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ABSORPTION SPECTRUM OF Pm⁺³ IN D₂0,DC1

John B. Gruber and John G. Conway

March 1960

ABSORPTION SPECIRUM OF Pm⁺³ IN D₂0,DC1

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March 1960

ABSTRACT

Under higher resolution than previously reported, the absorption spectrum of Pm^{+3} in D₂0,DCl was studied from 2700 to 19,000 A. Although additional structure is observed in the ultraviolet region, nothing is seen from 8233 to 19,000 A.

ABSORPTION SPECTRUM OF Pm⁺³ IN D₂0,DC1

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Three groups of investigators have already reported the general structure of the solution absorption spectrum in Pm^{+3} between 3000 and 10,000 A.^{1,2,3} In every case reported, the instrument employed was either a Model-LD or Model-DU Beckman spectrophotometer, and the largest amount of material handled was 5 mg.

We wish to report the absorption spectrum of Pm^{+3} in 0.023 M DCl (98% D_20) from 2600 A to 19,000 A under higher resolution than previously reported. Using a Cary Model-14 recording spectrophotometer, we have observed additional structure in the ultraviolet region. Molar extinction coefficients were calculated for all peaks from 2600 to 8233 A. No additional peaks were observed from 8233 to 19,000 A.

An emission-spectrum analysis of Pm^{+3} in 1 M HCl solution obtained from Oak Ridge National Laboratory indicated impurities of Nd, Sm, Al, Ca, and Am. Purification of 60 mg of Pm^{+3} was carried out by the use of a heated (87°C) Dowex-50 cation-exchange column with α -hydroxybutyric acid as eluting solution.⁴ After all other rare-earth impurities were separated from Pm^{+3} , the column was converted to a 12 N HCl column and Pm^{+3} was separated from actinide impurities.⁴

The PmCl₃ solution was then taken to complete dryness under a heat lamp, and 30 ml of DCl, D_2O solution added. The drying procedure was again repeated, and again new D_2O ,DCl solution added, giving a final solution of PmCl₃ in D_2O ,DCl.

The solution used in the absorption cells was analyzed before and after each run. The concentration of Pm^{+3} was determined by 4π beta counting, and the chloride concentration by the Volhard method. The amount of H_2O in the Pm^{+3} sample was obtained by comparison with known solutions of H_2O in the D_2O stock. One sample contained 30.0 mg Pm^{+3} per 5.23 ml 0.023 M DCl (98% D_2O).

The Cary 14 spectrophotometer was calibrated at the factory with an AH4 Hg arc. The Nd⁺³ and Am⁺³ standards were run in this laboratory in order to check the absolute values of peak wave lengths. The calibration results indicated the instrument to be correct to 1.5 A in the region from 2700 to 4900 A and 2 A from 4900 A to 2 μ . The resolving power of the monochromator is about 1.0 A in the ultraviolet and visible ranges and about 3.0 A in the near infrared. The wave length scale is reproducible to 0.5 A. Table 1 includes corrected wave length values. The uncertainty in peak locations is ≤ 2 A. Slit widths and molar excitation coefficients, ϵ , are also given.

The Pm^{+3} solution spectrum was compared with solution spectra of Eu^{+3} , Nd^{+3} , Sm^{+3} , and Am^{+3} . No trace of the rare-earth ions was observed. A trace of Am^{+3} was detected by α -assay (0.06 mg/ml). Consequently, the Am^{+3} peaks at 5033 and 8152 A were subtracted from the promethium spectrum and the remaining peaks taken as Pm^{+3} peaks. The solution absorption spectrum is shown in Fig. 1.

Since additional peaks are not observed from $0.8 \ \mu$ to $1.9 \ \mu$, the groundstate multiplets, ${}^{5}I_{\mu}$ to ${}^{5}I_{\beta}$, should be separated by less than 5400 cm⁻¹. The group of peaks around 8000 A are probably due to transitions from ${}^{5}I_{\mu}$ to the ${}^{5}F$ and ${}^{5}S$ multiplets. However, an analysis of the Pm⁺³ spectrum is best undertaken by studying the ion in a solid matrix. Such studies have already begun.

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Table I			
Absorption peaks of Pm ⁺³ in 0.023 M DC1 (98% D ₂ 0)			
λ, Wave of peak (A)	length Band width at half max. (A)	Slit width (mm)	<pre>€, molar excitation coefficient^a</pre>
2610	-2690	0.080	40 m 44 44
3074	3056-3081	0.075	0.32
3126'	3113-3139	0.061	0.77
3 153	3147-3160	0.061	0,31
3200	3187-3213	0.061	2.53
3281	3268-3294	0.061	4.96
3329	3316-3342	0.061	4.73
3440	3413-3460	0.061	0.39
3870	3845-3890	0.030	0.21
4015	4000-4057	0.021	0.51
4226	4200-4250	0.017	0,20
4496	4472-4520	0.016	0.41
4583	4566-4600	0.015	0.69
4933	4890-4986	0.013	1.41
5448	5431 -5 470	0.012	3.40
5476	5470-5502	0.012	3 .3 3
5679	5638-5700	0.013	3.77
5750	5726-5760	0.013	0.64
5905	5879-5929	0.013	0.23
6261	6226-6300	0.019	0.45
6838	6786-6886	0.048	2.13
69 80	6962-7000	0.069	2.14
7019	7000-7036	0.071	2.54
7152	7128-7176	0.075	0.36
7347	7872-7400	0.13	3.05
7824	7725-7872	0.40	1.54
8010	7974-8046	0.52	0.85
8057	8046-8080	0.52	0.74
8233	8200-8245	0.71	0.24
(No other absorption peaks were seen to 1.89μ)			
^a Log $\frac{I_0}{T} = A = \epsilon bc$, where A is the absorbance, ϵ is in liters x cm ⁻¹ x moles ⁻¹ ,			
b is the cell path length 2.001 cm, and c is in			
moles per liter.			

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FIGURE LEGEND

Figure 1. Solution absorption spectrum of 0.039 M Pm^{+3} in 0.023 M DCl (98% D_2^{0}).

(a) 6700 to 8300 A; (b) 6300 to 4700 A; and

(c) 4700 to 3000 A.

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