

einem heissen Luftstrom bis zu etwa 5 ml eingengt, durch eine Aluminiumoxydsäule (Aluminiumoxyd alkalifrei "Woelm"), 3 cm × 1,5 cm, filtriert, die Säule mit 5 ml Wasser ausgewaschen und das fast farblose Filtrat weiter, wie oben beschrieben, eingengt.

*Papierchromatographie:* Aus dem isolierten Zuckergemisch wurden variierende Mengen für die papierchromatographischen Untersuchungen entnommen. Die Chromatogramme (Whatman Filtrierpapier No. 1 in Bogen 45 × 18 cm) wurden mit absteigender mobiler Flüssigkeitsphase als 20—24-stündige Durchlaufschromatogramme entwickelt. Flüssigkeitsgemisch: Amylalkohol puriss. "Merck", Pyridin puriss. "Merck", Wasser, 7+7+6 Raumteile (einquasigiges Gemisch). Als Vergleichssubstanzen wurden auf jedes Chromatogramm Umbelliferose, Raffinose und Saccharose appliziert.

*Sprühreagens:* Eine gesättigte, wässrige Lösung von Harnstoff-Oxalat. Nach dem Besprühen des Chromatogramms wurde dies 5 Minuten auf 130—140° im Trockenschrank erwärmt. Ketosehaltige Zucker ergeben grünschwarze Flecke.

Für ökonomische Unterstützung dieser Arbeit bin ich *A/S Norsk Varekrævsforstyrings Fond* zu besonderem Dank verpflichtet.

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## The Electrostatic Model for Calculation of the Ligand Field Parameter of Octahedral Complexes

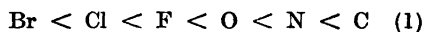
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Since 1951, several authors<sup>1,2</sup> have applied the ligand field theory to the absorption spectra of octahedral complexes with partly filled d-shells and found very good agreement with the observed energy levels, provided that reasonable values are chosen for the ligand field parameter  $\Delta$  (also denoted by  $(E_1 - E_2)$  or  $10 Dq$  or

$\frac{10}{21} K$ ), the energy difference between the high  $\gamma_3$ -orbital and the low  $\gamma_2$ -orbital (containing at most four and six electrons, respectively). All the wavenumbers of the Laporte-forbidden bands can be expressed as multiples of  $\Delta$  plus linear combinations of term distances, which seem<sup>3</sup> to have somewhat smaller values for complexes than the corresponding gaseous ions.

When the observed values of  $\Delta$  are compared, many regularities are conspicuous, which support the value of the treatment: For a given ligand,  $\Delta$  increases with the oxidation state of the central ion and with the principal quantum number 3d, 4d, and 5d. For a given central ion, Tsuchida's spectrochemical series can be expressed as increasing values of  $\Delta$ , depending mainly on the atom in the first coordination sphere:



Ilse and Hartmann<sup>4</sup> applied an electrostatic model to explain the absolute value of  $\Delta$ . Six point charges  $q$ , representing the ligands, perturb a hydrogen-like 3d-wavefunction yielding an energy difference in atomic units between the two possible energy levels  $\gamma_3$  and  $\gamma_2$ :

$$\Delta \cong \frac{8}{27} q \cdot \frac{Z_*}{3} \cdot G_4 \left( \frac{Z_*}{3} \cdot R \right) \quad (2)$$

where  $G_4(x) \cong \frac{14175}{8x^5}$

where  $Z_*$  is the effective charge acting on the hydrogen-like 3d-wavefunction and  $R$  the distance between the centre of the metal ion and the point charge. However, the actual 3d-radial function cannot be hydrogen-like; e. g. in a nickel(II) ion, the potential near the nucleus must necessarily correspond to  $Z = 28$  and for large distances  $r$  to  $Z = 3$ , while  $Z_*$  is some average value between these two limits. Recently, Hartree<sup>5</sup> calculated self-consistent field functions (with exchange) for gaseous ions which support this qualitative argument: When compared to a hydrogen-like function with the same average distance  $r$  of the electron from the nucleus, Hartree's function is larger both for small values of  $r$  (giving a smaller  $r_{\text{max}}$ ) and for large values of  $r$  (vanishing more slowly, corresponding to the external charge plus one), while it is smaller for intermediate  $r$ . Thus, it will be more generally valid to write eqn. 2 in the more old-fashioned way, discussed by Belford<sup>6</sup>:

$$\Delta \cong \frac{5}{3} q \cdot \frac{\bar{r}^4}{R^5} \quad (3)$$

As emphasized by Williams<sup>7</sup>, it is a very peculiar feature of the series (1) that neutral ligands such as H<sub>2</sub>O and NH<sub>3</sub> produce similar or larger values of  $\Delta$  than OH<sup>-</sup>, Cl<sup>-</sup> and other anions. The effect has been explained<sup>4,8</sup> as a perturbation from six dipoles with the point dipole moment  $\mu$ . It must be pointed out that the parameter  $\mu$  has no connection at all with the dipole moment of the ligand; only the negative end of a polarized molecule will have any appreciable effect (eqn. 3) independent of the distance to the positive end. Generally, the spatial distribution of charge will have larger effects, according to eqn. 3, than identical charges concentrated on a point. Thus,  $\Delta$  would be calculated as 3 000 K for  $q = 1$ ,  $Z_* = 7.2$  and  $R = 2.51$  Å from eqn. 2, while the CsNiCl<sub>6</sub>, studied by Asmussen and Bostrup<sup>9</sup> actually has  $\Delta = 6 900$  K, even though it contains octahedral environments, NiCl<sub>6</sub>, of the dimensions given above. However, this can easily be explained by the assumption of spherically symmetrical charge distributions (yielding, of course, no proof for the validity of the electrostatic model), since the most important contribution to  $\Delta$  is produced by the charge density just outside the nickel(II) ion with radius  $r_M$ .

If eqn. 3 is integrated for a sphere with radius  $r_L$  and charge  $q$  equally distributed in each volume element, one finds by neglecting the angular dependence of the perturbations from charge elements not on the axis containing the ligand's centre, that this expression can be derived:

$$\Delta \cong \frac{5}{12} q \cdot \frac{\bar{r}^4}{r_L^3 r_M^2} \quad (4)$$

The double segment common to the ligand and the sphere with  $r < r_0$  has the volume  $\frac{1}{3} \pi h_1^2 (3r_0 - h_1) + \frac{1}{3} \pi h_2^2 (3r_L - h_2)$ , which for  $r_0$  not much larger than  $r_M$  and  $r_L \gg r_M (\equiv h_1 \gg h_2)$  can be written  $\pi h_1^2 r_0$ , and thus, the volume element is  $2\pi r(r - r_M)dr$  and the charge element is  $\frac{3r(r - r_M)}{2r_L^3} dr$ , which then can be integrated from  $r_M$  outwards.

The expression (3) might of course be evaluated for different charge distributions, taking also the angular dependence of the perturbations into account; but these results would not have sufficiently quantitative significance, relative to the

necessary effort. The important feature of eqn. 4 is that  $\Delta$  is much increased, since  $r_L^{-3} r_M^{-2}$  generally is larger than  $4(r_L + r_M)^{-5}$ ; i. e. for  $r_L = 1.8$  Å and  $r_M = 0.7$  Å it is increased by a factor 9. The proportionality to  $r_L^{-3}$  seems confirmed to a certain degree by the series (1), even though the low values of  $\Delta$  for halide complexes (see the Table) may also be connected with  $\pi$ -bonding in the direction from the ligand to the central ion<sup>8</sup>.

|                           |                   |                   |                    |                   |
|---------------------------|-------------------|-------------------|--------------------|-------------------|
| Ligands:                  | 6 Br <sup>-</sup> | 6 Cl <sup>-</sup> | 6 H <sub>2</sub> O | 6 NH <sub>3</sub> |
| Nickel(II) <sup>9</sup>   | 6 500             | 6 900             | 8 500              | 10 800            |
| Rhodium(III) <sup>8</sup> | 18 900            | 20 300            | 27 000             | 33 900            |

The latter trend of thought was initiated by Van Vleck<sup>10</sup>, who demonstrated that the molecular orbital theory, assuming partly covalent bonding, implies nearly the same results as the electrostatic model. While much evidence for partly covalent bonding can be derived from the decrease of the  $F^k$ -integrals, relative to the gaseous ions<sup>11</sup>, the most conspicuous difficulty for the electrostatic theory, assuming pure d-orbitals, is the extension of the d-electrons. There is no doubt that a considerable amount of the partly filled shell in the gaseous ion is present<sup>6</sup> outside the crystallographic radius of the metal ion  $\sim 0.5 - 0.8$  Å, and this effect is further accentuated in the complexes<sup>3,11</sup>. However, the values of  $\Delta$  do not seem very much changed from those predicted by the electrostatic model. It is a rather general feature of the theoretical chemistry that the covalent and ionic structures have nearly the same energy, and the intermixing of them therefore does not produce large relative energy differences between the possible excited levels. Actually, the electrostatic model can be considered as yielding the perturbations, which are the further cause of introducing overlap with certain of the ligands' orbitals, as described by the group theory, of which the results are common to both theories.

Recently, several authors have attempted the difficult task of determining the absolute value of  $\Delta$  from combined electrostatic and molecular orbital theory. Kleiner<sup>12</sup> considered it impossible to apply the electrostatic theory to Cr(H<sub>2</sub>O)<sub>6</sub><sup>+++</sup>, since  $\Delta$  turned out to be slightly negative. However, it can easily be seen that this is caused by the neglect of orthogonality of

the d-wavefunction with the neighbourhood of the oxygen nuclei, since Hartree's function still has a large value there. From a magnetochemical study of  $\text{FeF}_2$  and  $\text{CoF}_2$ , rather small electrostatic field splittings have been obtained<sup>13</sup>, which nearly disappear or are reversed by introduction of the overlap. The level scheme does not agree well with the optical spectra of similar compounds, while Tanabe and Sugano<sup>14</sup> have taken up again the chromium(III) problem. Even though  $\Delta$  turns out to be of the right order of magnitude, it is a small effect as a difference between large quantities. So far, the electrostatic model seems still useful as a first order approximation, and there is much evidence that the partly covalent bonding\* has not yet reached the Pauling limiting value<sup>11</sup>, even for cobalt(III) and rhodium(III) complexes, while manganese(II) and nickel(II) complexes of the first transition group are nearer to the electrostatic case.

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\* Recently, Tinkham<sup>15</sup> investigated the binding of fluoride to Mn(II), Fe(II), Co(II), and Cr(III) by hyperfine-structure of paramagnetic resonance. It was concluded that both 2s, 2p, 3s, and 3p orbitals of fluorine are included, implying very complicated and uncertain expressions for the absolute magnitude of  $\Delta$ .

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### Absorption Spectra of Red Uranium(III)Chloro Complexes in Strong Hydrochloric Acid

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Someya<sup>1</sup> reported that solutions of Uranium(III) are red in concentrated hydrochloric acid, while they are greyish green in less acidic solutions. Fig. 1 gives the absorption spectra of grey uranium(III) solutions, which are identical in 2 M and 6 M HCl (and practically coincident with the spectrum, reported by Stewart<sup>2</sup> of the U(III) aquo ion in 1 M  $\text{HClO}_4$ ), and of a dark red solution in 11 M HCl. Since the normal redox potential<sup>3</sup> of U(III):U(IV) is  $-0.64$  V, a hydrogen activity, corresponding to  $10^{21}$  atm would be necessary to render the U(III) solutions thermodynamically stable; however, amalgamated zinc can in most cases produce a stationary state after one day, containing  $\sim 80\%$  U(III). It cannot be argued that the colour of the grey solution in 6 M HCl is caused by admixed pale green<sup>4</sup> U(IV), since it turns red by addition of a large excess of 12 M HCl after removal of the zinc.

The present author<sup>5</sup> identifies the narrow bands of grey U(III) in the visible as Laporte-forbidden transitions from the groundstate  $5f^3^4I_{9/2}$  to the other  $5f^3$ -levels, while the high and broad bands in the ultraviolet have  $5f^26d$ -levels as excited levels, to which the transitions are allowed by Laporte's rule. Similar  $f^n \rightarrow f^{n-1}d$  transitions have been observed<sup>6</sup> of Ce(III), Sm(II), Eu(II), Pa(IV), Np(III), and Pu(III). The individual  $5f^26d$ -levels are not easily identified; in U(III) both the ligand