Chapter II

EXPERIMENTAL
The experimental part of the work is divided into two parts (1) preparation of the uranyl compounds and (2) spectrographic procedure.

1. Preparation of the uranyl nitrate double compounds.

The different uranyl compounds required in the present investigations were prepared in our laboratory utilizing the methods if already available and developing the methods wherever necessary. Much work has been done on synthesizing the various uranyl salts. For our present work, the uranyl compounds in microcrystalline form were suitable. Thus the methods established already were followed for many cases.

In the present investigations the double salts CsUO$_2$(NO$_3$)$_3$, RbUO$_2$(NO$_3$)$_3$ and KUO$_2$(NO$_3$)$_3$ were prepared according to the methods available, the salts K$_2$UO$_2$(NO$_3$)$_4$ and Rb$_2$UO$_2$(NO$_3$)$_4$ were prepared by slightly modifying the available methods and the salt Cs$_2$UO$_2$(NO$_3$)$_4$ was prepared by developing a method for this salt. Similarly a method was devised to obtain a low temperature form of the potassium salt which is in all probability, the tripotassium uranyl nitrate salt (K$_3$UO$_2$(NO$_3$)$_5$).

For all the salts that were synthesized here UO$_2$(NO$_3$)$_2$·6H$_2$O was the starting material, which was mixed with various alkali nitrate salts to obtain
different uranyl nitrate double salts.

**Caesium uranyl nitrate** $\ce{CsUO_2(NO_3)_3}$: The method for the preparation of this salt has been described by Dieke and Duncan. A similar method was adopted in the present case also with a little difference in the starting materials in the present case were $\ce{CsNO_3}$ and $\ce{UO_2(NO_3)_2.6H_2O}$ instead of $\ce{Cs_2CO_3}$ and $\ce{UO_2(NO_3)_2.6H_2O}$ as used by Dieke and Duncan. Stoichiometric amounts of $\ce{CsNO_3}$ and $\ce{UO_2(NO_3)_2.6H_2O}$ were dissolved in concentrated nitric acid and evaporated slowly at room temperature ($26^\circ$C). However, the $\ce{CsUO_2(NO_3)_3}$ salt prepared by dissolving equimolar proportion of $\ce{CsNO_3}$ and $\ce{UO_2(NO_3)_2.6H_2O}$ in distilled water, showed some weak impurity bands in fluorescence spectrum which have been subsequently identified as due to $\ce{Cs_2UO_2(NO_3)_4}$.

**Rubidium uranyl nitrate** $\ce{RbUO_2(NO_3)_3}$: The salt was prepared and crystals obtained by following an exactly similar procedure as that for $\ce{CsUO_2(NO_3)_3}$.

**Potassium uranyl nitrate** $\ce{KUO_2(NO_3)_3}$: The preparation of $\ce{KUO_2(NO_3)_3}$ has been described by Nichols and Bowes. The preparation of the salt by dissolving stoichiometric amounts of $\ce{KNO_3}$ and $\ce{UO_2(NO_3)_2.6H_2O}$ in distilled water showed $\ce{K_2UO_2(NO_3)_4}$ bands in fluorescence with much more intensity. The microcrystals of $\ce{KUO_2(NO_3)_3}$ however were obtained by evaporating the
solution in nitric acid, on water bath. The formation of $\text{KUO}_2(\text{NO}_3)_3$ at a high temperature ($76^\circ\text{C}$) is in accordance with the observation by Dieke and Duncan\(^3\).

**Di-caesium uranyl nitrate** $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$: In the course of our investigations of the fluorescence spectrum of $\text{CsUO}_2(\text{NO}_3)_3$ irradiated by reactor radiations, it was found necessary to study the fluorescence spectrum of $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$.

Nichols and Howes\(^2\) describe the methods of preparation of $(\text{NH}_4)_2\text{UO}_2(\text{NO}_3)_4$ and $\text{K}_2\text{UO}_2(\text{NO}_3)_4$. Dieke and Duncan\(^3\) describe the preparation of $\text{Rb}_2\text{UO}_2(\text{NO}_3)_4$. However it seems attempts to synthesize $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$ were not successful\(^3\).

We have been successful in preparing this salt\(^4\). Attempts to grow $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$ crystals at room temperature with varied Cs/U ratios, only resulted in the formation mainly of $\text{CsUO}_2(\text{NO}_3)_3$ and a small amount of $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$. After several trials however, the following method was found to be satisfactory.

Caesium nitrate (BDH Analar) and uranyl nitrate hexahydrate were mixed together always taking care to see that a little excess of CsNO\(_3\) over that required to give di-caesium salt, is present. (This is necessary to avoid formation of small amounts of CsUO\(_2\)(NO\(_3\))\(_3\).) The
mixture is dissolved in dilute nitric acid and the solution is slowly evaporated to dryness on water bath. The salt is now dissolved again in distilled water. The evaporation and dissolution are carried out four or five times when the pH of the solution is '3'. The saturated solution is quickly cooled to 26°C (room temperature) and immediately transferred to a desiccator maintained at about 10°C in the refrigerator. Fused CaCl₂ is used as the desiccant. Yellowish green crystals of Cs₂UO₂(NO₃)₄ start appearing after about a week. With uranyl nitrate trihydrate as the starting material it is found that the number of dissolutions and evaporations can be reduced. Slight increase in the ratio of Cs/U content favours the formation of Cs₂UO₂(NO₃)₄ and reduces the chance of formation of CsUO₂(NO₃)₃. The crystals obtained by slow evaporation at 10°C are about a millimeter in cross section.

Microcrystalline powder of the dicaesium salt was obtained as follows. Stoichiometric amounts of CsNO₃ and UO₂(NO₃)₂·3H₂O are dissolved in distilled water and evaporated to dryness of water bath. The residue on dissolution and evaporation on a sand bath leaves a microcrystalline substance. The identity of this powder with the crystals grown at 10°C by slow
evaporation, is established by identical fluorescence spectra.

That the formation of $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$ is favoured under the condition mentioned above can be understood by the work of Yakimov et al.\textsuperscript{5} The Russian authors\textsuperscript{5} have studied the interaction of the components in the system CsNO$_3$-$\text{UO}_2(\text{NO}_3)_2$-$\text{H}_2\text{O}$. They have determined the composition in the solid phase in this system between the temperatures 0°-25°C. The solid phase of the system CsNO$_3$-$\text{UO}_2(\text{NO}_3)_2$-$\text{H}_2\text{O}$ was characterised by the existence of mixture of $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$ and $\text{CsUO}_2(\text{NO}_3)_3$ in the molar ratio of $\text{UO}_2(\text{NO}_3)_2$ : CsNO$_3$ :: 3.99-2.97 to 5.00-1.76 in systems containing 94% water at 25°C and only $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$ existed with the above molar ratio at 0°C. These complexes are formed by endothermic reactions. In the present case $\text{UO}_2(\text{NO}_3)_2$ : CsNO$_3$ :: 2.5 : 1 with solution in distilled water, crystallised at a low temperature of 10°C favours the formation of $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$.

That the chemical compound formed has a composition $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$ and not a mixture of individual components CsNO$_3$, $\text{UO}_2(\text{NO}_3)_2$-$\text{H}_2\text{O}$ or $\text{CsUO}_2(\text{NO}_3)_3$, is supported by the following observations.

1. Chemical analysis of the crystals isolated from the
TABLE 3
CHEMICAL ANALYSIS OF Cs$_2$UO$_2$(NO$_3$)$_4$

<table>
<thead>
<tr>
<th>Element</th>
<th>Value from expected chemical analysis</th>
<th>Value according to formula Cs$_2$UO$_2$(NO$_3$)$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td>33.6%</td>
<td>33.38%</td>
</tr>
<tr>
<td>U</td>
<td>29.2%</td>
<td>30.38%</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>Nil</td>
<td>Nil</td>
</tr>
</tbody>
</table>
mother liquor in different independent preparations gives the following results (Table 3) which is in conformity with the formula \( \text{Cs}_2\text{UO}_2(\text{NO}_3)_4 \). The fact that there is no water of crystallisation clearly shows absence of any free uranyl nitrate hexahydrate.

2. The fluorescence spectrum of the salt at 77°K has been reported\(^6\) and analysed in detail by us\(^7\). The analysis of the bands clearly indicates the similarity of the fluorescence spectrum with those of corresponding \( \text{Rb}_2\text{UO}_2(\text{NO}_3)_4 \) and \( \text{K}_2\text{UO}_2(\text{NO}_3)_4 \) salts. There is no trace of bands which arise due to fluorescence of either \( \text{CsUO}_2(\text{NO}_3)_3 \) or \( \text{UO}_2(\text{NO}_3)_2\cdot6\text{H}_2\text{O} \) in this preparation.

3. The infrared absorption spectra of \( \text{Cs}_2\text{UO}_2(\text{NO}_3)_4 \), \( \text{CsUO}_2(\text{NO}_3)_3 \) and \( \text{CsNO}_3 \) have been recorded in the range of 1200 cm\(^{-1}\) - 1600 cm\(^{-1}\) (Figure 2). \( \text{CsNO}_3 \) shows a broad absorption at \( \approx 1350 \text{ cm}\(^{-1}\) due to \( \nu_2 \) antisymmetric vibration of \( \text{NO}_3^- \) ion while the salts \( \text{CsUO}_2(\text{NO}_3)_3 \) and \( \text{Cs}_2\text{UO}_2(\text{NO}_3)_4 \) do not show any absorption at \( \approx 1350 \text{ cm}\(^{-1}\) indicating thereby, the absence of free \( \text{CsNO}_3 \).

Instead, in this region \( \text{CsUO}_2(\text{NO}_3)_3 \) shows an absorption band at 1270 cm\(^{-1}\) while \( \text{Cs}_2\text{UO}_2(\text{NO}_3)_4 \) shows absorption bands at 1279 cm\(^{-1}\), 1300 cm\(^{-1}\). The infrared absorption pattern in \( \text{Cs}_2\text{UO}_2(\text{NO}_3)_4 \) is thus different from that of \( \text{CsUO}_2(\text{NO}_3)_3 \). This therefore shows in the present case
the salt is not just a mixture of CsUO₂(NO₃)₃ and CeNO₃. The infrared absorption spectra of Rb₂UO₂(NO₃)₄ and K₂UO₂(NO₃)₄ have also been recorded and it is found that the infrared absorption in these two cases are similar to that of Cs₂UO₂(NO₃)₄ (Chapter 4).

4. X-ray powder diffraction pattern of Cs₂UO₂(NO₃)₄ has been recorded. This shows the similarity of the powder patterns of Cs₂UO₂(NO₃)₄ and that of Rb₂UO₂(NO₃)₄ (Saritzky and Walker). Table 4 shows that these patterns are different from that of CsUO₂(NO₃)₃.

Dirubidium uranyl nitrate \( \text{Rb}_2\text{UO}_2\text{(NO}_3\text{)}_4 \) : Deke and Duncan have described the formation of \( \text{Rb}_2\text{UO}_2\text{(NO}_3\text{)}_4 \). A saturated solution for \( \text{RbUO}_2\text{(NO}_3\text{)}_3 \) was allowed to crystallize at 6°C. Crystals having different habit from those of \( \text{RbUO}_2\text{(NO}_3\text{)}_3 \) appeared. First the new crystals were thought to be a dimorph of the \( \text{RbUO}_2\text{(NO}_3\text{)}_3 \) salt and thus it was called the low temperature form of \( \text{RbUO}_2\text{(NO}_3\text{)}_3 \). Later on, after careful analysis, it was ascertained that the so called low temperature form of \( \text{RbUO}_2\text{(NO}_3\text{)}_3 \) was nothing but dirubidium salt \( \text{Rb}_2\text{UO}_2\text{(NO}_3\text{)}_4 \). They could obtain very few crystals of \( \text{Rb}_2\text{UO}_2\text{(NO}_3\text{)}_4 \).

The multicrystals of \( \text{Rb}_2\text{UO}_2\text{(NO}_3\text{)}_4 \) were successfully grown in our laboratory by adopting a method similar to...
## TABLE 4

X-RAY POWDER DIFFRACTION DATA

<table>
<thead>
<tr>
<th></th>
<th>$\text{Hg}_2\text{UO}_2(\text{NO}_3)_4$</th>
<th>$\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$</th>
<th>$\text{Cs}_2\text{UO}_2(\text{NO}_3)_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>'d' (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intensity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.15</td>
<td>100</td>
<td>4.21</td>
<td>4.87</td>
</tr>
<tr>
<td>3.14</td>
<td>80</td>
<td>3.21</td>
<td>4.27</td>
</tr>
<tr>
<td>3.60</td>
<td>60</td>
<td>3.68</td>
<td>2.65</td>
</tr>
<tr>
<td>6.10</td>
<td>55</td>
<td>5.47</td>
<td>2.82</td>
</tr>
<tr>
<td>2.42</td>
<td>55</td>
<td>2.47</td>
<td>2.45</td>
</tr>
</tbody>
</table>

*Data from Saritzky, E and Walker, D.L.*

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*Note: The table provides X-ray powder diffraction data for three compounds, each listed with their respective 'd' values and intensities.*
that for $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$. Again use of $\text{UO}_2(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ and higher $\text{Rb}/\text{U}$ ratio favors the process of formation of $\text{Rb}_2\text{UO}_2(\text{NO}_3)_4$. The multiorystals of $\text{Rb}_2\text{UO}_2(\text{NO}_3)_4$ were grown at $10^\circ \text{C}$ in a refrigerator by slow evaporation of saturated solutions containing stoichiometric amounts of $\text{RbNO}_3$ and $\text{UO}_2(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$. The identity of the salt was again established by comparing the fluorescence spectrum with those obtained by Dieke and Duncan.

Dipotassium uranyl nitrate \(\text{K}_2\text{UO}_2(\text{NO}_3)_4\) : The preparation of $\text{K}_2\text{UO}_2(\text{NO}_3)_4$ has been described by Nichols and Howes, Seaborg. The salt has been prepared by Nichols and Howes by evaporation at temperature higher than $20^\circ \text{C}$ of a slightly acidic solution. Seaborg and Katz also describe the preparation of the salt at low temperature. It has been possible for us to synthesize $\text{K}_2\text{UO}_2(\text{NO}_3)_4$ at room temperature ($26^\circ \text{C}$).

The preparation of low temperature potassium salt $\text{K}_3\text{UO}_2(\text{NO}_3)_5$ has been described in Appendix I of part II of the thesis.

2. Spectrographic procedure.
   (a) Fluorescence spectra : Figure 3 shows the optical arrangement for recording the fluorescence spectrum.
   A 1600 watt high pressure Xenon lamp is used as a source
1) $\text{CsNO}_3$
2) $\text{Cs}_2\text{UO}_2(\text{NO}_3)_4$
3) $\text{Cs UO}_2(\text{NO}_3)_3$
FIG. 3
OPTICAL ARRANGEMENT FOR FLUORESCENCE STUDIES

XENON ARC LAMPS

CONDENSING LENSES

FOCUSING LENS

SAMPLE

TUNGSTEN FILAMENT LAMP

TO SPECTROGRAPH
of ultraviolet radiations. The radiations from xenon lamp are focussed on to the sample, through the Corning 9863 filter. This filter transmits wavelengths below 4200 Å and cuts off visible region between 4200 Å and 6000 Å which thus is useful in exciting fluorescence without interfering with the fluorescence spectrum.

The fluorescent radiation from the sample is now focussed onto the slit of the 3 prism (glass) Steinheil spectrograph. The sample was in a sealed vycor tube, immersed in a dewar flask containing liquid nitrogen. The lower portion of dewar flask was narrow and unsilvered and the sample was usually suspended in this portion. The narrow portion of the dewar reduces the loss of light due to scattering by bubbling liquid nitrogen surrounding the sample.

Spectrograph: For the purpose of recording the fluorescence spectra in the present case a 3 prism (glass) Steinheil spectrograph was used. Figure 4 shows the schematic diagram of the spectrograph. There are three different optics of the spectrograph which can be used for different purposes.

(i) Short focal length optics: In this case the focal length of the collimating lens is $f = 195 \text{ mm}$, and that of camera lens is $f = 255 \text{ mm}$. This setting has a dispersion of $45 \text{ Å/mm}$ and $14 \text{ Å/mm}$ at $5000 \text{ Å}$ and $4000 \text{ Å}$.
respectively. This setting is useful for Raman work or studies in which high light gathering power rather than high dispersion is desirable.

(ii) Medium focal length optics: In this setting the focal length of collimating lens used is 650 mm. and that of camera lens is 640 mm. This medium setting combines the advantages of both adequate dispersion and high aperture ratio. This medium setting was used for almost all the work on the fluorescence spectra of uranyl salts. The region covered for one particular setting of camera bracket adjustment was between 4200 Å to 7000 Å. This region was very much suitable for the present work because for almost all the uranyl salts the fluorescence spectrum lies in the region from 4700 Å to 7000 Å. The setting has a linear dispersion of 17 Å/mm. and 6.7 Å/mm. at 5000 Å and 4000 Å respectively. Usually panchromatic plates were used for photographing the fluorescence spectra. For many salts an exposure of about half an hour was sufficient to record the entire fluorescence spectrum including weak lines.

(iii) Long focal length optics: This has a collimating lens of f = 650 mm. and a camera lens of f = 1600 mm. giving linear dispersions of 7 Å/mm. and 2.6 Å/mm. at 5000 Å and 4000 Å respectively. This has lesser aperture
ratio $i/f = 1/25$. This is useful for high dispersion work. This setting was used in the present case for recording the fluorescence spectrum of CsUO$_2$(NO$_3$)$_3$.

In case of fluorescence spectra of uranyl salts at $77^\circ K$, the higher dispersion does not have any additional advantage because the fluorescence bands are already broad enough.

The advantage of using the spectrograph lies in the fact that it is easily convertible from one setting to another depending upon the requirements of the experiments.

(b) Low temperatures: Almost all the fluorescence spectra of the uranyl salts were obtained at liquid nitrogen temperature ($77^\circ K$). The temperature was easily obtained by immersing the sample in a dewar containing liquid nitrogen. Many times the bubbling of the liquid nitrogen introduced loss of light. The bubbling was reduced to some extent by covering the open end of the dewar flask by cotton wool. The turbidity of the liquid air reduced the intensity of light. To avoid this, (i) the liquid nitrogen was filtered through cotton wool to give clear liquid and (ii) the dewar flask was cleaned with tissue paper from inside to remove traces of moisture which otherwise contribute to turbidity of liquid nitrogen.
Fluorescence spectrum of CsUO$_2$(NO$_3$)$_3$ was also taken near the temperature of solid CO$_2$ (196°K). This was achieved by filling the narrow portion of the dewar flask by aether and the other portion of dewar with dry ice.

(c) Measurement: The spectra were measured on an Abbe comparator using iron arc lines as standard. The cross wire was focussed on the point of maximum density. Many bands in the fluorescence of UO$_2^{++}$ are not sharp even at the temperature of liquid nitrogen (77°K). The bands involving antisymmetric frequency (B) of UO$_2^{++}$ ion in particular, especially in monoalkali uranyl nitrate salts appear to be asymmetrically broadened towards longer wavelength side. Therefore the values obtained in the present case vary slightly from those of Dieke and Duncan, who have studied the spectrum at 20°K. Also the accuracy of measurement is different for different bands, being ± 0.1 Å for sharp bands and about ± 1 Å for intense broad bands. The data recorded represent mean values from two different spectrograms. In case of dialkali uranyl nitrate salts, many bands including those belonging to vibrations of UO$_2^{++}$ ion, are sharp. Therefore the accuracy of measurement in these cases is better than those in monoalkali uranyl nitrate salts.

(d) Infrared absorption: Infrared absorption spectra were obtained on a Perkin Elmer model-21 double beam
spectrophotometer. The double beam method gives the infrared absorption spectra free from atmospheric absorption peaks since these absorptions cancel out in the two beams.

Infrared absorption of the alkali uranyl nitrate double salts were recorded in the range of 650 cm⁻¹ to 2000 cm⁻¹ using NaCl prism. This range covered almost all expected fundamental vibration frequencies of UO₂⁺ and ONO₂⁻ ions.

The spectrophotometer was calibrated in different regions using standard absorption spectra of NH₃, CO₂ and H₂O. For recording the absorption spectrum slit-width, gain and response of the instrument are adjusted to get optimum resolution without undue noise.

Sample preparation: To record the absorption spectra of the samples in the solid state two methods are most generally used, (i) KBr pellet method and (ii) the mull method. In the first method many discrepancies occur due to the formation of solid solutions because of high pressures. The exchange of anions particularly in the presence of moisture also introduces anomalies. The pellet method has however certain advantages. For example the pellet can be preserved for a long time and the infrared absorption spectrum can be repeatedly mapped. But the anomalies outweigh these advantages.
particularly in the study of salts containing acidic radicals.

The mull method has been recognised as a generally accepted method for the study of solid state infrared absorption. The salt to be studied is finely ground and mixed with suitable medium in which it gets itself suspended. The mull so formed is held in between two transparent windows and the absorption recorded.

In the present case, as is common with many infrared absorption studies in the region 650 cm$^{-1}$ to 2000 cm$^{-1}$, we have chosen paraffin oil as mulling agent. The paraffin oil has strong absorption bands in the region between 1300 cm$^{-1}$ and 1500 cm$^{-1}$. To cover this region therefore, another organic medium viz., 'Hexachlorobutadiene' which does not have any strong absorption band between 1300 cm$^{-1}$ to 1500 cm$^{-1}$ is used (Figure 5).

The sample in the form of mull was held in between two sodium chloride windows and the absorption spectra were recorded. Care was taken to remove excess nitric acid from the salt which otherwise reacts with sodium chloride windows. The suspension in paraffin oil was comparatively easy to obtain as it is more viscous compared to hexachlorobutadiene. Care was also taken to avoid moisture during the process of
FIG. 5

HEXACHLOROBUTADIENE

% ABSORPTION

1200 1300 1400 1500 Cm⁻¹

0 50
Fluorescence Spectrum of CsUO₂(NO₃)₃ at 196°C
FIG 8(b).
grinding which otherwise introduces OH bands in the region at about 1600 cm\(^{-1}\) and interferes with the bands of interest. Though the smallest division on the recorded chart represents 2.5 cm\(^{-1}\), the accuracy of determination of absorption peaks for very sharp bands is as good as \(\pm 1\) cm\(^{-1}\).
REFERENCES


