ADVANCED CHEMISTRY

INORGANIC CHEMISTRY - SPRING - WEEK 8

Chapter 11

③ (a) ^2D $\quad 2S+1 = 2 \quad S = \frac{1}{2} \quad M_S = \pm\frac{1}{2}$

$L = 2 \quad M_L = \pm 2, \pm 1, 0$

(b) ^3G $\quad 2S+1 = 3 \quad S = 1 \quad M_S = \pm 1, 0$

$L = 4 \quad M_L = \pm 4, \pm 3, \pm 2, \pm 1, 0$

(c) ^4F $\quad 2S+1 = 4 \quad S = \frac{3}{2} \quad M_S = \pm\frac{3}{2}, \pm\frac{1}{2}$

$L = 3 \quad M_L = \pm 3, \pm 2, \pm 1, 0$

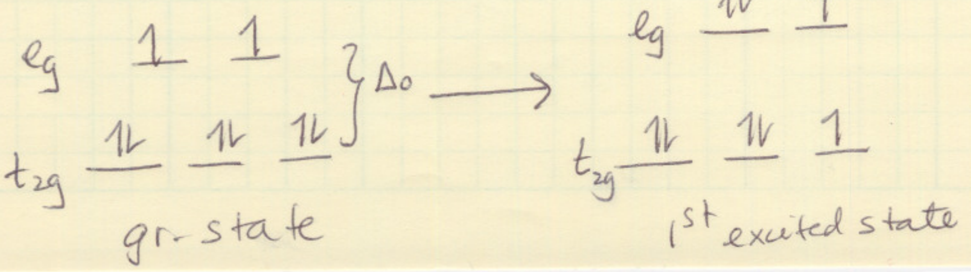
⑤ $\tilde{\nu} = 24{,}900\ \text{cm}^{-1} \quad \lambda = \dfrac{1}{24{,}900\ \text{cm}^{-1}} = 4.016 \times 10^{-5}\ \text{cm}$

$A = \epsilon c l \qquad \epsilon = 0.038\ \text{L mol}^{-1}\ \text{cm}^{-1}$

$$c = \frac{A}{\epsilon l} = \frac{0.10}{(0.038)\ \text{L mol}^{-1}\ \text{cm}^{-1}\ (1.00\ \text{cm})}$$

$$\underline{\underline{c = 2.63\ \text{mol L}^{-1}}}$$

⑧ $[Ni(H_2O)_6]^{2+}$ $\quad d^8$ configuration $\quad Ni(II)$



Energy required for ~~a~~ the ground state → first excited state transition } = Δ_o

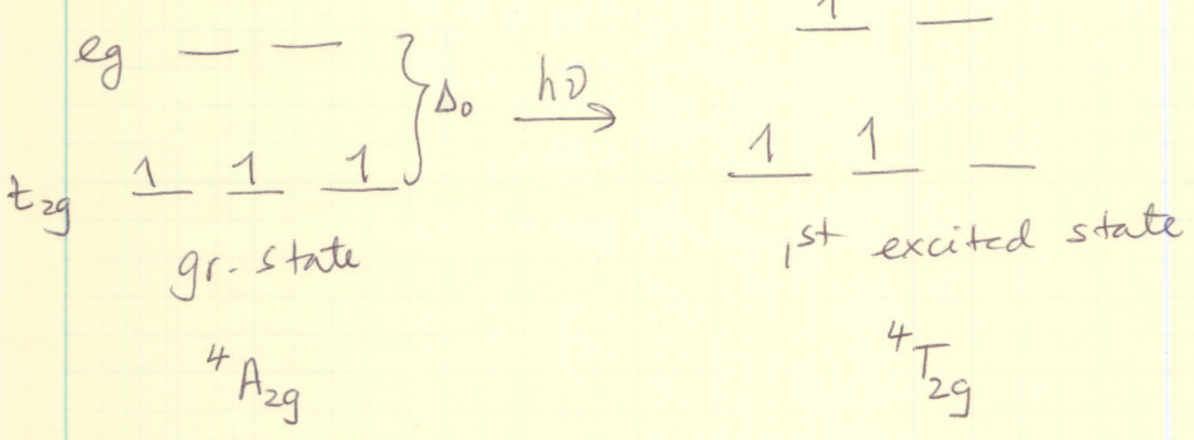
From the Tanabe-Sugano diagram this transition corresponds to $^3A_{2g} \longrightarrow {}^3T_{2g}$ } = Δ_o

from the spectra on Fig 11.8, the first transition occurs at ~ 8500 cm^{-1}

$$\therefore \Delta_o \approx 8500\ cm^{-1}$$

Ground state of this compound does not have Jahn-Teller distortions but the first excited state does have strong Jahn-Teller distortions. This is the reason for the splitting in the spectral bands.

⑨ (a) $[Cr(C_2O_4)_3]^{3-}$ $C_2O_4^{2-}$ strong field ligand
$Cr(III)$ d^3 case



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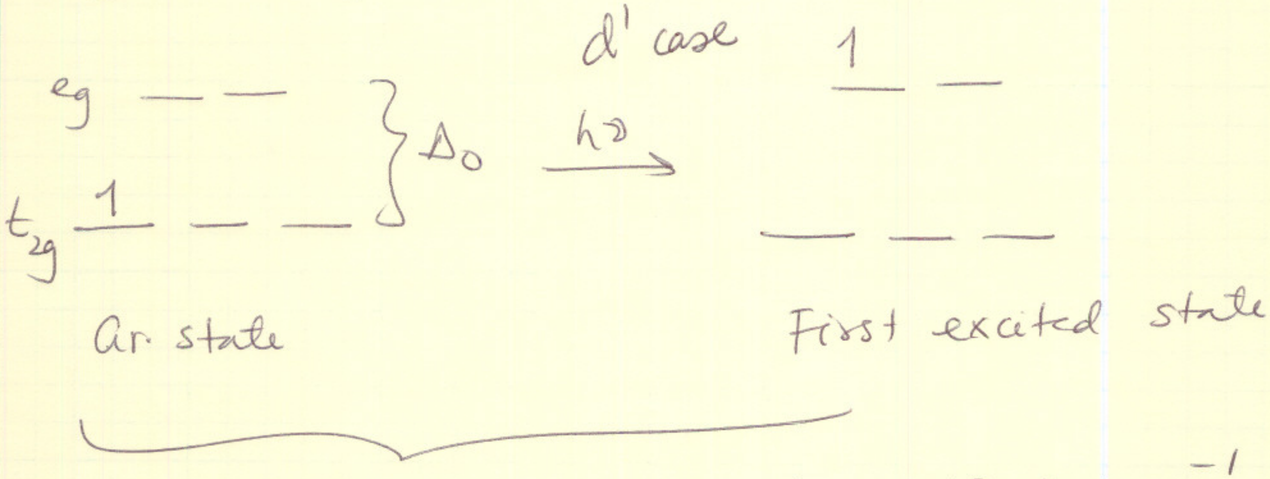
(b) $[Ti(NCS)_6]^{3-}$ Ti(III) [illegible]

d^1 case



energy of this transition $= \Delta_o = 18,400\ cm^{-1}$

Band is split due to Jahn-Teller distortions in the ground (weak) and excited (strong) states.

(c) $[Ni(en)_3]^{2+}$ d^8 case

The lowest energy band $({}^3A_{2g} \rightarrow {}^3T_{2g})$ corresponds to $\underline{\underline{\Delta_o = 11,200\ cm^{-1}}}$

(d) VF_6^{3-} V(III) d^2 case

Possible transitions $\left.\right\}$ ${}^3T_{1g}(F) \longrightarrow {}^3T_{2g}(F)$ $\nu_1 = 14,800\ cm^{-1}$

${}^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$ ν_2

${}^3T_{1g}(F) \longrightarrow {}^3A_{2g}(F)$ ν_3

$\left.\begin{matrix}\nu_2\\ \nu_3\end{matrix}\right\}$ one of these $=$ ~~23,500~~ cm^{-1} 23,250

Take the ration $\frac{23{,}250 \text{ cm}^{-1}}{14{,}800 \text{ cm}^{-1}} = 1.57$

Since ~~the~~ Fig 11.13 shows that $\nu_3 : \nu_1 \approx 2$

$\nu_2 = 23{,}250 \text{ cm}^{-1}$ $\quad \nu_1 = 14{,}800 \text{ cm}^{-1}$

when $\frac{\nu_2}{\nu_1} = 1.57$ $\quad \frac{\Delta_o}{B} \approx 28$ (From Fig 11.14)

Now using Fig 11.13

at $\frac{\Delta_o}{B} = 28$; $\quad \nu_2 \approx 37 \Rightarrow \frac{E}{B} = 37$

$$\frac{23{,}250 \text{ cm}^{-1}}{B} = 37$$

$$B = 628 \text{ cm}^{-1}$$

at $\frac{\Delta_o}{B} = 28$; $\nu_1 \approx 22 \Rightarrow \frac{E}{B} \approx 22$

$$\frac{14{,}800 \text{ cm}^{-1}}{B} \approx 22$$

$\therefore B = 672 \text{ cm}^{-1}$ $\quad$ average $B = 650 \text{ cm}^{-1}$

$$\Rightarrow \underline{\underline{\Delta_o = B \times 28 = 18{,}200 \text{ cm}^{-1}}}$$

(e) $VCl_3(CH_3CN)_3$ $V(\text{III})$ d^2 case

ν_1 = absorption band at 694nm

467 nm band is either ν_2 or ν_3

~~$694nm \times \frac{1m}{10^9 nm} \times \frac{1}{2.998 m s^{-1}} \times \frac{1}{6.626\times10^{-34} Js}$~~

$$\text{Energy of } \nu_1 = \frac{(6.626\times10^{-34} Js)(2.998\times10^{8} m s^{-1})}{(694\times10^{-9} m)}$$

$$= 2.845\times10^{-19} J$$

$$\text{Energy at } 467nm = \frac{(6.626\times10^{-34} Js)(2.998\times10^{8} m s^{-1})}{(467\times10^{-9} m)}$$

$$= 4.254\times10^{-19} J = \text{either } \nu_2 \text{ or } \nu_3$$

Take the ratio $\frac{4.254\times10^{-19} J}{2.845\times10^{-19} J} = 1.5$

$\therefore$ $4.254\times10^{-19} J$ must correspond to ν_2 (since $\nu_3 : \nu_1 = 2:1$ at all Δ_o)

Using Fig 11.14 $\frac{\nu_2}{\nu_1} = 1.5 \Rightarrow \frac{\Delta_o}{B} = 28$

Using Fig 11.13 at $\frac{\Delta_o}{B} = 28$; $\nu_2 = 37 \Rightarrow \frac{E}{B} = 37$

$\frac{4.254\times10^{-19} J}{B} = 37 \Rightarrow B = 1.149\times10^{-20} J$

at $\frac{\Delta_o}{B} = 28$; $\nu_1 = 22 \Rightarrow \frac{E}{B} = 22 \Rightarrow \frac{2.845\times10^{-19} J}{B} = 22$

$B = 1.29 \times 10^{-12}\ J$

$$\text{average } B = \frac{1.24 \times 10^{-20}\ J}{} \left(\frac{1}{6.626 \times 10^{-34}\ JS}\right) \times \left(\frac{1}{2.99 \times}\right.$$

$$= \underline{\underline{627\ cm^{-1}}}$$

$$\Delta_o = B(28) = \underline{\underline{17{,}547.45\ cm^{-1}}}$$

⑩ $[Co(NH_3)_6]^{2+}$ d^7 case

$$^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F) \qquad \nu_1 = 9000\ cm^{-1}$$

$$^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P) \qquad 21{,}100\ cm^{-1}$$

$$^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F) \qquad \text{too weak}$$

$$\frac{21{,}100\ cm^{-1}}{9{,}000\ cm^{-1}} = 2.34 \qquad \frac{\Delta_o}{B} = 11$$

$$\text{when } \frac{\Delta_o}{B} = 11 \ ; \ \text{for } \nu_1 \quad \frac{E}{B} = 9$$

$$\frac{9000\ cm^{-1}}{B} = 9 \qquad B = 1000\ cm^{-1}$$

$$\text{when } \frac{\Delta_o}{B} = 11 \quad \text{For } \nu_2 \quad \frac{E}{B} = 22 \Rightarrow \frac{21{,}100\ cm^{-1}}{B} = 22$$

$$B = 959\ cm^{-1}$$

$$\text{average } \underline{\underline{B = 980\ cm^{-1}}}$$

$$\Delta_o = B(10) = 9800\ cm^{-1}$$

⑫ ~~Strong Jahn-Teller effects are seen with~~

NH_3 is a weak field (high spin) ligand.

M^{3+}	Sc^{3+}	Ti^{3+}	V^{3+}	Cr^{3+}	Mn^{3+}	Fe^{3+}	Co^{3+}	Ni^{3+}	Cu^{3+}	Zn^{3+}
# d electrons	0	1	2	3	4	5	6	7	8	9
Jahn-Teller effect	none	weak	weak	none	strong	none	weak	weak	none	strong

⑭ ~~I~~ The iodide complex will have the lowest energy and the chloride will have the highest energy

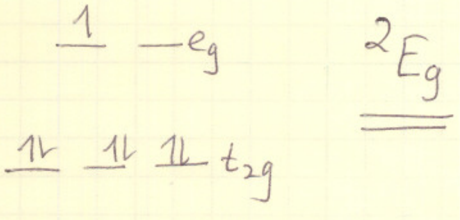
$$[Co(NH_3)_5 I]^{2+} < [Co(NH_3)_5 Br]^{2+} < [Co(NH_3)_5 Cl]^{2+}$$

This is because I atomic orbitals have higher energy than Br which is higher than Cl.

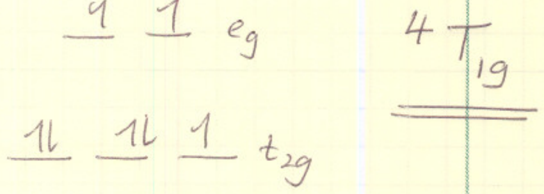
∴ I atomic orbitals are closer to the metal orbital.

∴ ~~MO~~ Bonding MO of the iodide complex are closer to the frontier t_{2g}/e_g orbitals compared to the chloride complex.

㉗ (a) bipy is a strong field ligand, NH_3 is a weak field ligand. Co^{2+} is d^7



$[Co(bipy)_3]^{3+}$

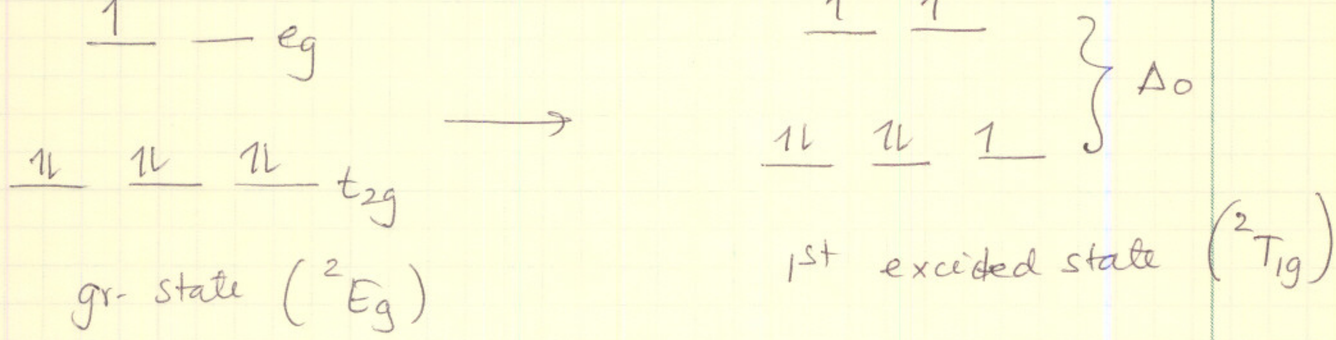


$[Co(NH_3)_6]^{2+}$

(b)

${}^2E_g \longrightarrow {}^2T_{1g}$	${}^4T_{1g} \longrightarrow {}^4T_{2g}$
${}^2E_g \longrightarrow {}^2T_{2g}$	${}^4T_{1g} \longrightarrow {}^4A_{2g}$
${}^2E_g \longrightarrow {}^2A_{1g}$	${}^4T_{1g} \longrightarrow {}^4T_{1g}$

(c) $[Co(bipy)_3]^{2+}$



$${}^2E_g \longrightarrow {}^2T_{1g} \quad \text{energy} = \Delta_o$$

$$\therefore \nu_1 = \Delta_o = 11{,}300\ cm^{-1}$$

$$LFSE = -6\left(\frac{2}{5}\Delta_o\right) + \frac{3}{5}\Delta_o = -\frac{9}{5}\Delta_o = -\frac{9}{5}(11{,}300\ cm^{-1})$$

$$= -20{,}340\ cm^{-1}$$

$[Co(NH_3)_6]^{2+}$ This is the same as problem # 10

(d) $[Co(bipy)_3]^{2+}$ will have strong Jahn-Teller distortions. ∴ Spectral bands will be broad.

$[Co(NH_3)_6]^{2+}$ will have weak Jahn-Teller distortions. Spectral bands will be narrower than the (bipy) complex.

(e) This is the same as for all octahedral complexes. For the (bipy) complex separation between t_{2g} and e_g orbitals will be larger than for (NH_3) complex.