

# 8. Molecular vibrations, infrared and Raman activity

## 8.1 Molecular vibrations: background

Group theory helps in finding the form of the dynamical matrix for molecular vibrations. Moreover, analogously to the electronic states it allows to classify the vibrational modes of a molecule.

In general, the Hamiltonian for a molecule reads

$$H = \sum_{i=1}^{N_e} \frac{\hat{p}_i^2}{2m_e} + \sum_{\mu=1}^{N_d} \frac{\hat{P}_\mu^2}{2M_\mu} - \sum_{i\mu} \frac{e^2 Z_\mu}{4\pi\epsilon_0 |\hat{r}_i - \hat{R}_\mu|} + \sum_{i,j} \frac{e^2}{4\pi\epsilon_0 |\hat{r}_i - \hat{r}_j|} + \sum_{\mu\nu} \frac{e^2 Z_\mu Z_\nu}{4\pi\epsilon_0 |\hat{R}_\mu - \hat{R}_\nu|}$$

If we perform the Born-Oppenheimer approximation, based on the observation  $m_\mu/m_e \gg 1$  and we solve the (still formidably complex) problem of  $N_e$  interacting electrons in presence of  $N_d$  nuclei fixed at the  $\vec{R}_\mu$  positions we obtain, to start with the configuration dependent ground state energy  $E_g(\{\vec{R}_\mu\})$ . The dynamic of the nuclei can be (classically) treated by the effective potential:

$$V_d(\{\vec{R}_\mu\}) = \sum_{\mu\nu} \frac{e^2 Z_\mu Z_\nu}{4\pi\epsilon_0 |\vec{R}_\mu - \vec{R}_\nu|} + E_g(\{\vec{R}_\mu\})$$

We are particularly interested in  $V_d(\{\vec{R}_\mu\})$  around the equilibrium coordinates  $\{\vec{R}_\mu^0\}$  which can be obtained by minimizing  $V_d(\{\vec{R}_\mu\})$  apart from rigid translation rotations. We take the zero of the energy at the potential minimum and expand  $V_d(\{\vec{R}_\mu\})$  in the displacements  $\vec{z}_\mu = \vec{R}_\mu - \vec{R}_\mu^0$ .

If we now introduce the generic coordinate index  $k = 1 \dots 3N_{at}$

$$L(\{\dot{z}_k, z_k\}) = \sum_k \frac{1}{2} m_k \dot{z}_k^2 - \sum_{k,l} \frac{1}{2} \frac{\partial^2 V_{el}}{\partial z_k \partial z_l} \Big|_{\{z_k=0\}} z_k z_l \quad (*)$$

The first order expansion vanishes by definition since  $\vec{R}_\mu^0$  is an equilibrium configuration (for the reference electronic state with energy  $E_g$ ).

The Hamiltonian (\*) gives rise to a secular equation in  $3N_{at}$  variables. The roots of the secular equation are the eigenfrequencies (squared)  $\omega_k^2$  and the eigenvectors denote the normal modes. The standard procedure consists in:

i) eliminating the mass

$$q_k = \sqrt{m_k} z_k \quad \phi_k = \frac{\partial L}{\partial q_k} = \frac{1}{\sqrt{m_k}} \frac{\partial L}{\partial \dot{z}_k} = \sqrt{m_k} \dot{z}_k$$

ii) turn into normal mode coordinates

$$q_k = \sum_K a_{kK} Q_K$$

$$V_{el}^{harm.} = \frac{1}{2} \sum_{k,l} \left( \frac{\partial^2 V}{\partial q_k \partial q_l} \right) a_{kK} a_{lL} Q_K Q_L = \frac{1}{2} \sum_K \omega_K^2 Q_K^2$$

where  $a_{kK} = a_{Kk}^T = (a^{-1})_{Kk}$  since  $\frac{\partial^2 V}{\partial q_k \partial q_l} \Big|_{\{z_k=0\}}$  is real and symmetric,

and  $\omega_K^2$  and  $a_{kK}$  are linked by the relation

$$\sum_{k,l} (a^{-1})_{Kk} \frac{\partial^2 V_{el}}{\partial q_k \partial q_l} \Big|_{\{z_k=0\}} a_{lL} = \omega_K^2 \delta_{KL}$$

Group theory helps to reduce  $\left. \frac{\partial^2 V}{\partial q_k \partial q_l} \right|_{\{q_k=0\}}$  into a block diagonal form and in classifying the symmetry and degeneracies of the eigenmodes. Moreover, by means of the projector operator technique, the normal mode can be "a priori" determined.

## 8.2 Application of group theory to molecular vibrations

The symmetry of the molecule is not changed by the normal modes, in the precise sense that  $\left. \frac{\partial^2 V}{\partial z_k \partial z_l} \right|_{\{z_k=0\}}$  is invariant under  $G$ .

$$\hat{R} P_{K'}^{(i,x)} = \sum_{K''=1}^{l_i} \Gamma_{K''K'}^{(i)}(R) P_{K''}^{(i,x)}$$

$i$  - irreducible representation

$x$  - extra label for (possible) multiple imp of the same type.

$P_{K'}^{(i,x)}$  - eigenmode associated to the frequency  $\omega_{K'}$ . is a vector of  $3N_{\text{at}}$  components. i.e. short notation for  $a_{K'}$ .  $P_{K'}$  is a mode degenerate with  $P_{K''}$ .

$\Gamma^{(i)}(R)$  - matrix representation of  $R$  in the eigenmode basis

$R$  - symmetry operation  $\in G$  the group of the molecule / or the Schrödinger equation.

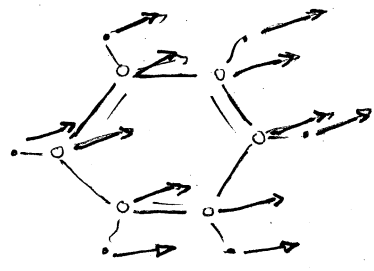
It is thus clear that the problem of finding  $P_{K'}$  is similar to the one of finding the eigenstates of the electronic Hamiltonian.

- As a first step one considers the representation of the atomic sites  $\Gamma^{a.s.}$ . One can associate it to the Hilbert space of  $N$  symmetry wave functions located around  $\{\vec{R}_\mu\}$ .  $\Rightarrow$  We are considering a representation of dimension  $N$ .

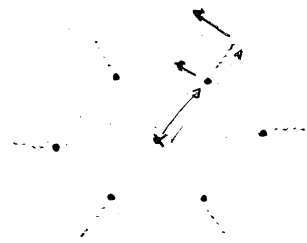
- Each atom can vibrate in 3 directions, independently of the others. The associated vector space is  $\mathbb{R}^3$  and the representation  $\Gamma^{vec}$  is the direct sum of the representations associated to the basis functions  $x, y, z$  in the character table.

- $\Gamma = \Gamma^{a.s.} \oplus \Gamma^{vec}$  has dimension  $3N_{at}$  and is the space of all possible deformations of the molecule. It is larger than the space of the normal modes since a molecule can also rigidly translate or rotate.

- The representation of the rigid translation coincides with  $\Gamma^{vec}$  since it corresponds to a generic deformation applied IDENTICALLY to ALL atoms.



- The representation of the rigid rotation is the one of the angular momentum (generically of the momentum of a vector)  $\Rightarrow$  the sum of the ones of the components of a pseudovector  $R_x, R_y, R_z$ .



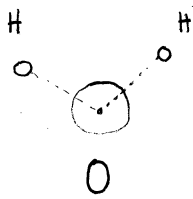
The pseudovector commut to all atomic displacements is  $\frac{1}{R_{\mu}^2} (\vec{R}_{\mu} \times \vec{z}_{\mu})$ , independent of  $\mu$ . Notice that the center of the rotation can be anywhere.

All together:

$$\Gamma_{\text{mol. vib}} = \Gamma^{\text{a.s.}} \otimes \Gamma^{\text{vec}} \ominus \Gamma^{\text{vec}} \ominus \Gamma^{\text{rot}}$$

- Finally  $\Gamma_{\text{mol. vib}}$  is reduced in terms of irreducible representations of  $G$ . With the help of the projection operators we can construct the  $f_k^{(i,x)}$  starting from a "generic" atom displacement.

Example: modes of the water molecule



The point group of  $\text{H}_2\text{O}$  is  $C_{2v}$  since the molecule has a  $C_2$  symmetry axis and 2 vertical symmetry planes. The character table

	E	$C_2$	$\sigma_v$	$\sigma_v'$	Basis functions
$A_1$	1	1	1	1	z
$A_2$	1	1	-1	-1	$R_z$
$B_1$	1	-1	1	-1	x, $R_y$
$B_2$	1	-1	-1	1	y, $R_x$

$$\Gamma^{a.s.} = \left\{ \begin{matrix} 3 & 1 & 3 & 1 \end{matrix} \right\} = 2A_1 \oplus B_1 \quad \text{as can be obtained from red. formula}$$

$$\Gamma^{rec} = A_1 \oplus B_1 \oplus B_2 = \left\{ \begin{matrix} 3 & -1 & 1 & 1 \end{matrix} \right\} \quad \text{associated to } x, y, z$$

$$\Gamma^{rot} = A_2 \oplus B_1 \oplus B_2 = \left\{ \begin{matrix} 3 & -1 & -1 & -1 \end{matrix} \right\} \quad \text{" " } R_x, R_y, R_z$$

$$\begin{aligned} \Gamma_{\text{mol.vib.}} &= (\Gamma^{a.s.} \otimes \Gamma_{rec}) \ominus \Gamma_{rec} \ominus \Gamma_{rot} = \\ &= (2A_1 \oplus B_1) \otimes (A_1 \oplus B_1 \oplus B_2) \ominus A_1 \ominus A_2 \ominus 2B_1 \ominus 2B_2 \end{aligned}$$

The direct product of representations has the character set:

$$\chi^{\Gamma_1 \otimes \Gamma_2}(\mathcal{C}_k) = \chi^{\Gamma_1}(\mathcal{C}_k) \chi^{\Gamma_2}(\mathcal{C}_k)$$

The further reduction of the representation follows the usual rules:

$$A_1 \otimes \Gamma = \Gamma \quad \forall \Gamma \quad B_1 \otimes B_1 = A_1 \quad B_1 \otimes B_2 = A_2$$

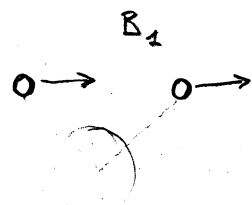
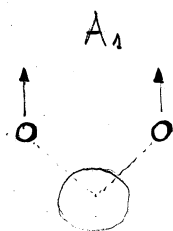
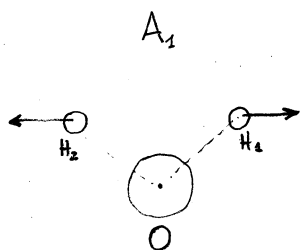
It follows that:

$$\begin{aligned} \Gamma_{\text{mol.vib.}} &= 2A_1 \oplus B_1 \oplus \cancel{2B_1} \oplus \cancel{A_2} \oplus \cancel{2B_2} \oplus \cancel{A_2} \ominus \cancel{A_1} \ominus \cancel{A_2} \ominus \cancel{2B_1} \ominus \cancel{2B_2} = \\ &= \boxed{2A_1 \oplus B_1} \end{aligned}$$

Since they are, the three of them, one dimensional representations, it is easier to obtain the normal modes. Assume as usual the deformation

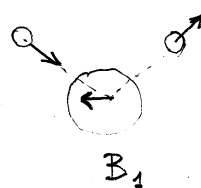
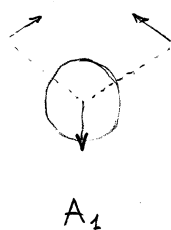
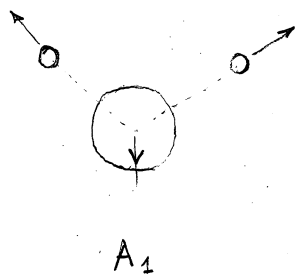
$$\mu_1 = (\hat{e}_{xH_2}, \vec{0}, \vec{0})$$

$$\mu_2 = (\hat{e}_{zH_2}, \vec{0}, \vec{0})$$



Notice that linear combinations of  $A_1$  are still  $A_1$ . Moreover we should require that the normal modes have

- no translation of the center of mass ( $\sum_{\mu} m_{\mu} \vec{z}_{\mu} = 0$ )
- no rotation ( $\sum_{\mu} \frac{m_{\mu}}{R_{\mu}^2} \vec{R}_{\mu} \otimes \vec{z}_{\mu} = 0 \quad \vec{L} = 0$ )
- are orthogonal



### 8.3 A more rigorous approach

A rigorous proof that  $\Gamma_{\text{vib}}$  and  $\Gamma_{\text{rot}}$  correspond to zero frequency eigenmodes of the force matrix  $F_{kl} = \frac{\partial^2 V_d}{\partial q_k \partial q_l} \Big|_{q_m = q_m^0}$ .

Let's organize the  $3N_{\text{at}}$  renormalized displacement coordinates as follows:

$$\begin{aligned}
 q_{3\mu-2} &= (m_{\mu})^{1/2} (x_{\mu} - x_{\mu}^0) & \mu &= 1 \dots N_{\text{at}} \\
 q_{3\mu-1} &= (m_{\mu})^{1/2} (y_{\mu} - y_{\mu}^0) & \vec{R}_{\mu} &= \begin{pmatrix} x_{\mu} \\ y_{\mu} \\ z_{\mu} \end{pmatrix} \quad \vec{R}_{\mu}^0 = \begin{pmatrix} x_{\mu}^0 \\ y_{\mu}^0 \\ z_{\mu}^0 \end{pmatrix} \\
 q_{3\mu} &= (m_{\mu})^{1/2} (z_{\mu} - z_{\mu}^0)
 \end{aligned}$$

Theorem If no external forces act on the molecule, the components of the force matrix  $F$  satisfy the following conditions

$$A - \sum_{\mu=1}^{N_{\text{at}}} (m_{\mu})^{1/2} F_{m, 3\mu-3+s} = 0 \quad m = 1 \dots 3N_{\text{at}} \quad s = 1, 2, 3$$

$$B - \sum_{\mu=1}^{N_{\text{at}}} (m_{\mu})^{1/2} \left\{ y_{\mu}^0 F_{m, 3\mu} - z_{\mu}^0 F_{m, 3\mu-1} \right\} = 0$$

$$C - \sum_{\mu=1}^{N_{\text{at}}} (m_{\mu})^{1/2} \left\{ z_{\mu}^0 F_{m, 3\mu-2} - x_{\mu}^0 F_{m, 3\mu} \right\} = 0 \quad m = 1 \dots 3N_{\text{at}}$$

$$D - \sum_{\mu=1}^{N_{\text{at}}} (m_{\mu})^{1/2} \left\{ x_{\mu}^0 F_{m, 3\mu-1} - y_{\mu}^0 F_{m, 3\mu-2} \right\} = 0$$

Proof: Let  $\vec{F}_{\mu}$  be the total force acting on the  $\mu$ -th nucleus. If there are only internal forces it must be  $\sum_{\mu=1}^{N_{\text{at}}} \vec{F}_{\mu} = 0$ . The first component of the equality gives:

$$0 = \sum_{\mu=1}^{N_{\text{at}}} \frac{\partial V_{\text{cl}}^{\text{hor.}}}{\partial x_{\mu}} = \sum_{\mu=1}^{N_{\text{at}}} (m_{\mu})^{1/2} \frac{\partial V_{\text{cl}}^{\text{hor.}}}{\partial q_{3\mu-2}}$$

Similarly for the other 2 directions  $\Rightarrow$  we can conclude

$$0 = \sum_{\mu=1}^{N_{\text{at}}} (m_{\mu})^{1/2} \frac{\partial V_{\text{cl}}^{\text{hor.}}}{\partial q_{3\mu-3+s}} \quad s = 1, 2, 3.$$

Now, we give the explicit form of  $V_{\text{cl}}^{\text{hor.}} = \frac{1}{2} \sum_{k, \ell=1}^{3N_{\text{at}}} F_{k\ell} q_k q_{\ell}$  from which we obtain

$$0 = \sum_{k=1}^{3N_{\text{at}}} \sum_{\mu=1}^{N_{\text{at}}} (m_{\mu})^{1/2} F_{k, 3\mu-3+s} q_k \quad \left( \begin{array}{l} \text{analogously we could} \\ \text{write exchanging indices} \\ \text{in } F \end{array} \right)$$

But, since the relation above should hold  $\forall$  (small) displacement  $\{q_k\}$ , we obtain the relation A.



In absence of external forces also the total force momentum vanishes:

$$\sum_{\mu=1}^{N_{\text{at}}} \vec{R}_{\mu}^0 \times \vec{F}_{\mu} = 0 \quad (*)$$

If we consider the first component of the equality above, we obtain:

$$0 = \sum_{\mu=1}^{N_{\text{at}}} \left( y_{\mu}^0 \frac{\partial V_{\text{cl}}^{\text{hor}}}{\partial z_{\mu}} - z_{\mu}^0 \frac{\partial V_{\text{cl}}^{\text{hor}}}{\partial y_{\mu}} \right) = \sum_{\mu=1}^{N_{\text{at}}} m_{\mu}^{1/2} \left( y_{\mu}^0 \frac{\partial V_{\text{cl}}^{\text{hor}}}{\partial q_{3\mu}} - z_{\mu}^0 \frac{\partial V_{\text{cl}}^{\text{hor}}}{\partial q_{3\mu-1}} \right)$$

By inserting the definition of  $V_{\text{cl}}^{\text{hor}}$ , we obtain:

$$\sum_{\mu=1}^{N_{\text{at}}} \sum_{k=1}^{3N_{\text{at}}} m_{\mu}^{1/2} \left( y_{\mu}^0 F_{k,3\mu} - z_{\mu}^0 F_{k,3\mu-1} \right) q_k = 0$$

And, due to the generic determination vector  $\{q_k\}$  one obtains

$$\sum_{\mu=1}^{N_{\text{at}}} m_{\mu}^{1/2} \left( y_{\mu}^0 F_{k,3\mu} - z_{\mu}^0 F_{k,3\mu-1} \right) = 0 \quad k=1 \dots 3N_{\text{at}}$$

The relations c and d are proven from the 2<sup>nd</sup> and 3<sup>rd</sup> component of (\*)

We can then construct 6 eigenstates of the force matrix  $F_{kl}$  with 0 eigenvalues:

Corollary Let  $c_1^{tz}$ ,  $c_2^{tz}$  and  $c_3^{tz}$  be the three translational vectors ( $3N_{\text{at}} \times 1$ )

$$p_1^{tz} = \begin{pmatrix} m_1^{1/2} \\ 0 \\ 0 \\ m_2^{1/2} \\ 0 \\ 0 \end{pmatrix} \quad p_2^{tz} = \begin{pmatrix} 0 \\ m_1^{1/2} \\ 0 \\ 0 \\ m_2^{1/2} \\ 0 \end{pmatrix} \quad p_3^{tz} = \begin{pmatrix} 0 \\ 0 \\ m_1^{1/2} \\ 0 \\ 0 \\ m_2^{1/2} \end{pmatrix}$$

and let  $c_1^{rt}$ ,  $c_2^{rt}$  and  $c_3^{rt}$  be the three rotational vectors ( $3N_{\text{at}} \times 1$ )

$$\begin{array}{l}
 f_1^{\text{rot}} = \begin{pmatrix} 0 \\ -m_1^{1/2} z_1^0 \\ m_1^{1/2} y_1^0 \\ 0 \\ -m_2^{1/2} z_2^0 \\ m_2^{1/2} y_2^0 \end{pmatrix} \quad
 f_2^{\text{rot}} = \begin{pmatrix} m_2^{1/2} z_1^0 \\ 0 \\ -m_1^{1/2} x_1^0 \\ m_2^{1/2} z_2^0 \\ 0 \\ -m_2^{1/2} x_2^0 \end{pmatrix} \quad
 f_3^{\text{rot}} = \begin{pmatrix} -m_1^{1/2} y_1^0 \\ m_1^{1/2} x_1^0 \\ 0 \\ -m_2^{1/2} y_2^0 \\ m_2^{1/2} x_2^0 \\ 0 \end{pmatrix}
 \end{array}$$

Then  $F C_s^{\text{tr}} = F C_s^{\text{rot}} = 0 \quad s=1,2,3$  i.e.  $C_s^{\text{tr}}$  and  $C_s^{\text{rot}}$  are 6 modes with 0 frequency.

proof:

$F C_s^{\text{tr}} = 0$  directly follows from equation A of the previous theorem.

$F C_s^{\text{rot}} = 0$  " " " " " B-D of the previous theorem.

Since A follows from the condition of no external forces it must be enclosed to rigid translation. The connection is readily established by expressing the mode coordinate in terms of the displacement coordinates.

$$Q_1^{\text{tr}} = f_1^{\text{tr}} \cdot \vec{q} = \sum_{\mu} m_{\mu} (x_{\mu} - x_{\mu}^0)$$

$$Q_2^{\text{tr}} = f_2^{\text{tr}} \cdot \vec{q} = \sum_{\mu} m_{\mu} (y_{\mu} - y_{\mu}^0)$$

$$Q_3^{\text{tr}} = f_3^{\text{tr}} \cdot \vec{q} = \sum_{\mu} m_{\mu} (z_{\mu} - z_{\mu}^0)$$

$$\vec{Q}^{\text{tr}} = \sum_{\mu=1}^{N_{\text{tot}}} m_{\mu} (\vec{R}_{\mu} - \vec{R}_{\mu}^0)$$

$Q_s^{\text{tr}}$  is the translation of the center of mass in  $x, y, \text{ or } z$  direction.

$$M \dot{\vec{Q}}^{\text{tr}} = \vec{P}_{\text{tot}} \text{ constant}$$

Analogously, the mode coordinates  $Q_s^{\text{rot}}$  can be grouped together

$$(Q_1^{\text{rot}}, Q_2^{\text{rot}}, Q_3^{\text{rot}}) = \sum_{\mu=1}^{N_{\text{tot}}} m_{\mu} \vec{R}_{\mu}^0 \times (\vec{R}_{\mu} - \vec{R}_{\mu}^0) = \sum_{\mu=1}^{N_{\text{tot}}} m_{\mu} (\vec{R}_{\mu}^0 \times \vec{R}_{\mu})$$

$$\Rightarrow \dot{\vec{Q}}^{\text{rot}} \approx \vec{L}_{\text{tot}} = \text{constant} \Rightarrow Q \propto \text{rotation angle.}$$

Now one should prove that  $f_1^{tr}, f_2^{tr}, f_3^{tr}$  generates the same representation as the functions  $x, y, z$ .

$$\hat{T} f_n^{tr} = \sum_{m=1}^3 \Gamma_{mn}^{tr}(T) f_m^{tr}$$

encl.  $\Gamma_{mn}^{tr}(T) \equiv \Gamma_{mn}^{rec}(T)$ .

The result is easily obtained since, if we define  $e_m = (e_m)_j = \delta_{jm}$

$m, j = 1, 2, 3$

$$\hat{T} e_n = \sum_{m=1}^3 \Gamma_{mn}^{rec}(T) e_m$$

$$f_n^{tr} = \begin{pmatrix} m_1^{1/2} \hat{e}_n \\ m_2^{1/2} \hat{e}_n \\ \vdots \\ m_{N_{tot}}^{1/2} \hat{e}_n \end{pmatrix}$$

$\hat{T} f_n^{tr} =$  permutes atoms with equal mass + rotate the vectors  $e_n$ .

$$= \begin{pmatrix} m_1^{1/2} \sum_m \Gamma_{mn}^{rec} \hat{e}_m \\ m_2^{1/2} \sum_m \Gamma_{mn}^{rec} \hat{e}_m \\ \vdots \\ m_{N_{tot}}^{1/2} \sum_m \Gamma_{mn}^{rec} \hat{e}_m \end{pmatrix} = \sum_m \Gamma_{mn}^{rec} \begin{pmatrix} m_1^{1/2} \hat{e}_m \\ m_2^{1/2} \hat{e}_m \\ \vdots \\ m_{N_{tot}}^{1/2} \hat{e}_m \end{pmatrix}$$

since  $m_{T(\mu)}^{1/2} = m_\mu^{1/2}$  given that  $T$  is a symmetry operation.

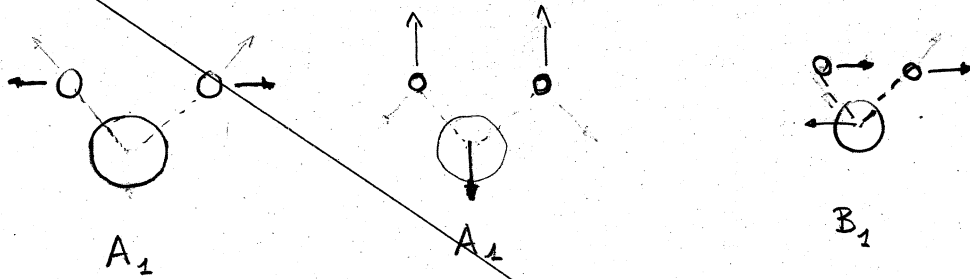
For the rotational representation one has:

$$f_n^{rot} = \begin{pmatrix} m_1^{1/2} \vec{R}_1^0 \times \hat{e}_n \\ m_2^{1/2} \vec{R}_2^0 \times \hat{e}_n \\ \vdots \\ m_{N_{tot}}^{1/2} \vec{R}_{N_{tot}}^0 \times \hat{e}_n \end{pmatrix}$$

$$\Pi(a \times b) = (\Pi a \times \Pi b) \det \Pi$$

And the transformation for zero vectors implies  $\Gamma_{mn}^{rot} = \det(\Pi^{rec}) \Gamma_{mn}^{rec}$ .

A simple orthogonalization though:



Notice that linear combinations of  $A_1$  modes are still  $A_1$ .  $A_1$  modes are defined apart from an overall translation in the  $z$  direction and  $B_2$  modes apart from a  $x$  translation and a rotation around  $y$ . To obtain the "true" modes one should require no center of mass motion and  $L_y = 0$ .

### 8.4 Infrared activity

$$H'_{\text{infrared}} = -\vec{E} \cdot \vec{\mu}$$

$E$  is the external electric field and  $\vec{\mu}$  is the dipole moment associated to the molecular deformation. Since the energy of the molecular vibration corresponds to the infrared part of the electromagnetic spectrum  $\Rightarrow$  infrared activity.  $\vec{\mu}$  transforms like a vector.

$$\vec{E} \cdot \langle f | \vec{\mu} | i \rangle \neq 0 \quad \Gamma_{\text{occ}} \otimes \Gamma_i \otimes \Gamma_f \text{ contains } A_1.$$

Using again the example of water. The molecule in its ground state is in  $A_1 = \Gamma_i$

$$(A_1 \oplus B_1 \oplus B_2) \otimes A_1 = A_1 \oplus B_1 \oplus B_2$$

since  $A_1 \otimes A_1 = A_1$   $B_1 \otimes B_1 = A_1$  and  $B_2 \otimes B_2 = A_1$

we conclude that all the three modes identified above are infrared active. In particular:

$A_1$  ← basis function  $z$  ⇒ stimulated by  $z$  polarized light  $\vec{E} = \hat{z}E$   
mode

and analogously for  $B_1$  with  $x$  polarized light. It is already an interesting observation that linearly polarized light  $\perp$  to the molecular plane (the  $y$  direction) cannot excite vibrations in the water molecule.

### 8.5 | The Raman effect

The Raman effect concerns the detection of inelastically scattered light from a system (a molecule, a crystal...)

The key quantity for its theoretical description is the induced dipole

$$\vec{\mu} = \vec{\alpha} \cdot \vec{E}_i \cos \omega t$$

connected to the (time dependent) incident electric field  $\vec{E}_i \cos \omega t$  by the polarization tensor  $\vec{\alpha}$ .  $\vec{\alpha}$  concerns the linear response of the dipole formation in a system ⇒ the relative motion of nuclei (or ions, more specifically) and (valence) electrons. It is thus natural to assume

$$\vec{\alpha} = \vec{\alpha}_0 + \Delta \vec{\alpha} \cos \omega_r t$$

where  $\omega_r$  is the vibrational frequency of a normal mode for the system. One obtains thus:

$$\vec{\mu} = (\vec{\alpha}_0 + \Delta \vec{\alpha} \cos \omega_r t) \vec{E}_i \cos \omega t =$$

$$= \vec{\alpha}_0 \vec{E}_i \cos \omega t + \frac{\Delta \vec{\alpha}}{2} \left[ \cos(\omega - \omega_R)t + \cos(\omega + \omega_R)t \right] \cdot \vec{E}_i$$

where we have used the relation  $\cos \alpha \cos \beta = \frac{1}{2} [\cos(\alpha - \beta) + \cos(\alpha + \beta)]$

It is thus possible to distinguish the

- elastic or Rayleigh contribution  $\vec{\alpha}_0 \vec{E}_i \cos \omega t$
- inelastic Stokes contribution  $\frac{\Delta \vec{\alpha}}{2} \cos(\omega - \omega_R)t \cdot \vec{E}_i$ ; emission of light
- inelastic anti-Stokes contribution  $\frac{\Delta \vec{\alpha}}{2} \cos(\omega + \omega_R)t \cdot \vec{E}_i$ ; absorption of light

From the group theoretical point of view it is important to derive the formal properties of the polarizability  $\vec{\alpha}$ . In short:

$\vec{\alpha}$  is a symmetric second rank tensor.

The fact that we are dealing with a second rank tensor is immediately clear from the equation:

$$\vec{u} = \vec{\alpha} \vec{E}$$

Written in components

$$u_i = \sum_j \alpha_{ij} E_j$$

A change in the coordinates system  $u'_i = \sum_j V_{ij} u_j$  immediately implies

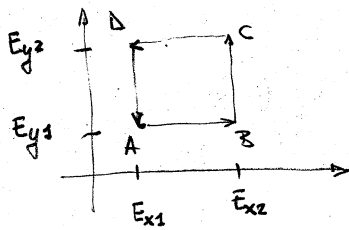
$$u'_i = \sum_{jklm} V_{ij} \alpha_{jk} V_{kl}^{\dagger} \underbrace{V_{lm} E_m}_{= E'_l}$$

$$\Rightarrow \alpha' = V \alpha V^{\dagger}$$

Moreover  $\vec{\alpha}$  is symmetric, i.e.  $\alpha_{ij} = \alpha_{ji}$ . We prove it following Feynmann: Let us calculate the variation of the energy density due to the induced polarization

$$dU_p = \vec{E} \cdot d\vec{P} = \vec{E} \cdot \vec{\alpha} \cdot d\vec{E}$$

Now let us construct the  $\oint dU_p = 0$  and take as a cycle:



$$\int_A^B \vec{E} \cdot d\vec{P} = \int_{E_{x1}}^{E_{x2}} \begin{pmatrix} \Sigma \\ E_{y1} \\ 0 \end{pmatrix} \cdot \vec{\alpha} \cdot \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} d\varepsilon = \int_{E_{x1}}^{E_{x2}} \begin{pmatrix} \Sigma \\ E_{y1} \\ 0 \end{pmatrix} \cdot \begin{pmatrix} \alpha_{xx} \\ \alpha_{yx} \\ \alpha_{zx} \end{pmatrix} d\varepsilon$$

$$= \int_{E_{x1}}^{E_{x2}} (\Sigma \alpha_{xx} + E_{y1} \alpha_{yx}) d\varepsilon = \frac{E_{x2}^2 - E_{x1}^2}{2} \alpha_{xx} + E_{y1} (E_{x2} - E_{x1}) \alpha_{yx}$$

$$\int_B^C \vec{E} \cdot d\vec{P} = \int_{E_{y1}}^{E_{y2}} \begin{pmatrix} E_{x2} \\ \Sigma \\ 0 \end{pmatrix} \cdot \vec{\alpha} \cdot \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} d\varepsilon = \int_{E_{y1}}^{E_{y2}} \begin{pmatrix} E_{x2} \\ \Sigma \\ 0 \end{pmatrix} \cdot \begin{pmatrix} \alpha_{xy} \\ \alpha_{yy} \\ \alpha_{zy} \end{pmatrix} d\varepsilon$$

$$= \int_{E_{y1}}^{E_{y2}} (E_{x2} \alpha_{xy} + \Sigma \alpha_{yy}) d\varepsilon = E_{x2} (E_{y2} - E_{y1}) \alpha_{xy} + \frac{E_{y2}^2 - E_{y1}^2}{2} \alpha_{yy}$$

$$\int_C^D \vec{E} \cdot d\vec{P} = \int_{E_{x2}}^{E_{x1}} \begin{pmatrix} \Sigma \\ E_{y2} \\ 0 \end{pmatrix} \cdot \vec{\alpha} \cdot \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} d\varepsilon = \frac{E_{x1}^2 - E_{x2}^2}{2} \alpha_{xx} + E_{y2} (E_{x1} - E_{x2}) \alpha_{yx}$$

$$\int_D^A \vec{E} \cdot d\vec{P} = \int_{E_{y2}}^{E_{y1}} \begin{pmatrix} E_{x1} \\ \Sigma \\ 0 \end{pmatrix} \cdot \vec{\alpha} \cdot \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} d\varepsilon = \frac{E_{y1}^2 - E_{y2}^2}{2} \alpha_{yy} + E_{x1} (E_{y1} - E_{y2}) \alpha_{xy}$$

$$\Rightarrow 0 = \oint \vec{E} \cdot d\vec{P} = (E_{x2} - E_{x1}) (E_{y2} - E_{y1}) (\alpha_{xy} - \alpha_{yx}) \Rightarrow \alpha_{xy} = \alpha_{yx}$$

An analogous treatment can be reserved to the other directions.

The consequences for the selection rules of Raman activity can be better appreciated when considering that a generic second rank tensor given by

$$\underline{T}^{(2)} = \vec{v} \otimes \vec{w} = \begin{pmatrix} v_x \\ v_y \\ v_z \end{pmatrix} \begin{pmatrix} w_x & w_y & w_z \end{pmatrix}$$

$\Rightarrow$  a symmetric one  $\underline{S}^{(2)} = \vec{v} \otimes \vec{v}$

The basis functions transforming as a vector are  $\begin{matrix} x \\ y \\ z \end{matrix}$ . Consequently the basis functions for a symmetric tensor are

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} (xyz) = \begin{pmatrix} x^2 & xy & xz \\ yx & y^2 & yz \\ zx & zy & z^2 \end{pmatrix}$$

$$x^2, y^2, z^2, xy, xz, yz.$$

For what concerns the selection rules we introduce the Raman Hamiltonian

$$H'_{\text{Raman}} = - \frac{\Delta \alpha}{2} E_i E_s \cos(\omega \pm \omega_r) t$$

The matrix element  $\langle \psi_f | H'_{\text{Raman}} | \psi_i \rangle \neq 0$  if  $\Gamma_i \otimes \Gamma_{H'_{\text{Raman}}}$  contains  $\Gamma_f$ . Interestingly Raman and infrared spectroscopy are complementary for what concerns systems with inversion symmetry since  $\Gamma_{IR} = \Gamma_u$  and  $\Gamma_{\text{Raman}} = \Gamma_g$ . In absence of inversion symmetry one can have vibrational modes which are both IR and Raman inactive: they are called silent modes.



## 8.5 Overtone and combination modes

The vibrations of molecules and solids are quantized. Moreover, being quantized excitations of harmonic oscillators they exhibit Bose-Einstein statistics. Thus it makes sense to create

$d_i^{\dagger 2} |0\rangle \leftarrow$  overtone with frequency  $2\omega_i$

$d_i^{\dagger} d_j^{\dagger} |0\rangle \leftarrow$  combination mode with frequency  $\omega_i + \omega_j$ .

Both the Raman and the IR activity can be computed also for overtones or combination modes. One has simply to take into account that  $\Gamma_{2\omega_i} = \Gamma_i \otimes \Gamma_i$  and  $\Gamma_{\omega_i + \omega_j} = \Gamma_i \otimes \Gamma_j$ . A simple consequence, for example is that all second overtones are Raman active since  $x^2 + y^2 + z^2$  is totally symmetric and  $\Gamma_i \otimes \Gamma_i$  always contains the totally symmetric irreducible representation.