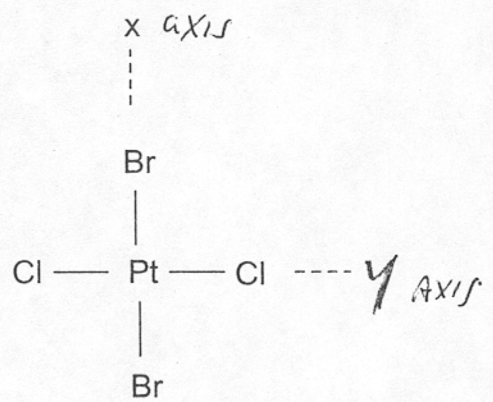
Problem Set 2.

1. Determine the reducible representation for molecular motion for:
a) PF_4Cl. The phosphorous-chlorine bond lies along the major axis of rotation.
b) CH_2Cl_2

3. The reducible representation for molecular motion for the square planar complex trans-dibromodichloroplatinum(II) is shown below.

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

where the molecular axes are defined as shown below.



Determine the group theory labels for molecular motion.
Determine the group theory labels for vibrational motion.
Determine separately the stretching and bending group theory labels for vibrational motion.
Predict the number of bands that you would expect to observe in the IR and Raman spectra of this complex.

4. Consider the tetrahedral complex, $ZnCl_2(pyridine)_2$. Determine its ideal symmetry (the inner coordination sphere of 2Cl and 2N donor atoms bound to Zn), and draw the molecular axes. Determine the group theory labels for ν(Zn-Cl) and ν(Zn-N) and their IR or Raman activity.

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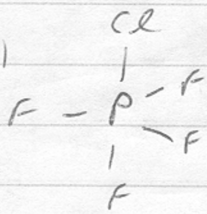
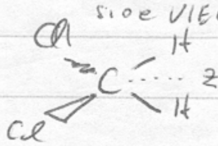
1. (a)



C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_{mol}	18	0	4

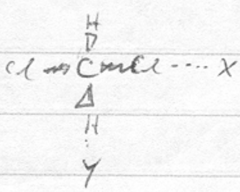
(b)

SIDE VIEW



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
Γ_{mol}	15	-1	3	3

END VIEW



NO QUESTION 2

3.

D_{2h}	E	$C_2(z)$	$C_2(x)$	$C_2(y)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
	15	-1	-3	-3	-3	5	3	3
For a_g	1	1	1	1	1	1	1	1

$$\tfrac{1}{8}(15 - 1 - 3 - 3 - 3 + 5 + 3 + 3) = \underline{2}$$

For b_{1g}	1	1	-1	-1	1	1	-1	-1

$$\tfrac{1}{8}(15 - 1 + 3 + 3 - 3 + 5 - 3 - 3) = \underline{2}$$

For b_{2g}	1	-1	1	-1	1	-1	1	-1

$$\tfrac{1}{8}(15 + 1 - 3 + 3 - 3 - 5 + 3 - 3)$$

$$= \underline{1}$$

For b_{3g} $\quad 1 \quad -1 \quad -1 \quad 1 \quad 1 \quad -1 \quad -1 \quad 1$

$$\tfrac{1}{8}(15 + 1 + 3 - 3 - 3 - 5 - 3 + 3)$$
$$= 1$$

For a_u $\quad 1 \quad 1 \quad 1 \quad 1 \quad -1 \quad -1 \quad -1 \quad -1$

$$\tfrac{1}{8}(15 - 1 - 3 - 3 + 3 - 5 - 3 - 3)$$
$$= 0$$

For b_{1u} $\quad 1 \quad 1 \quad -1 \quad -1 \quad -1 \quad -1 \quad 1 \quad 1$

$$\tfrac{1}{8}(15 - 1 + 3 + 3 + 3 - 5 + 3 + 3)$$
$$= 3$$

For b_{2u} $\quad 1 \quad -1 \quad 1 \quad -1 \quad -1 \quad 1 \quad -1 \quad 1$

$$\tfrac{1}{8}(15 + 1 - 3 + 3 + 3 + 5 - 3 + 3)$$
$$= 3.$$

For b_{3u} $\quad 1 \quad -1 \quad -1 \quad 1 \quad -1 \quad 1 \quad 1 \quad -1$

$$\tfrac{1}{8}(15 + 1 + 3 - 3 + 3 + 5 + 3 - 3)$$
$$= 3$$

$$\Gamma_{Tot} = 2a_g + 2b_{1g} + b_{2g} + b_{3g} + 3b_{1u} + 3b_{2u} + 3b_{3u}$$

$$\Gamma_{VIB} = \Gamma_{MOT} - \Gamma_{TRANS} - \Gamma_{VIB.}$$

$$= \Gamma_{MOT} - \underbrace{(b_{1u} + b_{2u} + b_{3u})}_{TRANS} - \underbrace{(b_{1g} + b_{2g} + b_{3g}}_{ROT}$$

$$= \underbrace{2a_g + b_{1g}}_{\text{RAMAN ACTIVE}} + \underbrace{2b_{1u} + 2b_{2u} + 2b_{3u}}_{\text{IR ACTIVE}}$$

RAMAN ACTIVE — IR ACTIVE

3 BANDS IN RAMAN SPECTRUM — 6 BANDS IN IR SPECTRUM

STRETCHING MODES ν

CAN CONSIDER M–X BONDS SEPARATELY OR ALL TOGETHER

D_{2h}	E	$C_2(z)$	$C_2(x)$	$C_2(y)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ_{Pt-Cl}	2	0	0	2	0	2	0	2
Γ_{Pt-Br}	2	0	2	0	0	2	2	0

AFTER FACTORING, YOU GET AS A FINAL SOLN.

$$\Gamma(Pt-Cl) = a_g + b_{2u}$$

$$\Gamma(Pt-Br) = a_g + b_{3u}$$

— TWO IR ACTIVE STRETCHES

TWO RAMAN ACTIVE

BENDING MOTIONS δ

$\angle Br\text{-}Pt\text{-}Cl$ BOND ANGLES ARE TO BE CONSIDERED

D_{2h}	E	$C_2(z)$	$C_2(x)$	$C_2(y)$	i	$\sigma(xy)$	$\sigma(xz)$	σ
$\Gamma_{\angle BrPtCl}$	4	0	0	0	0	4	0	

$$\Gamma_\delta = a_g + b_{1g} + b_{2u} + b_{3u}$$

IMPOSSIBLE TO HAVE AN a_g BEND

$$\therefore \quad \Gamma_\delta = b_{1g} + b_{2u} + b_{3u}$$

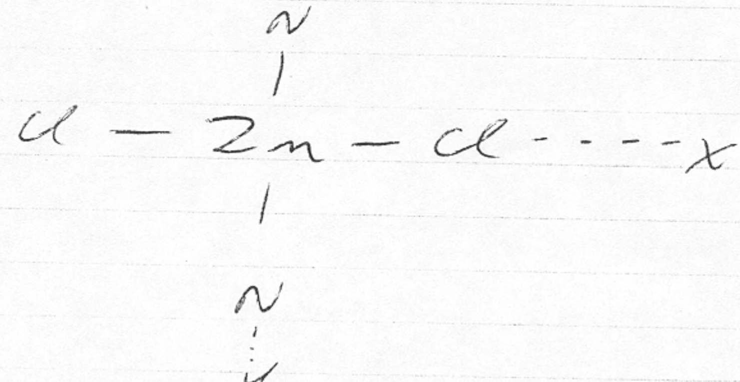
1 RAMAN ACTIVE BEND.

TWO ~~RAMAN~~ IR ACTIVE BENDS.

THE REST OF THE VIBRATIONS ARE OUT OF PLANE DEFORMATIONS OR ROCKING MODES

3. $ZnCl_2(Py)_2$ is tetrahedral with ideal symmetry $\underline{\underline{C_{2v}}}$

LOOKING DOWN THE MAJOR AXIS OF ROTATION (C_2, Z AXIS)



CHOOSE X + Y AXES SO THAT THEY ARE IN THE SAME PLANE AS THE BONDS

DETERMINE SYM. LABELS FOR ν(Zn−Cl)

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
$\Gamma_\nu(Zn\text{-}Cl)$	2	0	2	0

WHICH FACTORS TO

$$\Gamma_\nu(Zn\text{-}Cl) = a_1 + b_1$$ BOTH IR + RAMAN ACTIVE

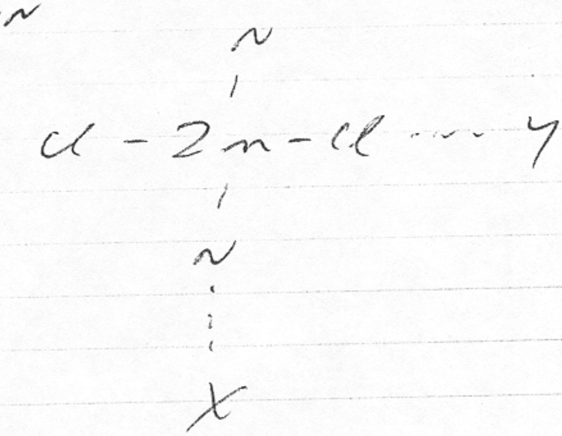
NOW, FOR ν(Zn−N)

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$

WHICH FACTORS TO

$\hat{\Gamma}_v(Zn-N) = a_1 + b_2$ BOTH IR + RAMAN ACTIVE

NOTE: IF YOU LABELLED X, Y AXIS AS SHOWN



YOU WOULD GET

$\hat{\Gamma}_v(Zn-N) = a_1 + b_1$

$\hat{\Gamma}_v(Zn-Cl) = a_1 + b_2$