

Energy Levels of Am IV in LaCl₃

John G. Conway

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tion band. With respect to the intensity of the second σ -polarized I -type transition we note that theory predicts a dipole strength which should hardly be observable spectroscopically. It can be shown, however, that this transition may steal some intensity by means of configuration interactions from the other transitions of the same direction of polarization.

The optical spectra in Figs. 3 and 5 further show that the location of the first strong absorption band in the spectra of the free ions goes through a maximum on passing from neptunium to pentacene whereas Fig. 3 suggests a continuous decrease in frequency in the same direction. A possible explanation for this change is that in a more extended approach the configurations I_1 and II will mix under the action of the electron correlation operator. Since this mixing will be stronger according to the same electronic theory is distributed over a smaller molecular system, the final answer will be the result of a competition between the negative trend of the one-electron excitation energy and the positive trend of the configuration mixing. This competition may lead to a maximum.

As for the γ -polarized transitions we could not obtain any evidence for the weak transitions I_2 of the dispersive band. Obviously this transition is too weak to be observed. For the mononegative ions we have in addition to I_2 the transition A which occurs also in the molecule itself. For the pentacene and neptunium mononegative ions we find this transition superimposed on the σ -polarized transition I_1 . In the spectrum of the neptunium mononegative ion we find two γ -polarized bands. Looking at Fig. 2 we see that the excitations A and I_2 are here fairly close together so that configuration interactions may give rise to a mixing between the two configurations and consequently I_2 may steal intensity from A . The spectrum of the neptunium mononegative ion again exhibits one γ -polarized band,⁹ which according to Fig. 2 can be here ascribed to the transition A . Here the transition I_2 will very likely be located near to the red tail hidden under the strong absorption I_1 .

In a subsequent paper we will study the influence of ion-pair formation on the spectra of these polyanions.

Energy Levels of Am IV in LaCl_3

JOHN G. CONWAY

Lawrence Radiation Laboratory, University of California, Berkeley, California

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It has been possible to split the II lowest energy level of Am IV by using Stark splittings and the complex spin-orbit structure, a II was obtained with 2^2 isotropic wavefunctions. This fit was then improved by using a fitting program and varying all free parameters. Comparison calculations using isotropic wavefunctions are made for Pu I . For Am IV the isotropic values are $F_2=3315 \text{ cm}^{-2}$ and $F_4=2015 \text{ cm}^{-2}$, the corresponding values for Pu I are $F_2=338.6 \text{ cm}^{-2}$ and $F_4=217.6 \text{ cm}^{-2}$.

INTRODUCTION

THE detailed analysis of the solid-state spectrum of Am IV ($5f^4$ ion) has not been possible with the available absorption and fluorescence data. This is due to several reasons; one is that with a ground state of $J=0$ and crystal symmetry of C_{2v} it is difficult to determine the J values.¹ A second difficulty is that in the actinide elements the LS coupling scheme is not followed and therefore one must perform rather detailed calculations in the intermediate coupling scheme before much of a gain in the spectrum can be obtained.²

The complete spin-orbit matrices have not been

calculated by Koster and Sklarov;³ earlier intermediate matrices of OsIII were used.⁴ The electrostatic interactions were originally calculated by Wybourne⁵ and Grotrian.⁶

There is some question as to the assignment made by Grotrian⁶ to the weak infrared-absorption peaks. A comparison between Pu I and Am IV (with $5f^6$) did not give us then an agreement as might be expected.⁷

¹ C. W. Sklarov has kindly sent us a type containing these matrices, entitled, "Energy Matrices for All Configurations of Equivalent f Electrons" by G. F. Koster and O. W. Sklarov, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts.

² G. S. Galt, Ph.D. thesis, The Johns Hopkins University, 1949.

³ H. G. Wybourne, *J. Chem. Phys.* **20**, 304 (1952).

⁴ J. S. Grotrian, *ZUR-6289* (1941).

⁵ J. S. Grotrian, *J. Chem. Phys.* **20**, 1015 (1952).

⁶ J. Sklarov, M. Fried, A. Grotrian, and H. E. Judd, *Comp. Rend.* **233**, 1011 (1952).

⁷ Work done under the auspices of the U. S. Atomic Energy Commission.

¹ K. T. Gaylor and A. Fried, *J. Chem. Phys.* **24**, 1211 (1956).

² J. H. Conner and J. G. Conway, *J. Chem. Phys.* **24**, 522 (1956).

TABLE I. Wavelengths of fluorescence lines excited by different energies.

Wavenumber (cm^{-1})	Wavelength (\AA)	Notes	Wavelength of exciting light ($\text{m}\mu$) ^a			Assignment
			510	462 ^b	368 ^b	
11 842	8441		7687	{ Same as 510 }	${}^6L_6-{}^7F_3$	
11 921	8385		7608			
11 975	8348		7554			
12 013	8321		7516			
12 027	8311		7502			
12 726	7855			{ 368 only }		
12 735	7849					
12 778	7823					
12 813	7802					
12 821	7797					
12 859	7774					
13 916	7183		7708	{ Same as 462 }	${}^6D_2-{}^7F_3$	
13 997	7142		7627			
14 050	7115		7573			
14 087	7096		7537			
14 125	7077		5404	{ Same as 510 }	${}^6L_6-{}^7F_2$	
14 154	7062		5375			
14 208	7035		5321			
14 248	7016		5281			
14 418	6933		5111			
14 450	6918		5079			
14 628	6834					
14 715	6793			{ 368 only }		
14 758	6773					
14 781	6763					
14 848	6732					
14 884	6716					
14 902	6708					
14 956	6684					
14 973	6676					
14 987	6670					
15 723	6358					
15 787	6332					
15 978	6256					
16 010	6244					
16 037	6233					
16 071	6220					
16 101	6208					
16 235	6157		5389	{ Same as 462 }	${}^6D_2-{}^7F_2$	
16 301	6132		5323			
16 334	6120		5294			
16 744	5970		2783	{ Same as 510 }	${}^6L_6-{}^7F_1$	
16 792	5953		2736			
17 406	5743			{ 368 only }		
18 840	5306		2783	{ Same as 462 }	${}^6D_2-{}^7F_1$	
18 924	5282		2700			
19 529	5119	Absorption line			${}^6L_6-{}^7F_0$	
19 822	5043			{ 368 only }		
19 879	5028					
20 008	4996					
20 961	4769					
21 041	4751					
21 624	4623	Absorption line			${}^6D_2-{}^7F_0$	
23 605	4235	uv-excited				
25 097	3982	uv-excited				

^a The numbers indicate the difference in reciprocal centimeters between the resonance level and the respective line.

^b All the lines that appeared in 510 also are in 462, and all those that appeared in 510 and 462 appear in 368.

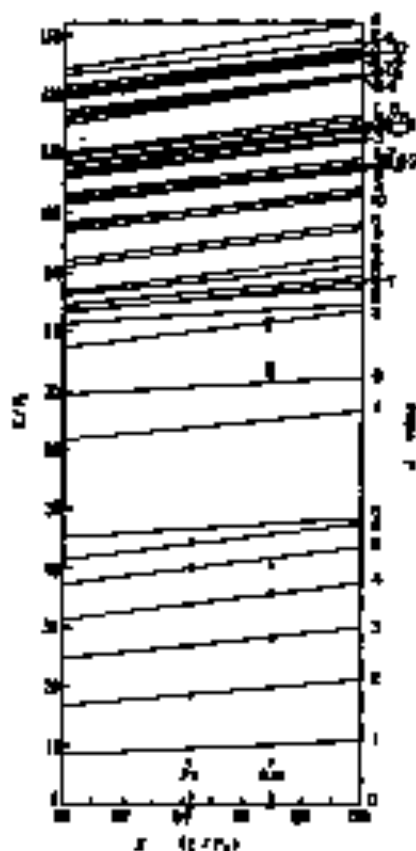


FIG. 1. Plot of E/F_2 vs x between $x=0$ and 10, 20 cm being used for F_2 and the square-root rectangle one for F_1 .

Furthermore, the selection rules of Oshits indicate that Graber should not have seen transitions between $J=0$ and $J=5$ or 4.¹¹ The $J=0$ to $J=1$ is a magnetic dipole transition and is expected to be weak.

This work was undertaken in an attempt to understand better some of these discrepancies and if possible, to assign some of the upper levels of Am IV.

The method chosen to study the low levels of Am IV was that of "selective excitation," where narrow bandwidths of light are used to excite fluorescence to low levels.¹² Near-infrared absorption experiments are used to obtain the higher levels of the ground multiplet.

EXPERIMENTAL

For the selective-excitation experiments a 1000-W Hg arc (AH6) was mounted in the source compartment of a Beckman DU monochromator with the output incident on the americium crystal mounted in a quartz Dewar filled with liquid nitrogen. The crystal was imaged on the slit of an $f/6.3$ spectrograph. Exposures from $\frac{1}{2}$ h to several days were taken throughout the

photographic range. The crystal is the same one used by Graber and Conway.¹¹

The fluorescence emitted by the crystal brightens as the wavelength of the exciting light coincides with the absorption peaks of the americium ion. There is a self-luminescence to the crystal which is excited by the energy of the radioactive decay. Any spectrum is, therefore, a mixture of both the selectively excited and self-luminescence emissions.

Wavelengths of 510, 410, and 366 m μ produced the brightest emissions and were therefore investigated first. The spectrum obtained upon irradiating with 510-m μ light is relatively simple, showing only three groups of lines. There are no absorption peaks in the region 5100 to 8000 \AA .

When 410-m μ light is used, many new emissions appear in addition to the groups excited by the 510-m μ light. The 510 groups are now weaker. A strong line appears at 8623 \AA where there is also a narrow absorption peak of the americium ion. Later experiments using 502-m μ light revealed that the lines assigned as inferred to 410 actually come from the 4623- \AA level. When 366-m μ light is used many new emissions appear but the previously observed groups also appear.

It appears that at the lowest energy all that happens is that transitions to the levels of the ground multiplet take place. But as the incident energy is increased it is possible to get emission to ground from this particular level and also a transfer of energy to the lower levels with emission to ground. This transfer of energy between upper levels and the accompanying emission greatly complicates the problem. The nature of the transfer between upper levels is not known. If the transfer is by collision, the lines would appear in the infrared beyond the region studied.

TABLE II. Wavelengths of the near-infrared lines from absorption data.

Wave number (cm ⁻¹)	Wavelength ^a (\AA)	Assignment
9 833	10 700	$F_2 - F_1$
9 533	10 480	
9 365	10 460	
9 267	10 132	
80 795	9 130	$G_1 - G_2$
80 943	9 133	
12 333	8 145	$F_1 - F_2$
12 253	8 139	
12 279	8 145	
12 217	8 123	
12 205	8 090	
12 413	8 088	
12 295	7 150	
12 274	7 150	

^a Data for the double and 4 025- \AA groups are from Graber.¹¹

¹¹J. B. Graber and J. G. Conway, *J. Chem. Phys.* **34**, 151 (1961).

¹G. S. Oshits, *J. Chem. Phys.* **17**, 311 (1949); *ibid.*, **18**, 1044, *Phys. Rev.* **129**, 239 (1948).

²Y. Yonemoto and G. G. Dicks, *J. Chem. Phys.* **21**, 1045 (1953).

TABLE III. Energy levels of Am³⁺ and Pu³⁺.

Term	Am ³⁺			Pu ³⁺			
	Expt. obsd. (cm ⁻¹)	Calculated by hyd. (cm ⁻¹)	Calculation obsd. (cm ⁻¹)	Expt. (cm ⁻¹)	Calc. (cm ⁻¹)	ξ obsd.	ξ calc.
⁷ F ₀	0	47	40	0.00	0	0	0
⁷ F ₁	2 720	2 667	2 744	2 763.85	2 175	1.425	1.4674
⁷ F ₂	5 329	5 268	5 368	4 329.57	4 210	1.258	1.2654
⁷ F ₃	7 269	7 267	7 051	6 144.35	6 195	1.478	1.4764
⁷ F ₄	9 589	9 523	9 568	7 774.85	7 438	1.467	1.4557
⁷ F ₅	10 820	11 143	11 229	9 139.05	9 273	1.436	1.4336
⁷ F ₆	12 280	12 280	12 280	10 231.95	10 131	1.434	1.4336
⁷ F ₇	19 426	19 038	19 126				
⁷ F ₈	21 055	21 261	21 351				
⁷ G ₄	21 210	21 268	21 210				

^a Expt. obs. or the spectroscopic values are $F_2=9723$, $F_3=10218$, $F_4=10614$, $F_5=11014$, $F_6=11413$. Obs. values are $F_2=10218$, $F_3=10718$, $F_4=11218$, $F_5=11718$, $F_6=12218$.

^b Obs. value of ξ in cm^{-1} .

^c The ξ calculations were for f wavefunctions and $F_2=232.6 \text{ cm}^{-1}$ and $F_3=267.8 \text{ cm}^{-1}$, or $\xi=17.65$ of cm^{-1} . The g values given by F_2 and F_3 had the same error.

This exchange of energy also indicates that there would be little hope of analyzing the usual fluorescence data which is obtained by irradiation with wide wavelength regions of ultraviolet light.

Table I presents the results of the selective-absorption experiments. The only new absorption data is for $J=5$. Two very weak lines are observed at 9236 and 9135 Å. This agrees with the very weak peaks seen by Caswell and Fields in the molten-salt solution of $\text{Am}(\text{NO}_3)_3$ in Li-K nitrate mixture.¹³ The position of these lines does not permit an accurate location of the $J=5$ level since they are only two of four possible lines and there are a total of seven possible levels. Table II has the data above 8000 Å that were used. Except for $J=5$, the data are due to Garber.⁷

RESULTS

An analysis of the data in Tables I and II makes possible the assignments for the 7F multiplet listed in Table III. The calculations were made by using the spin-orbit matrices of Koster and Nilsson.⁸ The calculations were made with $5f$ hydrogenic wavefunctions and were carried out using the term E/P_2 instead of energy, and $\chi(-7/P_2)$ instead of ξ . In this form the results are more easily applied to other $5f^2$ cases. Figure 1 is a plot of these results between χ of 9 and 10. It is possible on a plot of this nature to incorporate the data for Pu³⁺ and Am³⁺. These calculations for Pu³⁺ are an improvement over the previously published values since the matrices were included explicitly. Table III included the calculations for energy and g values for Pu³⁺. The calculations for Am³⁺ are for values $F_2=232.6 \text{ cm}^{-1}$ and $F_3=267.8 \text{ cm}^{-1}$; the Pu³⁺ values are $F_2=230.6 \text{ cm}^{-1}$ and $F_3=274.6 \text{ cm}^{-1}$.

Once the fit to hydrogenic values was obtained it was decided to vary the wavefunction parameters and to

¹³ W. E. Caswell and R. G. Fields, *Development in Applied Spectroscopy* (Plenum Press, Inc., New York, 1967), Vol. 2, p. 251.

see if it would be possible to obtain a new wavefunction that would better define the data. Now instead of only two variables there are four variables. A variable metric minimization program known as Vincent was used. (These calculations were done by T. P. Clements of the Lawrence Radiation Laboratory Mathematics and Computing Group.) The program in effect tries to minimize the sum of the squares of the differences between the observed and calculated values. The ground state is not fixed but can also vary. It has not been possible to carry these calculations to the completion due to the amount of computer time needed. It has been carried far enough to know that the parameters are not going to change by more than 1% of their values in going to completion. The $J=5$ was not used in this fitting process, but the lines marked level 6 and 7 of the ground levels were used. Table III also gives the fitted values. The fitted wavefunction is not much different from the hydrogenic.

The line at 21 956 cm^{-1} has a g value of 0.72.¹⁴ A calculation of the g value of the 7G_2 level using $5f$ hydrogenic wavefunctions is 0.65. The g value calculated for 7D_3 is 1.42; however, the line at 21 618 cm^{-1} is a very broad line and the line was observed to broaden in a magnetic field, but no measurement was possible. The 7D_3 and 7G_2 therefore satisfy the conditions of having the proper calculated and g values and agreeing with the calculations.

Before undertaking a study of the crystal-field parameters, more accurate measurements will be attempted on both the absorption and fluorescence.

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