ABSORPTION SPECTRUM OF POTASSIUM URANYL SULPHATE

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The electronic and infra-red absorption spectra of potassium uranyl sulphate ($K_2UO_2(SO_4)_2 \cdot 2H_2O$) have been reinvestigated in the solid state and solution. A tentative analysis has been proposed, on the basis of four systems with a common ground state, for the bands of the electronic absorption spectrum. For the infra-red absorption spectrum of the compound, most of the bands could be interpreted as due to the ground state frequencies of the uranyl ion and their overtones and combinations and one frequency of the sulphate radical.

The spectra of uranyl salts have been studied by a large number of workers from time to time. But there are many difficulties in the interpretation of the observed bands in the spectra as pointed out in the two recent reviews[1,2]. The most systematic investigation of these compounds has been carried out by Dieke & Duncan[3] and they have concluded that the fluorescence spectrum could be explained on the basis of a single electronic transition from an upper state to a ground state and the electronic absorption spectrum on the basis of different electronic transitions from the common ground state to the various upper states. The present study of the absorption spectrum of the potassium uranyl sulphate has been undertaken in continuation of our systematic reinvestigation of the uranyl compounds.

The electronic absorption spectrum of potassium uranyl sulphate has been previously studied by Dieke & Duncan[3] and Nichols & Howes[4] without proposing any analysis of the bands. However, Dieke & Duncan indicated the starting positions of some series. Pant[5] took the data of Nichols & Howes and analysed the bands on the basis of two electronic transitions from two close lying ground states to a common upper state. The defects of this type of analyis have been discussed earlier[6]. In the present reinvestigation, the earlier data are much extended and a new analysis of the bands has been proposed.

The electronic absorption spectrum of the compound in solution has also been studied to compare with the spectrum obtained from the solid state.

The infra-red absorption spectrum of potassium uranyl sulphate has been studied previously by Sevchenko & Stepanov[7] and they have come to the conclusion that the uranyl ion is bent in this compound. In the present investigation of the infra-red spectrum, use has been made of a better resolving instrument than the one used by the Russian workers. The interpretation of some of the bands has been proposed on the basis of uranyl frequencies and a few frequencies of the sulphate ion and the crystal lattice.

PREPARATION OF THE COMPOUND

This compound has been prepared thus: It readily separates out on cooling from a hot saturated solution of two salts, potassium sulphate and uranyl sulphate, mixed in equimolecular proportions. The salt has been filtered, washed free from the mother liquor and dried. The salt, prepared in this way, is a fine greenish-yellow crystalline powder which shows very bright fluorescence. From chemical analysis, its formula is found to be $K_2UO_2(SO_4)_2\, 2H_2O$.

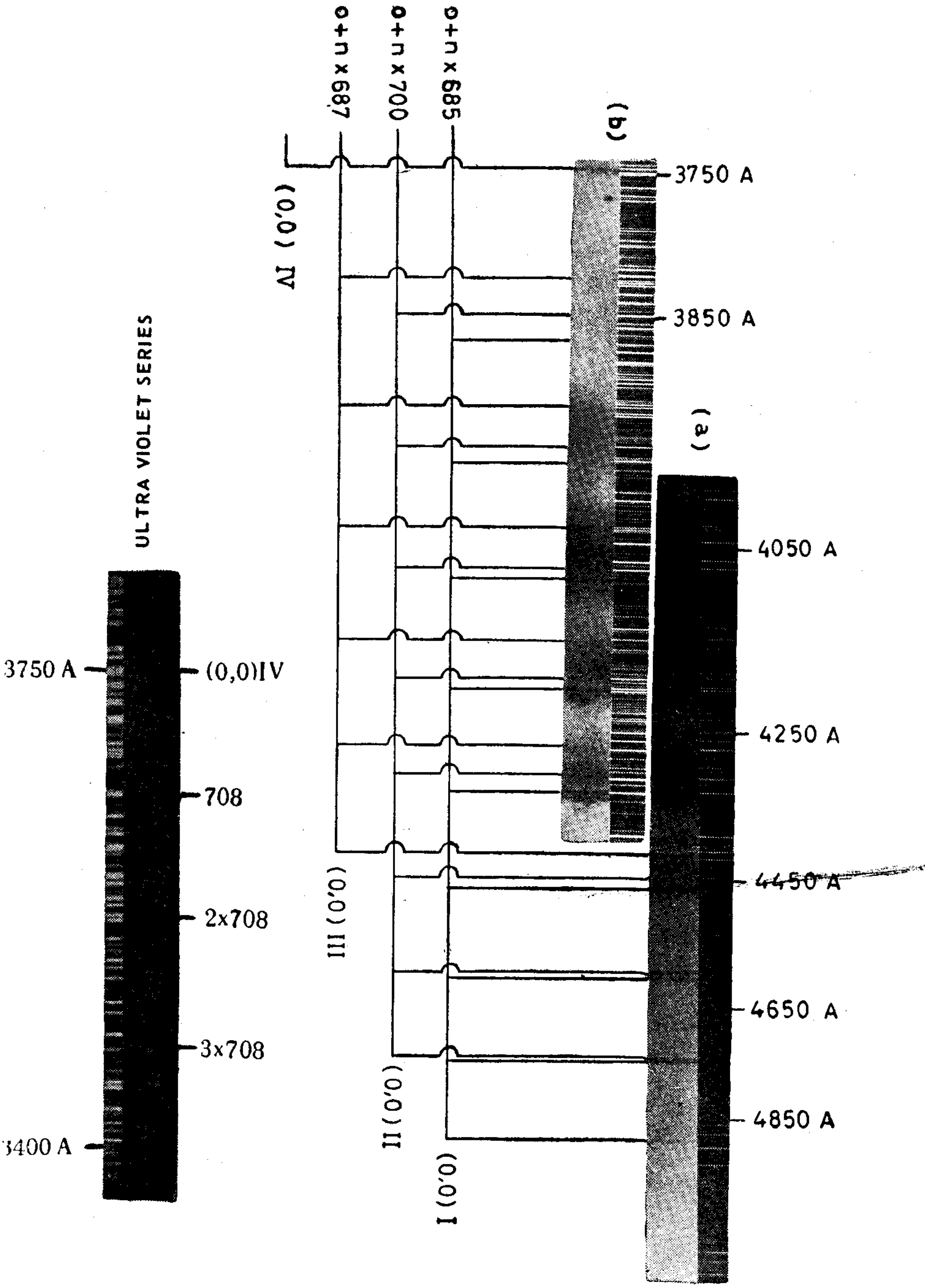

Fig. 1—Powder absorption spectrum of potassium uranyl sulphate at liquid air temperature. (Glass Littrow Spectrograph)

(*a*) Long path—length; (*b*) Short path—length.

TABLE 1

ABSORPTION BANDS OF POTASSIUM URANYL SULPHATE

Wave number of the band cm^{-1}		System I	System II	System III	System IV
With powder at —185°C	With solution at 25°C				
1	2	3	4	5	6
	18850				
20246 (1sh)		0—3×44	..	..	..
20310 (3sh)					
20377 (7sh)	20400	0, 0	..	..	
20441 (5sh)		0+2×30			
20469 (2sh)		0+3×30			
20488 (4sh)					
20515 (3sh)					
20563 (2sh)		0+186	..	..	..
20636 (3sh)		0+259			
20663 (3sh)		0+30+259			
20706 (4sh)					
20780 (2sh)		0+2×186	..	..	..
20816 (2sh)		0+439			
20849 (3sh)					
20907 (1sh)		0+2×259	..	..	..
20924 (2sh)		0+3×186			
20948 (4sh)					
20973 (1sh)					
20994 (4sh)		0+617	..	..	..
21062 (10sh)	21000	0+685			
21088 (10sh)	21150		0, 0		
21126 (2sh)		0+4×186			
21155 (3sh)		0+3×259			
21184 (2sh)		0+807			
21198 (1sh)					
21275 (2sh)			0+187	..	
21313 (2d)		0+685+259			
21339 (5sh)			0+251	..	
21373 (5sh)		0+996			
21391 (2msh)					
21418 (2msh)		0+4×259			
21490 (3sh)	21450	0+685+439			
21531 (4sh)			0+443		
21565 (3d)		0+186+996			
21587 (2d)			0+2×251		
21626 (2sh)		0+807+439			
21645 (2sh)		0+259+996			
21671 (2sh)		0+685+617			
21736 (10sh)	21650	0+2×685			
21788 (10sh)			0+700		
21849 (4d)		0+685+807			
21889 (3d)	21900		0+801		
21957 (2sh)			0+700+187		
21991 (1sh)		0+2×685+259			
22019 (2sh)			0+700+251		
22049 (2sh)		0+685+996			
22078 (2sh)			0+990		
22118 (2sh)			0+801+251		
22176 (1sh)		0+2×685+439			
22318 (1d)			0+251+990		
22398 (4sh)		0+2×685+617			
22412 (10sh)	22400	0+3×685			
22455 (4sh)					
22489 (5sh)			0+2×700		
22520 (1sh)					
22560 (7msh)		0+2×685+807			

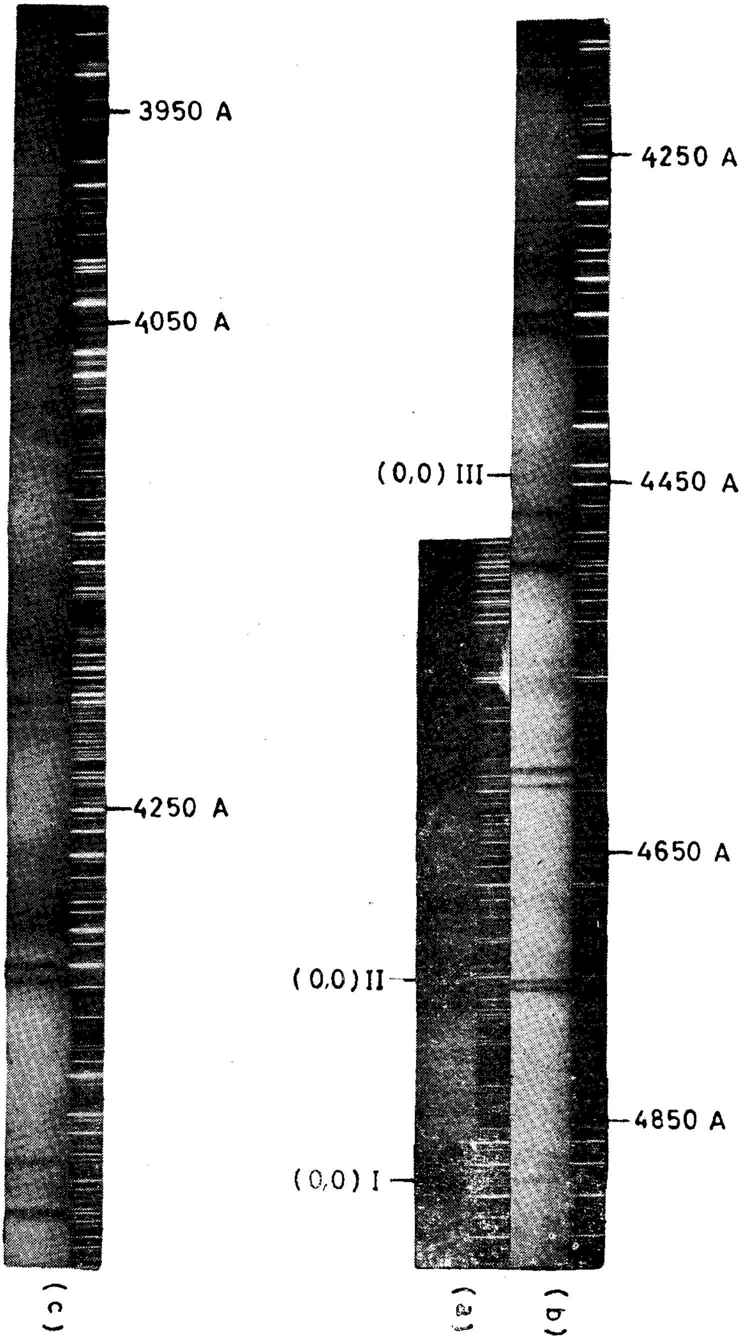

Fig. 2—Powder absorption spectrum of potassium uranyl sulphate at liquid air temperature. (Fuess Spectrograph)

(*a*) Long path-length; (*b*) & (*c*) Short path-length.

TABLE 1—*contd.*

1	2	3	4	5	6
22601 (1d)			0+700+801		
22663 (3d)				0, 0	
22733 (2d)	22750	0+2×685+996			
23004 (1sh)					
23068 (5sh)		0+3×685+617			
23108 (10sh)	23150	0+4×685			
23173 (2sh)					
23221 (5sh)			0+3×700		
23260 (5msh)		0+3×685+807			
23306 (2sh)			0+2×700+801		
23350 (2d)	23450			0+687	
23405 (2d)	23500				
23704 (2d)					
23723 (2d)					
23759 (4d)		0+4×685+617			
23797 (7sh)	23750	0+5×685			
23863 (5sh)			0+4×700		
23919 (5msh)		0+4×685+807			
23985 (3sh)	24050		0+3×700+801		
24111 (3d)				0+2×687	
24351 (2sh)					
24413 (4d)					
24440 (4d)		0+5×685+617			
24484 (7sh)	24500	0+6×685			
24553 (3d)			5×700		
24657 (3d)		0+5×685+807			
24795 (4d)				0+3×687	
24868 (2d)					
24960 (1d)					
25009 (1d)					
25053 (2sh)					
25115 (3msh)		0+6×685+617			
25165 (4sh)		0+7×685			
25207 (2sh)					
25267 (2d)			0+6×700		
25317 (2d)		0+6×685+807			
25457 (3d)	25400			0+4×687	
25552 (1d)					
25781 (1d)		0+7×685+617			
25846 (2d)		0+8×685			
25936 (2d)		0+7×685+807			
26027 (2d)	26050		0+7×700		
26140 (2d)				0+5×687	
26685 (10sh)	26900				
26875 (2d)					0, 0
27063 (2d)					0+190
27393 (10sh)	27550				0+708
27592 (2d)					
27811 (2d)					
28100 (5sh)					0+2×708
28799 (2d)					0+3×708

TABLE 2

INFRA-RED ABSORPTION BANDS OF POTASSIUM URANYL SULPHATE

Wave number of the bands		Assignment	
Authors	Sevchenko & Stepanov	Authors	Sevchenko & Stepanov
771 (vw)			
785 (vw)			
837 (ms)		ν_1 ;3×279	
924 (vs)	909	ν_3	ν_3
996 (s)	990	So_4	$5\nu_2$
1027 (vs)	1036	194+837	$\nu_1 + \nu_2$
1070 (w)			
1114 (s)		924+194; 4×279	
1141 (s)	1130		$\nu_3 + \nu_2$
1173 (s)		194+996	
1207 (vs)	1204	924+279	$6\nu_2$
1220 (s)		2×194+837	
1395 (vw)		5×279	
1444 (vs)		3×194+837	
1543 (vw)			
1600 (w)		4×194+837	
1638 (s)		2×837	
1704 (vw)		6×279	
1850 (vw)		2×924	
2008 (w)		2×924+194; 7×279	
2247 (vw)		8×279	
3106 (w)			
3226 (s) 3284 (s) 3334 (s)	Water of hydration		
3623 (ms)			
3658 (ms)			
3717 (ms)			

vs—very strong
s—strong
ms—medium strong
w—weak
vw—very weak

EXPERIMENTAL PROCEDURE

Since efforts to prepare single crystals of the compound have not been successful, fine powder of the compound has been prepared and the absorption spectra have been taken using thin layers of the powder as absorbing media at liquid air temperature. The spectra have been photographed on Fuess and Littrow spectrographs, having plate factors of 13A/mm and 7A/mm respectively at 4000A using Ilford selochrome and panchromatic plates. A 1000 watt tungsten filament ribbon lamp, free from any atomic lines, is used as the source of continuum in the region of absorption. The experimental set-up for recording the spectrum of the powder is the same as described earlier[6]. A very clear picture, with the weakestbands, is obtained in one hour exposure, while a few minutes exposure has brought out the strong bands of the spectrum.

The solution absorption spectra of the compound, dissolved in water, with different concentrations have been recorded at room temperature in the region 2000-7500A on a Perkin-Elmer spectracord Model 4000.

The infra-red absorption spectrum for the substance has been taken at room temperature on a Perkin-Elmer double beam spectrophotometer Model 221 with sodium chloride prism, both by potassium bromide pellet and Nujol-mull techniques.

DESCRIPTION AND NATURE OF BANDS

The electronic absorption spectrum of potassium uranyl sulphate obtained with the powders at liquid air temperature, extends from about 4940A in the visible region to 3470 A in the ultra-violet region as shown in Figs. 1 & 2. Dieke & Duncan[3] have given the data only upto 23822 cm^{-1} while in this investigation, bands have been obtained upto 28799 cm^{-1}, thus extending their data by 35 new bands. The data of bands, obtained, are given in column 1 of Table 1. The bands are quite sharp and intense in the visible region, while the sharpness of the bands decreases towards the short-wave length side. Again, the bands in the ultra-violet are sharp. The bands are crowded in the middle of the spectrum due to overlapping of the different systems.

In the solution absorption spectrum, recorded at room temperature, 19 bands have been obtained. The spectrum is shown in Fig. 3 and the data of the bands are given in Table 2.

~~In~~ the infra-red absorption spectrum about 28 bands have been recorded in the region 2 to ~~15~~μ. The spectra by Nujol-mull and KBr disc technique are shown in Fig. 4 and 5 respectively and the data of bands are given in Table 3.

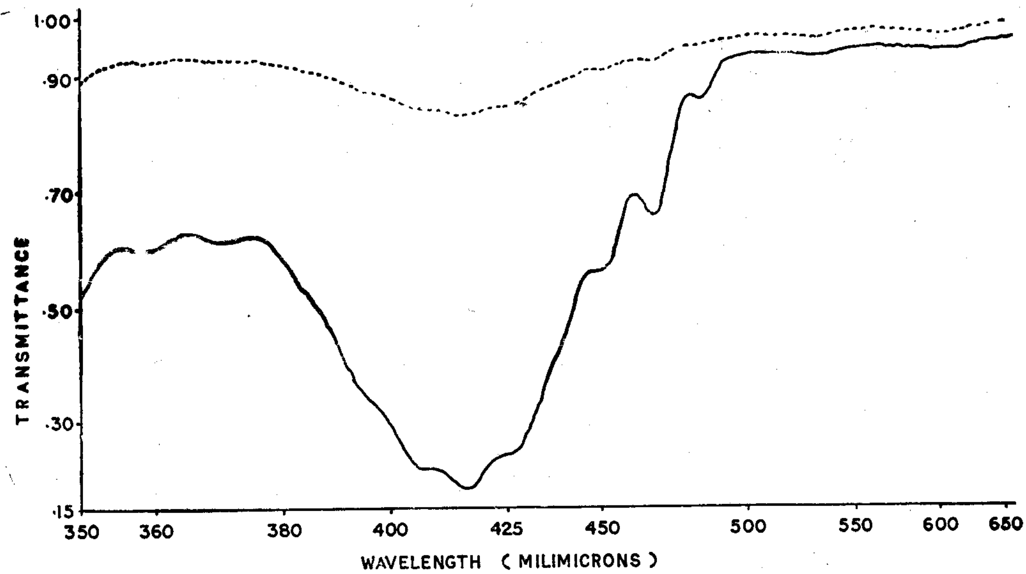

Fig. 3—Solution absorption spectrum of potassium uranyl sulphate at room temperature.
——Higher concentration (0·1N); .... Lower concentration (0·01N).

ANALYSIS OF ELECTRONIC ABSORPTION SPECTRUM

The present analysis has been carried out on the basis of four systems, involving four electronic transitions from common ground state to the various upper states. In the analysis, considerations have been made for the groupings and intensities of the bands. The 0,0 bands for the four systems have been found to be at 20377 cm^{-1}, 21088 cm^{-1}, 22663 cm^{-1} and 26685 cm^{-1}. In Table 1, the detailed interpretations of the absorption bands, obtained with powder at liquid air temperature, is given on the basis of the frequencies of the uranyl ion, sulphate ion and the crystal lattice. The intensities given are visual estimates from the spectrograms in the 1 to 10 scale.

System I

This system corresponds to the fluorescence series of Dieke. The first strong band on the long wavelength side is obtained at ν 20377 cm^{-1}. This band is taken as the 0,0 band of this series corresponding to the 0,0 band of fluorescence[8] (ν 20373 cm^{-1}). In the second group, a similar strong band has a shift of 685 cm^{-1} from the 0,0 corresponding to the symmetric stretching fundamental (ν_1) in the upper state. Similar bands, obtained up to the end of violet region, form a progression of $n \times \nu_1$ One band of moderate intensity at 21184 cm^{-1}, with a shift of 807 cm^{-1} from the 0,0 band, belongs to the ν_3 fundamental in the upper state corresponding to 915 cm^{-1} in the lower state obtained in fluorescence. Two other bands at 20563 cm^{-1} and 20636 cm^{-1}, appearing with moderate intensity in the spectrum, obtained with a thick layer of the substance, have frequency shifts of 186 cm^{-1} and 259 cm^{-1}, from the 0,0 corresponding to the in-plane and out-of-plane bending frequencies respectively in the upper state. It is already seen that the corresponding frequencies in the lower state have been obtained in the fluorescence spectrum. Three other fundamentals 439, 617 and 996 cm^{-1}, which possibly belong to the sulphate ion, have been obtained and these values agree well with the values given by Hibben[9]. Though the fundamentals of the crystal lattice are not obtained in the absorption spectrum, the values 44 cm^{-1} in the ground state and 30 cm^{-1} in the upper state have been taken from the fluorescence analysis to explain the satellite bands in the absorption spectrum. The combinations of all the above mentioned frequencies are also present in the analysis.

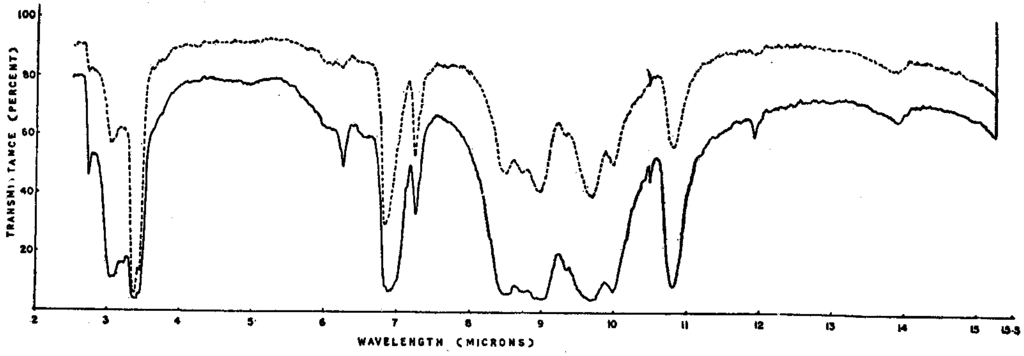

FIG. 4—Infra-red absorption spectrum of potassium uranyl sulphate. (Nujol-mull technique)

——— Higher concentration; ...... Lower concentration

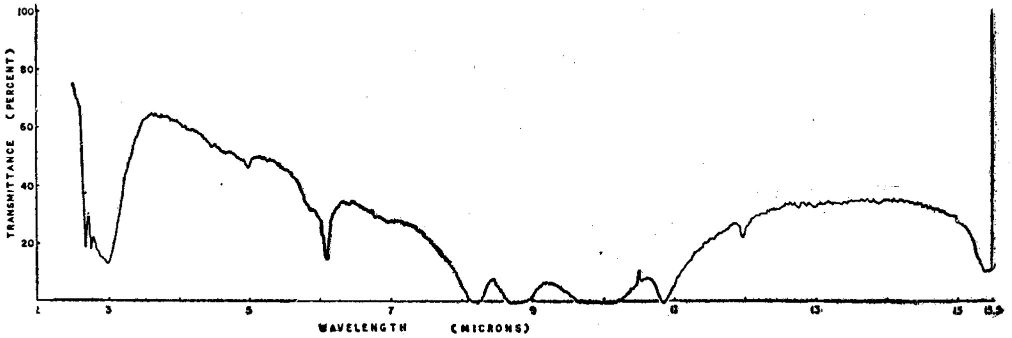

Fig. 5—Infra-red absorption spectrum of potassium uranyl sulphate. (Potassium-bromide disc technique)

System II

The second system in the absorption spectrum starts with a strong and sharp band at 21088 cm^{-1}which is close to the ν_1, fundamental of system I. The bands of the same type are found to occur in the higher groups. Therefore, this band at 21088 cm^{-1} is taken as the 0,0 of this system. A similar band in the next group has a frequency shift of 700 cm^{-1} from the 0,0, corresponding to the symmetric frequency ν_1, in the upper state. The bands of this frequency form a strong progression of $n \times \nu_1$, up to the violet region. In this system, the other bands are interpreted on the basis of the fundamentals 801 cm^{-1} (ν_3) 187 cm^{-1} and 251 cm^{-1} (in-plane and out-of-plane frequencies of the bending vibration ν_2) and 443 cm^{-1} and 990 cm^{-1} of sulphate ion frequencies.

The bands, due to the bending frequencies in the first and second systems, appear with considerable intensity and sharpness, indicating a possibility of the uranyl ion being bent in this compoound. Sevchenko & Stepanov[7] have also come to the same conclusion about the structure of the uranyl ion from their investigations of the infra-red spectrum of the compound.

System III

The diffuse series starts with a diffuse band at 22663 cm^{-1} agreeing well with the starting position of the diffuse series given by Dieke & Duncan[3]. All the bands of this system are diffuse in nature. The ν_1 fundamental has the value 685 cm^{-1} in the upper state. The bands of the higher members of this fundamental become more diffuse towards the short wave length side and, hence, there is an uncertainty in the measurements of these bands up to 30 cm^{-1}.

System IV

This system corresponds to the ultraviolet series of Dieke & Duncan. The bands of this system are again quite sharp possibly because the upper electronic level of this system is considerably away from the upper levels of other systems. The 0, 0 band for this system is found to be at 26685 cm^{-1} . The ν_1 fundamental, having a value 708 cm^{-1}, is obtained.

The bands corresponding to the overtones of this fundamental extend to the end of the spectrum forming a progression of $n \times \nu_1$. A band at 26875 cm^{-1} has a shift of 190 cm^{-1} from the 0, 0 band corresponding to the ν_2 fundamental in the upper state.

Since the solution absorption spectrum has been obtained at room temperature and with a spectrophotometer having dispersion less than the spectrograph employed for the solid state work, we can expect only a broad agreement between the two data (Column 1 and 2 in Table 1). Nichols & Howes have obtained only three bands in their solution absorption experiment at 20360, 21130 and 21890 cm^{-1} agreeing with our values 20400, 21150 and 21900 cm^{-1} respectively.

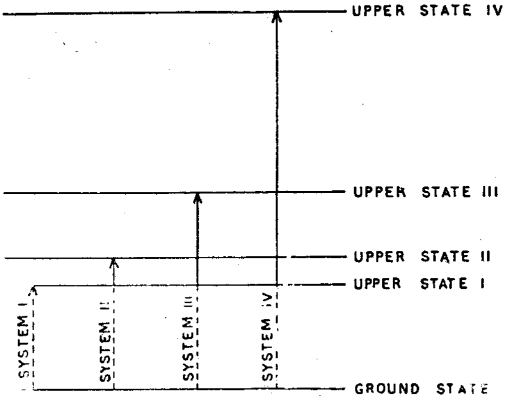

Fig. 6—Representative energy level diagram of potassium uranyl sulphate.

A representative energy level diagram for the electronic absorption spectrum of potassium uranyl sulphate has been shown in Fig. 6 involving a common ground state and the four upper states.

ANALYSIS OF INFRA-RED ABSORPTION SPECTRUM

Out of the 28 bands obtained in the infra-red absorption spectrum of potassium uranyl sulphate, only 19 bands could be interpreted on the basis of the vibrational frequencies of the uranyl ion, sulphate radical and water of hydration. The band corresponding to the ν_1 frequency, having the value 837 cm^{-1} is of medium intensity and the band corresponding to the ν_3 frequency, having a value 924 cm^{-1} is very strong as expected. The wave number values of these two fundamentals agree very well with these obtained in fluorescence[8]. Though the ν_2 fundamental is not obtained as such, as the investigation did not extend up to that limit, however, the values of ν_2 fundamentals (in-plane and out-of-plane vibrations) obtained in the fluorescence, have been used to explain a few combination bands and also overtones of these fundamentals which appear in the region of study. The fact that the bands of the ν_2 fundamentals and their combinations with ν_1 and ν_3 appear with sufficient intensity, give the evidence for the bent structure of the uranyl ion in the potassium uranyl sulphate, as suggested by Sevchenko & Stepanov[7]. A few overtone of the ν_2 fundamental are found to overlap with the bands of ν_1 and combinations of ν_2 and ν_3.

TABLE 3

CORRELATION OF FUNDAMENTAL FREQUENCIES—POTASSIUM URANYL SULPHATE

Type of vibration	Fluorescence (KVN)		Infra-red (Authors)	Infra-red (Sevchenko & Stepanov)	Electronic absorption (Authors)				
	Lower state	Upper state			System I		System II	System III	System IV
					Upper state	Lower state	Upper state	Upper state	Upper state
U-O Symmetric stretching (ν_1)	837	662	837	830	685		700	685	708
O-U-O Symmetric bending (ν_2) (in-plane)	194		194	200	186		187		190
O-U-O Symmetric bending (ν_2) out-of-plane)	279		279		259		251		
U-O antisymmetric stretching (ν_3)	915		924	920	807		801		
SO_4 ion frequency	417				439		443		
do.	597				617				
do.	1001		996		996		990		
Crystal lattice frequency.	44	30			30	44			

Sevchenko & Stepanov[7] interpreted the strong band at 990 cm^{-1} (our value is 996 cm^{-1}) as 5 ν_b, where ν_b is taken as 200 cm^{-1}, corresponding to the symmetric bending frequency. However, this band has been explained by us as the fundamental of the sulphate radical since it has been obtained in the fluorescence and electronic absorption of this compound and, moreover, this is the strongest of the sulphate ion fundamentals[8]. The strong bands at 3226, 3284 and 3334 cm^{-1} could be attributed to water of hydration.

Table 3 gives a correlation of the fundamental frequencies of potassium uranyl sulphate obtained from various data.

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