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On the Absorption Spectra of Complex Ions II

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The secular determinants obtained in the previous paper are solved for the energy levels which are important in the absorption spectra of the normal complex ions, leaving the crystalline field strength as a parameter. The values of B and C (Racah's parameters) there needed are determined from the observed spectra of free ions or in some cases by extrapolation.

The f-values of the transitions which connect the energy levels calculated are estimated and compared with the observed intensities. The difference of the spectral width among absorption bands and lines is also considered using the energy diagram obtained. Following the assignments determined by the above considerations, the calculated positions of lines and bands are rather in good agreement with the experimental data in divalent ions $[MX_6]^{2+}$ (M=Cr, Mn, Fe, Co, Ni), when we adjust the crystalline field parameter Dq suitably. In trivalent ions $[MX_6]^{3+}$ (M=Ti, V, Cr, Mn, Fe), it is necessary besides the adjustment of Dq to use smaller values of B and C than those of the free ions to obtain better agreement with experiments. The values of Dq thus determined are of reasonable magnitude close to those obtained in other ways. The decrease of B and C compared with those of the free ions might be connected with the recent Stevens' suggestion. It is interesting that, though the agreement is poor about $[Co(H_2O)_6]^{3+}$ and $[Co(NH_3)_6]^{3+}$ whose bindings are usually considered covalent, the qualitative explanation of their spectra is found possible in the crystalline field approximation.

§ Introduction

It has already been mentioned in the previous paper (1) that the complex ions under consideration show several forms of the absorption spectra, namely the relatively intense band, the weak band and the sharp line. No quantitative consideration, however, has been made to explain the origin of these differences.

We shall therefore investigate the nature of the transitions due to the optical absorption in these complexes in § 3. Then the comparison with the experimental data will be given in § 4 using the energy level diagram obtained in § 2.

§ 2. Determination of *B*, *C* and the Resulting Energy Level Diagram

Because most of the spectra of the free ions of the iron group elements are not yet completely known, in order to make the extrapolation possible, the values of B and C for the doubly or triply ionized states were estimated in the following way.

Since the term values of the elements in the d^2-isoelectronic sequence, i.e., Ti III, V IV, Cr V, Mn VI and Fe VII are experimentally known¹⁾, we have determined the values of B and C so that they will give the observed values for ^3F, ^3P and ^1G. When we plot these values of B and C against the atomic number Z²⁾, they approximately fall on a straight line: $B=145\ (Z-s)\ \mathrm{cm}^{-1}$. $C=705\ (Z-s)\ \mathrm{cm}^{-1}$ (compare with $B=129.5\ (Z-s)\ \mathrm{cm}^{-1}$, $C=514.5\ (Z-s)\ \mathrm{cm}^{-1}$ which one obtains using the Slater type wave function with $n^*=3$).

To obtain B and C in the d^3-isoelectronic sequence, we calculate $\Delta B=B(d^3)-B(d^2)$, $\Delta C=C(d^3)-C(d^2)$ using the observed value of the parent ion after Meshkov³⁾ (for the term value of $^1S(d^2)$ we adopt the calculated value, since the observed values are lacking), so that they give term values of ^4F, ^4P and ^2H correctly. In Table I, the column (diff. (I)) gives the differences between the values calculated in this way and the observed ones, and the column (diff. (II)) gives differences between the observed values and the values calculated in the usual way using the values of B and C determined so as to give ^4F, ^4P and ^2H correctly. The values of $B(d^3)$, $C(d^3)$ thus obtained also fall on a straight line parallel to the line for d^2 determined previously.

For d^n-isoelectronic sequences ($n\geq 4$) where we have few observed term values, this method cannot be applied, and the values of B and C were determined roughly from the observed three levels suitably chosen. Then they were adjusted so that they fall on straight lines which are parallel to the lines of d^2- and d^3-isoelectronic sequences and equally spaced with the distance between the d^2- and d^3-lines.

In Fig. 1 and 2 the points marked by × indicate the values thus determined for d^2 and d^3. But for d^4 B-values are not plotted, since if they were determined from ^5D, ^3H, ^3G we have far smaller values than those expected (smaller about by 130 cm^{-1}). C-values for d^4 determined from ^5D, ^{3}H, ^3G fall on the points expected from the graph. For d^5 B, C-values are the average of the two determined from ^6S, ^4G, ^4D and ^4P, ^4F respectively. For d^6 they were determined from ^5D,

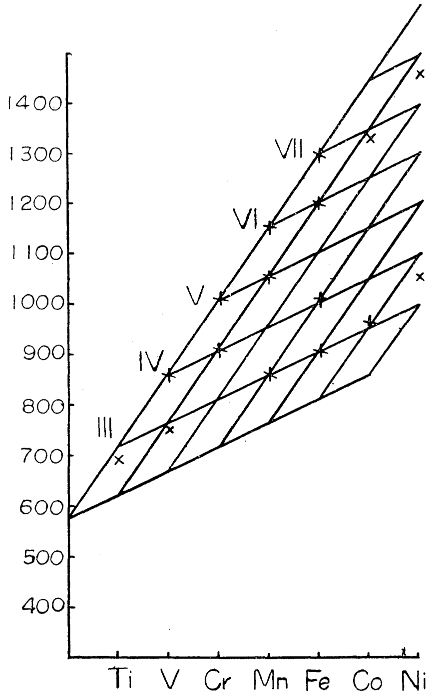

Fig. 1. B-values for various Z and ionicities.

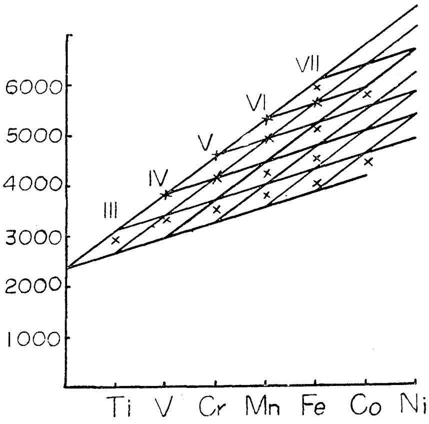

Fig. 2. C-values for various Z and ionicities.

Table I. The deviations of the calculated term values from those of the observed. (obs.—calc.) (Values are given in cm^{-1})

d^2

V IV		Diff.
^3F	419	
^1D	10960	−1397
^3P	13344	
^1G	18389	

$B=862$
$C=3815$

Cr V		Diff.
^3F	662	
^1D	13200	−1764
^3P	15868	
^1G	22060	

$B=1014$
$C=4617$

Mn VI		Diff.
^3F	964	
^1D	15336	−2065
^3P	18344	
^1G	25511	

$B=1159$
$C=5322$

Fe VII		Diff.
^3F	1346	
^1D	17475	−2335
^3P	20855	
^1G	28915	

$B=1301$
$C=5981$

d^3

V III		Diff. (I)	Diff. (II)
^4F	336		
^2P	11327	−3484	−5579
^4P	11668		
^2G	12089	− 43	−1040
^2D	16317	− 590	−2443
^2H	16907		

$B=755$
$C=3257$

Cr IV		Diff. (I)	Diff. (II)
^4F	554		
^4P	14324		
^2P	14229	−4341	−6985
^2G	15258	− 106	−1366
^2D	20487	− 788	−3652
^2H	21214		
^2F	36735	2506	1751

$B=918$
$C=4133$

Mn V		Diff. (I)	Diff. (II)
^4F	813		
^4P	16781		
^2G	18158	− 195	−1670
^2P	22961	908	−2190
^2D	24626	− 661	−3172
^2H	25150		

$B=1065$
$C=4919$

Fe VI		Diff. (I)	Diff. (II)
^4F	813		
^4P	19235		
^2G	20996	− 292	−1961
^2P	26297	820	−2685
^2D	28524	− 686	−3516
^2H	28981		

$B=1205$
$C=5659$

Table II. The values of B, C* and γ determined in the way described in § 2. (cm^{-1})

	B	C	C/B		B	C	C/B
Ti III	694.6	2910.4	4.190				
V	755.4	3257.2	4.312	V IV	861.6	3814.9	4.428
Cr	810.	3565.	4.401	Cr	918.	4132.7	4.502
Mn	860.	3850.	4.477	Mn	965.	4450.	4.611
Fe	917.	4040.	4.406	Fe	1015.	4800.	4.729
Co	971.	4497.	4.633	Co	1065.	5120.	4.808
Ni	1030.	4850.	4.709	Ni	1115.	5450.	4.888

* These B-values are not greatly different from those values recommended by Catalan et al.[5] after our calculation has been performed, and the value determined by Meshkov[4] for V III.

^3H, ^3G, and for d^7 B's were determined from ^4F, ^4P, ^2G and C's are the average of the two determined from ^4F, ^4P, ^2G and ^4P, ^2G, ^2H respectively. For d^8 B and C were determined from ^3F, ^3P.

The calculated term values using these B, C do not show so good agreement with the observed ones which were not used in the determination of these values ($\Delta E \simeq 2000$–$3000\,\mathrm{cm}^{-1}$ except some particular terms for which the error is even larger), so that we may expect that error of the same order would occur for the element, for example Co IV, for which spectral terms are not known yet. These errors are much larger than the errors that occur when one uses the values B, C determined by the least square method. But as our calculations are for molecular ions, we consider that the accuracy of such degree is sufficient for our purpose, judging from the nature of the crystalline field approximation. Values we adopt here are given in Table II. $\gamma=C/B$ is nearly constant for all elements and is about 4∼5, while, if we adopt the Slater type wave function, $\gamma=3.97$ and is independent of the effective nuclear charge.

With these values we solved the secular determinants including the interaction between configurations, and obtained the lowest eigenvalues among those belonging to the same $S\Gamma$. The results are shown in the energy diagrams in full line (Fig. 3–9). The other interesting levels were also solved neglecting the interaction between different configurations and are given in broken lines in the range $\Delta=Dq/B\geq 2$. Both the level energy (ordinate) which are measured always from the ground level and the strength of the crystalline field (abscissa) are scaled by B as unit. The values of γ and B used in the calculation of the level energy are also given. The observed term values and the lowest level of $d^{N-1}s$ configuration in the free state of the ion are indicated there.

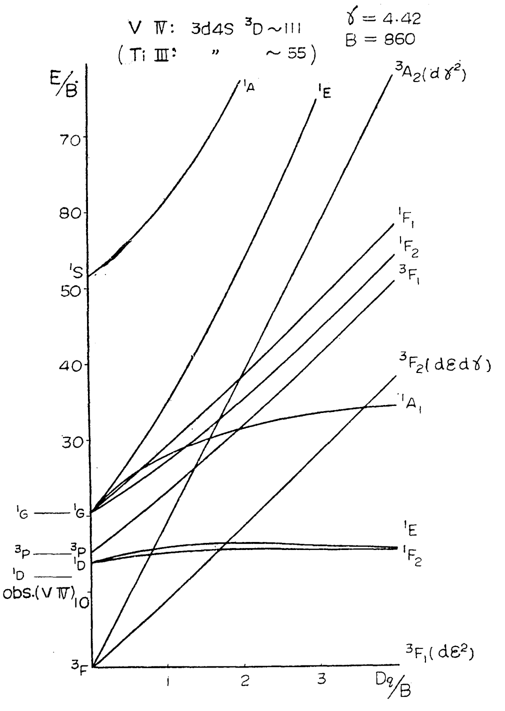

Fig. 3. The energy diagram for d².

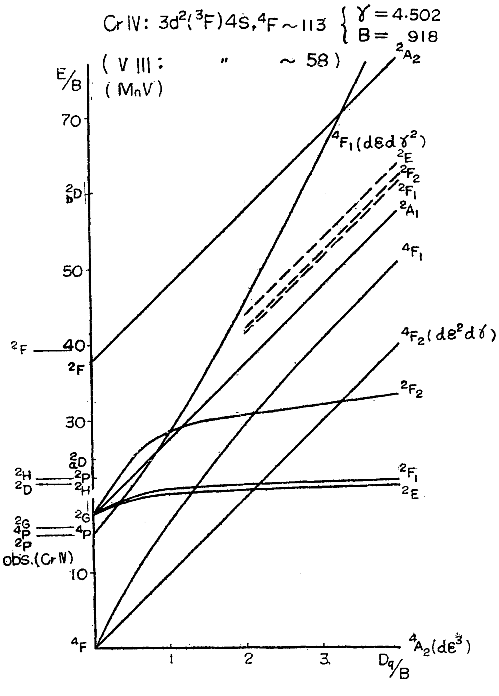

Fig. 5. The energy diagram for d³.

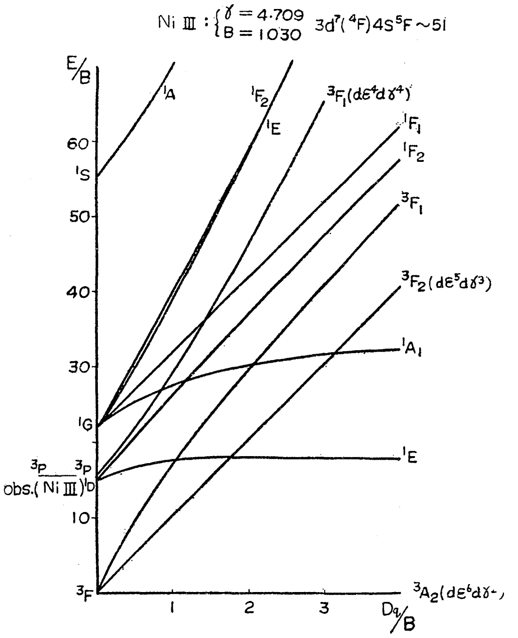

Fig. 4. The energy diagram for d⁸.

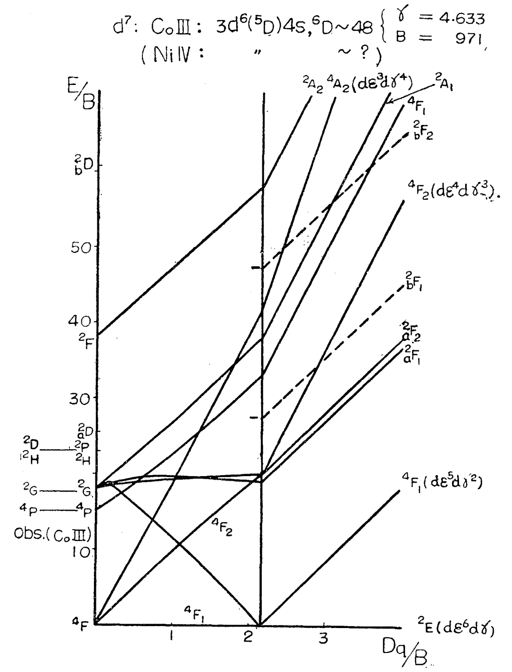

Fig. 6. The energy diagram for d⁷.

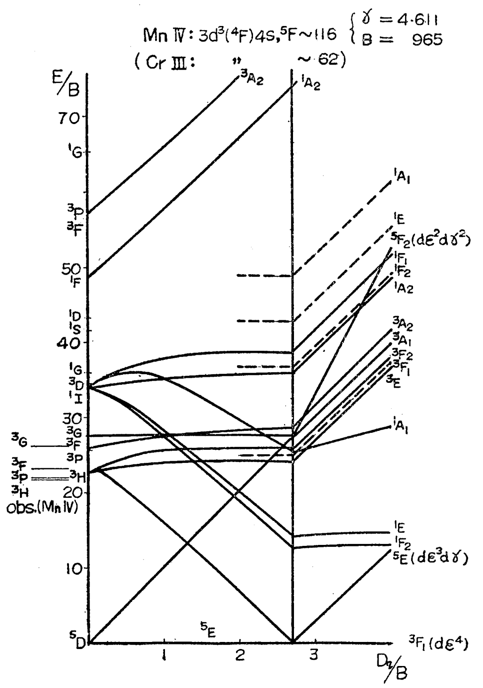

Fig. 7. The energy diagram for d⁴.

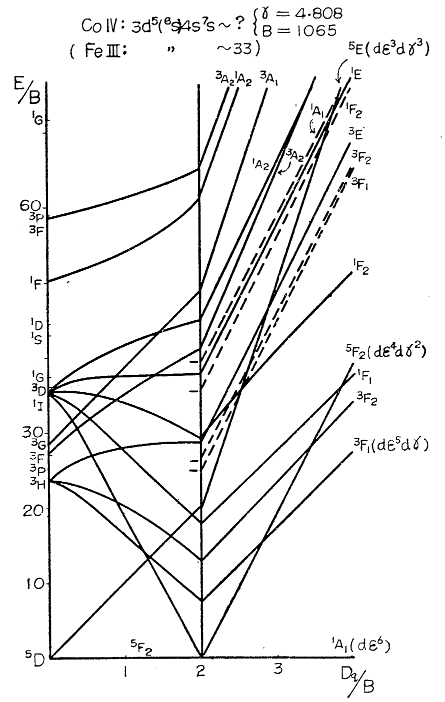

Fig. 8. The energy diagram for d⁶.

§ 3. Nature of the Transitions

In this section we shall consider the intensity of transitions, selection rules and the problem of the width of the observed absorption, in order to obtain some theoretical

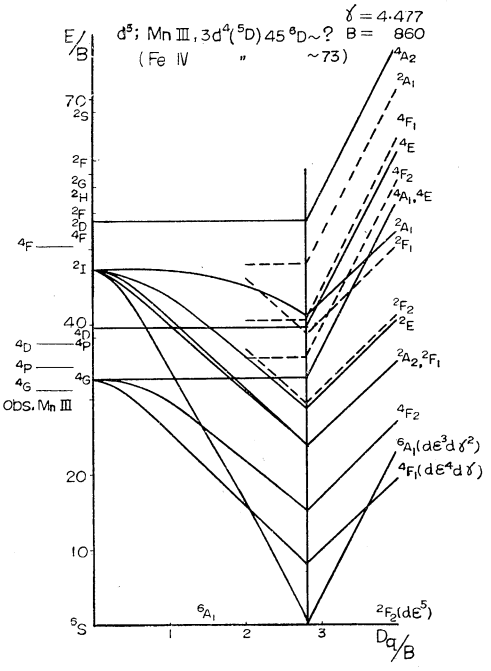

Fig. 9. The energy diagram for d⁵.

foundations for the interpretation of the observed spectra.

The relation between the absorption coefficient $k(\nu)$ and the oscillator strength f is given by the relation

$$f=\frac{mc}{\pi Ne^2}\int k(\nu)d\nu\ , \qquad (3.1)$$

where N is the number of the absorption centres per cubic centimeter, and ν the frequency measured in $\sec^{-1}$. For solutions, the intensity of the absorption is ordinarily given in terms of the extinction coefficient $\mathcal{E}$ defined through the relation $I=I_0 10^{-\mathcal{E}c_0x}$ where x is the thickness of the solution in cm and c_0 is the concentration in mol per litre, so that correspondingly to (3.1) we have

$$f=\frac{2.3\times10^3}{N_{\mathrm{Avog}}}\cdot\frac{mc}{\pi Ne^2}\int\mathcal{E}(\nu)d\nu\ , \qquad (3.2)$$

where N_{Avog} is the Avogadro number. For a rough estimation of f, we can replace the integral in (3.1) or (3.2) with $2.5\times k_{\max}\Delta\nu$ or $2.5\times\mathcal{E}_{\max}\Delta\nu$ in which $\Delta\nu$ represents the half width, assuming the absorption curve to be gaussian.

Experimentally it is known that in solutions all the bands in question have the values of $\log\mathcal{E}\simeq1\sim2$, $\Delta\nu\simeq10^{14}\sec^{-1}$ ($3000\,\mathrm{cm}^{-1}$) except for the case of $[Fe(H_2O)_6]^{3+}$, whose bands observed at 14300 cm^{-1} and 18200 cm^{-1} have rather small intensity $\log \mathcal{E} \simeq -1$ and the width $\Delta\nu \simeq 2\times 10^{14}$ sec^{-1}. Therefore, for the broad bands observed in solutions f-value can be estimated to be of the order of 2×10^{-4} if we take $\log \mathcal{E}=1$ (according to Sauer's measurement[6] for the bands of chrome alum, f is of the order of 10^{-3}), but for the weak bands of $[Fe(H_2O)_6]^{3+}$ it is about 4×10^{-6}.

On the other hand, the doublet lines of the chrome alums have the oscillator strength $f \simeq 3\times 10^{-8}$ according to Sauer's results. The line (though it is rather broad, the reason why we regard it as a line will be given later in § 4.) observed at 24600 cm^{-1} at room temperature has the values $\log \mathcal{E} \simeq -1$, $\Delta\nu \simeq 4\times 10^{13}$ sec^{-1}, so that its f-value becomes to be of the order of 10^{-6}.

All the observed absorption in question are thus considered to be due to forbidden transitions. This fact supports the interpretation that they are the transitions between the levels arising from the d^n-configuration, since all the levels then have the same parity so that the transitions between them are forbidden.

Among the forbidden transitions between the states with the same parity, the following transitions are able to have non-vanishing intensity; 1) the electric-dipole transition coupled with the vibration, 2) the electric-quadrupole transition and 3) the magnetic-dipole transition. Electric-dipole radiation due to naturally unsymmetric fields can be treated in a similar way to 1) and its transition probability may be of the same order of magnitude as those of 1), but we do not thuch it here because of its uncertainly. (See Van Vleck[7][8].)

We now estimate the f-values of those transitions in the same way as Van Vleck has done on the spectra of the rare earth salts.

For the intrasystem transition which connects the two states with the same multiplicity, the transition probability of the type 1) is given by

$$\sigma_{\rm I} \simeq \sigma_{\rm allow}(V_{\rm hem}/h\nu')^2 , \qquad (3.3)$$

where $V_{\rm hem}$ is a matrix element of the hemihedral part of the crystalline field, and ν' is the frequency interval separating the state in question from the excited states of the opposite parity, which are not limited to the excited states of the central metal ion but include those of the complex as a whole.

To obtain $V_{\rm hem}$ we expand the crystalline field $V(x,Q)$ in power series of Q where x denotes the electron coordinate and Q is the normal coordinates of the vibrational displacements

$$V(x,Q)=V_0(x)+\sum V_q{}^{(k)}Q_q{}^{(k)} + \tfrac{1}{2}\sum V_{qq}{}'^{(kk')}Q_q{}^{(k)}Q_q{}'^{(k')} , \qquad (3.4)$$

where $V_0(x)$ represents the crystalline field at the equilibrium position of the nuclei. We see that $V_q{}^{(k)}$ and $Q_q{}^{(k)}$ or $V_{qq'}{}^{(kk')}$ and $Q_q{}^{(k)}Q_{q'}{}^{(k)}$ have the same transformation properties, since the crystalline field has the properties

$$V(x,Q)=V(Rx,RQ) , \qquad (3.5)$$

where R denotes the symmetry operation. Now $V_{\rm hem}$ originates from the vibrational displacement with odd inversion symmetry F_{1u} and F_{2u}, that is, the main contribution to $V_{\rm hem}$ comes from $V_q(F_{1u})Q_q(F_{1u})$ and $V_q(F_{2u})Q_q(F_{2u})$ of the second term in (3.4). The order of magnitude of the second term is seen to be $(Q/r)V_0$. so that we can estimate $V_{\rm hem}$ using the relation

$$V_{\rm hem} \simeq (\delta R/\bar{r})V_0 , \qquad (3.6)$$

where δR is the zero-point amplitude of the vibration and $\bar{r}$ is the average of r. The amplitude δR is estimated from

$$2\pi^2\mu\nu_0{}^2(\delta R)^2=\tfrac{1}{2}h\nu_0 ,$$

where ν_0 is the fundamental frequency of the vibration and μ is the effective mass for the vibrating complex. For the numerical value of ν_0, we adopt 10^{13} sec^{-1} which may be compared with the infrared absorption at 2.4×10^{13} sec^{-1} and 4×10^{13} sec^{-1} of the cobalt complex recently found by Hill and Rosenberg[9]. For the value of μ, we take the mass of the central ion, $\mu \simeq 4\times 10^{-23}$ gr., as μ does not seem to differ from the mass of the central ion so much. Then we obtain the zero point amplitude to be of the order of 10^{-9} cm. Assuming the value $\bar{r} \simeq 10^{-8}$ cm, $V_0 \simeq 10^4$ cm^{-1}, we have $V_{\rm hem} \simeq 10^3$ cm^{-1}. With this and $\nu' \simeq 10^5$ cm^{-1}, we finally obtain

$$\sigma_{\rm I} \simeq 10^{-4}\cdot\sigma_{\rm allow} . \qquad (3.7)$$

The f-value of the allowed transition can be estimated from the relation

$$f \simeq \frac{8\pi^2 m}{3h}\nu\bar{r}^2 , \qquad (3.8)$$

where m is the electron mass and the frequency ν is assumed to be $6\times 10^{14}\,\mathrm{sec}^{-1}$, so that the f-value of the allowed transition may be considered to be of the order of unity. The f-value of the case 1) thus would be of the order of

$$f_{\mathrm{I}}\simeq 10^{-4}\,. \tag{3.9}$$

The transition probabilities of the case 2) and 3) for the intrasystem combinations are estimated from the relation

$$\text{for 2)}\qquad \sigma_{\mathrm{II}}=32\pi^6\nu^5 e^2 Q^2/5hc^5\,, \tag{3.10}$$

$$\text{for 3)}\qquad \sigma_{\mathrm{III}}=64\pi^4\nu^3 M^2/3hc^3\,. \tag{3.11}$$

Here Q is the "quadrupole amplitude" which can be estimated from the relation $Q\simeq\overline{r}^2$, and M is the matrix element of the magnetic moment connecting the states in question and considered of the order of the Bohr magneton. Then the corresponding f-values are

$$\text{for 2)}\qquad f_{\mathrm{II}}\simeq 2\times 10^{-7}\,, \tag{3.12}$$

$$\text{for 3)}\qquad f_{\mathrm{III}}\simeq 4\times 10^{-6}\,. \tag{3.13}$$

So that, for the intrasystem combinations, it seems to us that the electric-dipole transition coupled with the vibration predominates over the other two cases in our problem, though the intensity of the magnetic-dipole transition has the possibility to become comparable with that of the case 1) as our estimates may be in error by a factor of 10 or 100.

For the intersystem combinations we must take the spin-orbit interaction into account. We thus consider the contamination of the state with different multiplicity due to the spin-orbit interaction as follows[10)]

$$\Psi(\alpha_0\Gamma_T)=a\Psi(\alpha S\Gamma,\Gamma_T)+b\Psi(\alpha' S'\Gamma',\Gamma_T)\,, \tag{3.14}$$

where Γ_T is the irreducible representation of $S\times\Gamma$ and contamination occurs only among the states with the same Γ_T. Here it may generally be assumed that the coefficient a is nearly equal to unity, and b is of the order of magnitude $\Delta\nu/\nu$ where $\Delta\nu$ is the multiplet width and ν is the interval between different multiplets. Then the f-values of 1), 2) and 3) for the intersystem combinations are estimated from (3.9), (3.12) and (3.13) multiplying the factor b^2 respectively. Assuming the value of b as 3×10^{-2} which is estimated to be a little smaller than that of the rare earth salts, f-values thus obtained are

$$\left.\begin{aligned} &\text{for 1)}\qquad \overline{f}_{\mathrm{I}}\simeq 10^{-7}\,,\\ &\text{for 2)}\qquad \overline{f}_{\mathrm{II}}\simeq 2\times 10^{-10}\,,\\ &\text{for 3)}\qquad \overline{f}_{\mathrm{III}}\simeq 4\times 10^{-9}\,. \end{aligned}\right\} \tag{3.15}$$

From these considerations we now have some theoretical ground to say that, to the relatively strong absorption bands, the intrasystem transitions may be assigned in which electric-dipole transitions coupled with vibrations probably predominates, whose estimated f-value 10^{-4} should be compared with the observed ones $10^{-3}\sim 10^{-4}$, and that, to the weak bands of $[\mathrm{Fe(H_2O)_6}]^{3+}$ or to the lines, the intersystem transitions may correspond, where estimated f-value $\simeq 10^{-7}$ is not so different from those observed $10^{-6}\sim 10^{-8}$.

We shall briefly consider the fact that the absorption bands of the triply ionized complex show always a larger intensity than those of the doubly ionized one by a factor 10 in ε. This difference of the absorption intensity between the doubly and the triply ionized complexes is thought to come from the difference in the strength of the crystalline field and from that in ν', because the factor σ_{allow} does not differ greatly in both cases. The crystalline field is generally stronger in the triply ionized complex ions as will be seen later. Further ν' in the latter may be smaller than that of the former since the excited states with the odd parity likely exist at relatively lower positions in the more tightly bound triply ionized complexes owing to their departure from the atomic character. This supposition will be only justified when it is tested by a more thorough treatment of the complex as a molecule.

The selection rules were examined on the individual cases 1), 2) and 3) in each complexes. All assignment adopted in the following section do not break such selection rules. In our problem of the perfect cubic field, difference of the absorption due to the polarization of the incident light does not, of course, occur, but if we introduce the field of the lower symmetry that may really exist in crystals, or if some of the ligands are replaced with other atoms or molecules, i.e., in $[\mathrm{M\ X}_n\ \mathrm{Y}_{6-n}]^{2+,3+}$ complexes, this occurs and further investigation on the selection rules in these cases will give more precise information as to the nature of the absorption.

The coexistence of broad bands and lines in iron group complexes is an interesting phenomenon. In the energy diagrams (Fig. 3→Fig. 9), we can see that the energy intervals between the levels belonging to the same configuration $d\varepsilon^n d\gamma^{N-n}$ becomes to be almost independent of the strength of the crystalline field in the region where Dq is $\gtrsim 2B$ (this is really what happens in the iron group complexes), in other words, in this region interactions between configurations are negligible. But those belonging to different configurations are strongly dependent of the field strength, so that we are led to assign the transitions which connect the levels belonging to the same configurations to the lines and those belonging to different configurations to broad bands. Thus, we consider that the strong crystalline field in the iron group complexes is the cause of such a phenomenon. In rare earth salts where the crystalline field is much weaker than that of the iron group salts by a factor of 10^2, the broad bands has not been observed in the visible region as far as we know. (The broad bands observed in the ultraviolet region in Ce^{3+} 11) or Yb^{3+} 12) salts seem to be somewhat different from those of the iron group complex in their origin.)

The observed half width $3000\,cm^{-1}$ of the broad bands would be explained from this view-point, since the crystalline field could fluctuate with the amplitude of $V_{\text{hem}} \simeq 1000\,cm^{-1}$ even by the zero-point vibration of the system, coupled with which electric-dipole transitions are allowed to have non-vanishing intensities.

§ 4. Comparison with Experiments

We now compare our results with the experimental data in accordance with the considerations in the previous section, and determine Dq and, redetermine, if necessary, B and C which may be somewhat different from those determined previously from data for free ions, so as to give good agreement with the observation.

Measurements on these absorption spectra have been performed by many experimentalists, but the numbers of observed lines and bands available in the individual complex are often not so rich that the arbitrariness of the values of these parameters will exist in some cases.

$3d$: In the case of a single d-electron or hole, only a single absorption band is allowed to appear in our treatment. According to Hartmann an Schläfer13), $[Ti(H_2O)_6]^{3+}$ has a single band with intensity $\log \varepsilon \simeq 0.6$ and its absorption maximum is at $20300\,cm^{-1}$, which can be assigned to $(d\varepsilon)^2F_2 \rightarrow (d\gamma)^2E$ transition; the value of Dq thus determined is $Dq = 2030\,cm^{-1}$.

$3d^9$: Dreisch14) found a single band on $Cu^{2+}{}_{aq.}$; its absorption maximum is at $12200\,cm^{-1}$, which can be assigned to $(d\varepsilon^6 d\gamma^3)^2E \rightarrow (d\varepsilon^5 d\gamma^4)^2F_2$ transition. Then Dq is given as $1220\,cm^{-1}$.

$3d^2$: Hartmann and Schläfer15) found two bands in the $[V(H_2O)_6]^{3+}$ complex ion at room temperature:

	abs. max.	$\log \varepsilon$
$V(ClO_4)_3$ in $HClO_4$	$17.3 \times 10^3\,cm^{-1}$	0.74
	25.0	0.92
$NH_4V(SO_4)_2 \cdot 12H_2O_{aq.}$	17.8	0.54
	25.6	0.81
$CsV(SO_4)_2 \cdot 12H_2O_{aq.}$	17.8	0.65
	25.6	0.81

We assign these two bands to $(d\varepsilon^2)^3F_1 \rightarrow (d\varepsilon d\gamma)^3F_2$, $(d\varepsilon^2)^3F_1 \rightarrow (d\varepsilon d\gamma)^3F_1$ transitions respectively. Calculated values are $17300\,cm^{-1}$ for ${}^3F_1 \rightarrow {}^3F_2$ and $25400\,cm^{-1}$ for ${}^3F_1 \rightarrow {}^3F_1$, when we take the value of B as $640\,cm^{-1}$ which is determined using the fact that the energy interval between ${}^3F_2$ and ${}^3F_1$ should be aporoximately equal to $12B$. (In our treatment γ is always assumed not to be changed from those of the free ion.) The corresponding Dq is about $1860\,cm^{-1}$. It must be remarked here that our assignment of the second band is different from that adopted by Hartmann et al.,15) namely the second band in their treatment corresponds to $(d\varepsilon^2)^3F_1 \rightarrow (d\gamma^2)^3A_2$ transition in our case, which is considered to be strongly forbidden even if the coupling with vibrations were taken into account, for it corresponds to a two electron jump. Further, besides this broad band just mentioned, our treatment leads to the expectation that lines must be found corresponding to the transitions $(d\varepsilon^2)^3F_1 \rightarrow (d\varepsilon^2)^1E, {}^1F_2$ and $(d\varepsilon^2)^3F_1 \rightarrow (d\varepsilon^2)^1A_1$ at $9600\,cm^{-1}$ and $21000\,cm^{-1}$ respectiyely, which will be of course very weak.

$3d^8$: A. v. Kiss et al.16) measured the absorption spectra of the $[Ni(H_2O)_6]^{2+}$ complex ion, and obtained the following results:

	abs. max.	log. ε
$[Ni(H_2O)_6]SO_{4\,aq.}$	$13.9\times10^3\ cm^{-1}$ 15.2	0.32 0.27
	25.3	0.76
$[Ni(H_2O)_6]Cl_{2\,aq.}$	8.5	0.35
	13.9 15.2	0.36 0.27

But Dreisch and Trommer[17] reported the existence of three bands at 8400, 14100 and 25000 cm^{-1} respectively for this complex ion $NiSO_{4\,aq.}$, and Houston, Bose and Mookherji[18] also observed these three bands. So that we will take these values as the absorption maxima of the three bands.

Our assignment and calculated values are as follows:

transition	calc. val.	obs. max.
$(d\varepsilon^6 d\gamma^2)^3A_2 \to (d\varepsilon^5 d\gamma^3)^3F_2$	$8.2\times10^3\ cm^{-1}$	8.4
$\to (d\varepsilon^5 d\gamma^3)^3F_1$	13.9	14.1
$\to (d\varepsilon^4 d\gamma^4)^3F_1$	26.3	25.0

$$Dq = 824\ cm^{-1}\ ,$$

where we have used the same values of B and C as those of the free ion. Here again the third band corresponds to a two electron jump. However in this case, because of the smallness of Dq, the mixing of the two configurations $d\varepsilon^5 d\gamma^3$, $d\varepsilon^4 d\gamma^4$ occurs for the $^3F_1$ level and the intensity of the third band is thus considered to be stolen from that of the second band, while in the case of vanadium complex there was no counter-part of the state $d\gamma^2\,{}^3A_2$. For the first two bands of Ni tutton salts, the same assignment has been done by Griffth and Owen[19], using the value of the crystalline field parameter determined from their experimental data on the paramagnetic resonance absorption of Ni tutton salts. We have no resonable explanation as to the origin of the double maxima at 13900 and 15200 cm^{-1} found by A. v. Kiss at the position corresponding to the second band (14100 cm^{-1}).

For the optical absorption of $[Ni(NH_3)_6]^{2+}$, measurements are performed by Sone[20], Dreisch and Trommer[17], Bose and Mookherji[19] and for $[Ni(en)_3]Cl_{2\,aq.}$ by Sone[20]. Our results are the following, where the same assignments, the same B, C values were adopted as for $[Ni(H_2O)_6]^{2+}$:

$[Ni(NH_3)_6]^{2+}$	calc. val.	obs. max.	obs. log ε	
	$10.3\times10^3\ cm^{-1}$	10.6	0.92	Dreisch and Trommer
	17.0	17.5	0.75	Sone
	29.3	27.6	0.92	
		$Dq = 1030\ cm^{-1}$		
$[Ni(en)_3]^{2+}$	10.8	—	—	
	17.5	18.4	0.84	
	29.9	28.9	0.93	
		$Dq = 1080\ cm^{-1}$		

The first band must be found in the near infrared region for $[Ni(en)_3]^{2+}$ too. Further, a line due to the transition $(d\varepsilon^6 d\gamma^2)^3A_2 \to {}^1E$ must be found at 17500 cm^{-1} for the $[Ni(H_2O)_6]^{2+}$ complex ion (for the other two complexes, it will be masked by the broad bands). Actually Gielessen[21] reported the existence of the line in the region 17300–20500 cm^{-1} in the solid $[Ni(H_2O)_6]Cl_2$ at −189°C.

$3d^3$: For $[Cr(H_2O)_6]Cl_{3\,aq.}$, Tsuchida and Kobayashi[22] found two bands at 17500 cm^{-1} ($\log\varepsilon=1.02$) and 24500 cm^{-1} ($\log\varepsilon=1.20$) respectively, and later found one more absorption maximum at 36600 cm^{-1} ($\log\varepsilon=0.5$)[23]. This maximum is also found in the solution of $KCr(SO_4)_2\cdot12H_2O$, but its presence is obscured by the existence of the intense edge absorption. In solid states of chromic salts, however, it is clearly observed.

It is well known that the spectra of the chromic salts show sharp lines in many cases; Sauer[6], Joos and Schnetzler[24] have reported the existence of the lines in the crystals of $[Cr(H_2O)_6]Cl_3$ (14800 cm^{-1}, 14900 cm^{-1}), $[Cr(NH_3)_6]Cl_3\cdot H_2O$ (15200 cm^{-1}, 15400 cm^{-1}) and $[Cr(en)_3]Br_3$ (14900 cm^{-1}, 15400 cm^{-1}) at −180°C, and Spedding[25] further found a sharp absorption (21000 cm^{-1}) between the two bands. The same lines are also observed in the solution containing $[Cr(NH_3)_6]^{3+}$ or $[Cr(en)_3]^{3+}$ ion.

To compare our results with the observed spectra of $[Cr(H_2O)_6]^{3+}$, we will take the observed values of $KCr(SO_4)_2 \cdot 12H_2O$ crystal. The results are as follows:*

$[Cr(H_2O)_6]^{3+}{}_{\text{crys.}}$

	transition	calc. val.	obs. max.	obs. log α	
$(d\varepsilon^3)^4A_2$ (bands)	$\rightarrow(d\varepsilon^2 d\gamma)^4F_2$	17.2×10^3 cm^{-1}	18.0	0.5	
	$\rightarrow(d\varepsilon^2 d\gamma)^4F_1$	24.6	24.6	0.6	Tauchida at room temp.
	$\rightarrow(d\varepsilon d\gamma^2)^4F_1$	38.2	36.6	0.2	
(lines)	$\rightarrow(d\varepsilon^3)^2E$	14.9	14.9		Sauer at −190°C
	$\rightarrow(d\varepsilon^3)^2F_1$	15.3	15.1		
	$\rightarrow(d\varepsilon^3)^2F_2$	21.8	21.0		Spedding at liq. hydrg. temp.

$Dq=1720$ cm^{-1}

Here we changed the values of B and C from those of the free ion in the following way: The values of B and C of the free ion are determined previously to give the term values of ^4F, ^4P and ^2H correctly, so that if we use these B, C the agreement of the calculated term value of ^2G is not so good. This is unfortunate because as we see the lines originate from ^2G of the free ion in our treatment. So we replace γ so as to give the correct term value ^2G of the free ion (resulting γ being 4.0). But on comparing the result thus calculated with the observation we found that we further had to adjust the value of B, C in order to give the right positions of the lines. The value of B to be used here was 765 cm^{-1} (γ being the same as above 4.0) which is much smaller than those of the free ion 918 cm^{-1}. We cannot get better agreement with the observed spectra by adjusting only the parameter Dq as Finkelstein and Van Vleck[26] claimed in their paper on a similar calculation of the position of the doublet line of the chrome alum, since the energy interval between the states of the same configuration is almost independent of the crystalline field.

The third absorption band corresponds to the two electron excitation and the same consideration applies to this case as was mentioned for the two electron jump in the case of Ni complex. In this case, however Dq is rather large so that the degree of contamination may be small and consequently there remain doubts about our assignment of the observed third band to this transition. If this assignment were correct, this band would be nearly twice as broad as the first and second bands according to the considerations given at the end of § 3. The third band really seems rather broad, but it may be safe not to draw any definite conclusisn as to the origin of this third band.

It is doubtful whether the observed two lines do correspond to the transitions to ^2E and $^2F_1$ respectively or not. To make this clear, it would be necessary to take the deviation from the perfect cubic symmetry due to the Jahn-Teller effect[8] or to the trigonal field[27] exerted by the ions outside the complex ion in question, and the influence of the spin-orbit interaction into consideration. Moreover, if we consider the deformation of the $d\varepsilon$ orbital from the atomic d-character, the excited states ^2E and $^2F_1$ have no necessity to lie so close together. (Though the deformation of orbits may be taken into account in some degree in the adopted B, C values which is different from those of the free ion, we cannot include in this way the deformation that will remove the accidental degeneracy of ^2E and $^2F_1$ levels occurred in the strong crystalline field limit.)

For $[Cr(NH_3)_6]^{3+}$ complex ion, assuming the same assignment and the B, C values redetermined above to be correct, the comparison is as follows:

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* These data were used here with Tsuchida's which was obtained at room temperature, because for these lines the temperature shift is small. According to Sauer's experiments the doublet line at 14900 cm^{-1} shifts only about 20Å towards the longer wave leugth side when the temperature is changed from −190° to 18°C, while the bands shift as much as 150 Å.

$[Cr(NH_3)_6]^{3+}$	calc. val.	obs. max.	obs. log ε	
(bands)	21.4×10^3 cm^{-1}	21.5	1.62	
	29.4	28.5	1.57	Linhard[28]
	46.6	—	—	
(lines)	14.9	15.2		
	15.3	15.4		Joos and Schnetzler[24]
	21.8	—		

$$Dq=2140\ \mathrm{cm}^{-1}$$

For $[Cr(en)_3]^{3+}$, we shall omit the discussion, since its spectra are almost identical (though a slight decrease of the intensity is found) with those of $[Cr(NH_3)_6]^{3+}$.

$3d^7$: On the $[Co(H_2O)_6]Cl_2$ complex ion, many observations have been made (Houston[18], Dreisch[14], Dreisch and Trommer[17], Datta and Deb[29], Gielessen[21]) and, though there exist slight differences among them, the existence of the following the bands is generally accepted. The comparison is as follows.

trans.	calc. val.	obs. max.	obs. log ε	
$(d\varepsilon^5 d\gamma^2)^4F_1\to(d\varepsilon^4 d\gamma^3)^4F_2$	8.1×10^3 cm^{-1}	8.13	0.56	
$\to(d\varepsilon^4 d\gamma^3)^4F_1$	20.6	19.6	0.62	Dreisch and Trommer[17]

$$Dq=840\ \mathrm{cm}^{-1}$$

If we assume the value of Dq as above, the absorption lines to which the transitions $(d\varepsilon^5 d\gamma^2)^4F_1\to(d\varepsilon^5 d\gamma^2)a^2F_1$, a^2F_2 and $^4F_1\to b^2F_1$ have to be assigned must appear near 18000 cm^{-1} and $\sim$24000 cm^{-1} respectively. These positions of the lines, however, do not seem to be compatible with the line observed by Gielessen in the crystals at -189°C.

Transition $(d\varepsilon^5 d\gamma^2)^4F_1\to(d\varepsilon^6 d\gamma)^2E$ may give rise to a broad band with much weaker intensity, and, if it could actually be found, it would be very interesting because the dependence of its excitation energy on the strength of the crystalline field is different from those hitherto discussed. That is, this band is considered to have a different temperature shift (Fig. 6), if the magnitude of the temperature shift of the absorption maximum is predominantly due to the increase of the atomic distance caused by the thermal expansion. The absorption maximum of this band will then shift towards shorter wave length side when temperature is increased (Dq becomes smaller), while those of hitherto discussed will shift towards longer side as is often experimentally observed.

$3d^4$: For $[Mn(H_2O)_6]^{3+}$, Hartmann and Schläfer measured the absorption spectra of $CsMn(SO_4)_2\cdot12H_2O$[30], and found only one band at 21000 cm^{-1}. This band will correspond to the transition $(d\varepsilon^3 d\gamma)^5E\to(d\varepsilon^2 d\gamma^2)^5F_2$. If we determine Dq to be 2100 cm^{-1}, our calculation predicts the existence of the lines near 24000 cm^{-1} corresponding to the transitions to ^3E, $^3F_2$ etc.

Recently the absorption spectra of the aqueous solution of $CrSO_4\cdot7H_2O$ was measured by Tsuchida et al.*. According to their measurement, $[Cr(H_2O)_6]^{2+}$ shows a single band at 13900 cm^{-1} (log $\varepsilon\simeq0.8$). In this complex ion, we can also adopt the same assignment as above, and Dq value thus determined is 1390 cm^{-1}.

$3d^6$: The binding property of the $[Co(NH_3)_6]^{3+}$ complex ion has been considered to be covalent by the reasons that it has the diamagnetic normal state and that the atomic distance between the central ion and one of the ligands is relatively small. The same argument will apply for the $[Co(H_2O)_6]^{3+}$ complex, because a recent measurement on the susceptibility of this complex shows that this is also diamagnetic[31].

But an alternative explanation is possible in the ionic model that the small atomic distance means the strong crystalline field and at such strong field the change of the ground state could occur, i.e., the ground state could become singlet (Fig. 8)[32]. In our treatment we

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* This was reported at the meeting of the Chemical Society of Japan held in April, 1954.

shall adopt the latter explanation, and assume that the ionic structure will predominate over the covalent structure, so that the latter can be neglected.

For $[Co(H_2O)_6]^{3+}$, our assignment is as follows:

trans.	calc. val.	obs. max.	obs. log ε	
$(d\varepsilon^6)^1A_1\rightarrow(d\varepsilon^5d\gamma)^1F_1$	$16.0\times10^3\ \mathrm{cm}^{-1}$	16.3	1.62	Topp[33]
$(d\varepsilon^5d\gamma)^1F_2$	28.1	25.0	1.70	

$$Dq=1920\ \mathrm{cm}^{-1},$$

where we use a little smaller value of γ, so that the ground state is singlet when the value of Dq is determined to give the position of the first band correctly. The B value was not changed from that for the free ion. Assuming the parameter values to be as above, the third band corresponding to the transition $(d\varepsilon^6)^1A_1\rightarrow(d\varepsilon^4d\gamma^2)^1F_2$ must appear (which might be masked by an intense edge absorption in solution) and, moreover, according to our energy diagram a weak band due to the transition $^1A_1\rightarrow{}^3F_1$ and $^1A_1\rightarrow{}^3F_2$ must be found at the long wave length side of the first band.

In a similar way, the comparison of our results with observations for the $[Co(NH_3)_6]^{3+}$ complex ion is

$[Co(NH_3)_6]^{3+}{}_{aq.}$	calc. val.	obs. max.	obs. log ε	
	$20.4\times10^3\ \mathrm{cm}^{-1}$	21.1	1.78	
	33.6	29.5	1.74	Linhard[28]

$$Dq=2260\ \mathrm{cm}^{-1},$$

and for the $[Co(NH_3)_6]Cl_3$ crystal

$[Co(NH_3)_6]Cl_{3\ crys.}$	calc. val.	obs. max.	obs. log ε	
	19.2	21.6	1.35	
	32.0	28.6	1.29	Tsuchida[34]
$(d\varepsilon^6)^1A_1\rightarrow(d\varepsilon^4d\gamma^2)^1F_2$	39.4	35.4	1.25	

$$Dq=2260\ \mathrm{cm}^{-1},$$

where the third band is observed. However, as was mentioned earlier, the third band is considered to have an intensity much smaller than the first two bands, because Dq is also here rather large. So that the assignment for the third band is doubtful, judging from the comparative intensity of this band with the first two bands.

Calculated values do not show so good agreement with those of the observed as is seen above. When we adjust the value of B to give the relative positions of the bands correctly, the calculate absolute positions shift far from those of the observed values towards the longer wave length side. These facts perhaps mean that for this complex ion the approximation that assumes this complex as completely ionic is not so good as to give a quantitative agreement. But it suggests the possibility that this complex could be treated successfully starting from the ionic model and then taking the covalent structure into account. From this point of view, it is very interesting that the absorption band of relatively low intensity has recently been found* at the longer wave length side of the first band which seems to be due to the transition $^1A_1\rightarrow{}^3F_1$ or $^1A_1\rightarrow{}^3F_2$ in our ionic model.

For $[Fe(H_2O)_6]^{2+}$, only one band is observed by Dreisch and Kallscheuer[35] at 10300 cm^{-1} in the near infrared region. (Though Dreisch reports two maxima for $FeCl_{2\,aq.}$ at 9300 cm^{-1} ($\varepsilon=1.74$) and 10500 cm^{-1} ($\varepsilon=1.86$), we suspect that these two maxima would correspond to the vibrational structure of the band peaked at 10300 cm^{-1}.) Our energy diagram gives the observed value if we assign the transition $(d\varepsilon^4d\gamma^2)^5F_2\rightarrow(d\varepsilon^3d\gamma^3)^5E$ to the observed band and use the value of Dq as 1030 cm^{-1}.

$3d^5$ Absorption spectra of the complex ion $[Fe(H_2O)_6]^{3+}{}_{aq.}$ has been measured by Rabinowitch and Stockmayer[36] and A. v. Kiss[37], who found the same results, though the complex $[Fe(H_2O)_6]^{3+}$ is rather unstable and their results may possibly contain some error in details. Absorption spectra in $[Fe(H_2O)_6]^{3+}{}_{aq.}$

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* Private communication from Dr. Y. Kondo.

found by them consist of two weak bands and a relatively sharp one. Though the latter is broader than the lines found in other complexes, it is sharper than the bands which ordinarily appear, and we will therefore treat it as a line taking the possible error of the experiments into consideration. The results are as follows:

$[Fe(H_2O)_6]^{3+}{}_{aq.}$	trans.	calc. val.	obs. max.	obs. $\log \varepsilon$
$(d\varepsilon^3 d\gamma^2)^6A_1$	$\to(d\varepsilon^4 d\gamma)\ {}^4F_1$	14.3	14.3	−1.21
(bands)	$\to(d\varepsilon^4 d\gamma)\ {}^4F_2$	18.8	18.2	−1.00
(lines)	$\to(d\varepsilon^4 d\gamma^2)^4A_1, {}^4E$	25.0	24.6	−0.48

$Dq = 1350\ \mathrm{cm}^{-1}$,

where we recalculated the value of γ to give the term value of ^4G of the free ion correctly in the same way as was done for the chromium complexes, and adjusted the value of B to be 820 cm^{-1}—a value a little smaller than that of the free ion.

According to this assignment, just as was seen in the case of the transition $(d\varepsilon^5 d\gamma^2)^4F_1 \to (d\varepsilon^6 d\gamma)^2E$ in $3d^7$, the excitation energies of the two absorptions at 14300 cm^{-1} and 18200 cm^{-1}, show the opposite dependence on the crystalline field strength to the usual absorptions (Fig. 9), while a relatively sharp absorption found at 2400 cm^{-1} is insensitive to the crystalline field. Experimental study of this difference in temperature dependence will be interesting as was mentioned at the case of $3d^7$.

For $[Mn(H_2O)_6]^{2+}$, Kato[38] observed a band at 19600 cm^{-1} in $MnCl_{2\,aq.}$. Gielessen's measurement on $MnCl_2 \cdot 6H_2O$ crystal[21] shows that this has also line spectra near 25000 cm^{-1}. The comparison is as follows:

$[Mn(H_2O)_6]^{2+}$	trans.	calc. val.	obs. max.
(band)	$^6A_1 \to {}^4F_2$	$19.6 \times 10^3\ \mathrm{cm}^{-1}$	19.6
(line)	$\to {}^4A_1, {}^4E$	26.2	25.0

$Dq = 1230\ \mathrm{cm}^{-1}$,

where the value of γ was adjusted as before, but the B-value was assumed to be that of the free ion. This assignment leads to the existence of the weak band at 14600 cm^{-1} corresponding to the transition $^6A_1 \to {}^4F_1$ which is not reported yet.

§ 5. Conclusion

Though absorption spectra of many iron group complexes could be identified with our calculated energy diagram choosing the values of the parameters suitably and their observed behaviours were explained fairly well from the view-point of the crystalline field approximation, we do not feel the ground for justifying our treatment settled perfectly because of the shortage of available absorption data in the individual complex. In the following, however, we shall survey the results to show that the values of the parameters thus determined empirically are resonable ones and the arbitrariness of their values is not so large as one might suppose at first.

The calculated positions of lines and bands are rather in fair agreement with the experimental data in divalent ions, if we adjust only the crystalline field parameter Dq suitably. In trivalent ions, it was necessary, besides the adjustment of Dq, to use smaller values of B and C than those of the free ions to obtain better agreement with experiments. The values of B and Dq determined in this way are summarized below, where the corresponding values of B in free states are parenthesized. The values of C are not tabulated there because γ are not altered from those of the free ions.

	Ti^{3+}	V^{3+}	Cr^{3+}	Mn^{3+}	Fe^{3+}	Co^{3+}	
Dq (cm^{-1})	2030	1860	1720	2100	1350	1920?	
B (cm^{-1})		642	765	?	820	?	
		(862)	(918)	(965)	(1015)	(1065)	
			Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}
Dq (cm^{-1})			1390	1230	1030	840	820
B (cm^{-1})			810	860	917	971	1030
			(810)	(860)	(917)	(971)	(1030)

These values of Dq are of resonable magnitude, being close to those obtained in other ways, for instance, those obtained from the paramagnetic suceptibilities or the paramagnetic resonance absorption data. It is to be noticed that the values of Dq in trivalent complex ions are always larger than those of corresponding divalent complexes, and that in each isovalent complexes the Dq-value has a tendency to decrease as the atomic number Z increases. The Dq-value of Co^{3+} remarked by ? will have possibly a large error because of the particular binding property of Co^{3+} compiex ion as was mentioned in § 4.

We suppose that the decrease of B and C compared with those of free ions will be connected with Stevens' recent suggestion[39] on the interpretation of the paramagnetic resonance absorption, and a further theoretical investigation on B and C and Dq would be necessary.

Experimentally more detailed observation on the behavior of the absorption in the individual complex ions is highly desirable; particularly the detection of weak bands and lines which are usually obscured by relatively intense and broad bands; the measurement of the temperature shift of the absorption maxima or the temperature dependence of their intensities and all that will give the keys to these puzzles. Especially for Co^{3+} complexes, the absorption spectra of $[CoF_6]^{3-}$ will be interesting, since it has the paramagnetic normal state and its spectra may be identified with our energy level diagram where the value of Dq we must adopt is smaller than those at which the alteration of the ground state occur.

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