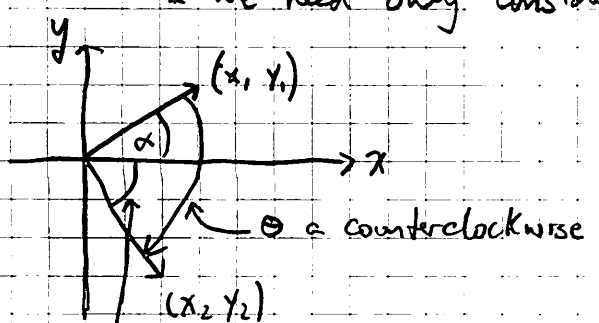
Solutions to PS # 2

1) a) $\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = E$ This matrix was explicitly derived in class

b) For proper rotation around any C_n Axis, the following analysis will hold!

* By convention, the C_n axis is the z-axis, so our z coordinate will not change upon rotation

* We need only consider how x + y project upon rotation



$-(\theta-\alpha) \Rightarrow$ This angle is negative because it is measured from the x axis in the opposite direction of α

$$x_1 = \vec{V}\cos\alpha \qquad y_1 = \vec{V}\sin\alpha \xrightarrow{C_n(\theta)} x_2 = \vec{V}\cos[-(\theta-\alpha)] = -\vec{V}\cos(\theta-\alpha) \qquad y_2 = \vec{V}\sin[-(\theta-\alpha)] = -\vec{V}\sin(\theta-\alpha)$$

Using the identity operation we get the following expression...

$$x_2 = -\vec{V}\cos(\theta-\alpha) = -\vec{V}[\cos\theta\cos\alpha + \sin\theta\sin\alpha] = -x_1\cos\theta - y_1\sin\theta$$

$$y_2 = -\vec{V}\sin(\theta-\alpha) = -\vec{V}[\sin\theta\cos\alpha - \cos\theta\sin\alpha] = -x_1\sin\theta + y_1\cos\theta$$

If we reformulate the above expressions in terms of a matrix representation, we get:

$$C_n(\theta)\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} -x_1\cos\theta - y_1\sin\theta \\ -x_1\sin\theta + y_1\cos\theta \\ z_1 \end{bmatrix} \quad \therefore \quad C_n(\theta) = \begin{bmatrix} -\cos\theta & -\sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \text{where } \theta = \frac{2\pi}{n}$$

The expression above is general for any C_n rotation.

For the case of C_3 $\begin{bmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

c) Using the same deviation + analysis above, we find

$$C_4 = \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

d)

$$i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$ This matrix was expressly derived in class

e)

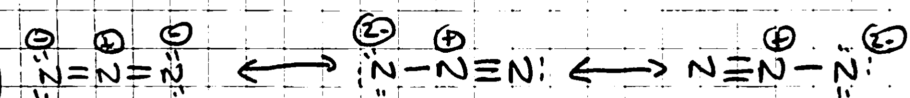
$$\sigma_h \quad \cdot \quad C_n(\theta) \quad = \quad S_n(\theta)$$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}\begin{bmatrix} -\cos\theta & -\sin\theta & 0 \\ -\sin\theta & -\cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \begin{bmatrix} -\cos\theta & -\sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

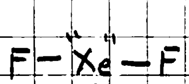
For S_4, $\theta = \frac{2\pi}{4}$ $\therefore$ $S_4 = \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

2a) $C_{\infty v}$ b) C_{3v} c) C_s d) $D_{\infty h}$ e) D_{2d} f) O_h g) D_{6h} h) T_d i) T_d

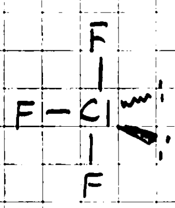
j) O_h k) D_{2d} l) D_{4h} m) C_s n) D_{3h} o) D_{2d} p) C_{2v} q) D_3

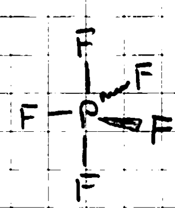
3a) 

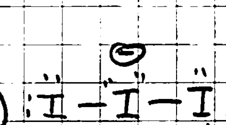
Linear

b) 

Linear

c) 

d) 

e) 

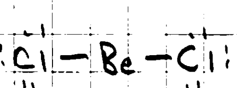
Linear

T-shaped

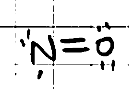
Trigonal Bipyramid

f) 

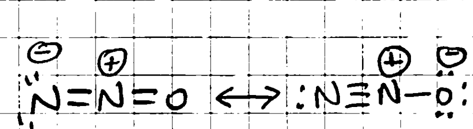
Linear

g) 

Linear

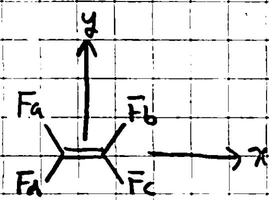
h) 

Linear

i) 

Linear

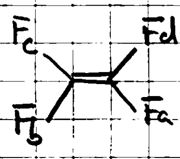
4)



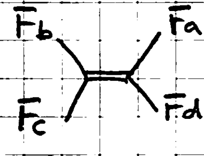
D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	$\cancel{S_4}$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
F_a	F_a	F_c	F_b	F_d		F_c	F_a	F_d	F_b

S_4 should not be included!

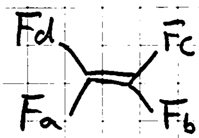
$C_2(z)$



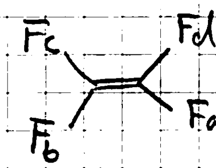
$C_2(y)$



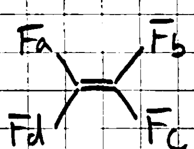
$C_2(x)$



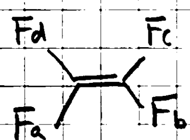
i



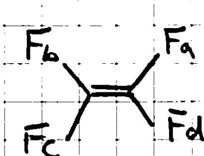
$\sigma(xy)$



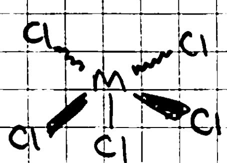
$\sigma(xz)$



$\sigma(yz)$

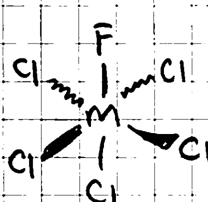


5a)



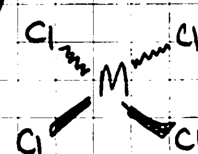
C_{4v}

b)



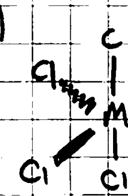
C_{4v}

c)



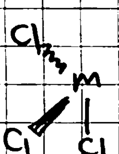
D_{4h}

d)



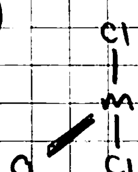
C_{2v}

e)



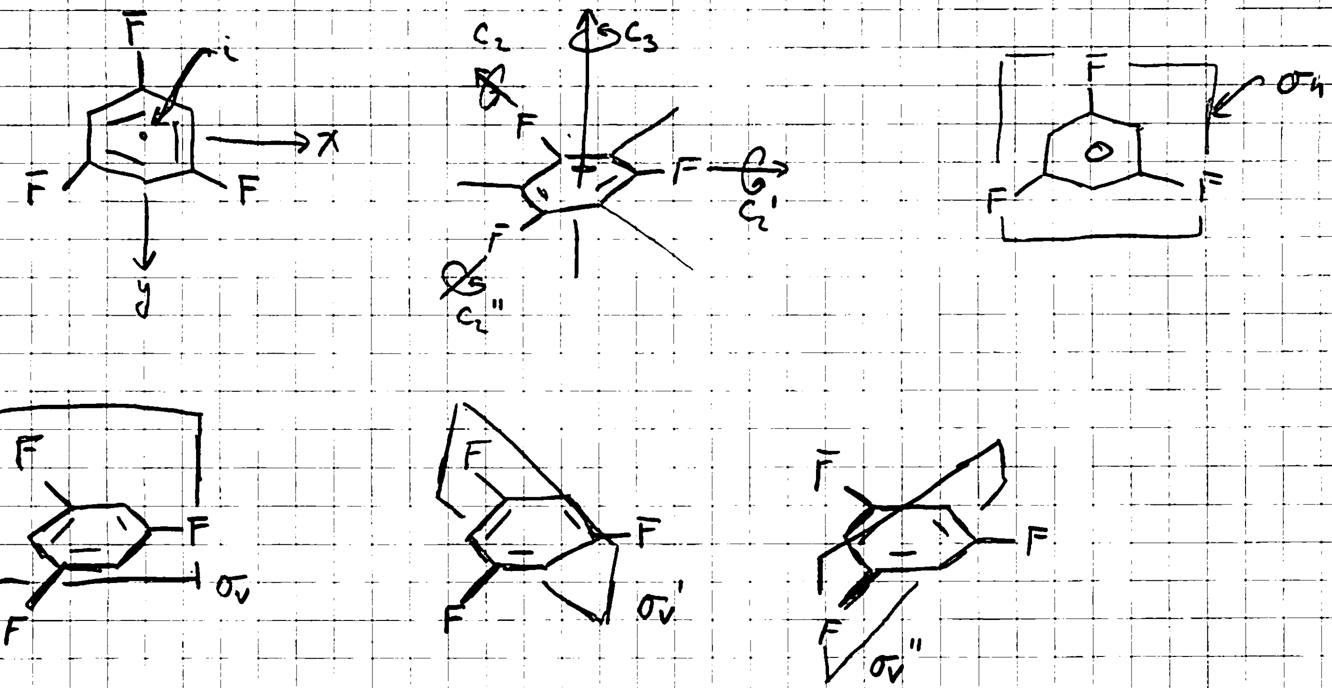
C_{3v}

f)



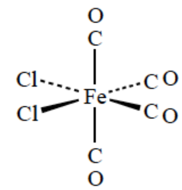
C_{2v}

6)



F
F
F
i
x
y
C_2
C_3
F
F
F
C_2'
C_2''
F
F
F
σ_h
F
F
F
σ_v
F
F
F
σ_v'
F
F
F
σ_v''

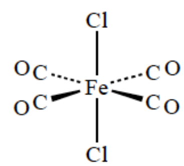
4.28 **a.** *cis*-$Fe(CO)_4Cl_2$ has C_{2v} symmetry.



The vectors for CO stretching have the representation Γ:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
Γ	4	0	2	2	
A_1	1	1	1	1	z
A_2	1	1	–1	–1	
B_1	1	–1	1	–1	x
B_2	1	–1	–1	1	y

$n(A_1) = 1/4[4 \times 1 + 0 \times 1 + 2 \times 1 + 2 \times 1] = 2$
$n(A_2) = 1/4[4 \times 1 + 0 \times 1 + 2 \times (-1) + 2 \times (-1)] = 0$
$n(B_1) = 1/4[4 \times 1 + 0 \times (-1) + 2 \times 1 + 2 \times (-1)] = 1$
$n(B_2) = 1/4[4 \times 1 + 0 \times (-1) + 2 \times (-1) + 2 \times 1] = 1$
$\Gamma = 2A_1 + B_1 + B_2$, all four IR active.



b. *trans*-$Fe(CO)_4Cl_2$ has D_{4h} symmetry.

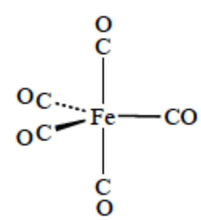
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
Γ	4	0	0	2	0	0	0	4	2	0	
A_{2u}	1	1	1	–1	–1	–1	–1	–1	1	1	z
E_u	2	0	–2	0	0	–2	0	2	0	0	(x,y)

Omitting the operations that have zeroes in Γ:

$n(A_{2u}) = 1/16[4 \times 1 + 2 \times 2 \times (-1) + 4 \times (-1) + 2 \times 2 \times 1] = 0$
$n(E_u) = 1/16[4 \times 2 + 2 \times 2 \times 0 + 4 \times 2 + 2 \times 2 \times 0] = 1$ (IR active)

Note: In checking for IR-active bands, it is only necessary to check the irreducible representations having the same symmetry as x, y, or z, or a combination of them.

c. $Fe(CO)_5$ has D_{3h} symmetry.



The vectors for C–O stretching have the following representation Γ:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
Γ	5	2	1	3	0	3	
E'	2	–1	0	2	–1	0	(x, y)
A_2''	1	1	–1	–1	–1	1	z

$n(E') = 1/12\,[(5 \times 2) + (2 \times 2 \times -1) + (3 \times 2)] = 1$
$n(A_2'') = 1/12\,[(5 \times 1) + (2 \times 2 \times 1) + (3 \times 1 \times -1) + (3 \times -1) + (3 \times 3 \times 1)] = 1$

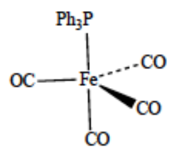
There are two bands, one matching E' and one matching A_2''. These are the only irreducible representations that match the coordinates x, y, and z.

4.29 In 4.28a, the symmetries of the CO stretching vibrations of *cis*-$Fe(CO)_4Cl_2$ (C_{2v} symmetry) are determined as $2\,A_1 + B_1 + B_2$. Each of these representations matches Raman-active functions: A_1 (x^2, y^2, z^2) ; A_2 (xy), B_1 (xz); and B_2 (yz), so all are Raman-active.

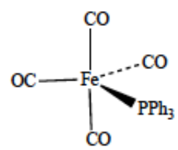
In 4.28b, the symmetries of the CO stretching vibrations of *trans*-$Fe(CO)_4Cl_2$ (D_{4h} symmetry) are $A_{1g} + B_{1g} + E_u$. Only A_{1g} ($x^2 + y^2, z^2$) and B_{1g} ($x^2 - y^2$) match Raman active functions; this complex exhibits two Raman-active CO stretching vibrations.

In 4.28c, the symmetries of the CO stretching vibrations of $Fe(CO)_5$ (D_{3h} symmetry) are $2\,A_1' + E' + A_2''$. Only A_1' ($x^2 + y^2, z^2$) and E' ($x^2 - y^2, xy$) match Raman-active functions; this complex exhibits four Raman-active CO stretching vibrations.

4.33 The possible isomers are as follows, with the triphenylphosphine ligand in either the axial (**A**) or equatorial (**B**) sites.



(**A**) C_{3v}



(**B**) C_{2v}

Note that the triphenylphosphine ligand is approximated as a simple L ligand for the sake of the point group determination. Rotation about the Fe–P bond in solution is expected to render the arrangement of the phenyl rings unimportant in approximating the symmetry of these isomers in solution. The impact of the phenyl rings would likely be manifest in the IR ν(CO) spectra of these isomers in the solid-state.

For **A**, we consider each CO bond as a vector to deduce the expected number of carbonyl stretching modes. The irreducible representation is as follows:

C_{3v}	E	C_3	$3\sigma_v$		
Γ	4	1	2		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

Reduction of the reducible representation affords $2\,A_1 + E$. These stretching modes are IR-active and three ν (CO) absorptions are expected for **A**.

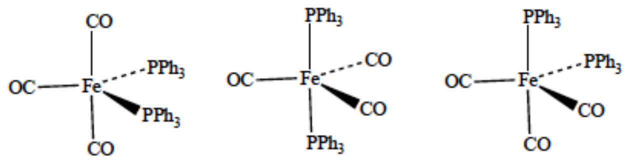
For **B**, a similar analysis affords the following irreducible representation:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
Γ	4	0	2	2		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

Reduction of the reducible representation affords $2\,A_1 + B_1 + B_2$. These stretching modes are IR-active, and four ν (CO) absorptions are expected for **A**.

The reported ν (CO) IR spectrum is consistent with formation of isomer **A**, with the triphenylphosphine ligand in the axial site.

4.34 As in 4.33, we consider the triphenylphosphine ligand as a simple L group for point group determination. The point groups for isomers A, B, and C are as follows:



(A) C_{2v} **(B)** D_{3h} **(C)** C_s

For **A**, the set of irreducible representations for the three CO stretching vibrational modes is $2A_1 + B_1$. These modes are all IR-active in the C_{2v} character table, and three ν (CO) IR absorptions are expected for isomer **A**.

For **B**, the set of irreducible representations for the three CO stretching vibrational modes is $A_1' + E'$. Only the E' mode is IR-active in the D_{3h} point group, and one ν (CO) IR absorption is expected for isomer **B**.

For **C**, the set of irreducible representations for the three CO stretching vibrational modes is $2A' + A''$. These modes are all IR-active in the C_s point group, and three ν (CO) IR absorptions are expected for isomer **C**.

The single ν (CO) IR absorption reported for $Fe(CO)_3(PPh_3)_2$ supports the presence of the D_{3h} isomer **B**.

The *trans* isomer B is reported in R. L. Keiter, E. A. Keiter, K. H. Hecker, C. A. Boecker, *Organometallics*, **1988**, *7*, 2466, and the authors observe splitting of the absorption associated with the E' mode in $CHCl_3$. The forbidden A_1' stretching mode was observed as a weak absorption.