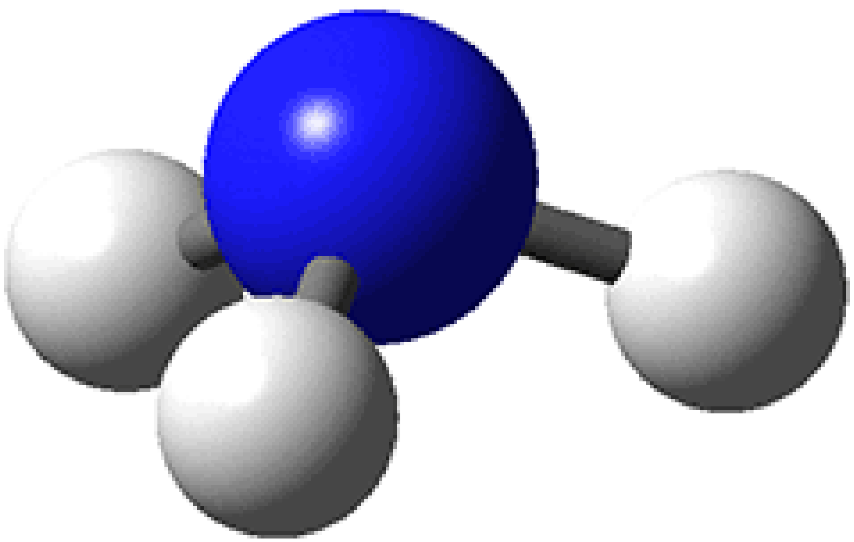
IR – spectroscopy Part III (Theory)

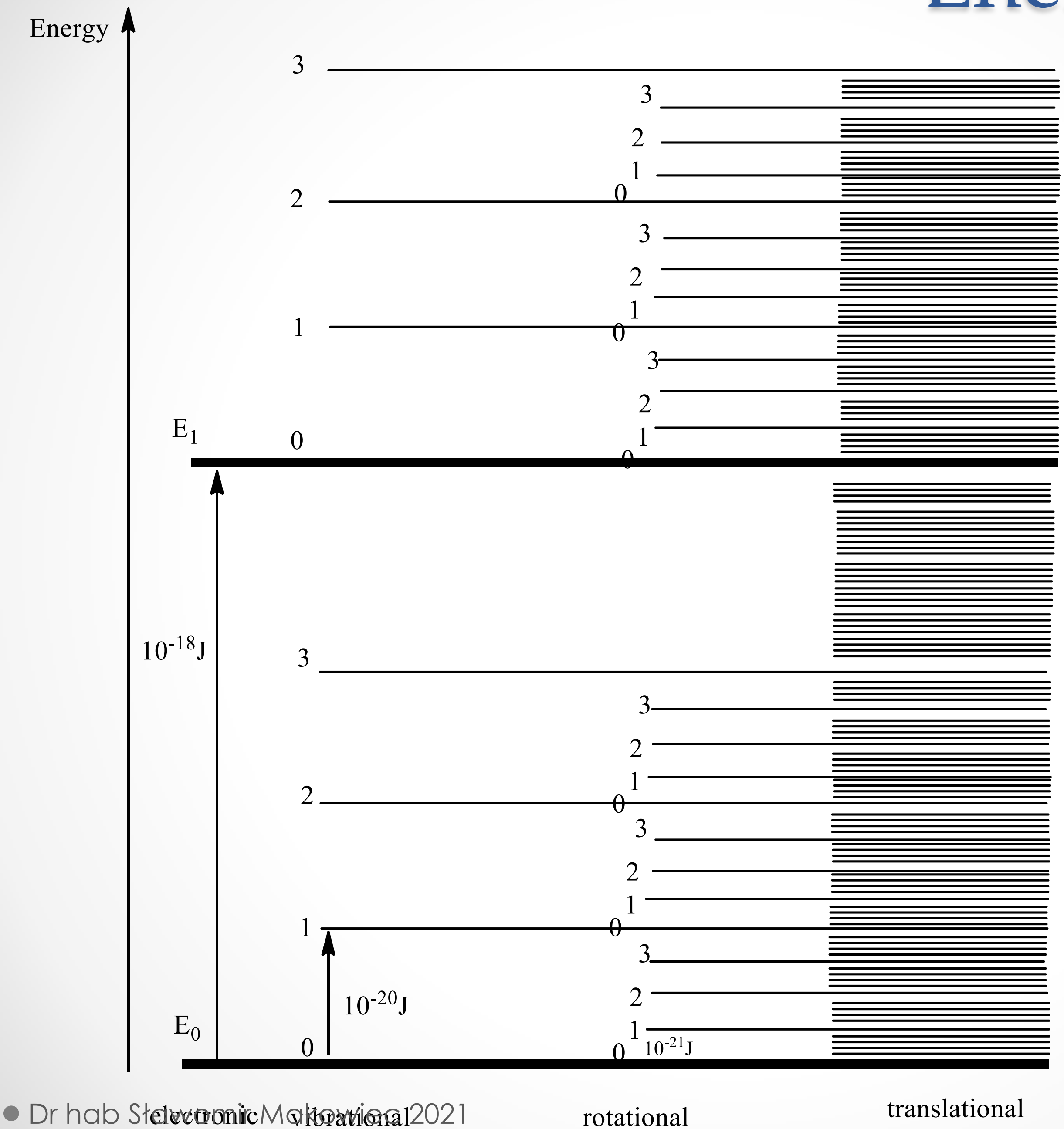


Department of Organic Chemistry
Dr hab. Sławomir Makowiec prof. PG

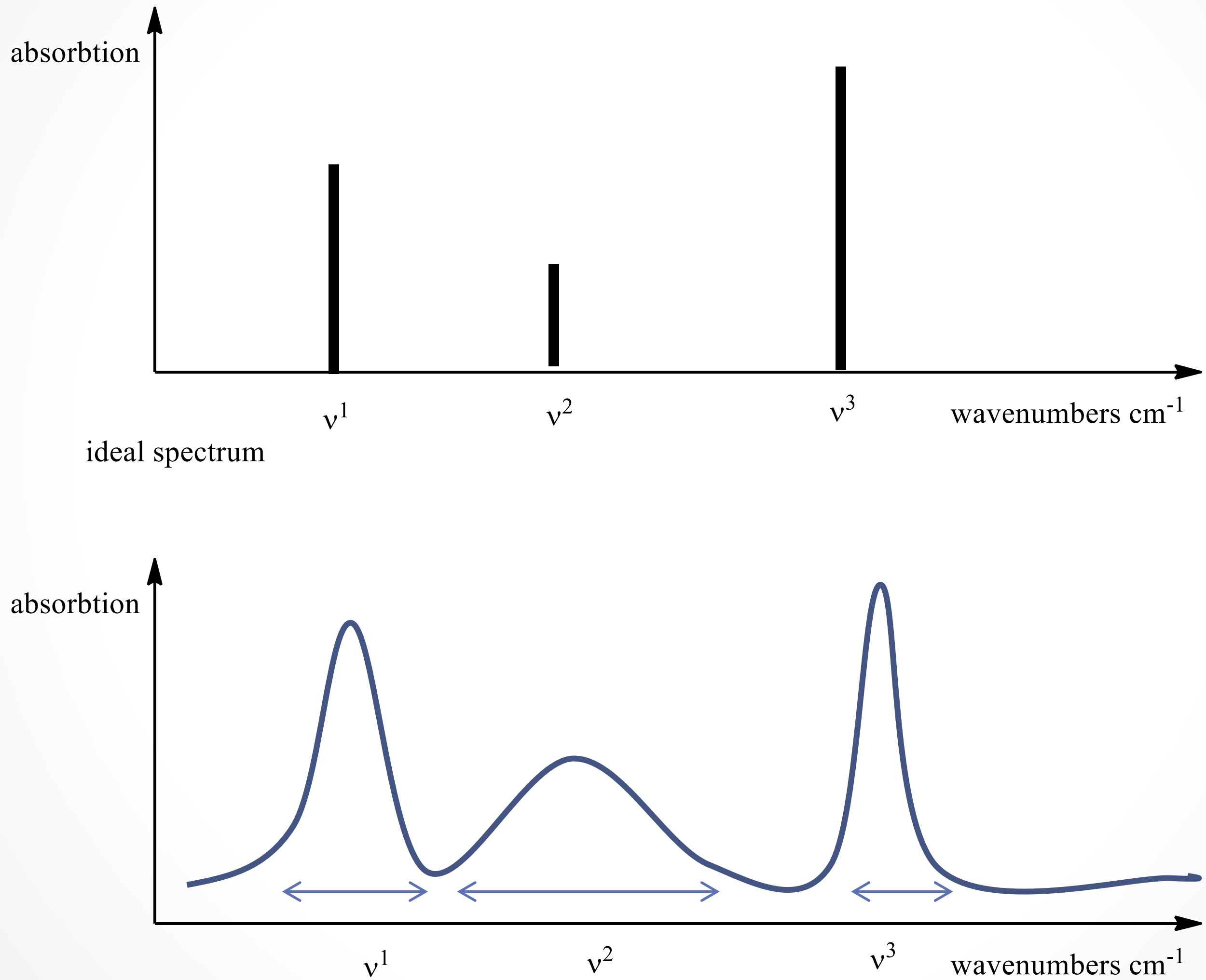
Electromagnetic spectrum

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 µm	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



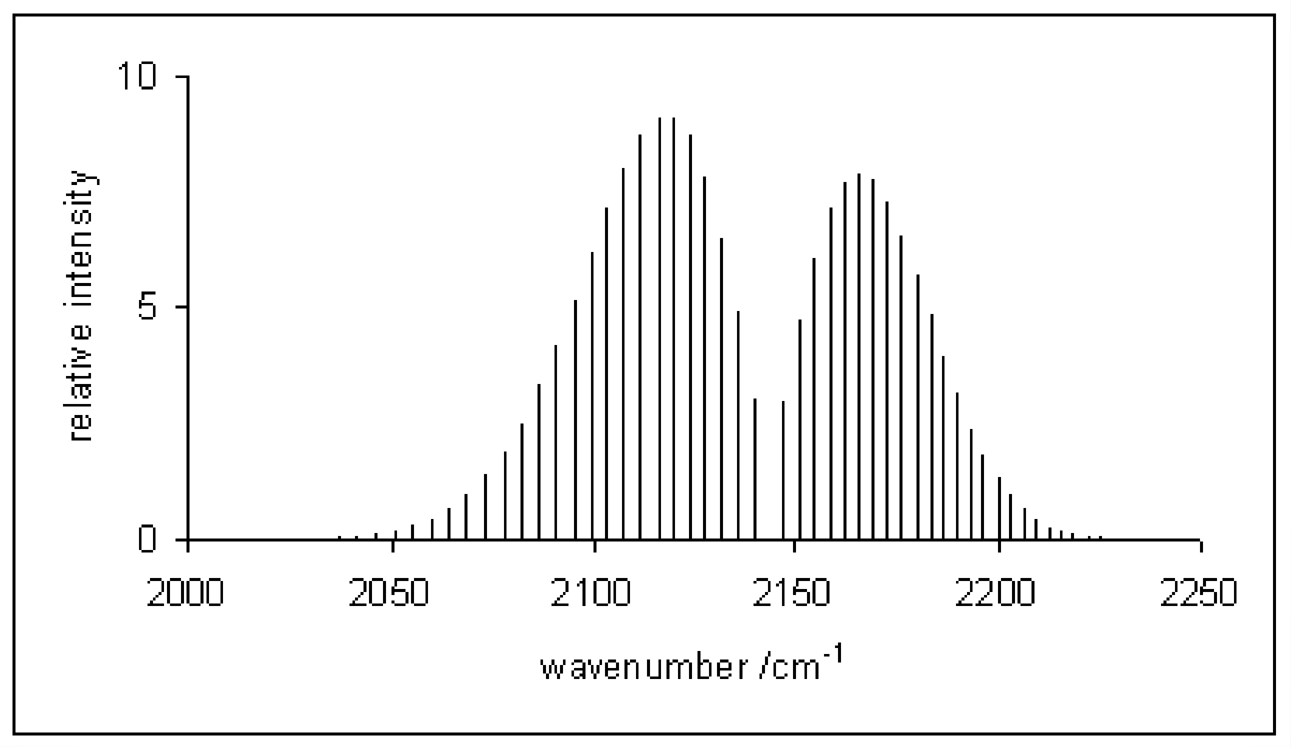
Width and shape of spectral lines



ideal spectrum

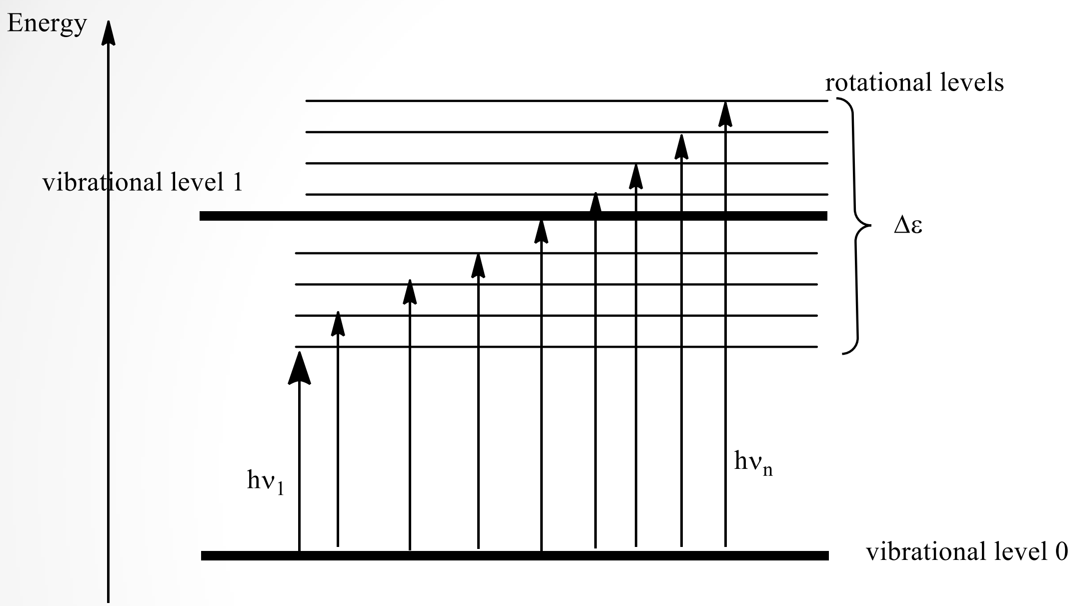
real spectrum

Rotational – vibrational spectrum



Simulation of vibration-rotation line spectrum of carbon monooxide

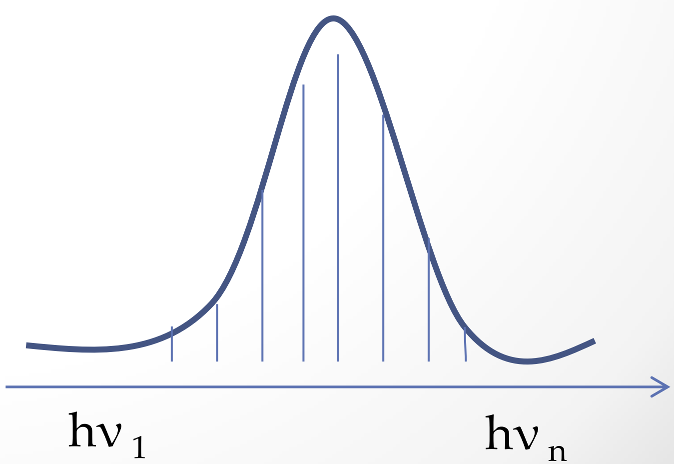
Line broadening



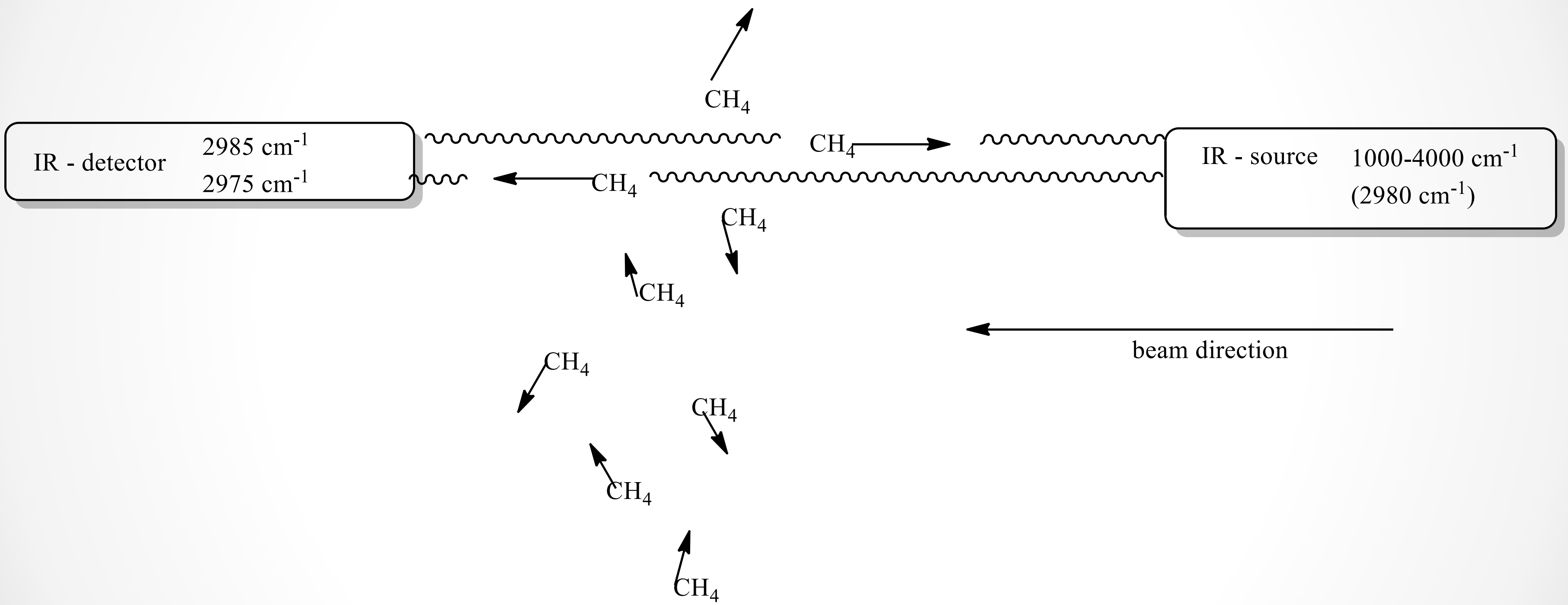
$\Delta\varepsilon$ = width of spectral line

Heisenberg's uncertainty principle
τ – particle lifetime on the energy level
$\Delta\varepsilon$ - width of spectral line

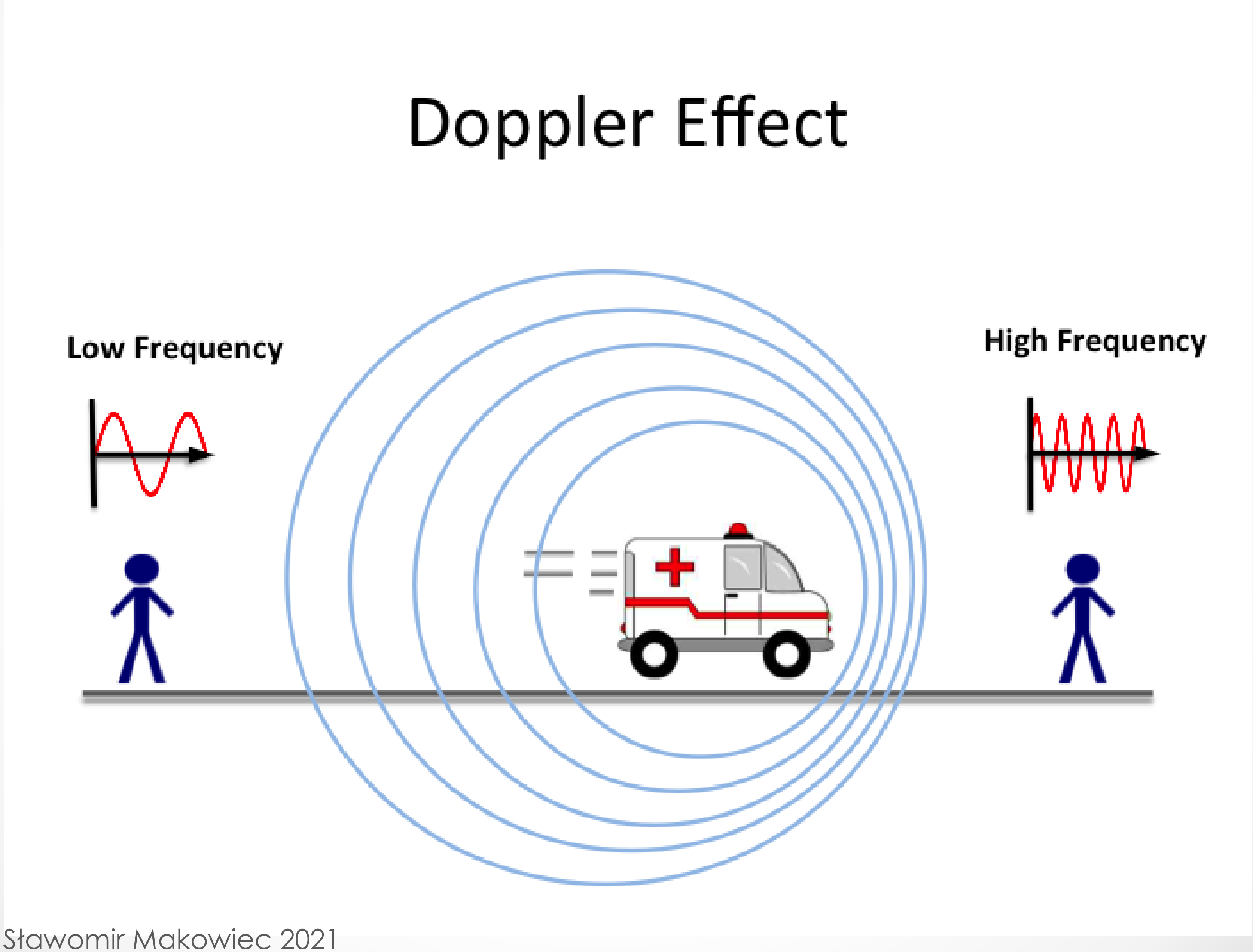
$\Delta\varepsilon\ \tau \geq h / 2\pi$



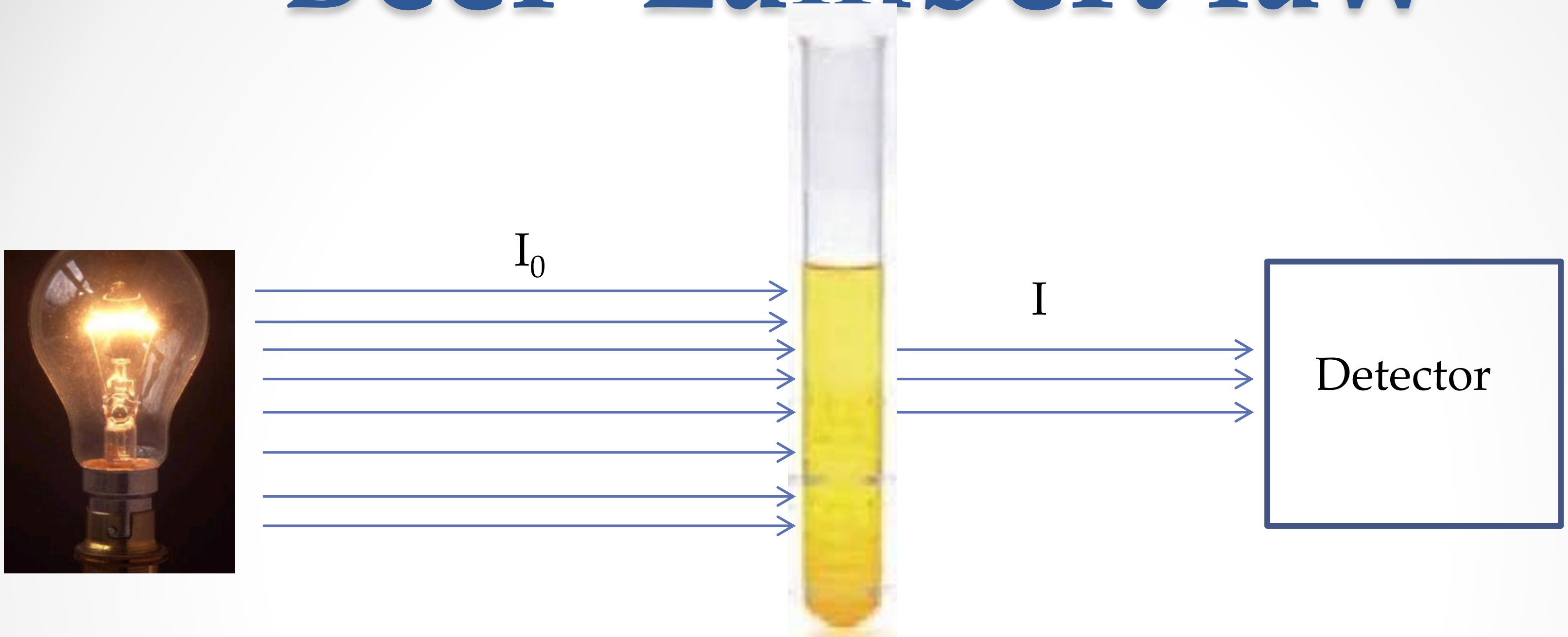
Line broadening – Doppler effect



Doppler effect



Beer–Lambert law

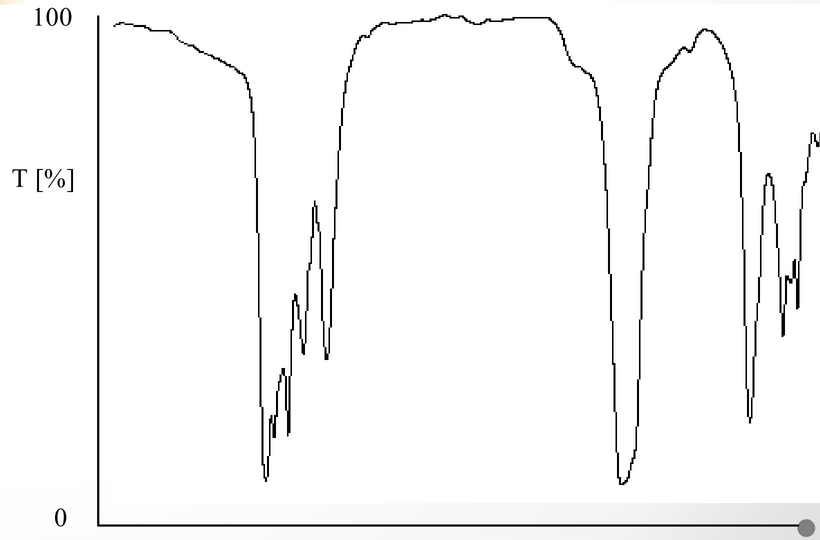


Transmitance

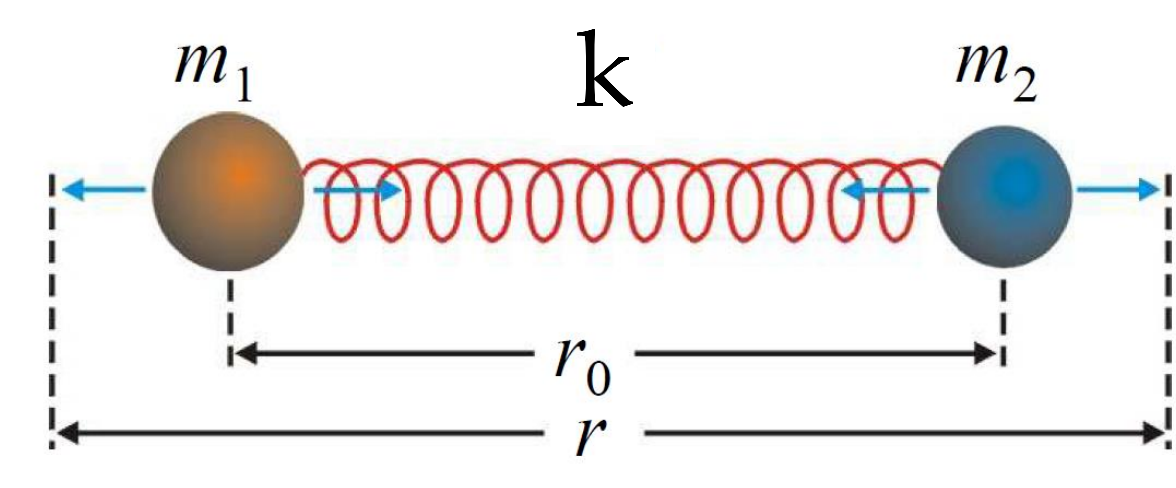
$$T = \frac{I}{I_0}$$

Absorbance

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



Harmonic oscillator

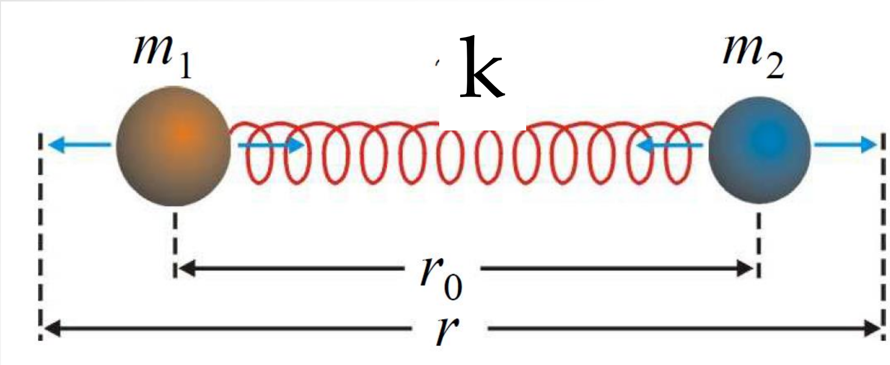


$$F = -kq$$

F = Force acting on the system
k = constant strength
q = r - r_0
r_0 position at equlibrum
r position at the moment

q (t) = Qcos2πνt
Q = amplitude
ν = frequency

Reduced mass



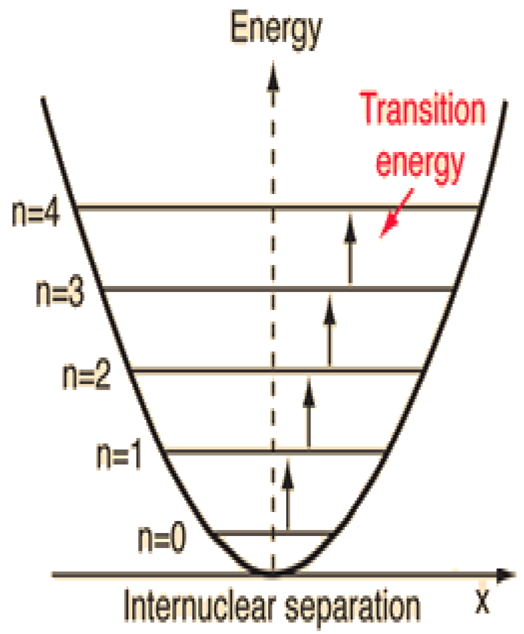
$$\frac{1}{m_{red}} = \frac{1}{m_1} + \frac{1}{m_2}$$

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

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

Bond Energies	Reduced mass
CH_3—CH_3 368 KJ/mol	(12*12)/(12+12) = 6
CH_3—H 431 KJ/mol	(12*1)/(12+1) = 0.92
CD_3—D 442 KJ/mol	(12*2)/(12+2) = 1 .71

Quantum harmonic oscillator



Schrodinger Equation for harmonic oscillator

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

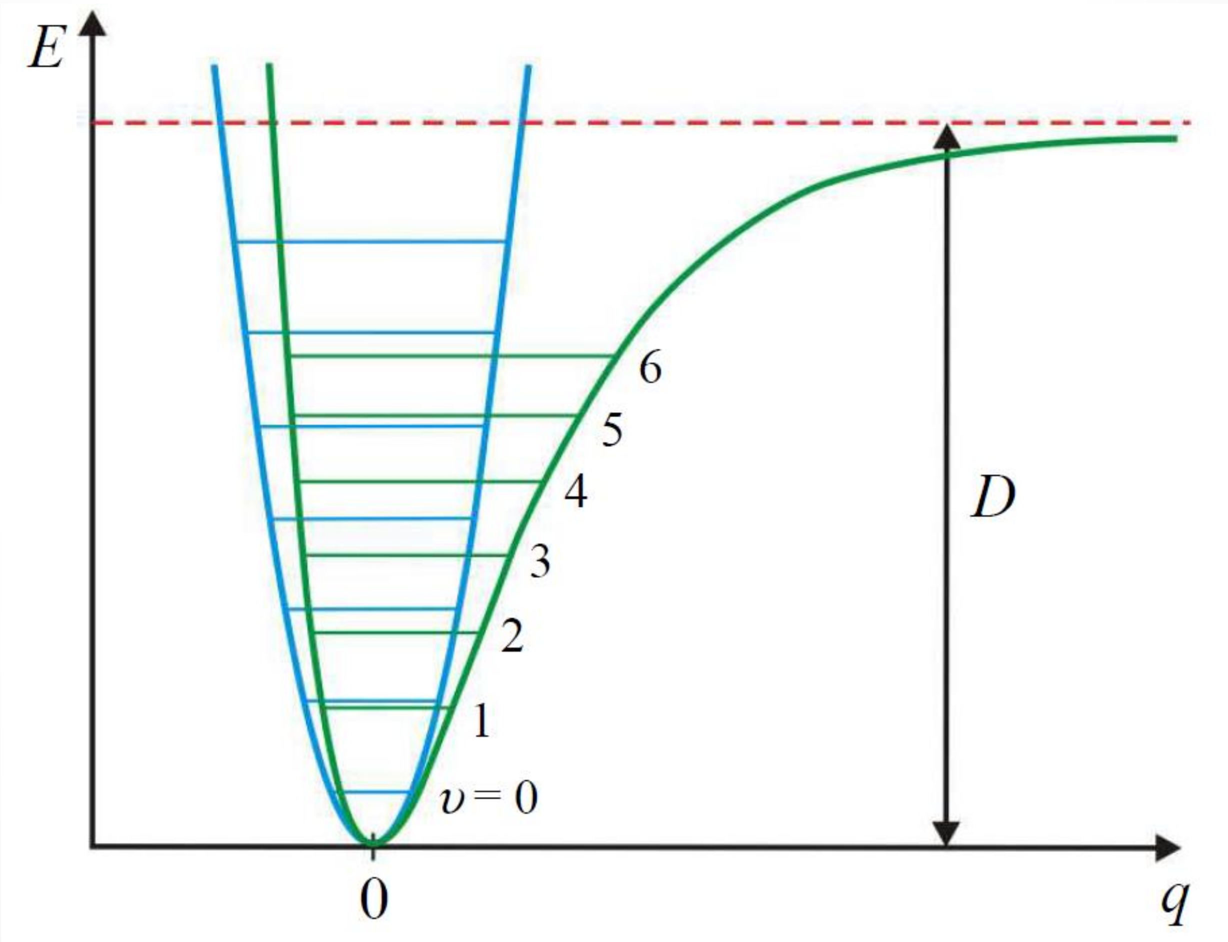
$$E_{osc} = \frac{h}{2\pi}\sqrt{\frac{k}{m_{red}}}\left(\nu+\frac{1}{2}\right)$$

Quantum number
$\upsilon = 0, 1, 2$

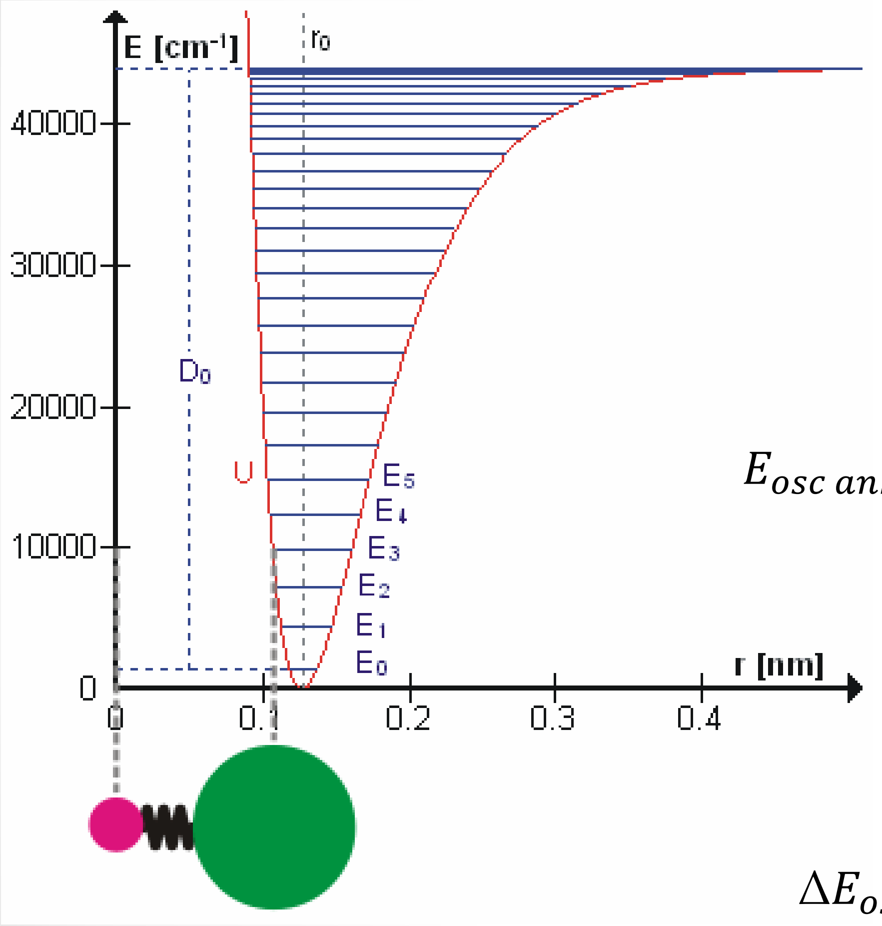
$$\Delta E_{osc} = E_{\nu+1} - E_{\nu} = \frac{h}{2\pi}\sqrt{\frac{k}{m_{red}}}$$

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

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

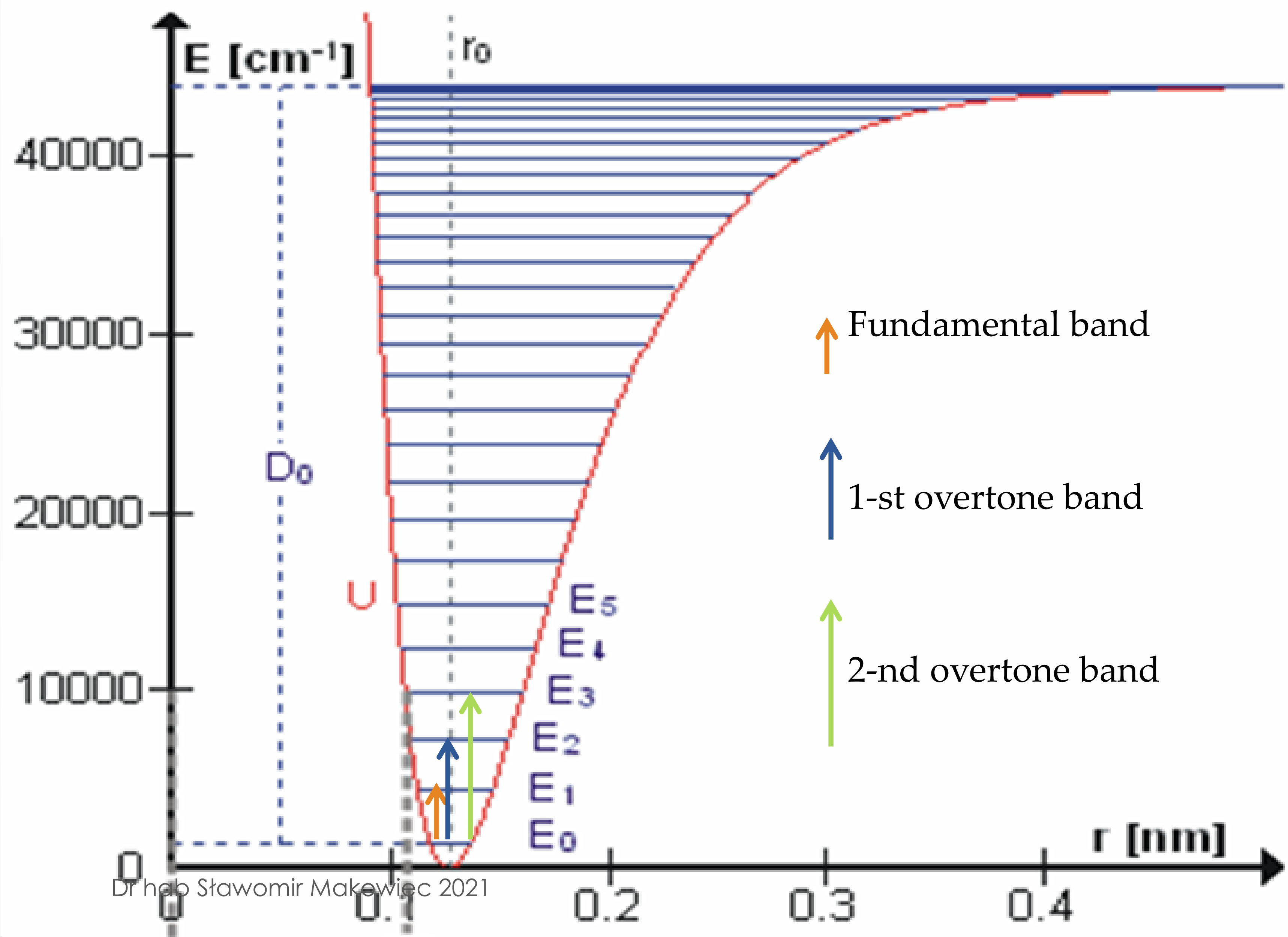
x -anharmonism factor

k_0 - constant strength for $\upsilon = 0$

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

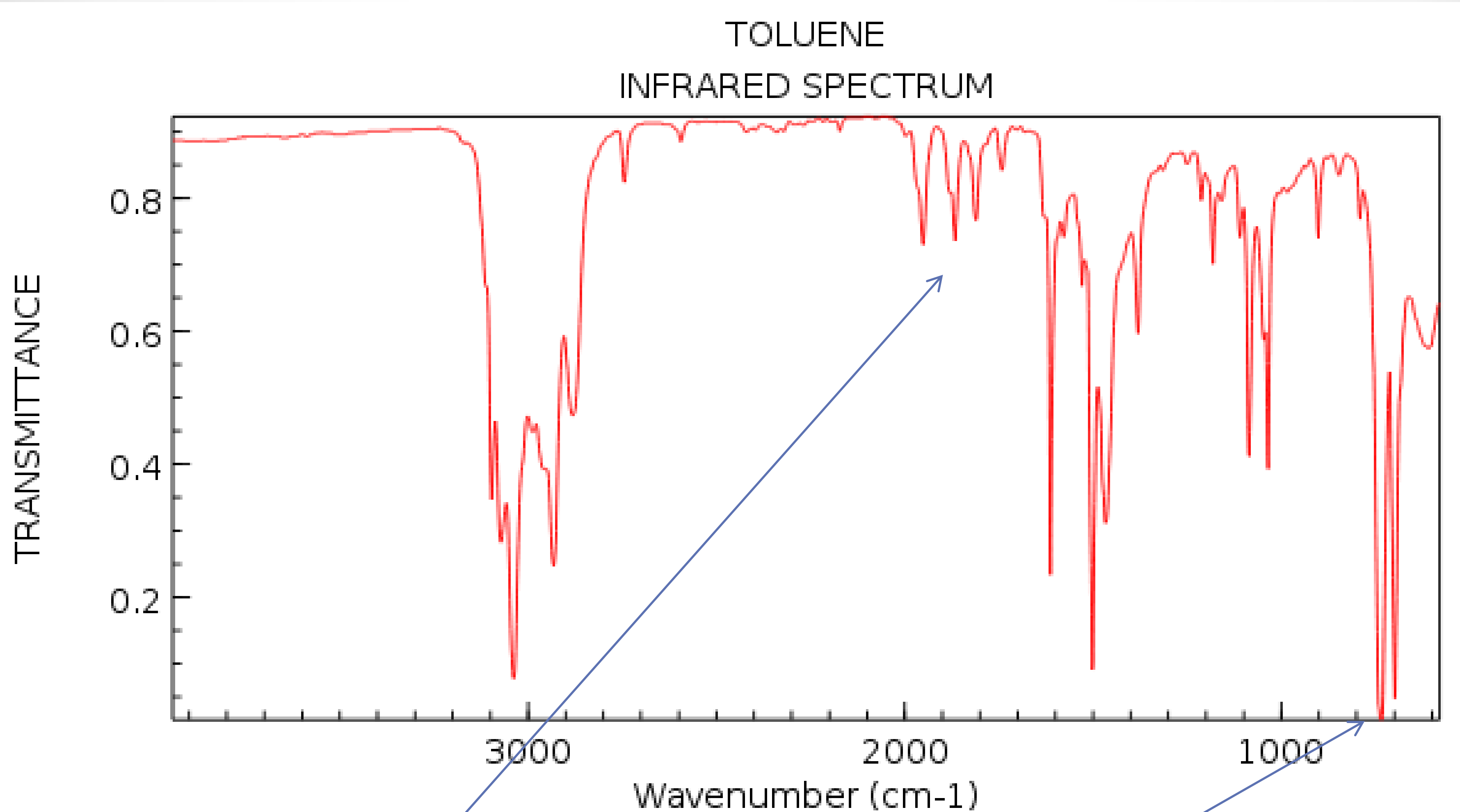
Selection rules Δν = +/- 1, +/-2, +/-3, ….

Overtones



E [cm⁻¹]
r₀
40000
30000
20000
10000
0
D₀
U
E₅
E₄
E₃
E₂
E₁
E₀
r [nm]
0
0.1
0.2
0.3
0.4
Fundamental band
1-st overtone band
2-nd overtone band

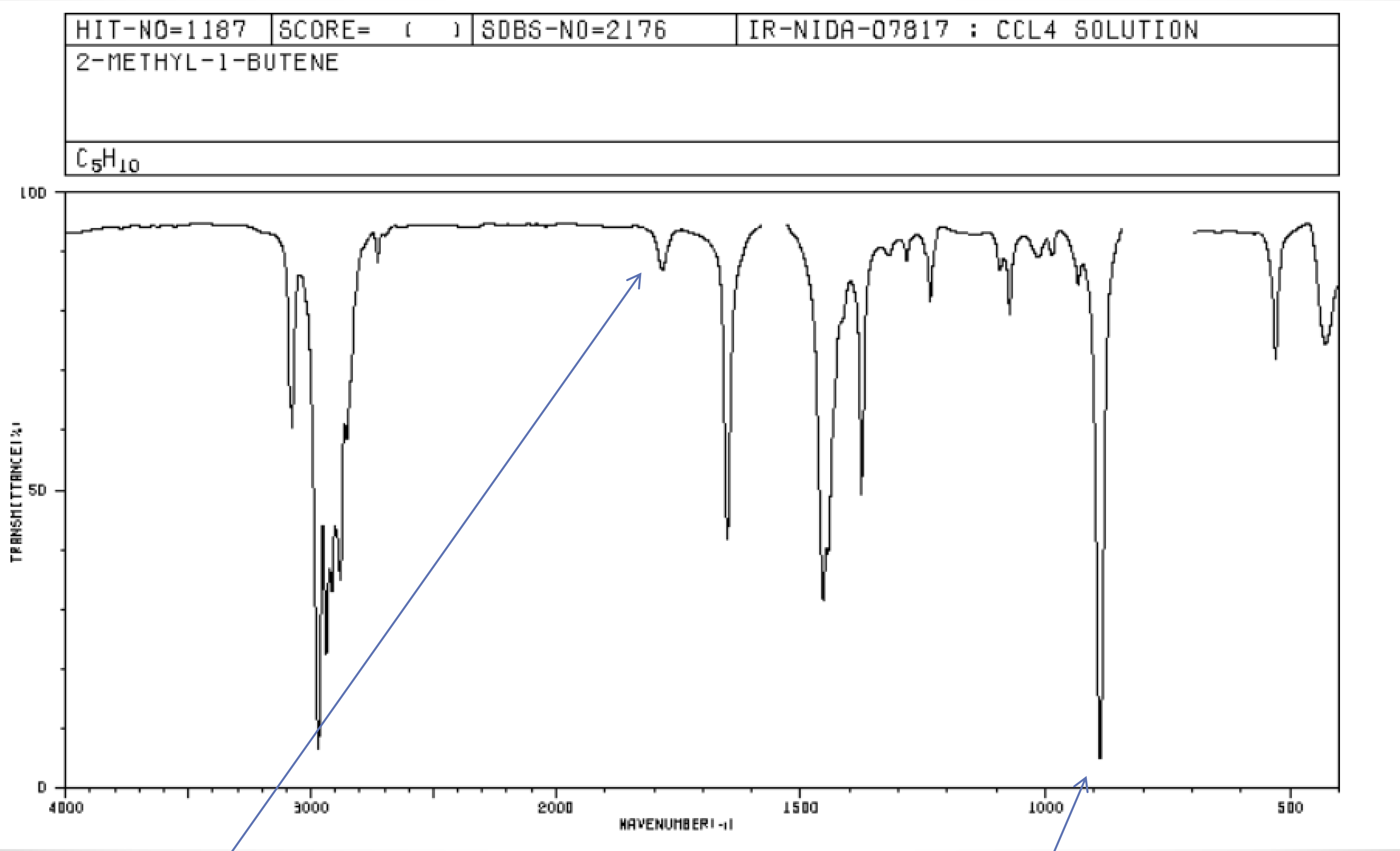
Overtones



Overtones or combinational bands

γ out of plane C_{ar} – H

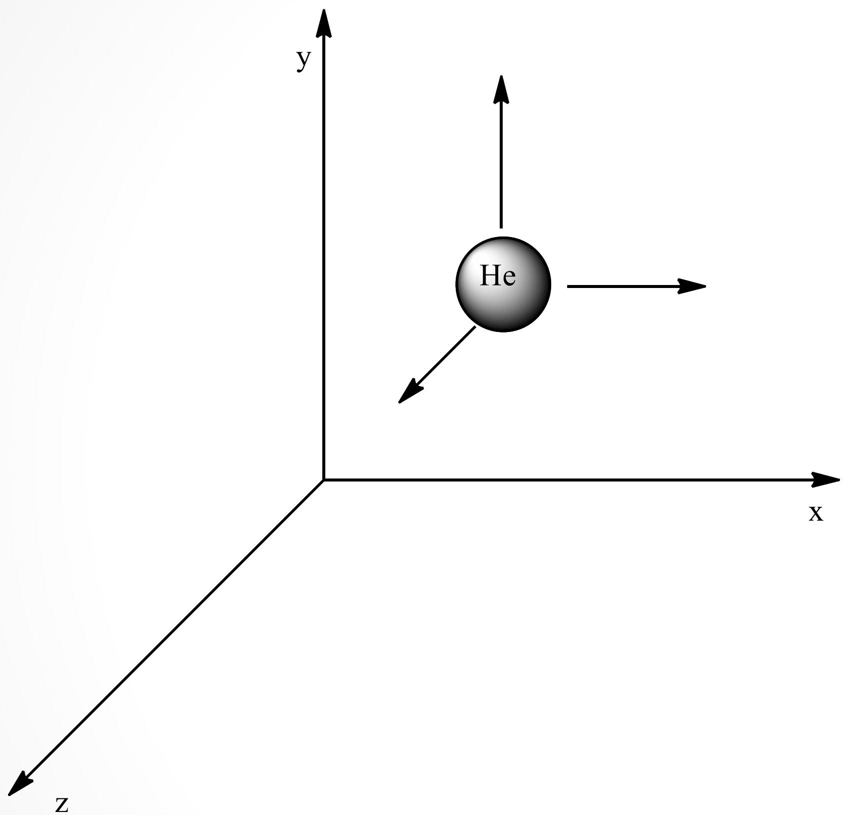
Overtones



Overtone 1783 cm^{-1}

(γ) out of plane $C{=}CH_2$ 883 cm^{-1}

Degrees of freedom

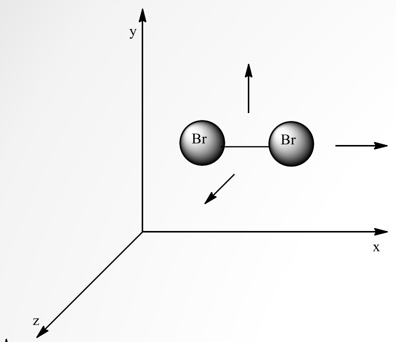


Translational Energy

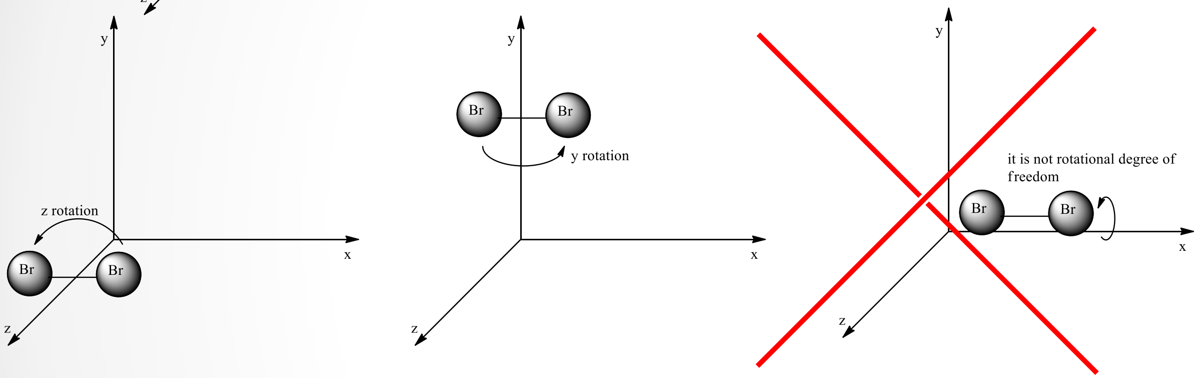
1 atom has three translational dergees of freedom

N – atomic molecule has 3N degrees of freedom

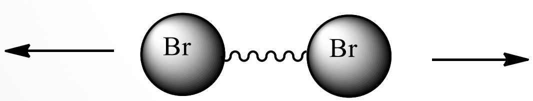
Degrees of freedom of molecule



Translational Energy
Molecule also has three translational degrees of freedom



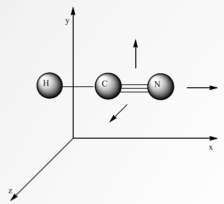
Rotational Energy
Two atomic (linear) molecule has two rotational degrees of freedom



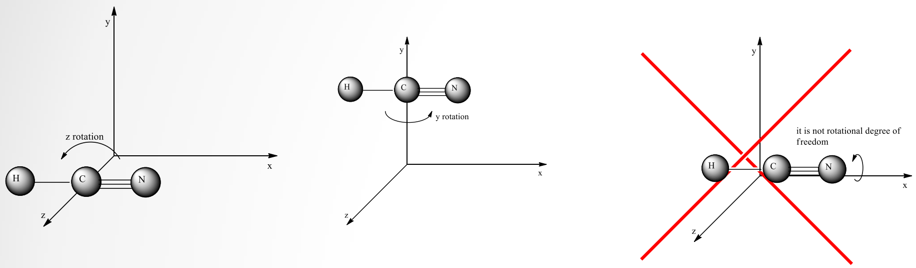
Vibrational Energy
Two atomic (linear) molecule has one vibrational degree of freedom

Number of vibrational degree of freedom is (2N – 5) for linear molecule

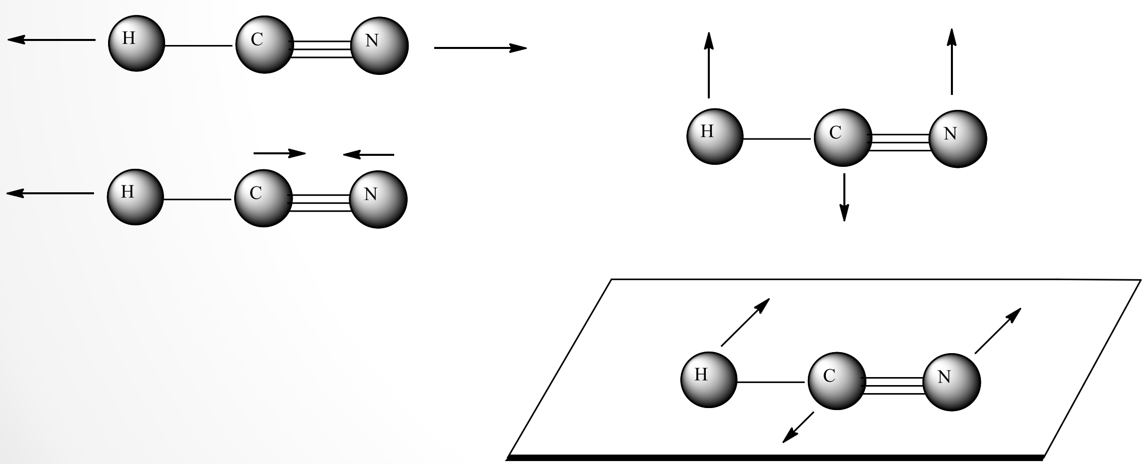
Degrees of freedom of molecule



Translational Energy
3N atomic linear molecule also has t**hree** translational degrees of freedom



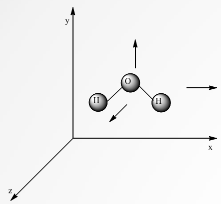
Rotational Energy
3N atomic linear molecule has **two** **Rotationa**l degrees of freedom



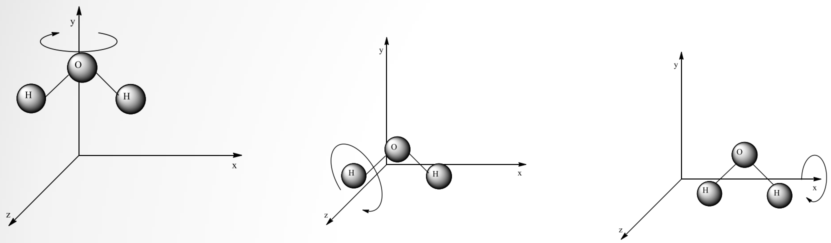
Vibrational Energy
Three atomic linear molecule has 4 vibrational degree of freedom

Number of vibrational degree of freedom is (3N – 5) for linear molecule

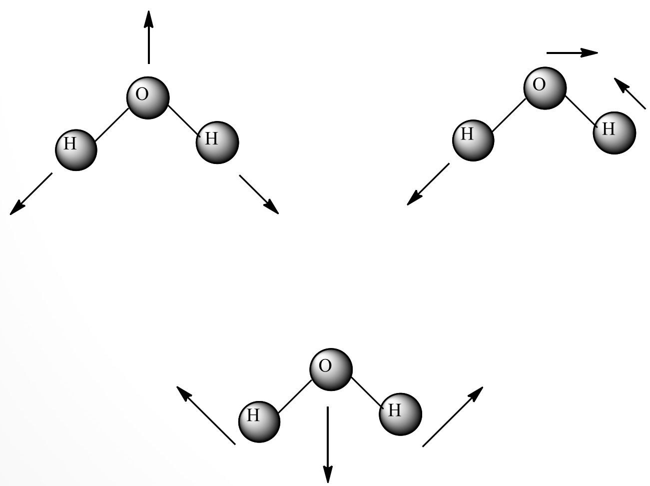
Degrees of freedom of molecule



Translational Energy
3N atomic nonlinear molecule also has t**hree** translational degrees of freedom



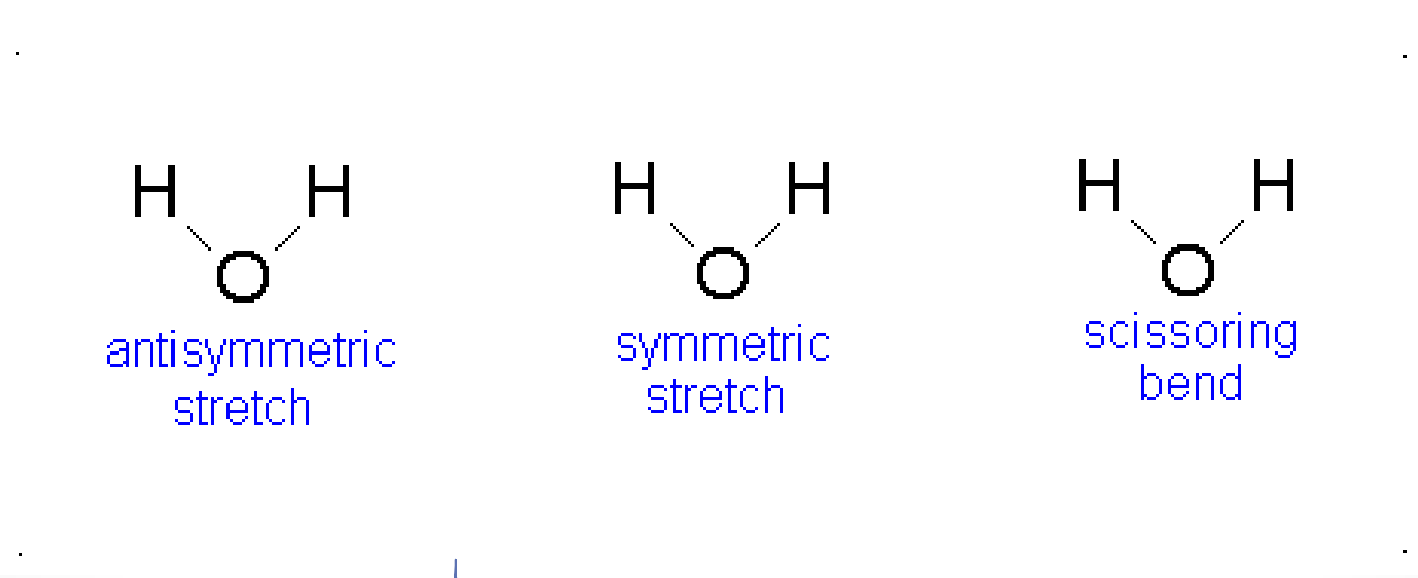
Rotational Energy
3N atomic non-linear molecule has **three** rotational degrees of freedom



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



The angle between the bonds does not change

The angle between bonds change

asymmetric stretch
ν_{as} OH 3756 cm^{-1}

symmetric stretch
ν_s OH 3657 cm^{-1}

Scissoring bend
δ_s HOH 1595 cm^{-1}

Vibrational modes - classification

Vibration with change of bond length

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

Vibration with change of an angle between the bonds

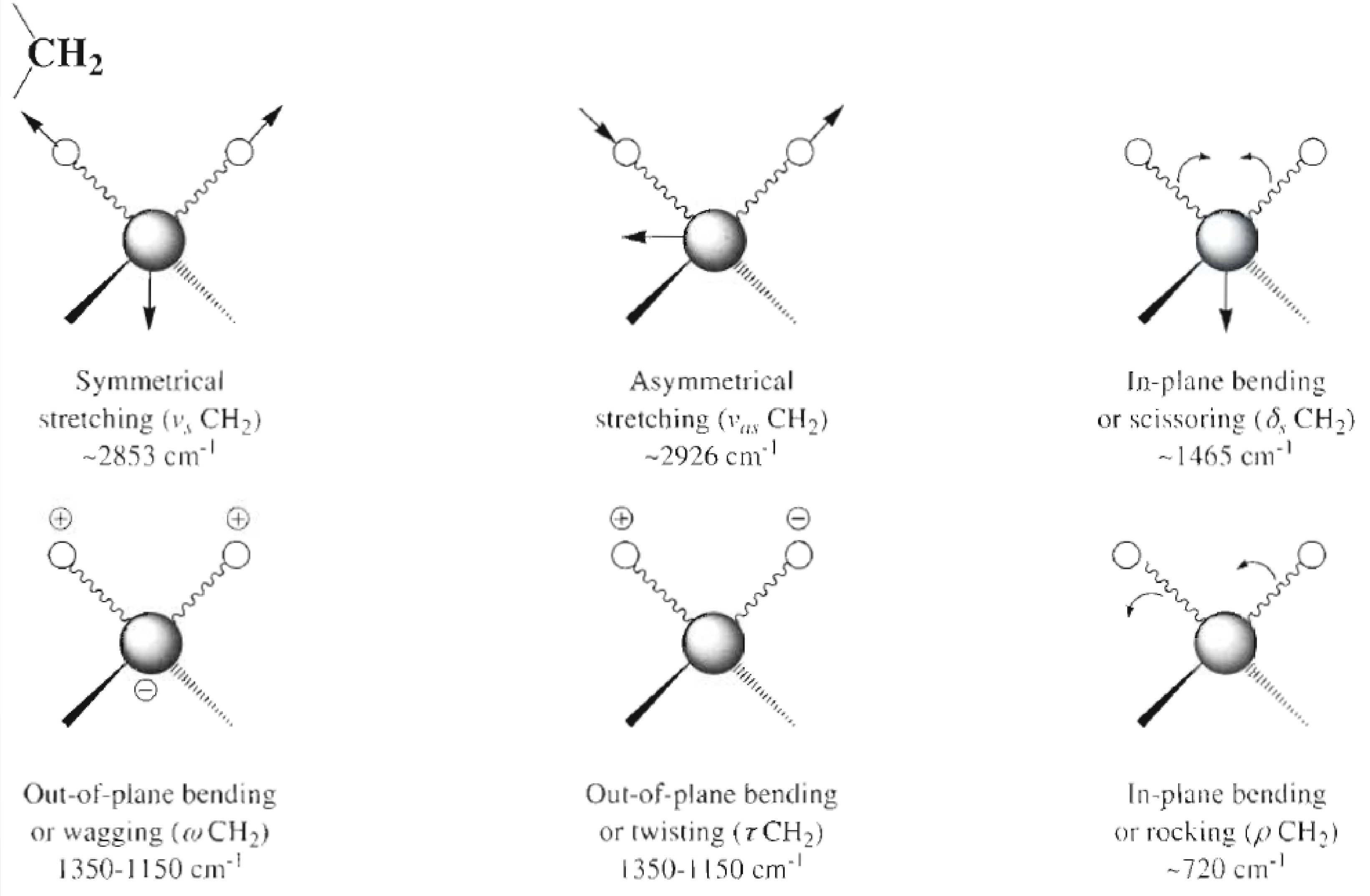
-- in-plane scissoring (bending) δ_s
-- in-plane bending (rocking) ρ
-- out-of-plane bending (wagging) ω
-- out-of-plane bending (twisting) τ

Classification in terms of symmetry (symmetric / asymmetric)

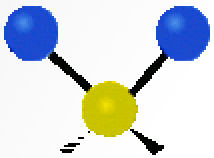
Classification in terms of plane of vibrations (in plane / out of plane (γ))

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

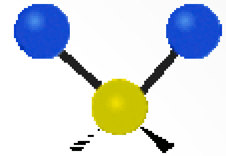
Vibrational modes for CH_2



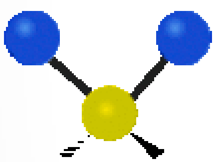
Vibrational modes for CH_2



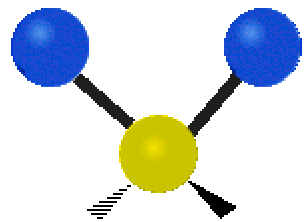
Symmetrical streching ν_s



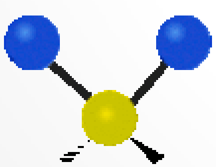
Asymmetrical streching ν_{as}



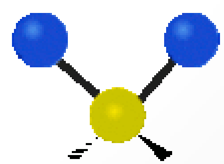
In-plane scissoring δ_s



In-plane bending ρ



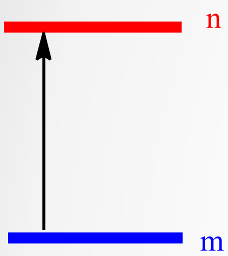
Out-of-plane bending (wagging) ω



Out-of-plane bending (twisting) τ

Probability of vibrational transition

Intensity of absorbtion



$I \approx |\mathrm{d}_{\mathrm{mn}}|^2$

Intensity of absorbtion is propotional to square of transition moment (transition dipol moment) d_{mn}
- transition between an initial state *m* and a final state *n*.

d_{mn} transiton moment between wave functions Ψm and Ψn

$$\mathrm{d}_{\mathrm{mn}} = \int_{-\infty}^{+\infty} \Psi^{*}{}_{m}\, \hat{\mu} \Psi_{n}\, dq$$

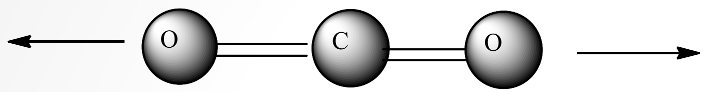
$\hat{\mu}$ - dipol moment operator
q - position

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

Intensity of absorbtion is propotional to square of the derivative of the dipol moment with respect to the normal coordinate of vibration

If the $\boldsymbol{\left(\frac{d\mu}{dq}\right)^2 = 0}$ ***electromagnetic wave is not absorbed***

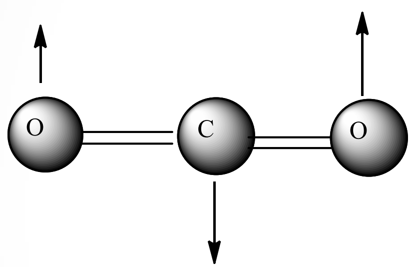
Vibrational modes of CO_2



$\nu_1 = 1343\ cm^{-1}$

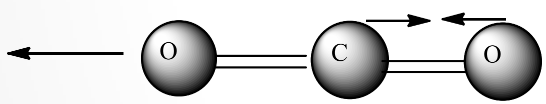
$$\left(\frac{d\mu}{dq}\right) = 0$$

Band inactive in IR



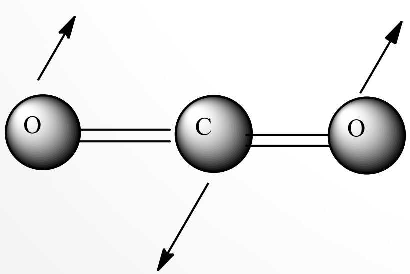
$\nu_2 = 667\ cm^{-1}$

$$\left(\frac{d\mu}{dq}\right) \neq 0$$



$\nu_3 = 2349\ cm^{-1}$

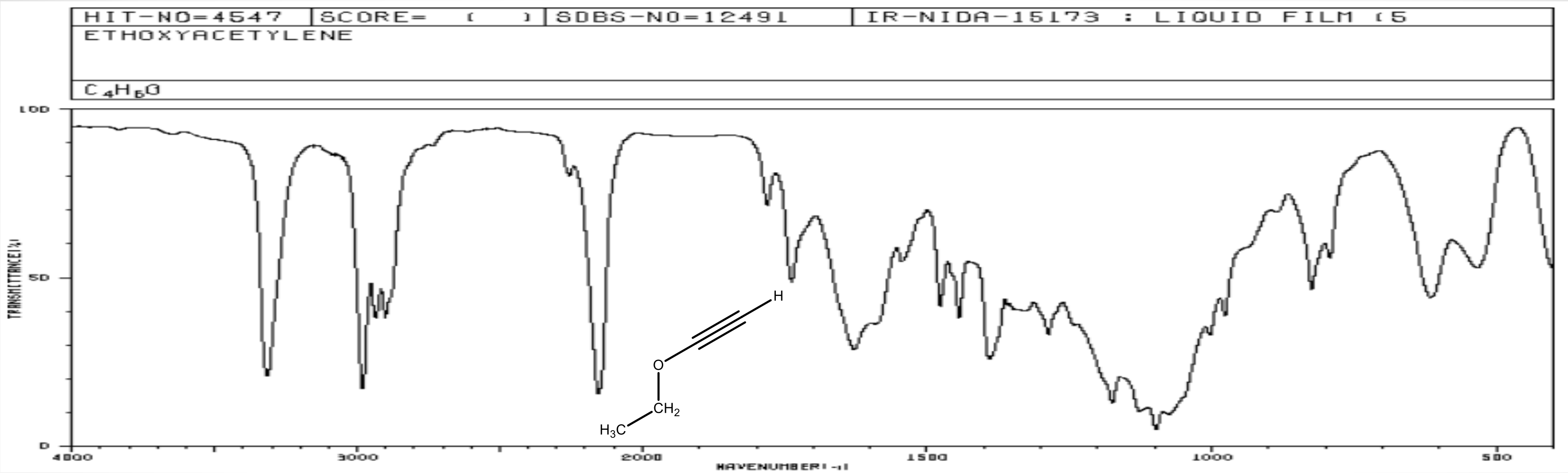
$$\left(\frac{d\mu}{dq}\right) \neq 0$$

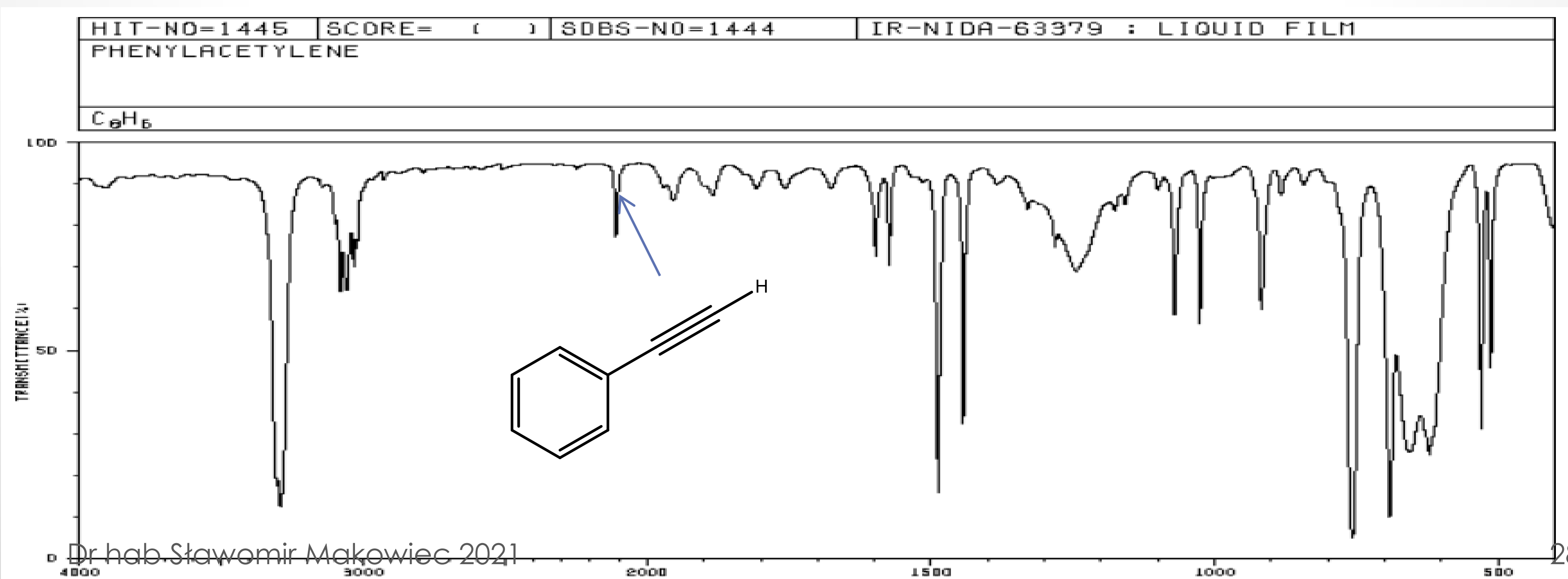


$\nu_4 = \nu_2 = 667\ cm^{-1}$

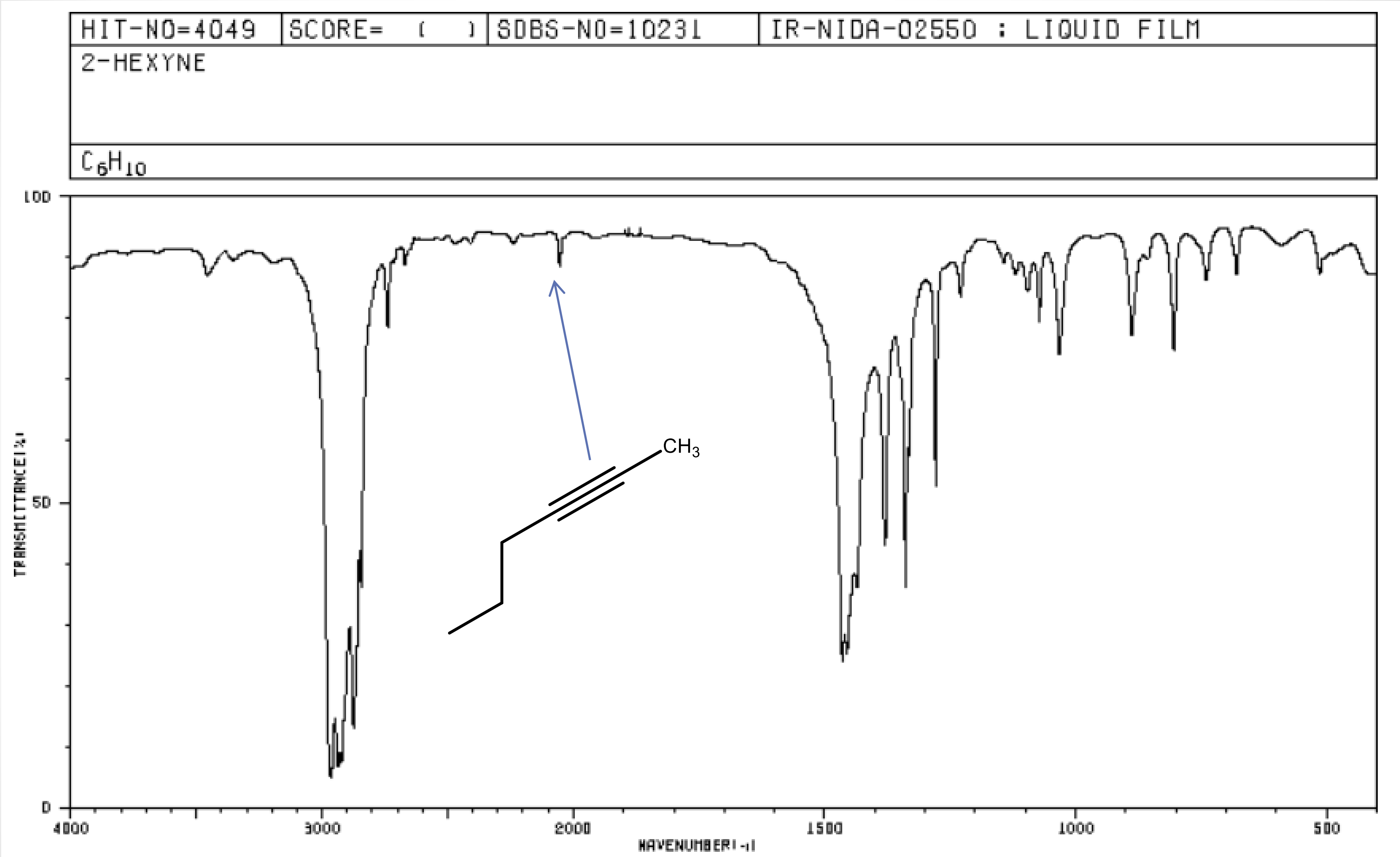
$$\left(\frac{d\mu}{dq}\right) \neq 0$$

Changes of dipol moment -vibrations





Vibrations - changes of dipol moment



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,. ✓

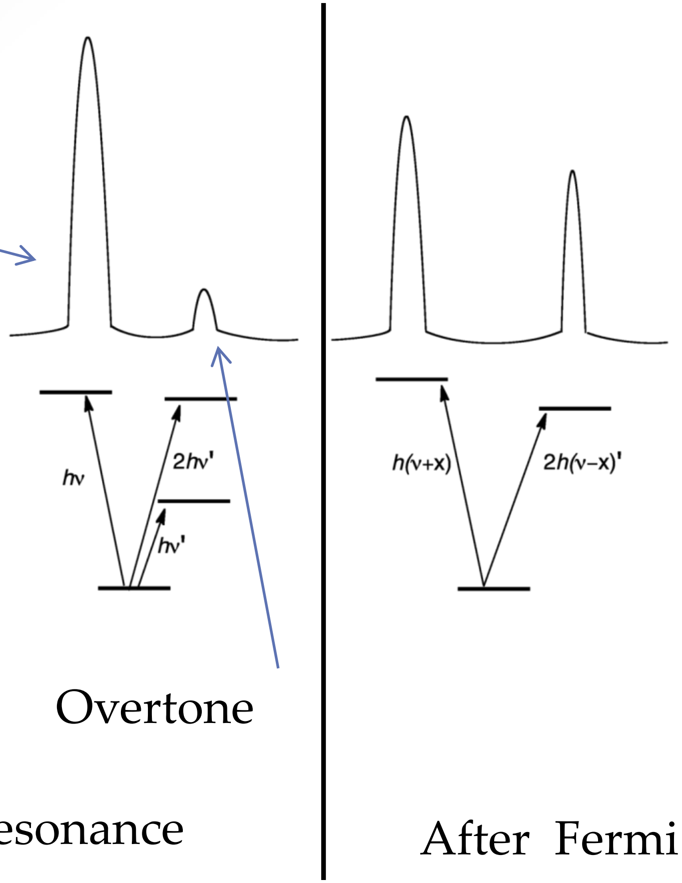
3. **Combination Bands**
   excitation is a sum of the two interacting bands $\nu_{combination} = \nu_1 + \nu_2$.

4. **Difference Bands**
   excitation is a difference between the two interacting bands $\nu_{dif} = \nu_1 - \nu_2$.
   (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



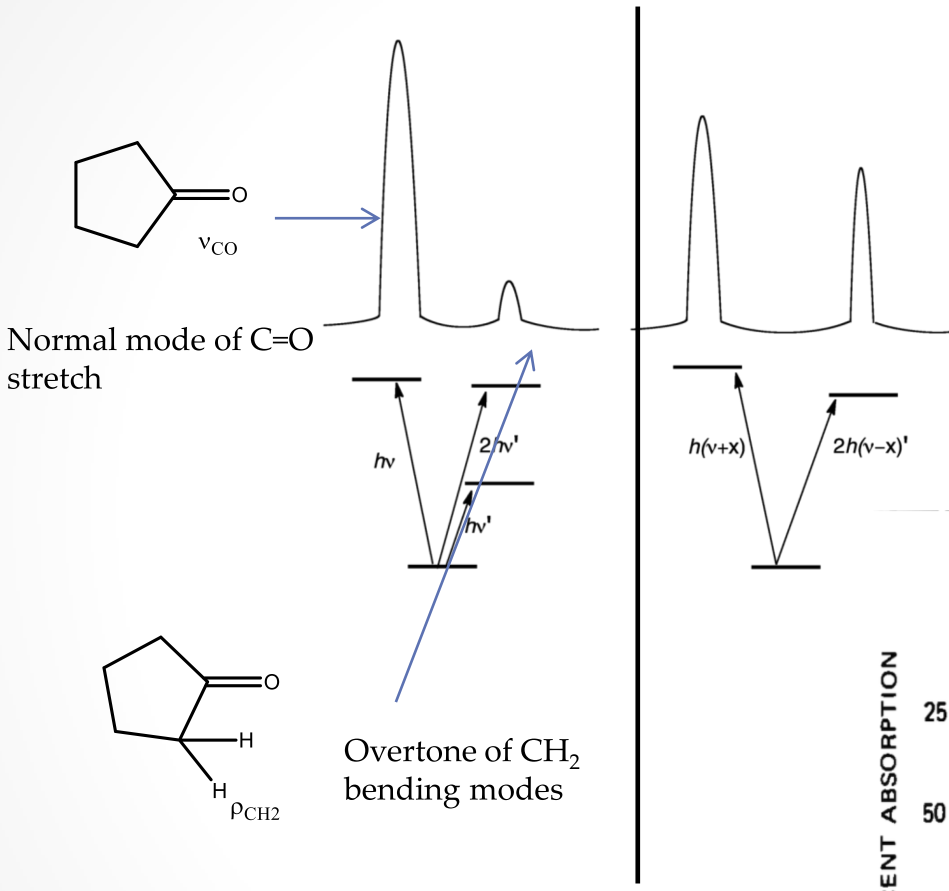
Resulting bands

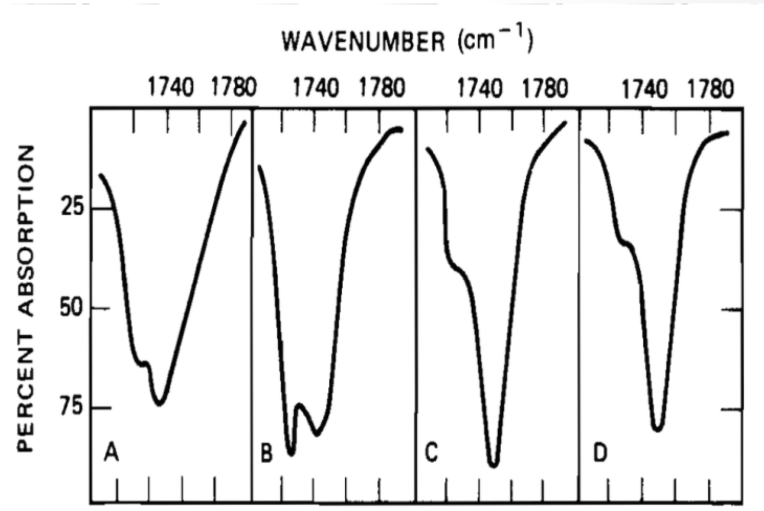
Overtone

Before Fermi resonance

After Fermi resonance

Fermi Resonance - ketones





IR spectrum of cyclopentanone in:
A. CCl_4 B. CS_2 C. $CHCl_3$ D. Thin film

Fermi Resonance – acyl chlorides