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INTRODUCTION

In recent years there has been considerable success in interpreting the spectra of 3+ actinides in solids[1] and solutions[2] and relating these results to the free-ion calculations. The U^{4+} ion has also been treated in the same way,[3] and Axe has reported on Pa^{4+}.[4]

It seems worthwhile now to investigate to see if a similar interpretation may be applied to the other 4+ ions of the actinide series.

Calculations

The complete f^n matrices were made available by Koster and Nielsen.[5] The configurations f^3, f^4, f^5, and f^6 were diagonalized for various values of χ and E/F_2; χ ($= \zeta/F_2$) was used instead of ζ, and energy was used in units of F_2 (E/F_2) because in this form the results may be compared with those for other atoms. In all cases the 5f hydrogenic wave function was used. This is the same assumption as was made in the interpretation of the 3+ ions.

Data

The only available data are for solutions or powdered solids, and all the data are at low resolution and room temperature; hence the energy is of low accuracy, and all the Stark components are not resolved. Intensity is on quite a relative basis. The Np^{4+} data are from a paper by Waggener on

the solution spectra of Np ions.[6] Waggener has kindly supplied me with a greatly enlarged copy of his Fig. 1, which was very convenient for obtaining the wavelength of the peaks.

The data on Pu^{4+} are from an unpublished collection of spectra of actinide elements that dates back to the late 1940's. The original experimenters are not known. The curve that showed the best resolution of peaks was a solution of Pu^{4+} in 16 M H_2SO_4. Curves in HCl and $HClO_4$ were not as distinctive as those in this very high concentration of H_2SO_4. Cohen has reported the Pu^{4+} spectrum over a more extensive wavelength region.[7] The main addition is his peak in the near infrared. The peak is quite asymetric and can be resolved into two peaks at 1.07 and 1.13 μ. The data for Am^{4+} and Cm^{4+} are from a paper by Asprey and Keenan and are for the solid fluorides suspended in fluorocarbon grease.[8]

Results

Figure 1 is a plot of the calculated and the experimental levels. The parameters used are listed in Table I.

It can be seen that even with the crude data it is possible to derive a set of parameters that can give a satisfactory explanation of the data. There are several conclusions that can be drawn from such a set of calculations. First, the magnitude of the crystal-field splitting is not so great as to overlap the level positions of the various free ions. This indicates that there is every reason to expect experiments on these ions to yield information about crystal-field parameters, as do experiments on the 3+ ions. Second, one gets a feeling for the magnitude of the Slater parameters and spin-orbit constants. The values of the parameters derived here are probably within 5% of the final values.

FOOTNOTE AND REFERENCES

*Work done under the auspices of the U. S. Atomic Energy Commission.

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Table I. Slater parameters and spin-orbit constants for Np^{4+}, Pu^{4+}, Am^{4+}, and Cm^{4+}

Ion	Pa^{4+}	U^{4+}	Np^{4+}	Pu^{4+}	Am^{4+}	Cm^{4+}
f^n	$5f^1$	$5f^2$	$5f^3$	$5f^4$	$5f^5$	$5f^6$
F_2	--	206	223.8	242.9	282.1	307.0
ζ	1490	1870	2193.	2429.	2821.	3042.

FIGURE CAPTION

Fig. 1. Experimental and calculated levels for Np^{4+}, Pu^{4+}, Am^{4+}, and Cm^{4+}. For Np^{4+} and Am^{4+}, the numbers associated with the calculation are equal to 2J. For Pu^{4+} and Cm^{4+}, the numbers are the J values.

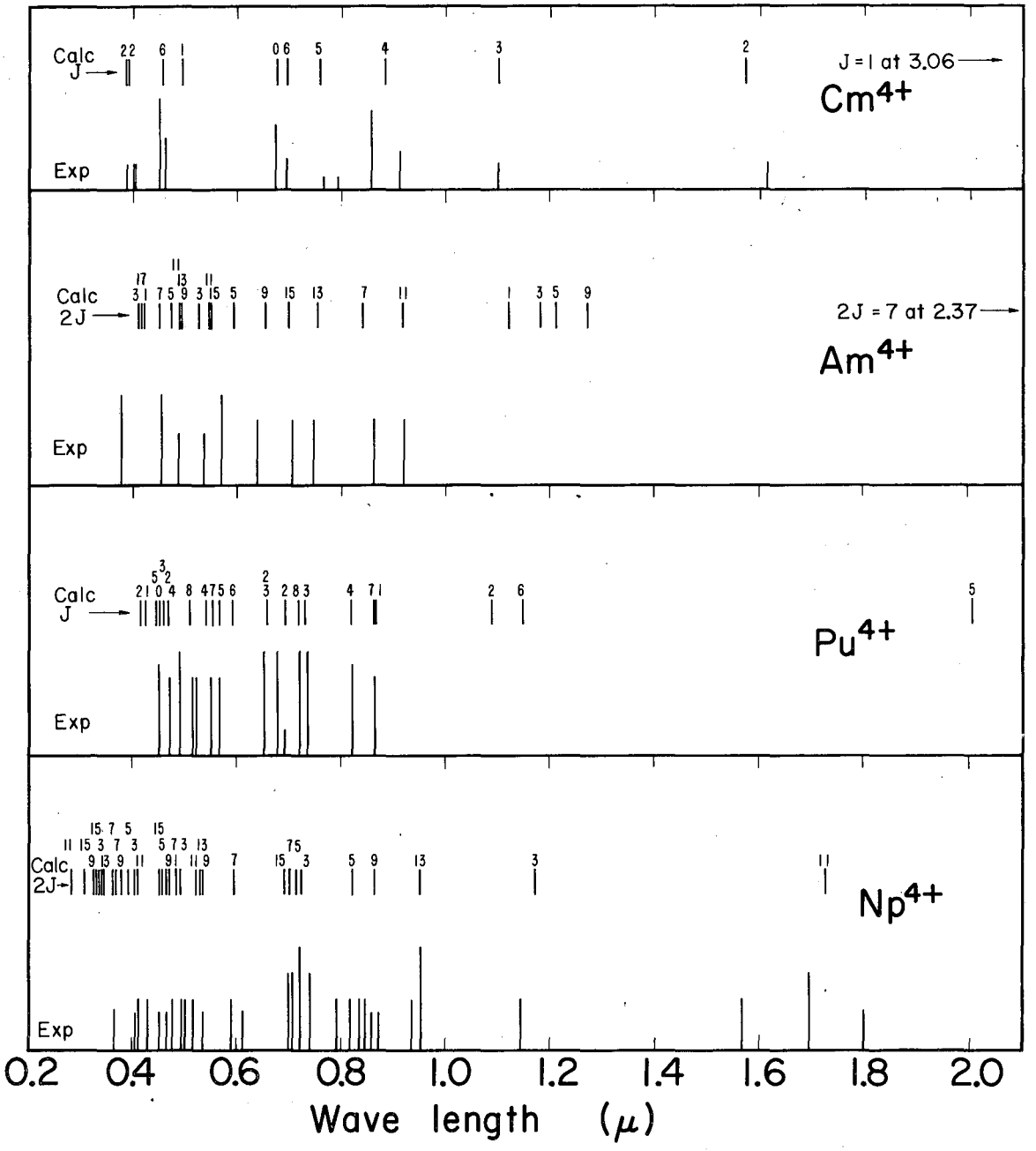

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Fig. 1