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ABSORPTION SPECTRA OF LANTHANIDE AND ACTINIDE RARE EARTHS.
III. THE HEAVIER LANTHANIDE ELEMENTS IN
AQUEOUS PERCHLORIC ACID SOLUTION

by

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ABSORPTION SPECTRA OF LANTHANIDE AND ACTINIDE RARE EARTHS
III. THE HEAVIER LANTHANIDE ELEMENTS IN AQUEOUS PERCHLORIC ACID SOLUTION

D. C. Stewart

Introduction

Two earlier reports[1,2] presented the light absorption spectra of solutions of those rare earth elements which were then available as high-purity compounds (lanthanum through terbium, and including promethium). Since that time, stocks of the heavier lanthanides of excellent quality have also been procured, and their spectra in solution have been determined in order to complete the set of reference curves. This information (on the elements terbium through lutecium) is contained in the present report.

In presenting the data, comparisons have been made as before with the limited number of pertinent values which have appeared in the more recent literature. (Older studies were generally made with materials of very uncertain composition. References to some of these very early values can be found in the papers by Jones and Anderson[3] and Yntema.[4]) The most comprehensive of the newer studies are those of Prandtl and Scheiner,[5] Rodden,[6] Moeller and Brantley,[7] and of a Dutch group whose work has been summarized by Hoogschagen and Gorter.[8] In most cases, data on molar extinction coefficients were not stated directly in the papers cited, so, when these appear in the tables of this report, they have generally been calculated from readings made at the peaks of absorption curve graphs presented in the studies quoted.

The rare-earth materials used in the present study were all available as oxides. These were individually dried, weighed, dissolved in standardized perchloric acid, and the resulting solutions diluted to known volume. The absorption spectra were taken over the 220 to 1400-millimicron wavelength range, using either a Beckman DU quartz prism spectrophotometer or its automatically recording counterpart, the Beckman DK spectrophotometer. Silica cells of one-centimeter path length were used to contain both the test solutions and the $0.6\underline{M}$ $HClO_4$ used as a comparison standard. All data were taken at room temperature.

A number of authors have emphasized the fact that the effective band width (extent of monochromatization) of the light passed through the test solutions is of particular importance in working with the rare earths because of the extreme sharpness of most of the absorption peaks. At a given wavelength, with the type of instruments here used, the effective band width is a function not only of the dispersive ability of the optical system, but also of

the slit width used in selecting a portion of the emergent light. Figure 1 shows the typical change of this experimentally determined slit width with wavelength for the two spectrophotometers employed. (The DU was used with the sensitivity knob left fixed at one full turn back from the counter-clockwise position. The DK sensitivity dial setting was 1.6.)

CURVE 1a: DU SPECTROPHOTOMETER, H_2 LAMP, UV SENSITIVE PHOTOTUBE
1b: DU SPECTROPHOTOMETER, W LAMP, UV SENSITIVE PHOTOTUBE
1c: DU SPECTROPHOTOMETER, W LAMP, RED SENSITIVE PHOTOTUBE
CURVE 2a: DK SPECTROPHOTOMETER, H_2 LAMP, PHOTOMULTIPLIER
2b: DK SPECTROPHOTOMETER, W LAMP, PHOTOMULTIPLIER
2c: DK SPECTROPHOTOMETER, W LAMP, RED SENSITIVE PHOTOTUBE
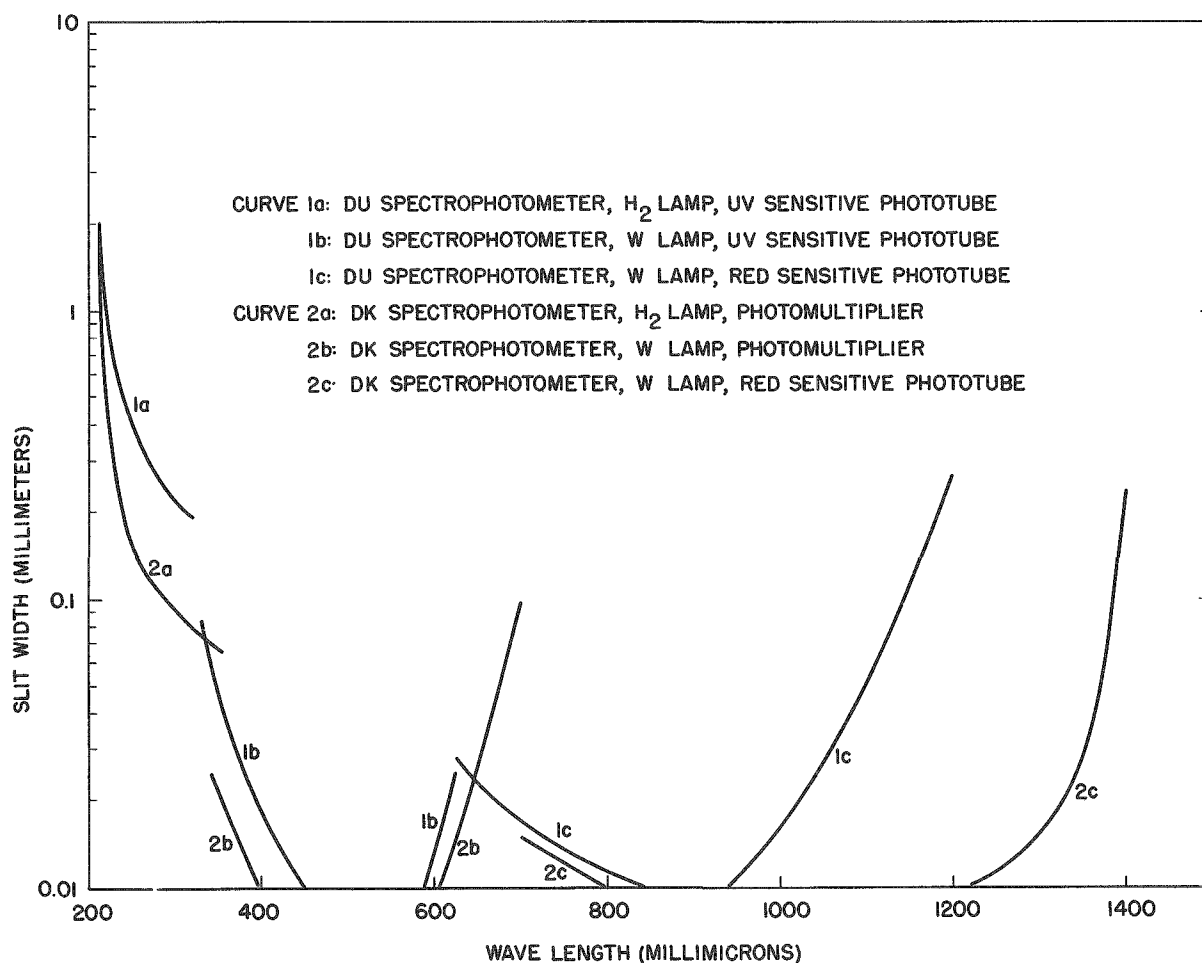
FIGURE 1
EXPERIMENTALLY DETERMINED SLIT WIDTHS

Table I lists the sources of the rare-earth materials used and presents data relative to their purity. The spectra of the individual elements in solution are discussed separately below.

Table 1

RARE-EARTH MATERIALS USED FOR SPECTRA DETERMINATIONS

Element	Compound*	Source	Purity**		
Terbium	(Tb_4O_7)	Natl. Bur. of Stands. "No. 50"	Dy-Up to 1% Gd-Up to 0.1% Y- Trace	Their Analysis	
	(Tb_4O_7)	Rare Earths, Inc. 99.9% terbium oxide	Y- 0.04%		
Dysprosium	Dy_2O_3	Ames, Iowa	Ho- 0.4% Y- 0.1%		
Holmium	(Ho_2O_3)	Rare Earths, Inc. 99.9% holmium oxide	No RF detected		
Erbium	Er_2O_3	Ames, Iowa	Yb- 0.1% Tm- 0.1% (?)		
Thulium	(Tm_2O_3)	Rare Earths, Inc. 99.9% thulium oxide	Yb- 0.1% Dy- 0.03% (?)		
Ytterbium	(Yb_2O_3)	Fairmount Chemical Co. 99.9% ytterbium oxide	Lu- 0.2% Tm- 0.3% Y- 0.2%		
Lutecium	(Lu_2O_3)	Rare Earths Inc. 99% Min. lutecium oxide	Tm- 0.4% Yb- 0.7% Y- 0.05% Non-RF cations- 0.25%		

* Parentheses indicate formulas assumed in weighing.

** Unless noted, purity values are on basis of spectrographic analyses
run by J. P. Faris, of the Argonne National Laboratory staff, using
the copper spark technique.

Terbium

  An absorption curve for this element was presented in the first of
the earlier reports,[1] and a portion of this (over the ultraviolet wavelength
range) is reproduced as part of Figure 2 of this paper. This earlier deter-
mination was made when only a very limited quantity of terbium oxide was
available, and this was known to contain some impurities, chiefly of dyspro-
sium. Therefore, when usable amounts of high purity oxide could be obtained,
the entire absorption spectrum was redetermined and is also shown in
Figure 2. The previously reported peaks at 255, 815-20 and 915 millimi-
crons can now be eliminated as having arisen from the dysprosium con-
tamination. In the earlier report, the small peaks at 351 and 358 mμ were
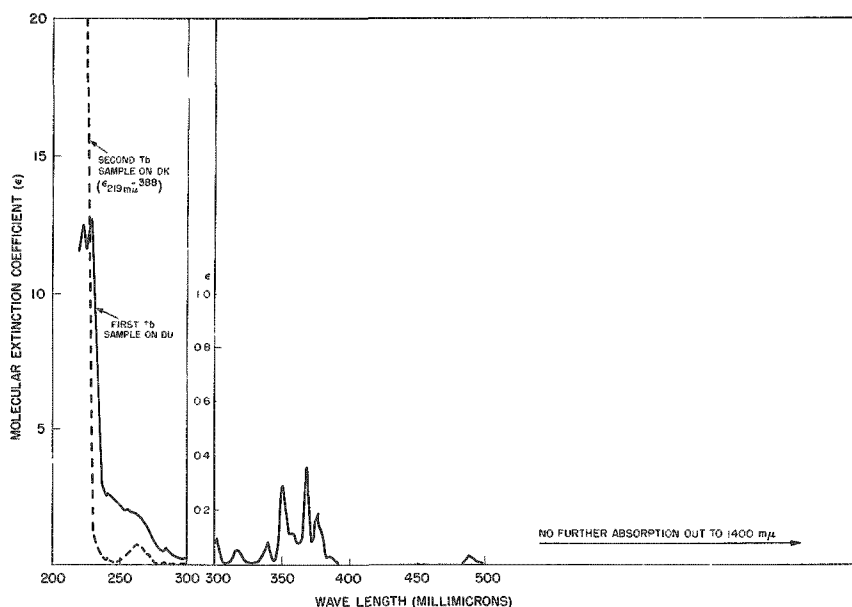
FIGURE 2

ABSORPTION SPECTRUM OF TERBIUM PERCHLORATE SOLUTION

also questioned, since they had not been reported in the exceptionally thorough summary of Prandtl and Scheiner.[5] However, they were again seen in the spectrum of the very pure oxide, and it is now believed that they are real and are attributable to terbium.

It will be seen that the absorption spectra in the ultraviolet are quite different for the two samples of oxide. In the earlier work, a double peak was seen at 224 and 230 $m\mu$ ($\epsilon \cong 12.6$). With the second sample a very intense absorption begins at about 230 $m\mu$, and examination of dilutions of both hydrochloric and perchloric acid solutions of the stock reveals a single peak at 219 $m\mu$ ($\epsilon \cong 388$). In order to try to resolve the contradiction between the two sets of data, the second terbium sample was put through a variety of chemical treatments to see if the large absorption peak could be made to disappear. It did not change appreciably, so it was concluded that the data presented earlier for the light absorption of terbium in the wavelength range below 300 $m\mu$ are probably incorrect. (The limited amount of material available at the time necessitated the use of microspectrophotometer cells, which in turn required special collimating slits. Light intensities were cut down and, as a result, the required slit widths were exceptionally large. This may have produced the error in the original curve.)

Table II summarizes the data relative to the two curves shown in Figure 2. (The earlier figures have been rounded off to make them more realistic in terms of significant numbers, and those peaks definitely attributable to Dy have been dropped.) The small peaks at 522.5 and 572.8 m were not seen at all in the second run.

Table II

LIGHT ABSORPTION OF TERBIUM IONS IN SOLUTION

Present Work (Figure 2), Perchlorate in Weak Acid		Ref. 1, Perchlorate in Weak Acid		Ref. 8, Chloride, 0.412$\underline{M}$		Ref. 5, Chloride in Weak Acid
λ_{max} (mμ)	ϵ	λ_{max} (mμ)	ϵ	λ_{max} (mμ)	ϵ	λ_{max} (mμ)
219	388					
		224	12.5			
		230	12.7			
242	0.23	242.0	2.4			241.8
258 (Sh.)	0.49					
264.0	0.74					
272 (Sh.)	0.38					
284.2	0.23					
303	0.09					305.2
						311.1
318	0.05	318	0.05			316 - 319.6
341.8	0.11	341.0	0.11			341.8
351	0.30	351.0	0.34			
358	0.14	358.0	0.14			
369	0.36	369.0	0.29	369.4*	0.25	369.4
378	0.19	378	0.18	377.3	0.14	375.2 - 379.7
487.5	0.03	487.5	0.03	487.0*	small	487.0
		522.5	0.02			522.5
		573	0.02			572.8

(Sh.) - Appears as a shoulder on a larger peak.
*Wavelength assignments from Prandtl and Scheiner.[5]

Dysprosium

The absorption curve of the plus-three dysprosium ion in weak perchloric acid solutions is shown in Figure 3 and the data pertinent to it are listed in Table III. It will be seen that much of the fine structure reported by Prandtl and Scheiner[5] is not seen in the absorption spectrum as taken with the Beckman instruments. The quoted ϵ (molar extinction coefficient) values for peaks below 320 millimicrons are somewhat uncertain, perhaps to a factor of two. With rare-earth solutions, a general absorption through this whole range often occurs, and it is difficult to apply any but arbitrary corrections to compensate for this. (This point will be discussed in more detail in the next report of this series.) In general, the ϵ values for peaks above 300 mμ have been found to be very reproducible.
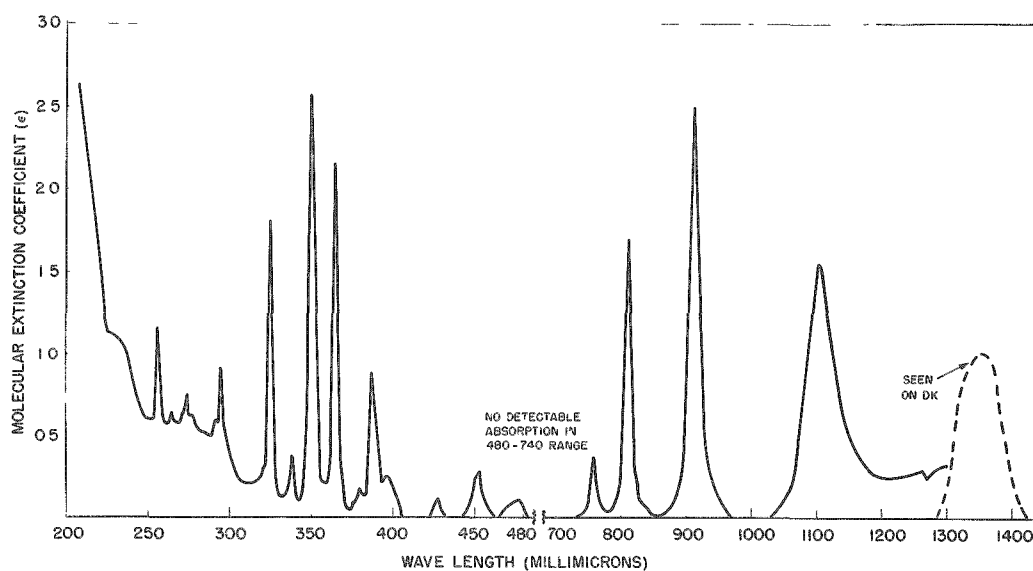
FIGURE 3

ABSORPTION SPECTRUM OF DYSPROSIUM PERCHLORATE SOLUTION

Table III

LIGHT ABSORPTION OF DYSPROSIUM IONS IN SOLUTION

Present Work (Figure 3), Perchlorate in Weak Acid		Ref. 9, Nitrate or Chloride		Ref. 10-11, Chemical Form not Specified		Ref. 6, Nitrate		Ref. 5, Chloride in Weak Acid	Ref. 4, Chloride in Weak Acid	Ref. 13, Neutral Chloride in H₂O	Ref. 14, Borax Beads (10-50% RE)
λ_{max} (mμ)	ε	λ_{max} (mμ)	ε	λ_{max} (mμ)	ε	λ_{max} (mμ)	ε	λ_{max} (mμ)	λ_{max} (mμ)	λ_{max}	λ_{max}
256.0	1.16							258.7			
264.7	0.64							262.8			
274.3	0.73							274.3			
								278.5			
294.8	0.92							291.2			
297	<0.1							296.0			
								298.7			
								299.4			
307	<0.1							302.2			
325.1	1.80							324.9			
338.3	0.38							338.2			
350.5	2.57							350.4			
								358.2			
364.7	2.16	364.9*	2.08			365	small	364.9			
379.5	0.27	380.3	0.26					379.6	380.0		
387.5	0.89	388.3*	0.98			390	small	387.9	387.3		
								388.3			
397	0.25	397.6*	0.26					397.5	399 0		
428	0.11	427.4*	0.12					427.4	427.5		
453	0.28	451.7	0.23					451.7	450.2		
								453.4	453.4		
477	0.11	474.0	0.10						475.4		
757.5	0.37	758.0	0.37						477.8		
809	1.87	805.5	1.87	810	1.80[10]	808	1.32				
911	2.51	909.0	2.56	908	2.33[11]	910	1.98			909	
1102	1.55	1103.5	1.61							1105	
1300**	1.0**										1250

*Wavelength assignments from Prandtl and Scheiner.[5]

**DK spectrophotometer data

The peak in the infrared at 1300 mμ has hitherto been unreported, although it is possibly the same as the one seen by Gobrecht[14] at 1250 mμ when he examined the infrared absorption spectra of rare-earth compounds fused in Borax beads.

Holmium

The holmium absorption spectrum in solution is shown in Figure 4 and the related data and literature comparisons are given in Table IV. Several hitherto unreported peaks were seen in the ultraviolet (219.5, 233.5, 260, 271.5, 274.5 mμ), but again there is some uncertainty as to the exact values of the "ϵ" figures quoted for that region. With the particular holmium oxide sample used, the ultraviolet background absorption was higher in hydrochloric acid solution as compared to the same material in perchloric acid solution.
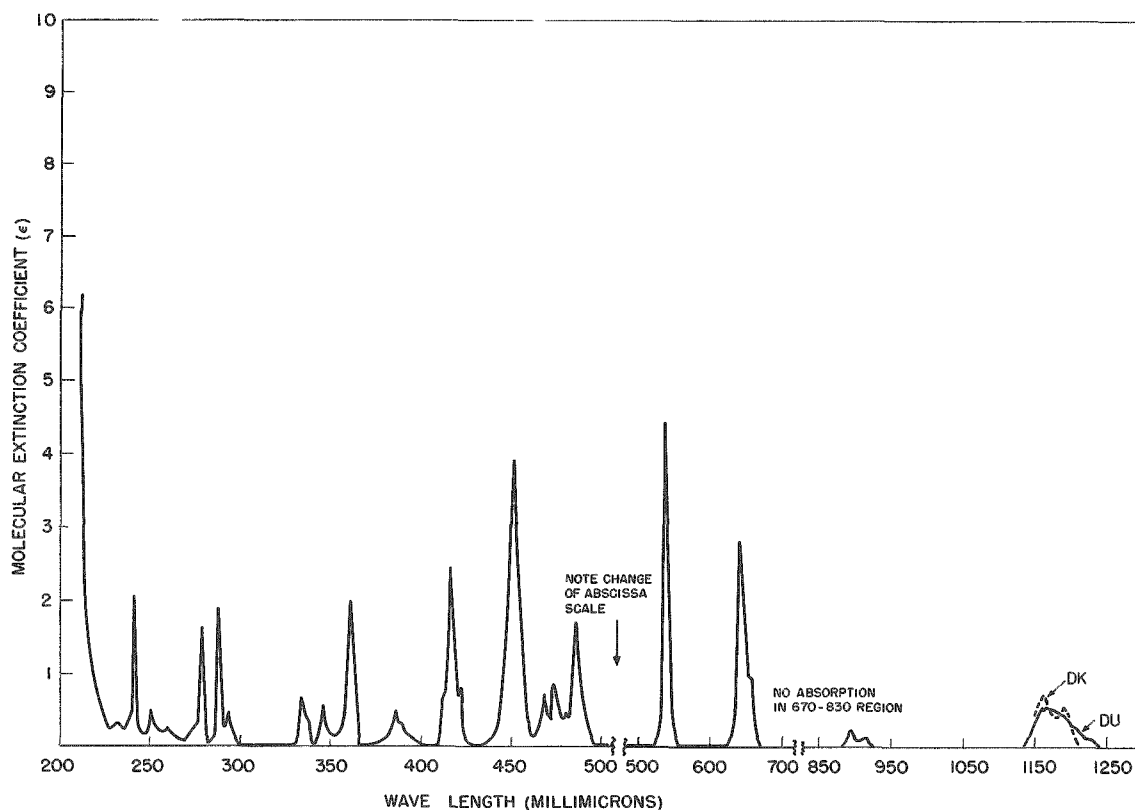

FIGURE 4

ABSORPTION SPECTRUM OF HOLMIUM PERCHLORATE SOLUTION

Table IV

LIGHT ABSORPTION OF HOLMIUM IONS IN SOLUTION

Present Work (Figure 4), Perchlorate in Weak Acid		Ref. 9, Chloride in H_2O		Ref. 10-11		Ref. 6, Nitrate		Ref. 5, Chloride in Weak Acid	Ref. 4, Chloride in Weak Acid	Ref. 13, Neutral Chloride in H_2O	Ref. 14, 10-50% RE in Borax Bead
λ_{max} (mμ)	ϵ	λ_{max} (mμ)	ϵ	max (mμ)	ϵ	max (mμ)	ϵ	max (mμ)	max (mμ)	λ_{max} (mμ)	λ_{max} (mμ)
219.5	0.55										
233.5	0.12										
238.7	0.28							238.0			
241.3	3.28							240.8			
250	0.45							249.8			
260	0.12										
271.5	0.13										
274.5	0.18										
278.3	1.98							277.8			
								278.3			
								284.7			
287.5	3.14							287.0			
289	1.20**										
293.5	0.45							292.0			
								295.6			
								326.6			
333.3	0.68							333.2			
345.5	0.55							345.2			
								347.2			
								350.0			
361.2	2.00	361.2*	1.73			360	small	361.2			
386	0.49	386.3*	0.48					386.3			
391	0.29**					390	small	389.6			
									415.9		
416.1	2.46	417.0*	3.16					417.0	417.4		
									419.2		
421.8	0.81	422.0*	0.87			420	small	422.0	422.0		
									427.3		
451	3.92	450.3*	5.10			452	1.94	450.3	450.5		
		450.9*	5.10					450.9	452.2		
									454.9		
468	0.73	467.7*	0.74					467.7	467.8		
473.5	0.82	473.4*	0.82					473.4	473.5		
480	0.47	479.9*	0.52			480	small	479.9	479.9		
									483.1		
485.5	1.71	485.2*	1.76					485.2	485.3		
		491.0*	0.35					491.0	491.0		
536.5	4.44	536.8*	5.25	536	2.11	539	2.11	536.8	536.5		
543	1.72**							543.4	543.5		
									549.3		
641	2.83	640.7*	3.34	643	1.89	643	1.89	640.7	640.5		
									643.3		
								652.5	653.0		
654	0.95**	656.7*	1.28					658.2	656.7		
893	0.21	891.0	0.13			900	small			893	
1160***	0.72										
1190***	0.55										1940

*Wavelength assignments from Prandtl and Scheiner.[5]

**Shoulder. Seen clearly only in more concentrated solutions.

***Observed on ГK spectrophotometer only. DU gives single peak at 1165. All UV data below 300 mμ based on DK curve.

The DU spectrophotometer has markedly less ability to resolve absorption peaks in the infrared than does the DK. With the former, a single new peak was seen in the holmium spectrum at 1165 $m\mu$, but with the latter instrument, this peak was shown to have two maxima at about 1160 and 1190 $m\mu$. (In general, infrared ϵ values taken with the DK will also be higher than those taken with the DU.)

In HCl solutions (and at slightly higher Ho concentrations) the recording instrument (DK) clearly showed the small peaks at 238.7, 271.5 and 274.5 $m\mu$, and the satellite peaks at 289 and 391 $m\mu$ were partially resolved, rather than appearing as shoulders. The large peak at 451 has two closely adjacent maxima, and the large peaks at 641, 536.5 and 416.1 $m\mu$ all have evidence of shoulders appearing on the redward side of the band. Some of this fine structure was missed when the perchlorate solution was checked with the DU.

Erbium

The light absorption curve of plus three erbium ions in weak perchloric acid solution is shown in Figure 5 and the data pertinent to it are given in Table V. No new, unreported peaks were seen.
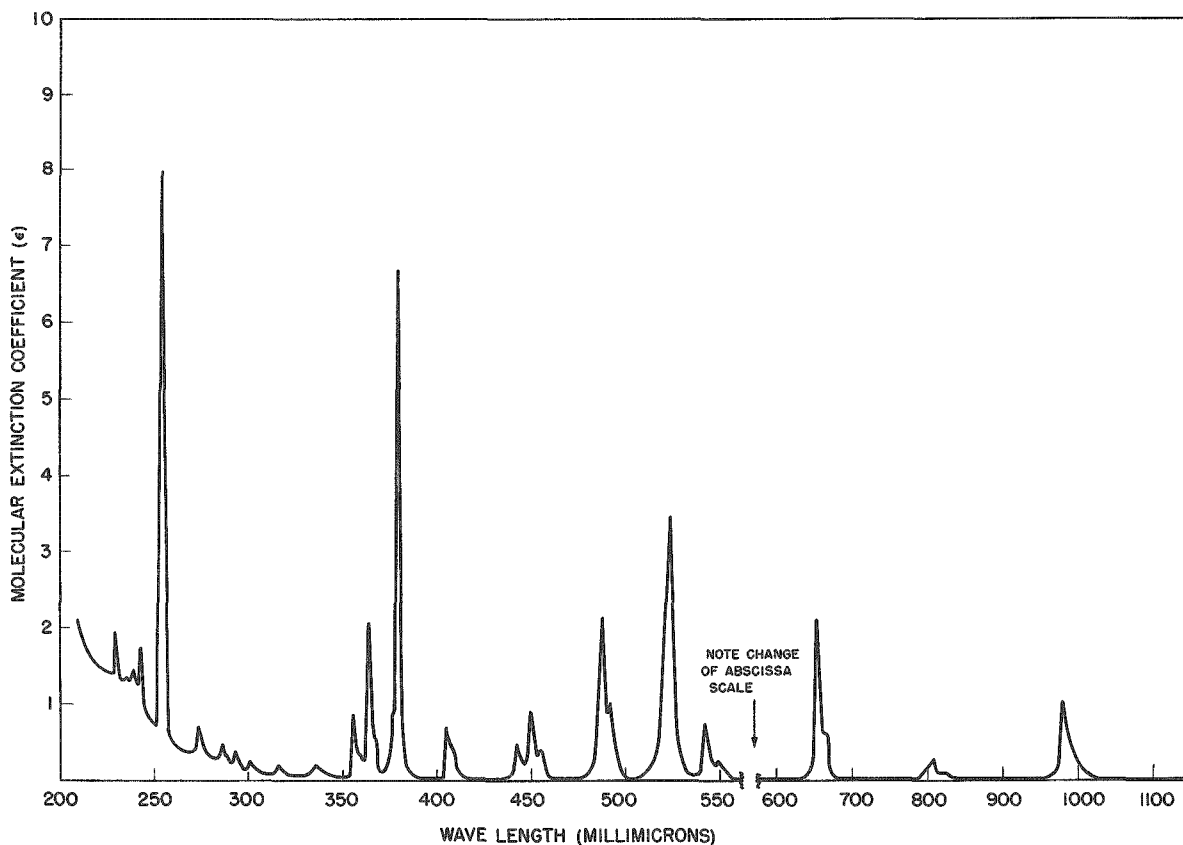

FIGURE 5

ABSORPTION SPECTRUM OF ERBIUM PERCHLORATE SOLUTION

Table V

LIGHT ABSORPTION OF ERBIUM IONS IN SOLUTION

Present Work (Figure 5), Perchlorate in Weak Acid		Ref. 8, Chloride		Ref. 7, Chloride		Ref. 6, Nitrate		Ref. 5, Chloride in Weak Acid	Ref. 4, Chloride in Weak Acid	Ref. 10-11		Ref. 13, Neutral Chloride in H_2O	Ref. 14, 10-50% RE in Borax Pearl	Ref. 15, Nitrate
λ_{max} (mμ)	ϵ	λ_{max} (mμ)	ϵ	λ_{max} (mμ)	ϵ	λ_{max} (mμ)	ϵ	λ_{max} (mμ)	λ_{max} (mμ)	λ_{max} (mμ)	ϵ	λ_{max} (mμ)	λ_{max} (mμ)	λ_{max} (mμ)
229.8	1.94							230.0						
236.1	1.42							235.9						
239.7	1.45													
243.1	1.73							243.7						
255.0	7.97			255.0*	5.7			255.0						
259	0.67							258.8						
273.5	0.68							273.3						
274.5	0.68							276.9						
286.3	0.44							285.8						
								289.4						
293	0.38							292.8						
								295.4						
301	0.25													
316	0.21							316.2						
336	0.19							335.5						
356.0	0.89			355.9*	0.75			355.9						
								359.0						
								364.0						
364.4	2.06			364.5*	1.31			364.5						
379.3	6.66			379.4	4.0**	381	1.16	379.4						
405	0.72	405.4*	0.61	405.4*	0.45	410	small	405.4	405.0					
									406.0					
		407.0*	0.48					407.0	407.2					
									410.4					
									412.3					
442.0	0.49	442.2*	0.39					442.2						
449.8	0.93	449.7	0.80			450	small	449.7	447.9					
453.5	0.43	453.4*	0.39	453.4*	0.50			453.4	453.7					
								455.3	455.5					
									484.9					482.1
487.5	2.15	487.1*	1.91	487.1*	1.26	489	0.81	487.1	487.1					484.5
														487.3
491.5	1.01	491.5*	0.81					491.5	491.3					492.5
														517.0
														519.3
								520.6	520.8					521.2
523.5	3.46	523.0*	2.90	523.0*	2.06	521	1.28	523.0	523.2	522***	3.13			522.8
														537
									539.6					539.5
542	0.76	541.3*	0.78	541.3*	0.5			541.3	541.6					541.4
549	0.24	548.8*	0.26					548.8	549.0					
									551.5					
								648.0	649.0					639.8
														648.5
654	2.12	652.5*	2.10	652.5*	1.21	653	1.28	652.5	652.6	653	4.0			652.5
		666.9	0.56					666.9	666.9					
807	0.29	801.5	0.33			800	small							
980	1.03	973.5	0.87	975	1.0	976	0.78			975	3.1	974.2		
													1260	

*Wavelength assignments from Prandtl and Scheiner.[5]

**Quoted value for perchloric acid solution. Other values calculated from their chloride curve.

***Ref. (11). Correction of value given earlier in Ref. (10).

Moeller and Brantley[7] pointed out that they had no independent means of checking their erbium salt for purity, which may account for the fact that their calculated ϵ values appear to run about a third lower than the values given in the present study. The figures calculated from the curves of Hoogschagen and Gorter[8] and the single value at 522 mμ recommended by Spedding and his associates[11] are also slightly lower, but in much better agreement with those of the present author.

With the DU spectrophotometer, the peak at 405 mμ seemed to have only one maxima. The DK tracing, however, showed this to be a double peak.

Thulium

The absorption curve of thulium perchlorate is given in Figure 6 and the related data and literature comparisons are shown in Table VI. The peaks in the ultraviolet (262.0, 273.5 and 284.3 mμ) have not been previously reported, nor has the one seen with the DU instrument at 1215 mμ. The DK spectrophotometer resolved this latter band into a double peak having maxima at 1185 and 1223 mμ.
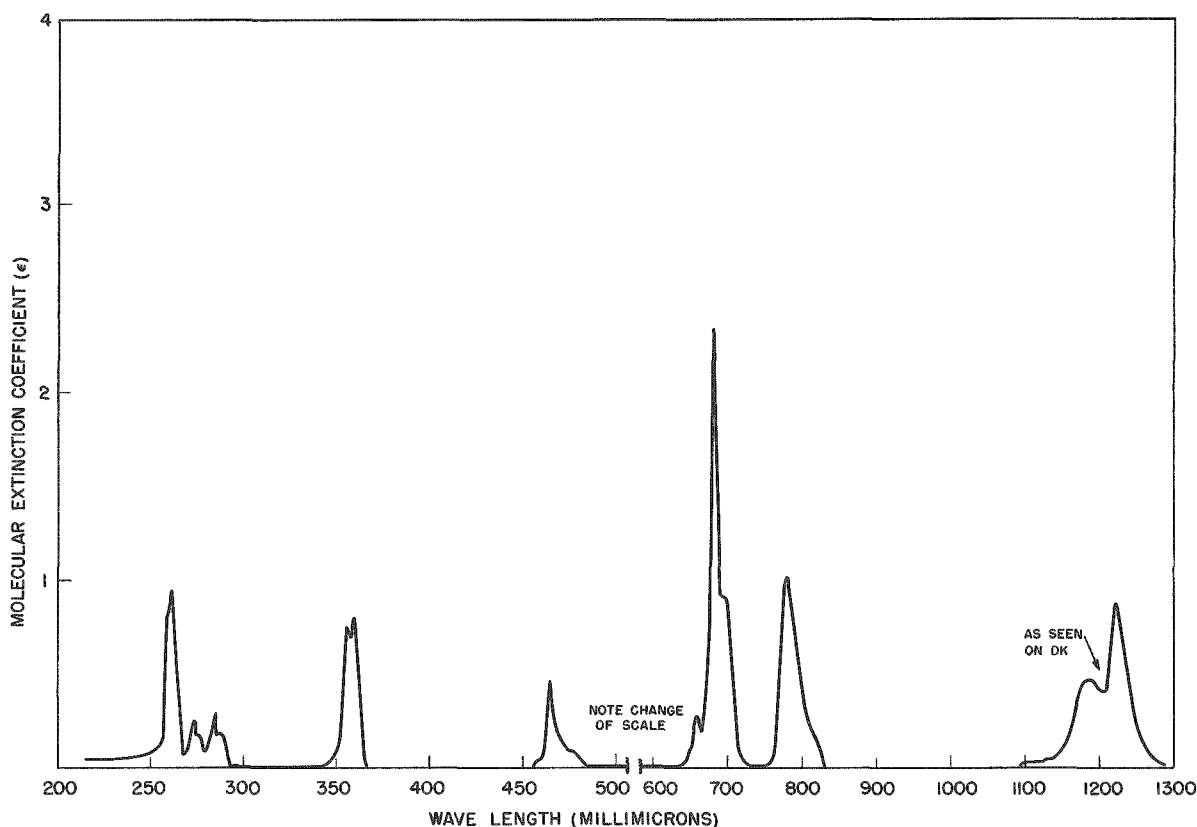

FIGURE 6

ABSORPTION SPECTRUM OF THULIUM PERCHLORATE SOLUTION

Table VI

LIGHT ABSORPTION OF THULIUM IONS IN SOLUTION

Present Work (Figure 6), Perchlorate in Weak Acid		Ref. 9, Chloride in H_2O		Ref. 7, Chloride		Ref. 6, Nitrate		Ref. 10, Form not Specified		Ref. 5, Chloride in Weak Acid	Ref. 4, Chloride in Weak Acid	Ref. 13, Neutral Chloride in H_2O
λ_{max} (mμ)	ε	λ_{max} (mμ)	ε	λ_{max} (mμ)	ε	λ_{max} (mμ)	ε	λ_{max} (mμ)	ε	λ_{max} (mμ)	λ_{max} (mμ)	λ_{max} (mμ)
262.0	0.95											
273.5	0.26											
284.3	0.29											
356.5	0.75	~357	1.84	~357	0.89							
360.0	0.79			~360	1.03	360	small					
464.2	0.46	464.2*	0.35	464.2*	0.56	470	small			464.2	464.3	
659	0.26	658.3*	0.17	658.3*	0.25	480	small			658.3	658.8	
682.5	2.34	682.5*	2.16	682.5	2.58	684	1.71	684	2.24	682.5	683.5	
		699.0*	0.70							699.0	699.9	
781	1.01	778.0	0.93	~781	1.10	780	0.96					No abs. in 820-1160 mμ range
1185**	0.46											
1223**	0.88											

*Wavelength assignments from Prandtl and Scheiner.[5]

**Seen as double peak with DK spectrophotometer. DU shows single peak at 1215 mμ. Peaks below 300 mμ taken from DK curve.

Ytterbium

As seen in Figure 7 and Table VII, the absorption spectrum of ytterbium in solution is a relatively simple one. Agreement with the published data of other authors using comparable instruments is quite good. The present work did not demonstrate a separate peak at 950 mμ, but the ε value at that shoulder is quoted because it may be of some value in analyzing for ytterbium in the presence of erbium, since an absorption peak of the latter directly interferes with the main Yb band at 978 mμ, but is only a minor interference at 950 mμ.

Lutecium

It would be predicted from theory that the lutecium spectrum would not exhibit the sharp light absorption peaks characteristic of most of the other rare earths in solution. These latter are believed to be due to electron
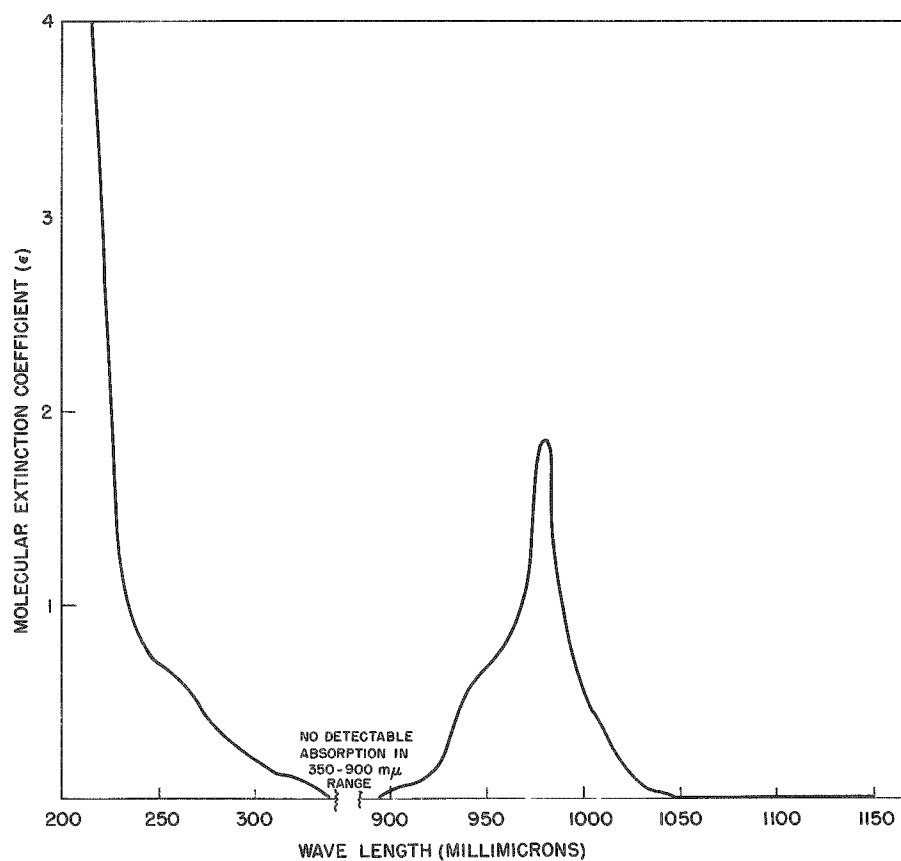
FIGURE 7

ABSORPTION SPECTRUM OF YTTERBIUM PERCHLORATE SOLUTION

Table VII

LIGHT ABSORPTION OF YTTERBIUM IONS IN SOLUTION

Present Work (Figure 7)		Ref. 12, Chloride or Nitrate		Ref. 7, Chloride		Ref. 6, Nitrate		Ref. 10, Nitrate	
λ_{max} (mμ)	ϵ	λ_{max} (mμ)	ϵ	λ_{max} (mμ)	ϵ	λ_{max} (mμ)	ϵ	λ_{max} (mμ)	ϵ
		937.0*	0.70						
950*	0.72	945.5	0.78	~950*	0.79				
978	2.00	973.5	2.10	975.0	1.96	973.0	2.34	973.0	1.80

*Appears as shoulder on larger peak.

transitions within the shielded 4f shell, and, in the case of lutecium, this should be completely filled, leaving no possibility for such intrashell changes. This was confirmed by the spectrum of the one lutecium sample examined, where only a generalized absorption was seen in the ultraviolet portion of the curve. Even this should not be taken very seriously, inasmuch as experience has amply demonstrated that such absorption is often not reproducible from one sample to another, and may depend primarily on the nature and level of trace impurities present.

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