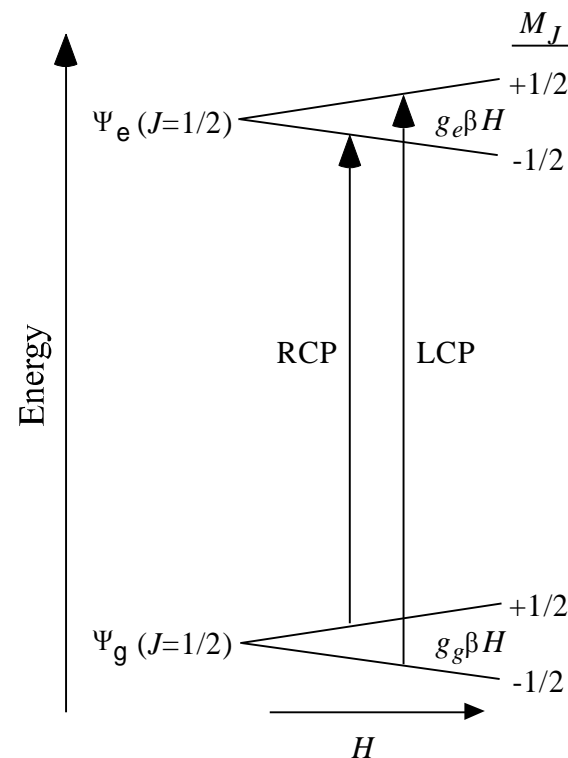
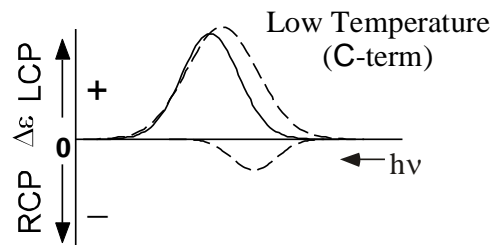
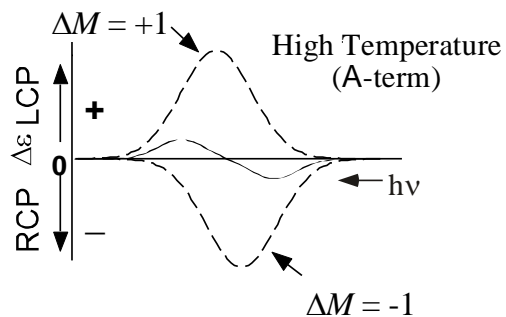


What happens if you apply a Magnetic Field in CD?

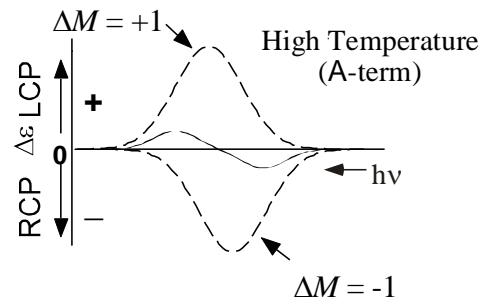
- Applying B to a paramagnetic systems changes everything
 - must consider Zeeman splitting $\rightarrow H'_{Zeeman} = -\vec{\mu}_J \cdot \vec{B} = -\hbar\gamma_e \vec{J} \cdot \vec{B} = g\mu_B \vec{J} \cdot \vec{B}$
 - causes splitting of ground & excited state levels
 - does not require optical activity!
- splitting of energy levels induces CD signal
 - for light propagating along the direction of the magnetic field the selection rules differ for CP:
 $LCP \mapsto \Delta M = +1$ $RCP \mapsto \Delta M = -1$



Categorization of MCD intensity mechanisms

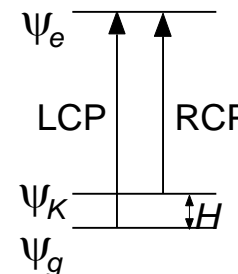
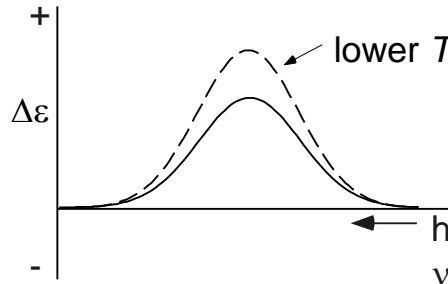
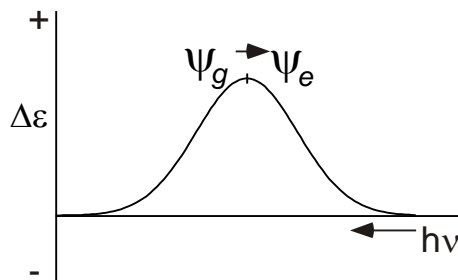
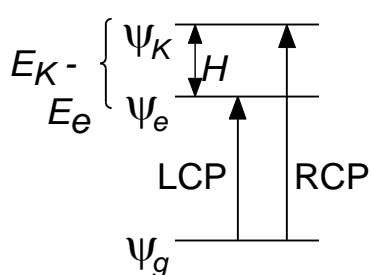
- A-term: T-indep derivative shape from degenerate GS and/or ES

$$A_1 = \frac{1}{d_g} \sum \left(\langle \Psi_e | L_z + 2S_z | \Psi_e \rangle - \langle \Psi_g | L_z + 2S_z | \Psi_g \rangle \right) \left(|\langle \Psi_g | m_- | \Psi_e \rangle|^2 - |\langle \Psi_g | m_+ | \Psi_e \rangle|^2 \right)$$



- B-term: field-induced mixing into non-degenerate GS and/or ES

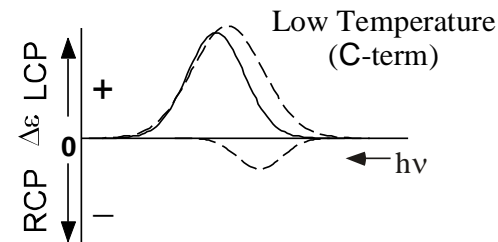
$$B_0 = -\frac{2}{d_g} \text{Re} \sum \left[\sum_{K, K \neq e} \frac{\langle \Psi_e | L_z + 2S_z | \Psi_K \rangle}{\Delta E_{Ke}} \langle \Psi_g | m_- | \Psi_e \rangle \langle \Psi_K | m_+ | \Psi_e \rangle - \langle \Psi_g | m_+ | \Psi_e \rangle \langle \Psi_K | m_- | \Psi_g \rangle \right. \\ \left. + \sum_{K, K \neq g} \frac{\langle \Psi_K | L_z + 2S_z | \Psi_g \rangle}{\Delta E_{Kg}} \langle \Psi_g | m_- | \Psi_e \rangle \langle \Psi_e | m_+ | \Psi_K \rangle - \langle \Psi_g | m_+ | \Psi_e \rangle \langle \Psi_e | m_- | \Psi_K \rangle \right]$$



3.1.3 Magnetic Circular Dichroism Spectroscopy

- C-term: T-dep absorption (at low temperatures) – simplification of A-term...

$$C_0 = -\frac{1}{d_g} \sum \langle \Psi_g | L_z + 2S_z | \Psi_g \rangle \left[\langle \Psi_g | m_- | \Psi_e \rangle^2 - \langle \Psi_g | m_+ | \Psi_e \rangle^2 \right]$$



- total MCD intensity $\rightarrow \frac{\Delta A}{E} = \frac{2N_A \pi^3 \alpha^2 C l \log e}{250 h c n} \beta \vec{H} \left[\underset{\substack{\uparrow \\ \text{derivative shape}}}{A_1 \left(\frac{\partial f}{\partial E} \right)} + \left(B_0 + \frac{C_0}{kT} \right) \underset{\substack{\uparrow \\ \text{absorption shape}}}{f} \right]$

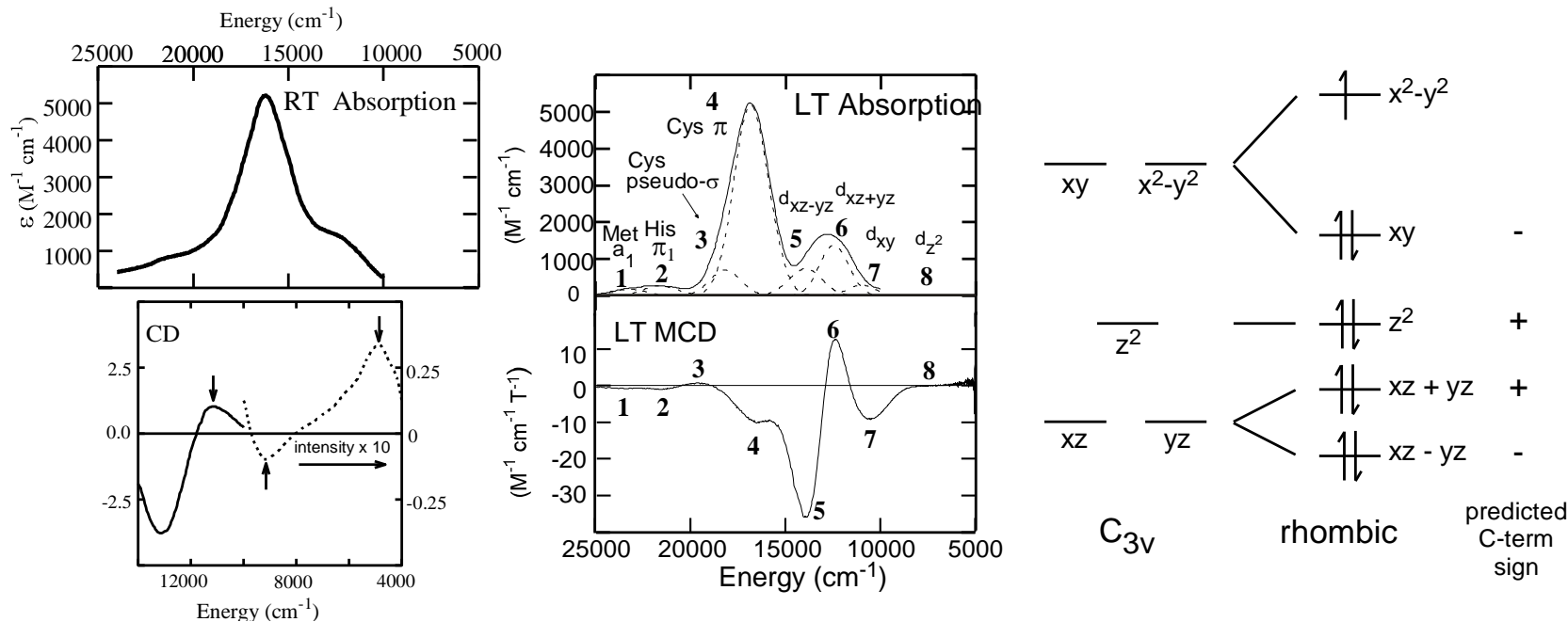
- at low temperatures (< 25K) \rightarrow C-term intensity dominates
- basic selection rules for C-term: $\Delta M_L = \pm 1, \Delta M_S = 0$
 - requires changes in orbital angular momentum, not spin state
 - will require **SOC** under most circumstances (*i.e.* same as EPR)

- SOC much larger in d-d transitions than CT transitions $\rightarrow C_0/D_0$ ratios $\frac{C_0}{D_0} = \frac{kT}{\beta H} \left(\frac{\Delta \epsilon}{\epsilon} \right)$
 - relative MCD intensity will be much larger for LF transitions

$$D_0 = -\frac{1}{d_g} \sum \left| \langle \Psi_g | M | \Psi_e \rangle \right|^2$$

3.1.3 Magnetic Circular Dichroism Spectroscopy

- e.g. blue copper centre in plastocyanins



- sign of MCD C-terms depends on specific contributions to SOC
 - calculated in similar way as g-values for EPR
 - predictions based on effect of $L_{x,y,z}$ operators on d -orbitals
 - useful in assigning LF transitions...