Absorption Spectra of Dysprosium(III), Holmium(III), and Erbium(III) Aquo Ions

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The narrow f^n-bands of aqueous Dy(III), Ho(III), and Er(III) perchlorates are measured in the range $800-210$ mμ. The application of the theory of Slater, Condon, Shortley, and Racah to the distribution of multiplet terms is discussed. The lowest term with the total spin S one unit lower than of the groundstate often decays with fluorescence in the lanthanides and actinides, *e.g.* Sm(III), Eu(III), Sm(II), Dy(III), Pu(III), and Am(III).

Stewart [1] investigated trivalent lanthanides lighter than terbium. The present author has studied thulium [2]. The remaining three lanthanides, Dy, Ho, Er, have not been completely measured in aqueous solutions by modern spectrophotometry. Thus, Gorter *et al.* [3] do not report the spectra below 360—370 mμ, and Holleck and Hartinger [4] and Banks and Klingman [5] indicate only the wavelengths of the high peaks of analytical interest. The former authors [4] assume the absorption limit at a wavelength so high that they do not recognize the erbium(III) band at 255.2 mμ, discovered by Moeller and Brantley [6]. Therefore, the present author has procured the pure Dy_2O_3, Ho_2O_3, and Er_2O_3, prepared by Professor F. H. Spedding, and has measured the spectra with high dispersion on a Cary spectrophotometer. It was not felt useful to duplicate the measurements [3-6] above 800 mμ on a Beckman DU. Tables 1—3 give the band groups.

A conspicuous result is the absence of strong bands, such as those caused by $4f^n \rightarrow 4f^{n-1}5d$ transitions in Ce(III), Sm(II), and Eu(II). The molar extinction coefficient ε of Dy(III), Ho(III), and Er(III) is well below 2 at 220 and 3 at 210 mμ. Likewise, Yb (III) does not exhibit such bands [7].

SEXTET AND QUARTET LEVELS OF DYSPROSIUM(III)

Dieke and Singh [8] have recently expressed doubt whether the present author [9] is correct in assuming the multiplet ^6F in the infra-red and ^6P in the near ultra-violet part of the Dy(III) spectrum. This illustrates two different opinions on the most practical method of identifying f^n-energy levels. Dieke and

Table 1. Absorption bands of dysprosium(III) aquo ions. The bands are arranged in groups thought to correspond with the levels of the gaseous ion. Shoulders are given in parenthesis. λ denotes the wavelength in mμ and σ the wavenumber in K $=$ cm^{-1} (not corrected for the refraction of air) of the maxima. δ is the half-width in K, *i.e.* the distance from the maximum to the wavenumber with half the value of ε, the molar extinction coefficient. $(-)$ and $(+)$ indicate the values of δ of unsymmetrical bands, towards lower and higher σ, respectively. The oscillator strength P is given in units of 10^{-6} from the equation $P = 9.2 \times 10^{-9}\ \varepsilon\delta$.

Group	λ	σ	ε	δ	P
1	760	13 160	0.32	100	0.3
2	475	21 050	0.09	—	0.11
3	453	22 080	0.23	—	⎫ 0.4
	(451)	22 170	0.21	—	⎭
4	427	23 420	0.08	—	0.1
5	394.5	25 350	0.22	250	0.5
6	(389.3)	25 620	0.40	—	⎫ 1.0
	385.8	25 920	0.81	125	⎭
	(378.6)	26 410	0.34	—	0.4
7	(366.1)	27 310	0.94	—	⎫ 2.2
	364.5	27 430	2.00	$(-)$115	⎭
8	(352.8)	28 340	1.39	—	⎫ 3.1
	350.6	28 520	2.40	$(-)$130	⎭
9	338.6	29 530	0.27	100	0.25
10	(326.6)	30 630	1.35	75	⎫
	325.5	30 720	1.68	85	⎬ 2.0
	(321.3)	31 120	0.15	—	⎭
11	302.6	33 050	0.09	—	0.07
12	299.6	33 380	0.19	—	⎫ 0.2
	298.7	33 480	0.19	—	⎭
13	295.5	33 840	0.63	90	0.5
14	292.3	34 210	0.18	—	0.15
15	278.7	35 880	0.03	—	0.02
16	275.3	36 320	0.12	—	⎫ 0.2
	274.5	36 430	0.15	—	⎭
17	264.5	37 810	0.09	—	0.1
18	258.0	38 760	0.28	75	0.2
19	256.2	39 030	0.64	70	0.4
20	239.6	41 740	0.05	—	—
21	235 ?	42 550	0.04	—	—

Singh prefer the (physically very sound) way to identify J of each level by different methods: selection rules for polarized light, Zeeman effect and, most important, the maximum number of possible sub-levels ($2J+1$ for an even and $J+\frac{1}{2}$ for an odd number of electrons). When J is known for all levels, they can be assembled in multiplets with defined L and S if the deviations from Russell—Saunders' coupling are not too large.

Although the success of this method is evident in some cases, it must be realized that it has developed rather slowly. The present author attempted to stimulate the search for correct assignments of energy levels by drawing attention [9,10] to the fact that the theory of Slater, Condon, and Shortley [11] as refined for f^n-configurations by Racah [12] seems remarkably close to the large-scale distribution of multiplets in the absorption spectra of lanthanides and actinides. Thus, the large gap between 10 000 K ($=$ cm^{-1}) and a fairly

Table 2. Absorption bands of holmium(III) aquo ions. Notation as in Table 1.

Group	λ	σ	ε	δ	P
1	655.7	15 250	1.05	(+)60	0.6
	652.3	15 330	1.03	—	0.6
	640.3	15 620	3.17	80	2.4
2	(548.4)	18 230	0.42	—	
	542.9	18 420	1.78	—	} 5.0
	536.5	18 640	4.42	(—)70	
3	(490.5)	20 390	0.37	—	
	484.9	20 620	1.85	75	} 1.3
	(483.2)	20 690	0.95	—	
4	479.5	20 850	0.48	—	0.1
5	473.4	21 120	0.86	100	0.8
6	467.6	21 390	0.84	45	0.3
7	(456.8)	21 890	0.73	—	
	(454.0)	22 030	1.96	—	
	451.4	22 150	3.94	} 150	} 5.5
	450.5	22 200	3.92		
	(447.5)	22 350	1.67	—	
8	421.2	23 740	0.86	20	
	(418.4)	23 890	1.41		
	(416.4)	24 010	2.33	} 130	} 3.0
	415.7	24 060	2.55		
9	393.0	25 450	0.13	—	0.1
	389.0	25 710	0.31	—	0.1
	384.7	26 000	0.50	35	0.2
	381.3	26 220	0.13	—	0.05
10	(363.6)	27 500	0.66	—	
	361.1	27 690	2.20	—	} 2.7
	(359.6)	27 810	1.50	—	
11	(347.8)	28 750	0.24	—	} 0.6
	345.6	28 940	0.57	120	
12	333.9	29 420	0.82	90	0.7
13	(295.0)	33 900	0.44	} 230	1.1
	293.8	34 030	0.55		
14	289.4	34 550	1.36	(—)25	
	287.6	34 770	3.37	(+)50	} 1.5
	(284.3)	35 170	0.04	—	
15	278.6	35 870	2.07	100	1.9
16	274.5	36 430	0.09	—	0.06
17	272.0	36 760	0.07	60	0.04
18	261.9	38 180	0.04	—	
	260.2	38 430	0.06	—	} 0.05
	258.8	38 640	0.03	—	
19	(251.2)	39 810	0.09	—	} 0.2
	250.0	40 000	0.20	105	
20	(242.4)	41 250	0.55	—	
	241.8	41 360	1.54	—	} 2.0
	241.1	41 470	3.52	(+)85,(—)35	
21	238.6	41 910	0.11	80	0.1
22	(233.7)?	42 790	0.06	—	—

high wavenumber in the middle of the lanthanide series is explained by the expected terms with the same S as the groundstate [10].

When the theory [11] has been previously applied to f^n-systems, unprobable ratios have been assumed between the parameters F^2, F^4 and F^6. Since the

Table 3. Absorption bands of erbium(III) aquo ions. Notation as in Table 1.

Group	λ	σ	ε	δ	P
1	666.8	15 000	0.51	(+)60	0.3
	652.9	15 320	1.92	(+)80	1.4
	(649.2)	15 400	1.04	(−)45	0.4
2	549.1	18 210	0.21	75	0.15
	542.0	18 450	0.72	50	0.3
3	(527.8)	18 950	0.40	—	
	523.3	19 110	3.10	(+) 45, (−) 105	
	(521.1)	19 190	1.98	—	} 2.1
	(518.3)	19 290	1.07	—	
4	491.4	20 350	0.94	(+)125	
	487.2	20 530	1.89	60	} 1.5
	(485.0)	20 620	0.81	—	
5	(455.6)	21 950	0.21	—	} 0.3
	453.5	22 050	0.38	—	
	449.8	22 230	0.89	50	0.4
	442.2	22 610	0.45	60	0.3
6	(410.5)	24 360	0.13	—	0.1
	407.0	24 570	0.53	} 110	0.6
	404.9	24 700	0.66		0.6
7	378.4	26 420	5 25	(+)55, (−) 90	
	(377.6)	26 480	3.81	—	} 3.8
	(376.0)	26 600	1.58	—	
8	(366.8)	27 260	0.45	(+)65	
	364.4	27 440	2.09	(+)38	} 0.8
	363.7	27 490	1.68	(−)34	
9	359.3	27 830	0.28	—	0.1
	356.2	28 070	0.81	43	0.3
10	317.0	31 550	0.11	50	0.05
11	(295.9)	33 800	0.08	—	0.02
	(294.4)	33 970	0.13	—	0.02
	293.5	34 070	0.17	23	0.04
12	287.2	34 820	0.17	48	0.1
13	275.1	36 350	0.32	33	} 0.2
	274.0	36 500	0.30	34	
14	261.0	38 310	0.06	—	
	260.3	38 420	0.11	—	} 0.1
	259.1	38 600	0.23	—	
15	255.2	39 180	6.45	(+)130, (−)145	8.2
16	243.3	41 100	0.64	70	0.4
	240.1	41 650	0.19	170	0.3
	236.1	42 350	0.08	35	0.03
17	230.1	43 460	0.49	80	0.4

energy differences between the terms with maximum S are multipla of one linear combination, E^3, of these parameters, Bethe and Spedding [13] and Satten [14] succeeded in identifying the spin-allowed bands of Tm(III) and Nd(III), respectively, while the spinforbidden bands of Nd(III) agree better [9] with ratios $F^2 \simeq 1.5\ F^4 \simeq 2\ F^6$. Independently, Judd [15] applied similar ratios to Eu(III) and Gd(III). Hence, it would be a surprising irregularity, if the order of ^6F and ^6P was reversed in Dy(III), especially since the hole-equivalent systems Sm(III) and Pu(III) exhibit analogous behaviour [9].

The present author does not believe that this reversal is finally proven. Dieke and Singh [8] have not observed the levels with $J = 11/2$, $9/2$, and $1/2$ of ^6F and hence concluded that the remaining levels actually are ^6P. It would not be surprising if the observed and calculated levels in Table 7, Ref. [9], were shifted one unit in J, since the interest was concentrated more on the multiplets than on the individual levels. However, the behaviour reported by Dieke and Singh [8] is more remarkable: the level called $^6P_{5/2}$ has five sub-levels, two more than the highest possible number. The collision between ^6H and ^6F may produce rather strong overlapping between levels, even with identical J, since the non-diagonal elements in intermediate coupling are zero [10] between levels with the maximum value of S. If $^6F_{1/2}$ is not the excited level at 13 200 K, the transition may be too weak to be observed with the large decrease of J from $^6H_{15/2}$. The two levels $^6F_{11/2}$ and $^6F_{9/2}$ may be hidden by the other levels, or simply be too improbable as final states for the fluorescence (in absorption they should occur below 9 000 K).

The fluorescent level at 20 958.8 K has seven sub-levels [8]. Dieke and Singh do not assume $J = 13/2$, but identify the level * as $^6F_{11/2}$ with subsequent ^6F-levels in the blue. Dieke and Singh [8] maintain that the intensity is too high for spin-forbidden transitions to quartet levels. However, in Table 1 there are three bands at 325.5, 350.6, and 364.5 mμ, which are 20 times stronger than the bands in the blue (cf. Fig. 1). The sextet character is evidently concentrated in the former bands. If they are identified as transitions to ^6P (they do not necessarily all have different values of J, but may be intermixed), E^3 is slightly greater than assumed previously [9], since the bands below 360 mμ were not known [3]. The new value $E^3 = 575$ K is more likely, compared to 480 K in Sm (III) and 630 K in Tm(III), than the old value 520 K.

Since $\zeta_{4f} = 1\ 920$ K in Dy(III)[16], the quartet levels $\sim$21 000 K are expected to have $\sim$6 % sextet character, as actually observed.

FLUORESCENCE OF TRIVALENT LANTHANIDES AND ACTINIDES

Dieke and Singh [8] remark, "Moreover, the whole intensity of the fluorescence spectrum is due to the transitions from the resonance level to sextet levels. It would be hard to explain this as quartet-sextet transitions. This could only be so if there were no quartet levels below the resonance level." In the author's opinion, the latter hypothesis corresponds to a rather necessary condition for a f^n-level to decay with fluorescence: it shall be the lowest level with S one unit lower than the groundstate. This condition is satisfied by $^5D_0$ in Eu(III)[17] (however, $^5D_1$ can also be observed) and by $^5D_4$ in Tb(III)[18]. Butement [19] observed a fluorescent level at 14 514 K of Sm(II) in $BaCl_2$. This result implies [28] that the F_k-integrals in Sm(II) are $\sim$16 % smaller than in the iso-electronic Eu(III).

The fluorescent level of Sm(III) at 17 800 K agrees well with the spin-forbidden band of lowest wavenumber; there is a gap without absorption bands

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* It can hardly have one of the very high J-values of ^4M, but is rather $^4I_{15/2}$ or $^4I_{13/2}$.

10 500—17 800 K in Sm(III), as there is between [*] 13 200—20 900 K in Dy(III). In Pu(III), the analogous gap [9] between 17 900 and 19 800 K is much smaller. Actually, a fluorescent level has been observed [20] of Pu(III) in LaCl₃ at 19 200 K, while Am(III)[21] in LaCl₃ has a group of fluorescent levels in the blue. The fluorescent levels of actinides can be utilized to find the excited levels of the ground multiplet (as initiated by Gobrecht [22] in the case of lanthanides) and hence to determine the large values of ζ_{5f}. Thus, a level seems to occur at 3 100 K in Pu(III), implying $\zeta_{5f} = 4\ 400$ K, if the effects of intermediate coupling are neglected. (However, ζ_{5f} is probably 20 % smaller, since Judd [16] has proven that the distances between the lowest levels of a ground multiplet generally are increased, and the distances between the highest levels decreased, compared to the Landé interval rule). It is interesting to compare the ^7F levels of Sm(II)[19], Eu(III), and Am(III) implied by fluorescence (f) and absorption (a):

$J =$	0	1	2	3	4	5	6
Sm(II)	0	269f	834f	1 493f	2 296f	?	?
Eu(III)	0	370f	1 058f	1 906f	2 872f	3 936f	4 964f
Am(III)	0	~800f	2 600f	5 300f	?	9 500a	12 300a

The wavenumbers have roughly the ratios 0.8 : 1 : 2.5. Although the determinants of intermediate coupling are not known, $^7F_4$ seems to be somewhat decreased in all cases.

ENERGY LEVELS OF HOLMIUM(III) AND ERBIUM(III)

It is common to f²-, f⁵-, f⁹-, and f¹²-systems that the P-term with maximum spin is 42 E^3 above [**] the ground term H, and the F-term only 9 E^3 above H. Thus, Pr(III), Sm(III), Dy(III), and Tm(III) all have a P-term at a high wavenumber, preceded by a large gap with no bands towards the red and spin-forbidden bands towards the blue limit. f³-, f⁴-, f¹⁰-, and f¹¹-systems have another characteristic distribution of terms with the maximum value of S: I, F, S, G, and D at 0, 21, 21, 33, and 54 E^3, respectively. Hence, two gaps exist, one in the near infra-red between I and F, and one in the near ultra-violet between G and D. The behaviour of Nd(III) and Pm(III) has previously been discussed [9]. Tables 2 and 3 and Fig. 1 present similar evidence from Ho(III) and Er(III).

The lowest triplet level of Ho(III) appears to occur at 20 600 K, probably $^3K_8$. It has a small chance to be fluorescent. It would be interesting to know, whether the excited states (before the fluorescent level is reached) decay with internal conversion into vibrational energy, or infra-red light is irradiated by sharp transitions.

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[*] The extremely weak bands reported [8] of DyCl₃, 6H₂O at 17 151, 18 462, and 18 486 K may be caused by impurities of Nd(III), Ho(III), etc.

[**] These energies refer to the baricenters, *i.e.* the average of the energy levels, when weighted by their degeneracy numbers.
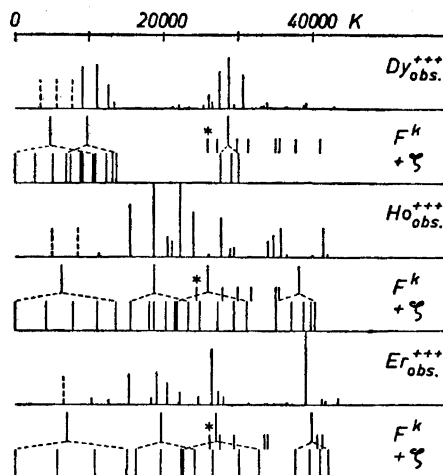
Fig. 1. The energy levels of dysprosium(III), holmium(III), and erbium(III). Three rows are given for each element: First, the wavenumbers of the observed band groups are indicated by lines, whose heights are proportional to the oscillator strength P (except the dotted lines in the infra-red, where P is not known). Second, the predicted baricenters of multiplets are given as high and low lines, representing terms with the maximum value of S and lower values, respectively. Third, the splitting of the terms with maximum value of S, assuming Russell-Saunders' coupling, is given. E^3, a linear combination of F_k-integrals [9], is estimated to 575 K, 590 K, and 610 K in the three ions (it is 460 K in Pr(III) and 630 K in Tm(III)) while the three values [16], [9] of ζ_{4f} are 1 920, 2 080, and 2 350 K (the values in Ce(III) is 644 K and in Yb(III) 2 950 K). The lowest multiplet with S one unit lower than of the groundstate is marked by an asterisk.

Especially in Fig. 1, a large gap is evident between the last level of Ho(III) with largely ^5G-character at 27 800 K and the likely ^5D-levels at 34 800—41 500 K. In the red, no bands are reported between the last ^5I-level * at 11 200 K and the first ^5F-level at 15 300 K.

The effects of intermediate coupling are very large in Er(III)[9], and the property "lowest spin-forbidden transition" to $^2H_{11/2}$ and to $^2H_{9/2}$ must be rather dispersed among the ^4I levels with the same J. The very high band at 39 200 K has probably some ^4D-character, but the exact nature is perhaps rather complicated. It has not been possible to observe an extremely narrow band of the type $^2P_{1/2}$ at 23 400 K of Nd(III). It may be connected with the low transition probablity of a transition in Er(III) from $^4I_{15/2}$ to a level with $J = 1/2$ (the $^2P_{1/2}$ of Nd(III) has $\sim$30 % quartet character, and nevertheless, the oscillator strength is only $\sim$2 % of ordinary $^4I_{9/2} \rightarrow$ quartet transitions in Nd(III)). Generally, transitions where J decreases strongly have rather low

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* The author has not been able to observe $^5I_4$ reported [22] at 13 300 K. This may be due either to vanishing intensity (the transition to $^5I_5$ is also very weak, *cf.* Fig. 1) or to a partial reversal of the upper-most levels of ^5I, as is perhaps the case in ^4I of Er(III) and certainly in ^3H of Tm(III). The latter effect corresponds to strong effects of 'averaged' intermediate coupling, as studied by Judd [16].

probabilities [9]. However, the absolute oscillator strengths, which probably are caused by forced electric dipole radiation induced by vibrations or ligand fields without a centre of inversion [23], are not easily calculated. Thus, some, but not all, bands of the acetylacetonates [24] are much higher than of the aquo ions. In particular, some bands of Ho aca$_3$ and Er aca$_3$ have ~50 times larger oscillator strengths than the corresponding bands of the aquo ions.

SUMMARIZING REMARKS

It is seen from Fig. 1 that the general distribution of spin-allowed and spin-forbidden transitions in Dy(III), Ho(III), and Er(III) agrees with the theory [9,10], as is also the case for the other trivalent lanthanides. This agreement is caused mainly by the fact that radial functions of highly different shape produce a smooth decrease of F_k with increasing k. Since interactions probably occur with other electron configurations (but not much more in the aquo ions than in the gaseous ions), the theory has always an uncertainty between 500 and 2 000 K of the baricenter of a given multiplet. On the other hand, it does not usually predict a multiplet 5 000 K in error.

It is hoped that this treatment may aid the future identification work, as J of a few levels of Ho(III) and Er(III) recently have been reported [25]. Especially the ultraviolet regions have been very little studied by more refined methods. It must be admitted that the determination of J of the individual levels is not yet completed, even in the much studied Nd(III) (the present author is inclined to believe that the groups at 680 and 630 mμ are caused by $^2H_{9/2}$ and $^2H_{11/2}$, respectively, and that the low J-values of ^4G must be dispersed in an irregular way between the stronger quartet bands of this ion). The intentions of ligand field studies of lanthanide salts at low temperature [26, 27] are very admirable, but they seem to be more fruitful when connected with the general theory of multiplet distribution in the f^n-systems.

EXPERIMENTAL

0.5 g Dy$_2$O$_3$ was dissolved by boiling with a slight excess of 2 M HClO$_4$ and measured in 2 cm silica cells. In the same way, 0.3 g Ho$_2$O$_3$ and 0.3 g Er$_2$O$_3$ were measured in 1 cm silica cells. The purity of the rare earths is better than 99.9 %. The spectra were measured twice (in opposite directions) at the lowest possible rate of dispersion change, viz. 1.25 mμ per division (0.83 cm of paper) in the visible and 0.5 mμ in the ultraviolet. No attempt was made to compare with HClO$_4$ in the double-beam Cary spectrophotometer 11 MS-50; rather, water was placed in the reference cell, and 2 M HClO$_4$ later measured against this water in order to evade spurious behaviour of the multipots.

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