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STUDIES OF ABSORPTION SPECTRA II

Theory of Copper (II)-Spectra

BY

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Theory of Copper (II) Spectra

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Most of the theoretical work concerning the constitution and the magnetic behaviour of the complexes of the transition elements has been done on the basis of Pauling's theory, developed in his famous paper and book.¹ While this theory naturally accounts for the stereochemistry of these as well as for many other chemical compounds, it does not tell anything directly about the very characteristic absorption spectra of complex ions in solution. These features, being connected with the low excited electronic states of the cation, may be described by a perturbation treatment, in which it is investigated how the different states of the ion will split up under the influence of the outer field created by the surrounding radicals, the so-called ligands.

Already in 1929, BETHE² had evaluated the splittings of different orbits due to the influences of various outer fields, and VAN VLECK and his school³ had used this view to account for different properties of crystals. The idea of using this crystal-field theory on complex ions in aqueous solution is due to HARTMANN and ILSE,⁴ who applied it to explain the absorption spectrum of the titanium (III) ion. Later they extended the theory to the spectrum of the vanadium (III) ion,⁵ and in a recent paper⁶ BJERRUM, KLIXBÜLL JÖRGENSEN, and the present author on the same basis discussed the simpler copper (II) complexes, particularly their spectra and constitution.

¹ PAULING, L.: J.A.C.S. **53**, (1931) 1367; "The Nature of the Chemical Bond", Cornell University Press 1940.

² BETHE, H.: Ann. Physik 5 Folge, **3** (1929) 133.

³ VAN VLECK, J. H.: The Theory of Electric and Magnetic Susceptibilities. Oxford 1932.

⁴ HARTMANN, H., and ILSE, F. E.: Z. physik. Chem. **197** (1951) 239.

⁵ HARTMANN, H., and ILSE, F. E.: Z. Naturforschg. **6a**, (1951) 751.

⁶ BJERRUM, J. BALLHAUSEN, C. J., and KLIXBÜLL JÖRGENSEN, C.: Acta Chem. Scand. **8** (1954), 1275.

In the present paper, the detailed calculations underlying the results quoted in ref. 6 are given. It is possible in a very simple way to obtain the formulae determining the absorption spectra of those first transition group elements whose cations have one "effective" d -electron. In general the five-fold degenerate ground electronic level will split up, the splittings determining e. g. the magnetic susceptibility of the complex⁷ as well as the spectrum, which results from transitions between the different levels.

The titanium (III) ion was treated in this way.⁴ The electronic configuration of Ti^{+++} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$, the ion in solution being surrounded by six water molecules arranged octahedrally. The cubic field resulting from the six water dipoles will split the level of the $3d$ electron into two, thus producing one band. The spectra and complexes of the titanium (III) ion are not well-known, however, but all the spectra of the complexes $[Cu(NH_3)_n(H_2O)_{N-n}]^{++}$ have been reported.⁸ (N is the coordination number, and n takes the integral values 0 to N). As the electronic configuration of the cupric ion is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$ we can use the so-called hole formalism,⁹ a description of missing electrons stating that for most purposes the holes in a shell behave as positive electrons. This is equivalent to the well-known rule that the number and type of terms are the same, e. g. for the atomic configurations d^n and d^{10-n} . We shall therefore treat the copper (II) ion as having one $3d$ positron besides the closed zinc (II) ion configuration.

We consider a cupric ion surrounded by N ligands, and as the models of the complexes the following configurations are used: the square-planar, the tetrahedral, the square-pyramidal and the octahedral configuration (Fig. 1). The choice of these particular models follows from considerations given in ref. 6. We shall first treat the octahedral configuration, as the square planar and square pyramidal configurations are included in this calculation.

We neglect the spin-orbit interaction since it is weak as compared with the ligand field, and as the unperturbed eigenfunctions for the $3d$ positron we take the hydrogen-like wave functions:

⁷ PENNEY, W. G., and SCHLAPP, R.: Phys. Rev. **42** (1932) 666.

⁸ BJERRUM, J.: Dan. Mat. Fys. Medd. **11** (1932) no. 10. *ibid.* **12** (1934) no. 15.

⁹ CORSON, E. M.: Perturbation Methods in Quantum Mechanics. (Blackie & Son 1951.)

$$\left. \begin{aligned} \psi_0 &= R \bar{Y}_2^0(\theta, \varphi) \\ \psi_1 &= R \bar{Y}_2^1(\theta, \varphi) \\ \psi_{-1} &= R \bar{Y}_2^{-1}(\theta, \varphi) \\ \psi_2 &= R \bar{Y}_2^2(\theta, \varphi) \\ \psi_{-2} &= R \bar{Y}_2^{-2}(\theta, \varphi) \end{aligned} \right\} \quad (1)$$

Here $\bar{Y}_n^m(\theta, \varphi)$ are the surface spherical harmonics normalized to unity, defined by $\bar{Y}_n^m = \bar{P}_n^m(\cos \theta) \frac{e^{im\varphi}}{\sqrt{2\pi}}$, $\bar{P}_n^m(\cos \theta)$ are the associated Legendre polynomials normalized to unity, R is the function $R = \sqrt{\frac{8}{45}} \left(\frac{Z}{3a_0}\right)^{3/2} r^2 e^{-\frac{Z}{3a_0}r}$, also normalized to unity, a_0 is the Bohr radius, and Z is the effective charge on the nucleus. We are especially interested in the first-order perturbations resulting from dipoles, but this result is most easily obtained after the calculation of the perturbations resulting from charges $-q$ placed on the sites of the dipoles has been performed.

The Hamiltonian operator becomes:

$$\mathbf{H} = -\frac{\hbar^2}{2m} \nabla^2 + \frac{Ze^2}{r} - e^2 \left(\frac{q_1}{r_1} + \frac{q_2}{r_2} + \frac{q_3}{r_3} + \frac{q_4}{r_4} + \frac{q_5}{r_5} + \frac{q_6}{r_6} \right)$$

or in terms of atomic units (used in this paper) we have for the perturbation term:

$$\mathbf{H}^{(1)} = -\left(\frac{q_1}{r_1} + \frac{q_2}{r_2} + \frac{q_3}{r_3} + \frac{q_4}{r_4} + \frac{q_5}{r_5} + \frac{q_6}{r_6} \right)$$

This quantity can be expanded in terms of the surface spherical harmonic as

$$\left. \begin{aligned} \mathbf{H}^{(1)} &= -\sum_{n=0}^{\infty} \sum_{m=-n}^n \sum_{N=1}^4 q_N \frac{4\pi}{2n+1} \cdot \frac{r_{<}^n}{r_{>}^{n+1}} \bar{Y}_n^m \left(\bar{Y}_n^m \left(\frac{\pi}{2}, N \right) \right)^* \\ &\quad - (q_5 + q_6) \sum_{n=0}^{\infty} \frac{r_{<}^n}{r_{>}^{n+1}} \sqrt{\frac{4\pi}{2n+1}} \bar{Y}_n^0 \end{aligned} \right\} \quad (2)$$

(A proof of this is given in ref. 10.) The first term in (2) is due to the charges in the plane, the second to the two charges placed

¹⁰ EYRING, H., WALTER, J., and KIMBALL, G. E.: Quantum Chemistry. (John Wiley & Sons 1944.)

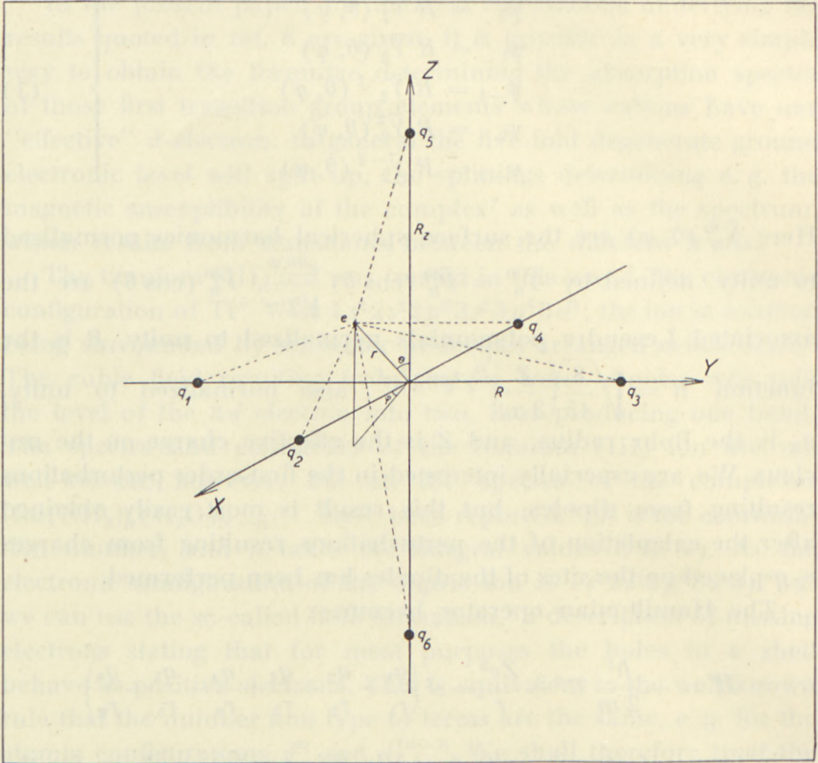


Fig. 1. Model of various types of configurations. The positions labelled 1—4 represent the square, 1—5 the square pyramid, and 1—6 the octahedron (or tetragonal bipyramid). Distances $r_1 - r_6$ from the ligands to the electron. Dipoles $\mu_1 - \mu_6$, and charges $q_1 - q_6$.

on the Z -axis. First we shall treat the perturbations due to the first term and obtain e. g. for $q_1 \neq q_2$ and $q_2 = q_3 = q_4$

$$\begin{aligned}
 H^{(1)} = & -q_1 \sum_{n=0}^{\infty} \sum_{m=-n}^n \frac{4\pi}{2n+1} \frac{r_{<}^n}{r_{>}^{n+1}} \bar{Y}_n^m \bar{Y}_n^{*m} \left(\frac{\pi}{2}, 0 \right) \\
 & -q_2 \sum_0^{\infty} \sum_{-n}^n \frac{4\pi}{2n+1} \frac{r_{<}^n}{r_{>}^{n+1}} \bar{Y}_n^m \bar{Y}_n^{*m} \left(\frac{\pi}{2}, \frac{\pi}{2} \right) \\
 & -q_2 \sum_0^{\infty} \sum_{-n}^n \frac{4\pi}{2n+1} \frac{r_{<}^n}{r_{>}^{n+1}} \bar{Y}_n^m \bar{Y}_n^{*m} \left(\frac{\pi}{2}, \pi \right) \\
 & -q_2 \sum_0^{\infty} \sum_0^n \frac{4\pi}{2n+1} \frac{r_{<}^n}{r_{>}^{n+1}} \bar{Y}_n^m \bar{Y}_n^{*m} \left(\frac{\pi}{2}, \frac{3\pi}{2} \right).
 \end{aligned}$$

Remembering that $\bar{Y}_n^m(\theta, \varphi) = e^{im\varphi} \bar{Y}_n^m(\varphi, 0)$ and $(\bar{Y}_n^m)^* = (-1)^m \bar{Y}_n^{-m}$ we have:

$$\mathbf{H}^{(1)} = -[q_1 + g(m) q_2] \sum_0^\infty \sum_{-n}^n \frac{4\pi}{2n+1} \frac{r_{<}^n}{r_{>}^{n+1}} \bar{Y}_n^m \bar{Y}_n^{*m} \left(\frac{\pi}{2}, 0 \right)$$

or

$$\mathbf{H}^{(1)} = -[q_1 + g(m) q_2] \frac{1}{\sqrt{2\pi}} \sum_0^\infty \sum_{-n}^n \frac{4\pi}{2n+1} \frac{r_{<}^n}{r_{>}^{n+1}} \bar{Y}_n^m \bar{P}_n^m(0),$$

where $g(m) = 3$ for $m = 0$ and ± 4
 $g(m) = -1$ for $m = \pm 1, \pm 2, \pm 3$.

In the general case we have for the first term in (2):

$$\mathbf{H}^{(1)} = -D(m, q) \frac{1}{\sqrt{2\pi}} \sum_{n=0}^\infty \sum_{m=-n}^n \frac{4\pi}{2n+1} \frac{r_{<}^n}{r_{>}^{n+1}} \bar{Y}_n^m(\theta, \varphi) \bar{P}_n^m(0) \quad (3)$$

in which expression $D(m) = q_1 \cdot f(m) + q_2 \cdot g(m)$.

The different terms $H_{NN'}^{(1)} = \int \psi_N \mathbf{H}^{(1)} \psi_{N'}^* d\tau$, must now be evaluated in order to get the secular equation.

We get

$$\left. \begin{aligned} \mathbf{H}_{NN'}^{(1)} &= \int R^2 \bar{Y}_2^{m'} (\bar{Y}_2^{m''})^* \mathbf{H}^{(1)} d\tau \\ &= \int R^2 [A \bar{Y}_4^m + B \bar{Y}_2^m + C \bar{Y}_0^m] \mathbf{H}^{(1)} d\tau, \end{aligned} \right\} \quad (4)$$

where

$$m = m' - m'',$$

and A, B and C are constants, related to the Wigner coefficients. (See CONDON and SHORTLEY¹¹ for the nomenclature and formulae of the Wigner coefficients.) The values of A, B and C are

$$A = \int \bar{Y}_2^{m'} (Y_4^m)^* (\bar{Y}_2^{m''})^* d\Omega = (-1)^{m''} \sqrt{\frac{5}{14\pi}} (22 m' - m'' | 224 m)$$

$$B = \int \bar{Y}_2^{m'} (\bar{Y}_2^m)^* (\bar{Y}_2^{m''})^* d\Omega = (-1)^{m''} \left(-\sqrt{\frac{5}{14\pi}} \right) (22 m' - m'' | 222 m)$$

$$C = \int \bar{Y}_2^{m'} (\bar{Y}_0^m)^* (\bar{Y}_2^{m''})^* d\Omega = (-1)^{m''} \sqrt{\frac{5}{4\pi}} (22 m' - m'' | 2200).$$

¹¹ CONDON, E. U., and SHORTLEY, G. H.: The Theory of Atomic Spectra, p. 73. (Cambridge 1953).

Further we have:

$$\left. \begin{aligned} \int \bar{Y}_n^m (\bar{Y}_{n'}^{m'})^* d\Omega &= \delta_{nn'} \delta_{mm'} \\ \delta_{nn'} &= \begin{cases} 0 & \text{for } n \neq n' \\ 1 & \text{for } n = n' \end{cases} \quad \delta_{mm'} = \begin{cases} 0 & \text{for } m \neq m' \\ 1 & \text{for } m = m' \end{cases} \end{aligned} \right\} \quad (5)$$

Now, from this it is seen that in

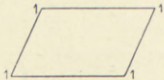
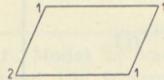
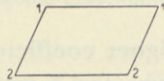
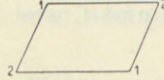
$$H_{NN'}^{(1)} = -D(m, q) \frac{1}{\sqrt{2\pi}} \int R^2 (A\bar{Y}_4^m + B\bar{Y}_2^m + C\bar{Y}_0^m) \sum_0^{\infty} \sum_{-n}^n \frac{4\pi}{2n+1} \frac{r_{>}^n}{r_{>}^{n+1}} \bar{Y}_n^m \bar{P}_n^m(0) dt$$

n can only be 4, 2 and 0 if $H_{NN'}^{(1)} \neq 0$.

As $\bar{P}_n^m = 0$ for $|m| = n - 1, n - 3, n - 5 \dots$ it also follows that $|m| = 0, 2, 4$.

The following table gives the values of $D(m)$ for different m :

TABLE 1.

Configuration	$ m $	$D(m, q)$
	0 and 4	$4 q_1$
	2	0
	0 and 4	$3 q_1 + q_2$
	2	$-q_1 + q_2$
	0 and 4	$2 q_1 + 2 q_2$
	2	0
	0 and 4	$2 q_1 + 2 q_2$
	2	$-2 q_1 + 2 q_2$

The secular equation is then:

$$\begin{vmatrix} H_{-2-2}^{(1)} - E^{(1)} & 0 & H_{20}^{(1)} & 0 & H_{-22}^{(1)} \\ 0 & H_{-1-1}^{(1)} - E^{(1)} & 0 & H_{-11}^{(1)} & 0 \\ H_{0-2}^{(1)} & 0 & H_{00}^{(1)} - E^{(1)} & 0 & H_{02}^{(1)} \\ 0 & H_{1-1}^{(1)} & 0 & H_{11}^{(1)} - E^{(1)} & 0 \\ H_{2-2}^{(1)} & 0 & H_{20}^{(1)} & 0 & H_{22}^{(1)} - E^{(1)} \end{vmatrix} = 0 \quad (6)$$

From the definition of $(\bar{Y}_n^m)^* = (-1)^m \bar{Y}_m^{-m}$ it is seen that when the indices are even

$$H_{NN'}^{(1)} = H_{-N-N'}^{(1)} \text{ and } H_{N-M}^{(1)} = H_{-NM}^{(1)} = H_{-MN}^{(1)}.$$

Using these relations, and by applying row and column additions and subtractions, it is possible to reduce the determinant to a diagonal form with the solutions

$$\left. \begin{aligned} E^{(1)} &= H_{11}^{(1)} + H_{1-1}^{(1)} \\ E^{(1)} &= H_{11}^{(1)} - H_{1-1}^{(1)} \\ E^{(1)} &= H_{22}^{(1)} - H_{2-2}^{(1)} \\ (E^{(1)})^2 - (H_{2-2}^{(1)} + H_{22}^{(1)} + H_{00}^{(1)})E^{(1)} + (H_{00}^{(1)}H_{2-2}^{(1)} + H_{00}^{(1)}H_{22}^{(1)} - 2(H_{20}^{(1)})^2) &= 0. \end{aligned} \right\} (7)$$

If we now look at the second term of (2), it is seen that for this term $m = 0$. This means that after (5) only the diagonal terms in (6) are affected, and we have in general

$$H_{NN'}^{(1)} = - \int R^2 (A \bar{Y}_n^m + B \bar{Y}_2^m + C \bar{Y}_0^m) \left[\frac{D(m, q)}{\sqrt{2\pi}} \sum_0^\infty \sum_{-n}^n \frac{4\pi}{2n+1} \frac{r_{>}^n}{r_{>}^{n+1}} \bar{Y}_n^m \bar{P}_n^m(0) \right. \\ \left. + (q_5 + q_6) \sum_0^\infty \frac{r_{>}^n}{r_{>}^{n+1}} \sqrt{\frac{4\pi}{2n+1}} \bar{Y}_n^0 \right] d\tau.$$

The evaluation of $H_{NN'}^{(1)}$, is now simple, the results being for ion-ion complexes: (the values of the G 's are determined individually by corresponding sets of R and q)

$$\left. \begin{aligned} H_{00}^{(1)} &= -D(0, q) \frac{8}{45} f \left[G_0 - \frac{1}{7} G_2 + \frac{3}{38} G_4 \right] \\ &\quad - \frac{8}{45} f(q_5 + q_6) \left[G_0 + \frac{2}{7} G_2 + \frac{2}{7} G_4 \right] \\ H_{11}^{(1)} &= -D(0, q) \frac{8}{45} f \left[G_0 - \frac{1}{14} G_2 - \frac{1}{14} G_4 \right] \\ &\quad - \frac{8}{45} f(q_5 + q_6) \left[G_0 + \frac{1}{7} G_2 - \frac{4}{21} G_4 \right] \\ H_{22}^{(1)} &= -D(0, q) \frac{8}{45} f \left[G_0 + \frac{1}{7} G_2 + \frac{1}{56} G_4 \right] \\ &\quad - \frac{8}{45} f(q_5 + q_6) \left[G_0 - \frac{2}{7} G_2 + \frac{1}{21} G_4 \right] \end{aligned} \right\} (8)$$

$$\left. \begin{aligned} H_{20}^{(1)} &= -D(2, q) \frac{8}{45} f \left[-\frac{5}{28\sqrt{6}} G_4 - \frac{3}{7\sqrt{6}} G_2 \right] \\ H_{2-2}^{(1)} &= -D(4, q) \frac{8}{45} f \frac{5}{24} G_4 \\ H_{1-1}^{(1)} &= -D(2, q) \frac{8}{45} f \left[\frac{5}{42} G_4 - \frac{3}{14} G_2 \right], \end{aligned} \right\} \quad (8)$$

where

$$G_n = \int_0^R f^6 r^6 e^{-2fr} \frac{r^n}{R^{n+1}} dr + \int_R^\infty f^6 r^6 e^{-2fr} \frac{R^n}{r^{n+1}} dr$$

and $f = \frac{Z}{3}$, using the nomenclature of Hartmann and Ilse.

Evaluating these integrals, we get

$$\begin{aligned} G_0 &= \frac{45}{8x} - \left(\frac{45}{8x} + \frac{75}{8} + \frac{15}{2}x + \frac{15}{4}x^2 + \frac{5}{4}x^3 + \frac{1}{4}x^4 \right) e^{-2x} \\ G_2 &= \frac{315}{4x^3} - \left(\frac{315}{4x^3} + \frac{315}{2x^2} + \frac{315}{2x} + 105 + \frac{105}{2}x + \frac{165}{8}x^2 + \frac{25}{4}x^3 + \frac{5}{4}x^4 \right) e^{-2x} \\ G_4 &= \frac{14175}{8x^5} - \left(\frac{14175}{8x^5} + \frac{14175}{4x^4} + \frac{14175}{4x^3} + \frac{4725}{2x^2} + \frac{4725}{4x} + \frac{945}{2} + \frac{315}{2}x \right. \\ &\quad \left. + 45x^2 + \frac{45}{4}x^3 + \frac{9}{4}x^4 \right) e^{-2x} \end{aligned}$$

when $x = fR$.

A few values of G_2 and G_4 are tabulated in Table 2.

TABLE 2.
Values of radial functions.

$x = fR$	G_2	G_4
7	0.2241	0.09533
8	0.1527	0.05200
9	0.1080	0.02960
10	0.0788	0.01772
11	0.0592	0.01100
12	0.0456	0.00712

$$x = \frac{Z}{3} \cdot R = fR \quad (R \text{ in a. u.})$$

For numerical calculations on copper (II) complexes Z is taken as 7.85 (cf. SLATER, Phys. Rev., 36, (1930) 57.)

With the help of Table 1, (7) and (8) we can now estimate the maxima of the absorption spectra of a cation — anion complex.

The ions CuCl_4^{--} and CuBr_4^{--} are of this type, even if according to the discussion in ref. 6, one might predict the composition to be $[\text{CuCl}_4(\text{H}_2\text{O})_2]^{--}$ in aqueous solution. It is not easy, however, to estimate the values of the parameters in the formula for the absorption of this complex, since the perturbation is due both to the charge of the halide ion and the induced dipole moment of the latter, caused by the influence of the cupric ion.

Both the chloro- and bromo-complexes have an absorption in the infrared. Now the distance $\text{Cu}^{++} - \text{Br}^-$ must be greater than the distance $\text{Cu}^{++} - \text{Cl}^-$, which means that the perturbation is smaller in the bromo-complex, and the absorption maximum is thus displaced towards the red in accordance with observation of the infrared band. (From $\lambda = 960 \text{ m}\mu$ in 13 M. HCl to $\lambda = 1100 \text{ m}\mu$ in 9 M. HBr.)

However, CuCl_4^{--} also has a very strong absorption in the ultraviolet passing into the violet, and the solution is therefore yellow.¹² CuBr_4^{--} has an absorption in the blue, passing into the infrared band; the solution is therefore red.

Thus the situation is more complicated than the simple description indicated before. There must be electron exchange between the anion and the cation of these complexes as the non-existence of copper (II) iodide seems to suggest.¹³ The strong absorption in the ultraviolet and visible regions may therefore be electron transfer spectra due to this exchange.

The spectra of the dipole — cation complexes are more interesting from the standpoint of this theory, since they have no absorption in the near ultraviolet. The absorption maxima for such complexes can be found in the following way:

We place a charge $-q$ at a distance R and a charge $+q$ at a distance $R + \Delta R$ from the cupric ion. As $\Delta X = f\Delta R$

$$\begin{aligned} H_{NN'}^{(1)} &= -D(m, q) \frac{8}{45} f \left[\sum_s K_s G_s(x) - \sum_s K_s G_s(x + \Delta x) \right] \\ &= D(m, q) \frac{8}{45} f \Delta x \sum_s K_s \frac{dG_s}{dx} = D(m, \mu) \frac{8}{45} f^2 \sum_s K_s B_s, \end{aligned}$$

¹² BJERRUM, J.: Dan. Mat. Fys. Medd. **22** (1946) no. 18.

¹³ FAJANS, K.: Naturwiss. **11** (1923) 165.

where μ is the point dipole equal to $eq\Delta R$. Then

$$\left. \begin{aligned}
 H_{00}^{(1)} &= D(0, \mu) \frac{8}{45} f^2 \left[B_0 - \frac{1}{7} B_2 + \frac{3}{28} B_4 \right] \\
 &\quad + \frac{8}{45} f^2 (\mu_5 + \mu_6) \left[B_0 + \frac{2}{7} B_2 + \frac{2}{7} B_4 \right] \\
 H_{11}^{(1)} &= D(0, \mu) \frac{8}{45} f^2 \left[B_0 - \frac{1}{14} B_2 - \frac{1}{14} B_4 \right] \\
 &\quad + \frac{8}{45} f^2 (\mu_5 + \mu_6) \left[B_0 + \frac{1}{7} B_2 - \frac{4}{21} B_4 \right] \\
 H_{22}^{(1)} &= D(0, \mu) \frac{8}{45} f^2 \left[B_0 + \frac{1}{7} B_2 + \frac{1}{56} B_4 \right] \\
 &\quad + \frac{8}{45} f^2 (\mu_5 + \mu_6) \left[B_0 - \frac{2}{7} B_2 + \frac{1}{21} B_4 \right] \\
 H_{20}^{(1)} &= D(2, \mu) \frac{8}{45} f^2 \left[-\frac{5}{28\sqrt{6}} B_4 - \frac{3}{7\sqrt{6}} B_2 \right] \\
 H_{2-2}^{(1)} &= D(4, \mu) \frac{8}{45} f^2 \frac{5}{24} B_4 \\
 H_{1-1}^{(1)} &= D(2, \mu) \frac{8}{45} f^2 \left[\frac{5}{42} B_4 - \frac{3}{14} B_2 \right]
 \end{aligned} \right\} (9)$$

q_1 and q_2 in the formula for $D(m)$ are altered to μ_1 and μ_2 , the values of the B 's are determined by corresponding sets of R and μ , and the functions used are:

$$\begin{aligned}
 \frac{dG_n}{dx} &= B_n \\
 B_0 &= -\frac{45}{8x^2} \left[+\frac{45}{8x^2} + \frac{45}{4x} + \frac{45}{4} + 6x + \frac{15}{4}x^2 + \frac{3}{2}x^3 + \frac{1}{2}x^4 \right] e^{-2x} \\
 B_2 &= -\frac{945}{4x^4} + \left[\frac{945}{4x^4} + \frac{945}{2x^3} + \frac{945}{2x^2} + \frac{315}{x} + \frac{315}{2} + \frac{255}{2}x + \frac{90}{4}x^2 \right. \\
 &\quad \left. + \frac{15}{2}x^3 + \frac{5}{2}x^4 \right] e^{-2x} \\
 B_4 &= -\frac{70875}{8x^6} + \left[\frac{70875}{8x^6} + \frac{70875}{4x^5} + \frac{70875}{4x^4} + \frac{23625}{2x^3} + \frac{23625}{4x^2} \right. \\
 &\quad \left. + \frac{4725}{2x} + \frac{1575}{2} + 225x + \frac{225}{4}x^2 + \frac{27}{2}x^3 + \frac{9}{2}x^4 \right] e^{-2x}
 \end{aligned}$$

The functions are tabulated in Table 3. A graphical representation is given in Fig. 2.

TABLE 3.
Values of derived radial functions.

$x = fR$	$-B_0$	$-B_2$	$-B_4$
3.0	0.2213	0.1054	0.0500
3.5	0.2527	0.2118	0.1619
4.0	0.2414	0.2489	0.2050
4.5	0.2203	0.2420	0.2012
5.0	0.1957	0.2136	0.1740
6.0	0.1491	0.1437	0.1067
7.0	0.1132	0.08980	0.05779
8.0	0.08754	0.05585	0.03022
9.0	0.06937	0.03563	0.01596
10.0	0.05625	0.02356	0.008859
11.0	0.04649	0.01614	0.005001
12.0	0.03906	0.01139	0.002967
13.0	0.03328	0.008272	0.001836
14.0	0.02868	0.006152	0.001177

With the aid of Table 1, (7), and (9), we are able to calculate the maximum of absorption for various types of ammine-cupric ions.

First, the square planar configuration, equal distances R and equal dipole moments: (The Γ notation is the notation of Bethe²)

$$\left. \begin{aligned} E(\Gamma_{3(t1)}) &= \mu f^2 \frac{8}{45} \left[4 B_0 - \frac{4}{7} B_2 + \frac{3}{7} B_4 \right] && \text{1-fold degenerate.} \\ E(\Gamma_{3(t3)}) &= \mu f^2 \frac{8}{45} \left[4 B_0 + \frac{4}{7} B_2 + \frac{19}{21} B_4 \right] && \text{1-fold degenerate.} \\ E(\Gamma_{5(t4)}) &= \mu f^2 \frac{8}{45} \left[4 B_0 + \frac{4}{7} B_2 - \frac{16}{21} B_4 \right] && \text{1-fold degenerate.} \\ E(\Gamma_{5(t5)}) &= \mu f^2 \frac{8}{45} \left[4 B_0 - \frac{2}{7} B_2 - \frac{2}{7} B_4 \right] && \text{2-fold degenerate.} \end{aligned} \right\} (10)$$

Next, the square pyramidal ($\alpha = 1$) and the distorted octahedron ($\alpha = 2$). R and μ the same in the plane, and perpendicular to the plane one or two dipoles μ_z at a distance R_z : (also here corresponding μ and R are to be taken together):

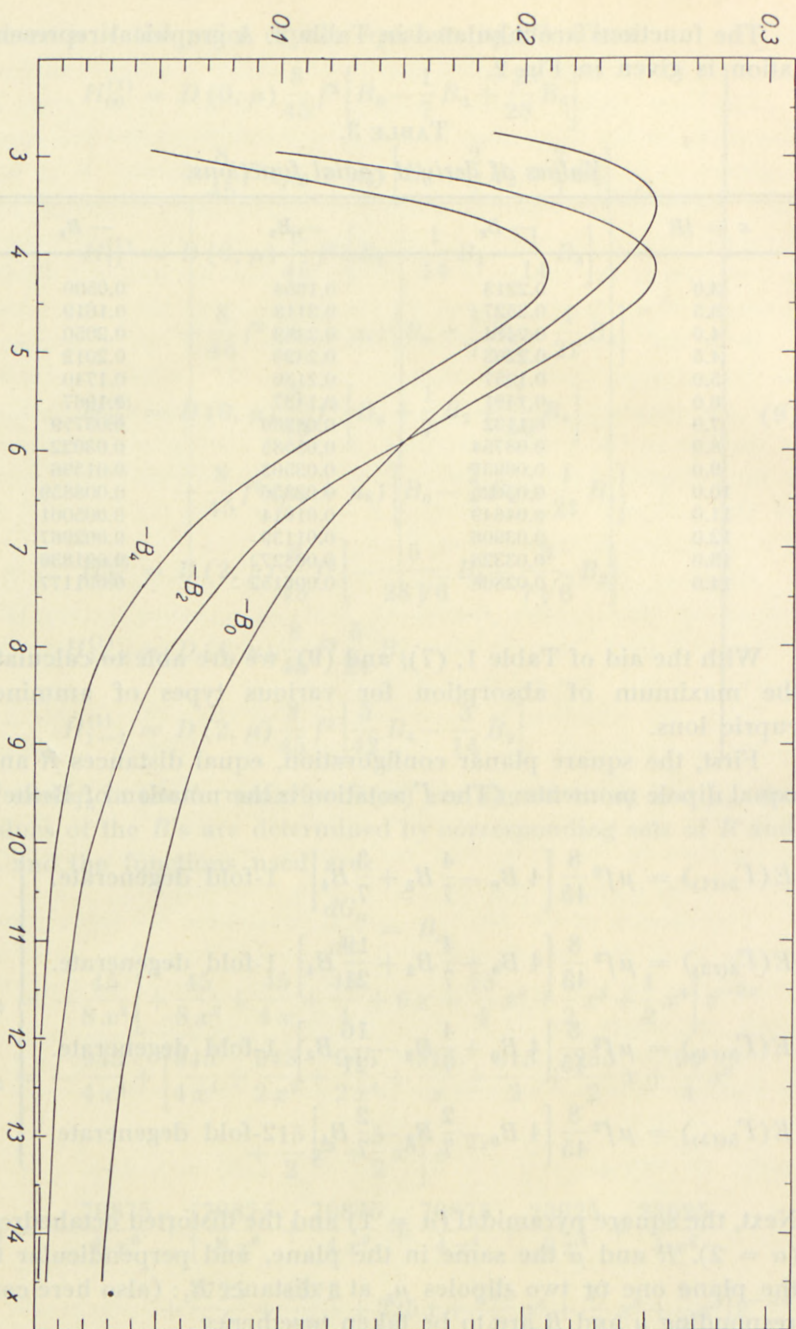


Fig. 2. Graphical representation of $-B_0$, $-B_2$ and $-B_4$ $x = l/R$ a. u.

$$\left. \begin{aligned}
 E(\Gamma_{3(t1)}) &= \mu f^2 \frac{8}{45} \left[4 B_0 - \frac{4}{7} B_2 + \frac{3}{7} B_4 \right] + \mu_z f^2 \frac{8}{45} \alpha \left[B_0 + \frac{2}{7} B_2 + \frac{2}{7} B_4 \right] \\
 E(\Gamma_{3(t3)}) &= \mu f^2 \frac{8}{45} \left[4 B_0 + \frac{4}{7} B_2 + \frac{19}{21} B_4 \right] + \mu_z f^2 \frac{8}{45} \alpha \left[B_0 - \frac{2}{7} B_2 + \frac{1}{21} B_4 \right] \\
 E(\Gamma_{5(t4)}) &= \mu f^2 \frac{8}{45} \left[4 B_0 + \frac{4}{7} B_2 - \frac{16}{21} B_4 \right] + \mu_z f^2 \frac{8}{45} \alpha \left[B_0 - \frac{2}{7} B_2 + \frac{1}{21} B_4 \right] \\
 E(\Gamma_{5(t5)}) &= \mu f^2 \frac{8}{45} \left[4 B_0 - \frac{2}{7} B_2 - \frac{2}{7} B_4 \right] + \mu_z f^2 \frac{8}{45} \alpha \left[B_0 + \frac{1}{7} B_2 - \frac{4}{21} B_4 \right]
 \end{aligned} \right\} (11)$$

The configuration of $\text{Cu}(\text{H}_2\text{O})_6^{++}$ is shown in ref. 6 to be a distorted octahedron. For this complex $\Gamma_{t3} < \Gamma_{t1} < \Gamma_{t4} < \Gamma_{t5}$.

If $\mu = \mu_z$ and $R = R_z$ (the regular octahedron) we obtain:¹⁴

$$\left. \begin{aligned}
 E(\Gamma_3) &= \frac{8}{45} f^2 \mu [6 B_0 + B_4] \quad \text{2-fold degenerate.} \\
 E(\Gamma_5) &= \frac{8}{45} f^2 \mu \left[6 B_0 - \frac{2}{3} B_4 \right] \quad \text{3-fold degenerate.} \\
 \Delta E &= \frac{8}{27} f^2 \mu B_4 \qquad E(\Gamma_5) > E(\Gamma_3)
 \end{aligned} \right\} (12)$$

It is seen that the distorted octahedral configuration will give three bands, the frequency of the maxima of the bands given

by: $h\nu_n = \Gamma_{t3} \rightarrow \begin{cases} \Gamma_{t5} \\ \Gamma_{t4} \\ \Gamma_{t1} \end{cases}$ if we look at $\text{Cu}(\text{H}_2\text{O})_6^{++}$. For the first two bands in this complex we shall have:

$$\frac{\nu_1}{\nu_2} = \frac{E(\Gamma_{t5}) - E(\Gamma_{t3})}{E(\Gamma_{t4}) - E(\Gamma_{t3})}$$

In this relation we have a connection between the absorption maxima and the values of the dipoles at the different sites. This

¹⁴ This result is identical with that of HARTMANN and ILSE.⁴ However, we disagree with their formula for G_0 and that for $E(B_{2g})$ on p. 242. For the coefficient to $H(4)$ we obtain $\frac{128}{945}$.

formula and the experimentally estimated ratio $\nu_1/\nu_2 = 1.33$ is used in ref. 6 to show that the configuration of $\text{Cu}(\text{H}_2\text{O})_6^{++}$ can only be slightly distorted. If the configuration is distorted much, it would be necessary to have $\mu_z > \mu$ in order to get the right absorption maximum, but it is known from chemical considerations that this is not the case. It is shown in ref. 6 that a good agreement between the experimentally known facts and the theory is obtained by using $N = 6$ for $\text{Cu}(\text{H}_2\text{O})_N^{++}$ in a slightly distorted octahedral configuration, where $R = 1.95 \text{ \AA}$ and $R_z = 2.00 \text{ \AA}$.

The formulae for the absorption of the mixed complexes are not written out because of their great length, but they are easily obtained with the help of Table 1, (7) and (9). Numerical calculations of the maxima of the first band for the various cupric ammine complexes are tabulated in ref. 6. The agreements between the known and calculated absorption maxima are remarkable.

If we treat the tetrahedral configuration with $N = 4$ and equal dipoles μ we similarly obtain:

$$\left. \begin{aligned} E(\Gamma_3) &= \mu f^2 \frac{8}{45} \left[4 B_0 - \frac{4}{9} B_4 \right] \quad \text{2-fold degenerate.} \\ E(\Gamma_5) &= \mu f^2 \frac{8}{45} \left[4 B_0 + \frac{8}{27} B_4 \right] \quad \text{3-fold degenerate.} \\ E(\Gamma_3) &> E(\Gamma_5). \end{aligned} \right\} \quad (13)$$

These results agree with those of BETHE,² who has proved that under the influence of a cubic field, such as that provided by the regular octahedral and tetrahedral configurations, the five fold $(2L + 1)$ degenerate 2D level will split up into two. The more unsymmetrical a field we put on the 2D level, the more splittings we get, until at last the degeneracy is completely removed. It follows from the above discussion that in the distorted octahedral complexes $[\text{Cu}(\text{NH}_3)_n(\text{H}_2\text{O})_{6-n}]^{++}$ the number of bands will depend only on the ligands in the co-planar positions 1 — 4. Four identical ligands ($\mu_1 = \mu_2 = \mu_3 = \mu_4$) or cis-placing of two identical ligands ($\mu_1 = \mu_2 \mp \mu_3 = \mu_4$) leads to 3 bands; the introduction of one different ligand ($\mu_1 \mp \mu_2 = \mu_3 = \mu_4$), or trans-placing ($\mu_1 = \mu_3 \mp \mu_2 = \mu_4$) will give 4 bands.

The ground level for nine d-electrons in the regular octahedron is 2-fold degenerate, but in the tetrahedral case this level is 3-fold degenerate. If we multiply the functions for the different levels by their degeneracy number and then add up the resulting terms, all the B 's except B_0 vanish. This means that the "centre of gravity" of the levels is not altered by applying a perturbation to the system (cf. ref. 2).

We may conclude from the calculations on dipole-cation complexes that electronic exchange between the ligands and the central ion cannot be very important for the absorption spectra of such complexes. Now it has been pointed out by ORGEL¹⁵ that the theories of PAULING and VAN VLECK are closely connected. In this respect it may be noted that the ground energy of the planar configuration given by (10) is lower than that of the tetrahedral configuration calculated in the same way (14) even when the electrostatic interaction of the ligands is taken into account.

A difficulty of the present theory is that dipole transitions between different levels are forbidden. The occurrence of "forbidden" transitions in such complicated systems as those we are dealing with can, however, have many reasons.¹⁶ Furthermore, there seems to be experimental evidence for the assumption that the intensity of the spectra (a rough measure of which is given by $\epsilon_{\max} \cdot \nu_{1/2}$, where ϵ_{\max} is the molar extinction coefficient of the maxima and $\nu_{1/2}$ the half-width of the band in cm^{-1}) is connected with the symmetry of the perturbing field. The intensity of e. g. the $[\text{Ni}(\text{NH}_3)_n(\text{H}_2\text{O})_{6-n}]^{++}$ complexes, which can be seen from the spectra computed by BJERRUM,¹⁷ is greatest for $n = 3$.

The spectra of high intensity ($\epsilon_{\max} \sim 2000$) we shall call electron transfer spectra, these being due to transfer of electrons from the ligands to the metal ion. The spectra due to the influence of ligands on the energy terms of the partially filled electron shells in the central atom we shall call transition group spectra, because they only occur in the transition groups of the periodic system. These latter spectra are mainly of two kinds, the first having a molar extinction coefficient $\epsilon \sim 10$, the second having $\epsilon \sim 0.1$. The ultraviolet spectrum of CuCl_4^{--} is an electron transfer spectrum;

¹⁵ ORGEL, L. E.: J. Chem. Soc. **1952**, 4756.

¹⁶ HERZBERG, C: Spectra of Diatomic Molecules. (D. VAN NOSTRAND 1950.)

¹⁷ BJERRUM, J.: Metal Ammine Formation in Aqueous Solution, p. 196. (Copenhagen 1941.)

the bands of the cupric amines are transition group spectra of the first kind, while all the bands of Mn^{++} are transition group spectra of the second kind. It is hoped that further investigations will throw more light on these questions.

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