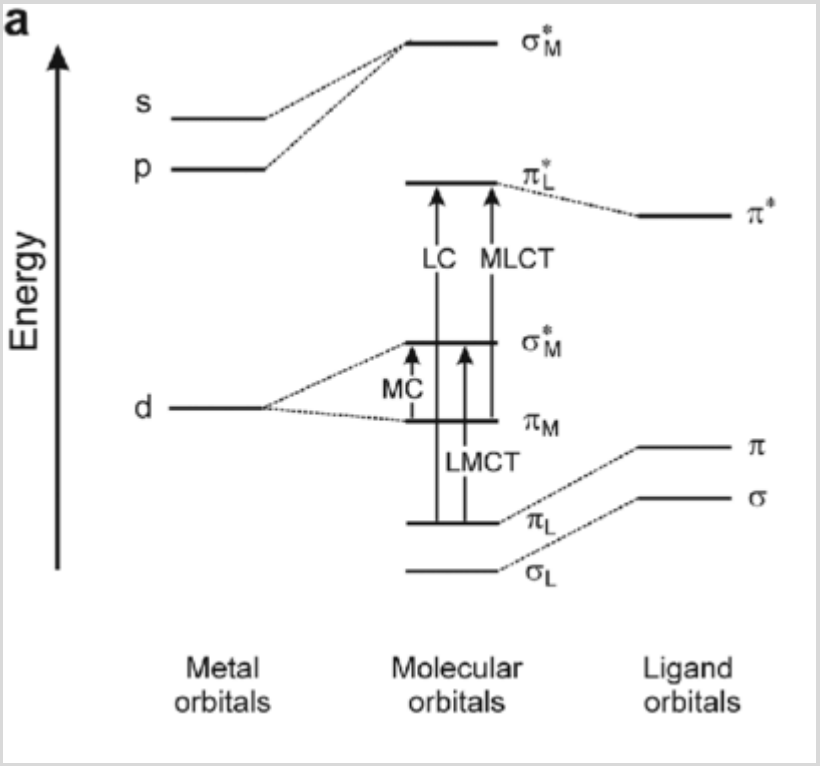
UV-vis Absorbance Spectroscopy of Transition Metal Complexes

Models/Topics Covered: Photochemistry, Jabłoński/Grotrian Diagrams, Beer-Lambert Law, Electronic Selection Rules, Orgel and Tanabe-Sugano Diagrams

This question sheet has an accompanying data sheet, and you may benefit from access to a ruler and calculator.



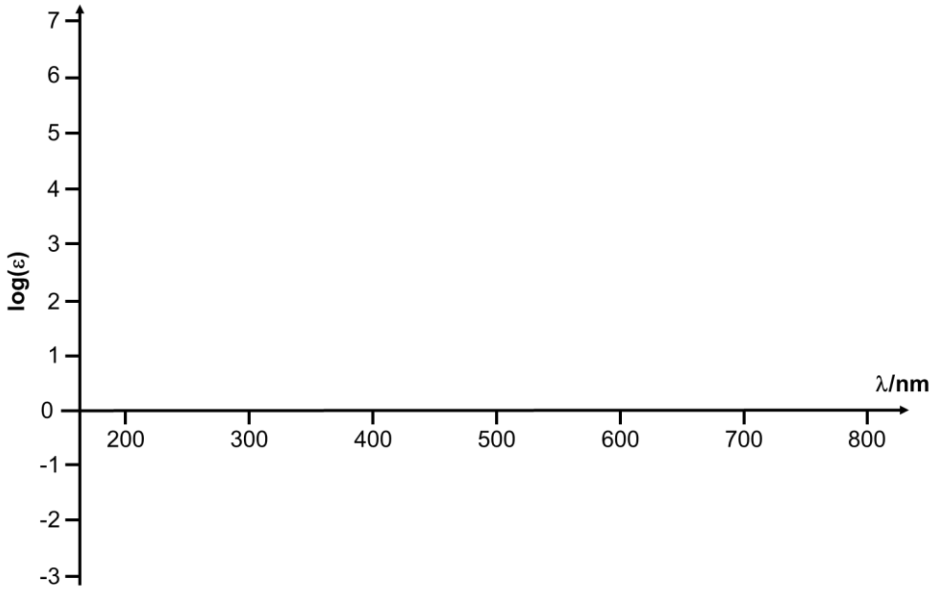
Reproduced from Ref[8] (Fig. 1)

Question 1 (Electronic Transitions)

(i). Draw a Jabłoński Diagram indicating the following processes: Absorption, Emission, Vibrational Relaxation, Intersystem Crossing between a Singlet and Triplet state, Fluorescence, Phosphorescence.

(ii). Using your diagram, explain why: (i) UV-vis absorption peaks are commonly broad, and (ii) rotational energy levels are usually not of interest to electronic spectroscopic techniques.

(iii). On a set of axes like those below, indicate the approximate ranges of absorbance and extinction coefficient for the following regions and transitions: Visible Region, Ligand-based π-π*, Charge Transfer, d-d (first row metals, octahedral), d-d (first row metals, tetrahedral), d-d (heavier metals). Support your answers with explanations in terms of the transitions between electronic energy levels and allowable transitions.



Question 2 (Charge Transfer)

Identify the type of charge transfer process providing colour in the following systems:

(i). $[Ru(bpy)_3]Cl_2$
(ii). $KMnO_4$, and explain why the $[ReO_4]^-$ anion is colourless
(iii). Sapphire, comprising corundum (Al_2O_3) with some aluminium sites replaced by Fe(II) and Ti(IV) impurities
(iv). Amethyst, comprising beryl ($Be_3Al_2Si_6O_{18}$) with Fe(IV) impurities

Question 3 (Term Symbols and Orgel Diagrams)

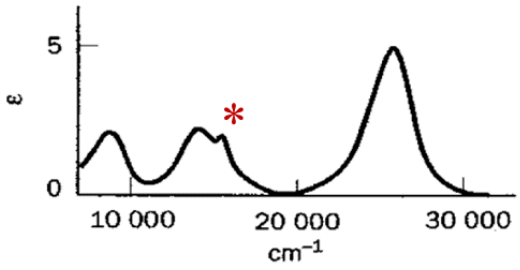
Orgel Diagrams can predict the difference in energy level of the various d-d transitions based on the strength of the crystal field a metal centre is exposed to.

(i). For a free d^2 metal ion, indicate why the ground state of the free ion is ^3F, and explain the importance of the ^3P state.
(ii). Introduction of the d^2 metal to a crystal field leads to splitting into four term symbols of different energies. What do these states correspond to in physical terms? Use energy level diagrams to help illustrate your answer.
(iii). With reference to Orgel Diagrams, explain the effect of increasing crystal field strength.
(iv). How many d-d transitions would you expect to observe via UV for a d^2 metal? What about a d^5 metal?

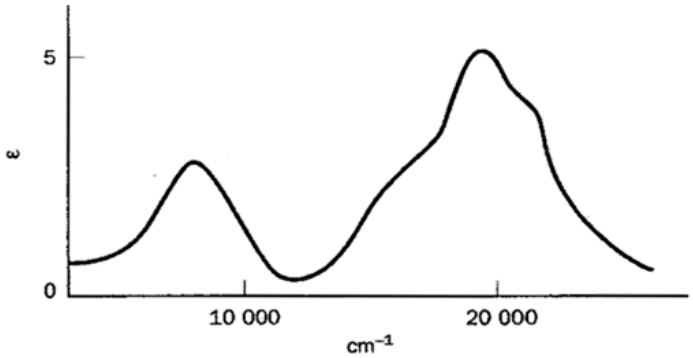
Question 4 (Tanabe-Sugano Diagrams)

Orgel Diagrams do not take into account interelectronic repulsion. Tanabe-Sugano diagrams allow for this through the inclusion of the Racah Parameter, B.

(i). Why are there no Tanabe-Sugano diagrams for d^1 or d^9 metals?
(ii). Identify the permitted transitions in the Tanabe-Sugano diagrams for a d^7 and a d^8 metal.
(iii). Indicate the origin of the starred peak in the UV spectrum of hexaaquanickel(II).
(iv). Indicate whether the UV spectrum of hexaaquacobalt(II) indicates this species is high or low spin.



d^8; the spectrum of $[Ni(H_2O)_6]^{2+}$.



d^7; the spectrum of $[Co(H_2O)_6]^{2+}$.

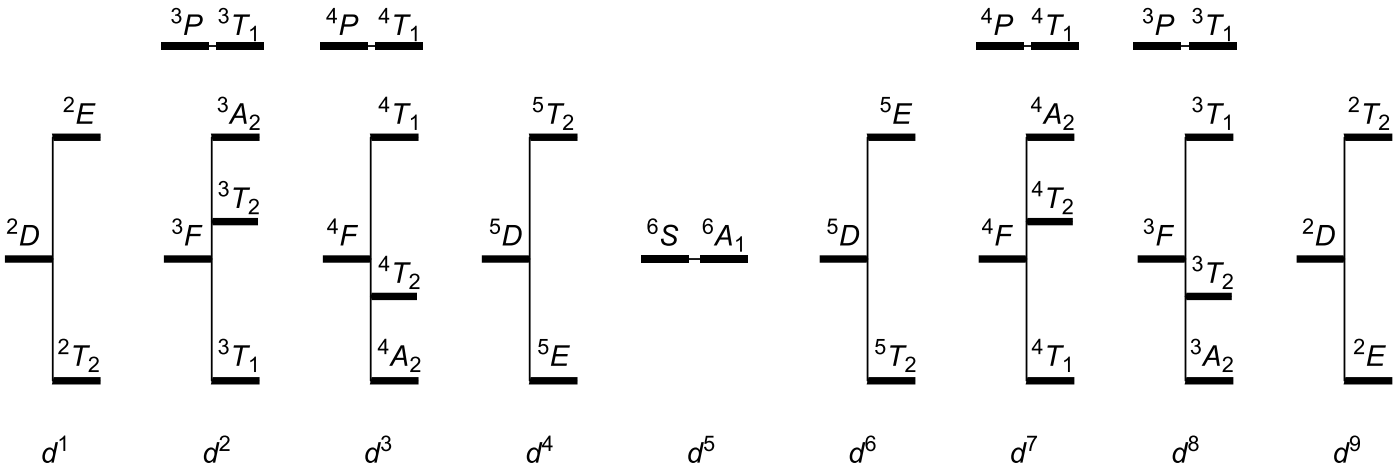
[1] Weller, Overton, Rourke, Armstrong. 2018. *Inorganic Chemistry*. 7th ed. New York, USA: Oxford University Press.
[2] Rankin, Mitzel, Morrison. 2013. *Structural Methods in Molecular Inorganic Chemistry.* 1st ed. Sussex, UK: John Wiley & Sons, Ltd. (Extra online resources available from: https://bcs.wiley.com/he-bcs/Books?action=index&itemId=0470972785&bcsId=7906)
[3] Ribas Gispert. 2008. *Coordination Chemistry.* 1st ed. Germany: Wiley-VCH.
[4] Halcrow. 2017. *Lecture 2 and 3: UV/vis Spectroscopy*. Lecture Notes, CHEM5600 I1, University of Leeds, delivered 2017.
[5] Lancashire, 2022. *The Russell Sanders Coupling Scheme*. Chemistry LibreTexts [Online] https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Spectroscopy/Electronic_Spectroscopy/Spin-orbit_Coupling/The_Russell_Saunders_Coupling_Scheme
[6] Alchemyst, 2019. *Electronic Spectroscopy*. [Online] https://alchemyst.co.uk/pdf/Inorganic/elec_spectroscopy.pdf (Website containing notes by an ex-Oxford Chemistry Student)
[7] Fritsch, Rossman. '*An Update on Color in Gems. Part 2: Colors involving Multiple Atoms and Color Centres*' Gems and Gemology, 1988 (Available: https://alchemyst.co.uk/pdf/Inorganic/elec_spectroscopy.pdf)
[8] Mauro et al. '*When self-assembly meets biology*' Chem. Soc. Rev. 2014, **43**(12), (DOI: 10.1039/c3cs60453e)
[9] Landskron, 2022. *Term splitting in ligand fields, selection rules, Tanabe-Sugano diagrams. Metal to ligand, and ligand to metal transitions.* Chemistry LibreTexts [Online] https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Inorganic_Coordination_Chemistry_(Landskron)/08%3A_Coordination_Chemistry_III_-_Electronic_Spectra/8.02%3A_Electronic_Spectra_of_Coordination_Compounds

***Data Sheet**: UV-vis Absorbance Spectroscopy of Transition Metal Complexes*

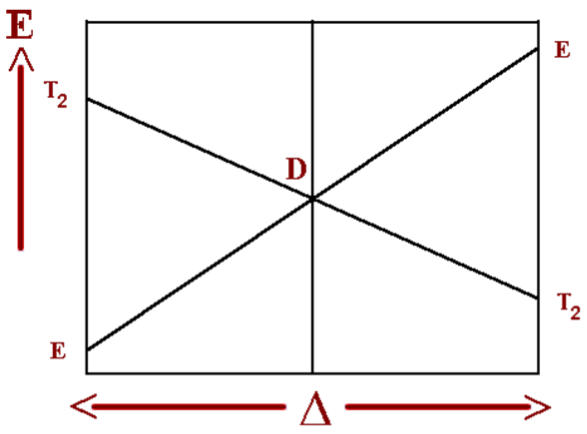
Mulliken Symbol Meanings

Mulliken Symbol for atomic and molecular orbitals	Explanation
a	Non-degenerate orbital; symmetric to principal C_n
b	Non-degenerate orbital; unsymmetric to principal C_n
e	Doubly degenerate orbital
t	Triply degenerate orbital
(subscript) g	Symmetric with respect to center of inversion
(subscript) u	Unsymmetric with respect to center of inversion
(subscript) 1	Symmetric with respect to C_2 perp. to principal C_n
(subscript) 2	Unsymmetric with respect to C_2 perp. to principal C_n
(superscript) '	Symmetric with respect to s_h
(superscript) "	Unsymmetric with respect to s_h

Term Symbols for Complexes with O_h Symmetry



Orgel Diagrams



d^1, d^6 tet
d^4, d^9 oct

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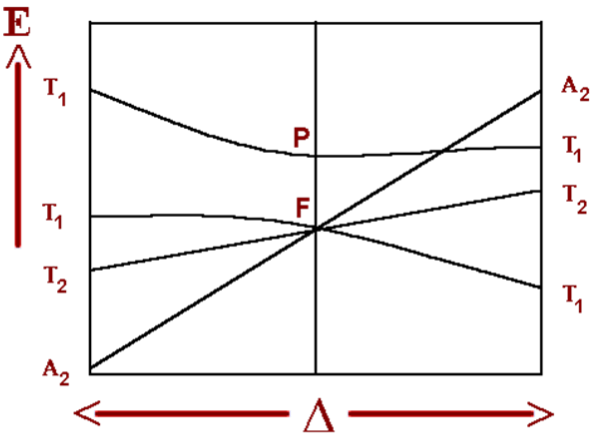
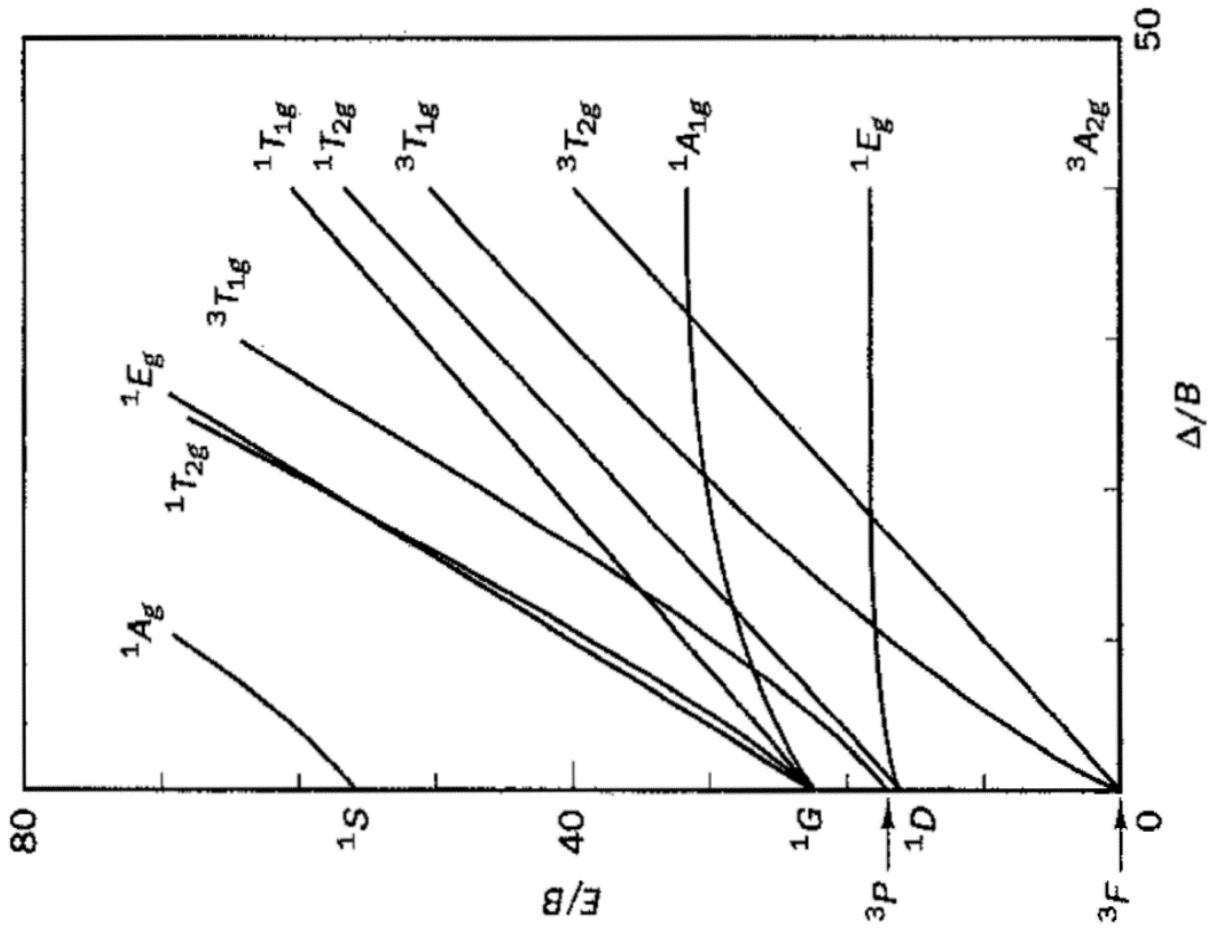
d^4, d^9 tet



d^2, d^7 tet
d^3, d^8 oct

d^2, d^7 oct
d^3, d^8 tet

Tanabe-Sugano Diagram for a d^8 Metal Centre



Tanabe-Sugano Diagram for a d^5 Metal Centre