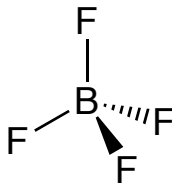


Chemistry 6330  
Problem Set 4 Answers

(1) (a)  $\text{BF}_4^-$  tetrahedral ( $T_d$ )



$T_d$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\Gamma_{xyz}$	3	0	-1	-1	1
$\Gamma_{\text{unmoved atoms}}$	5	2	1	1	3
$\Gamma_{\text{total}}$	15	0	-1	-1	3

If we reduce  $\Gamma_{\text{total}}$  we find that:

$$\Gamma_{\text{total}} = A_1 + E + T_1 + 3T_2$$

Looking at the character table, we can see that:

$$\Gamma_{\text{rotational}} = T_1$$

and

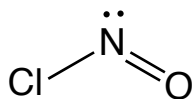
$$\Gamma_{\text{translational}} = T_2$$

therefore,

$$\Gamma_{\text{vibrational}} = A_1 + E + 2T_2$$

By inspection of the character table, the  $2T_2$  modes are IR active and  $A_1$ ,  $E$ , and  $2T_2$  modes are Raman active.

(b) ClNO bent ( $C_s$ )



$C_s$	E	$\sigma_h$
$\Gamma_{xyz}$	3	1
$\Gamma_{\text{unmoved atoms}}$	3	3
$\Gamma_{\text{total}}$	9	3

$$\Gamma_{\text{total}} = 6A' + 3A''$$

$$\Gamma_{\text{rotational}} = A' + 2A''$$

$$\Gamma_{\text{translational}} = 2A' + A''$$

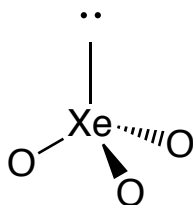
therefore,

$$\Gamma_{\text{vibrational}} = 3A'$$

$$\text{IR active: } 3A'$$

$$\text{Raman active: } 3A'$$

(c) XeO<sub>3</sub> trigonal pyramid (C<sub>3v</sub>)



C <sub>3v</sub>	E	2C <sub>3</sub>	3σ <sub>v</sub>
Γ <sub>xyz</sub>	3	0	1
Γ <sub>unmoved atoms</sub>	4	1	2
Γ <sub>total</sub>	12	0	2

$$\Gamma_{\text{total}} = 3A_1 + A_2 + 4E$$

$$\Gamma_{\text{rotational}} = A_2 + E$$

$$\Gamma_{\text{translational}} = A_2 + E$$

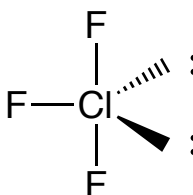
therefore,

$$\Gamma_{\text{vibrational}} = 2A_1 + 2E$$

$$\text{IR active: } 2A_1 + 2E$$

$$\text{Raman active: } 2A_1 + 2E$$

(d) ClF<sub>3</sub> t-shaped (C<sub>2v</sub>)



$C_{2v}$	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$
$\Gamma_{xyz}$	3	-1	1	1
$\Gamma_{\text{unmoved atoms}}$	4	2	2	4
$\Gamma_{\text{total}}$	12	-2	2	4

$$\Gamma_{\text{total}} = 4A_1 + A_2 + 3B_1 + 4B_2$$

$$\Gamma_{\text{rotational}} = A_2 + B_1 + B_2$$

$$\Gamma_{\text{translational}} = A_1 + B_1 + B_2$$

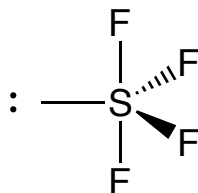
therefore,

$$\Gamma_{\text{vibrational}} = 3A_1 + B_1 + 2B_2$$

$$\text{IR active: } 3A_1 + B_1 + 2B_2$$

$$\text{Raman active: } 3A_1 + B_1 + 2B_2$$

(e)  $\text{SF}_4$  see-saw ( $C_{2v}$ )



$C_{2v}$	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$
$\Gamma_{xyz}$	3	-1	1	1
$\Gamma_{\text{unmoved atoms}}$	5	1	3	3
$\Gamma_{\text{total}}$	15	-1	3	3

$$\Gamma_{\text{total}} = 5A_1 + 2A_2 + 4B_1 + 4B_2$$

$$\Gamma_{\text{rotational}} = A_2 + B_1 + B_2$$

$$\Gamma_{\text{translational}} = A_1 + B_1 + B_2$$

therefore,

$$\Gamma_{\text{vibrational}} = 4A_1 + A_2 + 2B_1 + 2B_2$$

$$\text{IR active: } 4A_1 + 2B_1 + 2B_2$$

$$\text{Raman active: } 4A_1 + A_2 + 2B_1 + 2B_2$$

(2) (a)

Axes oriented such that z-axis goes through O-Xe-O bond and x-axis is through Xe, perpendicular to the plane of the molecule

$D_{2h}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_{xyz}$	3	-1	-1	-1	-3	1	1	1
$\Gamma_{\text{unmoved atoms}}$	5	3	3	1	1	3	3	5
$\Gamma_{\text{total}}$	15	-3	-3	-1	-3	3	3	5

$$\Gamma_{\text{total}} = 2A_g + B_{1g} + B_{2g} + 2B_{3g} + 3B_{1u} + 3B_{2u} + 3B_{3u}$$

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

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

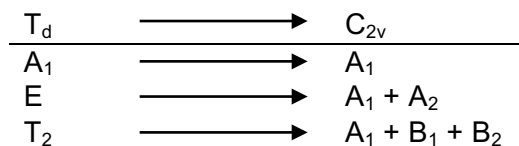
therefore,

$$\Gamma_{\text{vibrational}} = 2A_g + B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$$

(b) IR active:  $2B_{1u} + 2B_{2u} + 2B_{3u}$

Raman active:  $2A_g + B_{3g}$

(c) To solve this problem we need to look at what happens to  $A_1$ , E and  $T_2$  when lowering the symmetry from  $T_d$  to  $C_{2v}$  :



The normal modes for this molecule are:  $4A_1 + A_2 + 2B_1 + 2B_2$

(d) IR active:  $4A_1 + 2B_1 + 2B_2$

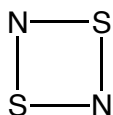
Raman active:  $4A_1 + A_2 + 2B_1 + 2B_2$

(e) There are several possible answers to this question:

(i) Neither structure is correct since neither has the correct number of IR bands.

(ii) Structure I, which gives 8 possible IR bands, is correct and one of the stretches is too weak to be seen or lies under another band.

(3)

 $D_{2h}$  symmetry

Axes oriented such that z-axis goes through the two N-atoms, y-axis goes through the two S-atoms and x axis is perpendicular to the plane of the molecule.

$D_{2h}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_{xyz}$	3	-1	-1	-1	-3	1	1	1
$\Gamma_{\text{unmoved atoms}}$	4	2	2	0	0	2	2	4
$\Gamma_{\text{total}}$	12	-2	-2	0	0	2	2	4

$$\Gamma_{\text{total}} = 2A_g + B_{1g} + B_{2g} + 2B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$$

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

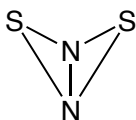
$$\Gamma_{\text{translational}} = B_{1u} + B_{2u} + B_{3u}$$

therefore,

$$\Gamma_{\text{vibrational}} = 2A_g + B_{3g} + B_{1u} + B_{2u} + B_{3u}$$

$$\text{IR active: } B_{1u} + B_{2u} + B_{3u}$$

$$\text{Raman active: } 2A_g + B_{3g}$$

 $C_{2v}$  symmetry

$C_{2v}$	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$
$\Gamma_{xyz}$	3	-1	1	1
$\Gamma_{\text{unmoved atoms}}$	4	0	2	2
$\Gamma_{\text{total}}$	12	0	2	2

$$\Gamma_{\text{total}} = 4A_1 + 2A_2 + 3B_1 + 3B_2$$

$$\Gamma_{\text{rotational}} = A_2 + B_1 + B_2$$

$$\Gamma_{\text{translational}} = A_1 + B_1 + B_2$$

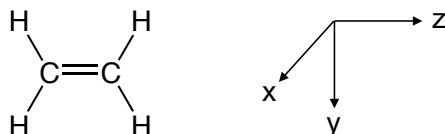
therefore,

$$\Gamma_{\text{vibrational}} = 3A_1 + A_2 + B_1 + B_2$$

IR active:  $3A_1 + B_1 + B_2$   
 Raman active:  $3A_1 + A_2 + B_1 + B_2$

If structure A is correct, the IR and Raman spectra should each have only three bands. If either, or both of the spectra contain more than three bands, this would indicate Structure B is correct.

- (4) Assume the molecule lies in the yz plane, with the z-axis going through the C-C bond, the x-axis perpendicular to the plane of the molecule and the y-axis pointing down.



(a)

$D_{2h}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_{xyz}$	3	-1	-1	-1	-3	1	1	1
$\Gamma_{\text{unmoved atoms}}$	6	2	0	0	0	0	2	6
$\Gamma_{\text{total}}$	18	-2	0	0	0	0	2	6

$$\Gamma_{\text{total}} = 3A_g + B_{1g} + 2B_{2g} + 3B_{3g} + A_u + 3B_{1u} + 3B_{2u} + 2B_{3u}$$

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

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

therefore,

$$\Gamma_{\text{vibrational}} = 3A_g + B_{2g} + 2B_{3g} + A_u + 2B_{1u} + 2B_{2u} + B_{3u}$$

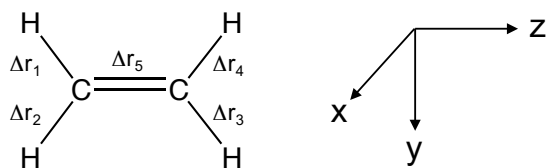
- (b) We can separate the bond internal coordinates into one C-C bond and 4 C-H bonds.

$D_{2h}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_{\text{CH}}$	4	0	0	0	0	0	0	4
$\Gamma_{\text{CC}}$	1	1	1	1	1	1	1	1

$$\Gamma_{\text{CC}} = A_g$$

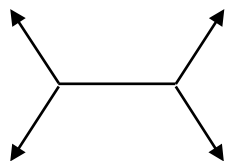
$$\Gamma_{\text{CH}} = A_g + B_{3g} + B_{1u} + B_{2u}$$

(c)

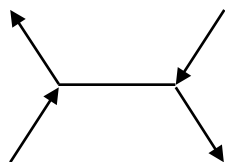


$$\hat{P}^{Ag}(\Delta r_5) \propto \Delta r_5$$

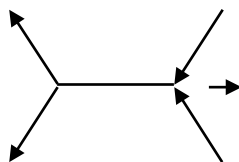
$$\hat{P}^{Ag}(\Delta r_1) \propto \Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4$$



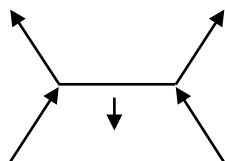
$$\hat{P}^{B_{3g}}(\Delta r_1) \propto \Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4$$



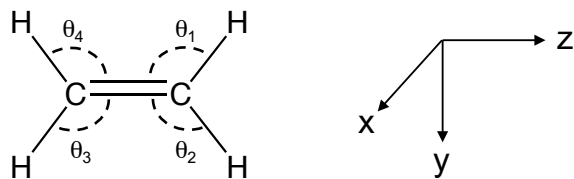
$$\hat{P}^{B_{1u}}(\Delta r_1) \propto \Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4$$



$$\hat{P}^{B_{2u}}(\Delta r_1) \propto \Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4$$



(d) We can use the four C-C-H angles as internal coordinates for in-plane bending modes:



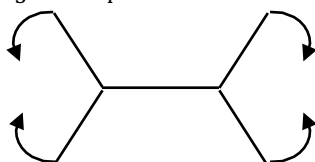
Each of these four angles can be varied independently of the others; we therefore expect no spurious modes.

$D_{2h}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_{\theta_1-\theta_4}$	4	0	0	0	0	0	0	4

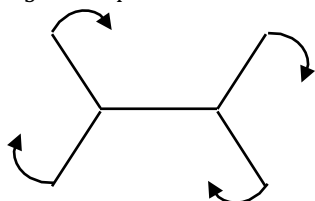
$$\Gamma_{\theta_1-\theta_4} = \Gamma_{CH} = A_g + B_{3g} + B_{1u} + B_{2u}$$

(e) We can use the results from Part C to write the SALC's easily:

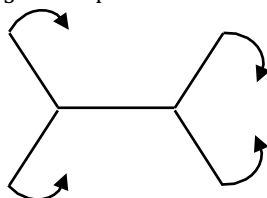
$$\hat{P}^{A_g}(\Delta\theta_1) \propto \Delta\theta_1 + \Delta\theta_2 + \Delta\theta_3 + \Delta\theta_4$$



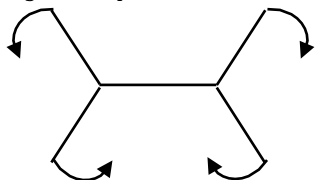
$$\hat{P}^{B_{3g}}(\Delta\theta_1) \propto \Delta\theta_1 - \Delta\theta_2 + \Delta\theta_3 - \Delta\theta_4$$



$$\hat{P}^{B_{1u}}(\Delta\theta_1) \propto \Delta\theta_1 + \Delta\theta_2 - \Delta\theta_3 - \Delta\theta_4$$



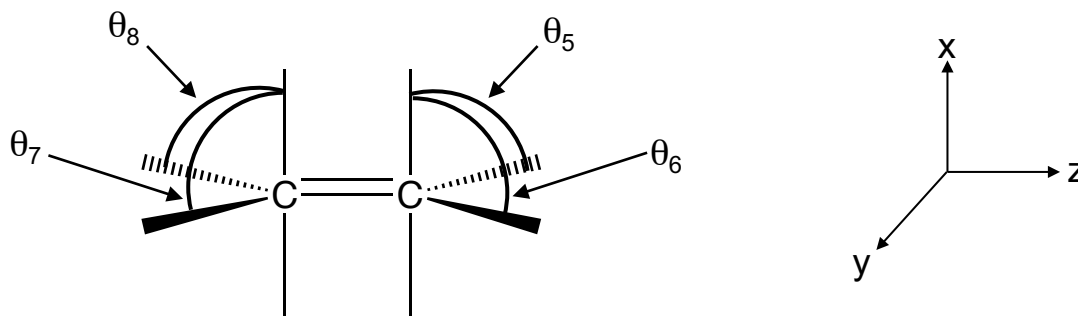
$$\hat{P}^{B_{2u}}(\Delta\theta_1) \propto \Delta\theta_1 - \Delta\theta_2 - \Delta\theta_3 + \Delta\theta_4$$



There are no spurious modes from this choice of in-plane internal coordinates.



- (f) The choice of internal coordinates for out-of-plane bends is more difficult. Imagine lines through the two C atoms, perpendicular to the plane of the molecule. We can use the angles from these lines to the H atoms:



$\theta_9$  "under"  $\theta_5$   
 $\theta_{10}$  "under"  $\theta_6$   
 $\theta_{11}$  "under"  $\theta_7$   
 $\theta_{12}$  "under"  $\theta_8$

$\theta_5 + \theta_9 = 180^\circ$ ;  $\theta_6 + \theta_{10} = 180^\circ$ ;  $\theta_7 + \theta_{11} = 180^\circ$ ;  $\theta_8 + \theta_{12} = 180^\circ$ ; we therefore expect 4 spurious modes.

Before we figure  $\Gamma_{\theta_5-\theta_{12}}$ , let's see what we expect. If we subtract the stretching and in-plane bending modes from  $\Gamma_{\text{vibrational}}$  we are left with

$$\Gamma_{\text{out-of-plane}} = B_{2g} + A_u + B_{3u}$$

$D_{2h}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_{\theta_5-\theta_{12}}$	8	0	0	0	0	0	0	0

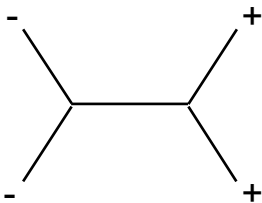
All of the operations except E move all of the angles. Reducing this rep gives us one irr. rep of each symmetry:

$$\Gamma_{\theta_5-\theta_{12}} = A_g + B_{1g} + B_{2g} + B_{3g} + A_u + B_{1u} + B_{2u} + B_{3u}$$

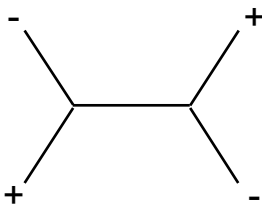
We cannot increase both  $\theta_5$  and  $\theta_9$  at the same time, for this is physically impossible. Likewise,  $\theta_6$  and  $\theta_{10}$ , and so forth. Because the supplementary angles are related by  $\sigma(yz)$ , any irr. rep for which  $\chi[\sigma(yz)] = \chi(E)$  will lead to a physically impossible mode. Thus, the spurious modes are  $A_g$ ,  $B_{3g}$ ,  $B_{1u}$ , and  $B_{2u}$ . (You should try using the projection operators of these irr. reps if you don't follow the logic used above.)

For the three remaining modes we expect:

$$\hat{P}^{B_{2g}}(\Delta\theta_5) \propto \Delta\theta_5 + \Delta\theta_6 - \Delta\theta_7 - \Delta\theta_8 - \Delta\theta_9 - \Delta\theta_{10} + \Delta\theta_{11} + \Delta\theta_{12}$$

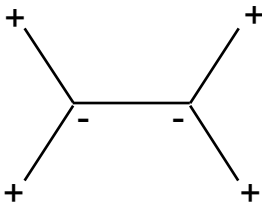


$$\hat{P}^{A_u}(\Delta\theta_5) \propto \Delta\theta_5 - \Delta\theta_6 + \Delta\theta_7 - \Delta\theta_8 - \Delta\theta_9 + \Delta\theta_{10} - \Delta\theta_{11} + \Delta\theta_{12}$$



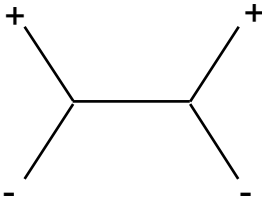
This mode corresponds to twisting the two CH<sub>2</sub> fragments relative to one another.

$$\hat{P}^{B_{3u}}(\Delta\theta_5) \propto \Delta\theta_5 + \Delta\theta_6 + \Delta\theta_7 + \Delta\theta_8 - \Delta\theta_9 - \Delta\theta_{10} - \Delta\theta_{11} - \Delta\theta_{12}$$



What about the  $B_{1g}$  mode, which has not yet been accounted for?

$$\hat{P}^{B_{1g}}(\Delta\theta_5) \propto \Delta\theta_5 - \Delta\theta_6 - \Delta\theta_7 + \Delta\theta_8 - \Delta\theta_9 + \Delta\theta_{10} + \Delta\theta_{11} - \Delta\theta_{12}$$



This is not actually a vibrational mode; it corresponds to rotation about the C-C axis ( $R_z$ ).