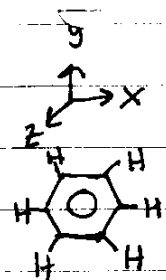


Practice Problems, March 5, 2019



D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_6$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$	
a) $\Gamma_{R_{3N}}$	36	0	0	0	-4	0	0	0	0	12	0	4	3N
d) $\Gamma_{R_{C-H}}$	6	0	0	0	2	0	0	0	0	6	0	2	C-H stretch

a) C_2' C_2' contains 4 atoms - $x \rightarrow x, y \rightarrow -y, z \rightarrow -z$
 $\chi = 4(-1) = -4$

C_2'' All atoms move. $\chi = 0$

σ_h All atoms stay. $x \rightarrow x, y \rightarrow y, z \rightarrow -z$
 $\chi = 12(1 + 1 - 1) = 12$

σ_v - contains C_2' σ_d - contains C_2''

Reducing Γ_R

$$\#A_{1g} = \frac{1}{24}(36 - 12 + 12 + 12) = 2$$

$$\#A_{2g} = \frac{1}{24}(36 + 12 + 12 - 12) = 2$$

etc.

$$\Gamma_{R(3N)} = 2A_{1g} + 2A_{2g} + 2B_{2g} + 2E_g + 4E_{2g} + 2A_{2u} + 2B_{1u} + 2B_{2u} + 4E_u + 2E_{2u}$$

Translations: $1e_u, 1a_{2u}$

Rotations: $1e_g, 1a_{2g}$

Vibrations: $2a_{1g}, 1a_{2g}, 2b_{2g}, 1e_g, 4e_{2g}, 1a_{2u}, 2b_{1u}, 2b_{2u}, 3e_u, 2e_{2u}$

b) $3N - 6 = 30$ vibrations. All 30 are represented above; the 'a' and 'b' representations represent 1 vibration each, but each 'e' represents 2 degenerate vibrations.

c) IR: e_{1u} and a_{2u} vibrations are IR-active.

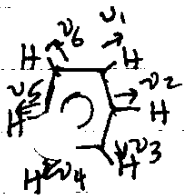
1 a_{2u} vibration \rightarrow 1 peak

3 e_{1u} reps - 3 degenerate pairs of vibrations \rightarrow 3 peaks

Total: 4 peaks in the IR

Raman: a_{1g} , e_{1g} and e_{2g} are Raman-active

2 a_{1g} , 1 e_{1g} , 4 e_{2g} \rightarrow 7 peaks in Raman spectrum



d) See Γ_{C-H} on pg. 1, representing 6 vectors, $v_1 \rightarrow v_6$.

e) $\Gamma_{C-H} = A_{1g} + E_{2g} + B_{1u} + E_{1u}$

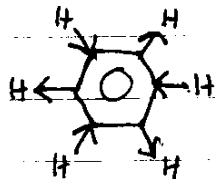
e_{1u} - 2 degenerate C-H stretching vibrations
 \rightarrow 1 C-H stretching peak in IR spectrum

f)

D6h	E	2C ₆	2C ₃	C ₂	3C _{2'}	3C _{2''}	i	2S ₆	2S ₆	σ_h	3 σ_d	3 σ_v
P(v_1)	v_1	v_2	v_3	v_4	v_1	v_2	v_4	v_3	v_2	v_1	v_2	v_1
		v_6	v_5		v_3	v_4		v_5	v_6		v_4	v_3
					v_5	v_6					v_6	v_5


$B_{1u} \quad 1 \quad -1 \quad 1 \quad -1 \quad 1 \quad -1 \quad -1 \quad 1 \quad -1 \quad 1 \quad -1 \quad 1$

$P(B_{1u}) = 4(v_1 - v_2 + v_3 - v_4 + v_5 - v_6)$




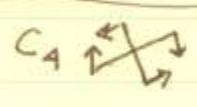
Note that Problems 2-4 are out of order here.

Problem #4

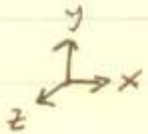


D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ	1	-1	1	-1	1	1	-1	1	-1	1

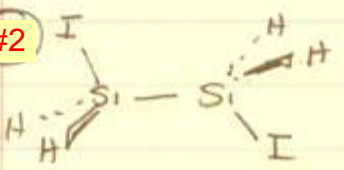
$\Gamma = B_{2g}$

E:  unchanged; $\chi=1$; C_4  $\chi=-1$ etc.

b) The vibration is not IR-active, as it does not result in a net translation (symmetry not the same as transl. along x, y, or z). It is Raman active - symmetry same as xy (representing a change in polarizability).



#2



C_{2h}	E	C_2	i	σ_h	
Γ_R	24	0	0	4	{3N vectors}

E: All atoms and all 24 x, y, z vectors stay in place. $\chi=24$.

C_2 : All atoms (and all 24 vectors) move. O's on diagg. $\rightarrow \chi=0$

i: All atoms move. $\chi=0$

σ_h : I, Si, Si, I stay in place. On each atom, $x \rightarrow x$ $y \rightarrow y$ $z \rightarrow -z$ $\chi = 4(1+1-1) = 4$

b) $\#A_g = \frac{1}{4}(24+4) = 7$

$\#B_g = \frac{1}{4}(24-4) = 5$

$\#A_u = \frac{1}{4}(24-4) = 5$

$\#B_u = \frac{1}{4}(24+4) = 7$

$\Gamma_R = 7A_g + 5B_g + 5A_u + 7B_u$

Transl.: $2B_u, A_u$

Rot.: $1A_g, 2B_g$

Vibr.: $6A_g, 3B_g, 4A_u, 5B_u$

#2

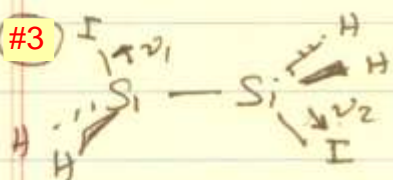
cont.

c) IR-active vibrations: $4A_u, 5B_u \rightarrow 9$ peaksRaman-active vibr.: $6A_g, 3B_g \rightarrow 9$ peaks

d)

They will be distinguishable. Although each contains 9 peaks, they arise from 2 distinct sets of vibrations ($4A_u + 5B_u$ for IR; $6A_g, 3B_g$ for Raman). These different vibrations will have different frequencies. [Recall that this is expected for molecules that contain i : no vibration can be both IR- and Raman-active.]

#3



C_{2v}	E	C_2	i	σ_h	
Γ_R	2	0	0	2	$\{\nu_1, \nu_2\}$

$$\Gamma_R = A_g + B_u$$

\downarrow \downarrow
 Raman IR

Expect one $\overset{\text{Si-I}}{\text{peak}}$ in the IR and one in the Raman. These will occur at different frequencies.

(The A_g is the symmetric stretch; the B_u is the anti-symmetric.)