Chapter III

MONOALKALI URANYL NITRATE SALTS
1. Caesium uranyl nitrate.

(a) Fluorescence spectrum at $77^\circ$K.

Cs$_2$UO$_2$(NO$_3$)$_3$ is assumed to be isomorphous with Rb$_2$UO$_2$(NO$_3$)$_3$, whose X-ray structural analysis is known in detail. This salt crystallises in rhombohedral division of the hexagonal system. Dieke and Duncan have studied the fluorescence spectrum of this salt at $20^\circ$K extensively. They used uranyl salts enriched in $^{235}$U, $^{18}$O and $^{15}$N to ascertain the nature of the vibrations involved. The fluorescence spectrum of this salt at $77^\circ$K has not been studied. To have a useful comparison with the other salts whose fluorescence spectra have been recorded at $77^\circ$K in the present investigations, it was thought necessary to investigate the fluorescence spectrum of this salt at $77^\circ$K.

The broad features of the fluorescence spectrum remain the same in going from $20^\circ$K to $77^\circ$K, in the case of Cs$_2$UO$_2$(NO$_3$)$_3$ (Figure 6). The fluorescence spectrum at $77^\circ$K is shifted towards long wave length side by $\sim 10$ cm$^{-1}$ from that at $20^\circ$K. The spectrum at $77^\circ$K contains less number of bands compared to that at $20^\circ$K. Many bands which remain unobserved at $77^\circ$K, belong to the lattice vibrations; of magnitudes between $20$ cm$^{-1}$ to $300$ cm$^{-1}$. This is owing to the fact that, at $77^\circ$K many of these already broad bands get broadened still and
overlap on the neighbouring bands. Almost all intense bands recorded at 20°K (Dieke and Duncan)\textsuperscript{1} have their corresponding bands in the fluorescence spectrum at 77°K, though shifted in position towards the longer wave side.

The fluorescence spectrum of CsUO\textsubscript{2}(NO\textsubscript{3})\textsubscript{3} at 77°K is shown in Figure 6. All the observed bands have been listed in Table 5 with assignments.

The intense band on the short wave limit of the fluorescence spectrum obviously represents the resonance band. This band also occurs on the long wave limit in absorption (Dieke and Duncan)\textsuperscript{1}. Thus the band at 21080 cm\textsuperscript{-1} in the fluorescence spectrum of this salt at 77°K represents a transition from vibrationless excited electronic state to the vibrationless ground electronic state.

The repetition frequency of the patterns in the fluorescence spectrum is known to be the totally symmetric vibration $\nu_1$ of $\text{UO}_2^{4+}$ (A). This has been ascertained by $^{235}\text{U}$ substitution by Dieke and Duncan\textsuperscript{1} which does not affect the symmetric vibration but only the antisymmetric one. Thus, the repetition frequency of 884 cm\textsuperscript{-1} in the fluorescence spectrum of CsUO\textsubscript{2}(NO\textsubscript{3})\textsubscript{3} is taken as the totally symmetric vibration of $\text{UO}_2^{4+}$. 
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<th>( \Delta \nu \text{from } R-nA ) cm(^{-1} )</th>
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* Notation from Dieke and Duncan¹
sh = sharp  b = broad
This vibration, which is represented by 'A' bands, occurs in several quanta. These bands have been designated as R-nA in Table 5, where R is the wave number of the resonance band, A the magnitude of the symmetric vibration and n an integer having values 1, 2, 3... In the fluorescence spectrum at 77°K four quanta of 'A' are observed.

The antisymmetric vibration ($\nu_2$) of UO$_2^{++}$ (B has been identified by Dieke and Duncan by the presence of $^{235}$U isotope shift of the expected order in the fluorescence spectrum of CsUO$_2$(NO$_3$)$_3$ at 20°K. The approximate value of 'B', the frequency of antisymmetric vibration of UO$_2^{++}$ can also be approximately calculated, knowing the value 'A', the symmetric vibration frequency by the relation

$$\frac{B}{A} = \sqrt{\frac{m + 2m}{M}} = 1.065$$

where m is the mass of the oxygen atom and M the mass of uranium atom. The above relation is based on the simplified linear model of UO$_2^{++}$. In the fluorescence spectrum the bands involving the antisymmetric vibration frequency (B) are the most intense. With all the above considerations and most of all, comparison with the already available data on the fluorescence spectrum of CsUO$_2$(NO$_3$)$_3$ at 20°K (Dieke and Duncan)$^1$, the band at
959.7 cm\(^{-1}\) on the longer wave lengths of the resonance band is assigned as the 'B' band. Similar corresponding bands in the subsequent groups belong to the series R-\(n\)A-B; \(n = 0, 1, 2\) etc., (Table 5). Because of the central heavy uranium atom in the UO\(_2\)\(^{2+}\) ion, the magnitude of the bending frequency is expected to be rather markedly low. Dieke and Duncan\(^1\) have associated the three intense bands at 209 cm\(^{-1}\), 213 cm\(^{-1}\) and 222 cm\(^{-1}\) in the fluorescence spectra at 20\(^\circ\)K to the bending vibration 'C'. In the fluorescence spectrum of CsUO\(_2\)(NO\(_3\))\(_3\) at 77\(^\circ\)K a band at 212.6 cm\(^{-1}\) is very intense and this has been taken as the 'C' band. Actually the doubly degenerate vibration 'C' is expected to split and show up as two components only. It appears that all the 'C' vibration assignments need further confirmation. The above values assigned to 'C' frequency are all of the right magnitude as can be seen from a comparison with data obtained from the Raman spectrum of UO\(_2\)\(^{2+}\) ion in solution\(^2\). Raman spectra of uranyl compounds in solutions have been obtained by Conn and Wu\(^3\) and Satyanarayana\(^2\). Two frequencies, one at 860 cm\(^{-1}\) and the other at 210 cm\(^{-1}\) were observed. The former obviously belongs to symmetric (A) vibration of UO\(_2\)\(^{2+}\) and the latter to the bending (C) vibration. Bands involving the 'C' vibration are designated as R-\(n\)A-C; \(n = 0, 1, 2\) etc., (Table 5).
Apart from the $\text{UO}_2^{2+}$ vibrations, nitrate vibrations (according to the present analysis the nitrate $\text{O}_2^-$) are also observed in the fluorescence spectrum of $\text{CsUO}_2(\text{NO}_3)_3$. This has been confirmed by $^{15}\text{N}$ isotope shift by Dieke and Duncan. As in the case of the $\text{UO}_2^{2+}$ vibrations, frequencies of the nitrate vibrations are not expected to undergo any significant changes in going from 20°K to 77°K and it has, in fact, been found so. With the help of assignments already made for $\text{CsUO}_2(\text{NO}_3)_3$ fluorescence at 20°K, we have identified and assigned various nitrate frequencies in the fluorescence spectrum at 77°K. These have been designated as R-nA-D, R-nA-E, R-nA-F, R-nA-G, R-nA-I and R-nA-K (Table 5). All these frequencies were attributed to the $\text{NO}_3^-$ ion by Dieke and Duncan. However, they are now believed to be due to the $\text{ONO}_2^-$ ion formed when one of the oxygen atoms of $\text{NO}_3^-$ ion co-ordinates with the central 'U' atom. The original $D_{3h}$ symmetry is then reduced to a lower symmetry, $C_{2v}$. This lowering of the symmetry brings about splitting of the degenerate vibrations $\nu_3$ and $\nu_4$ of $\text{NO}_3^-$ group and the $\text{ONO}_2^-$ radical has all the six fundamental vibrations nondegenerate. The significance of $D,E,F,G,I,J$ and $K$ vibrations in terms of fundamental vibrations of $\text{ONO}_2^-$ is explained in Table 6. The frequency 'H' (708 cm$^{-1}$) observed by Dieke and Duncan in the fluorescence spectrum of $\text{CsUO}_2(\text{NO}_3)_3$
### TABLE 6

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<td><strong>Resonance band</strong></td>
<td>$\gamma_9\text{ONO}_2^-$</td>
<td>$\gamma_9\text{ONO}_2^-$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---
at 20°K and attributed by them to the nitrate group has not been observed in the fluorescence spectrum at 77°K.

In the fluorescence spectrum at 20°K the bands involving the nitrate frequencies H, G, D, F are reported to have almost equal intensities. It is thus difficult to understand why 'H' frequency escaped observation in the fluorescence spectrum at 77°K while the other frequencies G, D and F are observed with moderate intensity. In the assignment of the nitrate frequencies, especially of 'I' and 'K' vibrations of ONO$_2^-$, use is made of the infrared absorption data obtained in the present investigations. The vibrational frequencies of 1023 cm$^{-1}$ and 1025 cm$^{-1}$ observed in the fluorescence spectrum at 20°K by Dieke and Duncan$^1$ and first recognised as ν$_{1}$ of ONO$_2^-$ by Gatehouse and Comyns$^5$, have not been detected in the fluorescence spectrum at 77°K. Probably they are too weak. Bands separated by 144 cm$^{-1}$ from R-nA bands can be supposed as involving ν$_{1}$ vibration of ONO$_2^-$. The broad nature of the bands makes one attribute them rather to the lattice vibrations. Some bands have been designated as R-nA-B-E etc., i.e., as involving two UO$_{2}^{++}$ and one nitrate vibrations. Such bands have also been observed in the spectrum at 20°K by Dieke and Duncan$^1$, who confirmed their assignment by $^{15}$N and $^{235}$U substitution.
The low frequencies observed in the fluorescence spectrum in the range of 40 to 300 cm\(^{-1}\) can be mainly attributed to lattice vibrations (Table 5). These bands are usually broad. Some low frequency lattice vibrations occur as antistokes bands also. The magnitudes of the lattice vibrations are expected to remain nearly the same both in the ground as well as in the excited state of the ion.

In the group of antistokes bands in the fluorescence spectrum at 77\(^{\circ}\)K, there is a band at an interval of 186 cm\(^{-1}\) from the resonance line (Table 5). This frequency does not appear to be a lattice frequency because no frequency of this magnitude is observed on the longer wave side of the resonance band. This can be another electronic level say \(G(0,0)\) above the lowest observed excited state, namely \(F(00)\), in which case it is natural to expect transitions from this level \(G(0,0)\) to the various vibrational levels of the ground state. Such antistokes bands have in fact been observed earlier, but only associated with R-nA transitions. These have been designated as \(C + R - nA; n = 0,1,2\) etc. These antistokes bands are understandably not observed at 20\(^{\circ}\)K for this salt\(^1\). This can be understood on the basis of the Boltzmann distribution. The intensity of these antistokes bands is temperature dependent - the
TABLE 7

FLUORESCENCE SPECTRUM OF CsUO$_2$(NO$_3$)$_3$
AT 196 K

<table>
<thead>
<tr>
<th>λ in Å</th>
<th>Visual intensity*</th>
<th>λ (vac) cm$^{-1}$</th>
<th>Δλ cm$^{-1}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>4718</td>
<td>4</td>
<td>21189</td>
<td>162</td>
<td>C+R</td>
</tr>
<tr>
<td>4754</td>
<td>8</td>
<td>21027</td>
<td>0</td>
<td>R</td>
</tr>
<tr>
<td>4924</td>
<td>5</td>
<td>20303</td>
<td>156</td>
<td>C+R$-A$</td>
</tr>
<tr>
<td>4962</td>
<td>10</td>
<td>20147</td>
<td>880</td>
<td>B$-A$</td>
</tr>
<tr>
<td>4980</td>
<td>10</td>
<td>20075</td>
<td>952</td>
<td>B$-B$</td>
</tr>
<tr>
<td>5146</td>
<td>5</td>
<td>19427</td>
<td>154</td>
<td>C+R$-2A$</td>
</tr>
<tr>
<td>5187</td>
<td>10</td>
<td>19273</td>
<td>874</td>
<td>B$-2A$</td>
</tr>
<tr>
<td>5209</td>
<td>10</td>
<td>19192</td>
<td>955</td>
<td>B$-A-B$</td>
</tr>
<tr>
<td>5383</td>
<td>3</td>
<td>18572</td>
<td>175</td>
<td>C+R$-3A$</td>
</tr>
<tr>
<td>5434</td>
<td>8</td>
<td>18397</td>
<td>876</td>
<td>B$-3A$</td>
</tr>
<tr>
<td>5704</td>
<td>4</td>
<td>17527</td>
<td>870</td>
<td>B$-4A$</td>
</tr>
</tbody>
</table>

♦All bands are very broad.

*All bands are very broad.
Intensity increasing with the temperature as can be seen from the fluorescence spectrum of CsUO$_2$(NO$_3$)$_3$ taken at liquid air and solid CO$_2$ temperatures (Figure 7). The bands observed therein are tabulated in Table 7 with the assignments. The nature of the level G(0,0) giving rise to the antistokes bands is not clearly known. There are two possibilities: (1) The G(0,0) level may be a pure electronic state, in which case, it is not clear why it does not show antistokes bands of the type R -nA-B (in addition to those of the type R -nA). (ii) The level can belong to one of the UO$_2^{2+}$ vibrations in the excited state. From the magnitude of the frequency, it can only be the bending (A$_2$) or C vibration of UO$_2^{2+}$ in the excited state. The symmetric frequency 'A' of UO$_2^{2+}$ in the excited state namely 734 cm$^{-1}$ (observed in absorption) bears a ratio of 3.9 to this 186 cm$^{-1}$ frequency. The A/C ratio in the ground state is 4.1, which is close to that in the excited state.

In the fluorescence spectrum there are some additional bands which are now recognised as belonging to Cs$_2$UO$_2$(NO$_3$)$_4$. These have been indicated in the Table No.5. The occurrence of Cs$_2$UO$_2$(NO$_3$)$_4$ impurity in CsUO$_2$(NO$_3$)$_3$ depends upon the way, the salt is synthesised. This has been discussed in Chapter 2.
(b) **Infrared absorption spectrum:** In the present investigation, the infrared absorption spectrum of CsUO$_2$(NO$_3$)$_3$ has been recorded in the range of 650 cm$^{-1}$ to 2000 cm$^{-1}$. The experimental details have been described in Chapter 2. The absorption bands observed in the present investigations are given in Table 8. Figure 8 (a) and Figure 8 (b) show the infrared absorption spectra of this salt in the regions 650 to 1000 cm$^{-1}$ and 1200 to 1600 cm$^{-1}$ respectively. In Table 8 the infrared absorption spectral data of Lipovskii and Khuzina$^7$ have also been included. The assignments to the various bands is based on the data available for RbUO$_2$(NO$_3$)$_3$ (Gatehouse and Comyns)$^5$. The corresponding frequencies observed in the fluorescence spectrum are also tabulated. From Table 8 it can be seen that there is a very close correspondence between the infrared absorption bands observed in the present investigations and the bands observed in the fluorescence at 77$^\circ$K. The ONO$_2^-$ radical belonging to the C$_{2v}$ symmetry is expected to have six fundamental vibrations$^4$, all of which are infrared active. The only vibration belonging to UO$_2^{++}$ (asymmetric vibration) in this range occurs at 960 cm$^{-1}$, as expected. The bending vibration of UO$_2^{++}$ (the $\delta_1 \propto C$ vibration) which is expected to occur at $\sim 200$ cm$^{-1}$ is out of this range. All the other frequencies are due to ONO$_2^-$ vibrations.
### TABLE 8

**INFRARED ABSORPTION SPECTRUM OF CsUO$_2$(NO$_3$)$_3$**

650 cm$^{-1}$ - 2000 cm$^{-1}$

<table>
<thead>
<tr>
<th>$\nu$ cm$^{-1}$</th>
<th>Nature</th>
<th>Assignment*</th>
<th>Lipovskii &amp; Khuzina$^7$ cm$^{-1}$</th>
<th>Fluorescence at 7°C K</th>
</tr>
</thead>
<tbody>
<tr>
<td>715</td>
<td>w.sh</td>
<td>$\gamma$ONO$_2^-$</td>
<td>710</td>
<td>-</td>
</tr>
<tr>
<td>743</td>
<td>v.s.sh</td>
<td>$\gamma$ONO$_2^-$</td>
<td>756</td>
<td>739.5</td>
</tr>
<tr>
<td>809</td>
<td>s.sh</td>
<td>$\gamma$ONO$_2^-$</td>
<td>803</td>
<td>804.7</td>
</tr>
<tr>
<td>960</td>
<td>v.s.b.</td>
<td>$\gamma$UO$_2^{++}$</td>
<td>956</td>
<td>939.7</td>
</tr>
<tr>
<td>1025</td>
<td>v.s.sh</td>
<td>$\gamma$ONO$_2^-$</td>
<td>1016</td>
<td>-</td>
</tr>
<tr>
<td>1270</td>
<td>v.s.b.</td>
<td>$\gamma$ONO$_2^-$</td>
<td>1270</td>
<td>127.7.4</td>
</tr>
<tr>
<td>1508</td>
<td>s.b</td>
<td></td>
<td>1501</td>
<td>-</td>
</tr>
<tr>
<td>1516</td>
<td>s.b</td>
<td></td>
<td>1517</td>
<td>15.9.9</td>
</tr>
<tr>
<td>1531</td>
<td>s.b</td>
<td></td>
<td>1536</td>
<td>-</td>
</tr>
<tr>
<td>1540</td>
<td>s.b</td>
<td></td>
<td>1552</td>
<td>-</td>
</tr>
<tr>
<td>1606</td>
<td>s.sh</td>
<td>$2\gamma$ONO$_2^-$</td>
<td>1605</td>
<td>-</td>
</tr>
<tr>
<td>1726</td>
<td>w.b</td>
<td>$2\gamma$ONO$_2^-$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1759</td>
<td>w.b</td>
<td>$2\gamma$ONO$_2^-$</td>
<td>1784</td>
<td>-</td>
</tr>
<tr>
<td>1828</td>
<td>v.w.b.</td>
<td>$2\gamma$ONO$_2^-$</td>
<td>1828</td>
<td>-</td>
</tr>
</tbody>
</table>

w = weak  sh = sharp  s = strong  b = broad
v.w = very weak  v.s = very strong

*Notation from Gatehouse and Comyns$^5$
The infrared data were particularly useful in identifying some of the nitrate vibrations, especially at $1270 \text{ cm}^{-1}$ and $1503 \text{ cm}^{-1}$ vibrations, in the fluorescence spectrum.

2. Rubidium uranyl nitrate.

(a) Fluorescence spectrum at 77°K.

Rubidium uranyl nitrate is known to crystallise in the rhombohedral form of the hexagonal system\textsuperscript{1}. It is one of the few uranyl salts whose X-ray structural analysis has been carried out in detail. Its fluorescence spectrum however is not known in detail. This is reverse of the situation obtained for CsUO$_2$(NO$_3$)$_3$ whose fluorescence spectrum is well known but not its X-ray structural analysis. A detailed study of the fluorescence spectrum of RbUO$_2$(NO$_3$)$_3$ was therefore felt necessary.

Dieke and Duncan\textsuperscript{1} gave a list of bands observed in fluorescence both at 20°K and 77°K. They have identified only the symmetric (A) and the antisymmetric (B) vibrational frequencies of UO$_2^{2+}$ observed in the fluorescence spectrum of the salt at 20°K. In order to facilitate a more detailed analysis, we have redecoded the fluorescence spectrum at 77°K (Figure 9) as is done for other uranyl salts under study. The wave lengths of the various bands observed in the present investigation are almost identical with those listed by Dieke and Duncan\textsuperscript{1}. 
So in Table 9 the wave numbers of the bands listed by Dieke and Duncan have been given. These bands are now analysed in detail in analogy with the fluorescence spectrum analysis of CsUO$_2$(NO$_3$)$_3$ and with the help of the infrared absorption data given by Gatehouse and Comyns$^5$. The relative intensity values included in the Table No.9 are taken from the spectrum obtained in the present investigation (Figure 9).

The fluorescence spectrum of RbUO$_2$(NO$_3$)$_3$ at 77°K is similar to that of CsUO$_2$(NO$_3$)$_3$ at 77°K. However the spectrum of RbUO$_2$(NO$_3$)$_3$ contains fewer bands (about 37) than those observed in the spectrum of CsUO$_2$(NO$_3$)$_3$ (about 70), in almost the same wave length range (4740 Å to 5790 Å). Also the bands in this case are broader than those of CsUO$_2$(NO$_3$)$_3$. Many frequencies in the range of 20 cm$^{-1}$ to 300 cm$^{-1}$ (from the resonance line) observed in the fluorescence spectrum of CsUO$_2$(NO$_3$)$_3$ at 77°K are either broadened too much or are not observed at all in the fluorescence spectrum of RbUO$_2$(NO$_3$)$_3$ at 77°K.

Compared to the fluorescence spectrum of RbUO$_2$(NO$_3$)$_3$ at 20°K, its spectrum at 77°K is shifted towards longer wave length side by about 7 cm$^{-1}$ and the bands are broader in general. There is no appreciable change in the values of the vibrational frequencies of UO$_2$ between
<table>
<thead>
<tr>
<th>Nature &amp; visual intensity</th>
<th>( \nu (\text{vac}) ) cm(^{-1})</th>
<th>( \Delta \nu ) cm(^{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>21192</td>
<td>0</td>
<td>R</td>
</tr>
<tr>
<td>2</td>
<td>21035</td>
<td>157</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>20958</td>
<td>224</td>
<td>R-C_1</td>
</tr>
<tr>
<td>8</td>
<td>20920</td>
<td>272</td>
<td>R-C_2</td>
</tr>
<tr>
<td>2</td>
<td>20499</td>
<td>693</td>
<td>C+R</td>
</tr>
<tr>
<td>sh 2</td>
<td>20450</td>
<td>742</td>
<td>R-E</td>
</tr>
<tr>
<td>sh 2</td>
<td>20387</td>
<td>805</td>
<td>R-D</td>
</tr>
<tr>
<td>8</td>
<td>20308</td>
<td>884</td>
<td>R-A</td>
</tr>
<tr>
<td>10</td>
<td>20235</td>
<td>957</td>
<td>R-B</td>
</tr>
<tr>
<td>8</td>
<td>20087</td>
<td>221</td>
<td>R-A-C_1</td>
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<tr>
<td>8</td>
<td>20034</td>
<td>274</td>
<td>R-A-C_2</td>
</tr>
<tr>
<td>sh 2</td>
<td>19910</td>
<td>1282</td>
<td>R-I</td>
</tr>
<tr>
<td>sh 2</td>
<td>19673</td>
<td>1519</td>
<td>R-K</td>
</tr>
<tr>
<td>1</td>
<td>19609</td>
<td>699</td>
<td>C+R-A</td>
</tr>
<tr>
<td>sh 1</td>
<td>19555</td>
<td>753</td>
<td>R-A-E</td>
</tr>
<tr>
<td>sh 1</td>
<td>19490</td>
<td>818</td>
<td>R-A-D</td>
</tr>
<tr>
<td>9</td>
<td>19419</td>
<td>869</td>
<td>R-2A</td>
</tr>
<tr>
<td>10</td>
<td>19349</td>
<td>959</td>
<td>R-A-B</td>
</tr>
<tr>
<td>9</td>
<td>19198</td>
<td>221</td>
<td>R-2A-C_1</td>
</tr>
<tr>
<td>9</td>
<td>19152</td>
<td>267</td>
<td>R-2A-C_2</td>
</tr>
<tr>
<td>sh 3</td>
<td>19025</td>
<td>394</td>
<td>R-A-I</td>
</tr>
<tr>
<td>sh 1</td>
<td>18785</td>
<td>734</td>
<td>R-2A-E</td>
</tr>
<tr>
<td>sh 1</td>
<td>18673</td>
<td>746</td>
<td>R-2A-E</td>
</tr>
<tr>
<td>sh 1</td>
<td>18598</td>
<td>821</td>
<td>R-2A-D</td>
</tr>
<tr>
<td>4</td>
<td>18537</td>
<td>882</td>
<td>R-3A</td>
</tr>
<tr>
<td>8</td>
<td>18468</td>
<td>951</td>
<td>R-2A-B</td>
</tr>
</tbody>
</table>
From Dieke and Duncan

| 1  | 18375 | 162 | 1 |
| 3  | 18317 | 220 | R-3A-C<sub>1</sub> |
| 3  | 18273 | 264 | R-3A-C<sub>2</sub> |
| sh | 18145 | 1274 | R-2A-I |
| sh | 17902 | 1517 | R-2A-K |
| 1  | 17728 | 809 | R-3A-B |
| 1  | 17669 | 888 | R-4A |
| 6  | 17593 | 944 | R-3A-B |
| sh | 17518 | 151 | 1 |
| 1  | 17439 | 230 | R-4A-C<sub>1</sub> |
| 1  | 17407 | 262 | R-4A-C<sub>2</sub> |
| 2  | 16780 | 889 | R-5A |
| 4  | 16270 | 949 | R-4A-B |

sh = sharp
20°K and 77°K. Slight apparent changes in the vibrational frequencies lie within the experimental error.

Table 9 lists the bands observed in the fluorescence spectrum of RbUO$_2$(NO$_3$)$_3$ at 77°K by Dieke and Duncan along with the assignments made by us. The intense band on the short wave limit of the fluorescence spectrum has been designated as resonance band (21192 cm$^{-1}$). This corresponds to the transition from a vibrationless excited electronic state to the vibrationless ground electronic state.

The repetition frequency of the patterns in the fluorescence spectrum of uranyl compounds is known to correspond to the symmetric vibration frequency of UO$_2^{++}$. This has been confirmed by $^{235}$U isotope shifts in the fluorescence spectrum of CsUO$_2$(NO$_3$)$_3$ (Dieke and Duncan). This frequency is forbidden in infrared absorption. The repetition frequency of the patterns in RbUO$_2$(NO$_3$)$_3$ is $\sim$ 884 cm$^{-1}$. This therefore corresponds to the totally symmetric vibration of UO$_2^{++}$ in RbUO$_2$(NO$_3$)$_3$. Bands involving this frequency have been designated as F-nA, where $n = 0, 1, 2$ etc (Table 9). This set of bands represents a transition from excited electronic state to the various 'nA' levels of the ground state.

The antisymmetric vibration (v$_2$ or B) of UO$_2^{++}$ is expected to bear the ratio of 1.065 to the symmetric
vibration (A). Once the symmetric vibration (A) has been identified, it is thus possible to calculate roughly the antisymmetric vibration (B). Moreover the bands belonging to 'B' are known to be the most intense in the fluorescence spectrum. With these two criteria and comparing the values of 'B' obtained in CsUO$_2$(NO$_3$)$_3$, the bands (B) involving the antisymmetric vibration of UO$_2^{2+}$ are identified in the fluorescence spectrum of RbUO$_2$(NO$_3$)$_3$. Thus the set of bands R-nA-B have been assigned based on the above considerations. The band corresponding to this vibration is observed strongly in infrared absorption as expected. Bands involving three fundamental vibrational frequencies of UO$_2^{2+}$ are known to comprise the most intense part of the fluorescence spectrum of the uranyl salts. Therefore the doubly degenerate bending vibration $\nu$ of UO$_2^{2+}$ is also expected to occur in an intense band in the fluorescence spectrum. One of the frequencies involved in the set of intense double bands at $\sim$ 224 cm$^{-1}$ and $\sim$ 272 cm$^{-1}$ from R-nA bands, may be associated with the bending vibration ($\nu_2$ or $\nu_3$). The magnitudes of these frequencies are comparable to those assigned as bending vibrations ($\nu_2$) in CsUO$_2$(NO$_3$)$_3$. Bands designated as R-nA-C in Table 9 belong to this category. However this assignment is not supported by any other evidence.
Apart from the $\text{UO}_2^{2+}$ vibrations, the nitrate vibrations (These are in fact, as mentioned earlier, vibrations to be associated with the radical $\text{ONO}_2^-$ of $C_{2v}$ symmetry and not with the $\text{NO}_3^-$ radical of $D_{3h}$ symmetry. For convenience, these are still referred to as $\text{NO}_3$ vibrations), are also observed in the fluorescence spectrum of $\text{RbUO}_2(\text{NO}_3)_3$. The identity of the bands involving the $\text{NO}_3$ vibrations has been confirmed by Dieke and Duncan$^4$ in $\text{CsUO}_2(\text{NO}_3)_3$ by $^{15}\text{N}$ isotope shifts. The various $\text{NO}_3$ frequencies are expected to undergo only slight changes in magnitude between the matrices $\text{CsUO}_2(\text{NO}_3)_3$ and $\text{RbUO}_2(\text{NO}_3)_3$ (Dieke and Duncan)$^4$. Comparing the various $\text{NO}_3$ frequencies obtained in $\text{CsUO}_2(\text{NO}_3)_3$ (Section 1 of this chapter) many bands in the fluorescence spectrum of $\text{RbUO}_2(\text{NO}_3)_3$ have been assigned to $\text{ONO}_2^-$ vibrations. The assignments of nitrate frequencies are given in Table 9. The frequencies $D, E, F, I, J, K$ .. belong to the various fundamental vibrations of $\text{ONO}_2^-$, as explained in the previous section. These bands have been designated as $R-nA-D$ etc.

The assignments of the band $R-nA-I$ and $R-nA-K$ are based on the information obtained from the infrared absorption studies$^5$. 

Low frequency vibrations are supposed to arise from the lattice vibrations. Only one such vibration has been observed in the fluorescence spectrum.

A set of bands at an interval of 690 cm$^{-1}$ from R-$\mathrm{nA}$ bands can be thought of as antistokes bands due to a transition from a level 191 cm$^{-1}$ above the normal excited state to the various 'nA' levels of the ground electronic state. Similar antistokes bands have also been observed in the case of $\text{CsUO}_2(\text{NO}_3)_3$. It is interesting to note that from the absorption spectrum of $\text{RbUO}_2(\text{NO}_3)_3$ at 20$^\circ$K an excited level is known at 199 cm$^{-1}$ above the normal excited state. The nature of this level giving rise to antistokes bands in fluorescence, is not known.

All the above vibrational frequencies except the symmetric vibration frequency occur each as a single quantum either alone or in combination with one or several quanta of 'A' vibration. In the fluorescence spectrum of $\text{RbUO}_2(\text{NO}_3)_3$ at 77$^\circ$K as many as 5 quanta of 'A' are observed and all these are accompanied by a single quantum of B and C vibrations.

Broadly the fluorescence spectrum of $\text{RbUO}_2(\text{NO}_3)_3$ is similar to that of $\text{CsUO}_2(\text{NO}_3)_3$. The various $\text{UO}_2^{++}$ and ONO$_2$ frequencies observed have been tabulated and compared with those of $\text{CsUO}_2(\text{NO}_3)_3$ in Table 11.
(b) Infrared absorption spectrum of RbUO$_2$(NO$_3$)$_3$.

The infrared absorption spectrum of RbUO$_2$(NO$_3$)$_3$ has been extensively studied by Gatehouse and Comyns$^5$. The ONO$_2^-$ vibrations have been identified with the help of $^{15}$N isotope shifts. The bands observed by them have been listed in Table 10. The intensities of the bands and the description of the bands are taken from the infrared absorption curves recorded in the present investigations. The corresponding bands observed in fluorescence have also been included in Table 10. From Table 10 one can see a close correspondence between the bands observed in infrared absorption and those observed in fluorescence. Many of the bands in the infrared absorption are explained in terms of fundamental vibrational frequencies of ONO$_2^-$.

Only one fundamental vibration ($\gamma_3$) of UO$_2^{4+}$ at 960 cm$^{-1}$ occurs strongly in infrared absorption, as expected.

3. Potassium uranyl nitrate.

(a) Fluorescence spectrum at 77°C.

The crystals of KUO$_2$(NO$_3$)$_3$ obtained from acidic solution have been described as belonging to rhombohedral system$^8$. Dieke and Duncan$^1$ have described the preparation of the potassium salt analogous to CsUO$_2$(NO$_3$)$_3$ and RbUO$_2$(NO$_3$)$_3$ at 78°C. Method of preparation of KUO$_2$(NO$_3$)$_3$ adopted in the present investigations has been described in Chapter 2.
<table>
<thead>
<tr>
<th>$\tilde{\nu}$ in cm$^{-1}$</th>
<th>Description</th>
<th>Assignment</th>
<th>Fluorescence data</th>
</tr>
</thead>
<tbody>
<tr>
<td>711 w.sh.</td>
<td>$\tilde{\nu}_s$ONO$_2^-$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>736 sh.</td>
<td>$\tilde{\nu}_s$ONO$_2^-$</td>
<td>734</td>
<td></td>
</tr>
<tr>
<td>803 s.sh.</td>
<td>$\tilde{\nu}_s$UO$_2^{++}$</td>
<td>805</td>
<td></td>
</tr>
<tr>
<td>960 s.b</td>
<td>$\tilde{\nu}_s$ONO$_2^-$</td>
<td>957</td>
<td></td>
</tr>
<tr>
<td>1023 s.sh.</td>
<td>$\tilde{\nu}_s$ONO$_2^-$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1276 s.b.</td>
<td>$\tilde{\nu}_s$ONO$_2^-$</td>
<td>1282</td>
<td></td>
</tr>
<tr>
<td>1429 -</td>
<td>$2\tilde{\nu}_s$ONO$_2^-$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1473 -</td>
<td>$2\tilde{\nu}_s$ONO$_2^-$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1536 s.b</td>
<td>$\nu_4$ONO$_2^-$</td>
<td>1519</td>
<td></td>
</tr>
<tr>
<td>1608 w.sh.</td>
<td>$2\tilde{\nu}_s$ONO$_2^-$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1727 w.sh.</td>
<td>$\nu_4+\tilde{\nu}_s$ONO$_2^-$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1761 w.sh.</td>
<td>$\nu_4+\tilde{\nu}_s$ONO$_2^-$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1845 v.w.sh.</td>
<td>A+B UO$_2^{++}$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1990 v.w.sh.</td>
<td>$\tilde{\nu}_s$ONO$_2^-$</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

From Gatehouse and Comyns$^5$

$w$ = weak  $s$ = strong
$sh$ = sharp  $v.w$ = very weak
$b$ = broad  $v.s$ = very strong
## TABLE 11

**VIBRATIONAL FREQUENCIES**

<table>
<thead>
<tr>
<th>Vibration</th>
<th>$\text{RbUO}_2(\text{NO}_3)_3$</th>
<th>$\text{CsUO}_2(\text{NO}_3)_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$77^\circ\text{K. cm}^{-1}$</td>
<td>$77^\circ\text{K. cm}^{-1}$</td>
</tr>
<tr>
<td><strong>UO}^{2+</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>884</td>
<td>884</td>
</tr>
<tr>
<td>B</td>
<td>957</td>
<td>960</td>
</tr>
<tr>
<td>C</td>
<td>224</td>
<td>212</td>
</tr>
<tr>
<td></td>
<td>272</td>
<td></td>
</tr>
<tr>
<td><strong>ONO}_2^-</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>805</td>
<td>805</td>
</tr>
<tr>
<td>E</td>
<td>742</td>
<td>749</td>
</tr>
<tr>
<td>F</td>
<td>734</td>
<td>740</td>
</tr>
<tr>
<td>G</td>
<td>-</td>
<td>716</td>
</tr>
<tr>
<td>I</td>
<td>1282</td>
<td>1277</td>
</tr>
<tr>
<td>K</td>
<td>1519</td>
<td>1520</td>
</tr>
</tbody>
</table>
The fluorescence spectrum of this salt at liquid air temperature has been first obtained and arranged in groups by Nichols and Howes. However, no detailed analysis of the fluorescence spectrum was done by these workers. Dieke and Duncan have given the $\text{UO}_2^{++}$ and $\text{NO}_3^-$ (in reality $\text{ONO}_2^-$) vibrational frequencies. Though they have listed the bands observed in the fluorescence spectrum of $\text{KUO}_2(\text{NO}_3)_3$ at $77^\circ\text{K}$, a detailed analysis of the spectrum has not been carried out.

We have recorded the fluorescence spectrum of $\text{KUO}_2(\text{NO}_3)_3$ at $77^\circ\text{K}$ and analysed the bands in detail. Many bands observed in the present investigations are in close agreement with those observed by Nichols and Howes and by Dieke and Duncan.

In general, the structure of the fluorescence spectrum is the same as that of $\text{CsUO}_2(\text{NO}_3)_3$ or $\text{RbUO}_2(\text{NO}_3)_3$ (Figure 10). A noteworthy feature is that the bands in $\text{KUO}_2(\text{NO}_3)_3$ are broader than those of $\text{RbUO}_2(\text{NO}_3)_3$ and $\text{CsUO}_2(\text{NO}_3)_3$. The Cs salt has the sharpest bands among the monoalkali uranyl nitrate salts. The fluorescence spectrum of $\text{KUO}_2(\text{NO}_3)_3$ contains a smaller number of bands compared to that of $\text{RbUO}_2(\text{NO}_3)_3$ in the same wave length range. One of the reasons for this feature may be broadening of the bands and the subsequent overlapping.
Compared to the fluorescence spectrum at 20°K the spectrum at 77°K is shifted towards longer wave side by 7 cm⁻¹. Same amount of shift was observed in the case of RbUO₂(NO₃)₃ whereas in the case of CsUO₂(NO₃)₃ the shift was 10 cm⁻¹.

The fluorescence spectrum of KUO₂(NO₃)₃ at 77°K is shown in Figure 10. The bands observed have been listed in Table 12. The accuracy of wave length measurements, ± 1 Å, is not high since the bands are broad.

The fluorescence spectrum has been recorded by Nichols and Howes⁸ as well as Dieke and Duncan¹. Dieke and Duncan¹ list only 13 bands while Nichols and Howes⁸ list as many as 37 bands in almost the same wave length range. As both the data were inadequate for the purpose of a detailed analysis, we have reinvestigated the fluorescence spectrum of KUO₂(NO₃)₃. The bands observed in the present investigation with vibrational assignments are shown in Table 12.

The intense band on the short wave limit of the fluorescence spectrum has been taken as the resonance band which represents a transition from vibrationless excited electronic state to the vibrationless ground electronic state (21176 cm⁻¹).
FLUORESCENCE SPECTRUM OF KUO₂(NO₃)₃ AT 77°K

FIG. 10.
FIG. 11(b)

$KUO_2(NO_3)_3$
FLUORESCENCE SPECTRUM OF Cs₂UO₂(NO₃)₄ AT 77°K

FIG. 12.
TABLE 12

FLUORESCENCE SPECTRUM OF KUO₂(NO₃)₃ AT 77K

<table>
<thead>
<tr>
<th>λ in air</th>
<th>Nature</th>
<th>ν (vac) cm⁻¹</th>
<th>Δν from R-nA cm⁻¹</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>4721</td>
<td>5</td>
<td>21176</td>
<td>0</td>
<td>R</td>
</tr>
<tr>
<td>4728</td>
<td>b 2</td>
<td>21144</td>
<td>32</td>
<td>1</td>
</tr>
<tr>
<td>4782</td>
<td>b 7</td>
<td>20906</td>
<td>270</td>
<td>R-C</td>
</tr>
<tr>
<td>4924</td>
<td>7</td>
<td>20303</td>
<td>873</td>
<td>R-A</td>
</tr>
<tr>
<td>4943</td>
<td>9</td>
<td>20224</td>
<td>952</td>
<td>R-B</td>
</tr>
<tr>
<td>4990</td>
<td>8</td>
<td>20034</td>
<td>269</td>
<td>R-A-C</td>
</tr>
<tr>
<td>5025</td>
<td>sh 2</td>
<td>19895</td>
<td>1281</td>
<td>R-I</td>
</tr>
<tr>
<td>5088</td>
<td>d</td>
<td>19649</td>
<td>654</td>
<td>C+R-2A</td>
</tr>
<tr>
<td>5094</td>
<td>d</td>
<td>19625</td>
<td>673</td>
<td>C+R-2A</td>
</tr>
<tr>
<td>5114</td>
<td>sh 2</td>
<td>19548</td>
<td>755</td>
<td>R-A-E</td>
</tr>
<tr>
<td>5145</td>
<td>8</td>
<td>19431</td>
<td>872</td>
<td>R-2A</td>
</tr>
<tr>
<td>5168</td>
<td>9</td>
<td>19344</td>
<td>959</td>
<td>R-A-B</td>
</tr>
<tr>
<td>5218</td>
<td>9</td>
<td>19159</td>
<td>272</td>
<td>R-2A-C</td>
</tr>
<tr>
<td>5260</td>
<td>sh 3</td>
<td>19006</td>
<td>1297</td>
<td>R-A-I</td>
</tr>
<tr>
<td>5322</td>
<td>d</td>
<td>18784</td>
<td>647</td>
<td>C+R-3A</td>
</tr>
<tr>
<td>5330</td>
<td>d</td>
<td>18756</td>
<td>675</td>
<td>C+R-3A</td>
</tr>
<tr>
<td>5352</td>
<td>sh 2</td>
<td>18679</td>
<td>752</td>
<td>R-2A-E</td>
</tr>
<tr>
<td>5366</td>
<td>sh 2</td>
<td>18631</td>
<td>800</td>
<td>R-2A-D</td>
</tr>
<tr>
<td>5374</td>
<td>sh 1</td>
<td>18602</td>
<td>829</td>
<td></td>
</tr>
<tr>
<td>5385</td>
<td>6</td>
<td>18565</td>
<td>866</td>
<td>R-3A</td>
</tr>
<tr>
<td>5409</td>
<td>8</td>
<td>18482</td>
<td>949</td>
<td>R-2A-B</td>
</tr>
<tr>
<td>5464</td>
<td>8</td>
<td>18296</td>
<td>269</td>
<td>R-3A-C</td>
</tr>
<tr>
<td>5510</td>
<td>sh 2</td>
<td>18148</td>
<td>1298</td>
<td>R-2A-I</td>
</tr>
<tr>
<td>5575</td>
<td>8</td>
<td>17615</td>
<td>949</td>
<td>R-3A-B</td>
</tr>
</tbody>
</table>

sh = sharp  b = broad  d = diffuse
The repetition of frequency of the fluorescence patterns is $\sim 873 \text{ cm}^{-1}$. On the basis of arguments put forward in previous sections it is clear that this repetition frequency is the same as the totally symmetric vibration ($\nu_1$) of $\text{UO}_2^{++}$ (A). So the set of bands involving this frequency has been designated as $R-nA$; $n = 0, 1, 2$ etc., (Table 12). This agrees well with the value tabulated by Dieke and Duncan $^1$ (875.46 cm$^{-1}$), for the fluorescence spectrum at 20°C.

The antisymmetric vibration of $\text{UO}_2^{++}$ occurs as a very strong band in the fluorescence spectrum. As explained in Section 1 of this chapter, the ratio $B/A$ should be close to the theoretical value of 1.065. This gives a value of $\sim 930 \text{ cm}^{-1}$ to be expected for the B vibration of $\text{UO}_2^{++}$ in $\text{KUO}_2(\text{NO}_3)_3$. In the infrared absorption spectrum obtained in the present investigations a strong and broad absorption band is observed at $\sim 952 \text{ cm}^{-1}$. In view of these, the strong band at $\sim 952 \text{ cm}^{-1}$ from the resonance band is taken to be due to the antisymmetric vibration (B) of $\text{UO}_2^{++}$. The set of bands involving this frequency is therefore represented as $R-nA-B$; $n = 0, 1, 2$ etc.

The other fundamental vibration of $\text{UO}_2^{++}$, the bending vibration ($\nu_4$), is also expected to occur with good intensity in fluorescence as in the case of $\text{CsUO}_2(\text{NO}_3)_3$. 
and \( \text{RbU}_2(\text{NO}_3)_3 \). A set of intense bands at an interval of 270 cm\(^{-1}\) from \( R-nA \) bands is taken as involving the \( C \) vibration. The bands are accordingly designated as \( R-nA-C; n = 0, 1, 2 \) etc. Only one intense band is observed in this range while for \( \text{RbU}_2(\text{NO}_3)_3 \) two equally intense bands are observed. The identification of 'C' vibration, as in other monoalkali salts, requires further confirmation.

Apart from the \( \text{UO}_2^{++} \) vibrations, one expects the nitrate \( (\text{ONO}_2^-) \) vibrations also to appear in the fluorescence spectrum as in the cases of \( \text{CsUO}_2(\text{NO}_3)_3 \) and \( \text{RbUO}_2(\text{NO}_3)_3 \). The values obtained for nitrate frequencies for the above two salts in fluorescence and that for \( \text{RbUO}_2(\text{NO}_3)_3 \) in infrared absorption helped in the present assignments of the nitrate \( (\text{ONO}_2^-) \) frequencies. Not all the nitrate frequencies observed in the case of \( \text{CsUO}_2(\text{NO}_3)_3 \) spectrum at 77°K, are observed in the fluorescence spectrum of \( \text{KUO}_2(\text{NO}_3)_3 \). Only \( R-nA-E, R-2A-D, R-nA-I \) series have been observed. The values of \( E \) and \( D \) frequencies agree well with those tabulated by Dieke and Duncan\(^1\) from the fluorescence spectrum of \( \text{KUO}_2(\text{NO}_3)_3 \) at 20°K. However the 'I' frequency, though it occurs with appreciable intensity in the fluorescence spectrum of \( \text{KUO}_2(\text{NO}_3)_3 \) at 77°K, has not been reported by Dieke and Duncan\(^1\). This assignment is based on those of
similar bands observed in CsUO$_2$(NO$_3$)$_3$ and RbUO$_2$(NO$_3$)$_3$
and also in the infrared absorption spectrum of
KUO$_2$(NO$_3$)$_3$ where a strong absorption band has been
observed at ~ 1272 cm$^{-1}$.

The set of bands at intervals of 654 cm$^{-1}$ and
678 cm$^{-1}$ from R-nA bands are not likely to belong to the
nitrate vibrations. Nitrate vibration of this magnitude
are not observed in infrared absorption of any of the
monoalkali uranyl nitrate salts. The bands are broad in
nature, unlike the other nitrate bands, which are
comparatively sharp. In all probability, these bands
may be antistokes bands arising from excited levels at
218 cm$^{-1}$ and 194 cm$^{-1}$ above the lowest excited electronic
state. Such antistokes bands have also been observed in
the fluorescence spectra of CsUO$_2$(NO$_3$)$_3$ and RbUO$_2$(NO$_3$)$_3$.
It is interesting to note that Dieke and Duncan$^1$ have
reported from an analysis of the absorption spectrum an
excited level at 21385 cm$^{-1}$ i.e., 200 cm$^{-1}$ above the
lowest excited state. These bands have been designated
as G'R-nA.

In general the fluorescence spectra at 77°K of all
the three monoalkali uranyl nitrate salts have a close
similarity.

\[ t - 2A A \]
(b) **Infrared absorption spectrum of KUO$_2$(NO$_3$)$_3$**

The infrared absorption spectrum of KUO$_2$(NO$_3$)$_3$ has been obtained for the first time. The experimental procedure has been given in Chapter 2. Figures 11 (a) and 11 (b) show the infrared absorption spectrum in the wave number ranges of 650 cm$^{-1}$ to 1100 cm$^{-1}$ and 1200 cm$^{-1}$ to 1600 cm$^{-1}$. The first one is recorded using paraffin oil as mull whereas the second one was taken with hexachlorobutadiene as the mulling agent. The absorption bands observed have been tabulated in Table 13. The vibration frequencies observed in fluorescence have also been included in the table for comparison. It can be seen that there is a close correspondence between the frequencies observed in fluorescence and those observed in infrared absorption. The assignments of the various bands is based on the assignment of similar bands of CsUO$_2$(NO$_3$)$_3$ and RbUO$_2$(NO$_3$)$_3$. The weak absorption band at 877 cm$^{-1}$ may involve the symmetric 'A' vibration of UO$_2^{2+}$. The totally symmetric vibration of UO$_2^{2+}$ is forbidden in infrared absorption only when the linear UO$_2^{2+}$ ion is free. But when UO$_2^{2+}$ is embedded in a crystal lattice, the usual selection rules no longer hold good strictly and it is possible that the forbidden transition occur in infrared absorption, though weakly.
TABLE 13

INFRARED ABSORPTION SPECTRUM OF KUO₂(NO₃)₃
650 cm⁻¹ - 2000 cm⁻¹

<table>
<thead>
<tr>
<th>ν in cm⁻¹</th>
<th>Description</th>
<th>Assignment</th>
<th>Fluorescence data</th>
</tr>
</thead>
<tbody>
<tr>
<td>741</td>
<td>s. sh</td>
<td>ν₂-ONO₂⁻</td>
<td>-</td>
</tr>
<tr>
<td>806</td>
<td>s. sh</td>
<td>ν₄-ONO₂²</td>
<td>800</td>
</tr>
<tr>
<td>877</td>
<td>w. sh</td>
<td>A UO₂²⁺</td>
<td>873</td>
</tr>
<tr>
<td>935</td>
<td>s. b</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>952</td>
<td>s. b</td>
<td>B UO₂²⁺</td>
<td>952</td>
</tr>
<tr>
<td>1027</td>
<td>vs. sh</td>
<td>ν₂-ONO₂⁻</td>
<td>-</td>
</tr>
<tr>
<td>1272</td>
<td>vs. b</td>
<td>ν₁-ONO₂−</td>
<td>1281</td>
</tr>
<tr>
<td>1508</td>
<td>s. sh</td>
<td>ν₄-ONO₂²</td>
<td>-</td>
</tr>
<tr>
<td>1606</td>
<td>w. b</td>
<td>ν₂-ONO₂⁻</td>
<td>-</td>
</tr>
<tr>
<td>1734</td>
<td>w.</td>
<td>ν₁+ν₂-ONO₂⁻</td>
<td>-</td>
</tr>
<tr>
<td>1764</td>
<td>w.</td>
<td>ν₁+ν₄-ONO₂⁻</td>
<td>-</td>
</tr>
<tr>
<td>1818</td>
<td>w. b</td>
<td>A+B UO₂²⁺</td>
<td>-</td>
</tr>
<tr>
<td>2000</td>
<td>w. sh</td>
<td>ν₁+ν₂-ONO₂⁻</td>
<td>-</td>
</tr>
</tbody>
</table>

w = weak  sh = sharp  s = strong
b = broad  v.w = very weak
vs = very strong

==============================================
B-nAr-I bands in the fluorescence spectrum were classified by the observation of \( \nu_1 \) vibration of \( \text{ONO}_2^- \) in infrared absorption. It is seen that most of the absorption bands in infrared belong to \( \text{ONO}_2^- \) (C\(_{2v}\) symmetry) radical and not to \( \text{NO}_3^- \) ion (D\(_{3h}\) symmetry).

The infrared absorption data and fluorescence data together give a detailed picture of the various vibrational levels in the ground state of \( \text{UO}_2^{2+} \) ion.

4. Discussions:

Nichols and Howes\(^8\) observed that there is a regular shift of the resonance band and consequently a general shift of the whole fluorescence spectrum towards longer wave length side as one proceeds from Cs to K. Deke and Duncan\(^1\) pointed out the need for spectroscopic study of a number of related uranyl salts in detail to understand more about the structure of the salts using \( \text{UO}_2^{2+} \) ion as the probe. They have, with the above purpose in mind, recorded the fluorescence spectra of many uranyl salts, particularly double nitrate salts. But the fluorescence spectra of all these salts were not obtained under similar conditions. The fluorescence spectrum of \( \text{CsUO}_2(\text{NO}_3)_3 \) was recorded at 20°K, that of \( \text{RbUO}_2(\text{NO}_3)_3 \) at 20°K and 77°K and that of \( \text{KUO}_2(\text{NO}_3)_3 \) at 77°K. In order to have a more meaningful comparison of the spectra of different salts it was thought necessary to record the
TABLE 14

VIBRATIONAL FREQUENCIES

<table>
<thead>
<tr>
<th>Vibration</th>
<th>CsUO$_2$(NO$_3$)$_3$</th>
<th>RbUO$_2$(NO$_3$)$_3$</th>
<th>KUO$_2$(NO$_3$)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_{2}^{2+}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>884</td>
<td>884</td>
<td>873</td>
</tr>
<tr>
<td>B</td>
<td>960</td>
<td>957</td>
<td>952</td>
</tr>
<tr>
<td>C</td>
<td>212</td>
<td>224</td>
<td>270</td>
</tr>
</tbody>
</table>

| ONO$_2^-$ |                        |                        |                        |
| D          | 805                    | 805                    | 806(I.R)               |
| E          | 749                    | 753                    | 755                    |
| F          | 739                    | 734                    | 741(I.R)               |
| G          | 715                    | 711(I.R)               | -                      |
| I          | 1277                   | 1282                   | 1281                   |
| K          | 1520                   | 1519                   | 1508(I.R)              |
| R          | 21080                  | 21192                  | 21176                  |

The values are from fluorescence spectra recorded at 77°CK unless otherwise mentioned.

I.R = Infrared absorption.
fluorescence and infrared spectra of all these salts under similar experimental conditions. In the foregoing sections we have described the results of the infrared and fluorescence spectral investigation of some alkali uranyl nitrate salts. Table 14 summarises the various frequencies of the $\text{UO}_2^{++}$ ion and the $\text{NO}_2^-$ group observed in these salts in fluorescence at 77°K. These frequencies are also in good agreement with the frequencies observed in the infrared absorption.

Compared with the fluorescence spectra at 20°K, the fluorescence spectra of these salts at 77°K contain less number of bands. This appears to be due to broadening and consequent overlapping of the bands at 77°K.

The fluorescence spectrum as a whole is shifted towards longer wave lengths by 7 to 10 cm$^{-1}$ between 20°K and 77°K for the three monoalkali uranyl nitrate salts.

There is no noticeable change in the magnitude of the various frequencies in going from 20°K to 77°K. The relative intensities of the bands do not also change appreciably between 20°K and 77°K.

The fluorescence spectrum of these salts at 77°K contains some new bands, not present in the same recorded
Usually in the fluorescence spectrum at low temperatures, say 20°K or below only transitions from the vibrationless level of the lowest excited electronic state to the various vibrational levels of the ground state are expected. This is indeed true for fluorescence spectra of the salts recorded at 20°K. At low temperatures, like liquid helium and liquid hydrogen temperatures, as per the Boltzmann distribution, there will be hardly any UO$_2^{2+}$ ions in excited states higher than the lowest excited state (to which all UO$_2^{2+}$ ions fall before fluorescence, irrespective of to what excited state, the absorbing light has taken them). However, as the temperature increases, other excited states close to the lowest excited state get increasingly populated and fluorescence transitions originating from such levels get recorded. Thus, for instance, at 77°K the excited levels lying at 186 cm$^{-1}$ in Cs, 191 cm$^{-1}$ in Rb and 200 cm$^{-1}$ in K from the lowest excited level get enough populated so that fluorescence transitions originating from them could be observed. Such transitions are responsible for the new bands observed in the fluorescence spectra of the salts at 77°K and which were not observed in the spectra at 20°K.

Coming to the identity of these new excited states G(0,0), there are two possibilities (1) - hey
could be new excited electronic levels or (ii) they could be vibronic levels resulting from the association of the bending vibration $\nu_2$ with the lowest excited state. If the levels were independent electronic levels, one would expect transitions from them to all the vibrational levels of the ground state i.e., all the bands in the fluorescence spectrum should have a companion at about 290 cm$^{-1}$ on short wave side. This is not the case. The new levels seem to combine only with 'A' levels of the ground state. In the absorption spectra at 20°K, it was found that bands involving transitions to these levels are polarised. The magnitude of the frequencies involved in these transitions are also in good agreement with the expected values of the $\nu_2$ vibrations in the excited state. Thus in all probability the $G(0,0)$ levels appear to be vibrational levels ($\nu_2$ bending vibrations of UO$_2^{++}$) associated with the excited states. Among the three spectra, the fluorescence spectrum of CsUO$_2$(NO$_3$)$_3$ shows the sharpest bands, followed by the spectrum of RbUO$_2$(NO$_3$)$_3$. The bands of KUO$_2$(NO$_3$)$_3$ are broad and diffuse. There is no apparent regularity in the shift of the resonance band in going from Cs to K as can be seen from the Table No.14. The symmetric vibration frequency of UO$_2^{++}$ is maximum (888 cm$^{-1}$) for RbUO$_2$(NO$_3$)$_3$ and minimum 875 cm$^{-1}$ for KUO$_2$(NO$_3$)$_3$. On the other
hand the value of the antisymmetric vibration \( B \) decreases regularly from Cs to K.

The relative intensities in the group of bands between 210 cm\(^{-1}\) and 270 cm\(^{-1}\) from the R-nA bands in going from Cs to K affords interesting study. In CsUO\(_2\)(NO\(_3\))\(_3\) the band at \( \sim 213 \) cm\(^{-1}\) from R-nA bands is the most intense in the group (and hence assigned to \( \nu_2\) bending vibration of UO\(^{2+}\)). In RbUO\(_2\)(NO\(_3\))\(_3\), however, there are two bands with high (an equal) intensity in the group at 224 cm\(^{-1}\) and 272 cm\(^{-1}\). In KUO\(_2\)(NO\(_3\))\(_3\) the band with maximum intensity in the group occurs at a still larger separation of 270 cm\(^{-1}\). As has been assumed earlier, if the most intense band in the group indeed involves the C vibration, the above values point out that its magnitude increases as one goes from CsUO\(_2\)(NO\(_3\))\(_3\) to KUO\(_2\)(NO\(_3\))\(_3\) through RbUO\(_2\)(NO\(_3\))\(_3\).

The magnitude of nitrate vibrations is seen to be almost unaffected by the change of the alkali atom. The nitrate vibrations, however, appear more prominently in the fluorescence spectrum of CsUO\(_2\)(NO\(_3\))\(_3\) and not so prominently in that of KUO\(_2\)(NO\(_3\))\(_3\).

The fluorescence spectrum of CsUO\(_2\)(NO\(_3\))\(_3\) at 77°K obtained in the present investigations does not show the impurity bands reported by Dieke and Duncan\(^1\). However, in some cases the fluorescence spectra of
CsUO₂(NO₃)₃ and RbUO₂(NO₃)₃ showed bands due to Cs₂UO₂(NO₃)₄ and Rb₂UO₂(NO₃)₄ respectively, though weakly in the case of RbUO₂(NO₃)₃. These salts were crystallised from solutions using distilled water as solvent. The variation in the composition of the crystals due to slight variations in the method of preparation is already discussed in Chapter 2. Bands due to the 'A' and 'B' frequencies of ^18O^16O⁴⁺ have escaped detection in our spectra, probably because they have been eclipsed by other bands.

The behaviour of 'E' frequency in fluorescence and infrared absorption spectrum is interesting. The 'E' frequency belongs to the ₂ ô vibration of ONC₂ involving NO₂ symmetric bending vibration. This is the only nitrate frequency which combines with the UO₂⁺⁺ antisymmetric frequency B. This B + E combination frequency has been observed in fluorescence at 2(°K) as well as at 77°K for CsUO₂(NO₃)₃. The assignment has been confirmed by the ²³⁵U and ¹⁵N isotope shifts by Dieke and Duncan. The 'E' frequency however occurs in combination with the symmetric frequency 'A' in all the three salts.

The infrared absorption spectra of the three alkali uranyl nitrate salts show that all the observed bands can be assigned to UO₂⁺⁺ or to ONO₂ vibrations.
There are no bands which could be attributed to the \( \text{NO}_3^- \) ion. This indicates that in all these molecules the nitrate groups are co-ordinately bound to the central 'U' atom. This observation is in conformity with the results on X-ray structural analysis carried out by Hoard and Stroupe\(^1\) on \( \text{RbUO}_2(\text{NO}_3)_1 \).
REFERENCES


