6.2. Introduction to Spectroscopic states and term symbols

From the number of absorption bands we have already seen that usually more d-d transitions are observed than expected from a simplified picture where one electron is excited from a $t_{2g}$ orbital to an $e_g$ orbital. An electron configuration, e.g., $(t_{2g})^1(e_g)^1$, turns out to be a rather simplistic picture. For a better, more detailed description, spectroscopists introduced term symbols. When labeling spectroscopic states for transition-metal complexes, we have two choices to describe these states. (a) We can look at the isolated (gas-phase) metal cation, start from its electron configuration ($d^n$), and look at the ground and excited states. (b) On the other hand, we can look at the complex of a certain point symmetry and use appropriate Mulliken labels.

6.2.1 Gas-phase metal cation:

A single electron exhibits two types of angular momenta: a spin (intrinsic angular momentum) and an orbital angular momentum. The quantum numbers that describe the size of the angular momenta are: $s$ (for the spin angular momentum, which is always $\frac{1}{2}$ for a single spin) and $l$ (for the orbital angular momentum). The quantum numbers, $m_s$ and $m_l$, specify the orientation of the angular momenta with respect to a primary axis (the $z$-axis). As discussed in an earlier chapter, $m_s$ can have values of $l, l-1, l-2, \ldots, -(l-1), -(l-2), \ldots, -1, -\frac{1}{2}, \frac{1}{2}, \ldots, -\frac{1}{2}$ only $\frac{1}{2}$ and $-\frac{1}{2}$ are possible, due to the restriction of $s$). Another way of looking at these quantum numbers is the consideration that $l$ and $s$ are given my the largest number of $m_l$ and $m_s$.

In order to describe a spectroscopic state of a cation, we have to consider the total angular momentum $L$ and the overall electron spin $S$. Both are related to the angular momentum quantum number, $l$, and spin quantum number, $s$, for single electrons, respectively. We also have to consider $M_l$ and $M_s$ quantum numbers for the atoms/cations.

(i) Term symbols for the Mg atom:

Let’s start with a simple example: the neutral Mg atom. In the ground state, both valence electrons are in an s orbital with opposite spin directions:

- electron (1): $m_l=0, m_s=\frac{1}{2}$
- electron (2): $m_l=0, m_s=-\frac{1}{2}$

Because of the Pauli exclusion principle, we do not have another choice in combining these electrons differently in this ground state. The whole atom in the ground state has a total angular momentum: $M_l=m_l(1)+m_l(2)=0+0=0$ and an overall spin: $M_s=m_s+m_s=\frac{1}{2}+(-\frac{1}{2})=0$.

Therefore, our $L$ and $S$ values for the Mg are both 0. Instead of using these two numbers directly for the description of the state, spectroscopists use term symbols. Similar to the orbital notation (s orbital for $l=0$, p orbital for $l=1$, etc), the following convention is used: $L = 0, 1, 2, 3, 4, \ldots$. Note that capital letters are used for term symbols. The spin is described by the spin multiplicity $= 2S+1$ and placed as the superscript in front of the angular momentum notation. $M$, also 2Q+1, provides information about how many different states are possible with a particular quantum number, $Q$. We can also define an orbital multiplicity, $2L+1$. For example, a P term has an orbital multiplicity of $2\cdot1+1 = 3$; three states are described by P. Compare this to the number of p orbitals. The ground state of the Mg atom is therefore described with the term $1S$ (read: singlet S).

In the excited state of Mg*, one electron is excited to a p orbital. Now we have to distinguish between different microstates, resulting in 12 possible combinations. Microstates can be best illustrated by placing electrons in orbitals, which are defined by the quantum numbers, $m_l$, and $m_s$. The spins of the s- and p electrons can be parallel or antiparallel and the excited electron can reside in the $p_x$, $p_y$, or $p_z$ orbital. In the absence of electron interaction (repulsion) all microstates would be degenerate. Due to electron repulsion, the degeneracy between the microstates is lifted and we can obtain the following terms symbols, which describe groups of microstates. Let’s start with the distinction between the parallel and antiparallel spin

Parallel maximum $M_l=l(1)+l(2)=0+1=1$ maximum $M_s=m_s=m_s=m_s=\frac{1}{2}+\frac{1}{2}=1$
Therefore, $L=1$ and $S=1$ term symbol: $3P$ (read: triplet P)

Antiparallel maximum $M_l=l(1)+l(2)=0+1=1$ maximum $M_s=m_s+m_s=\frac{1}{2}+(-\frac{1}{2})=0$
Therefore, $L=1$ and $S=0$ term symbol: $1P$ (read: singlet P)

The term symbol $1P$ describes three degenerate microstates: spin multiplicity of 1 and orbital multiplicity of 3. On the other hand, the $3P$ term describes nine degenerate microstates, arising from a spin multiplicity of 3 and an orbital multiplicity of 3. This way we accounted for all microstates.

(ii) Term symbols for a d^2 configuration: Ti^{2+}

The first step is to write down all microstates for the ground state of Ti^{2+}. In Table 13.1 of the text book (p. 441) all microstates are given for the $d^2$ configuration in terms of $(m(1)^+m(2)^-)$ and $-\frac{1}{2}$ and $\frac{1}{2}$ indicating a $m_s$ values for $\frac{1}{2}$ and $-\frac{1}{2}$. These microstates are represented by the terms, $1G, 3F, 1D, 3P$, and $1S$. Taking into account the spin and orbital multiplicities of each term, we obtain 45 microstates.

<table>
<thead>
<tr>
<th>Term</th>
<th>Number of microstates</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1G$</td>
<td>9×1= 9</td>
</tr>
<tr>
<td>$3F$</td>
<td>7×3= 21</td>
</tr>
<tr>
<td>$1D$</td>
<td>5×1= 5</td>
</tr>
<tr>
<td>$3P$</td>
<td>3×3= 9</td>
</tr>
<tr>
<td>$1S$</td>
<td>1×1= 1</td>
</tr>
</tbody>
</table>

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(ii) Relative energies of spectroscopic terms

**Hund’s rules**

We have encountered Hund’s rule as a rule how to fill orbitals with electrons. In order to distinguish the relative energies of terms, and especially to identify the ground state, we can use the extended version of Hund’s rules.

1. **The term with the greatest spin multiplicity lies lowest in energy.**
   
   This rule states that the triplet states are more stable than singlet states. This is in accordance with the simpler version of Hund’s rule, that states that electrons in different orbitals with the same spin direction are more stable than those with opposite spin direction.

2. **For a given multiplicity, the greater the value of L of a term, the lower the energy.**
   
   When L is high, each electron can stay clear of its partner and hence feels lower coulombic interactions.

Using these rules, the following order of terms for Ti$^{2+}$ is predicted:

\[ ^3F < ^3P < ^1G < ^1D < ^1S \]

However, the observed order is:

\[ ^3F < ^1D < ^3P < ^1G < ^1S \]

It turns out that Hund’s rules are reliable only for the determination of the ground state.

**Racah parameters**

In order to assign energies to terms, electronic repulsion integrals would have to be rigorously analysed. Fortunately, the repulsion integrals can be combined into three parameters: the so-called **Racah parameters** $A$, $B$, and $C$. These Racah parameters are sums of repulsion integrals and the energies of the terms are expressed as linear combinations of the Racah parameters. For the $d^2$ electron configuration, the energies are given as

\[
E(^1S) = A + 14B + 7C
E(^1G) = A + 4B + 2C
E(^1D) = A - 3B + 2C
E(^3P) = A + 7B
E(^3F) = A - 8B
\]

All three Racah parameters are positive and their values of the Racah parameters are determined empirically by fitting the observed energies of the terms to the above expressions. Since the first parameter, $A$, is present for all terms, it can be disregarded for energy comparisons.

In the case that $C > 5B$ the order of the terms is close to that predicted by Hund’s rules. If $C < 5B$ high orbital angular momentum becomes more important compared to having a high spin multiplicity.

The Table on the right-hand side gives Racah parameters for some d-block ions.

### 6.2.2 Metal cation complexes:

As soon as ligands are coordinated to a transition-metal centre, a molecular symmetry is imposed and the d orbital split according to the ligand field. In these cases, **molecular term symbols** have to be used.

**Molecular term symbols**

Since $L$ is not a good quantum number in complexes, which are non-spherical, states are labeled using symmetry species of the correct point group. The simplest example is a transition-metal centre with $d^1$ configuration, e.g., the Ti$^{3+}$ cation. This electron can reside either in the $t_{2g}$ or $e_g$ orbital sets. Therefore, the molecular term symbols for the ground state (electron configuration: $t_{2g}^1$) is $^2T_{2g}$ and for the excited state (electron configuration: $e_g^1$) is $^2E_g$. To remind us, let’s look at the term symbol for gas-phase Ti$^{3+}$. Since we have a single unpaired electron, we are automatically dealing with doublet states (spin multiplicity of two; $2 \cdot \frac{1}{2} + 1$). The is located in a d-orbital ($l=2,1,0,-1,-2$) with a maximum angular momentum quantum number of $l = 2$. Hence, the term for the ground state is $^2D$, which has an orbital multiplicity of $2 \cdot 2 + 1 = 5$, which represents the five different d orbitals which the electron can reside in. We are not concerned about term symbols of the excited states since

<table>
<thead>
<tr>
<th>Atomic Term</th>
<th>Number of States</th>
<th>Terms in $O_h$ Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>1</td>
<td>$A_{1g}$</td>
</tr>
<tr>
<td>P</td>
<td>3</td>
<td>$T_{1g}$</td>
</tr>
<tr>
<td>D</td>
<td>5</td>
<td>$T_{2g} + E_g$</td>
</tr>
<tr>
<td>F</td>
<td>7</td>
<td>$T_{1g} + T_{2g} + A_{2g}$</td>
</tr>
<tr>
<td>G</td>
<td>9</td>
<td>$A_{1g} + E_g + T_{1g} + T_{2g}$</td>
</tr>
</tbody>
</table>
those states would involve excitation from or to a different type of orbitals. The ground state of the free ion \( ^2D \) splits into the two molecular terms \( ^2T_{2g} \) and \( ^2E_g \) upon formation of an octahedral complex. From ligand field theory, we know that the \( ^2T_{2g} \) state is lower in energy compared to \( ^2E_g \).

But most of the time electron repulsion must be considered and a \( e_g \leftrightarrow t_{2g} \) transition is not an unambiguous description of a transition. For example, \( d_{z^2} \leftrightarrow d_{xy} \) and \( d_{z^2} \leftrightarrow d_{xz} \) transitions fall into this category, but they are not necessarily degenerate if other electrons are present. Group-theoretical treatment provides us with tables that correlate atomic terms with molecular terms (table for \( O_6 \) complexes shown below). In that table we can find the splitting of the atomic \( D \) term that we derived above.

**Correlation diagrams**

We can draw a correlation diagram between atomic terms and molecular terms. For the \( d^1 \) electron configuration we split the \( ^2D \) term into \( ^2T_{2g} \) and \( ^2E_g \). The degree of splitting depends on the strength of the ligand field and has a value of \( \Delta_o \) as shown below.

For the \( d^2 \) electron configuration of a transition metal cation, two triplet terms have to be considered: \( ^3F \) and \( ^3P \). Using the table with correlates the atomic terms to molecular terms, we can derive four molecular triplet terms: \( ^3A_{2g} \), \( ^3T_{2g} \), \( ^3T_{1g} \). The \( ^3A_{2g} \), \( ^3T_{2g} \), and \( ^3T_{1g} \) terms correspond to the \( e_g^1 \), \( t_{2g}^1 \), and \( t_{2g}^2 \) electron configurations, respectively. The energies of these terms can be written in terms of \( \Delta_o \):

\[
\begin{align*}
E(t_{2g}^2, ^3T_{1g}) &= 2(-2/5 \Delta_o) = -0.8 \Delta_o \\
E(e_g^1, ^3T_{2g}) &= (-2/5+3/5) \Delta_o = 0.2 \Delta_o \\
E(e_g^1, ^3A_{2g}) &= 2(3/5 \Delta_o) = 1.2 \Delta_o
\end{align*}
\]

As a result, the energies relative to that of the lowest term are:

\[
\begin{align*}
E(t_{2g}^2, ^3T_{1g}) &= 0 \\
E(e_g^1, ^3T_{2g}) &= \Delta_o \\
E(e_g^1, ^3A_{2g}) &= 2 \Delta_o
\end{align*}
\]

The correlation diagram above illustrates the splittings of the molecular terms and their relative energies in terms of \( \Delta_o \). The relative energies of the atomic terms are given using the Racah parameters.

In these diagrams, we can distinguish between two extreme cases: (a) the weak-field limit and (b) the strong-field limit. The weak-field limit is found on the left side of the diagram, where electron-electron repulsion is dominating the energy and terms can be expressed as linear combinations of Racah parameters. Labels using atomic term symbols are a good approximation. In the strong-field limit, the ligand field is dominating the relative energies. Molecular term symbols have to be used.

**Tanabe-Sugano diagrams**

Correlation diagrams between energies of atomic and molecular terms can draw as so-called Tanabe-Sugano diagrams for each electron configuration of free ions. The ground state is the reference point and is along the x-axis. Energy
values in a Tanabe-Sugano diagram are only given relative to the ground state. The simple correlation diagram had multiples of B (the Racah parameter) on the energy axis to denote the relative energies of the atomic terms. In the Tanabe-Sugano diagrams, the energy axis has units of E/B. The x-axis has units of $\Delta_0/B$. Each Tanabe-Sugano diagram is given for only one specific B/C ratio (the best value). For example, the Tanabe-Sugano diagram for d³ complexes is given for C = 4.5 B.

On the right-hand side, Tanabe-Sugano diagrams for d² and d³ configurations are given. So far we have encountered straight lines in correlation diagrams. The curved lines in the Tanabe-Sugano diagrams for d² and d³ configurations are a consequence of the non-crossing rule. Terms of the same symmetry cannot cross and will ‘repel’ each other (see section 3.2.3).

Excitations of electrons are transition between electronic states. Usually, we are concerned about transitions from the ground state to an excited state. Therefore, in a Tanabe-Sugano diagram we start from the x-axis (ground state) and measure the height of an arrow to an excited state, which provides us with the energy separation. Depending on the ligand-field splitting, the energy of these transitions will vary. How many spin-allowed transition do you expect for octahedral d²- and d³-transition-metal complexes?

The UV-visible spectrum given above is an absorption spectrum for a d³ complex. The transitions are indicated in term symbols as well as with the corresponding electron configuration. The ratio of energies (wavenumbers) of the two spin-allowed d-d transitions can be used to obtain experimental values for B and $\Delta_0$. The ratio of the energies can be found in the Tanabe-Sugano diagram, providing a specific value for $\Delta_0/B$. The Racah parameter B can be calculated form the E/B value for the low-energy transitions taking the energy (wavenumber) of the transition as E. Using this Racah parameter, the ligand field splitting, $\Delta_0$, can be calculated.

The nephelauxetic effect
So far, we considered the interelectronic repulsion parameters, B and C (the Racah parameters) as fixed. However, the experimentally determined value for B of the [Cr(NH₃)₆]³⁺ complex is 657 cm⁻¹. For the free Cr³⁺ ion B is 1030 cm⁻¹, giving a 64% reduction of B in going from the free ion to the complex. This finding means that the electron-electron repulsion between d electrons is reduced in the hexammine complex, relative to the free ion. The reduction of interelectronic repulsion is a consequence of delocalization of d-electron density onto the ligands. In MO terms, the distance between the electrons in complexes increases as a result of the formation of larger MO’s upon combination of metal and ligand orbitals. This effect is called nephelauxetic effect from the Greek words for ‘cloud expanding’. The reduction of B is usually reported in terms of the nephelauxetic parameter, $\beta$:

$$\beta = \frac{B(\text{complex})}{B(\text{free ion})}$$

Smaller $\beta$ corresponds to larger reduction of interelectronic repulsion. Different ligands result in different nephelauxetic parameters. Hence, we can write a nephelauxetic series of ligands:

$$F^- > H_2O > Cl^- > CN^- > Br^- > N_3^- > I^-$$

Soft ligands, like the iodo ligand, form more covalent coordinative bonds, resulting in larger delocalization of the metal-d electrons.

Selection rules
We have seen in the previous chapter that some transitions are not allowed, for example transitions where the spin of the electron in changed are spin-forbidden. This does not mean that such a transition will never occur, but that it is less likely and that the intensity (molar absorption coefficient) of such an absorption band is very low. Whether transitions are allowed or forbidden, and to what degree they may be forbidden depends on selection rules:

(i) **spin selection rule**

Electromagnetic radiation usually cannot change the relative orientation of an electron spin. The selection rule states that the overall spin \( S \) of a complex must not change during an electronic transition, hence, \( \Delta S = 0 \).

This selection rule can be relaxed by spin-orbit coupling, i.e., coupling between spin angular momentum and orbital angular momentum. However, spin-forbidden transitions remain generally much weaker than spin-allowed transitions. Spin-orbit coupling is particularly strong for heavy d-metals. In the 3d series, spin-forbidden transitions have \( \varepsilon_{\text{max}} = 1 \text{ L mol}^{-1} \text{ cm}^{-1} \).

In an octahedral \( d^3 \) transition-metal complex, the \( ^2E_g \leftarrow ^4A_{2g} \) transition is spin-forbidden. It is still visible as a very weak absorption band in the UV-visible spectrum (see above).

(ii) **Laporte selection rule**

The Laporte selection rule is particularly applicable for centrosymmetric molecules, i.e., molecules with an inversion centre. Orbitals and states in such molecules can be described with the symmetry labels \( g \) (gerade) and \( u \) (ungerade). Laporte-allowed transitions are accompanied with a change of parity (\( g \) and \( u \)); this means, transitions from a \( g \)-state to a \( u \)-state and vice versa are Laporte-allowed and transitions from a \( g \)-to a \( g \)-state and from a \( u \)-to a \( u \)-state are Laporte-forbidden. All d orbitals are gerade (have \( g \) symmetry). Therefore, d-d transitions, e.g., \( ^4T_{2g} \leftarrow ^4A_{2g} \) in an octahedral \( d^3 \) complex, are Laporte-forbidden.

The Laporte selection rule is relaxed by (a) deviation of perfect centrosymmetric symmetry due to ligands of less symmetry or chelate ligands and (b) asymmetric vibrations. While d orbitals are always centrosymmetric by themselves, for a non-centrosymmetric ligand field the Laporte selection rule is strictly not applicable anymore. As a consequence, Laporte-forbidden d-d transitions have \( \varepsilon_{\text{max}} = 20 \text{ to } 100 \text{ L mol}^{-1} \text{ cm}^{-1} \), while Laporte-allowed d-d transitions have \( \varepsilon_{\text{max}} = \text{ca. } 500 \text{ L mol}^{-1} \text{ cm}^{-1} \).

(iii) **Symmetry-allowed transitions**

Transitions which are not governed by symmetry restrictions (e.g. Laporte rule) have much larger intensities in the electronic absorption spectra. Such transitions are usually charge transfer band that give rise to intense colorations.

### Intensities of spectroscopic bands in 3d complexes

<table>
<thead>
<tr>
<th>Band type</th>
<th>( \varepsilon_{\text{max}} / \text{L mol}^{-1} \text{ cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin-forbidden</td>
<td>(&lt;1)</td>
</tr>
<tr>
<td>Laporte-forbidden d-d</td>
<td>20-100</td>
</tr>
<tr>
<td>Larport-allowed d-d</td>
<td>ca. 500</td>
</tr>
<tr>
<td>Symmetry-allowed (e.g. CT)</td>
<td>1000 – 50 000</td>
</tr>
</tbody>
</table>