TABLE VI

ELECTRONIC ABSORPTION SPECTRA OF $M_2Re_4Br_{15}$ COMPOUNDS

Compd. and state or solvent	Wave lengths of maximum (ϵ[a] or rel. intens.)						
(1) $(QnH)_2Re_4Br_{15}$ (mull)	775–800 (m)	667 (vw)	560 (m, sh)	470 (s)	440 (s)	375 (s)	335 (s)
(2) $[(C_2H_5)_4N]_2Re_4Br_{15}$ (acetone)	778 (~600)	670 (~13)	~540 (sh[b])				
(3) $(pyH)_2Re_4Br_{15}$ (acetone)	777 (~600)	672 (~13)	~540 (sh[b])				
(4) $(QnH)_2Re_3Br_{11}$ (acetone)	777 (606)		535 (sh)				
(5) $Re_3Br_9((C_2H_5)_2C_6H_5P)_3$ (chloroform)	770 (600)		535 (sh)				
(6) K_2ReBr_6 (1 *N* HBr)[c]	755 (11.3)	665 (11.8)				353 (10^4)	325 (10^4)

[a] ϵ represents decadic molar extinction coefficient. [b] sh indicates that the shoulder was so poorly resolved as to preclude a meaningful intensity estimate, that is, one which does not include a major contribution from the underlying absorption which is rising steeply into the ultraviolet; see Figure 2. [c] Taken from C. Rulfs and R. Meyer, *J. Am. Chem. Soc.*, **77**, 4505 (1955).

an Re_3Br_9 group in compound 5 has already been demonstrated by the isomorphism of that compound with $Re_3Cl_9[(C_6H_5)(C_2H_5)_2P]_3$, which has been shown by X-ray structural work[6] to contain the Re_3Cl_9 group. An extensive series of other compounds,[21] including compound 4, also contain the Re_3Br_9 group and characteristically have absorption bands at ~780 and ~540 mμ.

Acknowledgments.—We thank the M.I.T. Computation Center for use of the I.B.M. 7094 computer and Dr. R. M. Wing for helpful discussions.

[21] F. A. Cotton, S. J. Lippard, and J. T. Mague, *Inorg. Chem.*, in press.

CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY,
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Analysis of the Absorption Spectrum of Cesium Uranium(V) Hexafluoride[1]

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The optical absorption spectrum of $CsUF_6$ has been measured from 300 to 50,000 cm.$^{-1}$, and the results have been analyzed in terms of the crystal field theory. The UF_6^- ion, characterized by a single 5f electron on the uranium, has a slightly distorted octahedral configuration. The crystal field parameters found are $\zeta_{5f} = 1955$ cm.$^{-1}$, $A_4^0\langle r^4\rangle = 2351$ cm.$^{-1}$, and $A_6^0\langle r^6\rangle = 208.8$ cm.$^{-1}$. The spectrum is largely vibronic in character, and values of the fundamental vibrational frequencies have been deduced from the splittings observed in the near-infrared and visible regions.

We have previously reported some preliminary results on the near-infrared absorption spectrum of several compounds of the type MUF_6, containing uranium in the pentavalent state.[2] It is the purpose of this work to report on the complete spectral analysis of $CsUF_6$ and to ascertain the magnitude of the crystal field parameters responsible for the salient features of the observed absorption spectrum.

Although intensive investigation of the optical behavior of the first inner transition series, characterized by the presence of 4f electrons, has been carried out, relatively little data have appeared on the actinide elements with the $5f^n$ electronic configuration.[3-5] In particular, of those elements possessing a $5f^1$ configuration in chemically accessible valence states, only three have been prepared: Pa(IV), U(V), and Np(VI). The optical and magnetic properties of Pa(IV) have previously been treated[6] as have those for Np(VI),[7-9] and it was therefore felt to be desirable to augment these data with information on U(V).

The optical absorption spectra of compounds containing actinide ions may be explained in terms of the incomplete 5f electronic shell, and consist in the main of fairly sharp groups of lines corresponding to transitions between the ground state and the upper Stark levels of the ions. The free ion splittings, due to interelectronic repulsion and spin–orbit coupling, are further augmented by the electrostatic field generated by the other ions present in the environment. These surrounding charges distort the free-ion electronic wave functions and give rise to crystal field splittings of the order of several thousand cm.$^{-1}$, whereas the analogous splittings in lanthanide complexes are a factor of ten smaller. We may envision the following cases according to the relative strengths

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] M. J. Reisfeld and G. A. Crosby, *J. Mol. Spectry.*, **10**, 232 (1963).

[3] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Ltd., Oxford, England, 1962.

[4] B. R. Judd, "Operator Techniques in Atomic Spectroscopy," McGraw-Hill Book Co., Inc., New York, N. Y., 1963.

[5] D. S. McClure, *Solid State Phys.*, **9**, 399 (1959).

[6] J. D. Axe, "The Electronic Structure of Octahedrally Co-ordinated Protactinium(IV)," University of California Radiation Lab. Rept. UCRL-9293 (1960).

[7] J. C. Eisenstein and M. H. L. Pryce, *Proc. Roy. Soc.* (London), **A255**, 181 (1960).

[8] G. L. Goodman, Doctoral Dissertation, Harvard University, 1959.

[9] G. L. Goodman and M. Fred, *J. Chem. Phys.*, **30**, 849 (1959).

of the various interactions: (1) Crystal-field < spin-orbit < electronic repulsion. This case is typical of the 4f lanthanide ions. (2) Spin-orbit < crystal-field < electronic repulsion. This situation, the so-called "weak-field," is found in the ions of the d-level transition ions. (3) Spin-orbit < electronic repulsion < crystal-field. This is the "strong-field" case found also in d-level ions and 5f ions of the type NpO_2^{2+}. (4) Spin-orbit $\simeq$ crystal-field $\simeq$ electronic repulsion. This, the "intermediate-field" case, corresponds to the observed spectra in the case of many of the 5f actinide ions.

In the case of a free ion having the $5f^1$ configuration the situation is considerably simplified, for the interelectronic repulsion terms within the shell vanish. Only two different energy levels ($^2F_{5/2}$, $^2F_{7/2}$) arise, although they are 6- and 8-fold degenerate, respectively. The expected absorption spectrum of the free ion would consist of a single line corresponding to a transition between these levels. In practice, however, the spectrum is complicated by the appearance of additional transitions, arising from the removal of the degeneracies by the crystal field. It is possible, however, from an assignment of the observed transitions to the proper electronic levels, to determine theoretically both the free-ion separation and the magnitude of the crystalline field interactions. These types of calculations form the domain of crystal field theory.

Experimental

Two different procedures were used for the preparation of $CsUF_6$. The first method utilized a dry preparation in which UF_5 was mixed and heated with CsF under anhydrous conditions.[10] The second preparation involved the dissolution of anhydrous UF_5 in a concentrated (48% by weight) aqueous solution of HF at 0°.[11] An ice-blue solution results which is stable when chilled, but slowly turns green when allowed to remain at room temperature. An equimolar quantity of CsF in concentrated HF was added to the blue solution, whereupon a light blue precipitate formed. The supernatant liquid was centrifuged off and the precipitate was dried on filter paper. X-Ray analysis of the precipitate showed it to be identical in structure with the material formed by the dry preparation. Spectra from both preparations were identical.

The spectral region 2000–25,000 Å. was examined using a Cary Model 14MR spectrophotometer. The samples of $CsUF_6$ were ground into mulls with Fluorolube[12] and placed between calcium fluoride disks. Low-temperature spectra were measured, utilizing the same mulls in a liquid nitrogen cell with KBr windows. Infrared spectra of mineral oil mulls between cesium bromide windows were obtained on a Perkin-Elmer Model 421 spectrophotometer.

It was soon found that upon moderate exposure to the radiation, the blue $CsUF_6$ decomposed into an emerald-green material which exhibited a totally different absorption spectrum. These latter spectra were quite similar to those characteristic of tetravalent uranium.[13-15] The green material was not characterized further.

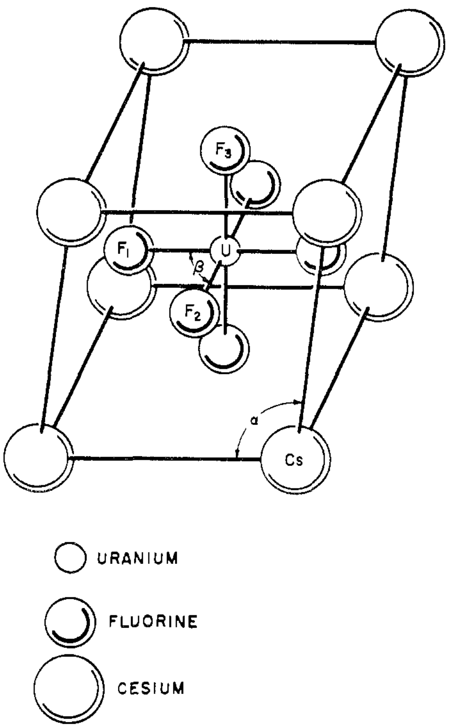

Figure 1.—Rhombohedral unit cell of $CsUF_6$.

Table I
Structural Data for $CsUF_6$ Unit Cell

a_0, Å.	8.036	$R_{F_1-F_2}$, Å.	2.74
c_0, Å.	8.388	$R_{F_1-F_3}$, Å.	2.86
a_{rhomb}, Å.	5.42	R_{Cs-F}, Å.	3.05
α_{rhomb}	95.8°	$\beta_{F_1-U-F_2}$	92.5°
R_{U-F}, Å.	1.98	α_{Cs-U-F_1}	42.5°

An attempt was made to observe the Raman spectrum of $CsUF_6$ using the powdered material in a cone-shaped solid sample cell on a Cary Model 81 Raman spectrophotometer. No peaks were observed which could be ascribed to $CsUF_6$ due to the rapid formation of the green U(IV) compound.

Theory

According to the crystal-field approximation, the Hamiltonian for the ion imbedded in a complex or crystal is expressed as a sum of the Hamiltonian for the free ion plus a potential, V_0, arising from the surrounding ligands or atoms. Since V_0 must transform as the totally symmetric representation in the symmetry group of the molecule it is necessary that the point group of the complex be known. In the case of $CsUF_6$ it was found that this compound was isostructural with rhombohedral $KOsF_6$, giving hexagonal dimensions $a_0 = 8.036$, $c_0 = 8.388$ Å.[10] The unit cell group is $R\bar{3}$ ($C_{3i}^2 = S_6^2$) and the site group is $C_{3i}(S_6)$. Transformation to a rhombohedral unit cell leads to the conclusion that the UF_6^- ion is a slightly irregular octahedron with F-U-F bond angles of 92.5 and 87.5°. Structural data on $CsUF_6$ are given in Table I, and the rhombohedral $CsUF_6$ unit cell is depicted in Figure 1.

Owing to the small deviation from regularity ($\Delta\beta = 2.5°$), it was decided to use the undistorted octahedral model for further calculations.

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[10] R. A. Penneman, G. D. Sturgeon, and L. B. Asprey, *Inorg. Chem.*, **3**, 126 (1964).

[11] L. B. Asprey and R. A. Penneman, *ibid.*, **3**, 727 (1964).

[12] Fluorolube "S-30," Hooker Electrochemical Co.

[13] D. M. Gruen, *J. Am. Chem. Soc.*, **76**, 3850 (1954).

[14] J. L. Ryan, *Inorg. Chem.*, **3**, 211 (1964).

[15] R. A. Penneman, F. H. Kruse, R. S. George, and J. S. Coleman, *ibid.*, **3**, 309 (1964).

Upon expansion in spherical harmonics of a generalized charge distribution, V_0, the crystal-field Hamiltonian acting on the ith electron, is

$$V_0 = e\sum_{n=0}^{\infty}\sum_{m=-n}^{+n} r_i^n C_n^m Y_n^m(\theta, \phi) \qquad (1)$$

where the Y_n^m are the usual spherical harmonics and C_n^m is a geometric factor. The Y_n^m form a basis for the $2n + 1$ dimensional irreducible representation D_l of the rotation group R_3; thus, if the crystal-field matrix elements are to be nonvanishing, we find that n must lie in the range $0 \leq n \leq 2l$, where l is the angular momentum quantum number of the electron. For a single 5f electron, then, the sum over n in eq. 1 is limited from $n = 0$ to $n = 6$. In addition, the Y_n^m also form bases for a reducible representation Γ_i of the octahedral group, since the Hamiltonian must have the same symmetry as does the point group.

Since J is half-integral for the $5f^1$ system ($J = {}^5/_2, {}^7/_2$), the "double group" representation O_h' was employed for the decomposition of the representation of the sphere group. The results, using the character tables for O_h', are

$$\begin{aligned} J &= 2 \rightarrow \Gamma_3 + \Gamma_5 \\ J &= 3 \rightarrow \Gamma_2 + \Gamma_4 + \Gamma_5 \\ J &= {}^5/_2 \rightarrow \Gamma_7 + \Gamma_8 \\ J &= {}^7/_2 \rightarrow \Gamma_6 + \Gamma_7' + \Gamma_8' \end{aligned} \qquad (2)$$

Also, the crystal field matrix elements vanish if the Y_n^m have negative parity. Therefore, with the above considerations in mind, the octahedral crystal-field Hamiltonian, V_0, for i 5f electrons may be written as

$$V_0 = a_4^0\sum_i r_i^4[Y_4^0 + \sqrt{5/14}(Y_4^4 + Y_4^{-4})]_i + a_6^0\sum_i r_i^6[Y_6^0 - \sqrt{7/2}(Y_6^4 + Y_6^{-4})]_i \qquad (3)$$

a_4^0 and a_6^0 are related to the ion–ligand distance and the effective charge on the ligand. In general, the a_i are regarded as parameters evaluated from a fit of the experimental data.

For the evaluation of the matrix elements, the unperturbed free-ion wave functions in the $SLJJ_z$ representation were employed and the operator-equivalent approach[16-18] was adopted for the evaluation of the matrix elements. Rewriting eq. 3 in the notation now employed in studies of lanthanides and actinides, we arrive at

$$V_0 = A_4^0[V_4^0 + 5V_4^4] + A_6^0[V_6^0 - 21V_6^4] \qquad (4)$$

The potentials V_i^j as well as the eigenfunctions and matrix elements for a $5f^1$ electron are given in the Appendix. The eigenvalues are written in terms of ζ, the spin–orbit coupling constant; and θ and Δ, which are functions of the $A_j^0\langle r^j\rangle$.[6] In the earlier work on NpF_6 by Goodman,[8,9] which initiated much of the work on interpretation of the spectra of actinide ions, the separation of the crystal-field levels, denoted here by θ and Δ, were defined as $7Q$ and $7R$, respectively.

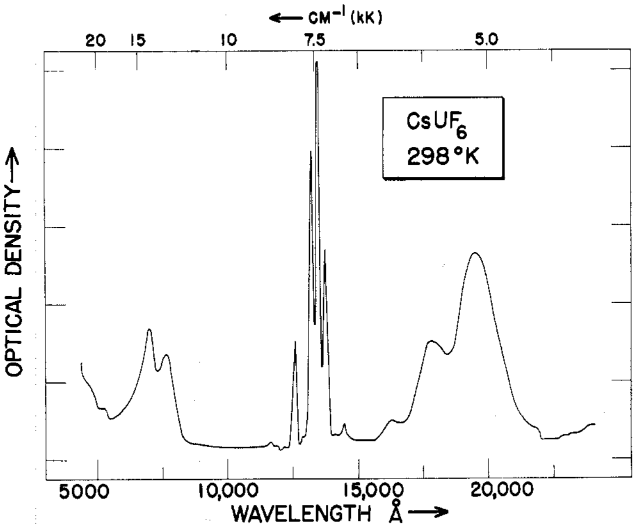

Figure 2.—Room temperature spectrum of $CsUF_6$ in Fluorolube.

As may be observed from the reduction of the free-ion states $J = {}^5/_2$ and $J = {}^7/_2$ (eq. 2) under the influence of the crystal field, five states result, two arising from the lower $J = {}^5/_2$ level and three from the upper $J = {}^7/_2$ level. The Γ_6 and Γ_7 states are Kramers doublets while the Γ_8 state is orbitally twofold degenerate (a set of two Kramers doublets). In the absence of a magnetic field, then, four transitions should be observed in fields of octahedral symmetry. Figure 4 shows the energy level distribution as a function of the relative strength of the crystal field. At the left-hand portion of the graph are located the free-ion levels, split by the spin–orbit coupling; and at the extreme right are located the "strong-field" states corresponding to the reduction of $J = 3$ under the site symmetry O_h. The spacings of the levels have been scaled to unity in the two extreme cases. As may be seen over most of the range, the order of the levels in increasing energy is Γ_7, Γ_8, Γ_7', Γ_8', and Γ_6.

Results and Discussion

The observed spectra of $CsUF_6$ at room temperature and liquid nitrogen temperature are shown in Figures 2 and 3. The absorption peaks arising from the U(IV) contaminant and the Fluorolube medium have been deleted. Two additional bands have not been shown. One, located in the infrared, consists of a broad peak centered at 503 cm.$^{-1}$, and the second consists of three lines at 36,000, 40,000, and 44,000 cm.$^{-1}$ of very much greater intensity. Table II lists the lines observed at both 298 and 75°K. The peaks arising from U(IV) and Fluorolube are shown in parentheses.

As may be observed from the room temperature spectrum there are seven groups of absorption bands centered at approximately 19,610, 17,775, 16,325, 13,510, 12,660, 7575, and 6940 Å. Transforming the wave lengths to a wave number basis places these bands at 5100, 5625, 6125, 7400, 7900, 13,200, and 14,400 cm.$^{-1}$. The low-temperature spectrum reveals further small splittings within each group of peaks. Since the point group of the UF_6^- ion is almost octahedral and would

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[16] K. W. H. Stevens, *Proc. Phys. Soc.* (London), **A65**, 209 (1952).

[17] R. J. Elliott and K. W. H. Stevens, *Proc. Roy. Soc.* (London), **A219**, 387 (1953).

[18] J. M. Baker, B. Bleaney, and W. Hayes, *ibid.*, **A247**, 141 (1958).

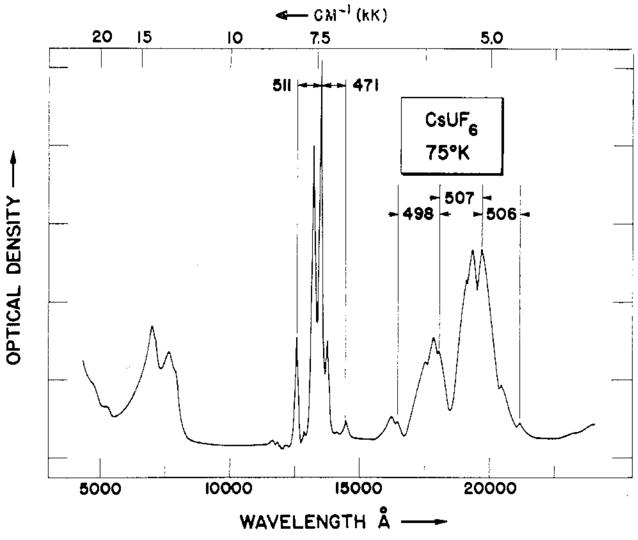

Figure 3.—Low-temperature spectrum of $CsUF_6$ in Fluorolube.

Table II
Observed Frequencies (cm.$^{-1}$) in $CsUF_6$

75°K.	298°K.	75°K.	298°K.
503	503	8,010	
4587		8,157	
4941		8,368	
5093		8,529	
	5102	(8,929)	(8,929)
5196		9,434	(9,398)
5600		(10,707)	(10,695)
	5624	(10,989)	(10,990)
5674		13,055	
5792		13,208	13,200
6098		14.245	
	6126	14,395	14,400
6180		15,049	(15,130)
(6600)		15,760	(15,670)
	(6765)	16,736	
(6812)			(18,380)
6928	6930	18,587	
7249	7249		(18,690)
7399	7399	20,619	
7540	7540	21,097	(21,053)
7569		23,810	(24,213)
7741		36,000	36,000
(7857)		40,000	40,000
7910		44,000	44,000
7946	7912		

therefore lead to the presence of only four peaks for pure electronic transitions, it remains to explain the presence of the additional features of the observed spectra. As has been shown by the work of Satten and others[19-21] on UCl_6^{2-} complexes ($5f^2$ configuration), the absorption spectrum may be understood on the basis of vibronic coupling involving electric dipole transitions arising from a simultaneous change in electronic state and a quantum of an odd vibrational mode of the UCl_6^{2-} complex. Similar considerations would be expected to apply for the UF_6^- complex studied here.

Assignment of Vibrational Frequencies

For a molecular point group of O_h symmetry the representations and their usual designation and optical activity are: $A_{1g} = \nu_1$ (Raman), $E_g = \nu_2$ (Raman), $T_{1u} = \nu_3$ (infrared), $T_{1u} = \nu_4$ (infrared), $T_{2g} = \nu_5$ (Raman), and $T_{2u} = \nu_6$ (inactive). The absorption band at 503 cm.$^{-1}$ may be assigned to the highest infrared-active T_{1u} mode ν_3 by analogy with the data on $NOUF_6$, $\nu_3 = 550$ cm.$^{-1}$.[22] It is therefore to be expected that a coupling will occur between some electronic states and one quantum of ν_3. The low-temperature spectrum indicates a peak at 4587 cm.$^{-1}$ (21,800 Å.) located 506 cm.$^{-1}$ below the strong absorption at 5093 cm.$^{-1}$ (19,635 Å.) and another peak at 6928 cm.$^{-1}$ (14,434 Å.) lying 471 cm.$^{-1}$ below the 7399 cm.$^{-1}$ (13,515 Å.) peak. If these peaks arose from a vibrational hot band corresponding to $\Delta\nu_3 = -1$, they would have disappeared from the low-temperature spectrum due to the depopulation of the level in accordance with the Boltzmann distribution. Since they do not disappear at low temperatures, we assume them to arise from a vibronic interaction of the $0 \rightarrow 0$ transition with one quantum of ν_3 (503 cm.$^{-1}$). Therefore, the electronic levels Γ_8 and Γ_7' will be assigned as 4587 and 6928 cm.$^{-1}$, respectively.

A further interesting feature is the spacing between the three lowest lying bands, amounting to 507 and 498 cm.$^{-1}$. The vibrational selection rules indicate that the totally symmetric vibrational mode A_{1g} can couple with the vibronic transitions to give further allowed transitions of diminished intensity ($A_{1g} + T_{1u}$, $2A_{1g} + T_{1u}$, . .). With such a scheme, we assign the A_{1g} infrared-inactive vibration ν_1 as 506 ± 10 cm.$^{-1}$. Further confirmation of this assignment may be found by the appearance of an absorption at 7910 cm.$^{-1}$, displaced 511 cm.$^{-1}$ from the prominent peak at 7399 cm.$^{-1}$. The threefold splitting centered at 7399 cm.$^{-1}$ with peaks at approximately ±145 cm.$^{-1}$ probably arises from the coupling of an additional vibrational mode with the vibronic level. This is confirmed by the diminution in intensity of the long wave length component at low temperature. The Boltzmann factor of $e^{-2.08} = 0.125$, expected from a $\Delta\nu = -1$ transition, corresponds to the observed decrease in absorption. This mode could be the T_{2g} Raman-active ν_5 vibration, but no Raman peaks were observed due to the presence of the highly colored U(IV) species formed. Since the combination band $T_{1u} + \gamma_i$ must be of odd order to enable vibronic features to appear, γ_i must be an even mode (E_g or T_{2g}). The even fundamental mode E_g (ν_2) lies at 535 cm.$^{-1}$ in the gaseous UF_6,[23] whereas the T_{2g} (ν_5) appears at 202 cm.$^{-1}$. Since we do not expect a very large shift in the vibrational fundamental frequencies upon going from octahedral UF_6 gas to octahedral UF_6^- in the present case, we assign the 145 cm.$^{-1}$ frequency in $CsUF_6$ as T_{2g} (ν_5).

The lowest band, centered at approximately 5195

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(19) R. A. Satten, *J. Chem. Phys.*, **30**, 590 (1959).

(20) R. A. Satten, D. J. Young, and D. M. Gruen, *ibid.*, **33**, 1140 (1960).

(21) S. A. Pollack and R. A. Satten, *ibid.*, **36**, 804 (1962).

(22) J. R. Geichman, E. A. Smith, S. S. Trond, and P. R. Ogle, *Inorg. Chem.*, **1**, 661 (1962).

(23) H. H. Claassen, *J. Chem. Phys.*, **30**, 968 (1959).

cm.$^{-1}$, shows a threefold splitting different in appearance from the group at 7399 cm.$^{-1}$. The components are not resolved at room temperature but exhibit a splitting of ± 103 cm.$^{-1}$ at 75°K. A similar splitting of ± 96 cm.$^{-1}$ is observed on the next higher frequency band at 5674 cm.$^{-1}$. Since we have assigned these bands as arising from an $E_7 \rightarrow E_8 + T_{1u}$ (ν_3) and an $E_7 \rightarrow E_8 + T_{1u}$ (ν_3) + A_{1g} (ν_1) transition, respectively, we would expect that these states would couple vibronically with an even (Γ_g) vibrational mode. However, since the UF_6^- is not quite centrosymmetric, it is possible that an additional odd vibration might be involved. The remaining unassigned vibrational modes are E_g (ν_2), T_{1u} (ν_4), and T_{2u} (ν_6), which appear in gaseous UF_6 at 535, 181, and 140 cm.$^{-1}$, respectively. The above-mentioned splittings of ~100 cm.$^{-1}$ in the 5195 cm.$^{-1}$ band of $CsUF_6$ should correspond to one of these modes. A shift of over 400 cm.$^{-1}$ from UF_6 to $CsUF_6$ seems unlikely, and we disregard E_g (ν_2) as the vibrational level involved. This level is then either the T_{1u} (ν_4) or T_{2u} (ν_6) mode.

There are three other absorption peaks of interest, located ~150 cm.$^{-1}$ toward the long wave length sides of the bands at 5093, 13,208, and 14,397 cm.$^{-1}$. The bands are resolved only at low temperature. The fact that they do not disappear at 75°K. may be taken as indicative of the fact that they do not arise from a $\Delta\nu = -1$ transition. This frequency of 150 cm.$^{-1}$ probably corresponds to either the odd T_{1u} (ν_4) or T_{2u} (ν_6). Since we had previously determined a frequency of ~100 cm.$^{-1}$ as ν_4 or ν_6, by analogy with UF_6 we will place the higher level as ν_4 (T_{1u}).

We then arrive at the following infrared frequencies (cm.$^{-1}$) for $CsUF_6$: A_{1g} (ν_1) = 506, T_{1u} (ν_3) = 503, T_{1u} (ν_4) = 150, T_{2g} (ν_5) = 145, and T_{2u} (ν_6) = 100. The close similarity between ν_1 and ν_3 and ν_4 and ν_5 is somewhat surprising, but an analogous situation is found in octahedral NpF_6,[23] where $\nu_1 = 648$, $\nu_3 = 624$, $\nu_4 = 200$, and $\nu_5 = 206$ cm.$^{-1}$.

Since the $\Gamma_7 \rightarrow \Gamma_8$ transition became vibronically allowed by a coupling with ν_3, it seems reasonable to assign ν_3 as the enabling frequency for the $\Gamma_7 \rightarrow \Gamma_8'$ transition. On this basis the Γ_8' level is placed at 12,705 cm.$^{-1}$ (13,208 − 503). The one remaining level to be assigned, Γ_6, was placed at 14,245 cm.$^{-1}$, corresponding to the observed intense band location at 14,395 cm.$^{-1}$ less the odd mode T_{1u} frequency of 150 cm.$^{-1}$. All of the assigned parent electronic levels were observed with the exception of Γ_8' and possessed the expected weak intensity.

The remaining prominent features of the spectrum appear in the ultraviolet region with very much greater intensity than the already considered crystal-field spectra. This region of heightened absorption strongly indicates that these peaks arise from Laporte-allowed transitions. It is, however, not clear whether these arise from the $5f^1 \rightarrow 6d$ promotion or from the so-called "change-transfer" bands, involving either electron transfer from the central ion antibonding π-orbitals to the nonbonding ligand orbitals or *vice versa*. A choice as to which of these mechanisms corresponds to the observed peaks cannot be unambiguously made in the present study. However, if we take the reported values of the 5f → 6d transition for U^{3+} as 25.5, 28.6, and 31.2 kK.[24] [1 kK. = 1000 cm.$^{-1}$], and those for U^{4+} as 31.8, 33.0, 35.7, and 40.0 kK.,[25] then the values observed here for U^{5+} of 36.2, 40.0, and 44.0 kK. might reasonably be presumed to arise from a similar Laporte-allowed $5f^1 \rightarrow 6d$ transition.

TABLE III

COMPARISON OF EXPERIMENTAL AND CALCULATED CRYSTAL FIELD ENERGY LEVELS FOR $CsUF_6$

Level	Frequency, cm.$^{-1}$ (exptl.)[a]	Frequency, cm.$^{-1}$ (calcd.)
Γ_6	14,245	14,840
Γ_8'	12,705	12,107
Γ_7'	6,928	6,928
Γ_8	4,587	3,989
Γ_7	0	0

[a] The experimental electronic levels have been assigned from observed absorptions and deduced vibrational frequencies.

The final assignment of the 0–0 electronic transitions is shown in Table III. With these assignments the secular determinants were evaluated and the crystal-field parameters calculated by least-squares fit on an electronic computer. The energy levels predicted by the parameters are also shown in Table III along with those transitions observed experimentally. The values of the parameters for $CsUF_6$ are listed in Table IV, along with those for the isoelectronic species $PaCl_6^{2-}$ and NpF_6.[6,7] Figure 4 depicts the energy levels for the three $5f^1$ compounds as calculated from the experimental crystal-field parameters. In Figure 5 we have shown the vibronic scheme for the $\Gamma_7 \rightarrow$

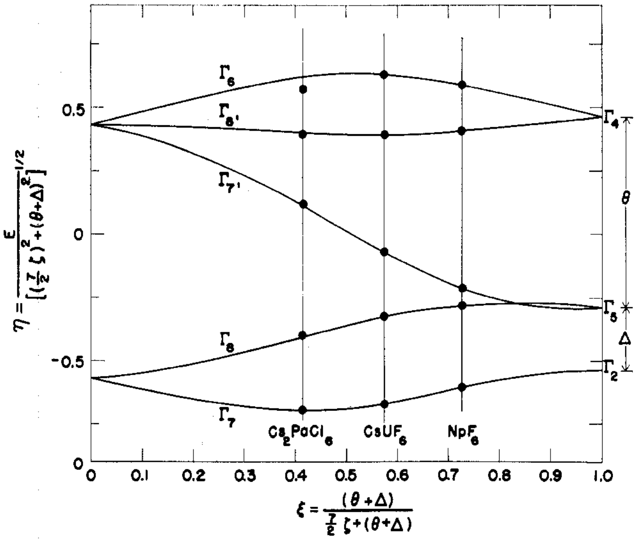

Figure 4.—Energy level diagram of a $5f^1$ electronic system under the influence of an octahedral field. At the extreme left are shown the free ion states and at the right are the pure crystal-field levels with no spin–orbit coupling. The curves have been calculated for a particular value of $\theta/\Delta = 3.0$. For Pa^{4+} this value is actually closer to 1.5, which accounts for the slight discrepancy in the fit for Cs_2PaCl_6.

[24] C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, London, 1962, p. 156.

[25] J. L. Ryan and C. K. Jørgensen, *Mol. Phys.*, **7**, 17 (1963–1964).

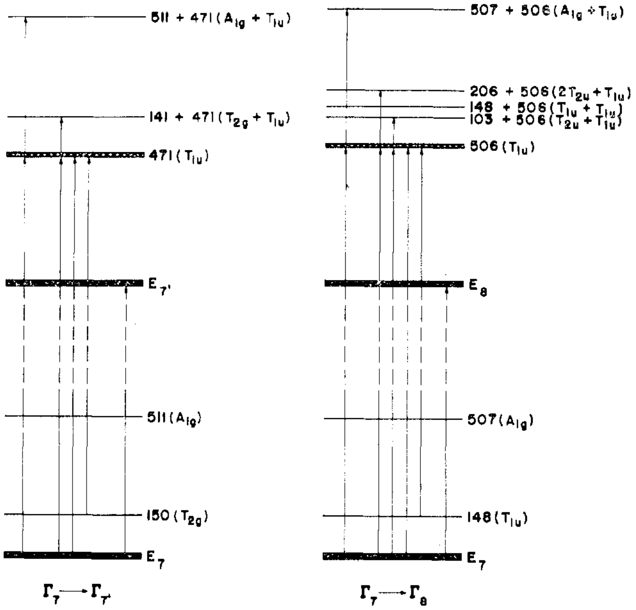

Figure 5.—Vibronic energy levels for $\Gamma_7 \rightarrow \Gamma_7'$ and $\Gamma_7 \rightarrow \Gamma_8$ transitions. The arrows indicate those transitions actually observed. The energy spacings are to scale except for the regions of the dotted lines which are of the order of 10,000 cm.$^{-1}$.

Γ_7' and $\Gamma_7 \rightarrow \Gamma_8$ transitions as deduced from the arguments given above.

With the main features of the spectrum thus accounted for, it remains to examine the reasonableness of the parameters derived from the data. In Table IV the crystal field parameters for Pa(IV) and Np(VI) are listed, along with those found here. Linear interpolation of the ζ_{5f} values, corrected for atomic number and ionic charge, predicts ζ_{5f} for U(V) to be 1947 cm.$^{-1}$ as compared to the experimental value of 1955 cm.$^{-1}$. No simple rule for θ and Δ exists, however, and we will, therefore, employ the following arguments. For a pure octahedral point charge model, the coefficients A_4^0 and A_6^0 are given by

$$A_4^0 = \frac{7Ze^2}{16R^5} \qquad A_6^0 = \frac{3Ze^2}{64R^7} \tag{5}$$

where Z is the ligand charge and R is the ion-ligand distance. The values for R are also shown in Table IV, and by computing the ratio A_4^0/A_6^0 and comparing it to $A_4^0\langle r^4\rangle/A_6^0\langle r^6\rangle$; we may calculate $\langle r^4\rangle/\langle r^6\rangle$. The values for Pa(IV), U(V), and Np(VI) are 0.294, 0.308, and 0.290. The rather good agreement of these values (0.297 ± 0.007) for the radial wave function ratio, which should be a constant for the point-charge crystal field model, along with the agreement with theory as shown by Figure 4, indicates consistent sets of parameters for the 5f^1 compounds treated thus far. By comparison, a SCF calculation for U^{5+} gives $\langle r^4\rangle/\langle r^6\rangle = 0.2178$.[26]

Table IV
Crystal Field Parameters for 5f^1 Ions

	Pa(IV)[6]	U(V)	Np(VI)[7]
ζ_{5f}, cm.$^{-1}$	1490	1955	2,405
Δ, cm.$^{-1}$	1496	2429	5,455
θ, cm.$^{-1}$	2160	6739	16,770
$A_4^0\langle r^4\rangle$, cm.$^{-1}$	888	2351	5,738
$A_6^0\langle r^6\rangle$, cm.$^{-1}$	41.9	208.8	540.5
$\langle r^4\rangle/\langle r^6\rangle$	0.294	0.308	0.290

Finally, then, it may be seen that the spectrum of $CsUF_6$ is dominated by vibronic transitions with the parent electronic states almost absent. The simple crystal-field treatment gives reasonable agreement with the experimental data and provides an excellent check with data gathered for other 5f^1 systems.

Appendix

The eigenfunctions for the 5f^1 orbitals under O_h' are given below. The functions are denoted by $|\Gamma_i^j)$ where i denotes the irreducible representation of the octahedral double group.

$$\begin{array}{lll}
{}^2F_{5/2} & |\Gamma_8^1) = & |1/2) \\
 & |\Gamma_8^2) = & |-1/2) \\
 & |\Gamma_8^3) = & -(1/\sqrt{6})[\sqrt{\ }\,|5/2) + |-3/2)] \\
 & |\Gamma_8^4) = & (1/\sqrt{6})[|3/2) + \sqrt{5}|-5/2)] \\
 & |\Gamma_7^1) = & (1/\sqrt{6})[|5/2) - \sqrt{5}|-3/2)] \\
 & |\Gamma_7^2) = & (1/\sqrt{6})[\sqrt{5}|3/2) - |-5/2)] \\
{}^2F_{7/2} & |\Gamma_6^1) = & (1/2\sqrt{3})[\sqrt{5}|7/2) + \sqrt{7}|-1/2)] \\
 & |\Gamma_6^2) = & (1/2\sqrt{3})[\sqrt{7}|1/2) + \sqrt{5}|-7/2)] \\
 & |\Gamma_8^1) = & (1/2)[|5/2) + \sqrt{3}|-3/2)] \\
 & |\Gamma_8^2) = & (1/2)[\sqrt{3}|3/2) + |-5/2)] \\
 & |\Gamma_8^3) = & (1/2\sqrt{3})[\sqrt{7}|7/2) - \sqrt{5}|-1/2)] \\
 & |\Gamma_8^4) = & (1/2\sqrt{3})[\sqrt{5}|1/2) - \sqrt{7}|-7/2)] \\
 & |\Gamma_7^1) = & (1/2)[|3/2) - \sqrt{3}|-5/2)] \\
 & |\Gamma_7^2) = & (-1/2)[\sqrt{3}|5/2) - |-3/2)]
\end{array}$$

After simultaneous diagonalization of both crystal-field and spin-orbit interactions, the following secular determinants are obtained.

$$\Gamma_6 \quad \left| (3/2)\zeta + (1/7)(4\theta + \Delta) - E \right| = 0$$

$$\Gamma_7 \quad \begin{vmatrix} (3/2)\zeta - (3/7)(\theta + \Delta) - E & 2\sqrt{3}\Delta/7 \\ 2\sqrt{3}\Delta/7 & -2\zeta - (1/7)(3\theta + 2\Delta) - E \end{vmatrix} = 0$$

$$\Gamma_8 \quad \begin{vmatrix} (3/2)\zeta - (1/14)(\theta - 2\Delta) - E & 3\sqrt{5}\theta/14 \\ 3\sqrt{5}\theta/14 & -2\zeta + (1/14)(3\theta + 2\Delta) - E \end{vmatrix} = 0$$

where

$$\Delta = (16/33)[5A_4^0\langle r^4\rangle - (420/13)A_6^0\langle r^6\rangle]$$
$$\theta = (16/33)[4A_4^0\langle r^4\rangle + (280/13)A_6^0\langle r^6\rangle]$$

The octahedral potentials V_i^j are given below.

$$V_4^0 = \Sigma(35z^4 - 30z^2r^2 + 3r^4)$$
$$V_4^4 = \Sigma(x^4 - 6x^2y^2 + y^4)$$
$$V_6^0 = \Sigma(231z^6 - 315z^4r^2 + 105z^2r^4 - 5r^6)$$
$$V_6^4 = \Sigma[(x^4 - 6x^2y^2 + y^4)(11z^2 - r^2)]$$

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(26) D. T. Cromer, Los Alamos Scientific Laboratory, Los Alamos N. M., private communication.