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ABSTRACT

The absorption spectrum of U^{+4} has been observed from 2000 Å to 8μ. All the terms that can arise from two f electrons have been found. Terms have been assigned to all the absorption peaks. The radial integral, F_2, is found to be 206 cm^{-1} and the spin-orbit coupling ζ_{5f}, is 1870 cm^{-1}.

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INTRODUCTION

The spectrum of U^{+4} is one of the most observed of all the actinide elements. This is because its compounds are readily available, and it should have a relatively simple spectra since it contains only two $5\underline{f}$ electrons. The spectrum of Pr^{+3} $(4\underline{f}^2)$ has been successfully interpreted, and good agreement exists between theory and experiment.[1-4] It is natural that similar results have been sought for in U^{+4}. Many workers have looked for and reported certain features in U^{+4} to be analogous to the multiplets which have been seen in Pr^{+3}.[5-8] In this study the U^{+4} ion in solid solution has been observed throughout the optical spectrum, and all the multiplets have been observed and can be fitted to theory.

It is generally mentioned in work on compounds of U^{+4} that the lines are broad. This has been the case with most of the materials looked at in preparation for this study. One material, however, exhibits sharp or relatively sharp lines. This material is UF_4 dissolved in a matrix of CaF_2. The absorption lines although sharp were still not sharp enough to be able to observe Zeeman effects.

EXPERIMENTAL

Crystals

Three different concentrations of UF_4 in CaF_2 were prepared and observed. The concentrations were approximately 0.1, 1, and 10% by weight. The crystals, or clear crystalline masses, were prepared in an electron bombardment furnace (Fig. 1). Such a furnace efficiently uses the power available and allows for slow growth of the crystal.

It was not necessary to grow these crystals slowly since preparation of the CaF_2 crystal was easy and took only a few hours. The resulting material was optically clear, which sufficed for this work. The CaF_2 is a cubic structure, and therefore polarization work could not be done. The CaF_2 starting material was purchased from Harshaw Chemical Company as pieces of synthetic crystals.

It is necessary to prepare the CaF_2 crystals in a vacuum so that all bubbles are removed from the melt. Attempts to prepare CaF_2 in another furnace at atmospheric pressure were not successful.

The UF_4 was precipitated from an acid solution with HF. The precipitate was dried at $100^{\circ}C$ in air and then transferred to a nickel tube. The nickel tube measuring 1/2-in. diam. by 8-in. long was closed on one end. The loaded tube was placed in a vacuum system and pumped on until a vacuum of 10^{-6} mm of mercury was obtained. The closed end containing the dried UF_4 was heated to $1000^{\circ}C$ for 1 hour. This vacuum-sublimed UF_4 was used in the preparation of all the crystals.

Spectroscopic Equipment

The spectrum range covered was from 2000 A to 8 μ. For the range of 2000 to 8000 A a 3.4-m focal length Wadsworth-mount spectrograph containing a 15000-lines-per-inch grating and having a 5.2 A/mm dispersion was used. The range from 8000 to 11000 A was covered with the same instrument containing a 7500-lines-per-inch grating and having 10.4 A/mm dispersion. The light sources used were a 1000-watt mercury lamp (AH6), a 300-watt concentrated zirconium-arc lamp, and a 100-watt tungsten-ribbon-filament lamp. Dewar flasks of both Pyrex and quartz were used.

For the infrared region of 1 μ to 8 μ, a Perkin-Elmer spectrometer was used. The spectrometer with a NaCl prism was used to survey the region.

There was no absorption above 2.5 μ. The spectrometer was then converted to a grating operation and the NaCl prism was used as a foreprism. Two gratings were used, one with a blaze at 1.6 μ and the other blazed at 12 μ. When the spectrometer was used with a grating, the light source was moved back, and a fused quartz lens added to the optical system. The light source was focused on the crystal located in a quartz Dewar flask by the reflection optics normally used with the spectrometer. The lens then focused the image of the crystal on the slit of the spectrometer. Thermocouple and PbS detectors were used.

The lines of UF_4 in CaF_2 were not sharp enough to show reasonable or interpretable patterns in a Zeeman experiment at liquid-hydrogen temperature and a magnetic field of 37,700 gauss. A few lines showed broadening, but this fact was not useable. In one experiment, the absorption spectra was observed at liquid-helium temperature, but the additional sharpening of the lines was so insignificant that the remaining work was at liquid-nitrogen temperature.

The net result is that I have a list of lines somewhat grouped together. The additional aids usually used, such as polarization, Zeeman effect, and crystal-field selection rules were not available. The symmetry of the U^{+4} ion in CaF_2 is not known.

DATA

Table I lists all the observed lines together with a very rough estimation of intensity and the assignment as obtained from this work. The calculated values were obtained by solving the intermediate field equations for $\chi = 4.52$ and multiplying by $F_2 = 206\ cm^{-1}$.

RESULTS

The equations of Spedding for the $\underline{f}^2$ electron system were used to make the intermediate field calculations.[9] A plot of the levels with the ground state normalized to zero is shown in Fig. 2. Certain assumptions had to be made before this plot could be made. The ratios of F_4/F_2 and F_6/F_2 were taken from the paper by Elliott, Judd, and Runciman.[10] They suggest that $F_4/F_2 = 0.145$ and $F_6/F_2 = 0.0164$ for the 5$\underline{f}$ elements based on hydrogenic wave functions. The energy levels in units of F_2 for the 5$\underline{f}^2$ system are given in Table II.

Table I

Wavelengths and term assignments of UF_4 in CaF_2

Wavelength (A)	Intensity	Wave numbers (cm^{-1})		Term assignment
		Observed	Calculated	
2349	6	42558	39482	$^1S_0$
3920	2	25503	23330	$^3P_2$
4193	2	23843	23330	$^3P_2$
4291	1	23298	23330	$^3P_2$
4418	2	22628	23330	$^3P_2$
4745	2	21069	19480	$^1I_6$
4803	2	20815	19480	$^1I_6$
4813	2	20771	19480	$^1I_6$
4823	2	20728	19480	$^1I_6$
4831	2	20694	19480	$^1I_6$
4837	5	20668	19480	$^1I_6$
4847	5	20626	19480	$^1I_6$
5256	7	19020	18503	$^3P_1$
5391	9 s	18544	18503	$^3P_1$
6269	5	15947	15672	$^3P_0$
6488	6	15411	15413-$^1D_2$	$^1D_2$ or $^1G_4$
6507	8	15364	15664-$^1G_4$	$^1D_2$ or $^1G_4$
6545	2	15274	15664	$^1D_2$ or $^1G_4$
6562	2	15235	15664	$^1D_2$ or $^1G_4$
6569	2	15219	15664	$^1D_2$ or $^1G_4$
6578	6	15198	15664	$^1D_2$ or $^1G_4$

Table I (cont'd.)

Wavelengths and term assignments of UF_4 in CaF_2

Wavelength (A)	Intensity	Wave numbers (cm^{-1})		Term assignment
		Observed	Calculated	
6592	6	15166	15664	$^1D_2$ or $^1G_4$
6600	6	15147	15664	$^1D_2$ or $^1G_4$
6659	2	15013	15664	$^1D_2$ or $^1G_4$
7715	3	12958	10922	$^3H_6$
8788	2	11476	10922	$^3H_6$
8935	3	11189	10922	$^3H_6$
8955	4	11164	10922	$^3H_6$
8965	3	11151	10922	$^3H_6$
8981	3	11127	10922	$^3H_6$
8995	2	11114	10922	$^3H_6$
9157	2	10918	10922	$^3H_6$
9179	2	10891	10922	$^3H_6$
9199	2	10868	10922	$^3H_6$
9298	2	10752	10922	$^3H_6$
10979	10	9108	8619-$^3F_4$	$^3F_3$ or $^3F_4$
11080	4	9025	8574-$^3F_3$	$^3F_3$ or $^3F_4$
11128	4	8986	8574	$^3F_3$ or $^3F_4$
1.17[a]		8547	8574	$^3F_3$ or $^3F_4$
1.569	8	6373	5875	$^3H_5$
1.592	3	6281	5875	$^3H_5$
1.603	4	6238	5875	$^3H_5$

Table I (cont'd.)

Wavelengths and term assignments of UF_4 in CaF_2

Wavelength (A)	Intensity	Wave numbers (cm^{-1})		Term assignment
		Observed	Calculated	
1.674	5	5974	5875	$^3H_5$
1.684	4	5938	5875	$^3H_5$
1.697	7	5893	5875	$^3H_5$
1.704	8	5869	5875	$^3H_5$
1.716	5	5828	5875	$^3H_5$
2.42[b]	2	4132	4031	$^3F_2$

---

[a] Broad

[b] Very broad

Table II

Energy levels (in units of F_2 for $5\underline{f}^2$ electrons
(for $F_4/F_2 = 0.145$; $F_6/F_2 = 0.0164$)

^3H	0
^3F	13.1
^1G	18.0
^1D	48.9
^1I	58.9
^3P	61.3
^1S	149.4

It should be pointed out that the F_6 value cannot be ignored. The equations for $\underline{f}^2$ quickly show this.[11]

Figure 3 shows the variation of the levels with F_2, F_4, and F_6. The plot is energy in units of F_2 against various values of F_4/F_2. The equations of Condon and Shortley[11] were solved with the variable F_4/F_2 and then the value of F_6/F_2 taken as 1/10 the F_4/F_2 value. Those levels that change greatly with the electrostatic parameters might be expected to show the poorest fit to Fig. 2 since this has in it fixed ratios of F_2, F_4, and F_6. The level $^1S_0$ does in fact fit the poorest.

The best fit of the experimental data to Fig. 2 is obtained for $F_2 = 206 \pm 4$ cm^{-1}. The lines for this value of F_2 are shown on the plot. The fit gives a value of $\chi = 4.52 \pm .04$ which gives $\zeta = 935$ cm^{-1} in the notation of Spedding[9] or $\zeta_{5\underline{f}} = 1870$ cm^{-1} as used by Judd.[3]

These values are reasonable for U^{+4}. The F_2 is proportional to $(Z - \sigma)$. The value usually used for the screening constant (σ) of the actinide elements is 58,[12] so that the ratio of the F_2's for Th^{++} and U^{+4} should be $\frac{90-58}{92-58}$ or 1.06. The F_2 for Th^{++} is reported as 193 cm^{-1} by Racah.[13] This gives a value of 205 cm^{-1} for uranium extrapolated from thorium. So the value of 206 cm^{-1} for U^{+4} is reasonable.

The ζ value is proportional to the fourth power $(Z - \sigma)$. Extrapolated from Th^{++} whose value is 520 cm^{-1}, the value for uranium is 670 cm^{-1}. This is compared to 935 cm^{-1} found in this work. While this is not good agreement, it does point out that the value found is reasonable.

The solution of the 3 by 3 matrix elements, by the use of an IBM-650 program gives eigenvectors from which the percentage composition of the $^3H_4$ ground state may be obtained. The $^3H_4$ at $\chi = 4.52$ is composed of 87.7% $^3H_4$, 1% $^3F_4$, and 11.3% $^1G_4$. The limiting value for $\underline{j}$-$\underline{j}$ coupling of the $^3H_4$ state is 74.8% $^3H_4$, 2.7% $^3F_4$, and 22.4% $^1G_4$.[13]

Acknowledgment

Discussion of this work with Ralph D. McLaughlin and John D. Axe, was very helpful. This work was performed under the auspices of the U. S. Atomic Energy Commission.

REFERENCES

1. Sayre, Sancier, and Freed, J. Chem. Phys. 23, 2060 (1955); J. Chem. Phys. 29, 242 (1958).
2. A. M. Hellwege and K. H. Hellwege, Z. Physik 130, 549 (1951).
3. B. R. Judd, Proc. Roy. Soc. (London) A241, 414 (1957).
4. G. H. Dieke and R. Sarup, J. Chem. Phys. 29, 741 (1958).
5. K. M. Sancier and S. Freed, J. Chem. Phys. 20, 349 (1952).
6. D. M. Gruen, J. Am. Chem. Soc. 76, 3850 (1954).
7. C. K. Jorgensen, Kgl. Danske Videnskab. Selskab, Mat. fys. Medd. 29, No. 7 (1955).
8. T. V. Alexanian, Doklady Akad. Nauk. S.S.S.R. 115, 333 (1957).
9. F. H. Spedding, Phys. Rev. 58, 255 (1940).
10. Elliott, Judd, and Runciman, Proc. Roy. Soc. (London) A240, 509 (1957).
11. E. V. Condon and G. H. Shortley, The Theory of Atomic Spectrum (Cambridge University Press, Cambridge, 1953) p. 207.
12. Dawson, Mandleberg, and Davies, J. Chem. Soc., 2047 (1951).
13. G. Racah, Physica 16, 651 (1950).

Figure Legends

Fig. 1. Electron bombardment furnace.

Fig. 2. Energy levels of U V in the intermediate field region. Curves for the ${}^3F_3$ and ${}^3F_4$ levels, although actually separate, are not resolved in this figure.

Fig. 3. Energy levels as a function of $F_2:F_4:F_6$.

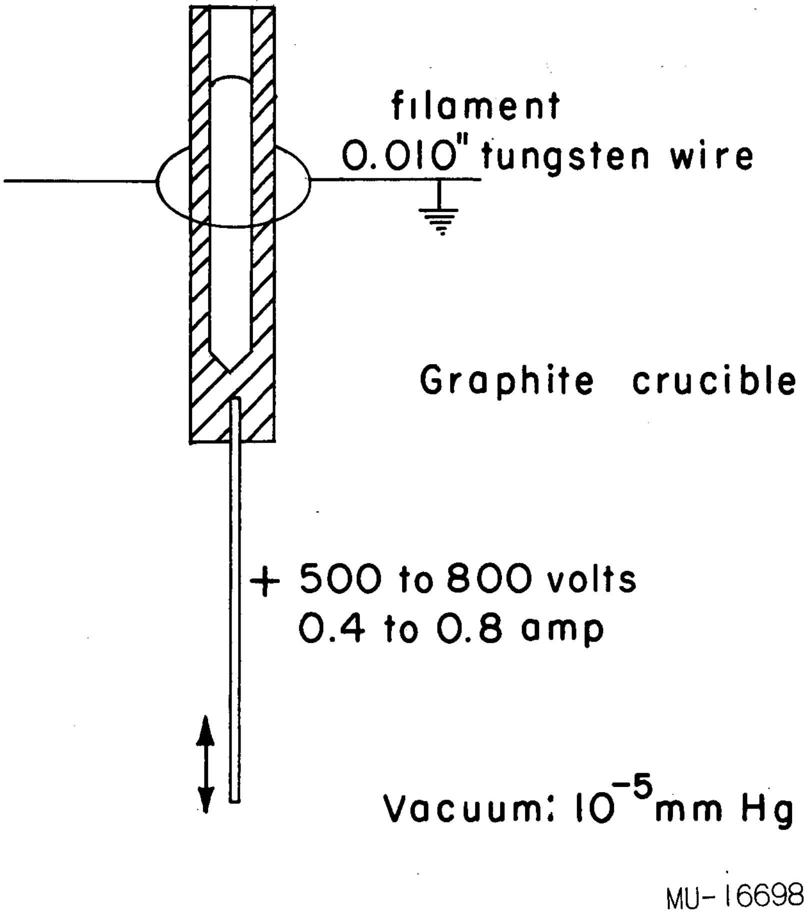
filament
0.010" tungsten wire
Graphite crucible
+ 500 to 800 volts
0.4 to 0.8 amp
Vacuum: 10⁻⁵ mm Hg
MU-16698

Fig. 1.

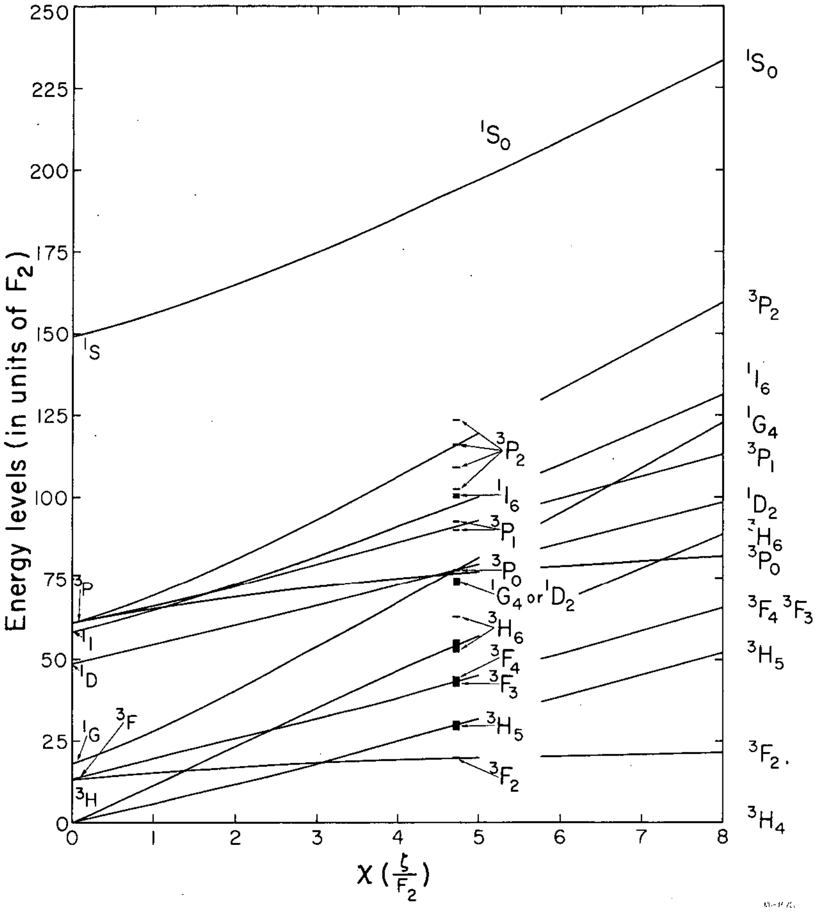
Energy levels (in units of F₂)
250
225
200
175
150
125
100
75
50
25
0
0
1
2
3
4
5
6
7
8
χ (ζ/F₂)
¹S
³P
¹I
¹D
¹G
³F
³H
¹S₀
³P₂
¹I₆
³P₁
³P₀
¹G₄ or ¹D₂
³H₆
³F₄
³F₃
³H₅
³F₂
¹S₀
³P₂
¹I₆
¹G₄
³P₁
¹D₂
³H₆
³P₀
³F₄ ³F₃
³H₅
³F₂.
³H₄

Fig. 2.

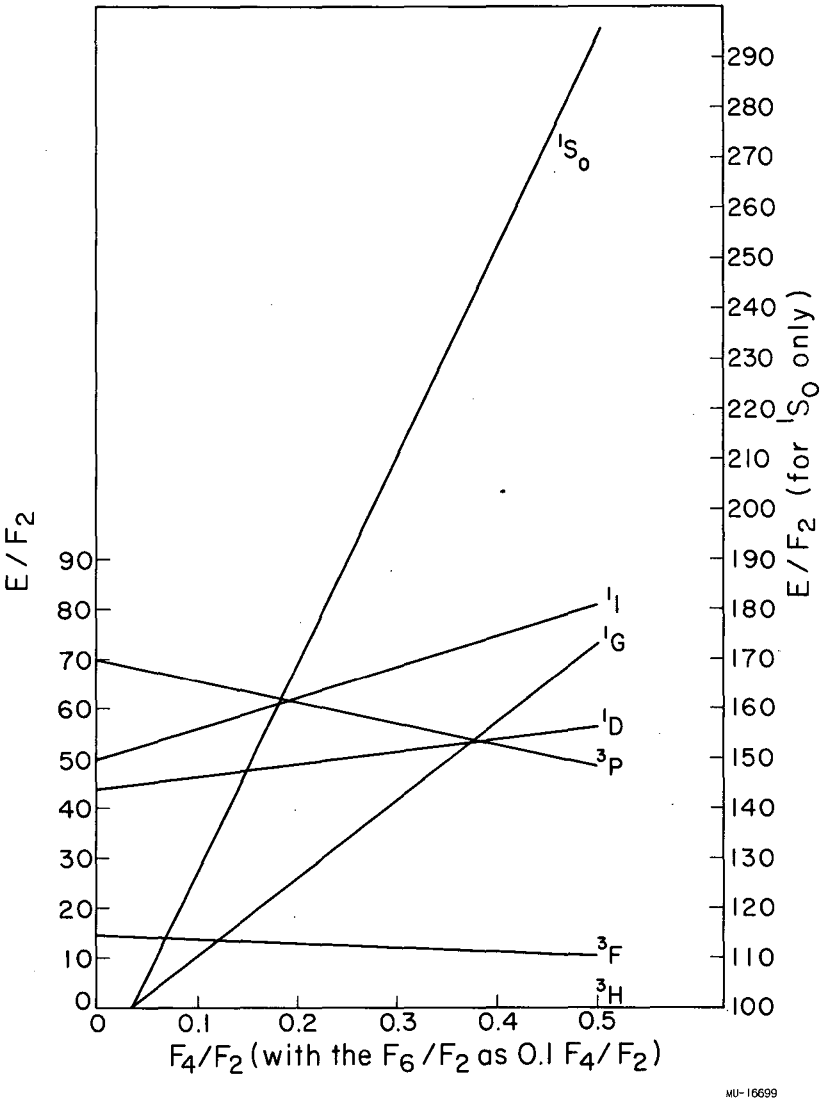
E / F2
90
80
70
60
50
40
30
20
10
0
E / F2 (for 1S0 only)
290
280
270
260
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
1S0
1I
1G
1D
3P
3F
3H
0
0.1
0.2
0.3
0.4
0.5
F4/F2 (with the F6/F2 as 0.1 F4/F2)
MU-16699

Fig. 3.