CHAPTER-I

INTRODUCTION
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Uranium, the fourth member of the actinide series, is considered as prototype of three elements actinium, thorium and protactinium due to its chemical resemblance with them. In commercial field it creates great interest due to its nuclear energy. The present concept of the actinide elements is largely based on the development of nuclear fission. The study of nuclear technology improves the process and techniques of nuclear fission procedures. Such procedures as ion exchange separations, solvent extraction and handling of microgram quantities of material or of reactive or intensely radioactive substances have been perfected in the nuclear energy programmes.

Earlier, uranium was considered as a member of the group VI-A of the periodic table along with chromium, molybdenum and tungsten because of its dominating hexavalence. It was placed below tungsten—an element of the sixth period, in which 5d electron shell is being filled up.

Later on extensive physico-chemical studies such as absorption spectra both in aqueous solution and in solid state, crystallographic and magnetic susceptibility data suggest that uranium is a member of the second series of inner transitional element (f-block elements) and the actinides are a parallel block like lanthanides. Now it is ascertained that uranium atom contains
at least three 5f electrons in both ground and excited states\(^4\,5\) with the outer electronic configuration \(5f^26d^17s^2\).

Uranium exists in four oxidation states varying from \(U^{2+}\) to \(U^{6+}\) of which the typical valencies are \(U^{4+}\) and \(U^{6+}\). Among the four oxidation states of uranium, the most stable state is \(U^{6+}\). In the hexavalent state, uranium forms \(UO_2^{2+}\) ion in almost all the compounds of U(VI). The exception is \(UF_6\) and \(UCI_6\) salts which contain \(U^{6+}\) ion in the absence of moisture. Dittrich\(^6\) established the existence of the dioxouranium (VI) ion \(UO_2^{2+}\) in aqueous solution on the basis of cryoscopic data. The characteristic feature of this group is that the distance between uranium and two oxygen atoms \((1.7-2.0 \, \text{Å})\) are shorter than the distances between uranium and any of the other elements entering into the composition of the various compounds. This group has a linear structure. The strength of this group is related to the fact that the uranium atoms have at their disposal a large number of 6d and 5f orbitals, some of which remain free even after the formation of covalent bands between uranium and the oxygen atoms, \(O=U=O\). It is an outstanding stable oxocation having unique ability to form complex salts. In fact, the hexavalent chemistry of uranium is mainly the complex salts of \(UO_2^{2+}\) species. So the structure of this ion has been exclusively discussed in minute detail.

**Stereochemistry**

The stereochemistry of the uranium compounds and of other actinide compounds have been worked out theoretically on the
basis of the angular distributions and relative strengths of various orbitals and combinations of f orbitals in the same way as for light elements. Thus hybridisations Sf-linear, Sf\(^3\)-tetrahedral, Sf\(^2\)d-square and d\(^2\)Sf\(^3\)-octahedral, observed to hold good in PuO\(_2^+\), NpCl\(_4\) and UCl\(_6\). However, due to closeness in the energy levels of electrons in the valence shells and the mutual overlap of orbitals of comparable size in these heavy atoms, several equally probable pictures can be mentioned in a single case. Thus for the present cases, the orbitals actually used are mixed orbitals of all possible sets and evidently bonding is not restricted to any single set.

In a particular oxidation state, different coordination numbers are possible. We are interested only with the dioxouranium(VI), detailed study of this species are cited in the text.

Dioxouranium(VI) UO\(_2^+\) ion and the molecular polyhedra of its complexes

Literature survey reveals that more than 50 mononuclear oxo-cations are known having the general formula M\(_{0x}^n\) where \(x = 1,2,3\) and \(n = 1,2,3,4\) and 5. Of the oxo-ions of uranium UO\(_2^+\) is a peculiar one for its higher stability. Dioxouranium(VI) UO\(_2^+\) ion with covalent U-O axial bonds forms complexes with anions and neutral molecules in which uranyl ion behaves like metallic cation exhibiting intermediate properties between M\(^+\) and M\(^2+\) ions and ions of similar size but greater charge. Linearity of UO\(_2^+\) is proved by Infrared and Raman spectral data. Moreover, crystallographic results indicate the presence of four, five or six ligand
atoms in equatorial plane perpendicular to the O-U-O group though the coplannarity of the ligand atom is dependent on the environment.

With neutral monodentate ligands, $\text{UO}_2^{2+}$ forms complexes of the type $\text{UO}_2(\text{lig})_6^{2+}$ which can be diagrammatically represented as follows:

\[ \text{U} \quad \text{O} \quad \text{Lig} \quad \text{Lig} \quad \text{Lig} \quad \text{Lig} \quad \text{Lig} \quad \text{Lig} \quad \text{O} \]

The two oxygen atoms attached to U(VI) are actually perpendicular to the plane drawn, one above and the other below the plane.

With neutral bidentate ligands, the model of the complexes should be as follows:

\[ \text{U} \quad \text{Lig} \quad \text{Lig} \quad \text{Lig} \quad \text{Lig} \quad \text{Lig} \quad \text{Lig} \quad \text{Lig} \quad \text{O} \]

\[ \text{O} \]

\[ 2^+ \]
The coordination polyhedra of the uranyl ion have been well studied in the solid state especially by X-ray investigation. The hexacoordination is generally found for this dioxo ion in its highest oxidation state (+6) which corresponds to a minimum ionic radius. The type of polyhedron occurred in the complexes is influenced by the nature of the ligands and the configuration geometries of the ligands. Ligands are usually characterised by their rigidity, coplannarity and the distance of the donor atoms (bite). Out of various possible types of ligands the oxygen or nitrogen donors have received priority in the field of study. The ligands which are much more in compact forms have smaller bites and are more effective to form the high coordination structures. Peroxo group (bite 1.5 Å) and nitrato group (bit 2.1 Å) are very compact ligands. In the oxinato (bite 2.6 Å) and tropolonato (bite 2.6 Å) the more compact plannar conformation and the minor intraligand repulsion factor allow eight coordination number while in β-diketonato (bite 2.7 Å) and salicylaldiminato (bite 2.9 Å) adducts, $\text{UO}_2^{2+}$ reaches the maximum value of seven coordination number.

Hepta coordination number was also experienced in the adducts formed by the reaction of $\text{UO}_2(\text{C}_2\text{O}_4)$ with sulphoxides, phosphine oxides, arsine oxide and pyridine (PhCH$_2$)$_2$SO, Ph$_3$PO, trioctyl phosphine oxide, Ph$_3$AsO or pyridine N-oxide.

Seven Coordination

In uranyl ion the presence of linear trans O-U-O group confines the polyhedron to be of the geometry of mononuclear
pentagonal bipyramidal\(^8\) as shown below. In \(\text{UO}_2\)(acac)\(_2\), \(\text{UO}_2\)(trop)\(_2\) and \(\text{UO}_2\)(salen) complexes the stability arises out of bridging of two metal ions by an oxygen atom of the ligand giving polynuclear geometry\(^8\).

\[\text{A} \quad \text{B} \quad \text{B} \quad \text{B} \quad \text{B} \quad \text{B} \quad \text{A} \]

**Eight Coordination**

The uranyl ion gives a hexagonal bipyramidal geometry to accommodate the coordination sites in this coordination as illustrated below. The hexagonal bipyramid has two sets of non equivalent ligand sites A and B and its shape is specified by the ratio of the bond lengths \(\gamma_A/\gamma_B\). This polyhedron is energetically less favoured and bound only in case of O-U-O linear group for example, \(\text{UO}_2(\text{O}_2)^2\) may be stated.

\[\text{A} \quad \text{B} \quad \text{B} \quad \text{B} \quad \text{B} \quad \text{B} \quad \text{A} \]
However, generally, $\text{UO}_2^{2+}$ forms complexes with five or six ligand molecules or atoms at the equatorial plane. These complexes are more common and stable than those with puckered hexagonal configurations. A standard example is the structure of the triacetate ion $\text{UO}_2(\text{CH}_3\text{COO})_3^{-}$ where the acetato group is a bidentate ligand and is bound through the two oxygen atoms of the acetate group with the central oxo-ion. All the six oxygen atoms are distributed in one plane perpendicular to the O-U-O axis. The distribution of the acetate groups around the uranyl group, whose axis is perpendicular to the plane of the drawing is shown in Figure 1.1. The coordination number of the $\text{UO}_2^{2+}$ ion is six in the above mentioned acetato complex. It may be noted that the complexes $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$, $\text{UO}_2(\text{NO}_3)_2(\text{OP}($$\text{OEt}_3$)$_2$ and $\text{Rb}$$\text{UO}_2(\text{NO}_3)_3^{-}$ exhibit similar structures.

To prove the composition of the complex ion in a solution, it must be isolated in the form of various derivatives. For example, to establish the coordinating pattern of dioxalato uranyl $\text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2$ Chernyaev et al. prepared five derivatives $M_2$$\text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2$$\cdot$$n\text{H}_2\text{O}$ where $M' = \text{K}^+$, $\text{NH}_4^+$, $\text{CN}_3\text{H}_6^+$, $\text{Rb}^+$ and $\text{Cs}^+$; $n = 0$ or 1. The inner sphere of the uranyl complex compound thus preserves a constant composition while the coordination number of uranyl group is six. Water molecule can either enter the composition of the inner sphere of the complex or can exist as water of crystallisation. The nature of such water molecules is revealed by physicochemical measurements.
Fig. I-1. Structure of the anion in Na[UO$_2$(OOC$_3$H$_7$)$_3$]
(projection to the equatorial plane)
The $\text{UO}_2^{2+}$ group, in several compounds such as $\text{K}_3\text{UO}_2\text{F}_5\text{I}$, $\text{UO}_2\text{Cl}_2\cdot 2\text{H}_2\text{O}$, $\text{UO}_2\text{C}_2\text{O}_4\cdot 3\text{H}_2\text{O}$, $\text{UO}_2\text{SO}_4\cdot 3\text{H}_2\text{O}$ etc. can be considered as coordinatively unsaturated. $\text{UO}_2(\text{acac})_2$ where acac = acetonil acetone, readily forms adducts with neutral ligand containing nitrogen or oxygen as donor sites. The compound is dimeric as established by ebullioscopic measurements in benzene solution. Both the facts clearly indicate that $\text{UO}_2(\text{acac})_2$ is coordinatively unsaturated. For this the following configuration has been proposed.

In several other compounds the pentagonal bipyramidal structure was observed for such unsaturated uranyl complexes. It has been suggested that the coordinative unsaturation of $\text{UO}_2^{2+}$ is to a certain extent caused by steric hindrances arising during the formation of the inner sphere of the complex compounds.

Electronic structure of the uranyl group - Bonding and Molecular orbital approach of $\text{UO}_2^{2+}$ ion

In $\text{UO}_2^{2+}$ ion, twelve electrons are involved in the formation of molecular orbitals (six outer electrons of U, $5f^36d^7s^2$, and four electrons from each of the oxygen atom i.e. two valence 2p electrons and one unshared pair of 2p electrons); two of the electrons are eliminated for the bipositive charge to the ion.
Now, in the ground state the distribution of electrons in the molecular orbitals can be represented in the following way\textsuperscript{14,15}.

\[
\begin{array}{cccc}
|1\sigma_u^+|^2 & |1\sigma_g^+|^2 & |1\pi_u|^4 & |1\pi_g|^4 \\
\end{array}
\]

This electronic configuration explains the formation of metal oxygen triple bond in axial positions constituting of two \(\sigma\) and four \(\pi\) bonds between two oxygens and one uranium in the triatomic uranyl ion

\[
\text{O} \equiv \text{U} \equiv \text{O}
\]

The above molecular orbitals are formed by the combination of linear symmetrical atomic orbitals and therefore it is supposed that only 5f\(_z^3\), 5f\(_{xz}\), 5f\(_{yx}\), 6d\(_{yz}\), 6d\(_z^2\), 7p\(_x\), 7p\(_y\) and 7p\(_z\) atomic orbitals of uranium are involved. A consideration of the high stability of the UO\(_2^+\) ion and overlap criterion lead to the conclusion that the low lying empty orbitals \(\phi_u\) and \(\delta_u\) are commonly connected with the electronic transitions\textsuperscript{15}

\[
\begin{align*}
\phi_u & \equiv 5f_{xy}^2, 5f_{yx}^2 \\
\delta_u & \equiv 5f_{xyz}, 5f_{zx}^2 \\
\delta_g & \equiv 6d_{x^2-y^2}, 6d_{xy}
\end{align*}
\]

Moreover, uranium forms donor acceptor bonds in the equatorial plane. Keeping in mind the fact that equatorial \(\pi\) bonds are weaker than the \(\sigma\) bonds, it is suggested that only those orbitals
which have some electron density normal to internuclear (Z) axis involve in bond formation. Therefore, according to preliminary assumption, the orbitals involved should be \( f_{xy}^2 \), \( f_{yx}^2 \), \( f_{xz}^2 \), \( d_{x^2-y^2} \), \( d_{xy} \), \( d_{z^2} \) and \( S \). The remaining five orbitals viz., \( f_{xyz} \), \( f_{zx}^2 \), \( f_{z^3} \), \( d_{xz} \) and \( d_{yz} \) generally do not take part in the equatorial bonding. However, a small contribution from these last give orbitals is suggested in the cases where the equatorial coordination deviates from planarity.

From theoretical point of view McGlynn, Smith and Neely suggested that bonding between uranyl and ligand is possible when only the \( b_{1u} \) and \( e_{2g} \) orbitals of the ligand in the equatorial plane mix with the empty \( f_{x}(x^2-y^2) \) component of the atomic orbitals \( \delta_u \) and \( d_{x^2-y^2} \) and \( d_{xy} \) components of the atomic orbitals \( \delta_g \) respectively. Similarly \( \pi \) bonding between ligand and uranyl results by the combination of bonding (\( e_{2u} \)) with empty \( f_{z}(x^2-y^2) \) and \( f_{xyz} \) components of \( \delta_u \).

The above complication in bonding evidently makes it difficult to interpret the anomalous properties of the uranyl group; e.g. short interatomic distance, high valency, vibration frequency, variation of polarizability and magnetic susceptibility. However, extensive studies of different uranyl compounds conclude that these properties depend on the atoms and groups which enter into the coordination sphere of uranium and form bonds with it in the equatorial plane. For instance, the valency vibration frequencies of the \( UO_2^2+ \) group decrease when the donor properties of the
ligands are strengthened or when the number of the donor ligands in
the inner sphere of the complex is increased.

To explain such anomalies, a new theory, though qualitative
in nature is developed by Dyatkina, Markov, Taspkina and Mikhailov.17
According to these authors the real valencies of uranium and oxygen
atoms are higher than are usually taken into account. Here also it
is suggested that besides six valence electrons of uranium there are
still a large number of free orbitals in the 6d and 5f subshells,
thereby uranium can serve as an electron acceptor with its empty
orbitals. At the same time oxygen can also increase its valency by
using its unshared electron pairs. Again extensive studies by
Syrkin18 lead to an opinion that in the uranyl group, besides the
double U=O bonds, an additional donor acceptor reaction between the
unshared electron pairs of the oxygen atoms and the empty orbitals
of the uranium atom is realised, subsequently leading to an increase
of the real bond order value of each of the U=O bonds above that of
a double bond character. The structural formula of the uranyl
group then can be represented by the following form

\[ \circlearrowright O \quad U \quad \circlearrowright O \]

A partial displacement of the negative charge from the oxygen atom
to uranium takes place due to formation of such additional donor-
acceptor bonds in the equatorial plane. Obviously this should
hinder the displacement of electrons from the uranyl oxygen atoms
towards the uranium since the acceptor possibilities of uranium
are not unlimited. Therefore, a competition between the donor-
acceptor bonds of uranium with the ligands in the equatorial plane and an additional reaction with the unshared electron pairs of the \( \text{UO}_2^{2+} \) group oxygen atoms goes on. Stronger the donor properties of the ligands, greater is the competition. However, this concept leads to a weakening of the \( \text{U} = 0 \) bond, their elongation, a decrease in the valence vibration frequencies and also a change in those properties which are decided by the electron density in the bonds, namely the polarizability and the diamagnetic susceptibility.

This concept of additional reaction favours in explaining the anomalies in the properties of the uranyl group. McGlynn and Smith\textsuperscript{14} developed analogous views but their discussion is mainly within the area of the molecular orbitals of the \( \text{UO}_2^{2+} \) group.

For a thorough understanding regarding the uranyl ion the absorption spectra of the corresponding complexes should be studied well. A short summary on this aspect has been tried to develop here.

**Electronic spectra of uranyl complexes**

The electronic spectral studies of uranyl compounds are essentially the study of the electronic spectra of uranyl moiety as established in earlier works\textsuperscript{14, 15, 19-35}. Characteristics of this ion were examined by Dieke and Duncane\textsuperscript{36}. The binding properties of \( \text{UO}_2^{2+} \) ion in nucleic acids were used by Beer et al\textsuperscript{37} to determine base sequencies by electron microscopy. Lastly, the work of McGlynn and Smith\textsuperscript{14} presents the basis for the interpretation of the electronic spectra of the uranyl group.
Electronic spectra is primarily influenced by the axial field, though a minor effect of the equatorial field on the spectrum has been noted on various uranyl compounds. Furthermore, in \( \text{UO}_2^{2+} \) entity the axial U-O bond distance is much shorter than the equatorial U-O bond length. The concept of molecular orbitals of the \( \text{UO}_2^{2+} \) ion is of great importance for the interpretation of spectroscopic and magnetic data. MO-calculations have been worked out assuming the \( \text{UO}_2^{2+} \) ion to be \( D_{\infty h} \) symmetry. The atomic orbitals of the oxygen and uranium atoms according to \( D_{\infty h} \) symmetry can be classified as represented in Table I.1.

The rules of quantum mechanics stress that only the atomic orbitals belonging to the same type of symmetry can interact one another giving the particular molecular orbitals arising in the \( \text{UO}_2^{2+} \) moiety. Thus the molecular orbitals 1 \( \sigma_g^+ \), 2 \( \sigma_g^+ \) and 3 \( \sigma_g^+ \) can arise from the group orbitals of the atoms \( p \sigma_1 \) and \( p \sigma_2 \) and two atomic orbitals of the uranium atom belonging to the same type of symmetry (\( S, d_{z^2} \)). Among these orbitals, 1 \( \sigma_g^+ \) is bonding and 2 \( \sigma_g^+ \) and 3 \( \sigma_g^+ \) are loose or antibonding orbitals. In the same way, three orbitals 1 \( \sigma_u^+ \), 2 \( \sigma_u^+ \) and 3 \( \sigma_u^+ \) can arise from a group orbitals of two oxygen atoms and two atomic orbitals \( p_z, f_{z^2} \), out of which 1 \( \sigma_u^+ \) is a bonding orbital while the remaining two are loose or antibonding. Again, three pairs of degenerate \( \pi_u \) orbitals arise from the \( (p_{x_1} - p_{x_2}) \) and \( (p_{y_1} + p_{y_2}) \) orbitals of the oxygen atoms and the \( p_x, f_{x^2}, p_y, f_{y^2} \) orbitals. Among the three orbitals 1 \( \pi_u \) is the bonding orbital and 2 \( \pi_u \) and 3 \( \pi_u \) orbitals are loose or antibonding. Furthermore, two pairs of degenerate molecular
Table I.1 - Classification of atomic orbitals of uranium and group orbitals of oxygen atoms in D<sup><h1></sup>_h symmetry

<table>
<thead>
<tr>
<th>Type of symmetry</th>
<th>Atomic orbitals of uranium</th>
<th>Group orbitals of oxygen</th>
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</thead>
<tbody>
<tr>
<td>Σ&lt;sub&gt;g&lt;/sub&gt;</td>
<td>S { d&lt;sub&gt;z^2&lt;/sub&gt; }</td>
<td>( \frac{1}{2} (p_{z_1} + p_{z_2}) )</td>
</tr>
<tr>
<td>Σ&lt;sub&gt;u&lt;/sub&gt;</td>
<td>P&lt;sub&gt;z&lt;/sub&gt; { f&lt;sub&gt;z^3&lt;/sub&gt; }</td>
<td>( \frac{1}{2} (p_{z_1} - p_{z_2}) )</td>
</tr>
<tr>
<td>Λ&lt;sub&gt;u&lt;/sub&gt;</td>
<td>P&lt;sub&gt;x&lt;/sub&gt; { f&lt;sub&gt;xz^2&lt;/sub&gt; }, P&lt;sub&gt;y&lt;/sub&gt; { f&lt;sub&gt;yz^2&lt;/sub&gt; }</td>
<td>( \frac{1}{2} (p_{x_1} + p_{y_2}) )</td>
</tr>
<tr>
<td>Λ&lt;sub&gt;g&lt;/sub&gt;</td>
<td>d&lt;sub&gt;xz&lt;/sub&gt; { d&lt;sub&gt;yz&lt;/sub&gt; }</td>
<td>( \frac{1}{2} (p_{x_1} - p_{x_2}) )</td>
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<tr>
<td>δ&lt;sub&gt;u&lt;/sub&gt;</td>
<td>f&lt;sub&gt;z(x^2-y^2)&lt;/sub&gt; { f&lt;sub&gt;xyz&lt;/sub&gt; }</td>
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<td>φ&lt;sub&gt;u&lt;/sub&gt;</td>
<td>f&lt;sub&gt;x(x^2-y^2)&lt;/sub&gt; { f&lt;sub&gt;y(x^2-y^2)&lt;/sub&gt; }</td>
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<tr>
<td>δ&lt;sub&gt;g&lt;/sub&gt;</td>
<td>(d&lt;sub&gt;x^2-y^2&lt;/sub&gt;, d&lt;sub&gt;xy&lt;/sub&gt;)</td>
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orbitals of which the bonding $1\pi_g$ and the loose $2\pi_g$ orbitals arise from the $(px_1 - px_2)$ and $(py_1 - py_2)$ orbitals of the oxygen and the $d_{xz}$ and $d_{yz}$ orbitals. The atomic orbitals of the metal of the type $f^a_{x^2-y^2}$, $f^b_{x^2-y^2}$, $f^c_{x^2-y^2}$, $f_{xyz}$, $d_{x^2-y^2}$, $d_{xy}$ have no analogs within the atomic orbitals of oxygen and therefore remain as antibonding atomic orbitals.

McGlynn and Smith have arranged the above mentioned molecular orbitals in ascending order of energy content which is illustrated in Figure 1.2. The arrangement is done considering the principal properties of the molecular orbitals, the overlapping and the similarity of the energies of the atomic orbitals forming a given molecular orbital. Taking this fact into account it may be concluded that the deepest are the bonding orbitals, above them are the antibonding and still higher are the loose orbitals, the $\sigma$-orbitals are situated below the $\pi$-orbitals. Evidently the same relationship is expected to hold in the placement of antibonding orbitals in the molecule and in the free atom of metal. From the above discussion, it is evident that $1\sigma_g^+$ and $1\sigma_u^+$ orbitals having least amount of energy should be placed in the lower part of the diagram of the molecular orbitals. Although $1\sigma_g^+$ orbital has been placed above $1\sigma_u^+$ orbital, in practice it is difficult to say which of these is the deeper one. The controversy, however, is needless since both the $1\sigma_u^+$ and $1\sigma_g^+$ are electron saturated and consequently do not take part in bonding. Obviously the remaining bonding orbitals $1\pi_g$ and $1\pi_u$ are placed behind $\sigma$-orbitals. McGlynn et al. placed $\pi_u$ orbitals below $\pi_g$ orbitals considering the overlap nodal
Fig. I.2. The molecular orbitals in UO$_2^{2+}$
and the relative atomic orbital energy. However, since the spectral characteristics are dependent on higher placed molecular orbital, the site of electron excitation, and both \(1\pi_u\) and \(1\pi_g\) can serve the purpose of the band relation remain unambiguous and the disposition of several \(\pi\) orbital is uncertain.

Between the atomic orbitals of the type \(\delta_u\) and \(\phi_u\), \(\delta_u\) are placed above the bonding orbitals. In the \(\text{UO}_2^+\) group with the axial symmetry a splitting off takes place and the orbitals with the greater, angular moment with respect to the \(\phi_u\) axis are placed lower than \(\delta_u\). But the magnitude and the sign of the splitting depend on the field created by the ligands situated on the axis, so the real positions of the \(\phi_u\) and \(\delta_u\) orbitals remain ambiguous.

The relative disposition of the next seven molecular orbitals namely \(2\sigma_u^+, 3\sigma_u^+, 2\sigma_g^+\), \(3\sigma_g^+, 2\pi_u\), \(3\pi_u\) and \(2\pi_g\) remain undetermined. However, these orbitals are not important for the electronic spectrum of \(\text{UO}_2^+\) group due to high energy content of the orbitals. Therefore, only the orbitals \(1\pi_g\), \(1\pi_u\), \(\delta_u\) and \(\phi_u\) are involved for relevant spectral and magnetic studies of the uranyl group.

Another remarkable fact is the extent of equatorial coordination effect over the energies of the molecular orbitals of \(\text{UO}_2^+\) ion and the energies of the resultant states. The representation generated by six equivalent equatorial bonds contains the irreducible representations \(a_{1g}, b_{1u}, e_{1u}\) and \(e_{2g}\) of the \(D_{6h}\) point group. These have been shown in Tables I.2 to I.4. On complex
Table 1.2 - Representations to which atomic orbitals conform in relevant point groups

<table>
<thead>
<tr>
<th>Point group</th>
<th>S</th>
<th>pxpy</th>
<th>pz</th>
<th>d_{x^2-y^2}</th>
<th>d_{xz}</th>
<th>d_{yz}</th>
<th>d_{z^2}</th>
<th>f_x(x^2-y^2)</th>
<th>f_y(x^2-y^2)</th>
<th>f_z(x^2-y^2)</th>
<th>f_{xyz}</th>
<th>f_{xz^2}</th>
<th>f_{yz^2}</th>
<th>f_{z^3}</th>
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<tr>
<td>D_{6h}</td>
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<td>b_{3g}</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table I.3 - Ligand group orbitals of a D_{6h} uranyl ion Complex

<table>
<thead>
<tr>
<th>Orbital</th>
<th>$\mathcal{T}$ orbital</th>
<th>$\mathcal{A}$ I orbital</th>
<th>$\mathcal{A}$ II orbital</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6) $^{1/2}(a_1-a_2 + a_3 - a_4 + a_5 - a_6)$</td>
<td>$b_{1u}$</td>
<td>$b_{2g}$</td>
<td>$a_{2g}$</td>
<td>$\mathcal{T} - 2\beta_m$</td>
</tr>
<tr>
<td>(6) $^{1/2}(a_2 - a_3 + a_5 - a_6)$</td>
<td>${e_{2g}}$</td>
<td>${e_{2g}}$</td>
<td>${e_{1u}}$</td>
<td>$\mathcal{T} - \beta_m$</td>
</tr>
<tr>
<td>(12) $^{1/2}(2a_1 - a_2 - a_3 + 2a_4 - a_5 - a_6)$</td>
<td>${e_{1u}}$</td>
<td>${e_{1g}}$</td>
<td>${e_{2g}}$</td>
<td>$\mathcal{T} + \beta_m$</td>
</tr>
<tr>
<td>(6) $^{1/2}(a_2 + a_3 - a_5 - a_6)$</td>
<td>${e_{1u}}$</td>
<td>${e_{1g}}$</td>
<td>${e_{2g}}$</td>
<td>$\mathcal{T} + 2\beta_m$</td>
</tr>
</tbody>
</table>
Table 1.4 - Ligand group-orbitals of a $D_{2h}$ ($V_b$) uranyl ion complex

| Orbital                  | $\Sigma$ | $\Pi_{\perp}$ | $\Pi_{||}$ | Energy                                           |
|--------------------------|----------|---------------|------------|--------------------------------------------------|
| $(4+2s^2)^{-\frac{1}{2}}(sl_1-a_2+a_3-sl_4+a_5-a_6)$ | $b_{3u}$ | $b_{2g}$      | $b_{1g}$   | $(4\delta m + 2s^2\lambda L - 3s\beta_{Lm}) / (4+2s^2)$ |
| $(4+2q^2)^{-\frac{1}{2}}(ql_1-a_2-a_3+ql_4-a_5-a_6)$ | $a_g$    | $b_{1u}$      | $b_{2u}$   | $(4\delta m + 2q^2\lambda L - 3q\beta_{Lm}) / (4+2q^2)$ |
| $(\mp)(a_2-a_3+a_5-a_6)$       | $b_{1g}$ | $a_u$         | $b_{3u}$   | $\lambda - \beta m$                              |
| $(\mp)(a_2+a_3-a_5-a_6)$      | $b_{2u}$ | $b_{3g}$      | $a_g$      | $\lambda + \beta m$                              |
| $(4+2r^2)^{-\frac{1}{2}}(rl_1+a_2-a_3-rl_4-a_5+a_6)$ | $b_{3u}$ | $b_{2g}$      | $b_{1g}$   | $(4\delta m + 2r^2\lambda L + 3r\beta_{Lm}) / (4+2r^2)$ |
| $(4+2p^2)^{-\frac{1}{2}}(pl_1+a_2+a_3+pl_4+a_5+a_6)$ | $a_g$    | $b_{1u}$      | $b_{2u}$   | $(4\delta m + 2p^2\lambda L + 3p\beta_{Lm}) / (4+2p^2)$ |
formation, among the valence orbitals only $f_x(x^2-y^2)$ transforms as $b_{1u}$ and the degenerate pair $d_{xy}$, $d_{x^2-y^2}$ transform as $e_{2g}$ (all in $D_{6h}$). The $\phi u$-MO and the $f_y(x^2-y^2)$ components of the $\phi u$-MO are unaffected by the equatorial ligation and will remain atomic in character throughout. Based on a MO analysis of ligand uranyl ion interaction recently Glebov\textsuperscript{38} proposed a new covalent scheme of bonding in uranyl complexes with $D_{6h}$ symmetry. The new scheme with the energy transfer from uranyl bonds to U-ligand bonds and vice versa, is in good agreement with the known interatomic distances in uranyl compounds.

The effect of the crystal field of equatorial ligands, CFEL on electronic structure of uranyl compounds was described by Glebov\textsuperscript{39}. According to the ionic model an increase in ionicity, i.e. weakening of the $UO_2$ bond in the uranyl moiety leads to an increase in $U-O$ interatomic distance $R_{UO}$. He also established a relation between $R_{UO}$ and the difference in crystal field generated by the equatorial ligands on U and $\omega$ atoms of uranyl group. Accordingly at $\Delta$ CFEL $> 5$ eV, the $R_{UO}$ vs CFEL dependence is linear. At $\Delta$ CFEL $< 5$ eV, the role of CFEL is less important than the electron donor interaction of the $UO_2^{2+}$ with ligands indicating the inapplicability of the ionic model. Later on Glebov and Nefedov\textsuperscript{40} studied the effect of $U-O$ interatomic distance ($R_{UO} = 1.7-2.5 \, \AA$) and the crystal field of equatorial ligands (CFEL $\leq 16.21$ eV) on the electronic structure of $UO_2^{2+}$ by quasirelativistic MO LCAO method. According to them the charge $d$ distribution in the various AO depends only slightly on $R_{UO}$. There is a decrease in population
of outer vacant AO of U, with increasing CFEL, while the population of inner 6p3/2-AO changes only slightly. The population of overlap MO of UO$_2^{2+}$ decreases as R$_{U0}$ and CFEL increases where the population of the inner overlap MO is more sensitive to this change than that of the outer overlap.

The uranyl ion having the electronic configuration in its ground state, $(1_{\Sigma_u}^+)^2 (1_{\Sigma_g}^-)^2 (1\pi_u)^4 (1\pi_g)^4$ emphasises that uranium oxygen axial bond is a triple bond consisting of one $\sigma$ and two $\pi$ linkages and this triple bond character is indispensable to explain the spectroscopic nature and the unique stability often associated with the UO$_2^{2+}$ ion. This idea is very similar to that proposed by Dyatkina, Markov, Tsapkina and Michailov. Moreover, the $\sigma$- and $\pi$-bonds have been well characterised by McGlynn, Smith and Neely in connection with the ligation effects on the Infrared spectrum of the uranyl ion.

The successive order of the molecular orbitals adopted in the UO$_2^{2+}$ group suggests that the monoelectronic transitions are possible from the state $|1\pi_g|^4 1\Sigma_u^+ \rightarrow$ into the state $|1\pi_g|^3 |\phi_u|^1$; $1\Delta_u$, $1\Sigma_u$, $1\Delta_u$, $1\Sigma_u$, and $|1\pi_g|^3 |\delta_u|^1$; $1\Delta_u$, $1\Sigma_u$, $1\Sigma_u$. Transitions into the states $\Delta$ and $\Gamma$ are orbitally forbidden and those into the $\pi$ and $\phi$ states are allowed; the component of the latter transition into the $\pi$ state should be polarised in the xy plane. Though it is difficult to decide which of these transition is lowest in energy but it will be most likely the transition of the type singlet $\rightarrow$ triplet (S $\rightarrow$ T). In the spectrum of UO$_2^{2+}$ (in the
Table I.5 - Absorption spectrum of the UO$_2^+$ ion

<table>
<thead>
<tr>
<th>Region</th>
<th>$f$</th>
<th>$\nu_{\text{max}}, \text{cm}^{-1}$</th>
<th>$\tau$, sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.29 \times 10^{-5}$</td>
<td>22050</td>
<td>$4.76 \times 10^{-4}$</td>
</tr>
<tr>
<td>2</td>
<td>$1.13 \times 10^{-4}$</td>
<td>24125</td>
<td>$4.39 \times 10^{-5}$</td>
</tr>
<tr>
<td>3</td>
<td>$3.45 \times 10^{-5}$</td>
<td>27000</td>
<td>$1.21 \times 10^{-4}$</td>
</tr>
<tr>
<td>4</td>
<td>$7.71 \times 10^{-2}$</td>
<td>34000</td>
<td>$9.80 \times 10^{-7}$</td>
</tr>
<tr>
<td>5</td>
<td>$2.65 \times 10^{-2}$</td>
<td>43000</td>
<td>$1.69 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
form of hydrated ion or in the monocrystal $\text{Rb}_2\text{UO}_2(\text{NO}_3)_3$ five absorption regions are found which have been shown in Table I.5 along with the oscillator strength $f$ and survival time $\gamma$.

The low value of multiple splitting ($\sim 2500 \text{ cm}^{-1}$) prevents their attribution to the $3\phi$ or $3\Gamma$ states and makes their attribution to the $3\Xi$ or $3\Delta$ states. The investigation of the vibrational structure of these bands exhibits that the corresponding transition is allowed when the vibration is of the type $\Sigma^+_g (\gamma_1)$ and subsequently these bands should be related to the transition into the $3\Xi$ state. A tentative assignment of the absorption band is shown in Figure I.3.

The low energy absorption in the excited triplet state is due to excitation of an electron from a bonding orbital, $1\pi_g$ to a non-bonding $5f$-atomic orbital of uranium. This type of electron transfer, though theoretically independent of hexagonal equatorial ligation is influenced to some extent by the ligands in the equatorial plane and in most cases bands exhibit in the visible region.

Belford and Belford26 examined the $\overline{\pi}$-bonding in uranyl ion in connection with the electronic spectra of the compounds and calculated the overlap integral values of the uranium and oxygen atoms as represented in Table I.6. These data indicate that like the $\Sigma$ bonds, the formation of $\overline{\pi}$ bonds are completely real. Again $f$-bonds are weaker type than $d$-bonds since overlap integrals in the bonds due to the $f$-orbitals are much smaller than those of the $d$-orbitals. The authors26 considered that in the ground state
Fig. I-3. Tentative assignments of the absorption bands in the spectrum of $\text{USe}_2$. 

1. $\Sigma_{1u}$
2. $\Sigma_{0u}$ or $\Delta_{2u}$
3. $\Pi_u$
4. $\Sigma_g^+$

Energy levels at:
- $48000 \text{ cm}^{-1}$
- $34000 \text{ cm}^{-1}$
- $27000 \text{ cm}^{-1}$ ($\Omega = 2$)
- $24125 \text{ cm}^{-1}$ ($\Omega = 1$)
- $22050 \text{ cm}^{-1}$ ($\Omega = 0$)
orbital energies to be in the order $e_{1g} < a_{1g} < a_{2u} < e_{1u}$ for the purpose of calculation. Newman\textsuperscript{27}, on the other hand calculated $\pi$-orbital overlap integrals using Belford and Belford's primary bond and Hartree-Fock relativistic wave function and arranged the four occupied orbitals in order of increasing energy as $e_{1g} < a_{1g} < e_{1u} < a_{2u}$. This order indicates that the overlap between a uranium 5f orbital and an oxygen 2p orbital is larger than the corresponding $\sigma$-overlap. Newman took into account the effects of spin-orbit coupling, trigonal field and lattice interactions for his calculation and observed that energy required for the first excited system to be 48,000 cm$^{-1}$ in contrast to 25,000 cm$^{-1}$ as found by McGlynn et al. However, the spectral interpretations in the region 19,200-27,000 cm$^{-1}$ have essentially been singlet $\rightarrow$ triplet in character.

Based on the experimental work of Gorlter-Walrand and Jeager\textsuperscript{24}, Gorlter-Walrand and Vanquickenborne\textsuperscript{22,23} have interpreted that band system at 20,000-30,000 cm$^{-1}$ is due to singlet-singlet transition. The authors have shown that the spectra of the

<table>
<thead>
<tr>
<th>Distance</th>
<th>$\psi d$</th>
<th>$\pi d$</th>
<th>$\psi f$</th>
<th>$\pi f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.67</td>
<td>0.175</td>
<td>0.269</td>
<td>0.066</td>
<td>0.075</td>
</tr>
<tr>
<td>1.92</td>
<td>0.193</td>
<td>0.192</td>
<td>0.052</td>
<td>0.047</td>
</tr>
</tbody>
</table>

Table I.6 - Overlap integrals
uranyl compounds are virtually independent of the chemical nature of the equatorial ligands but dependent on the total symmetry and equatorial coordination number which perhaps can explain the similarity of the spectrum of Na\(^+\)UO\(_2\)(CH\(_3\)COO)\(_3\)\(^-\) and (n-Bu\(_4\)N)\(^+\)UO\(_2\)(NO\(_3\))\(_3\)\(^-\). Only four transitions are found by Gorller-Walrand and Jeagere in the band analysis of the acetato-complex and these observations were further explained by Gorller-Walrand and Vanquickenborne presuming Newman's approach for the UO\(_2^{2+}\) ion in the ground state. However, according to these authors the band system situated at 20,000-22,000 cm\(^{-1}\) is due to a \(1\Sigma_g^+ \rightarrow 1\Phi_g\) transition while the band system at 22,500-27,000 cm\(^{-1}\) is due to a \(1\Sigma_g^+ \rightarrow 1\Delta_g\) transition.

Bell examined the spectrum of UO\(_2^{2+}\) ion in the region 1800-5000 Å. In his investigation seven major bands having almost equal spacings (represented in Table 1.7) were observed.

Brint and McCaffery investigated the electronic spectrum of (Bu\(_4\)N)\(^+\)UO\(_2\)(NO\(_3\))\(_3\)\(^-\) in polymer solution (methyl acrylate) at liquid-helium temperature within 20,000-35,000 cm\(^{-1}\). The authors favoured the energies of the orbitals in the order of \(e_{1g} < a_{1g} < a_{2u} < e_{1u}\) and the low energy bands were said to be arising out of the transitions to the triplet states \(^3\Sigma_{1g}\) and \(^3\Sigma_{2g}\) (Figure I.4 and Figure I.5). The higher energy band structure corresponds to transition to the state \(^3\Sigma_{1u}\) (Figure I.6). They have shown that the intensity of the absorption spectra is independent on the symmetry D\(\alpha\)\(<h\) but depends on the most effective molecular symmetry.
Fig. 1-4. Orbital energies for the uranyl ion.
Fig. I-5 Lowest energy triplets and splittings under first and second order spinorbit interactions
Fig. I-6. Correlation of states between $D_{\infty h}$ and $D_3 h$
Table 1.7 - Energies and spacings of the seven major absorption bands of the aqueous uranyl ion

<table>
<thead>
<tr>
<th>Band</th>
<th>Band Centre (cm⁻¹)</th>
<th>Band spacings (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24,107</td>
<td>7260</td>
</tr>
<tr>
<td>2</td>
<td>31,367</td>
<td>5506</td>
</tr>
<tr>
<td>3</td>
<td>36,873</td>
<td>5944</td>
</tr>
<tr>
<td>4</td>
<td>42,817</td>
<td>6113</td>
</tr>
<tr>
<td>5</td>
<td>48,930</td>
<td>6020</td>
</tr>
<tr>
<td>6</td>
<td>54,950</td>
<td>5980</td>
</tr>
<tr>
<td>7</td>
<td>60,930</td>
<td></td>
</tr>
</tbody>
</table>

D₃. They have also examined the spectrum of dinitrocomplex in various solvents and have obtained quantitative estimates of reduction in symmetry from changes in the excited state moment (Figure 1.7). They classified the spectrum into two major regions.

(1) 20,000-28,000 cm⁻¹ (ν max \(\approx 50\))

In this region transitions occur from the totally symmetric ground state to electronic levels resulting from two triplet states \(3E_{1g}, 3E_{2g}\) (from \(f\rightarrow f\) type transition). These are close in
Fig. I-7. Change in the orbital and state designations resulting from reduction of symmetry in the $\text{UO}_2^{2+}$ ion.
energy and therefore interact strongly through spin orbit coupling.

(ii) 28,000-35,000 cm\(^{-1}\) \((\lambda_{\text{max}} \approx 500)\) 

This region corresponds to transitions to levels arising from an odd parity triplet state (from \(f \rightarrow d\) type excitation).

Pasini et al\(^{29}\) investigated the electronic spectra of the uranyl complexes with optically active quadridentate Schiff bases using different solvents. They observed three detectable bands in the region 470, 385 and 345 nm corresponding to molar extinction coefficient \((\lambda \approx 500, 5000, 8000\) respectively. The spectral data indicate that these bands are not much affected by the solvents. Two types of transition may occur according to the authors. They are (i) transfer of electron from apical oxygen \(\rightarrow f\)-transition of the uranyl moiety, (ii) transfer of charge from equatorial ligands to uranium atom. The former transition is generally ascertained with low intensity peak and lower molar extinction coefficient values whereas the latter type corresponds to high intensity peaks and high molar extinction coefficient values.

A band at 225 nm exhibited in uranyl complexes of glutathione is assigned to the \(n \rightarrow \pi^*\) electronic transition of carbonyl group by Marzotto\(^{41}\). The dramatic effect induced by \(\text{UO}_2^{2+}\) on this band can be correlated with a bonding interaction of this group to uranyl ion.

During their intensive study on the electronic spectra of uranyl complexes with 1,2-disubstituted benzene Kim, Miyake and
Imoto observed one or two new bands characterised by much higher intensity and complete lack of vibrational structures between 340-500 nm in the uranyl complexes. The authors assigned these bands to charge transfer transition.

Seminara, Siracusa and Cassol studied cyclic polythene uranyl complexes and reasoned the band in the region 350-500 nm solely due to triatomic uranyl moiety and not due to charge transfer from ligand to uranium.

R.G. Denning et al. studied the electronic structure of uranyl ion in Cs$_2$UO$_2$(NO$_3$)$_3$ using polarised single crystal absorption spectra of 4.2K. For this purpose they employed natural C-D, m-C-D, Zeeman effect and isotropic substitution measurements and observed that there is a large intensity in the $\sigma$-spectrum of Cs$_2$UO$_2$(NO$_3$)$_3$ in comparison with that in the $\pi$-spectrum. The authors identified seven electronic states in Cs$_2$UO$_2$(NO$_3$)$_3$ and Na$_2$UO$_2$(CH$_3$COO)$_3$ between 21,000 and 30,000 cm$^{-1}$. On the basis of both experimental and exhaustive theoretical calculations the authors gave their report which is in disagreement of previous workers and simultaneously put forward the descriptions for the electronic excited state. An abstract of their approach along with their comments is illustrated in Table I.8.

Now, based on Denning and his coworkers model, Flint et al interpreted the luminescence spectra of Rb$_2$UO$_2$(NO$_3$)$_3$ which is structurally similar to Cs$_2$UO$_2$(NO$_3$)$_3$. According to
Table I.8 - Summary of observed electronic excited states in CsUO$_2$(NO$_3$)$_3$ and NaUO$_2$(CH$_3$COO)$_3$

<table>
<thead>
<tr>
<th>Origin</th>
<th>Wave number cm$^{-1}$</th>
<th>Excited state symmetry</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>21090</td>
<td>$\kappa_g$ $E''$ $E$</td>
<td>Fluorescent origin. Positive MCD term ($\mu = 0.01 \mu_B$)</td>
</tr>
<tr>
<td>II</td>
<td>21694</td>
<td>$\Delta_g$ $E'$ $E$</td>
<td>Associated with strongest absorption. Only state to show resolvable first order Zeeman splitting ($\mu = 1.1 \mu_B$)</td>
</tr>
<tr>
<td>III</td>
<td>C.22300</td>
<td>$\phi_g$ $A_1''$ $A_1$</td>
<td>Inferred from $\pi$-polarised vibronic structure.</td>
</tr>
<tr>
<td>IV</td>
<td>C.23250</td>
<td>$?$ $A_1'$ $A_1$</td>
<td>Inferred from a $\kappa$-polarised feature with a large negative vibrational isotope shift implying $\gamma_{asym}$ (UO$_2$).</td>
</tr>
<tr>
<td>V</td>
<td>C.23475</td>
<td>$\Delta_g$ $E'$ $E$</td>
<td>Observed as new broad structure above the second repeat of structure on II in the $\gamma$-spectrum.</td>
</tr>
<tr>
<td>VI</td>
<td>26640</td>
<td>$\phi_g$ $A_1''$ $A_1$</td>
<td>Inferred from location of vibronic structure in both polarizations.</td>
</tr>
<tr>
<td>VII</td>
<td>27430</td>
<td>$\phi_g$ $A_2''$ $A_2$</td>
<td>Static electric dipole intensity parallel to OUO. Vibronic structure of comparable intensity in both polarizations. Some magnetic dipole intensity polarized parallel to OUO.</td>
</tr>
<tr>
<td>Origin</td>
<td>Wave number/ cm(^{-1})</td>
<td>Excited state symmetry</td>
<td>Magnetic moment (\mu_B)</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------</td>
<td>------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>A(_1)</td>
<td>21104.1 (\Delta_g) E</td>
<td>0.075</td>
<td>+ve</td>
</tr>
<tr>
<td>A(_2)</td>
<td>21135.7 (\pi_g) E</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>21896.3 (\phi_g?) (A_1?)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>C(_1)</td>
<td>21915.0 (\Delta_g) E</td>
<td>(\sim 1.0)</td>
<td>-ve</td>
</tr>
<tr>
<td>C(_2)</td>
<td>21925.6 (\phi_g?) (A_2?)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>C(_3)</td>
<td>21937.6 (\phi_g?) (A_1?)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>(\sim 23620) (\Delta_g) E</td>
<td>(\sim 0.3)</td>
<td>-ve</td>
</tr>
<tr>
<td>E</td>
<td>23677.7 (\phi_g?) (A_2?)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>27122.0 (\phi_g?) (A_1?)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>G(_1)</td>
<td>27794.7 (\phi_g) (A_2)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>G(_2)</td>
<td>27804</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the authors\textsuperscript{45}, it consists of an electronic origin accompanied by a large number of vibronic origins corresponding to lattice modes and the vibrations of the UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{3} entity. The uranium oxygen distance of the UO\textsubscript{2}\textsuperscript{2+} grouping is appreciably larger than in the ground state so that Frank-Condon progressions in the uranium-oxygen symmetric stretching mode (\upsilon_1) appear based on all these electronic and vibronic origins. However, the antisymmetric uranyl stretching mode \upsilon_2 (and some of the nitrate modes) have higher wave number than \upsilon_1 so some overlapping of spectral features occurs. The pure electronic origin of the 10-K luminescence spectrum of Rh\textsubscript{2}UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{3} occurs as a sharp medium strength band at 21,207 cm\textsuperscript{-1}. Between this origin and 21000 cm\textsuperscript{-1} at least 15 weak features are resolved. These correspond to vibronic origins involving low-frequency vibrations of the lattice and uranium nitrate deformations. Progressions in the totally symmetric stretching mode \upsilon_1 on the electronic origin and all these vibronic origins may be followed up to about six members, with the expected Franck-Condon patterns. The positions of these progressions on the origin and the \upsilon_2 vibronic origin are given in Table 1.9.

The observed \upsilon_1 wave number is confirmed by the Raman Spectrum. The progression on the origin thus occurs 74 cm\textsuperscript{-1} to high energy of the \upsilon_2 vibronic origin. However, if a large splitting does occur this will produce four strong bands in the region of the \Pi_g \rightarrow \Sigma_g^+ + \upsilon_1 and \Pi_g \rightarrow \Sigma_g^+ + \upsilon_2 transitions together with further features due to other vibrational modes.
Table 1.9 - Wave numbers and Assignments of Progressions in \( \nu_1 \) on the Electronic Origin and \( \nu_2 \) vibronic Origin for \( \text{RbUO}_2(\text{NO}_3)_3 \) at 15 K

<table>
<thead>
<tr>
<th>Band position/cm(^{-1})</th>
<th>Assignment</th>
<th>Band position/cm(^{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>21207</td>
<td>Origin(0'(\rightarrow)0)</td>
<td>20244</td>
<td>0'(\rightarrow)0 + ( \nu_2 )</td>
</tr>
<tr>
<td>20318</td>
<td>0'(\rightarrow)0 + ( \nu_1 )</td>
<td>19362</td>
<td>0'(\rightarrow)0 + ( \nu_2 + \nu_1 )</td>
</tr>
<tr>
<td>19434</td>
<td>0'(\rightarrow)0 + 2 ( \nu_1 )</td>
<td>18481</td>
<td>0'(\rightarrow)0 + ( \nu_2 + 2 \nu_1 )</td>
</tr>
<tr>
<td>18552</td>
<td>0'(\rightarrow)0 + 3 ( \nu_1 )</td>
<td>17604</td>
<td>0'(\rightarrow)0 + ( \nu_2 + 3 \nu_1 )</td>
</tr>
<tr>
<td>17672</td>
<td>0'(\rightarrow)0 + 4 ( \nu_1 )</td>
<td>16725</td>
<td>0'(\rightarrow)0 + ( \nu_2 + 4 \nu_1 )</td>
</tr>
<tr>
<td>16794</td>
<td>0'(\rightarrow)0 + 5 ( \nu_1 )</td>
<td>15855</td>
<td>0'(\rightarrow)0 + ( \nu_2 + 5 \nu_1 )</td>
</tr>
<tr>
<td>15913</td>
<td>0'(\rightarrow)0 + 6 ( \nu_1 )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
However, an examination of the electronic spectra of the uranyl complexes in different solvents reveals the following characteristic features which lead to the conclusion that electronic spectra occur due to (i) transition within the $\text{UO}_2^{2+}$ moiety (ii) charge transfer from equatorial ligands to $\text{UO}_2^{2+}$ ion and (iii) intraligand transitions of the organic ligand molecules.

**Circular Dichroism (C.D.) Spectral Study**

Pasini et al. studied the circular dichroism (C.D.) spectra on uranyl complexes with tetradentate optically Schiff bases derived from salicyaldehyde and a variety of C-substituted ethylene diamines and informed that the result of these investigations helped in predicting the conformation of chelate rings as well as the distortion of the complex molecules as a whole. In the above cases the coordination number is seven. C.D. spectra of the complex with salstien (Figure 1.8) carried out in different solvents show significant changes in CHCl$_3$ solution where the five coordination in the equatorial plane is removed by dissociation of the neutral additional ligand. This change however, is not detected in UV spectra, thus suggesting that the C.D. spectra are more useful test for detecting changes in the coordination number.

In the study of visible spectra of these complexes (Figure 1.9) in different solvents, three strong and easy picking bands around 470 nm (shoulder, $\xi \approx 500$), 395 nm (shoulder, $\xi \approx 5000$) and 345 nm ($\xi \approx 8000$) are observed. These are nearly solvent independent...
Fig. I-8. C.D. spectra in different solvents of $\text{UO}_2\text{Sal}(-)$ Stien; $\text{CHCl}_3$, $\text{CH}_3\text{OH}$, $\text{DMF}$ (Stien-stilbenediamine).

Fig. I-9. Electronic spectra in different solvents of $\text{UO}_2\text{Sal}(-)$ Stien; $\text{CHCl}_3$, $\text{CH}_3\text{OH}$, $\text{DMF}$. 
Although in some uranyl complexes $\nu_1$, $\nu_3$ and $\nu_2$ appear in both IR and Raman spectra, the linearity of the uranyl group is no longer a matter of doubt. After coordination the symmetry of the O-U-O group may be disturbed and thus Feldman et al. suggested that during the formation of uranyl complexes with tridentate ligands like malate, citrate and tartarate, the linearity of the UO$_2$ group may be distorted due to electrostatic repulsion between the oxygen atoms of the O-U-O group and the oxygen atoms of the ligands. Consequently, the possible bent structure for UO$_2^{2+}$ moiety in some stray cases does not contradict the well elucidated linear and symmetrical structure of the UO$_2$ group.

During their investigation on the spectra of the uranyl complexes of $(R_3PH)_2\text{UO}_2\overline{X_4}$ ($R =$ ethyl, n-propyl or phenyl, $X =$ Cl, Br, and I) Day and Venanzi observed a weak band in the region 800–900 cm$^{-1}$ which corresponds to the symmetric stretching frequency ($\nu_1$) of the uranyl entity. To explain this phenomenon it has been interpreted that the cation $(R_3PH)^+$ is linked with uranyl oxygen by a hydrogen bond and the U-0...H configuration would be angular and such an arrangement at one or both ends of the uranyl group could compute for the anomalous symmetric stretch.

The valence vibration frequencies and other properties (the force constant and bond length) of the U-0 bond are not fixed in different uranyl compounds but depend mainly on the nature of the ligand which enters into the coordination sphere of uranium and
forms bonds with the $\text{UO}_2^{2+}$ ion. McGlynn, Smith and Neely \(^1\) during their study on a series of complexes of the type $\text{K}_x\text{UO}_2\text{Lig(NO}_3\text{)}_2\text{L}$ found both the $\nu_3$ and $\nu_1$ frequencies of the $\text{UO}_2^{2+}$ decreased in the following order:

$$\text{NO}_3^- > \text{F}^- > \text{H}_2\text{O} > \text{O-phen} > \text{py} > \text{ONO}^- > \text{NCS}^- > \text{NH}_3^- > \text{en}^- > \text{CN}^-$$

Similar results were obtained by Babaeva, Evstaf'eva, Markov and Tsapkina \(^6\) on the study of the frequency changes on addition of urea to binary uranyl compounds. Despite uncertainty it concludes that the frequencies are decreased when the donor properties are strengthened or when the number of donor ligands in the inner sphere of the complex is increased.

The ligand field effect on the spectrum of uranyl ion is best explained by McGlynn et al. \(^6\). They have taken into account various factors like $\sigma(L\rightarrow M)$, $\pi(L\rightarrow M)$ and $\pi(M\rightarrow L)$ which are participant in equatorial bondings. The stabilisation energy (S.E.) is an important factor for an equatorial bonding. For an isolated $D_{6h}$ uranyl complex it is represented by

$$\text{S.E.} = \text{electrostatic effect} + \sigma(L\rightarrow M)$$
$$+ \pi(L\rightarrow M) \pm \pi(M\rightarrow L) \text{ where the } \sigma(L\rightarrow M) \text{ term predominates.}$$

It is concluded that $\nu_3$ is primarily influenced by the ligand's electrostatic field and a relationship can be drawn as

$$\Delta\nu_3 \text{ (or } \nu_1 \text{)} = \text{electrostatic effect} - \sigma(L\rightarrow M) - \pi(L\rightarrow M)$$
$$\pm \pi(M\rightarrow L)$$
where the choice of sign of the $\chi(M \rightarrow L)$ term is determined by comparison with experiment. The changes in $\gamma_1$ and $\gamma_3$ are mainly due to $\gamma(L \rightarrow M)$ effect i.e. ligand orbitals of appropriate symmetry overlap with empty $d_{x^2-y^2}$, $d_{xy}$, $f_x(x^2-y^2)$, $f_y(x^2-y^2)$, $f_z(x^2-y^2)$ and $f_{xyz}$ metal orbitals leasing to a shift of electron density to the metal. The effect is best demonstrated in the reduction of $UO_2(VI)$ to $UO_2(V)$.

The extensive systematic investigations of the uranyl compounds reveal that $\gamma_3$ values of the $UO_2^{2+}$ moiety in different complexes depend on the following factors:

1. nature and number of equatorial ligands;
2. ligand bite; (3) equatorial number attained in a particular complex; (4) nature of the cations outside the coordination sphere for anionic uranyl complexes.

McGlynn et al have deduced a relation between valence vibration frequencies of the uranyl group and other parameters which are as follows:

$$\gamma_1 = \left( \frac{f}{M_{Mo}} \right) \frac{1}{2} \left( \frac{1}{2} \chi C \right) \text{ cm}^{-1}$$

$$\gamma_2 = \left( 2d(1 + \frac{2M_{Mo}}{M_{U}}) \right) / M_{Mo} \frac{1}{2} \left( \frac{1}{2} \chi C \right) \text{ cm}^{-1}$$

$$= \gamma_3 (2d/f)^{\frac{1}{2}}$$

$$\gamma_3 = \left( (1 + \frac{2M_{Mo}}{M_{U}}) f / M_{Mo} \right) \frac{1}{2} \left( \frac{1}{2} \chi C \right) \text{ cm}^{-1}$$

$$= \gamma_1 (1 + \frac{2M_{Mo}}{M_{U}})^{\frac{1}{2}}$$
where \( M_o \) and \( M_U \) are the atomic masses of oxygen and uranium respectively; \( f \) (\( F_{U0} \) notation used here) is the elastic force constant in the direction of the U-O bond \( d \), that in the direction perpendicular to the U-O bond.

Substituting the values of \( F_{U0} \) in the Badger's rule modified by Jones
\[
E^q_j = \frac{F_{U0}}{3} + d_{U0}
\]
where \( \beta = 1.03; d_{U0} = 1.17 \), U-O axial bond length can be calculated in angstrom unit. Jones calculated U-O bond length of some uranyl complexes where the results differ from crystallographic data by a small value (1-1.5%). A change of 3.5% in U-O bond length causes a 0.35% variation in force constant values. Several authors calculated \( F_{U0} \) (millidyynes / \( \AA \)) and the U-O bond length (in Angstrom \( \AA \)) putting the \( \gamma_j \) values (cm\(^{-1}\)) in the above equation except where the bond length is greater than 1.25 \( \AA \).

Bullock established two equations related to the stretching and interaction force constants of the linear symmetrical triatomic molecules of the type \( XY_2 \) and the fundamental frequencies \( \gamma_1 \) and \( \gamma_3 \). The relationships have been represented as follows:

\[
4 \pi^2 c^2 m_1 \gamma_1^2 = \frac{K_1 + K_{1,2}}{m_y}
\]
and
\[
4 \pi^2 c^2 m_1 \gamma_3^2 = (1 + \frac{2m_y}{mx}) \left( \frac{K_1 - K_{1,2}}{m_y} \right)
\]
where \( m_1 \) is 1/16th of the mass of the \( O^{16} \) atom, \( K_1 \) is the force constant describing the stretching of the \( X-Y \) bonds, \( K_{1,2} \) is the
force constant which depicts the force acting on an $Y$-atom from $X$ is changed; $m_x$ and $m_y$ are the atomic weights of $X$ and $Y$ respectively and the remaining symbols having their usual significances. The value of $\nu_i$ was obtained from Raman spectra. Incidentally, the small value of $K_{1,2}$ resulted from this method of calculation suggests that the assumptions of valence forces and of a linear symmetrical model for $UO_2^{2+}$ are true.

Yakshin et al.\textsuperscript{65}, during their theoretical analysis of frequencies of uranyl group absorption in IR spectra of the complexes, established the relation, $(\nu_{as})^2 = 1.281 (\nu_{s})^2 - 50991$, which characterises the relationship between the asymmetric and symmetric valence vibrations of the $U-O$ bond in the $UO_2$ group. The values of $\nu_{as}$ obtained in this way give more precise bond energies of solvated $UO_2$ compounds with organic ligands.

Ohwada\textsuperscript{66} suggested that the bending frequency $(\nu_2)$ of the $UO_2^{2+}$ group may be used to calculate the $U-O$ bond distance according to the following equation

$$2 \chi^2 c^2 \nu_2^2 = \left( \frac{m_U + 2m_o}{m_U} \right) \frac{1}{m_o} \cdot \frac{K_\delta}{R_{U-O}^2}$$

where $m_o$ and $m_U$ are the atomic masses of oxygen and uranium and $R_{U-O}$ ($\AA$) is the equilibrium distance between uranium and oxygen; $K_\delta$ is the bending force constant. The value of $K_\delta$ can be evaluated from the equation

$$K_\delta = A \nu_2^2 + B$$
where $A = 1.66$, $B = -0.167 \times 10^5$. Substituting the value of $K$ in the above equation, the following equation is obtained

$$R_{UO} = \left[ \frac{(m_U + 2mo) (A'V_l + B)}{2\pi^2 C^2 V_l^2 \mu_m u} \right]^{1/2}$$

**Polarizability and Magnetic Susceptibility**

Polarizability is measured in terms of refraction. Since the refraction of the multiple bonds are more than that of single bond it is a measure of the electron density and the bond order value of the U-O bonds. Markov and Tsapkina measured the refraction of a series of uranyl compounds and tentatively allotted the refractions into segments, one for uranyl ion and other for the remaining ions in the complex. The values are listed in the Table I.11 which indicates a regular decrease in the refraction of the uranyl group with increasing number of urea molecules. Minc and Kecki also concluded that the polarizability of the $UO_2^{2+}$ group is decreased when the donor properties of the equatorial ligands are strengthened.

According to the report given by Belova, Syrkin, Markov and Tsapkina, uranyl compounds are characterised by small diamagnetism. When the sums of the diamagnetic increments for the remaining molecules and ions participating in the complex compound from their measured magnetic susceptibilities are deduced, a small paramagnetic susceptibility is attributed over $UO_2^{2+}$ ion. Obviously, this includes the diamagnetic components of uranium and oxygen as well as an additional paramagnetic component. The paramagnetism is of
Table 1.11 - Values of the refraction for uranyl compounds and the portion due to the $UO_2^{2+}$ ion

<table>
<thead>
<tr>
<th>Compound</th>
<th>$R_D$ cm$^{-1}$</th>
<th>$R_{DUO_2^{2+}}$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$UO_2SO_4\cdot 2CO(NH_2)_2$</td>
<td>54.44</td>
<td>11.55</td>
</tr>
<tr>
<td>$UO_2SO_4\cdot 3CO(NH_2)_2$</td>
<td>67.35</td>
<td>10.30</td>
</tr>
<tr>
<td>$UO_2SO_4\cdot 4CO(NH_2)_2$</td>
<td>81.29</td>
<td>10.08</td>
</tr>
<tr>
<td>$UO_2(NO_3)_2\cdot 2CO(NH_2)_2$</td>
<td>62.98</td>
<td>13.44</td>
</tr>
<tr>
<td>$UO_2(NO_3)_2\cdot 4CO(NH_2)_2$</td>
<td>93.90</td>
<td>12.23</td>
</tr>
<tr>
<td>$UO_2(NO_3)_3\cdot 5CO(NH_2)_2$</td>
<td>106.48</td>
<td>10.75</td>
</tr>
<tr>
<td>$UO_2C_2O_4\cdot CO(NH_2)_2$</td>
<td>45.45</td>
<td>13.82</td>
</tr>
<tr>
<td>$UO_2C_2O_4\cdot 3CO(NH_2)_2$</td>
<td>72.77</td>
<td>12.82</td>
</tr>
</tbody>
</table>
the order of $10^{-5}$-$10^{-6}$ which is independent of temperature, so that it does not appear to be connected with the spin, in accord with the $\text{UC}_2^{2+}$ ion having no unpaired electrons in the ground state. The magnetic data as listed in Table I.12, indicate that the paramagnetism of $\text{UC}_2^{2+}$ increases with the increasing number of the donor ligands. The reason for the rise in the paramagnetic susceptibility is difficult to interpret but it is assumed that it may be caused both by a decrease in the diamagnetic part and by an increase in the paramagnetic increment. Assuming that the paramagnetic susceptibility of the $\text{UC}_2^{2+}$ ion is always fixed, it can be concluded that this increase is connected with a diminution in the diamagnetic component.

In the study of the properties of the uranyl compounds the changes of asymmetric stretching frequency $\nu_3$, the magnetic susceptibility $\chi$ and the refraction $R_D$ of the uranyl group are observed. The variation of these physical properties as listed in Table I.13 indicates that the values of $\nu_3$ and $R_D$ of $\text{UC}_2^{2+}$ decrease with the increasing number of urea molecules in the compound as well as when water molecules are interchanged by urea molecules; thereby it results the successive increment of the magnetic susceptibility of the $\text{UC}_2^{2+}$ group. Dyatkina et al.\textsuperscript{17} explained this variation in physical characteristics of the $\text{UC}_2^{2+}$ group considering the electronic structure of the uranyl group with equatorial ligands.

According to Eisenstein and Pryce\textsuperscript{70} temperature independent paramagnetism is resulted by the excitation of a bonding $5f\sigma_u^+$ electron into a level of the $1\pi_u$ type which is not involved in
Table I.12 - The magnetic susceptibility of $\text{UO}_2^{2+}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Magnetic susceptibility due to $\text{UO}_2^{2+}$ ($\times 10^6$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{UO}_2\text{SO}_4$</td>
<td>46</td>
</tr>
<tr>
<td>$\text{UO}_2\text{SO}_4\cdot2\text{CO(NH}_2\text{)}_2$</td>
<td>63</td>
</tr>
<tr>
<td>$\text{UO}_2\text{SO}_4\cdot3\text{CO(NH}_2\text{)}_2$</td>
<td>71</td>
</tr>
<tr>
<td>$\text{UO}_2\text{SO}_4\cdot4\text{CO(NH}_2\text{)}_2$</td>
<td>70</td>
</tr>
<tr>
<td>$\text{UO}_2\text{SO}_4\cdot3\text{H}_2\text{O}$</td>
<td>68</td>
</tr>
<tr>
<td>$(\text{C}_{10}\text{H}_3\text{N}_2\text{H})_2\cdot\text{UO}_2(\text{SO}_4)\cdot2\text{CO(NH}_2\text{)}_2\cdot3\text{H}_2\text{O}$</td>
<td>79</td>
</tr>
<tr>
<td>$\text{UO}_2(\text{NO}_3)_2\cdot2\text{CO(NH}_2\text{)}_2$</td>
<td>61</td>
</tr>
<tr>
<td>$\text{UO}_2(\text{NO}_3)_2\cdot4\text{CO(NH}_2\text{)}_2\cdot3\text{H}_2\text{O}$</td>
<td>68</td>
</tr>
<tr>
<td>$\text{UO}_2(\text{NO}_3)_2\cdot5\text{CO(NH}_2\text{)}_2\cdot3\text{H}_2\text{O}$</td>
<td>75</td>
</tr>
<tr>
<td>$\text{UO}_2\text{Cl}_2\cdot2\text{CO(NH}_2\text{)}_2\cdot3\text{H}_2\text{O}$</td>
<td>63</td>
</tr>
<tr>
<td>$\text{UO}_2\text{Cl}_2\cdot3\text{CO(NH}_2\text{)}_2\cdot3\text{H}_2\text{O}$</td>
<td>67</td>
</tr>
</tbody>
</table>
Table I.13 - Variations of the physical characteristics of the UO$_2^{2+}$ group in the uranyl urea compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_3$, cm$^{-1}$</th>
<th>$\chi \times 10^6$</th>
<th>$R_D$, cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_2$(NO$_3$)$_2$·2CO(NH$_2$)$_2$</td>
<td>939</td>
<td>61</td>
<td>13.44</td>
</tr>
<tr>
<td>UO$_2$(NO$_3$)$_2$·4CO(NH$_2$)$_2$</td>
<td>915</td>
<td>68</td>
<td>12.23</td>
</tr>
<tr>
<td>UO$_2$(NO$_3$)$_2$·5CO(NH$_2$)$_2$</td>
<td>915</td>
<td>75</td>
<td>10.75</td>
</tr>
<tr>
<td>UO$_2$SO$_4$·2CO(NH$_2$)$_2$</td>
<td>932</td>
<td>63</td>
<td>11.55</td>
</tr>
<tr>
<td>UO$_2$SO$_4$·3CO(NH$_2$)$_2$</td>
<td>917</td>
<td>71</td>
<td>10.30</td>
</tr>
<tr>
<td>UO$_2$SO$_4$·4CO(NH$_2$)$_2$</td>
<td>917</td>
<td>70</td>
<td>10.08</td>
</tr>
<tr>
<td>UO$_2$C$_2$O$_4$·3H$_2$O</td>
<td>957, 939</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>UO$_2$C$_2$O$_4$·CO(NH$_2$)$_2$</td>
<td>946, 935</td>
<td>60</td>
<td>13.82</td>
</tr>
<tr>
<td>UO$_2$C$_2$O$_4$·3CO(NH$_2$)$_2$</td>
<td>921, 900</td>
<td>62</td>
<td>12.82</td>
</tr>
<tr>
<td>(NH$_4$)$_2$UO$_2$(C$_2$O$_4$)$_2$(H$_2$O)$_2$.H$_2$O</td>
<td>938, 913</td>
<td>70</td>
<td>-</td>
</tr>
<tr>
<td>K$_2$UO$_2$(C$_2$O$_4$)$_2$(H$_2$O)CO(NH$_2$)$_2$</td>
<td>907, 891</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(NH$_4$)$_2$UO$_2$(C$_2$O$_4$)$_2$(H$_2$O)(CO(NH$_2$)$_2$</td>
<td>904, 885</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
the bond formation of the $\text{UO}_2^{2+}$ group and of the $6d_{\sigma_g}^+\uparrow$ electron to
the $1\pi_g$ level. The value of the paramagnetic contribution is cal-
culated using the expression $16N\lambda^2/\Delta$, where $N$ is the Avogadro
number, $\lambda$ is Bohr magneton, $\lambda$ is the probability of locating the
electron in the bond and $\Delta$ is energy required to promote $5f_{\sigma}$
 bonding electron to a $5f_{\pi}$ state. Assuming $\lambda \sim 0.5$ and $\Delta \sim 400,000$
$\text{cm}^{-1}$ for the $5f$ electron, the estimated contribution of the $5f$
electron from the $1\sigma_u^+$ orbital is $60 \times 10^{-6}$ while in the case
of the $6d$ electron from the $1\sigma_g^+$ orbital, the analogous contribu-
tion amounts to $20 \times 10^{-6}$. Though the paramagnetic value has a
correct order of magnitude it should not be considered as decisive
factor for the arbitrary values of the parameters adopted.

Freed and Kasper, from a measurement of the magnetic sus-
ceptibility of the uranyl ion at different temperatures observed
that the susceptibility decreased slightly and uniformly with a
decrease in temperature. The results have been shown in Table I.14.

Table I.14 - The magnetic susceptibility of $\text{UO}_2^{2+}$ at different
temperatures ($^\circ\text{K}$)

<table>
<thead>
<tr>
<th>Temperature ($^\circ\text{K}$)</th>
<th>Magnetic susceptibility due to $\text{UO}_2^{2+}$ ($\times 10^5$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.2</td>
<td>57.03</td>
</tr>
<tr>
<td>116.3</td>
<td>56.28</td>
</tr>
<tr>
<td>90.8</td>
<td>55.93</td>
</tr>
<tr>
<td>69.8</td>
<td>53.97</td>
</tr>
</tbody>
</table>
However, the paramagnetism of the uranyl ion may be accepted owing to the fact that 5f electrons are involved in bonding. The paramagnetism should be markedly anisotropic being zero along the UO$_2^{2+}$ axis and maximum perpendicular to this axis$^{14,70}$.

Belford$^{72}$ calculated the paramagnetism of UO$_2^{2+}$ ion applying the molecular orbitals diagram designed by him and arbitrarily considering the value of excitation energy $\Delta$ at 20,000 cm$^{-1}$. He established a linear relationship between the formal charge on the uranium atom and the calculated magnetic susceptibility of UO$_2^{2+}$ ion. The displacement of electron from the donor ligand in the equatorial plane to uranium atom decreases the effective positive charge over uranium and subsequent decrease in the U-O force constant values. According to Belford, a decrease in the formal charge on uranium corresponds to an increase in the magnetic susceptibility of UO$_2^{2+}$. Since the force constant of the U-O bond is related to asymmetric stretching frequency ($\gamma_3$), a linear relation with negative slope is quite expected between $\gamma_3$ and magnetic susceptibility and such an opinion was established by the report of Sahakari and Mukhedkar$^{73}$.

**NMR Spectral Studies on Uranyl Complexes**

The proton-nmr spectra of uranyl complexes with organic ligands have been extensively studied by a number of workers$^{30,74-82}$. Subramanian and Viswanatha$^{31}$ also put forward their report on $^{19}$F-nmr spectral study.
Siddal and Prohaska\textsuperscript{76} have taken into account the magnetic anisotropy of the uranyl group as the most important factor of the chemical shifts for the protons in the uranyl nitrate adducts of methylene diphosphonates. But Subramanian et al\textsuperscript{78,79,81} suggested that in the compounds $\text{UO}_2\text{L}_2\text{X}$ ($\text{L} = \beta$-diketone; $\text{X} = \text{pyridine N-oxide or its para derivatives}$), complexation would cause deshielding of protons due to transmittance of electron density from the ligand oxygen to the metal ion.

Both the above grounds for the chemical shifts were established by Kim et al\textsuperscript{30} during their study on the uranyl complexes with $1,2$-disubstituted benzenes.

Pople et al\textsuperscript{77} proposed an equation to calculate the chemical shifts for the protons in the neighbourhood of an anisotropic field of the uranyl ion,

$$\Delta \xi_m = \Delta \xi_{\text{atomic}} \left(1 - 3 \cos^2 \gamma \right) / 3R^3$$

where $\Delta \xi_{\text{atomic}} = \xi_{\text{atomic (parallel to axis)}} - \xi_{\text{atomic (perpendicular to axis)}}$

'R' is the distance of proton from the anisotropic atom (or group in this case), and $\gamma$ is the angle between the line joining the proton to the centre of the anisotropic group and the axis of symmetry of the anisotropic group.

According to Kim et al\textsuperscript{30} the chemical shifts for phenyl ring in the $1,2$-disubstituted benzenes depend on the nature
(electron withdrawing or electron donating) of the substituents at the X and Y positions (Figure I.11).

The authors examined the spectral study on phthalic acid (X = Y = COOH, electron withdrawing group), pyrocatechol (X = Y = OH, electron donating group) and O-phenylene diamine (X = Y = NH$_2$, electron donating group) and observed the resonance peaks for the protons at 2.39, 3.32 and 3.58 ppm respectively and hence it is concluded that the phenyl ring protons in each molecule are nearly equivalent. Furthermore, the results indicate that the drainage of electron density from phenyl ring to the substituents or from the latter to the former causes the downfield or upfield shift equally for all phenyl ring protons without any significant difference of the chemical shifts between Ha and Hb protons.

It is suggested that the deshielding of both Ha and Hb protons due to the anisotropic field of uranyl group and the change of the drainage of electron density from ligand to metal are caused by complexation. However, the difference of the chemical shifts, $\gamma_{AB}$ between Ha and Hb protons for phthalic acid and O-phenylenediamine complexes is attributed to the effect of the anisotropic field of the uranyl ion, because Ha and Hb protons seem to remain equivalent even if some change of the drainage of electron density between ligand and metal occurs by complexation. Assuming the symmetric structures of the complexes with the distance of 2.9 Å between carboxylate oxygen and uranium and 2.7 Å between the nitrogen and uranium, $\gamma_{AB}$ in these complexes can be
Fig I. 11
calculated by substituting $\Delta \chi = -2.74 \times 10^{-23}$ and $\gamma = \pi/2$ into the previously stated equation. The evaluated values are 0.41 and 0.31 ppm correspond to the observed values 0.42 and 0.32 ppm for the phthalic acid and o-phenylenediamine complexes respectively which support the assumption that $\nu_{AB}$ in the uranyl complexes should be caused by the anisotropic field of uranyl ion. On the otherhand, Subramanian and Manchanda\textsuperscript{79} explained $\nu_{AB}$ for their compounds considering only deshielding effect due to the drainage of electron density from ligand to the metal.

Bong-il-Kim et al\textsuperscript{30} succeeded in calculating the anisotropic field effect of the uranyl ion, $\Delta \sigma_m$ and the shielding effect caused by the drainage of electron density between ligand and metal $\Delta \sigma_d$. They also suggested that back donation from metal to ligand occurs through the covalent bond U-O (phenol), not through the electrostatic bond U-O (carboxylate).

\textbf{X-ray structural analysis}

The determination of the crystalline structure of the uranyl compounds by X-ray analysis suffers very serious experimental trouble due to its specificity. It is very difficult to localise the light atoms like oxygen, carbon, nitrogen and fluorine in the presence of the heavy uranium atom now and then. Possibly, for this reason the available data on the structure of the uranyl compounds are most unsystematic. The uranium-ligand distances are known only in the case of ligands bonded through oxygen, fluorine and nitrogen atoms though few structures have been
investigated completely. Moreover, high degree of accuracy is not found for all the structures described fully.

It was Zachariasen\textsuperscript{83}, who first determined the structure of potassium pentafluorouranilate $K_3\textsuperscript{3-}\text{UO}_{2}\text{F}_5\textsuperscript{7-}$ by $X$-ray analysis using precise diffractometer with a high degree of accuracy. The error in the determination of the interatomic distances between uranium and the light atom is not more than $\pm 0.02$-$0.03$ $\AA$. Zachariasen and Plettinger\textsuperscript{11} investigated the structure of sodium-triacetatouranilate $Na_2\textsuperscript{2-}\text{UO}_2(\text{CH}_3\text{COO})_3\textsuperscript{7-}$ on a diffractometer allowing for the absorption and extinction factor by introducing a correction for the temperature effect of uranium and the light atoms. This appears to be one of the better $X$-ray structural investigations of uranyl compounds and indicates that the position of the lighter atoms can be determined with an accuracy of upto $\pm 0.03\AA$, even in the presence of uranium.

Chernyaev\textsuperscript{78} has reconsidered the $X$-ray data of a number of uranyl compounds which suggest that the $UO_2^{2+}$ radicals has a symmetrical linear structure though there are few reports of deviations from this structure. They are two comparatively short U-O bonds usually known as 'primary' along with four, five or six uranium-ligand equatorial bonds termed as 'secondary' coordinated around the uranyl group. The ligands are accommodated in the plane perpendicular to the axis of the O-U-O group attaining a bipyramidal structure. For some compounds the experimental results indicate the forms of the coordination polyhedra around the central uranium
atom and the magnitudes of the valence angles.

The structures of uranyl complexes with tropolone, 8-hydroxyquinoline, Schiff base, cupferron, carboxylic acids, fluorides have been studied. Though the available data are not plentiful but are of considerable importance in the crystallo-chemistry of the uranyl compounds.

Complex Compounds of Uranyl Ion, UO$_2$$^{2+}$

Among the large contingent of ligands carbonate, peroxide, hydroxide, fluoride, acetate, oxalate, sulphate, nitrate, chloride, bromide, ioddine, cyanate and thiocyanate ions, were a few used for preparing uranyl complexes. In all the complexes UO$_2$$^{2+}$ : ligand ratio varies from 1:0.5 to 1:6 for monodentate ligands and 1:0.5 to 1:3 for bidentate ligands. Even, some mixed ligand complexes where both mono and bidentate ligands remain in the innersphere have been well established. The previously considered simple salts like UO$_2$SO$_4$·3H$_2$O; UO$_2$(C$_2$O$_4$)·3H$_2$O and UO$_2$(NO$_3$)$_2$·6H$_2$O are now the examples of complex salts and thus uranyl nitrate hexahydrate is better written as $\left[UO_2(H_2O)_6\right](NO_3)_2$.

Water is considered as a typical ligand since it is not only coordinated with uranyl ion, but also displaces certain ligands like NO$_3^-$, SO$_4^{2-}$ etc. from the innersphere. Investigations of the uranyl complexes indicate that in the displacement series ligands can be arranged in the following order: CO$_3^{2-}$$>$$O_2^{-}$$>$$OH^{-}$$>$$F^{-}$$>$$CH_3COO^{−}$$>$$C_2O_4^{2−}$$>$$SO_4^{2−}$$>$$Cl^{−}$$>$$NO_3^{−}$$>$$amines$$>$$Br^{−}$$>$$I^{−}$. This
series can be used to indicate the synthetic methods which may be used for the preparation of mixed ligand complexes and to predict the direction which will be taken by the reaction of intraspheric substitution.

Formerly, the possible isolation of uranyl amine from alcoholic as well as aqueous solution was controversial but at present it is well established that the chemical affinity of uranium for nitrogen is much weaker than its affinity for oxygen or fluorine atoms, for which the synthesis of uranyl amines is difficult to perform. On the otherhand, in most of the cases the amines have fairly strong basic properties, in basic aqueous solution the uranyl ion is hydrolysed forming hydroxy compounds.

\[ \text{UO}_2^{2+} + 2\text{OH}^- \rightarrow \text{UO}_2(\text{OH})_2 \]

\[ \text{UO}_2(\text{OH})_2 + 2\text{OH}^- \rightarrow \text{UO}_2(\text{OH})_4^{2-} \]

On the contrary in acid medium the uranyl amines are also difficult to prepare because of the considerable tendency of amine nitrogen to add protons forming corresponding cations. Grinberg and Vdovenko isolated some uranyl amines from non-aqueous solutions. Later on Markov and Tsapkin have reported the preparation of uranyl amines, with amines of weaker basic properties, from aqueous solution. At present the reactions between various uranyl salts with 1,10-phenanthroline, 2-2'-dipyridyl, acridine and \( \beta \)-naphthoquinoline can be carried out both in aqueous and non aqueous solution. In these uranyl complexes the uranyl ion is coordinatively unsaturated due to steric effect since the heterocyclic amines occupy a large volume in the innersphere, thereby hinder the entry of the fellow ligands to give
the maximum coordination number six.

**Uranyl Complexes with Organic Ligands**

A good number of uranyl complexes with organic ligands have been isolated and characterised. Comynes\(^9\) reviewed some uranyl complexes with organic ligands containing oxygen, nitrogen and phosphorous as donors. Later on Chernyaev\(^7\) has listed as many as 250 uranyl complexes with different organic ligands which have been characterised briefly by IR, UV, X-ray and thermogravimetric analyses. After his work many other interesting compounds with organic chelating ligands like tropolone, 8-hydroxyquinoline, \(\beta\)-diketone, schiff bases, azoderivatives, glutathione, pyridine-2,6-dicarboxylate, \(p\)-nitroso-N,N-dimethylaniline, crown ether, pyridine N-oxides, 2-2'-bipyridyl-N-Oxide, 1,10-phenanthroline N-oxide, Neo-cupferron, hydroxamic acids etc. have been prepared and characterised by various physicochemical methods which have greatly enriched our present day knowledge and the structure and bondings in uranyl complexes\(^3,4,1\)\(^-\)\(^2\)\(^0\).  

**Analytical applications of uranyl complexes**

The use of uranyl complexes for the determination of various metal ions is not a new chapter in analytical chemistry. However, we are dealing only with the gravimetric methods out of the widely used area and in the process some important uranyl complexes are quoted here.

**Acetato Complexes of uranyl ion**

The acetato complexes of dioxygenium(VI) have been widely used as gravimetric reagent. In the presence of acetic acid and
alkali metal acetates, diaquodiacetato uranyl $\text{UO}_2(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2\cdot 7\text{H}_2\text{O}$
in aqueous solution gives triacetatouranylates, $\text{M}^I\text{UO}_2(\text{CH}_3\text{COO})_3\cdot 7\text{H}_2\text{O}$
where $\text{M}^I$ is Li$^+$, Na$^+$, K$^+$, NH$_4^+$, Rb$^+$ and Cs$^+$. The reaction of triacetatouranylates
of bivalent cations of the type $\text{M}''\text{UO}_2(\text{CH}_3\text{COO})_3\cdot 7\text{H}_2\text{O}$
with the solution of sodium or lithium salts forms triacetates with
double cations in the outer sphere, i.e. of the type
$\text{M}'\text{M}''\text{UO}_2(\text{CH}_3\text{COO})_3\cdot 7\cdot 2\text{H}_2\text{O}$
where $\text{M}''$ is a bivalent cation. Due to low
solubility of these compounds they are suitable for the quantitative
estimation of sodium or lithium. The bivalent cations may be Mg$^{2+}$,
Zn$^{2+}$, Cu$^{2+}$, Fe$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Co$^{2+}$ or Cd$^{2+}$ of which the zinc and
magnesium compounds are most extensively studied.$^{121-134}$

8-Quinolinolato Complexes of uranyl ion

8-Quinolinol has been used as a good precipitating agent for
uranyl ion$^{135}$. The red crystalline precipitate with composition
$\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2\cdot \text{C}_9\text{H}_5\text{NOH}$ was long regarded as normal uranyl 8-quinolinolate
with an 'extra' molecule of 8-quinolinol. The composition
of the above red compound is $\text{H}\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_3\cdot 7$ according to Bullwinkel
and Noble$^{102}$ and they have prepared the sodium, tetraethyl ammonium
and tetraphenyl arsonium salts corresponding to this free acid.

Cupferronato and neo-cupferronato Complexes of uranyl ion

The reaction of cupferron (ammonium salt of $\alpha$-nitrosophenyl
hydroxylamine) with uranyl ion was first studied by Horton$^{33}$ and
latter Szoke$^{136}$ who prepared ammonium tricupferronatouranylate having
the composition $\text{NH}_4\text{UO}_2(\text{C}_9\text{H}_5\text{N}_2\text{O}_2)_3\cdot 7$. 

-56-
Horton also prepared sodium, potassium, rubidium and caesium salts of the anion, $\sqrt[3]{\text{UO}_2\left(\text{C}_6\text{H}_5\text{N}_2\text{O}_3\right)^{-}}$, by reacting the respective alkali cupferrates with uranyl ion. In turn, alkali cupferrates were obtained by replacing ammonium ion from cupferron by the corresponding alkali metals. Three cupferronato units are equivalent in the ammonium compound as suggested by the crystallographic data.

Kundu and Banerjee prepared sodium triscupferronatouranylate and found this sodium salt as an effective precipitant for gravimetric determination of ammonium, potassium, rubidium, caesium, calcium, strontium and barium. Using the same reagent Sarkar and Kundu established the conditions for estimating silver, cadmium, thallium, zinc and lead. They obtained satisfactory results from their experiments.

Bera and Kundu, however, prepared a new compound sodium tris(neo-cupferronato) dioxouranium(VI), $\text{Na}\sqrt[3]{\text{UO}_2\left(\text{C}_{10}\text{H}_{7}\text{N}_2\text{O}_3\right)^{-}}\cdot 2\text{H}_2\text{O}$, formed by the reaction of sodium salt of neo-cupferron ($\beta$-nitrosodimethylhydroxylamine) with uranyl ion. They used this sodium salt as precipitant for the gravimetric determination of silver, thallium(I) and barium.

Recently, Bhattacharya and Kundu prepared sodium tris-(benzhydroxamato)dioxouranium(VI) dihydrate, $\text{Na}\sqrt[3]{\text{UO}_2\left(\text{C}_7\text{H}_6\text{O}_2\text{N}\right)^{-}}\cdot 2\text{H}_2\text{O}$, by the reaction of sodium salt of benzhydroxamic acid with uranyl nitrate. They observed this sodium salt as a suitable reagent for the gravimetric determination of alkali-metals like rubidium,
caesium, barium, thallium(I) and lead. They also separated rubidium and caesium from potassium with this reagent.

**Bio-inorganic aspects of Uranium Chemistry**

Recent emphasis on nuclear projects simultaneously associated with enhanced major health hazards due to radioactive exposures leads to the bio-inorganic study of the actinides. Uranium belonging to a member of actinide series is no longer exception of these studies. The maximum permissible body burden$^{141}$ of M.P.B.B. expressed in $\mu$Ci unit for $^{233}$U is 0.07 and for $^{238}$U is 0.5.

**A. Toxicity**

The acute toxicity of parenterally injected aqueous uranyl nitrate at 30 days ranges from 0.1 to 0.3 mg/kg in the rabbit and guineapig to as much as 20 to 25 mg/kg in C57B1 mice causes death to then. Most of the deaths happened between day 14 and 21. The change in toxicity between the species has been ascribed to differences of pH of the urine. As herbivores have a very acidic urine the clearance of the uranyl cation by dialysis from plasma in the form of its bicarbonate complex, is partially suppressed, thus favouring retention of the cation in the animal.

Rothstein$^{142}$ work with yeasts furnished the mechanism of toxicity of uranium which is due to the suppression of glucose metabolism by interaction of $\text{UO}_2^{2+}$ with the cell surface. The inhibition of glucose metabolism was found to be directly proportional to the amount of $\text{UO}_2^{2+}$ present. The suppression of glucose metabolism could be neutralised either by addition to excess phosphate to the system.
or by administration of some other complexing agent. This mechanism of cellular death by suppression of respiration of the cell is supported by the rate of onset and the nature of histological changes in the kidney. The only tissue damaged is the proximal kidney tubule.

B. Routes of entry into the body

Alike other actinides uranium possesses few or no chemical properties which are typical of elements which enter into bio-chemical process, the low gastronomical uptake of UO$_2$$^+$ is not astonishing. Possibly, uptake through food chain is the strongest pathways.

C. Transport of Uranium in body fluids

(a) Blood

There have been a very few investigation of the chemical form of uranium in blood. According to Neumen$^{143}$ and Dounce$^{144}$, 50% of U(VI) in serum was associated with proteins and 50% with bicarbonate. The equilibrium of UO$_2$$^+$ between the proteins and bicarbonate is established rapidly. In the first few minutes after the intravenous injection about 80-90% of the element remain ultrafilterable and flows out of the vascular compartment into extracellular fluid. The level of the element in blood decreases with the uptake by bone and release through kidney and thus facilitating the diffusion of the element into extracellular fluid. U$^+$, bound to proteins is discharged very slowly in comparison to UO$_2$$^+$. Perhaps, the limited interaction of uranium in the line of other actinides, with the bio-inorganic chemistry of iron is caused
by the Fe$^{3+}$/Fe$^{2+}$ cycle of oxidation and reduction. In this continuation it is proposed that iron insufficiency may help increased uptake.

(b) Urine

On the basis of the report of homologous actinides such as plutonium, americium and curium it is presumed that U$^{4+}$ and U$^{3+}$ will be excreted in urine as the citrate complexes and UO$_2^{2+}$ as bicarbonate complex.

D. Uptake of Uranium into

(a) Liver

Uranium, being a typical hard acid may be expected to strongly bound to phosphates. Thus if this results a strong complex of uranium with phospholipids is expected; the same can act as ionospheres in the concentration of the elements in liver.

Ballon and Gies$^{145}$ reported a little or no UO$_2^{2+}$ uptake by the liver of normal animals. Indeed, the undergoing study by Bullman$^{141}$ deserved a clear uptake of UO$_2^{2+}$ into the livers of thioacetamide intoxicated animals.

(b) Bone

The concentration of uranium on bone was overlooked before the establishment of work of Neuman$^{143}$. In Vitro studies evidence that UO$_2^{2+}$ was taken up onto bone surface by ion-exchange such that two calcium ion were replaced by one uranyl ion on the bone crystal surface. Of course, renal filtration interferes with this uptake.
Administration of uranyl nitrate deposits more uranium on mouse skeleton than the bicarbonate species. With a more vascular immature skeleton having larger surface area of mineralising tissue the uptake of $\text{UO}_2^{2+}$ reaches highest level. The uptake of uranium into trabecular bones (ribs and vertebra) was 4 to 20 times higher than into long bone shafts (compact bones) as reported by Tannebaum\textsuperscript{146}. Autoradiographic studies indicate the association of uranyl ion with bone surfaces which are in close proximity to the circulation system. In spite of the resembling of the incorporating process of $\text{UO}_2^{2+}$ and $\text{Ca}^{2+}$ into bone the basic analogy is comprised in the penetrating capacity of $^{45}\text{Ca}^{2+}$ through microcirculation of bone with subsequent exchange with non-active $\text{Ca}^{2+}$ which is entirely forgotten in crystals remote from circulation and in non-availability of uranium in new deposits of bone after the injection of radioactive $^{45}\text{Ca}^{2+}$. These dissimilarities are caused as kidney can resort efficiently the released calcium ion whilst the physiological uranyl ions released from bone are easily cleared through kidney.

E. \textbf{Decorporation Procedure}

The cell fractionation and liver perfusion investigations act as a major impetus in the rethinking of techniques for departing actinides from the liver. Diethylene triamine penta acetic acid (DTPA) which was found to be the potent for plutonium has a little value in clearing uranium from the body. Ballon \textit{et al}\textsuperscript{145} supposed that this lack of success is related to the relatively low stability of the DTPA chelate complex.
F. Conclusion

Several investigations into the mechanisms of uptake of the uranium and the actinides as well as their possible methods of removal which is now under progress over the globe could throw some new light upon the treatment of iron storage diseuses and Wilson's disease. It may also give some insight into the possible influence of intracellular calcium concentrations upon the onset of cancer.

The Present Research

A. Physicochemical studies and nature of bondings in complexes of dioxouranium(VI) with phenylacetoxydioxouranium acid

The uranyl ion, more properly known as dioxouranium(VI), combines with phenylacetoxydioxouranium acid in the stoichiometric ratio of (1:3). The general formulae of the complexes are \( M_{I} \overset{\text{UO}_2(\text{C}_8\text{H}_8\text{O}_2\text{N})_3}{\sim} \cdot n\text{H}_2\text{O} \) where \( M_{I} \) is a monovalent cation like \( \text{Li}^+ \), \( \text{NH}_4^+ \), \( \text{K}^+ \), \( \text{Rb}^+ \), \( \text{Tl}^+ \) and \( \text{Hg}^{2+} \) and \( M_{II} \overset{\text{UO}_2(\text{C}_8\text{H}_8\text{O}_2\text{N})_3}{\sim} \cdot 2\cdot n\text{H}_2\text{O} \) where \( M_{II} \) is a divalent cation like \( \text{Mg}^{2+} \), \( \text{Ca}^{2+} \), \( \text{Sr}^{2+} \), \( \text{Ba}^{2+} \), \( \text{Zn}^{2+} \), \( \text{Cd}^{2+} \), \( \text{Hg}^{2+} \) and \( \text{Pb}^{2+} \) and \( n = 0, 1, 2, 3 & 4 \).

Of the above mentioned compounds potassium tris(phenylacetoxydioxouranium(VI)) was prepared first by the reaction of phenylacetoxydioxouranium acid with uranyl ion in presence of potassium.
hydroxide in aqueous medium of pH nearly equal to 9.00. Similarly lithium and ammonium salts have been prepared using lithium hydroxide and ammonium hydroxide respectively instead of potassium hydroxide. Other compounds of the series have been prepared by the metathesis reaction between the aqueous solution of corresponding metallic cations and the potassium salt in methanol at pH range 6. All the complex salts are well crystalline, coloured solid, highly soluble in DMF and DMSO. Mercurous salt has low solubility in DMF. Lithium salt is soluble in methanol, ethanol and acetone. Potassium salt is soluble only in methanol. Other salts are insoluble in all other common solvents.

The newly isolated compounds are well characterised and their structures have been elucidated through elemental analyses and various physico-chemical studies such as conductance, TGA, reflectance, electronic and infrared spectroscopy. Thermal stability of the complexes has been established by TGA data. Electronic spectral result indicates charge transfer spectra from ligand to uranium. \( \nu_3(\text{cm}^{-1}) \) values i.e., the asymmetric stretching frequency of UC\textsuperscript{2+} from IR data has been used to calculate the force constant \( F_{UC} \) in m dyne/Å\(^2\) and subsequently the U-O axial bond lengths \( R_{UC} \) also have been calculated in Å. Absence of \( \nu_1 \), the symmetric stretching frequency of UC\textsuperscript{2+} ion in all the complexes suggests the linearity of the UC\textsuperscript{2+} group.
B. Studies on the mixed ligand complexes of dioxouranium(VI) with phenylacetohydroxamic acid

Dioxouranium(VI) forms 1:2 complexes of the type \([\text{UO}_2L_2^-]\), where \(L\) is the anion of phenylacetohydroxamic acid (\(\text{C}_9\text{H}_7\text{O}_2\text{N}\)). The compound is coordinately unsaturated since four equatorial positions of the \(\text{UO}_2^{2+}\) group are occupied by two bidentate ligands leaving two positions vacant. Several anions and coordinating amines along with phenylacetohydroxamic acid have been successfully employed for coordination and subsequent expansion of coordination number of dioxouranium(VI). The general compositions of the complexes are

\[(\text{NH}_4)_2\text{UO}_2\text{L}_2\text{X}_2^-\]
\[\text{NH}_4\text{UO}_2\text{L}_2\text{X}^-\]
\[\text{UO}_2\text{L}_2\text{B}^-\]

where \(L\) is the anion of phenylacetohydroxamic acid (\(\text{C}_9\text{H}_7\text{O}_2\text{N}\)), \(X = \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{CH}_3\text{COO}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{NO}_3^-; B = 1,10\text{-phenanthroline}, 2\text{-2'}\text{-dipyridyl}, 2\text{C}0(\text{NH}_2)_2\). They are insoluble in common solvents but are soluble in DMF and DMSO. The stoichiometry of the complexes has been established on the basis of elemental analyses. Various physicochemical studies such as conductance, TGA, DTA, reflectance and electronic spectra and far IR spectra have been adopted to predict the geometry of the complexes and the coordinating behaviour of the anions in order to elucidate the structural arrangements.

Conductance values establish both electrolytic and non-electrolytic nature of the compounds. Thermal nature of the compounds
as revealed by the TGA and DTA data indicates the expulsion of various portion in course of formation of final product. Electronic spectra characterises the charge-transfer bands from ligand to uranium. The IR, particularly far IR offers the conclusive proof for chelation of anions and amines other than phenylacetohydroxamic acid and also geometry of the complexes. $\nu_2$, the bending frequency of O-U-O, appears in far IR. The $\nu_1$, being absent in all the complexes, indicates the linearity of the UO$_2^+$ group. The force constant $F_{UO}$ (in m dynes/A°) and axial U-O bond lengths $R_{UO}$ (in A°) have been calculated from $\nu_3$ values.

C. Studies on the Coordination of salicylhydroxamic acid with dioxouranium(VI) and elucidation of their structures through physicochemical methods

Dioxouranium(VI) successfully coordinates with salicylhydroxamic acid giving two series of compounds. In one series, metal-ligand ratio is 1:1.5 or 2:3 which can be represented as $M_2\Gamma(UO_2)_2(L')_{3/2}nH_2O$ where $L'$ is the anion of salicylhydroxamic acid (C$_7$H$_5$O$_3$N)$_2$; $M = Na^+$, $K^+$ and $Rb^+$. In the other series, the metal-ligand ratio is 1:3 which can be represented by the general formulae $M_{11}UO_2(L)_{3/2}nH_2O$ and $M_{11}UO_2(L)_{3/2}nH_2O$ where $L$ is the anion of salicylhydroxamic acid (C$_7$H$_5$O$_3$N)$_2$; $M_{11} = Na^+$, $K^+$, $Rb^+$, $Cs^+$, $Tl^+$, $NH_3CH^+$, $N_2H^+$, (C$_6$H$_5$)$_4$As$^+$ and (NH$_2$)$_2$C = NH$_2^+$; $M_{11} = Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$ and $Zn^{2+}$ and $n = 0$ to 4.

The first type of compounds are soluble in water, therefore, they are prepared in alcohol (methanol and absolute alcohol) at a pH~8.0. Of the second type of compounds sodium and potassium salts being liable to be hydrolysed in water, prepared in absolute alcohol.
Other compounds of this series can be prepared by the direct metathesis reaction of aqueous solution of sodium or potassium tris-(salicylhydroxato)dioxouranium(VI) instantly prepared in water at pH 8.5 with the aqueous solution of corresponding metallic cations. The compounds are coloured and well crystalline. Except sodium and potassium salts other compounds, being insoluble in common solvents, are soluble in DMF and DMSO.

The stoichiometry of the complexes are established on the basis of elemental analyses and they are characterised through various physicochemical studies. Conductance values are appreciably low due to the big size of the anions in comparison to the cations. TGA data predict the exclusion of three salicylhydroxamic acid unit at a time at the decomposition temperature indicating the uniform attachment of three salicylhydroxamic acid unit to uranyl moiety. Electronic spectra characterise the charge transfer band as well as transition within the uranyl entity. Appearance of $\nu_3$ (asymmetric stretching frequency) and absence of $\nu_1$ (symmetric stretching frequency) support the linear model of $\text{UO}_2^{2+}$ ion. Force constant ($F_{UO}$) in m dynes/Å and U-0 axial bond length ($R_{UO}$) in Å have been calculated as usual from $\gamma_2$(cm$^{-1}$) values.

D. Studies and nature of bondings in mixed ligand complexes of dioxouranium(VI) with salicylhydroxamic acid

It is well established that dioxouranium(VI) forms 1:2 complexes with salicylhydroxamic acid having the formula $\text{UO}_2(C_7H_6O_3N)_2(H_2O)_2$. Dioxouranium(VI) also forms a series of
mixed ligand complexes with salicylhydroxamic acid along with some anionic ligands and coordinating amines. The general formulae of the complexes are:

(i) \((\text{NH}_4)_2\text{UO}_2\text{L}_2\text{X}_2\cdot n\text{H}_2\text{O}\)

(ii) \(\text{NH}_4\text{UO}_2\text{L}_2\cdot \text{H}_2\text{O} \cdot n\text{H}_2\text{O}\)

(iii) \(\text{UO}_2\text{L}_2\text{B} \cdot n\text{H}_2\text{O}\)

where L is the anion of salicylhydroxamic acid (C\text{H}_6\text{O}_3\text{N}), X = \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{C}_2\text{O}_4^{2-}, \text{CH}_3\text{COO}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{NO}_3^-; \text{B} = \text{1,10-phenanthroline}, \text{2,2'-dipyridyl}, \text{2CO(NH}_2\text{)}_2\text{, and } n = 0, 1, 2 \text{ and } 3. \text{ They are insoluble in common solvents but are soluble in DMF and DMSO.}

They have been characterised through elemental analyses, conductance, TGA, DTA, far IR and electronic spectral data. Both the electrolytic and non-electrolytic character of the compounds have been established from conductance values. The relative thermal stabilities of the complexes as established from DTA and TGA data are sulphato < 1,10-phenanthroline < urea < bromo 2,2'-dipyridyl < oxalato < chloro < carbonato < iodo < nitrato < acetato. The occurrence of bands in the electronic spectra indicates the charge transfer spectra from ligand orbitals to 5f and/or 6d orbitals of \text{UO}_2^{2+} moiety as well as transition within 5f orbitals.

Particular attention has been paid towards the far IR spectra which have been utilised to predict the geometry of the complexes and the coordinating behaviour of the anions and amines other than salicylhydroxamic acid. In the present complexes \(\nu\text{asymmetric}
stretching frequency) and $\gamma_3$ (bending vibration) of the uranyl group are IR active but $\gamma_1$ (symmetric stretching frequency) is IR forbidden which maintain the linearity of the $\text{UO}_2^{2+}$ group. The value of $\gamma_3 (\text{cm}^{-1})$ of the $\text{UO}_2^{2+}$ entity has been used to calculate the force constant $F_{\text{UO}}$ in $\text{m dynes/A}^0$ and the U-O axial bond length ($R_{\text{UO}}$) in $\text{Å}$.

E. Gravimetric determination of strontium, barium and thallium(I) with potassium tris(phenylacetohydroxamato)dioxouranium(VI) as an analytical reagent

Potassium tris(phenylacetohydroxamato)dioxouranium(VI) was found to be an effective and suitable reagent for the quantitative estimation of strontium, barium and thallium(I). About 1% reagent solution was prepared by dissolving the salt in methanol. The red coloured solution was used immediately after its preparation. The reagent solution with suitable concentration was utilised for the quantitative precipitation of the above mentioned ions. The precipitate thus obtained are well crystalline and thermally highly stable. So the precipitates having exact stoichiometry were dried at 120°C and weighed to constant weight. Due to higher thermal stability and low solubility product of these precipitates, this method offers a great advantage in the field of gravimetric determination. Moreover, high molecular weight of the precipitates provides a better approach to accuracy, thereby, favouring the effectiveness of this method.

(a) Strontium was precipitated quantitatively from a solution of strontium nitrate with 1% solution of the reagent at pH 6.2 to 6.9.
so that the supernatant liquid contains an excess of 0.33% (w/v) reagent. The precipitated strontium tris(phenylacetohydroxamato)dioxouranium(VI), dihydrate Sr\(\left[\text{UO}_2(C_9H_8O_2N)\right]_2\cdot2H_2O\) thus obtained was allowed to settle for 6-7 hours or preferably overnight at room temperature. After drying at 120°C the constant weight residue having the composition Sr\(\left[\text{UO}_2(C_9H_8O_2N)\right]_2\) was weighed. Alkali metals other than sodium and lithium and alkaline earth metals, lead, thallium(I) interfere with the precipitation of strontium. The anhydrous strontium tris(phenylacetohydroxamato)dioxouranlum(VI) begins to decompose from 180°C onwards. The solubility product of the precipitate was determined to be \(6.4 \times 10^{-9}\) at 25°C.

(b) Barium has been estimated by precipitating the metal as barium tris(phenylacetohydroxamato)dioxouranium(VI), tetrahydrate, Ba\(\left[\text{UO}_2(C_9H_8O_2N)\right]_2\cdot4H_2O\) at pH 6.3 to 7.6. The precipitation is quantitative when the supernatant liquid contains 0.34% (w/v) of the reagent in excess. The precipitate is highly crystalline and can be dried at 120°C with the definite composition Ba\(\left(C_9H_8O_2N\right)_2\). Lead, thallium(I) and other alkaline earth metals interfere with the precipitation of barium.

The anhydrous barium tris(phenylacetohydroxamato)dioxouranium(VI) is stable up to 135°C. The solubility product was determined to be \(4.9 \times 10^{-12}\) at 25°C.

(c) Thallium(I) has been determined quantitatively by precipitating thallium(I) as thallium(I) tris(phenylacetohydroxamato)dioxouranium(VI) from a solution of thallous sulphate at pH 6.2 to
The reagent concentration in supernatant liquid required for complete precipitation of thallium(I) was found to be 0.17% (w/v) in excess. The precipitate thus obtained are highly crystalline and thermally stable upto 160°C. So the precipitate was dried at 120°C and weighed to a constant weight with the composition Tl\(\text{UO}_2\)(C\(_6\)H\(_3\)O\(_2\)N\(_3\))\(_2\)\(_7\).

Zinc, cadmium, lead and alkaline earth metals interfere with the precipitation of thallium(I). The solubility product is \(1.6 \times 10^{-10}\) at 23-25°C.

Gravimetric determination of metals by potassium tris-(phenylacetohydroxamato)dioxouranium(VI) offers an easy, quick as well as accurate method for the estimation of these metals. The precision of each method has been ascertained by calculating standard deviation of the results from a series of identical determinations.
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