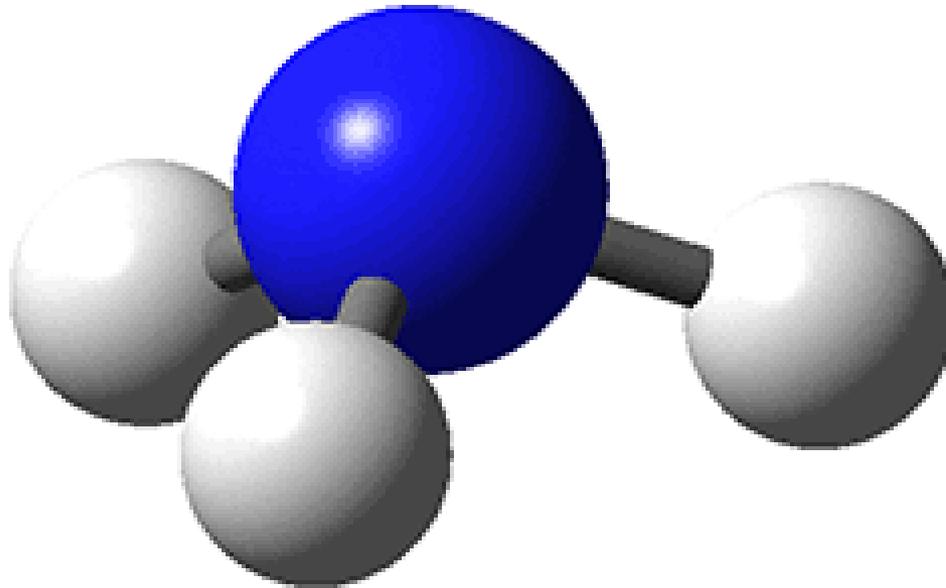


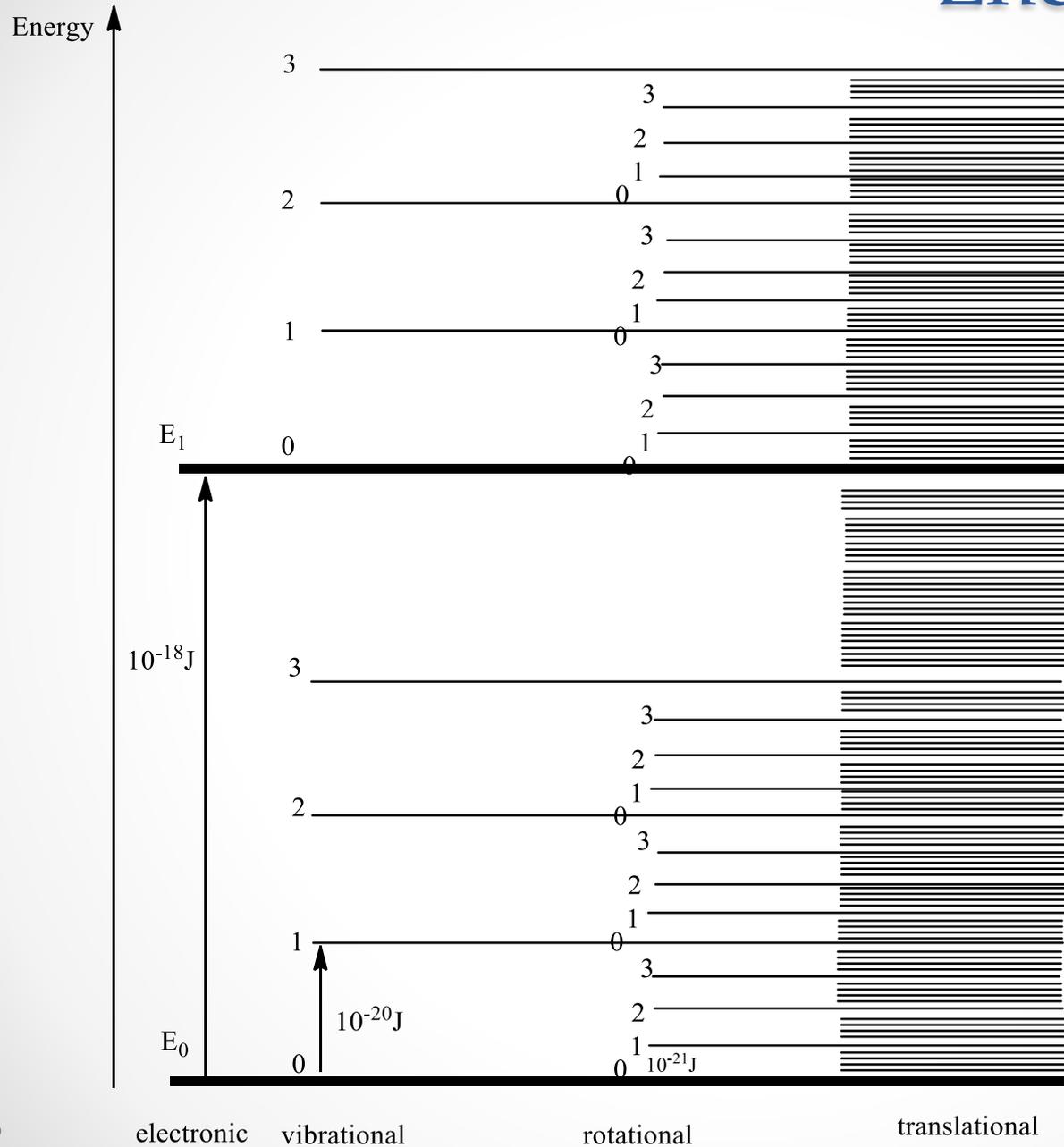
IR – spectroscopy Part III (Theory)



Electromagnetic spectrum

Spectral region	VHF	UHF	Microwave	Infrared	Visible	Ultraviolet	X-rays	γ -rays
Common usage	NMR	EPR	rotational transitions	vibrational transitions	electronic transitions		ionisation	nuclear effects
Frequency (Hz)	5×10^8	3×10^{10}	3×10^{11}	3×10^{13}	6×10^{14}	1.2×10^{15}	3.0×10^{17}	1.5×10^{19}
Wavelength	0.6 m	1 cm	1 mm	10 μ m	500 nm	250 nm	1 nm	20 pm
Wavenumber (cm^{-1})	0.017	1.0	10.0	1000	20,000	40,000	1.0×10^7	5.0×10^8
Single photon energy (eV)	2.07×10^{-6}	1.24×10^{-4}	1.24×10^{-3}	1.24×10^{-1}	2.5	5.0	1.24×10^3	6.2×10^4
Photon energy (kJ mol^{-1})	2.03×10^{-4}	1.20×10^{-2}	1.20×10^{-1}	12.0	239	479	1.2×10^5	6×10^6

Energy levels



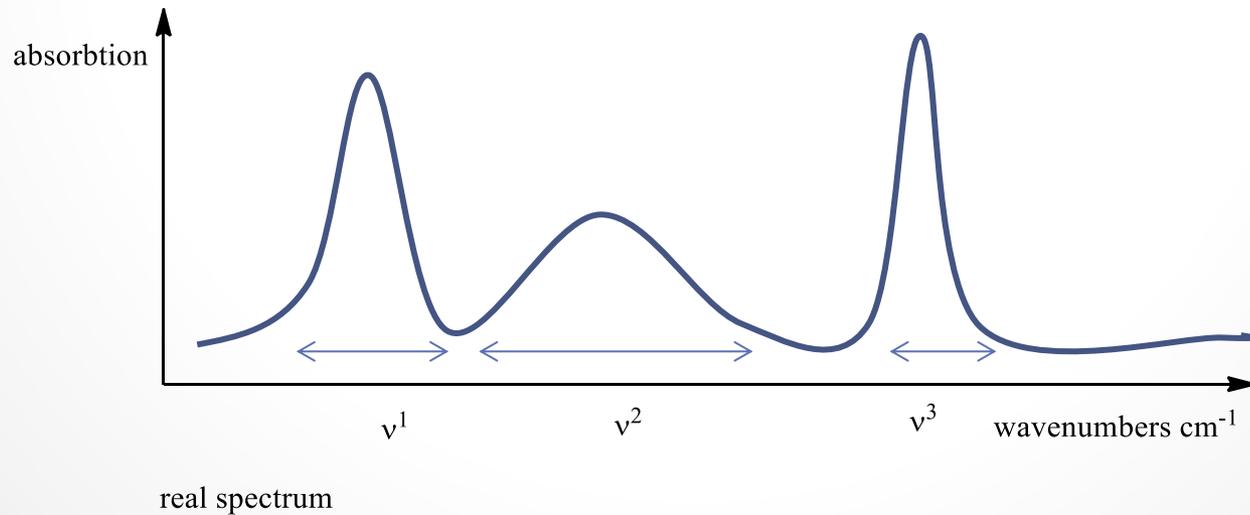
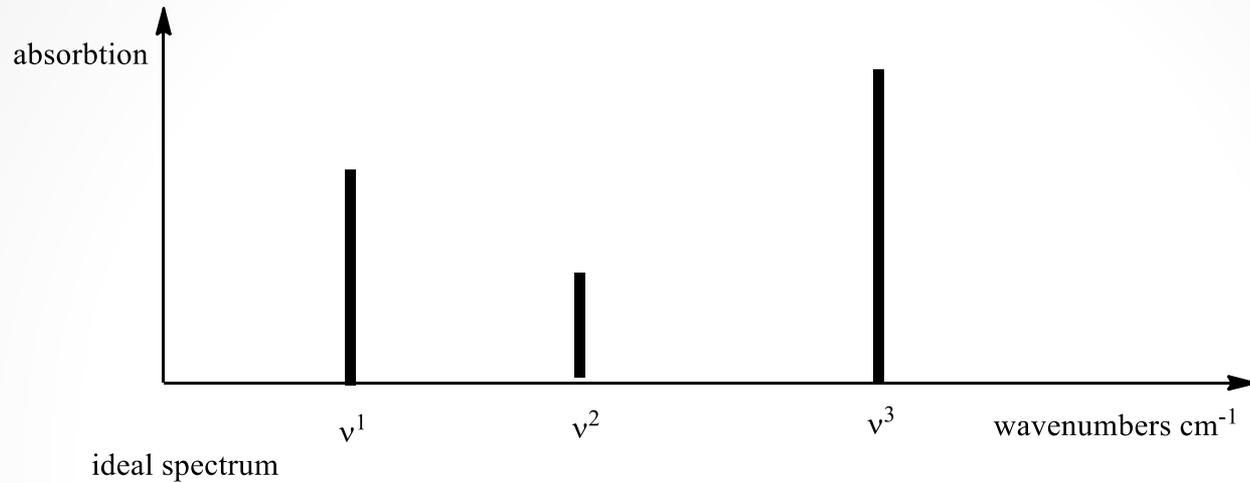
● electronic

vibrational

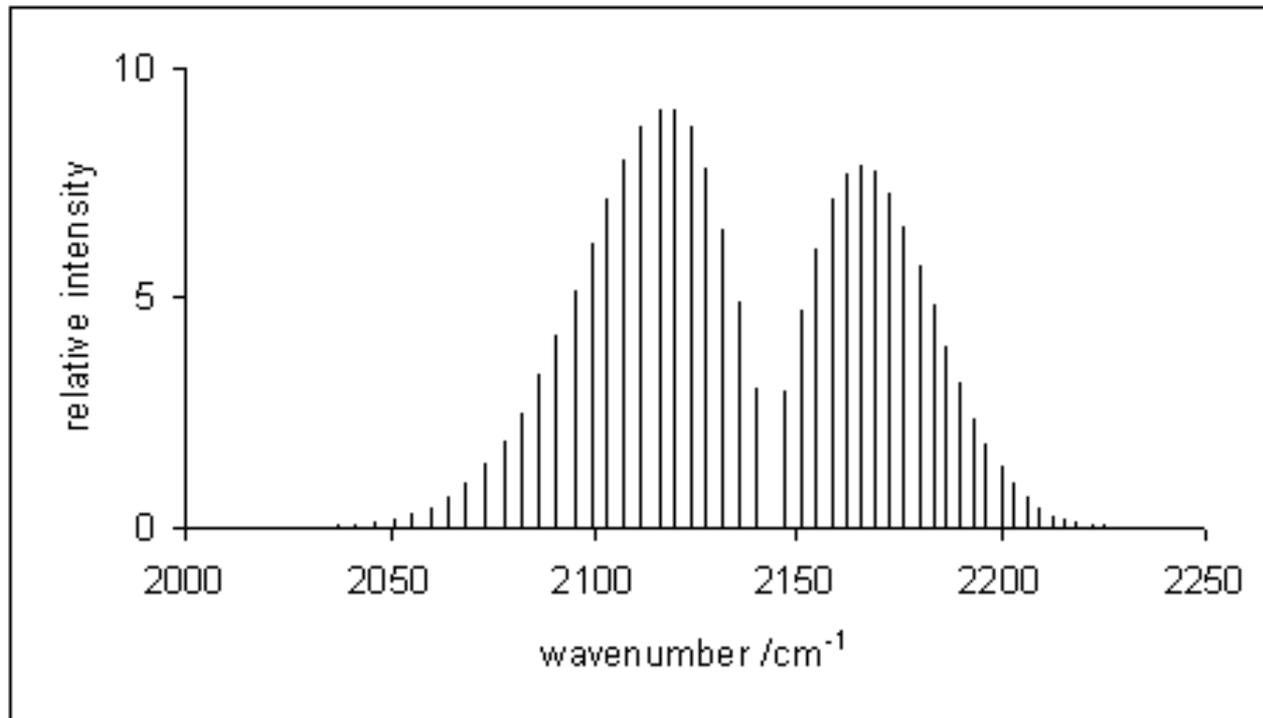
rotational

translational ●

Width and shape of spectral lines

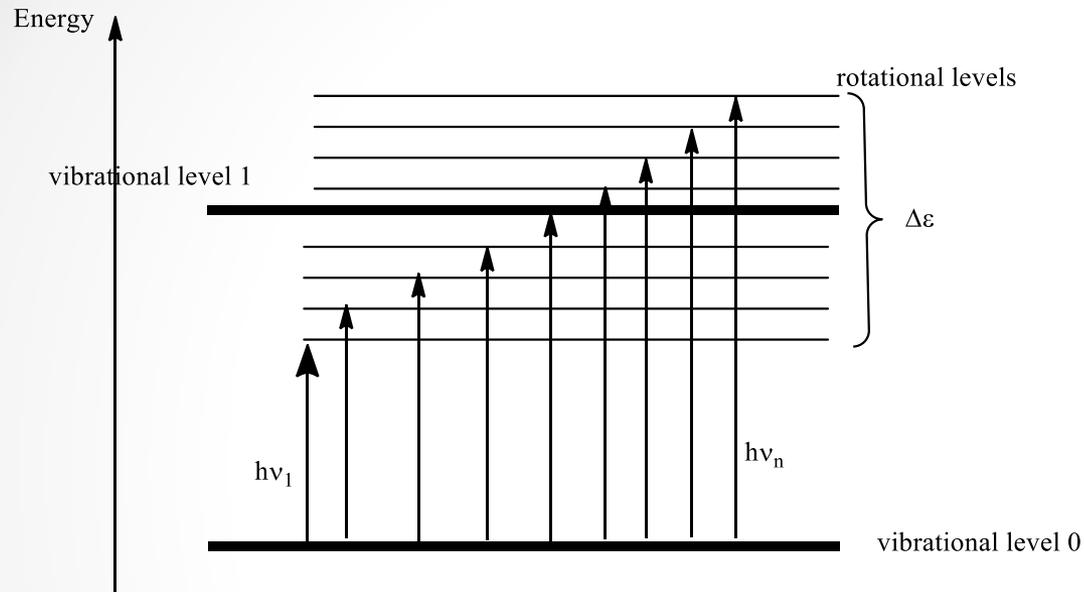


Rotational – vibrational spectrum



Simulation of vibration-rotation line spectrum of carbon monoxide

Line broadening



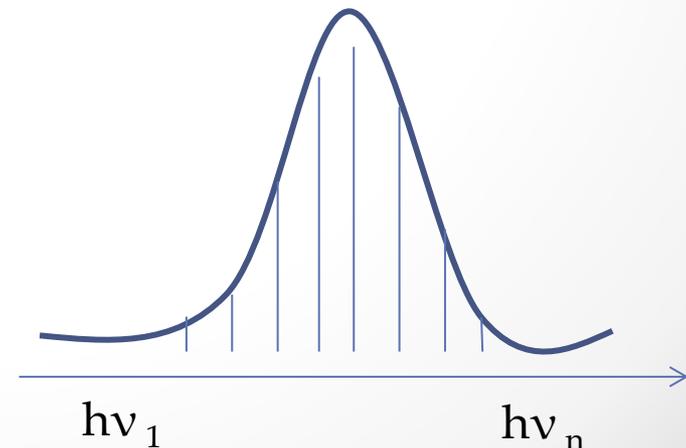
$\Delta\varepsilon =$ width of spectral line

Heisenberg's uncertainty principle

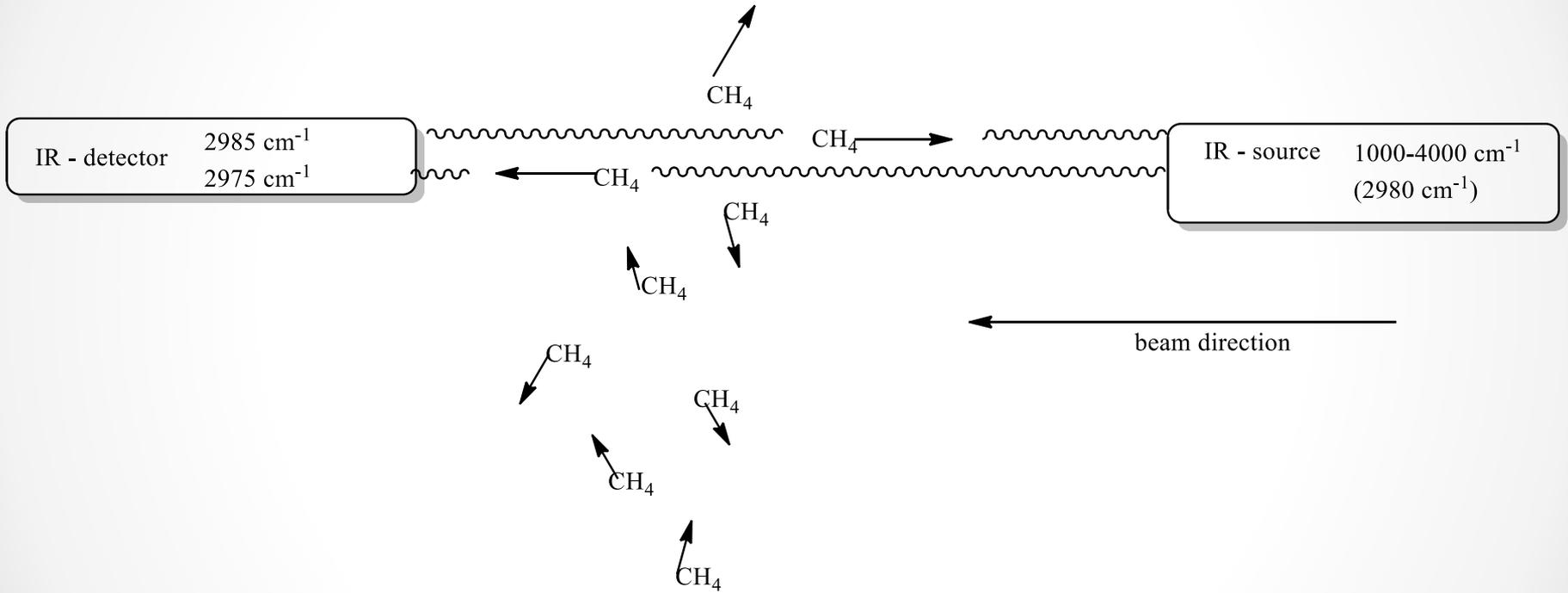
τ – particle lifetime on the energy level

$\Delta\varepsilon$ - width of spectral line

$$\Delta\varepsilon \tau \geq h / 2\pi$$

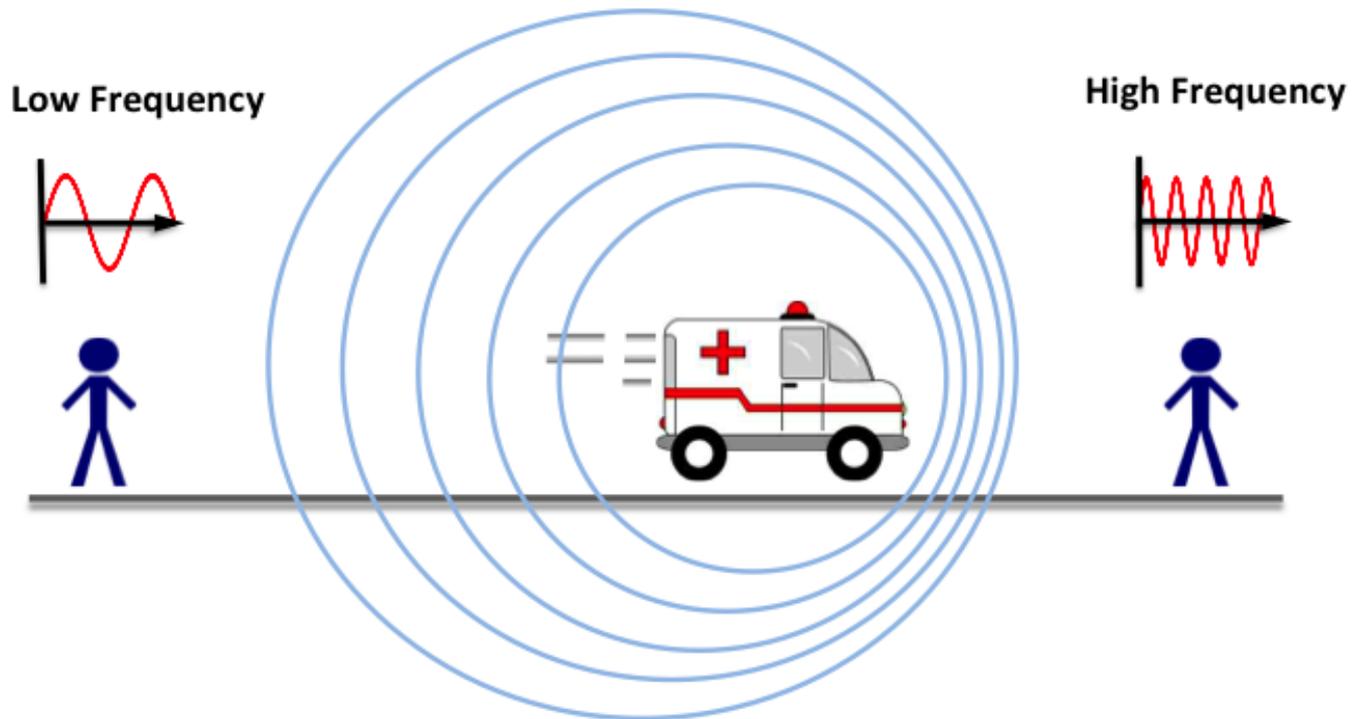


Line broadening – Doppler effect

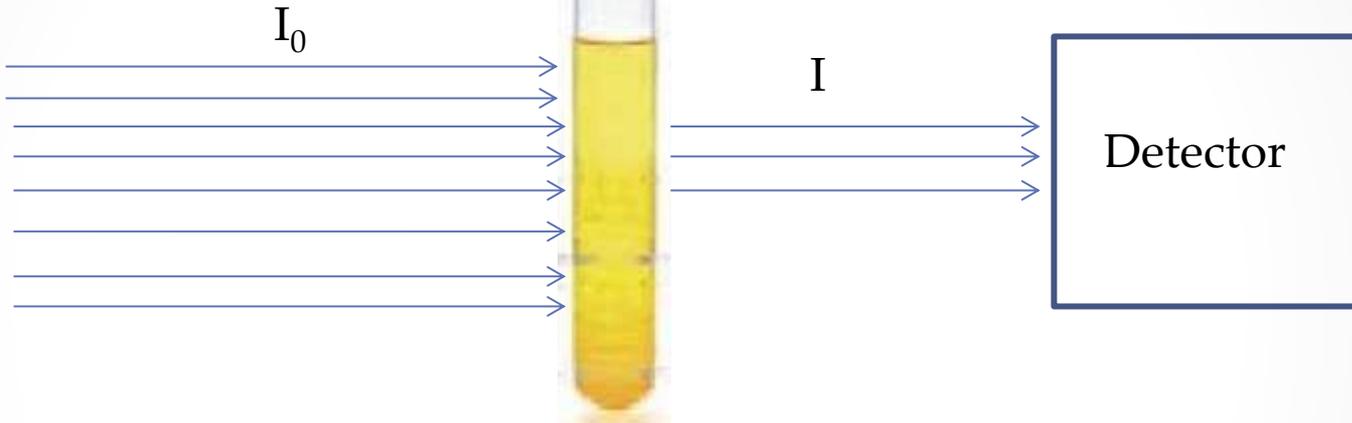


Doppler effect

Doppler Effect



Beer–Lambert law

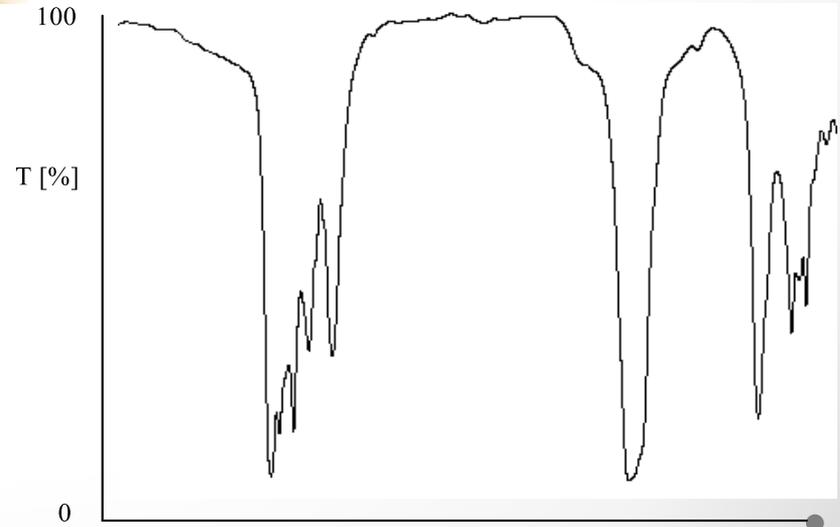


Transmittance

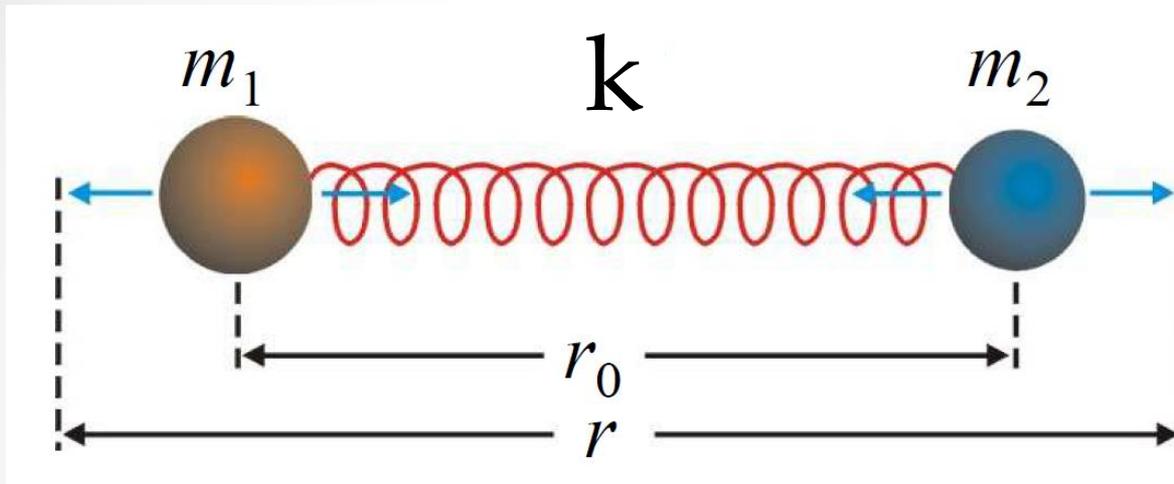
$$T = \frac{I}{I_0}$$

Absorbance

$$A = \log \frac{1}{T}$$



Harmonic oscillator



$$F = -kq$$

F = Force acting on the system

k = constant strength

$q = r - r_0$

r_0 position at equilibrium

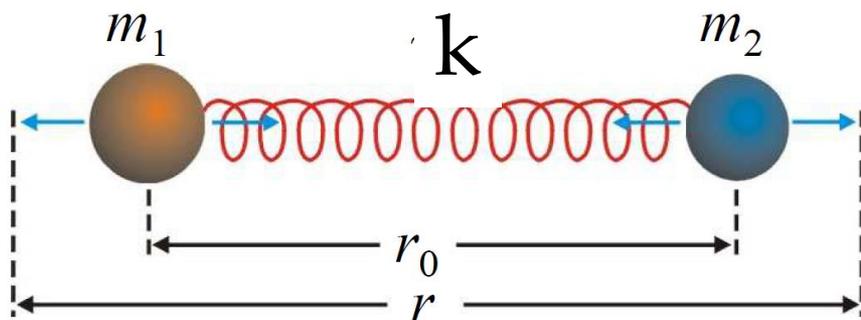
r position at the moment

$q(t) = Q \cos 2\pi \nu t$

Q = amplitude

ν = frequency

Reduced mass



$$\frac{1}{m_{red}} = \frac{1}{m_1} + \frac{1}{m_2}$$

$$\frac{1}{\mu} = \frac{1}{m_{red}}$$

$$\mu = \frac{1}{\frac{1}{m_1} + \frac{1}{m_2}} = \frac{m_1 m_2}{m_1 + m_2}$$

Bond Energies

CH₃—CH₃ 368 KJ/mol

CH₃—H 431 KJ/mol

CD₃—D 442 KJ/mol

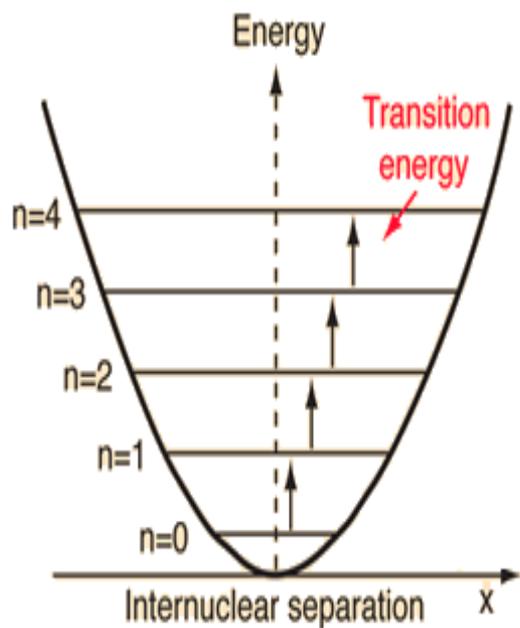
Reduced mass

(12*12)/(12+12) = 6

(12*1)/(12+1) = 0.92

(12*2)/(12+2) = 1.71

Quantum harmonic oscillator



Schrodinger Equation for harmonic oscillator

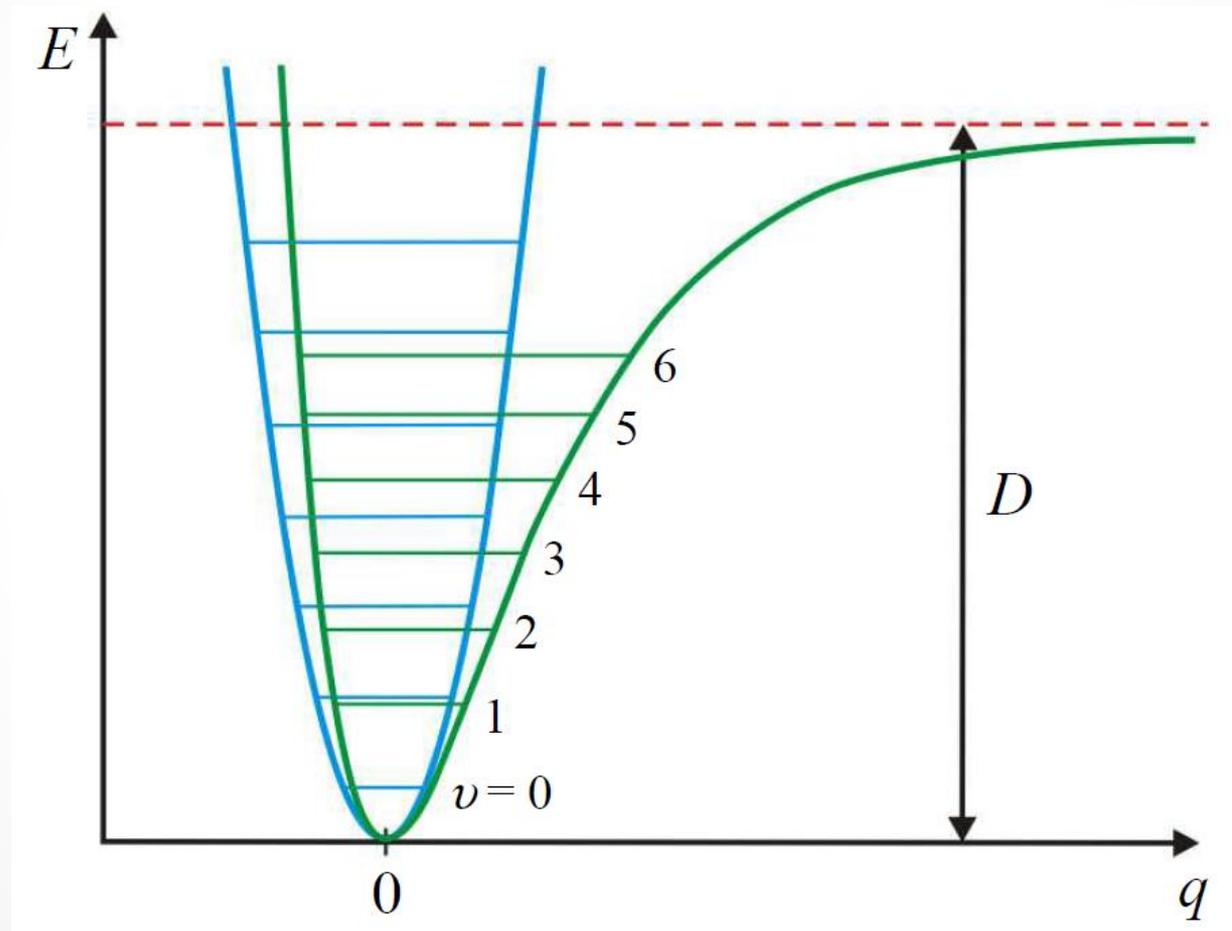
$$-\frac{h^2}{8\pi^2 m_{red}} \frac{d^2\Psi}{dq^2} + \frac{1}{2} kq^2\Psi = E\Psi$$

$$E_{osc} = \frac{h}{2\pi} \sqrt{\frac{k}{m_{red}}} \left(\nu + \frac{1}{2} \right) \quad \text{Quantum number } \nu = 0, 1, 2$$

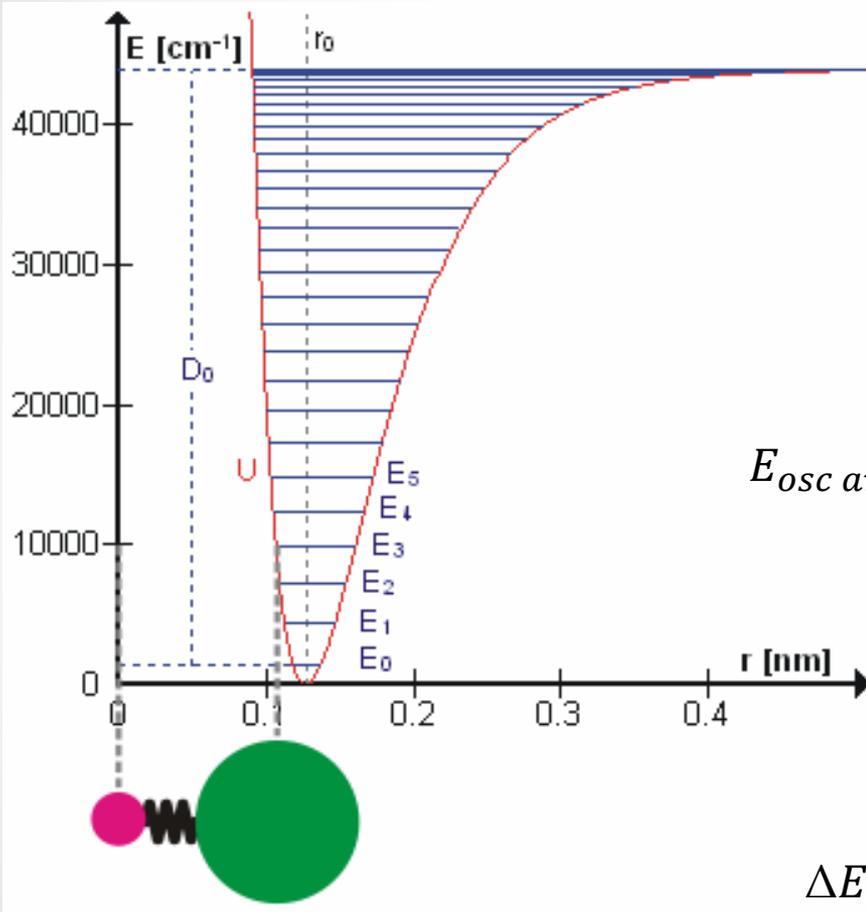
$$\Delta E_{osc} = E_{\nu+1} - E_{\nu} = \frac{h}{2\pi} \sqrt{\frac{k}{m_{red}}}$$

Selection rule $\Delta\nu = +/- 1$

Quantum harmonic and anharmonic oscillator



Anharmonic oscillators



$$U(q) = \frac{1}{2} f(q)q^2$$

Equation of potential energy of anharmonic oscillator

$$E_{osc\ anh} = \frac{h}{2\pi} \sqrt{\frac{k_0}{m_{red}}} \left(v + \frac{1}{2} \right) - \frac{hx}{2\pi} \sqrt{\frac{k_0}{m_{red}}} \left(v + \frac{1}{2} \right)$$

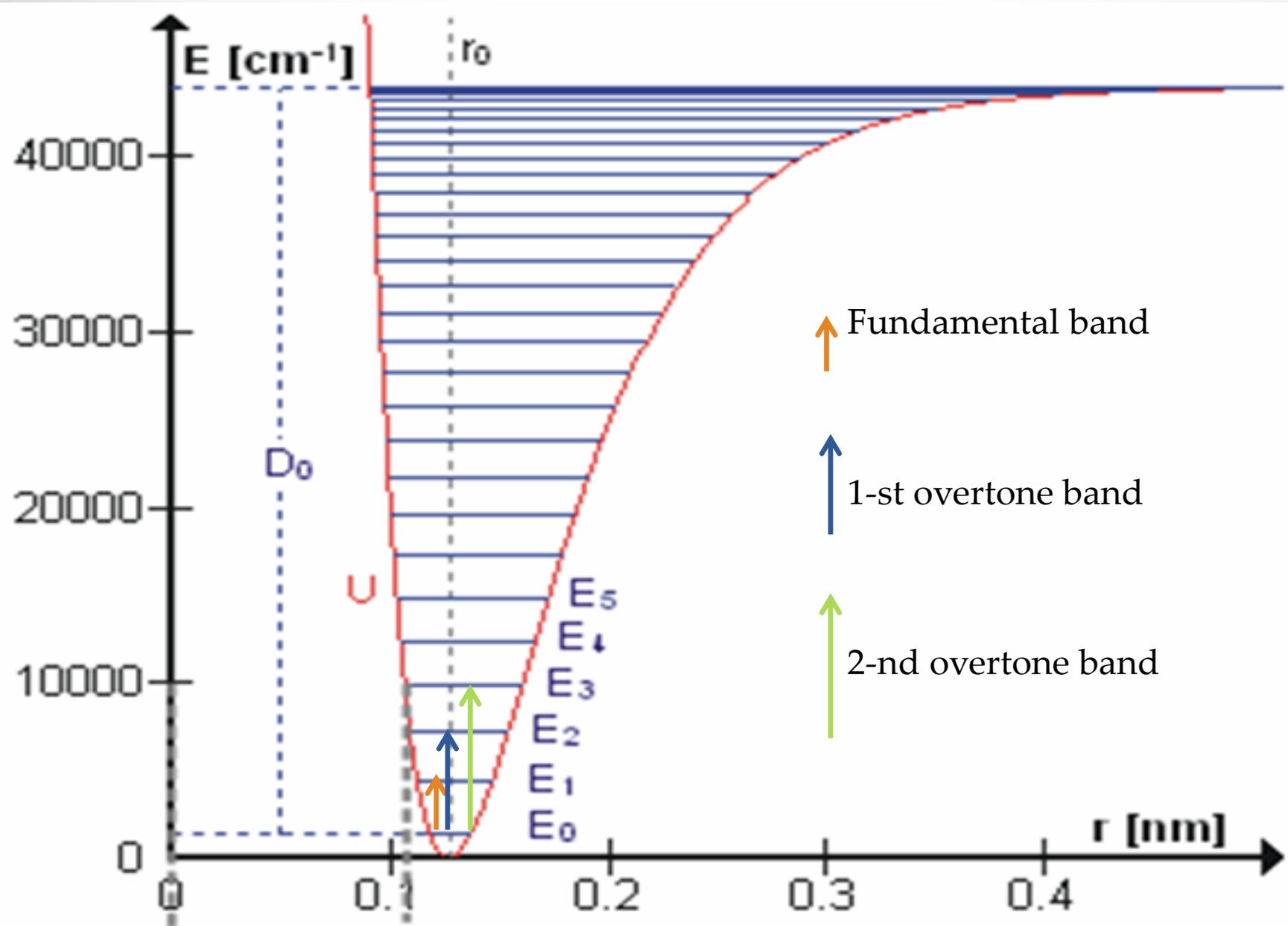
x - anharmonism factor

k_0 - constant strength for $v = 0$

$$\Delta E_{osc} = E_{v+1} - E_v = \frac{h}{2\pi} \sqrt{\frac{k_0}{m_{red}}} [1 - 2x(v + 1)]$$

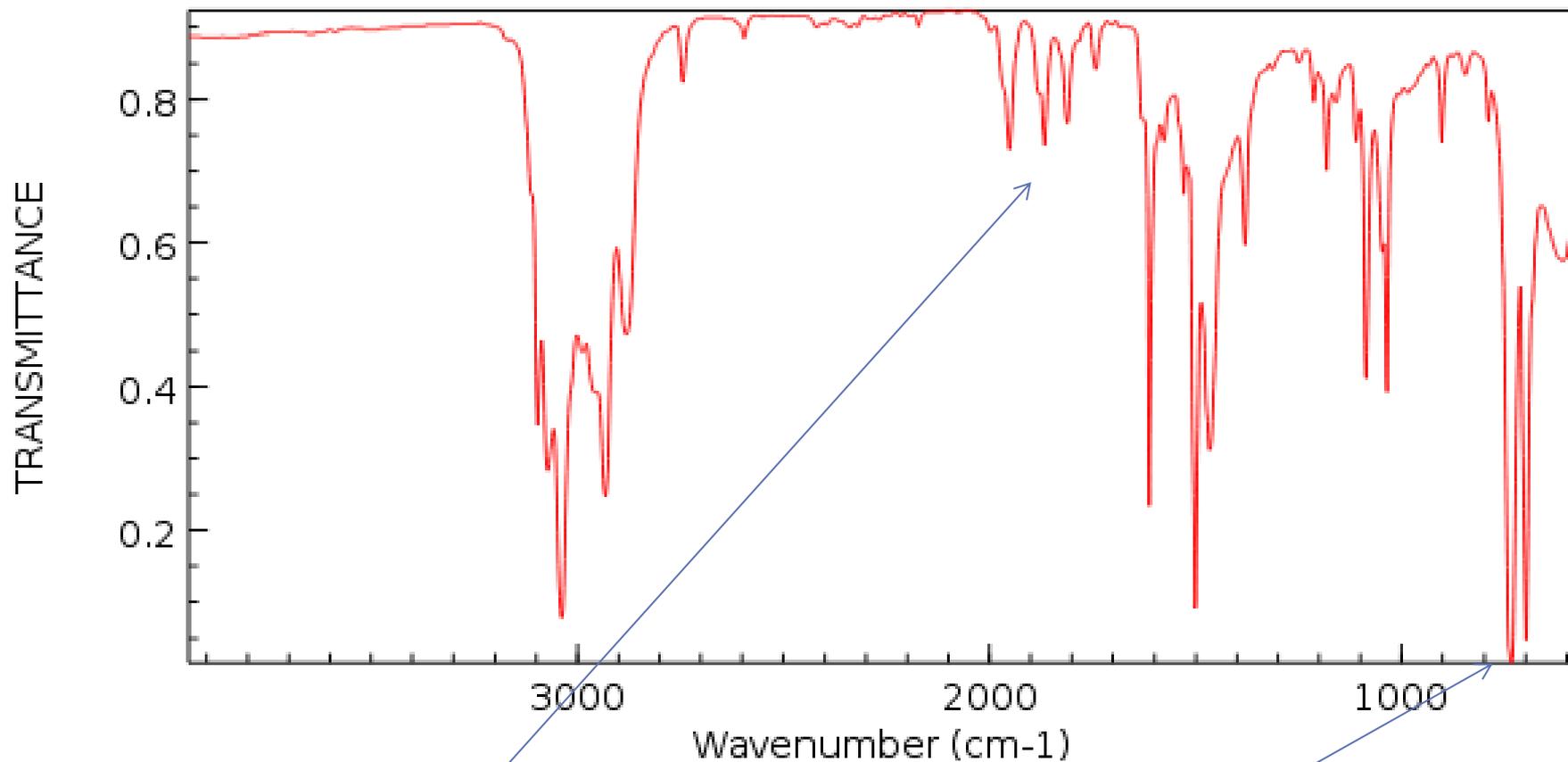
Selection rules $\Delta v = +/- 1, +/- 2, +/- 3, \dots$

Overtone



Overtone

TOLUENE
INFRARED SPECTRUM



Overtone or combinational bands

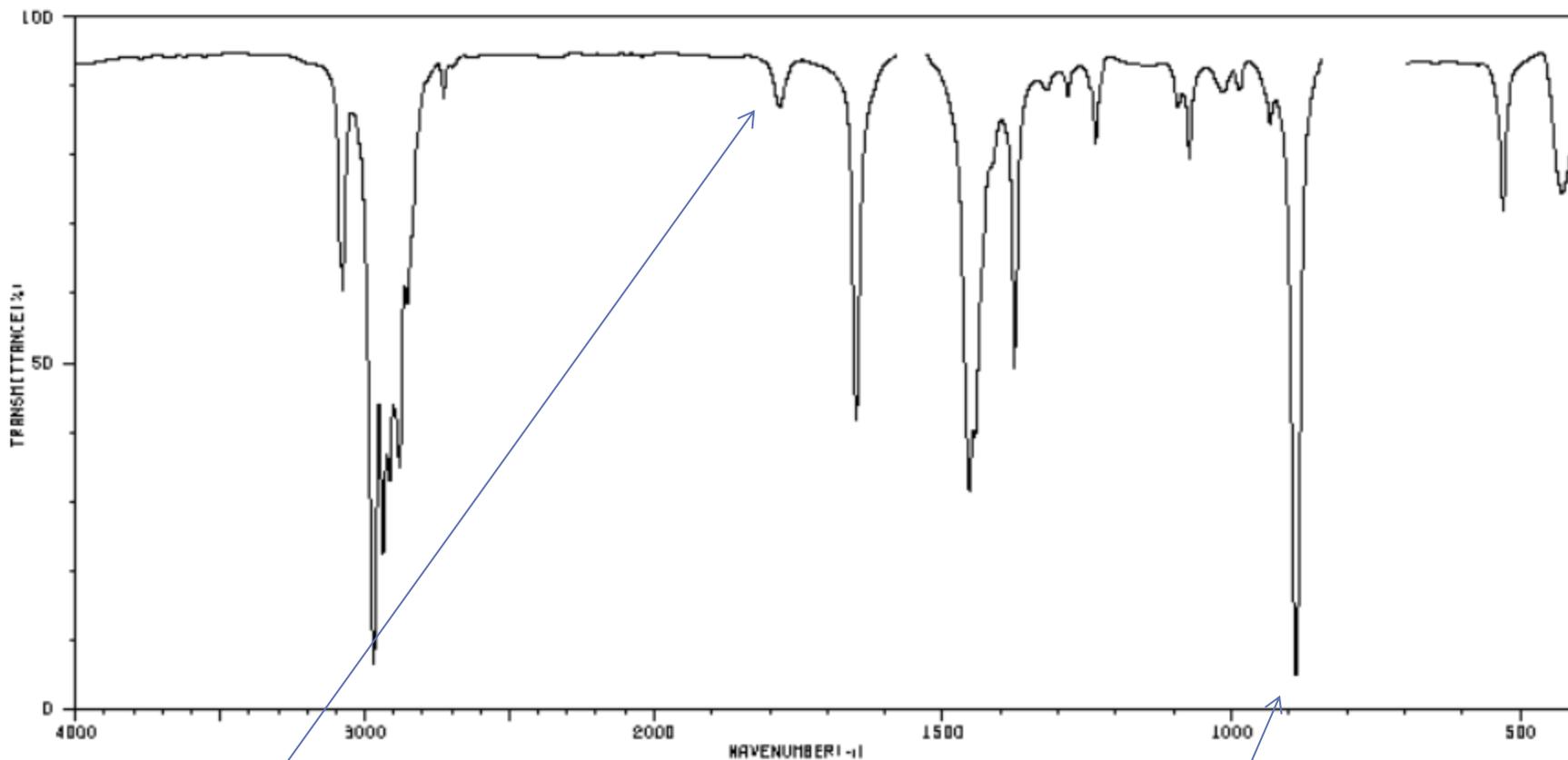
γ out of plane $C_{ar}-H$

Overtone

HIT-NO=1187 SCORE= () SDBS-NO=2176 IR-NIDA-07817 : CCL4 SOLUTION

2-METHYL-1-BUTENE

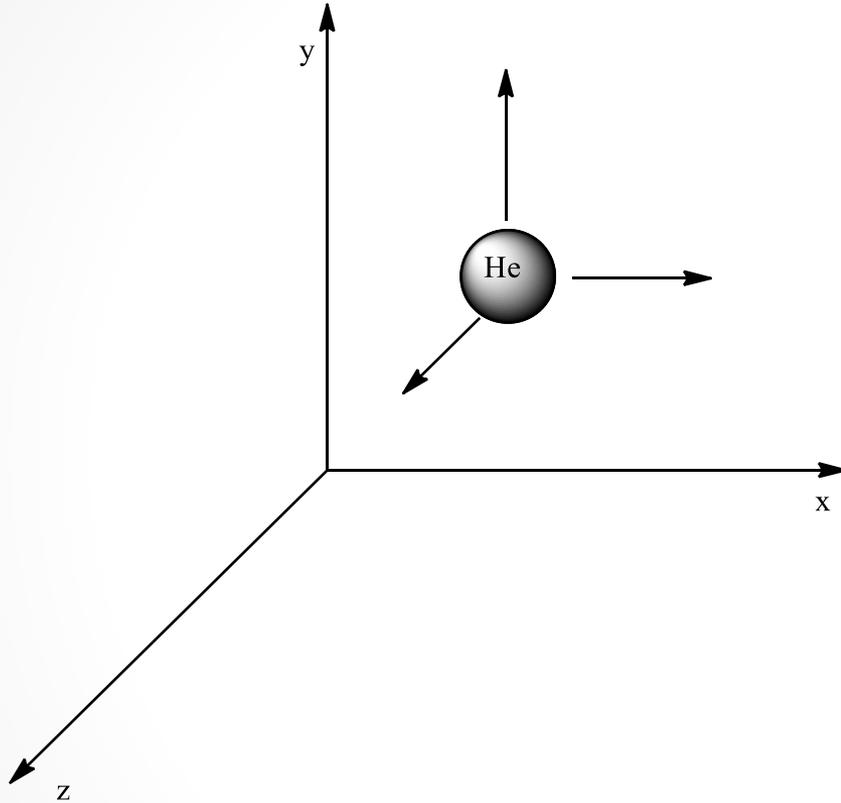
C5H10



● Overtone 1783 cm^{-1}

(γ) out of plane $\text{C}=\text{CH}_2$ 883 cm^{-1} ●

Degrees of freedom



Translational Energy

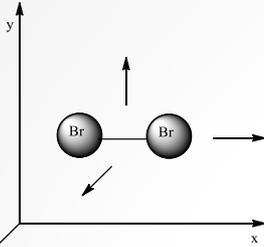
1 atom has three translational degrees of freedom

N – atomic molecule has $3N$ degrees of freedom

Degrees of freedom of molecule

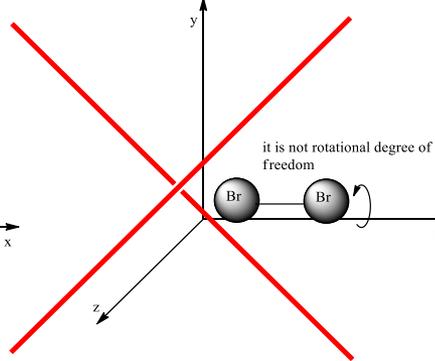
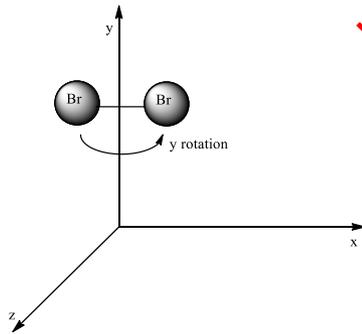
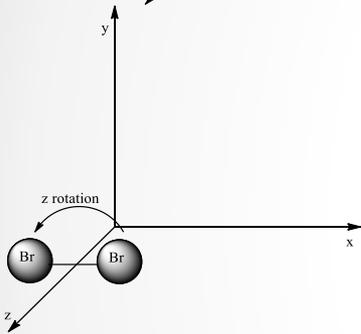
Translational Energy

Molecule also has three translational degrees of freedom



Rotational Energy

Two atomic (linear) molecule has two rotational degrees of freedom



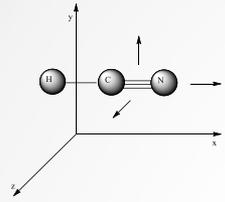
Vibrational Energy

Two atomic (linear) molecule has one vibrational degree of freedom



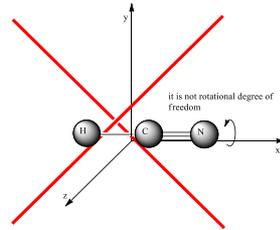
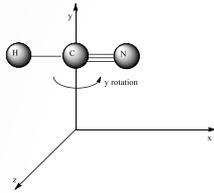
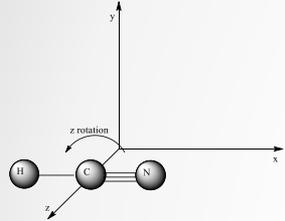
Number of vibrational degree of freedom is $(3N - 5)$ for linear molecule.

Degrees of freedom of molecule



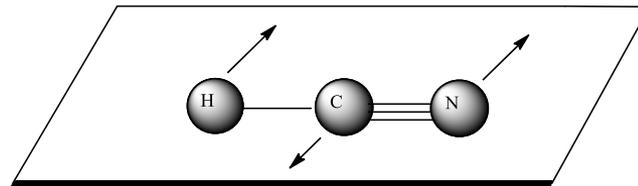
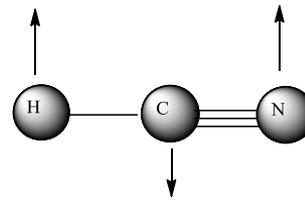
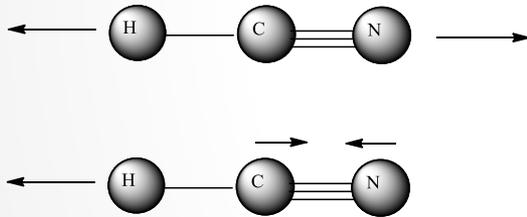
Translational Energy

3N atomic linear molecule also has **three** translational degrees of freedom



Rotational Energy

3N atomic linear molecule has **two** **Rotational** degrees of freedom

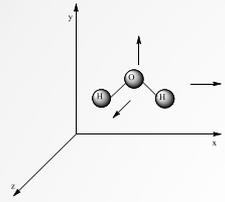


Vibrational Energy

Three atomic linear molecule has 4 vibrational degree of freedom

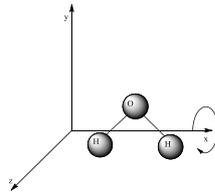
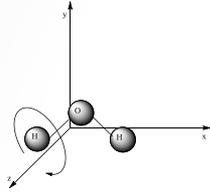
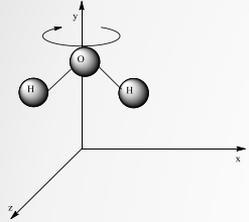
Number of vibrational degree of freedom is $(3N - 5)$ for linear molecule.

Degrees of freedom of molecule



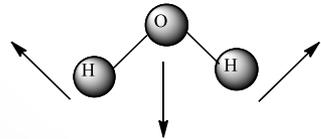
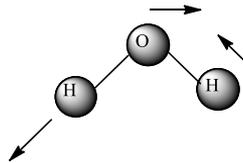
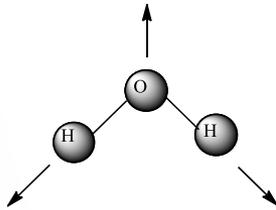
Translational Energy

3N atomic non-linear molecule also has **three** translational degrees of freedom



Rotational Energy

3N atomic non-linear molecule has **three** rotational degrees of freedom

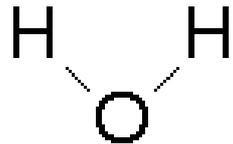


Vibrational Energy

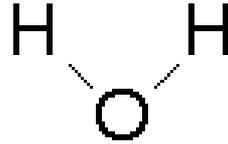
3N atomic non-linear molecule molecule has $(3N-6)$ vibrational degree of freedom

● Number of vibrational degree of freedom is $(3N - 6)$ for non-linear molecule ●

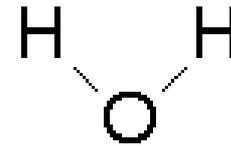
Vibrational modes - water



antisymmetric
stretch



symmetric
stretch



scissoring
bend

The angle between the bonds does not change

asymmetric stretch
 $\nu_{\text{as}} \text{OH}$ 3756 cm^{-1}

symmetric stretch
 $\nu_{\text{s}} \text{OH}$ 3657 cm^{-1}

The angle
between bonds change

Scissoring bend
 $\delta_{\text{s}} \text{HOH}$ 1595 cm^{-1}

Vibrational modes - classification

Vibration with change of bond length

-- stretching vibration ν_s and ν_{as} (vibration in plane)

Vibration with change of an angle between the bonds

-- in-plane scissoring (bending) δ_s

-- in-plane bending (rocking) ρ

-- out-of-plane bending (wagging) ω

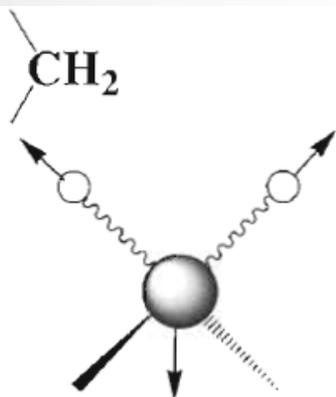
-- out-of-plane bending (twisting) τ

Classification in terms of symmetry (symmetric / asymmetric)

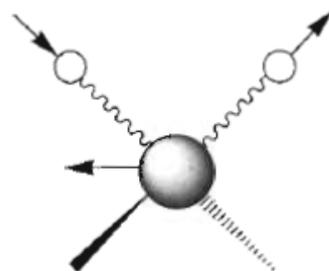
Classification in terms of plane of vibrations (in plane / out of plane (γ))

Greek small letters ν (Nu), δ (Delta), ρ (Rho), ω (Omega), τ (Tau), γ (Gamma)

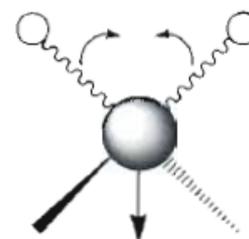
Vibrational modes for CH₂



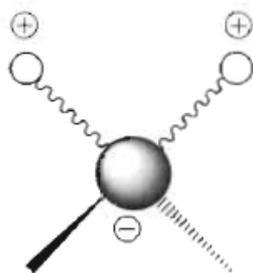
Symmetrical stretching (ν_s CH₂)
~2853 cm⁻¹



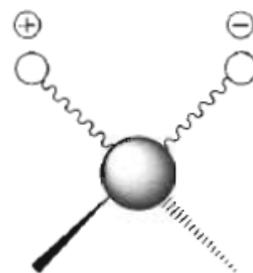
Asymmetrical stretching (ν_{as} CH₂)
~2926 cm⁻¹



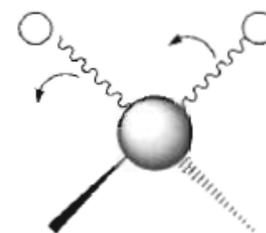
In-plane bending or scissoring (δ_s CH₂)
~1465 cm⁻¹



Out-of-plane bending or wagging (ω CH₂)
1350-1150 cm⁻¹

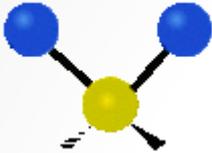


Out-of-plane bending or twisting (τ CH₂)
1350-1150 cm⁻¹

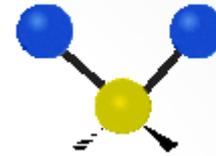


In-plane bending or rocking (ρ CH₂)
~720 cm⁻¹

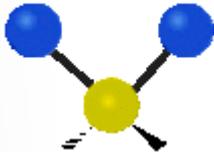
Vibrational modes for CH₂



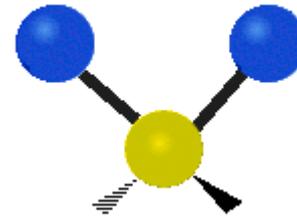
Symmetrical stretching ν_s



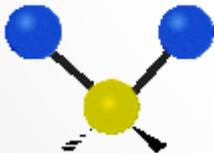
Asymmetrical stretching ν_{as}



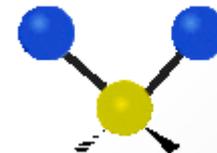
In-plane scissoring δ_s



In-plane bending ρ



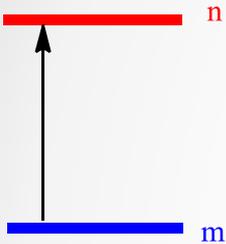
Out-of-plane bending (wagging) ω



Out-of-plane bending (twisting) τ

Probability of vibrational transition

Intensity of absorption



$$I \approx |d_{mn}|^2$$

Intensity of absorption is proportional to square of transition moment (transition dipole moment) d_{mn}
- transition between an initial state m and a final state n .

d_{mn} transition moment between wave functions Ψ_m and Ψ_n

$$d_{mn} = \int_{-\infty}^{+\infty} \Psi_m^* \hat{\mu} \Psi_n dq$$

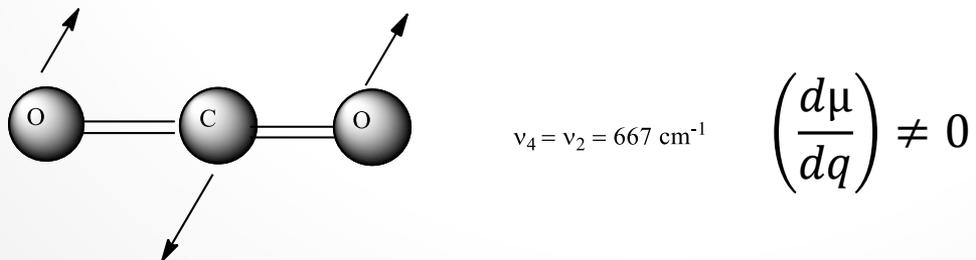
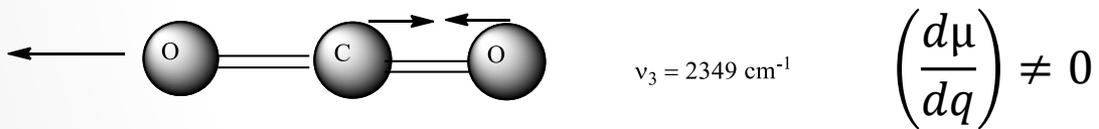
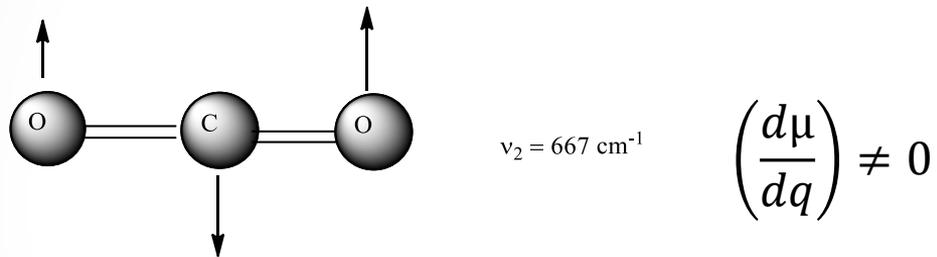
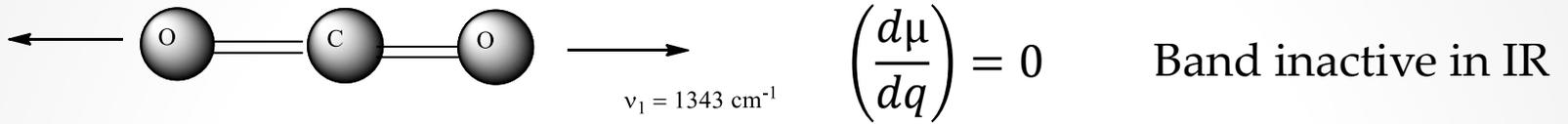
$\hat{\mu}$ - dipole moment operator
 q - position

$$I \approx \left(\frac{d\mu}{dq} \right)_{q=0}^2$$

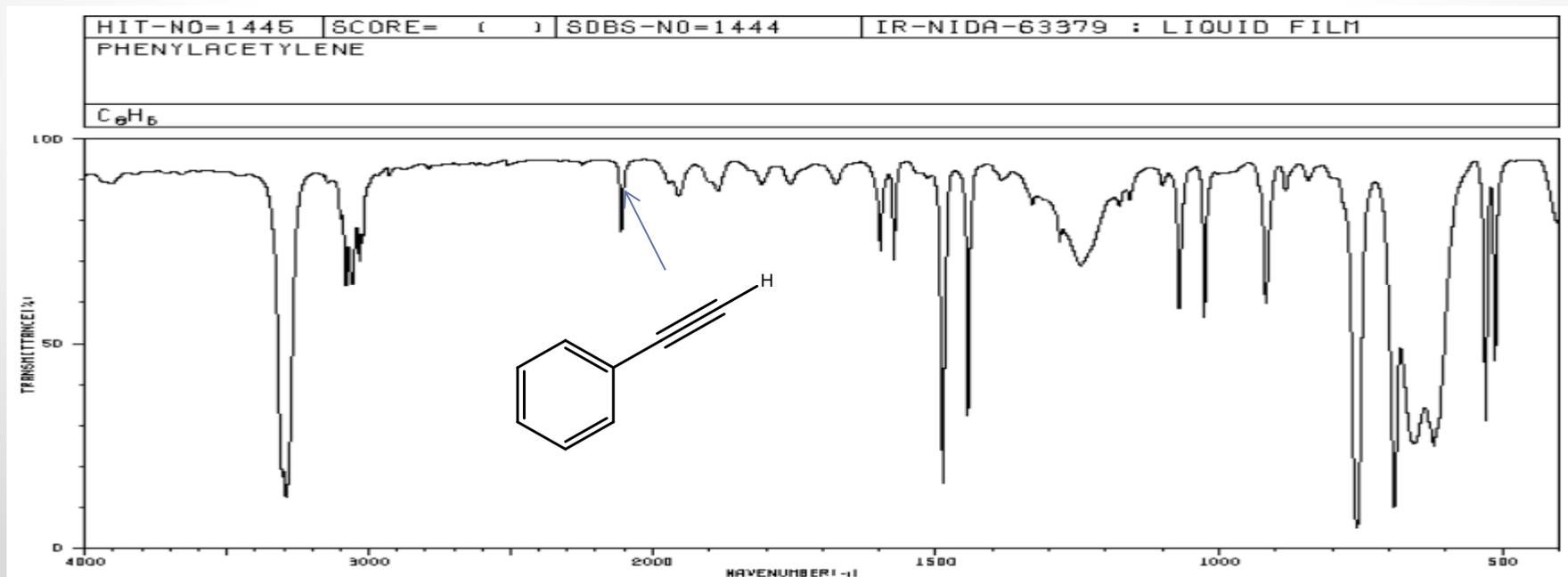
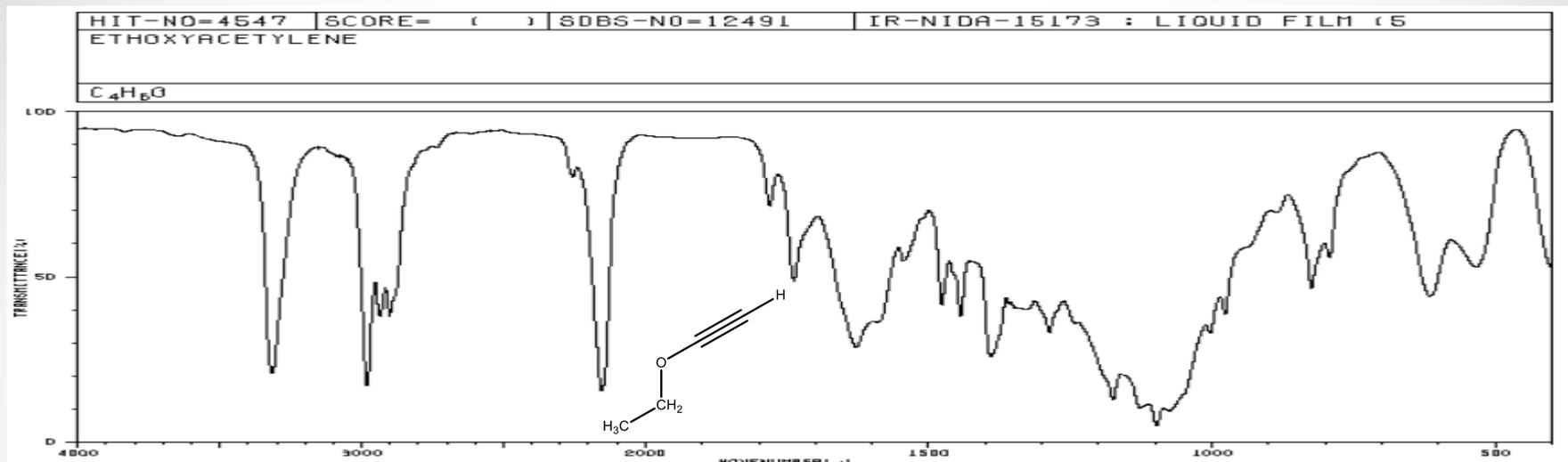
Intensity of absorption is proportional to square of the derivative of the dipole moment with respect to the normal coordinate of vibration

If the $\left(\frac{d\mu}{dq} \right)_{q=0} = 0$ electromagnetic wave is not absorbed

Vibrational modes of CO₂



Changes of dipole moment -vibrations

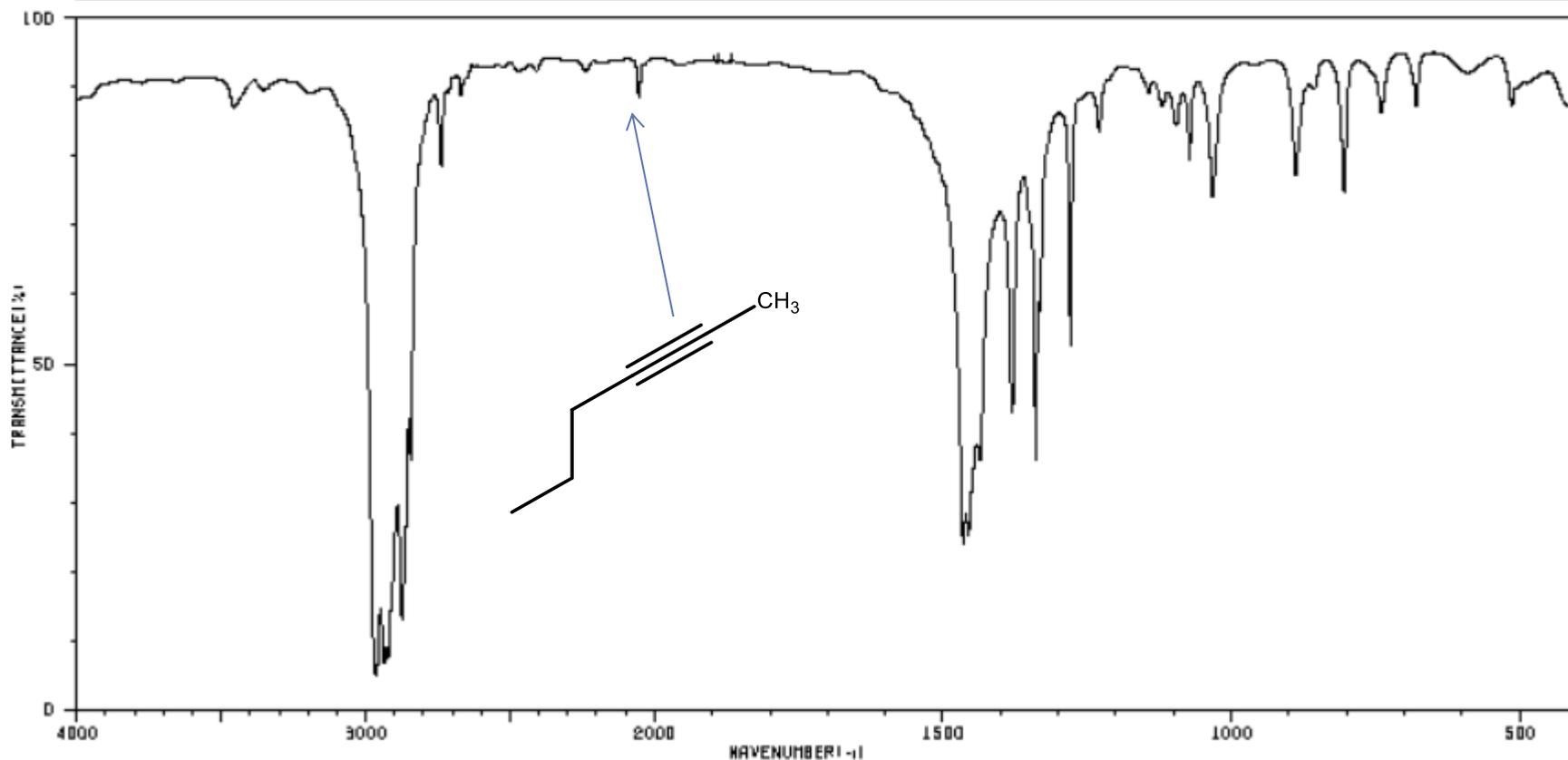


Vibrations - changes of dipol moment

HIT-NO=4049 SCORE= () SDBS-NO=10231 IR-NIDA-02550 : LIQUID FILM

2-HEXYNE

C_6H_{10}



Classification of bands

1. Fundamental bands

excitation from ground state to the lowest-energy excited state.



2. Overtone Bands

excitation from ground state to higher energy excited states,



3. Combination Bands

excitation is a sum of the two interacting bands $\nu_{\text{combination}} = \nu_1 + \nu_2$.

4. Difference Bands

excitation is a difference between the two interacting bands $\nu_{\text{dif}} = \nu_1 - \nu_2$.

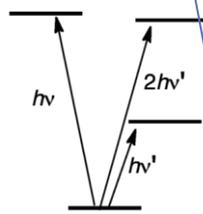
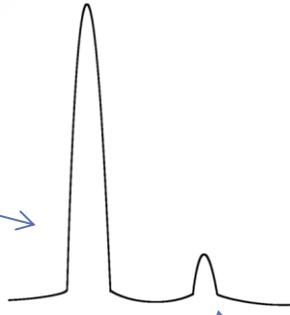
(Simultaneous absorption on one oscillator and emission from the second oscillator)

5. Fermi Resonance

Coupling of a fundamental vibration with an overtone

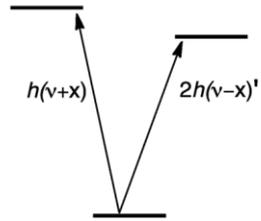
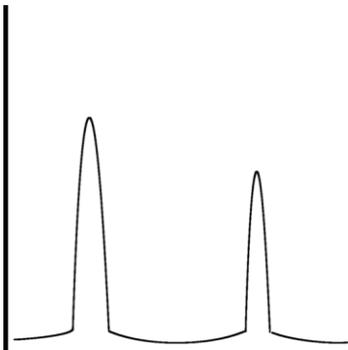
Fermi Resonance

Fundamental vibration



Overtone

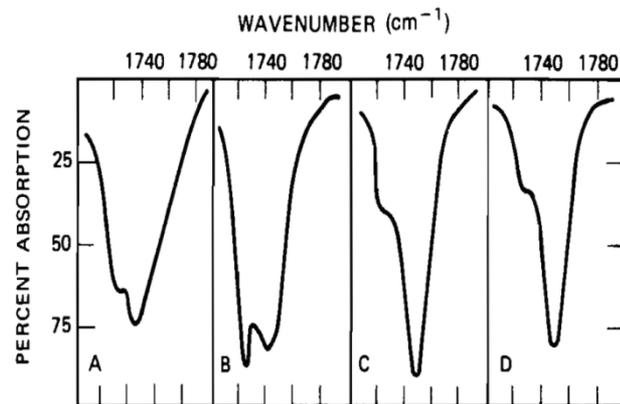
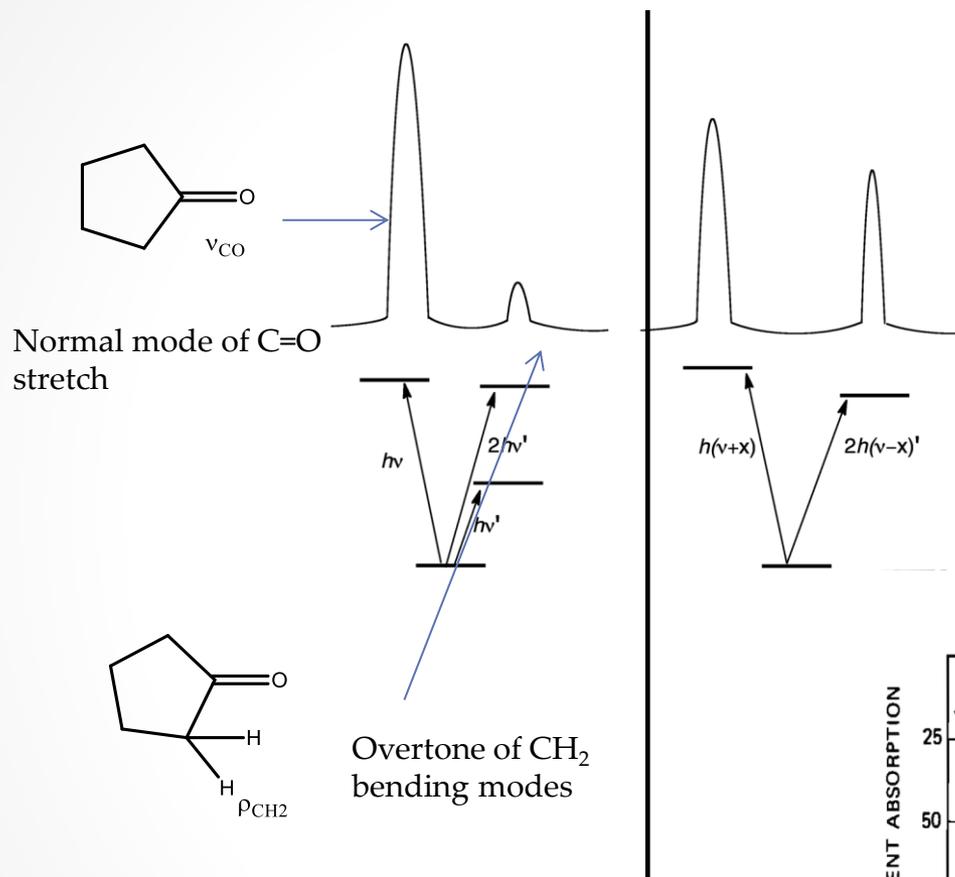
Before Fermi resonance



Resulting bands

After Fermi resonance

Fermi Resonance - ketones



IR spectrum of cyclopentanone in:
 A. CCl₄ B. CS₂ C. CHCl₃ D. Thin film

Fermi Resonance – acyl chlorides

