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LOW TEMPERATURE ABSORPTION SPECTRUM OF URANIUM(+3) FORMATE ENERGY LEVEL SCHEME OF URANIUM(+3)*

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ABSTRACT

The absorption spectrum of thin films of $U(HCOO)_3$ was measured at 298, 77 and 4°K in the range 4,000-24,000 cm^{-1}. Electrostatic, spin-orbit and configuration interaction parameters were obtained by least-squares fitting to 12 observed levels for $U(HCOO)_3$. The obtained parameter values (in cm^{-1}) are: $E^1 = 2779$, $E^2 = 14.1$, $E^3 = 271.6$, $\zeta_{5f} = 1656.4$, $\alpha = 17.5$, $\beta = -479$, $\gamma = 1000$. A good agreement with experiment is observed for all calculated levels and a number of new assignments of excited levels of U(+3) is proposed. Intensity calculations were carried out and considered in the problem of level assignment.

INTRODUCTION

The absorption spectra of the U^{+3} ion have been reported in aqueous solutions,[1-6] organic solvents,[7] molten eutectics[8,9] and also have been studied at low temperatures in the U^{+3}; CaF_2[10-12] and U^{+3}; $LaCl_3$[13,14] systems. In all these spectra the low lying bands occur with approximately the same energy. Significant differences in energy and intensity are observed in the range above 13,000 cm^{-1}. The U^{+3} dopped CaF_2 single crystals obtained from Optovac Inc. apparently have more than one site symmetry and hence the validity of the analysis of that spectrum[12] seems to be uncertain.

In the present study a thin film of the Uranium(+3) Formate and Halowax* mixture has been used for a spectroscopic investigation at room, liquid nitrogen and liquid helium temperatures. Single crystals of Uranium(+3) Formate could not be prepared. Uranium(+3) Formate is a stable compound with a known, C_{3v}^5, field symmetry.[15]

The data obtained from this technique are sufficiently precise for a theoretical analysis of the "free ion" energy levels of $U(HCOO)_3$, in the range 4,000-22,000 cm^{-1}. The first theoretical treatment of the U^{+3} spectrum was reported by Jørgensen.[3] An attempt to identify the energy levels of the U^{+3} ion was given by Carnall and Wybourne.[6] These authors have diagonalized the energy matrices for a $5f^3$ configuration, keeping the F_k ratios fixed as determined by Judd[16] for a 5f-hydrogen like eigenfunction. The values of ζ_{5f} = 1666 cm^{-1} and F_2 = 196 cm^{-1} were found to give the best fit for the identified, lowest observed levels. In this paper the problem of the level assignment and theoretical fit to the data in the recorded region, including configuration interaction and intensity correlation, is discussed.

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*Chlorinated napthalene, index of refraction = 1.635.

EXPERIMENTAL

Uranium(+3) Formate was prepared according to the procedure given in Ref. 15. An Uranium(+3) Formate/Halowax mixture was placed between two quartz windows, approximately 1 cm in diameter, and pressed to get a clear and uniform film. Absorption spectra of such Uranium(+3) Formate films were taken at room temperature, at liquid nitrogen and liquid helium temperatures on a Cary 14 Spectrophotometer, in the range 4,000-23,000 cm^{-1}. (Fig. 1.) A thin layer of Halowax oil was used in the reference cell. For low temperature runs, the cell was directly cooled with liquid nitrogen or liquid helium, inside a double all-glass Dewar. The obtained data are presented in Table I. It is interesting to note that in a commercial metal Dewar in which the cell was indirectly cooled with liquid helium by thermal contact with a copper block, we were not able to reach even liquid nitrogen temperature. We also recorded the optical spectrum of an U^{+3}; CaF_2 crystal obtained from Optovac Inc., at liquid nitrogen temperature, in the range 4,000-23,000 cm^{-1}. The spectroscopic data correspond closely to those given in Ref. 12, but indicate more than one site symmetry.

ENERGY-LEVEL CALCULATIONS

Since the theoretical treatment of lanthanide and actinide spectra is discussed in detail in numerous articles and books[17-20] it will not be presented in this paper. The notation used by Wybourne[17] is followed. The energy matrices for the f^3 configuration contained the electrostatic, spin-orbit and configuration interaction elements. In the first step of the U^{+3} energy level identification, only the terms of the electrostatic energy

interaction (E^k) and the spin-orbit interaction constant (ζ_{5f}) were treated as free parameters in a least-squares fit to the experimental centers of the low-lying absorption line groups. Approximate values for these parameters were taken from Carnall and Wybourne's data.[6] In this step of the calculation we were able to make an approximate assignment of 11 levels. In order to assign more levels and obtain better agreement between calculated and observed "free ion" levels, the inclusion of the effects of configuration interaction was essential. The parameters α and β have been previously determined for some actinide ions. Hence the expected values for a $5f^3$ configuration are; $\alpha \approx 20$ cm^{-1}, $\beta = -409$ cm^{-1}.[21] The γ term has not been well determined, however, a value of +1000 is expected to be correct.

More than 100 least-squares fit of seven parameters (E^1, E^2, E^3, ζ_{5f}, α, β and γ) to different combinations of the experimental energy levels were carried out. In the fitting process, first α, β and γ were kept constant. In the final fitting process, only γ was kept constant at 1,000 cm^{-1} while the remaining 6 parameters were freely varied.

A satisfactory agreement between all calculated and observed experimental levels is reached in a fit of 6 parameters (γ was kept constant at 1,000 cm^{-1}) to the following 8 levels: $^4I_{9/2}$(300 cm^{-1}), $^4I_{11/2}$(4,610 cm^{-1}), $^4F_{3/2}$(7,160 cm^{-1}), $^4I_{13/2}$(8,280 cm^{-1}), $^4G_{7/2}$(13,320 cm^{-1}), $^4F_{9/2}$(14,770 cm^{-1}), $^4D_{3/2}$(16,280 cm^{-1}), and $^2K_{15/2}$(18,375 cm^{-1}). The mean energy difference remain within the possible deviations from the experimental centers of gravity. The following levels: $^2H_{11/2}$(15,350 cm^{-1}), $^2K_{13/2}$(15,640 cm^{-1}), $^4D_{5/2}$(17,640 cm^{-1}), and $^2I_{11/2}$(21,370 cm^{-1}) were included in the final calculation. Since the choice of the experimental centers of gravity for the remaining levels is

arbitrary, the results obtained in the fit to 12 experimental levels are preferred. (Table II.) The inclusion of more than 12 levels do not influence the values of the parameters or the position of the levels. It is interesting to note, that we could find only one order of the calculated levels which remained in good agreement with experiment. In some cases, small changes in order were possible and are discussed in the following sections.

The inclusion of γ into the calculation does not have an influence of the results (rms), but may have an influence on the F_k ratios since γ and E^1 are related by a common term $S(S + 1)$ in their coefficients. Hence a change in γ causes a change in E^1 (or F_2) and consequently in the F_k ratios. It is interesting to note, that the calculated ratios of the Slater integrals F_k are very close to that of the hydrogenic approximation. The ratios of the 5f hydrogen-like Slater radial integrals are: $F_4/F_2 = 0.14218$ and $F_6/F_2 = 0.0161$. The corresponding ratios of the obtained F_k parameters are 0.142 and 0.0159.

We found a close dependence between some of the U^{+3} levels. A change in energy of one of these levels, cause a proportional change in the corresponding level in spite of varying the electrostatic and spin-orbit parameters over a wide range ($E^1 \cong 2{,}500$ to $4{,}200$ cm^{-1}, $E^2 \cong 13.0$ to 28.0 cm^{-1}, $E^3 \cong 240$ to 310 cm^{-1}, $\zeta_{5f} = 1{,}480$ to $1{,}740$ cm^{-1}). In these calculations, the configuration interaction parameters were held constant or were not included in the fitting procedure. A close dependence was found between the following levels: $^4F_{3/2}$ and $^4S_{3/2}$, $^4S_{3/2}$ and $^4D_{3/2}$, $^4G_{5/2}$ and $^4G_{7/2}$, $^4F_{7/2}$ and $^4F_{9/2}$, $^4F_{9/2}$ and $^2G_{7/2}$, $^2K_{13/2}$ and $^2K_{15/2}$.

INTENSITY CONSIDERATION

Intensity calculation based upon the derived values of E^k and ζ_{5f}, were carried out in order to get the approximate relative intensities of the allowed transitions and to confirm the assumed "free ion" energy level assignment. We have followed the theory of intensities of f^N transitions in the form derived by Judd[22] and applied by Carnall et al. for various lanthanides and actinides spectra.[20,23-25] The intensity of a particular induced electric dipole transition between the levels $\psi J \rightarrow \psi' J'$ within the f^N configuration may be expressed by the equation:

$$P = \sum_{\lambda=2,4,6} T_\lambda \sigma (f^N \psi J \| U^{(\lambda)} \| f^N \psi J')^2$$

where P is the oscillator strength of a transition between the levels ψJ and $\psi' J'$, or the measured band are for different excited levels with the same J value, assigned to a particular "free ion" level. $\sigma(cm^{-1})$ is the frequency of the baricenter of the transition. $U^{(\lambda)}$ are the matrix elements of a tensor $U^{(\lambda)}$ of rank 2. T_λ are quantities usually treated as parameters to be determined from experimental oscillator strengths or the above mentioned absorption bands area's. The matrix elements $U^{(\lambda)}$ were calculated for us by W. T. Carnall for two different sets of E^k and ζ_{5f} values.

The values of the free ion parameters used are given below:

	E^1	E^2	E^3	ζ_{5f}	α	β	γ
Set I	2747.5	14.7	278.7	1600.1	(23.4	-210.5	933.0)
Set II	3188.8	14.1	274.9	1625.7	(20.0	-400.	-1000.)

The values of the matrix elements $U^{(\lambda)}$ for both sets were found to be very close and insensitive to small changes of E^k and ζ_{5f}.

Using the values of $U^{(\lambda)}$, one can determine quantities proportional to T_λ. Since some free ion levels are very close to each other (see Table I), the experimentally observed components of these levels, may be overlapped. For these levels we were not able to separate the band area's or accurately determine the energy of its baricenters. In such cases, one baricenter was chosen and the area of all bands were measured and compared to the corresponding sum of the matrix elements of $U^{(\lambda)}$. The intensity calculation was made for the spectrum recorded at room temperature. The first six or eight area of absorption band groups were used in a least-squares calculation. The results are presented in Table III. In this fitting process, we obtained the following values, proportional to the T_λ parameter:

$t_2 = 0.00868$, $t_4 = 0.00017$, $t_6 = 0.00407$, (for 7 band areas), and

$t_2 = 0.00554$, $t_4 = 0.00662$, $t_6 = 0.00363$, (for 8 band areas).

Errors may arise from:

(i) some degree of arbitrariness in the choice of the base (zero absorption) line of the spectrum as well as the centers of the absorption line groups.

(ii) the impossibility of separating, in some cases, the areas of absorption line groups, assigned to the corresponding free ion energy level. This is due to the possible overlapping of the components of close centered energy levels.

Considering these remarks, one should not overestimate the results presented in Table III, however, they are given as evidence supporting the assignment of the U^{+3} free ion energy levels in $U(HCOO)_3$.

RESULTS

In the investigated spectral range it is possible to separate 10 line groups. We arbitrary designate them by the capital letters ABC ... . In the following discussion, a detailed review of the various line groups is presented.

Group A (~ 300 cm^{-1})

Since the Uranium(+3) Formate does not exhibit fluorescence, little is known about its ground level structure. By comparison with the determined centers of gravity of the $^4I_{9/2}$ level for the $Np^{+4}/Pb\ N_6O_4$ [26] and U^{+3}/CaF_2 [12] systems, we assumed for U^{+3} a value of 300 cm^{-1}.

Group B (~ 4,600 cm^{-1})

This band was first observed by Carnall and Wybourne[6] in $DClO_4$ and molten LiCl-KCl eutectic solutions of U^{+3}. Studies of the crystal absorption spectra[10-13] confirmed the assignment of that band to the first U^{+3} excited level with J = 11/2 and more than 83% of ^4I character. This assignment determines at the same time the approximate positions of the $^4I_{13/2}$, $^4I_{15/2}$ and $^4F_{3/2}$ levels at ~ 8,200, 11,300 and 7,150 cm^{-1}, respectively, since large deviations from this energy give unreasonable values of ζ_{5f} and E^k. Some of the 10 components found may be vibronic, but without further investigations they can not be easily identified since they do not show an apparent pattern. The band observed at room temperature, at 4,345 cm^{-1}, is an example of temperature dependent satellite line since the peak disappears on cooling. Similar satellite lines appear at 7,960, 9,124, 10,600 and 13,077 cm^{-1}, all centered at ~ 300 cm^{-1} from one of the electronic lines.

Group C (~ 7,160 cm^{-1})

This group, assigned to the $^4F_{3/2}$ level, consists as expected for the C_{3v} symmetry of two components at 7,139 and 7,184 cm^{-1}. Since this is one of

the 5 well-separated bands, a nearly exact agreement between the observed and calculated energy is indispensable in a correct energy scheme.

Group D (7,878-8,700 cm^{-1})

There are observed all 7 components, expected for the $^4I_{13/2}$ level, however, it can not be excluded that some of them may be vibronic.

Group E (9,419-10,274 cm^{-1})

Five bands were recorded for this group, which correspond to the transitions to the $^2H_{9/2}$ and $^4F_{3/2}$ levels. The positions of its centers of gravity can not be well estimated, since the band centered at 9,734 can be associated with either the $^2H_{9/2}$ or the $^4F_{5/2}$ level. Depending on the assignment, baricenters will shift.

Group F (10,911-11,958 cm^{-1})

The 9 recorded bands corresponds to transitions to the $^4S_{3/2}$, $^4G_{5/2}$, $^4I_{15/2}$ and $^4F_{7/2}$ levels. According to the intensity calculation, the band centered at 10,911 cm^{-1} should be a component of the $^4G_{5/2}$ level. We noticed that in the results of the various fitting processes, the distance between the $^4G_{5/2}$ and the next $^4G_{7/2}$ levels was always kept nearly constant. Since the experimental center of gravity of the $^4G_{7/2}$ level can not be placed below 13,320 cm^{-1}, the calculated energy of the $^4G_{5/2}$ level can not occur below 11,100 cm^{-1}. The energy of the $^4F_{7/2}$ level is found to be proportional to that of the $^2H_{9/2}$ level, whose center of gravity is assumed to be above 14,600 cm^{-1}. Consequently, the energy of the $^4F_{7/2}$ level occur above 11,500 cm^{-1}. The positions of the $^4S_{3/2}$ and $^4I_{15/2}$ levels depends upon the earlier assignments, hence they may vary slightly around 11,100 and 11,400 cm^{-1}, respectively.

Since it is apparent that the components of these levels are overlapped and the centers of gravity can not be determined, they could not be included in the fitting calculations.

Group G (~ 13,320 cm^{-1})

The observed components of the band at 13,271, 13,374, and 13,623 cm^{-1} are well isolated from other absorption bands by more than 1,000 cm^{-1}. We found this can only be the $^4G_{7/2}$ level.

Group H (14,637-17,077 cm^{-1})

Since most of the components of the "free ion" levels, centered in that range may be overlapped, an exact assignment of the various observed lines to the calculated levels, has little physical meaning. In the following group G, the theory predicts the most intense transition to the $^2K_{15/2}$ level, which must therefore be centered at 18,375 cm^{-1}. This assignment, in addition to those made earlier: $^4I_{11/2}$ at 4,600 cm^{-1}, $^4F_{3/2}$ at 7,160 cm^{-1}, $^4I_{13/2}$ at 8,200 cm^{-1} and $^4G_{7/2}$ at 13,320 cm^{-1}, immediately determined the final order and approximate energy of the "free ion" levels as well in the H group for the whole observed spectrum, however, some changes in energy and order are still possible. The calculated order of levels in this group is as follows; $^4F_{9/2}$, $^2H_{11/2}$, $^2K_{13/2}$, $^2D_{3/2}$, $^2P_{1/2}$, $^2G_{7/2}$ and $^4G_{9/2}$. According to the intensity calculations, the most intense transitions in this group, should be to the $^2K_{13/2}$ and $^2D_{3/2}$ levels. In the course of the various fittings procedures, we found that the energy of the $^2K_{13/2}$ level is proportional to that of $^2K_{15/2}$, but can vary from ~ 15,100 to ~ 15,700 cm^{-1} causing proportional shifts on the $^4F_{9/2}$ and $^2K_{13/2}$ levels, while the assigned levels are kept constant. However, the $^4F_{9/2}$ level should occur with a relatively weak intensity, its center of gravity may not

be expected below 14,700 cm^{-1}. Hence, the first 8 bands, centered between 14,637 and 16,054 cm^{-1} should belong to the $^4F_{9/2}$, $^2H_{11/2}$ and $^2K_{13/2}$ levels, with the centers of gravity at 14,770, 15,350 and 15,670 cm^{-1}. The next 2 intense bands, recorded at 16,263 and 16,295 cm^{-1} have to be assigned to the $^2D_{3/2}$ level. This level can not change its position without a significant influence on the energy of the $^4F_{3/2}$ and $^4S_{3/2}$ levels. In the fitting process, it was found that the energy of the $^2P_{1/2}$ level remain nearly constant around 16,650 cm^{-1}. The last bands observed in that group, centered between 16,883 and 17,077 cm^{-1}, should then be assigned to the $^2G_{7/2}$ and $^4G_{9/2}$ levels. Their energy depends on those of the assigned levels; $^4G_{7/2}$ and $^4F_{9/2}$, respectively. In the least-squares fit, only the experimental centers of gravity of the $^4F_{9/2}$, $^2H_{11/2}$, $^2K_{13/2}$ and $^2D_{3/2}$ may be considered.

Group I (17,508-20,450 cm^{-1})

In that group, the transitions with the highest intensity occur to the $^2K_{15/2}$ and $^2D_{3/2}$ levels, and are therefore centered at 18,375 and around 19,200 cm^{-1}, respectively. The first 3, relatively weak bands, observed between 14,670 and 15,006 cm^{-1} should be assigned to transitions to the $^4D_{5/2}$ level, while the bands recorded between 19,344 and 20,432 are assigned to the $^2I_{11/2}$ and $^2D_{5/2}$ levels.

Group J (21,082-21,500 cm^{-1})

The 3 bands, recorded at 21,082, 21,371 and ~ 21,500 cm^{-1}, belong to the $^4I_{11/2}$ and $^2G_{9/2}$ levels.

CONCLUDING COMMENTS

The present analysis includes more levels and gives a much better fit to the data in the whole investigated region as compared to earlier work. This was accomplished by inclusion of the configuration interaction parameters into the calculation. The free ion energy level parameters obtained in a fit where all except γ were freely varied, are close to those expected. Since we were able to determine only 12 centers of gravity of the experimental line groups, the evaluation of γ in this fit would have little physical meaning.

We would like to point out that, according to our calculation, the given level assignment appears as the only one which gives a good agreement with experiment. It should be emphasized, however, that the calculated energy for most of the levels may easily be changed up to 300 cm^{-1} with only a slight change of the free ion parameters.

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FOOTNOTES AND REFERENCES

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Table I. Energy-level assignments.

Line group	Level assignment[a]	Observed at liquid helium temperature mμ	Observed at liquid helium temperature cm^{-1}	Center of gravity cm^{-1}	Calculated energy levels cm^{-1}	Composition of eigenvectors of the free ion levels						
A	$^4I_{9/2}$			300*	324	$-0.0282\,^4F$	$-0.0479\,^4G$	$-0.9095\,^4I$	$0.0837\,^2G1$	$-0.0788\,^2G2$	$-0.1208\,^2H1$	$0.3767\,^2H2$
		2350.7	4254									
		2231.4	4479									
		2204.6	4534									
		2190.8	4561									
		2183.0	4579									
B	$^4I_{11/2}$	2175.7	4595	4610*	4603	$0.0373\,^4G$	$0.9733\,^4I$	$0.0829\,^2H1$	$-0.2082\,^2H2$	$-0.0333\,^2I$		
		2151.5	4646									
		2148.0	4654									
		2121.3	4712									
		2064.5	4842									
C	$^4F_{3/2}$	1400.3	7139	7160*	7147	$0.1691\,^4S$	$0.0981\,^4D$	$-0.7967\,^4F$	$0.2669\,^2P$	$-0.4715\,^2D1$	$0.1832\,^2D2$	
		1301.5	7184									
		1269.0	7878									
		1231.9	8115									
D	$^4I_{13/2}$	1207.2	8281	8280*	8267	$0.9605\,^4I$	$-0.0984\,^2I$	$0.2603\,^2K$				
		1197.2	8350									
		1172.4	8527									
		1161.3	8608									
		1149.1	8700									

(continued)

Table I (continued)

Line group	Level assignment[a]	Observed at liquid helium temperature mμ	Observed at liquid helium temperature cm^{-1}	Center of gravity cm^{-1}	Calculated energy levels cm^{-1}	Composition of eigenvectors of the free ion levels						
		1061.3	9419									
	$^2H_{9/2}$	1054.3	9482		9514	$0.3436\,^4F$	$0.2660\,^4G$	$-0.3558\,^4I$	$-0.4317\,^2G1$	$0.3798\,^2G2$	$0.2089\,^2H1$	$-0.5571\,^2H2$
E		1027.0	9734									
	$^4F_{5/2}$	991.3	10084		9869	$-0.0404\,^4D$	$-0.7868\,^4F$	$0.4647\,^4G$	$-0.2942\,^2D1$	$-0.0621\,^2D2$	$0.1964\,^2F1$	$0.1443\,^2F2$
		973.0	10274									
		916.2	10911									
		914.5	10931									
	$^4S_{3/2}$	898.2	11130		11118	$0.7861\,^4S$	$0.0960\,^4D$	$0.3811\,^4F$	$0.4711\,^2P$	$-0.0759\,^2D1$	$-0.0012\,^2D2$	
F	$^4G_{5/2}$	886.8	11273		11275	$-0.0690\,^4D$	$0.5064\,^4F$	$0.8125\,^4G$	$0.1552\,^2D1$	$-0.0905\,^2D2$	$0.1598\,^2F1$	$0.1443\,^2F2$
	$^4I_{15/2}$	880.2	11360		11441	$-0.8977\,^4I$	$-0.4195\,^2K$	$0.1351\,^2L$				
	$^4F_{7/2}$	867.6	11522		11501	$0.0166\,^4D$	$0.7152\,^4F$	$0.2909\,^4G$	$-0.0590\,^2F1$	$-0.0833\,^2F2$	$-0.4743\,^2G1$	$0.4142\,^2G2$
		860.2	11624									
		849.0	11775									
		836.0	11958									
		753.3	13271									
G	$^4G_{7/2}$	747.5	13374	13320*	13318	$0.0405\,^4D$	$0.4702\,^4F$	$-0.8414\,^4G$	$-0.1229\,^2F1$	$-0.1434\,^2F2$	$0.1049\,^2G1$	$-0.1504\,^2G2$
		733.8	13623									

(continued)

Table I (continued)

Line Group	Level assignment[a]	Observed at liquid helium temperature mμ	Observed at liquid helium temperature cm^{-1}	Center of gravity cm^{-1}	Calculated energy levels cm^{-1}	Composition of eigenvectors of the free ion levels						
		683.0	14637									
	$^4F_{9/2}$	676.8	14771	14770*	14776	$0.7903\,^4F$	$-0.2104\,^4G$	$0.1695\,^4I$	$-0.2266\,^2G1$	$0.0873\,^2G2$	$-0.0665\,^2H1$	$0.4889\,^2H2$
		665.5	15022									
		652.1	15331									
	$^2H_{11/2}$	650.5	15368	15350*	15355	$0.5240\,^4G$	$-0.1918\,^4I$	$0.1520\,^2H1$	$-0.7802\,^2H2$	$0.2382\,^2I$		
		640.5	15608									
	$^2K_{13/2}$	638.0	15670	15640*	15634	$-0.2760\,^4I$	$-0.2165\,^2I$	$0.9365\,^2K$				
H		622.7	16054									
		614.7	16263									
	$^4D_{3/2}$	613.5	16295	16280*	16280	$0.4708\,^4S$	$-0.4984\,^4D$	$-0.3793\,^4F$	$-0.3167\,^2P$	$0.3809\,^2D1$	$-0.3752\,^2D2$	
	$^2P_{1/2}$	605.5	16510		16683	$0.6713\,^4D$	$0.7411\,^2P$					
	$^2G_{7/2}$	593.9	16833		16877	$0.0374\,^4D$	$-0.5042\,^4F$	$-0.4143\,^4G$	$-0.0746\,^2F1$	$-0.0744\,^2F2$	$-0.5720\,^2G1$	$0.4842\,^2G2$
	$^4G_{9/2}$	592.0	16877		16990	$0.0186\,^4F$	$0.9016\,^4G$	$0.1064\,^4I$	$0.0488\,^2G1$	$0.0880\,^2G2$	$-0.2862\,^2H1$	$0.2889\,^2H2$
		585.4	17077									
		571.0	17508									
	$^4D_{5/2}$	567.3	17622	17640*	17635	$-0.6508\,^4D$	$0.1629\,^4F$	$-0.2224\,^4G$	$-0.3422\,^2D1$	$-0.5629\,^2D2$	$0.1907\,^2F1$	$0.1735\,^2F2$
		562.5	17772									
		554.5	18029									
		545.5	18326									
	$^2K_{15/2}$	542.6	18424	18375*	18367	$0.4013\,^4I$	$-0.6514\,^2K$	$0.6440\,^2L$				

(continued)

Table I (continued)

Line group	Level assignment[a]	Observed at liquid helium temperature mμ	Observed at liquid helium temperature cm^{-1}	Center of gravity cm^{-1}	Calculated energy levels cm^{-1}	Composition of eigenvectors of the free ion levels						
I		536.0	~ 18650									
	$^4D_{3/2}$	523.2	19108		19248	$-0.2669\,^4S$	$-0.6204\,^4D$	$0.1543\,^4F$	$0.3748\,^2P$	$-0.4407\,^2D1$	$-0.4305\,^2D2$	
		515.5	19393									
	$^2H_{11/2}$	510.0	19602		19569	$0.5063\,^4G$	$0.1151\,^4I$	$-0.7168\,^2H1$	$0.2845\,^2H2$	$0.3684\,^2I$		
		505.1	19792									
		495.4	20180									
	$^2D_{5/2}$	488.8	20450		20221	$-0.4243\,^4D$	$-0.2909\,^4F$	$-0.0445\,^4G$	$0.8506\,^2D1$	$-0.0570\,^2D2$	$0.0463\,^2F1$	$0.0665\,^2F2$
		474.2	21082									
J	$^2I_{11/2}$	467.8	21371	21370*	21391	$0.6116\,^4G$	$-0.0151\,^4I$	$0.1260\,^2H1$	$0.2093\,^2H2$	$-0.7524\,^2I$		
	$^2G_{9/2}$	468.4	21622		21618	$-0.4826\,^4F$	$-0.0508\,^4G$	$0.0755\,^4I$	$-0.5608\,^2G1$	$0.3880\,^2G2$	$0.3095\,^2H1$	$0.4450\,^2H2$
	$^4D_{1/2}$				21946	$0.7411\,^4D$	$-0.6713\,^2P$					
	$^4D_{7/2}$				22921	$0.9623\,^4D$	$-0.0360\,^4F$	$0.0831\,^4G$	$-0.2227\,^2F1$	$-0.0952\,^2F2$	$0.0834\,^2G1$	$0.0095\,^2G2$
	$^2D_{3/2}$				23447	$-0.1999\,^4S$	$0.4161\,^4D$	$-0.2118\,^4F$	$0.4877\,^2P$	$0.4288\,^2D1$	$-0.5660\,^2D2$	
	$^2I_{13/2}$				24074	$0.0358\,^4I$	$0.9713\,^2I$	$0.2351\,^2K$				
	$^2L_{15/2}$				24487	$0.1822\,^4I$	$-0.6322\,^2K$	$-0.7531\,^2L$				
	$^2H_{9/2}$				24731	$0.1381\,^4F$	$0.2551\,^4G$	$-0.0210\,^4I$	$0.1143\,^2G1$	$-0.4450\,^2G2$	$0.8277\,^2H1$	$0.1389\,^2H2$
	$^2L_{17/2}$				25231	$1.0000\,^2L$						
	$^2D'_{5/2}$				25833	$-0.5454\,^4D$	$-0.0348\,^4F$	$0.2330\,^4G$	$-0.1825\,^2D1$	$0.3148\,^2D2$	$-0.4491\,^2F1$	$-0.5593\,^2F2$

(continued)

Table I (continued)

Line group	Level assignment[a]	Observed at liquid helium temperature mμ	Observed at liquid helium temperature cm^{-1}	Center of gravity cm^{-1}	Calculated energy levels cm^{-1}	Composition of eigenvectors of the free ion levels						
	$^2D_{3/2}$				27014	$0.1440\,^4S$	$0.4179\,^4D$	$0.0871\,^4F$	$-0.4777\,^2P$	$-0.4988\,^2D1$	$-0.5657\,^2D2$	
	$^2H_{11/2}$				28536	$0.3060\,^4G$	$0.0495\,^4I$	$0.6636\,^2H1$	$0.4723\,^2H2$	$0.4903\,^2I$		
	$^2F_{7/2}$				30610	$0.2185\,^4D$	$0.1007\,^4F$	$-0.1475\,^4G$	$0.4393\,^2F1$	$0.8225\,^2F2$	$-0.2073\,^2G1$	$-0.0892\,^2G2$
	$^2D_{5/2}$				30978	$-0.2984\,^4D$	$0.1098\,^4F$	$-0.1327\,^4G$	$-0.1184\,^2D1$	$0.7524\,^2D2$	$0.4188\,^2F1$	$0.3546\,^2F2$
	$^2G_{9/2}$				32929	$0.0651\,^4F$	$-0.0467\,^4G$	$0.0008\,^4I$	$0.6522\,^2G1$	$0.6969\,^2G2$	$0.2732\,^2H1$	$0.0894\,^2H2$
	$^2G_{7/2}$				33365	$-0.0588\,^4D$	$0.0367\,^4F$	$-0.0652\,^4G$	$-0.1654\,^2F1$	$0.3153\,^2F2$	$0.5957\,^2G1$	$0.7137\,^2G2$
RMS[b]					19.7							

[a]Major component of eigenvector

[b]RMS = $\sum_i (\Delta_i^2/n)^{1/2}$ where Δ_i is the difference between observed and calculated energies, and n is the number of observed levels used in the fitting procedure.

*Levels included in the least-squares fit.

Table II. Free ion parameters obtained from the fitting routine to 12 experimental levels.

E^0	E^1	E^2	E^3	ζ_{5f}	α	β	γ
12,350	2,779	14.1	272	1,656	17.5	-479	1,000

Table III. Intensity Correlations

Level assignment S'L'J'	Center of band energy (cm^{-1})	Matrix Elements of $U^{(\lambda)}$ U(2)	U(4)	U(6)	Observed band area (Abs.×cm^{-1})	Calculated band area for six groups	for eight groups
$^4I_{9/2}$	269	0.0683	0.1051	0.3855			
$^4I_{11/2}$	4610	0.0215	0.1051	1.0724	16.5	21.0	21.7
$^4F_{3/2}$	7160	0.0000	0.1092	0.0100	2.8	0.4	5.4
$^4I_{13/2}$	8280	0.0071	0.0095	0.5006	36.8	17.4	15.9
$^2H_{9/2}$	9700	0.0567	0.0485	0.4368	46.8	48.6	78.0
$^4F_{5/2}$		0.1971	0.5910	0.2251			
$^4S_{3/2}$	11400	0.0000	0.0561	0.2676	121.5	121.5	110.2
$^4G_{5/2}$		0.7101	0.2032	0.1679			
$^4I_{15/2}$		0.0000	0.0188	0.1004			
$^4F_{7/2}$		0.0344	0.0006	0.4816			
$^4G_{7/2}$	13320	0.0891	0.2924	0.0028	18.5	11.1	32.5

(continued)

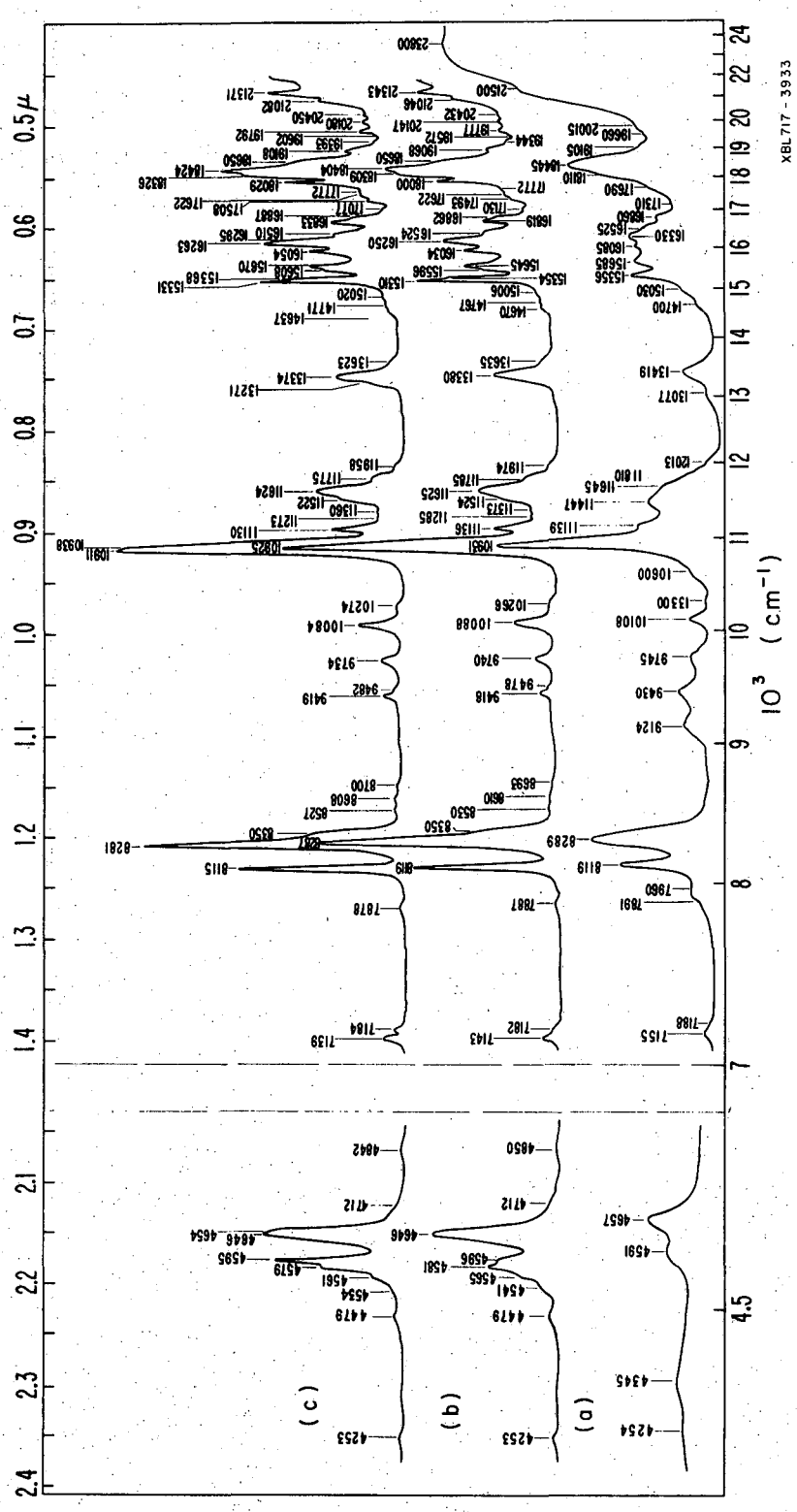
Table III (continued)

Level assignment S'L'J'	Center of band energy (cm^{-1})	Matrix Elements of $U^{(\lambda)}$ U(2)	U(4)	U(6)	Observed band area (Abs × cm^{-1})	Calculated band area for six groups	for eight groups
$^4F_{9/2}$		0.0021	0.0347	0.0088			
$^2H_{11/2}$		0.0026	0.0283	0.0253			
$^2K_{13/2}$		0.0342	0.0001	0.1237			
$^4D_{3/2}$	16200	0.0000	0.1210	0.0115	121.7		65.4
$^2P_{1/2}$		0.0000	0.0154	0.0233			
$^2G_{7/2}$		0.0044	0.1817	0.0000			
$^4G_{9/2}$		0.0016	0.0727	0.0227			
$^4D_{5/2}$		0.0000	0.0346	0.0360			
$^2K_{15/2}$	18425	0.0000	0.1125	0.0924	87.6		46.3
$^4D_{3/2}$		0.0000	0.0967	0.0117			

FIGURE CAPTION

Fig. 1. Absorption spectrum of $U(HCOO)_3$:

(a) at 298°K; (b) 77°K; (c) 4°K.


0.5 μ
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21
22
23
24
4.5
10^3 (cm^{-1})
(a)
(b)
(c)
XBL 717 - 3933

Fig. 1

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