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THE SOLUTION ABSORPTION SPECTRUM OF Es<sup>3+</sup>

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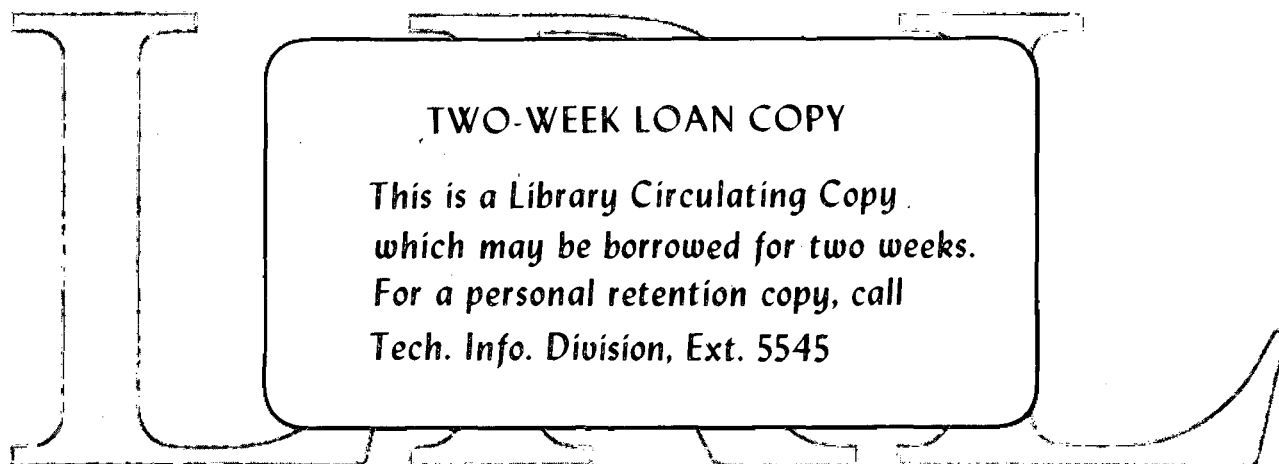
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## THE SOLUTION ABSORPTION SPECTRUM OF $\text{Es}^{3+}$

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### Introduction

Our first observations of the absorption spectrum of approximately 1  $\mu\text{g}$  of  $^{253}\text{Es}$  in hydrochloric acid solutions have been reported previously (1). The availability of a larger quantity of einsteinium made confirmatory experiments possible. Presented here are the results of recent experiments which produced much improved spectra in the wavelength region from 3,700 A to 10,600 A.

### Material

Approximately 7.5  $\mu\text{g}$  of einsteinium produced in the HFIR at Oak Ridge National Laboratory were used in the work reported here. Analysis of this material showed the following isotopic composition at the time of its use: 99.47%  $^{253}\text{Es}$ , 0.49%  $^{254}\text{Es}$ , and 0.04%  $^{255}\text{Es}$ . This einsteinium was carefully purified by a series of cation exchange columns as described in our previous report.

### Spectra

All spectra were obtained in 3-6 M HCl solutions with  $\text{Es}^{3+}$  concentrations of  $\sim 0.1$  M to  $\sim 5$  M; solution volumes ranged from  $\sim 100$  nanoliters

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down to ~3 nanoliters.

Two sets of spectra were obtained: (a) in the wavelength region from 3,400 A to 7,500 A using ~3.5  $\mu\text{g}$   $^{253}\text{Es}$  within 33 hr of the separation from its decay product  $^{249}\text{Bk}$  by cation exchange; (b) in the wavelength region from 3,300 A to 10,600 A using ~3  $\mu\text{g}$   $^{253}\text{Es}$  within 56 hr following the separation from berkelium.

Absorption peak positions were measured independently by two observers and the results averaged.

#### Absorption Cell

The general construction details and techniques of operation of the micro-absorption light-pipe cell, adapted for use with the Cary Model-14 Recording Spectrophotometer, have already been described (1,2). In the present instance, light transmission through the micro-absorption cell was improved further by coating the entrance light pipe with chromium overlayers with silicon monoxide up to the light exit face.

Preliminary test scans with ~3  $\text{M}$   $\text{Nd}^{3+}$  solutions yielded excellent spectra in the wavelength region from 2,500 A to 10,000 A. Peaks having molar absorptivities  $> 0.1$  in the ultraviolet and visible light region (2,500 A to 7,500 A) and  $> 0.2$  in the infrared region (7,500 A to 10,600 A) were readily detected. Baseline deviations due to instrumental effects were investigated by scanning the wavelength region of interest with air or a water droplet between the light pipes. These cell blank scans indicated the presence of minor absorption "peaks" at ~7,650 A and ~9,650 A. The  $\text{Nd}^{3+}$  and  $\text{Es}^{3+}$  spectra were corrected for these spurious effects.

### Results and Discussion

The best  $\text{Es}^{3+}$  solution absorption spectrum in the wavelength region from 3,500 A to 7,200 A observed on the Cary spectrophotometer traces is shown in Fig. 1. At the shorter wavelengths the high background absorbance is believed to be caused by the presence of such radiolytic decomposition products as  $\text{Cl}_2$ ,  $\text{H}_2\text{O}_2$ , etc. produced by  $^{253}\text{Es}$  (a 20.47 day alpha emitter) in the hydrochloric acid solutions. No peaks in the region from 7,000 A to 10,600 A having molar absorptivities  $> 0.2$  were observed.

A total of 18 absorption bands were observed in the wavelength region from 3,700 to 10,600 A. These observed  $\text{Es}^{3+}$  peaks are listed in Table 1. The tabulated peak positions are the statistical averages of measurements by two observers on many wavelength scans.

The peak positions reported earlier were confirmed to within the experimental error limits of the measurements (average difference = 16 A) except for that at 3,625 A which was not clearly evident in the present experiments due to the high background absorption in the ultraviolet region.

The molar absorptivities of the observed peaks were found to be small. Although accurate calculations could not be performed due to the variation of  $\text{Es}^{3+}$  concentrations during wavelength scans, the molar absorptivity of the most prominent peak at 4,950 A was estimated to be  $\sim 5$ .

The observed  $\text{Es}^{3+}$  solution spectrum was compared with the two theoretically-derived spectra for the  $5f^{10}$  ( $\text{Es}^{3+}$ ) configuration calculated by Fields, Wybourne, and Carnall (3) and by Conway (4). The agreement between calculated and experimental levels is considered unsatisfactory in each case. The detection of absorption bands in the infrared region (perhaps masked in

the present experiments by the instrument-caused absorptions mentioned previously) hopefully would allow assignments of J values to the low-lying energy levels; the resulting calculated energy levels would then possibly show an improved "fit" with the observed levels. Significant chloride ion complexing could have occurred at the maximum HCl concentration with consequent influence on the spectrum.

It is of current interest to determine the energy of the first excited electronic state of  $\text{Es}^{3+}$  in the  $5f^{10}$  configuration. The theoretical calculations referred to above locate this level at approximately  $10,400 \text{ cm}^{-1}$  (9,600 Å). Recent luminescence measurements on an einsteinium beta-diketone by Nugent, et al. (5) suggest that the first excited electronic state of  $\text{Es}^{3+}$  lies at an energy lower than  $9,800 \text{ cm}^{-1}$  (10,200 Å). In the present experiments, we extended the measurements to  $9,450 \text{ cm}^{-1}$  (10,600 Å) and demonstrated the absence of  $\text{Es}^{3+}$  peaks having molar absorptivities  $> 0.2$  in this portion of the infrared region. In future investigations, we shall carefully re-examine this wavelength region and attempt to extend our measurements farther into the infrared.

#### Acknowledgements

We wish to express our appreciation to Dr. Albert Ghiorso who made available to us the einsteinium remaining after the preparation of a nuclear reaction target. We are also grateful to Dr. John Conway, who furnished a revised set of calculated energy levels for  $\text{Es}^{3+}$ . One of the co-authors, Dr. J. R. Peterson, wishes to acknowledge the financial support of The University of Tennessee which made his stay at the Lawrence Radiation Laboratory possible. This work was done under the auspices of the U. S. Atomic Energy Commission.



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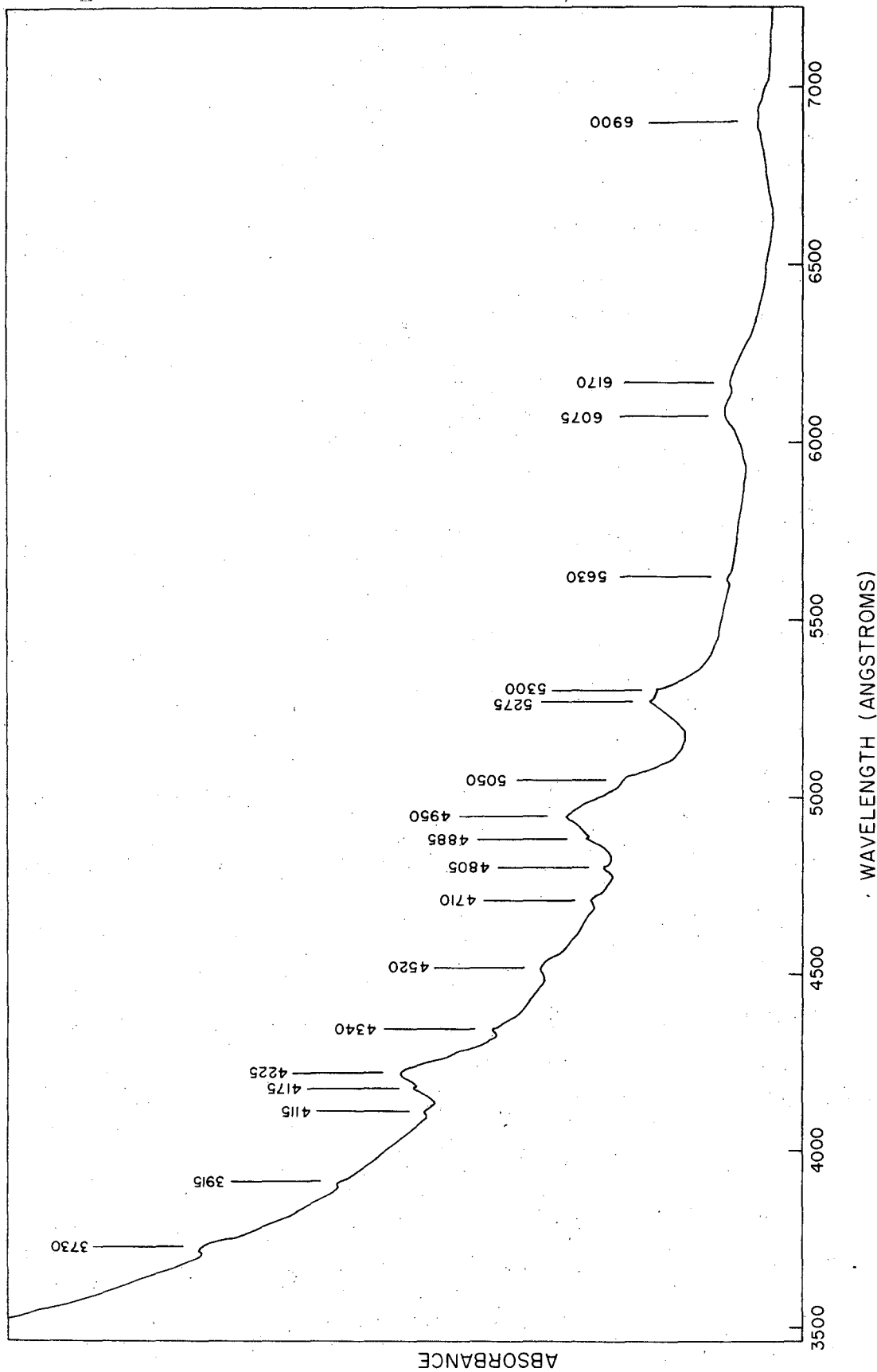


FIG. 1  
THE ABSORPTION SPECTRUM OF  $Es^{3+}$

Table 1Absorption Spectrum of  $\text{Es}^{3+}$  in 3-6 M HCl Solution

| Observed peak position (Å)<br>(This work) | Observed peak positions (Å)<br>(Reference 1) | Peak Description                          |
|---|--|---|
| 6900 ± 100                                | -----  | moderate intensity; very broad            |
| 6170 ± 15                                 | -----  | moderate-strong; broad                    |
| 6075 ± 15                                 | 6050 ± 50                                    | moderate-strong; broad                    |
| 5630 ± 15                                 | 5625 ± 30                                    | very weak                                 |
| 5300 ± 15                                 |  | moderate; sharp                           |
| 5275 ± 15                                 | 5296 ± 20                                    | moderate; sharp                           |
| 5050 ± 20                                 | -----  | very weak; broad; shoulder on strong peak |
| 4950 ± 20                                 | 4960 ± 30                                    | strongest; sharp                          |
| 4885 ± 10                                 | -----  | weak shoulder on strong peak              |
| 4805 ± 10                                 | -----  | moderate; sharp                           |
| 4710 ± 15                                 | -----  | moderate                                  |
| 4520 ± 20                                 | -----  | moderate; broad; on bkgd absorption       |
| 4340 ± 15                                 | -----  | weak; on bkgd absorption                  |
| 4225 ± 15                                 | 4230 ± 30                                    | strong; sharp; on bkgd absorption         |
| 4175 ± 15                                 | -----  | weak shoulder on strong peak              |
| 4115 ± 10                                 | -----  | weak; on bkgd absorption                  |
| 3915 ± 15                                 | -----  | weak; high bkgd absorption                |
| 3730 ± 20                                 | -----  | moderate; high bkgd absorption            |
| -----                                     | 3625 ± 25                                    | high bkgd absorption                      |

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