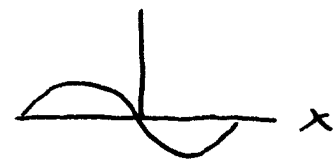
direct product $\chi(\psi_{e,2} \cdot \hat{O} \cdot \psi_{e,1}) = \chi(\psi_{e,2}) \otimes \chi(\hat{O})$
$\otimes\ \chi(\psi_{e,1})$

"contains" the totally symmetric representation.

Generalization of $\int_{-\infty}^{\infty} f_{odd}(x)\,dx = 0$



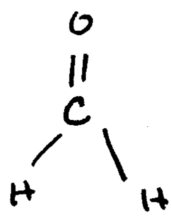
Group: E, i(x)

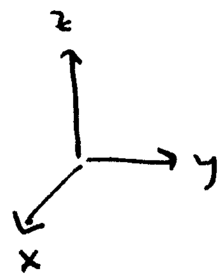
$\int_{-\infty}^{\infty} f_{even}(x)\,dx \neq 0$ in all cases

Selection Rules: $\hat{O} = \mu_i$ $\chi(\psi_{e2} \cdot \mu_i \cdot \psi_{e1})$

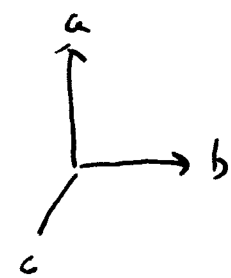
<u>Example:</u>

<u>C_{2v}</u>





or



Permanent moment μ_a only, but we don't require a permanent moment for electronic transitions.
Can consider $\mu_{x,y,z}$ or $\mu_{a,b,c}$ $\Delta S = 0$ also

<u>μ_z</u> $\chi(\mu_z)$ is A_1 $\chi(\psi_2) \otimes \chi(\mu_z) \otimes \chi(\psi_1)$
$= \chi(\psi_2) \otimes \chi(\psi_1)$

Ground State $^1A_1$ $\chi(\psi_1)$ A_1 so $\chi(\psi_2)$ A_1 as well

$^1A_1 - {}^1A_1$ other allowed transitions: $A_2 - A_2$ $B_1 - B_1$
$B_2 - B_2$

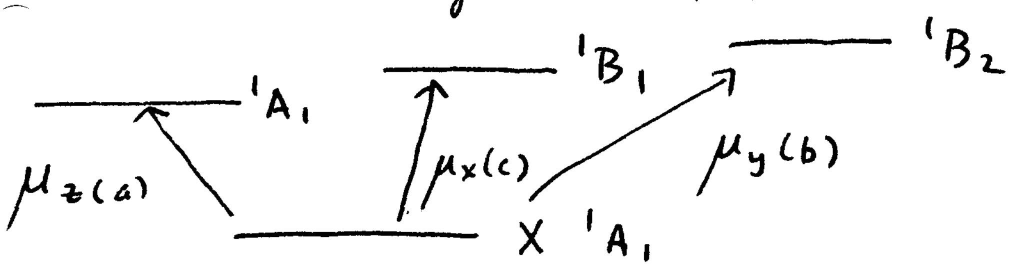
<u>μ_x</u> $\chi(\mu_x)$ is B_1 $\underbrace{\chi(\psi_2) \otimes \chi(\psi_1)}_{B_1} \otimes B_1$ must be A_1

From ground state $^1B_1 \leftrightarrow {}^1A_1$ also $B_2 - A_2$

μ_y $\chi(\mu_y)$ is B_2 $\underbrace{\chi(\psi_2) \otimes \chi(\psi_1)}_{B_2} \otimes B_2$ must be A_1

From ground state $^1B_2 - {}^1A_1$ also $B_1 - A_2$

From the ground $^1A_1$ state:

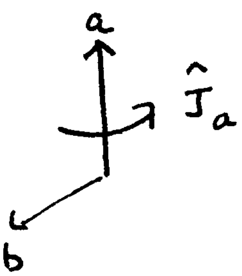


What about vibrational spectroscopy? Must learn more.

skip 2007

Rotational Transitions: One Special Group

based on Hamiltonian: $\mathcal{H}_{rot}/h = A\hat{J}_a^2 + B\hat{J}_b^2 + C\hat{J}_c^2$



$$C_2^{(a)}\hat{J}_a = \hat{J}_a$$
$$C_2^{(b)}\hat{J}_a = C_2^{(c)}\hat{J}_a = -\hat{J}_a$$

$R\psi_{rot} = (\pm 1)\psi_{rot}$ ∴ $\mathcal{H}_{rot}$ invariant to symmetry operation E, $C_2^{(c)}$, $C_2^{(b)}$, $C_2^{(c)}$

Viergruppe (4-group) ∴ ψ_{rot} bases

unusual notation

	E	$C_2^{(a)}$	$C_2^{(b)}$	$C_2^{(c)}$	μ_i	$\psi_{K_{-1}K_{+1}}$	
A	1	1	1	1		ee	
B_a	1	1	-1	-1	μ_a	eo	R_a
B_b	1	-1	1	-1	μ_b	oo	R_b
B_c	1	-1	-1	1	μ_c	oe	R_c

a-type $\mu_a \neq 0$ $\chi(\mu_a)$ is B_a

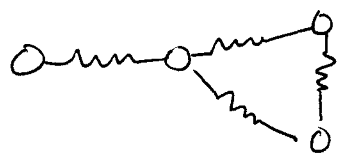
$$\chi(\psi_2) \otimes B_a \otimes \chi(\psi_1) \text{ must be } A$$
$$\chi(\psi_2) \otimes \chi(\psi_1) \text{ is } B_a \quad (B_a \otimes B_a = A)$$

Possibilities: $A \leftrightarrow B_a$ (ee – eo) $\Delta K_{-1} = 0, \pm 2, \pm 4$
$B_b \leftrightarrow B_c$ (oo – oe) $\Delta K_1 = \pm 1, \pm 3$.

Can't deduce strength from symmetry

22. Vibrational Spectroscopy of Polyatomic Molecules

A. Classical Motion + Normal Modes



Even if we assume chemical bonds to be simple harmonic oscillators, the overall vibrational motions are complex. Let's first consider the motion classically in Cartesian coordinates.

$\xi_i \quad i = 1, 3N$ Cartesian coordinates of displacement from equilibrium position.

$$2T = \sum_i m_i \dot{\xi}_i^2 \qquad V = \underbrace{V_e}_{\text{can be set to zero}} + \sum_i \underbrace{\left(\frac{\partial V}{\partial \xi_i}\right)_e}_{0} \xi_i + \frac{1}{2}\sum_{i,j}\left(\frac{\partial^2 V}{\partial \xi_i \partial \xi_j}\right)_e \xi_i \xi_j + \cdots$$

$$2V = \sum_{i,j} b'_{ij}\, \xi_i \xi_j$$

Switching to mass-weighted coordinates:

$$\eta_i = \sqrt{m_i}\, \xi_i \qquad \xi_i = m_i^{-1/2}\, \eta_i$$

$$\therefore\ 2T = \sum_i \dot{\eta}_i^2 \qquad 2V = \sum_{i,j} b_{ij}\, \eta_i \eta_j \qquad b_{ij} = b_{ji}$$

$\mathcal{L} = T - V$; Lagrangian formulation $\dfrac{d}{dt}\dfrac{\partial \mathcal{L}}{\partial \dot{\eta}_k} - \dfrac{\partial \mathcal{L}}{\partial \eta_k} = 0 \quad k = 1,2,3 \ldots 3N$

$$\frac{\partial \mathcal{L}}{\partial \dot{\eta}_k} = \frac{\partial T}{\partial \dot{\eta}_k} = \dot{\eta}_k \qquad \frac{\partial \mathcal{L}}{\partial \eta_k} = -\frac{\partial V}{\partial \eta_k} = -\sum_j b_{kj}\, \eta_j$$

$$\ddot{\eta}_k + \sum_j b_{kj}\, \eta_j = 0 \qquad k = 1,2,3, \ldots 3N$$

$\Rightarrow$ Attempt a harmonic solution $\eta_k = \eta_k^0 \sin(\sqrt{\lambda}\, t + \delta)$

in which all atoms move with same frequency $\omega = \sqrt{\lambda}$ and phase δ.

$$\ddot{\eta}_k = -\lambda \eta_k \quad \therefore \quad -\lambda \eta_k + b_{kk}\eta_k + \sum_{j \neq k} b_{kj}\eta_j = 0$$

Cancelling out the sin terms:

$$-\lambda \eta_k^\circ + b_{kk}\eta_k^\circ + \sum_{j \neq k} b_{kj}\eta_j^\circ = 0$$

$$\sim \quad (b_{kk} - \lambda)\eta_k^\circ + \sum_{j \neq k} b_{kj}\eta_j^\circ = 0$$

To avoid the trivial solution ($\eta_i^\circ = 0$) we set the secular determinant equal to zero:

$$\begin{vmatrix} b_{11} - \lambda & b_{12} & b_{13} & \cdots \\ b_{21} & b_{22} - \lambda & & \\ & & b_{33} - \lambda & \\ \vdots & & & \ddots \end{vmatrix} = 0$$

Solution of $|b_{kj} - \lambda \delta_{kj}| = 0$ yields $3N$ roots for λ
$\sqrt{\lambda} = \omega = 2\pi\nu$ "normal frequencies of vibration".
They need not be distinct and will be zero for non-vibrational modes. The classical motion is a linear combination of the motions in all modes. It depends on the initial conditions. To obtain the relationships among the η_k° in any one mode, substitute the λ into the linear equations.

e.g. $\lambda = \lambda_m$ $\quad (b_{11} - \lambda_m)\eta_1^\circ + b_{12}\eta_2^\circ + \cdots + b_{1,3N}\eta_{3N}^\circ = 0$

$$\vdots$$

$$b_{3N,1}\eta_1^\circ + b_{3N,2}\eta_2^\circ + \cdots + (b_{3N,3N} - \lambda_m)\eta_{3N}^\circ = 0$$

only 3N-1 eq. are independent. They lead to ratios of the η_k° rather than to absolute values. One can use normalization to obtain a full set.

For $\lambda = \lambda_m$, label the η_k° as $\eta_{1m}^\circ, \eta_{2m}^\circ, \ldots \eta_{3N,m}^\circ$

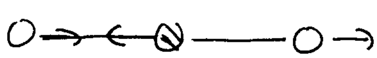
Let $\quad l_{km} = N_m \eta_{km}^\circ \qquad \sum_k l_{km}^2 = 1$

The l_{km} for each mode can be represented by column vectors; e.g.:

$$m=1 \quad \lambda_1 = \omega_1^2 \quad \begin{pmatrix} l_{11} \\ l_{21} \\ l_{31} \\ \vdots \\ l_{3N,1} \end{pmatrix} \qquad m=2 \quad \lambda_2 = \omega_2^2 \quad \begin{pmatrix} l_{12} \\ l_{22} \\ \vdots \\ l_{3N,2} \end{pmatrix}$$

from unitary matrix

which themselves are often represented by displacement arrows:



> We refer to the collective modes as "normal modes".

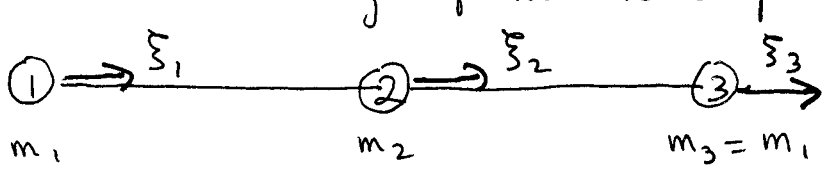
The overall motion is $\eta_i = \sum_m a_m \eta_{im}$

i = atomic coordinate ... m modes

$$\eta_k = \sum_m a_m \underset{l_{km}}{\eta_{km}^\circ} \sin(\sqrt{\lambda_m}\, t + \delta_m)$$

<u>A Simple Example</u> : <u>the Linear B-A-B Molecule</u>

- 3 coordinates only if motion confined to 1-dimension



displacement from equilibrium

$$2V = k(\xi_2-\xi_1)^2 + k(\xi_3-\xi_2)^2$$
$$= k(\xi_1^2 - 2\xi_1\xi_2 + \xi_2^2) + k(\xi_2^2 - 2\xi_2\xi_3 + \xi_3^2)$$

$$2V = k(\xi_1^2 + 2\xi_2^2 + \xi_3^2 - 2\xi_1\xi_2 - 2\xi_2\xi_3)$$

$$2T = m_1\dot{\xi}_1^2 + m_2\dot{\xi}_2^2 + m_1\dot{\xi}_3^2 \qquad \eta_i = \sqrt{m_i}\,\xi_i$$

$$2T = \dot{\eta}_1^2 + \dot{\eta}_2^2 + \dot{\eta}_3^2$$

$$2V = \sum_{i,j} b_{ij}\eta_i\eta_j = k\left\{ \frac{\eta_1^2}{m_1} + \frac{2\eta_2^2}{m_2} + \frac{\eta_3^2}{m_1} - \frac{2\eta_1\eta_2}{\sqrt{m_1m_2}} - \frac{2\eta_2\eta_3}{\sqrt{m_1m_2}} \right\}$$

$$b_{11} = \frac{k}{m_1} \quad b_{22} = \frac{2k}{m_2} \quad b_{33} = \frac{k}{m_1} \quad b_{13} = b_{31} = 0$$

$$b_{12} = b_{21} = -\frac{k}{\sqrt{m_1m_2}} = b_{23} = b_{32}$$

$$|b_{kj} - \lambda\delta_{kj}| = 0 = \begin{vmatrix} \frac{k}{m_1}-\lambda & -k/\sqrt{m_1m_2} & 0 \\ -k/\sqrt{m_1m_2} & \frac{2k}{m_2}-\lambda & -k/\sqrt{m_1m_2} \\ 0 & -k/\sqrt{m_1m_2} & \frac{k}{m_1}-\lambda \end{vmatrix}$$

$$\left(\frac{k}{m_1}-\lambda\right)^2\left(\frac{2k}{m_2}-\lambda\right) - 2\left(\frac{k}{m_1}-\lambda\right)\frac{k^2}{m_1m_2} = 0$$

$$\left(\frac{k}{m_1}-\lambda\right)\left\{\left(\frac{2k}{m_2}-\lambda\right)\left(\frac{k}{m_1}-\lambda\right) - 2k^2/m_1m_2\right\} = 0$$

$$\lambda_1 = \frac{k}{m_1} \qquad \left[\lambda^2 - \lambda\left(\frac{k}{m_1}+\frac{2k}{m_2}\right)\right] = 0$$

$$\lambda_3 = 0 \text{ (translation)} \qquad \lambda_2 = k\left(1/m_1 + 2/m_2\right)$$

$$\omega_1 = \sqrt{k/m_1} = 2\pi\nu_1 \qquad \omega_2 = \sqrt{k(1/m_1 + 2/m_2)} = 2\pi\nu_2 > \omega_1$$

$$\omega_3 = 0$$

The Motion of The Modes

$$(b_{11} - \lambda)\eta_1^0 + b_{12}\eta_2^0 + b_{13}\eta_3^0 = 0$$

$$b_{12}\eta_1^0 + (b_{22} - \lambda)\eta_2^0 + b_{23}\eta_3^0 = 0$$

$$b_{13}\eta_1^0 + b_{23}\eta_2^0 + (b_{33} - \lambda)\eta_3^0 = 0$$

OR

$$(k/m_1 - \lambda)\eta_1^0 - k/\sqrt{m_1 m_2}\,\eta_2^0 = 0 \qquad (1)$$

$$-k/\sqrt{m_1 m_2}\,\eta_1^0 + \left(\frac{2k}{m_2} - \lambda\right)\eta_2^0 - \frac{k}{\sqrt{m_1 m_2}}\eta_3^0 = 0 \qquad (2)$$

$$-k/\sqrt{m_1 m_2}\,\eta_2^0 + \left(\frac{k}{m_1} - \lambda\right)\eta_3^0 = 0 \qquad (3)$$

a) $\lambda_3 = 0$ $\quad (1) \Rightarrow \dfrac{k}{m_1}\eta_1^0 = \dfrac{k}{\sqrt{m_1 m_2}}\eta_2^0$

$$\therefore \eta_1^0 = \eta_3^0$$

$(3) \Rightarrow \dfrac{k}{m_1}\eta_3^0 = \dfrac{k}{\sqrt{m_1 m_2}}\eta_2^0$

$$\eta_2^0 = \frac{\sqrt{m_1 m_2}}{m_1}\eta_1^0 = \sqrt{m_2/m_1}\,\eta_1^0$$

$\eta_i = \sqrt{m_i}\,\xi_i \qquad \xi_1^0 = \xi_3^0;\ \sqrt{m_2}\,\xi_2^0 = \sqrt{\dfrac{m_2}{m_1}}\sqrt{m_1}\,\xi_1^0 \;\therefore\; \xi_1^0 = \xi_2^0$

$\xi_1^0 = \xi_2^0 = \xi_3^0$ all equal $\quad \xi_i = \xi_i^0 \sin\delta$ all equa

$\circ\!\longrightarrow \quad \circ\!\longrightarrow \quad \circ\!\longrightarrow$ translation

(CAN SHOW THAT A SPECIFIC SOLN TO EQ'S : ALL $\xi_i = At$)

23. Vibrational Spectroscopy (cont.)

In column vector format. mode 3 = $\frac{1}{\sqrt{3}}\begin{pmatrix}1\\1\\1\end{pmatrix}$ or $N\begin{pmatrix}1\\ \sqrt{m_2/m_1}\\ 1\end{pmatrix}$

(ξ_i representation)

b) $\lambda_1 = \frac{k}{m_1}$ (1) $\Rightarrow$ $\eta_2^0 = 0$ (as does (3)) η_i represent.

(2) $\Rightarrow$ $\eta_3^0 = -\eta_1^0$

Or, $\xi_2^0 = 0$ $\xi_3^0 = -\xi_1^0$ $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\0\\-1\end{pmatrix}$ ← O—◎—O →

--> <--

"symmetric stretch"

c) $\lambda_2 = k(1/m_1 + 2/m_2)$

$$(1) \Rightarrow -\frac{k\cdot 2}{m_2}\eta_1^0 - \frac{k}{\sqrt{m_1 m_2}}\eta_2^0 = 0$$

$$(3) \Rightarrow -\frac{k}{\sqrt{m_1 m_2}}\eta_2^0 - \frac{2k}{m_2}\eta_3^0 = 0$$

$\Big\}$ $\eta_1^0 = \eta_3^0$

$$(1) \Rightarrow \eta_2^0 = -\frac{2k}{m_2}\frac{\sqrt{m_1 m_2}}{k}\eta_1^0 = -2\sqrt{m_1/m_2}\,\eta_1^0$$

In terms of ξ_i^0: $\xi_1^0 = \xi_3^0$ $\sqrt{m_2}\,\xi_2^0 = -2\sqrt{\frac{m_1}{m_2}}\sqrt{m_1}\,\xi_1^0$

or $\xi_2^0 = -2\frac{m_1}{m_2}\xi_1^0$

Note that $m_1\xi_1^0 + m_2\xi_2^0 + m_1\xi_3^0 = 2m_1\xi_1^0 + m_2\left(-\frac{2m_1}{m_2}\right)\xi_1^0$

$= 0$

$\therefore$ center of mass invariant (true for all vibrations)