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# STUDIES OF ABSORPTION SPECTRA VI

Actinide Ions with two 5 *f*-Electrons

BY

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## Introduction.

The absorption spectrum of uranium (IV) ions is interpreted as the atomic spectrum of the free ion with little influence from crystal fields. It is compared with the theoretical predictions of CONDON and SHORTLEY for systems with two  $f$ -electrons. The identification is supported by the behaviour of the spectrum of different complexes and by a new band in the ultraviolet. The energy levels are related to the actinide hypothesis, and chemical conclusions drawn from the absence of very strong absorption bands.

The absorption spectra of the lanthanide and actinide ions consist of narrow bands, which are not much influenced by chemical changes in the complexes. They are supposed to be practically the same as the atomic spectra of the free ions in vacuo, while the ordinary transition group ions have absorption spectra that are strongly dependent on the crystal field perturbations of the ligands.

The theoretical interpretation of the lanthanide spectra has been successful in simple cases. According to Pauli's equivalence theorem of electrons and holes,  $f^n$  gives the same number of terms as  $f^{14-n}$ . Thus,  $f^2$  and  $f^{12}$  both correspond to two effective electrons, as found in  $Pr^{+++}$  and  $Tm^{+++}$ . The absorption spectrum of the praseodymium ion is discussed by ELLIS,<sup>1</sup> GOBRECHT,<sup>2</sup> LANGE,<sup>3</sup> and SPEDDING,<sup>4</sup> while BETHE and SPEDDING<sup>5</sup> interpreted the thulium ion spectrum. Recently, the 3-electron system  $Nd^{+++}$  has been described by SATTEN.<sup>6</sup> Besides this, only the ground-levels and some few other levels of the complicated lanthanide ions have been identified.

The atomic spectra of  $4f^2$  are best known from  $La^+$ , studied by RUSSELL and MEGGERS.<sup>7</sup> Later the  $5f^2$ -system  $Th^{++}$  was

studied by DE BRUIN, KLINKENBERG and SCHUURMANS.<sup>8</sup> Of the 5  $f^2$ -systems of chemical interest  $U^{+4}$  is perhaps the best known. The absorption spectra of uranium (IV) complexes are the main subject of the following discussion.

### Theoretical Predictions.

CONDON and SHORTLEY<sup>9</sup> give a general treatment of the interaction between a few electrons by different coupling-schemes, which are idealized simplifications of the observed distribution of energy levels. In particular, the intermediate cases between ( $L, S$ ) coupling (the Russell-Saunders case) and ( $j, j$ ) coupling are discussed. Although ( $j, j$ ) coupling is most prominent in the heavy atoms, particularly at the ends of the periods, ( $L, S$ ) coupling will presumably be predominant in  $U^{+4}$ .

The electrostatic interaction of two equivalent  $f$ -electrons is given<sup>9</sup> as functions of the integrals  $F_0$ ,  $F_2$ ,  $F_4$ , and  $F_6$ , which are determined by the electric field of the kernel, in this case the emanation configuration. SATTEN<sup>6</sup> points out that the inequalities

$$F_4 \leq 0.202 F_2 \text{ and } F_6 \leq 0.0306 F_2 \quad (1)$$

are valid from the definition of these integrals<sup>9</sup> (The inequality  $F_6 \leq 0.00306 F_2$  is erroneously given in Satten's paper).

In the cases\*  $La^+$ ,  $Pr^{+++}$ , and  $Th^{++}$  (ref. 7, 4, and 8, respectively) these integrals are given in the energy unit  $\text{cm}^{-1}$ .

	$F_2$	$F_4$	$F_6$
$La^+$ . . . . .	93.3 $\text{cm}^{-1}$	21.6 $\text{cm}^{-1}$	0.26 $\text{cm}^{-1}$
$Pr^{+++}$ . . . . .	232	47	
$Th^{++}$ . . . . .	208	42	4.6

It is most probable that the ratio  $F_4/F_2$  has nearly the maximum value, i. e. 0.2.

The possibility of  $F_6$  being approximately  $0.03 F_2$  is very important for the position of some of the terms. Table 1 in the first two columns gives the electrostatic interaction of  $f^2$  in the two

\* RACAH<sup>41</sup> has later given the parameters  $F_2 = 193$ ,  $F_4 = 36$ , and  $F_6 = 3.4 \text{ cm}^{-1}$  for  $Th^{++}$ , while KLINKENBERG<sup>42</sup> gives the values 200, 55, and  $4.3 \text{ cm}^{-1}$ , respectively.

cases ( $F_4 = 0.2 F_2$  and  $F_6 = 0$ ) and ( $F_4 = 0.2 F_2$  and  $F_6 = 0.02 F_2$ ). The energy  $2 F_0$ , which is constant for all the given terms, is not considered.

The next column of Table 1 gives the interval splitting, expressed<sup>9</sup> by the Landé interval factor  $\zeta$ . This energy is added to the electrostatic interaction to give the energy of the level relative to the other levels of  $f^2$ .

Only in the limiting case where  $\zeta = 0$  the Russell-Saunders ( $L, S$ ) coupling is completely in concordance with the experimental data. For increasing values of  $\zeta$  the atom will approximate to ( $j, j$ ) coupling, and eventually  $L$  and  $S$  will no longer have physical significance, but only the vector sum  $J$  from the  $j$  of the individual electrons. The intermediate coupling cases can be quantitatively treated by the perturbation theory, e. g. as applied by SPEDDING.<sup>4</sup> For the values of  $J$  where only one level is represented in the configuration (as in the case of  $f^2$ , with odd  $J$  values), no perturbation is predicted. In the cases where two ( $J = 0$  and 6) or three ( $J = 2$  and 4) levels exist with the same  $J$ , the perturbation energy is given as a function of  $\zeta$  and the distances between the levels which perturb each other. The secular determinants producing these functions are given by SPEDDING.<sup>4</sup> In the simple case with only two levels the energies are thus:

$$E_6 = \frac{I + H + 5 \zeta}{2} \pm \left\{ \left( \frac{I - H - 5 \zeta}{2} \right)^2 + 6 \zeta^2 \right\}^{\frac{1}{2}}$$

and

$$E_0 = \frac{S + P - 2 \zeta}{2} \pm \left\{ \left( \frac{S - P + 2 \zeta}{2} \right)^2 + 48 \zeta^2 \right\}^{\frac{1}{2}},$$

where  $S, P, H$ , and  $I$  are the electrostatic energies of the terms. The negative sign of the square root is used for the energy of the lower of the two perturbed levels, and the positive sign for the higher energy.

The last column of Table 1 gives the sign of the perturbation energy. In the cases of  $J = 2$  and 4 the outermost levels are perturbed to greater distances, and the displacement of the middle one is determined by the position of the two other levels.

This theory does not consider the perturbation from electron configurations other than  $f^2$  (see ref. 9, chapter 15). This con-

TABLE 1. The Condon-Shortley energies of  $f^2$ .

Level	Electrostatic interaction energy		Multiplet splitting due to $(L, S)$ interaction	Sign of perturbation energy
	$F_4 = 0.2 F_2$ $F_6 = 0$	$F_4 = 0.2 F_2$ $F_6 = 0.02 F_2$		
${}^3H_4$	$-35.2 F_2$	$-35.5 F_2$	$-6 \zeta$	—
${}^3H_5$	$-35.2$	$-35.5$	$-1$	0
${}^3H_6$	$-35.2$	$-35.2$	$+5$	—
${}^3F_2$	$-16.6$	$-22.3$	$-4$	—
${}^3F_3$	$-16.6$	$-22.3$	$-1$	0
${}^3F_4$	$-16.6$	$-22.3$	$+3$	$+ \text{ or } -$
${}^1G_4$	$-10.4$	$-9.0$	0	$+$
${}^1D_2$	$-0.8$	$+13.5$	0	$+ \text{ or } -$
${}^1I_6$	$+26.8$	$+26.8$	0	$+$
${}^3P_0$	$+51.6$	$+25.0$	$-2$	—
${}^3P_1$	$+51.6$	$+25.0$	$-1$	0
${}^3P_2$	$+51.6$	$+25.0$	$+1$	$+$
${}^1S_0$	$+99.6$	$+133.9$	0	$+$

figuration interaction takes place between terms with the same  $L, S$  and parity. Thus all configurations  $[Em] 6d^2$ ,  $[Em] 5g 7s$ , and  $[Em] 5f 7p$  are able to interact with some terms of  $[Em] 5f^2$ . In many cases, the configuration interactions in heavy atoms will remove the physical significance of electron configurations. The wave-functions of the individual terms will be mixtures of the corresponding hydrogen-like wave-functions of the pure electron configurations. It is almost impossible to predict the direction of the displacement of the levels, due to configuration interaction, before the atomic spectrum of e. g.  $U^{+4}$  is analyzed. This refinement cannot be expected yet, since the very complicated line spectra of the actinide elements are extremely difficult to disentangle. The chemical absorption spectroscopy may here give information to atomic spectroscopists about the terms of the lowest configuration of the given ion.

### Experimental.

Most absorption spectra of dissolved uranium (IV) salts have been measured on the sulphate, chloride or bromide. While ÅHRLAND and LARSSON<sup>10</sup> in the two last cases have shown that

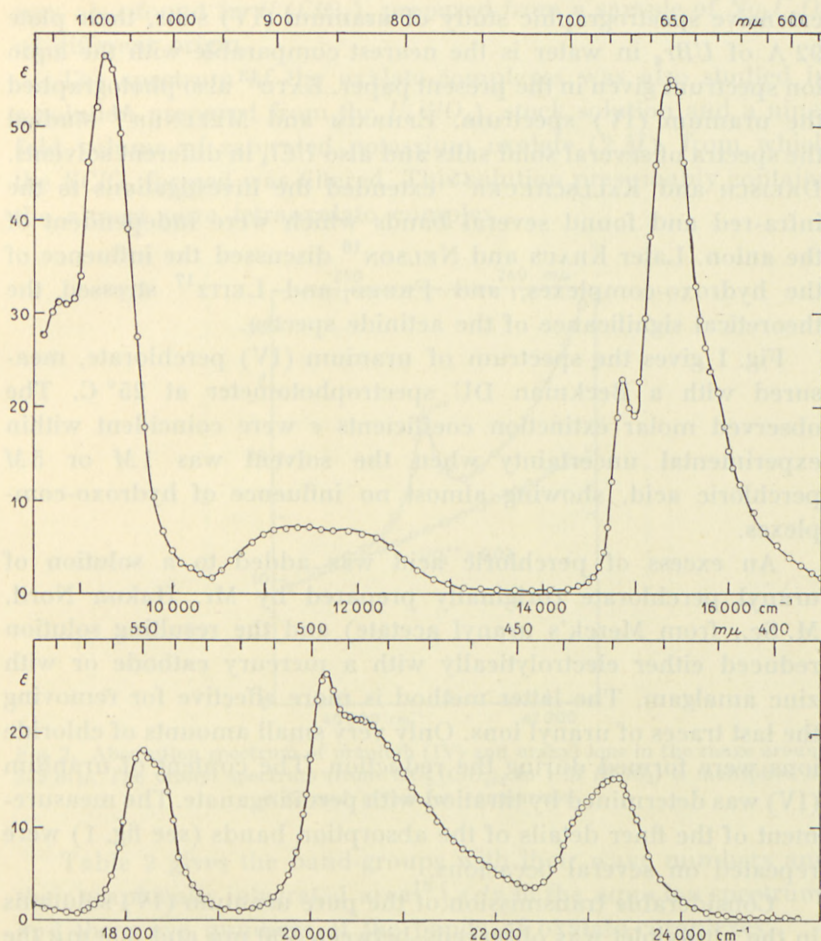


Fig. 1. Absorption spectrum of aquo uranium (IV) ions from measurements in 1 M and 5 M  $HClO_4$  at 25° C. The molar extinction coefficient  $\epsilon = \frac{\log_{10} I_0 - \log_{10} I}{cl}$  is given as a function of the wave number in the range 8500—25500  $cm^{-1}$ . The path width  $l$  is 1 cm and the concentration  $c$  of  $U^{+4}$  is 0.1 M and 0.02 M.

the halide complexes are not very strong, the aquo ion can best be studied in uranium (IV) perchlorate with enough perchloric acid added to suppress formation of hydroxo compounds.

Among the spectra given in the literature FORMANEK<sup>11</sup> investigated solutions in hydrochloric acid, which also clearly showed uranium (III) bands. JONES and STRONG<sup>12</sup> made a very

extensive spectrographic study of uranium (IV) salts, their plate 92 A of  $U\text{Br}_4$  in water is the nearest comparable with the aquo ion spectrum given in the present paper. KATO<sup>13</sup> also photographed the uranium (IV) spectrum. EPHRAIM and MEZENER<sup>14</sup> studied the spectra of several solid salts and also  $U\text{Cl}_4$  in different solvents. DREISCH and KALLSCHEUER<sup>15</sup> extended the investigations to the infra-red and found several bands which were independent of the anion. Later KRAUS and NELSON<sup>16</sup> discussed the influence of the hydroxo-complexes, and FREED and LEITZ<sup>17</sup> stressed the theoretical significance of the actinide spectra.

Fig. 1 gives the spectrum of uranium (IV) perchlorate, measured with a Beckman DU spectrophotometer at 25° C. The observed molar extinction coefficients  $\epsilon$  were coincident within experimental uncertainty when the solvent was 1M or 5M perchloric acid, showing almost no influence of hydroxo-complexes.

An excess of perchloric acid was added to a solution of uranyl perchlorate (originally prepared by Mr. Hakon Nord, M. Sc., from Merck's uranyl acetate) and the resulting solution reduced either electrolytically with a mercury cathode or with zinc amalgam. The latter method is more effective for removing the last traces of uranyl ions. Only very small amounts of chloride ions were formed during the reduction. The content of uranium (IV) was determined by titration with permanganate. The measurement of the finer details of the absorption bands (see fig. 1) were repeated on several occasions.

Considerable transmission of the pure uranium (IV) solutions in the ultraviolet was observed—between 400  $m\mu$  and 300  $m\mu$  the molar extinction coefficient is well below 1. When further measurement with the hydrogen lamp were performed at shorter wave lengths it was evident that uranyl ions formed by oxidation were the most prominent absorbing material. However, a new band appeared at 245  $m\mu$ , narrow and with a moderate extinction coefficient, maximally about 20. This band resembles the other bands found in the visible spectrum. Fig. 2 shows that it cannot reasonably be attributed to oxidation, since the uranyl spectrum increases in the interesting range without the faintest sign of a peak. The background in the uranium (IV) spectrum is presumably only partially due to the uranyl impurities. The narrow band



was also found in  $U(ClO_4)_4$  prepared from a sample of  $Na_2U_2O_7$  of different origin.

The spectrum of the oxalato-complexes was also studied in a solution prepared from the  $U(ClO_4)_4$  stock solution and a nine-fold volume of saturated potassium oxalate (2 M), from which the  $KClO_4$  formed was filtered. This solution presumably contains the almost pure tetraoxalato complex.

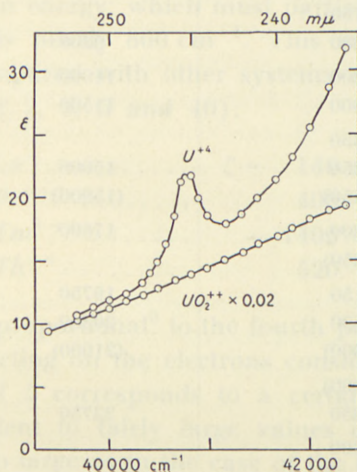


Fig. 2. Absorption spectrum of uranium (IV) and uranyl ions in the range around 245 m $\mu$ . The uranyl spectrum (from  $UO_2(ClO_4)_2$  in 1 M  $HClO_4$ ) is multiplied by 0.02 and given for comparison.

Table 2 gives the band-groups with their wave numbers and their graphically integrated area<sup>18</sup>  $\int \epsilon d\nu$  in the aquo ion spectrum, and the wave numbers of the bands of oxalato-complexes.

Since the spectrum of uranium (IV) complexes is not highly influenced by complex formation, the crystal field perturbations are small as compared with the multiplet splitting determined by the Landé factor  $\zeta$ . Since the thermal energy is small as compared with  $\zeta$  ( $kT$  at room temperature corresponding to 210  $cm^{-1}$ ) the higher levels of ground-term  $^3H$  are only negligibly populated, and all the narrow absorption bands must be due to transitions from  $^3H_4$ .

It appears from Table 2 that the bands of oxalato-complex are displaced on the average 400  $cm^{-1}$  towards lower wave numbers as compared with the aquo ion spectrum. Presumably

TABLE 2. The uranium (IV) bands observed.

Band group no.	Wave numbers of maxima in $\text{cm}^{-1}$ (shoulders in parenthesis)		Area = $\int \epsilon d\nu$
	$Uaq_N^{+4}$	$Uox_4^{-4}$	$Uaq_N^{+4}$
1.....	{ 6550 } { (6900) } (ref. 15)		
2.....	{ (8750) } { 9300 }	9200	} $5 \cdot 10^4 \text{ cm}^{-1}$
3.....	{ 11200 } { 12000 }	11000 11500	} 1.3 ·
4.....	{ 14850 } { 15350 } { (15850) }	15000 15000 (15800)	} 4.8 ·
5.....	{ 18200 } { (18350) }	17800	} 1.2 ·
6.....	{ 20150 } { 20500 } { (21300) }	19750 20300 (21000)	} 3.6 ·
7.....	{ (23000) } { 23350 }	22750	} 1.5 ·
8.....	40800		} $\sim 1$ ·

the lowest of the levels into which  ${}^3H_4$  is split by the crystal field from the ligands is some hundred  $\text{cm}^{-1}$  lower in the aquo ion than in the oxalato complex (cf. the theory of BETHE<sup>19</sup>). The symmetry of the uranium (IV) complexes discussed here seems to be cubic or nearly cubic. MARCHI and McREYNOLDS<sup>20</sup> maintain that the tetraoxalato complex most probably has the Archimedean anti-prism configuration.

All the uranium (IV) bands have relatively large half widths of about four hundred  $\text{cm}^{-1}$  (as in  $Pr^{+++}$ ), while no observed band is very narrow, as e. g. the band at  $427 \mu$  of  $Nd^{+++}$ . Thick layers of concentrated uranium (IV) solutions transmit light in such narrow parts of the visible spectrum between the absorption bands that they can be used for optical filters in some cases.

### Identification of the Uranium (IV) Bands.

In a following section the arguments will be given for the electron configuration in uranium (IV) complexes being  $[Em] 5f^2$ . Under this assumption the theoretical predictions are compared with the observed spectra: One of the most certain identifications of the band groups in Table 2 is the very strong group 2 as  ${}^3H_4 - {}^3H_6$ . According to Table 1, the energy difference is  $11 \zeta$  besides some perturbation energy, which must partially cancel. Thus the Landé factor  $\zeta$  is nearly  $800 \text{ cm}^{-1}$ . This is a very reasonable value if it is compared with other systems with two effective  $f$ -electrons (see ref. 7, 4, 5 and 40):

$La^+$ .....	$\zeta \sim 140 \text{ cm}^{-1}$
$Pr^{+++}$ .....	400
$Tm^{+++}$ .....	-1400
$Th^{++}$ .....	520

$\zeta$  is formally proportional<sup>9</sup> to the fourth power of the effective nuclear charge acting on the electrons considered.

This value of  $\zeta$  corresponds to a certain amount of  $(j, j)$  coupling, equivalent to fairly large values of the perturbation energy, but not so large as in the case of the thulium ion (which has a nearly closed shell and correspondingly inverted multiplets with a highly negative Landé factor). It is predicted that the selection rule of  $S$  will be obeyed in some degree, giving higher intensities, *inter alia* to the triplet transitions, than to the singlets from the triplet ground-state. The intensities are presumably increasing with the value of  $J$ , but configuration interaction may cause peculiar intensity values.

The electrostatic interaction parameter  $F_2$  can next be determined to  $380 \text{ cm}^{-1}$  from the identification of the ultraviolet band (no. 8 in Table 2) with  ${}^3H_4 - {}^3P_2$ . If the first column of Table 1 is chosen, the energy of this transition corresponds to

$$\{ 86.8 F_2 + 7 \zeta + \text{some perturbation energy} \}.$$

The alternative possibility of representing  ${}^3P_2$  by band No. 7 would give a much more compressed\* energy scale with  $F_2$  only

\* Good agreement is obtained, if  $F_6$  is large ( $\sim 10 \text{ cm}^{-1}$ ). But then a band is masked by others in the visible part of the spectrum, presumably  ${}^1I_6$ , and the other identifications are not altered much.

about  $180 \text{ cm}^{-1}$ . This would not agree well with  $F_2$  in  $Th^{++}$ , which is<sup>8</sup>  $208 \text{ cm}^{-1}$ , since  $F_2$  is roughly proportional to  $Z + 1$ , where  $Z$  is the external charge of the ion (cf. the discussion of the first transition group by CONDON and SHORTLEY<sup>9</sup>). From Table 1 it follows that  ${}^3F_2$  and  ${}^3H_5$  must be placed at essentially smaller wave numbers than one is able to measure on the Beckman *DU* spectrophotometer. The bands of lower intensity than  ${}^3H_6$ , which were discovered in the infra-red by DREISCH and KALLSCHEUER<sup>15</sup> are presumably due to these transitions. The low band group 3 is due to  ${}^3F_3$  and the four other band groups in the visible, Nos. 4, 5, 6 and 7, can tentatively be assigned to the transitions from  ${}^3H_4$  to  ${}^3F_4$ ,  ${}^1D_2$ ,  ${}^1G_4$ , and  ${}^1I_6$ , respectively. Then no observed band-group remains unidentified and predicted bands are only missed at about  $36000 \text{ cm}^{-1}$  ( ${}^3P_0$ ) and  $38000 \text{ cm}^{-1}$  ( ${}^3P_1$ ) in addition to the unobservable  ${}^1S_0$  at  $58000 \text{ cm}^{-1}$ .

When the perturbation energies are found from the determinantal equations given by SPEDDING,<sup>4</sup> curious consequences are found if  $F + 3\zeta$  is nearly equal to  $G$ , where  $F$  and  $G$  are the electrostatic interaction energies found from the Condon-Shortley theory (see Table 1) for the terms  ${}^3F$  and  ${}^1G$ . The difference between two of the three roots of the equation for  $J = 4$  will then be approximately  $7.7\zeta$  (in this case  $6160 \text{ cm}^{-1}$ ) while the lowest root is placed  $750 \text{ cm}^{-1}$  below  $H - 6\zeta$  by the perturbation. The former difference agrees reasonably well with the difference found between the two strong band groups Nos. 4 and 6, although the average wave number calculated is too low.

The question which of the two highest levels with  $J = 4$  is  ${}^3F_4$  and which is  ${}^1G_4$  has no physical significance. The wave functions will be intermixed with nearly equal coefficients, and the triplet character transferred so much to both states that the intensity can be nearly equal. This is often the case, e. g., in the heavy atoms of the inert gases.<sup>21</sup>

This identification is supported by the shapes of the band groups, whose fine structure is due to the crystal field splitting of the excited state and the ground-state,  ${}^3H_4$ . According to the theory of BETHE<sup>19</sup> these weak crystal field perturbations will only depend on  $J$ . The bands identified here as being due to transitions to states with  $J = 6$  thus have very similar structures with a

satellite towards lower wave numbers. The two band groups with  $J = 4$  have the complicated structure with three or more partial bands in the spectrum of uranium (IV) aquo ion (see fig. 1). The case of  $J = 3$  has another structure.

The succession of  ${}^1D_2$  and  ${}^1G_4$  has been inverted in the identification, due to the fine structure. The weakest point is the position of  ${}^1I_6$ , which further has too small an intensity. But it is necessary to assume that it is the last band before  ${}^3P$ . The energy of  ${}^1I_6$  seems also to be depressed<sup>8</sup> in  $Th^{++}$  and is perhaps affected by configuration interactions.

It is remarkable that the Condon-Shortley theory, which has not met with very great success in dealing with the heavy atoms, is in so good agreement with the experimental data for the uranium (IV) spectrum. Table 3 gives the results with  $F_2 = 380 \text{ cm}^{-1}$ ,  $F_4 = 76 \text{ cm}^{-1}$ ,  $F_6 = 0 \text{ cm}^{-1}$  (which seems to be the best approximation),  $\zeta = 800 \text{ cm}^{-1}$ , and the perturbation energies calculated by the method of SPEDDING,<sup>4</sup> as compared with the observed wave number of the centre of gravity of the band group in the aquo ion spectrum.

TABLE 3. Calculated and observed levels of  $U^{+4}$ .

	Calculated	Observed
${}^3H_5$	4750 $\text{cm}^{-1}$	—
${}^3H_6$	9350	9200 $\text{cm}^{-1}$
${}^3F_2$	7700	6600 (ref. 15)
${}^3F_3$	11800	11600
${}^3F_4$ ( ${}^1G_4$ )	12050	15400
${}^1D_2$	19500	18250
${}^1G_4$ ( ${}^3F_4$ )	18700	20500
${}^1I_6$	29350	23200
${}^3P_0$	35500	—
${}^3P_1$	37700	—
${}^3P_2$	40000	40800
${}^1S_0$	58200	—

The average value of the absolute deviation  $|v_{\text{obs}} - v_{\text{calc}}|$  is thus  $1800 \text{ cm}^{-1}$  for the 8 observed bands. The calculations of SPEDDING<sup>4</sup> show the average deviation  $440 \text{ cm}^{-1}$  for the 10 bands of  $Pr^{+++}$  and of BETHE and SPEDDING<sup>5</sup>  $1170 \text{ cm}^{-1}$  for the 7 observed bands of  $Tm^{+++}$ .

### The Other Actinide Elements.

The suggestion that uranium is an ordinary transition element without  $f$ -electrons was rejected by KIESS, HUMPHREYS and LAUN,<sup>22</sup> who proved that the ground-state is  $^5L_6$  from the configuration  $[Em] 5f^3 6d 7s^2$ . SCHUURMANS<sup>23</sup> demonstrated that the lowest configuration of  $U^+$  is  $[Em] 5f^3 7s^2$  closely followed by  $[Em] 5f^3 6d 7s$ . Since in the transition groups the electrons with the highest principal quantum numbers are removable by ionization, it is almost certain that the fourth ionization state of uranium has the configuration  $[Em] 5f^2$ . There is no contradiction in the fact\* that  $[Em] 5f 6d$  has lower energy ( $15000 \text{ cm}^{-1}$ ) in  $Th^{++}$  than  $[Em] 5f^2$ , since  $f$ -electrons have steeply decreasing energies with increasing atomic number in the lanthanide and actinide elements.

Experimentally, attention has been concentrated on the magnetic properties. HUTCHINSON and ELLIOT<sup>24</sup> and HOWLAND and CALVIN<sup>25</sup> concluded that all the ions of the elements with atomic numbers from 92 to 95 have the general configuration  $[Em] 5f^n$ . But some evidence for  $[Em] 6d^2$  has been found in the case of solid uranium (IV) compounds. While  $5f^2$  in ( $L, S$ ) coupling should give a magnetic moment of 3.58 Bohr magnetons and in ( $j, j$ ) coupling 3.84 B.m.,  $6d^2$  is presumed to have its orbital moment quenched and to give the value 2.83 B.m. calculated from spin moment only. DAWSON<sup>26</sup> measured solid solutions of  $UF_4$  in  $ThF_4$  and (analogous to TRZEBIATOWSKI and SELWOOD<sup>27</sup>)  $UO_2$  in  $ThO_2$ , and found decreasing magnetic moment by dilution with the diamagnetic thorium compounds, varying from 3.3 to 2.9 B.m. The  $5f$ -electrons are not so effectively shielded in the actinides as the  $4f$ -electrons in the lanthanides. If the levels of  $^3H_4$  split by crystal fields are not equally populated, magnetic effects may be produced. According to NYHOLM,<sup>28</sup> the magnetic moment of sodium plutonyl acetate measured by DAWSON<sup>29</sup> is not a definite proof of the configuration  $[Em] 6d^2$  of  $PuO_2^{++}$ .

Spectroscopic evidence is strongly against the possibility of  $[Em] 6d^2$  for  $U^{+4}$ , which would give very broad bands as the ordinary transition group complexes. The green  $UF_4$  according

\* The configuration  $[Em] 6d^2$  seems<sup>41</sup> to be placed  $810 \text{ cm}^{-1}$  below  $[Em] 5f 6d$  in  $Th^{++}$ .

to EPHRAIM and MEZENER<sup>14</sup> has a reflection spectrum composed of bands at nearly same places as the aquo ion. An interesting case is the brown  $UO_2$ , which has not the usual colour of  $U^{+4}$  (compare e. g. the lanthanide sesquioxides which are coloured by the trivalent lanthanide ions alone). Recently, GRUEN<sup>30</sup> has studied solid solutions of  $UO_2$  in  $ThO_2$ . While pure  $UO_2$  has a steeply increasing absorption below 600  $m\mu$  besides an absorption band at 670  $m\mu$ , the mixtures with much  $ThO_2$  have narrow bands (as other  $U^{+4}$  salts have) at 655, 600, 540, and 515  $m\mu$ , while the strong absorption begins here at 460  $m\mu$ . The molecular spectrum below 460  $m\mu$  may be due to admixtures of higher oxidation states, analogous to the change of colour of  $CeO_2$  by the presence of very small impurities. GRUEN<sup>30</sup> mentions the analogous change of absorption spectrum and electrical conductivity of olive-green nickel (II) oxide by admittance of some  $10^{-4}$  molar excess of oxygen.

The absorption spectra of the actinide ions can further illustrate the problems discussed in SEABORG's famous paper.<sup>31</sup> The spectrum of uranium (IV) ions seems not only to indicate that the  $5f$ -electrons have lower energy than the  $6d$ -electrons, but also that there must be a considerable energy difference. If this were not the case, transitions  $5f^2-5f6d$  should occur in the spectrum. These would correspond to very strong bands, since the two combining terms are even and odd in contrast to the usual bands, which are forbidden as free dipole radiation *qua* transitions between even terms. The strong bands are known in the ultraviolet cerium (III)<sup>32</sup> solutions, which must be caused by  $[Xe] 4f \rightarrow [Xe] 5d$  or  $[Xe] 6s$ . They are very broad and have molar extinction coefficients near 500. The ultraviolet part of the uranium (IV) spectrum shows no sign of such bands above the steep absorption limit at  $\sim 230 m\mu$ . As pointed out by SEABORG,<sup>31</sup> the ordinary bands of the actinide ions are about ten times intenser than those of the lanthanide ions,<sup>32</sup> which is in good agreement with the present results. No molecular spectrum is observed in the aquo uranium (IV) ion either. This is presumably due to the low electron affinity of  $U^{+4}$ , which shows no great tendency to transfer electrons from the ligands.<sup>33</sup>

Uranium (III) salts do not exhibit very strong absorption bands, at least over 400  $m\mu$  (from preliminary measurements in

10 M HCl after reduction with zinc amalgam). The terms originating from  $[Em] 5f^2 6d$  are thus probably considerable higher than the terms from  $[Em] 5f^3$  which produce the many bands in the visible spectrum.

Two other systems with two electrons outside the emanation shell are quinevalent neptunium and sexavalent plutonium, best known as the oxo-complexes  $NpO_2^+$  and  $PuO_2^{++}$ . These ions have each a very high, narrow band in the infra-red, and a large number of small bands with extinction coefficients near 10 (see ref. 31, p. 1042 and pp. 560, 592, respectively). The high bands at  $983 m\mu$  in neptunium (V) and  $833 m\mu$  in plutonium (VI) can tentatively be identified as  ${}^3H_4-{}^3H_6$  giving the Landé factor  $\zeta$  the probable values  $900$  and  $1000 \text{ cm}^{-1}$ . The number of bands in neptunium (V) in the visible is remarkably large. Measurements by HINDMAN, MAGNUSSON and LA CHAPELLE (ref. 31, p. 1042) give the wave numbers  $\nu$  and maximum extinction coefficients  $\epsilon$  for 1 M HCl solutions:

No.	$\nu$	$\epsilon$	No.	$\nu$	$\epsilon$
1	$9759 \text{ cm}^{-1}$	3.5	7	$16180 \text{ cm}^{-1}$	23.5
2	10170	325	8	16610	4.5
3	10900	2.8	9	16830	5.5
4	13000	5 (broad)	10	21000	8.5
5	14530	5.2	11	23250	8.5
6	15900	9.0	12	27400	7

The group Nos. 6—9 resemble the  ${}^3H_4-{}^3F_4$  ( ${}^1G_4$ ) and the three last bands the singlet transitions for  ${}^1D_2$ ,  ${}^1G_4$  ( ${}^3F_4$ ), and  ${}^1I_6$  of the uranium (IV) ion. But the vibrational structure<sup>34</sup> imparted by the two firmly bound oxygen atoms may disturb the identification. The electrostatic interaction  $F_2$  seems to be slightly larger than in  $U^{+4}$ , as is also to be expected if the hypothesis of  $[Em] 5f^2$  is correct. Recently, GRUEN and HUTCHINSON<sup>35</sup> have given magnetochemical evidence for this electron configuration of neptunium (V). The values of  $\zeta$  are larger *inter alia* for the actinide ions than for the lanthanide ions, as also found from magnetic properties of americium (III).<sup>25</sup>

Uranium (V) in  $UO_2^+$  has no absorption bands in the range  $360-1000 m\mu$ <sup>36</sup>. The configuration  $[Em] 5f$  would only show one band in the far infra-red, since  $\frac{7}{2}\zeta$  is so small an energy. In



contrast to this, systems such as  $[Xe] 4f^{13}$  in ytterbium (III) have so large a (negative) Landé factor that the internal doublet splitting of  ${}^2F$  is  $10200 \text{ cm}^{-1}$ . BOUSSIÈRES and HAISSINSKY<sup>37</sup> give no absorption spectrum of their protactinium (IV) compounds. Neptunium (VI) in  $NpO_2^{++}$  has a larger number of low bands<sup>34</sup> which, analogous to the uranyl ion spectrum, are not yet explained by the atomic spectra.\*

The absorption spectra discussed here show that the  $5f$ -electrons seem to have considerably lower energy than the  $6d$ -electrons, when two electrons are considered in atoms with atomic numbers of at least 92. It is hoped to investigate later the systems with more  $5f$ -electrons, e. g.  $U^{+++}$ , encouraged by the success of the Condon-Shortley theory.<sup>9</sup> The actinide hypothesis of SEABORG<sup>31</sup> seems to be valid to a higher degree than is often concluded from chemical evidence. The higher oxidation states found in the actinide elements are only a continued development of the tendency, also found in cerium and praseodymium in the beginning of the lanthanide series.

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\* If the electron transfer theory of molecular spectra can be applied to the uranyl ion, the bands  $\sim 22000 \text{ cm}^{-1}$  of low intensity are perhaps due to transitions of less probability to  $f$ -states in contrast to the high bands  $\sim 45000 \text{ cm}^{-1}$  caused by  $d$ -states.

### Additional Note.

Recently, two papers have been published on the  $[Em] 5f^2$ -systems of chemical interest. SANCIER and FREED<sup>38</sup> have directly compared the reflection spectra of anhydrous  $PrCl_3$  and  $UCl_4$ . While the experimental results of these authors are very valuable (e. g. the continuous absorption<sup>39</sup> below  $400 m\mu$  of  $UCl_3$ ), the identification of most of the visible bands of  $UCl_4$  with  ${}^3H_4-{}^1I_6$  does not seem convincing without further proof. For this purpose, solid salts of  $U^{+4}$  (and especially the chloride with the strongly split bands<sup>14</sup>) are not so useful as the aquo ion in solution. The crystal field in the liquid state is averaged over the contributions of low symmetry, while strong deviations from cubic symmetry can occur in the rigid crystal. The continuous absorption at  $300 m\mu$  of  $UCl_4$  is presumably<sup>38</sup> a molecular spectrum which can also be obtained in concentrated  $HCl$ -solutions of uranium (IV).

GRUEN<sup>40</sup> calculates the spectra of  $NpO_2^+$  and  $PuO_2^{++}$  from given values of  $\zeta$  and the known terms of  $Th^{++}$ <sup>41, 42</sup> after addition of about ten per cent. It might seem more reasonable to use this experimentally determined electrostatic interaction in the place of the Condon-Shortley parameters which only are a first-order approximation. But there is a possibility of transferring configuration interactions from  $Th^{++}$  to the heavier atoms which are not necessarily similar.

It may be inquired whether the electrostatic interaction is really proportional to  $Z-58$  in the actinides<sup>40</sup> and  $Z-34$  in the lanthanides,<sup>6</sup> where  $Z$  is the atomic number. The strong increase of  $F_2$  from  $La^+$  to  $Pr^{+++}$  corresponds rather to proportionality to the external charge  $+1$ , thus in this case  $Z-55$ . Also in the actinides evidence can be found for increasing electrostatic interaction: The isoelectronic species  $Np^{+++}$  and  $Pu^{+4}$  ( $[Em] 5f^4$ ) have a nearly biunique correspondance between their absorption bands:

$Np^{+++}$ (ref. 31, p. 1053)		$Pu^{+4}$ (ref. 16)	
$\nu$	$\epsilon_{\max}$	$\nu$	$\epsilon_{\max}$
10000 $\text{cm}^{-1}$ .....	29	12200 $\text{cm}^{-1}$ .....	21
11700 .....	23	13700 .....	14
12700 .....	46	15300 .....	35
15100 .....	29	18100 .....	14
16600 .....	25	19800 .....	11
18100 .....	41	21300 .....	54

On an average 19 per cent higher wave numbers are observed among the band maxima of  $Pu^{+4}$ , as compared with  $Np^{+3}$ . This is of course partially due to the increased Landé interval factor  $\zeta$ , which also causes larger perturbations. But the electrostatic interaction seems definitely to have increased more than three per cent found from the strong-shielding theory. The deviation may be connected with the strong dependence of the ionic radius on the external charge.

If the Gruen hypothesis<sup>40</sup> is applied to  $U^{+4}$ , the identifications of the band-groups of Table 2 would be: No. 2  ${}^3H_6$ , No. 3 uncertain, No. 4 most of  ${}^3P$  and  ${}^1G_4$ , No. 5 perhaps  ${}^3P_1$ , No. 6  ${}^1I_6$ , No. 7  ${}^1D_2$ , and No. 8  ${}^1S_0$ . It is interesting to note that a very large  $\zeta$  (over  $1100 \text{ cm}^{-1}$ ) also could explain some features of the observed spectrum: Band group No. 2 now being  ${}^3F_4$ , No. 4  ${}^3H_6$  and some  ${}^3P$ -levels, No. 6  ${}^1G_4$ , and No. 8  ${}^1S_0$ . But the primary hypothesis, the relatively low energy of  ${}^3P$  and high  ${}^1D$ , does not seem totally justifiable. As also given by RACAH<sup>41</sup> for  $Th^{++}$ , it corresponds to a large value of  $F_6$  and relatively small value of  $F_2$ .

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## References.

1. ELLIS, C. B. *Phys. Rev.* **49** (1936) 875.
2. GOBRECHT, H. *Ann. d. Physik* [5] **28** (1937) 673.
3. LANGE, H. *Ann. d. Physik* [5] **31** (1938) 609.
4. SPEDDING, F. H. *Phys. Rev.* **58** (1940) 255.
5. BETHE, H. and SPEDDING, F. H. *Phys. Rev.* **52** (1937) 454.
6. SATTEN, R. A. *J. Chem. Phys.* **21** (1953) 637.
7. RUSSELL, N. H. and MEGGERS, W. F. *J. Res. Nat. Bur. Stand.* **9** (1932) 625.
8. BRUIN, T. L. DE, KLINKENBERG, P. F. A. and SCHUURMANS, PH. *Z. Physik* **118** (1941—42) 58.
9. CONDON, E. U. and SHORTLEY, G. H. *The Theory of Atomic Spectra*, Cambridge 1953.
10. AHRLAND, S. and LARSSON, R. *Acta Chem. Scand.* **8** (1954) 137.
11. FORMANÉK, J. *Die qualitative Spektralanalyse*. Berlin 1905.
12. JONES, H. C. and STRONG, W. W. *A Study of the Absorption Spectra . . .*, Carnegie Inst. Publ. **130** Washington 1910.
13. KATO, S. *Scient. Paper Inst. Phys. Chem. Res.* **13** (1930) 49.
14. EPHRAIM, F. and MEZENER, M. *Helv. Chim. Acta* **16** (1933) 1260.
15. DREISCH, TH. and KALLSCHEUER, O. *Z. Physik. Ch. B* **45** (1939) 19.
16. KRAUS, K. A. and NELSON, F. *The Hydrolytic Behaviour . . . U.S. Atomic Energy Comm. Doc. 1888* (1948).
17. FREED, S. and LEITZ, F. J. *The Absorption Spectra . . . U.S. Atomic Energy Comm. Doc. 1890* (1948).
18. JØRGENSEN, C. KLIXBÜLL, *Acta Chem. Scand.* **8** (1954) 1495.
19. BETHE, H. *Ann. d. Physik* [5] **3** (1929) 133.
20. MARCHI, L. E. and McREYNOLDS, J. P. *J. Am. Chem. Soc.* **65** (1943) 333 and MARCHI, L. E. *ibid.* **65** (1943) 2257.
21. RASMUSSEN, E. *Serier i de ædle Luftarters Spektre . . .* Thesis. Copenhagen 1932.
22. KIESS, C. C., HUMPHREYS, C. J. and LAUN, D. D. *J. Res. Nat. Bur. Stand.* **37** (1946) 57.
23. SCHUURMANS, PH. *Physica* **11** (1946) 419.
24. HUTCHINSON, C. A. and ELLIOT, N. J. *Chem. Phys.* **16** (1947) 920.
25. HOWLAND, J. J. and CALVIN, M. J. *Chem. Phys.* **18** (1950) 239.
26. DAWSON, J. K. *J. Chem. Soc.* **1952**, 1185.
27. TRZEBIATOWSKI, W. and SELWOOD, R. W. *J. Am. Chem. Soc.* **72** (1950) 4504.

28. NYHOLM, R. S. Quarterly Rev. **7** (1953) 377.
  29. DAWSON, J. K. J. Chem. Soc. **1952** 2705.
  30. GRUEN, D. M. J. Am. Chem. Soc. **76** (1954) 2117.
  31. SEABORG, G. T. The Transuranium Elements. Nat. Nuclear Energy Ser. Div IV, **14 B** (1949) 1492.
  32. STEWART, D. C. Light Absorption . . . U.S. Atomic Energy Comm. Doc. **2389** (1948).
  33. JØRGENSEN, C. KLIXBÜLL. Acta Chem. Scand. **8** (1954) 1502.
  34. SJOBLOM, R. and HINDMAN, J. C. J. Am. Chem. Soc. **73** (1951) 1744 and JONES, L. H. and PENNEMAN, R. A. J. Chem. Phys. **21** (1953) 542.
  35. GRUEN, D. M. and HUTCHINSON, C. A. J. Chem. Phys. **22** (1954) 386.
  36. KRAUS, K. A., NELSON, F. and JOHNSON, G. L. J. Am. Chem. Soc. **71** (1949) 2510.
  37. HAISSINSKY, M. and G. BOUSSIÈRES. J. Chem. Soc. **1949** S. 256.
  38. SANCIER, K. M. and FREED, S. J. Chem. Phys. **20** (1952) 349.
  39. FREED, S. and SANCIER, K. M. J. Chem. Phys. **22** (1954) 928.
  40. GRUEN, D. M. J. Chem. Phys. **20** (1952) 1818.
  41. RACAH, G. Physica **16** (1950) 651.
  42. KLINKENBERG, P. F. A. Physica **16** (1950) 618.
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