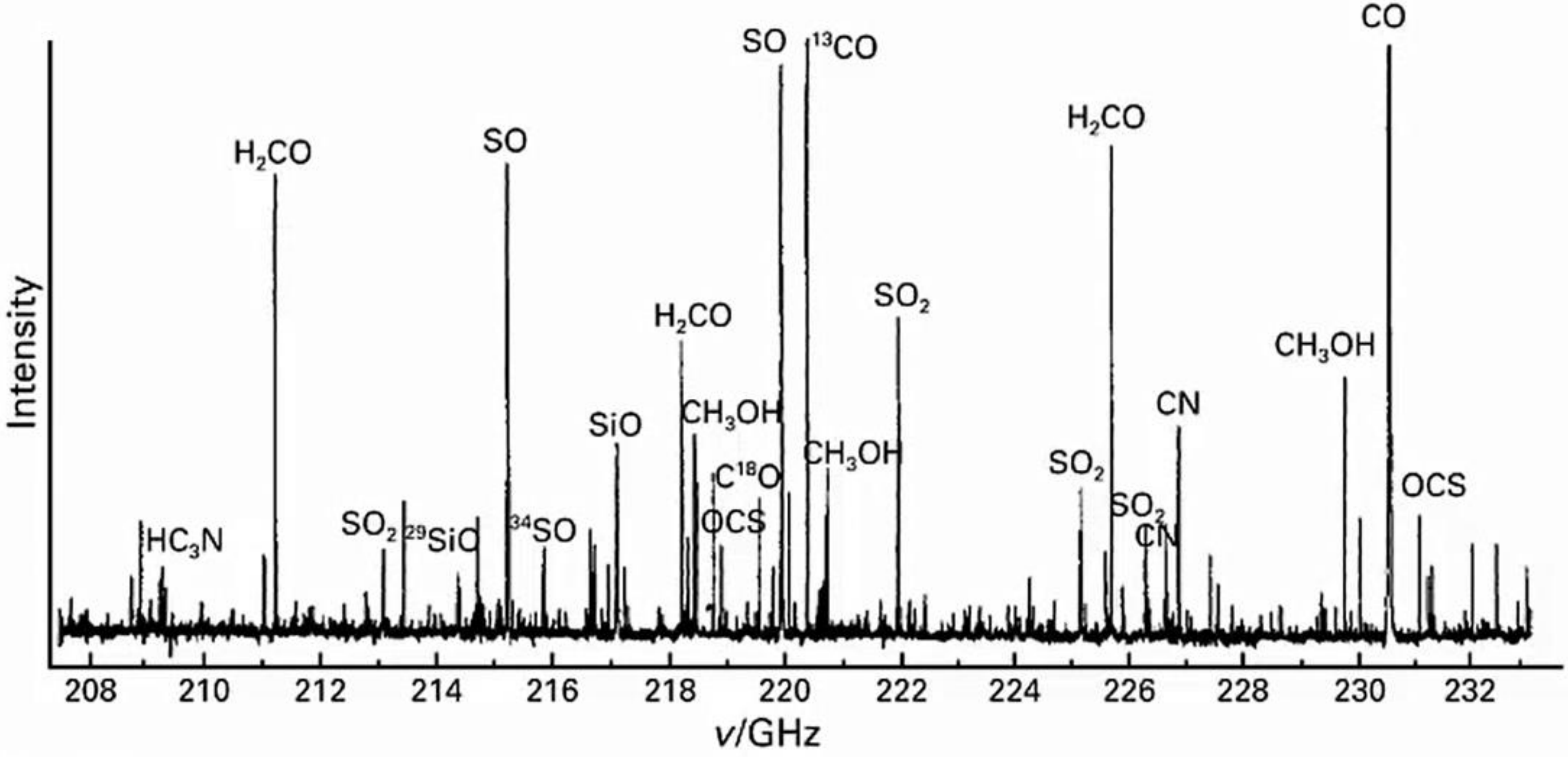
$$\frac{\tilde{B}(^{12}\mathrm{C}^{16}\mathrm{O})}{\tilde{B}(^{13}\mathrm{C}^{16}\mathrm{O})} = \frac{\mu(^{13}\mathrm{C}^{16}\mathrm{O})}{\mu(^{12}\mathrm{C}^{16}\mathrm{O})} = 1.046$$

Microwave studies have determined the atomic weight of ^{13}C to be 13.0007 [Gilliam *et al.*, *Phys. Rev.*, 78, 140, 1950]

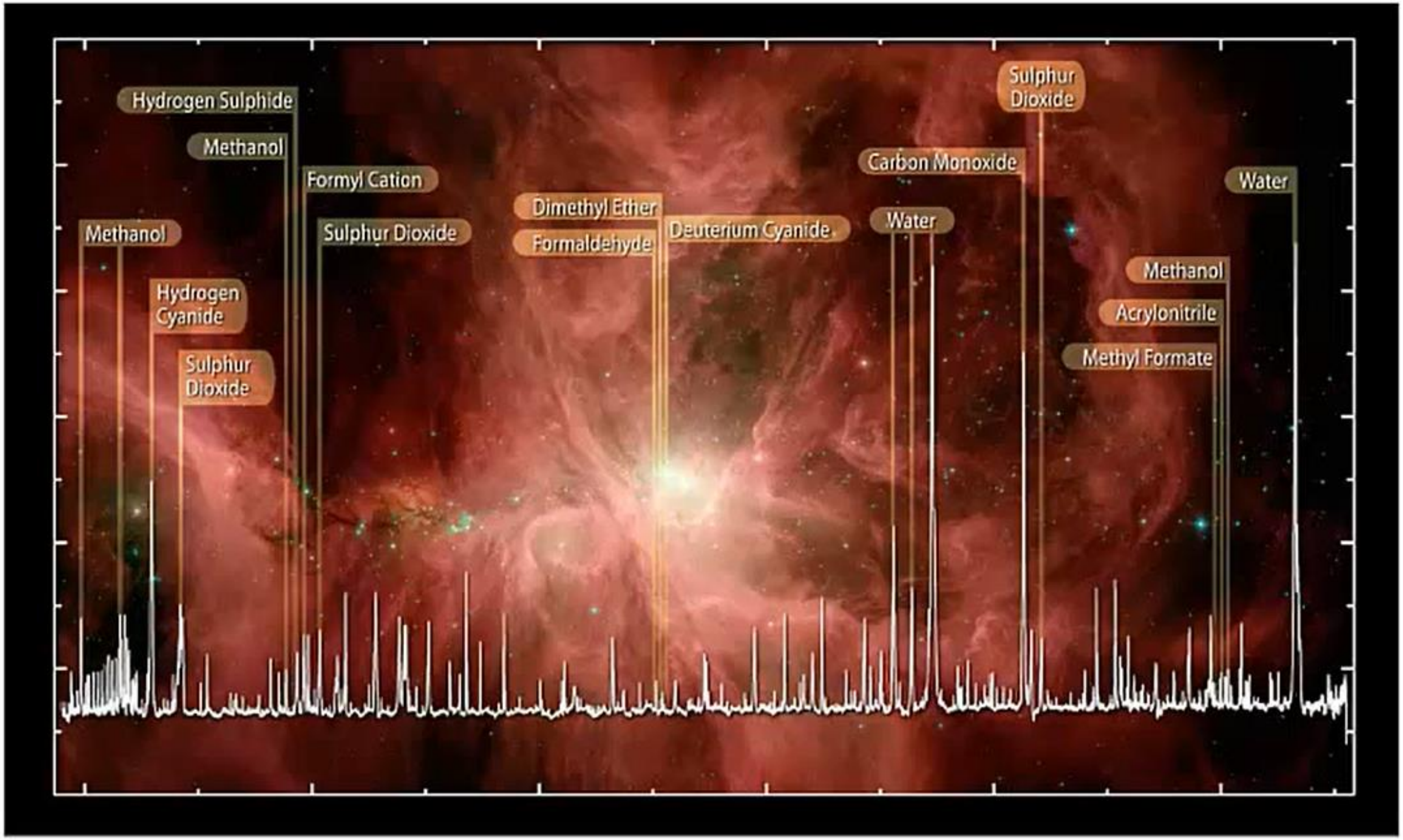
Determination of natural abundance of isotope from the comparison of intensities of spectra



- Allows identification of compounds with known rotational spectrum, *e.g.* detection of interstellar molecules

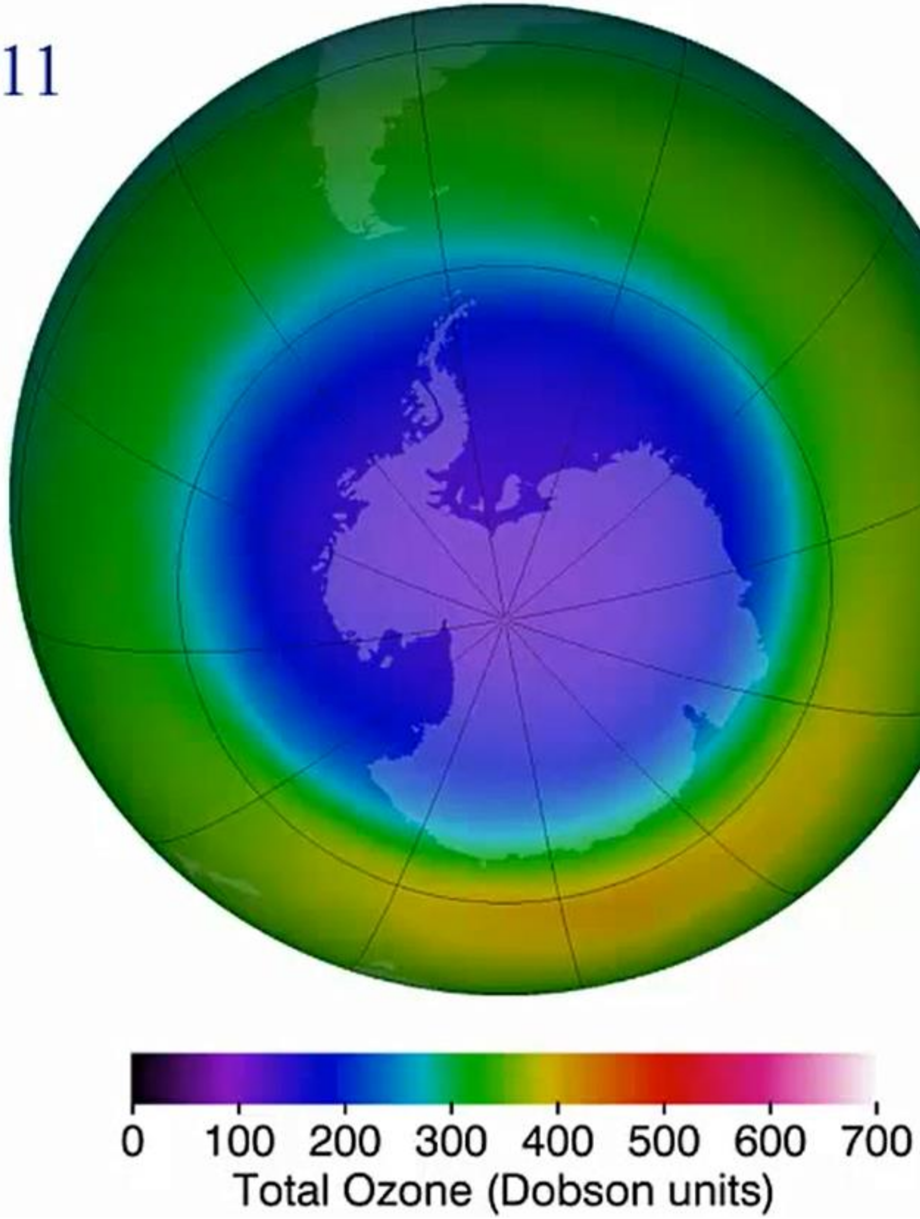


- The Orion Nebula: data from the HIFI instrument aboard the Herschel Space Observatory



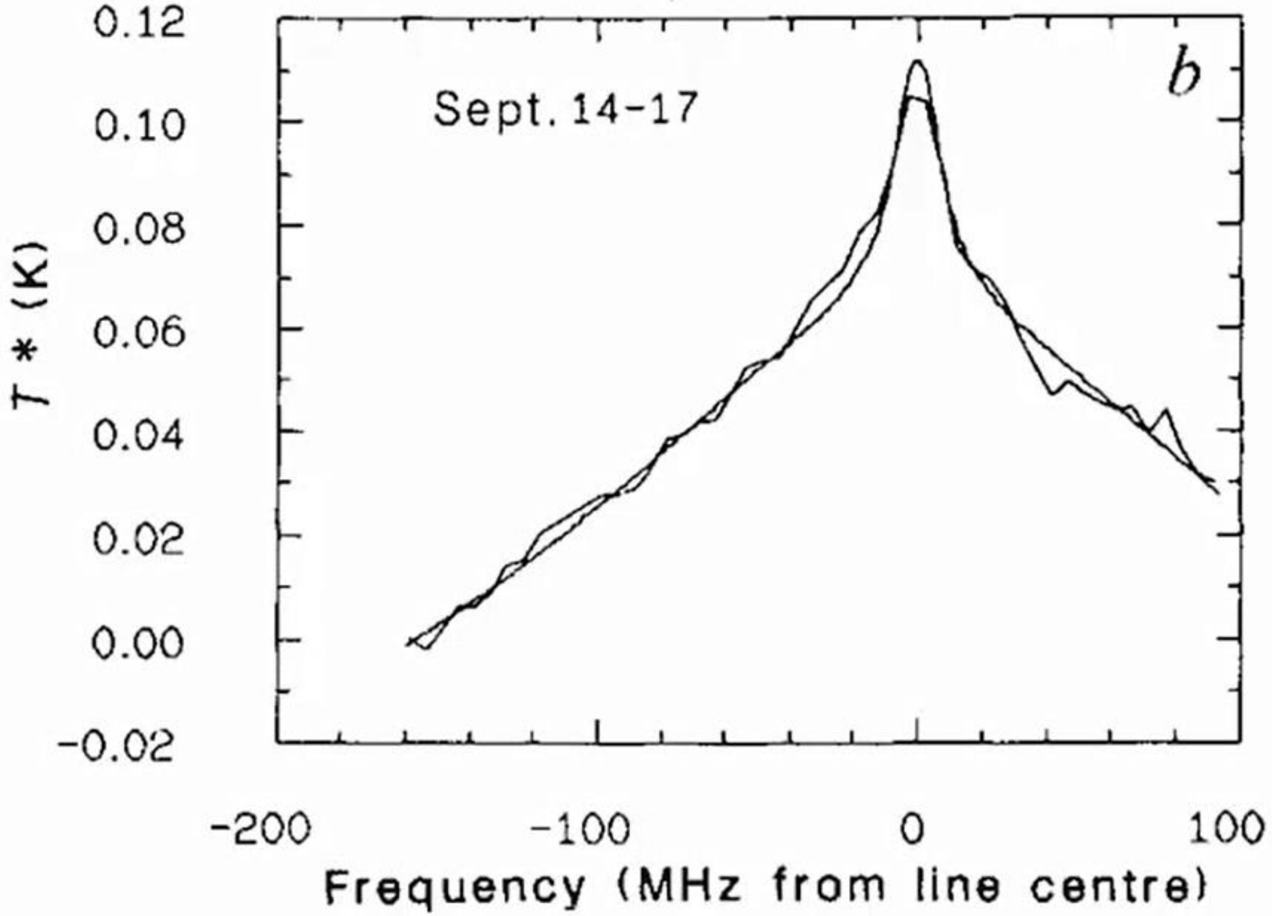
Antarctic Ozone Hole

- October 2011



Ground-based microwave data of ClO

- Solomon *et al.*, 1987



END

The pure rotational spectrum of $^{12}C^{16}O$ has transitions at 3.863 and 7.725 cm $^{-1}$. Calculate the internuclear distance and predict the transitions for the given two lines.

So, $2\bar{B} = (7.725 - 3.863)\ cm^{-1}$

$= 3.862\ cm^{-1}$

$\Rightarrow \bar{B} = \frac{3.862}{2}\ cm^{-1}$

$= 1.931\ cm^{-1}$

$\bar{B} = \frac{h}{8\pi^2 Ic} = 1.931\ cm^{-1}$

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

$= \frac{6.626 \times 10^{-27}\ gm\ cm^2\ sec}{8 \times 3.14^2 \times 1.93 \times 3 \times 10^{10}}$

$= 1.45 \times 10^{-39}\ gm\ cm^2$

$I = \mu r^2 \Rightarrow \frac{\frac{12 \times 16}{6.023\times10^{23}\ 6.023\times10^{23}}}{\frac{12+16}{6.023\times10^{23}}}$ $\mu = \frac{12 \times 16}{12+16} \times 1.6603 \times 10^{-24}$

$= 1.13 \times 10^{-23}$

$I = \mu r^2$

$r^2 = I/\mu = \frac{1.45 \times 10^{-39}}{1.13 \times 10^{-23}}$

$= 1.28 \times 10^{-16}$

$= 1.13 \times 10^{-8}$ cm

$= 1.13$ Å

Now, $\Delta\bar{\nu} = 2\bar{B}(J+1)$.

$3.863 = 2\bar{B}(J+1)$

$\Rightarrow 3.863 = 3.863(J+1)$.

$\Rightarrow J+1 = 1$

$\Rightarrow J = 0$.

$J=0 \rightarrow J=1$.

$\Delta\bar{\nu} = 2\bar{B}(J+1)\ cm^{-1}$.

$\Rightarrow 7.725 = 3.863(J+1)$

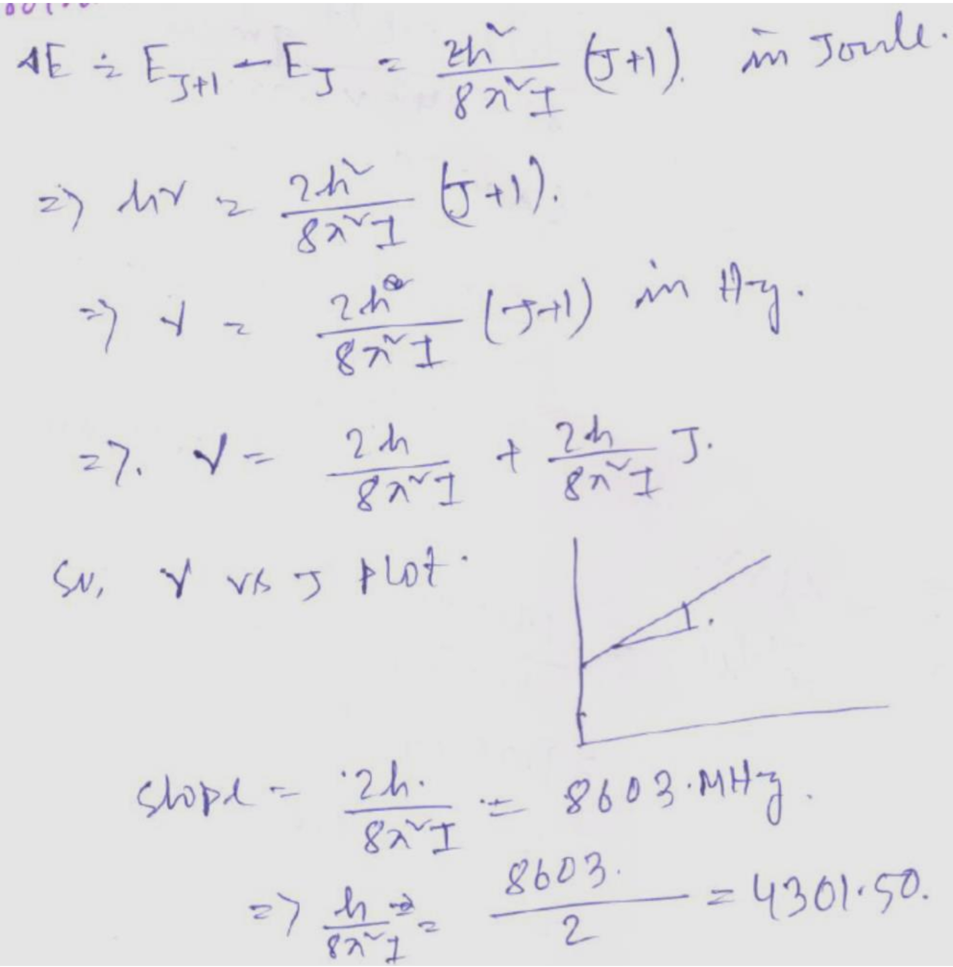
$\Rightarrow$ ~~$\bar{B}$~~ $J+1 = 2$

$\Rightarrow J = 1$.

$\Rightarrow J=1 \rightarrow J=2$.

$\Delta J = \pm 1$.

The γ vs J plot for different rotational transition for a particular molecule is showing a slope of 8603 MHz. Calculate the rotational quantum no. for the highest populated state at 25°C



$\Delta E = E_{J+1} - E_J = \frac{2h^2}{8\pi^2 I}(J+1)$ in Joule.

$\Rightarrow h\nu = \frac{2h^2}{8\pi^2 I}(J+1)$.

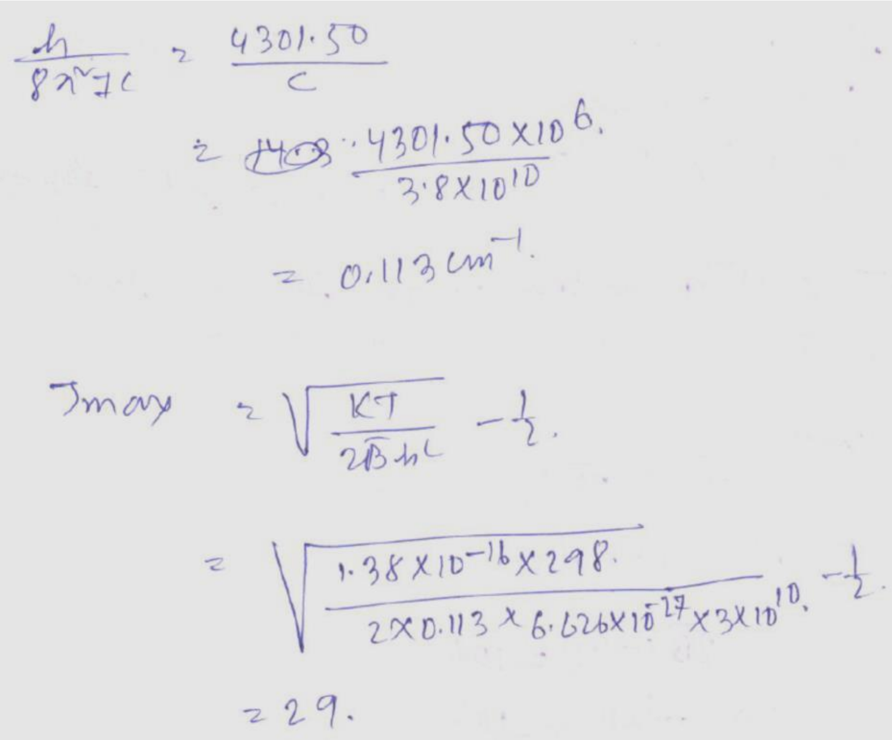
$\Rightarrow \nu = \frac{2h}{8\pi^2 I}(J+1)$ in Hz.

$\Rightarrow \nu = \frac{2h}{8\pi^2 I} + \frac{2h}{8\pi^2 I} J$.

So, ν vs J plot.

slope $= \frac{2h}{8\pi^2 I} = 8603$ MHz.

$\Rightarrow \frac{h}{8\pi^2 I} = \frac{8603}{2} = 4301.50$.



$\frac{h}{8\pi^2 I c} = \frac{4301.50}{c}$

$= \frac{4301.50 \times 10^6}{3.8 \times 10^{10}}$

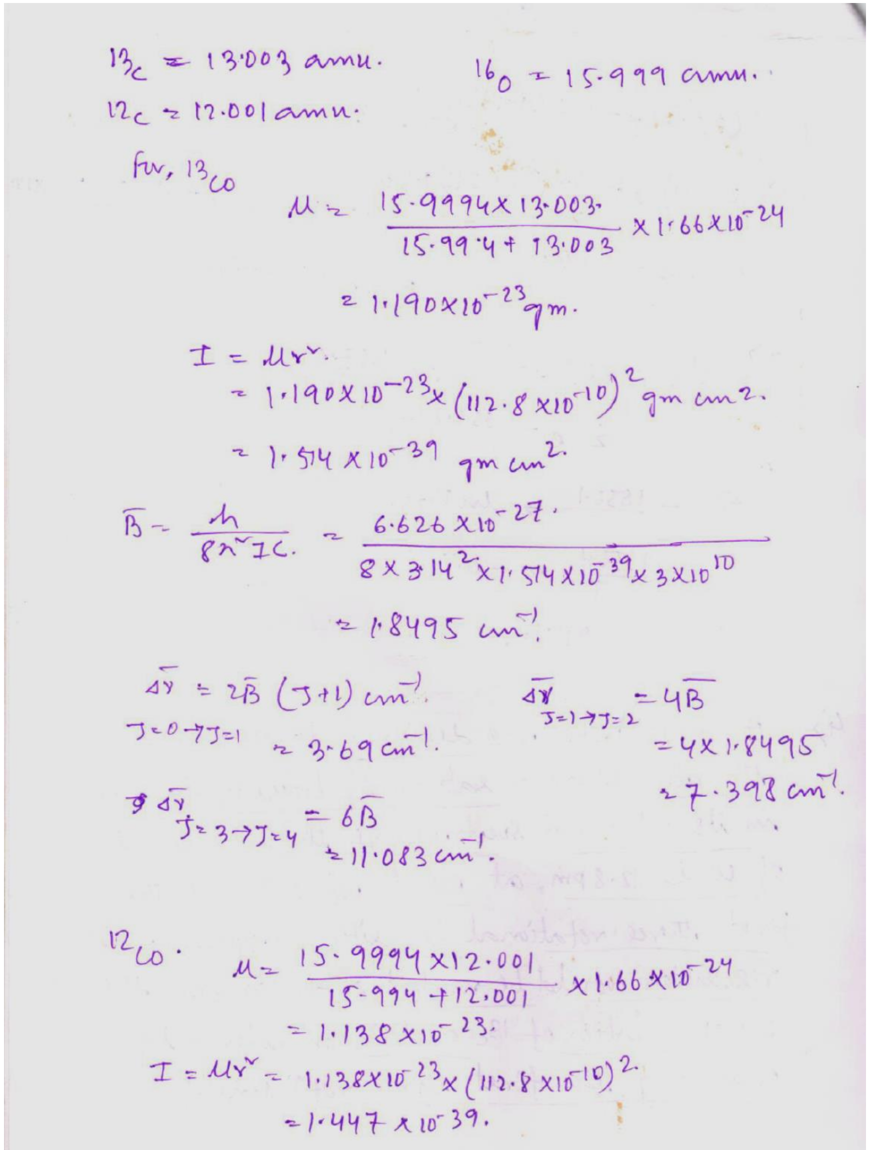
$= 0.113\ \text{cm}^{-1}$.

$J_{max} = \sqrt{\frac{KT}{2Bhc}} - \frac{1}{2}$.

$= \sqrt{\frac{1.38 \times 10^{-16} \times 298}{2 \times 0.113 \times 6.626 \times 10^{-27} \times 3 \times 10^{10}}} - \frac{1}{2}$.

$= 29$.

A space probe was designed to seek CO in the atmosphere of saturn by looking for lines in its rotational spectrum. If the bond length of CO is 112.8 pm , at what wave no. Do the first three rotational transitions appear? What resolution would be needed to determine the isotopic ratio of ^{13}C and ^{12}C on saturn by observing the first three rotational lines?



$^{13}C = 13.003$ amu. $\quad ^{16}O = 15.999$ amu.

$^{12}C = 12.001$ amu.

For, ^{13}CO

$$\mu = \frac{15.9994 \times 13.003}{15.994 + 13.003} \times 1.66 \times 10^{-24}$$

$$= 1.190 \times 10^{-23} \text{ gm.}$$

$$I = \mu r^2.$$

$$= 1.190 \times 10^{-23} \times (112.8 \times 10^{-10})^2 \text{ gm cm}^2.$$

$$= 1.514 \times 10^{-39} \text{ gm cm}^2.$$

$$\bar{B} = \frac{h}{8\pi^2 I c.} = \frac{6.626 \times 10^{-27}.}{8 \times 3.14^2 \times 1.514 \times 10^{-39} \times 3 \times 10^{10}}$$

$$= 1.8495 \text{ cm}^{-1}.$$

$\Delta\bar{\nu} = 2\bar{B}(J+1) \text{ cm}^{-1}.$

$\Delta\bar{\nu}_{J=0 \to J=1} = 3.69 \text{ cm}^{-1}.$

$\Delta\bar{\nu}_{J=1 \to J=2} = 4\bar{B}$

$= 4 \times 1.8495$

$= 7.398 \text{ cm}^{-1}.$

$\Delta\bar{\nu}_{J=3 \to J=4} = 6\bar{B}$

$= 11.083 \text{ cm}^{-1}.$

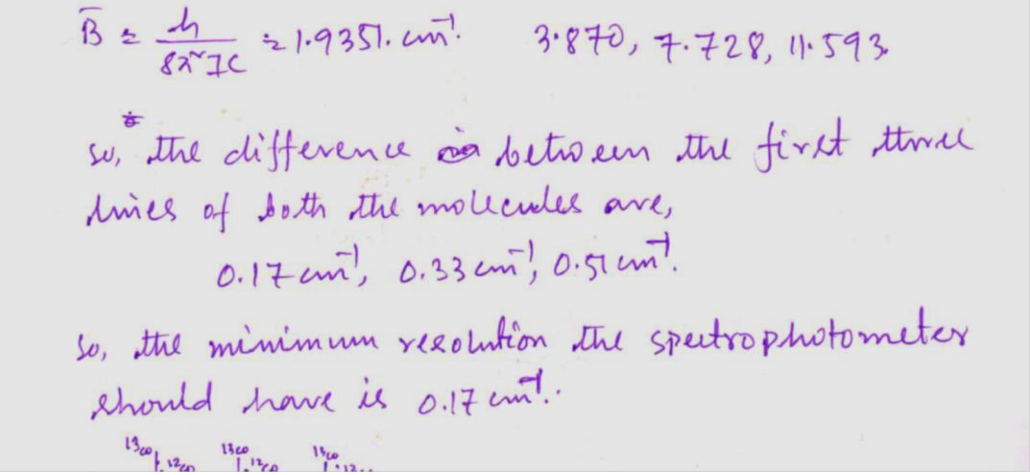
$^{12}CO.$

$$\mu = \frac{15.9994 \times 12.001}{15.994 + 12.001} \times 1.66 \times 10^{-24}$$

$$= 1.138 \times 10^{-23}.$$

$$I = \mu r^2 = 1.138 \times 10^{-23} \times (112.8 \times 10^{-10})^2.$$

$$= 1.447 \times 10^{-39}.$$



$\bar{B} = \frac{h}{8\pi^2 I c} = 1.9351. \text{ cm}^{-1}.$ $\quad 3.870, 7.728, 11.593$

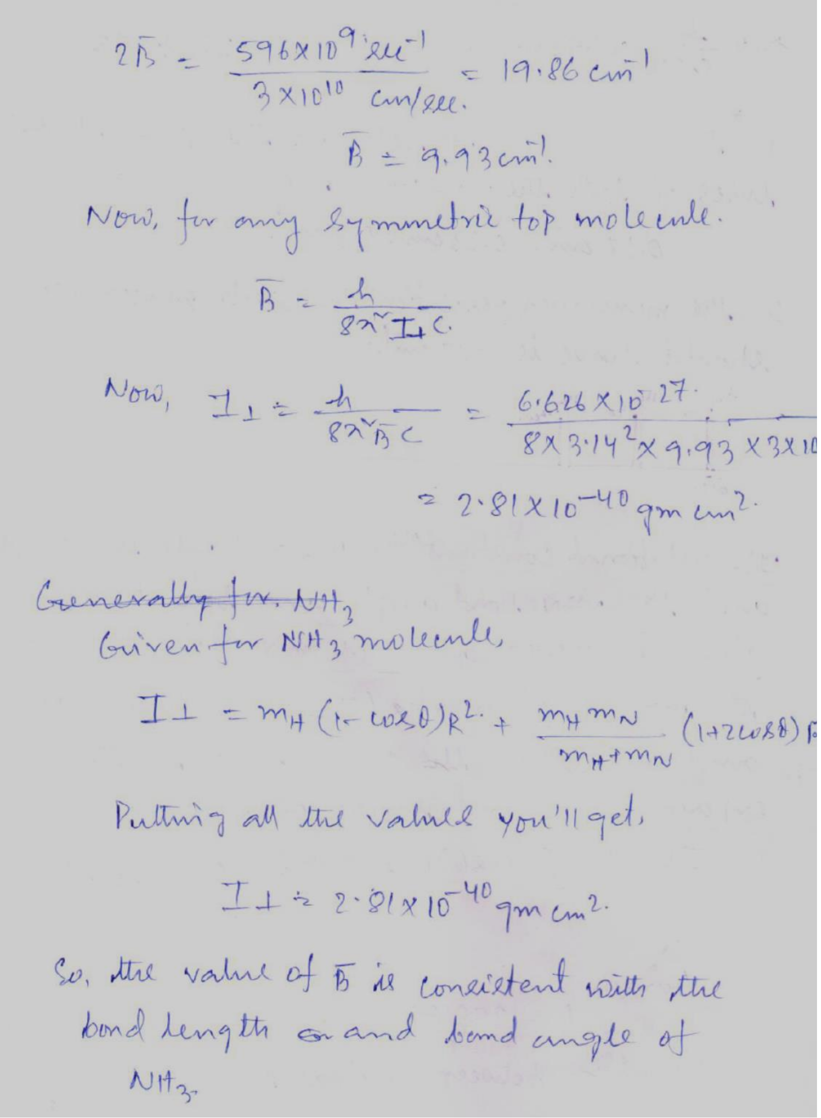
so, the difference between the first three lines of both the molecules are,

$0.17 \text{ cm}^{-1}, 0.33 \text{ cm}^{-1}, 0.51 \text{ cm}^{-1}.$

so, the minimum resolution the spectrophotometer should have is 0.17 cm^{-1}.

The rotational constants(B)and for NH_3 molecule is 298 Ghz and the NHN bond angle and bond length are given as 106.78° and 101.4 pm respectively. Calculate the moment of inertia ($I_\perp$) for the molecule and also show the consistency in the experimental and theoretical value of $I_\perp$

$$I_\perp = m_H (1-\cos^{\theta}\Theta) R^2 + m_H m_N/m_H+m_N (1+2\cos\Theta)R^2$$



$$2\bar{B} = \frac{596\times10^{9}\ sec^{-1}}{3\times10^{10}\ cm/sec} = 19.86\ cm^{-1}$$

$$\bar{B} \doteq 9.93\ cm^{-1}.$$

Now, for any symmetric top molecule.

$$\bar{B} = \frac{h}{8\pi^2 I_\perp c}.$$

Now, $I_\perp \doteq \dfrac{h}{8\pi^2 \bar{B} c} = \dfrac{6.626\times10^{-27}}{8\times3.14^2\times9.93\times3\times10}$

$$= 2.81\times10^{-40}\ gm\ cm^2.$$

~~Generally for NH$_3$~~

Given for NH_3 molecule,

$$I_\perp = m_H(1-\cos\theta)R^2 + \frac{m_H m_N}{m_H+m_N}(1+2\cos\theta)$$

Putting all the values you'll get,

$$I_\perp \doteq 2.81\times10^{-40}\ gm\ cm^2.$$

So, the value of $\bar{B}$ is consistent with the bond length ~~or~~ and bond angle of NH_3.

In the pure rotational emission spectrum of $H^{35}Cl$ gas , lines at 106 cm^{-1} and 233.2 cm^{-1} are observed to have equal intensity. What is the temperature of the gas?? The rotational constant B for $H^{35}Cl$ is 10.6 cm^{-1} and ratio of hC/K has the value 1.44 cm deg.

As the Probability of transition for both the molecules are same.

$$(2J'+1)e^{-BJ'(J'+1)\frac{hc}{KT}} = (2J''+1)e^{-BJ''(J''+1)\frac{hc}{KT}}.$$

⇒ J' ⇒ rotⁿ quantum no. for the first line
J'' ⇒ " " " " " 2nd ".

Since,

$\Delta\bar{\nu} = 2B(J+1)$ cm⁻¹.

For, the first line,

$$2\bar{B}(J'+1) = 106$$

$$\Rightarrow J'+1 = \frac{106}{2\times10.6} = 5.$$

$J' = 4.$

Transition, $J'=5 \rightarrow J'=4.$ (Because its an emission line, ✓

For the 2nd line,

$$2\bar{B}(J''+1) = 233.2$$

$$\Rightarrow J''+1 = \frac{233.2}{2\times10.6} = 11.$$

Transition

$J''=11 \rightarrow J''=10.$

Now,

$$(2J'+1)e^{-BJ'(J'+1)\frac{hc}{KT}} = (2J''+1)e^{-BJ''(J''+1)\frac{hc}{KT}}.$$

$$\Rightarrow (2\times5+1)\,e^{-\frac{10.6\times5(5+1)1.44}{T}} = (2\times11+1)\,e^{-\frac{10.6\times11(11+1)\times1.44}{T}}$$

$$\Rightarrow 11\cdot e^{-\frac{457.9}{T}} = 23\cdot e^{-2014.8/T}.$$

$$\Rightarrow \frac{11}{23} = e^{-\frac{2014.8}{T}}\cdot e^{\frac{457.9}{T}} = e^{-1556.1/T}.$$

$$\Rightarrow -\frac{1556.1}{T} = \ln 11/23.$$

$$\Rightarrow -\frac{1556.1}{T} = -0.737.$$

$$\Rightarrow T = 2111°K.$$

HCl has a B value of 10.593 $cm^{-1}$and a centrifugal distortion constant D of $5.3*10^{-4}$ cm^{-1}. Estimate the vibrational frequency and force constant of the molecule

Vibrational frequency

$$\bar{\omega}^2 = \frac{4B^3}{D}$$

$$= \frac{4 \times (10.593\ cm^{-1})^3}{5.3 \times 10^{4}\ cm^{-1}}$$

$$= 897.100 \times 10^4\ cm^{-2}$$

$$= 2995.16\ cm^{-1}$$

$$K = 4\pi^2 \bar{\omega}^2 c^2 \mu$$

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

$$= \frac{\cancel{108}\ 1 \times 1.66 \times 10^{-27}\ Kg \times 35.5 \times 10^{-27} \times 1.66}{1.66 \times 10^{-27}\ (1 + 35.5)}$$

$$= 1.614 \times 10^{-27}\ Kg$$

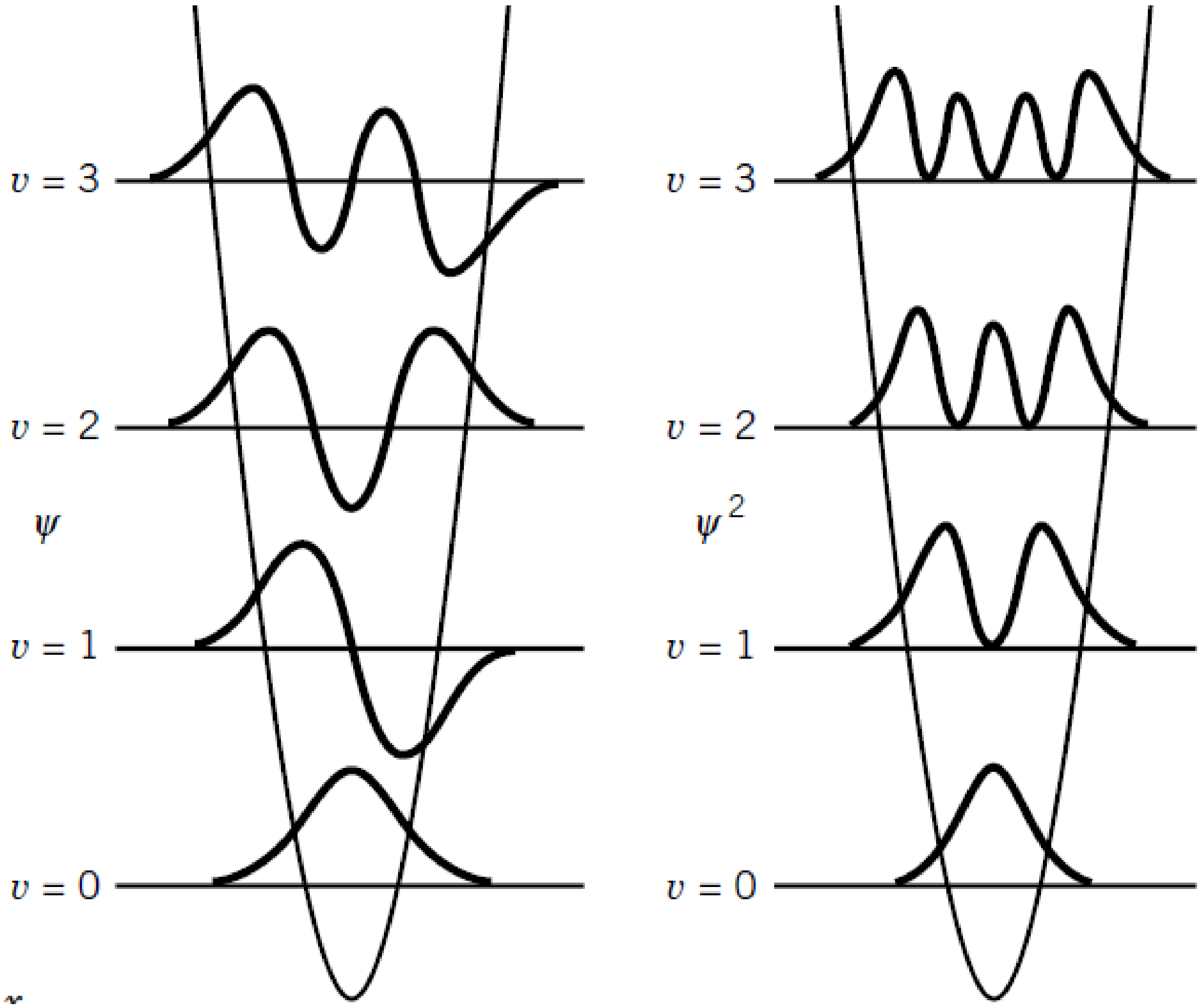
$$= 1.614 \times 10^{-24}\ gm$$

$$K = 4 \times 3.14^2 (3 \times 10^{10}) (2995.16)^2 \times 1.614 \times 10^{-24}$$

$$= 513931.6\ gm\ sec^{-2}$$

02/02/2017

Harmonic Oscillator Wave functions



Selection Rule

$$\mu_z = \mu_0 + \left(\frac{d\mu}{dx}\right)_{x=0} x + \ldots\ldots$$

$V \rightarrow V^{/}$

$$\mu_z^{V,V^{/}}(x) = \int \psi_V^*(x)\mu_z(x)\psi_{V^{/}}(x)dx$$

$$= \int \psi_V^*(x)\left[\mu_0 + x\left(\frac{d\mu}{dx}\right)_{x=0} + \ldots\right]\psi_{V^{/}}(x)dx$$

$$= \int \psi_V^*(x)\mu_0\psi_{V^{/}}(x)dx + \int \psi_V^*(x)x\left(\frac{d\mu}{dx}\right)_{x=0}\psi_V(x)dx$$

$$= \mu_0\int \psi_V^*(x)\psi_{V^{/}}(x)dx + \left(\frac{d\mu}{dx}\right)_{x=0}\int \psi_V^*(x)x\,\psi_{V^{/}}(x)dx$$

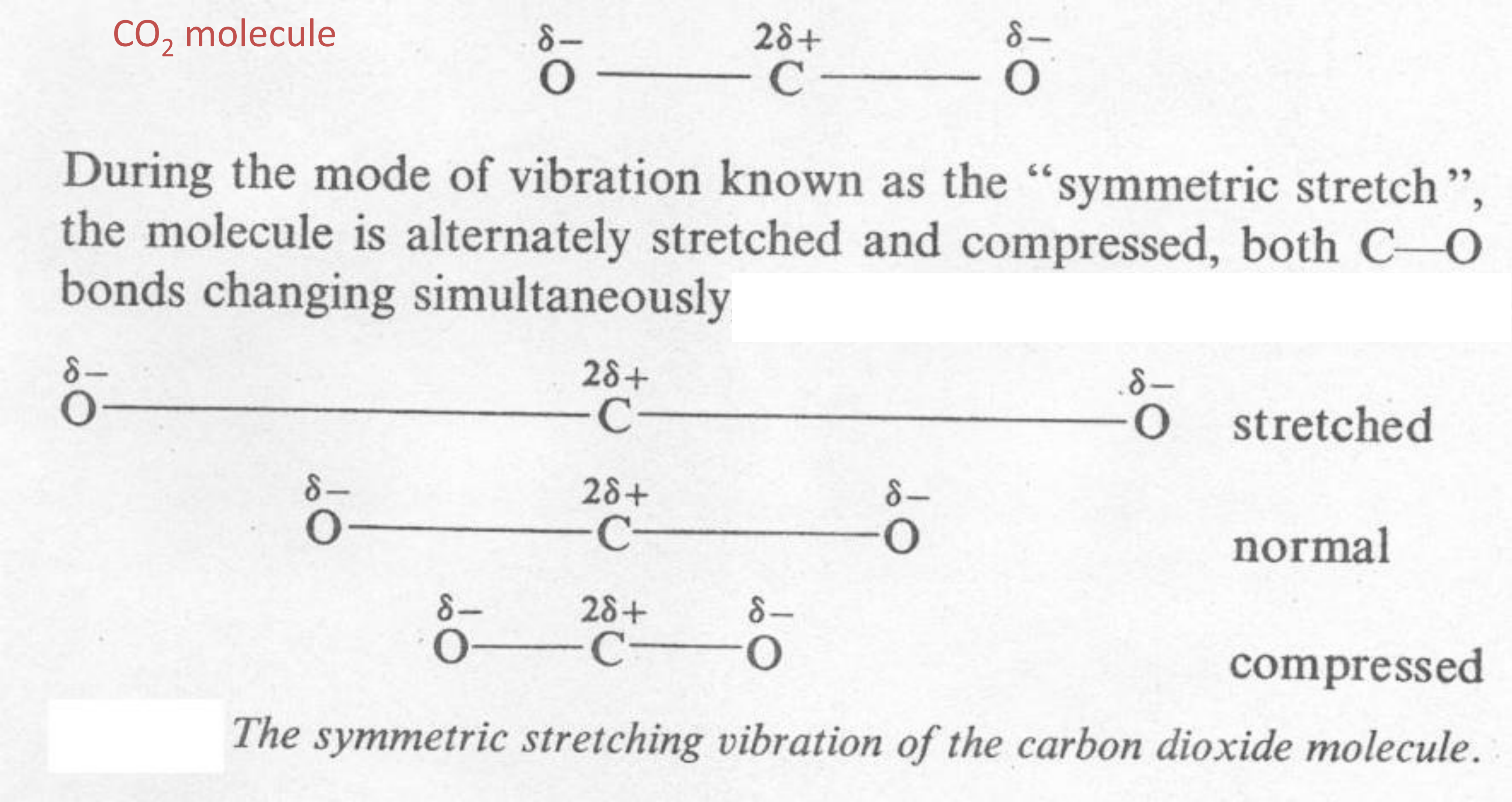
Gross Selection Rule:

A molecule will show vibrational spectrum only if the dipole moment changes with internuclear distance.

Specific Selection Rule:

$$\Delta V = \pm 1$$

Vibrational Spectrum of Carbon Dioxide



CO_2 molecule

$$\overset{\delta-}{O}\text{———}\overset{2\delta+}{C}\text{———}\overset{\delta-}{O}$$

During the mode of vibration known as the "symmetric stretch", the molecule is alternately stretched and compressed, both C—O bonds changing simultaneously

$$\overset{\delta-}{O}\text{——————————}\overset{2\delta+}{C}\text{——————————}\overset{\delta-}{O}$$

stretched

$$\overset{\delta-}{O}\text{—————}\overset{2\delta+}{C}\text{—————}\overset{\delta-}{O}$$

normal

$$\overset{\delta-}{O}\text{——}\overset{2\delta+}{C}\text{——}\overset{\delta-}{O}$$

compressed

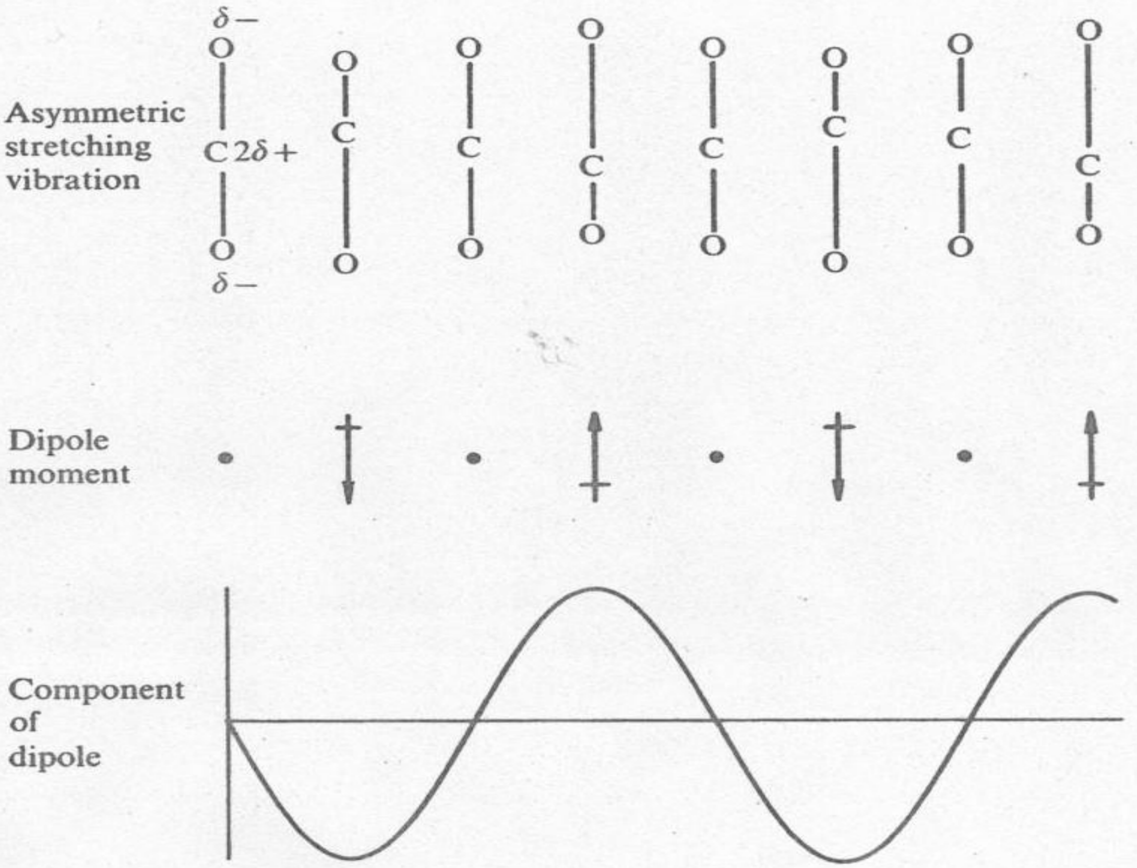
The symmetric stretching vibration of the carbon dioxide molecule.

This stretching mode results in no peak because the dipole moment is zero does not change during vibration

Vibrational Spectrum of Carbon Dioxide

Asymmetric stretching results in a change in dipole moment during vibration and produces a peak in the IR spectrum.

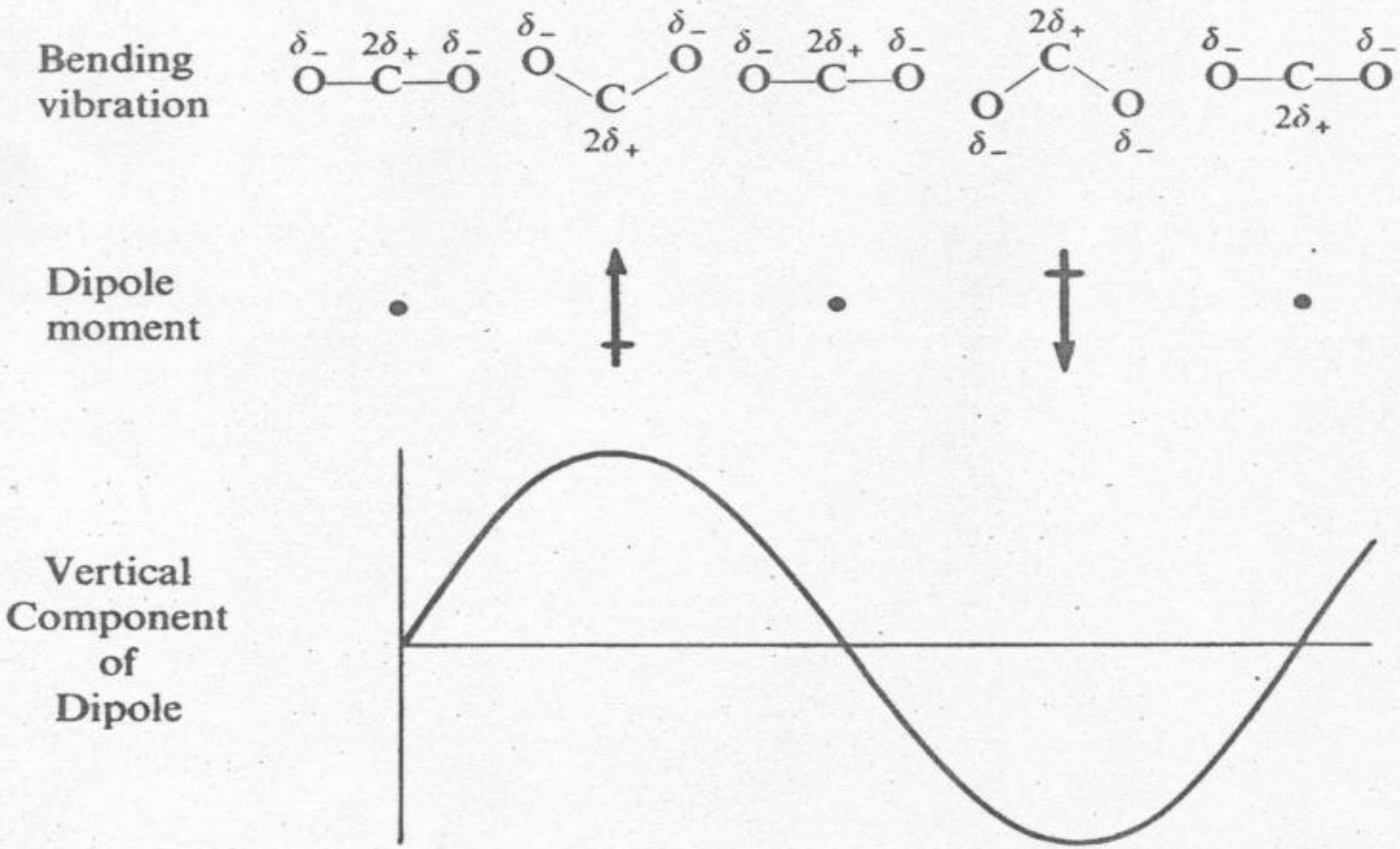
REGIONS OF THE SPECTRUM 11



The asymmetric stretching vibration of the carbon dioxide molecule showing the fluctuation in the dipole moment.

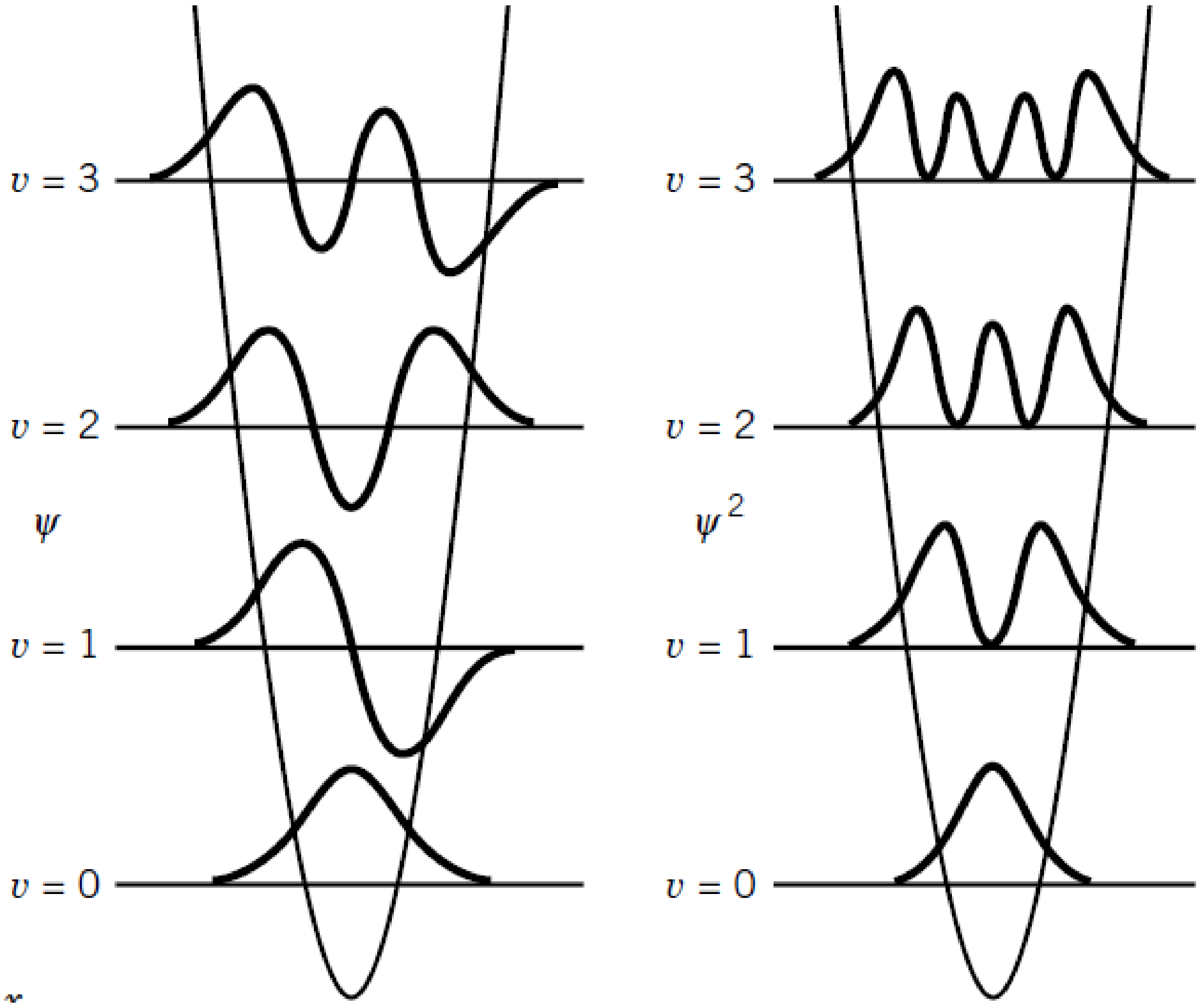
Vibrational Spectrum of Carbon Dioxide

The bending mode of vibration gives a peak in the IR spectrum



The bending motion of the carbon dioxide molecule and its associated dipole fluctuation.

Harmonic Oscillator Wave functions



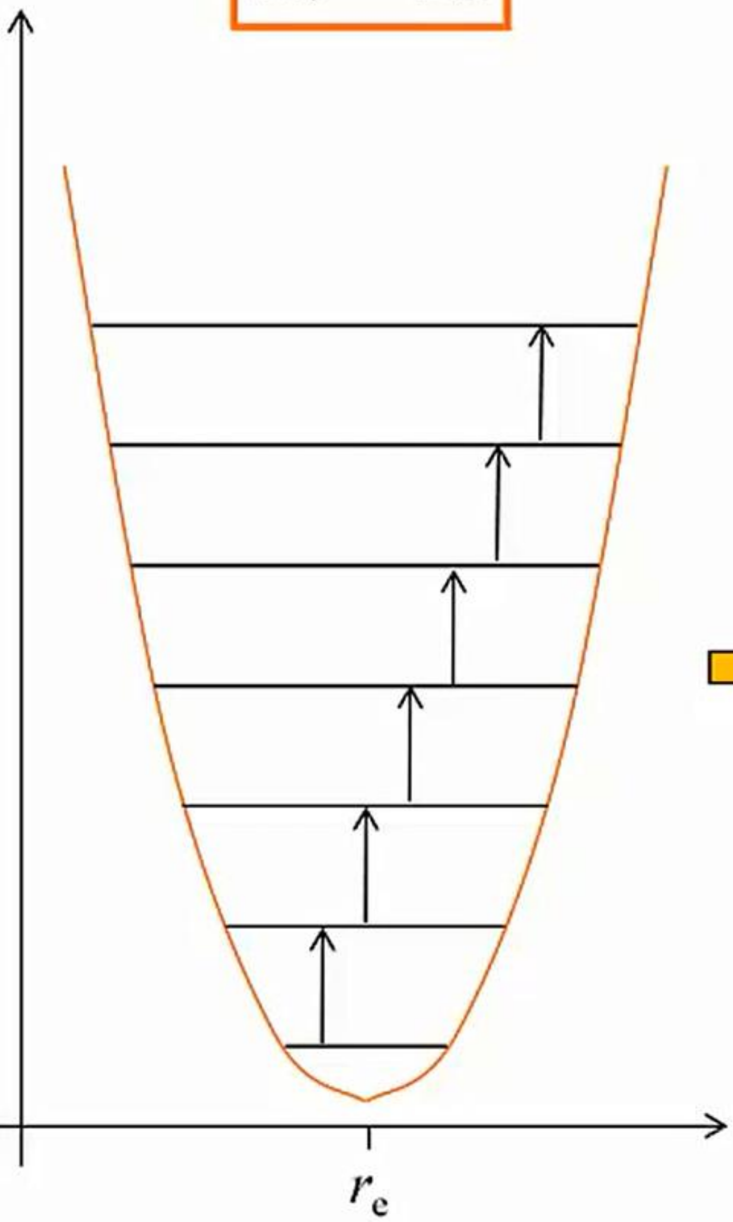
Vibrational Transitions

- For the transition $v \rightarrow v + 1$, ΔE is:

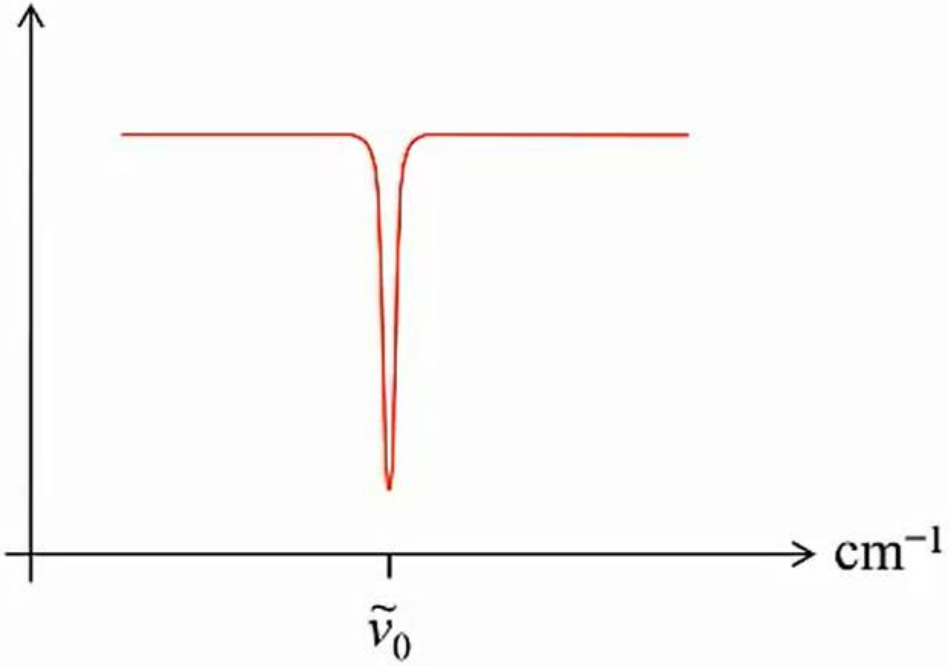
$$\begin{aligned}\frac{\Delta E}{h\tilde{c}} = \tilde{\nu} = \tilde{G}(v+1) - \tilde{G}(v) \\ = \left(v+1+1/2\right)\tilde{\nu}_0 - \left(v+1/2\right)\tilde{\nu}_0 \\ = \tilde{\nu}_0\end{aligned}$$

- Thus for the harmonic oscillator approximation, we expect that all transitions will give rise to a single spectral line at $\tilde{\nu}_0$

$$\boxed{\Delta v = \pm 1}$$



$$\boxed{\tilde{G}(v) = \left(v + 1/2\right)\tilde{\nu}_0}$$



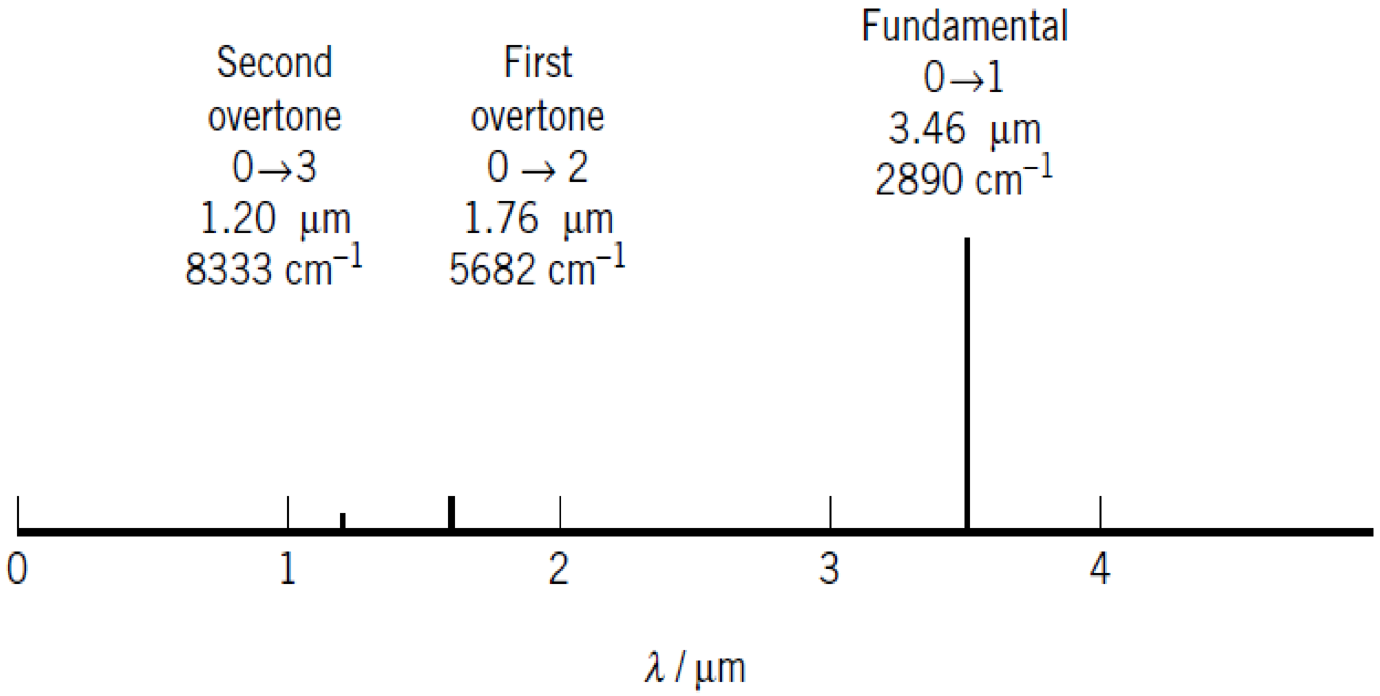
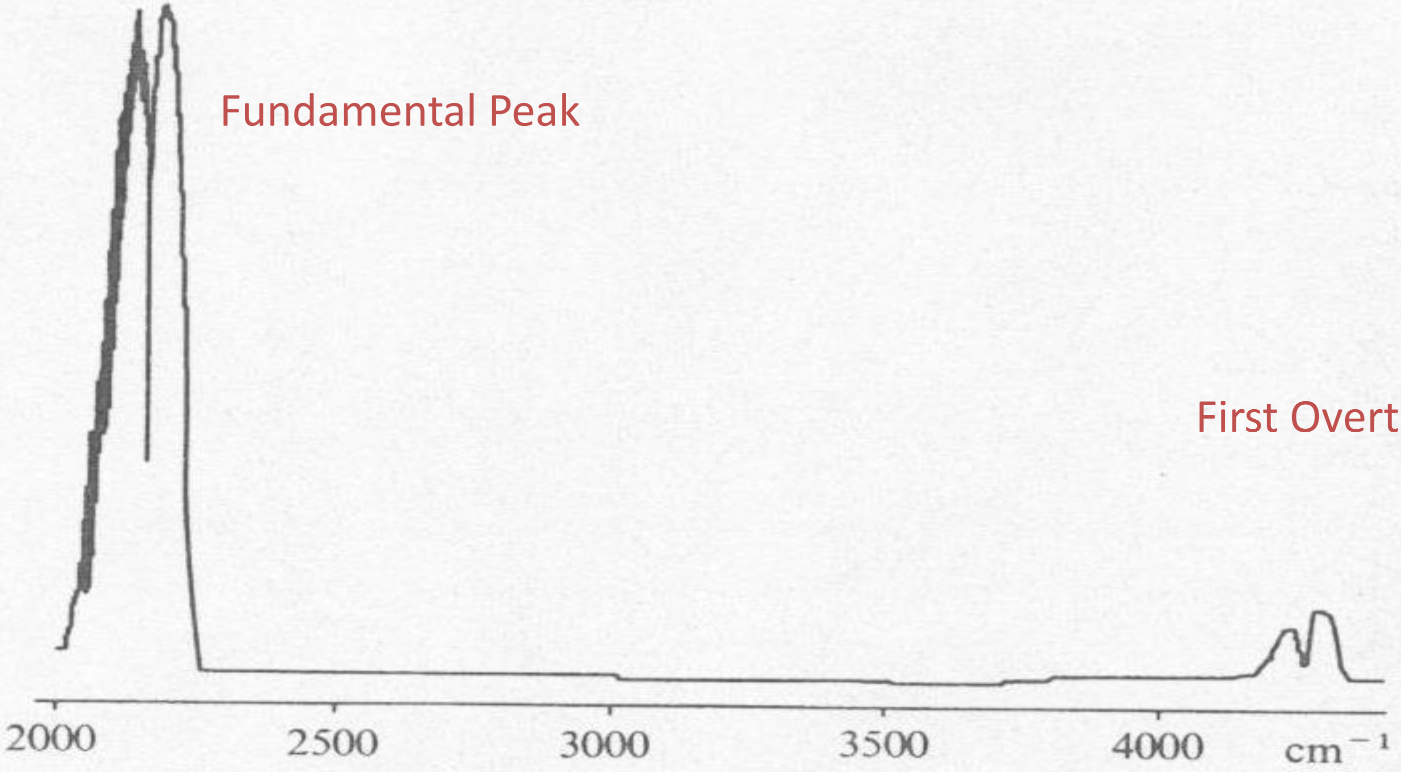


Figure 13.7 "Stick" representation of the vibrational absorption spectrum of $H^{35}Cl$. The relative intensities of the lines fall off five times as fast as indicated.

IR Spectrum of Carbon Monoxide (CO)

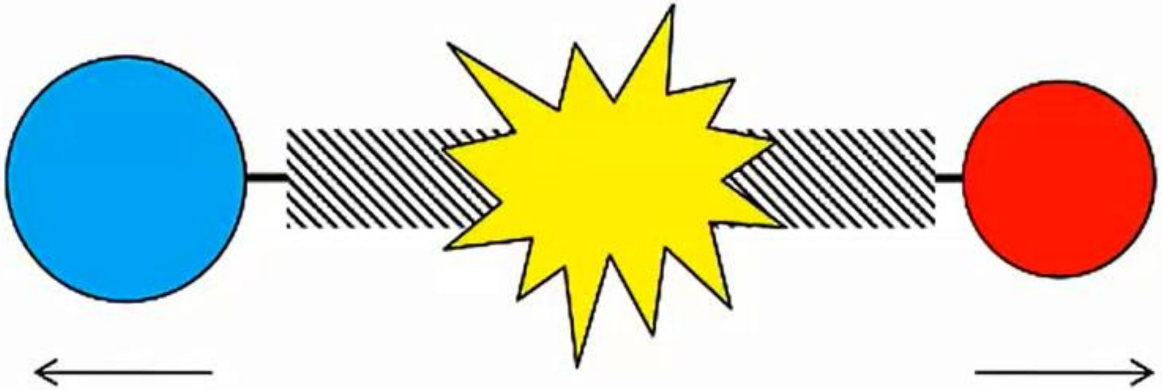


Fundamental Peak

First Overtone

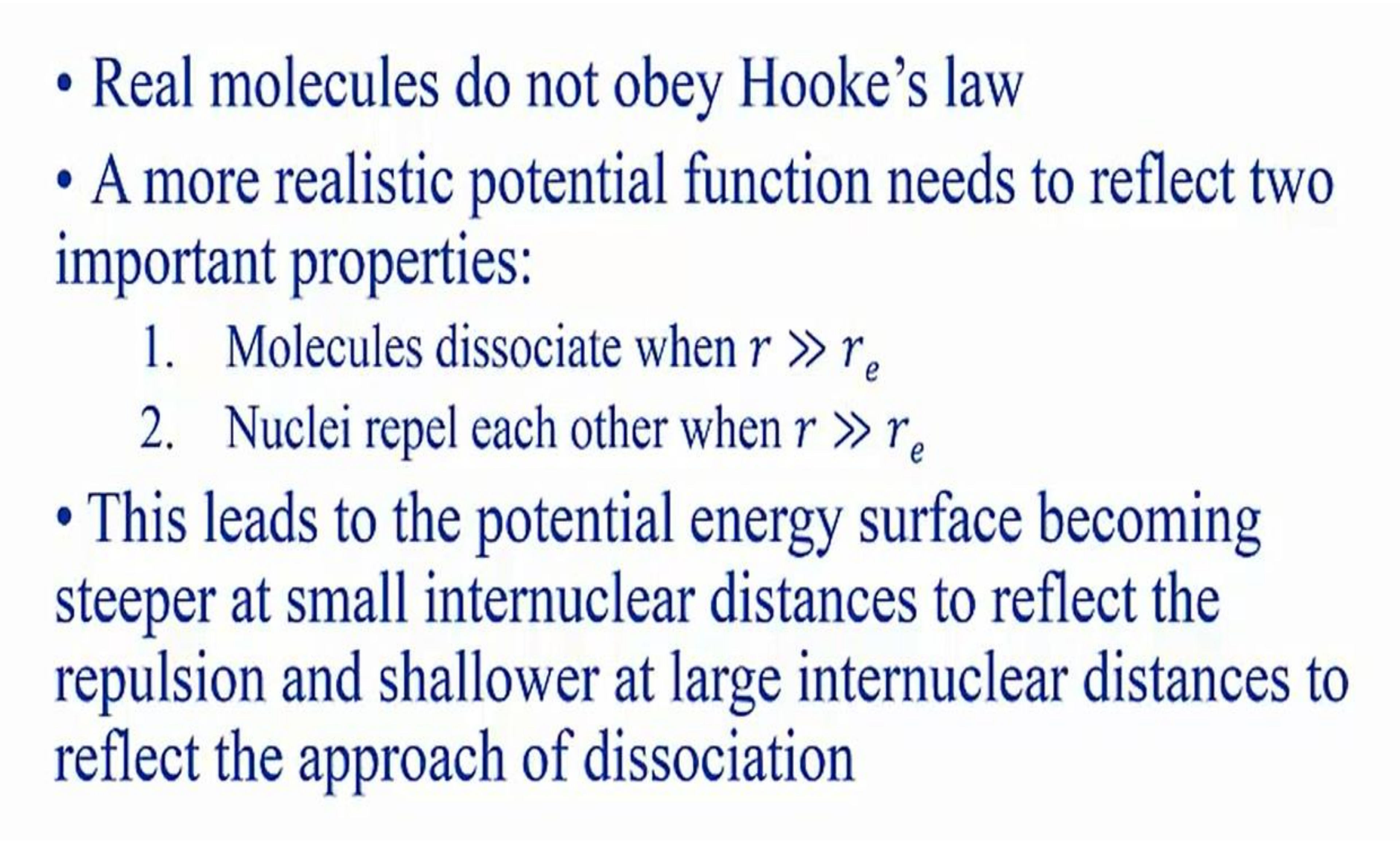
The fundamental absorption (centred at about 2143 cm^{-1}) and the first overtone (centred at about 4260 cm^{-1}) of carbon monoxide; the fine structure of the P branch in the fundamental is partially resolved. (Gas pressure 650 mm Hg in a 10 cm cell.)

- However, if molecular bonds are stretched too much, there comes a point at which they will break, *i.e.* the molecules dissociate



The harmonic model approximation fails!

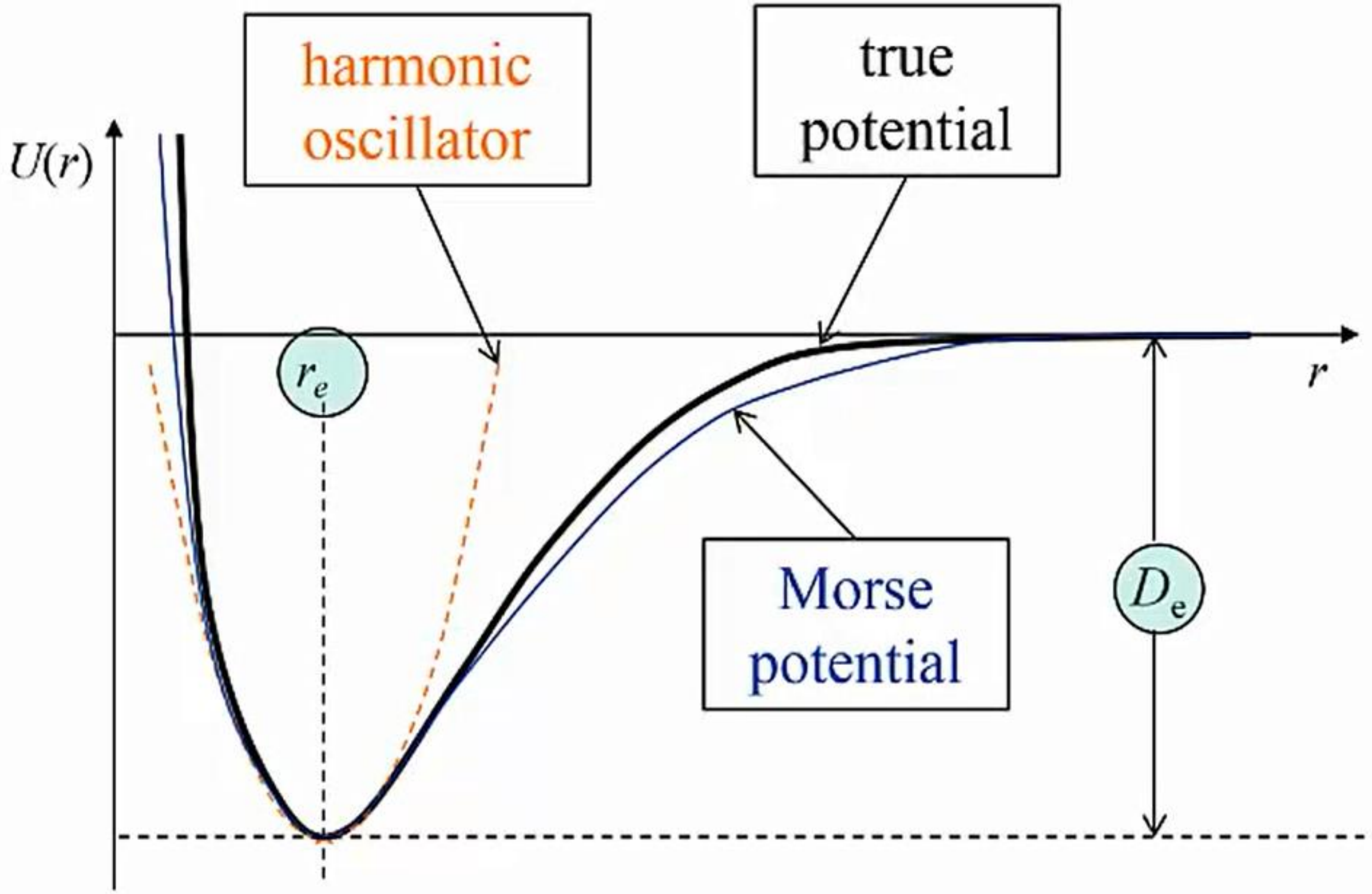
Important Points Need to be Considered:



- Real molecules do not obey Hooke's law
- A more realistic potential function needs to reflect two important properties:
    1. Molecules dissociate when $r \gg r_e$
    2. Nuclei repel each other when $r \gg r_e$
- This leads to the potential energy surface becoming steeper at small internuclear distances to reflect the repulsion and shallower at large internuclear distances to reflect the approach of dissociation

Anharmonic Model

Morse Potential



$$U(r) = D_e\{1-\mathrm{e}^{-a(r-r_e)}\}^2$$

$$= D_e\{1-\exp(-a\ \mathbf{x}\ \}^2$$

- D_e is the equilibrium dissociation constant and a is a molecular parameter

Vibrational Energy

- Set up the Schrödinger equation for the anharmonic oscillator using a Morse function:

$$\hat{H}\Psi = E\Psi$$

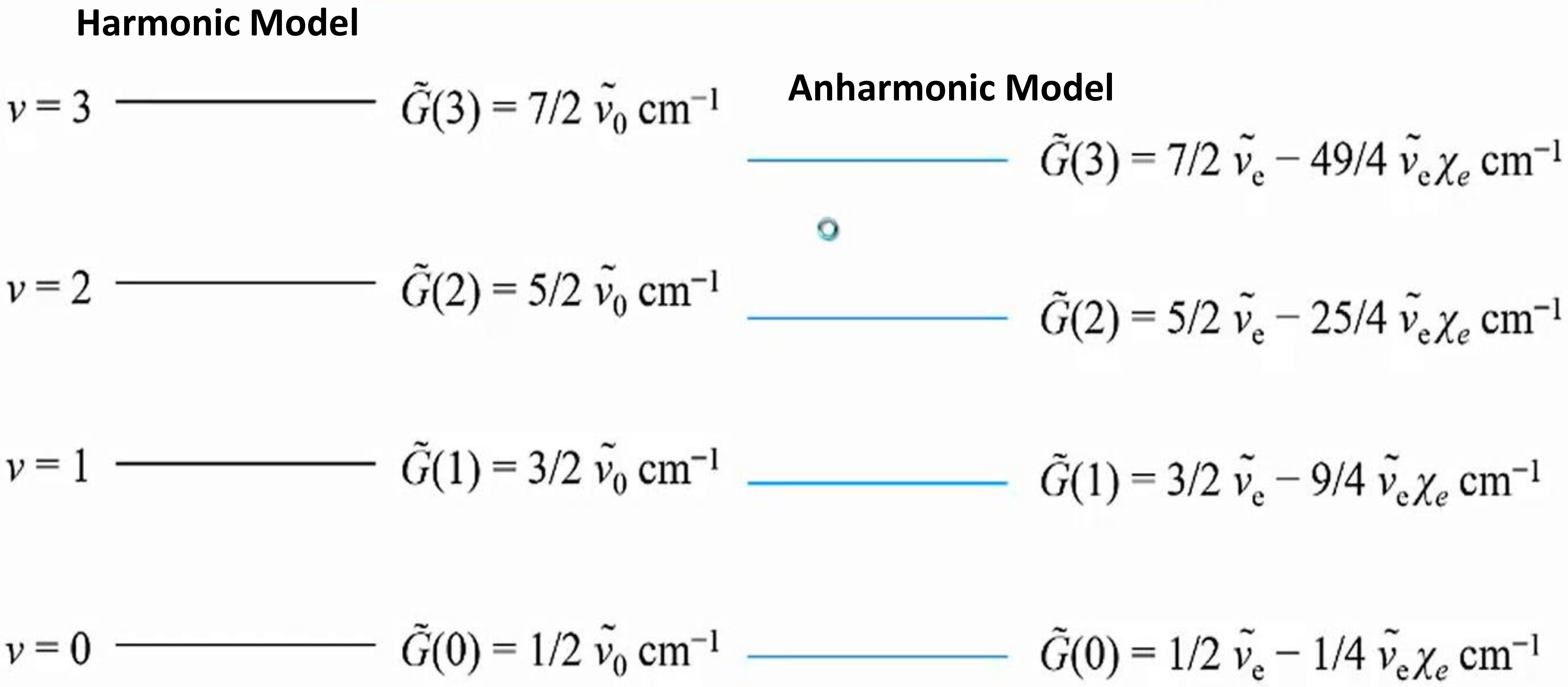
$$\left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + D_e\left\{1-\exp(-a x)\right\}^2\right)\Psi_{\mathrm{vib}} = E_{\mathrm{vib}}\Psi_{\mathrm{vib}}$$

- Solving this equation reveals that the vibrational energy levels are quantised

$$\tilde{G}(v) = (v+1/2)\tilde{\nu}_e - (v+1/2)^2\,\tilde{\nu}_e\chi_e \qquad \boxed{\mathrm{cm}^{-1}}$$

Vibrational Energy Level Diagram

$$\boxed{\tilde{G}(v) = (v+1/2)\tilde{\nu}_e - (v+1/2)^2\,\tilde{\nu}_e\chi_e}$$



Harmonic Model

$v = 3$ $\tilde{G}(3) = 7/2\ \tilde{\nu}_0\ \text{cm}^{-1}$

$v = 2$ $\tilde{G}(2) = 5/2\ \tilde{\nu}_0\ \text{cm}^{-1}$

$v = 1$ $\tilde{G}(1) = 3/2\ \tilde{\nu}_0\ \text{cm}^{-1}$

$v = 0$ $\tilde{G}(0) = 1/2\ \tilde{\nu}_0\ \text{cm}^{-1}$

Anharmonic Model

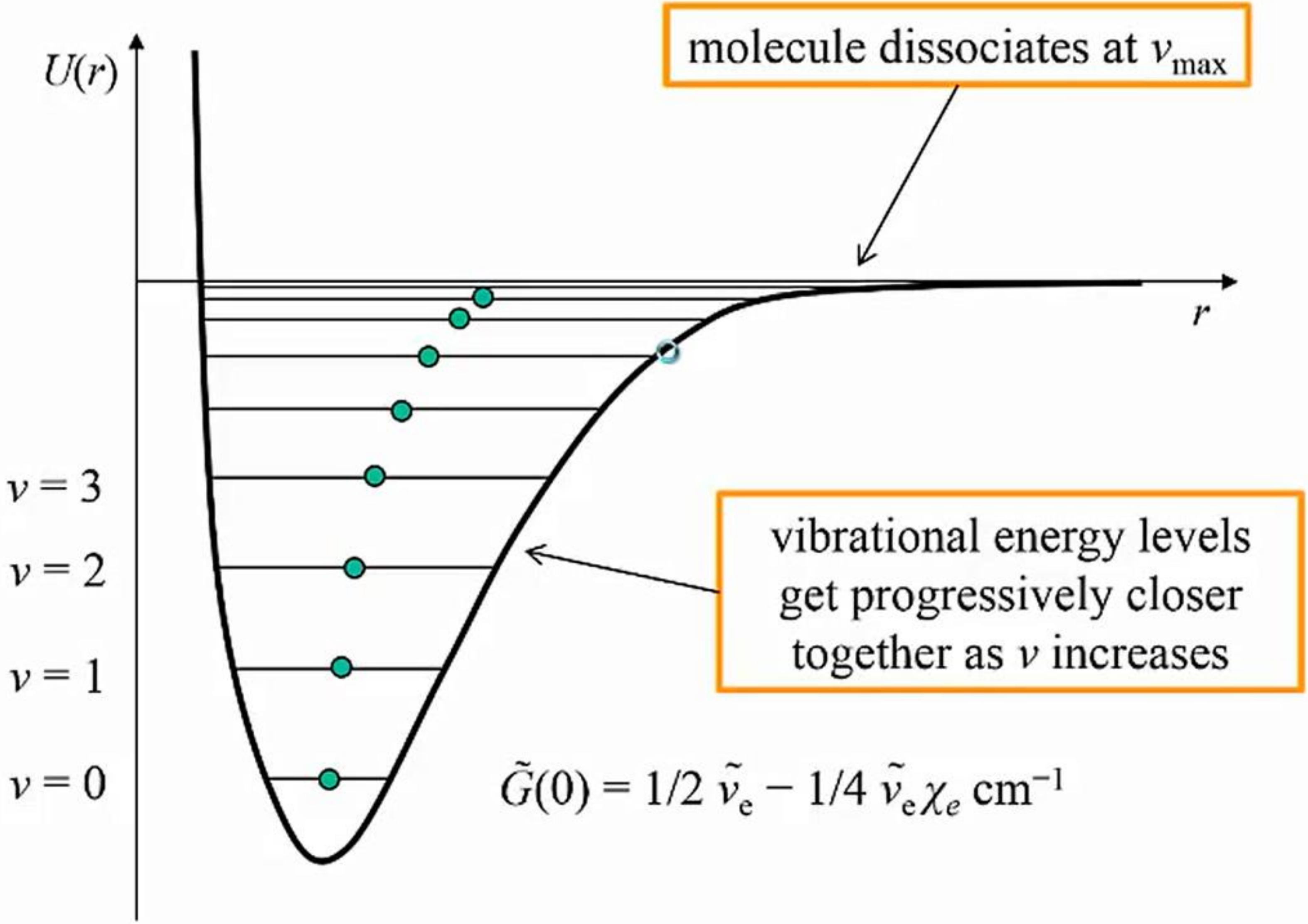
$\tilde{G}(3) = 7/2\ \tilde{\nu}_\text{e} - 49/4\ \tilde{\nu}_\text{e}\chi_e\ \text{cm}^{-1}$

$\tilde{G}(2) = 5/2\ \tilde{\nu}_\text{e} - 25/4\ \tilde{\nu}_\text{e}\chi_e\ \text{cm}^{-1}$

$\tilde{G}(1) = 3/2\ \tilde{\nu}_\text{e} - 9/4\ \tilde{\nu}_\text{e}\chi_e\ \text{cm}^{-1}$

$\tilde{G}(0) = 1/2\ \tilde{\nu}_\text{e} - 1/4\ \tilde{\nu}_\text{e}\chi_e\ \text{cm}^{-1}$

Anharmonic Oscillator



molecule dissociates at v_{max}

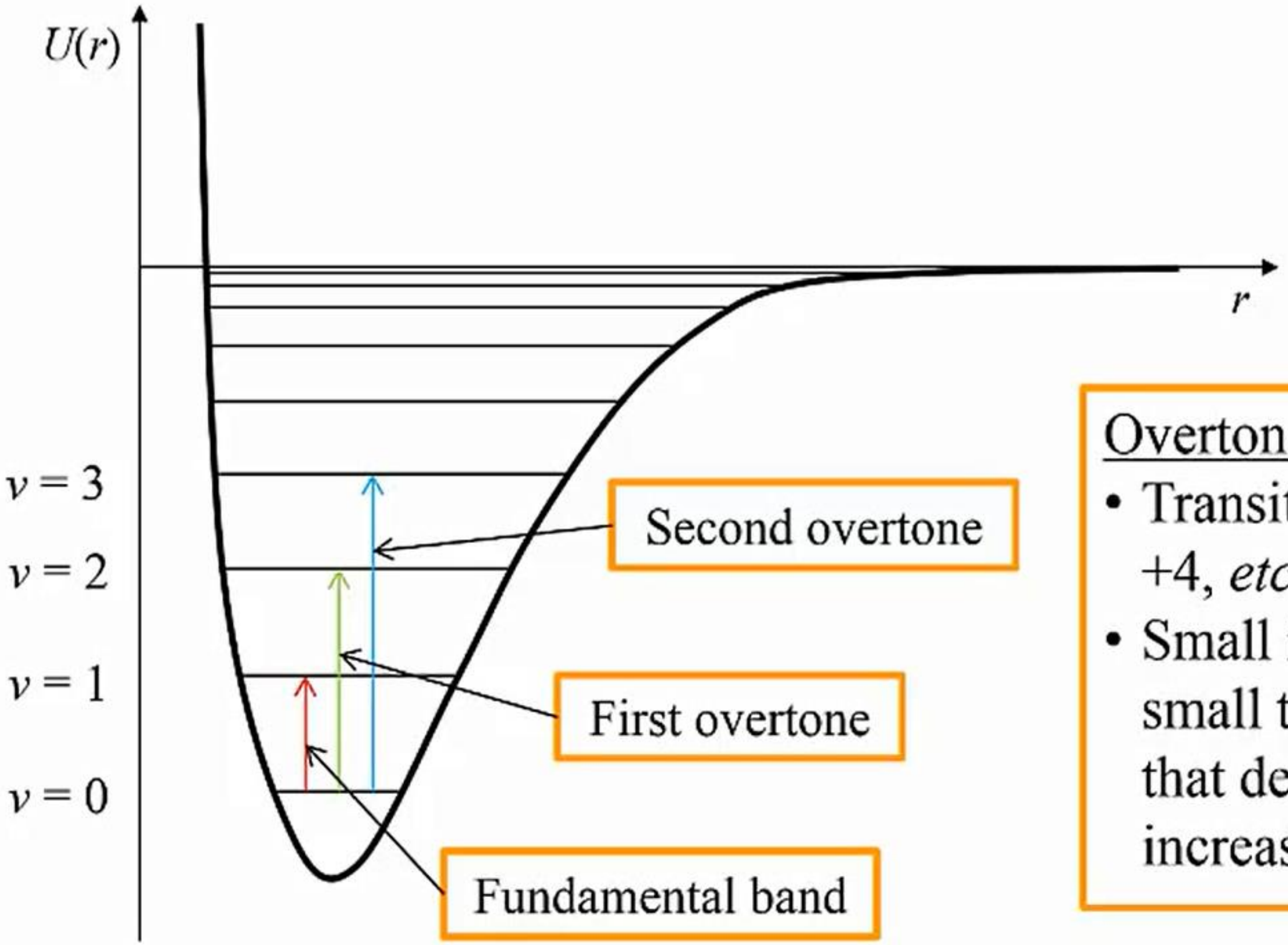
vibrational energy levels get progressively closer together as v increases

$$\tilde{G}(0) = 1/2\ \tilde{\nu}_{\mathrm{e}} - 1/4\ \tilde{\nu}_{\mathrm{e}}\chi_e \ \mathrm{cm}^{-1}$$

Effects of Anharmonicity

- Breakdown of the $\Delta v = \pm 1$ selection rule
- Shift of energy levels
- For an anharmonic oscillator, Δv is arbitrary, but intensities are weaker for $|\Delta v| > 1$
    - This is because the transition moment is small
- Thus we expect to see more transitions than a single peak

Overtone Bands



<u>Overtone bands</u>

- Transitions $\Delta v = +2, +3, +4$, *etc.*
- Small intensity due to small transition moment that decreases as Δv increases

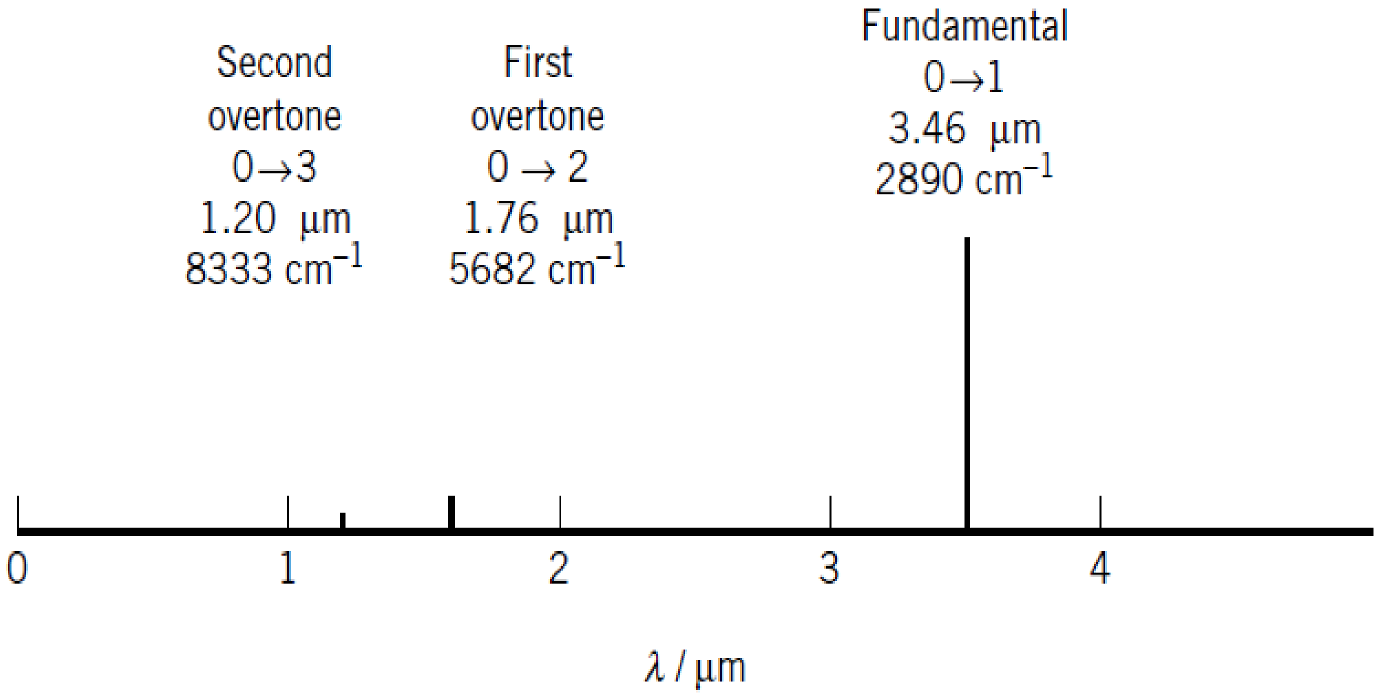
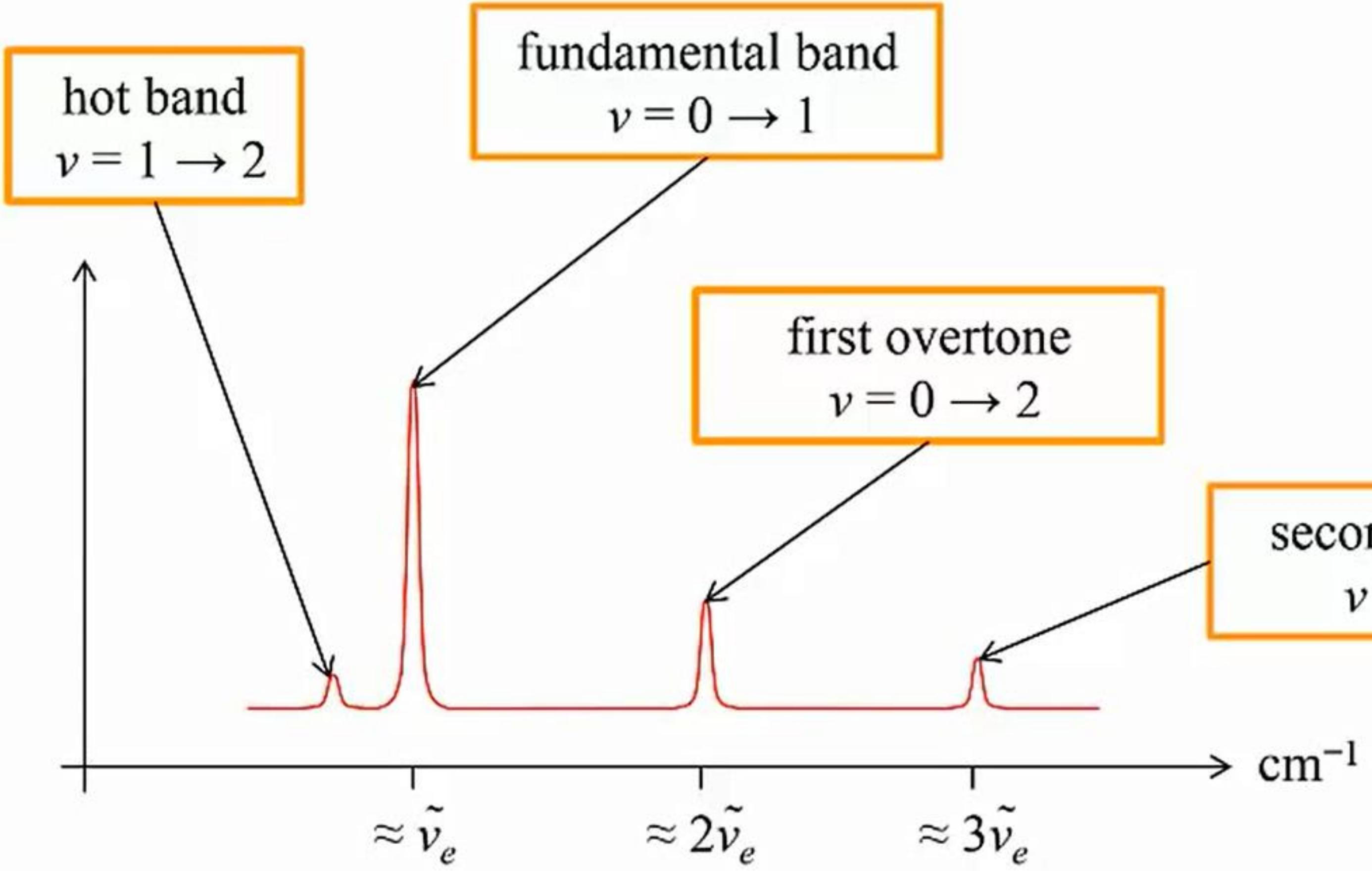


Figure 13.7 "Stick" representation of the vibrational absorption spectrum of $H^{35}Cl$. The relative intensities of the lines fall off five times as fast as indicated.

Vibrational Spectrum of a Diatomic Molecule



hot band
$v = 1 \rightarrow 2$

fundamental band
$v = 0 \rightarrow 1$

first overtone
$v = 0 \rightarrow 2$

second overtone
$v = 0 \rightarrow 3$

- If χ_e is small, $\tilde{\nu}_0 = \tilde{G}(1) - \tilde{G}(0) \approx \tilde{\nu}_e$
- If χ_e is not small, $\tilde{\nu}_0 = \tilde{G}(1) - \tilde{G}(0) = \tilde{\nu}_e - 2\tilde{\nu}_e \chi_e$

The spacing between vibrational level is 10^3cm^{-1}.

$$\frac{N_{v=1}}{N_{v=0}} = \exp\left\{-\frac{6{\cdot}63 \times 10^{-34} \times 3 \times 10^{10} \times 10^{3}}{1{\cdot}38 \times 10^{-23} \times 300}\right\}$$

$$\approx \exp(-4{\cdot}8) \approx 0{\cdot}008.$$

Thus to a very good approximation, we may ignore all transitions originating from ϑ= 1 or more.

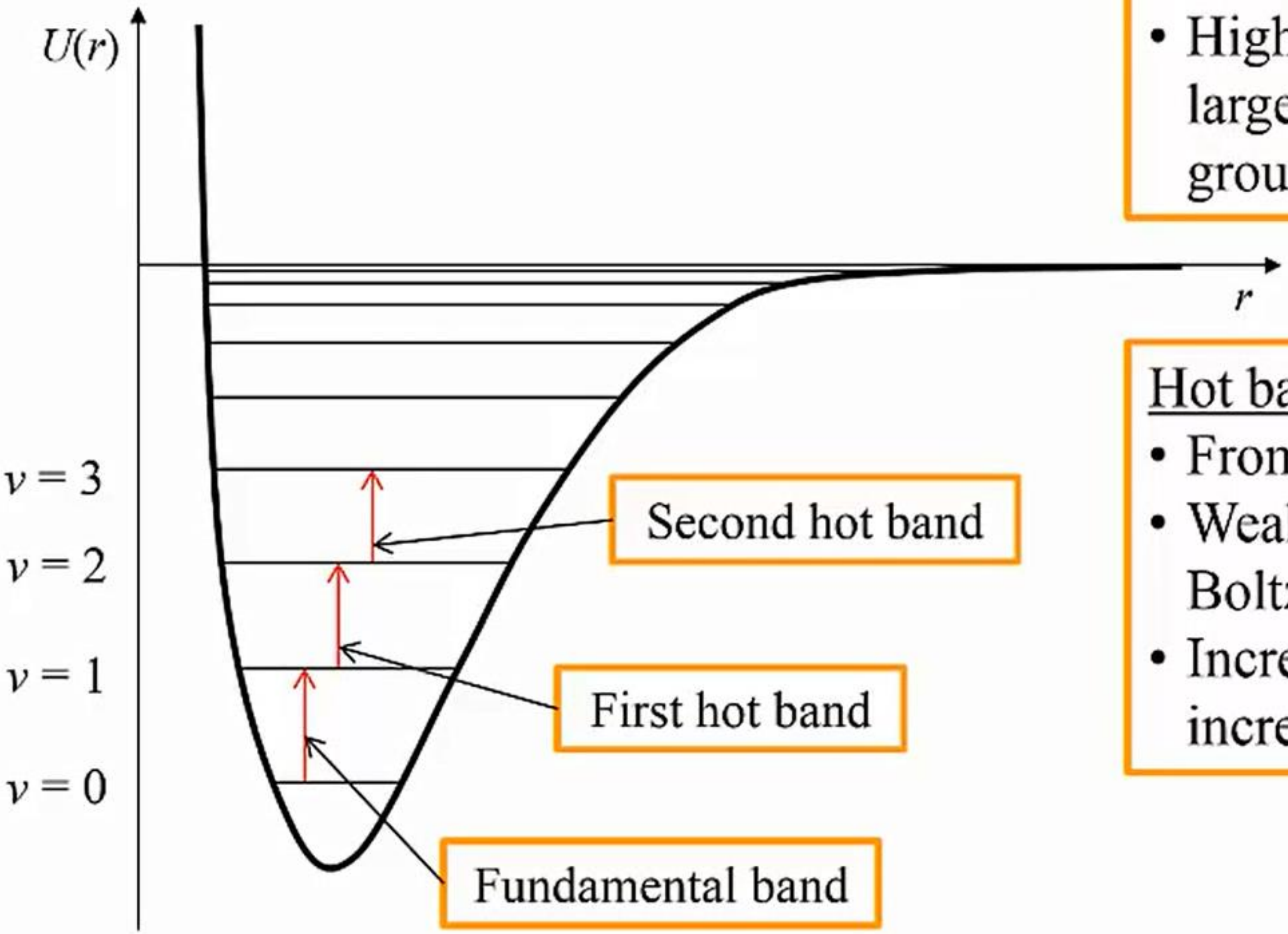
ΔE_{rot} = 10-100 Joul/mole

ΔE_{vib} = 10000 Joul/mole

$k_B T \approx$ 2.4 kJ/mole

ΔE_{ele} = 100 **KJ/** mole

Fundamental Band *vs*. Hot Bands

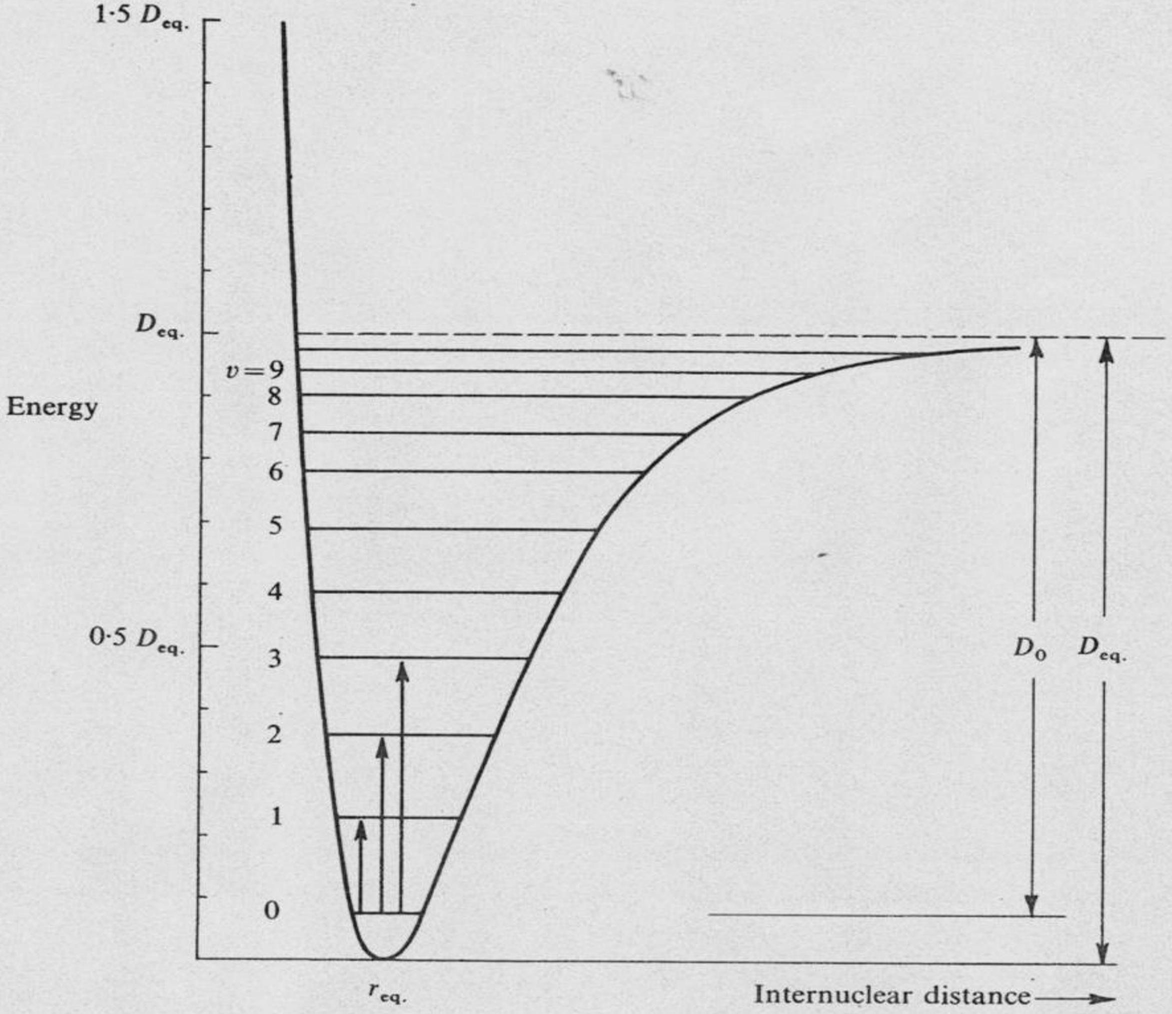


Fundamental band

- $v = 0 \rightarrow v = 1$
- High intensity due to a large population of the ground state

Hot bands

- From $v = 1$ or higher
- Weak intensity due to Boltzmann distribution
- Increases as temperature increases


1·5 $D_{eq.}$
$D_{eq.}$
Energy
$v=9$
8
7
6
5
4
0·5 $D_{eq.}$
3
2
1
0
D_0
$D_{eq.}$
$r_{eq.}$
Internuclear distance

Vibrational Frequency

- The force constant for the Morse potential, k_{M}, is determined from the curvature:

$$k_{\mathrm{M}} = \left(\frac{d^2 U(r)}{dr^2} \right)_{r=r_e} = 2D_e a^2$$

- Thus the frequency is given by

$$\nu_e = \frac{1}{2\pi} \sqrt{\frac{k_{\mathrm{M}}}{\mu}} = \frac{1}{2\pi} \sqrt{\frac{2D_e a^2}{\mu}}$$

1. $v = 0 \rightarrow v = 1$, $\Delta v = +1$, with considerable intensity.

$$\Delta\varepsilon = \varepsilon_{v=1} - \varepsilon_{v=0}$$

$$= \bar{\omega}_e(1 - 2x_e) \quad \text{cm}^{-1}$$

2. $v = 0 \rightarrow v = 2$, $\Delta v = +2$, with small intensity.

$$= 2\bar{\omega}_e(1 - 3x_e) \quad \text{cm}^{-1}$$

3. $v = 0 \rightarrow v = 3$, $\Delta v = +3$, with normally negligible intensity.

$$= 3\bar{\omega}_e(1 - 4x_e) \quad \text{cm}^{-1}$$

Note:

$$\bar{\nu}_e = \bar{\omega}_e$$

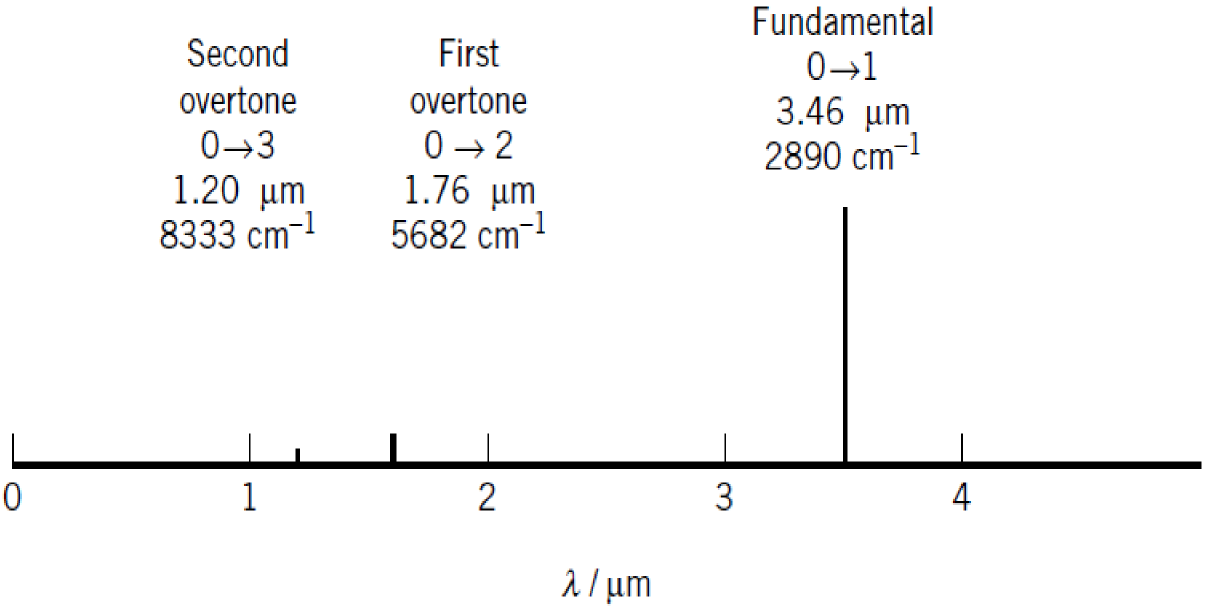


Figure 13.7 “Stick” representation of the vibrational absorption spectrum of $H^{35}Cl$. The relative intensities of the lines fall off five times as fast as indicated.

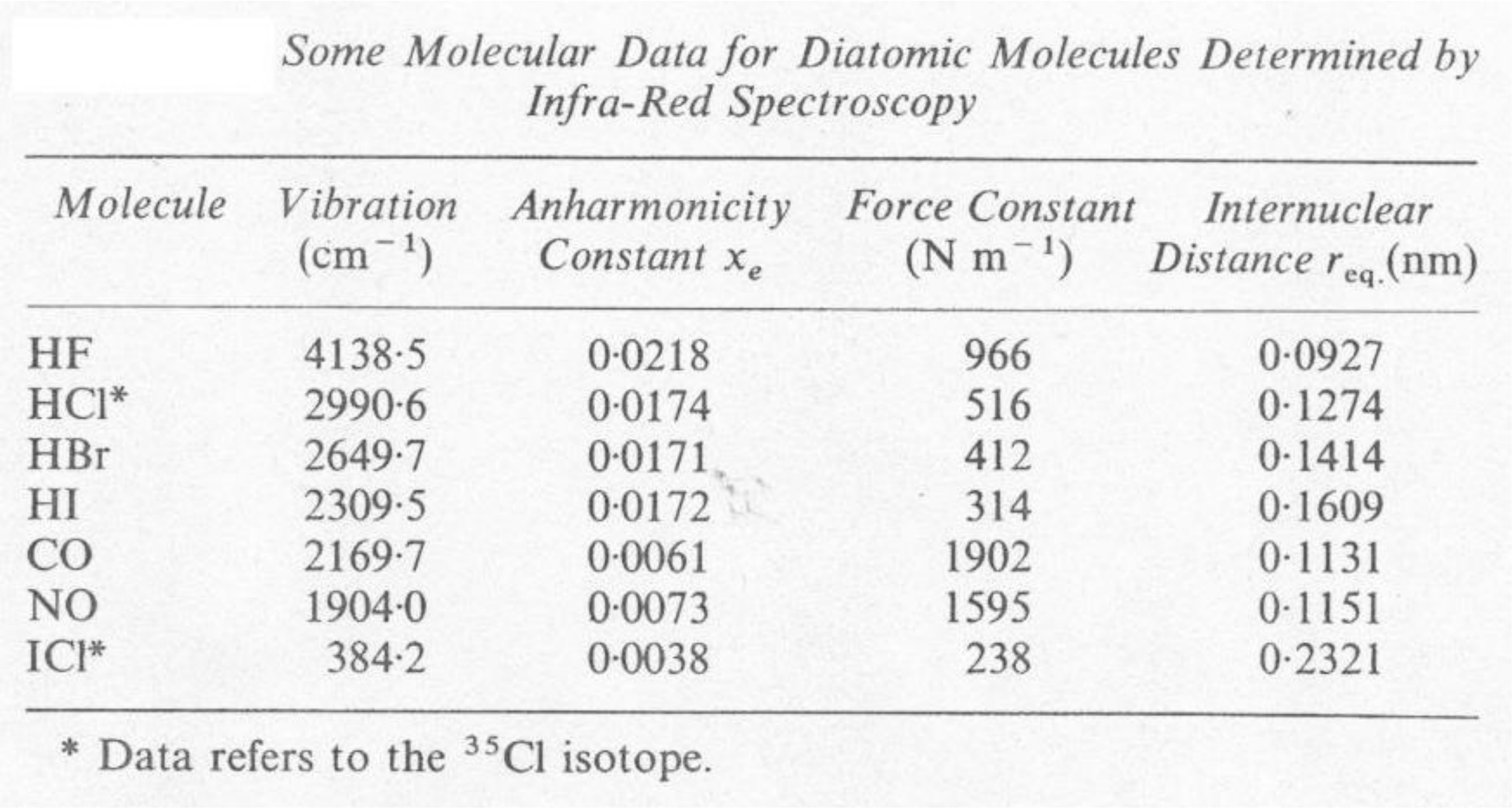
$$= \bar{\omega}_e(1 - 2x_e) \quad \text{cm}^{-1} \qquad = 2890$$

$$= 2\bar{\omega}_e(1 - 3x_e) \quad \text{cm}^{-1} \qquad = 5682$$

$$= 3\bar{\omega}_e(1 - 4x_e) \quad \text{cm}^{-1} \qquad = 8333$$

$\bar{\omega}_e$ **= 2990 cm^{-1}** $\qquad x_e = 0{\cdot}0174$

Fundamental vibration peak in the IR spectrum and the force constants for some diatomic molecules



Some Molecular Data for Diatomic Molecules Determined by Infra-Red Spectroscopy

Molecule	*Vibration* (cm^{-1})	*Anharmonicity Constant* x_e	*Force Constant* (N m^{-1})	*Internuclear Distance* $r_{eq.}$ (nm)
HF	4138·5	0·0218	966	0·0927
HCl*	2990·6	0·0174	516	0·1274
HBr	2649·7	0·0171	412	0·1414
HI	2309·5	0·0172	314	0·1609
CO	2169·7	0·0061	1902	0·1131
NO	1904·0	0·0073	1595	0·1151
ICl*	384·2	0·0038	238	0·2321

* Data refers to the ^{35}Cl isotope.

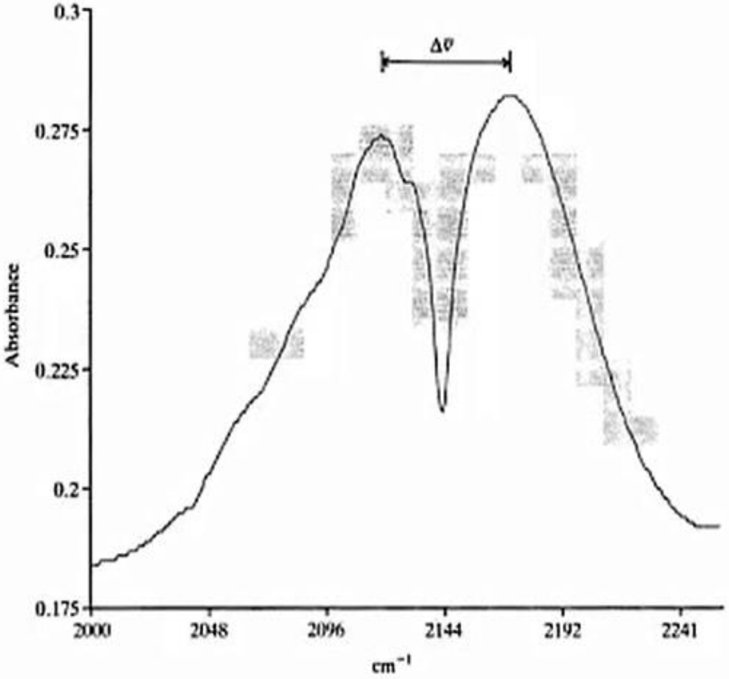
How to experimentally determine about D_e and D_0?

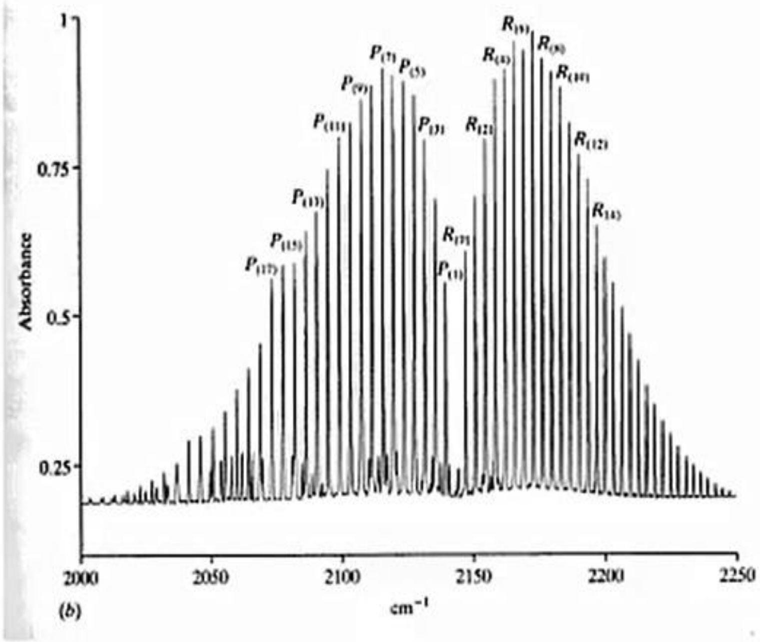
Hint:

$$\tilde{G}(\vartheta) = \tilde{v}_e\,(\vartheta+1/2) - \tilde{v}_e\,\tilde{\chi}_e\,(\vartheta+1/2)^2.$$

06/02/2017

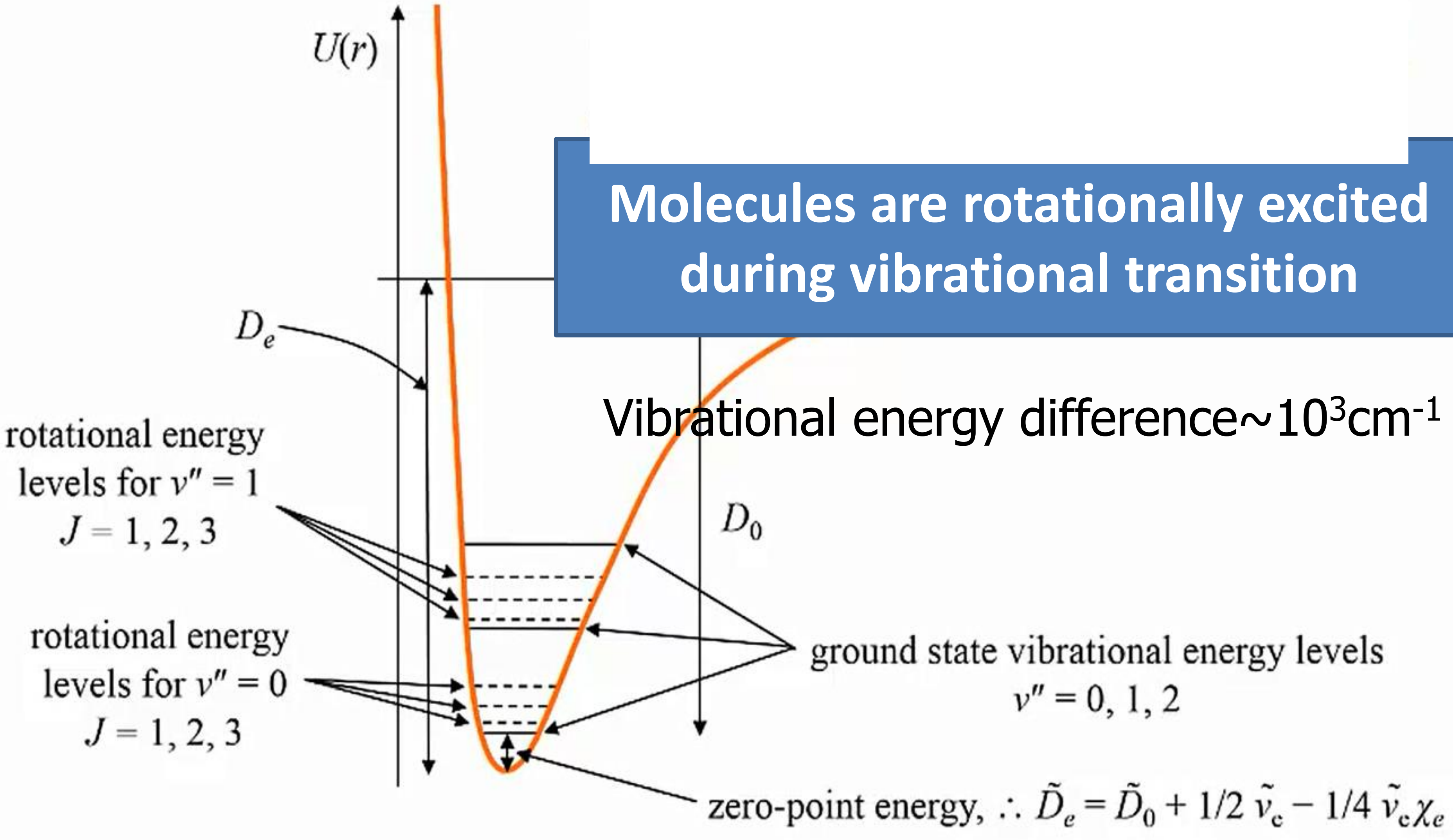
Vibrational Spectrum of CO





- At low resolution, cannot resolve the separation of the fine rotational lines:
- At high resolution, rovibrational lines are resolved:

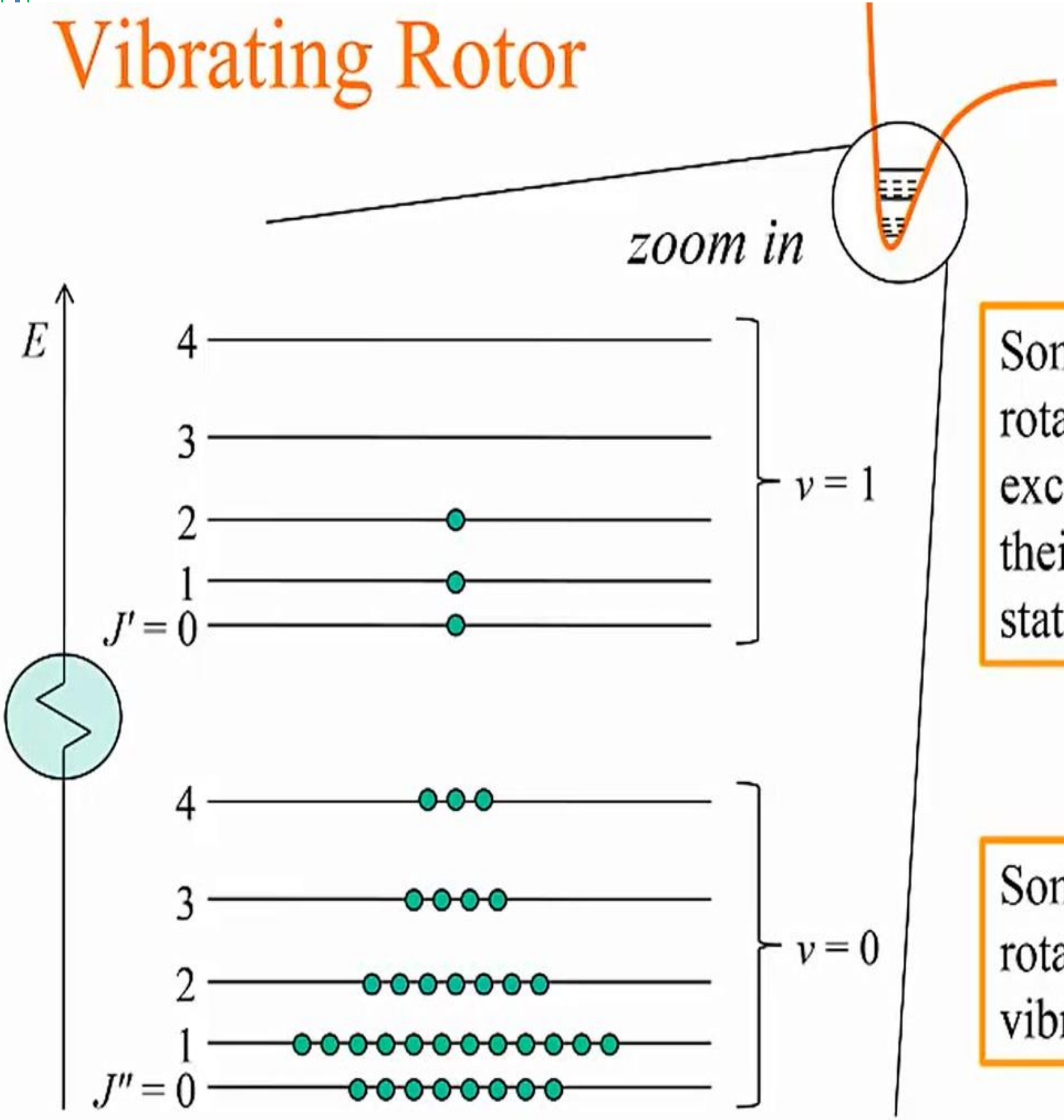
Diatomic Vibrating Rotor



Molecules are rotationally excited during vibrational transition

Vibrational energy difference~10^3cm^{-1}

Vibrating Rotor



Some molecules are rotationally excited or de-excited when promoted to their vibrational excited states

Some molecules are rotationally excited in their vibrational ground states

Rovibrational Energy of rigid diatomic molecules

Absorption of infrared region, molecules can change vibrational and rotational states because vibrational transitions can couple with rotational transitions to give rovibrational spectra.

By Treating as harmonic oscillator and rigid rotor, energy of vibration and rotation can expressed as:

- **Total energy of rovibration motion:**

$$\mathbf{E_{rovib} = E_{rot} + E_{vibr}}$$

Independent Vibrations and Rotations

- Ignoring centrifugal distortion

$$\tilde{S}(v,J)=\tilde{G}(v)+\tilde{F}(J) \qquad \boxed{\text{cm}^{-1}}$$

$$\tilde{S}(v,J)=\underbrace{(v+1/2)\tilde{\nu}_e-(v+1/2)^2\,\tilde{\nu}_e\chi_e}_{\boxed{\text{vibrational energy}}}+\underbrace{\tilde{B}J(J+1)}_{\boxed{\text{rotational energy}}}$$

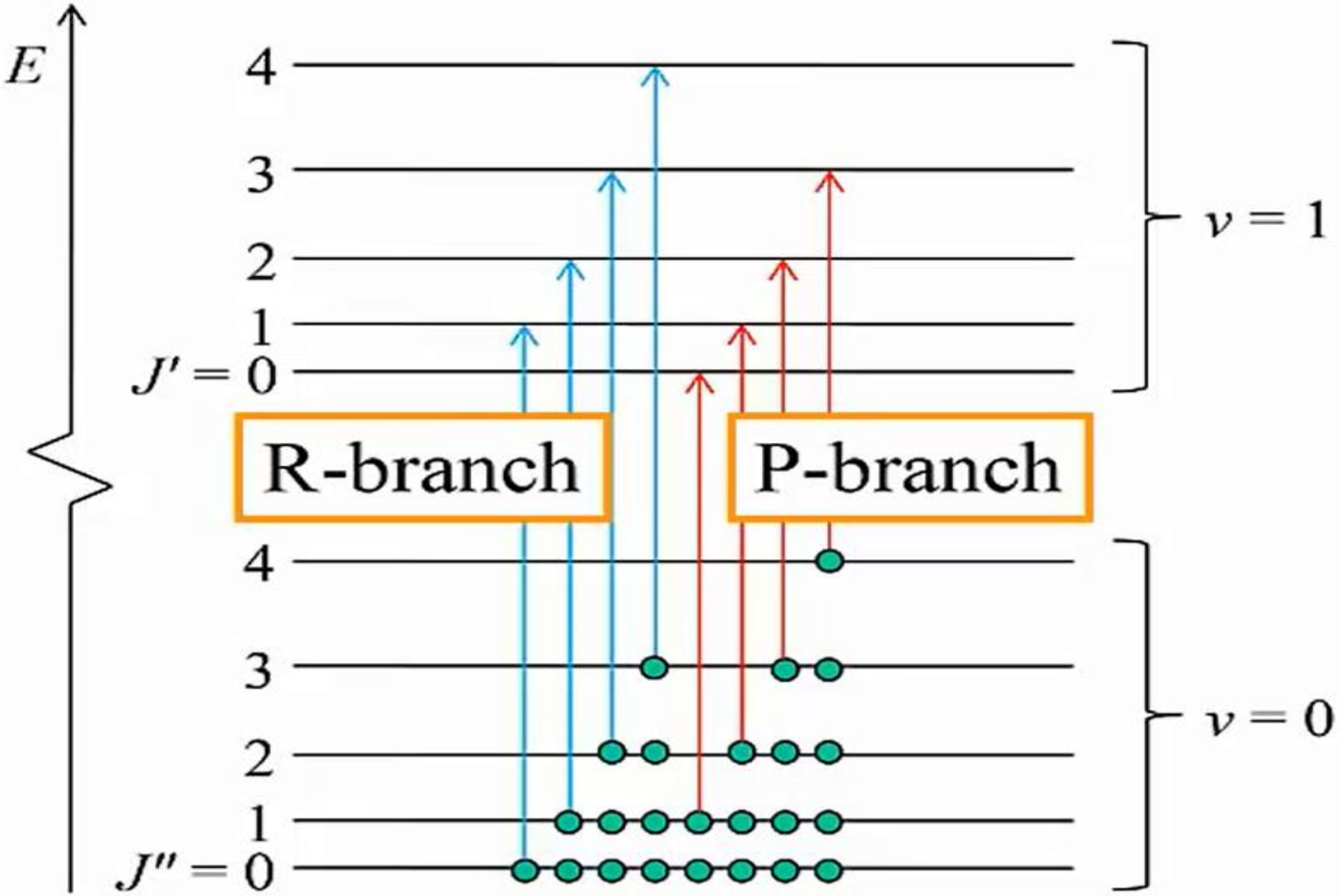
- Total energy is just a simple sum of the vibrational and rotational energies

- Two selection rules apply:

$$\boxed{\Delta v=\pm 1,\pm 2,\ldots} \qquad \boxed{\Delta J=\pm 1}$$

Fundamental Band ($v = 0 \rightarrow 1$)

$$\boxed{\Delta J = \pm 1}$$



Rotational Structure of the Fundamental Band

- P-branch ($J'' \rightarrow J' = J'' - 1$) during $v = 0 \rightarrow 1$ transition

ΔJ = -1

$$\tilde{\nu}_{P(J')} = \tilde{G}(1) + \tilde{B}J'(J'+1) - \tilde{G}(0) - \tilde{B}J''(J''+1)$$

$$= \boxed{\tilde{\nu}_e - 2\tilde{\nu}_e\chi_e} + \tilde{B}J'(J'+1) - \tilde{B}(J'+1)(J'+2)$$

$$= \tilde{\nu}_0 - 2\tilde{B}(J'+1)$$

band origin or band centre

- R-branch ($J'' \rightarrow J' = J'' + 1$) during $v = 0 \rightarrow 1$ transition

ΔJ = +1

$$\tilde{\nu}_{R(J'')} = \tilde{G}(1) + \tilde{B}J'(J'+1) - \tilde{G}(0) - \tilde{B}J''(J''+1)$$

$$= \boxed{\tilde{\nu}_e - 2\tilde{\nu}_e\chi_e} + \tilde{B}(J''+1)(J''+2) - \tilde{B}J''(J''+1)$$

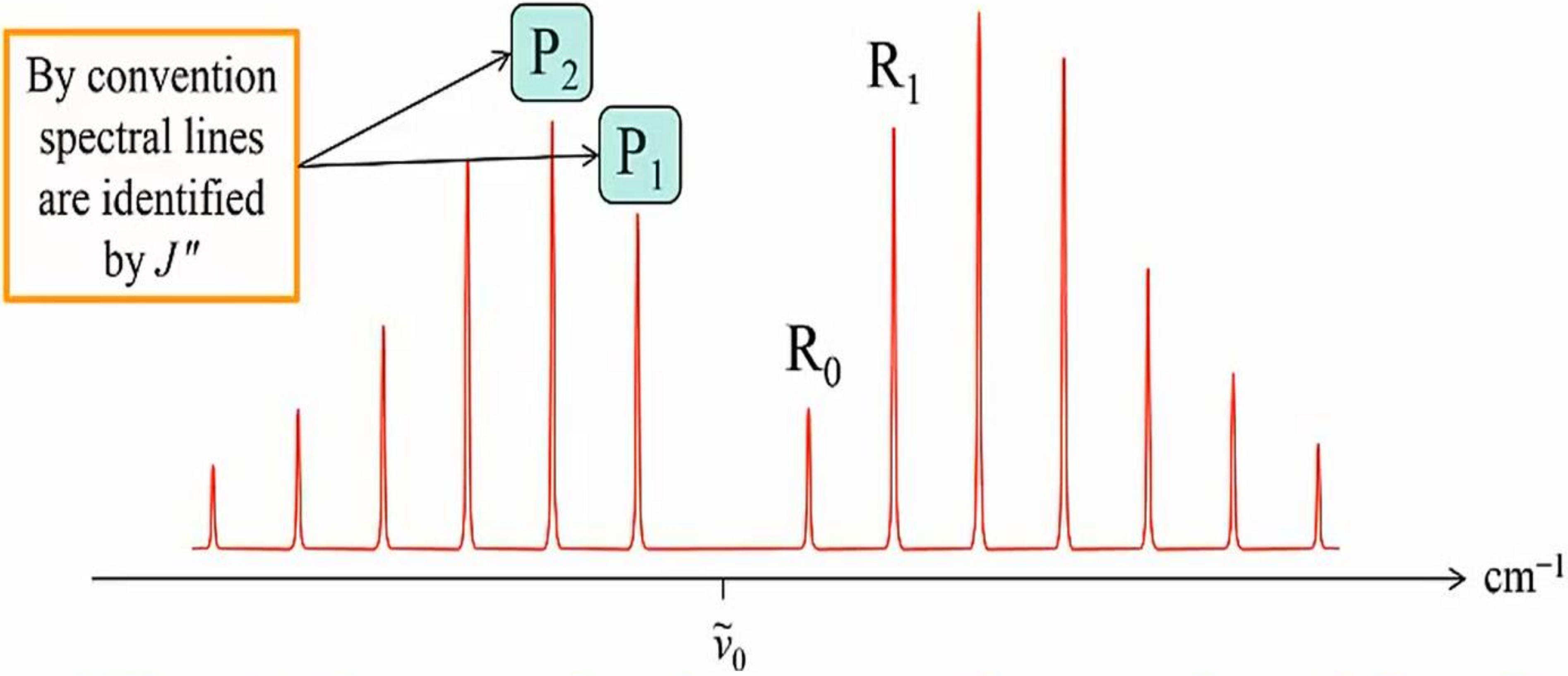
$$= \tilde{\nu}_0 + 2\tilde{B}(J''+1)$$

Rovibrational Spectrum

$$\tilde{\nu}_{P(J')} = \tilde{\nu}_0 - 2\tilde{B}(J'+1)$$

$$\tilde{\nu}_{P(J'')} = \tilde{\nu}_0 - 2\tilde{B}J''$$

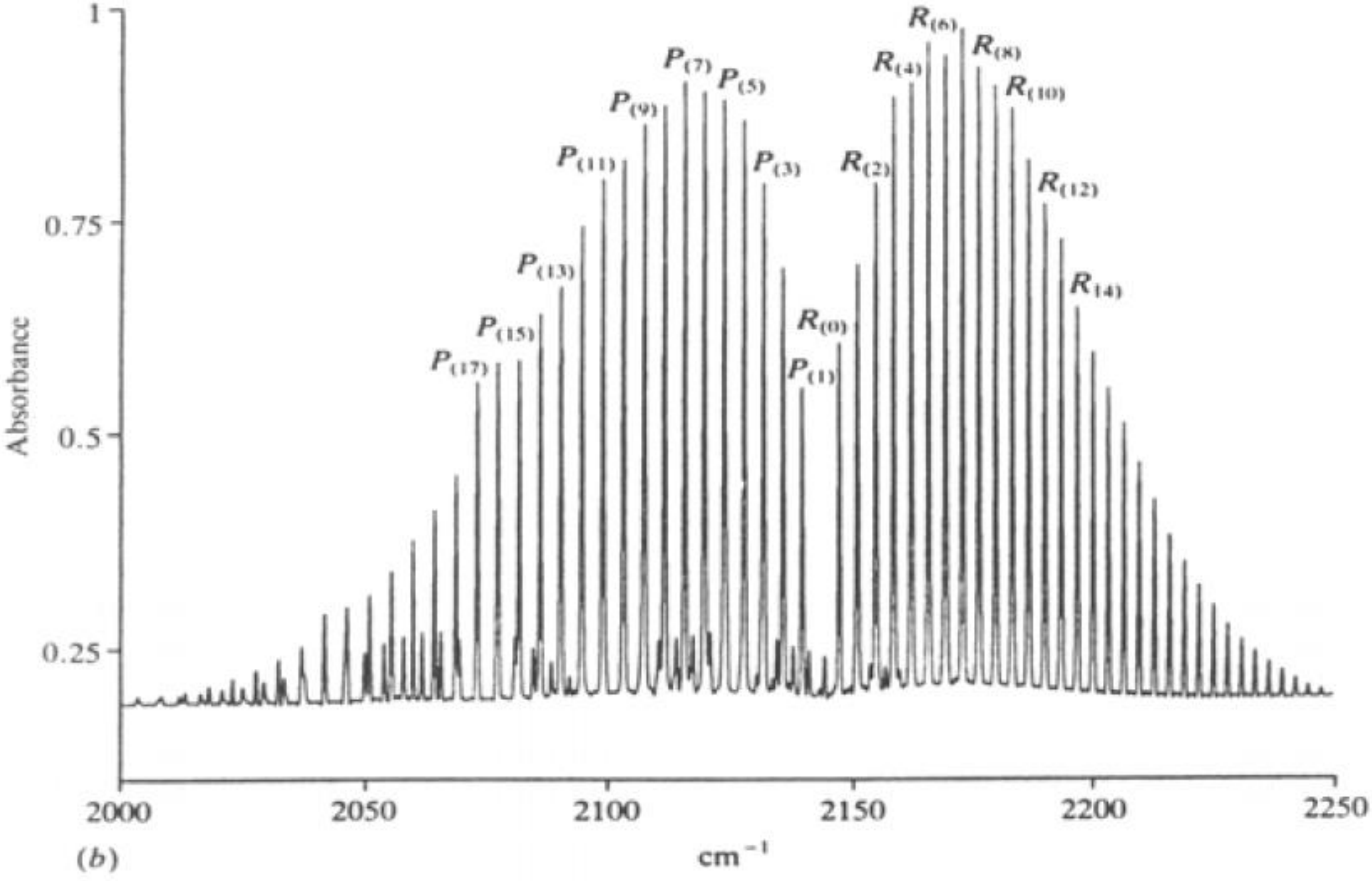
$$\tilde{\nu}_{R(J'')} = \tilde{\nu}_0 + 2\tilde{B}(J''+1)$$



By convention spectral lines are identified by J''

- What is the spacing between the rotational lines?

Vibration-rotational Spectra of Carbon Monoxide



08/02/2017

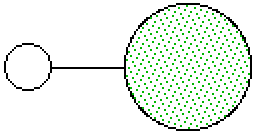
Vibrational feature of Polyatomic Molecules

Vibrations in Molecules

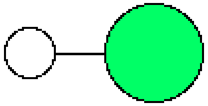
Sym. Stretching

8086 cm^{-1} = 1 eV

HCl $\nu = 2991\ \text{cm}^{-1}$



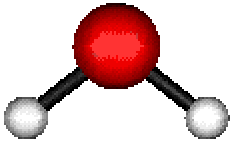
HF $\nu = 4139\ \text{cm}^{-1}$



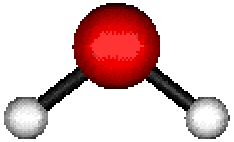
Asym. Stretching

Sym. Bending

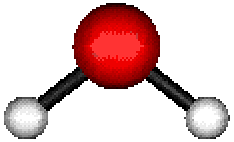
H_2O $\nu_1 = 3835\ \text{cm}^{-1}$



$\nu_3 = 3939\ \text{cm}^{-1}$

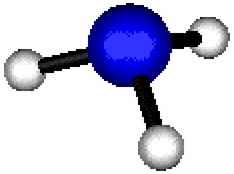


$\nu_2 = 1648\ \text{cm}^{-1}$

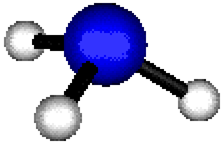


Asym. Bending

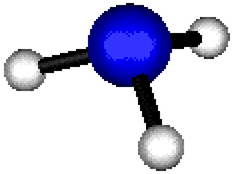
NH_3 $\nu_1 = 3505.7\ \text{cm}^{-1}$



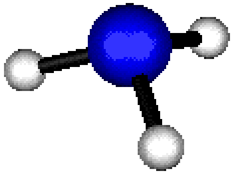
$\nu_3 = 3573.1\ \text{cm}^{-1}$



$\nu_2 = 1022\ \text{cm}^{-1}$



$\nu_4 = 1689.7\ \text{cm}^{-1}$

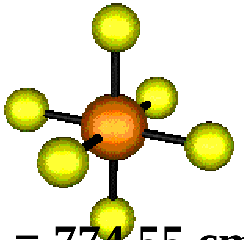


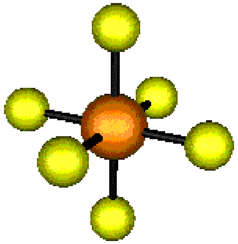
SF_6

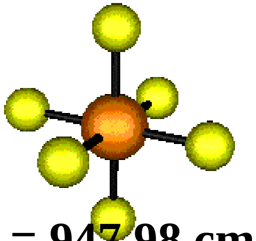
$\nu_5 = 643.35\ \text{cm}^{-1}$

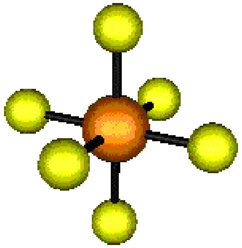
$\nu_2 = 615.02\ \text{cm}^{-1}$

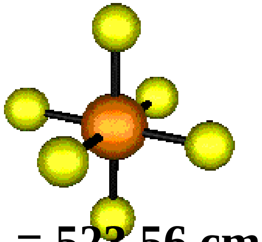
$\nu_6 = 348.08\ \text{cm}^{-1}$

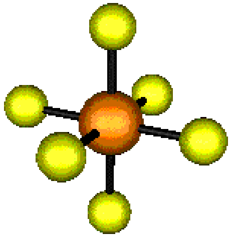












$\nu_1 = 774.55\ \text{cm}^{-1}$

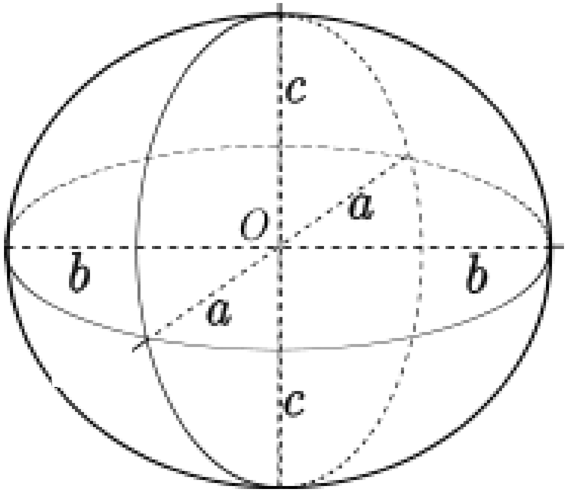
$\nu_3 = 947.98\ \text{cm}^{-1}$

$\nu_4 = 523.56\ \text{cm}^{-1}$

Concept of normal modes in a molecule

- There are 3N possible movements in a molecule made of N atoms, each of which moving in one of three directions, x, y and z.
  - There are three transitional movements: all atoms in the molecule moving in x, y or z direction at the same time.
  - There are three rotational movements around x, y or z-axis
    - Linear molecules are exceptions because two axes that are perpendicular to the molecular axis are identical.
  - The rest of movements are vibrational movements
    - For linear molecules, 3N – 5 movements
    - For non-linear molecules, 3N – 6 movements
  - **All vibrational movements of the sample can be described as linear combinations of vibrational normal modes**.

Classes of Rotating Molecules



b should be replaced by a

★ Molecules can be classified into five main groups depending on their moments of inertia.

1.	$I_C = I_B , I_A = 0$	Linear molecules
2.	$I_C = I_B = I_A$	Spherical top
3.	$I_C = I_B > I_A$	Prolate symmetric top
4.	$I_C > I_B = I_A$	Oblate symmetric top
5.	$I_C > I_B > I_A$	Asymmetric top

Normal Modes of Vibrations:

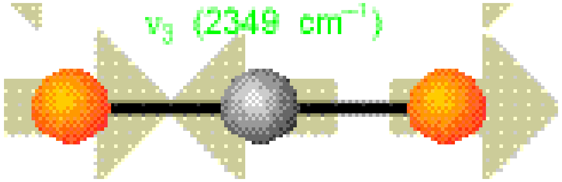
N isolated atoms have $3N$ degrees of freedom (x, y, z translations for each)

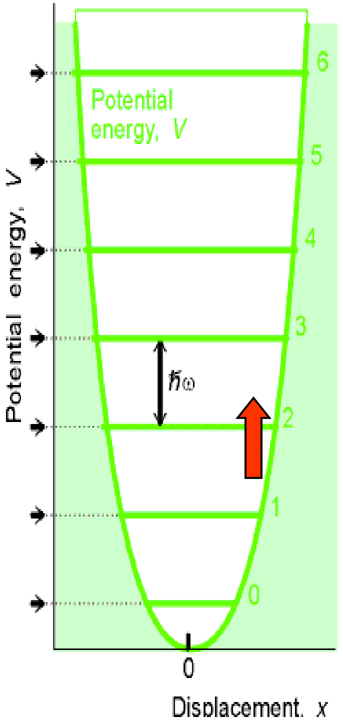
N atoms in a molecule have $3N$ degrees of freedom arranged amongst translations, vibrations and rotations:

Molecule:	**Linear**	**Non-linear**
no. translations =	**3**	**3**
no. rotations =	**2**	**3**
$\therefore$ no. vibrations =	**$3N-5$**	**$3N-6$**

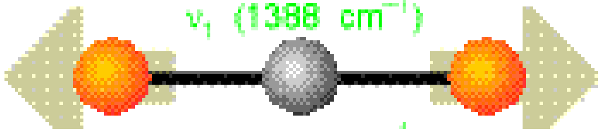
Vibrational Modes of Carbon Dioxide

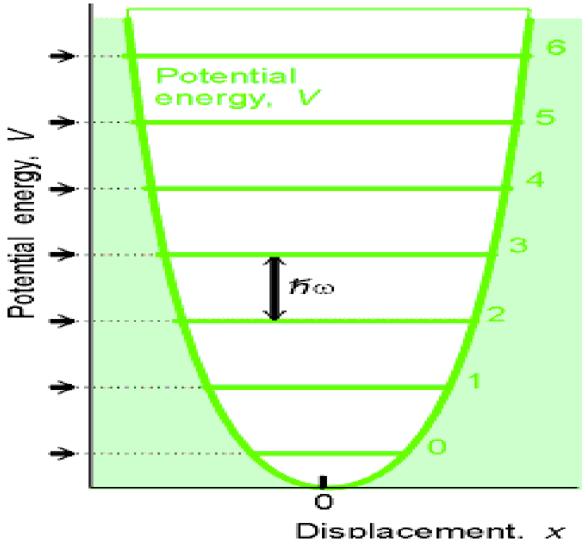
Antisymmetric stretching





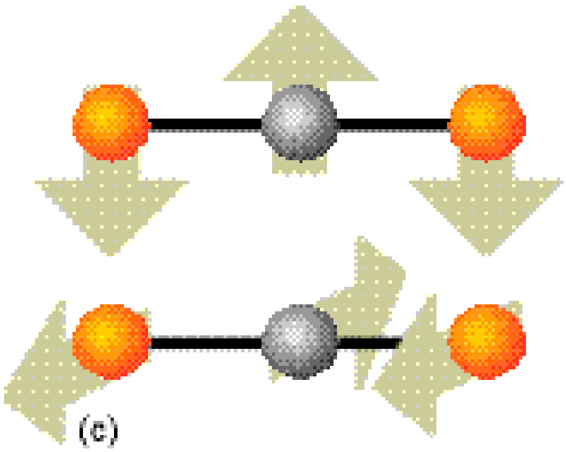
Symmetric stretching

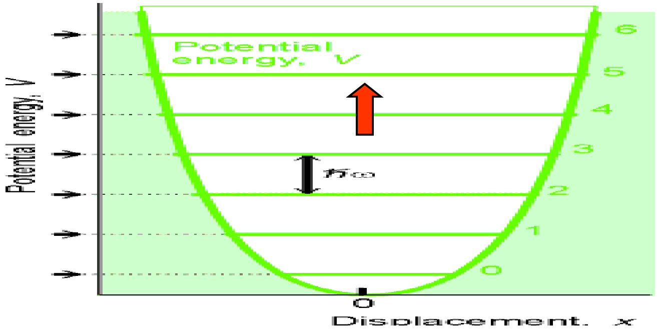




Not IR Active

2 Bending modes of same frequency



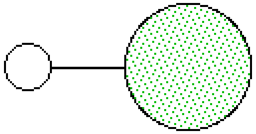


Vibrations in Molecules

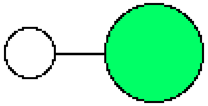
Sym. Stretching

8086 cm^{-1} = 1 eV

HCl $\nu = 2991\ \mathrm{cm}^{-1}$



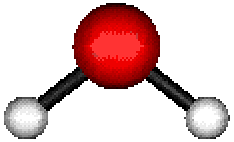
HF $\nu = 4139\ \mathrm{cm}^{-1}$



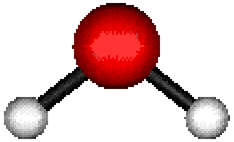
Asym. Stretching

Sym. Bending

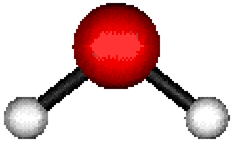
H_2O $\nu_1 = 3835\ \mathrm{cm}^{-1}$



$\nu_3 = 3939\ \mathrm{cm}^{-1}$

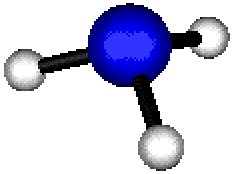


$\nu_2 = 1648\ \mathrm{cm}^{-1}$

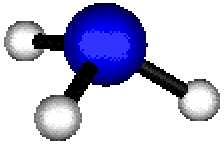


Asym. Bending

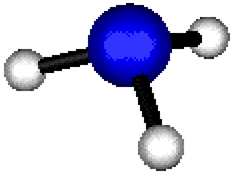
NH_3 $\nu_1 = 3505.7\ \mathrm{cm}^{-1}$



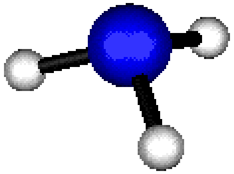
$\nu_3 = 3573.1\ \mathrm{cm}^{-1}$



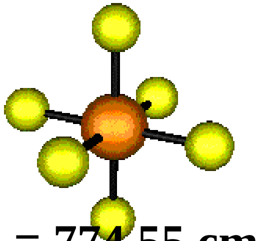
$\nu_2 = 1022\ \mathrm{cm}^{-1}$



$\nu_4 = 1689.7\ \mathrm{cm}^{-1}$

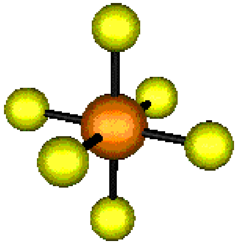


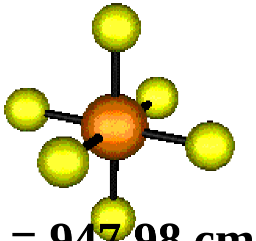
SF_6



$\nu_1 = 774.55\ \mathrm{cm}^{-1}$

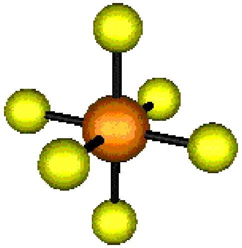
$\nu_5 = 643.35\ \mathrm{cm}^{-1}$

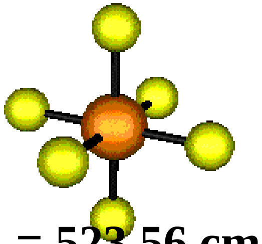




$\nu_3 = 947.98\ \mathrm{cm}^{-1}$

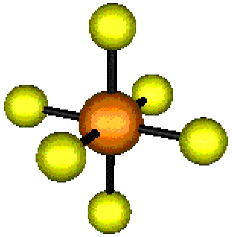
$\nu_2 = 615.02\ \mathrm{cm}^{-1}$





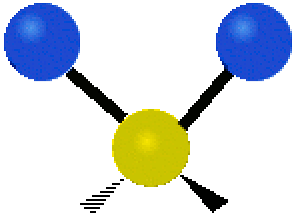
$\nu_4 = 523.56\ \mathrm{cm}^{-1}$

$\nu_6 = 348.08\ \mathrm{cm}^{-1}$

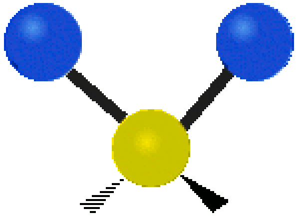


Vibrations of a methylene group ($-CH_2-$) in a molecule for illustration

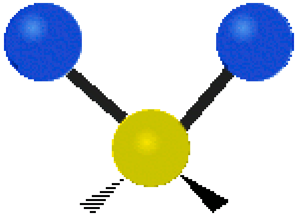
Symmetrical stretching

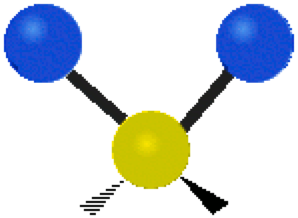


Asymmetrical stretching

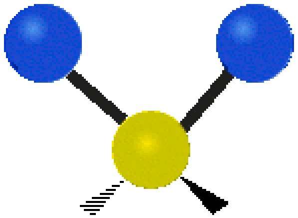


Scissoring (Bending)

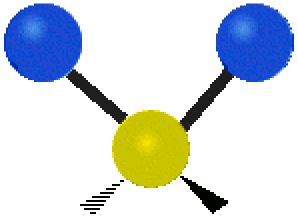




Rocking



Wagging



Twisting

In the normal coordinate system, the vibrational Hamiltonian of polyatomic system can be written as:

$$H = \sum_{i=1}^{3N-6} H_i(Q_i) = H_1(Q_1) + H_2(Q_2) + H_3(Q_3) + \ldots$$

$$H = \sum_{i=1}^{3N-6} \left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} k_i Q_i^2 \right]$$

$$H = \left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial Q_1^2} + \frac{1}{2} k_1 Q_1^2 \right] + \left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial Q_2^2} + \frac{1}{2} k_2 Q_2^2 \right] + \left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial Q_3^2} + \frac{1}{2} k_3 Q_3^2 \right] + \ldots$$

Therefore, the wave function is of the form :

$$\Psi = \prod_{i=1}^{3N-6} \psi_i(Q_i) = \psi_1(Q_1) \bullet \psi_2(Q_2) \bullet \psi_3(Q_3) \bullet \ldots$$

The total vibrational energy is:

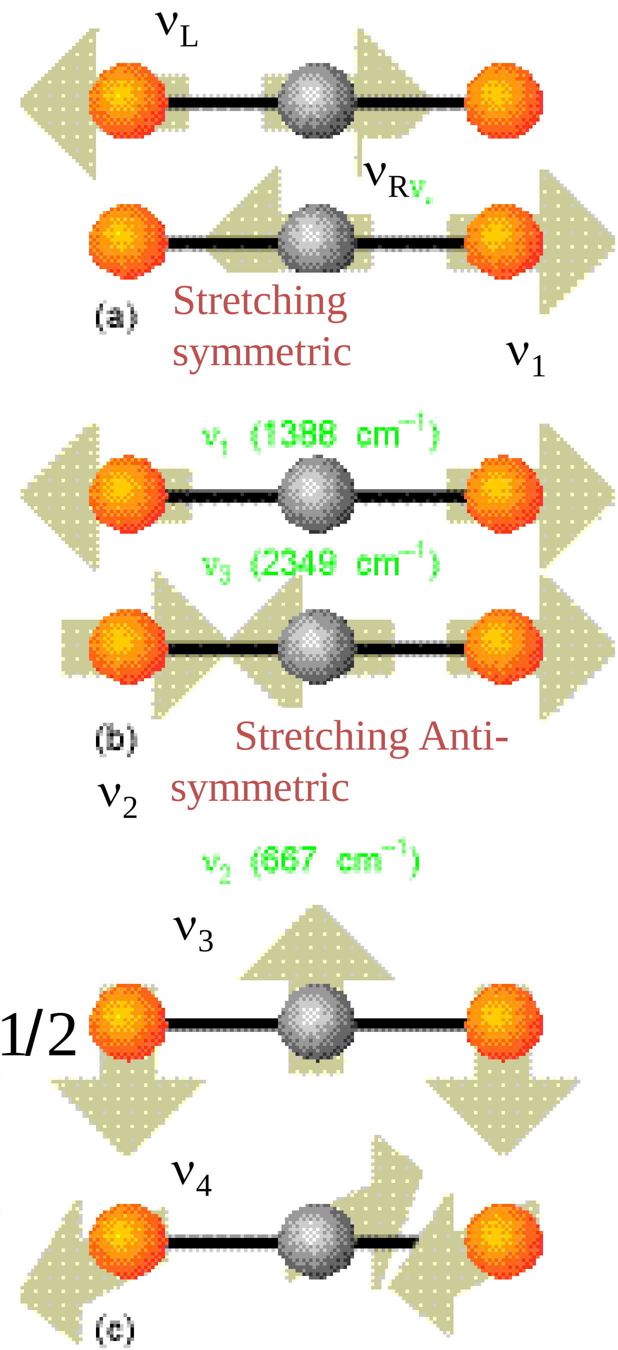
$$E(n_1 n_3 n_3 \ldots) = \sum_{i=1}^{3N-6} \left(n_i + \frac{1}{2} \right) h\nu_i = \left(n_1 + \frac{1}{2} \right) h\nu_1 + \left(n_2 + \frac{1}{2} \right) h\nu_2 + \left(n_3 + \frac{1}{2} \right) h\nu_3 + \ldots$$

◆**Example: CO_2 , 3 atoms, 3N-5= 4 modes**

➔ It's possible to find specific modes that are independent, that is **if one is excited, it does not excite the other**: these are the normal modes. For CO_2, these are: ν_1, ν_2, ν_3 and ν_4.

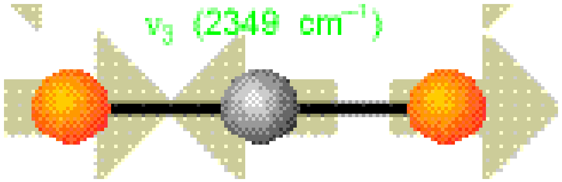
➔ **Each normal mode q behaves like an independent harmonic oscillator** (approximation), so has a series of terms $G_q(\upsilon)$ where is the wavenumber of the mode q and depends on the force constant k_q and the effective mass of the mode m_q.

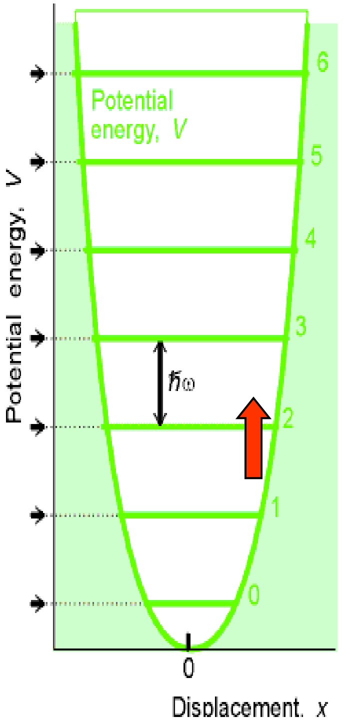
$$G_q(\upsilon) = \left(\upsilon + \frac{1}{2}\right)\tilde{\nu}_q \;\; ; \;\; \upsilon = 0,1,2,\ldots \qquad \tilde{\nu}_q = \frac{1}{2\pi c}\left(\frac{k_q}{m_q}\right)^{1/2}$$



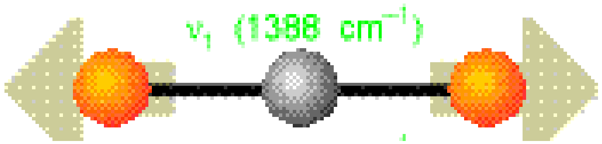
Vibrational modes of C0$_2$

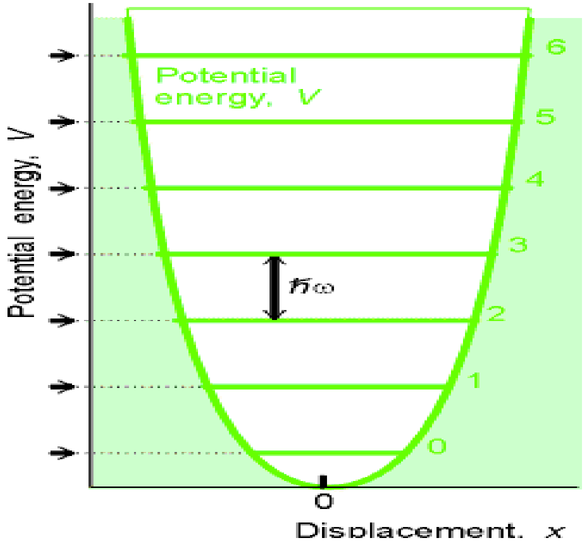
Antisymmetric stretching





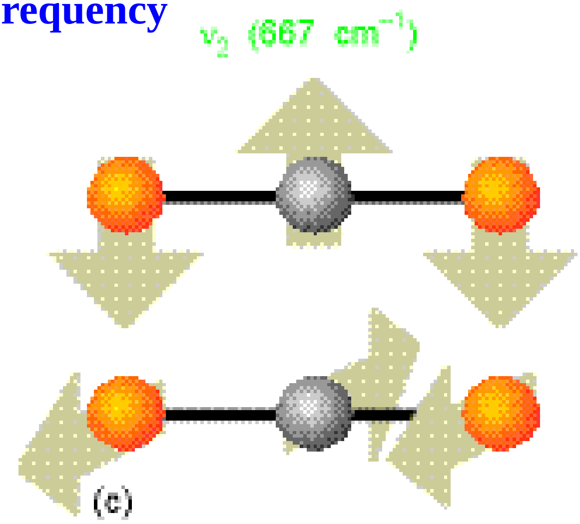
Symmetric stretching

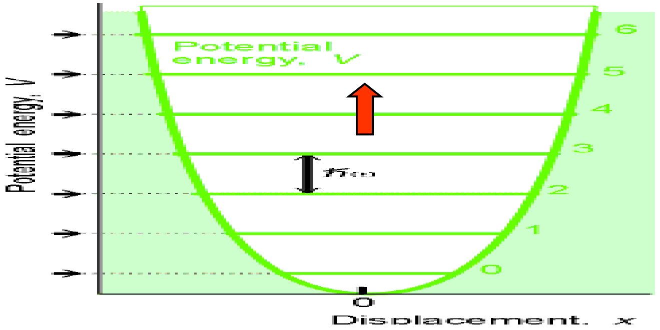




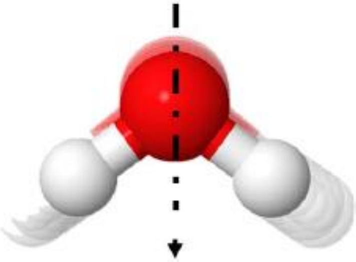
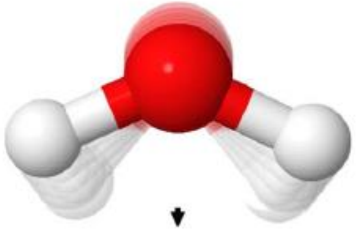
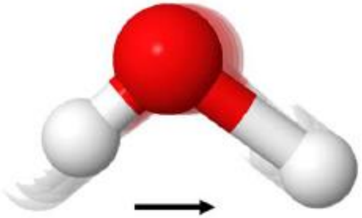
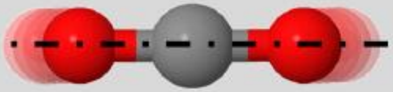
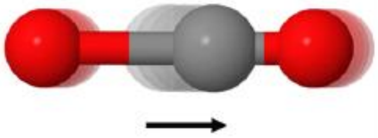
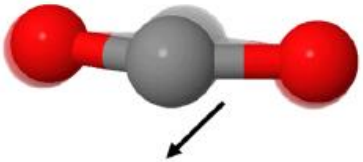
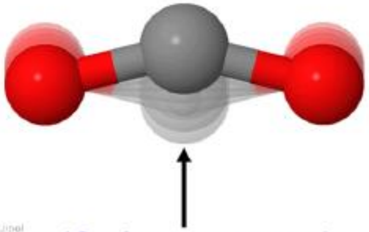
Not IR Active

2 Bending modes of same frequency





- Parallel and perpendicular modes

Examples:	**Parallel (||)** Dipole changes are || to the main axis of symmetry		**Perpendicular (⊥)** Dipole changes are ⊥ to the main axis of symmetry	
H_2O ($3x3-6=3$ vib. modes)	 Symmetric stretch $\nu_1=3652cm^{-1}$	 Symmetric bending $\nu_2=1595cm^{-1}$	 Asymmetric stretch $\nu_3=3756cm^{-1}$	
CO_2 ($3x3-5=4$ vib. modes)	 No dipole moment Not IR-active! Symmetric stretch $\nu_1=1330cm^{-1}$	 Asymmetric stretch $\nu_3=2349cm^{-1}$		
			Symmetric bending (2 degenerate) $\nu_2=667cm^{-1}$	

4.2. Types of bands

- Vibrational partition function

$$\boxed{Q_{vib} = \prod_{i}^{\text{modes}} \left[1 - \exp\left(-\frac{hc\omega_{e,i}}{kT}\right)\right]^{-g_i}}$$

E.g., NH$_3$: 3N-6 = 6 vib. modes

Degenerate

$$Q_{vib} = \left[1 - \exp\left(-\frac{hc\omega_{e,1}}{kT}\right)\right]^{-1}\left[1 - \exp\left(-\frac{hc\omega_{e,2}}{kT}\right)\right]^{-1}\left[1 - \exp\left(-\frac{hc\omega_{e,3}}{kT}\right)\right]^{-2}\left[1 - \exp\left(-\frac{hc\omega_{e,4}}{kT}\right)\right]^{-2}$$

Vibration	**Frequency [cm^{-1}]**	**Type**	**Description**
ν_1	3337	||	Symmetric stretch
ν_2	950	||	Symmetric bend
ν_3	3444	⊥	Asymmetric stretch (Degenerate)
ν_4	1627	⊥	Asymmetric bend (Degenerate)

IR Spectrum of Complex Molecules

There are many possible vibrational modes giving rise to complicated spectra with many peaks.

IR spectra are mainly used to identify unknown compounds

The peak positions and intensities of an unknown can be compared with the spectrum of known suspects in the same manner that police use fingerprints

IR Spectrum of Complex Molecules

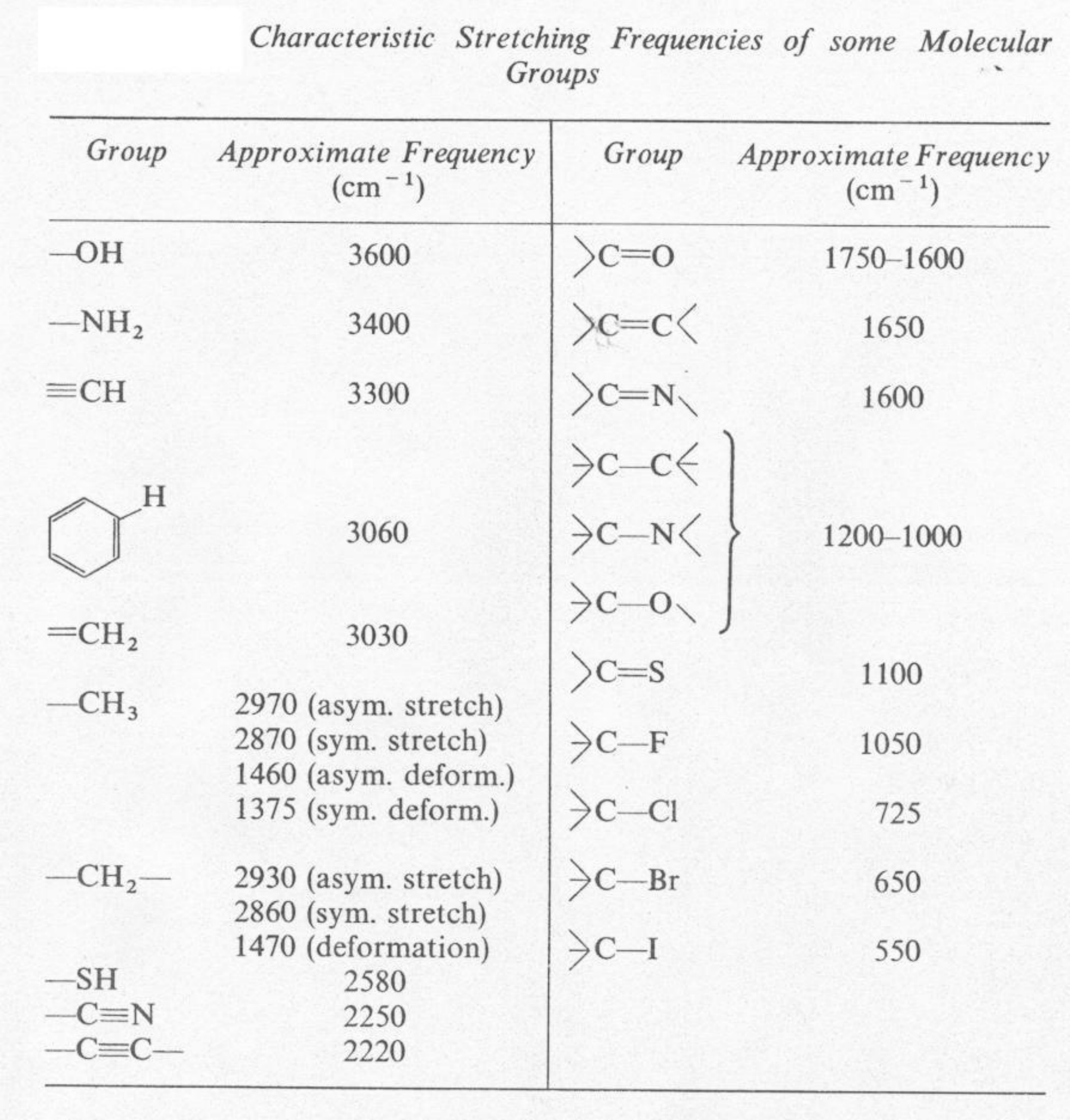
vibrational modes are categorized in the following way:

1. Skeletal vibrations where all the atoms in the molecule move about to some extent.

   These vibrations give rise to absorption peaks in the range 700 – 1400 cm^{-1} which is called the fingerprint region.

2. Functional group vibrations in which only the atoms in that functional group vibrate appreciably.

   Each functional group gives rise to an absorption peak at a characteristic frequency, no matter what the rest of the molecule contains. These peaks can be used to identify the functional groups present in the molecules.



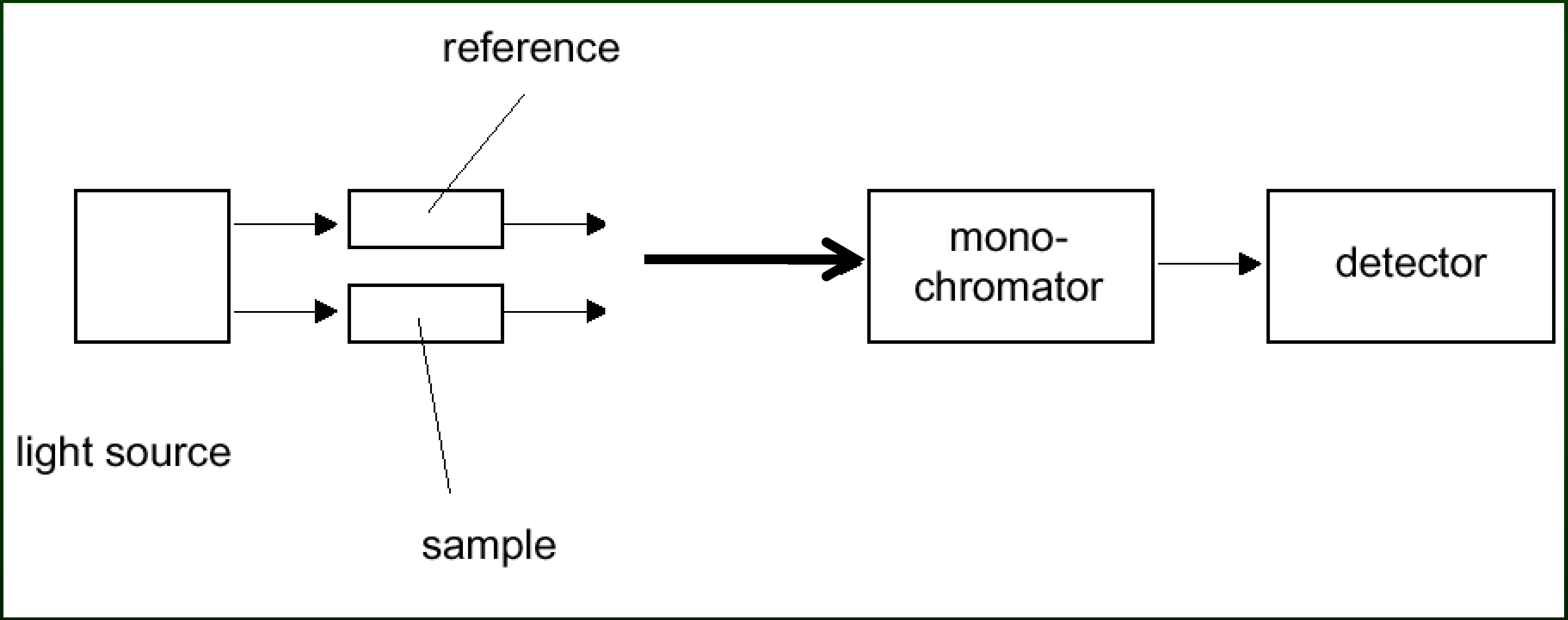
Characteristic Stretching Frequencies of some Molecular Groups

Group	*Approximate Frequency* (cm^{-1})	*Group*	*Approximate Frequency* (cm^{-1})
—OH	3600	>C=O	1750–1600
—NH_2	3400	>C=C<	1650
≡CH	3300	>C=N\	1600
H	3060	>C—C<	1200–1000
		>C—N<	
		>C—O\	
=CH_2	3030	>C=S	1100
—CH_3	2970 (asym. stretch) 2870 (sym. stretch) 1460 (asym. deform.) 1375 (sym. deform.)	>C—F	1050
		>C—Cl	725
—CH_2—	2930 (asym. stretch) 2860 (sym. stretch) 1470 (deformation)	>C—Br	650
		>C—I	550
—SH	2580		
—C≡N	2250		
—C≡C—	2220		

- Dispersive instruments: with a monochromator to be used in the mid-IR region for spectral scanning and quantitative analysis.
- Fourier transform IR (FTIR) systems: widely applied and quite popular in the far-IR and mid-IR spectrometry.
- Nondispersive instruments: use filters for wavelength selection or an infrared-absorbing gas in the detection system for the analysis of gas at specific wavelength.

Dispersive IR spectrophotometers

Modern dispersive IR spectrophotometers are invariably double-beam instruments, but many allow single-beam operation via a front-panel switch.



Simplified diagram of a double beam infrared spectrometer

Dispersive spectrophotometers Designs

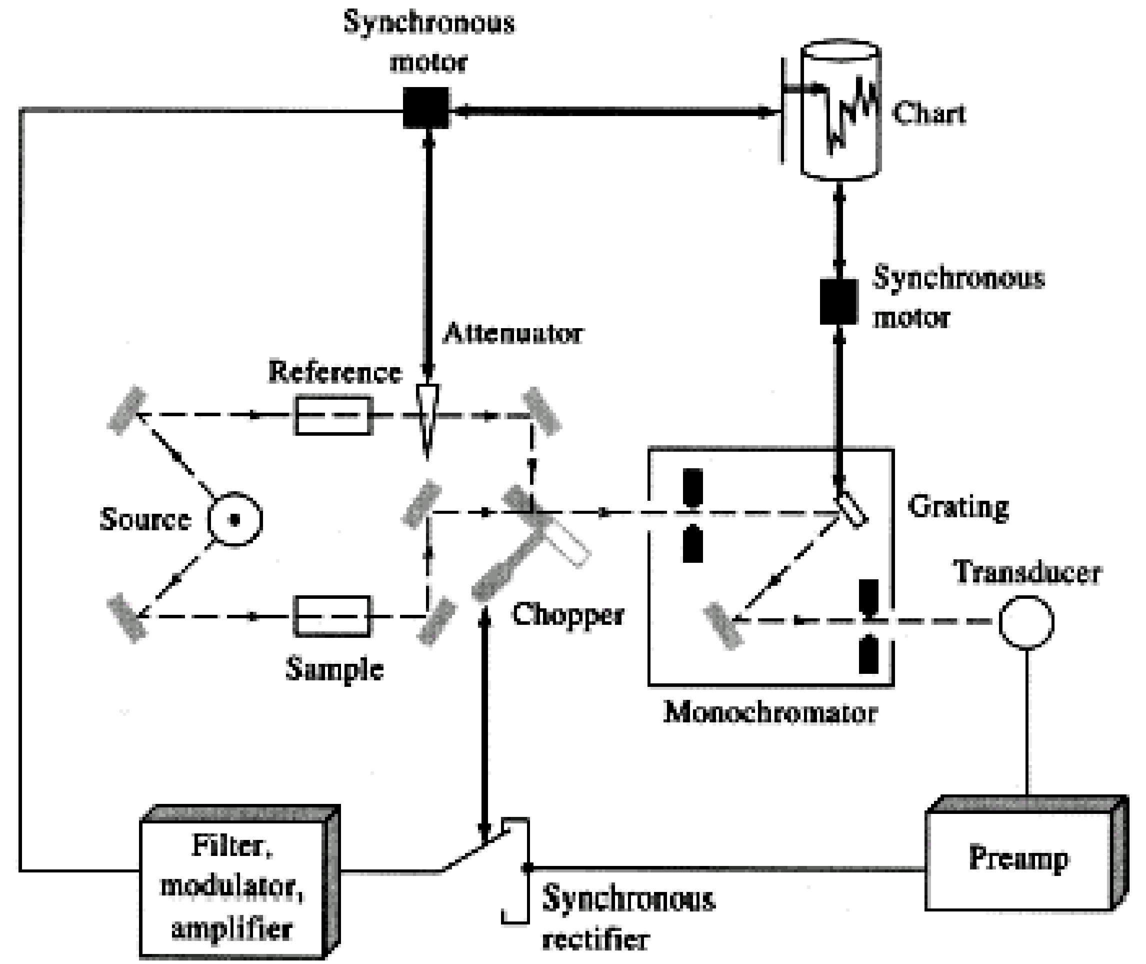
Null type instrument

Double Beam Instrument

Source separated into two separate beams.

Sample and background collected simultaneously.

Monochromator scans through wavelength region



Dispersive Double Beam IR Spectrophotometer

Components of dispersive spectrophotometers

1. IR source

Nernst Glower	heated rare earth oxide rod (~1500 K)	1-50 µm (mid- to far-IR)
Globar	heated SiC rod (~1500 K)	1-50 µm (mid- to far-IR)
W filament lamp	1100 K	0.78-2.5 µm (Near-IR)
Hg arc lamp	plasma	50 - 300 µm (far-IR)
CO2 laser	stimulated emission lines	9-11 µm

2. Detector / transducer

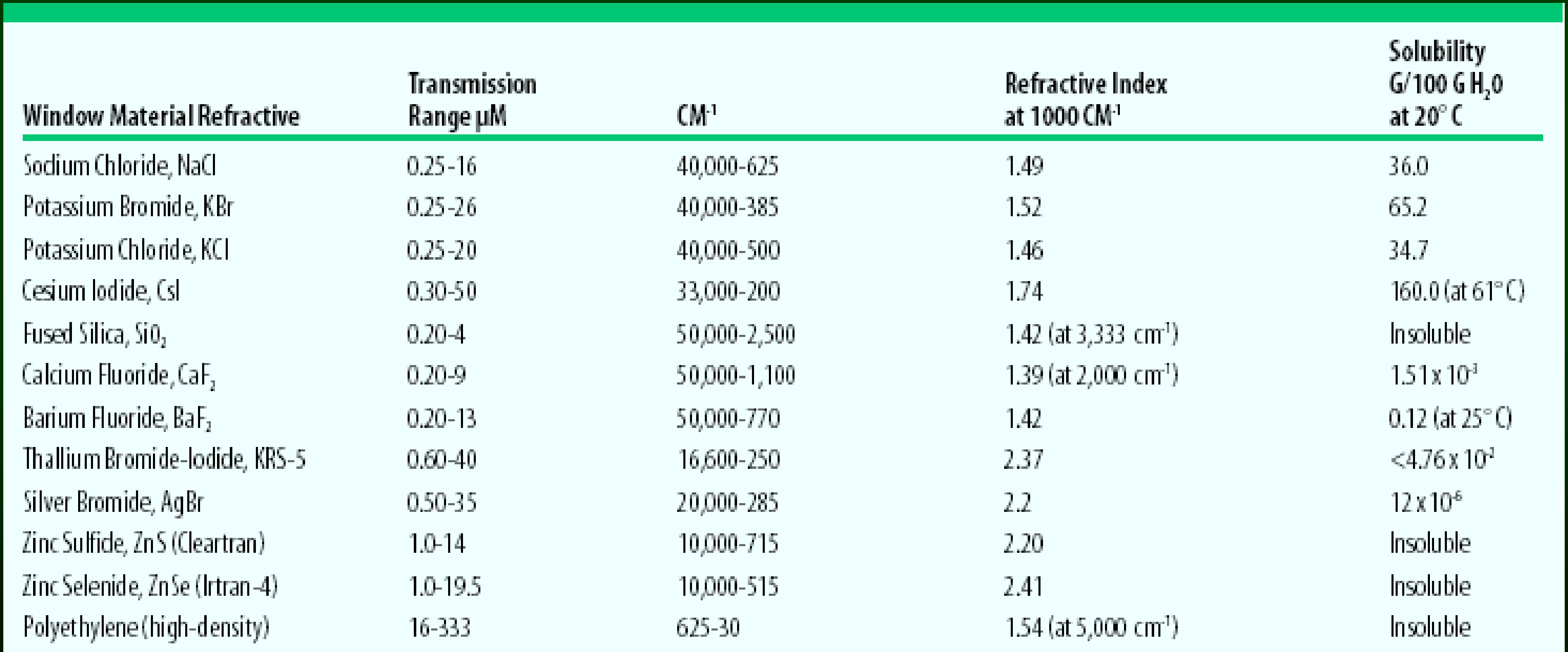
Thermocouple	thermoelectric effect - dissimilar metal junction	cheap, slow, insensitive
Bolometer	Ni, Pt resistance thermometer (thermistor)	Highly sensitive $<400\ \text{cm}^{-1}$
Pyroelectric	Tri glycine sulfate piezoelectric material	fast and sensitive (mid IR)
Photoconducting	PbS, CdS, Pb Se light sensitive cells	fast and sensitive (near IR)

•**Windows** are used for sample cells and to permit various compartment to be isolated from the environment.

→ transparent to IR over the wavelength region

→ inert to the various chemicals analyzed

→ capable of being shaped, ground, and polished to the desired optical quality



Window Material Refractive	Transmission Range µM	CM^{-1}	Refractive Index at 1000 CM^{-1}	Solubility G/100 G H_20 at 20° C
Sodium Chloride, NaCl	0.25-16	40,000-625	1.49	36.0
Potassium Bromide, KBr	0.25-26	40,000-385	1.52	65.2
Potassium Chloride, KCl	0.25-20	40,000-500	1.46	34.7
Cesium Iodide, CsI	0.30-50	33,000-200	1.74	160.0 (at 61° C)
Fused Silica, SiO_2	0.20-4	50,000-2,500	1.42 (at 3,333 cm^{-1})	Insoluble
Calcium Fluoride, CaF_2	0.20-9	50,000-1,100	1.39 (at 2,000 cm^{-1})	1.51 x 10^{-3}
Barium Fluoride, BaF_2	0.20-13	50,000-770	1.42	0.12 (at 25° C)
Thallium Bromide-Iodide, KRS-5	0.60-40	16,600-250	2.37	<4.76 x 10^{-2}
Silver Bromide, AgBr	0.50-35	20,000-285	2.2	12 x 10^{-6}
Zinc Sulfide, ZnS (Cleartran)	1.0-14	10,000-715	2.20	Insoluble
Zinc Selenide, ZnSe (Irtran-4)	1.0-19.5	10,000-515	2.41	Insoluble
Polyethylene (high-density)	16-333	625-30	1.54 (at 5,000 cm^{-1})	Insoluble

END

1. The fundamental line in the IR spectrum of $^{12}C^{16}O$ occurs at 2143 cm^{-1}, and the first overtone occurs at 4260 cm^{-1}. Calculate the values of $\tilde{\nu}_e$ and $\tilde{\chi}_e$ for $^{12}C^{16}O$.

2. Vibrational energy of a diatomic molecule is given by the following expression
$\tilde{G}(\vartheta) = \tilde{\nu}_e(\vartheta+1/2) - \tilde{\nu}_e\tilde{\chi}_e(\vartheta+1/2)^2$.
In the limit of dissociation of the molecule, show that $\vartheta_{max} = ½(1/\tilde{\chi}_e - 1)$. Now show that the energy liberated during the dissociation of the molecule is given by the expression $D_e = \tilde{\nu}_e / 4\tilde{\chi}_e$.

3. Assume the following data for the molecule $^1H^{35}Cl$:
Bond length: 127.5 pm
Bond force constant 516.3 Nm^{-1}
Assume bond length and bond force constant is not changing in going from $\vartheta = 0 \rightarrow 1$.
Atomic masses: $^1H = 1.673 \times 10^{-27}$ kg, $^{35}Cl = 58.066 \times 10^{-27}$ kg
Do the following, giving answers in cm^{-1}:
(a) Calculate the zero point energy. (Ans:1502cm^{-1})
(b) Calculate the wavenumbers of the lines $P_{(1)}$, $P_{(2)}$, $R_{(0)}$, $R_{(1)}$, $R_{(2)}$.

Ans: 2994 cm-1, 2974.6 cm^{-1}, 3035 cm^{-1}, 3055 cm^{-1}, 3075 cm^{-1}.

Q/1

$$E_n = \left[(n+1/2)\bar{\nu}_e - (n+1/2)^2 \bar{\nu}_e x_e \right] \text{cm}^{-1}$$

x_e = Anh - const
$\bar{\nu}_e$ = eq. vib freq.

For $n=0 \rightarrow n=1$

$$\Delta \epsilon_{0\rightarrow 1} = \left[3/2\, \bar{\nu}_e - (3/2)^2 \bar{\nu}_e x_e - 1/2\, \bar{\nu}_e + (1/2)^2 \bar{\nu}_e x_e \right]$$

$$\Delta \epsilon_{0\rightarrow 1} = \bar{\nu}_e - 2\bar{\nu}_e x_e$$

For $n = 0 \rightarrow n = 2$

$$\Delta \epsilon_{0\rightarrow 2} = (2\bar{\nu}_e - 6\bar{\nu}_e x_e)$$

$\Delta \epsilon_{0\rightarrow 1} = 2143 \text{ cm}^{-1}$ (fundamental line) . . (1)
$\Delta \epsilon_{0\rightarrow 2} = 4260 \text{ cm}^{-1}$ (1st overtone) . . (2)

(1) × (3) − (2)

$$\bar{\nu}_e = 2169 \text{ cm}^{-1}$$

from equn (1)

$$\bar{x}_e = 0.0059$$

$$\underset{\text{Energy}}{\tilde{G}(v)} = \bar{\nu}_e\left(v+\tfrac{1}{2}\right) - \bar{\nu}_e\tilde{x}_e\left(v+\tfrac{1}{2}\right)^2$$

$$\frac{d\tilde{G}(v)}{dv} = \bar{\nu}_e \times \tfrac{3}{2} - \bar{\nu}_e\tilde{x}_e \, 2\left(v+\tfrac{1}{2}\right)\cdot\tfrac{3}{2}$$

$$= \tfrac{3}{2}\bar{\nu}_e - 3\bar{\nu}_e\tilde{x}_e\left(v+\tfrac{1}{2}\right)$$

At $v = v_{max}$

$$\frac{d\tilde{G}(v)}{dv} = 0$$

$$\tfrac{3}{2} - 3\tilde{x}_e\left(v_{max}+\tfrac{1}{2}\right) = 0$$

$$\Rightarrow \tilde{x}_e\left(v_{max}+\tfrac{1}{2}\right) = \tfrac{1}{2}$$

$$\Rightarrow v_{max}+\tfrac{1}{2} = \frac{1}{2\tilde{x}_e}$$

$$\Rightarrow v_{max} = \tfrac{1}{2}\left(\frac{1}{\tilde{x}_e} - 1\right)$$

Energy liberated during dissociation

$$E_{v_{max}} = D_e$$

$$D_e = \bar{\nu}_e\left(\frac{1}{2\tilde{x}_e} - \tfrac{1}{2} + \tfrac{1}{2}\right) - \bar{\nu}_e\tilde{x}_e\left(\frac{1}{2\tilde{x}_e} - \tfrac{1}{2} + \tfrac{1}{2}\right)^2$$

~~$\frac{1}{2}\bar{\nu}_e \quad \frac{1}{4}\bar{\nu}_e$~~

$$= \frac{\bar{\nu}_e}{2\tilde{x}_e} - \frac{\bar{\nu}_e}{4\tilde{x}_e} \quad \cancel{= \tfrac{1}{2}\bar{\nu}_e - \tfrac{1}{4}\bar{\nu}_e\tilde{x}_e}$$

$$= \frac{1}{4}\frac{\bar{\nu}_e}{\tilde{x}_e} \quad \text{(proved)}$$

Q.3) Assume the following data for the molecule $^{1}H^{35}Cl$

Bond length = 127.5 pm

Bond force constant = 516.3 N m^{-1}

Assume bond length and bond force constant is not changing in going from $v = 0 \rightarrow 1$

Atomic masses ; $^{1}H = 1.673 \times 10^{-27}$ kg

$^{35}Cl = 58.066 \times 10^{-27}$ kg

a) Calculate the zeropoint energy

b) Calculate the wave numbers of the line $P(1), P(2), R(0), R(1), R(2)$

Rotational const = $B = \dfrac{h}{8\pi^2 I c}$

~~I = Moment of inertia~~ Reduced mass μ = $\dfrac{m_1 m_2}{m_1 + m_2}$

$= \dfrac{1.673 \times 58.066}{(1.673 + 58.066)} \times 10^{-27}$ kg

$= \dfrac{97.144418}{59.739} \times 10^{-27}$ kg

$= 1.626 \times 10^{-27}$ kg

Moment of Inertia = ~~B = 3×10^8~~ $\mu = I r^2$ $= 1.626 \times 10^{-27}$ kg × $(127.5 \times 10^{-12})^2$ m^2

$= 2.64 \times 10^{-47}$ kg m^2

$$B = \frac{6.626 \times 10^{-34} \text{ J-s}}{8 \times (3.14)^2 \times (\cancel{1.626}\ 2.64 \times 10^{-47} \text{ kg m}^2) \times 3 \times 10^{8} \text{ m s}^{-1}}$$

= ~~0.017 × 10^5 m^-1~~ ~~624.7~~

= ~~(0.017 × 10^5)(100 cm)^-1~~ ~~624.7~~

= ~~0.017 × 10^5 × 10^-2 cm^-1~~

= ~~0.017 × 10^17 cm^-1~~

$= 0.0106 \times 10^{5}$ m^{-1}

$= 1060.66$ ~~×100~~ m^{-1}

$= 10.6$ cm^{-1}

$$\bar{\omega}_0 = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

K → Bond force const

μ → reduced mass

$= 2994.9$ cm^{-1}

Zeropoint energy $\frac{1}{2}\bar{\omega}_0 = 1497.98$ cm^{-1}

Waveno of lines

$E_{vib} + E_{Rot} = E_{tot}$

$\Rightarrow (v + 1/2)\,\overline{\omega_0} + B(J+1)J = E_{tot}$

(In this case)

For $v = 0 \rightarrow 1 \rightarrow J'$ $\overset{J''}{\uparrow}$

$\Delta E_{Total} = B J'(J'+1) + 3/2\,\overline{\omega_0} - BJ''(J''+1) - 1/2\,\overline{\omega_0}$

$= \overline{\omega}_0 + B\left[(J' - J'')(J' + J'' + 1)\right]$

Now

$J' - J'' = \pm 1$.

case-I

$J' - J'' = -1$

$\Delta E = \overline{\omega_0} - B\left[J' + J'' + 1\right]$

$P(1) = \overline{\omega}_0 - 2B = 2991.9 - 2 \times 10.6 = 2979.7\ cm^{-1}$

$P(2) = \overline{\omega}_0 - 4B = 2994.9 - \overset{4}{\cancel{2}} \times 10.6 = 2952.5\ cm^{-1}$

$P(3) = \overline{\omega}_0 - 6B = 2991.9 - \overset{6}{\cancel{2}} \times 10.6 = 2931.3\ cm^{-1}$

$J' - J'' = 1$

$\Delta E = \overline{\omega_0} + B\left[J' + J'' + 1\right]$

$R(0) = \overline{\omega}_0 + 2B = 2991.9 + 2 \times 10.6 = 3016.1\ cm^{-1}$

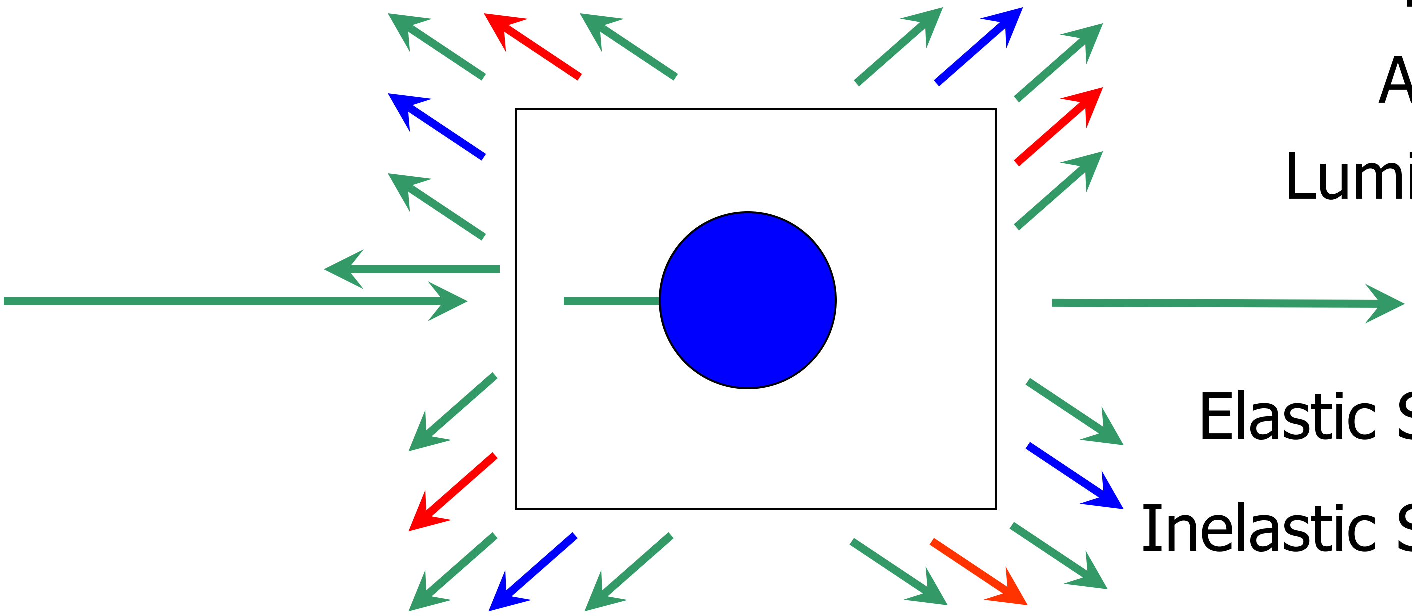
$R(1) = \overline{\omega}_0 + 4B = 2994.9 + 4 \times 10.6 =$ ~~[illegible]~~ 3037.4 cm^{-1}

$R(2) = \overline{\omega}_0 + 6B = 2994.9 + 6 \times 10.6 = 3058.5\ cm^{-1}$

Raman Spectroscopy


RAMAN'S SPECTROGRAPH
THE FIRST RAMAN SPECTRUM WAS
OBTAINED WITH THIS SPECTROGRAPH
IN 1928.

What happens when light falls on a material?



Transmission

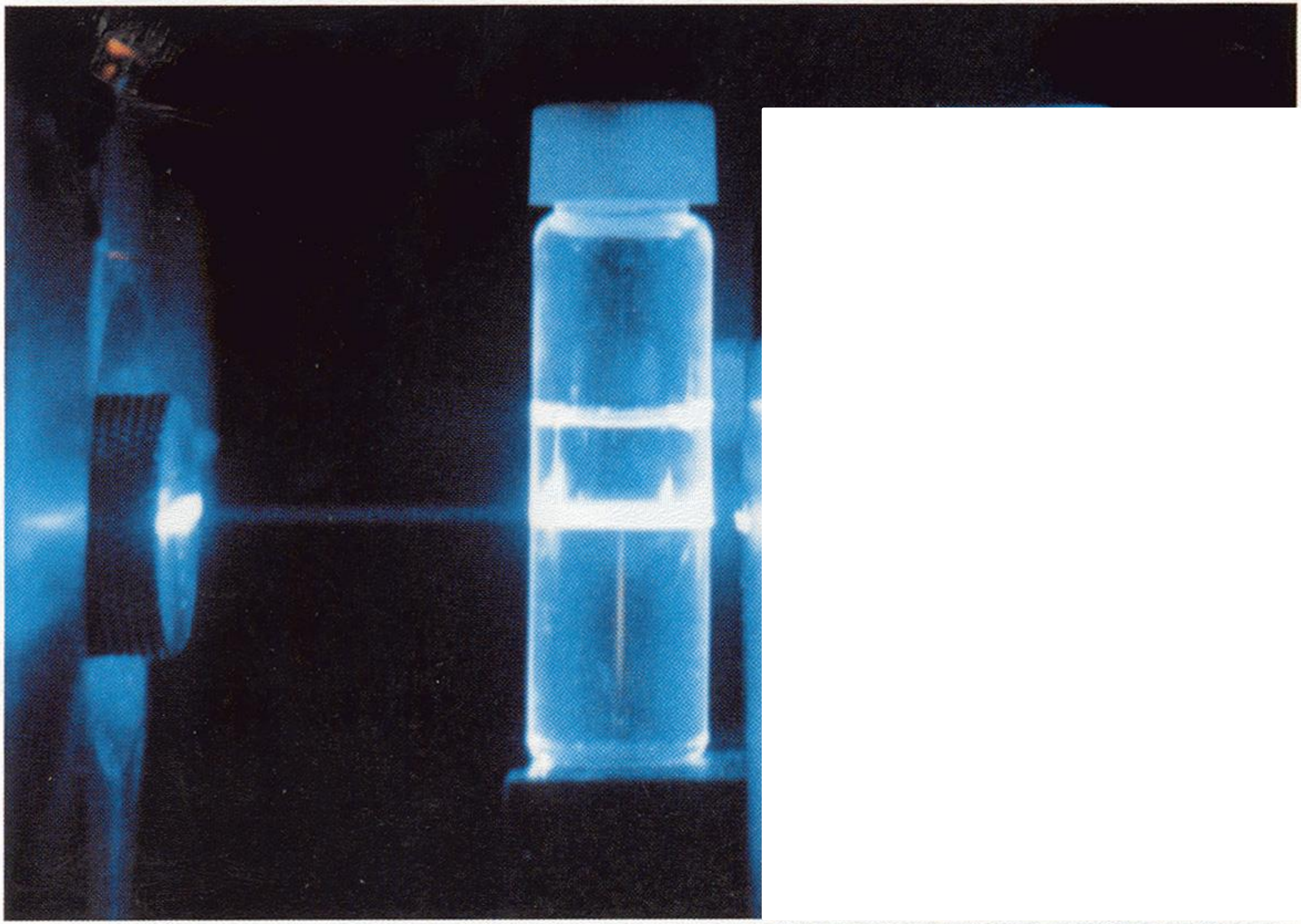
Reflection

Absorption

Luminescence

Elastic Scattering

Inelastic Scattering

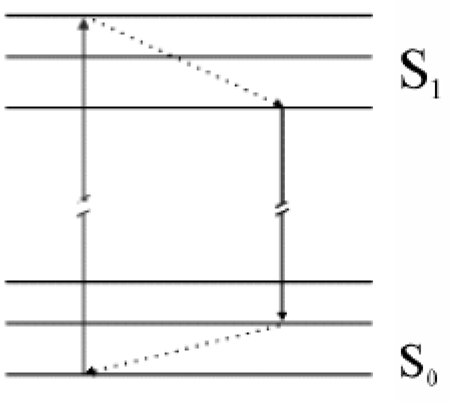


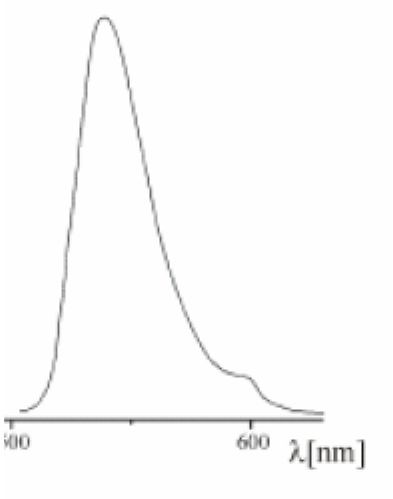
Raman scattering visible to the unaided eye, from a 488 nm laser beam passing through liquid cyclohexane. Left vial exhibits mostly Rayleigh scattering which obscures much weaker Raman scattering. Right vial is viewed through a 488 nm band rejection filter, which permits observation of longer wavelength Raman scattering.

Raman, Fluorescence and IR

Absorption

and emission





6.1 Scattering

In addition to being absorbed and emitted by atoms and molecules, photons may also be *scattered* (approx. 1 in 10^7 in a transparent medium). This is not due to defects or dust but a molecular effect which provides another way to study energy levels.

This scattering may be:

Elastic and leave the molecule in the same state (Rayleigh Scattering) or

Inelastic and leave the molecule in a *different* quantum state (Raman Scattering)

Nobel Prize 1904
(physics)

Nobel Prize 1930
(physics)

6.2 Rayleigh Scattering

Lord Rayleigh calculated that a dipole scatterer << λ scatters with an intensity:

no. of scatterers

polarizability

$$\boxed{I = I_0 \frac{8\pi N\alpha^2}{\lambda^4 R^2}\left(1+cos^2\theta\right)}$$

wavelength

distance
scatterer - observer

n.b., $\boxed{I \propto \frac{1}{\lambda^4}}$

5 times more effective for 400nm than 600nm
Hence the sky is blue!

Raman Scattering

Scattering is not an oscillating dipole phenomenon!

The presence of an electric field *E* induces a polarization in an atom/ molecule given by

$$\mathbf{P} = \overset{\text{polarizability}}{\alpha}\mathbf{E}$$

If the field is oscillating (e.g., photon) $\mathbf{P} = \alpha \mathbf{E}_0 \cos(2\pi\nu_0 t)$

In atoms the polarizability is isotropic, and the atom acts like an antenna and re-radiates at the incident frequency – Rayleigh Scattering only

In molecules the polarizability may be anisotropic, and depends on the rotational and vibrational coordinates. This can also give rise to Raman Scattering.

Gross Selection Rule:

To be Raman active a molecule must have anisotropic polarizability

[Less restrictive than the need for a dipole moment, symmetric molecules can be Raman active]

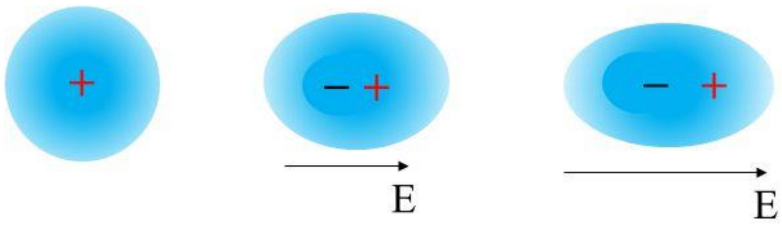
Polarization

Amount of polarization $\vec{p}$ in most materials is *proportional* to the magnitude of the applied electric field:

$$\vec{p} = \alpha \vec{E}$$

α - "*polarizability*" of a material

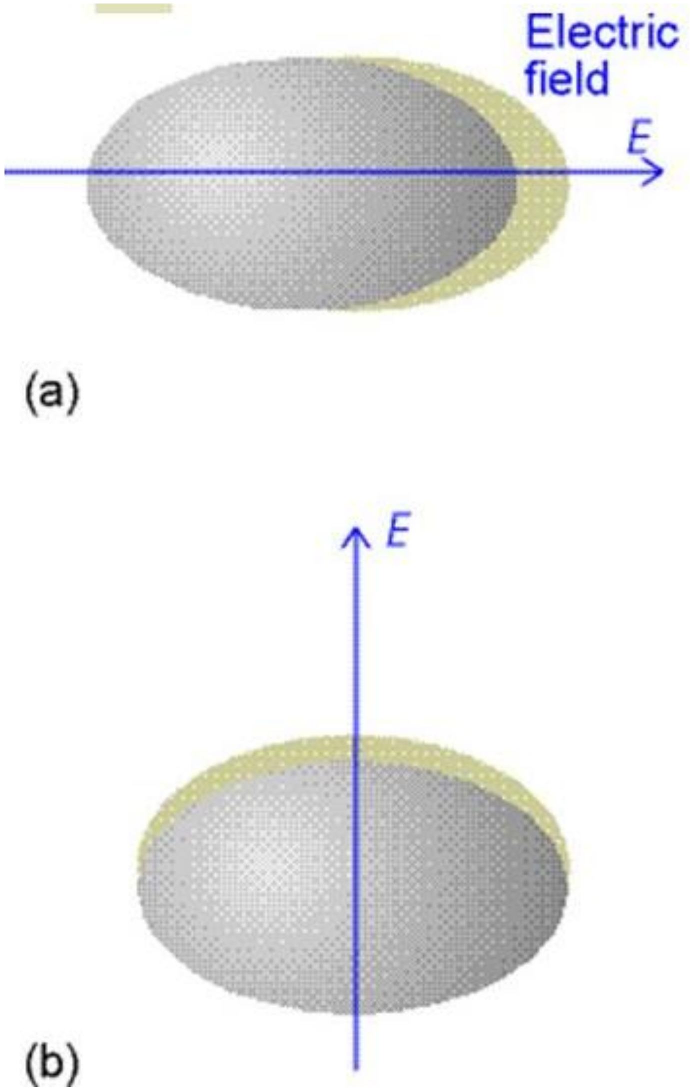
In an induced dipole, is the distance between the charges fixed?
The distance is proportional to the strength of the applied field.



As discussed, when an atom or molecule is brought into an electric field E , an electric dipole moment μ is induced in the system. The magnitude of this induced dipole moment is proportional to the electric field, μ = α E where α is known as the polarizability.

- Except for the case of spherical symmetry, the magnitude of the induced dipole moment depends on the direction of the electric field. For example, in case of a diatomic molecule, the induce dipole moment will be higher in magnitude when the electric field direction is along the inter-nuclear axis than that of the perpendicular to the inter-nuclear axis.

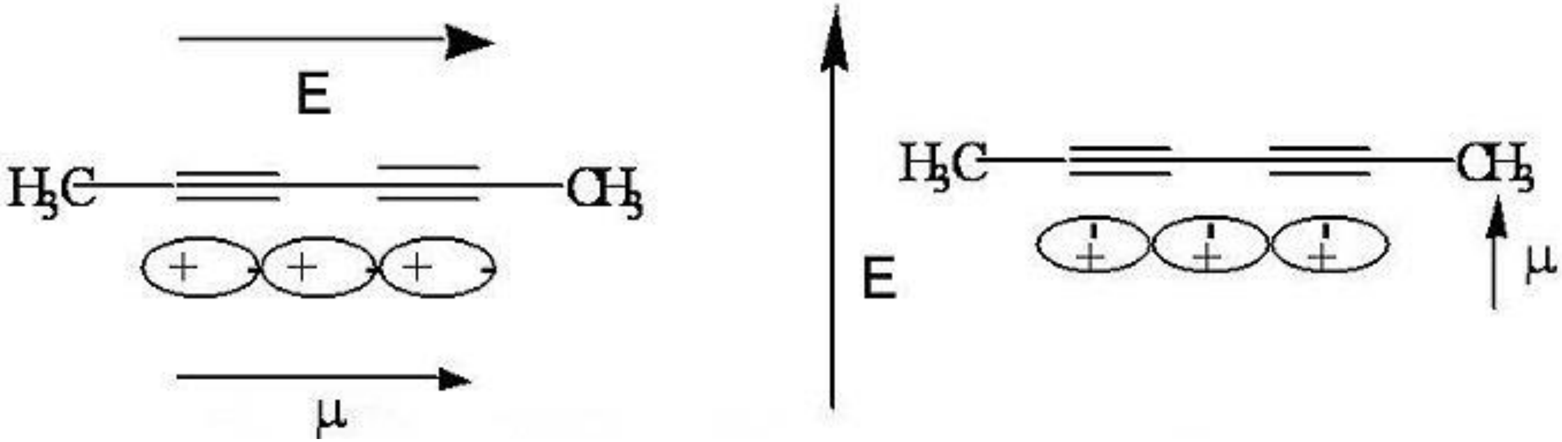
Change in Polarizability



An electric field applied to a molecule results in its distortion, and the distorted molecule acquires a contribution to its dipole moment (even if it is nonpolar initially). The polarizability may be different when the field is applied (a) parallel or (b) perpendicular to the molecular axis (or, in general, in different directions relative to the molecule); if that is so, then the molecule has an anisotropic polarizability.

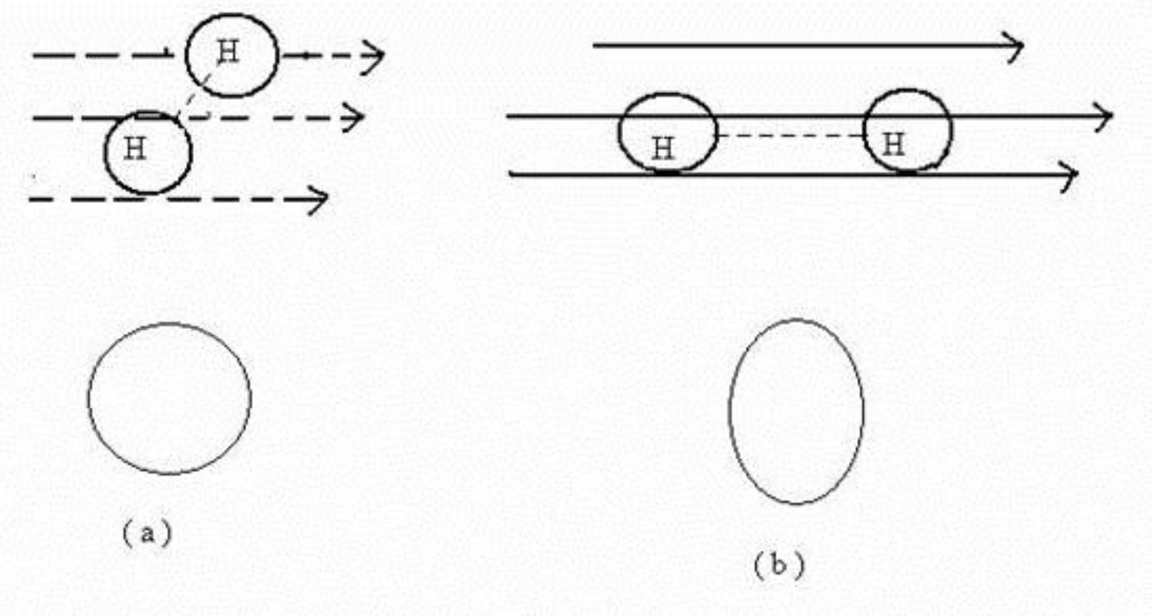
Anisotropic Nature of Polarizability

- The polarization of a molecules need not be identical in all directions.



Polarisability Change during Rotation

In case of a diatomic and linear molecule, the ***induce dipole moment*** will be higher in magnitude when the electric field direction is along the inter-nuclear axis than that of the perpendicular to the inter-nuclear axis.



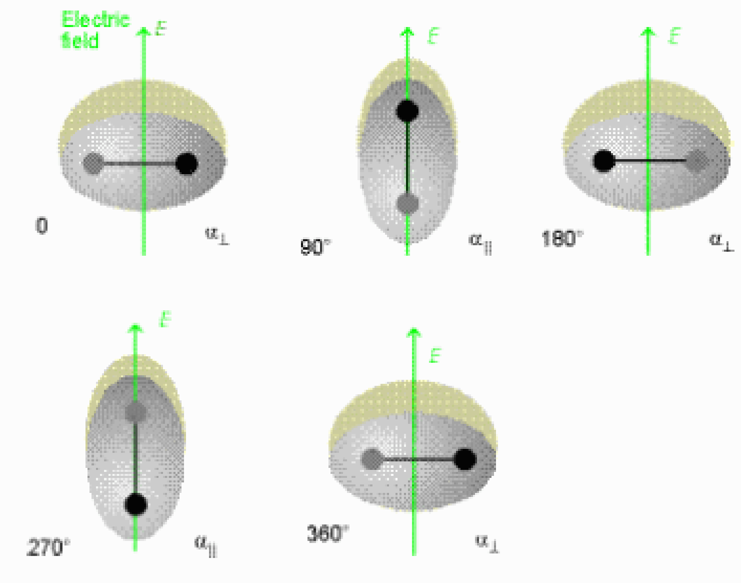
Polarisability Ellipsoid of Hydrogen in two different orientations.

Classical theory Raman scattering: Rotational Raman

$$P_{in} = \propto E$$

$$\propto = \propto_0 + \Delta\propto \cos(2\omega t)$$

$$E = E_0 \cos(2\pi v_0 t)$$



$$P_{in} = (\propto_0 + \Delta\propto \cos(2\omega t)) \times E_0 \cos(2\pi v_0 t)$$

$$= \propto_0 E_0 \cos(2\pi v_0 t) + \frac{1}{2} E \Delta\propto \{\cos(2\pi v_0 - 2\omega)t + \cos(2\pi v_0 + 2\omega)t\}$$

Rayleigh **Stokes** **Anti-Stokes**

$$\Delta\alpha \neq 0$$

Polarizability should be changed during rotation

Classical theory Raman scattering : Vibrational Raman

- An oscillating electric field (incident photon) causes the molecule to have an ***induced*** dipole:

$$\mathbf{P} = \alpha \mathbf{E} \qquad \mathbf{E} = \mathbf{E}_0 \cos(2\pi \nu_0 t)$$

$$\mathbf{P} = \alpha \mathbf{E}_0 \cos(2\pi \nu_0 t)$$

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial r}\right)_{r_0} (r - r_0) + \ldots$$

- $$\mathbf{P} = \alpha_0 \mathbf{E}_0 \cos(2\pi \nu_0 t) + \left(\frac{\partial \alpha}{\partial q_i}\right)_0 \mathbf{E}_0 \cos(2\pi \nu_0 t) q_i^0 \cos(2\pi \nu_i t)$$

$$= \underbrace{\alpha_0 \mathbf{E}_0 \cos(2\pi \nu_0 t)}_{\textit{Rayleigh}} + \frac{1}{2}\left(\frac{\partial \alpha}{\partial q_i}\right)_0 \mathbf{E}_0 q_i^0 \left[\underbrace{\cos\left(2\pi(\nu_0 - \nu_i)t\right)}_{\textbf{Stokes}} + \underbrace{\left(\cos 2\pi(\nu_0 + \nu_i)t\right)}_{\textbf{Anti-Stokes}}\right]$$

$$\left(\frac{\partial \alpha}{\partial r}\right)_{r_0} \neq \mathbf{0}$$

In order for a vibrational mode to be Raman active, the polarizability must change during the vibration, and for a rotation to be Raman active, the polarizability must change as the molecule rotates in an electric field.

$$I_{\text{scatt}} \propto \left|\mathbf{P} \cdot \mathbf{E}_0\right|^2 = \left|\left(\partial\alpha/\partial q_i\right)_0\right|^2 I_0^2$$

Thus, the polarizability must change linearly with vibrational motion for vibrational Raman scattering to occur. The greater the change, the more intense the Raman scattering. If α is unchanged or at a minimum/maximum, there is no Raman scattering.

Quantum Picture of Raman scattering : Vibrational Raman

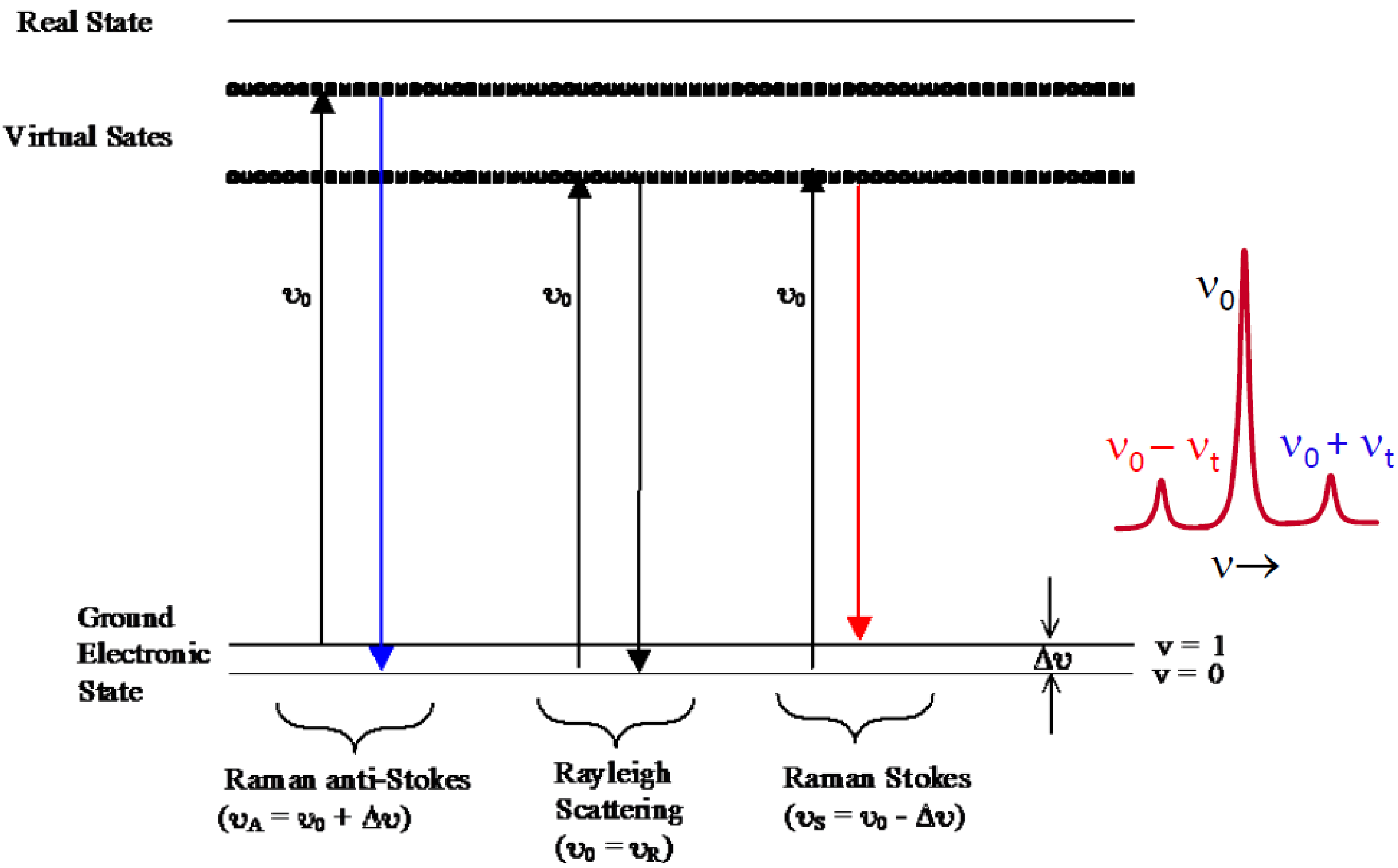
$$\mu_{\mathrm{fi}} = \left\langle v_{\mathrm{f}} \middle| \alpha(0) + \left(\frac{\mathrm{d}\alpha}{\mathrm{d}x}\right)_0 x + \cdots \middle| v_{\mathrm{i}} \right\rangle \mathcal{E}$$

$$= \langle v_{\mathrm{f}}|v_{\mathrm{i}}\rangle \alpha(0)\mathcal{E} + \left(\frac{\mathrm{d}\alpha}{\mathrm{d}x}\right)_0 \langle v_{\mathrm{f}}|x|v_{\mathrm{i}}\rangle \mathcal{E} + \cdots$$

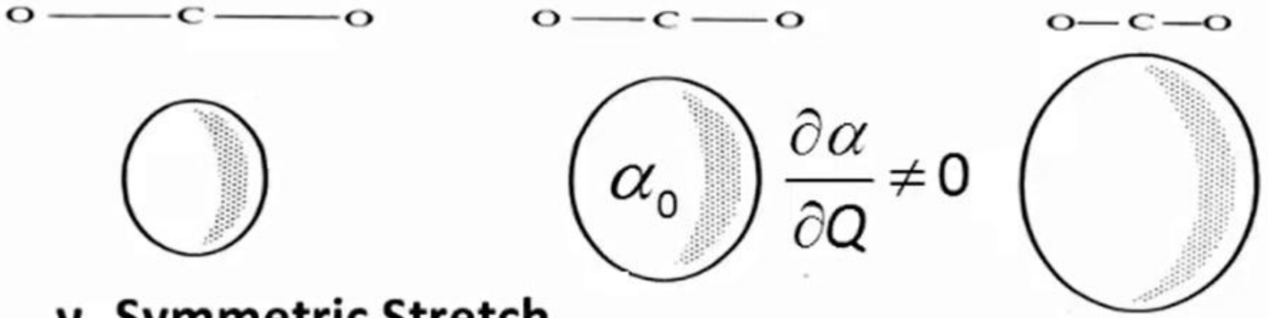
$\langle v_{\mathrm{f}}|v_{\mathrm{i}}\rangle = 0 \qquad \mathrm{f} \neq \mathrm{i}$

Raman active if $(\mathrm{d}\alpha/\mathrm{d}x)_0 \neq 0$ and $\langle v_{\mathrm{f}}|x|v_{\mathrm{i}}\rangle \neq 0$. Therefore, the polarizability of the molecule must change during the vibration; this is the gross selection rule of Raman spectroscopy. Also, we already know that $\langle v_{\mathrm{f}}|x|v_{\mathrm{i}}\rangle \neq 0$ if $v_{\mathrm{f}} - v_{\mathrm{i}} = \pm 1$; this is the specific selection rule of Raman spectroscopy.

Molecular Picture of Scattering Events

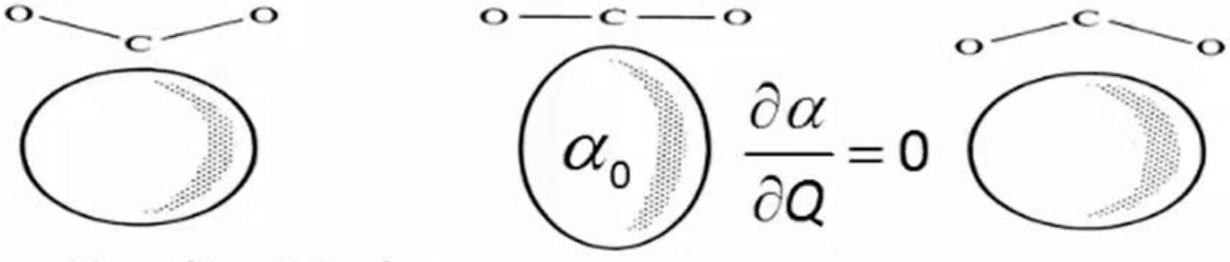


Polarizability Ellipsoids of CO_2



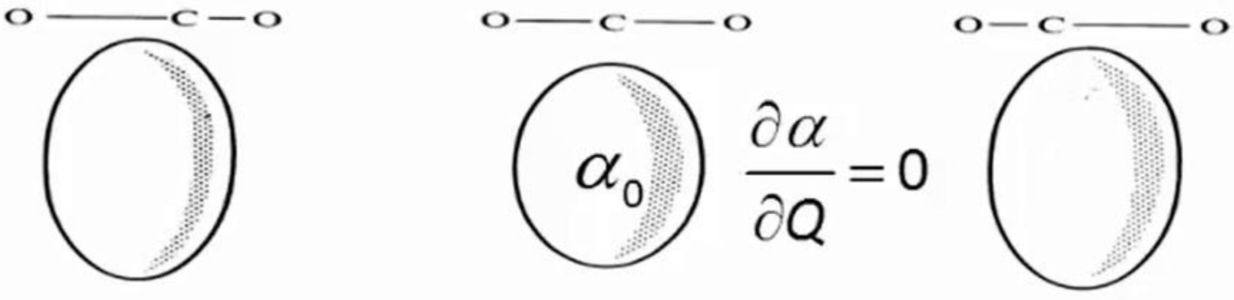
$$\alpha_0 \quad \frac{\partial \alpha}{\partial Q} \neq 0$$

ν_1 Symmetric Stretch



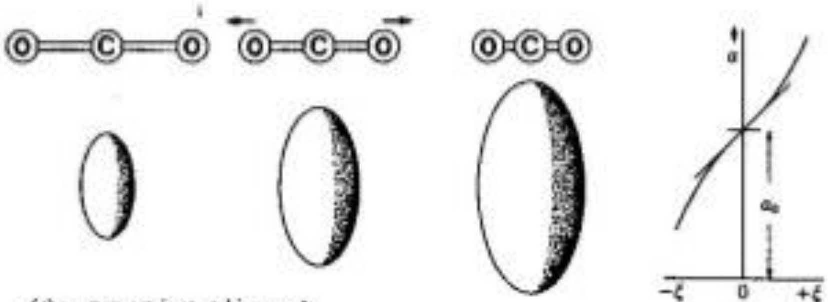
$$\alpha_0 \quad \frac{\partial \alpha}{\partial Q} = 0$$

ν_2 Bending Mode

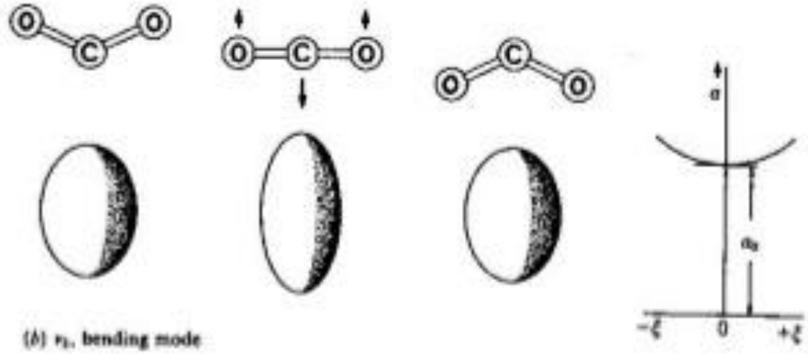


$$\alpha_0 \quad \frac{\partial \alpha}{\partial Q} = 0$$

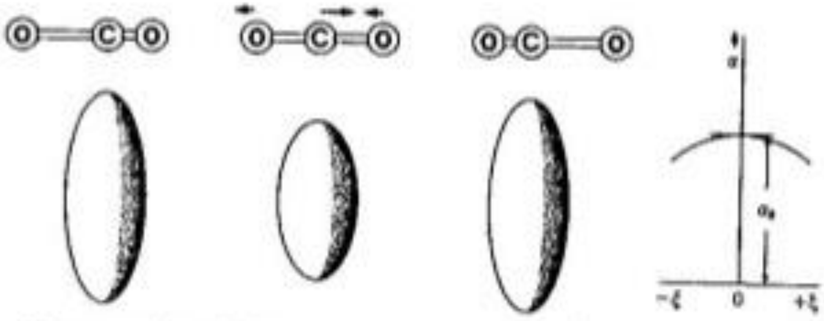
Raman Activity of CO_2 Vibrations



(*a*) ν_1, symmetric stretching mode



(*b*) ν_2, bending mode



(*c*) ν_3, asymmetric stretching mode

Figure 4.7 The changes in the polarizability ellipsoid of carbon dioxide during its vibrations, and a graph showing the variation of the polarizability, α, with the displacement coordinate, ξ, during each vibration.

Rotational Raman

Linear molecules $\Delta J = 0, \pm 2$

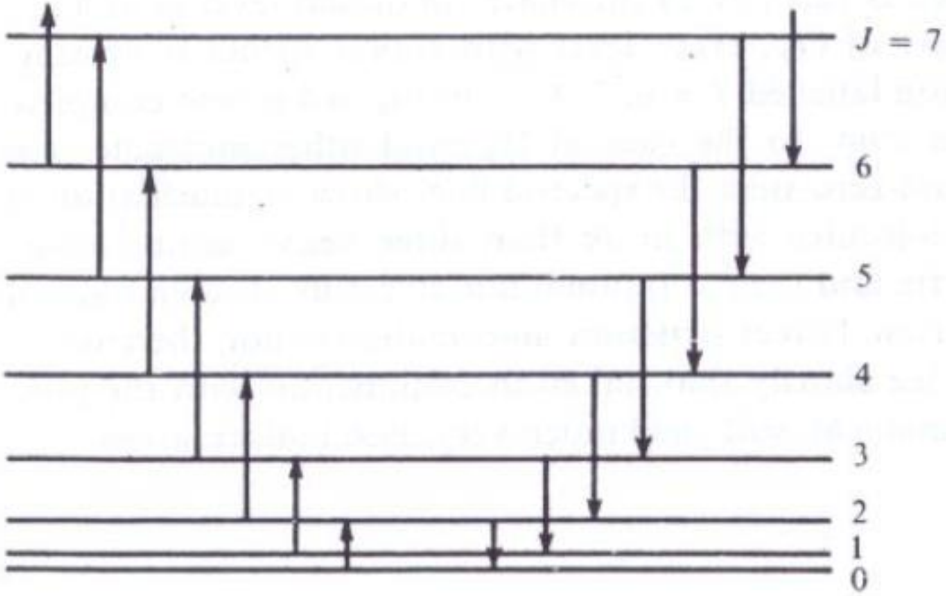
For Linear Molecules

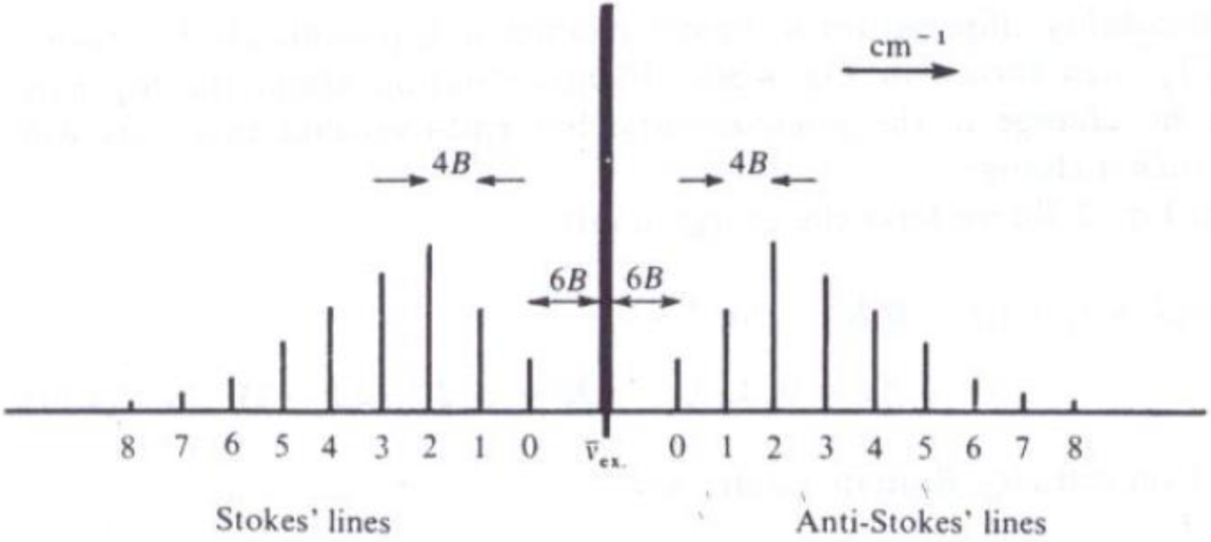
$$\Delta\tilde{\nu}_{\mathrm{R}} = \tilde{B}J'(J'+1) - \tilde{B}J''(J''+1)$$

$$\Delta\tilde{\nu}_{\mathrm{R}} = \boldsymbol{v_0 \pm \tilde{B}\,(4J+6)}$$

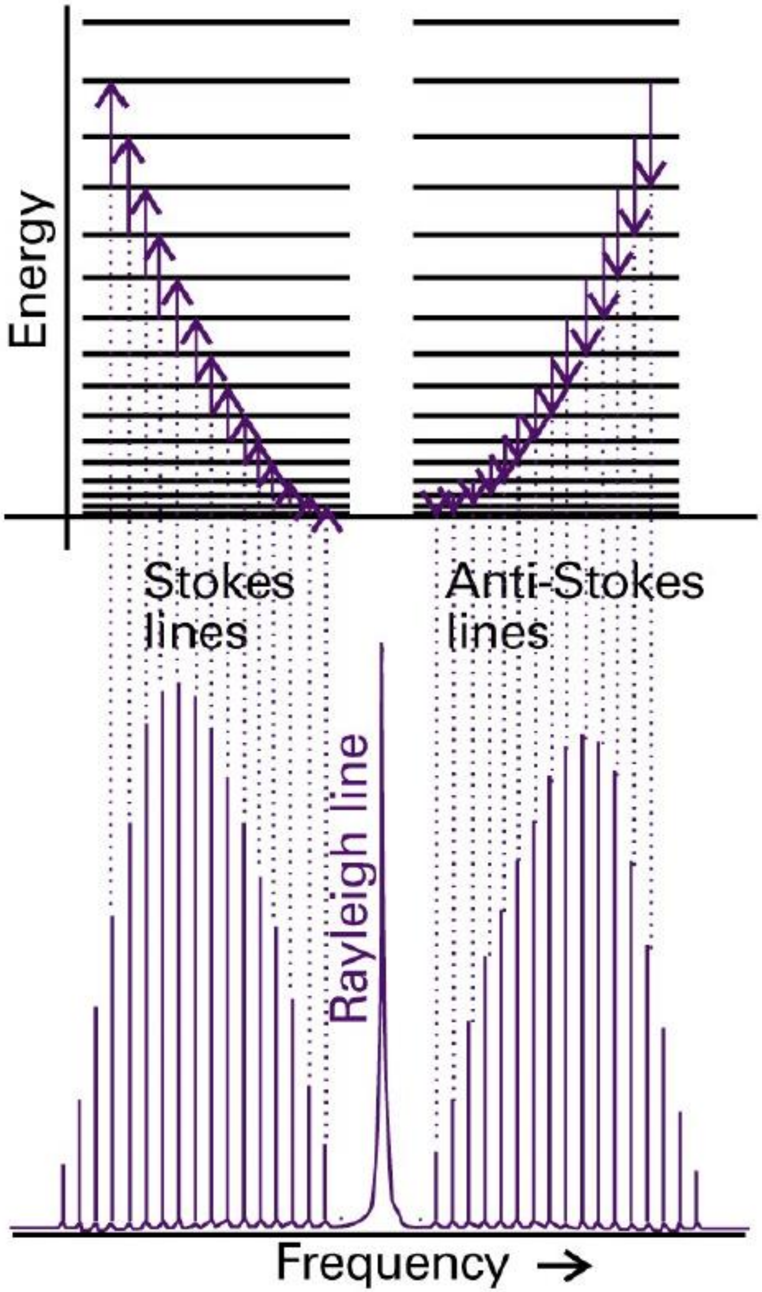
Stokes (-) **anti-stokes (+)**

- a gap of 6*B* between ν_0 and 1st lines of each branch
- lines in each branch of equal spacing = 4*B*

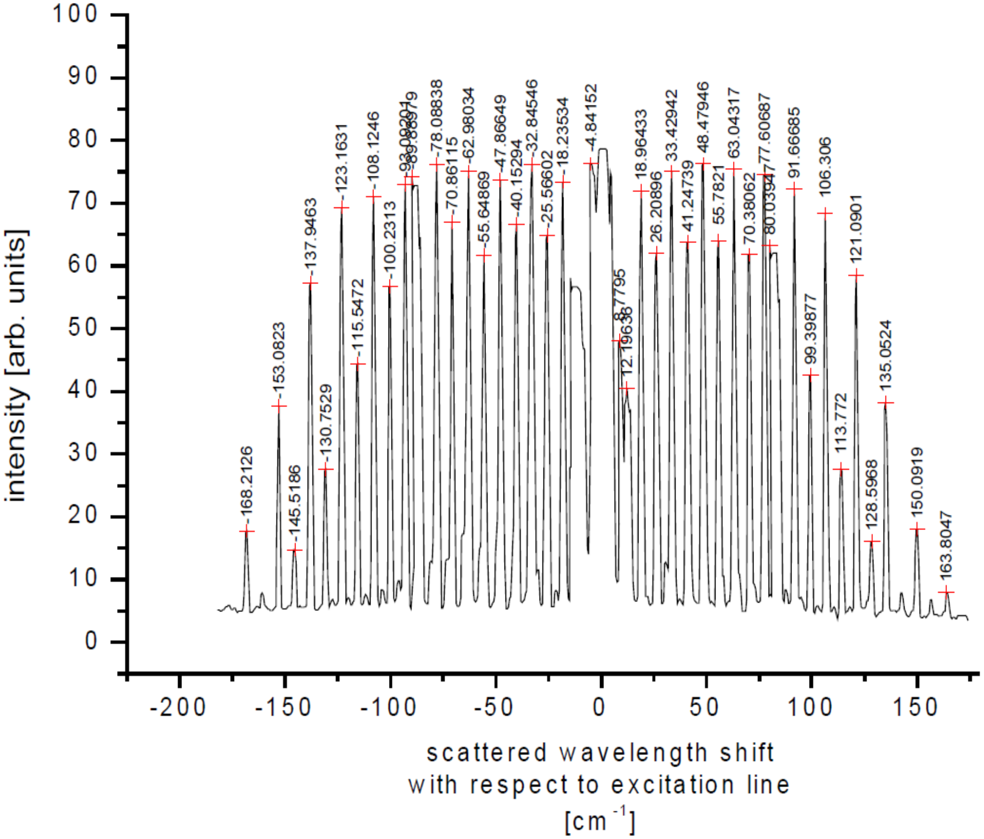

$J = 7$
6
5
4
3
2
1
0


cm^{-1}
$4B$
$4B$
$6B$
$6B$
8 7 6 5 4 3 2 1 0
$\bar{\nu}_{\text{ex.}}$
0 1 2 3 4 5 6 7 8
Stokes' lines
Anti-Stokes' lines

Rotational Raman spectra of Diatomic Molecule



Rotational Raman Spectrum of $^{15}N_2$



Why ΔJ = ± 2?

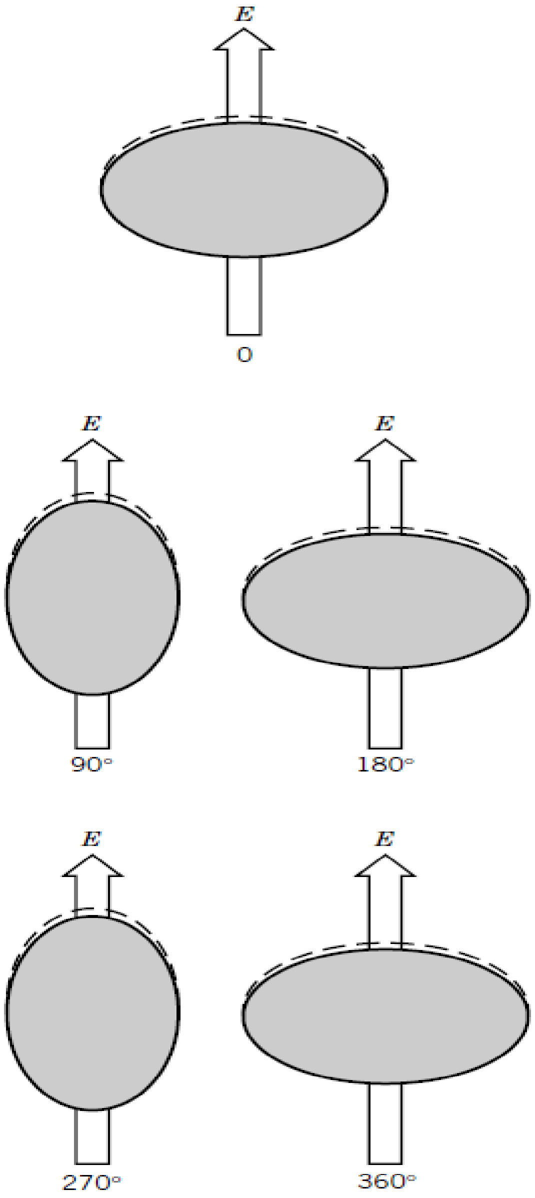


Figure 13.16 Polarizability ellipsoid for a molecule that returns to its initial value twice in a 360° revolution.

Pure Rotational Raman Spectra of Symmetric top molecules

$$\Delta J = 0, \pm 1, \pm 2, \Delta K = 0 \qquad \text{when } K \neq 0$$

$$\left.\begin{aligned} \bar{\nu}_R &= \bar{\nu}_{\text{ex.}} \pm \Delta\varepsilon_R = \bar{\nu}_{\text{ex.}} \pm 2B(J+1)\ \text{cm}^{-1} \qquad (J = 1, 2, \ldots) \\ \bar{\nu}_S &= \bar{\nu}_{\text{ex.}} \pm \Delta\varepsilon_S = \bar{\nu}_{\text{ex.}} \pm B(4J+6)\ \text{cm}^{-1} \qquad (J = 0, 1, 2, \ldots) \end{aligned}\right\}$$

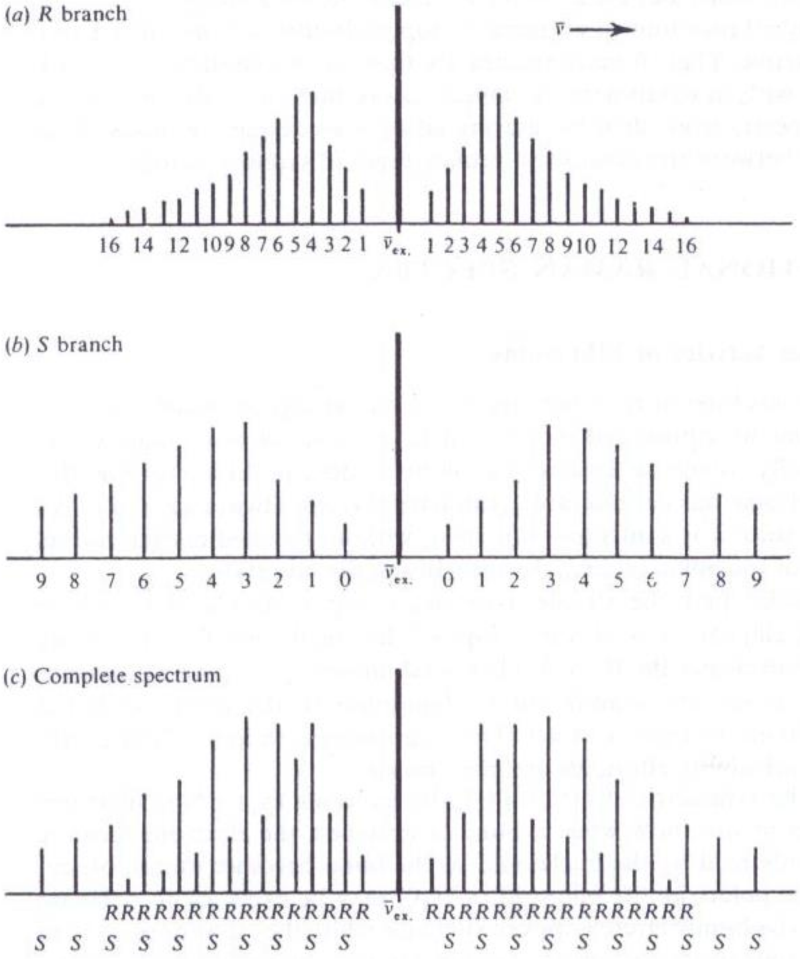
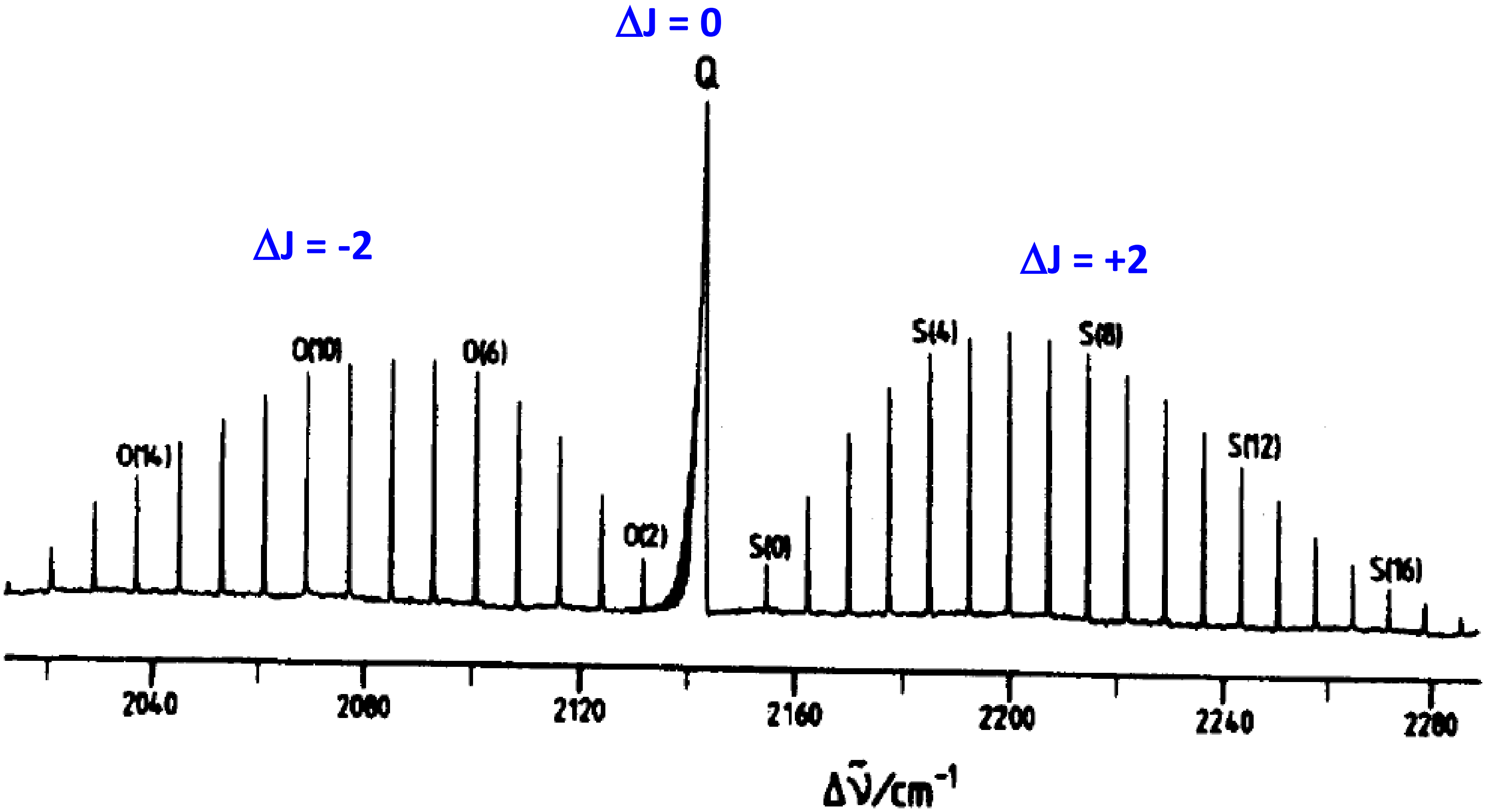


Figure 4.5 Rotational Raman spectrum of a symmetric top molecule. The *R* and *S* branch lines are shown separately in (*a*) and (*b*) respectively, with the total spectrum in (*c*).

Vibrational Raman Spectroscopy
(with rotational (sub)-structure)

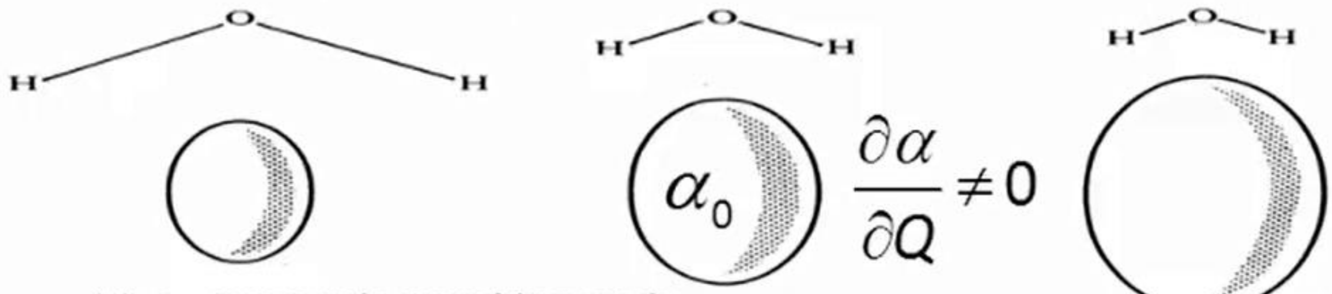
ϑ = 0 to ϑ = 1 transition



The 1–0 Stokes vibrational Raman spectrum of CO showing the *O*-, *Q*-, and *S*-branch rotational structure

Polarizability Ellipsoids of H_2O Vibrational Modes and Raman Activity

Size

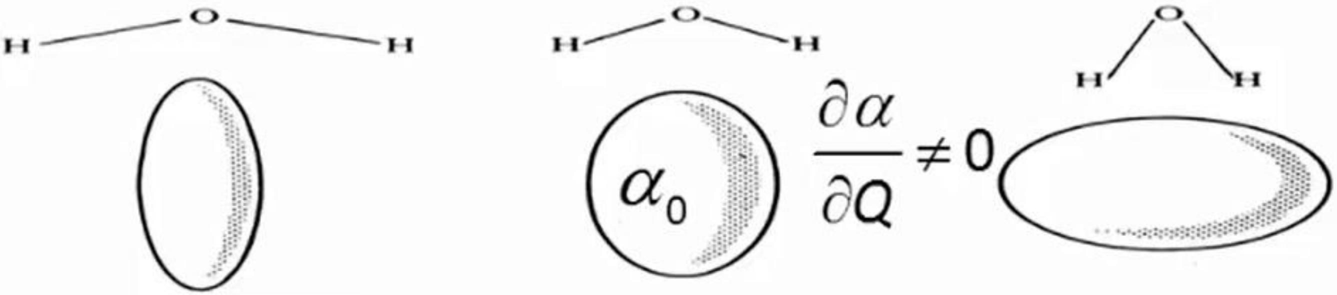


(a) ν_1, symmetric stretching mode

$$\frac{\partial \alpha}{\partial Q} \neq 0$$

Raman Active

Shape

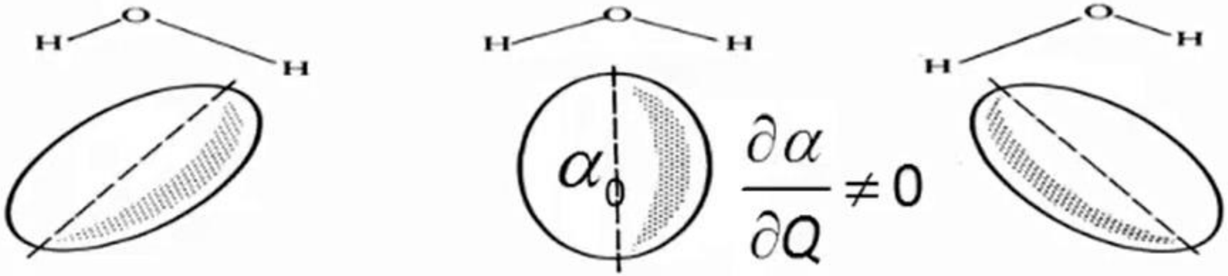


(b) ν_2, bending mode

$$\frac{\partial \alpha}{\partial Q} \neq 0$$

Raman Active

Orientation



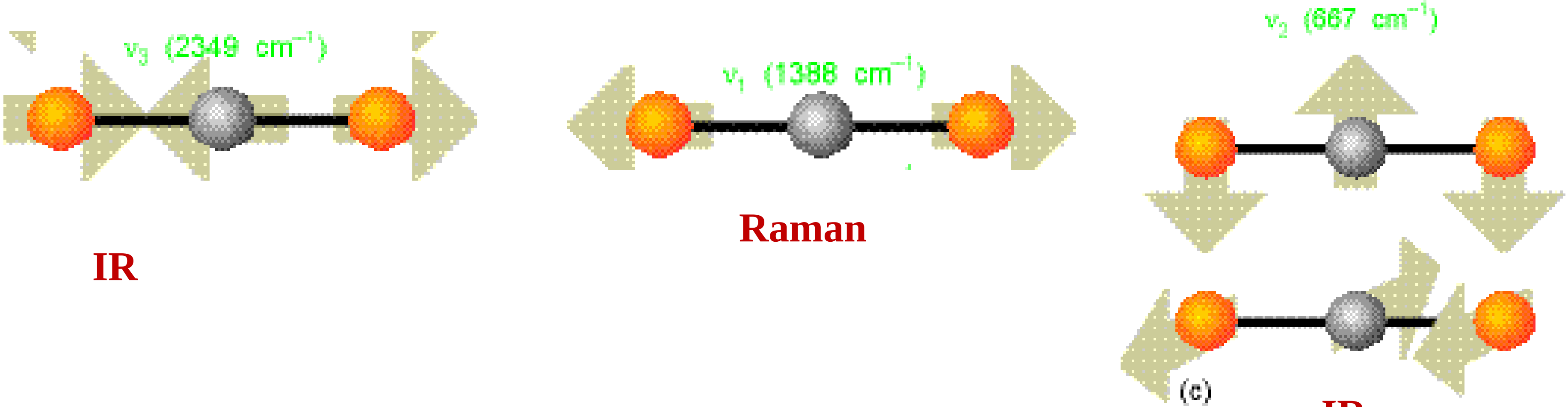
(c) ν_3, asymmetric stretching mode

$$\frac{\partial \alpha}{\partial Q} \neq 0$$

Raman Active

Mutual Exclusion Principle

For molecules with a center of symmetry, no IR active transitions are Raman active and vice versa



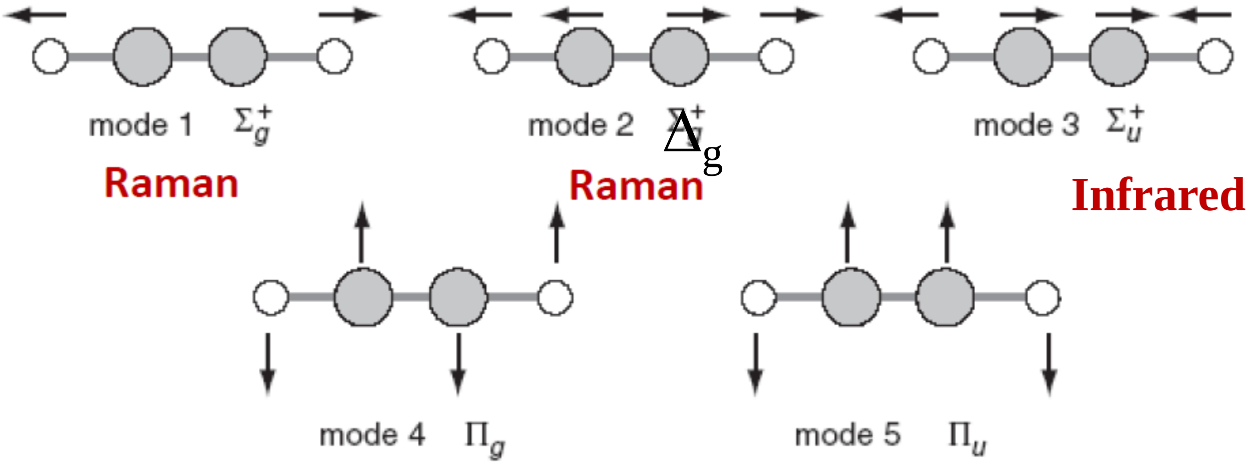
IR

Raman

IR

acetylene

$D_{\infty h}$



Raman

Raman

Infrared

Raman

Infra Red

The *Vibrational Raman Spectra of Homonuclear diatomic molecules* are of Special interest because they yield force constants and rotational constants that are not available from microwave and Infrared Absorption spectroscopy.

Advantages of Raman over IR

- Water can be used as solvent.

- Very suitable for biological samples in native state (because water can be used as solvent).

- Although Raman spectra result from molecular vibrations at IR frequencies, spectrum is obtained using visible light or NIR radiation.

=>Glass and quartz lenses, cells, and optical fibers can be used. Standard detectors can be used.

- Few intense overtones and combination bands => few spectral overlaps.

- Totally symmetric vibrations are observable.

- Raman intensities α to concentration and laser power.

Advantages of IR over Raman

- Simpler and cheaper instrumentation.
- Less instrument dependent than Raman spectra because IR spectra are based on measurement of intensity *ratio*.
- Lower detection limit than (normal) Raman.
- Background fluorescence can overwhelm Raman.
- More suitable for vibrations of bonds with very low polarizability (e.g. C–F).

Raman and Fraud

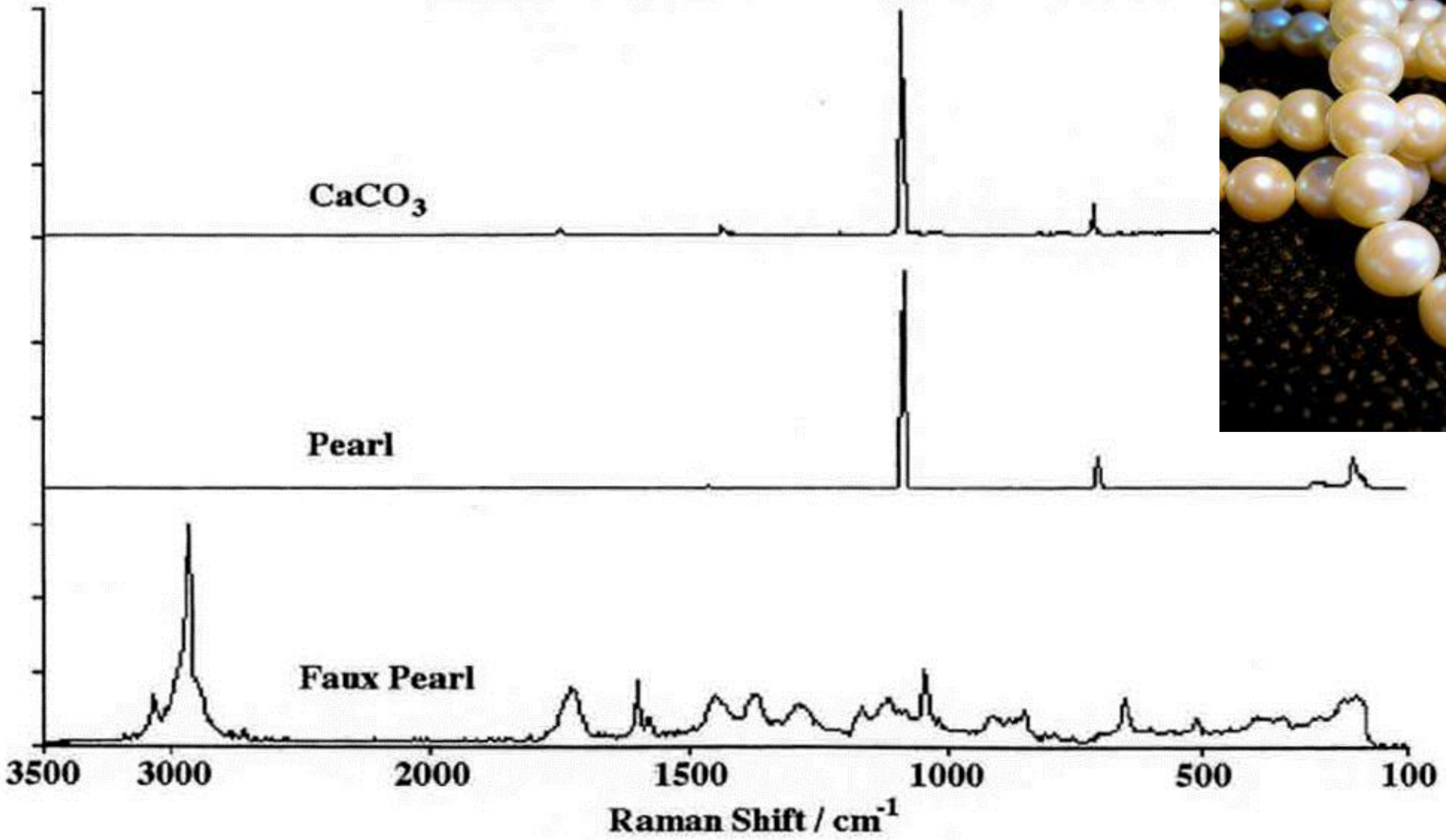


Figure 3 The Raman spectra of calcium carbonate (top), natural pearl (middle), and faux pearl (bottom). (Adapted with permission from Ref. 9.)

Lewis, I. R.; Edwards, H. G. M., *Handbook of Raman Spectroscopy: From the Research Laboratory to the Process Line,* Marcel Dekker, New York: 2001.0

Raman Instrumentation