

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

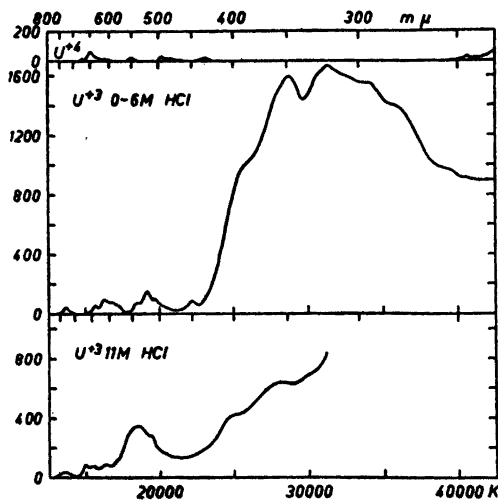


Fig. 1. The absorption spectra of uranium (IV) aquo ions<sup>4</sup> in  $\text{HClO}_4$ , and of 0.001 M to 0.008 M uranium(III) in 2 M–6 M HCl (several solutions of the grey form) and in 11 M HCl (the dark red chloro complexes). Measured on a Cary spectrophotometer at 25°C. The content of U(IV) is corrected<sup>2</sup> for from the absorption  $\sim 650 \text{ m}\mu$ . The half-life time for spontaneous evolution of hydrogen is  $\sim 10$  minutes in 11 M HCl and longer in more dilute acids.

field parameters and the intermediate coupling (i. e.  $\zeta_{5f}$  and  $\zeta_{6d}$ ) are not small compared to the energy differences between the multiplet terms with given values of  $L$  and  $S$ , while usually only one of these conditions prevails (in the  $d^n$ -complexes and in the lanthanides, respectively). Thus most of the  $\frac{14 \cdot 13}{2} \cdot \frac{10}{2} = 455$

possible  $5f^2 6d$ -levels may have different energy. In addition to the two principal peaks<sup>2</sup> at 350 and 319  $\text{m}\mu$ , the shoulders at 390, 327, 294, 280, and  $\sim 250 \text{ m}\mu$  are probably caused by such levels or by superposed  $f^2$ -transitions. It is remarkable that the broad bands seem only to occur<sup>2</sup> in a range between 400 and 250  $\text{m}\mu$ .

The narrow  $f^2$ -peak at 521  $\text{m}\mu$  is shifted to a comparatively broad and high band at 540  $\text{m}\mu$ , having an area and thus an oscillator strength  $\sim 5$  times larger for the red solution in 11 M HCl than for the

grey aquo ion. (The reflection spectrum<sup>6,7</sup> of anhydrous  $\text{UCl}_5$  exhibits a similar shift to  $\sim 545 \text{ m}\mu$ , compared to<sup>7</sup>  $\sim 510 \text{ m}\mu$  for  $\text{UF}_5$ ). In the ultraviolet, the  $5f^2 6d$ -bands are lower and shifted towards higher wavelengths; only the shoulders at 401, 361, and 330  $\text{m}\mu$  can be observed, because U(IV) in 12 M HCl (as  $\text{UCl}_6^{2-}$ ?) has an electron transfer band at 286.5  $\text{m}\mu$  ( $\epsilon = 2300$ ,  $\delta(-) = 1400 \text{ K}$ ), which is shifted towards shorter wavelengths by dilution and has disappeared in 4 M HCl. The U(IV) aquo ion is remarkably non-absorbing in the ultraviolet<sup>4</sup> (see the Figure). U(III) in 9 M HBr has a spectrum similar to that of the grey solutions in  $< 6 \text{ M HCl}$ .

It cannot be completely excluded that the red colour in 11 M HCl is caused by a mixed oxidation state U(III, IV) analogous to Ti(III, IV)<sup>8</sup>. However, it is much more probable that a chloro complex of U(III) is formed. Actually, the actinides exhibit other exchange ion properties in strong HCl than do the lanthanides<sup>9</sup>, and recently, Ward and Welch<sup>10</sup> reported equilibria between chloride ions and Pu(III), Am(III), and Cm(III): The decreased affinities to cation exchange resins imply formation constants of the monochloro complexes of all three metals equal to 15, when extrapolated to infinite dilution, and 1 to 2.5 in the actual solutions. Further, Pu(III) is strongly bound to anion exchangers in 12.6 M HCl (implying the partial presence of  $\text{PuCl}_4^-$  or higher complexes). This is not the case for Am(III) or Cm(III) in 12.6 M HCl, nor for Pu(III) in 10 M HCl. Kraus, Moore and Nelson<sup>11</sup> have made a comparative study of quadrivalent metals in HCl and found strong adsorption on anion exchangers of U(IV) above 5.5 M and of Zr(IV) above 7 M HCl, while Th(IV) was not extracted at all.

It is surprising that the trivalent actinides (and also Ce(III)<sup>10</sup>) should occur mainly as monochloro complexes in 1 M HCl, since no change of absorption spectrum can be observed below 6 M HCl. Thus, Hindman<sup>3</sup> investigated Pu(III), and the spectrum of Nd(III)<sup>12</sup> changes only above 6 M HCl. Of course, the  $f^2$ -transitions might be less perturbed than the  $f^2 \rightarrow f^2 1d$  transitions. However, the three high bands of Ce(III) at 253, 240, and 222  $\text{m}\mu$  are identical within the experimental uncertainty of 0.002 M  $\text{CeCl}_3$  in  $\text{H}_2\text{O}$ , 1 M, 3 M, and 5 M HCl. Only in stronger HCl, a new spectrum appears<sup>12</sup>. The evidence for U(III) in this note is analogous.

It may be questioned whether the chloro complex formation, implied by physico-chemical methods, apply to association in the second co-ordination sphere (analogous to  $\text{Co}(\text{NH}_3)_6^{+++}$ ,  $\text{I}^-$ ) or to substitutions of water in the first co-ordination sphere. The old statement that changes of the absorption spectra occur only in the latter case<sup>13</sup> has been highly justified for d<sup>n</sup>-transitions in the recent years. The present author believes that the first co-ordination sphere of the aquo ions of trivalent lanthanides and actinides is not changed to a large extent in solutions, containing less than 4 M HCl, while in concentrated HCl actual complexes are formed with one or more chloride ions bound directly to the central ion. J. Bjerrum<sup>14</sup> investigated the case of Cu(II) and the strongly increasing chloride activity of strong HCl. The mass-action law on concentration units is very far from being valid; this is probably caused by the strong tendency towards dehydration of the aquo ions in strong HCl of low H<sub>2</sub>O-activity<sup>15</sup>. It is interesting that Katzin effect<sup>16</sup>, *i. e.* that complexes with anions are much more readily formed in anhydrous alcohols than in aqueous solutions or in alcohols with 10 % water content, can be described a similar dehydration effect: the spectral changes of Ce(III) in above 10 M aqueous HCl are reproduced by 0.002 M CeCl<sub>3</sub> alone in absolute ethanol<sup>12</sup>, but not of Ce(ClO<sub>4</sub>)<sub>3</sub>. Thus, water (and amines) have an extraordinarily large tendency to occupy the whole of the first co-ordination sphere (rather independently of the dielectric constant of the solvent), thus displacing anions to form second-sphere associates or leading to complete ionic dissociation.

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## The Hump of Ionization Potentials at Half-Filled Shells and the Influence of Spin-Pairing Energy on Standard Oxidation Potentials

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Recently, many properties of chemical complexes have been related to atomic spectroscopy<sup>1</sup>. Especially, the ligand field stabilization of partly filled d-shells has been evaluated<sup>2</sup> in terms of the parameter  $\Delta$  (also called ( $E_1 - E_2$ ) or 10 *Dq*), determined from the absorption spectra.

The standard oxidation potentials<sup>3</sup> (with the opposite sign of that used by Latimer) express the ionization potentials in aqueous solutions when corrected for the energy necessary for the reaction  $\frac{1}{2}\text{H}_2 \rightarrow \text{H}_{\text{aq}}^+ + \text{e}^-$ . Since the latter energy probably is between 4.5 and 5 eV, the ionization potentials in solution are much lower, 4–7 eV, than for the gaseous ions known from atomic spectroscopy<sup>4</sup>. The divalent and trivalent hexaaquo ions of the first transition group represent the only case where the redox potentials are known for systems having several different numbers of d-electrons. In Table I, these potentials<sup>3</sup> are corrected for the influence of ligand field stabilization<sup>2</sup> (1 eV = 8 067