

FLUORESCENCE OF URANYL SALTS

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It is well known that the uranyl salts give rise to discrete fluorescent spectra. They consist generally of three to eight band groups having a similar internal structure at low temperatures and having a constant difference in frequency equal to about 860 cm.^{-1} . The emission spectrum lies between the blue and the red region of the spectrum; their absorption spectrum starts from the green region and goes up to the ultra-violet region. The frequency difference between the successive bands in absorption is a smaller constant equal to about 710 cm.^{-1} . These intervals remain fairly the same for all the salts with a maximum variation of about 40 cm.^{-1} among the different salts. Thus the observed emission and absorption bands of uranyl salts can be represented by an energy level diagram. These bands are diffuse at the laboratory temperature, but on cooling to such low temperatures as those of liquid air they become sharp.

While the uranium compounds containing UO_2^{++} ions fluoresce, the uranium compounds not containing the uranyl group do not emit light at all. The characteristics of the spectra are so similar for all uranyl salts. It is obvious that the UO_2^{++} ion intimately influences the spectra and that this radical has a definite vibration-electronic scheme of levels. The intervals in fluorescence or in absorption are not much influenced either by the negative ion or by the metal in the double salts. Moreover, the same intervals appear even in the fluorescence of the salt solutions. Van Heel¹ put forward the idea that the spectrum is due to an electronic jump modified by the oscillation energy of the uranyl ion. That the interval of 860 cm.^{-1} arises from the symmetric vibration of the bent uranyl ion has been confirmed by the determination of the Raman effect of the uranyl salts.²

G. H. Dieke and Van Heel³ first drew up a scheme of levels (Fig. 2) for explaining the fluorescence as well as absorption at room temperatures. They assumed 'm' to represent the electronic quantum number; $m = 0$ is the ground state while $m = 1$ represents the first excited state. n is used to denote the vibrational quantum number for excited as well as the ground states, the intervals in them being 710 cm.^{-1} and 860 cm.^{-1} . At liquid-air temperature, Van Heel introduced one more quantum number p which would influence the vibrational quantum numbers. As the resolution of the spectra vanishes in solutions and solid solutions even at low temperatures, it was concluded that

the small intervals disappear with the destruction of crystal structure. So p was identified with the space lattice vibrations. For example, he drew the scheme for the spectra of uranyl potassium double chloride at 20°C . Well-formed crystals of this substance have different absorption along their different axes. Along the axis, where there is greater absorption, the fluorescence is greater and also better polarised; this spectrum has been called the green spectrum. Along the other axis the white spectrum is emitted. Van Heel has also studied the fluorescence of other double salts, such as autunite and uranyl potassium sulphate at low temperatures.

In the present paper the fluorescence of uranyl nitrate has been studied. Uranyl nitrate is the most common uranyl salt which crystallises with six molecules of water of crystallisation. Large and clear crystals may be easily procured by slowly evaporating a slightly acidic solution. The substance

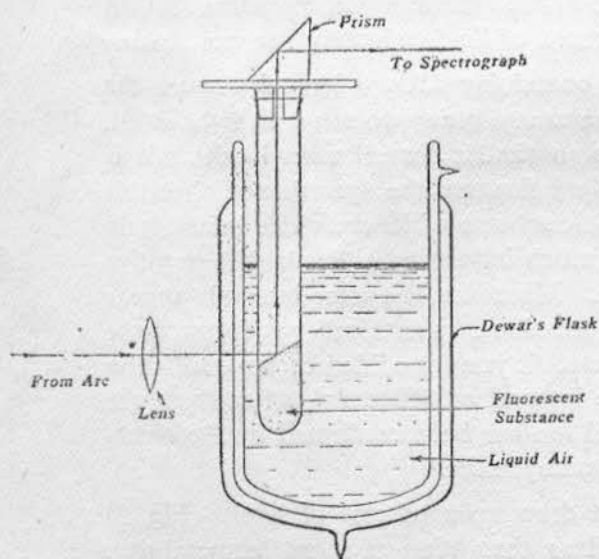


FIG. 1

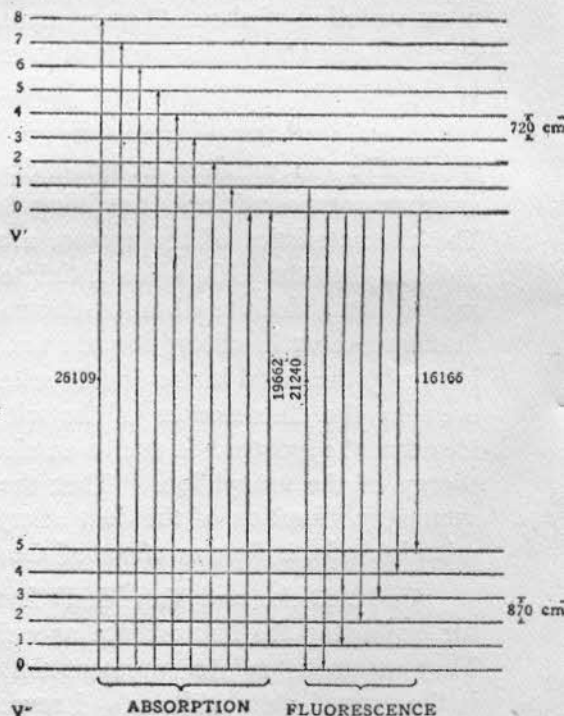


FIG. 2

crystallises in the rhombic system. The data of the spectrum obtained from the monograph on the fluorescence of the uranyl salts by Nichols and Howes⁴ were supplemented by a redetermination of the frequencies of the prominent bands using a high dispersion Hilger E_1 spectrograph with glass train. For this purpose, the uranyl nitrate was placed in a pyrex glass tube and illuminated

by means of a mercury arc as shown in Fig. 1. The fluorescent light was obtained from the top by means of a right-angled prism placed on a glass plate attached to the stopper with a central hole in it. The surface of the powder was suitably tilted in order that maximum amount of fluorescent light may be focussed on the spectrograph when the substance was illuminated. Fairly intense spectrograms could be got after an exposure of about two hours on hypersensitive panchromatic plates. At room temperature, the bands are very wide having a width of about 80 Å. At liquid-air temperature, the tube was surrounded by triple-walled transparent Dewar flask. The tube was placed very near the walls of the flask containing liquid air so that the absorption of incident light by liquid air may be reduced. The fluorescence of the salt increases and the bands exhibit structure. The difference between the fluorescence at room temperature and liquid-air temperature may be clearly noticed in the spectrogram (Plate I, Figs. *a* and *b*). It seems as though crests of the bands at room temperature shift to a great extent towards longer wave-length side from the intense bands at -185°C . Nichols and Howes are of the opinion that the shift in the bands is due to the change in the intensity of the individual components with temperature. They believe that the stronger bands at liquid-air temperature are suppressed at room temperature and that the weaker bands correspondingly rise in intensity.

The following tables give the fluorescence and absorption bands of the nitrate at room temperatures.

Fluorescence of uranyl nitrate at 20° C.

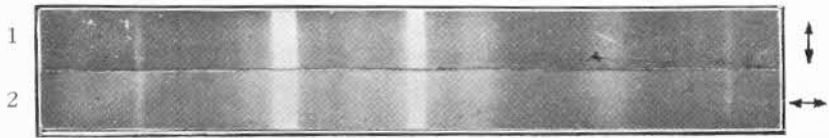
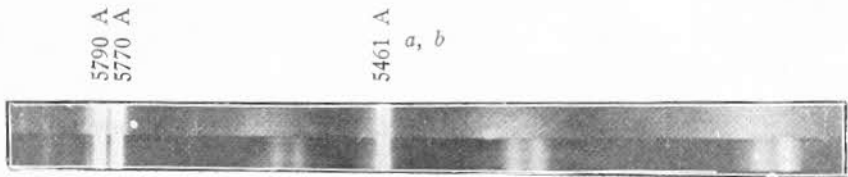
Absorption of uranyl nitrate at 20° C.

Wave-numbers of bands	Transitions v' to v''		Wave-numbers of bands	Transitions v'' to v'	
16166	0	5	19662	1	0
17047	0	4	20534	0	0
17905	0	3	21256	0	1
18765	0	2	21978	0	2
19662	0	1	22701	0	3
20534	0	0	23392	0	4
21240	1	0	23981	0	5
			24691	0	6
			25413	0	7
			26109	0	8

It was deemed interesting to examine whether the fluorescent light from the surface exhibited any polarisation. No changes could be detected even though the incident light was polarised by means of a nicol and the fluorescence examined by means of the double-image prism. The photographs are reproduced in Plate I. Figures *c* and *d* are the spectra of the fluorescence of uranyl nitrate at room and liquid-air temperatures respectively. 1 and 2 represent the fluorescence with the vibration vectors vertical and horizontal respectively. The polarised fluorescence of uranyl sulphate and uranyl acetate at liquid-air temperatures are reproduced in Figures *e* and *f* respectively. Neither the structure of the bands nor their intensities show any marked difference in the two polarised components.

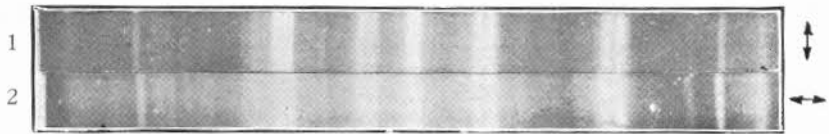
An interesting point has come into light in this study of the fluorescence spectra. The intensities of certain bands vary when the substance is cooled to liquid-air temperature from the ordinary temperature. The most intense band in the whole set at the laboratory temperature shifts to the next band on the shorter wave-length side at -185°C . For example, at $+25^{\circ}\text{C}$., the band with a wave-number corresponding to 18750 is the brightest in the emission spectrum of uranyl nitrate. On the other hand, the 19650 cm^{-1} band is the most intense at the lower temperature. The intensities of the other bands on either side gradually decrease. This fact would play an important part in fixing the principal electronic transition in the spectra. This shift of the intensity of the bands towards the red at the higher temperature is consistent with energy considerations. The Boltzmannian population of the higher vibrational levels in the ground state would naturally increase with the temperature; hence the intensity also would shift more and more towards the red.

Though the spectra of the salts arising out of the vibration of the uranyl ion are remarkably similar, a full variety is displayed in the finer structure of the bands at low temperatures. The crystal structure seems to be very important in influencing the structure of the bands. The water of crystallisation is very closely associated with the uranyl radical and entirely alters the crystal structure also. For example, uranyl nitrate hexahydrate is rhombic, uranyl nitrate trihydrate is triclinic and uranyl nitrate dihydrate is rhombic. Lack of similarity in the structure of the bands due to these different nitrates is obvious. But a crystalline structure seems to be essential for the presence of the narrow components in the spectrum. In the case of canary glass, a rather unusually broad vague doublet occurs at $+20^{\circ}\text{C}$. At the temperature of liquid air, the doublet is partially resolved, but no narrow components appear. It is clear that the absence of the components

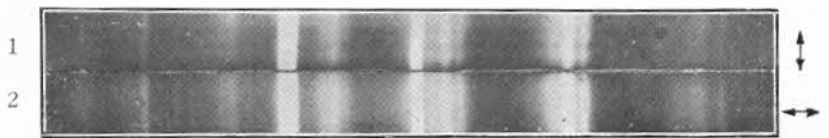


5790 A
5770 A

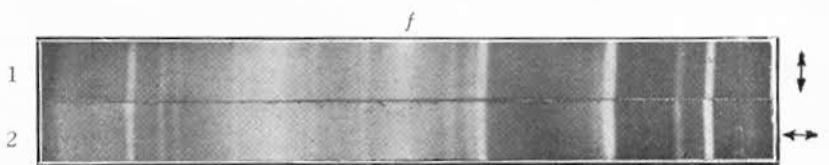
c
5461 A



d



e



f

even at low temperatures is to be traced directly to the non-crystalline structure of the substances.

All these considerations lead us to infer that the effect of the acid radical which is associated with the uranyl ion, will be to subject the vibrational levels to a type of Stark effect⁵ thus introducing a close splitting in them with its magnitude depending on the acid radical and the crystal fields. The splitting in the levels may also be interpreted as arising from a combination of the lattice frequencies with the vibration states since the lattice oscillations are governed by the associated acid radical and the crystal structure. Besides these two conditions, the splitting is also conditioned in the same uranyl salt by the amount of water of crystallisation, which gives rise to different hydrates of varying crystal structure. The close splitting of vibration levels caused either by lattice oscillations or by a Stark effect should be capable of explaining the structure of the bands at low temperatures.

Summary

The spectra of the fluorescence of uranyl nitrate both at laboratory and liquid-air temperatures have been studied under high dispersion. The fluorescent spectra of uranyl salts excited by polarised light reveal complete depolarisation. The width and intensity variations of the bands at different temperatures are accounted for. The structure of the bands prominently displayed at low temperatures is considered to arise out of a Stark splitting of levels due to crystal fields. The fusion of these close levels at laboratory temperatures would account for the observed width of the bands.

Finally, it is my pleasant duty to tender my hearty thanks to Dr. L. Sibaiya for his kind guidance during the course of the investigation.

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