

Chapter 18

Interpretation of Spectra

In the previous chapter the topic of spectral studies on coordination compounds was introduced only briefly in connection with ligand field theory, and some of the attendant problems that are associated with interpreting the spectra were described. In this chapter, a more complete description will be presented of the process of interpreting spectra of complexes. It is from the analysis of spectra that we obtain information about energies of spectroscopic states in metal ions and the effects produced by different ligands on the d orbitals. However, it is first necessary to know what spectroscopic states are appropriate for various metal ions. The analysis then progresses to how the spectroscopic states for the metal ions are affected by the presence of the ligands and how ligand field parameters are determined for spectral data.

18.1 SPLITTING OF SPECTROSCOPIC STATES

As we have seen, an understanding of spin-orbit coupling is necessary to determine the spectroscopic states that exist for various electron configurations, d^n (see Section 2.6). Because they will be needed frequently in this chapter, the spectroscopic states that result from spin-orbit coupling in d^n ions that have degenerate d orbitals are summarized in Table 18.1.

The spectroscopic states shown in Table 18.1 are those that arise for the so-called *free* or *gaseous* ion. When a metal ion is surrounded by ligands in a coordination compound, those ligands generate an electrostatic field that removes the degeneracy of the d orbitals. The result is that e_g and t_{2g} subsets of orbitals are produced. Because the d orbitals are no longer degenerate, spin-orbit coupling is altered so that the states given in Table 18.1 no longer apply to a metal ion *in a complex*. However, just as the d orbitals are split in terms of their energies, the *spectroscopic states* are split in the ligand field. The spectroscopic states are split into components that have the same multiplicity as the free ion states from which they arise. A single electron in a d orbital gives rise to a 2D term for the gaseous ion, but in an octahedral field the electron will reside in a t_{2g} orbital, and the spectroscopic state for the t_{2g}^1 configuration is $^2T_{2g}$. If the electron were excited to an e_g orbital, the spectroscopic state would be 2E_g . Thus, transitions between $^2T_{2g}$ and 2E_g states would not be spin forbidden because both states are doublets. Note that lowercase letters are used to describe *orbitals*, whereas capital letters describe *spectroscopic states*.

Table 18.1 Spectroscopic States for Gaseous Ions Having d^n Electron Configurations^a.

Ion	Spectroscopic states
d^1, d^9	2D
d^2, d^8	$^3F, ^3P, ^1G, ^1D, ^1S$
d^3, d^7	$^4F, ^4P, ^2H, ^2G, ^2F, ^2D, ^2P$
d^4, d^6	$^5D, ^3H, ^3G, ^2^3F, ^3D, ^2^3P, ^1I, ^2^1G, ^1F, ^2^1D, ^2^1S$
d^5	$^6S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2G, ^2F, ^3^2G, ^3^2D, ^2P, ^2S$

^a $^2^3F$ means two distinct 3F terms arise, etc.

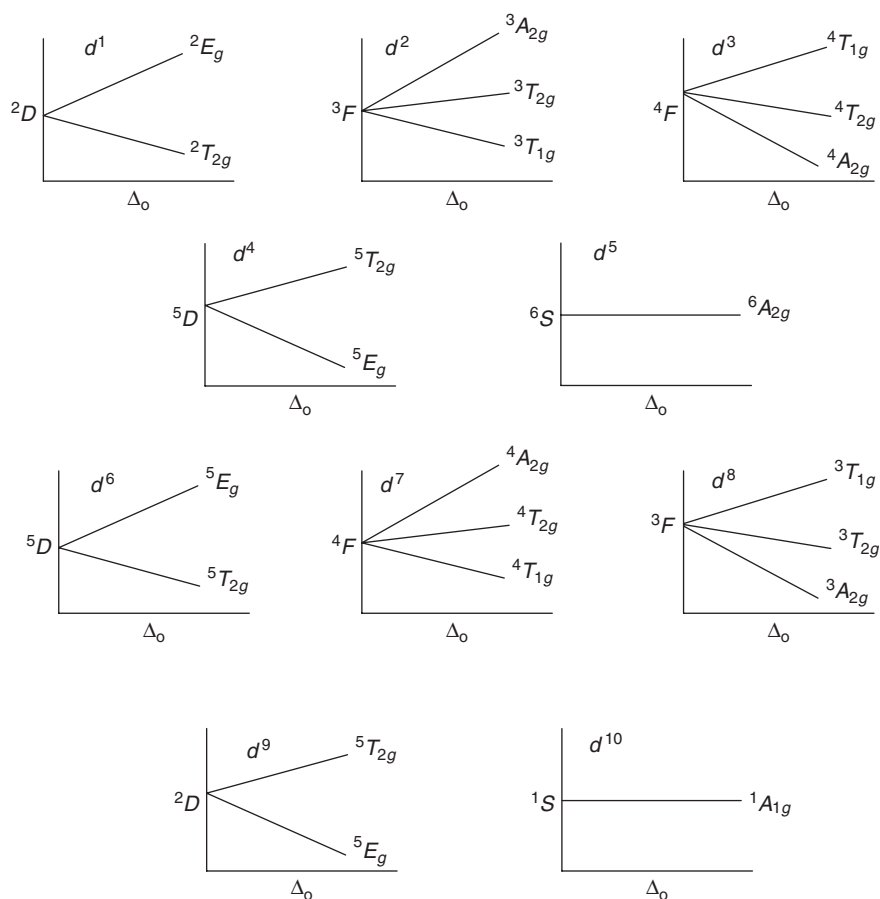
Table 18.2 Splitting of Spectroscopic States in a Ligand Field^a.

Gaseous ion spectroscopic state	Components in an octahedral field	Total degeneracy
S	A_{1g}	1
P	T_{1g}	3
D	$E_g + T_{2g}$	5
F	$A_{2g} + T_{1g} + T_{2g}$	7
G	$A_{1g} + E_g + T_{1g} + T_{2g}$	9
H	$E_g + 2 T_{1g} + T_{2g}$	11
I	$A_{1g} + A_{2g} + E_g + T_{1g} + 2 T_{2g}$	13

^aLigand field states have the same multiplicity as the spectroscopic state from which they arise.

A gaseous ion having a d^2 configuration gives rise to a 3F ground state as a result of spin-orbit coupling. Although they will not be derived, in an octahedral ligand field the t_{2g}^2 configuration gives three different spectroscopic states that are designated as $^3A_{2g}$, $^3T_{1g}$, and $^3T_{2g}$. These states are often referred to as *ligand field states*. The energies of the three states depend on the strength of the ligand field, but the relationship is not a simple one. The larger the ligand field splitting, the greater the difference between the ligand field states of the metal. For the time being, we will assume that the function is linear, but it will be necessary to refine this view later. Table 18.2 shows a summary of the states that result from splitting the gaseous state terms of metal ions in an octahedral field produced by six ligands.

Figure 18.1 shows the approximate energies of the ligand field spectroscopic states as a function of the field strength for all d^n ions. In the drawings, the states are assumed to be linear functions of Δ_o , but this is not correct over a wide range of field strength. For the d^1 ion, the 2D ground state is split into $^2T_{2g}$ and 2E_g states in the ligand field. As the field strength, Δ_o , increases, a center of energy is maintained



■ FIGURE 18.1 The splitting patterns for ground-state D and F terms in an octahedral field.

for the energies of the ${}^2T_{2g}$ and 2E_g states in exactly the same way that a center of energy is maintained by the t_{2g} and e_g orbital subsets. Therefore, in order to give no *net* change in energy, the slope of the line for the 2E_g state is $+(3/5)\Delta_o$, whereas that of the ${}^2T_{2g}$ state is $-(2/5)\Delta_o$.

Note that the ground-state terms for d^n ions (except for d^5) are all either D or F terms and that the state splitting occurs so that the center of energy is maintained. For the ligand field states that are produced by splitting the 3F term (which results from a d^2 configuration), the center of energy is also preserved even though there are three states in the ligand field. By looking at Table 18.2, it can be seen that all of the states that arise from splitting the D and F ground states for the gaseous ions have T , E , or A designations. When describing the splitting of the d orbitals in an octahedral field (see Chapter 17), the “ t ” orbitals were seen to be triply degenerate, whereas the “ e ” orbitals were doubly degenerate. We can consider the *spectroscopic states* in the ligand field to have the same degeneracies as the *orbitals*,

which makes it possible to preserve the center of energy. For example, the lines representing the ${}^2T_{2g}$ and 2E_g states have slopes of $-(2/5)\Delta_o$ and $+(3/5)\Delta_o$, respectively. Taking into account the degeneracies of the states, the energy of *sum* of the two subsets is

$$3[-(2/5)\Delta_o] + 2[+(3/5)\Delta_o] = 0$$

This result shows that even though the two states have energies that depend on the magnitude of the ligand field splitting, the *overall* energy change is 0. For purposes of determining the center of energy, an “A” state can be considered as being singly degenerate. When the 3F state corresponding to the d^2 configuration is split into ${}^3A_{2g}$, ${}^3T_{1g}$, and ${}^3T_{2g}$ components, the slopes of the lines must be such that the overall energy change is 0. Thus, the slopes of the lines and the multiplicities are related by

$$\underset{(T)}{3[-(3/5)\Delta_o]} + \underset{(T)}{3[+(1/5)\Delta_o]} + \underset{(A)}{1[+(6/5)\Delta_o]} = 0$$

which shows that the three ligand field states yield the energy of the 3F gaseous ion state as the center of energy.

From the diagrams shown in Figure 18.1, it can be seen that the splitting pattern for a d^4 ion is like that for d^1 ion except for being inverted and the states having the appropriate multiplicities. Likewise, the splitting pattern for a d^3 ion is like that for d^2 except for being inverted and the multiplicity being different. The reason for this similarity is the “electron-hole” behavior that is seen when the spectroscopic states for configurations such as p^1 and p^5 are considered. Both give rise to a 2P spectroscopic state, and only the J values are different. It should be apparent from the diagrams shown in Figure 18.1 that the ligand field splitting pattern is the same for d^1 and d^6 , d^2 and d^7 , and so forth, except for the multiplicity. In fact, it is easy to see that this will be true for any d^n and d^{5+n} configurations. It is also apparent that the singly degenerate “A” states that arise from the S states for d^5 and d^{10} configurations are not split in the ligand field. All of the ligand field components and their energies in an octahedral field are summarized in Table 18.3.

When a transition metal ion is surrounded by ligands that generate a tetrahedral field, the splitting pattern of the d orbitals is inverted when compared to that in an octahedral field. As a result, the e orbitals lie lower than the t_2 set (note that there is no subscript “g” because a tetrahedron does not have a center of symmetry). A further consequence is that the energies of the ligand field spectroscopic states shown in Table 18.3 are also reversed in order compared to their order in octahedral fields. For example, in an octahedral field, the d^2 ion gives the states (in order of increasing energy) ${}^3T_{1g}$, ${}^3T_{2g}$, and ${}^3A_{2g}$ as shown in Table 18.3. In a tetrahedral field, the order of increasing energy for the states arising from a d^2 ion would be 3A_2 , 3T_2 , and 3T_1 .

For a specific d^n electron configuration, there are usually several spectroscopic states that correspond to energies above the ground state term. However, they may not have the same *multiplicity* as the ground state. When the spectroscopic state for the free ion becomes split in an octahedral field, each ligand field component has the same multiplicity as the ground state (see Table 18.3). *Transitions between spectroscopic states having different multiplicities are spin forbidden.* Because the T_{2g} and E_g spectroscopic

Table 18.3 Energies of Octahedral Ligand Field States in Terms of Δ_o .

Ion	State	Octahedral field states	Energies in octahedral field
d^1	2D	${}^2T_{2g} + {}^2E_g$	$-(2/5)\Delta_o + (3/5)\Delta_o$
d^2	3F	${}^3T_{1g} + {}^3T_{2g} + {}^3A_{2g}$	$-(3/5)\Delta_o + (1/5)\Delta_o + (6/5)\Delta_o$
d^3	4F	${}^4A_{2g} + {}^4T_{2g} + {}^4T_{1g}$	$-(6/5)\Delta_o - (1/5)\Delta_o + (3/5)\Delta_o$
d^4	5D	${}^5E_g + {}^5T_{2g}$	$-(3/5)\Delta_o + (2/5)\Delta_o$
d^5	6S	${}^6A_{1g}$	0
d^6	5D	${}^5T_{2g} + {}^5E_g$	$-(2/5)\Delta_o + (3/5)\Delta_o$
d^7	4F	${}^4T_{1g} + {}^4T_{2g} + {}^2A_{2g}$	$-(3/5)\Delta_o + (1/5)\Delta_o + (6/5)\Delta_o$
d^8	3F	${}^3A_{2g} + {}^3T_{2g} + {}^3T_{1g}$	$-(6/5)\Delta_o - (1/5)\Delta_o + (3/5)\Delta_o$
d^9	2D	${}^2E_g + {}^2T_{2g}$	$-(3/5)\Delta_o + (2/5)\Delta_o$
d^{10}	1S	1A_g	0

Ligand field state of lowest energy given first, and energies are listed in the same order.

states in a ligand field have the same multiplicity as the ground states from which they arise, it can be seen that the $T_{2g} \rightarrow E_g$ transition is the only spin-allowed transition for ions that have D ground states. In cases where the ground state is an F term, there is a P state of higher energy that has the same multiplicity. That state gives a T_{1g} state (designated as $T_{1g}(P)$) having the same multiplicity as the ground-state T_{1g} term. Accordingly, spectroscopic transitions are possible from the ground state in the ligand field to the T state that arises from the P term. Therefore, for ions having T and A ground states, the spin-allowed transitions in an octahedral field are as follows:

Octahedral Field			
For T ground states:		For A ground states:	
ν_1	$T_{1g} \rightarrow T_{2g}$	ν_1	$A_{2g} \rightarrow T_{2g}$
ν_2	$T_{1g} \rightarrow A_{2g}$	ν_2	$A_{2g} \rightarrow T_{1g}$
ν_3	$T_{1g} \rightarrow T_{1g}(P)$	ν_3	$A_{2g} \rightarrow T_{1g}(P)$

The spin-allowed transitions for ions having T and A ground states in tetrahedral fields are as follows:

Tetrahedral Field			
For T ground states:		For A ground states:	
ν_1	$T_1 \rightarrow T_2$	ν_1	$A_2 \rightarrow T_2$
ν_2	$T_1 \rightarrow A_2$	ν_2	$A_2 \rightarrow T_1$
ν_3	$T_1 \rightarrow T_1(P)$	ν_3	$A_2 \rightarrow T_1(P)$

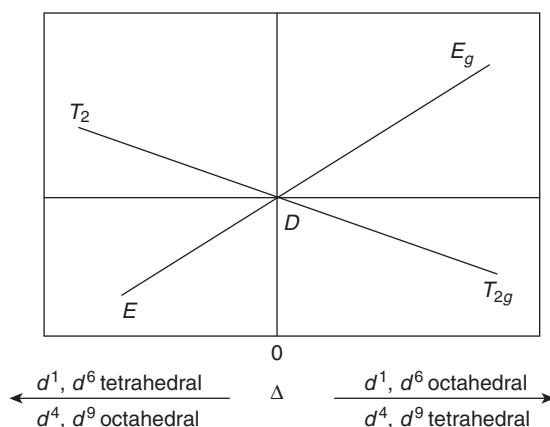
As shown, for both octahedral and tetrahedral complexes, *three* absorption bands are expected. Many complexes do, in fact, have absorption spectra that show three bands. However, charge transfer absorption makes it impossible in some cases to see all three bands, so spectral analysis must often be based on only one or two observed bands.

18.2 ORGEL DIAGRAMS

The splitting patterns of the spectroscopic states that are shown in Table 18.3 can be reduced to graphical presentation in two diagrams. These diagrams were developed by L. E. Orgel, and they have since become known as *Orgel diagrams*. Figure 18.2 shows the Orgel diagram that is applicable for ions that give *D* ground states.

In an Orgel diagram, energy is represented as the vertical dimension, and the vertical line in the center of the diagram represents the gaseous ion where there is no ligand field ($\Delta = 0$). Note that the right-hand side of the diagram applies to d^1 and d^6 ions in *octahedral* fields or d^4 and d^9 ions in *tetrahedral* fields. This situation arises because the ligand field states are inverted for the two cases, and the electron-hole formalism also causes the orbitals to be inverted. As a result, the ligand field states are the same for a d^1 ion in an octahedral field as they are for a d^4 ion in a tetrahedral field.

The left-hand side of the Orgel diagram shown in Figure 18.2 applies to d^4 and d^9 ions in *octahedral* fields or to d^1 and d^6 ions in *tetrahedral* fields. Note that the *g* subscripts have been deleted on the left-hand side of the diagram. Although *both* sides of the diagram can apply to tetrahedral or octahedral complexes in some cases, it is customary to show the *g* on one side of the diagram but not on the other. This does *not* mean that one side of the diagram applies to tetrahedral complexes and the other to octahedral complexes. *Both* sides apply to *both* types of complexes. It should also be remembered that the magnitude of the splitting is quite different for the two types of complexes because Δ_t is approximately $(4/9)\Delta_o$.

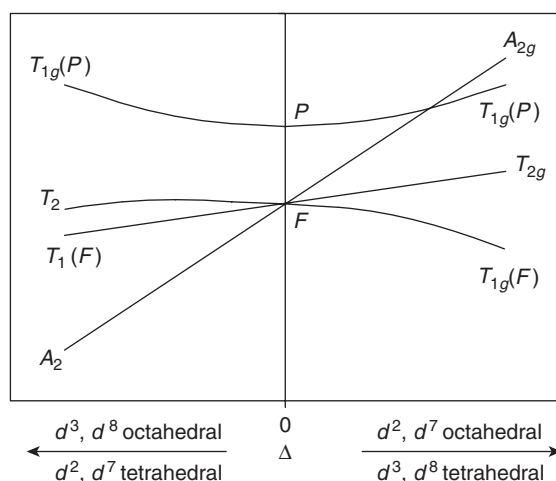


■ **FIGURE 18.2** An Orgel diagram for metal ions having *D* spectroscopic ground states. The multiplicity of the *D* state is not specified because it is determined by the number of electrons in the *d* orbitals of the metal ion.

The Orgel diagram that applies to ions that have F spectroscopic ground states is shown in Figure 18.3. This diagram also includes the P state, which has higher energy because in an octahedral ligand field that state becomes a T_{1g} state (T_1 in a tetrahedral field) that has the same multiplicity as the ground state. Therefore, spectral transitions are spin-allowed between the ground state and the excited state arising from the P state.

For octahedral complexes containing d^2 and d^7 ions, the ground state is T_{1g} , which we will designate as $T_{1g}(F)$ to show that it arises from the F ground state of the free ion rather than the P state. Note that the lines representing the $T_{1g}(F)$ and $T_{1g}(P)$ in the Orgel diagram are curved, with the curvature increasing as the magnitude of Δ increases. These states represent quantum mechanical states that have identical designations, and it is a characteristic of such states that they cannot represent the same energy. Therefore, these states interact strongly and repel each other. This phenomenon is often referred to as the *noncrossing rule*.

As has been stated, the multiplicity of the ligand field states is the same as the multiplicity of the ground-state term from which they arise. Therefore, a d^2 ion gives a 3F ground state that is split into the triplet $^3T_{1g}$, $^3T_{2g}$, and $^3A_{2g}$ states in an octahedral field. From the diagram, we can see that the possible spectral transitions are those from the $^3T_{1g}$ state to the three ligand field states of higher energy. On this basis, the Orgel diagram allows us to predict that three bands should be observed in the spectrum for a d^2 ion in an octahedral field. Frequently, the spectra of such complexes contain fewer than three bands, and there may be some ambiguity in assigning the bands to specific transitions. One reason why the assignment of some bands may be uncertain is that there may be charge transfer bands that occur in the same region of the spectrum (see Section 18.8). These bands are often intense, and they may mask the so-called $d-d$ transitions. Another factor that may complicate band assignment is that some of the bands are quite weak so they may be difficult to identify in the presence of other strong



■ **FIGURE 18.3** An Orgel diagram for metal ions having F spectroscopic ground states. The multiplicity of the F state is not specified. The P state having the same multiplicity as the ground state is also shown.

bands. The point is that for many complexes, matching the observed bands in the spectrum is not necessarily a simple, straightforward matter. Moreover, the Orgel diagrams are only qualitative, so we need a more quantitative method if we are to be able to perform calculations to obtain Δ and other ligand field parameters.

In the previous discussion, only the ligand field states that arise from the free ion ground state and excited states having the same multiplicity were considered. However, other spectroscopic terms exist for the free ion (see Table 18.1). For example, if a d^2 ion is considered, the ground state is 3F , but the other states are 3P , 1G , 1D , and 1S . When spectral transitions are considered, only the 3F and 3P states concern us. We do need to understand that because of the noncrossing rule, some of the energies of the states will deviate from linear functions of Δ . A d^2 electron configuration corresponds to Ti^{2+} , V^{3+} , and Cr^{4+} ions, but even for the free ions the spectroscopic states have different energies. For the free ions, the energies of the spectroscopic states are shown in Table 18.4.

The energies shown in Table 18.4 make it clear that a *complete* energy level diagram for a d^2 ion in an octahedral ligand field will be dependent on the specific metal ion being considered. Furthermore, the energies of states that have identical designations will obey the noncrossing rule so that they will vary in a nonlinear way with the field strength.

18.3 RACAH PARAMETERS AND QUANTITATIVE METHODS

From the preceding discussion, it is clear that we should expect a maximum of three spin-allowed transitions regardless of the d^n configuration of the metal ion. Because of spin-orbit coupling, the interelectronic repulsion is different for the various spectroscopic states in the ligand field. The ability of the electrons to be permuted among a set of degenerate orbitals and interelectron repulsion are both important considerations (see Chapter 2). By use of quantum-mechanical procedures, these energies can be expressed as integrals. One of the methods makes use of integrals that are known as the Racah parameters. There are three parameters, A , B , and C , but if only *differences* in energies are considered, the parameter A is not needed. The parameters B and C are related to the coulombic and exchange

Table 18.4 Energies of Spectroscopic Terms for Gaseous d^2 Ions.

Term	Spectroscopic state energies, cm^{-1}		
	Ti^{2+}	V^{3+}	Cr^{4+}
3F	0	0	0
1D	8,473	10,540	13,200
3P	10,420	12,925	15,500
1G	14,398	17,967	22,000
$349.8\ cm^{-1} = 1\ kcal\ mol^{-1} = 4.184\ kJ\ mol^{-1}$.			

energies, respectively, that are a result of electron pairing. For an ion that has a d^2 configuration, it can be shown that the 3F state has an energy that can be expressed as $(A - 8B)$, whereas that of the 3P state is $(A + 7B)$. Accordingly, the difference in energy between the two states can be expressed in terms of B only because the parameter A cancels. When states having a different multiplicity than the ground state are considered, the difference in energy is expressed in terms of both B and C .

Although the energies of the spectroscopic states of first row d^2 ions were shown in Table 18.4, compilations exist for all gaseous metal ions. The standard reference is a series of volumes published by the National Institute of Standards and Technology (C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular 467, Vol. I, II, and III, 1949). Table 18.5 shows the energies for the spectroscopic states in d^n ions in terms of the Racah B and C parameters.

For the cases where the ground state of a free ion is an F term, the difference in energy between the ground state and the first excited state having the same multiplicity (a P term) is defined as $15B$, which is $(A + 7B) - (A - 8B)$. This is analogous to the case of splitting of d orbitals in a ligand field where the difference in energy is represented as $10Dq$. The parameter B is simply a unit of energy whose numerical value depends on the particular ion considered. For d^2 and d^8 ions,

$$15B = {}^3F \rightarrow {}^3P \quad (18.1)$$

where ${}^3F \rightarrow {}^3P$ means the energy difference between the two states. For d^3 and d^7 ions,

$$15B = {}^4F \rightarrow {}^4P \quad (18.2)$$

It can be seen from Table 18.5 that all excited spectroscopic states having a multiplicity that is *different* from the ground state have energies that are expressed in terms of both B and C . As we have seen from the previous discussion, spin-allowed transitions occur only between states having the *same* multiplicity. Therefore, in the analysis of spectra of complexes only B must be determined. It is found for some complexes that $C \approx 4B$, and this approximation is adequate for many uses.

The discussion so far has concerned the Racah parameters for *gaseous* ions. For example, the d^2 ion Ti^{2+} has a 3P state that lies $10,420 \text{ cm}^{-1}$ above the 3F ground state, so $15B = 10,420 \text{ cm}^{-1}$ and B is 695 cm^{-1} for this ion. Using this value for B results in an approximate value of 2780 cm^{-1} as the value of C for

Table 18.5 Energies of Spectroscopic States for Free Ions in Terms of Racah Parameters.

d^2, d^8		d^3, d^7		d^5	
1S	$22B + 7C$	2H	$9B + 3C$	4F	$22B + 7C$
1G	$12B + 2C$	2P	$9B + 3C$	4D	$17B + 5C$
3P	$15B$	4P	$15B$	4P	$7B + 7C$
1D	$5B + 2C$	2G	$4B + 3C$	4G	$10B + 5C$
3F	0	4F	0	6S	0

the gaseous ion. For many complexes of +2 ions of first-row transition metals, B is in the range of 700 to 1000 cm^{-1} and C is approximately 2500 to 4000 cm^{-1} . For +3 ions of first-row metals, B is normally in the range 850 to 1200 cm^{-1} . For second- and third-row metal ions, the value of B is usually only about 600 to 800 cm^{-1} because interelectron repulsion is smaller for the larger ions.

When *complexes* of the metal ions are considered, the situation is considerably more complicated. The differences between energy states in the ligand field are related not only to the Racah parameters, but also to the magnitude of Δ (or Dq). As a result, the energies for the three spectral bands must be expressed in terms of both Dq and the Racah parameters. Because the observed spectral bands represent differences in energies between states having the same multiplicity, only the Racah B parameter is necessary. Even so, B is not a constant because it varies with the magnitude of the effect of the ligands on the d orbitals of the metal (the ligand field splitting). Analysis of the spectrum for a complex involves determining the value of Dq and B for *that complex*. Of course $\Delta = 10Dq$, and we have used Δ to describe orbital splitting more frequently up to this point. When dealing with spectral analysis, the discussion can also be presented with regard to Dq .

For metal ions having d^2 , d^3 , d^7 , and d^8 configurations, the ground state is an F state, but there is an excited P state that has the same multiplicity. For d^2 and d^7 ions in an *octahedral* field, the spectroscopic states are the same (except for the multiplicity) as they are for d^3 and d^8 ions in *tetrahedral* fields. Therefore, the expected spectral transitions will also be the same for the two types of complexes. The three spectral bands are assigned as follows ($T_{1g}(F)$ means the T_{1g} state arising from the F spectroscopic state):

$$\begin{aligned}\nu_1 T_{1g} & (F) \rightarrow T_{2g} \\ \nu_2 T_{1g} & (F) \rightarrow A_{2g} \\ \nu_3 T_{1g} & (F) \rightarrow T_{1g}(P)\end{aligned}$$

For octahedral complexes of d^2 and d^7 metal ions (or d^3 and d^8 ions in tetrahedral complexes), the energies corresponding to ν_1 , ν_2 , and ν_3 can be shown to be

$$E(\nu_1) = 5Dq - 7.5B + (225B^2 + 100Dq^2 + 180DqB)^{1/2} \quad (18.3)$$

$$E(\nu_2) = 15Dq - 7.5B + (225B^2 + 100Dq^2 + 180DqB)^{1/2} \quad (18.4)$$

$$E(\nu_3) = (225B^2 + 100Dq^2 + 180DqB)^{1/2} \quad (18.5)$$

The third band corresponds to the difference in energy between the $T_{1g}(F)$ and $T_{1g}(P)$ states that arises from splitting the F and P states. In the limit where $Dq = 0$ (as it is for a gaseous ion), the energy reduces to $(225B^2)^{1/2}$, which is $15B$. That is precisely the difference in energy between the F and P spectroscopic states.

The corresponding energies for the spectral transitions that occur for d^3 and d^8 ions in octahedral fields (or d^2 and d^7 ions in tetrahedral fields) are as follows:

$$E(\nu_1) = 10Dq \quad (18.6)$$

$$E(\nu_2) = 15Dq + 7.5B - 1/2(225B^2 + 100Dq^2 - 180DqB)^{1/2} \quad (18.7)$$

$$E(\nu_3) = 15Dq + 7.5B + 1/2(225B^2 + 100Dq^2 - 180DqB)^{1/2} \quad (18.8)$$

For these complexes, the first band corresponds directly to $10Dq$. If all three of the spectral bands are observed in the spectrum, it can be shown that

$$\nu_3 + \nu_2 - 3\nu_1 = 15B \quad (18.9)$$

The foregoing discussion applies to complexes that are weak-field cases. Spectral analysis for strong-field cases is somewhat different and will not be discussed here. For complete analysis of the spectra of strong-field complexes, see the book by A. B. P. Lever, *Inorganic Electronic Spectroscopy*, listed in the references at the end of this chapter.

It is possible to solve Eqs. (18.3) through (18.8) to obtain Dq and B for situations where two or more of the spectral bands can be identified. The resulting equations giving Dq and B as functions of frequencies of the spectral bands are shown in Table 18.6. Although the equations shown in Table 18.6 can be used to evaluate Dq and B , the positions of at least two spectral bands must be known and correctly assigned. Historically, other approaches to evaluating ligand field parameters have been developed, and they are still useful. In the remainder of this chapter, some of the other approaches will be described. In many cases, unambiguous interpretations of spectra are difficult because of factors such as charge transfer bands, absorptions by ligands, and lack of ideal symmetry caused by Jahn-Teller distortion (see Chapter 17). The discussion that follows will amplify the introduction presented so far, but for complete details of spectral interpretation, consult the reference works by Ballhausen, Jørgensen, and Lever listed in the references.

18.4 THE NEPHELAUXETIC EFFECT

When a metal ion is surrounded by ligands in a complex, the ligand orbitals being directed toward the metal ion produce changes in the total electron environment of the metal ion. One consequence is that the energy required to force pairing of electrons is altered. Although the energy necessary to force electron pairing in the gaseous ion can be obtained from tabulated energy values for the appropriate spectroscopic states, those values are not applicable to a metal ion that is contained in a complex. When ligands bind to a metal ion, the orbitals on the metal ion are "smeared out" over a larger region of space. The molecular orbital terminology for this situation is that the electrons become more delocalized in the complex than they are in the free ion. The expansion of the electron cloud is known as the *nephelauxetic effect*.

As a result of the nephelauxetic effect, the energy required to force pairing of electrons in the metal ion is somewhat smaller than it is for the free ion. When ligands such as CN^- are present, the nephelauxetic effect is quite large owing to the ability of the ligands to π bond to the metal as a result of back donation. As discussed in Chapter 17, antibonding orbitals on the CN^- have appropriate symmetry

Table 18.6 Equations for Calculating Dq and B from Spectra.	
Spectral bands known	Equations
Ions having "T" ground states	
ν_1, ν_2, ν_3	$Dq = (\nu_2 - \nu_1)/10$ $B = (\nu_2 + \nu_3 - 3\nu_1)/15$
ν_1, ν_2	$Dq = (\nu_2 - \nu_1)/10$ $B = \nu_1(\nu_2 - 2\nu_1)/(12\nu_2 - 27\nu_1)$
ν_1, ν_3	$Dq = [(5\nu_3^2 - (\nu_3 - 2\nu_1)^2)^{1/2} - 2(\nu_3 - 2\nu_1)]/40$ $B = (\nu_3 - 2\nu_1 + 10Dq)/15$
ν_2, ν_3	$Dq = [(85\nu_3^2 - 4(\nu_3 - 2\nu_2)^2)^{1/2} - 9(\nu_3 - 2\nu_2)]/340$ $B = (\nu_3 - 2\nu_2 + 30Dq)/15$
Ions having "A" ground states	
ν_1, ν_2, ν_3	$Dq = \nu_1/10$ $B = (\nu_2 + \nu_3 - 3\nu_1)/15$
ν_1, ν_2	$Dq = \nu_1/10$ $B = (\nu_2 - 2\nu_1)(\nu_2 - \nu_1)/(15\nu_2 - 27\nu_1)$
ν_1, ν_3	$Dq = \nu_1/10$ $B = (\nu_3 - 2\nu_1)(\nu_3 - \nu_1)/(15\nu_3 - 27\nu_1)$
ν_2, ν_3	$Dq = [(9\nu_2 + \nu_3) - (85(\nu_2 - \nu_3)^2 - 4(\nu_2 + \nu_3)^2)^{1/2}]/340$ $B = (\nu_2 + \nu_3 - 30Dq)/15$
Adapted from Y. Dou, J. Chem. Educ. 1990, 67, 134.	

to form π bonds to nonbonding d orbitals on the metal ion. As a result, the Racah parameters B and C for a metal ion are variables whose exact values depend on the nature of the ligands attached to the ion. The change in B from the free ion value is expressed as the *nephelauxetic ratio*, β , which is given by

$$\beta = \frac{B'}{B} \quad (18.10)$$

where B is the Racah parameter for the free metal ion and B' is the same parameter for the metal ion in the complex. C. K. Jørgensen devised a relationship to express the nephelauxetic effect as the product of a parameter characteristic of the ligand, h , and another characteristic of the metal ion, k . The mathematical relationship is

$$(1 - \beta) = hk \quad (18.11)$$

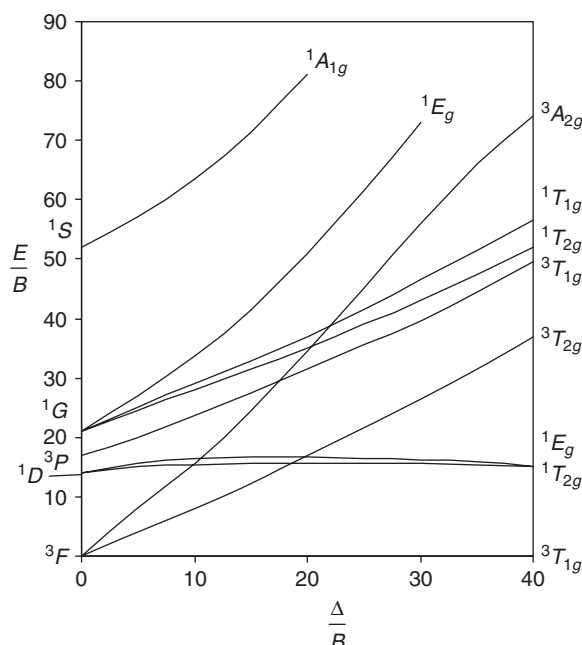
Table 18.7 Nephelauxetic Parameters for Metal Ions and Ligands*.			
Metal Ion	<i>k</i> value	Ligand	<i>h</i> value
Mn ²⁺	0.07	F [−]	0.8
V ²⁺	0.1	H ₂ O	1.0
Ni ²⁺	0.12	(CH ₃) ₂ NCHO	1.2
Mo ³⁺	0.15	NH ₃	1.4
Cr ³⁺	0.20	en	1.5
Fe ³⁺	0.24	ox ^{2−}	1.5
Rh ³⁺	0.28	Cl [−]	2.0
Ir ³⁺	0.28	CN [−]	2.1
Co ³⁺	0.33	Br [−]	2.3
Mn ⁴⁺	0.5	N ₃ [−]	2.4
Pt ⁴⁺	0.6	I [−]	2.7
Pd ⁴⁺	0.7		
Ni ⁴⁺	0.8		
*From C. K. Jørgensen, <i>Oxidation Numbers and Oxidation States</i> , Springer Verlag, New York, 1969, p. 106.			

After substituting B'/B for β , the equation can be written as

$$B' = B - Bhk \quad (18.12)$$

From this equation, we see that the Racah parameter for the metal ion in a complex, B' , is the value for the gaseous ion *reduced* by a correction (expressed as Bhk) for the cloud-expanding effect. As should be expected, the effect is a function of the nature of the particular metal ion and ligand. As a result, analysis of the spectrum for a complex must be made to determine both Dq and B (which is actually B' for the complex). Table 18.7 shows values of the nephelauxetic parameters for ligands and metal ions.

The data shown in Table 18.7 indicate that the ability of a ligand to produce a nephelauxetic effect increases as the softness of the ligand increases. Softer ligands such as N₃[−], Br[−], CN[−], or I[−] show a greater degree of covalency when bonded to metal ions, and they can more effectively delocalize electron density. It is also apparent that the nephelauxetic effect is greater for metal ions that are more highly charged. This is to be expected because these smaller, harder metal ions will experience a greater reduction in interelectronic repulsion by expanding the electron cloud than will a larger metal ion of lower charge. As the data show, the nephelauxetic effect correlates well with the hard-soft interaction principle.



■ **FIGURE 18.4** A complete Tanabe-Sugano diagram for a d^2 metal ion in an octahedral field. When $\Delta = 0$, the spectral terms (shown on the left vertical axis) are those of the free gaseous ion. Spectroscopic transitions occur between states having the same multiplicity.

18.5 TANABE-SUGANO DIAGRAMS

Qualitatively, the Orgel diagrams are energy level diagrams in which the vertical distances between the lines representing the energies of spectroscopic states are functions of the ligand field splitting. Although they are useful for summarizing the possible transitions in a metal complex, they are not capable of being interpreted quantitatively. The problems associated with B having values that depend on the ligand field splitting make it difficult to prepare a specific energy level diagram for a given metal ion. Y. Tanabe and S. Sugano circumvented part of this problem by preparing energy level diagrams that are based on spectral energies and Δ , but they prepared the graphs with E/B and Δ/B as the variables. When plotted in this way, the energy of the ground state becomes the horizontal axis and the energies of all other states are represented as curves above the ground state. Figure 18.4 shows a complete Tanabe-Sugano diagram for a d^2 ion. Even though the axes on Tanabe-Sugano diagrams have numerical scales (unlike an Orgel diagram), they are still not exactly quantitative. One reason is that B is not a constant. The nephelauxetic ratio, B'/B , varies from approximately 0.6 to 0.8 depending on the nature of the ligands. Some of the spectroscopic states have multiplicities that are different from that of the ground state as a result of electron pairing. The energies of those states are functions of both the Racah B and C parameters. However, the ratio C/B is not strictly a constant, and the calculations that are carried out to produce a Tanabe-Sugano diagram are based on a specific C/B value, usually in the range 4 to 4.5.

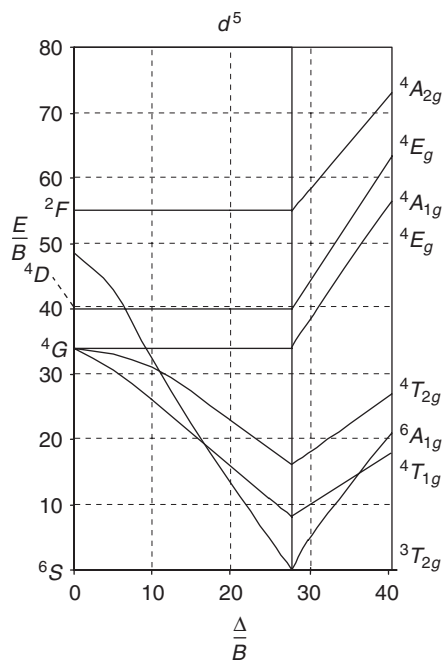
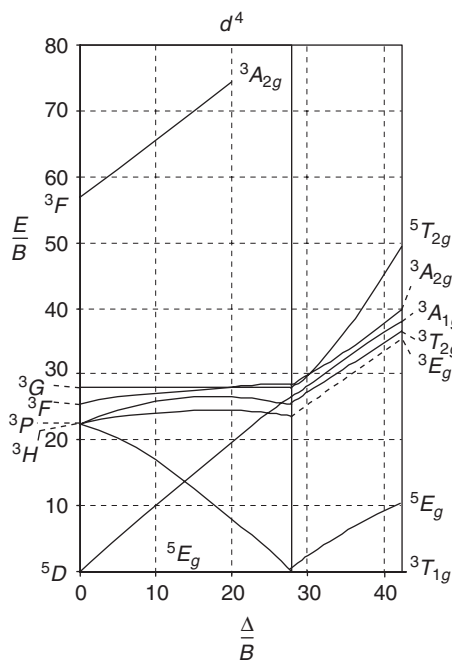
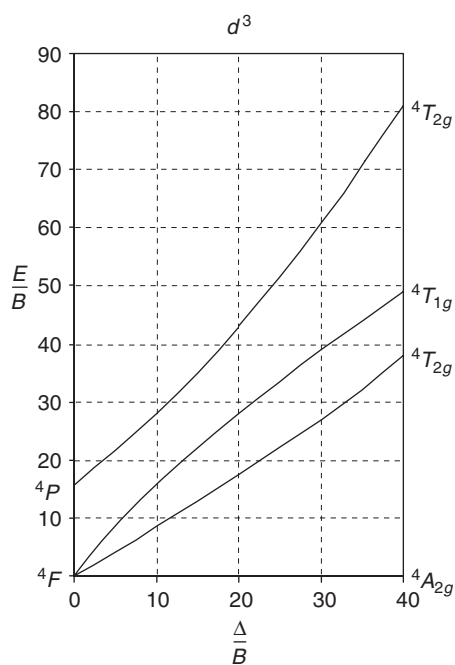
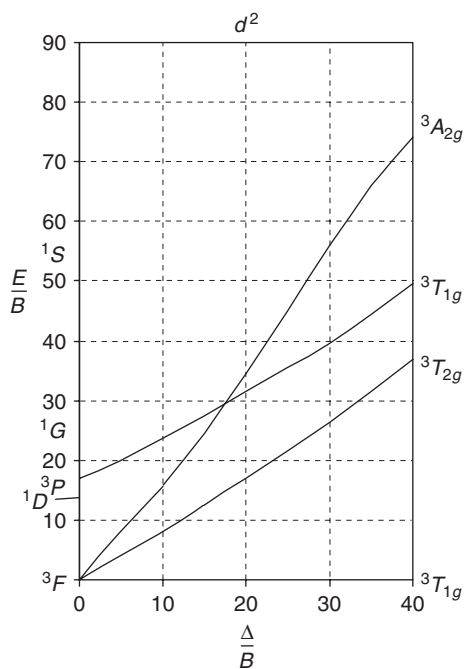
By looking at Tables 18.2 and 18.3, we see that for most metal ions there will be a sizeable number of spectroscopic states in a ligand field. A *complete* Tanabe-Sugano diagram shows the energies of *all* of these states as plots of E/B versus Δ/B . However, in the analysis of spectra of complexes, it is usually necessary to consider only states having the same multiplicity as the ground state. Therefore, only a small number of states must be considered when assigning spectral transitions. The Tanabe-Sugano diagrams shown in this chapter do not include some of the excited states but rather show only the states involved in $d-d$ transitions. The result is a less cluttered diagram that still presents the details that are necessary for spectral analysis. The simplified Tanabe-Sugano diagrams for d^2 through d^8 ions are shown in Figure 18.5. Note that the diagrams for d^4 , d^5 , d^6 , and d^7 have a vertical line that typically occurs in the Δ/B range of 20 to 30. This is the result of electron spin pairing when the ligand field becomes sufficiently strong. Note that the ground state continues to be the horizontal axis, but the multiplicity is different and corresponds to that of the complex with fewer unpaired electrons.

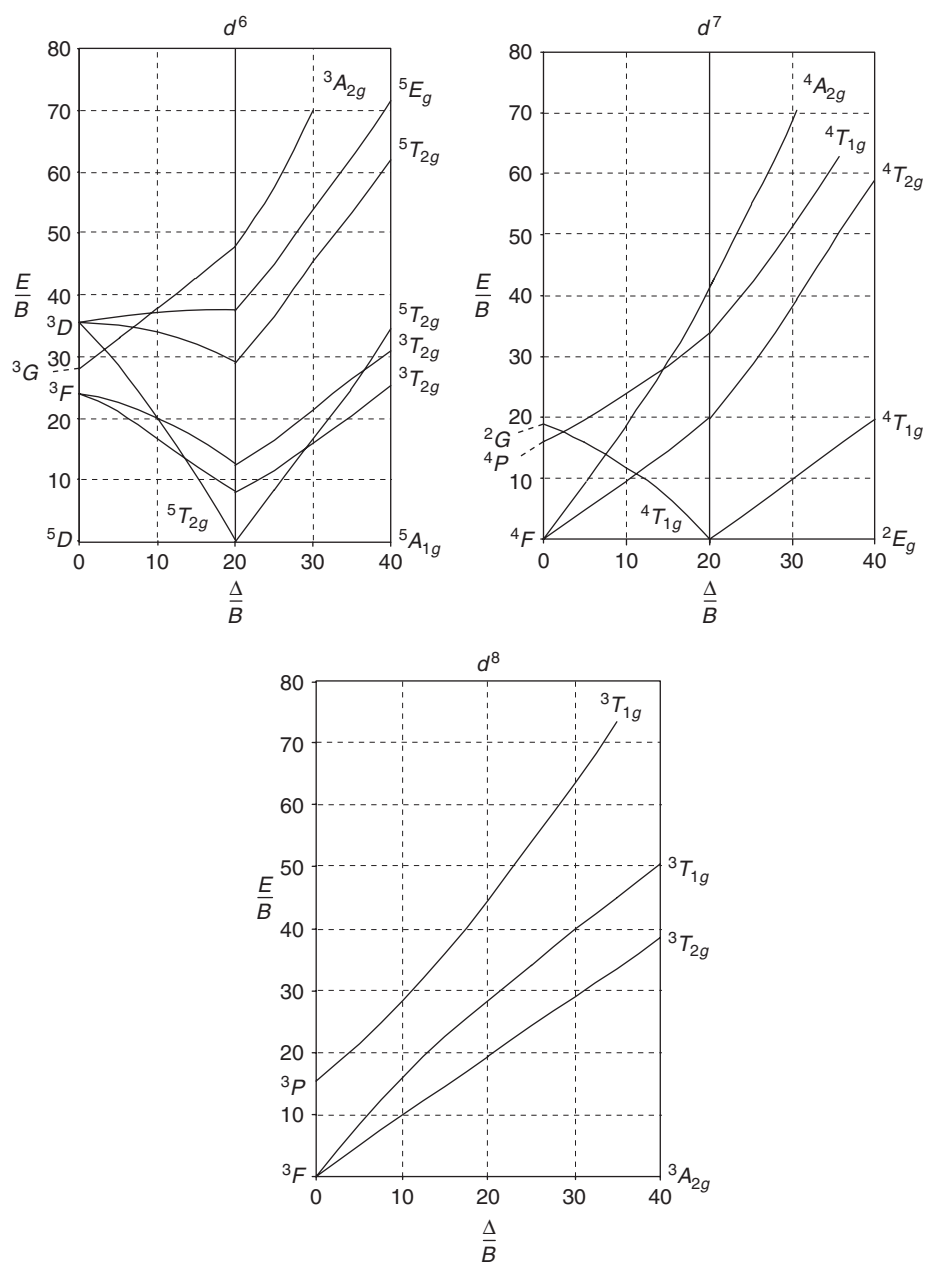
The use of a Tanabe-Sugano diagram in spectral analysis is relatively simple. Figure 18.6 shows a simplified Tanabe-Sugano diagram for a d^3 metal ion. Transitions between the $^4A_{2g}$ ground state and excited states having the same multiplicity can be represented as vertical lines between the horizontal axis and the lines representing the excited states. Suppose a complex CrX_6^{3-} has two absorption bands, $\nu_1 = 11,000\text{ cm}^{-1}$ and $\nu_3 = 26,500\text{ cm}^{-1}$, and that Dq and B are to be determined from the diagram shown in Figure 18.6. For this complex, $\nu_3/\nu_1 = 2.4$, so the ratio of the lengths of the lines representing the third and first transitions must have this value. Because the lines representing the excited states *diverge* as Δ changes, there is only one point on the horizontal axis where this ratio of 2.4 is satisfied. That value of Δ/B is the one where the distances from the ground state (the horizontal axis) up to the first and third excited states have the ratio 2.4. The problem is to find the correct point on the Δ/B axis.

On Figure 18.6, a trial value of $\Delta/B = 30$ is shown that yields the vertical lines representing ν_3 and ν_1 . The measured lengths of these lines gives a ratio of 2.19, which is somewhat lower than the ratio of the experimental spectral energies. At a trial value of 10 for Δ/B (also shown on the figure), the lengths of the lines give a ratio of 3.11, which is higher than the ratio of the spectral energies. By carefully measuring the lengths of the lines corresponding to the transitions, it is found that the correct value of Δ/B is approximately 16. This value corresponds to values of E_1/B of approximately 14 and E_3/B of about 35 (by reading on the vertical axis). Because it is known that the energy of the ν_1 band is $E_1 = 11,000\text{ cm}^{-1}$,

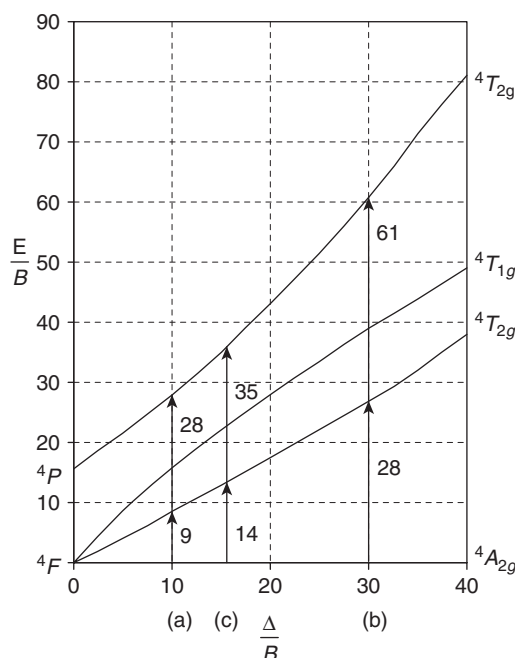
$$\frac{E_1}{B} = 14 = \frac{11,000\text{ cm}^{-1}}{B} \quad (18.13)$$

so B is approximately 780 cm^{-1} . We have already determined that Δ/B is approximately 16, so it is now possible to evaluate Δ , which we find to be approximately $12,000$ to $13,000\text{ cm}^{-1}$. If the calculations are repeated using the data for $E_3 = 26,500\text{ cm}^{-1}$ and $\Delta/B = 16$, values of approximately 760 cm^{-1} and $12,100\text{ cm}^{-1}$ are indicated for B and Δ , respectively. For Cr^{3+} , the free ion B value is 1030 cm^{-1} , so the value indicated for B in the CrX_6^{3-} complex is, as expected, approximately 75% of the free ion value.





■ **FIGURE 18.5** Simplified Tanabe-Sugano diagrams for d^n metal ions in octahedral fields. The drawings have been simplified by omitting several states that have multiplicities that do not permit spin allowed transitions.



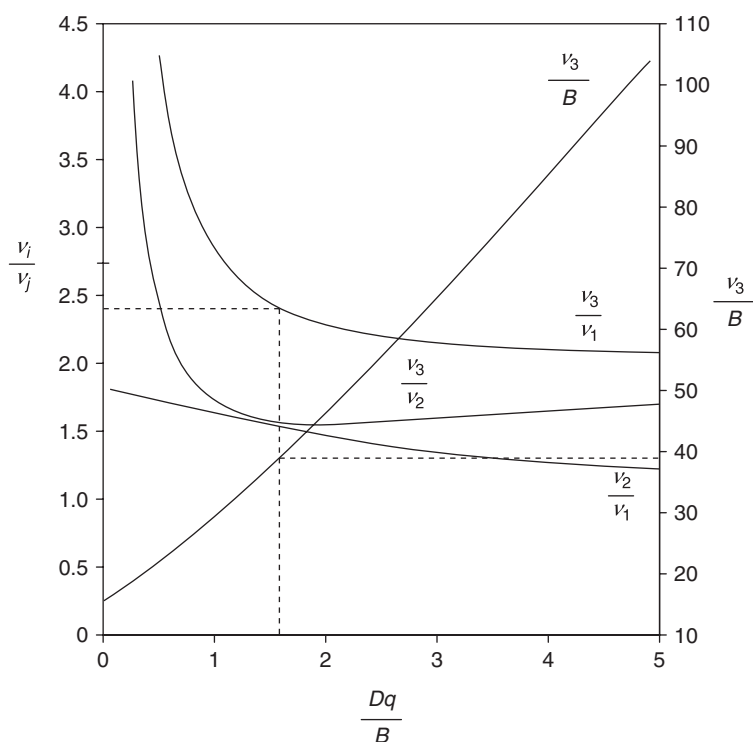
■ **FIGURE 18.6** The simplified Tanabe-Sugano diagram for a d^3 ion in an octahedral field and its use for determining ligand field parameters (see text). At point (a) ($\Delta/B = 10$) on the figure, $\nu_3/\nu_1 = 28/9 = 3.11$. At point (b) ($\Delta/B = 30$) on the figure, $\nu_3/\nu_1 = 61/28 = 2.19$. At point (c) ($\Delta/B = 16$), $\nu_3/\nu_1 = 35/14 = 2.50$, which is approximately the correct value. Therefore, 16 is approximately the correct value for Δ/B .

In the foregoing illustration, we have assumed that ν_2 either is not observed or has an unknown energy. Having found that $\Delta/B = 16$, we can read from the Tanabe-Sugano diagram the energy of the ${}^4T_{1g}$ state corresponding to that value of Δ/B to find $E_2/B = 23$, which shows that the second spectral band should be at approximately $16,500\text{ cm}^{-1}$.

Because a value of E/B can be read directly from the graph, B can be determined owing to the fact that the energies of the bands in the spectrum are already known. With B and Δ/B having been determined, Δ is readily obtained. Note, however, that this measurement is not particularly accurate, which means that Δ/B is not known very accurately. In fact, Tanabe-Sugano diagrams are not normally used to determine Δ and B quantitatively. They are useful as a basis for interpreting spectra, but the equations shown in Table 18.6 or other graphical or numerical procedures are generally used for determining Δ and B . One such graphical procedure will now be described.

18.6 THE LEVER METHOD

A method described by A. B. P. Lever (1968) provides an extremely simple and rapid means of evaluating Dq and B for metal complexes. In this method, the equations for $E(\nu_1)$, $E(\nu_2)$, and $E(\nu_3)$ are used with a wide range of Dq/B values to calculate the ratios ν_3/ν_1 , ν_3/ν_2 , and ν_2/ν_1 . These values are shown

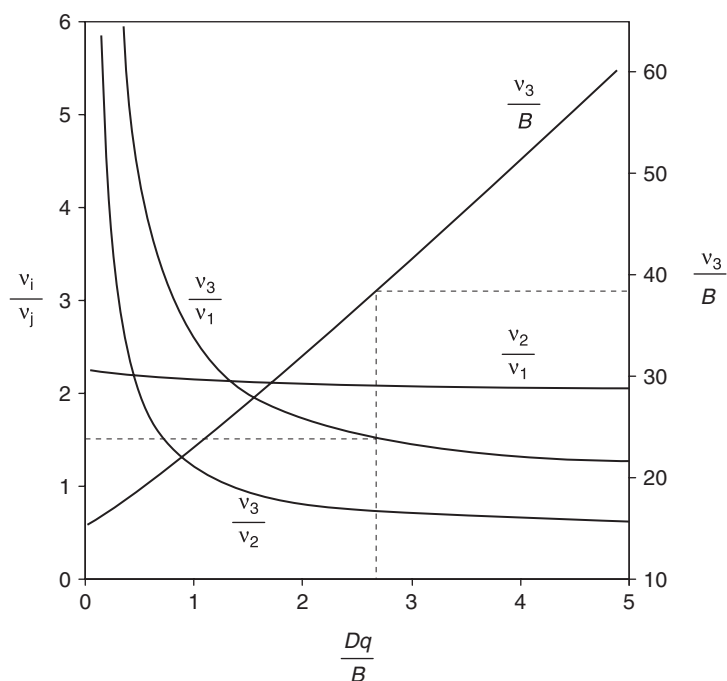


■ **FIGURE 18.7** Diagram for using the Lever method to determine Dq and B for ions having A spectroscopic ground states. (Drawn using data presented by Lever, 1968).

as extensive tables along with ν_3/B ratios in the original literature, but they can also be shown graphically as in Figure 18.7 (for ions having A ground states) and Figure 18.8 (for ions having T ground states).

When using the Lever method, experimental band maxima are used to calculate the ratios ν_3/ν_1 , ν_3/ν_2 , and ν_2/ν_1 . The ratios are then located on the appropriate line on the graph, and by reading *downward* to the horizontal axis, the value of Dq/B is determined. Once the ν_i/ν_j ratio is located, the ν_3/B value can also be identified by reading to the right-hand axis, whether or not ν_3 is available from the spectrum. Therefore, because Dq/B and ν_3 are both known, it is a simple matter to calculate Dq and B . When using the Lever method, it is best to use either the original tables of values or a large-scale graph with grid lines to be able to read values more accurately.

The procedure for using the Lever method will be illustrated by considering the CrX_6^{3-} complex described earlier in using the Tanabe-Sugano diagram. In this case, absorption bands were presumed to be seen at $11,000$ and $26,500\text{ cm}^{-1}$ and to represent ν_1 and ν_3 , respectively. Therefore $\nu_3/\nu_1 = 2.41$. Because Cr^{3+} is a d^3 ion, the ground state is ${}^4A_{2g}$, so Figure 18.7 is the appropriate one to use. Reading



■ **FIGURE 18.8** Diagram for using the Lever method to determine Dq and B for ions having T spectroscopic ground states. (Drawn using data presented by Lever, 1968).

across to the vertical axis opposite the value $\nu_3/\nu_1 = 2.41$ corresponds to a value of Dq/B equal to about 1.6 on the horizontal axis. Similarly, the value ν_3/B is found to be about 38.5. Therefore,

$$Dq/B = 1.6 \quad (18.14)$$

$$\nu_3/B = 38.5 \quad (18.15)$$

so that $B = Dq/1.6$ and $B = \nu_3/38.5$. From Eqs. (18.14) and (18.15) we find that

$$Dq = \nu_3 \times 1.6/38.5 = 26,500 \text{ cm}^{-1} \times 1.6/38.5 = 1100 \text{ cm}^{-1}$$

which leads to a value of approximately 690 cm^{-1} for B . These values are in fair agreement with the values of 1200 cm^{-1} and 760 cm^{-1} estimated for Dq and B , respectively, from the Tanabe-Sugano diagram. Because B for the gaseous Cr^{3+} ion is 1030 cm^{-1} , the nephelauxetic ratio for this complex is $B = 690 \text{ cm}^{-1}/1030 \text{ cm}^{-1} = 0.67$, which is a typical value for this parameter.

When using the Lever method, the question naturally arises regarding the situation in which the identities of the bands in the spectrum are unknown. Assuming that we do not know that the observed bands are actually ν_1 and ν_3 , we calculate from the previous example that $\nu_i/\nu_j = 2.41$. It is readily apparent that this ratio could not be ν_2/ν_1 because the entire range of values presented for this ratio is approximately 1.2 to 1.8. If the 2.41 value actually represented ν_3/ν_2 , a value of Dq/B of about 0.52 is

indicated. From our previous discussions, it has been seen that for first-row +3 metal ions, Δ_o is about 15,000 to 24,000 cm⁻¹ (Dq approximately 1500–2400 cm⁻¹) depending on the ligands. It has also been shown that B values for first-row metals are typically about 800 to 1000 cm⁻¹. Therefore, for this situation a ratio of Dq/B of 0.52 is clearly out of the realm of possibility for an octahedral complex of this type. For that reason, a ratio of band energies of 2.41 is consistent only with the bands being assigned as ν_3 and ν_1 . It can be shown that this is the case for other complexes as well. It is not actually necessary to know the assignments of the bands in most cases to use the Lever method to determine Dq and B . Assuming that the complexes have realistic values for Dq and B leads to the conclusion that only one set of assignments is possible. Also, only two band positions need to be known because the ratio of these gives both the Dq/B and ν_3/B values from the figures.

Let us consider the case of VF_6^{3-} , which has bands at 14,800 cm⁻¹ and 23,000 cm⁻¹. Because ν^{3+} is a d^2 ion, the ground-state term is ${}^3T_{1g}$, and in this case, $\nu_3/\nu_1 = 1.55$. From Figure 18.8 it can be seen (from the dotted lines) that a value of 1.55 for the ratio ν_3/ν_1 corresponds to $Dq/B = 2.6$ and $\nu_3/B = 38$. Therefore, using these values it is found that

$$B = \nu_3 / 38 = Dq / 2.6 \quad (18.16)$$

so that $Dq = 23,000 \text{ cm}^{-1} \times 2.6/38 = 1600 \text{ cm}^{-1}$ and B is 600 cm⁻¹. These values for Dq and B are in agreement with those obtained for this complex using other procedures.

From the discussion earlier in this chapter, we know that a value of 16,000 cm⁻¹ for Δ_o is typical of most complexes of a +3 first-row transition metal ion. For V^{3+} , the free-ion B value is 860 cm⁻¹, so the value 600 cm⁻¹ found for V^{3+} in the complex indicates a value of 0.70 for the nephelauxetic ratio, β . All of these values are typical of complexes of first-row transition metal ions. Therefore, even though the identity of the bands may be uncertain, performing the analysis will lead to B and Dq values that will be reasonable only when the correct assignment of the bands has been made.

In the previous example, if an incorrect assumption is made that the bands represent ν_3 and ν_2 , the ratio of energies having a value of 1.49 would indicate a value of Dq/B of only about 0.80. Using this value and the experimental spectral band energies leads to unrealistic values for Dq and B for a complex of a +3 first-row metal ion. Thus, even if the assignment of bands is uncertain, the calculated ligand field parameters will be consistent with the typical ranges of values for Dq and B for such complexes for only one assignment of bands. The Lever method is a simple, rapid, and useful method for analyzing spectra of transition metal complexes to extract values for ligand parameters. It is fully applicable to tetrahedral complexes as well by using the diagram that corresponds to the correct ground-state term for the metal ion.

18.7 JØRGENSEN'S METHOD

An interesting approach to predicting the ligand field splitting for a given metal ion and ligand has been given by Christian Klixbüll Jørgensen. In Jørgensen's approach, the equation that has been developed to predict the ligand field splitting in an octahedral field, Δ_o , is

$$\Delta_o(\text{cm}^{-1}) = fg \quad (18.17)$$

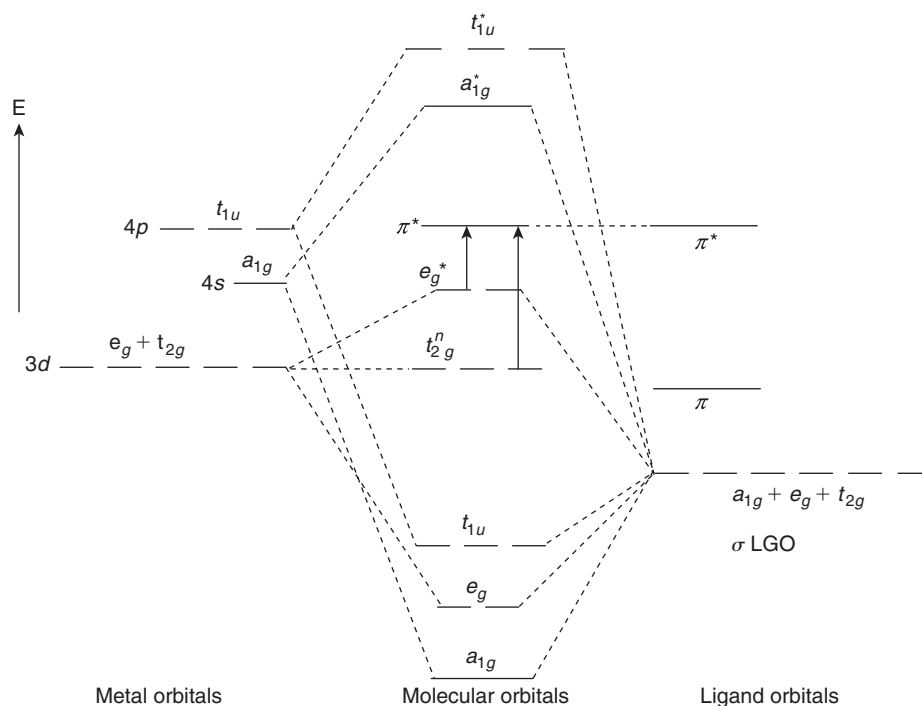
Table 18.8 Selected Values for the f and g Parameters for Use in Jørgensen's Equation.			
Metal Ion	g	Ligand	f
Mn ²⁺	8,000	Br [−]	0.72
Ni ²⁺	8,700	SCN [−]	0.73
Co ²⁺	9,000	Cl [−]	0.78
V ²⁺	12,000	N ₃ [−]	0.83
Fe ³⁺	14,000	F [−]	0.9
Cr ³⁺	17,400	H ₂ O	1.00
Co ³⁺	18,200	NCS [−]	1.02
Ru ²⁺	20,000	py	1.23
Rh ³⁺	27,000	NH ₃	1.25
Ir ³⁺	32,000	en	1.28
Pt ⁴⁺	36,000	CN [−]	1.7
From C. K. Jørgensen (1971). <i>Modern Aspects of Ligand Field Theory</i> , pp. 347–348. North Holland, Amsterdam.			

where f is a parameter characteristic of the ligand and g is a parameter characteristic of the metal ion. The values for parameters in this equation are based on the assignment of a value of $f = 1.00$ for water as a ligand and values for other ligands were determined by fitting the spectral data to known ligand field splittings. Table 18.8 shows representative values for f and g parameters for several metal ions and ligands.

Equation (18.17) predicts values for Δ_o that are in reasonably good agreement with the values determined by more robust methods. In many instances, an approximate value for the ligand field splitting is all that is required, and this approach gives a useful approximation for Δ_o rapidly with a minimum of effort.

18.8 CHARGE TRANSFER ABSORPTION

Up to this point, the discussion of spectra has been related to the electronic transitions that occur between spectroscopic states for the metal ion in the ligand field. However, these are not the only transitions for which absorptions occur. Ligands are bonded to metal ions by donating electron pairs to orbitals that are essentially metal orbitals in terms of their character. Transition metals also have non-bonding e_g or t_{2g} orbitals (assuming an octahedral complex) arising from the d orbitals that may be partially filled, and the ligands may have empty nonbonding or antibonding orbitals that can accept electron density from the metal. For example, both CO and CN[−] have empty π^* orbitals that can



■ **FIGURE 18.9** Interpretation of $M \rightarrow L$ charge transfer absorption in an octahedral complex using a modified molecular orbital diagram. The transitions are from e_g^* or t_{2g} orbitals on the metal to π^* orbitals on the ligands.

be involved in this type of interaction (see Chapter 16). Movement of electron density from metal orbitals to ligand orbitals and vice versa is known as *charge transfer*. The absorption bands that accompany such shifts in electron density are known as *charge transfer bands*.

Charge transfer (CT) bands are usually observed in the ultraviolet region of the spectrum, although in some cases they appear in the visible region. Consequently, they frequently overlap or mask transitions of the $d-d$ type. Charge transfer bands are of the spin-allowed type, so they have high intensity. If the metal is in a low oxidation state and easily oxidized, the charge transfer is more likely to be of the metal-to-ligand type, indicated as $M \rightarrow L$. A case of this type occurs in $\text{Cr}(\text{CO})_6$ where it is easy to move electron density from the metal atom (which is in the 0 oxidation state), especially because the CO ligands have donated six pairs of electrons to the Cr. The empty orbitals on the CO ligands are π^* orbitals. In this case, the electrons are in nonbonding t_{2g} orbitals on the metal so the transition is designated as $t_{2g} \rightarrow \pi^*$. In other cases, electrons in the e_g^* orbitals are excited to the empty π^* orbitals on the ligands. Figure 18.9 shows these cases on a modified molecular orbital diagram for an octahedral complex. Although CO is a ligand that has π^* acceptor orbitals, other ligands of this type include NO, CN^- , olefins, and pyridine.

The intense purple color of MnO_4^- is due to a charge transfer band that occurs at approximately $18,000\text{ cm}^{-1}$ and results from a transfer of charge from oxygen to the Mn^{7+} . In this case, the transfer is indicated as $\text{L} \rightarrow \text{M}$, and it results from electron density being shifted from filled p orbitals on oxygen atoms to empty orbitals in the e set on Mn. As a general rule, the charge transfer will be $\text{M} \rightarrow \text{L}$ if the metal is easily oxidized, whereas the transfer will be $\text{L} \rightarrow \text{M}$ if the metal is easily reduced. Therefore, it is not surprising that Cr^0 in $\text{Cr}(\text{CO})_6$ would have electron density shifted *from the metal to the ligands* and Mn^{7+} would have electron density shifted *from the ligands to the metal*. The ease with which electron density can be shifted from the ligands to the metal is related in a general way to how difficult it is to ionize or polarize the ligands.

We have not yet addressed the important topic of absorption by the ligands in complexes. For many types of complexes, this type of spectral study (usually infrared spectroscopy) yields useful information regarding the structure and details of the bonding in the complexes. This topic will be discussed later in connection with several types of complexes containing specific ligands (e.g., CO , CN^- , NO_2^- , and olefins).

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■ QUESTIONS AND PROBLEMS

- For the following high spin ions, describe the nature of the possible electronic transitions and give them in the order of increasing energy.
(a) $[\text{Ni}(\text{NH}_3)_6]^{2+}$; (b) $[\text{FeCl}_4]^-$; (c) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$; (d) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$; (e) $[\text{FeF}_6]^{4-}$; (f) $[\text{Co}(\text{H}_2\text{O})_2]^{2+}$
- Use Jørgensen's method to determine Δ_o for the following complexes:
(a) $[\text{MnCl}_6]^{4-}$; (b) $[\text{Rh}(\text{py})_6]^{3+}$; (c) $[\text{Fe}(\text{NCS})_6]^{3-}$; (d) $[\text{Co}(\text{NH}_3)_6]^{2+}$; (e) $[\text{PtBr}_6]^{2-}$
- Spectral bands are observed at $17,700\text{ cm}^{-1}$ and $32,400\text{ cm}^{-1}$ for $[\text{Cr}(\text{NCS})_6]^{3-}$. Use the Lever method to determine Dq and B for this complex. Where would the third band be found? What transition does it correspond to?
- Some values for the Racah B parameter are 918 , 766 , and 1064 cm^{-1} . Match these values to the ions Cr^{3+} , V^{2+} , and Mn^{4+} . Explain your assignments.
- Spectral bands are observed at 8350 and $19,000\text{ cm}^{-1}$ for the complex $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. Use the Lever method to determine Dq and B for this complex. Determine where the missing band should be observed. What transition does this correspond to?
- A complex VL_6^{3+} has the two lowest energy transitions at $11,500$ and $17,250\text{ cm}^{-1}$.
(a) What are the designations for these transitions?
(b) Use the Lever method to determine Dq and B for this complex.
(c) Where should the third spectral band be observed?
- Use Jørgensen's method to determine Dq and B for $[\text{Co}(\text{en})_3]^{3+}$. What would be the approximate positions of the three spectral bands?
- Peaks are observed at 264 and 378 nm for $[\text{Cr}(\text{CN})_6]^{3-}$. What are Dq and B for this complex?
- For the complex $[\text{Cr}(\text{acac})_3]$ (where acac = acetylacetonate ion), ν_1 is observed at $17,860\text{ cm}^{-1}$ and ν_2 is at $23,800\text{ cm}^{-1}$. Use these data to determine Dq and B for this complex.
- For the complex $[\text{Ni}(\text{en})_3]^{2+}$ (where en = ethylenediamine), ν_1 is observed at $11,200\text{ cm}^{-1}$, ν_2 is at $18,450\text{ cm}^{-1}$, and ν_3 is at $29,000\text{ cm}^{-1}$. Use these data to determine Dq and B for this complex.
- For each of the following, tell whether you would or would not expect to see charge transfer absorption. For the cases where you would expect CT absorption, explain the type of transitions expected.
(a) $[\text{Cr}(\text{CO})_3(\text{py})_3]$; (b) $[\text{Co}(\text{NH}_3)_6]^{3+}$; (c) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$; (d) $[\text{Co}(\text{CO})_3\text{NO}]$; (e) CrO_4^{2-}