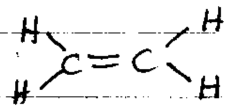
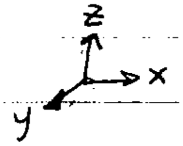
Ch 4, Part B: # 21, 22, 24, 25(#5), 27(+Raman), 28&29(a,b)

21.

a) D_{2h}: E, $C_2(z)$, $C_2(y)$, $C_2(x)$, i, $\sigma(xy)$, $\sigma(xz)$, $\sigma(yz)$

b) 



(May not match your coordinate system; that's OK.)

E $(x,y,z) \to (x,y,z)$
$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \chi = 3$$

$C_2(z)$ $(x,y,z) \to (-x,-y,z)$
$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \chi = -1$$

$C_2(y)$ $(x,y,z) \to (-x,y,-z)$
$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad \chi = -1$$

$C_2(x)$ $(x,y,z) \to (x,-y,-z)$
$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad \chi = -1$$

i $(x,y,z) \to (-x,-y,-z)$
$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad \chi = -3$$

$\sigma(xy)$ $(x,y,z) \to (x,y,-z)$
$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad \chi = 1$$

$\sigma(xz)$ $(x,y,z) \to (x,-y,z)$
$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \chi = 1$$

$\sigma(yz)$ $(x,y,z) \to (-x,y,z)$
$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \chi = 1$$

c)

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
Γ_R	3	-1	-1	-1	-3	1	1	1	(x,y,z)
d) Γ_x	1	-1	-1	1	-1	1	1	-1	x
Γ_y	1	-1	1	-1	-1	1	-1	1	y
Γ_z	1	1	-1	-1	-1	-1	1	1	z

e) $\Gamma_x * \Gamma_y = (1*1) + (-1*-1) + (1*-1) + (1*-1) + (-1^2) + (1^2) + 2(1*-1) = 0$ ✓

$\Gamma_x * \Gamma_z = 1 - 1 + 1 - 1 + 1 - 1 + 1 - 1 = 0$ ✓

$\Gamma_y * \Gamma_z = 1 - 1 - 1 + 1 + 1 - 1 - 1 + 1 = 0$ ✓

All are mutually orthogonal.

22. D_{2d}

a) $h = 8$ $(E, 2S_4, C_2, 2C_2', 2\sigma_d)$

b) $E * A_1 = (2*1) + (0*1) + (-2*1) + (0*1) + (0*1) = 0$

similar for other 3 irreducible reps (A_2, B_1, B_2).

(Note that each has a character of 1 for the E and C_2 classes, for which the E representation has characters of 2 and -2, respectively.)

c) $A_1: 1^2 + 2(1^2) + 1^2 + 2(1^2) + 2(1^2) = 8 = h$ ✓

$A_2: 1^2 + 2(1^2) + 1^2 + 2(-1^2) + 2(-1^2) = 8$ ✓

$B_1: 1^2 + 2(-1^2) + 1^2 + 2(1^2) + 2(-1^2) = 8$ ✓

$B_2: 1^2 + 2(-1^2) + 1^2 + 2(-1^2) + 2(1^2) = 8$ ✓

$E: 2^2 + (-2)^2 = 8$ ✓

d)

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$
Γ_1	6	0	2	2	2
Γ_2	6	4	6	2	0
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
E	2	0	-2	0	0

Reduce Γ_1: $\#A_1 = \frac{1}{8}(6 + 0 + 2 + 4 + 4) = 2$ $\quad \#B_1 = \frac{1}{8}(6 + 0 + 2 + 4 - \cancel{4}) = 1$

$\#B_2 = \frac{1}{8}(6 + 0 + 2 - 4 + 4) = 1$ $\quad \#E = \frac{1}{8}(12 - 4) = 1$

$\boxed{\Gamma_1 = 2A_1 + B_1 + B_2 + E}$

Reduce Γ_2:

$\#A_1 = \frac{1}{8}(6 + 8 + 6 + 4) = 3$ $\quad \#A_2 = \frac{1}{8}(6 + 8 + 6 - 4) = 2$

$\#B_1 = \frac{1}{8}(6 - 8 + 6 + 4) = 1$

$\boxed{\Gamma_2 = 3A_1 + 2A_2 + B_1}$

Pg 3.

23.

NOT assigned for 2015

C_{3v}	E	$2C_3$	$3\sigma_v$	$h=6$
Γ_1	6	3	2	
Γ_2	5	-1	-1	
A_1	1	1	1	
A_2	1	1	-1	
E	2	-1	0	

Γ_1

$\#A_1 = \frac{1}{6}(6+6+6) = 3$

$\#A_2 = \frac{1}{6}(6+6-6) = 1$

$\#E = \frac{1}{6}(12-6) = 1$

$\boxed{\Gamma_1 = 3A_1 + A_2 + E}$

Γ_2

$\#A_1 = \frac{1}{6}(5-2-3) = 0$ $\quad \#A_2 = \frac{1}{6}(5-2+3) = 1$

$\#E = \frac{1}{6}(10+2) = 2$

$\boxed{\Gamma_2 = A_2 + 2E}$

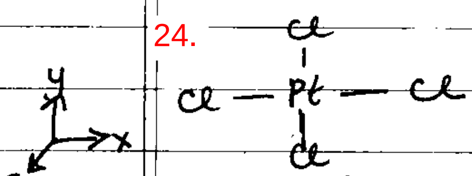
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	$h=48$
Γ	6	0	0	2	2	0	0	0	4	2	

$\#A_{1g} = (6+12+6+12+12)\frac{1}{48} = 1$ $\quad \#A_{2g} = \frac{1}{48}(6-12+6+12-12) = 0$

$\#E_g = \frac{1}{48}(12+0+12+24) = 1$ $\quad \#T_{1u} = \frac{1}{48}(18+12-6+12+12) = 1$

$\boxed{\Gamma = A_{1g} + E_g + T_{1u}}$

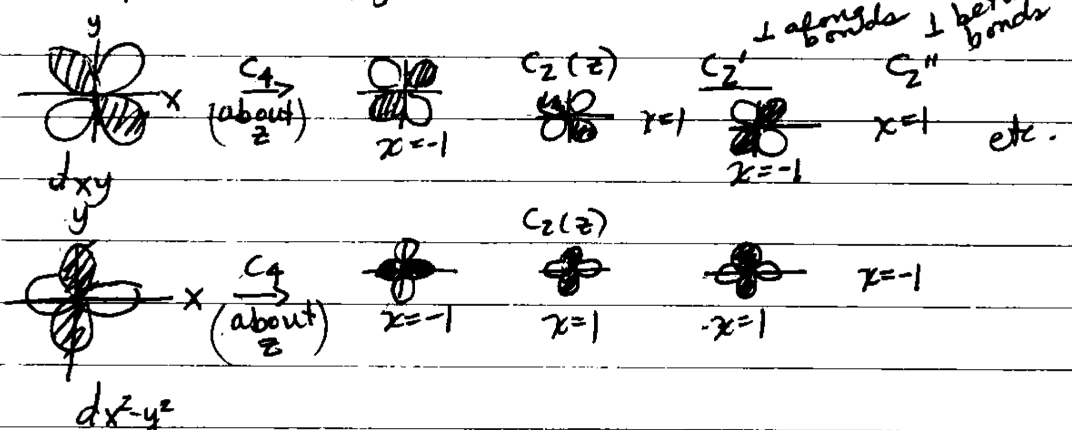
24.



square planar

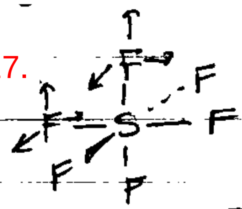
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
$\Gamma_{d_{xy}}$	1	-1	1	-1	1	1	-1	1	-1	1	$=B_{2g}$
$\Gamma_{d_{x^2-y^2}}$	1	-1	1	1	-1	1	-1	1	1	-1	$=B_{1g}$

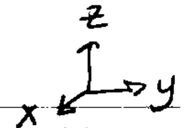
⊥ along bonds ⊥ between bonds



The point here is to subject each orbital to the operations of the D_{4h} group + determine the characters (+1 if unchanged, -1 if sign change). Then compare to table to label the representation.

25. #5 e. O_2F_2 (has only C_2) and i. $[Cr(C_2O_4)_3]^{3-}$ (has C_3 and $\perp C_2$).

27. 



Multiple coordinate systems would work here.

$3 \cdot 7 = 21$ total

Basis set = x, y, z vectors on each atom:

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 = C_4^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
Γ_R	21	0	-1	3	-3	-3	-1	0	5	3	{3N vectors}

$8C_3$: only S stays in place, but axes interconvert $\chi = 0$

$6C_2$ - between bonds - S stays in place. Two axes interconvert, one goes into the opposite of itself $\chi = -1$

$6C_4$ S and two F's stay in place. One axis on each is unchanged → $\chi = 3(1) = 3$

$3C_2 = C_4^2$ S and two F's stay. One axis on each is unchanged; the other 2 axes transform to the opposite of themselves.
e.g. $z \to z$, $x \to -x$, $y \to -y$ $\quad 3(1 + -1 + -1) = -3$

i S stays. $x \to -x$, $y \to -y$, $z \to -z$ $\quad \chi = -3$

S_4 (colinear with C_4): S stays. ~~e.g. $z \to z$~~ One axis goes into the opposite of itself; the other two interchange
(e.g. $z \to -z$, $y \to x$, $x \to -y$) $\quad \chi = -1$

S_6 colinear with C_3. S stays, but Axes interchange. $\chi = 0$

$3\sigma_h$ S and four Fs stay in place. On each, two axes are unchanged and one transforms to the opposite of itself.
(e.g. $z \to -z$, $x \to x$, $y \to y$ $\quad 5(1 + 1 + -1) = 5$)

$6\sigma_d$ (between bonds) S and two F's in plane; others move.
On each atom, one axis is unchanged; others interchange (e.g., $z \to z$, $y \to -x$, $x \to -y$). $\chi = 3(1) = 3$

27. cont.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2=C_4^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
Γ_R	21	0	-1	3	-3	-3	-1	0	5	3	3N v 3
A_{1g}	1	1	1	1	1	1	1	1	1	1	
E_g	2	-1	0	0	2	2	0	-1	2	0	
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x,y,z)
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	

b)

#motions 1 + 2 + 3 + 3 + 3(3) + 3 = 21 total ✓

$$\Gamma_R = A_{1g} + E_g + T_{1g} + T_{2g} + 3T_{1u} + T_{2u}$$

$$\#A_{1g} = \tfrac{1}{48}(21 - 6 + 18 - 9 - 3 - 6 + 15 + 18) = 1$$

$$\#E_g = \tfrac{1}{48}(42 - 18 - 6 + 30) = 1$$

$$\#T_{1g} = \tfrac{1}{48}(63 + 6 + 18 + 9 - 9 \cancel{+6} - 33) = 1$$

$$\#T_{2g} = \tfrac{1}{48}(63 - 6 - 18 + 9 - 9 + 6 - 15 + 18) = 1$$

$$\#T_{1u} = \tfrac{1}{48}(63 + 6 + 18 + 9 + 9 + 6 + 15 + 18) = 3$$

$$\#T_{2u} = \tfrac{1}{48}(63 - 6 - 18 + 9 + 9 - 6 + 15 - 18) = 1$$

c) Translations (3 total motions) → 1 T_{1u} (x, y, z transform together)

Rotations → 1 T_{1g} (represents 3 degenerate rotations)

Vibrations: $A_{1g} + E_g + T_{2g} + 2T_{1u} + T_{2u}$

motions: 1 + 2 + 3 + 2(3) + 3 = 15 = 3N−6 ✓

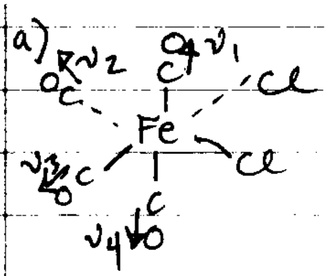
d) "IR-active vibrations: $2\,T_{1u}$ → 6 vibrations, but only 2 bands in spectrum, each representing 3 degenerate motions.

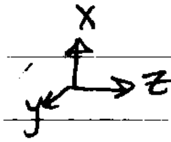
Regarding Raman activity

Of the vibrations listed in part (c) above, the A_{1g}, E_g, and T_{2g} are Raman-active. Three peaks are predicted – one for the A_{1g} vibration, one for the two degenerate E_g vibrations, and one for the three degenerate T_{2g} vibrations.

28 and 29.

a)





C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
Γ_R	4	0	2	2	$\{\nu_1 \rightarrow \nu_4\}$	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1		xy
B_1	1	-1	1	-1	x	xz
B_2	1	-1	-1	1	y	yz

Reduce Γ_R:

$\# A_1 = \frac{1}{4}(4+2+2) = 2$ $\qquad$ $\# A_2 = \frac{1}{4}(4-2-2) = 0$

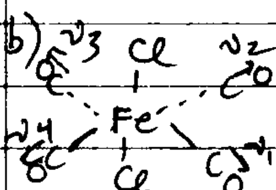
$\# B_1 = \frac{1}{4}(4+2-2) = 1$ $\qquad$ $\# B_2 = \frac{1}{4}(4-2+2) = 1$

$$\Gamma_R = 2A_1 + B_1 + B_2$$

IR-active C-O stretches: $2A_1$, B_1, B_2 $\rightarrow$ 4 total

Raman-active : $2A_1$, B_1, B_2 $\rightarrow$ 4 total

b)



D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
Γ_R	4	0	0	2	0	0	0	4	2	0	ν's
A_{1g}	1	1	1	1	1	1	1	1	1	1	x^2+y^2
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	x^2-y^2
E_u	2	0	-2	0	0	-2	0	2	0	0	(x,y)

Reduce Γ_R:

$\# A_{1g} = \frac{1}{16}(4+4+4+4) = 1$ $\qquad$ $\# B_{1g} = \frac{1}{16}(16) = 1$

$\# E_u = \frac{1}{16}(8+8) = 1$

$$\Gamma_R = A_{1g} + B_{1g} + E_u$$

IR-active: E_u $\rightarrow$ (one band representing 2 motions)

Raman-active: A_{1g}, B_{1g} $\rightarrow$ 2 bands