

# ANALYSIS OF THE FLUORESCENCE BANDS OF THE URANYL SALTS

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## 1. INTRODUCTION

It has been known for a long time that the fluorescence spectra of uranyl salts at low temperatures consist of several discrete and sharp bands which usually fall into six regularly spaced groups. The bands contained in a group are the members of the several series which have been earlier designated as A, B, C, D, E, etc. The frequency interval between the two successive members of the same series is nearly  $860 \text{ cm.}^{-1}$  which in the complementary absorption spectra diminishes to nearly  $700 \text{ cm.}^{-1}$ . These intervals, however, vary slightly from one spectrum to another, and sometimes regular as well as irregular variations in them are also noticed from series to series in the same spectrum.

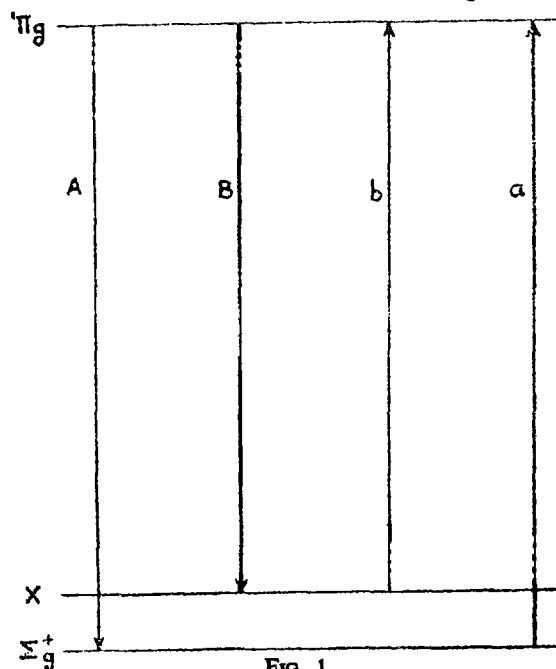
The regularity in the spectra and the fact that only those compounds of uranium which possess the uranyl group are fluorescent, led Nichols and Howes (1919) to suggest that the constant frequency intervals were due to the uranium oxide. Several arguments can now be advanced in favour of this suggestion and particularly the appearance of the  $860 \text{ cm.}^{-1}$  frequency in the Raman and infra-red spectra of uranyl salts (Conn and Wu, 1938; Satyanarayana, 1942) leaves no doubt as to its correctness. The earlier contention of Dieke and Van Heel (1925) that the constancy of the frequency intervals is due to a simultaneous change of the electric moment and the oscillation of the nuclei of the  $\text{UO}_2$  group is also, therefore, correct. The difficulty of explaining the large number of bands and the smaller frequency intervals, however, still remains on this simple idea. In a subsequent paper Van Heel (1925) assuming the existence of one more frequency which he attributed to the vibration of  $\text{UO}_2$  in the crystalline space lattice attempted an interpretation of the bands, but no further work seems to have been done in this direction since then. As is indicated by a remark by Pringsheim (1933) that Van Heel's analysis is analogous to that for the benzene spectrum, presumably his interpretation has finally been taken as satisfactory. This, however, is not true for several reasons to be given in the following section where Van Heel's analysis is discussed in detail.

2. REMARKS ON VAN HEEL'S ANALYSIS

Van Heel has interpreted the spectra at liquid-air temperature of only uranyl potassium sulphate and autunite. In the former case, two frequencies N and P representing respectively the oscillation frequency of the nuclei and the vibrational frequency of  $\text{UO}_2$  in the crystalline space lattice have been taken.  $N = 833 \text{ cm.}^{-1}$  and  $678 \text{ cm.}^{-1}$  respectively in the ground and the excited states and its quantum number can change by any integer, *e.g.*, 0, 1, 2, 3, 4, etc.  $P = 77$  in the ground state and not more than one quantum of this frequency takes part. In the excited state without any change in its quantum number, the value of this frequency changes to 88, 113, 127, 137, 144, 149 and  $149 \text{ cm.}^{-1}$  in the successive group. This would, of course, lead to the assumption of a peculiar type of anharmonicity factor where the frequency of vibration changes without any change in its quantum number, but may still be understood as being due to an extremely strong coupling between the N and P vibrations. This apart, the transitions from (2, 0), *i.e.*,  $N = 2$  and  $P = 0$ , in the excited state to (6, 0) or (7, 0) in the ground state have little significance when the spectrum extends only up to the 6th group (*i.e.*,  $N = 5$ ). Some several relatively strong bands also do not find a place in the analysis. But as we have very little knowledge of the coupling together of the electronic and vibrational energies in the condensed state of matter and also of the various complicated factors that may influence the energy states, the discrepancies outlined above should not be stressed too far. The most outstanding objection to the term scheme, however, is that it is in contradiction with the experimental results. Van Heel's own observations show that the entire fluorescence spectrum appears when the frequency of the exciting radiation equals the electronic frequency. It is also known that whatever may be the frequency of the exciting radiation, the same spectrum always appears. In other words, the luminescence of uranyl salts is a phenomenon of true fluorescence, not of resonance. This obviously demands that the transition to the ground state should be from a single electronic level in the excited state. Whatever may be the absorbed energy, the surplus vibrational energy must be lost by some internal mechanism (*e.g.*, collisions, etc.) and the excited molecule must fall to the upper electronic state before luminescence can occur. In Van Heel's scheme, however, the electronic frequency is  $20383 \text{ cm.}^{-1}$ , while bands are shown to arise from several vibrational levels extending up to  $22554 \text{ cm.}^{-1}$  above the ground state, *i.e.*, up to  $2171 \text{ cm.}^{-1}$  above the excited electronic state. In the absorption spectrum at  $-185^\circ \text{C}$ . also, bands arise from levels as high as  $2577 \text{ cm.}^{-1}$  above the ground level. Thus, it is easily seen that the scheme is quite unsatisfactory.

## 3. BASIS FOR THE NEW ANALYSIS

In spite of the emitter being the same, minor variations in the spectra of various uranyl salts, undoubtedly due to the interaction of the crystalline fields, are observed. It is, however, necessary to have a common interpretation for all the spectra, slight modifications of which would be sufficient to satisfy the more complicated cases. The interpretation has to be consistent with the observational fact mentioned above which imposes the strict condition that the bands should arise out of a single (if more, they should be closely spaced) electronic level in the upper state. With this restriction and the unavoidable lack of knowledge of the energy states of free  $\text{UO}_2^{++}$  molecule, the problem becomes more complicated. Any useful information for further progress can, only be had from a coordinated study of the fluorescence and the absorption spectra, although the Raman and the infra-red spectral data should also be of great help. Taking for example, the fluorescence and the absorption spectra of uranyl fluoride II at  $-185^\circ \text{C}$ ., it is observed (previous paper) that the first two bands designated as A and B in the fluorescence spectrum appear also in



absorption (named  $a$  and  $b$ ) with the important difference that while in fluorescence B is far stronger than A, in absorption  $a$  is stronger than  $b$ . This fact naturally leads to the suggestion that the three levels which give rise to these bands are situated as shown in Fig. 1. (It should be mentioned,

however, that  $\Sigma_g - X$  interval is only 150  $\text{cm.}^{-1}$ ]. The names given to the levels may be taken to be arbitrary for the present.) It requires that  ${}^1\Sigma_g - {}^1\Pi_g$  transition is forbidden while  ${}^1\Pi_g - X$  is allowed. In absorption, at low temperatures, due to the prohibitive Boltzmann factor, the X level will be very much less populated than the  ${}^1\Sigma_g$  level with the result that in spite of the higher  $X - {}^1\Pi_g$  transition probability, the *a* band will be stronger than the *b* band.

#### 4. INTERPRETATION OF THE FLUORESCENCE SPECTRA

##### (a) *Simpler Cases*

*Uranyl fluoride II.*—The three frequencies of the  $\text{UO}_2^{++}$  molecule are known from the Raman and the infra-red spectral studies. The symmetric valence frequency  $\nu_1 = 860 \text{ cm.}^{-1}$ , the deformational frequency  $\nu_2 = 210 \text{ cm.}^{-1}$  and the anti-symmetric valence frequency  $\nu_3 = 930 \text{ cm.}^{-1}$ . The A-B (or  $\Sigma_g - X$ ) interval of 150  $\text{cm.}^{-1}$  does not represent any of these known vibrational frequencies, hence our assumption that both  $\Sigma_g$  and X are electronic levels. The average A-C interval = 230  $\text{cm.}^{-1}$ . The presence of the E band is very doubtful for several reasons, but if it is present B-E interval = 247  $\text{cm.}^{-1}$ . These intervals indeed represent the  $\nu_2$  frequency. The intervals such as A-A, B-B and C-C which are nearly equal have an average value of 863  $\text{cm.}^{-1}$ . This is due to the symmetric valence frequency  $\nu_1$ . The several bands of the spectrum can now be interpreted as in Table I.

TABLE I

Int.	Desig.	$\nu$ Obs.	$\nu$ Cal.	Assignment	Remarks
0	A	20234	20232	$A_0$	Electronic frequency Do.
8	B	20082	20082	$B_0$	
2	A	19366	19369	$A_0 - \nu_1$	Group II Average
10	B	19217	19219	$B_0 - \nu_1$	
4	C	19137	19137 <sup>a</sup>	$A_0 - \nu_1 - \nu_2$	
0?	E	18970?	18972	$B_0 - \nu_1 - \nu_2$	
1	A	18504	18506	$A_0 - 2\nu_1$	Group III Average
9	B	18353	18356	$B_0 - 2\nu_1$	
4	C	18276	18276	$C_0 - 2\nu_1 - \nu_2$	
0	A	17641	17643	$A_0 - 3\nu_1$	Group IV Average
4	B	17492	17493	$B_0 - 3\nu_1$	
4	C	17415	17413	$A_0 - 3\nu_1 - \nu_2$	
0	B	16640	16630	$B_0 - 4\nu_1$	Visually estimated Do.
0	C	16577	16550	$A_0 - 4\nu_1 - \nu_2$	

*Autunite*.—The spectrum has been studied by Van Heel. He has also suggested an analysis for it. But the analysis again suffers from the same defects. We give in Table II the analysis of the bands on the same basis as above.  $A-B = 114 \text{ cm.}^{-1}$ ,  $\nu_2 = 218 \text{ cm.}^{-1}$  and  $\nu_1 = 820 \text{ cm.}^{-1}$ . The spectrum extends only up to the 4th group, and the data do not appear to be complete.

TABLE II

Int.	Desig.	$\nu$ Obs.	$\nu$ Cal.	Assignment	Remarks
5	A	..	19962	$A_0$	Not observed
	B	19848	19848	$B_0$	Do Group I
	C	..	19744	$A_0 - \nu_2$	
1	E	19629	19620	$B_0 - \nu_2$	
1	F	19535	19526	$A_0 - 2\nu_2$	
1	G	19400	19402	$B_0 - 2\nu_2$	
5	B	19028	19028	$B_0 - \nu_1$	Group II
3	C	18929	18924	$A_0 - \nu_1 - \nu_2$	
1	E	18830	18810	$B_0 - \nu_1 - \nu_2$	
1	F	18714	18706	$A_0 - \nu_1 - 2\nu_2$	
1	G	18586	18592	$B_0 - \nu_1 - 2\nu_2$	
5	B	18206	18208	$B_0 - 2\nu_1$	Group III
3	C	18098	18104	$A_0 - 2\nu_1 - \nu_2$	
1	E	18006	17990	$B_0 - 2\nu_1 - \nu_2$	
1	F	17901	17986	$A_0 - 2\nu_1 - 2\nu_2$	
1	G	17784	17772	$B_0 - 2\nu_1 - 2\nu_2$	
2	B	17388	17388	$B_0 - 3\nu_1$	Group IV

(b) *More Complicated Cases*

The spectral analysis becomes more complicated if in addition to the A, B, C and E bands the D bands also appear. Since the A-C and B-E intervals are equal to the deformational frequency, the position of the D bands between C and E becomes difficult to explain as neither the A-D nor the B-D interval corresponds to any of the three known vibrational frequencies of the  $\text{UO}_2^{++}$  molecule.\* Although most of the series, namely, A, B, C, E, F, G, H, I, K and L could be explained in a manner as given above, the D bands cannot be ignored. Arbitrarily explaining the frequencies without regard to the peculiar behaviour of these bands, would have no meaning. We have seen already the unstable nature of these bands in the uranyl chloride spectrum. They appear only at  $-185^\circ \text{C}$ . and disappear even at temperatures as low as  $-110^\circ \text{C}$ . They are accompanied by extended diffuseness, lose their discrete character easily and can be made

\* A frequency close to the  $\nu_2$  frequency observed by Satyanarayana in the Raman spectrum of the solution of uranyl chloride, however, does correspond to the B-D. interval.

to appear as short continua. It is evident that the D bands should have their origin in some unstable state, unlike the other bands. A satisfactory explanation cannot be given before the several possibilities which could give rise to such characteristics are fully discussed. In the following, therefore, we give the analysis for the spectra of the uranyl sulphate, the acetate, the nitrate, the chloride, fluoride II and uranyl potassium sulphate without proposing a definite assignment for the D bands.

TABLE III

Int.	Desig.	$\nu$ Obs.	$\nu$ Cal.	Assignment	Remarks
<i>m</i>	A	20494	20496	$A_0$	Group I
<i>s</i>	B	20332	20332	$B_0$	
<i>d</i>	C	20245	20238	$A_0 - \nu_2$	
<i>v.d.</i>	D	20139	20149	$D_0$	
<i>v.d.</i>	E	20071	20074	$B_0 - \nu_2$	
<i>m</i>	F	19978	19980	$A_0 - 2\nu_2$	
<i>d</i>	F'	19887	19891	$D_0 - \nu_2$	
<i>d</i>	G	19786	19816	$B_0 - 2\nu_2$	
<i>d</i>	H	19714	19722	$A_0 - 3\nu_2$	
<i>d</i>	A	19637	19639	$A_0 - \nu_1$	Group II
<i>s</i>	B	19469	19475	$B_0 - \nu_1$	
<i>m</i>	C	19383	19381	$A_0 - \nu_1 - \nu_2$	
<i>d</i>	D	19292	19294	$D_0 - \nu_1$	
<i>d</i>	E	19218	19219	$B_0 - \nu_1 - \nu_2$	
<i>v.d.</i>	F	19122	19122	$A_0 - \nu_1 - 2\nu_2$	
<i>d</i>	F'	19021	19036	$D_0 - \nu_1 - \nu_2$	
<i>v.d.</i>	G	18934	18959	$B_0 - \nu_1 - 2\nu_2$	
<i>v.d.</i>	H	18869	18865	$A_0 - \nu_1 - 3\nu_2$	
<i>v.d.</i>	A	18792	18782	$A_0 - 2\nu_1$	Group III
<i>s</i>	B	18620	18618	$B_0 - 2\nu_1$	
<i>m</i>	C	18534	18524	$A_0 - 2\nu_1 - \nu_2$	
<i>v.d.</i>	D	18435	18435	$D_0 - 2\nu_1$	
<i>d</i>	E	18344	18360	$B_0 - 2\nu_1 - \nu_2$	
<i>v.d.</i>	F	18250	18269	$A_0 - 2\nu_1 - 2\nu_2$	
<i>d</i>	F'	18160	18177	$D_0 - 2\nu_1 - \nu_1$	
<i>v.d.</i>	G	18065	18102	$B_0 - 2\nu_1 - 2\nu_2$	
<i>v.d.</i>	H	18010	18011	$A_0 - 2\nu_1 - 3\nu_2$	
<i>v.d.</i>	A	17935	17925	$A_0 - 3\nu_1$	Group IV
<i>m</i>	B	17757	17761	$B_0 - 3\nu_1$	
<i>m</i>	C	17672	17667	$A_0 - 3\nu_1 - \nu_2$	
<i>d</i>	D	17582	17578	$D_0 - 3\nu_1$	
<i>d</i>	E	17490	17503	$B_0 - 3\nu_1 - \nu_2$	
<i>v.d.</i>	F	17418	17409	$A_0 - 3\nu_1 - 2\nu_2$	
<i>v.d.</i>	H	17157	17151	$A_0 - 3\nu_1 - 3\nu_2$	
<i>v.d.</i>	A	17068	17068	$A_0 - 4\nu_1$	
<i>v.d.</i>	B	16904	16905	$B_0 - 4\nu_1$	
<i>d</i>	C	16825	16821	$A_0 - 4\nu_1 - \nu_2$	
<i>v.d.</i>	D	16729	16721	$D_0 - 4\nu_1$	
<i>d</i>	E	16637	16647	$B_0 - 4\nu_1 - \nu_2$	
<i>v.d.</i>	F	16535	16553	$A_0 - 4\nu_1 - 2\nu_2$	
<i>d</i>	B	16065	16048	$B_0 - 5\nu_1$	Group VI
<i>d</i>	C	15985	15964	$A_0 - 5\nu_1 - \nu_2$	

## URANYL SULPHATE

We have  $A-B = 165 \text{ cm.}^{-1}$ ,  $B-D = 183 \text{ cm.}^{-1}$ ,  $\nu_2 = 258 \text{ cm.}^{-1}$  and  $\nu_1 = 857 \text{ cm.}^{-1}$

The  $\lambda$  values given by Nichols and Howes have been used after converting them into wave numbers. The designations of the bands are our own. Similar bands in all the spectra have similar designations.

*Uranyl Acetate*

We have  $A-B = 150 \text{ cm.}^{-1}$ ,  $B-D = 150 \text{ cm.}^{-1}$ ,  $\nu_1 = 855 \text{ cm.}^{-1}$  and  $\nu_2 = 235 \text{ cm.}^{-1}$

TABLE IV

Int.	Desig.	$\nu$ Obs.	$\nu$ Cal.	Assignment	Remarks
<i>v.d.</i>	A	20728	20733	$A_0$	Group I
<i>m</i>	B	20583	20583	$B_0$	
<i>..</i>	C	..	20498	$A_0 - \nu_2$	
<i>d</i>	D	20436	20433	$D_0$	
<i>m</i>	E	20349	20348	$B_0 - \nu_2$	
<i>m</i>	F	20278	20263	$A_0 - 2\nu_2$	
<i>d</i>	G	20148	20113	$B_0 - 2\nu_2$	
<i>v.d.</i>	A	19887	19878	$A_0 - \nu_1$	Group II
<i>s</i>	B	19730	19728	$B_0 - \nu_1$	
<i>m</i>	C	19641	19643	$A_0 - \nu_1 - \nu_2$	
<i>v.d.</i>	D	19576	19578	$C_0 - \nu_1$	
<i>a</i>	E	19488	19493	$B_0 - \nu_1 - \nu_2$	
<i>d</i>	F	19416	19408	$A_0 - \nu_1 - 2\nu_2$	
<i>v.d.</i>	G	19352	?	$B_0 - \nu_1 - 2\nu_2$	
<i>v.d.</i>	A	19013	19023	$A_0 - 2\nu_1$	Group III
<i>s</i>	B	18863	18873	$B_0 - 2\nu_1$	
<i>m</i>	C	18785	18777	$A_0 - 2\nu_1 - \nu_2$	
<i>v.d.</i>	D	18714	18723	$D_0 - 2\nu_1$	
<i>d</i>	E	18627	18635	$B_0 - 2\nu_1 - \nu_2$	
<i>d</i>	F	18565	18553	$A_0 - 2\nu_1 - 2\nu_2$	
<i>v.d.</i>	G	18376	18400	$B_0 - 2\nu_1 - 2\nu_2$	
<i>v.d.</i>	A	18164	18168	$A_0 - 3\nu_1$	Group IV
<i>s</i>	B	18013	18018	$B_0 - 3\nu_1$	
<i>m</i>	C	17932	17933	$A_0 - 3\nu_1 - \nu_2$	
<i>v.d.</i>	E	17757	17783	$B_0 - 3\nu_1 - \nu_2$	
<i>v.d.</i>	F	17700	17699	$A_0 - 3\nu_1 - 2\nu_2$	

In the last two groups only the B and C bands are present.

*Uranyl Nitrate*

The B, C, D and E bands (E, D, C, B bands of Nichols and Howes) of the spectrum of uranyl nitrate agree with the corresponding bands of the

above spectrum. No separate analysis is, therefore, given. There is a slight difference in the  $\nu_1$  and  $\nu_2$  frequencies and other intervals. Thus  $A-B = 167 \text{ cm.}^{-1}$ ,  $B-D = 165 \text{ cm.}^{-1}$ ,  $\nu_2 = 250 \text{ cm.}^{-1}$  and  $\nu_1 = 859 \text{ cm.}^{-1}$

*Uranyl Chloride*

The peculiarity of the D bands in this spectrum is that they continuously shift towards the B band in the successive groups. A-D interval in the first group =  $196 \text{ cm.}^{-1}$ , but in the 4th group it has already fallen to  $72 \text{ cm.}^{-1}$ . The D-D interval is, however, constant and is equal to  $854 \text{ cm.}^{-1}$ . B-B or C-C or E-E intervals are equal to  $876 \text{ cm.}^{-1}$ . We have, therefore,  $\nu_1 = 854 \text{ cm.}^{-1}$  and  $876 \text{ cm.}^{-1}$ ,  $\nu_2 = 246 \text{ cm.}^{-1}$ .  $A-B = 174 \text{ cm.}^{-1}$

TABLE V

Int.	Desig.	$\nu$ Obs.	$\nu$ Cal.	Assignment	Remarks
..	A	..	20709	$A_0$	
9	B	20535	20535	$B_0$	
1	C	20462	20463	$A_0 - \nu_2$	
6	D	20339	20339	$D_0$	
8	E	20286	20289	$B_0 - \nu_2$	
1	F	20130	20117	$A_0 - 2\nu_2$	
2	F'	20093	20093	$D_0 - \nu_2$	
1	G	20051	20043	$B_0 - 2\nu_2$	
1	H	19882	19871	$A_0 - 3\nu_2$	
1	A	19833	19833	$A_0 - \nu_1$	Other weaker bands are masked by the general diffuseness
10	B	19655	19659	$B_0 - \nu_1$	
6	C	19574	19577	$A_0 - \nu_1 - \nu_2$	
6	D	19489	19495	$D_0 - \nu_1$	
6	E	19405	19413	$B_0 - \nu_1 - \nu_2$	

Other bands in the higher groups can also be similarly explained.

*Uranyl Fluoride I*

In this spectrum both the C and the D bands shift apart in the successive groups. As above, although the B-C and the B-D intervals considerably change, the B-B, the C-C and the D-D intervals are constant but different. This gives the  $\nu_1$  frequency to be  $819 \text{ cm.}^{-1}$ ,  $827 \text{ cm.}^{-1}$  and  $795 \text{ cm.}^{-1}$  respectively.  $\nu_2 = 176 \text{ cm.}^{-1}$



TABLE VI

Int.	Desig.	$\nu$ Obs.	$\nu$ Cal.	Assignment	Remarks
..	A	..	20188	$A_0$	
6	B	20095	20095	$B_0$	
10	C	20012	20012	$A_0 - \nu_2$	
3	D	19967	19967	$D_0$	
4	E	19912	19919	$B_0 - \nu_2$	
..	F	..	19836	$A_0 - 2\nu_2$	
0	F'	19794	19791	$D_0 - \nu_2$	
3	G	19728	19743	$B_0 - 2\nu_2$	
1	H	19661	19666	$A_0 - 3\nu_2$	
3	I	19578	19567	$B_0 - 3\nu_2$	
10	B	19274	19276	$B_0 - \nu_1$	Coincide
12	C	19183	19185	$A_0 - \nu_1 - \nu_2$	
..	D	19173	19172	$D_0 - \nu_1$	
8	E	19112	19100	$B_0 - \nu_1 - \nu_2$	
1	F	19028	19009	$A_0 - \nu_1 - 2\nu_2$	
3	H	18846	18833	$A_0 - \nu_1 - 3\nu_2$	
3	I	18718	18748	$B_0 - \nu_1 - 3\nu_2$	
1	A	18521	18534	$A_0 - 2\nu_1$	The order of C and D is reversed. With the D band diffuseness starts. End of the diffuseness.
8	B	18455	18457	$B_0 - 2\nu_1$	
3	D	18390	18377	$D_0 - 2\nu_1$	
10	C	18345	18358	$A_0 - 2\nu_1 - \nu_2$	
8	E	18286	18281	$B_0 - 2\nu_1 - \nu_2$	
1	F'	18198	18201	$D_0 - 2\nu_1 - \nu_2$	
1	G	18066	18105 ?	$B_0 - 2\nu_1 - 2\nu_2$	
2	I	17923	17929	$B_0 - 2\nu_1 - 3\nu_2$	
0	A	17686	17609	$A_0 - 3\nu_1$	Beginning of diffuseness
5	B	17636	17638	$B_0 - 3\nu_1$	
3	D	17573	17582	$D_0 - 3\nu_1$	
10	C	17523	17533	$A_0 - 3\nu_1 - \nu_2$	End of diffuseness
8	E	17457	17462	$B_0 - 3\nu_1 - \nu_2$	
1	F'	17399	17406	$D_0 - 3\nu_1 - \nu_2$	
1	I	17085	17110	$B_0 - 3\nu_1 - 3\nu_2$	

The rest of the bands belonging to the higher groups can similarly be explained.

#### *Uranyl Potassium Sulphate*

We have  $A-B = 90 \text{ cm.}^{-1}$ ,  $B-D = 120 \text{ cm.}^{-1}$ ,  $\nu_1 = 833 \text{ cm.}^{-1}$  and  $\nu_2 = 172 \text{ cm.}^{-1}$ . The spectrum contains a large number of bands which have been measured by Nichols and Howes.

TABLE VII

Int.	Desig.	$\nu$ Obs.	$\nu$ Cal.	Assignment	Remarks
<i>v.d.</i>	A	20475	20475	$A_0$	The two have probably coincided
<i>m</i>	B	20385	20385	$B_0$	
<i>d</i>	C	20313	20303	$A_0-\nu_2$	
<i>m</i>	D	20265	20265	$D_0$	
<i>m</i>	E	20197	20213	$B_0-\nu_2$	
<i>s</i>	F	20109	20131	$A_0-2\nu_2$	
<i>..</i>	F'	..	20093	$D_0-\nu_2$	
<i>v.d.</i>	G	20047	20041	$B_0-2\nu_2$	
<i>d</i>	H	19973	19959	$A_0-3\nu_2$	
<i>m</i>	J	19910	19921	$D_0-2\nu_2$	
<i>d</i>	K	19786	19782	$A_0-4\nu_2$	
<i>d</i>	L	19726	19697	$B_0-4\nu_2$	
<i>m</i>	A	19634	19642	$A_0-\nu_1$	
<i>s</i>	B	19554	19552	$B_0-\nu_1$	
<i>m</i>	C	19467	19470	$A_0-\nu_1-\nu_2$	
<i>v.d.</i>	D	19440	19432	$D_0-\nu_1$	
<i>d</i>	E	19365	19380	$B_0-\nu_1-\nu_2$	
<i>m</i>	F	19772	19298	$A_0-\nu_1-2\nu_2$	
<i>..</i>	F'	..	19260	$D_0-\nu_1-\nu_2$	
<i>v.d.</i>	G	19234	19208	$B_0-\nu_2-2\nu_2$	
<i>d</i>	H	19134	19122	$A_0-\nu_1-3\nu_2$	
<i>v.d.</i>	J	19084	19088	$D_0-\nu_1-2\nu_2$	
<i>v.d.</i>	K	18952	18950	$A_0-\nu_1-4\nu_2$	
<i>v.d.</i>	L	18886	18864	$B_0-\nu_1-4\nu_2$	

The other groups can be explained in a similar way. It will, however, be mentioned here that in the last three groups there are no D, F or J bands while A, B, C, F, G, H are present.

## 5. DISCUSSION

It is known from the study of the molecular spectra that the iso-electronic molecules are similar in many respects. The 16 electron molecules, for example,  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{HgCl}_2$ , etc., all have the closed configuration  $\sigma_g^2 \sigma_u^2 \sigma_g^2 \sigma_u^2 \pi_u^4 \pi_g^4$  and have a  ${}^1\Sigma_g^+$  ground state. They are all, without exception, linear molecules belonging to the  $D_{\infty h}$  symmetry. The  $\text{UO}_2^{++}$  molecule has also 16 electrons, namely, the four 5 *d* bonding electrons of the  $\text{U}^{++}$  ion (configuration  $5s^2 5p^6 5d^4$ ) and 12 *sp* bonding and non-bonding electrons of the two oxygen atoms. The X-ray analysis of Fankuchen (1936) shows that the molecule is linear. Conn and Wu, however, suggest a bent structure for it, primarily on the basis of the appearance of the  $\nu_2$  frequency in the Raman spectra of the solutions of uranyl salts. However the  $\text{UO}_2^{++}$  may still be linear in the solid state, as the strong infra-red absorption of the  $\nu_3$  frequency appears to show. The closed configuration of the molecule will have  ${}^1\Sigma_g^+$  ground state. Definite magnetic data are

lacking to test this point, although uranyl nitrate is reported to be diamagnetic in confirmation with the suggestion.\* The next state (X) cannot be due to spin and may be a separate level altogether. The excited state may be a  $(\pi^{-1}g)og$ ,  ${}^1Ilg$  state as observed in other similar molecules (Mulliken, 1941). The  ${}^1Ilg \rightarrow {}^1\Sigma g$  transition would then be forbidden, as already observed. The transition to the X state is probably allowed or is at least more favoured.

Now, both in crystals (Van Vleck, 1937) and in polyatomic molecules (Spomer, 1941), the violation of selection rules is of a frequent occurrence. A forbidden transition can be made allowed by the excitation of a non-totally symmetric vibration. (An allowed transition in the neighbourhood and the effect of the crystalline field would also increase the probability of the transition.) The vibrational structure of such a transition, however, differs in a characteristic way from that of an allowed transition. In the forbidden transition, there must occur a change of a non-totally symmetrical vibration by at least one quantum number upon which will then be superposed the changes of a totally symmetrical vibration. In such a transition the (0, 0) band should be either absent or should be very weak. The weak intensity of the (0, 0) band, *i.e.*, A band of the first group and of the A series which is a pure  $\nu_1$  progression is readily understood. The high intensity of the C bands which are due to a (0, 1) transition of a non-totally symmetric  $\nu_2$  vibration ( $UO_2^{++}$  being assumed to be linear) upon which the changes of the totally symmetric vibration  $\nu_1$  are superposed is again clear. The A and the D series in our spectra closely resemble the I and the A series of the fluorescence spectrum of solid benzene (Kronenberger, 1930). The analysis of Spomer and others of these bands is also exactly the same as ours for the A and the C bands. The increase in the intensity of the C bands after at least one quantum of  $\nu_1$  is superposed on the (0, 1)  $\nu_2$  transition also agrees with the observations of the spectrum of benzene.

The vibrational structure of the  ${}^1Ilg \rightarrow X$  transition agrees well with an allowed transition. The (0, 0) band should be strong and the totally symmetrical vibration should be the only one to change by any quantum number so as to give rise to strong bands. The strong B series which is a pure  $\nu_1$  progression is what should be expected. The B and the D are the only two series which appear with high intensity in all the spectra studied. The intensities of the other series, however, greatly vary from spectrum to spectrum. Such cases must be attributed to the effect of the crystalline field. The general increase in the intensity of the bands in the second

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\* *Vide International Critical Tables*, Vol. VI, p. 359.

group denotes the slight relative displacement of the positions of the energy minima in the ground and the excited states.

The shifting of the C bands in the fluoride I spectrum finds a natural explanation in our scheme, *i.e.*, it is due to the  $\nu_1$  frequency being slightly different for the molecule in the  ${}^1\Sigma_g$  and X states. If the B-C interval were due to a vibrational frequency, a strong coupling between this vibration and  $\nu_1$  would have been necessary to explain the shifting. Similar remarks may also apply to the D bands.

In conclusion, the author wishes to thank Sir C. V. Raman for helpful discussions.

#### SUMMARY

From some direct experimental evidence, it is concluded that the entire fluorescence spectrum of the uranyl salts arises out of a transition from a single excited state (designated  ${}^1Ilg$ ) to the several vibrational states of two close ground levels (designated  ${}^1\Sigma_g$  and X) and that the  ${}^1Ilg \rightarrow {}^1\Sigma_g$  transition is much less favoured than the  ${}^1Ilg-X$  transition. The  $\nu_1$  and  $\nu_2$  frequencies taking part in the transition agree with those observed in the Raman and infra-red spectra;  $\nu_1$  is, however, very much more prominent. The vibrational structure of the  ${}^1Ilg-{}^1\Sigma_g$  transition resembles that of a forbidden transition, while the structure of the other is that of an allowed one. The intensity distribution of the A, B and C bands is explained. No specific explanation of the D bands is given. Van Heel's analysis is shown to be unsatisfactory.

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