

8.6.2: Selection Rules

Electronic transitions between states of different energies give rise to electronic spectra. However, some transitions are more probable, and thus more intense, than others. In UV-vis spectroscopy, for example, the transitions that are "allowed" can give rise to absorption bands that are much more intense than transitions that are "forbidden". To be clear, "forbidden" transitions are still possible, and are sometimes observable, but are less intense because they happen less frequently than "allowed" transition when the molecules are exposed to electromagnetic radiation.

Selection Rules that govern Electronic Transitions

The Selection Rules governing transitions between electronic energy levels (including microstates and terms) are:

1. **The Spin Selection Rule**, $\Delta S = 0$.
2. **The Laporte (or orbital) Selection Rule**, for centrosymmetric molecules $g \rightarrow u$ or $u \rightarrow g$, or $\Delta l = \pm 1$.

Selection rules that govern electronic transitions

Spin selection rule

The Spin Selection Rule forbids transitions between states with different total spin, and thus different spin multiplicity. This rule allows transitions only between states with the same total intrinsic spin ($\Delta S = 0$), and thus the same spin multiplicity value in the term symbol. In other words, the direction of the promoted electron's spin should not change. Just in case it is not obvious yet, the spin multiplicity is the left superscript in the term symbol, so this rule allows transitions between terms with the same superscript. For example, this rule would allow a transition from a 3T term to a 3A term, but not from 3T to 2D .

Laporte (orbital) Selection Rule

The Laporte Selection Rule applies to molecules that have a center of symmetry (aka center of inversion, centrosymmetric). This rule forbids transitions between states with the same parity (symmetry) with respect to an inversion center (i). Parity is indicated on molecular orbitals and on term symbols with subscripts g (gerade, or even) and u (ungerade, or uneven). Transitions between u and g terms are allowed (eg $T_{2g} \rightarrow T_{1u}$ is allowed), but those between two g or two u terms are forbidden (eg $T_{2g} \rightarrow T_{1g}$ is forbidden). Because different types of orbitals have different symmetries with respect to i , this rule is sometimes referred to as the "orbital selection rule". It forbids transitions within one type of orbital subshell. For example, p orbitals are antisymmetric with respect to i , while both s and d orbitals are symmetric with respect to i . This rule forbids $s \rightarrow s$, $p \rightarrow p$, $d \rightarrow d$, and $d \rightarrow s$ transitions, but allows transition between $d \rightarrow p$ and $d \rightarrow s$ orbitals. This rule is important in transition metal complexes because it forbids $d-d$ transitions in centrosymmetric geometries, including octahedral and linear coordination geometries.

Despite these selection rules, $d \rightarrow d$ transitions are a hallmark feature of octahedral transition metal complexes, and are often responsible for their brilliant colors. These $d \rightarrow d$ transitions, and other forbidden transitions may still occur, primarily through relaxation of these rules in specific cases.

Breaking the rules!

Relaxation of the Laporte and Spin Selection Rules can occur through:

- **Vibronic coupling:** the bonds of metal complexes vibrate and may cause temporary distortions in molecular symmetry. These distortions can cause temporary loss in symmetry (as well as some orbital mixing), and thus allow $d \rightarrow d$ transitions in those moments of distortion. Despite being forbidden by the Laporte Selection rule, the $d \rightarrow d$ transitions in octahedral complexes appear, but are weak (of low intensity) with molar absorptivities $\leq 100 \text{ M}^{-1} \text{ cm}^{-1}$.
- **Orbital Mixing:** In the case of octahedral complexes, π -acceptor and π -donor ligands can mix with the d -orbitals so that transitions are no longer purely $d \rightarrow d$ (but these are usually considered "charge transfer" transitions, not $d \rightarrow d$). In the case of tetrahedral complexes, the molecule has no center of symmetry (thus no u or g subscripts on the terms). In the valence orbital model, a tetrahedral molecule is said to have sp^3 and sd^3 hybridized orbitals, while MO theory predicts MO's with mixtures of some s , p , and d character - this mixing of orbital types can allow transitions between "mixed" orbitals that would otherwise be forbidden in "pure" orbitals. A similar phenomenon would occur in octahedrons with significant distortion, or in other coordination geometries that provide potential for orbital mixing.

- **Spin-Orbit coupling:** This gives rise to spin-forbidden bands of low intensity, usually with very weak molar absorptivities approximately $\leq 1 M^{-1} cm^{-1}$. This phenomenon is usually more important for transition metals of the second row $4d$ and beyond.

? Exercise 8.6.2.1

Consider the d^2 case presented in a [previous section](#). The free ion terms for d^2 were found to be 3F , 1G , 3P , 1D , 1S . First, identify the ground state term. Then identify the Spin-Allowed excitations starting from the ground state.

Answer

The ground state is 3F . There is only one spin-allowed transition: $^3F \rightarrow ^3P$.

The spin-forbidden transitions from 3F include $^3F \rightarrow ^1D$, $^3F \rightarrow ^1G$, and $^3F \rightarrow ^1S$.

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