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We report here the first observations of the absorption spectrum of Es^{3+} in 3-6 M HCl in the wavelength region 3200-6500 Å.

Material

The einsteinium used for the first observations of the Es^{3+} spectrum on January 24, 1966, consisted of ~500 ng of Es^{253} , which had been purified on January 17-24, 1966, by a series of standard cation ion exchange separations: an α -hydroxyisobutyrate column, a 2 M HCl clean-up column, a saturated alcoholic HCl column, and a final 2 M HCl clean-up column.

Confirmatory experiments recently became possible, as a result of the availability of ~2.8 μg of Es, having the approximate isotopic composition: 97.5% Es^{253} and 2.5% Es^{254} .

This sample was isolated and chemically purified at Oak Ridge National Laboratory by a LiCl column, two high-pressure α -hydroxyisobutyrate columns, and three clean-up columns.

Spectra

All spectra reported here were run in 3-6 M HCl solution; solid material was present along with the einsteinium when the first spectra were taken, but was absent in the confirmatory runs. Spectra were taken at Es

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concentrations varying from about 0.03 M to about 2 M, and in solution volumes ranging from about 60 nanoliters down to about one nanoliter. In the recent confirmatory experiments, two sets of spectra were taken: a) using about one third of the material as prepared at Oak Ridge National Laboratory and b) using about half of the material within two hours of repurification by cation exchange with α -hydroxyisobutyric acid as eluting agent, followed by a 2 M HCl clean-up column.

In general, peak positions on the charts were marked and read independently by three different observers, and the results averaged.

Absorption Cell

The micro-absorption cell (1) employed in this work was developed especially for use with the Cary Model-14 Recording Spectrophotometer, on extremely limited quantities of the heavier actinide elements.

Its general construction is indicated in Fig. 1a-1b below:

XBL 677-3508

Fig. 1a-1b

Microabsorption Cell

In test runs prior to the einsteinium experiments, excellent spectra of Na^{3+} were obtained in the wavelength region from 2700-15,000 Å; peaks having molar absorptivities >0.1 were readily detected.

The microcell design used by us possesses important technical advantages over the capillary cells usually employed with limited amounts of material; the very high concentrations of the absorbing species of interest minimizes the importance of background absorption by other species added to maintain acidity, etc., while the large free surface-to-volume ratio of the small droplet of solution allows rapid diffusion of radiolytically-generated gases and prevents supersaturation and bubbling. Water loss by evaporation and radiolysis may be readily replenished by pumping.

The chief problem associated with the use of the cell is the necessity for precise optical alignment. This was solved by providing externally accessible screw controls for adjusting the cell carriage after insertion into the spectrophotometer cell compartment.

Procedure

Einsteinium in about 1 μl of 6 M HCl was drawn into a clean quartz capillary pipet (held in a micromanipulator), expelled to form a droplet on the outside of the pipet tip, allowed to evaporate to a volume of about 0.06 μl and transferred to the gap between the entrance light pipe and catcher pipe. The cell was then closed, sealed with "Apiezon Q" and the sealed cell attached to a holder which was inserted into the light-condensing and collecting system.

At the beginning and end of each spectral sweep the drop diameter was monitored with a microscope fitted with an ocular micrometer. Drop diameters were easily maintained in the UV and visible regions of the spectrum, but the heating associated with infra-red scanning caused rapid evaporation of the droplet.

In this preliminary paper we report only the most obvious features of the spectrum, seen in all three samples examined, and reproduced at least six times. These peaks are listed in Table 1.

TABLE 1
Absorption Peaks of Es^{3+} in 3-6 M HCl Solution

Peak Position (A)	Remarks
3625±25	
3760±30	prominent
4230±30	most prominent
4960±30	prominent
5296±20	
5625±30	
6050±50	very broad, weak

Molar absorptivities of these peaks are small, of the order of five or less. Peaks at wavelengths below about 4500 Å appeared as shoulders above a general absorption which increased strongly with decreasing wavelength. This background absorption may be due to such radiolytic decomposition products as Cl_2 , H_2O_2 , etc.

In Fig. 2 we present a comparison between the observed low-lying energy levels of the $5f^{10} (\text{Es}^{3+})$ configuration and those calculated (a) by Fields, Wybourne and Carnall (2), using hydrogenic wave functions and a value of the Slater radial integral F_2 and the spin-orbit coupling constant, ζ , extrapolated from data on the lighter actinides, and (b) by Conway (3), using somewhat different values for F_2 and ζ , and including the effect of configuration interaction. The root mean squares of the deviations between the observed and the nearest calculated levels are 880 cm^{-1} and 416 cm^{-1} for the results by Fields et al. and Conway, respectively. Clearly the calculations by Conway are in better agreement with the experimental data presented here.

XBL677-3629

Fig. 2

Observed and Calculated Levels of Es^{3+} Acknowledgments

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References

- (1) B. B. CUNNINGHAM and T. C. PARSONS, unpublished.
- (2) P. R. FIELDS, B. G. WYBOURNE, and W. T. CARNALL, Argonne National Laboratory Report, ANL-6911, July 1964.
- (3) J. G. CONWAY, private communication, Lawrence Radiation Laboratory, 1967.

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