C734b 2008
Problem Set #6 Solutions

① CH_3D point group $= C_{3v}$ $\Gamma_{x,y,z} = A_1 \oplus E$

a)

C_{3v}	E	$2C_3$	$3\sigma_v$
N_R	5	2	3
Γ_{xyz}	3	0	1
$N_R \cdot \Gamma_{xyz}$	15	0	3

reduction yields $\Gamma_{3N} = 4A_1 \oplus A_2 \oplus 5E$

$\Gamma_{Rot} = A_2 \oplus E$ $\Gamma_{trans} = A_1 \oplus E$

$\therefore \Gamma_{vib} = \Gamma_{3N-6} = 3A_1 \oplus 3E$

$$\left.\begin{array}{l} A_1 \otimes A_1 = A_1 = \Gamma_z, \Gamma_{z^2} \\ A_1 \otimes E = E = \Gamma_{x,y}, \Gamma_{xy,yz} \end{array}\right] \text{ both are ir / Raman active.}$$

$\uparrow$ groundstate, excited normal mode

b) Correlation table construction

T_d:	$\boxed{E}$	$\boxed{8C_3}$	$3C_2$	$6S_4$	$\boxed{6\sigma_d}$
C_{3v}	E	$2C_3$			$3\sigma_v$

boxes ⇒ common classes.

	C_{3v}	E	$2C_3$	$3\sigma_v$	
IRs in T_d	A_1	1	1	1	$= A_1$ in C_{3v}] by inspection
	E	2	−1	0	$= E$ in C_{3v}
	T_2	3	0	1	

↳ reduction yields $T_2 (T_d) = A_1 \oplus E \; (C_{3v})$

$\because$ there are $2T_2$ vibrational modes in T_d

$\Rightarrow \underbrace{A_1 \oplus E \oplus 2T_2}_{T_d} \rightarrow \underbrace{3A_1 \oplus 3E}_{C_{3v}}$ in C_{3v} in agreement with part a)

(2.) $np\,n'p\,n''p \Rightarrow \ell_1 = 1 \quad s_1 = \frac{1}{2}$

a) $\ell_2 = 1 \quad s_2 = \frac{1}{2}$

$\ell_3 = 1 \quad s_3 = \frac{1}{2}$

$\therefore L_{12} = (1+1) - |1-1| = 2, 1, 0$

$\therefore L = L_{12} + \ell_3 \rightarrow |L_{12} - \ell_3|$

$L_{12} = 2 \qquad L = (2+1) \rightarrow |2-1| = 3, 2, 1$

$L_{12} = 1 \qquad L = (1+1) \rightarrow |1-1| = 2, 1, 0$

$L_{12} = 0 \qquad L = (0+1) \rightarrow |0-1| = 1$

$L = S(1x),\ P(3x),\ D(2x),\ F(1x).$

$S_{12} = (\frac{1}{2}+\frac{1}{2}) - |\frac{1}{2}-\frac{1}{2}| = 1, 0$

$S = S_{12} + S_3 \rightarrow |S_{12} - S_3|$

$S_{12} = 1 \qquad S = (1+\frac{1}{2}) - |1-\frac{1}{2}| = 3/2, \frac{1}{2}$

$S_{12} = 0 \qquad S = (0+\frac{1}{2}) - |0-\frac{1}{2}| = \frac{1}{2}$

parity $= (-1)^{\sum_i \ell_i} = (-1)^{1+1+1} = (-1)^3 = -1 \Rightarrow$ all terms are u-terms.

$2S+1 = 4, 2(2x)$

$\therefore$ terms are $^{2S+1}L = {}^4F_u(1x),\ {}^4D_u(2x),\ {}^4P_u(3x),\ {}^4S_u(1x)$

${}^2F_u(2x),\ {}^2D_u(4x),\ {}^2P_u(6x),\ {}^2S_u(2x)$

$\vec{J} = \vec{L} + \vec{S}$

$4F \Rightarrow J = (3+3/2) - |3-3/2| = 9/2, 7/2, 5/2, 3/2$

$2F \Rightarrow J = (3+\frac{1}{2}) - |3-\frac{1}{2}| = 7/2, 5/2$

$4D \Rightarrow J = (2+3/2) - |2-3/2| = 7/2, 5/2, 3/2, \frac{1}{2}$

${}^2D \Rightarrow J = (2+\frac{1}{2}) - |2-\frac{1}{2}| = 5/2, 3/2$

$4P \Rightarrow J = (1+3/2) - |1-3/2| = 5/2, 3/2, \frac{1}{2}$

$2P \Rightarrow J = (1+\frac{1}{2}) - |1-\frac{1}{2}| = 3/2, \frac{1}{2}$

$^4S \Rightarrow J = (0 + 3/2) \to |0 - 3/2| = 3/2$

$^2S \Rightarrow J = (0 + 1/2) \to (0 - 1/2) = 1/2$

$\therefore$ terms are $^{2S+1}L_J \equiv$

$$\boxed{\begin{array}{l} ^4F_{u\,9/2,7/2,5/2,3/2}\ (1x);\quad ^4D_{u\,7/2,5/2,3/2,1/2}\ (2x);\quad ^4P_{u\,5/2,3/2,1/2}\ (3x);\quad ^4S_{u\,3/2}\ (1x) \\ ^2F_{u\,7/2,5/2}\ (2x);\quad ^2D_{u\,5/2,3/2}\ (4x);\quad ^2P_{u\,3/2,1/2}\ (6x),\quad ^2S_{u\,1/2}\ (2x) \end{array}}$$

b) (ns np nd nf) : $l_1 = 0 \quad l_2 = 1 \quad l_3 = 2 \quad l_4 = 3$

$s_1 = 1/2 \quad s_2 = 1/2 \quad s_3 = 1/2 \quad s_4 = 1/2$

$L_{12} = (0+1) - |0-1| = 1$

$L_{123} = |1+2| - |1-2| = 3, 2, 1$

$\vec{L} = \vec{L}_{123} + \vec{l}_4$: $L_{123} = 3 : L = (3+3) - |3-3| = 6, 5, 4, 3, 2, 1, 0$

$L_{123} = 2 : L = (2+3) - |2-3| = 5, 4, 3, 2, 1$

$L_{123} = 1 : L = (1+3) - |1-3| = 4, 3, 2$

$\therefore L = S(1x), P(2x), D(3x), F(3x), G(3x), H(2x), I(1x)$

use part a) $S_{123} = 3/2\ (1x), 1/2\ (2x)$

$\therefore \vec{S} = \vec{S}_{123} + \vec{s}_4$: $S_{123} = 3/2 \Rightarrow S = (3/2 + 1/2) - |3/2 - 1/2| = 2, 1$

$S_{123} = 1/2 \Rightarrow S = (1/2, 1/2) - |1/2, 1/2| = 1, 0$

$\therefore S = 2\,(1x), 1\,(3x), 0\,(2x) \Rightarrow 2S+1 = 5\,(1x), 3\,(3x), 1\,(2x)$

$\therefore$ terms $\equiv$ ^{2S+1}L = $^5S\ (1x)$; $^3S\ (3x)$; $^1S\ (2x)$; $^5P\ (2x)$, $^3P\ (6x)$, $^1P\ (4x)$

$^5D\ (3x)$, $^3D\ (9x)$, $^1D\ (6x)$; $^5F\ (3x)$; $^3F\ (9x)$; $^1F\ (6x)$

$^5G\ (3x)$, $^3G\ (9x)$; $^1G\ (6x)$; $^5H\ (2x)$; $^3H\ (6x)$; $^1H\ (4x)$

$^5I\ (1x)$; $^3I\ (3x)$; $^1I\ (2x)$

parity $= (-1)^{\sum_i l_i} = (-1)^{0+1+2+3} = (-1)^6 = +1 \Rightarrow$ all terms have g-parity

$\vec{J} = \vec{L} + \vec{S}$:

$^5S \Rightarrow J = (2+0) - |2-0| = 2$

$^3S \Rightarrow J = (1+0) - |1-0| = 1$

$^1S \Rightarrow J = (0+0) - |0-0| = 0$

$^5P \Rightarrow J = (2+1) - |2-1| = 3, 2, 1$

$^3P \Rightarrow J = (1+1) - |1-1| = 2, 1, 0$

$^1P \Rightarrow J = (1+0) - |1-0| = 1$

$^5D \Rightarrow J = (2+2) - |2-2| = 4, 3, 2, 1, 0$

$^3D \Rightarrow J = (2+1) - |2-1| = 3, 2, 1$

$^1D \Rightarrow J = (2+0) - |2-0| = 2$

$^5F \Rightarrow J = (2+3) - |2-3| = 5, 4, 3, 2, 1$

$^3F \Rightarrow J = (3+1) - |3-1| = 4, 3, 2$

$^1F \Rightarrow J = (3+0) - |3-0| = 3$

$^5G \Rightarrow J = (4+2) - |4-2| = 6, 5, 4, 3, 2$

$^3G \Rightarrow J = (4+1) - |4-1| = 5, 4, 3$

$^1G \Rightarrow J = (4+0) - |4-0| = 4$

$^5H \Rightarrow J = (5+2) - |5-2| = 7, 6, 5, 4, 3$

$^3H \Rightarrow J = (5+1) - |5-1| = 6, 5, 4$

$^1H \Rightarrow J = (5+0) - |5-0| = 5$

$^5I \Rightarrow J = (6+2) - |6-2| = 8, 7, 6, 5, 4$

$^3I \Rightarrow J = (6+1) - |6-1| = 7, 6, 5$

$^1I \Rightarrow J = (6+0) - |6-0| = 6$

$\therefore$ terms $= \boxed{{}^{2S+1}L_J =}$ $^5S_{2g}$ (1x), $^3S_{1g}$ (3x), $^1S_{0g}$ (2x); $^5P_{3,2,1g}$ (2x); $^3P_{2,1,0g}$ (6x), $^1P_{1g}$ (4x)

$^5D_{4,3,2,1,0g}$ (3x), $^3D_{3,2,1g}$ (9x); $^1D_{2g}$ (6x); $^5F_{5,4,3,2,1g}$ (3x); $^3F_{4,3,2g}$ (9x); $^1F_{3g}$ (6x)

$^5G_{6,5,4,3,2g}$ (3x), $^3G_{5,4,3g}$ (9x); $^1G_{4g}$ (6x); $^5H_{7,6,5,4,3g}$ (2x); $^3H_{6,5,4g}$ (6x); $^1H_{5g}$ (4x)

$^5I_{8,7,6,5,4g}$ (1x); $^3I_{7,6,5g}$ (3x); $^1I_{6g}$ (2x)

(3) $nd\,nf \quad \ell_1 = 2 \quad s_1 = \tfrac{1}{2} \qquad \ell_2 = 3 \quad s_2 = \tfrac{1}{2}$.

$L = |\ell_1 + \ell_2| \to |\ell_1 - \ell_2| = |2+3| - |2-3| = 5, 4, 3, 2, 1$

$S = |s_1 + s_2| \to |s_1 - s_2| = \tfrac{1}{2} + \tfrac{1}{2} - |\tfrac{1}{2} - \tfrac{1}{2}| = 1, 0$

$J = L + S - |L - S|$

$(L, S) \quad (5,1) : J = 5+1 \to |5-1| = 6, 5, 4$

$(5,0) : J = 5$

$(4,1) : J = 4+1 \to |4-1| = 5, 4, 3$

$(4,0) : J = 4$

$(3,1) : J = 3+1 \to |3-1| = 4, 3, 2$

$(3,0) : J = 3$

$(2,1) : J = 2+1 \to |2-1| = 3, 2, 1$

$(2,0) : J = 2$

$(1,1) : J = 1+1 \to |1-1| = 2, 1, 0$

$(1,0) : J = 1$

Terms are $^3H_{6,5,4}$, $^1H_5$, $^3G_{5,4,3}$, $^1G_4$, $^3F_{4,3,2}$, $^1F_3$

$^3D_{3,2,1}$, $^1D_2$, $^3P_{2,1,0}$, $^1P_1$

parity $= (-1)^{2+3} = -1$ <u>all</u> are u-states

Count distinct J-states:

$J = 6\ (\times 1),\ 5\ (\times 3),\ 4\ (\times 4),\ 3\ (\times 4),\ 2\ (\times 4),\ 1\ (\times 3),\ 0\ (\times 1)$

Next: do j-j coupling; couple ℓ_i, s_i to make j_i; then couple j_i's

$\ell_1 = 2 \quad s_1 = \tfrac{1}{2} \qquad j_1 = 2 + \tfrac{1}{2} \to |2 - \tfrac{1}{2}| = 5/2, 3/2$

$\ell_2 = 3, \quad s_2 = \tfrac{1}{2} \qquad j_2 = 3 + \tfrac{1}{2} \to |3 - \tfrac{1}{2}| = 7/2, 5/2$

$J = j_1 + j_2 \to |j_1 - j_2|$

(j_1, j_2): $(5/2, 7/2) \Rightarrow J = 5/2 + 7/2 \rightarrow |5/2 - 7/2| = 6, 5, 4, 3, 2, 1$

$(5/2, 5/2) \Rightarrow J = 5/2 + 5/2 \rightarrow |5/2 - 5/2| = 5, 4, 3, 2, 1, 0$

$(3/2, 7/2) \Rightarrow J = 3/2 + 7/2 \rightarrow |3/2 - 7/2| = 5, 4, 3, 2$

$(3/2, 5/2) \Rightarrow J = 3/2 + 5/2 \rightarrow |3/2 - 5/2| = 4, 3, 2, 1$

Distinct J-states are $6(\times 1)$, $5(\times 3)$, $4(\times 4)$, $3(\times 4)$, $2(\times 4)$, $1(\times 3)$, $0(\times 1)$

SAME # !

4 a) CN^- $\Rightarrow$ $Mo^{n+} + 8CN^- = -3 \Rightarrow n = 5$ $\quad Mo^{5+} \Rightarrow d^1$

$Mo^{n+} + 8CN^- = -4 \Rightarrow n = 4$ $\quad Mo^{4+} = d^2$

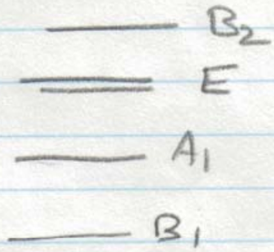
b) In D_{2d} the d orbitals transform as follows:

d_{xy} : B_2

d_{yz}, d_{xz} : E

d_{z^2} : A_1

$d_{x^2-y^2}$: B_1



c) $Mo(CN)_8^{3-}$ ground state configuration $= b_1^1 = B_1$

$Mo(CN)_8^{4-}$ " " " $= b_1^2 = A_1$ $(= b_1 \otimes b_1)$

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for $Mo(CN)_8^{3-}$

$(b_1)^1 : B_1 \rightarrow (a_1)^1\ A_1 \qquad A_1 \otimes B_1 = B_1 \Rightarrow$ forbidden

$(b_1)^1\ B_1 \rightarrow (b_2)^1\ B \qquad B_2 \otimes B_1 = A_2 \Rightarrow$ forbidden

$(b_1)^1\ B_1 \rightarrow (e)^1\ E \qquad B_1 \otimes E = E \Rightarrow (x,y)$ allowed

$\Rightarrow$ only symmetry allowed transition polarized in (x,y) plane

$2S+1 = 2$

$\Rightarrow$ transition $= {}^2B_1 \rightarrow {}^2E$

for $Mo(CN)_8^{4-}$

$(b_1)^2 : {}^1A_1 \rightarrow b_1^1 e^1 \Rightarrow {}^1E, {}^3E$ allowed (x,y)

$(b_1)^2 : A_1 \rightarrow b_1^1 a_1^1 \Rightarrow {}^1B_1, {}^3B_1$ forbidden

$(b_1)^2\ A_1 \rightarrow b_1^1 b_2^1 = {}^1A_2, {}^3A_2$ forbidden.

$\Rightarrow$ only symmetry allowed transition polarized in (x,y) plane is ${}^1A_1 \rightarrow {}^1E$

${}^1A_1 \rightarrow {}^3E$ becomes allowed through spin orbit coupling.

d) From character table $\Gamma_z = B_2$, $\Gamma_{x,y} = E$

$\therefore B_1 \otimes \Gamma(Q_k) \subset B_2$ or E

$\Rightarrow \Gamma(Q_k) = A_2$ or E respectively.