Normal Modes of Vibration

C734b 2008

Internal vibrational modes of a molecule containing N atoms is made up of the superposition of 3N-(5 or 6) simple harmonic vibrations called **normal modes**

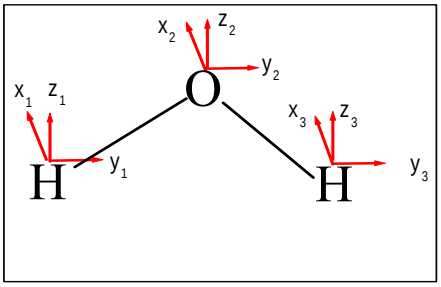
-5 for linear molecules ≡ (3 translations + 2 rotations)
-6 for nonlinear molecules ≡ (3 translations + 3 rotations)

Normal coordinates , Q_k, are linear combinations of atomic displacements x_i, y_i, z_i from the equilibrium positions of the atoms.

$\{Q_k\}$ are **properties of the molecules** and are determined by molecular symmetry
→ each transforms according to one or other IR of the molecular point group.

To find the normal modes study the transformation of the atomic displacements $\{x_i\ y_i\ z_i\}$ by setting up a local basis set $(e_{i1}\ e_{i2}\ e_{is})$ on each atom.

Example: H_2O (C_{2v}) 3N = 3x3 = 9 vectors



Molecule lies in the yz plane C_{2v}: {E, C_2, $\sigma_v(xz)$, $\sigma_v'(xz)$

Γ(R) will be a 9x9 matrix

$$\Gamma(E)=\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

← atom 1

← atom 2

← atom 3

$$\chi(E)=9$$

$\Gamma(C_2)$: $x_1 \rightarrow -x_3$ $x_2 \rightarrow -x_2$ $x_3 \rightarrow -x_1$
$y_1 \rightarrow -y_3$ $y_2 \rightarrow -y_2$ $y_3 \rightarrow -y_1$
$z_1 \rightarrow z_3$ $z_2 \rightarrow z_2$ $z_3 \rightarrow z_3$

$$\Gamma(C_2) = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

← atom 3
← atom 2
← atom 1

$$\chi(C_2) = -1$$

$\Gamma[\sigma_v(xz)]$: $x_1 \rightarrow x_3$ $x_2 \rightarrow x_2$ $x_3 \rightarrow x_1$
$y_1 \rightarrow -y_3$ $y_2 \rightarrow -y_2$ $y_3 \rightarrow -y_1$
$z_1 \rightarrow z_3$ $z_2 \rightarrow z_2$ $z_3 \rightarrow z_1$

$$\Gamma(\sigma_v(xz)) = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

← atom 3
← atom 2
← atom 1

$$\chi[\sigma_v(xz)] = +1$$

$\Gamma[\sigma_v'(yz)]$:

$x_1 \rightarrow -x_1$, $y_1 \rightarrow y_1$, $z_1 \rightarrow z_1$ | $x_2 \rightarrow -x_2$, $y_2 \rightarrow y_2$, $z_2 \rightarrow z_2$ | $x_3 \rightarrow -x_3$, $y_3 \rightarrow y_3$, $z_3 \rightarrow z_3$

$$\Gamma\left(\sigma_{v'}(yz)\right) = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

← **atom 1**

← **atom 2**

← **atom 3**

$$\chi\left[\sigma_{v'}(yz)\right] = +3$$

Reducible character set is:
$\chi = \{9, -1, +1, +3\}$

Don't want to do this for large molecules!

Shortcut: recognize that $\chi(R)$ contribution = 0 from atoms which move because they contribute only to off-diagonal matrix elements.
Let N_R = # atoms which do not move for a given symmetry operation, R.

$$\therefore \chi(R) = \chi_{\Gamma_{x,y,z}} \cdot N_R$$

$\chi_{\Gamma_{x,y,z}}$ = character representation for (x,y,z)

This may require doing a direct sum

$\Gamma_{x,y,z}(C_{2v}) = A_1 \oplus B_1 \oplus B_2$ Can read this off the character table

$$\Rightarrow \chi_{\Gamma_{x,y,z}} = \{3,-1,+1,+1\} \quad \Rightarrow \chi_{\Gamma_{x,y,z}} \cdot N_R = \{3\times 3,-1\times 1,+1\times 1,+1\times 3\}$$

$=\{9,-1,1,3\} \equiv$ same reducible representation as before.

Do reduction in C_{2v}

$$a_1 = \frac{1}{4}[(9)(1)(1)+(1)(-1)(1)+(1)(1)(1)+(3)(1)(1)] = 3$$

$$a_2 = \frac{1}{4}[(9)(1)(1)+(1)(-1)(1)+(1)(-1)(1)+(3)(1)(-1)] = 1$$

$$b_1 = \frac{1}{4}[(9)(1)(1)+(1)(-1)(-1)+(1)(1)(1)+(3)(1)(-1)] = 2$$

$$b_2 = \frac{1}{4}[(9)(1)(1)+(1)(-1)(-1)+(1)(-1)(1)+(3)(1)(1)] = 3$$

$$\therefore \Gamma_{\text{total}} = 3A_1 \oplus A_2 \oplus 2B_1 \oplus 3B_2$$

From character table: $\Gamma_{\text{translation}}$ transforms as $\Gamma_x \oplus \Gamma_y \oplus \Gamma_z = B_1 \oplus B_2 \oplus A_1$

Γ_{rotation} transforms as $\Gamma_{R_x} \oplus \Gamma_{R_y} \oplus \Gamma_{R_z} = B_2 \oplus B_1 \oplus A_2$

Subtract from $\Gamma_{\text{total}} = \Gamma_{\text{vib}} = \Gamma_{\text{total}} - \Gamma_{\text{translation}} - \Gamma_{\text{rotation}}$

$$\Rightarrow \Gamma_{\text{vib}} = 2A_1 \oplus B_2$$

Note: 3N-6 = 3 for $H_2O \equiv$ # modes deduced!

Allowed transitions

It can be shown that the transformation of atomic displacements $\{x_i, y_i, z_i\}$ to a set of normal coordinates $\{Q_k\}$ results in a Hamiltonian which is a sum of one-dimensional harmonic oscillators.

Therefore the wave function is a product of 1D harmonic oscillator wave functions:

$$\psi_{n_k} \equiv |n_k\rangle = N_k H_{n_k}(\gamma_k Q_k) e^{-\frac{\gamma_k^2 Q_k^2}{2}}$$

where $\gamma_k = \frac{\omega_k}{\hbar}$ and $n_k \equiv$ vibrational quantum number of the k^{th} mode.

$$\Rightarrow \psi_{n_1,n_2,\cdots}(Q_1,Q_2,\cdots) = \prod_{k=1}^{3N-\binom{5}{6}} \psi_{n_k}(Q_k)$$

or $$|n_1,n_2,\cdots\rangle = |n_1\rangle|n_2\rangle\cdots = \prod_k |n_k\rangle$$

Typically, most molecules are in their ground vibrational ground state where $n_k = 0$ for k =1, …, 3N-6 or 3N-5

Note: $H_0 \equiv$ constant $\Rightarrow \psi = \prod_k e^{\frac{\gamma_k^2 Q_k^2}{2}}$

which is invariant under any point symmetry operation; that is, its totally symmetric.

Ground states of all normal modes transform as the totally symmetric IR of the point group of the molecule

Excited vibrational state symmetry is determined by the symmetry products of the particular Hermite polynomials of the normal mode(s) involved.

Most common transitions are fundamental transition where only a single vibrational mode is excited.

$$\Delta n_i = 0; \quad n_i \neq n_k \qquad \Delta n_k = 1$$

$$\Rightarrow |0,0,\cdots,0,\cdots,0\rangle \rightarrow |0,0,\cdots,1,\cdots,0\rangle$$

Note: $H_1(x) = 2x$ which means the ground state transforms like Γ_1 and the excited state transforms like Q_k.

Transitions are induced by infrared radiation. The operator responsible is the electric dipole moment operator, **D**.

$$\hat{D} = -e\vec{r}$$

A transition is allowed if the matrix element $\langle 0,0,\cdots 1,\cdots,0 | \hat{D} | 0,0,\cdots,0,\cdots,0\rangle \neq 0$

Thus:

A fundamental transition is allowed only if the normal coordinate Q_k for that mode forms a basis for the same IR as x, y, and/or, z.

For water in C_{2v}, A_1 transforms as z, B_1 transforms as x, and B_2 transforms as y.

$$\because \Gamma_{vib} = 2A_1 \oplus B_2$$ all 3 vibrations are allowed.

Note: only light polarized along the z-axis and the y axis will excite water.
Not an issue in gases or liquids since
i) the light sources are often incoherent sources (random polarizations), and

ii) the molecules tumble about. Such polarization effects could arise using lasers and exciting solid samples whose orientation have been fixed.
It can also have a bearing on samples adsorbed onto surfaces.

Raman Scattering

Raman scattering is an inelastic scattering process.

Photon looses (or gains) one quantum of vibrational energy to (or from) the molecule.

Here, the electric field of the light indices an electric dipole in the molecule, a process that depends on the polarizability of the molecule, α.

$$\Rightarrow \vec{D} = \alpha \vec{E}$$

α is a tensor which has the form: $\begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}$ $\alpha_{ij} = \alpha_{ji}$

The components of the polarizability transform like the binary products of coordinates, x^2, y^2, xz, etc.

Thus:

A fundamental transition is Raman active if a normal mode forms a basis for one or more components of the polarizability

For H_2O A_1, A_2, B_1, and B_2 are all Raman active. This means there are 3 Raman bands and therefore 3 coincidences with the infrared absorption spectrum.
Here coincidence implies the same frequency.

Some general points:

1.) If the symmetry of the molecule is lowered by a perturbation, this may remove degeneracies and/or permit transitions that were forbidden in the more symmetric molecule.

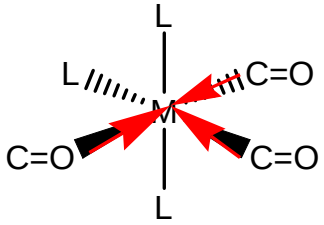
2.) The number of Raman and infrared bands can sometimes be used to distinguish between various structures.

3.) Molecules having an inversion center will have Raman and infrared bands but **no** coincidences.

4.) Stretching modes (for example C=O bonds) can often be analyzed separately because they come in a characteristic region of the infrared spectrum.

This means a full vibrational analysis is unnecessary. Instead, study the transformation of the unit vectors directed along the appropriate ligands.

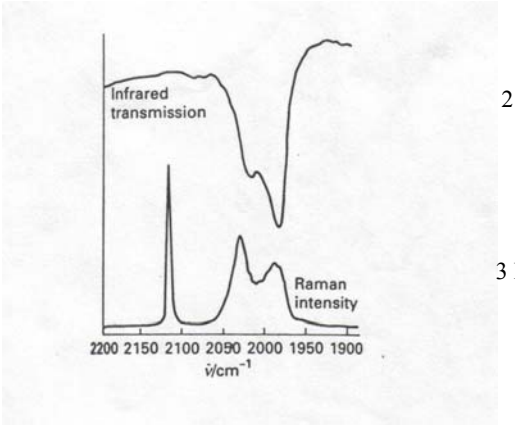
For example: $ML_3(CO)_3$



It is only necessary to study the 3 vectors in C_{2v} symmetry to determine the symmetry of the CO stretching modes.

Example: Consider the case of $Fe(CO)_5$

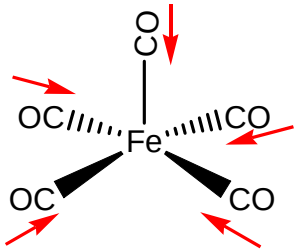
Raman and IR spectra of the molecule in the region of the CO stretches.



2 IR bands

3 Raman bands

The molecule can have two geometries. Do these spectra help to distinguish them?

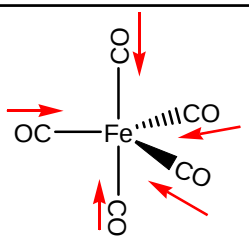


C_{4v}

	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
Γ_{CO}	5	1	1	3	1

	IR active?	Raman active?
$\Gamma_{CO} = 2A_1$	Yes	Yes
$\oplus$		
B_1	No	Yes
$\oplus$		
E	Yes	Yes

Predict 3 IR bands and 5 Raman bands



D_{3h}

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{CO}	5	2	1	3	0	3

		IR active?	Raman active?
$\Gamma_{CO} = 2A_1'$		No	Yes
	$\oplus$		
	E'	Yes	Yes
	$\oplus$		
	A_2''	Yes	No

Expect 2 IR bands and 3 Raman bands

The spectra is most consistent with $Fe(CO)_5$ having a D_{3h} geometry.

This was ultimately confirmed to be the case by X-ray crystallography.