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Relative Intensities of the Ligand-field Transition Bands in Tetragonal Chromium(III) and Cobalt(III) Complexes

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On the basis of a tetragonal (D_{4h}) model, the procedures for calculating the vibronically induced transition moment have been described, and a correlation in the band intensity between two nondegenerate transition components (A_2 and B_2) has been shown. The correlation has then been applied to understanding the characteristic absorption spectra of the *trans*-$[CrClF(NH_3)_4]^+$ and *trans*-$[CrF_2(NH_3)_4]^+$ complexes. Furthermore, an effect upon the band intensity caused by the configuration interactions among the E states has been proposed in order to explain the characteristic spectra of the *trans*-$[Co(C_2O_4)_2(py)_2]^-$ and *trans*-$[Co(CO_3)_2(py)_2]^-$ complexes. This treatment has been applied also to the spectra of cobalt(III) complexes with C_{4v} symmetry.

It is well known that the absorption spectra of *trans* complexes of the $[MX_2(NH_3)_4]^+$ type (M=Co and Cr; X=Cl and Br) exhibit marked splittings in the first absorption bands, this fact being well understood on the basis of the ligand-field theory.1) Recently, it has been reported that the absorption spectra of a few chromium(III) complexes, such as *trans*-$[Cr(OH)_2(NH_3)_4]^+$, *trans*-$[CrF(OH)(NH_3)_4]^+$ and *trans*-$[CrF_2(NH_3)_4]^+$, show marked splittings in the second absorption bands, while the first bands are at the same time poorly or clearly split, the assignments of the bands being made on the basis of the angular overlap model.2) Similar splittings in the second absorption bands have been reported with the *trans* complexes of the $[Co(OO)_2(py)_2]^-$ type (OO represents CO_3^{2-} or $C_2O_4^{2-}$), and the assignment of the split bands has been attempted by means of the angular overlap model.3) These interesting aspects of the behavior of the splittings suggest that there is a certain correlation among the intensities of the split bands.

Early works on the band intensities of the ligand-field transitions were carried out by several workers4–8) with respect to cubic complexes. Griffith9) first applied the so-called tensor method to the calculation of the intensity, and then several workers10–12) used the method for the parameterization of the band intensity with respect to complexes of rare earth elements.

There have also been a few investigations of the band intensity with respect to complexes with symmetry lower than the cubic. Dubicki and Day13) measured the temperature dependence of the intensity of the ^4E_g ($^4T_{2g}$ parentage) band for *trans*-$[CrX_2(en)_2]ClO_4$ (X=Br or Cl) and found that the ^4E_g band borrows its intensity from the charge-transfer (CT) bands by means of the vibronic mechanism. In their treatment, however, only the admixtures of the excited ligand-field states with the ligand-to-metal CT states were taken into consideration.

The purpose of the present work was to find the correlation of the band intensities in a tetragonal cobalt(III) or a chromium(III) complex by applying the treatment of Dubicki and Day, with some modifications. That is, all kinds of admixtures of the ligand-field states with the CT states were considered in our treatment. In the first part of this paper, the mathematic formulation of the relative intensities of the ligand-field transitions will be described according to a model distorted weakly from a regular octahedron, and then the resultant formula will be proved by means of the spectral data of a few chromium(III) complexes. In the later part, the effect due to configuration interactions among the E states upon the band intensity will be discussed in connection with the spectral data for several cobalt(III) complexes.

Experimental

The *trans*-$[CoCl_2(NH_3)_4]Cl$, $[CoCl(NH_3)_5]Cl_2$, $[CoBr(NH_3)_5]Br_2$ and $[Cr(NH_3)_6](ClO_4)_3$ complexes were synthesized by the usual methods, while the *trans*-$[Co(CN)_2(NH_3)_4]Cl$ complex was prepared according to the literature.14) The measurements of the absorption spectra in an aqueous solution were carried out with a Hitachi 323 recording spectrophotometer at room temperature. However, the spectrum of *trans*-$[CoCl_2(NH_3)_4]Cl$ was measured in a DMF solution. The absorption spectral data of the *trans*-$[CrF_2(NH_3)_4]^+$, *trans*-$[CrClF(NH_3)_4]^+$ and $[CoCl(CN)_5]^{3-}$ complexes were cited from the literature.2,15) The curve analysis3) of the absorption spectra was carried out at the Data Processing Center, Kanazawa University.

Methods of Calculation

Matrix Elements. The ligand-field transition between even-parity states is induced through odd-parity vibrations. The dipole-moment matrix element for the A'→B' transition is given by6)

$$\langle A'|\mathbf{P}|B'\rangle = \sum_{D}\frac{\langle A|\mathbf{P}|D\rangle\langle D|\mathbf{H}_v|B\rangle}{E_B-E_D} + \sum_{C}\frac{\langle B|\mathbf{P}|C\rangle\langle C|\mathbf{H}_v|A\rangle}{E_A-E_C}, \qquad (1)$$

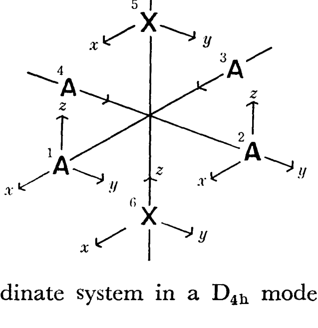

Fig. 1. Coordinate system in a D_{4h} model.

where the first term expresses the part caused by the admixtures of the D odd-parity states with the B excited-ligand-field states, and the second term, the part caused by the admixtures of the C odd-parity states with the A ground state. The $\mathbf{H}_v$ symbol denotes the vibrational Hamiltonian in a tetragonal complex. By adopting the coordinate system as in Fig. 1, $\mathbf{H}_v$ is written as follows:[16)]

$$
\begin{aligned}
\mathbf{H}_v(\mathrm{E_u^x}(\mathrm{a})) &= (x_5+x_6-2x_0)(\partial/\partial x)(V_5+V_6)/2,\\
\mathbf{H}_v(\mathrm{E_u^x}(\mathrm{b})) &= (x_2+x_4-2x_0)(\partial/\partial x)(V_2+V_4)/2, \qquad (2)\\
\mathbf{H}_v(\mathrm{E_u^x}(\mathrm{c})) &= (x_1+x_3-2x_0)(\partial/\partial x)(V_1+V_3)/2,\\
\mathbf{H}_v(\mathrm{A_{2u}}(\mathrm{a})) &= (z_1+z_2+z_3+z_4-4z_0),\\
&\quad \times(\partial/\partial z)(V_1+V_2+V_3+V_4)/4,\\
\mathbf{H}_v(\mathrm{A_{2u}}(\mathrm{b})) &= (z_5+z_6-2z_0)(\partial/\partial z)(V_5+V_6)/2,\\
\mathbf{H}_v(\mathrm{B_{2u}}) &= (z_1+z_3-z_2-z_4)(\partial/\partial z)(V_1+V_3-V_2-V_4)/4,
\end{aligned}
$$

where $V_j(j=1—6)$ represents the ligand-field potential at the jth position, and where x_j and z_j denote the nuclear displacements.

In a model of octahedron with weak tetragonal distortion, the excited-ligand-field states in a Co(III) complex are usually approximated by[8)]

$$
\begin{aligned}
|\mathrm{E_g^x}(\mathrm{a})\rangle &= \{(yz)(y^2-z^2)\},\\
|\mathrm{E_g^x}(\mathrm{b})\rangle &= \{(yz)(x^2)\}, \qquad (3)\\
|\mathrm{A_{2g}}\rangle &= \{(xy)(x^2-y^2)\},\\
|\mathrm{B_{2g}}\rangle &= \{(xy)(z^2)\}.
\end{aligned}
$$

In the above determinants, each state is represented by a d-orbital component of the t_{2g} "hole" (yz or xy) and a d-orbital component of the occupied e_g orbital (y^2-z^2, x^2, x^2-y^2 or z^2). Thus, the wave function for $\mathrm{E_g^x}(\mathrm{a})$ is:

$$
\begin{aligned}
\{(yz)(y^2-z^2)\} = \{|\cdots\overset{+}{(yz)}\overset{-}{(y^2-z^2)}\overset{+}{(zx)}\overset{-}{(zx)}\overset{+}{(xy)}\overset{-}{(xy)}|\\
+|\cdots\overset{+}{(y^2-z^2)}\overset{-}{(yz)}\cdots|\}/\sqrt{2}.
\end{aligned}
$$

On the other hand, there are two CT states which can be used as the odd-parity states; one is that of the ligand-to-metal charge transfer (LMCT), and the other, the metal-to-ligand charge transfer (MLCT). The CT states obtained by the use of the symmetry ligand orbitals listed in Table 1 are given in Table 2.

Our attention was given to the matrix elements in (1) in order to determine the CT states which contribute greatly to the intensities of the ligand-field transition bands; the Wigner-Eckart theorem[17)] was useful in finding the non-vanishing matrix elements (the vibronic selection rule used in the calculation is given in Table 3). Among the non-vanishing matrix elements thus found, the elements such as $\langle y^2-z^2|\boldsymbol{\Gamma}|\pi_\eta\rangle$, $\langle y^2-z^2|\boldsymbol{\Gamma}|\sigma_\alpha\rangle$ and $\langle xy|\boldsymbol{\Gamma}|\pi_\alpha\rangle$ ($\boldsymbol{\Gamma}$ represents $\mathbf{H}_v$ and $\mathbf{P}$) were considered to have small values because of the poor overlap integrals of the metal orbitals with the ligand orbitals. Furthermore, when the ligand-field potentials in a $\mathbf{H}_v$ lay outside the positions of the ligand orbitals used, the matrix elements associated with the $\mathbf{H}_v$ were considered to be quite small because of the three-centered integral. Since the numerators in (1) were expressed by products of the matrix elements of the $\mathbf{P}$ and those of the $\mathbf{H}_v$, the contribution from a product to the induced dipole moment was regarded to be negligible, at least when either of the two matrix elements was extraordinarily small.

TABLE 1. SYMMETRY LIGAND ORBITALS IN THE D_{4h} POINT GROUP

Symmetry	Orbitals
E_u	$\sigma_\alpha=(\sigma_1+\sigma_3)/\sqrt{2}$ $\sigma_\beta=(\sigma_2+\sigma_4)/\sqrt{2}$
E_u	$\pi_\alpha=(x_5+x_6)/\sqrt{2}$ $\pi_\beta=(y_5+y_6)/\sqrt{2}$
E_u	$\pi_\xi=(x_2+x_4)/\sqrt{2}$ $\pi_\eta=(y_1+y_3)/\sqrt{2}$
A_{2u}	$\sigma_\gamma=(\sigma_5+\sigma_6)/\sqrt{2}$
A_{2u}	$\pi_\gamma=(z_1+z_2+z_3+z_4)/2$
B_{2u}	$\pi_\zeta=(z_1-z_2+z_3-z_4)/2$

TABLE 2. ODD-PARITY CHARGE-TRANSFER STATES IN THE TETRAGONAL Co(III) COMPLEX

Representation	LMCT	MLCT
$\vert E_u^x\rangle$	$\{(\sigma_\alpha)(y^2-z^2)\}$	$\{(zx)(\sigma_\gamma)\}$
	$\{(\sigma_\alpha)(x^2)\}$	$\{(xy)(\sigma_\beta)\}$
	$\{(\pi_\xi)(y^2-z^2)\}$	$\{(xy)(\pi_\eta)\}$
	$\{(\pi_\xi)(x^2)\}$	$\{(zx)(\pi_\gamma)\}$
	$\{(\pi_\alpha)(y^2-z^2)\}$	$\{(zx)(\pi_\zeta)\}$
	$\{(\pi_\alpha)(x^2)\}$	$\{(xy)(\pi_\beta)\}$
$\vert A_{2u}\rangle$	$\{(\sigma_\gamma)(z^2)\}$	$[\{(yz)(\sigma_\beta)\}+\{(zx)(\sigma_\alpha)\}]/2$
	$\{(\pi_\gamma)(z^2)\}$	$[\{(yz)(\pi_\eta)\}+\{(zx)(\pi_\xi)\}]/2$
	$\{(\pi_\zeta)(x^2-y^2)\}$	$[\{(yz)(\pi_\beta)\}+\{(zx)(\pi_\alpha)\}]/2$
$\vert B_{2u}\rangle$	$\{(\sigma_\gamma)(x^2-y^2)\}$	$[\{(yz)(\sigma_\beta)\}-\{(zx)(\sigma_\alpha)\}]/2$
	$\{(\pi_\gamma)(x^2-y^2)\}$	$[\{(yz)(\pi_\eta)\}-\{(zx)(\pi_\xi)\}]/2$
	$\{(\pi_\zeta)(z^2)\}$	$[\{(yz)(\pi_\beta)\}-\{(zx)(\pi_\alpha)\}]/2$

TABLE 3. VIBRONIC SELECTION RULES IN TETRAGONAL Co(III) AND Cr(III) COMPLEXES

	Transition	**P**	Admixture with excited state		Admixture with ground state	
			$\mathbf{H}_v$	D	$\mathbf{H}_v$	C
Co	${}^1A_{1g}\rightarrow{}^1A_{2g}$	E_u	E_u	E_u	E_u	E_u
	${}^1A_{1g}\rightarrow{}^1B_{2g}$	E_u	E_u	E_u	E_u	E_u
	${}^1A_{1g}\rightarrow{}^1E_g$	A_{2u}	E_u	A_{2u}	E_u	E_u
		E_u	A_{2u}	E_u	A_{2u}	A_{2u}
			B_{2u}	E_u	B_{2u}	B_{2u}
Cr	${}^4B_{1g}\rightarrow{}^4A_{2g}$	E_u	E_u	E_u	E_u	E_u
	${}^4B_{1g}\rightarrow{}^4B_{2g}$	E_u	E_u	E_u	E_u	E_u
	${}^4B_{1g}\rightarrow{}^4E_g$	A_{2u}	E_u	B_{2u}	E_u	E_u
		E_u	A_{2u}	E_u	B_{2u}	A_{2u}
			B_{2u}	E_u	A_{2u}	B_{2u}

Using the curled determinants, the states in a Cr(III) complex were easily correlated with the corresponding states in a Co(III) complex. The correlation table thus obtained is listed in Table 4. The states belonging to the A and B representations in the Co(III) complex correspond in turn to the states belonging to the B and A representations in the Cr(III) complex, while

Table 4. Correlation table of representations in tetragonal Co(III) and Cr(III) complexes

O_h Co(III) Complex	D_{4h} Co(III) Complex	D_{4h} Cr(III) Complex
$T_{1g}(t_{2g}{}^5e_g)$	E_g	$E_g(t_{2g}{}^2e_g)$
	A_{2g}	$B_{2g}(t_{2g}{}^2e_g)$
$T_{2g}(t_{2g}{}^5e_g)$	E_g	$E_g(t_{2g}{}^2e_g)$
	B_{2g}	$A_{2g}(t_{2g}{}^2e_g)$
$A_{1g}(t_{2g}{}^6)$	A_{1g}	$B_{1g}(t_{2g}{}^3)$
T_{1u}(CT)	E_u	E_u(CT)
	A_{2u}	B_{2u}(CT)
T_{2u}(CT)	E_u	E_u(CT)
	B_{2u}	A_{2u}(CT)

the states belonging to the E representation are common to both metal complexes.

Fenske[8] has stated that the LM(t_{2g})CT transitions make no contribution to the intensities of the ligand-field transition bands. On this basis, the CT states listed in Table 2 were used for a Cr(III) complex only by exchanging A for B (or B for A). The intensity calculation for Cr(III) complexes was performed in the same way as that for Co(III) complexes.

Relative Intensities. *Admixture with LMCT*: In the case of Co(III) complexes, the matrix elements of the $^1A_{1g}\rightarrow{}^1A_{2g}$ transition were found to be the same as those of the $^1A_{1g}\rightarrow{}^1B_{2g}$ transition, although the coefficients differed from one another (see Table 5). On the basis of this result, in the case of a complex with only a σ-donating ligand such as NH_3 in the xy plane, the ratio of the oscillator strengths[18] of the $^1A_{2g}$ transition, $f(A_2)$, to that of the $^1B_{2g}$ transition, $f(B_2)$, was expressed by

$$\frac{f(A_2)}{f(B_2)}=k\frac{E(A_2)}{E(B_2)}\times\left(\frac{E(\mathrm{CT})-E(B_2)}{E(\mathrm{CT})-E(A_2)}\right)^2. \tag{4}$$

In this equation, $E(A_2)$, $E(B_2)$, and E(CT) denote energy corresponding to each transition, and k is a coefficient, found to be 3 in this case. Hereinafter, the mechanism associated with L(σ)MCT (or ML(σ)CT) will be called the L(σ)-vibronic mechanism.

As is shown in Table 5, two L(π)MCT participated in each transition through the vibronic mechanism (hereinafter called the L(π)-vibronic mechanism); for instance, with regard to the $^1A_{2g}$ transition, the $\langle x^2|\mathbf{P}|\pi_\xi\rangle$ and $\langle y^2-z^2|\mathbf{P}|\pi_\xi\rangle$ dipole moments appeared in the summation of the first term in (1). From the differences in the normalization constants of the (y^2-z^2) and (x^2) orbitals, it can easily be shown that

$$\langle y^2-z^2|\mathbf{P}|\pi_\xi\rangle=\sqrt{3}\langle x^2|\mathbf{P}|\pi_\xi\rangle. \tag{5}$$

On this basis, if the denominators in (1) were replaced by a mean value of the L(π)MCT transition energies, the oscillator strengths in this L(π)-vibronic mechanism were evaluated by adding the two products of the matrix elements; consequently, the same equation as (4) was obtained, with the coefficient of 3/5. Similar equations were also derived between the $f(E_g(a))$ of the $^1E_g(a)$ and the $f(E_g(b))$ of the $^1E_g(b)$ transitions in both the L(σ)- and L(π)-vibronic mechanisms.

Admixture with MLCT: As is shown in Table 5, the matrix elements of the $^1T_{1g}$ parentage bands dif-

Table 5. Non-vanishing matrix elements

$\langle B|\mathbf{H}_v(E_u^y)|D(E_u^x)\rangle\langle D(E_u^x)|\mathbf{P}(E_u^x)|A\rangle$

	$A_{1g}\rightarrow A_{2g}$	$A_{1g}\rightarrow B_{2g}$
D : LMCT	$(-\sqrt{6}/2)\langle xy|\mathbf{H}_v|\sigma_\alpha\rangle\langle x^2|\mathbf{P}|\sigma_\alpha\rangle$	$(\sqrt{2}/2)\langle xy|\mathbf{H}_v|\sigma_\alpha\rangle\langle x^2|\mathbf{P}|\sigma_\alpha\rangle$
	$(-\sqrt{6}/2)\langle xy|\mathbf{H}_v|\pi_\xi\rangle\langle x^2|\mathbf{P}|\pi_\xi\rangle$	$(\sqrt{2}/2)\langle xy|\mathbf{H}_v|\pi_\xi\rangle\langle x^2|\mathbf{P}|\pi_\xi\rangle$
	$(\sqrt{2}/2)\langle xy|\mathbf{H}_v|\pi_\xi\rangle\langle y^2-z^2|\mathbf{P}|\pi_\xi\rangle$	$(\sqrt{6}/2)\langle xy|\mathbf{H}_v|\pi_\xi\rangle\langle y^2-z^2|\mathbf{P}|\pi_\xi\rangle$
D : MLCT	$\sqrt{2}\langle x^2-y^2|\mathbf{H}_v|\sigma_\beta\rangle\langle\sigma_\beta|\mathbf{P}|xy\rangle$	$\sqrt{2}\langle z^2|\mathbf{H}_v|\sigma_\beta\rangle\langle\sigma_\beta|\mathbf{P}|xy\rangle$
	$\sqrt{2}\langle x^2-y^2|\mathbf{H}_v|\pi_\eta\rangle\langle\pi_\eta|\mathbf{P}|xy\rangle$	$\sqrt{2}\langle z^2|\mathbf{H}_v|\pi_\eta\rangle\langle\pi_\eta|\mathbf{P}|xy\rangle$

$\langle B(E_g^x)|\mathbf{H}_v(E_u^y)|D(A_{2u})\rangle\langle D(A_{2u})|\mathbf{P}(A_{2u})|A\rangle$[a]

	$A_{1g}\rightarrow E_g(a)$	$A_{1g}\rightarrow E_g(b)$
D : LMCT	$(\sqrt{6}/2)\langle yz|\mathbf{H}_v|\sigma_\gamma\rangle\langle z^2|\mathbf{P}|\sigma_\gamma\rangle$	$(\sqrt{2}/2)\langle yz|\mathbf{H}_v|\sigma_\gamma\rangle\langle z^2|\mathbf{P}|\sigma_\gamma\rangle$
	$(\sqrt{6}/2)\langle yz|\mathbf{H}_v|\pi_\gamma\rangle\langle z^2|\mathbf{P}|\pi_\gamma\rangle$	$(\sqrt{2}/2)\langle yz|\mathbf{H}_v|\pi_\gamma\rangle\langle z^2|\mathbf{P}|\pi_\gamma\rangle$
	$(\sqrt{2}/2)\langle yz|\mathbf{H}_v|\pi_\zeta\rangle\langle x^2-y^2|\mathbf{P}|\pi_\zeta\rangle$	$-(\sqrt{6}/2)\langle yz|\mathbf{H}_v|\pi_\zeta\rangle\langle x^2-y^2|\mathbf{P}|\pi_\zeta\rangle$
D : MLCT	$1/\sqrt{2}\langle y^2-z^2|\mathbf{H}_v|\sigma_\beta\rangle\{\langle\sigma_\beta|\mathbf{P}|yz\rangle+\langle\sigma_\alpha|\mathbf{P}|zx\rangle\}$	$(1/\sqrt{2})\langle x^2|\mathbf{H}_v|\sigma_\beta\rangle\{\langle\sigma_\beta|\mathbf{P}|yz\rangle+\langle\sigma_\alpha|\mathbf{P}|zx\rangle\}$
	$1/\sqrt{2}\langle y^2-z^2|\mathbf{H}_v|\pi_\beta\rangle\{\langle\pi_\beta|\mathbf{P}|yz\rangle+\langle\pi_\alpha|\mathbf{P}|zx\rangle\}$	$(1/\sqrt{2})\langle x^2|\mathbf{H}_v|\pi_\beta\rangle\{\langle\pi_\beta|\mathbf{P}|yz\rangle+\langle\pi_\alpha|\mathbf{P}|zx\rangle\}$

$\langle B(E_g^x)|\mathbf{H}_v(A_{2u},B_{2u})|D(E_u^y)\rangle\langle D(E_u^y)|\mathbf{P}(E_u^y)|A\rangle$

	$A_{1g}\rightarrow E_g(a)$	$A_{1g}\rightarrow E_g(b)$
D : LMCT	$(\sqrt{6}/2)\langle yz|\mathbf{H}_v|\sigma_\beta\rangle\langle y^2|\mathbf{P}|\sigma_\beta\rangle$	$(\sqrt{2}/2)\langle yz|\mathbf{H}_v|\sigma_\beta\rangle\langle y^2|\mathbf{P}|\sigma_\beta\rangle$
	$(\sqrt{6}/2)\langle yz|\mathbf{H}_v|\pi_\beta\rangle\langle y^2|\mathbf{P}|\pi_\beta\rangle$	$(\sqrt{2}/2)\langle yz|\mathbf{H}_v|\pi_\beta\rangle\langle y^2|\mathbf{P}|\pi_\beta\rangle$
	$(\sqrt{2}/2)\langle yz|\mathbf{H}_v|\pi_\beta\rangle\langle z^2-x^2|\mathbf{P}|\pi_\beta\rangle$	$-(\sqrt{6}/2)\langle yz|\mathbf{H}_v|\pi_\beta\rangle\langle z^2-x^2|\mathbf{P}|\pi_\beta\rangle$
D : MLCT	$\sqrt{2}\langle y^2-z^2|\mathbf{H}_v|\sigma_\gamma\rangle\langle\sigma_\gamma|\mathbf{P}|yz\rangle$	$\sqrt{2}\langle x^2|\mathbf{H}_v|\sigma_\gamma\rangle\langle\sigma_\gamma|\mathbf{P}|yz\rangle$
	$\sqrt{2}\langle y^2-z^2|\mathbf{H}_v|\pi_\gamma\rangle\langle\pi_\gamma|\mathbf{P}|yz\rangle$	$\sqrt{2}\langle x^2|\mathbf{H}_v|\pi_\gamma\rangle\langle\pi_\gamma|\mathbf{P}|yz\rangle$
	$\sqrt{2}\langle y^2-z^2|\mathbf{H}_v|\pi_\zeta\rangle\langle\pi_\zeta|\mathbf{P}|yz\rangle$	$\sqrt{2}\langle x^2|\mathbf{H}_v|\pi_\zeta\rangle\langle\pi_\zeta|\mathbf{P}|yz\rangle$

a) $\langle B(E_g^x)|\mathbf{P}(E_u^y)|C(B_{2u})\rangle\langle C(B_{2u})|\mathbf{H}_v(B_{2u})|A\rangle$ is included in this case.

fered from those of the $^1T_{2g}$ parentage bands, though every coefficient was equal to $\sqrt{2}$ in both parentages. However, we could also show similar relations to (5) between the matrix elements in the transitions to the nondegenerate states (and between those in the transitions to the degenerate states). The same equations as (4) could be derived in both the L(σ)- and L(π)-vibronic mechanisms, where the k values were equal to 3.

In the case of the Cr(III) complexes, the resultant equations were also expressed by (4); however, the A_2 subscript (or B_2) had to be exchanged with B_2 (or A_2).

Results and Discussion

Nature of the A_2 and B_2 Transitions. Only a half of the calculated matrix elements of the first term in (1) are listed in Table 5, because the other half can easily be obtained by considering the symmetry. The matrix elements concerning the second term in (1) were obtained by exchanging the $\mathbf{P}$ in the first term with the $\mathbf{H}_v$.

From the present model of weak tetragonal distortion, it can be predicted that the intensities of the transitions to the nondegenerate excited states are independent of the ligand on the z axis (X in Fig. 1), since they are only related with the ligand orbitals on the xy plane (π_ξ, π_η, σ_α, and σ_β) through the E odd-vibrations occurring on the plane. This prediction is confirmed by the fact that the intensities of the $^4A_{2g}$ band in *trans*-$[CrX_2(NH_3)_4]^+$ ($X=F^-$ and OH^-), whose tetragonal distortions seem to be small, are almost invariable, in comparison with the considerable variations in the intensities of the ^4E_g(b) bands. Moreover, the fact that the intensities of the $^4A_{2g}$ (or $^4B_{2g}$) bands are nearly equal to one-third of the intensity of the $^4T_{1g}$ (or $^4T_{2g}$) band in $[Cr(NH_3)_6]^{3+}$ supports the prediction from the present model.

The present model is applicable to the problem of A_2 and B_2 transitions in a C_{4v} complex for the following reason: The wave functions associated with the ligand orbitals on the xy plane are the same as those in the D_{4h} complexes. According to the ligand-field theory,19) the ligand-field potential in a C_{4v} complex can be divided into two potentials in D_{4h} symmetry:

$$U_{C_{4v}} = U_{D_{4h}}(A_{2u}) + U_{D_{4h}}(A_{1g}).$$

The first term can mix the states coming from even-parity states in D_{4h} with the states coming from odd-parity states under static conditions, and contributes only to the intensities of the E bands. On the other hand, the second term can mix the states coming from the odd-parity states in D_{4h} symmetry under vibronic conditions. In fact, in *trans*-$[CrF(OH)(NH_3)_4]^+$ the above-mentioned prediction holds.

Application to Tetragonal Complexes. As for Co(III) complexes, no absorption spectrum has been reported to exhibit distinct splittings in both the first and second absorption band regions. However, as for Cr(III) complexes, it has been reported that the absorption spectra in *trans*-$[CrF_2(NH_3)_4]^+$ and *trans*-$[CrClF(NH_3)_4]^+$ 2) show such splittings. Now, let us apply (4) to these complexes. Note that, in this application, the A_2 and B_2 subscripts in (4) must be exchanged with B_2 and A_2 respectively. The E(CT) values in these complexes are assumed to be *ca.* 55000 cm^{-1}, while the E(CT) value in $[Cr(NH_3)_6](ClO_4)_3$ lies above 52000 cm^{-1}. The $f(B_2)/f(A_2)$ value in (4) was calculated from the numerical data listed in Table 6, and found to be 1.36. On the other hand, the ratio calculated from the observed $f(B_2)$ and $f(A_2)$ values was 1.24 for the difluoro complex. As for *trans*-$[CrClF(NH_3)_4]^+$, the value calculated from the data of Table 6 was 1.52, and the value calculated from the observed data was 1.34, the two being roughly equal.

The angular overlap model20) suggested that the extent of the tetragonal distortion due to M-L σ-bonding is expressed by the difference between two antibonding energies, $\sqrt{3}/4\{\langle z^2|\mathbf{A}|z^2\rangle-\langle x^2-y^2|\mathbf{A}|x^2-y^2\rangle\}$. In the case of the *trans*-$[M(X)_2(A)_4]$-type complex, the difference is rewritten as $\sqrt{3}(e_\sigma(X)-e_\sigma(A))/2$, where e_σ denotes the σ-antibonding parameter. It is known2) that the σ-parameter related with the Cr–F bonding, $e_\sigma(F)$, is slightly larger than that of the $Cr-NH_3$ bonding, $e_\sigma(N)$. When these findings are taken into consideration, the tetragonal distortions in the Cr(III) complexes concerned are regarded as very small, and the excited states are sufficiently approximated by Eq. 3. Thus, it seems reasonable to use our model for the Cr(III) complexes with small distortions.

The Effect of Configuration Interactions. In a previous paper,3) the band intensity in *trans*-$[Co(C_2O_4)_2$-

TABLE 6. ABSORPTION SPECTRAL DATAa) OF Cr(III) COMPLEXES ($\tilde{\nu}$ in $10^3\ cm^{-1}$)

	$\tilde{\nu}_{max}$	ε_{max}	$f\times10^7$	Assignment
trans-$[CrF_2(NH_3)_4]^+$ b)	18.6(17.8)	13.8(8.8)	(0.98)	E_g(a)
	20.3(20.5)	14.9(14.7)	(2.62)	B_{2g}
	25.0(24.4)	10.9(8.5)	(1.12)	E_g(b)
	27.9(27.9)	11.1(10.8)	(2.10)	A_{2g}
trans-$[CrClF(NH_3)_4]^+$ b)	17.8(17.7)	21.3(20.9)	(2.19)	E(a)
	20.2(20.7)	16.7(14.6)	(2.69)	B_2
	24.3(24.3)	16.8(15.4)	(1.96)	E(b)
	26.5(27.1)	17.2(12.8)	(2.01)	A_2
$[Cr(NH_3)_6]^{3+}$	21.0	47.9		T_{2g}
	29.4	39.8		T_{1g}

a) Analyzed values in parentheses. b) Ref. 2.

Table 7. Absorption spectral data of Co(III) complexes ($\tilde{\nu}$ in $10^3\,cm^{-1}$)

	$\tilde{\nu}_{max}$	ε_{max}	$f \times 10^7$	Assignment
trans-$[Co(CN)_2(NH_3)_4]^+$	20.3	15.4	1.81	A_{2g}
	24.0	66.3	12.2	$E_g(a)$
	31.4	67.6	14.9	$(B_{2g}, E_g(b))$
trans-$[Co(Cl)_2(NH_3)_4]^+$	15.9	42.7	5.11	$E_g(a)$
	20.7	21.8	3.96	A_{2g}
	26.3	44.6	11.8	$(B_{2g}, E_g(b))$
$[CoCl(NH_3)_5]^{2+}$	18.5	34.9	4.21	E(a)
	20.6	32.2	6.09	A_2
	27.7	49.1	9.34	$(B_2$, E(b))
$[CoBr(NH_3)_5]^{2+}$	18.0	44.4	5.64	E(a)
	20.5	35.4	6.50	A_2
trans-$[Co(CO_3)_2(py)_2]^-$ [a)]	18.3	89.1	12.0	$E_g(a)$, (A_{2g})
	23.4	35.5	5.58	B_{2g}
	26.5	57.5	6.51	$E_g(b)$
trans-$[Co(C_2O_4)_2(py)_2]^-$ [a)]	18.4	57.5	8.25	$E_g(a)$, (A_{2g})
	24.1	17.8	2.11	B_{2g}
	26.7	61.7	10.0	$E_g(b)$
$[CoCl(CN)_5]^{3-}$ [b)]	25.5	200		E(a)
	32.2	97		A_2
$[Co(NH_3)_6]^{3+}$	21.0	47.9		T_{1g}
	29.4	39.8		T_{2g}
$[Co(CN)_6]^{3-}$	32.1	240		T_{1g}
	38.5	178		T_{2g}
$[Co(C_2O_4)_3]^{3-}$	16.6	148		T_{1g}
	23.6	200		T_{2g}

a) Ref. 3. b) Ref. 15.

$(py_2)]^-$ was treated by considering only the L(σ)-vibronic mechanism under a weak tetragonal distortion, and the intensity of the $^1A_{2g}$ band, which was not observed in the absorption spectrum, was estimated. The value reported there, $\varepsilon_{max}=19$, now seems to somewhat large in the light of the maximum ($\varepsilon_{max}=57.5$) of the observed band (the spectral data are summarized in Table 7). If the L(π)MCT contributes to the $^1A_{2g}$ band intensity, the ε_{max} value may be evaluated as a smaller one. However, in the case of *trans*-$[Co(C_2O_4)_2(py)_2]^-$, such a contribution seems to be negligible because the π-ligand orbitals of the O donors on the xy plane are utilized for σ-hybridizations. Thus, we re-evaluated that value by considering the configuration interactions among the E states.

When the distortion becomes large, the one-electron wave functions, y^2-z^2, x^2, z^2-x^2, and y^2, which have been used in the E states must be altered by the following respective functions:[20)]

$$\begin{aligned} \phi_a(x) &= a\phi(y^2-z^2) - b\phi(x^2), \\ \phi_b(x) &= b\phi(y^2-z^2) + a\phi(x^2), \\ \phi_a(y) &= -a\phi(z^2-x^2) - b\phi(y^2), \\ \phi_b(y) &= -b\phi(z^2-x^2) + a\phi(y^2), \\ \text{where } & a^2 + b^2 = 1. \end{aligned} \tag{6}$$

When an expression for the $f(A_2)/f(B_2)$ ratio in a Co(III) complex was derived from these new wave functions of the E states, the expression was found to be the same as (4), although the k value varied as a function of the a coefficient. The change is illustrated in Fig. 2. When the L(σ)-vibronic mechanism participates and the $e_\sigma(X)$ is larger than the $e_\sigma(A)$, the k value decreases rapidly from 3 to 1.5 in the initial section of the a^2 value. On the other hand, in the case of $e_\sigma(X)<e_\sigma(A)$, the change of k with a^2 is quite different.

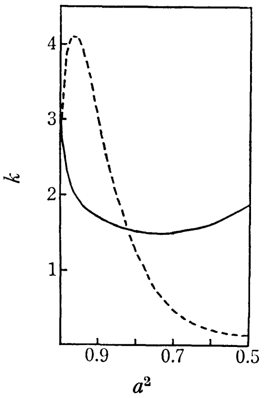

Fig. 2. Relationships between the coefficients k and a^2; —— $e_\sigma(X) > e_\sigma(A)$, ---- $e_\sigma(X)<e_\sigma(A)$.

It is reasonable to consider that $e_\sigma(py)$ is larger than $e_\sigma(O)$ in *trans*-$[Co(C_2O_4)_2(py)_2]^-$; if a sufficiently strong distortion is considered, the ε_{max} value of the $^1A_{2g}$ band is evaluated to be 10 for the bis(oxalato) complex. When the same calculations are carried out with a related dicarbonato complex, the results give $\varepsilon_{max}=16$. These values are much smaller than the observed ε_{max} values in the first absorption-band region ($\varepsilon_{max}=57.5$ for the bis(oxalato) complex and $\varepsilon_{max}=89.1$ for the dicarbonato complex). It is also possible to find an effect of the same kind in the polarized crystal spectra of *trans*-$K_2[Co(CN)(mal)_2(OH_2)]\cdot H_2O$;[21)] two split bands have been observed in the second absorption-band region, while only one band assignable to E(a) has been observed in the first absorption-band region. This phenomenon can now be understood by considering the intensity of the A_2 band, which is too weak, compared with that of the B_2 band.

Whether or not a band splitting can be observed depends upon both the magnitude of the intensities and the extent of the energy separation of the split bands, but the latter is not discussed in this paper. The formula (4) derived in this paper is useful in evaluating the intensity of an unobservable band from the observed intensity of the other band. Thus, let us discuss the behavior of band intensities in cobalt(III) complexes in terms of the tetragonal distortion. Three cases—Case a, $e_\sigma(X)>e_\sigma(A)$; Case b, $e_\sigma(X)\simeq e_\sigma(A)$, and Case c, $e_\sigma(X)<e_\sigma(A)$—will be considered. In Case a, the intensity of the $^1A_{2g}$ band observed at the longest wavelength is quite small in comparison with that of the $^1B_{2g}$ band, because the calculated value of the energy part in (4) becomes small as a result of the large separation between the $^1A_{2g}$ and $^1B_{2g}$ bands, and because k also has a small value. This kind of complex will often exhibit marked

splittings in the $^1T_{2g}$ bands. In Case b, the $^1A_{2g}$-band intensity is anticipated to be comparable to the $^1B_{2g}$-band intensity because of the large k value ($k \simeq 3$). In this case, band splittings will be observed only in a complex with ligands showing a strong π-bonding or π-antibonding contribution. No typical example of this is found in Co(III) complexes, but the spectrum of *trans*-$[Co(CN)_2(NH_3)_4]^+$ probably is such a case, for the intensity of the $^1A_{2g}$ band is almost one-third of the intensity of the $^1T_{1g}$ band in $[Co(NH_3)_6]^{3+}$. This probability is supported by the fact that the π-bonding contribution of the CN^- ligand has been found through the infrared spectral[22] and the absorption spectral studies.[23] In Case c, the $f(A_2)/f(B_2)$ ratio becomes larger than unity, except for an extremely distorted complex, because the energy part in (4) takes a large value as a result of the small separation of the $^1A_{2g}$ and $^1B_{2g}$ bands, and because k also takes a large value. In this case, it will be easier to observe band splitting in the $^1T_{1g}$-band region rather than in the $^1T_{2g}$-band region. This seems to correspond to the large intensities of the $^1A_2$ bands in $[CoX(NH_3)_5]^{2+}$ ($X=Cl^-$ and Br^-) and $[CoCl(CN)_5]^{3-}$. When the distortion becomes extremely large, the $f(A_2)/f(B_2)$ ratio takes a value of roughly unity on account of the small value of k. An example is seen in the spectrum of *trans*-$[CoCl_2(NH_3)_4]^+$; the broad band in the $^1T_{2g}$-band region suggests that the $^1B_{2g}$-band intensity is comparable to the $^1A_{2g}$-band intensity.

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