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THE SOLUTION ABSORPTION SPECTRUM OF Cf³⁺*

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Recently, several hundred micrograms of californium were isolated from highly neutron irradiated curium targets. This represents the largest amount of the element ever processed and made available at one time. We have used this material to conduct the first investigation on a macro scale of the solution absorption spectrum of californium in the trivalent state. Earlier attempts to observe the absorption spectrum in aqueous solution and in a LaCl₃ matrix⁽¹⁾ were limited by the small amount of material available, and were confined to the visible region of the spectrum. We have been able to demonstrate the existence of approximately 21 absorption bands in a spectral range extending from 5,500 to 36,000 cm⁻¹.

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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EXPERIMENTAL

The chemical procedures employed were similar to those used in previous work.⁽¹⁾ Two entirely separate experiments were performed. Initially, only 167 $\mu\text{gm.}$ of californium was available, and it was examined in several different concentrations both as CfCl_3 in 0.5M DCl and as $\text{Cf}(\text{ClO}_4)_3$ in $\sim 1\text{M}$ DClO_4 . The highest concentration observed at this time was 0.0063M Cf^{3+} in $\sim 1\text{M}$ DClO_4 . Deuterated solvents were employed to increase the range over which the near infrared spectral region could be investigated.

Several months later, after more californium had been processed, the measurements were repeated. At this time 592 $\mu\text{gm.}$ of californium was used, and the highest concentration studied was 0.016M Cf^{3+} in $\sim 1\text{M}$ DClO_4 .

The spectrophotometer cells were specially designed and were fabricated from silica capillary tubing with high purity silica windows. Two different cell sizes were used; 5 cm. path length with a 1 mm. i.d. and 2 cm. path length with a 2 mm i.d.

Isotopically the californium was $\sim 80\%$ Cf^{252} [$t_{1/2}(\alpha) = 2.73\text{y}$; $t_{1/2}(\text{S.F.}) = 85.5\text{y}$]⁽²⁾ and $\sim 20\%$ Cf^{254} [$t_{1/2}(\alpha) = 61.9\text{d}$]⁽²⁾. The release of the corresponding large amounts of energy in the small volumes employed produced samples which had bubbling characteristics of fine California champagne. The cells had to be emptied and refilled frequently as the light path became blocked with gas bubbles. Fully deuterated methanol was added to the solutions in

some of the experiments to help reduce the bubbling. However, individual runs never exceeded two minutes.

The spectrophotometer used was a high resolution prism-grating instrument equipped with special cell compartments and cell holders suitable for remote handling of samples. The entire instrument was placed inside a cave area with 4-foot thick walls⁽³⁾ to prevent exposure of personnel to the intense neutron emission due to the spontaneous fission of the Cr^{252} .

RESULTS AND DISCUSSION

The experimental problems associated with the present investigation were manifold, but in particular the conditions encountered made it necessary to present a composite of the spectra measured. As a result of the intense bubbling, it was never possible to obtain spectra over more than a few thousand Angstrom units before the light path was blocked. Thus repeated runs, all of which were superimposed on a constantly increasing absorption background, were required. An intercomparison of the spectra in these runs showed that smooth hand drawn curves could be subtracted from the sets of experimental data to give a consistent set of molar absorptivities. Thus the results presented in Figure 1 and Table 1 represent an average of a number of runs in which the apparent background was subtracted. Of course, such an operation introduces an artificiality and some degree of error. However, this error could be shown to be very small except possibly in the near infrared region where the

bands were superimposed on D_2O stretching frequency overtones and in the ultraviolet where strong absorption, probably due in part to H_2O_2 , was encountered. Three energy levels were predicted for the near infrared region⁽⁴⁾ where we obtained experimental evidence for two absorption bands. Attempts are now underway to theoretically interpret the spectrum and derive the applicable spectroscopic parameters. Theoretical intensity calculations will then be possible.

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TABLE 1.--Molar Absorptivity Values (ϵ)
for Cf^{3+} in 1 M DClO_4

cm^{-1}	$\text{m}\mu$	ϵ	cm^{-1}	$\text{m}\mu$	ϵ
6410.	1.560	5.3	21280.	.4699	8.9
8260.	1.211	1.6	22620.	.4421	10.3
11900.	.8403	2.5	23000.	.4348	9.8
12990.	.7698	6.3	24880.	.4019	0.9
13420.	.7452	6.4	28300.	.3534	1.0
14840.	.6738	2.5	29940.	.3340	1.5
15620.	.6402	1.7	30770.	.3250	3.8
16610.	.6020	4.9	32800.	.3049	1.1
20410.	.4900	1.9	33900.	.2950	2.4
			35210.	.2840	1.9

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FIGURE CAPTION

Figure 1. The Absorption Spectrum of Cf^{3+} in 1 M DClO_4 .

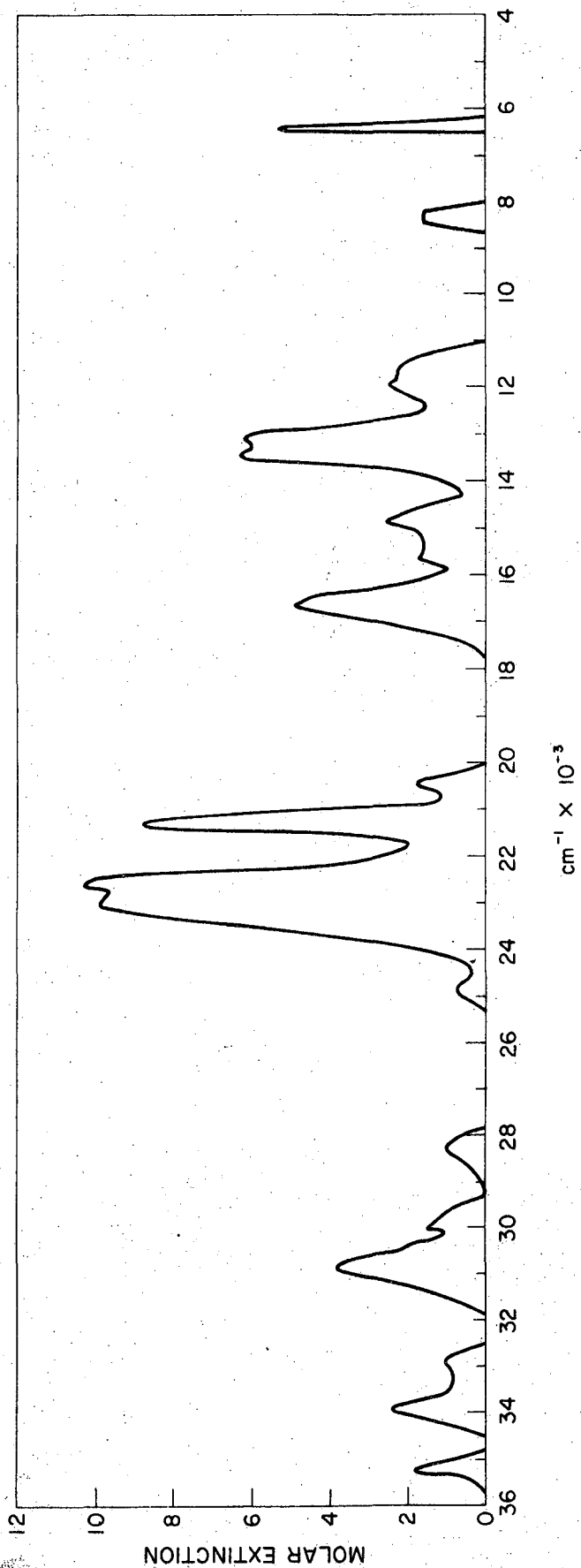


Fig. 1

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