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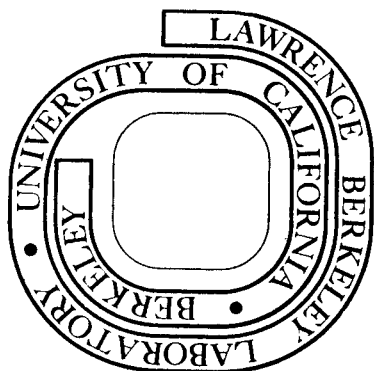
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SPECTRAL PROPERTIES OF $(\text{Et}_4\text{N})_2\text{UI}_6$ AND $(\text{Et}_4\text{N})_2\text{UF}_6$ [†]

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ABSTRACT

The optical spectra of $(\text{NEt}_4)_2\text{UI}_6$ and $(\text{NEt}_4)_2\text{UF}_6$ are presented and analyzed. With these data the electrostatic, spin-orbit, and crystalline field parameters have been obtained for the series of octahedral compounds UX_6^{2-} ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$). The Slater parameter F^2 diminishes approximately 20% as the halide ion changes from F^- to I^- . The crystalline (or ligand) field parameters for comparable PaX_6^{2-} and UX_6^{2-} compounds vary markedly.

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Introduction

The preparation and spectral properties of octahedral compounds of the type $(\text{NEt}_4)_2\text{PaX}_6$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) have recently been investigated.¹⁻³ The trends in the ligand field parameters θ and Δ for these $5f^1$ complexes were explained qualitatively in terms of molecular orbital theory by large variations in σ bonding dominating the total ligand field splitting and changing markedly as the halide ion varied. This same trend was also found for salts of the hexahalogenouranates(V). As part of the above program the corresponding $(\text{NEt}_4)_2\text{UX}_6$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) salts were prepared and their optical spectra obtained at 77 K.^{2,3} The most thorough analyses of the octahedral UX_6^{2-} spectra ($X = \text{Cl}, \text{Br}$) have been given by Satten and coworkers from data obtained at 4 K on U^{4+} diluted in single crystals.⁴⁻⁶ We report in this paper the analyses of the spectra of $(\text{NEt}_4)_2\text{UX}_6$ ($X = \text{I}, \text{F}$) and compare the trends in the parameters obtained for the U^{4+} series ($5f^2$) as the halide ion is varied, with the corresponding parameters in the $5f^1$ series.

Experimental and Calculations

The preparation of $(\text{NEt}_4)_2\text{UI}_6$ and $(\text{NEt}_4)_2\text{UF}_6$ and the recording of their spectra at room temperature and 77 K have been described previously.^{2,3,7}

Calculated energies were obtained by the simultaneous diagonalization of the combined electrostatic, spin-orbit, and crystalline field matrices which were constructed by the tensor operator methods described by Judd⁸ and Wybourne.⁹ These matrices were factored by the crystal quantum number, μ , into a 25x25 matrix ($\mu = 0$, Γ_1 and Γ_2 states); a 24x24 matrix ($\mu = 2$, Γ_3 and Γ_4 states); and two 21x21 matrices ($\mu = 1$, a doubly

degenerate Γ_5 state). Matrices of these ranks can be easily diagonalized by existing computer programs so no further factoring was necessary. Experimental energies were compared with calculated energies and the parameters of the above interactions were adjusted to provide the best fit. Our computer program was checked by reproducing the energy levels for Cs_2UBr_6 and Cs_2UCl_6 given by Satten et al.⁴ using their parameters.

The crystal field Hamiltonian for octahedral symmetry was defined as

$$\begin{aligned} \mathcal{H}_c = & B_0^4 [C_0^{(4)} + (5/14)^{1/2} (C_{-4}^{(4)} + C_4^{(4)})] \\ & + B_0^6 [C_0^{(6)} - (7/2)^{1/2} (C_{-4}^{(6)} + C_4^{(6)})] \end{aligned}$$

following the nomenclature given by Wybourne.⁹ For our calculations we set the ratios of $F^4/F^2 = .74$ and $F^6/F^2 = .55$.^{10,11} These ratios were obtained from a review of the data available from spectra of free ions and trivalent 4f and 5f ions in the solid state and were found to be constant for a wide range of measurements.¹²

Results

Figure 1 shows the spectra obtained for $(\text{NEt}_4)_2\text{UX}_6$ ($X = \text{Cl}, \text{Br}, \text{I}$) and for Cs_2UCl_6 . As can be seen immediately the general features of these spectra are very similar, the UI_6^{2-} spectrum showing shifts to lower energies when compared to the UBr_6^{2-} and UCl_6^{2-} spectra. The situation for $(\text{NEt}_4)_2\text{UF}_6$ is quite different as shown in Figure 2. This spectrum shows almost no similarity to the other UX_6^{2-} spectra and the peaks are strongly shifted to higher energies.

High resolution optical spectra of UCl_6^{2-} and UBr_6^{2-} have been studied in great detail by Satten and coworkers.⁴⁻⁶ These spectra are

dominated by vibronic transitions which appear at regularly spaced intervals on either side of the pure electronic transitions. For O_h symmetry the pure electronic dipole transition within an ℓ^n configuration is forbidden; however, vibrations of ungerade character break the inversion symmetry and are observed superimposed upon the pure electronic transition. In some instances the pure electronic transitions are not observed but are deduced from the vibronic assignments. Satten and coworkers have interpreted in this fashion the spectra of UCl_6^{2-} and UBr_6^{2-} . We make use of their assignments and similarly assign the UI_6^{2-} spectrum.

The vibrational frequencies for UBr_6^{2-} and UCl_6^{2-} have been studied extensively^{4-6,13-15} and we estimate the corresponding values for UI_6^{2-} by use of the following equation,³

$$\nu_i(I) = \sqrt{\frac{M(\text{Cl or Br})}{M(I)}} (\nu_i(\text{Cl or Br})) \quad (1)$$

where ν_i is the frequency of the halide atom-metal vibration and M is the mass of the halide atom, and the data reported by Brown, et al.¹⁶ The calculated values are given in Table I and compared with the available measurements.

From the estimated and measured vibrational frequencies and by comparison with other UX_6^{2-} ($X = \text{Cl, Br}$) spectra we assigned eight electronic levels as shown in Table II. The vibrational frequencies observed do not fit well with the values expected for ν_3 and ν_4 . The discrepancies could be due to errors in choosing the centers of overlapping peaks and/or the possibility of other normal modes or combinations of normal modes falling in these ranges also. However, the assignments were primarily made on the basis of the similarities with other UX_6^{2-} ($X = \text{Cl, Br}$) spectra.

By comparing the experimental energies with the calculated spectrum we were able to make three more assignments as shown in Table III. This table also shows the calculated and experimental energy levels. The parameters obtained by the "best fit" are given in Table IV. We also observed a small shift in the spectra of $(\text{NEt}_4)_2\text{UX}_6$ ($X = \text{Br}, \text{Cl}$) from that found by Satten, et al. for the Cs_2UX_6 ($X = \text{Cl}, \text{Br}$). We assigned these spectra and obtained the "best fit" parameters shown in Table IV and the energy levels given in Figure 3.

The interpretation of the spectrum of $(\text{NEt}_4)_2\text{UF}_6$ posed a more difficult problem. The vibrational frequencies expected were calculated by use of equation (1) and are given in Table I along with the reported values obtained from the vibronic spectrum of PaF_6^{2-} and ir measurements on UF_6^{2-} .^{2,17} The vibrational frequencies for UF_6^{2-} are much higher than for the other halides so they were well resolved in the spectrum. The most consistent vibrational frequency was observed at $\sim 360 \text{ cm}^{-1}$. This value corresponds with that calculated for ν_3 (see Table I) but disagrees with the assignment obtained from the ir spectrum.² The energy levels for UF_6^{2-} were shifted strongly to higher energies but the same general ordering was expected as found for the other UX_6^{2-} complexes. On this basis the assignments given in Table II were made. For levels above 12000 cm^{-1} the assignments were determined by the proximity of the calculated and observed levels. The parameters are given in Table IV and the energy levels are shown in Figure 3.

It can be seen from Figure 3 that several pairs of energy levels for UF_6^{2-} are interchanged when compared to the energy levels of the other halide complexes. This change in order was necessary to obtain good agreement between the calculated and observed levels. In one case this changeover can be directly traced from the spectra. The spectrum of $(\text{NEt}_4)_2\text{UI}_6$ shows well-resolved lines at 6640 cm^{-1} (Γ_5) and

7169 cm^{-1} (Γ_4). For the UBr_6^{2-} complex these two lines come closer and for UCl_6^{2-} we observe only a broad line with unresolved structure. Finally in $(\text{NEt}_4)_2\text{UF}_6$ we find again two well-resolved levels with the inverse order, (8290 cm^{-1} , Γ_4 ; 8577 cm^{-1} , Γ_5).

Discussion

The electrostatic, spin-orbit, and crystalline field parameters obtained from our analyses and from Satten, et al.⁴ are tabulated in Table IV. One trend is immediately evident. All parameters except B_0^6 increase as the halide ion is changed from I^- to F^- . The change is most abrupt from Cl^- to F^- as expected from the spectra. The crystalline field parameters for the analogous PaX_6^{2-} and UX_6^{2-} compounds were expected to be similar, with the Pa parameters larger due to the greater magnitude of the radial expectation values $\langle r^n \rangle$. The effects due to the larger radial values for Pa^{4+} would be offset to a degree by the smaller ionic radius of U^{4+} . In fact, except for the fluoride complexes, the crystalline field parameters given in Table IV show none of the expected trends.

The differences between the PaX_6^{2-} and UX_6^{2-} arises from the addition of a 5f electron so that in the $5f^2$ case we have the additional electrostatic parameters F^2 , F^4 , and F^6 . Our calculations were performed with fixed ratios for F^4/F^2 and F^6/F^2 so we discuss only F^2 . One of the surprising results of our analysis is the great change in F^2 as the halide ion is varied; of the order of 20%. In order to check this result we have also calculated the effect of fixed values for the configuration interaction parameters, α , β , γ (obtained from the results of the analysis of Np^{3+} diluted in LaCl_3)¹⁸ and found no significant change in the fit of experimental and calculated levels nor in the empirical parameters.

We compare in Table V the values of Δ and θ ,¹ the parameters obtained from ligand field theory, for the PaX_6^{2-} and UF_6^{2-} complexes. The value of Δ , the parameter which depends only on π bonding, is the same for the UF_6^{2-} and PaF_6^{2-} complexes; but although it is diminished for the other UX_6^{2-} complexes relative to the PaX_6^{2-} complexes, it is approximately constant. However, θ , which depends on both π and σ bonding is relatively constant for the entire UX_6^{2-} series, in striking contrast to the PaX_6^{2-} which shows a substantial lowering as the halide ion is changed from F^- to I^- . The spin-orbit coupling constant ζ , also changes more markedly for the UX_6^{2-} series than for the PaX_6^{2-} series.

Let us consider only the electrostatic and spin-orbit parameters. For the PaX_6^{2-} complexes the spin-orbit parameters are approximately equal for all three compounds while for the UX_6^{2-} complexes there is a significant decrease in this parameter between UF_6^{2-} and the other compounds. Qualitatively, we can attribute a reduction in the spin-orbit parameter to covalency effects, which would then appear to be significant in the chloride, bromide, and iodide complexes and in PaF_6^{2-} , but not in the UF_6^{2-} complex. Again, the difference between the PaF_6^{2-} and UF_6^{2-} complex may be attributed to the greater radial extent of the 5f wavefunction for Pa^{4+} . B.R. Judd¹⁹ has pointed out that the observed values of F^2 for the UX_6^{2-} compounds correlate in a roughly linear way with the polarizability of the halide ion, and a qualitative calculation has shown that a nearby polarizable atom or ion will always reduce the effective coulombic interaction in a second ion.²⁰ However, these qualitative models suggest larger values for the crystalline field parameters for the Pa complexes, contrary to the observed trends of the

chloride, bromide, and iodide compounds.

Another way of interpreting the change in F^2 in this series of complexes is by use of the nephelauxetic effect.²¹ We would then expect the electron cloud about the metal ion to expand toward the ligands with the effect to be largest for I^- and smallest for F^- . If we define β' as the ratio $\frac{F^2(\text{complex})}{F^2(\text{free ion})}$ and assume $\beta' = 1$ for UF_6^{2-} , then we find $\beta' = .87$ for UCl_6^{2-} ; $\beta' = .82$ for UBr_6^{2-} , and $\beta' = .77$ for UI_6^{2-} . This trend follows that found in the d transition series,²¹ and will explain the changes in F^2 . However, it does not explain the large differences between the ligand field parameters of the PaX_6^{2-} and UX_6^{2-} complexes.

Let us assume the crystal field parameters for the PaX_6^{2-} complexes should be valid for the UX_6^{2-} complexes, and then consider the differences in the crystal field defined as,

$$\Delta CF = CF(U) - CF(Pa) \quad (2)$$

where $CF = \theta + \Delta$. As can be seen from Tables IV and V the crystal (or ligand) field in the series of ligands (I-Br-Cl-F) increases much more rapidly for the PaX_6^{2-} complexes than for the UX_6^{2-} complexes. There will be a point where $CF(U) = CF(Pa)$, ($\Delta CF = 0$) for a hypothetical ligand at a certain bond distance. We call this point "equilibrium" and consider the value found for F^2 at this point as the "correct" value. Figure 4 shows a plot of ΔCF vs F^2 . Qualitatively ΔCF decreases from the iodide to the fluoride as the value of F^2 increases. From this definition of "equilibrium" the value of F^2 appears to be too large for UF_6^{2-} and too small for other members of the UX_6^{2-} series.

This work shows that the parameters obtained in the usual method for analyzing optical data of 4f and 5f series may not have the same meaning for free ion spectra and solid state spectra. Our studies suggest the Slater parameter F^2 is strongly affected by the type of ligand in the complex and may absorb some of the effects of the ligand field. Such effects have been predicted by theoretical calculations.^{22,23} This is also true to a lesser degree for the spin-orbit coupling constant. If F^2 and ζ are affected by the ligands then the values found for the ligand field parameters may also not be the "correct" values.

Finally, we wish to point out that our analysis is consistent with the excellent studies of Satten, et al.⁴⁻⁶ The $5f^2$ optical spectra observed in octahedral symmetry are dominated by the vibronic transitions. Furthermore, the electrostatic, spin-orbit, and crystalline field parameters increase as the ligand changes from I^- to F^- . In the $5f^1$ series the crystalline field and spin-orbit parameters also increase with higher oxidation state on the metal ion. The reported analysis of the optical spectrum of $CsNpF_6$ ²⁴ does not fit the above trends. We suggest this discrepancy should be studied further.

Conclusion

We have analyzed the optical spectra of $(NEt_4)_2UF_6$ and $(NEt_4)_2UI_6$. The electrostatic, spin-orbit, and crystal field parameters for the entire UX_6^{2-} ($X = F, Cl, Br, I$) have been obtained and where applicable compared to corresponding parameters for PaX_6^{2-} . It was noted that the Slater parameter F^2 changes by approximately 20% for the series and the crystal field parameters are dissimilar for the comparable PaX_6^{2-} and UX_6^{2-} complexes.

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Table I. Estimated Vibrational Frequencies for $(\text{Et}_4\text{N})_2\text{UF}_6$ and $(\text{Et}_4\text{N})_2\text{UI}_6$.

	UF_6^{2-}				UI_6^{2-}			
	Calc. from		Observed		Calc. from		Observed	
	UBr_6^{2-a}	UCl_6^{2-b}	PaF_6^{2-c}	UF_6^{2-c}	UBr_6^{2-a}	UCl_6^{2-b}	PaI_6^{2-d}	UI_6^{2-d}
$\nu_1(\text{cm}^{-1})$	371	404			143	156		
$\nu_2(\text{cm}^{-1})$	308	—			119	—		
$\nu_3(\text{cm}^{-1})$	369	351	404	406	143	135	143	143
$\nu_4(\text{cm}^{-1})$	168	155	148	155	65	60	60	60
$\nu_5(\text{cm}^{-1})$	170	162			66	62		
$\nu_6(\text{cm}^{-1})$	121	114			47	44		

a) Ref. 15.

b) Ref. 5, Ref. 13.

c) Ref. 2.

d) Ref. 3.

Table II. Observed Electronic and Vibronic Lines and Assignments (in cm^{-1}).

$(\text{NEt}_4)\text{UCl}_6$				$(\text{NEt}_4)_2\text{UCl}_6$			
Vibronic Lines	Vibrational Frequencies	Electronic Transition	Assignment	Vibronic Lines	Vibrational Frequencies	Electronic Transition	Assignment
4596	-41			5181	-457		
—	0	4637	Γ_5	5348	-290		
4680	+43			—	0	5638	Γ_5
4753	+116			6094	+456		
4769	0	4769	Γ_3	6006	-665		
6112	-72			6215	-456		
6143	-41			6309	-362		
6184	0	6184	Γ_4	—	0	6671	Γ_3
6250	+66			7032	+361		
6285	+101			7087	+416		
6549	-91			7342	+671		
6640	0	6640	Γ_5	6605	-412		
6734	+94			6821	-196		
7092	-77			—	0	7017	Γ_4
7169	0	7169	Γ_4	7189	+184		
7262	+93			7452	+435		
7570	-93			7692	+675		
7663	0	7663	Γ_3	7849	-441		
7782	+119			7930	-360		
8643	-98			—	0	8290	Γ_4
8741	0	8741	Γ_5	8651	+361		
8842	+101			8787	+497		
9606	-114			8945	+655		
9671	-49			7981	-596		
—	0	9720	Γ_4	8137	-440		
9747	+27			8210	-367		
9852	+132			—	0	8577	Γ_5
				8945	+368		
				9225	+648		
				9901	-661		
				10111	-451		
				—	0	10562	Γ_5
				11013	+451		
				11274	+712		
				11587	-448		
				11655	-380		
				—	0	12035	Γ_4
				12330	+295		
				12484	+449		

Table III. Calculated and Observed Electronic Transitions.

$(Et_4N)_2UI_6$			$(Et_4N)_2UF_6$		
Γ	Exptl(cm^{-1})	Calc(cm^{-1})	Γ	Exptl(cm^{-1})	Calc(cm^{-1})
1	0	102	1	0	46
4		892	4		1129
3		1189	3		1311
5		2234	5		3303
5	4637	4632	5	5638	5631
3	4769	4821	3	6671	6596
4	6184	6184	4	7017	7006
5	6640	6840	4	8290	8256
4	7169	6927	5	8577	8550
3	7663	7463	1	8787	8751
1		7718	3	9085	9079
4		8760	5		10418
5	8741	8866	4	10562	10713
3		9317	2		10816
2		9420	3		11193
4	9720	9584	4	12035	12015
5		10333	5	12804	12811
3	10776	10812	3	13038	13093
5		10848	5	13263	13282
2	11468	11621	2		13967
5	12180	12219	1		14572
1		12439	5	14925	14949
4		12507	4		15242
1		13673	1	16584	16551
4		14597	4	17301	17330
3		14622	3	18051	18119
5		15086	5		18910
1		15628	5		20036
3		15864	3		20056
5		16312	1		20065
4		17724	4		22482
5		18363	5		22619
1		18384	1		23025
4		18536	4		23183
2		19219	2		24387
5		19946	5		25149
3		20085	3		25382
5		21861	5		27121
3		23106	3		28780
1		35750	1		45447

Table IV. Electrostatic, Spin-Orbit, and Crystalline Field Parameters for UX_6^{2-} and PaX_6^{2-} .

	UF_6^{2-a}	UCl_6^{2-a}	UBr_6^{2-a}	UI_6^{2-a}	UCl_6^{2-b}	UBr_6^{2-b}	PaF_6^{2-c}	$PaCl_6^{2-c}$	$PaBr_6^{2-c}$	PaI_6^{2-c}
$F^2(\text{cm}^{-1})$	49699 ± 465	43170 ± 2181	40867 ± 2739	38188 ± 2422	42606	41425	—	—	—	—
$\zeta(\text{cm}^{-1})$	1970 ± 10	1774 ± 35	1756 ± 41	1724 ± 39	1800	1792	1508	1523	1535	1542
$B_0^4(\text{cm}^{-1})$	10067 ± 113	7463 ± 432	6946 ± 609	6338 ± 676	7211	6593	14736	6666	5413	4191
$B_0^6(\text{cm}^{-1})$	22 ± 72	992 ± 258	999 ± 252	941 ± 289	1367	1195	1423	394	-68	-282
$\Delta_{\text{rms}}(\text{cm}^{-1})^d$	67	168	176	188	—	—	—	—	—	—
$\Delta_{\text{med}}(\text{cm}^{-1})^e$	39	76	95	106	—	—	—	—	—	—

- a) This work.
 b) Reference 4.
 c) Reference 3.
 d) Root mean square deviation.
 e) Mean energy deviation.

Table V. Ligand Field Parameters for UX_6^{2-} and PaX_6^{2-} .

	$\Theta^a(\text{cm}^{-1})$		$\Delta^a(\text{cm}^{-1})$		$\zeta(\text{cm}^{-1})$	
	M = Pa ^b	M = U	M = Pa ^b	M = U	M = Pa ^b	M = U
MF_6^{2-}	4502	2455	3074	3029	1508	1969 ± 10
MCl_6^{2-}	1873	2457	1634	1290	1523	1774 ± 35
MCl_6^{2-c}		2640		847		1800
MBr_6^{2-}	1268	2336	1707	1127	1535	1756 ± 41
MBr_6^{2-c}		2378		828		1792
MI_6^{2-}	832	2151	1546	999	1542	1724 ± 39

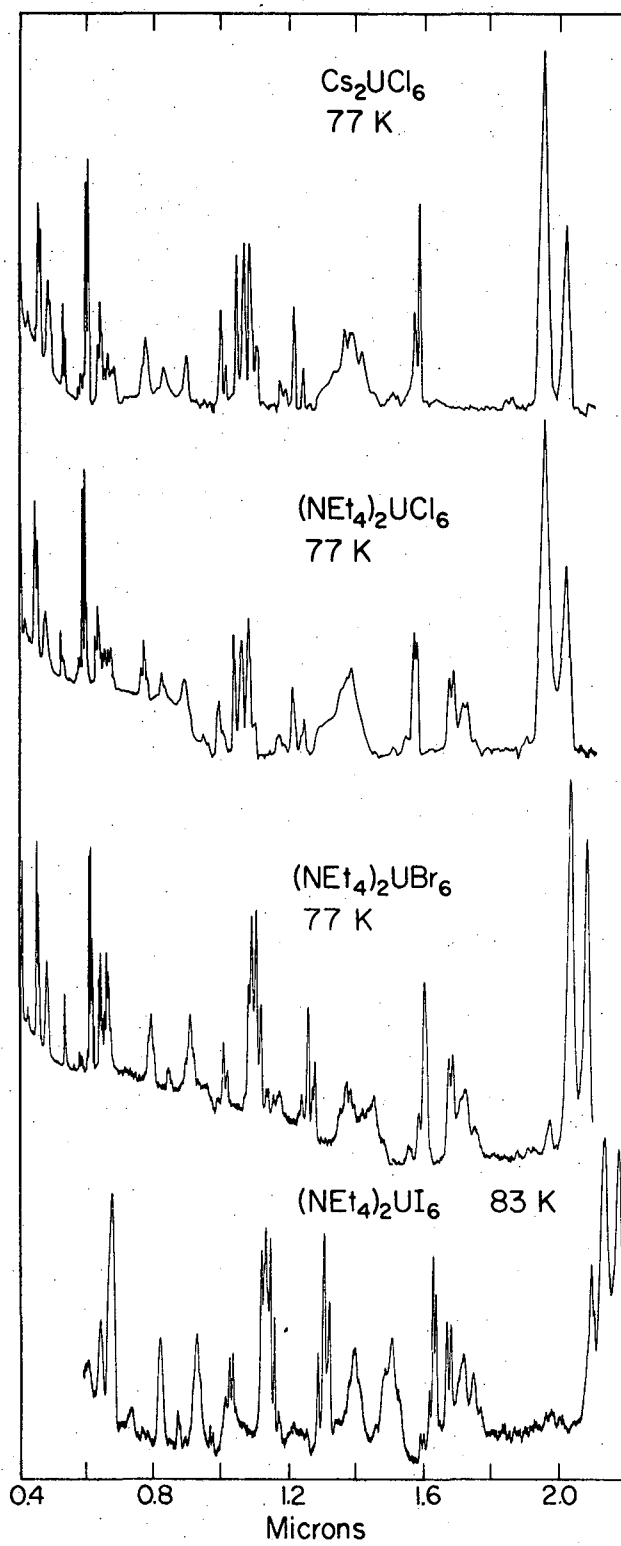
a) Total ligand field splitting = $\Delta + \Theta$. (See Reference 1 for definitions.)

b) Reference 3.

c) Reference 5.

Figure Captions

- Fig. 1. Spectra obtained for various UX_6^{2-} ($X = Cl, Br, I$) compounds at $\sim 77^\circ K$. The lines at $\sim 1.7\mu$ are from the $(NEt_4)^+$ cation.
- Fig. 2. Spectrum of $(NEt_4)_2UF_6$ at $77^\circ K$. The lines at $\sim 1.7\mu$ are from the $(NEt_4)^+$ cation.
- Fig. 3. Energy level diagram for UX_6^{2-} ($X = F, Cl, Br, I$). The LSJ state listed for each level is the component having the largest value.
- Fig. 4. Differences in ligand field parameters for UF_6^{2-} and PaF_6^{2-} vs F^2 for UX_6^{2-} .



XBL 756-3233

Fig. 1

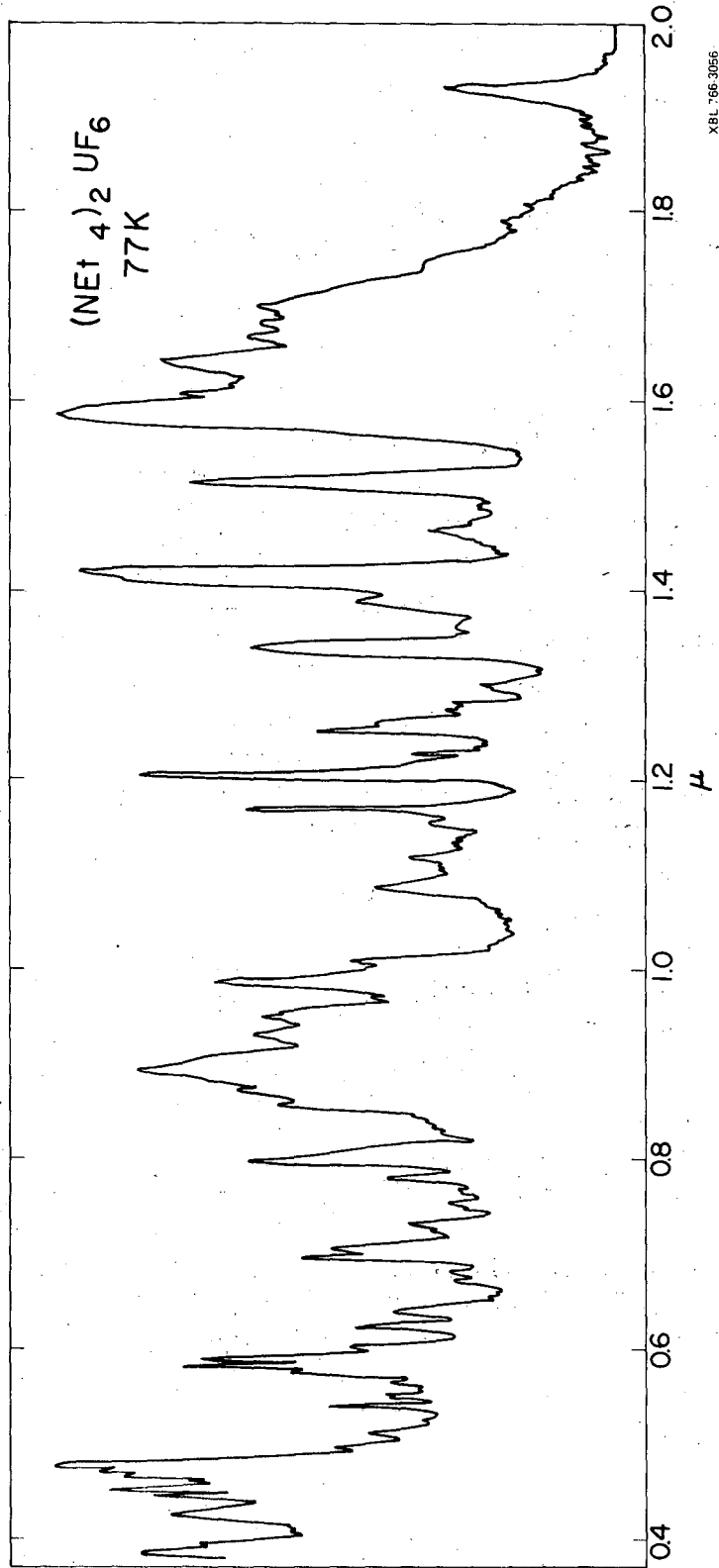


Fig. 2

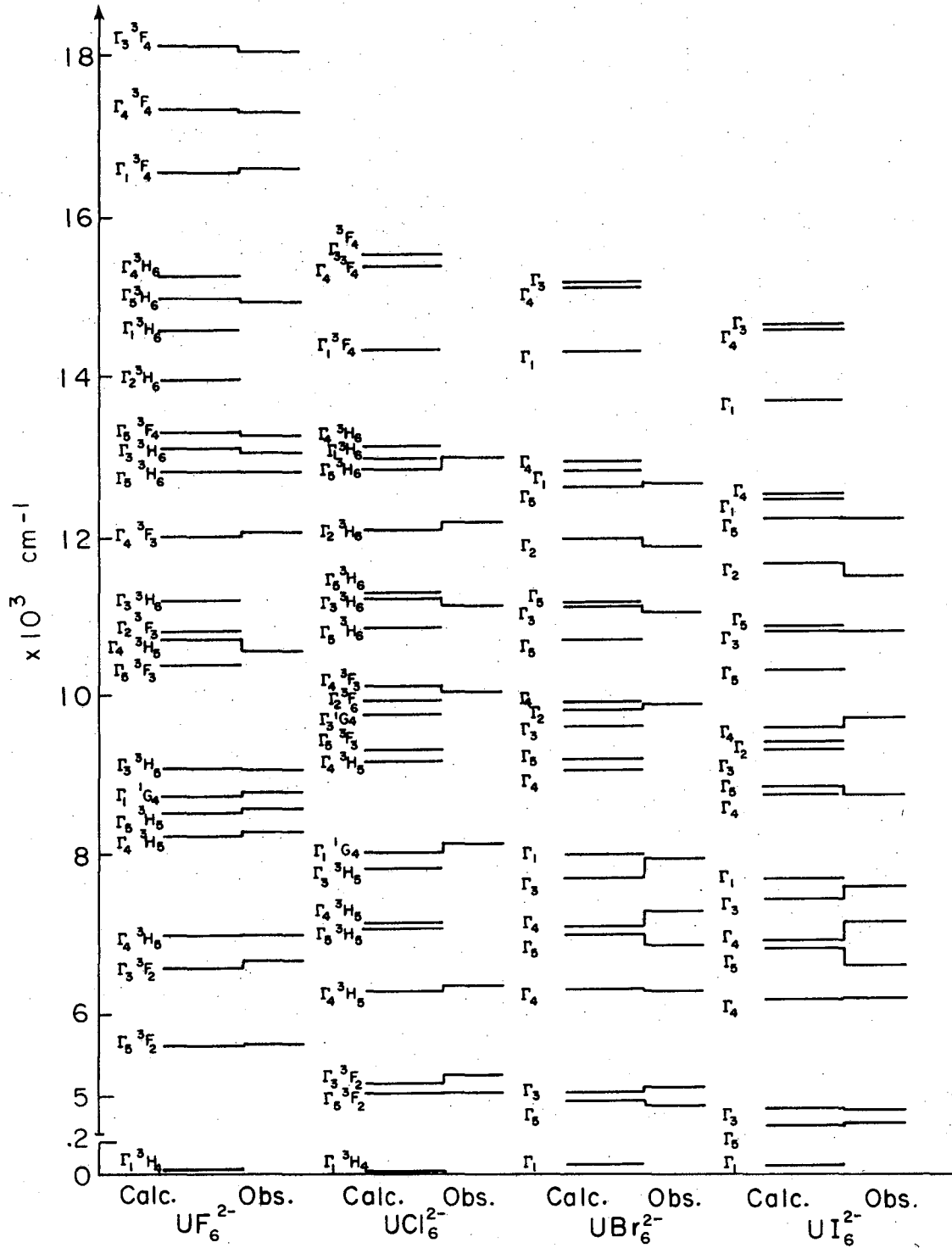
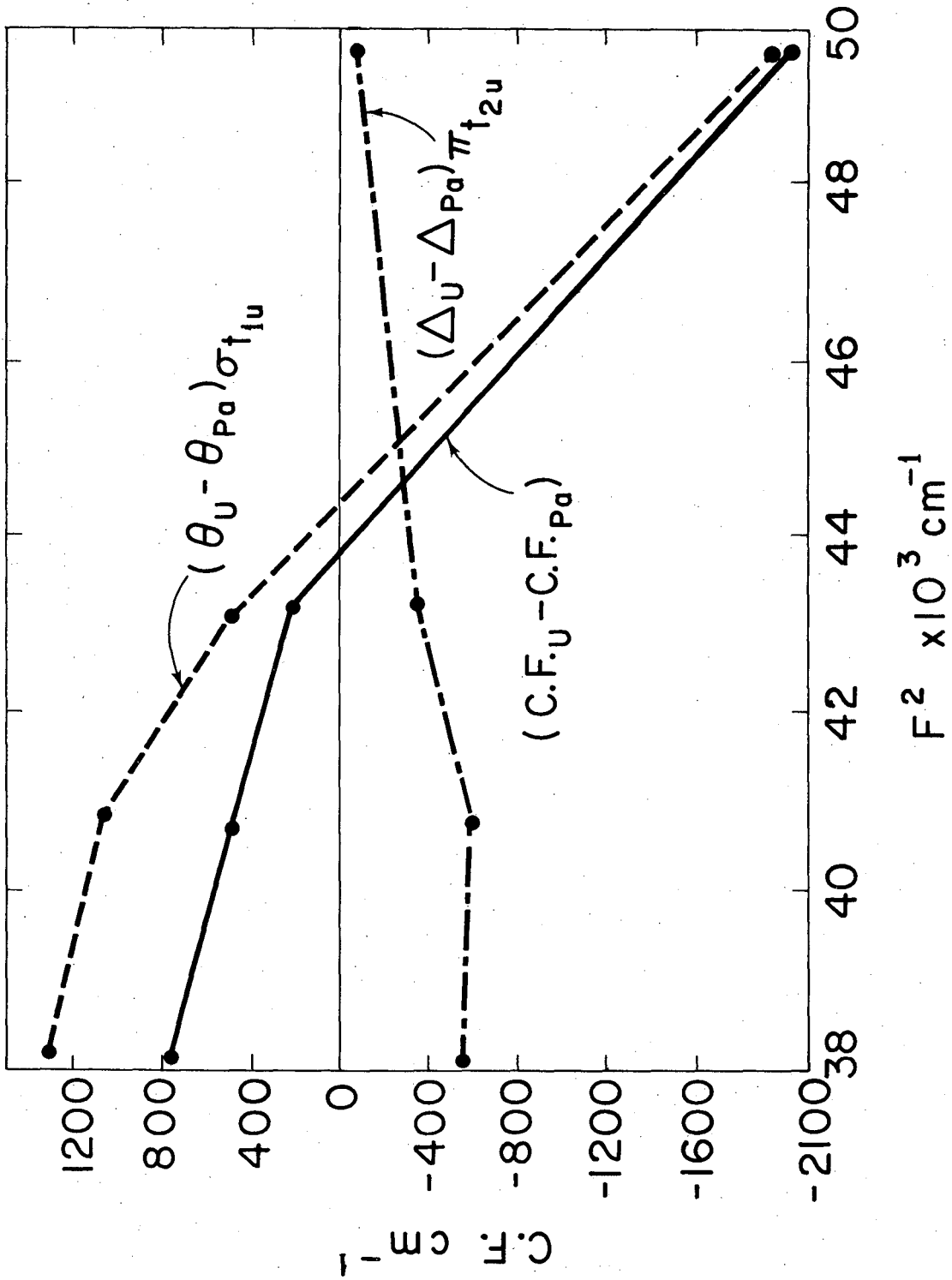


Fig. 3

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Fig. 4

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