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STUDIES OF ABSORPTION SPECTRA VII

Systems with three and more *f*-Electrons

BY

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Introduction.

The sixth paper of this series discussed systems with two $5f$ -electrons¹ and a preliminary note² mentioned some features of the absorption spectra of lanthanide and actinide ions containing more f -electrons. The present paper is an attempt to identify the energy levels of these systems.

In the first transition group, the energy levels of the free ion in vacuo are usually well known and the influence from the surrounding molecules determining the observed spectra.^{3, 4, 5, 6} In contrast to this behaviour the lanthanide and actinide ions show relatively small chemical effects in the spectra, but the terms of the free ion are not known from atomic spectroscopy.

Thus, the most important part of the identification is the calculation of the energies of the different terms originating from the electron configuration $[Xe] 4f^n$ in the lanthanides and $[Em] 5f^n$ in the actinides. CONDON and SHORTLEY⁷ have presented a very extensive theory of the electrostatic interaction between the electrons in partially filled shells.

The calculation of the energy levels proceeds in three steps of refinement: First, the electrostatic interaction can be expressed in terms of the parameters F_2 , F_4 , and F_6 (F_0 is disregarded in the present paper, since its contribution is invariant within the same configuration), as outlined in ref. 7, p. 174. But in the case where two or more terms of the given configuration present the same set of quantum numbers L and S , only the average energy of these terms can be obtained directly. Next, these cases can be treated by construction of the appropriate eigen-functions and by finding the different eigen-values. RACAH⁸ has developed very useful group-theoretical methods for calculating the energies of especially f^n -configurations. If q terms present the same combination of L and S , the energy of the terms can be found as

the eigen-values of a matrix of the order q , while the results are independent of all other terms (in the Condon-Shortley theory it is necessary to calculate all the energy levels in a certain order). The third achievement of a first-order calculation is the introduction of the intermediate coupling-scheme, where the mutual perturbations between the levels in the pure Russell-Saunders' case are given as functions of the Lande interval factor ζ . For instance, ISHIZU and OBI⁹ have given the corresponding matrices for f^3 -systems. The values of ζ in the individual multiplets, expressed in terms of ζ_{4f} or ζ_{5f} can also be found by the two first steps of the Condon-Shortley method mentioned above.

f^3 -systems.

The first Condon-Shortley treatment of any f^3 -system was given by SATTEN¹⁰ for Nd^{+++} in crystals of $Nd(BrO_3)_3 \cdot 9 H_2O$. He pointed out that the energy differences between the quartet terms are multiples of $5 F_2 + 6 F_4 - 91 F_6$. It is very convenient for purposes of identification that the ratio between the single parameters in this case is unimportant. The strong bands observed in Nd^{+++} imply most certainly $5 F_2 + 6 F_4 - 91 F_6 = 1400 \text{ cm}^{-1}$ and $\zeta_{4f} = 900 \text{ cm}^{-1}$, which can also be extrapolated* from Pr^{+++} . ζ in the quartets equals $\frac{1}{3} \zeta_{4f}$, while f^2 -systems have $\zeta = \frac{1}{2} \zeta_{nf}$.

But the relative values of F_2 , F_4 and F_6 are important for the positions of the doublet terms. From the definition of the parameters, SATTEN implies the inequalities $F_4 < 0.203 F_2$ and $F_6 < 0.00306 F_2$, but the correct value⁷ in the last case is $F_6 < 0.0306 F_2$, as is also given by SATTEN in the fraction in eq. 11. Whenever F_6 is negligibly small and $F_4 = 0.2 F_2$, the doublets do not give as good agreement with experimental results as do the quartet terms. Rather, a value of $F_6 = 0.02 F_2$ can be used² as a tentative proposal. Table 1 gives the centre of gravity for each term in the two cases.

In the cases where the doublet terms are represented twice

* As also from $\zeta_{4f} = 644 \text{ cm}^{-1}$ in Ce^{+++} , known from atomic spectroscopy⁵⁵. Nevertheless, the quite small splitting of the multiplet 4D might support ζ_4 considerably $< 900 \text{ cm}^{-1}$ in Nd^{+++} .

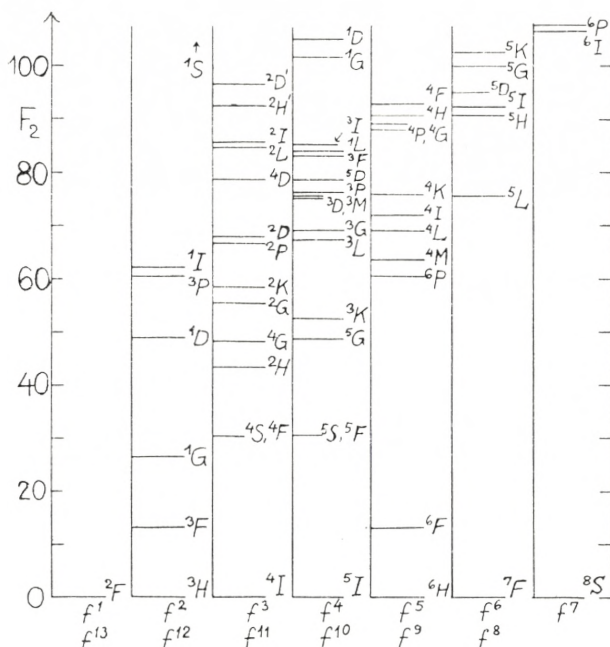


Fig. 1. Centres of gravity of multiplets in f^n -systems, expressed in the Condon-Shortley parameter F_2 , assuming $F_4 = 0.2 F_2$ and $F_6 = 0.02 F_2$.

(in the righthand column), the complicated energy expressions are not linear in F_6 , while they are so in the other terms.

Fig. 1 gives the terms of the f^n -systems with the second choice of parameters $F_4 = 0.2 F_2$ and $F_6 = 0.02 F_2$, and with the lowest term at 0 F_2 .

TABLE 1. Electrostatic interaction of f^3 for selected values of the Condon-Shortley parameters.

	$F_4 = 0.2 F_2$ $F_6 = 0$	$F_4 = 0.2 F_2$ $F_6 = 0.02 F_2$		$F_4 = 0.2 F_2$ $F_6 = 0$	$F_4 = 0.2 F_2$ $F_6 = 0.02 F_2$
4I	— 93.2 F_2	— 97.6 F_2	2H	— 62.0 F_2	— 54.2 F_2
4F	— 49.8	— 67.0	$^2H'$	— 2.6	— 5.1
4S	— 49.8	— 67.0	2G	— 39.7	— 40.8
4G	— 25.0	— 49.4	$^2G'$	+ 63.5	+ 39.8
4D	+ 18.4	— 18.8	2F	+ 7.8	+ 20.6
2L	— 12.6	— 13.0	$^2F'$	+ 124.4	+ 113.6
2K	— 39.8	— 39.0	2D	— 40.3	— 30.5
2I	— 6.2	— 12.3	$^2D'$	+ 13.7	— 1.2
2P	— 33.8	— 30.9			

TABLE 2. Doublet term levels for Nd^{+++} .

	Without intermediate coupling	With approx. intermediate coupling	Observed ¹¹
${}^2H_{9/2}$	17300 cm^{-1}	16600 cm^{-1}	15700 cm^{-1}
${}^2H_{11/2}$	17900	17600	16000
${}^2G_{7/2}$	21300	21500	20800
${}^2G_{9/2}$	22400	24000	21000
${}^2K_{13/2}$	21400	21300	21300
${}^2K_{15/2}$	23500	23200	21700
${}^2P_{1/2}$	25100	24500	23400
${}^2P_{3/2}$	25100	25900	23900
${}^2D_{3/2}$	23300	21700	23100
${}^2D_{5/2}$	26400	26000	26300
${}^2L_{15/2}$	30000	30500	..
${}^2L_{17/2}$	31900	31900	30400
${}^2I_{11/2}$	30900	30900	31800
${}^2I_{13/2}$	31400	31500	..
${}^2H'_{9/2}$	32200	32400	33500
${}^2H'_{11/2}$	34700	34700	34400
${}^2D'_{3/2}$	35000	35700	..
${}^2D'_{5/2}$	34600	35000	..
${}^2F_{5/2}$	40600	41100	38500
${}^2F_{7/2}$	42700	42600	39900
${}^2G'_{7/2}$	48700	49200	..
${}^2G'_{9/2}$	47800	47900	..
${}^2F'_{5/2}$	72600	72700	..
${}^2F'_{7/2}$	71500	71500	..

Table 2 gives the doublet levels for the f^3 -system Nd^{+++} , if $F_2 = 325 \text{ cm}^{-1}$, $F_4 = 65 \text{ cm}^{-1}$, $F_6 = 6,5 \text{ cm}^{-1}$, $\zeta_{4f} = 900 \text{ cm}^{-1}$ and the centre of ${}^4I = 3300 \text{ cm}^{-1}$.

There are calculated levels in two cases: (1) without intermediate coupling effects and (2) an approximate treatment of the perturbations given by ISHIDZU and OBL.⁹ If the secular determinant is written

$$\begin{vmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \dots & \dots & \dots & \dots \\ a_{n1} & a_{n2} & \dots & a_{nn} \end{vmatrix} = 0, \quad (1)$$

where $a_{pq} = a_{qp}$, and especially $a_{qq} = E_q - E$ and $a_{pq} = k_{pq} \zeta_{4f} (p \neq q)$. E_q is the energy of the unperturbed level and k_{pq}

the non-diagonal elements;⁹ then different roots of E are the perturbed levels. If one of the unperturbed levels, E_q , has a larger distance from all the other E_p than the order of magnitude of $k_{pq} \zeta_{4f}$, it is a good approximation to write one of the roots

$$E = E_q + \sum_{p \neq q} \frac{k_{pq}^2 \zeta_{4f}^2}{E_q - E_p}. \quad (2)$$

When $|E_q - E_p|$ decreases, the formula gives too large perturbations, and in the limit $E_p = E_q$ the mutual repulsion of the levels are given by

$$E = E_q \pm k_{pq} \zeta_{4f}. \quad (3)$$

If only two levels coincide, their centre of gravity can be used as a level and be perturbed by all the contributions, acting separately on them.

The third column of Table 2 gives the wave numbers of the bands, observed by STEWART¹¹ in the spectrum of aqueous solutions of neodymium perchlorate. In some cases, e. g. the weak bands in the blue due to 2G and 2K , the aquo ion in solution shows the four predicted bands more distinctly than the crystal. The absorption spectrum of the solid is very valuable for investigations of the fine structure,¹⁰ but is not so useful for detection of the atomic level, which is split more by crystal fields of lower symmetry in the rigid crystal.

The single band at $427.5 \text{ m}\mu$ (23400 cm^{-1}) is presumably due to the transition to ${}^2P_{1/2}$, which is the state with $J = \frac{1}{2}$ sought for by SATTEN.

Fig. 2 shows the observed spectra of the f^3 - and f^4 -systems; in the case of Nd^{+++} the measurements by STEWART¹¹ are given.

The electron configuration $[Em] 5f^3$ is exemplified by U^{+++} , Np^{+4} , PuO_2^+ , and AmO_2^{++} . The absorption spectrum of U^{+++} in aqueous solution has been reported by KATO,¹² SEABORG,¹³ and is extensively discussed by STEWART.¹⁴ The infra-red part of the spectrum has been investigated by ROHMER et al.¹⁵ These authors found two weak bands at 7070 and 10320 cm^{-1} , and two strong bands at 8230 and $11240 - 11490 \text{ cm}^{-1}$, whereas the band at 9430 cm^{-1} presumably¹⁵ is due to impurities of U^{+4} , while STEWART¹⁴ assigns the band to U^{+3} . The reflection spectrum of solid UCl_3 has been studied among others by FREED and

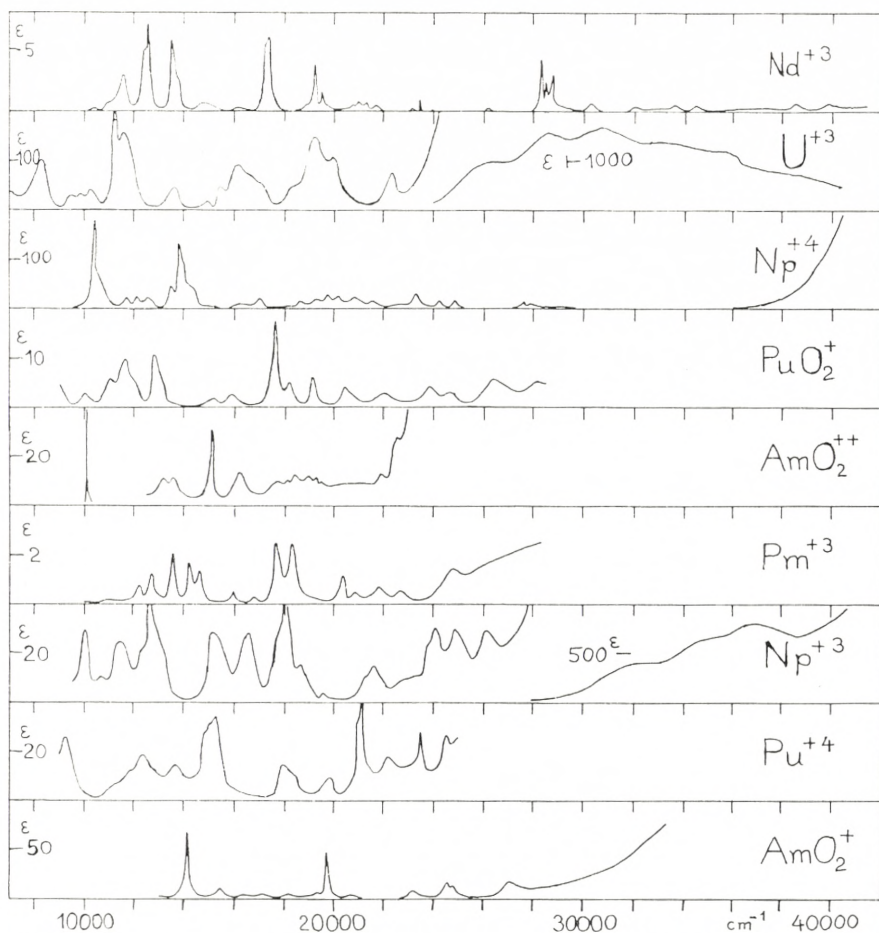


Fig. 2. Observed spectra of f^3 - and f^4 -systems in aqueous solution. Neodymium (III),¹¹ uranium (III),¹⁴ neptunium (IV),¹⁷ plutonium (V),¹³ americium (VI),^{18, 56} promethium (III),²¹ neptunium (III),¹⁷ plutonium (IV),²² and americium (V).¹⁸

SANCIER.¹⁶ Np^{+4} was studied by SJOBLÖM and HINDMAN¹⁷ in 1 M HCl and 1 M H_2SO_4 , giving evidence for the pure aquo ion in solution, while PuO_2^+ in 0.5 M HCl was studied by CONNICK, KASHA, McVEY and SHELIN (ref. 13, p. 559). AmO_2^{++} was investigated* by STEPHANAU, NIGON and PENNEMAN.¹⁸

If the transition is $^4I_{9/2} - ^4I_{15/2}$, then $\zeta_{5f} = 1700\text{ cm}^{-1}$, 2100 cm^{-1} and 2700 cm^{-1} can be implied from the strong bands with centres at 11300 cm^{-1} (U^{+3}), 13800 cm^{-1} (Np^{+4}) and 17600 cm^{-1}

* ASPREY, STEPHANAU and PENNEMAN⁵⁶ found a high, narrow band at 10100 cm^{-1} .

(PuO_2^+). This is in good agreement with the value of $\zeta_{5f} = 1600 \text{ cm}^{-1}$ in U^{+4} (ref. 1). The bands at 8200 cm^{-1} (U^{+3}), 10400 cm^{-1} (Np^{+4}), and 11700 cm^{-1} or 12900 cm^{-1} (PuO_2^+) are then probably ${}^4I_{9/2} - {}^4I_{13/2}$. The identification of the higher terms is rendered difficult by the large value of ζ_{5f} . The three bands with increasing intensity at 13800 , 16400 , and 19100 cm^{-1} in U^{+3} and 16800 , ~ 20000 , and 23300 cm^{-1} in Np^{+4} are perhaps due to ${}^4F_{5/2}$, ${}^4F_{7/2}$, and ${}^4F_{9/2}$, respectively. This gives the distance between the centre of gravity ${}^4F - {}^4I$ equal to $16400 - 6000 = 10400 \text{ cm}^{-1}$ in U^{+3} and $20000 - 7400 = 12600 \text{ cm}^{-1}$ in Np^{+4} . This is slightly larger than the 10000 cm^{-1} of Nd^{+3} , and the displacement towards higher wave numbers in the actinides is thus mainly due to larger values of ζ . The other bands, on the basis of this theory, are due to levels of 2H , 4G , ${}^2K \dots$, but the observed bands over 20000 cm^{-1} cannot be identified with certainty as yet. In U^{+3} only one such band at 22200 cm^{-1} , which is weak and narrow, is observed.

Table 3 illustrates the choice of parameters $\zeta_{5f} = 1700 \text{ cm}^{-1}$, $F_2 = 340 \text{ cm}^{-1}$, $F_4 = 68 \text{ cm}^{-1}$, and $F_6 = 6.8 \text{ cm}^{-1}$ for U^{+3} . The second column gives the approximate influence (within an accuracy of $\sim 200 \text{ cm}^{-1}$) of intermediate coupling, cf. eq. 2 and ref. 9. The ground-state ${}^4I_{9/2}$ is decreased 1200 cm^{-1} by the perturbations of other levels with $J = \frac{9}{2}$.

The wave numbers of Table 3, when multiplied by 1.2, apply quite well to Np^{+4} and they explain the large number of bands observed between 19000 and 25000 cm^{-1} in this spectrum. Over 24000 cm^{-1} in U^{+3} appears the broad and intense absorption due to the transitions¹ $[Em] 5 f^3 \rightarrow [Em] 5 f^2 6 d$ with maxima* at

* Measured in $10 M HCl$ by Messrs. K. G. POULSEN, M. Sc., and F. WOLDBYE, M. Sc., using the new Cary spectrophotometer. The scarlet colour, produced by reduction with zinc, disappears at room temperature in less than a minute. Solutions in $6 M HClO_4$ are reduced much more slowly under formation of traces of chloride by metals, but the bluish grey solutions are of more prolonged stableness. FONTANA⁵³ measured the reaction rate with water in perchlorate medium and found it strongly increasing with the ionic strength, but not dependent *inter alia* on the hydrogen ion concentration. The colour change with HCl is peculiar, since no particular effect on the uranium (III) spectrum could be observed. It is perhaps connected with the shift of the uranium (IV) bands in chloro complexes, which cause different overlappings of the absorption bands. Mixtures of trivalent and quadrivalent uranium in concentrated hydrochloric acid are olive-brown, because only light in a narrow range about $560 m\mu$ contributes to the visual impression. Cf. the observations of SOMEYA.⁶⁰

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

	Calc. without intermediate coupling	With approx. intermediate coupling	Observed
$^4J_{11/2}$	3100 cm^{-1}	4100 cm^{-1}	—
$^4I_{13/2}$	6900	7800	8200 cm^{-1}
$^4I_{15/2}$	11100	11700	11300
$^4F_{3/2}$	13100	12600	—
$^4F_{5/2}$	14500	15000	13800
$^4S_{3/2}$	16500	16600	15700
$^4F_{7/2}$	16500	17300	16400
$^4G_{5/2}$	18200	18800	19100
$^4F_{9/2}$	19100	18100	19800
$^2H_{9/2}$	20100	19700	—
$^4G_{7/2}$	20200	20900	22200
$^2H_{11/2}$	21200	22200	..
$^4G_{9/2}$	22800	23200	..
$^2K_{13/2}$	23900	25100	..
$^2G_{7/2}$	24400	26500	..
$^4G_{11/2}$	25900	26300	..

25800, 28500, and 31000 cm^{-1} with molar extinction coefficients ~ 1000 .

Np^{+4} does not show this type of absorption¹⁷ below 40000 cm^{-1} , which shows the increasing energy difference between 5 f - and 6 d -electrons with increasing atomic number by the same oxidation state, i. e. state of ionization. PuO_2^+ also has quite weak bands in the measured range (10000—28500 cm^{-1}), and there seems to be a tendency towards lower intensities with higher oxidation state. This was likewise observed for the iso-electronic sequence $Np^{+3} - Pu^{+4} - AmO_2^+$ discussed in the next section. The high narrow bands^{18, 56} of AmO_2^{++} at 10100 and 15100 cm^{-1} and the weaker bands at 13200, 13700, and 16200 cm^{-1} are presumably due to f^n -transitions, while the absorption at higher wave numbers is a molecular spectrum of the UO_2^{++} -type.¹

f^4 -systems.

The electrostatic interaction is for the quintet terms:

$$\left. \begin{array}{l} {}^5I \quad - 95 F_2 \quad - 240 F_4 \quad - 1079 F_6 \\ {}^5G \quad - 40 \quad - 174 \quad - 2080 \\ {}^5F \quad - 60 \quad - 198 \quad - 1716 \\ {}^5D \quad - 5 \quad - 132 \quad - 2717 \\ {}^5S \quad - 60 \quad - 198 \quad - 1716 \end{array} \right\} (4)$$

It is seen in all cases that the energy is $30 F_2 + 99 F_4 + 858 F_6$ lower than the quartet terms of f^3 with the same L , and especially, the energies of 5F and 5S are equal. The interval factor ζ for all the quintet terms equals $\frac{1}{4} \zeta_{nf}$. Two of the triplet terms are represented only once in f^4 :

$$\left. \begin{array}{l} {}^3M \quad - 55 F_2 \quad - 150 F_4 \quad - 211 F_6 \quad \zeta = \frac{1}{6} \zeta_{nf} \\ {}^3L \quad - 70 \quad - 105 \quad - 316 \quad \zeta = \frac{5}{24} \zeta_{nf} \end{array} \right\} (5)$$

while the others are represented twice or more times. RAO¹⁹ has calculated the matrices of electrostatic interaction in these cases by Slater's method.⁷ REILLY²⁰ recalculated these matrices by means of Racah's method⁸ and corrected several errors. Their elements are given in the parameter system of RACAH as the linear combinations

$$e_0 E^0 + e_1 E^1 + e_2 E^2 + e_3 E^3,$$

$$\left. \begin{array}{l} \text{where } E^0 = F_0 - 10 F_2 - 33 F_4 - 286 F_6 \\ E^1 = \frac{1}{9} \{ 70 F_2 + 231 F_4 + 2002 F_6 \} \\ E^2 = \frac{1}{9} \{ F_2 - 3 F_4 + 7 F_6 \} \\ E^3 = \frac{1}{3} \{ 5 F_2 + 6 F_4 - 91 F_6 \}. \end{array} \right\} (6)$$

It is valid⁸ for all the terms of the configuration f^n ($n \leq 7$)

$$e_0 = \frac{n(n-1)}{2}, \quad (7)$$

and $e_0 E^0$ can thus be used for convenience as zero-point of the energy-scale. e_1 is given as function of n , the seniority number⁸ v (which can be n , $n-2$, $n-4$ or $n-6$ and at least 0) and the total spin S :

$$e_1 = \frac{9(n-v)}{2} + \frac{v(v+2)}{4} - S(S+1). \quad (8)$$

The non-diagonal elements contain only $e_2 E^2 + e_3 E^3$ contributions. Since $e_2 E^2$ and $e_3 E^3$ are of the same order of magnitude and mostly smaller than E^1 , it is seen that the terms are divided into groups with the same v and S (and the highest values of S and v have the lowest energy *inter alia*), whose structure is determined by the $e_2 E^2 + e_3 E^3$ values.

The matrices of REILLY²⁰ are used with the assumptions that $F_4 = 0.2 F_2$ and $F_6 = 0.02 F_6$ (giving $E^1 = 17.36 F_2$, $E^2 = 0.06 F_2$, and $E^3 = 1.46 F_2$) and $E^0 = 0$. The energies below $60 F_2$ are then:

$$\left. \begin{array}{ll} {}^5_4I_{20} & - 30.7 F_2 & {}^3_4D_{20} & 42.9 F_2 \\ {}^5_4S_{00} & 0 & {}^3_4M_{30} & 44.7 \\ {}^5_4F_{10} & 0 & {}^3_4P_{11} & 45.7 \\ {}^5_4G_{20} & 17.5 & {}^5_4D_{20} & 48.2 \\ {}^3_4K_{30} & 21.6 & {}^3_4F_{30} & 52.3 \\ {}^3_4L_{21} & 36.6 & {}^1_4L_{22} & 52.9 \\ {}^3_4G_{21} & 38.5 & {}^3_4I_{20} & 54.1 \end{array} \right\} \quad (9)$$

The superscript is as usual the multiplicity $2S+1$, the left subscript the seniority number v and the right subscript the quantum numbers U , which can be found in ref. 8, Table 1. They denote a group-theoretical classification of the terms in f^n -systems.

It is seen that f^3 - and f^4 -systems are likely to have their strong absorption bands in the visible spectrum at nearly the same places. Really, Pm^{+++} has, according to LANTZ and PARKER,²¹ a group of strong bands between 12000 and 22000 cm^{-1} as also Nd^{+++} . The continuous absorption given at the higher wave numbers can perhaps be ascribed to the influence of the strong radioactivity on the solvent. The molar extinction coefficients in the figures are erroneously multiplied by 1000.

The electron configuration $[Em] 5f^4$ is exhibited by ions

Np^{+3} , Pu^{+4} , and AmO_2^+ . Fig. 2 gives the spectra measured of the neptunium (III) aquo ion¹⁷ and of americium (V).¹⁸ The monomer aquo ion of plutonium (IV) was studied by HINDMAN.²²

The broad bands at ~ 32000 , 34500 , 37500 , and 42000 cm^{-1} of Np^{+++} are due to transitions $[Em] 5f^4 \rightarrow [Em] 5f^3 6d$ with the excited states 5L , $^5K \dots$. In contrast to this atomic spectrum, the strong bands of plutonium (IV) complexes in the ultraviolet are presumably due to electron transfer, i. e. internal redox processes.^{2, 5} Chloro complexes of U^{+4} have their "electron transfer spectrum" over 34000 cm^{-1} , but this is found below 25000 cm^{-1} in chloro complexes²² of Pu^{+4} , since the latter ion is a stronger oxidizing agent, i. e. has greater electron affinity.

The narrow bands of Pu^{+4} have an average of 19 per cent higher wave numbers¹ than Np^{+3} . Similar results were obtained above for Np^{+4} and U^{+3} . Thus, the external charge seems to have a strong influence on the screening of the f -electrons. The screening constant is presumed to be quite constant 34 in the trivalent lanthanides²³ and 58 in the actinides.²⁴ But the f -electrons seem not screened much in ions of low charge,* e.g. ζ_{4f} is -0.1 cm^{-1} in neutral cesium and 64 cm^{-1} in Ba^+ , and ζ_{5f} is only 81 cm^{-1} in Ra^+ while it is 1236 cm^{-1} in Th^{+3} . The hydrogen-like f -wave functions are only smaller than the kernel in ions with high external charge. Even in the trivalent ions, "external screening" prevents very large energy decrease of the f -electrons.

The strong bands at 12700 cm^{-1} (Np^{+3}), 15200 cm^{-1} (Pu^{+4}), and 19700 cm^{-1} (AmO_2^+) are presumably due to $^5I_4 - ^5I_8$, thus giving $\zeta_{5f} = 1900$, 2300 , and 3000 cm^{-1} , respectively, if intermediate coupling effects are not considered. The bands at 10000 cm^{-1} (Np^{+3}), 12300 cm^{-1} (Pu^{+4}), and 14100 cm^{-1} (AmO_2^+) are possibly due to 5I_7 . The values of $J = 2, 3, 4$, and 5 are represented in both 5F and 5G and give intermediate coupling effects. The high values of $J (= 6, 7 \text{ and } 8)$ in 3K will also give strong bands. It is not possible to identify them, until methods for determination of J from crystal field studies are developed, cf. SATTEN.¹⁰

* Cf. MEISSNER and WEINMANN⁶¹, RASMUSSEN⁶², ⁶³ KLINKENBERG and LANG³⁸.

f^5 -systems.

By direct use of Condon-Shortley's method the following energies can be determined:*

$$\left. \begin{array}{l} {}^6H \quad - 115 F_2 \quad - 348 F_4 \quad - 2587 F_6 \\ {}^6F \quad - 100 \quad - 330 \quad - 2860 \\ {}^6P \quad - 45 \quad - 264 \quad - 3861 \\ {}^4M \quad - 105 \quad - 231 \quad - 1089 \end{array} \right\} \begin{array}{l} \zeta = \frac{1}{5} \zeta_{nf} \\ \zeta = \frac{1}{9} \zeta_{nf} \end{array} \quad (10)$$

It is seen that the sextet terms are displaced $9 E^0$ below the corresponding f^2 -triplets. By Racah's method (using $10 E^0$ as zero-point for the energy-scale) it is possible to calculate the following diagonal elements for the matrices:

TABLE 4. Diagonal elements for electrostatic interaction in f^5

$$\left(S = \frac{5}{2} \text{ and } \frac{3}{2}, v = 5 \right).$$

${}^6_5H_{11}$	—	$9 E^3$			
${}^6_5F_{10}$		0			
${}^6_5P_{11}$	+	$33 E^3$			
${}^4_5M_{30}$	$5 E^1$	—	$50 E^2$	— $23 E^3$	
${}^4_5L_{21}$	5	+	85	— 23	
${}^4_5K_{21}$	5	—	219	— 13/3	
${}^4_5K_{30}$	5	+	188	+	16/3
${}^4_5J_{20}$	5	+	40	— 2	
${}^4_5J_{30}$	5	—	50	— 11	
${}^4_5H_{11}$	5	+	0	— 2	
${}^4_5H_{21}$	5	+	197	+	26
${}^4_5H_{30}$	5	—	176	+	14
${}^4_5G_{20}$	5	—	$1040/7$	+	$8/7$
${}^4_5G_{21}$	5	+	$1089/7$	+	$11/21$
${}^4_5G_{30}$	5	+	104	+	$22/3$
${}^4_5F_{10}$	5	+	0	+	0
${}^4_5F_{21}$	5	—	65	+	3
${}^4_5F_{30}$	5	—	76	+	42
${}^4_5D_{20}$	5	+	$1144/7$	+	$22/7$
${}^4_5D_{21}$	5	—	$1781/7$	+	$202/7$
${}^4_5P_{11}$	5	+	0	+	$44/3$
${}^4_5P_{30}$	5	+	104	—	$14/3$

* SCHUURMANS⁵⁴ has calculated the energies of quintet terms of f^4 and sextet terms of f^5 and f^7 by means of Condon and Shortley's method.

The seniority numbers 3 and 1 are not considered here. For instance the quartet terms with $\nu = 3$ have $9 E^1$, thus much higher energy levels than the ($\nu = 5$) cases. The non-diagonal elements can be calculated individually from Racah's theory. Some cases of interest for the low-lying energy levels are:

$$\left. \begin{aligned}
 ({}^4_5K_{21} \parallel {}^4_5K_{30}) &= 8\sqrt{17} E^2 + \frac{8}{3}\sqrt{17} E^3 \\
 ({}^4_5I_{20} \parallel {}^4_5I_{30}) &= -120\sqrt{3} E^2 + 2\sqrt{3} E^3 \\
 ({}^4_5H_{11} \parallel {}^4_5H_{30}) &= -10\sqrt{39} E^2 - \frac{5}{3}\sqrt{39} E^3 \\
 ({}^4_5G_{20} \parallel {}^4_5G_{21}) &= -\frac{16}{7}\sqrt{2145} E^2 + \frac{5}{21}\sqrt{2145} E^3 \\
 ({}^4_5F_{10} \parallel {}^4_5F_{21}) &= -\frac{1}{3}\sqrt{165} E^3 \\
 ({}^4_5P_{11} \parallel {}^4_5P_{30}) &= 130\sqrt{11} E^2 - \frac{5}{3}\sqrt{11} E^3
 \end{aligned} \right\} \quad (11)$$

With the same assumption ($E^1 = 17.36 F_2$, $E^2 = 0.06 F_2$, and $E^3 = 1.46 F_2$) the levels given in Fig. 1 are obtained from these values. Fig. 3 gives the observed spectra of the systems with five and more f -electrons.

The distribution of the sextet terms agrees with Sm^{+++} . The many strong bands in the infra-red are due to levels of 6H and 6F , and the only other strong band at 24800 cm^{-1} is due to ${}^6H_{5/2} - {}^6P_{7/2}$. Thus, E^3 is increased only ten per cent as compared with Pr^{+++} , if intermediate coupling or configuration interaction⁷ effects can be excluded. From the spectrum in the infra-red and fluorescence spectra GOBRECHT²³ found $\zeta_{4f} = 1200 \text{ cm}^{-1}$ in Sm^{+++} .

Since Sm^{+++} has¹¹ weak bands distributed at wave numbers over 17900 cm^{-1} , some quartet terms must occur at slightly lower energies than expected from the parameter ratio $F_4 = 0.2 F_2$ and $F_6 = 0.02 F_2$, as also in Pr^{+++} , where E^1 (or F_6) is relatively small. The calculations show that 4M with the J -values $\frac{15}{2}$, $\frac{17}{2}$, $\frac{19}{2}$, and $\frac{21}{2}$ should be the lowest quartet term. The positions

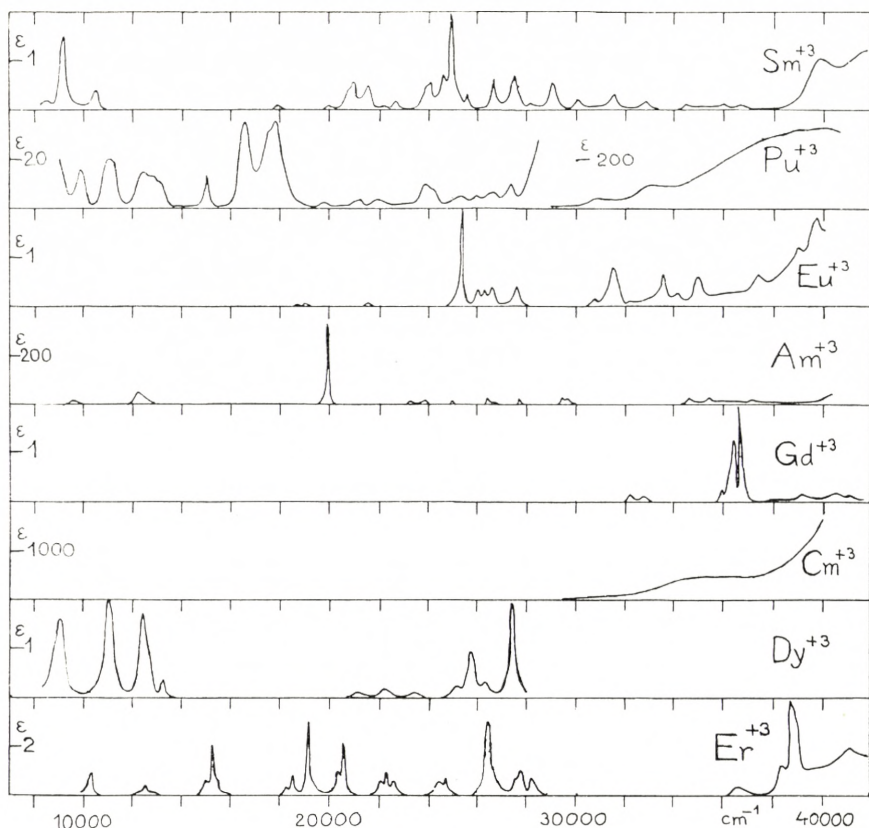


Fig. 3. Observed spectra of f^5 -, f^6 -, f^7 -, f^9 - and f^{11} -systems in aqueous solution. Samarium (III),¹¹ plutonium (III),^{14, 22} europium (III),¹¹ americium (III),¹⁸ gadolinium (III),¹¹ curium (III),³⁵ dysprosium (III),⁴⁷ and erbium (III).^{48, 49}

of the different levels of the multiplet can be found from the general formula:

$$E = E_0 + \frac{\zeta}{2} \{ J(J+1) - L(L+1) - S(S+1) \}, \quad (12)$$

where E_0 is the centre of gravity of the term and ζ is ζ_{nf} multiplied by a constant characteristic of the term. These constants have been calculated for many f^n -cases by RAO.²⁵

HINDMAN²² has given the absorption spectrum of plutonium (III) aquo ions (cf. ref. 13, p. 574). Table 5 gives the results for the two low sextets 6H and 6F , if their centres of gravity are assumed to have the distance $9 E^3 = 6000 \text{ cm}^{-1}$ and $\zeta_{5f} = 2500$

TABLE 5. Calculated and observed sextet levels of Pu^{+++} .

	Calc.	Obs.
${}^6H_{13/2}$	10000 cm^{-1}	9900 cm^{-1}
${}^6F_{5/2}$	10500	11100
${}^6F_{7/2}$	12250	122—13200
${}^6H_{15/2}$	13750	15000
${}^6F_{9/2}$	14500	16600
${}^6F_{11/2}$	17250	17900
$({}^6P_{7/2})$	36750	—

cm^{-1} (as extrapolated from the other trivalent actinide ions). The bands at 19800, 21200, and 21900 cm^{-1} have only intensities about ten per cent of the strong bands and they are due to quartet levels. At the limit of the measured range, 28500 cm^{-1} , an absorption begins which is either a strong f^5 -band (6P) or the much stronger $[Em] 5 f^5 \rightarrow [Em] 5 f^4 6 d$ transitions. STEWART¹⁴ gives shoulders at 31000 and 33500 cm^{-1} before a broad band at 40000 cm^{-1} (see Fig. 3), but no definite conclusion can be drawn.

No information has been given on the absorption spectrum of Am^{+4} , which probably occurs in solid AmO_2 or AmF_4 .

f^6 -systems.

By direct diagonalization according to CONDON and SHORTLEY can be found:

$$\left. \begin{array}{l} {}^7F \quad - 150 F_2 \quad - 495 F_4 \quad - 4290 F_6 \quad \zeta = \frac{1}{6} \zeta_{nf} \\ {}^5L \quad - 140 \quad - 336 \quad - 2582 \quad \zeta = \frac{1}{16} \zeta_{nf} \end{array} \right\} \quad (13)$$

It is seen that 7F has the energy $-15 E^0$. Using Racah's method, the terms with $S = 2$ and the seniority number $\nu = 6$ have the energies in Table 5, when $-15 E^0$ is used as zero-point of the energy scale.

TABLE 6. Diagonal elements of electrostatic interaction of $f^6(S = 2, v = 6)$.

$$\begin{aligned}
 {}^5_6P_{11} &= 6 E^1 + 0 E^2 + 11 E^3 \\
 {}^5_6D_{20} &= 6 + 858/7 + 11 \\
 {}^5_6D_{21} &= 6 - 1131/7 + 18 \\
 {}^5_6F_{21} &= 6 - 195 + 15 \\
 {}^5_6G_{20} &= 6 - 780/7 + 4 \\
 {}^5_6G_{21} &= 6 + 1683/7 + 11 \\
 {}^5_6H_{11} &= 6 + 0 - 3 \\
 {}^5_6H_{21} &= 6 - 21 + 6 \\
 {}^5_6I_{20} &= 6 + 30 - 7 \\
 {}^5_6K_{21} &= 6 + 135 - 7 \\
 {}^5_6L_{21} &= 6 - 105 - 15
 \end{aligned}$$

Some non-diagonal elements are:

$$\left. \begin{aligned}
 ({}^5_6H_{11} \parallel {}^5_6H_{21}) &= -12 \sqrt{455} E^2 \\
 ({}^5_6G_{20} \parallel {}^5_6G_{21}) &= -\frac{24}{7} \sqrt{4290} E^2 \\
 ({}^5_6D_{20} \parallel {}^5_6D_{21}) &= \frac{234}{7} \sqrt{132} E^2
 \end{aligned} \right\} \quad (14)$$

These values are used for the f^6 -levels in Fig. 1. Fig. 3 gives the observed spectra of $Eu^{+++11,18}$ and Am^{+++18} .

GOBRECHT²³ found $\zeta_{4f} = 1450 \text{ cm}^{-1}$ in Eu^{+++} from fluorescence studies. The band of Am^{+++} at 12300 cm^{-1} , identified as ${}^7F_0 - {}^7F_6$, gives $\zeta_{5f} = 3500 \text{ cm}^{-1}$ when no intermediate coupling effects are considered. The most characteristic features of the two spectra are the extremely weak bands (compared with the other lanthanides and actinides, respectively) due to the change of S from 3 to 2. But the bands at 25300 cm^{-1} in Eu^{+++} and 19900 cm^{-1} in Am^{+++} have quite normal intensities.

The latter case is presumably due to the transition ${}^7F_0 - {}^5L_6$. Since the distance between the two levels with $J = 6$ is not much greater than ζ_{5f} , the excited state intermixes strongly¹ with 7F_6 . The only difficulty is the great change of J by the transition, since usually only $|\Delta J| \leq 4$ are allowed with reasonable probability.²⁶ 5I_4 and 5H_4 are thus also possible explanations of the band in Eu^{+++} .

The extremely narrow and weak bands of Eu^{+++} at 19000 and 21500 cm^{-1} have been investigated by SPEDDING, MOSS, and WALLER²⁷ and by FREED, WEISSMAN, and FORTRESS.²⁸ According to HELLWEGE and KAHLE²⁹ the bands are due to transitions to 5D_1 and 5D_2 , while the very strongly forbidden transition to 5D_0 has been observed at 17250 cm^{-1} . FREED³⁰ assumes the two first bands to be due to levels with $J = 2$ and 3. The occurrence of 5D seems peculiar; compare Table 5. It can be connected with strong interaction with the 5D -term with seniority number 4, which has the diagonal element of energy $9E^1 + 143/7E^3$. The non-diagonal elements with the two other terms are rather large:

$$({}^5D_{20} \parallel {}^5D_{20}) = \frac{22}{7} \sqrt{14} E^3 \quad \text{and} \quad ({}^5D_{20} \parallel {}^5D_{21}) = \frac{12}{7} \sqrt{462} E^3.$$

Nevertheless, none of the 5D -terms should pass below 5L . The multiplet splitting of the term is strong, $\zeta \simeq \zeta_{4f}$, as is often the case with the lowest of the two interacting multiplets with the same L and S ⁹, and the interaction with the levels of the ground-state can be rather high, due to the low values of J .

The isoelectronic species Sm^{++} was studied by BUTEMENT and TERRY.³¹ BUTEMENT³² later discussed this and other divalent lanthanides and assumed that the broad and intense bands, giving the orange-red colour of samarium (II) salts, are due to $[Xe] 4f^6 \rightarrow [Xe] 4f^5 5d$. As shown in the next section, divalent ions will have considerably less energy differences for this type of process than the trivalent ions.

f^7 -systems.

By direct diagonalization according to CONDON and SHORTLEY was found:

$$\left. \begin{array}{l} {}^8S \quad - 210 F_2 \quad - 693 F_4 \quad - 6006 F_6 \\ {}^6I \quad - 175 \quad \quad - 504 \quad \quad - 4291 \quad \zeta = 0 \text{ for all sextet terms.} \end{array} \right\} (15)$$

If the energy of 8S , $-21E^0$, is used as zero-point of the energy-scale, the following energies of the sextet terms are obtained by Racah's method:

$$\left. \begin{aligned}
 {}^6_7J_{20} &= 7 E^1 - 70 E^2 - 7 E^3 \\
 {}^6_7G_{20} &= 7 \quad + 260 \quad + 4 \\
 {}^6_7D_{20} &= 7 \quad - 286 \quad + 11 \\
 {}^6_5H_{11} &= 9 E^1 + 9 E^3 \\
 {}^6_5F_{10} &= 9 E^1 \\
 {}^6_5P_{11} &= 9 E^1 - 33 E^3
 \end{aligned} \right\} (16)$$

It is seen that analogously to the positions of d^2 - and d^5 -terms (ref. 8, p. 1363) the energies of 8S , 6I , 6G , 6D , 6H , 6F , and 6P in f^7 -systems are exactly opposite in value to 1S , 1I , 1G , 1D , 3H , 3F , and 3P in f^2 -systems. Thus, the relative position of 6I and 6P will depend¹ on F_6/F_2 (or E^1/E^3), but they will be the lowest terms highly over the ground-state 8S . The spectrum¹¹ of Gd^{+++} has bands only at wave numbers over 32000 cm^{-1} , and the most prominent of the weak, ΔS -forbidden bands are the group at 39000 cm^{-1} , which presumably is due to the high J -values of 6I . Since $\zeta = 0$, all multiplet splitting is due to intermediate coupling effects. If the assumptions of Fig. 1 are used, the energy difference ${}^6I - {}^8S$ correspond to $106.7 F_2$, thus F_2 is 365 cm^{-1} , which agrees well with $F_2 = 325 \text{ cm}^{-1}$ in Nd^{+++} under the same assumptions.

The information on the absorption spectrum of Cm^{+++} has been quite divergent. WERNER and PERLMAN^{33,34} investigated solution in $0.5 M HCl$, having a high (ϵ maximally 483^{33} or 1140^{34}) and broad band at 28400 cm^{-1} and a weak shoulder at 21700 cm^{-1} . The strong α -activity of the solution is liable to produce absorbing impurities, e. g. chlorine. CRANE and PERLMAN³⁵ give the spectrum of $0.0013 M Cm(ClO_4)_3$ as a steep absorption limit at 40000 cm^{-1} , a shoulder ($\epsilon \sim 400$) at 35000 cm^{-1} , and nearly no absorption below 29000 cm^{-1} (Fig. 3). It would be very interesting to know the reflection spectrum of curium (III) fluoride or another compound (oxide, sulphate) without the tendency of a molecular spectrum. The narrow bands of $[Em]5f^7$ in the ultraviolet of Cm^{+++} have not yet been detected.

FREED and KATCOFF³⁶ studied the absorption spectrum of Eu^{++} in crystals. These authors concluded that the strong bands with vibrational structure in the range $25000\text{--}34000 \text{ cm}^{-1}$ are

due to $[Xe]4f^7 \rightarrow [Xe]4f^6 5d$ or even to transfer of electrons out in the crystal lattice, the opposite direction of the usual "electron transfer spectra". The real f^7 -bands of Eu^{++} are presumably masked by the strong bands near 30000 cm^{-1} .

On the analogy of the transition groups, it can be predicted that the energy difference between d - and f -electrons in a given

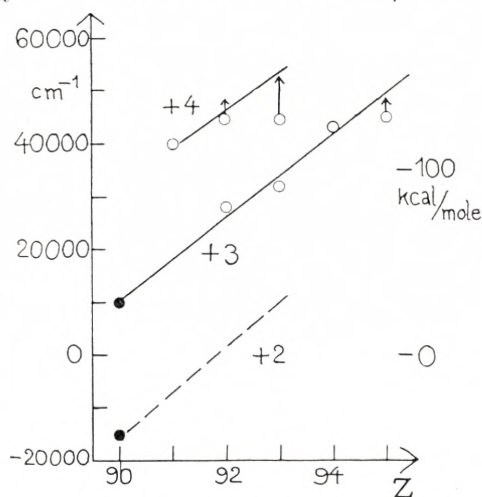


Fig. 4. The energy difference between the lowest terms of the electron configurations $[Em] 5f^{n-1} 6d$ and $[Em] 5f^n$. Filled circles from atomic spectroscopy.^{37, 38} Upward arrows by minimum values from chemical absorption spectra (no transition observed in measured range of wave lengths).

lanthanide or actinide element will decrease with decreasing oxidation state. Fig. 4 shows the energy difference between the lowest term of $[Em] 5f^{n-1} 6d$ and of $[Em] 5f^n$ in the actinides. The filled circles represent measurements from atomic spectroscopy (for Th^{++} of KLINKENBERG³⁷ and for Th^{+++} of KLINKENBERG and LANG³⁸). Open circles represent the results obtained from chemical absorption spectra discussed above. Upward arrows represent minimum values for the energy difference. The value for protactinium (IV) is derived from the measurements of R. E. ELSON.³⁹ This oxidation state* has broad bands at 35000 and 40000 cm^{-1} in $1\text{ M H}_2\text{SO}_4$ and at 40000 cm^{-1} 2 M HClO_4 .

It is seen from Fig. 4 that divalent actinides most probably will have strong absorption bands in the visible part of the

* Cf. the recent measurements by FRIED and HINDMAN.⁶⁴

spectrum, due to the relatively small energy necessary to excite a $5f$ -electron to a $6d$ -state.

The internal f^n -transitions are possible only because some states with opposite parity are slightly intermixed in the real states, which have no absolutely pure electron configuration.^{7,26} These interactions are due to fields with no centre of symmetry²⁶ acting on the excited electron configurations of which the $f^{n-1}d$ discussed above are the nearest to the ground-state. It is remarkable that the intensities of the narrow f^n -bands generally decrease with increasing distance between $f^{n-1}d$ and f^n , e. g. in the series Pr^{+++} , Nd^{+++} , Pm^{+++} , Sm^{+++} . In the actinides, a similar trend is not only found at increasing atomic number, but especially with increasing ionization state. This corresponds strictly to the energy difference between $6d$ - and $5f$ -electrons, as shown by Fig. 4. If this configuration interaction is the most important cause of intensity, it can be predicted that values of L which do not occur in the $f^{n-1}d$ -configuration, would exhibit weaker bands *inter alia*. This is perhaps the explanation of the anomalously low intensity of 1I_6 in Pr^{+++} as compared with Tm^{+++} .

f^9 -systems.

The electrostatic interaction in f^{14-n} -systems is completely equivalent to the f^n -systems. Since the intermediate coupling effects are quite important in the heavy end of the lanthanides, only some remarks will be made here about f^9 - and f^{11} -systems, which show some recognizable features. All the work done on these ions has been concentrated on the actions of crystal fields — MEEHAN and NUTTING⁴⁰ studied the sulphates of dysprosium, holmium, erbium, and thulium, SPEDDING⁴¹ the erbium (III) ion; SEVERIN has measured the fine structure of several holmium (III)⁴² and erbium (III) salts,⁴³ and ROSA⁴⁴ dysprosium. Recently, HELLWEGE⁴⁵ has treated the crystal field problems theoretically,** and GIESEKUS⁴⁶ especially the conditions in

* This band is not yet observed in Pr^{+3} , if HELLWEGE⁴⁵ is correct in assigning 1D_2 to the band at 16900 cm^{-1} . F_6 seems to be 64 times too small in the calculations of TREFFTZ.⁶⁶ As will be discussed elsewhere, the corrected value ($F_6 = 0.0152 F_2$) satisfies the observed data. The supposed⁵² 1I_6 of Tm^{+3} at 28000 cm^{-1} has been measured 12 times less intense than given by HOOGSCHAGEN.²⁶

** The influence of unsymmetrical crystal fields of citrate, ethylenediamine-tetraacetate and many other complexes of lanthanides has been investigated among others by HOLLECK and ECKHARDT⁶⁷.

TABLE 7. Calculated and observed sextet levels of Dy^{+++} .

	Calc.	Obs. (ref. 47)
${}^6H_{13/2}$	2700 cm^{-1}	—
${}^6H_{11/2}$	5000	—
${}^6F_{11/2}$	6500	—
${}^6H_{9/2}$	7000	7600 cm^{-1}
${}^6H_{7/2}$	8600	8100
${}^6F_{9/2}$	8500	9100
${}^6H_{5/2}$	9900	—
${}^6F_{7/2}$	10100	11000
${}^6F_{5/2}$	11400	12400
${}^6F_{3/2}$	12300	13200
${}^6F_{1/2}$	12800	—
${}^6P_{7/2}$	25400	25100
${}^6P_{5/2}$	26700	25800, 26300
${}^6P_{3/2}$	27600	27400

crystals of bromate enneahydrates. However, the atomic energy levels have not received much attention.

The dysprosium (III) aquo ion in solution was studied by HOOGSCHAGEN, SCHOLTE, and KRUYER⁴⁷ (see Fig. 3). The spectrum has strong bands below 13200 cm^{-1} , due to 6H and 6F , three weak bands at 21100, 22100, and 23400 cm^{-1} , presumably due to 4M , and strong bands in the range 25100—27400 cm^{-1} due to 6P . Table 7 gives the calculated and observed sextet levels of Dy^{+++} with $E^3 = 520 \text{ cm}^{-1}$ and $\zeta_{4f} = 1800 \text{ cm}^{-1}$ (cf. GOBRECHT²³). No measurements of californium (III) have been published, but the 6F -bands must be distributed over most of the visible spectrum with ζ_{5f} about 4500 cm^{-1} .

The absorption bands of Dy^{+++} also resemble those of Sm^{+++} by their width, which can even compete with Pr^{+++} and Tm^{+++} . In contrast to this, the bands of Eu^{+++} and Tb^{+++} are very narrow. These similarities between f^n - and f^{14-n} -systems are connected with the sensitivity to crystal field perturbations.⁴⁶

f^{11} -systems.

These systems, which are equivalent to f^3 -systems, are exemplified by Er^{+++} (a spectrophotometric study was made by HOOGSCHAGEN and GORTER⁴⁸ and by MOELLER and BRANTLEY⁴⁹). The absorption spectrum of centurium (III) has not yet been reported.

TABLE 8. The lowest levels of Er^{+++} .

	Without intermediate coupling	Approx. inter- mediate coupling (eq. 2, 3)	Observed
${}^4I_{13/2}$	6000 cm^{-1}	6500 cm^{-1}	6500 cm^{-1} (ref. 50)
${}^4I_{11/2}$	11200	11400	10300 (ref. 48)
${}^4I_{9/2}$	15600	14300	12500
${}^4F_{9/2}$	15800	14500	15300
${}^4F_{7/2}$	19400	19600	18300, 19100
${}^4G_{11/2}$	21700	21000	20400
${}^4F_{5/2}$	22600	21600	22200
${}^2H_{11/2}$	23900	25000	26500 (ref. 49)
${}^2H_{9/2}$	25400	23200	24600
${}^4G_{9/2}$	26100	27500	27500
${}^2K_{15/2}$	27900	27800	28100

GOBRECHT²³ identified the band at 15300 cm^{-1} in Er^{+++} with ${}^4I_{15/2} - {}^4I_{9/2}$ giving $\zeta_{4f} = 2350 \text{ cm}^{-1}$ (while the f^{13} -system Yb^{+++} has $\zeta_{4f} = 2950 \text{ cm}^{-1}$). In opposition to most other spectroscopic evidence, GOBRECHT maintained that transitions with decreasing values of J had the highest probability, thus giving the strongest bands. In the author's opinion, it is rather difficult to find the highest levels of these inverted multiplets (from more than seven f -electrons), because they have the lowest values of J . The high value of ζ_{4f} gives strong perturbations between the levels with the same J . These will distribute the levels of 4F , 4G , and 2H , which are responsible for most of the visible bands of erbium (III) in a rather irregular way. Table 8 illustrates a reasonable choice of parameters, $F_2 = 400$, $F_4 = 80$, $F_6 = 8 \text{ cm}^{-1}$, and $\zeta_{4f} = 2400 \text{ cm}^{-1}$. Approximate calculations of intermediate coupling are also given. ${}^4I_{15/2}$ is then decreased 800 cm^{-1} . The levels with $J = 9/2$ intermix strongly.

Table 9 gives the found values of the electrostatic interaction parameter $E^3 = \frac{5}{3}F_2 + 2F_4 - \frac{91}{3}F_6$, which determines the distance between the multiplets of highest multiplicity. The values for Pr^{+++} and Tm^{+++} are given in ref. 51 and 52, for Nd^{+++} in ref. 10, and for U^{+4} in ref. 1.

Besides crystal field studies,^{10, 45, 46} further identification of the lanthanide and actinide terms will be promoted by atomic

TABLE 9. The electrostatic interaction parameter E^3 .

f^2	Pr^{+++}	460 cm^{-1}			$U^{+4} \sim 780 \text{ cm}^{-1}$
f^3	Nd^{+++}	480	U^{+++}	500 cm^{-1}	Np^{+4} 610
f^4	Pm^{+++}	~ 500	Np^{+++}	~ 550	$Pu^{+4} \sim 650$
f^5	Sm^{+++}	480	Pu^{+++}	~ 670	
f^9	Dy^{+++}	520			
f^{11}	Er^{+++}	580			
f^{12}	Tm^{+++}	630			

spectroscopy, if a light-source can be constructed which ionizes the metal atoms strongly, at least to triply charged ions, but which does not excite them very much over their respective ground-states. Then, the transitions from $f^{n-1}s$, $f^{n-1}d$ and $f^{n-1}g$ to f^n will give strong emission lines, and the selection rules and Zeeman effect can be used for identification of the values of J .

Additional Note.

SATTEN⁵⁸ has commented on the note.² He is correct in pointing out that $F_4 = 0.2 F_2$ implies $F_6 = 0.03 F_2$. It might be preferred to use the ratio $F_4 = 0.17 F_2$ and $F_6 = 0.02 F_2$, which give slightly decreasing F^k integrals, as RACAH⁵⁹ found in Th^{++} . But such a change from the set $F_4 = 0.02 F_2$, $F_6 = 0.02 F_2$ used here would have almost no significance for the numerical results derived here. The most important difference, in the author's opinion, is between F_6 being negligibly small, as really found in the strongly perturbed⁷ La^+ and probably¹ also in U^{+4} , and F_6 being considerably over half its maximum value, as in⁵⁹ Th^{++} and in the author's opinion in most other lanthanides* and actinides. The influence on the Racah parameters⁸ discussed above can be seen from this table:

F_4/F_2	F_6/F_2	E^1	E^2	E^3	E^1/E^3
0.20	0.03	19.58 F_2	0.068 F_2	1.12 F_2	17.5
0.20	0.02	17.36	0.060	1.46	11.9
0.17	0.02	16.60	0.070	1.40	11.8
0.15	0.02	16.08	0.077	1.36	11.8
0.15	0.01	13.85	0.069	1.66	8.3
0.15	0.00	11.62	0.061	1.97	5.9

* also in Pr^{+3} , see the note p. 22.

Since the energy differences between terms with the same multiplicity and seniority number are mainly determined by E^3 , while the differences between such groups are multiples of E^1 (see eq. 8), the weak bands due to lower multiplicity will be displaced towards higher wave numbers, compared to the strong bands of the highest multiplicity, by increasing ratio E^1/E^3 .

The statement of SATTEN⁵⁸ that ${}^2P_{1/2}$ of Nd^{+++} cannot be placed so high as at 23400 cm^{-1} with any choice of F_k parameters, seems objectionable. The set $F_2 = 340\text{ cm}^{-1}$ $F_4 = 55\text{ cm}^{-1}$ and $F_6 = 7\text{ cm}^{-1}$ is adjusted to SATTEN's¹⁰ quartet terms and gives with $\zeta_{4f} = 900\text{ cm}^{-1}$ the energy ${}^2P_{1/2} - {}^4I_{9/2} = 24630\text{ cm}^{-1}$ without intermediate coupling. The interaction with ${}^4D_{1/2}$ will then depress the energy $\sim 600\text{ cm}^{-1}$. The interesting suggestion of SATTEN⁵⁸ that crystal fields intermix states as ${}^2G_{9/2}$ and ${}^2P_{1/2}$ is made somewhat uncertain by the fact that the wave number of the 4273 \AA -line seems only to shift in different complexes due to change of the energy of the ground-state ${}^4I_{9/2}$ and its crystal field splittings. The two last arguments have been accepted by SATTEN in a private communication.

Acknowledgment.

I am very much indebted to Professor Jannik Bjerrum for his interest in the work.

Summary.

The atomic energy levels causing the narrow bands of lanthanide and actinide elements are investigated. The case of Nd^{+++} , studied by SATTEN, is discussed with particular respect to the doublet terms, and the other systems with three effective f -electrons are considered. The electrostatic interaction of 4, 5, 6, and 7 f -electrons is computed from RACAH's and simpler cases from CONDON and SHORTLEY's theory. The relative positions of the multiplets agree well with the observed spectra, while the certain identification of the different levels is difficult, due to effects of intermediate coupling. In most of the actinide ions, the Lande interval factor ζ_{5f} is found to be rather more than 2

ζ_{4f} in the corresponding lanthanide ions. The electrostatic interaction, which separates the terms, seems to be quite similar in the two cases, except for an increase with increasing oxidation state, due to variations in effective charge. The transitions $[Em] 5f^n \rightarrow [Em] 5f^{n-1}6d$, causing broad and intense absorption bands, are used to estimate the very high energy difference between 6 *d*- and 5 *f*-electrons in the actinide ions (see Fig. 4). Some spectra due to molecular transfer of electrons are discussed and the spectrum of Cm^{+++} is shown not to be the predicted f^7 -spectrum. Observed spectra of Dy^{+++} and Er^{+++} are compared with the theory. Several tables give numerical results, and especially Table 9 gives the values of electrostatic interaction in the investigated cases of lanthanide and actinide ions.

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