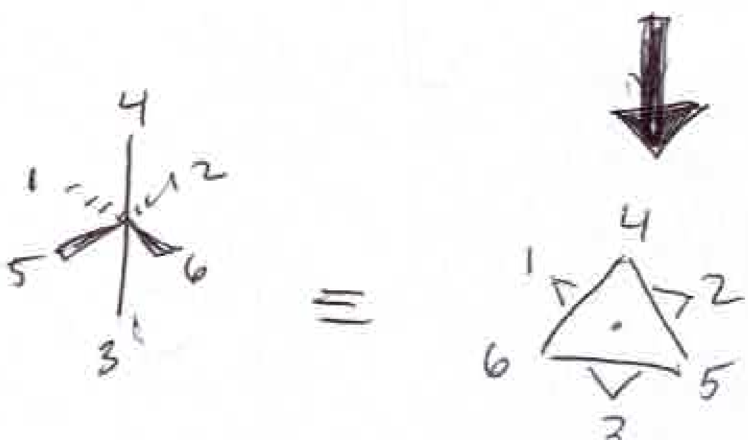
Lecture 10 CH431 9/29/16

Midterm

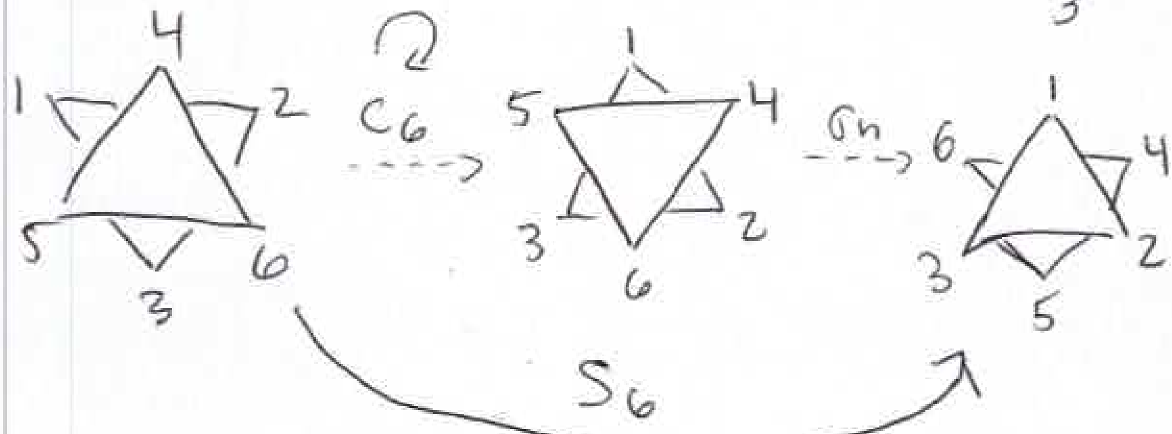
$S_{2n} \rightarrow$ coincides w/ a C_n

$S_6 \rightarrow$ coincides w/ a C_3

triangle representation of octahedral symmetry molecule



C_3, S_6 axis pos.



Γ gamma

symbol for a reducible representation

Γ_{3N} reducible representation for all the 3N degrees of freedom for a molecule

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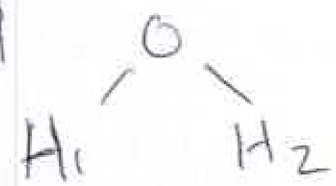
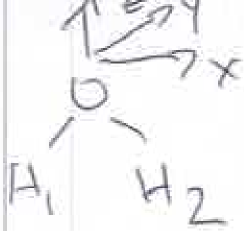


$$\Gamma_{xyz} = \underset{x}{\underset{\uparrow}{B_1}} + \underset{y}{\underset{\uparrow}{B_2}} + \underset{z}{\underset{\uparrow}{A_1}}$$

	E	C2	σ_{xz}	σ_{yz}
B_1	1	−1	1	−1
B_2	1	−1	−1	1
A_1	1	1	1	1
Γ_{xyz}	3	−1	1	1

* Under E symmetry operation, the character of $\Gamma_{x,y,z}$ <u>always</u> = 3

under E symmetry operation the character equals 3 for $\Gamma_{x,y,z}$



	E	C_2	σ_{xz}	σ_{yz}
unmoved atoms	3	1	3	1

O, H_1, H_2 stay in place

O stays in place, H_1 & H_2 move

	E	C_2	σ_{xz}	σ_{yz}
Γ_{xyz}	3	-1	1	1
X unmoved	3	1	3	1
Γ_{3N}	9	-1	3	1

multiply

equals degrees of freedom

Reduction formula

$h = 4$

$$n(A_1) = \frac{1}{4}\left[1(9)(1) + 1(-1)(1) + 1(3)(1) + 1(1)(1)\right]$$

$$= \frac{1}{4}(12) = \boxed{3}$$

Note: this should be a positive integer or zero, will never be negative or a fraction

$$n(A_2) = \frac{1}{4}[1(9)(1) + 1(-1)(1) + 1(3)(-1) + 1(1)(-1)]$$
$$= \frac{1}{4}(4) = \boxed{1}$$

$$n(B_1) = \frac{1}{4}[1(9)(1) + 1(-1)(-1) + 1(3)(1) + 1(1)(-1)]$$
$$= \frac{1}{4}(12) = \boxed{3}$$

$$n(B_2) = \frac{1}{4}[1(9)(1) + 1(-1)(-1) + 1(3)(-1) + 1(1)(1)]$$
$$= \frac{1}{4}(8) = \boxed{2}$$

$$\Gamma_{3N} = 3A_1 + A_2 + 3B_1 + 2B_2$$

$$\Gamma_{translational} = B_1 + B_2 + A_1$$
$$(x \quad y \quad z)$$

$$\Gamma_{rotational} = B_2 + B_1 + A_2$$
$$(R_x \quad R_y \quad R_z)$$

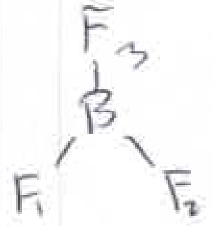
$$\Gamma_{vibrational} = 2A_1 + (0A_2) + B_1 + 0B_2$$
$$= \boxed{2A_1 + B_1}$$

$\Gamma_{vibrational} = 2A_1 + B_1$

IR & Raman active

IR & Raman active

 $\rightarrow$ 3 IR and 3 Raman signals



D_{3h}

		E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$
① Γ_{xyz} : E'	(x,y)	2	-1	0	2	-1	0
+ A_2''	z	1	1	-1	-1	-1	1
Γ_{xyz}		3	0	-1	1	-2	1
X	unmoved	4	1	2	4	1	2
Γ_{3N}		12	0	-2	4	-2	2

② $\boxed{h=12}$

$$n(A_1') = \frac{1}{12}\left(1(12)(1) + 2(0)(1) + 3(-2)(1) + 1(4)(1) + 2(-2)(1) + 3(2)(1)\right)$$
$$= \frac{12}{12} = 1$$

$$n(E') = \frac{1}{12}\left(1(12)(2) + 2(0)(-1) + 3(-2)(0) + 1(4)(2) + 2(-2)(-1) + 3(2)(0)\right)$$
$$= \frac{36}{12} = 3$$

$\downarrow$

$$\Gamma_{3N} = A_1' + A_2' + 3E' + 2A_2'' + E''$$

③ $\Gamma_{trans} = \underset{(x,y)}{E'} + \underset{(z)}{A_2''}$

$\Gamma_{rot} = \underset{(R_x,R_y)}{E''} + \underset{(R_z)}{A_2'}$

$\Gamma_{vib} = A_1' + 2E' + A_2''$

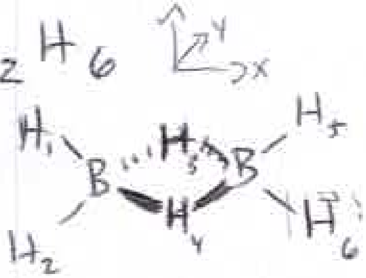
A_1': Raman; $2E'$: Raman, IR; A_2'': IR

3 Raman, 3 IR stretches

Challenge example: try at home!

Challenge example: try at home and look at vibrations on Molecules 360

B_2H_6 D_{2h}



① Γ_{3N}

Γ_{xyz} :

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
B_{3u}	1	-1	-1	1	-1	1	1	-1
B_{2u}	1	-1	1	-1	-1	1	-1	1
B_{1u}	1	1	-1	-1	-1	-1	1	1
Γ_{xyz}	3	-1	-1	-1	-3	1	1	1
χ unmoved	8	0	2	2	0	4	6	2
Γ_{3N}	24	0	-2	-2	0	4	6	2

② $h = 8$

$$n(A_g) = \tfrac{1}{8}\big(1(24)(1) + 1(0)(1) + 1(-2)(1) + 1(-2)(1) + 1(0)(1) + 1(4)(1) + 1(6)(1) + 1(2)(1)\big) = \frac{32}{8} = 4$$

$$n(B_{1g}) = \tfrac{1}{8}\big(1(24)(1) + 1(0)(1) + 1(-2)(-1) + 1(-2)(-1) + 1(0)(1) + 1(4)(1) + 1(6)(-1) + 1(2)(-1)\big) = \frac{24}{8} = 3$$

$\downarrow$ etc.

$$\Gamma_{3N} = 4A_g + 3B_{1g} + 3B_{2g} + 2B_{3g} + A_u + 4B_{1u} + 3B_{2u} + 4B_{3u}$$

③ $\Gamma_{trans} = B_{1u} + B_{2u} + B_{3u}$

$\Gamma_{Rot} = B_{1g} + B_{2g} + B_{3g}$

$\Gamma_{vib} = 4A_g + 2B_{1g} + 2B_{2g} + B_{3g} + A_u + 3B_{1u} + 2B_{2u} + 3B_{3u}$

18 total vibrations!

IR: B_{1u}, B_{2u}, B_{3u} x, y, z

$\rightarrow 3B_{1u} + 2B_{2u} + 3B_{3u} \Rightarrow 8$ IR vibrations

Raman: $A_g, B_{1g}, B_{2g}, B_{3g}$ → quadratic functions

$4A_g + 2B_{1g} + 2B_{2g} + B_{3g} \Rightarrow 9$ Raman vibrations