

What we have learnt till now?

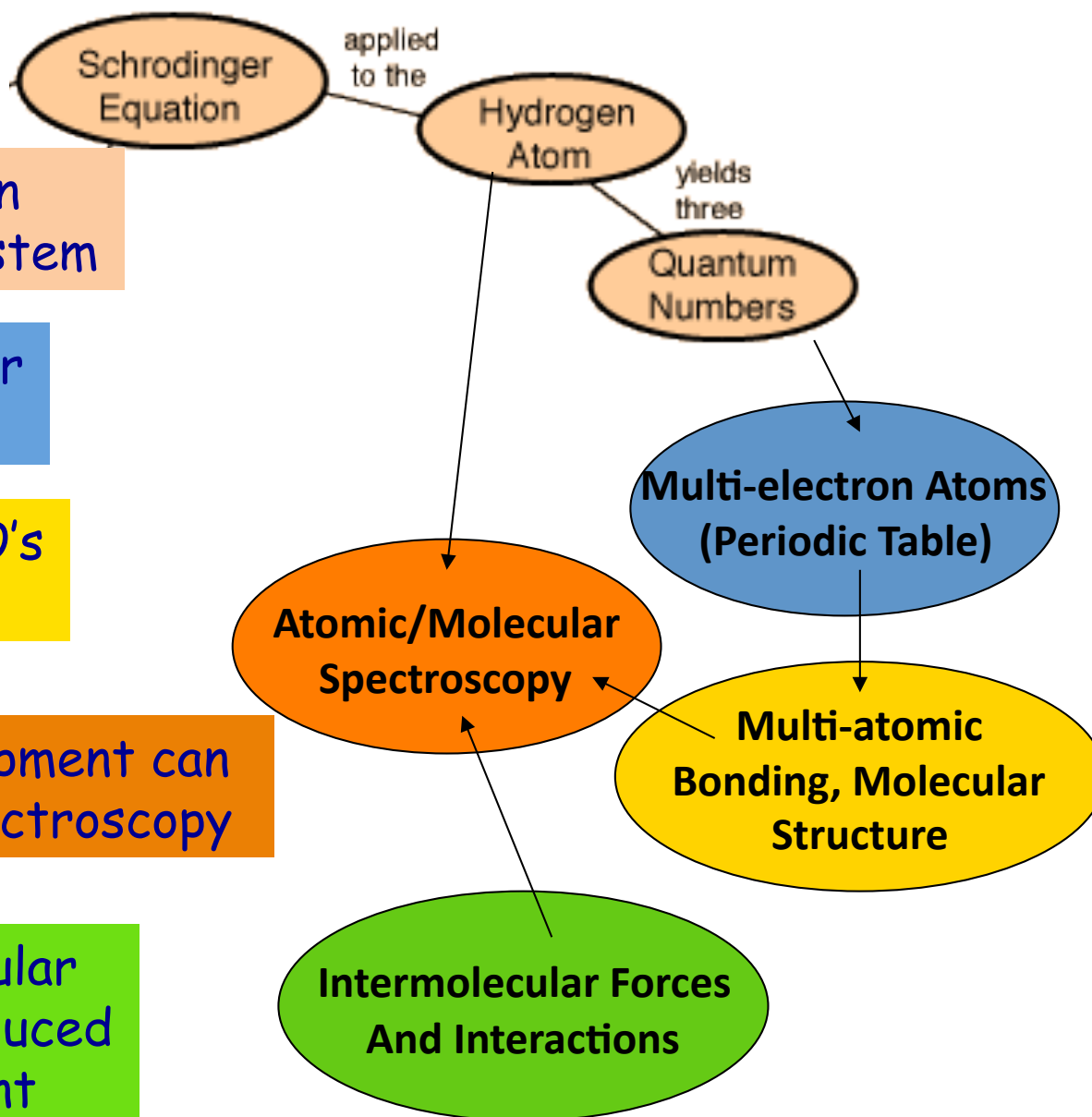
We used QM/TISE to obtain eigen states for single e^- system

We extend the same idea for Multi electronic system

We learned to construct MO's for different molecules

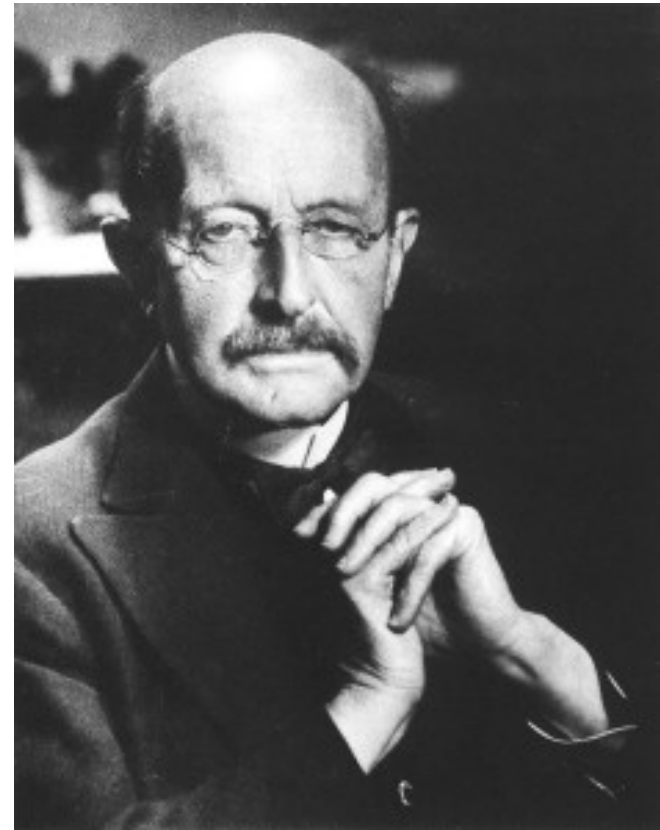
All these theoretical development can only be verified through spectroscopy

We talked about intermolecular forces/potentials and introduced the concept of Dipole moment and polarisability



Experiment is the only means of knowledge at our disposal. Everything else is poetry, imagination

- Max Planck



Molecular Spectroscopy

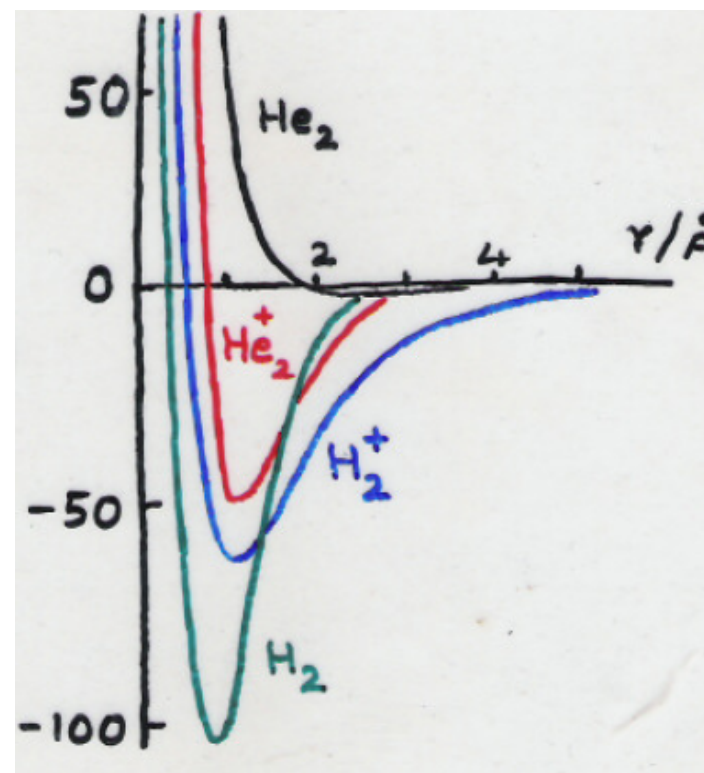
Important information's for chemist

★ Bond Length

How to find out bond length of **any molecule**?

★ Bond Strength

How to find out bond strength of **any molecule**?

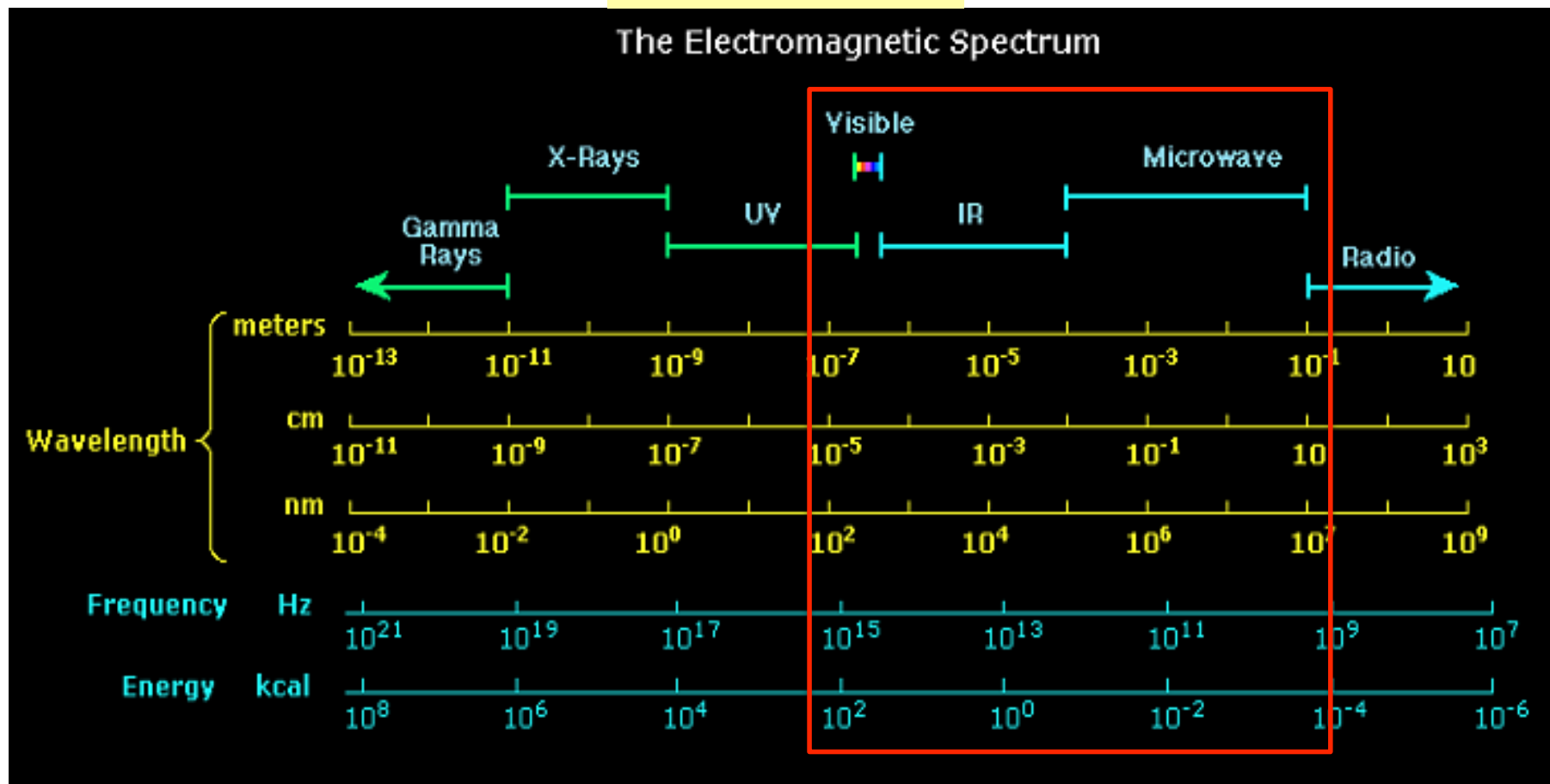


Species	Number of electrons	Ground-state electron configuration	Bond order	Bond length/pm	Binding energy/ $\text{kJ} \cdot \text{mol}^{-1}$
H_2^+	1	$(\sigma_g 1s)^1$	1/2	106	268
H_2	2	$(\sigma_g 1s)^2$	1	74	457
He_2^+	3	$(\sigma_g 1s)^2(\sigma_u 1s)^1$	1/2	108	241
He_2	4	$(\sigma_g 1s)^2(\sigma_u 1s)^2$	0	≈ 6000	$\ll 1$

Electromagnetic Spectrum

The frequency at which energy is absorbed or emitted is related to the energy levels involved in the transitions by

$$h\nu = |E_2 - E_1|$$

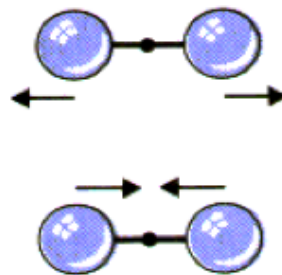


Electromagnetic Spectrum of interest

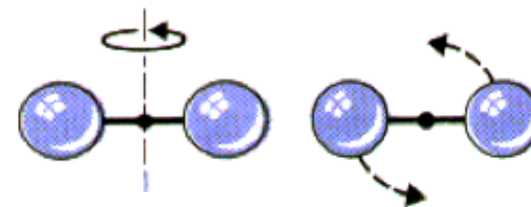
	UV-Visible	IR	Microwave
Energy (ΔE)	10^2 Kcal	1 Kcal	10^{-2} Kcal
Frequency	10^{15} Hz	10^{12} Hz	10^9 Hz
Time scale	10^{-15} Sec	10^{-12} Sec	10^{-9} Sec

Related to
Electronic motion

Related to
Nuclear motion



Vibrational motion

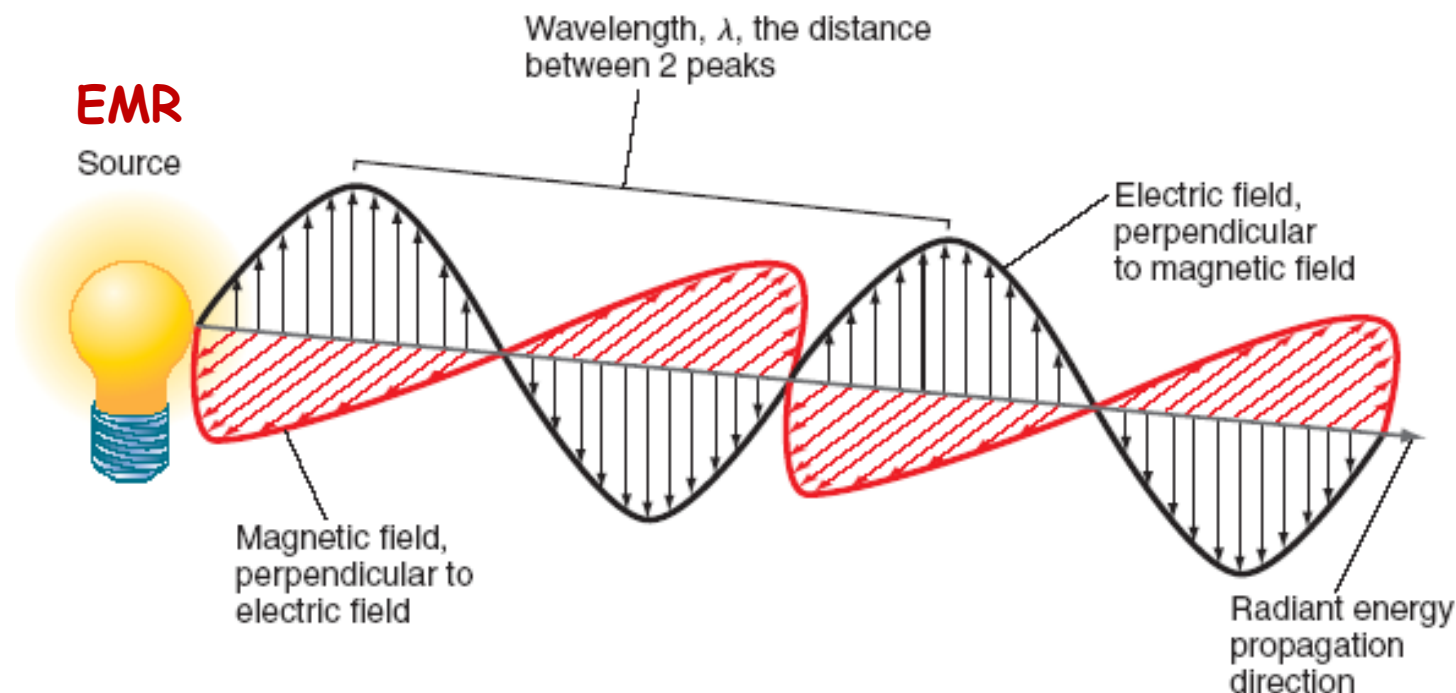


Rotational motion

Born-Oppenheimer Approximation

We can analyze spectroscopically each motion separately

The molecule must interact with light!



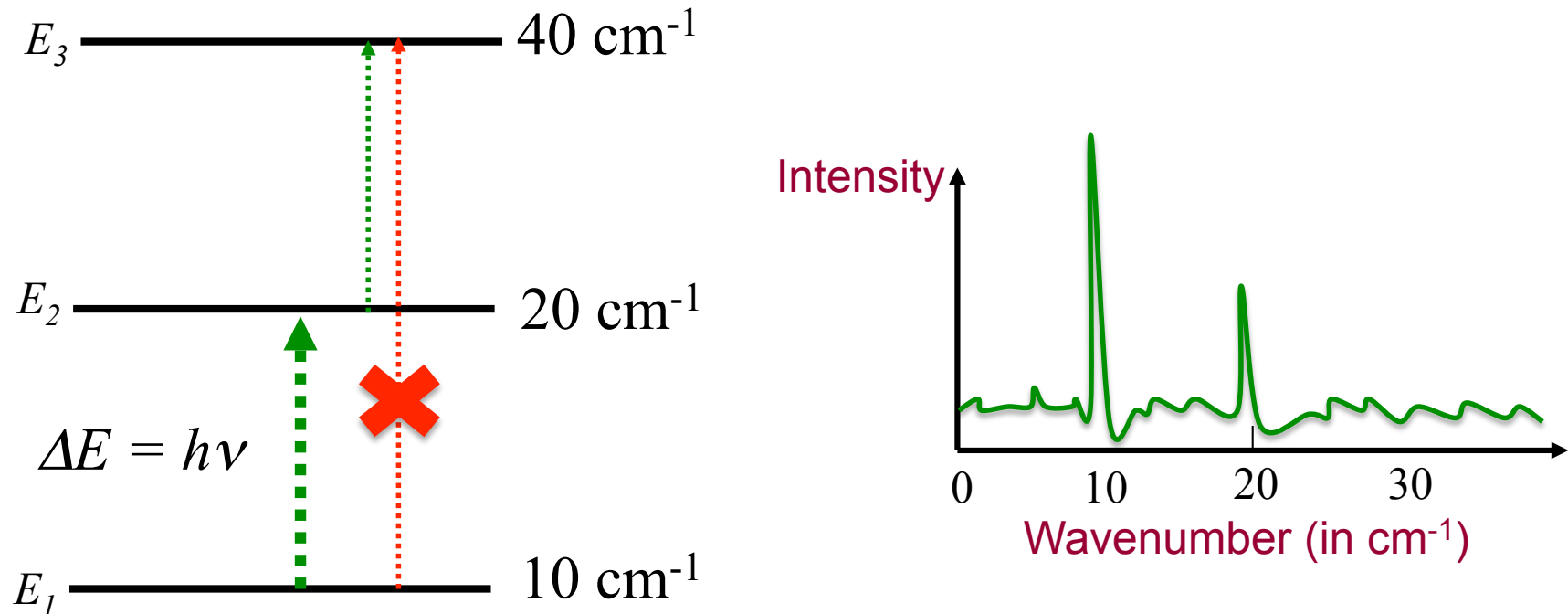
- ☀ The molecule must have a permanent dipole moment which will eventually produce an oscillating field for either rotational or vibrational motion

HCl

- ☀ For molecule with zero dipole moment, a fluctuating induced dipole moment must be produced for any one of the rotational or vibrational Motion

H₂

The information captured in an experimentally recorded spectra



- ☀ Frequencies or wavenumbers of the spectral transitions

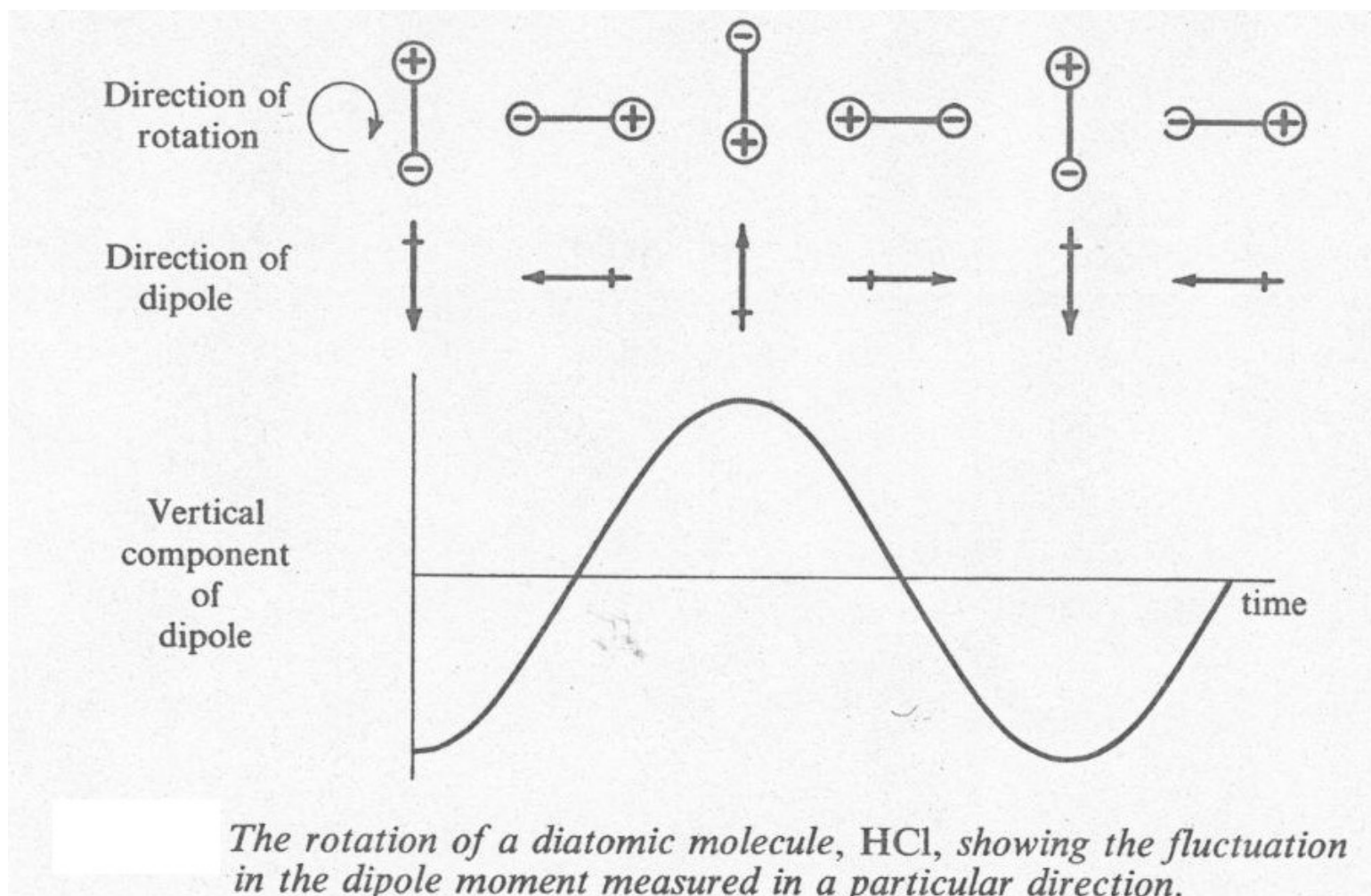
- ☀ Not all the transitions are allowed
 - Selection rule (can be derived using QM calculations)

- ☀ Intensity ratio's of the spectral lines
 - Populations of the states (Boltzmann Distribution)

Number of molecules in level j at equilibrium $n_j \propto g_j \exp(-\epsilon_j / kT)$

How to find out bond length of HCl ?

A diatomic molecule with permanent dipole moment



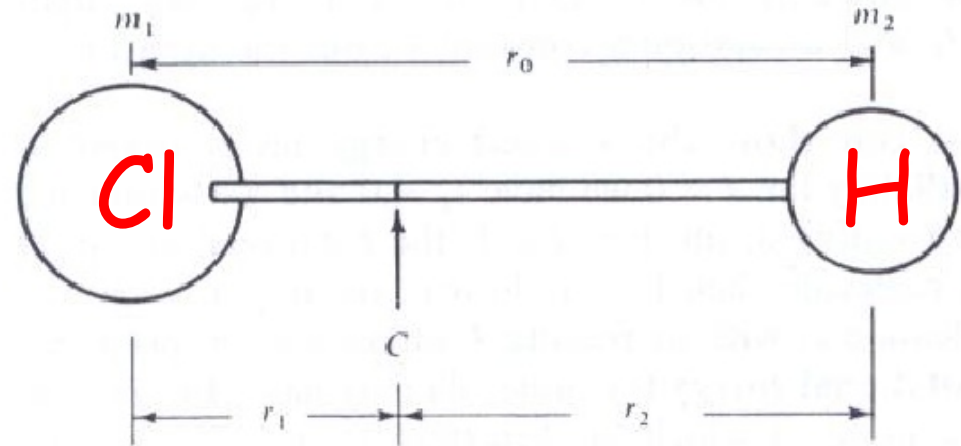
Rotational motion can create a fluctuating dipole

HCl is rotationally active molecule

Rigid Rotor model

Assumption: The diatomic bond is rigid

Solving the Schrödinger equation, it can be shown that the rotational energy levels allowed to the rigid diatomic molecule will be



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

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

Calculating the Rotational transition energies (ΔE)

$$E_J = \frac{h}{8\pi^2 I_c} J(J+1) \text{ cm}^{-1}, \text{ where } J = 0, 1, 2, \dots$$

$$E_J = BJ(J+1) \text{ cm}^{-1}, \text{ where } B = \frac{h}{8\pi^2 I_c} = \text{Rotational Constant}$$

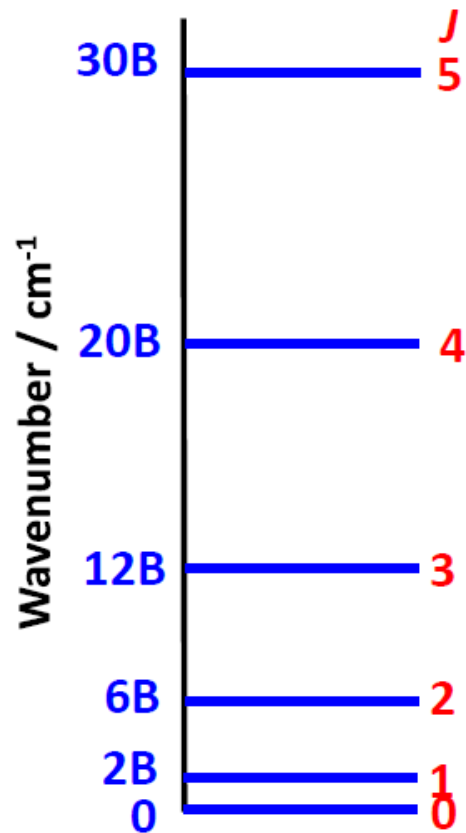
Selection Rule: $\Delta J = \pm 1$

$$\Delta E = E(J_{\text{final}}) - E(J_{\text{initial}})$$

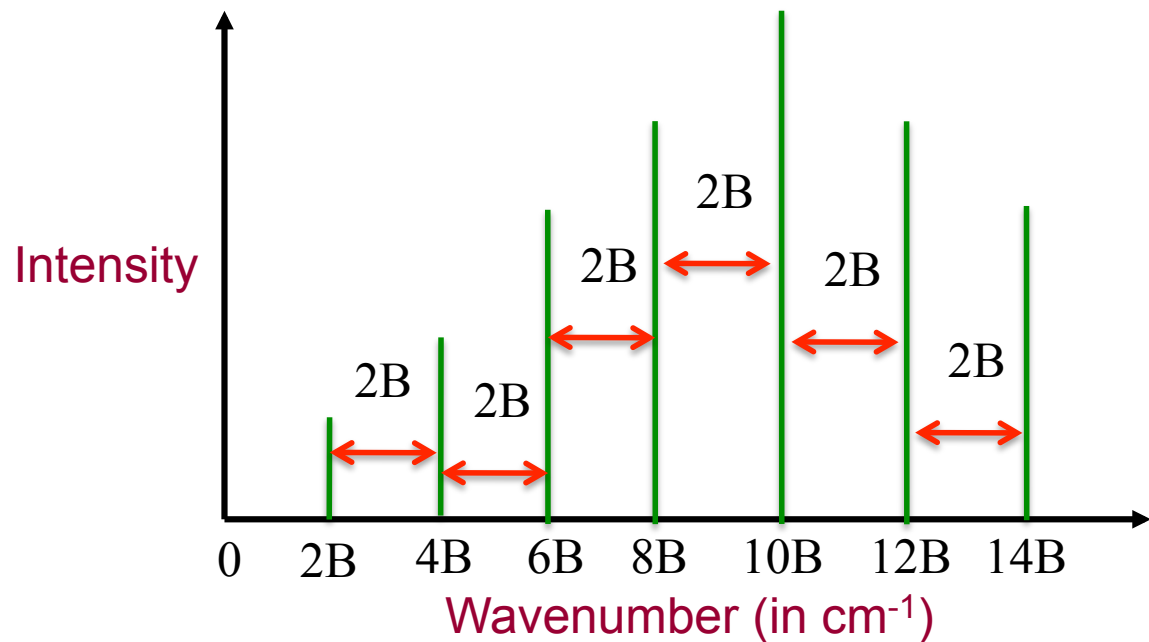
for $\Delta J = +1$

$$\Delta E = B(J+1)(J+2) - BJ(J+1) = 2B(J+1)$$

Spectral features for Rotational Spectra



Rotational energy level
get more widely spaced
with increasing J

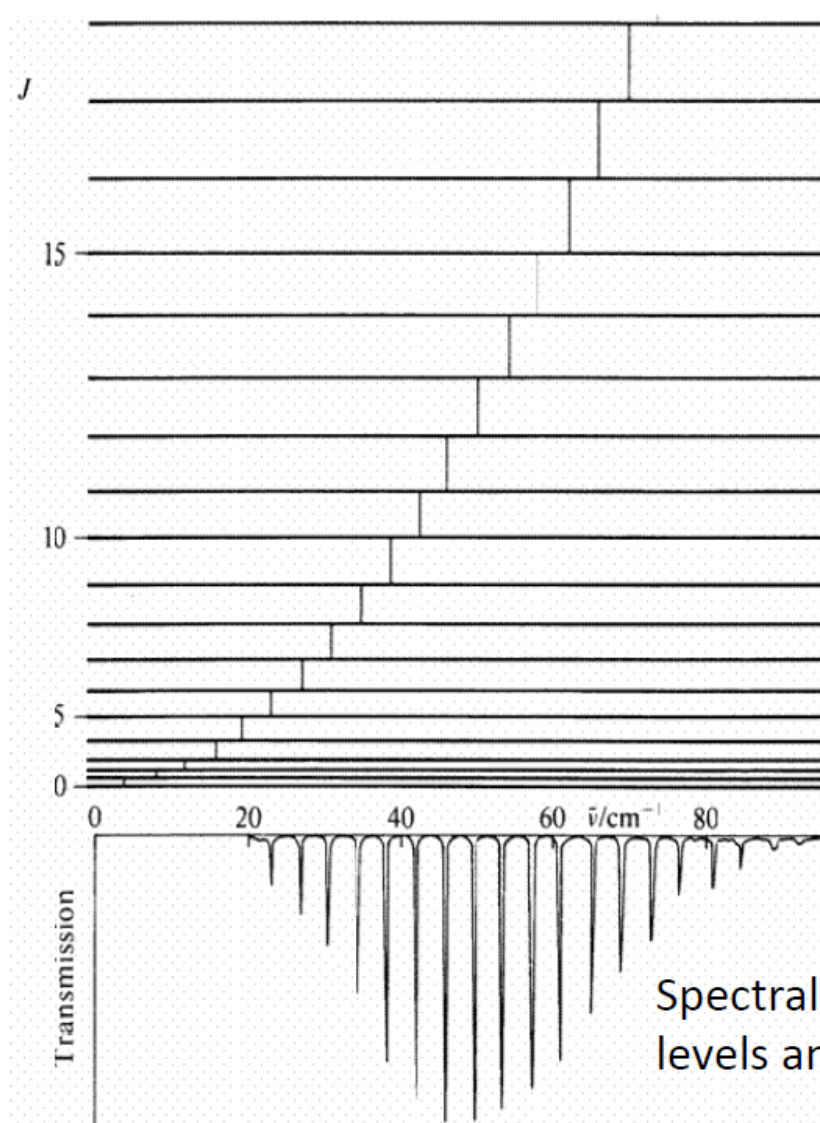


Rotational spectral lines
are all equally spaced

Spectral lines have
different intensities Why?

A real rotational spectra for CO

Rotational Spectrum of CO



Rotational spectrum
of CO (300K)

$$\begin{aligned}\tilde{\nu} &= F_{J+1} - F_J \\ &= \tilde{B}(J+1)(J+2) - \tilde{B}J(J+1) \\ &= 2\tilde{B}(J+1)\end{aligned}$$

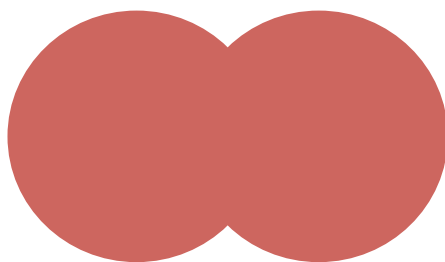
Transitions in the microwave region:
 $1\text{-}100\text{ cm}^{-1}$ ($\lambda = 1\text{ cm} - 100\text{ }\mu\text{m}$)

Lines *spaced* by $2\tilde{B}$

Spectral Profile governed by population of lower
levels and J dependence of the transition strength.

How to find out bond strength of HCl ?

A diatomic molecule with permanent dipole moment



Basic assumption:

- The bond between two atom behaves like spring

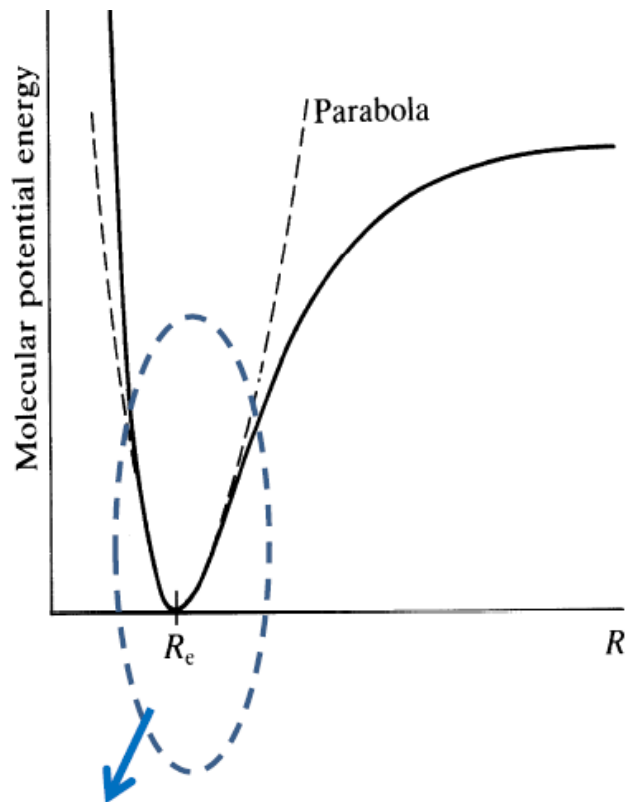


- The atoms vibrate approximately like an harmonic oscillator obeying Hooke's Law:

$$F = -k(r_{eq} - r) \quad k \text{ is the force constant}$$

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

Modeling diatomic chemical bond as simple harmonic oscillator



SHO a good approx.
at small x (low v)

Eigenvalues:

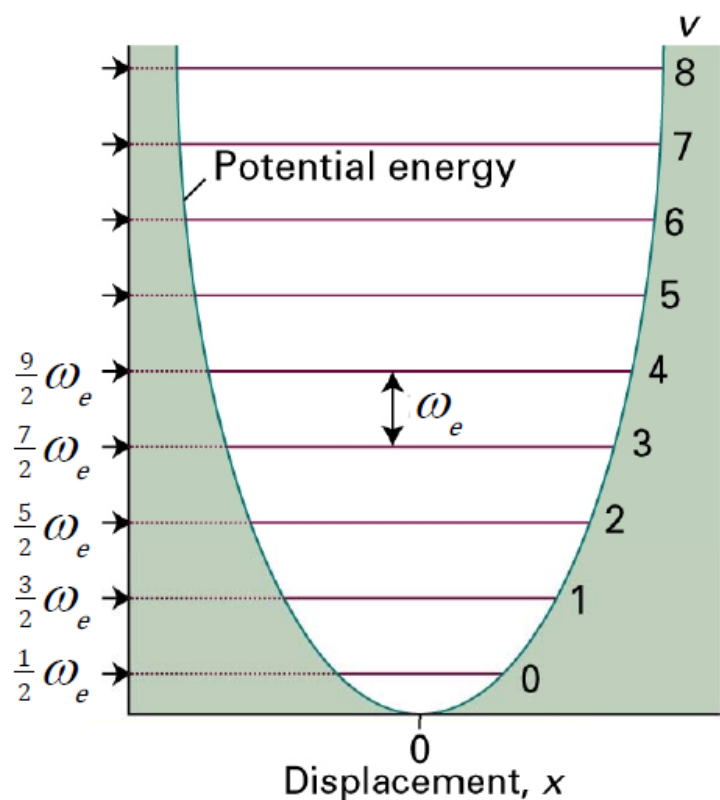
The vibrational terms

$$\tilde{G}_v = \left(v + \frac{1}{2}\right) \omega_e \quad \omega_e / \text{cm}^{-1} = \frac{\nu_{vib}}{\tilde{c}} = \frac{1}{2\pi\tilde{c}} \sqrt{\frac{k_F}{\mu}}$$

v is the vibrational quantum number = 0, 1, 2, ...
 ω_e the vibrational constant (in cm^{-1}),
 k_F is the Force Constant,
 μ is the reduced mass

Concept of Zero Point Energy

Modeling diatomic chemical bond as simple harmonic oscillator



Eigenvalues:

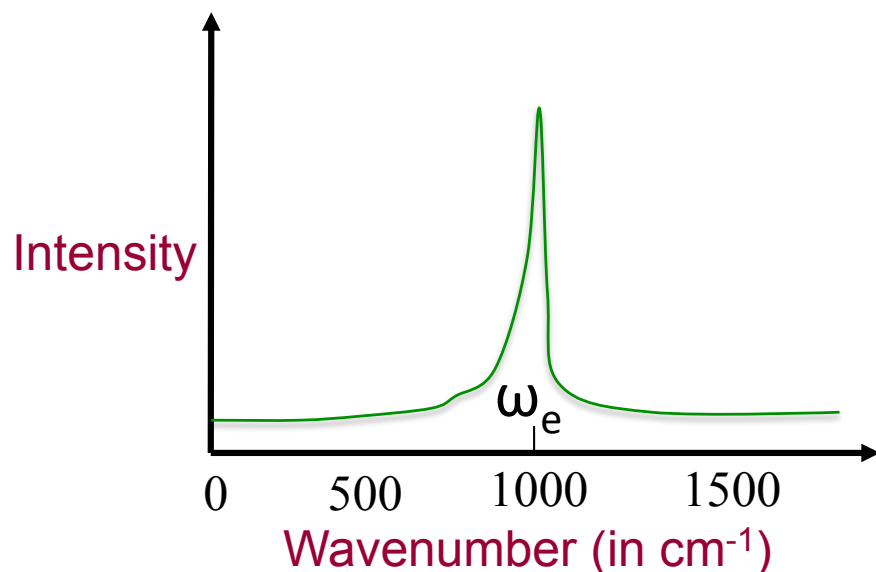
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Concept of Zero Point Energy

Spectral features for Vibrational Spectra



Vibrational Terms:

$$\tilde{G}_v = \left(v + \frac{1}{2}\right) \omega_e$$

Selection Rule:

$$\Delta v = \pm 1$$

Transitions at:

$$\tilde{\nu} = \tilde{G}_{v+1} - \tilde{G}_v = \omega_e$$

n.b. In absorption, only see transitions from $v=0$ since, except at very high T , this is the only level populated:

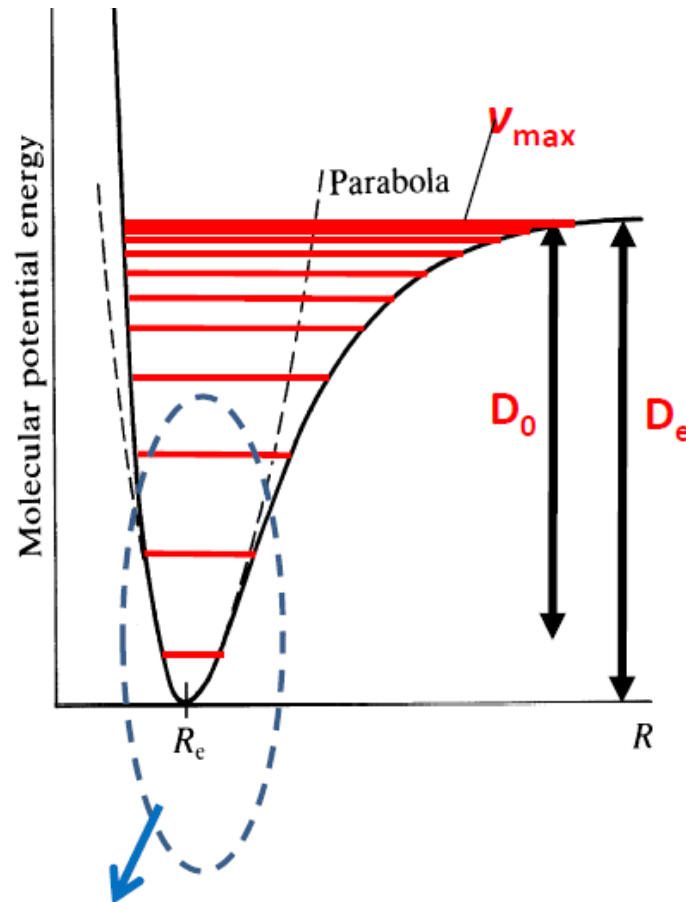
e.g., if $\omega_e = 1000 \text{ cm}^{-1}$, $T = 300 \text{ K}$

$$\frac{n_{v=1}}{n_{v=0}} = \frac{\cancel{g_1}^1}{g_0} \exp\left\{\frac{-h\tilde{c}\omega_e}{kT}\right\} = 0.008$$

How to break a HCl bond?

Concept of Anharmonic oscillator

Morse Potential



SHO a good approx.
at small x (low v)

$$V(R) = D_e \left[1 - \exp(-\beta(R - R_e)) \right]^2$$

Energy Eigenvalues:

$$\tilde{G}_v = \left(v + \frac{1}{2}\right)\omega_e - \left(v + \frac{1}{2}\right)^2\omega_e x_e$$

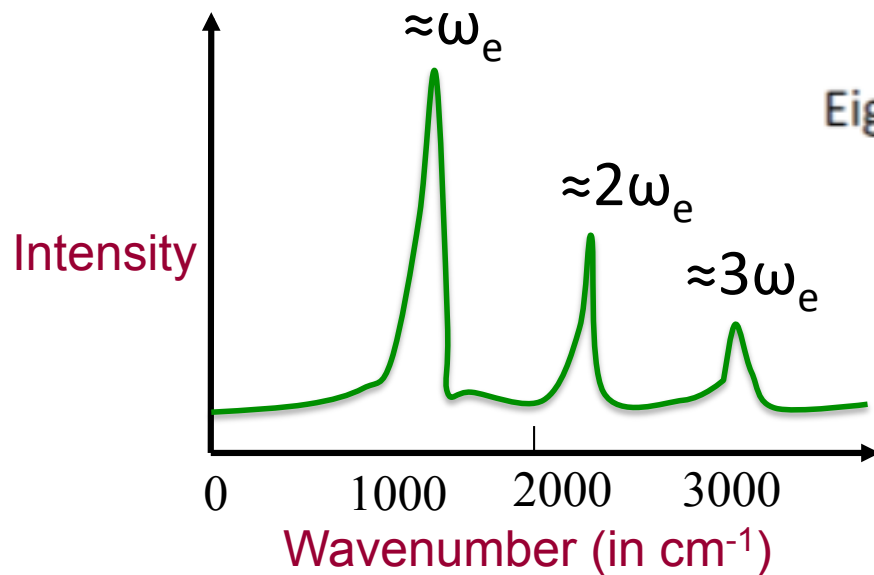
$$v = 0, 1, 2, 3, \dots, v_{\max}$$

x_e is the (dimensionless)
anharmonicity constant:

$$x_e = \frac{\omega_e}{4D_e}$$

the experimental dissociation energy, $D_0 = D_e - \text{ZPE}$

Spectral features for Anharmonic Vibrational Spectra

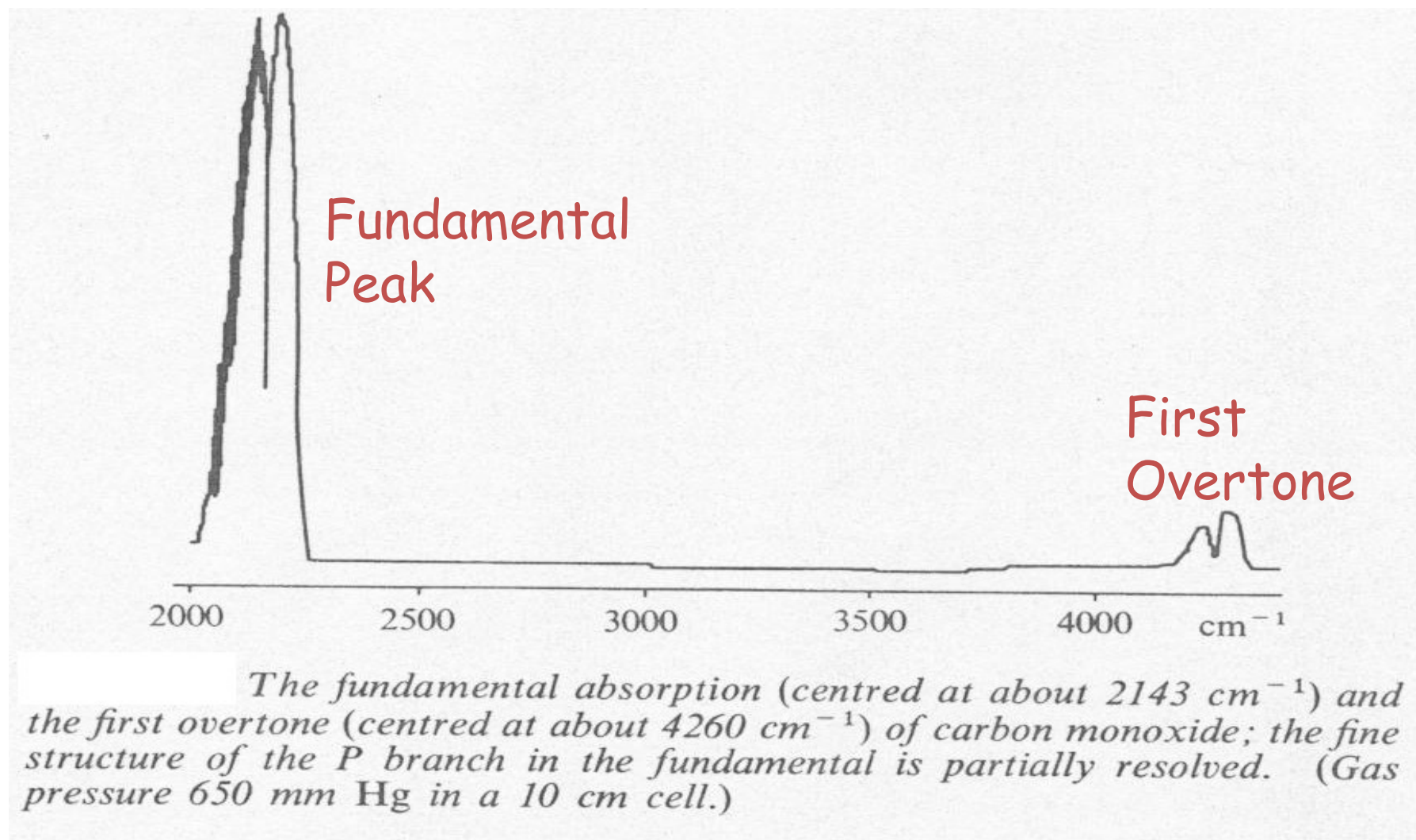


Eigenvalues: $\tilde{G}_v = (v + \frac{1}{2})\omega_e - (v + \frac{1}{2})^2\omega_e X_e$
 $v = 0, 1, 2, 3, \dots$

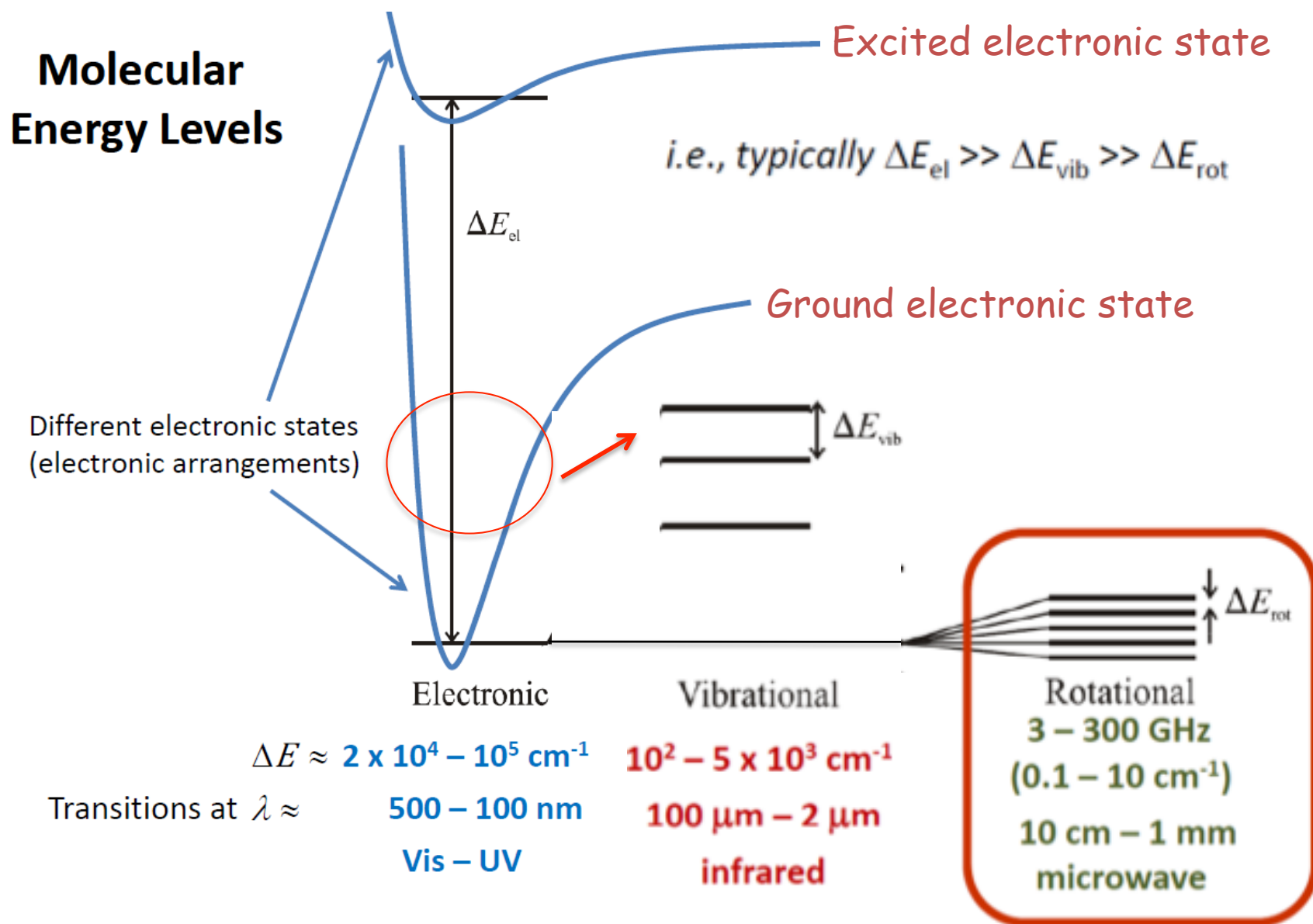
Specific Selection rule: $\Delta v = \pm 1, (\pm 2, \pm 3, \text{ weaker})$

Transitions: fundamental $(0 \rightarrow 1) \quad \tilde{\nu} = \omega_e - 2\omega_e X_e$
 1^{st} overtone $(0 \rightarrow 2) \quad \tilde{\nu} = 2\omega_e - 6\omega_e X_e$

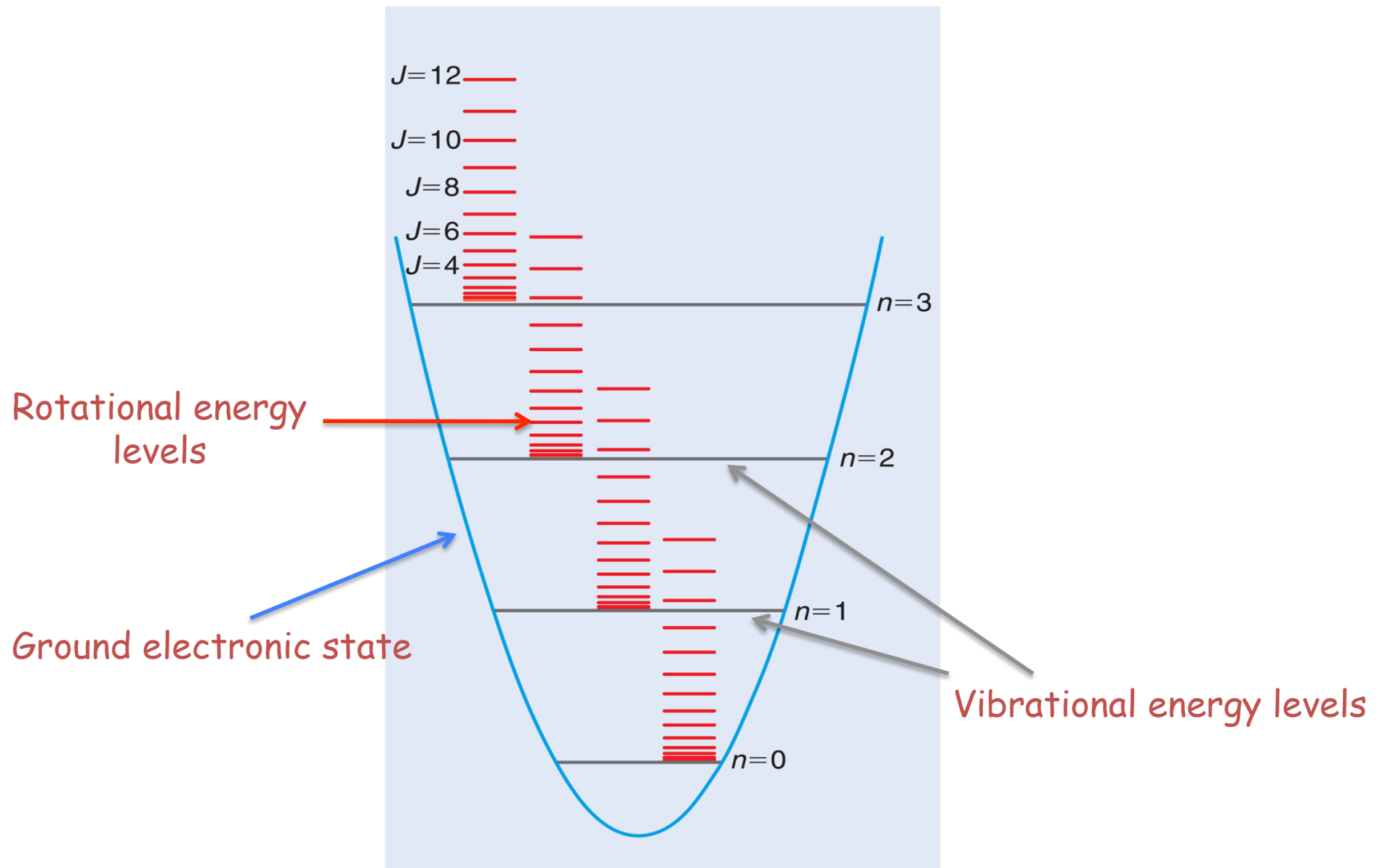
IR Spectrum of Carbon Monoxide (CO)



Different Energy Levels within a molecule



Different Energy Levels within a molecule



How to find out bond length of H_2 ?

A diatomic molecule without permanent dipole moment

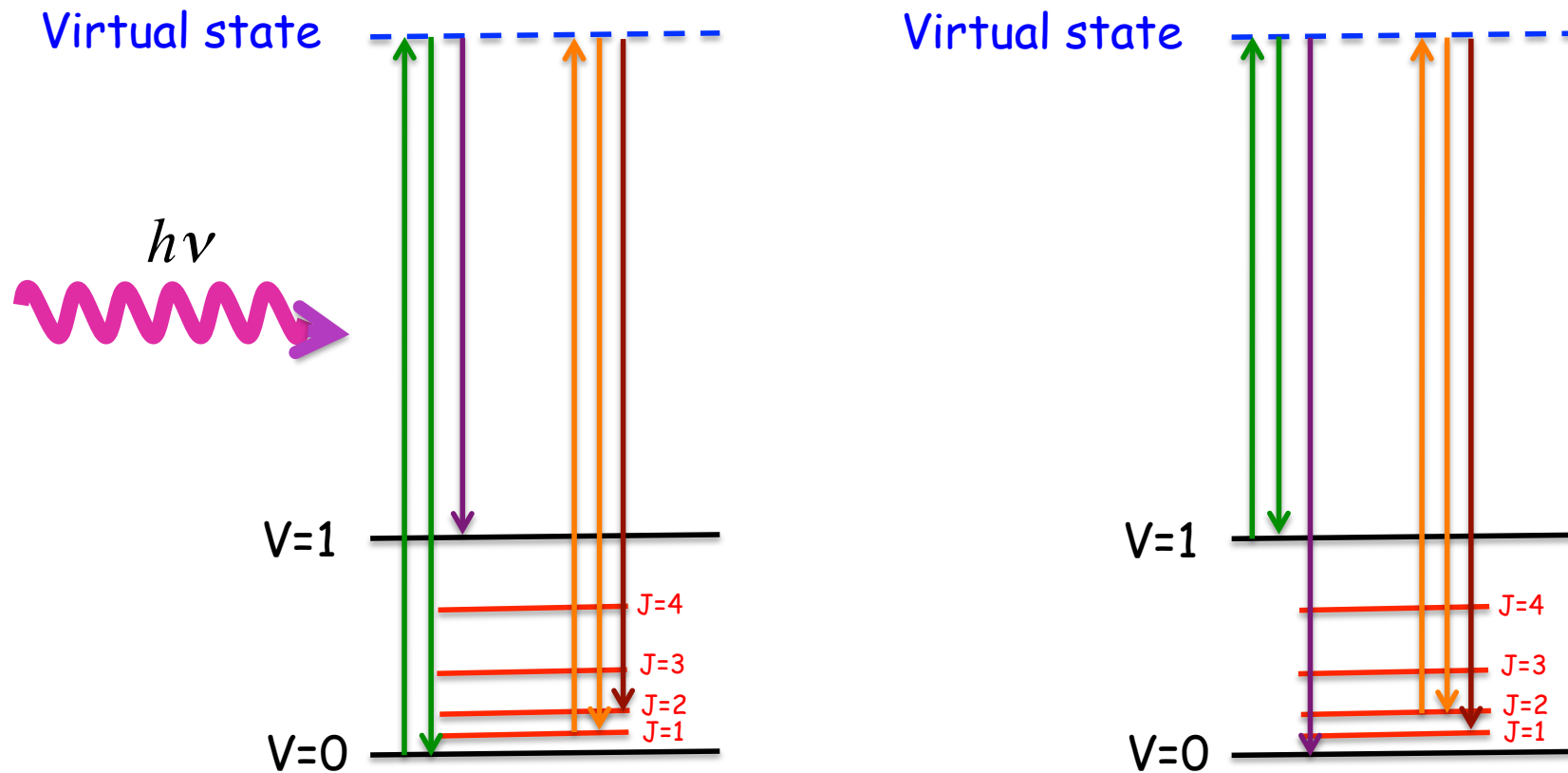
H_2 does have polarisability thus dipole moment can be induced

Molecular rotation or vibration can transform this into an oscillating induced dipole

Raman Spectroscopy

- Different principles. Based on scattering of (usually) visible monochromatic light by molecules of a gas, liquid or solid
- Two kinds of scattering encountered:
 - Rayleigh (1 in every 10,000) same frequency
 - Raman (1 in every 10,000,000) different frequencies

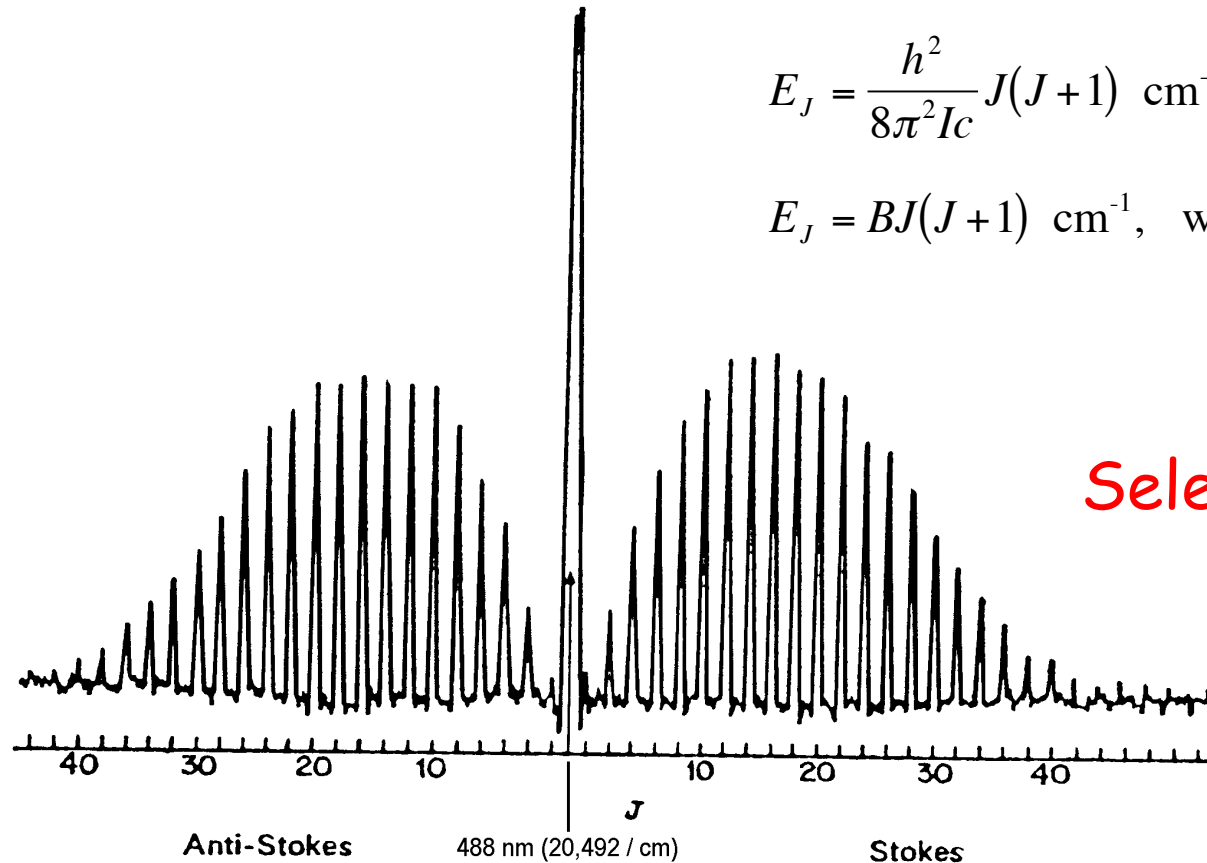
Raman Spectroscopy



- **Rayleigh scattering:** no change in wavenumber of light
- **Raman scattering:**
either greater than original or less than original by a constant amount determined by molecular energy levels & independent of incident light frequency

Rotational Raman Spectroscopy

Rotational Raman, carbon dioxide, 200 /cm



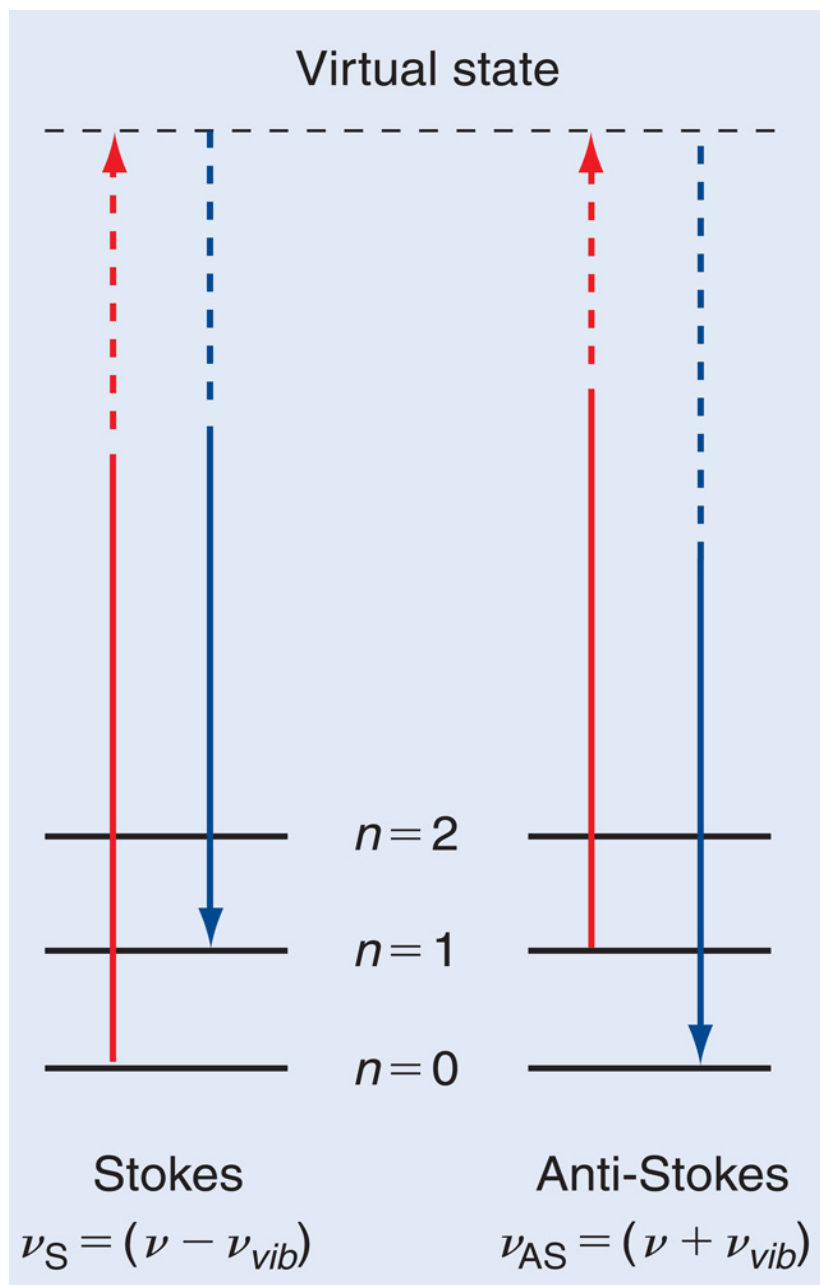
$$E_J = \frac{h^2}{8\pi^2 I_C} J(J+1) \text{ cm}^{-1}, \text{ where } J = 0, 1, 2, \dots$$

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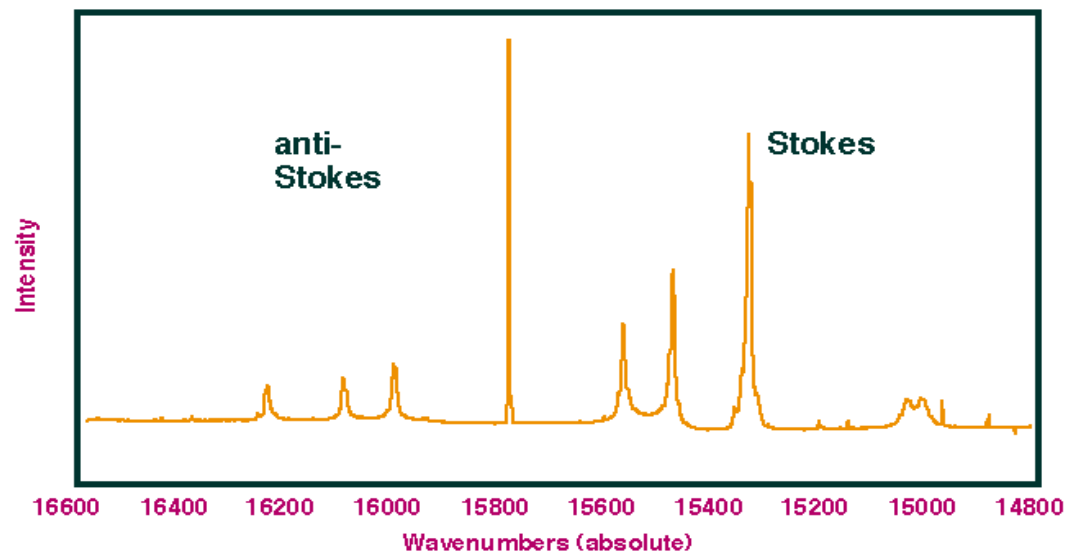
Selection Rule: $\Delta J = 0, \pm 2$

In Raman Spectra we measure spectral shift

Vibrational Raman Spectroscopy



Raman spectrum of CCl_4



Eigenvalues:

$$\tilde{G}_v = \left(v + \frac{1}{2}\right)\omega_e - \left(v + \frac{1}{2}\right)^2\omega_e X_e$$

$$v = 0, 1, 2, 3, \dots, v_{max}$$

Selection Rule: $\Delta v = 0, \pm 1, \pm 2, \dots$

It doesn't matter how beautiful your theory is,
it doesn't matter how smart you are. If it
doesn't agree with experiment, it's wrong.



R. P. Feynman

What we achieved in Ch-107 course?

PH-107

CH-107

