UCRL-17692
c.2

University of California

Ernest O. Lawrence Radiation Laboratory

THE ABSORPTION SPECTRUM OF Es^{3+}
IN HYDROCHLORIC ACID SOLUTIONS

B. B. Cunningham, J. R. Peterson,
R. D. Baybarz, and T. C. Parsons

August 14, 1967

RECEIVED
LAWRENCE
RADIATION LABORATORY
NOV 6 1967
LIBRARY AND
DOCUMENTS SECTION

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

UCRL-17692
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Submitted to Inorganic and
Nuclear Chemistry Letters

UCRL-17692
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

THE ABSORPTION SPECTRUM OF Es^{3+} IN HYDROCHLORIC ACID SOLUTIONS

B. B. Cunningham, J. R. Peterson, R. D. Baybarz, and T. C. Parsons

August 14, 1967

THE ABSORPTION SPECTRUM OF Es^{3+} IN HYDROCHLORIC ACID SOLUTIONS

B. B. Cunningham, J. R. Peterson, R. D. Baybarz*, and T. C. Parsons

Department of Chemistry and Lawrence Radiation Laboratory
University of California, Berkeley, California

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

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

*Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

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:

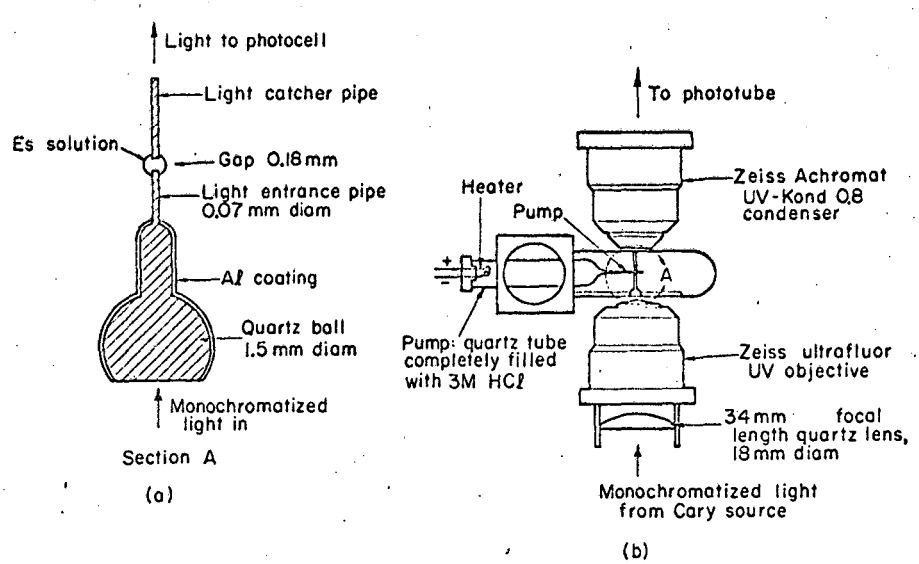

Fig. 1a-1b

Microabsorption Cell

In test runs prior to the einsteinium experiments, excellent spectra of Nd^{3+} were obtained in the wavelength region from 2700-15,000 A; 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.

Results and Discussion

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 A 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 $5f^{10}$ (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.

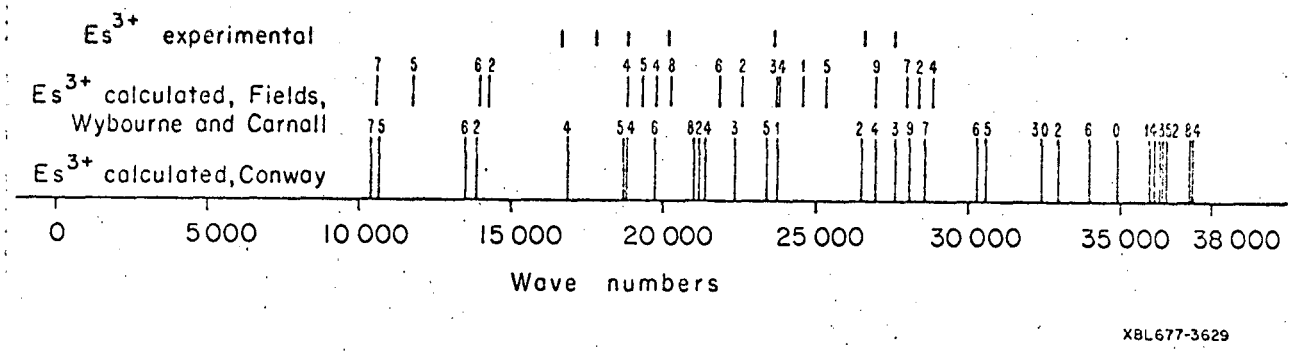

Fig. 2

Observed and Calculated Levels of Es^{3+}

Acknowledgments

We wish to express our appreciation to Dr. N. Edelstein, who carried out one of the sets of spectral readings, to John Conway, who supplied one of the sets of calculated levels, to Dennis Fujita, Lester Morss, and Ray Dod, who assisted in column operation and radiometric assays, and to the Health Chemistry Group for monitoring assistance.

This work was done under the auspices of the U. S. Atomic Energy Commission.

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.

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.