

Relative intensities for multiplet and crystal-field-split transition-metal-ion photoemission spectra

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Previously, the photoemission spectra of the d levels of ionic transition-metal systems have been analyzed assuming localized-ion levels and taking into account the multiplet and crystal-field splitting of the final states. However, theoretical analyses of the relative intensities of these levels given in several recent papers are inconsistent and usually incorrect. The analysis required to obtain geometrical intensity rules for systems with several open shells (i.e., t_{2g} and e_g shells in transition-metal systems) is quite involved and difficult. In this paper, we review and physically interpret the analysis. We explicitly state the main assumptions used and show where they enter the problem. Finally, we present tables of our results for d^n ions ($n = 1-9$) in octahedral and in tetrahedral coordination.

The photoemission spectra of the d levels of ionic transition-metal systems^{1,2} and the f levels of rare earths³ may be quite complex. Analyses¹⁻⁵ of the spectra, assuming localized-metal levels and taking into account the multiplet and crystal-field splitting of the final states, have been qualitatively successful. However, theoretical analyses of the relative intensities of these levels given in several recent papers are not correct.^{1,2,4,5} A recent publication⁶ presented the correct intensities, but did not detail their derivation. The intensity analysis for systems with several open shells is quite involved and difficult.^{6,7} In this Note, we review the analysis^{6,7} and describe the physical origins of the various terms which arise. The main assumptions used in the analysis are explicitly stated. Finally, application is made to the d -level spectra of transition-metal ions in order to correct previous work.^{1,2,4,5}

It is essential to first state a notation for the quantum numbers and characteristics of systems with several open shells.

(i) The initial ground state is denoted by Ψ_I with total spin and orbital symmetries S_T^I and L_T^I . (For Co^{2+} in octahedral coordination, for example, the ground state is 5T_2 ; $S_T^I = 2$ and $L_T^I = T_2$.) The final state after photoemission consists of an ion Ψ_F with quantum numbers S_T^F and L_T^F and an electron in a continuum orbital χ . Clearly $S_T^F = S_T^I \pm \frac{1}{2}$ for a dipole-allowed one-electron transition from Ψ_I to $\Psi_F\chi$. The total space and spin quantum numbers for ψ_I and ψ_F are the resultant of vector coupling of the space and spin quantum numbers between two or more shells. We shall now describe these shells.

(ii) The shell from which the electron is removed upon ionization is called the active shell. In Ψ_I , the shell contains N_a electrons and in Ψ_F , $N_a - 1$. The N_a electrons couple in the initial state to S_a^I and L_a^I spin and space symmetries. In the ion, the $N_a - 1$ electrons couple to S_a^F and L_a^F . N_a electrons of the active shell will be denoted by a^{N_a} . The one-electron space symmetry of the active shell is denoted by l_a ; its spin s_a is of course $\frac{1}{2}$. Following the notation of Griffith,⁸ the fractional parentage coefficient, $C(I, F)$, of $|a^{N_a} a^{-1}(S_a^I L_a^I)\rangle$ in $|a^{N_a} a^{-1}(S_a^F L_a^F)\rangle$ is written

$$C(I, F) = \langle a^{N_a} a^{-1}(S_a^F L_a^F), a^{\frac{1}{2}} l_a | a^{N_a} S_a^I L_a^I \rangle. \quad (1)$$

(iii) All shells other than the active shell are grouped together and described as passive shells. The spin and space symmetries for this group of shells are denoted by S_p and L_p . Clearly, S_p and L_p must be the same in both Ψ_I and Ψ_F or the photoionization transition will be forbidden. [If, in addition to ionization from shell a , L_p and/or S_p are changed, this will correspond to at least a two-electron change from Ψ_I to $\Psi_F\chi$. Since the transition involves a one-electron operator, $\sum_i \vec{p}_i \cdot \vec{\epsilon} e^{i\vec{k}\cdot\vec{r}_i}$, the matrix element will vanish.⁹]

(iv) The degeneracies of the various states are denoted by¹⁰ $\lambda(S_T^F)$, $\lambda(L_T^F)$, $\lambda(S_a^I)$, $\lambda(L_a^I)$, etc. The notation described above is illustrated in Table I for ionization from the t_2 shell of a d^6 system (Fe^{2+}) in octahedral coordination.

For systems with several open shells, Cox *et al.*⁷ have derived a formula for the total photoionization cross section σ . Before we discuss this formula and its consequences, we enumerate the assumptions used to derive it to apply it to cases of interest to us.

TABLE I. Illustration of the notation described in the text for the photoionization of a system with two open shells. The example is high-spin d^6 (Fe^{2+}) in octahedral coordination.

Initial state	$\Psi_I = t_2^4({}^3T_1)e^2({}^3A_2); {}^5T_2$
Final state	$\Psi_F = t_2^3({}^4A_2)e^2({}^3A_2); {}^6A_1$ + (continuum electron in χ)
	$S_T^I = 2, L_T^I = T_2, \lambda(S_T^I) = 5, \lambda(L_T^I) = 3$
	$S_F^F = \frac{5}{2}, L_F^F = A_1, \lambda(S_F^F) = 6, \lambda(L_F^F) = 1$
	active shell $t_2; l_a = T_2$
	$S_a^I = 1; L_a^I = T_1, \lambda(S_a^I) = 3, \lambda(L_a^I) = 3$
	$S_a^F = \frac{3}{2}, L_a^F = A_2, \lambda(S_a^F) = 4, \lambda(L_a^F) = 1$
	passive shells; e plus all closed shells
	$S_p = 1, L_p = A_2, \lambda(S_p) = 3, \lambda(L_p) = 1$

(i) The *total* cross section is obtained. That is, $\sigma(h\nu)$ is summed over all directions of the emitted electron and averaged over all directions of polarization of the incident photon.

(ii) Both Ψ_I and Ψ_F are represented by *sums* of antisymmetrized products of orbitals (Slater determinants) chosen to have the appropriate space and spin symmetries described above. The orbitals are symmetry adapted.¹¹ In particular, we neglect many electron effects due to correlation (as might be obtained by, e.g., configuration interaction).

(iii) The *same* orbitals are used to construct both Ψ_I and Ψ_F . The process of photoionization is assumed to remove an electron from the bound shell a and place it into the continuum orbital χ ; all other orbitals are unchanged. In other words, we neglect relaxation for Ψ_F .

As a direct consequence of this and of assumption (ii) above, we neglect changes in the relative intensities of the main one-electron peaks due to losses into many electron (shake-up) satellites. These losses can be significant. As an example, for the NiO ionic crystal, self-consistent-field cluster calculations¹² on NiO_6 show that relaxation effects change the intensity ratios among the various Ψ_F by up to 7%. Correlation effects lead to even larger changes¹² of up to 24%. As a second example, for the K -shell ionization of molecular oxygen¹³ where these losses are quite large, the deviation of the observed multiplet intensity ratio from the simple $(S+1)/S$ rule is 23.5%. Of this amount, 14% is due to relaxation and the remaining 10% to other many-electron effects [the breakdown of assumption (ii)].

(iv) The photon energy is large enough so that the one-electron transition-matrix element varies only very slowly with the kinetic energy of the

ejected electron. That is, we assume that the matrix element is not affected by the differences of the kinetic energies of the electrons for all of the final states ψ_F which may arise from ionization of a given atomic subshell (nl). Clearly, this assumption will not hold for photon energies at or near the ionization threshold.⁴ In this region, the cross section may be expected to vary strongly and, in particular, effects due to the presence of neighboring atoms will be quite important. This has been shown dramatically by calculations¹⁴ for N_2 . Namely, the K -shell photoionization cross section changes by a factor of 2 in a 4-eV energy range at 10 eV above threshold.

The formula for σ uses the average value of this matrix element which, for ionization from shell a , we denote $\bar{\mu}_a$. For our application to ionic crystals, we assume $\bar{\mu}_a = \bar{\mu}_b$ if shells a and b are crystal-field-split shells with a common atomic origin. (For example, the t_2 and e shells arising in a T_d or O_h environment from the atomic d shell.) The equality $\bar{\mu}_a = \bar{\mu}_b$ requires (in addition to the independence of the matrix element on electron energy) that crystal-field and covalency effects on the "radial" parts of the orbitals of shells a and b are negligible.

In terms of the notation given above, the expression for the total cross section σ derived by Cox *et al.*⁷ is

$$\sigma = N_a |\bar{\mu}_a|^2 [C(I, F)]^2 SL; \quad (2a)$$

$$S = \lambda(S_T^I) \lambda(S_T^F) \lambda(S_a^I) \left[W \begin{pmatrix} S_a^F & S_a^I & \frac{1}{2} \\ S_T^I & S_T^F & S_p \end{pmatrix} \right]^2; \quad (2b)$$

$$L = \lambda(L_T^I) \lambda(L_T^F) \lambda(L_a^I) \left[W \begin{pmatrix} L_a^F & L_a^I & l_a \\ L_T^I & L_T^F & L_p \end{pmatrix} \right]^2. \quad (2c)$$

The contribution to σ of space and spin symmetries factor into the terms L and S , respectively. The Racah W coefficients^{7,15} ($6-j$ coefficients) represent the effect of the active and passive shells.

We shall next derive three rules that determine relative intensities in these systems. First, using sum rules for the W coefficients [Eq. (4.13) of Ref. 8 and Eq. (11.15) of Ref. 11], we have

$$\sum_{\text{allowed } S_T^F} S = \lambda(S_T^I) \quad (\text{fixed } S_a^F), \quad (3)$$

$$\sum_{\text{allowed } L_T^F} L = \lambda(L_T^I) \quad (\text{fixed } L_a^F).$$

The sums are over all possible multiplets of Ψ_F which can arise for a fixed final coupling of the active shell, S_a^F and L_a^F . In effect, Eqs. (3) state that the total intensity going into the coupling

S_a^F, L_a^F is distributed over allowed multiplets S_T^F, L_T^F according to the values of S and L . The $C(I, F)$ obey the sum rule^{16,17}

$$\sum_{\substack{\text{allowed} \\ S_a^F \text{ and } L_a^F}} [C(I, F)]^2 = 1. \quad (4)$$

Combining Eqs. (2) and (3), we have

$$\sum_{\substack{\text{allowed } S_a^F \text{ and } L_a^F \\ \text{for fixed } S_T^F \text{ and } L_T^F}} = N_a |\bar{\mu}_a|^2 [C(I, F)]^2 \lambda(S_T^I) \lambda(L_T^I). \quad (5a)$$

This means that the total cross section for photoexcitation from shell a which ends with S_a^F, L_a^F symmetry in shell a is equal to the square of the coefficient of fractional parentage for $S_a^F L_a^F$ symmetry times factors depending *only* on the initial state.

Finally, we obtain an expression that states that the *total* cross section for photoexcitation from shell a is equal to the number of electrons in shell a times the average one-electron matrix element (squared) for shell a times the *total* orbital and spin degeneracies of the *initial* state.

$$\frac{I1}{I2} = \frac{\lambda(S1_T^F)}{\lambda(S2_T^F)} \left[W \left(\begin{matrix} S_a^F & S_a^I & \frac{1}{2} \\ S_T^I & S1_T^F & S_p \end{matrix} \right) / W \left(\begin{matrix} S_a^F & S_a^I & \frac{1}{2} \\ S_T^I & S2_T^F & S_p \end{matrix} \right) \right]^2 \frac{\lambda(L1_T^F)}{\lambda(L2_T^F)} \left[W \left(\begin{matrix} L_a^F & L_a^I & l_a \\ L_T^I & L1_T^F & L_p \end{matrix} \right) / W \left(\begin{matrix} L_a^F & L_a^I & l_a \\ L_T^I & L2_T^F & L_p \end{matrix} \right) \right]^2. \quad (6)$$

The relative intensity is given by the ratio of space and spin degeneracies of the final multiplets *times* an additional factor of the ratio of Racah W coefficients to account for the recoupling of spin and space symmetries [from Eq. (2)]. It is this second factor which is often neglected. This rule *only* applies in the case of ionization from an open shell when other open shells are present. If the passive shells are totally symmetric, $S_p = 0$ and $L_p = A_1$, only one set of symmetries $S_T^F = S_a^F$ and $L_T^F = L_a^F$ are possible.

We note that rules (i) and (ii) permit us to compute relative cross sections for *classes* of transitions. Rule (i) compares the *total* intensity of emission from a given *shell* to that of another shell; rule (ii) compares the total intensity for a given *final symmetry* of the active shell to that of different final symmetries for the *same* active shell. In cases where there is more than one *final state* associated with this *final symmetry* of the active shell, one must use rule (iii) to compare the intensity of these final states.

As an example, let us apply the above rules to Fe^{2+} in FeO . The two open shells are t_2 and e . The d^6 ground state ψ_I is $t_2^4(3T_1)e^2(3A_2); 5T_2$ (as discussed in Table I). The possible final states ψ_F

$$\sum_{\substack{\text{all allowed final} \\ \text{states for ionization} \\ \text{from shell } a}} \sigma = N_a |\bar{\mu}_a|^2 \lambda(S_T^I) \lambda(L_T^I). \quad (5b)$$

We may now state the following rules which, sequentially applied, determine relative intensities of photoelectron peaks:

(i) *The dependence on which shell is ionized.* The ratio of the intensities summed over all final states ψ_F arising from ionization from shell a to those arising from shell b is N_a/N_b . This requires the assumption that the average transition moments are equal, $|\bar{\mu}_a| = |\bar{\mu}_b|^2$. This follows directly from Eq. (5b).

(ii) *The dependence on the final spin and orbital symmetries of the active shell a .* For ionization from shell a , the ratio of the intensities summed over all final states ψ_F arising from final symmetry $S1_a^F, L1_a^F$ of shell a to those arising from a different symmetry $S2_a^F, L2_a^F$ is $[C(I, F1_a)]^2 / [C(I, F2_a)]^2$. This follows directly from Eq. (5a).

(iii) *The dependence on the final state ψ_F .* For ionization from shell a and with final symmetry S_a^F, L_a^F of shell a , the ratio of the intensity of final state $\psi1_F (S1_T^F, L1_T^F)$ to $\psi2_F (S2_T^F, L2_T^F)$ is

are listed in Table II.

Rule (i) tells us that the sum of the intensities for states $\langle 1 \rangle$ and $\langle 2 \rangle$ (emission from shell e) divided by the sum of the intensities for states $\langle 3 \rangle, \langle 4 \rangle, \langle 5 \rangle, \langle 6 \rangle,$ and $\langle 7 \rangle$ (emission from shell t_2) will be $2/4 = \frac{1}{2}$, i.e.,

$$\frac{I(1) + I(2)}{I(3) + I(4) + I(5) + I(6) + I(7)} = \frac{1}{2}. \quad (7)$$

TABLE II. Possible final ion states for photoionization of (high spin d^6) Fe^{2+} in octahedral coordination.

S_a^I	L_a^I	S_a^F	L_a^F	S_p	L_p	$\Psi_F(S_T^F, L_T^F)$	State number
1	A_2	$\frac{1}{2}$	E	1	T_1	$4T_2(\frac{3}{2}, T_2)$	1
1	A_2	$\frac{1}{2}$	E	1	T_1	$4T_1(\frac{3}{2}, T_1)$	2
1	T_1	$\frac{3}{2}$	A_2	1	A_2	$6A_1(\frac{5}{2}, A_1)$	3
1	T_1	$\frac{3}{2}$	A_2	1	A_2	$4A_1(\frac{3}{2}, A_1)$	4
1	T_1	$\frac{1}{2}$	E	1	A_2	$4E(\frac{3}{2}, E)$	5
1	T_1	$\frac{1}{2}$	T_1	1	A_2	$4T_2(\frac{3}{2}, T_2)$	6
1	T_1	$\frac{1}{2}$	T_2	1	A_2	$4T_1(\frac{3}{2}, T_1)$	7

Since states $\langle 3 \rangle$ and $\langle 4 \rangle$ arise from the same final symmetry of the active shell, rule (ii) tells us how to relate the intensities for states $\langle 5 \rangle$, $\langle 6 \rangle$, and $\langle 7 \rangle$ to the *sum* of the intensities for states $\langle 3 \rangle$ and $\langle 4 \rangle$. We obtain

$$\frac{I(3)+I(4)}{I(5)} = \frac{[C(^3T_1, ^4A_2)]^2}{[C(^3T_1, ^2E)]^2} = \frac{\frac{1}{3}}{\frac{1}{6}} = 2, \quad \frac{I(3)+I(4)}{I(6)} = \frac{[C(^3T_1, ^4A_2)]^2}{[C(^3T_1, ^2T_1)]^2} = \frac{\frac{1}{3}}{\frac{1}{4}} = \frac{4}{3}, \quad \frac{I(3)+I(4)}{I(7)} = \frac{[C(^3T_1, ^4A_2)]^2}{[C(^3T_1, ^2T_2)]^2} = \frac{\frac{1}{3}}{\frac{1}{4}} = \frac{4}{3}. \quad (8)$$

TABLE III. Relative intensities of multiplet and crystal-field-split d -level photoionization peaks of high-spin transition-metal ions in octahedral coordination.

	Initial state	Final ion state	Intensity (arbitrary units)
d^1	$t_2^1(^2T_2)$	$t_2^0(^1A_1)$	1
d^2	$t_2^2(^3T_1)$	$t_2^1(^2T_2)$	1
d^3	$t_2^3(^4A_2)$	$t_2^2(^3T_1)$	1
d^4	$t_2^3(^4A_2)e^1(^2E); ^5E$	$t_2^3(^4A_2)$	1
d^5	$t_2^3(^4A_2)e^2(^3A_2); ^6A_1$	$t_2^2(^3T_1)e^1(^2E)$	$\left. \begin{matrix} ^4T_2 \\ ^4T_1 \end{matrix} \right\} \frac{3}{2}$
		$t_2^3(^4A_2)e^1(^2E); ^5E$	$\frac{2}{2}$
		$t_2^2(^3T_1)e^2(^3A_2); ^5T_2$	3
d^6	$t_2^4(^3T_1)e^2(^3A_2); ^5T_2$	$t_2^4(^3T_1)e^1(^2E)$	$\left. \begin{matrix} ^4T_2 \\ ^4T_1 \end{matrix} \right\} 1$
		$t_2^3(^4A_2)e^2(^3A_2)$	$\left. \begin{matrix} ^6A_1 \\ ^4A_1 \end{matrix} \right\} \frac{6}{5}$
		$t_2^3(^2E)e^2(^3A_2); ^4E$	$\frac{2}{3}$
		$t_2^3(^2T_1)e^2(^3A_2); ^4T_2$	1
		$t_2^3(^2T_2)e^2(^3A_2); ^4T_1$	1
		$t_2^5(^2T_2)e^1(^2E)$	$\left. \begin{matrix} ^3T_2 \\ ^3T_1 \end{matrix} \right\} 1$
		$t_2^4(^3T_1)e^2(^3A_2)$	$\left. \begin{matrix} ^5T_2 \\ ^3T_2 \end{matrix} \right\} \frac{5}{2}$
d^7	$t_2^5(^2T_2)e^2(^3A_2); ^4T_1$	$t_2^4(^1T_2)e^2(^3A_2)$	3T_1 1
		$t_2^4(^1E)e^2(^3A_2)$	3E $\frac{2}{3}$
		$t_2^4(^1A_1)e^2(^3A_2)$	3A_2 $\frac{1}{3}$
		$t_2^6(^1A_1)e^1(^2E)$	2
		$t_2^5(^2T_2)e^2(^3A_2)$	$\left. \begin{matrix} ^4T_1 \\ ^2T_1 \end{matrix} \right\} 4$
		$t_2^5(^2T_2)e^2(^3A_2)$	2
d^8	$t_2^6(^1A_1)e^3(^2E)$	$t_2^6(^1A_1)e^2(^3A_2)$	$\frac{3}{2}$
		$t_2^6(^1A_1)e^2(^1E)$	1
		$t_2^6(^1A_1)e^2(^1A_1)$	$\frac{1}{2}$
		$t_2^5(^2T_2)e^3(^2E)$	$\left. \begin{matrix} ^3T_2 \\ ^3T_1 \\ ^1T_2 \\ ^1T_1 \end{matrix} \right\} \frac{9}{4}$
d^{10}	$t_2^6(^1A_1)e^4(^1A_1)$	$t_2^6(^1A_1)e^3(^2E)$	4
		$t_2^5(^2T_2)e^4(^1A_1)$	6

TABLE IV. Relative intensities of d -level photoionization peaks of high-spin transition-metal ions in tetrahedral coordination.

	Initial state	Final ion state	Intensity (arbitrary units)
d^1	$e^1(^2E)$	$e^0(^1A_1)$	1
d^2	$e^2(^3A_2)$	$e^1(^2E)$	1
d^3	$e^2(^3A_2)t_{\frac{1}{2}}(^2T_2); ^4T_1$	$e^2(^3A_2)$	1
		$e^1(^2E)t_{\frac{1}{2}}(^2T_2) \begin{cases} ^3T_2 \\ ^3T_1 \end{cases}$	1 1
d^4	$e^2(^3A_2)t_{\frac{1}{2}}(^3T_1); ^5T_2$	$e^2(^3A_2)t_{\frac{1}{2}}(^2T_2) \quad ^4T_1$	2
		$e^1(^2E)t_{\frac{1}{2}}(^3T_1) \begin{cases} ^4T_2 \\ ^4T_1 \end{cases}$	1 1
d^5	$e^2(^3A_2)t_{\frac{3}{2}}(^4A_2); ^6A_1$	same as octahedral case	
d^6	$e^3(^2E)t_{\frac{3}{2}}(^4A_2); ^5E$	$e^3(^2E)t_{\frac{3}{2}}(^3T_1) \begin{cases} ^4T_2 \\ ^4T_1 \end{cases}$	$\frac{3}{2}$ $\frac{3}{2}$
		$e^2(^3A_2)t_{\frac{3}{2}}(^4A_2) \begin{cases} ^6A_1 \\ ^4A_1 \end{cases}$	$\frac{6}{5}$ $\frac{3}{10}$
		$e^2(^1E)t_{\frac{3}{2}}(^4A_2); ^4E$	1
		$e^2(^1A_1)t_{\frac{3}{2}}(^4A_2); ^4A_2$	$\frac{1}{2}$
d^7	$e^4(^1A_1)t_{\frac{3}{2}}(^4A_2); ^4A_2$	$e^4(^1A_1)t_{\frac{3}{2}}(^3T_1); ^3T_1$	3
		$e^3(^2E)t_{\frac{3}{2}}(^4A_2) \begin{cases} ^5E \\ ^3E \end{cases}$	$\frac{5}{2}$ $\frac{3}{2}$

Rule (iii) tells us the relationship between the intensity of state (1) to that of state (2), and the relationship between the intensity of state (3) to that of state (4). We obtain

$$\frac{I(1)}{I(2)} = \frac{\lambda(\frac{3}{2})}{\lambda(\frac{3}{2})} \frac{W^2 \begin{pmatrix} \frac{1}{2} & 1 & \frac{1}{2} \\ 2 & \frac{3}{2} & 1 \\ \frac{1}{2} & 1 & \frac{1}{2} \end{pmatrix}}{W^2 \begin{pmatrix} \frac{1}{2} & 1 & \frac{1}{2} \\ 2 & \frac{3}{2} & 1 \\ \frac{1}{2} & 1 & \frac{1}{2} \end{pmatrix}} \frac{\lambda(T_2)}{\lambda(T_1)} \frac{W^2 \begin{pmatrix} E & A_2 & E \\ T_2 & T_2 & T_1 \\ E & A_2 & E \end{pmatrix}}{W^2 \begin{pmatrix} E & A_2 & E \\ T_2 & T_1 & T_1 \end{pmatrix}} = \frac{4}{4} \times \frac{1}{12} \times \frac{3}{3} \times \frac{1}{6} = 1, \quad (9)$$

$$\frac{I(3)}{I(4)} = \frac{\lambda(\frac{5}{2})}{\lambda(\frac{3}{2})} \frac{W^2 \begin{pmatrix} \frac{3}{2} & 1 & \frac{1}{2} \\ 2 & \frac{5}{2} & 1 \\ \frac{3}{2} & 1 & \frac{1}{2} \end{pmatrix} \lambda(A_1)}{W^2 \begin{pmatrix} \frac{3}{2} & 1 & \frac{1}{2} \\ 2 & \frac{3}{2} & 1 \\ \frac{3}{2} & 1 & \frac{1}{2} \end{pmatrix} \lambda(A_1)} \frac{W^2 \begin{pmatrix} A_2 & T_1 & T_2 \\ T_1 & A_1 & A_2 \\ A_2 & T_1 & T_2 \end{pmatrix}}{W^2 \begin{pmatrix} A_2 & T_1 & T_2 \\ T_2 & A_1 & A_2 \end{pmatrix}} = \frac{6}{4} \times \frac{1}{120} \times \frac{1}{1} \times \frac{1}{3} = 9.$$

Combining Eqs. (7)–(9), we have six linear equations in seven unknowns. We therefore solve for six unknowns in terms of the seventh. If we use $I(1) \equiv 1$ as the seventh unknown we obtain the results shown in Table III for d^6 .

In the case that the active shell is closed in the initial state, ($S_a^I = 0$, $L_a^I = A_1$, $S_a^F = \frac{1}{2}$, and $L_a^F = l_a$) an important simplification of (iii) arises. Using the symmetry properties of the W coefficients for permutation of indices together with Eq. (11.12) of

Ref. 15 and Eq. (4.2) of Ref. 8, we have

$$\left[W \begin{pmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ S_T^I & S_T^F & S_p \end{pmatrix} \right]^{-2} = \lambda(\frac{1}{2}) \lambda(S_T^I),$$

$$\left[W \begin{pmatrix} l_a & A_1 & l_a \\ L_T^I & L_T^F & L_p \end{pmatrix} \right]^{-2} = \lambda(l_a) \lambda(L_T^I);$$

where the values are independent of S_T^F and L_T^F . Equation (6) then reduces to the ratio of multi-

plicities:

$$\frac{I_1}{I_2} = \frac{\lambda(S1^F_T) \lambda(L1^F_T)}{\lambda(S2^F_T) \lambda(L2^F_T)}. \quad (6a)$$

Because of their practical interest, we apply the formulas described above to high-spin transition-metal ions as encountered in a crystal-field treat-

ment of ionic crystals. The relative intensities of the various d -level photoelectron peaks are given in Table III and IV for ions in octahedral, O_h , and tetrahedral, T_d , coordination. Values of the W coefficients for these two groups are the same and are given by Griffith.⁸ The W coefficients required for spin are tabulated by Rotenberg *et al.*¹⁸

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