

Electronic spectra from transition metal ions and complexes are observed in the visible and UV regions. Absorption spectra show the particular wavelengths of light absorbed, that is the particular amount of energy required to promote an electron from one energy level to a higher level, whilst emission spectra show the energy emitted when the electron falls back from the excited level to a lower level. Transitions involving the outer shell of electrons are generally observed in the wavenumber region  $100\,000\text{ cm}^{-1}$  to  $10\,000\text{ cm}^{-1}$ , but most spectra are measured in the  $50\,000\text{--}10\,000\text{ cm}^{-1}$  region (200–1000 nm). The interpretation of spectra provides a most useful tool for the description and understanding of the energy levels present.

### ENERGY LEVELS IN AN ATOM

The energy levels in an atom are described in Chapter 1 in terms of four quantum numbers:

1.  $n$  the principal quantum number which may have values 1, 2, 3, 4... corresponding to the first, second, third or fourth shell of electrons around the nucleus.
2.  $l$  the subsidiary quantum number, which may have values 0, 1, 2... ( $n - 1$ ), and describes the orbital angular momentum or shape of the orbital. Thus

$n = 1$	$l = 0$	spherical $s$ orbital
$n = 2$	$l = 0$	spherical $s$ orbital
	$l = 1$	dumb-bell shaped $p$ orbital
$n = 3$	$l = 0$	$s$ orbital
	$l = 1$	$p$ orbital
	$l = 2$	$d$ orbital

3.  $m$  the magnetic quantum number may have values from  $+l, (l - 1) \dots 0, \dots -l$ .
4.  $m_s$  the electron spin quantum number which has a value of either  $+\frac{1}{2}$  or  $-\frac{1}{2}$ .



Each of these arrangements corresponds to an electronic arrangement sometimes called a spectroscopic state, which is described by a full term symbol. The letter  $D$  indicates that the  $L$  quantum number has a value of two,  $P$  indicates that  $L = 1$  and  $S$  denotes a value of  $L = 0$  as described previously. The lower right hand subscript denotes the value of the total quantum number  $J$ , and the upper left superscript indicates the multiplicity, which has the value of  $2S + 1$  (where  $S$  is the resultant spin quantum number). The relation between the number of unpaired electrons, the resultant spin quantum number  $S$ , and the multiplicity is given in Table 32.1.

Table 32.1

Unpaired electrons	$S$	Multiplicity	Name of state
0	0	1	Singlet
1	$\frac{1}{2}$	2	Doublet
2	1	3	Triplet
3	$1\frac{1}{2}$	4	Quartet
4	2	5	Quintet

$m$   
 $S$   
 $J$   
 $S = \text{state}$   
 $J = \text{resultant angular quantum no.}$   
 $m = \text{multiplicity}$   
 $= 2S + 1$   
 $S = \text{resultant spin quantum no.}$

(Thus the symbol  $^3D_2$  (pronounced triplet  $D$  two) indicates a  $D$  state, hence  $L = 2$ ; the multiplicity is three, hence  $S = 1$  and the number of unpaired electrons is 2; and the total quantum number  $J = 2$ .)

(All of the spectroscopic terms derived above for a  $p^2$  configuration would occur for an excited state of carbon  $1s^2, 2s^2, 2p^1, 3p^1$ . However, in the ground state of the atom  $1s^2, 2s^2, 2p^2$  the number of states is limited by the Pauli exclusion principle since no two electrons in the same atom can have all four quantum numbers the same. In the ground state configuration, the two  $p$  electrons both have the same values of  $n = 2$  and  $l = 1$  so they must differ in at least one of the remaining quantum numbers  $m$  or  $m_s$ . This restriction reduces the number of terms from  $^3D, ^3P, ^3S, ^1D, ^1P$  and  $^1S$  to  $^1D, ^3P$  and  $^1S$ .)

This can be shown by writing down only those electronic arrangements of  $m$  and  $m_s$  which do not violate the Pauli exclusion principle. For  $p$  electrons, the subsidiary quantum number  $l = 1$ , and the magnetic quantum number  $m$  may have values from  $+l \rightarrow 0 \rightarrow -l$ , giving in this case values of  $m = +1, 0$  and  $-1$ . There are 15 possible combinations (Table 32.2). The values of  $M_s$  and  $M_L$  (the total spin and total orbital quantum numbers in the  $z$  direction) are obtained by adding the appropriate  $m_s$  and  $m$  values:

$$M_s = \sum m_s$$

$$M_L = \sum m$$

$M_L$  has values from  $+L \dots 0 \dots -L$  (a total of  $2L + 1$  values) and  $M_s$  has values from  $+S \dots 0 \dots -S$  (a total of  $2S + 1$  values)



Table 32.2 Allowed values of  $m$  and  $m_s$  for the  $p^2$  configuration

$m = +1 \ 0 \ -1$			$M_S$	$M_L$	Term symbol
1	↑↓		0	2	$^1D$
2		↑↓	0	-2	$^1D$
3	↑↓		0	0	$\left. \begin{array}{l} ^3P, ^1D, ^1S \end{array} \right\}$
4	↑	↓	0	0	
5	↓	↑	0	0	
6	↑↓		0	1	$\left. \begin{array}{l} ^3P, ^1D \end{array} \right\}$
7	↓↑		0	1	
8		↑↓	0	-1	$\left. \begin{array}{l} ^3P, ^1D \end{array} \right\}$
9		↓↑	0	-1	
10	↑↑		1	1	$^3P$
11	↑	↑	1	0	$^3P$
12		↑↑	1	-1	$^3P$
13	↓↓		-1	1	$^3P$
14	↓	↓	-1	0	$^3P$
15		↓↓	-1	-1	$^3P$

The  $L$  and  $S$  quantum numbers associated with each electronic configuration (and hence the spectroscopic term symbol) can be worked out from the  $M_L$  and  $M_S$  quantum numbers in Table 32.2. First choose the maximum  $M_S$  value, and select the maximum  $M_L$  associated with it. This gives  $M_S = 1$  and  $M_L = 1$  (number 10 in table), and corresponds to a group of terms where  $L = 1$  and  $S = 1$ . Since  $L = 1$ , this must be a  $P$  state, and since  $S = 1$ , the multiplicity  $(2S + 1) = 3$ , so it is in fact a triplet  $P$  state  $^3P$ . Using the equations above:

if  $L = 1$ ,  $M_L$  may have the values  $+1, 0$  and  $-1$

and

if  $S = 1$ ,  $M_S$  may have the values  $+1, 0$  and  $-1$

There are nine combinations of these two terms:

$$M_L = +1 \quad M_S = +1, 0, -1$$

$$M_L = 0 \quad M_S = +1, 0, -1$$

$$M_L = -1 \quad M_S = +1, 0, -1$$

Examination of Table 32.2 shows that 13 of the allowed values could be assigned a  $^3P$  term symbol.

From the unassigned combinations we next pick out the maximum  $M_S$  and  $M_L$ . In this case  $M_S = 0$  and  $M_L = 2$ . From this it is deduced that  $L = 2$  and  $S = 0$ . Since  $L = 2$  this must be a  $D$  state. The value of  $S = 0$  gives a multiplicity of  $2S + 1 = 1$ , so it is a singlet  $D$  state  $^1D$ .

If  $L = 2$ , then  $M_L$  may have values  $+2, +1, 0, -1$  and  $-2$ , and since  $S = 0$ ,  $M_S = 0$ . This gives five combinations of  $M_L$  and  $M_S$ . Examination of



Table 32.2 shows that nine of the allowed values could be assigned a  $1P$  term symbol.

The  $^3P$  and  $^1D$  states account for  $9 + 5 = 14$  combinations, and the remaining one which corresponds to  $M_L = 0$  and  $M_S = 0$ , must correspond to  $L = 0$  and  $S = 0$ . This gives a singlet  $S$  state  $^1S$ . Thus all 15 permissible electronic arrangements are accounted for by the  $^1S$ ,  $^3P$  and  $^1D$  states. Where two or more allowed electronic configurations have the same values for  $M_L$  and  $M_S$  (for example configurations 3, 4 and 5 in Table 32.2), more than one term symbol will describe the arrangement. In these cases a linear combination of the functions should be taken, and it is incorrect to attribute any one term to a particular arrangement.

### DETERMINING THE GROUND STATE TERMS = HUND'S RULES

Once the terms are known, they can be arranged in order of energy, and the ground state term identified by using Hund's rules:

1. The terms are placed in order depending on their multiplicities and hence their  $S$  values. The most stable state has the largest  $S$  value, and stability decreases as  $S$  decreases. The ground state therefore possesses the most unpaired spins because this gives the minimum electrostatic repulsion.
2. For a given value of  $S$ , the state with the highest  $L$  value is the most stable.
3. If there is still ambiguity, for given values of  $S$  and  $L$ , the smallest  $J$  value is the most stable if the subshell is less than half filled, and the biggest  $J$  is most stable if the subshell is more than half filled.

(Hund's rules should not be used to predict the order of excited configurations such as C  $1s^2, 2s^2, 2p^1, 3p^1$ .)

Applying the first rule to the terms arising from  $p^3$  in the ground state of carbon the  $^3P$  state must be the ground state since there is only one triplet state,  $^1D$  and  $^1S$  being singlets. Using the second rule, the  $^1D$  state corresponds to a value of  $L = 2$  and is more stable than the  $^1S$  state where  $L = 0$ . Finally, the triplet  $P$  state has three terms  $^3P_2, ^3P_1$  and  $^3P_0$  so from the third rule  $^3P_0 < ^3P_1 < ^3P_2$ . The experimentally measured energies for the terms arising from the ground state of carbon are shown in Figure 32.9. It can be seen that for a light atom like carbon, the splitting of the  $^3P$  terms because of the  $J$  terms from spin orbit coupling is much smaller than the splitting into  $^1S, ^1D$  and  $^3P$  terms resulting from coupling of  $l$  quantum numbers. For the lighter elements below atomic number 30, the splitting of levels of different  $J$  is small compared with the splitting of levels of different  $L$  (see Figure 32.9); hence Russell-Saunders coupling gives the correct result for the sequence of energy levels or terms for the first row of transition elements. For the heavier elements, the  $J$  splitting is greater than the  $L$  splitting and Russell-Saunders coupling can no longer be used and an alternative form of  $j-j$  coupling is used instead.



## ELECTRONIC SPECTRA OF TRANSITION METAL COMPLEXES

Spectra arise because electrons may be promoted from one energy level to another. Such electronic transitions are of high energy, and in addition much lower energy vibrational and rotational transitions always occur. The vibrational and rotational levels are too close in energy to be resolved into separate absorption bands, but they result in considerable broadening of the electronic absorption bands in  $d-d$  spectra. Band widths are commonly found to be of the order of  $1000-3000 \text{ cm}^{-1}$ .

The spectrum of a coloured solution may be measured quite easily using a spectrophotometer. A beam of monochromatic light obtained using a prism and a narrow slit is passed through the solution and on to a photoelectric cell. The amount of light absorbed at any particular frequency can be read off, or a whole frequency range can be scanned, and the absorbance  $A$  plotted as a graph on a paper chart recorder. The absorbance was formerly called the optical density. If  $I_0$  is the intensity of the original beam of light, and  $I$  the intensity after passing through the solution, then

$$\log \left( \frac{I_0}{I} \right) = A$$

The molar absorption coefficient  $\epsilon$  is usually calculated from the absorbance

$$\epsilon = \frac{A}{cd}$$

where  $c$  is the concentration of the solution in  $\text{mol l}^{-1}$ , and  $l$  is the path length in centimetres. (Cells are commonly 1 cm long.)

Not all of the theoretically possible electronic transitions are actually observed. The position is formalized into a set of selection rules which distinguish between 'allowed' and 'forbidden' transitions. 'Allowed' transitions occur commonly. 'Forbidden' transitions do occur, but much less frequently, and they are consequently of much lower intensity.

Laporte 'orbital' selection rule

$\Delta l = \pm 1$  Laporte allowed

$\Delta l = 0$  Laporte forbidden

Transitions which involve a change in the subsidiary quantum number  $\Delta l = \pm 1$  are 'Laporte allowed' and therefore have a high absorbance. Thus for Ca,  $s^2 \rightarrow s^1 p^1$ ,  $l$  changes by  $+1$  and the molar absorption coefficient  $\epsilon$  is  $5000-10000 \text{ litres per mol per centimetre}$ . In contrast  $d-d$  transitions are 'Laporte forbidden', since the change in  $l = 0$ , but spectra of much lower absorbance are observed ( $\epsilon = 5-10 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) because of



## SPECTRA

**Table 32.7** Molar absorption coefficients for different types of transition

Laporte (orbital)	Spin	Type of spectra	$\epsilon$	Example
Allowed	Allowed*	Charge transfer	10 000	$[\text{TiCl}_6]^{2-}$ <i>3d<sup>2</sup>4s<sup>2</sup></i>
Partly allowed, some <i>p-d</i> mixing	Allowed	<i>d-d</i>	500	$[\text{CoBr}_4]^{2-}$ , $[\text{CoCl}_4]^{2-}$
Forbidden	Allowed	<i>d-d</i>	8-10	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , $[\text{V}(\text{H}_2\text{O})_6]^{3+}$
Partly allowed, some <i>p-d</i> mixing	Forbidden	<i>d-d</i>	4	$[\text{MnBr}_4]^{2-}$ <i>3d<sup>3</sup>4s<sup>2</sup></i>
Forbidden	Forbidden	<i>d-d</i>	0.02	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

slight relaxation in the Laporte rule. When the transition metal ion forms a complex it is surrounded by ligands, and some mixing of *d* and *p* orbitals may occur, in which case transitions are no longer pure *d-d* in nature. Mixing of this kind occurs in complexes which do not possess a centre of symmetry, for example tetrahedral complexes, or asymmetrically substituted octahedral complexes. Thus  $[\text{MnBr}_4]^{2-}$  which is tetrahedral and  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  which is octahedral but non-centrosymmetric are both coloured. Mixing of *p* and *d* orbitals does not occur in octahedral complexes which have a centre of symmetry such as  $[\text{Co}(\text{NH}_3)_6]^{3+}$  or  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ . However, in these cases the metal-ligand bonds vibrate so that the ligands spend an appreciable amount of time out of their centrosymmetric equilibrium position. Thus a very small amount of mixing occurs, and low-intensity spectra are observed. Thus Laporte allowed transitions are very intense, whilst Laporte forbidden transitions vary from weak intensity if the complex is non-centrosymmetric to very weak if it is centrosymmetric (Table 32.7).

**Spin selection rule**  $\Delta S = 0$  *no change in e<sup>-</sup> spin but exceptions in some cases*

During transitions between energy levels, an electron does not change its spin, that is  $\Delta S = 0$ . There are fewer exceptions than for the Laporte selection rule. Thus in the case of  $\text{Mn}^{2+}$  in a weak octahedral field such as  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  the *d-d* transitions are 'spin forbidden' because each of the *d* orbitals is singly occupied. Many  $\text{Mn}^{2+}$  compounds are off white or pale fleshy coloured, but the intensity is only about one hundredth of that for a