

ON THE FLUORESCENCE SPECTRUM OF DI-CAESIUM URANYL NITRATE AT 77° K.

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INTRODUCTION

THE fluorescence spectra of mono-alkali uranyl nitrates have received much attention in the past. Similarly, the fluorescence spectra of di-rubidium uranyl nitrate and di-potassium uranyl nitrate have also been studied. The various vibration frequencies of UO_2^{++} ion and NO_3^- ion in these salts have been identified by Dieke and Duncan¹ and a detailed list of these is available. The fluorescence spectrum of di-caesium uranyl nitrate however has not been studied by these authors because it could not be prepared.¹ In recent communications^{2,3} we have reported the successful preparation of this salt and an outline of its fluorescence spectrum. This paper deals with a detailed study of the spectrum.

EXPERIMENTAL

Multi-crystals of $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$ were grown by the methods described elsewhere.³ Micro crystals of $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$ were packed and sealed in a pyrex tube which was, in turn, held in a Dewar flask containing liquid nitrogen. Fluorescence was excited by the radiations from a high pressure 1600-watt xenon lamp filtered through an ultra-violet filter (Corning, 9863). The spectrum was recorded on a 3-prism glass Steinheil spectrograph with a dispersion of 17 Å/mm. at 5000 Å. Band heads were measured on an Abbe comparator focusing the cross-wire on the position of maximum intensity in the band near to the head. The accuracy of measurements is therefore different for sharp bands and for diffuse bands. The accuracy is on an average ± 0.1 Å in the case of very sharp bands while for broad bands it is ± 1 Å.

RESULTS AND DISCUSSIONS

The spectrum obtained is given in Fig. 1. The wavelengths of bands measured and other data are given in Table I which includes also the assign-

ments proposed for the bands. Broadly, the spectrum at 77° K. consists of groups of similar bands repeating at intervals of 855 cm.⁻¹ with the band at 20751 cm.⁻¹ as the resonance band. Compared to the fluorescence spectrum of mono-salt, the spectrum of di-caesium salt is shifted towards the

TABLE I
Fluorescence spectrum of Cs₂UO₂(NO₃)₄

λ (air) Å	Visual intensity Max. 100	ν (vac.) cm. ⁻¹	$\Delta\nu$ from R-nA in cm. ⁻¹	Assign- ment R-
4801.9	b 5	20819.3	68.3	+L ₂
4808.2	b 5	20792.0	41.0	+L ₁
4817.7	sh 5	20751.0	0	Resonance
4827.7	b 10	20708.0	43.0	L ₁
4834.1	b 20	20680.6	70.4	L ₂
4837.6	b 4	20665.6	85.4	L ₃
4843.7	b 30	20639.6	111.4	L ₄
4849.1	b 20	20616.6	134.4	L ₅
4854.3	b 3	20594.5	156.5	L ₆
4858.5	b 20	20576.7	174.3	L ₇
4863.1	b 4	20557.3	193.7	L ₈
4870.6	b 20	20525.6	225.4	L ₉
4878.6	sh 50	20492.0	259.0	C
4883.0	bb 50	20473.5	277.5	L ₁₀
4981.5	sh 5	20068.7	682.3	G
4993.9	sh 10	20019.0	732.0	F
4998.8	sh 5	19999.2	751.8	E
5017.0	b 10	19926.2	824.8	D
5017.2	sh 30	19925.9	825.1	
5025.3	sh 80	19893.8	857.2	A
5035.7	bb 50	19852.7	41.1	A+L ₁
5045.3	b 100	19814.9	936.9	B
5053.5	sh 70	19782.5	111.3	A+L ₄
5059.3	bb 70	19760.1	133.7	A+L ₅
5064.5	sh 5	19739.8	154.0	A+L ₆
5069.4	sh 10	19720.7	173.1	A+L ₇
5074.2	sh 10	19702.0	191.8	A+L ₈
5082.4	sh 10	19670.2	223.6	A+L ₉
5091.1	sh 80	19636.6	257.2	A+C
5097.9	b 80	19610.4	283.2	A+L ₁₀

TABLE I. (Contd.)

λ (air) Å	Visual intensity Max. 100	ν (vac.) cm.^{-1}	$\Delta\nu$ from R-nA in cm.^{-1}	Assign- ment R-
5102.8	<i>b</i> 5	19591.6	302.2	..
5130.0	<i>b</i> 5	19487.7	406.1	..
5141.5	<i>sh</i> 40	19444.2	449.6	..
5187.9	<i>sh</i> 5	19270.2	623.6	..
5190.9	<i>sh</i> 5	19259.1	634.7	..
5204.0	<i>sh</i> 10	19210.4	683.4	A+G
5217.3	<i>sh</i> 20	19161.7	732.1	A+F
5222.4	<i>sh</i> 1	19142.9	750.9	A+E
5242.4	<i>sh</i> 20	19069.9	823.9	A+D
5245.6	<i>sh</i> 10	19058.2	835.6	B+E
5250.6	<i>sh</i> 80	19040.1	853.7	2A
5261.3	<i>bb</i> 20	19001.4	38.7	2A+L ₁
5271.6	<i>b</i> 100	18964.3	929.5	A+B
5282.1	<i>sh</i> 80	18926.6	113.5	2A+L ₄
5292.4	<i>sh</i> 5	18889.8	150.3	2A+L ₆
5292.7	<i>sh</i> 20	18888.7	151.4	2A+L ₆
5303.2	<i>sh</i> 20	18851.3	188.8	2A+L ₈
5313.3	<i>sh</i> 10	18815.5	224.6	2A+L ₉
5322.7	<i>sh</i> 80	18732.2	257.9	2A+C
5327.8	<i>b</i> 80	18764.2	275.9	2A+L ₁₀
5352.0	<i>sh</i> 10	18679.4	360.7	..
5372.6	<i>sh</i> 10	18607.8	432.3	..
5378.5	<i>sh</i> 60	18587.4	452.7	..
5429.6	<i>sh</i> 5	18412.4	627.7	..
5433.1	<i>sh</i> 4	18400.6	639.5	..
5446.5	<i>sh</i> 10	18355.3	684.8	2A+G
5461.4	<i>sh</i> 10	18305.2	734.9	2A+F
5468.7	<i>b</i> 5	18280.8	759.3	2A+E
5484.1	<i>sh</i> 10	18229.5	810.6	..
5488.5	<i>sh</i> 10	18214.8	825.3	2A+D
5491.1	<i>sh</i> 20	18206.2	833.9	A+B+E
5496.8	<i>sh</i> 60	18187.3	852.8	3A

TABLE I (Contd.)

λ (air) Å	Visual intensity Max. 100	ν (vac.) cm. ⁻¹	$\Delta\nu$ from R-nA in cm. ⁻¹	Assign- ment R-
5506.4	<i>b</i> 5	18155.6	31.7	..
5510.2	<i>b</i> 5	18143.1	44.2	3A+L ₁
5518.8	<i>b</i> 100	18114.8	925.3	3A+B
5531.4	<i>sh</i> 80	18073.6	113.7	3A+L ₄
5542.4	<i>sh</i> 5	18037.7	149.6	3A+L ₆
5549.9	<i>sh</i> 10	18013.3	174.0	3A+L ₇
5553.3	<i>sh</i> 10	18002.3	185.0	3A+L ₈
5564.9	<i>sh</i> 10	17964.8	222.5	3A+L ₉
5576.0	<i>sh</i> 60	17929.0	258.3	3A+C
5580.5	<i>sh</i> 60	17914.6	272.7	3A+L ₁₀
5608.1	<i>sh</i> 10	17826.1	361.2	..
5631.0	<i>sh</i> 20	17753.9	433.4	..
5638.0	<i>sh</i> 40	17731.9	455.4	..
5696.2	<i>bb</i> 10	17550.7	636.6	..
5727.0	<i>sh</i> 5	17456.3	731.0	3A+F
5751.3	<i>sh</i> 10	17382.5	804.8	..
5758.1	<i>sh</i> 30	17362.0	825.3	3A+D
5765.0	<i>sh</i> 20	17341.2	846.1	4A
5788.0	<i>b</i> 90	17272.3	915.0	3A+B
5802.2	<i>sh</i> 40	17230.1	111.1	4A+L ₄
5823.4	<i>sh</i> 5	17167.3	173.9	4A+L ₇
5825.5	<i>sh</i> 4	17161.1	180.1	4A+L ₈
5850.6	<i>sh</i> 50	17087.5	253.7	4A+C
5855.2	<i>sh</i> 50	17074.1	267.1	4A+L ₁₀
5920.4	<i>sh</i> 3	16886.1	455.1	..
6082.1	<i>sh</i> 70	16437.1	904.1	4A+B
6411.7	<i>sh</i> 30	15592.2	844.9*	5A+B

b = broad; *bb* = very broad.; *sh* = sharp.

* $\Delta\nu = \nu_{R-(4A+B)} - \nu_{R-(5A+B)}$.

long wavelength side by about 340 cm.⁻¹ and slightly shrunk in extent owing to the decrease in magnitude of the vibration frequencies of UO₂⁺⁺, the emitter of the spectrum (Table II).

TABLE II

UO₂⁺⁺ vibration frequencies in mono- and di-caesium uranyl nitrates

V	A differences		B differences		C differences	
	di-salt cm. ⁻¹	mono-salt cm. ⁻¹	di-salt cm. ⁻¹	mono-salt cm. ⁻¹	di-salt cm. ⁻¹	mono-salt cm. ⁻¹
0	857	884	936	956	259	..
1	854	880	930	952	257	..
2	853	879	925	948	258	..
3	846	876	915	943	258	..
4	..	874	904	937	254	..
R	20751	21089·6

The data on mono-salt are from Dieke and Duncan.¹

The resonance band at 20751 cm.⁻¹ is an intense sharp line on the short wave end of the spectrum and is the (0-0) band due to the electronic transition between the excited and normal states of the UO₂⁺⁺. There is an intense sharp band 857 cm.⁻¹ away from the resonance band on the longer wavelength side. From our previous knowledge of uranyl spectra we know that the repetition frequency occurring in the groups of bands is the symmetric vibration of linear UO₂⁺⁺ ion. The band at 5025·3 Å, 857 cm.⁻¹ away on the longer wavelength side of the resonance line is thus a transition from the excited electronic state with zero vibration to the first quantum of the symmetric vibration of UO₂⁺⁺ ion in the ground electronic state. Since the symmetric vibration frequencies are denoted by 'A', this band is designated as R-A. There are similar sharp bands in all other groups at intervals of 854 cm.⁻¹, 853 cm.⁻¹ and 846 cm.⁻¹. These are designated as R-2A, R-3A, R-4A, etc., respectively and lie in the spectrum at 5025 Å, 5250 Å, 5497 Å, 5765 Å, respectively. The decrease in the symmetric frequency for higher vibrational quantum number indicates a marked anharmonicity of the symmetric frequency.

The intense band at 5045 Å, 936 cm.⁻¹ from the resonance band is identified as due to the antisymmetric vibration. This assignment is supported

by the presence in the infra-red absorption spectrum* of this salt of a strong band at 928 cm.^{-1} . The band is designated as R-B (B being the antisymmetric frequency) and arises out of a transition from the excited electronic state to the first antisymmetric vibrational level of the ground state. Similar intense bands are found in other groups at intervals which are approximately the repetition or the symmetric frequency. These are due to vibrational quanta of the symmetric frequency each of which however is now loaded with one quantum of antisymmetric vibration. Thus the band at 5272 Å is designated as R-(A + B) and those at 5518 Å , 5788 Å , 6082 Å and 6411 Å as R-(2A + B), R-(3A + B), R-(4A + B) and R-(5A + B), respectively. These form the most intense set of bands, in the fluorescence spectrum. The antisymmetric frequency thus appears to occur in a single quantum either alone or in combination with one or several quanta of the symmetric frequency.

There is a fairly intense sharp band at 4878 Å , 259 cm.^{-1} from the resonance band. The magnitude of the frequency and the intensity of the band lead one to think that this may be the bending frequency of UO_2^{++} . There are also similar bands at 5091 Å , 5322 Å , 5576 Å and 5851 Å which can be designated as R-(A + C), R-(2A + C), R-(3A + C) and R-(4A + C) respectively as in the case of $nA + B$ band. Here again the bending frequency occurs as a single quantum either alone or in combination with one or several quanta of A.

There is a striking difference between the fluorescence spectrum of the mono- and the di-salts as regards the relative intensity of A and A + B bands. In case of $\text{CsUO}_2(\text{NO}_3)_3$, A and A + B bands are almost of equal intensity. But in the case of $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$ the intensity of A bands gets reduced by a factor of two or more. At the same time the A bands in $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$ are much sharper than the corresponding A bands in mono-caesium salt. Similar intensity relations for A and B bands are also observed¹ in $\text{Rb}_2\text{UO}_2(\text{NO}_3)_4$ and $\text{K}_2\text{UO}_2(\text{NO}_3)_4$.

There are a set of weak but sharp bands at 682 cm.^{-1} , 732 cm.^{-1} , 752 cm.^{-1} and 825 cm.^{-1} from the resonance band. On comparing these values with the nitrate frequencies of $\text{Rb}_2\text{UO}_2(\text{NO}_3)_4$ and $\text{K}_2\text{UO}_2(\text{NO}_3)_4$ (Table III) one can see that these are the nitrate frequencies associated with the UO_2^{++} spectrum in $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$. Thus following Dieke and Duncan¹ we designate these bands as G, F, E, D bands respectively. As in the case of antisymmetric and bending frequencies there are bands at 5204 Å , 5446 Å which

* From unpublished results obtained here.

TABLE III
Nitrate frequencies in cm.^{-1}

Vibrations	$\text{K}_2\text{UO}_2(\text{NO}_3)_4$	$\text{Rb}_2\text{UO}_2(\text{NO}_3)_4$	$\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$	$\text{CsUO}_2(\text{NO}_3)_3$	$\text{KUO}_2(\text{NO}_3)_3$
(D)	825	825	825	804	803
(E)	750	751	752	749	715
(F)	736	734	732	739	742
(G)	691	688	682	712	

The data except those for $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$ are from Dieke and Duncan.¹

can be designated as $\text{R}-(\text{A}+\text{G})$, $\text{R}-(2\text{A} + \text{G})$ respectively and bands at 5217 Å, 5461 Å, 5727 Å designated as $\text{R}-(\text{A} + \text{F})$, $\text{R}-(2\text{A}+\text{F})$ and $\text{R}-(3\text{A}+\text{F})$ bands respectively. Similarly bands corresponding to $\text{R}-(\text{A} + \text{E})$, $\text{R}-(2\text{A}+\text{E})$ and $\text{R}-(\text{A}+\text{D})$, $\text{R}-(2\text{A}+\text{D})$ and $\text{R}-(3\text{A}+\text{D})$ are obtained (Table I). Thus these nitrate frequencies also occur in a single quantum either alone or coupled with one or more quanta of the symmetric frequency as in other alkali uranyl nitrates. It is of interest to note that the magnitude of the frequencies is comparable to those in the di-alkali salts rather than in the mono-alkali salts.

There is a band at 5246 Å which is sharp and is approximately of the same intensity as the nitrate bands. This band can be fitted in as $\text{R}-(\text{B} + \text{E})$ band. There is one more band of this type at 5491 Å which can be designated as $\text{R}-(\text{A} + \text{B} + \text{E})$ band. This supports the proposed analysis of similar bands in the mono-caesium uranyl nitrate by Dieke and Duncan,¹ who adduce an isotope shift evidence for their proposed analysis. But why only E frequency of nitrate is coupled with the antisymmetric vibration is not known.

This anomaly of 'E' frequencies of nitrate combining with the antisymmetric vibration B can be avoided if these bands at 5245.6 Å and 5491.1 Å are interpreted as components of ν_2 out-of-plane bending vibration.⁽²⁾ In the case of KNO_3 in crystalline state the observed infra-red spectra show some weak components accompanying the out-of-plane bending non-degenerate ν_2 frequency (826 cm.^{-1} for $^{14}\text{NO}_3$ and 811 cm.^{-1} for $^{15}\text{NO}_3$). These are explained on the basis of coupling between $^{14}\text{NO}_3$ and $^{15}\text{NO}_3$.⁴ If similar coupling is assumed, the bands at 5246 and 5491 Å can be regarded as components of D vibration as found in the case of KNO_3 . Similarly bands at 5017 Å,

5484 Å, 5751 Å which are not designated in Table I can also be designated as components of 'D' vibration.

We now come to a set of broad weak bands in the frequency range of 40 cm^{-1} to 277 cm^{-1} . There are two such bands on the short wave side of the resonance band at 41 cm^{-1} and 68 cm^{-1} . There are a series of similar bands on the long wavelength side also. These appear to be due to the so-called lattice vibrations. The two bands on the short wave side of the resonance band arise due to these lattice vibrations being superimposed on the excited electronic state, while the rest of the bands on the longer wavelength side are due to similar vibrations superimposed on the ground electronic state. These lattice vibrations each with only one quantum are also associated with the symmetric A frequency. The mean values of these lattice vibrations observed in the present spectrum are collected together in Table IV. A band at 112 cm^{-1} of these lattice frequencies is intense and sharp as compared to others.

TABLE IV

Mean values of lattice vibrations

Vibrations in cm^{-1}	Designation
41	L ₁
69	L ₂
85	L ₃
112	L ₄
134	L ₅
152	L ₆
174	L ₇
187	L ₈
224	L ₉
275	L ₁₀

Apart from these there are some bands in the frequency range of 300 cm.^{-1} and 650 cm.^{-1} which are not designated. They may be due to combination frequencies. There is however one prominent band at 19444 cm.^{-1} which is 1307 cm.^{-1} away from the resonance band. This agrees with the magnitude of the antisymmetric vibration of NO_3^- . It will be interesting to test this assignment by a study of the nitrogen isotopic shift for this band.

SUMMARY

It is shown that the fluorescence spectrum of $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$ consists mainly of sequences starting off from the resonance band R followed by 'C' the bending frequency and each consisting of bands which can be assigned as (A, B, A + C), (2A, A + B, 2A + C), (3A, 2A + B, 3A + C), etc., where A is the symmetric vibration frequency, B the antisymmetric frequency and C the bending frequency of the linear UO_2^{++} ion in this lattice. In addition are observed several fundamental frequencies of the nitrate ion and the lattice either alone or coupled to the symmetric frequency A and its overtones. The relevant constants are:

Symmetric frequency	A = 857 cm.^{-1}
Antisymmetric frequency	B = 936 cm.^{-1}
Bending frequency	C = 259 cm.^{-1}
Resonance frequency	R = 20751 cm.^{-1}

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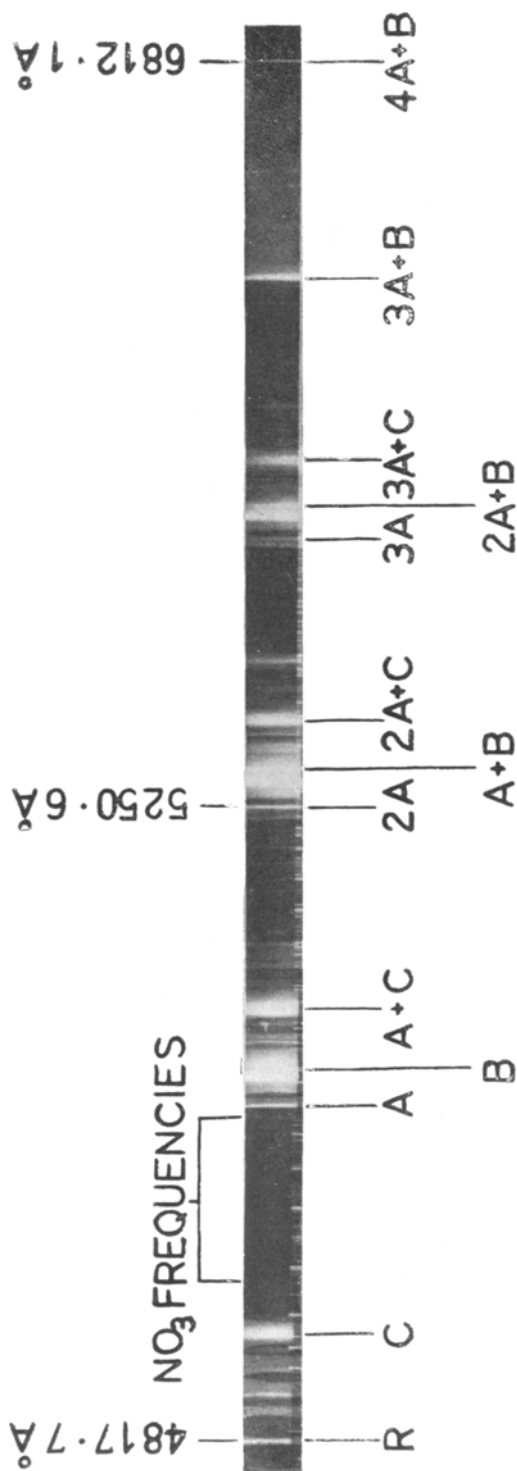


FIG. 1. Fluorescence spectrum of $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$ at 77°K .