


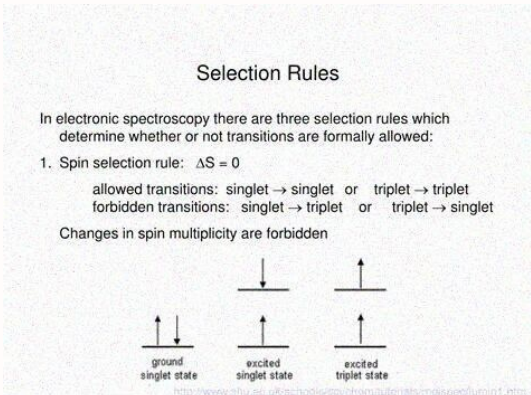
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Electronic spectra selection rules. Selection rules spectroscopy.



c) π -acceptor and π -donor ligands can mix with the d-orbitals so transitions are no longer purely d-d. Types of transition Charge transfer, either ligand to metal or metal to ligand. These are often extremely intense and are generally found in the UV but they may have a tail into the visible. d-d, these can occur in both the UV and visible region but since they are forbidden transitions have small intensities. Expected intensities of electronic transitions Transition type Example Typical values of ϵ /m²mol⁻¹ Spin forbidden, Laporte forbidden [Mn(H₂O)₆]²⁺ 0.1 Spin allowed (octahedral complex), Laporte forbidden [Ti(H₂O)₆]³⁺ 1 - 10 Spin allowed (tetrahedral complex), Laporte partially allowed by d-p mixing [CoCl₄]²⁻ 50 - 150 Spin allowed, Laporte allowed e.g. charge transfer bands [TiCl₆]²⁻ or MnO₄⁻ 1000 - 106 Expected Values The expected values should be compared to the following rough guide. For M²⁺ complexes, expect Δ = 7500 - 12500 cm⁻¹ or λ = 800 - 1350 nm. For M³⁺ complexes, expect Δ = 14000 - 25000 cm⁻¹ or λ = 400 - 720 nm. For a typical spin-allowed but Laporte (orbitally) forbidden transition in an octahedral complex, expect ϵ < 10 m²mol⁻¹. Extinction coefficients for tetrahedral complexes are expected to be around 50-100 times larger than for octrahedral complexes. B for first-row transition metal free ions is around 1000 cm⁻¹. Depending on the position of the ligand in the nephelauxetic series, this can be reduced to as low as 60% in the complex.

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Relaxation of the Rules can occur through: a) Spin-Orbit coupling - this gives rise to weak spin forbidden bands b) Vibronic coupling - an octahedral complex may have allowed vibrations where the molecule is asymmetric. Absorption of light at that moment is then possible. c) π -acceptor and π -donor ligands can mix with the d-orbitals so transitions are no longer purely d-d.

Selection rules of atomic spectra(review)

$$\text{TDM} \propto \int Y_{l'm_l'}^* (Y_{10} \text{ or } Y_{1\pm1}) Y_{lm_l} \sin \theta d\theta d\varphi \times \delta_{m_l'm_l}$$

- From the mathematical properties of spherical harmonics, this integral is zero unless

$$\Delta l = l' - l = \pm 1$$
$$\Delta m_l = m_{l'} - m_l = 0, \pm 1$$
$$\Delta m_s = 0$$

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