AN OPTICAL STUDY OF α -UF₅ AND β -UF₅

H. G. HECHT*, J. G. MALM and W. T. CARNALL

Chemistry Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439 (U.S.A.)

(Received February 15, 1985)

Summary

The optical absorption spectra of polycrystalline samples of both α and β -UF₅ have been measured in the range 2700 - 500 nm at 4, 77 and about 293 K using a recording spectrophotometer. It was assumed that the crystal field in both cases was dominated by weak covalent interactions; consequently crystal-field analyses were developed based on the angular overlap model. Crystal-field parameters consistent with the experimental data were derived.

1. Introduction

There has been considerable interest expressed in the spectroscopy and electronic structure of UF₅ as a product of the photodecomposition of UF₆. However, the experimental [1] and theoretical [2] investigations reported in the literature have been based on matrix-isolated molecules of UF₅ which are generally taken to have C_{4v} symmetry. On aggregation to form bulk UF₅, either the α or β structure must begin to emerge depending on the conditions. We consider it desirable to have well-characterized spectra of these two polymorphs available as an aid to understanding the overall reduction process. In addition, the ability to model these simpler 5f¹ configurations should provide a basis for subsequent analysis of the more complex spectra expected for NpF₅ (5f²) and PuF₅ (5f³).

Uranium pentafluoride was first prepared in 1911 by Ruff and Heinzelmann [3] through hydrofluorination of UCl₅. During the course of the Manhattan Project it was established that UF₅ exists in two polymorphic forms, structures for which were given by Zachariasen [4] in 1949. The structure proposed for the low-temperature β form was a highly distorted pentagonal bipyramid with four corners shared. Single crystals of β -UF₅ were subsequently obtained from a solution of UF₆ in anhydrous HF which

^{*}Permanent address: Department of Chemistry, South Dakota State University, Brookings, SD 57007, U.S.A.

had stood under fluorescent illumination for several weeks, and a diffraction study of these showed that the uranium atom in fact has eightfold coordination (space group, $I\bar{4}2d$) with a geometry intermediate between a dodecahedron and a square antiprism [5]. A more recent analysis of X-ray diffraction data for a single crystal of the high-temperature α phase of UF₅ (space group, I4/m) confirmed the chain-like structure of octahedrally coordinated uranium atoms proposed by Zachariasen, but with much shorter nonbridging U—F bond lengths [6].

We have prepared both α -UF₅ and β -UF₅ and have examined the absorption spectra (2700 - 500 nm) of polycrystalline samples at 4, 77 and about 293 K. Analyses of the two different crystal fields were carried out, based on the observed absorption features, and crystal-field parameters derived.

2. Experimental details

 β -UF₅ was prepared by the reaction of PF₃ with excess UF₆ at 298 K. The pale yellow product was identified by X-ray powder diffraction [5]. A sample of the product completely dissolved in liquid anhydrous hydrogen fluoride containing NaF. Lower valent uranium fluorides are insoluble in this medium.

 α -UF₅ was prepared by heating β -UF₅ with excess UF₆ at 473 K for 16 hours. The very pale blue product, identified by X-ray diffraction [6], was also shown to be completely soluble in the liquid anhydrous HF-NaF solution.

Samples were prepared for spectral analysis by thorough mixing of the appropriate polycrystalline material with powdered Teflon [7]. The mixture was loaded into a 13 mm die, and pressed at about 6000 lbf. All operations were conducted in a dry box. The pellet was immediately transferred under dry nitrogen gas to an optical Dewar equipped with quartz windows, and the spectra were recorded using a Cary 17 spectrophotometer at 4 K, about 77 K and about 293 K. After a few days the pellets began to show the presence of dark green patches which are characteristic of U⁴⁺, despite the maintenance of anhydrous conditions. The α -form is reported to be particularly sensitive to traces of moisture [6]. The spectra of the α and β forms at room temperature (about 293 K) and 4 K are shown in Figs. 1 and 2. The spectra recorded at about 77 K have been omitted for the sake of clarity; they are intermediate in resolution between the two extremes shown, and provide little additional information.

3. Structural considerations and spectroscopic analysis

The U-F bond angles of the α -form are required to be precisely 90° by the uranium site symmetry (4/m), so that the only parameters needed to



Fig. 1. Spectra of Teflon pellets of α -UF₅ and β -UF₅ recorded at room temperature and liquid helium temperatures.



Fig. 2. IR spectrum of a concentrated Teflon pellet of α -UF₅ at room temperature and liquid helium temperatures.

TABLE 1	
---------	--

Coordinates for the fluorine atoms in α -UF₅ and β -UF₅ (with the uranium atom at the origin)

α -UF ₅ (D_{4h}		β -UF 5					
$\overline{R(\text{\AA}) \theta(\text{deg})}$		ϕ (deg)	Actual coordinates			Idealized coordinates (D_{4d})		
			R (Å)	θ (deg)	φ (deg)	\overline{R} (Å)	θ (deg)	φ (deg)
2.2351	0	0	1.9590	54.46	69.61	2.19	57.5	67.5
2.2351	180	0	1.9590	125.54	-69.61	2.19	122.5	-67.5
1.9957	90	0	2.2849	61.49	157.90	2.19	57.5	157.5
1.9957	90	90	2.2849	118.51	-157.90	2.19	122.5	-157.5
1.9957	90	180	2.1967	51.79	-112.64	2.19	57.5	-112.5
1.9957	90	270	2.1967	128.21	112.64	2.19	122.5	112.5
			2,3190	62.20	-24.20	2.19	57.5	-22.5
			2.3190	117.80	24.20	2.19	122.5	22.5

specify the bonding within the first coordination sphere about the uranium atom are the U—F bond distances. The lengths reported are 2.235(1) Å along the -U-F-U- (bridging) chain, and 1.995(7) Å for the four non-bridging U—F bonds [6]. The bonding may be described as an octahedron subjected to a tetragonal elongation (D_{4h}), with coordinates as given in Table 1.

The bonding in β -UF₅ is much more irregular. Using the structural parameters given by Ryan *et al.* [5], the actual coordinates shown in Table 1 may be obtained by translating the uranium atom to the origin and rotating coordinates. An analysis using the actual structure would involve far too many crystal-field terms to be practical. As noted above, the structure is intermediate between a dodecahedron and a square antiprism (D_{4d}), whose idealized coordinates are listed in the last three columns of Table 1. Because of the approximate nature of this representation only a qualitative interpretation can be expected, but it does result in a crystal-field hamiltonian with only three axial terms so that the problem becomes tractable.

There are indications that the crystal field may be dominated by weak covalent rather, than electrostatic interactions in both UF₅ phases [8]. The angular overlap model (AOM) offers a way of relating the crystal-field terms for metal atoms bonded to similar ligands [9], and so it lends itself quite naturally to development of a basis for analysis of the present spectra. In addition, the model has already seen application in recent years to complexes involving f-orbital bonding [10 - 13]. (Although it does not affect the calculations reported in the present communication, Urland (private communication) has pointed out that there is an error in Table 3 of ref. 10 concerning the parameter $R_6 c_{62} (B_2^{-6})$: the coefficient $\overline{E} = 2/5(26\pi/7)^{1/2}$ should read $\overline{E} = 2/5(52\pi/7)^{1/2}$.) In the subsequent discussion we follow the definition of crystal-field terms given by Wybourne [14] and make the usual assumption that the bonding is predominately of σ and π character (*i.e.*, $e_{\delta} = e_{\phi} = 0$). An interpretation of the crystal-field structure is first developed in terms of the AOM, then, based on the established assignments, the crystal-field and spin-orbit parameters are allowed to vary freely to obtain the best fit to the experimental data.

We consider first the case of α -UF₅. With the coordinates given in Table 1 and the transformation matrices for f-orbitals given by Urland [10], it is found that the crystal-field parameters may be written

$$B_{0}^{2} = -1.429e_{\sigma} - 2.143e_{\pi} + 1.429e_{\sigma}' + 2.143e_{\pi}'$$

$$B_{0}^{4} = 1.929e_{\sigma} + 0.643e_{\pi} + 2.571e_{\sigma}' + 0.857e_{\pi}'$$

$$B_{4}^{4} = 2.689e_{\sigma} + 0.896e_{\pi}$$

$$B_{0}^{6} = -2.321e_{\sigma} + 3.482e_{\pi} + 3.714e_{\sigma}' - 5.571e_{\pi}'$$

$$B_{4}^{6} = -2.606e_{\sigma} + 3.909e_{\pi}$$
(1)

where e_{σ} and e_{π} are the angular overlap parameters for the equatorial ligands (at 1.9957 Å) and e_{σ}' , e_{π}' are those for the axial ligands (at 2.2351 Å). We introduce two additional approximations at this point. First, with various other workers [12, 13, 15] we assume that the angular overlap parameters vary with the seventh power of the distance and write

$$e_{\lambda}' = e_{\lambda} \left(\frac{1.9957}{2.2351}\right)^7 = 0.452e_{\lambda}$$
 (2)

Second, we take the ratio of π bonding to σ bonding to be constant. The value given by Warren [11] to characterize the bonding in the UF₆⁻ is assumed as an initial estimate:

$$\frac{e_{\pi}}{e_{\sigma}} = 0.413 \tag{3}$$

With these approximations the crystal-field parameters can be expressed in terms of the single variable e_{σ} :

$$B_{0}^{2} = -1.269e_{\sigma}$$

$$B_{0}^{4} = 3.515e_{\sigma}$$

$$B_{4}^{4} = 3.060e_{\sigma}$$

$$B_{0}^{6} = -0.245e_{\sigma}$$

$$B_{4}^{6} = -0.992e_{\sigma}$$
(4)

The energy matrix for the f^1 configuration was diagonalized within the L, S, J, J_z manifold under the simultaneous application of the crystalfield and spin-orbit coupling interactions. The energy levels are shown in



Fig. 3. Calculated energy level diagram for the f^1 ion in a field of D_{4h} symmetry using the AOM as described in the text. The broken line is drawn for the best values of e_{σ} and ξ_{5f} obtained by fitting to the spectrum of α -UF₅.

Figure 3, where they are scaled such that pure spin-orbit coupling is represented on the left, and pure crystal-field splitting on the right. We assume that a reasonable value for ζ_{5f} would be approximately 1900 cm⁻¹, somewhat reduced from the free-ion value of $\zeta = 2172$ cm⁻¹ [16]. An examination of the parameters, published by Warren [11] suggests that we might expect e_{σ} to be in the region 4000 - 5000 cm⁻¹ in this case. Comparison of Figs. 1 - 3 indicates that all but the lowest-lying pure electronic transitions have probably been observed.

IR and Raman spectra were recorded and shown to be equivalent to those published by Jacob [17], but no detailed analysis of the vibronic structure has been attempted. We note that our samples, particularly α -UF₅, showed obvious decomposition during attempts to obtain laser Raman spectra. Since the peaks at 1623, 1320, 660 and 582 nm, all have rather similar structure toward higher energies at 4 K, we have assumed them to be the pure electronic transitions, Table 2. The structure of the vibronic transitions is similar to that reported for the UF₆⁻ ion, [18] with some additional splittings due to the tetragonal distortion. A very low-frequency band is

TABLE 2

α - UF_5		β -UF ₅		
Assigned level	Calculated level ^a	Assigned level	Calculated level ^b	
	$0 (\Gamma_2^{-})$		0 (Γ ₁₀ ⁻)	
3650	3773 (Γ_6^{-})	—	1136 (Γ_9^{-})	
6161	6030 (Γ_{7}^{-})		$3061(\Gamma_{11}^{-1})$	
7579	7673 (Γ_7^{-1})	6671	6671 (Γ_{10}^{-})	
10730	10684 (Γ_6^{-})	7474	7474 (Γ_8)	
15152	14919 (Γ_7^{-})	9434	9434 (Γ ₁₁ ⁻)	
17182	17399 (Γ_6^-)	11601	11601 (Г 9 ⁻)	

Observed and calculated energy levels for α -UF₅ and β -UF₅

All values are in reciprocal centimeters.

^aThe parameters used to generate these levels are given as Set B, Table 3.

^bThe parameters used to generate these levels are given as Set D, Table 3.

also apparent at about 42 - 43 cm⁻¹ which is possibly due to a non-localized mode which propagates along the chain-like structure. The broad, weak absorption in the range 1000 - 1150 nm in α -UF₅, Fig. 1, may be due to small amounts of UF₄ and/or β -UF₅ in the sample, which is thought also to be responsible for some of the absorption at 1400 - 1500 nm. The peak at 932 nm is weak, but it also has a structure to the blue side which is reminiscent of that seen more clearly in the more intense transitions. This is assigned to the pure electronic transition expected in this region (see Fig. 3).

Figure 3 suggests that the transition to the Γ_6^- level from the ${}^2F_{5/2}$ state in zero field might lie just outside the range of our well-defined measurements. We consistently found strong poorly resolvable absorption in the approximate range 2600 - 2800 nm at low temperatures. A room temperature scan failed to show any evidence of the Γ_6^- level near 2600 nm, but a very concentrated pellet revealed what appears to be part of the vibronic structure associated with this transition, Fig. 2. By comparison with the vibronic structure of the other bands, we estimate that the pure electronic transition is at about 2740 nm or 3650 cm⁻¹.

The parameter values which give the best fit to the six transitions identified for α -UF₅ assuming approximations (2) and (3) are $\zeta = 1608 \text{ cm}^{-1}$ and $e_{\sigma} = 5714 \text{ cm}^{-1}$. The standard deviation of this fit is 459 cm⁻¹, and corresponding crystal-field parameters are shown in Table 3, Set A. If we now adopt the energy level assignments deduced with the aid of the AOM, but treat all the crystal-field terms and the spin-orbit interaction as freely varying parameters, the computed energy levels are those given in Table 2, and are shown as Set B, Table 3. In this case the standard deviation of the calculated and observed energy levels, Table 2, is 220 cm⁻¹. By relaxing approximation (3) but retaining approximation (2), the values of e_{σ} and e_{π} obtained by a least-squares fit to the parameters of Set B are 5523 cm⁻¹ and 1337 cm⁻¹ respectively. The resulting ratio $e_{\pi}/e_{\sigma} = 0.242$ is somewhat

	α -UF ₅		β -UF ₅		
	Set A	Set B	Set C	Set D	
B_0^2	-7251	-5920	-2325	-1185	
B_0^4	20084	16442	-15049	-15354	
B_4^{4}	17485	17786			
B_0^{6}	-1400	-2986	6120	3314	
B_4^{6}	-5668	-6298			
٢	1608	1884	1836	1926	

TABLE 3 Crystal-field parameter values

All values in reciprocal centimeters.

dent on the single parameter e_{α} ":

lower than that of the original estimate, but the crystal-field parameter values appear to be consistent with those estimated based on the AOM and the final value of ζ is in better agreement with expectations of a moderate reduction from the free-ion value.

As already noted the actual symmetry of β -UF₅ is rather low. The absorption bands are correspondingly broad and ill-resolved, and we expect the parameters to be more approximate. With the idealized model described above the crystal-field hamiltonian is axial and the parameters are given by

$$B_0^2 = -0.383e_{\sigma}'' - 0.574e_{\pi}''$$

$$B_0^4 = -3.528e_{\sigma}'' - 1.176e_{\pi}''$$

$$B_0^6 = 4.288e_{\sigma}'' - 6.432e_{\pi}''$$
(5)

$$B_0^2 = -0.620 e_{\sigma}''$$

$$B_0^4 = -4.013 e_{\sigma}''$$

$$B_0^6 = 1.632 e_{\sigma}''$$
(6)

The energy levels for this case are shown in Fig. 4 using a scaling which is the equivalent of that used for Fig. 3.

Comparison of Fig. 4 with Fig. 1 suggests that the four prominent bands observed for β -UF₅ are just those coming from the ${}^{2}F_{7/2}$ state. We take the longest wavelength absorption for each of these four bands at liquid helium temperature to be the pure electronic transition, Table 2, and fit to them by treating ζ_{5f} and e_{σ}'' as free parameters. The best fit obtained in this way gave $\zeta_{5f} = 1836 \text{ cm}^{-1}$ and $e_{\sigma}'' = 3750 \text{ cm}^{-1}$, for which the standard deviation was 280 cm⁻¹. The corresponding crystal-field parameters are shown as Set C, Table 3. If we now adopt the assignments based on the



Fig. 4. Calculated energy level diagram for the f¹ ion in a field of D_{4d} symmetry using the AOM as described in the text. The broken line is drawn for the best values of e_{σ} " and ζ_{5f} obtained by fitting to the spectrum of β -UF₅.

AOM, but treat the crystal-field and spin-orbit parameters as variables, the corresponding parameter set is given as Set D, Table 3, and the energy levels derived from this set are those shown in Table 2. The standard deviation is of course zero since there are as many parameters as levels fit.

If we relax approximation (3) for the β -UF₅ case, the best values of e_{σ}'' and e_{π}'' implied by the parameters of Set D are 3816 cm⁻¹ and 1053 cm⁻¹ respectively, giving $e_{\pi}''/e_{\sigma}'' = 0.276$. No positive identification has yet been made of the two electronic transitions which are predicted by this model to occur in the IR range in β -UF₅.

In view of the qualitative nature of the models used, particularly for the β -UF₅, the parameters determined should be regarded as approximate. They do, however, give a reasonable account of the dominant structural features in these two polymorphic forms of UF₅. The range of U—F bond distances in β -UF₅ is large enough to bracket the two values of α -UF₅, but to the extent that the average value 2.19 Å of the idealized model may be taken as representative, we would expect the e_{σ} " value of β -UF₅ to be smaller than the e_{σ} value for the equatorial U-F bonds of α -UF₅ by the factor,

$$\left(\frac{1.9957}{2.19}\right)^7 = 0.52$$

The values determined for this ratio from our analysis are 0.66 and 0.69 for the crude and more refined fits respectively, which is in satisfactory agreement considering the approximations involved in the analysis. It is also of interest to note that our analyses give rather consistent values for the ratio of π bonding to σ bonding in the two compounds, namely $e_{\pi}/e_{\sigma} = 0.242$ for α -UF₅ and $e_{\pi}''/e_{\sigma}''' = 0.276$ for β -UF₅. These values are somewhat lower than the ratio 0.413 reported for the UF₆⁻ ion [11].

Finally, one might hope to use the wavefunctions derived from the above analysis to calculate the g tensors or magnetic susceptibilities and thereby obtain an independent verification of the parameters. The susceptibility of β -UF₅ has been reported by Nguyen-Nghi et al. [19], but the values we calculate are about a factor of 5-10 too small. An agreement with their data can be brought about only through a change of sign of the B_0^2 term. An examination of eqn. (5) shows that the sign of B_0^2 cannot be positive if the parameters are to have any physical significance. We conclude that the observed susceptibility of neat β -UF₅ is dominated by exchange coupling of the uranium ions, and the same is likely to be true of α -UF₅. The uranium atoms of both α -UF₅ and β -UF₅ are in rather close proximity, which facilitates the exchange interaction and leads to spin-orbit coupling constants which are smaller than those found in other uranium(V) fluorides, such as $CsUF_6$ [20]. Since there is no obvious diluent available in this case, an experimental study of the magnetic behavior of the unperturbed ion is problematical.

Acknowledgment

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under Contract W-31-109-ENG-38.

References

- 1 R. T. Paine, R. S. McDowell, L. B. Asprey and L. H. Jones, J. Chem. Phys., 64 (1976) 3081;
 - B. J. Krohn, W. B. Person and J. Overend, J. Chem. Phys., 65 (1976) 969;
 - L. H. Jones and S. Ekberg, J. Chem. Phys., 67 (1977) 2591.
- 2 D. H. Maylotte, R. L. St. Peters and R. P. Messmer, Chem. Phys. Lett., 38 (1976) 181.
- 3 O. Ruff and H. Heinzelmann, Z. Anorg. Allgem. Chem., 72 (1911) 63.

- 4 W. H. Zachariasen, Acta Crystallogr., 22 (1949) 296.
- 5 R. R. Ryan, R. A. Penneman, L. B. Asprey and R. T. Paine, Acta Crystallogr., Sect. B, 32 (1976) 3311.
- 6 P. G. Eller, A. C. Larson, J. R. Peterson, D. D. Ensor and J. P. Young, Inorg. Chim. Acta, 37 (1979) 129.
- 7 E. Schmieder, E. Dornberger and B. Kanellakopulos, Appl. Spectrosc., 24 (1970) 499.
- 8 M. Gerloch and R. C. Slade, Ligand-Field Parameters, Cambridge University Press, London, 1973.
- 9 C. K. Jørgensen, R. Pappalardo and H. H. Schmidtke, J. Chem. Phys., 39 (1963) 1422;
 - C. E. Schäffer and C. K. Jørgensen, Molec. Phys., 9 (1965) 401.
- 10 W. Urland, Chem. Phys., 14 (1976) 393.
- 11 K. D. Warren, Inorg. Chem., 16 (1977) 2008.
- 12 W. Urland, Chem. Phys. Lett., 50 (1977) 445; 53 (1978) 296; 62 (1979) 525; Z. Naturforsch., 34a (1979) 1507; Ber. Bunsenges. Phys. Chem., 83 (1979) 1042.
- 13 H.-D. Amberger, W. Grape and E. Stumpp, J. Less-Common Met., 95 (1983) 181.
- 14 B. G. Wybourne, Spectroscopic Properties of Rare Earths, Wiley-Interscience, New York, 1965.
- 15 J. D. Axe and G. Burns, Phys. Rev., 152 (1966) 331.
- 16 V. Kaufman and L. J. Radziemski, J. Opt. Soc. Am., 66 (1976) 599.
- 17 E. Jacob, Z. Anorg. Allgem. Chem., 400 (1973) 45.
- 18 E. Soulie, Rep. CEA-R-4849 (1977).
- 19 Nguyen-Nghi, M. Marquet-Ellis and A.-J. Dianoux, C. R. Acad. Sci., Paris, 259 (1964) 4683.
- 20 E. Soulie, J. Phys. Chem. Solids, 39 (1978) 695.