Part II
Molecular Spectroscopy

Prof. Dr. Xin Lu (吕鑫)
Office: 曾成奎楼 B301、卢嘉锡楼234
Email: xinlu@xmu.edu.cn
http://pcossgroup.xmu.edu.cn/old/users/xlu/group/
http://pcossgroup.xmu.edu.cn/old/users/xlu/group/courses/theochem/

Recommended books

- ***Fundamentals of Molecular Spectroscopy***, C. N. Banwell and E. M. McCash, 4th Edition, McGraw Hill
  A good introductory level
- ***Physical Chemistry***, Donald A McQuarrie and John D. Simon
  University Science Books
  Good for other parts of the course too

	$J \cdot mol^{-1}$	$cal \cdot mol^{-1}$	eV	cm^{-1}
$1\ J \cdot mol^{-1}$	1	0.2390	1.036×10^{-5}	8.359×10^{-2}
$1\ cal \cdot mol^{-1}$	4.184	1	4.336×10^{-5}	0.3497
$1\ eV$	9.649×10^{4}	2.306×10^{4}	1	8.065×10^{3}
$1\ cm^{-1}$	1.196×10	2.859	1.240×10^{-4}	1

The Electromagnetic Spectrum

- To convert frequency in rad s^{-1} to wavenumbers divide by $2\pi\tilde{c}$ ($\tilde{c}$ ~ the speed of light in $cm \cdot s^{-1}$)

$\tilde{c} = 2.997925 \times 10^{10} cm \cdot s^{-1}$

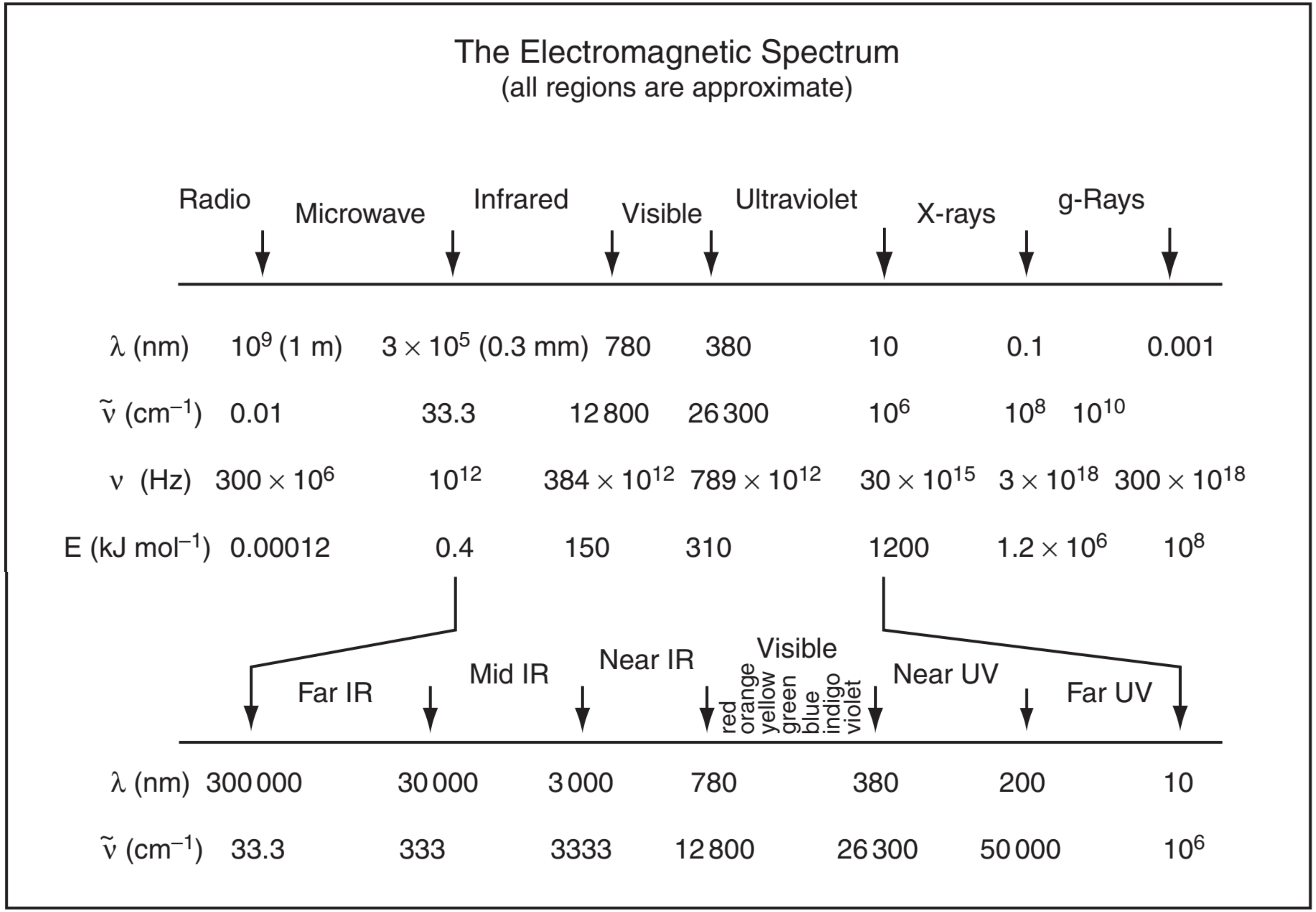
Wave length

Wavenumber

$\nu = c/\lambda$ ← ***Freq. in Hz***

$E = hc/\lambda$ ← ***Energy***

- To convert wavenumbers to energy in joules, multiply by $h\tilde{c}$ (1 eV ≡ 8065.5 cm^{-1}).



λ (nm)	10^9 (1 m)	3×10^5 (0.3 mm)	780	380	10	0.1	0.001
$\tilde{\nu}$ (cm^{-1})	0.01	33.3	12 800	26 300	10^6	10^8	10^{10}
ν (Hz)	300×10^6	10^{12}	384×10^{12}	789×10^{12}	30×10^{15}	3×10^{18}	300×10^{18}
E (kJ mol^{-1})	0.00012	0.4	150	310	1200	1.2×10^6	10^8

λ (nm)	300 000	30 000	3 000	780	380	200	10
$\tilde{\nu}$ (cm^{-1})	33.3	333	3333	12 800	26 300	50 000	10^6

1. Introduction

Spectroscopy may be defined as the interaction of electromagnetic radiation with matter.

◆ **NMR** and **IR** (*learnt*) : qualitative tools to determine the structure of molecules.

◆ In this part, we shall study:

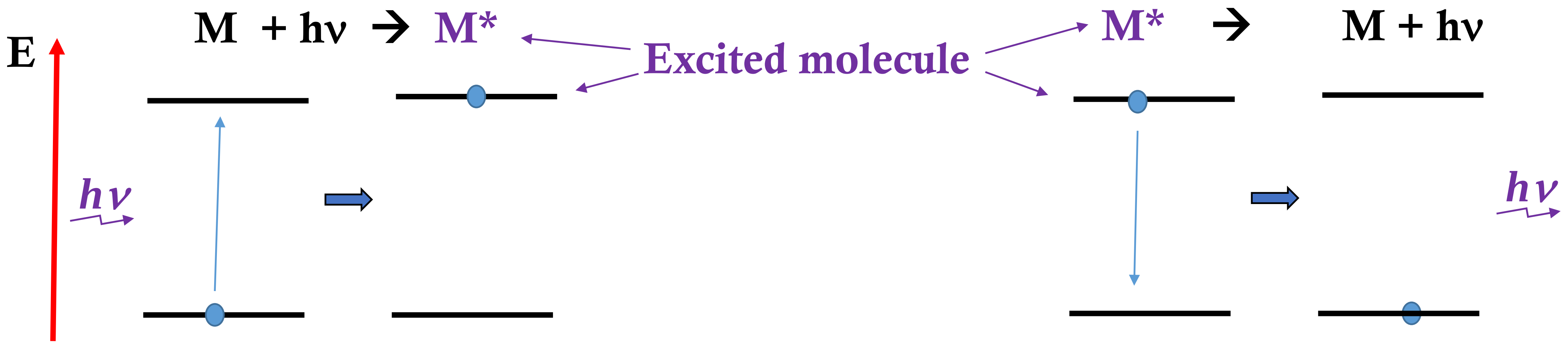
i) ***the more fundamental principles of spectroscopy*** using the ideas of Quantum Mechanics. (Spectroscopy provides some of the best experimental evidence for many of the ideas of quantum mechanics!)

ii) ***how to determine fundamental parameters such as bond lengths and energy levels*** by analyzing the fine structure of spectra.

Quantization of energy :

- In QM, the energy that a molecule possesses is quantized.
- When a molecule is excited from one energy level to higher one, electromagnetic radiation (light) is absorbed.
- When a molecule relaxes from a higher energy level to a lower one, light is given out.
- These processes give rise to ***absorption*** and ***emission*** *spectra*, respectively.

Absorption: **Spontaneous emission:**

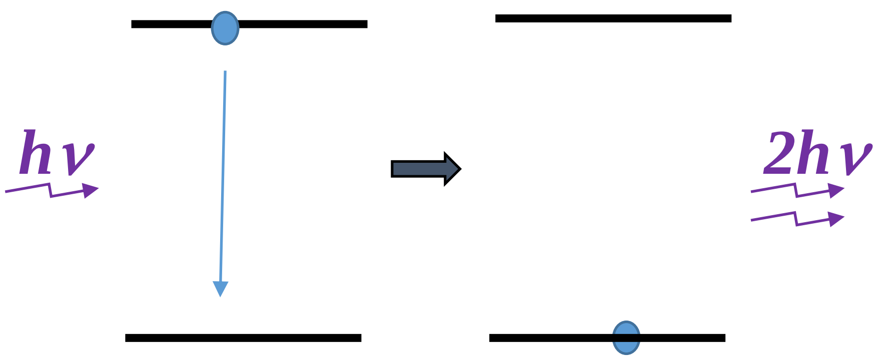


Stimulated emission

- The emission of a photon may either be spontaneous, as above, or it could be stimulated by another photon.
- In this process a photon of the correct energy stimulates the molecule to return to a lower energy level with the emission of a photon of the same energy.

Stimulated emission

$$M^* + h\nu \rightarrow M + 2h\nu$$



The most important application of stimulated emission is laser (Light Amplification by Stimulated Emission of Radiation)!

Contributions to the total energy of a molecule

Consider the molecules in the gas phase:

- Constantly moving around (**translation**al energy), **rotating**, and **vibrating**.
- Given enough energy, their electrons could be ***excited*** to higher energy levels.
- All of these energies are ***quantized***.
- But we can ***disregard translational energy levels*** i) because they are so close in energy and ii) because light does not cause a transition between translational energy levels.
- We can assume that these energies are independent of one another:

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

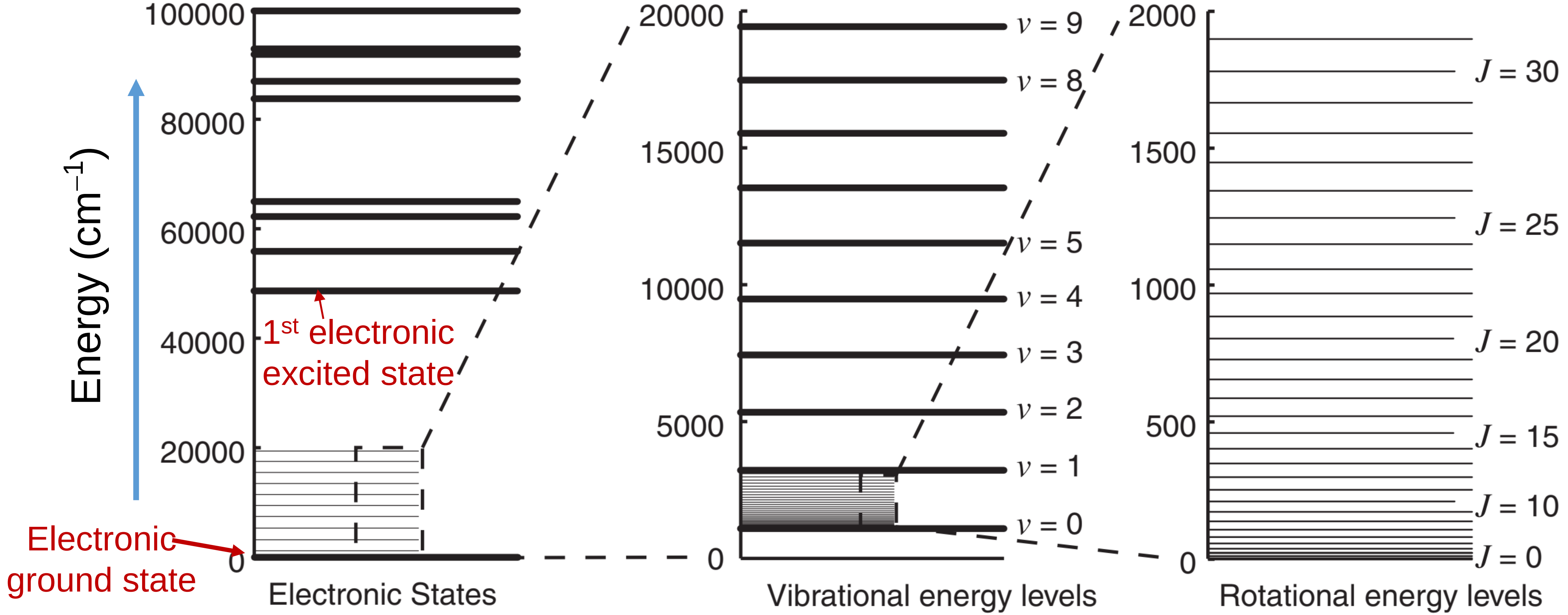
(Born-Oppenheimer Approximation)

- Similarly, when a molecule is promoted from one energy level to another, we can approximate the change in energy as,

$$\Delta E_{\text{total}} = \Delta E_{\text{electronic}} + \Delta E_{\text{vibrational}} + \Delta E_{\text{rotational}}$$

$$\textit{with } \Delta E_{\text{electronic}} >> \Delta E_{\text{vibrational}} >> \Delta E_{\text{rotational}}$$

The different energy levels for carbon monoxide



- Each electronic state has *many* vibrational energy levels associated with it.
- Each vibrational state has *many* rotational energy levels.

Since the energies required for the different types of transition vary considerably, they correspond to absorptions or emissions in different parts of the electromagnetic spectrum.

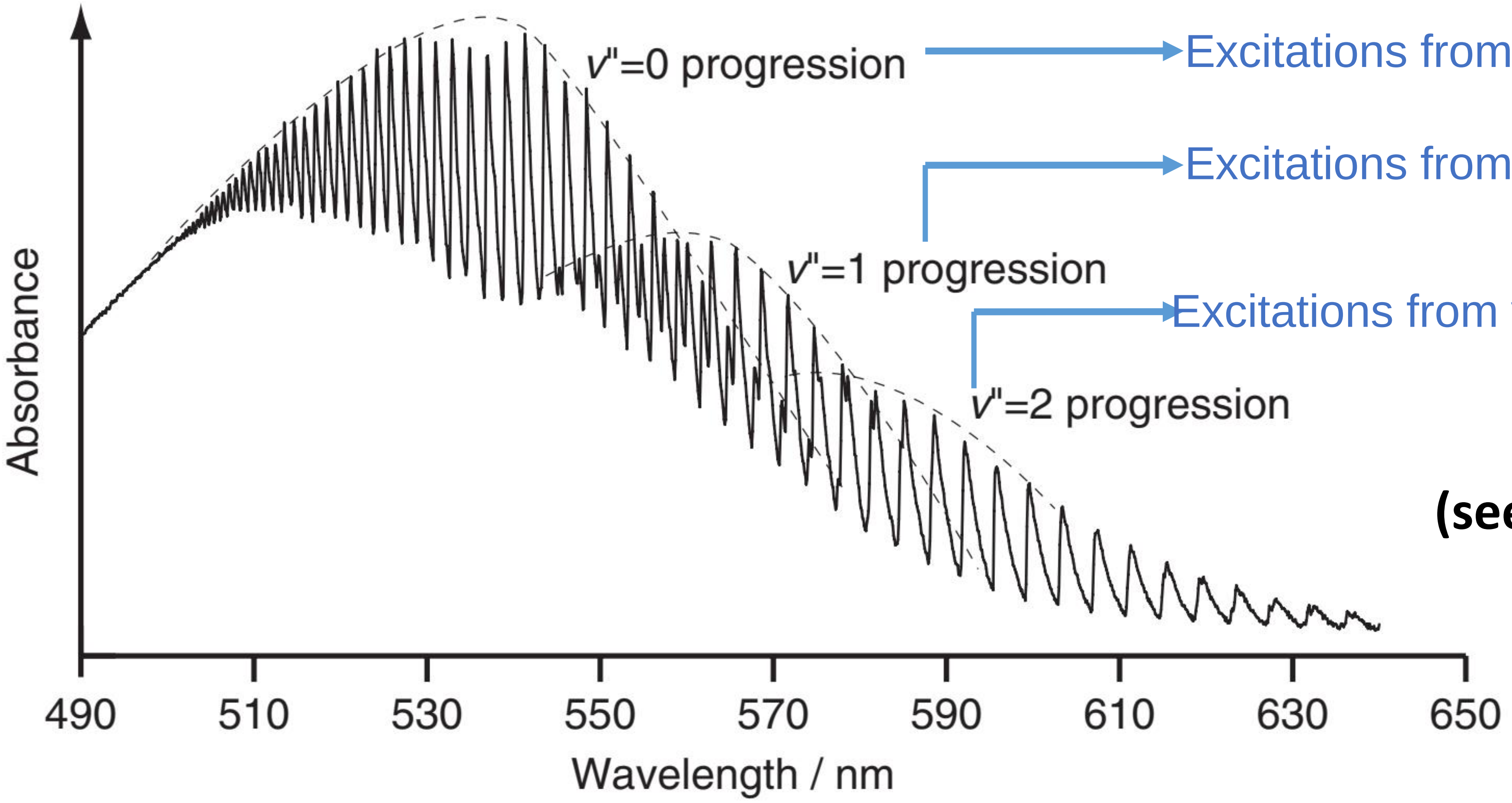
• $\Delta E_{electronic}$ typically 10,000s cm^{-1}	Visible/UV, possible x-ray for core e^{-}
• $\Delta E_{vibrational}$ typically 1,000s cm^{-1}	Infra-red (IR)
• $\Delta E_{rotational}$ typically a few cm^{-1}	Microwave/radiowave

- A *IR* photon that causes a *vibrational transition* can also cause a concomitant *rotational transition*. Spectral phenomena?
- Almost all molecules when they are vibrationally excited are also simultaneously rotationally excited.
- The same is true for electronic transitions -- each is usually accompanied by a simultaneous vibrational and rotational transition. Spectral phenomena?

Iodine vapor, *violet* due to absorbing light in the yellow-green part.

I_2 + hv (~540 nm) → I_2^* *(see its UV-vis spectrum given below!)*

Each of these peaks corresponds to the ***same electronic transition*** but with a different change in the vibrational (and indeed, rotational) energy of the iodine molecule.



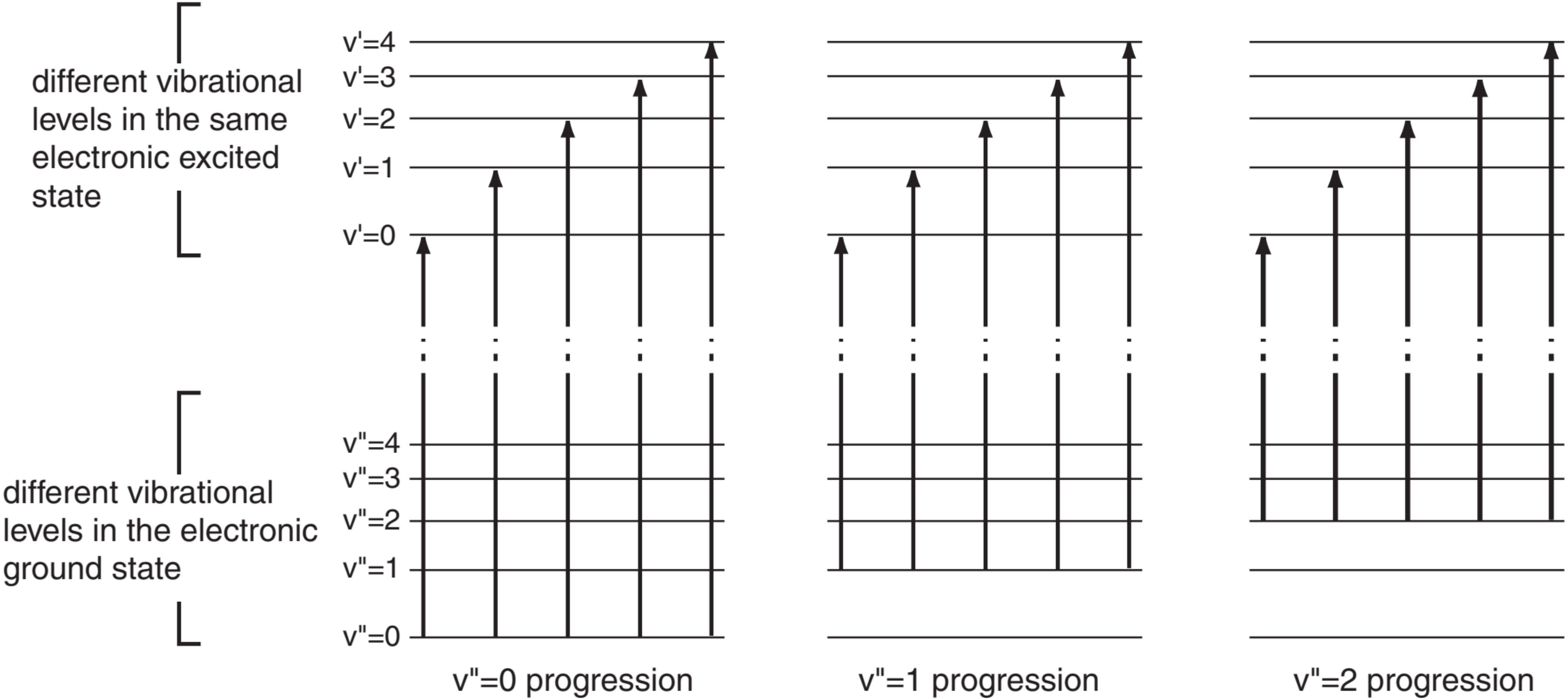
Excitations from vibrational ground state

Excitations from vibrational 1st excited state

Excitations from vibrational 2nd excited state

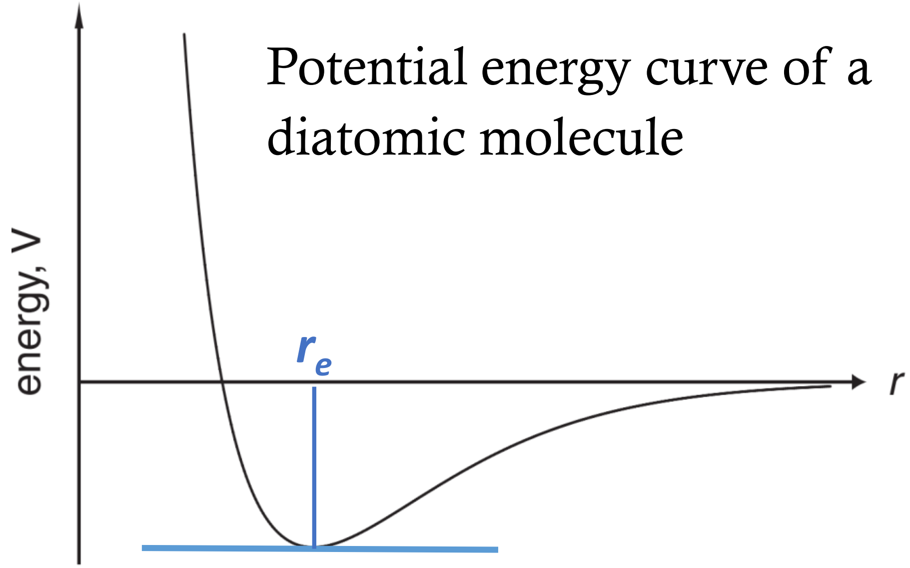
(see next page for details)

The ultrafine structure of UV-vis Spectrum

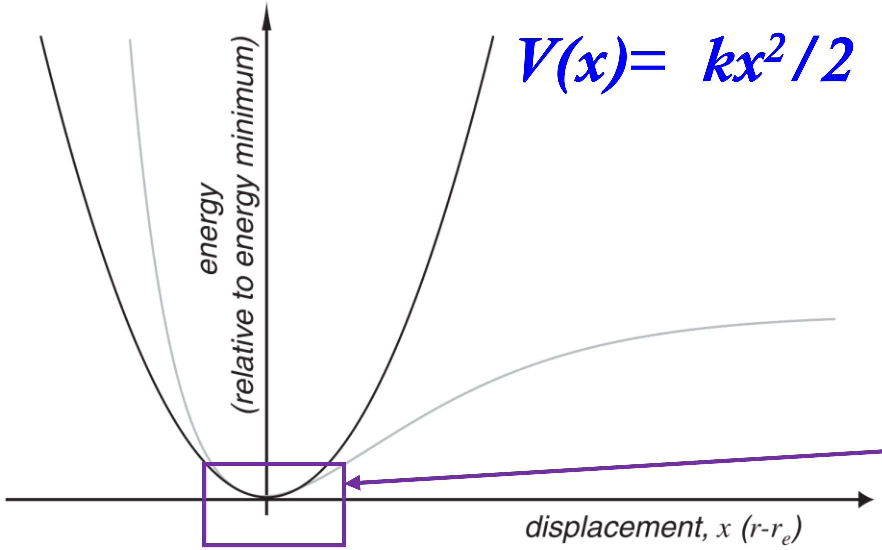


- Transitions from the vibrational ground state.
- Transitions from the 1st vibrational excited state.
- Transitions from the 2nd vibrational excited state.

2. Vibrational Spectroscopy - *the Harmonic Oscillator*



Potential energy curve of a diatomic molecule



$V(x) = kx^2/2$

- Restoring force acting on the molecule : $-dV/dr$
- At the equilibrium separation r_e, $-dV/dr = 0$
- The simplest assumption:

  restoring force $\propto -(r-r_e) = -kx$ (let $x = r-r_e$)

  k = ***force constant*** (in N m^{-1}),

  larger k, harder it is to stretch/compress the bond.

- The potential energy can thus be given by:

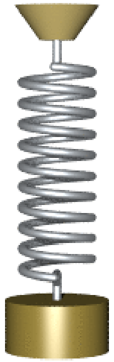
  $V(x) = -\int -kx\,dx = kx^2/2 + constant$

  $constant = 0$, so $V(0) = 0$;

- A good approximation for ***small displacements from r_e***.

Ex.1

Classical harmonic oscillator



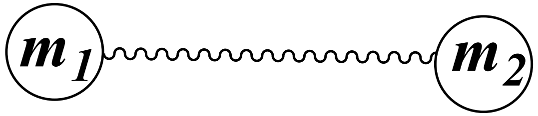
Mass-spring

◆ For a classic harmonic oscillator, e.g., a weight of mass ***m*** on a spring.

- *The frequency of oscillation is constant*, but the amplitude varies.
- At larger amplitudes, the energy of the system is greater, i.e., *greater stretch, greater potential energy*, but the frequency of oscillation remains the same.
- This *intrinsic frequency* of oscillation, given the symbol ***ω***, is given by:

$$\omega = \sqrt{k/m} \quad \text{(in rad s}^{-1}\text{)}$$

◆ For a system comprised of two vibrating masses, m_1 and m_2, the frequency depends on their reduced mass, ***μ***.



$$\omega = \sqrt{k/\mu} \quad \text{(in rad s}^{-1}\text{)} \quad \text{with } \mu = m_1m_2/(m_1+m_2)$$

◆ To convert to ***Hz***, the frequency in ***rad s^{-1}*** is divided by ***2π***.

$$\omega \ \text{(in Hz)} = \omega \ \text{(in rad s}^{-1}\text{)}/2\pi = (2\pi)^{-1}\sqrt{k/\mu}$$

- In vibrational and rotational spectroscopy, ***wavenumbers*** are often used as a measure of frequency (the wavenumber representing the number of waves in one centimeter).

$\tilde{\nu}$ = wavenumber in cm^{-1} = $1/\lambda$ (λ in cm) *non-standard symbol of freq.*

$\boldsymbol{\tilde{\omega}}$ (in cm^{-1}) = $(2\pi\tilde{c})^{-1}\sqrt{\boldsymbol{k}/\mu}$

($\tilde{c}$ non-standard symbol for the speed of light in cm s^{-1})

$$\boldsymbol{\nu = c/\lambda}$$

$$\boldsymbol{\nu}\ \textbf{\textit{(in Hz)}} = \boldsymbol{\tilde{c}}/\lambda\,(\lambda \text{ in cm}) = \boldsymbol{\tilde{c}}\tilde{\nu}$$

QM Treatment for Harmonic Oscillator

- Vibrational energies are quantized and found by solving the ***Schrödinger equation*** for the harmonic oscillator:

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{d^2x}+\frac{1}{2}kx^2\psi = E\psi$$

Kinetic energy associated with the *wavefunction.*

Potential energy associated with the *wavefunction.*

→ There are infinite number of solutions, ψ_v, with corresponding energy E_v:

E_v *(in Joules)* $= (v + ½)\hbar\omega$

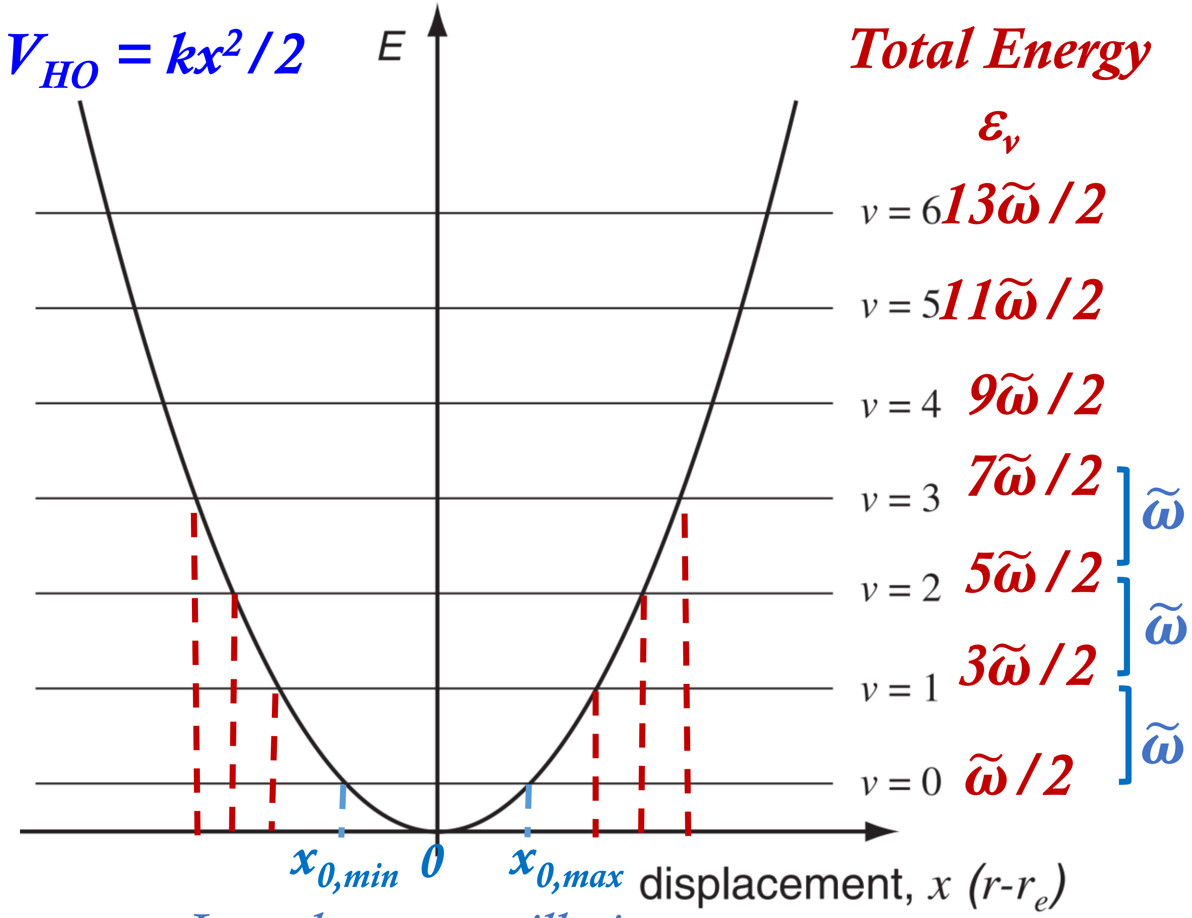
(v *~ vibrational quantum number, 0,1,2,3…)*

(ω *in rad* s^{-1}*)*

or ε_v *(in* cm^{-1}*)* $= (v + ½)\tilde{\omega}$ $\longleftarrow$ *(*$\tilde{\omega}$ *in* cm^{-1}*)*

Quantized energies of harmonic oscillator

- The energies of the first seven wavefunctions of the harmonic oscillator are shown below together with the potential energy function.



In each state, oscillating between these extremes.

- For each quantum state of the HO,

i) At $x = x_{v,max}$ or $x_{v,min}$, $E_k = 0$, $V=V_{v,max} = E_v$

ii) At $x = 0$, $V = 0$, $E_k = E_{k,v,max} = E_v$

- The lowest energy $\varepsilon_0 = \tilde{\omega}/2$ is known as the *zero-point energy*, i.e., a bond is always vibrating, even in its lowest energy state.
- Selection rule for transitions: $\Delta v = +/-1$
- ***Spectral phenomenon?***

Ex.3,4

The Morse Oscillator

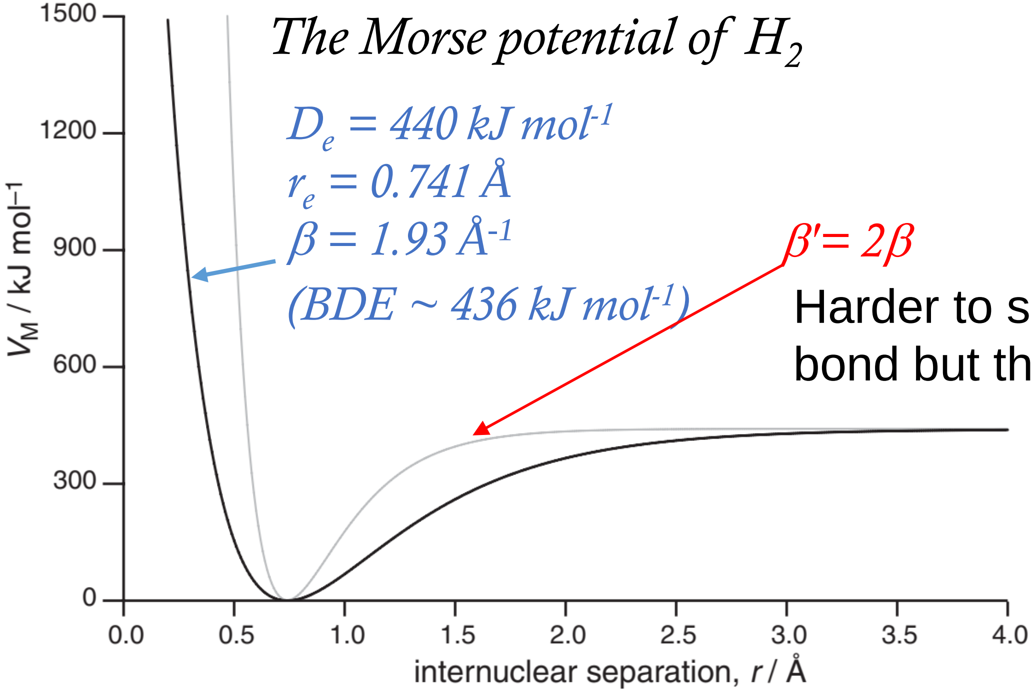
- The harmonic oscillator description is problematic for *larger displacements of a bond(?)*.
- A much better description of an oscillator can be gained using the empirical ***Morse potential*** (V_M) that agrees much better with experiment.

$$V_M(x) = D_e\,[1 - \exp(\underbrace{-\beta x}_{\text{must be dimensionless!}})]^2$$

($x = r - r_e$; D_e – Depth of the well; β – steepness of the well)

must be dimensionless!

units of reciprocal length



The Morse potential of H_2

$D_e = 440$ kJ mol^{-1}

$r_e = 0.741$ Å

$\beta = 1.93$ Å^{-1}

(BDE ~ 436 kJ mol^{-1})

$\beta' = 2\beta$

Harder to stretch the bond but the same BDE!

- For small displacements ($x \ll 1/\beta$),

$$e^{-\beta x} \approx 1 - \beta x \quad (e^{-\theta} = 1 - \theta + \theta/2! - \theta/3!\ \ldots)$$

$$\rightarrow V_M(x) \approx D_e\beta^2 x^2 = kx^2/2$$

$$(\text{with } k = 2D_e\beta^2)$$

i.e., the oscillator becomes harmonic.

QM Description of the Morse Oscillator

- The ***Schrödinger equation*** for the ***Morse Oscillator***,

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{d^2x}+V_M\psi=E\psi$$

$$\rightarrow E_v\,(\text{in joules})=(v+½)\hbar\omega-(v+½)^2\hbar\omega x_e$$

$$x_e=\frac{\hbar\beta^2}{2\mu\omega}\quad(\textit{anharmonicity constant})$$

$$\text{or}\quad \varepsilon_v\,(\text{in cm}^{-1})=(v+½)\,\tilde{\omega}-(v+½)^2\tilde{\omega}x_e$$

- ➢ From ω (and μ), k_M can be calculated. $k_M=\mu\omega^2$ Note: $\omega=2\pi\tilde{c}\tilde{\omega}$ in rad·s^{-1}

- ➢ Then from x_e, β and D_e can be calculated. $\beta=\sqrt{2\mu\omega x_e/\hbar}$

Effects of x_e (anharmonicity constant)

Typically $0 < x_e < 0.1.$

Morse oscillator

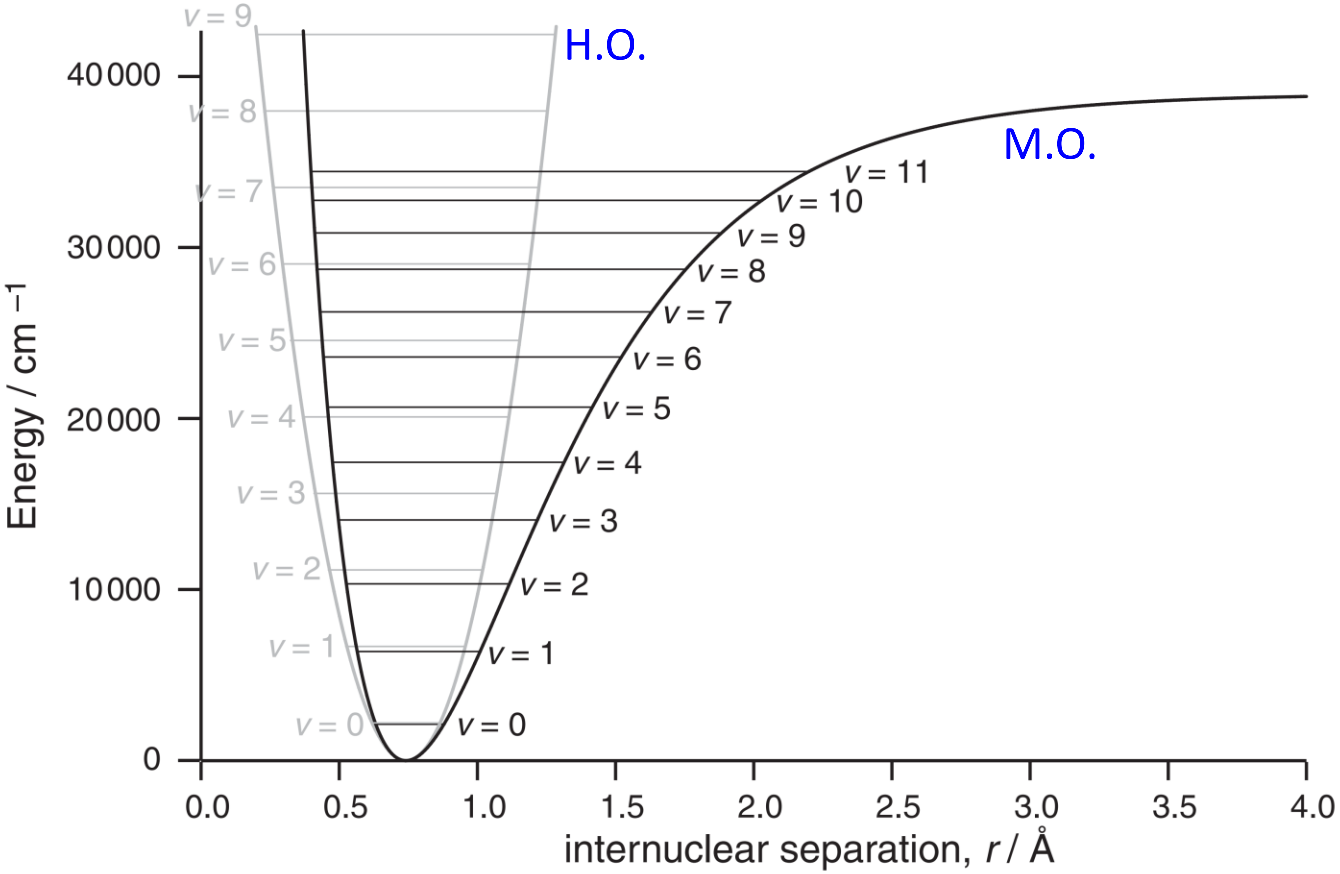
$$E_v^{M} = (v + ½)\hbar\omega - (v + ½)^2\hbar\omega x_e$$

$$\Delta E_v^{M} = E_v^{M} - E_{v-1}^{M} = \hbar\omega - 2v\hbar\omega x_e$$

Harmonic oscillator

$$E_v^{HO} = (v + ½)\hbar\omega$$

$$\Delta E_v^{HO} = E_v^{HO} - E_{v-1}^{HO} = \hbar\omega$$



i) E_v^{M} *always* $< E_v^{HO}$

ii) ΔE_v^{M} *always* $< \Delta E_v^{HO}$

iii) ΔE_v^{M} *gets smaller with increasing **v**, eventually approaching 0. That is,* E_v *reaches its maximum.*

Ex.2

Maximum of $E_v(\varepsilon_v)$

$$\varepsilon_v\ (\text{in cm}^{-1}) = (v + ½)\tilde{\omega} - (v + ½)^2\tilde{\omega}x_e$$

$$\Delta\varepsilon_v^M = \varepsilon_v^M - \varepsilon_{v-1}^M = \hbar\tilde{\omega} - 2v\hbar\tilde{\omega}x_e \quad v\uparrow,\ \Delta\varepsilon_v^M\downarrow;\quad \Delta\varepsilon_v^M \leq 0,\ \varepsilon_v{}^M{}_{max} = D_e!$$

- Eventually the ε_v^M reaches a *maximum* at v_{max} and then falls.
- This ε_v^M corresponds to the energy D_e.

To determine v_{max} and D_e, define

$$d\varepsilon_v/dv = 0 \rightarrow$$

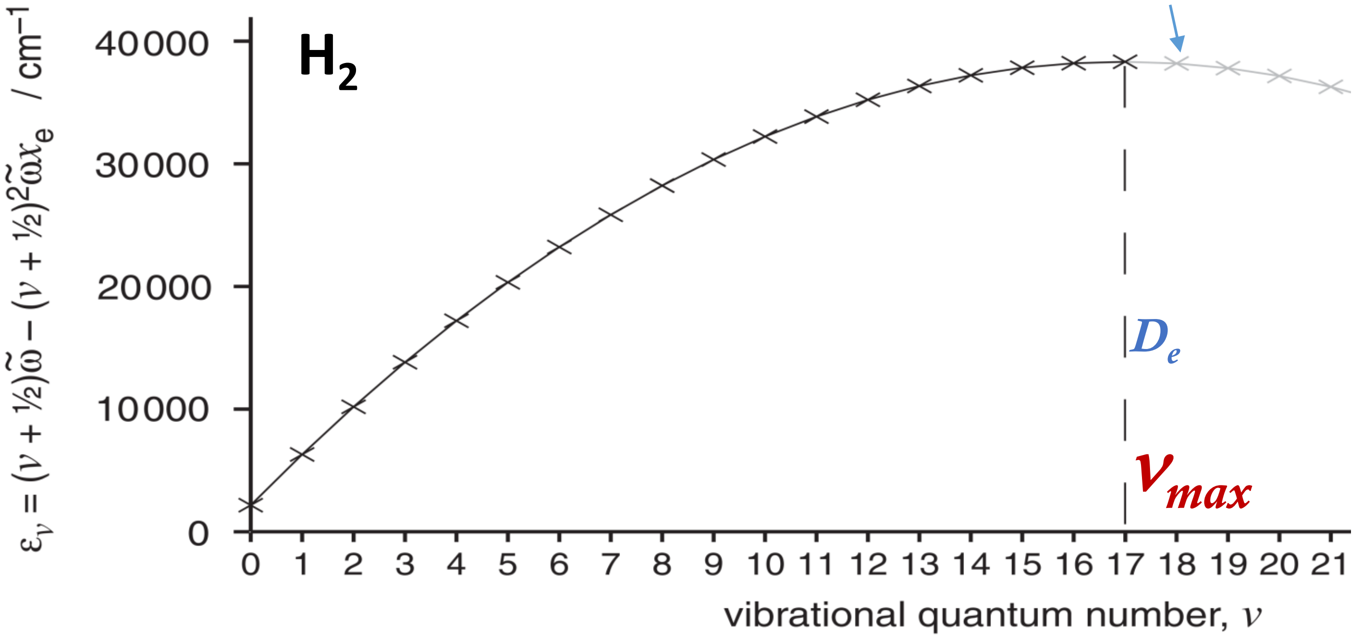
$$d[(v + ½)\tilde{\omega} - (v + ½)^2\tilde{\omega}x_e]/dv=0$$

$$\rightarrow v_{max} = (x_e^{-1} - 1)/2$$

$$\rightarrow D_e = (v_{max} + ½)\ \tilde{\omega} - (v_{max} + ½)^2\tilde{\omega}x_e$$

$$\rightarrow \tilde{D}_e\ (\text{in cm}^{-1}) = \tilde{\omega}(4x_e)^{-1}$$

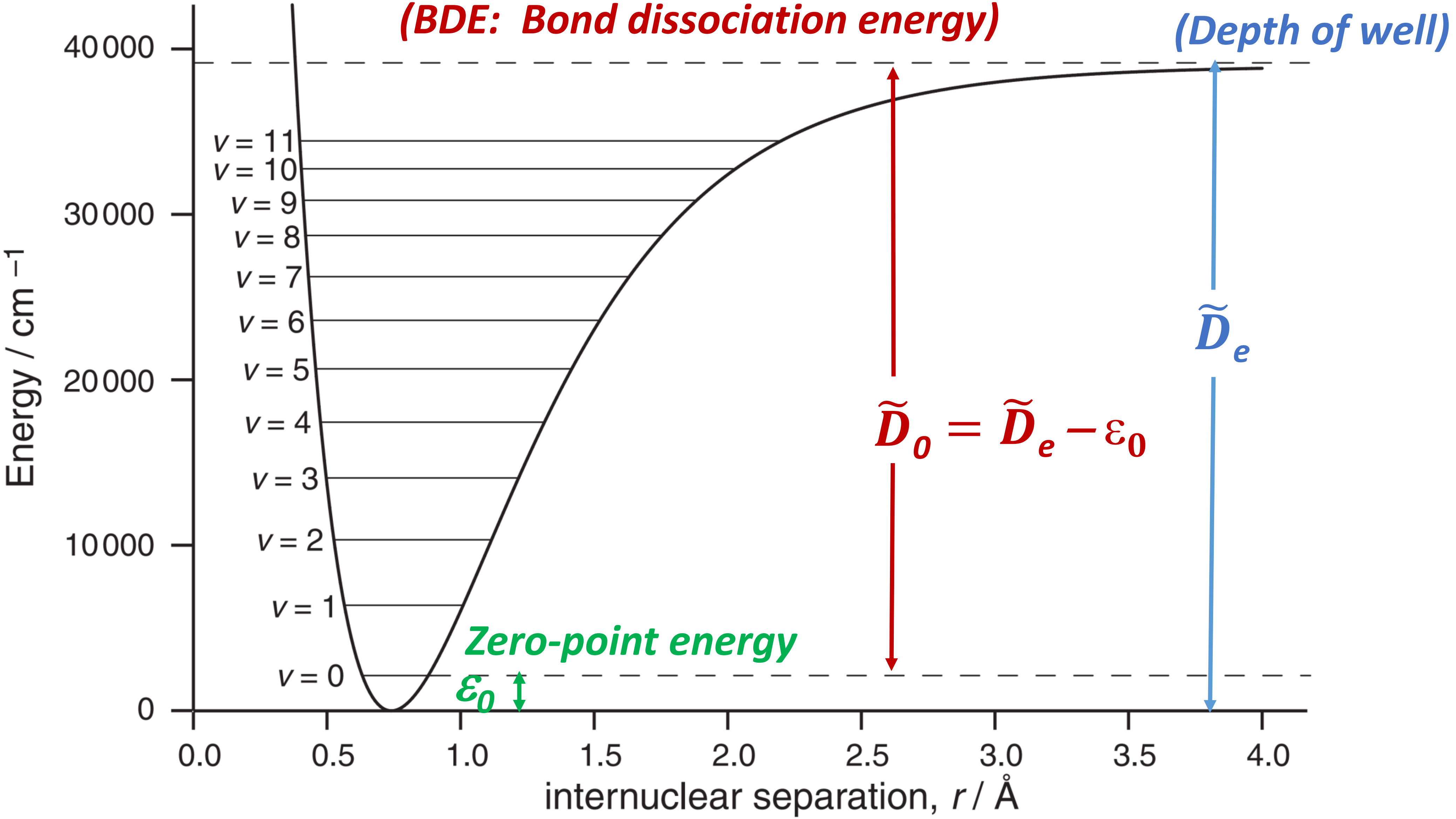
$$\text{or}\quad D_e\ (\text{in joules}) = \hbar\omega(4x_e)^{-1}$$



These points have no physical meaning!

Q: In practice, is the as-derived v_{max} an integer? Can we first determine the integer v_{max} and then use it to derive D_e? Why?

Dissociation energy D_e and D_0



(BDE: Bond dissociation energy)

(Depth of well)

$\tilde{D}_e$

$$\tilde{D}_0 = \tilde{D}_e - \varepsilon_0$$

Zero-point energy

ε_0

Populations of the different energy levels

Populations of the different vibrational energy levels are given by the ***Boltzmann distribution***.

- The probability of an oscillator to occupy the *v*th level is

$$P_v = e^{-E_v/kT} / \sum_v e^{-E_v/kT}$$

- The ratio of N_v, the population of the *v*th level, to N_0, the population of the ground state ($v = 0$) is given by:

$$N_v/N_0 = e^{-\Delta E/kT} \qquad (\Delta E = E_v - E_0)$$

- Since ΔE is large relative to kT, only the ground state is significantly populated at room temperature. (***Boltzmann constant*** $k = 1.380649\times10^{-23}$ J/K = 0.69503476 cm^{-1}/K)

- For example, $\Delta E_{1\text{-}0}$ = 2000 cm^{-1}, kT (T=300K) ≈ 200 cm^{-1}

$$N_1/N_0 \approx e^{-10} \approx 5\times10^{-5}$$

Transitions in the Anharmonic Oscillator

◆Selection rule for *Harmonic oscillator*: $\Delta v = \pm 1$, $\Delta \varepsilon = \varpi$ (a single line in spectrum!)

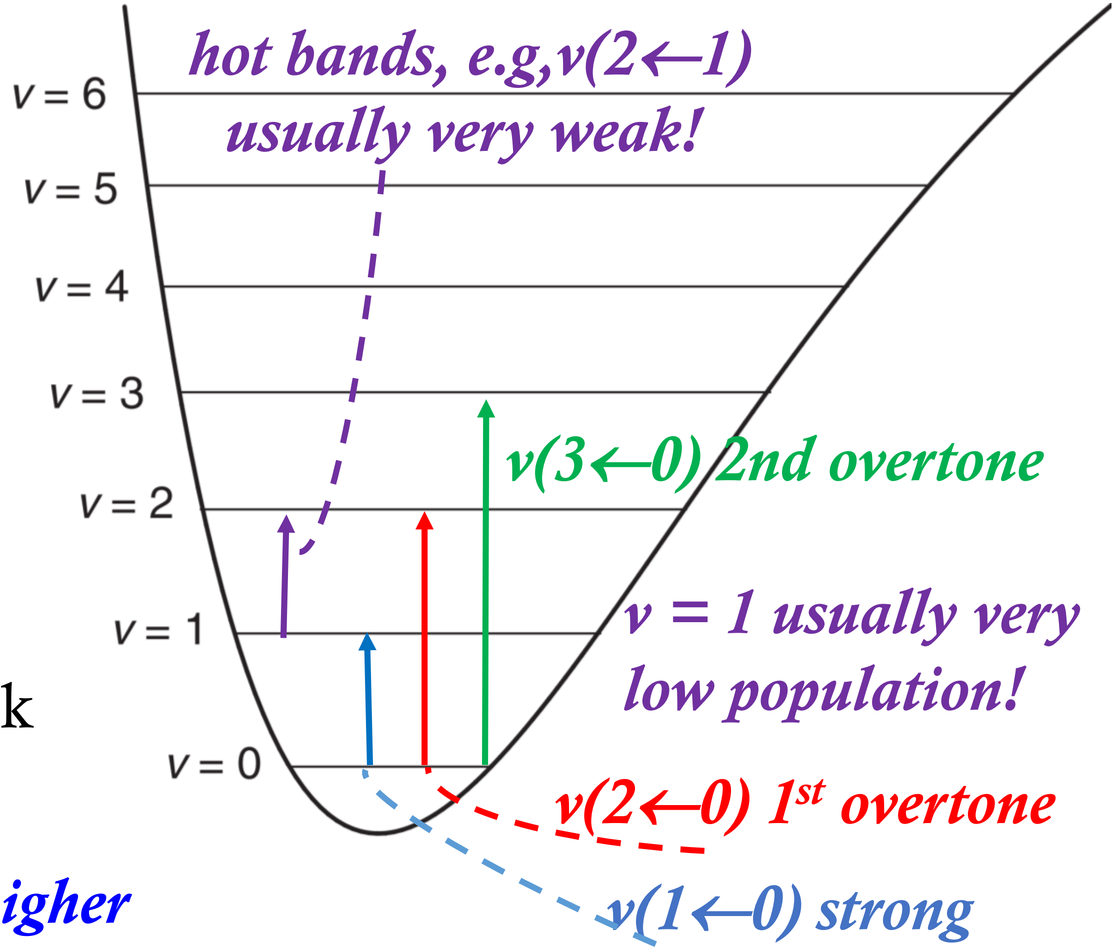
◆ Selection rules for *anharmonic oscillator*:

- $\Delta v = \pm 1, \pm 2, \pm 3, \ldots$ ***(Less strict!)***
- A ***change in dipole moment*** during vibration!

◆Allowed transitions are not equally intense, depending on the population of the level excited.

◆The transition from $v=0$ to $v=1$, labeled $v(1\text{-}0)$ or $v(1\leftarrow 0)$, is usually very strong, but transitions to higher vibrational levels rapidly become very weak in intensity (hardly observable!)

◆The transitions that become more important at ***higher temperatures*** are called ***hot bands***.



hot bands, e.g, $v(2\leftarrow 1)$ usually very weak!

$v(3\leftarrow 0)$ 2nd overtone

$v = 1$ usually very low population!

$v(2\leftarrow 0)$ 1^{st} overtone

$v(1\leftarrow 0)$ strong Fundamental

Frequencies of transitions

$$\varepsilon_v \text{ (in cm}^{-1}) = (v + ½)\tilde{\omega} - (v + ½)^2\tilde{\omega}x_e$$

- v=0 to v=1; $v(1\leftarrow 0)$ *The fundamental absorption! (基频吸收(峰))*

$$\Delta\varepsilon = \varepsilon_1 - \varepsilon_0$$

$$= (1 + ½)\tilde{\omega} - (1 + ½)^2\tilde{\omega}x_e - [(0 + ½)\tilde{\omega} - (0 + ½)^2\tilde{\omega}x_e]$$

$$= \tilde{\omega}(1 - 2x_e) < \tilde{\omega}$$

(基频峰值略小于振子的特征振动频率！)

- v=0 to v=2; $v(2\leftarrow 0)$ *1st overtone(第一泛频), weak in intensity!*

$$\Delta\varepsilon = \varepsilon_2 - \varepsilon_0$$

$$= (2 + ½)\tilde{\omega} - (2 + ½)^2\tilde{\omega}x_e - [(0 + ½)\tilde{\omega} - (0 + ½)^2\tilde{\omega}x_e]$$

$$= 2\tilde{\omega}(1 - 3x_e)$$

Just a little less than twice freq. of fundamental!

Frequencies of transitions

$$\varepsilon_v \text{ (in cm}^{-1}\text{)} = (v + ½)\,\tilde{\omega} - (v + ½)^2\tilde{\omega}x_e$$

- v=0 to v=3; $v(3 \leftarrow 0)$ ---- *2nd overtone, very weak!*

$$\Delta\varepsilon = \varepsilon_3 - \varepsilon_0$$

$$= (3 + ½)\tilde{\omega} - (3 + ½)^2\tilde{\omega}x_e - [(0 + ½)\,\tilde{\omega} - (0 + ½)^2\tilde{\omega}x_e]$$

$$= 3\tilde{\omega}(1 - 4x_e)$$

- v=1 to v=2; $v(2 \leftarrow 1)$ ---- ***hot band*** *(visible at high temperature!)*

$$\Delta\varepsilon = \varepsilon_2 - \varepsilon_1$$

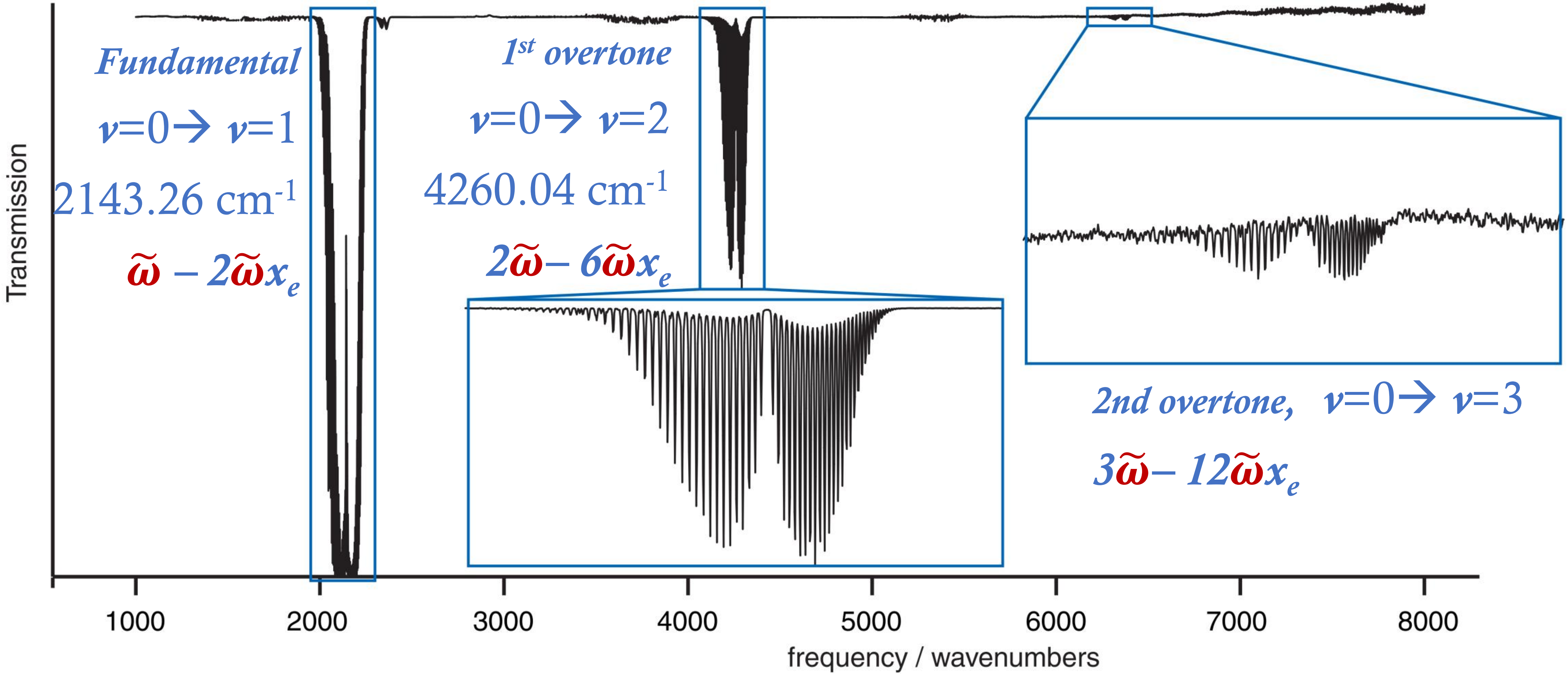
$$= (2 + ½)\,\tilde{\omega} - (2 + ½)^2\tilde{\omega}x_e - [(1 + ½)\,\tilde{\omega} - (1 + ½)^2\tilde{\omega}x_e]$$

$$= \tilde{\omega}\,(1 - 4x_e)$$

----Almost the same *freq.* as the *fundamental*!

An IR Spectrum of Carbon Monoxide

Ex. 5,6



Fundamental

$v=0 \rightarrow v=1$

2143.26 cm^{-1}

$\tilde{\omega} - 2\tilde{\omega}x_e$

1st overtone

$v=0 \rightarrow v=2$

4260.04 cm^{-1}

$2\tilde{\omega} - 6\tilde{\omega}x_e$

2nd overtone, $v=0 \rightarrow v=3$

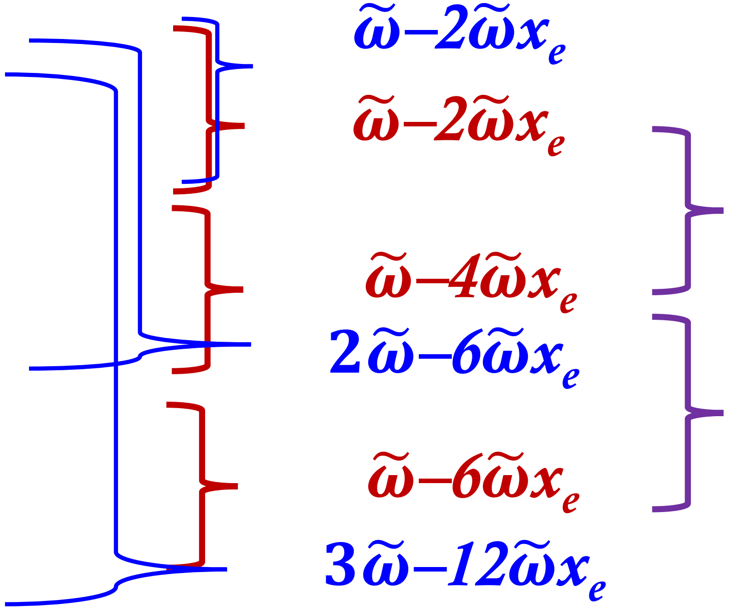
$3\tilde{\omega} - 12\tilde{\omega}x_e$

Q1: What do the fine structures in each of the absorption bands mean?

Q2: From the spectrum, how to determine $\tilde{\omega}$ and x_e, and hence k_M, D_e, D_0 and β?

Practical way

The easiest way to find these parameters in practice is to take the differences between ***successive lines in the spectrum***.



v	$\varepsilon_v = (v + \frac{1}{2})\,\tilde{\omega} - (v + \frac{1}{2})^2\tilde{\omega}x_e$	$\Delta\varepsilon_{(v+1\leftarrow v)}$	$\Delta\varepsilon_{(v+1\leftarrow v)} - \Delta\varepsilon_{(v+2\leftarrow v+1)}$
0	$\tilde{\omega}/2 - \tilde{\omega}x_e/4$	$\tilde{\omega} - 2\tilde{\omega}x_e$	
		$\tilde{\omega} - 2\tilde{\omega}x_e$	
1	$3\tilde{\omega}/2 - 9\tilde{\omega}x_e/4$		$2\tilde{\omega}x_e$
		$\tilde{\omega} - 4\tilde{\omega}x_e$	
2	$5\tilde{\omega}/2 - 25\tilde{\omega}x_e/4$	$2\tilde{\omega} - 6\tilde{\omega}x_e$	$2\tilde{\omega}x_e$
		$\tilde{\omega} - 6\tilde{\omega}x_e$	
3	$7\tilde{\omega}/2 - 49\tilde{\omega}x_e/4$	$3\tilde{\omega} - 12\tilde{\omega}x_e$	

$$2\tilde{\omega}x_e = 2\Delta\varepsilon_{(1\leftarrow 0)} - \Delta\varepsilon_{(2\leftarrow 0)}$$

e.g., CO

$\nu\,(1\leftarrow 0) \sim 2143.26\ \mathrm{cm^{-1}}$

$\nu\,(2\leftarrow 0) \sim 4260.04\ \mathrm{cm^{-1}}$

$\nu\,(2\leftarrow 1) \sim 2116.78\ \mathrm{cm^{-1}}$

$$2\tilde{\omega}x_e = \Delta\varepsilon_{(1\leftarrow 0)} - \Delta\varepsilon_{(2\leftarrow 1)} = 26.48\ \mathrm{cm^{-1}}$$

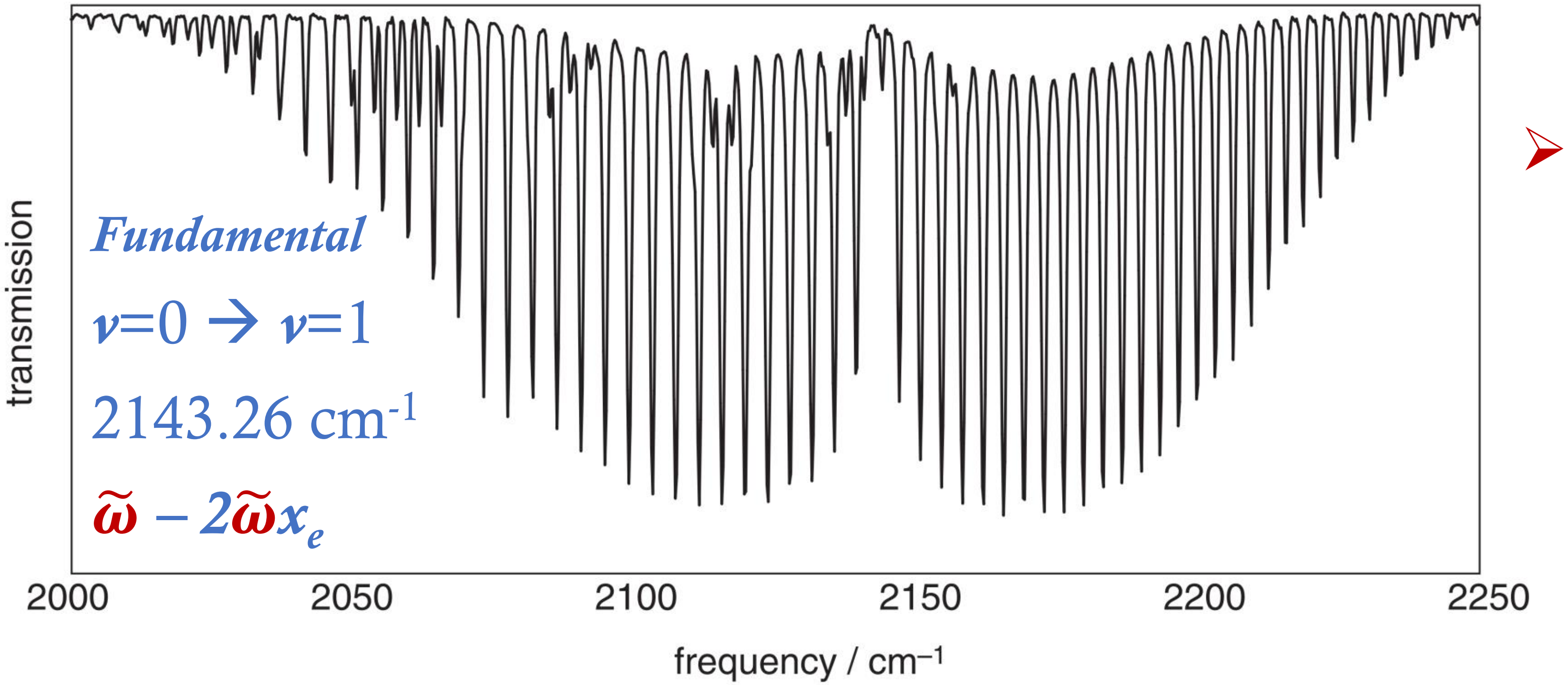
$$\tilde{\omega} = \Delta\varepsilon_{(1\leftarrow 0)} + 2\tilde{\omega}x_e = 2169.74\ \mathrm{cm^{-1}}$$

$$x_e = 2\tilde{\omega}x_e/(2\tilde{\omega}) = 0.006102$$

Q： Can we get such information that is related to bond length from a vibrational spectrum?

Vibration-rotation spectrum

- The fundamental absorption in the IR spectrum of CO is a band of many peaks.
- Each peak in this band corresponds to ***the same vibrational transition*** from $v = 0$ to $v = 1$ but accompanied by a ***different rotational transition***.
- This is so-called ***vibration-rotation spectrum*** of CO.



Fundamental

$v=0 \rightarrow v=1$

2143.26 cm^{-1}

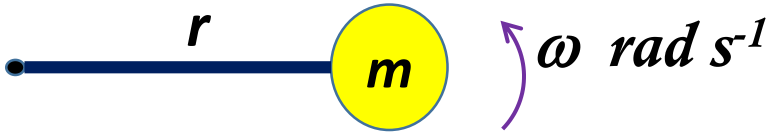
$\tilde{\omega} - 2\tilde{\omega}x_e$

- To understand the physical meaning of these fine structures, we need to look at pure rotational spectroscopy first.

3. Rotational (microwave) spectroscopy

Transitions between rotational energy levels in molecules usually give rise to peaks in the microwave / radio region of the electromagnetic spectrum.

Rotational angular momentum



The ***momentum of inertia*** of the rotating mass (in an ***angular velocity*** ω) is given by,

$$I = mr^2$$

Analogous to mass in linear motion.

The ***rotational angular momentum*** (L) is given by,

$$L = I\omega$$

Analogous to $p=mv$.

The ***kinetic energy*** (E_k) associated with the rotating mass is given by,

$$E_k = I\omega^2/2 = L^2/(2I)$$

Analogous to $E_k = mv^2/2 = p^2/2m$.

In general for a three-dimensional object, its total angular momentum can be resolved into its components about the x, y, z axes.

$$L_{total} = L_x + L_y + L_z$$

The component rotational angular momenta are given by the equations,

$$L_x = I_x\omega_x, \quad L_y = I_y\omega_y, \quad L_z = I_z\omega_z$$

I_x ~ the momentum of inertia about the x axis

ω_x ~ the component of angular velocity about x axis

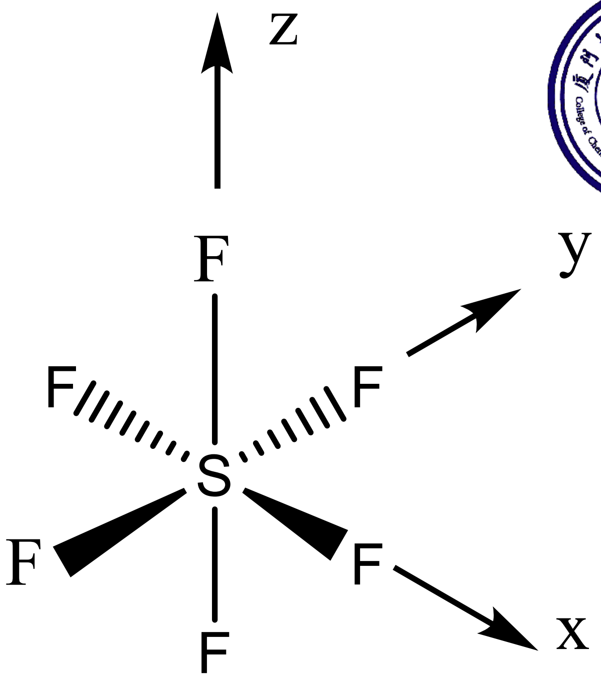
- Thus a molecule has three principal moments of inertia, one about each axis.
- For a rotating molecule, the x, y and z axes are chosen by a set of conventions. For example, the z-axis is chosen to be *the highest order of rotational symmetry*.

e.g., **SF_6**

- Moment of inertia about each axis is the same:

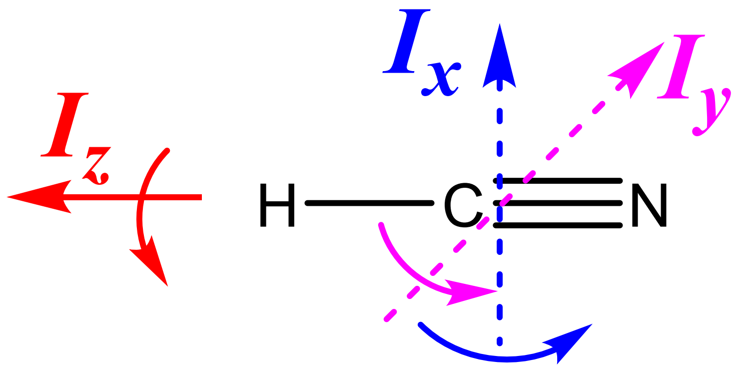
$$I_x = I_y = I_z$$

- Such a molecule is classified as a '***spherical top***'.

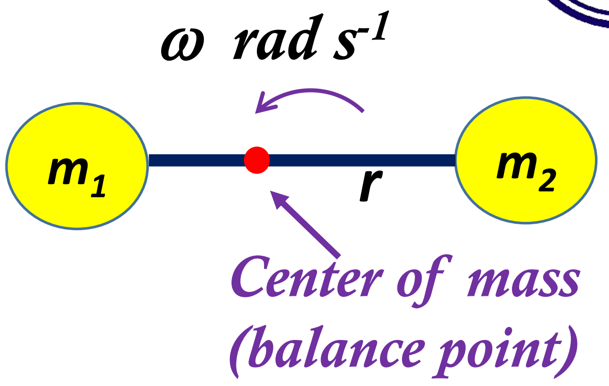


e.g., **H-C≡N**

- Linear molecule, bond axis as *z*-axis!
- Moment of inertia about *z* axis, I_z, is negligible.
- $I_x = I_y$



The rigid rotor model for a rotating molecule



A simple rotating diatomic molecule may be model by a ***rigid rotor*** consisting of two masses.

The ***moment of inertia*** for such a system is given by:

$I = \mu r^2$, $\mu = m_1m_2/(m_1+m_2)$ ~ ***reduced mass***

Ex.7

Solving the Schrödinger equation for the rigid rotor gives an expression for the energy it may possess: $E_J = BJ(J+1)$, J *(rotational quantum number)* $= 0,1,2,3,\ldots$

$$(\text{Note: } E = L^2(2I)^{-1} \;\&\; L^2 = \hbar^2 J(J+1) \quad)$$

B is the ***rotational constant*** for a particular rotor given by:

$$B = \hbar^2/(2I) \quad (\text{joules}) \xrightarrow{B = h\tilde{c}\tilde{B}} \tilde{B}\ (\text{in cm}^{-1}) = \frac{h}{8\pi^2\tilde{c}I}$$

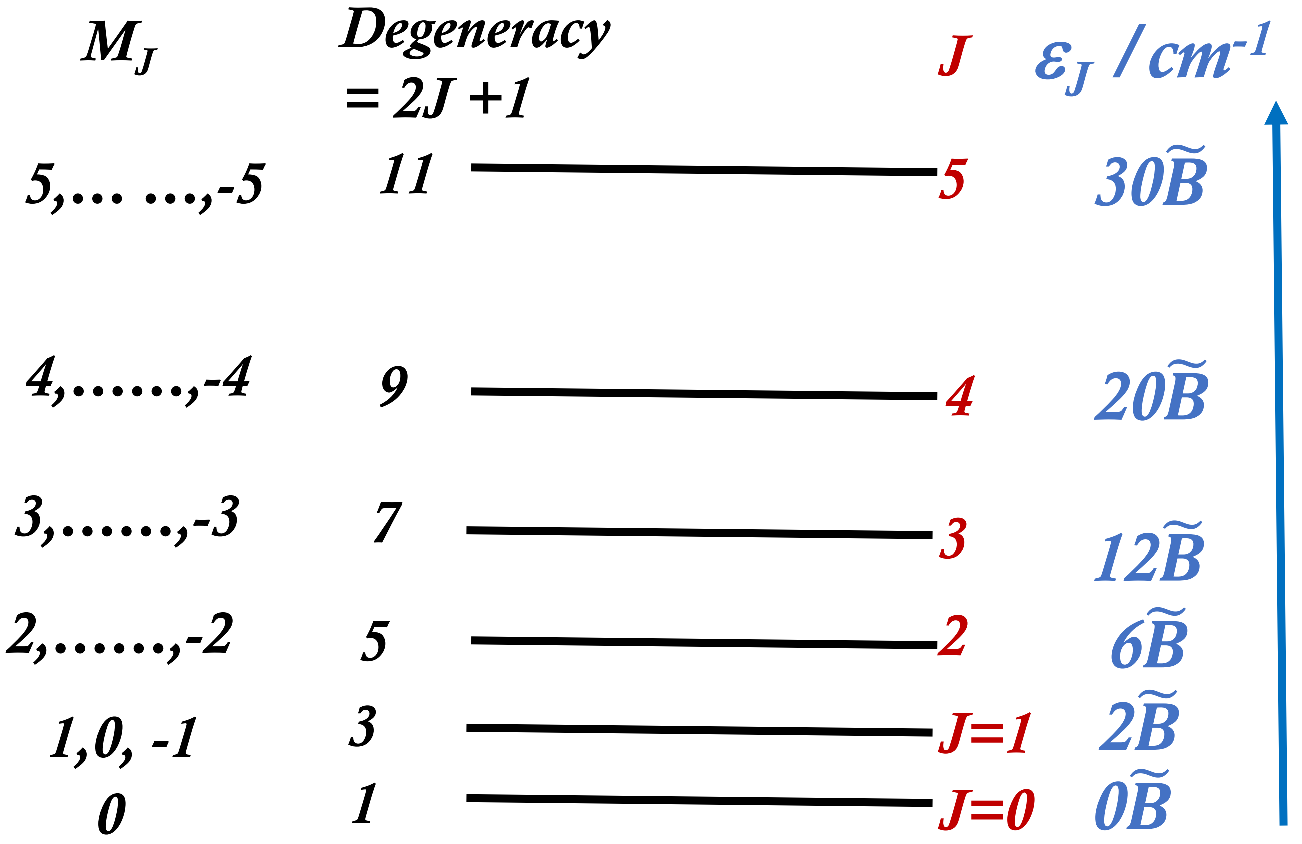
Ex.9-12

Energy levels for a rigid rotor

The energy levels for the rigid rotor in wavenumbers are given by:

$$\varepsilon_J = \tilde{B}J(J+1) \qquad J = 0,1,2,3,\ldots$$

Hence the spacing between adjacent rotational energy levels increases with ***J***.



M_J	Degeneracy $= 2J+1$	J	ε_J / cm^{-1}
5,… …,-5	11	5	$30\tilde{B}$
4,……,-4	9	4	$20\tilde{B}$
3,……,-3	7	3	$12\tilde{B}$
2,……,-2	5	2	$6\tilde{B}$
1,0, -1	3	J=1	$2\tilde{B}$
0	1	J=0	$0\tilde{B}$

- In the absence of an external field, each of the rotational energy levels has a degeneracy of ***(2J + 1)*** with the different sub-levels being distinguished by a quantum number M_J which takes values from ***+J*** to ***–J***.
- ***J*** defines the number and the magnitude of angular momentum the rotor possesses, M_J defines how it is oriented.

Magnitude and direction of angular momentum

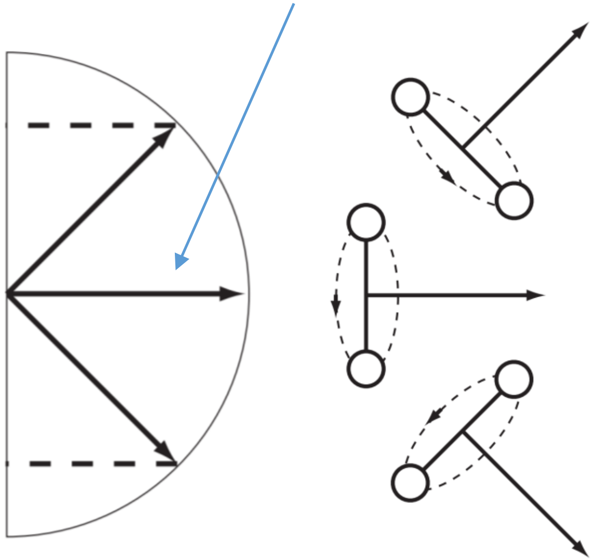
- Energy for the rotor = kinetic energy only = $\frac{1}{2}I\omega^2 = L^2/2I$

but $E = \hbar^2 J(J+1)/2I$ → $L^2 = \hbar^2 J(J+1)$ → $|L| = \sqrt{J(J+1)}\hbar$

- The value of M_J defines the component of the angular momentum along a given reference axis, e.g., z axis with $L_z = M_J\hbar$.

For J =1:

Unit in ħ



$|L| = \sqrt{2}\hbar$

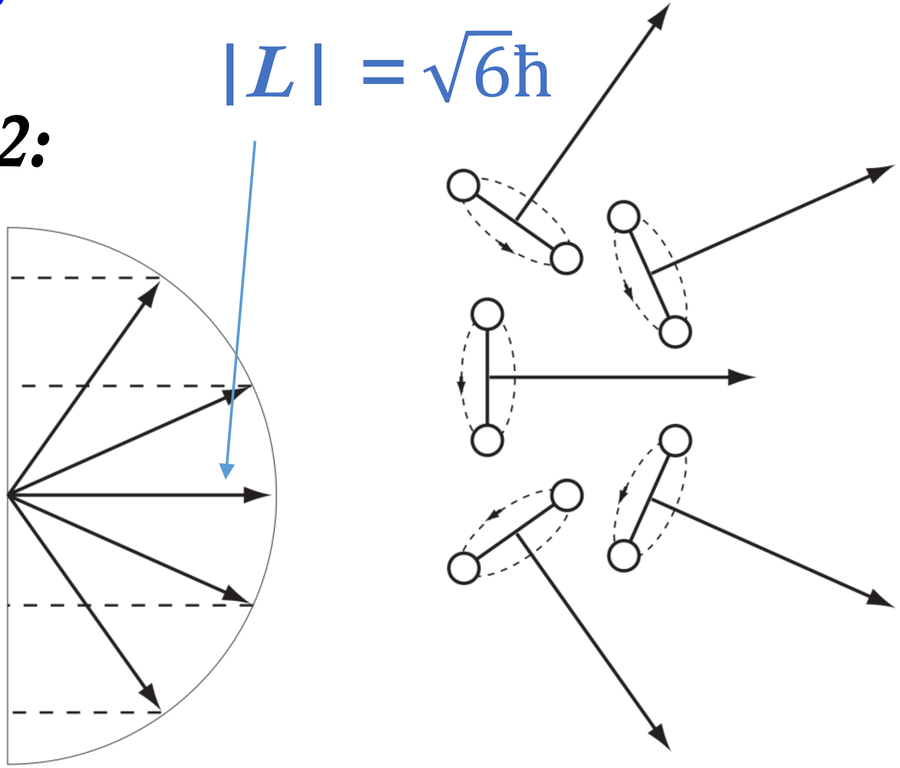
$M_J = +1$

$M_J = 0$

$M_J = -1$

For J =2:

Unit in ħ



$|L| = \sqrt{6}\hbar$

$M_J = +2$

$M_J = +1$

$M_J = 0$

$M_J = -1$

$M_J = -2$

Populations of the different energy levels

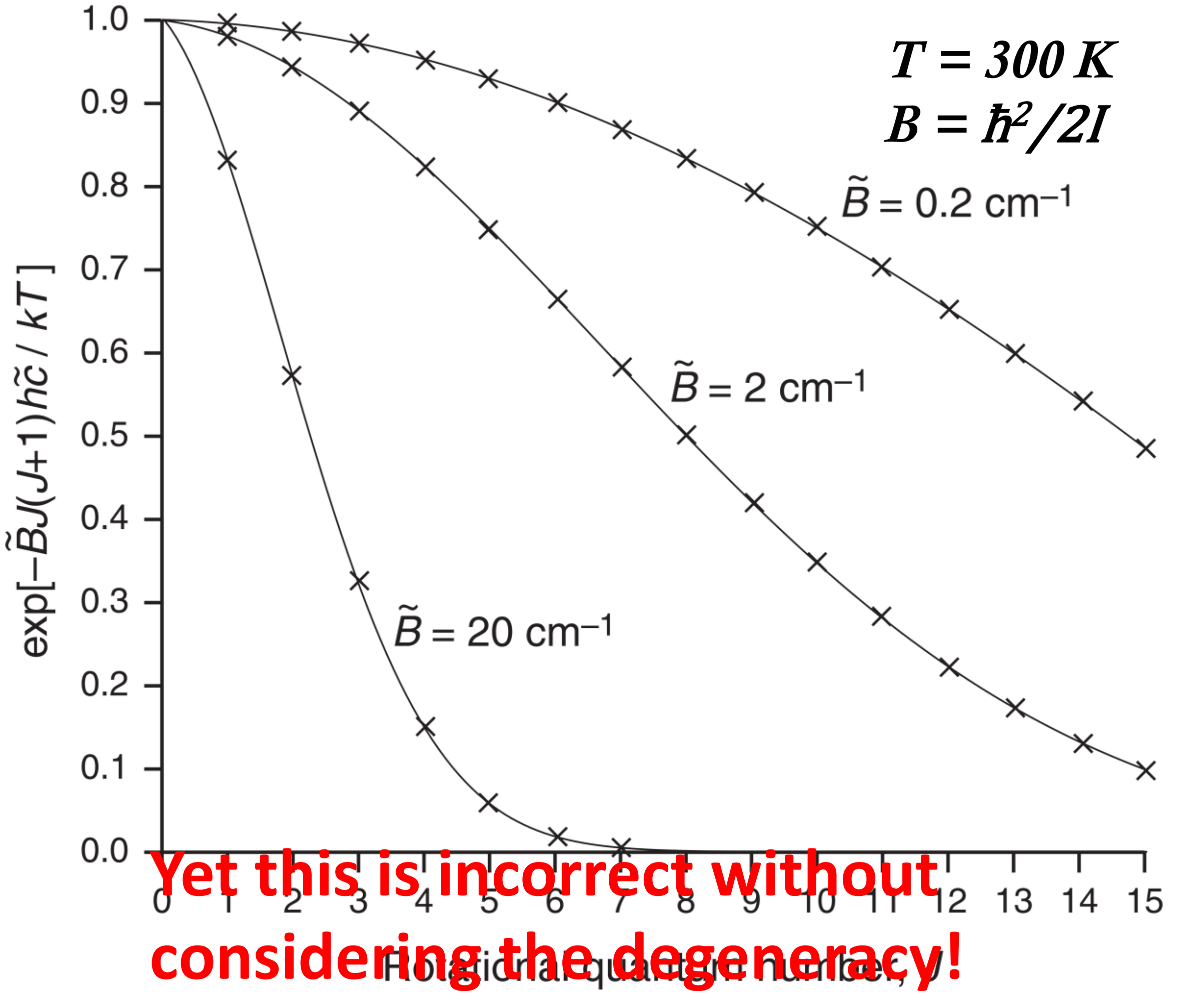
- Rotational energy levels are close enough in energy that many are occupied at R.T., *i.e.* a given sample will have molecules rotating at various different frequencies.

- The populations of the different rotational energy levels are given by the ***Boltzmann distribution***.

- The ratio of N_J, the population of the Jth level, to N_0, the population of the ground state ($J = 0$) is given by:

$$N_J/N_0 = e^{-\Delta E/kT} \quad (\Delta E = E_J) \ ?$$

$$\rightarrow \ N_J/N_0 = \exp\left(-\frac{h\tilde{c}\tilde{B}J(J+1)}{kT}\right)$$



***T* = 300 K**

$B = \hbar^2/2I$

Yet this is incorrect without considering the degeneracy!

Effects of the degeneracy of energy levels

- Taking the different degeneracies (i.e., *2J +1*) of the energy levels into account, the populations of the different energy levels is given by:

population ∝ $(2J+1)\exp(-E_J/kT)$

→ $\partial[(2J+1)\exp(-E_J/kT)]/\partial J = 0$

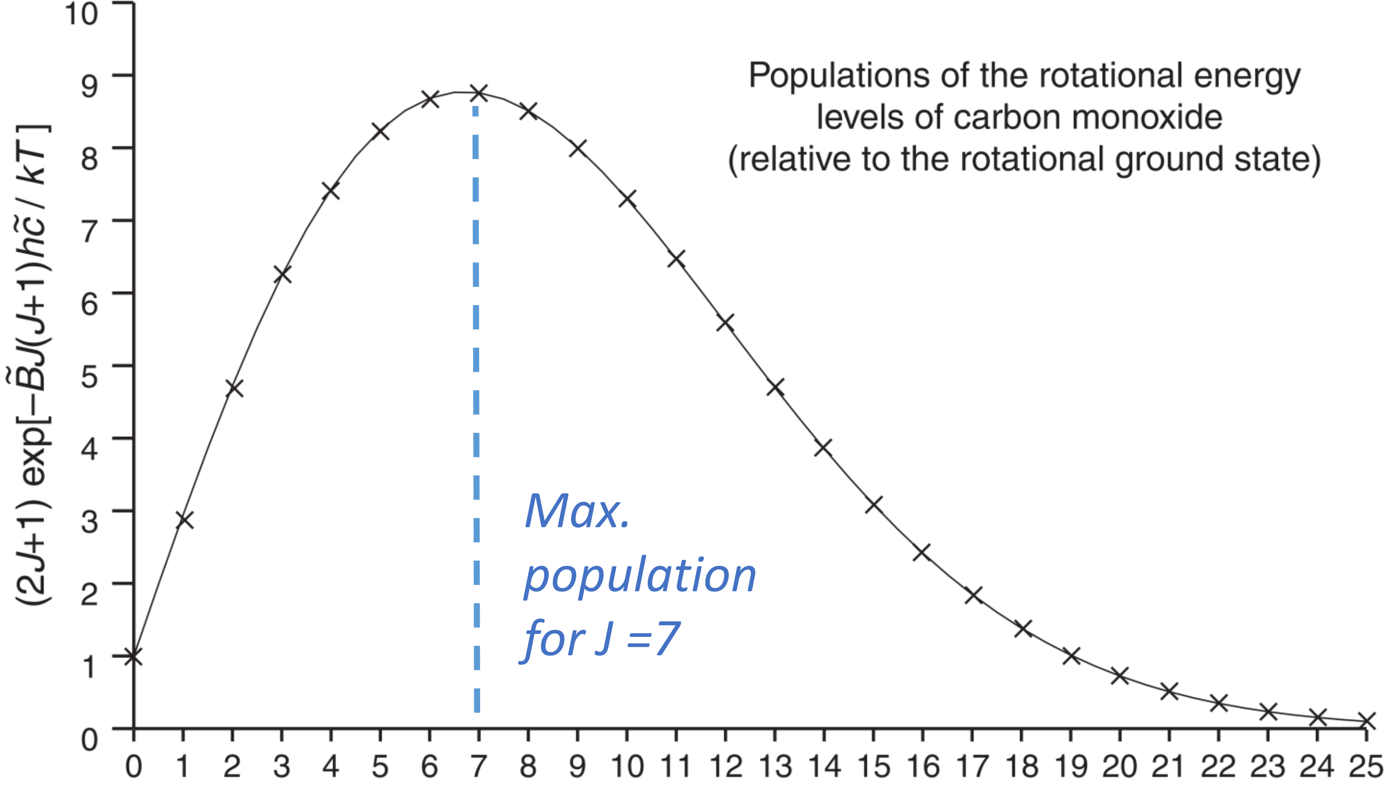
→ J_{max}

→ $N_J/N_0 = (2J+1)\exp\left(-\dfrac{h\tilde{c}\tilde{B}J(J+1)}{kT}\right)$

- Overall the population of the different levels rises to a maximum and then decreases.
- The value of ***J*** for the energy level with the maximum population, denoted J_{max}, may be found to be:

$$J_{max} \approx \sqrt{\frac{kT}{2h\tilde{c}\tilde{B}}} - \frac{1}{2}$$

Ex.13


Populations of the rotational energy levels of carbon monoxide (relative to the rotational ground state)

Max. population for *J* =7

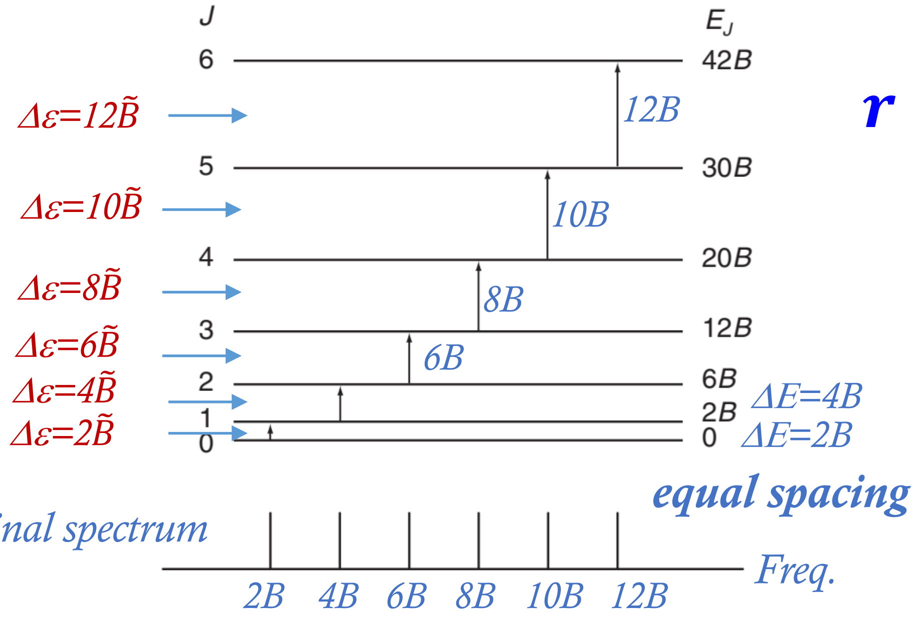
Transition between rotational levels

Ex.8

Molecules can be promoted from one rotational energy level to the next with the absorption of a photon but there are certain restrictions. For the rigid diatomic rotor the ***selection rules*** are:

1. The molecule must possess ***a permanent dipole moment*** to absorb EM radiation.
2. During the transition J must change by **±1** only (*i.e.* $\Delta J = \pm 1$). $\varepsilon_J = \tilde{B}J(J+1)$, $J = 0,1,2,3,\ldots$
3. There are also restrictions on ΔM_J but these are less important.

Allowed transitions

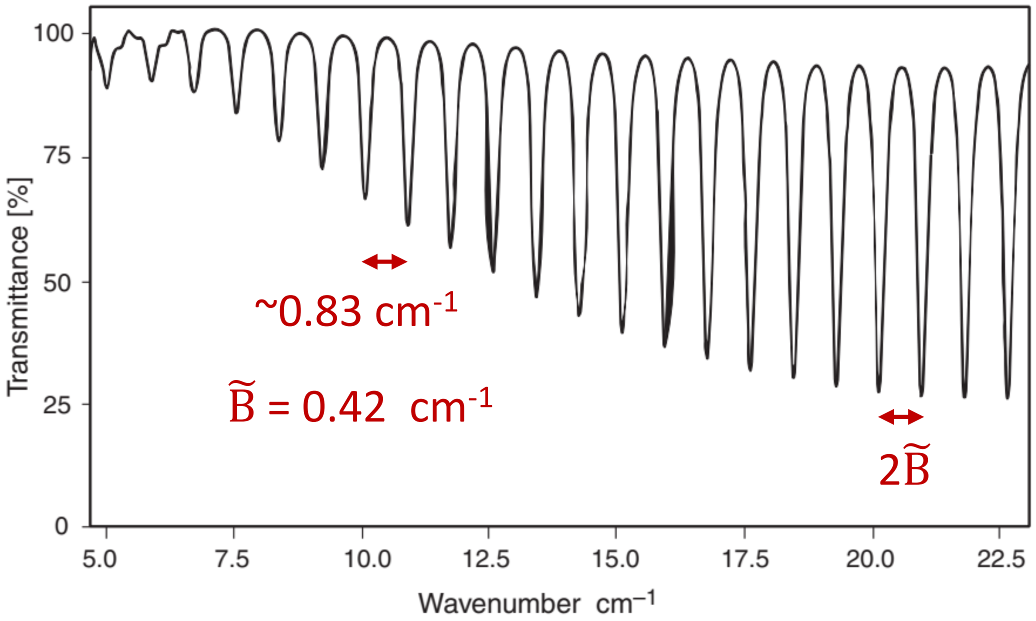


equal spacing of lines !

For a diatomic rotor

$$r = \sqrt{\frac{h}{8\pi^2 \tilde{c}\tilde{B}\mu}}$$

The rotational spectrum for N_2O



Intensities of the spectrum lines

- The relative intensities of the peaks depend on the populations of the energy levels.
- The intensities of the peaks in the spectrum first rise with increasing ***J*** and then fall off again.
- The relative intensities of the peaks in the spectrum are not determined *solely* by the populations of the energy levels.
- For example, when the higher rotational energy levels are occupied, *emission processes* (both stimulated and spontaneous) need to be taken into account as well as *absorption*.
- As a result, whilst the maximum population for a rotational level for CO is ***J* =7**, the most intense peak actually is due to the transition **J = 12 → 13**.

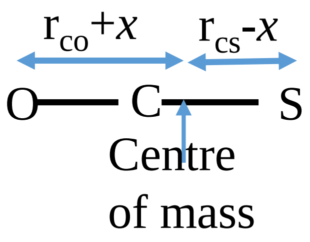
Polyatomic molecules

◆For linear polyatomic molecules, the spectra have the same form for the diatomic molecules.

- The peaks are still separated by ***2B***, from which the *moment of inertia* can be deduced!
- ×→ bond lengths ! More info. needed.

For example: carbon oxysulphide, **O=C=S**.

$r_{co} < r_{cs}$



The molecule balances on its centre of mass. →

$$m_C x + m_O(r_{CO} + x) = m_S(r_{CS} - x)$$

The moment of inertia is the sum of the moments of inertia of each atom rotating about the centre of mass. It is given by:

$$I = m_C x^2 + m_O(r_{CO} + x)^2 + m_S(r_{CS} - x)^2$$

Eliminating ***x*** from both equations gives,

$$I = m_O r^2_{CO} + m_S r^2_{CS} - (m_O r_{CO} - m_S r_{CS})^2 / M \qquad (M = m_S + m_C + m_O)$$

While ***I*** can be deduced from ***B***, both r_{CO} and r_{CS} are to be determined! Yet need more info.

Isotopes substitution

Thus in the above example, if we measured $\boldsymbol{B}$ for ^{18}O=C=S and calculated the new moment of inertia, $\boldsymbol{I'}$, we would have a second equation where the only unknowns were the two bond lengths, r_{CO} and r_{CS}, which we assume are unchanged.

$$I' = m_{18O}r^2_{CO} + m_S r^2_{CS} - (m_{18O}r_{CO} - m_S r_{CS})^2/M \qquad (M = m_S + m_C + m_{18O})$$

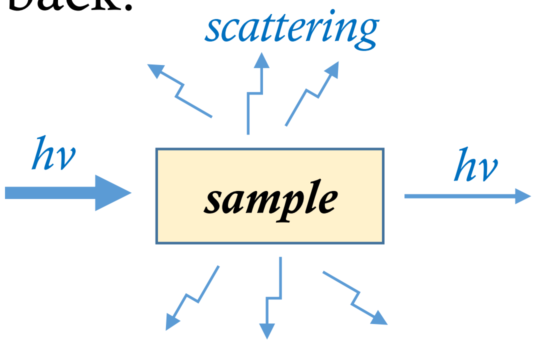
Solving the equations for $\boldsymbol{I}$ and $\boldsymbol{I'}$ allow the bond lengths r_{CO} and r_{CS} to be determined.

4 Rotational Raman spectroscopy

◆In order for a rotor to absorb electromagnetic radiation, it must have a dipole moment. So, for example, whilst CO will absorb in the microwave region of the spectrum ***N_2 will not***.

◆ ***Raman spectroscopy*** can be used to circumvent the aforementioned drawback.

◆If light is passed through a transparent substance, most passes straight through, unchanged, but some is scattered at different angles.

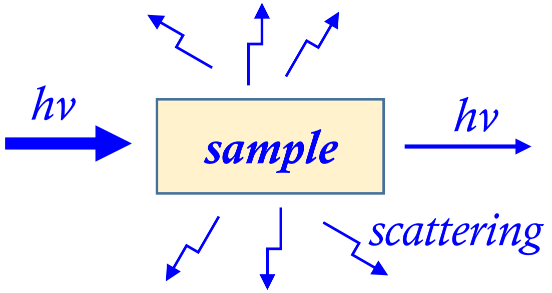


➢Most of the scatter light is ***Rayleigh scattering***, having the same freq. as the incident light.

➢Some of the scattered light has frequencies greater or less than that of the incident light.

◆ ***How to understand and to further make use of such phenomena?***

4 Rotational Raman spectroscopy



X_J + *Incident laser light (freq.)* $\longrightarrow$ $[X_J]$

Molecule in rotational level J

No explicit transition but inducing a dipole!

virtual state

$X_{higher\ J}$ + *lower freq. light (Stokes)*

X_J + *same freq. light (Rayleigh)*

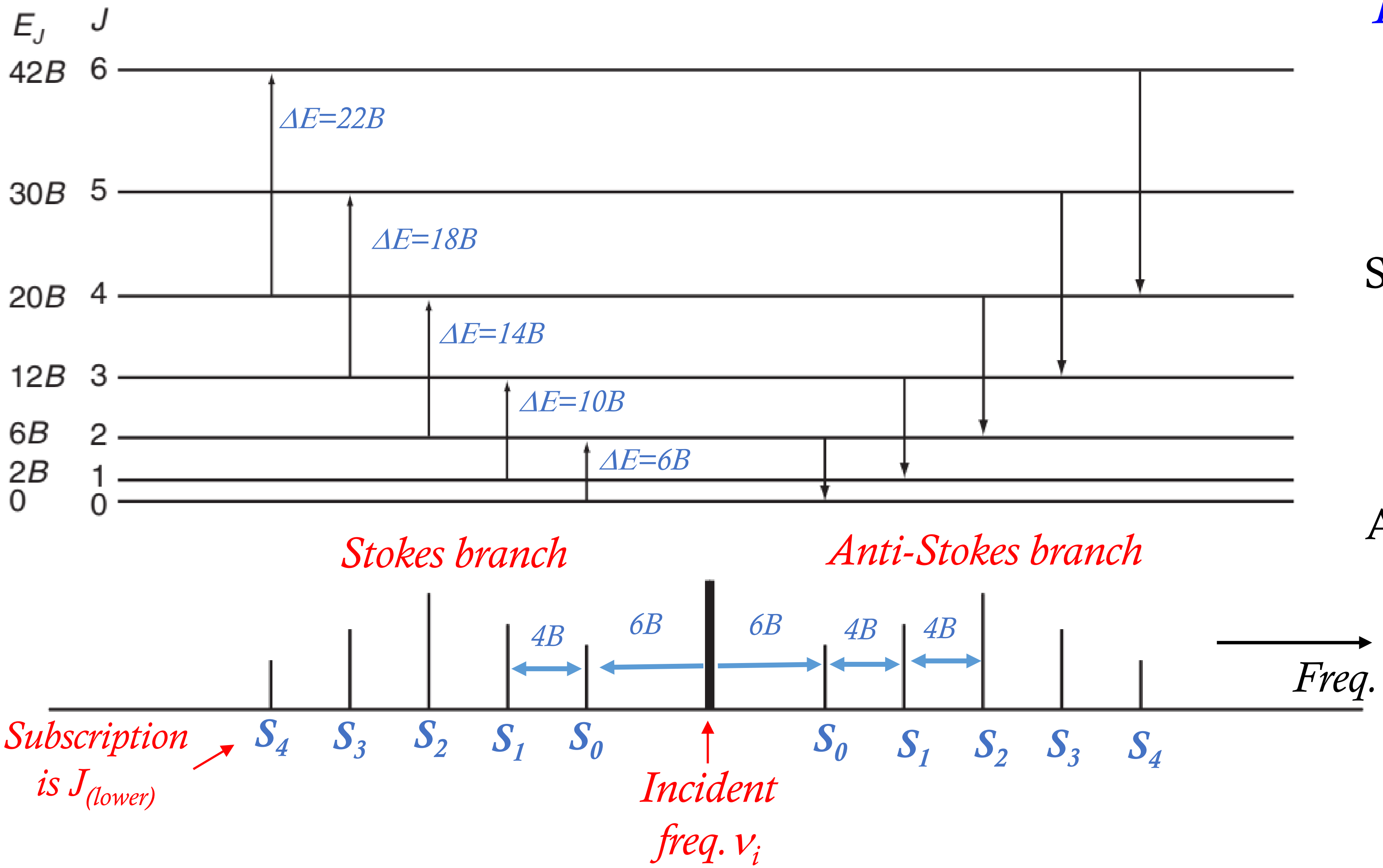
$X_{lower\ J}$ + *higher freq. light (anti-Stokes)*

The *selection rules* for a linear molecule in *Raman spectroscopy* are: $\Delta J = 0, +/-2$

Note: ΔJ is defined by convention as J(upper level) $-J$(lower level) and thus is always positive!

4 Rotational Raman spectroscopy

A schematic diagram for some allowed transitions and the resulting ***Raman spectrum***



Let $J = J_{lower}$ & $J_{upper} = J + 2$,

$$\Delta\varepsilon_J = \varepsilon_{Jupper} - \varepsilon_{Jlower}$$

$$= \tilde{B}(4J+6)\ cm^{-1}$$

Stokes lines appear at:

$$\nu_{incident} - \tilde{B}(4J+6)\ cm^{-1}$$

$$(J = 0,1,2,\dots)$$

Anti-Stokes lines appear at:

$$\nu_{incident} + \tilde{B}(4J+6)\ cm^{-1}$$

$$(J=0,1,2,\dots)$$

The frequencies of the transitions observed in Raman spectrum are given by:

$$\Delta\varepsilon_J = \varepsilon_{Jupper} - \varepsilon_{Jlower} = \tilde{B}J_{upper}(J_{upper}+1) - \tilde{B}J_{lower}(J_{lower}+1)$$

$$= \tilde{B}(4J+6)\ \ cm^{-1}$$

(Let $J_{lower} = J$,
then $J_{upper} = J+2$)

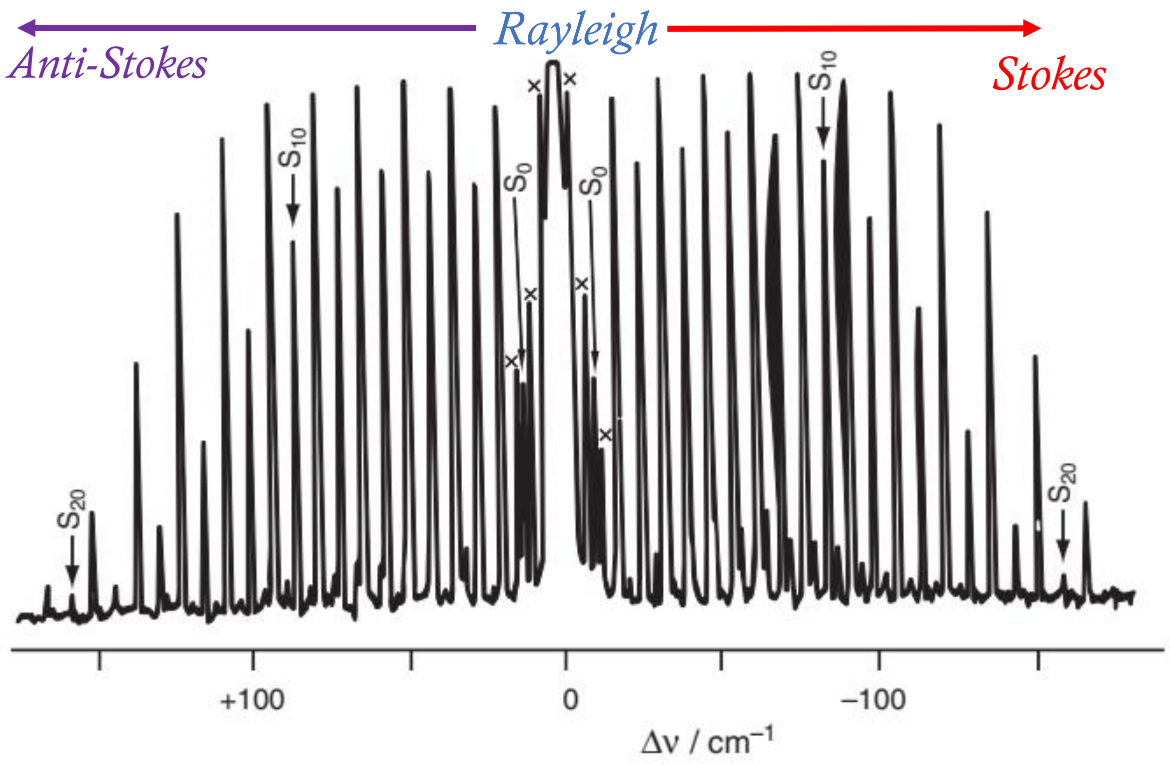
Stokes lines appear at:

$$\nu_{incident} - \tilde{B}(4J+6)\ \ cm^{-1}\ (J = 0,1,2,\ldots)$$

Anti-Stokes lines appear at:

$$\nu_{incident} + \tilde{B}(4J+6)\ \ cm^{-1}\ (J=0,1,2,\ldots)$$

The pattern of intensities will be discussed later.



Raman spectrum of $^{15}N_2$

Ex.14,15

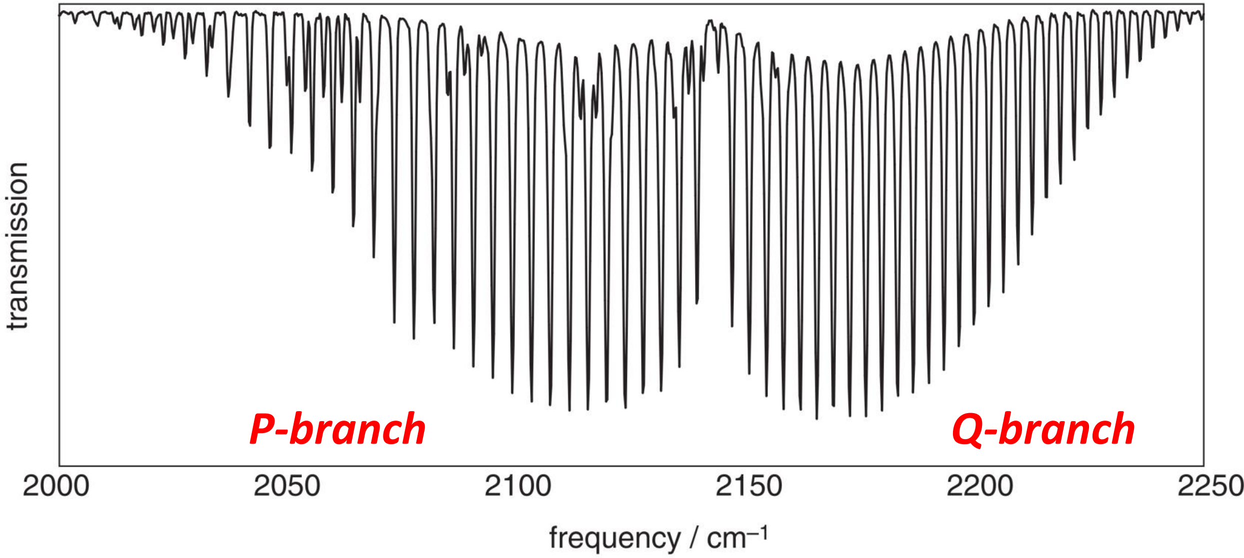
5 *The vibrating rotator*

Now we are able to understood the fine structure in the IR spectrum of CO.

- The peaks in the IR spectrum correspond to the same vibrational transition ($v\ 1 \leftarrow 0$);
- For each peak there is a different change in the rotational energy.
- The selection rules for a simultaneous change of both vibrational energy and rotational energy in a diatomic molecule are: $\Delta v = 0, \pm 1, \pm 2, \pm 3, \ldots$, *etc.* $\Delta J = \pm 1$.

- $\Delta v = 0$ ~ solely rotational transitions.
- $\Delta J = 0$ is impossible for a diatomic mol.!

Pure vibrational transition is absent in the spectrum. Each vibrational change must be accompanied by change in rotational energy!



Fine structures in IR spectrum

- The lines to the low frequency side of the band origin are designated the ***P*-branch** whilst those to the high frequency side are designated the ***R*-branch**.

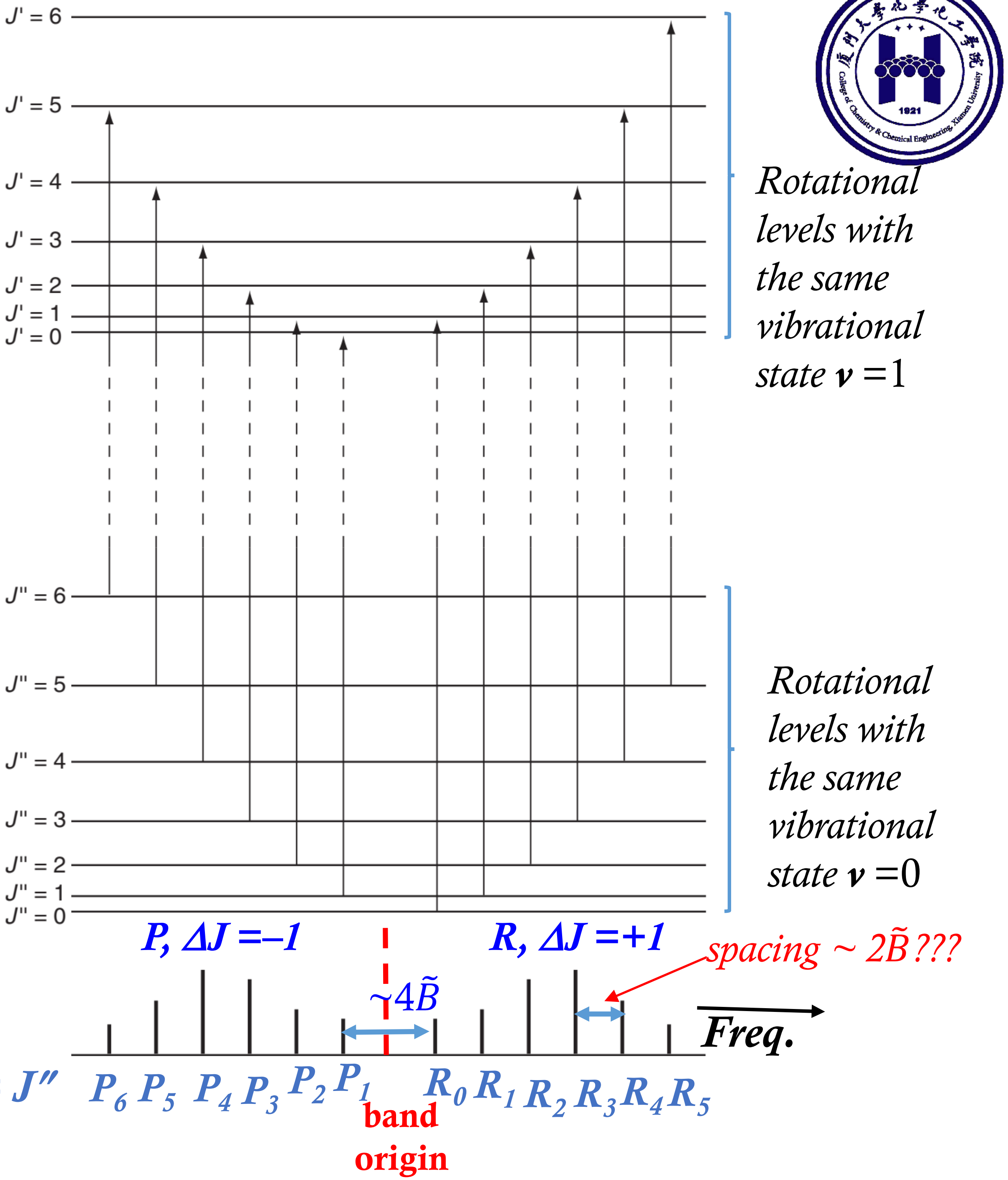
Lines arising from

$$\Delta J = -2,\ \ -1,\ \ 0,\ \ +1,\ \ +2$$

called **O** **P** **Q** **R** **S** branch

Seen in Raman

- Only the **P** and **R** branches are seen in the vibrational spectra of diatomic molecules, but others may appear in the spectra of other molecules.



Subscript $J_{lower} = J''$

Using the BO approximation, the energy of the vibrating-rotor is simply the sum of its component parts: $E_{\text{total}} = E_{\text{vibrational}} + E_{\text{rotational}}$

$$= (v + \tfrac{1}{2})\tilde{\omega} - (v + \tfrac{1}{2})^2\tilde{\omega}x_e + \tilde{B}J(J+1)$$

- However, the rotational constant ***B*** is not exactly the same in the $v = 0$ state and the $v = 1$ state.
- The more the molecule vibrates, the greater average bond length $<r>$ becomes. (the larger I) !
- As $I \propto <r>^2$ & $B \propto 1/I$ → The smaller ***B*** for the higher v !
- Define B_0 for $v=0$ and B_1 for $v=1$. Then $B_0 > B_1$.
- The spacings in the spectrum are not even; the lines in the ***R***-branch tend to ***crowd*** together with *increasing freq*. and the lines in the ***P***-branch tend to become more ***widely spaced*** with *decreasing freq.* (plz confirm this statement!)
- The energy for any observable transition:

$$\begin{aligned}\varepsilon_{upper} - \varepsilon_{lower} &= [(1 + \tfrac{1}{2})\tilde{\omega} - (1 + \tfrac{1}{2})^2\tilde{\omega}x_e + \tilde{B}_1 J'(J'+1)] \qquad (\tilde{\omega}_0 = \tilde{\omega} - 2\tilde{\omega}x_e \sim \text{band origin}) \\ &\quad - [(0 + \tfrac{1}{2})\tilde{\omega} - (0 + \tfrac{1}{2})^2\tilde{\omega}x_e + \tilde{B}_0 J''(J''+1)] = \tilde{\omega}_0 + \tilde{B}_1 J'(J'+1) - \tilde{B}_0 J''(J''+1)\end{aligned}$$

How to derive B_1 and B_0 from a IR spectrum

The energy for any observable transition is

$$\varepsilon_{upper} - \varepsilon_{lower} = \tilde{\omega}_0 + \tilde{B}_1 J'(J'+1) - \tilde{B}_0 J''(J''+1)$$

$$(\tilde{\omega}_0 = \tilde{\omega} - 2\tilde{\omega}x_e \sim \text{band origin})$$

➢To determine B_1, we consider two transitions with the same J'' value.

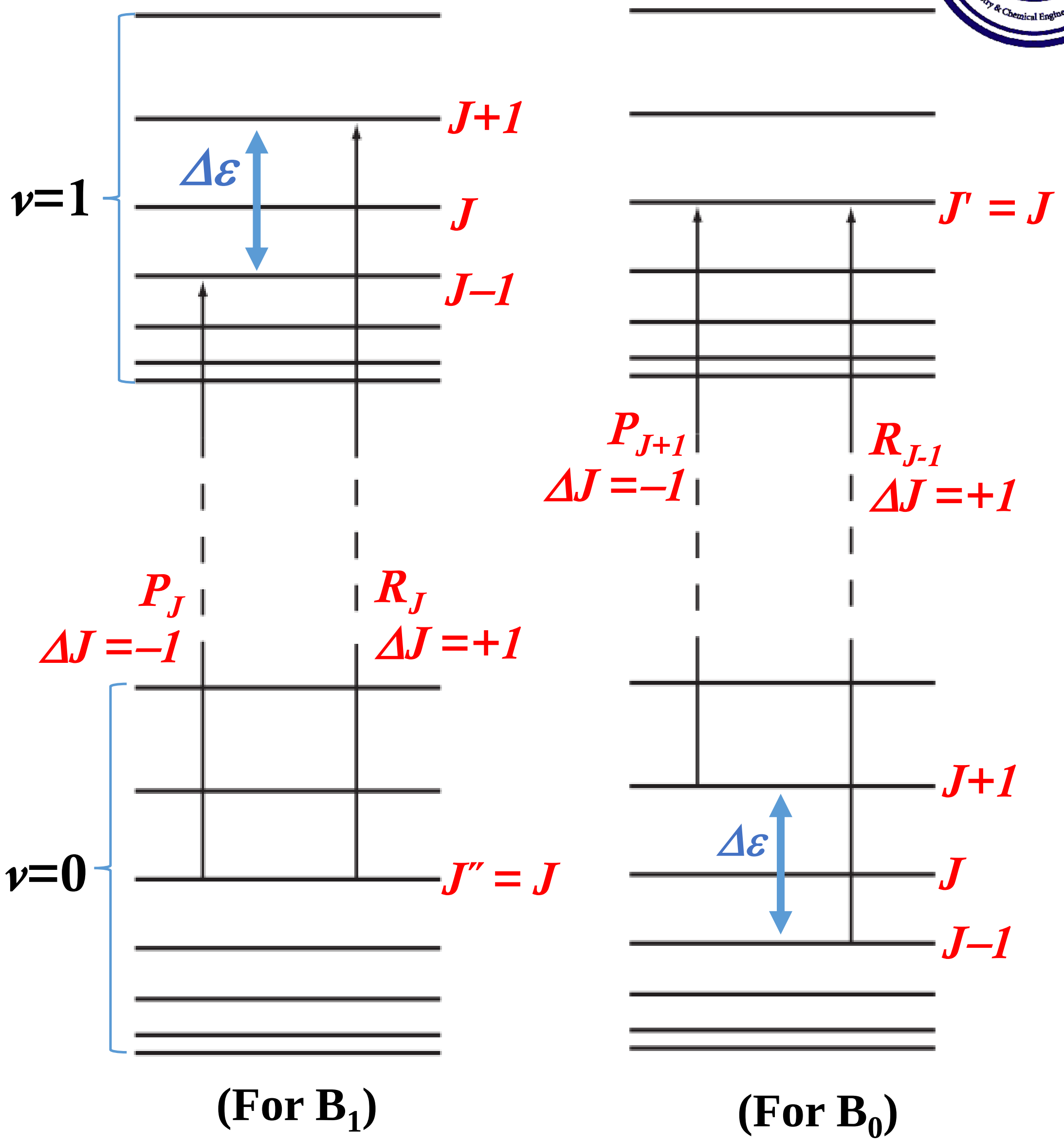
$$\Delta\varepsilon = \tilde{R}_J - \tilde{P}_J = 2(2J+1)\tilde{B}_1$$

$$\text{e.g., } R_3 - P_3 = 14\,\tilde{B}_1$$

➢To determine B_0, we choose two transitions with the same J' value.

$$\Delta\varepsilon = \tilde{R}_{J-1} - \tilde{P}_{J+1} = 2(2J+1)\tilde{B}_0$$

$$\text{e.g., } R_1 - P_3 = 10\,\tilde{B}_0$$



Ex.16

- Once B_1 and B_0 have been determined, the moments of inertia I (= $\hbar^2(2B)^{-1}$) and hence bond lengths ($r=(I/\mu)^{1/2}$) in the ***upper*** and ***lower*** vibrational levels, r_1 and r_0, may also be found.

- The rotational constant for a molecule in a given vibrational energy level, B_v, varies with the vibrational quantum number, v, according to the following equation:

$$\tilde{B}_v = \tilde{B}_e - \tilde{\alpha}(v+\tfrac{1}{2}) \qquad \rightarrow \tilde{\alpha} = \tilde{B}_0 - \tilde{B}_1$$

Hypothetic rotational constant for the molecule with its equilibrium bond length at the bottom of the potential energy curve.

a small positive number with the same units as ***B***.

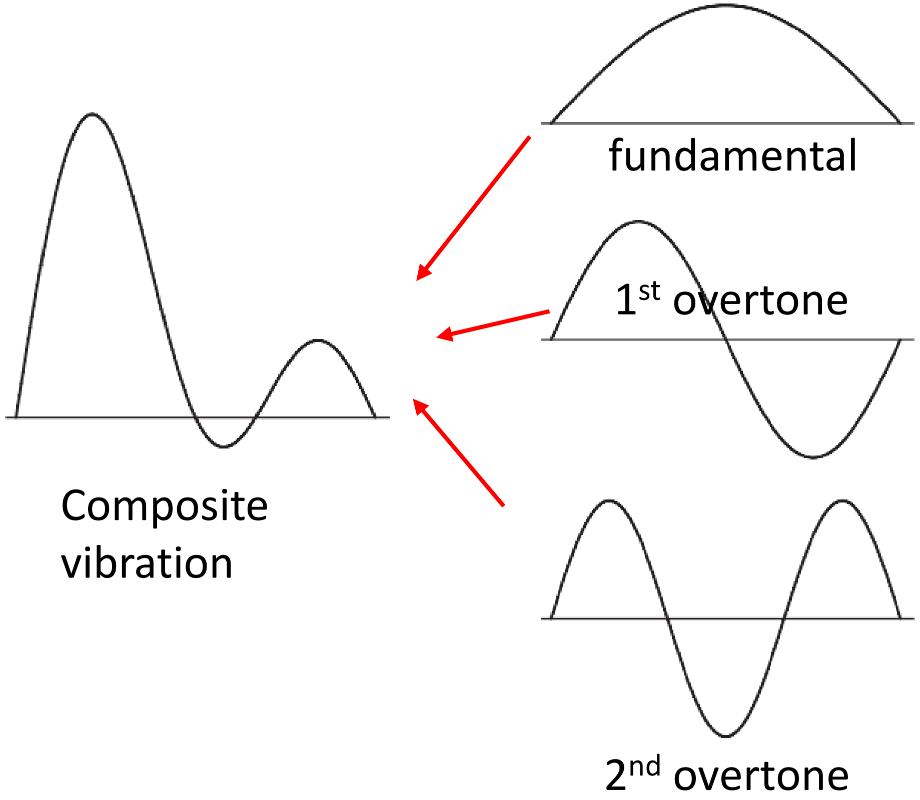
- Using this expression, once B_e has been found from B_0 and B_1, the equilibrium bond length, r_e, (corresponding to the bond length at the minimum of the potential energy curve), may also be determined.

6. Normal modes and degrees of freedom

- Imagine a simple string vibrating, such as a guitar string. Usually, the vibration would be rather more complex, but nonetheless it could still be broken down into combinations from the fundamental vibration and various contributions from the overtones.

- Similarly, whilst the exact way in which a molecule may be vibrating may be rather complicated, it too could be broken down into a number of more simple vibrational modes.

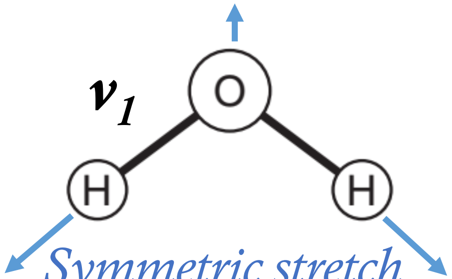
- The molecule (with the exception of a diatomic) has more than one fundamental mode of vibration and, as we have already seen, the overtones in the spectra of molecules are usually less significant.



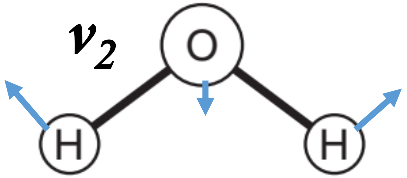
Degrees of freedom

A ***N***-atom molecule has ***3N*** *degrees of freedom, including* ***3*** *translational ones,* ***2*** *(for linear molecule）or* ***3*** *(for non-linear one) rotational ones, and* ***3N-6*** *(for non-linear molecule) or* ***3N-5*** *(for linear molecule) normal modes of vibration.*

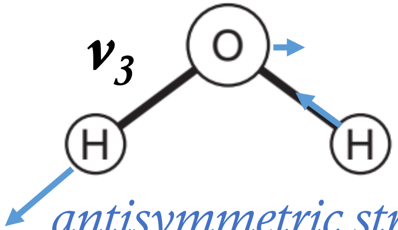
- A non-linear three-atom molecule (e.g., $\mathbf{H_2O}$) has ***3*** normal modes of vibration.



Symmetric stretch
3651.7 cm^{-1}



bend
1595.0 cm^{-1}

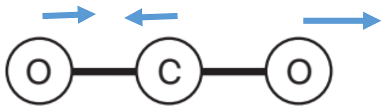


antisymmetric stretch
3755.8 cm^{-1}

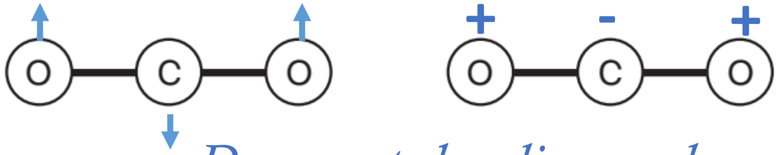
The order of the normal modes is based on the symmetries of the vibrations (This will be concerned later).

- A linear three-atom molecule (e.g., $\mathbf{CO_2}$) has ***4*** normal modes of vibration.

Symmetric stretch
$\nu_1 = 1330\ cm^{-1}$



Anti-symmetric stretch
$\nu_3 = 2349.3\ cm^{-1}$



Degenerate bending modes
$\nu_2 = 667.3\ cm^{-1}$

- For an acyclic molecule with ***N*** atoms, there is (***N-1***) bonds and so (***N-1***) stretching modes of vibration.

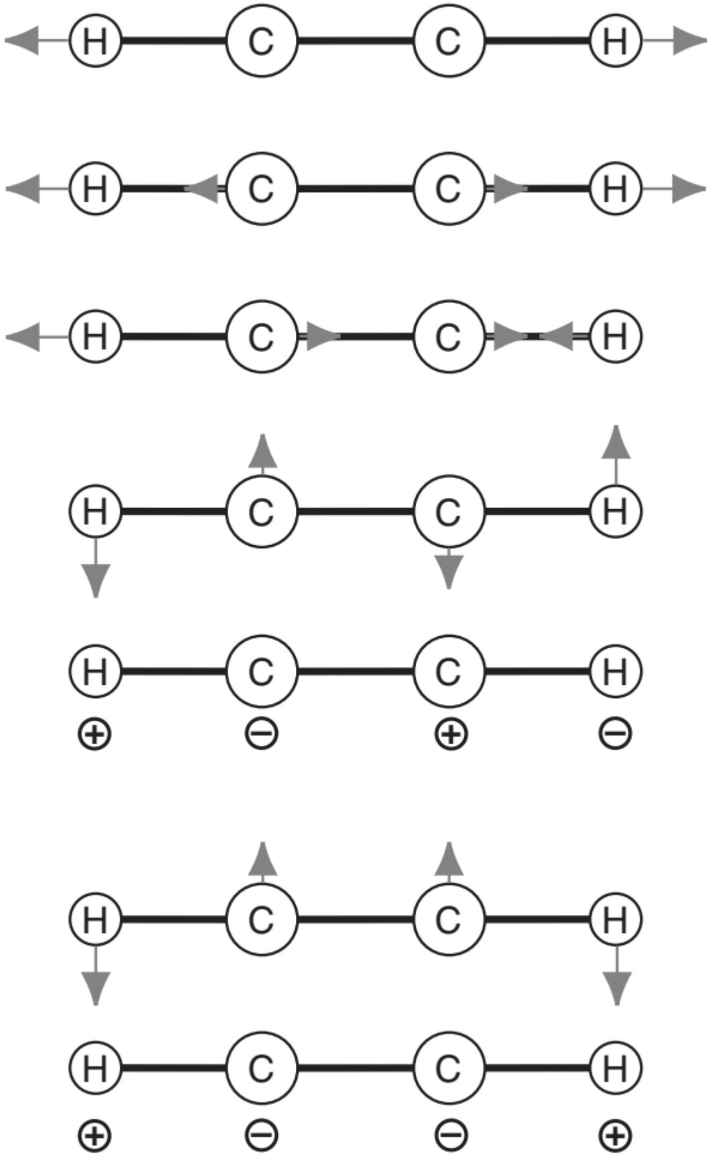
e.g., **C_2H_2**.

3N-5 = **7** normal modes, including

N-1 = **3** stretching modes

2N-4 = **4** bending modes

Ex.18



C-H symmetric stretch
$\nu_1 = 3374\ cm^{-1}$

C-C stretch
$\nu_2 = 1974\ cm^{-1}$

antisymmetric stretch
$\nu_3 = 3287\ cm^{-1}$

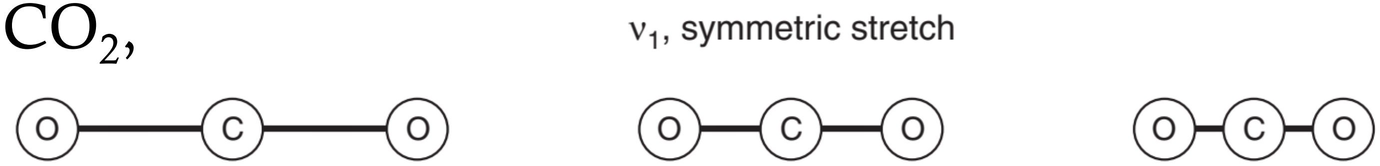
Degenerate trans bend
$\nu_4 = 615\ cm^{-1}$

Degenerate cis bend
$\nu_5 = 729\ cm^{-1}$

Perpendicular and parallel vibrations

- To be ***IR-active***, the dipole moment of the molecule must change during the vibration.

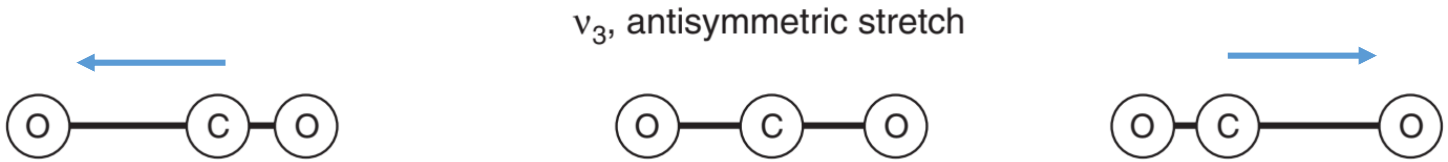
e.g., CO_2,



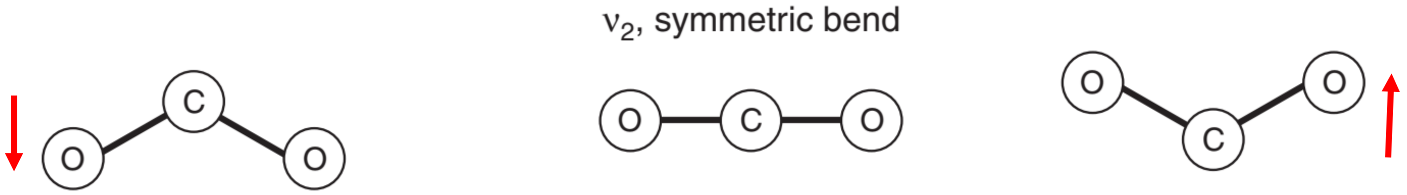
Never any dipole moment!

→ ***IR inactive***!

During the other vibrational modes, the change in the dipole moment may either be ***parallel*** to the principal axis or ***perpendicular*** to it.



No dipole



change in dipole moment parallel to the principal axis!

change in dipole moment perpendicular to the principal axis!

Q: Which normal modes of C_2H_2 can be observed in IR spectroscopy? **Ex. 17**

Perpendicular and parallel vibrations

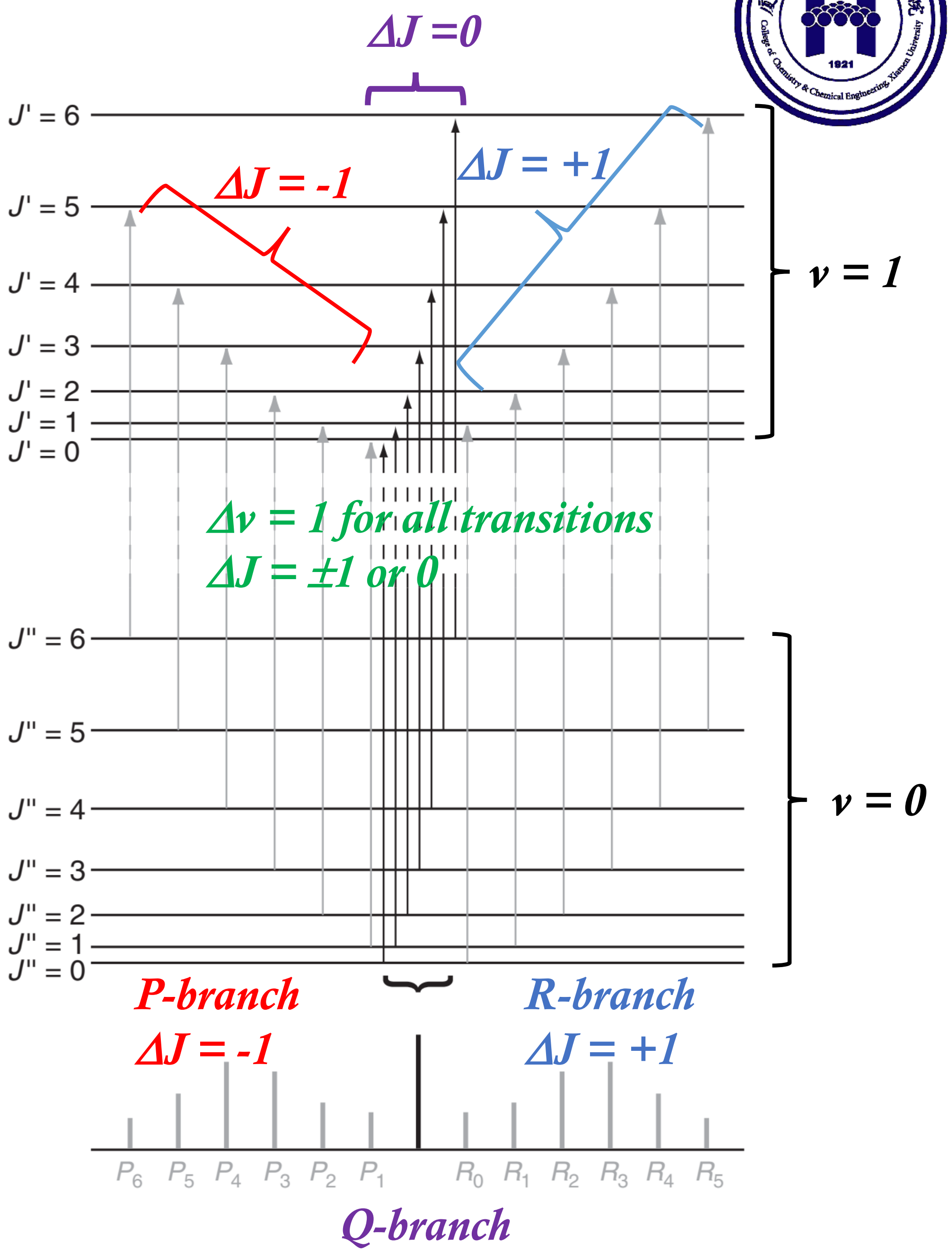
- ***The selection rules*** for a simultaneous vibration-rotation transition in a ***diatomic molecule*** (where the change in dipole moment is ***parallel to the principle axis***), are

  $\Delta v = \pm 1, \pm 2, \pm 3, \ldots$, etc. $\Delta J = \pm 1$ ($\Delta J \neq 0$)

  The selection rule ***ΔJ = – 1*** gives rise to the ***P-branch*** and ***ΔJ = + 1*** to the ***R*-branch**.

- These same selection rules hold for any linear molecule, but **only** for ***parallel*** vibrations.

- For vibrations where the dipole-moment change is ***perpendicular*** to the principle axis, the transition may occur with ***ΔJ = 0***, giving rise to a ***Q-branch*** in the spectrum.



The energy of the lines in the ***Q-branch*** are given by:

$$\varepsilon_{upper} - \varepsilon_{lower}$$

$$= [(1 + \tfrac{1}{2})\tilde{\omega} - (1 + \tfrac{1}{2})^2\tilde{\omega}x_e + \tilde{B}_1 J(J+1)]$$

$$- [(0 + \tfrac{1}{2})\tilde{\omega} - (0 + \tfrac{1}{2})^2\tilde{\omega}x_e + \tilde{B}_0 J(J+1)]$$

$$= \tilde{\omega} - 2\tilde{\omega}x_e + (\tilde{B}_1 - \tilde{B}_0)J(J+1)$$

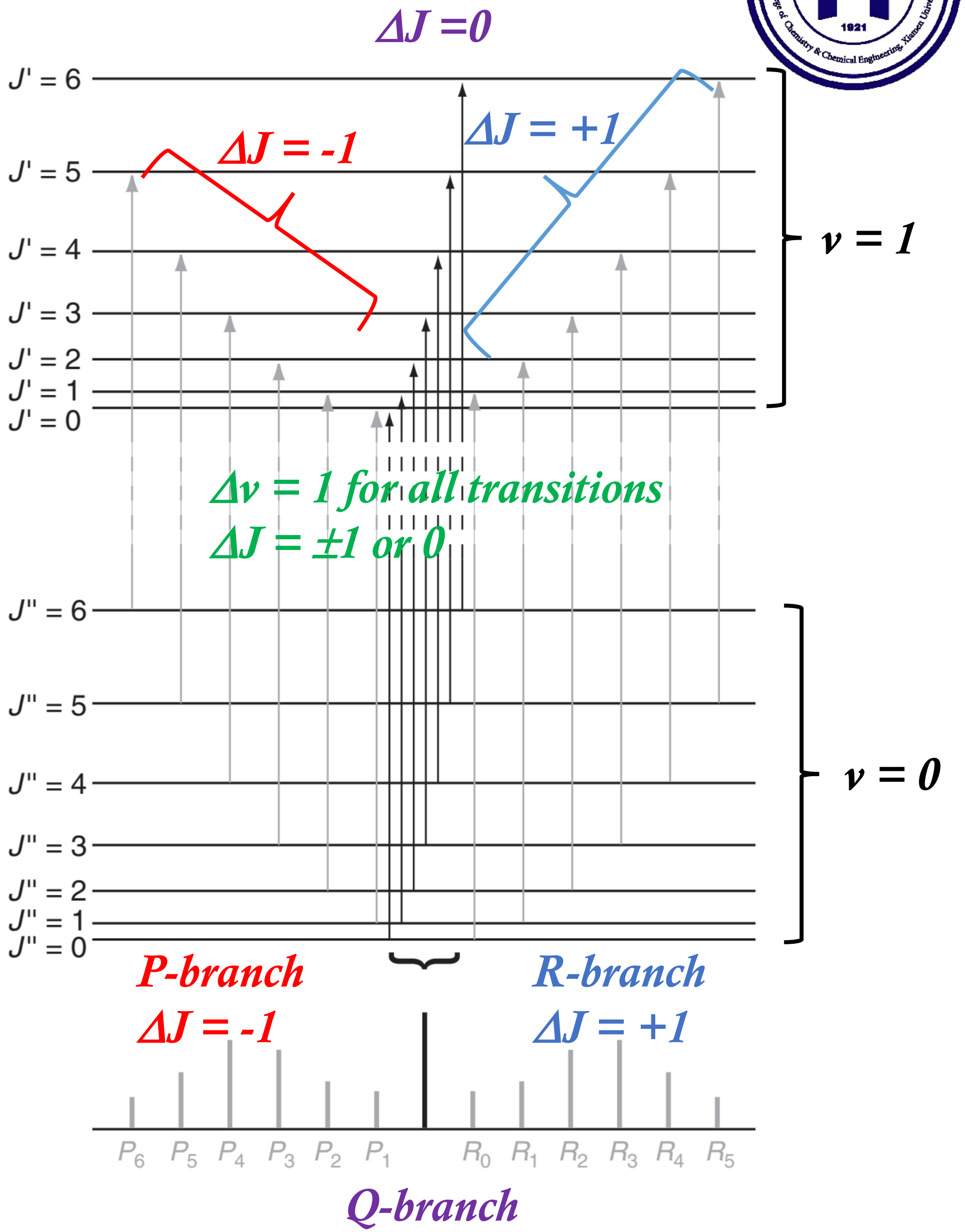
$$= \tilde{\omega}_0 + (\tilde{B}_1 - \tilde{B}_0)J(J+1)$$

$$\tilde{\omega}_0 = \tilde{\omega} - 2\tilde{\omega}x_e \sim \text{band origin}$$

$$(\tilde{B}_1 - \tilde{B}_0) \neq 0$$

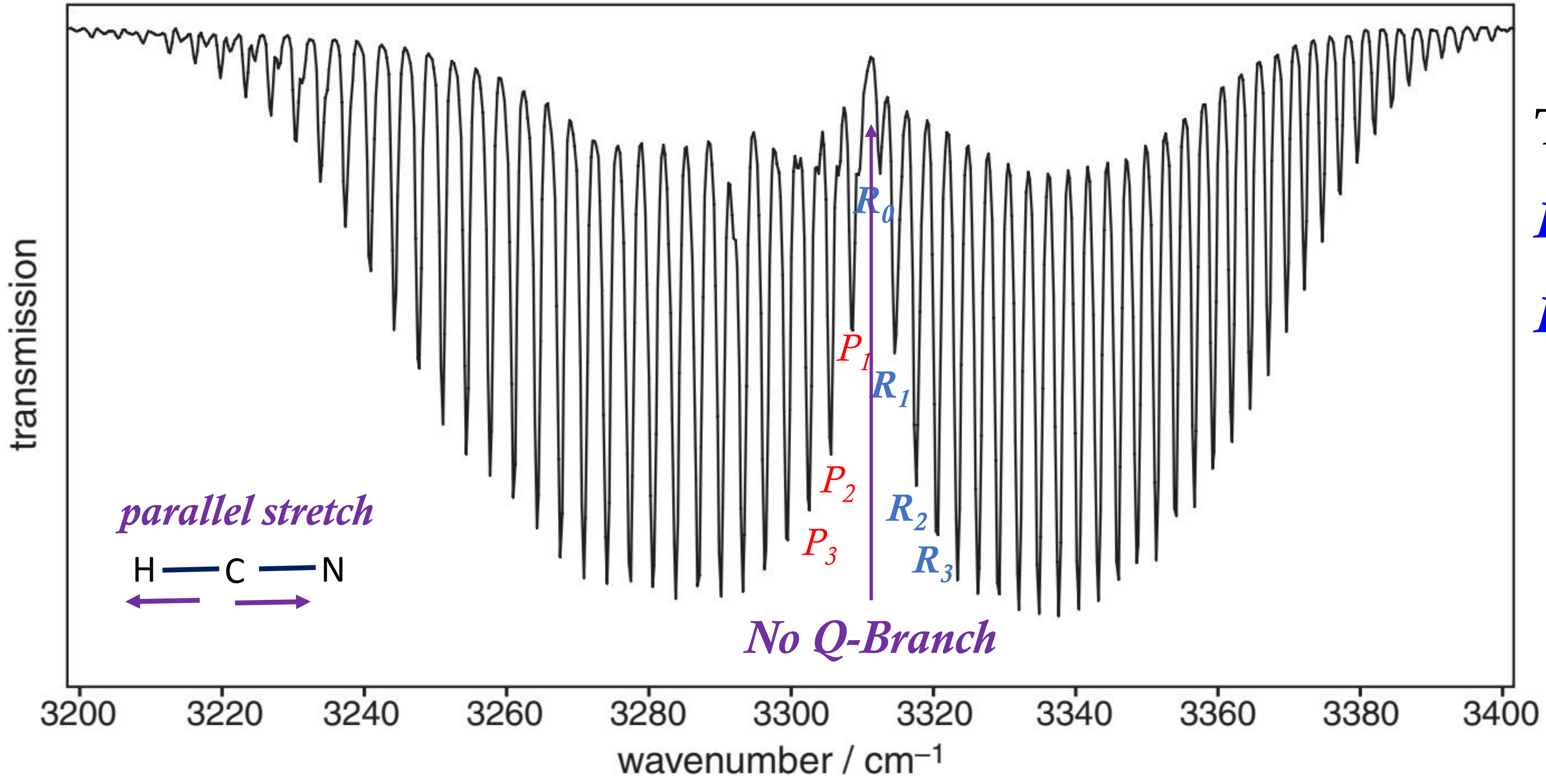
→ The lines are not coincident!

→ The ***Q-branch*** is broadened.



Perpendicular and parallel vibrations

- The parallel CH stretching mode for HCN is shown below.



The spacing between

P_1 - P_2,

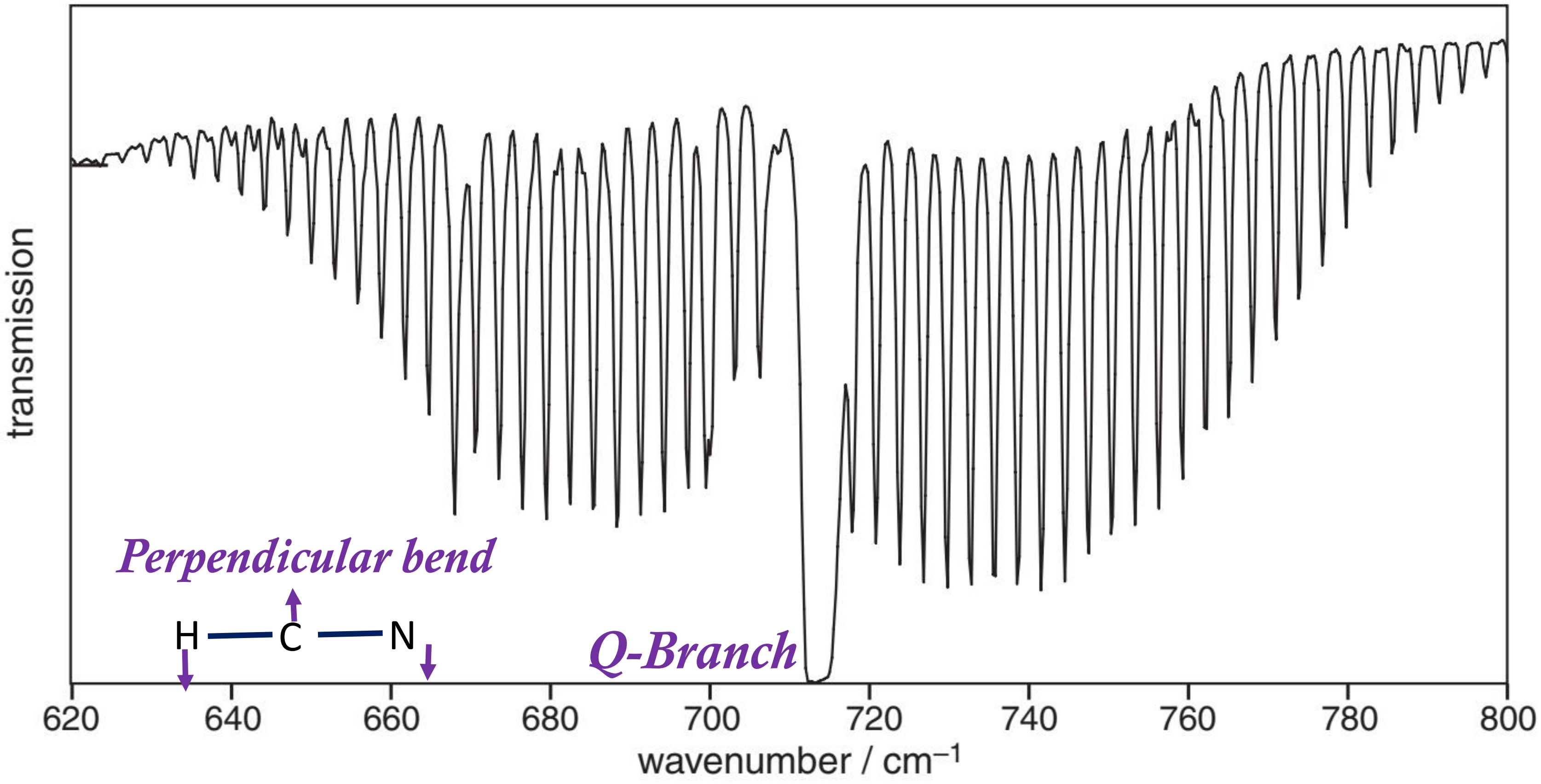
R_1 - R_0 etc is $\approx 2\tilde{B}$,

R_0 - P_1 $\approx 4\tilde{B}$.

The fact that there is no Q branch means the molecule has to be linear!

Perpendicular and parallel vibrations

- The perpendicular CH bending mode for HCN is shown below.



Bending → ***I*** decreasing

$\boldsymbol{B \propto 1/I}$

→ $\boldsymbol{B_1 > B_0}$ **&** $\boldsymbol{B_1 - B_0 > 0}$**.**

$$\Delta\varepsilon = \tilde{\omega}_0 + (\tilde{B}_1 - \tilde{B}_0)J(J+1)$$

The lines in the Q branch are not all on top of one another as would be the case if $B_1 = B_0$, but spread out on the high frequency side of ω_0 as J increases.

7. Raman spectroscopy revisited: polarizability

- The key point in deciding if a vibration will be ***Raman active*** is whether or not there is ***a change*** in the ***polarizability*** of the molecule.
- When a molecule is put into ***an electric field***, it will be ***distorted*** with the nuclei being attracted towards the negative pole of the field and the electrons being attracted towards the positive pole.
- This distortion therefore sets up an ***induced dipole moment*** in the molecule and the molecule is said to ***be polarized***. The size of the ***induced dipole moment***, μ, is proportional to the *strength of the electric field*, E.

$$\mu = \alpha E$$

α ~ *polarizability of a molecule*

- How polarizable an atom or molecule is depends on how easy it is to distort its electron cloud.

7. Raman spectroscopy revisited: *polarizability*

Average polarizabilities of some atoms and molecules without permanent dipole moment

	α / Å^3		α / Å^3		α / Å^3
		H_2	0.8	He	0.2
Li_2	34	F_2	1.3	Ne	0.2
Na_2	30	Cl_2	4.6	Ar	1.6
K_2	61	Br_2	6.5	Kr	2.5
Rb_2	68	I_2	12.3	Xe	4.0
Cs_2	91			Rn	5.3

Electrons more easily distorted!

→ Larger α!

→ *increasing Z_{eff}*

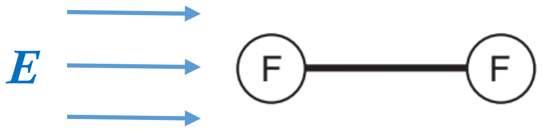
smaller, more compact atom, harder to distort, smaller α

7.1 Dependence of Polarizability

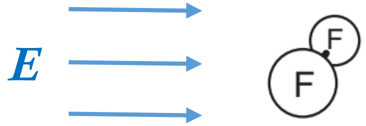
Why do we use '***average polarizability***'?

The polarizability varies with how the molecule is aligned in the electric field.

i) Orientation dependence:



easiest to polarize
along the bond axis



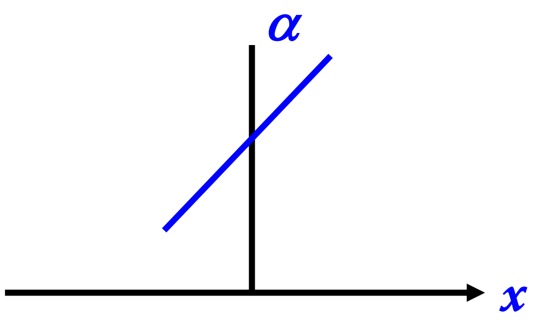
harder to polarize
across the bond axis

ii) Vibration dependence:

$\boldsymbol{x < 0}$,
harder to polarize

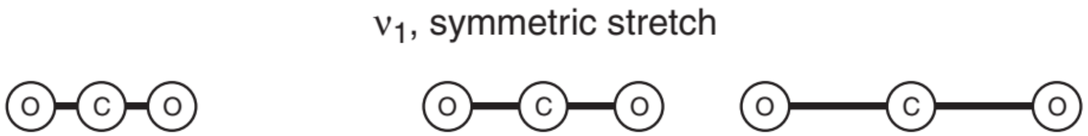
$\boldsymbol{x = 0}$, no displacement
from equilibrium position

$\boldsymbol{x > 0}$,
easier to polarize



Thus between the extremes of the vibration, the polarizability of the molecule changes significantly!
This vibration is of course *Raman active*.

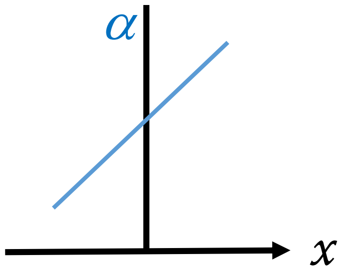
Example: vibrational modes of CO_2



$x < 0$,
less polarizable

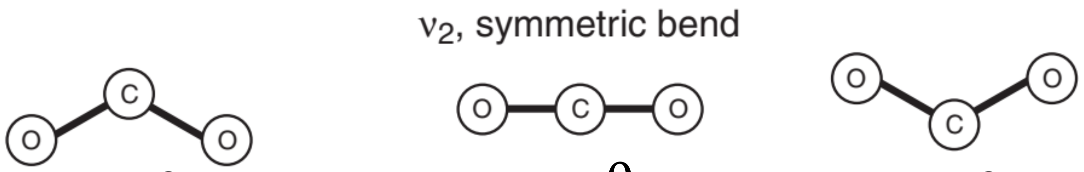
$x = 0$

$x > 0$,
more polarizable



large change in α!
Raman active!

no change in μ!
IR inactive!

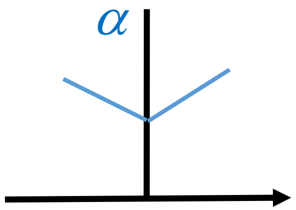


$x < 0$

$x = 0$

$x > 0$

equally polarizable
(doubly degenerate!)

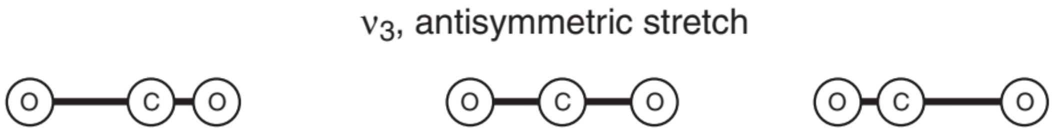


$d\alpha/dx$ (at x=0) = 0 !

no change in α!

Raman inactive!

large change in μ!
IR active!

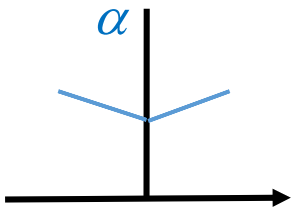


$x < 0$

$x = 0$

$x > 0$

equally polarizable



$d\alpha/dx$ (at x=0) = 0 !

no change in α!
Raman inactive!

change in μ!
IR active!

→ Rule of mutual exclusion of molecules having a symmetry centre!

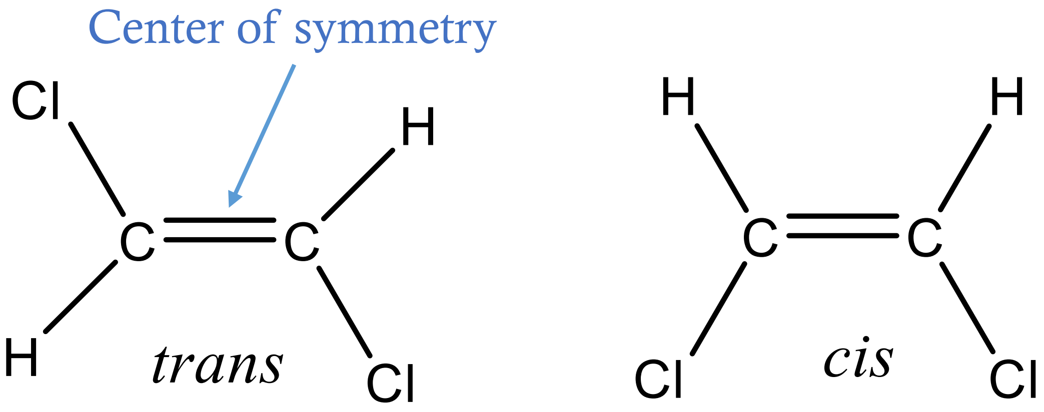
7.2 Rule of mutual exclusion

Ex.19,20

- If a molecule has ***a center of symmetry*** (***i***) then if a vibration is ***Raman active***, it will be ***IR inactive*** and ***vice versa***.

- If there is ***no center of symmetry***, some vibrations *may* be both ***Raman and IR active***.

This rule could be used to distinguish isomers. e.g., isomers of 1,2-dichloroethene.



Center of symmetry

trans

cis

3N-6 =***12*** normal modes.

For ***cis***, most are IR/Raman active.

For ***trans***, none can be simultaneously both IR and Raman active.

7.3 Words of warning

- ***Molecules other than linear structures***: Most molecules, including simple ***bent*** triatomic molecules have spectra that are very difficult, if not impossible, to interpret fully.

- ***Overtones and combinations***:

i) Occasionally *overtones* are possible in vibrational spectroscopy.

ii) The *normal modes* and/or their harmonics for molecules can also combine.

iii) ***Combination bands*** arise from the addition of two or more fundamental frequencies or overtones, such as ν_1 +/– ν_2, ν_1+ ν_2+/– ν_3, 2ν_1+/–ν_3, etc.

e.g., CO_2.

symmetric stretch $\boldsymbol{\nu_1}$, ~ 1330 cm^{-1}

the 1st overtone (~1334 cm^{-1}) of the bending mode $\boldsymbol{\nu_2}$

interacts → Two signals

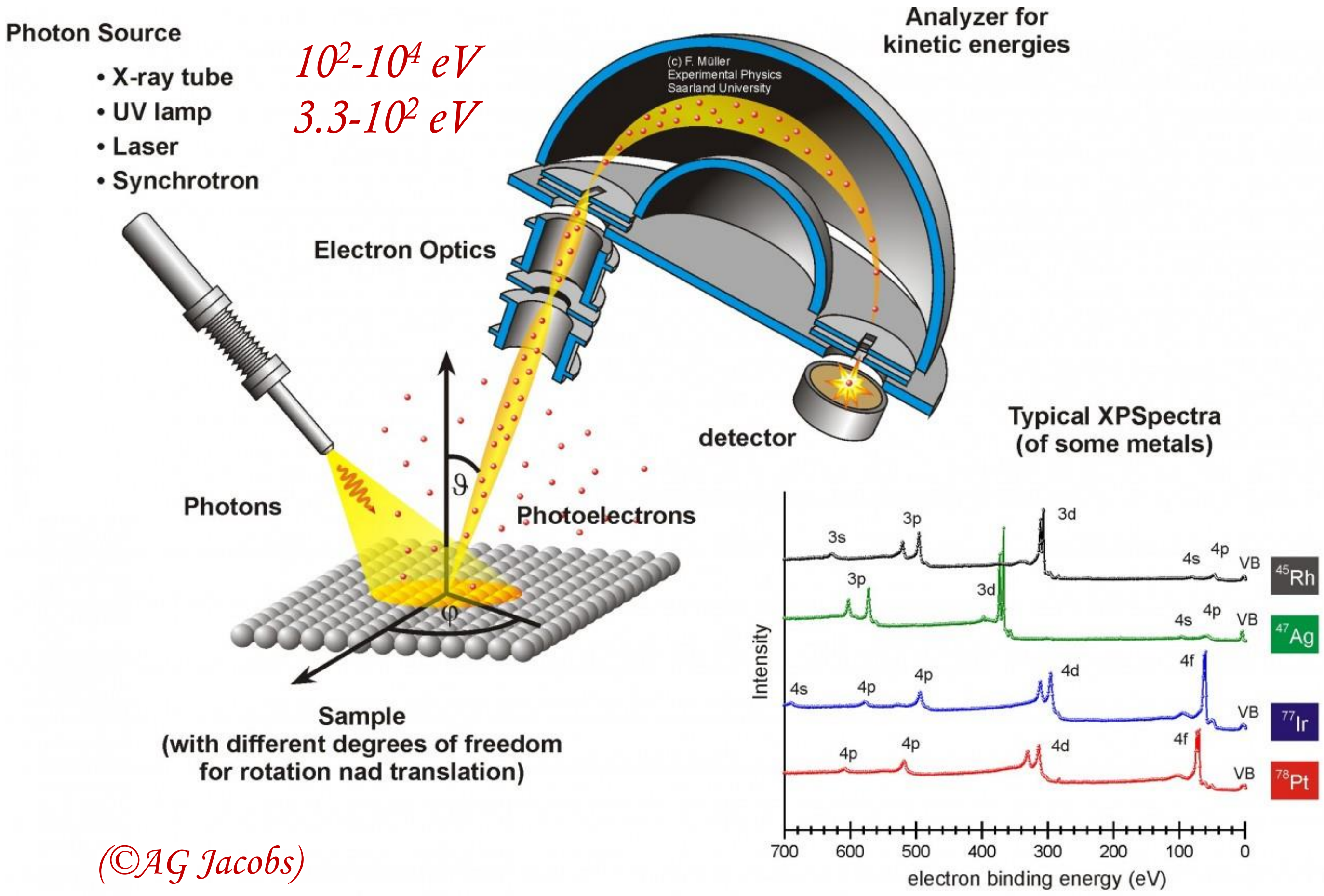
1285 and 1385 cm^{-1}

itself Raman inactive!

8. Photoelectron spectroscopy (PES)

XPS & UPS

PES can give an indication of the energies of the different occupied orbitals in atoms or molecules and, in the case of molecules, whether the orbitals are bonding, non-bonding or antibonding. It is an excellent tool to confirm the predictions from **MO** theory.



10^2-10^4 eV

3.3-10^2 eV

(©AG Jacobs)

- For *atoms*, $KE = h\nu - I_i$

KE ~ kinetic energy of the ejected electron.

I_i ~ energy to ionize an electron from *i*th orbital.

- For ***molecules***, part of the photon energy can also promote the ion to ***a higher vibrational-rotational state***.

$$KE = h\nu - I_i - \Delta E_{vib} - \Delta E_{rot}$$

PES thus can also reveal information concerning the vibrational energy levels in the resulting ion.

8.1 Ionization energy vs. orbital energy

The ***ionization energy*** is not simply equal to minus the corresponding orbital energy but the difference in energy between the starting material and the product,

For $\mathbf{M} \rightarrow \mathbf{M}^{+} + \mathbf{e}^{-}$: $\boldsymbol{I_i} = E^{\text{electrons}}(M^{+}) - E^{\text{electrons}}(M) \neq \boldsymbol{\varepsilon_i}$

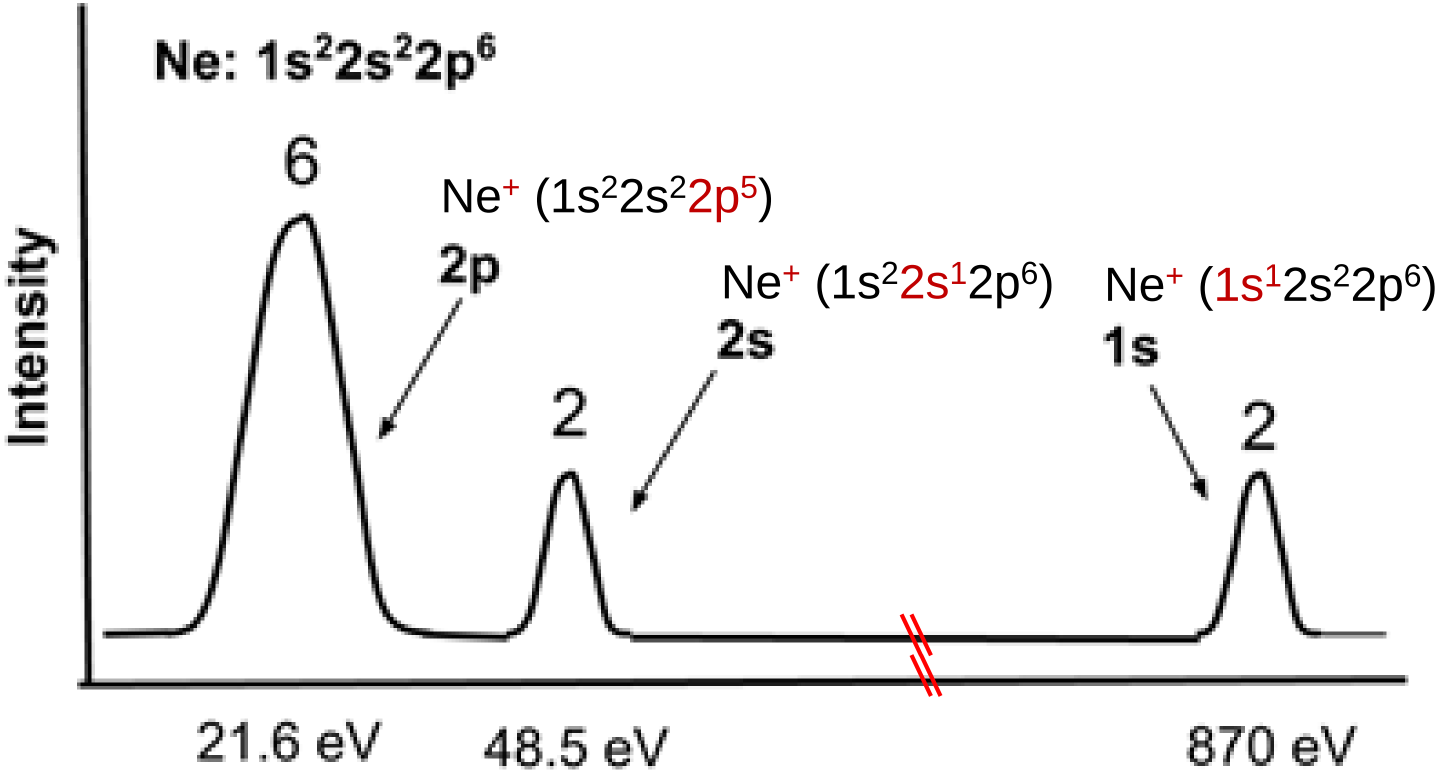
($\boldsymbol{\varepsilon_i}$ ~ energy of the *i*th orbital from which the electron was ejected.)

Whilst not exact (*?*), the ionization energies are a good indication of the energies of molecular/atomic orbitals.

8.2 Photoelectron spectra of atoms

➢The PES of neon gas:

- ***Three peaks*** -- removal of an electron from the ***1s***, ***2s*** and ***2p*** orbitals, respectively.
- The ratio of the peaks: ***2s*:*2p* ≈ *1*:*3***



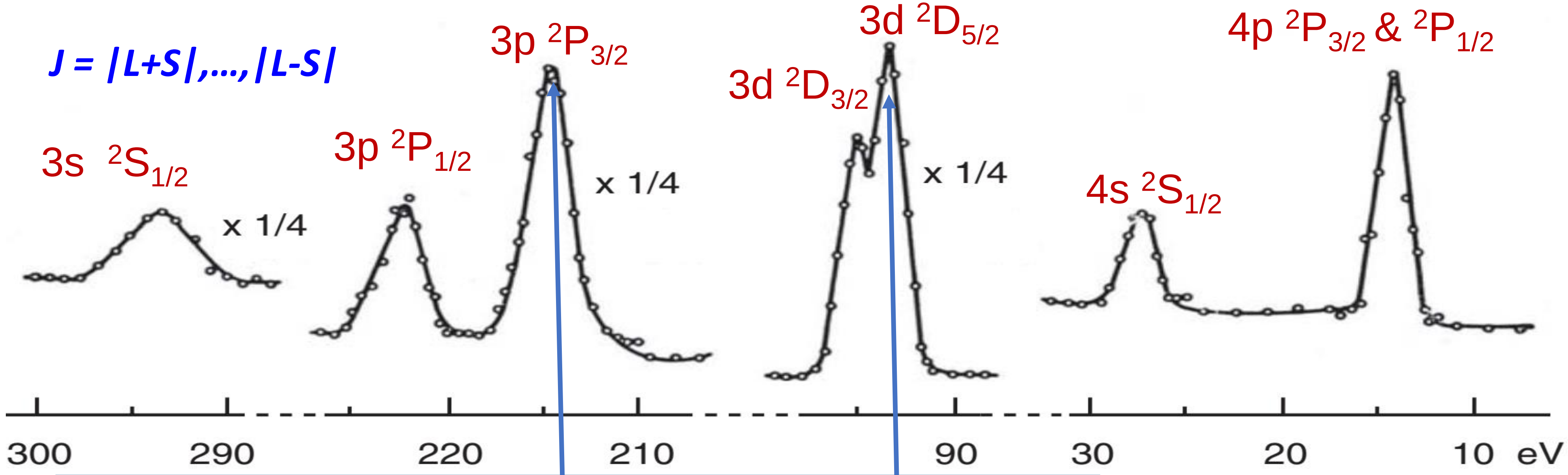
8.2 Photoelectron spectra of atoms

$I_i = E^{\text{electrons}}(M^+) - E^{\text{electrons}}(M)$

- When looking at the PE spectra of atoms, we should really *use the term symbols* to represent the different levels of the ions produced. This is essential when *spin-orbit coupling* becomes significant, e.g., PES of *Krypton* ([Ne]$3s^23p^63d^{10}4s^24p^6$).

Kr^+ …$3s^13p^6$… …$3s^23p^5$… …$3p^63d^9$… …$4s^14p^6$… …$4s^24p^5$…

$J = |L+S|,\dots,|L-S|$



lower IE for the state of lower energy of the cation.

8.2 Photoelectron spectra of atoms

Ex.21

- The degeneracy of a given level is given by the general formula ***(2J + 1)*** – the degeneracies are the main contributor to the observed intensity ratio of the peaks in the PE spectrum.

$^2P_{3/2}$:$^2P_{1/2}$ = 4:2

- Two factors influence the magnitude of the ***spin-orbit coupling***.

i) the nuclear charge ***Z*** – the greater ***Z***, the greater the coupling.

ii) the ***e-n*** separation – the further away the electron, the smaller the interaction.

The energies of the different levels formed on removing an electron from the ***p*** orbitals in krypton are given here.

Level	IE / eV	Spin-orbit splitting / eV
4 $^2P_{3/2}$	14.0	0.6 (not resolved)
4 $^2P_{1/2}$	14.6	
3 $^2P_{3/2}$	214.4	7.8
3 $^2P_{1/2}$	222.2	
2 $^2P_{3/2}$	1679.3	52.5
2 $^2P_{1/2}$	1731.8	

e closer to *n*

8.3 Photoelectron spectra of molecules

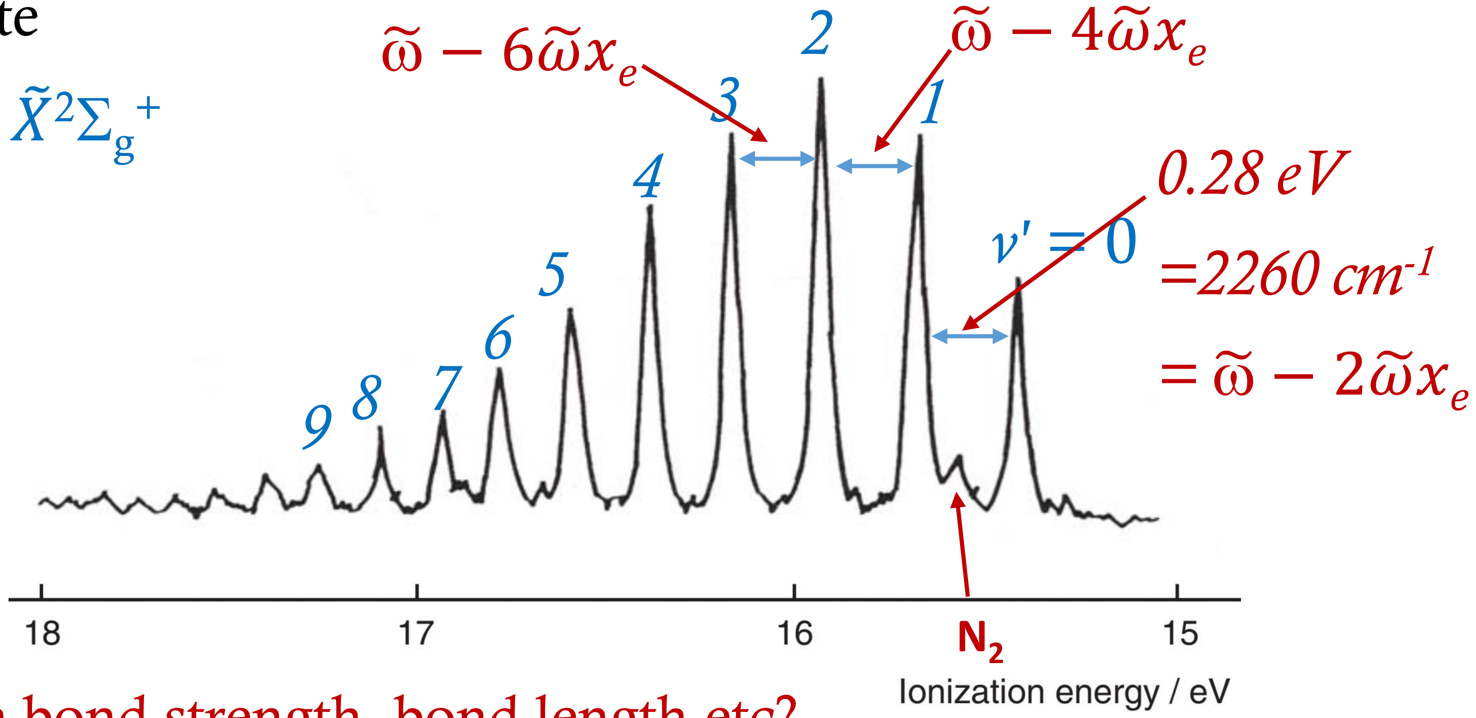
The PE spectra for molecules show a series of bands, each consisting of a number of peaks corresponding to the removal of an electron from a particular molecular orbital.

- Some of the energy of the incident photon is used to vibrationally excite the ion.
- The different peaks in the spectrum of H_2 correspond to the final ion being left in different vibrational states.

$H_2^+ \sim 2260\ \text{cm}^{-1}$

$H_2 \sim 4280\ \text{cm}^{-1}$

$H_2\ (1\sigma_g^2) \rightarrow H_2^+\ (1\sigma_g^1) + e^-$



The change in bond strength, bond length etc?

Why does the v′=2 state give the highest intensity?

$I_i = h\nu - KE$

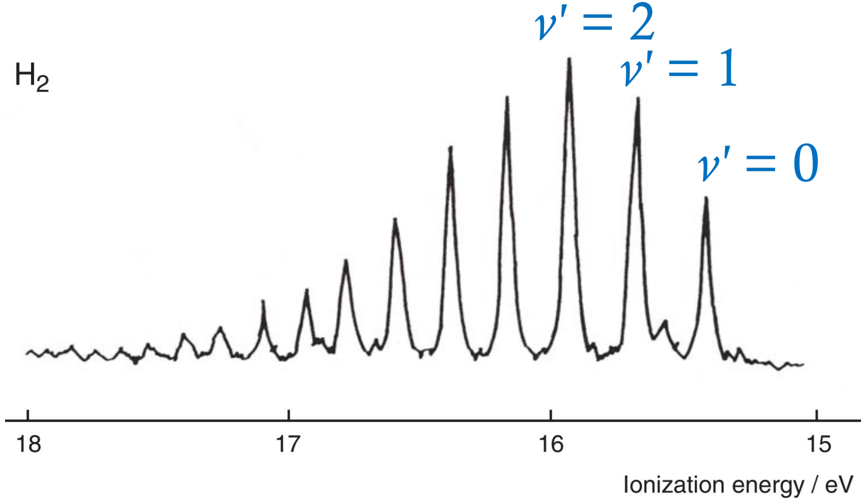
8.3.1 The Frank-Condon principle

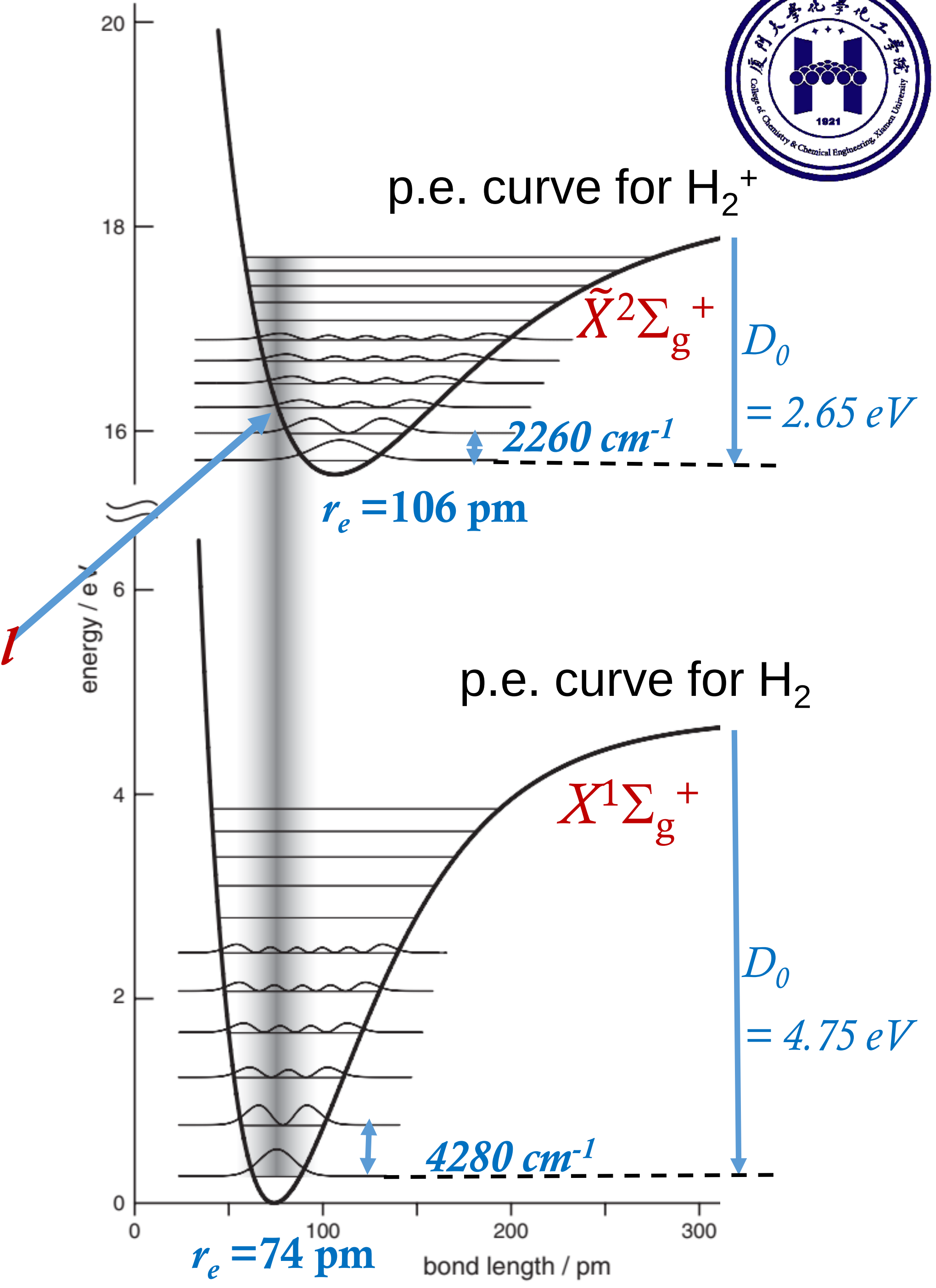
- The time needed for the photoelectron effect to take place is extremely short – of the order of *femto seconds* (10^{-15} seconds), much quicker than the time of vibrating.
- Consequently, during the electronic transition there is ***no appreciable change in the geometry*** of the molecule, i.e the bond length stays the same. This is known as the ***Franck-Condon principle***.
  - At room temperature, the only significantly populated vibrational level for the neutral molecule is the $v'' = 0$ level. The probability density for this level is at a maximum for bond lengths near to the equilibrium separation, r_e.
  - Since the bond length does not change during the electronic transition, the only levels that can be populated in the cation immediately after ionization are those whose population densities have maxima at this same separation.

8.3.1 The Frank-Condon principle

- In the PE spectrum of H_2, the peak with the maximum intensity is not the one where the ion is left in the vibrational ground state (with ***v*'= 0**), but in a vibrational excited state (with ***v*'= 2**).

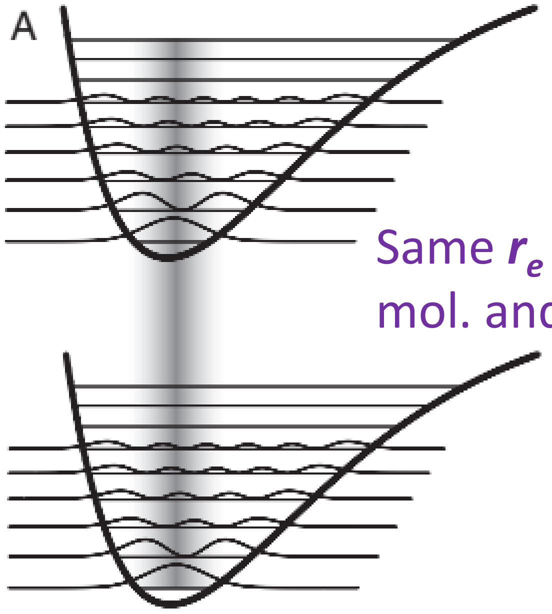
- Since the left-edge of the potential curve rises steeply at short bond lengths, ***there are a number of higher vibrational energy levels*** with their maxima around the bond lengths indicated by the shaded bar.





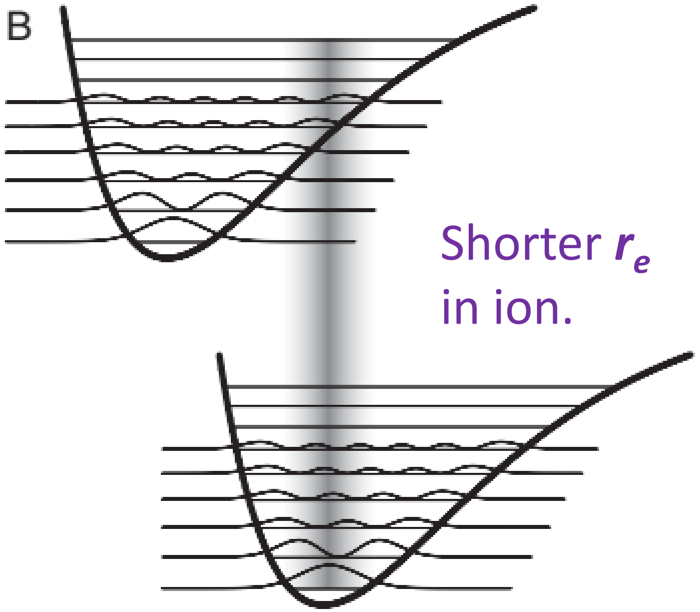
The Frank-Condon principle (More cases)

- In case the internuclear separation in the ion is the same as that in the neutral molecule (i.e., electron ejected from a non-bonding MO), the most likely transition upon ionization is to the vibrational ground state in the ion. ***Few peaks can be seen in the PE spectrum***!



Same r_e in mol. and ion.

- In case the bond length in the ion is shorter than the neutral molecule (i.e., electron likely ejected from an anti-bonding MO), ***few peaks can be seen in the PE spectrum***.



Shorter r_e in ion.

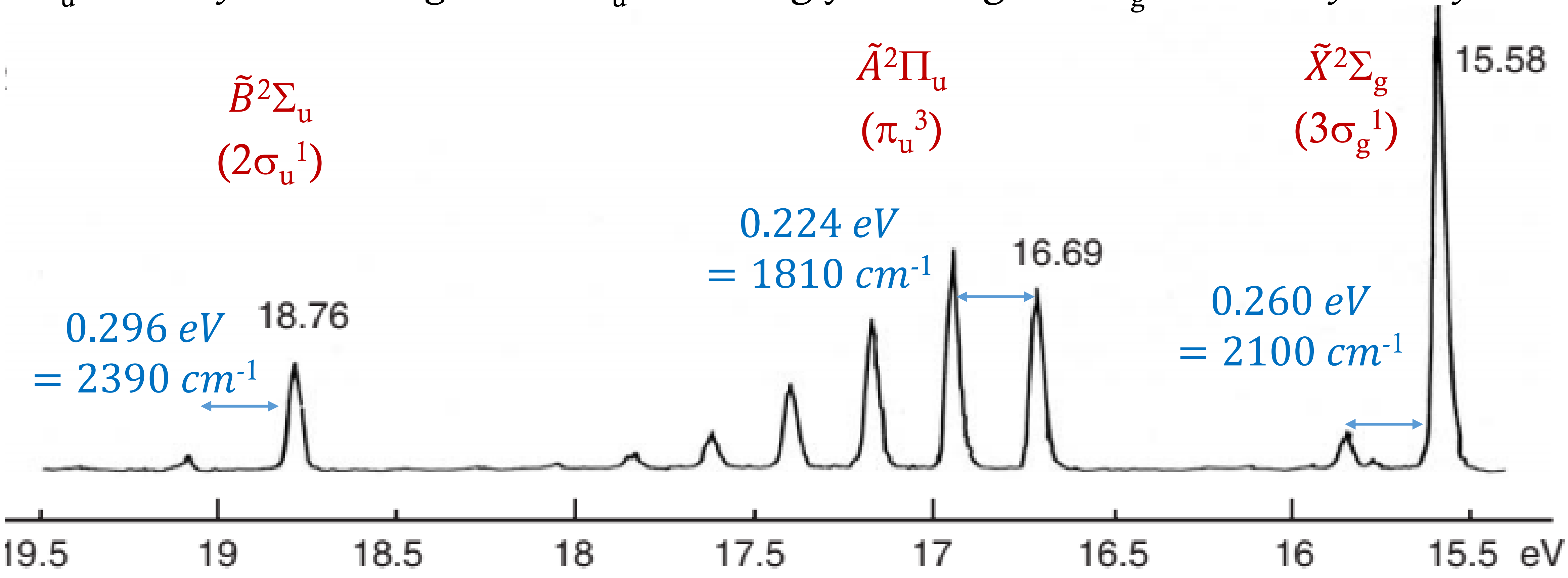
The PE spectrum of N_2

$N_2\ X^1\Sigma_g^+\ (\ldots\ 2\sigma_g^2\ 2\sigma_u^2 1\pi_u^4\ 3\sigma_g^2)$

~ 2345 cm^{-1}

These peaks can be observed in the PES spectrum of H_2 with N_2 inpurity.

$2\sigma_u$~ *weakly antibonding* $1\pi_u$ ~ strongly bonding $3\sigma_g$ ~ *relatively weakly bonding*



$\tilde{B}^2\Sigma_u$ $(2\sigma_u^1)$

$\tilde{A}^2\Pi_u$ (π_u^3)

$\tilde{X}^2\Sigma_g$ $(3\sigma_g^1)$

$0.296\ eV = 2390\ cm^{-1}$

$0.224\ eV = 1810\ cm^{-1}$

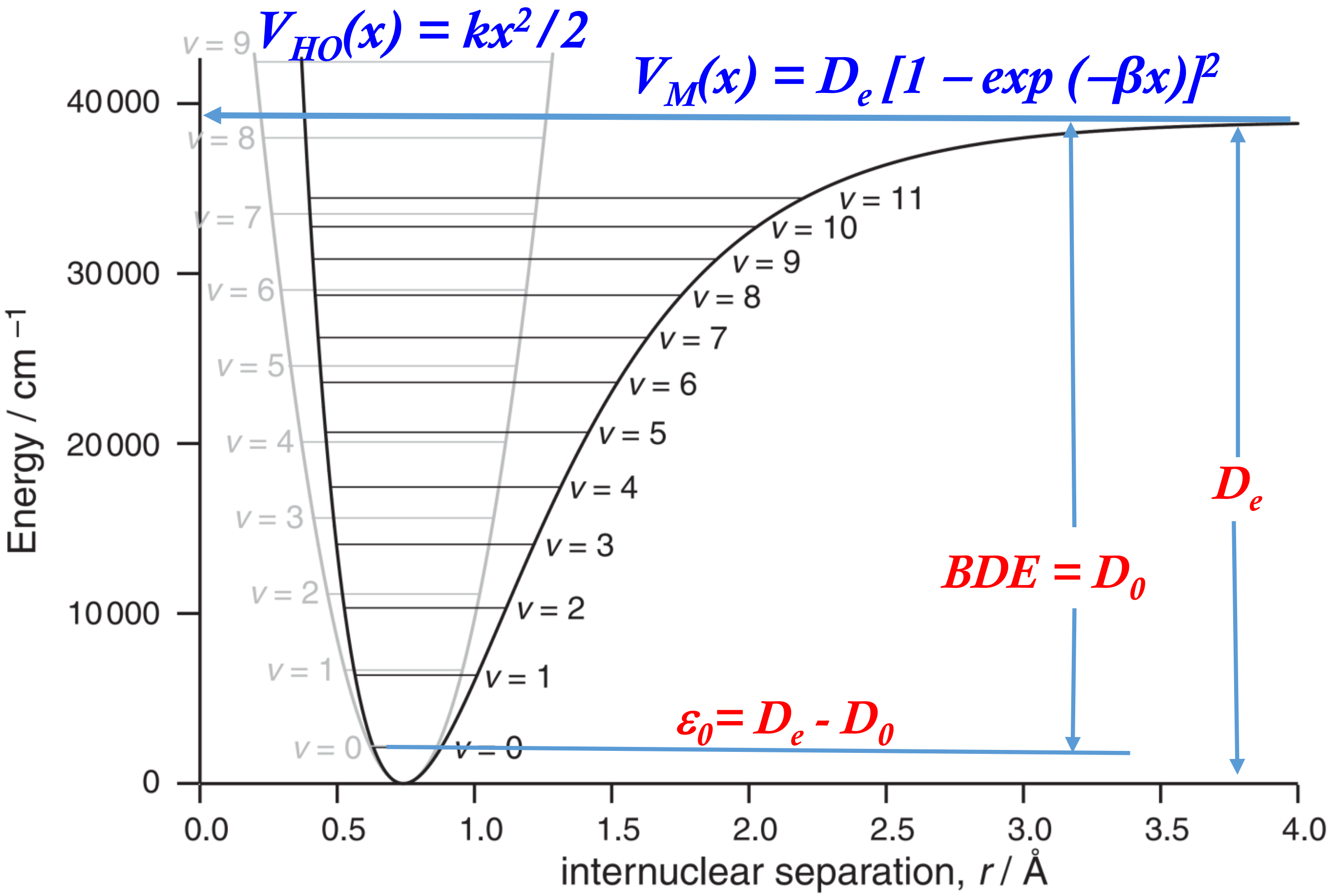
$0.260\ eV = 2100\ cm^{-1}$

Summary

- Vibration of diatomics can be modelled by either ***harmonic oscillator*** ($\varepsilon_v = (v + \tfrac{1}{2})\tilde{\omega}$) or the more realistic ***Morse oscillator*** ($\varepsilon_v = (v + \tfrac{1}{2})\tilde{\omega} - (v + \tfrac{1}{2})^2\tilde{\omega}x_e$).
- ***Selection rule*** for an allowed transition:

  i) **H.O.** ~ *dipolar*, $\Delta v = \pm 1$;

  ii) **M.O.** ~ *dipolar*, $|\Delta v| \geq 1$;



$V_{HO}(x) = kx^2/2$

$V_M(x) = D_e\,[1 - \exp(-\beta x)]^2$

BDE = D_0

D_e

$\varepsilon_0 = D_e - D_0$

- ***For H.O.***: $\Delta E_{v+1\leftarrow v} = \hbar\tilde{\omega}$ $\quad \Delta\varepsilon_{v\leftarrow v-1} = \tilde{\omega}$
- ***For M.O.*** : $v_{max} = (x_e^{-1} - 1)/2$

  $\tilde{D}_e$ *(in cm^{-1})* $= \tilde{\omega}(4x_e)^{-1}$

$\Delta E_{v\leftarrow v-1} = \hbar\omega - 2v\hbar\omega x_e$

$\Delta\varepsilon_{v\leftarrow v-1} = \tilde{\omega} - 2vx_e\tilde{\omega}$

Summary

- Molecular rotation can be modelled by rigid rotor ($I = \mu r^2$, $E_J = BJ(J+1)$, $B = \hbar^2/2I$, $B = h\tilde{c}\tilde{B}$).

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

$$J_{max} \approx \sqrt{\frac{kT}{2h\tilde{c}\tilde{B}}} - \frac{1}{2}$$

- Transitions between rotational energy levels in molecule can be observed:

i) in microwave spectrum with the ***Selection rule*** (*dipolar*, $\Delta J = \pm 1$) and ***peak distance of*** ***2B.***

ii) in rotational Raman scattering spectrum with the ***selection rule*** (lineal molecule): $\Delta J = 0, \pm 2$, and as Stokes lines and anti-Stokes lines by $(4J + 6)\tilde{B}$ cm^{-1} lower and higher than the incident line, respectively.

iii) as fine structures in vibrational IR spectrum: with the ***selection rule***: $\Delta J = \pm 1$ *(for diatomics)* and $\Delta J = 0$ *for dipole moment change perpendicular to the principle axis.*

The End of Molecular Spectroscopty

吸收：

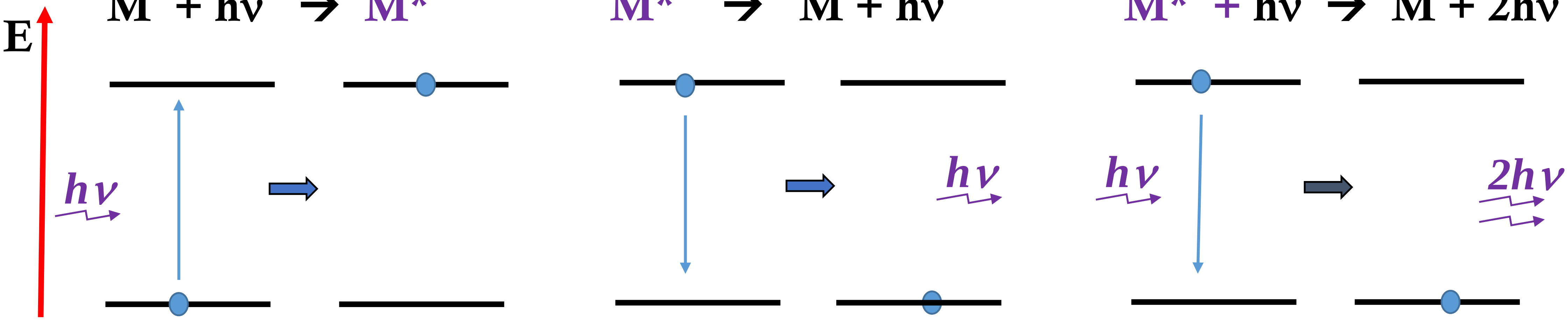
$M + h\nu \rightarrow M^*$

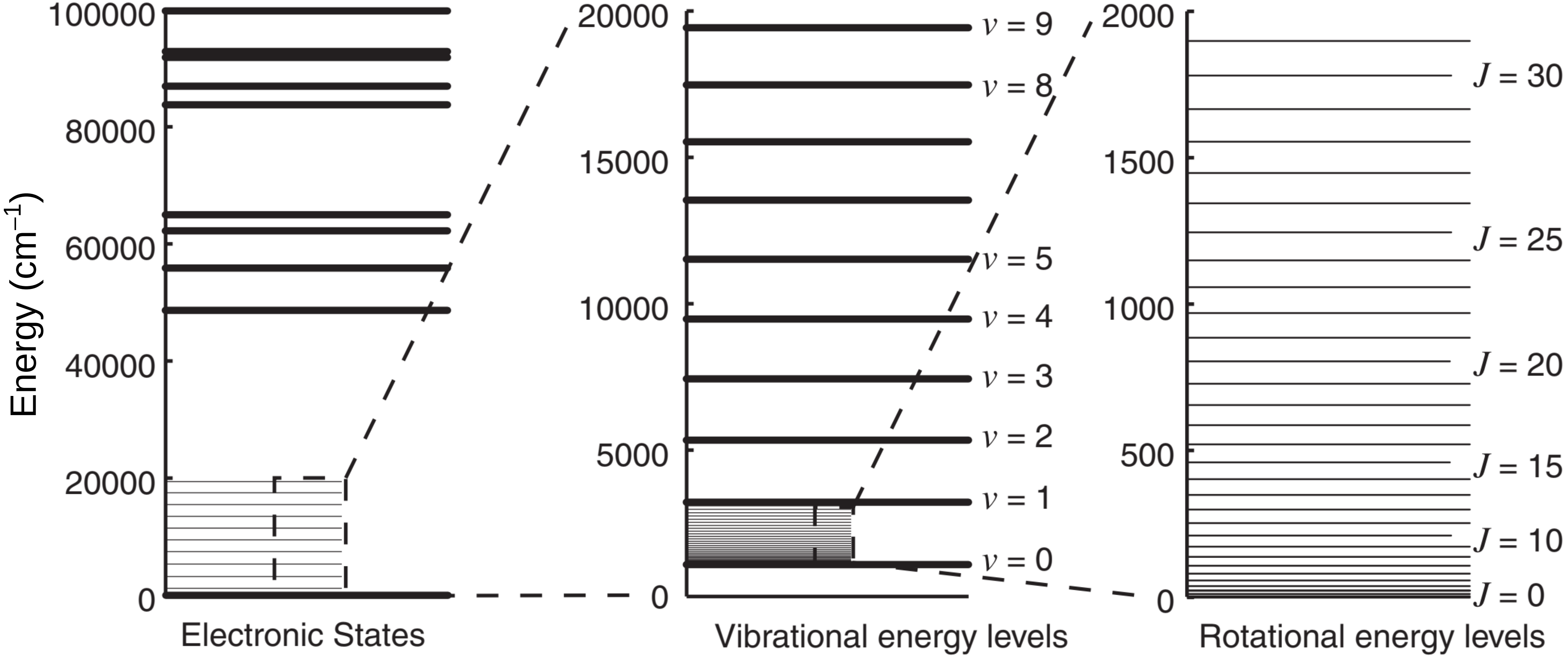
自发发射：

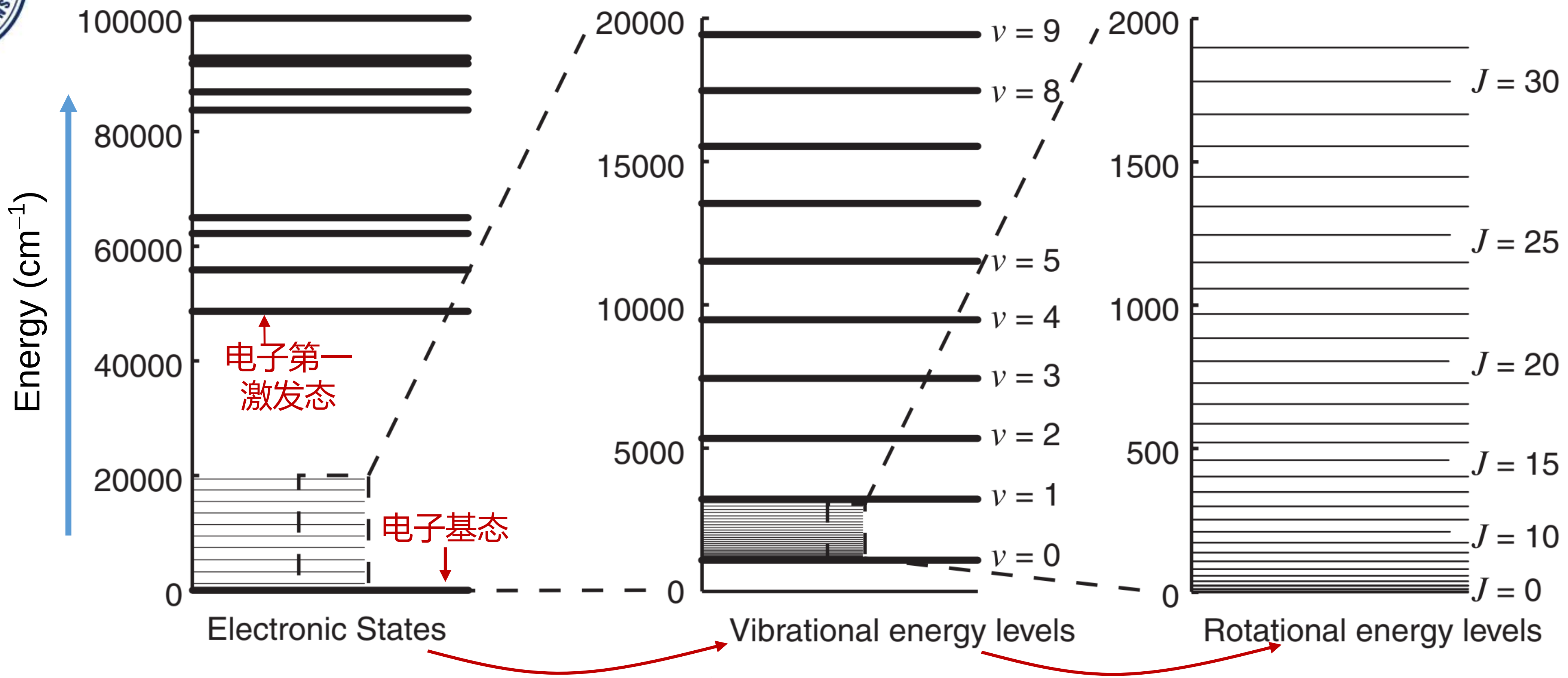
$M^* \rightarrow M + h\nu$

受激发射

$M^* + h\nu \rightarrow M + 2h\nu$




Energy (cm^{-1})
100000
80000
60000
40000
20000
0
Electronic States
20000
15000
10000
5000
0
v = 9
v = 8
v = 5
v = 4
v = 3
v = 2
v = 1
v = 0
Vibrational energy levels
2000
1500
1000
500
0
J = 30
J = 25
J = 20
J = 15
J = 10
J = 0
Rotational energy levels



电子第一激发态

电子基态

每个电子态有许多振动能级

每个振动态有许多转动能级