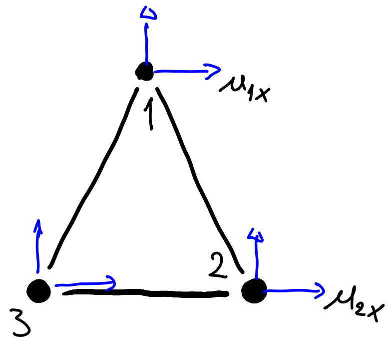
7. Molecular vibrations



- atomic displacements $\{\boldsymbol{u}_i\}$ transform like a representation Γ of the symmetry point group

- character of rotations :
  - for each atom that transforms into itself

$\chi(R(\theta)) = 1 + 2\cos\theta$ proper rotation

$\chi(\bar{R}(\theta)) = -(1 + 2\cos\theta)$ improper rotation

- decompose Γ in irreps $\Gamma = \Gamma_{trans} + \Gamma_{rot} + \Gamma_{vib}$

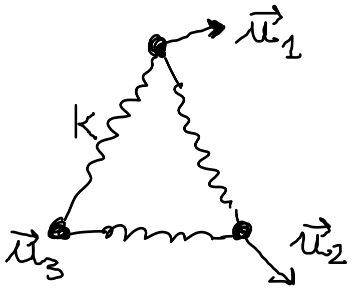
CM (x,y,z) (R_x, R_y, R_z)

Ozone molecule $\bar{6}$m2 $\Gamma_{vib} = \underbrace{A_1'}_{\text{singlet}} + \underbrace{E'}_{\text{doublet}}$

$\bar{6}\,m2$ (D_{3h})		E	m_z	3_z [2]	$\bar{6}_z$ [2]	2_y [3]	m_x [3]	
Γ_1	A'_1	1	1	1	1	1	1	x^2+y^2, z^2
Γ_2	A'_2	1	1	1	1	–1	–1	R_z
Γ_3	A''_1	1	–1	1	–1	1	–1	
Γ_4	A''_2	1	–1	1	–1	–1	1	z
Γ_6	E'	2	2	–1	–1	0	0	(x, y), $(x^2–y^2, xy)$
Γ_5	E''	2	–2	–1	1	0	0	(xz, yz), (R_x, R_y)

Group theory gives **degeneracies & symmetries**, but not order of energy levels

Microscopic model for Ozone vibrations



eq^n of motion $\qquad m\ddot{\vec{u}}_i = -\dfrac{\partial E}{\partial \vec{u}_i}$ $\qquad$ elastic energy

oscillations $\qquad \vec{u}_i(t) \sim e^{i\omega t}$

$$-m\omega^2 \begin{bmatrix} U_{1x} \\ \vdots \\ \vdots \end{bmatrix} = -K \underbrace{\begin{bmatrix} \quad & \quad \\ \quad & \quad \end{bmatrix}}_{h} \begin{bmatrix} U_{1x} \\ \vdots \\ \vdots \end{bmatrix}$$

$$(h - \lambda \underline{I}) \begin{bmatrix} U_{1x} \\ \vdots \\ \vdots \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ \vdots \end{bmatrix} \qquad \lambda = \frac{m\omega^2}{K}$$

$$\lambda = 3 \qquad \omega_1 = \sqrt{\frac{3K}{m}} \qquad \begin{array}{cccccccc} & 1x & 1y & 2x & 2y & 3x & 3y \\ U_1 = [& 0 & -2 & -\sqrt{3} & 1 & \sqrt{3} & 1 &] \end{array}$$

$$\lambda = \frac{3}{2} \qquad \omega_2 = \sqrt{\frac{3}{2}\frac{K}{m}} \qquad U_2 = \left[-\frac{1}{2} \quad \frac{\sqrt{3}}{2} \quad -\frac{1}{2} \quad -\frac{\sqrt{3}}{2} \quad 1 \quad 0 \right]$$

double

$$U_3 = \left[-\frac{\sqrt{3}}{2} \quad -\frac{1}{2} \quad \frac{\sqrt{3}}{2} \quad -\frac{1}{2} \quad 0 \quad 1 \right]$$