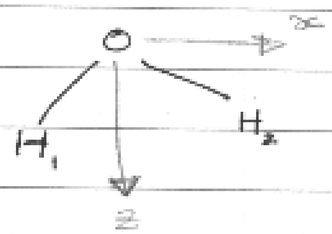
H_2O Molecule

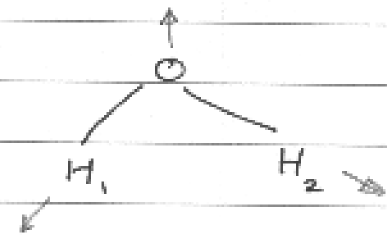
H_2O has $3N-6 = 3(3)-6 = 3$ normal modes

Defining axis



Q_1 at 3652 cm^{-1}

(symmetric stretch)

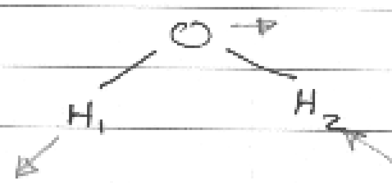


$$Q_1 = a_1 Z_{H_1} - b_1 X_{H_1} - a_2 Z_O + a_3 Z_{H_2} + b_3 X_{H_2}$$

a_i and b_i are constant

Q_2 at 3765 cm^{-1}

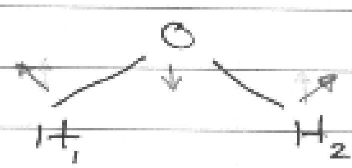
(antisymmetric stretch)



$$Q_2 = a_1 Z_{H_1} - b_1 X_{H_1} + b_2 X_O - b_3 Z_{H_2} - a_3 Z_{H_2}$$

Q_3 at 1545 cm^{-1}

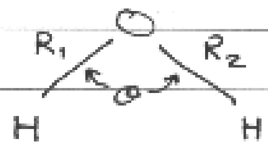
(angle bending)



$$Q_3 = -a_1 Z_{H_1} - b_1 X_{H_1} + a_2 Z_O - a_3 Z_{H_2} + b_3 X_{H_2}$$

The potential energy (V) can be expressed in terms of "internal coordinates" for H_2O:

$$2V = f_{R_1R_1}(\Delta R_1)^2 + f_{R_2R_2}(\Delta R_2)^2 + f_{\Theta}(\Delta\Theta)^2$$
$$+ 2f_{R_1R_2}(\Delta R_1)(\Delta R_2) + 2f_{R_1\Theta}(\Delta R_1)(\Delta\Theta)$$
$$+ 2f_{R_2\Theta}(\Delta R_2)(\Delta\Theta)$$



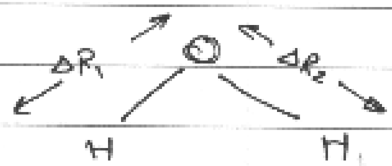
$f_{R_1R_1}$, $f_{R_2R_2}$ and f_{Θ} are diagonal force constants.

$f_{R_1R_2}$, $f_{R_1\Theta}$ and $f_{R_2\Theta}$ are interaction (off-diagonal) force constants.

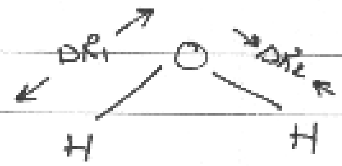
Symmetry Coordinates

Equivalent internal coordinates may be combined using "symmetry rules" to generate symmetry coordinates

$S_1 = \Delta R_1 + \Delta R_2$



$S_3 = \Delta R_1 - \Delta R_2$



$S_2 = \Delta\Theta$

Projection operator P^{γ} of symmetry species γ is used and applied to internal coordinates to generate a set of 3N-6 symmetry coordinates with "symmetry rules" being satisfied.

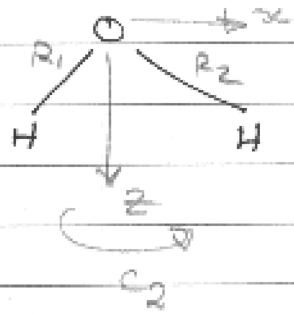
This method is also know as " Symmetry-adapted linear combinations" SALCs.

$$P^{\gamma} = \sum_R (\chi_R^{\gamma})\, \hat{O}_R\, \mathrm{Int}$$

Example of SALCs on H_2O molecule

For $Int = R_1$

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	SALCs
$O_R(R_1)$	R_1	R_2	R_1	R_2	
A_1	1	1	1	1	$2R_1 + 2R_2$
A_2	1	1	-1	-1	$R_1+R_2-R_1-R_2=0$
B_1	1	-1	1	-1	$2R_1 - 2R_2$
B_2	1	-1	-1	1	$R_1-R_2+R_1+R_2=0$



C_{2v}

For $Int = R_2$

Same results will be obtained as above.

For a resultant combination:

$$S_i = a_1 Int_1 + a_2 Int_2 + \cdots$$

The normalization constant is:

$$\eta = (a_1^2 + a_2^2 + \cdots)^{-1/2} \qquad = \frac{1}{\sqrt{8}} = \frac{1}{2\sqrt{2}}$$

Thus: $S_1 = \frac{1}{\sqrt{2}}(R_1 + R_2)$

$S_2 = \frac{1}{\sqrt{2}}(R_1 - R_2)$

for Int = Θ

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	SALCs
$O_R(\Theta)$	Θ	Θ	Θ	Θ	
A_1	1	1	1	1	4Θ
A_2					0
B_1					0
B_2					0

$$S_2 = \frac{1}{4}(4\Theta)$$

$$= \Theta$$

$$\eta = \frac{1}{(4^2)^{1/2}} = \frac{1}{4}$$