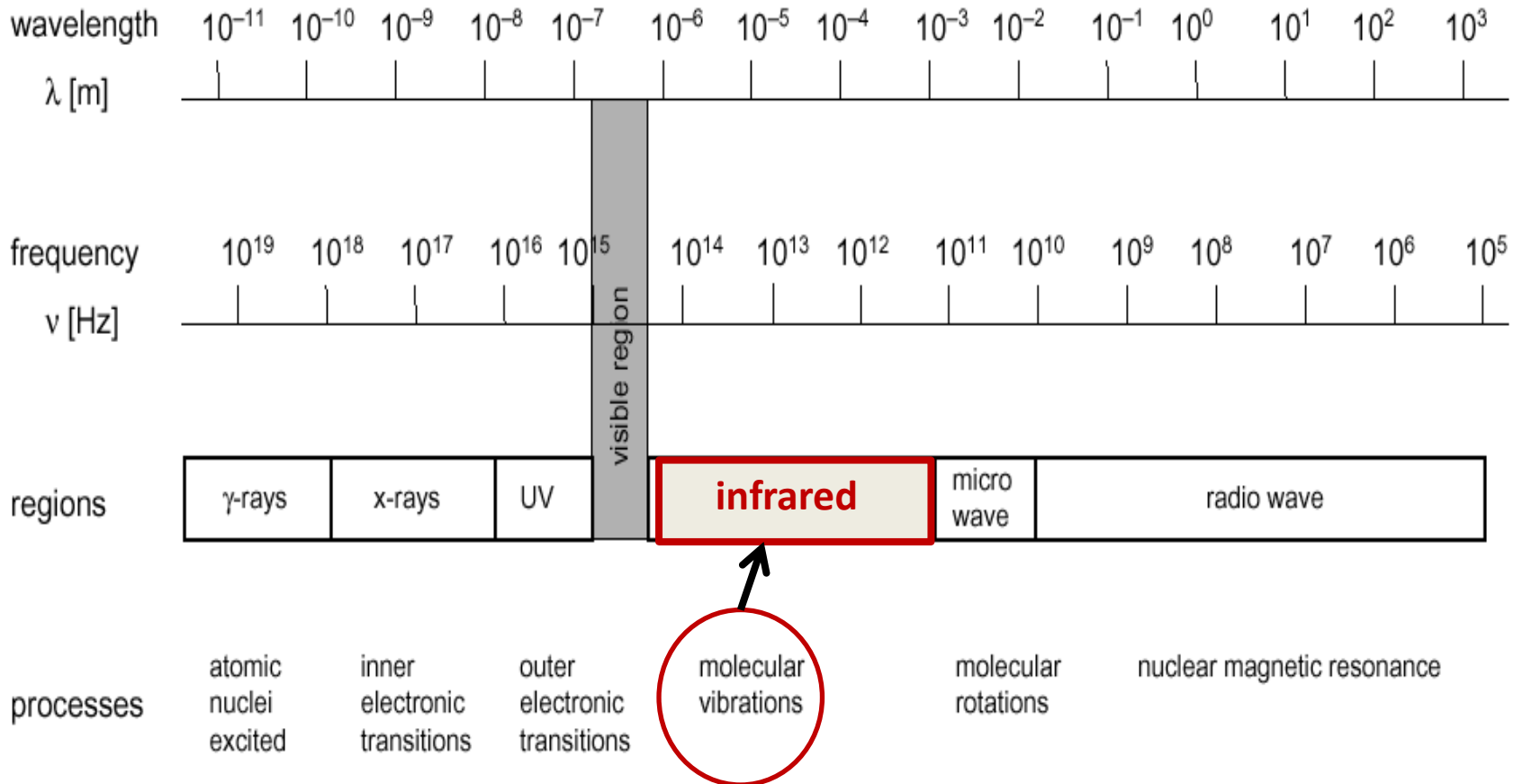


10.5.12 lecture PCIII

Chemische Bindung und Molekulare Spektroskopie (Lehramt)

Schwingungsspektroskopie

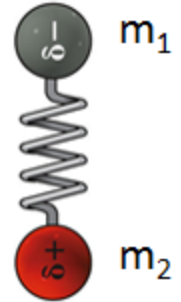
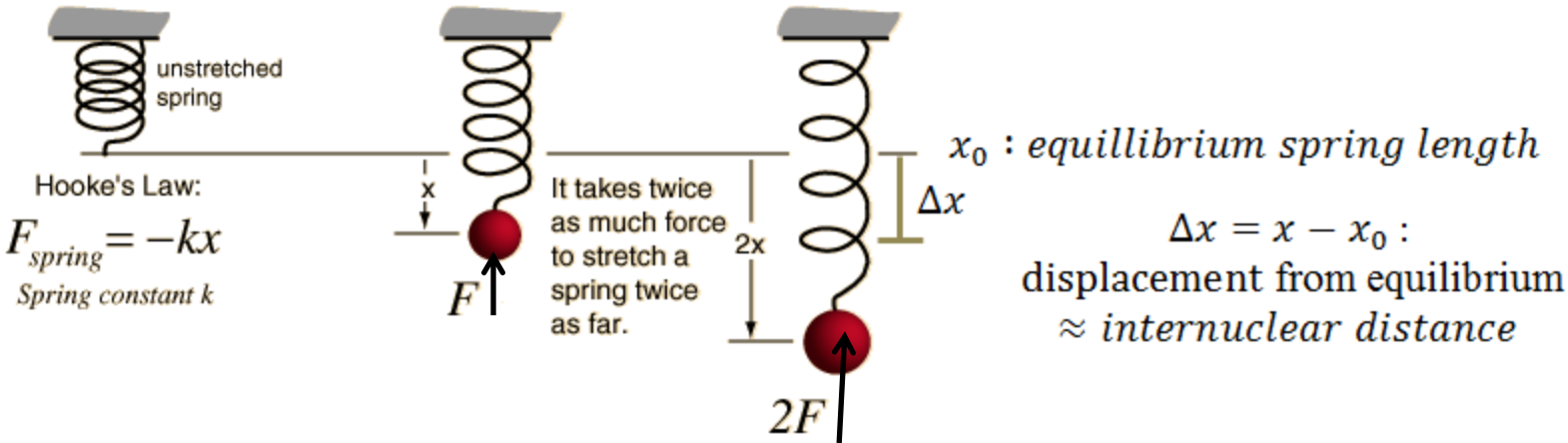
Whereabouts



describing molecular vibrations

- Classical model : simple Harmonic Oscillator (SHO)
- Quantum SHO (QSHO)
- first example with potential energy in Hamiltonian operator
- Difference between classic/QM models : Zero Point Energy (ZPE)

Classical model (Harmonischer Oszillator)



1D-problem

2D-problem

Hook's law Newton's second law

$$F = -kx, F = ma = m \frac{d^2}{dx^2}$$

$$\frac{d^2}{dx^2} + \left(\frac{k}{m}\right) x = 0$$

ω^2 : oscillation frequency

$$x(t) = A(\sin \omega t + b)$$

$$\omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ (Hz)}, \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$\mu =$ reduced mass (Reduzierte Masse)

Quantum SHO (QSHO)

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

- free particle : $V(x) = 0$

Quantized systems

- particle in box: $V(x) = 0$

- vibration : $V(x) = \frac{1}{2} k x^2$

What makes difference between systems is the potential term definition

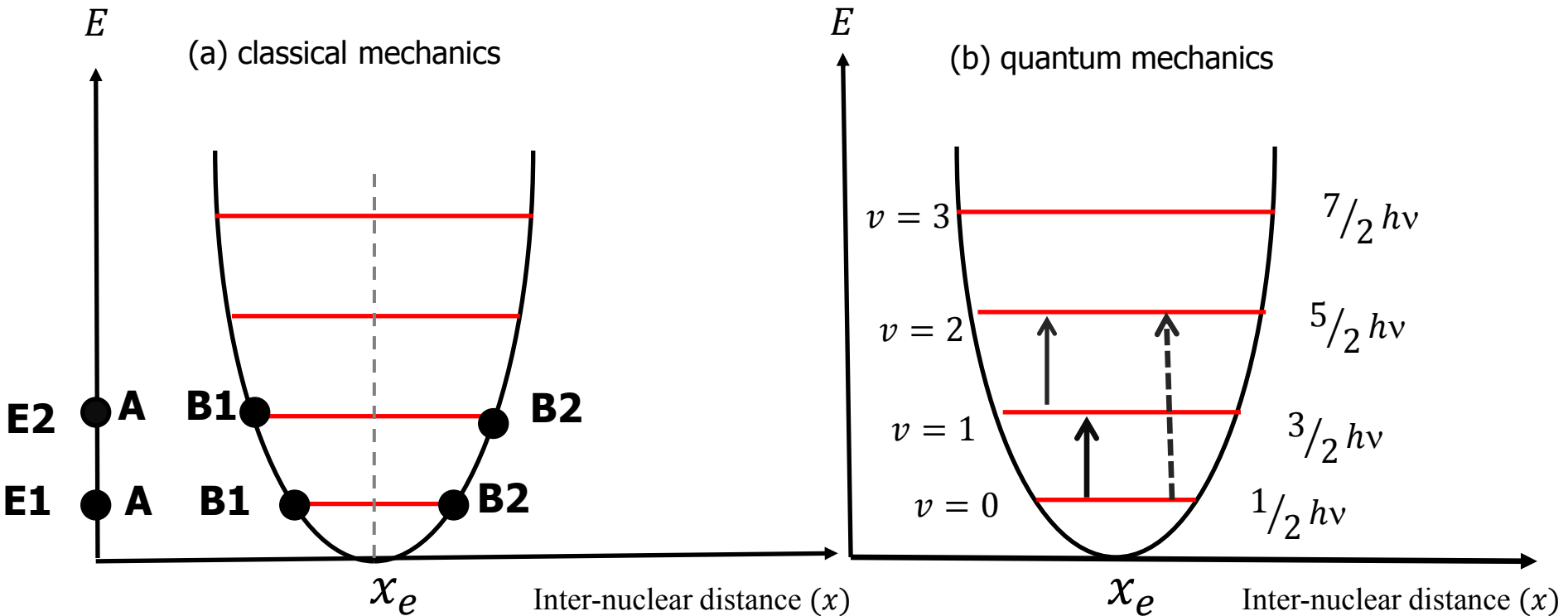
Solutions to the problem :

$$\psi_{vib} = f(x) \cdot \exp\left(-\frac{\alpha x^2}{2}\right) \text{ (vibrational wave function)}$$

$$E_{vib} = \sum_{i=1}^{3N-6} \left(v_i + \frac{1}{2}\right) h\nu, v_i = 0,1,2,3 \text{ (vibrational quantum number)}$$

selection rule : $\Delta v = \mp 1$

classical vs. quantum mechanics, energy curves



$$E = \frac{1}{2} k(x - x_e)^2$$

$$x = x_e \rightarrow E = 0$$

$$E_{vib} = (v_i + \frac{1}{2})h\nu$$

- ZPE : Zero point energy = $\frac{1}{2} h\nu$
- allowed and forbidden transitions (selection rules)
- transition energies = $h\nu$

QHSO- wave functions

$$\psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

$$\psi_1 = \sqrt{2} \left(\frac{\alpha}{\pi}\right)^{1/4} \alpha^{1/2} x e^{-\alpha x^2/2}$$

$$\psi_2 = \frac{1}{\sqrt{2}} \left(\frac{\alpha}{\pi}\right)^{1/4} (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

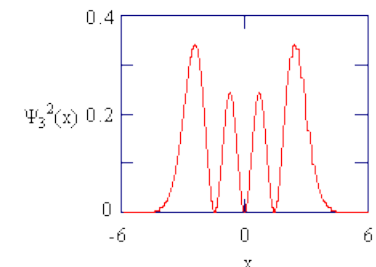
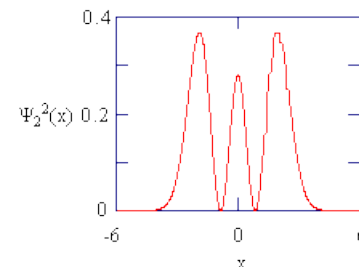
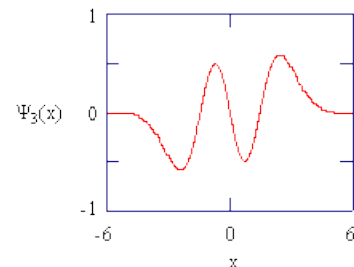
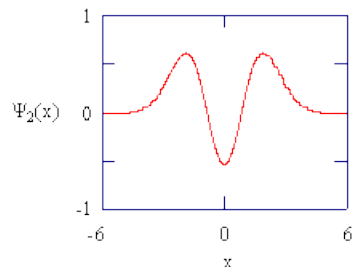
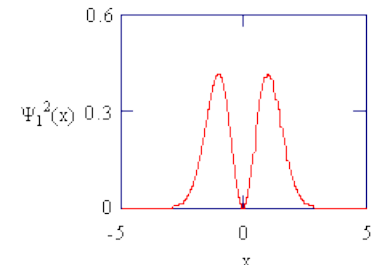
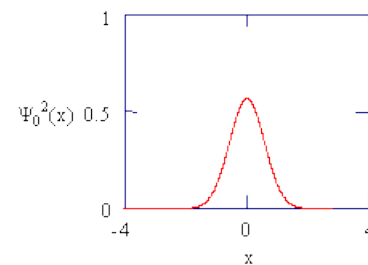
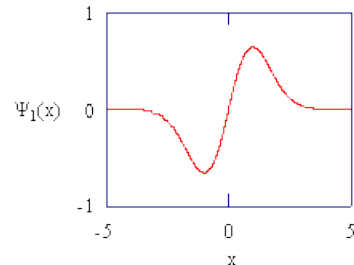
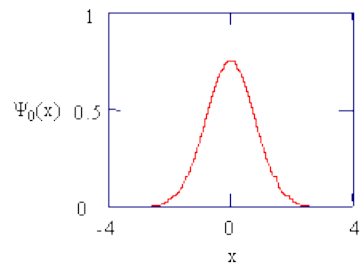
$$\psi_3 = \sqrt{3} \left(\frac{\alpha}{\pi}\right)^{1/4} (2\alpha^{3/2} x^3/3 - \alpha^{1/2} x) e^{-\alpha x^2/2}$$

$$\psi_4 = \frac{1}{\sqrt{6}} \left(\frac{\alpha}{\pi}\right)^{1/4} (2\alpha^2 x^4 - 6\alpha x^2 + 3/2) e^{-\alpha x^2/2}$$

$$\psi_5 = \frac{1}{\sqrt{15}} \left(\frac{\alpha}{\pi}\right)^{1/4} (2\alpha^{5/2} x^5 - 10\alpha^{3/2} x^3 + 15\alpha^{1/2} x/2) e^{-\alpha x^2/2}$$

$$\psi_\nu = \left(\frac{1}{2^\nu \nu!}\right)^{1/2} \left(\frac{\alpha}{\pi}\right)^{1/4} H_\nu(\alpha^{1/2} x) e^{-\alpha x^2/2}, \quad \alpha = \mu\omega/\hbar$$

Hermite polynomials



Normal modes (Normalschwingungen)

linear molecule: $3N - 5$

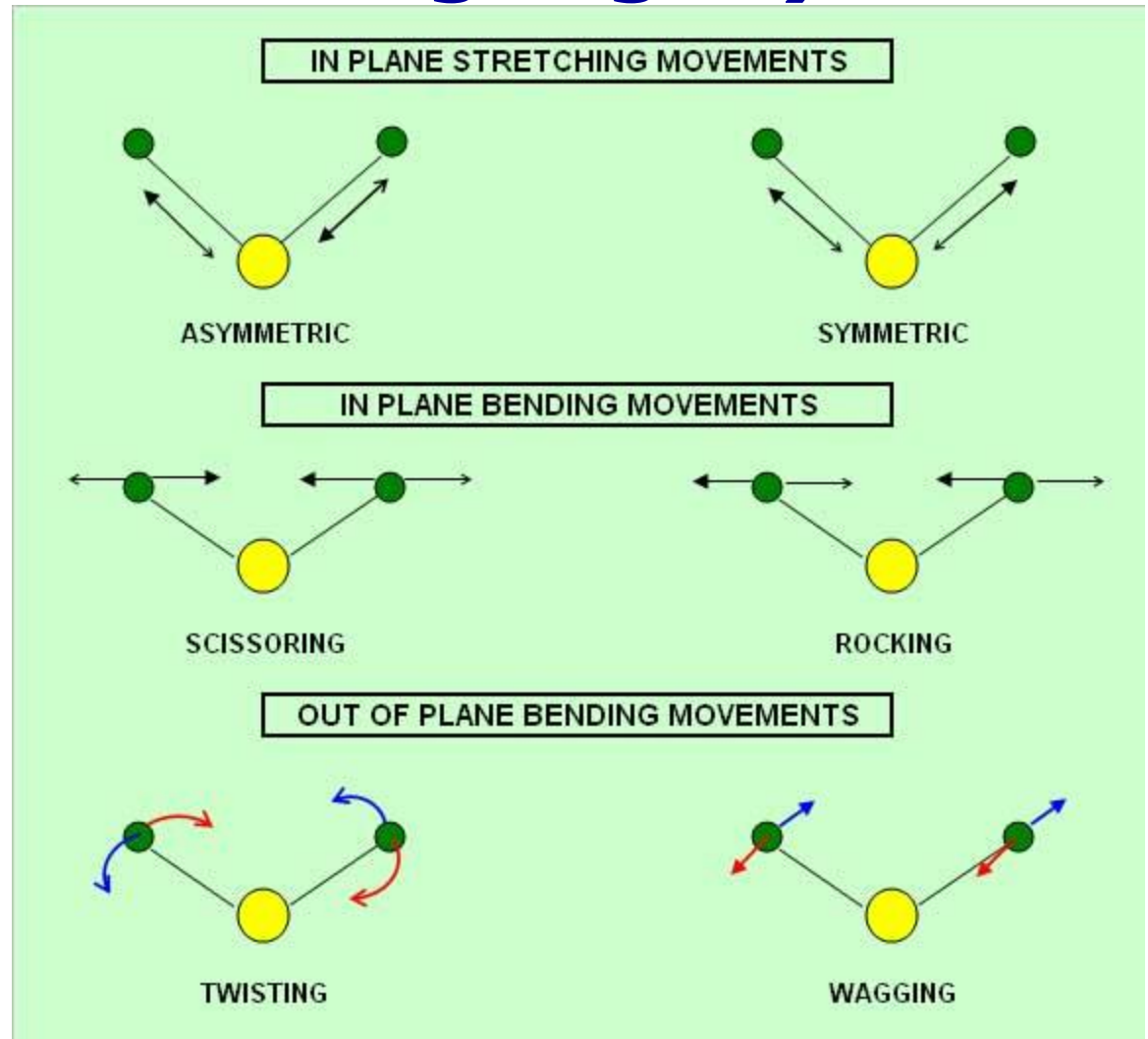
non linear molecule: $3N - 6$

basic movements:

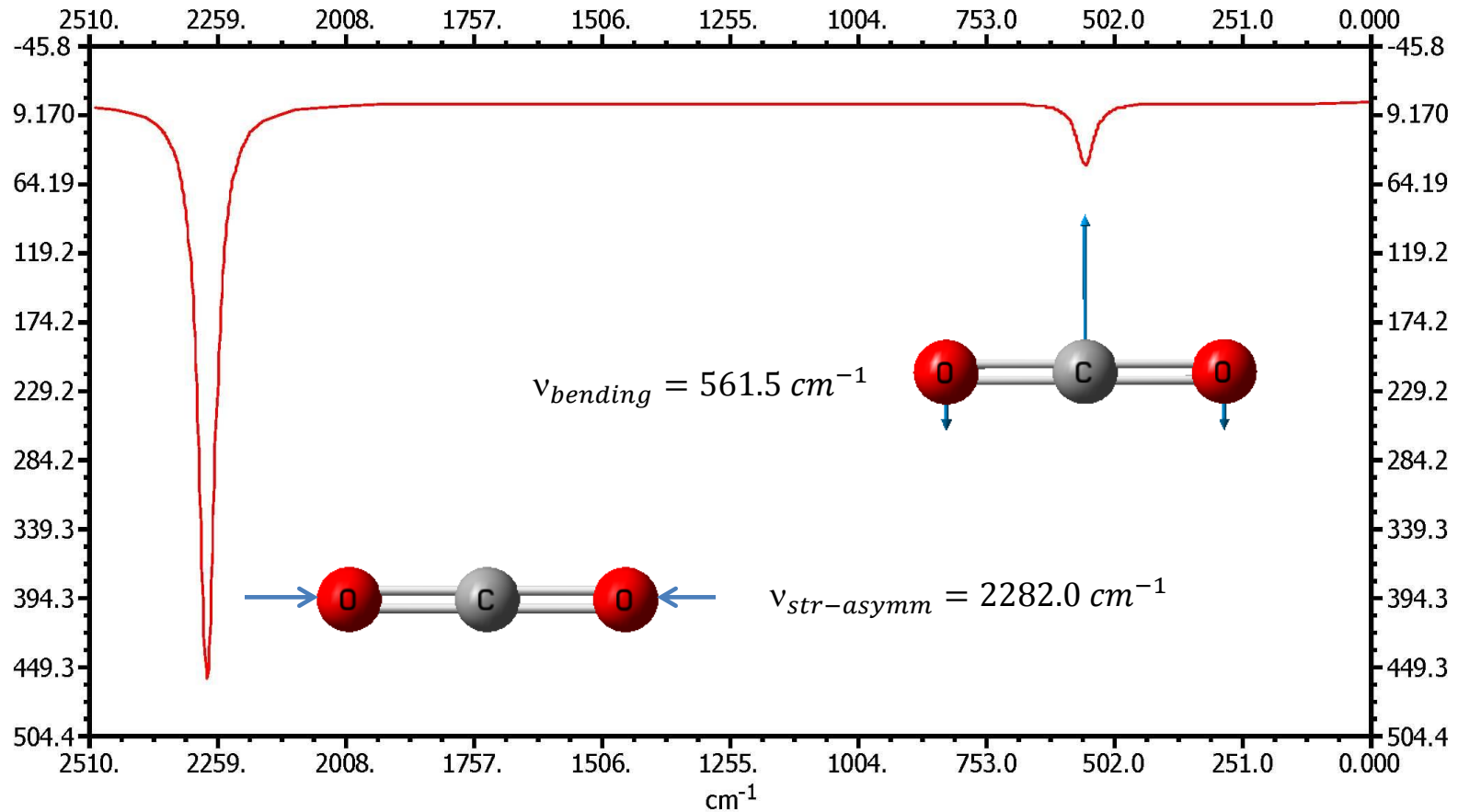
1,2) stretching (symm – asymm)
(Symmetrische/Asymmetrische
Streckschwingung)

3) bending
(Deformationsschwingungen
Oder Biege/Beugeschwingungen)

$$\nu_{str-asymm} > \nu_{str-symm} > \nu_{bend}$$



Example1: linear carbon dioxide

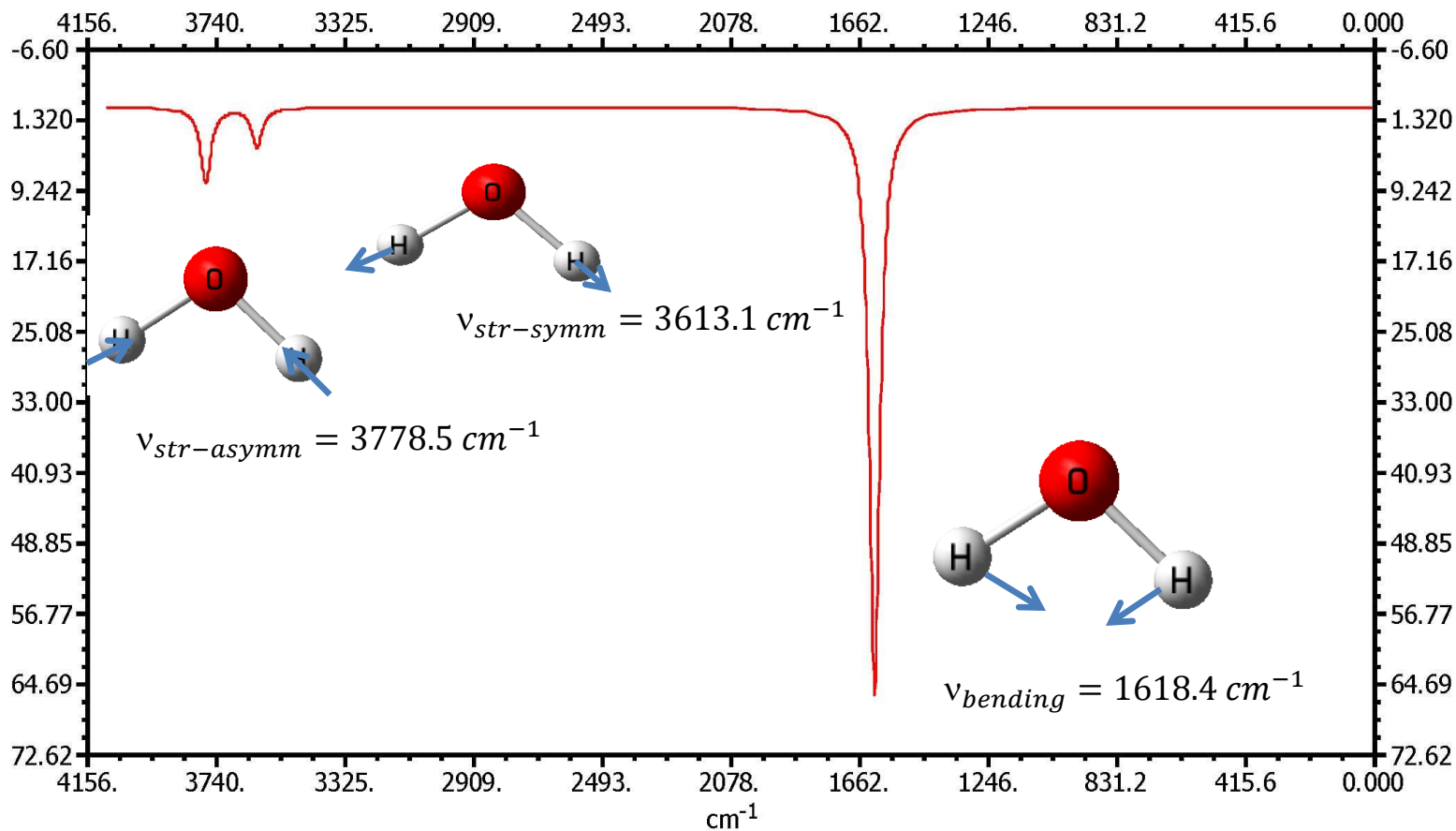


$$\neq \text{ normal modes : } 3N - 5 = 4,$$

experimental values : $\nu_{\text{str-asyymm}} = 2349 \text{ cm}^{-1} > \nu_{\text{str-symm}} = 1340 \text{ cm}^{-1} > \nu_{\text{bending}} = 667 \text{ cm}^{-1}$

Points to remember: line intensity, degeneracy

Example2: non linear water



$$\neq \text{normal modes} : 3N - 6 = 3,$$

experimental values : $\nu_{str-asymm} = 3755.9 \text{ cm}^{-1} > \nu_{str-symm} = 3657.1 \text{ cm}^{-1} > \nu_{bending} = 1594.7 \text{ cm}^{-1}$