Chapter 8. Molecular vibration, Infrared, and Raman activity

8.1 Molecular vibration: background

Group theory helps in finding the solution of the dynamical matrix for molecular vibrations. In general the Hamiltonian for a molecule reads:

$$H = \sum_{i=1}^{N_{el}} \frac{\hat{p}_i^2}{2m_e} + \sum_{\mu=1}^{N_{at}} \frac{\hat{P}_\mu^2}{2m_\mu} - \sum_{i\mu} \frac{e^2 Z_\mu}{4\pi\varepsilon_0 |\hat{r}_i - \hat{R}_\mu|}$$

$$+ \sum_{i,j} \frac{e^2}{4\pi\varepsilon_0 |\hat{r}_i - \hat{r}_j|} + \sum_{\mu\nu} \frac{e^2 Z_\mu Z_\nu}{4\pi\varepsilon_0 |\hat{R}_\mu - \hat{R}_\nu|}$$

If now we do the Born-Oppenheimer approximation and we solve the (formidably complex) problem of N_{el} interacting electrons in presence of N_{at} nuclei fixed at positions $\vec{R}_\mu$ we obtain, to start with, the $E_g(\{\vec{R}_\mu\})$, ground state electronic energy. The dynamic of the nuclei can be treated by the effective potential:

$$V(\{\vec{R}_\mu\}) = \sum_{\mu\nu} \frac{e^2 Z_\mu Z_\nu}{4\pi\varepsilon_0 |\vec{R}_\mu - \vec{R}_\nu|} + E_g(\{\vec{R}_\mu\})$$

We are particularly interested into $V(\{\vec{R}_\mu\})$ around the equilibrium coordinates $\{\vec{R}_\mu^0\}$. We take the zero of the energy at the potential minimum and expand $V(\{\vec{R}_\mu\})$ in the displacements $\vec{\xi}_\mu = \vec{R}_\mu - \vec{R}_\mu^0$. If now we introduce the generic coordinate index $\kappa = 1 \dots 3N_{at}$

$$H = \sum_\kappa \frac{1}{2} m_\kappa \dot{\xi}_\kappa^2 + \sum_{\kappa,\ell} \frac{1}{2} \frac{\partial^2 V}{\partial \xi_\kappa \partial \xi_\ell}\Big|_{\{\xi_k = 0\}} \xi_\kappa \xi_\ell \qquad (*)$$

The first order expansion vanishes by definition since $\vec{R}_\mu^0$ is an equilibrium configuration.

The hamiltonian (*) becomes give rise to a $(3N_{at} \times 3N_{at})$ secular equation. The roots of the secular equation are the eigenfrequencies ω_K^2 and the eigenvectors denote the normal modes. The standard procedure consists in

i) eliminating the mass:

$$q_k = \sqrt{m_k}\, \xi_k$$

ii) Turn into normal mode coordinates

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

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

where $a_{kK} = a^T_{Kk} = (a^{-1})_{Kk}$ since $\dfrac{\partial^2 V}{\partial q_k \partial q_l}$ is real and symmetric.

and ω_K^2 and a_{kK} are linked by the relation

$$\sum_{k,l} (a^{-1})_{Kk} \frac{\partial^2 V}{\partial q_k \partial q_l} a_{lL} = \omega_K^2 \delta_{KL}$$

Group theory helps in reducing $\left. \dfrac{\partial^2 V}{\partial q_k \partial q_l} \right|_{\{q_n\}=0}$ into a block diagonal form and in classifying the symmetry of the

normal modes.

8.2 Application of Group Theory to Molecular Vibrations

Group theory helps in the diagonalization of $V_{kl} \equiv \frac{\partial^2 V}{\partial q_k \partial q_l}$, in the classification of the normal modes and in determining their interaction with radiation. The fundamental idea:

The symmetry of the molecule is not changed by the normal modes. It follows that

$$\hat{P}_R \, f_K^{(i,\alpha)} = \sum_{K'=1}^{l_i} D^{(i)}(R)_{K'K} \, f_{K'}^{(i,\alpha)}$$

i - representation

α - labels equal representations

f_K - the eigenmode associated to the frequency ω_K
($f_{K'}$ eigenmode degenerate with f_K)

$D^{(i)}(R)$ - matrix representation of the eigenmode

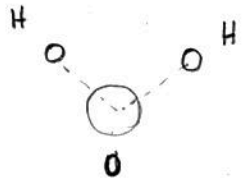
R - operation $\in G$, the group of the Schrödinger equation

Notice: f_K (and $f_{K'}$) is made of $3N_{at}$ components!

The problem of finding the f_K is similar to the one of finding the eigenstates of the electronic Hamiltonian.

4] $\Gamma_{\text{mol. vib.}}$ is expanded in terms of irreducible representations of G. With the help of the projection operator we can construct the $f_k^{(i,\alpha)}$ starting from a "generic" atom displacement.

Example: the water molecule:



The point group of H_2O is C_{2v} since the molecule has a C_2 symmetry axis and 2 vertical symmetry planes.

The character table

		E	C_2	σ_v	$\sigma_{v'}$
z	A_1	1	1	1	1
R_z	A_2	1	1	-1	-1
R_y, x	B_1	1	-1	1	-1
R_x, y	B_2	1	-1	-1	1

$\Gamma^{a.s.} = \{ 3 \;\; 1 \;\; 3 \;\; 1 \}$

↑ = number of atoms (3 = all atoms are showing this symmetry plane; 1 = only O is invariant)

$\Gamma^{a.s} = 2A_1 \oplus B_1$ as can be easily checked.

$\Gamma^{vec} = A_1 \oplus B_1 \oplus B_2$ (encircled for x, y, z)

$\Gamma^{rot} = A_2 \oplus B_1 \oplus B_2$ (" " R_x, R_y, R_z)

$$\Gamma_{mol.\,vib} = \left(\Gamma^{a.s.} \otimes \Gamma_{vec}\right) - \Gamma_{vec} - \Gamma_{tot}$$

$$= \left(2A_1 \oplus B_1\right) \otimes \left(A_1 \oplus B_1 \oplus B_2\right) \ominus A_1 \ominus A_2 \ominus 2B_1 \ominus 2B_2$$

The product of (irreducible) representations has a character set which is the class by class product of the character sets:

$$\chi^{\Gamma_1 \otimes \Gamma_2}(C_k) = \chi^{\Gamma_1}(C_k)\,\chi^{\Gamma_2}(C_k)$$

The further decomposition of the representation follows the usual rules.

$$A_1 \otimes \Gamma = \Gamma \qquad \forall\ \Gamma$$

$$B_1 \otimes B_1 = A_1$$

$$B_1 \otimes B_2 = A_2$$

It follows that $\Gamma_{mol.\,vib} = 2A_1 \oplus 2B_1 \oplus \cancel{2B_2} + B_1 \oplus A_1 \oplus \cancel{A_2}$

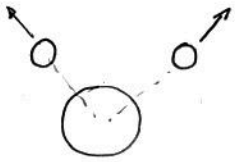
$$\ominus A_1 \ominus \cancel{A_2} \ominus 2B_1 \ominus \cancel{2B_2} =$$

$$= \boxed{2A_1 \oplus B_1}$$

Since they are the three of them one dimensional representations, I can obtain the normal mode by application of the projector operator technique.

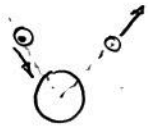
$$\vec{N}_{H_1} = \hat{e}_x + \hat{e}_y \qquad \vec{N}_O = \hat{e}_x + \hat{e}_y \qquad \vec{N}_{H_2} = 0$$

A simple orthogonalization though:



A_1

A_1



B_1

where oxigen does not move. Notice that A_1 modes are defined apart from an overall translation in the z direction and B_1 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 $L_y = 0$