Light-Induced Spin-State Switching in Transition Metal Complexes

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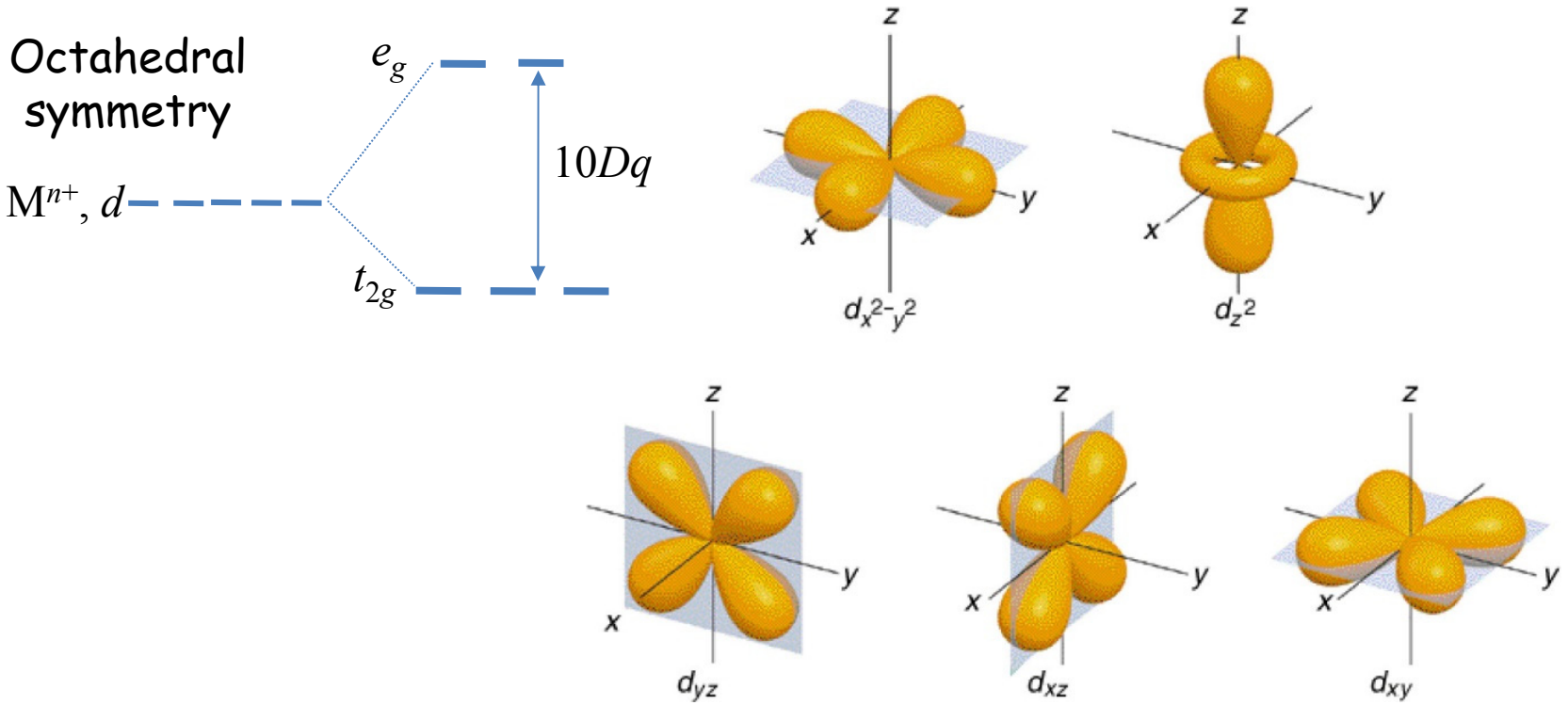
Splitting of d-Orbitals by the Ligand Field

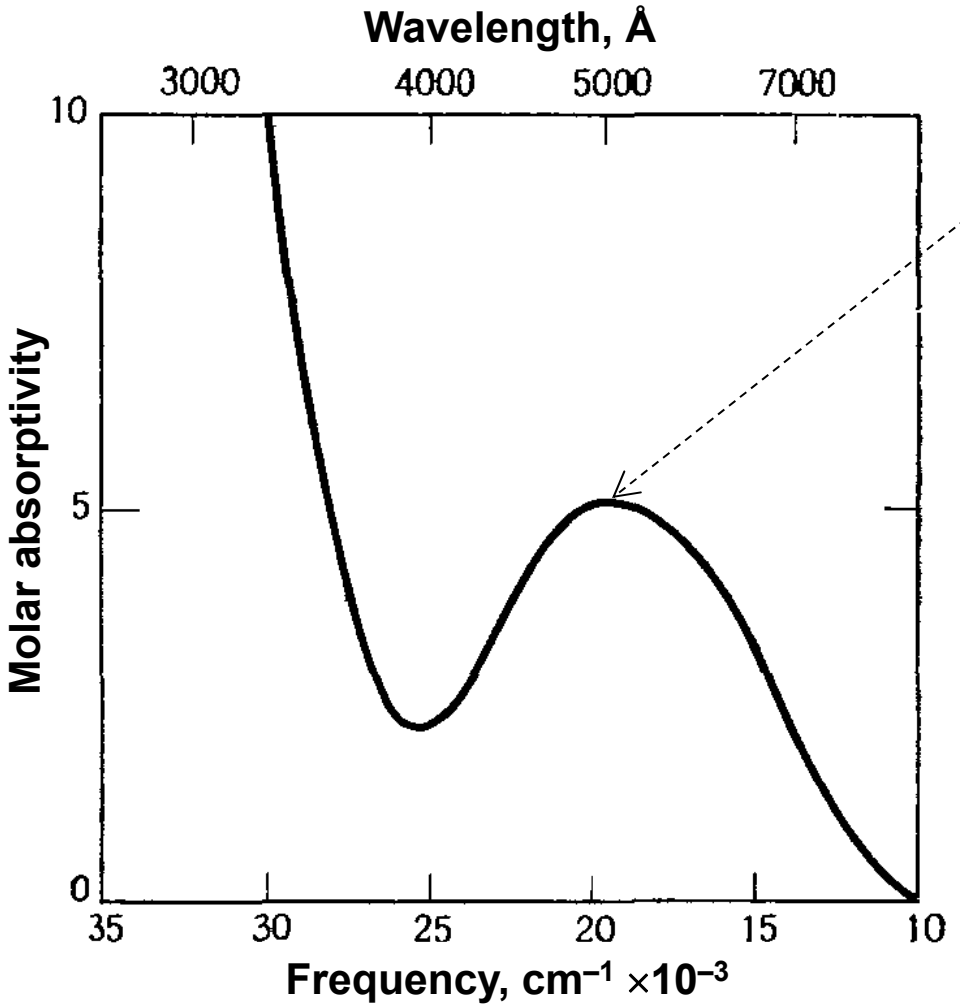


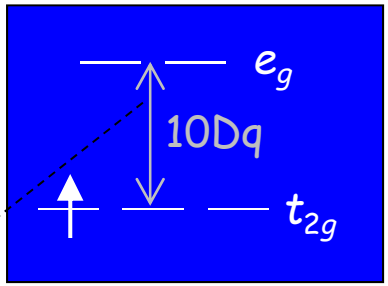
Spectrochemical series of ligand-field strength:

$I^- < Br^- < Cl^- < SCN^- < NO_3^- < F^- < OH^- < H_2O <$
$NCS^- < py < NH_3 < en < NO_2^- < PPh_3 < CN^- < CO$

Absorption Spectroscopy

Optical absorption spectrum of $[Ti(H_2O)_6]^{3+}$



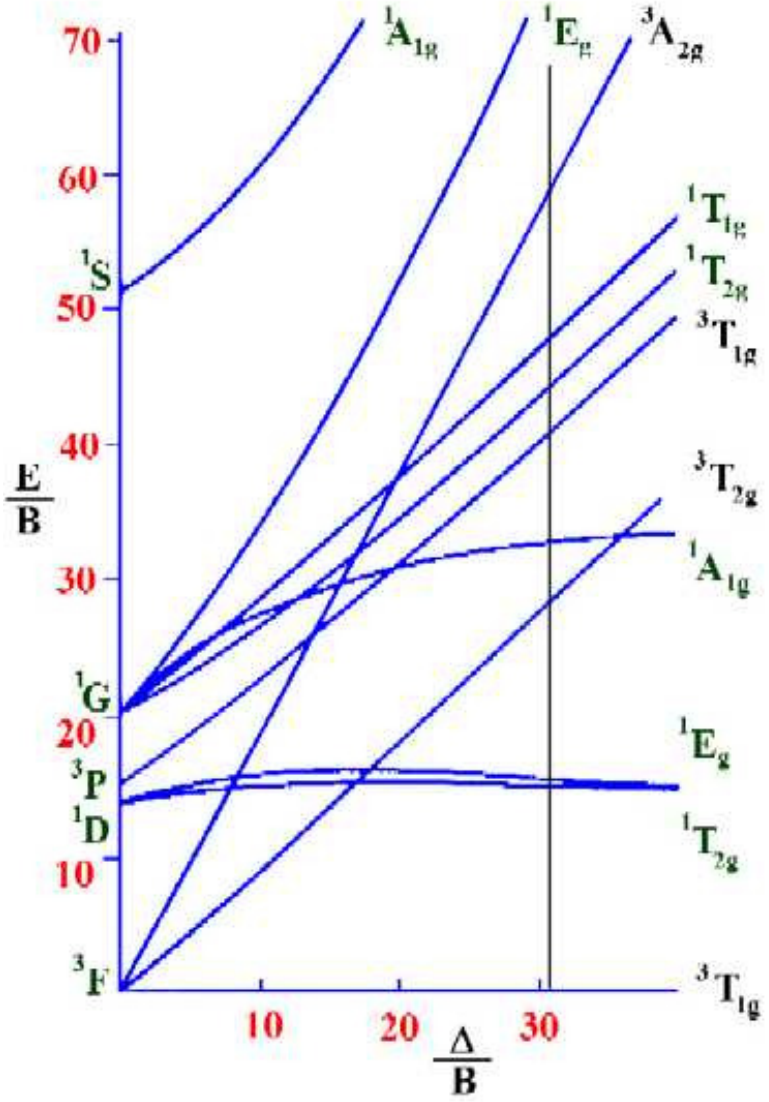


Ti^{3+}, $3d^1$

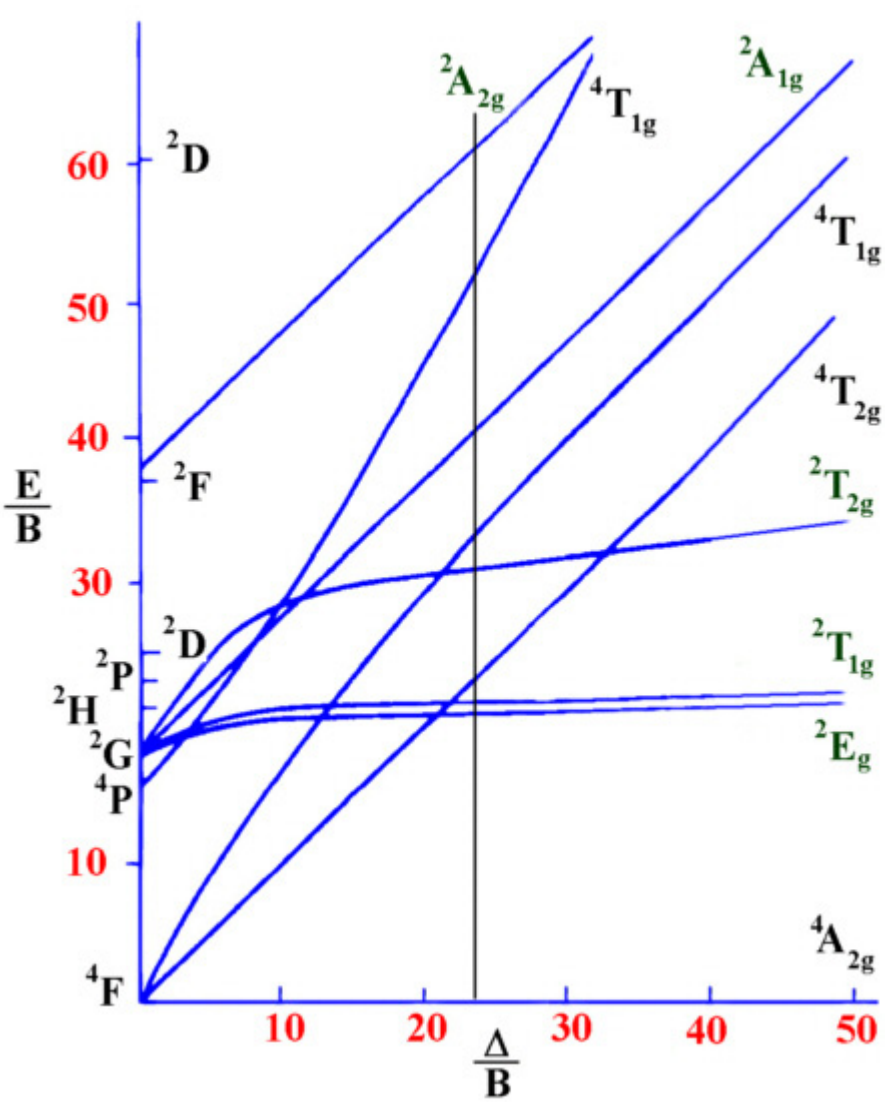
$10Dq = \Delta_o \approx 20{,}000\ cm^{-1}$

Tanabe-Sugano Diagrams

d^2 Ion

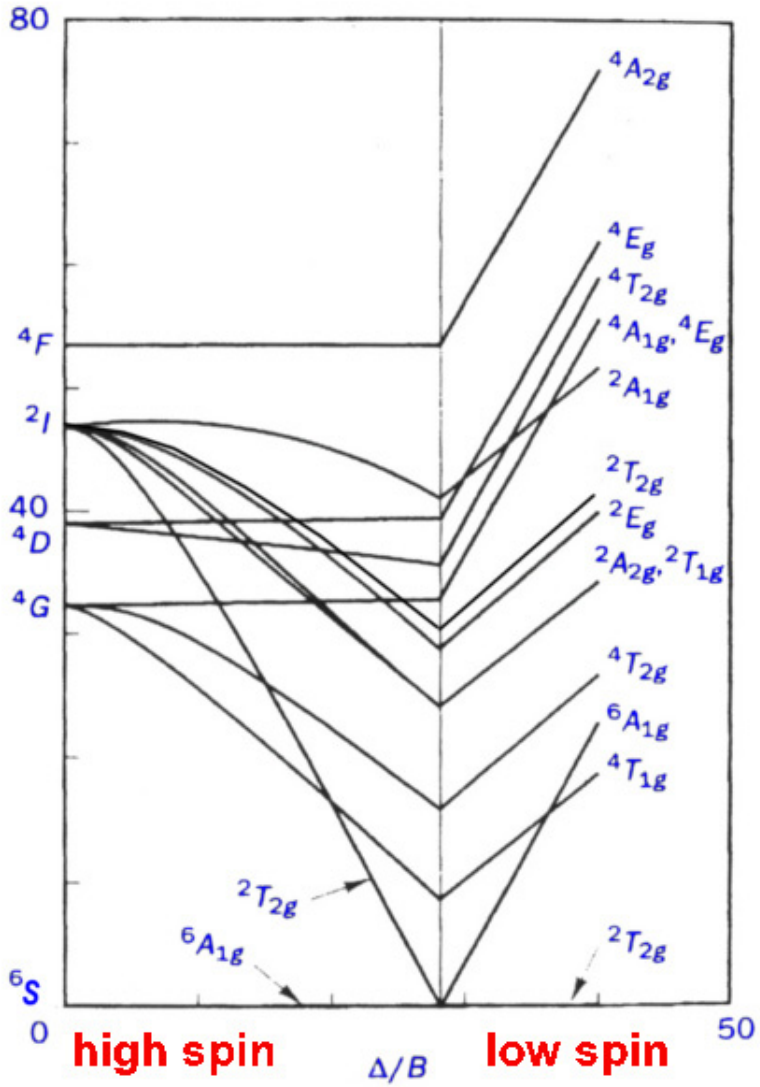


d^3 Ion

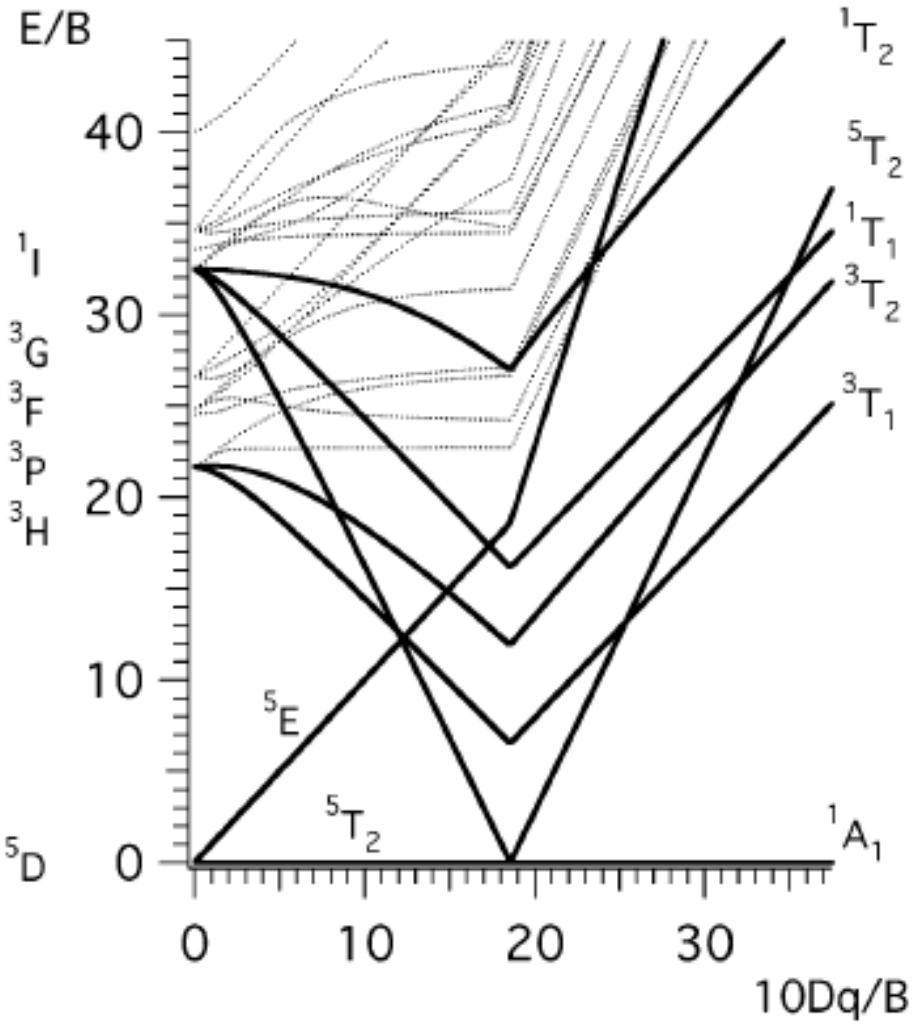


Tanabe-Sugano Diagrams

d^5 Ion



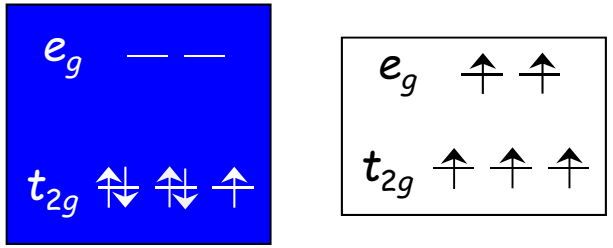
d^6 Ion



The History of SCO Phenomenon

- Observed for d^4, d^5, d^6, d^7 metal ions
- These ions exhibit two possible electron configurations in the octahedral ligand field
- Switching between the states is achieved by changing temperature, pressure, or by photoexcitation

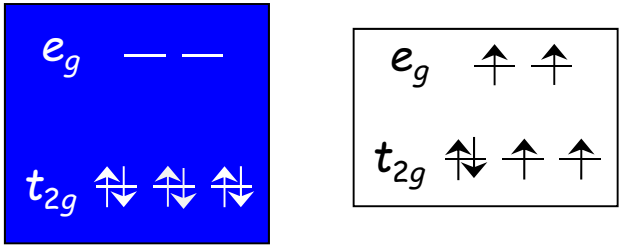
Example – d^5 ion



LS, S = 1/2 HS, S = 5/2

- 1931 – Cambi and Szego observed SCO in Fe(III) dithiocarbomates
- Pauling initially explained their results by the change in the bond type from covalent to ionic
- Orgel was the first to suggest the correct explanation based on the change in the spin state of the ion

Example – d^6 ion



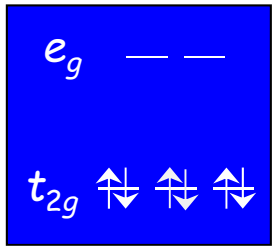
LS, S = 0 HS, S = 2

Cambi, L.; Szegö, L. *Ber. Deutsch. Chem. Gesell.* **1931**, *64*, 167.
Pauling, L. *J. Am. Chem. Soc.* **1937**, *59*, 633.
Orgel, L. E. 10th Chemical Conference, Brussels, **1956**, 289.

Spin Crossover (SCO) in Fe(II) complexes

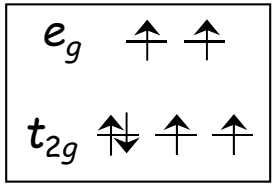
About 90% of reported cases of SCO have been observed in Fe(II) complexes

LS, S = 0



10Dq > Π

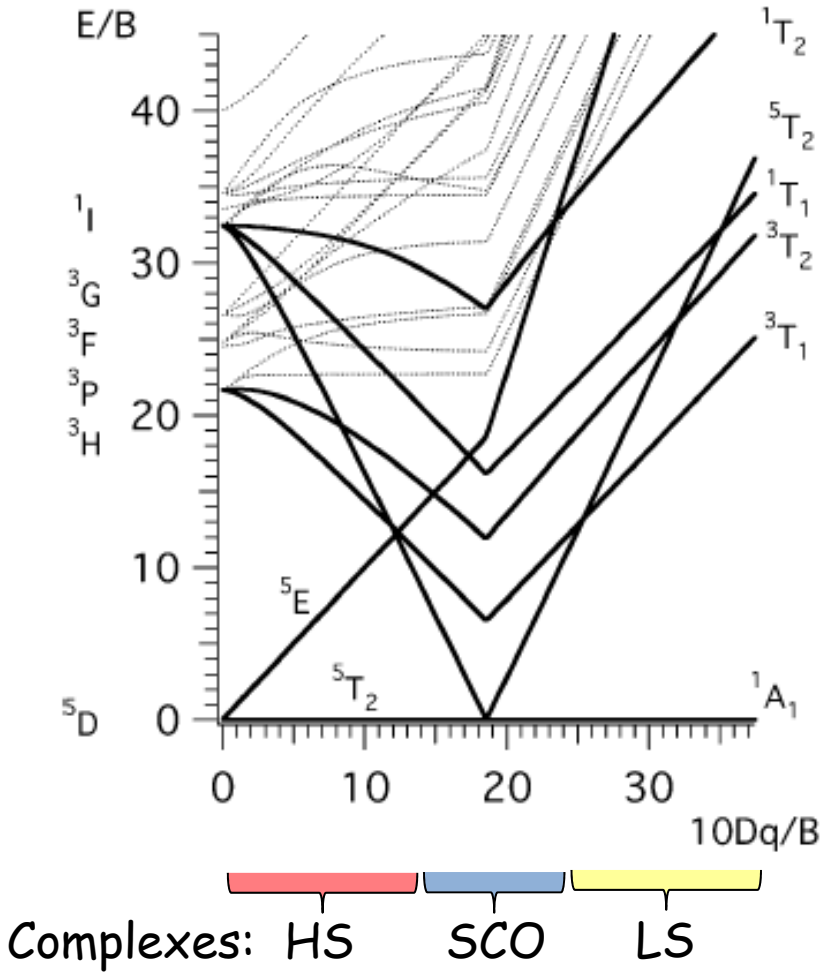
HS, S = 2



10Dq < Π

10Dq – ligand-field splitting

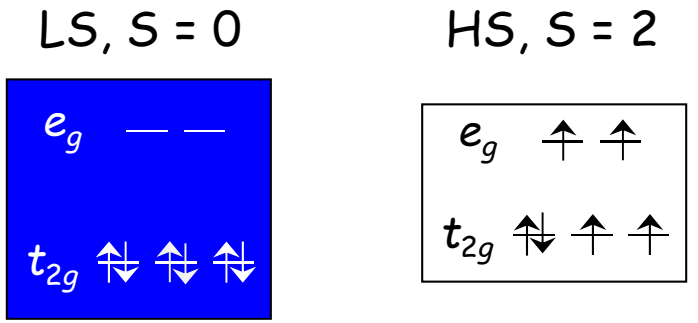
Π – electron pairing energy



Hauser, A. *Top. Curr. Chem.* **2004**, *233*, 49-58.

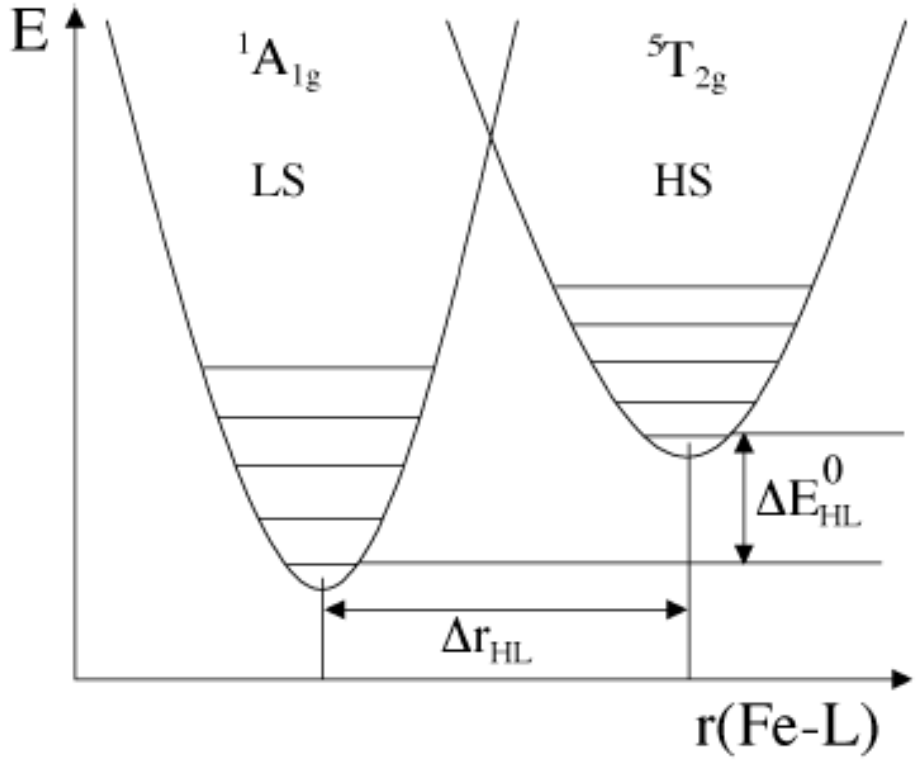
Metal-Ligand Distances

The antibonding orbitals (e_g*) are populated only in the HS state



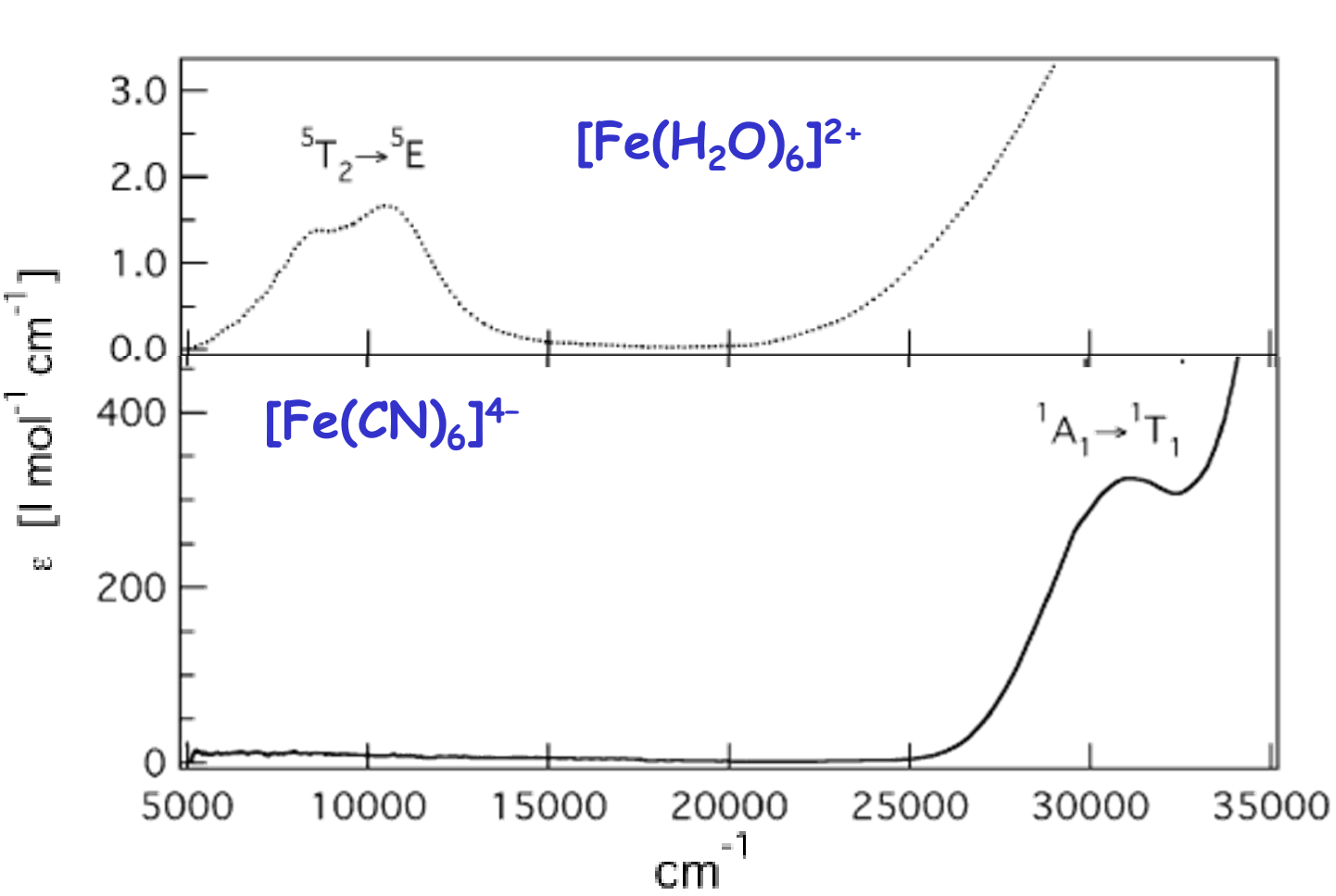
r(Fe–L): 1.95-2.00 Å 2.15-2.20 Å

- Useful relationship:
  $10Dq \sim 1/r^n$ (n = 5 – 9)
- Using the average r(Fe-L) for SCO complexes, one can estimate that $10Dq_{LS}/10Dq_{HS} \sim 1.75$
- Important: the Fe-N bond lengths and orbital overlap change upon SCO, and therefore 10Dq is different for the LS and HS states of the same complex



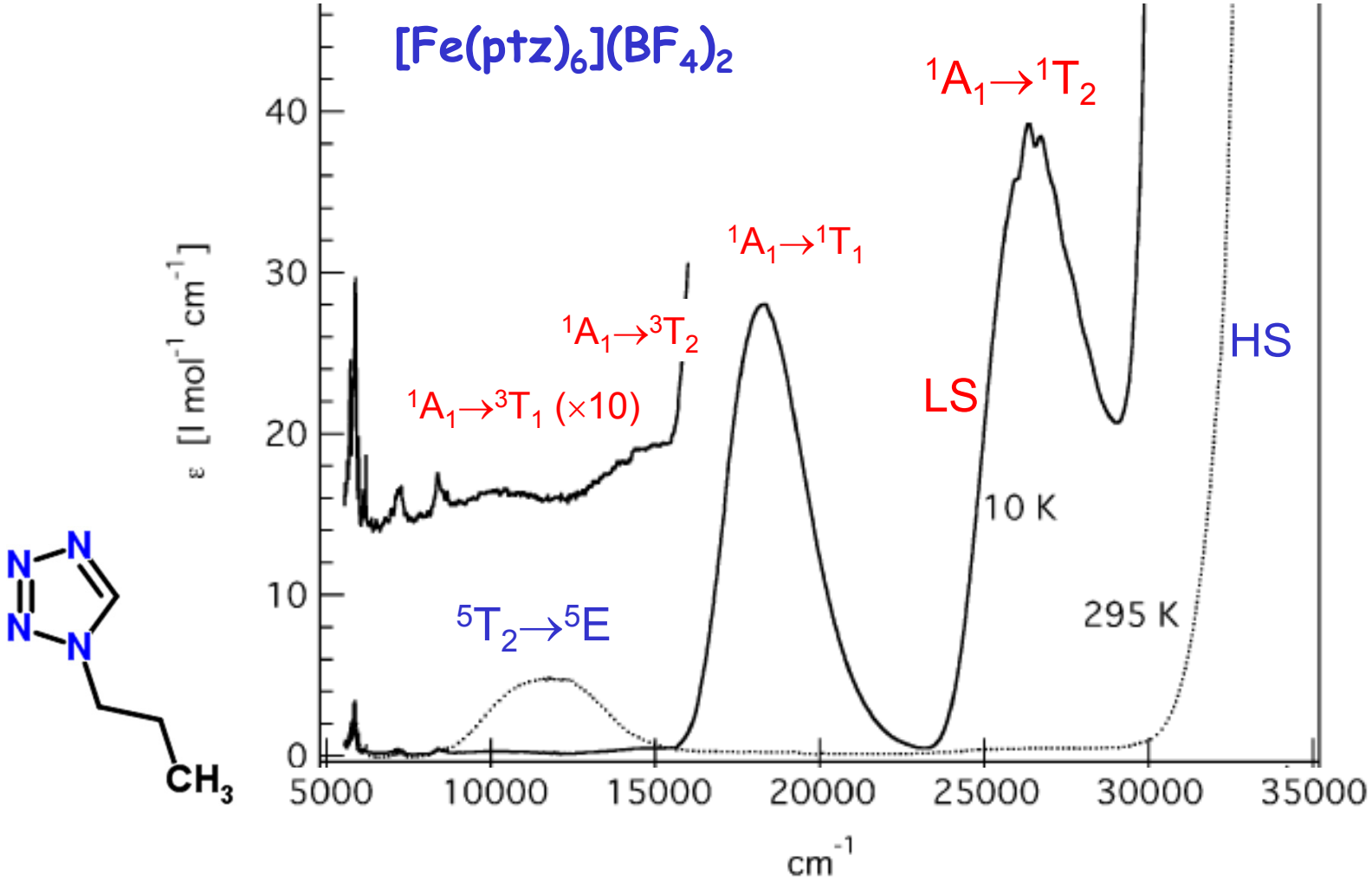
Hauser, A. *Top. Curr. Chem.* **2004**, *233*, 49-58.

Absorptions Spectra of HS and LS Complexes



Hauser, A. *Top. Curr. Chem.* **2004**, *233*, 49-58.

Absorption Spectra of SCO Complexes



$10Dq^{HS}$ = 11 800 cm^{-1} **$10Dq^{LS}$ = 19 410 cm^{-1}**

Hauser, *A. J. Chem. Phys.* **1991**, *94*, 2741.

Pairing Energy and Ligand-Field Strength

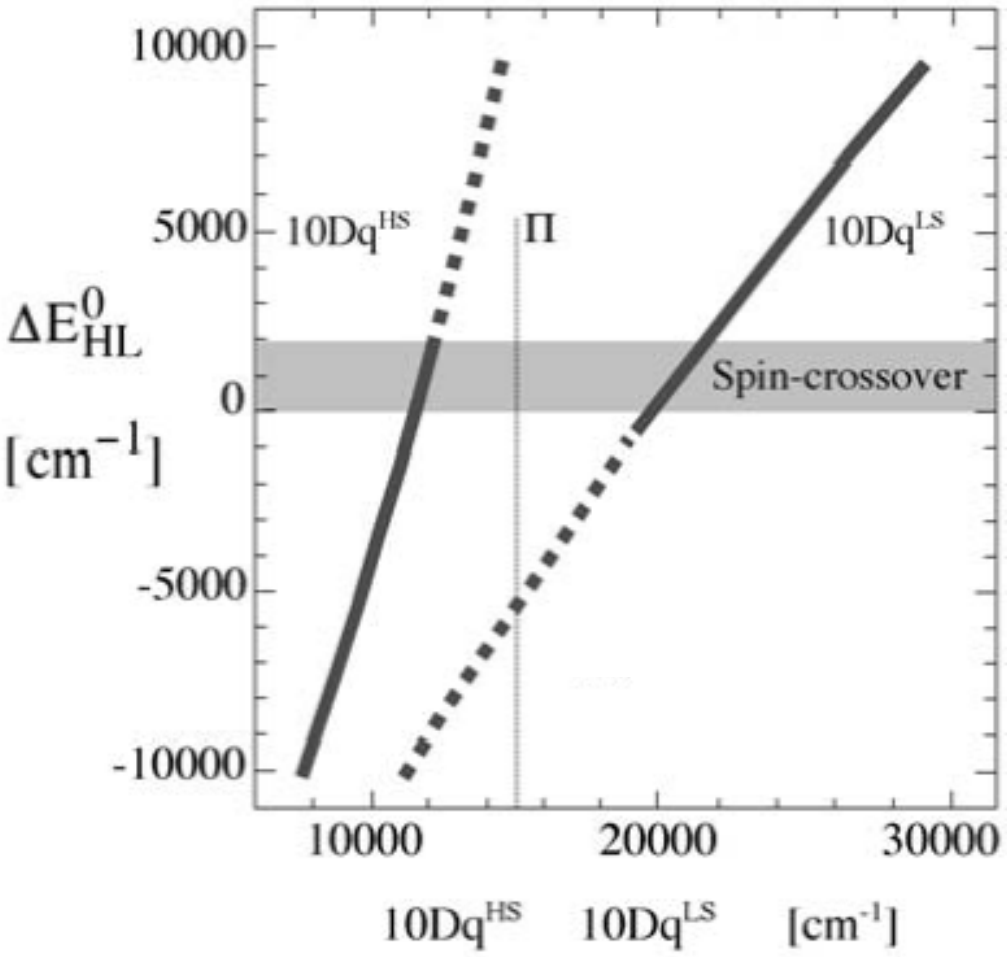
- The pairing energy is about the same in the LS and HS states: $\Pi \approx$ **15,000 cm^{-1}** for Fe(II) complexes
- 10Dq is changing during the spin transition:

  $10Dq_{HS} < 10Dq_{LS}$

- If $10Dq_{HS} < 10{,}000$ cm^{-1} or $10Dq_{LS} > 23{,}000$ cm^{-1}, the *SCO* is impossible
- Conditions for observation of *SCO* in Fe(II) complexes:

$10Dq_{HS} \approx 11{,}000 - 12{,}500$ cm^{-1}

$10Dq_{LS} \approx 19{,}000 - 22{,}000$ cm^{-1}



$$\Delta E^0_{HL} = E^0_{HS} - E^0_{LS}$$

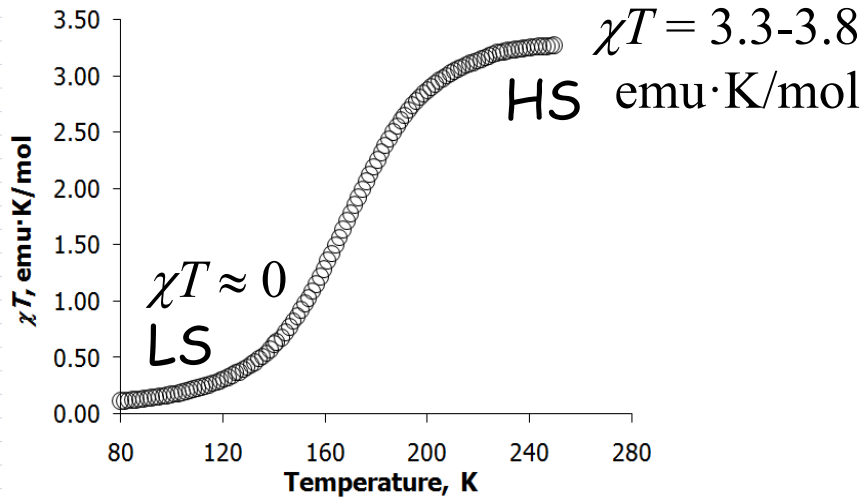
Hauser, A. *Top. Curr. Chem.* **2004**, *233*, 49-58.

Characterization Methods

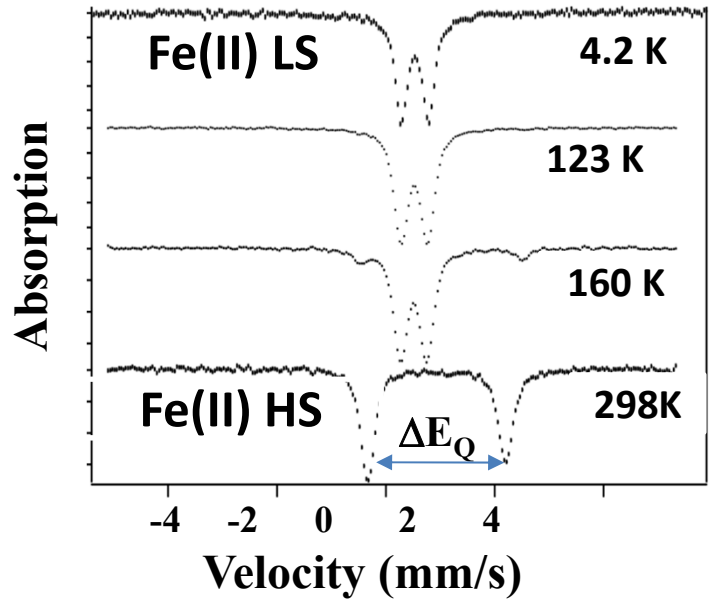
Crystallography

	LS	HS
d(Fe^{II}-N) (Å)	1.95-2.00	2.15-2.20

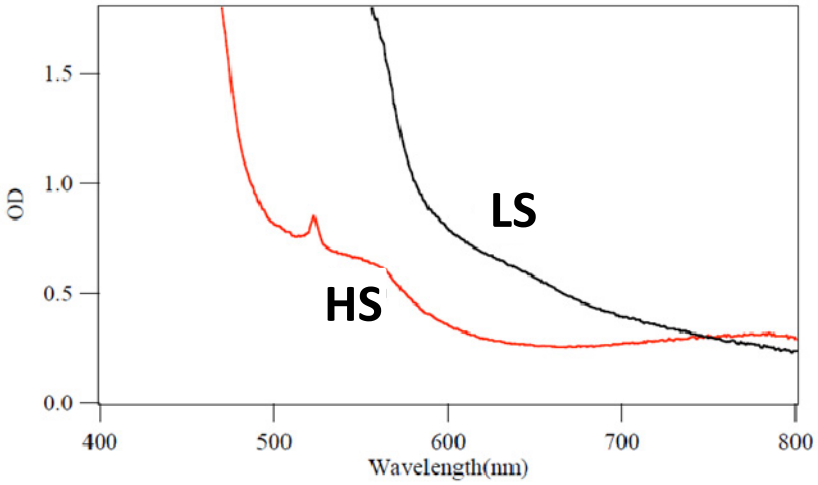
Mangetometry



^{57}Fe Mössbauer Spectroscopy

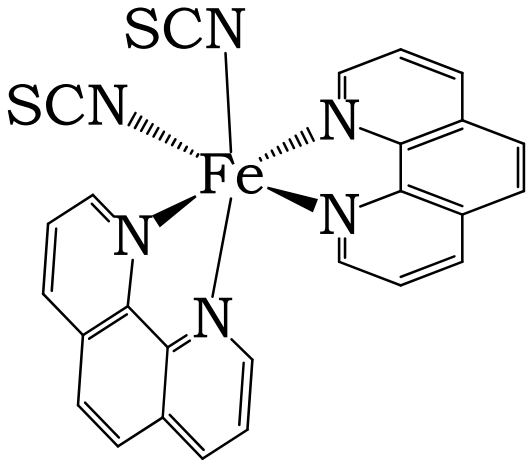


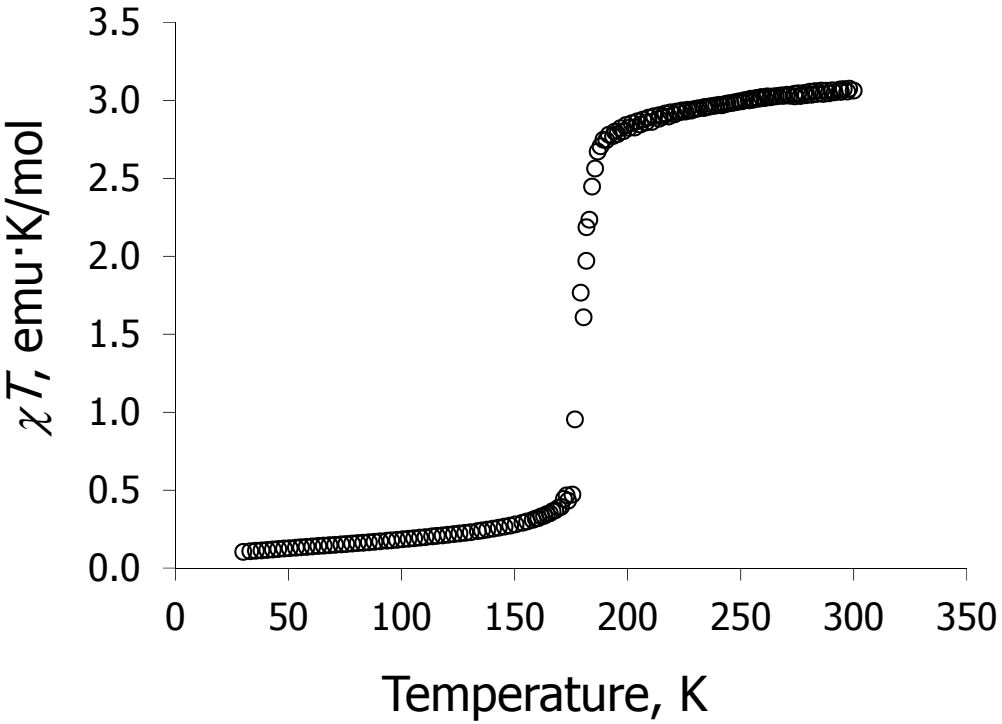
Other spectroscopic techniques



Magnetometry

The first reported SCO complex of Fe(II)





At $T_{1/2}$ = 180 K,

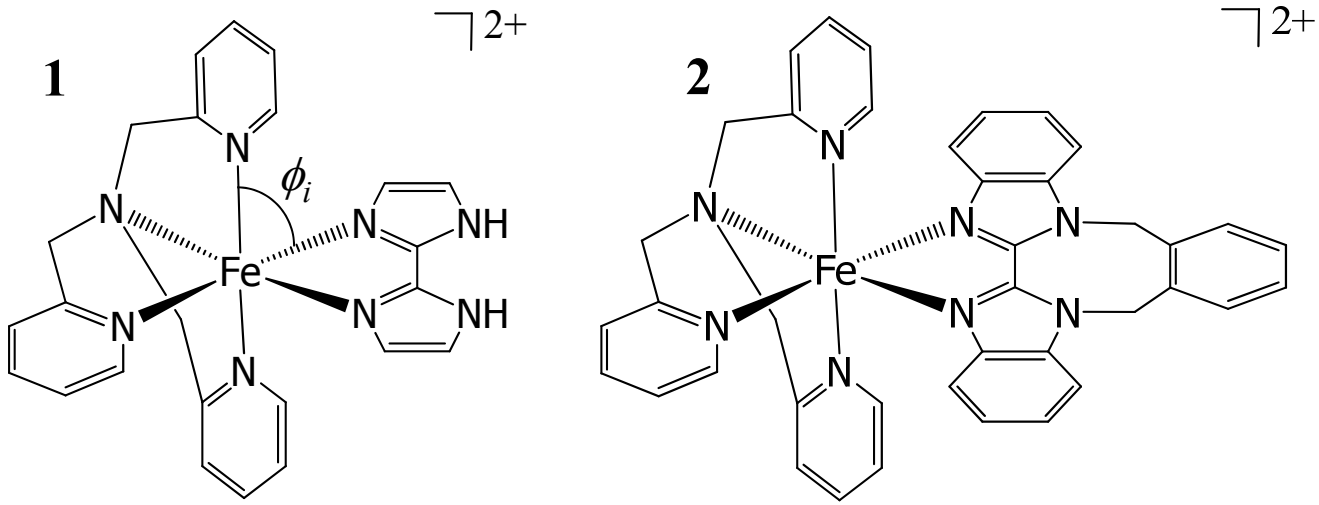
$$\gamma_{HS} = \frac{[Fe]_{HS}}{[Fe]_{total}} = \frac{[Fe]_{HS}}{[Fe]_{HS} + [Fe]_{LS}}$$

König, Madeja *Chem. Commun.* **1966**, 61-62.

Crystallography

Formula	$FeCl_2O_8N_8C_{32}H_{30}$ (**1**)		$FeCl_2O_{9.2}N_8C_{41.2}H_{38.8}$ (**2**·1.5CH_3OH)	
Temperature	123 K	210 K	123 K	210 K
Space group (No.)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/n$ (11)	$P2_1/n$ (11)
V, Å^3	3231.06	3372.03	4716.8	4768.89
d(Fe–N)$_{av}$, Å	2.002(4)	2.184(4)	2.188(4)	2.188(3)
Σ(N-Fe-N), deg	71.9(2)	118.1(2)	166.9(2)	165.5(1)

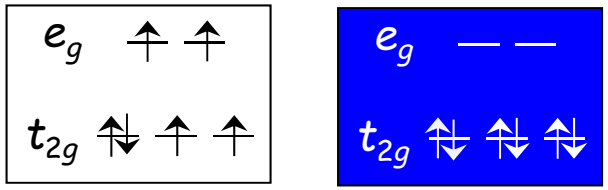
$$\Sigma = \sum_{i=1}^{12} |\phi_i - 90|$$



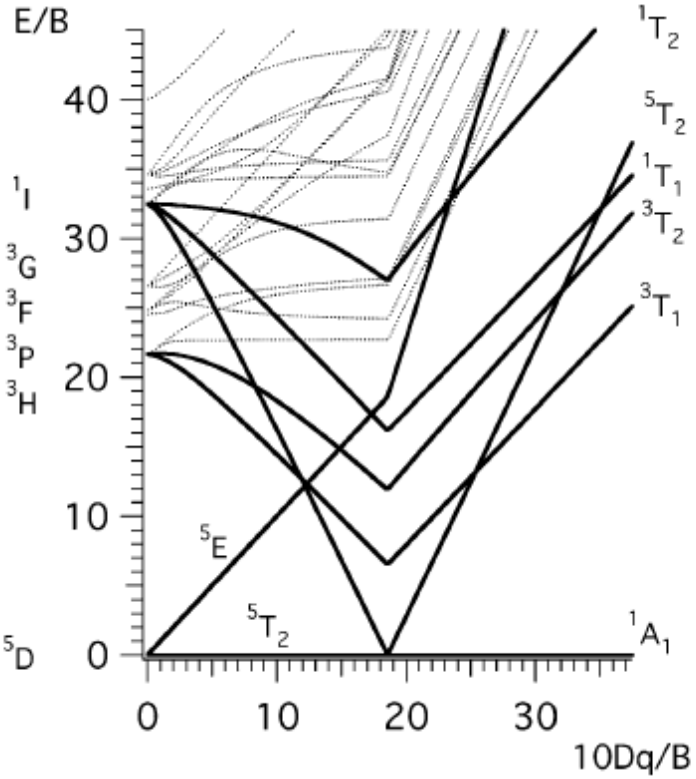
Phan, H.; Chakraborty, P.; Chen, M.; Calm, Y. M.; Kovnir, K.; Keniley, L. K.; Hoyt, J. M.; Knowles, E. S.; Besnard, C.; Meisel, M. W.; Hauser, A.; Achim, C.; Shatruk, M. *Chem. Eur. J.* **2012**, *18*, 15805-15815.

The Physics of Spin Crossover

Fe(II), d^6

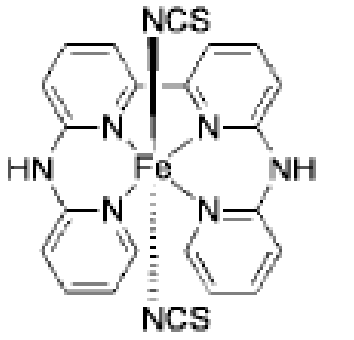


HS, S = 2 LS, S = 0



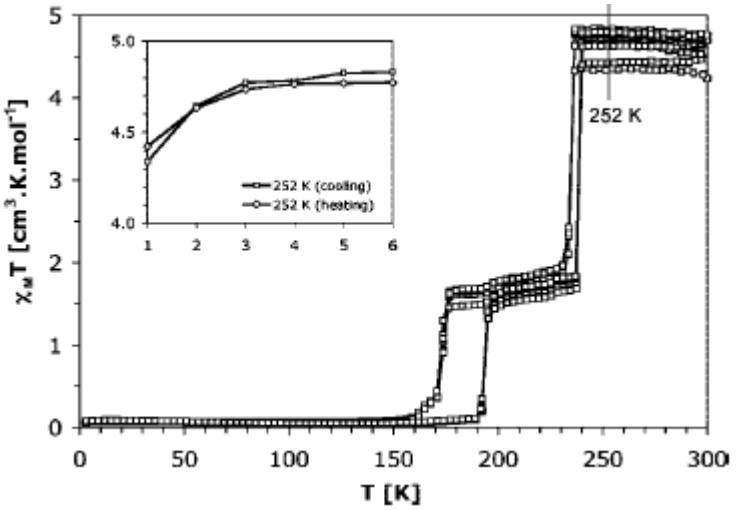
- Two contributions to the total electron energy are important:
  - d-orbital splitting, $10Dq$
  - d-electron pairing energy, $\Pi \approx 15{,}000\ \mathrm{cm}^{-1}$ for Fe^{2+}
- SCO is possible when
  $$10Dq_{HS} < \Pi < 10Dq_{LS}$$
- SCO is not possible when
  $$10Dq_{HS} < 10{,}000\ \mathrm{cm}^{-1} \text{ or}$$
  $$10Dq_{LS} > 23{,}000\ \mathrm{cm}^{-1}$$
- Conclusion:
  The SCO depends on the ligand field and the charge on the metal ion
- Spectrochemical series:
  $I^- < Br^- < Cl^- < SCN^- < NO_3^- < F^- < OH^- < H_2O < NCS^- < py < NH_3 < en < NO_2^- < PPh_3 < CN^- < CO$

Cooperativity of the Spin Transition

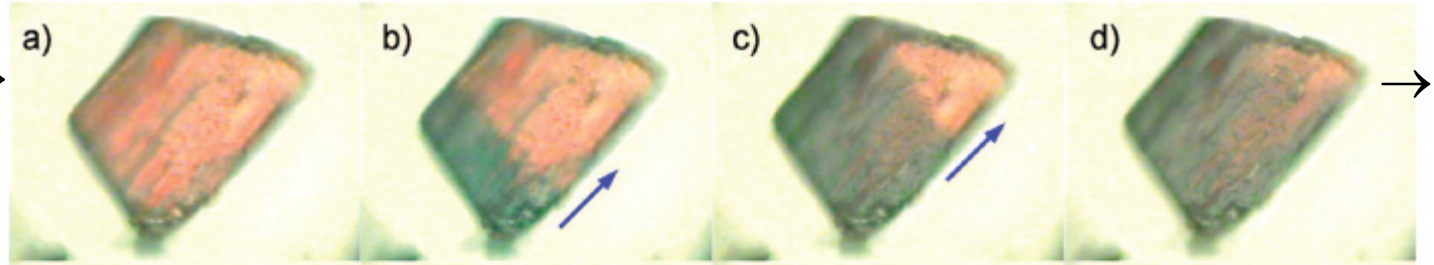


1
trans-[Fe(bapbpy)(NCS)$_2$]

Two-step *SCO*

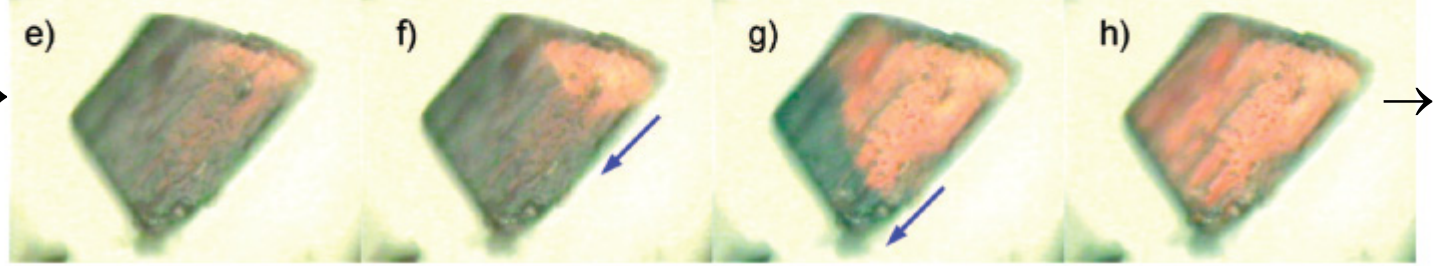


253 K →



→ 243 K

243 K →

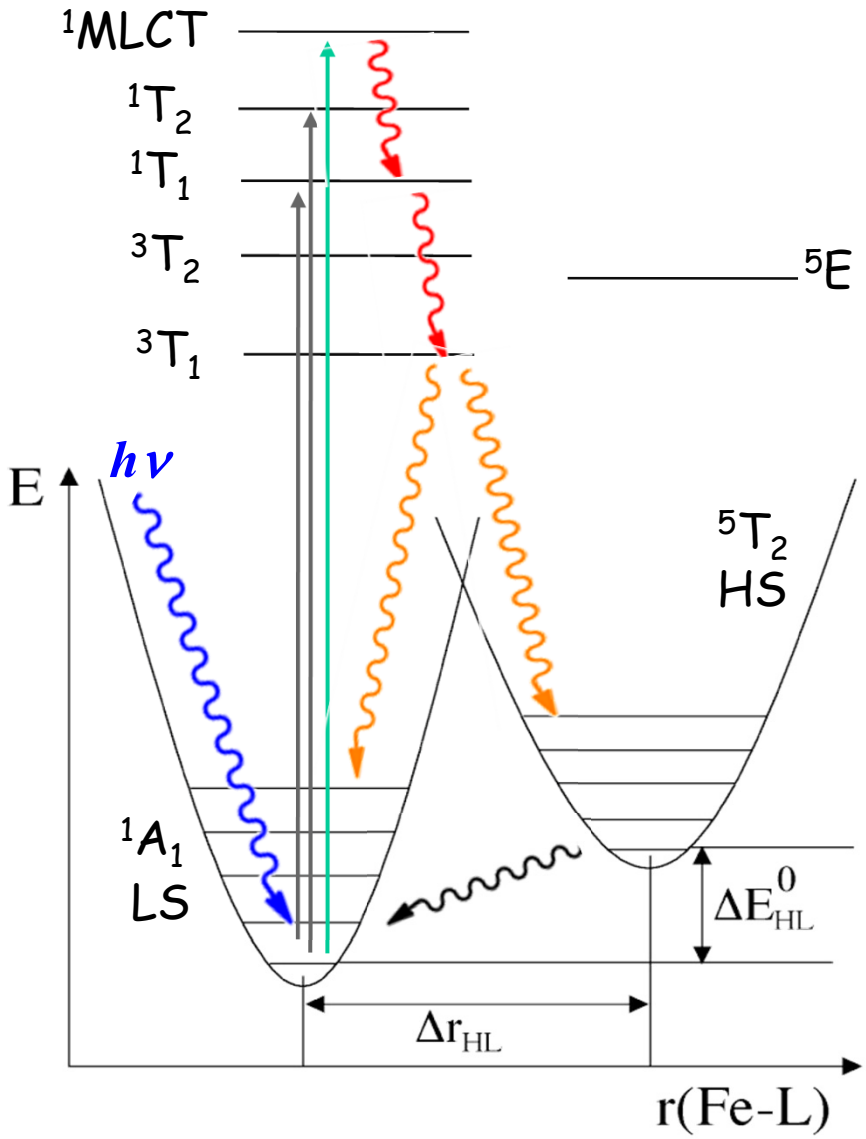


→ 253 K

Reedijk, J. et al. *Chem. Mater.* **2009**, *21*, 1123.

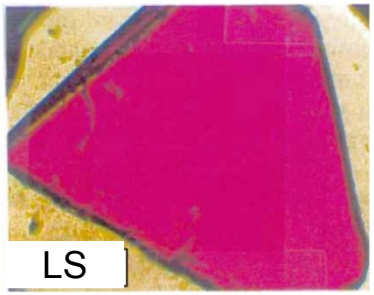
Photoinduced SCO (LIESST)

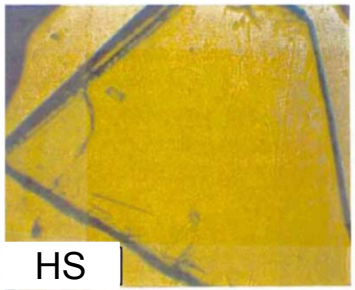
- Irradiation into characteristic absorption bands of the LS state results in photoinduced population of the metastable HS state.
- This phenomenon is known as Light-Induced Excited Spin State Trapping, or **LIESST**



Hauser, A. *Top. Curr. Chem.* **2004**, *234*, 155-198.

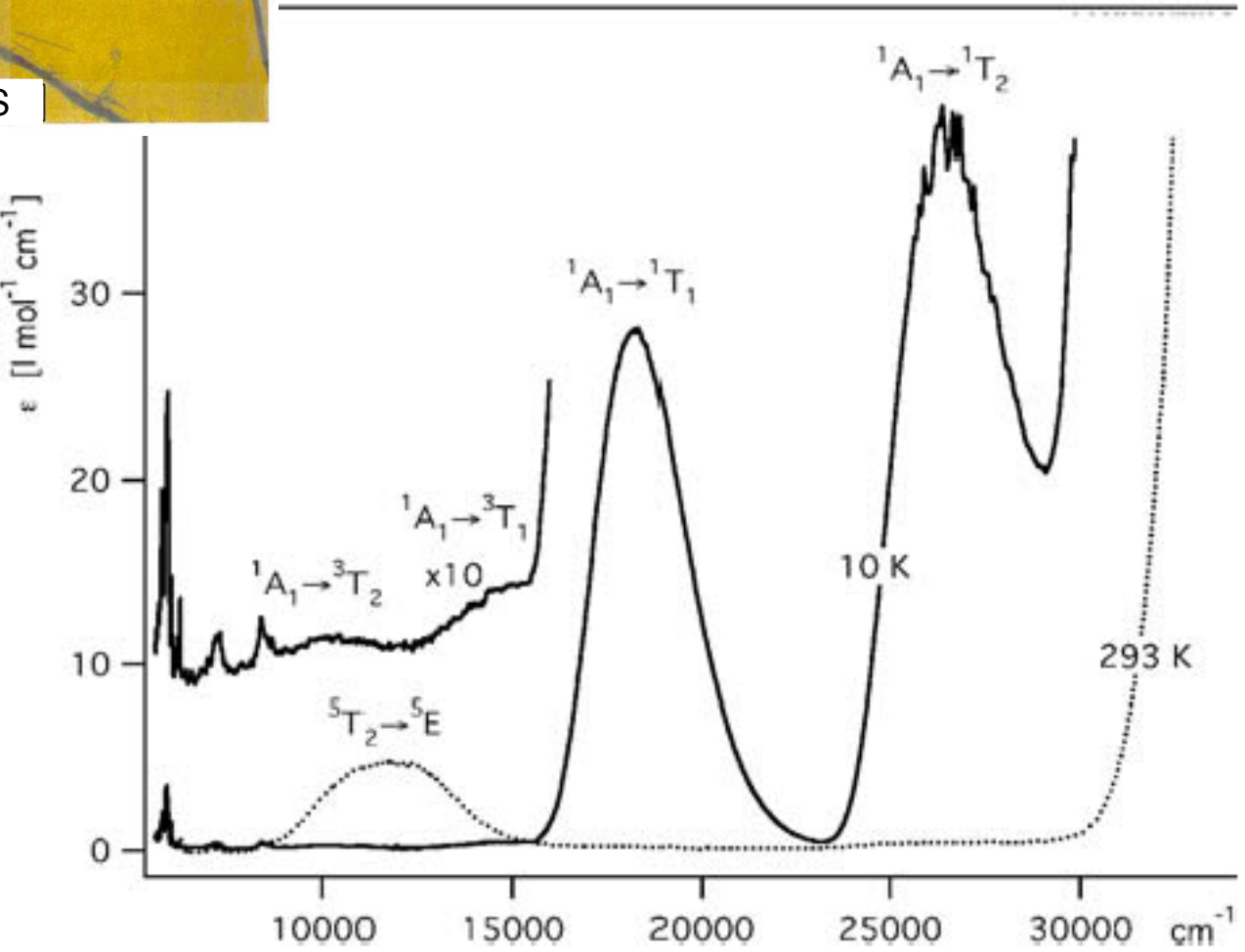
LIESST: The First Observation





$[Fe(ptz)_6](BF_4)_2$

Ground States:
- LS = $^1A_1$
- HS = $^5T_2$



Hauser, A. *Chem. Phys. Lett.* **1986**, *124*, 543.

LIESST: The First Observation

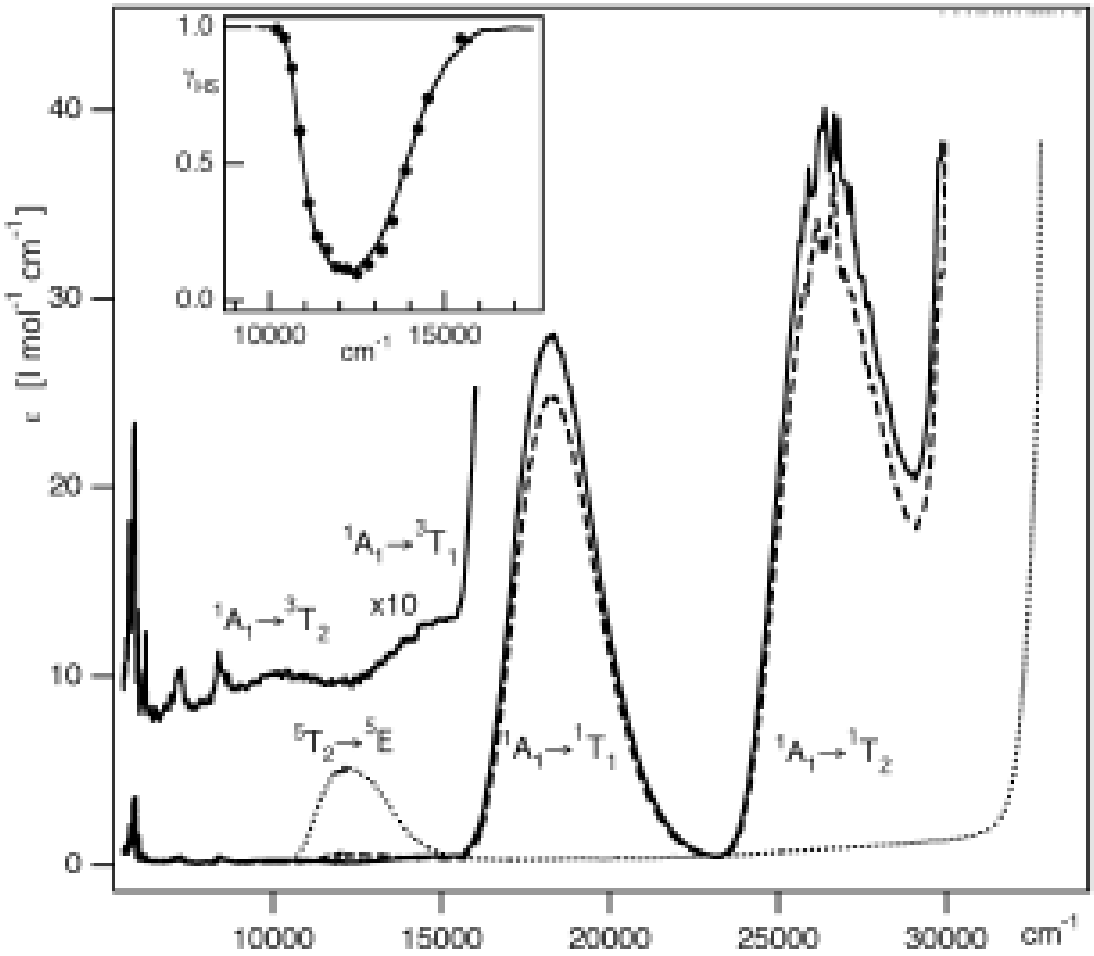
$[Fe(ptz)_6](BF_4)_2$

Three spectra at 10 K:

— after slow cooling from 300 K to 10 K, the complex is in the LS state

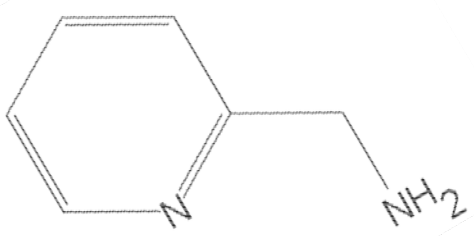
···· irradiation with λ = 515 nm at 10 K causes spin transition (LIESST) into the metastable HS state

--- irradiation with λ =830 nm at 10 K causes a reverse spin transition (RLIESST) into the ground LS state



Hauser, A. *Chem. Phys. Lett.* **1986**, *124*, 543.

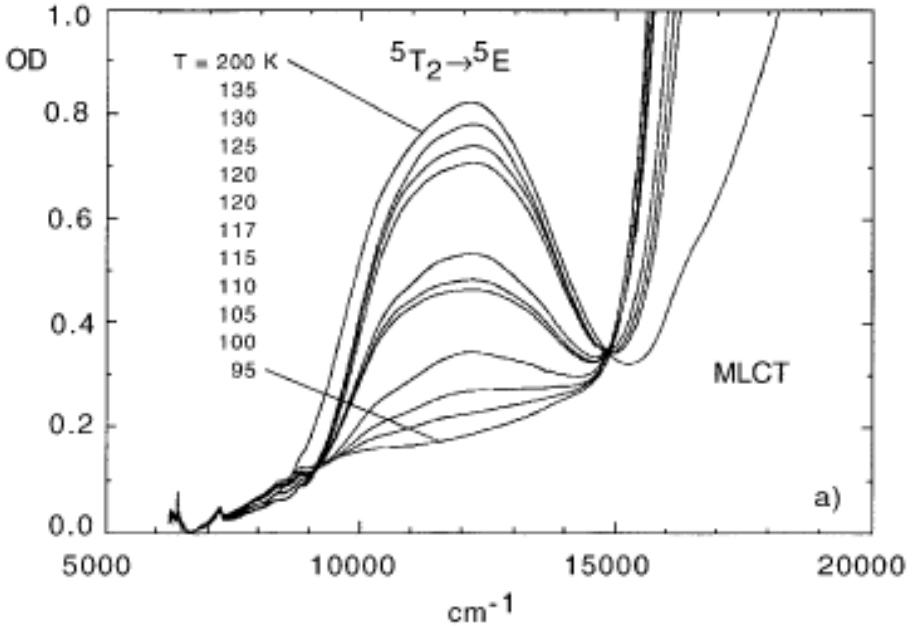
LIESST: Stability of Crystals



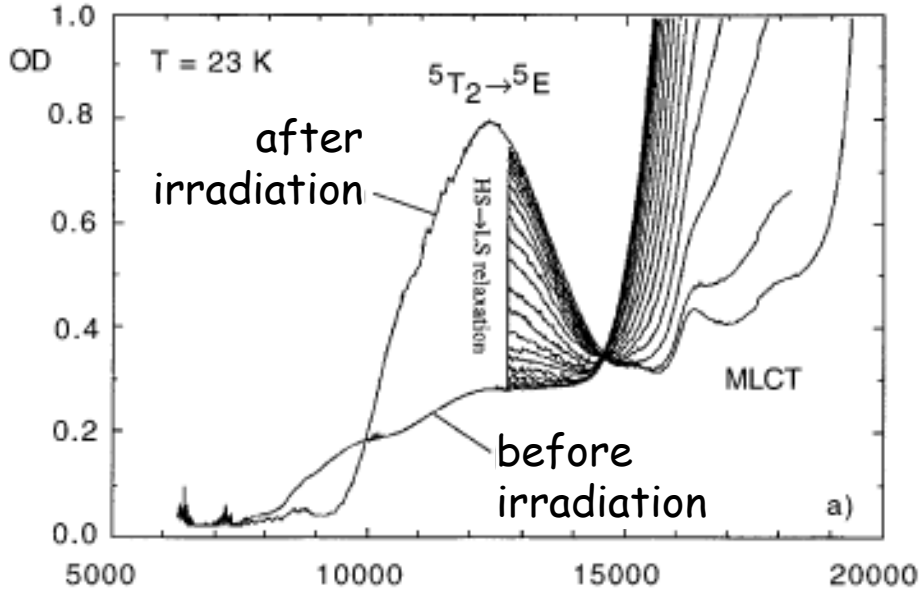
$[Fe(pic)_3]Cl_2$

- Crystals of this compound are converted into fine powder under irradiation at 23 K (λ = 515 nm)

Temperature-dependent spectra



Before and after irradiation at 23 K



Romstedt, H.; Hauser, A.; Spiering, H. *J. Phys. Chem. Solids* **1998**, *59*, 265.
Vef, A.; Manthe, U.; Gütlich, P.; Hauser, A. *J. Chem. Phys.* **1994**, *101*, 9326.