10.2 LIGAND-FIELD SPECTRA OF OCTAHEDRAL COMPLEXES[1]

▶ 10.2.1 Energy States from Spectral Terms

Spectral terms in atoms or ions arise from coupling of the angular momentum (l) of individual electrons in ways limited by the Pauli exclusion principle to afford states of differing total angular momentum (L) and different energy (arising from differences in electron repulsion; see page 34): The values of l associated with the various hydrogenlike orbitals arise from the solution of the Schrödinger equation for H, a problem having spherical symmetry. On placing a transition metal ion in an electric field of less-than-spherical symmetry such as O_h, l ceases to be a valid quantum number and orbitals are described by their symmetry labels (irreducible representations) for O_h, or the appropriate symmetry, instead. A physical manifestation of this is sometimes the splitting of a set of orbitals which were degenerate in the free ion.

In spherical symmetry the character of the representation for a state having an orbital angular momentum quantum number of l (or L) under an operation of the spherical group $R_h(3)$ (Douglas and Hollingsworth, pp. 87–90, see General References) is given by

$$\chi[C(\phi)] = \frac{\sin(l + \tfrac{1}{2})\phi}{\sin \phi/2} \quad \text{for rotation by an angle of } \phi \text{ radians} \tag{10.1}$$

$$\chi[S(\phi)] = \pm\frac{\sin(l + \tfrac{1}{2})(\phi + \pi)}{\sin \tfrac{1}{2}(\phi + \pi)} \quad \begin{array}{l}\text{for an improper rotation by an angle of } \phi \\ \text{radians (minus sign for } ungerade \text{ states)}\end{array} \tag{10.2}$$

from which the more specific equations for symmetry operations E, σ, and i below are easily obtained:

$$\chi(E) = 2l + 1 \qquad \begin{array}{l}\text{(the character under the identity operation} \\ \text{is the degeneracy of the orbital set)}\end{array} \tag{10.3}$$

$$\chi(\sigma) = \pm\sin(l + \tfrac{1}{2})\pi \qquad \begin{array}{l}\text{(minus sign for } ungerade \text{ states, } \sigma \\ \text{represents a symmetry plane)}\end{array} \tag{10.4}$$

$$\chi(i) = \pm(2l + 1) \qquad \text{(minus sign for } ungerade \text{ states)} \tag{10.5}$$

To obtain the symmetry species into which a set of orbitals split in a symmetry lower than spherical, one obtains the appropriate characters by Equations (10.1)–(10.5) and reduces the representation by means of Equation (3.13). Thus, for a set of d orbitals ($l = 2$) or a D spectroscopic term ($L = 2$) in O_h symmetry, one obtains the following representation which reduces to $e_g + t_{2g}$ for d and $E_g + T_{2g}$ for D:

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[1] This section uses the notation and terminology of group theory but does not require the detailed manipulations of Section 3.5. The material of Sections 1.4 and 1.5 is useful as background.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
Γ_d	5	-1	1	-1	1	5	-1	-1	1	1	$\longrightarrow e_g + t_{2g}$ or $D \rightarrow E_g + T_{2g}$

The e_g orbitals (d_{z^2} and $d_{z^2-y^2}$) and t_{2g} orbitals (d_{xy}, d_{xz}, d_{yz}) are shown in Figure 9.8. As you can verify for yourself, by using the operations on p orbitals or using the equations above, an octahedral field does not split the p orbitals. They remain triply degenerate and are characterized by their symmetry properties as t_{1u}. Likewise, the nondegenerate, totally symmetric s orbital becomes a_{1g}. See R. L. DeKock, A. L. Kromminga, and T. S. Zwier, *J. Chem. Educ.* **1979**, *56*, 510.

Ions in symmetric ligand fields have different energy states which result not only from differences in electron repulsion energy (as they do in free ions) but also from the splitting of orbital degeneracies by the ligand field. The d^1 case is quite simple because there is no electron repulsion. The electron is in the t_{2g} orbital in the ground state in an octahedral field. The d^1 ion $[Ti(H_2O)_6]^{3+}$ shows a single absorption band in the visible region of the spectrum corresponding to the transition $t_{2g}^1 \rightarrow e_g^1$ (see Figure 9.11). The energy of the band maximum is the splitting parameter $10Dq$. *The energy states of the complex follow by analogy to the behavior of orbitals in going from the free ion to the ion in the complex.* Just as the $d(l = 2)$ orbitals split into $t_{2g} + e_g$, so the ^2D term ($L = 2$) of the d^1 configuration splits into $^2T_{2g}$ and ^2E_g with the same spin multiplicity in an O_h field.

In a similar fashion, $S(L = 0)$ terms become A_{1g} and P terms become T_{1g} in an octahedral field. In a centrosymmetric point group (e.g., O_h), *all* spectral terms arising from d^n configurations give g states. Terms arising from p^n or f^n configurations give states which are u if n is odd and g if n is even ($u \times u = g$). If the point group is noncentrosymmetric (e.g., T_d), the g or u subscript is omitted. Table 10.1 lists the states arising from various spectral terms for d^n configurations in an O_h field. Note that the degeneracy (5-fold for D, 7-fold for F, etc.; the same as for the corresponding orbital sets) is conserved.

EXAMPLE 10.1: What states are expected in an octahedral field from a ^1G free ion term? Verify the result as the same degeneracy as ^1G.

Solution: From Table 10.1 the singlet states in O_h are $^1A_{1g}$, ^1E_g, $^1T_{1g}$, and $^1T_{2g}$. The degeneracy is $1 + 2 + 3 + 3 = 9$.

Table 10.1 Splitting of spectral terms for d^n configurations in an octahedral field

Term	Degeneracy	States in an octahedral field
S	1	A_{1g}
P	3	T_{1g}
D	5	$E_g + T_{2g}$
F	7	$A_{2g} + T_{1g} + T_{2g}$
G	9	$A_{1g} + E_g + T_{1g} + T_{2g}$
H	11	$E_g + T_{1g} + T_{1g} + T_{2g}$
I	13	$A_{1g} + A_{2g} + E_g + T_{1g} + T_{2g} + T_{2g}$

▶ *10.2.2*   *Selection Rules*

Not every possible transition is seen in a spectrum. In studying any type of spectrum, one object is to learn what the characteristics of the ground and excited states must be, in order that transitions between them may be observed. The statements of required characteristics are called **selection rules**. If ground and excited states for a possible transition possess the required characteristics, the transition is said to be **allowed**. If they do not, the transition is **forbidden**.

The selection rules are derived from specific idealized theoretical models of the absorption process. It often happens that the ground- and excited-state wavefunctions are not the simple ones assumed in theoretical treatments. In such cases, "forbidden" transitions are often observed. However, forbidden transitions have low probability and, consequently, their observed intensities are generally low.

The model for absorption of electromagnetic radiation which is most often applicable in spectroscopy is the **electric dipole model**. In this model, radiation absorption is accompanied by a change in the electric dipole moment of the molecule, and the intensity of an electronic transition is proportional to the dipole strength, D. The dipole strength is the square of an integral involving the wavefunctions for the ground and excited states and an operator called the **dipole moment vector;** $d\tau$ is a volume element.

$$D = \left[\int \Psi_{ground} \, (operator) \Psi_{excited} \, d\tau \right]^2 \tag{10.6}$$

The operator (the dipole moment vector) transforms as a vector having components in the x, y, and z directions and thus has the form $a\vec{x} + b\vec{y} + c\vec{z}$.

LaPorte's Rule

A couple of generally applicable selection rules can be derived from Equation (10.6). **LaPorte's Rule** states that *in centrosymmetric environments, transitions can occur only between states of opposite parity ($u \to g$ or $g \to u$)*. This means that $d \to p$, $s \to p$, and so on, are allowed, but not $d \to d$, $s \to d$, and so on. Transitions allowed by LaPorte's rule are quite intense, having $\varepsilon \cong 10,000$.

That Equation (10.6) leads to LaPorte's rule can be demonstrated readily. The dipole moment operator transforms as x, y, and z which in any centrosymmetric point group must be odd (u). The product of the operator and the wavefunctions in the integral must be g if the integral is not to equal zero. [The integral of an odd (u) function vanishes when integrated over all space because the positive and negative portions cancel one another.] Thus, even products result from $g \times g = g$ and $u \times u = g$, but an odd product results from $g \times u = u$. These dictate that because the operator is odd (or u), the integrand is g only if the product of the wavefunctions is also u. This is, the basis for LaPorte's rule.

Actually, the selection rules are even more restrictive than this. The function involved in the integral must not only be even, it must be *totally symmetric*—it must belong to the totally symmetric representation (A_{1g} for the O_h case). The product of two representations

is A_{1g} (or contains A_{1g} for a reducible representation) *only* if the two representations are identical. Therefore, the *product of the representations* for the ground and excited states (this product is called the **symmetry of the transition**) must belong to the *same representation* as that of one of the vectors **x**, **y**, and **z**. This provides a basis for detailed assignments of transitions.

Transitions involving only d orbitals ($d \rightarrow d$ transitions) are LaPorte-forbidden in centrosymmetric point groups; yet, as we shall soon see, they do appear—however, with intensities ($\varepsilon \cong 5{-}100$) that are only about 10^{-2} of allowed transitions. The intensity-giving mechanism is the so-called **vibronic mechanism** which relaxes partially LaPorte's rule for complexes. A vibration of odd parity (e.g., T_{1u}) distorts an octahedron, for example, destroying the center of symmetry so that the g and u designations are not applicable during the time required for the transition and allows mixing of d and p orbitals. The vibrational and electronic transitions are coupled (**vibronic**). Because the energy contribution of the vibrational part of the transition is so much less than that of the electronic transition, the energies of the absorptions may be related to differences in electronic energy levels alone.

If a complex lacks a center of inversion, then the *gerade* and *ungerade* labels no longer have meaning. LaPorte's rule might not be expected to apply to tetrahedral complexes or to trigonal bipyramidal complexes that are noncentrosymmetric. Indeed, such complexes show more intense $d \rightarrow d$ absorptions ($\varepsilon \cong 100{-}200$) than do octahedral complexes, but they are still much weaker than LaPorte-allowed transitions.

Spin Selection Rule

A second selection rule is the **spin selection rule,** which states that *transitions may occur only between energy states with the same spin multiplicity.* That this should be so is not obvious from the general form of the integral in Equation (10.6). However, it can be shown that the integral should vanish unless the spin function of both Ψ_{ground} and $\Psi_{excited}$ are the same. Allowed transitions involve promotion of electrons without change of spin. Spin-forbidden transitions are less intense ($\varepsilon \cong 10^{-2} - 1$) than those of spin-allowed transitions. The fact that they are seen at all is because the wavefunctions are often not as simple as those corresponding to Russell–Saunders coupling which have well-defined values of S. In particular, the j–j coupling scheme (page 37), which applies especially to the heavier elements, mixes the orbital and spin-angular momentum through so-called spin–orbit coupling to yield states of the same *total* angular momentum made up partly of orbital and partly of spin contributions. Thus, the spin function is no longer separable and well-defined; that is, the experimental situation does not fully correspond to the assumption of definite values for S. This effect becomes more important for the heavier elements of the second and third transition series. Hence, **spin-forbidden** transitions become more common for complexes of these complexes. Spin–orbit coupling makes the interpretation using Russell–Saunders coupling for the free-ion states (which we assume in examples used here) less reliable and thus introduces greater uncertainty in the prediction of spectra for these elements.[2]