

ELECTRONIC TRANSITIONS OF URANYL ION*

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INTRODUCTION

THE absorption spectra of uranyl salts have been studied by a large number of workers both in the solution and the crystalline state.¹⁻³ The crystalline state spectra have been studied in the region 5000 Å to 3400 Å, after which the absorption coefficient becomes high. In the solution state it has been possible to record spectra upto 1900 Å. The region from 5000 Å to 3400 Å was once supposed to be a single electronic band system^{4, 5} on account of its apparent mirror symmetry with the fluorescence. It is now believed⁶⁻⁸ that the regularity in the banded region is due to a fortuitous coincidence caused by the overlapping of several electronic transitions. Dieke and Duncan,² on the basis of the spectra of some crystalline salts, classified the electronic transitions observed in the region 5000 Å to 3400 Å as: F, M, D, U series. McGlynn and Smith⁷ have divided the region 5000 Å to 3400 Å into three electronic transitions arising from three levels of a triplet. In fact the differential changes in absorption intensity and contour shapes show, as will be evident in this paper, that their region (2) is composed of two separate electronic transitions. Bell and Biggers²⁸ have also attempted to resolve the absorption envelope into 14 bands of Gaussian shape by means of computer techniques and the bands have been divided into three groups to form the three vibronic transitions from ground state to a triplet in accordance with the model proposed by McGlynn and Smith. It is to be noted, however, that the intensity distribution in the bands does not satisfy Franck-Condon distribution. Considerable changes are observed in the contour shapes, band positions and intensities if an extra perturbation is brought about in the sphere of solvation or co-ordination by changing pH, concentration, etc. In discussing the molecular species which may be present in the various solutions of uranyl nitrate studied by

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them, Kaplan, Kildebrandt and Ader (cited by Rabinowitch and Belford⁸) thought to recognise six spectral types in the absorption spectra. We believe that these differential changes in the intensity distribution, contour shapes and band positions with varying pH, etc., provide evidence for separate electronic transitions. Even under perturbed conditions in the solvation sphere major changes in the spectra do not take place; hence it is natural to expect the differential changes as arising due to perturbation of different electronic transitions to varying extents. A detailed study has been made in this laboratory on the absorption spectra of uranyl salts and solutions both at room temperature (R.T.) and at liquid air temperature (L.A.T.). The purpose of this paper is to present a concise account of this work and discuss the results with a view to elucidating the various overlapping electronic transitions in the region 5000 Å to 1900 Å.

The curves reported include unpublished data of Bist⁹ and Khandelwal.¹⁰ The room temperature spectra were obtained with the help of Hilger Uvispec Spectrophotometer or on Beckman Recording Spectrophotometer DK-2 (at Iowa State University, Iowa). For recording the spectra at L.A.T. a Bellingham and Stanley monochromator with a photomultiplier and galvanometer arrangement was suitably adapted to measure the optical density. The chemicals used were A.R. grade, recrystallised before use from solutions in double distilled water.

ANALYSIS OF EXPERIMENTAL RESULTS

(a) Absorption Studies on Crystalline Salts

The absorption spectrum of uranyl nitrate hexahydrate (UNH) has been classified by Dieke and Duncan² into four series. A similar analysis obtained in our laboratory is summarised below:

(i) The fluorescence series (F) starts at *ca* 4855 Å and the successive bands fall after intervals of *ca* 700 cm^{-1} . The maximum intensity is attained in the second band. The fine structure of these bands can be explained by assuming two vibrational frequencies $\nu_1 = 700 \text{ cm}^{-1}$ and $\nu_2 = 725 \text{ cm}^{-1}$ of the excited uranyl ion along with a frequency *ca* 30 cm^{-1} superposed on the (0, 0) band.

(ii) The second series called the magnetic series (M) starts at *ca* 4650 Å. The third band is the most intense in the series which can be traced upto its seventh member. The first two groups show a splitting of *ca* 150 cm^{-1} and the bands occur with an interval of *ca* 705 cm^{-1} .

(iii) The third and the most intense series starts from *ca* 4300 Å and is called the diffuse series (D). It attains its maximum intensity in the violet component band of the second group and can be followed upto the seventh member. The average interval between the bands of this series is *ca* 710 cm^{-1} and each group has two prominent bands with a separation of *ca* 160 cm^{-1} .

(iv) The ultra-violet series (U) starts from a *ca* 5670 Å and has comparatively sharper doublets with irregular spacings. The main bands fall at intervals of *ca* 710 cm^{-1} .

The M, D and U transitions show in general a doublet splitting varying from 150 cm^{-1} to 400 cm^{-1} . In some cases a splitting of *ca* 150 cm^{-1} was recognised in the fluorescence series also by Pant¹¹ and by Pant and Pande,¹² the so-called A and B series. Beyond U-series the absorption has not been studied in detail. In some cases a new series has been reported by Pande¹³ to start after the second or third member of U-series. In the case of uranyl sulphate trihydrate (S_1), uranyl chloride (S_1), $\text{Cs}_2\text{UO}_2\text{Cl}_4$ and potassium uranyl chloride, such a series starts at about 3491 Å, 3486 Å and 3581 Å respectively. This series, hereafter called the second ultra-violet (SU), has also been observed in this laboratory in pyridine uranyl chloride complexes.¹⁴ Data on the various electronic transitions observed in a number of crystals of uranyl salts are given in Table I.

(b) *Absorption of Molten Uranyl Nitrate Hexahydrate (UNH) Snap Frozen to 80° K.*

The frozen melt, unless snap frozen, shows the usual spectrum of UNH. The spectrum of snap frozen melt resembles that of concentrated acidic solutions and the bands are without any fine structure. From the photographic and photometric records 12 bands have been recorded. Their positions are given in Table II along with the assignments, the justification for which follows.

The fluorescence series a' (so named after the a' series in fluorescence¹⁵) is violet shifted with respect to the (0, 0) band of crystal both in fluorescence and absorption.

The interval between the first and the second band is somewhat larger than between successive bands thereafter. Moreover, the optical density shows almost a ten-fold increase on going from first band to the second band, and does not rise appreciably thereafter. This gives a strong suggestion that another electronic transition starts from *ca* 4622 Å, which there-

TABLE I

Origins of the various electronic transitions in crystalline uranyl salts

Salts	Transitions cm. ⁻¹					
	F	M	D	U	SU	
Chlorides:						
S ₁	(13)	20535	21180	22362	26690	28677
S ₂	(13)	20335	21080	23347	26636	..
Cs ₂ UO ₂ Cl ₄	(13)	20088	20629	22233	26185	27693
K ₂ UO ₂ Cl ₄ ·2H ₂ O	(13)	19975	20511	22232	26269	27917
Rb ₂ UO ₂ Cl ₄ ·2H ₂ O	(2)	19961	22279
Pyridine uranyl chloride:						
Form I	(14)	20064	20660	22644	25730	27771
Form II	(14)	20027	20598	22581	25596	..
Deutero-pyridine uranyl chloride:						
Form I	(14)	20063	20656	22645	25739	..
Form II	(14)	20027	20603	22583	25596	..
Acetates:						
S ₁	(13)	20592	21245	22435	26650	..
S ₂	(13)	20288	21270	22379
S ₅	(13)	20690	21601
NaUO ₂ Ac ₃	(13)	21127	21915	23832	27140	..
NH ₄ UO ₂ Ac ₃	(2)	21056	21811	23740	26876	..
Pyridine uranyl acetate:						
MgUO ₂ Ac ₄	(2)	20996	21725	23636	27568	..
Sulphates:						
S ₁	(13)	20326	21150	22295	26532	28636
S ₂	(13)	20540	21377	22533
S ₃	(13)	20428	21328	22382
S ₃	(13)	20306	20943	22013	26553	..
(NH ₄) ₂ UO ₂ (SO ₄) ₂	(2)	20358	..	22544	27635	..
(K ₂ UO ₂)(SO ₄) ₂	(2)	20389	..	22680	27702	..
Cs ₂ UO ₂ (SO ₄) ₂ ·3H ₂ O	(2)	20593
Rb ₂ UO ₂ (SO ₄) ₂	(2)	20390
Nitrates:						
Hexahydrate	(13)	20588	21487	23212	27278	..
Trihydrate	(2)	20778
KUO ₂ (NO ₃) ₃	(2)	21183	21873
K ₂ UO ₂ (NO ₃) ₄	(2)	20807
CsUO ₂ (NO ₃) ₃	(2)	21090	21693	23740	26832	..
RbUO ₂ (NO ₃) ₃	(2)	21199	21697	23808	26959	..
K ₂ UO ₂ (CO ₃) ₂	(2)	20943	27775	..
Uranyl fluoride	(2)	20065	21214	22469

fore, corresponds to the violet component of M-series of UNH. The violet component of M-series seems to gain intensity in the melt. The broad

though well-resolved bands of M-series overlap the bands due to weaker fluorescence series which fall at the longer wavelength slope of the bands. The D-series is weaker in the spectrum of melt as compared to crystal. The origin of D-series seems to be masked by the stronger 4324 Å band of M-series. The doublet structure can, however, be estimated from the second member. The extrapolated (0, 0) band falls at *ca* 4270 Å which is also violet shifted with respect to the corresponding band in the crystal.

TABLE II

Absorption bands in the snap-frozen uranyl nitrate hexahydrate melt at L.A.T.

Band No.	λ in Å	ν in cm.^{-1}	$\frac{\text{Optical density}^*}{\text{Intensity (visual)}}$	Observed $\Delta\nu$	Assignment
1	4805	20806	0.17*
2	4622	21631	1.70*	825	M ₀
3	4467	22380	1.90*	749	M ₁
4	4324	23120	1.80*	740	M ₂
5	4190	23860	..	740	M ₃
6	4145	24119	vd	259	D ₁
	4095	24413	vd
7	4025	24838	vd	719	D ₂
	3980	25119	vd
8	3912	25555	vd	717	D ₃
	3883	25746	vw, vd
9	3805	26274	vw, vd	719	D ₄
10	3645	27627	w	1153	U ₀
	3618	27656	w	228	..
11	3515	28281	w	626	U ₁
12	3460	28894	w	613	U ₂
	3430	29146	vw

w—weak ; vw—very weak ; vd—very diffuse.

The U-series can, however, be easily separated from the extended portions of M and D-series. The first doublet band of U-series appears with rather low intensity, being violet-shifted with respect to the corresponding bands of the crystal. So far as intensity is concerned, U-series is not much affected in melt. The bands of this series can be traced upto the third member after which the absorption could not be studied. The absorption spectrum of snap-frozen uranyl nitrate hexahydrate melt is shown in Fig. 1.

(c) *Absorption of Acidic Solutions Frozen into a Glass at 80° K.*

The influence on the absorption spectrum of variation of uranyl content in nitric acid (16 N) may be summarised as follows:

The F-series consists of the α' bands, as in the spectrum of the melt. The intensity of M-series is high in acidic solutions. Comparison with crystal spectrum shows that of the two components of the M-series the violet one is the stronger in the spectrum of the melt, while the red component gains in intensity with increase of H^+ ion concentration. The D-series remains weak as in the spectrum of melt. The U-series remains unchanged.

(d) *Absorption of Concentrated Aqueous Glasses at 80° K.*

The absorption spectra of frozen aqueous glasses having uranyl concentrations from 5 M to 2 M show the following changes on dilution:

There is a marked diminution in the intensity of α' bands without any appreciable shift. Simultaneously a new series of bands α begin to appear on the longer wavelength side of α' , the first member of α being close to the F-series of UNH. The intensity of M-series diminishes rapidly on dilution and the optical density of the first band of M-series decreases from 1.72 in 5 M to 0.40 in 3.5 M uranyl glass.¹⁰ The intensity of D-series, however, increases remarkably on aqueous dilution. The band peaks are closer to the violet component of the D-series in UNH and show a red shift with respect to the corresponding bands of the melt. The U-series is present with almost usual intensity and gets slightly red-shifted on aqueous dilution. A representative of the spectrum of frozen aqueous glasses is shown in Fig. 1.

(e) *Absorption Spectra of Uranyl Solutions at R.T.*

Some representatives of the spectra of aqueous solutions at R.T. are shown in Fig. 2. The details are reported by Khandelwal.⁶ We interpret

the remarkable changes in the contour of the absorption curves as being due to differential perturbation brought about by ligands in different electronic transitions. Thus in acidic solutions the M-series is stronger and D-series is weaker, while in aqueous and alkaline solutions the reverse is true. The acidic solutions resemble the melt. The F-series gets violet-shifted in acidic solutions and red-shifted with increase of pH.

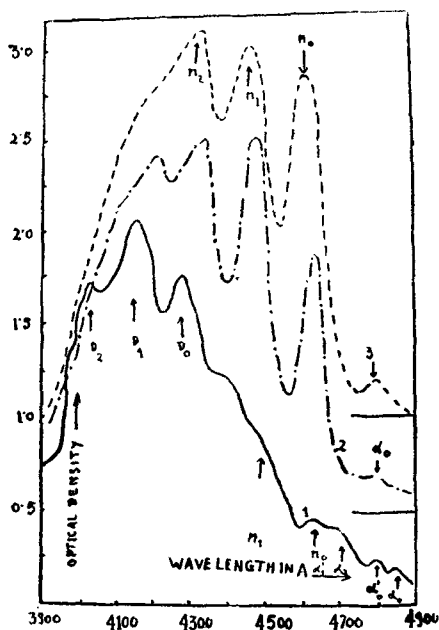


FIG. 1

FIG. 1. Absorption spectra of UNH solutions at L.A.T: (1) Aqueous solution 2.0 M, (2) Acidic solution 3.5 M, (3) Snap-frozen UNH melt.

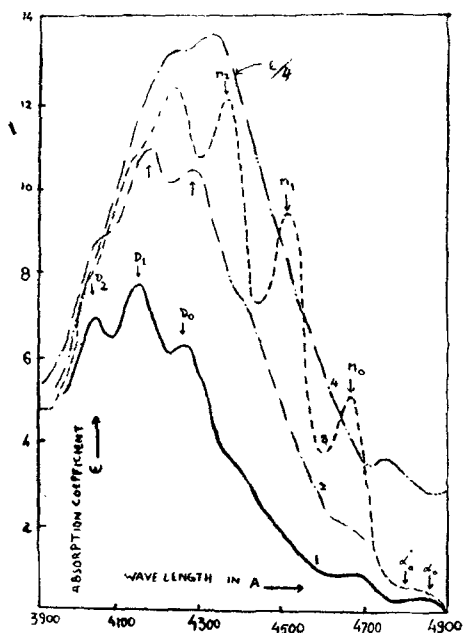


FIG. 2

FIG. 2. Absorption spectra of UNH solutions at R.T. : (1) Aqueous solution 0.1 M, (2) Aqueous solution 2.08 M, (3) 0.1 M solution in HNO_3 (16 N), (4) 0.1 M solution (highly alkaline).

(f) *The Full Absorption Curve for Uranyl Solutions at R.T.*

The full absorption curve from 5000 Å to 1900 Å for 0.01 M aqueous solutions of uranyl nitrate, uranyl chloride and uranyl perchlorate, obtained on Beckmann spectrophotometer, is shown in Fig. 3. This figure also contains the absorption curve of UNH from 5000 Å to 3400 Å, obtained on Hilger Uvispec Spectrophotometer. The banded region is observable upto 3000 Å for all the three substances. Of this region, the portion upto 3400 Å has already been shown to consist of four electronic transitions F, M, D, U.

however, the ϵ_{max} for the SU-series will be much smaller since there is contribution to the absorption by the tail part of yet another continuous type of electronic transition which follows it on the shorter wavelength side. It is found that on increasing pH a band develops around 3400 Å in uranyl nitrate solutions along with two more bands which develop at *ca* 3050 Å and at 2550 Å respectively.⁶ This behaviour has also been observed in uranyl acetate solutions.⁹ With increasing pH all these bands get red-shifted but to varying extents (Fig. 4).

Below 3000 Å there is again a steep rise in ϵ , which becomes more evident on subtracting the contribution due to the SU-transition. This indicates the starting of yet another electronic transition from about 3050 Å, where a band is found to develop on increasing pH. The maximum value of ϵ for this transition, which we call third ultra-violet (TU) transition, is about 200. The discontinuity in the contour shape is also evident from the inspection of the reported absorption curves of various uranyl salt solutions by Ahrlund¹⁷ which suggests starting of new electronic transitions.

There is again a discontinuity in the contour and yet steeper rise in ϵ occurs from about 2550 Å. The band developing at *ca* 2000 Å in the solution of uranyl nitrate is due to nitrate ion. The very steep rise in ϵ in uranyl chloride and uranyl perchlorate solutions at about 1900 Å is due to the corresponding anions. As remarked earlier, a band develops around 2550 Å in alkaline solutions and may be thought to be due to the perturbation of still another electronic transition, lying in this region. Another interesting observation is by Osada¹⁶ who found that in uranium glasses an absorption band develops at *ca* 2350 Å. We shall call the electronic transition starting at *ca* 2550 Å as the fourth ultra-violet (FU) transition. The last two electronic transitions, *viz.*, TU and FU do not show any vibrational structure.

THEORETICAL CONSIDERATIONS

Theoretical approach towards understanding of uranyl ion has started recently.^{7, 18, 19} It seems worthwhile to quote the remark by Rabinowitch and Belford.³ "Since the uranyl compounds involve far too many electrons and nuclei to be given detailed description based purely on first principles, all the theoretical treatments for some time are sure to be at best semi-empirical—whether explicitly or in a disguised manner." The ground state of a free uranyl ion is established to be a $^1\Sigma_g^+$ state the electron configuration however is still not settled. McGlynn and Smith⁷ gave the electron

configuration to be $(1\sigma_u^+)^2 (1\sigma_g^+)^2 (1\pi_u)^4 (1\pi_g)^4$ while Newman¹⁹ has proposed σ bond to be highest.

TABLE III

Data on the electronic transitions of uranyl ion

Electronic transition	Approximate position in Å	$\epsilon_{\max.}$	Mean vibrational frequency in cm.^{-1}
Fluorescence series			
(band origin) F_0	4850	0.7	720
Magnetic series			
(band origin) M_0	4620	7	700
Diffuse series			
(band origin) D_0	4280	10	700
Ultra-violet series			
(band origin) U_0	3620	3	690
Second ultra-violet series			
(band origin) SU_0	3440	20	700
Third ultra-violet transition			
TU			
$\lambda_{\max.}$	3050	200	..
Fourth ultra-violet transition			
FU			
$\lambda_{\max.}$	2550	1000	..

The triplet model proposed by these workers for excited states has, however, been criticised.^{3, 20} There is ambiguity in the explanation of the Zeeman effect which is observed in some uranyl compounds. Another point is that the separation F-M and M-D should be equal, which it is not, were these transitions to bear their origin to the three components $\Omega = 0, 1, 2$ of $^3\Pi_u$ state.²¹ Moreover the F-series, if it is due to a $^3\pi_0$ upper state, should show a magnetic splitting contrary to experimental findings of Dieke *et al.* We shall examine the manners in which ground state and the excited states arise for a hypothetical free linear symmetrical uranyl ion and present briefly an alternative point of view.

Free uranium atom is supposed to have six valence electrons in the configuration of $5f^3 6d' 7s^2$. The U^{6+} ion and similarly the two O^{--} ions, which may be supposed as constituents of uranyl ion, have inert gas electron configuration. The three ions at large distances will be diamagnetic and remain so when uranyl ion is formed (Pascal's law) or may possess a feeble temperature-independent paramagnetism. This view is supported by the

magnetic susceptibility measurements on uranyl salts. Apart from electrostatic binding there should be covalent binding as demonstrated by Crandall.²² Eisenstein²³ has suggested the use of fd hybrids for uranyl ion. In the field of cylindrical symmetry the atomic d and f orbitals of uranium split giving orbitals designated as $|2, 0\rangle$, $|2, 1\rangle$, $|2, 2\rangle$ and $|3, 0\rangle$, $|3, 1\rangle$, $|3, 2\rangle$, $|3, 3\rangle$ respectively in the increasing order of energy with increasing value of m_l . The linear combinations of these give various fd hybridised orbitals. The orbitals $|2, 0\rangle \pm |3, 0\rangle$ and $|2, 1\rangle \pm |3, 1\rangle$ give rise to σ and π bonds respectively by overlapping with appropriate $2p$ orbitals of oxygens and we get a triple bonded uranyl ion with ground state ${}^1\Sigma_g^+$. The σ and π bonding MO's are in fact linear combinations of hybridised f , d orbitals and oxygen group orbitals. This means that a correlation can be found in the picture of electrons in the MO's of uranyl ion and the picture when constituent ions are separated. Such a correlation should also be there for excited uranyl ion. The excited states, at least some of them, should thus be described by MO's which are linear combinations of central uranium orbitals and oxygen group orbitals. This assertion, if accepted, restricts the value of spin to zero and the excited states thus resulting will be singlet states. The absorption coefficient for uranyl ion in the visible and near UV region is rather low, indicative of the disallowed nature of transitions and that in the region beyond is greater by one or more orders of magnitude. The above refers to the co-ordinated uranyl ion, however, for the free uranyl ion which is being considered the state of affairs grossly should not have been much different. It is probably for the above reason that a triplet-excited state was proposed by McGlynn *et al.* The disallowed nature equally suggests crystal field type transitions, the excited states arising by a rearrangement of coupling between inner electrons and the transitions are parity-forbidden. Another point is that the vibrational frequency in the excited states does not change much. The symmetric frequency in the ground state is *ca* 860 cm^{-1} which in all excited states becomes about 700 cm^{-1} . This decrease can be accounted for by removing nearly half a bond from the three bonds of uranyl ion. Qualitatively f , d combinations other than those used in the ground state produce half as much overlap. The five transition showing vibronic structure may thus be supposed due to excitation in the states arising by a rearrangement of coupling of f and d electrons, of course, with the restriction on resulting MO's as already stated. The excited state MO's may be written²⁴ as

$$\phi = A \psi_{fd \text{ hybrid}} + \frac{\sqrt{1-A^2}}{2} \psi_{oxy}$$

where A is a mixing coefficient, ψ_{oxy} are oxygen group orbitals and ψ_{fd} hybrid are central ion functions. The explicit inclusion of oxygen orbitals, while limits the number of crystal field transitions, give rise to possibility of charge transfer spectra. Thus transitions may occur from orbitals having a predominant central ion character (ground state MO's) to those having predominating ligand character. The observed spectrum is put in this category if the intensity is much greater than crystal field spectra. Finally, depending on whether a σ bond (Newman) or π bond (McGlynn and Smith) is higher energetically, the excitation will take place from either bond. In view of fact that overlap integrals are a sensitive of the U-O distance which itself depends on the environment we could expect to get three schemes for a co-ordinated uranyl ion, viz., (i) excitation taking place from σ bond, (ii) σ and π bond both at the same level and both being excited and finally (iii) π bond being excited, following the common belief that in optical spectra most loosely bound electron take part. The possibility. of anomalous excitation cannot, however, be ruled out.

SUMMARY

The discussion of the experimental results outlined above points out the existence of at least seven different electronic transitions in the region 5000 Å to 1900 Å. Of these the first five show a *vibronic* structure and appear with a rather low intensity. The analysis is supported by the differential intensity changes and frequency shifts brought about by the proximity of various perturbing ions in the solvation sphere. In dilute aqueous solutions, the M-series is weak and the D-series is more discrete and intense. In melt and strongly acidic solutions M-series is enhanced, the D-series becomes very weak, but the U-series is not much affected. The F-series gets violet-shifted with no appreciable change in intensity. With change in concentration (dilution) the M-series becomes weak with no shift and the D-series gains in intensity with a slight red shift. Similarly the U-series shows a red shift as also does the F-series where α bands appear towards the lower frequency side of α' series on lowering the concentration in aqueous solutions. The changes observed at R.T. with changes of pH, etc., follow the same pattern as the frozen glasses. The SU-series gains intensity on increasing pH accompanied with a red shift as also the TU and FU transitions.

The changes in contour shapes can be understood in terms of the differential changes of intensity and shifts in the known electronic transitions identified in the study of crystals and help in the identification of some new

electronic transitions. Even uranyl nitrate hexahydrate crystals gives at room temperature a spectrum like that of slightly acidulated dilute aqueous solutions while the $\text{CsUO}_2(\text{NO}_3)_3$ gives a spectrum like that of a strongly acidic solution.

Recent theoretical approaches to the understanding of uranyl transitions are also examined and an alternative point of view has been put forward in which the necessity of triplet, excited state is ruled out.

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