

Molecular Spectroscopy



By

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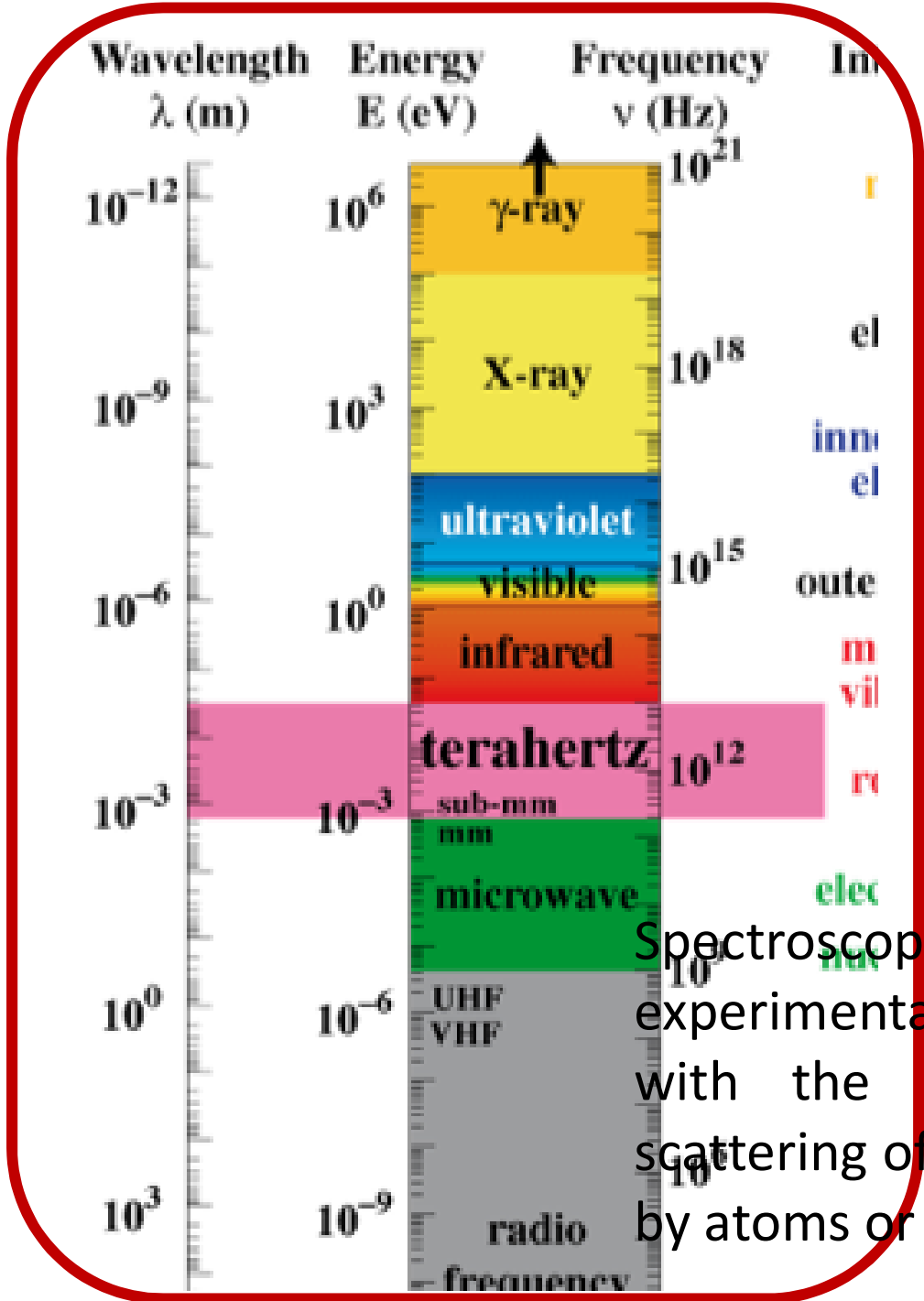
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Spectroscopy ????

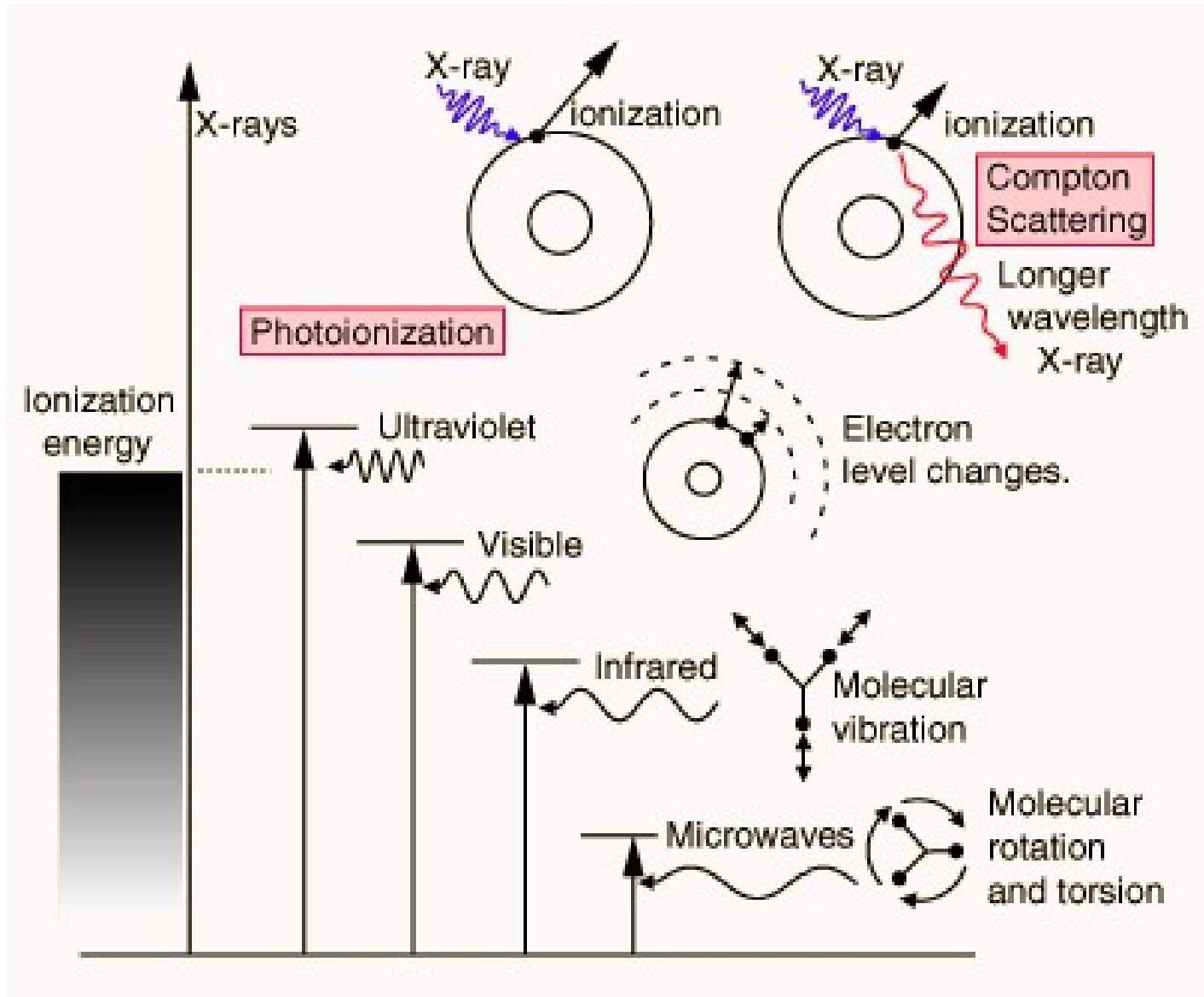


Interaction of electromagnetic radiations with matter



Spectroscopy is basically an experimental subject and is concerned with the absorption, emission or scattering of electromagnetic radiation by atoms or molecules

The interaction of radiation with matter



Different types of Energy

Connecting macroscopic thermodynamics to a molecular understanding requires that we understand how energy is distributed on a molecular level.

ATOMS: The electrons: **Electronic energy**. Increase the energy of one (or more) electrons in the atom.

Nuclear motion: **Translational energy**. The atom can move around (translate) in space.

MOLECULES:

The electrons: **Electronic energy**. Increase the energy of one (or more) electrons in the molecule.

Nuclear motion:

Translational energy. The entire molecule can translate in space.

Vibrational energy. The nuclei can move relative to one another.

Rotational energy. The entire molecule can rotate in space.

Energy is quantized



Planck, 1900

Planck suggests that radiation (light, energy) can only come in quantized packets that are of size $h\nu$.

Energy (J) → $E = h\nu$

Planck's constant
 $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$

Frequency (s^{-1})

Note that we can specify the energy by specifying *any one* of the following:

1. The frequency, ν (units: Hz or s^{-1}):

$$E = h\nu$$

2. The wavelength, λ , (units: m or cm or mm):

Recall: $\nu\lambda = c$

$$E = \frac{hc}{\lambda}$$

3. The wavenumber, $\tilde{\nu}$ (units: cm^{-1} or m^{-1})

Recall: $\tilde{\nu} = \frac{1}{\lambda}$

$$E = hc\tilde{\nu}$$

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

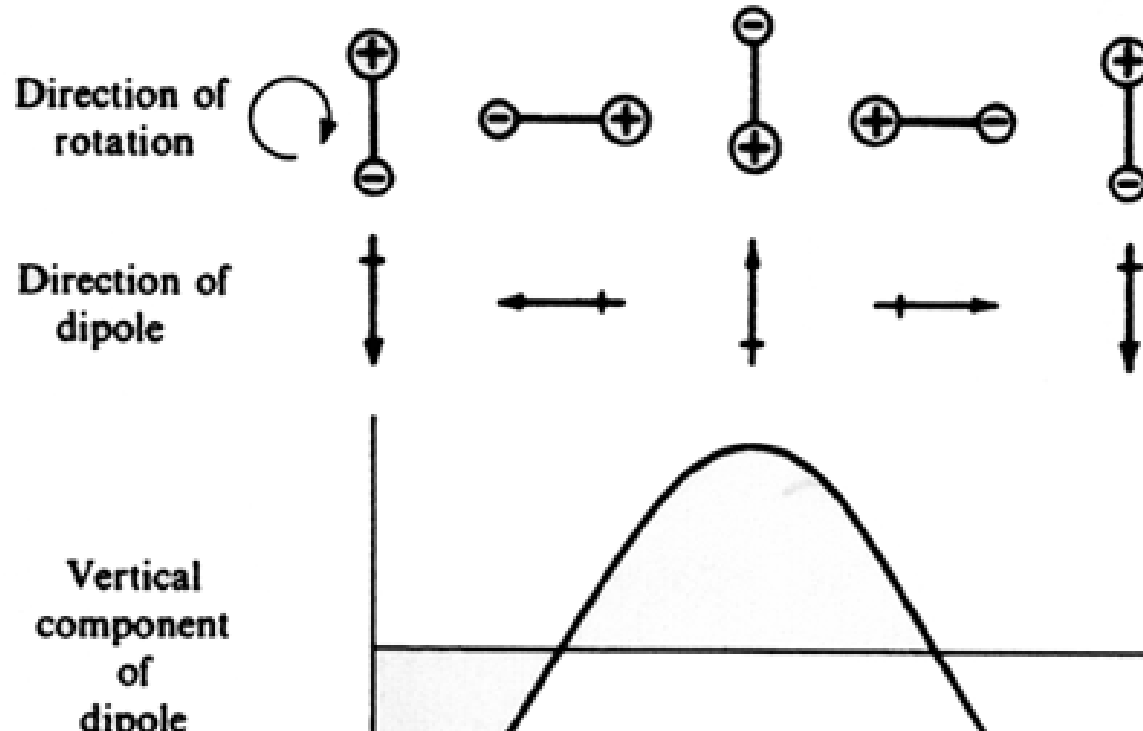
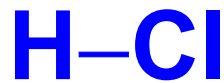
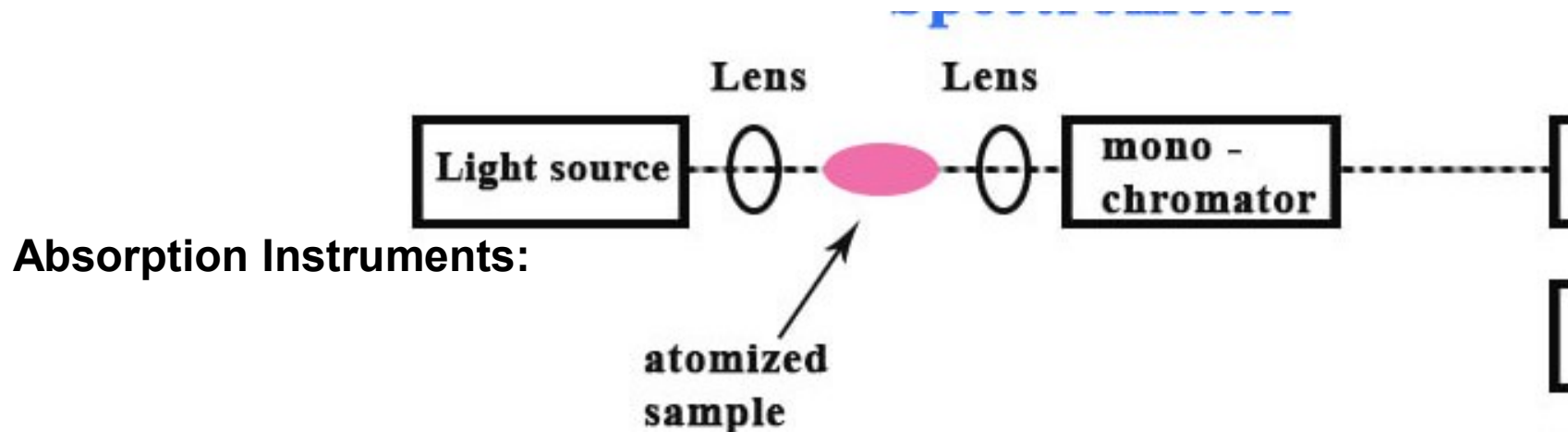
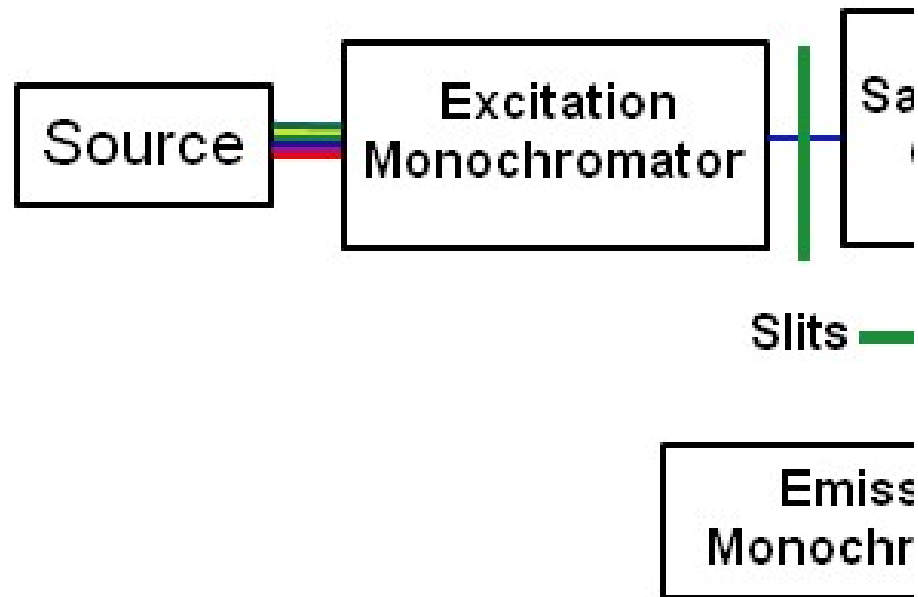


Fig. The rotation of a polar diatomic molecule, showing the fluctuation in the dipole moment measured in a particular direction

Basic Elements of Practical Spectroscopy



Emission Instruments:



Resolving Power

The ability of an optical instrument to produce separate images of two objects very close together is called resolving power.

Rayleigh criterion: When the central maximum in the diffraction pattern of one point source coincides with the first minimum in the diffraction pattern of the other point source, then the two sources



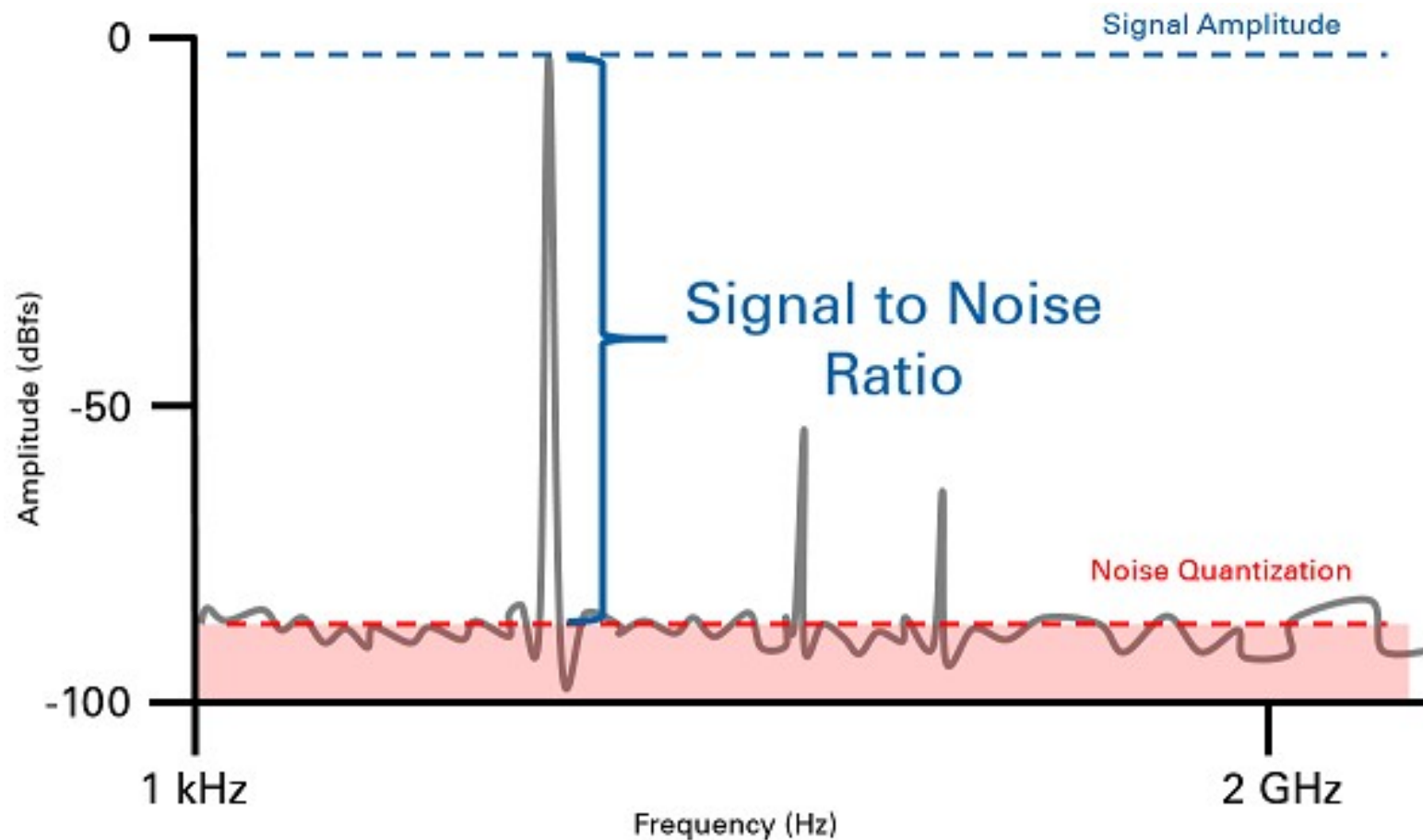
are said to have been resolved by the optical instrument.



Signal-to-Noise Ratio

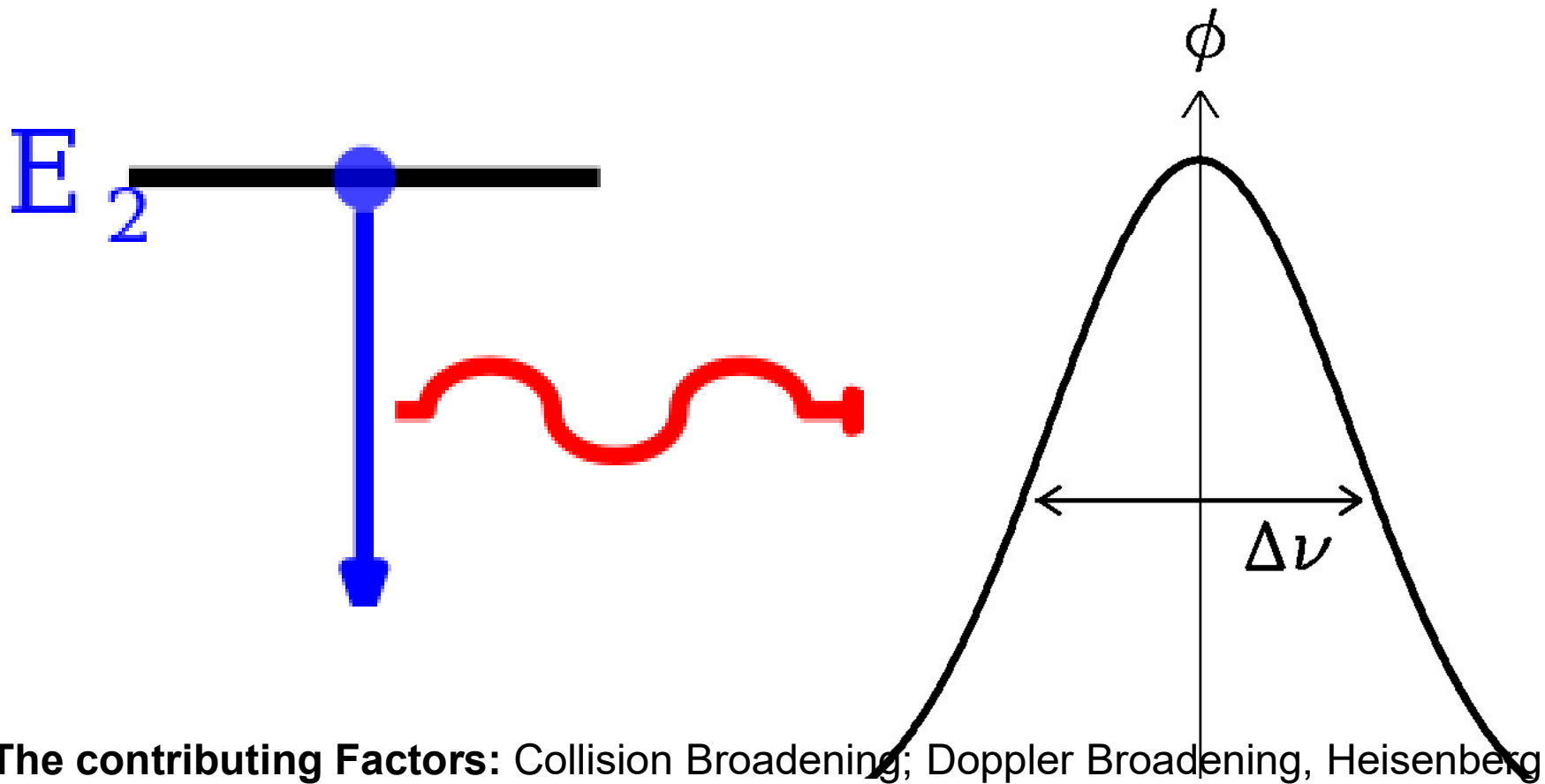
Electronic amplification to magnify signal

The recorded spectrum has a background of random fluctuations by the source or detector or generated by amplifying equipments



Width of Spectral Lines

- Range of Frequencies rather than a single frequency and every molecules are having natural line width
- Natural line width (inherent minimum width in atomic and molecular transitions)



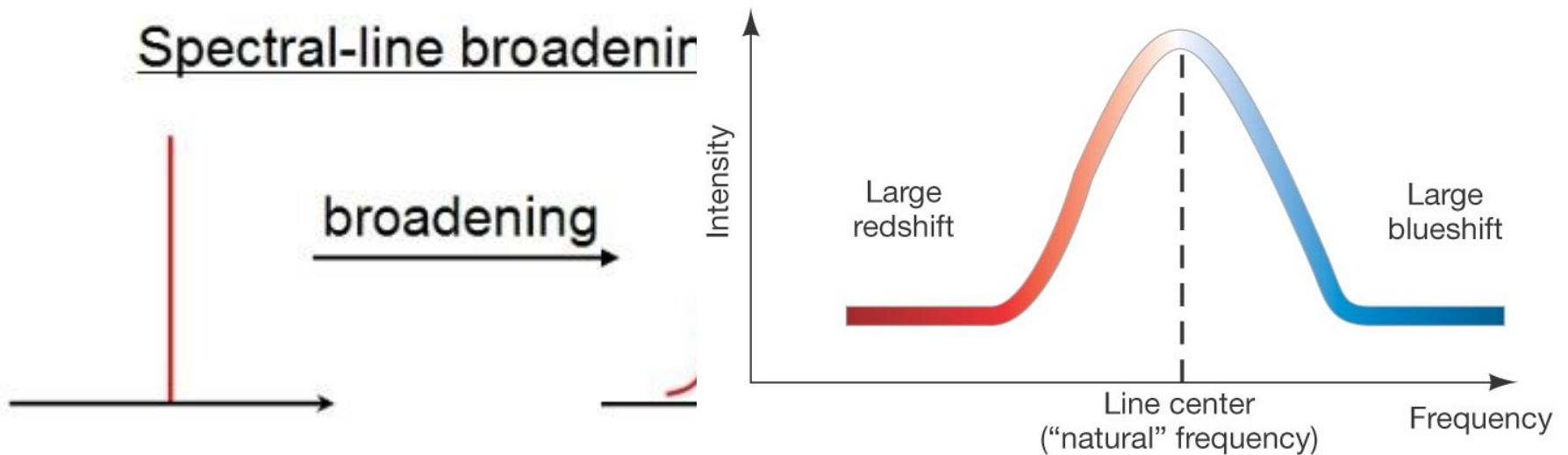
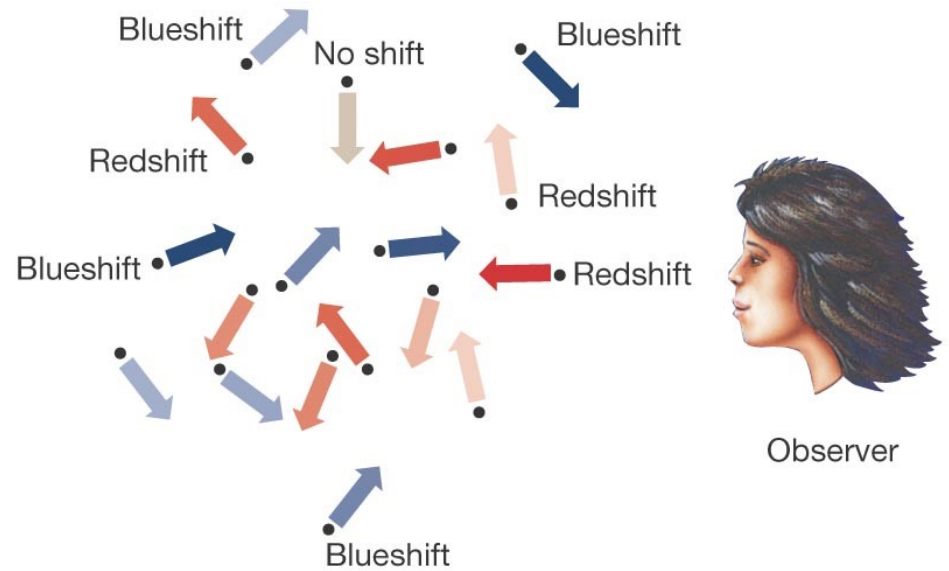
The contributing Factors: Collision Broadening; Doppler Broadening, Heisenberg uncertainty principle

Collision Broadening

In gas and Liquid: Due to collision of an atom with other atoms, ions, free electrons or the walls of the container.

In Solids Due to the interaction of with the phonons of the lattice It leads to the change of relative phase between atomic dipole moment and that of a incident wave Collision

In solid particles are more limited: Hence solid phase spectra's are more sharper

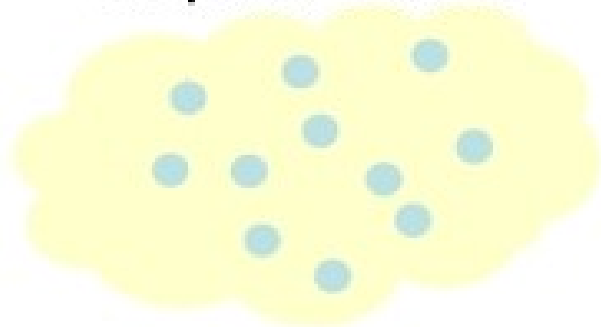


Doppler Broadening

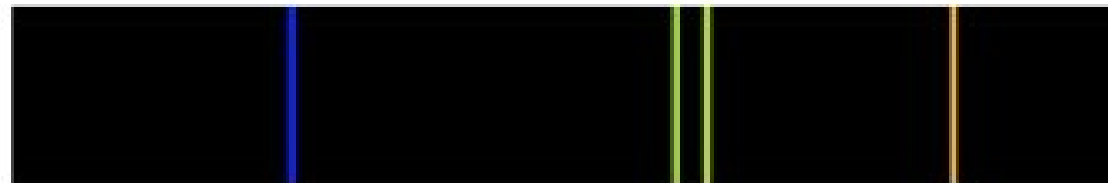
Doppler broadening is the broadening of spectral lines due to the **Doppler effect** caused by a distribution of velocities of atoms or molecules

Thermal Doppler broadening: at kT particles are not at rest position having different velocities

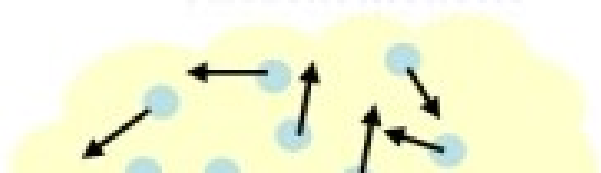
Gas particles at rest



Emission line spectrum with narrow li



Gas particles with random motions

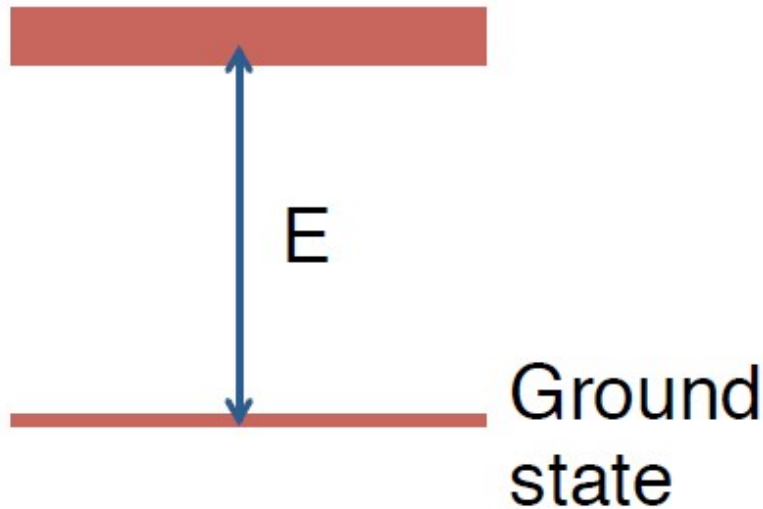


Emission line spectrum with thermal line broadening



Shift because of motion of particles: Its random so high and low frequencies

Heisenberg Uncertainty Principle



Consider excited state E above the ground state
Electrons in excited state there for average time Δt decaying to ground state

Uncertainty principle: energy of a level is uncertain amount ΔE given by:

If $\Delta t = \infty$ then $\Delta E = 0$

$$\Delta E \Delta t \approx \frac{h}{2\pi}$$

Intensity of Spectral Lines

Depends on:

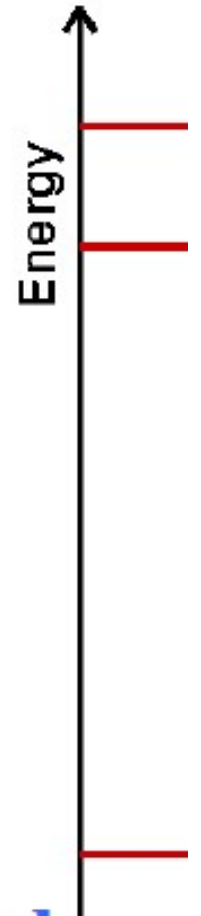
- the transition probability between the two states (selection rules)

- population of states

$$\frac{N_{\text{upper}}}{N_{\text{lower}}} = \exp(-\Delta E/kT)$$

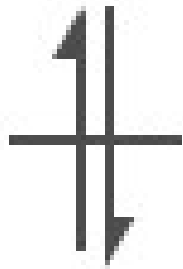
Boltzmann constant

- in absorption, the sample path length and concentration

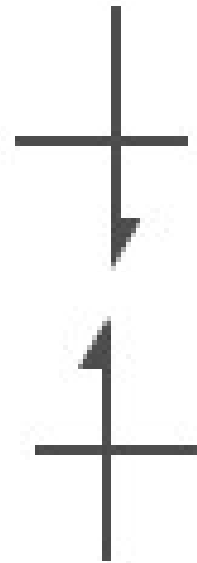


Transition Probability (Selection Rule)

Selection Rules determine the probability of the transition



Ground



Excited

Selection Rules

- During the transition, there must be a change in the **dipole moment** of the molecule:
 - if there is a large change, the light / molecule interaction is strong and many photons are absorbed:
large area or intense bands → intense colour
 - if there is a small change, the light / molecule interaction is weak and few photons are absorbed:
low area or weak bands → weak colour
 - If there is no change, there is no interaction and **no** photons are absorbed.



Population of States (Boltzmann Distribution)

Relative Population (N_2/N_1)

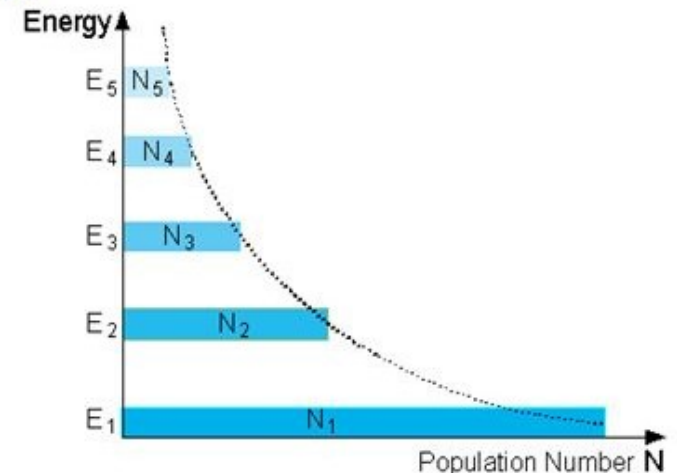
The relative population (N_2/N_1) of two energy levels E_2 compared to E_1 is:

$$N_2/N_1 = \text{const} * \exp(-E_2/kT) / \text{const} * \exp(-E_1/kT)$$

$$\frac{N_2}{N_1} = \exp\left(-\frac{E_2 - E_1}{kt}\right)$$

The proportionality constant (const) is cancelled by division of the two population numbers.

The Figure below shows the population of each energy level at thermal equilibrium.



Path Length of the Sample (Molar Absorption Coefficient)

The Beer-Lambert Law (λ specific):

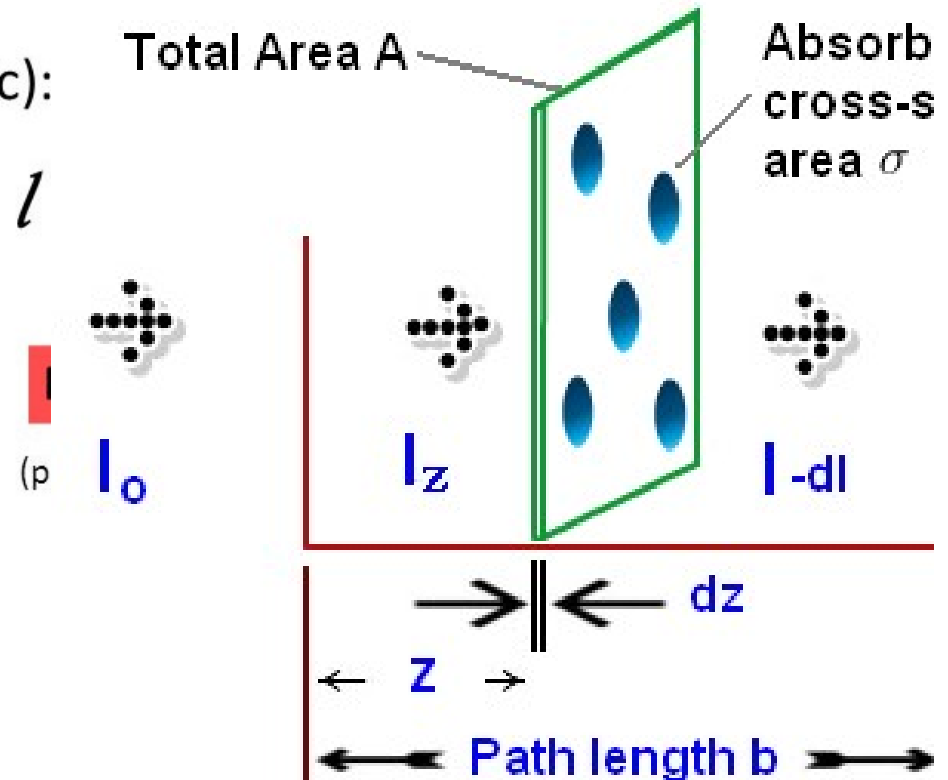
$$\text{Log} (I_0/I) = A = \epsilon c l$$

A = absorbance (unitless, $A = \log_{10} P_0/P$)

ϵ = molar absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$)

l = path length of the sample (cm)

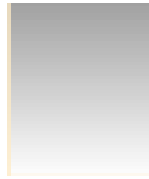
c = concentration (mol/L or M)



Concentration	↑	Absorbance	↑
Path length	↑	Absorbance	↑
Molar Abs.	↑	Absorbance	↑

Microwave interactions

Small number of available states, almost transparent.

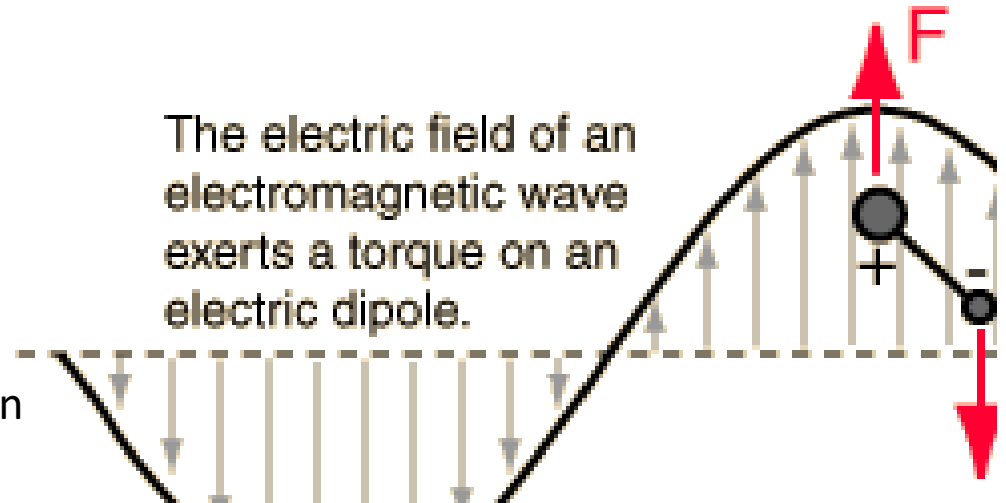


Microwaves rotate molecules

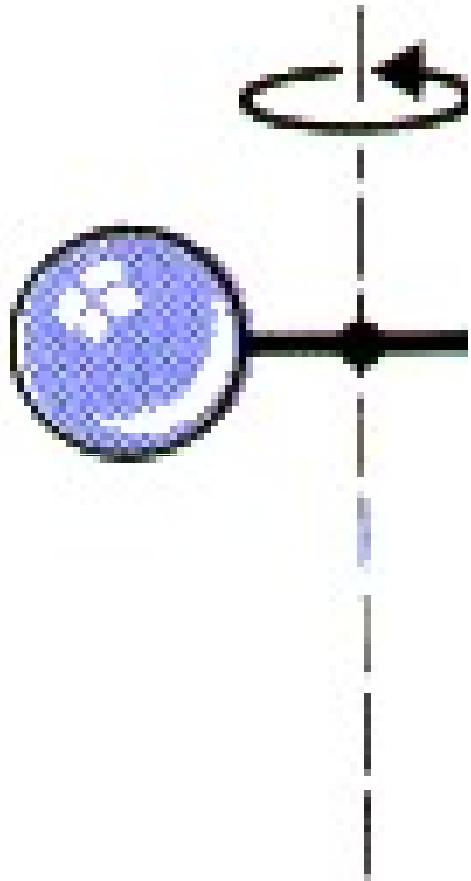
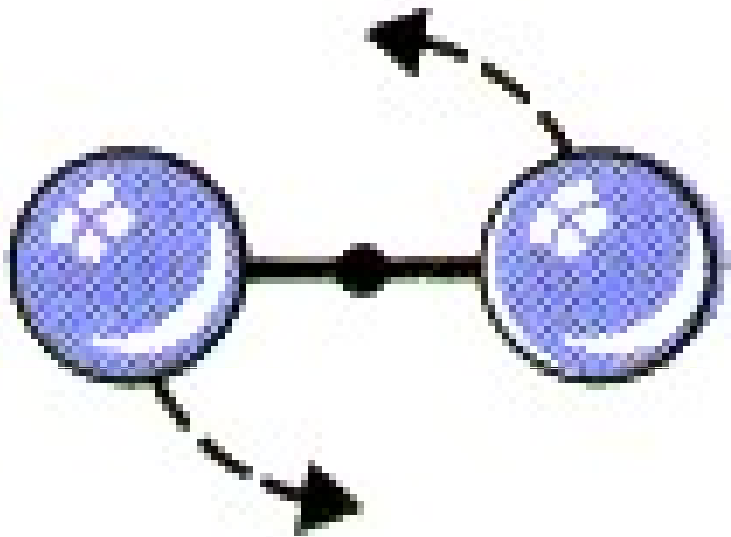


- Quantum energy of microwave photons (0.00001-0.001 eV) matches the ranges of energies separating quantum states of **molecular rotations and torsion**
- Note that *rotational motion of molecules is quantized*, like electronic and vibrational transitions → associated absorption/emission lines

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

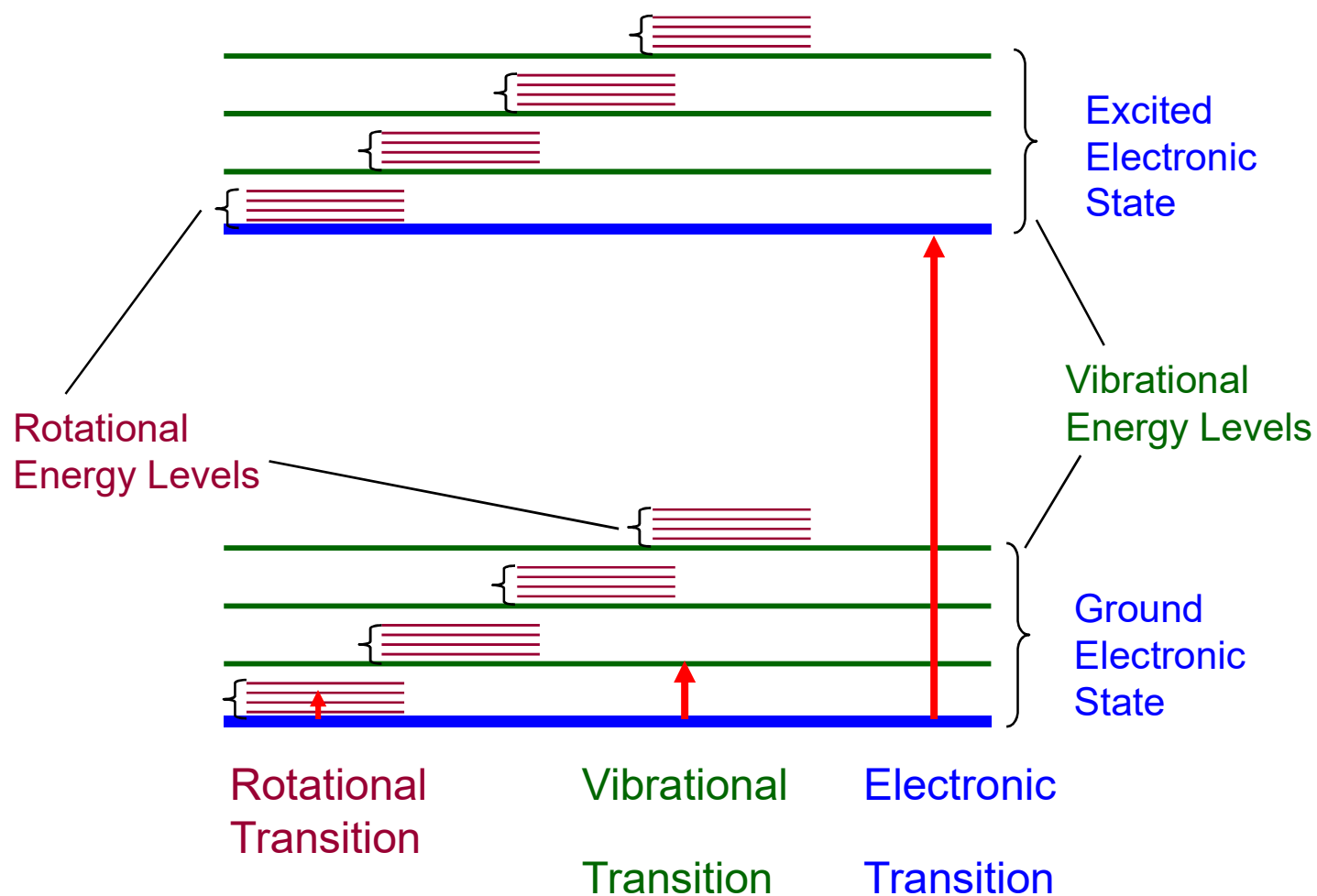


- Absorption of microwave radiation causes heating due to increased molecular rotational activity



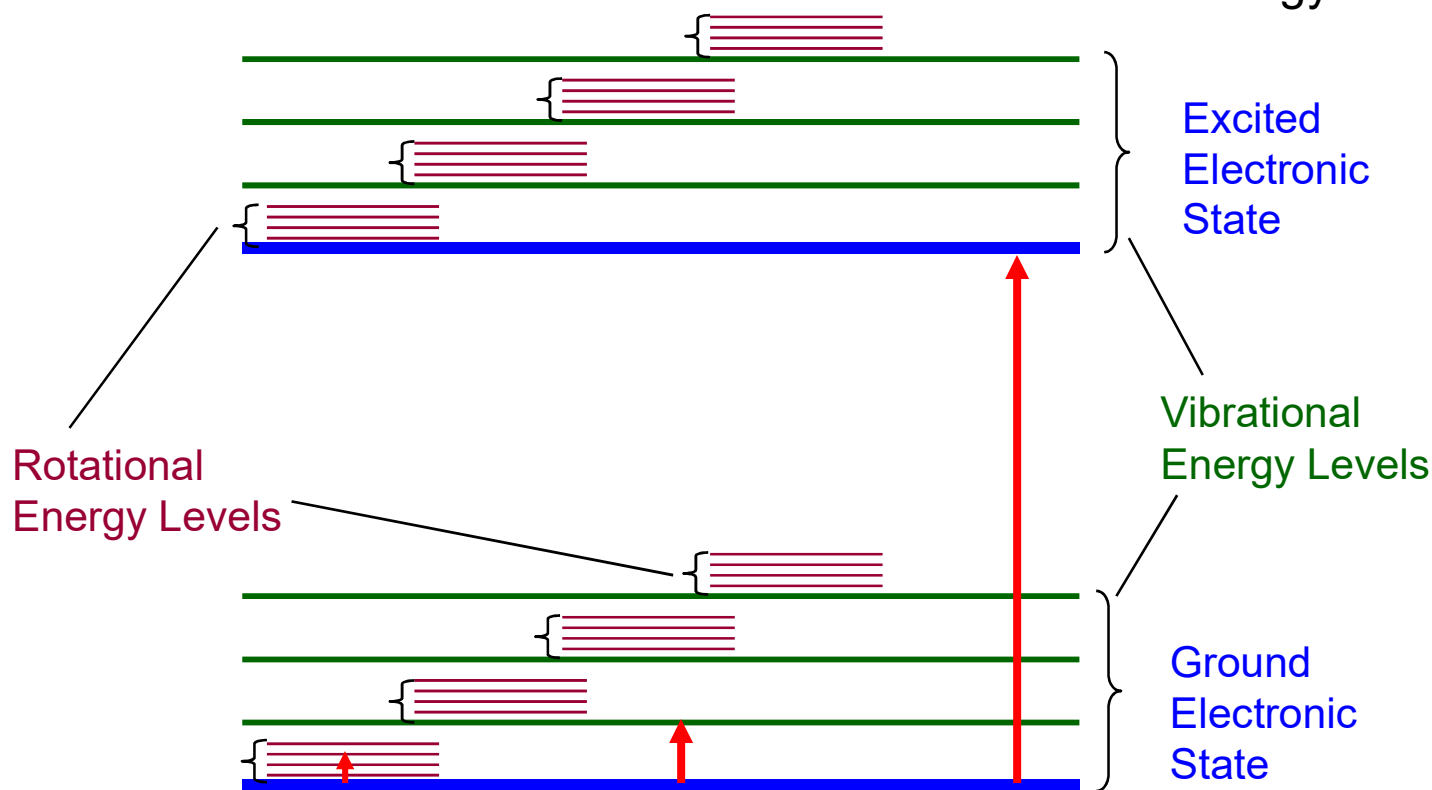
Molecular Energy Levels

Radiation can be absorbed or emitted if the molecule changes any of its energy states



Molecular Energy Levels

All forms of the energy are quantized



Rotational
Transition
1-20 cm^{-1}
Microwave

Vibrational
Transition
2000-4000 cm^{-1}
Infrared

Electronic
Transition
10000-50000 cm^{-1}
UV-Visible

Rigid Molecules

Non-Rigid Molecules

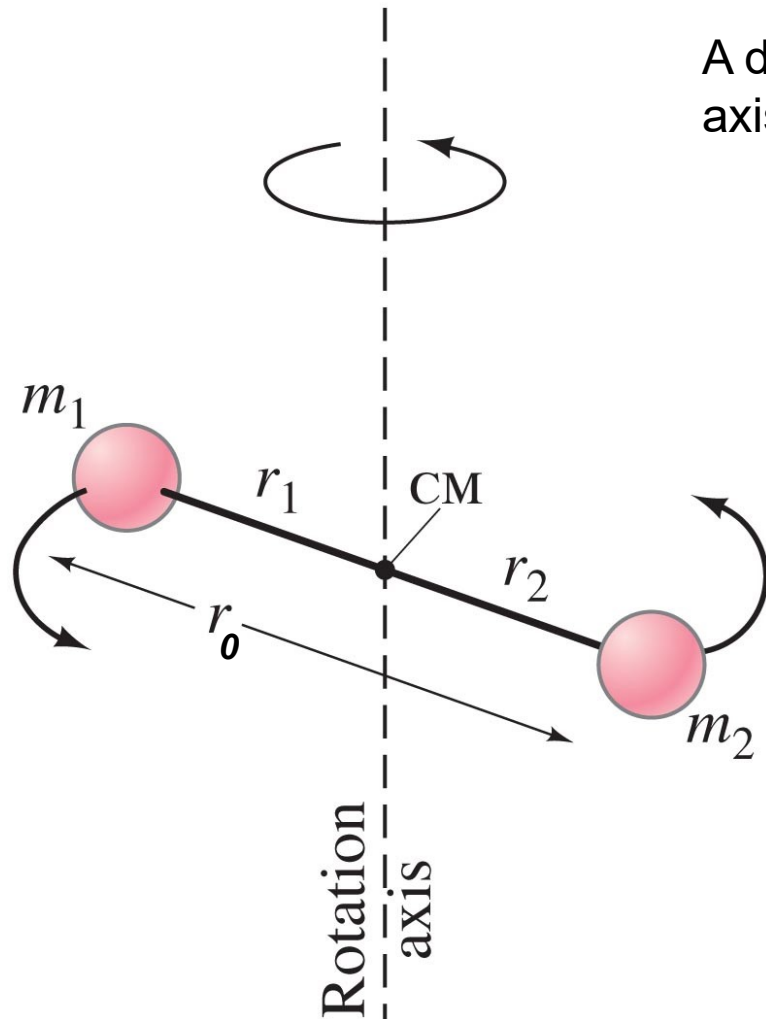
Rotational Spectra

Diatomic Molecules

Polyatomic Molecules

Rigid Diatomic Molecules

For simplicity, we can consider only rotational motion of rigid diatomic molecule



A diatomic molecule can rotate around a vertical axis. The rotational energy is quantized.

Assume a rigid (not elastic) bond

$$r_0 = r_1 + r_2$$

For rotation about center of gravity, C :

$$\begin{aligned} m_1 r_1 &= m_2 r_2 \\ &= m_2 (r_0 - r_1) \end{aligned}$$

$$r_1 = \frac{m_2 r_0}{m_1 + m_2}$$

$$r_2 = \frac{m_1 r_0}{m_1 + m_2}$$

RIGID ROTOR

Moment of inertia about C:

$$I_C = m_1 r_1^2 + m_2 r_2^2 = m_2 r_2 r_1 + m_1 r_1 r_2 = r_1 r_2 (m_1 + m_2)$$

$$\Rightarrow I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2 \quad \mu = \text{reduced mass,} \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

A diatomic molecule can rotate around a vertical axis. The rotational energy is quantized. By using the Schrödinger equation, the rotational energy levels allowed to the rigid diatomic molecule are given by,

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

J = Rotational quantum number ($J = 0, 1, 2, \dots$)

I = Moment of inertia = mr^2

μ = reduced mass = $m_1 m_2 / (m_1 + m_2)$

r = internuclear distance

Rotational Spectra of Rigid Diatomic molecule

Rotational Energy Levels for rigid rotor:

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

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 I c} J(J + 1) \text{ cm}^{-1} \quad (J = 0, 1, 2, \dots)$$

$$\varepsilon_J = BJ(J + 1) \text{ cm}^{-1} \quad (J = 0, 1, 2, \dots)$$

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

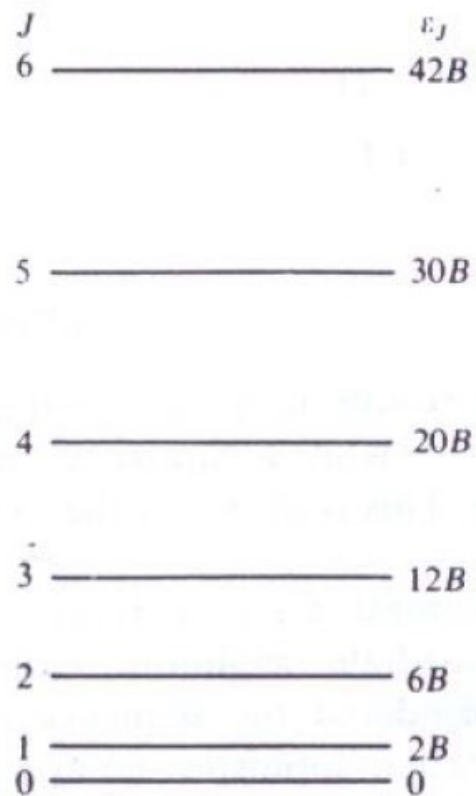
Where $I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2$

Rotational Spectra of Rigid Diatomic molecule

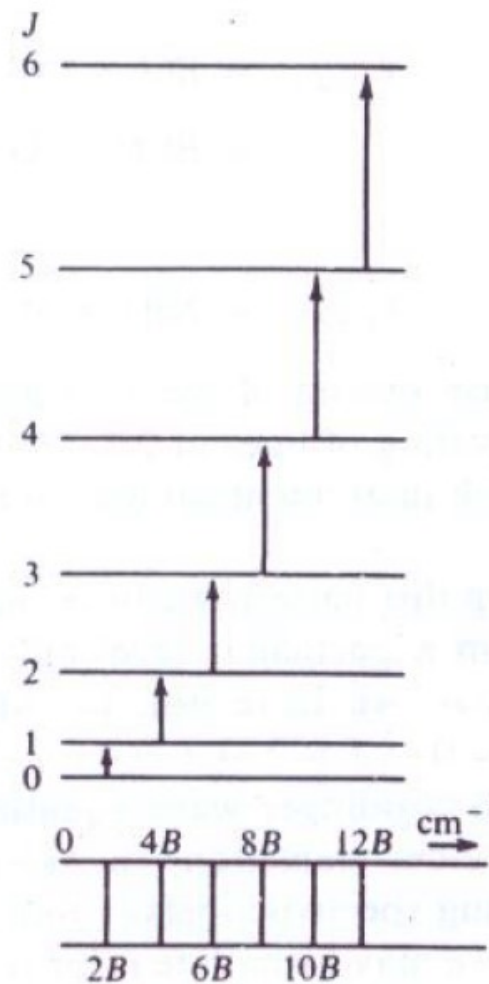
For rigid rotor, $J \rightarrow J + 1$,

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

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

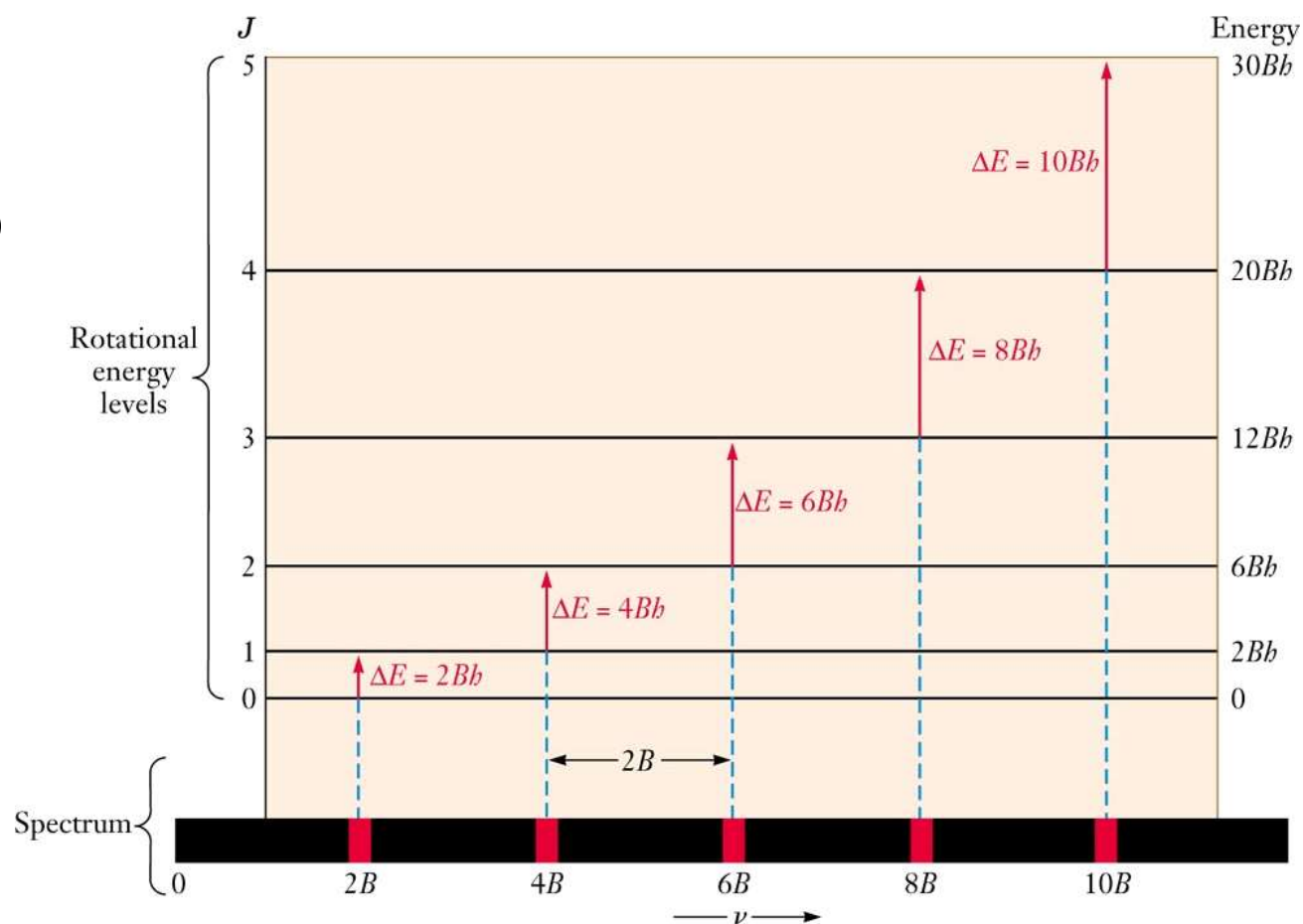
Rotational Spectra of Rigid Rotor

Selection Rule: Apart from **Specific rule**, $\Delta J = \pm 1$, **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.**

$$\Delta j = \pm 1$$

$$\Delta j = +1 \text{ (absorption)}$$

$$\Delta j = -1 \text{ (emission)}$$



Appearance of rotational spectrum We can calculate the energy corresponding to rotational transitions

$$\Delta E = E_{J'} - E_J \quad \text{for } \Delta J = J_{final} - J_{initial} = +1$$

Or generally:

$$\begin{aligned} J \rightarrow J + 1 \quad \bar{\nu} &= B(J+1)(J+2) - BJ(J+1) \\ &= 2B(J+1) \text{ cm}^{-1} \end{aligned}$$

Microwave absorption lines should appear at

$$\begin{aligned} J = 0 \quad \rightarrow J = 1 : \quad \bar{\nu} &= 2B - 0 = 2B \text{ cm}^{-1} \\ J = 1 \quad \rightarrow J = 2 : \quad &= \quad \quad = 4B \text{ cm}^{-1} \end{aligned}$$

Note that the selection rule is $\Delta J = \pm 1$, where + applies to absorption and - to emission.

Find $r(\text{C—O})$

$$I = \frac{h}{8\pi^2 Bc} = \frac{2.7992774 \times 10^{-46}}{B} \text{ kgm}^2$$
$$= \mu r^2$$

$$B = 1.921175 \text{ cm}^{-1}; \quad \mu = 1.1386378 \times 10^{-26} \text{ kg}$$

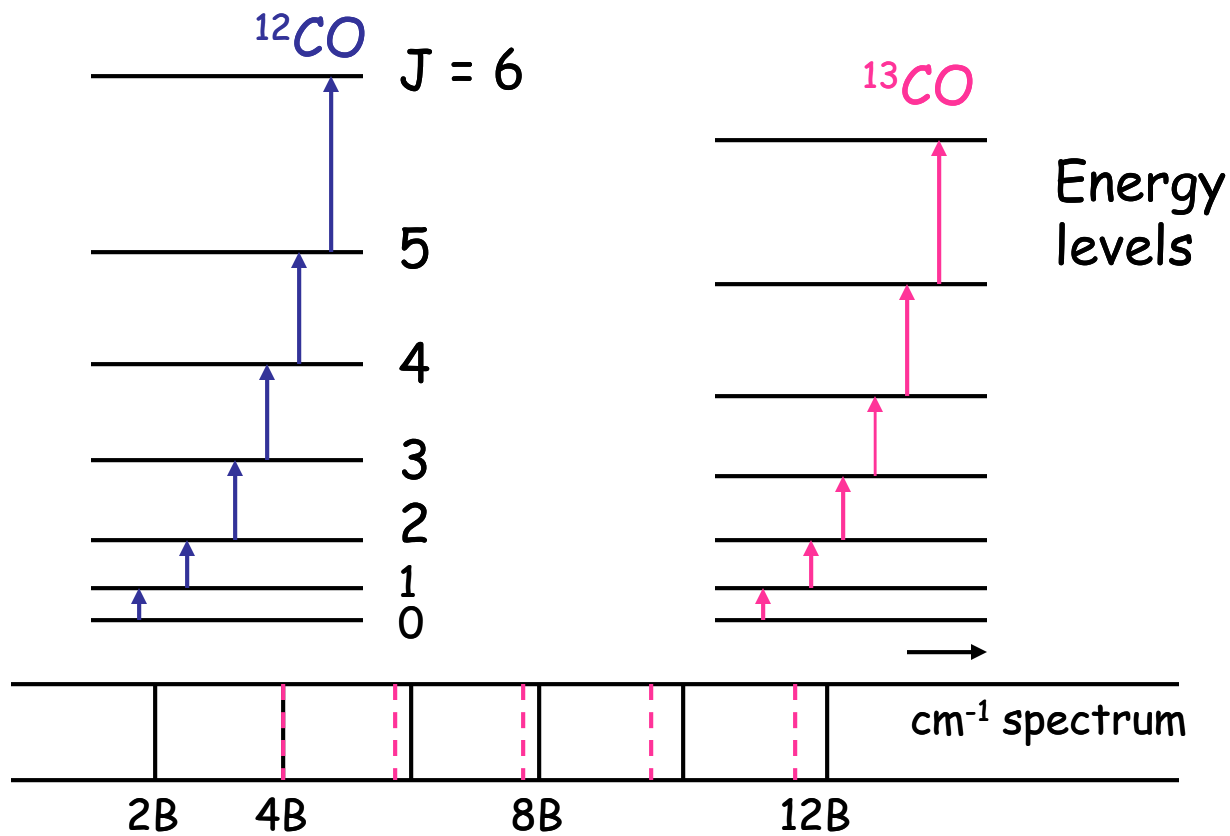
$$\Rightarrow = 1.131 \times 10^{-10} \text{ m}$$

$$\Rightarrow 0.1131 \text{ nm} \quad r = \sqrt{\frac{I}{\mu}}$$

Answer: C-O bond length is 0.1131 nm.

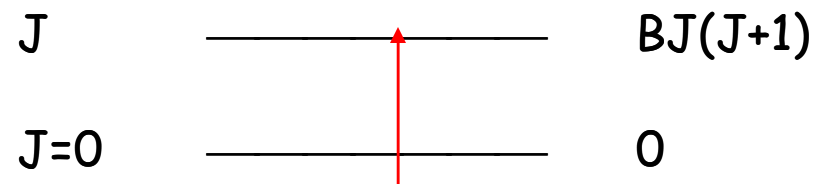
Effect of isotopes

From $^{12}\text{C}^{16}\text{O} \rightarrow ^{13}\text{C}^{16}\text{O}$, mass increases, B decreases ($\propto 1/I$), so energy levels lower.



Relative Intensities of rotation spectral lines

Now we understand the locations (positions) of lines in the microwave spectrum, we can see which lines are strongest.



Intensity depends upon two factors:

Intensity depends upon two factors:

1. Greater initial state population gives stronger spectral lines. This population depends upon temperature, T.

$k =$ Boltzmann's constant, $1.380658 \times 10^{-23} \text{ J K}^{-1}$

$$(k = R/N) \frac{N_J}{N_0} \propto \exp\left(-\frac{E_J}{kT}\right) = \exp\left(-\frac{hc \bar{\nu}}{kT}\right)$$

We conclude that the population is smaller for higher J states.

$$\frac{N_J}{N_0} \propto e\left(-\frac{1.52034\bar{\nu}}{T}\right) \quad \frac{hc}{k} = 1.52034 \text{ cmK}$$

2. Intensity also depends on degeneracy of initial state.

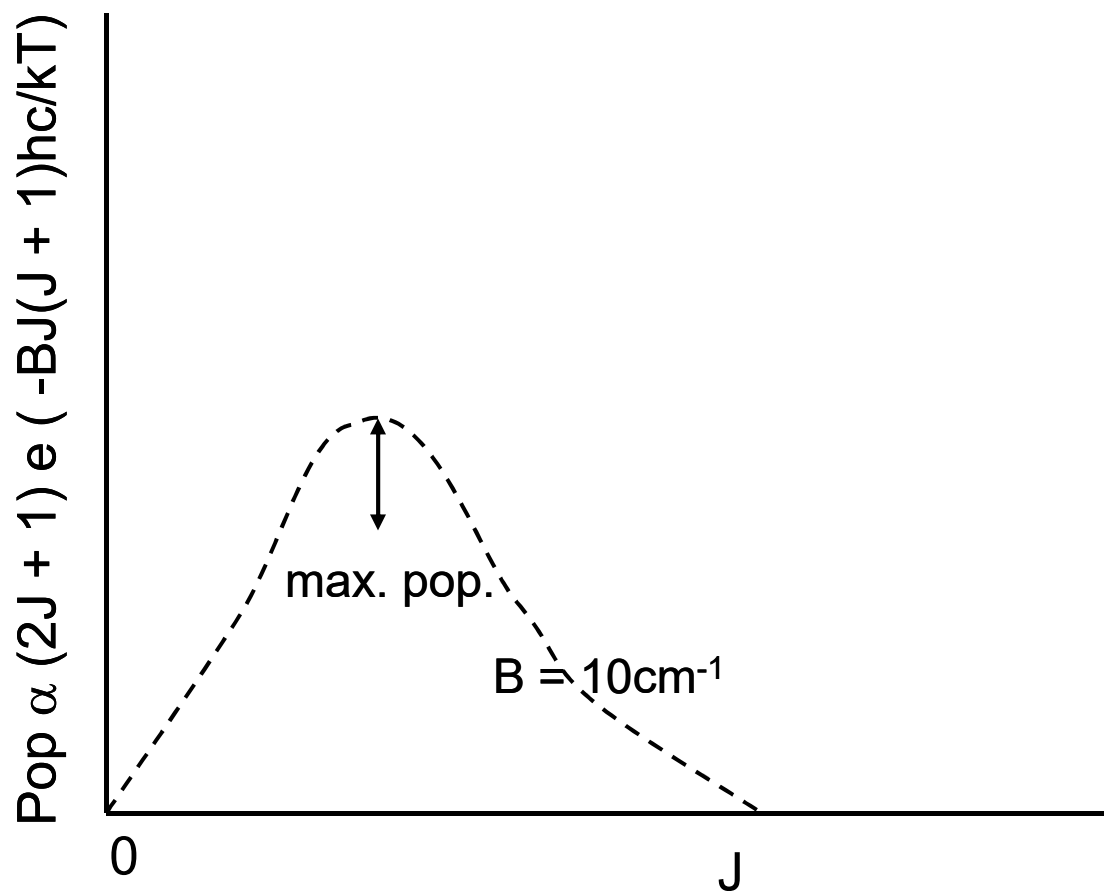
(degeneracy = existence of 2 or more energy states having exactly the same energy)

Each level J is $(2J+1)$ degenerate

⇒ **population is greater for higher J states.**

To summarize: Total relative population at energy $E_J \propto (2J+1) \exp(-E_J / kT)$ & maximum population occurs at nearest integral J value to :

Look at the values of N_J/N_0 in the figure, .



Plot of population of rotational energy levels versus value of J .

The Non-Rigid Rotor

If the shape of the molecule is allowed to distort upon rotation, Then the restriction of the rigid rotor is lifted.

It may be expected that as the rotational energy increases the molecule will have it's bond lengthened because of the centrifugal distortion.

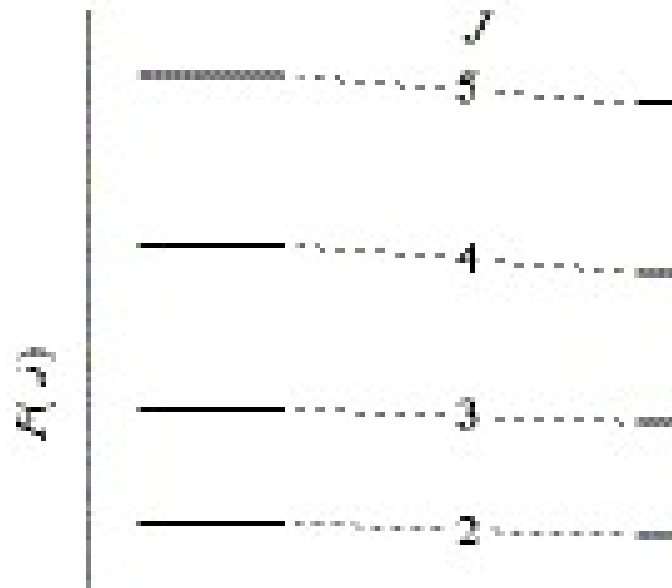
This will lead to an effective decrease in the rotational energy since the longer bond will lead to a decrease in the rotational energy.

We can refine the theory by adding a correction term, containing the centrifugal distortion constant, D , which corrects for the fact that the bond is not rigid.

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

Here, D is the **centrifugal distortion constant**. For the $J \rightarrow J + 1$ transitions, the absorption frequency is given by

$$\begin{aligned}\tilde{\nu} &= F(J + 1) - F(J) \\ &= 2\tilde{B}(J + 1) - 4\tilde{D}(J + 1)^3 \quad J = 0, 1, 2, \dots\end{aligned}$$



$$D = \frac{h^3}{32\pi^4 I^2 r^2 k c} \text{cm}^{-1}$$

$$= \frac{4B^3}{\bar{\nu}_{\text{vib}}^2}$$

where $\bar{\nu}_{\text{vib}}$ is bond stretch wavenumber.

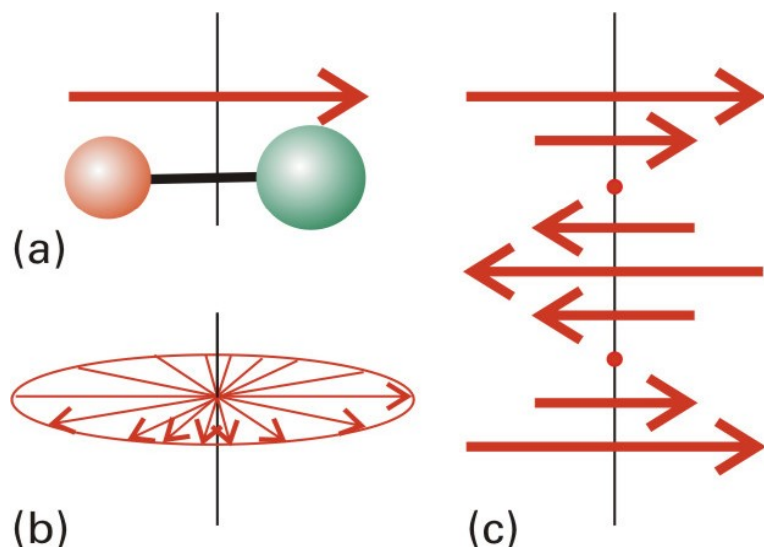
i) can find J values of lines in a spectrum - fitting 3 lines gives 3 unknowns: J, B, D.

ii) We can estimate $\bar{\nu}_{\text{vib}}$ from the small correction term, D.

Rotational spectroscopy

- **Gross selection rule:** The molecules must have a permanent electric dipole moment so that the molecules are polar.

Classical description



To an observer, a rotating polar molecule has an electric dipole that appears to oscillate. This oscillating dipole can interact with the EM field.

Rotational-inactive molecules: Molecules without rotational spectrum

Homonuclear diatomic molecules: N_2 , O_2

Symmetric linear molecules: CO_2

Tetrahedral molecules: CH_4

Octahedral molecules: SF_6 , C_6H_6

Rotational-active molecules: Molecules with rotational spectrum

Heteronuclear diatomic molecules: HCl

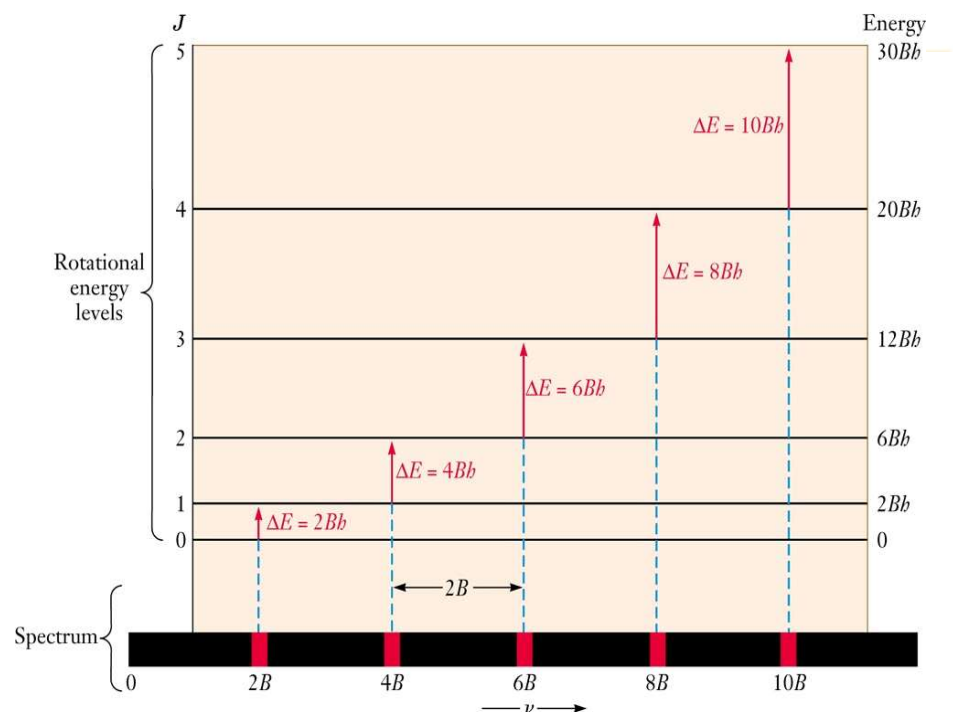
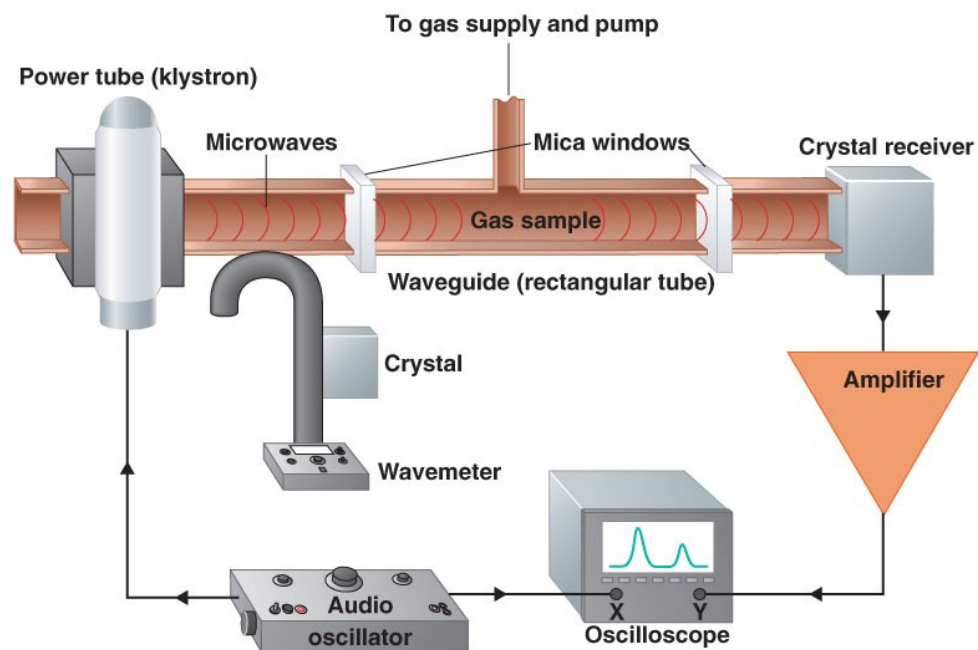
Less symmetric polar molecules: NH_3 , H_2O

Microwave Spectroscopy

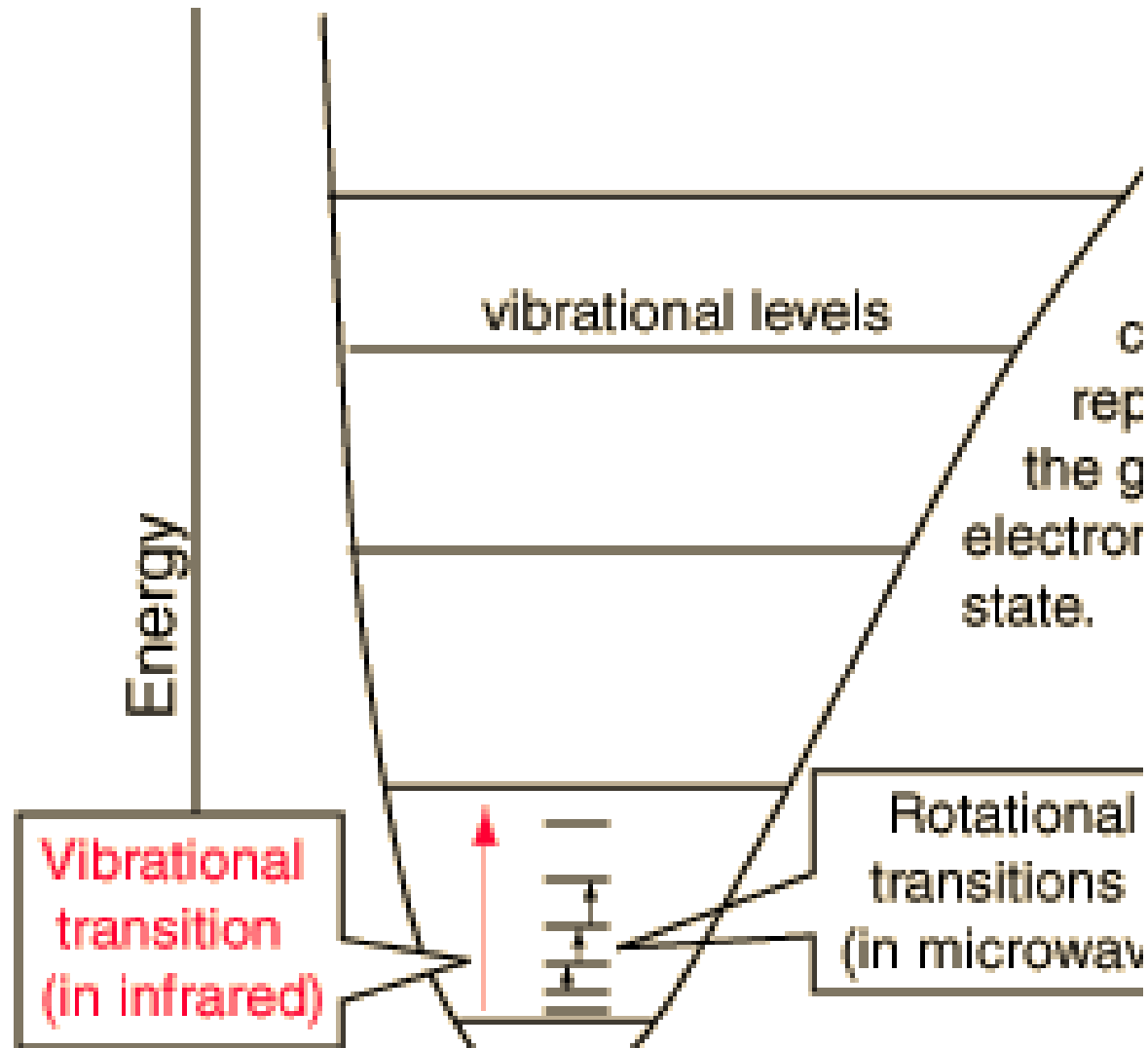
Incident electromagnetic waves can excite the rotational levels of molecules provided they have an electric dipole moment. The electromagnetic field exerts a torque on the molecule.

IMPORTANT

- ❖ **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 dipole moment (polar compound) -- change of dipole occurs during the rotation – hence interaction with radiation takes place – Therefore, heteronuclear diatomic molecules are microwave active.**



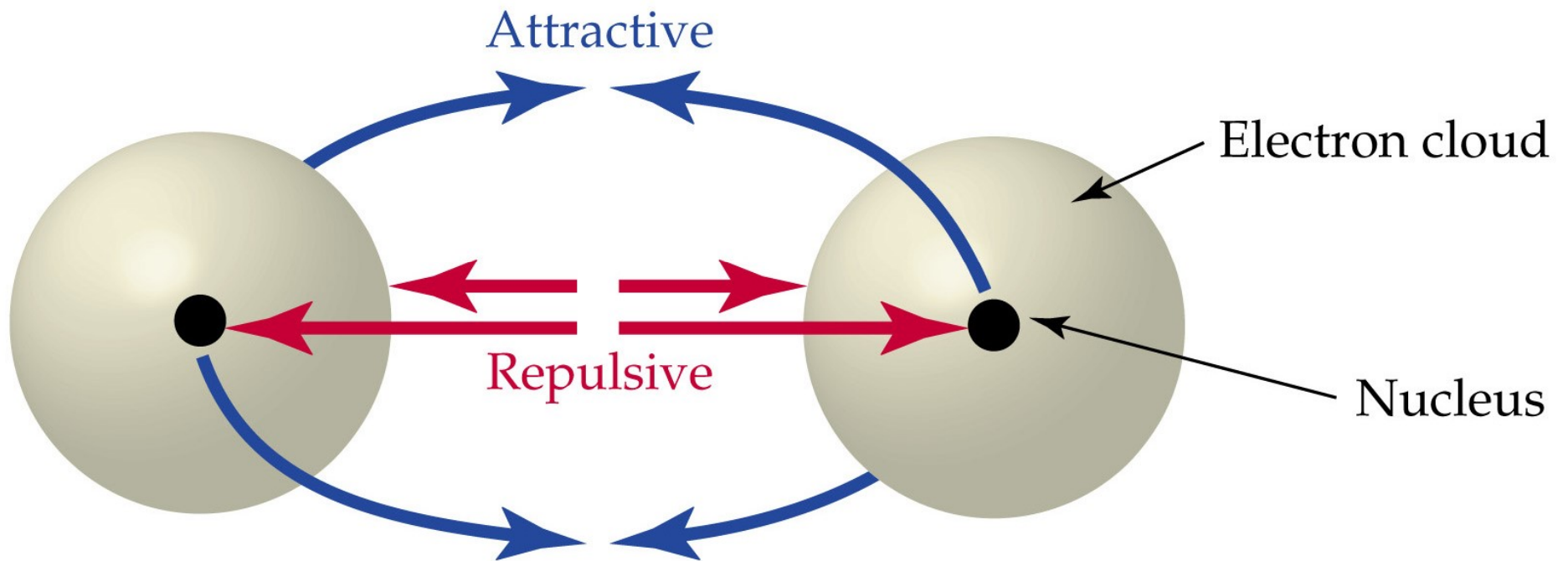
Rotational Energy levels



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

Vibrational Spectroscopy

Chemical Bond Formation



The two atoms settle at a mean internuclear distance such that these forces are just balanced and the total energy of the whole system is a minimum

Vibrational Energy of Diatomic Molecules

- The bonds between atoms behave like springs



- The atoms vibrate approximately like an harmonic oscillator obeying Hooke's Law:

$$F = -k(r - r_{eq})$$

k is the force constant

$$E_{PE} = \frac{1}{2}k(r - r_{eq})^2$$

Vibrational Energy of Diatomic Molecules

$$\omega_{\text{osc}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ Hz}$$

$$\omega_{\text{osc}} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1}$$

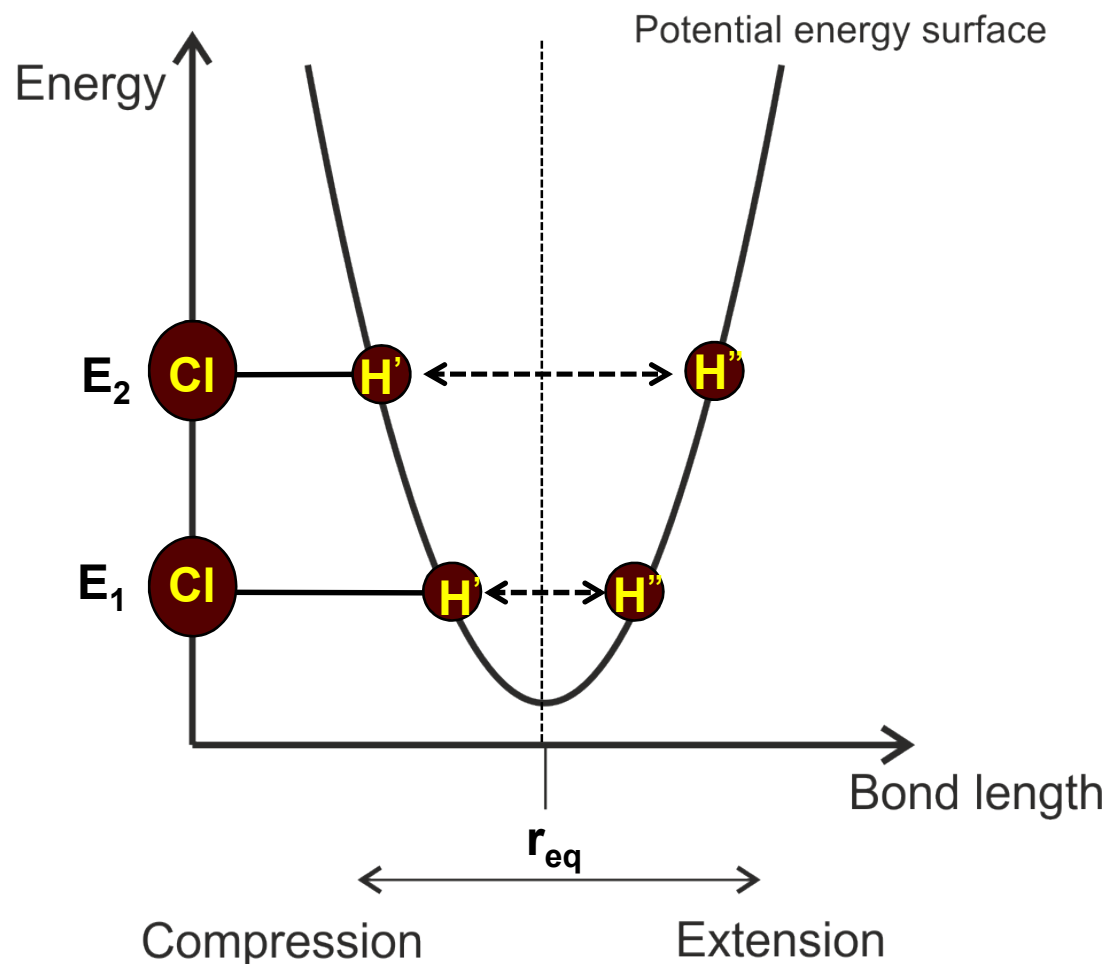
Allowed vibrational energy levels

$$E_{\text{vib}} = (v + \frac{1}{2})h\omega_0 \text{ J}$$

$$v = 0, 1, 2, \dots$$

$$E_v = (v + \frac{1}{2}) h\omega_{\text{osc}} \text{ cm}^{-1}$$

Exchange of PE and KE during vibration



Vibrational spectra: Harmonic oscillator model

Oscillation Frequency,

$$\omega_{\text{osc.}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{Hz}$$

k is the force constant
 μ = reduced mass,

$$\bar{\omega}_{\text{osc.}} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \text{cm}^{-1}$$

Vibrational frequency only dependent on the mass of the system and the force constant .

From Schrodinger equation, Vibrational energies for **simple harmonic oscillator**,

$$E_v = (v + \frac{1}{2})h\omega_{\text{osc.}} \quad \text{joules} \quad (v = 0, 1, 2, \dots)$$

where v is called the *vibrational quantum number*.

$$\epsilon_v = \frac{E_v}{hc} = (v + \frac{1}{2})\bar{\omega}_{\text{osc.}} \quad \text{cm}^{-1}$$

Vibrational spectra: Harmonic oscillator model

Oscillation Frequency,

$$\omega_{\text{osc.}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ Hz}$$

k is the force constant
 μ = reduced mass,

The vibrational frequency is increasing with:

- ❖ increasing force constant k (= increasing bond strength)
- ❖ decreasing atomic mass

• **Example:** $k_{\text{C}\equiv\text{C}} > k_{\text{C}=\text{C}} > k_{\text{C}-\text{C}}$

Vibrational Energy of Diatomic Molecules

Allowed vibrational energy levels

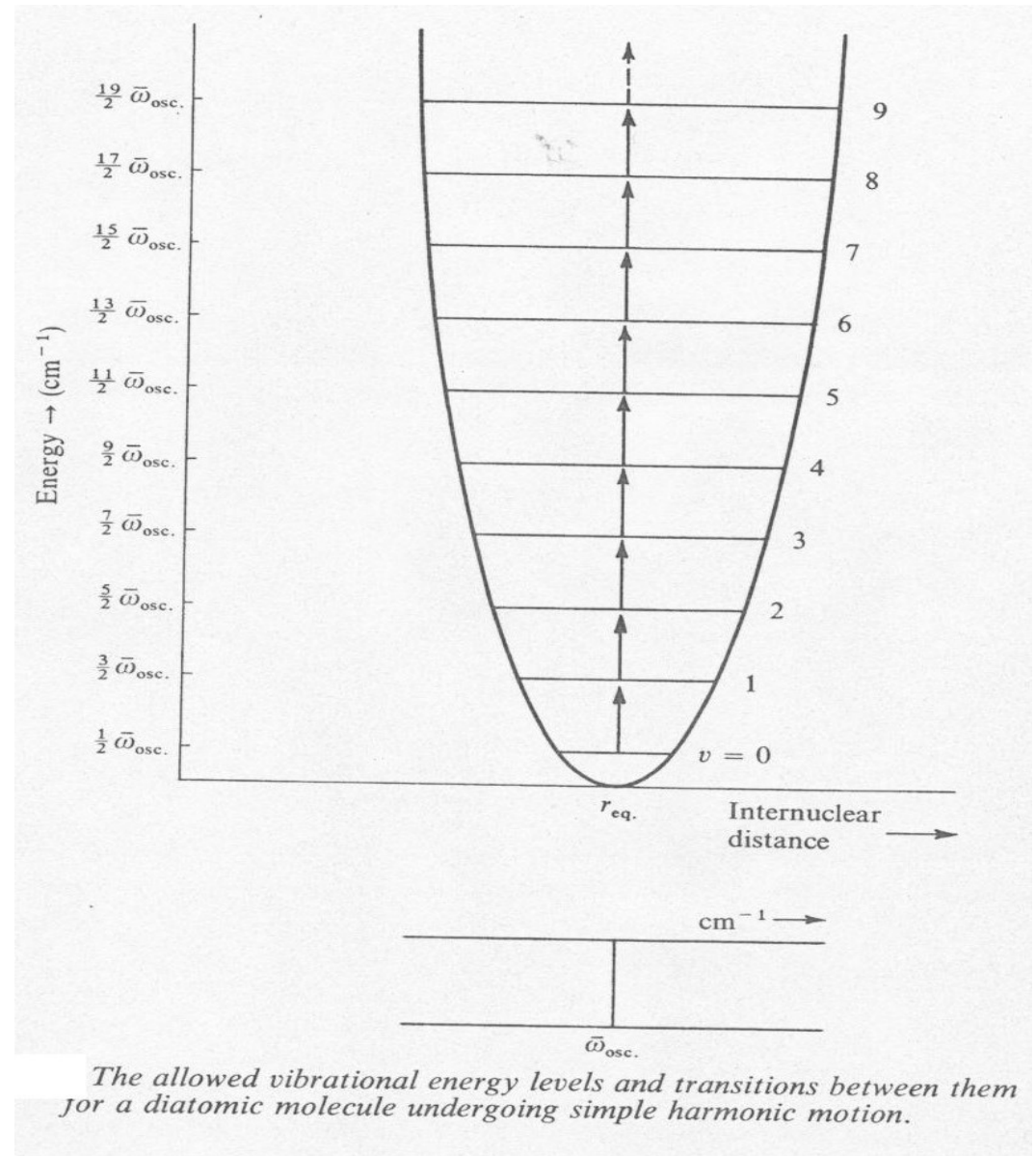
$$E_{\text{vib}} = (v + \frac{1}{2})\omega_0 \text{ cm}^{-1}$$

$$V = 0, 1, 2, \dots$$

Allowed transitions

$$\Delta v = \pm 1$$

Thus expect only one vibrational peak in the IR spectrum



Vibrational Spectrum of Diatomic Molecules

Interaction between EMR and the vibrational energy of molecules can only occur if the bond is polar and a change of dipole moment occurs during oscillation.

Thus only polar bonds generate peaks in the infrared spectrum of molecules.

Thus HCl, CO and HF absorb EMR and have an IR spectrum but H₂ and N₂ do not.

Infrared Spectroscopy

$$\omega_{\text{osc.}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ Hz}$$

POSITION	REDUCED MASS	LIGHT ATOMS → HIGH FREQUENCY
	BOND STRENGTH (STIFFNESS)	STRONG BONDS → HIGH FREQUENCY

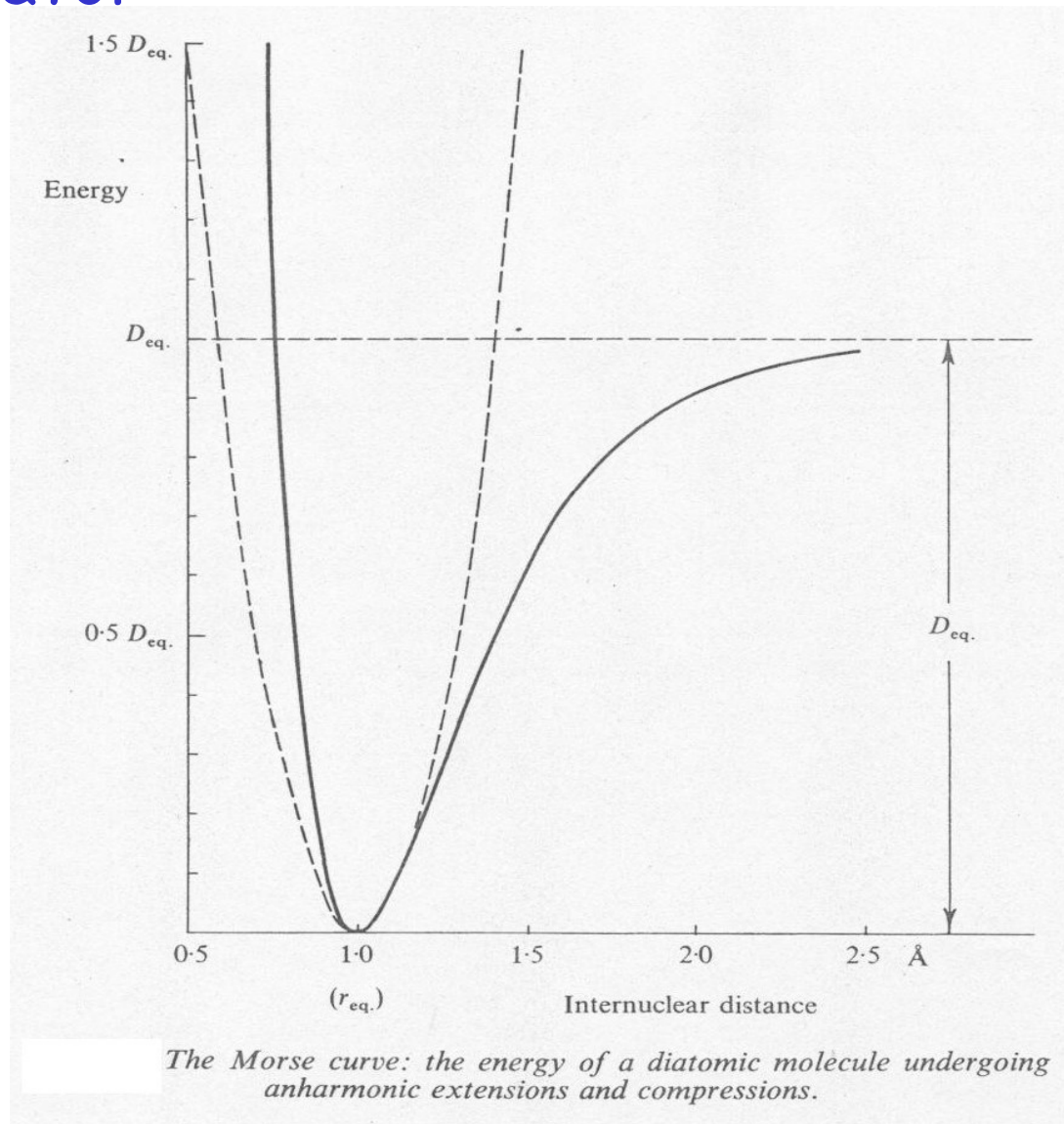
The vibrational frequency is increasing with:

- increasing force constant k (= increasing bond strength)
- decreasing atomic mass

Vibrational Energy of Diatomic Molecules

The Anharmonic Oscillator

Deviations in the energy profile of a real molecule undergoing anharmonic vibration.



Vibrating Diatomic Molecule

The Anharmonic Oscillator

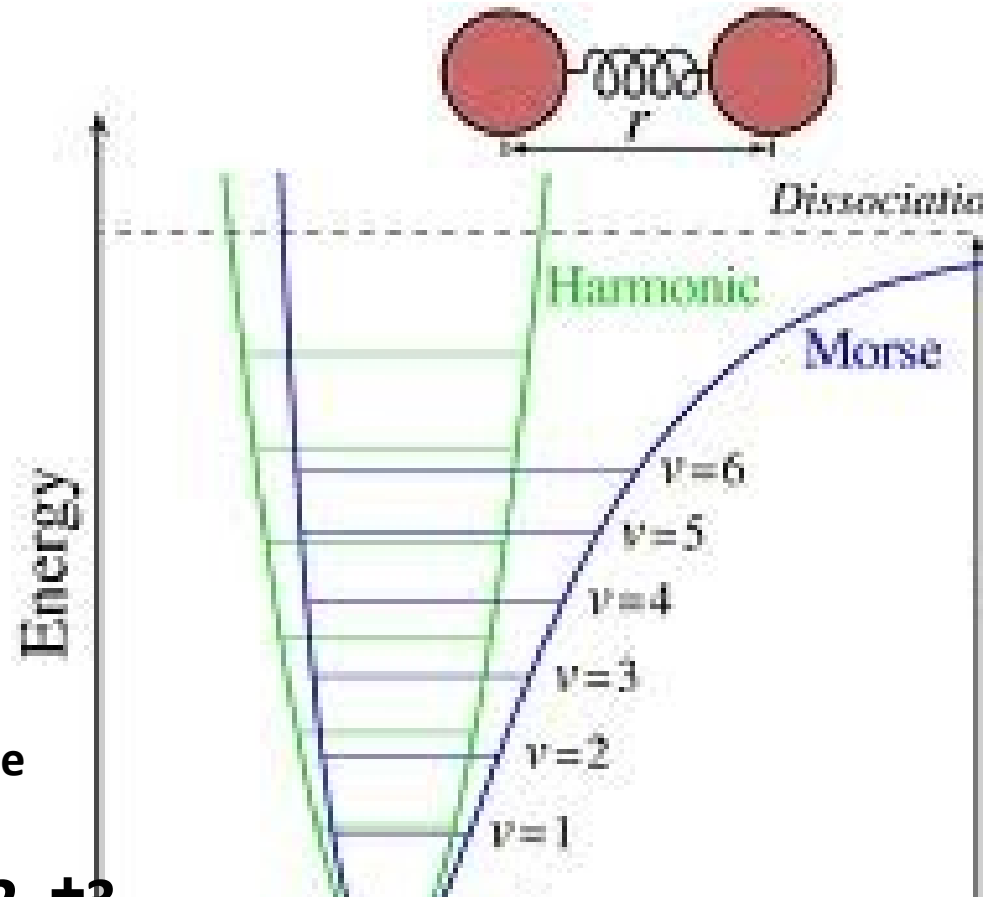
$$\omega_{\text{osc}} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$E_v = (v + 1/2) \omega_{\text{osc}}$$

$\Delta v = \pm 1$ for Harmonic Oscillator

$$E_v = (v + 1/2) \omega_e - (v + 1/2)^2 \omega_e \chi_e$$

Anharmonic Oscillator $\Delta v = \pm 1, \pm 2, \pm 3 \dots$

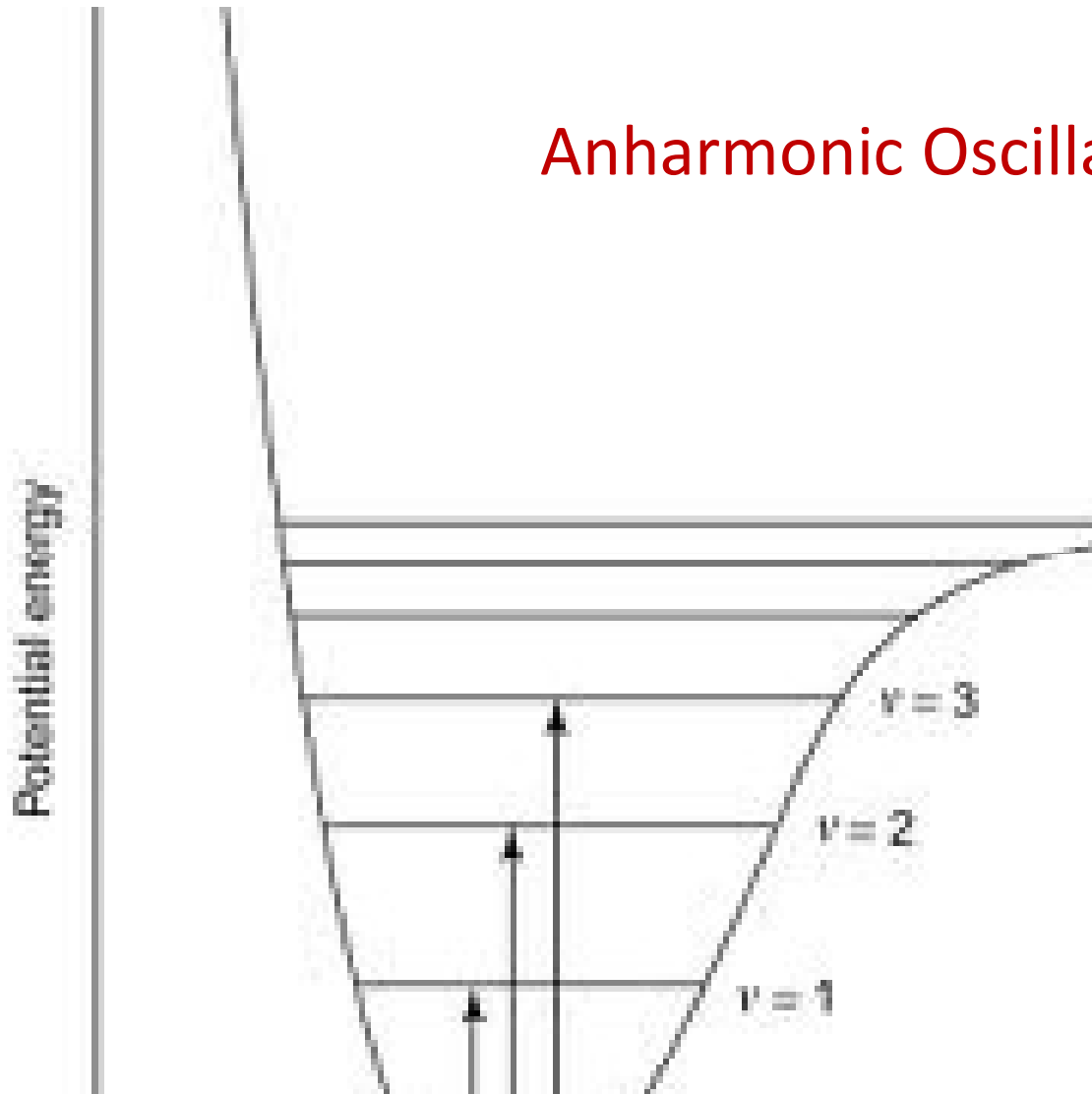


Real Molecules do not obey Hooke's law.....bcz bonds are not elastic

Overtone and hot bands.....

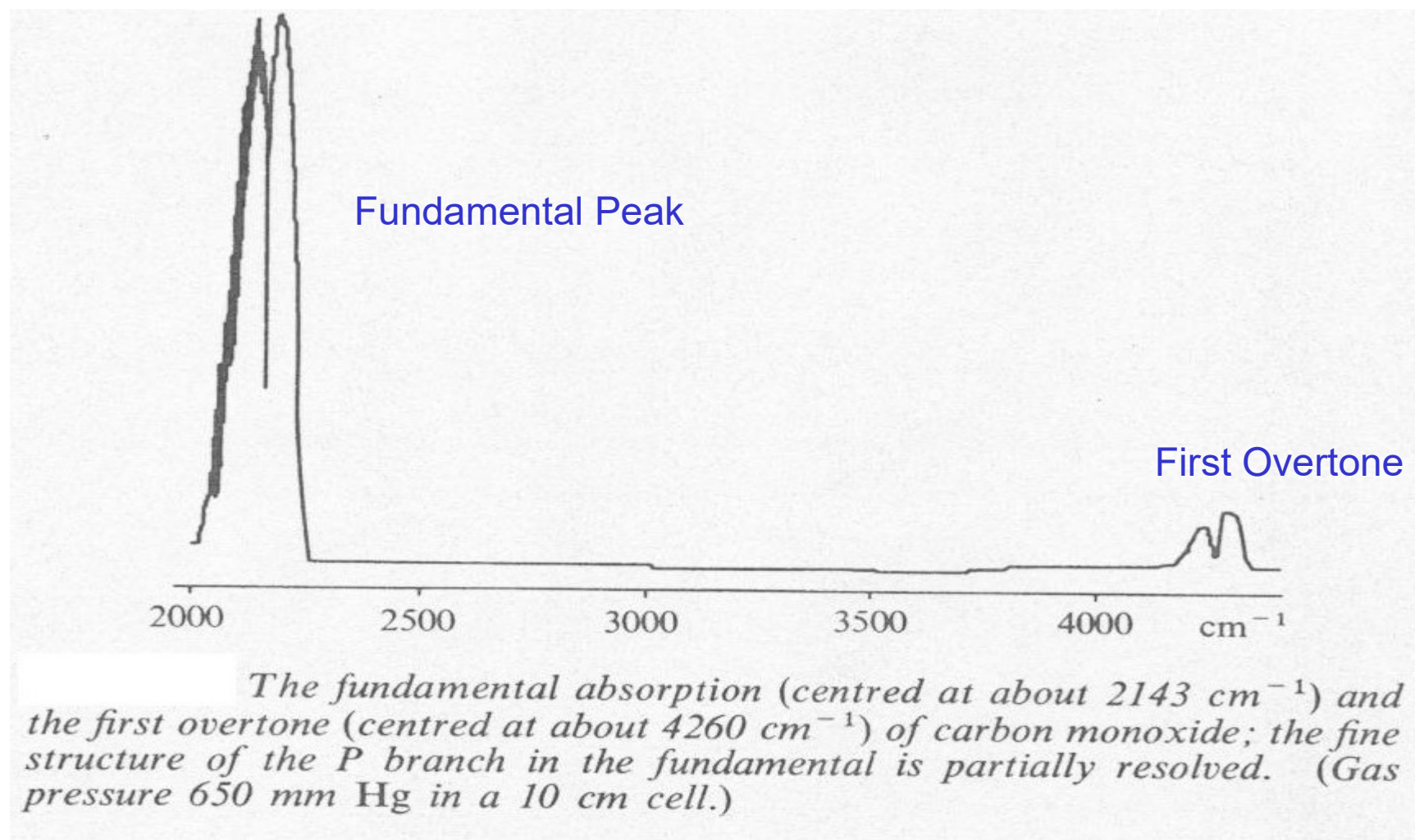
Anharmonic Vibrating Energy Levels

Anharmonic Oscillator $\Delta v = \pm 1, \pm 2, \pm 3, \dots$

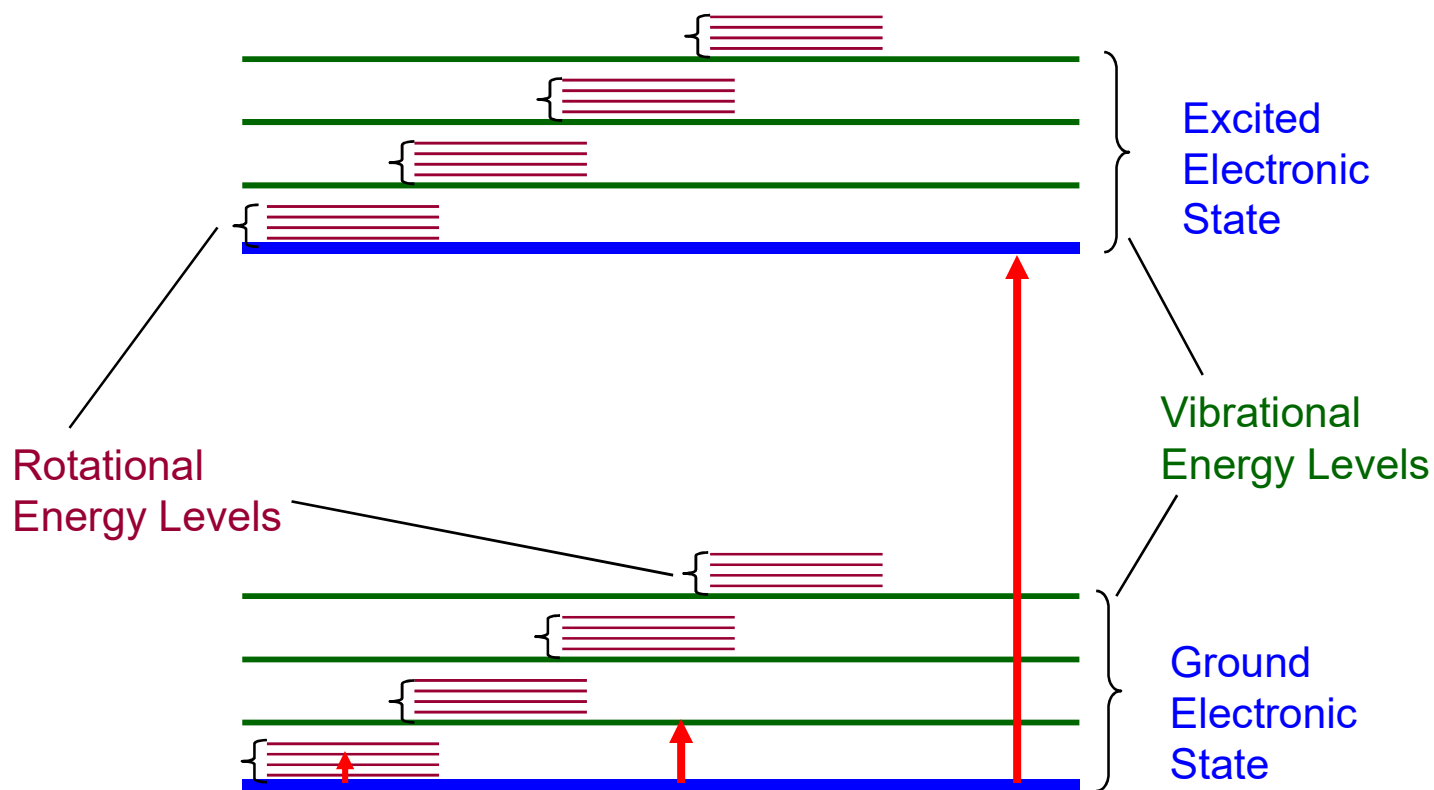


Overtones and hot bands.....

IR Spectrum of Carbon Monoxide (CO)



Molecular Energy Levels



Rotational
Transition

1-20 cm^{-1}

Microwave

Vibrational
Transition

2000-4000 cm^{-1}

Infrared

Electronic
Transition

10000-50000 cm^{-1}

UV-Visible

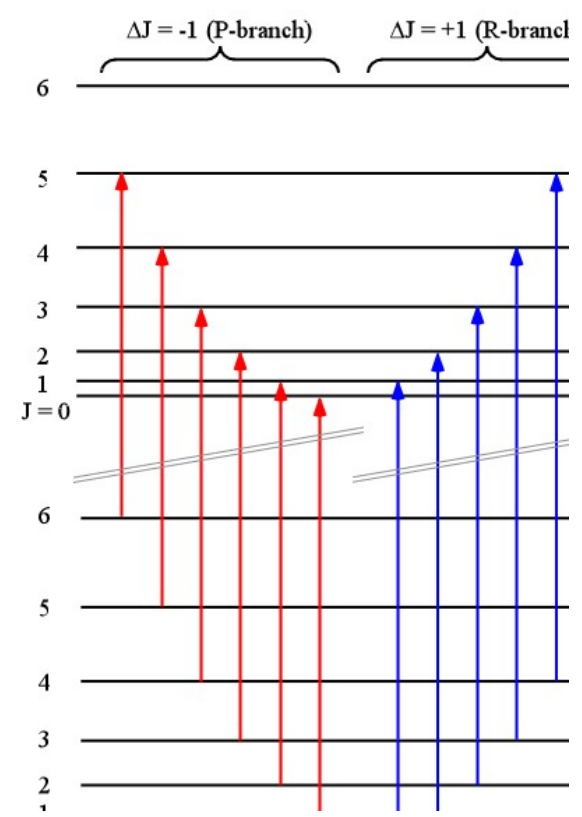
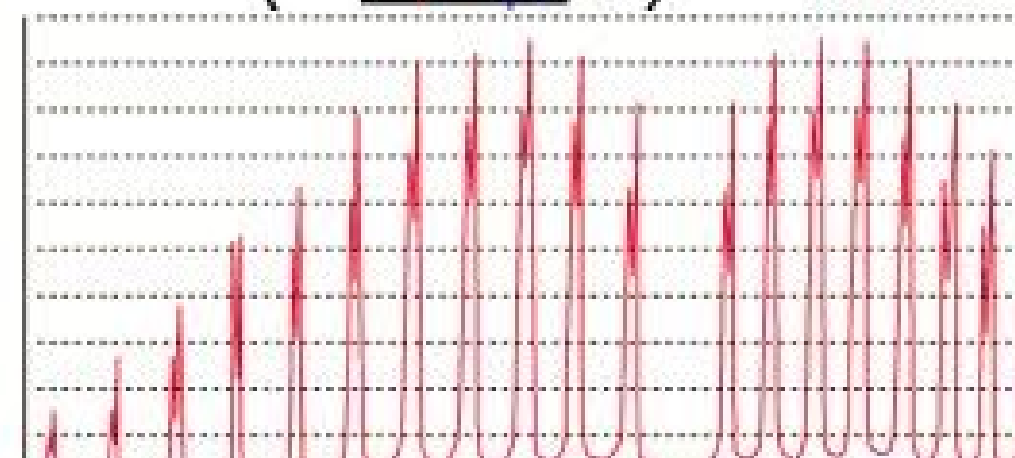
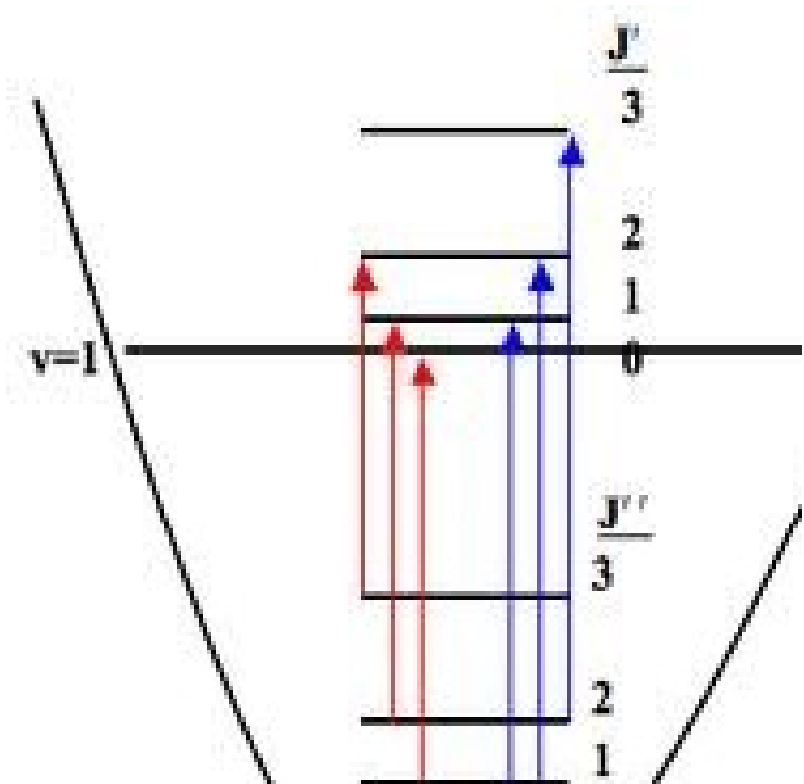
Diatomic Vibrating Rotator

• **Born-Oppenheimer Approximation:** Energies are simply sum of separate energies

$$E_{\text{total}} = E_{\text{rot}} + E_{\text{vib}}$$

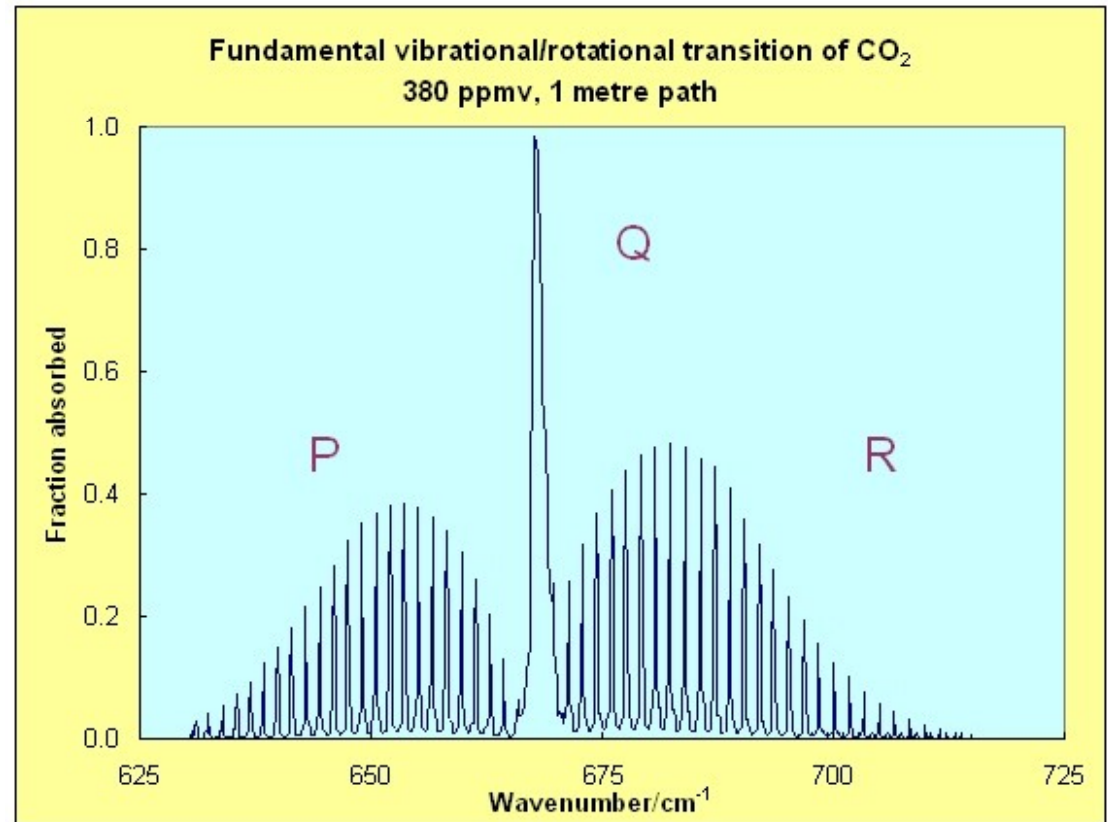
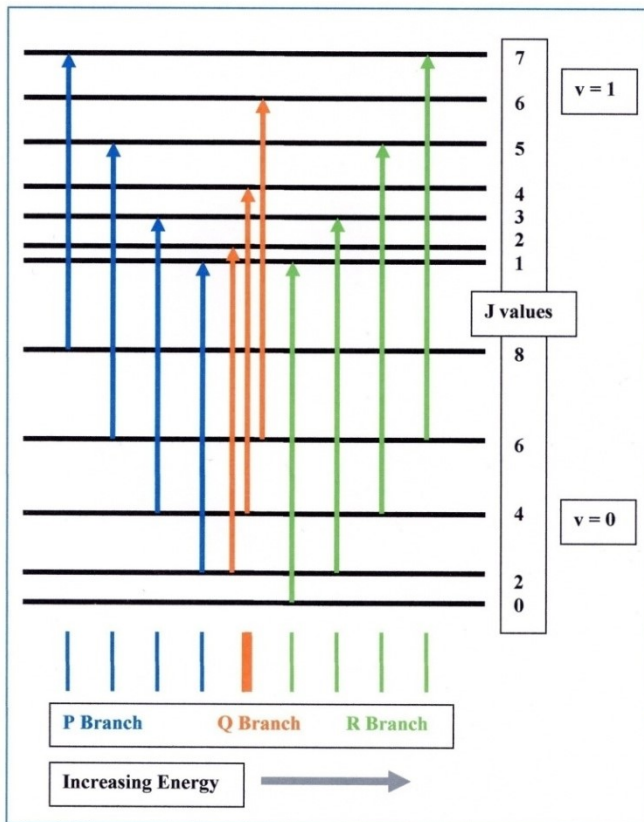
$\Delta v = \pm 1, \pm 2$ etc. and $\Delta J = \pm 1$

ΔJ	-2	-1	0	+1	+2
Branch	O	P	Q	R	S



Interactions of Rotations and Vibrations

- Breakdown of Born-Oppenheimer Approximation
- Bond-length changes with vibrational energy
- Rotational constant (B) varies with $1/r^2$
- B is smaller for upper state than lower state Energies are simply sum of separate energies ($B_1 < B_0$) $\Delta v = \pm 1$, and $\Delta J = 0, \pm 1$



Molecular Motion and Spectroscopy

Spectroscopy

- **Study of Interaction of Matter and Light (Photon)**
- **Molecular Spectroscopy**
 - Information about molecules such as geometry and energy levels are obtained by the interaction of **molecules** and **photons**
- **Molecular motions: Translation, Rotation, Vibration**
 - determines the energy levels for the absorption or emission of photons

Degrees of Freedom: Translation, Rotation, and Vibration

Consider a single Ar atom moving in 3-D space:

- Moving motion is referred to as **Translation**
- To analyze the translation of an Ar, we need to know
 position (x, y, z) and momentum (p_x, p_y, p_z)
Where it is *Where it is headed*
- Each coordinate-momentum pair [for example, (x, p_x)] is referred to as a **Degree of Freedom (DF)**
- An Ar atom moving through 3-D space has **three DFs**

**N argon atoms possesses 3N DFs:
All translational DFs**



Internal Motions

- A collection of N atoms possesses $3N$ DFs
- If N atoms happen to be bonded together into an N -atom molecule, the number of DFs is still $3N$.
- But, atoms in a molecule cannot translate independently of each other → No $3N$ translational DFs → Contribution of DFs to **Internal Motions**
- **Two types: Rotation and Vibration**

Center of Mass (Balanced Point)

- A point mass that can represent the molecule**
- Motion of the center of mass requires 3 DFs to describe it**
- In general, regardless of its size or complexity, a molecule has 3 translational DFs**
- Thus, $(3N - 3)$ DFs for the internal motions of rotation and vibration**

Molecular vibrations

Translation - the movement of the entire molecule while the positions of the atoms relative to each other remain fixed: **3 degrees of translational freedom**.

Rotational transitions – interatomic distances remain constant but the entire molecule rotates with respect to three mutually perpendicular axes: **3 rotational freedom (nonlinear), 2 rotational freedom (linear)**.

Fundamental Vibrations

Vibrations – relative positions of the atoms change while the average position and orientation of the molecule remain fixed.

Degrees of freedom	linear	non-linear
Translational	3	3
Rotational	2	3
Vibrational	$3N-5$	$3N-6$
Total	$3N$	$3N$

N = number of atoms in molecule

Molecular vibrations

TABLE 8.1

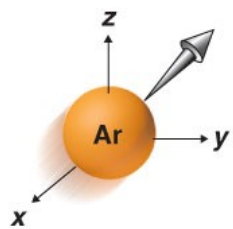
Classification of degrees of freedom

Molecule	Total	Translational	Rotational	Vibrational
<i>N</i> -atom molecule	$3N$	3	2 if linear 3 if nonlinear	$3N-5$ if linear $3N-6$ if nonlinear
N ₂	6	3	2	1
CO ₂	9	3	2	4
H ₂ O	9	3	3	3
CH ₄	15	3	3	9

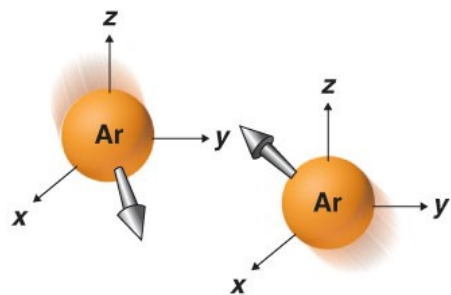
Atoms

Degrees of freedom
(3N)

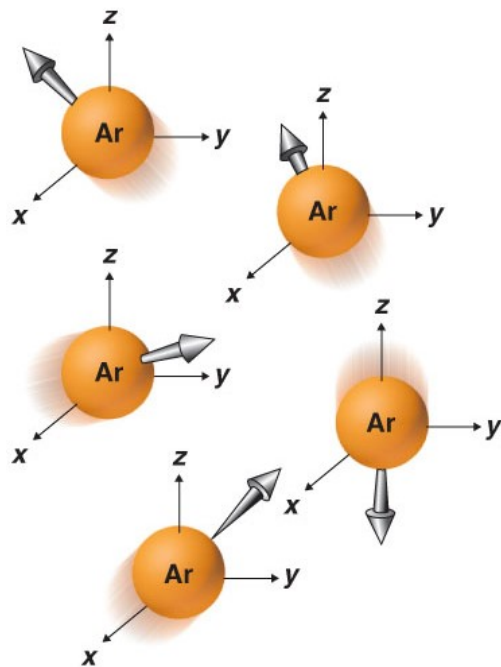
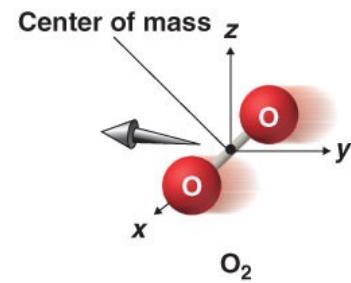
Molecules



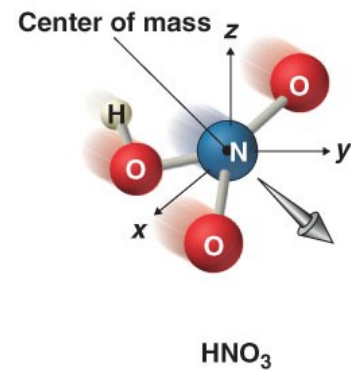
$$3 \times 1 = 3$$

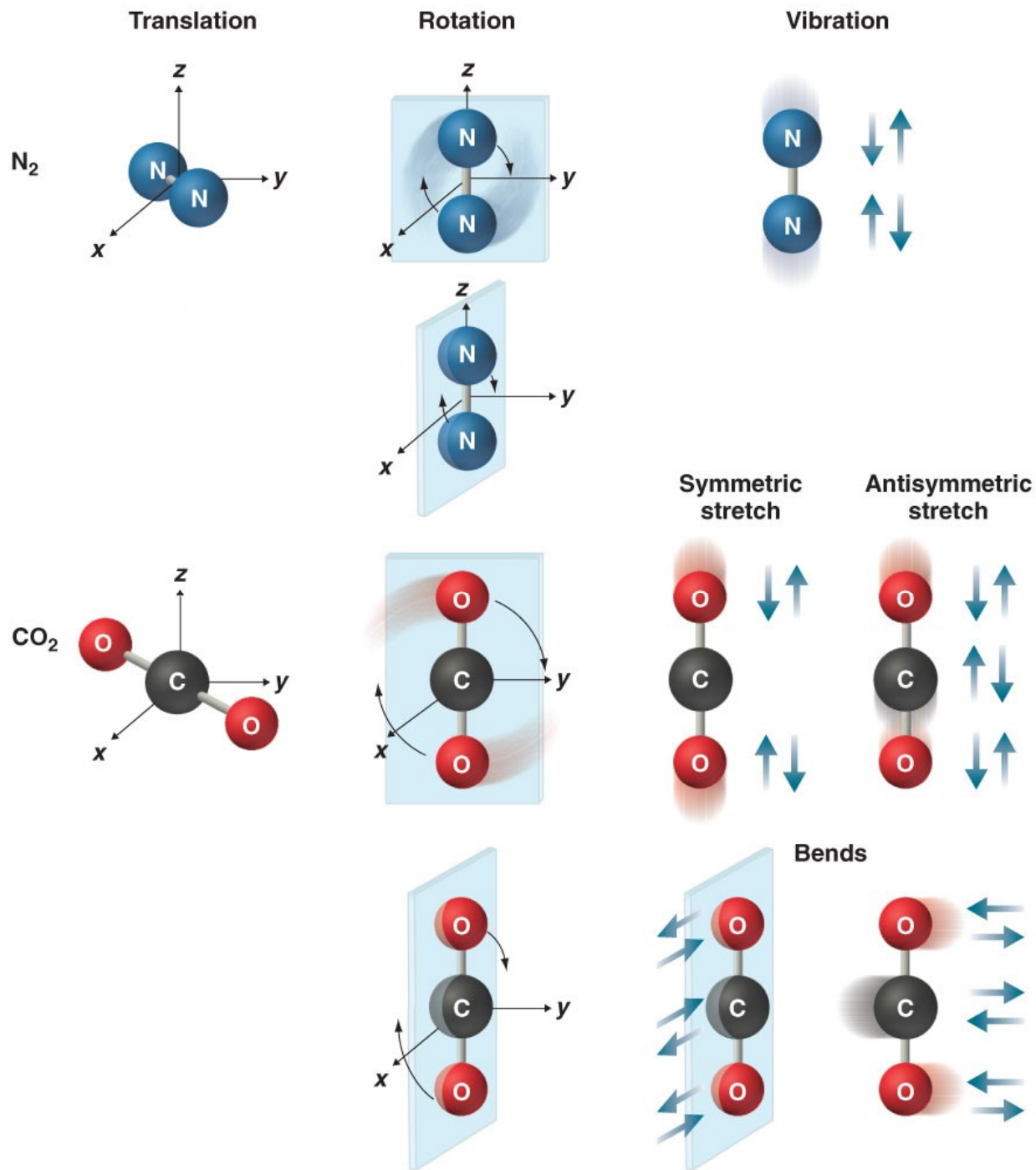


$$3 \times 2 = 6$$

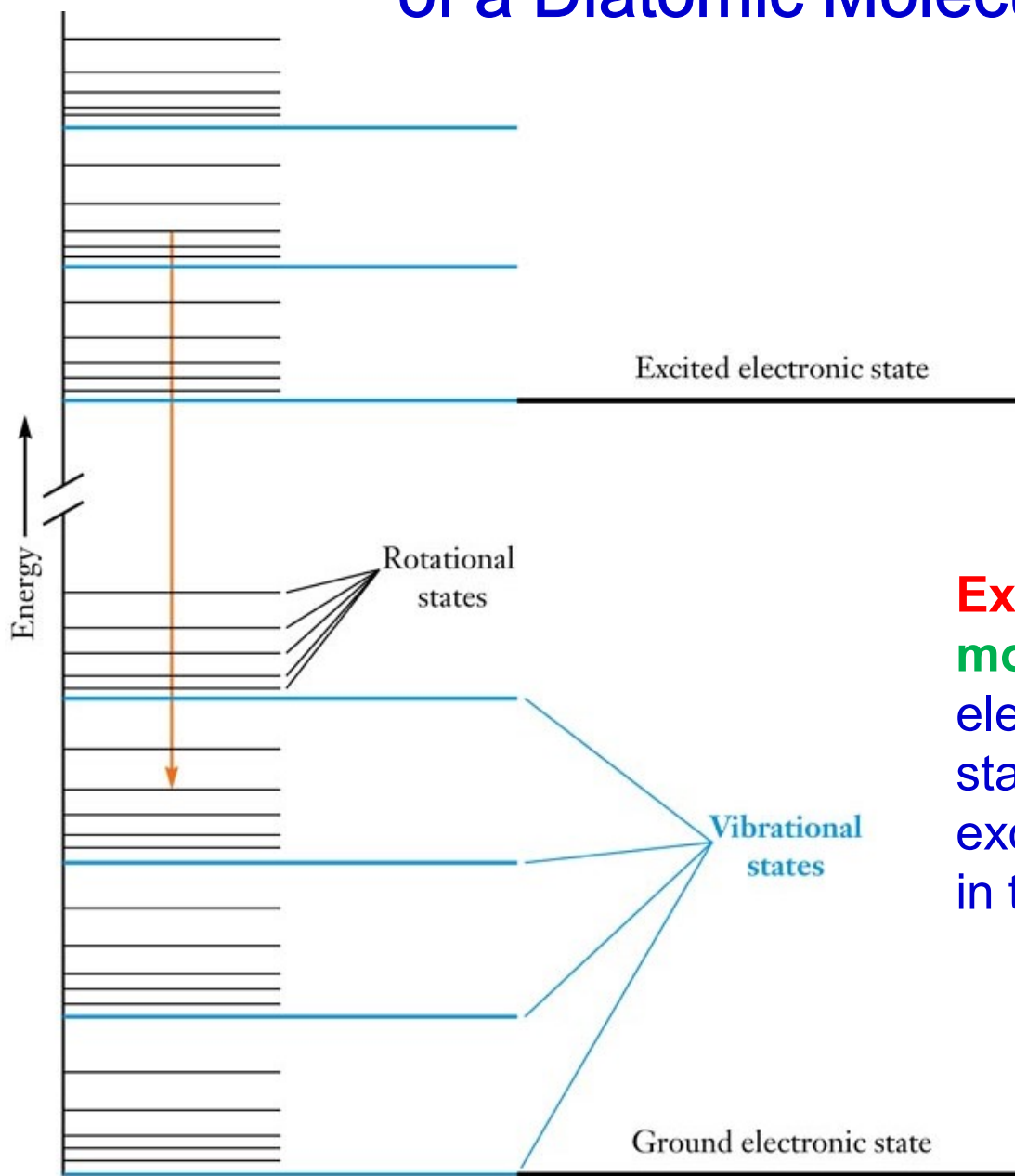


$$3 \times 5 = 15$$

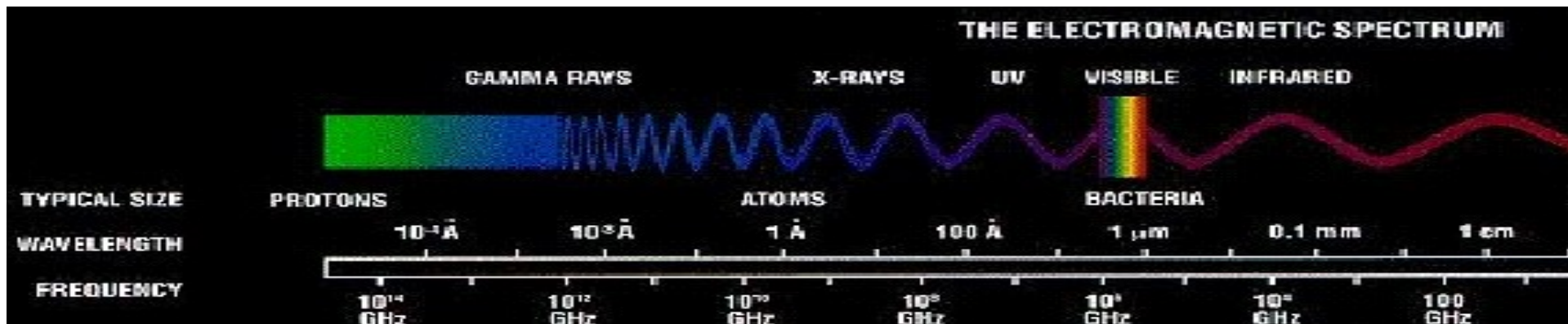




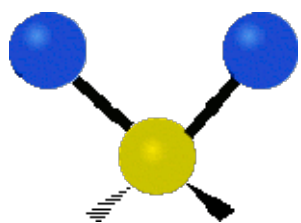
Electronic, Vibrational, and Rotational Energy Levels of a Diatomic Molecule



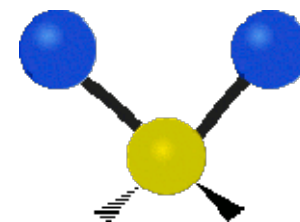
Exercise: Indicate the **molecular state** in which it is electronically in the ground state, vibrationally in the first excited state, and rotationally in the ground state.



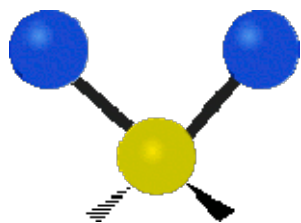
Vibrational Motions



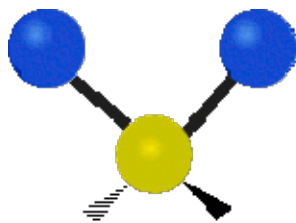
Symmetric Stretch



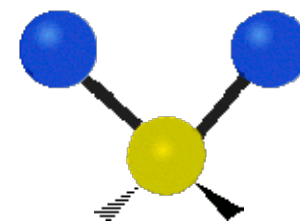
Asymmetric Stretch



Scissoring



Rocking



Twisting

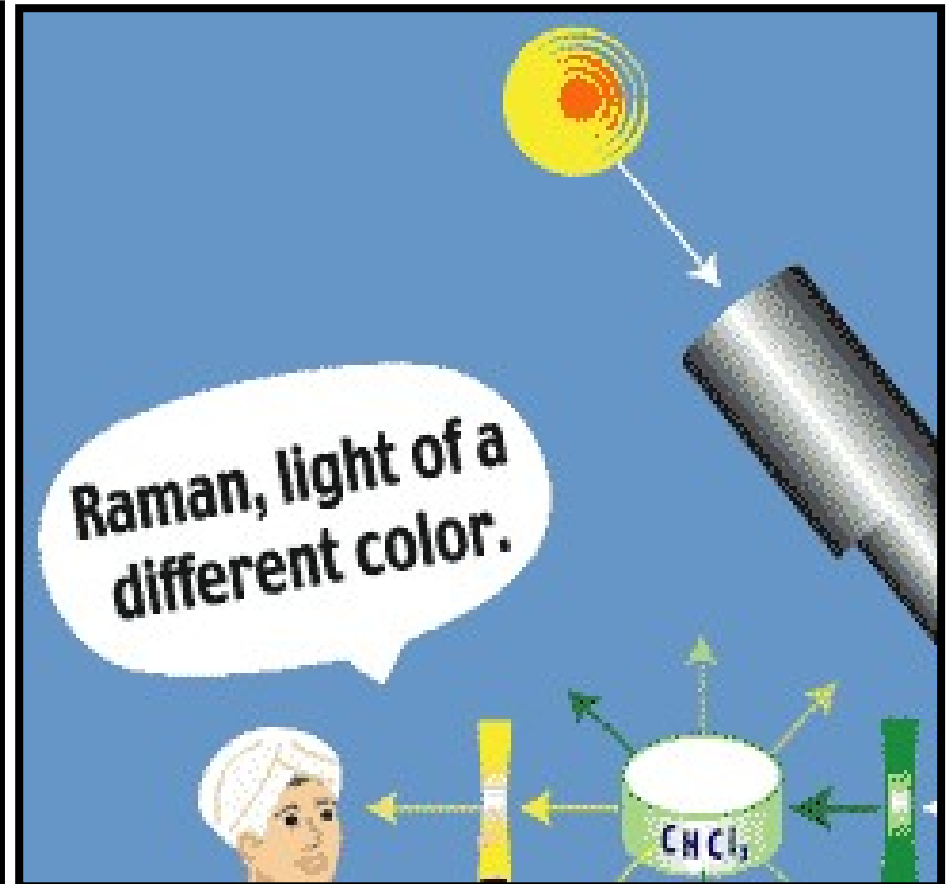
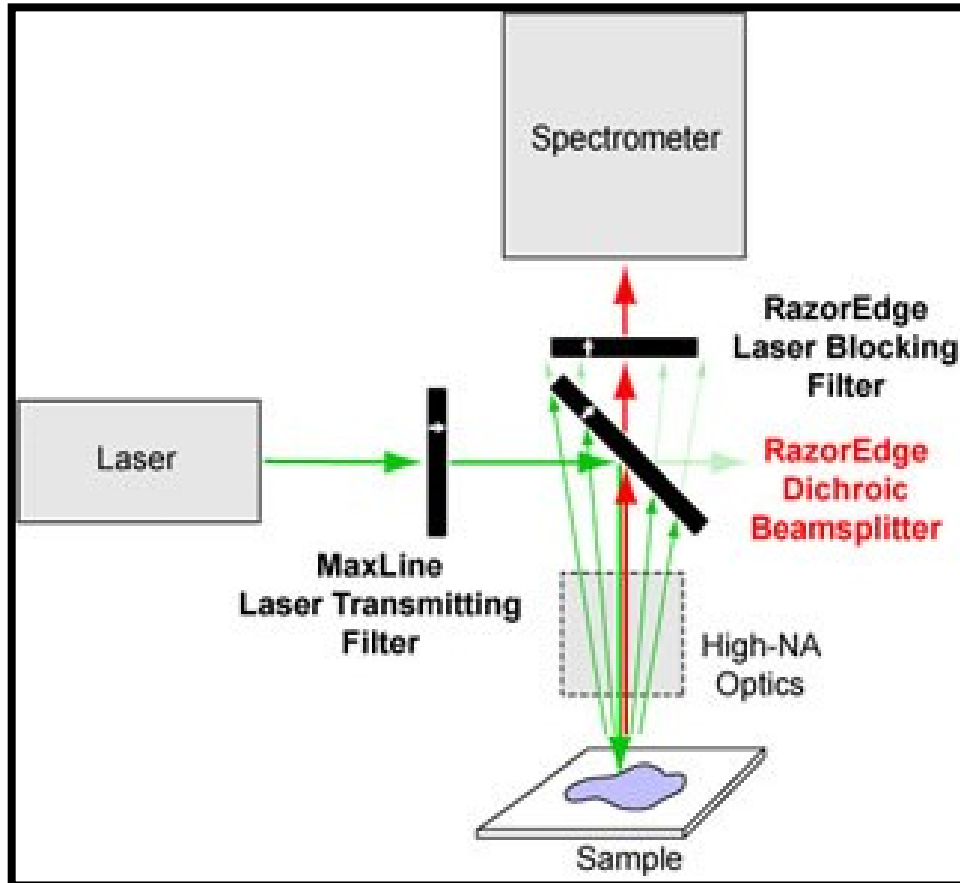
Raman Spectroscopy

Transparent Materials.....

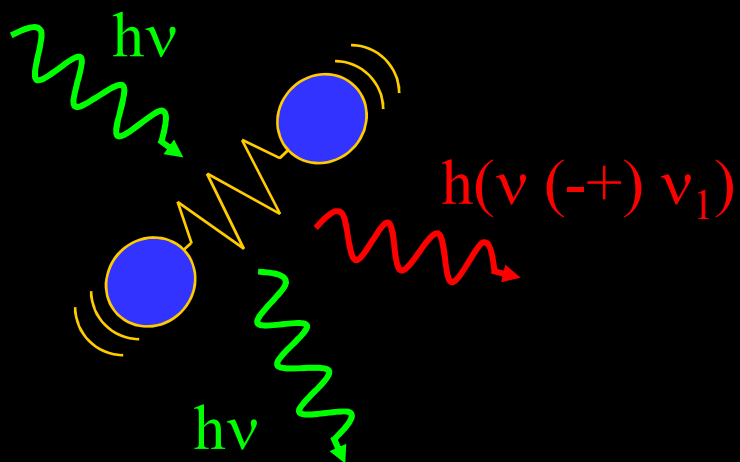
Scattering of Light (0.01%)

Elastic : Raleigh Scattering ; Inelastic: Change in frequency

(Stokes and Anti-stokes)

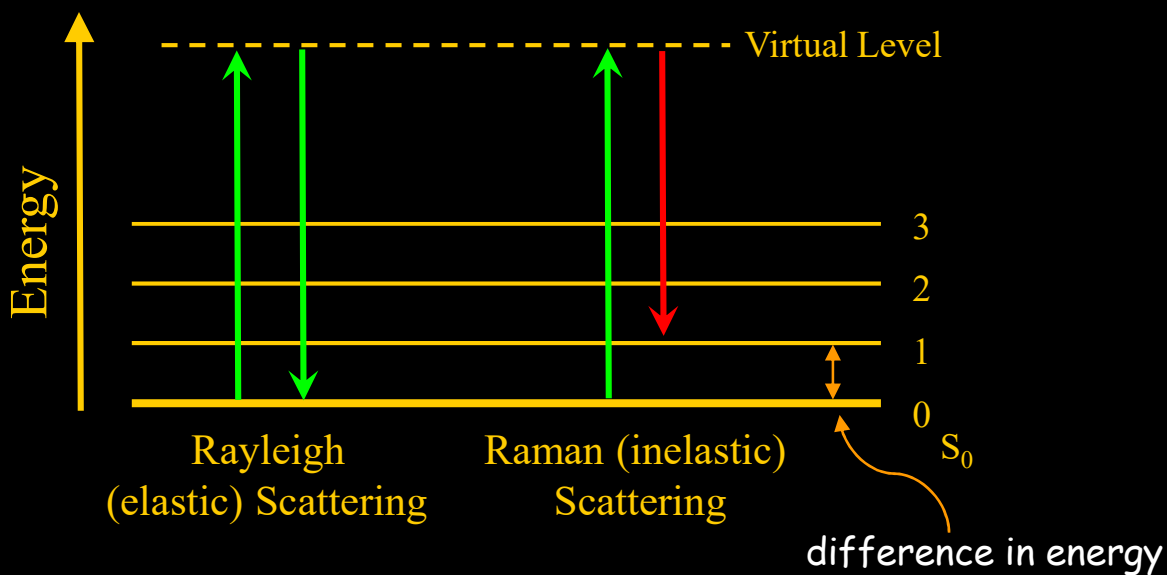


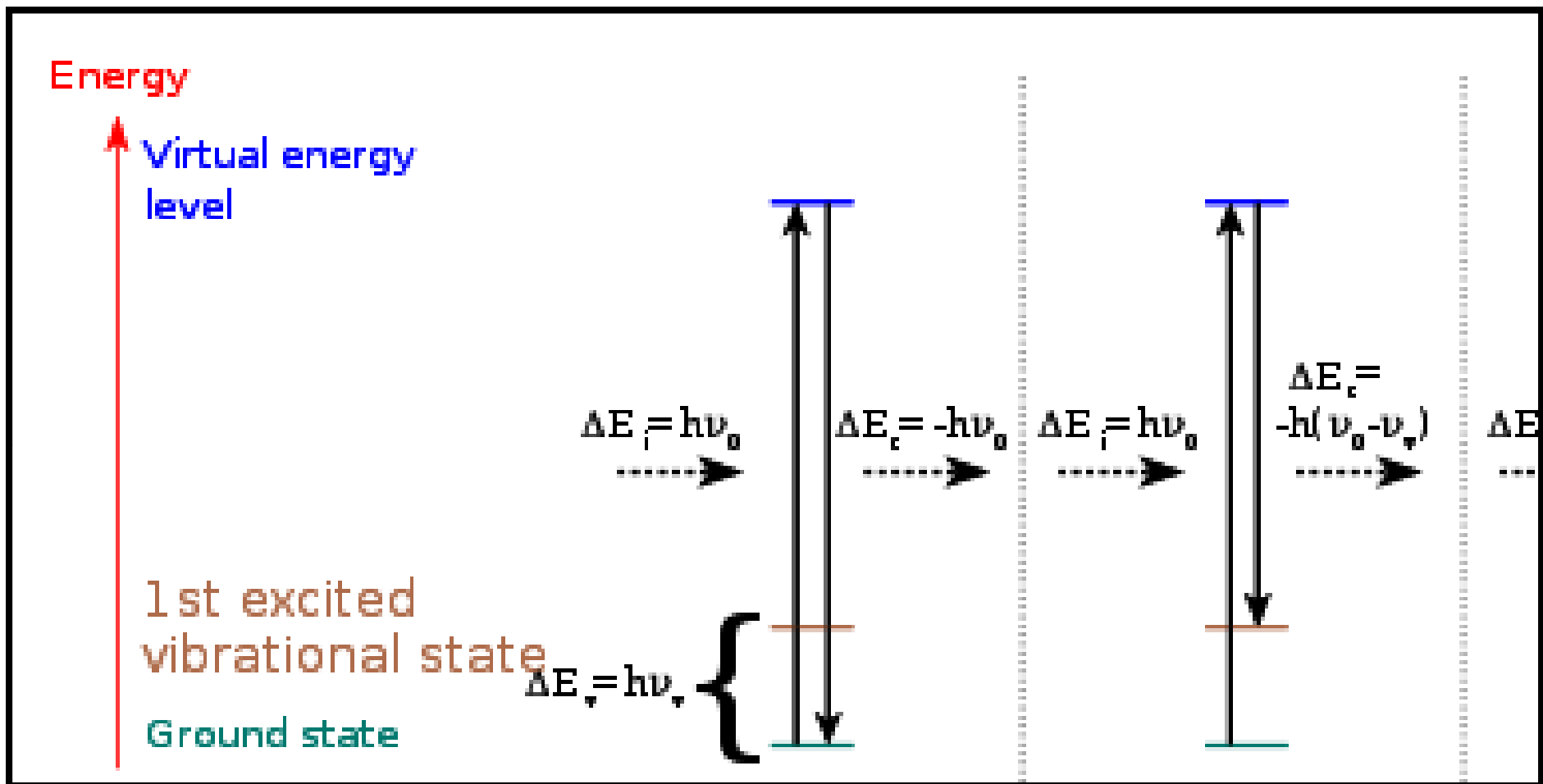
Quantum Theory of the Raman Effect

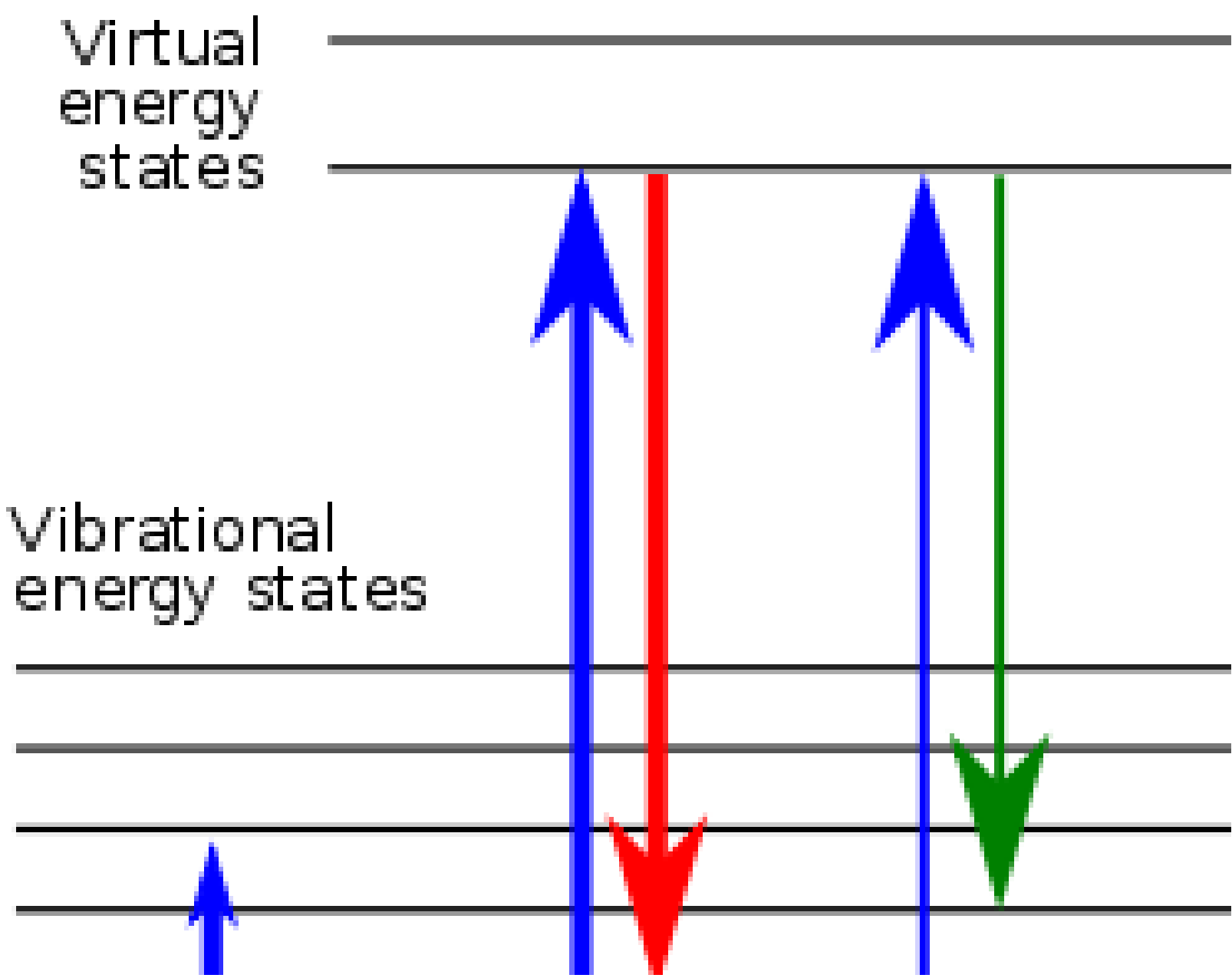


Inelastic Scattering

- Energy transferred from incident light to molecular vibrations







Virtual energy states

Vibrational energy states

Classical Theory of the Raman Effect: Molecular Polarizability

- Spatial charge separation under influence of electric field

→ induced dipole moment μ :

$$\mu = \alpha E$$

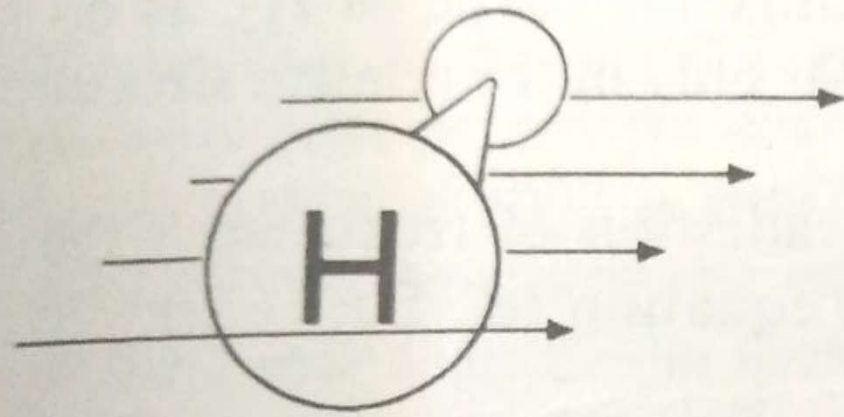
α : polarizability

- Electric field E due to electromagnetic wave with frequency ν

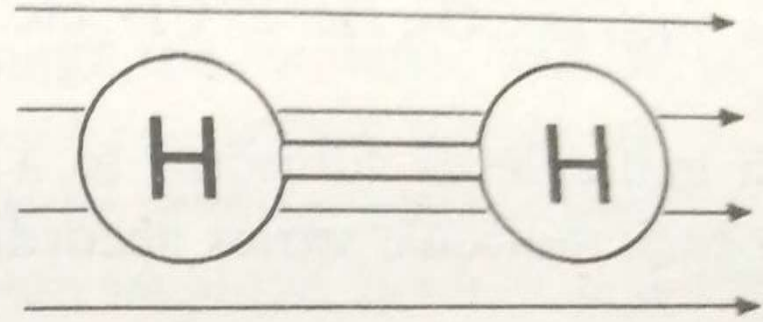
$$E = E_0 \cos 2\pi \nu t$$

$$\rightarrow \mu = \alpha E_0 \cos 2\pi \nu t$$

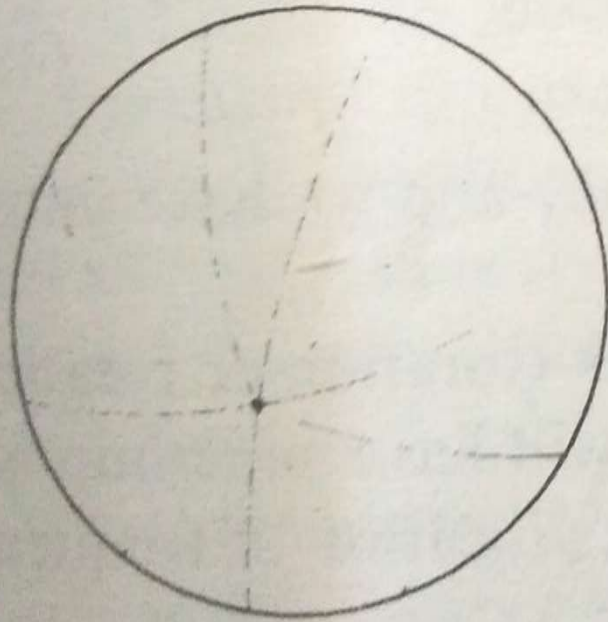
→ emission of light at same frequency ν



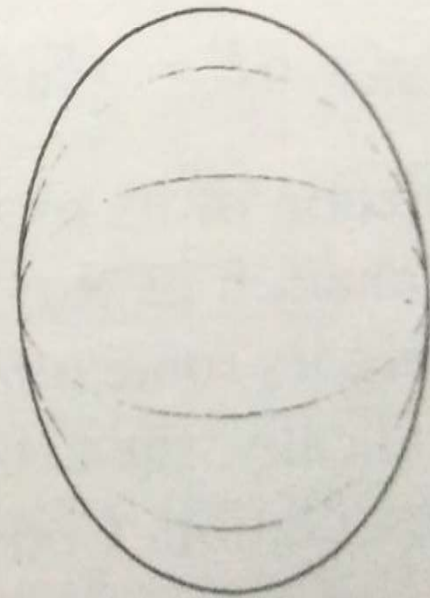
(a)



(b)



(c)



(d)

-
- Internal vibrational motion with Eigenfrequency ν_M

$$q = q_0 \cos 2\pi \nu_M t$$

- Polarizability $\alpha \rightarrow$ develop in series

$$\alpha = \alpha_{q=0} + (\partial\alpha/\partial q)_{q=0} q + \text{higher order terms}$$

$$\rightarrow \boldsymbol{\mu} = \alpha \mathbf{E}$$

$$= (\alpha_{q=0} + (\partial\alpha/\partial q)_{q=0} q_0 \cos 2\pi \nu_M t) \mathbf{E}_0 \cos 2\pi$$

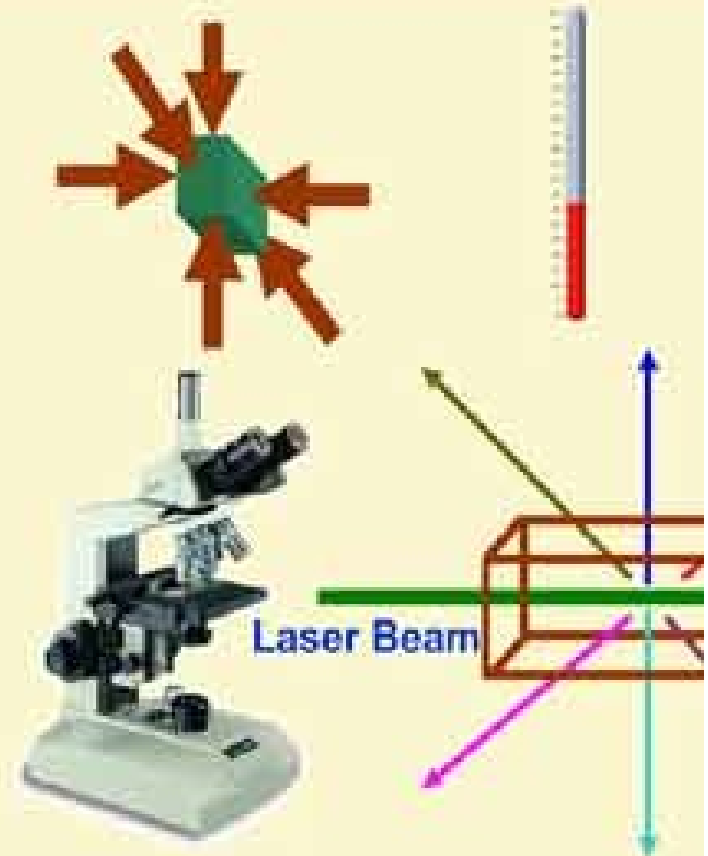
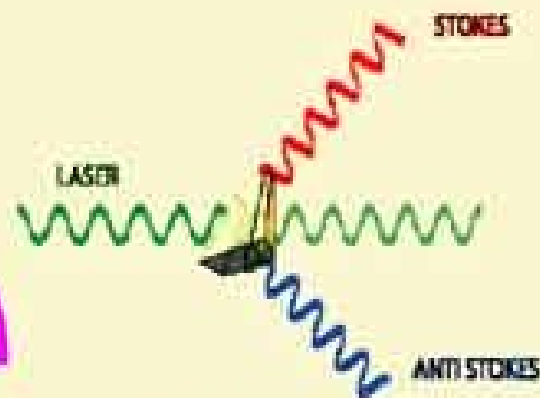
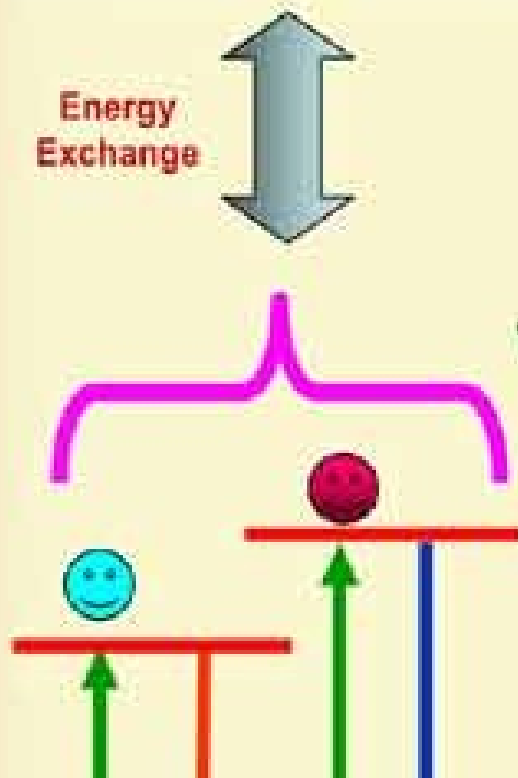
$$= \alpha_{q=0} \mathbf{E}_0 \cos 2\pi \nu_0 t + \frac{1}{2} (\partial\alpha/\partial q)_{q=0} q_0 \mathbf{E}_0 [\cos$$

→ harmonic oscillator: $\Delta v = \pm 1$

inelastic impact	elastic impact	in
$\Delta E_M > 0$	$\Delta E_M = 0$	
$v = v_0 - v_{\text{vib}} < v_0$	$v = v_0$	v'

Raman Spectroscopy: The Molecular De

- Phonons
(Rotational, Vibrational)
- Magnons
- Plasmons



- Investigating isolated SWNTs.
- Studying ultra thin films.
- Studying Phase transitions under High Pressure and Temperature.

